Supporting Information

Base- and Additive-free Ir-Catalyzed *ortho*-Iodination of Benzoic Acids: Scope and Mechanistic Investigations

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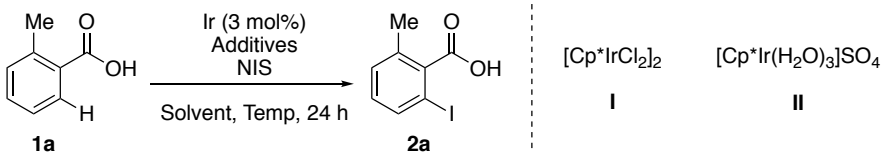
General information

All reagents were used as obtained from commercial sources without further purification. Flash chromatography was performed with 60 Å (35-70 μm) silica gel (GC 60A 35-70 Micron, DAVISIL) using mixtures petroleum ether / EtOAc as eluent. Analytical TLC was performed on aluminum plates pre-coated (0-25 mm) with silica gel (Merck, Silica Gel 60 F254). Compounds were detected by exposure to UV light or by revealing the plates in a solution of 5% $KMnO_4$ in water. Melting points were recorded in metal block and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz respectively on a Bruker Advance spectrometer. Chemical shifts (δ) are shown in ppm, using as a reference the residual peaks of $CH(D)Cl_3$ (δ_H 7.26 and δ_C 77.00). Coupling constants (J) are given in Hz. NMR yields were calculated using 1 equiv. of 2,3,5,6-tetrachloro-4-nitrobenzene as internal standard. High-resolution mass spectra (HRMS) were recorded on Brucker microTOF ESI-TOF mass spectrometer.

Optimization studies

Table S1. Screening studies of the reaction conditions.[a]

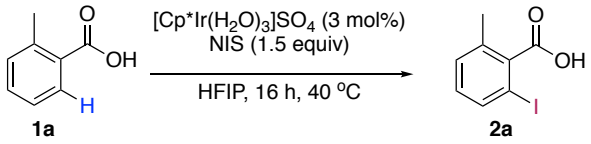


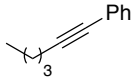
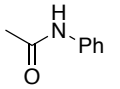
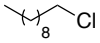
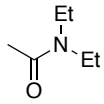
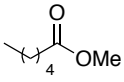
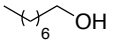
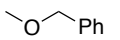
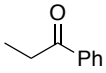
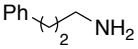
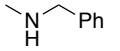
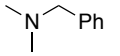
Entry	Solvent	T (°C)	Cat	Additives	NIS (equiv.)	Yield (%)[b]
1[c]	Acetone	60	**I**	$AgCO_3$	1	<5%
2[c]	DCE[d]	60	**I**	$AgCO_3$	1	-
3	Acetone	60	**I**	$AgBF_4$/ NaOAc	3	25
4	DCE	60	**I**	$AgBF_4$/ NaOAc	3	32
5	TFE	60	**I**	$AgBF_4$/ NaOAc	3	78
6	HFIP	60	**I**	$AgBF_4$/ NaOAc	3	86
7	HFIP	60	**II**	$AgBF_4$/ NaOAc	3	90
8	HFIP	40	**II**	$AgBF_4$/ NaOAc	3	86
9[e]	HFIP	40	**II**	NaOAc	1.2	80
10	HFIP	40	**II**	-	3	88
11	**HFIP**	**40**	**II**	**-**	**1.5**	**98**
12	Acetone	40	**II**	-	1.5	5
13	DCE	40	**II**	-	1.5	0
14	Toluene	40	**II**	-	1.5	0
15	THF	40	**II**	-	1.5	0
16	^{i}PrOH	40	**II**	-	1.5	0
17	^{t}BuOH	40	**II**	-	1.5	5
18	TFE[f]	40	**II**	-	1.5	73
19	AcOH	40	**II**	-	1.5	0
20	TFA[g]	40	**II**	-	1.5	0

[a]Experiments were carried out under air atmosphere on 0.15 mmol scale and 0.1 M of solvent. $AgBF_4$ (20 mol %), NaOAc (30 mol %). [b]Determined by ^{1}H NMR spectroscopy with respect to an internal standard (1,2,4,5-tetrachloro-3-nitrobenzene). [c]The reaction was carried out with 1 equiv. of $AgCO_3$. [d]DCE = 1,2-dichloroethane. [e]The reaction was carried out with 1 equiv. of NaOAc. [f]TFE = 2,2,2-trifluoroethanol. [g]TFA = trifluoroacetic acid.

Robustness studies

Table S2. Robustness screening test.



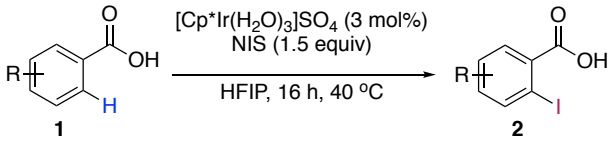
Entry	Additive	yield **2a** (%)	yield additive (%)	yield **1a** (%)	Entry	Additive	yield **2a** (%)	yield additive (%)	yield **1a** (%)
0	-	99	-	-	9		0	0	99
1		0	97	0	10		30	70	70
2		99	78	0	11		70	100	0
3		99	84	0	12		73	81	0
4		0	56	99	13		70	85	0
5		0	60	99	14		0	99	99
6		0	26	0	15		46	50	0
7		0	0	99	16		80	100	0
8		0	0	75					

The standard reaction is undertaken in the presence of one equivalent of the given additive. The yield of **2a**, remaining additive and starting material after reaction is given by internal standard.

Procedure for the synthesis of $[Cp^*Ir(H_2O)_3]SO_4$ II

$AgSO_4$ (0.754 mmol, 235 mg) was added to a suspension of $[Cp^*IrCl_2]_2$ (0.377 mmol, 300 mg) in H_2O (2.5 mL). The mixture was stirred at room temperature. After 12 h, the yellow suspension was filtered thought celite and the filtrate was evaporated and dried in vacuo to yield $[Cp^*Ir(H_2O)_3]SO_4$ as a yellow powder (173 mg, 98% yield).

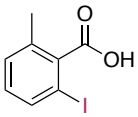
General procedure for the *ortho*-Iodination of Benzoic Acids 1



Benzoic acid **1** (0.5 mmol), $[Cp^*Ir(H_2O)_3]SO_4$ (3.0 mol%, 0.015 mmol, 7 mg) and *N*-iodosuccinimide (0.75 mmol, 169 mg) was dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP, 0.1 M, 5.0 mL) under air atmosphere in a capped vial and stirred at 40 °C for 16 hours. The reaction was quenched by addition of $Na_2S_2O_3$ (sat) (2 mL) and then acidified by HCl (1.0 M) to pH <2. The aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL), and the combined organic phases were washed with brine (10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The product was purified by column chromatography (petroleum ether / ethyl acetate (2% of AcOH)) providing the *ortho*-iodobenzoic acid **2**.

Synthesis and characterization data for *ortho*-iodobenzoic acids 2

2-Iodo-6-methylbenzoic acid (2a)

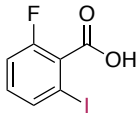


The title compound was prepared according the general procedure from 2-methylbenozic acid (**1a**, 68 mg). Purification by column chromatography (SiO_2;

petroleum ether / ethyl acetate (2% of AcOH), 90:10) afforded **2a** as a colorless solid (128 mg, 98%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 11.08 (s, br, 1H), 7.72 (d, J = 7.9 Hz, 1H), 7.24 (d, J = 7.6 Hz, 1H), 7.05 (t, J = 7.8 Hz, 1H), 2.49 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.7, 139.0, 136.7, 136.6, 131.0, 129.9, 91.5, 20.3 ppm. HRMS (ESI): m/z calcd for $C_8H_7IO_2$-H: 260.9418 $[M-H]^-$; found: 260.9424.

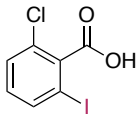
2-Fluoro-6-iodobenzoic acid (2b)



The title compound was prepared according the general procedure from 2-fluorobenzoic acid (**1b**, 70 mg) at 60 °C. Purification by column chromatography (SiO_2; petroleum ether / ethyl acetate (2% of AcOH), 90:10) afforded **2b** as a colorless solid (98 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.40 (s, 1H), 7.77–7.64 (m, 1H), 7.22–7.10 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.99, 159.27 (d, $^{1}J_{C-F}$ = 257.0 Hz), 135.54 (d, $^{3}J_{C-F}$ = 3.6 Hz), 132.98 (d, $^{3}J_{C-F}$ = 8.6 Hz), 126.99 (d, $^{2}J_{C-F}$ = 18.1 Hz), 115.99 (d, $^{2}J_{C-F}$ = 21.5 Hz), 92.52 (d, $^{4}J_{C-F}$ = 2.3 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ 109.31 ppm. HRMS (ESI): m/z calcd for $C_7H_4IO_2F$-H: 264.9167 $[M-H]^-$; found: 264.9145

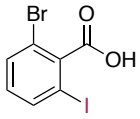
2-Chloro-6-iodobenzoic acid (2c)



The title compound was prepared according the general procedure from 2-chlorobenzoic acid (**1c**, 78 mg) at 60 °C. Purification by column chromatography (SiO_2; petroleum ether / ethyl acetate (2% of AcOH), 80:20) afforded **2c** as a colorless solid (138 mg, 98%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.43 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.08 (t, *J* = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.63, 138.68, 137.50, 131.75, 130.86, 129.24, 91.52 ppm. HRMS (ESI): m/z calcd for $C_7H_4IO_2{}^{35}Cl$-H: 280.8872 $[M-H]^-$; found: 280.8849.

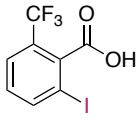
2-Bromo-6-iodobenzoic acid (2d)



The title compound was prepared according the general procedure from 2-bromobenzoic acid (**1d**, 101 mg) at 60 °C. Purification by column chromatography (SiO_2; petroleum ether / ethyl acetate (2% of AcOH), 80:20) afforded **2d** as a colorless solid (114 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.77 (s, br, 1H), 7.81 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.59 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.00 (t, *J* = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.0, 140.6, 138.0, 132.3, 132.0, 118.6, 91.4 ppm. HRMS (ESI): m/z calcd for $C_7H_4{}^{79}BrIO_2$-H: 324.8361 $[M-H]^-$; found: 324.8351.

2-Iodo-6-(trifluoromethyl)benzoic acid (2e)

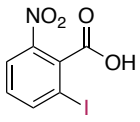


The title compound was prepared according the general procedure from 2-trifluoromethylbenzoic acid (**1e**, 90 mg) at 60 °C. Purification by column chromatography (SiO_2; petroleum ether / ethyl acetate (2% of AcOH), 80:20) afforded **2e** as a colorless solid (96 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.58 (s, 1H), 8.12–8.07 (m, 1H), 7.75–7.69 (m, 1H), 7.32–7.25 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.0, 142.9, 136.9 (q, $^{3}J_{C\text{-}F}$

= 2.2 Hz), 131.0, 128.8 (q, $^{2}J_{C\text{-}F}$ = 32.7 Hz), 125.9 (q, $^{3}J_{C\text{-}F}$ = 4.6 Hz), 122.4 (q, $^{1}J_{C\text{-}F}$ = 274.4 Hz), 93.1 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ 59.97 ppm. HRMS (ESI): m/z calcd for $C_8H_4F_3IO_2$-H: 314.9135 $[M\text{-}H]^-$; found: 314.9190.

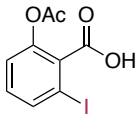
2-Iodo-6-nitrobenzoic acid (2f)



The title compound was prepared according the general procedure from 2-nitrobenzoic acid (**1f**, 84 mg) at 60 °C. Purification by column chromatography (SiO_2; petroleum ether / ethyl acetate (2% of AcOH), 80:20) afforded **2f** as a colorless solid (54 mg, 37%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23–8.19 (m, 2H), 7.34 (t, *J* = 8.1 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.9, 146.1, 145.1, 134.8, 131.4, 124.1, 93.4 ppm. HRMS (ESI): m/z calcd for $C_7H_4INO_4$-H: 291.9107 $[M\text{-}H]^-$; found: 291.9141.

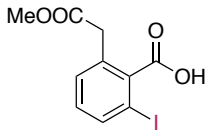
2-Acetoxy-6-iodobenzoic acid (2g)



The title compound was prepared according the general procedure from acetyl salicylic acid (**1g**, 90 mg). Purification by column chromatography (SiO_2; petroleum ether / ethyl acetate (2% of AcOH), 80:20) afforded **2g** as a colorless solid (88 mg, 58%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.17 (s, 1H), 7.78 (m, 1H), 7.21–7.15 (m, 2H), 2.30 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 169.0, 148.2, 137.4, 132.3, 131.7, 123.2, 92.4, 20.9 ppm. HRMS (ESI): m/z calcd for $C_9H_7IO_4$-H: 304.9305 $[M\text{-}H]^-$; found: 304.9276.

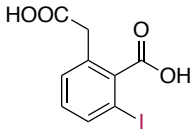
2-Iodo-6-(2-methoxy-2-oxoethyl)benzoic acid (2h)



The title compound was prepared according the general procedure from 2-(2-methoxy-2-oxoethyl)benzoic acid (**1h**, 97 mg) at 60 °C. Purification by column chromatography (SiO_2; petroleum ether / ethyl acetate (2% of AcOH), 80:20) afforded **2h** as a colorless solid (134 mg, 84%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (dd, J = 8.0, 1.1 Hz, 1H), 7.33 (dd, J = 7.8, 1.1 Hz, 1H), 7.13 (t, J = 7.8 Hz, 1H), 5.65 (s, br, 1H), 3.81 (s, 2H), 3.74 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4, 171.3, 139.0, 138.8, 132.9, 131.3, 130.5, 92.6, 52.5, 39.6 ppm. HRMS (ESI): m/z calcd for $C_{10}H_8IO_4$-H: 318.9467 $[M-H]^-$; found: 318.9452.

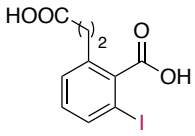
2-(Carboxymethyl)-6-iodobenzoic acid (2i)



The title compound was prepared according the general procedure from 2-(carboxymethyl)benzoic acid (**1i**, 45 mg) at 40 °C. Purification by column chromatography (SiO_2; dichloromethane / methanol, 80:20) afforded **2i** as a colorless solid (38 mg, 50%).

^{1}H NMR (400 MHz, MeOD-d_4): δ 7.80 (d, J = 7.8 Hz, 1H), 7.36 (d, J = 7.8 Hz, 1H), 7.11 (t, J = 7.8 Hz, 1H), 3.70 (s, 2H) ppm. ^{13}C NMR (100 MHz, MeOD-d_4): δ 172.0, 171.6, 147.4, 139.3, 133.9, 131.8, 131.6, 92.4, 40.0 ppm. HRMS (ESI): m/z calcd for $C_9H_7IO_4$ Na^+: 328.9281 $[M+Na^+]^+$; found: 328.9289.

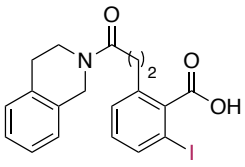
2-(2-Carboxyethyl)-6-iodobenzoic acid (2j)



The title compound was prepared according the general procedure from 2-(2-carboxyethyl)benzoic acid (**1j**, 97 mg). Purification by column chromatography (SiO_2; petroleum ether / ethyl acetate (2% of AcOH), 80:20) afforded **2j** as a colorless solid (125 mg, 78%).

^{1}H NMR (400 MHz, MeOD): δ 7.74 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.34 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.09 (t, *J* = 7.8 Hz, 1H), 3.00–2.92 (m, 2H), 2.65–2.59 (m, 2H) ppm. ^{13}C NMR (100 MHz, MeOD): δ 176.0, 172.4, 142.7, 140.0, 138.3, 131.6, 130.0, 92.1, 36.3, 30.5 ppm. HRMS (ESI): m/z calcd for $C_{10}H_9IO_4$-H: 318.9467 $[M-H]^-$; found: 318.9429.

2-(3-(3,4-Dihydroisoquinolin-2(1*H*)-yl)-3-oxopropyl)-6-iodobenzoic acid (2k)

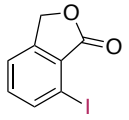


The title compound was prepared according the general procedure from 2-(3-(3,4-dihydroisoquinolin-2(1*H*)-yl)-3-oxopropyl)benzoic acid (**1k**, 155 mg). Purification by column chromatography (SiO_2; petroleum ether / ethyl acetate (2% of AcOH), 80:20) afforded **2k** as a colorless solid (143 mg, 66%).

^{1}H NMR (500 MHz, DMSO-d_6, 90 ^{o}C): δ 7.72 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.09 (dd, *J* = 7.8, 7.6 Hz, 1H), 4.64 (s, 2H), 3.70 (t, *J* = 6.2 Hz, 2H), 2.93 (dd, *J* = 9.5, 6.2 Hz, 2H), 2.85 (t, *J* = 6.0 Hz, 2H), 2.74 (dd, *J* = 9.3, 6.4 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, as a mixture of 2 rotamers, 25 ^{o}C): δ 171.7, 171.6, 170.4, 170.4, 140.8, 138.6, 138.5, 137.7, 137.6, 134.7, 133.8, 132.8, 131.7, 130.7,

130.6, 128.8, 128.2, 128.2, 128.1, 127.2, 126.9, 126.8, 126.7, 126.5, 126.1, 92.7, 92.7, 47.3, 44.6, 43.4, 40.4, 34.8, 34.7, 29.2, 28.9, 28.8, 28.3 ppm. HRMS (ESI): m/z calcd for $C_{19}H_{18}INO_3$-H: 434.0259 $[M-H]^-$; found: 434.0286.

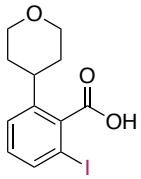
2-(Hydroxymethyl)-6-iodobenzoic acid (2l)



The title compound was prepared according the general procedure from 2-(hydroxymethyl)benzoic acid (**1l**, 76 mg). Purification by column chromatography (SiO_2; CH_2Cl_2) afforded **2l** as a colorless solid (52 mg, 35%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (dt, *J* = 7.8, 0.8 Hz, 1H), 7.51–7.44 (m, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 5.21 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 148.7, 140.4, 134.7, 126.9, 121.9, 92.4, 67.5 ppm. GC-MS: m/z calcd for $C_8H_5IO_2$: 260.0 $[M+H]^+$; found: 261.0.

2-Iodo-6-(tetrahydro-2*H*-pyran-4-yl)benzoic acid (2m)

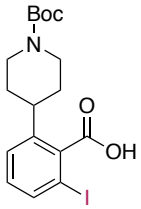


The title compound was prepared according the general procedure from 2-(tetrahydro-2*H*-pyran-4-yl)benzoic acid (**1m**, 103 mg). Purification by column chromatography (SiO_2; petroleum ether / ethyl acetate (2% of AcOH), 80:20) afforded **2m** as a colorless solid (101 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 1H), 7.13 (t, *J* = 7.9 Hz, 1H), 4.12–4.09 (m, 2H), 3.53 (td, *J* = 11.5, 2.8 Hz, 2H), 2.96–2.86 (m, 1H), 1.85–1.81 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 143.9,

138.9, 137.1, 131.3, 126.0, 91.6, 68.2, 40.0, 33.7 ppm. HRMS (ESI): m/z calcd for $C_{12}H_{13}IO_3$-H: 330.9837 $[M-H]^-$; found: 330.9805.

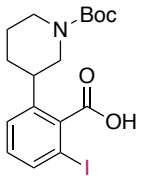
2-(1-(*tert*-Butoxycarbonyl)piperidin-4-yl)-6-iodobenzoic acid (2n)



The title compound was prepared according the general procedure from 2-(1-(*tert*-butoxycarbonyl)piperidin-4-yl)benzoic acid (**1n**, 152 mg). Purification by column chromatography (SiO_2; petroleum ether / ethyl acetate (2% of AcOH), 90:10) afforded **2n** as a colorless solid (87 mg, 40%).

^{1}H NMR (500 MHz, $CDCl_3$, 50 °C): δ 7.68 (dd, J = 7.8, 1.1 Hz, 1H), 7.24 (dd, J = 7.9, 1.1 Hz, 1H), 7.05 (t, J = 7.9 Hz, 1H), 4.23 (d, J = 13.2 Hz, 2H), 2.95–2.87 (m, 1H), 2.85–2.77 (m, 2H), 1.90–1.86 (m, 2H), 1.63–1.58 (m, 2H), 1.49 (s, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.0, 154.9, 144.2, 139.5, 137.1, 130.8, 125.9, 91.9, 79.6, 44.2, 40.5, 28.5, 26.2 ppm. HRMS (ESI): m/z calcd for $C_{17}H_{22}INO_4$-H: 430.0521 $[M-H]^-$; found: 430.0538.

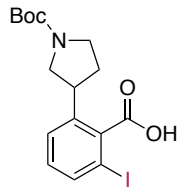
2-(1-(*tert*-Butoxycarbonyl)piperidin-3-yl)-6-iodobenzoic acid (2o)



The title compound was prepared according the general procedure from 2-(1-(*tert*-butoxycarbonyl)piperidin-3-yl)benzoic acid (**1o**, 152 mg) at 40 °C. Purification by column chromatography (SiO_2; petroleum ether / ethyl acetate (2% of AcOH), 90:10) afforded **2o** as a colorless solid (128 mg, 59%).

^{1}H NMR (500 MHz, $CDCl_3$, 50 °C): δ 7.69 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.25 (d, *J* = 8.8 Hz, 1H), 7.05 (t, *J* = 7.9 Hz, 1H), 4.24–4.16 (m, 2H), 3.76–3.73 (m, 2H), 2.95–2.81 (m, 1H), 2.75–2.72 (m, 2H), 1.81–1.68 (m, 2H), 1.47 (s, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.8, 154.6, 141.9, 140.2, 137.3, 130.6, 125.8, 92.0, 79.6, 50.2, 44.0, 32.0, 28.3, 26.2, 25.3 ppm. HRMS (ESI): m/z calcd for $C_{17}H_{22}INO_4$-H: 430.0521 $[M-H]^-$; found: 430.0540.

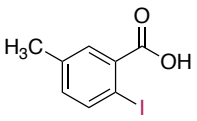
2-(1-(*tert*-Butoxycarbonyl)pyrrolidin-3-yl)-6-iodobenzoic acid (2p)



The title compound was prepared according the general procedure from 2-(1-(*tert*-butoxycarbonyl)pyrrolidin-3-yl)benzoic acid (**1p**, 146 mg) at 40 °C. Purification by column chromatography (SiO_2; petroleum ether / ethyl acetate (2% of AcOH), 90:10) afforded **2p** as a colorless solid (113 mg, 54%).

^{1}H NMR (500 MHz, $CDCl_3$, 50 °C): δ 7.71 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.07 (t, *J* = 7.9 Hz, 1H), 3.92–3.67 (m, 2H), 3.67–3.50 (m, 2H), 3.47–3.31 (m, 1H), 2.35–2.19 (m, 1H), 2.05–1.91 (m, 1H), 1.48 (s, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.0, 154.4, 140.3, 137.6, 130.9, 125.7, 92.0, 79.4, 45.5, 32.7, 28.5, 28.1, 26.2 ppm. HRMS (ESI): m/z calcd for $C_{16}H_{20}INO_4$-H: 416.0364 $[M-H]^-$; found: 416.0405.

2-Iodo-5-methylbenzoic acid (2q)

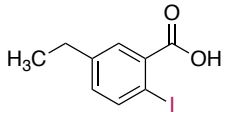


The title compound was prepared according the general procedure from 3-methylbenozic acid (**1q**, 68 mg). Purification by column chromatography (SiO_2;

petroleum ether / ethyl acetate (2% of AcOH), 80:20) afforded **2q** as a colorless solid (85 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.1 Hz, 1H), 7.84 (dd, *J* = 2.3, 0.9 Hz, 1H), 7.03 (m, 1H), 2.36 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 141.7, 138.2, 134.6, 132.9, 132.8, 90.6, 20.8 ppm. HRMS (ESI): m/z calcd for $C_8H_7IO_2$-H: 260.9412 $[M-H]^-$; found: 260.9465.

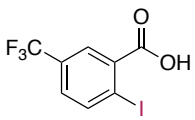
5-Ethyl-2-iodobenzoic acid (2r)



The title compound was prepared according the general procedure from 3-ethylbenzoic acid (**1r**, 68 mg). Purification by column chromatography (SiO_2; petroleum ether / ethyl acetate (2% of AcOH), 80:20) afforded **2r** as a colorless solid (83 mg, 60%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 2.3 Hz, 1H), 7.05 (dd, *J* = 8.1, 2.3 Hz, 1H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 144.5, 141.7, 133.4, 132.9, 131.6, 90.9, 28.2, 15.2 ppm. HRMS (ESI): m/z calcd for $C_9H_9IO_2$-H: 274.9574 $[M-H]^-$; found: 274.9550.

2-Iodo-5-(trifluoromethyl)benzoic acid (2s)

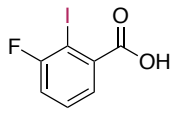


The title compound was prepared according the general procedure from 3-(trifluoromethyl)benzoic acid (**1s**, 95 mg) at 60 °C using 5 mol% of catalyst loading.

Purification by column chromatography (SiO_2; petroleum ether / ethyl acetate (2% of AcOH), 80:20) afforded **2s** as a colorless solid (96 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J = 2.3 Hz, 1H), 8.22 (dd, J = 8.2, 0.9 Hz, 1H), 7.45 (dd, J = 8.3, 2.3 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5, 142.9, 133.9, 130.9 (q, $^2J_{C-F}$ = 33.6 Hz), 129.7 (q, $^3J_{C-F}$ = 3.5 Hz), 128.7 (q, $^3J_{C-F}$ = 3.8 Hz), 123.3 (q, $^1J_{C-F}$ = 272.5 Hz), 99.2 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ −63.2 (s) ppm. HRMS (ESI): m/z calcd for $C_8H_4F_3IO_2$-H: 314.9130 [M-H]$^-$; found: 314.9141.

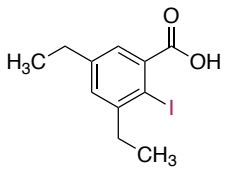
3-Fluoro-2-iodobenzoic acid (2t)



The title compound was prepared according the general procedure from 3-fluorobenzoic acid (**1t**, 70 mg). Purification by column chromatography (SiO_2; petroleum ether / ethyl acetate (2% of AcOH), 80:20) afforded **2t** as a colorless solid (57 mg, 43%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (ddd, J = 7.8, 1.5, 0.8 Hz, 1H), 7.42 (ddd, J = 8.2, 7.7, 5.3 Hz, 1H), 7.28−7.22 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 162.33 (d, J_{C-F} = 244.9 Hz), 135.6, 129.78 (d, J_{C-F} = 8.3 Hz), 127.59 (d, J_{C-F} = 3.1 Hz), 119.16 (d, J_{C-F} = 25.8 Hz), 83.60 (d, J_{C-F} = 27.4 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ −85.9 (s) ppm. HRMS (ESI): m/z calcd for $C_7H_4FIO_2$-H: 264.9219 [M-H]$^-$; found: 264.9156.

3,5-Diethyl-2-iodobenzoic acid (2u)

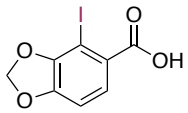


The title compound was prepared according the general procedure from 3,5-diethylbenzoic acid (**1u**, 89 mg). Purification by column chromatography (SiO_2;

petroleum ether / ethyl acetate (2% of AcOH), 80:20) afforded **2u** as a colorless solid (79 mg, 52%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 2.2 Hz, 1H), 7.22 (d, J = 2.2 Hz, 1H), 2.86 (q, J = 7.5 Hz, 2H), 2.64 (q, J = 7.6 Hz, 2H), 1.27–1.21 (m, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 148.6, 144.4, 136.5, 131.5, 128.0, 95.7, 35.3, 28.1, 15.2, 14.7 ppm. HRMS (ESI): m/z calcd for $C_{11}H_{13}IO_2$-H: 302.9890 $[M-H]^-$; found: 302.9890.

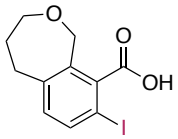
4-Iodobenzo[*d*][1,3]dioxole-5-carboxylic acid (2v)



The title compound was prepared according the general procedure from benzo[*d*][1,3]dioxole-5-carboxylic acid (**1v**, 83 mg). Purification by column chromatography (SiO_2; petroleum ether / ethyl acetate (2% of AcOH), 90:10) afforded **2v** as a colorless solid (130 mg, 89%).

^{1}H NMR (400 MHz, Acetone-d_6): δ 7.63 (d, J = 8.2 Hz, 1H), 6.91 (d, J = 8.2 Hz, 1H), 6.18 (s, 2H) ppm. ^{13}C NMR (100 MHz, Acetone-d_6): δ 165.6, 151.2, 148.6, 127.2, 126.7, 107.3, 101.3, 71.7 ppm. HRMS (ESI): m/z calcd for $C_8H_5IO_4$-H: 292.9216 $[M-H]^-$; found: 292.9154.

8-Iodo-1,3,4,5-tetrahydrobenzo[*c*]oxepine-9-carboxylic acid (2w)

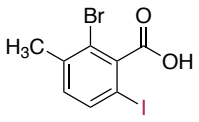


The title compound was prepared according the general procedure from 1,3,4,5-tetrahydrobenzo[*c*]oxepine-9-carboxylic acid (**1w**, 96 mg) at 40 °C. Purification by

column chromatography (SiO_2; petroleum ether / ethyl acetate (2% of AcOH), 80:20) afforded **2w** as a colorless solid (84 mg, 53%).

^{1}H NMR (400 MHz, MeOD): δ 7.65 (d, *J* = 7.9 Hz, 1H), 6.97 (d, *J* = 7.9 Hz, 1H), 4.64 (s, 2H), 4.08–3.86 (m, 2H), 3.05–2.99 (m, 2H), 1.87–1.73 (m, 2H) ppm. ^{13}C NMR (100 MHz, MeOD): δ 172.8, 142.7, 142.2, 141.6, 137.9, 131.7, 90.9, 76.2, 74.7, 33.3, 30.8 ppm. HRMS (ESI): m/z calcd for $C_{11}H_{11}IO_3$-H: 316.9680 $[M-H]^-$; found: 316.9680.

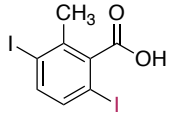
2-Bromo-6-iodo-3-methylbenzoic acid (2x)



The title compound was prepared according the general procedure from 2-bromo-3-methylbenzoic acid (**1x**, 108 mg). Purification by column chromatography (SiO_2; petroleum ether / ethyl acetate (2% of AcOH), 80:20) afforded **2x** as a colorless solid (157 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 5.90 (s, br, 1H), 2.40 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.6, 141.0, 138.9, 137.6, 132.7, 121.0, 87.3, 23.0 ppm. HRMS (ESI): m/z calcd for $C_8H_6{}^{79}BrIO_2$-H^+: 338.8518 $[M-H]^-$; found: 338.8518.

3,6-Diiodo-2-methylbenzoic acid (2y)

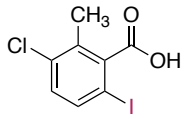


The title compound was prepared according the general procedure from 3-iodo-2-methylbenzoic acid (**1y**, 131 mg) at 40 °C. Purification by column chromatography

(SiO_2; petroleum ether / ethyl acetate (2% of AcOH), 80:20) afforded **2y** as a colorless solid (136 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.3 Hz, 1H), 7.36 (dd, *J* = 8.3, 0.7 Hz, 1H), 2.54 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 141.4, 139.6, 139.0, 137.8, 101.8, 90.9, 26.6 ppm. HRMS (ESI): m/z calcd for $C_8H_6I_2O_2$-H: 386.8384 [M-H]$^-$; found: 386.8378.

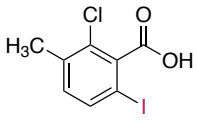
3-Chloro-6-iodo-2-methylbenzoic acid (2z)



The title compound was prepared according the general procedure from 3-chloro-2-methylbenzoic acid (**1z**, 85 mg). Purification by column chromatography (SiO_2; petroleum ether / ethyl acetate (2% of AcOH), 80:20) afforded **2z** as a colorless solid (145 mg, 98%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.5 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 2.47 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 140.8, 137.5, 135.4, 134.4, 131.6, 88.5, 18.1 ppm. HRMS (ESI): m/z calcd for $C_8H_6{}^{35}ClIO_2$-H: 294.9023 [M-H]$^-$; found: 294.9014.

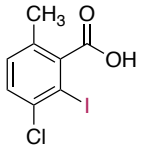
2-Chloro-6-iodo-3-methylbenzoic acid (2aa)



The title compound was prepared according the general procedure from 2-chloro-3-methylbenzoic acid (**1aa**, 85 mg). Purification by column chromatography (SiO_2; petroleum ether / ethyl acetate (2% of AcOH), 80:20) afforded **2aa** as a colorless solid (133 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.1 Hz, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 5.98 (s, br, 1H), 2.36 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.2, 138.8, 137.02, 136.97, 132.9, 130.8, 87.5, 19.9 ppm. HRMS (ESI): m/z calcd for $C_8H_6{}^{35}ClIO_2$-H: 294.9023 $[M-H]^-$; found: 294.9028.

3-Chloro-2-iodo-6-methylbenzoic acid (2ab)

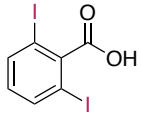


The title compound was prepared according the general procedure from 5-chloro-2-methylbenzoic acid (**1ab**, 85 mg). Purification by column chromatography (SiO_2; petroleum ether / ethyl acetate (2% of AcOH), 80:20) afforded **2ab** as a colorless solid (130 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.70 (s, br, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.17 (d, *J* = 8.2 Hz, 1H), 2.42 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.7, 141.9, 136.9, 134.0, 131.3, 129.7, 95.8, 19.6 ppm. HRMS (ESI): m/z calcd for $C_8H_6{}^{35}ClIO_2$-H: 294.9023 $[M-H]^-$; found: 294.9034.

Synthesis and characterization data for *ortho*-diiodobenzoic acids 3

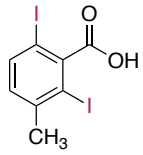
2,6-Diiodobenzoic acid (3ac)



The title compound was prepared according the general procedure from benzoic acid (**1ac**, 62 mg) at 65 °C and 2 equiv. of NIS. Purification by column chromatography (SiO_2; petroleum ether / ethyl acetate (2% of AcOH), 80:20) afforded **3ac** as a colorless solid (127 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8.0 Hz, 2H), 6.81 (t, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.8, 144.4, 138.7 (2C), 132.1, 90.7 (2C) ppm. HRMS (ESI): m/z calcd for $C_7H_4I_2O_2$-H: 372.8222 $[M-H]^-$; found: 372.8235.

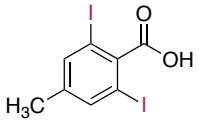
2,6-Diiodo-3-methylbenzoic acid (3q)



The title compound was prepared according the general procedure from 2-toluic acid (**1q**, 68 mg) at 65 °C and 3 equiv. of NIS. Purification by column chromatography (SiO_2; petroleum ether / ethyl acetate (2% of AcOH), 80:20) afforded **3q** as a colorless solid (116 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, J = 8.1 Hz, 1H), 6.99 (d, J = 8.1 Hz, 1H), 2.45 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.1, 145.3, 142.7, 138.6, 131.5, 97.8, 86.5, 28.6 ppm. HRMS (ESI): m/z calcd for $C_8H_6I_2O_2$-H: 386.8379 $[M-H]^-$; found: 386.8482.

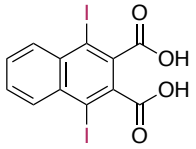
2,6-Diiodo-4-methylbenzoic acid (3ad)



The title compound was prepared according the general procedure from 4-methylbenozic acid (**1ad**, 68 mg). Purification by column chromatography (SiO_2; petroleum ether / ethyl acetate (2% of AcOH), 90:10) afforded **3ad** as a colorless solid (146 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 0.8 Hz, 2H), 2.28 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.8, 142.8, 141.6, 139.4 (2C), 90.4 (2C), 20.3 ppm. HRMS (ESI): m/z calcd for $C_8H_6I_2O_2$-H: 386.8379 $[M-H]^-$; found: 386.8370.

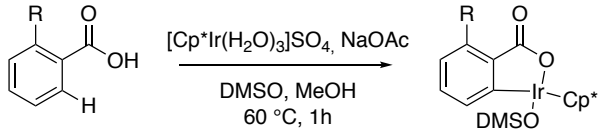
1,4-Diiodonaphthalene-2,3-dicarboxylic acid (3ae)



The title compound was prepared according the general procedure from naphthalene-2,3-dicarboxylic acid (**1ae**, 108 mg) at 40 °C and 3 equiv. of NIS. Purification by column chromatography (SiO_2; petroleum ether / ethyl acetate (2% of AcOH), 80:20) afforded **3ae** as a colorless solid (150 mg, 64%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60–8.55 (m, 2H), 7.96–7.92 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0 (2C), 137.6 (2C), 135.4 (2C), 132.5 (2C), 129.3 (2C), 102.5 (2C) ppm. HRMS (ESI): m/z calcd for $C_{12}H_6I_2O_4$-H: 466.8277 $[M-H]^-$; found: 466.8346.

Synthesis of Iridacycle 6a, 6c, 6e and 6f[1]

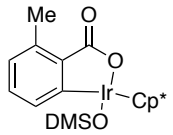


1 **6**

The benzoic acid derivative **1** (0.18 mmol), $[Cp^*Ir(H_2O)_3]SO_4$ (0.18 mmol, 80.4 mg), NaOAc (0.36 mmol, 29.4 mg) and DMSO (0.36 mmol, 28.2 mg, 25.6 µl) were dissolved in MeOH (0.05 M, 3.6 mL), heated to 60 ^{o}C and stirred for 1 h. The solvent was evaporated and the crude was dissolved in dichloromethane (5 mL). The iridacycle **6** was washed by stirring over $NaHCO_3$ (sat., 5 mL) for 10 min, and the phases were then separated. The organic phase was then washed further by stirring

over Na_2SO_4 (sat., 5 mL) for 10 minutes. The organic phase was collected, the solvent evaporated and the iridacycle **6** was collected as yellow crystals.

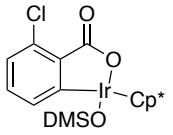
Iridacycle 6a



Iridacycle **6a** was prepared according to the general procedure from 2-methylbenzoic acid (**1a**) (0.20 mmol, 27.2 mg). The reaction afforded **6a** as yellow crystals (85 mg, 90%).

^{1}H NMR (400 MHz, MeOD): δ 7.49 (d, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 2.87 (s, 3H), 2.67 (s, 3H), 2.52 (s, 3H), 1.77 (s, 15H) ppm. ^{13}C NMR (100 MHz, MeOD): δ 185.2, 152.8, 141.3, 134.5, 133.7, 131.4, 127.5, 94.4, 42.7, 40.6, 18.4, 7.5 ppm. HRMS (ESI): m/z calcd for $C_{18}H_{21}O_2IrNa^+$: 485.1063 [M-DMSO+Na^+]$^+$; found: 485.1066.

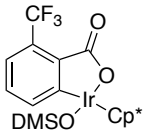
Iridacycle 6c



Iridacycle **6c** was prepared according to the general procedure from 2-chlorobenzoic acid **1c** (0.05 mmol, 7.83 mg). The reaction afforded **6c** as yellow crystals (13 mg, 46%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52–7.46 (m, 1H), 7.19–7.07 (m, 2H), 3.03 (s, 3H), 2.50 (s, 3H), 1.76 (s, 15H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.3, 154.0, 136.1, 134.2, 133.2, 131.9, 127.3, 94.4, 43.6, 43.2, 8.8 ppm. HRMS (ESI): m/z calcd for $C_{17}H_{18}O_2{}^{35}ClIrNa^+$: 505.0509 [M-DMSO+$Na^+$]$^+$; found: 505.0520.

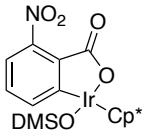
Iridacycle 6e



Iridacycle **6e** was prepared according to the general procedure from 2-chlorobenzoic acid **1e** (0.36 mmol, 68 mg) during 16 h. The reaction afforded **6e** as yellow crystals (100 mg, 48%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.4 Hz, 1H), 7.40 (d, J = 7.6 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 2.95 (s, 3H), 2.42 (s, 3H), 1.69 (s, 15H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 152.6, 139.6, 135.1, 130.5, 130.3 (q, $^{2}J_{C\text{-}F}$ = 31.5 Hz), 123.4 (q, $^{1}J_{C\text{-}F}$ = 274.0 Hz), 122.8 (q, $^{3}J_{C\text{-}F}$ = 7 Hz), 94.3, 43.4, 42.7, 8.6 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ -58.61 ppm. HRMS (ESI): m/z calcd for $C_{18}H_{18}F_3O_2IrNa^+$: 539.0780 $[M\text{-}DMSO+Na^+]^+$; found: 539.0768.

Iridacycle 6f

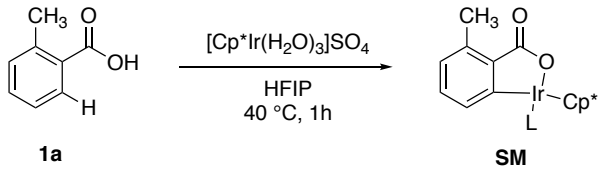


Iridacycle **6f** was prepared according to the general procedure from 2-chlorobenzoic acid **1f** (0.32 mmol, 53.5 mg) during 16 h. The reaction afforded **6f** as yellow crystals (160 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, J = 7.5, 1.0 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H), 7.02 (dd, J = 7.7, 1.0 Hz, 1H), 2.96 (s, 3H), 2.48 (s, 3H), 1.70 (s, 15H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.8, 178.1, 153.0, 151.4, 137.4, 131.6, 128.4, 117.5, 94.4, 43.8, 42.8, 8.7 ppm. HRMS (ESI): m/z calcd for $C_{17}H_{18}NO_4IrNa^+$: 516.0758 $[M\text{-}DMSO+Na^+]^+$; found: 516.0823.

Experimental control experiments

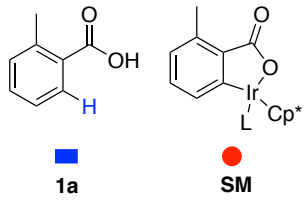
Synthesis of iridacycle SM under the reaction conditions used in catalytic experiments:



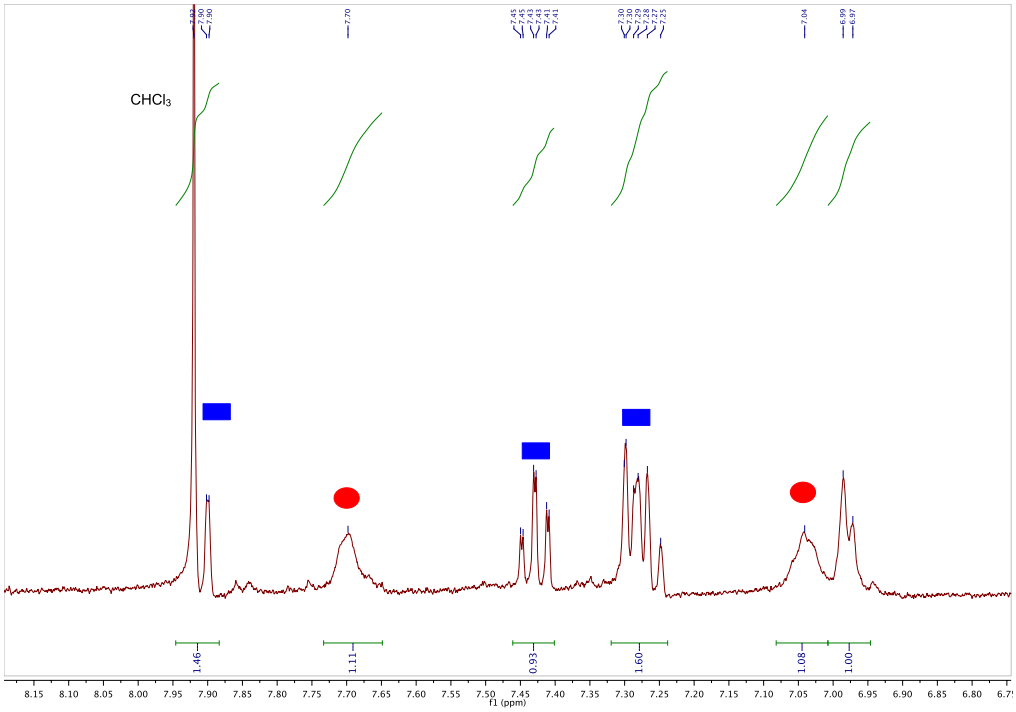
1a **SM**

2-Methylbenzoic acid **1a** (0.05 mmol, 6.7 mg) and $[Cp^*Ir(H_2O)_3]SO_4$ (0.055 mmol, 26.4 mg) were dissolved in HFIP (0.01 M, 0.5 mL), heated to 40 °C and stirred for 1 h. The solvent was evaporated and the unreacted carboxylic acid was removed with $CHCl_3$. The remaining yellow solid was dissolved in MeOD-d_4 and analyzed by ^1H NMR spectroscopy. The iridacycle was observed in a *ca.* 1:1 mixture with acid **1a**. The yield could not be estimated.

