Photocatalytic Decarboxylative Reduction of Carboxylic Acids and its Application in Asymmetric Synthesis

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Supporting Information

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A. General Information

All commercial chemicals and solvents were used as received without prior purification. All reactions were monitored by TLC (Merck silica gel 60 F_{254}), GC or ^{1}H-NMR. Conversions and yields provided by GC was obtained with a Varian 3900 with an auto sampler equipped with an EQUITYTM-5 column (30 m * 0.25 mm * 0.25 µm), and using hydrogen as carrier gas. *n*-Dodecane was used as internal standard, standardized by calibrating against authentic samples of pure products. Conversions and yields provided by ^{1}H-NMR was obtained using 2,5-dimethylfuran as the internal standard. Enantiomeric excess was determined by GC using a CP-Chirasil-Dex CB column (25 m * 0.32 mm * 0.25 µm) from Varian or by HPLC using a CHIRALPAK AD-H column from Chiral Technologies Europe, together with a solvent delivery system from Varian (9012Q) and UV-Vis detector operating at 254 nm also from Varian (9050). ^{1}H- and ^{13}C-NMR spectra were obtained at 400 and 100 MHz, respectively, using a Varian 400 spectrometer. Residual solvent peaks were used as reference. ^{19}F-NMR spectra were obtained using a Varian 400 spectrometer and referenced with hexafluorobenzene at -164.9 ppm. Column chromatography was performed by manual flash chromatography (wet-packed silica, 0.04 - 0.063 mm) or by automated column chromatography on a Biotage SP-4 instrument using pre-packed silica columns. LC-MS analysis was performed on a API SCIEX 150 EX Perkin Elmer ESI-MS (30 eV) connected to a Perkin Elmer gradient pump system and a C8 column (Gemini) using acetonitrile and 1% formic acid in MQ-water as mobile phases with a gradient of 5 to 95% acetonitrile over 4 min. HRMS analysis was performed on a SCIEX Qstar XL (Q-TOF) mass spectrometer with an Acquity UPLC CSH C18 (pH 4) column eluting with a gradient of 1-99% acetonitrile in MQ-water containing 0.1% formic acid. IR absorption was measured on a Biotools ChiralIR-2X instrument and optical rotations were measured on a PerkinElmer 341LC Polarimeter.

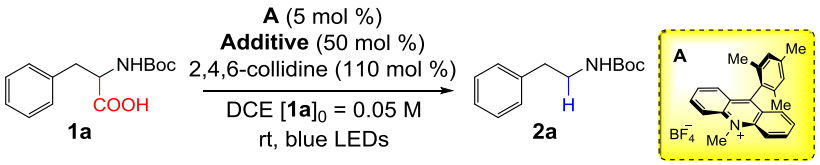
DCE = 1,2-dichloroehane; DCM = dichloromethane; DMSO = dimethyl sulfoxide; DMF = dimethylformamide

Materials

Commercially available reagents were purchased from Sigma Aldrich, Alfa Aesar and NovaBiochem and used as received unless otherwise noted.

B. Optimization Studies

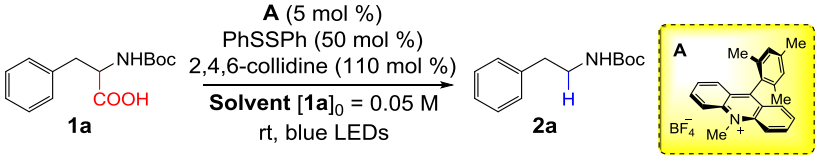
Table S1. Additive Screening



Entry	Additive	Yield (%)[a]
1	PhSH	20
2	Fluorene	0
3	*N*-hydroxysuccinimide	0
4	PhSSPh	75

[a] Determined by ^{1}H NMR of the crude reaction mixture using 2,5-dimethylfuran as the internal standard.

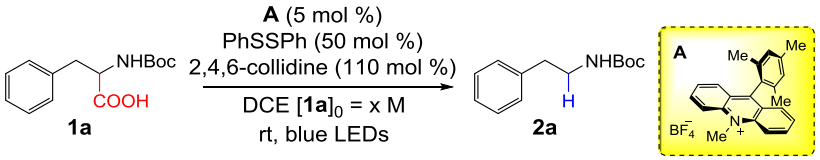
Table S2. Solvent Screening



Entry	Solvent	Yield (%)[a]
1	1,2-dichloroethane (DCE)	75
2	dichloromethane	60
3	α,α,α-Trifluorotoluene	20
4	acetonitrile	12
5	DMSO	0
6	DMF	0
7	H_2O	6

[a] Determined by ^{1}H NMR of the crude reaction mixture using 2,5-dimethylfuran as the internal standard.

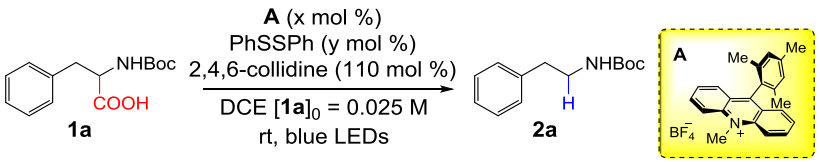
Table S3. Concentration Effect



Entry	x	Yield (%)[a]
1	0.2	35
2	0.1	49
3	0.05	75
4	0.025	>95

[a] Determined by ^{1}H NMR of the crude reaction mixture using 2,5-dimethylfuran as the internal standard.

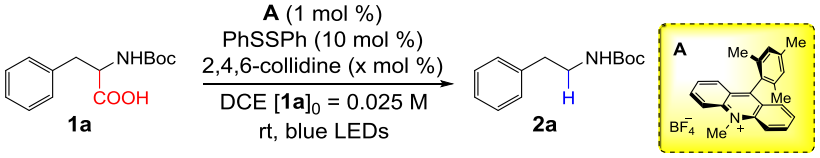
Table S4. Catalyst and Disulfide Loading



Entry	x	y	Yield (%)[a]
1	5	50	>95
2	2.5	50	>95
3	1	50	79
4	1	10	80

[a] Determined by ^{1}H NMR of the crude reaction mixture using 2,5-dimethylfuran as the internal standard.

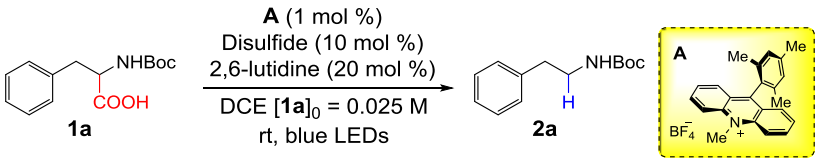
Table S5. Base Loading



Entry	x	Yield (%)[a]
1	100	80
2	50	80
3	20	85
4[b]	20	95

[a] Determined by ^{1}H NMR of the crude reaction mixture using 2,5-dimethylfuran as the internal standard. [b] 2,6-lutidine was used as the base.

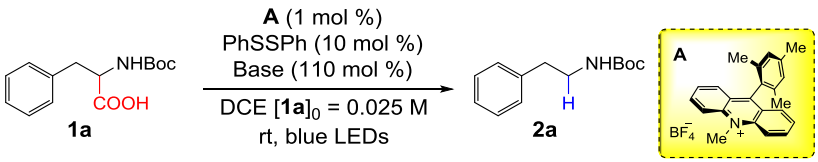
Table S6. Disulfide Screening



Entry	Disulfide	Yield (%)[a]
1	diphenyl disulfide	95
2	bis(4-methoxyphenyl)disulfide	93
3	bis(4-chlorophenyl)disulfide	>95

[a] Determined by ^{1}H NMR of the crude reaction mixture using 2,5-dimethylfuran as the internal standard.

Table S7. Base Screening



Entry	Base	Yield (%)[a]
1	2,4,6-collidine	80
2	$NaHCO_3$	42
3	Cs_2CO_3	4
4	CsF	55
5	4-methoxypyridine	69
6	2,6-lutidine	83

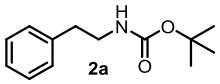
[a] Determined by ^1H NMR of the crude reaction mixture using 2,5-dimethylfuran as the internal standard.

C. General Procedure for the Photocatalytic Decarboxylative

General procedure: The carboxylic acid (0.2 mmol) and the bis(4-chlorophenyl)disulfide (DDDS) (5.7 mg, 0.02 mmol) were added into a 10mL vial equipped with a Teflon coated magnetic stirring bar. The vial was sealed with a septum-cap and the internal atmosphere exchanged with nitrogen *via* three repeated cycle of vacuum-refill. Then 8 mL of a 0.25 mM solution of the photocatalyst in degassed 1,2-dichloroethane (sparged with nitrogen for 20 minutes) was added followed by 2,6-lutidine (4.7 µL, 0.04 mmol). The above mixture was then sparged with nitrogen for further 5 minutes. The vial was sealed with Teflon tape and irradiated (at approximately 4 cm away from the light source) with 8 W blue LEDs (λ_{max} = 460 nm) under vigorous stirring. After 14 hours the solvent was reduced under vacuum to approximately 1 mL. Purification of the crude mixture by flash chromatography on silica gel provided the desired product.

D. Product Characterization

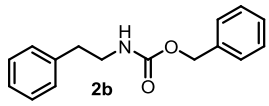
***Tert*-butyl phenethylcarbamate (2a - Scheme 2)**



The reaction was carried out following the general procedure starting from Boc-Phe-OH. Purification by flash column chromatography (gradient eluent from hexane to 95:5 hexane/ethyl acetate) afforded the title compound as a white solid (44 mg, 99% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.44 (s, 9H), 2.80 (t, 2H, *J* = 7.1 Hz), 3.38 (q, 2H, *J* = 6.7 Hz), 4.58(bs, 1H), 5.11 (s, $2H_{min}$), 7.16-7.25 (m, 3H), 7.27-7.34 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.3, 36.1, 41.7, 79.1, 126.3, 128.5, 128.7, 138.9, 155.8 ppm. Spectral data are in agreement with literature values.[1]

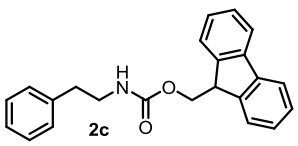
Benzyl phenethylcarbamate (2b - Scheme 2)



The reaction was carried out following the general procedure starting from *Z*-Phe-OH. Purification by flash column chromatography (gradient eluent from hexane to 95:5 hexane/ethyl acetate) afforded the title compound as a white solid (48 mg, 94% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.83 (t, 2H, *J* = 7.0 Hz), 3.48 (q, 2H, *J* = 6.7 Hz), 4.81(bs, 1H), 5.11 (s, $2H_{min}$), 7.15-7.27 (m, 3H), 7.28-7.40 (m, 7H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ36.0, 42.2, 66.6, 126.5, 128.1, 128.5, 128.6, 128.7, 136.5, 138.7, 156.2 ppm. Spectral data are in agreement with literature values.[1]

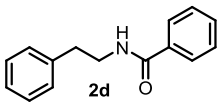
(9H-Fluoren-9-yl)methyl phenethylcarbamate (2c - Scheme 2)



The reaction was carried out following the general procedure starting from Fmoc-Phe-OH. Purification by flash column chromatography (gradient eluent from hexane to 90:10 hexane/ethyl acetate) afforded the title compound as a white solid (65 mg, 95% yield). HRMS *calcd* for ($C_{23}H_{21}NO_2$+H): 344.1651, found 344.1669.

^{1}H NMR ($CDCl_3$, 400 MHz, 8:1 mixture of two rotamers): δ 2.66 (bs, $2H_{min}$), 2.84 (t, $2H_{maj}$, *J* = 7.0 Hz), 3.33 (bs, $2H_{min}$), 3.48 (q, $2H_{maj}$, *J* = 6.7 Hz), 4.24 (t, $1H_{maj}$, *J* = 6.9 Hz), 4.43 (d, $2H_{maj}$, *J* = 6.9 Hz), 4.52 (bs, $2H_{min}$), 4.62 (bs, $1H_{min}$), 4.84 (b2, $1H_{maj}$), 7.06-7.22 (m, 2H), 7.22-7.29 (m, 1H), 7.30-7.38 (m, 2H), 7.39-7.47 (m, 1H), 7.60 (d, 2H, J = 7.53 Hz), 7.79 (d, 2H, *J* = 7.54 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 36.1, 42.2, 47.3, 120.0, 126.5, 127.0, 127.6, 128.6, 128.8, 138.8, 141.3, 143.9, 156.3 ppm. IR (DCM, cm^{-1}) 3449, 3437, 3066, 3053, 3029, 2949, 2897, 1723, 1604, 1514, 1450, 1326, 1269, 1231, 1198, 1137 and 1050.

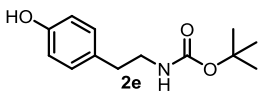
_N_-Phenethylbenzamide (2d - Scheme 2)



The reaction was carried out following the general procedure starting from *N*-benzoylphenylalanine. Purification by flash column chromatography (gradient eluent from hexane to 80:20 hexane/ethyl acetate) afforded the title compound as a white solid (44 mg, 98% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.93 (t, 2H, *J* = 7.0 Hz), 3.68-3.75 (m, 2H), 6.32 (bs, 1H), 7.21-7.27 (m, 3H), 7.29-7.35 (m, 2H), 7.36-7.42 (m, 2H), 7.44-7.50 (m, 1H), 7.68-7.72 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ33.6, 41.1, 126.5, 126.7, 128.47, 128.48, 128.6, 128.7, 131.3, 134.5, 138.8, 167.4 ppm. Spectral data are in agreement with literature values.[2]

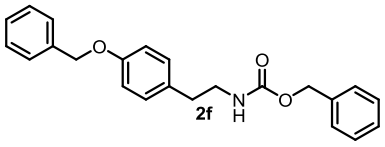
***Tert*-butyl (4-hydroxyphenethyl)carbamate (2e - Scheme 2)**



The reaction was carried out following the general procedure using 5 mol % of the photocatalyst together with 1 equiv. of bis(4-cholophenyl)disulfide (DDDS) and starting from Boc-Tyr-OH. Purification by flash column chromatography (gradient eluent from hexane to 70:30 hexane/ethyl acetate) afforded the title compound as colorless oil (24 mg, 51% yield). Performing the reaction using 1 mol % of the photocatalyst and 10 mol % of DDDS afforded the product in 29% isolated yield.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.44 (s, 9H), 2.93 (t, 2H, *J* = 7.0 Hz), 3.68-3.75 (m, 2H), 6.32 (bs, 1H), 7.21-7.27 (m, 3H), 7.29-7.35 (m, 2H), 7.36-7.42 (m, 2H), 7.44-7.50 (m, 1H), 7.68-7.72 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ28.4, 35.2, 42.0, 79.4, 115.4, 129.8, 130.6, 154.4, 156.0 ppm. Spectral data are in agreement with literature values.[3]

Benzyl (4-(benzyloxy)phenethyl)carbamate (2f - Scheme 2)

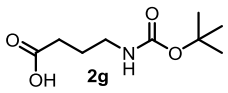


The reaction was carried out following the general procedure starting from Z-Tyr-(Bzl)-OH. Purification by flash column chromatography (gradient eluent from hexane to 90:10 hexane/ethyl acetate) afforded the title compound as a white solid (50 mg, 70% yield). HRMS *calcd* for ($C_{23}H_{23}NO_3$+H): 362.1756, found 362.1726.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.76 (t, 2H, *J* = 7.0 Hz), 3.43 (q, 2H, *J* = 6.7 Hz), 4.76 (bs, 1H), 5.05 (s, 2H), 5.10 (s, 2H), 6.88-6.96 (m, 2H), 7.10 (d, 2H, *J* = 8.3 Hz), 7.28-7.46 (m, 10H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ35.1, 42.3, 66.5, 69.9, 114.9, 127.3, 127.8, 128.0, 128.4, 128.5, 129.0, 130.0, 136.5, 137.0, 156.2, 157.4

ppm. IR (DCM, cm^{-1}) 3445, 3436, 3053, 3033, 2983, 2935, 2869, 1719, 1610, 1509, 1452, 1235, 1174, 1135, 1056, 1026 and 1013.

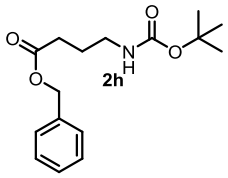
4-((*Tert*-butoxycarbonyl)amino)butanoic acid (2g - Scheme 2)



The reaction was carried out following the general procedure using 5 mol % of the photocatalyst together with 1 equiv. of bis(4-cholophenyl)disulfide (DDDS) and starting from Boc-Glu-OH. Purification by flash column chromatography (50:50 hexane/ethyl acetate) afforded the title compound as colorless oil (36 mg, 88% yield). Performing the reaction using 1 mol % of the photocatalyst and 10 mol % of DDDS afforded the product in 35% isolated yield.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.43 (s, 9H), 1.81 (quint, 2H, *J* = 7.0 Hz), 2.39 (t, 2H, *J* = 7.2 Hz), 3.05-3.25 (m, 2H), 4.69 (bs, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ25.1, 28.3, 31.2, 39.7, 79.5, 156.1, 178.1 ppm. Spectral data were in agreement with literature values.[4]

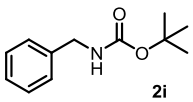
Benzyl 4-((*tert*-butoxycarbonyl)amino)butanoate (2h - Scheme 2)



The reaction was carried out following the general procedure starting from Boc-Glu(OBzl)-OH. Purification by flash column chromatography (gradient eluent from hexane to 90:10 hexane/ethyl acetate) afforded the title compound as a white solid (49 mg, 84% yield). HRMS *calcd* for ($C_{16}H_{23}NO_4$+H): 294.1705, found 294.1704.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.43 (s, 9H), 1.83 (quint, 2H, *J* = 7.1 Hz), 2.40 (t, 2H, *J* = 7.4 Hz), 3.16 (q, 2H, *J* = 6.6 Hz), 4.65 (bs, 1H), 5.11 (s, 2H), 7.29-7.40 (m, 5H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.2, 28.3, 31.5, 39.8, 66.3, 79.1, 128.1, 128.2, 128.5, 135.8, 155.9, 177.0 ppm. IR (DCM, cm^{-1}) 3449, 3436, 3055, 2979, 2934, 1728, 1510, 1502, 1367, 1244 and 1167.

***Tert*-butyl benzylcarbamate (2i - Scheme 2)**

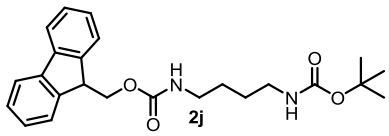


The reaction was carried out following the general procedure using 5 mol % of the photocatalyst together with 1 equiv. of bis(4-cholophenyl)disulfide (DDDS) and starting from Boc-Phg-OH. Purification by flash column chromatography (gradient eluent from hexane to 90:10 hexane/ethyl acetate) afforded the title compound as white solid (27 mg, 66% yield). Performing the reaction using 1 mol % of the photocatalyst and 10 mol % of DDDS afforded the product in 21% isolated yield.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.46 (s, 9H), 4.32 (d, 2H, *J* = 4.3 Hz), 4.83 (bs, 1H), 7.23-7.36 (m, 5H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ28.4, 44.6, 79.4, 127.3, 127.,4, 128.5, 138.8, 155.8 ppm. Spectral data were in agreement with literature values.[5]

(9H-fluoren-9-yl)methyl tert-butyl butane-1,4-diyldicarbamate (2j - Scheme 2)

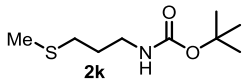
The reaction was carried out following the general procedure starting from Fmoc-Orn-(Boc)-OH. Purification by flash column chromatography (gradient eluent from hexane to 70:30 hexane/ethyl acetate)



afforded the title compound as a white solid (69 mg, 84% yield). HRMS *calcd* for ($C_{24}H_{30}N_2O_4$+H): 411.2284, found 411.2226.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.45 (s, 9H), 1.47-1.57 (m, 4H), 2.98-3.28 (m, 4H), 4.21 (t, 1H, *J* = 6.9 Hz), 4.40 (d, 2H, *J* = 6.9 Hz), 4.59 (bs, 1H), 4.92 (bs, 1H), 7.31 (td, 2H, J_t = 7.4 Hz, J_d = 1.2 Hz), 7.37-7.43 (m, 2H), 7.60 (d, 2H, *J* = 7.5 Hz), 7.76 (d, 2H, *J* = 7.5 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 27.1, 27.3, 28.3, 40.1, 40.6, 47.2, 66.4, 79.1, 119.9, 125.0, 126.9, 127.6, 141.2, 143.9, 155.9, 156.4 ppm. IR (DCM, cm^{-1}) 3448, 2977, 2938, 1719, 1713, 1605, 1513, 1503, 1451, 1367, 1276, 1243, and 1170.

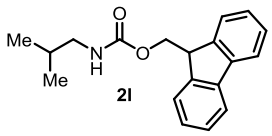
Tert-butyl (3-(methylthio)propyl)carbamate (2k - Scheme 2)



The reaction was carried out following the general procedure starting from Boc-Met-OH. Purification by flash column chromatography (gradient eluent from hexane to 90:10 hexane/ethyl acetate) afforded the title compound as colorless oil (37 mg, 90% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.42 (s, 9H), 1.77(quint, 2H, *J* = 7.1 Hz), 2.08 (s, 3H), 2.50 (t, 2H, *J* = 7.1 Hz), 3.20 (q, 2H, *J* = 6.6 Hz), 4.66 (bs, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ15.4, 28.3, 29.2, 31.4, 39.5, 79.1, 155.9 ppm. Spectral data were in agreement with literature values.[6]

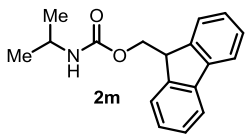
(9H-fluoren-9-yl)methyl isobutylcarbamate (2l - Scheme 2)



The reaction was carried out following the general procedure starting from Fmoc-Val-OH. Purification by flash column chromatography (gradient eluent from hexane to 70:30 hexane/ethyl acetate) afforded the title compound as a white solid (69 mg, 84% yield). HRMS *calcd* for ($C_{19}H_{21}NO_2$+H): 296.1615, found 296.1607.

^{1}H NMR ($CDCl_3$, 400 MHz,): δ0.91 (bs, 6H$_{min}$), 0.94 (t, 6H$_{maj}$, *J* = 6.7 Hz), 1.65 (bs, 1H$_{min}$), 1.79 (sep, 1H$_{maj}$, *J* = 6.7 Hz), 2.91 (bs, 2H$_{min}$), 3.05 (t, 2H$_{maj}$, *J* = 6.5 Hz), 4.21-4.31 (m, 1H), 4.44 (d, 2H$_{maj}$, *J* = 6.9 Hz), 4.49 (bs, 2H$_{min}$), 4.70 (bs, 1H$_{min}$), 4.88 (bs, 1H$_{maj}$), 7.34 (td, 2H, J_t = 7.4 Hz, J_d = 1.2 Hz), 7.42 (t, 2H, *J*= 7.5 Hz), 7.62 (d, 2H, *J* = 7.4 Hz), 7.79 (d, 2H, *J* = 7.6 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ19.8, 28.7, 47.2, 48.4, 66.4, 119.8, 124.9, 126.9, 127.5, 141.2, 143.9, 156.4 ppm. IR (DCM, cm^{-1}) 3446, 2962, 2931, 2898, 2872, 1722, 1604, 1515, 1468, 1450, 1226, 1140 and 1010.

(9H-fluoren-9-yl)methyl isopropylcarbamate (2m - Scheme 2)

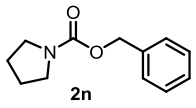


The reaction was carried out following the general procedure starting from Fmoc-Aib-OH. Purification by flash column chromatography (gradient eluent from hexane to 90:10 hexane/ethyl acetate) afforded the title compound as a white solid (48 mg, 86% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.18 (d, 6H, *J* = 6.5 Hz), 3.75-3.95 (m, 1H), 4.15-4.30 (m, 1H), 4.41 (d, 2H, *J* = 6.9 Hz), 4.64 (bs, 1H), 7.33 (td, 2H, J_t = 7.5 Hz, J_d = 1.2 Hz), 7.41 (tt, 2H, J_1 = 7.5 Hz, J_2 = 1.0 Hz), 7.61 (ddd, 2H, J_1 = 7.4 Hz, J_2 = 0.9 Hz, J_3 = 0.9 Hz), 7.77 (dt, 2H, J_d = 7.6 Hz, J_t = 1.0 Hz) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz)

δ 22.9, 43.0, 47.2, 66.2, 119.9, 124.9, 126.9, 127.5, 141.2, 144.0, 155.5 ppm. Spectral data were in agreement with literature values.[7]

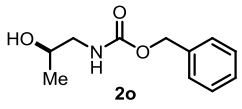
Benzyl pyrrolidine-1-carboxylate (2n - Scheme 2)



2n

The reaction was carried out following the general procedure starting from Z-Pro-OH. Purification by flash column chromatography (gradient eluent from hexane to 90:10 hexane/ethyl acetate) afforded the title compound as a white solid (37 mg, 91% yield).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.80-1.92 (m, 4H), 3.34-3.46 (m, 4H), 5.14 (s, 2H), 7.26-7.40 (m, 5H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.9, 25.7, 45.7, 46.2, 66.5, 127.7, 128.3, 137.1, 154.8 ppm. Spectral data were in agreement with literature values.[8]

Benzyl (R)-(2-hydroxypropyl)carbamate (2o - Scheme 2)

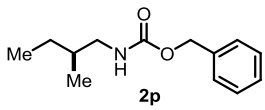


2o

The reaction was carried out following the general procedure using 5 mol % of the photocatalyst together with 1 equiv. of bis(4-cholophenyl)disulfide (DDDS) and starting from Z-Thr-OH. Purification by flash column chromatography (gradient eluent from 70:30 to 50:50 hexane/ethyl acetate) afforded the title compound as a white solid (37 mg, 90% yield) with an enantiomeric excess >99%. HRMS *calcd* for ($C_{11}H_{15}NO_3$+H): 210.1130, found 210.1142.
^{1}H NMR ($CDCl_3$, 400 MHz,): δ 1.17 (d, 3H, *J* = 6.3 Hz), 2.57 (bs, 1H), 2.94-3.11 (m, 1H), 3.20-3.40 (m, 1H), 3.89 (bs, 1H), 5.10 (s, 2H), 5.30 (bs, 1H), 7.27-7.38 (m, 5H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.6, 48.2, 66.8, 67.4, 128.1, 128.1, 128.5, 136.3, 157.0 ppm. $[\alpha]^{20}_D$ = -16.4° (c = 1.04, $CHCl_3$, >99% *ee*). Spectral data were in agreement with literature values.[9]

The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak AD-H column, 85:15 hexane:*i*PrOH, flow rate 0.5 mL/min, λ = 254 nm: τmajor = 14.7 min, τminor = 15.3 min. The enantiomeric excess found in the isolated product reflect the enantiopurity of the starting L-amino acid derivative (>99% *ee*).

Benzyl (S)-(2-methylbutyl)carbamate (2p - Scheme 2) (gram-scale reaction)

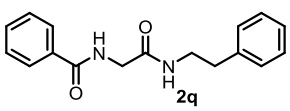


2p

Z-Ile-OH (1.060 g, 4 mmol) and the bis(4-cholophenyl)disulfide (115 mg, 0.4 mmol) were added into a 150mL cylindrical flask (4.8 cm of external diameter and 15 cm of total high) equipped with a Teflon coated magnetic stirring bar. The vial was sealed with a rubber septum and the internal atmosphere exchanged with nitrogen *via* three repeated cycle of vacuum-refill. Then 140 mL of a 0.28 mM solution of the photocatayst in degassed 1,2-dichloroehtane (sparged with nitrogen for 30 minutes) was added followed by 2,6-lutidine (93 µL, 0.8 mmol). The above mixture was then sparged with nitrogen for further 10 minutes. The flask was sealed with Teflon tape and irradiated (at approximately 2 cm away from the light source) with 24 watt blue LEDs (λ_{max} = 460 nm) under vigorous stirring. After 36 hours the solvent was reduced under vacuum to approximately 3 mL. Purification of the crude mixture by flash chromatography on silica gel (gradient eluent from hexane to 90:10 hexane/ethyl acetate) provided the desired product as a colorless oil (725 mg, 82% yield).

^{1}H NMR ($CDCl_3$, 400 MHz,): δ 0.86-0.94 (m, 6H), 1.07-1.21 (m, 1H), 1.32-1.46 (m, 1H), 1.47-1.61 (m, 1H), 2.95-3.06 (m, 1H), 3.08-3.20 (m, 1H), 4.79 (bs, 1H), 5.10 (s, 2H), 7.28-7.39 (m, 5H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 11.2, 16.9, 17.0, 26.7, 35.1, 46.7, 66.5, 128.0, 128.1, 128.5, 135.6, 156.5 ppm. $[\alpha]^{20}_{D}$ = +3.8° (c = 0.95, $CHCl_3$, >99% *ee*).

_N_-(2-oxo-2-(phenethylamino)ethyl)benzamide (2q - Scheme 2)

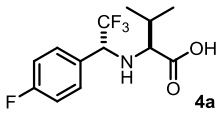


The reaction was carried out following the general procedure using 5 mol % of the photocatalyst together with 1 equiv. of bis(4-cholophenyl)disulfide (DDDS) and starting from *N*-Benzoyl-Gly-Phe. Purification by flash column chromatography (gradient eluent from 50:50 to 40:60 hexane/ethyl acetate) afforded the title compound as a white solid (48 mg, 85% yield). Performing the reaction using 1 mol % of the photocatalyst and 10 mol % of DDDS afforded the product in 55% isolated yield. HRMS *calcd* for ($C_{17}H_{18}N_2O_2$+H): 283.1447, found 283.1449.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.82 (t, 2H, *J* = 7.1 Hz), 3.54 (q, 2H, *J* = 7.1 Hz), 4.06 (d, 2H, *J* = 5.1 Hz), 6.70 (bs, 1H), 7.13-7.26 (m, 5H), 7.37 (bs, 1H), 7.40-7.47 (m, 2H), 7.49-7.55 (m, 1H), 7.79-7.84 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 35.5, 40.7, 43.8, 126.5, 127.1, 128.5, 128.5, 128.6, 131.8, 133.3, 138.5, 167.7, 169.0 ppm. IR (DCM, cm^{-1}) 3673, 3666, 3602, 3444, 3435, 3426, 3061, 3030, 2928, 2857, 1689, 1679, 1659, 1650, 1642, 1604, 1582, 1546, 1524, 1513, 1503, 1484, 1276 and 1229.

Chiral amines **4a-d** were prepared according to the literature procedure described in reference 10. The crudes obtained following this methodology were purified by column chromatography on silica-gel affording the desired compounds.

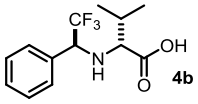
((*R*)-2,2,2-trifluoro-1-(4-fluorophenyl)ethyl)-L-valine (4a - Table 2)



Prepared according to ref.10 using L-Valine methyl ester hydrochloride (731 mg, 4.02 mmol), 2,2,2,4′-Tetrafluoroacetophenone (672 mg, 3.5 mmol) was purified by flash column chromatography (gradient eluent from hexane to 5:1 hexane/ethyl acetate). The title compound **4a** was obtained as a white solid (573 mg, 56% overall yield). The d.r. was determined by ^{19}F NMR to be 11 to 1. HRMS: calc. for $C_{13}H_{15}F_4NO_2$ (M+H) : 294.117; found 294.1109.

^{1}H ($CDCl_3$, 400 MHz, major diasteroisomer): δ 0.97 (d, 6H, *J* = 7.0 Hz), 1.99-2.13 (m, 1H), 2.90 (d, 1H, *J* = 5.1 Hz), 4.19 (q, 1H, *J* = 7.0 Hz), 7.05-7.13 (m, 2H), 7.44 (dd, 2H, J_1 = 8.6 Hz, J_2 = 5.5.0 Hz) ppm. ^{13}C ($CDCl_3$, 100 MHz, major diasteroisomer): δ 17.7, 19.5, 31.4, 62.7 (q, *J* = 28.2 Hz), 63.1, 115.8 (d, *J* = 21.7 Hz), 124.8 (q, *J* = 280.8 Hz), 128.6, 130.9 (d, *J* = 8.4 Hz), 163.4 (d, *J* = 248.7 Hz), 182.7 ppm. ^{19}F ($CDCl_3$, 376 MHz): δ 76.9 (d, *J* = 6.8 Hz, minor), 78.1 (d, *J* = 6.8 Hz, major) ppm. IR (DCM, cm^{-1}) 3058, 2967, 2933, 2877, 1766, 1746, 1709, 1609, 1513, 1351, 1274, 1228, 1178, 1159, 1126 and 834. $[\alpha]^{20}_{D}$ = -99.3° (c = 0.785, $CHCl_3$, d.r. 11:1).

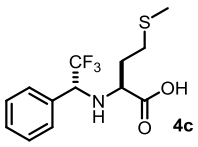
((*S*)-2,2,2-trifluoro-1-phenylethyl)-D-valine (4b - Table 2)



Prepared according to ref. 10 using D-Valine methyl ester hydrochloride (731 mg, 4.02 mmol), 2,2,2-Trifluoroacetophenone (491 µL, 3.5 mmol) was purified by flash column chromatography (gradient eluent from hexane to 5:1 hexane/ethyl acetate). The title compound **4b** was obtained as a white solid (490 mg, 51% overall yield). The d.r. was determined by ^{19}F NMR to be 46 to 1. The ^{1}H, ^{13}C were found to be in agreement with the literature.[10] The absolute configuration of **4b** was assigned in accordance with the data reported in reference 10.

