Supporting Information

Rhodium-Catalyzed Double Alkyl-Oxygen Bond Cleavage: An Alkyl Transfer Reaction from Bis/Tris(*o*-alkyloxyphenyl)phosphine to Aryl Acids

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Table of Contents

1. General information

Experimental: All nonaqueous manipulations were using standard Schlenk techniques. All reactions were set up under an inert atmosphere (argon or N_2) utilizing glassware that was flame-dried and cooled under vacuum. Reactions were monitored using thin-layer chromatography (TLC) on silica gel plates. Visualization of the developed plates was performed under UV light (254 nm) or $KMnO_4$ stain. Silica gel flash column chromatography was performed on synthware 40-63 μm silica gel.

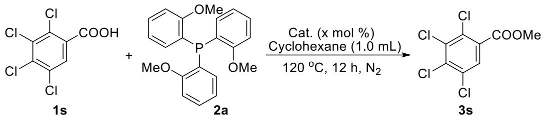
Instrumentation: All NMR spectra were run at 400 MHz (^{1}H NMR) or 100 MHz (^{13}C NMR/^{31}P NMR) in $CDCl_3$ or d_6-DMSO solution. NMR spectra were internally referenced to tetramethylsilane. ^{13}C NMR spectra were internally referenced to the residual solvent signal. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m= multiplet, br = broad), coupling constants (J) were reported in Hz. High resolution mass spectra (HRMS) were recorded on Bruker MicrOTOF-QII mass instrument (ESI).

Materials: Unless otherwise indicated, starting catalysts and materials were obtained from Sigma Aldrich, TCI, Alfa Aesar, Adamas or Acros Co. Ltd. Moreover, commercially available reagents were used without additional purification. Phosphines[1-2] and amine[3] with different substitutes were prepared according to literature procedures.

2. Optimization of the Reaction Conditions

Benzoic acid **1** (0.1mmol), $(2\text{-MeOPh})_3P$ **2** (0.05-0.14mmol), and catalyst (4.0-10 mol%) was added to a flame-dried Schlenck tube which charged with a magnetic stir bar in 1.0 mL of dry solvent. The resulting suspension was stirred at the specified temperature under N_2 for 12 h. Until the reaction completed (monitored by TLC), the crude products thus obtained and the conversion of the reaction was determined by gas chromatography with an internal standard.

Table S1. The effect of different catalysts



entry[a]	cat.	cat. (x mol%)	yield (%)[b]
1	--	--	0
2	Ag(OTf)	10	N.R.
3	$Ni(OAc)_2$	10	13
4	$Ni(acac)_2$	10	34
5	$Fe(acac)_3$	10	20
6	$Pd_2(dba)_3$	10	65
7	$Pd_2(allyl)_2Cl_2$	10	76
8	$PdCl_2$	10	21
9	$Pd(OAc)_2$	10	52
10	$Pd(OTf)_2$	10	48
11	$Sc(OTf)_3$	10	22
12	$[Rh(COD)Cl]_2$	10	85
13	$Rh_2(OAc)_4$	10	98
14	**$Rh_2(OAc)_4$**	**8**	**95 (91)**[c]
15	$Rh_2(OAc)_4$	5	68
16	$Rh_2(OAc)_4$	4	46

[a] Reaction conditions: a mixture of **1s** (0.1 mmol), **2a** (0.12 mmol) and catalyst in cyclohexane (1.0 mL) at 120 °C for 12 h under nitrogen atmosphere. [b] Determined by GC analysis using a standard. [c] Yield of isolated product is given in parentheses.

Table S2. Solvent effects

entry[a]	solvent	concentration	yield (%)[b]
1	1,4-dioxane	0.1	89
2	DCM	0.1	21
3	toluene	0.1	90
4	*p*-xylene	0.1	91
5	DMF	0.1	54
6	1,3,5-trimethylbenzene	0.1	92
7	CH_3CN	0.1	40
8	DCE	0.1	64
9	chlorobenzene	0.1	70
10	ethyl acetate	0.1	87
11	**cyclohexane**	0.1	**95 (91)**[c]
12	ethyl ether	0.1	92
13	cyclohexane	0.07	90
14	cyclohexane	0.05	76

[a] Reaction conditions: a mixture of **1s** (0.1 mmol), **2a** (0.12 mmol) and $Rh_2(OAc)_4$ (8 mol%) in solvent (x mL) at 120 °C for 12 h under nitrogen atmosphere. [b] Determined by GC analysis using a standard. [c] Yield of isolated product is given in parentheses.

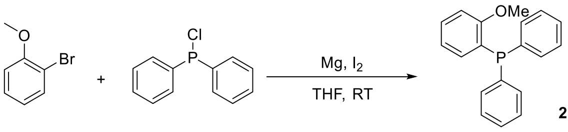
Table S3. Temperature and phosphine loading

entry[a]	temp. (℃)	phosphine (mol%)	yield (%)[b]
1	120	50	42
2	120	80	68
3	120	100	88
4	**120**	**120**	**95(91)**[c]
5	120	140	93
6	100	120	80
7	140	120	85

[a] Reaction conditions: a mixture of **1s** (0.1 mmol), **2a** (50-140 mol%) and $Rh_2(OAc)_4$ (8 mol%) in cyclohexane (1 mL) at 100-140°C for 12 h under nitrogen atmosphere. [b] Determined by GC analysis using a standard. [c] Yield of isolated product is given in parentheses.

3. General procedures for the synthesis of phosphines 2d-f

These compounds were obtained on multigrams scale by a slightly modified published procedure.[1-2]



2d

Figure S1. Synthesis of (2-methoxyphenyl)diphenylphosphane **2d**

A solution of 2-bromobenzylmethyl ether (0.94 g, 5 mmol) in dry THF was dropped into a suspension of magnesium (0.12 g) in THF (6 mL), previously activated with iodine. The mixture was refluxed until magnesium disappeared, a solution of chlorodiphenylphosphine (0.89 g, 4.0 mmol, 0.8 equiv.) in dry THF (1 mL) was added at room temperature, and the reaction mixture was then heated to reflux for 1 h. After cooling, the mixture was poured into a mixture of ice (ca. 5 g) and HCl (6 mL, 1 N) and stirred until magnesium dissolution. The aqueous phase was extracted with Et2O (3×30 mL), the combined organic layers were dried over with anhydrous Na_2SO_4, the solvent was removed under reduced pressure. The residue was recrystallized with MeOH to obtain the desired compound **2d**. Yield: 1.0 g (85%), white crystal. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.38 – 7.26 (m, 11H), 6.94 – 6.82 (m, 2H), 6.71 – 6.65 (m, 1H), 3.75 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 161.23, 161.08, 136.79, 136.69, 133.98, 133.78, 133.63, 130.32, 128.55, 128.37, 128.30, 125.71, 125.59, 121.03, 110.25, 110.23, 77.36, 77.04, 76.72, 55.70, 55.66; **^{31}P NMR** (100 MHz, $CDCl_3$) δ = -16.77.

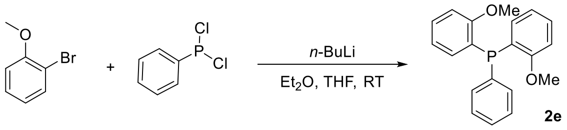


Figure S2. Synthesis of bis(2-methoxyphenyl)(phenyl)phosphane **2e**

To an ether solution (10 mL) of 1-bromo-2-methoxylbenzene (1.88 g, 10 mmol, 2.5 equiv) was added a hexane solution of *n*-butyllithium (1.6 M, 6.4 mL, 10.2 mmol) at -78 °C, then resulting solution was warmed to 0 °C and stirred for 1 h until many white solid salts were produced. THF (10 mL) was added to the reaction mixture, and cooled down to -78 °C. Dichlorophenylphosphine (0.71 g, 4 mmol) was added to the reaction system slowly, and stirred for 1 h, gradually warmed to room temperature, and stirred until completion. After addition of a saturated solution of NH_4Cl, the mix-ture was extracted with ethyl acetate (EA). The organic layer was washed with brine and dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The residue was recrystallized with EtOH to obtain the de-sired compound **2e**. Yield: 1.2 g (95%), white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.38 – 7.25 (m, 7H), 6.94 – 6.80 (m, 4H), 6.73 – 6.64 (m, 2H), 3.74 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 161.33, 136.50, 134.11, 133.81, 130.08, 128.51 – 128.00, 125.20, 120.90, 110.20, 77.34, 77.02, 76.70, 55.66; **^{31}P NMR** (100 MHz, $CDCl_3$) δ = -27.88.

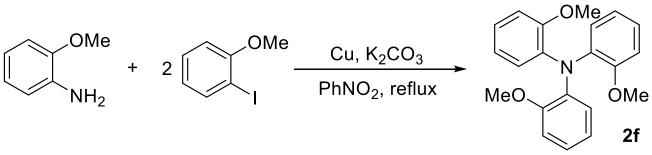


Figure S3. Synthesis of tris(2-methoxyphenyl)amine **2f**

To a three-necked flask fitted with a reflux condenser, thermometer, and nitrogen purge line was added 0.64 g (5.2 mmol) of o-anisidine, 2.3 g (10 mmol) of o-iodoanisole, 3 g of ball-milled K_2CO_3, 0.64 g of spongy copper powder and 2 g of nitrobenzene. The flask was then heated at reflux for about 3 h under a nitrogen purge. When the reaction was complete (monitored by TLC), the mixture was poured into saturated NH_4Cl (aq); then the aqueous phase was extracted with ethyl acetate (3×35 mL) and the combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude product was then recrystallized from acetone to obtain the desired compound **2f**. Yield: 1.15 g (65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.05 (ddd, *J* = 8.1, 6.3, 2.7 Hz, 3H), 6.85 (ddd, *J* = 7.1, 6.4, 4.4 Hz, 9H), 3.59 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 153.11, 137.76, 124.50, 123.73, 120.64, 112.59, 77.36, 77.04, 76.73, 55.76, 55.72.

4. General procedures for the synthesis of triphenylphosphine 2a-^{18}O

According to the procedure.[4-6]

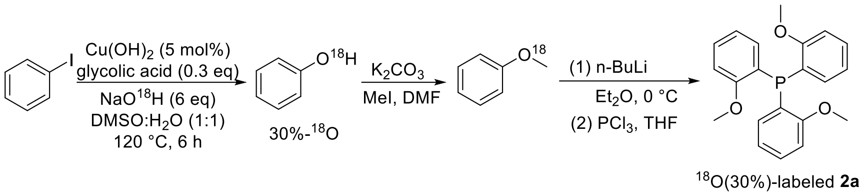


Figure S4. Synthesis of ^{18}O-labeled **2a**

Procedure 1: A Schlenk tube was charged with PhI (0.2 g, 10 mmol), $Cu(OH)_2$ (4.9 mg, 0.05 mmol), glycolic acid (22.8 mg, 0.3 mmol), NaOH (240 mg, 6.0 mmol), and DMSO/H_2O (1.0 mL/1.0 mL). The mixture was stirred at 120 ℃ for 6 h under Ar. The reaction mixture was allowed to cool to room temperature, poured into water (3 mL), and then acidified to pH=1 with 2 N HCl. The aqueous phase was extracted twice with EA, and the combined organic layer was washed with H_2O and brine, dried over anhydrous Na_2SO_4, and concentrated under vacuum. Purification of the crude product by silica gel column chromatography (EtOAc/PE) afforded the phenol in up to 99% yield.

Procedure 2: The phenol (0.56 g, 6 mmol) was added to a two-necked flask with K_2CO_3 (12 mmol, 2 equiv) as the dehydrogenating base in DMF (10 mL), then MeI (3 equiv) was added, and the reaction mixture was stirred for 8 h. Et_2O (30 mL) was added to the mixture, and the organic phases were washed with water, then dried over anhydrous Na_2SO_4, and concentrated by rotary (under low temperature) to gain the crude product. The pure methyl ether was obtained in 92% yield by silica gel column chromatography.

Procedure 3: TMEDA (15 mmol, 0.15 equiv) was added to a hexane solution of *n*-butyllithium (1.6 M, 3.1 mL, 5 mmol) slowly via syringe at 0 ^{o}C under an argon atmosphere. The reaction mixture was stirred at 60 ^{o}C for 18 h and a copious amount of precipitate produced. ^{18}O-Labeled ether (5.1 mmol) was then added to the reaction mixture and stirred for 20-24 h. After cooling to -78 ^{o}C, 5 mL THF and PCl_3 (1.5 mmol) were successively added and stirred for 3 h at this temperature, then allowed to warm to -10 ℃ and 2 mL HCl (aq, 2 M) solution was added. The aqueous solution was extracted with Et_2O (3×30 mL) and the combined organic phases were dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The crude product was purified via silica gel column chromatography to afford the desired product **2a-**^{18}O in 91% yield (eluent, petroleum ether (PE)/EA=20:1).

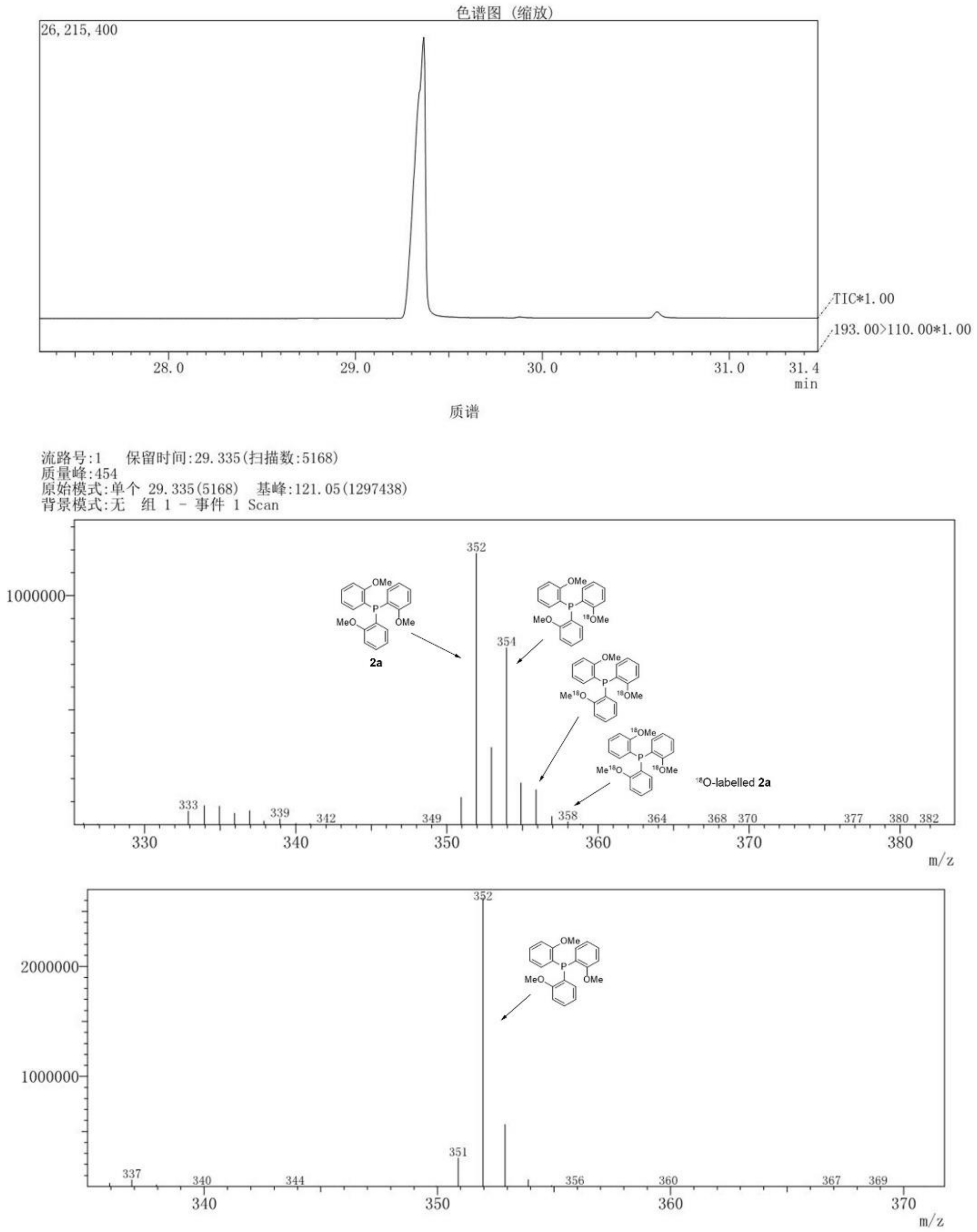


Figure S5. GC-MS spectroscopy of compound ^{8}O-labeled **2a** and **2a**

5. Synthesis of choloridorhodium complex and stoichiometric experiment

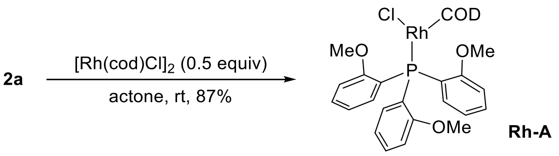


Figure S6. Synthesis of compound **Rh-A**

To a solution of the complex $[RhCl(cod)]_2$ (100 mg, 0.203 mmol) in acetone (5 mL) was added $(2\text{-MeOPh})_3P$ **2a** (2.0 equiv). The color of the solution quickly changed from orange to yellow. The mixture was stirred at room temperature and checked for completion by TLC. After the solvent was removed in vacuo, the desired single crystal **Rh-A** was obtained.

*Chlorido($^{\eta}$-cycloocta-1,5-diene)[tris(2-methoxyphenyl)-phosphine]rhodium (***Rh-A***)*

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.35 (t, *J* = 7.7 Hz, 4H), 6.95 (t, *J* = 7.3 Hz, 4H), 6.83 (dd, *J* = 8.0, 4.0 Hz, 4H), 5.23 (s, 2H), 3.86 (s, 2H), 3.54 (d, *J* = 18.2 Hz, 9H), 2.36 (s, 4H), 2.01 – 1.79 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.43, 160.39, 131.17, 120.57, 120.47, 119.96, 119.54, 110.66, 110.62, 98.24, 77.45, 77.13, 76.82, 71.53, 55.12, 33.21, 29.19.

^{31}P NMR (100 MHz, $CDCl_3$) δ = 16.51, 15.60.

HRMS (ESI) m/z $[C_{29}H_{33}ClO_3PRh+H]^+$ calcd. 599.0989, found 599.0990.

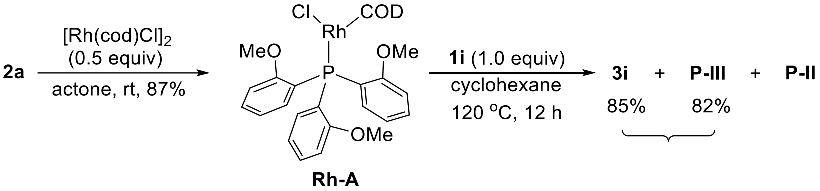


Figure S7. Stoichiometric experiment between **Rh-A** and **1i**

Stoichiometric experiment: **Rh-A** (50 mg) and benzoic acid **1i** (1.0 equiv) were added to a flame-dried Schlenk tube with a magnetic stir bar in 1.5 mL of cyclohexane, which was stirred at 120 ℃ for 12 h, resulting in **3i** in 85% yield and **P-II** in 82% yield.

6. Process of the Esterification of Various Aryl Acids via Rh-Catalyzed Cleavage of Me-O bond in $(2\text{-MeOPh})_3P$

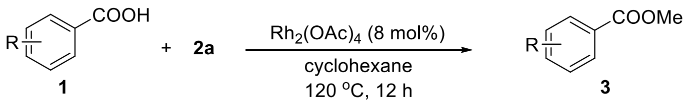


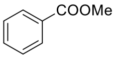
Figure S8. General procedure for the esterification of various acids

To a flame-dried Schlenck tube charged with a magnetic stir bar were added benzoic acid **1a-t** (0.1mmol), $(2\text{-MeOPh})_3P$ **2a** (0.12mmol) and $Rh_2(OAc)_4$ (8.0 mol%) in 1.0 mL of dry cyclohexane. The resulting suspension was stirred at 120 ℃ under N_2 for 12 h. When the reaction was complete (monitored by TLC), the organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layers were dried ($MgSO_4$), filtered, concentrated in vacuo, and purified by flash chromatography (1-5% ethyl acetate in petroleum ether) to afford pure products **3a-t** (58-91% yields).

Compounds ***3a***,[8] ***3b***,[9] ***3c***,[10] ***3d***,[11] ***3e***,[12] ***3f***,[12] ***3g***,[13] ***3h,***[14] ***3i***,[15] ***3j***,[16] ***3k,***[17] ***3l,***[14] ***3m,***[14] ***3n,***[14] ***3o,*** [17] ***3p,***[12] ***3q,***[12] ***3r,***[19] ***3s,***[18] ***3t***[19]***,*** *and* ***3rb***[14] *have previously been reported and their structure has been confirmed by comparison with the published spectral data.*

7. Experimental characterization data for products:

*methyl benzoate (***3a***)*

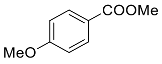


The title compound was prepared according to the general procedure as colorless oil (8.3 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 (d, *J* = 7.4 Hz, 2H), 7.58 (t, *J* = 6.7 Hz, 1H), 7.47 (t, *J* = 6.9 Hz, 2H), 3.95 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.11, 129.70, 129.41, 128.12, 77.40, 77.08, 76.76, 52.09.

*methyl 4-methoxybenzoate (***3b***)*

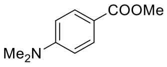


The title compound was prepared according to the general procedure as colorless oil (14.8 mg, 89%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (d, J = 8.5 Hz, 2H), 6.91 (d, J = 8.5 Hz, 2H), 3.88 (s, 3H), 3.84 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.88, 163.32, 131.59, 122.58, 113.59, 77.38, 77.06, 76.75, 55.41, 51.87.

*methyl 4-(dimethylamino)benzoate (***3c***)*

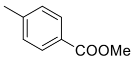


The title compound was prepared according to the general procedure as white solid (15.9 mg, 89%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 (d, *J* = 9.1 Hz, 2H), 6.69 (d, *J* = 9.0 Hz, 2H), 3.90 (s, 3H), 3.08 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.46, 153.25, 131.22, 116.96, 110.69, 77.38, 77.06, 76.74, 51.46, 40.01.

*methyl 4-methylbenzoate (***3d***)*

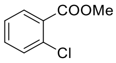


The title compound was prepared according to the general procedure as colorless oil (12.8 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 3.89 (s, 3H), 2.40 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.14, 143.50, 129.56, 129.03, 127.42, 77.33, 77.02, 76.70, 51.89, 21.60.

*methyl 2-chlorobenzoate (***3e***)*

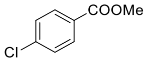


The title compound was prepared according to the general procedure as colorless oil (15.1 mg, 89%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.44 (dtd, *J* = 9.6, 8.0, 1.5 Hz, 2H), 7.32 (td, *J* = 7.5, 1.5 Hz, 1H), 3.95 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.12, 133.64, 131.37, 130.00, 77.44, 77.12, 76.80, 52.41.

*methyl 4-chlorobenzoate (***3f***)*

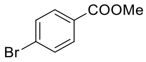


The title compound was prepared according to the general procedure as colorless oil (15.8 mg, 93%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 3.95 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.24, 139.37, 130.97, 128.71, 128.57, 77.36, 77.04, 76.73, 52.29.

*methyl 4-bromobenzoate (***3g***)*

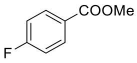


The title compound was prepared according to the general procedure as white solid (17.8 mg, 83%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 (d, *J* = 7.7 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 3.96 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.40, 131.89, 131.72, 131.12, 129.03, 128.06, 77.34, 77.02, 76.71, 52.

*methyl 4-fluorobenzoate (***3h***)*

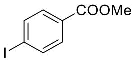


The title compound was prepared according to the general procedure as light yellow oil (10.8 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 – 8.00 (m, 2H), 7.09 (dd, *J* = 9.6, 7.8 Hz, 2H), 3.90 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.00, 132.25, 132.16, 132.05, 131.93, 126.37, 52.06.

*methyl 4-iodobenzoate (***3i***)*

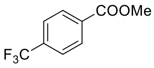


The title compound was prepared according to the general procedure as white solid (23.8 mg, 91%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84 (d, *J* = 8.6 Hz, 2H), 7.78 (d, *J* = 8.6 Hz, 2H), 3.95 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.59, 137.72, 131.03, 129.59, 100.75, 77.37, 77.05, 76.74, 52.31.

*methyl 4-(trifluoromethyl)benzoate (***3j***)*

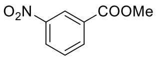


The title compound was prepared according to the general procedure as colorless oil (11.8 mg, 58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.11 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 3.92 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.74, 134.50, 134.17, 133.30, 129.89, 125.29 (q, *J* = 3.8 Hz), 77.30, 76.98, 76.66, 52.36.

*methyl 3-nitrobenzoate (***3k***)*

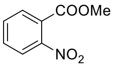


The title compound was prepared according to the general procedure as colorless oil (14.7 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.84 (s, 1H), 8.40 (dd, *J* = 19.0, 7.7 Hz, 2H), 7.68 (t, *J* = 7.9 Hz, 1H), 4.00 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.85, 148.19, 135.19, 131.79, 131.69, 129.61, 127.30, 124.46, 77.39, 77.08, 76.76, 52.75, 52.70.

*methyl 2-nitrobenzoate (***3l***)*

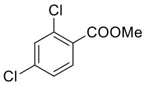


The title compound was prepared according to the general procedure as colorless oil (15.4 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.96 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.79 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.75 – 7.65 (m, 2H), 3.97 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.90, 132.95, 131.79, 129.86, 127.57, 123.94, 77.36, 77.04, 76.73, 53.30.

*methyl 2,4-dichlorobenzoate (***3m***)*

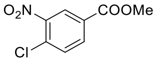


The title compound was prepared according to the general procedure as colorless oil (17.6 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.82 (d, *J* = 8.4 Hz, 1H), 7.48 (s, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 3.94 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.16, 138.32, 134.93, 132.53, 130.99, 128.13, 126.98, 77.41, 77.09, 76.77, 52.56.

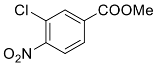
*methyl 4-chloro-3-nitrobenzoate (***3n***)*



The title compound was prepared according to the general procedure as white solid (18.8 mg, 87%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.56 (s, 1H), 8.21 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 4.02 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.12, 133.54, 132.15, 131.54, 130.02, 126.51, 77.38, 77.06, 76.74, 52.91.