^1H NMR (400 MHz, MeOD-d_4): δ 7.74–7.65 (m, br, 1H), 7.09–7.01 (m, br, 1H), 7.01-6.92 (m, br, 1H), 2.75 (s, 3H), 1.68 (s, 15H) ppm.



1a **SM**



Study of the reaction by ^{1}H NMR spectroscopy. Characterization of reaction intermediates:

2-Methylbenzoic acid **1a** (0.05 mmol, 6.7 mg) and $[Cp^*Ir(H_2O)_3]SO_4$ (0.05 mmol, 25 mg) were dissolved in HFIP (0.01 M, 0.5 mL). The solution was transferred into a 5 mm NMR tube, and a 3 mm NMR tube filled with DMSO-d_6 used for external referencing was assembled inside. The coaxial tubes were then transferred to the NMR spectrometer (500 MHz) at 25 °C. The iridacycle **SM** (yellow marks) was observed in a *ca.* 1:1.5 mixture with 2-methylbenzoic acid **1a** (pink marks) (Figure S1).

In a second experiment, 2-methylbenzoic acid **1a** (0.05 mmol, 6.7 mg) and $[Cp^*Ir(H_2O)_3]SO_4$ (0.05 mmol, 25 mg) were dissolved in HFIP (0.01 M, 0.5 mL). After 5 min, NIS (0.03 mmol, 7 mg) was added and the mixture was transferred into a 5 mm NMR tube. A a 3 mm NMR tube filled with DMSO-d_6 used for external referencing was assembled inside. The coaxial tubes were then transferred to the NMR spectrometer (500 MHz) at 25 °C. an NMR tube, fitted with a capillary tube filled with DMSO-d_6. The tube was then transferred to the NMR spectrometer (500 MHz) at 25 °C. In addition to iridacycle **SM** and 2-methylbenzoic acid **1a**, a new iridacycle **INT** (blue marks) was observed after 5 min at rt. This new iridacycle is only formed upon addition of NIS. The mixture consisted of *ca.* 1:1.1:2.4 mixture of **INT**:**SM**:**1a** (Figure S2). Then, ^{1}H NMR experiments were measured at different times at 40 °C (5 min, 2 h, 13 h). As shown in Figure S3, formation of product **2a** was observed as the concentration of iridacycles diminished.

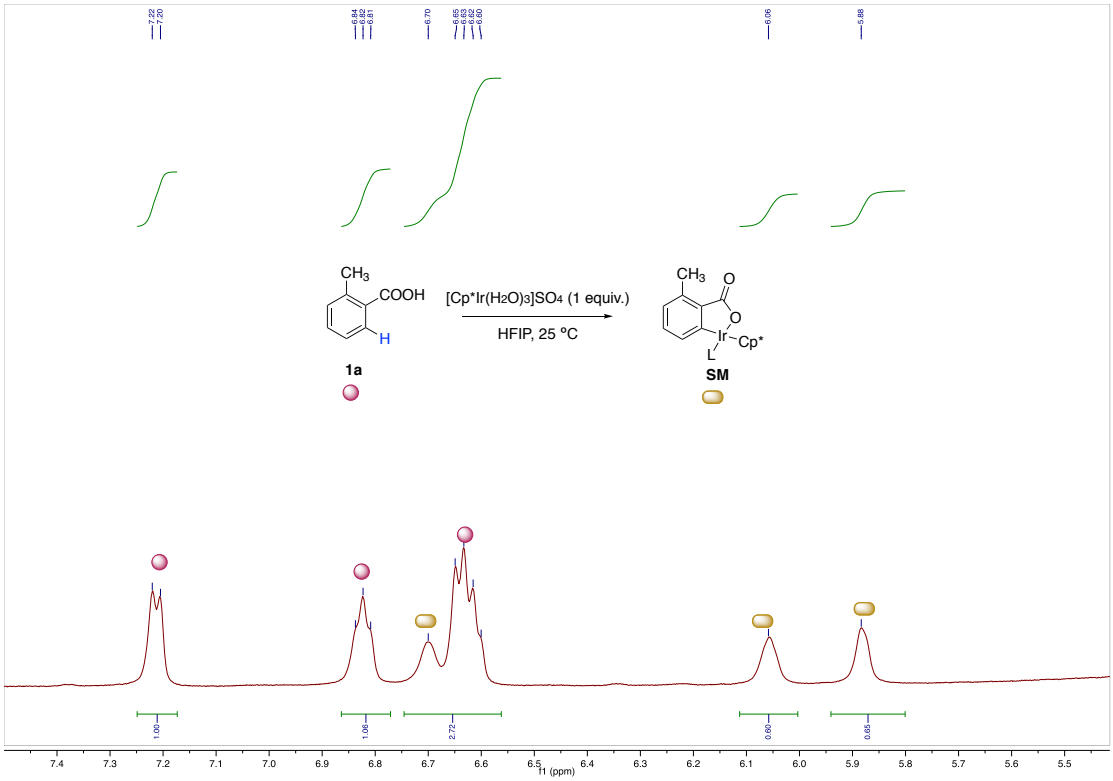


Figure S1. ^{1}H NMR experiment of **1a** with catalyst **II**.

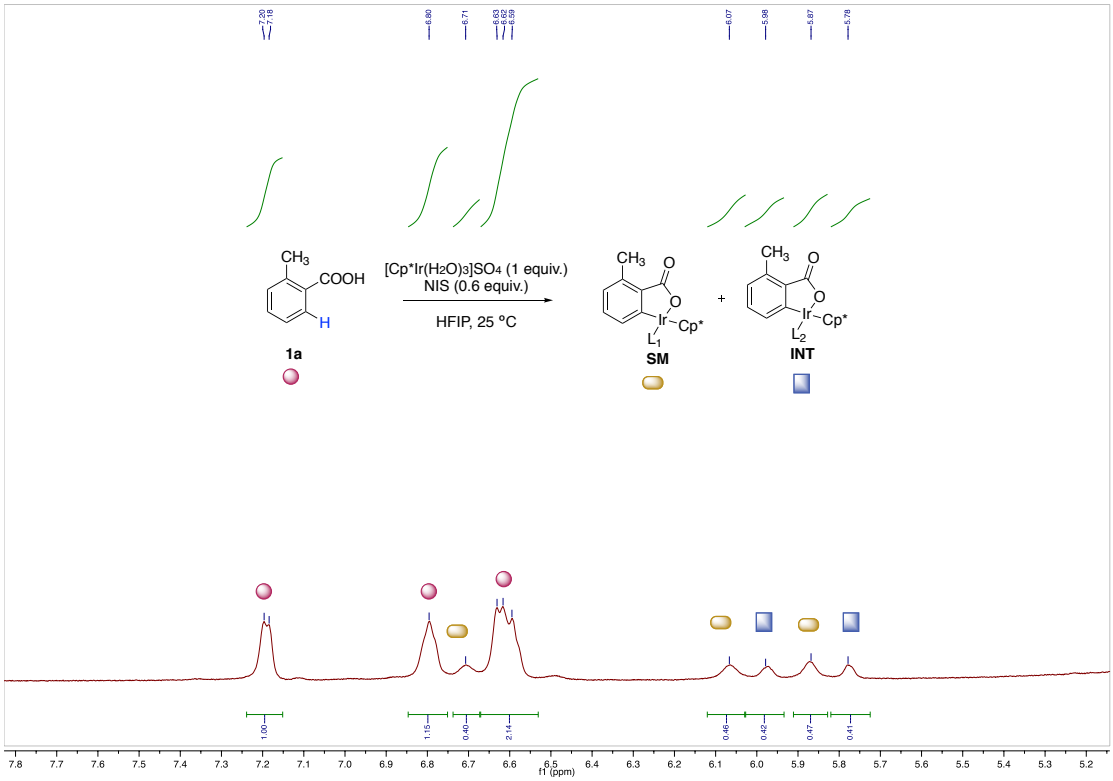


Figure S2. ^{1}H NMR experiment of **1a** with catalyst **II** and NIS after 10 mins at rt.

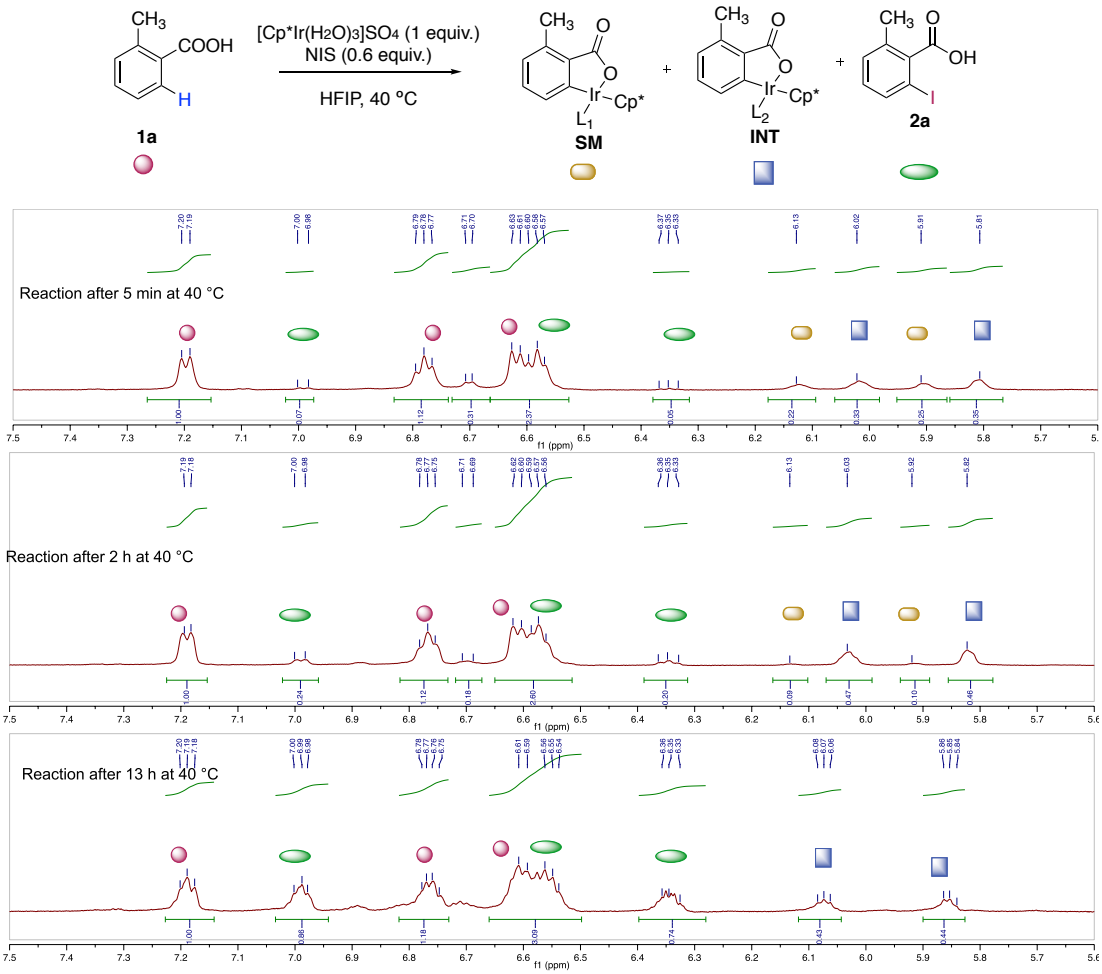
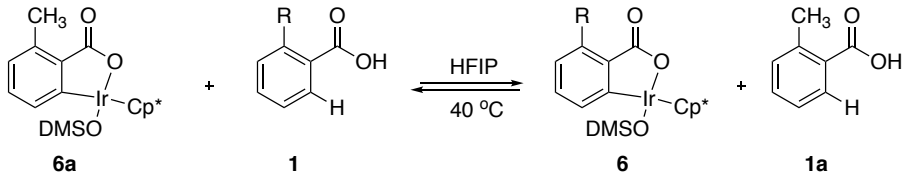


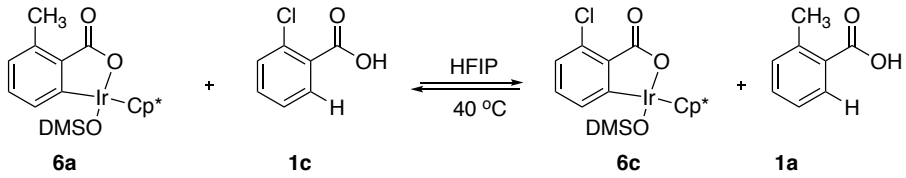
Figure S3. ^{1}H NMR experiments of **1a** with catalyst **II** and NIS at 40 °C.

Reversibility of the C–H activation:



Iridacycle **6a** (0.037 mmol, 20 mg) and corresponding *ortho*-substituted benzoic acid **1** (0.037 mmol) was dissolved in HFIP (0.1M, 0.37 mL) and stirred at 40 °C for 1 h. The solvent was evaporated and the crude mixture dissolved in $CDCl_3$ and analyzed by ^{1}H NMR. The same experiment was repeated for 16 h.

- Reversibility of the C–H activation (**6a** +**1c**):

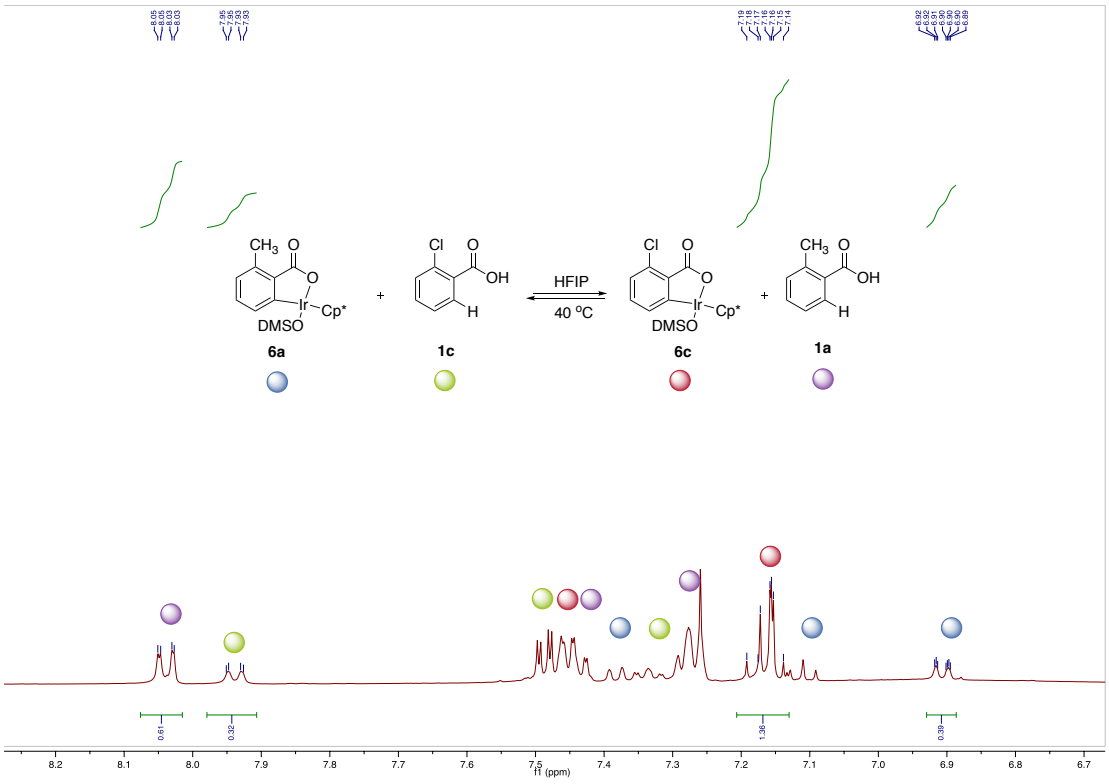


t = 0 **6a** : **1c** : **6c** : **1a** = 1.00 : 1.00 : 0.00 : 0.00

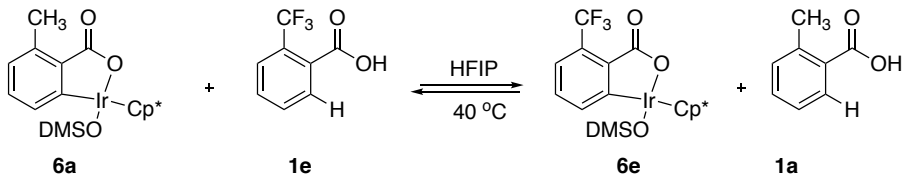
t = 1 h **6a** : **1c** : **6c** : **1a** = 0.30 : 0.41 : 0.59 : 0.70

t = 16 h **6a** : **1c** : **6c** : **1a** = 0.39 : 0.32 : 0.68 : 0.61

A mixture of **6a**, **1c**, **6c**, and **1a** was obtained in both experiments (see above). The ^{1}H NMR spectrum after 16 h is shown below. The ratio was therefore estimated to: **6a** : **1c** : **6c** : **1a** = 0.39 : 0.32 : 0.68 : 0.61 ca = 0.4 (blue) : 0.3 (green) : 0.7 (pink) : 0.6 (purple) after 16 h. The ratio was essentially the same after only 1 h.



- Reversibility of the C–H activation (**6a** +**1e**):

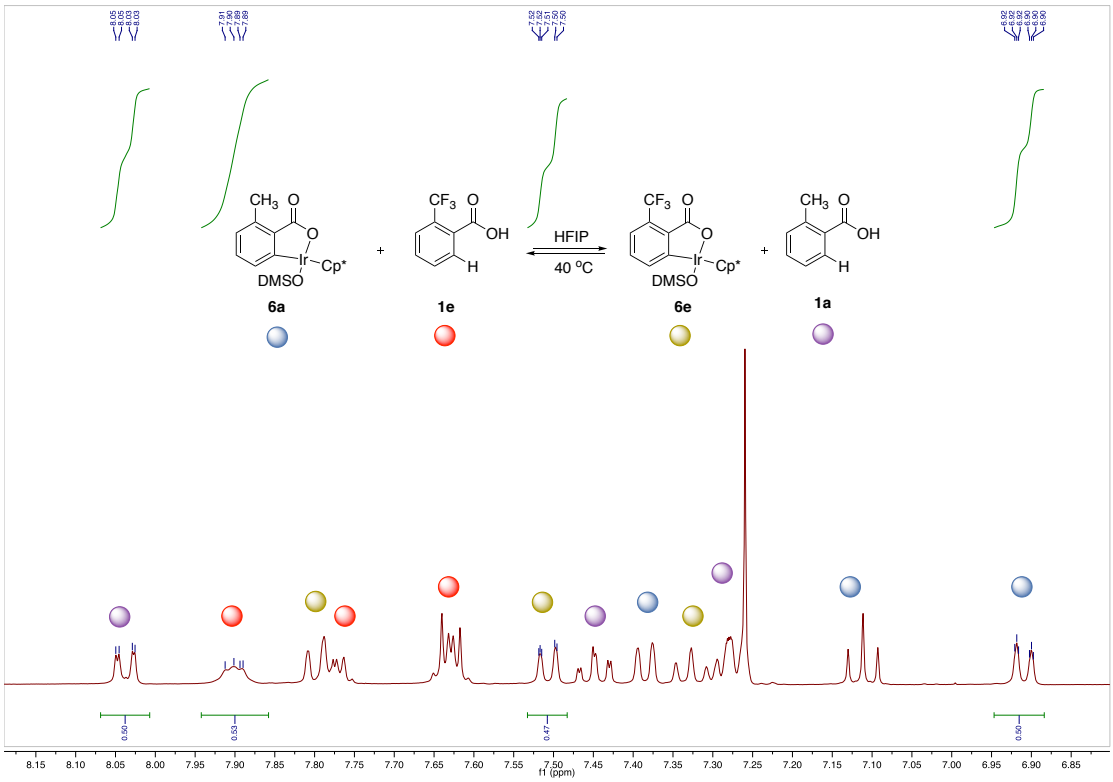


t = 0 **6a** : **1e** : **6e** : **1a** = 1 : 1 : 0 : 0

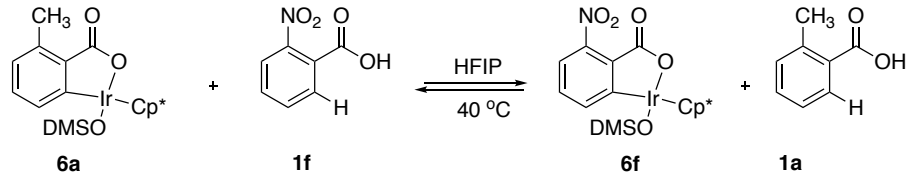
t = 1 h **6a** : **1e** : **6e** : **1a** = 0.45 : 0.58 : 0.55 : 0.42

t = 16 h **6a** : **1e** : **6e** : **1a** = 0.50 : 0.53 : 0.47 : 0.50

A mixture of **6a**, **1e**, **6e**, and **1a** was obtained in both experiments (see above). The ^{1}H NMR spectrum after 16 h is shown below. The ratio was therefore estimated to: **6a** : **1e** : **6e** : **1a** = 0.50 : 0.53 : 0.47 : 0.50 ca = 0.5 (blue) : 0.5 (red) : 0.5 (yellow) : 0.5 (purple) after 16 h. The ratio was essentially the same after only 1 h.



- Reversibility of the C–H activation (**6a** +**1f**):

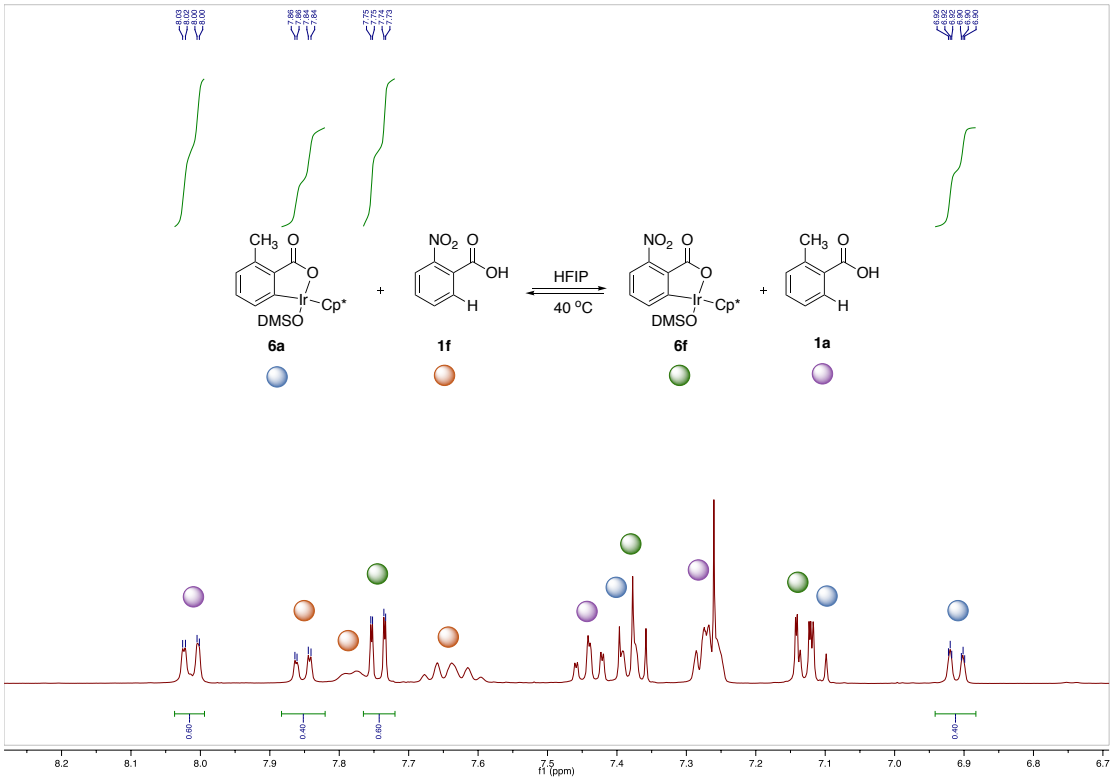


t = 0 **6a** : **1f** : **6f** : **1a** = 1 : 1 : 0 : 0

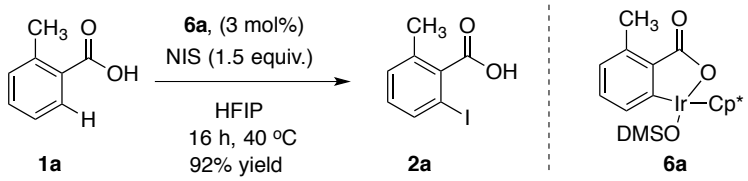
t = 1 h **6a** : **1f** : **6f** : **1a** = 0.41 : 0.49 : 0.51 : 0.59

t = 16 h **6a** : **1f** : **6f** : **1a** = 0.40 : 0.40 : 0.60 : 0.60

A mixture of **6a**, **1f**, **6f**, and **1a** was obtained in both experiments (see above). The ^{1}H NMR spectrum after 16 h is shown below. The ratio was therefore estimated to: **6a** : **1f** : **6f** : **1a** = 0.40 : 0.40 : 0.60 : 0.60 ca = 0.4 (blue) : 0.4 (orange) : 0.6 (green) : 0.6 (purple) after 16 h. The ratio was essentially the same after only 1 h.

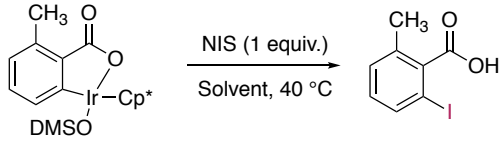


***ortho*-Iodination of 1a catalyzed by iridacycle 6a:**



Benzoic acid 1 (0.5 mmol), iridacycle 6a (3.0 mol%, 0.015 mmol, 8 mg) and *N*-iodosuccinimide (0.75 mmol, 169 mg) was dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP, 0.1 M, 5.0 mL) under air atmosphere in a capped vial and stirred at 40 °C for 16 hours. The reaction was quenched by addition of $Na_2S_2O_3$ (sat) (2 mL) and then acidified by HCl (1.0 M) to pH <2. The aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL), and the combined organic phases were washed with brine (10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. ^{1}H NMR yields of 2a (92% yield) was calculated using 1 equiv. of 2,3,5,6-tetrachloro-4-nitrobenzene as internal standard.

Reaction of iridacycle 6a with NIS in different solvents:



6a **2a**

Iridacycle **6a** (0.037 mmol, 20 mg) and NIS (0.037 mmol, 9 mg) were dissolved in the solvent (0.1 M, 0.4 mL) in a capped vial. The solution was transferred into an NMR tube with an internal tube for the D_2O, which was then transferred to the NMR spectrometer with the probe preheated at 40 °C. Signals from the aromatic protons of the product were used to monitor the formation of 2-iodo-6-methylbenzoic acid (**2a**).

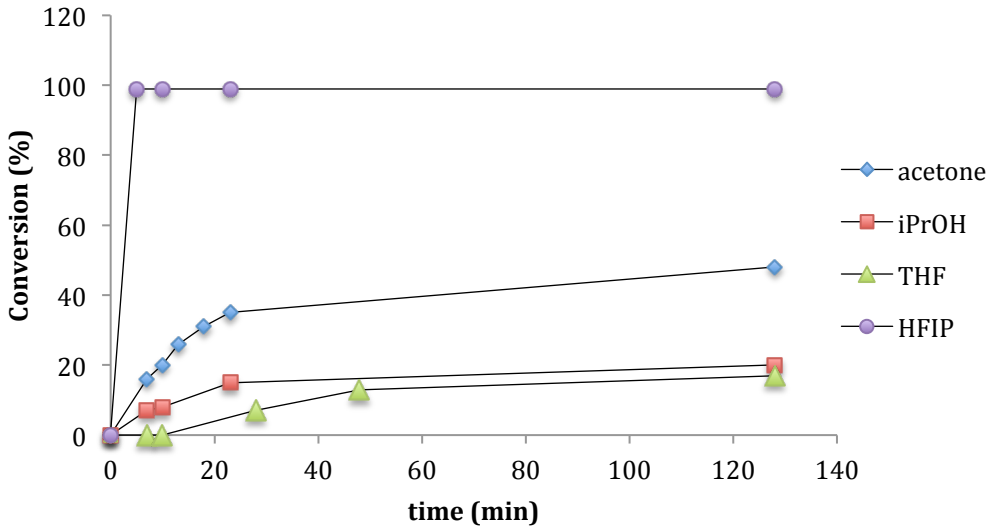
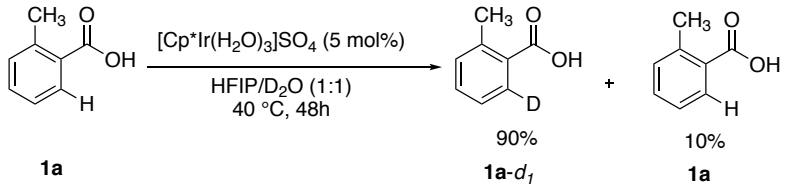


Figure S4. Kinetic profile of Iridacycle **6a** with NIS in several solvents.

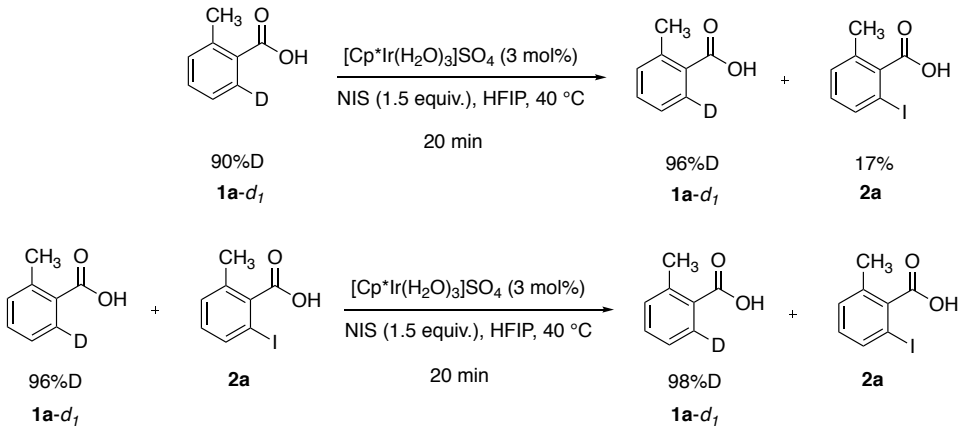
Synthesis of 2-iodobenzoic-6-d_1 acid (1a-d_1)

The synthesis was performed by treating **1a** with $[Cp^*Ir(H_2O)_3]SO_4$ in HFIP / D_2O (see details below). Since only a 90% D was obtained, we took advantage of the KIE /*vide infra*) and subjected **1a**-d_1 (90% D) to the iodination conditions for a short reaction time. The non-reacted starting material was recovered. This last iodination process was repeated to finally obtained **1a**-d_1 (98% D):

Benzoic acid **1a** (0.5 mmol, 68 mg), $[Cp^*Ir(H_2O)_3]SO_4$ (5.0 mol%, 0.025 mmol, 12 mg) was dissolved in HFIP / D_2O (1:1) (0.1 M, 5.0 mL) in a capped vial and stirred at 40 ^oC for 48 h. The reaction was quenched by addition of $Na_2S_2O_3$ (sat) (2 mL) and then acidified by HCl (1.0 M) to pH <2. The aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL), and the combined organic phases were washed with brine (10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The product was purified by column chromatography (petroleum ether / ethyl acetate (2% of AcOH)) providing the *ortho*-iodobenzoic acid **1a**-d_1 with 90% D.



The *ortho*-iodobenzoic acid **1a**-d_1 (90% D, 0.365 mmol, 50 mg) was then treated with $[Cp^*Ir(H_2O)_3]SO_4$ (3.0 mol%, 0.011 mmol, 5 mg) and NIS (0.546 mmol, 123 mg) and was dissolved in HFIP (0.1 M, 3.7 mL) in a capped vial and stirred at 40 °C for 20 mins. The reaction was quenched by addition of $Na_2S_2O_3$ (sat) (2 mL) and then acidified by HCl (1.0 M) to pH <2. The aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL), and the combined organic phases were washed with brine (10 mL), dried over $MgSO_4$, and concentrated under reduced pressure recovering **1a**-d_1 (96% D) in 83% yield. Without any purification the mixture was treated to the iodination condition again for 20 mins. The starting material was recovered by column chromatography (petroleum ether / ethyl acetate (2% of AcOH)) providing the 2-iodobenzoic acid **1a**-d_1 with 78% yield (98% D).



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (t, J = 7.5 Hz, 1H), 7.30–7.28 (m, 2H), 2.68 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 141.4, 133.0, 131.9, 131.3 (t, $^1J_{C\text{-}^2H}$ = 24.9 Hz), 128.2, 125.7, 22.1 ppm. HRMS (ESI): m/z calcd for $C_8H_6DO_2$-H: 136.0509 $[M\text{-}H]^-$; found: 136.0510.

Kinetic isotope effect

Two parallel reactions, one with 2-methylbenzoic acid (**1a**) and another with 2-methylbenzoic acid-6-d_1 (98% D, **1a**-d_1), were carried out. Benzoic acid **1** or **1a**-d_1 (0.2 mmol), $[Cp^*Ir(H_2O)_3]SO_4$ (3.0 mol%, 0.006 mmol, 3 mg) and NIS (0.3 mmol, 68 mg) were dissolved in HFIP / $CDCl_3$ (2:1) (0.1 M, 2.0 mL) in a capped vial. The solution was transferred into an NMR tube and the tube was transferred to the NMR spectrometer with the probe preheated at 40 °C. Signals from the aromatic protons of the product were used to monitor the formation of 2-iodo-6-methylbenzoic acid (**2a**). ^{1}H NMR spectra were recorded every 1 min. Each experiment was done three times. The average of the initial rate plots for the experiments with each acid (**1a**, **1a**-d_1) are given in Figure S2. A KIE of 2.90 ± 0.36 was obtained.

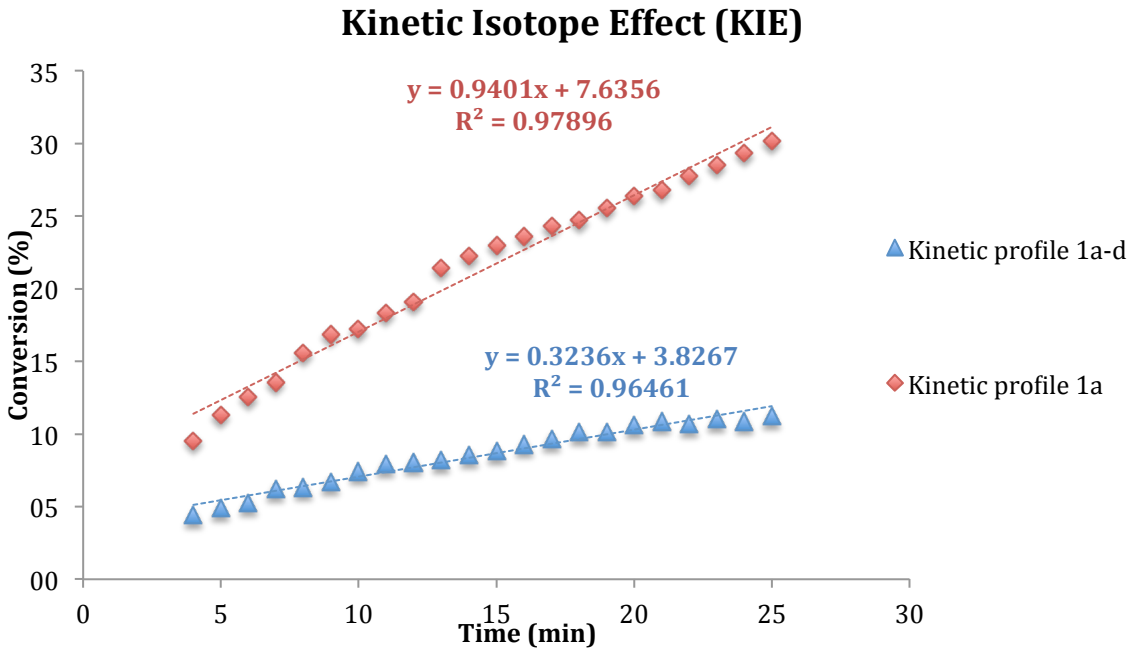
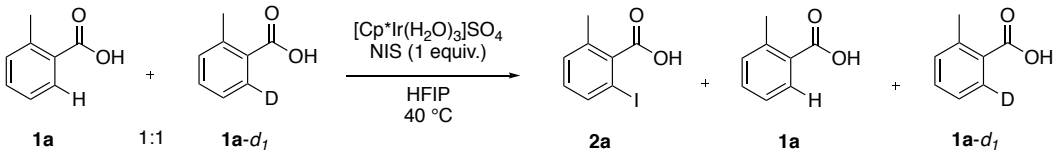


Figure S5. KIE of parallel reactions.

Selectivity determining step: The iodination of both **1a** and **1a**-d_1 in the same NMR tube (competition conditions) was also carried out. For this experiment the amount of deuterated and non-deuterated substrates could be adjusted, so that in solution an exact ratio of 1:1 of **1a** : **1a**-d_1 was present. Therefore, a mixture of benzoic acid **1a** (0.19 mmol) and benzoic acid **1a**-d_1 (0.19 mmol) was treated with $[Cp^*Ir(H_2O)_3]SO_4$ (3.0 mol%, 0.006 mmol, 3 mg) and NIS (0.196 mmol, 44 mg, note: this is the limiting reagent!) was dissolved in HFIP / $CDCl_3$ (2:1) (0.1 M, 2.0 mL) in a capped vial. The solution was transferred into an NMR tube and the tube was transferred to the NMR spectrometer with the probe preheated at 40 °C. Signals from the aromatic protons of the substrates and product were used to monitor the formation of 2-iodo-6-methylbenzoic acid (**2a**). NMR spectra were recorded after 25, 30, 35, 40, 45, 90 and 120 min. Each experiment was done three times. A KIE of 1.78 ± 0.18 was obtained (Figure S6).



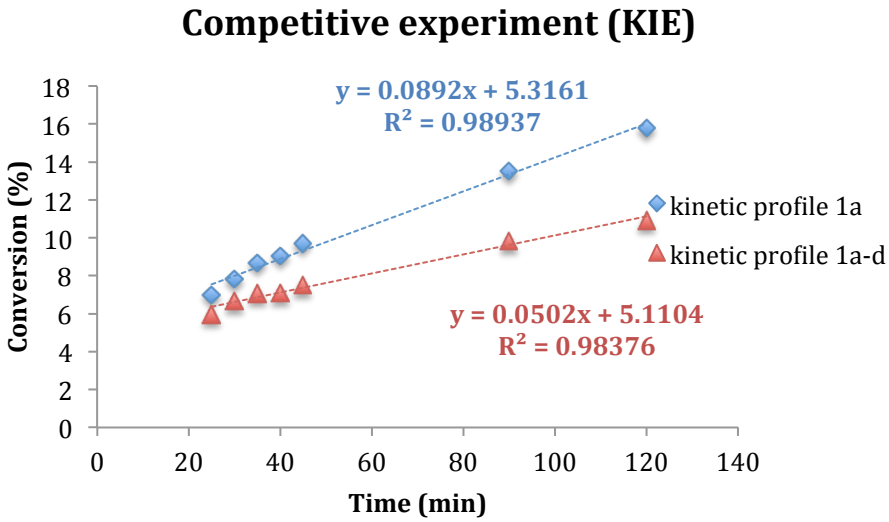


Figure S6. KIE of competition reaction.

Computational studies

Computational Methods:

All structures were initially optimized using density functional theory (DFT) by using the M06[2] functional as implemented in Gaussian 09.[3] Optimizations were carried out in a solvent model (IEFPCM, solvent = 2,2,2-trifluoroethanol)[4] by using the 6-311G** basis set for non-metallic atoms and SDD[5] for the iridium. The critical stationary points were characterized by frequency calculations in order to verify that they have the right number of imaginary frequencies, and the intrinsic reaction coordinates (IRC)[6] were followed to verify the energy profiles connecting the key transition structures to the correct associated local minima.

The energies showed in the manuscript are Free Gibbs energies and are given in kcal/mol. These energies are relative to the NIS-coordinated iridacycle (**INT-1**), marked as G = 0.0 kcal/mol.

As mentioned in the manuscript, the catalytic cycle was computed in the absence (Figure S7) and in the presence of HFIP (Figure S9 and Figure 1 in the manuscript). Also, as shown in Figure S8, the CH activation step is endergonic, and thus reversible even in the presence of a soft acid like NHS.