^{1}H ($CDCl_3$, 400 MHz, major diasteroisomer): δ 0.96 (d, 6H, J = 7.0 Hz), 1.98-2.13 (m, 1H), 2.94 (d, 1H, J = 5.1 Hz), 4.19 (q, 1H, J = 7.0 Hz), 7.35-7.50 (m, 5H) ppm. ^{13}C ($CDCl_3$, 100 MHz, major diasteroisomer): δ 17.7, 19.4, 31.4, 63.28, 63.5 (q, *J* = 28.2 Hz), 124.9 (q, *J* = 280.8 Hz), 128.7, 129.2, 129.5, 132.8, 179.3 ppm. ^{19}F ($CDCl_3$, 376 MHz): δ76.7 (d, *J* = 6.8 Hz, minor), 77.8 (d, *J* = 6.8 Hz, major) ppm. $[\alpha]^{20}_{D}$ = +81.2° (c = 0.884, $CHCl_3$, d.r. 46 : 1).

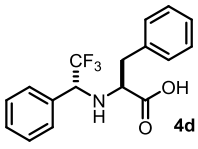
((*R*)-2,2,2-trifluoro-1-phenylethyl)-L-methionine (4c - Table 2)



Prepared according to ref. 10 using L-Methionine methyl ester hydrochloride (803 mg, 4.02 mmol), 2,2,2-Trifluoroacetophenone (491 µL, 3.5 mmol) was purified by flash column chromatography (gradient eluent from hexane to 4:1 hexane/ethyl acetate). The title compound **4c** was obtained as a white solid (666 mg, 62% overall yield). The d.r. was determined by ^{19}F NMR to be 6 to 1.

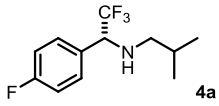
^{1}H ($CDCl_3$, 400 MHz): δ 1.79-1.93 (m, 1H), , 1.98-2.05 (m, 1H), 2.06 (s, 3H), 2.50-2.76 (m, 2H), 3.28-3.35 (m, 1H), 4.22-4.33 (m, 1H), 6.55 (bs, 1H), 7.38-7.46 (m, 5H) ppm. ^{13}C ($CDCl_3$, 100 MHz, major diasteroisomer): δ 15.2, 30.4, 32.6, 56.9, 63.3 (q, *J* = 28.9 Hz), 124.8 (q, *J* = 281.6 Hz), 128.8, 129.0, 129.6, 132.6, 178.1 ppm. ^{19}F ($CDCl_3$, 376 MHz): δ76.8 (d, *J* = 6.8 Hz, minor), 77.9 (d, *J* = 6.8 Hz, major) ppm. IR (DCM, cm^{-1}) 2920, 1765, 1752, 1713, 1602, 1367, 1274, 1167 and 1122. $[\alpha]^{20}_{D}$ = -66.3° (c = 0.953, $CHCl_3$, d.r. 6 : 1).

((*R*)-2,2,2-trifluoro-1-phenylethyl)-L-phenylalanine (4d - Table 2)



Prepared according to ref. 10 using L-Phenylalanine methyl ester hydrochloride (868 mg, 4.02 mmol), 2,2,2-Trifluoroacetophenone (491 µL, 3.5 mmol) was purified by flash column chromatography (gradient eluent from hexane to 4:1 hexane/ethyl acetate). The title compound **4d** was obtained as a white solid (742 mg, 66% overall yield). The d.r. was determined by ^{19}F NMR to be 18 to 1. HRMS: calc. for $C_{17}H_{16}F_3NO_2$ (M+H): 324.1211; found 324.1175.
^{1}H ($CDCl_3$, 400 MHz): δ 2.85 (dd, 1H, J_1 = 13.3 Hz, J_2 = 9.0 Hz), 3.15 (dd, 1H, J_1 = 13.3 Hz, J_2 = 4.3 Hz), 3.38 (dd, 1H, J_1 = 9.0 Hz, J_2 = 4.3 Hz), 4.11 (q, 1H, *J* = 7.0 Hz), 6.94-7.02 (m, 2H), 7.06-7.14 (m, 2H), 7.20-7.40 (m, 6H) ppm. ^{13}C ($CDCl_3$, 100 MHz): δ38.9, 59.7, 63.3 (q, *J* = 28.7 Hz), 124.7 (q, *J* = 280.7 Hz), 127.3, 128.3, 128.8, 128.9, 129.2, 123.3, 132.1, 135.8, 175.7 ppm. ^{19}F ($CDCl_3$, 376 MHz): δ77.1 (d, *J* = 6.8 Hz, minor), 77.9 (d, *J* = 6.8 Hz, major) ppm. IR (DCM, cm^{-1}) 3072, 3033, 2927, 1771, 1755, 1713, 1603, 1496, 1453, 1359, 1336, 1275, 1175 and 1126.. $[\alpha]^{20}_{D}$ = -31.6° (c = 0.90, $CHCl_3$, d.r. 18 : 1).

(*R*)-2-methyl-N-(2,2,2-trifluoro-1-(4-fluorophenyl)ethyl)propan-1-amine (5a - Table 2)



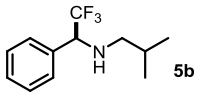
4a

The reaction was carried out following the general procedure starting from amino acid **4a**. Purification by flash column chromatography (gradient eluent from hexane to 95:5 hexane/ethyl acetate) afforded the title compound as a colorless oil (36 mg, 72% yield) with an enantiomeric excess of 83%. HRMS *calcd* for ($C_{12}H_{15}F_4N$+H): 250.1219, found 250.1221.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.89 (d, 3H, *J* = 6.6 Hz), 0.91 (d, 3H, *J* = 6.6 Hz), 1.71 (sep, 1H, *J* = 6.7 Hz), 2.29 (dd, 1H, J_1 = 11.3 Hz, J_2 = 7.4 Hz), 2.40 (dd, 1H, J_1 = 11.3 Hz, J_2 = 6.3 Hz), 4.11 (q, 1H, *J* = 7.4 Hz), 7.05-7.12 (m, 2H), 7.37-7.44 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.3, 20.5, 28.4, 55.4, 64.1 (q, *J* = 29.0 Hz), 115.5 (d, *J* = 22.1 Hz), 125.3 (q, *J* = 281.5 Hz), 129.4, 130.3, 130.3, 130.4, 163.0 (d, *J* = 247.2 Hz) ppm. ^{19}F ($CDCl_3$, 376 MHz): δ 77.6 (d, *J* = 6.8 Hz) ppm. IR (DCM, cm^{-1}) 2962, 2930, 2852, 1608, 1275, 1253, 1227, 1173, 1119, 833 and 792. $[\alpha]^{20}_D$ = -18.2° (c = 0.525, $CHCl_3$, *ee* 83%).

The enantiomeric excess was determined by GC analysis on a Varian Chrompack Capillary Column (CP-Chiralsil-DEX CB 25m, 0.32mm, 0.25µm), using an isotherm method at 80° with a flow rate 1.5 mL/min (hydrogen gas as carrier): τ_{major} = 30.9 min, τ_{minor} = 31.6 min.

(*S*)-2-methyl-N-(2,2,2-trifluoro-1-phenylethyl)propan-1-amine (5b - Table 2)



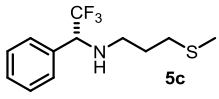
5b

The reaction was carried out following the general procedure starting from amino acid **4b**. Purification by flash column chromatography (gradient eluent from hexane to 95:5 hexane/ethyl acetate) afforded the title compound as a colorless oil (35 mg, 75% yield) with an enantiomeric excess of 97%. HRMS *calcd* for ($C_{12}H_{16}F_3N$+H): 232.1313, found 232.1310.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.88 (d, 3H, *J* = 6.6 Hz), 0.90 (d, 3H, *J* = 6.6 Hz), 1.71 (sep, 1H, *J* = 6.6 Hz), 2.29 (dd, 1H, J_1 = 11.3 Hz, J_2 = 7.0 Hz), 2.40 (dd, 1H, J_1 = 11.7 Hz, J_2 = 6.6 Hz), 4.09 (q, 1H, *J* = 7.4 Hz), 7.35-7.43 (m, 5H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.3, 20.5, 28.4, 55.6, 64.8 (q, *J* = 28.3 Hz), 125.3 (q, *J* = 281.5 Hz), 128.4, 128.6, 128.8, 134.8 ppm. ^{19}F ($CDCl_3$, 376 MHz): δ 77.3 (d, *J* = 8.2 Hz) ppm. IR (DCM, cm^{-1}) 2961, 2932, 2910, 2870, 1604, 1469, 1391, 1367, 1265, 1171 and 1119. $[\alpha]^{20}_D$ = -51.4° (c = 0.8083, $CHCl_3$, *ee* 97%).

The enantiomeric excess was determined by GC analysis on a Varian Chrompack Capillary Column (CP-Chiralsil-DEX CB 25m, 0.32mm, 0.25µm), using an isotherm method at 50° with a flow rate 2.0 mL/min (hydrogen gas as carrier): τ_{minor} = 83.3 min, τ_{major} = 84.8 min.

(*R*)-3-(methylthio)-N-(2,2,2-trifluoro-1-phenylethyl)propan-1-amine (5c - Table 2)



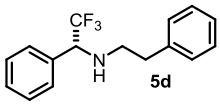
5c

The reaction was carried out following the general procedure starting from amino acid **4c**. Purification by flash column chromatography (gradient eluent from hexane to 95:5 hexane/ethyl acetate) afforded the title compound as a colorless oil (40 mg, 76% yield) with an enantiomeric excess of 69%.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.71-1.81 (m, 2H), 2.07 (m,2H), 2.47-2.59 (m, 2H), 2.61-2.73 (m, 2H), 4.11 (q, 1H, *J* = 7.4 Hz), 7.35-7.42 (m, 5H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.47, 29.28, 31.7, 46.5, 64.7 (q, *J* = 29.0 Hz), 125.4 (d, *J* = 281.3 Hz), 128.4, 128.6, 128.9, 134.5 ppm. ^{19}F ($CDCl_3$, 376 MHz): δ 77.3 (d, *J* = 8.2 Hz) ppm. IR (DCM, cm^{-1}) 3053, 2923, 2856, 1605, 1589, 1352, 1168, 1122, and 849. $[\alpha]^{20}_D$ = -31.6° (c = 1.014, $CHCl_3$, *ee* 69%).

The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak AD-H column, 98:2 hexane:*i*PrOH, flow rate 0.5 mL/min, λ = 254 nm: τ_{major} = 9.2 min, τ_{minor} = 10.1 min.

(*R*)-2,2,2-trifluoro-N-phenethyl-1-phenylethan-1-amine (5d - Table 2)

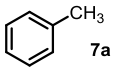


5d

The reaction was carried out following the general procedure starting from amino acid **4d**. Purification by flash column chromatography (gradient eluent from hexane to 90:10 hexane/ethyl acetate) afforded the title compound as a colorless oil (21 mg, 37% yield) with an enantiomeric excess of 88%. HRMS *calcd* for ($C_{16}H_{16}F_3N$+H): 280.1313, found 280.1323.
^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.75 (m, 4H), 4.14(q, 1H, *J* = 7.4 Hz), 7.11-7.17 (m, 2H), 7.18-7.23 (m, 1H), 7.25-7.38 (m, 7H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 36.2, 48.8, 64.6 (q, *J* = 28.3 Hz), 125.4 (d, *J* = 281.5 Hz), 126.3, 128.4, 128.5, 128.6, 128.6, 128.9, 134.3, 139.3 ppm. ^{19}F ($CDCl_3$, 376 MHz): δ 77.2 (d, *J* = 6.8 Hz) ppm. IR (DCM, cm^{-1}) 3031, 2929, 2856, 1604, 1500, 1455, 1380, 1355, 1267, 1170, 1126, 1084, 907 and 846. $[\alpha]^{20}_D$ = -44.4° (c = 0.734, $CHCl_3$, *ee* 88%).

The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak AD-H column, 98:2 hexane:*i*PrOH, flow rate 0.5 mL/min, λ = 254 nm: τ_{major} = 8.0 min, τ_{minor} = 8.5 min.

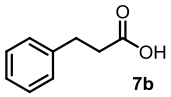
Toluene (7a - Scheme 3)



7a

The reaction was carried out following the general procedure using 5 mol % of the photocatalyst together with 1 equiv. of bis(4-cholophenyl)disulfide (DDDS) and starting from Phenylacetic acid. The product was not isolated due to its high volatility. GC-yield = 34%.

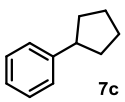
3-phenylpropanoic acid (7b - Scheme 3)



7b

The reaction was carried out following the general procedure using 5 mol % of the photocatalyst together with 1 equiv. of bis(4-cholophenyl)disulfide (DDDS) and starting from Phenylsuccinic acid. Purification by flash column chromatography (70:30 hexane/ethyl acetate) afforded the title compound as a white solid (24 mg, 80% yield).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.71 (t, 2H, *J* = 8.2 Hz), 2.98 (t, 2H, *J* = 8.2 Hz), 7.20-7.26 (m, 3H), 7.28-7.37 (m, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 30.5, 35.6, 126.3, 128.2, 128.5, 140.1, 178.9 ppm. Spectral data were in agreement with literature values.[11]

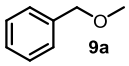
cyclopentylbenzene (7c - Scheme 3)


7c

The reaction was carried out following the general procedure using 5 mol % of the photocatalyst together with 1 equiv. of bis(4-cholophenyl)disulfide (DDDS) and starting from 1-Phenyl-1-cyclopentanecarboxylic acid. Purification by flash column chromatography (pentane 100%) afforded the title compound as a white solid (24 mg, 82% yield).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.55-1.88 (m, 6H), 2.04-2.13 (m, 2H), 3.01 (tt, J_1 = 9.8 Hz, J_2 = 7.4 Hz), 7.16-7.21 (m, 1H), 7.24-7.33 (m, 4H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.5, 34.6, 45.9, 125.6, 127.1, 128.2, 146.5 ppm.

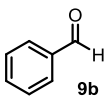
(methoxymethyl)benzene (9a - Scheme 4)



9a

The reaction was carried out following the general procedure using 5 mol % of the photocatalyst together with 1 equiv. of bis(4-cholophenyl)disulfide (DDDS) and starting from (±)-α-Methoxyphenylacetic acid. After 14h the crude mixture was transferred in a round bottom flask and the solvent evaporated under vacuum. The crude was then dissolved in deuterated chloroform and 2,5-Dimethylfuran (0.1 mmol) was added before NMR analysis. From the integration of the picks at 2.21 (6H, internal standard), 5.83 ppm (2H, internal standard) and 3.40 (3H, product), 4.47 ppm (2H, product) the NMR-yield was found to be 84%.
Spectral data were in agreement with literature values.[12]

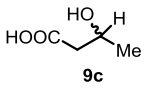
Benzaldehyde (9b - Scheme 4)



9b

The reaction was carried out following the general procedure using 5 mol % of the photocatalyst together with 1 equiv. of bis(4-cholophenyl)disulfide (DDDS) and starting from (±)-Mandelic acid. After 14h the crude mixture was transferred in a round bottom flask and the solvent evaporated under vacuum. The crude was then dissolved in deuterated chloroform and 2,5-Dimethylfuran (0.1 mmol) was added before NMR analysis. From the integration of the picks at 5.83 ppm (2H, internal standard) and 10.0 (1H, product) the NMR-yield was found to be >95%.
Spectral data were in agreement with literature values.[13]

3-hydroxybutanoic acid (9c - Scheme 4)



9c

The reaction was carried out following the general procedure using 5 mol % of the photocatalyst together with 1 equiv. of bis(4-cholophenyl)disulfide (DDDS) and starting from Citramalic acid. Purification by flash column chromatography (gradient eluent from hexane/ethyl acetate 70:30 to ethyl acetate) afforded the title compound as a colorless oil (21 mg, 37% yield) afforded the title compound as a white solid (11 mg, 52% yield).
^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.55-1.88 (m, 6H), 2.04-2.13 (m, 2H), 3.01 (tt, J_1 = 9.8 Hz, J_2 = 7.4 Hz), 7.16-7.21 (m, 1H), 7.24-7.33 (m, 4H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.5, 34.6, 45.9, 125.6, 127.1, 128.2, 146.5 ppm. $[\alpha]^{20}_{D}$ = 0.0° (c = 1.051, $CHCl_3$). Spectral data were in agreement with literature values.[14]

E. References

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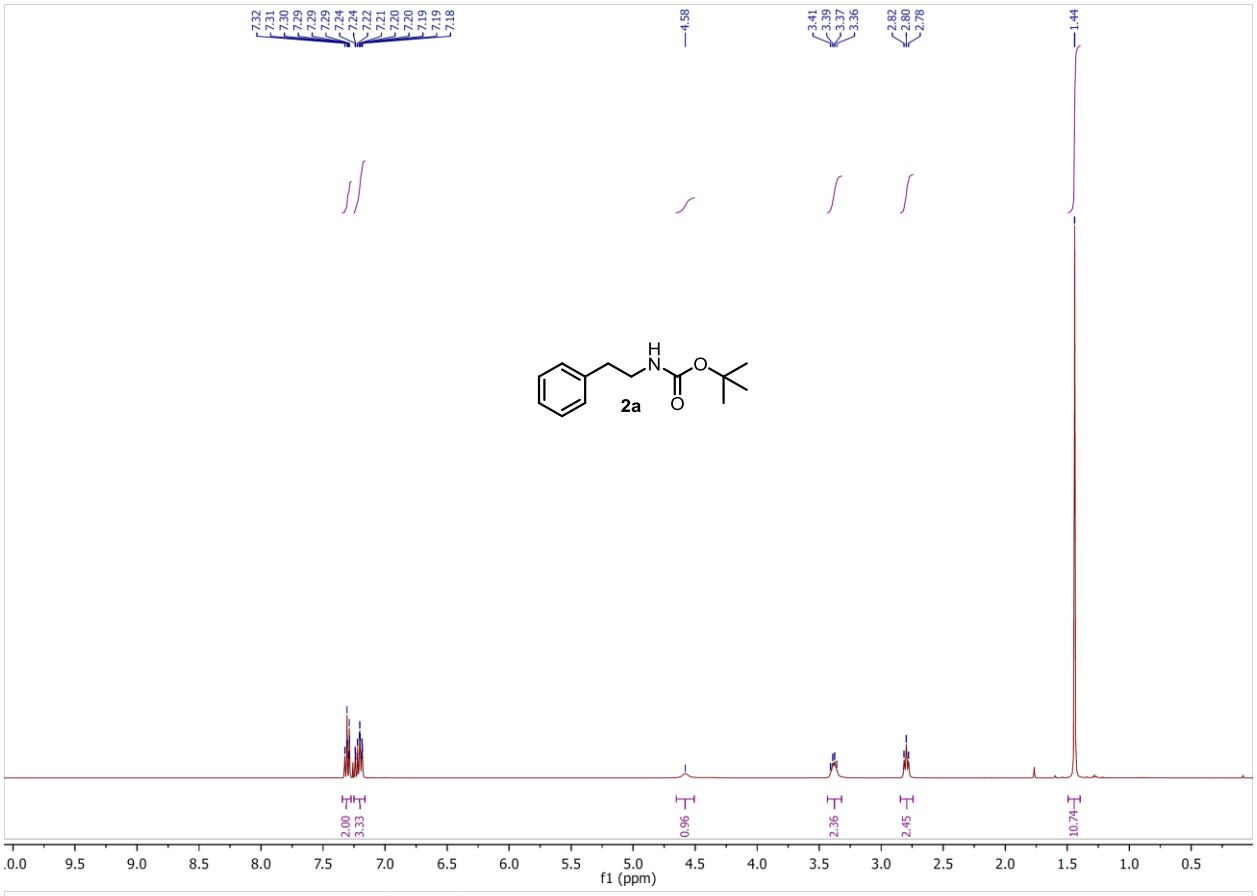
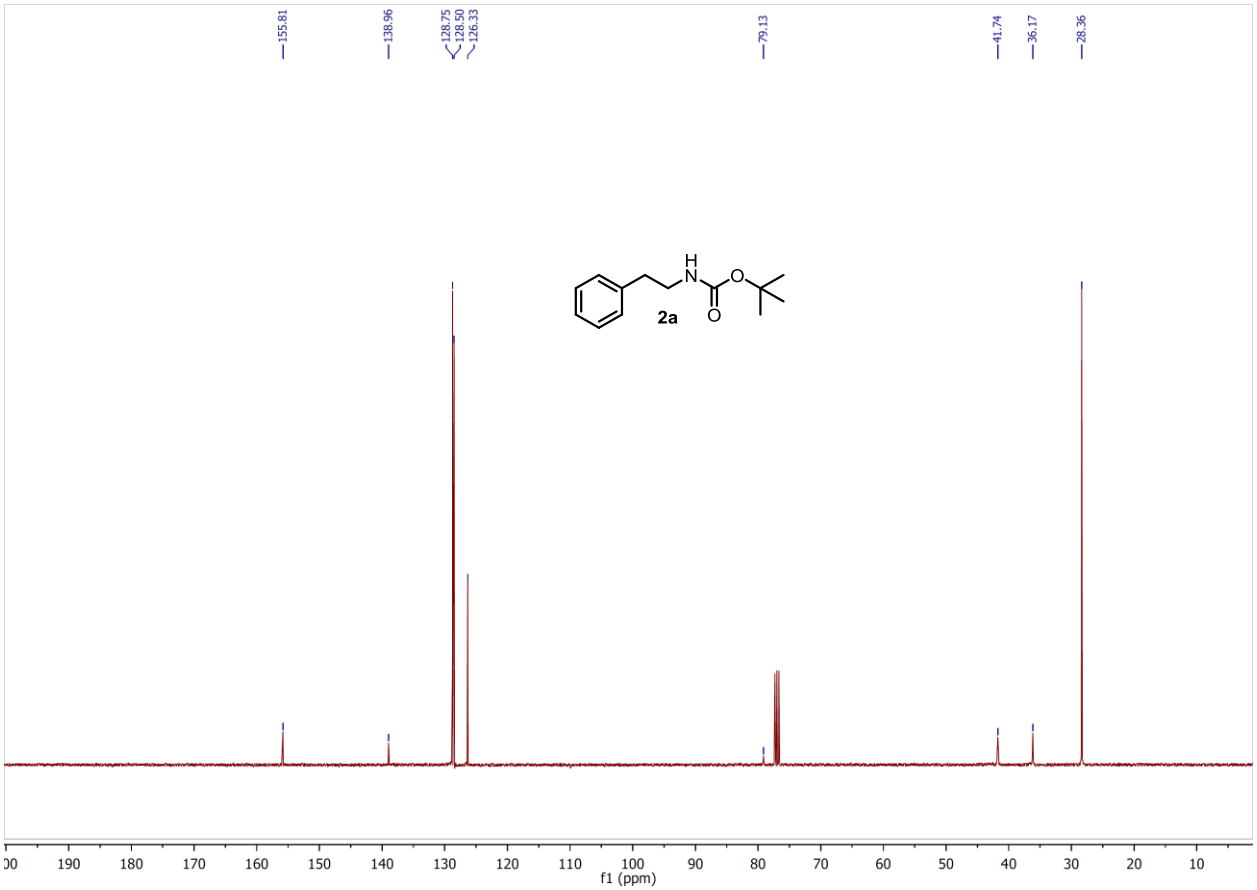
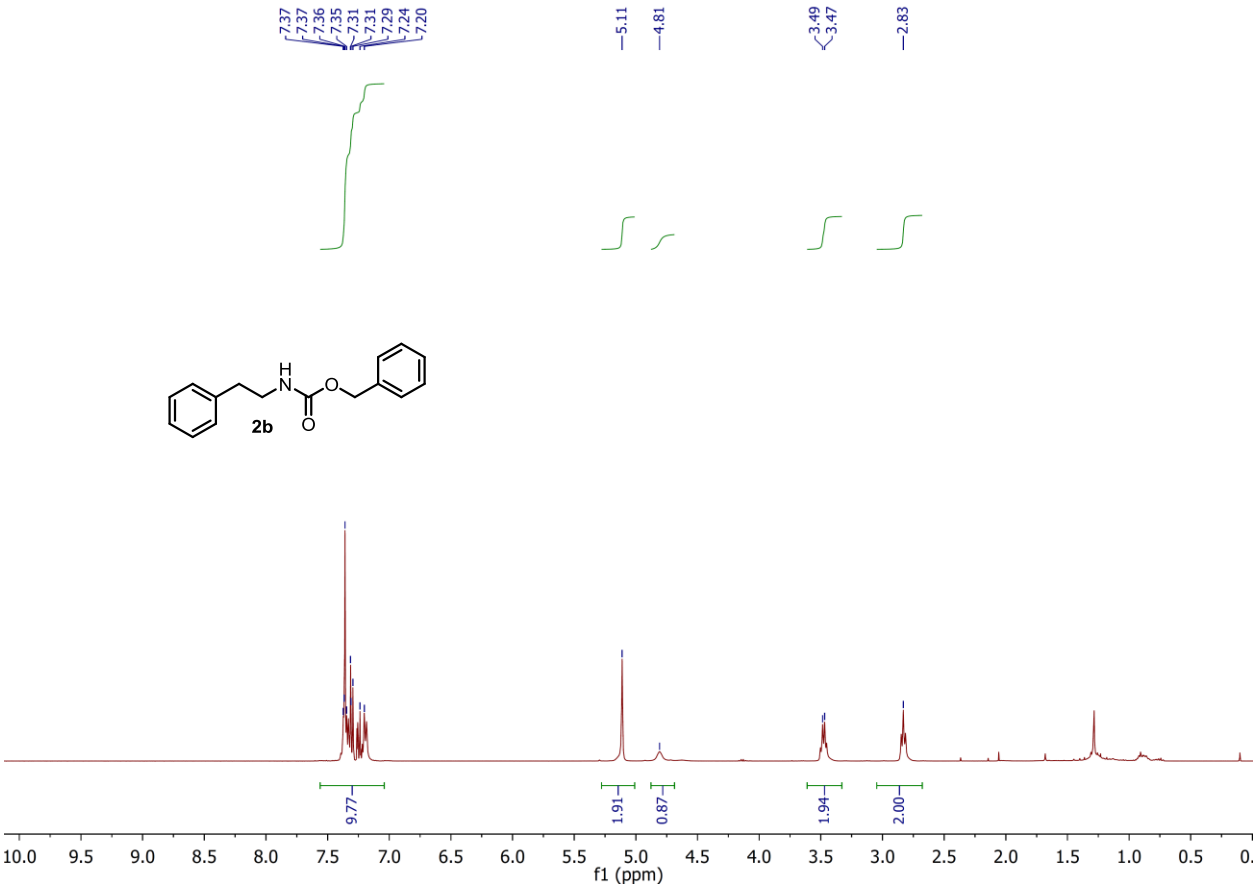
F. NMR Spectra