*methyl 3-chloro-4-nitrobenzoate (***3o***)*

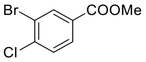


The title compound was prepared according to the general procedure as light yellow solid (19.0 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.22 (d, *J* = 1.7 Hz, 1H), 8.08 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 4.00 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.09, 150.44, 134.36, 133.08, 128.76, 127.09, 125.39, 77.39, 77.07, 76.75, 53.07.

*methyl 3-bromo-4-chlorobenzoate (***3p***)*

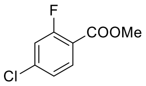


The title compound was prepared according to the general procedure as colorless oil (20.5 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.32 (d, *J* = 1.9 Hz, 1H), 7.94 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 3.97 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.07, 139.52, 134.95, 129.95, 122.64, 77.36, 77.04, 76.72, 52.57.

*methyl 4-chloro-2-fluorobenzoate (***3q***)*

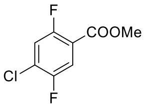


The title compound was prepared according to the general procedure as colorless oil (15.1 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.90 (t, *J* = 8.1 Hz, 1H), 7.24 – 7.14 (m, 2H), 3.94 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.01, 163.97, 163.07, 160.44, 139.94, 133.02, 77.40, 77.08, 76.76, 52.42.

*methyl 4-chloro-2,5-difluorobenzoate (***3r***)*

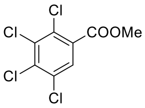


The title compound was prepared according to the general procedure as colorless oil (15.5 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78 – 7.69 (m, 1H), 7.26 (dd, *J* = 9.1, 5.9 Hz, 1H), 3.96 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.04, 162.99, 158.60, 156.01, 155.21, 152.76, 119.03, 52.70.

*methyl 2,3,4,5-tetrachlorobenzoate (***3s***)*

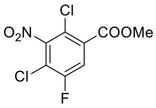


The title compound was prepared according to the general procedure as white solid (24.9 mg, 91%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86 (s, 1H), 3.99 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.04, 136.25, 135.07, 132.26, 131.83, 130.48, 129.63, 77.34, 77.02, 76.70, 53.07.

*methyl 2,4-dichloro-5-fluoro-3-nitrobenzoate (***3t***)*

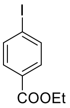


The title compound was prepared according to the general procedure as colorless oil (16.3 mg, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.87 – 7.80 (m, 1H), 4.03 – 3.91 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.62, 157.60, 155.06, 130.64, 130.57, 119.98, 119.74, 77.33, 77.02, 76.70, 53.38.

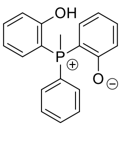
*ethyl 4-iodobenzoate (***3ib***)*



The title compound was prepared according to the general procedure as colorless oil (72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.80 (d, *J* = 8.7 Hz, 2H), 7.75 (d, *J* = 8.6 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H).

2-((2-hydroxyphenyl)(methyl)(phenyl)phosphonio)phenolate (**P-I**)



The title compound was prepared according to the general procedure as white solid (26.5 mg, 86%).

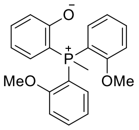
^{1}H NMR(400 MHz, DMSO) δ = 7.67 (dd, *J* = 20.5, 7.4 Hz, 6H), 7.36 (t, *J* = 7.7 Hz, 2H), 6.88 (dd, *J* = 14.6, 7.6 Hz, 2H), 6.66 (t, *J* = 7.2 Hz, 3H), 2.76 (d, *J* = 14.9 Hz, 3H).

^{13}C NMR(101 MHz, DMSO) δ = 167.39, 167.23, 136.84, 136.21, 134.39, 134.28, 133.35, 132.62, 132.51, 131.71, 129.76, 129.63, 118.72, 116.38, 116.31, 116.15, 104.84, 103.91, 40.40, 40.18, 39.97, 39.76, 39.54.

^{31}P NMR (101 MHz, DMSO) δ = 57.09, 56.33, 18.79, 16.51.

HRMS (ESI) m/z $[C_{19}H_{17}O_2P+H]^+$ calcd. 309.1044, found 309.1040.

*2-(bis(2-methoxyphenyl)(methyl)phosphonio)phenolate (*__P-II__)



The title compound was prepared according to the general procedure as white solid with 5% yield.

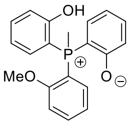
^{1}H NMR (400 MHz, DMSO) δ = 7.85 – 7.70 (m, 3H), 7.24 – 7.13 (m, 3H), 7.13 – 7.07 (m, 3H), 6.97 – 6.85 (m, 3H), 3.79 (s, 6H), 2.63 (d, J = 15.2 Hz, 3H).

^{13}C NMR (100 MHz, DMSO) δ = 161.69, 161.66, 137.42, 137.40, 134.37, 134.28, 129.79, 129.77, 129.75, 122.19, 122.06, 112.70, 112.63, 106.46, 105.52, 56.27, 11.85, 11.23.

^{31}P NMR(101 MHz, DMSO) δ = 20.09.

HRMS (ESI) m/z $[C_{21}H_{21}O_3P+H]^+$ calcd. 353.1307, found 353.1304.

*2-((2-hydroxyphenyl)(2-methoxyphenyl)(methyl)phosphonio)phenolate (*__P-III__*)*



The title compound was prepared according to the general procedure as white solid (30.1 mg, 89%).

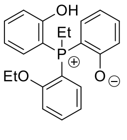
^{1}H NMR (400 MHz, DMSO) δ = 7.87 – 7.68 (m, 1H), 7.46 – 7.31 (m, 3H), 7.17 (dd, *J* = 12.1, 7.4 Hz, 2H), 6.99 – 6.54 (m, 6H), 3.76 (s, 3H), 2.71 (dd, *J* = 15.6, 8.4 Hz, 3H).

^{13}C NMR (100 MHz, DMSO) δ = 173.36, 166.22, 165.95, 165.09, 161.93, 136.83, 135.22, 134.86, 134.05, 131.69, 121.93, 118.86, 117.91, 113.78, 109.53, 107.89, 105.11, 103.64, 101.90, 56.71, 52.28.

^{31}P NMR(101 MHz, DMSO) δ = 18.50, 17.69.

HRMS (ESI) m/z $[C_{20}H_{19}O_3P+H]^+$ calcd. 339.1150, found 339.1142.

*2-((2-ethoxyphenyl)(ethyl)(2-hydroxyphenyl)phosphonio)phenolate (*__P-IV__*)*



The title compound was prepared according to the general procedure as light yellow solid (21.9 mg, 65%).

^{1}H NMR (400 MHz, DMSO) δ 7.86 – 7.61 (m, 3H), 7.48 – 7.35 (m, 3H), 7.31 – 7.11 (m, 3H), 7.06 – 6.55 (m, 3H), 4.14 – 3.97 (m, 2H), 3.19 – 3.02 (2, 2H), 1.13 (dt, J = 21.5, 7.6 Hz, 3H), 0.97 (t, J = 6.9 Hz, 3H).

^{31}PNMR (101 MHz, DMSO) δ = 25.30.

HRMS (ESI) m/z $[C_{22}H_{23}O_3P+H]^+$ calcd. 367.1463, found 367.1453**.**

References:

[1] Nishina, N.; Yamamoto, Y.*Synlett*, **2007**, *11*, 1767-1770.

[2] Muller, A.; Otto, S.; Roodt, A. *Dalton. Trans*, **2008**, *5*, 650-657.

[3] Alvarez, R.; Mehl, G. H.; *Liquid crystals*, **2005**, *32*, 469-476.

[4] Xiao, Y.; Xu, Y.; Cheon, H. S. *J. org. chem*, **2013**, *78*, 5804-5809.

[5] Maurya, R. A.; Park, C. P.; Lee, J. H. *Angew. Chem. Int. Ed*, **2011**, *50*, 5952-5955.

[6] Takeda, N.; Tagawa, T.; Unno, M. *Heteroatom. Chem*, **2014**, *25*, 628-635.

[7] Tiburcio, J.;*Polyhedron*,**2006**,*25*,1549-1554.

[8] Liu, Q.; Lan, Y.; Lei, A. *J. Am. Chem. Soc*, **2009**, *131*, 10201-10210.

[9] Gao, H. Y.; Ha, C. Y.;*Synthetic commun*, **2006**, *36*, 3283-3286.

[10] Yamamoto, Y. *Adv. Synth. Catal*, **2010**, *352*, 478-492.

[11] Won, J. E.; Kim, H. K.;Yoon, Y. J.*Tetrahedron*, **2007**, *63*, 12720-12730.

[12] Dawar, P.; Raju, M. B.; Ramakrishna, R. A. *Tetrahedron. Lett*, **2011**, *52*, 4262-4265.

[13] Irfan, M.; Glasnov, T. N.; Kappe, C. O. *Org. lett*, **2011**, *13*, 984-987.

[14] Zhang, X.; Chen, Z. K.; Loh, K. P. *J. Am. Chem. Soc*, **2009**, *131*, 7210-7211.

[15] Liu, C.; Wang, J.; Lei, A.*Angew. Chem. Int. Ed*, **2011**, *123*, 5250-5254.

[16] Wang, Z.; Kang, J.; Yu, M. *J. Chem. Res*, **2007**, 2007, 323-324.

[17] Haydon, D. J.; Bennett, J. M.; Brown, D.*J. med. chem*, **2010**, *53*, 3927-3936.

[18] Sorna, V.; Theisen, E. R.; Stephens, B.*J. med. chem*, **2013**, *56*, 9496-9508.

[19] Boyarskiy, V. P.; Fonari, M. S.*J. Fluorine. Chem*, **2010**, *131*, 81-85.