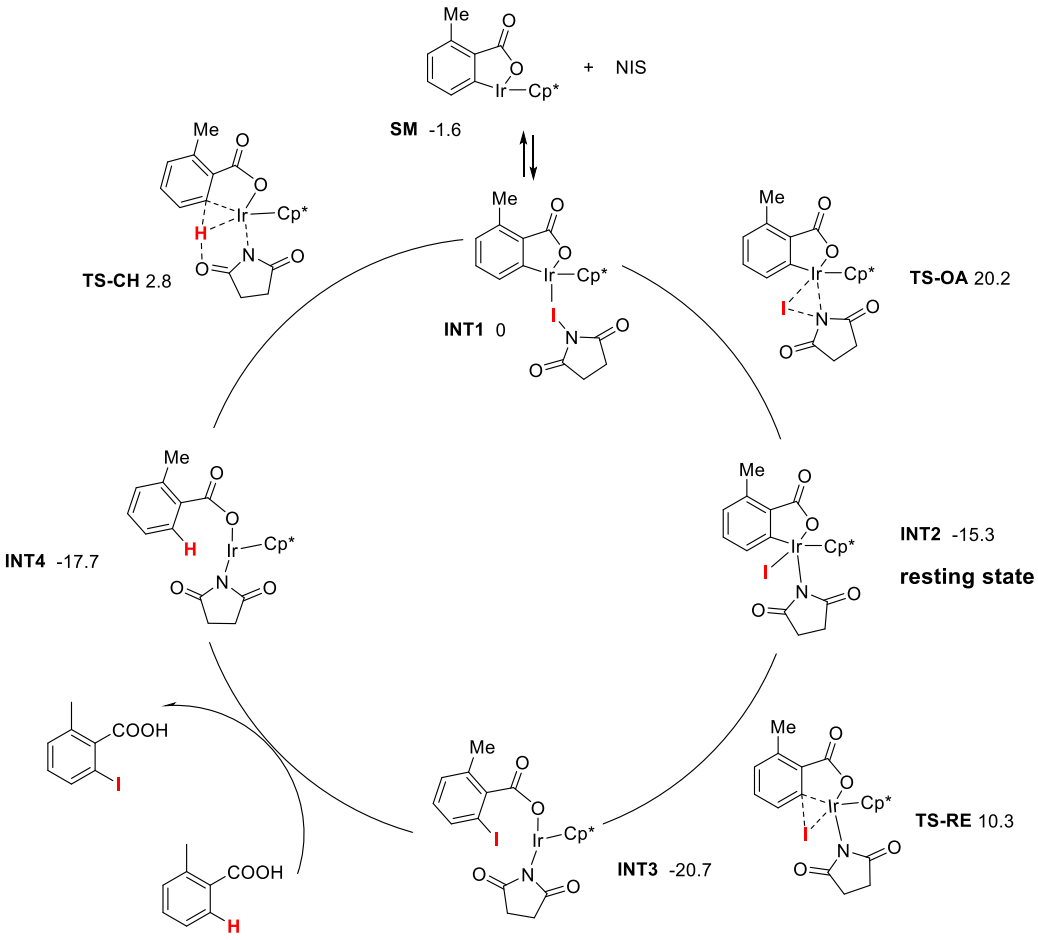


Figure S7. Mechanistic pathway in the absence of HFIP

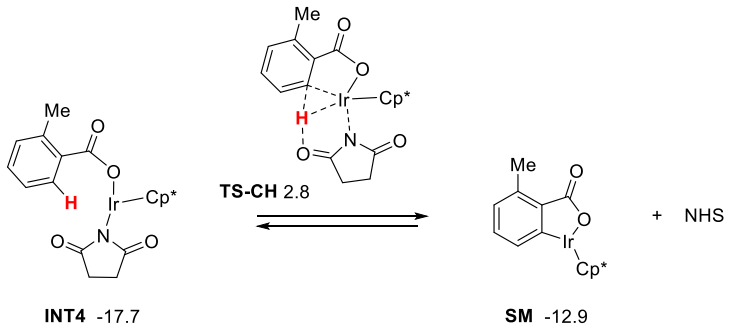


Figure S8. Reversibility of the C-H activation step

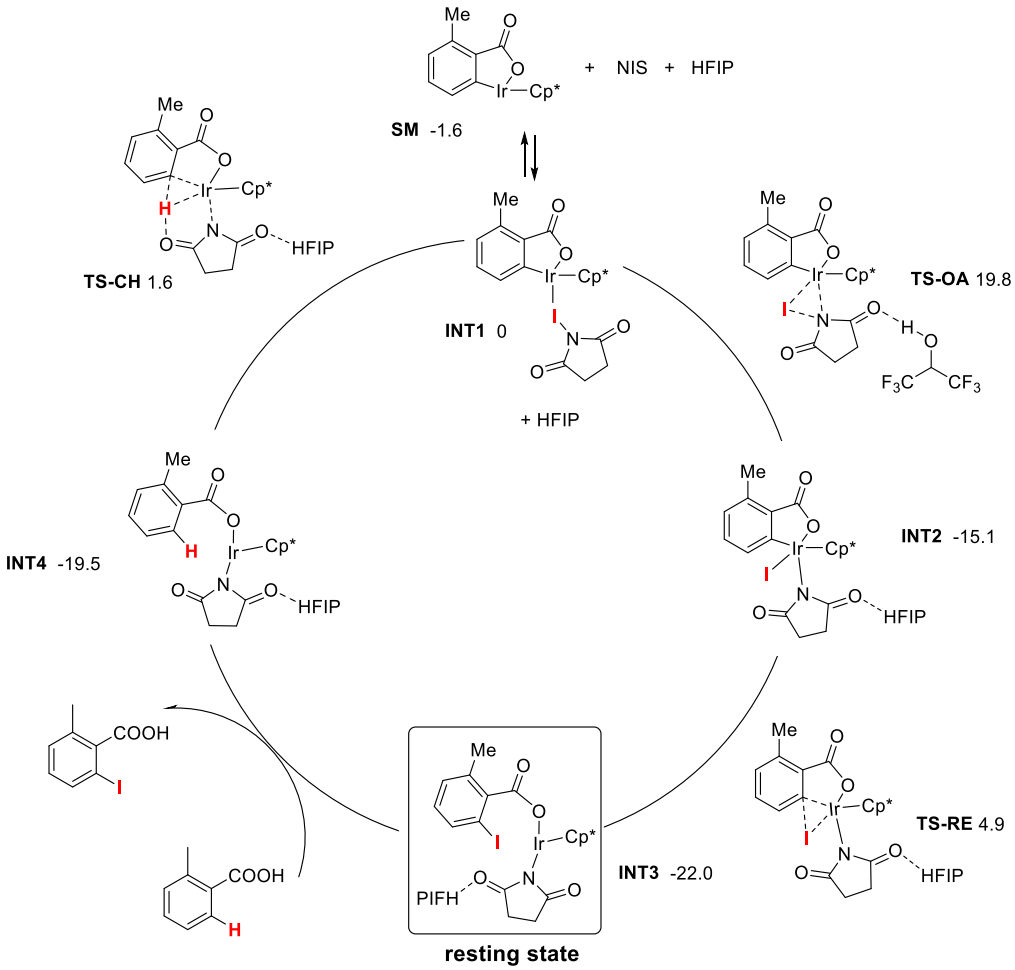
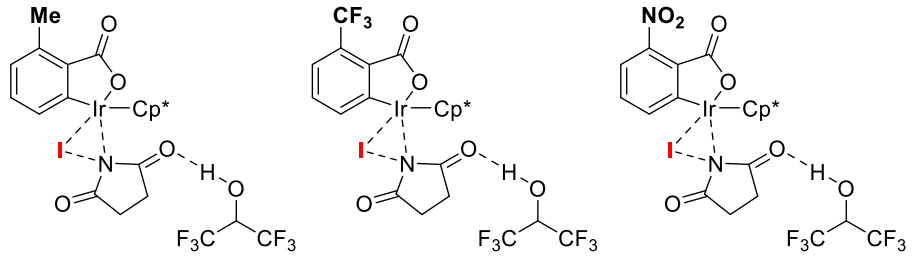


Figure S9. Mechanistic pathway in the presence of HFIP



TS-OA 21.4 **TS-OA** 22.6 **TS-OA** 23.8

Figure S10. Transition state energies of the oxidative addition of benzoic acids **1e** and **1f**.

Cartesian Coordinates of the computed structures:

SM

G at M06/6-311G** (SDD, Ir) (IEFPCM, CF_3CH_2OH) = -952.747906 Hartrees

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.027040	-0.924959	0.000604
2	6	0	-2.065642	-1.723762	-0.000236
3	6	0	-3.172558	2.403468	-0.000187
4	6	0	-3.890566	0.070411	0.000176
5	6	0	-2.528854	-0.299821	-0.000166
6	6	0	-1.830465	2.016909	-0.000493
7	6	0	-4.184526	1.442454	0.000167
8	6	0	-1.482838	0.657255	-0.000451
9	6	0	2.527966	-0.656695	-0.701663
10	6	0	2.527023	-0.654276	0.705543
11	6	0	2.030090	0.658693	1.152487
12	6	0	1.833573	1.496380	-0.002042
13	6	0	2.031421	0.654628	-1.153563
14	77	0	0.395226	-0.174799	-0.000081
15	1	0	-4.984594	-1.581782	0.874102
16	1	0	-4.985010	-1.582077	-0.872687
17	8	0	-0.737381	-1.869389	-0.000432
18	8	0	-2.803876	-2.703638	-0.000145
19	1	0	-5.224623	1.758475	0.000442
20	1	0	-3.433836	3.458887	-0.000191
21	1	0	-1.060820	2.780922	-0.000750
22	1	0	-5.987549	-0.401985	0.000762
23	6	0	1.594633	2.976015	-0.004787
24	1	0	2.555185	3.505613	-0.005696
25	1	0	1.041332	3.296516	-0.890281
26	1	0	1.041288	3.299740	0.879508
27	6	0	1.956987	1.088051	-2.584454
28	1	0	2.945922	1.425850	-2.919874
29	1	0	1.647254	0.267332	-3.235451
30	1	0	1.256039	1.914589	-2.716548
31	6	0	2.940663	-1.770973	-1.613781
32	1	0	3.954046	-1.592649	-1.993485
33	1	0	2.939958	-2.734398	-1.100174
34	1	0	2.275621	-1.846894	-2.478181
35	6	0	2.938597	-1.765338	1.622044
36	1	0	3.950835	-1.584684	2.003698
37	1	0	2.271521	-1.839316	2.485055
38	1	0	2.940263	-2.730320	1.111384
39	6	0	1.954123	1.096881	2.581855
40	1	0	2.942626	1.435971	2.917249
41	1	0	1.252869	1.923712	2.710427
42	1	0	1.643813	0.278285	3.235256

NIS

G at M06/6-311G** (SDD, Ir) (IEFPCM, CF_3CH_2OH) = -371.274279 Hartrees

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	53	0	-1.501030	0.000001	-0.000234
2	7	0	0.560738	0.000001	0.000119
3	6	0	1.312278	1.175616	0.000024
4	6	0	2.762358	0.761335	0.000152
5	6	0	2.762353	-0.761343	0.000608
6	6	0	1.312271	-1.175616	0.000517
7	1	0	3.243318	1.198314	0.879042
8	1	0	3.243449	-1.198311	-0.878214
9	8	0	0.860061	-2.286262	-0.000056
10	8	0	0.860071	2.286263	0.000320
11	1	0	3.242938	-1.197775	0.879976
12	1	0	3.243086	1.197750	-0.879148

NHS

G at M06/6-311G** (SDD, Ir) (IEFPCM, CF_3CH_2OH) = -360.497372 Hartrees

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-0.000007	-1.969661	-0.000198
2	7	0	0.000000	-0.956404	-0.000166
3	6	0	-1.166198	-0.210221	-0.000143
4	6	0	-0.761727	1.245127	-0.000014
5	6	0	0.761725	1.245127	0.000354
6	6	0	1.166200	-0.210221	-0.000051
7	1	0	-1.198585	1.726278	0.879005
8	1	0	1.198585	1.726594	-0.878491
9	8	0	2.279299	-0.666210	-0.000015
10	8	0	-2.279297	-0.666211	-0.000052
11	1	0	1.198088	1.725897	0.879833
12	1	0	-1.198092	1.726213	-0.879320

INT-1

G at M06/6-311G** (SDD, Ir) (IEFPCM, CF_3CH_2OH) = -1324.020179 Hartrees

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	-0.964320	-0.064238	0.130110
2	6	0	-2.931020	0.648936	-0.706525
3	6	0	-3.092396	-0.612188	-0.050357
4	6	0	-2.694733	-0.430985	1.339529
5	6	0	-2.453359	1.006366	1.549350
6	6	0	-2.586358	1.656580	0.309031
7	6	0	-0.105884	-1.847297	-0.420186
8	6	0	1.250725	-4.259938	-0.922175
9	6	0	-0.482208	-2.661990	-1.497716
10	6	0	0.980985	-2.256730	0.388654

11	6	0	1.674179	-3.466971	0.152119
12	6	0	0.192984	-3.860438	-1.741696
13	1	0	-1.294575	-2.368436	-2.155937
14	1	0	-0.106082	-4.488157	-2.578027
15	1	0	1.763154	-5.197420	-1.122466
16	6	0	1.359734	-1.287040	1.459929
17	8	0	2.311757	-1.425293	2.236395
18	8	0	0.594783	-0.208739	1.508300
19	53	0	0.833734	1.248213	-1.598232
20	7	0	2.490689	1.576058	-0.347704
21	6	0	2.469196	2.512003	0.694468
22	8	0	1.581767	3.313353	0.897272
23	6	0	3.577627	0.687909	-0.314209
24	8	0	3.775757	-0.201630	-1.113469
25	6	0	3.767841	2.333214	1.470112
26	1	0	3.543489	2.292259	2.538057
27	6	0	4.399308	1.046067	0.914589
28	1	0	5.453620	1.138348	0.646853
29	6	0	2.841777	-3.929410	0.992360
30	1	0	3.674009	-3.221512	0.939281
31	1	0	2.575409	-4.001346	2.050371
32	1	0	3.190751	-4.907654	0.648827
33	1	0	4.288214	0.204970	1.606935
34	1	0	4.389381	3.216472	1.293817
35	6	0	-2.103616	1.612151	2.873822
36	1	0	-2.978730	1.611188	3.534277
37	1	0	-1.314397	1.039053	3.368745
38	1	0	-1.760365	2.643097	2.770503
39	6	0	-2.818228	-1.449501	2.432731
40	1	0	-3.806413	-1.381142	2.904660
41	1	0	-2.699818	-2.463686	2.045804
42	1	0	-2.066134	-1.290760	3.209182
43	6	0	-2.445544	3.122292	0.028601
44	1	0	-1.907802	3.305969	-0.905842
45	1	0	-3.436552	3.581337	-0.072150
46	1	0	-1.915541	3.639768	0.830058
47	6	0	-3.312358	0.956598	-2.125987
48	1	0	-3.138186	0.101443	-2.782640
49	1	0	-4.378486	1.210541	-2.180361
50	1	0	-2.753300	1.807946	-2.520655
51	6	0	-3.691313	-1.854976	-0.632571
52	1	0	-3.237474	-2.757837	-0.219861
53	1	0	-4.763206	-1.879758	-0.400127
54	1	0	-3.587579	-1.885456	-1.718780

TS-OA

G at M06/6-311G** (SDD, Ir) (IEFPCM, CF_3CH_2OH) = -1323.987915 Hartrees
Frequencies: -209.3

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	-0.215828	-0.571254	0.170316
2	6	0	-1.980804	-1.784042	-0.762623
3	6	0	-0.750365	-2.512970	-0.748117
4	6	0	-0.346488	-2.641236	0.644551
5	6	0	-1.440896	-2.104908	1.477402
6	6	0	-2.423694	-1.586693	0.618892

7	6	0	1.588066	-0.389255	-0.783454
8	6	0	4.197950	-0.256982	-1.801650
9	6	0	1.807815	-0.487261	-2.162470
10	6	0	2.693807	-0.209553	0.075624
11	6	0	4.017452	-0.145042	-0.418080
12	6	0	3.109292	-0.416041	-2.663518
13	1	0	0.974280	-0.604307	-2.848137
14	1	0	3.278332	-0.486412	-3.735373
15	1	0	5.204407	-0.212137	-2.209386
16	6	0	2.338648	-0.027757	1.508626
17	8	0	3.130449	0.185671	2.426929
18	8	0	1.027727	-0.071370	1.743444
19	53	0	-1.267645	1.753300	-1.703660
20	7	0	-0.520162	1.870229	0.503781
21	6	0	-1.449694	2.157282	1.521436
22	8	0	-2.615365	1.816702	1.517494
23	6	0	0.666140	2.624086	0.674410
24	8	0	1.525328	2.772546	-0.168187
25	6	0	-0.752520	2.964641	2.608938
26	1	0	-0.766468	2.383376	3.535045
27	6	0	0.658792	3.227436	2.071956
28	1	0	0.916771	4.287255	2.004828
29	6	0	5.220900	0.042828	0.475595
30	1	0	5.166076	0.986751	1.025509
31	1	0	5.287465	-0.743397	1.233116
32	1	0	6.138537	0.035443	-0.119379
33	1	0	1.437276	2.727579	2.655116
34	1	0	-1.327967	3.877728	2.785806
35	6	0	-1.440440	-2.134309	2.973367
36	1	0	-1.566691	-3.161948	3.333842
37	1	0	-0.490060	-1.760023	3.365946
38	1	0	-2.245885	-1.526925	3.389752
39	6	0	0.789425	-3.470214	1.162833
40	1	0	0.444702	-4.493847	1.353628
41	1	0	1.609928	-3.518140	0.444471
42	1	0	1.176386	-3.066075	2.100867
43	6	0	-3.753045	-1.011601	0.993244
44	1	0	-3.971012	-0.102839	0.430704
45	1	0	-4.538000	-1.745358	0.770551
46	1	0	-3.806181	-0.767909	2.054531
47	6	0	-2.818037	-1.519348	-1.973889
48	1	0	-2.205285	-1.309985	-2.853631
49	1	0	-3.427889	-2.404657	-2.194913
50	1	0	-3.495915	-0.677635	-1.822755
51	6	0	-0.106277	-3.190870	-1.917489
52	1	0	0.974349	-3.274444	-1.795946
53	1	0	-0.516700	-4.204133	-2.009001
54	1	0	-0.306635	-2.665488	-2.852958

INT-2

G at M06/6-311G** (SDD, Ir) (IEFPCM, CF_3CH_2OH) = -1313.044623 Hartrees

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	0.202197	-0.295444	0.063416
2	6	0	1.827756	-1.335981	1.387317
3	6	0	0.578208	-1.412858	2.075693

4	6	0	-0.323050	-2.217979	1.261215
5	6	0	0.377418	-2.627852	0.074022
6	53	0	2.316535	0.765352	-1.551049
7	6	0	1.711560	-2.133371	0.164748
8	6	0	-1.841039	0.015939	0.448190
9	6	0	-4.581096	0.393791	0.695618
10	6	0	-2.357809	0.440584	1.669526
11	6	0	-2.674222	-0.170105	-0.659813
12	6	0	-4.073774	0.004080	-0.549148
13	6	0	-3.738153	0.623673	1.785155
14	1	0	-1.713442	0.641974	2.517196
15	1	0	-4.156704	0.949619	2.733418
16	1	0	-5.652020	0.537767	0.807802
17	6	0	-1.966618	-0.455167	-1.933322
18	8	0	-2.498063	-0.654424	-3.022408
19	8	0	-0.644651	-0.470417	-1.818212
20	7	0	0.125066	1.751852	0.545034
21	6	0	-0.525975	2.706773	-0.232284
22	6	0	-0.339267	4.087235	0.389872
23	6	0	0.504797	3.832792	1.638152
24	6	0	0.754543	2.328934	1.630121
25	1	0	0.147838	4.738703	-0.341307
26	1	0	1.468180	4.350345	1.631216
27	8	0	1.420015	1.735925	2.472009
28	8	0	-1.147080	2.485524	-1.259338
29	6	0	-5.012786	-0.190612	-1.715031
30	1	0	-4.786256	0.505004	-2.528204
31	1	0	-4.923463	-1.193892	-2.140217
32	1	0	-6.046489	-0.033440	-1.395895
33	1	0	-1.322371	4.516002	0.603664
34	1	0	-0.000377	4.099948	2.570966
35	6	0	0.334546	-1.006613	3.494311
36	1	0	0.776734	-1.765688	4.151803
37	1	0	0.796467	-0.043834	3.707658
38	1	0	-0.729234	-0.953914	3.726870
39	6	0	3.112791	-0.816251	1.943148
40	1	0	2.930079	-0.010481	2.650746
41	1	0	3.629086	-1.637612	2.456432
42	1	0	3.768629	-0.446290	1.153088
43	6	0	-1.642419	-2.763952	1.692933
44	1	0	-1.462840	-3.757446	2.123868
45	1	0	-2.119271	-2.145964	2.451762
46	1	0	-2.330302	-2.883439	0.854558
47	6	0	-0.145717	-3.532583	-0.995524
48	1	0	0.164847	-4.562553	-0.784170
49	1	0	-1.235236	-3.514293	-1.043191
50	1	0	0.246427	-3.254382	-1.975427
51	6	0	2.838261	-2.576159	-0.706395
52	1	0	3.158434	-3.563102	-0.345272
53	1	0	2.530083	-2.688368	-1.747099
54	1	0	3.690691	-1.900912	-0.660400

TS-RE

G at M06/6-311G** (SDD, Ir) (IEFPCM, CF_3CH_2OH) = -1324.003761 Hartrees

Frequencies: -232.5

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	0.608289	0.235965	0.174155
2	6	0	2.048094	1.838189	-0.552510
3	6	0	2.043248	1.708263	0.905935
4	6	0	2.615911	0.415627	1.228795
5	6	0	2.912353	-0.250848	0.005379
6	6	0	2.475089	0.601368	-1.106387
7	6	0	-1.205663	2.069155	-1.518881
8	6	0	-1.669084	2.343894	0.709858
9	6	0	-1.342486	-0.967496	-0.594447
10	53	0	0.481653	-2.675434	-0.469355
11	6	0	-2.198825	-0.982220	0.516932
12	6	0	-3.596777	-0.963189	0.308055
13	6	0	-4.065163	-0.938520	-1.013231
14	1	0	-5.136767	-0.926523	-1.190180
15	6	0	-3.190219	-0.936604	-2.103415
16	1	0	-3.584342	-0.924574	-3.115730
17	6	0	-1.810720	-0.974206	-1.907699
18	1	0	-1.130617	-1.010691	-2.748133
19	6	0	-2.364586	3.061239	-1.493972
20	1	0	-3.192059	2.648579	-2.078139
21	1	0	-2.050593	3.987539	-1.983988
22	6	0	-2.686288	3.231471	-0.009222
23	1	0	-2.580680	4.258605	0.350518
24	1	0	-3.691825	2.894403	0.258894
25	7	0	-0.886649	1.679440	-0.226024
26	8	0	-1.570650	2.255459	1.925741
27	8	0	-0.635082	1.692250	-2.535853
28	6	0	-1.569410	-0.931275	1.873122
29	8	0	-2.135540	-1.312000	2.898776
30	8	0	-0.343426	-0.457556	1.890008
31	6	0	-4.587264	-0.948964	1.449034
32	1	0	-4.526168	-1.867934	2.037411
33	1	0	-4.387737	-0.127523	2.142671
34	1	0	-5.604174	-0.842446	1.062159
35	6	0	3.703307	-1.507151	-0.133582
36	1	0	3.512244	-2.210715	0.678495
37	1	0	3.519132	-2.009850	-1.083150
38	1	0	4.766889	-1.236463	-0.099105
39	6	0	2.661661	0.298633	-2.560578
40	1	0	3.670870	0.584192	-2.881417
41	1	0	2.535037	-0.767371	-2.761093
42	1	0	1.936025	0.847706	-3.162285
43	6	0	1.797086	3.113138	-1.288077
44	1	0	2.726980	3.695776	-1.271393
45	1	0	1.511229	2.938714	-2.323289
46	1	0	1.026054	3.715713	-0.804991
47	6	0	1.791036	2.814135	1.881678
48	1	0	2.707334	3.404315	2.007265
49	1	0	1.001387	3.482452	1.536344
50	1	0	1.502932	2.422317	2.858175
51	6	0	2.888385	-0.079544	2.614217
52	1	0	3.760793	0.438546	3.028539

53	1	0	2.036077	0.113434	3.270227
54	1	0	3.092165	-1.151351	2.624866

INT-3

G at M06/6-311G** (SDD, Ir) (IEFPCM, CF_3CH_2OH) = --1324.053124 Hartrees

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.919734	3.151945	-2.745565
2	6	0	-1.724920	3.951598	-1.453090
3	6	0	-1.834753	1.690113	-2.303384
4	6	0	-1.594489	2.882364	-0.369646
5	7	0	-1.648539	1.627396	-0.938407
6	6	0	1.475884	0.071592	1.053082
7	6	0	5.275991	2.073054	0.571199
8	6	0	3.798843	0.270908	0.008968
9	6	0	2.805988	0.772259	0.850848
10	6	0	4.297440	2.593293	1.418605
11	6	0	5.032787	0.901801	-0.145013
12	6	0	3.059090	1.962504	1.572041
13	6	0	-3.370149	-1.051404	-0.150098
14	6	0	-3.207355	-0.751520	1.242469
15	6	0	-2.081138	-1.542877	1.761060
16	6	0	-1.535037	-2.292874	0.685288
17	6	0	-2.297248	-1.951764	-0.518968
18	77	0	-1.414085	-0.123782	0.193823
19	1	0	-1.152818	3.343428	-3.501274
20	1	0	-2.562872	4.611692	-1.212077
21	8	0	-1.920105	0.721484	-3.054951
22	8	0	-1.475230	3.101547	0.834485
23	8	0	0.537502	0.541010	0.268294
24	8	0	1.352814	-0.795678	1.912456
25	1	0	5.788085	0.493233	-0.806242
26	1	0	6.231867	2.577093	0.465242
27	1	0	4.495738	3.506011	1.973298
28	1	0	-0.819258	4.565747	-1.455945
29	1	0	-2.890917	3.323138	-3.219750
30	6	0	-1.636378	-1.579954	3.188021
31	1	0	-1.863890	-0.642441	3.700177
32	1	0	-2.162029	-2.384997	3.716258
33	1	0	-0.562565	-1.755624	3.253317
34	6	0	-0.432036	-3.300690	0.764912
35	1	0	-0.853474	-4.286907	0.995177
36	1	0	0.104467	-3.382012	-0.182761
37	1	0	0.285032	-3.033388	1.540790
38	6	0	-2.092429	-2.528406	-1.881881
39	1	0	-2.790636	-3.361023	-2.034662
40	1	0	-2.276038	-1.771162	-2.646031
41	1	0	-1.077829	-2.911426	-2.006790
42	6	0	-4.445229	-0.552939	-1.067333
43	1	0	-4.034799	-0.307411	-2.048420
44	1	0	-5.212277	-1.325859	-1.194019
45	1	0	-4.931431	0.338080	-0.665439
46	6	0	-4.091893	0.125259	2.071320
47	1	0	-4.584522	0.887155	1.464678
48	1	0	-4.869432	-0.485861	2.546106
49	1	0	-3.531663	0.626123	2.863685

50	6	0	2.009432	2.540319	2.494216
51	1	0	1.105890	2.824527	1.944001
52	1	0	1.708438	1.811239	3.254482
53	1	0	2.390523	3.426149	3.007581
54	53	0	3.463678	-1.541518	-1.133424

INT-4

G at M06/6-311G** (SDD, Ir) (IEFPCM, CF_3CH_2OH) = -1313.252649 Hartrees

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.994824	4.128406	-0.661664
2	6	0	-0.576467	4.099818	0.812178
3	6	0	-1.110772	2.653594	-1.050417
4	6	0	-0.554278	2.612581	1.163030
5	7	0	-0.848545	1.861537	0.046726
6	6	0	2.100846	-0.860253	0.421018
7	6	0	6.234371	-0.080341	-0.522941
8	6	0	4.394159	-1.575788	-0.134778
9	6	0	3.530541	-0.493466	0.103309
10	6	0	5.389979	0.999500	-0.265835
11	6	0	5.733889	-1.381495	-0.457131
12	6	0	4.031017	0.829612	0.042546
13	6	0	-2.913214	-0.633666	-0.461690
14	6	0	-2.640081	-1.131865	0.853793
15	6	0	-1.624902	-2.189867	0.748405
16	6	0	-1.246065	-2.308057	-0.615733
17	6	0	-2.005362	-1.306786	-1.369947
18	77	0	-0.822456	-0.233089	0.069406
19	1	0	-0.268999	4.617880	-1.317064
20	1	0	-1.268358	4.621971	1.478817
21	8	0	-1.395272	2.242618	-2.173322
22	8	0	-0.320768	2.148610	2.277232
23	8	0	1.212888	0.067918	0.134414
24	8	0	1.833441	-1.964188	0.901919
25	1	0	6.379406	-2.233479	-0.648771
26	1	0	7.278614	0.095835	-0.765449
27	1	0	5.792055	2.008738	-0.301559
28	1	0	0.419471	4.518479	0.986338
29	1	0	-1.960590	4.615337	-0.828424
30	6	0	-1.135209	-3.028117	1.885564
31	1	0	-1.162042	-2.476260	2.828070
32	1	0	-1.783409	-3.906414	1.995919
33	1	0	-0.112345	-3.360548	1.711669
34	6	0	-0.284568	-3.300070	-1.191651
35	1	0	-0.797148	-4.252363	-1.373411
36	1	0	0.121153	-2.953622	-2.144621
37	1	0	0.547757	-3.470179	-0.507989
38	6	0	-1.958930	-1.094723	-2.848121
39	1	0	-2.777999	-1.649441	-3.322975
40	1	0	-2.069144	-0.034587	-3.083162
41	1	0	-1.019070	-1.449936	-3.275026
42	6	0	-3.955326	0.369565	-0.852336
43	1	0	-3.586849	1.030853	-1.638251
44	1	0	-4.846119	-0.150253	-1.224439
45	1	0	-4.258293	0.983327	-0.001693
46	6	0	-3.340353	-0.741794	2.117293

47	1	0	-3.762871	0.262145	2.048977
48	1	0	-4.161298	-1.442507	2.313550
49	1	0	-2.664006	-0.772322	2.974404
50	6	0	3.200940	2.063036	0.318610
51	1	0	2.491463	2.256954	-0.490881
52	1	0	2.606155	1.960180	1.229189
53	1	0	3.851529	2.936161	0.422008
54	1	0	3.985180	-2.577437	-0.059554

TS-CH

G at M06/6-311G** (SDD, Ir) (IEFPCM, CF_3CH_2OH) = -1313.219961 Hartrees
Frequencies: -1200.3

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.798939	0.959182	-1.355865
2	6	0	1.937773	3.765129	0.919119
3	6	0	3.091120	3.297957	0.025487
4	6	0	0.989038	2.592205	0.878044
5	6	0	2.683570	1.892843	-0.416063
6	7	0	1.453873	1.553365	0.165840
7	6	0	-1.755640	1.103048	-1.641274
8	6	0	-3.541509	0.129622	2.147110
9	6	0	-3.843063	0.703941	-0.213316
10	6	0	-2.441219	0.768998	-0.342675
11	6	0	-2.157160	0.197337	2.003527
12	6	0	-4.366178	0.370274	1.047542
13	6	0	-1.579486	0.507276	0.756400
14	6	0	0.822481	-1.950028	1.305042
15	6	0	1.991501	-1.662543	0.517830
16	6	0	1.671102	-1.857220	-0.879633
17	6	0	0.291908	-2.308371	-0.943923
18	6	0	-0.230221	-2.374280	0.385326
19	77	0	0.352240	-0.258465	-0.046014
20	1	0	-4.560040	0.343067	-2.226776
21	1	0	-4.741424	1.996807	-1.695031
22	1	0	1.426554	4.659813	0.553262
23	1	0	4.051100	3.243820	0.545866
24	8	0	-0.137745	2.581468	1.443814
25	8	0	3.325829	1.176065	-1.163644
26	8	0	-0.482059	0.784954	-1.691134
27	8	0	-2.332345	1.650222	-2.585522
28	1	0	-5.444892	0.308195	1.166098
29	1	0	-3.981691	-0.104478	3.112633
30	1	0	-1.517883	0.050800	2.869862
31	1	0	-5.825538	0.746332	-1.044653
32	1	0	3.233210	3.923547	-0.859590
33	1	0	2.231915	3.958222	1.955062
34	1	0	-0.690704	1.465570	1.064267
35	6	0	-1.560928	-2.942311	0.775218
36	1	0	-2.312872	-2.778033	0.000835
37	1	0	-1.463543	-4.024929	0.922340
38	1	0	-1.933024	-2.509260	1.704179
39	6	0	-0.433392	-2.688171	-2.198363
40	1	0	-0.224545	-3.736428	-2.443961
41	1	0	-1.514050	-2.578899	-2.088284
42	1	0	-0.112632	-2.077525	-3.045072

43	6	0	2.633413	-1.832510	-2.028405
44	1	0	3.111020	-2.814831	-2.136806
45	1	0	2.123616	-1.608386	-2.968752
46	1	0	3.405176	-1.079234	-1.876896
47	6	0	3.341423	-1.308564	1.063608
48	1	0	3.911829	-2.228079	1.244003
49	1	0	3.900945	-0.689177	0.362649
50	1	0	3.262954	-0.776028	2.014148
51	6	0	0.770153	-2.032314	2.802124
52	1	0	1.106146	-3.022192	3.135852
53	1	0	1.418195	-1.286740	3.268610
54	1	0	-0.243366	-1.884385	3.179105

TS-OA--HFIP

G at M06/6-311G** (SDD, Ir) (IEFPCM, CF_3CH_2OH) = -2113.698998 Hartrees
Frequencies: -114.2

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	-1.343916	0.756775	-0.041335
2	6	0	-1.847564	2.094566	-1.761257
3	6	0	-2.005079	2.763832	-0.477879
4	6	0	-0.664248	2.957467	0.078312
5	6	0	0.278373	2.371463	-0.800197
6	6	0	-0.460210	1.773766	-1.909704
7	6	0	-3.182551	-0.162214	0.049209
8	6	0	-5.738151	-1.242893	0.449630
9	6	0	-3.897718	-0.688283	-1.031724
10	6	0	-3.759405	-0.198982	1.337105
11	6	0	-5.049126	-0.732721	1.558268
12	6	0	-5.168999	-1.231645	-0.825030
13	1	0	-3.473846	-0.688988	-2.029850
14	1	0	-5.722373	-1.643972	-1.665310
15	1	0	-6.732056	-1.659458	0.590784
16	6	0	-2.871151	0.288671	2.429869
17	8	0	-3.175353	0.360604	3.620982
18	8	0	-1.652436	0.625057	2.019008
19	53	0	-0.680388	-2.678605	-1.747985
20	7	0	-0.330978	-1.247981	0.024125
21	6	0	1.067437	-0.918257	0.136791
22	8	0	1.801553	-0.741761	-0.819793
23	6	0	-0.709139	-1.928046	1.286413
24	8	0	-1.684435	-2.618120	1.393770
25	6	0	1.480553	-0.927202	1.596963
26	1	0	1.621122	0.104401	1.931245
27	6	0	0.340030	-1.632808	2.336458
28	1	0	0.641130	-2.581459	2.788393
29	6	0	-5.699654	-0.781756	2.920895
30	1	0	-5.102992	-1.364029	3.628906
31	1	0	-5.794111	0.216684	3.357130
32	1	0	-6.695384	-1.228472	2.848682
33	1	0	-0.119125	-1.012307	3.108109
34	1	0	2.446218	-1.433296	1.676922
35	6	0	1.769350	2.453953	-0.703639
36	1	0	2.127634	3.303351	-1.299031
37	1	0	2.104607	2.609149	0.324532
38	1	0	2.251969	1.558302	-1.096042

39	6	0	-0.377556	3.690763	1.351268
40	1	0	0.623982	3.474071	1.727370
41	1	0	-0.450208	4.771727	1.181936
42	1	0	-1.099293	3.426268	2.127737
43	6	0	0.170011	1.137235	-3.111467
44	1	0	-0.533109	0.486833	-3.635122
45	1	0	0.495381	1.916047	-3.812562
46	1	0	1.042322	0.543841	-2.834592
47	6	0	-2.908945	1.938599	-2.806027
48	1	0	-3.897322	1.800566	-2.365777
49	1	0	-2.938120	2.846002	-3.422142
50	1	0	-2.707660	1.095091	-3.469438
51	6	0	-3.251296	3.433253	0.022582
52	1	0	-3.270648	3.476713	1.113990
53	1	0	-3.301816	4.462453	-0.353450
54	1	0	-4.148430	2.909086	-0.312553
55	1	0	3.563477	-0.903123	-0.484171
56	8	0	4.452234	-1.159568	-0.161620
57	6	0	5.072997	-0.061064	0.438911
58	6	0	5.974213	-0.607303	1.549544
59	6	0	5.836776	0.753305	-0.614796
60	1	0	4.374222	0.632921	0.921524
61	9	0	6.402575	1.854908	-0.085472
62	9	0	6.863212	-1.501708	1.084885
63	9	0	6.657158	0.381077	2.158574
64	9	0	6.802547	0.036106	-1.213758
65	9	0	4.969625	1.154603	-1.570991
66	9	0	5.219008	-1.222774	2.480999

INT-2--HFIP

G at M06/6-311G** (SDD, Ir) (IEFPCM, CF_3CH_2OH) = -2113.754553 Hartrees

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	-1.442793	-0.333094	0.183962
2	6	0	-0.244203	-1.872642	1.499854
3	6	0	-0.175994	-0.597455	2.138136
4	6	0	-1.534396	-0.215618	2.503884
5	6	0	-2.431850	-1.256891	2.080813
6	53	0	-1.468888	-2.294811	-1.894430
7	6	0	-1.645375	-2.299307	1.507080
8	6	0	-1.745970	1.727371	0.474251
9	6	0	-2.396234	4.411560	0.768462
10	6	0	-0.753494	2.626387	0.856404
11	6	0	-3.041106	2.168444	0.182643
12	6	0	-3.395106	3.528647	0.341975
13	6	0	-1.091825	3.974040	1.006044
14	1	0	0.267759	2.305973	1.025133
15	1	0	-0.329284	4.685850	1.309956
16	1	0	-2.639663	5.462392	0.896943
17	6	0	-3.938354	1.134129	-0.390260
18	8	0	-5.110205	1.298106	-0.717286
19	8	0	-3.354758	-0.047300	-0.554016
20	7	0	-0.155806	0.526434	-1.248501
21	6	0	-0.582536	1.274422	-2.355073
22	6	0	0.631203	1.702696	-3.172973
23	6	0	1.810708	1.004810	-2.495924

24	6	0	1.196322	0.358753	-1.265280
25	1	0	0.482574	1.415320	-4.216577
26	1	0	2.250043	0.214745	-3.113178
27	8	0	1.840413	-0.256289	-0.402840
28	8	0	-1.739830	1.542622	-2.618655
29	6	0	-4.782064	4.047987	0.050771
30	1	0	-5.057225	3.881903	-0.994563
31	1	0	-5.537921	3.532346	0.649442
32	1	0	-4.835365	5.118914	0.263520
33	1	0	0.704624	2.793916	-3.139781
34	1	0	2.624961	1.671455	-2.200288
35	6	0	1.063656	0.076488	2.632179
36	1	0	1.279906	-0.305939	3.638035
37	1	0	1.917375	-0.131530	1.991531
38	1	0	0.938114	1.156150	2.719099
39	6	0	0.905670	-2.767820	1.170840
40	1	0	1.820059	-2.200745	1.012092
41	1	0	1.058319	-3.456093	2.012137
42	1	0	0.704776	-3.367181	0.280709
43	6	0	-1.911040	0.909765	3.406867
44	1	0	-1.940196	0.513439	4.430206
45	1	0	-1.188956	1.724073	3.378902
46	1	0	-2.900022	1.307402	3.174843
47	6	0	-3.903952	-1.320660	2.337035
48	1	0	-4.087791	-1.911576	3.242007
49	1	0	-4.332364	-0.329513	2.491124
50	1	0	-4.429598	-1.797900	1.507927
51	6	0	-2.145872	-3.674590	1.220524
52	1	0	-2.217780	-4.198885	2.183307
53	1	0	-3.141908	-3.662443	0.775083
54	1	0	-1.474433	-4.236014	0.573461
55	1	0	3.440432	-0.524024	-0.708325
56	8	0	4.424951	-0.569720	-0.823009
57	6	0	4.982598	0.364315	0.047348
58	1	0	4.269375	1.132996	0.370485
59	6	0	6.101693	1.097257	-0.696509
60	6	0	5.467443	-0.340712	1.321094
61	9	0	5.966676	0.526471	2.224099
62	9	0	4.422735	-0.976173	1.900803
63	9	0	6.411916	-1.263425	1.066841
64	9	0	6.725777	1.992592	0.095870
65	9	0	7.031657	0.250310	-1.173377
66	9	0	5.582001	1.768613	-1.744087

TS-RE--HFIP

G at M06/6-311G** (SDD, Ir) (IEFPCM, CF_3CH_2OH) = -2113.722737 Hartrees
Frequencies: -205.3

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	1.477307	-0.488257	0.065714
2	6	0	2.532685	-1.978276	1.415684
3	6	0	1.448475	-2.594136	0.646781
4	6	0	1.841552	-2.575289	-0.748082
5	6	0	3.109540	-1.928508	-0.838525
6	6	0	3.497752	-1.476209	0.500952
7	6	0	1.198940	0.846921	2.865876

8	6	0	-0.801557	0.004955	2.163067
9	6	0	1.182936	1.889354	-0.140765
10	53	0	2.533462	1.225581	-2.139096
11	6	0	-0.184355	2.053479	-0.419870
12	6	0	-0.847930	3.213543	0.041336
13	6	0	-0.096939	4.161119	0.752048
14	1	0	-0.590391	5.060856	1.107893
15	6	0	1.264552	3.978697	1.010023
16	1	0	1.818082	4.733185	1.561795
17	6	0	1.929803	2.844776	0.547106
18	1	0	2.991040	2.715331	0.713287
19	6	0	0.207678	1.275676	3.943546
20	1	0	0.216343	2.367299	4.010012
21	1	0	0.536798	0.886275	4.910804
22	6	0	-1.131443	0.704862	3.475021
23	1	0	-1.566013	-0.022280	4.166685
24	1	0	-1.892921	1.466802	3.284456
25	7	0	0.527494	0.158657	1.853978
26	8	0	-1.616917	-0.625283	1.484330
27	8	0	2.401372	1.062341	2.892595
28	6	0	-0.880203	0.928859	-1.115243
29	8	0	-1.951748	1.060087	-1.716200
30	8	0	-0.261360	-0.225183	-1.050029
31	6	0	-2.323145	3.451801	-0.181203
32	1	0	-2.558783	3.517447	-1.246128
33	1	0	-2.930468	2.634214	0.214930
34	1	0	-2.628677	4.380669	0.307801
35	6	0	3.983793	-1.889886	-2.044959
36	1	0	3.411545	-1.840767	-2.972726
37	1	0	4.687729	-1.057954	-2.021005
38	1	0	4.565857	-2.821013	-2.060015
39	6	0	4.793551	-0.815533	0.855901
40	1	0	5.574603	-1.571696	1.001028
41	1	0	5.125631	-0.138546	0.065899
42	1	0	4.692521	-0.241975	1.778232
43	6	0	2.650580	-2.024389	2.903155
44	1	0	3.081904	-2.996813	3.172886
45	1	0	3.296645	-1.237069	3.286247
46	1	0	1.677406	-1.952081	3.391260
47	6	0	0.299057	-3.364781	1.215165
48	1	0	0.609618	-4.403083	1.386380
49	1	0	-0.031097	-2.950163	2.168112
50	1	0	-0.552260	-3.372771	0.533089
51	6	0	1.068179	-3.188899	-1.871741
52	1	0	1.266681	-4.266129	-1.913692
53	1	0	-0.004945	-3.047300	-1.729051
54	1	0	1.345645	-2.753061	-2.832963
55	1	0	-3.286894	-0.395839	1.412969
56	8	0	-4.248110	-0.250929	1.235598
57	6	0	-4.459363	-0.371231	-0.141197
58	1	0	-3.611218	-0.023697	-0.747375
59	6	0	-5.645724	0.524585	-0.498364
60	6	0	-4.704412	-1.840393	-0.509499
61	9	0	-5.798295	-2.349449	0.090931
62	9	0	-4.850045	-2.012484	-1.839879
63	9	0	-3.646695	-2.584075	-0.117102
64	9	0	-6.749982	0.223861	0.212361
65	9	0	-5.962280	0.430199	-1.806455
66	9	0	-5.343014	1.814692	-0.244768