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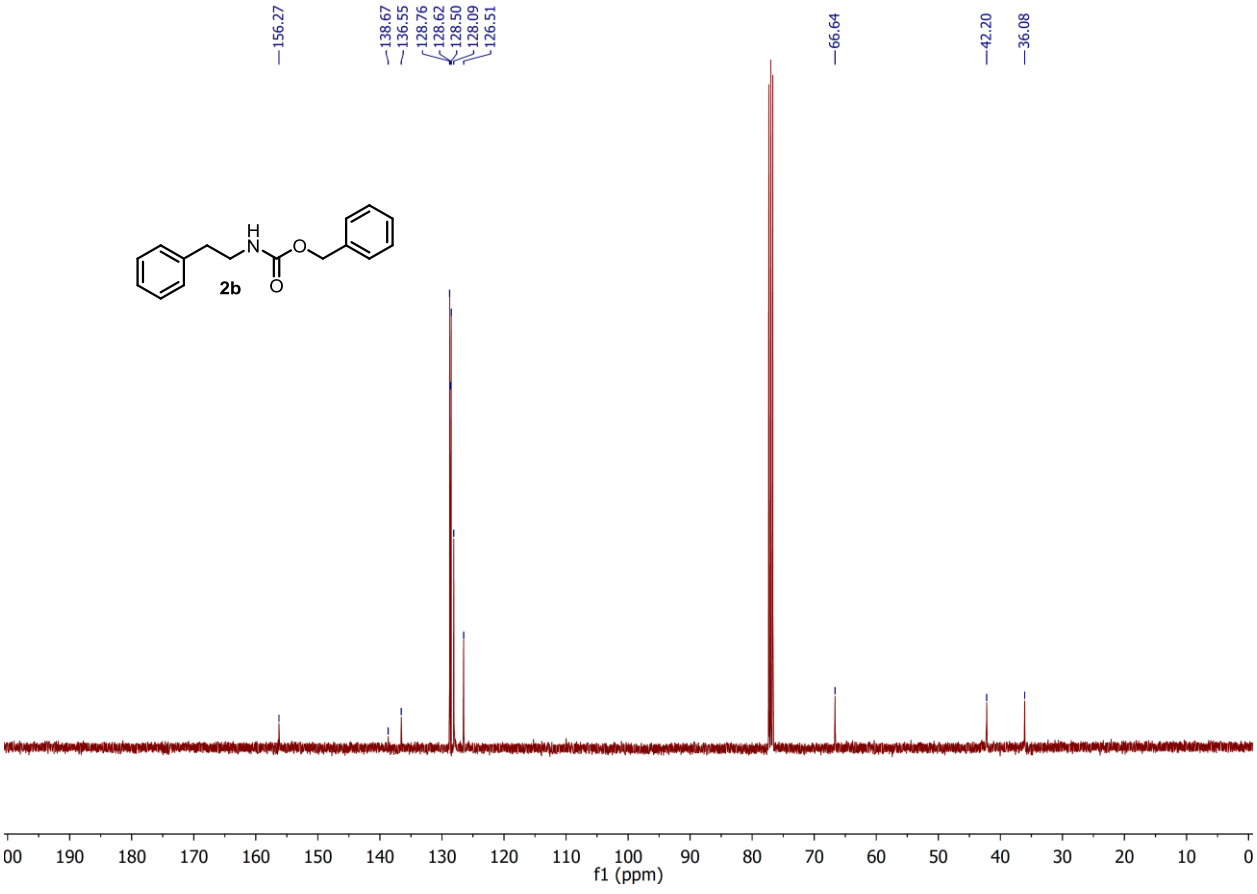
7.36
7.35
7.31
7.31
7.29
7.24
7.20
5.11
4.81
3.49
3.47
2.83
2b
9.77
1.91
0.87
1.94
2.00
f1 (ppm)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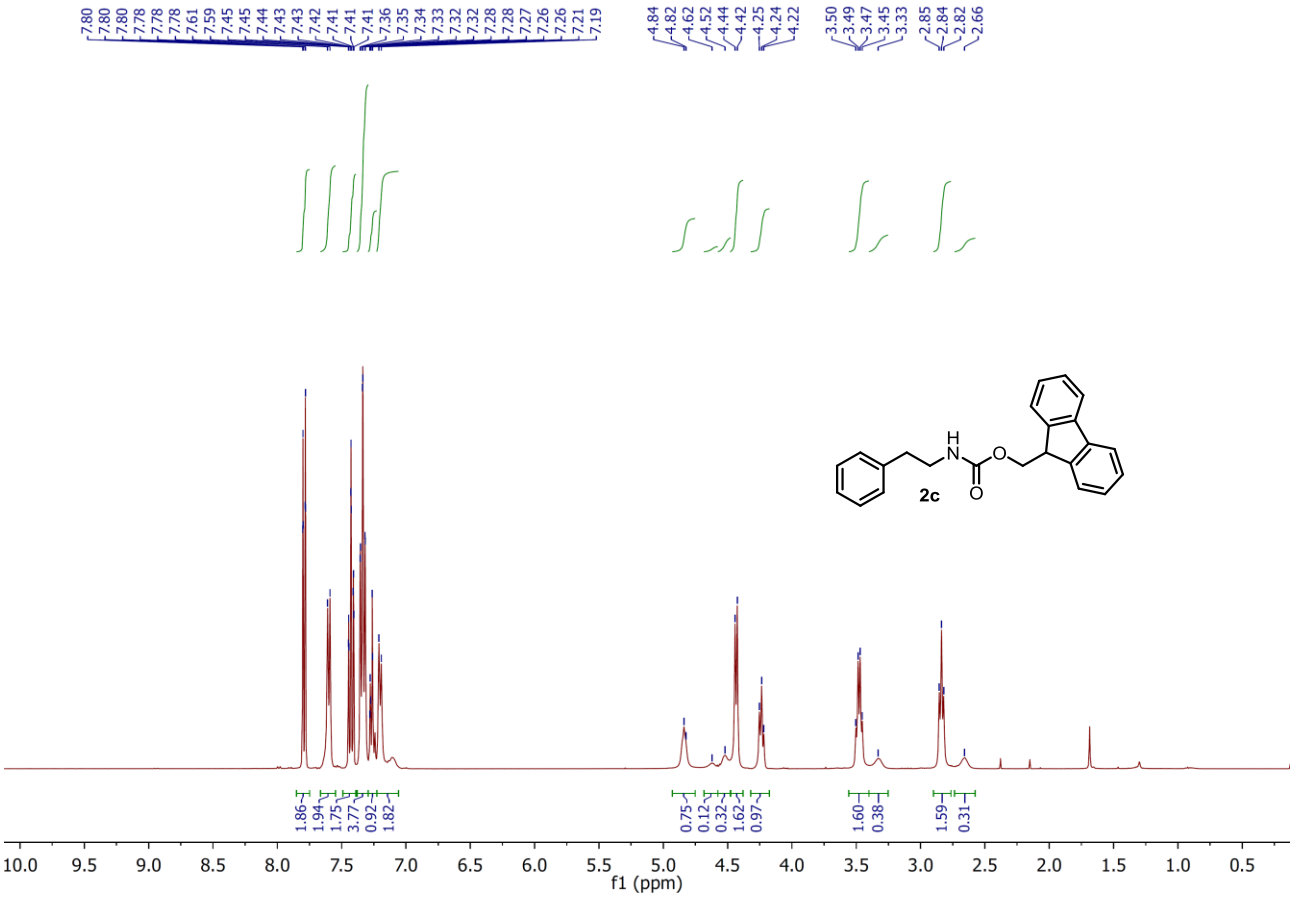
128.09
126.51
66.64
42.20
36.08
2b
f1 (ppm)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7.42
7.41
7.41
7.41
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7.35
7.34
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7.27
7.26
7.26
7.21
7.19
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4.82
4.62
4.52
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3.49
3.47
3.45
3.33
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2.66
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3.77
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0.75
0.12
0.32
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0.97
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0.38
1.59
0.31
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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2.5
2.0
1.5
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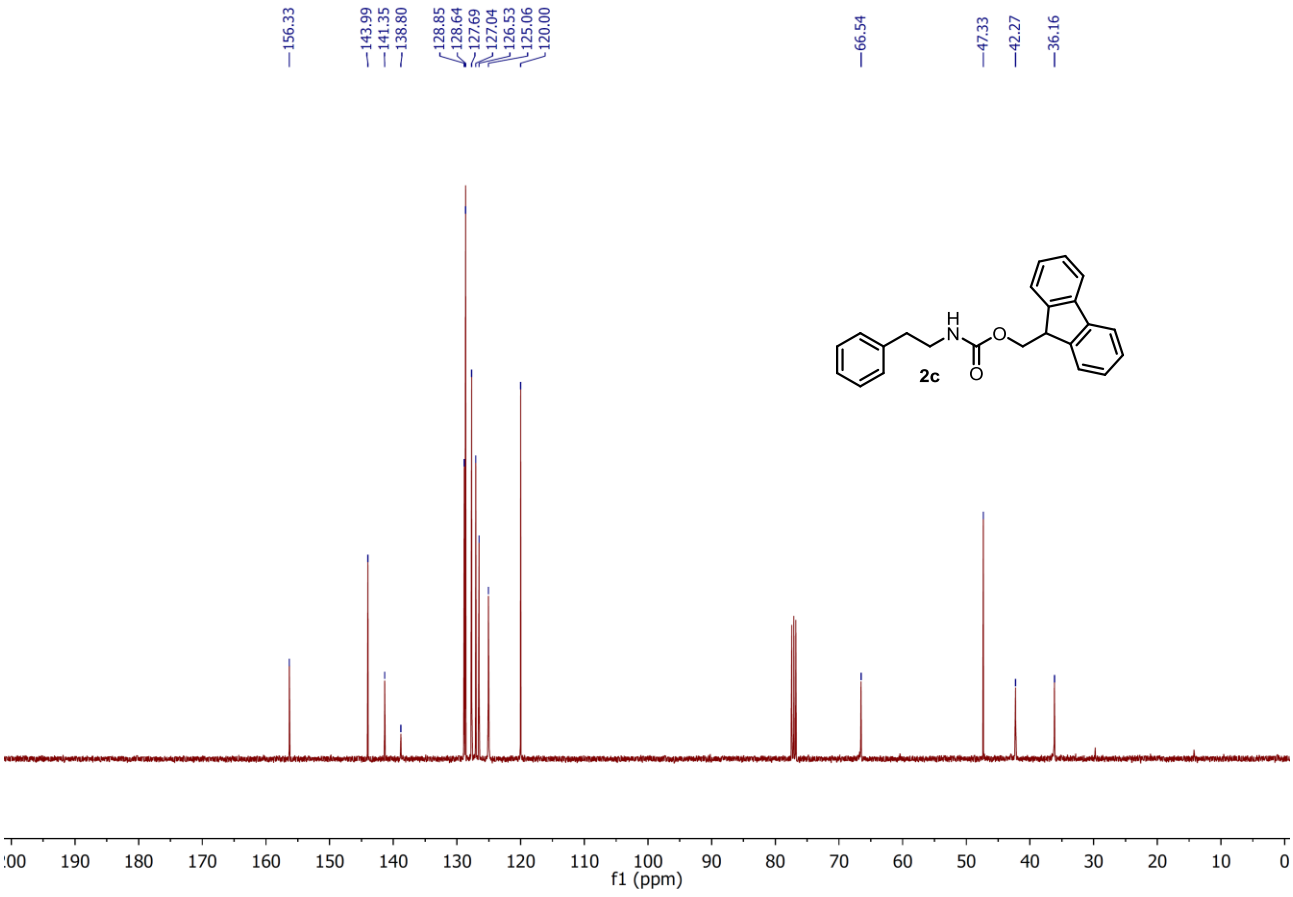
0.5
f1 (ppm)
H
N
O
O
2c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125.06
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42.27
36.16
200
190
180
170
160
150
140
130
120
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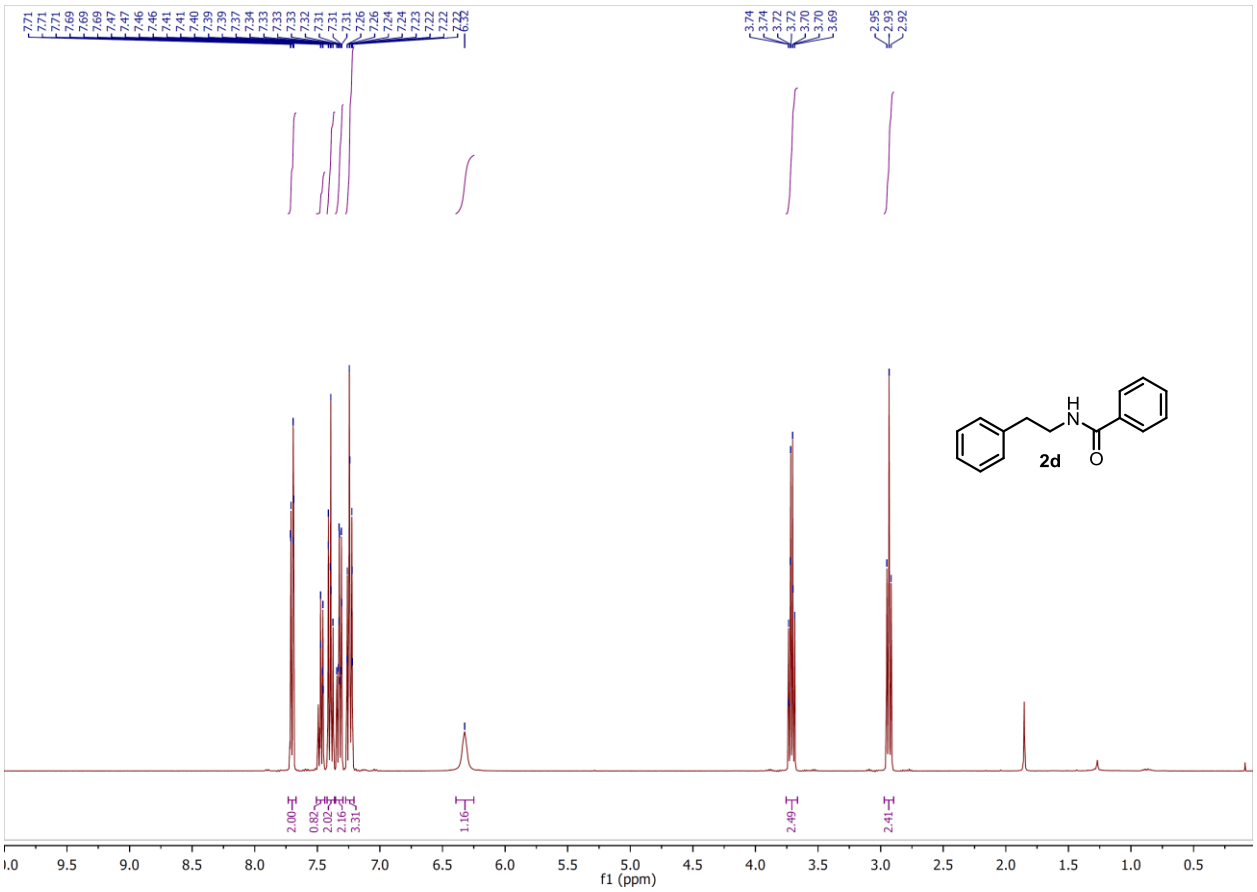
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
H
N
O
O
2c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3.72
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3.70
3.70
3.69
2.95
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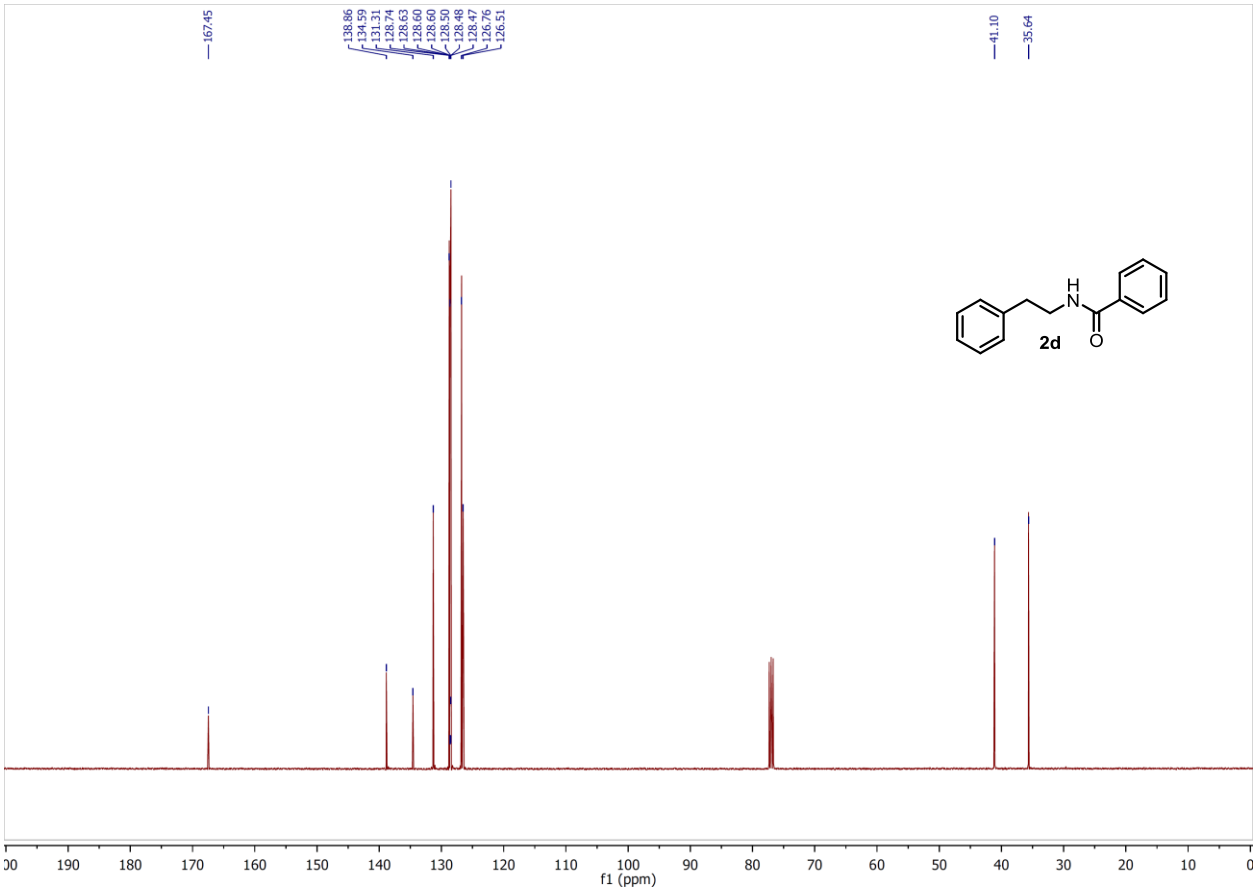
2.41
f1 (ppm)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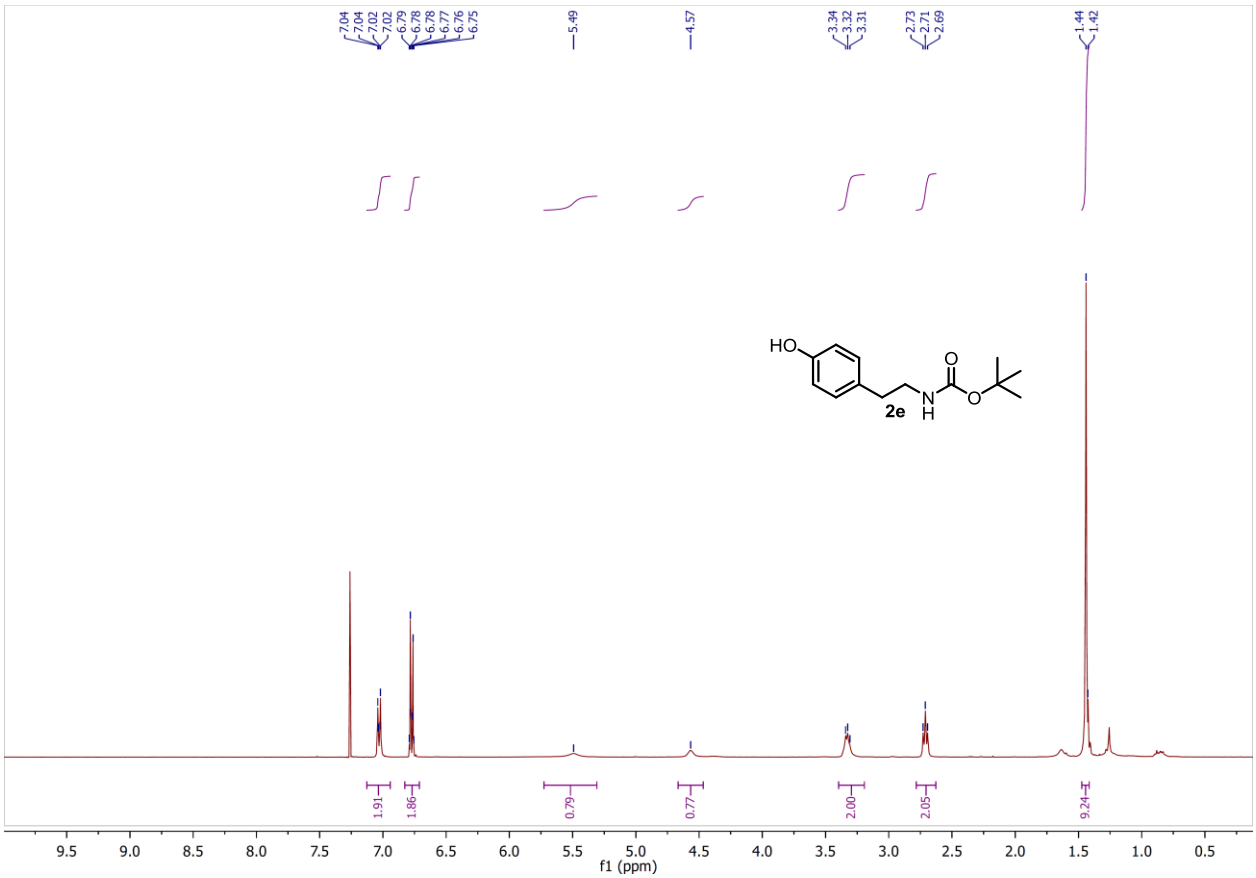
126.51
41.10
35.64
2d
f1 (ppm)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3.31
2.73
2.71
2.69
1.44
1.42
HO
O
N
H
O
2e
1.91
1.86
0.79
0.77
2.00
2.05
9.24
9.5
9.0
8.5
8.0
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7.0
6.5
6.0
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3.0
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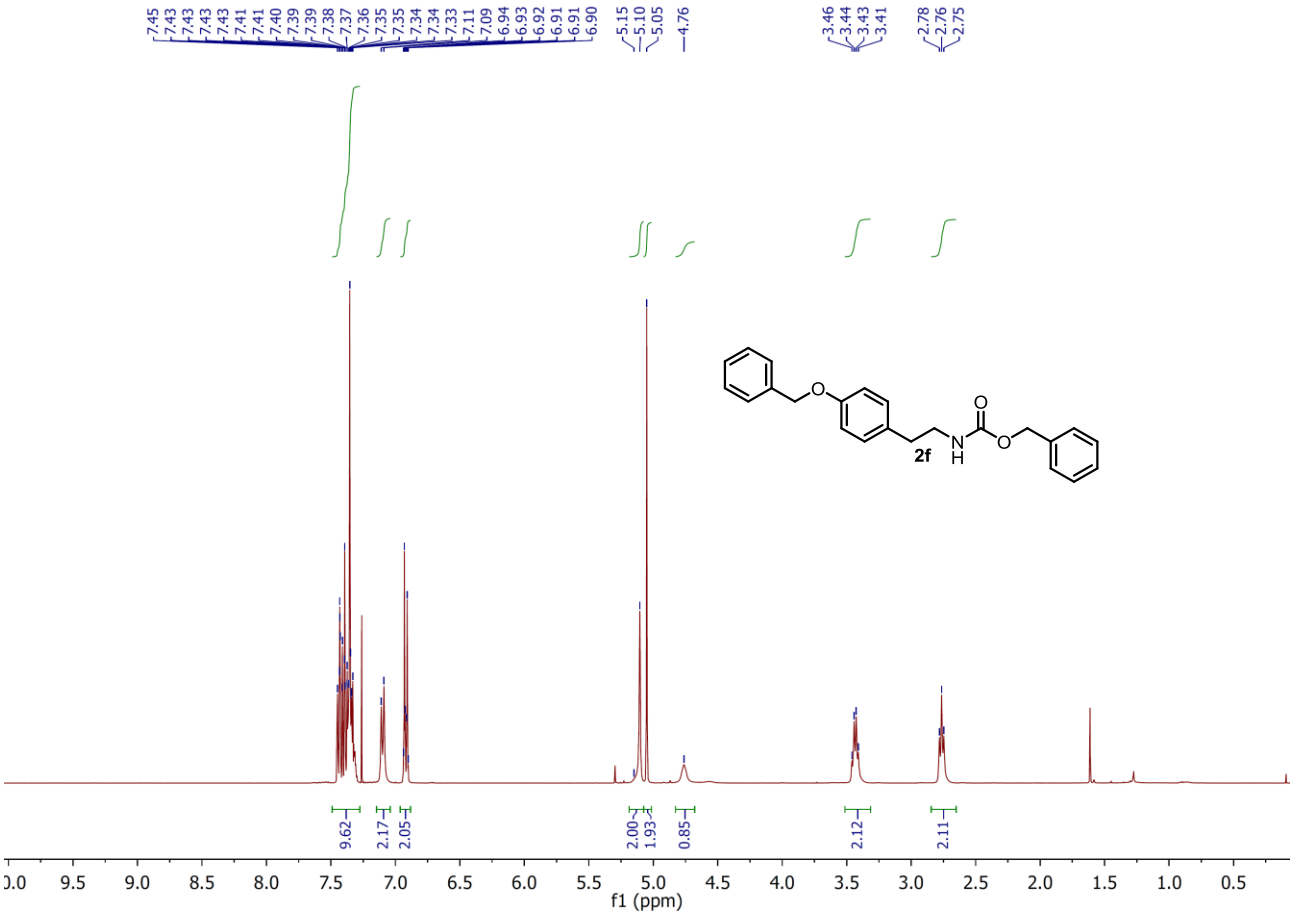
1.5
1.0
0.5
f1 (ppm)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7.35
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6.91
6.91
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3.46
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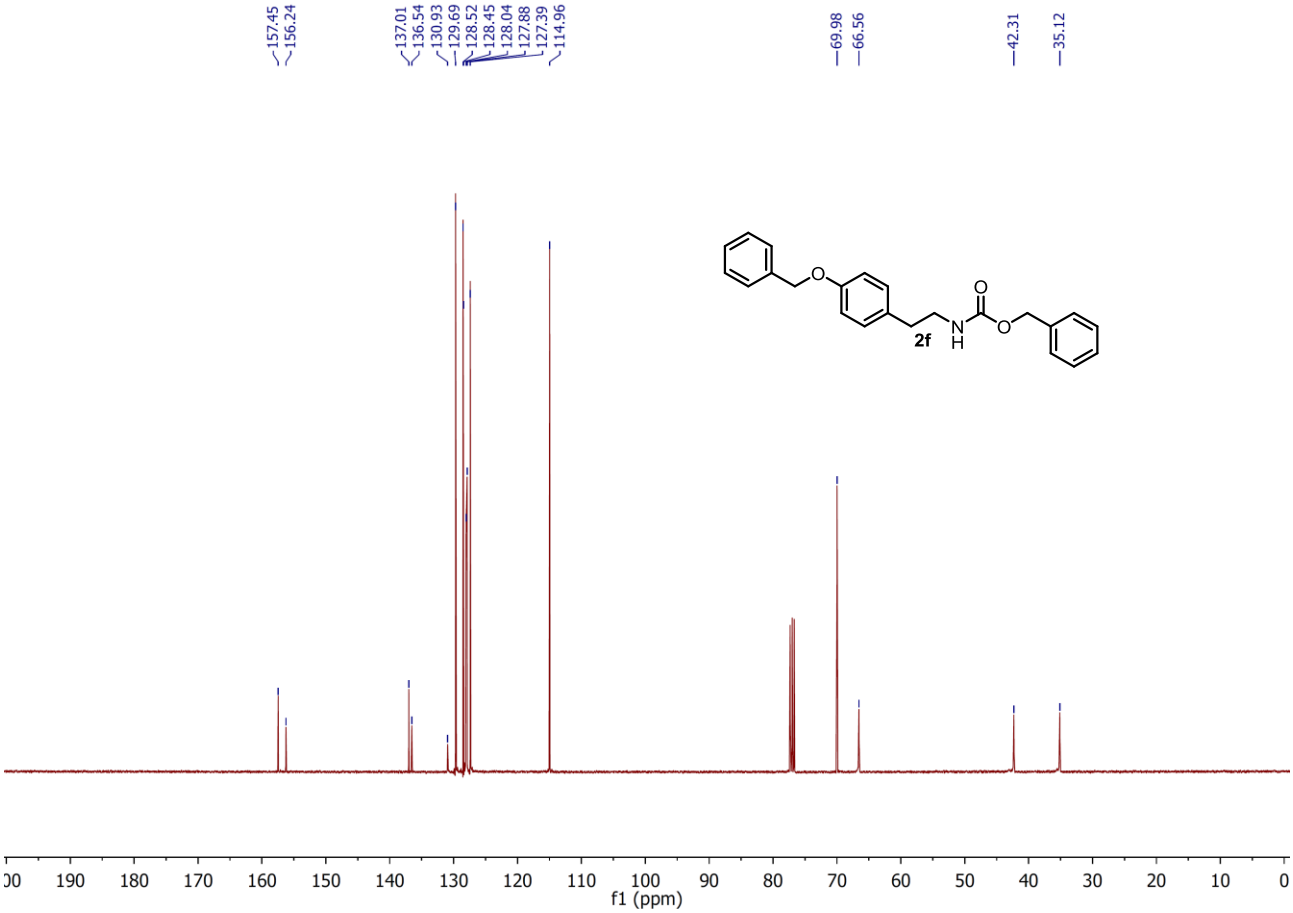
f1 (ppm)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42.31
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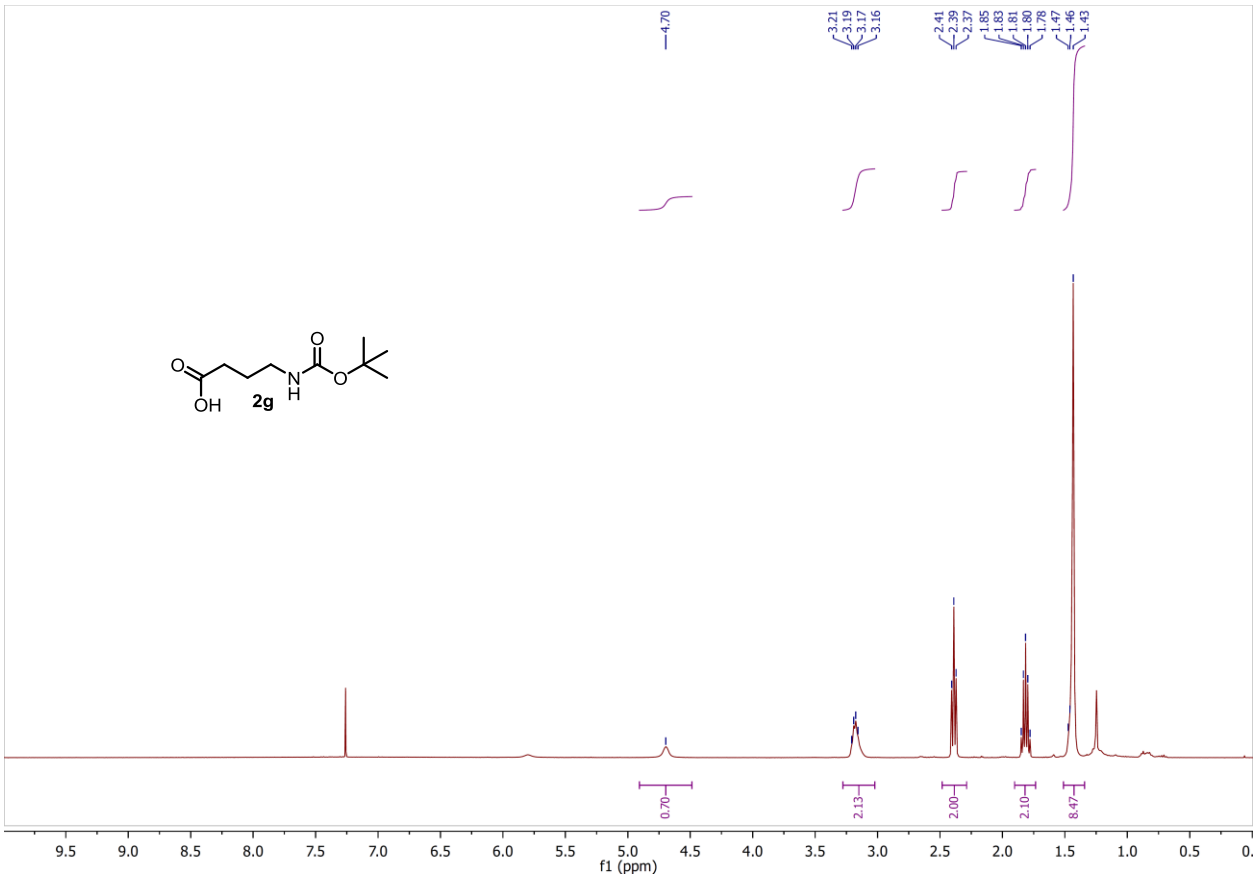
2f
f1 (ppm)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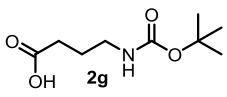
f1 (ppm)


2g

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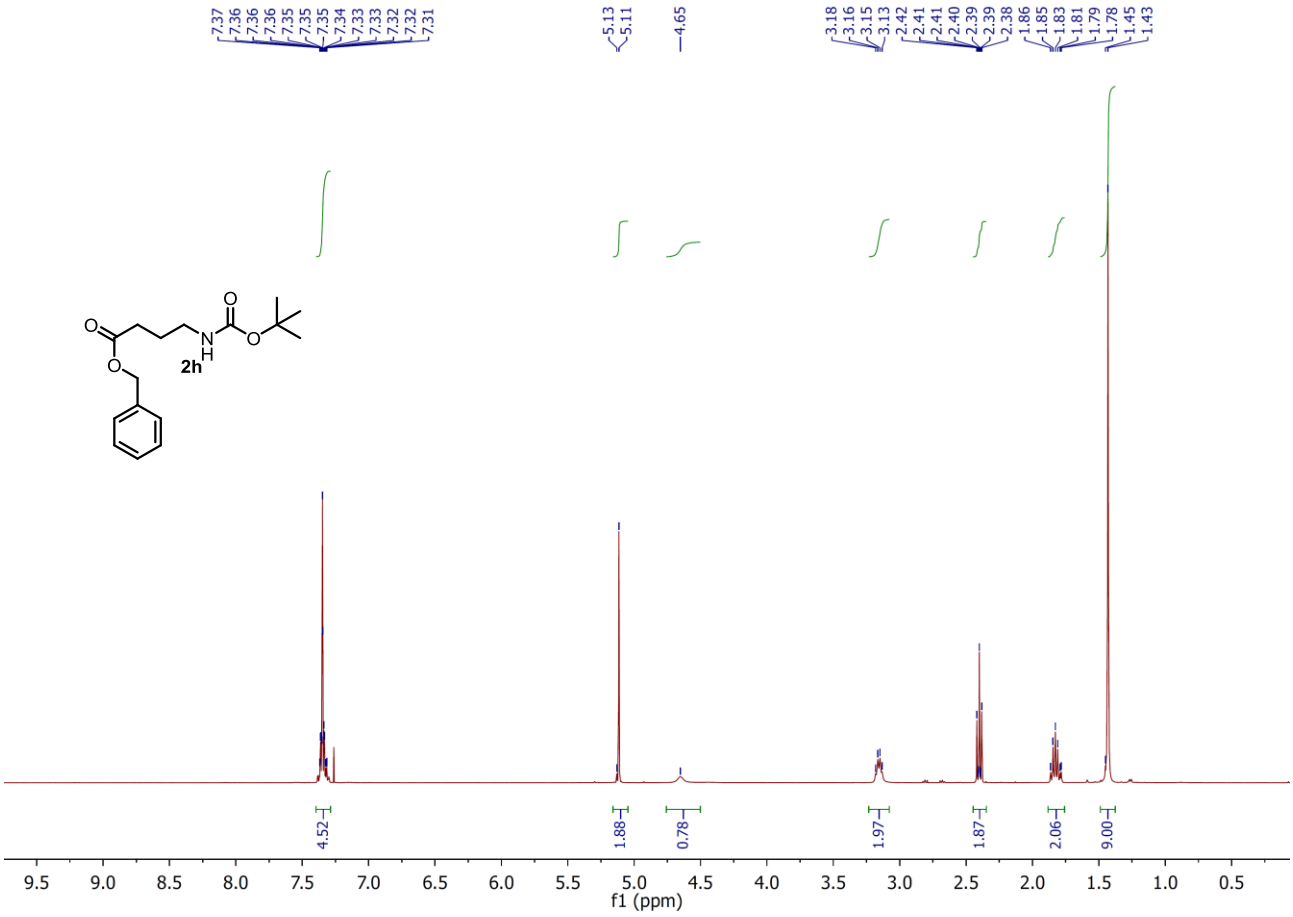
28.35
25.19
f1 (ppm)

