Semi-heterogeneous Dual Iron/Photocatalytic Decarboxylative C(sp^3)-C(sp^3) Cross-Coupling via Radical Sorting

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Contents

1. General Information

All reactions were performed under argon atmosphere with glass storage tube unless otherwise stated. Reagents were purchased from commercial sources and were used as received. Solvents were purified by VG-P7 solvent drying system or commercial dry solvent. Thin layer chromatography (TLC) was performed to monitor reactions by UV light (254 nm) or phosphomolybdate chromogenic agent. Silica gel column chromatography was performed using 200-300 Mesh silica gel.

The reaction tube used in the experiment was a 10 mL liquid storage sealed tube with a polytetrafluoroethylene thread plug. The photoreactor was an optical parallel reaction instrument produced by Shanghai Shanshi Technology SSSTECH-AF3. (Figure S1).

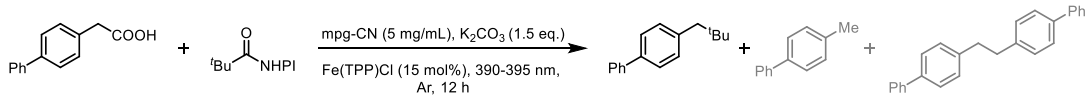
^{1}H NMR spectra and ^{13}C NMR spectra were recorded at 400 MHz, 100 MHz on a Bruker Avance 400 spectrometer. All chemical shifts in ^{1}H NMR spectra are reported in parts per million (ppm) relative to residual $CDCl_3$ (7.26 ppm) as internal standards. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, br = broad), the number of protons (n) for a given resonance was indicated by nH. Coupling constants were reported as a J value in Hz. ^{19}F NMR chemical shiftswere reported in ppm. ^{13}C NMR chemical shifts are reported in ppm relative to the central peak of $CDCl_3$ (77.16 ppm) as internal standards. HRMS data were obtained by ESI or APCI method with Bruker mass spectrometer (MAXIS). EPR were recorded with Bruker E500 electron paramagnetic spectrometer. UV-Vis absorption spectra were collected on a PerkinEImer Lambda 365 UV-VIS Spectrophotometer. The X-Ray Diffraction (XRD)patterns were collected on Rigaku D/Max2550VB+/PC (Cu Kα source) at a scan rateof 2.4° min^{-1}. Scanning Electron Microscopy (SEM) images were obtained on a fieldemission scanning electron microscope (HITACHI SU8220 microscope) at anacceleration voltage and the applied current of 5 kV and 10 μA. For the SEM test, thepowder samples were glued on an aluminium SEM specimen holder with theconductive resin, and then the specimen holder was directly put into SEM for testingwithout gold spraying. X-Ray Photoelectron Spectroscopy (XPS) spectra weredetermined on a VG ESCALAB 250 XPS system with a monochromatized Al Kα Xray source (15 kV, 200 W). The BET test was performed on a fully automatic specific surface area and pore analyzer, model ASAP2460.

Figure S1. Pictures of photoreactors

(Note: The temperature of the reaction mixture is room temperature due to return water, and the reactor has no external heating devices)

2. Optimization of reaction conditions

Table S1. Screening of solvent.

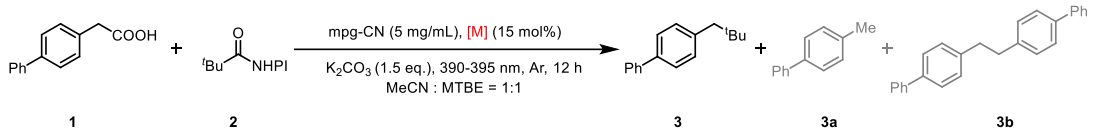


1 **2** **3** **3a** **3b**

Entry	Solvent	Yield (%)		
		3	**3a**	**3b**
1	MeCN	56	10	16
2	THF	33	10	25
3	MTBE	54	19	12
4	acetone	48	7	20
5	1,4-Dioxane	24	18	21
6	DMSO	6	trace	trace
7	**MeCN + MTBE**	65	9	12
8	MeCN + DCE	32	5	27
9	MeCN + acetone	41	8	23
10	MeCN + EA	50	8	20

Reaction conditions: **1** (0.2 mmol), **2** (1.2 equiv.), mpg-CN (5 mg/mL), Fe(TPP)Cl (15 mol%), K_2CO_3 (1.5 equiv.), solvent (0.1 M), 390-395 nm, Ambient temperature refers to 28-33 °C, 12 h, Ar. Yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

Table S2. Screening of Fe catalyst.

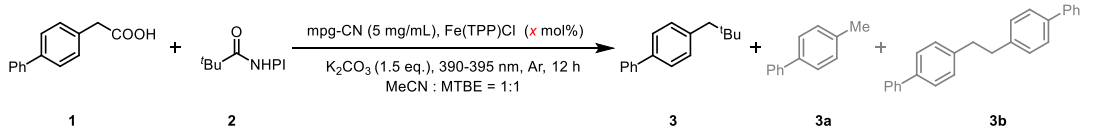


1 **2** **3** **3a** **3b**

Entry	[M]	Yield (%)		
		3	**3a**	**3b**
1	Fe(TPP)Cl	65	9	12
2	Fe(OEP)Cl	65	11	12
3	Co(TPP)Cl	11	56	14
4	Mn(TPP)Cl	20	12	33
5	Ni(TPP)Cl	20	21	17

Reaction conditions: **1** (0.2 mmol), **2** (1.2 equiv.), mpg-CN (5 mg/mL), Fe catalyst (15 mol%), K_2CO_3 (1.5 equiv.), MeCN : MTBE = 1:1 (0.1 M), 390-395 nm, Ambient temperature refers to 28-33 °C, 12 h, Ar. Yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

Table S3. Screening of Fe(TPP)Cl loading.

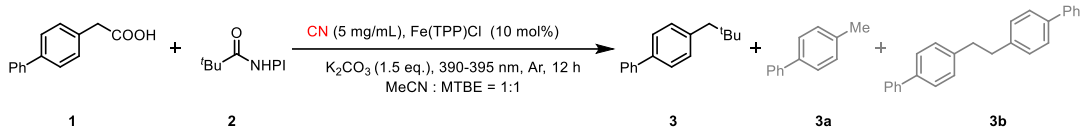


1 **2** **3** **3a** **3b**

Entry	x	Yield (%)		
		3	**3a**	**3b**
1	5	61	7	15
2	10	72	7	10
3	15	65	9	12
4	20	63	8	14

Reaction conditions: **1** (0.2 mmol), **2** (1.2 equiv.), mpg-CN (5 mg/mL), Fe catalyst (*x* mol%), K_2CO_3 (1.5 equiv.), MeCN : MTBE = 1:1 (0.1 M), 390-395 nm, Ambient temperature refers to 28-33 °C, 12 h, Ar. Yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

Table S4. Screening of carbon nitride (CN).

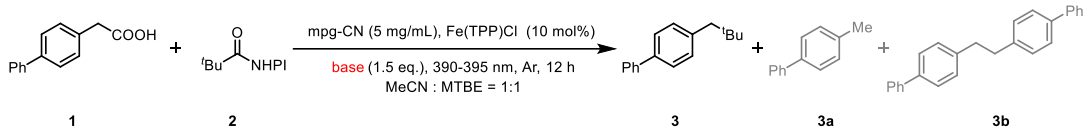


1 **2** **3** **3a** **3b**

Entry	CN	Yield (%)		
		3	**3a**	**3b**
1	mpg-CN	72	7	10
2	mpg-CN-Q	35	4	20
3	g-C_3N_4	32	6	10
4	CN-OA-m	56	7	17
5	$BiVO_4$	33	10	6

Reaction conditions: **1** (0.2 mmol), **2** (1.2 equiv.), CN (5 mg/mL), Fe(TPP)Cl (10 mol%), K_2CO_3 (1.5 equiv.), MeCN : MTBE = 1:1 (0.1 M), 390-395 nm, Ambient temperature refers to 28-33 °C, 12 h, Ar. Yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

Table S5. Screening of the base.

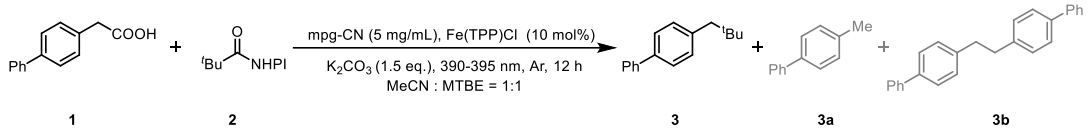


1 **2** **3** **3a** **3b**

Entry	base	Yield (%)		
		3	**3a**	**3b**
1	K_2CO_3	72	7	10
2	Cs_2CO_3	65	10	10
3	K_3PO_4	66	9	12
4	K_2HPO_4	48	7	15
5	KOH	24	44	12
6	DIPEA	41	40	9
7	DBU	trace	trace	trace
8	Et_3N	19	49	12
9	DMTHPM	17	20	19

Reaction conditions: **1** (0.2 mmol), **2** (1.2 equiv.), mpg-CN (5 mg/mL), Fe(TPP)Cl (10 mol%), base (1.5 equiv.), MeCN : MTBE = 1:1 (0.1 M), 390-395 nm, Ambient temperature refers to 28-33 °C, 12 h, Ar. Yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

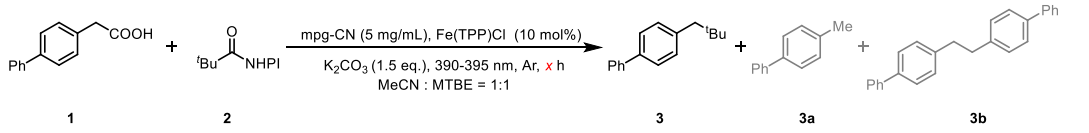
Table S6. Screening of optical power.



Entry	390-395 nm	Yield (%)		
		3	**3a**	**3b**
1	15 W	72	7	10
2	10 W	72	6	9
3	5 W	66	8	13
4	2 W	63	6	11

Reaction conditions: **1** (0.2 mmol), **2** (1.2 equiv.), mpg-CN (5 mg/mL), Fe(TPP)Cl (10 mol%), K_2CO_3 (1.5 equiv.), MeCN : MTBE = 1:1 (0.1 M), 390-395 nm, Ambient temperature refers to 28-33 °C, 12 h, Ar. Yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

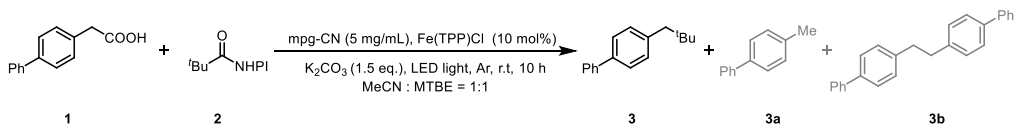
Table S7. Screening of reaction time.



Entry	Time (h)	Yield (%)		
		3	**3a**	**3b**
1	6	62	8	9
2	8	63	10	10
3	10	72	6	10
4	12	72	6	9

Reaction conditions: **1** (0.2 mmol), **2** (1.2 equiv.), mpg-CN (5 mg/mL), Fe(TPP)Cl (10 mol%), base (1.5 equiv.), MeCN : MTBE = 1:1 (0.1 M), 390-395 nm, Ambient temperature refers to 28-33 °C, *x* h, Ar. Yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

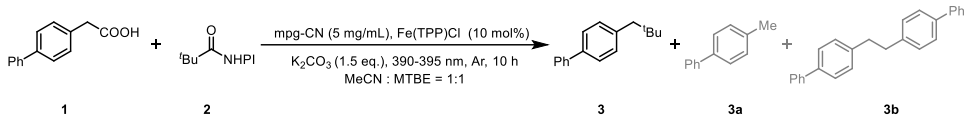
Table S8. Screening of different light sources.



Entry	LED light	Yield (%)		
		3	**3a**	**3b**
1	390-395 nm	72	6	9
2	460-465 nm	33	4	16
3	530-535 nm	8	2	8
4	620-630 nm	trace	trace	trace

Reaction conditions: **1** (0.2 mmol), **2** (1.2 equiv.), mpg-CN (5 mg/mL), Fe(TPP)Cl (10 mol%), K_2CO_3 (1.5 equiv.), MeCN : MTBE = 1:1 (0.1 M), 390-395 nm, Ambient temperature refers to 28-33 °C, 10 h, Ar. Yields were determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

Table S9. Control experiments.



1 **2** **3** **3a** **3b**

Entry	Deviation from the standard conditions	Yield (%)		
		3	**3a**	**3b**
1	none	72	6	9
2	no light	n.r	n.r	n.r
3	no mpg-CN	15	1	6
4	no Fe	23	19	26
5	no K_2CO_3	29	6	9
6	air	trace	n.r	n.r

Reaction conditions: **1** (0.2 mmol), **2** (1.2 equiv.), mpg-CN (5 mg/mL), Fe(TPP)Cl (10 mol%), K_2CO_3 (1.5 equiv.), MeCN : MTBE = 1:1 (0.1 M) , 390-395 nm, Ambient temperature refers to 28-33 °C, 10 h, Ar. Yields were determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as internal standard.

3. Preparation of mpg-CN and raw materials.

3.1 Preparation of mpg-CN.

mpg-CN was synthesized according to the literature procedure[1]. A mixture of cyanamide (3.00 g) and colloidal silica aqueous solution (Ludox HS-40, 40 wt.%, 7.50 g) was stirred in a glass vial at room temperature for about 15 minutes until cyanamide was dissolved completely. Water was slowly evaporated upon stirring the mixture overnight at 60 °C. Magnetic stirring bar was removed and the white solid was transferred into a porcelain crucible and calcinated at 550 °C for ca. 4 h under flow of nitrogen in a muffle oven. The oven was allowed to cool to room temperature, the content from the crucible was transferred into a polypropylene bottle, The resulting brown-yellow powder was treated with a 4 M NH_4HF_2 for 24 h to remove the silica template. The powders were then centrifuged and washed three times with distilled water and twice with ethanol, and dried overnight in a vacuum oven (60 °C).

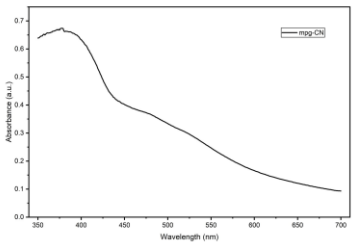
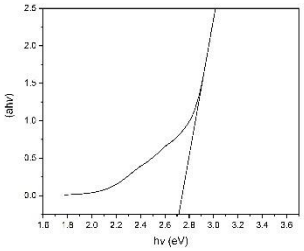
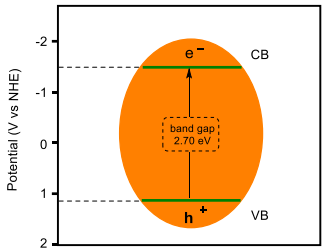
UV-vis spectra of mpg-C_3N_4	Tauc plot derived from DR UV-Vis absorption spectrum assuming the direct allowed transition in mpg-CN	Band gap of mpg-CN
		

Figure S2 Characterization of mpg-CN

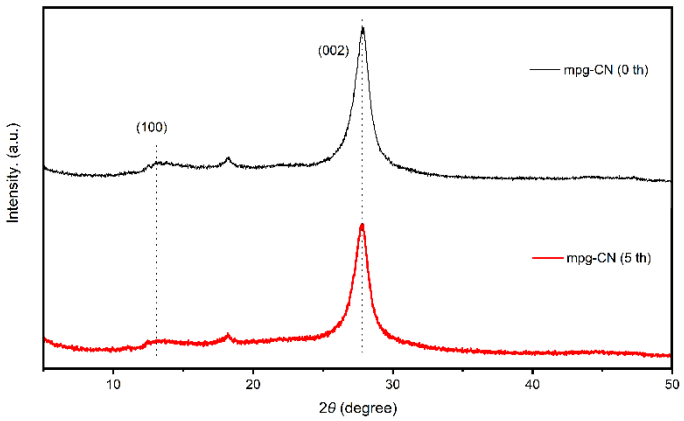


Figure S3 Powder X-Ray diffraction pattern of mpg-CN

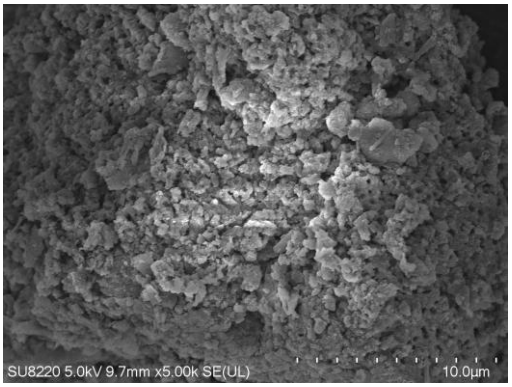
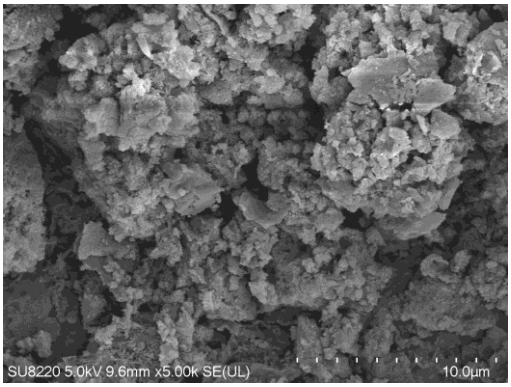
SEM of mpg-CN (0 th)	SEM of recycled mpg-CN (5 th)
	

Figure S4 SEM of mpg-CN

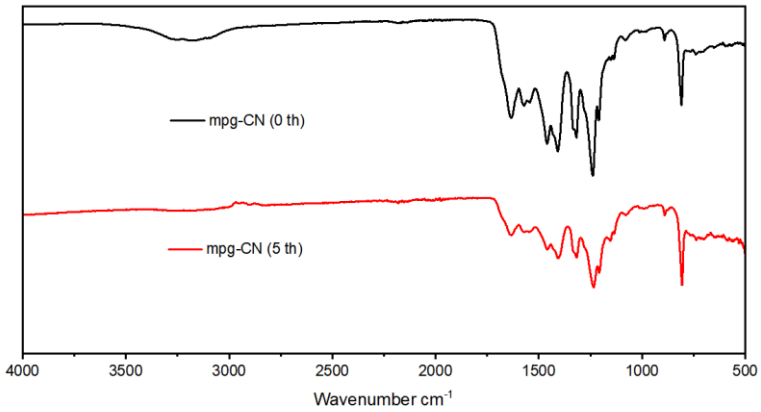


Figure S5 FTIR spectra of mpg-CN

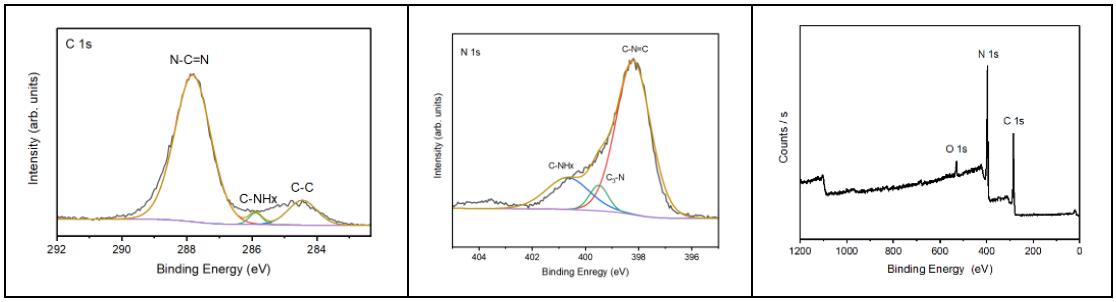


Figure S6 XPS of mpg-CN (0 th)

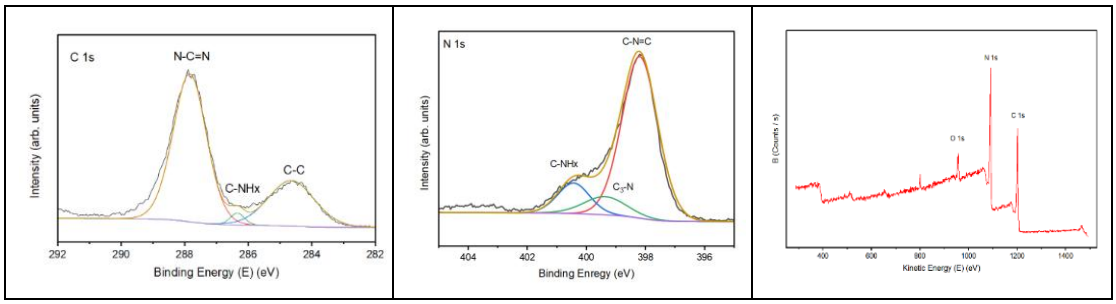


Figure S7 XPS of recycled mpg-CN (5th)

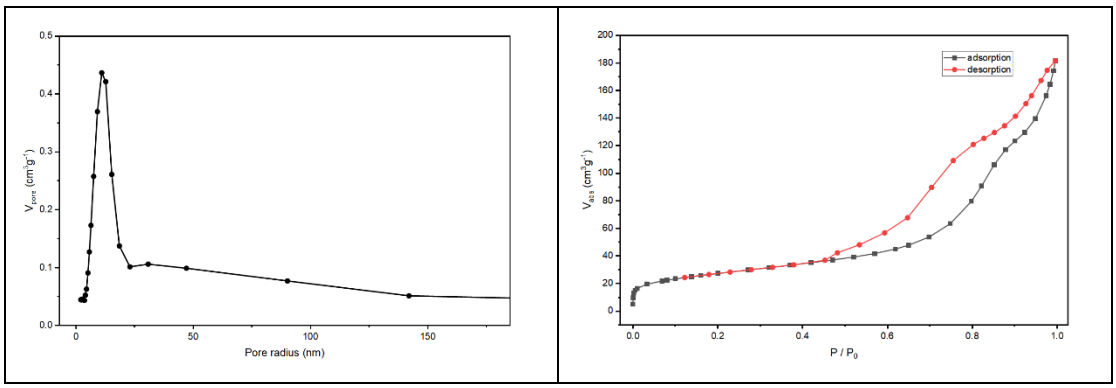


Figure S8 BET of mpg-CN (0 th)