INT-3--HFIP

G at M06/6-311G** (SDD, Ir) (IEFPCM, CF_3CH_2OH) = -2113.765522 Hartrees

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.992500	0.713135	2.813951
2	6	0	-1.174403	-0.148526	3.782511
3	6	0	-1.486158	0.294909	1.439829
4	6	0	-0.246168	-0.953665	2.873968
5	7	0	-0.501183	-0.635784	1.547206
6	6	0	3.247068	-0.110785	0.168936
7	6	0	5.588308	3.008285	2.030259
8	6	0	4.176901	2.266315	0.240067
9	6	0	4.043290	1.004161	0.819563
10	6	0	5.465659	1.754606	2.629495
11	6	0	4.940121	3.275857	0.825148
12	6	0	4.699275	0.741782	2.044758
13	6	0	-1.018600	-2.704130	-0.954693
14	6	0	0.056433	-3.532880	-0.483738
15	6	0	1.267021	-3.205051	-1.250343
16	6	0	0.946316	-2.152213	-2.149893
17	6	0	-0.462335	-1.802265	-1.938759
18	77	0	0.561075	-1.469173	-0.068809
19	1	0	-1.820866	1.786408	2.940392
20	1	0	-1.785152	-0.838644	4.371551
21	8	0	-1.903484	0.744485	0.358174
22	8	0	0.587033	-1.772197	3.243243
23	8	0	2.005679	-0.154099	0.591137
24	8	0	3.781240	-0.882942	-0.619786
25	1	0	5.028989	4.248667	0.355844
26	1	0	6.188800	3.782102	2.498774
27	1	0	5.973299	1.555305	3.568903
28	1	0	-0.573589	0.435231	4.485256
29	1	0	-3.072937	0.553284	2.872583
30	6	0	2.579238	-3.909983	-1.126913
31	1	0	2.743805	-4.266152	-0.107291
32	1	0	2.587885	-4.783188	-1.790974
33	1	0	3.402807	-3.250131	-1.397747
34	6	0	1.849253	-1.548670	-3.178844
35	1	0	1.805533	-2.144477	-4.098703
36	1	0	1.544748	-0.530140	-3.427664
37	1	0	2.879370	-1.520993	-2.823877
38	6	0	-1.222523	-0.774920	-2.712130
39	1	0	-1.590959	-1.226376	-3.642235
40	1	0	-2.076098	-0.398165	-2.148050
41	1	0	-0.585864	0.070703	-2.981192
42	6	0	-2.453553	-2.762837	-0.528764
43	1	0	-2.892133	-1.764249	-0.491792
44	1	0	-3.028949	-3.363039	-1.242896
45	1	0	-2.560836	-3.219600	0.456792
46	6	0	-0.040951	-4.628850	0.528786
47	1	0	-0.887191	-4.482173	1.201742
48	1	0	-0.177376	-5.588505	0.015115
49	1	0	0.868954	-4.697561	1.128953
50	6	0	4.567456	-0.607029	2.715081
51	1	0	3.543324	-0.778920	3.064940
52	1	0	4.814357	-1.419881	2.024433

53	1	0	5.234912	-0.678874	3.576880
54	53	0	3.176365	2.735153	-1.624900
55	1	0	-3.203190	1.744097	0.382016
56	8	0	-4.094521	2.185540	0.387550
57	6	0	-5.035098	1.201003	0.096183
58	1	0	-4.636715	0.183914	0.196562
59	6	0	-6.182899	1.317758	1.102730
60	6	0	-5.497369	1.342196	-1.360130
61	9	0	-5.713805	1.104681	2.350559
62	9	0	-6.752591	2.536165	1.083594
63	9	0	-7.149580	0.406734	0.869469
64	9	0	-6.388791	0.390573	-1.705463
65	9	0	-6.059671	2.540356	-1.601641
66	9	0	-4.430783	1.218114	-2.179371

INT-4--HFIP

G at M06/6-311G** (SDD, Ir) (IEFPCM, CF_3CH_2OH) = -2102.965937 Hartrees

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.618104	1.837833	2.032814
2	6	0	-0.759376	1.525289	3.262165
3	6	0	-1.024279	0.954317	0.942915
4	6	0	0.297606	0.552327	2.741294
5	7	0	0.063670	0.280564	1.400744
6	6	0	3.638173	0.676774	-0.466622
7	6	0	5.374599	4.535740	-1.281560
8	6	0	5.127892	2.186468	-1.721197
9	6	0	4.197421	2.062061	-0.675529
10	6	0	4.468846	4.417548	-0.227616
11	6	0	5.709149	3.410709	-2.036683
12	6	0	3.855814	3.197658	0.098601
13	6	0	-0.112938	-2.732435	0.156709
14	6	0	1.119037	-3.105680	0.796221
15	6	0	2.208051	-2.977538	-0.182104
16	6	0	1.655742	-2.473640	-1.390329
17	6	0	0.216993	-2.280567	-1.174831
18	77	0	1.251409	-1.016690	0.236576
19	1	0	-1.545616	2.882173	1.713122
20	1	0	-1.319792	1.041783	4.067774
21	8	0	-1.464075	0.863599	-0.217660
22	8	0	1.205914	0.064190	3.402018
23	8	0	2.453240	0.638024	0.115176
24	8	0	4.265552	-0.313915	-0.843870
25	1	0	6.416625	3.484778	-2.857159
26	1	0	5.820523	5.500802	-1.505253
27	1	0	4.227440	5.295230	0.366301
28	1	0	-0.266591	2.402464	3.689815
29	1	0	-2.681353	1.615892	2.155647
30	6	0	3.629838	-3.379032	0.048373
31	1	0	3.903024	-3.297279	1.102792
32	1	0	3.763576	-4.426414	-0.249625
33	1	0	4.307399	-2.754050	-0.532359
34	6	0	2.389139	-2.235729	-2.672784
35	1	0	2.490910	-3.180174	-3.220995
36	1	0	1.851642	-1.534998	-3.315176
37	1	0	3.382758	-1.830939	-2.476216

38	6	0	-0.758272	-1.822475	-2.210324
39	1	0	-1.098008	-2.688849	-2.792091
40	1	0	-1.628099	-1.342446	-1.761045
41	1	0	-0.298484	-1.114347	-2.902896
42	6	0	-1.489074	-2.803602	0.744642
43	1	0	-2.113659	-1.985036	0.382102
44	1	0	-1.967468	-3.747757	0.459850
45	1	0	-1.462699	-2.756400	1.834976
46	6	0	1.269670	-3.653247	2.179507
47	1	0	0.463341	-3.317833	2.833873
48	1	0	1.244817	-4.749419	2.143304
49	1	0	2.220838	-3.354174	2.624740
50	6	0	2.901086	3.168617	1.270798
51	1	0	1.869686	3.009041	0.944833
52	1	0	3.133580	2.356151	1.963802
53	1	0	2.949376	4.115139	1.816358
54	1	0	5.383818	1.294380	-2.282392
55	1	0	-2.904178	1.582868	-0.507810
56	8	0	-3.845506	1.893671	-0.601607
57	6	0	-4.670693	0.786515	-0.423069
58	1	0	-4.161888	-0.060453	0.053982
59	6	0	-5.813740	1.189183	0.513148
60	6	0	-5.162242	0.282696	-1.786813
61	9	0	-5.313459	1.517277	1.723888
62	9	0	-6.494067	2.253394	0.051615
63	9	0	-6.693667	0.183815	0.695730
64	9	0	-5.940149	-0.813474	-1.674784
65	9	0	-5.862696	1.219109	-2.452272
66	9	0	-4.096936	-0.049260	-2.547583

TS-CH--HFIP

G at M06/6-311G** (SDD, Ir) (IEFPCM, CF_3CH_2OH) = -2102.932257 Hartrees
Frequencies: -1208.0

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.359006	4.208205	1.046235
2	6	0	-2.304337	-1.798929	3.847251
3	6	0	-1.759414	-3.083563	3.212871
4	6	0	-2.212979	-0.803509	2.716482
5	6	0	-1.443442	-2.691341	1.770094
6	7	0	-1.787264	-1.347652	1.564415
7	6	0	0.723592	1.212585	0.929984
8	6	0	-2.436062	4.104297	0.706141
9	6	0	-0.040286	3.651585	0.917546
10	6	0	-0.332825	2.273720	0.877204
11	6	0	-2.709212	2.738168	0.671316
12	6	0	-1.118727	4.547532	0.819654
13	6	0	-1.666859	1.794360	0.744935
14	6	0	-3.360645	-0.282320	-1.569588
15	6	0	-2.782946	-1.603224	-1.518562
16	6	0	-1.426728	-1.533385	-2.004093
17	6	0	-1.185506	-0.157024	-2.419089
18	6	0	-2.368936	0.602408	-2.174066
19	77	0	-1.613519	-0.212743	-0.222613
20	1	0	2.034494	3.781672	0.300413
21	1	0	1.790967	3.968556	2.021845

22	1	0	-1.718542	-1.439941	4.697728
23	1	0	-2.478437	-3.907149	3.209239
24	8	0	-2.488428	0.420914	2.827667
25	8	0	-0.961524	-3.427192	0.926871
26	8	0	0.368710	0.036881	0.512947
27	8	0	1.874340	1.437364	1.365102
28	1	0	-0.914788	5.614684	0.841323
29	1	0	-3.246555	4.825794	0.651694
30	1	0	-3.739663	2.396221	0.628128
31	1	0	1.344817	5.295040	0.928252
32	1	0	-0.846786	-3.447531	3.691933
33	1	0	-3.344494	-1.877826	4.177304
34	1	0	-2.105981	0.946961	1.680245
35	6	0	-2.606182	2.018360	-2.601487
36	1	0	-1.687924	2.608569	-2.588185
37	1	0	-2.990987	2.020118	-3.628674
38	1	0	-3.340245	2.517956	-1.969055
39	6	0	0.068531	0.340422	-3.069577
40	1	0	0.039068	0.118613	-4.143418
41	1	0	0.179007	1.420594	-2.955079
42	1	0	0.956864	-0.138330	-2.654424
43	6	0	-0.498812	-2.685727	-2.241146
44	1	0	-0.669067	-3.104487	-3.241125
45	1	0	0.545457	-2.368370	-2.188339
46	1	0	-0.651304	-3.469918	-1.500371
47	6	0	-3.502904	-2.846911	-1.096334
48	1	0	-4.030138	-3.266474	-1.961884
49	1	0	-2.810836	-3.597430	-0.715356
50	1	0	-4.247898	-2.637722	-0.325386
51	6	0	-4.793186	0.063713	-1.288556
52	1	0	-5.402705	-0.080743	-2.189343
53	1	0	-5.208449	-0.567277	-0.499613
54	1	0	-4.902775	1.105347	-0.979763
55	1	0	2.898637	0.195907	1.143522
56	8	0	3.596699	-0.496494	0.950732
57	6	0	4.599007	0.096741	0.193268
58	1	0	4.658926	1.185227	0.325010
59	6	0	4.343472	-0.145382	-1.302879
60	6	0	5.943589	-0.476005	0.654091
61	9	0	3.175711	0.438809	-1.658162
62	9	0	4.246576	-1.454103	-1.598103
63	9	0	5.309587	0.383703	-2.081831
64	9	0	6.132557	-0.207296	1.959376
65	9	0	6.002149	-1.812986	0.499157
66	9	0	6.977813	0.060343	-0.027448

Final Product

G at M06/6-311G** (SDD, Ir) (IEFPCM, CF_3CH_2OH) = -470.640586 Hartrees

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	53	0	1.974371	-0.078206	0.023547
2	6	0	-0.057573	-0.742870	-0.011346
3	6	0	-0.295692	-2.108219	-0.037579
4	6	0	-1.101681	0.171977	0.012271
5	6	0	-1.607149	-2.556797	-0.046607

6	1	0	0.529064	-2.811415	-0.051833
7	6	0	-2.427321	-0.282391	0.009056
8	6	0	-2.658233	-1.652833	-0.023398
9	1	0	-1.806491	-3.623292	-0.070698
10	1	0	-3.682978	-2.012943	-0.030649
11	6	0	-3.565108	0.691219	0.047765
12	1	0	-3.582875	1.239292	0.995661
13	1	0	-3.484938	1.434007	-0.753478
14	1	0	-4.521893	0.177381	-0.063950
15	6	0	-0.856667	1.645414	0.075582
16	8	0	-0.879699	2.293211	1.086625
17	8	0	-0.642633	2.161058	-1.135760
18	1	0	-0.496334	3.114709	-1.034425

TS-OA (CF_3)

G at M06/6-311G** (SDD, Ir) (IEFPCM, CF3CH2OH) = -2411.453653 Hartrees

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	0.945118	0.862700	0.103550
2	6	0	1.183996	2.578915	1.526531
3	6	0	1.499689	2.954309	0.157190
4	6	0	0.245996	2.940369	-0.596689
5	6	0	-0.794064	2.507865	0.264315
6	6	0	-0.203859	2.224843	1.568792
7	6	0	2.799204	0.051627	0.459881
8	6	0	5.420235	-0.922176	0.700595
9	6	0	3.346371	-0.205249	1.723316
10	6	0	3.568046	-0.209015	-0.692776
11	6	0	4.891721	-0.687712	-0.571104
12	6	0	4.646388	-0.694815	1.840165
13	1	0	2.760506	-0.033285	2.619298
14	1	0	5.066424	-0.894562	2.821818
15	1	0	6.434428	-1.287007	0.801208
16	6	0	2.831107	-0.009154	-1.984161
17	8	0	3.298557	-0.164616	-3.106984
18	8	0	1.560136	0.331829	-1.813855
19	53	0	0.210741	-2.232143	2.382890
20	7	0	0.007927	-1.125938	0.340979
21	6	0	-1.385157	-0.893105	0.050736
22	8	0	-2.209671	-0.579669	0.890800
23	6	0	0.519370	-2.014588	-0.732572
24	8	0	1.522338	-2.663289	-0.623340
25	6	0	-1.659244	-1.186651	-1.412421
26	1	0	-1.791029	-0.237300	-1.939332
27	6	0	-0.436188	-1.966692	-1.904924
28	1	0	-0.668376	-2.994228	-2.196542
29	6	0	5.786251	-0.965697	-1.760717
30	1	0	0.077799	-1.480769	-2.736714
31	1	0	-2.601222	-1.736420	-1.483528
32	6	0	-2.258492	2.484533	-0.046787
33	1	0	-2.701398	3.452332	0.219771
34	1	0	-2.447106	2.320736	-1.110438
35	1	0	-2.787818	1.719220	0.522516
36	6	0	0.123905	3.347732	-2.031145
37	1	0	-0.851223	3.086462	-2.445441

38	1	0	0.253642	4.432482	-2.121460
39	1	0	0.895161	2.867011	-2.638632
40	6	0	-0.972267	1.848267	2.799314
41	1	0	-0.324984	1.393496	3.551486
42	1	0	-1.419885	2.747479	3.240685
43	1	0	-1.775037	1.146744	2.569826
44	6	0	2.099130	2.709701	2.704350
45	1	0	3.143218	2.555402	2.428298
46	1	0	2.007074	3.722983	3.114661
47	1	0	1.845742	2.007550	3.501006
48	6	0	2.788768	3.552638	-0.323461
49	1	0	2.934359	3.376653	-1.391651
50	1	0	2.783263	4.637180	-0.160784
51	1	0	3.646276	3.136946	0.209471
52	1	0	-3.917411	-0.946989	0.434177
53	8	0	-4.734753	-1.307569	0.032477
54	6	0	-5.364504	-0.309133	-0.715652
55	6	0	-6.176654	-1.014228	-1.804580
56	6	0	-6.218726	0.579810	0.198674
57	1	0	-4.666091	0.359478	-1.233741
58	9	0	-6.786694	1.596910	-0.476109
59	9	0	-7.048046	-1.899183	-1.291464
60	9	0	-6.869198	-0.129965	-2.548010
61	9	0	-7.193460	-0.107271	0.817050
62	9	0	-5.421522	1.112510	1.152571
63	9	0	-5.344127	-1.683420	-2.625739
64	9	0	5.975767	0.123808	-2.536334
65	9	0	7.026352	-1.357821	-1.364182
66	9	0	5.319363	-1.960258	-2.545932

TS-OA (NO_2)

G at M06/6-311G** (SDD, Ir) (IEFPCM, CF3CH2OH) = -2278.886755 Hartrees

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	-1.174285	0.823036	-0.056755
2	6	0	-1.412053	2.326763	-1.703330
3	6	0	-1.816473	2.861369	-0.414039
4	6	0	-0.606710	3.002778	0.396478
5	6	0	0.497705	2.521121	-0.353580
6	6	0	-0.008622	2.039471	-1.634375
7	6	0	-2.953231	-0.128707	-0.446261
8	6	0	-5.502680	-1.316857	-0.693983
9	6	0	-3.402209	-0.607519	-1.684337
10	6	0	-3.790147	-0.250356	0.678368
11	6	0	-5.059935	-0.816441	0.525463
12	6	0	-4.659007	-1.207526	-1.801790
13	1	0	-2.770623	-0.531832	-2.562149
14	1	0	-4.991304	-1.585683	-2.763876
15	1	0	-6.487608	-1.762055	-0.776581
16	6	0	-3.169245	0.098004	1.992501
17	8	0	-3.710031	-0.061935	3.081949
18	8	0	-1.929105	0.545149	1.877479
19	53	0	-0.198253	-2.591139	-1.783373
20	7	0	-0.135248	-1.106928	0.081532
21	6	0	1.249910	-0.817448	0.358890
22	8	0	2.069623	-0.560663	-0.503506

23	6	0	-0.653177	-1.846480	1.256593
24	8	0	-1.635460	-2.534768	1.219649
25	6	0	1.530123	-0.968529	1.840513
26	1	0	1.772431	0.011843	2.259984
27	6	0	0.262174	-1.589228	2.434957
28	1	0	0.435446	-2.532977	2.956573
29	1	0	-0.263853	-0.913223	3.113711
30	1	0	2.421404	-1.593856	1.947640
31	6	0	1.942078	2.610492	0.025023
32	1	0	2.373001	3.519841	-0.412829
33	1	0	2.077442	2.670927	1.106899
34	1	0	2.518264	1.766105	-0.354337
35	6	0	-0.578302	3.596616	1.769605
36	1	0	0.364174	3.392558	2.280290
37	1	0	-0.703396	4.683847	1.705993
38	1	0	-1.392561	3.201308	2.381963
39	6	0	0.841225	1.550643	-2.767252
40	1	0	0.263492	0.948339	-3.470884
41	1	0	1.247019	2.410288	-3.315264
42	1	0	1.677394	0.950386	-2.407987
43	6	0	-2.269071	2.257594	-2.928308
44	1	0	-3.314228	2.059619	-2.686172
45	1	0	-2.222794	3.224669	-3.444162
46	1	0	-1.924149	1.493554	-3.627323
47	6	0	-3.155653	3.445332	-0.074081
48	1	0	-3.363535	3.366200	0.995336
49	1	0	-3.180200	4.508395	-0.341835
50	1	0	-3.960334	2.943239	-0.614652
51	1	0	3.791131	-0.901271	-0.125125
52	8	0	4.670885	-1.225644	0.158950
53	6	0	5.419931	-0.150050	0.641706
54	6	0	6.545437	-0.737268	1.497504
55	6	0	5.942596	0.703533	-0.523713
56	1	0	4.849418	0.524311	1.293430
57	9	0	6.587364	1.803512	-0.092438
58	9	0	7.290632	-1.622197	0.812919
59	9	0	7.364223	0.231146	1.953841
60	9	0	6.773909	0.021040	-1.328940
61	9	0	4.891764	1.110558	-1.273607
62	9	0	6.024474	-1.374233	2.562199
63	7	0	-6.014957	-0.872297	1.647071
64	8	0	-6.409276	0.192581	2.112827
65	8	0	-6.406205	-1.984178	2.001271

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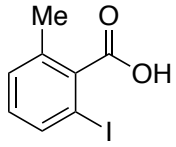
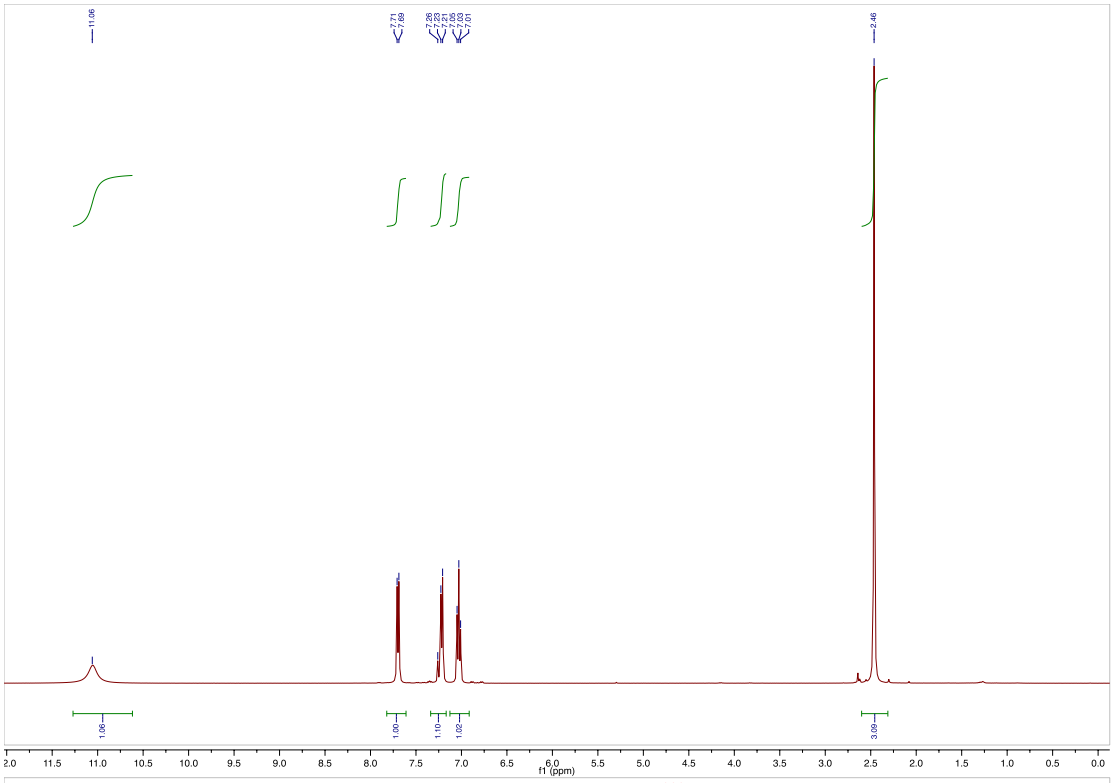
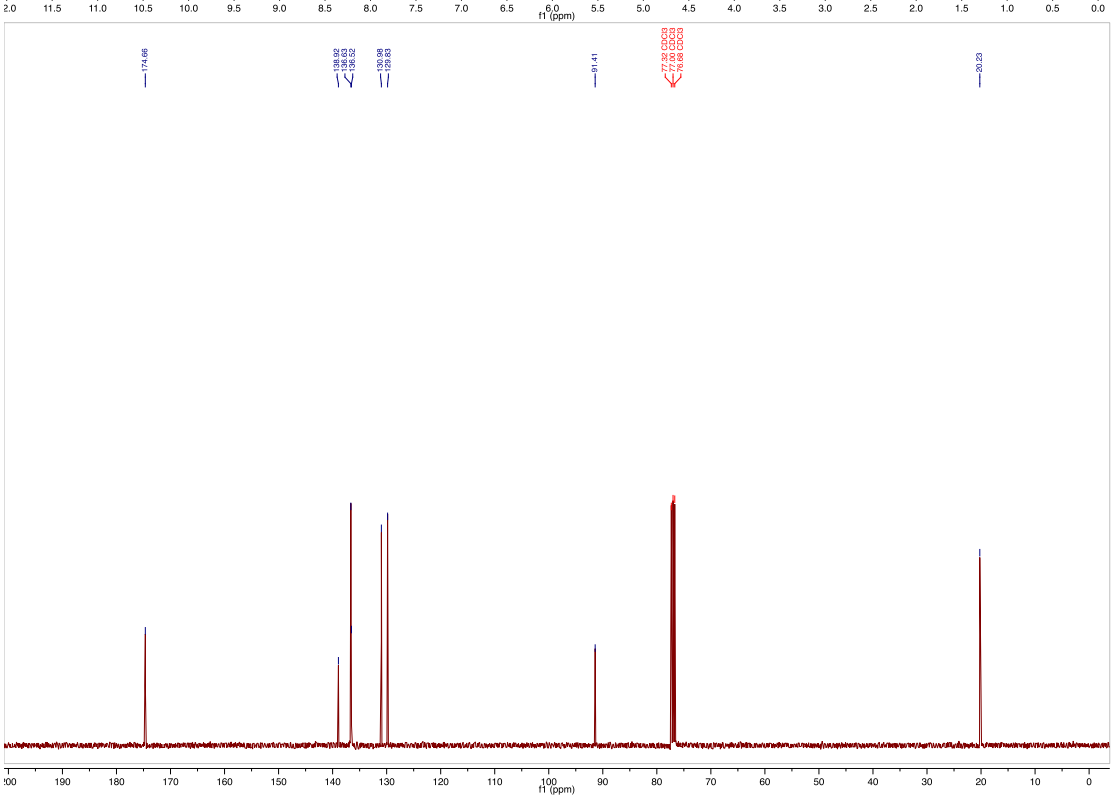
^{1}H NMR and ^{13}C NMR of iodobenzoic acids 2 and 3

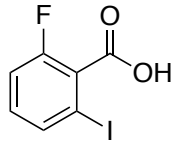
2-Iodo-6-methylbenzoic acid (2a)

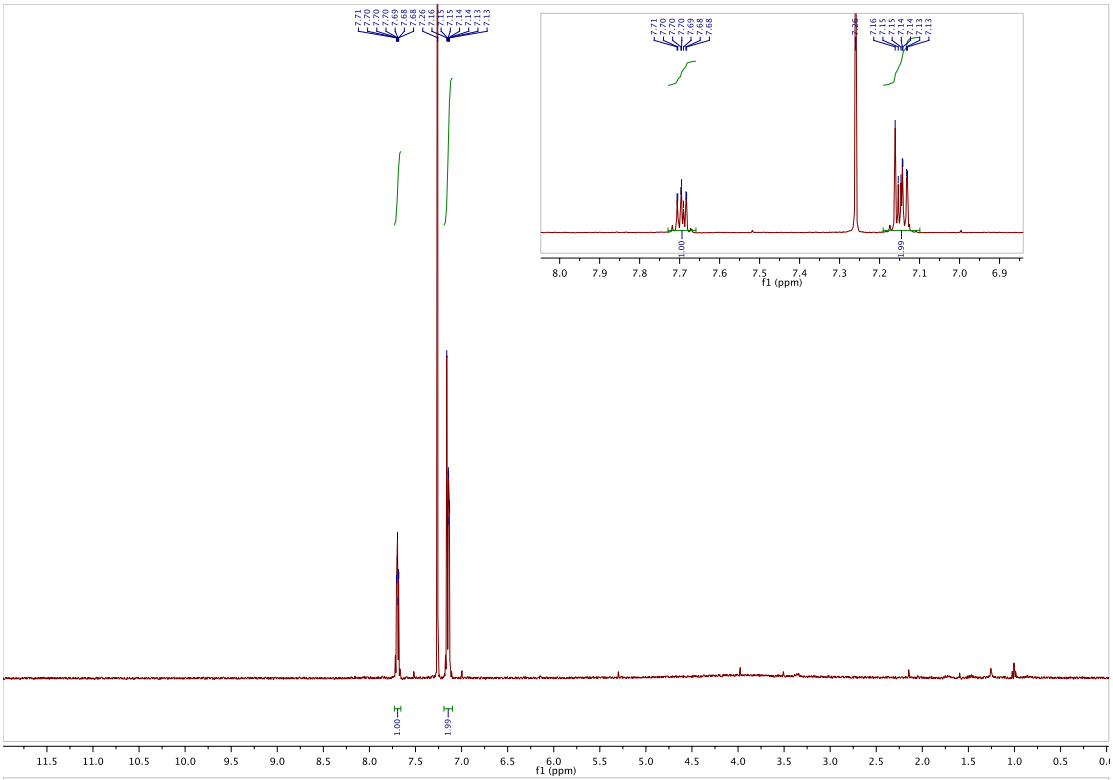


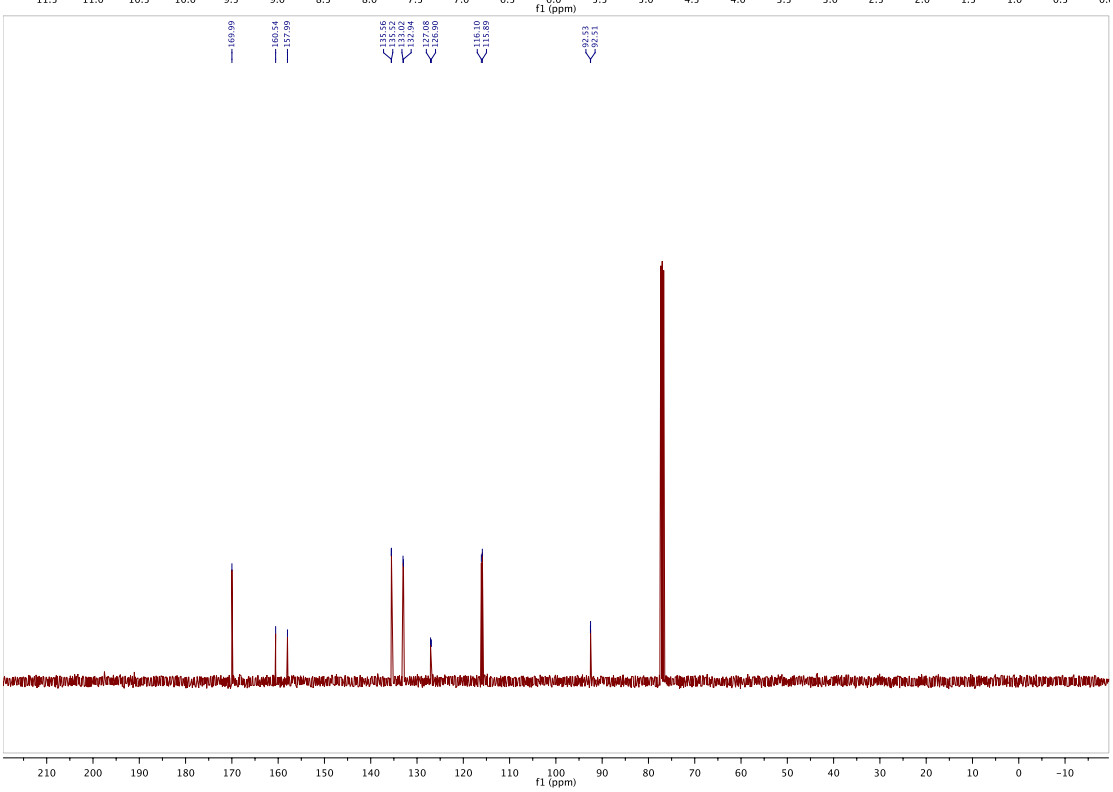




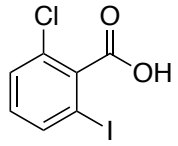
2-Fluoro-6-iodobenzoic acid (2b)

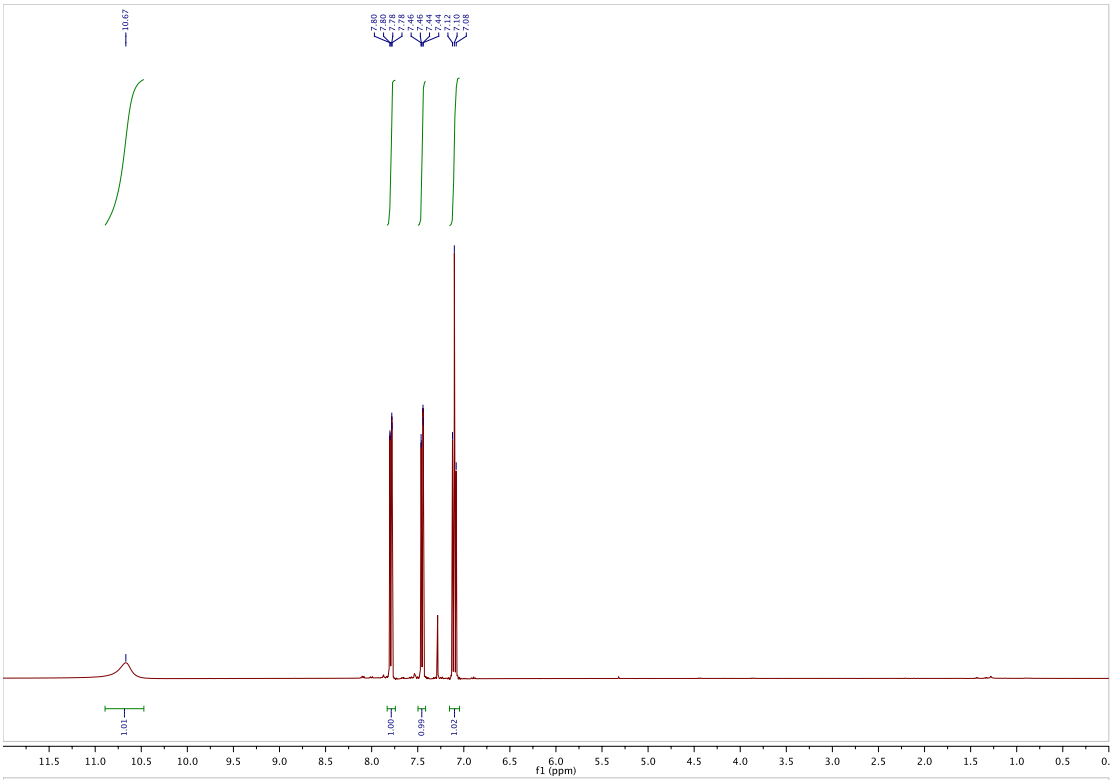


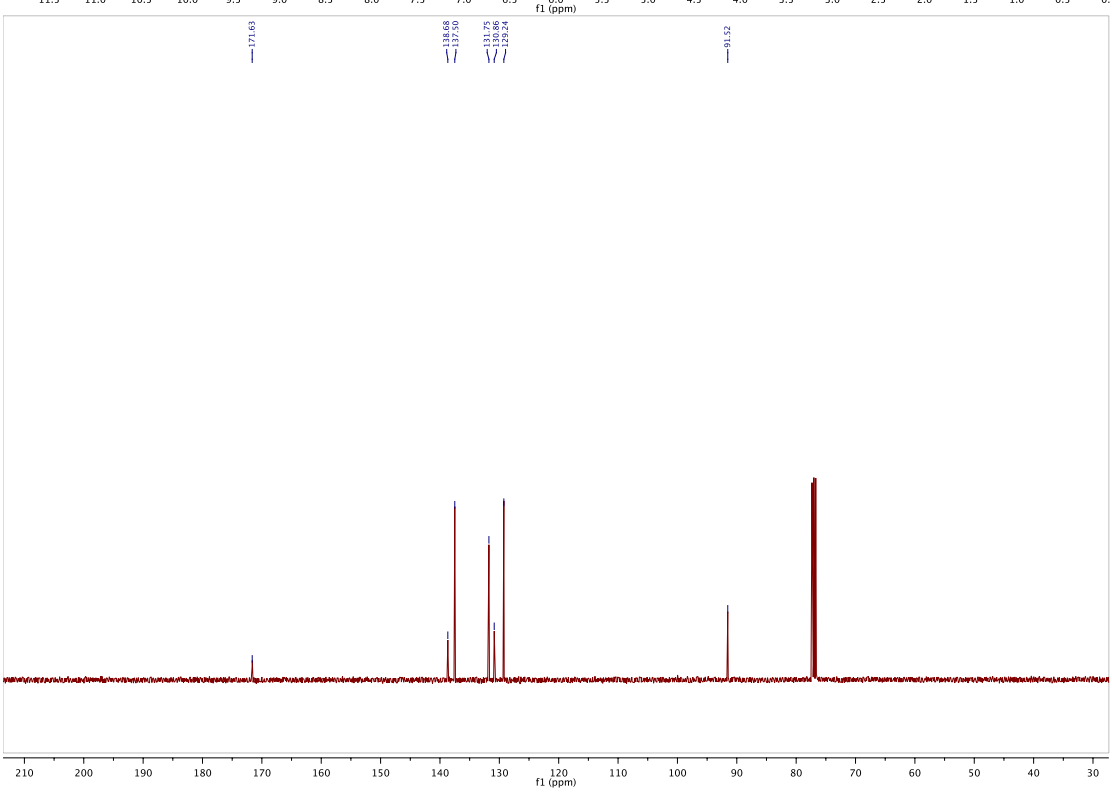




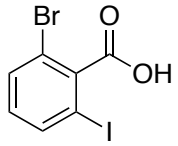
2-Chloro-6-iodobenzoic acid (2c)

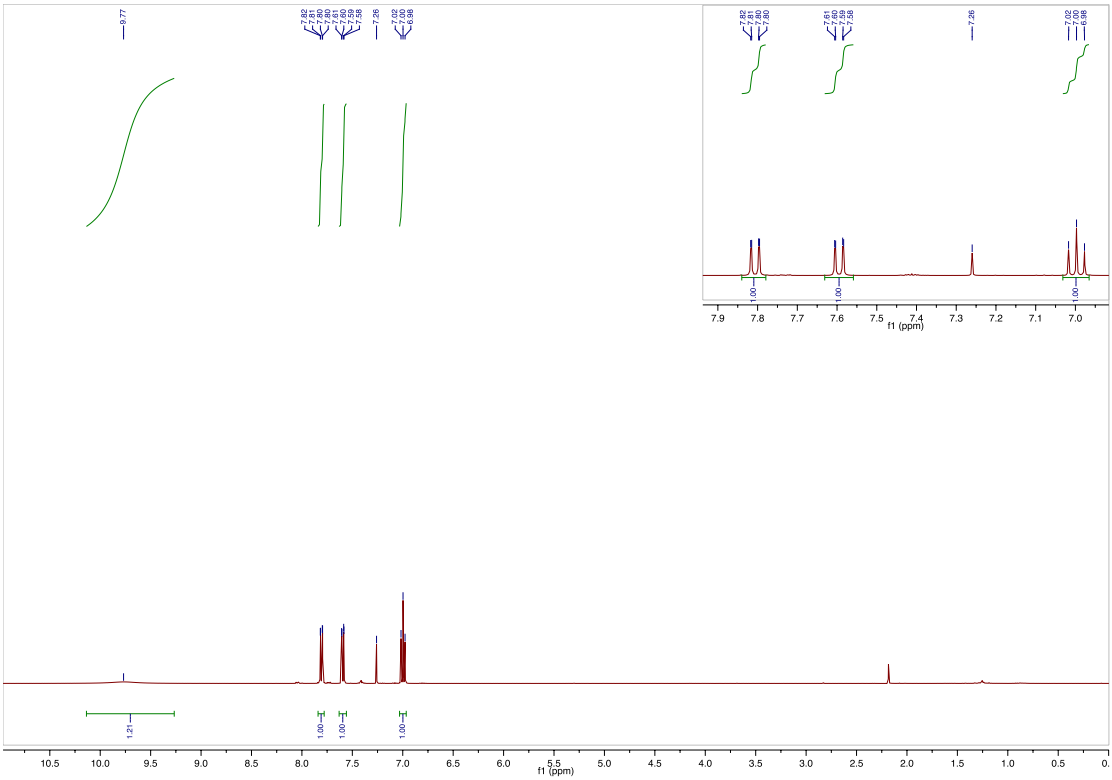


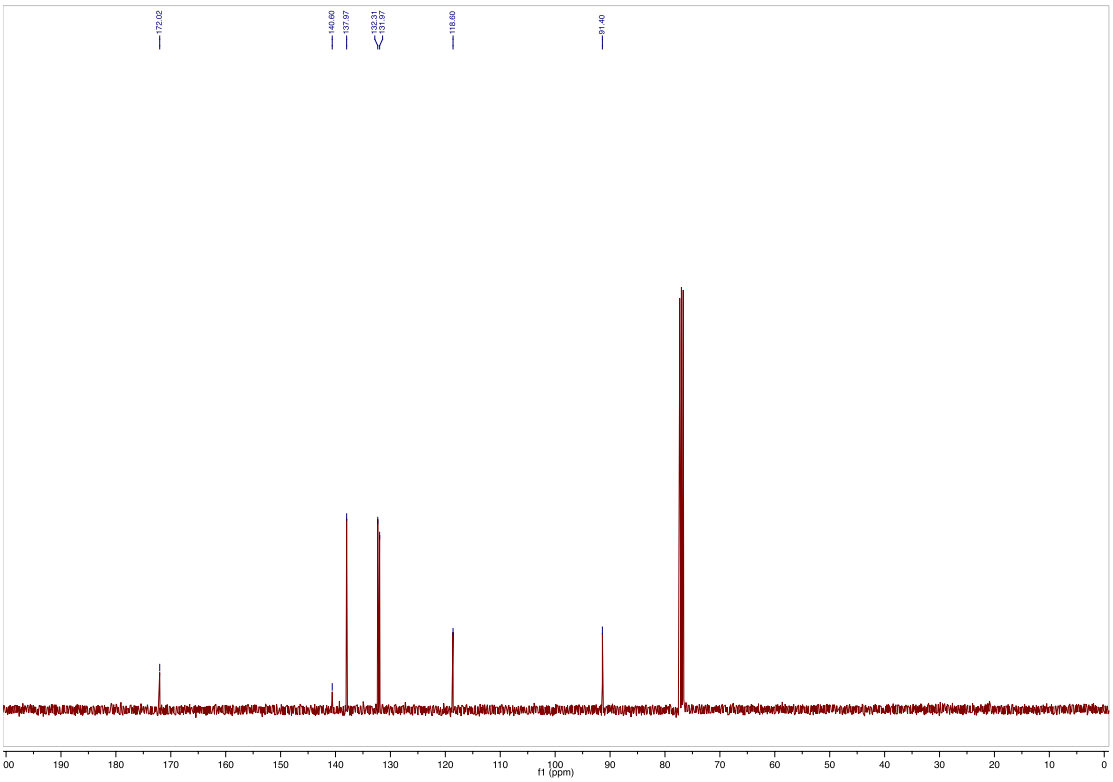




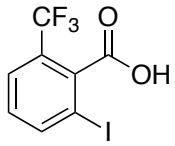
2-Bromo-6-iodobenzoic acid (2d)