8. ^{1}H and ^{13}C NMR spectra for all compounds

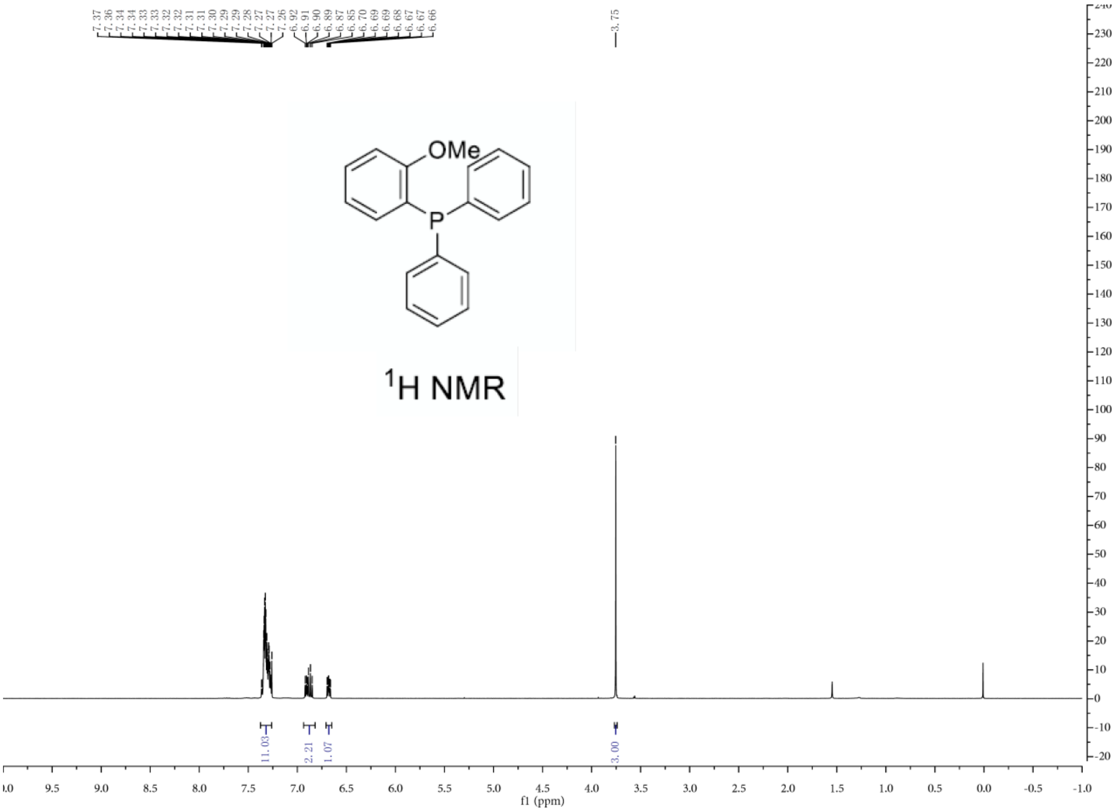


Figure S9. ^{1}H NMR of **2d** $CDCl_3$ at RT

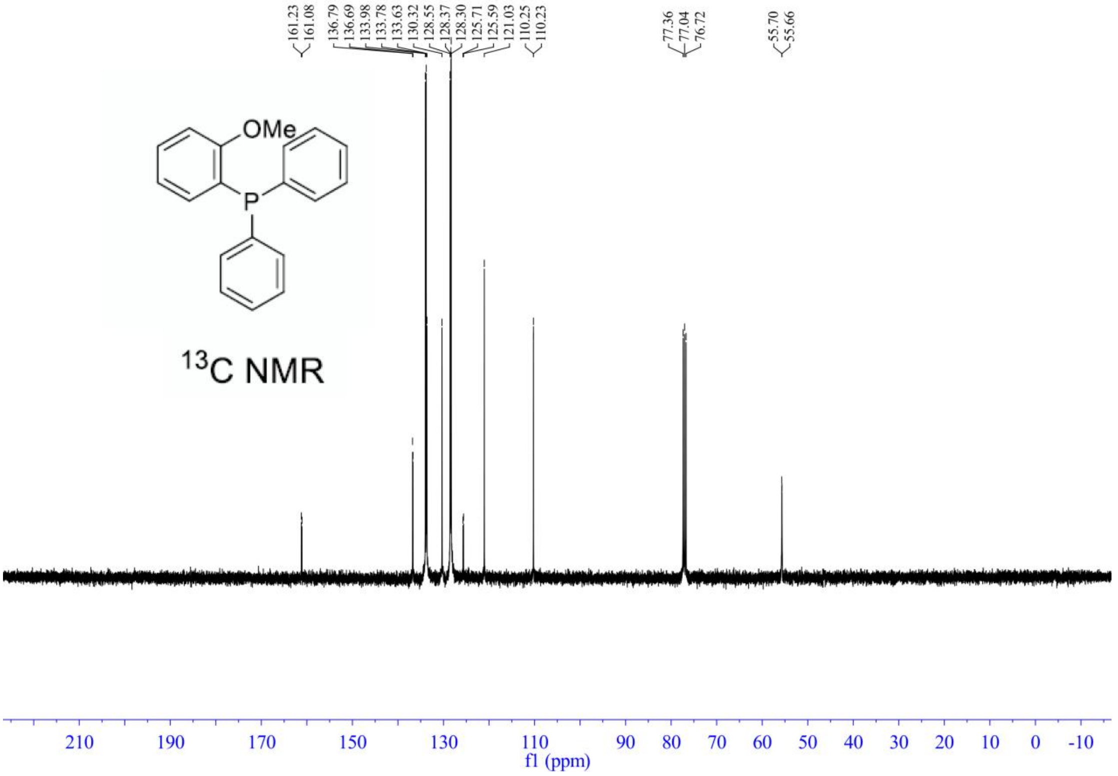


Figure S10. ^{13}C NMR of **2d** $CDCl_3$ at RT

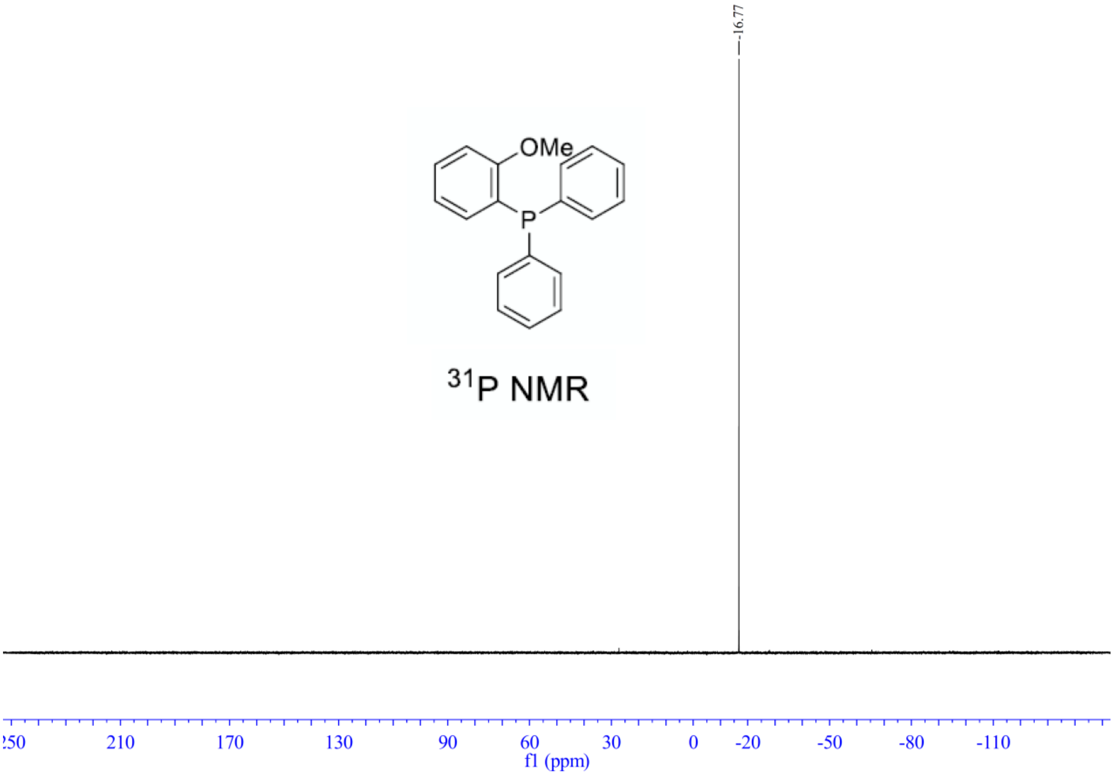


Figure S11. ^{31}P NMR of **2d** $CDCl_3$ at RT

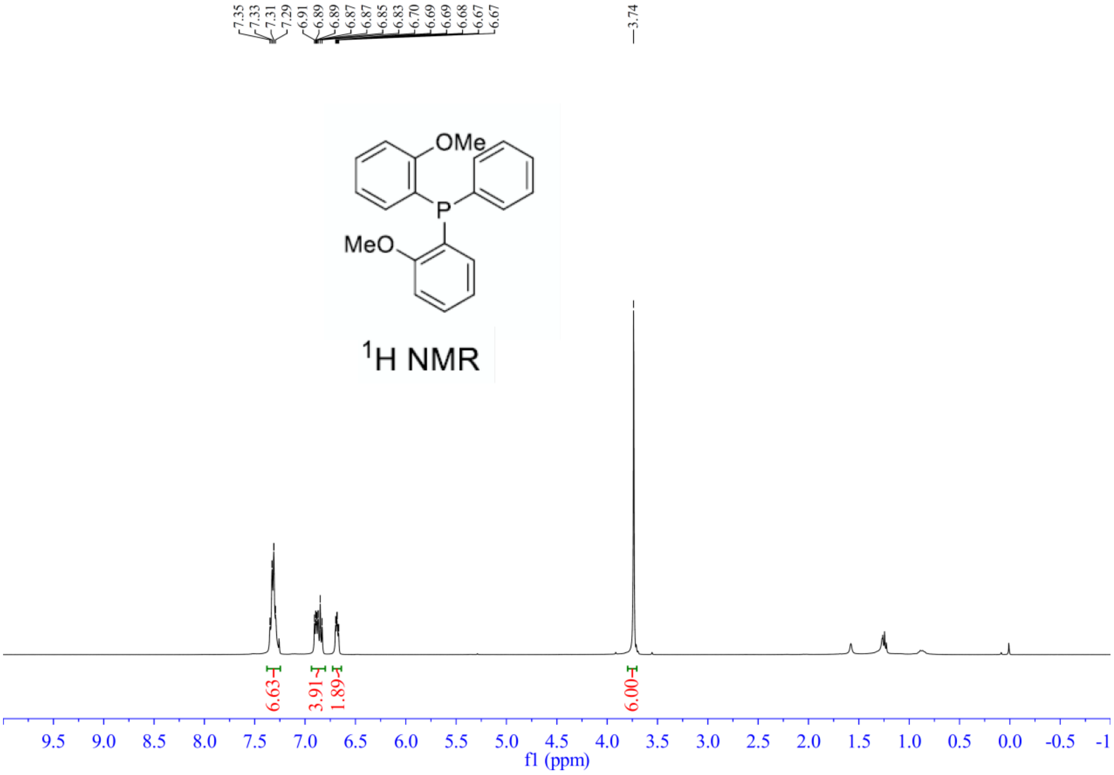


Figure S12. ^{1}H NMR of **2e** $CDCl_3$ at RT

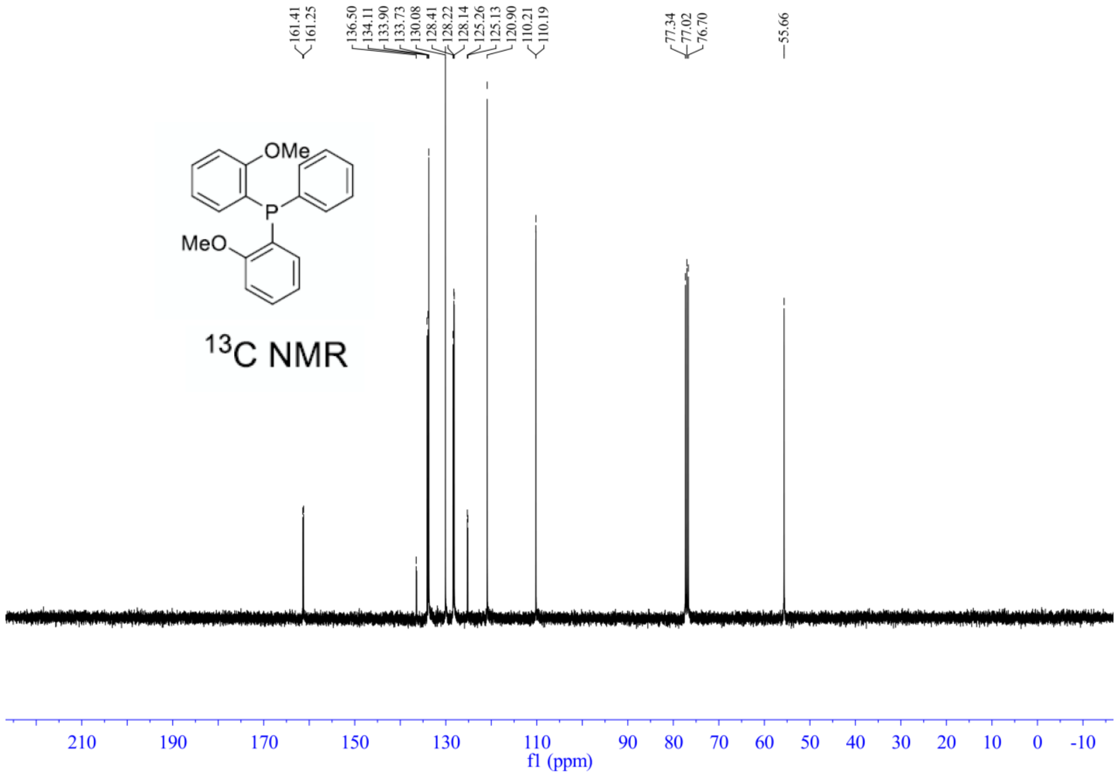


Figure S13. ^{13}C NMR of **2e** $CDCl_3$ at RT

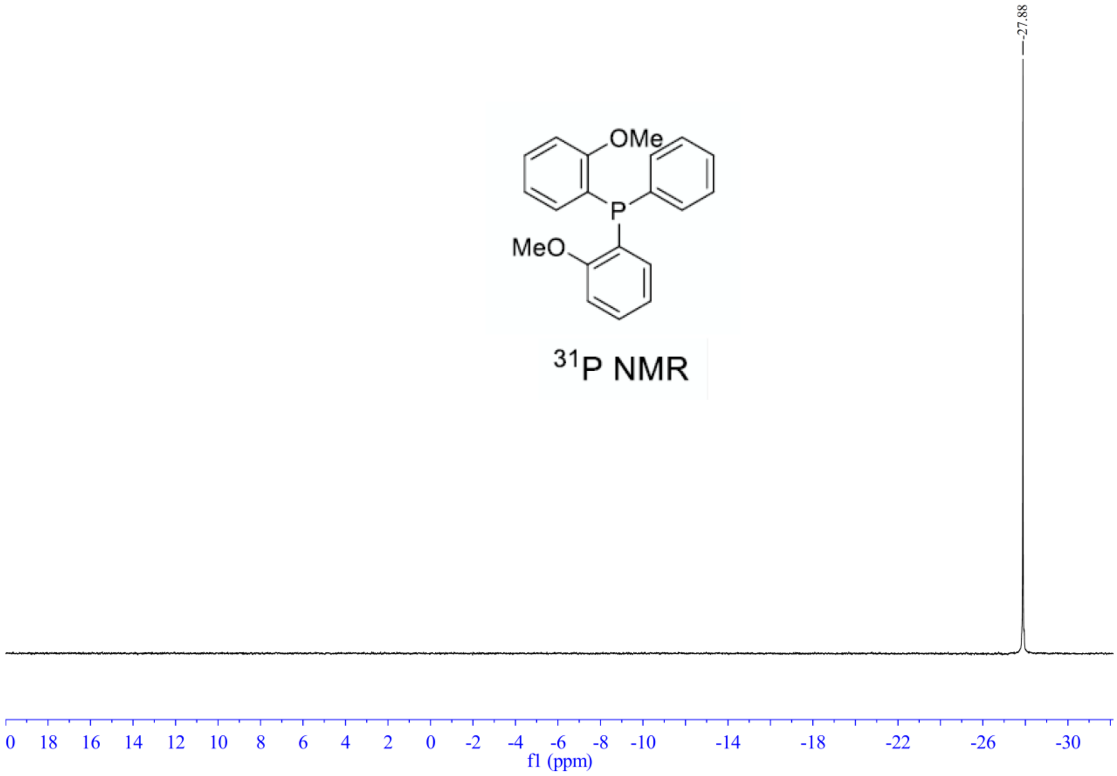


Figure S14. ^{31}P NMR of **2e** $CDCl_3$ at RT

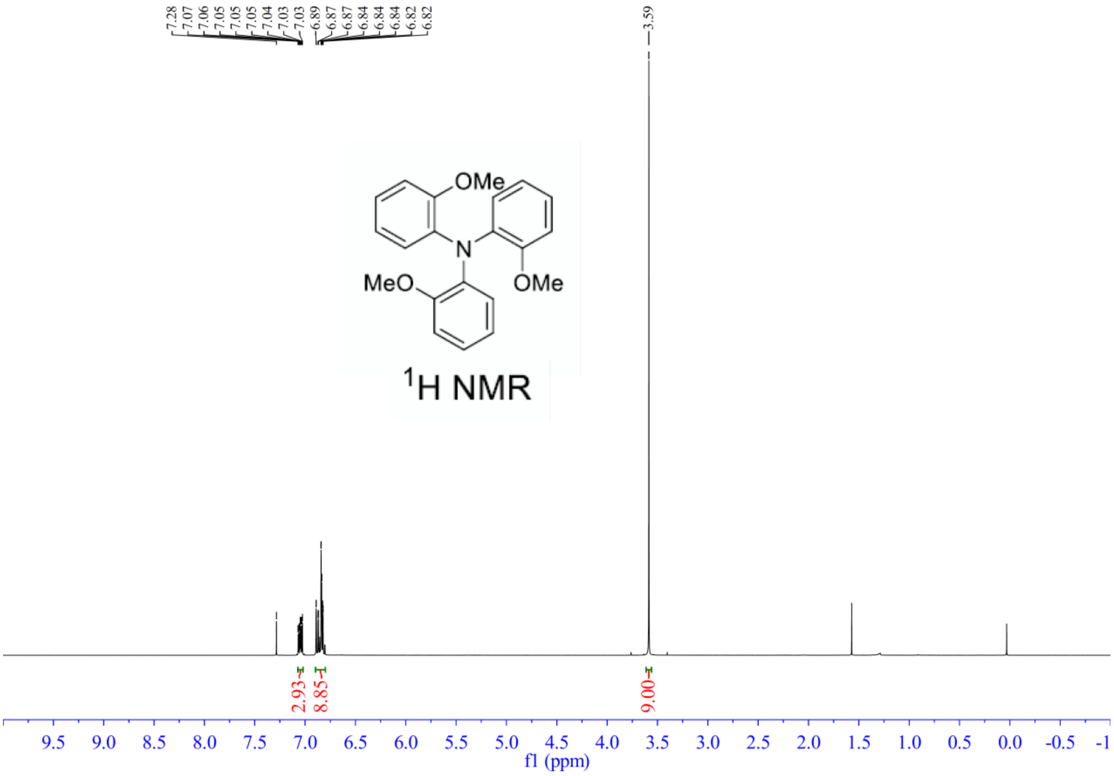


Figure S15. ^{1}H NMR of **2f** $CDCl_3$ at RT

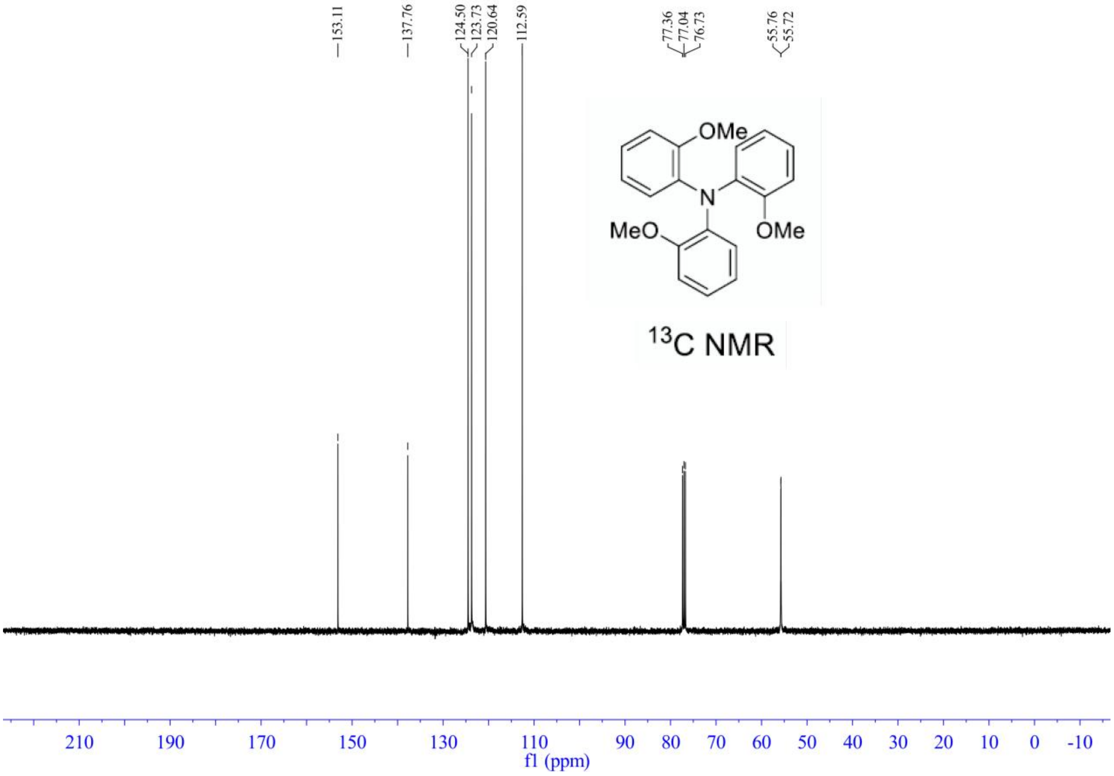


Figure S16. ^{13}C NMR of **2f** $CDCl_3$ at RT

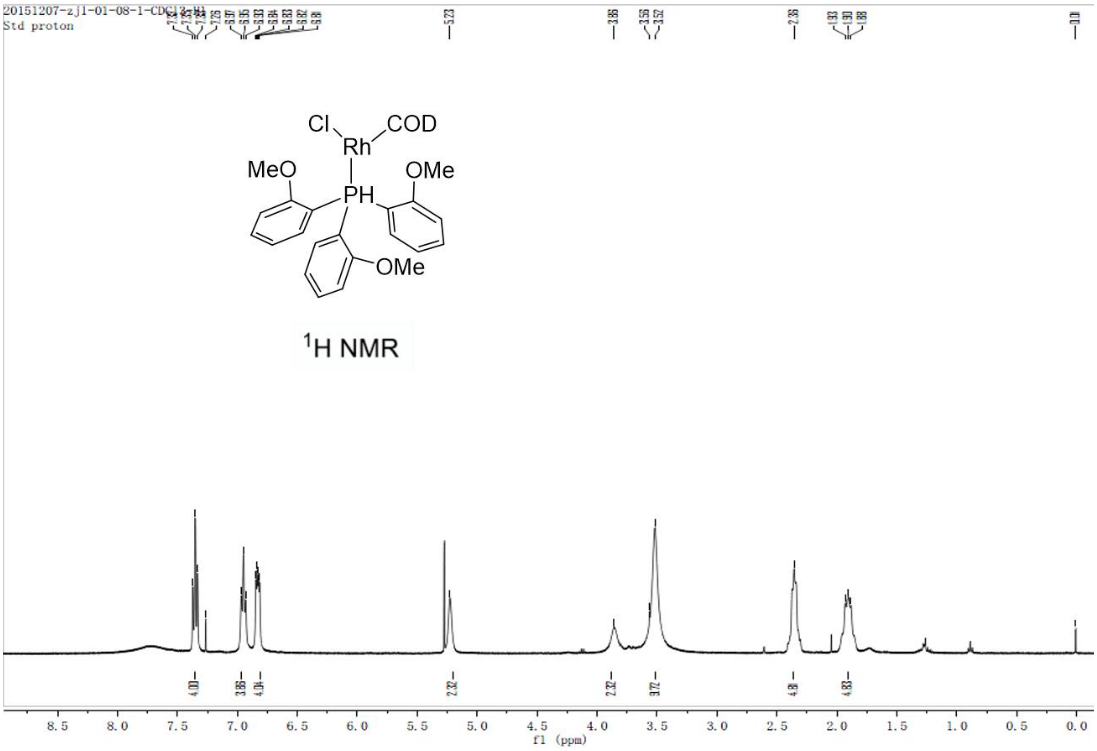


Figure S17. ^{1}H NMR of **Rh-A** CDCl$_3$ at RT

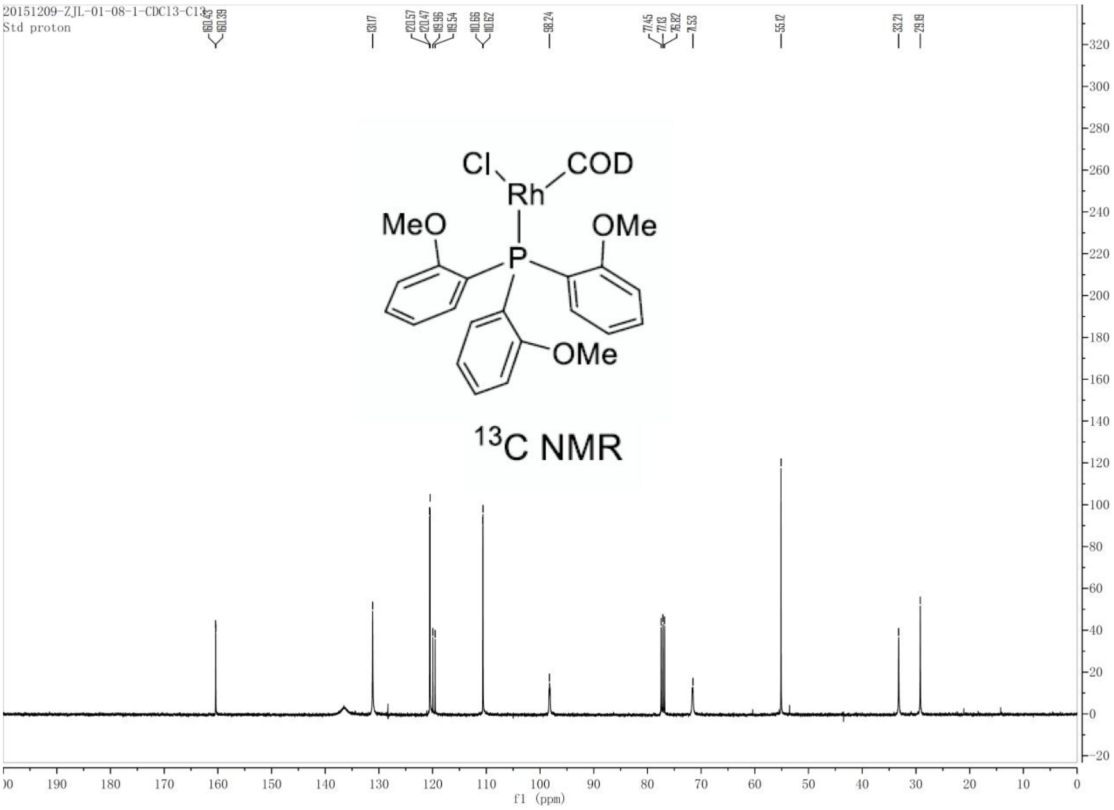


Figure S18. ^{13}C NMR of **Rh-A** CDCl$_3$ at RT