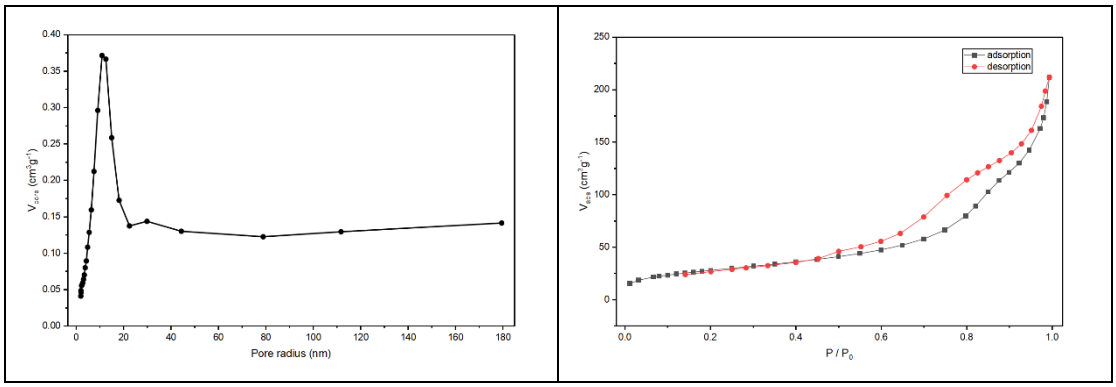
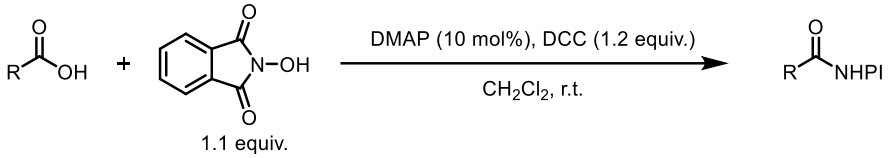
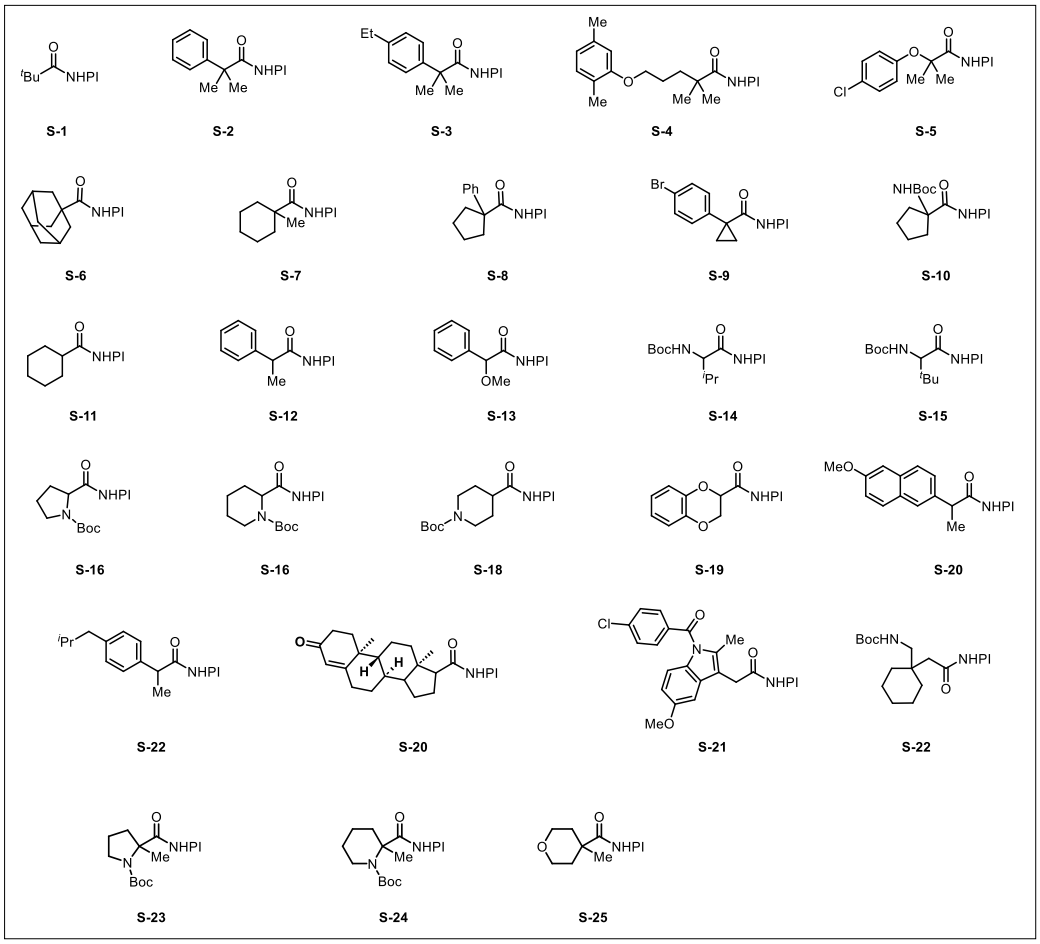


Figure S9 BET of recycled mpg-CN (5 th)

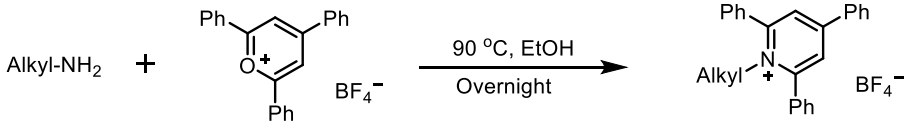
3.2 General procedure for preparation of redox active esters (RAEs).



RAEs were prepared using alkyl carboxylic acid as starting materials according to the literature procedure.[2] The corresponding alkyl carboxylic acid (10.0 mmol, 1.0 equiv.), *N*-hydroxyphthalimide (11.0 mmol, 1.1 equiv.), and 4-dimethylaminopyridine (1.0 mmol, 10 mol%) were mixed in a flask with a magnetic stirring bar. Dry CH_2Cl_2 (40 mL) was added. Then a solution of *N*, *N′*-dicyclohexylcarbodiimide (11.0 mmol, 1.1 equiv.) in CH_2Cl_2 (15 mL) was added slowly at room temperature. The reaction mixture was monitored by TLC at room temperature. After completed, the white precipitate was filtered off and the solution was concentrated under vacuum. Corresponding redox active esters were purified by column chromatography on silica gel (petroleum ether/ethyl acetate as eluent).

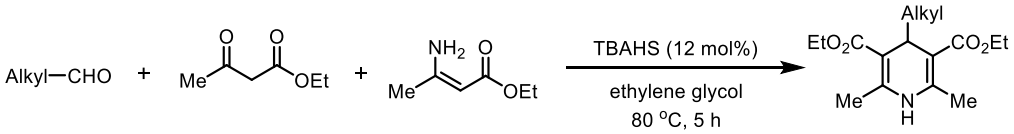


3.3 Synthesis of pyridinium salts.[3]



A magnetic stir bar, primary amine (1.2 equiv.) was added to a suspension of 2,4,6- triphenylpyrylium tetrafluoroborate (1.0 equiv.) and EtOH (1.0 M) in a round-bottom flask. The mixture was stirred and heated at reflux in an oil bath at 85 °C to 90 °C for 4 h. The mixture was then allowed to cool to room temperature. If product precipitation occurred after cooling to room temperature, the solid was filtered, washed with EtOH and then Et_2O, and dried under high vacuum.

3.4 Synthesis of 1,4-dihydropyridines (DHP).[4]

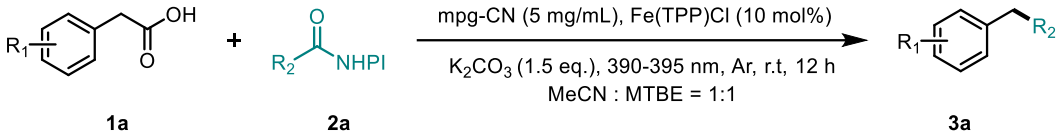


A magnetic stir bar, Bu_4NHSO_4 (12 mol%) ethyl 3-aminocrotonate (1.0 equiv.), ethyl acetoacetate (1.0 equiv.), aldehyde (1.0 equiv.), and d ethylene glycol (2.5 M) were added into a round-bottom flask, which was closed with a rubber stopper with argon balloon and heated at 80 °C for overnight. After cooling to room temperature, the reaction mixture was diluted with water, extracted with ethyl acetate,

dried over Na_2SO_4 and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel using the solvent system afforded the desired product.

4. General procedure for the catalytic reactions

4.1 Standard procedure for the synthesis of products

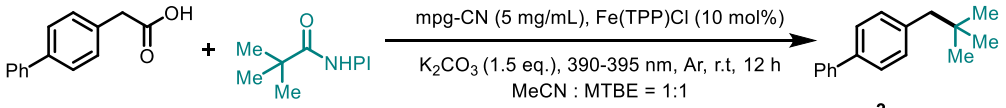


1a **2a** **3a**

To an oven-dried 10 mL glass storage tube with a stir bar were added acid (1.0 equiv., 0.2 mmol), redox active ester (1.2 equiv., 0.24 mmol), mpg-CN (10 mg), Fe(TPP)Cl (10 mol%) and K_2CO_3 (1.5 equiv., 0.3 mmol). The mixture was evacuated and backfilled with argon for 3 times before mixed solvent (MeCN : MTBE = 1 : 1) (2.0 mL) were added. The reaction mixture was placed in a photo reactor, and maintained at approximately room temperature. The mixture was then stirred rapidly and irradiated for 12-24 hours. mpg-CN was obtained by rapid filtration of the reaction mixture, and the filtrate was concentrated under vacuo. The product was purified via flash column chromatography on silica gel (petroleum ether/ethyl acetate = 200:1~50:1).

4.2 Standard procedure for gram-scale synthesis

An oven-dried 100 mL flask equipped with a magnetic stir bar was sequentially charged with 2-([1,1'-biphenyl]-4-yl)acetic acid (1.0 equiv., 4.0 mmol), tertiary butyl redox active ester (1.2 equiv., 4.8 mmol), mpg-CN (200 mg) and Fe(TPP)Cl (10 mol%) and K_2CO_3 (1.5 equiv., 0.3 mmol). The mixture was evacuated and backfilled with argon for 3 times before mixed solvent (MeCN : MTBE = 1: 1) (40.0 mL) were added. The reaction mixture was placed in a photo reactor, and maintained at approximately room temperature. The mixture was then stirred rapidly and irradiated for 12 hours. mpg-CN was obtained by rapid filtration of the reaction mixture, and the filtrate was concentrated under vacuo. The product was purified via flash column chromatography on silica gel (petroleum ether/ethyl acetate = 200:1~50:1).



1, 4 mmol **2, 1.2 eq.** **3**

547.5 mg, 61% yield

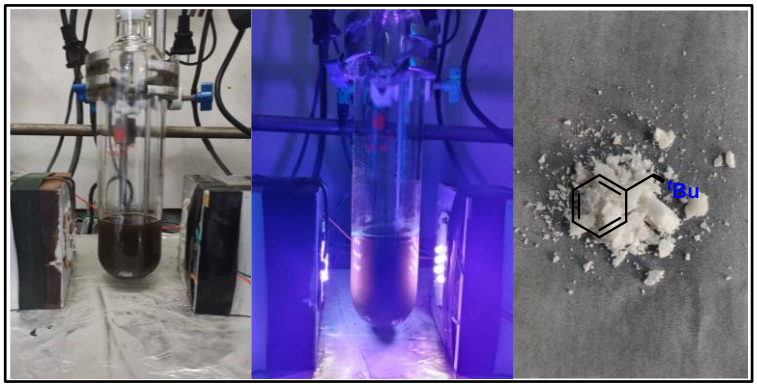
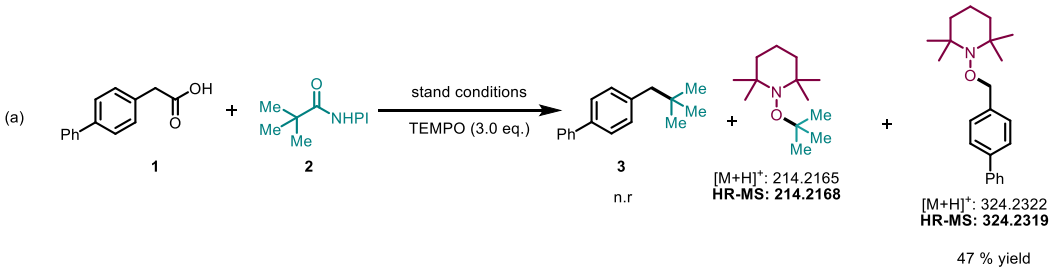


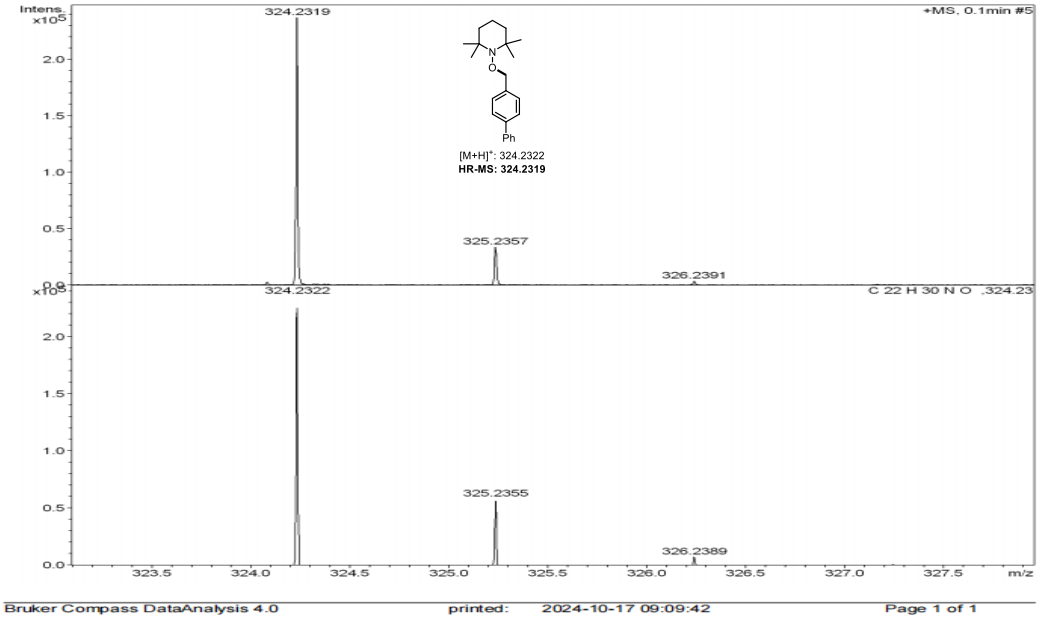
Figure S10 gram-scale synthesis

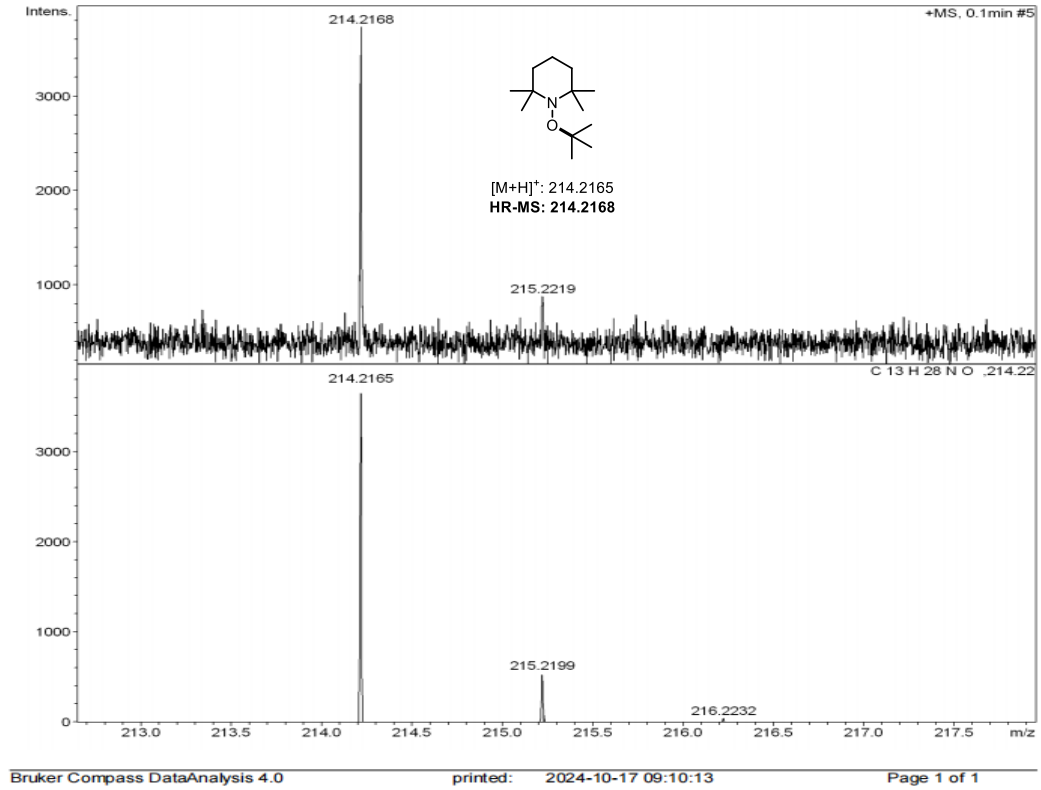
5. Mechanism research

5.1 radical trapping experiment

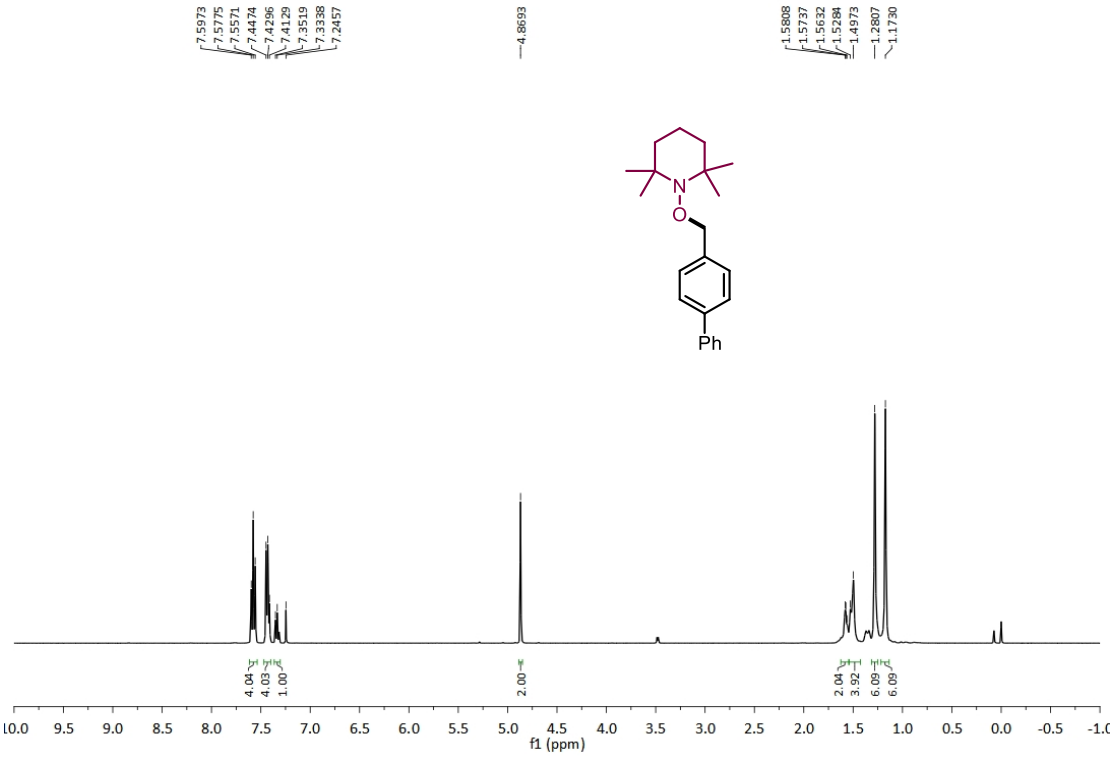


To an oven-dried 10 mL glass storage tube with a stir bar were added acid (1.0 equiv., 0.2 mmol), redox active ester (1.2 equiv., 0.24 mmol), mpg-CN (10 mg), Fe(TPP)Cl (10 mol%) and K_2CO_3 (1.5 equiv., 0.3 mmol), TEMPO (3.0 eq., 0.6 mmol) The mixture was evacuated and backfilled with argon for 3 times before mixed solvent (MeCN : MTBE = 1 : 1) (2.0 mL) were added. The reaction mixture was placed in a photo reactor, and maintained at approximately room temperature. The mixture was then stirred rapidly and irradiated for 12 hours. mpg-CN was obtained by rapid filtration of the reaction mixture, and the filtrate was concentrated under vacuo. The product was purified via flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1~50:1).