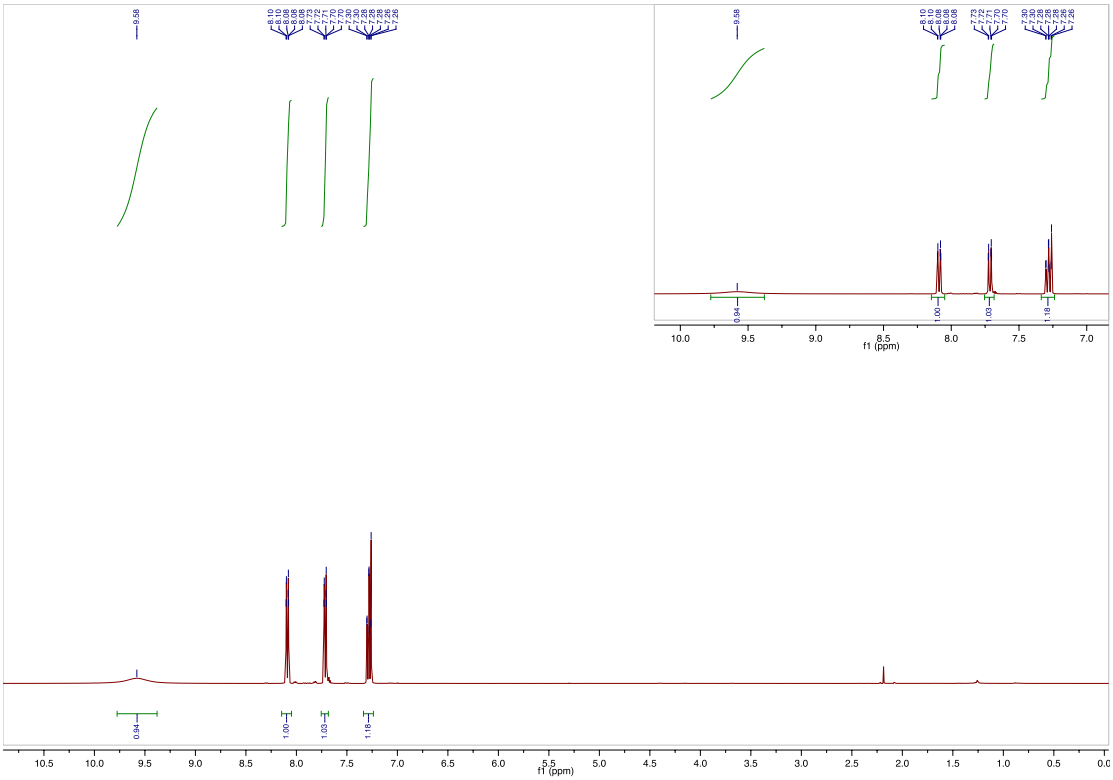


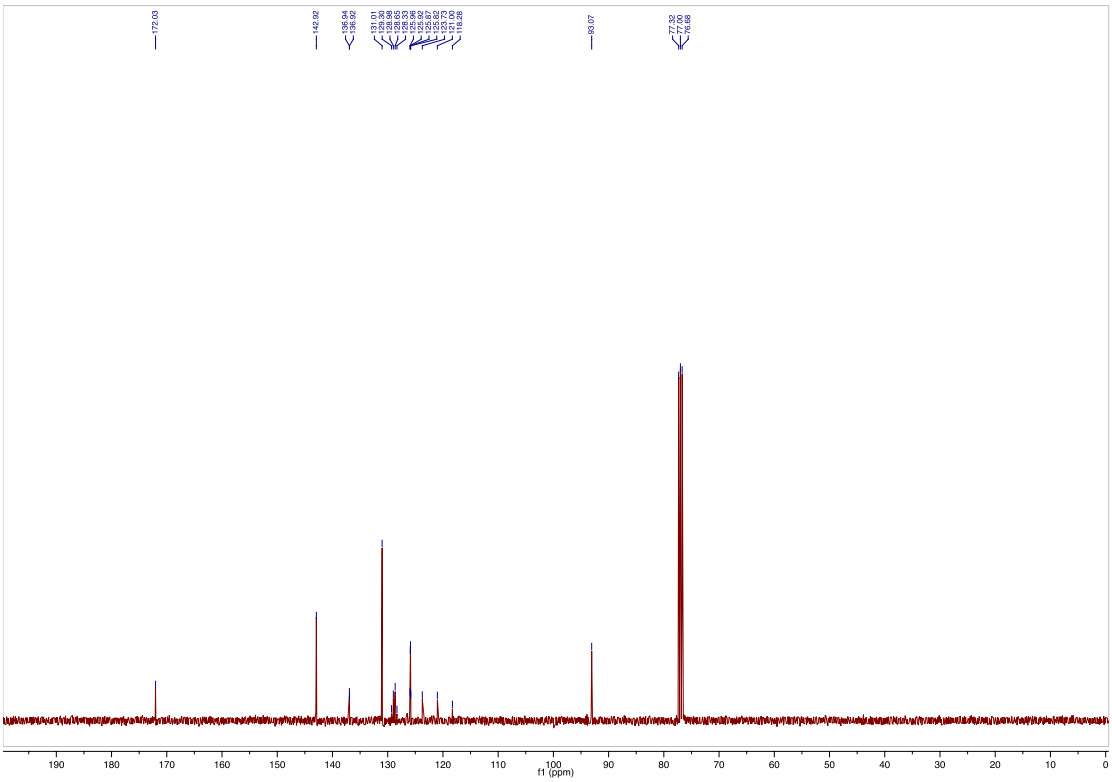




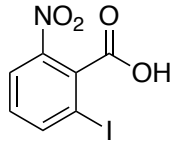
2-Iodo-6-(trifluoromethyl)benzoic acid (2e)

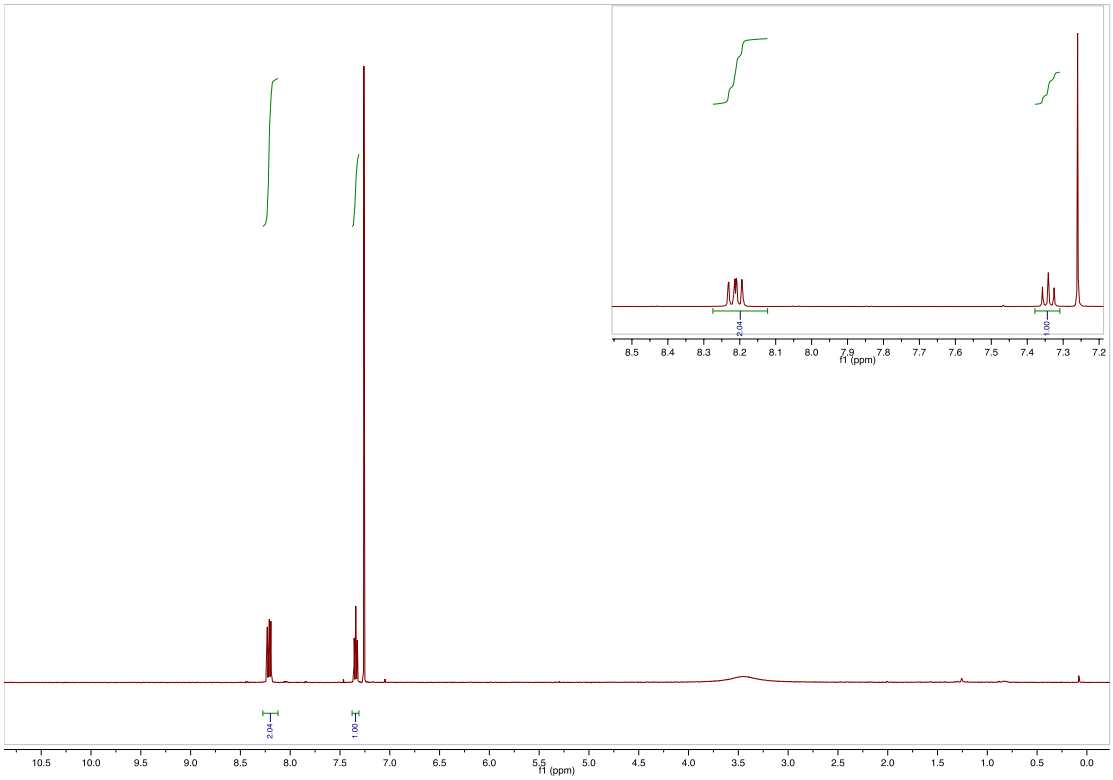


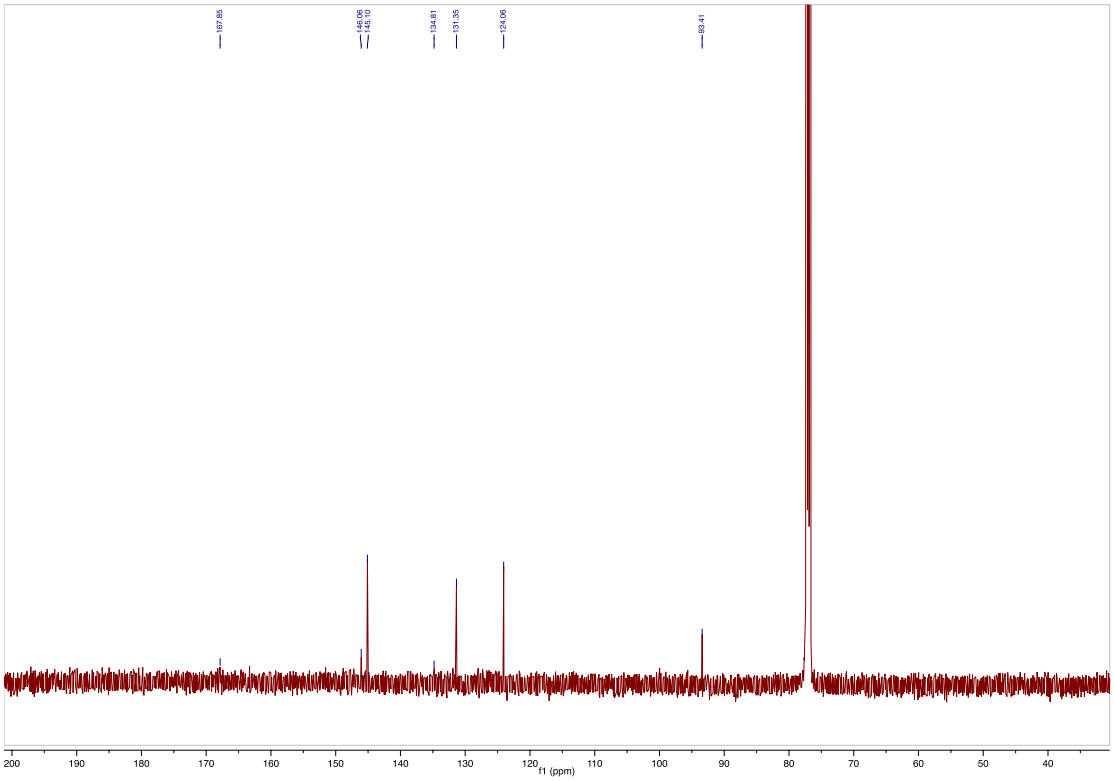




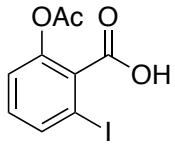
2-Iodo-6-nitrobenzoic acid (2f)

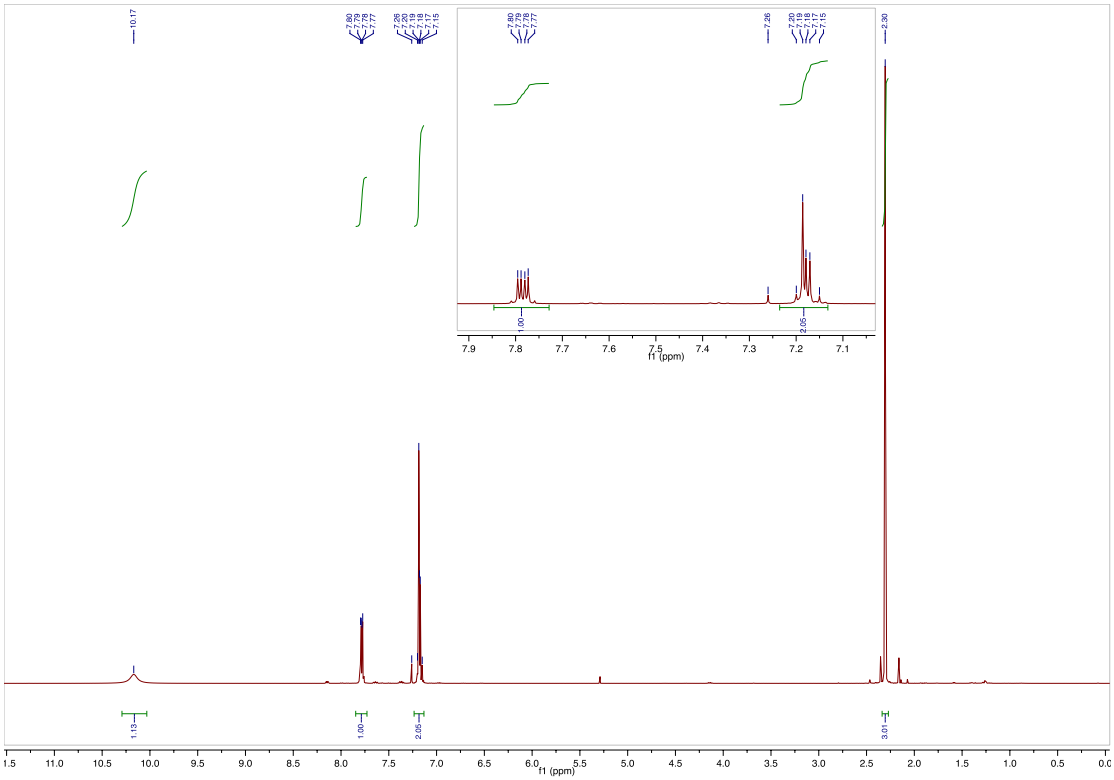


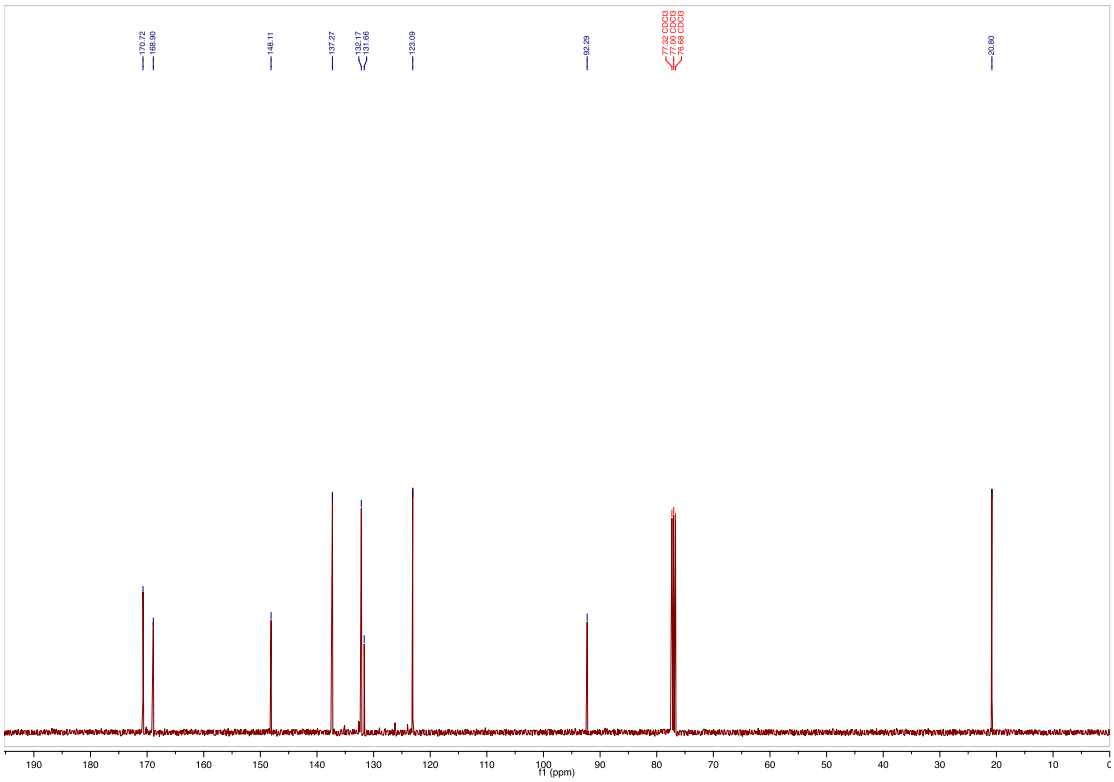




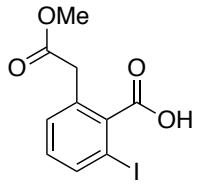
2-Acetoxy-6-iodobenzoic acid (2g)

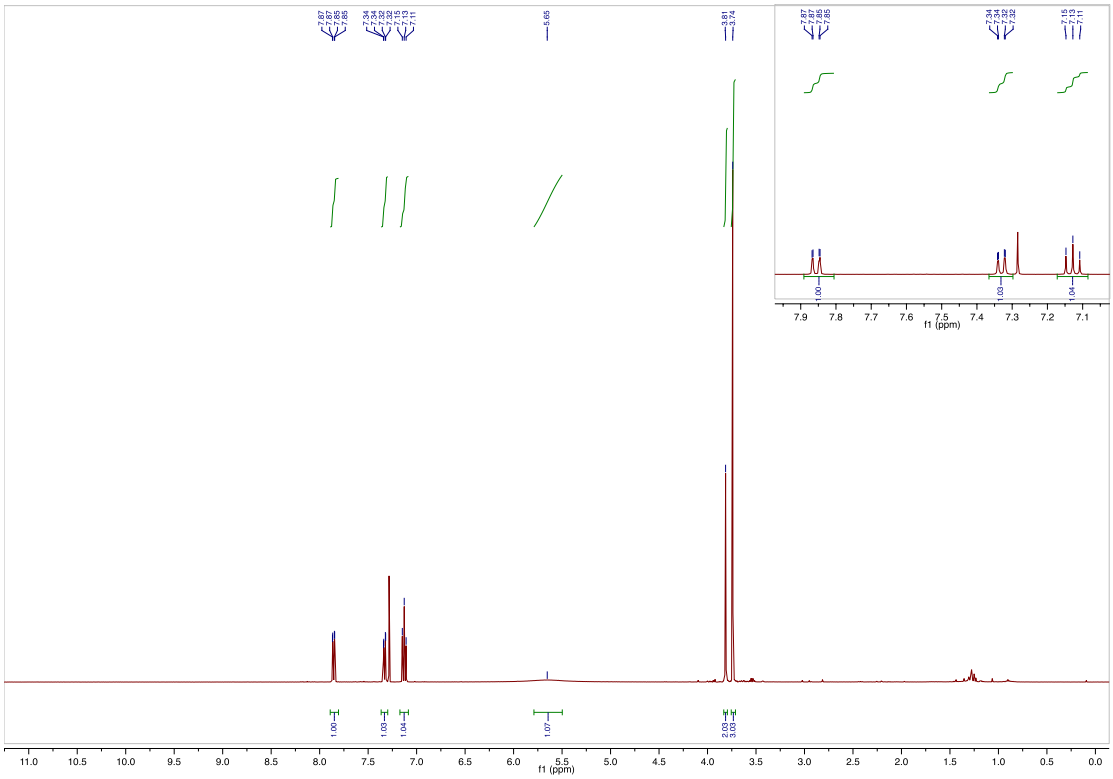


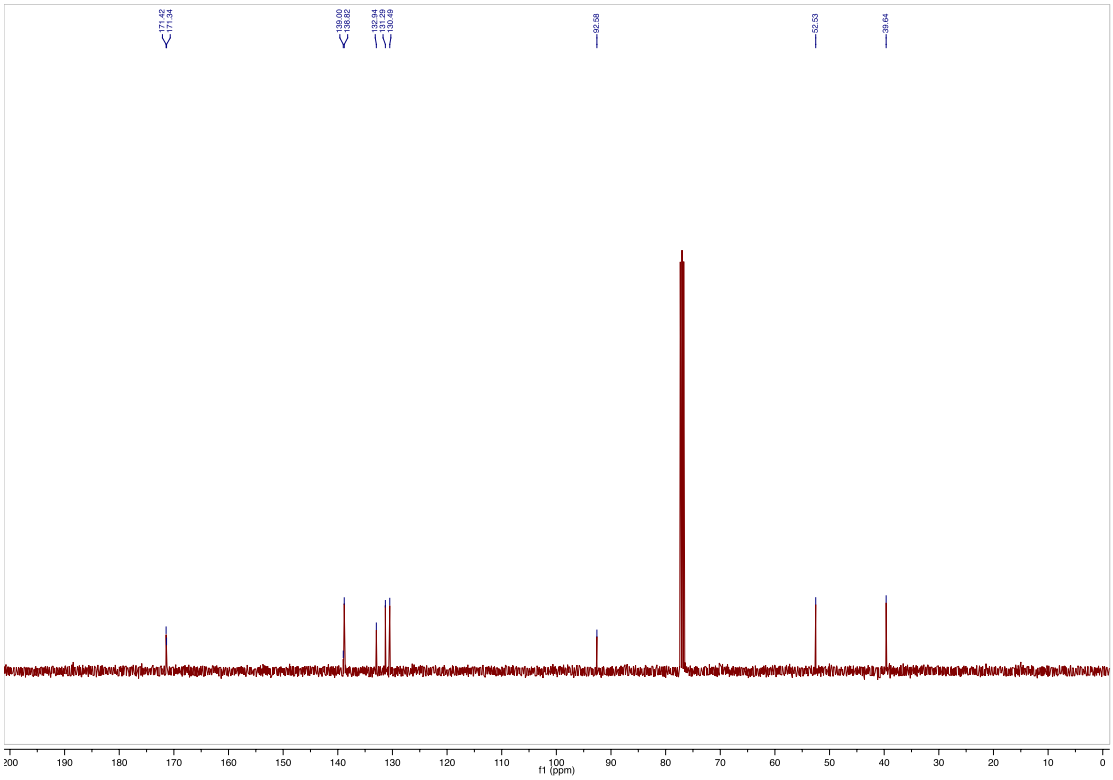




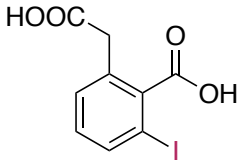
2-Iodo-6-(2-methoxy-2-oxoethyl)benzoic acid (2h)

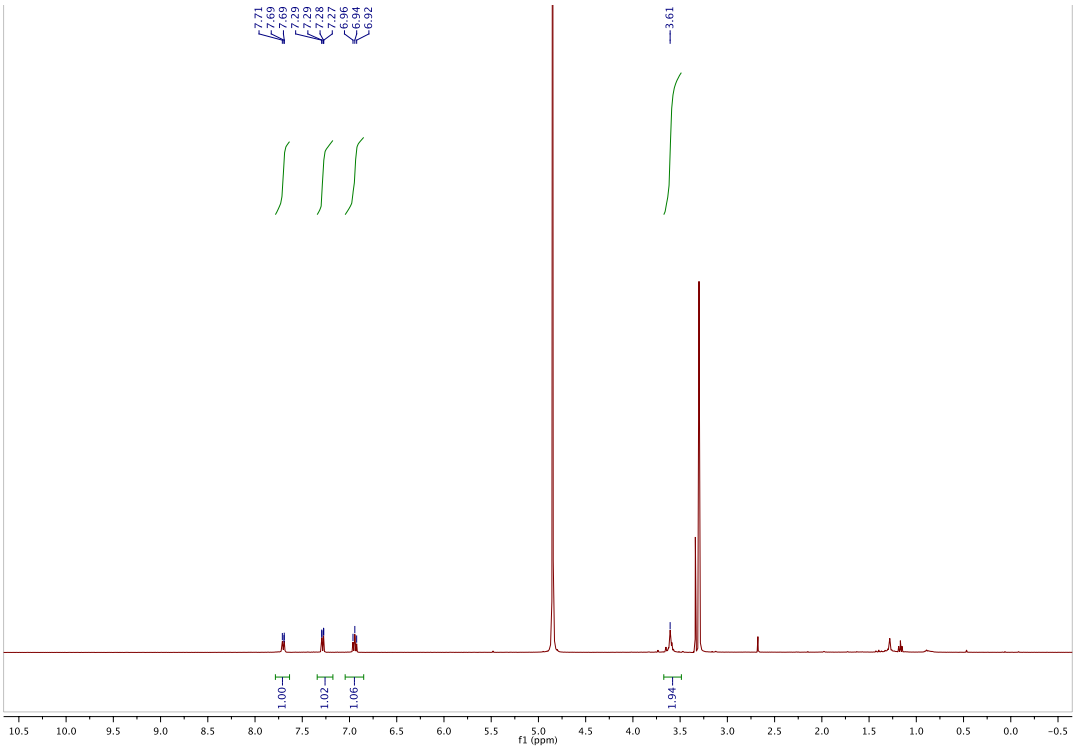


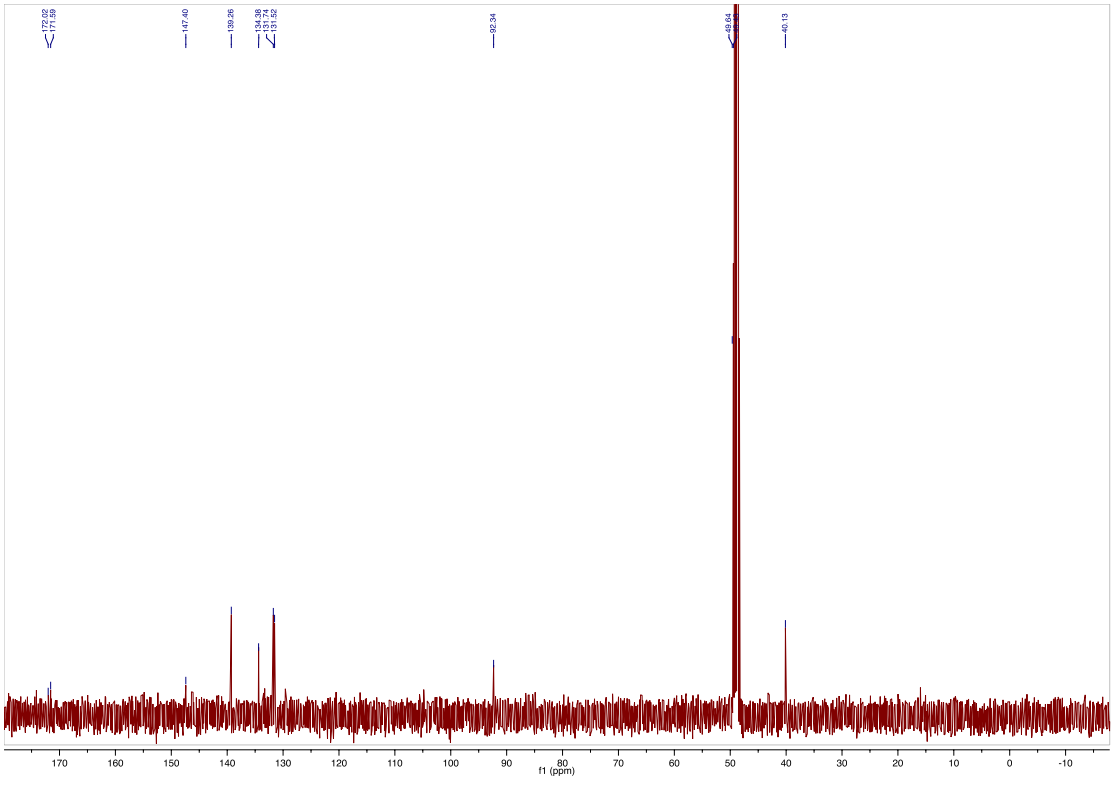




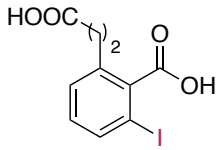
2-(Carboxymethyl)-6-iodobenzoic acid (2i)

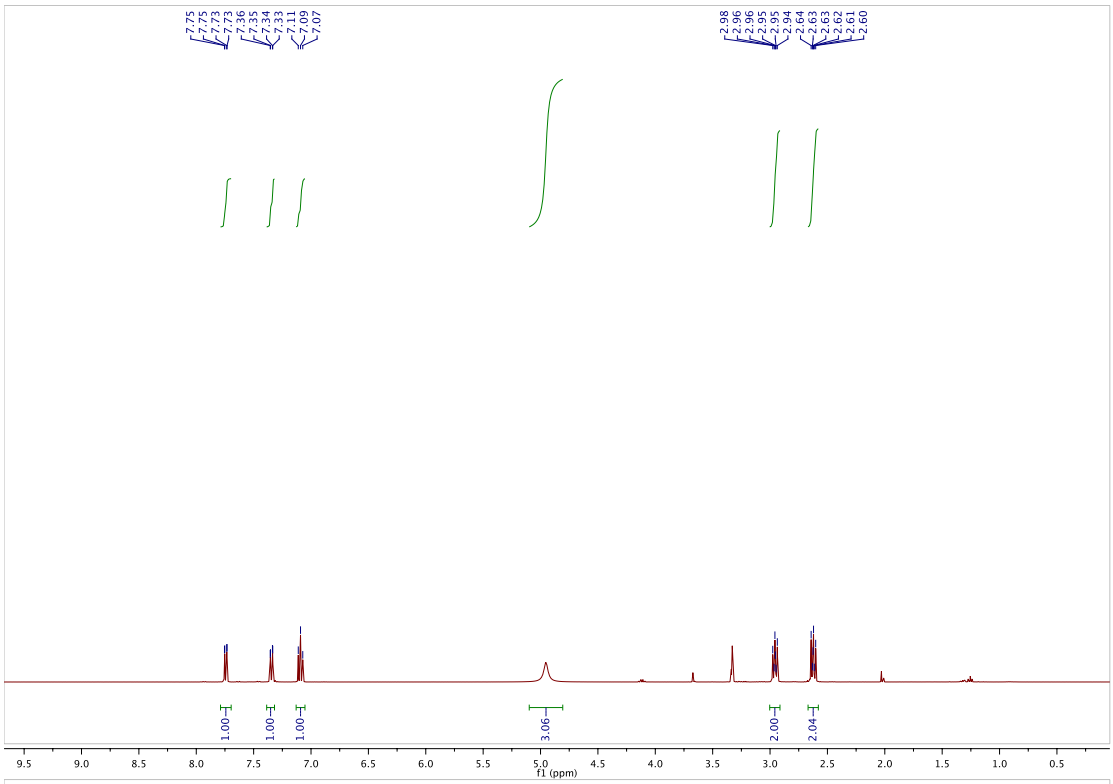


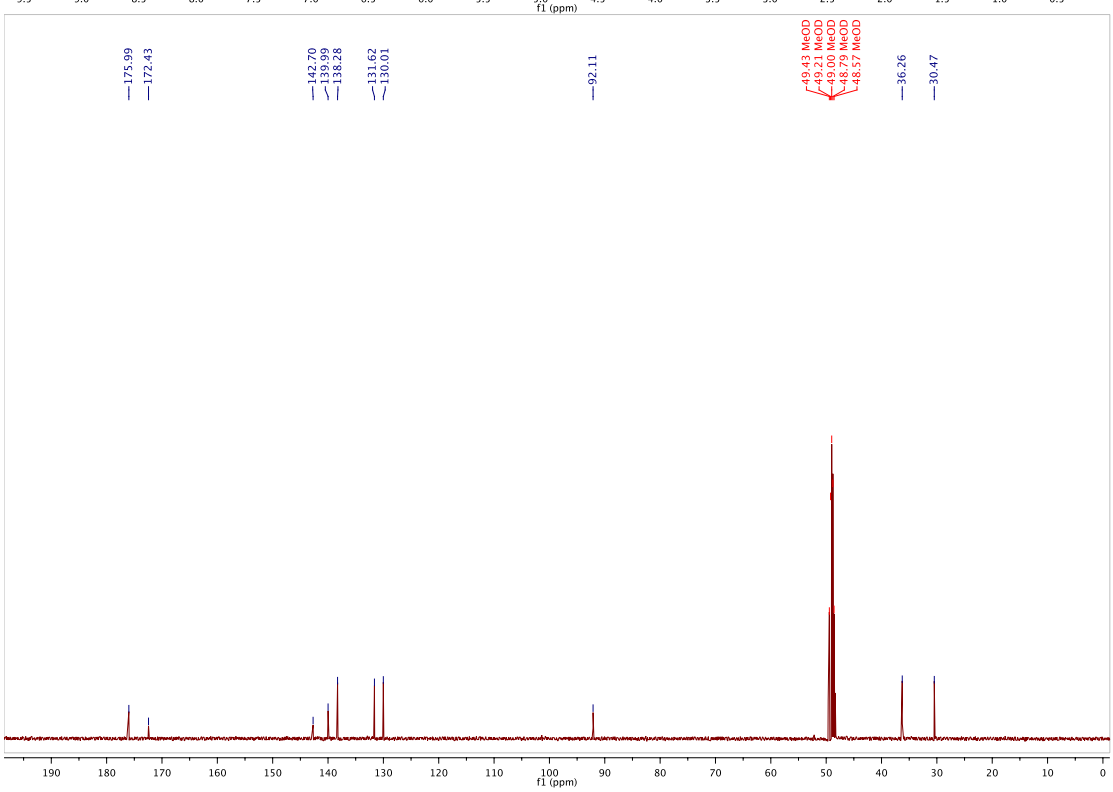




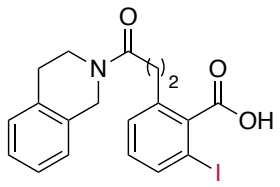
2-(2-Carboxyethyl)-6-iodobenzoic acid (2j)

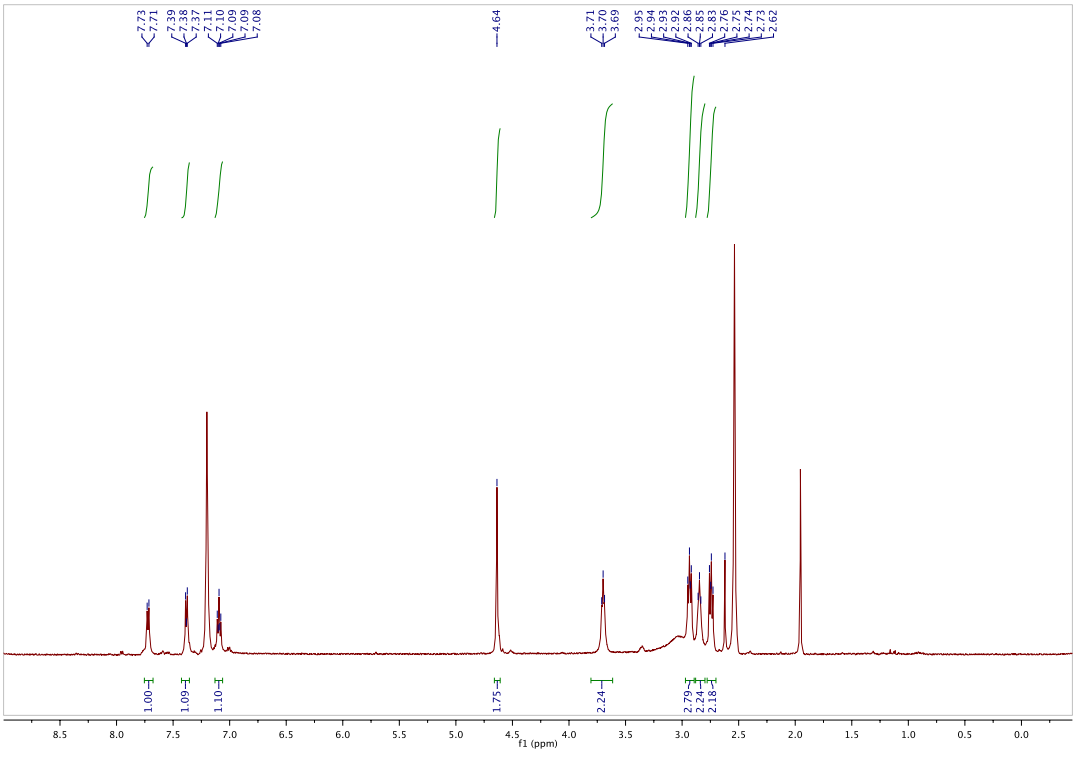


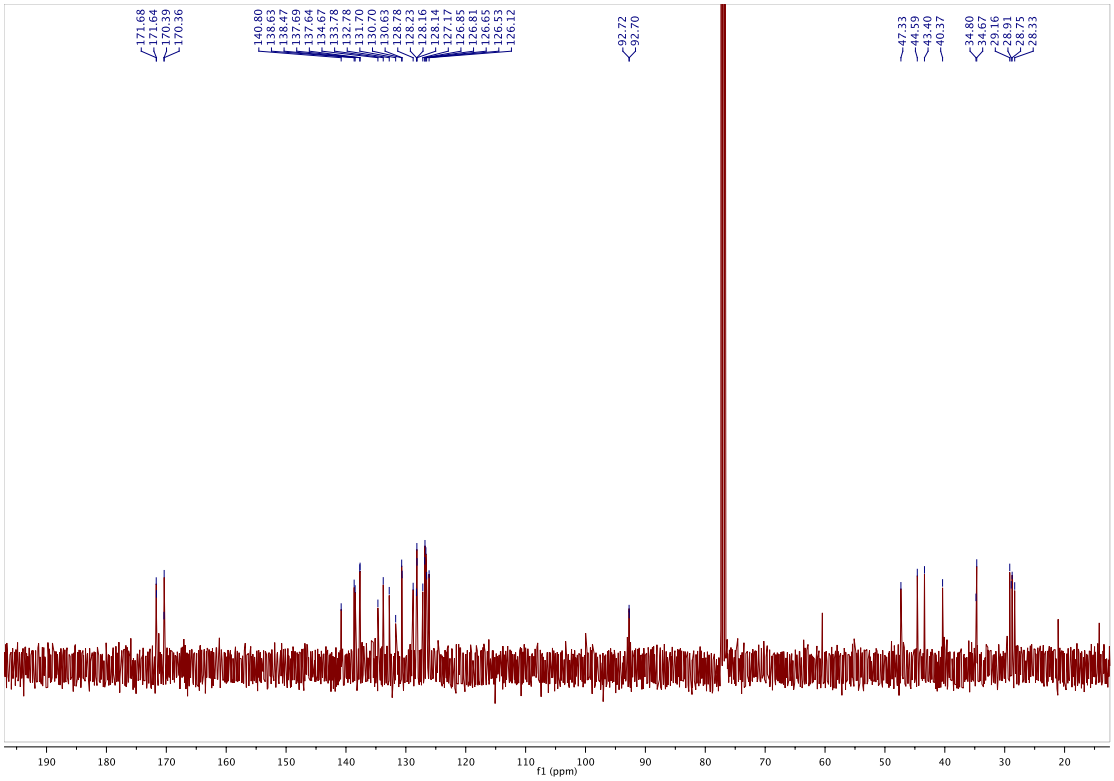




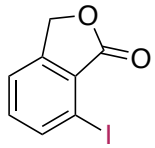
2-(3-(3,4-Dihydroisoquinolin-2(1*H*)-yl)-3-oxopropyl)-6-iodobenzoic acid (2k)

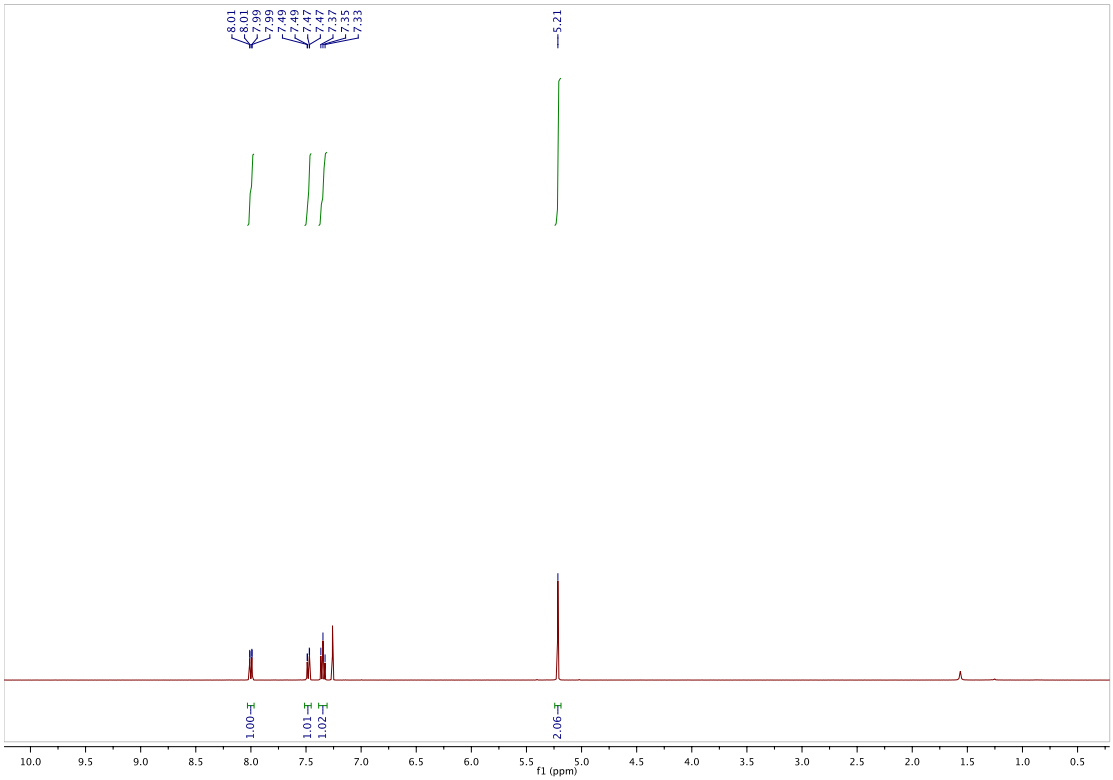


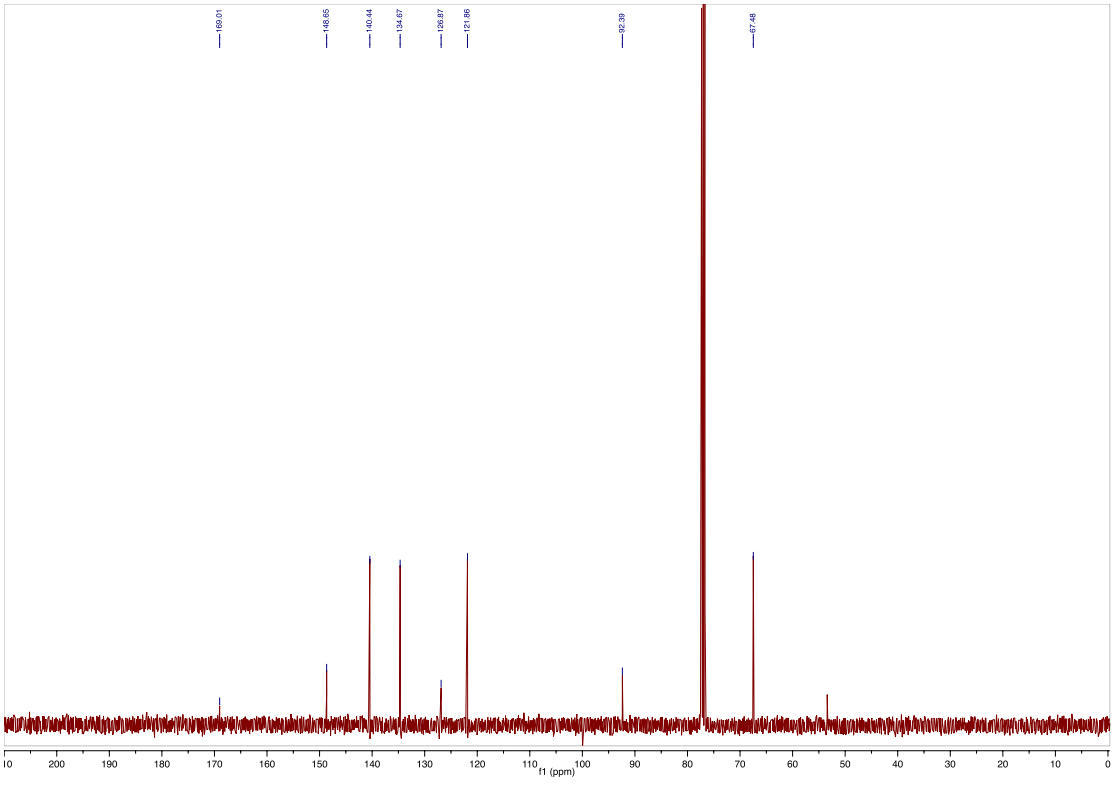




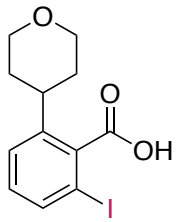
2-(Hydroxymethyl)-6-iodobenzoic acid (2l)