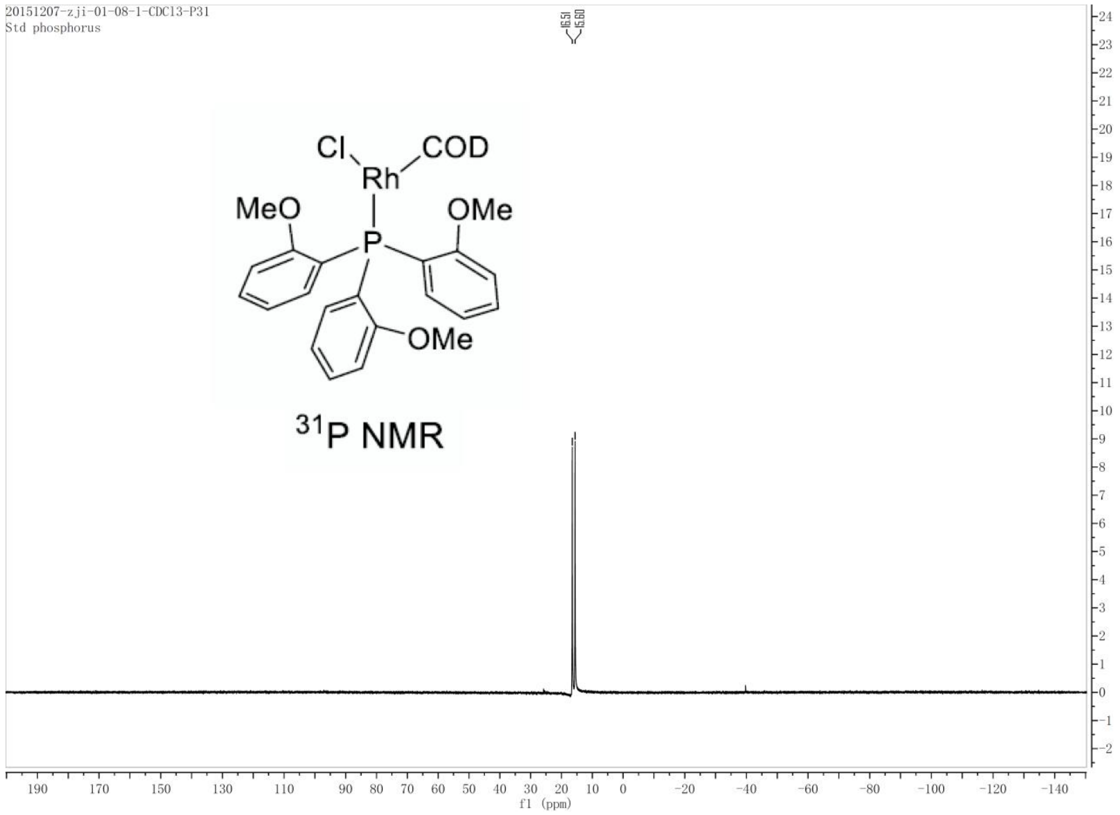


Figure S19. ^{31}P NMR of **Rh-A** CDCl$_3$ at RT

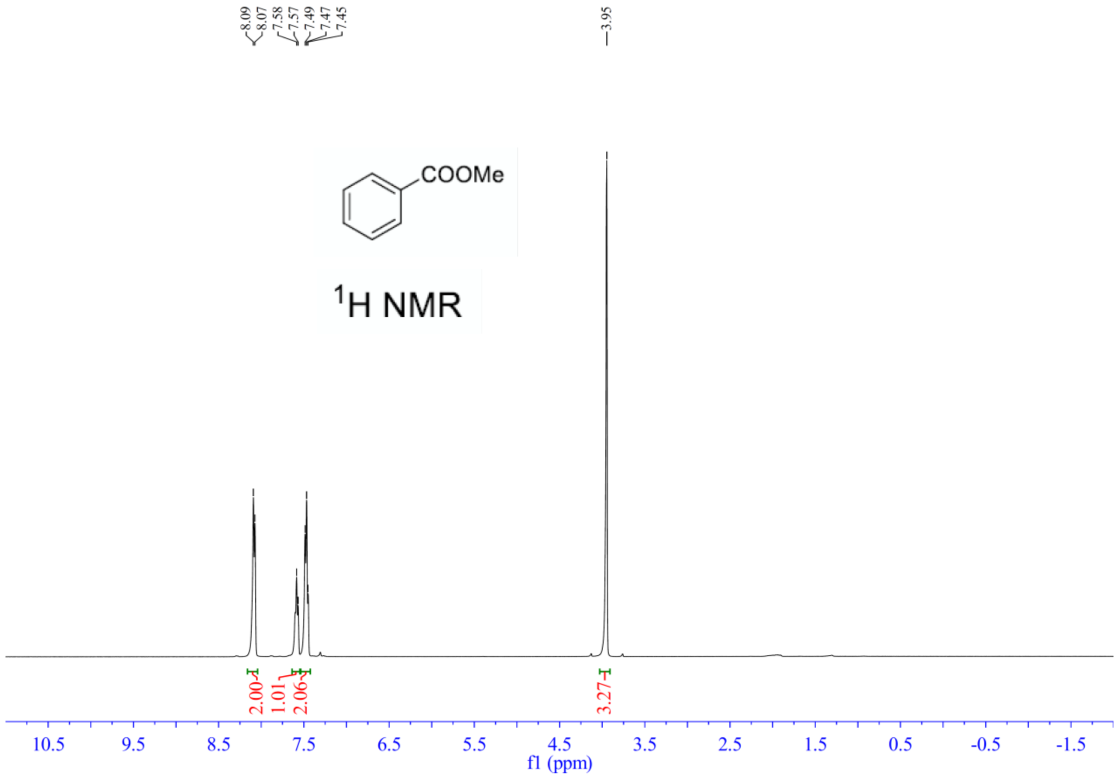


Figure S20. ^{1}H NMR of **3a** CDCl$_3$ at RT

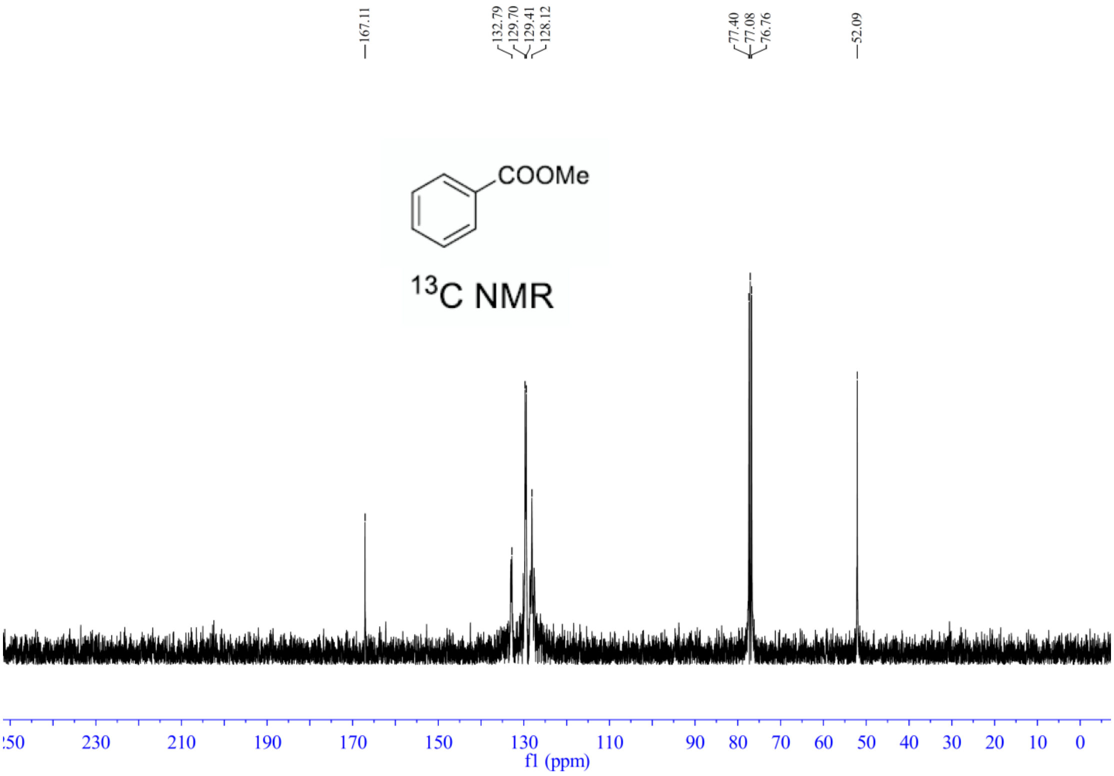


Figure S21. ^{13}C NMR of **3a** $CDCl_3$ at RT

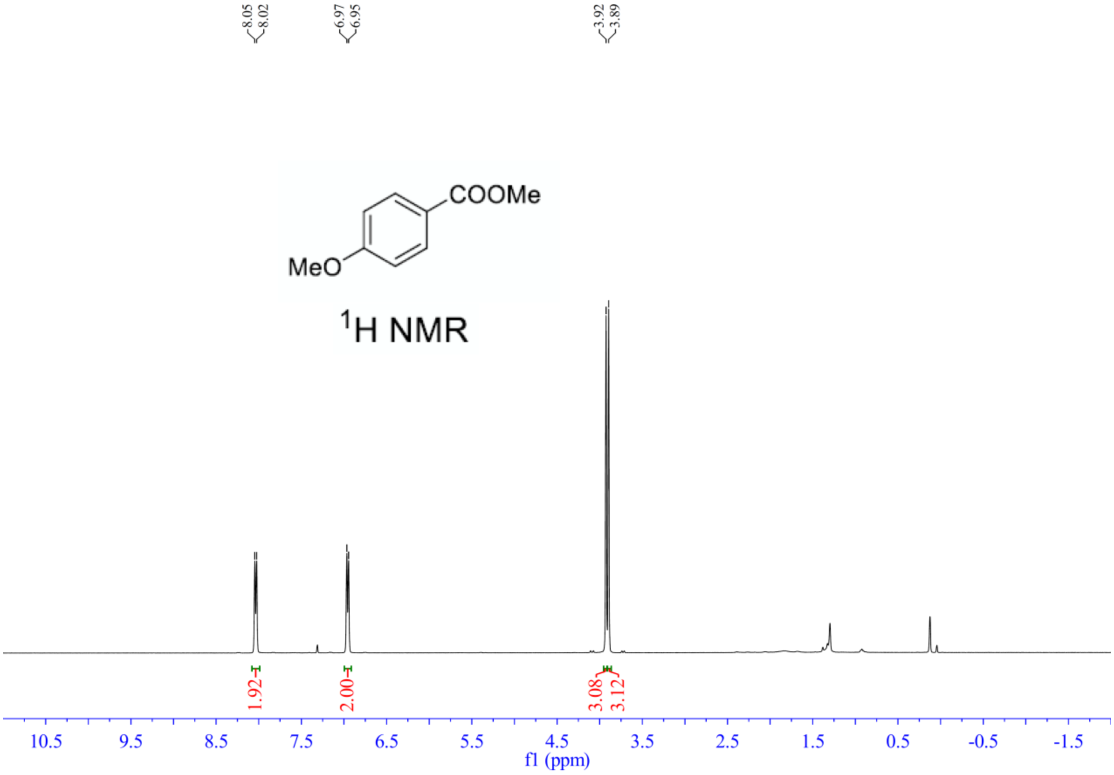


Figure S22. ^{1}H NMR of **3b** $CDCl_3$ at RT

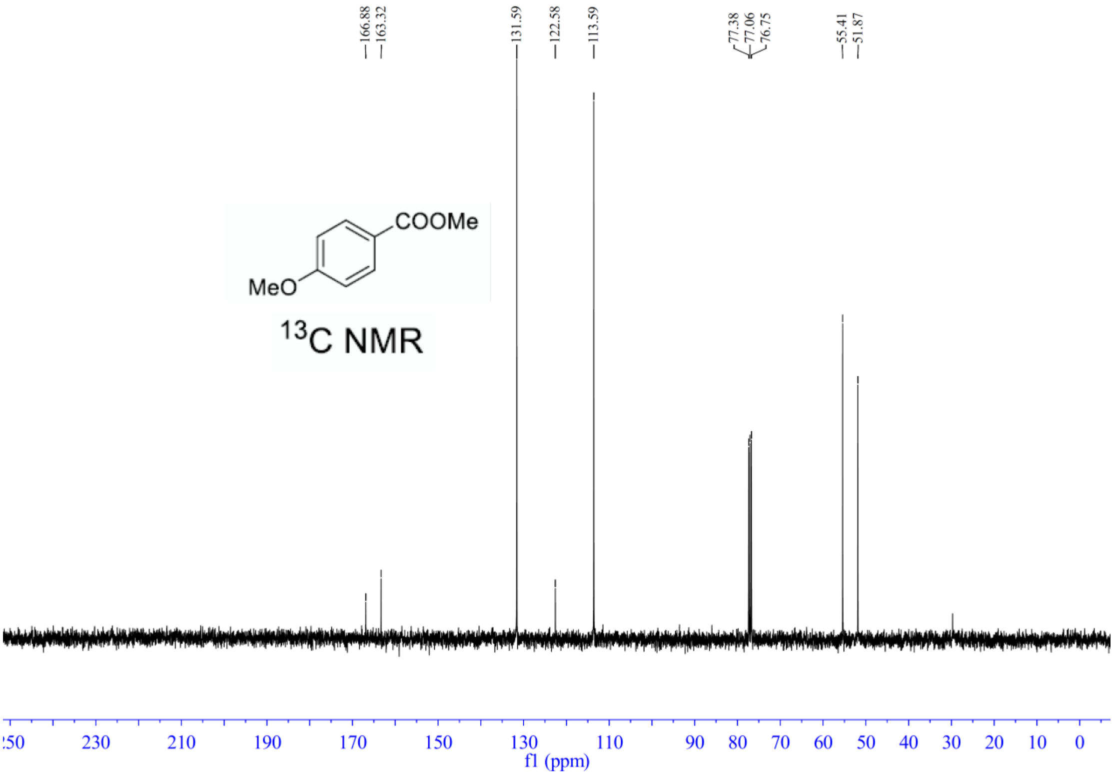


Figure S23. ^{13}C NMR of **3b** $CDCl_3$ at RT

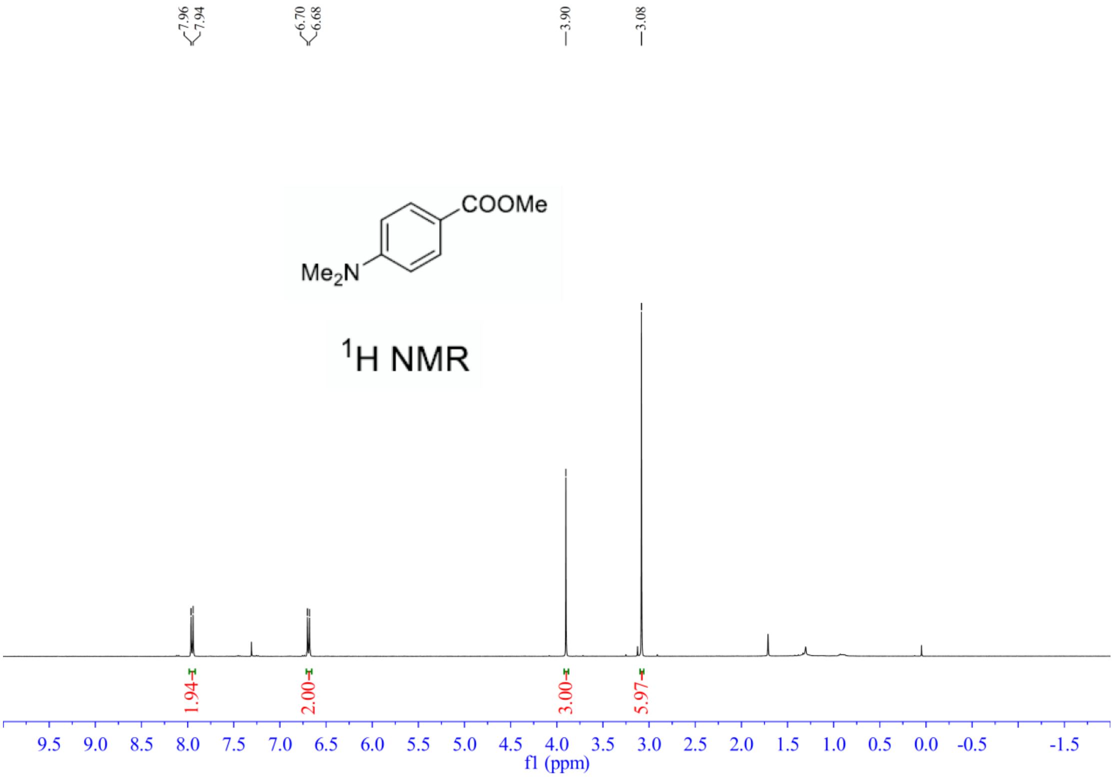


Figure S24. ^{1}H NMR of **3c** $CDCl_3$ at RT

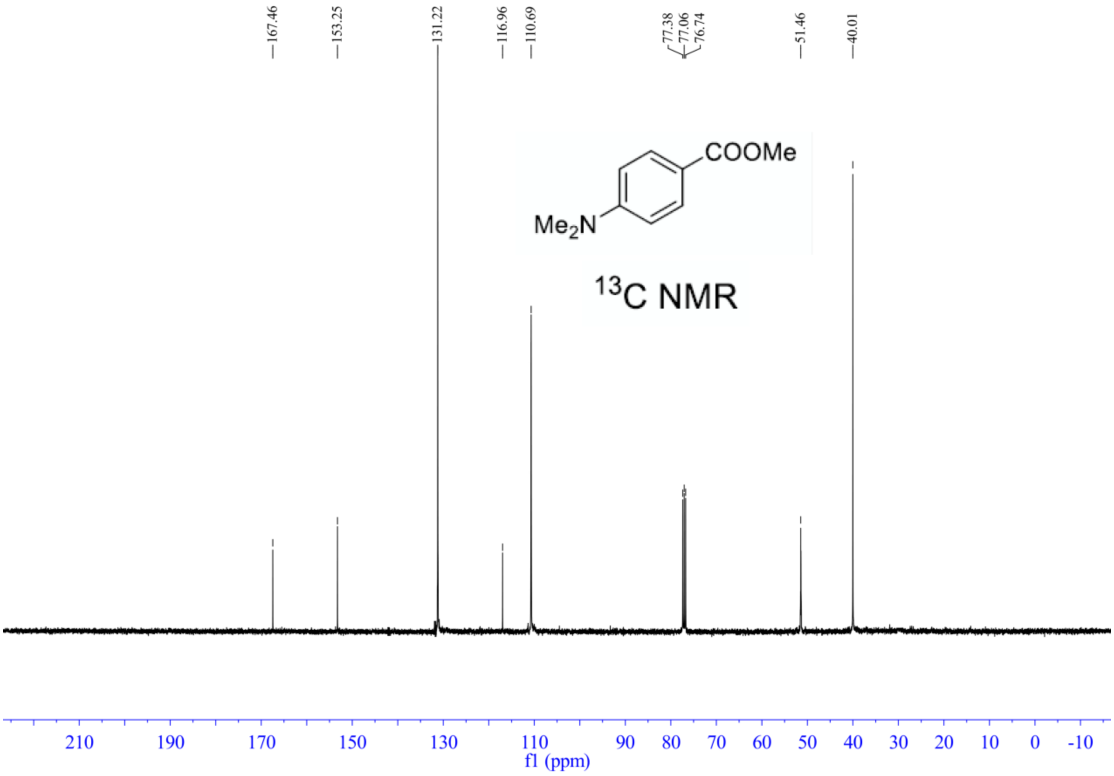


Figure S25. ^{13}C NMR of **3c** $CDCl_3$ at RT

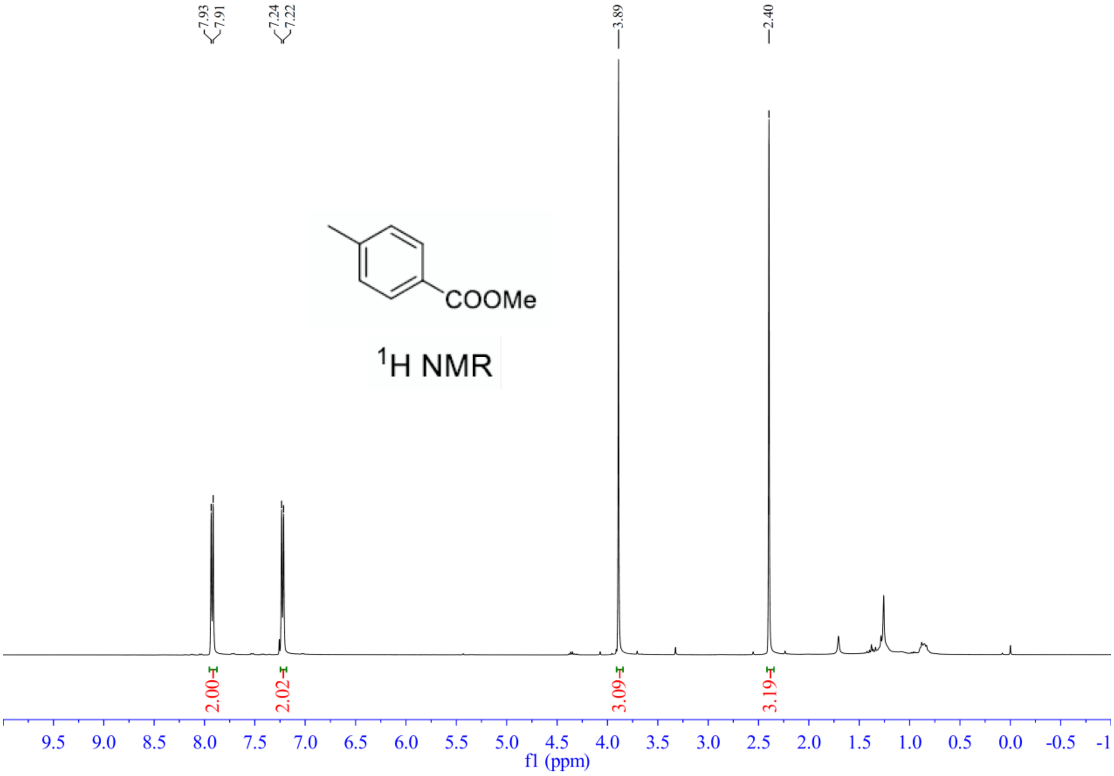


Figure S26. ^{1}H NMR of **3d** $CDCl_3$ at RT

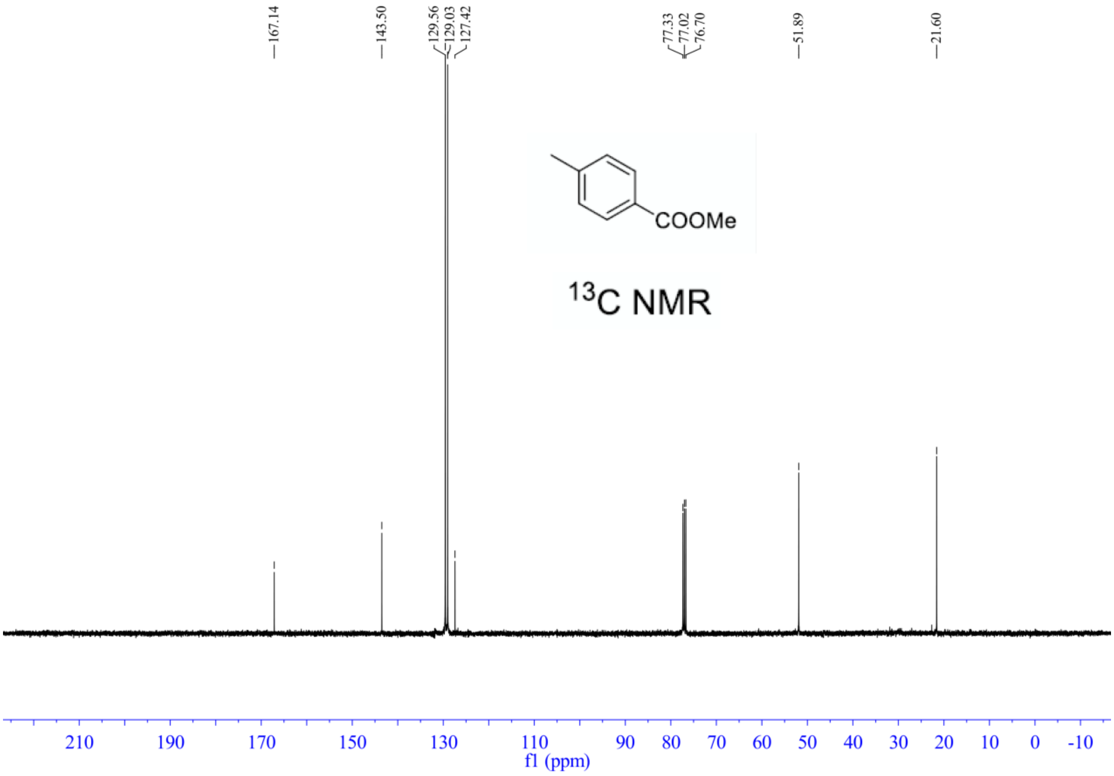


Figure S27. ^{13}C NMR of **3d** $CDCl_3$ at RT

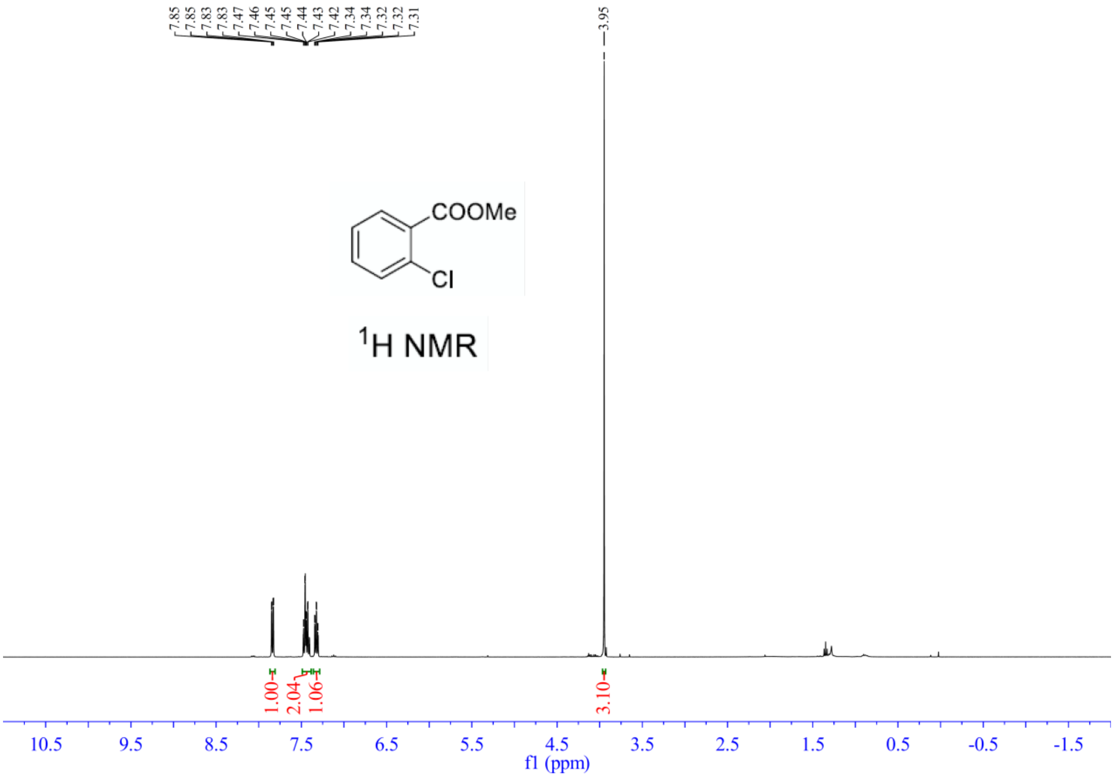


Figure S28. ^{1}H NMR of **3e** $CDCl_3$ at RT

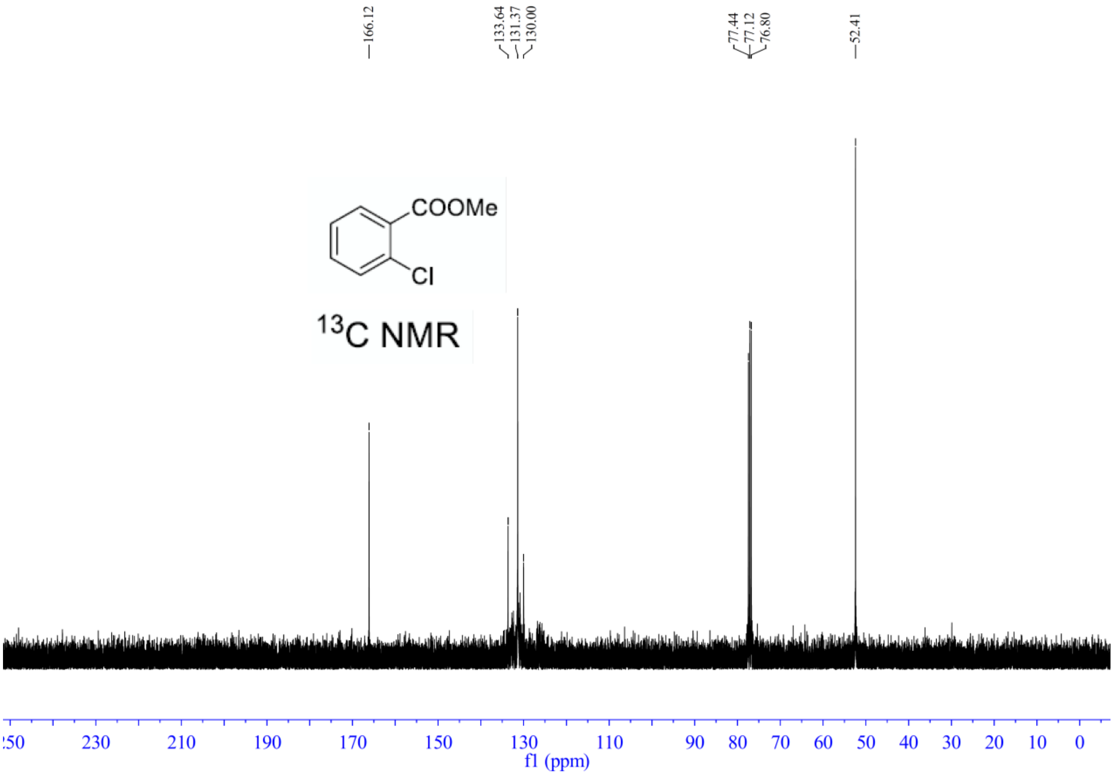