^{1}H NMR (400 MHz, $CDCl_3$) δH 7.58 (t, J = 8.0 Hz, 4H), 7.43 (m, 4H), 7.34 (d, J = 7.3 Hz, 1H), 4.87 (s, 2H), 1.57 (m, 2H), 1.51 (d, J = 12.4 Hz, 4H), 1.28 (s, 6H), 1.17 (s, 6H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 141.2, 140.5, 137.5, 128.9, 128.1, 127.3, 127.26, 127.19, 78.6, 60.2, 39.9, 33.3, 20.5, 17.3.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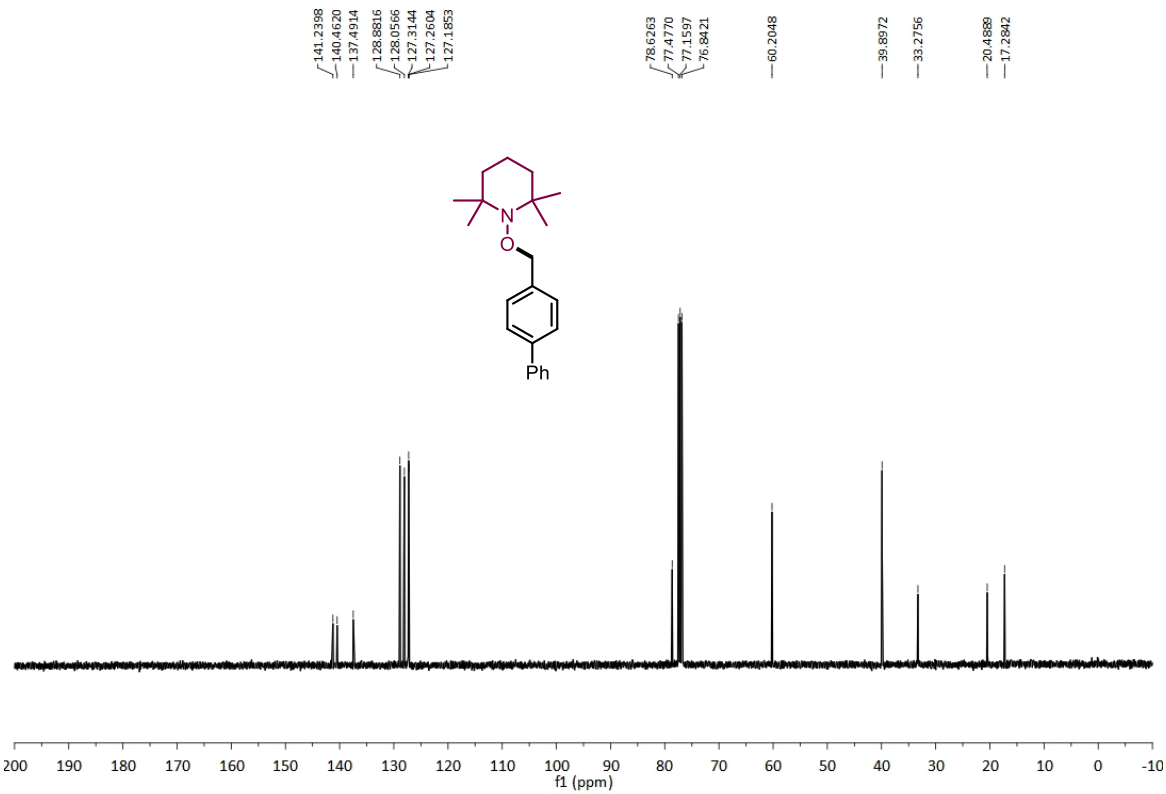
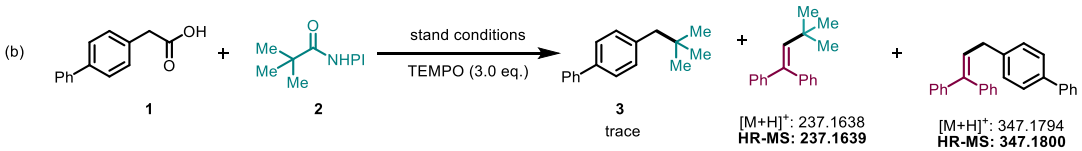
7.5775
7.5571
7.4474
7.4296
7.4129
7.3519
7.3338
7.2457
4.8693
1.5808
1.5737
1.5632
1.5284
1.4973
1.2807
1.1730
N
O
Ph
4.04
4.03
1.00
2.00
2.04
3.92
6.09
6.09
f1 (ppm)


141.2398
140.4620
137.4914
128.8816
128.0566
127.3144
127.2604
127.1853
78.6263
77.4770
77.1597
76.8421
60.2048
39.8972
33.2756
20.4889
17.2842
N
O
Ph
f1 (ppm)

(b)


stand conditions
TEMPO (3.0 eq.)
1
2
3
trace
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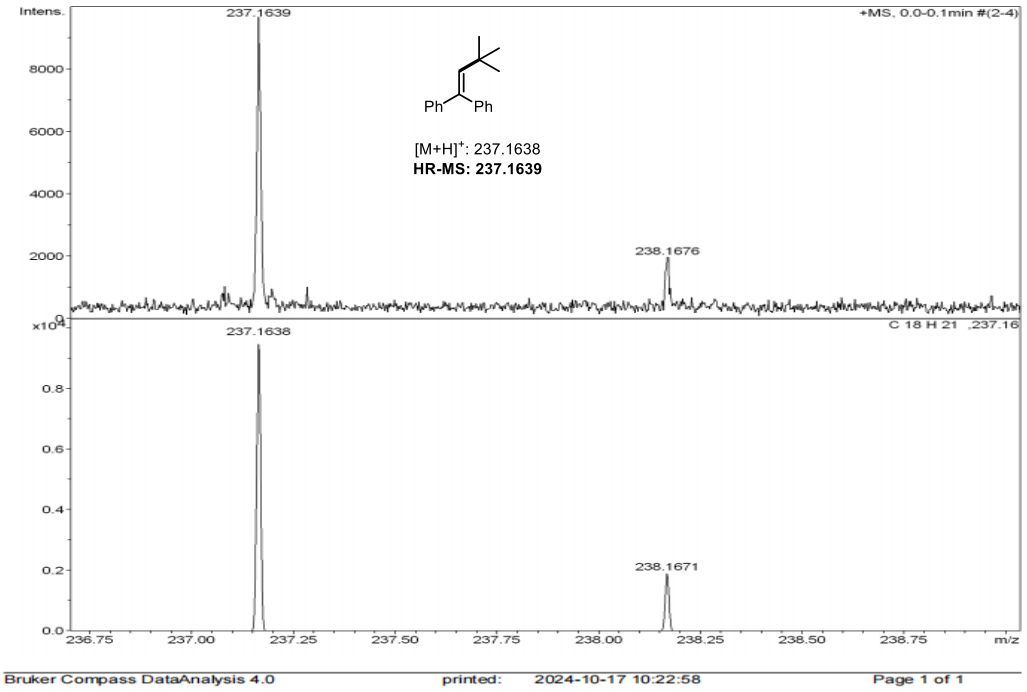
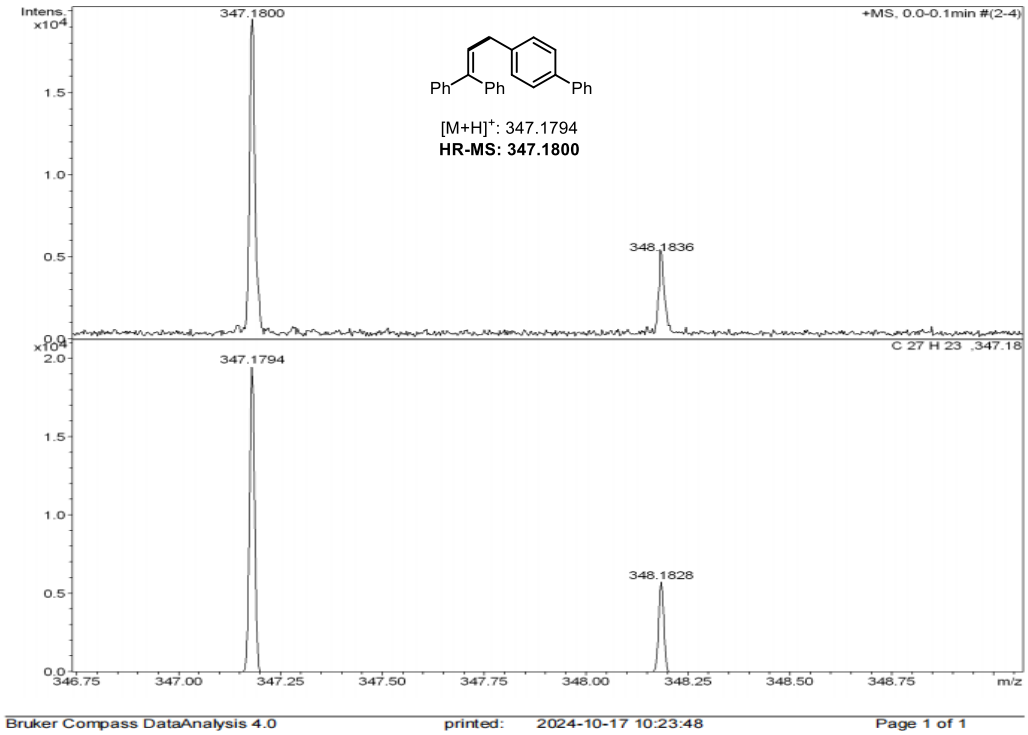
HR-MS: 237.1639
[M+H]+: 347.1794
HR-MS: 347.1800


Intens.
237.1639
+MS, 0.0-0.1min #(2-4)
[M+H]+: 237.1638
HR-MS: 237.1639
238.1676
237.1638
C 18 H 21 ,237.16
238.1671
m/z
Bruker Compass DataAnalysis 4.0
printed: 2024-10-17 10:22:58
Page 1 of 1


Intens.
347.1800
+MS, 0.0-0.1min #(2-4)
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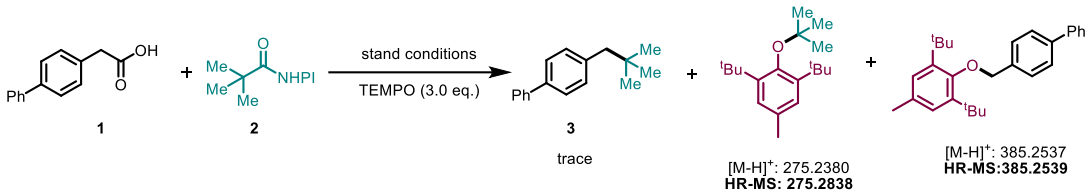
HR-MS: 347.1800
348.1836
347.1794
C 27 H 23 ,347.18
348.1828
m/z
Bruker Compass DataAnalysis 4.0
printed: 2024-10-17 10:23:48
Page 1 of 1

(c)

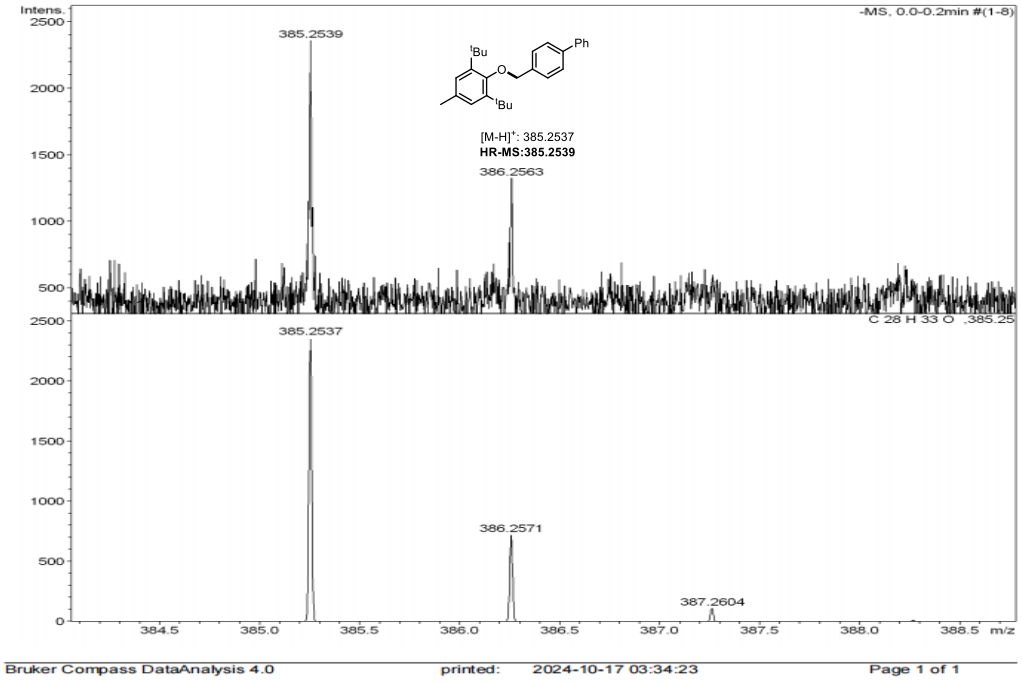


1 2 3

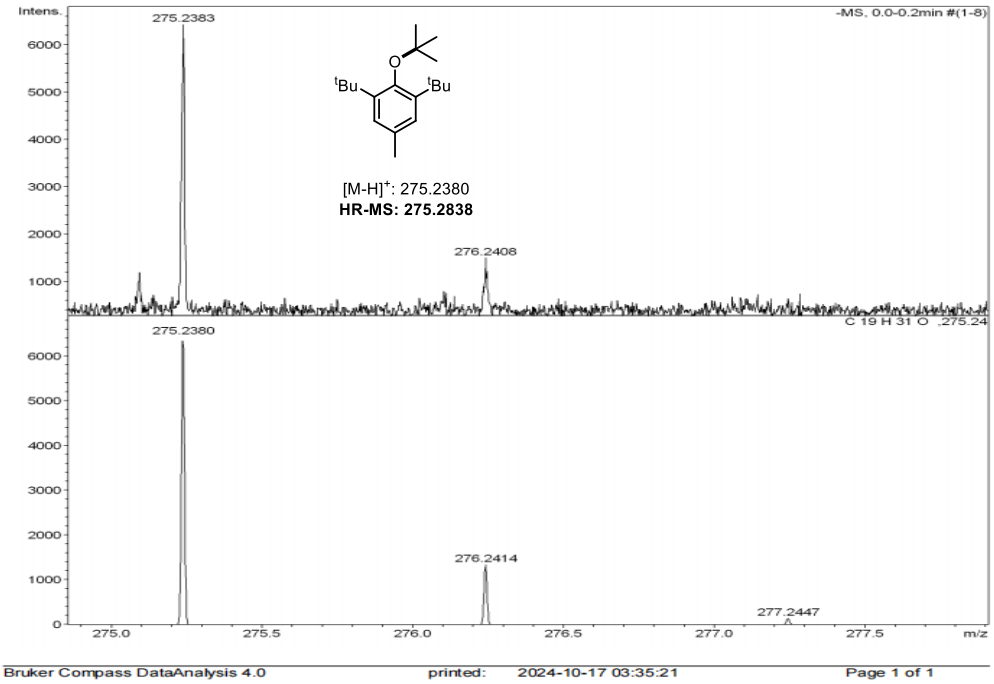
trace

$[M-H]^+$: 275.2380
HR-MS: 275.2838

$[M-H]^+$: 385.2537
HR-MS:385.2539

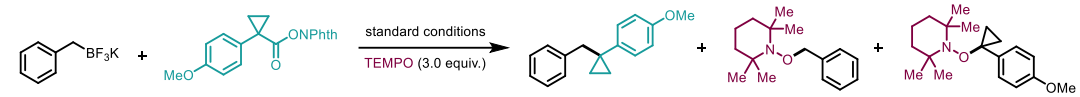


Bruker Compass DataAnalysis 4.0 printed: 2024-10-17 03:34:23 Page 1 of 1



Bruker Compass DataAnalysis 4.0 printed: 2024-10-17 03:35:21 Page 1 of 1

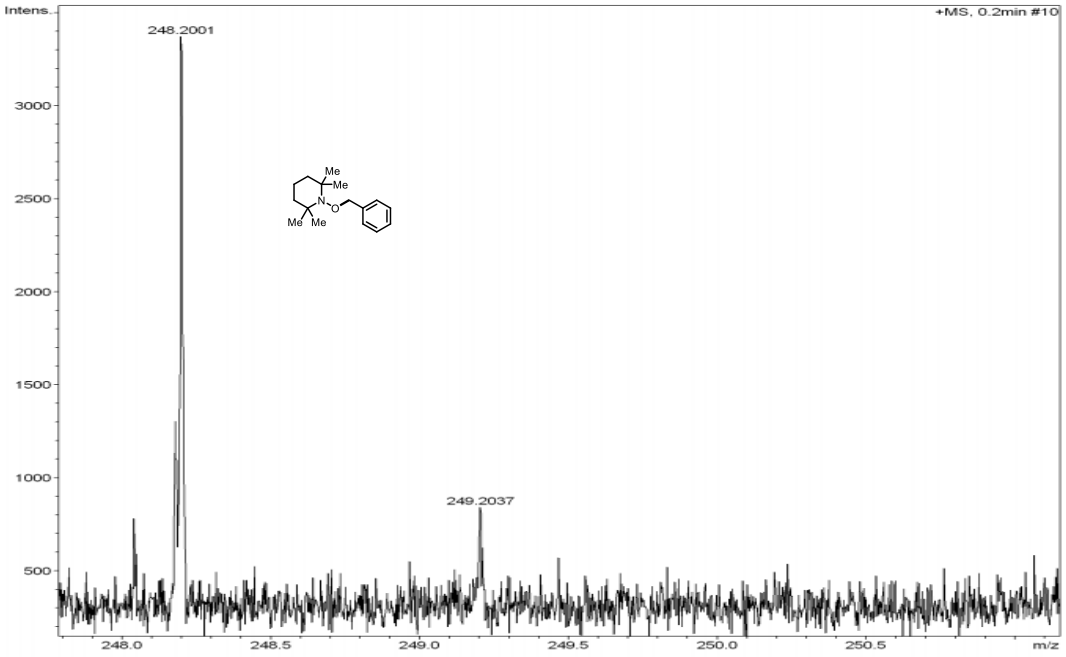
(d)

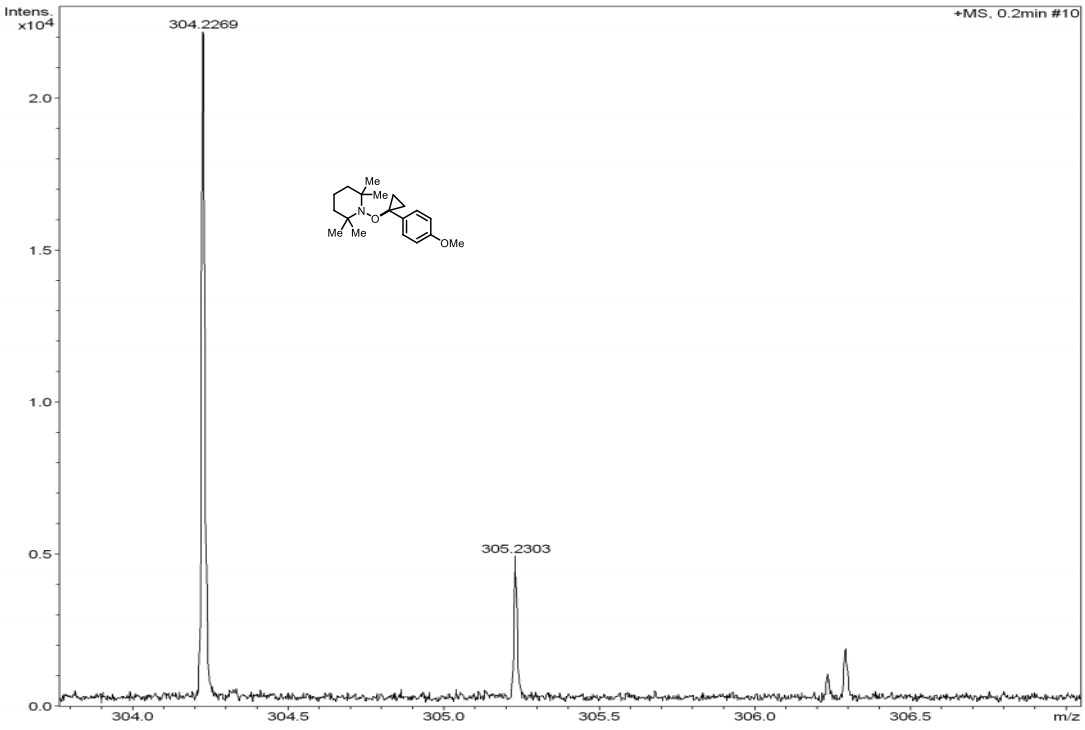


50 **51** **37**, N.D **52**, detected by HRMS **53**, detected by HRMS

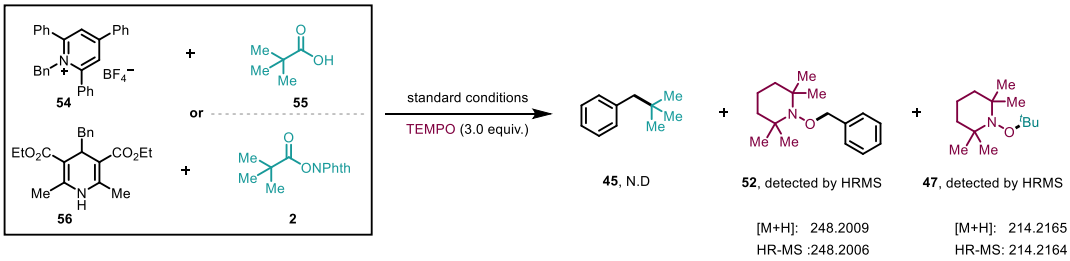
[M+H]: 248.2009 [M+H]: 304.2271

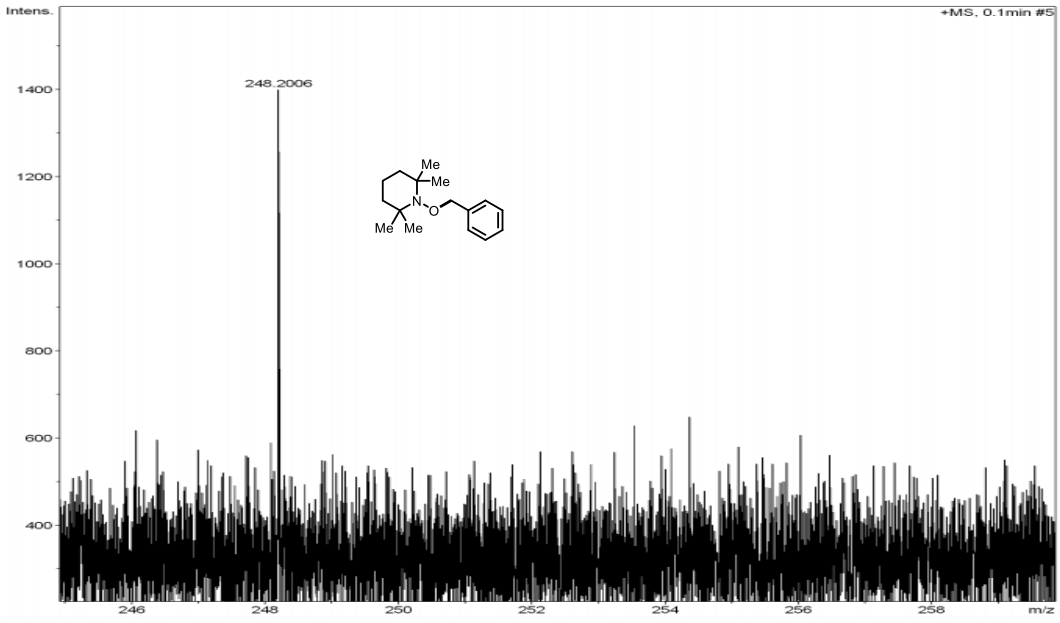
HR-MS: 248.2001 HR-MS: 304.2269





(e)