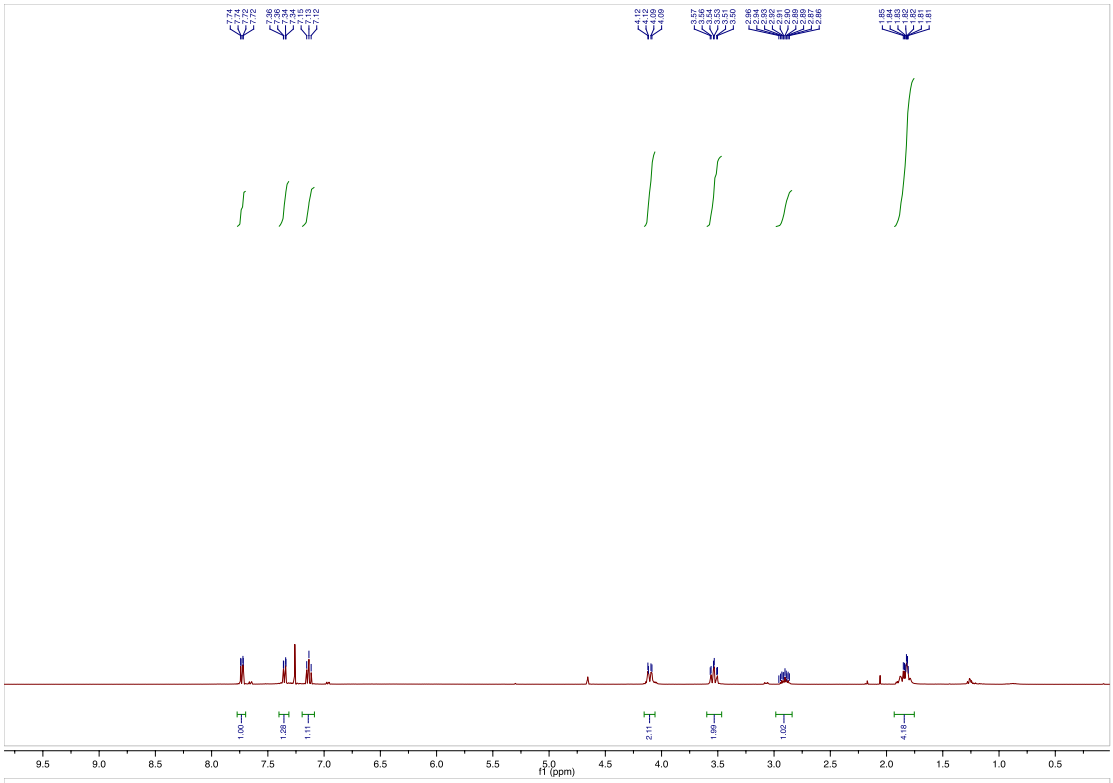


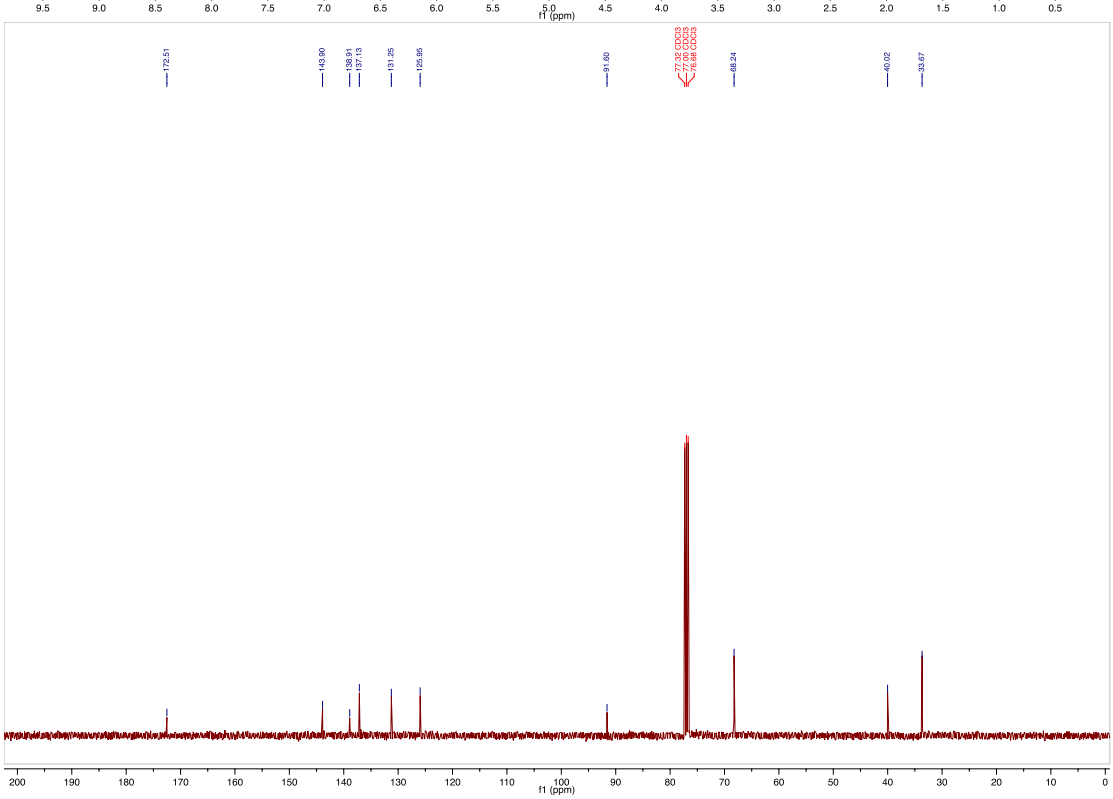




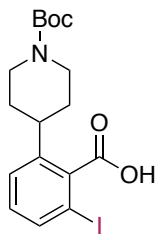
2-Iodo-6-(tetrahydro-2*H*-pyran-4-yl)benzoic acid (2m)

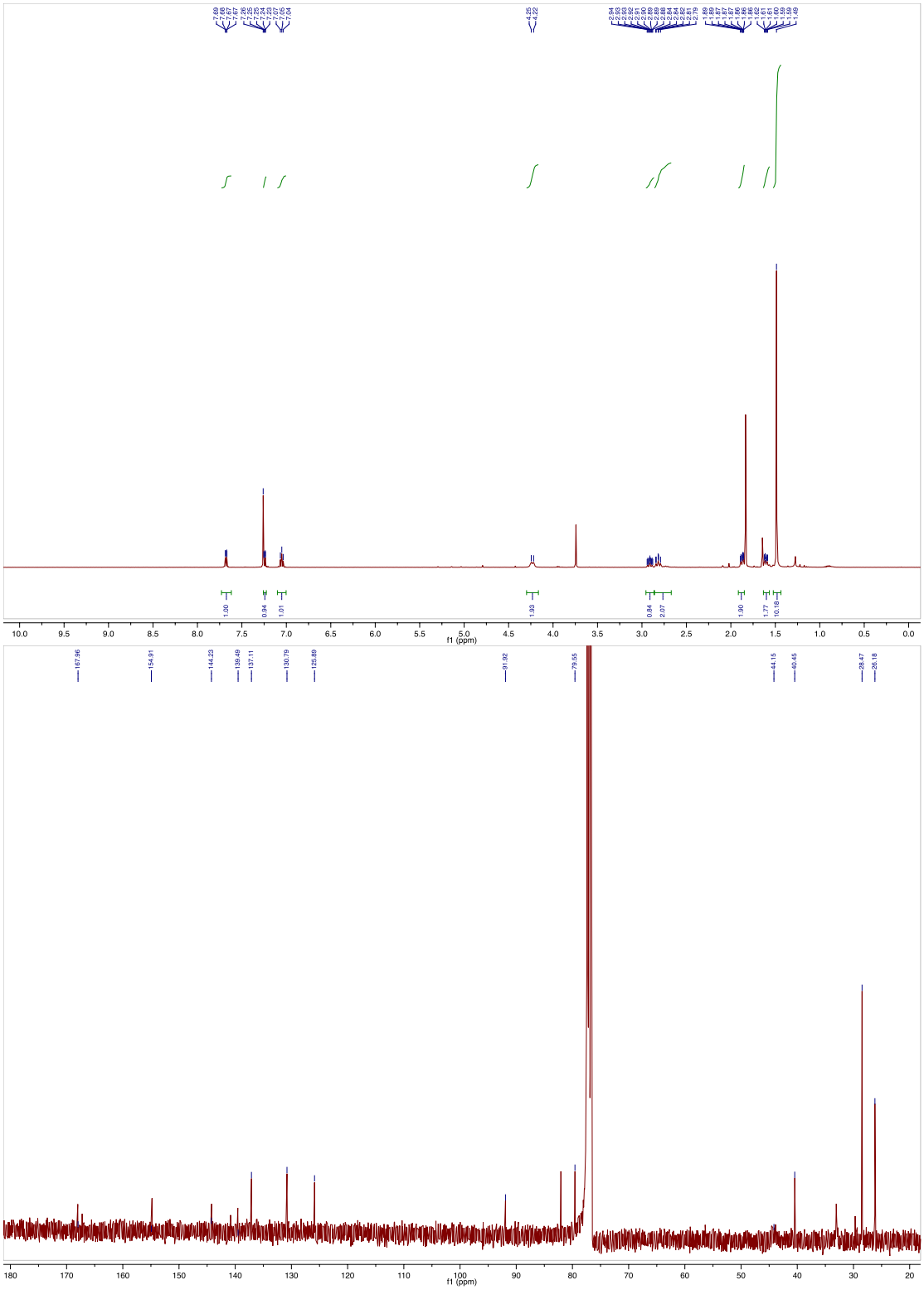




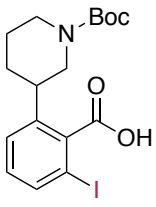


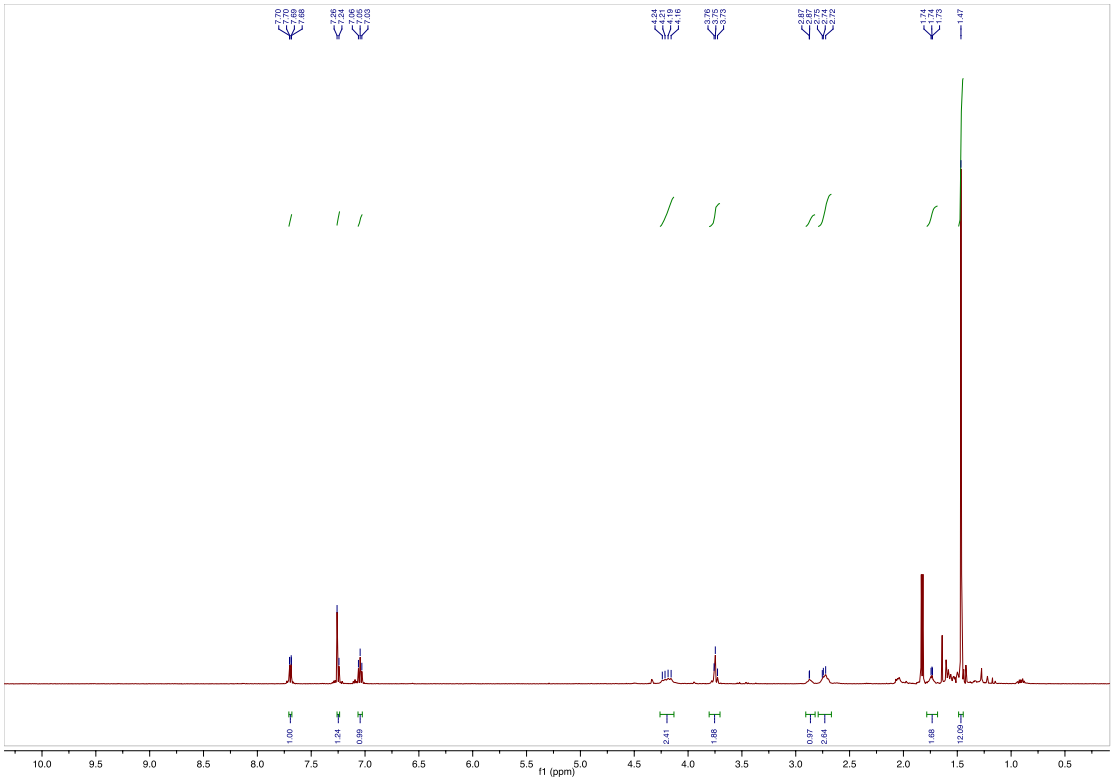
2-(1-(*tert*-Butoxycarbonyl)piperidin-4-yl)-6-iodobenzoic acid (2n)

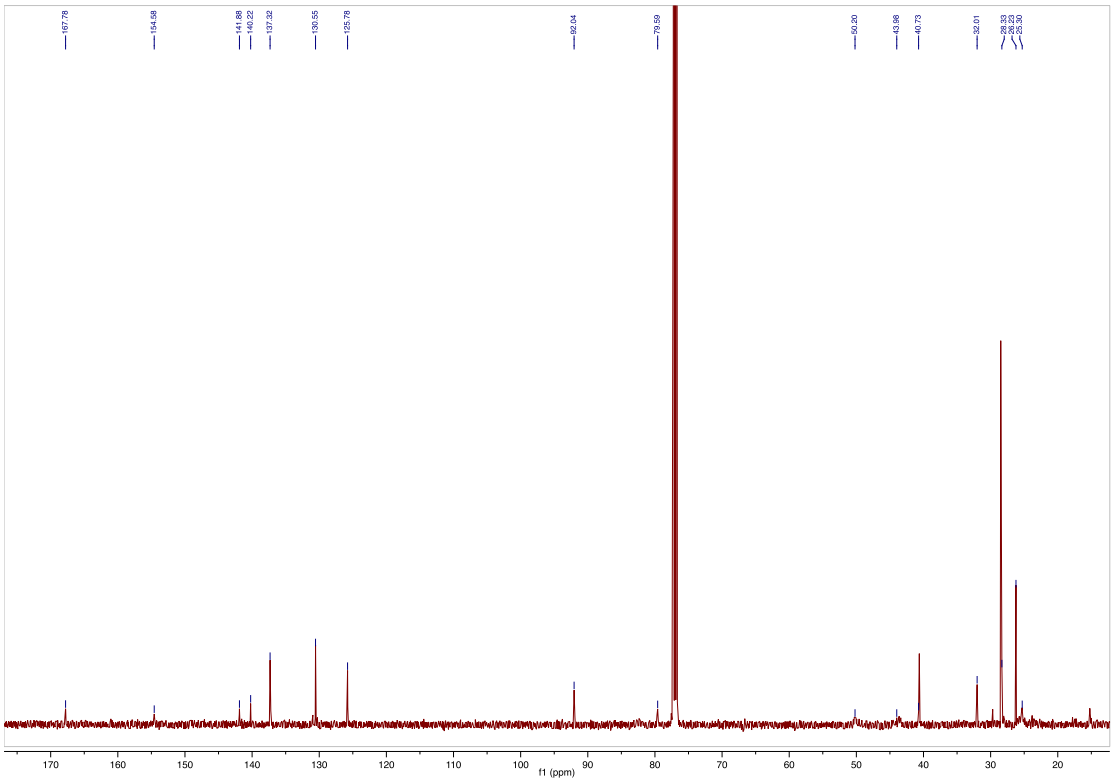




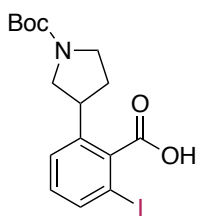
2-(1-(*tert*-Butoxycarbonyl)piperidin-3-yl)-6-iodobenzoic acid (2o)

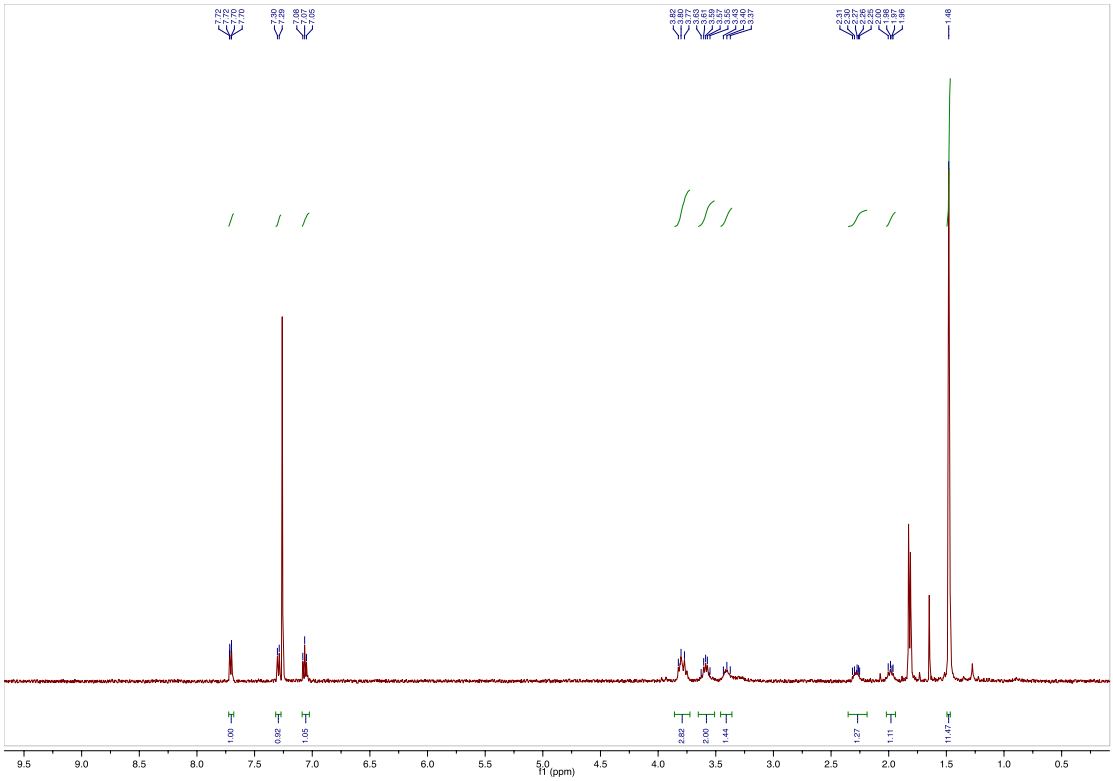


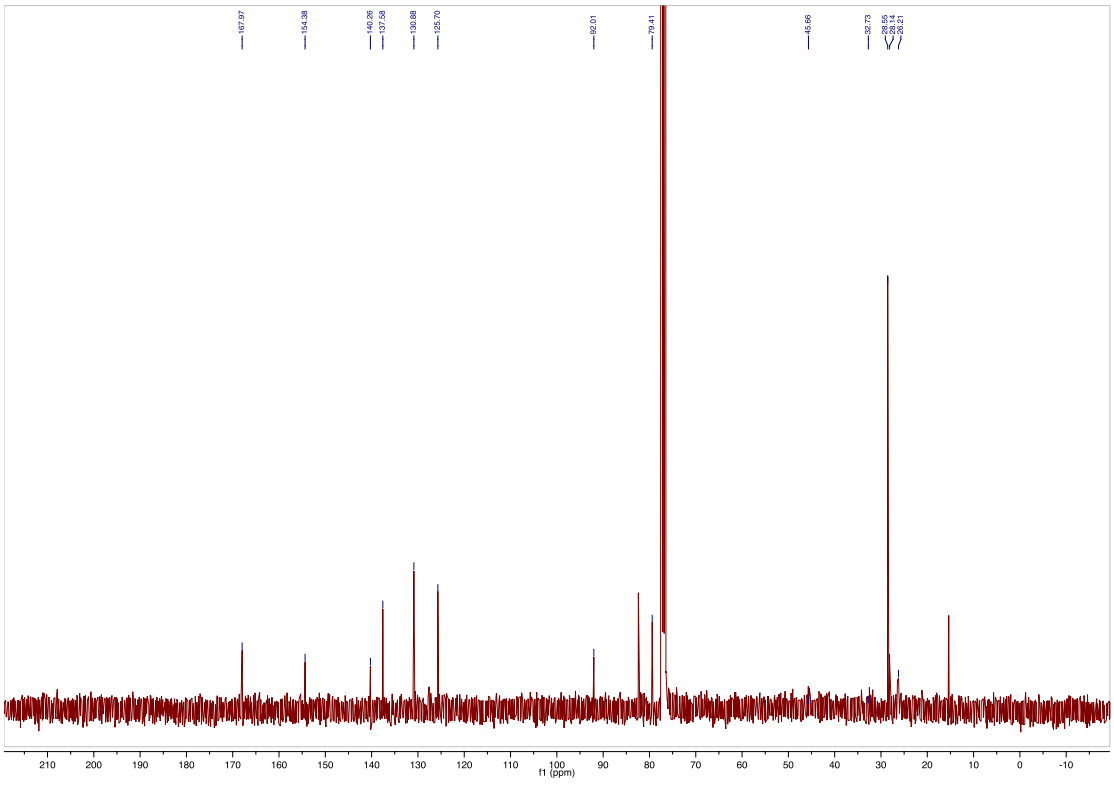




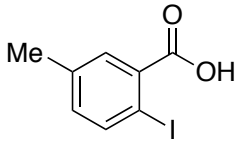
2-(1-(*tert*-Butoxycarbonyl)pyrrolidin-3-yl)-6-iodobenzoic acid (2p)

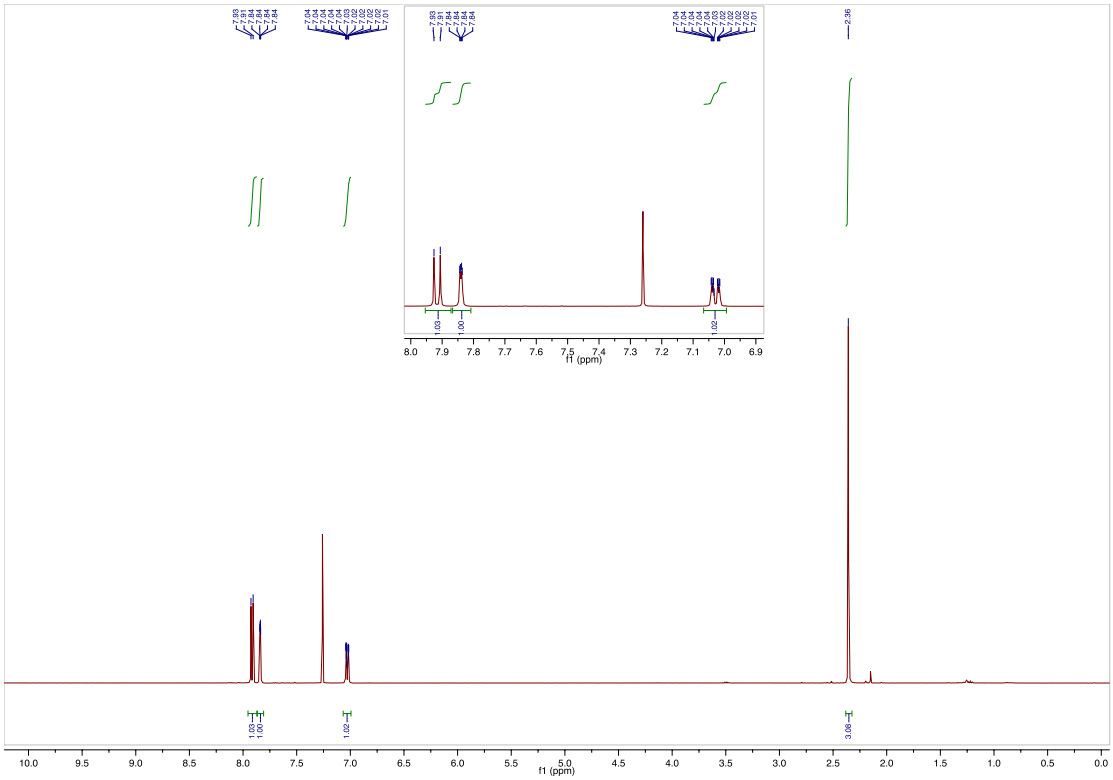


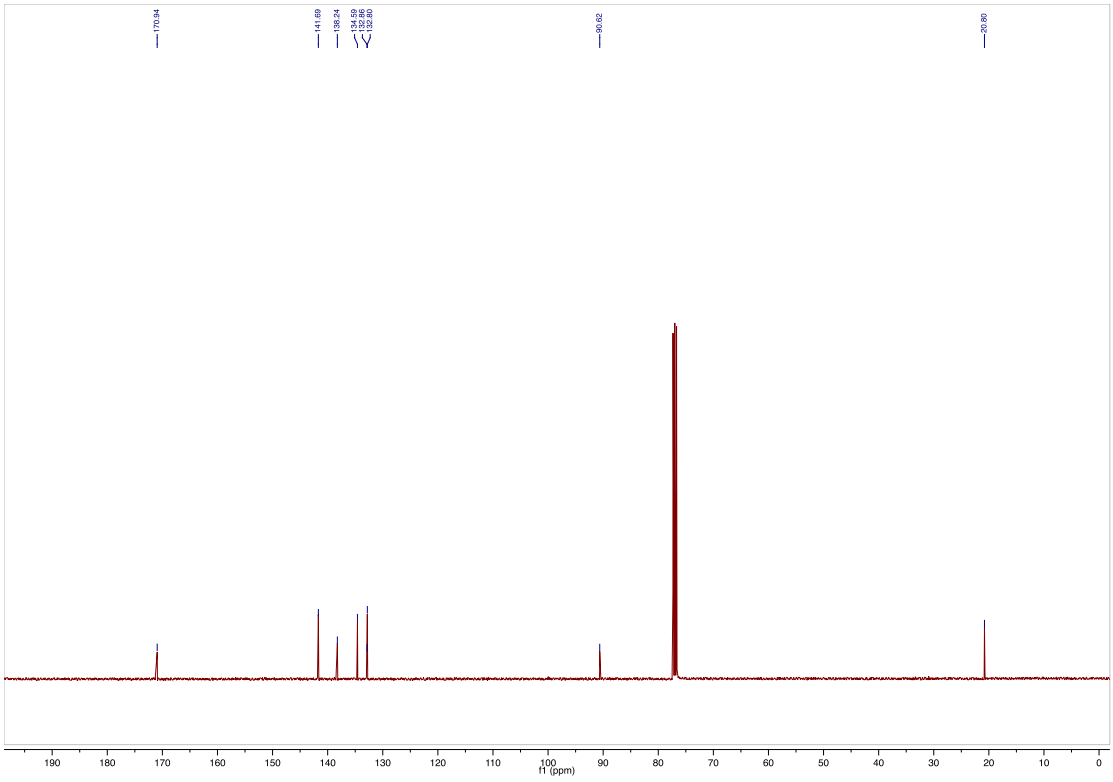




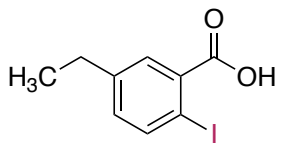
2-Iodo-5-methylbenzoic acid (2q)

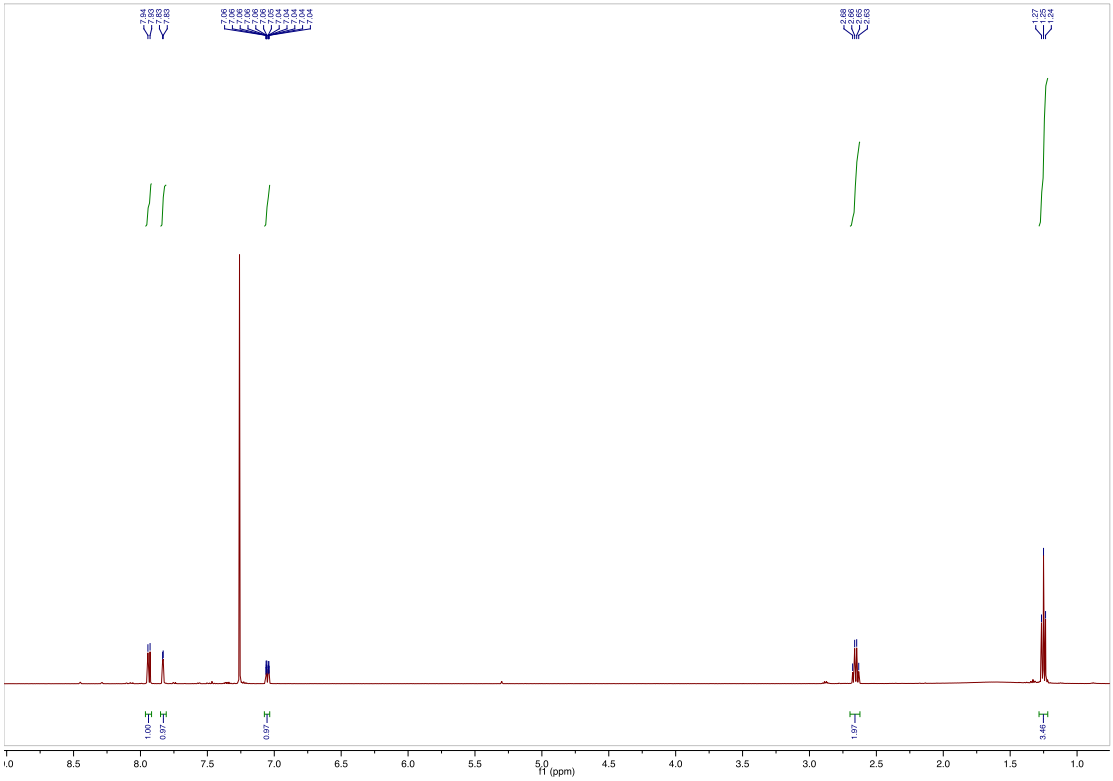


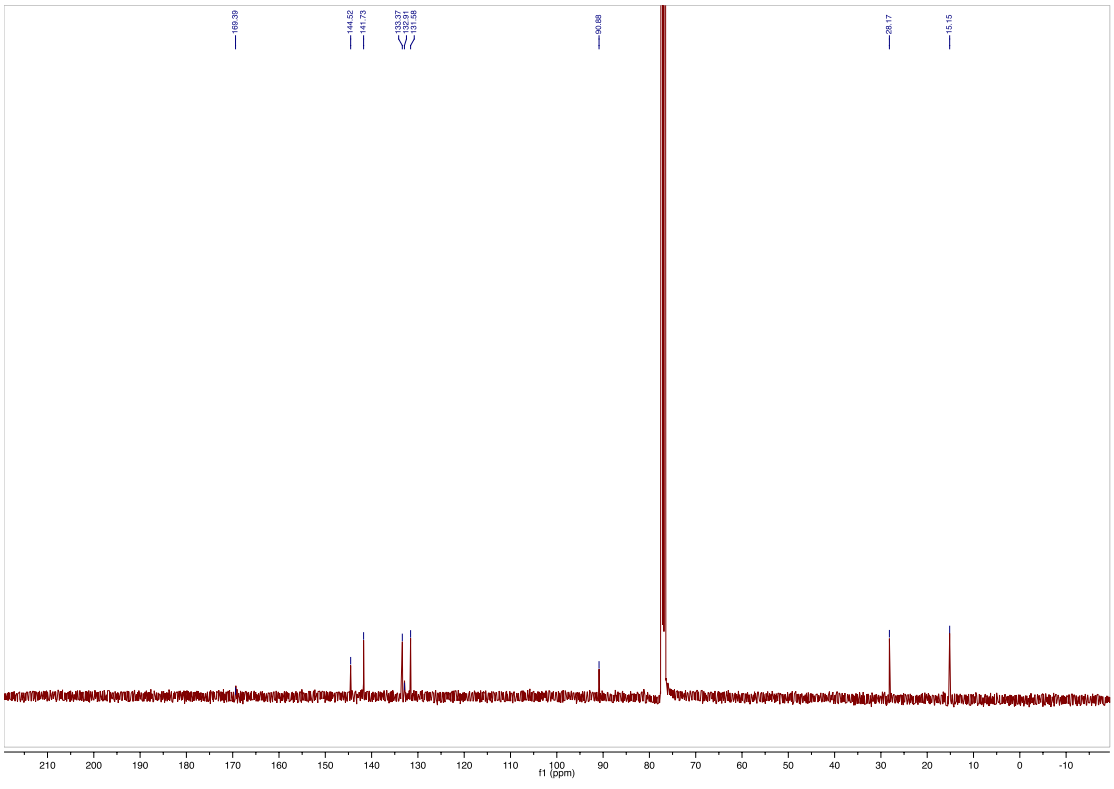




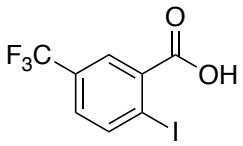
5-Ethyl-2-iodobenzoic acid (2r)

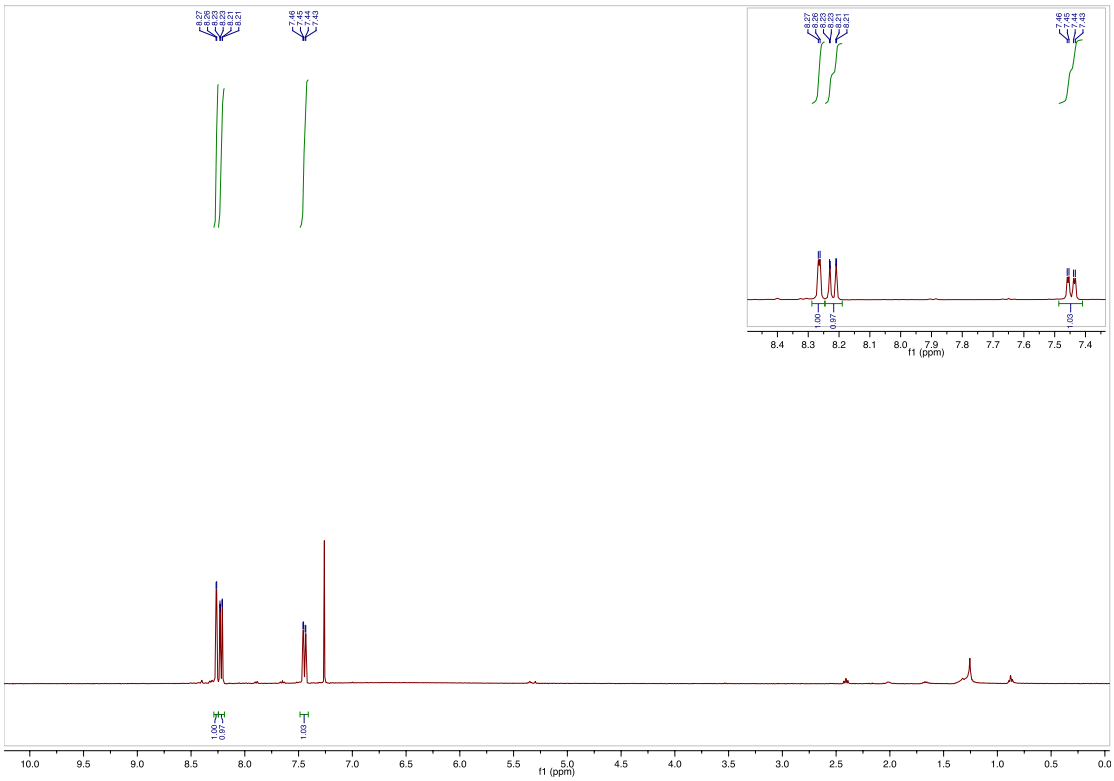


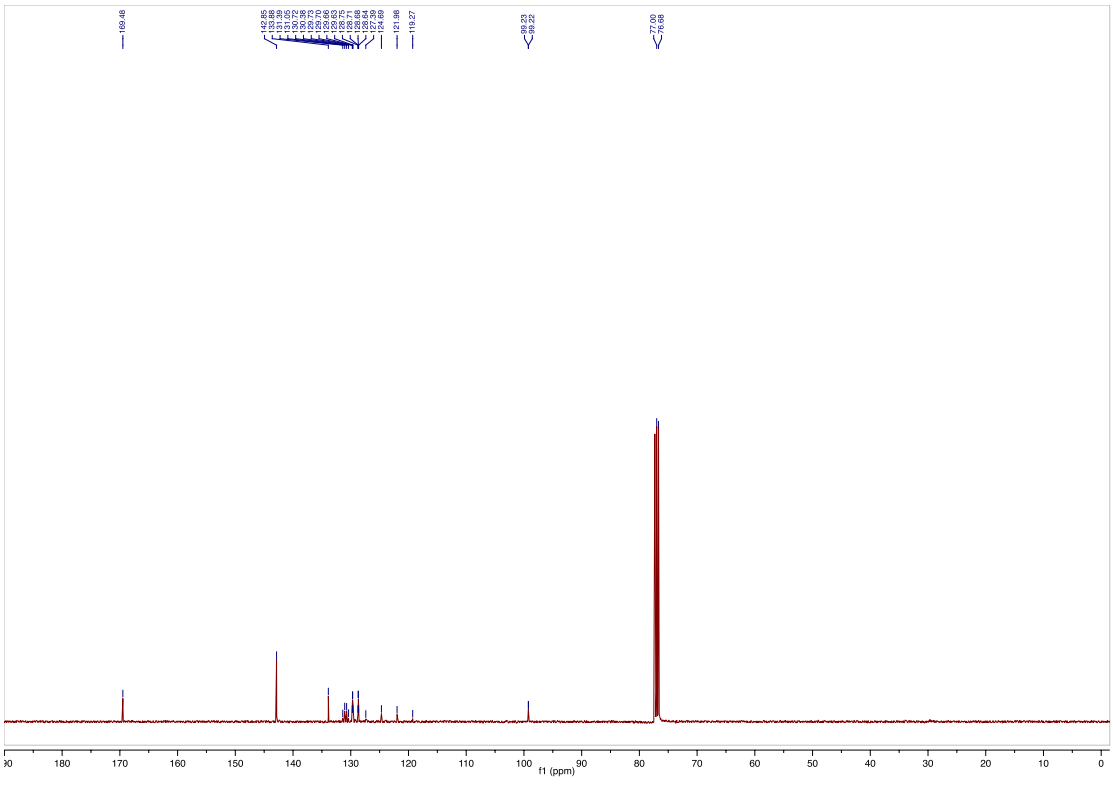




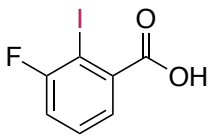
2-Iodo-5-(trifluoromethyl)benzoic acid (2s)

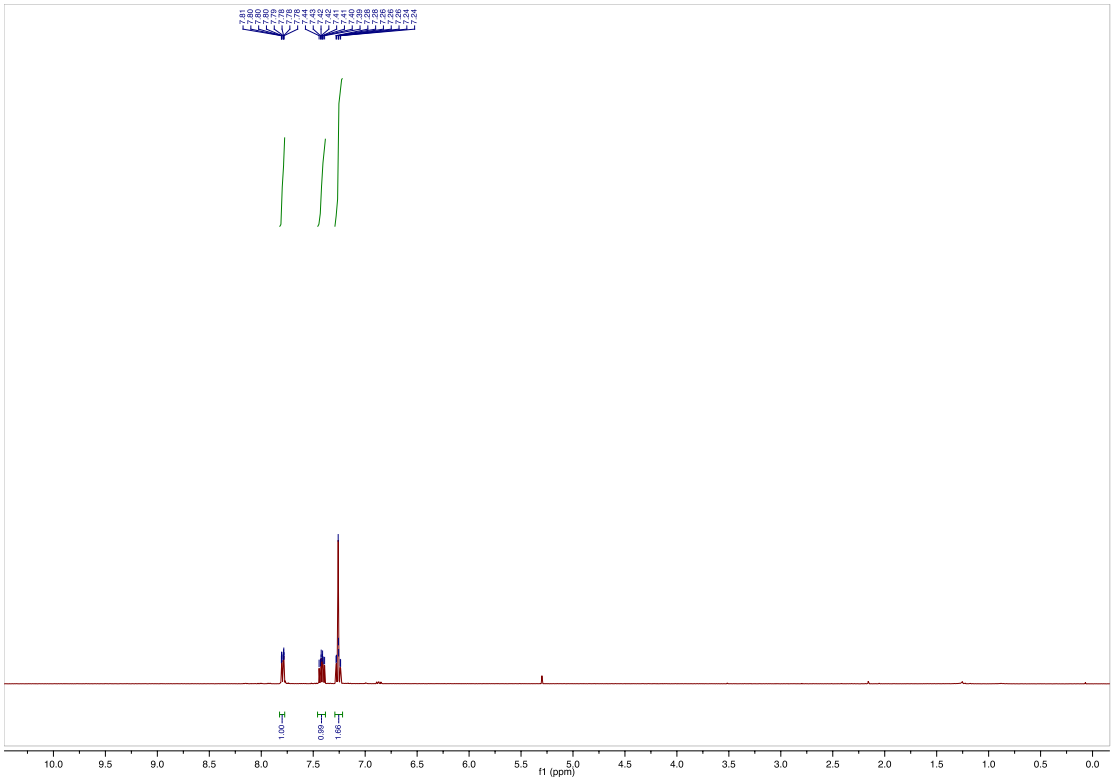


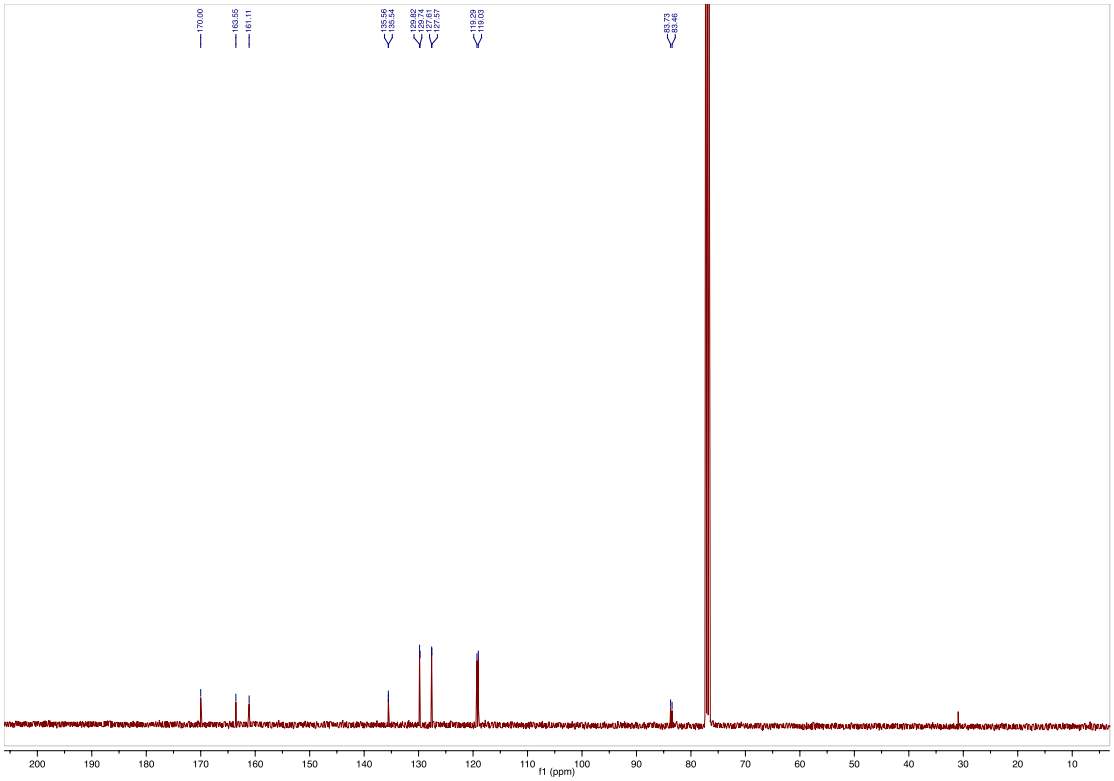




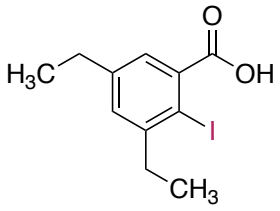
5-Fluoro-2-iodobenzoic acid (2t)