2g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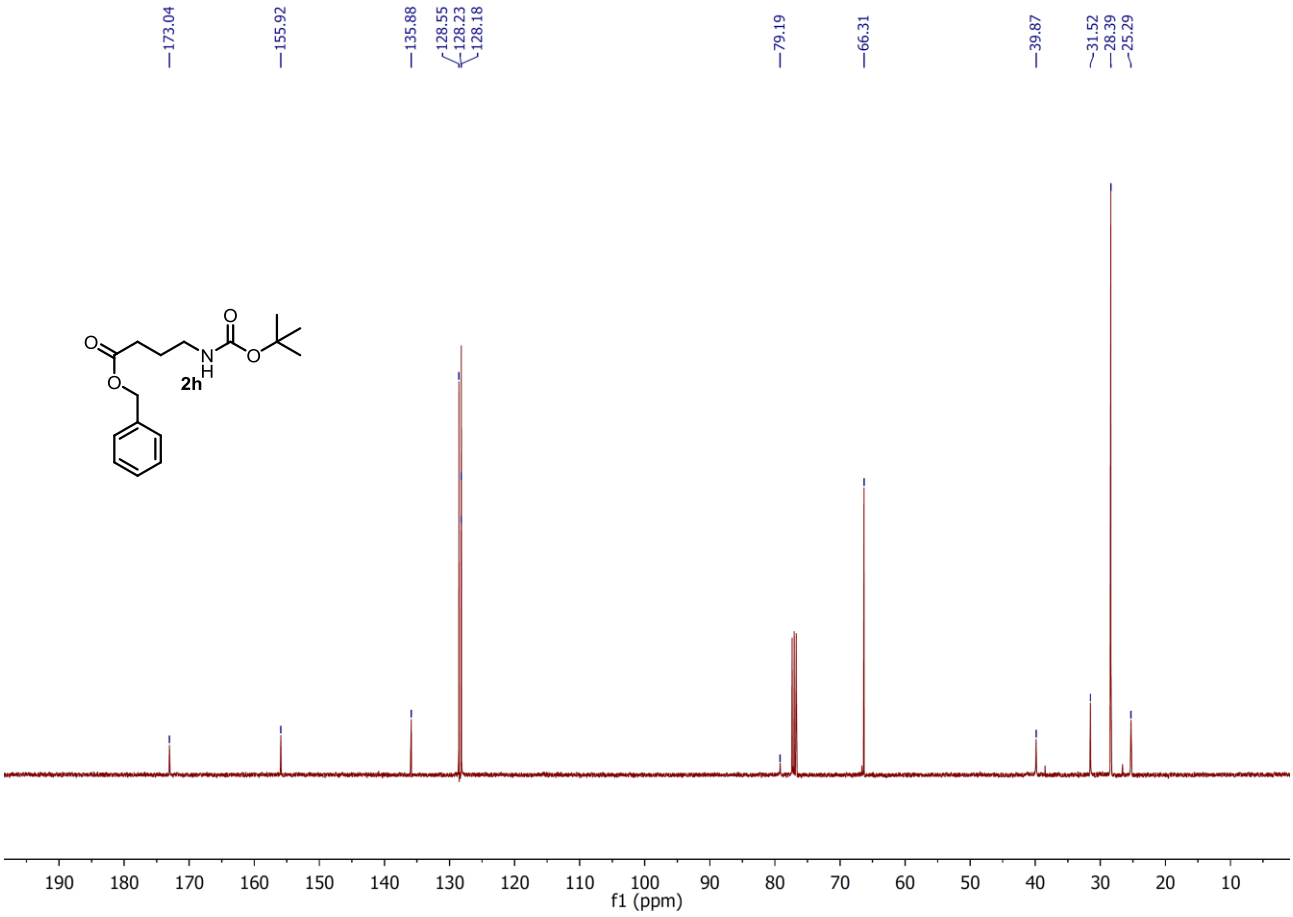
1.83
1.81
1.79
1.78
1.45
1.43
O
O
N
H
O
O
2h
4.52
1.88
0.78
1.97
1.87
2.06
9.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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31.52
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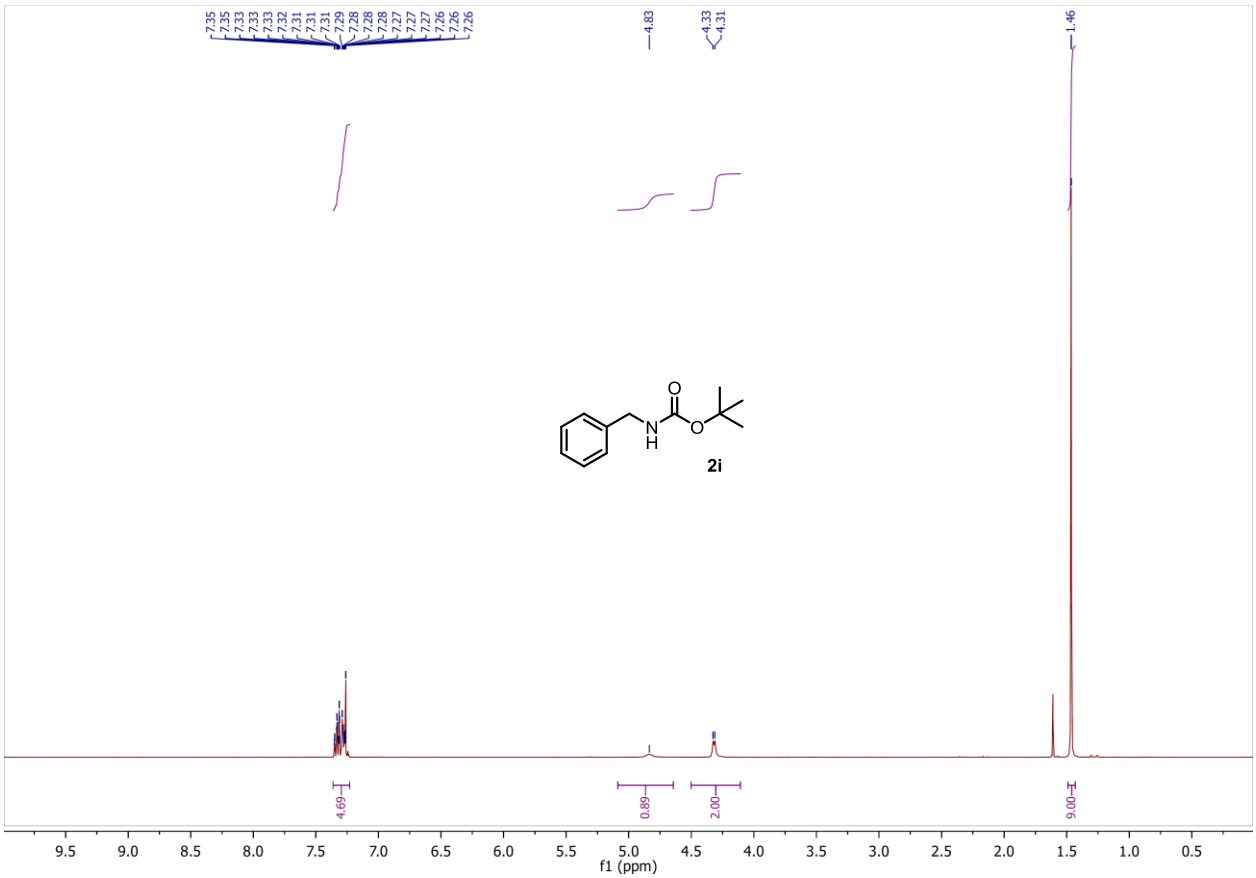
f1 (ppm)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7.27
7.27
7.27
7.26
7.26
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4.33
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0.89
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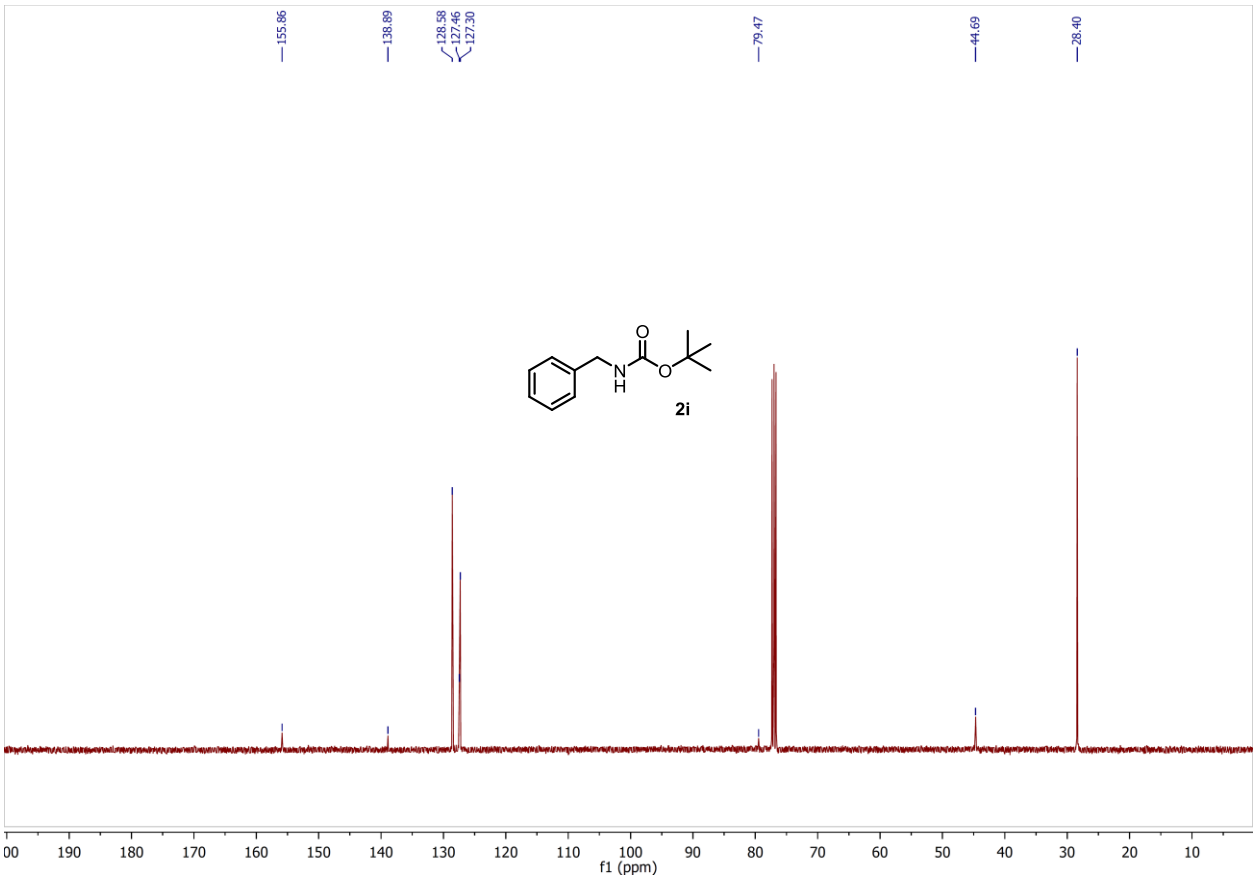
9.00
f1 (ppm)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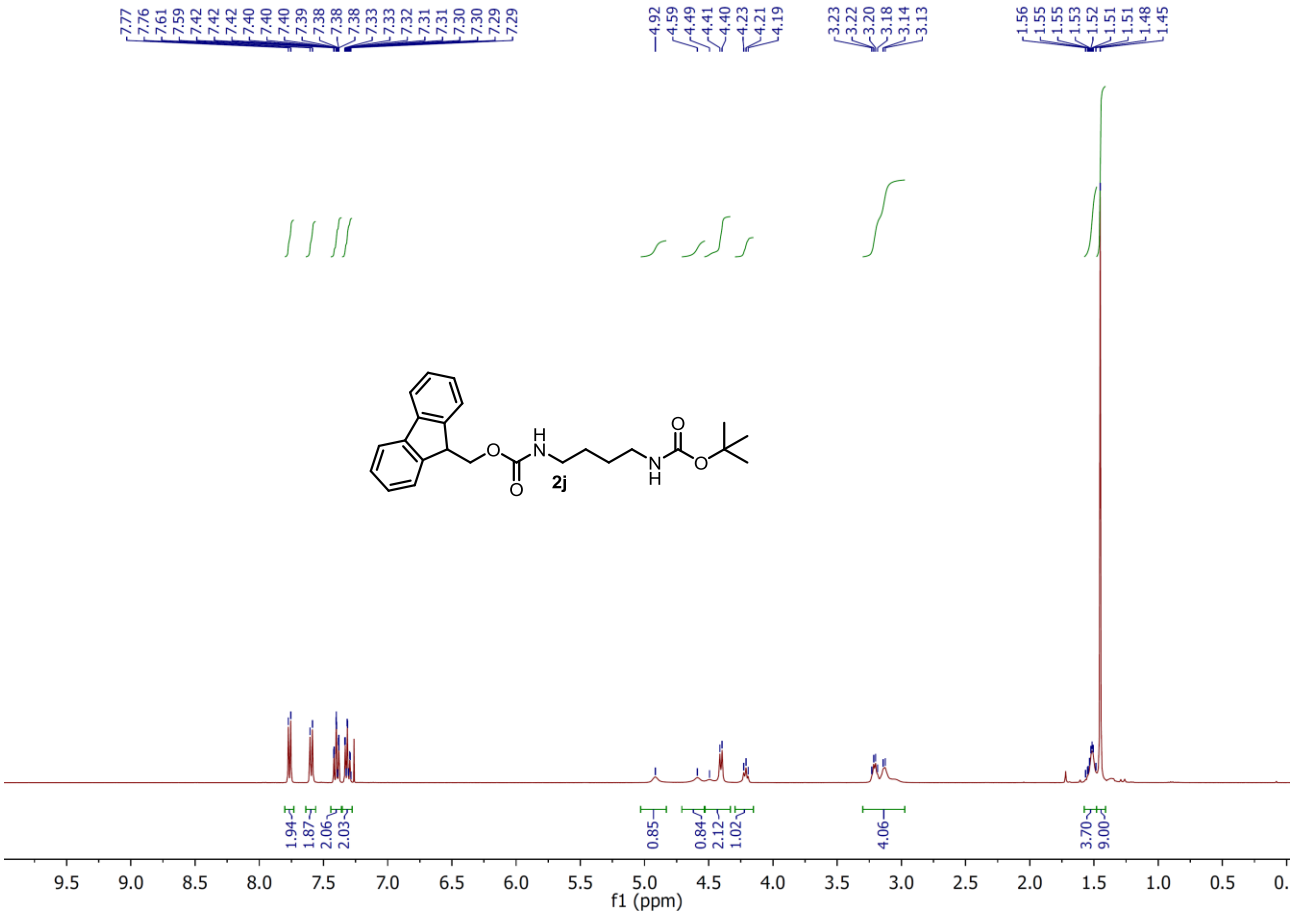
2i
f1 (ppm)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7.38
7.33
7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.29
4.92
4.59
4.49
4.41
4.40
4.23
4.21
4.19
3.23
3.22
3.20
3.18
3.14
3.13
1.56
1.55
1.55
1.53
1.52
1.51
1.51
1.48
1.45
2j
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1.87
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2.03
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0.84
2.12
1.02
4.06
3.70
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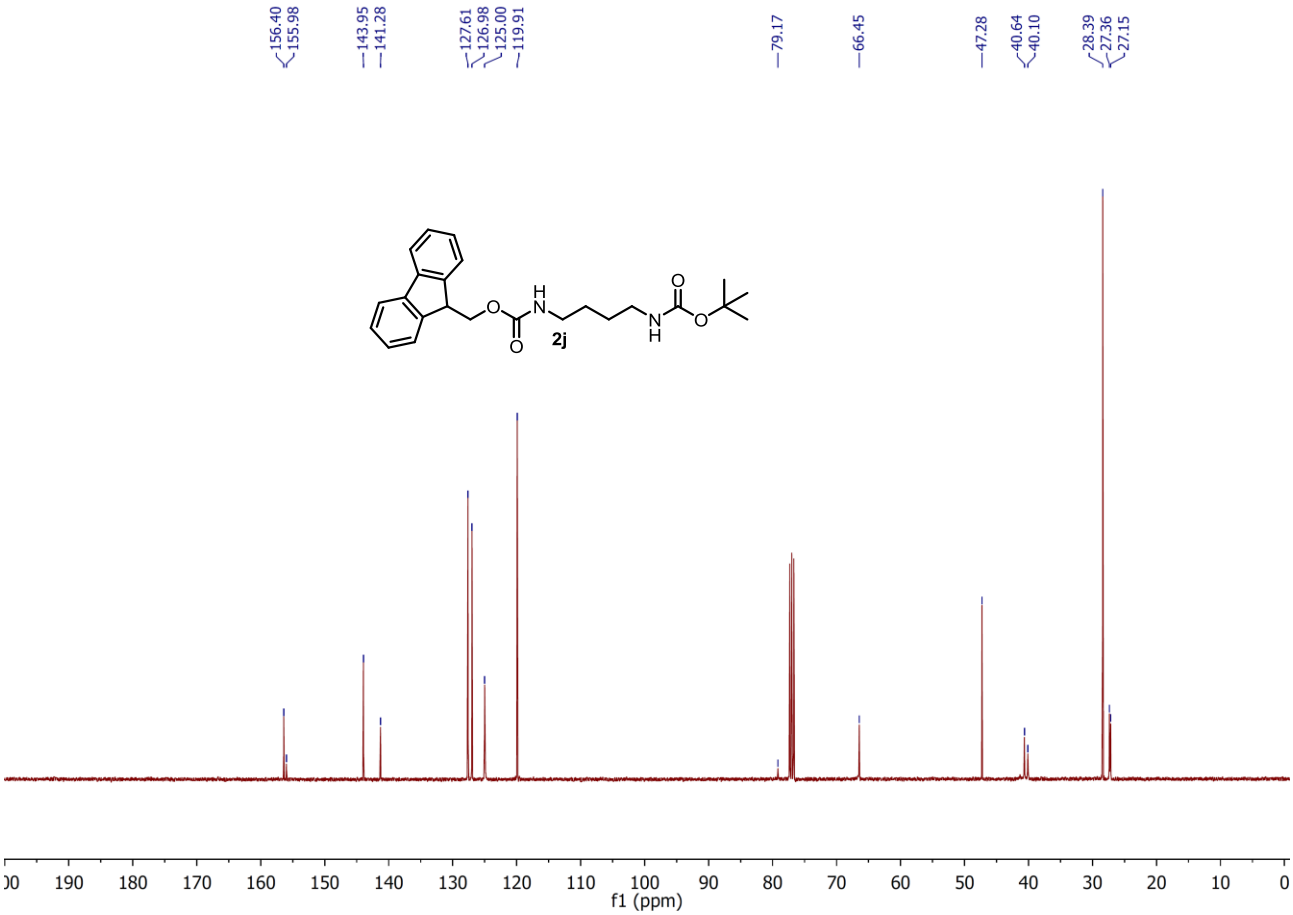
f1 (ppm)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126.98
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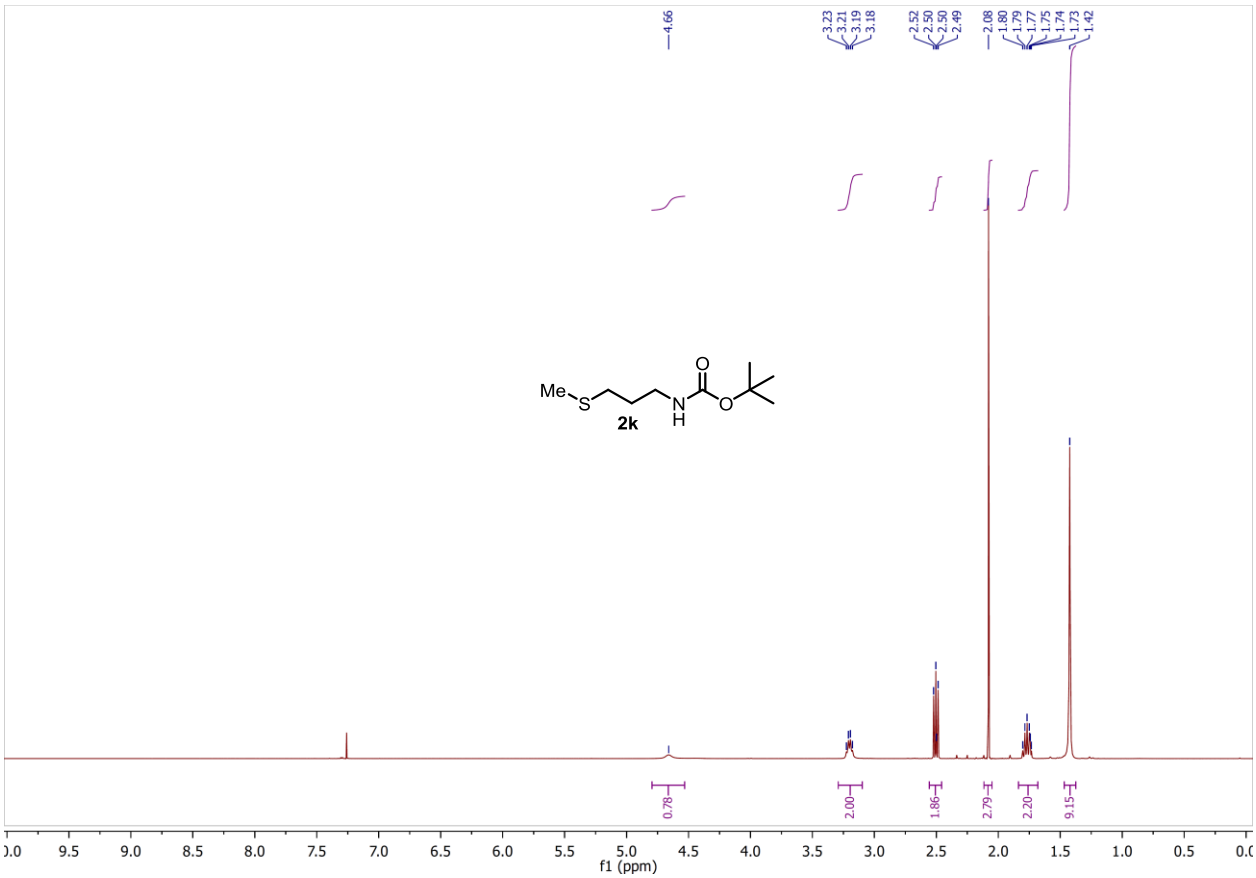
119.91
79.17
66.45
47.28
40.64
40.10
28.39
27.36
27.15
2j
f1 (ppm)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1.80
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1.77
1.75
1.74
1.73
1.42
Me
S
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H
O
O
2k
0.78
2.00
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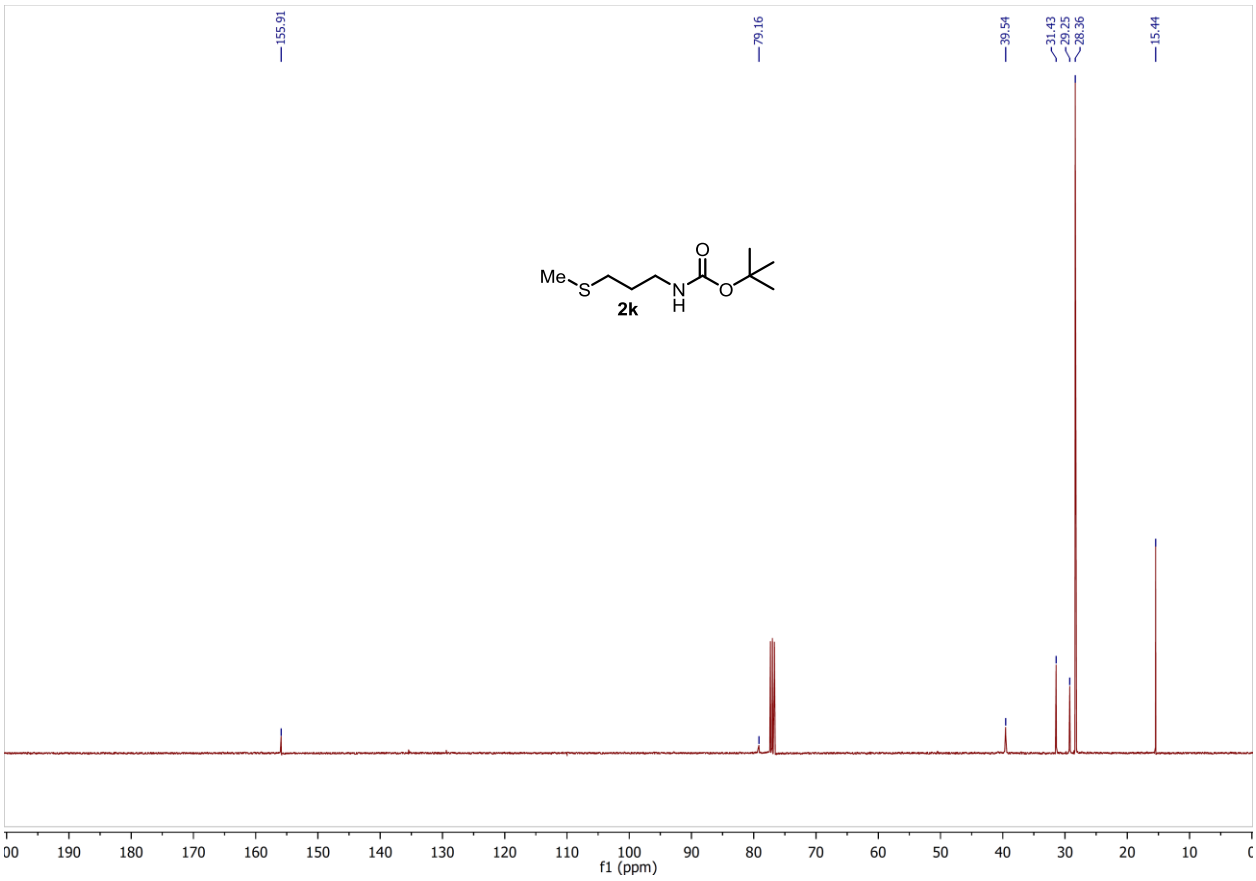
2.79
2.20
9.15
f1 (ppm)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S
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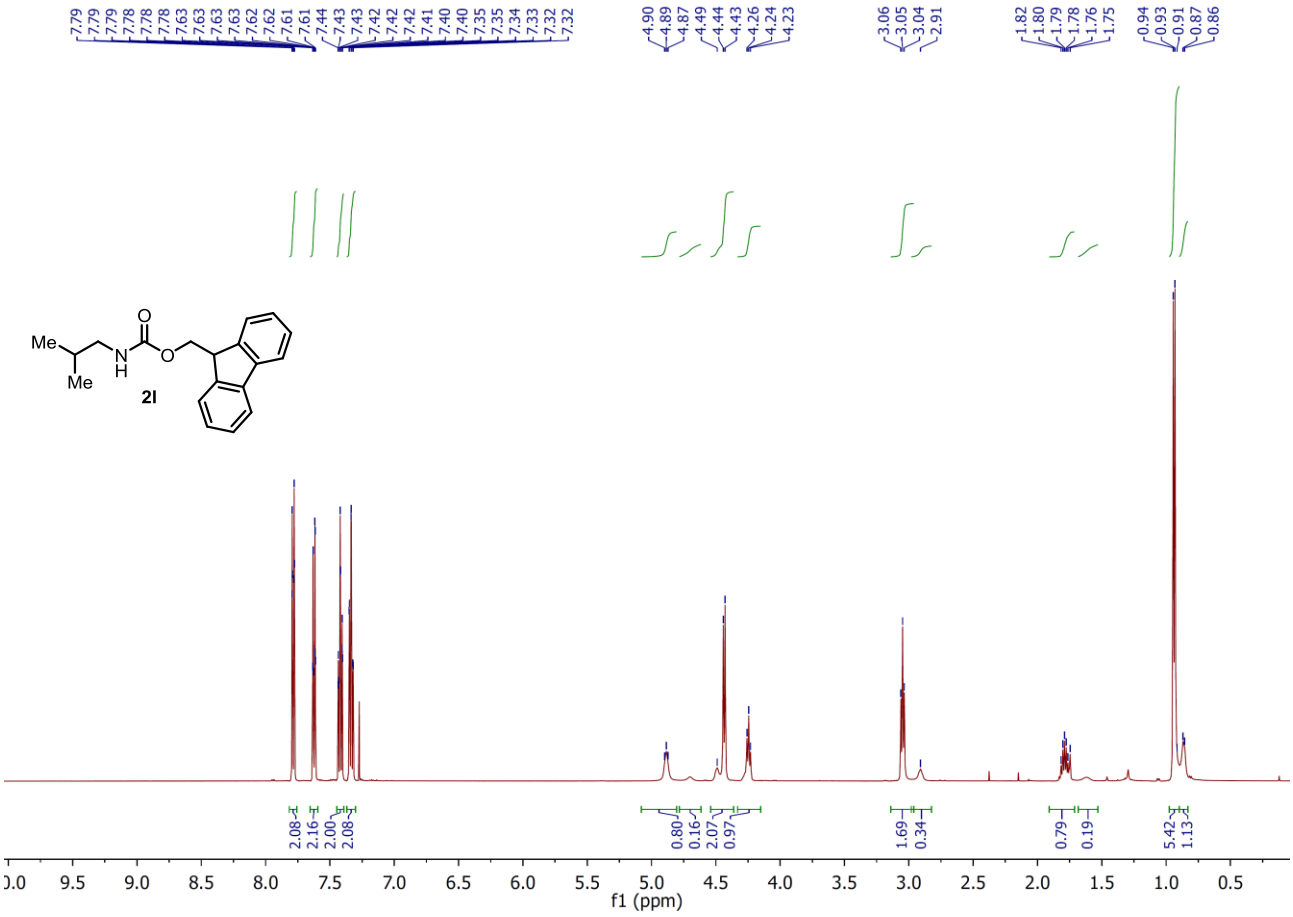
H
O
O
2k
f1 (ppm)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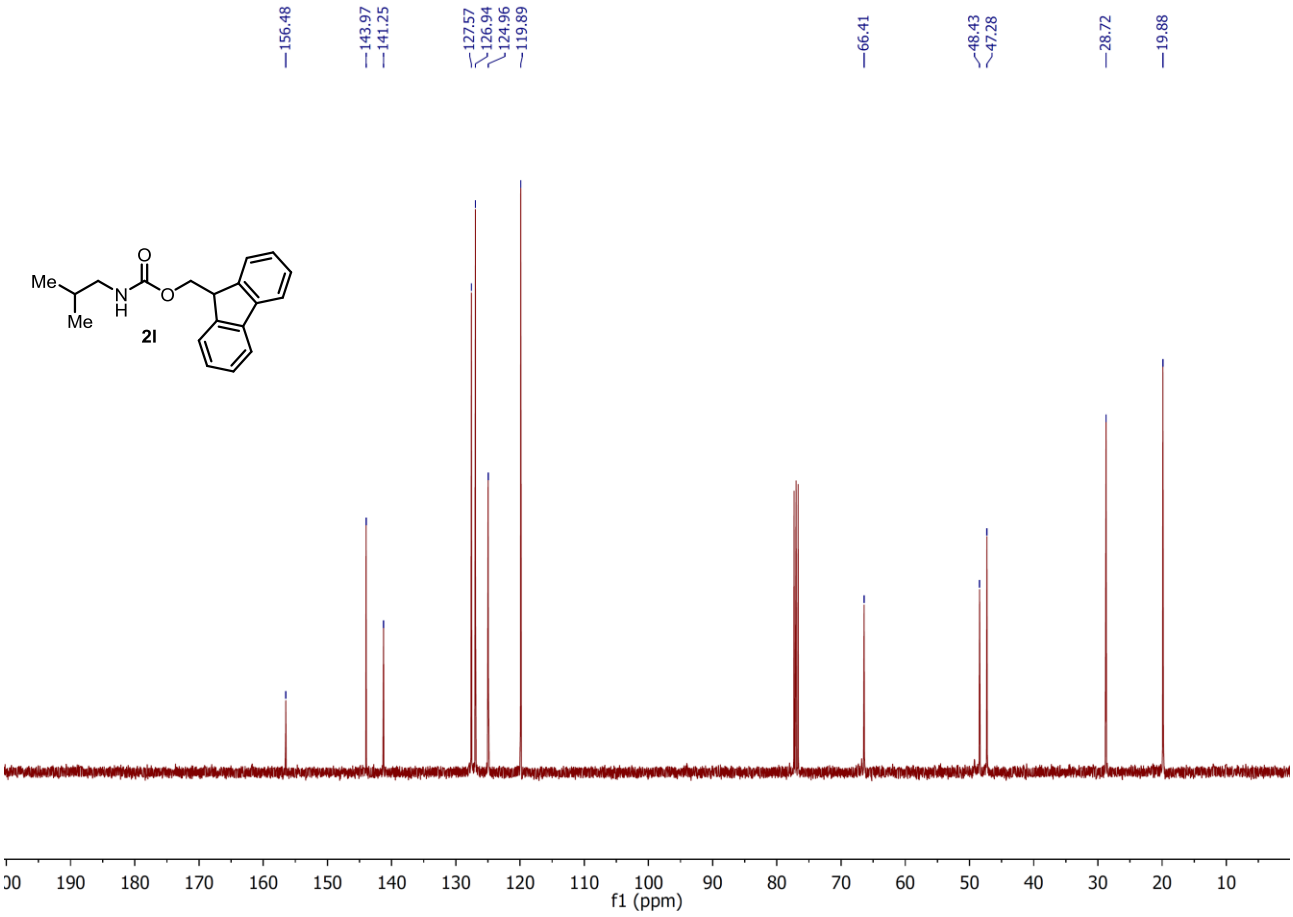
4.90 4.89 4.87 4.49 4.44 4.43 4.26 4.24 4.23
3.06 3.05 3.04 2.91
1.82 1.80 1.79 1.78 1.76 1.75
0.94 0.93 0.91 0.87 0.86
Me
Me
N
H
O
O
2l
2.08 2.16 2.00 2.08 0.80 0.16 2.07 0.97 1.69 0.34 0.79 0.19 5.42 1.13
f1 (ppm)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47.28
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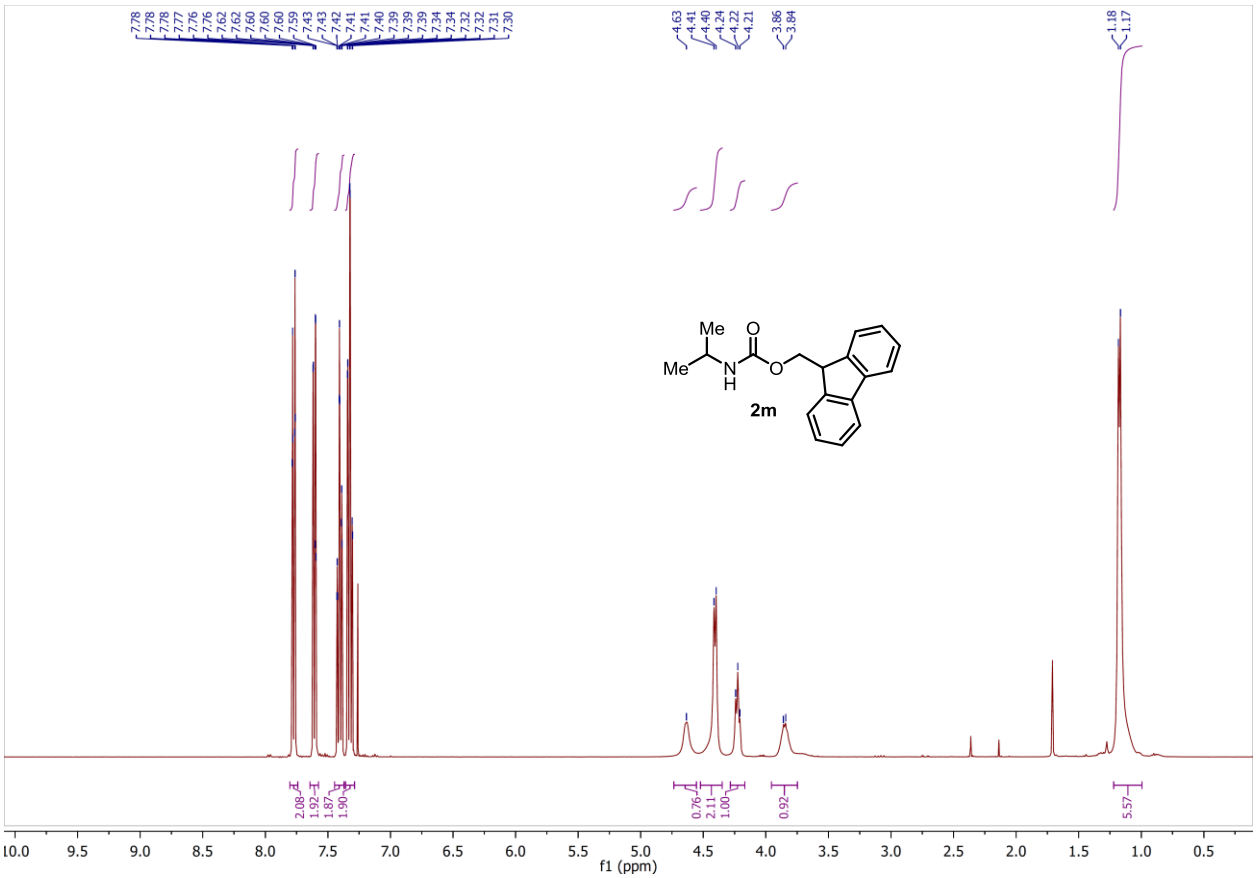
19.88
Me
Me
N
H
O
O
2l
f1 (ppm)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7.41
7.40
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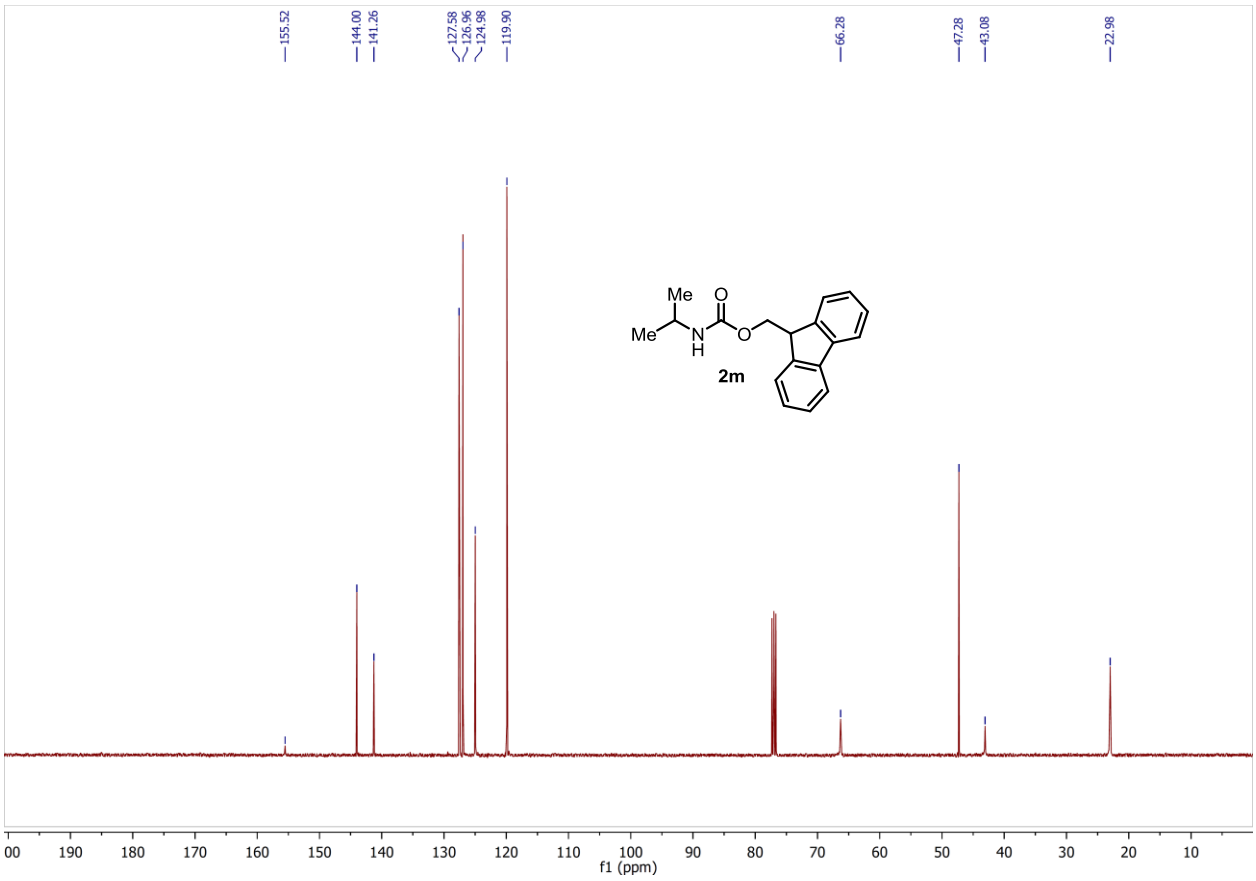
7.39
7.34
7.34
7.32
7.32
7.31
7.30
4.63
4.41
4.40
4.24
4.22
4.21
3.86
3.84
1.18
1.17
Me
O
Me
N
H
O
2m
2.08
1.92
1.87
1.90
0.76
2.11
1.00
0.92
5.57
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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144.00
141.26
127.58
126.96
124.98
119.90
66.28
47.28
43.08
22.98
Me
O
Me
N
H
O
2m
00
190
180
170
160
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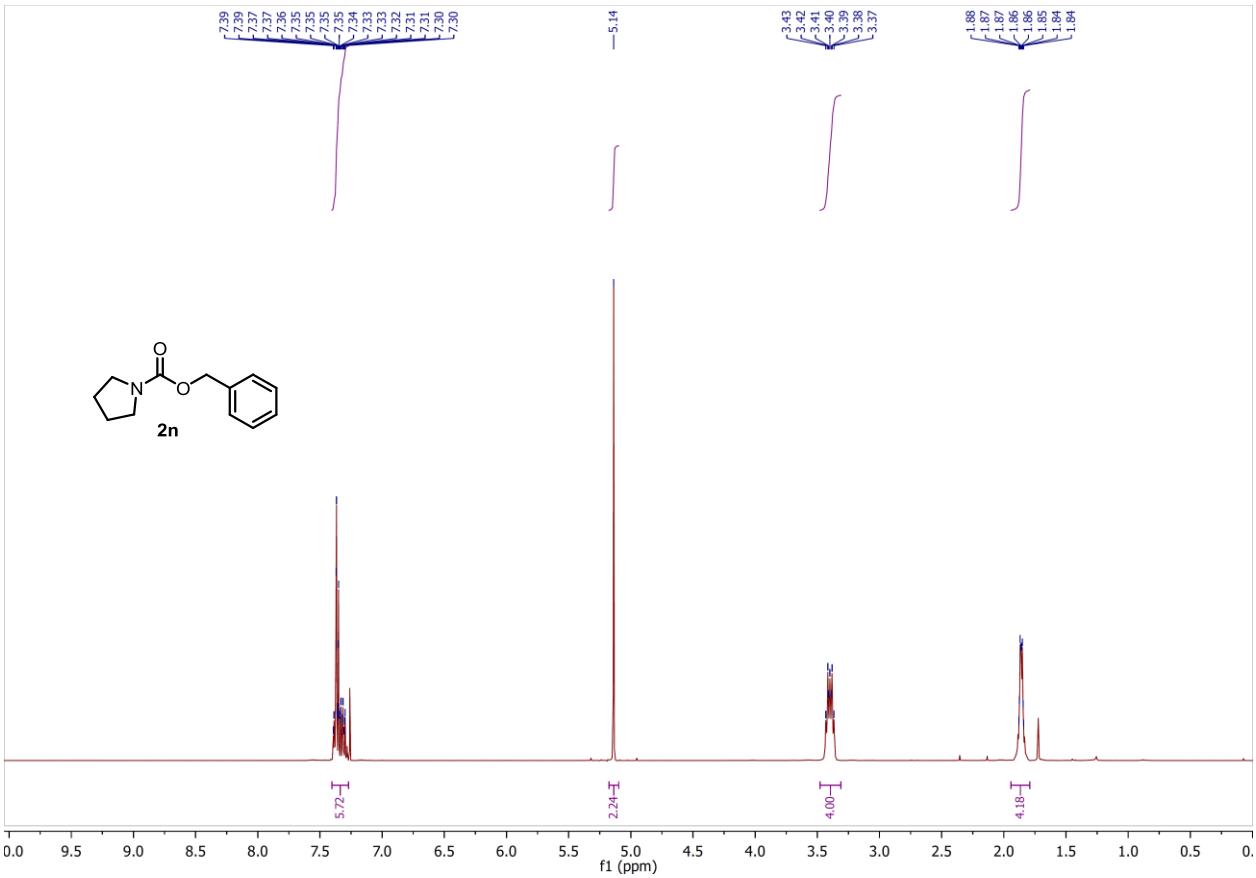
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.32
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7.31
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3.42
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3.40
3.39
3.38
3.37
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1.87
1.87
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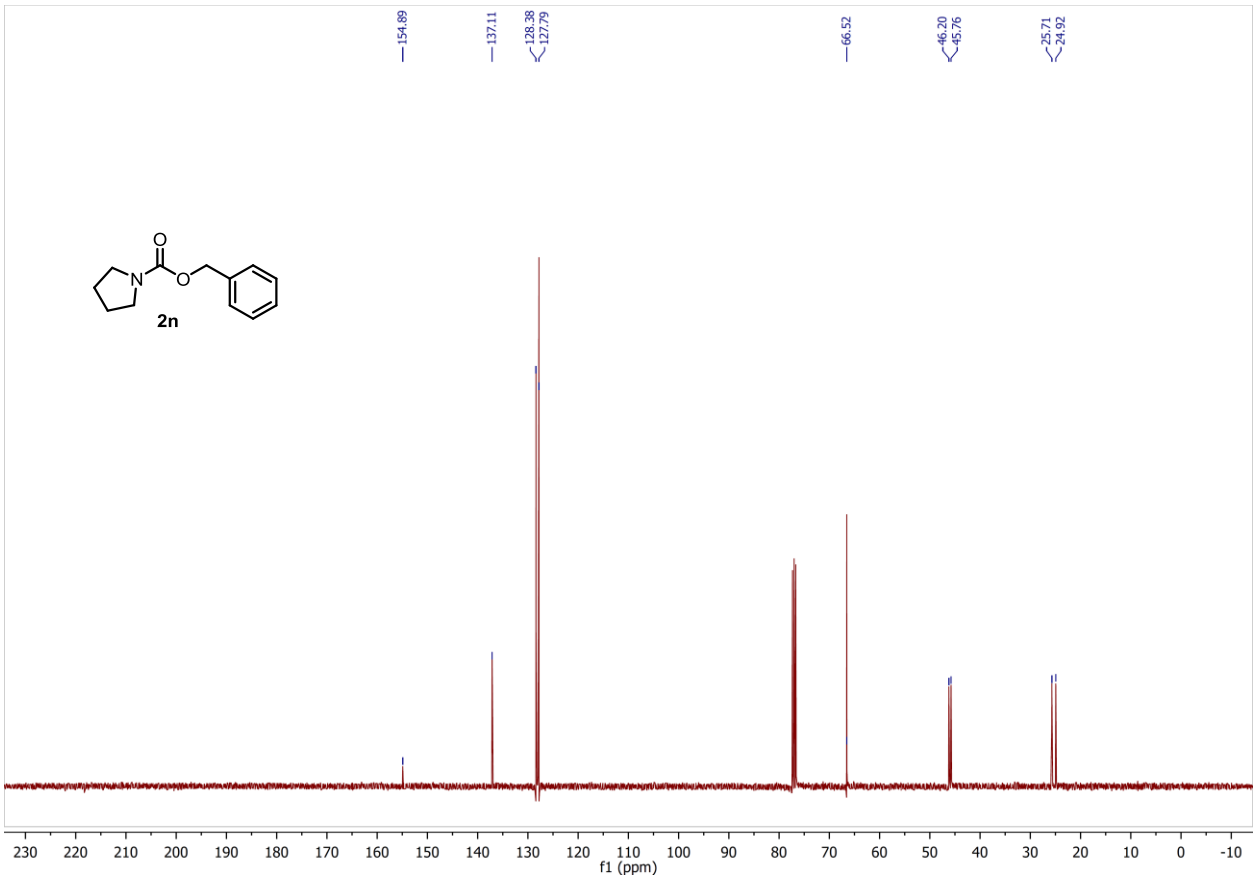
1.85
1.84
1.84
5.72
2.24
4.00
4.18
f1 (ppm)
2n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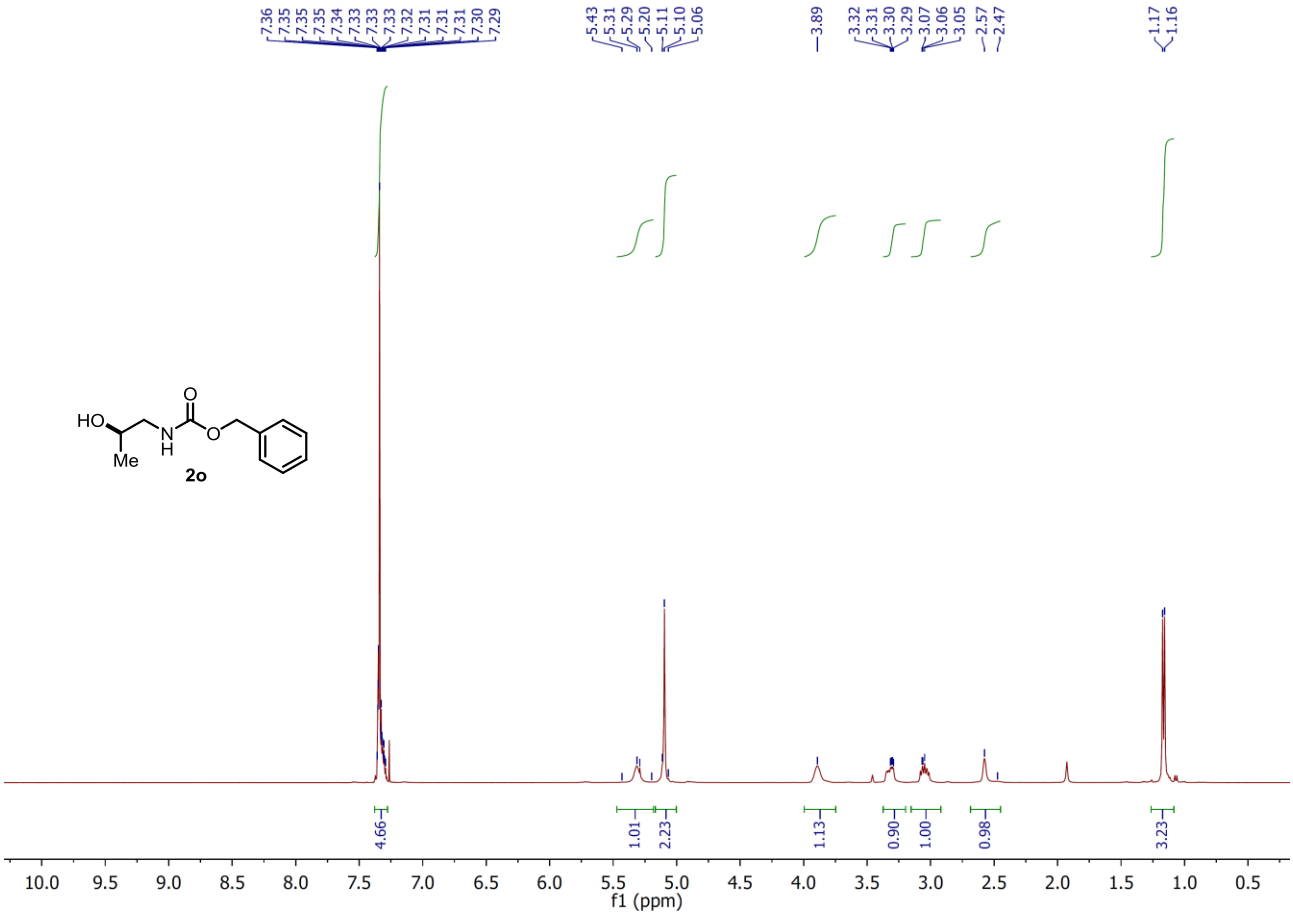
66.52
46.20
45.76
25.71
24.92
f1 (ppm)
2n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7.33
7.32
7.31
7.31
7.31
7.30
7.29
5.43
5.31
5.29
5.20
5.11
5.10
5.06
3.89
3.32
3.31
3.30
3.29
3.07
3.06
3.05
2.57
2.47
1.17
1.16
HO
N
H
O
O
Me
2o
4.66
1.01
2.23
1.13
0.90
1.00
0.98
3.23
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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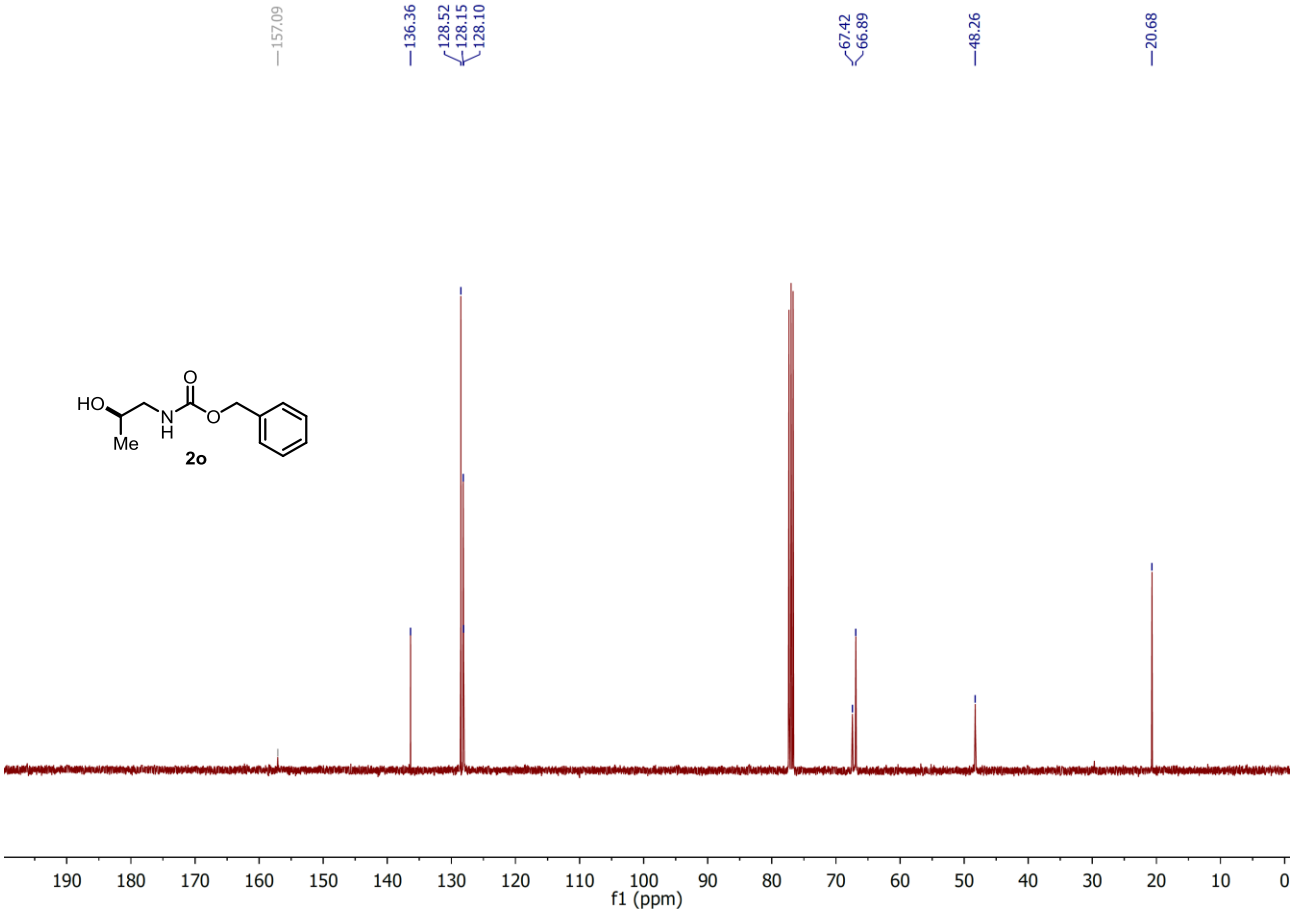
f1 (ppm)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20.68
HO
N
H
O
O
Me
2o
190
180
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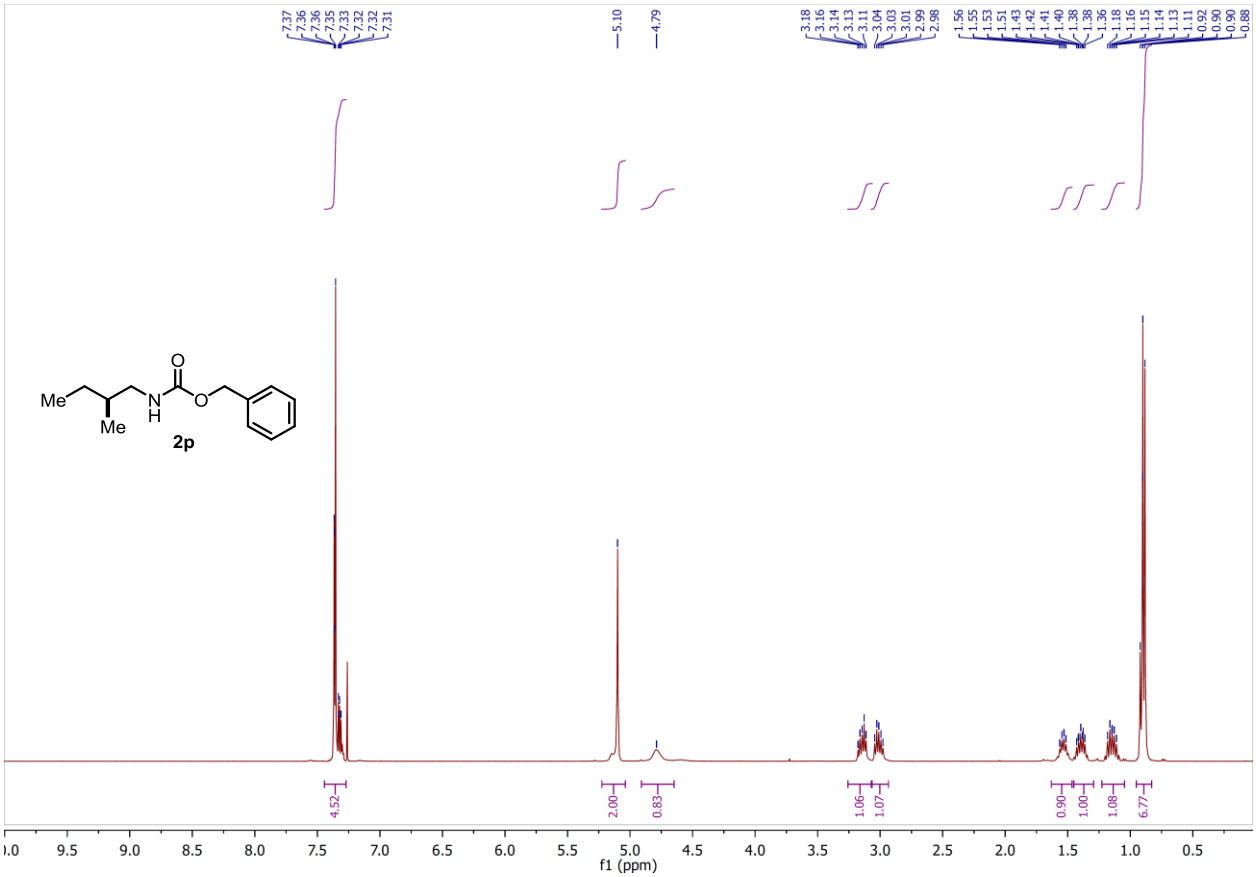
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.31
5.10
4.79
3.18
3.16
3.14
3.13
3.11
3.04
3.03
3.01
2.99
2.98
1.56
1.55
1.53
1.51
1.43
1.42
1.41
1.40
1.38
1.38
1.36
1.18
1.16
1.15
1.14
1.13
1.11
0.92
0.90
0.90
0.88
Me
Me
N
H
O
O
2p