54
55
or
56
2
standard conditions
TEMPO (3.0 equiv.)
45, N.D
52, detected by HRMS
47, detected by HRMS
[M+H]: 248.2009
HR-MS :248.2006
[M+H]: 214.2165
HR-MS: 214.2164


Intens.
+MS, 0.1min #5
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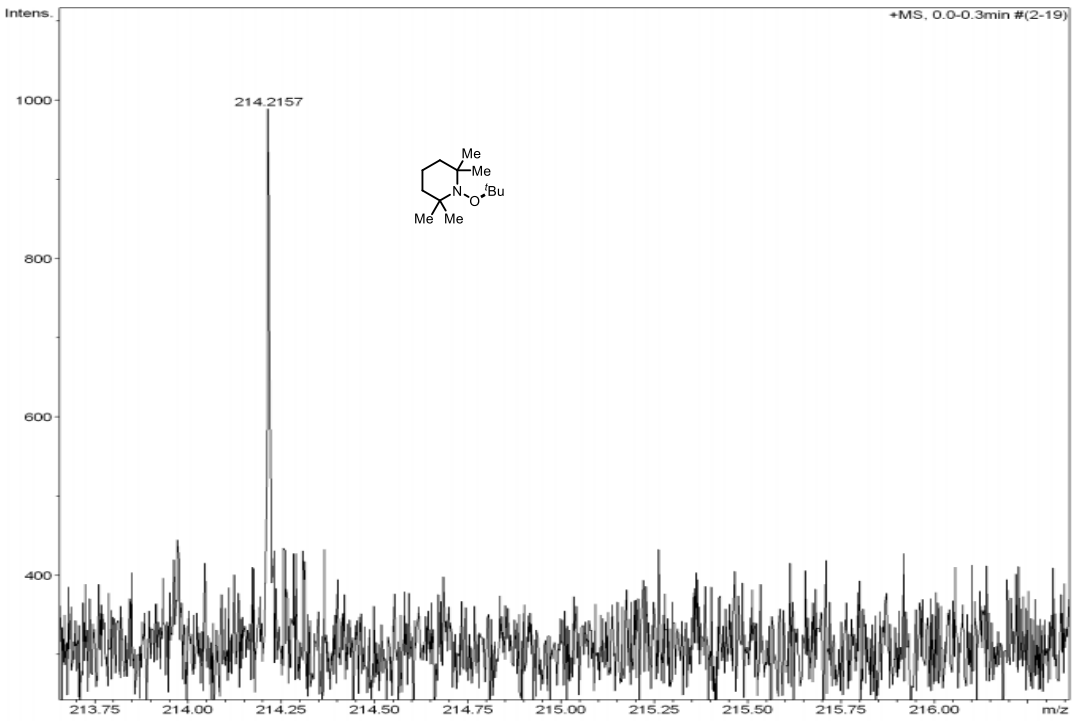
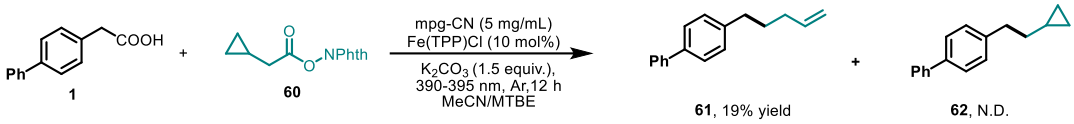
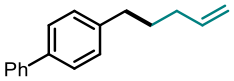
1400
1200
1000
800
600
400
246
248
250
252
254
256
258
m/z


Intens.
+MS, 0.0-0.3min #(2-19)
214.2157
1000
800
600
400
213.75
214.00
214.25
214.50
214.75
215.00
215.25
215.50
215.75
216.00
m/z

5.2 Radical Clock Experiments



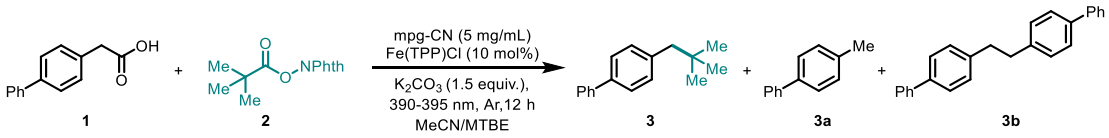
To an oven-dried 10 mL glass storage tube with a stir bar were added acid (1.0 equiv., 0.2 mmol), redox active ester (1.2 equiv., 0.24 mmol), mpg-CN (10 mg), Fe(TPP)Cl (10 mol%) and K_2CO_3 (1.5 equiv., 0.3 mmol), The mixture was evacuated and backfilled with argon for 3 times before mixed solvent (MeCN : MTBE = 1 : 1) (2.0 mL) were added. The reaction mixture was placed in a photo reactor, and maintained at approximately room temperature. The mixture was then stirred rapidly and irradiated for 12 hours. mpg-CN was obtained by rapid filtration of the reaction mixture, and the filtrate was concentrated under vacuo. The product was purified via flash column chromatography on silica gel (petroleum ether/ethyl acetate = 250: 1~200:1).



4-(pent-4-en-1-yl)-1,1'-biphenyl (**61**)[20]: The product **61** was purified by column chromatography (petroleum ether/ethyl acetate = 250:1~200:1). white solid, 19% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.51 (d, *J* = 7.0 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.25 (d, *J* = 7.4 Hz, 1H), 7.18 (t, *J* = 4.6 Hz, 2H), 5.83-5.73 (m, 1H), 5.0-4.9 (m, 2H), 2.60 (t, *J* = 7.8 Hz, 2H), 2.05 (q, *J* = 7.2 Hz, 2H), 1.73-1.65 (m, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 141.6, 141.1, 138.7, 138.6, 128.9, 128.7, 127.1, 127.0, 126.9,114.8, 35.0, 33.3, 30.6.

5.3 Kinetic Studies



Kinetic profiles of substrate **1** at different initial concentrations (from 0.05 M to 0.15 M) are shown in figure S11, left. A linear relationship was observed between the observed rate constant Kobs and the concentration of 1, indicating a first-order kinetic dependence on **1**

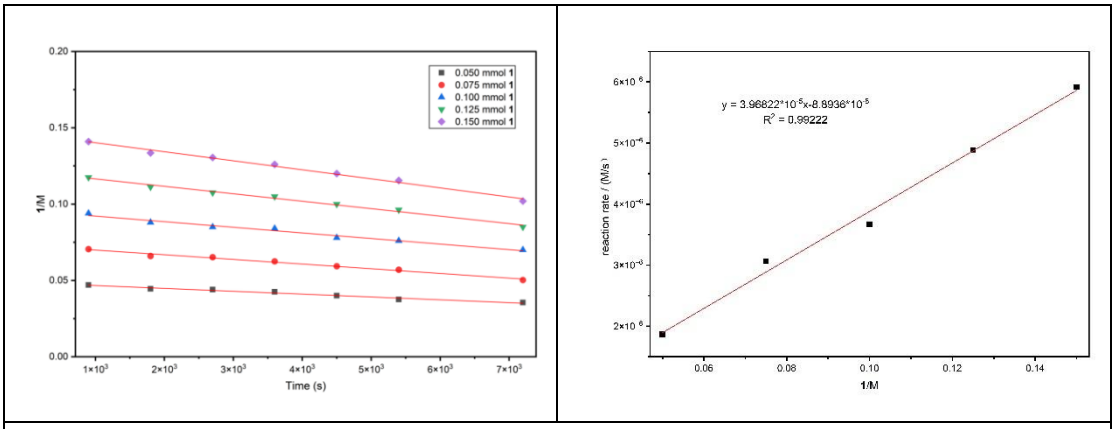


Figure S11 Kinetic studies of **1**

Kinetic profiles of substrate 2 at different initial concentrations (from 0.080 M to 0.160 M) are shown in figure S12, left. A linear relationship was observed between the observed rate constant Kobs and the concentration of **2**, indicating a zero-order kinetic dependence on **2**.

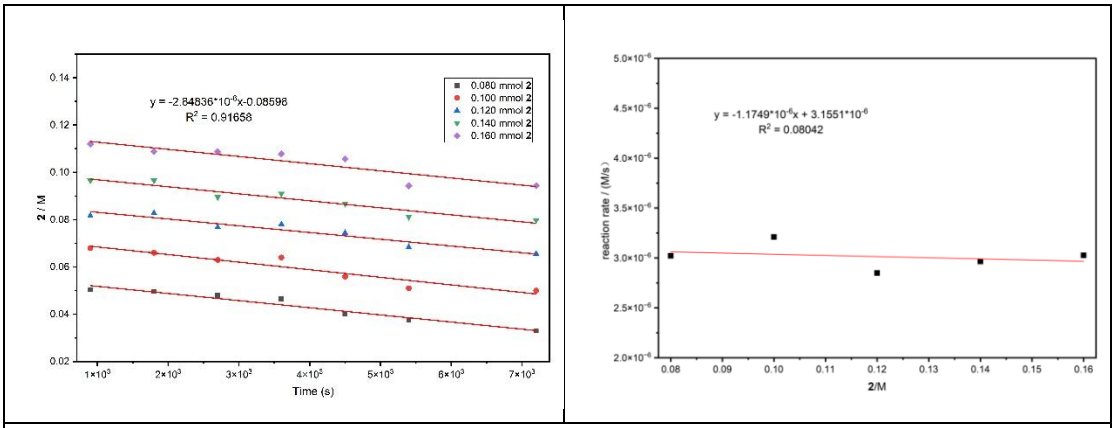


Figure S12 Kinetic studies of **2**

5.4 Cyclic Voltammograms Profiles.

Samples were prepared by mixing 0.002 mmol of the substrate in 20 mL of 0.1 M nBu_4NPF_6 in anhydrous DMF. Measurements employed a glassy carbon working electrode, platinum wire counter electrode, saturated calomel electrode (SCE) reference electrode, and a scan rate of 1000 mV/s. The solution was sparged with nitrogen for 5 minutes before data collection. $E_{1/2}$ was obtained using Origin.

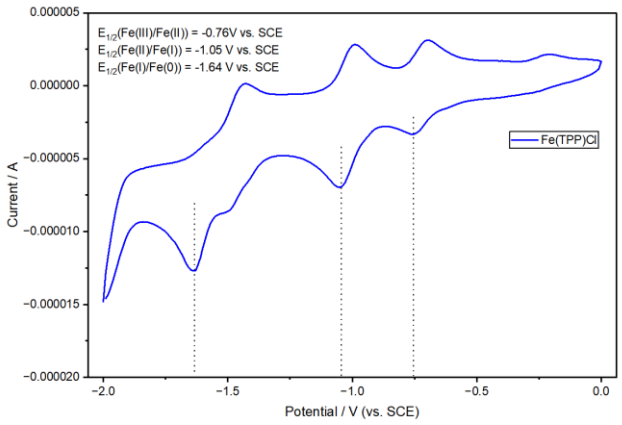
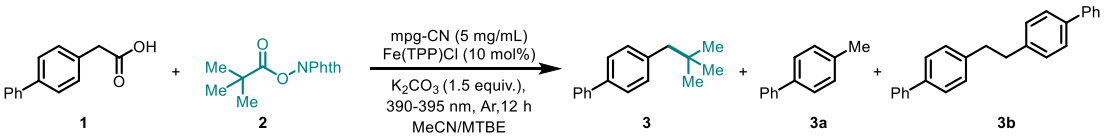


Figure S13 CV data of Fe(TPP)Cl

5.5 Product distribution for a model primary/tertiary cross-carboxylic acid coupling reaction



control conditions	product	3°-3° dimer	3°- H	1°-1° dimer	1°- H	[product] /[3°-3° dimer]	[product] /[1°-1° dimer]
no Fe(TPP)Cl	28%	36%	trace	26%	16%	0.78	1.07
with Fe(TPP)Cl	57%	21%	trace	10%	10%	2.71	5.70
fold change In the presence of Fe(TPP)Cl	↑ 2.0x	↓ 1.7x	--	↓ 2.6	↓ 1.6	↑ 3.5x	↑ 5.3x

Scheme S4 Product distribution for a model primary/tertiary cross-carboxylic acid coupling reaction

Data from the 1º–3º double decarboxylative acid coupling (Scheme S4) also support a meaningful radical sorting effect. The presence of the Fe(TPP)Cl catalyst enhanced the formation of cross-coupled product by 2.04-fold while decreasing the 1º homodimerization by 2.6-fold, resulting in a net 5.3-fold boost of selective formation of cross-coupled product over the 1º homodimerization. Although the degree of 3º homodimerization showed a very marginal increase (1.7-fold) in the presence of the Fe(TPP)Cl catalyst, the net selectivity of cross-coupled product formation over 3º homodimerization reflects a 3.5-fold enhancement. The sorting coefficients for stochastic 1º and 3º radical recombination in this reaction are 1.07 and 0.78, respectively, whereas adding a Fe(TPP)Cl catalyst increases the sorting coefficients to 5.7 and 2.7, respectively. The observed higher preference for decreased 1º homodimerization and hydrogenation side product in the presence of the Fe(TPP)Cl catalyst would imply a favorable binding of the less substituted 1º radical, consistent with the radical sorting effect. As such, the aforementioned

5.7-fold enhancement of 1º sorting coefficient would also reinforce a more favorable pathway between a more substituted 3º radical and an Fe-1º alkyl complex, thus further supporting that the iron-mediated radical sorting effect is operative in these decarboxylative cross-coupling reactions.

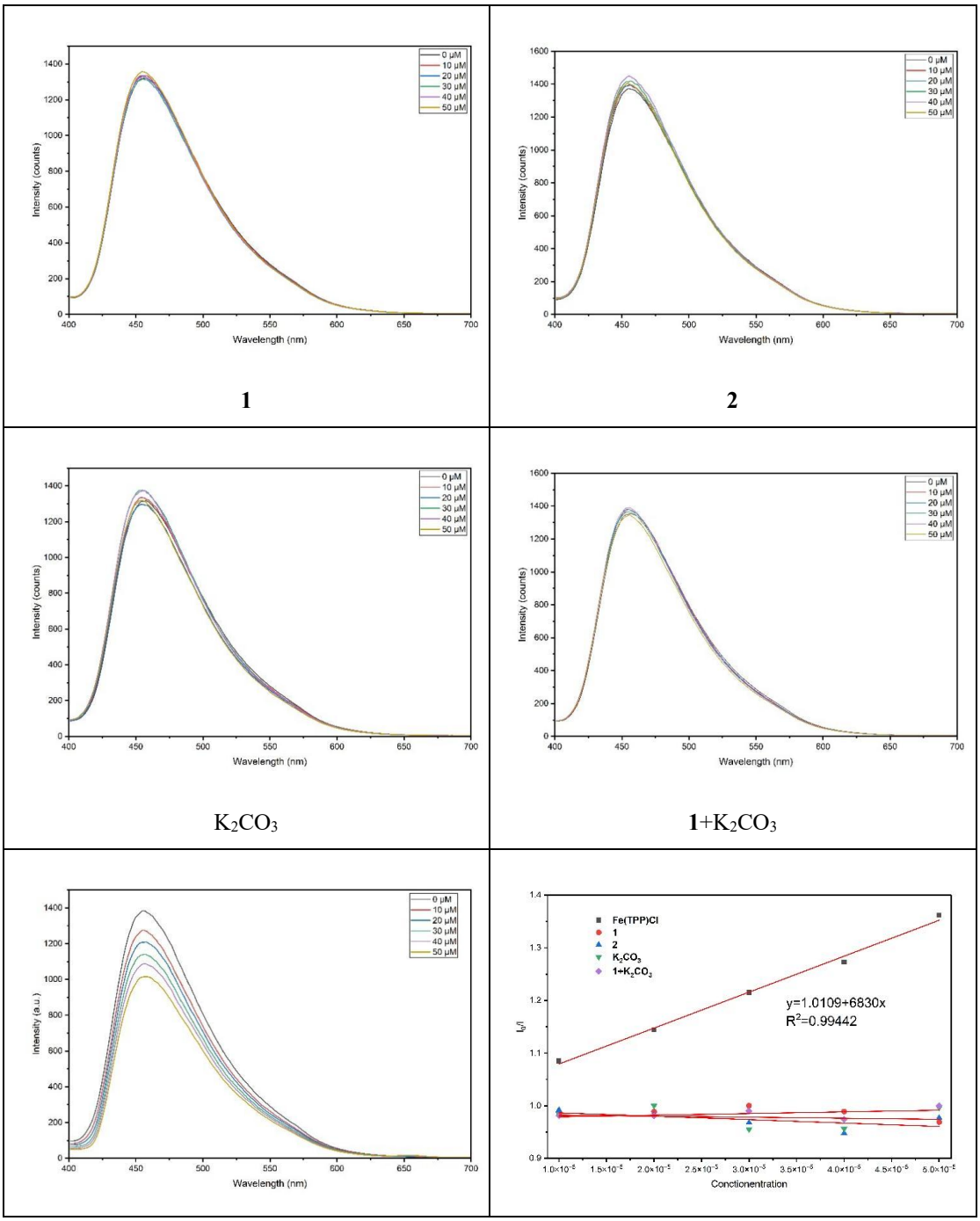
5.6 Comparison of our catalytic system with Macmillan's S_H2 system

	Our work	MacMillan's S_H2 system
Catalytic system	Semi-heterogeneous Dual Catalysis: mpg-CN/Fe(TPP)Cl)	Homogeneous Dual Catalysis TXO or 4CzIPN with $Ni(acac)_2$/K[Tp*]
Metal center and ligand property	Fe(TPP)Cl：The porphyrin ligand provides a stable coordination environment and features a relatively weak metal–carbon bond, which facilitates S_H2 substitution. This system selectively captures less hindered alkyl radicals and does not form tertiary alkyl–iron complexes	Ni $(acac)_2$/K [Tp*] ： The scorpionate ligand modulates the coordination selectivity of the Ni center, stabilizing binding exclusively with methyl or primary alkyl radicals, while secondary or tertiary radicals remain free and participate in the reaction.
Radical cross-coupling types	3°-1°, 2°-1°, 1°-1°	3°-1°, 2°-1°, 1°-1°
Radical precursors	Carboxylic acids、 redox-active esters 、 potassium trifluroborates 、 Katritzky salts 、 DHPs No requirement of external activating agent	Limited to carboxylic acid Requiring excess amount of $MesI(OAc)_2$ as activating reagents
Reaction conditions and application potential	Semi-heterogeneous system: mpg-CN (recycle for 5 times) gram-scale synthesis broad functional group tolerance mild reaction conditions (390-395 nm)	Homogeneous system: no data for recyclability of TXO or 4CzIPN no gram-scale synthesis broad scope UV or visible light

5.7 Stern-Volmer experiments.

The Stern-Volmer measurements were conducted in a 2 mL suspension of mpg-CN in acetonitrile (0.25 mg mL^{-1}). The measurements were carried out in a 1 cm pathlength quartz cuvette, with continuous stirring of the suspension to ensure homogeneity. The sample was excited using a 375 nm continuous-wave (CW) laser operating at a power of 550 μW. The emitted light was filtered through a dichroic mirror

to eliminate scattered laser light before being collected by a Fluorescence spectra were acquired/recorded using a Hitachi F-7000 fluorescence spectrophotometer. The excitation wavelength of 375 nm was specifically chosen to avoid overlap or interference with the mpg-CN emission spectra. For each experiment, a 1000 µM stock solution of the molecule to analyze was prepared in a 1:1 mixture of water and acetonitrile. Incremental additions of 20 µL of this stock solution were made every 5 minutes to the cuvette containing the mpg-CN suspension, resulting in a stepwise concentration increase of 10 µM per addition.