Figure S29. ^{13}C NMR of **3e** $CDCl_3$ at RT

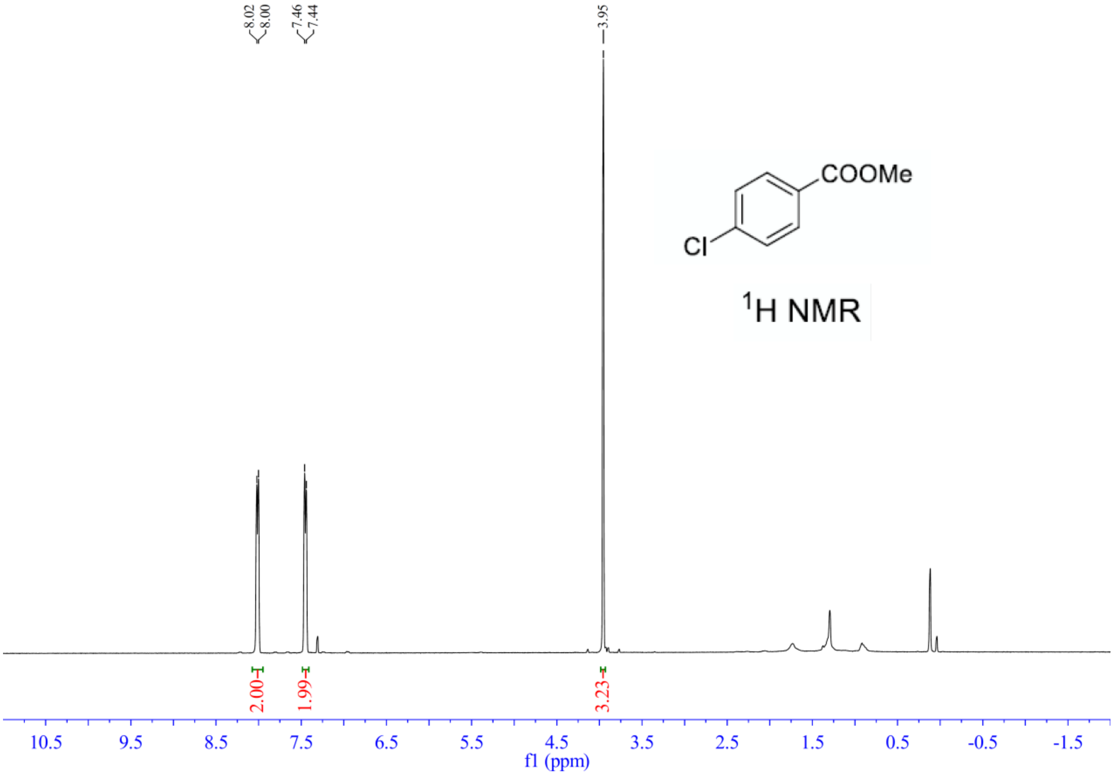


Figure S30. ^{1}H NMR of **3f** $CDCl_3$ at RT

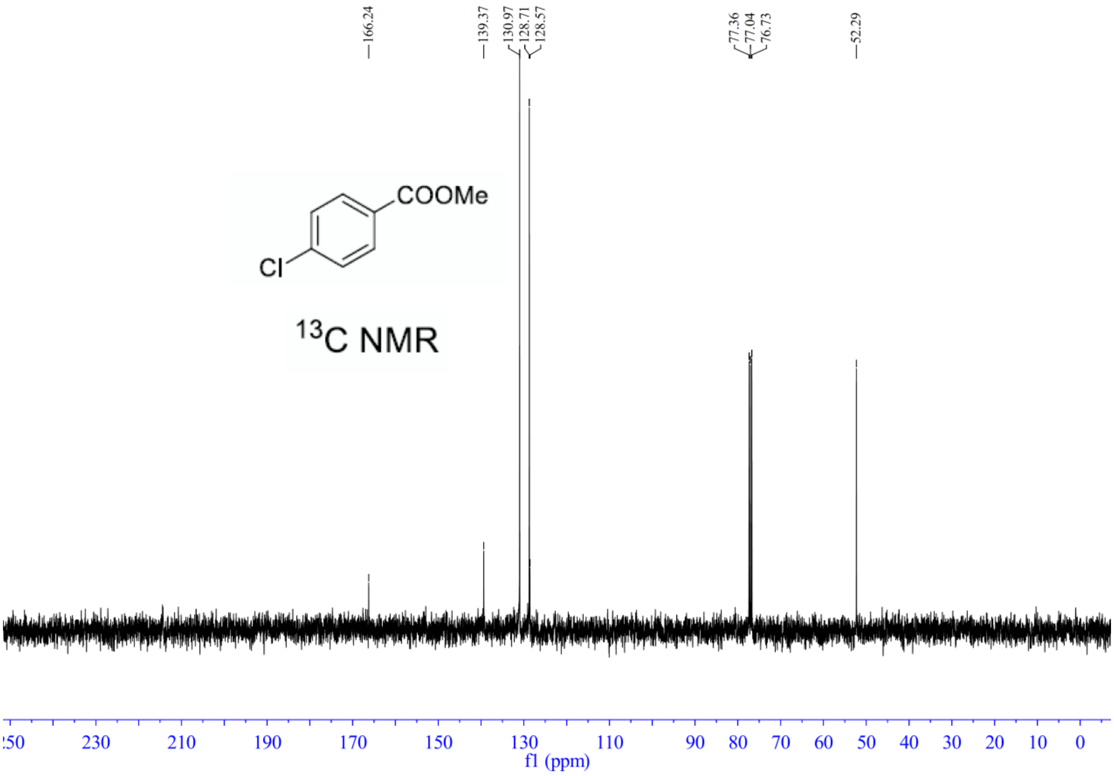


Figure S31. ^{13}C NMR of **3f** CDCl$_3$ at RT

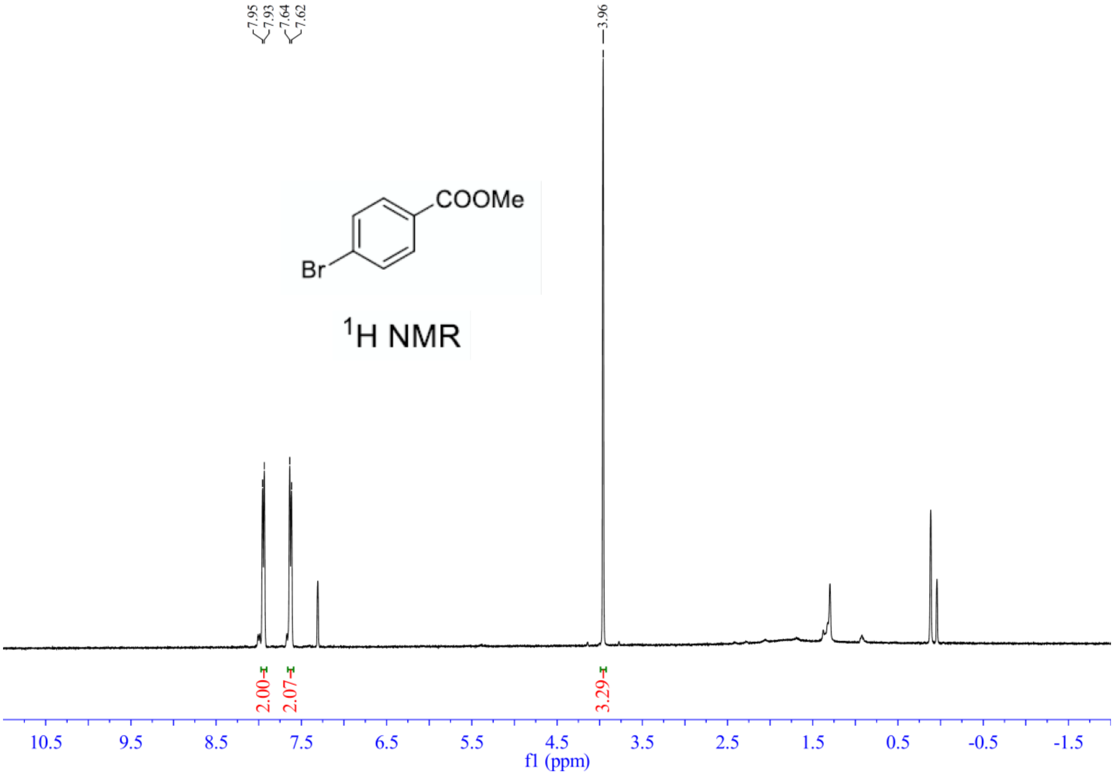


Figure S32. ^{1}H NMR of **3g** CDCl$_3$ at RT

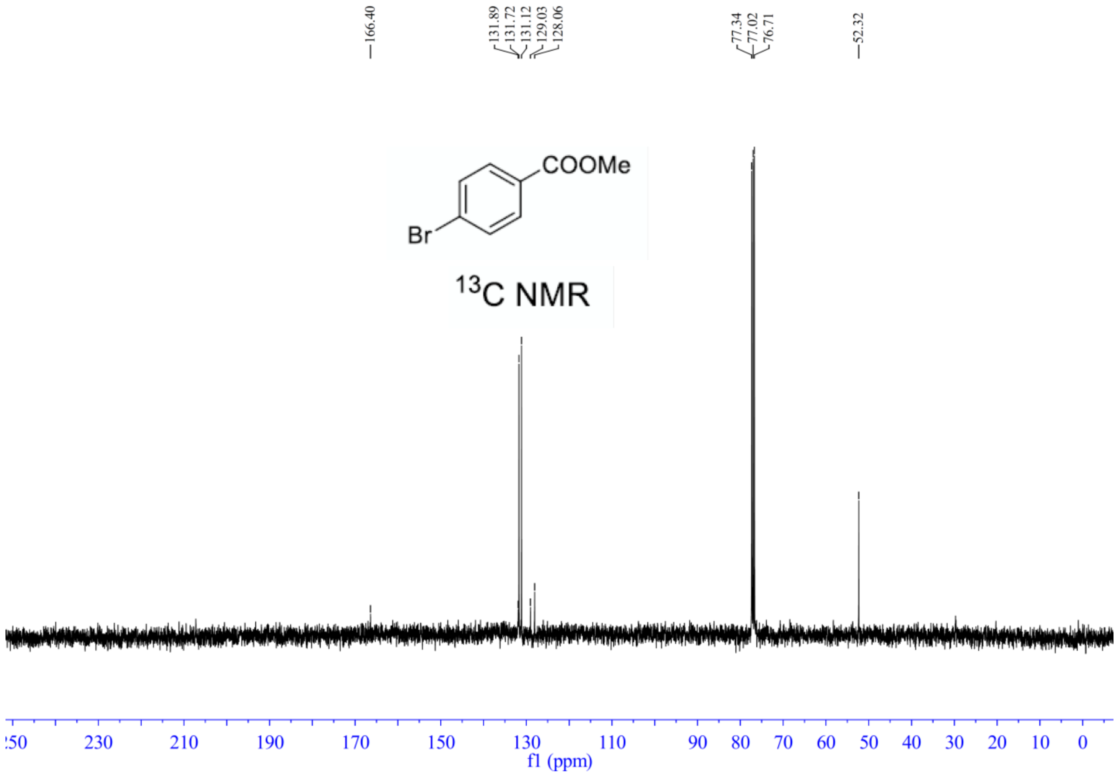


Figure S33. ^{13}C NMR of **3g** $CDCl_3$ at RT

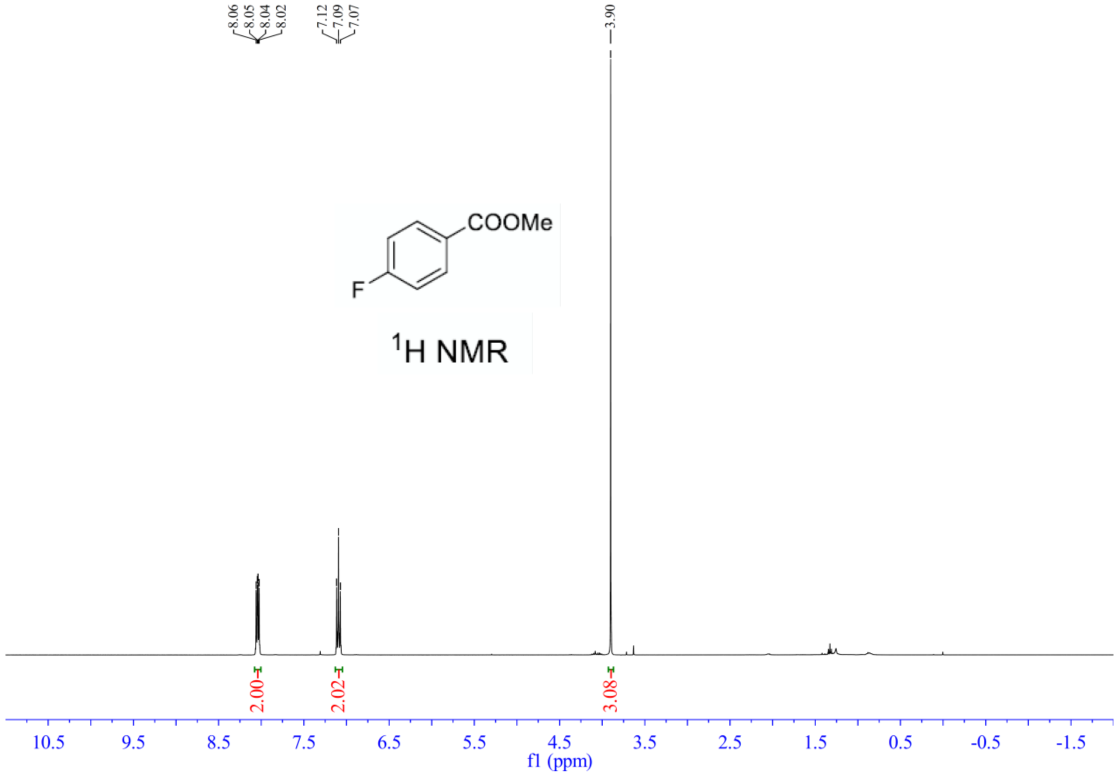


Figure S34. ^{1}H NMR of **3h** $CDCl_3$ at RT

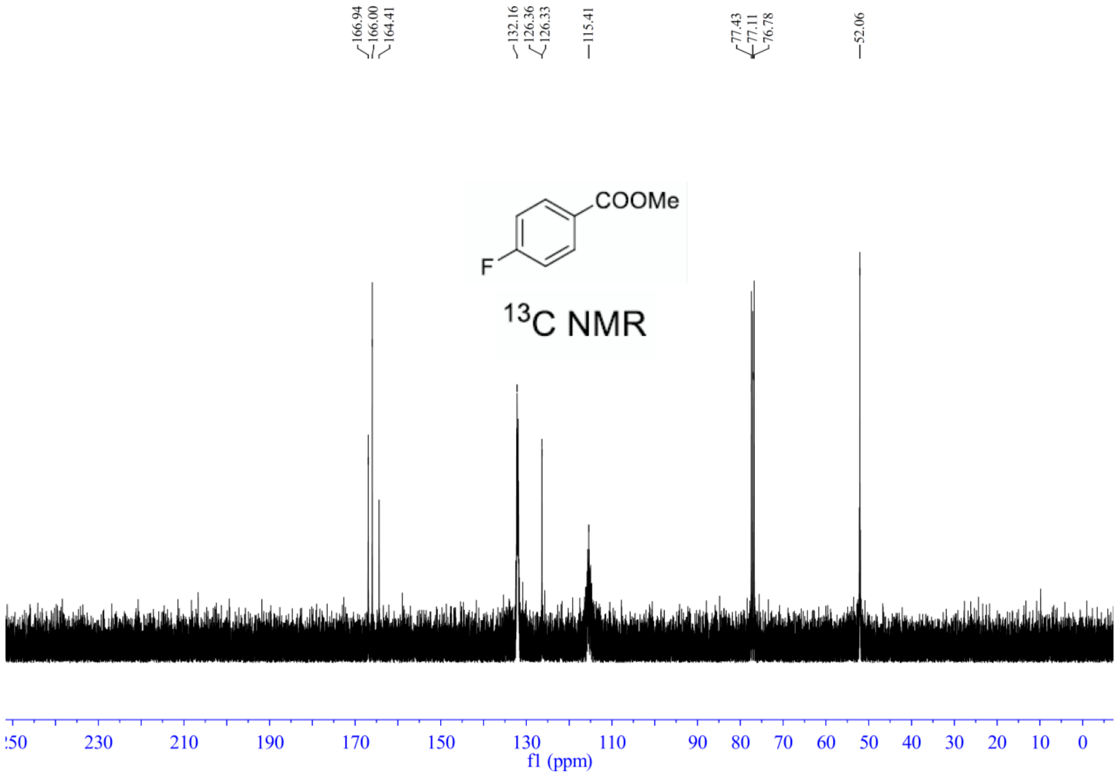


Figure S35. ^{13}C NMR of **3h** $CDCl_3$ at RT

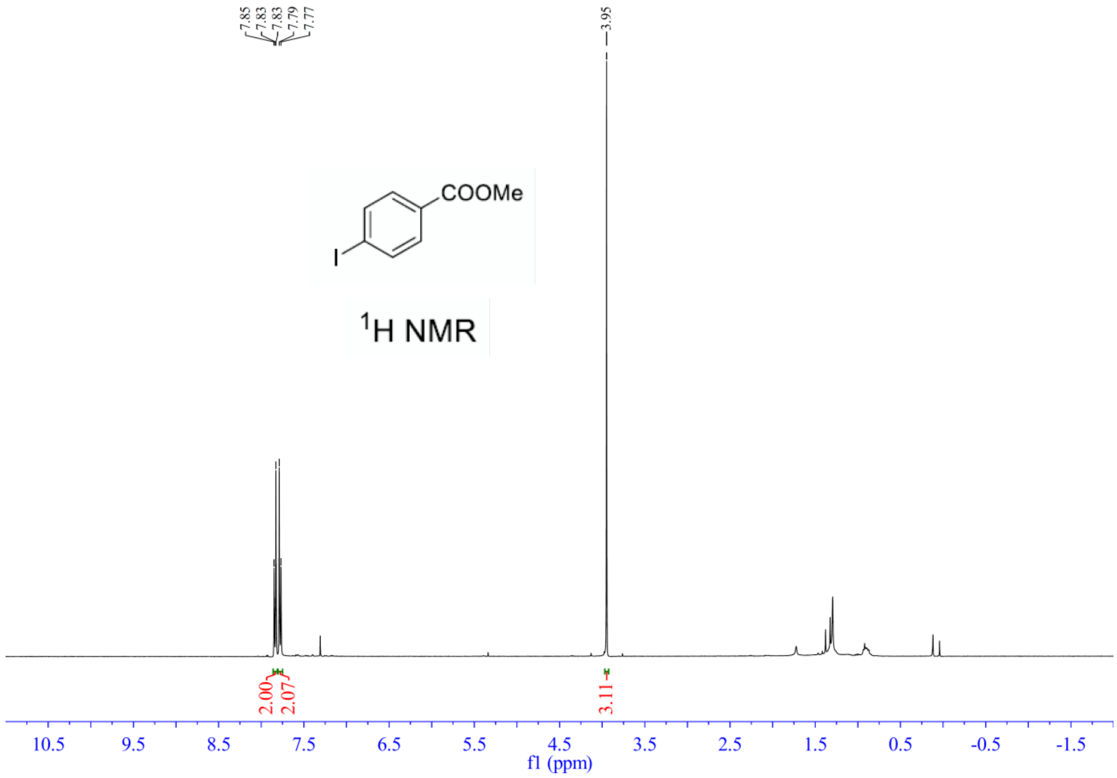


Figure S36. ^{1}H NMR of **3i** $CDCl_3$ at RT

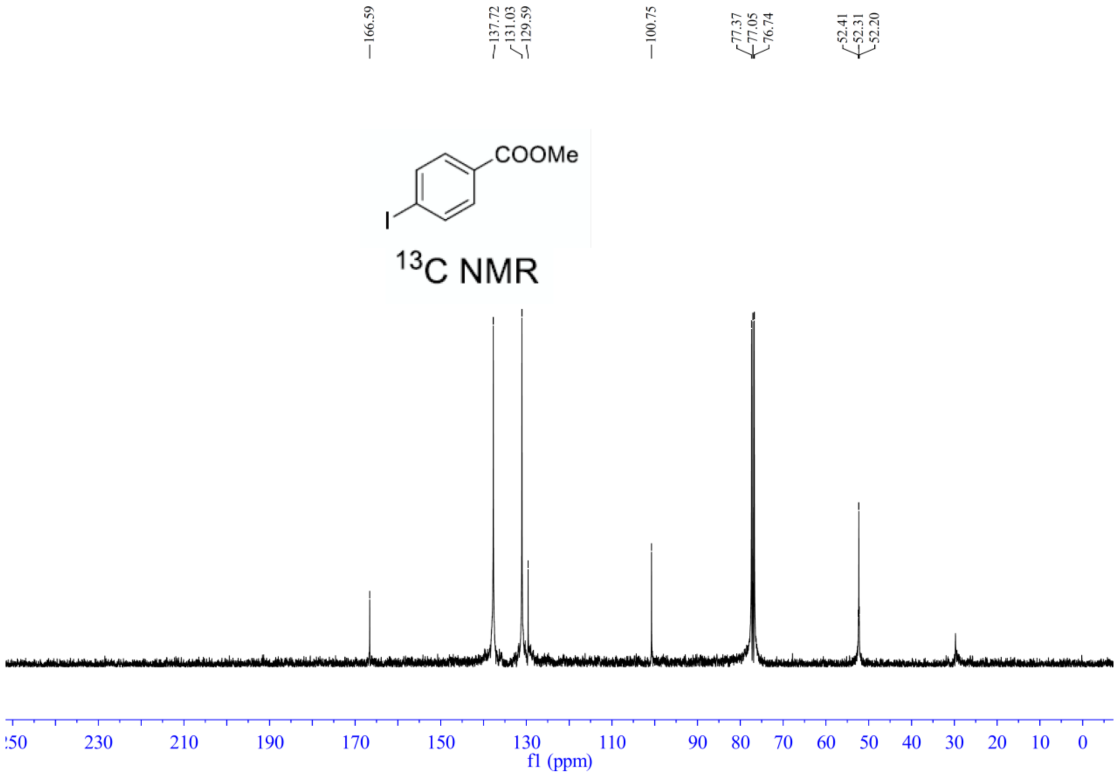


Figure S37. ^{13}C NMR of **3i** $CDCl_3$ at RT

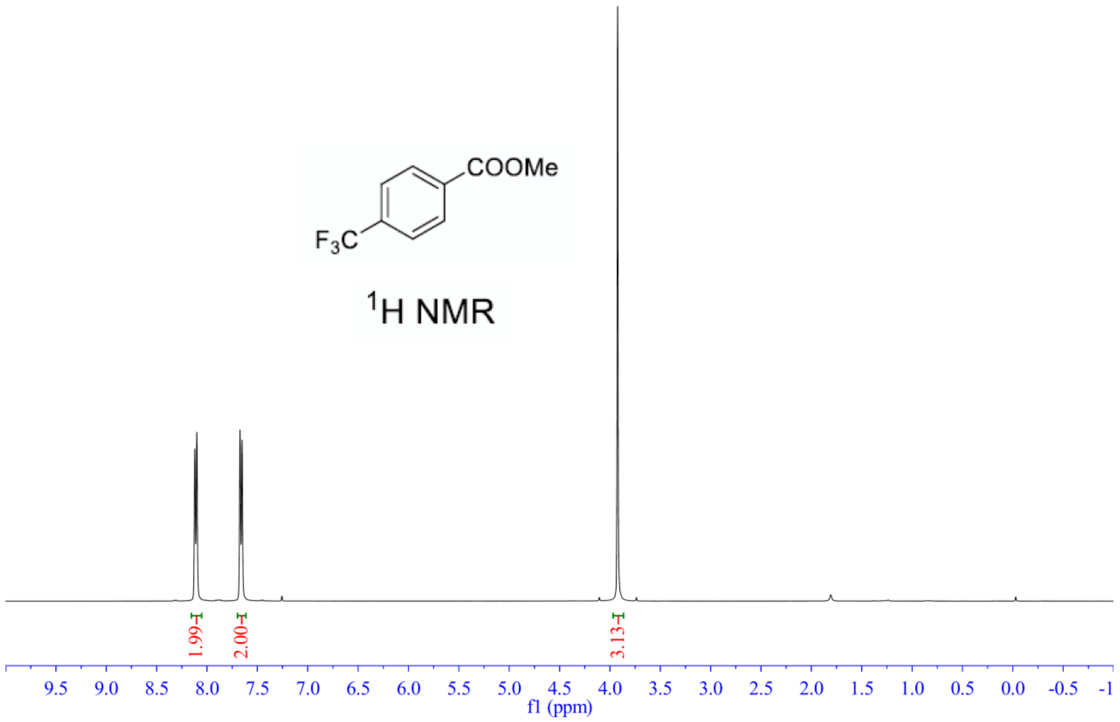


Figure S38. ^{1}H NMR of **3j** $CDCl_3$ at RT

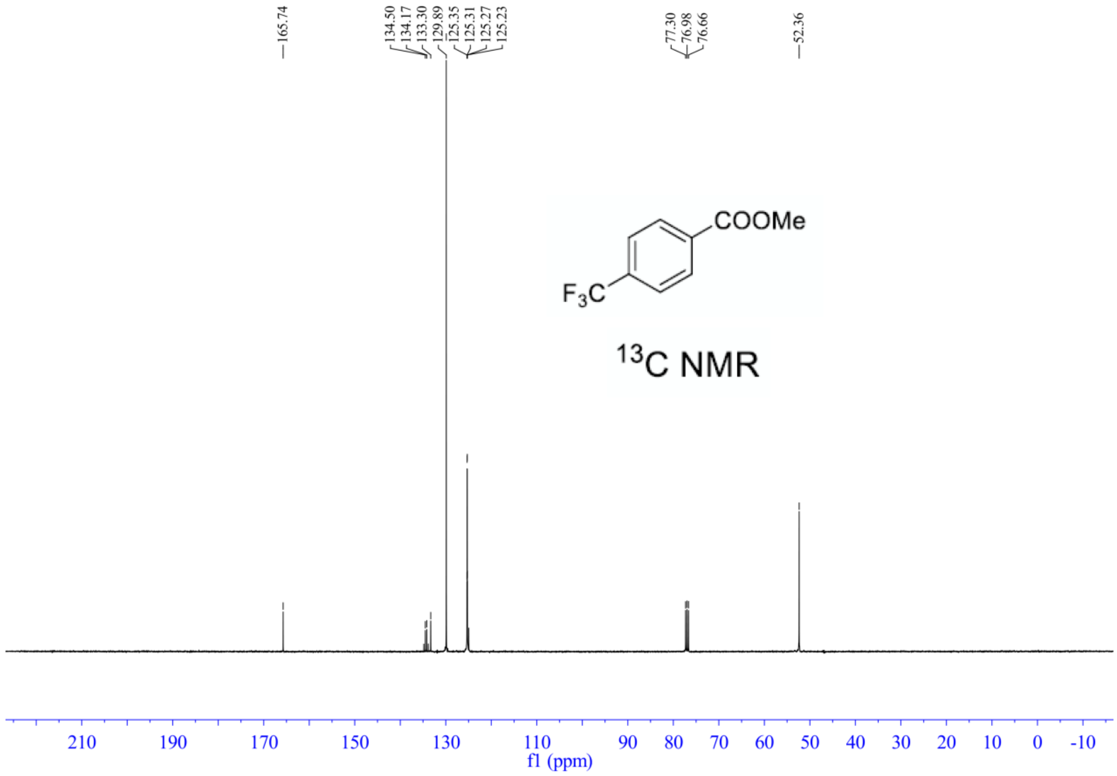


Figure S39. ^{13}C NMR of **3j** $CDCl_3$ at RT