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2.00
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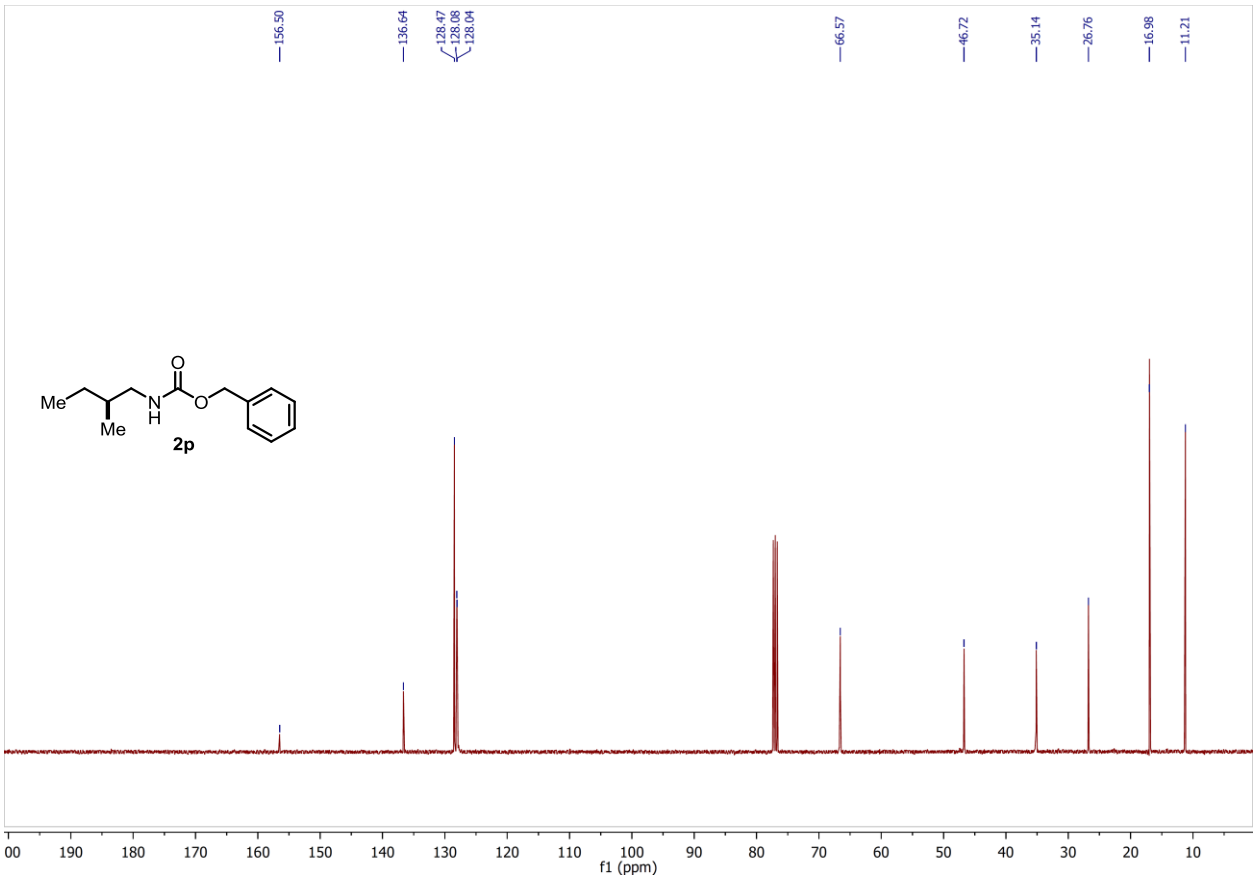
1.06
1.07
0.90
1.00
1.08
6.77
f1 (ppm)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128.04
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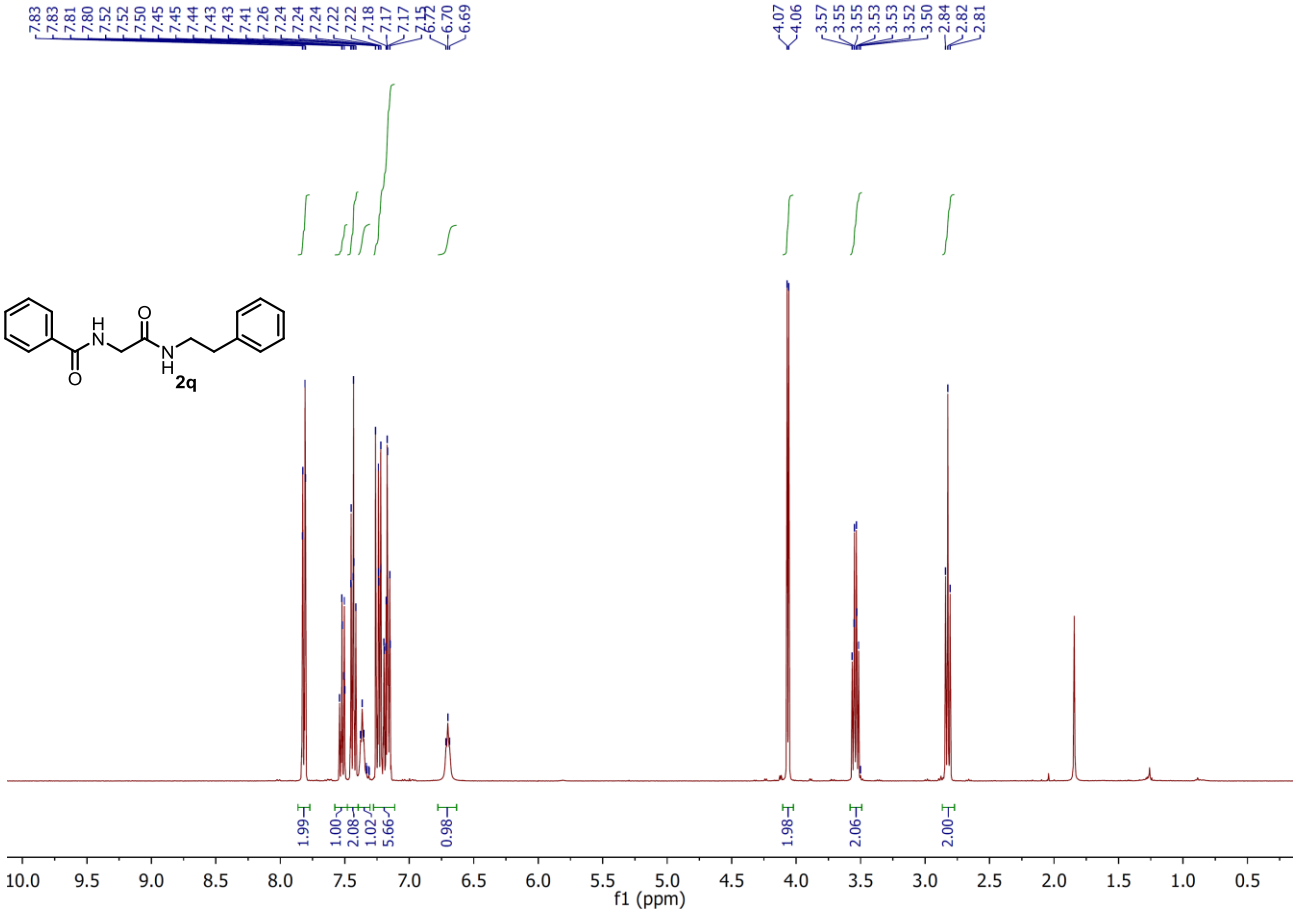
35.14
26.76
16.98
11.21
Me
Me
N
H
O
O
2p
f1 (ppm)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7.50
7.45
7.45
7.44
7.43
7.43
7.41
7.26
7.24
7.24
7.24
7.22
7.22
7.18
7.17
7.17
6.72
6.70
6.69
4.07
4.06
3.57
3.55
3.55
3.53
3.53
3.52
3.50
2.84
2.82
2.81
2q
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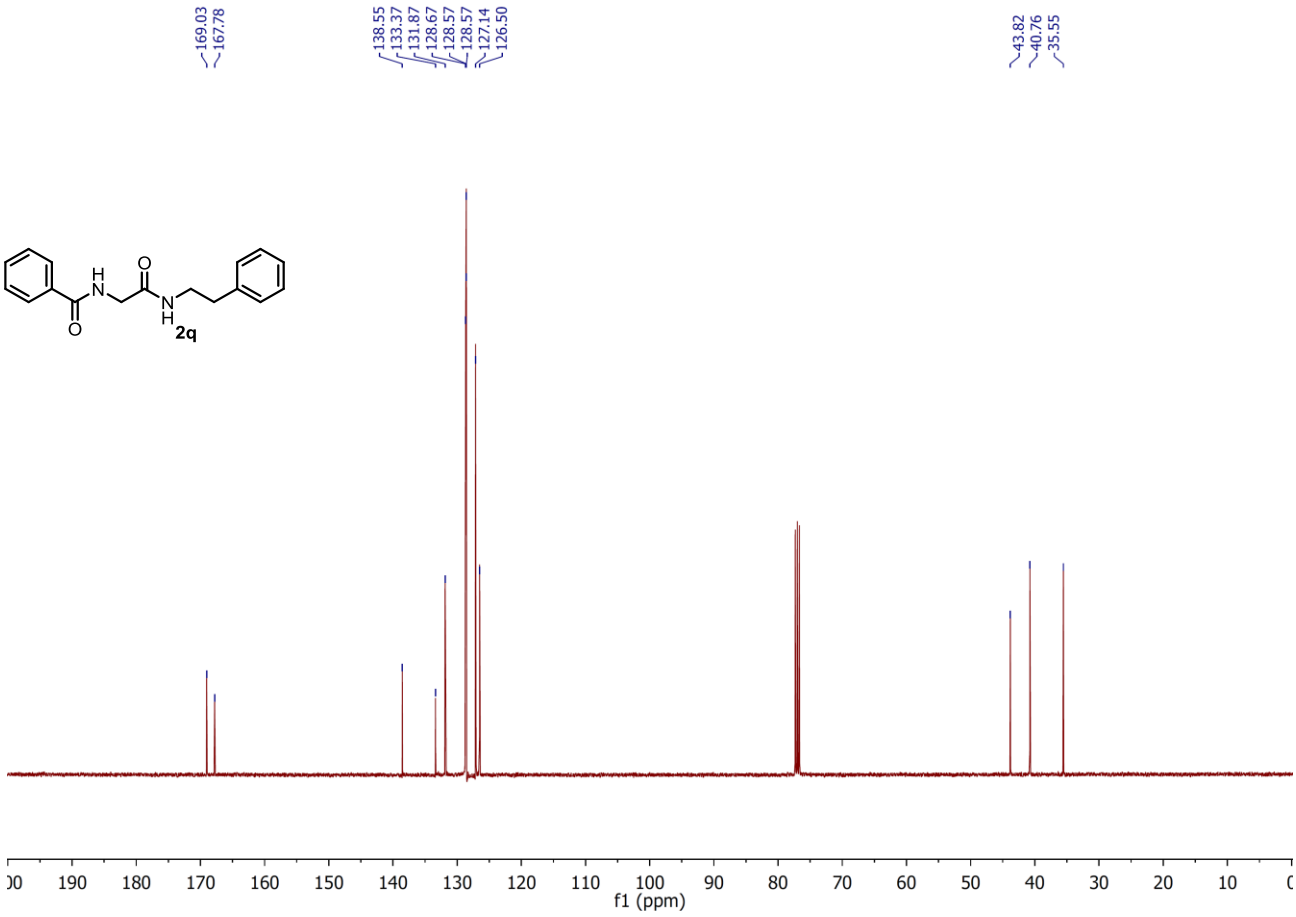
1.00
2.08
1.02
5.66
0.98
1.98
2.06
2.00
f1 (ppm)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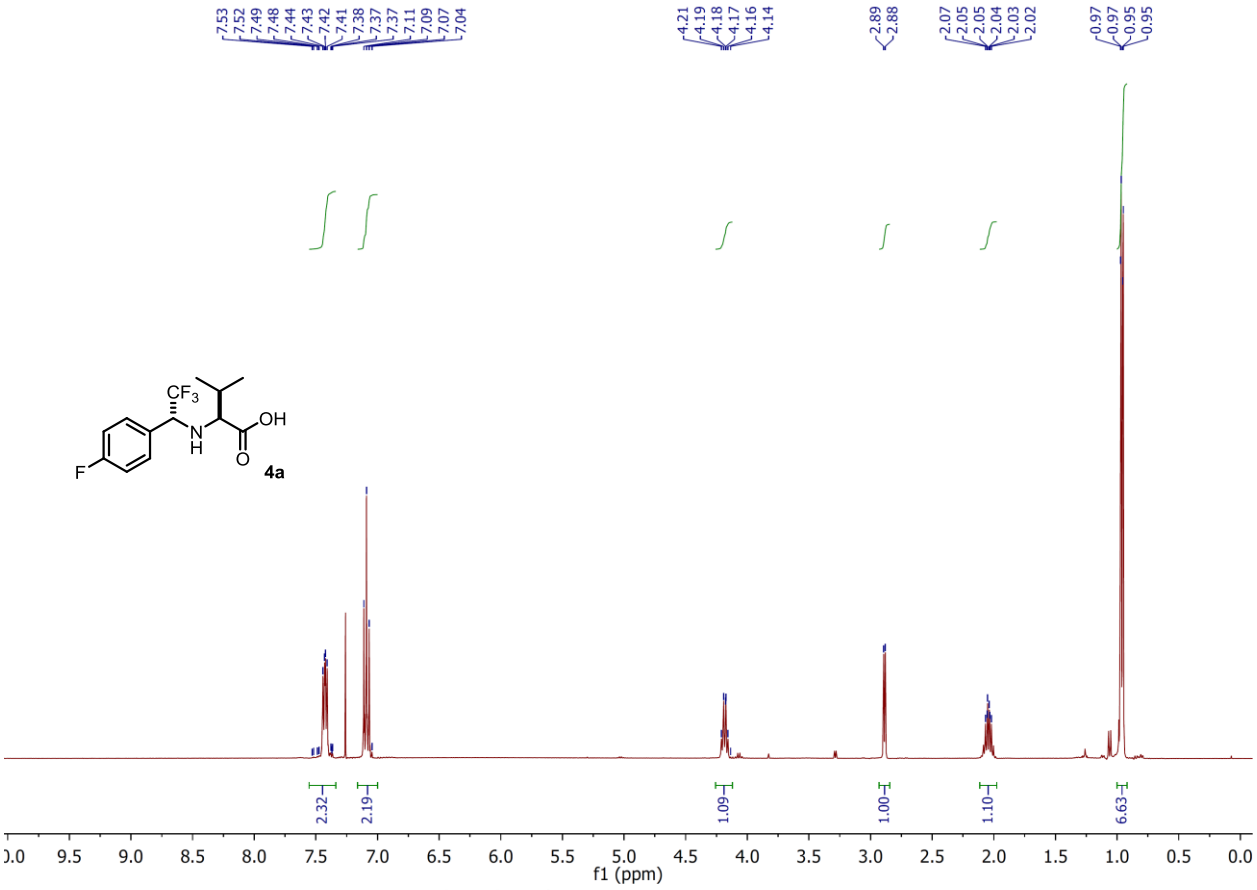
128.57
128.57
127.14
126.50
43.82
40.76
35.55
2q
f1 (ppm)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7.37
7.37
7.11
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7.07
7.04
4.21
4.19
4.18
4.17
4.16
4.14
2.89
2.88
2.07
2.05
2.05
2.04
2.03
2.02
0.97
0.97
0.95
0.95
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H
O
F
4a
2.32
2.19
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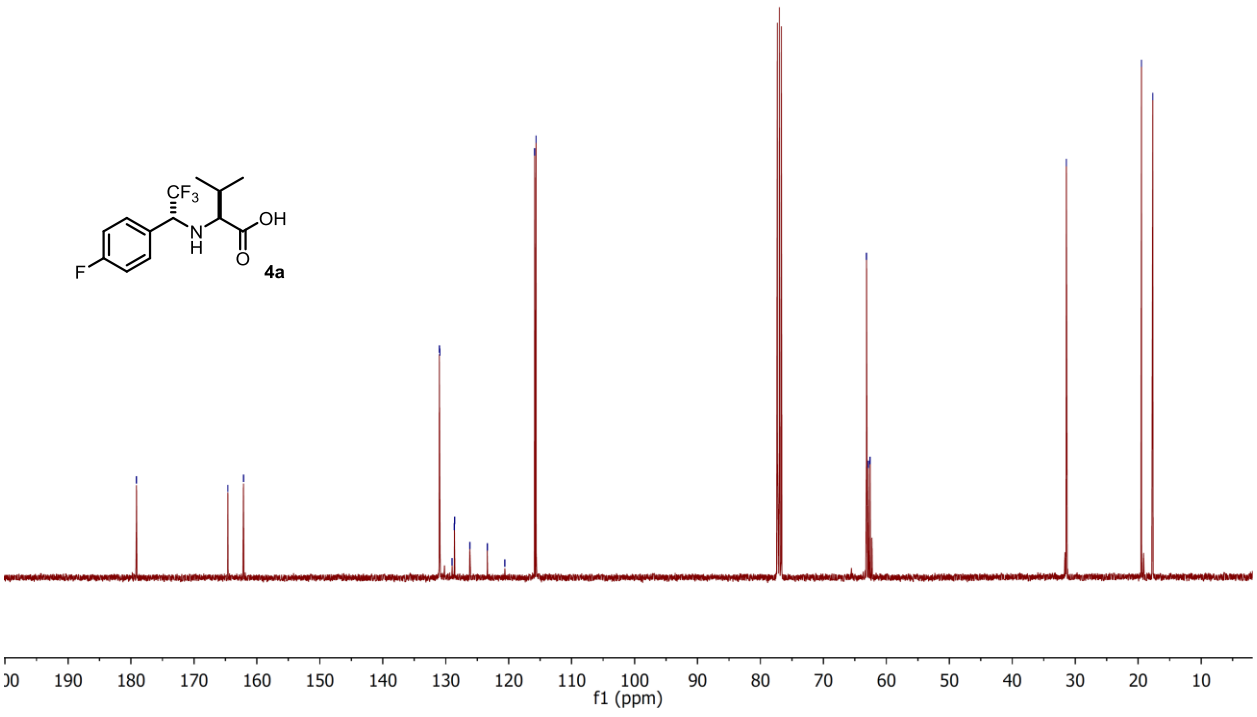
1.00
1.10
6.63
f1 (ppm)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115.65
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31.40
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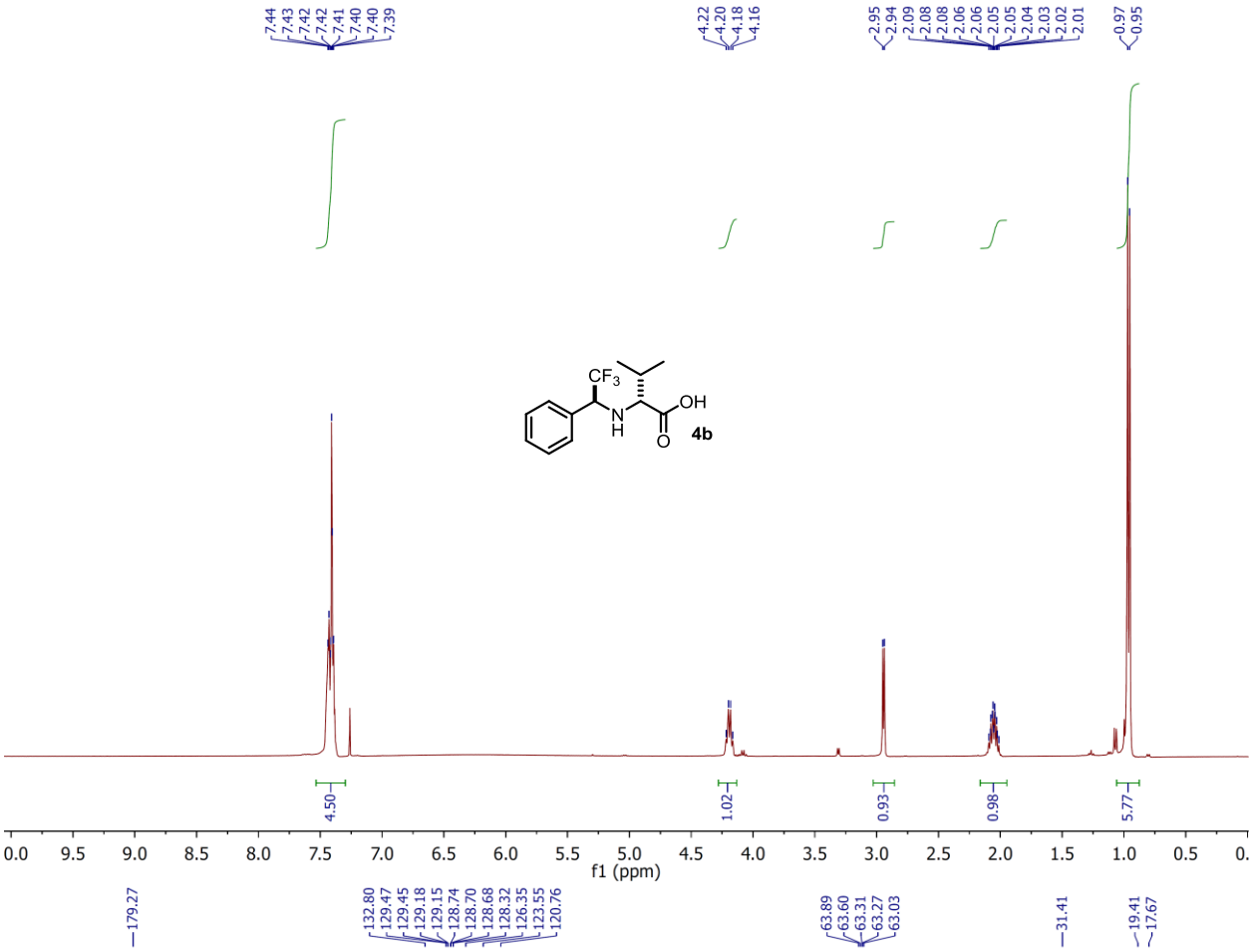
CF3
OH
N
H
O
F
4a
f1 (ppm)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4.22
4.20
4.18
4.16
2.95
2.94
2.09
2.08
2.08
2.06
2.06
2.05
2.05
2.04
2.03
2.02
2.01
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H
OH
O
4b
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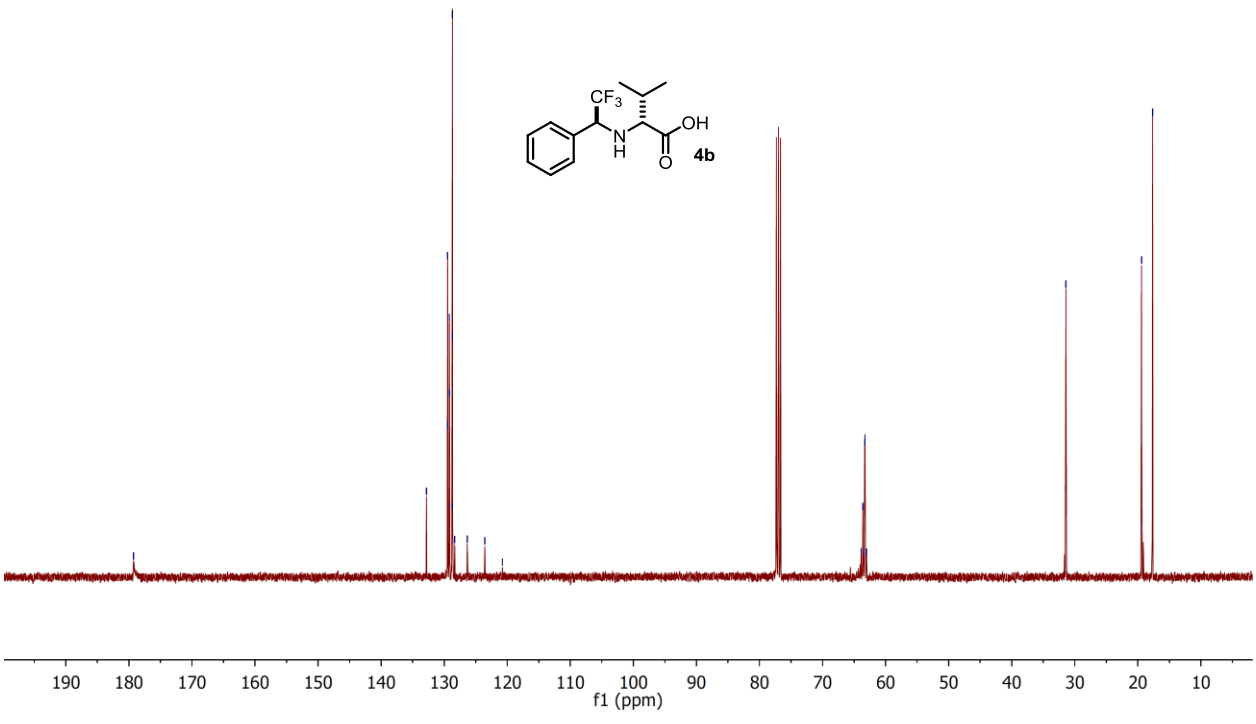
5.77
f1 (ppm)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123.55
120.76
63.89
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63.31
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63.03
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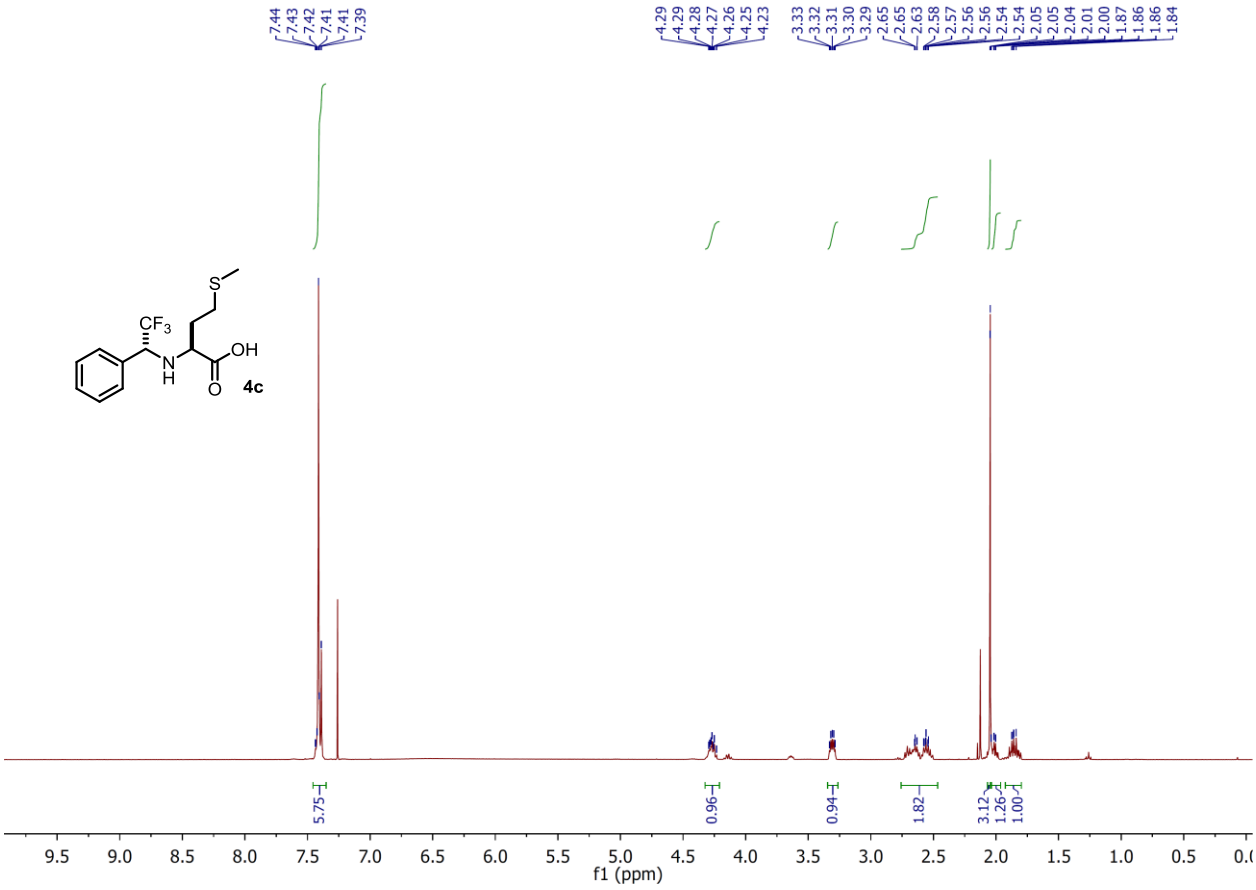
19.41
17.67
CF3
N
H
OH
O
4b
f1 (ppm)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4.23
3.33
3.32
3.31
3.30
3.29
2.65
2.65
2.63
2.58
2.57
2.56
2.56
2.54
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2.01
2.00
1.87
1.86
1.86
1.84
S
CF3
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H
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O
4c
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0.94
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3.12
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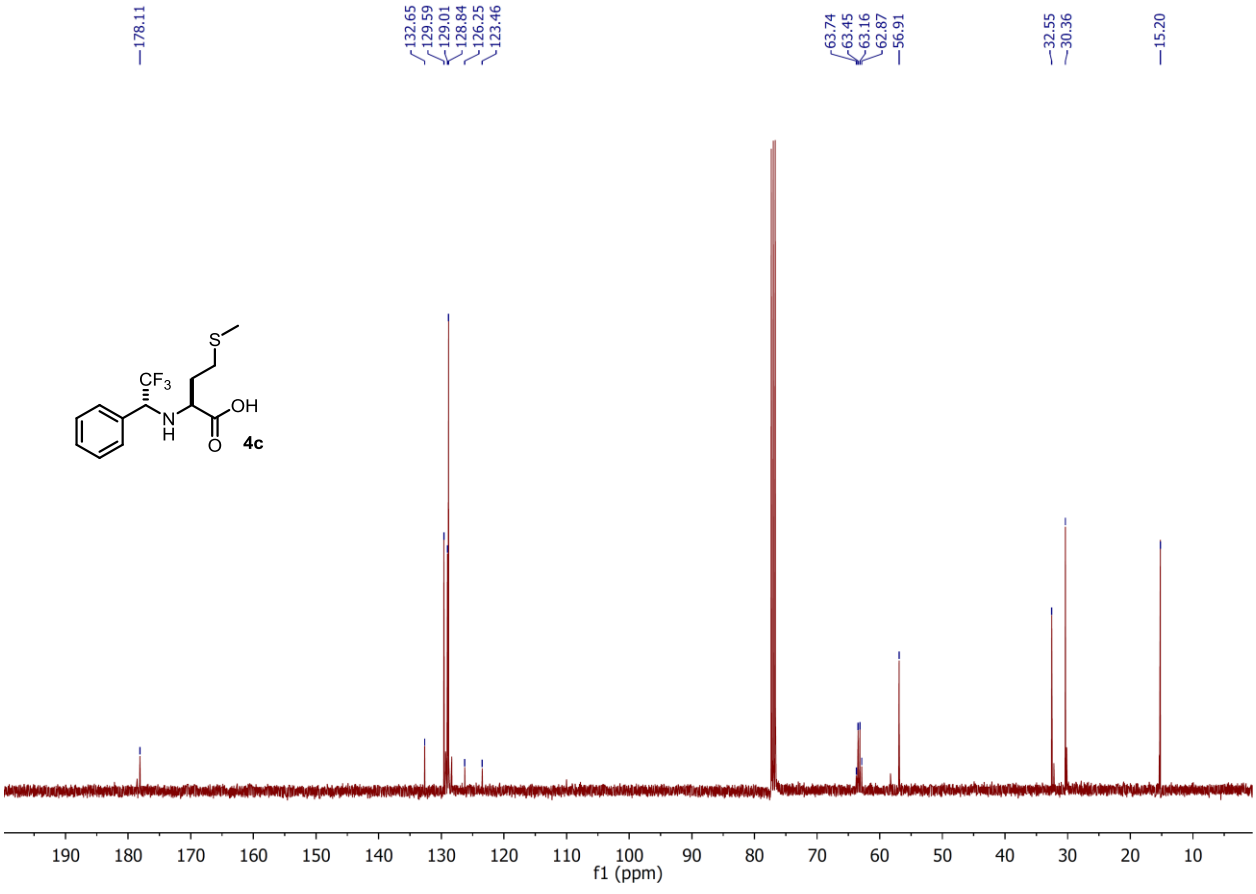
1.00
f1 (ppm)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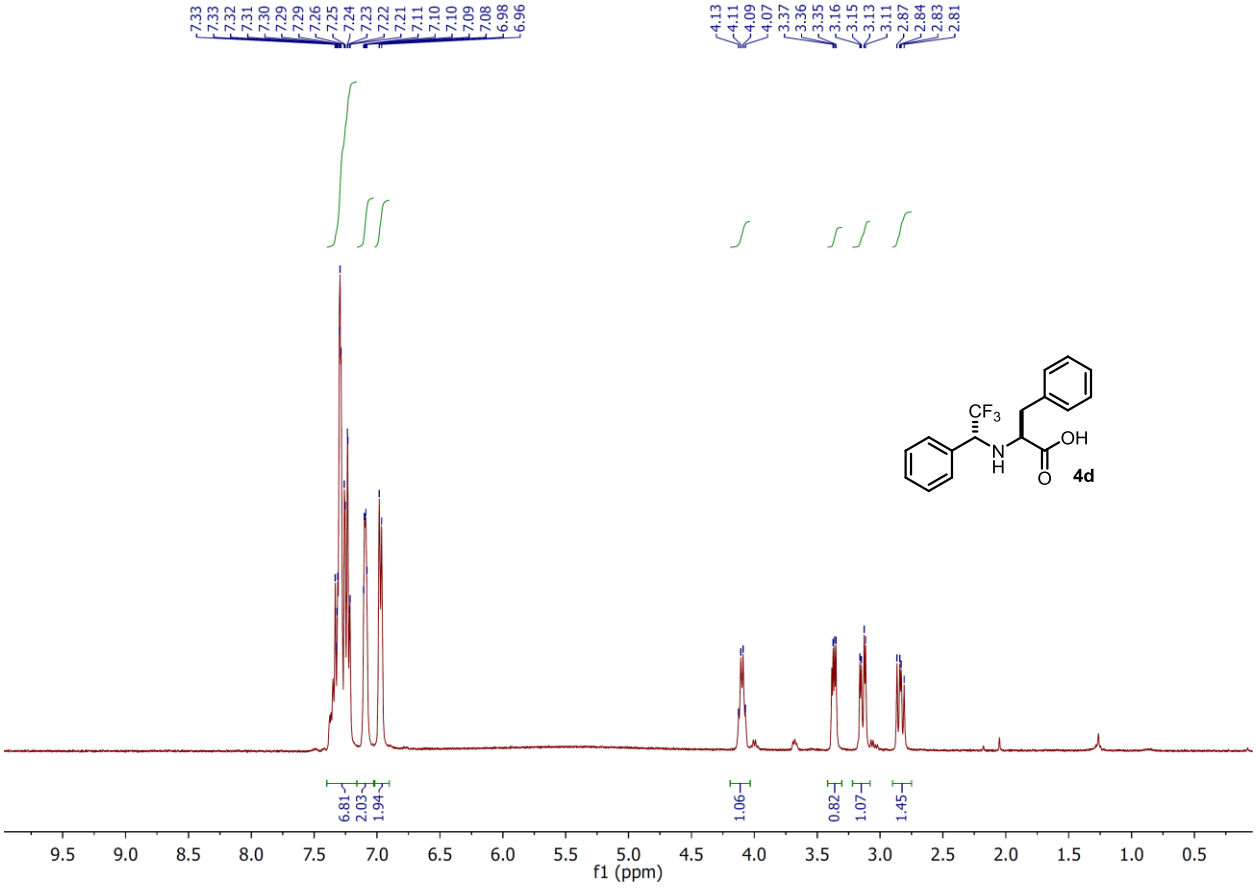
32.55
30.36
15.20
S
CF3
N
H
OH
O
4c
f1 (ppm)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7.21
7.11
7.10
7.10
7.09
7.08
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6.96
4.13
4.11
4.09
4.07
3.37
3.36
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3.15
3.13
3.11
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2.84
2.83
2.81
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O
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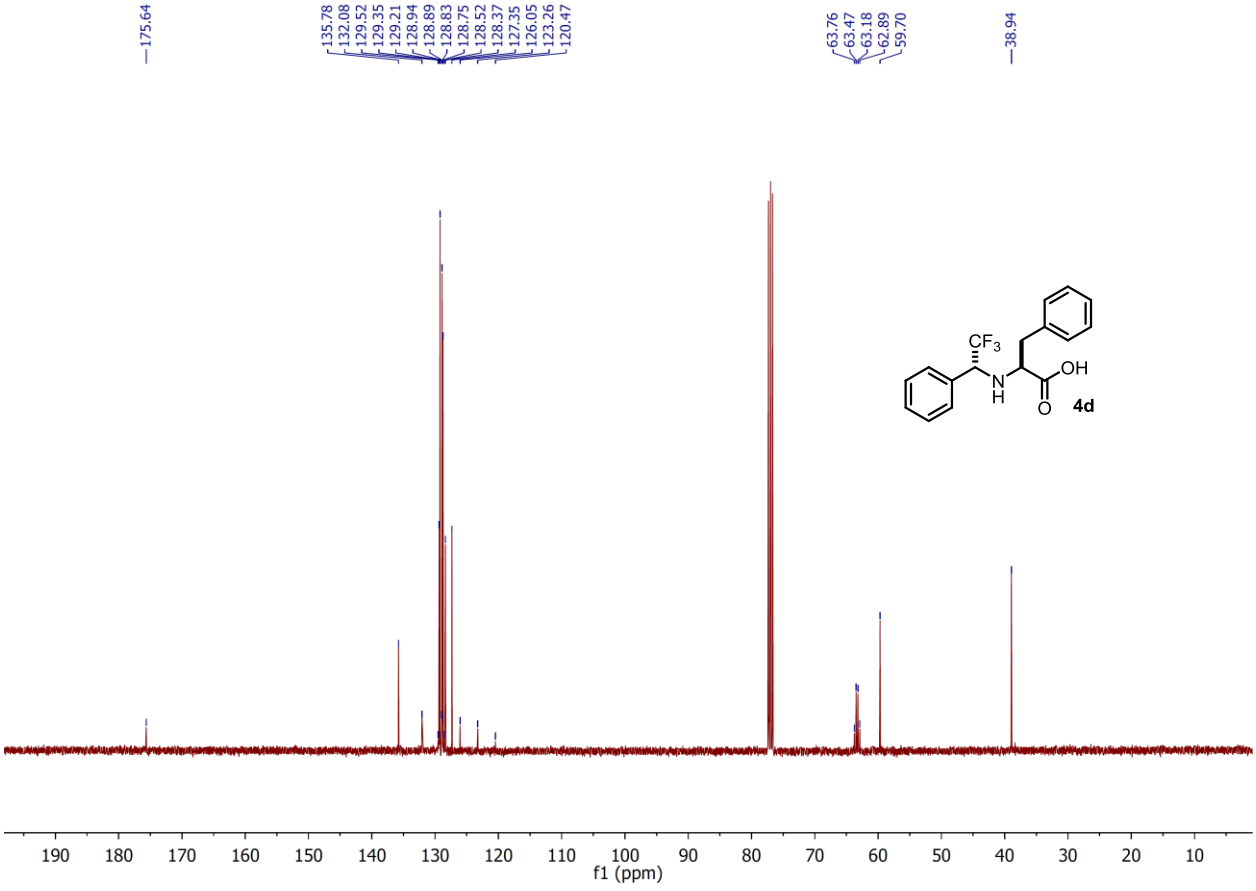
2.03
1.94
1.06
0.82
1.07
1.45
f1 (ppm)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128.52
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127.35
126.05
123.26
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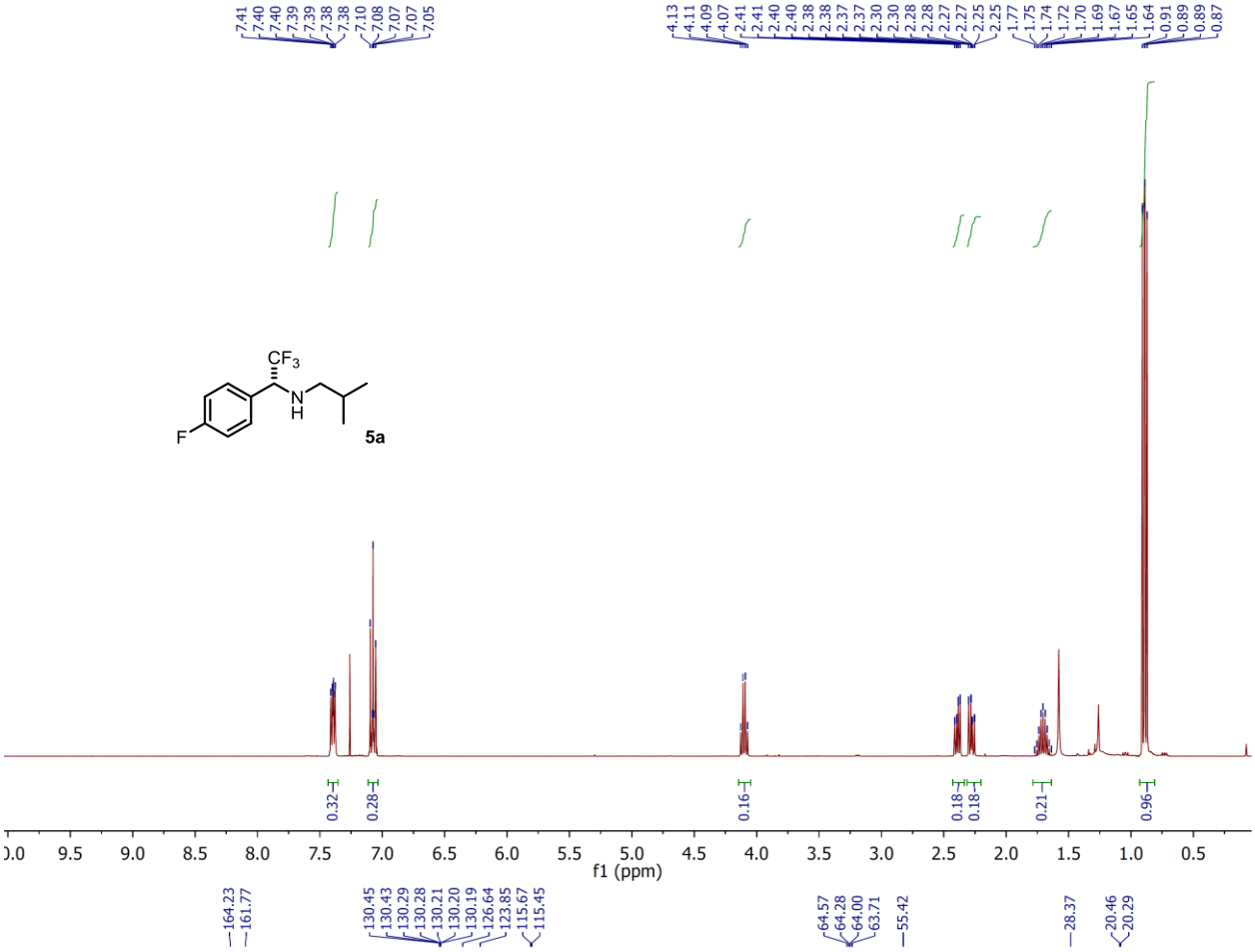
63.18
62.89
59.70
38.94
CF3
N
H
OH
O
4d
f1 (ppm)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4.11
4.09
4.07
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2.40
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2.38
2.37
2.37
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2.28
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2.27
2.25
2.25
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1.74
1.72
1.70
1.69
1.67
1.65
1.64
0.91
0.89
0.89
0.87
CF3
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F
5a
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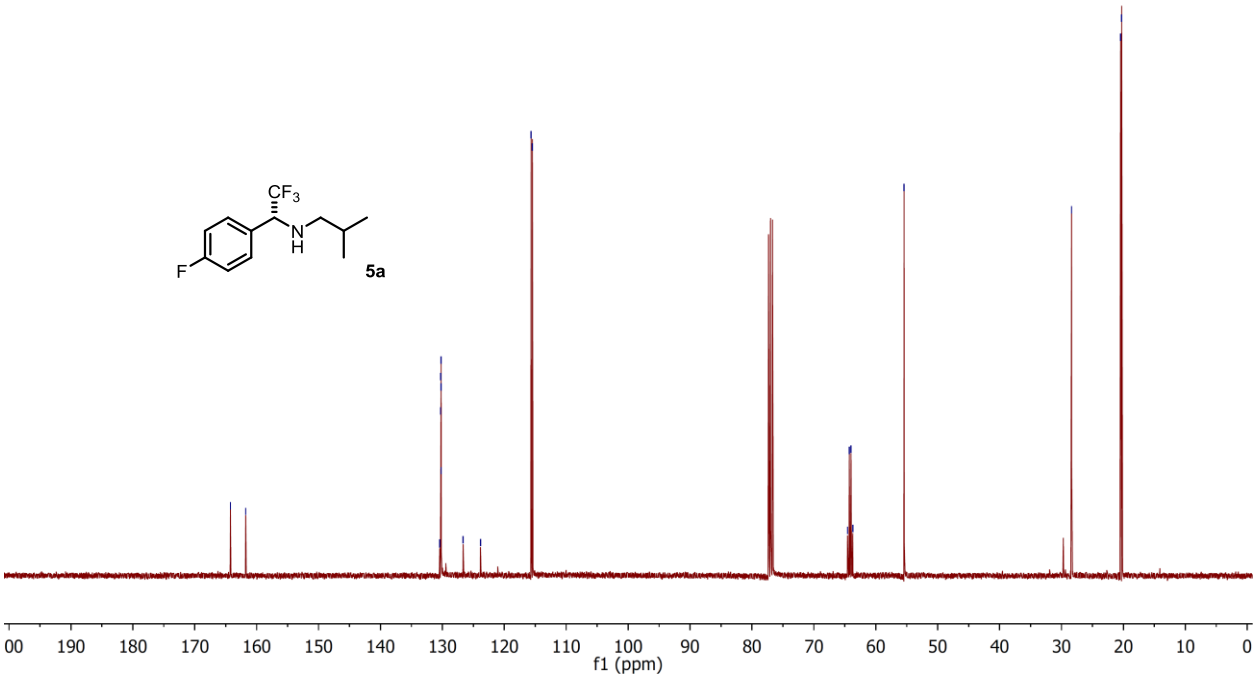
f1 (ppm)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64.57
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28.37
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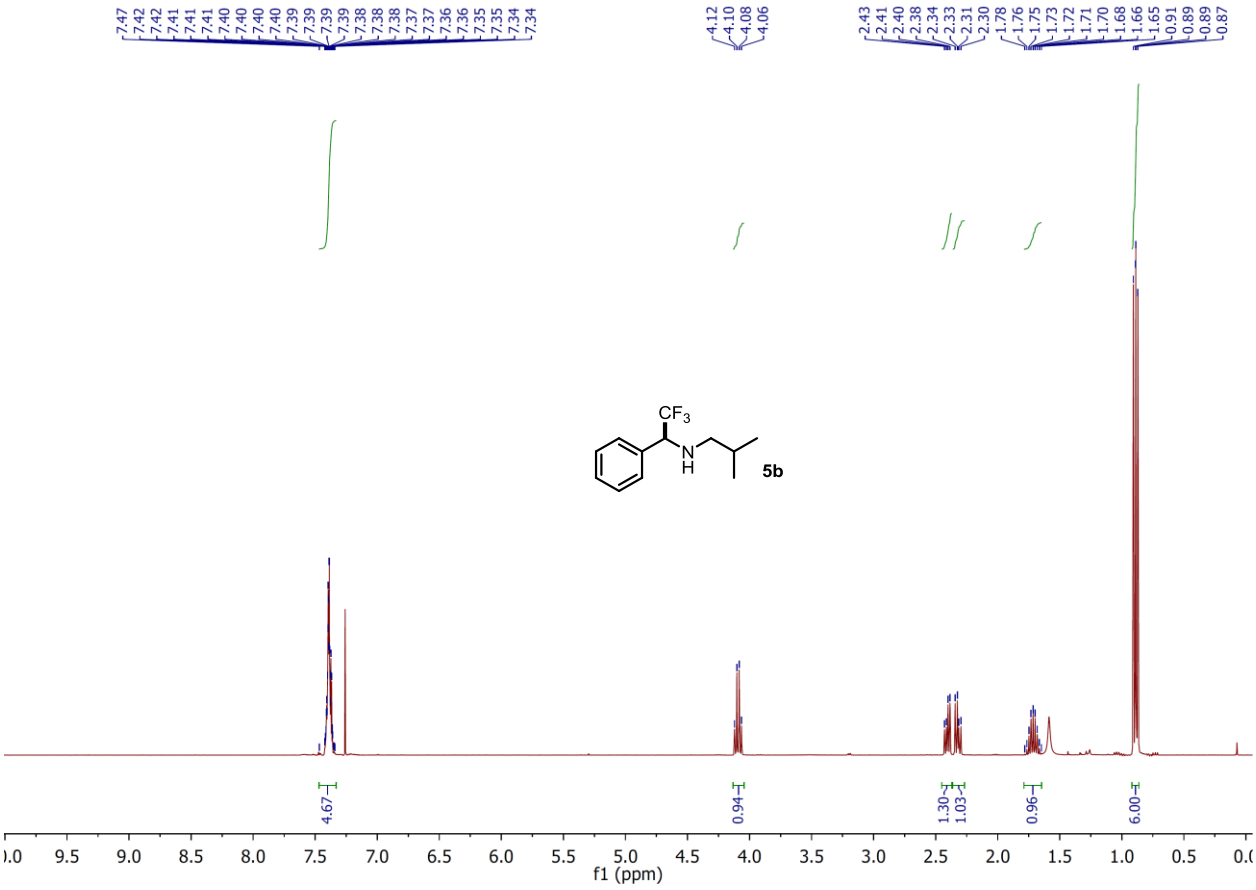
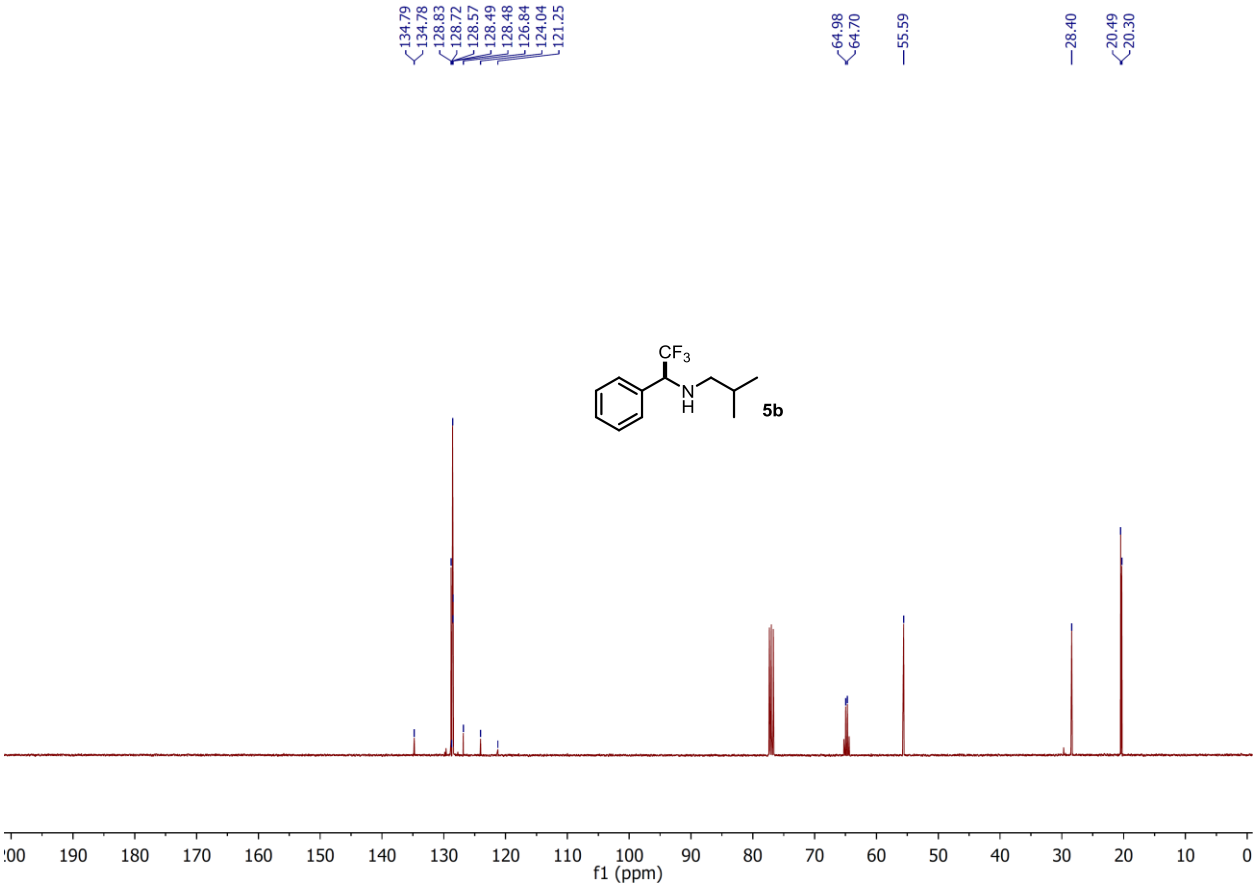
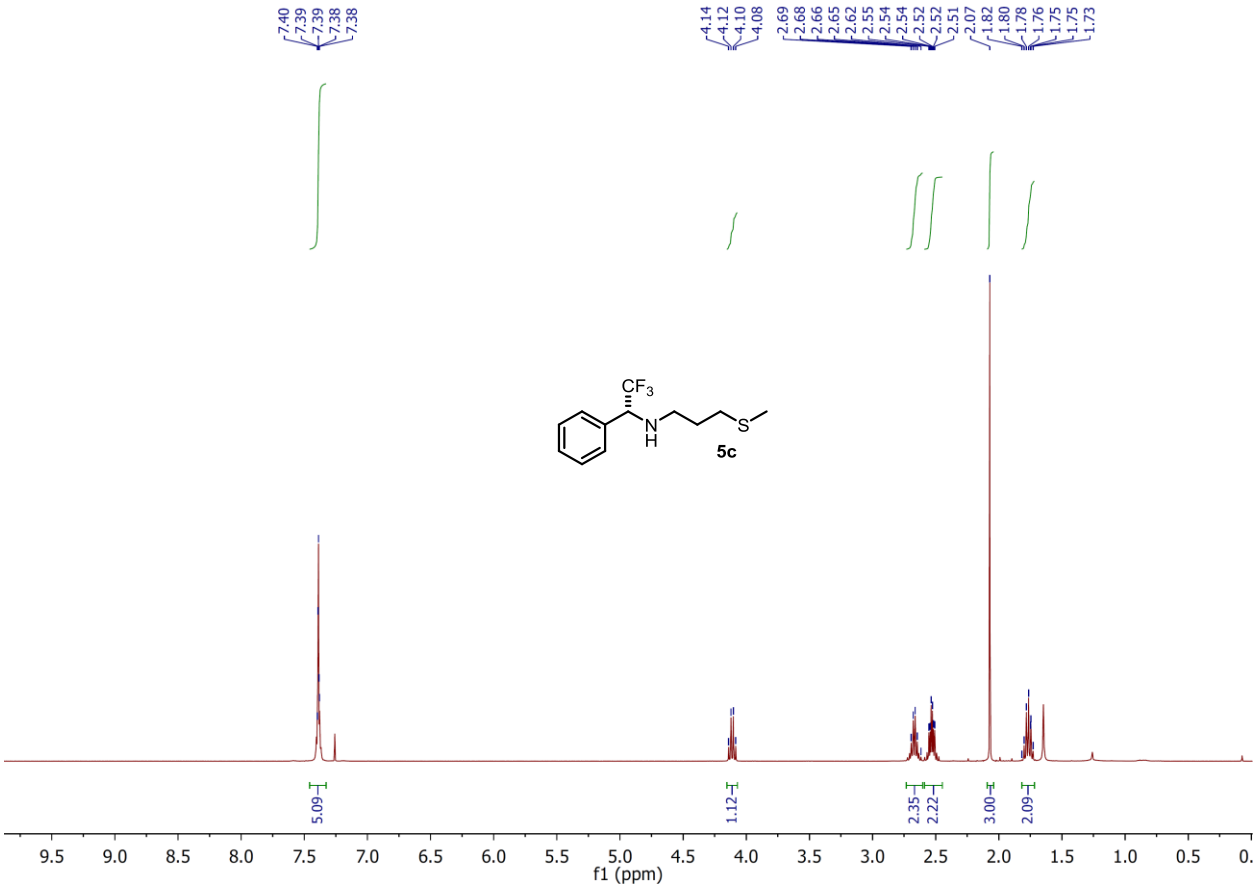
20.29
CF3
N
H
F
5a
f1 (ppm)