Fe(TPP)Cl	Quenching plots of different species

Figure S14 Stern-Volmer quenching experiments and quenching plots of different species

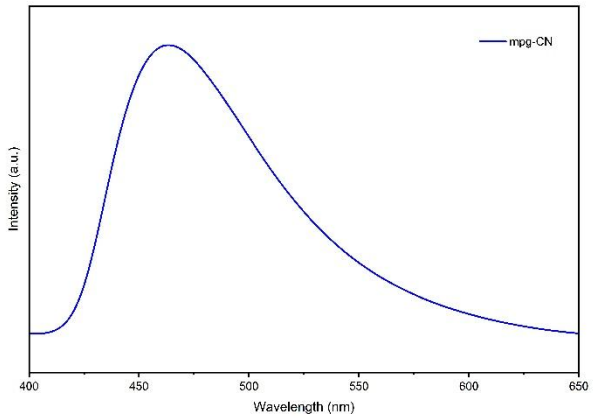


Figure S15 The photoluminescence (PL) spectra of mpg-CN.

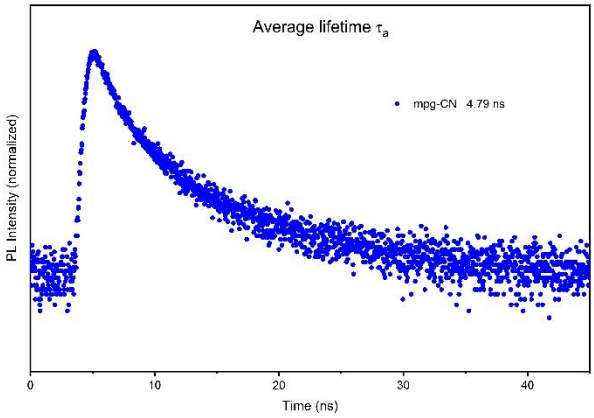
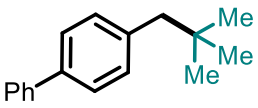


Figure S16 Time-resolved photoluminescence (TRPL) spectra of different mpg-CN.

$$\tau_{av} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}$$

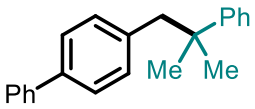
Time-resolved photoluminescence (TRPL) spectra monitored at the corresponding emission peaks give the average radiative lifetimes (τ) of the recombining charge carriers. The radiative lifetimes of mpg-CN were 4.79 ns, respectively (**Figure S16**). suggesting a reduced recombination rate of photogenerated electron-hole pairs. This extended lifetime implies that photogenerated electrons are more effectively sustained during the reaction, thereby enhancing the overall photocatalytic efficiency.

5.8 Characterization of compounds



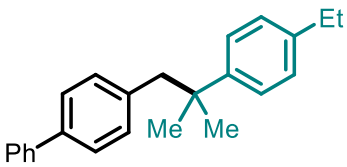
4-neopentyl-1,1'-biphenyl (**3**)[5]: The product **3** was purified by column chromatography (petroleum ether/ethyl acetate = 200:1~100:1). white solid, 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.62 (d, *J* = 7.3 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 2H), 2.56 (s, 2H), 0.96 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 141.3, 139.1, 138.7, 131.0, 128.8, 127.12, 127.11, 126.5, 50.0, 32.0, 29.6.



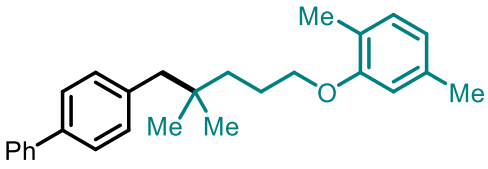
4-(2-methyl-2-phenylpropyl)-1,1'-biphenyl (**4**)[6]: The product **4** was purified by column chromatography (petroleum ether/ethyl acetate = 200:1~100:1). white solid, 62% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.47 (dd, *J* = 5.2, 3.4 Hz, 2H), 7.35-7.27 (m, 4H), 7.27- 7.18 (m, 5H), 7.15-7.09 (m, 1H), 6.80 (d, *J* = 8.1 Hz, 2H), 2.83 (s, 2H), 1.27 (s, 6H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 149.1, 141.2, 138.8, 138.2, 130.9, 128.8, 128.1, 127.1, 127.0, 126.4, 126.3, 125.8, 50.9, 39.0, 28.4.; HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{23}$ 287.1794; Found 287.1796.



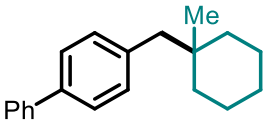
4-(2-(4-ethylphenyl)-2-methylpropyl)-1,1'-biphenyl (**5**)[7]: The product **5** was purified by column chromatography (petroleum ether/ethyl acetate = 200:1~100:1). white solid, 47% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.48 (d, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 8.6 Hz, 4H), 7.23 (d, *J* = 7.4 Hz, 1H), 7.16 (t, *J* = 5.5 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.82 (d, *J* = 8.0 Hz, 2H), 2.81 (s, 2H), 2.57 (q, *J* = 7.6 Hz, 2H), 1.25 (s, 6H), 1.17 (t, *J* = 7.6 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 146.5, 141.6, 141.2, 138.8, 138.3, 131.0, 128.8, 127.5, 127.09, 127.06, 126.3, 126.2, 50.9, 38.7, 28.4, 28.39, 15.7. HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{27}$ 315.2107; Found 315.2100.



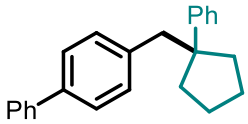
4-(5-(2,5-dimethylphenoxy)-2,2-dimethylpentyl)-1,1'-biphenyl (**6**): The product **6** was purified by column chromatography (petroleum ether/ethyl acetate = 150:1~100:1). white solid, 43% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.51 (d, *J* = 7.3 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.12 (m, 2H), 6.93 (d, *J* = 7.4 Hz, 1H), 6.57 (m, 2H), 3.85 (t, *J* = 6.5 Hz, 2H), 2.50 (s, 2H), 2.23 (s, 3H), 2.11 (s, 3H), 1.78 (m, 2H), 1.33 (m, 2H), 0.86 (s, 6H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 157.2, 141.2, 138.8, 138.6, 136.5, 131.1, 130.4, 128.8, 127.12, 127.10, 126.5, 123.8, 120.8, 112.1, 68.7, 48.1, 38.2, 34.3, 27.1, 24.6, 21.6, 16.0. HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{33}O$ 373.2526; Found 373.2526.



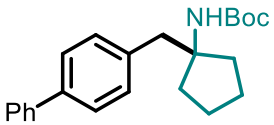
4-((1-methylcyclohexyl)methyl)-1,1'-biphenyl (**7**): The product **7** was purified by column chromatography (petroleum ether/ethyl acetate = 250:1~100:1). white solid, 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.51 (m, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 7.3 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 2.49 (s, 2H), 1.50-1.36 (m, 5H), 1.26-1.18 (m, 5H), 0.79 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 141.2, 139.6, 138.4, 131.1, 129.5, 128.7, 127.0, 126.3, 48.5, 37.2, 34.2, 26.5, 24.7, 22.2. HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{25}$ 265.1951; Found 265.1946.



4-((1-phenylcyclopentyl)methyl)-1,1'-biphenyl (**8**): The product **8** was purified by column chromatography (petroleum ether/ethyl acetate = 200:1~100:1). light yellow solid, 63% yield.

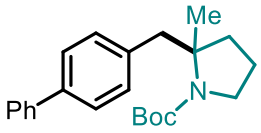
^{1}H NMR (400 MHz, $CDCl_3$) δH 7.46 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.31 (dd, *J* = 10.4, 4.8 Hz, 2H), 7.19 (m, 5H), 7.10-7.09 (m,1H), 7.02-7.00 (m, 2H), 6.57 (d, *J* = 8.1 Hz, 2H), 2.79 (s, 2H), 1.79 (m, 8H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 148.3, 141.2, 138.6, 138.3, 130.7, 128.8, 127.8, 127.6, 127.1, 127.0, 126.1, 125.7, 52.6, 47.3, 36.9, 23.1.



tert-butyl (1-([1,1'-biphenyl]-4-ylmethyl)cyclopentyl)carbamate (**9**): The product **9** was purified by

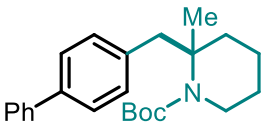
column chromatography (petroleum ether/ethyl acetate = 100:1~20:1). white solid, 47% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.51 (d, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 7.3 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 4.19 (s, 1H), 3.02 (s, 2H), 1.76 (s, 2H), 1.64 (s, 6H), 1.41 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 155.0, 141.2, 139.1, 138.3, 130.8, 128.9, 127.2, 127.1, 126.8, 78.9, 64.3, 42.0, 38.0, 29.8, 23.2. HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{30}NO_2$ 352.2271; Found 352.2265.



tert-butyl 2-([1,1'-biphenyl]-4-ylmethyl)-2-methylpyrrolidine-1-carboxylate (**10**): The product **10** was purified by column chromatography (petroleum ether/ethyl acetate = 80:1~20:1). colorless oily liquid, 45% yield.

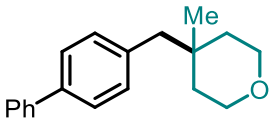
The major rotamer: ^{1}H NMR (400 MHz, $CDCl_3$) δH 7.60 (dd, *J* = 7.8, 2.4 Hz, 2H), 7.43 (dd, *J* = 7.8, 2.2 Hz, 2H), 7.43 (t, *J* = 6.6 Hz, 2H), 7.33 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.25-7.20 (dd, *J* = 10.6, 7.6 Hz, 2H), 3.53-3.28 (m, 2H), 3.32-3.01 (m, 1H), 2.84-2.79 (m, 1H), 2.07-2.02 (m, 1H), 1.64-1.44 (m, 14H), 1.29-1.24 (m, 1H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 154.4, 141.0, 139.1, 138.1, 130.9, 128.8, 127.1, 126.9, 126.8, 79.6, 63.6, 48.6, 44.0, 39.1, 28.8, 27.1, 21.7.; **The minor rotamer**: ^{1}H NMR (400 MHz, $CDCl_3$) δH 7.60 (dd, *J* = 7.8, 2.4 Hz, 2H), 7.43 (dd, *J* = 7.8, 2.2 Hz, 2H), 7.43 (t, *J* = 6.6 Hz, 2H), 7.33 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.25-7.20 (dd, *J* = 10.6, 7.6 Hz, 2H), 3.53-3.28 (m, 2H), 3.32-3.01 (m, 1H), 2.84-2.79 (m, 1H), 2.07-2.02 (m, 1H), 1.64-1.44 (m, 14H), 1.29-1.24 (m, 1H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC: 153.7, 140.9, 138.8, 137.8, 130.7, 128.7, 127.0, 126.9, 126.5, 78.6, 63.1, 48.5, 42.8, 37.8, 28.7, 26.0, 21.3.; HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{30}NO_2$ 352.2271; Found 352.2272.



tert-butyl 2-([1,1'-biphenyl]-4-ylmethyl)-2-methylpiperidine-1-carboxylate (**11**): The product **11** was purified by column chromatography (petroleum ether/ethyl acetate = 50:1~20:1). light yellow solid, 51% yield.

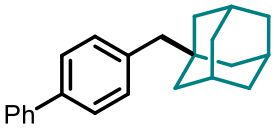
^{1}H NMR (400 MHz, $CDCl_3$) δH 7.59 (d, *J* = 7.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 7.6 Hz,

2H), 7.33 (t, J = 7.3 Hz, 1H), 7.24 (d, J = 8.0 Hz, 2H), 3.82-3.76 (m, 1H), 3.33 (d, J = 13.2 Hz, 1H), 2.92 (d, J = 13.2 Hz, 1H), 2.87-2.79 (m, 1H), 1.82-1.75 (m, 1H). 1.67-1.56 (m, 3H), 1.51 (s, 3H), 1.49 (s, 9H), 1.33-1.29 (m, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 156.0, 141.0, 138.9, 137.6, 131.0, 128.7, 127.1, 127.0, 126.6, 79.4, 57.9, 42.6, 41.1, 34.6, 28.7, 26.7, 22.9, 17.4. HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{32}NO_2$ 366.2428; Found 366.2427.



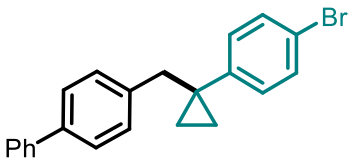
4-([1,1'-biphenyl]-4-ylmethyl)-4-methyltetrahydro-2H-pyran (**12**): The product **12** was purified by column chromatography (petroleum ether/ethyl acetate = 60:1~20:1). white solid, 65% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.50 (d, J = 7.6 Hz, 2H), 7.42 (d, J = 8.2 Hz, 2H), 7.35 (t, J = 7.8 Hz, 2H), 7.24 (t, J = 77.4 Hz, 1H), 7.11 (d, J = 8.0 Hz, 2H), 3.74-3.69 (m, 2H), 3.58-3.52 (m, 2H), 2.55 (s, 2H), 1.57-1.51 (m, 2H),1.27-1.21 (m, 2H), 0.91 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 141.0, 139.0, 137.1, 131.1, 128.8, 127.1, 127.0, 126.5, 64.0, 48.8, 37.5, 32.1, 23.4.; HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{119}H_{233}O$ 267.1743; Found 267.1740.



1-([1,1'-biphenyl]-4-ylmethyl)adamantane (**13**)[7]: The product **13** was purified by column chromatography (petroleum ether/ethyl acetate = 250:1~100:1). light yellow solid, 33% yield.

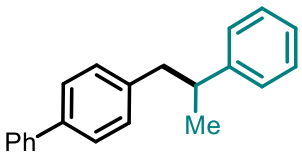
^{1}H NMR (400 MHz, $CDCl_3$) δH 7.60 (d, J = 7.3 Hz, 2H), 7.49 (d, J = 8.1 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.33 (d, J = 7.3 Hz, 1H), 7.15 (d, J = 8.1 Hz, 2H), 2.40 (d, J = 5.9 Hz, 2H), 1.95 (m, 3H), 1.69-1.66 (m, 3H), 1.60-1.55 (m, 4H), 1.52-1.51 (m, 5H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 141.3, 138.7, 137.6, 131.1, 129.6, 128.8, 127.1, 126.3, 51.0, 42.6, 37.2, 33.8, 28.9. HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{27}$ 303.2107; Found 303.2108.



4-((1-(4-bromophenyl)cyclopropyl)methyl)-1,1'-biphenyl (**14**): The product **14** was purified by column

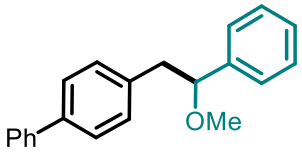
chromatography (petroleum ether/ethyl acetate = 200:1~100:1). white solid, 39% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.49 (d, *J* = 7.3 Hz, 2H), 7.35 (m, 4H), 7.25 (m, 3H), 6.97 (m, 4H), 2.86 (s, 2H), 0.83 (d, *J* = 3.6 Hz, 2H), 0.79 (d, *J* = 3.6 Hz, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 144.0, 140.9, 138.9, 138.5, 131.0, 130.9, 129.8, 128.7, 127.1, 126.9, 126.7, 119.7, 45.2, 26.1, 12.9. HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{20}Br$ 363.0743; Found 363.0742; 365.0747.



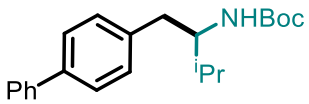
4-(2-phenylpropyl)-1,1'-biphenyl (**15**)[9]: The product **15** was purified by column chromatography (petroleum ether/ethyl acetate = 200:1~100:1).white solid, 64% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.49 (m, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.22 (dd, *J* = 15.7, 7.4 Hz, 3H), 7.12 (m, 3H), 7.07 (d, *J* = 8.1 Hz, 2H), 2.93 (m, 2H), 2.72 (dd, *J* = 12.9, 7.9 Hz, 1H), 1.19 (d, *J* = 6.8 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 147.1, 141.2, 140.1, 138.9, 129.7, 128.8, 128.5, 127.2, 127.1, 127.09, 126.9, 126.2, 44.8, 42.0, 21.4.



4-(2-methoxy-2-phenylethyl)-1,1'-biphenyl (**16**): The product **16** was purified by column chromatography (petroleum ether/ethyl acetate = 200:1~100:1). white solid, 50% yield.

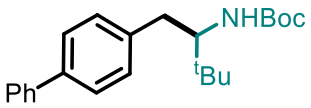
^{1}H NMR (400 MHz, $CDCl_3$) δH 7.50 (d, *J* = 7.9 Hz, 2H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.26 (m, 3H), 7.18 (m, 3H), 7.10 (d, *J* = 7.9 Hz, 2H), 4.29 (m, 1H), 3.14 (s, 3H), 3.08 (dd, *J* = 13.8, 7.7 Hz, 1H), 2.86 (dd, *J* = 13.8, 5.6 Hz, 1H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 141.8, 141.2, 139.1, 137.8, 130.0, 128.8, 128.5, 127.8, 127.2, 127.1, 127.0, 126.9, 85.1, 56.9, 44.6. HRMS (APCI-TOF) m/z: $[M - H]^+$ Calcd for $C_{21}H_{21}O$ 287.1436; Found287.1429.



2-([1,1'-biphenyl]-4-ylmethyl)-2,3-dihydro-1H-indene (**17**): The product **17** was purified by column chromatography (petroleum ether/ethyl acetate = 150:1~20:1). white solid, 45% yield.

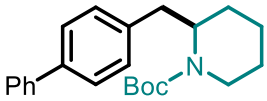
^{1}H NMR (400 MHz, $CDCl_3$) δH 7.49 (d, *J* = 7.4 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2xH), 7.35 (t, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 7.3 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 2H), 4.28 (d, *J* = 9.3 Hz, 1H), 3.71 (s, 1H), 2.77 (dd,

J = 13.8, 6.1 Hz, 1H), 2.64 (dd, *J* = 13.4, 8.2 Hz, 1H), 1.72-1.52 (m, 1H), 1.29 (s, 9H), 0.91 (d, *J* = 6.8 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 155.9, 141.2, 139.2, 138.0, 129.8, 128.8, 127.2, 127.1, 79.1, 56.7, 38.5, 30.9, 28.5, 19.9, 17.4. HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{30}NO_2$ 340.2271; Found 340.2272.



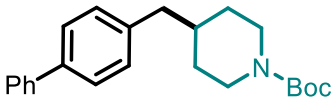
tert-butyl (1-([1,1'-biphenyl]-4-yl)-3,3-dimethylbutan-2-yl)carbamate (**18**): The product **18** was purified by column chromatography (petroleum ether/ethyl acetate = 150:1~20:1) white solid, 53% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.47 (d, *J* = 7.4 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 7.3 Hz, 1H), 7.18 (m, 2H), 4.18 (d, *J* = 10.4 Hz, 1H), 3.66 (td, *J* = 11.2, 3.2 Hz, 1H), 2.99 (dd, *J* = 14.1, 3.1 Hz, 1H), 2.28 (dd, *J* = 14.0, 11.7 Hz, 1H), 1.15 (s, 9H), 0.92 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 155.9, 141.4, 139.1, 138.7, 129.9, 129.6, 128.8, 127.1, 127.0, 78.8, 60.0, 36.6, 35.0, 28.4, 26.6. HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{32}NO_2$ 354.2428; Found 354.2431.



tert-butyl (R)-2-([1,1'-biphenyl]-4-ylmethyl)piperidine-1-carboxylate (**19**): The product **19** was purified by column chromatography (petroleum ether/ethyl acetate = 150:1~20:1). white solid, 56% yield.

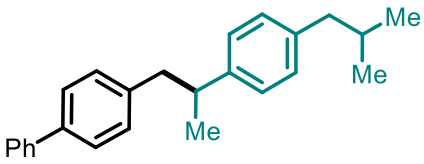
^{1}H NMR (400 MHz, $CDCl_3$) δH 7.48 (d, *J* = 7.4 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.17 (m, 2H), 4.38 (s, 1H), 4.00 (d, *J* = 11.8 Hz, 1H), 2.86 (m, 2H), 2.71 (m, 1H), 1.65-1.51 (m, 5H), 1.41-1.34 (m, 1H), 1.24 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 155.0, 141.3, 139.3, 138.6, 129.8, 128.8, 127.2, 127.16, 127.12, 79.2, 52.6, 39.1, 35.9, 28.4, 27.6, 25.7, 19.1. HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{30}NO_2$ 352.2271; Found 352.2270.



tert-butyl 4-([1,1'-biphenyl]-4-ylmethyl)piperidine-1-carboxylate (**20**): The product **20** was purified by column chromatography (petroleum ether/ethyl acetate = 150:1~20:1). white solid, 44% yield.