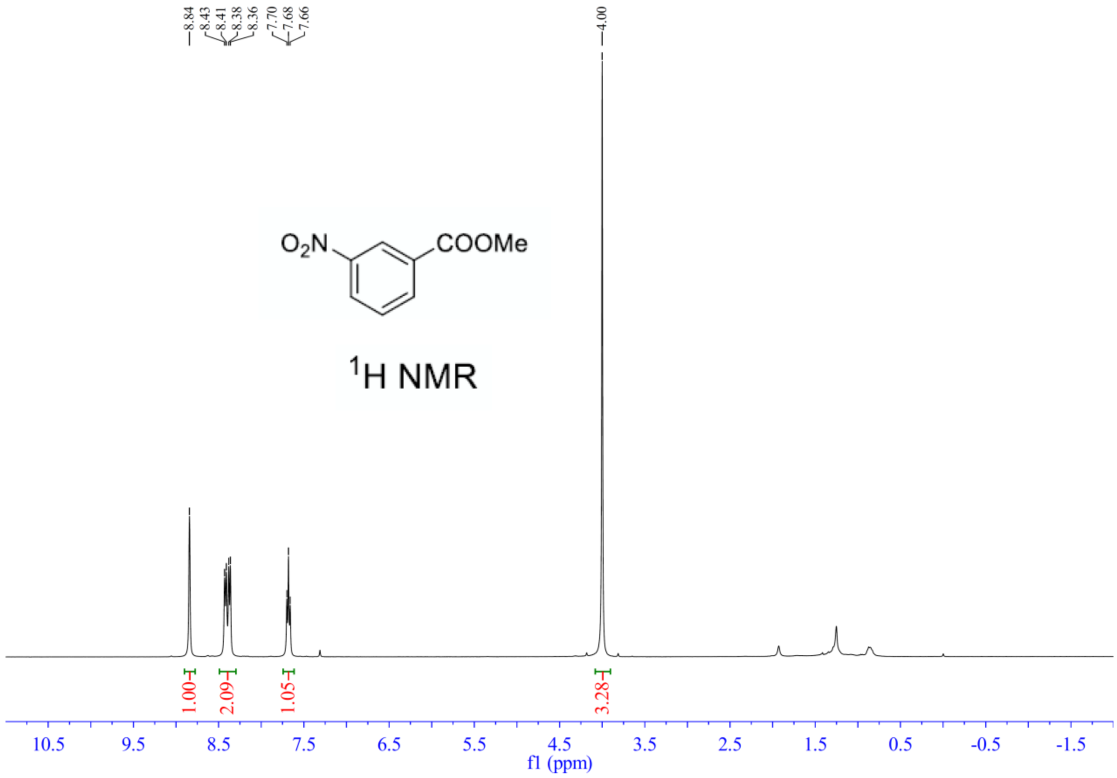


Figure S40. ^{1}H NMR of **3k** $CDCl_3$ at RT

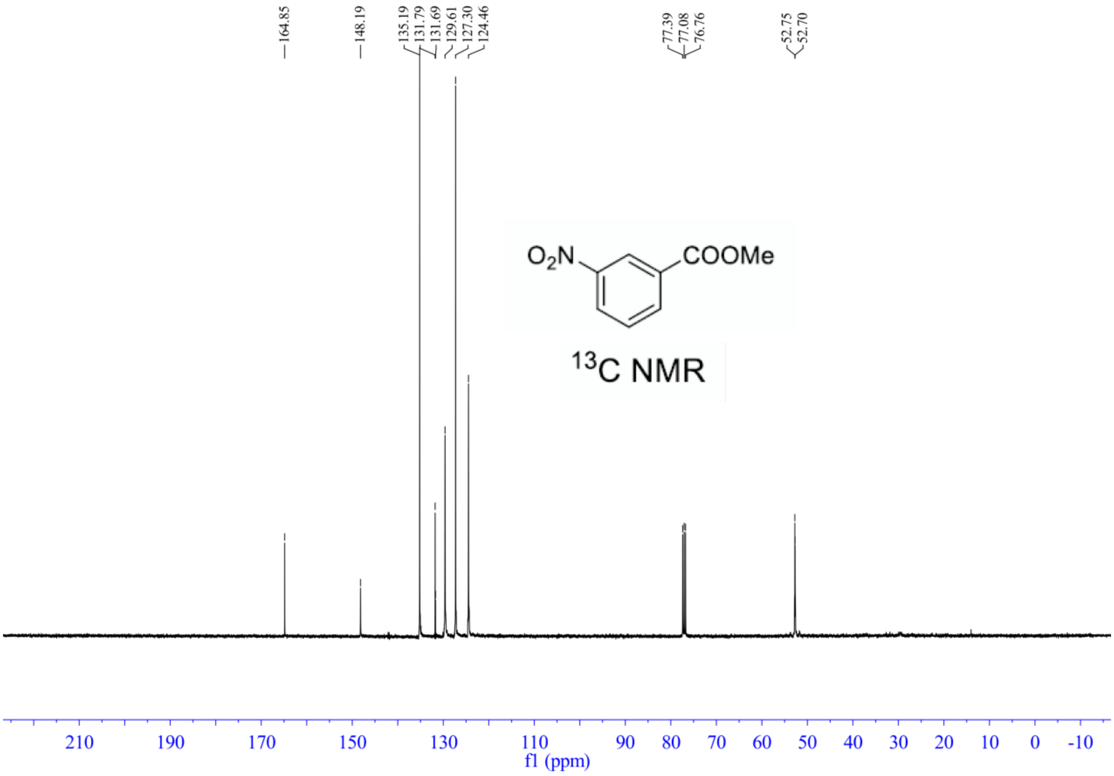


Figure S41. ^{13}C NMR of **3k** $CDCl_3$ at RT

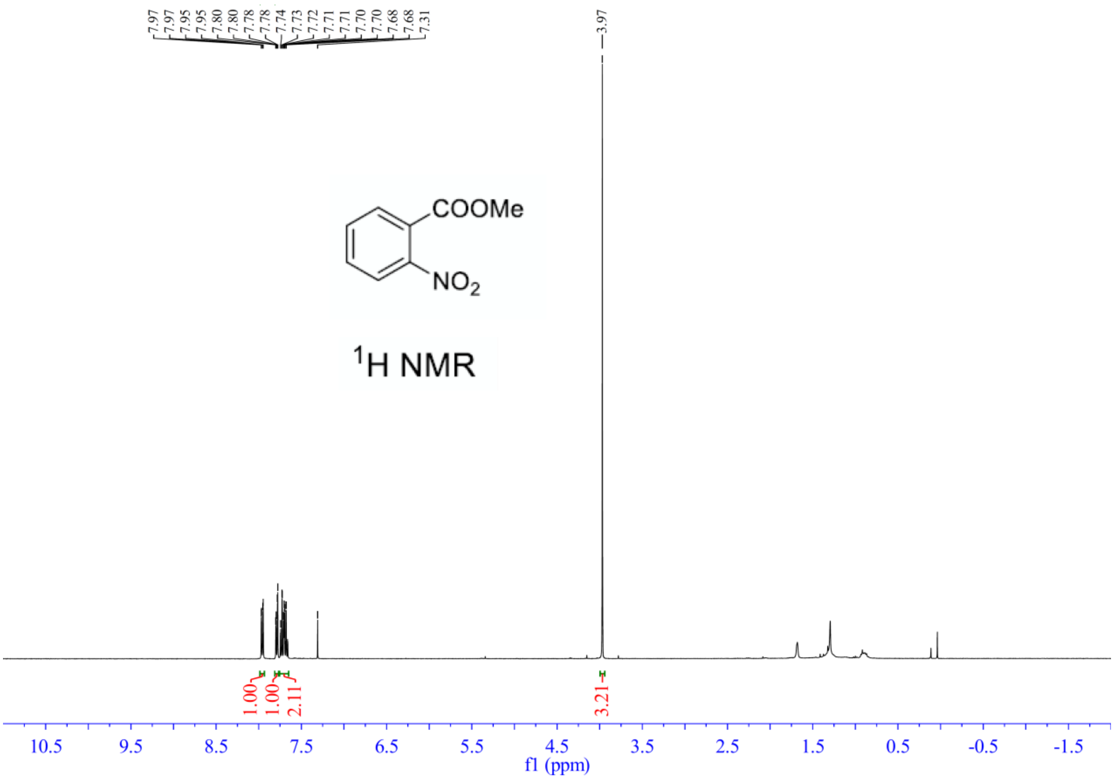


Figure S42. ^{1}H NMR of **3l** $CDCl_3$ at RT

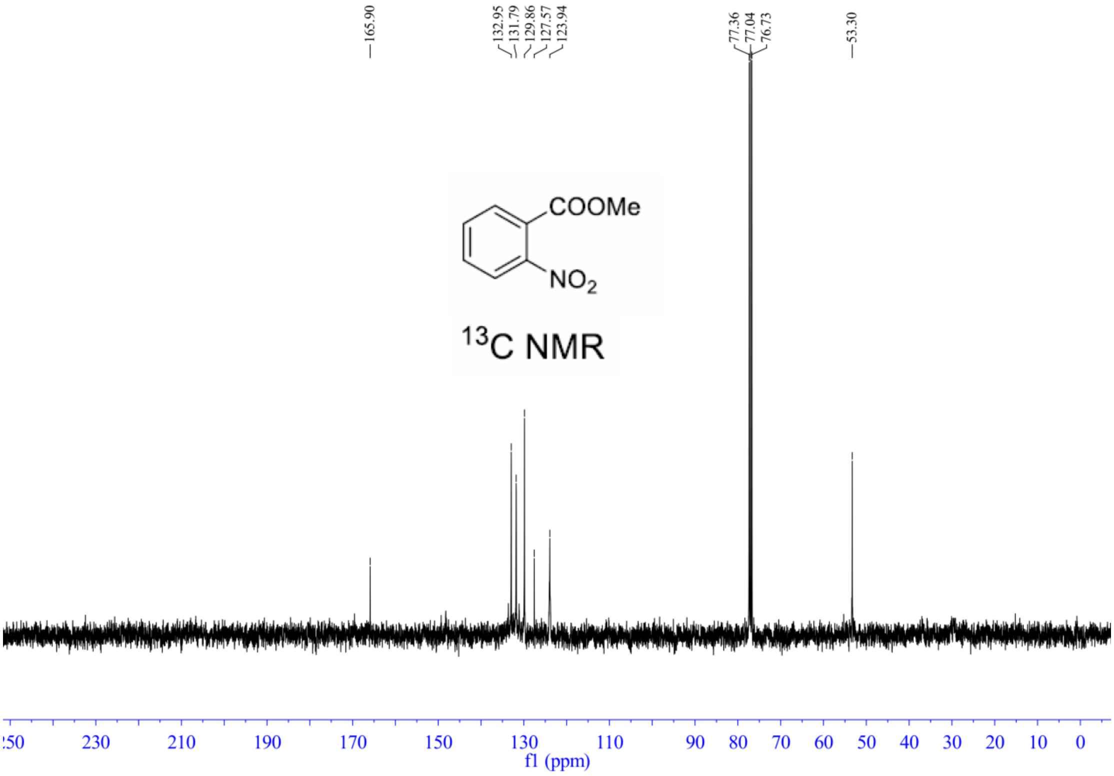


Figure S43. ^{13}C NMR of **3l** $CDCl_3$ at RT

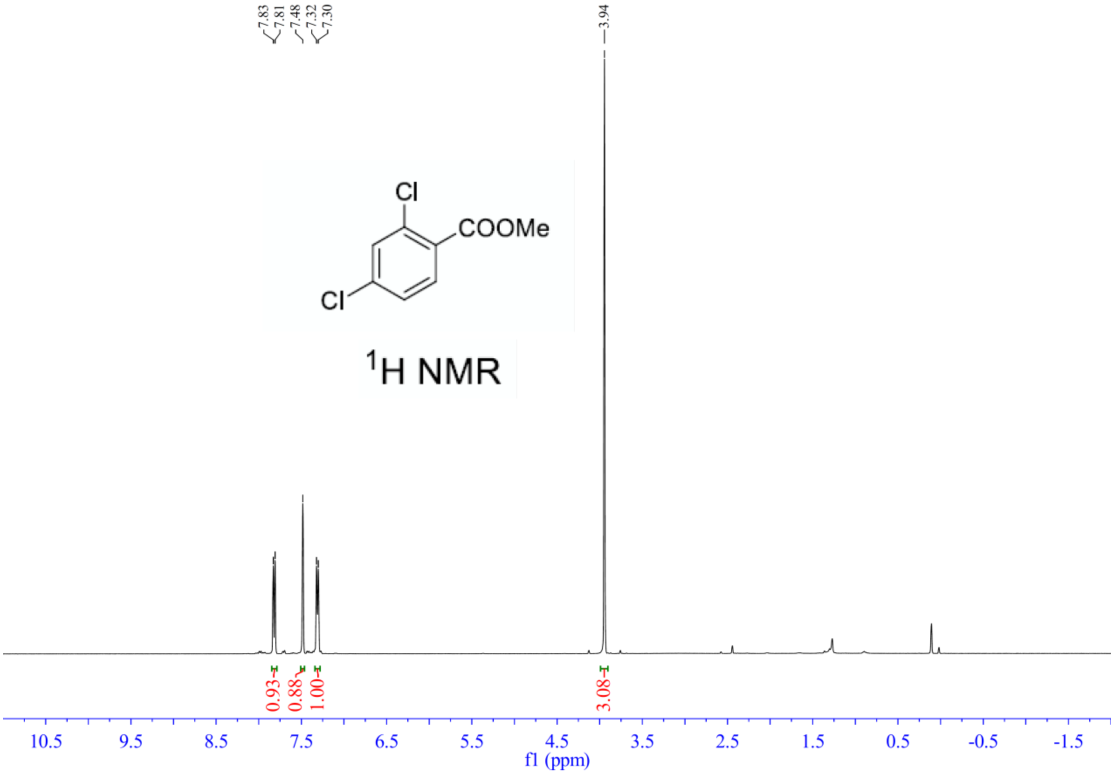


Figure S44. ^{1}H NMR of **3m** $CDCl_3$ at RT

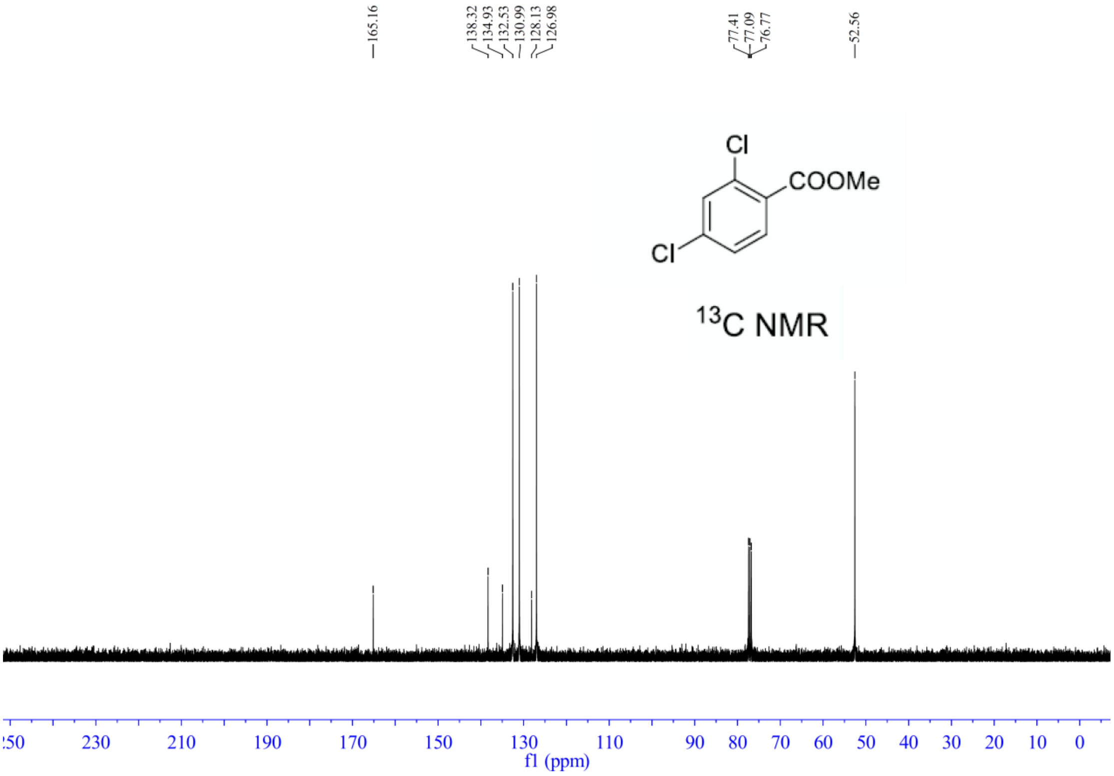


Figure S45. ^{13}C NMR of **3m** $CDCl_3$ at RT

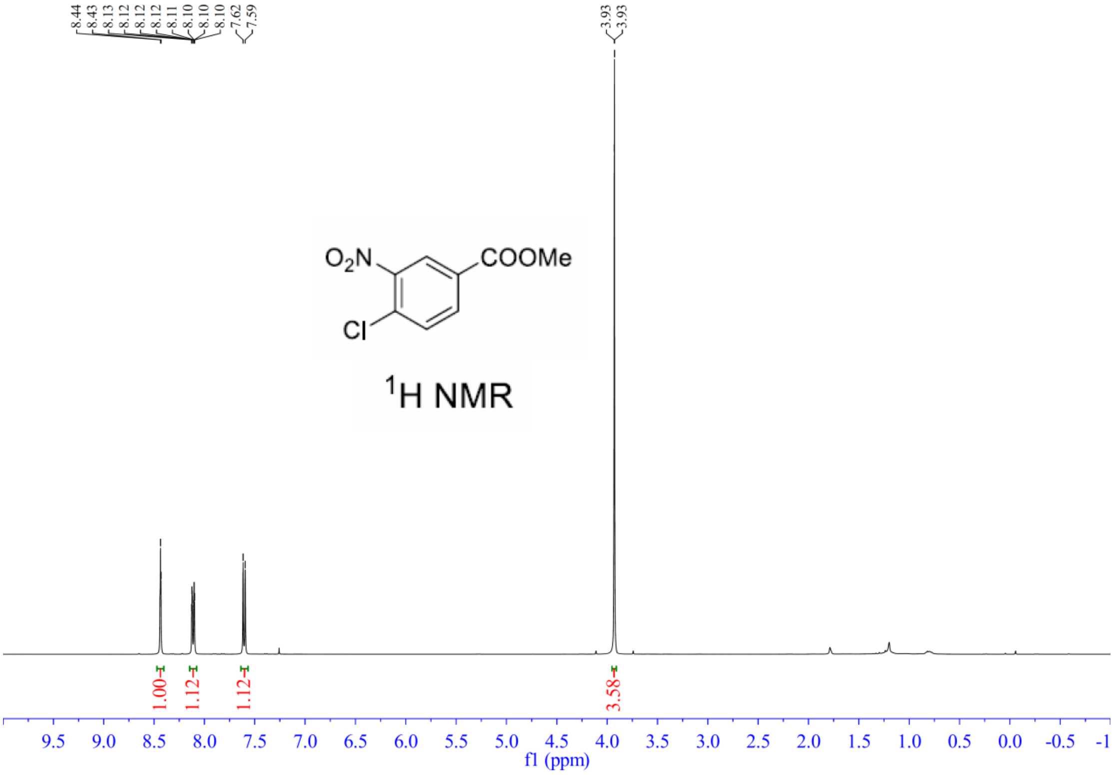


Figure S46. ^{1}H NMR of **3n** $CDCl_3$ at RT

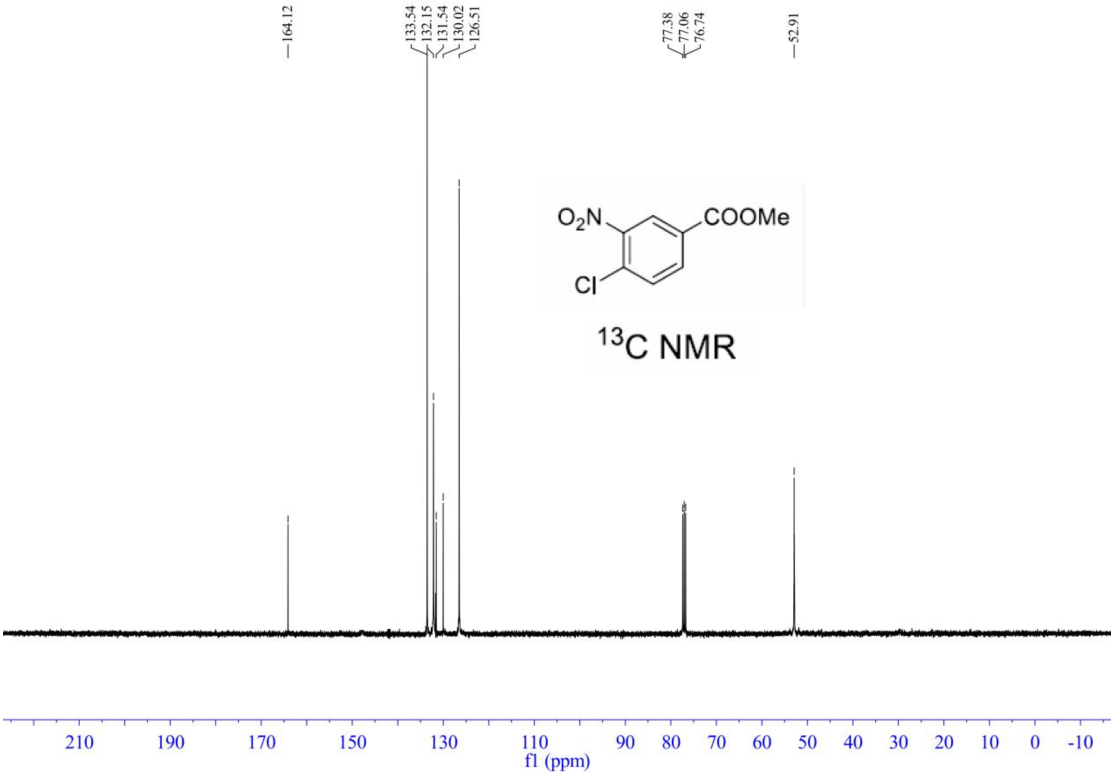


Figure S47. ^{13}C NMR of **3n** $CDCl_3$ at RT

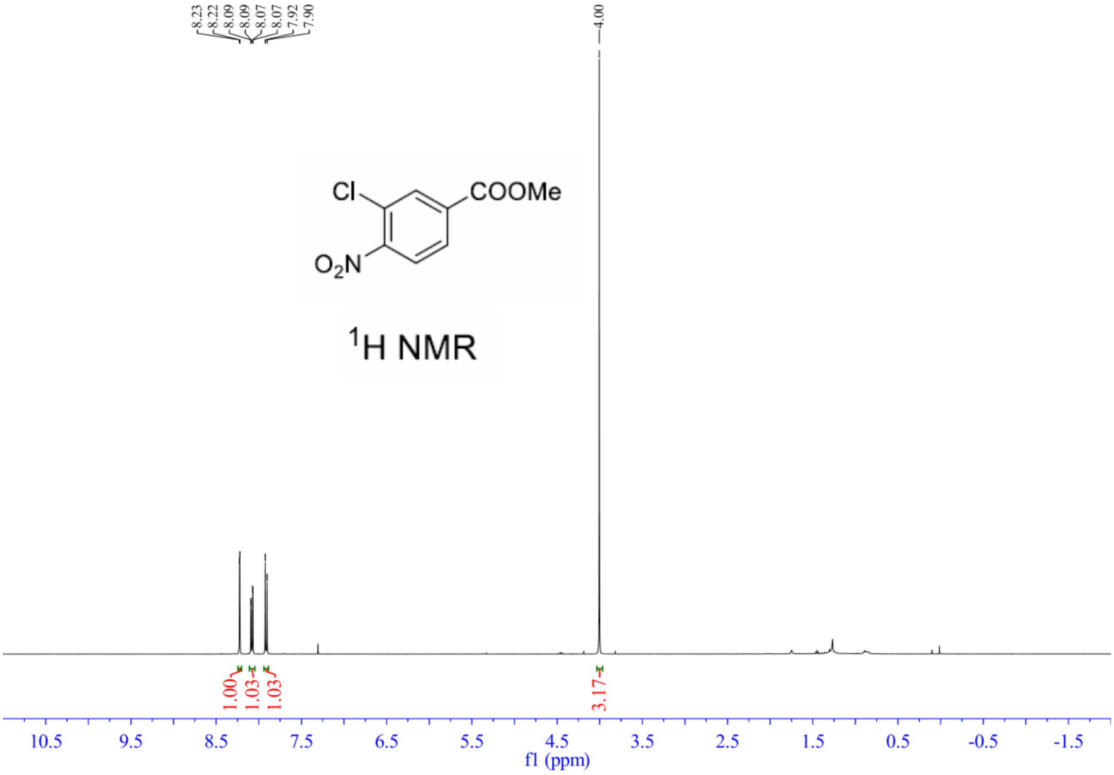


Figure S48. ^{1}H NMR of **3o** $CDCl_3$ at RT

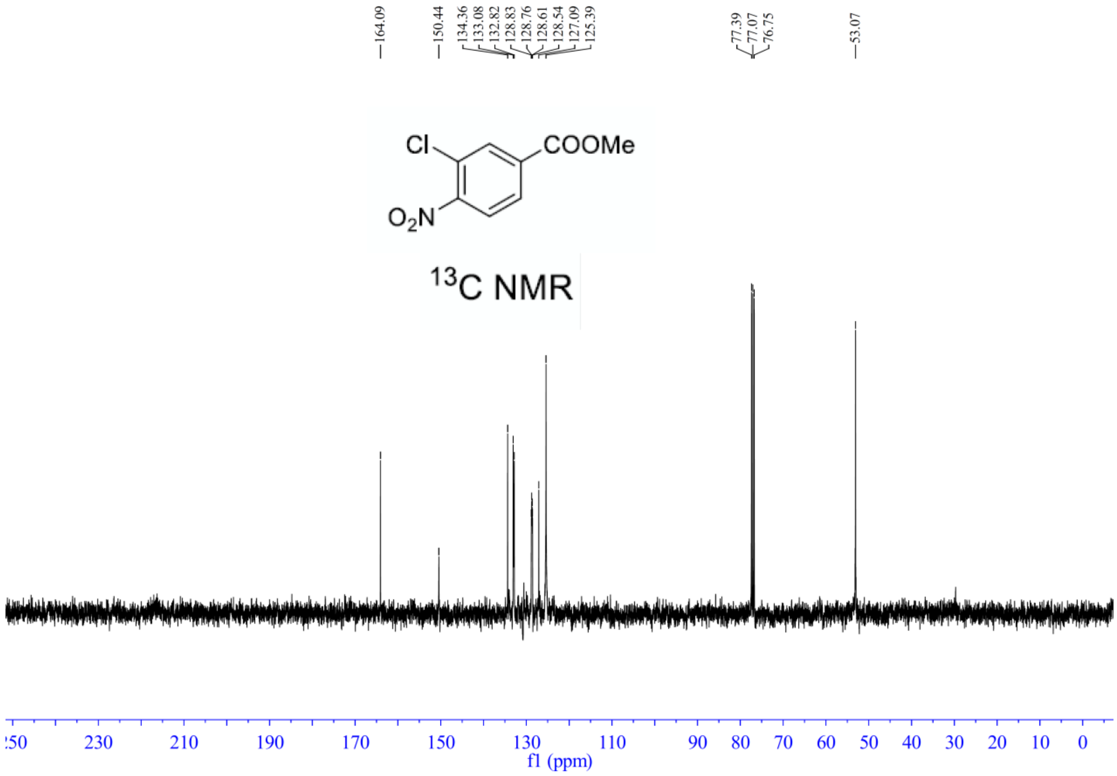


Figure S49. ^{13}C NMR of **3o** $CDCl_3$ at RT