7.47 7.42 7.42 7.41 7.41 7.41 7.40 7.40 7.40 7.40 7.39 7.39 7.39 7.39 7.38 7.38 7.38 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.34
4.12 4.10 4.08 4.06
2.43 2.41 2.40 2.38 2.34 2.33 2.31 2.30 1.78 1.76 1.75 1.73 1.72 1.71 1.70 1.68 1.66 1.65 0.91 0.89 0.89 0.87
CF3
N
H
5b
4.67 0.94 1.30 1.03 0.96 6.00
f1 (ppm)


134.79 134.78 128.83 128.72 128.57 128.49 128.48 126.84 124.04 121.25
64.98 64.70 55.59 28.40 20.49 20.30
CF3
N
H
5b
f1 (ppm)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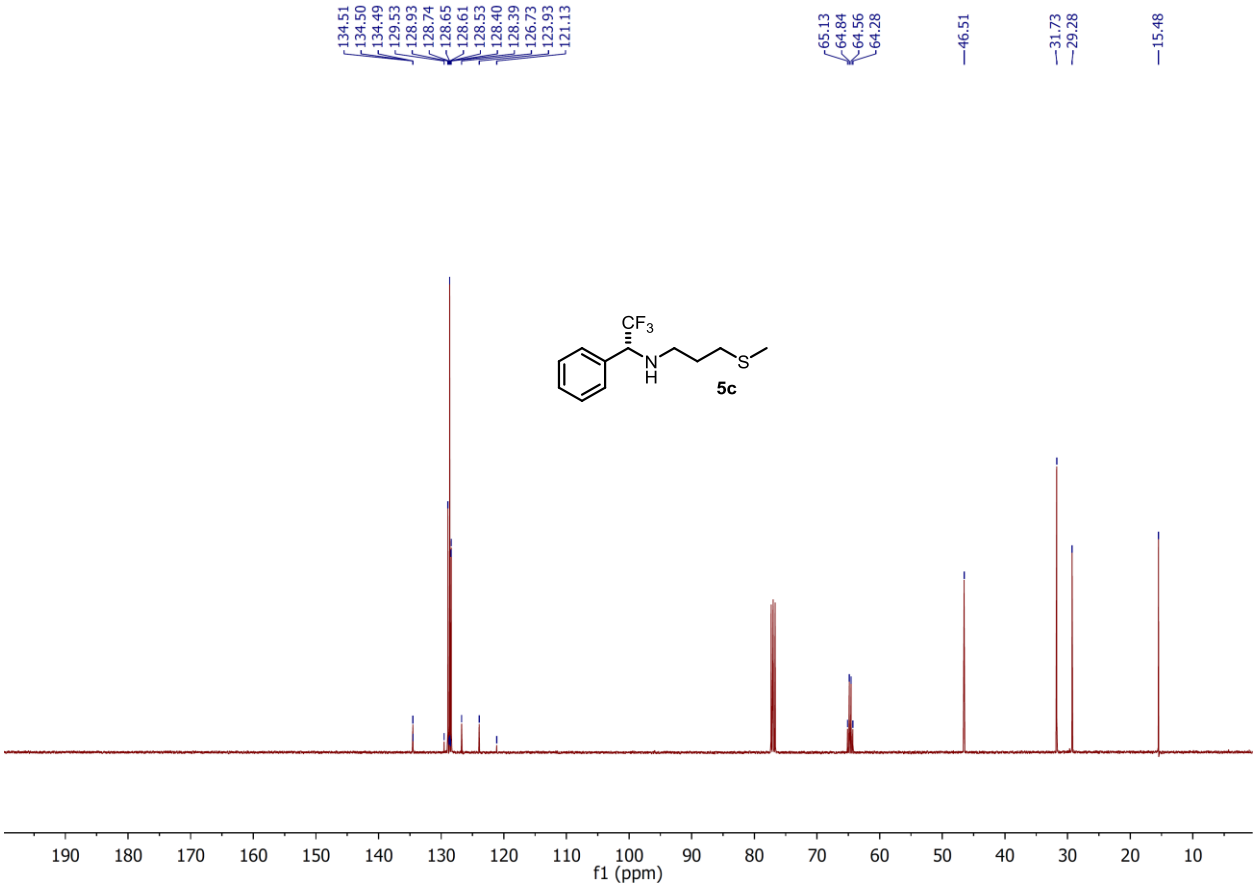
7.39
7.39
7.38
7.38
4.14
4.12
4.10
4.08
2.69
2.68
2.66
2.65
2.62
2.55
2.54
2.54
2.52
2.52
2.51
2.07
1.82
1.80
1.78
1.76
1.75
1.75
1.73
CF3
N
H
S
5c
5.09
1.12
2.35
2.22
3.00
2.09
f1 (ppm)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128.65
128.61
128.53
128.40
128.39
126.73
123.93
121.13
65.13
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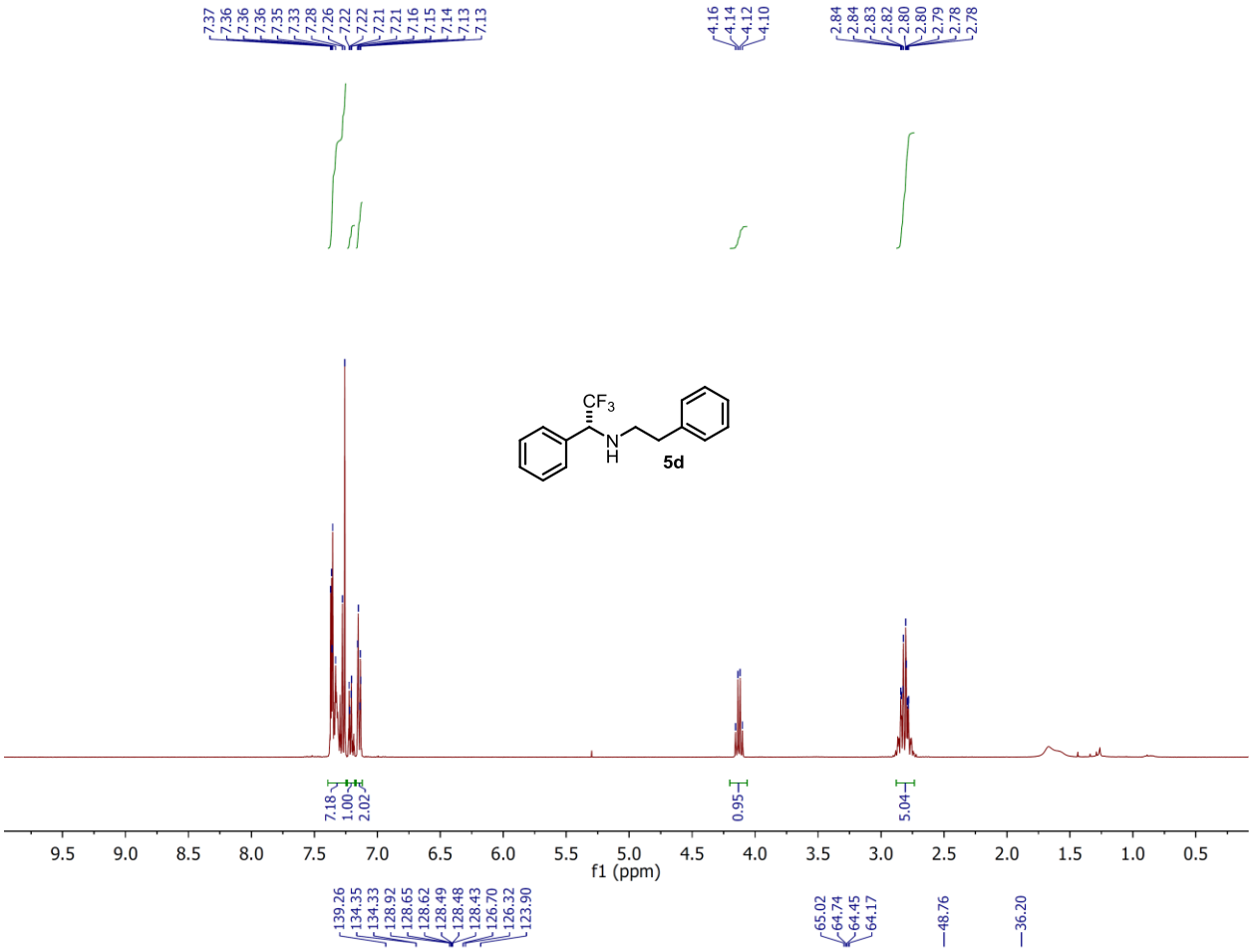
64.28
46.51
31.73
29.28
15.48
CF3
N
H
S
5c
f1 (ppm)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7.36
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7.33
7.28
7.26
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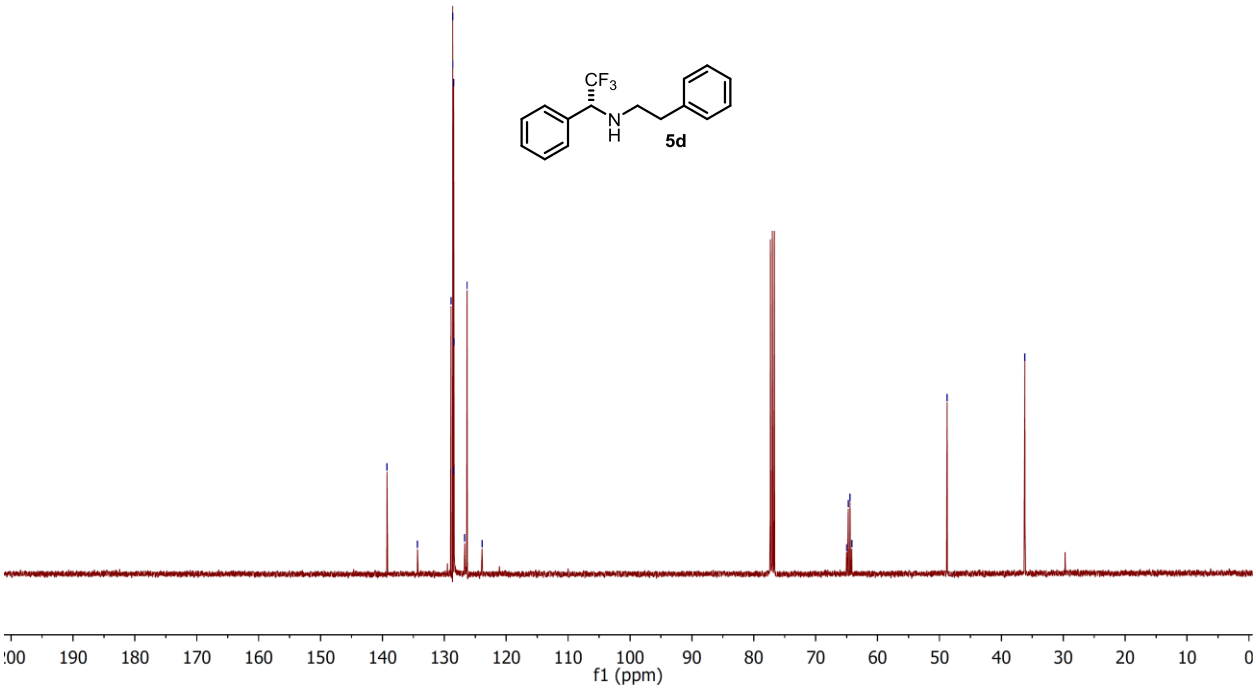
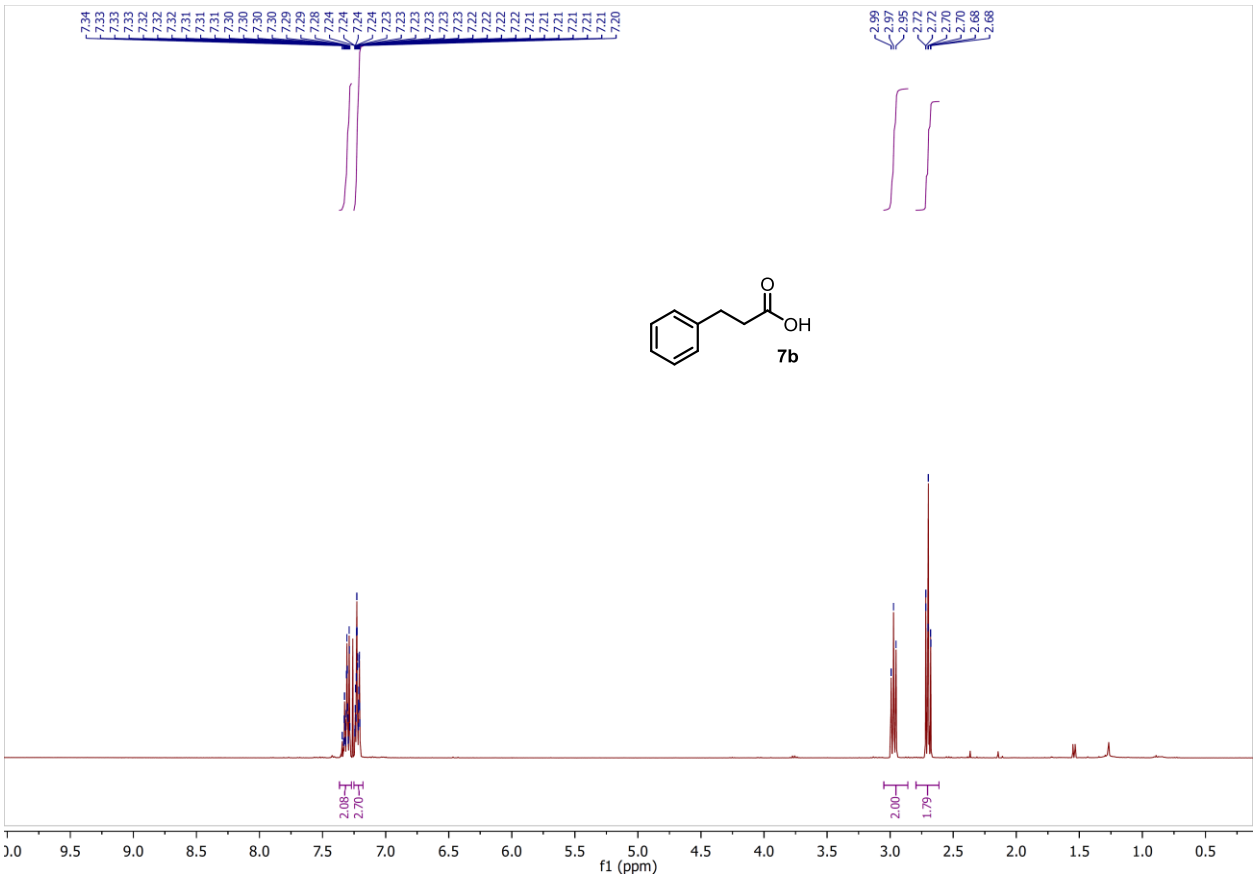
7.22
7.21
7.21
7.16
7.15
7.14
7.13
7.13
4.16
4.14
4.12
4.10
2.84
2.84
2.83
2.82
2.80
2.80
2.79
2.78
2.78
CF3
N
H
5d
7.18
1.00
2.02
0.95
5.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