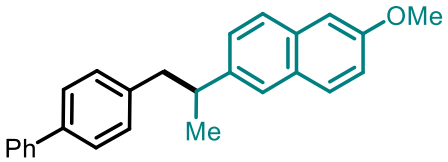
^{1}H NMR (400 MHz, $CDCl_3$) δH 7.51 (d, *J* = 7.5 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 7.3 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 4.01 (d, *J* = 12.7 Hz, 2H), 2.58 (t, *J* = 11.9 Hz, 2H), 2.51 (d, *J* = 6.8 Hz, 2H), 1.60-1.53 (m, 5H), 1.38 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 155.0,

141.2, 139.5, 139.1, 129.7, 128.9, 127.2, 127.1, 127.1, 79.4, 44.1, 42.9, 39.3, 32.2, 28.6. HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{30}NO_2$ 352.2271; Found 352.2264.



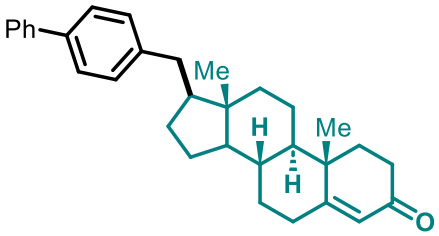
4-(2-(4-isobutylphenyl)propyl)-1,1'-biphenyl (**21**): The product **21** was purified by column chromatography (petroleum ether/ethyl acetate = 200:1~100:1)white solid, 56% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.49 (d, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.05 (dd, *J* = 11.5, 8.1 Hz, 4H), 6.98 (d, *J* = 8.0 Hz, 2H), 2.95-2.87 (m, 2H), 2.72-2.67 (m, 1H), 2.37 (d, *J* = 7.2 Hz, 2H), 1.80-1.74 (m, 1H), 1.17 (d, *J* = 6.6 Hz, 3H), 0.82 (d, *J* = 6.6 Hz, 6H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 144.2, 141.1, 140.2, 139.3, 138.7, 129.6, 129.1, 128.7, 127.0, 127.0, 126.8, 126.8, 45.2, 44.9, 41.6, 30.4, 22.5, 21.3. HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{29}$ 329.2264; Found 329.2270.



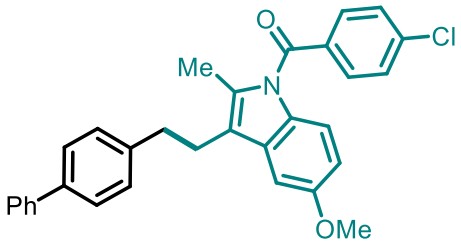
2-(1-([1,1'-biphenyl]-4-yl)propan-2-yl)-6-methoxynaphthalene (**22**): The product **22** was purified by column chromatography (petroleum ether/ethyl acetate = 200:1~50:1). white solid, 38% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.60 (dd, *J* = 8.9, 6.1 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 3H), 7.39 (d, *J* = 7.9 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.26 (dd, *J* = 13.1, 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 6.4 Hz, 2H), 3.84 (s, 3H), 3.10 (dd, *J* = 14.2, 7.0 Hz, 1H), 2.98 (m, 1H), 2.81 (dd, *J* = 13.3, 8.1 Hz, 1H), 1.27 (d, *J* = 6.9 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 157.4, 142.3, 141.2, 140.1, 138.9, 133.4, 129.7, 129.3, 129.2, 128.8, 127.1, 127.0, 126.96, 126.9, 126.6, 125.2, 118.8, 105.8, 55.4, 44.8, 41.9, 21.5. HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{25}O$ 353.1900; Found 353.1905.



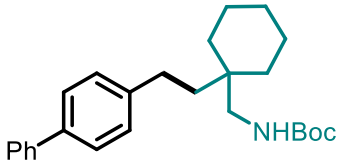
(8R,9R,10S,13S,17S)-17-([1,1'-biphenyl]-4-ylmethyl)-10,13-dimethyl-1,2,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-3H-cyclopenta[a]phenanthren-3-one (**23**): The product **23** was purified by column chromatography (petroleum ether/ethyl acetate = 150:1~50:1)white solid, 46% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.58 (d, *J* = 7.7 Hz, 2H), 7.50 (d, *J* = 7.9 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.23 (m, 2H), 5.74 (s, 1H), 2.87 (dd, *J* = 13.4, 4.1 Hz, 1H), 2.43-2.37 (m, 4H), 2.19 (t, *J* = 12.9 Hz, 1H), 2.06-2.03 (m, 2H), 1.91-1.89 (m, 1H), 1.79-1.48 (m, 9H), 1.32-1.24 (m, 3H), 1.20 (s, 3H), 0.97 (t, *J* = 11.2 Hz, 1H), 0.88 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 199.7, 171.6, 141.2, 141.1, 138.6, 129.6, 128.8, 127.1, 127.0, 126.9, 123.9, 54.0, 50.5, 49.0, 43.3, 38.8, 37.4, 36.2, 35.9, 34.1, 33.1, 32.6, 27.1, 25.8, 21.1, 20.9, 17.6. HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{32}H_{39}O$ 439.2995; Found 439.2992.



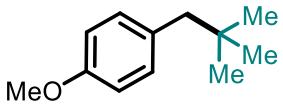
N-(1-(6-methylquinolin-2-yl)-2-phenylethyl)acetamide (**24**): The product **24** was purified by column chromatography (petroleum ether/ethyl acetate = 100:1~15:1). light yellow solid, 41% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.48 (t, *J* = 7.8 Hz, 4H), 7.42 (d, *J* = 7.9 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.28 (m, 3H), 7.12 (d, *J* = 7.8 Hz, 2H), 6.99 (d, *J* = 9.0 Hz, 1H), 6.84 (d, *J* = 1.9 Hz, 1H), 6.62 (dd, *J* = 9.0, 2.1 Hz, 1H), 3.75 (s, 3H), 2.88 (s, 4H), 1.91 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 168.4, 156.1, 141.1, 140.9, 139.2, 139.0, 134.4, 134.3, 131.3, 131.14, 131.11, 129.3, 129.1, 128.9, 127.3, 127.2, 127.1, 118.9, 115.2, 111.2, 101.6, 55.9, 35.6, 26.4, 13.2. HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{27}ClNO_2$ 480.1725; Found 480.1726; 482.1715.



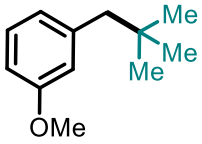
tert-butyl ((1-(2-([1,1'-biphenyl]-4-yl)ethyl)cyclohexyl)methyl)carbamate (**25**): The product **25** was purified by column chromatography (petroleum ether/ethyl acetate = 150:1~20:1)light yellow solid, 36 % yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.57 (d, *J* = 7.7 Hz, 2H), 7.50 (d, *J* = 7.9 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.27 (d, *J* = 9.6 Hz, 2H), 4.53 (s, 1H), 3.15 (d, *J* = 6.4 Hz, 2H), 2.59 (m, 2H), 1.60-1.57 (m, 2H), 1.49-1.39 (m, 17H), 1.31-1.29 (m, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 156.4, 142.7, 141.3, 138.8, 129.0, 128.8, 127.2, 127.16, 127.11, 79.2, 47.0, 36.8, 33.7, 29.8, 29.3, 28.6, 26.4, 21.6. HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{36}NO_2$ 394.2741; Found 394.2747.



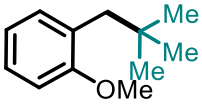
1-methoxy-4-neopentylbenzene (**26**)[10]: The product **26** was purified by column chromatography (petroleum ether/ethyl acetate = 200:1~100:1). white solid, 62% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.04 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 3.79 (s, 3H), 2.43 (s, 2H), 0.88 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 157.9, 132.0, 131.5, 113.2, 55.3, 49.5, 31.9, 29.4.



1-methoxy-3-neopentylbenzene (**27**)[10]: The product **27** was purified by column chromatography (petroleum ether/ethyl acetate = 200:1~100:1). white solid, 46% yield.

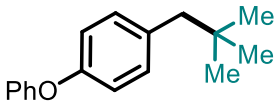
^{1}H NMR (400 MHz, $CDCl_3$) δH 7.04 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 3.79 (s, 3H), 2.43 (s, 2H), 0.88 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 159.2, 141.5, 128.6, 123.2, 116.6, 111.0, 55.3, 50.4, 31.9, 29.6.



1-methoxy-2-neopentylbenzene (**28**)[10]: The product **28** was purified by column chromatography

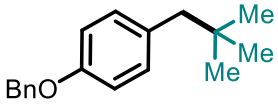
(petroleum ether/ethyl acetate = 200:1~100:1). light yellow solid, 45% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.18 (t, *J* = 7.9 Hz, 1H), 6.74 (m, 2H), 6.68 (s, 1H), 3.80 (s, 3H), 2.47 (s, 2H), 0.91 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 159.2, 141.5, 128.6, 123.2, 116.6, 111.0, 55.3, 50.4, 31.9, 29.6.



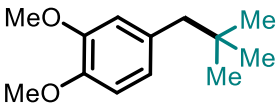
1-neopentyl-4-phenoxybenzene (**29**): The product **29** was purified by column chromatography (petroleum ether/ethyl acetate = 150:1~100:1). white solid, 54% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.31 (t, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 3H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.3 Hz, 2H), 2.47 (s, 2H), 0.90 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 157.8, 155.3, 134.9, 131.7, 129.8, 123.0, 118.7, 118.4, 49.6, 31.9, 29.5. HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{21}O$ 241.1587; Found 241.1587.



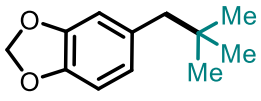
1-(benzyloxy)-4-neopentylbenzene (**30**): The product **30** was purified by column chromatography (petroleum ether/ethyl acetate = 200:1~100:1). white solid, 47% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.43 (d, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.32 (d, *J* = 7.1 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 5.03 (s, 2H), 2.43 (s, 2H), 0.88 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 157.2, 137.4, 132.3, 131.5, 128.7, 128.0, 127.7, 114.1, 70.2, 49.5, 31.9, 29.5. HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{23}O$ 255.1743; Found 255.1739.



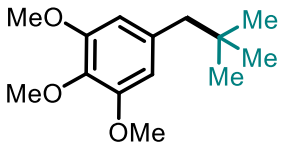
1,2-dimethoxy-4-neopentylbenzene (**31**)[12]: The product **31** was purified by column chromatography (petroleum ether/ethyl acetate = 200:1~100:1). white solid, 60% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 6.78 (d, *J* = 7.8 Hz, 1H), 6.66 (d, *J* = 8.1 Hz, 2H), 3.86 (s, 6H), 2.44 (s, 2H), 0.90 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 148.2, 147.3, 132.5, 122.6, 114.1, 110.7, 56.0, 55.9, 50.0, 31.9, 29.5.



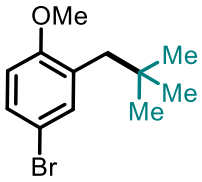
5-neopentylbenzo[d][1,3]dioxole (**32**): The product **32** was purified by column chromatography (petroleum ether/ethyl acetate = 150:1~50:1). white solid, 40% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 6.72 (d, *J* = 7.8 Hz, 1H), 6.63 (s, 1H), 6.57 (d, *J* = 7.9 Hz, 1H), 5.92 (s, 2H), 2.41 (s, 2H), 0.89 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 147.1, 145.7, 133.7, 123.4, 111.0, 107.7, 100.8, 50.1, 31.9, 29.5. HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{17}O_2$ 193.1223; Found 193.1229.



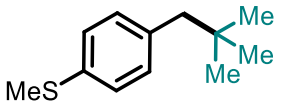
1,2,3-trimethoxy-5-neopentylbenzene (**33**): The product **33** was purified by column chromatography (petroleum ether/ethyl acetate = 150:1~100:1). white solid, 72% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 6.33 (s, 2H), 3.84 (s, 9H), 2.43 (s, 2H), 0.92 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 152.5, 136.4, 135.6, 107.7, 61.0, 56.2, 50.8, 31.9, 29.6. HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{23}O_3$ 239.1642; Found 239.1641.



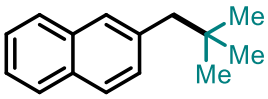
4-bromo-1-methoxy-2-neopentylbenzene (**34**): The product **34** was purified by column chromatography (petroleum ether/ethyl acetate = 200:1~100:1). white solid, 72% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.26 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.17 (d, *J* = 2.3 Hz, 1H), 6.71 (d, *J* = 8.7 Hz, 1H), 3.75 (s, 3H), 2.50 (s, 2H), 0.89 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 157.4, 134.8, 131.0, 129.8, 129.75, 112.2, 55.4, 42.6, 32.6, 29.6. HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{23}O_3$ 239.1642; Found 239.1641. $C_{12}H_{18}BrO$ 257.0536; Found 257.0534, 259.0512.



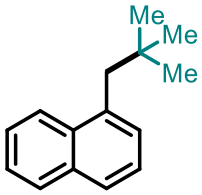
methyl(4-neopentylphenyl)sulfane (**35**)[11]: The product **35** was purified by column chromatography (petroleum ether/ethyl acetate = 200:1~100:1). white solid, 52% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.17 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 2.47 (s, 3H), 2.45 (s, 2H), 0.89 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 136.9, 135.2, 131.0, 126.4, 49.7, 31.8, 29.3, 16.2.



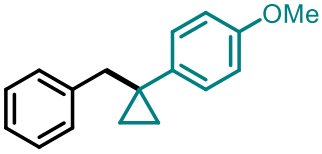
2-neopentylnaphthalene (**38**)[13]: The product **38** was purified by column chromatography (petroleum ether/ethyl acetate = 150:1~100:1). white solid, 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.83 (t, *J* = 8.1 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.60 (s, 1H), 7.46 (t, *J* = 6.9 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 1H), 2.70 (s, 2H), 0.99 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 137.6, 133.4, 132.1, 129.6, 128.7, 127.69, 127.68, 127.0, 125.8, 125.2, 50.5, 32.2, 29.6.



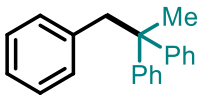
1-neopentylnaphthalene (**39**)[14]: The product **39** was purified by column chromatography (petroleum ether/ethyl acetate = 150:1~100:1). white solid, 53% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 8.12 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 7.5 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.42 (m, 3H), 7.29 (d, *J* = 7.0 Hz, 1H), 3.02 (s, 2H), 0.97 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 136.4, 134.0, 133.4, 129.0, 128.7, 126.8, 125.34, 125.32, 125.2, 125.1, 45.1, 33.2, 30.3.



1-(1-benzylcyclopropyl)-4-methoxybenzene (**40**)[16]: The product **40** was purified by column chromatography (petroleum ether/ethyl acetate = 200:1~100:1). white solid, 52% yield.

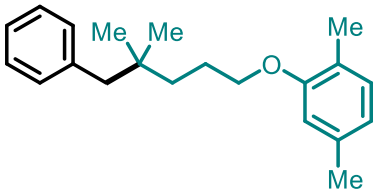
^{1}H NMR (400 MHz, $CDCl_3$) δH 7.19-7.14 (m, 3H), 7.05 (dt, *J* = 6.5, 2.1 Hz, 2H), 6.97 (dd, *J* = 8.0, 2.0 Hz, 2H), 6.73 (dd, *J* = 6.6, 2.2 Hz, 2H), 3.75 (s, 3H), 2.87 (s, 2H), 0.81 (d, *J* = 2.0 Hz, 4H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 155.7, 139.9, 137.2, 130.2, 129.5, 127.8, 125.9, 113.6, 55.2, 46.1, 25.9, 12.6.



propane-1,2,2-triyltribenzene (**41**)[17]: The product **41** was purified by column chromatography (petroleum ether/ethyl acetate = 200:1~100:1). white solid, 39% yield.

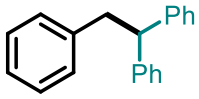
^{1}H NMR (400 MHz, $CDCl_3$) δH 7.27-7.22 (m, 4H), 7.20-7.16 (m, 6H), 7.12-7.03 (m, 3H), 6.59 (dt, *J* = 6.8, 1.7 Hz, 2H), 3.43 (s, 2H), 1.54 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 149.3, 138.1, 130.8, 127.9,

127.8, 127.3, 160.0, 125.8, 47.7, 47.2, 27.0.



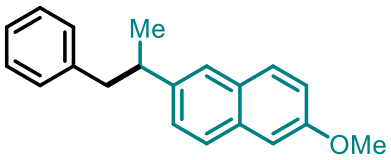
2-((4,4-dimethyl-5-phenylpentyl)oxy)-1,4-dimethylbenzene (**43**): The product **43** was purified by column chromatography (petroleum ether/ethyl acetate = 150:1~100:1) white solid, 52% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.28-7.19 (m, 3H), 7.13 (d, *J* = 7.0 Hz, 2H), 7.00 (d, *J* = 7.4 Hz, 1H), 6.65 (d, *J* = 7.5 Hz, 1H), 6.62 (s, 1H), 3.92 (t, *J* = 6.5 Hz, 2H), 2.54 (s, 2H), 2.31 (s, 3H), 2.18 (s, 3H), 1.86-1.82 (m, 2H), 1.40-1.36 (m, 2H), 0.90 (s, 6H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 157.1, 139.3, 136.5, 130.6, 130.3, 127.7, 125.8, 123.7, 120.6, 112.0, 68.6, 48.4, 38.1, 34.0, 26.9, 24.5, 21.5, 15.9. HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{28}O$ 297.2213; Found 297.2211.



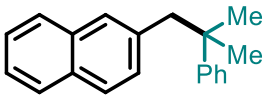
ethane-1,1,2-triyltribenzene (**44**)[18]: The product **44** was purified by column chromatography (petroleum ether/ethyl acetate = 200:1~100:1). white solid, 38% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.26-7.19 (m, 8H), 7.18-7.11 (m, 5H), 6.99 (dd, *J* = 6.6, 2.0 Hz, 2H), 4.23 (t, *J* = 7.8 Hz, 1H), 1.23 (d, *J* = 7.8 Hz, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 144.5, 140.3, 129.1, 128.4, 128.1, 126.2, 125.9, 53.1, 42.1.



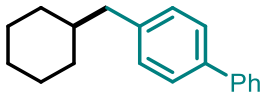
2-methoxy-6-(1-phenylpropan-2-yl)naphthalene (**45**): The product **45** was purified by column chromatography (petroleum ether/ethyl acetate = 150:1~80:1). white solid, 54% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.67-7.64 (m, 2H), 7.51 (d, *J* = 1.8 Hz, 1H), 7.31 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.23-7.19 (m, 2H), 7.16-7.08 (m, 5H), 3.89 (s, 3H), 3.11 (m, 1H), 3.02 (dd, *J* = 13.3, 6.5 Hz, 1H), 2.83 (dd, *J* = 13.3, 8.2 Hz, 1H), 1.30 (d, *J* = 6.9 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 157.2, 142.2, 140.9, 133.2, 129.2, 129.1, 129.1, 128.1, 126.7, 126.5, 125.9, 125.0, 118.6, 105.6, 55.3, 45.0, 41.8, 21.3. HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{21}O$ 277.1587; Found 277.1594.



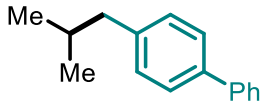
2-((4,4-dimethyl-5-phenylpentyl)oxy)-1,4-dimethylbenzene (**46**): The product **46** was purified by column chromatography (petroleum ether/ethyl acetate = 150:1~50:1). white solid, 41% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.76-7.74 (m, 1H), 7.68-7.65 (m, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.41-7.38 (m, 2H), 7.32-7.27 (m, 5H), 7.23-7.19 (m, 1H), 6.87 (dd, *J* = 8.4, 1.8 Hz, 1H), 3.03 (s, 2H), 1.37 (s, 6H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 148.9, 136.6, 133.1, 132.0, 129.2, 128.8, 128.0, 127.6, 127.5, 126.7, 126.3, 125.7, 125.6, 125.1, 51.3, 39.1, 28.3. HRMS (APCI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{21}$ 261.1638; Found 261.1633.



4-(cyclohexylmethyl)-1,1'-biphenyl (**47**)[8]: The product **47** was purified by column chromatography (petroleum ether/ethyl acetate = 200:1~100:1). white solid, 39% yield.

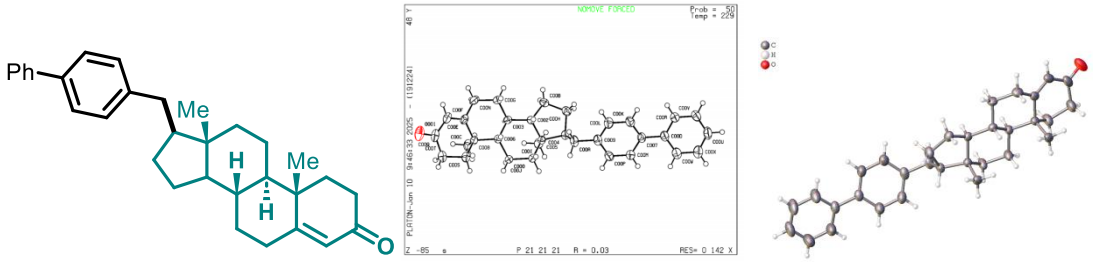
^{1}H NMR (400 MHz, $CDCl_3$) δH 7.59 (m, 2H), 7.51 (dd, *J* = 8.3, 2.1 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.33 (m, 1H), 7.23 (m, 2H), 2.53 (d, *J* = 7.1 Hz, 2H), 1.74-1.55 (m, 5H), 1.26-1.83 (m, 4H), 1.04-0.96 (m, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 141.3, 140.7, 138.6, 129.7, 128.8, 127.1, 127.07, 126.9, 43.9, 39.9, 33.3, 26.7, 26.5.