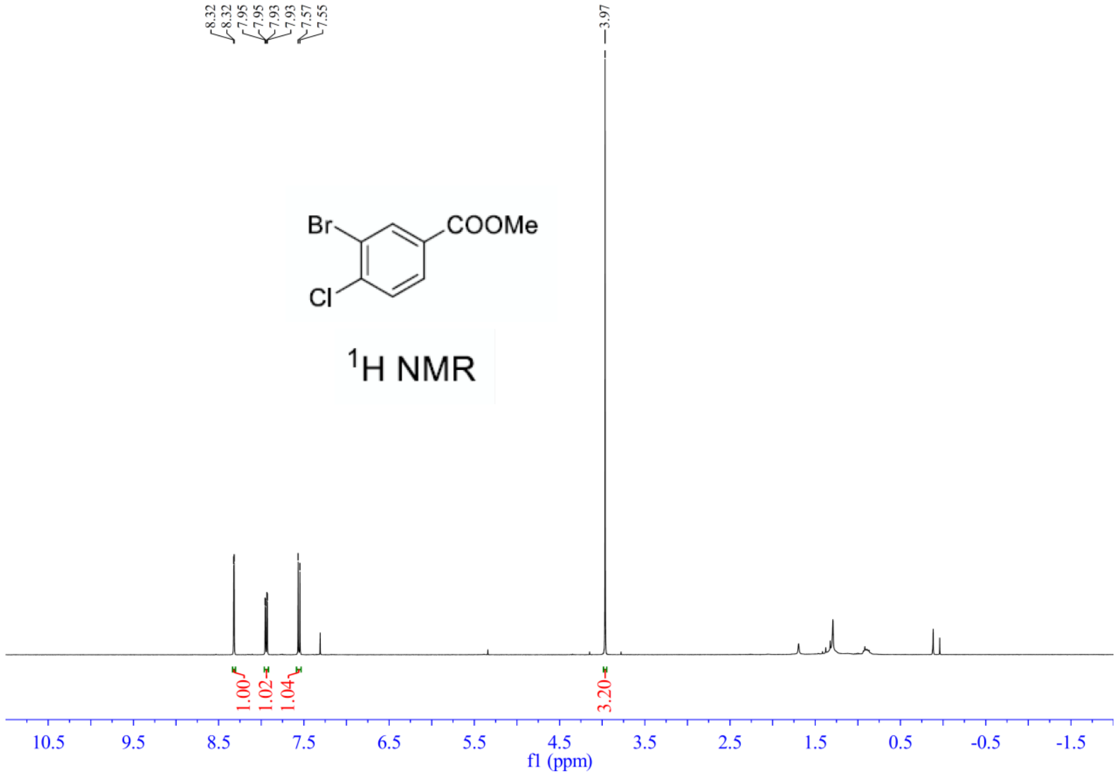


Figure S50. ^{1}H NMR of **3p** $CDCl_3$ at RT

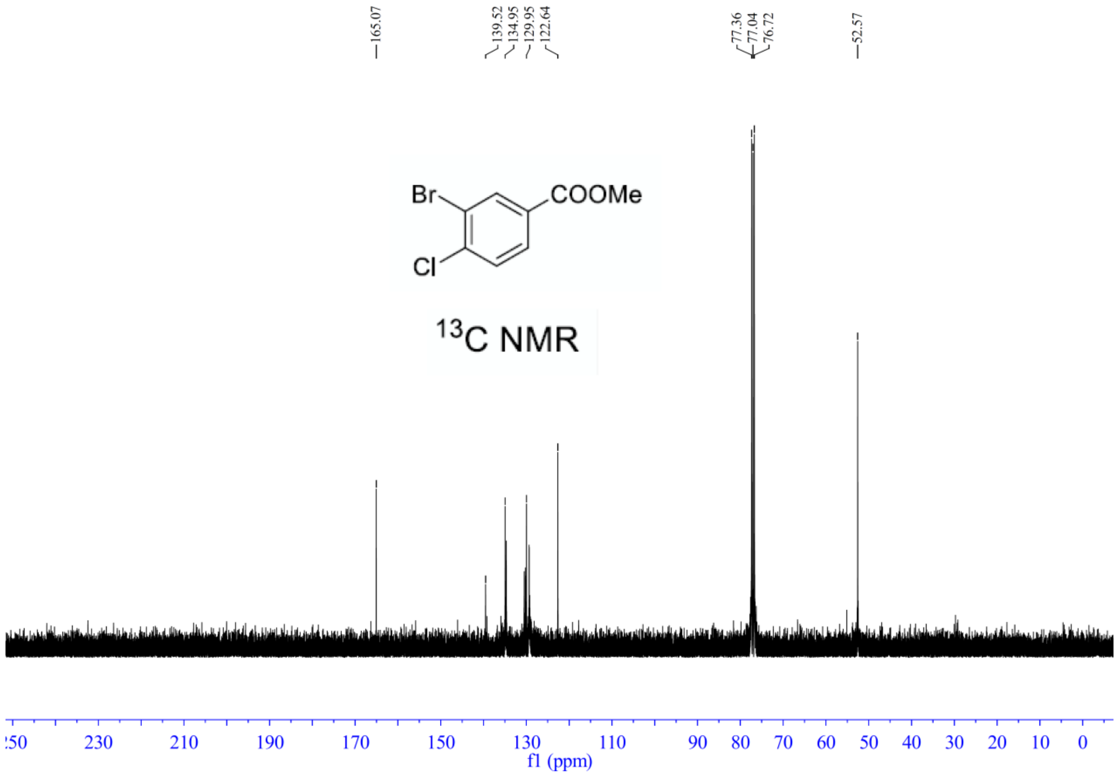


Figure S51. ^{13}C NMR of **3p** $CDCl_3$ at RT

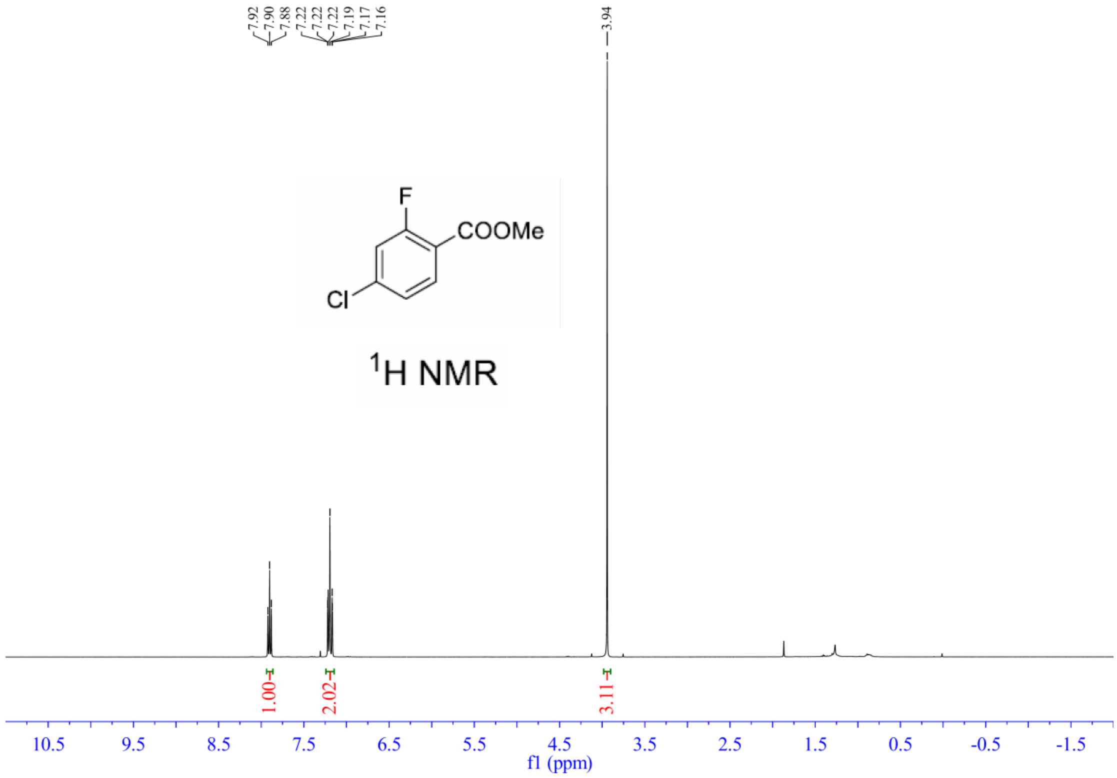


Figure S52. ^{1}H NMR of **3q** $CDCl_3$ at RT

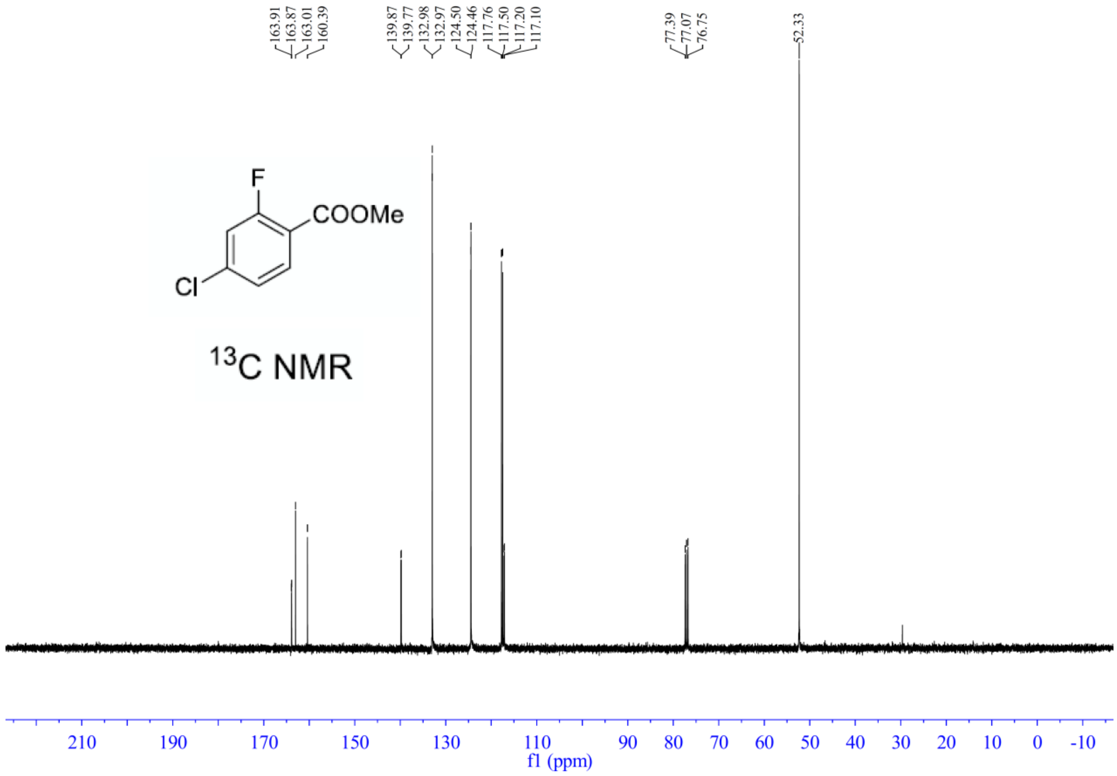


Figure S53. ^{13}C NMR of **3q** $CDCl_3$ at RT

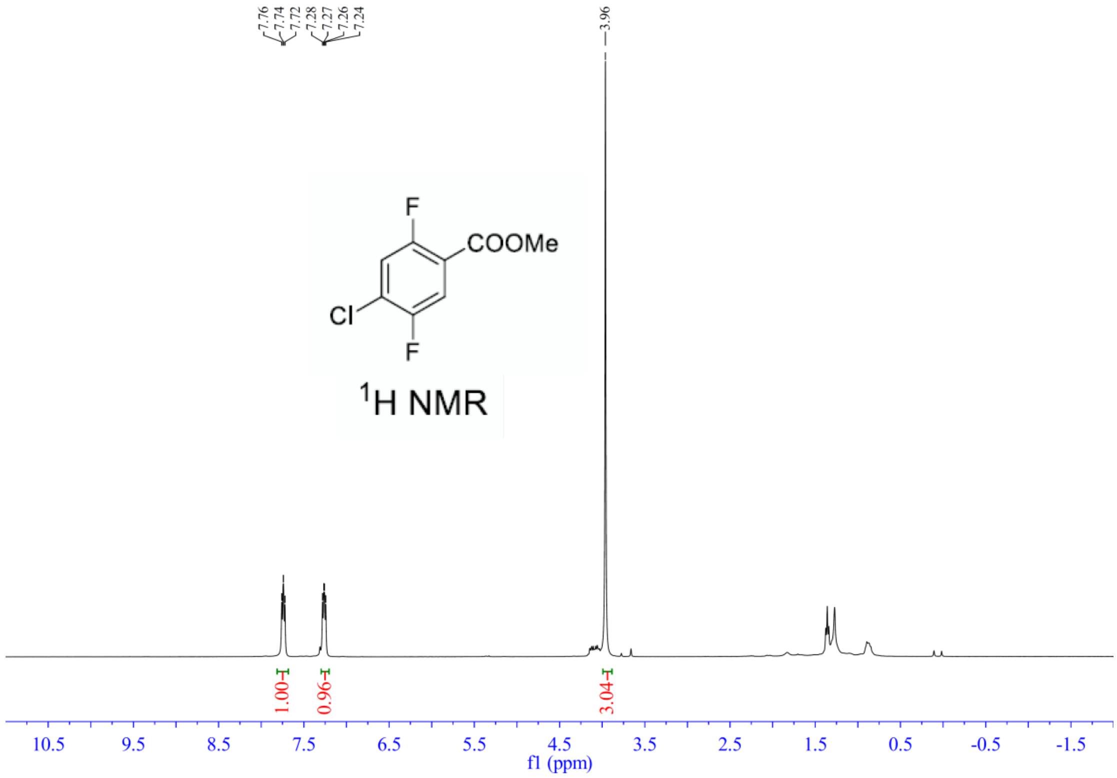


Figure S54. ^{1}H NMR of **3r** $CDCl_3$ at RT

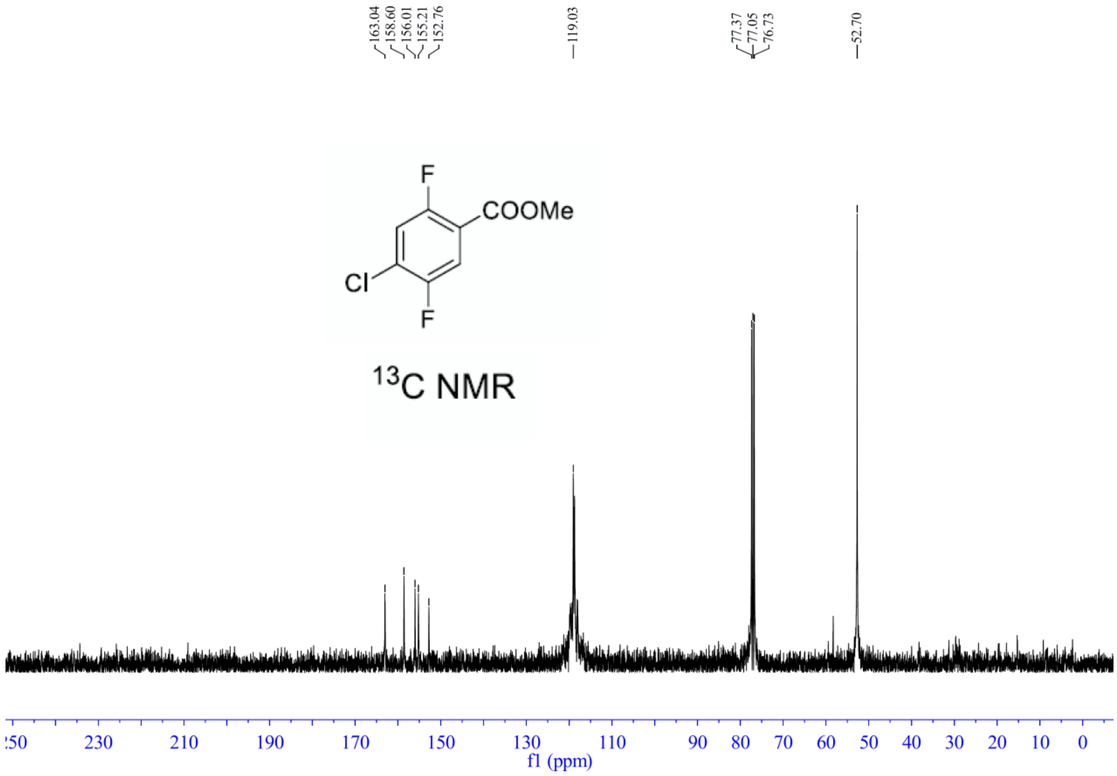


Figure S55. ^{13}C NMR of **3r** $CDCl_3$ at RT

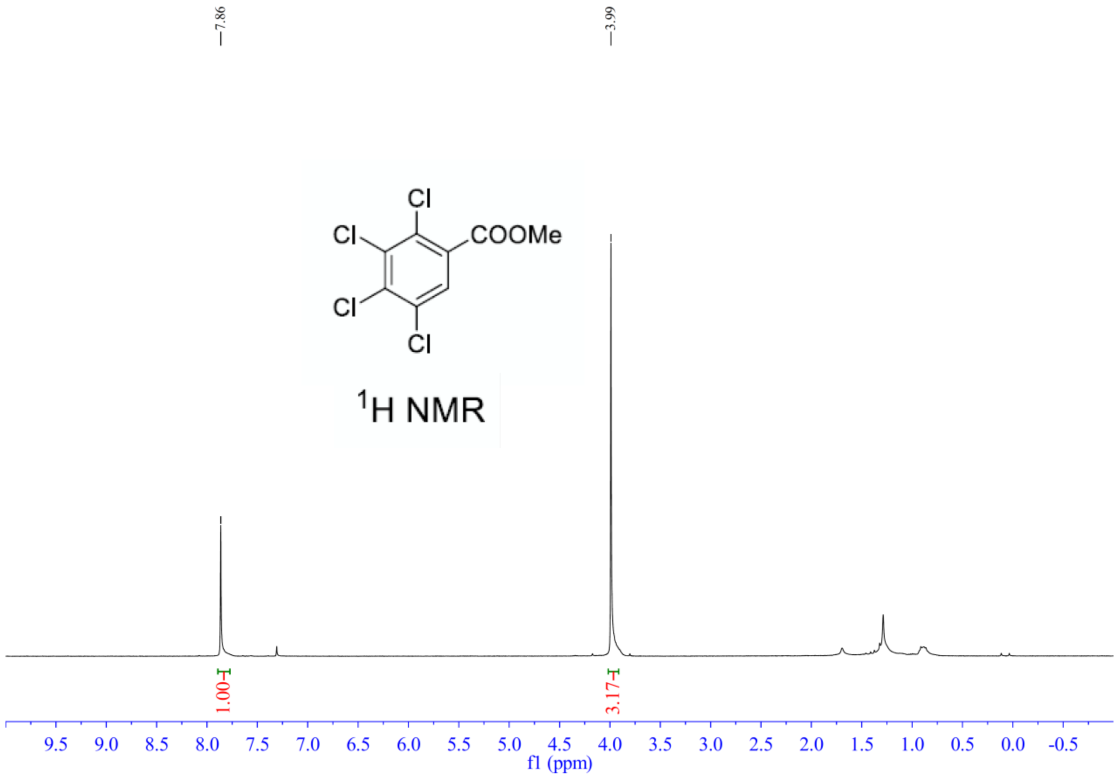


Figure S56. ^{1}H NMR of **3s** $CDCl_3$ at RT

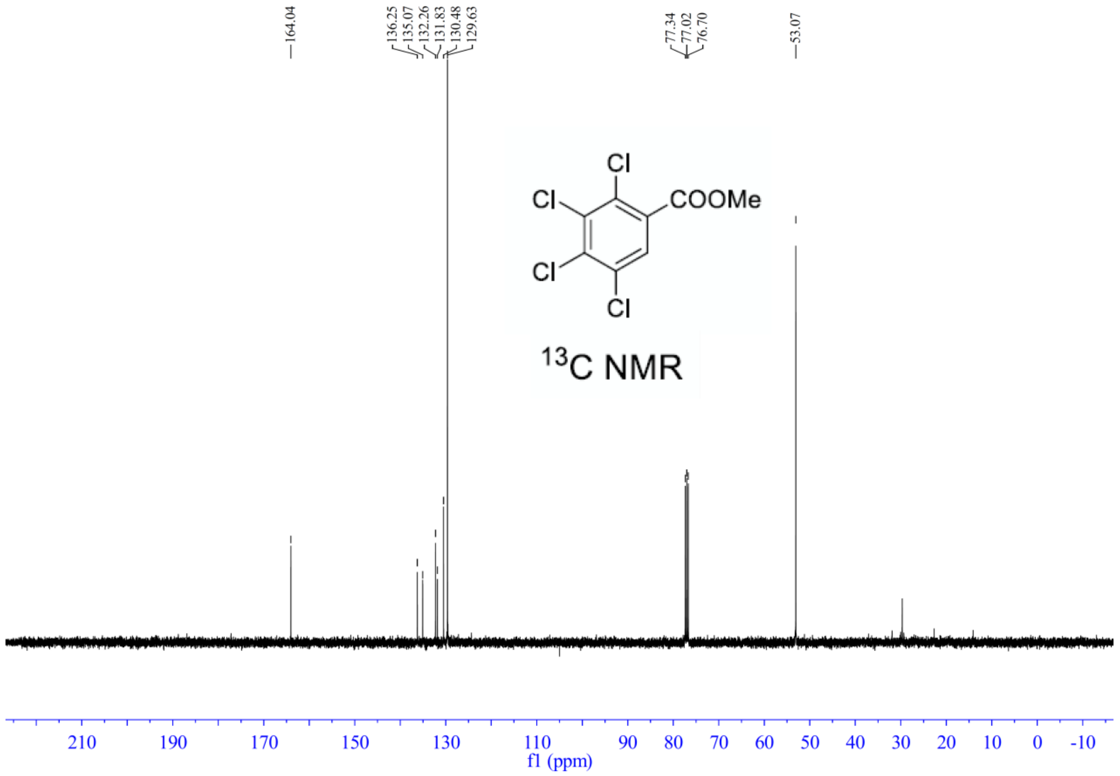


Figure S57. ^{13}C NMR of **3s** CDCl$_3$ at RT

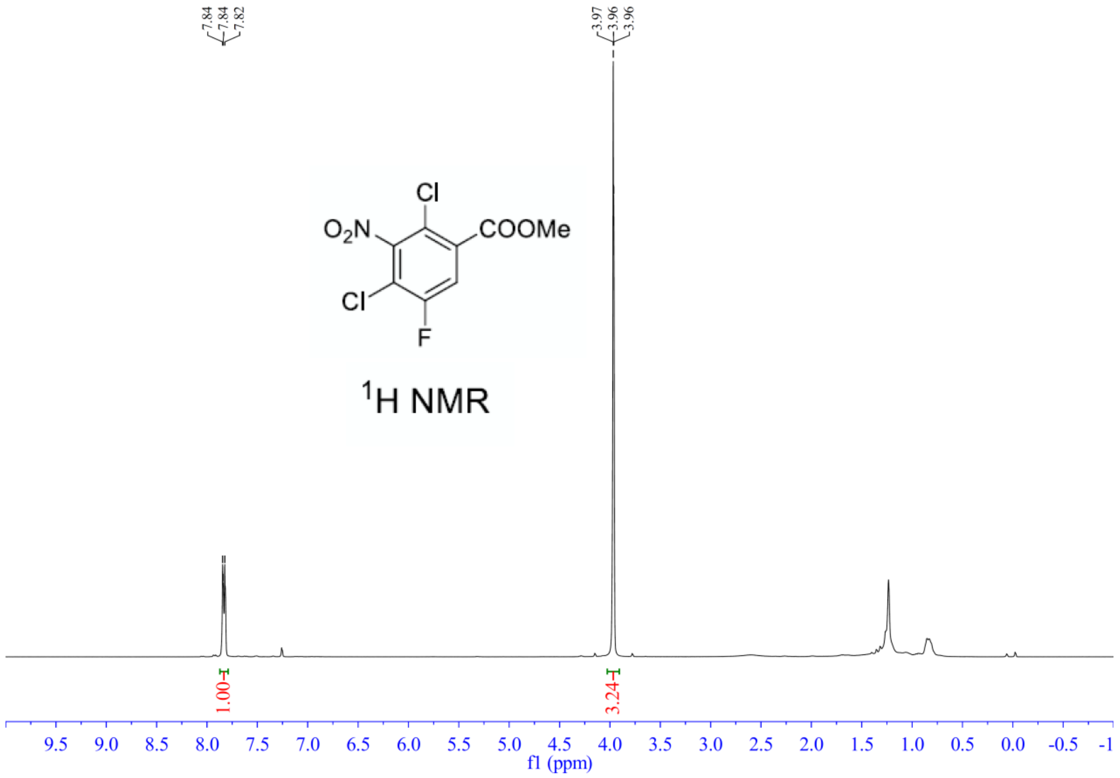


Figure S58. ^{1}H NMR of **3t** CDCl$_3$ at RT

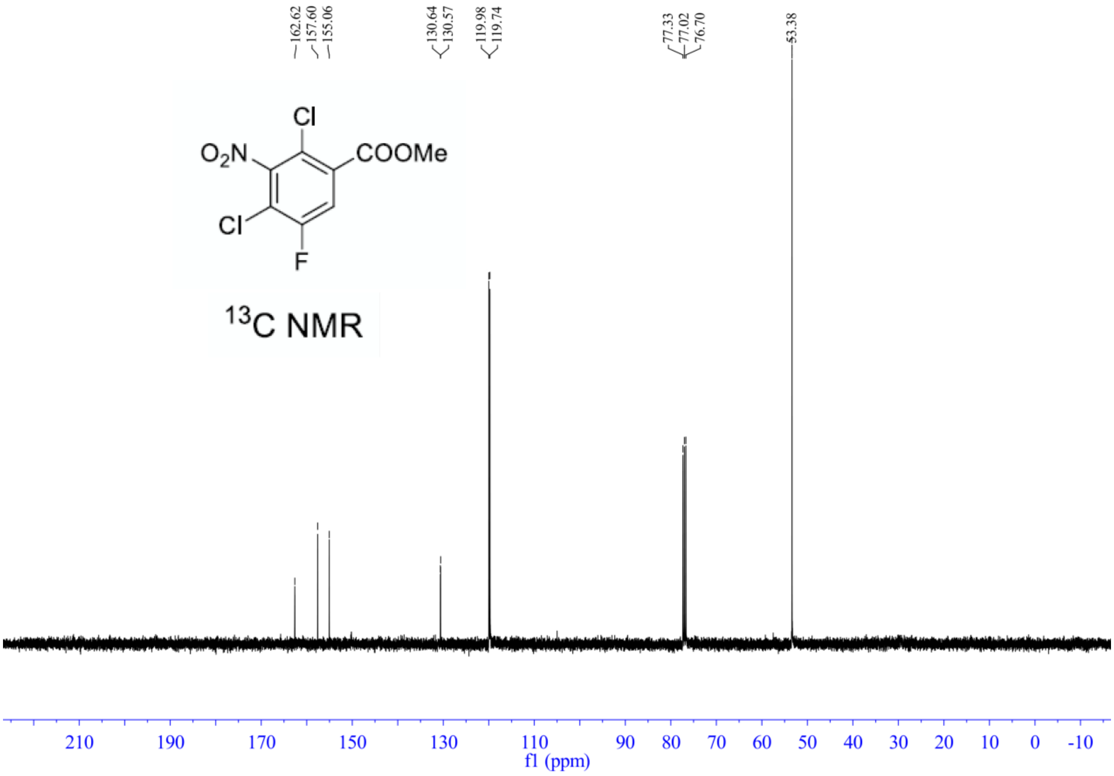


Figure S59. ^{13}C NMR of **3t** $CDCl_3$ at RT

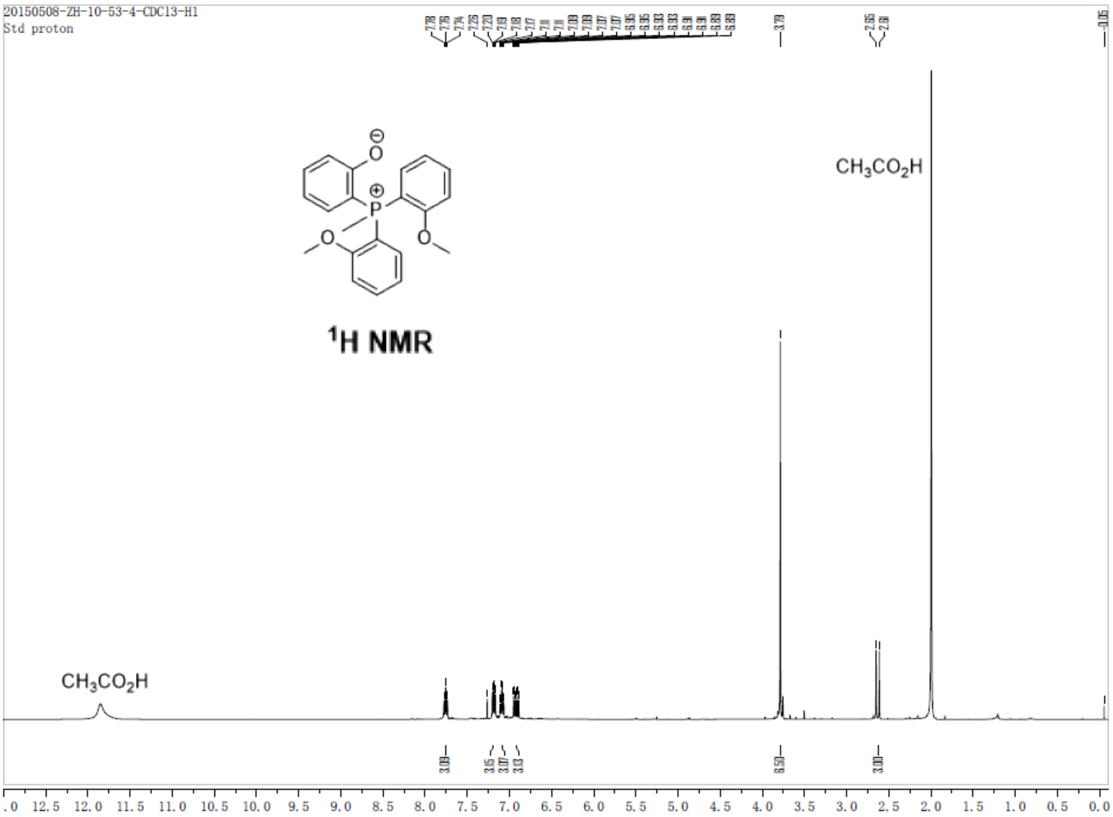