139.26
134.35
134.33
128.92
128.65
128.62
128.49
128.48
128.43
126.70
126.32
123.90
65.02
64.74
64.45
64.17
48.76
36.20
CF3
N
H
5d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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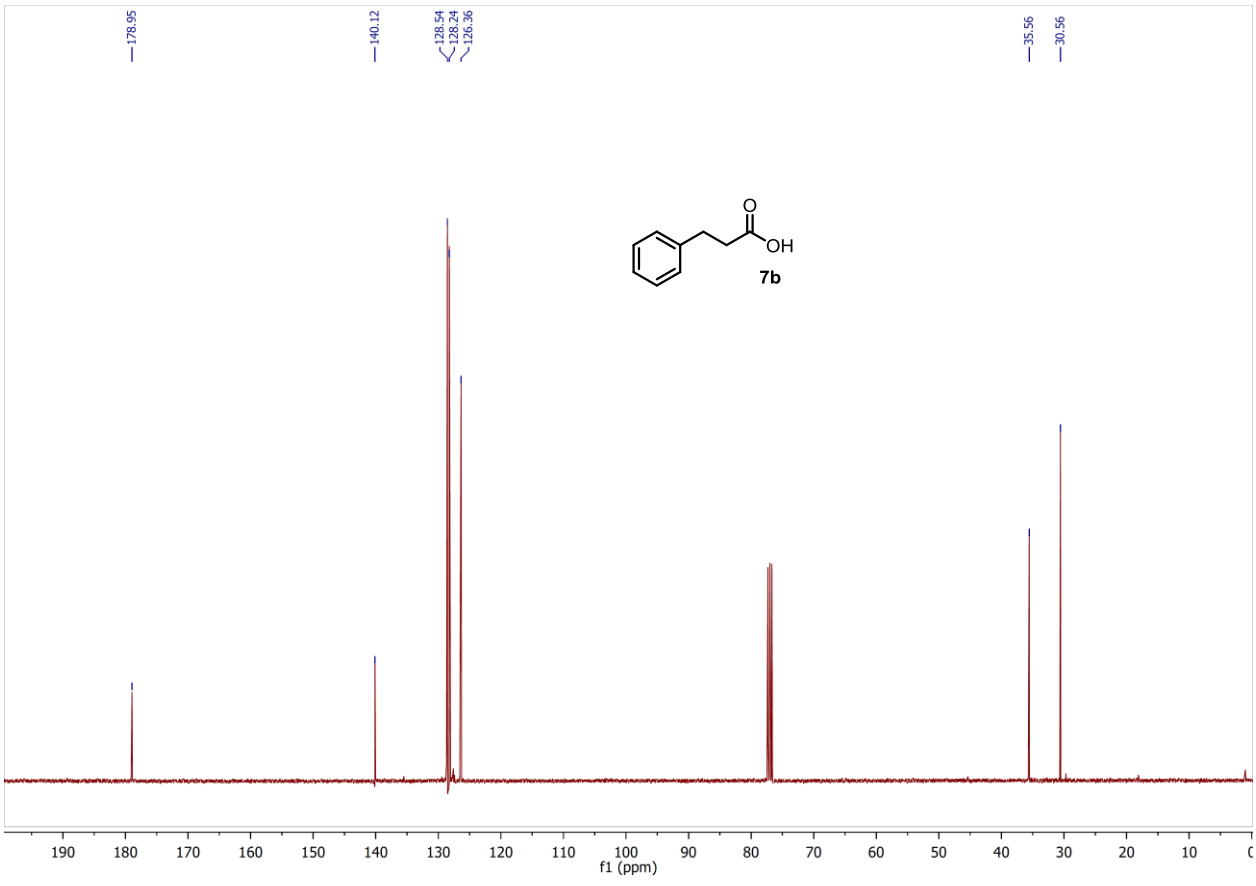
2.99 2.97 2.95 2.72 2.72 2.70 2.70 2.68 2.68
O
OH
7b
2.08
2.70
2.00
1.79
f1 (ppm)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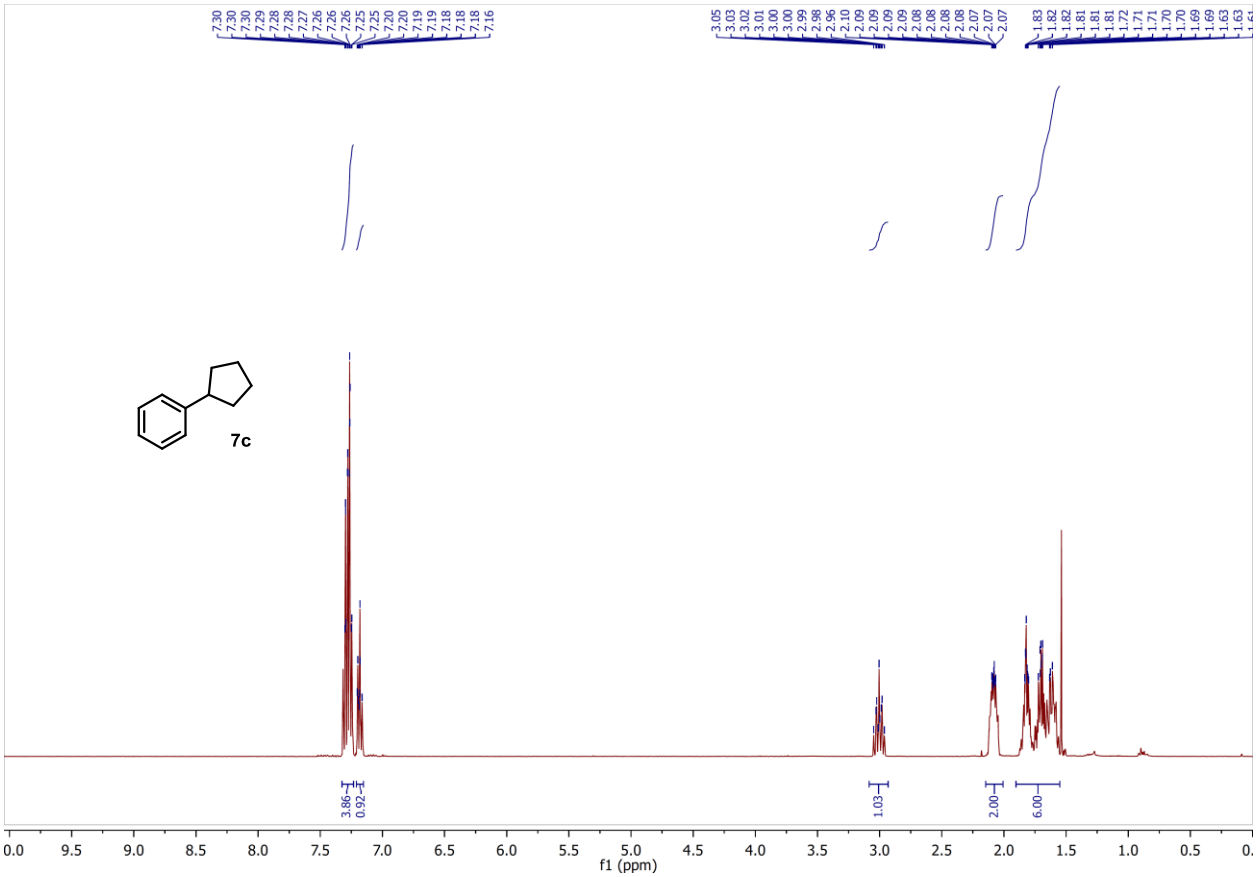
140.12
128.54
128.24
126.36
35.56
30.56
O
OH
7b
f1 (ppm)