4-isobutyl-1,1'-biphenyl (**48**): The product **48** was purified by column chromatography (petroleum ether/ethyl acetate = 200:1~100:1). white solid, 36% yield. [19]

^{1}H NMR (400 MHz, $CDCl_3$) δH 7.60-7.57 (m, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.00 (t, *J* = 7.4 Hz, 2H), 7.32 (d, *J* = 7.3 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 2H), 2.51 (d, *J* = 7.2 Hz, 2H), 1.94-1.87 (m, 1H), 0.93 (d, *J* = 6.6 Hz, 6H).; ^{13}C NMR (100 MHz, $CDCl_3$) δC 141.2, 140.9, 138.6, 129.5, 128.7, 127.0, 127.0, 126.8, 45.1, 30.3, 22.4.

5.9 Determination of absolute configuration of compound 26



CCDC: 2416104

Table 1 Crystal data and structure refinement for 26.

Identification code	s
Empirical formula	$C_{32}H_{38}O$
Formula weight	438.62
Temperature/K	229.00
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.2977(4)
b/Å	14.2719(9)
c/Å	27.7472(18)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2493.9(3)
Z	4
ρ_{calc}g/cm^3	1.168
μ/mm^{-1}	0.514
F(000)	952.0
Crystal size/mm^3	0.3 × 0.1 × 0.1
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.37 to 136.608
Index ranges	-6 ≤ h ≤ 7, -17 ≤ k ≤ 17, -33 ≤ l ≤ 31

Reflections collected	45421
Independent reflections	4510 [R_{int} = 0.0307, R_{sigma} = 0.0141]
Data/restraints/parameters	4510/0/300
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0326, wR_2 = 0.0891
Final R indexes [all data]	R_1 = 0.0330, wR_2 = 0.0894
Largest diff. peak/hole / e $Å^{-3}$	0.15/-0.12
Flack parameter	0.04(6)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for s. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
O001	7778(3)	-2525.9(11)	7249.8(6)	63.0(4)
C002	6322(2)	2607.9(11)	6465.5(5)	27.0(3)
C003	5930(2)	1803.7(11)	6816.0(5)	27.3(3)
C004	5174(3)	3693.6(11)	5852.4(6)	30.5(3)
C005	4451(3)	2795.7(11)	6123.9(5)	28.5(3)
C006	5420(2)	909.1(11)	6528.2(5)	28.5(3)
C007	6760(3)	6171.5(11)	4604.8(6)	34.9(4)
C008	4984(3)	39.0(11)	6855.0(6)	30.9(3)
C009	6612(3)	4430.2(11)	5097.8(6)	37.2(4)
C00A	6423(3)	3532.4(12)	5382.3(6)	40.6(4)
C00B	6831(3)	3579.7(11)	6667.7(6)	33.8(4)
C00C	2884(3)	149.0(14)	7139.8(7)	44.0(4)
C00D	6810(3)	7098.3(12)	4354.7(6)	38.2(4)
C00E	6769(3)	-62.1(12)	7222.8(6)	32.9(4)
C00F	7663(3)	-892.3(14)	7323.9(6)	39.8(4)
C00G	7838(3)	1630.7(12)	7143.0(6)	35.9(4)

C00H	6492(3)	4237.3(12)	6235.1(6)	40.2(4)
C00I	2409(3)	3067.2(14)	6398.5(7)	39.4(4)
C00J	4073(3)	1912.2(11)	5829.0(6)	38.1(4)
C00K	8461(3)	5852.3(13)	4877.5(7)	43.8(4)
C00L	8392(3)	4999.2(13)	5118.2(7)	44.0(4)
C00M	4992(3)	5584.3(13)	4576.6(7)	42.1(4)
C00N	7432(3)	811.2(13)	7483.4(6)	40.1(4)
C00O	3636(3)	1067.3(12)	6156.7(6)	38.4(4)
C00P	4937(3)	4735.3(13)	4816.4(7)	42.3(4)
C00Q	6933(3)	-1785.7(13)	7136.1(7)	44.2(4)
C00R	8316(4)	7765.0(14)	4468.9(8)	56.8(6)
C00S	4902(4)	-836.8(12)	6536.9(7)	45.6(5)
C00T	5029(4)	-1756.8(13)	6817.7(8)	53.0(5)
C00U	6934(5)	8836.6(14)	3887.5(8)	57.3(6)
C00V	8374(5)	8623.7(15)	4237.2(8)	64.5(7)
C00W	5390(4)	7327.4(16)	3992.6(10)	63.1(6)
C00X	5443(5)	8187.4(17)	3762.6(10)	70.2(7)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for s. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O001	74.3(11)	48.2(8)	66.5(10)	19.7(7)	5.8(8)	21.9(8)
C002	25.1(7)	30.2(8)	25.8(7)	-1.3(6)	2.0(6)	-1.3(6)
C003	24.6(7)	32.4(8)	24.9(7)	0.1(6)	-0.5(6)	0.0(6)
C004	35.1(8)	26.4(7)	29.9(8)	2.0(6)	2.7(6)	1.0(6)
C005	29.2(8)	30.2(8)	26.1(7)	3.6(6)	-0.3(6)	-2.0(6)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for s. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C006	29.5(7)	30.6(8)	25.3(7)	3.4(6)	0.0(6)	-1.6(6)
C007	45.1(9)	30.5(8)	29.2(7)	-0.3(6)	6.7(7)	-2.5(7)
C008	27.8(7)	33.9(8)	31.0(8)	8.9(7)	-2.4(6)	-1.3(7)
C009	49.8(10)	29.9(8)	31.8(8)	-0.5(7)	11.1(8)	0.0(7)
C00A	56.4(11)	29.7(8)	35.6(8)	2.9(7)	12.1(8)	0.5(8)
C00B	34.8(8)	33.0(8)	33.6(8)	-5.3(7)	0.9(7)	-3.2(7)
C00C	28.4(8)	50.7(10)	52.8(11)	22.7(9)	3.0(8)	-0.5(8)
C00D	52.2(10)	30.0(8)	32.5(8)	-0.9(6)	6.7(8)	-3.9(8)
C00E	26.1(7)	44.1(9)	28.6(8)	11.6(7)	3.1(6)	0.7(7)
C00F	30.6(8)	51.3(10)	37.7(9)	17.2(8)	1.6(7)	4.7(8)
C00G	32.9(8)	40.6(9)	34.2(8)	2.1(7)	-9.3(7)	-1.6(7)
C00H	50.5(10)	29.8(8)	40.2(9)	-2.1(7)	-1.2(8)	-5.1(8)
C00I	26.3(8)	46.8(10)	45.1(10)	12.1(8)	2.5(7)	1.7(7)
C00J	52.1(10)	31.2(8)	31.1(8)	5.2(7)	-12.5(8)	-7.4(8)
C00K	42.6(10)	39.0(9)	49.8(10)	7.5(8)	3.0(9)	-7.9(8)
C00L	42.8(10)	42.8(9)	46.4(10)	9.8(8)	4.5(8)	0.4(9)
C00M	48.7(11)	39.9(9)	37.7(9)	5.8(8)	-4.3(8)	-7.6(8)
C00N	40.3(9)	51.1(10)	29.0(8)	5.7(8)	-8.1(7)	-0.2(8)
C00O	50.1(10)	31.6(8)	33.6(8)	6.8(7)	-16.0(8)	-10.2(8)
C00P	50.1(11)	37.2(9)	39.6(9)	1.8(7)	1.8(8)	-12.5(8)
C00Q	46.7(10)	43.2(10)	42.6(9)	19.1(8)	11.1(9)	9.5(9)
C00R	82.1(16)	41.4(10)	46.9(11)	8.9(8)	-20.2(11)	-19.2(11)
C00S	62.8(12)	31.3(9)	42.8(10)	7.2(8)	-11.5(9)	-1.9(9)
C00T	68.4(14)	33.2(9)	57.6(12)	12.1(9)	-9.2(11)	-3.6(10)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for s. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C00U	90.6(17)	31.2(9)	50.0(11)	8.9(8)	1.0(12)	-5.4(11)
C00V	99.7(19)	39.1(11)	54.8(12)	5.7(9)	-15.0(13)	-26.9(12)
C00W	63.0(14)	46.6(12)	79.9(16)	21.2(11)	-20.5(12)	-14.8(11)
C00X	76.9(16)	51.8(13)	81.9(17)	26.2(12)	-21.7(14)	-8.0(13)

Table 4 Bond Lengths for s.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O001	C00Q	1.224(2)	C009	C00A	1.510(2)
C002	C003	1.525(2)	C009	C00L	1.385(3)
C002	C005	1.536(2)	C009	C00P	1.383(3)
C002	C00B	1.530(2)	C00B	C00H	1.539(2)
C003	C006	1.540(2)	C00D	C00R	1.380(3)
C003	C00G	1.526(2)	C00D	C00W	1.384(3)
C004	C005	1.555(2)	C00E	C00F	1.341(3)
C004	C00A	1.540(2)	C00E	C00N	1.500(3)
C004	C00H	1.555(2)	C00F	C00Q	1.452(3)
C005	C00I	1.544(2)	C00G	C00N	1.525(2)
C005	C00J	1.522(2)	C00J	C00O	1.535(2)
C006	C008	1.562(2)	C00K	C00L	1.389(3)
C006	C00O	1.541(2)	C00M	C00P	1.383(2)
C007	C00D	1.494(2)	C00Q	C00T	1.490(3)
C007	C00K	1.389(3)	C00R	C00V	1.385(3)
C007	C00M	1.396(3)	C00S	C00T	1.529(2)

Table 4 Bond Lengths for s.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C008	C00C	1.549(2)	C00U	C00V	1.362(4)
C008	C00E	1.525(2)	C00U	C00X	1.364(4)
C008	C00S	1.531(2)	C00W	C00X	1.384(3)

Table 5 Bond Angles for s.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C003	C002	C005	113.63(12)	C00P	C009	C00L	117.12(16)
C003	C002	C00B	118.85(13)	C009	C00A	C004	110.88(14)
C00B	C002	C005	103.23(13)	C002	C00B	C00H	103.75(13)
C002	C003	C006	109.09(12)	C00R	C00D	C007	121.20(18)
C002	C003	C00G	111.93(13)	C00R	C00D	C00W	116.60(17)
C00G	C003	C006	109.77(13)	C00W	C00D	C007	122.19(18)
C005	C004	C00H	103.69(12)	C00F	C00E	C008	122.19(16)
C00A	C004	C005	115.89(13)	C00F	C00E	C00N	121.08(15)
C00A	C004	C00H	112.34(15)	C00N	C00E	C008	116.69(14)
C002	C005	C004	102.62(13)	C00E	C00F	C00Q	124.60(16)
C002	C005	C00I	112.23(12)	C00N	C00G	C003	111.13(14)
C00I	C005	C004	106.02(13)	C00B	C00H	C004	107.61(13)
C00J	C005	C002	107.90(13)	C005	C00J	C00O	111.12(13)
C00J	C005	C004	117.91(13)	C007	C00K	C00L	121.68(18)
C00J	C005	C00I	110.05(15)	C009	C00L	C00K	121.30(18)
C003	C006	C008	113.24(12)	C00P	C00M	C007	121.27(19)
C003	C006	C00O	112.17(13)	C00E	C00N	C00G	112.67(13)
C00O	C006	C008	112.11(12)	C00J	C00O	C006	112.35(14)

Table 5 Bond Angles for s.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C00K	C007	C00D	121.83(17)	C009	C00P	C00M	121.91(18)
C00K	C007	C00M	116.68(16)	O001	C00Q	C00F	121.85(19)
C00M	C007	C00D	121.48(17)	O001	C00Q	C00T	121.8(2)
C00C	C008	C006	111.46(13)	C00F	C00Q	C00T	116.31(16)
C00E	C008	C006	109.50(13)	C00D	C00R	C00V	121.4(2)
C00E	C008	C00C	107.33(13)	C00T	C00S	C008	113.93(15)
C00E	C008	C00S	109.46(14)	C00Q	C00T	C00S	111.59(17)
C00S	C008	C006	108.67(13)	C00V	C00U	C00X	119.19(19)
C00S	C008	C00C	110.39(15)	C00U	C00V	C00R	120.7(2)
C00L	C009	C00A	122.68(18)	C00X	C00W	C00D	121.9(2)
C00P	C009	C00A	120.16(18)	C00U	C00X	C00W	120.1(2)

Table 6 Torsion Angles for s.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O001	C00Q	C00T	C00S	-152.5(2)	C00B	C002	C005	C004	44.21(14)
C002	C003	C006	C008	-179.85(12)	C00B	C002	C005	C00I	-69.18(16)
C002	C003	C006	C00O	-51.74(17)	C00B	C002	C005	C00J	169.41(13)
C002	C003	C00G	C00N	-178.79(13)	C00C	C008	C00E	C00F	103.06(19)
C002	C005	C00J	C00O	57.58(19)	C00C	C008	C00E	C00N	-74.62(18)
C002	C00B	C00H	C004	16.78(18)	C00C	C008	C00S	C00T	-71.7(2)
C003	C002	C005	C004	174.29(12)	C00D	C007	C00K	C00L	178.57(17)
C003	C002	C005	C00I	60.90(17)	C00D	C007	C00M	C00P	-178.72(17)
C003	C002	C005	C00J	-60.51(17)	C00D	C00R	C00V	C00U	0.0(4)
C003	C002	C00B	C00H	-164.45(14)	C00D	C00W	C00X	C00U	0.6(4)

Table 6 Torsion Angles for s.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
C003	C006	C008	C00C	68.37(17)	C00E	C008	C00S	C00T	46.3(2)
C003	C006	C008	C00E	-50.24(17)	C00E	C00F	C00Q	O001	-178.18(19)
C003	C006	C008	C00S	-169.76(14)	C00E	C00F	C00Q	C00T	-1.3(3)
C003	C006	C00O	C00J	52.21(19)	C00F	C00E	C00N	C00G	132.88(17)
C003	C00G	C00N	C00E	53.6(2)	C00F	C00Q	C00T	C00S	30.5(3)
C004	C005	C00J	C00O	173.11(15)	C00G	C003	C006	C008	57.17(17)
C005	C002	C003	C006	57.41(16)	C00G	C003	C006	C00O	-174.71(13)
C005	C002	C003	C00G	179.09(13)	C00H	C004	C005	C002	-32.96(16)
C005	C002	C00B	C00H	-37.61(16)	C00H	C004	C005	C00I	84.92(16)
C005	C004	C00A	C009	167.46(16)	C00H	C004	C005	C00J	-151.33(15)
C005	C004	C00H	C00B	10.08(18)	C00H	C004	C00A	C009	-73.6(2)
C005	C00J	C00O	C006	-55.4(2)	C00I	C005	C00J	C00O	-65.17(18)
C006	C003	C00G	C00N	-57.51(18)	C00K	C007	C00D	C00R	-14.9(3)
C006	C008	C00E	C00F	-135.80(16)	C00K	C007	C00D	C00W	163.8(2)
C006	C008	C00E	C00N	46.52(19)	C00K	C007	C00M	C00P	1.1(3)
C006	C008	C00S	C00T	165.82(17)	C00L	C009	C00A	C004	97.2(2)
C007	C00D	C00R	C00V	179.8(2)	C00L	C009	C00P	C00M	-2.0(3)
C007	C00D	C00W	C00X	179.9(2)	C00M	C007	C00D	C00R	164.9(2)
C007	C00K	C00L	C009	-0.3(3)	C00M	C007	C00D	C00W	-16.4(3)
C007	C00M	C00P	C009	0.6(3)	C00M	C007	C00K	C00L	-1.2(3)
C008	C006	C00O	C00J	-179.08(14)	C00N	C00E	C00F	C00Q	171.61(16)
C008	C00E	C00F	C00Q	-6.0(3)	C00O	C006	C008	C00C	-59.78(19)
C008	C00E	C00N	C00G	-49.4(2)	C00O	C006	C008	C00E	-178.38(14)
C008	C00S	C00T	C00Q	-54.3(2)	C00O	C006	C008	C00S	62.09(18)
C00A	C004	C005	C002	90.62(17)	C00P	C009	C00A	C004	-80.2(2)

Table 6 Torsion Angles for s.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
C00A	C004	C005	C00I	-151.50(15)	C00P	C009	C00L	C00K	1.9(3)
C00A	C004	C005	C00J	-27.7(2)	C00R	C00D	C00W	C00X	-1.3(4)
C00A	C004	C00H	C00B	-115.79(15)	C00S	C008	C00E	C00F	-16.8(2)
C00A	C009	C00L	C00K	-175.62(17)	C00S	C008	C00E	C00N	165.55(15)
C00A	C009	C00P	C00M	175.53(17)	C00V	C00U	C00X	C00W	0.5(4)
C00B	C002	C003	C006	179.16(13)	C00W	C00D	C00R	C00V	1.0(4)
C00B	C002	C003	C00G	-59.16(19)	C00X	C00U	C00V	C00R	-0.8(4)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for s.

Atom	x	y	z	U(eq)
H002	7541.76	2422.44	6261.62	32
H003	4688.28	1961.78	7019.33	33
H004	3895.54	4068.35	5775.08	37
H006	6713.71	760.2	6340.44	34
H00A	7844.36	3296.7	5459.26	49
H00B	5696.63	3058.57	5186.92	49
H00C	8300.44	3610.64	6783.03	41
H00D	5872.44	3740.21	6933.31	41
H00E	2885.44	744.85	7307.92	66
H00F	2756.82	-356.63	7371.64	66
H00G	1693.47	127.57	6918.19	66
H00H	8844.85	-895.95	7530.84	48
H00I	9090.53	1496.75	6945.11	43
H00J	8129.94	2196.47	7331.88	43

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for s.

Atom	x	y	z	U(eq)
H00K	7863.13	4426.09	6099.29	48
H00L	5728.21	4801.98	6336.78	48
H00M	2085.05	2588.89	6635.68	59
H00N	1239.45	3120.03	6172.62	59
H00O	2619.83	3663.22	6559.5	59
H00P	5324.13	1784.23	5629.52	46
H00Q	2859.23	2009.53	5613.8	46
H00R	9691.44	6222.77	4899.89	53
H00S	9575.7	4804.24	5298.51	53
H00T	3815.85	5769.57	4391.04	51
H00U	8729.14	682.24	7667.03	48
H00V	6319.18	986.69	7713.05	48
H00W	3484.76	504.09	5957.62	46
H00X	2292.1	1166.31	6327.35	46
H00Y	3726.02	4354.54	4787.31	51
H00Z	9324.58	7633	4709.31	68
H00	3578.07	-828.99	6351.54	55
H	6082.52	-813.13	6307.04	55
H1	3746.4	-1828.96	7014.14	64
HA	5087.02	-2281.78	6590.37	64
H2	6968.37	9423.69	3734.05	69
H3	9417.83	9064.65	4322.1	77
H4	4360.53	6885.77	3900.22	76
H5	4448.52	8324.5	3519.93	84