Figure S60. ^{1}H NMR of **P-II** $CDCl_3$ at RT

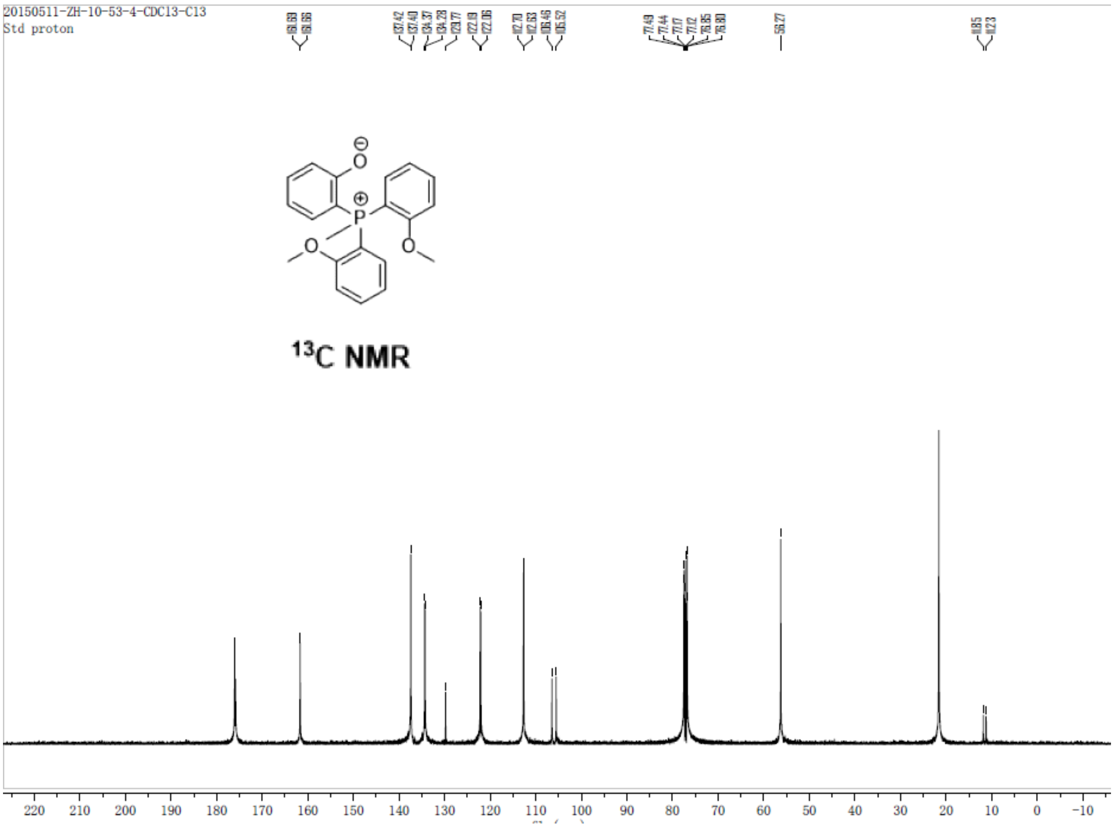


Figure S61. ^{13}C NMR of **P-II** DMSO-6d at RT

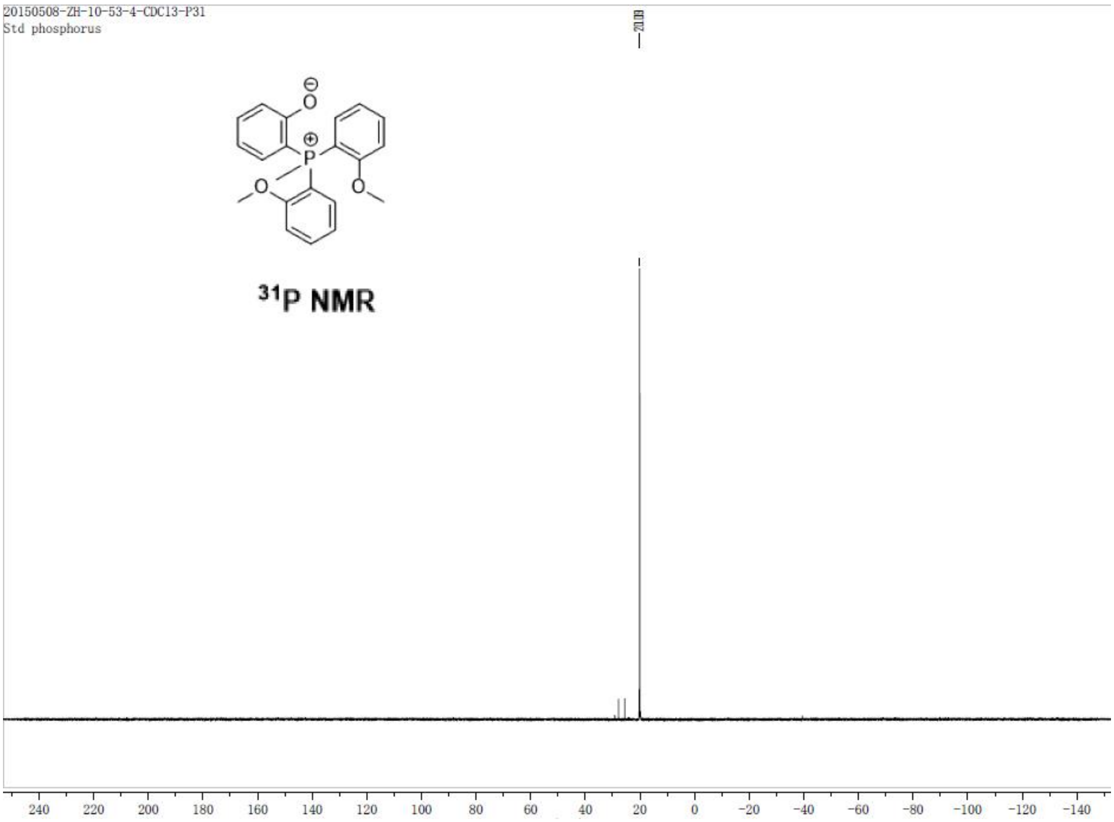


Figure S62. ^{31}P NMR of **P-II** DMSO-6d at RT

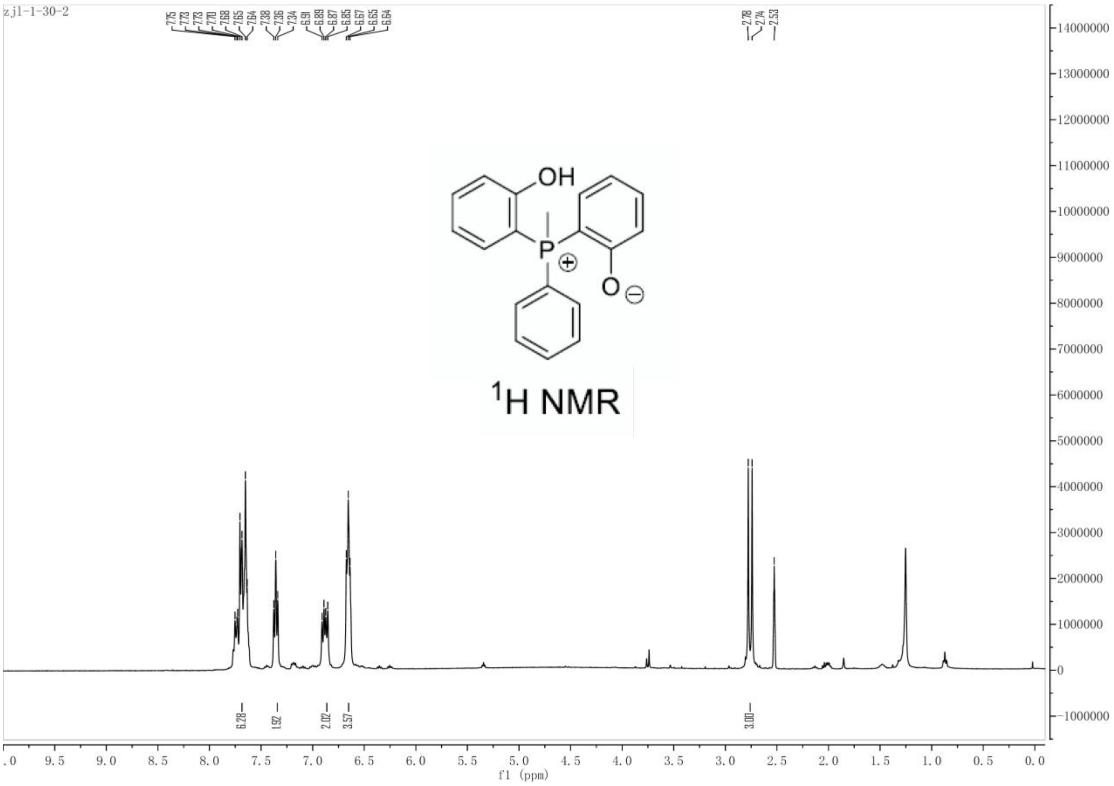


Figure S63. ^{1}H NMR of **P-I** DMSO-6d at RT

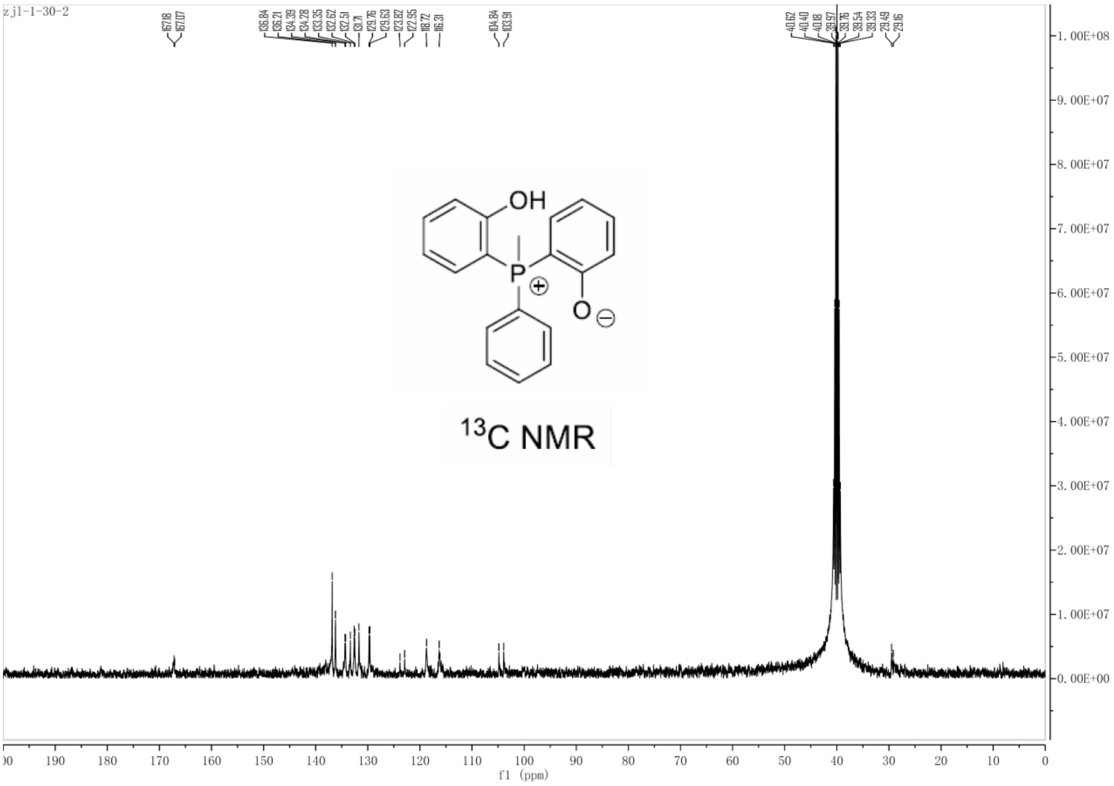


Figure S64. ^{13}C NMR of **P-I** DMSO-6d at RT

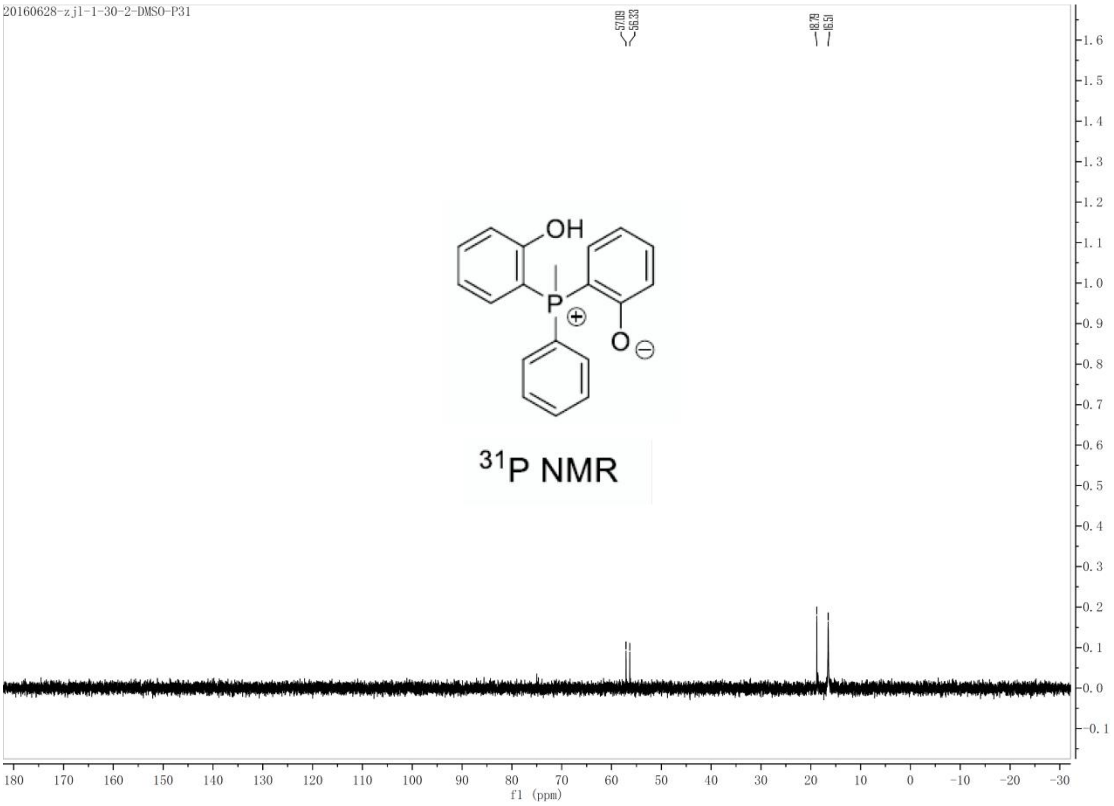


Figure S65. ^{31}P NMR of **P-I** DMSO-6d at RT

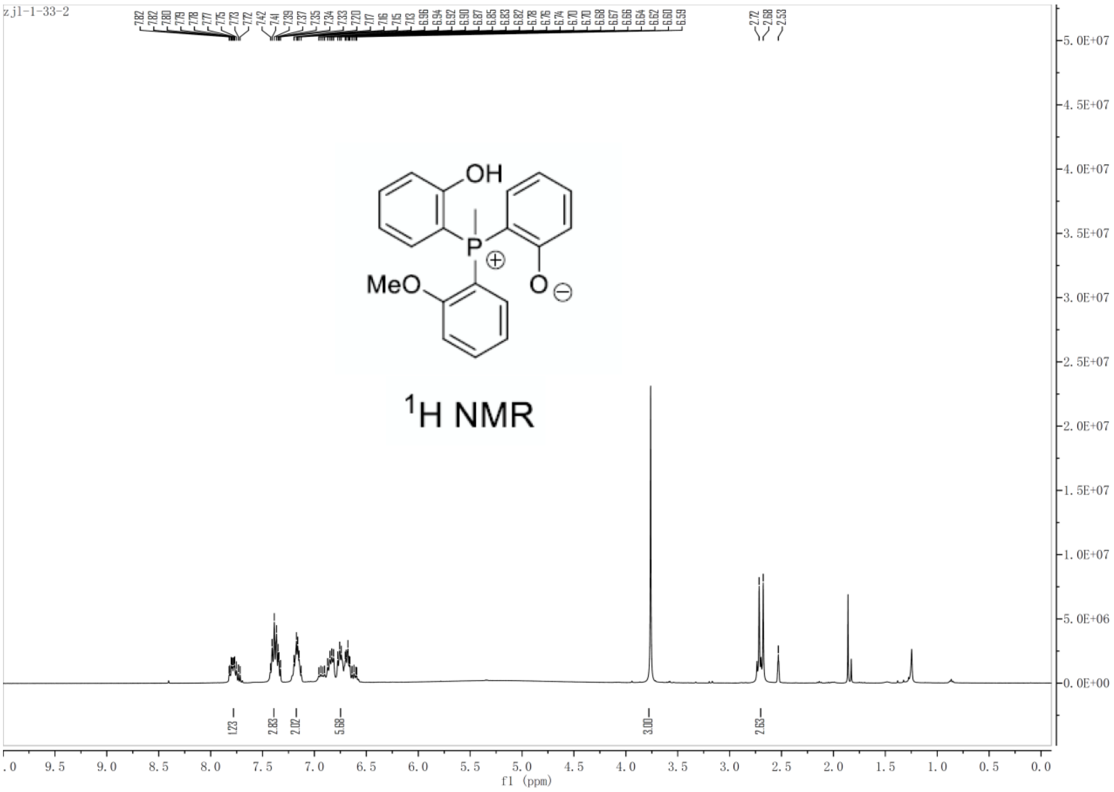


Figure S66. ^{1}H NMR of **P-III** DMSO-6d at RT

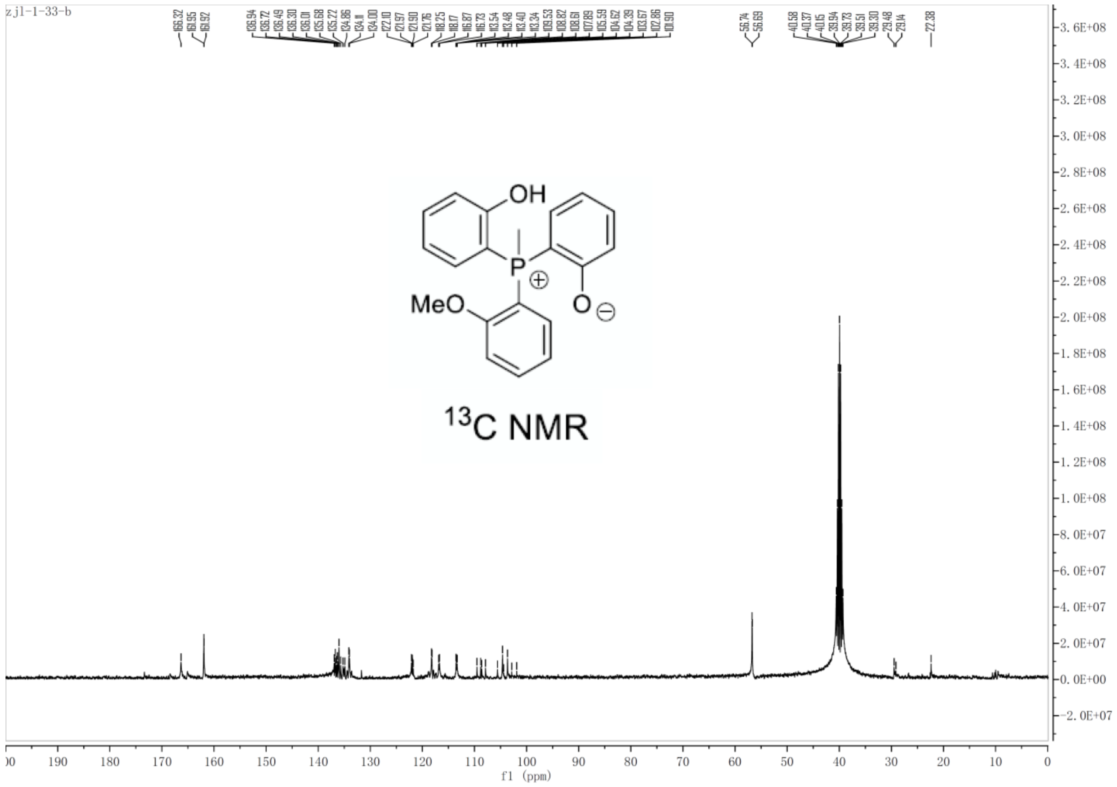


Figure S67. ^{13}C NMR of **P-III** DMSO-6d at RT

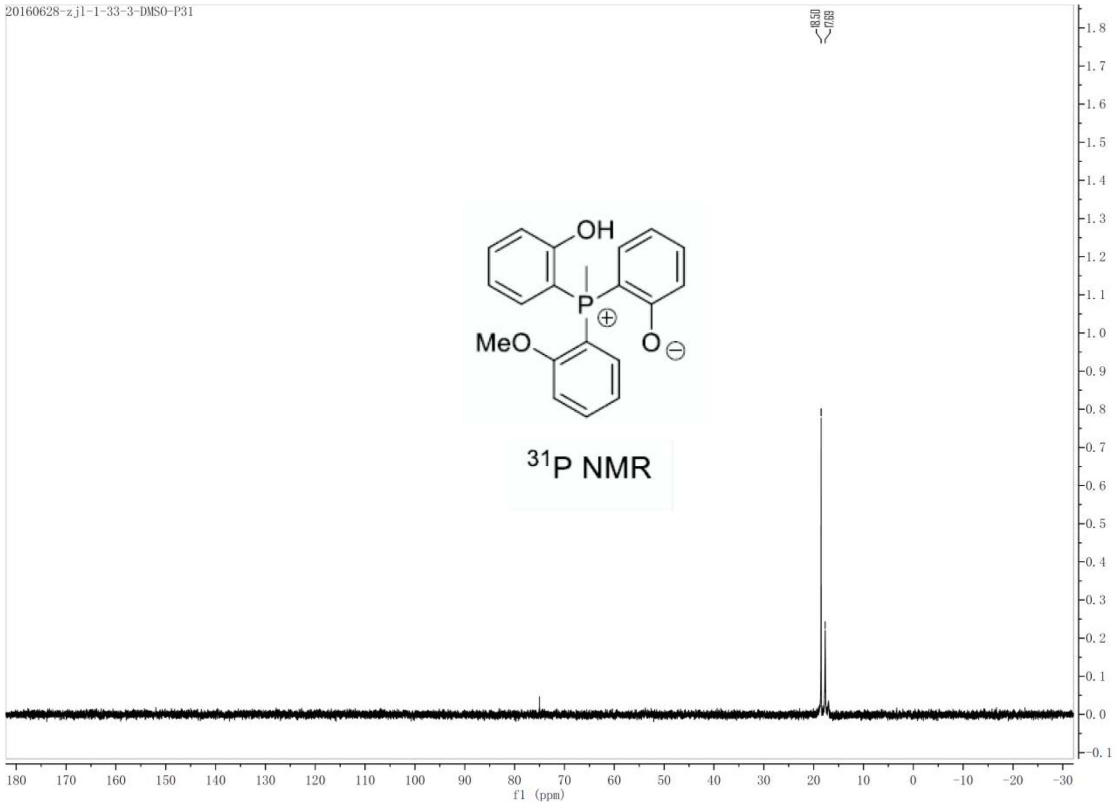


Figure S68. ^{31}P NMR of **P-III** DMSO-6d at RT

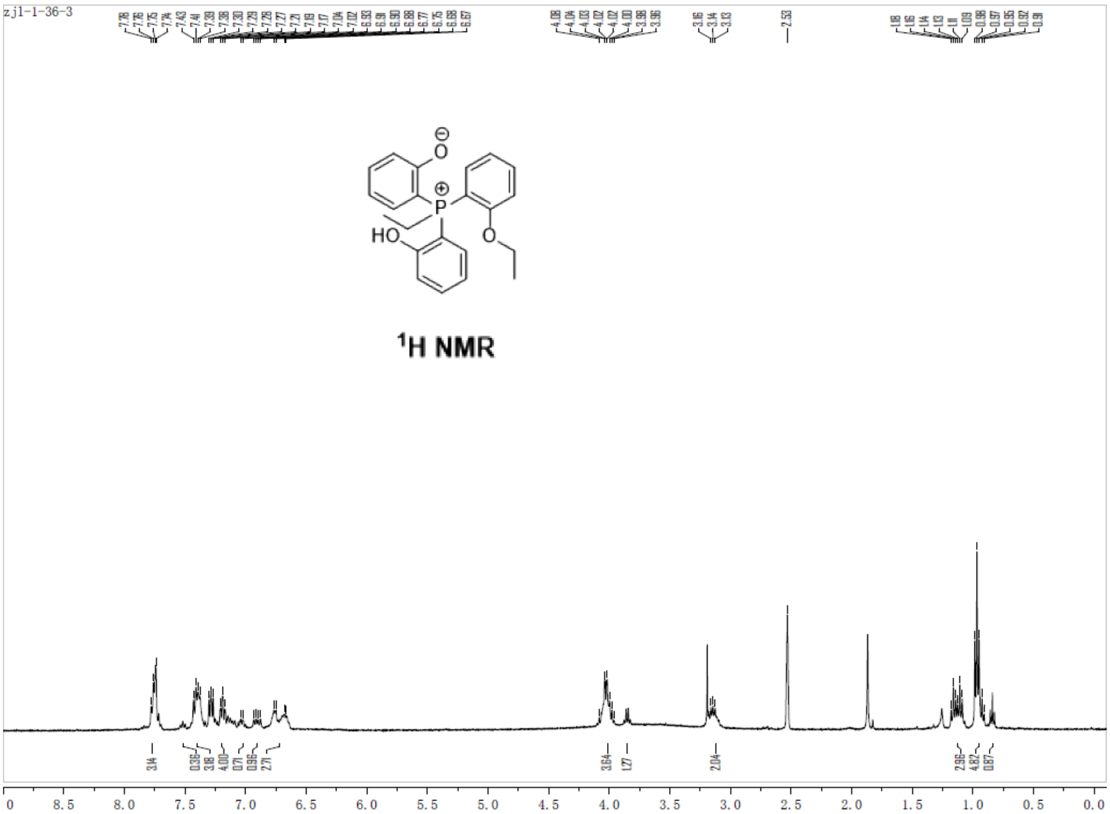


Figure S69. ^{1}H NMR of **P-IV** DMSO-6d at RT

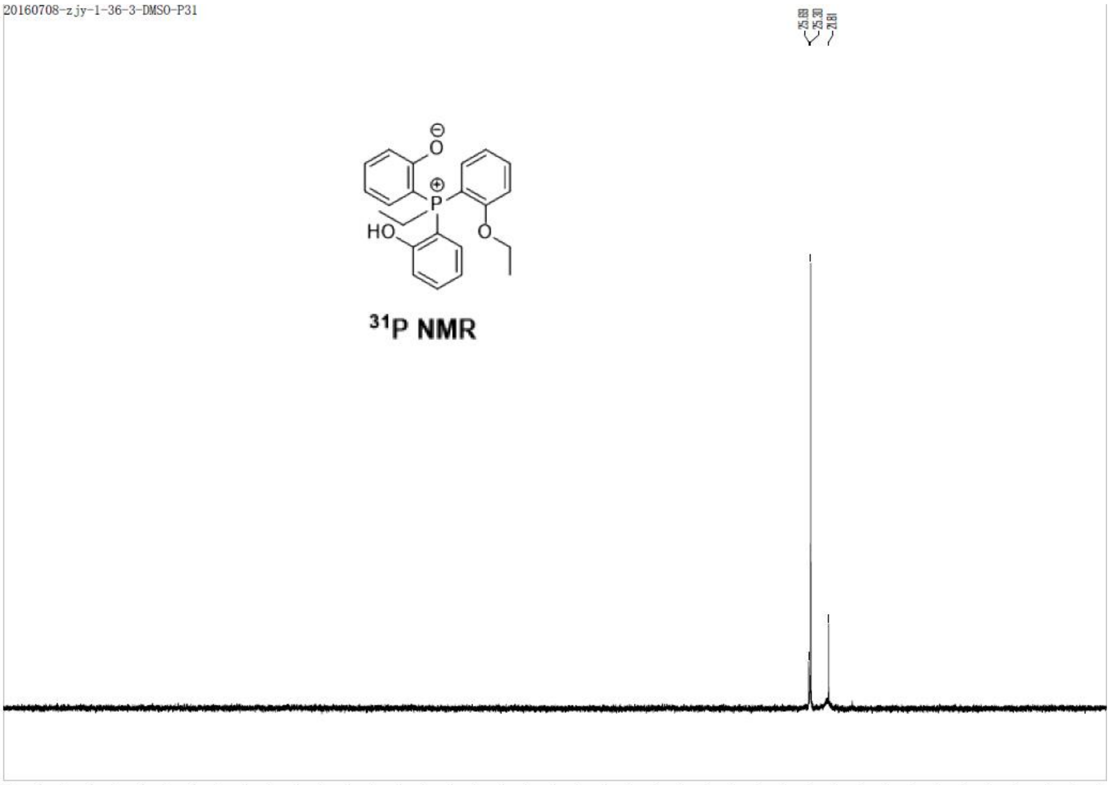


Figure S70. ^{31}P NMR of **P-IV** DMSO-6d at R