7.30
7.30
7.30
7.29
7.28
7.28
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7.26
7.26
7.26
7.25
7.25
7.20
7.20
7.19
7.19
7.18
7.18
7.18
7.16
3.05
3.03
3.02
3.01
3.00
3.00
2.99
2.98
2.96
2.10
2.09
2.09
2.09
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2.08
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2.07
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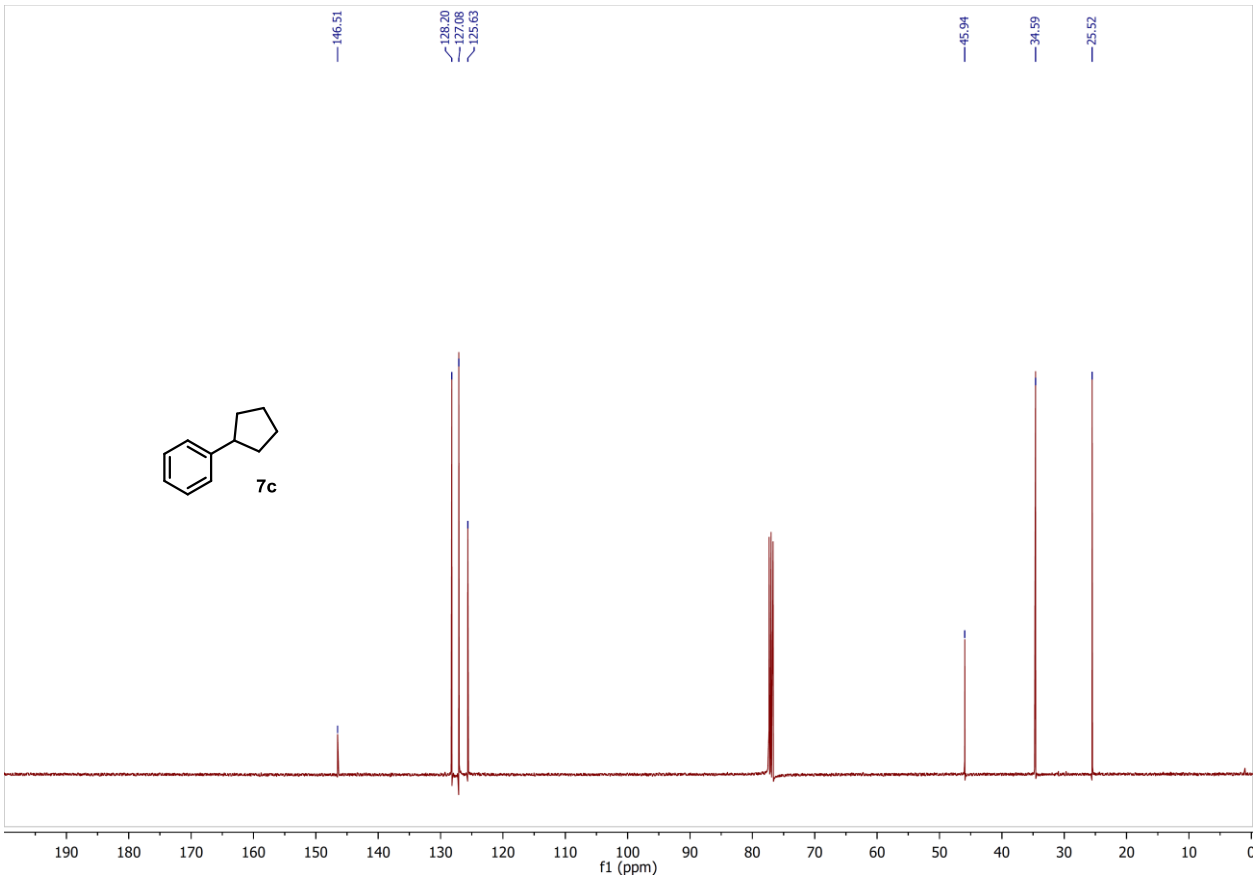
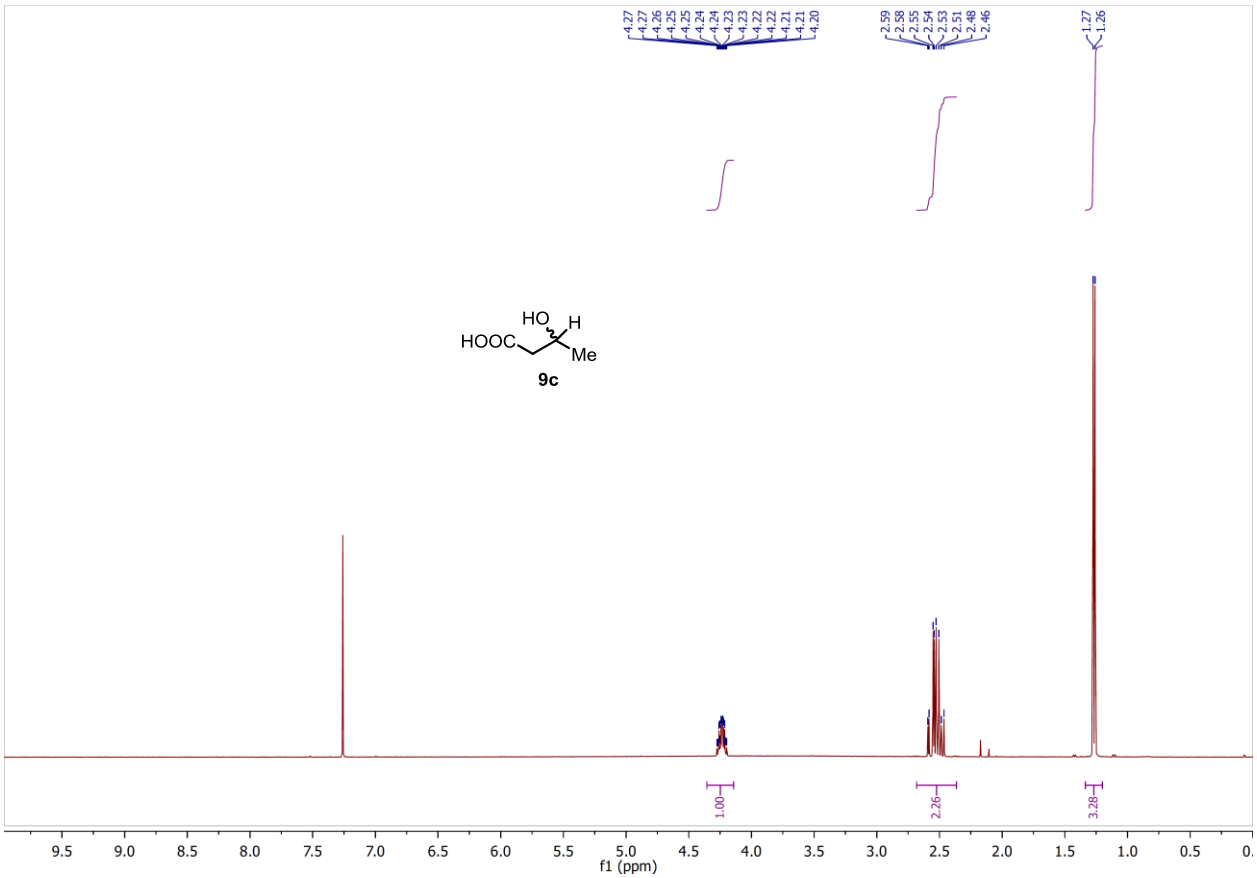
1.81
1.72
1.71
1.71
1.70
1.70
1.69
1.69
1.63
1.63
7c
3.86
0.92
1.03
2.00
6.00
f1 (ppm)


146.51
128.20
127.08
125.63
45.94
34.59
25.52
7c
f1 (ppm)


4.27
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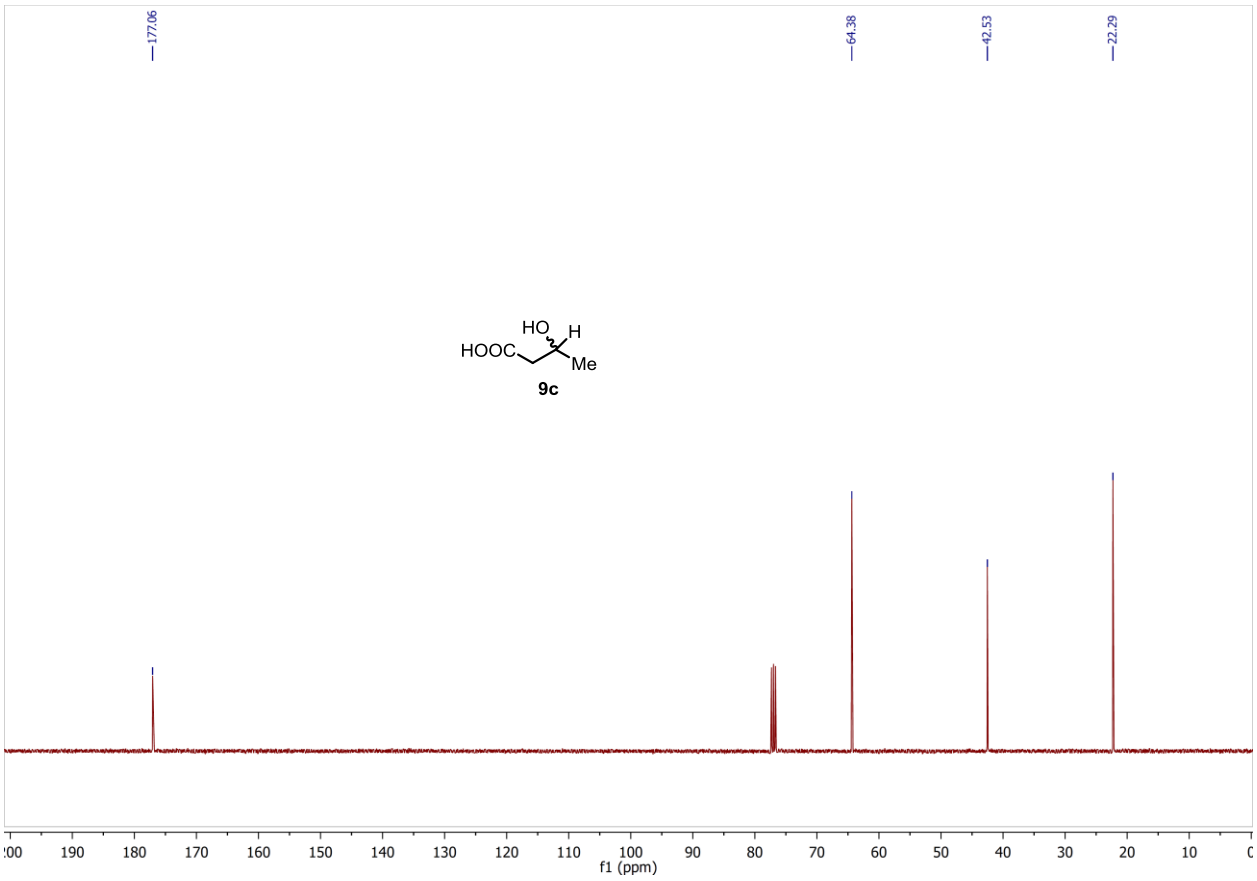
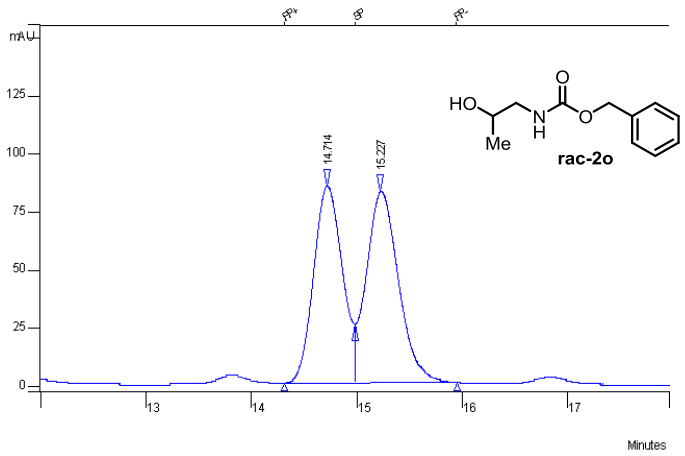
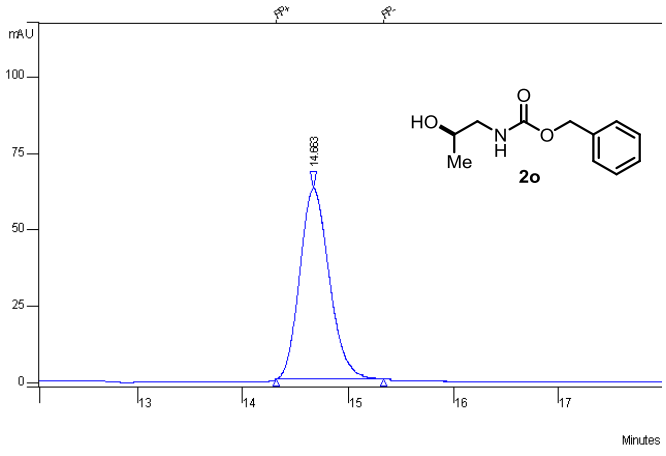
4.26
4.25
4.25
4.24
4.24
4.23
4.23
4.22
4.22
4.21
4.21
4.20
2.59
2.58
2.55
2.54
2.53
2.51
2.48
2.46
1.27
1.26
HO
H
HOOC
Me
9c
1.00
2.26
3.28
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


177.06
64.38
42.53
22.29
HO
H
HOOC
Me
9c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

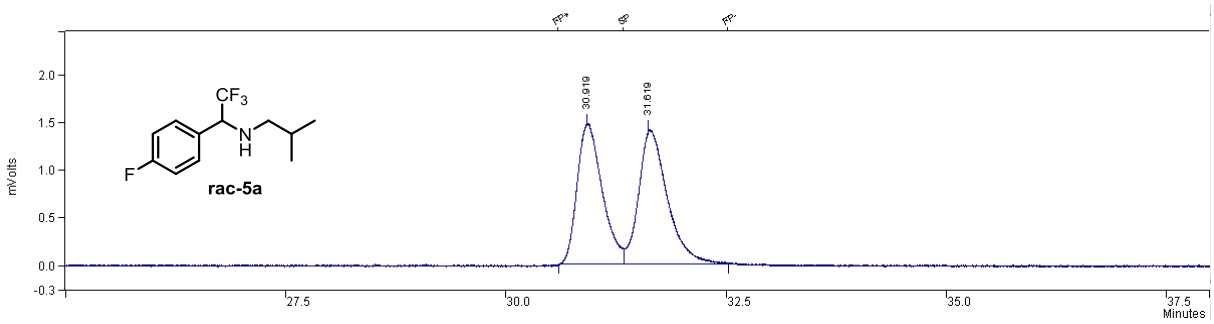
G. HPLC and GC Traces



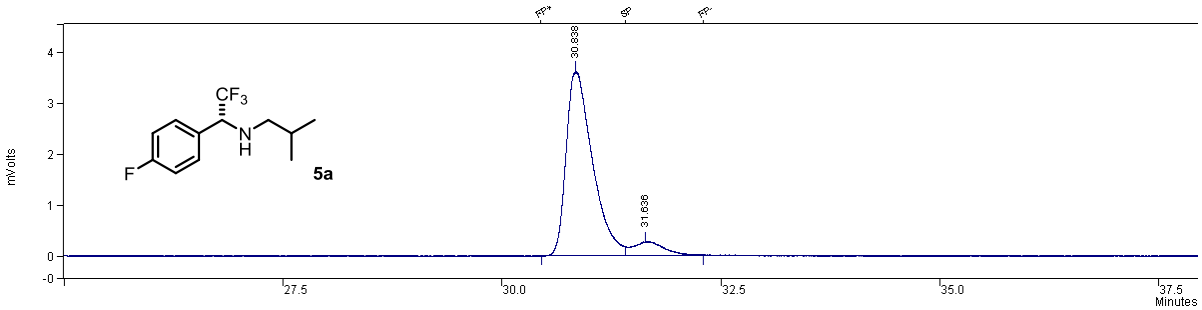
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		48.1628	14.714	0.000	862231
2		51.8372	15.227	0.000	928013
	Totals:	100.0000		0.000	1790244



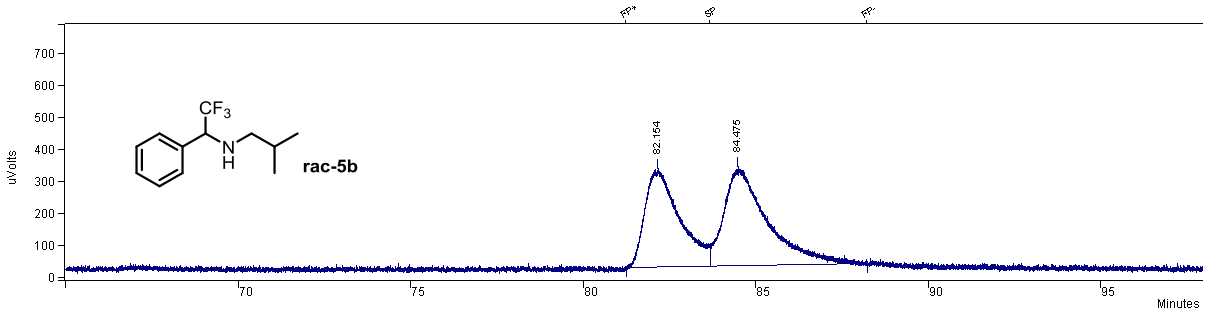
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		100.0000	14.663	0.000	647321
	Totals:	100.0000		0.000	647321



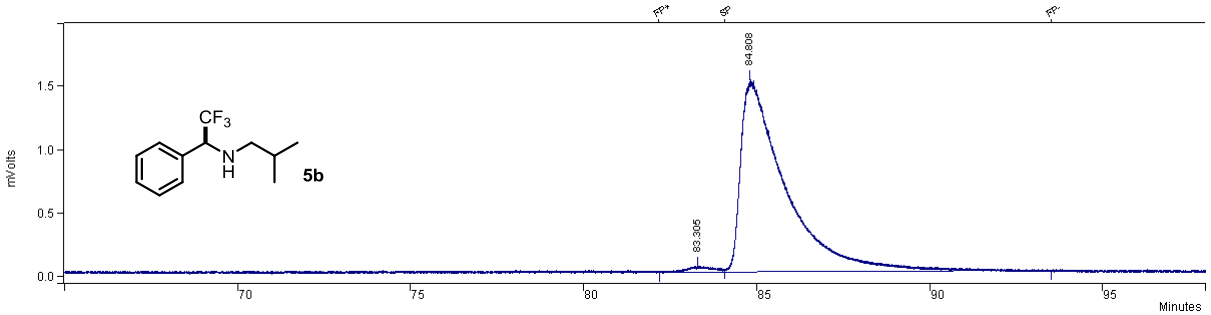
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		48.0018	30.919	0.000	29224
2		51.9982	31.619	0.000	31657
	Totals:	100.0000		0.000	60881



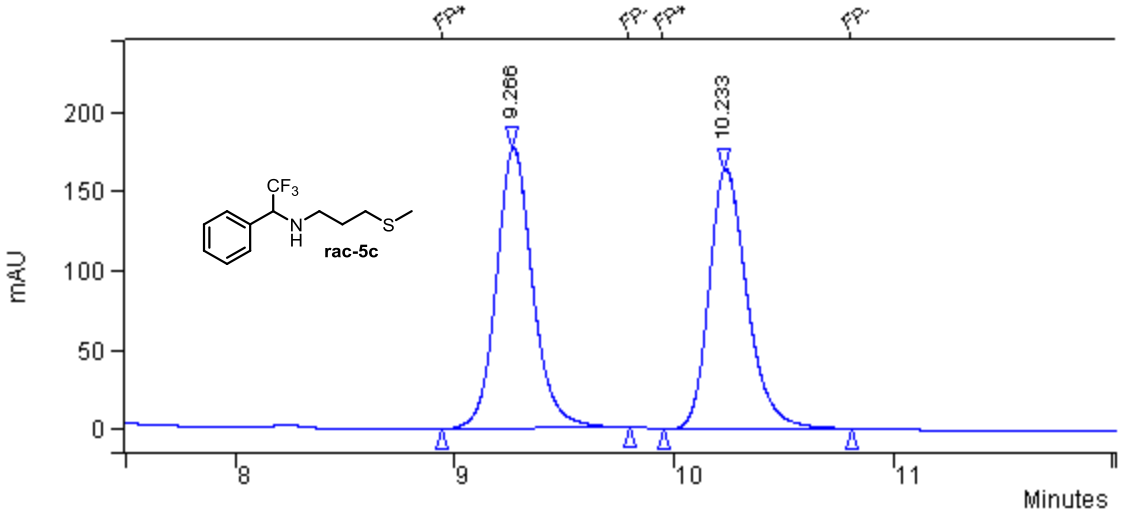
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		91.7740	30.838	0.000	76050
2		8.2260	31.636	0.000	6817
	Totals:	100.0000		0.000	82867



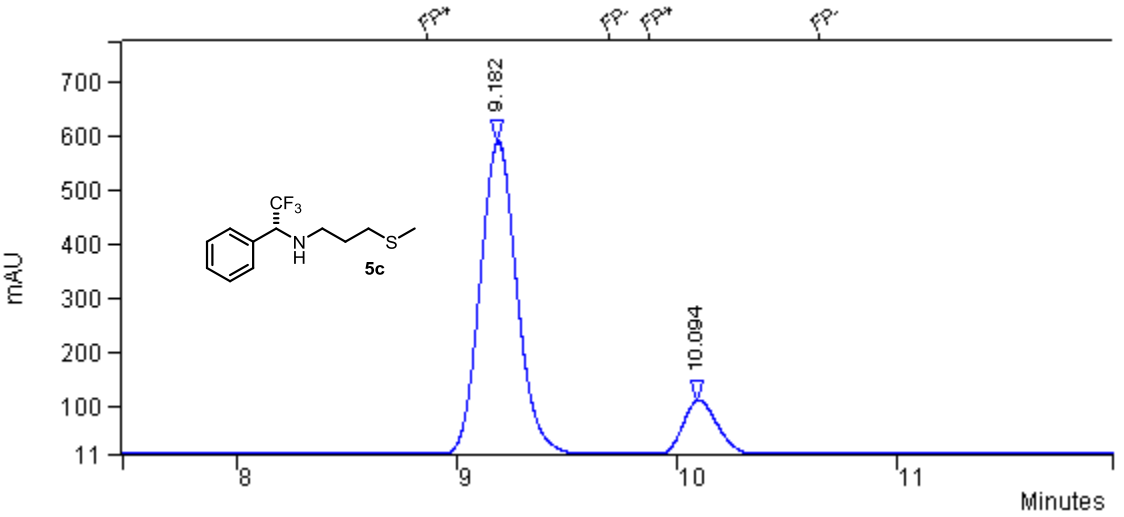
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		44.4216	82.154	0.000	21474
2		55.5784	84.475	0.000	26867
Totals:		100.0000		0.000	48341



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		1.6035	83.305	0.000	2218
2		98.3965	84.808	0.000	136105
Totals:		100.0000		0.000	138323

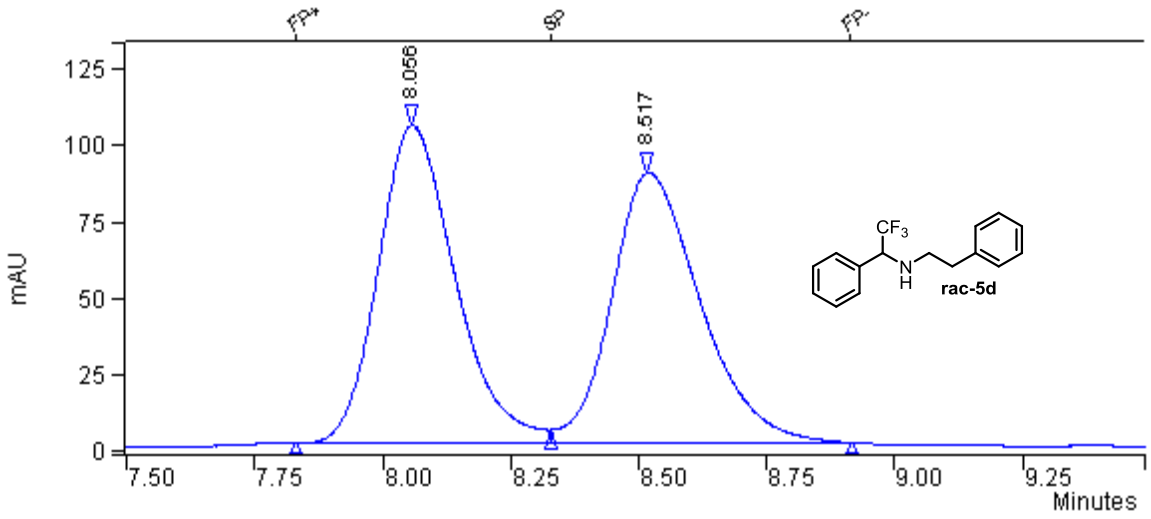


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		50.9255	9.266	0.000	1081421
2		49.0745	10.233	0.000	1042116
	Totals:	100.0000		0.000	2123537

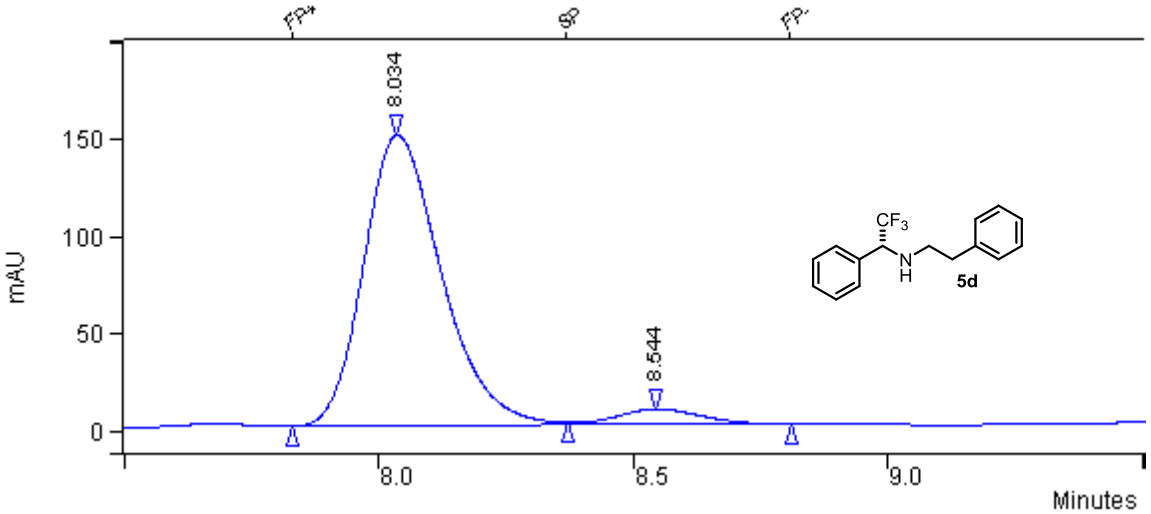


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		84.6384	9.182	0.000	3613404
2		15.3616	10.094	0.000	655824
	Totals:	100.0000		0.000	4269228

5D



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		50.6306	8.056	0.000	574733
2		49.3694	8.517	0.000	560416
	Totals:	100.0000		0.000	1135149



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)
1		94.2493	8.034	0.000	842600
2		5.7507	8.544	0.000	51412
	Totals:	100.0000		0.000	894012