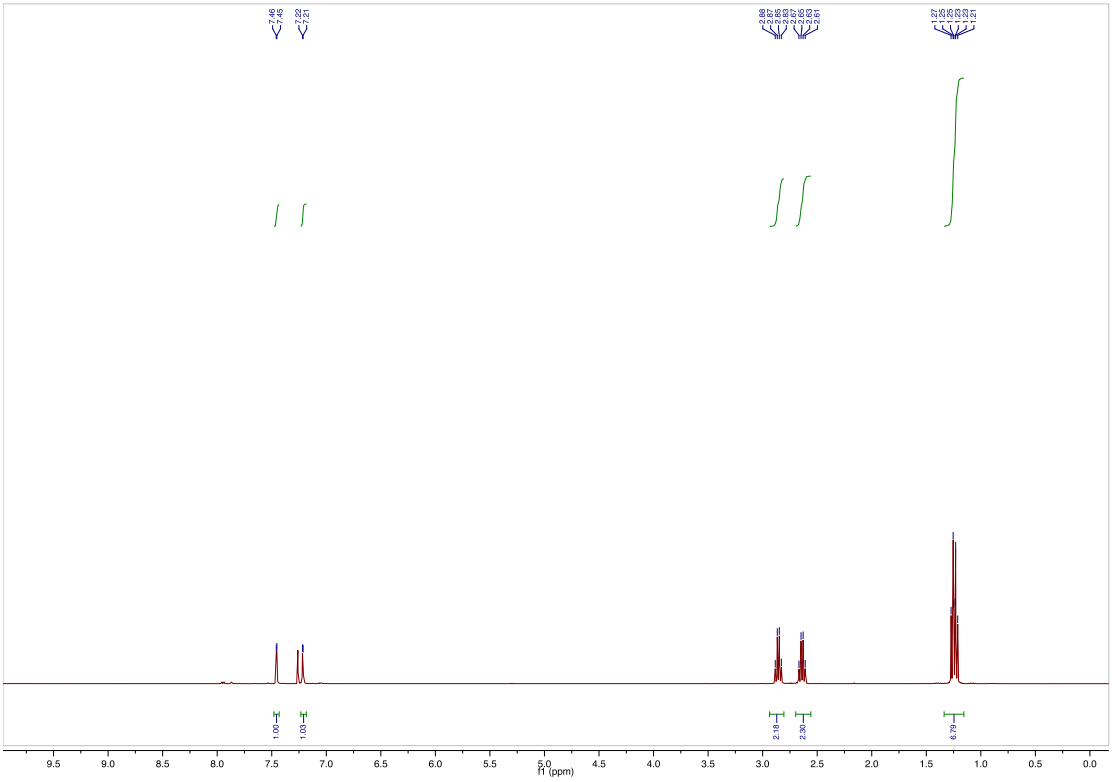


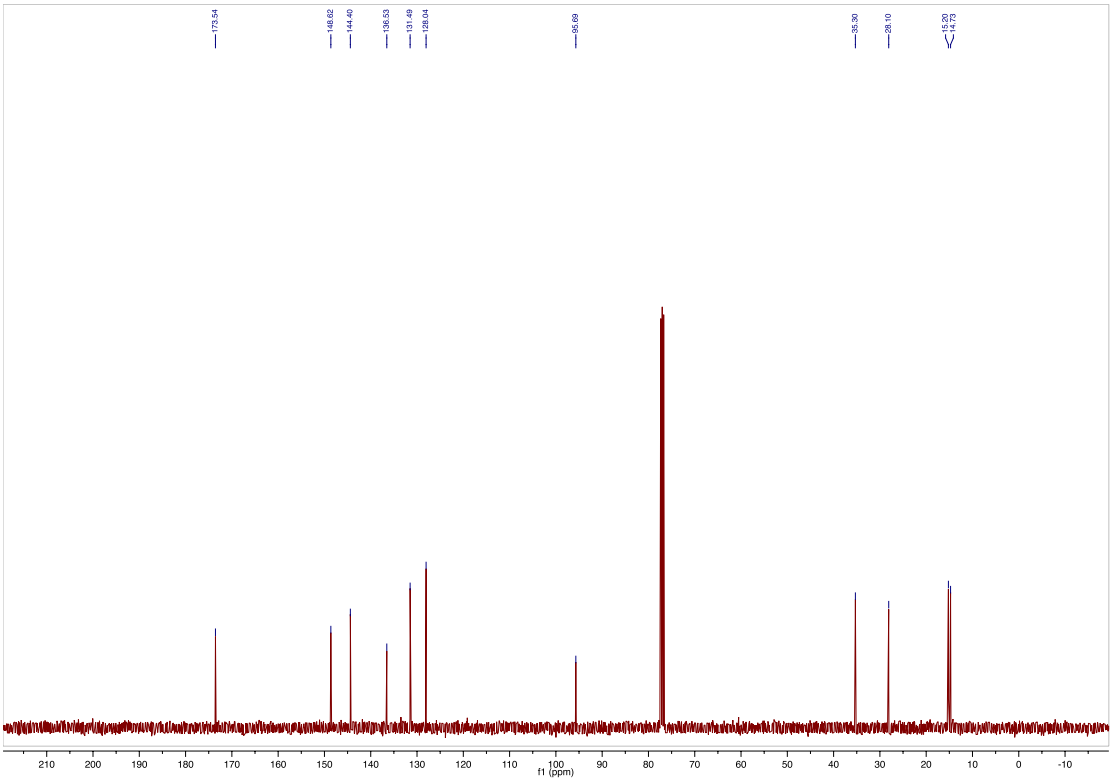




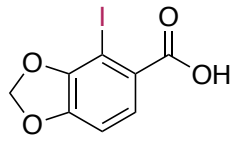
3,5-Diethyl-2-iodobenzoic acid (2u)

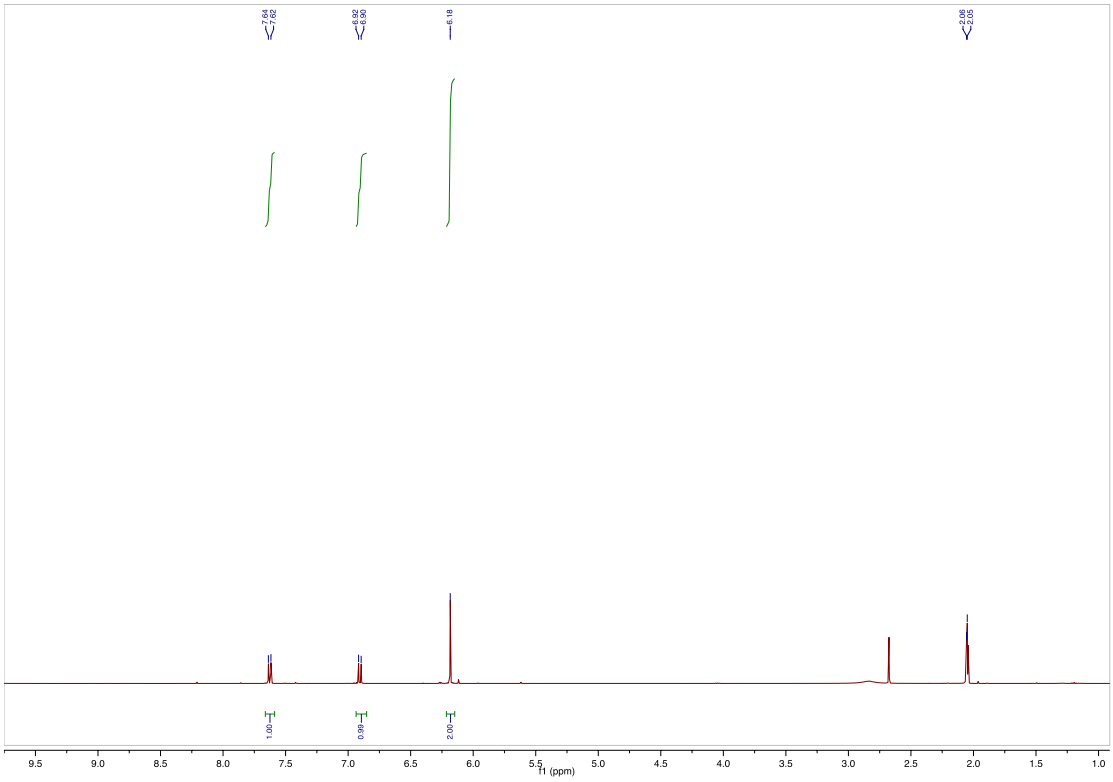


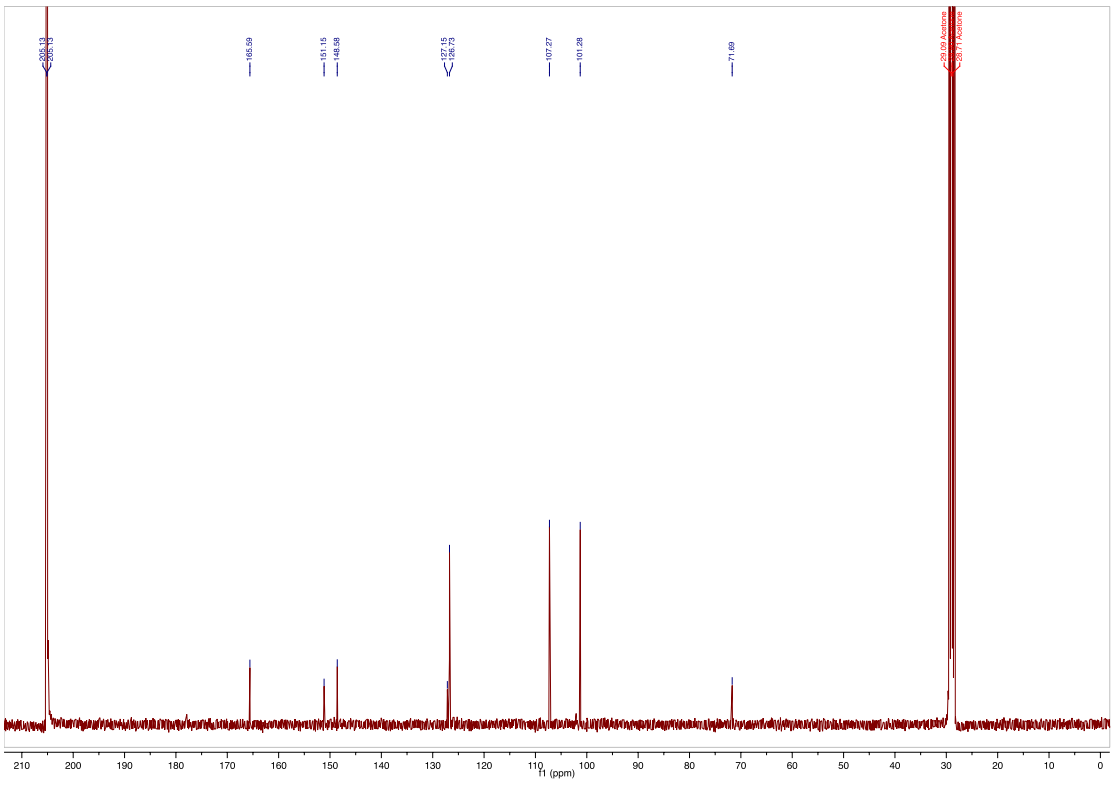




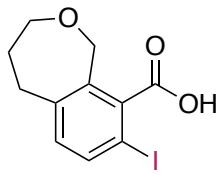
4-Iodobenzo[*d*][1,3]dioxole-5-carboxylic acid (2v)

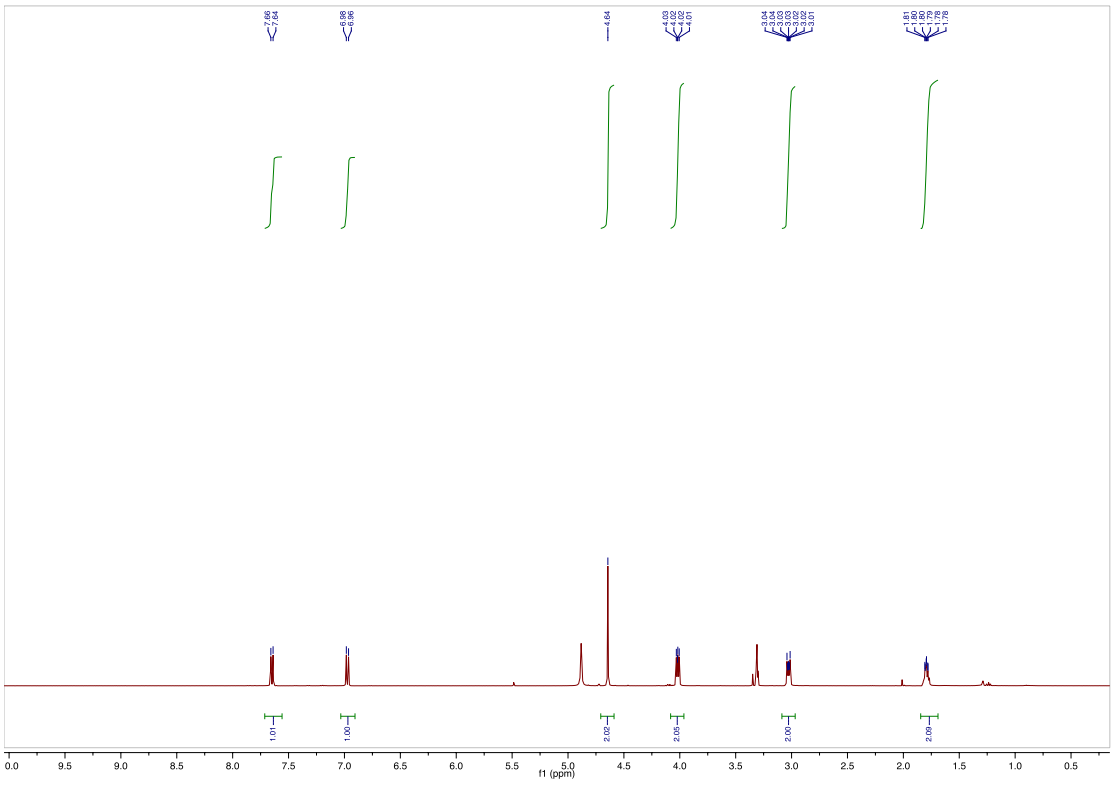


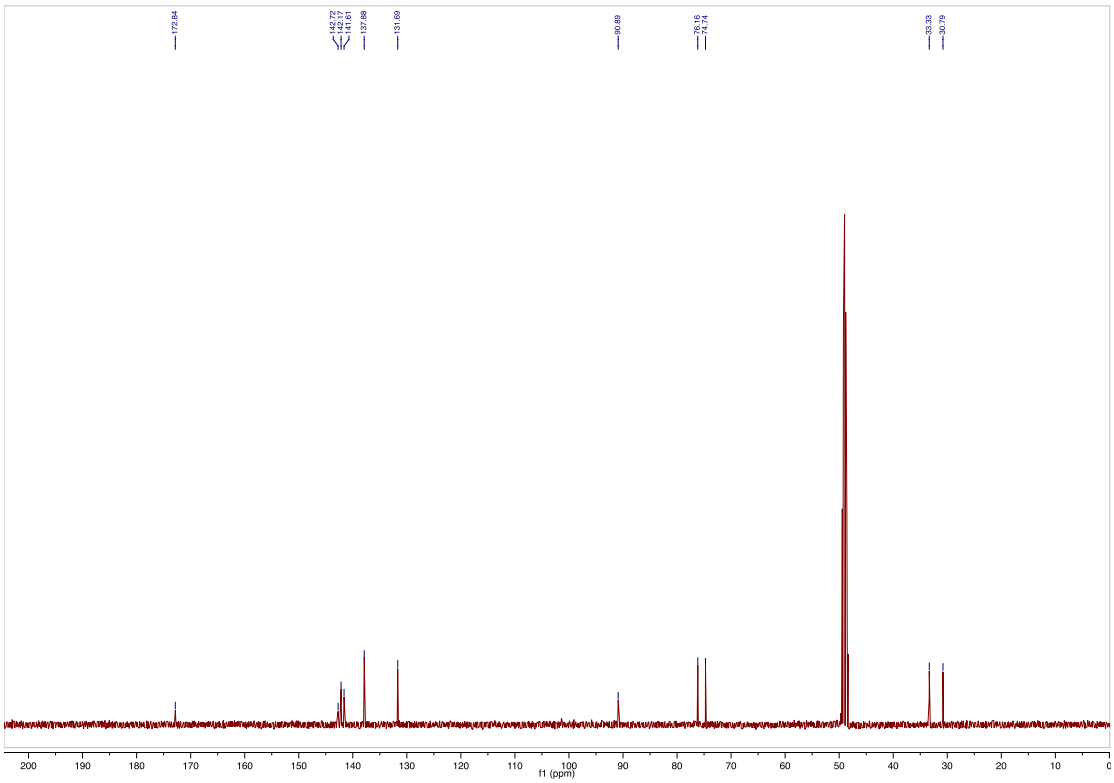




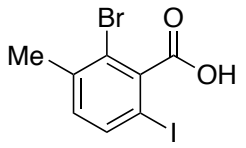
8-Iodo-1,3,4,5-tetrahydrobenzo[*c*]oxepine-9-carboxylic acid (2w)

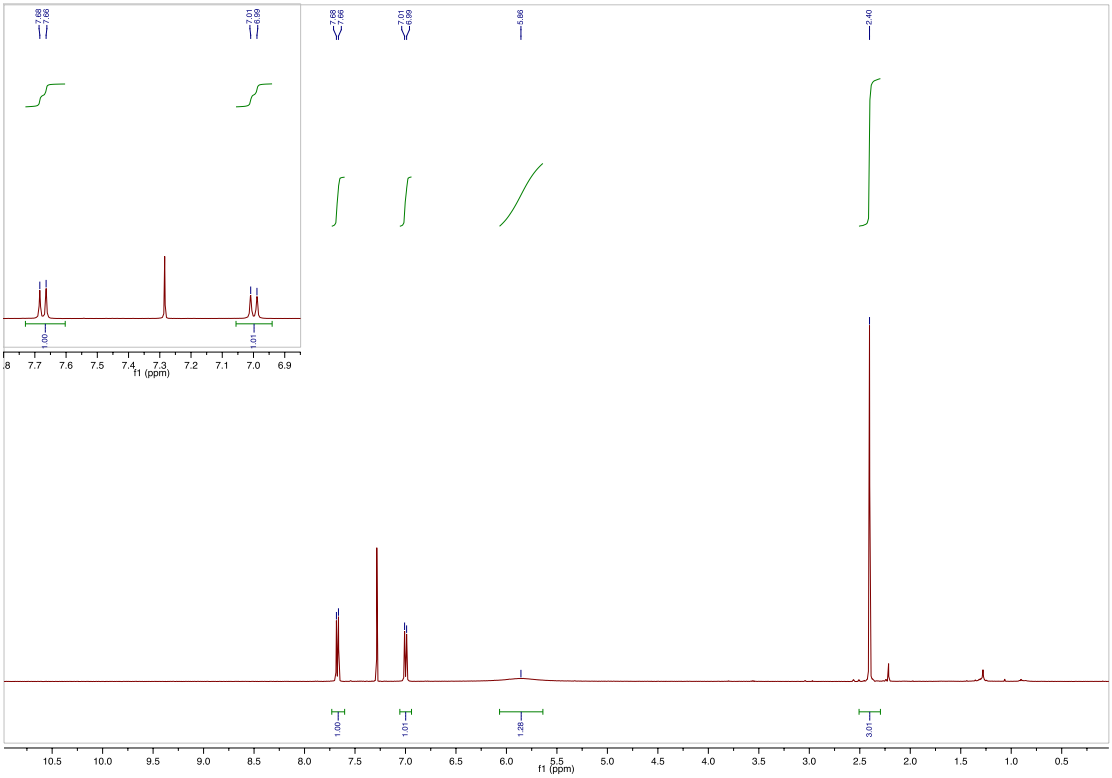


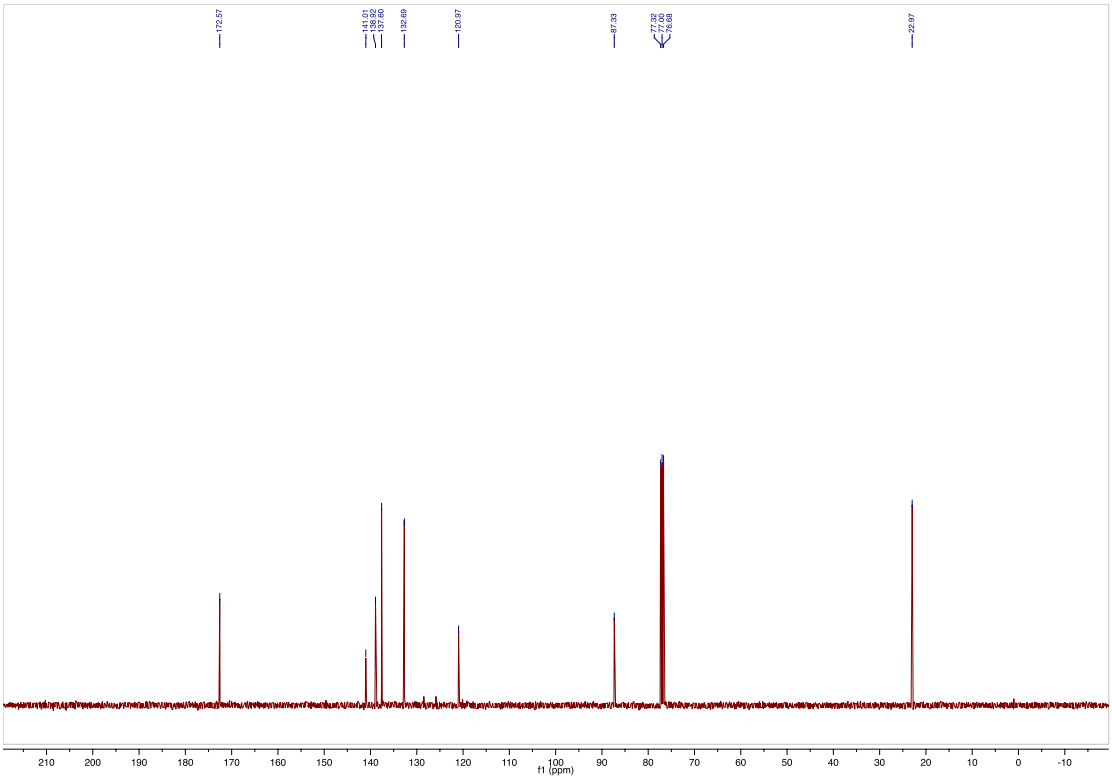




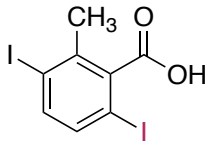
2-Bromo-6-iodo-3-methylbenzoic acid (2x)

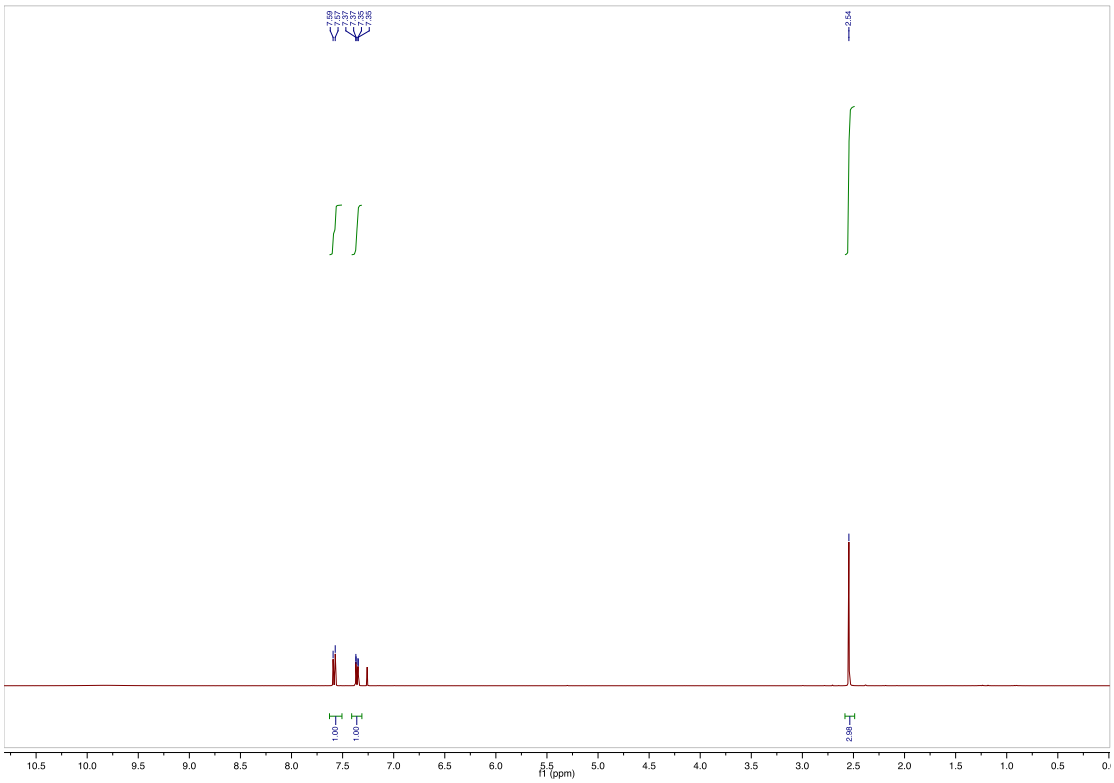


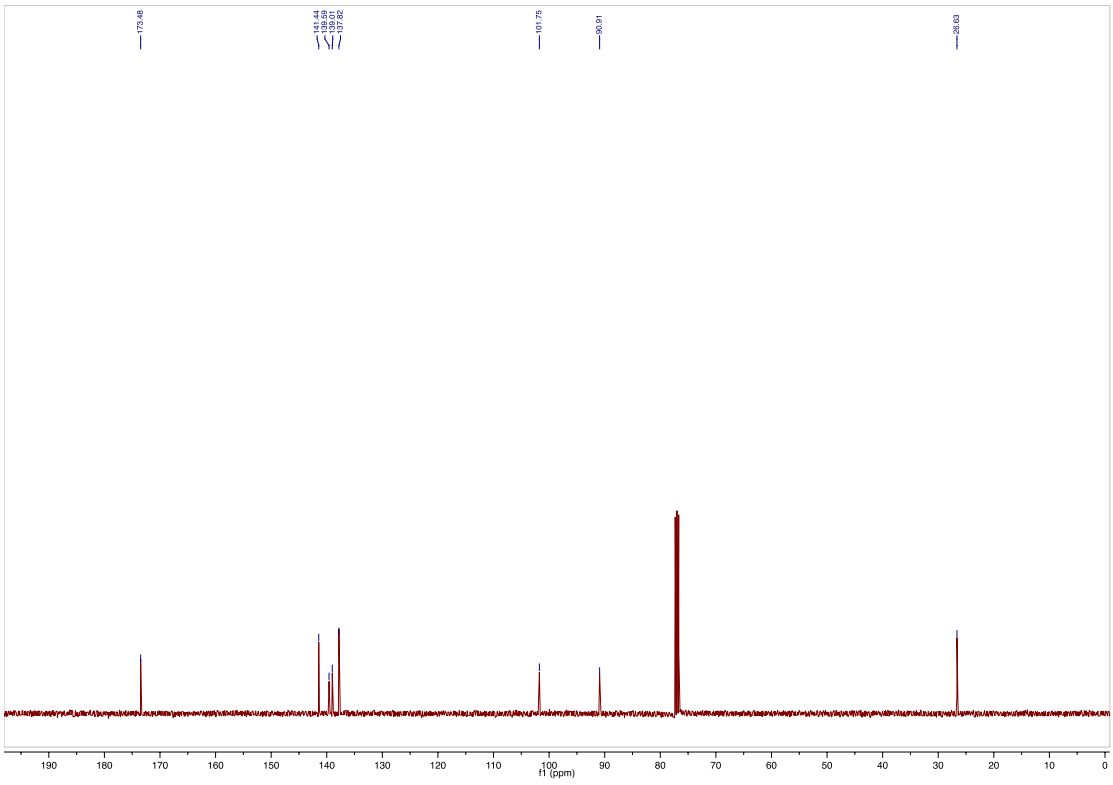




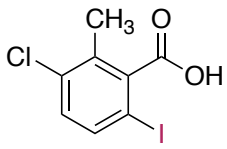
3,6-Diiodo-2-methylbenzoic acid (2y)

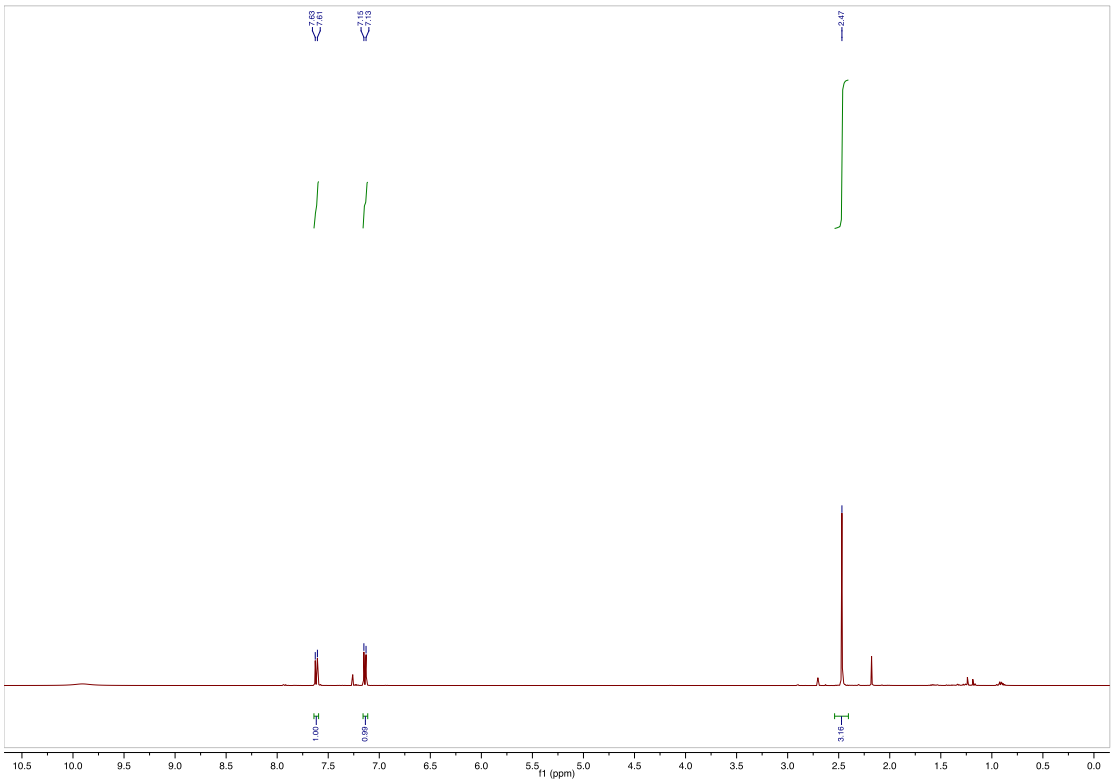


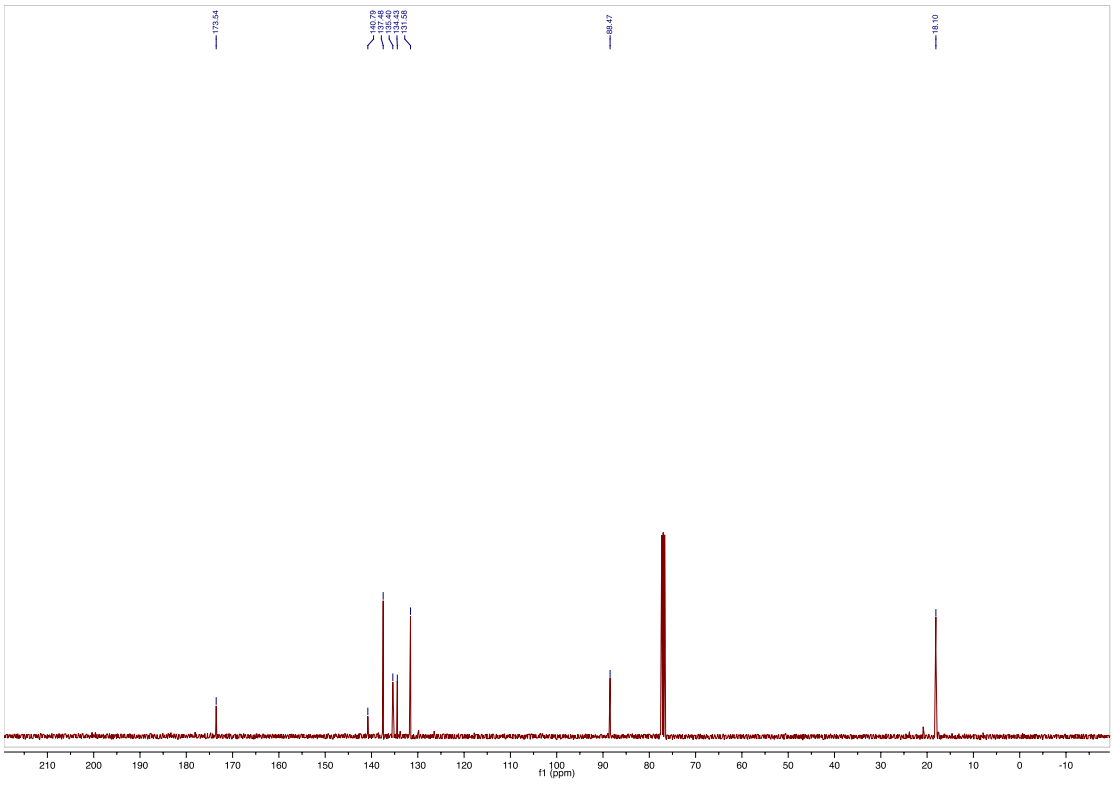




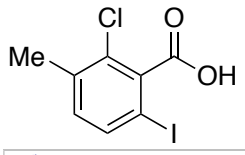
3-Chloro-6-iodo-2-methylbenzoic acid (2z)

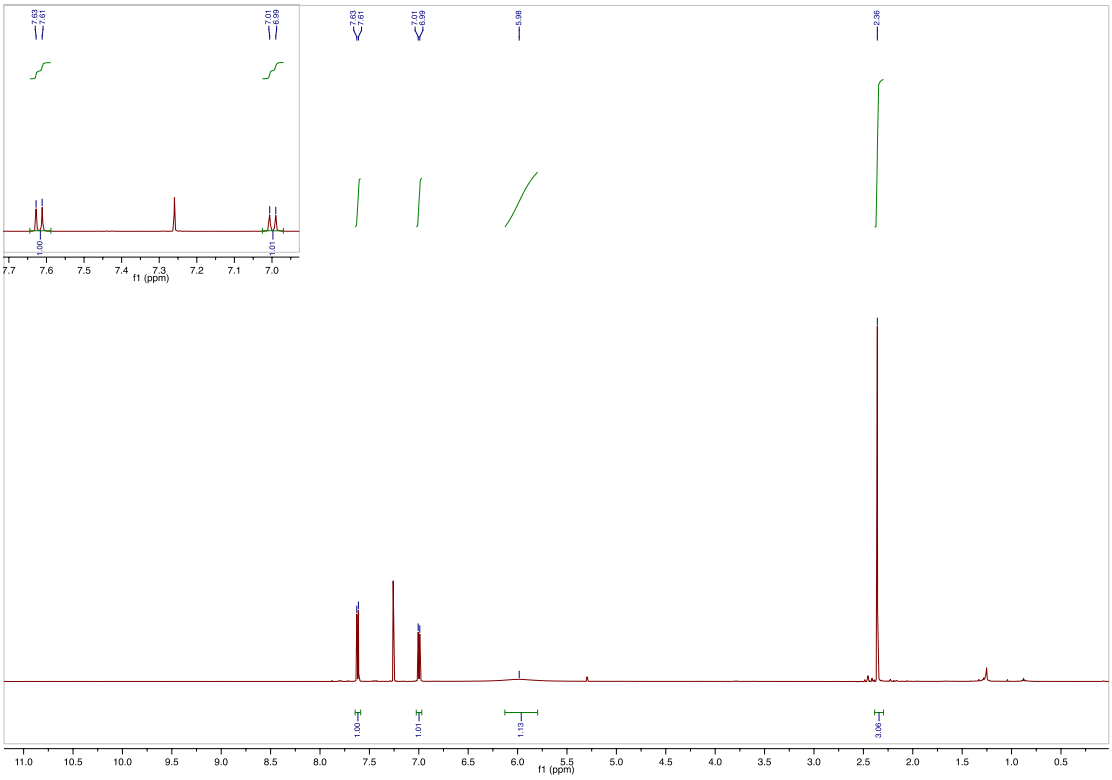


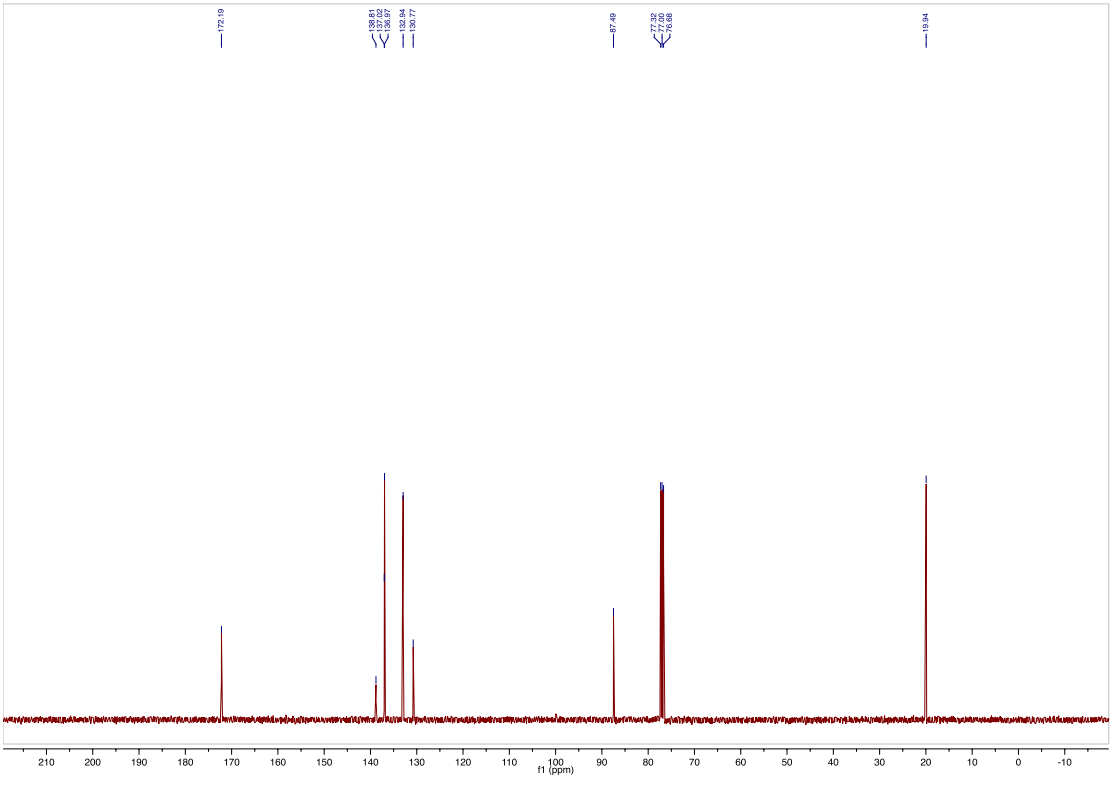




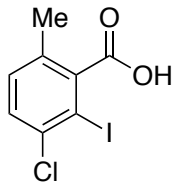
2-Chloro-6-iodo-3-methylbenzoic acid (2aa)

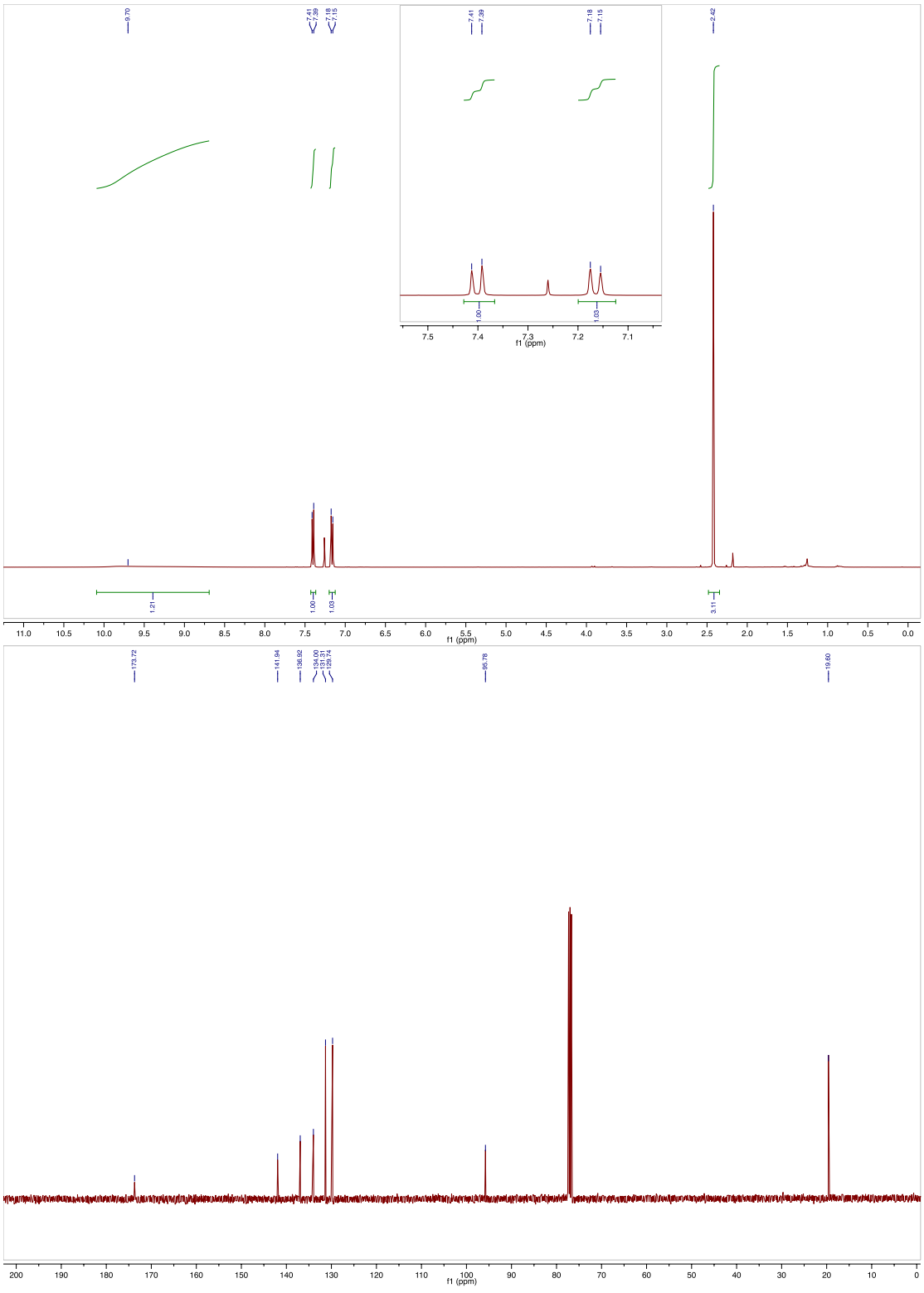




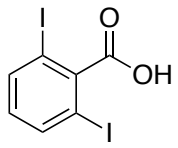


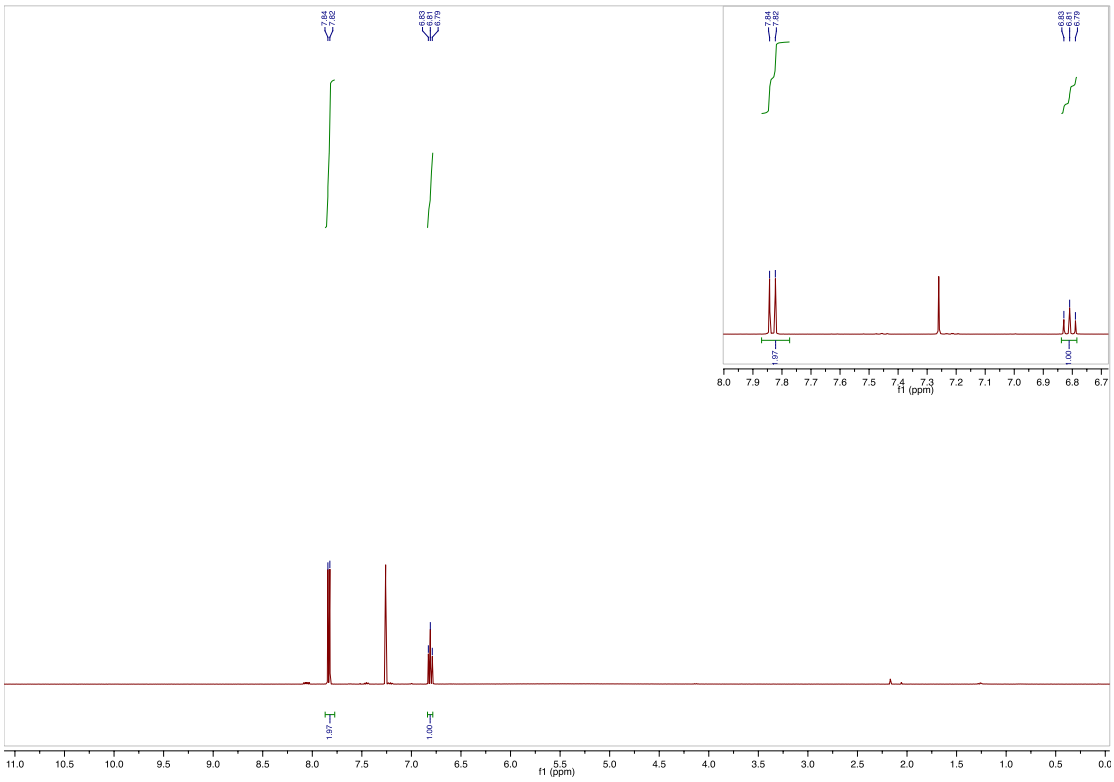
3-Chloro-2-iodo-6-methylbenzoic acid (2ab)

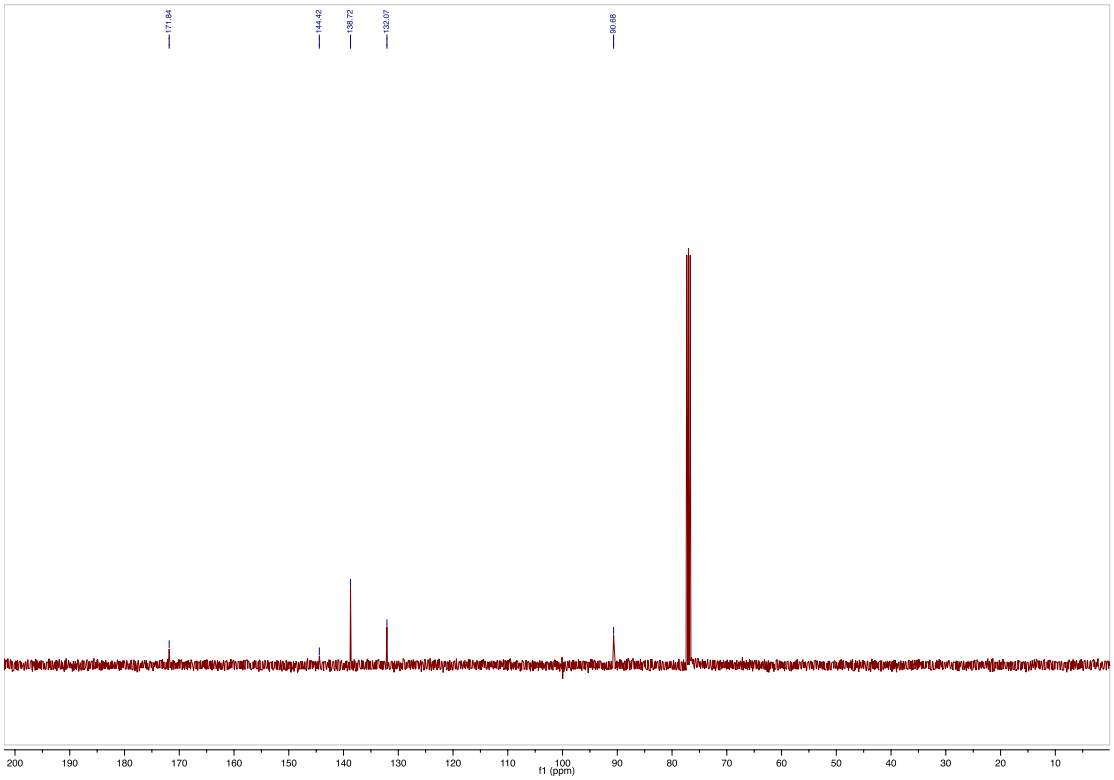




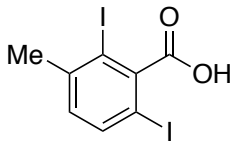
2,6-Diiodobenzoic acid (3ac)

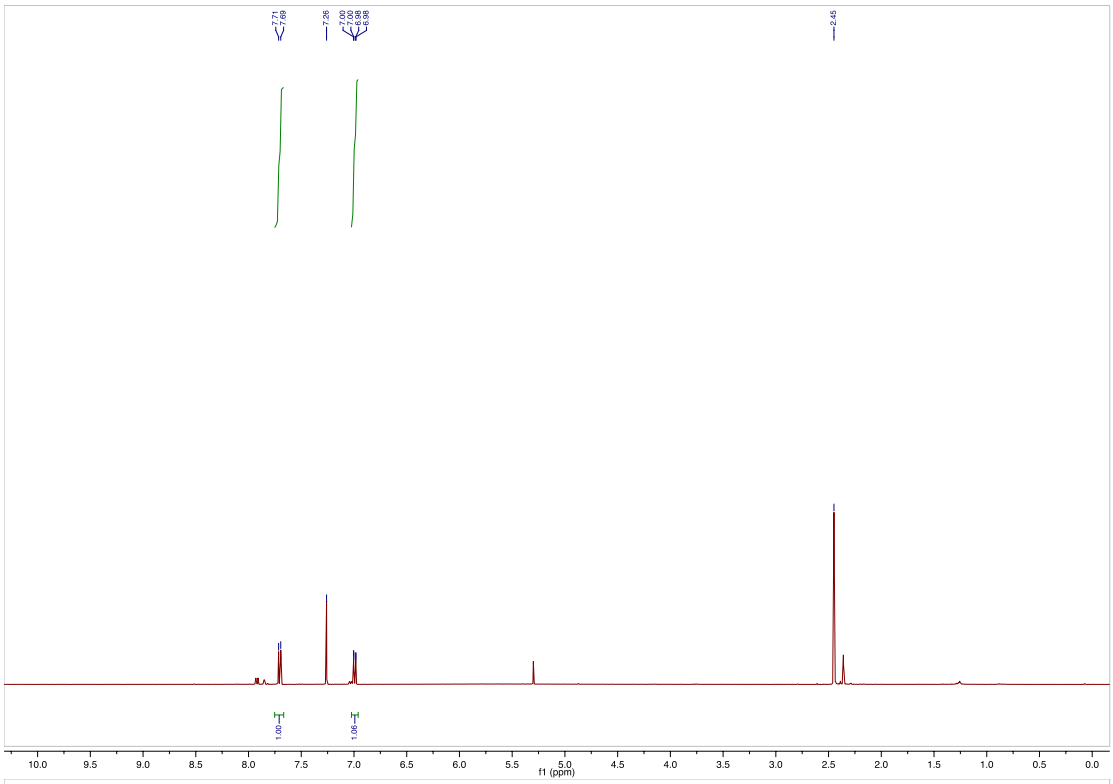


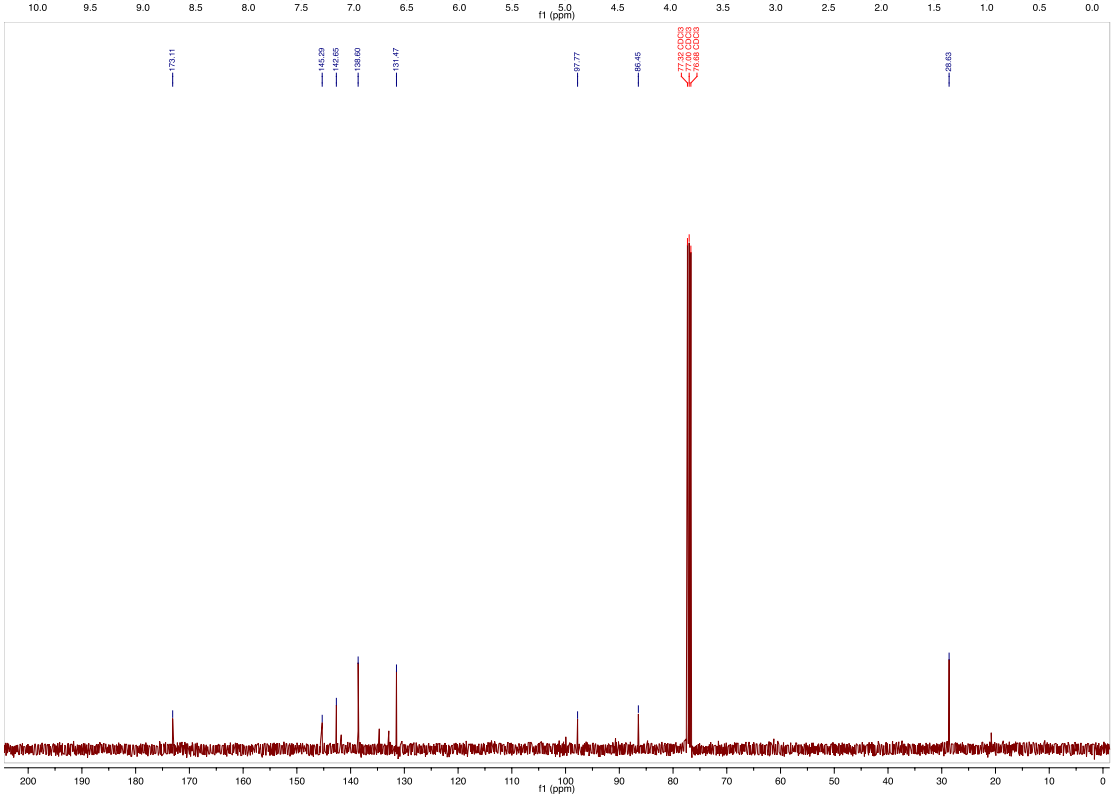




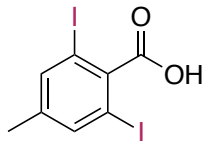
2,6-Diiodo-3-methylbenzoic acid (3q)

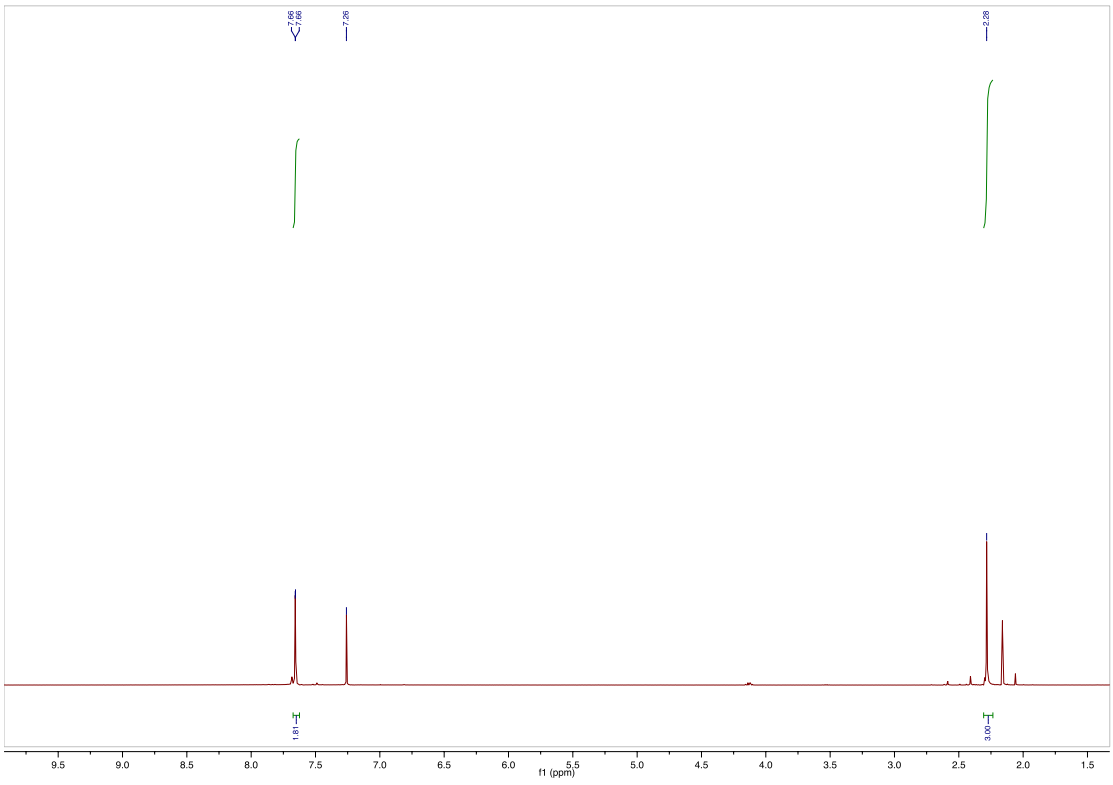


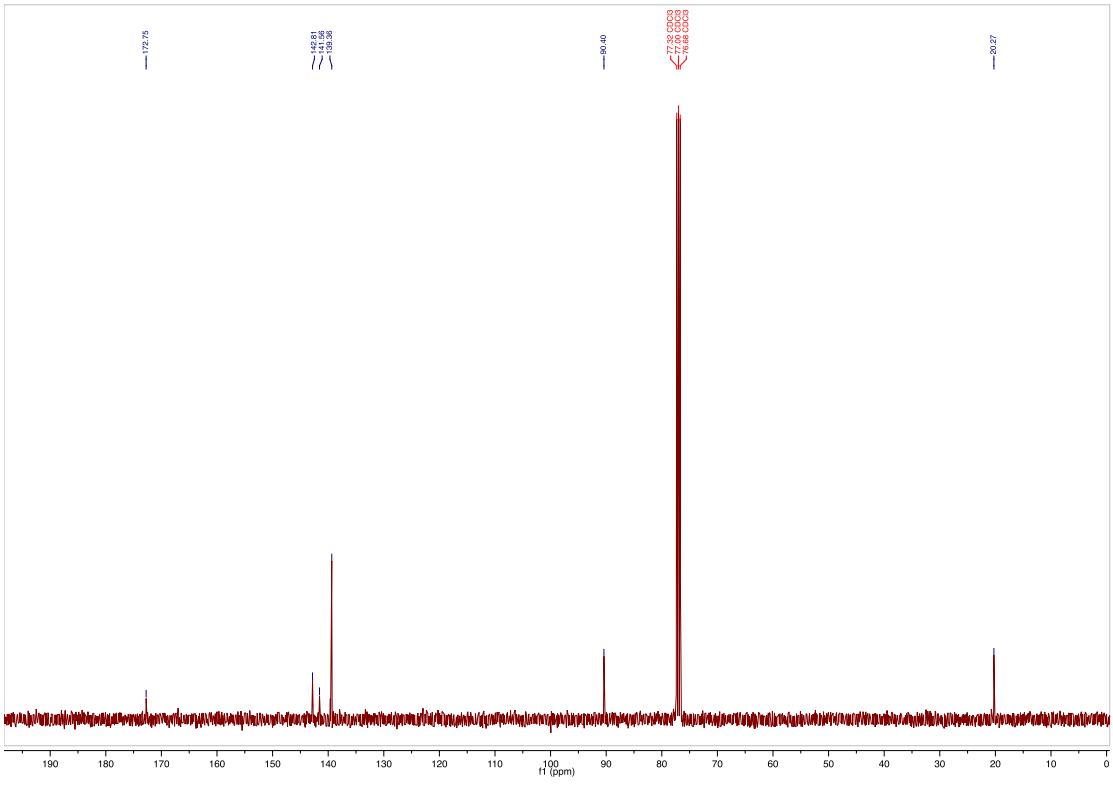




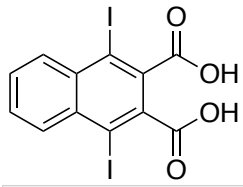
2,6-Diiodo-4-methylbenzoic acid (3ad)

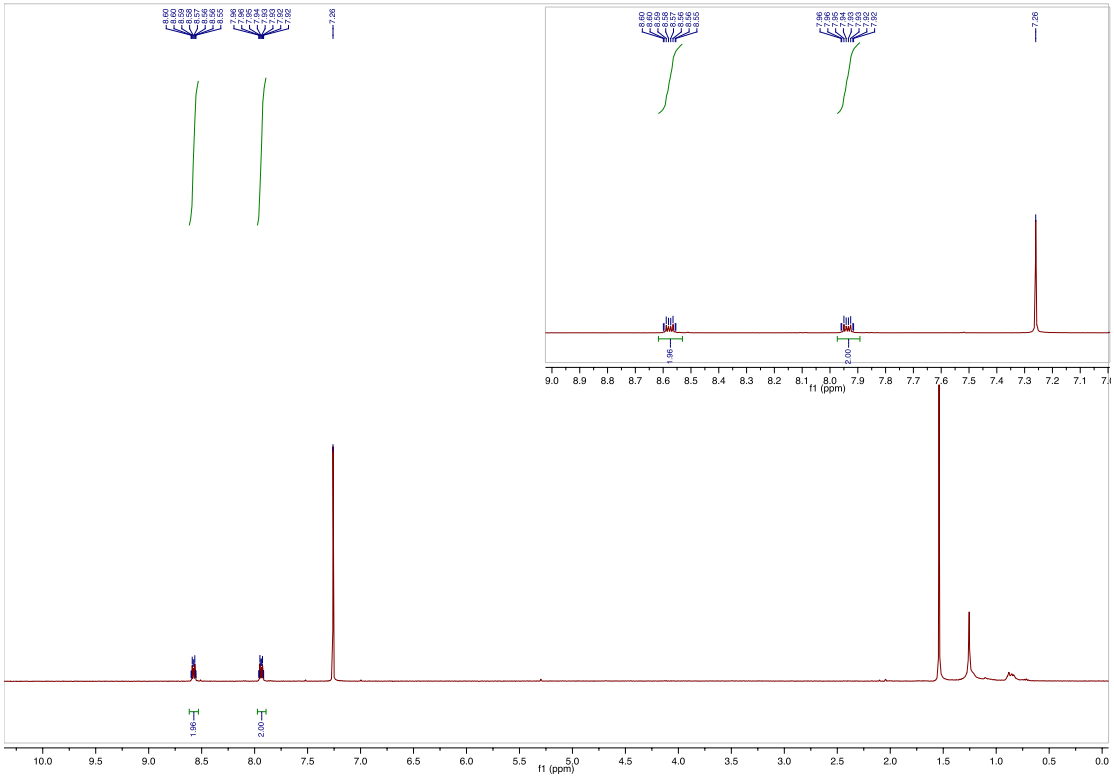


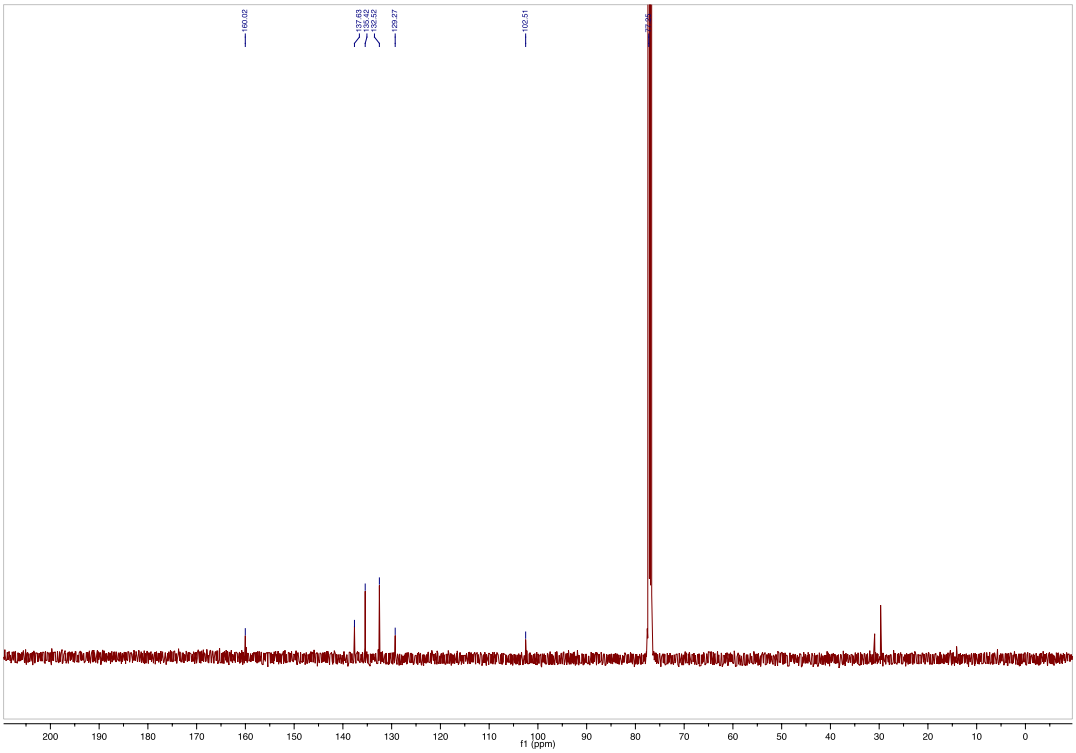




1,4-Diiodonaphthalene-2,3-dicarboxylic acid (3ae)

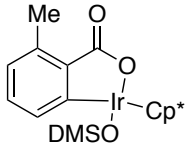


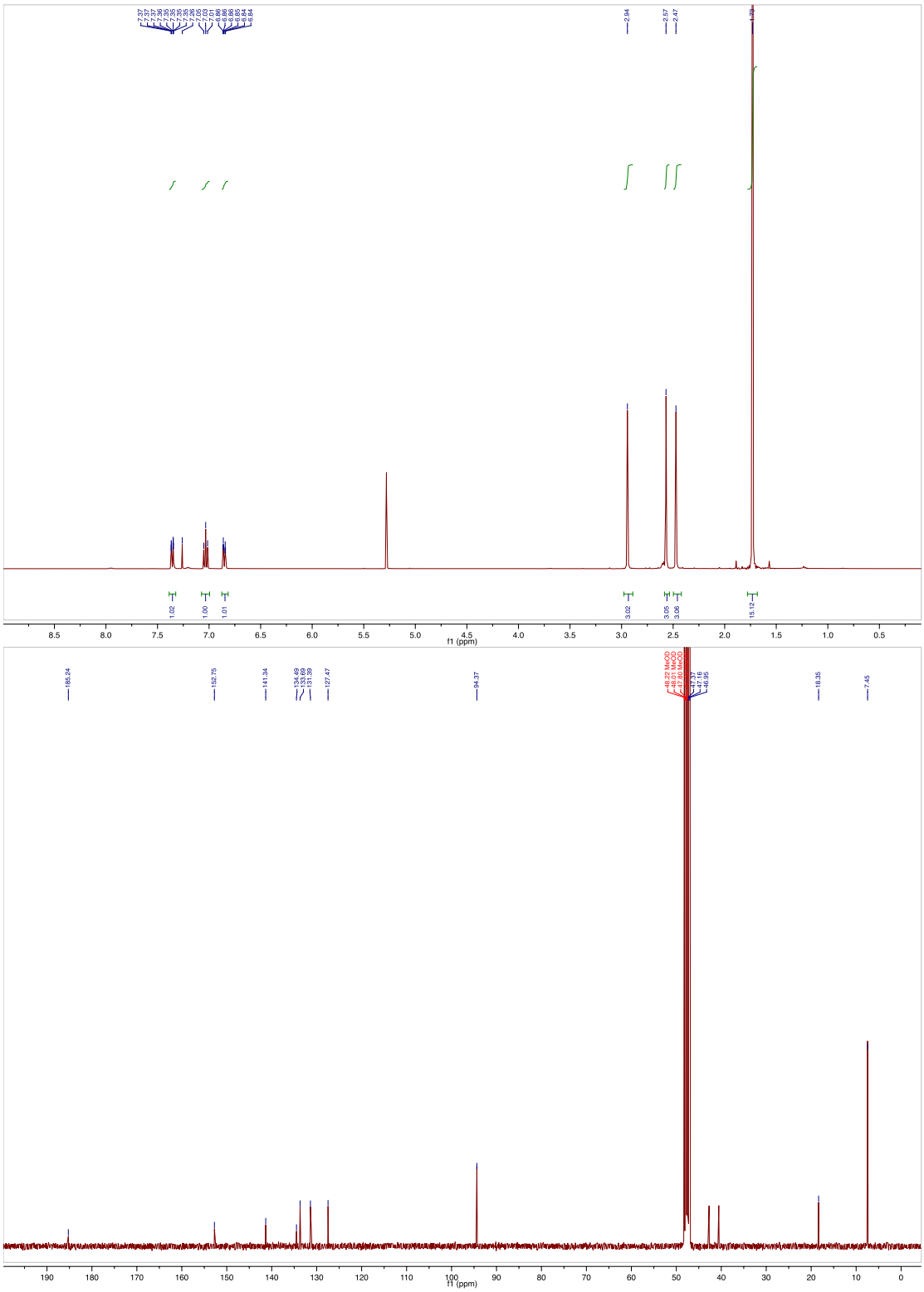




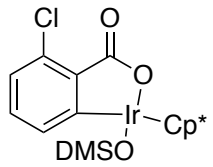
^{1}H NMR, ^{13}C NMR of iridacycle 6a, 6c, 6e and 6f

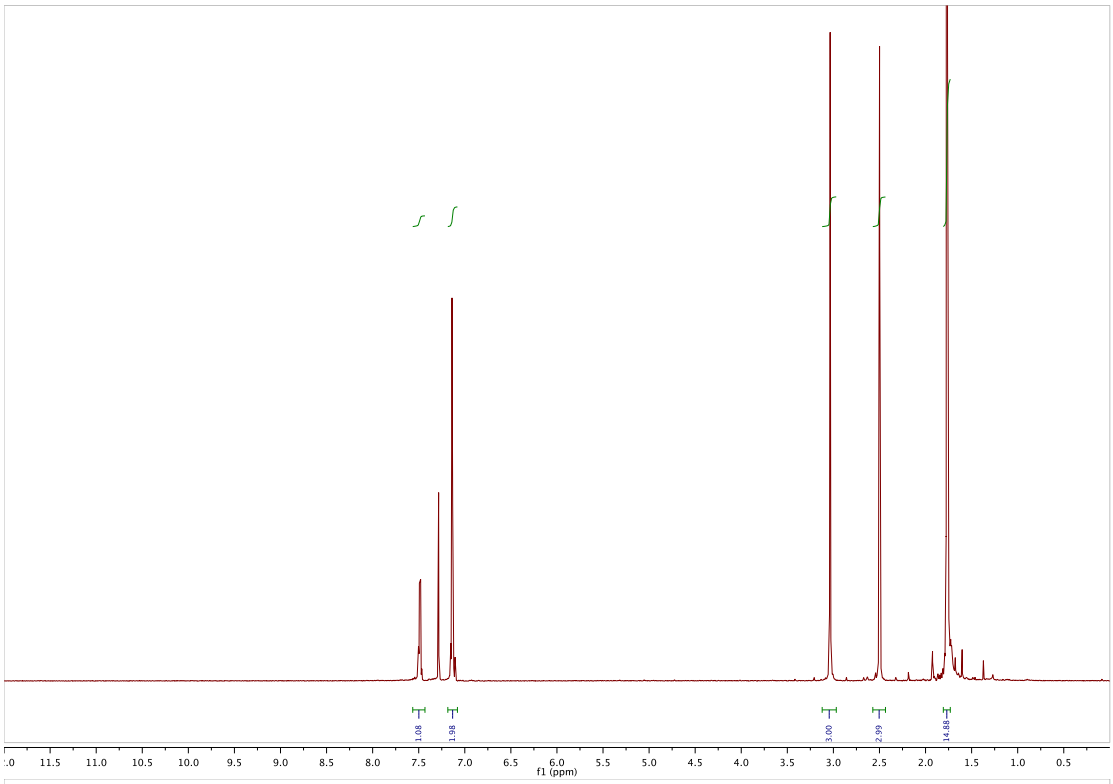
Iridacycle 6a

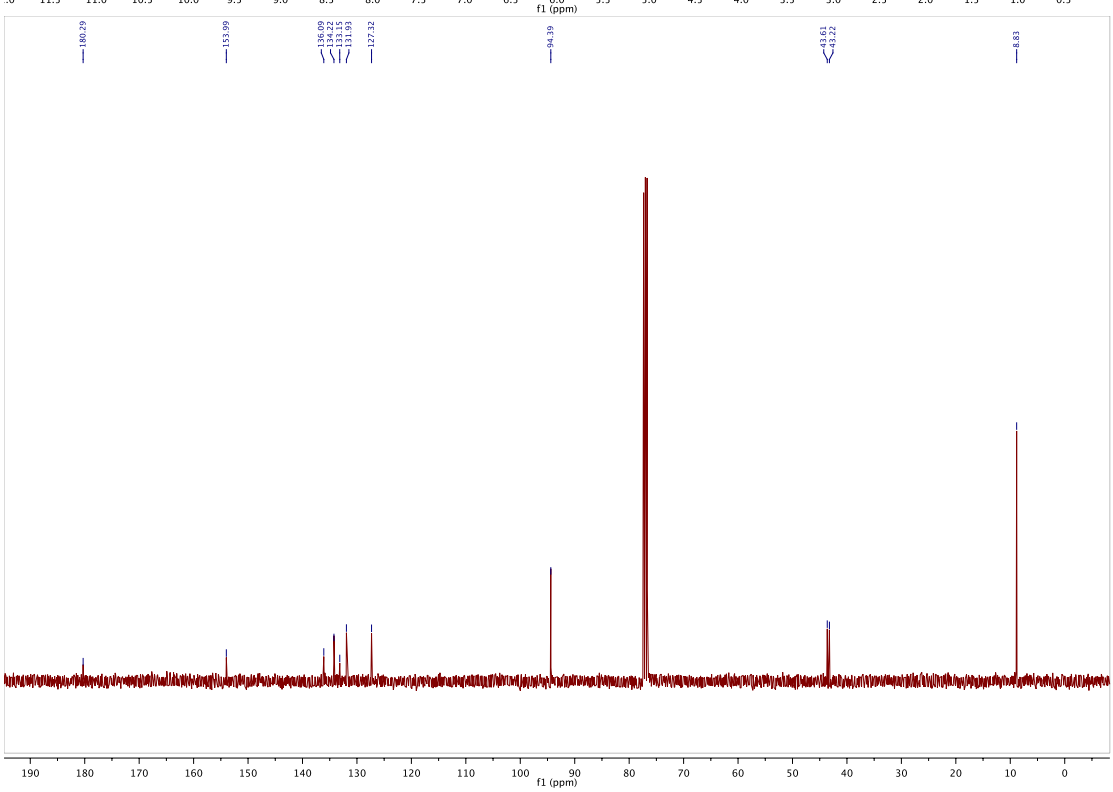




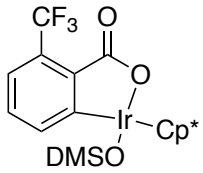
Iridacycle 6c

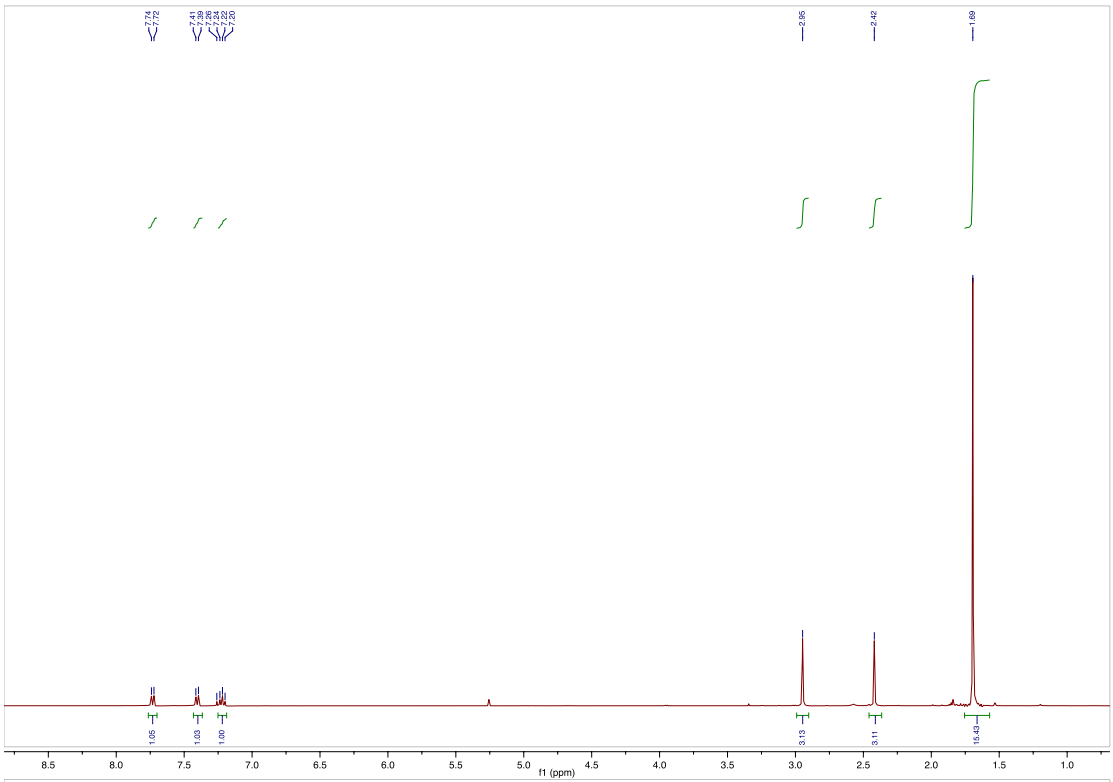

Cl
O
O
Ir
Cp*
DMSO

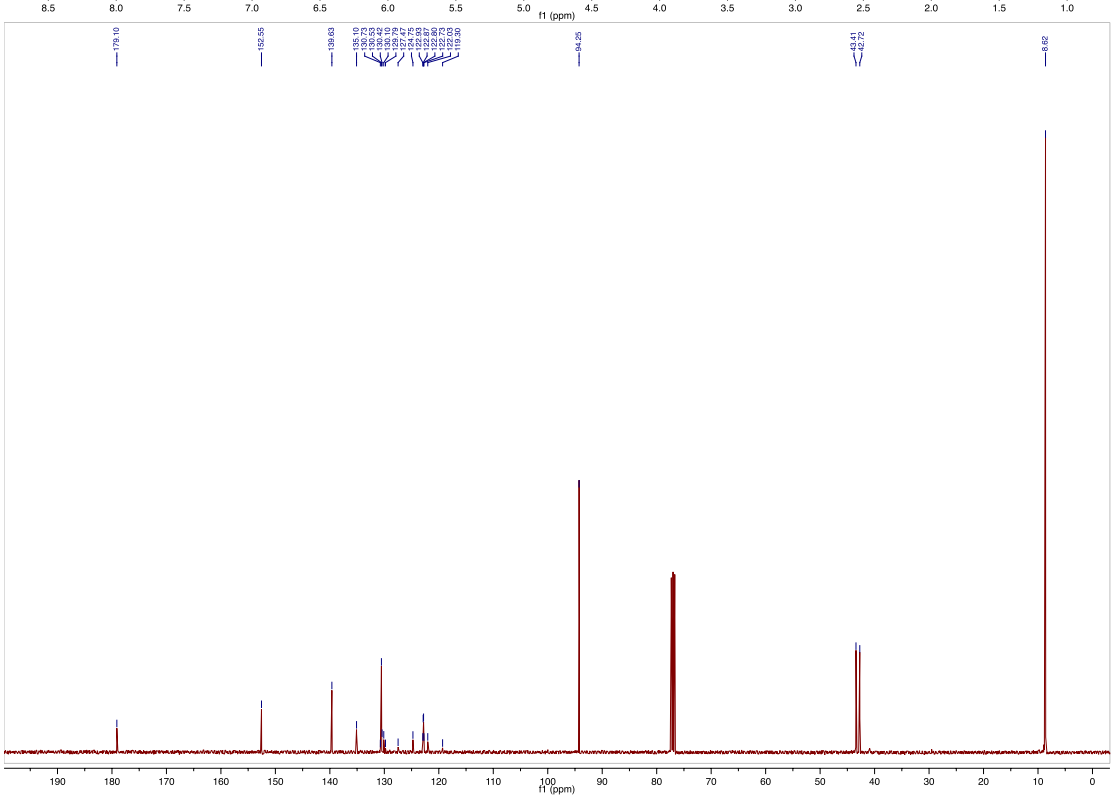

1.08
1.98
3.00
2.99
14.88
f1 (ppm)


180.29
153.99
136.09
134.22
133.15
131.93
127.32
94.39
43.61
43.22
8.83
f1 (ppm)

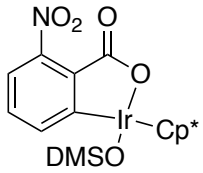
Iridacycle 6e

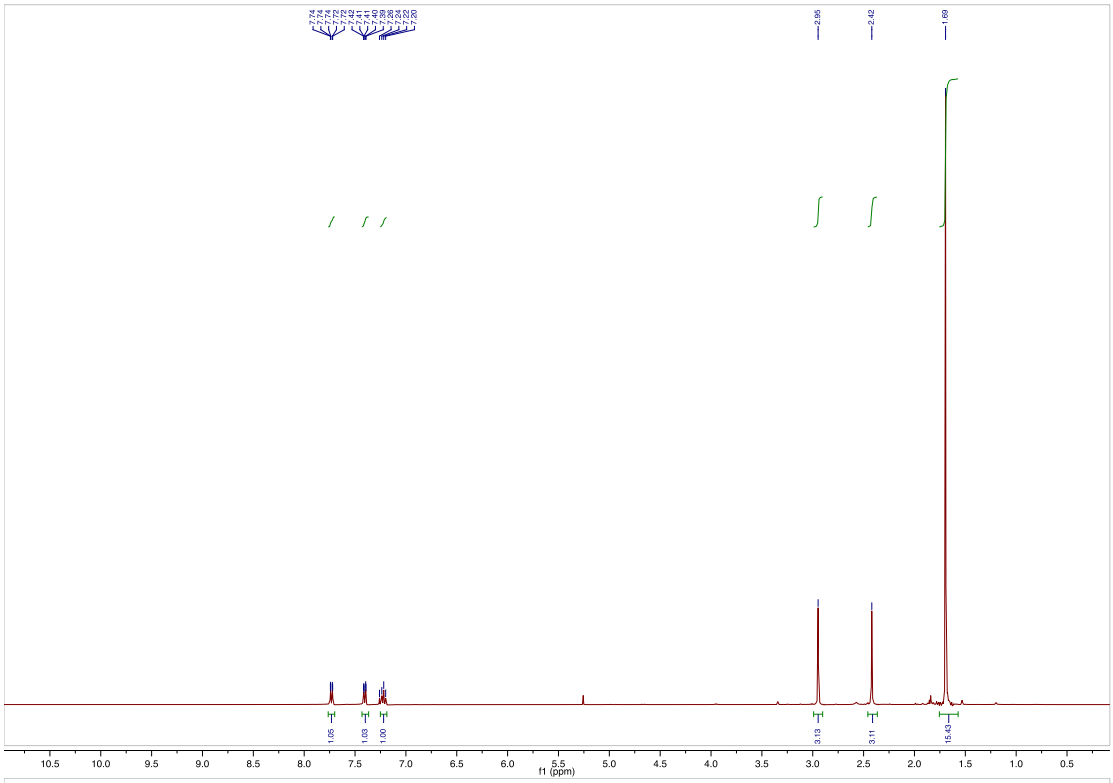


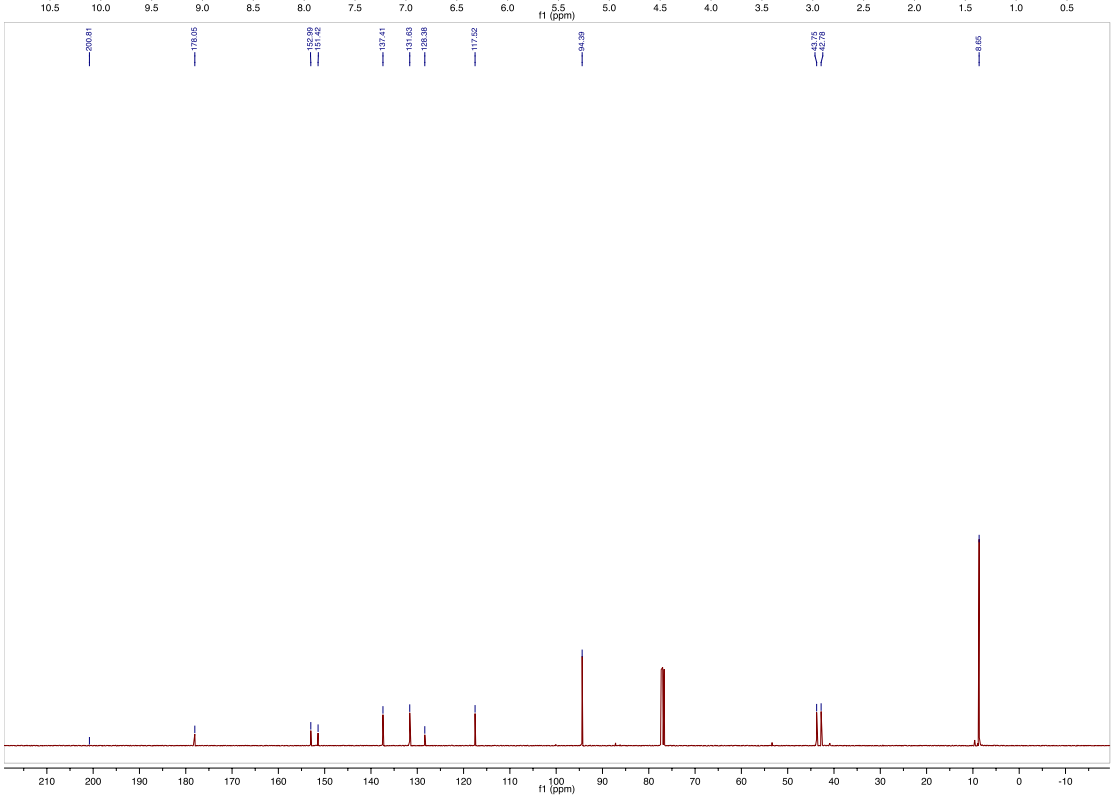




Iridacycle 6f







^{1}H NMR, ^{13}C NMR of of 2-iodobenzoic-6-*d* acid (1a-d_1)

2-methylbenzoic-6-*d* acid (1a-d_1)