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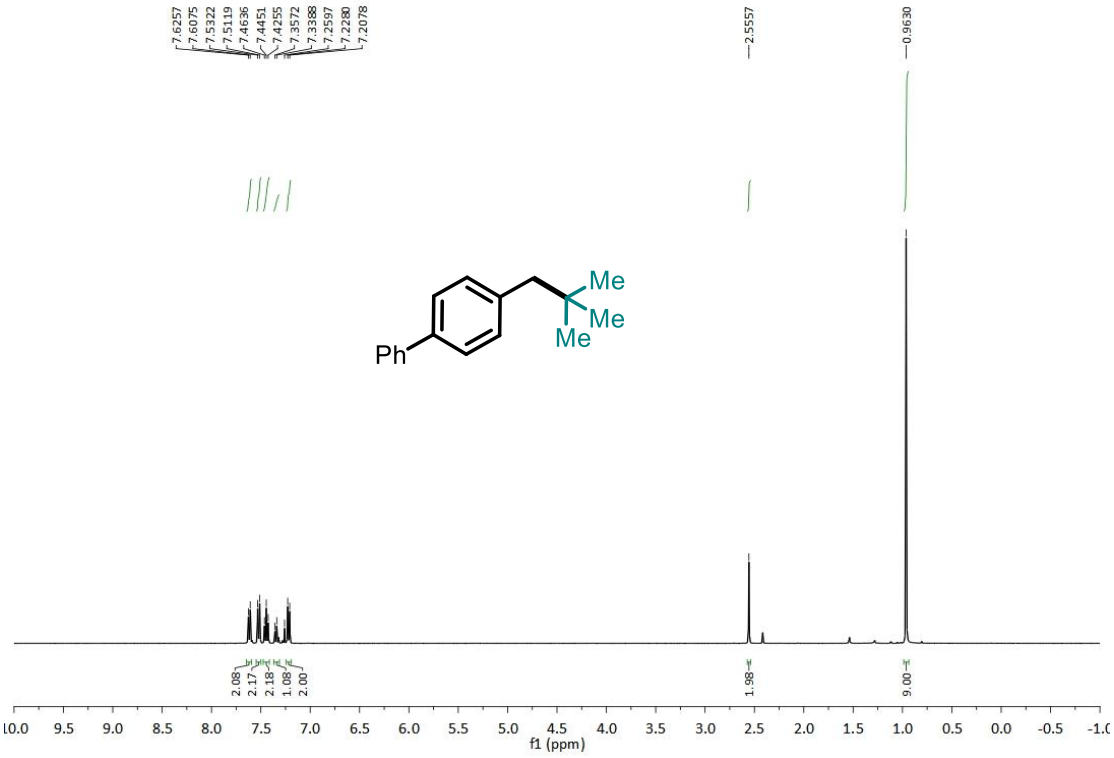
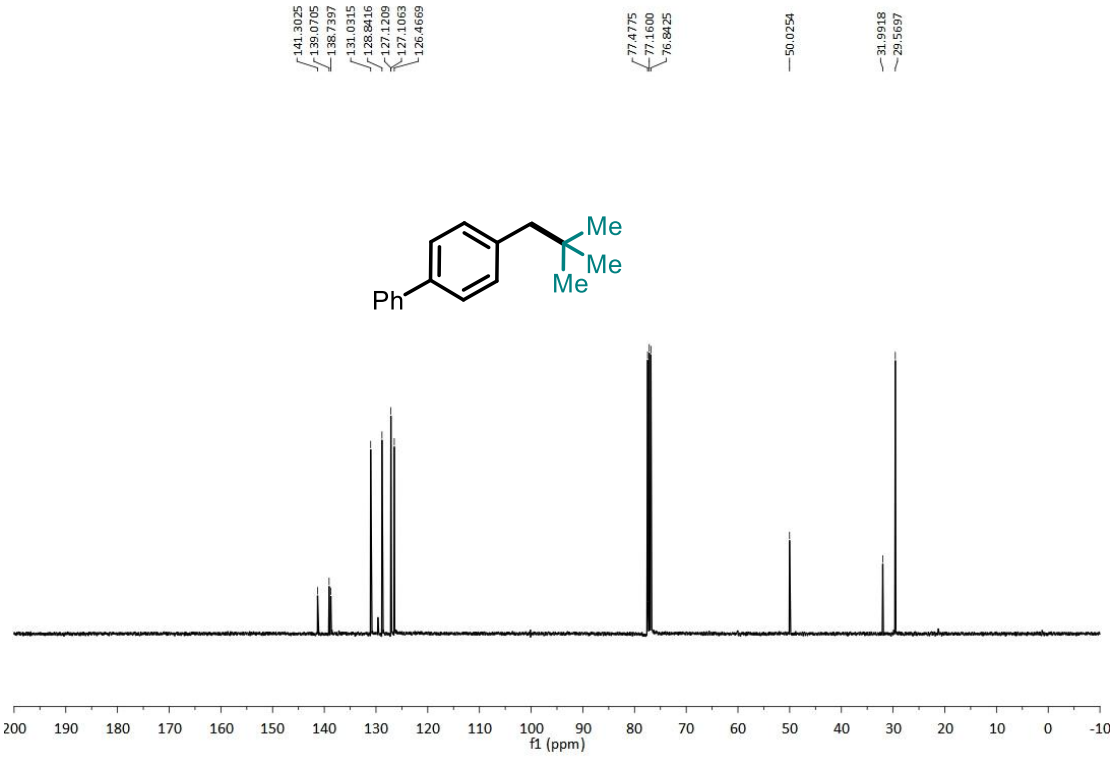
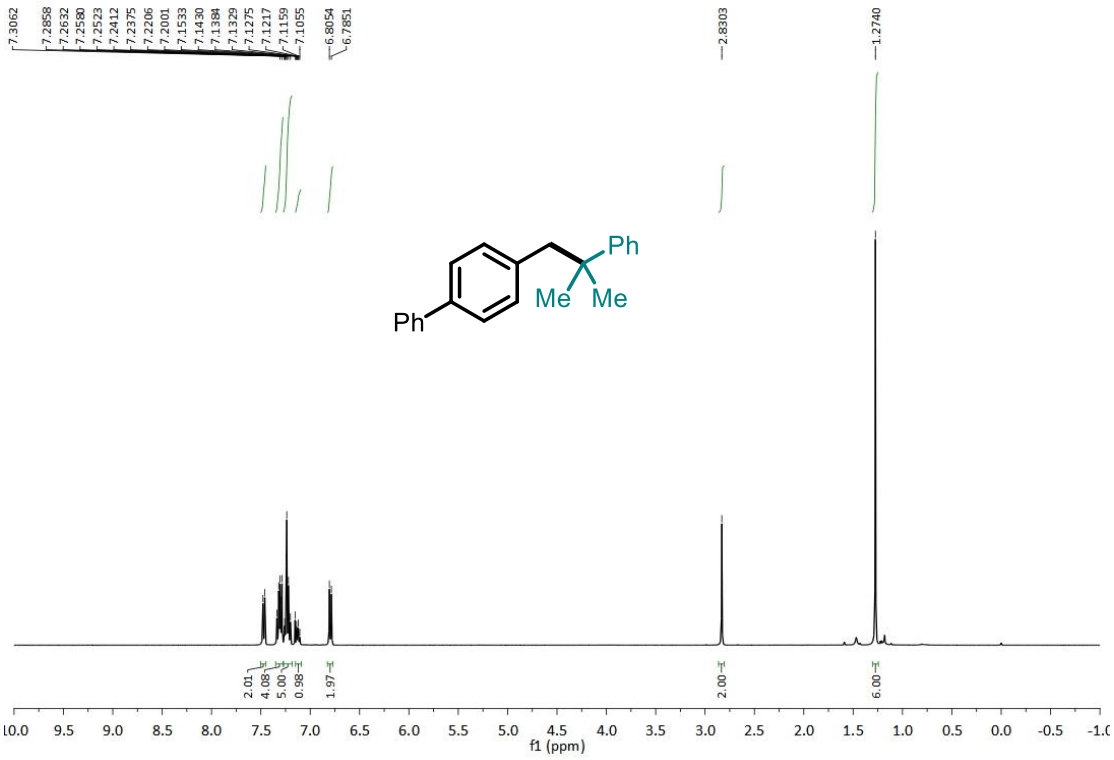
7. NMR spectral data for compounds



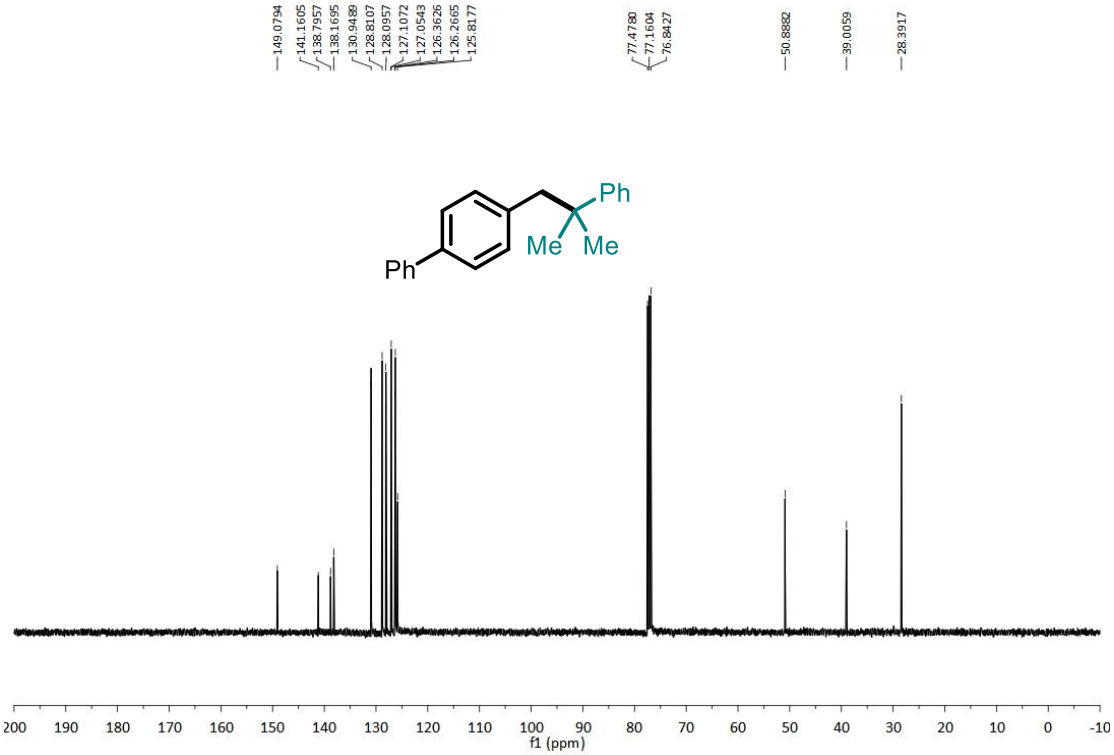
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3**



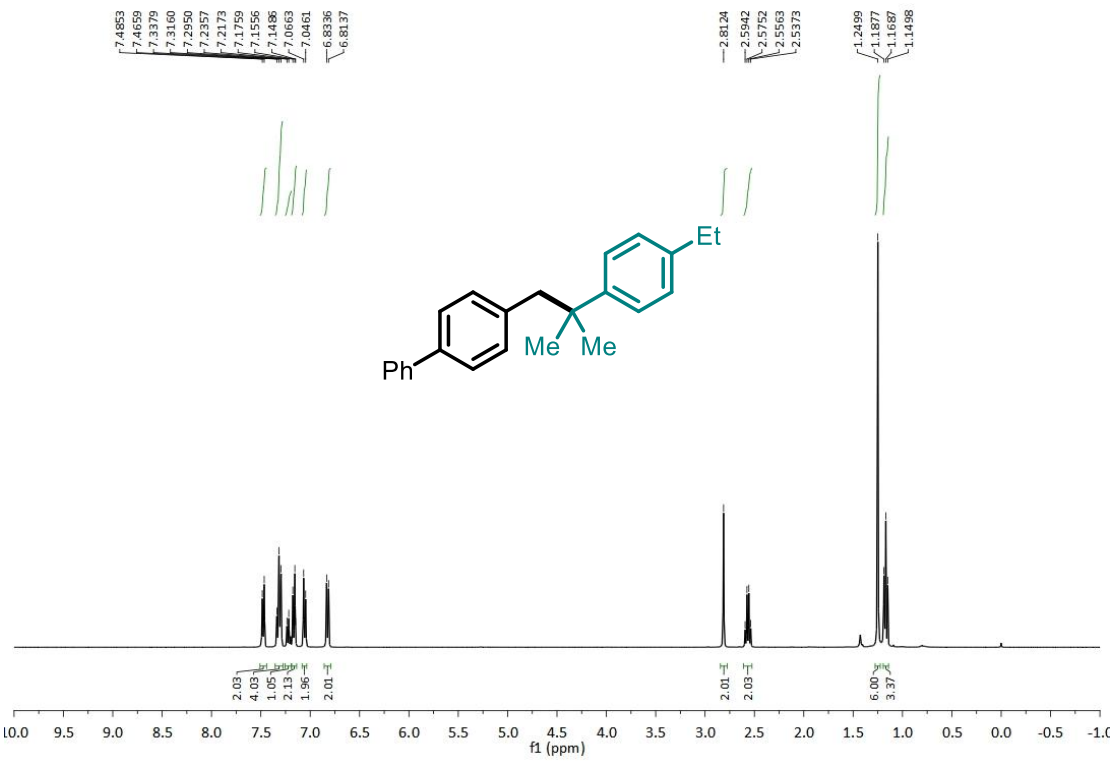
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **3**



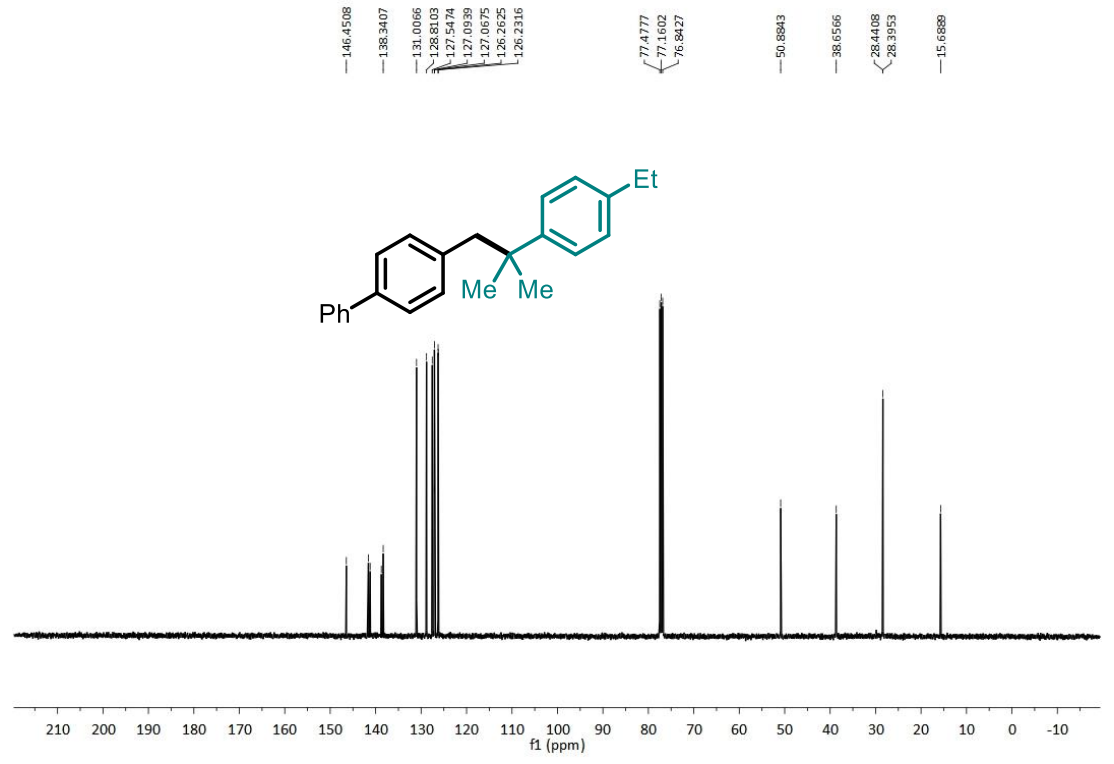
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **4**



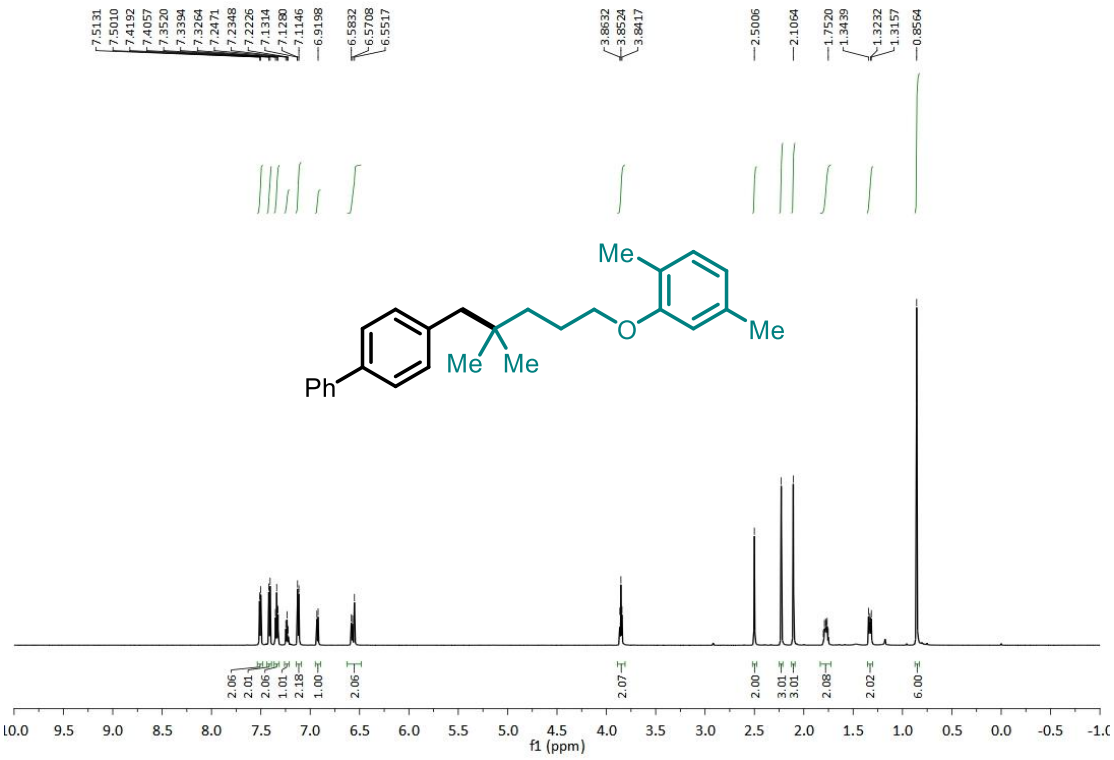
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **4**



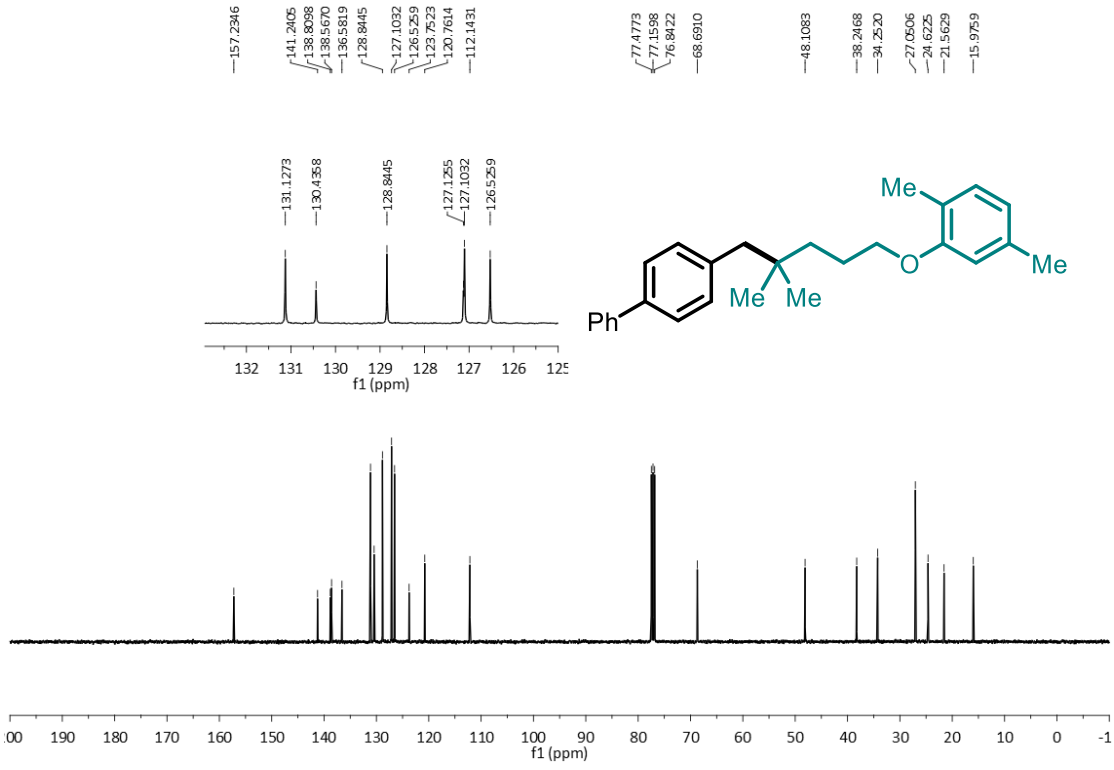
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5**



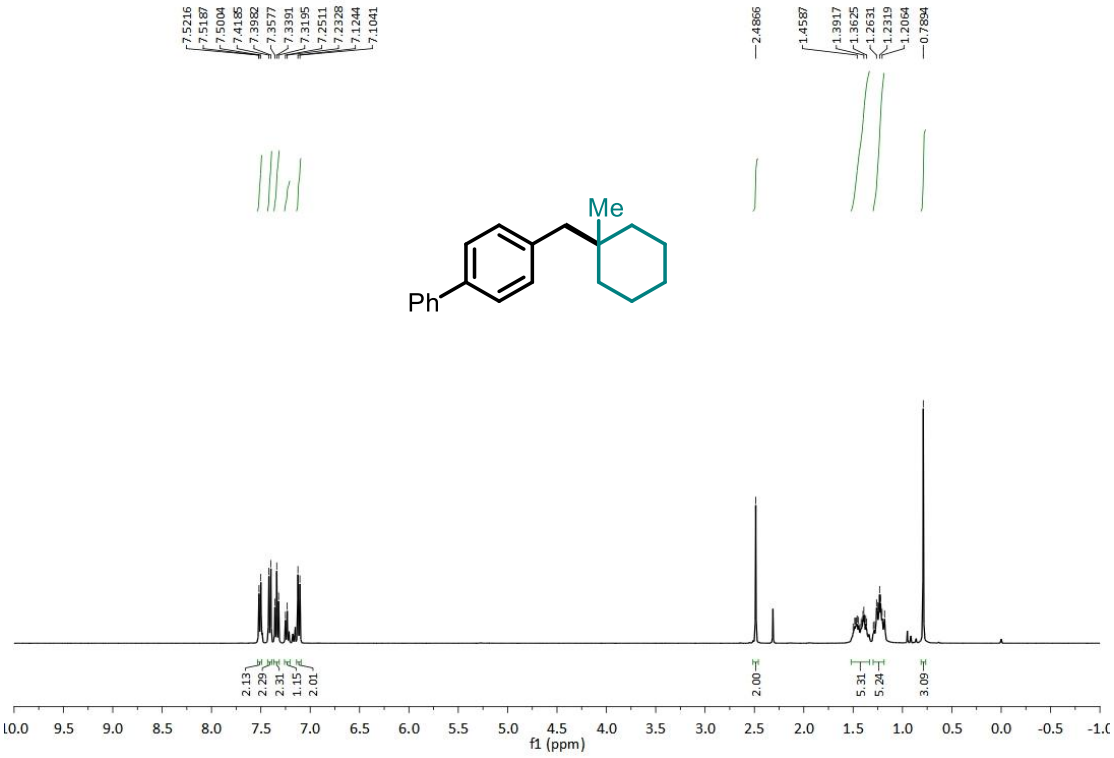
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **5**



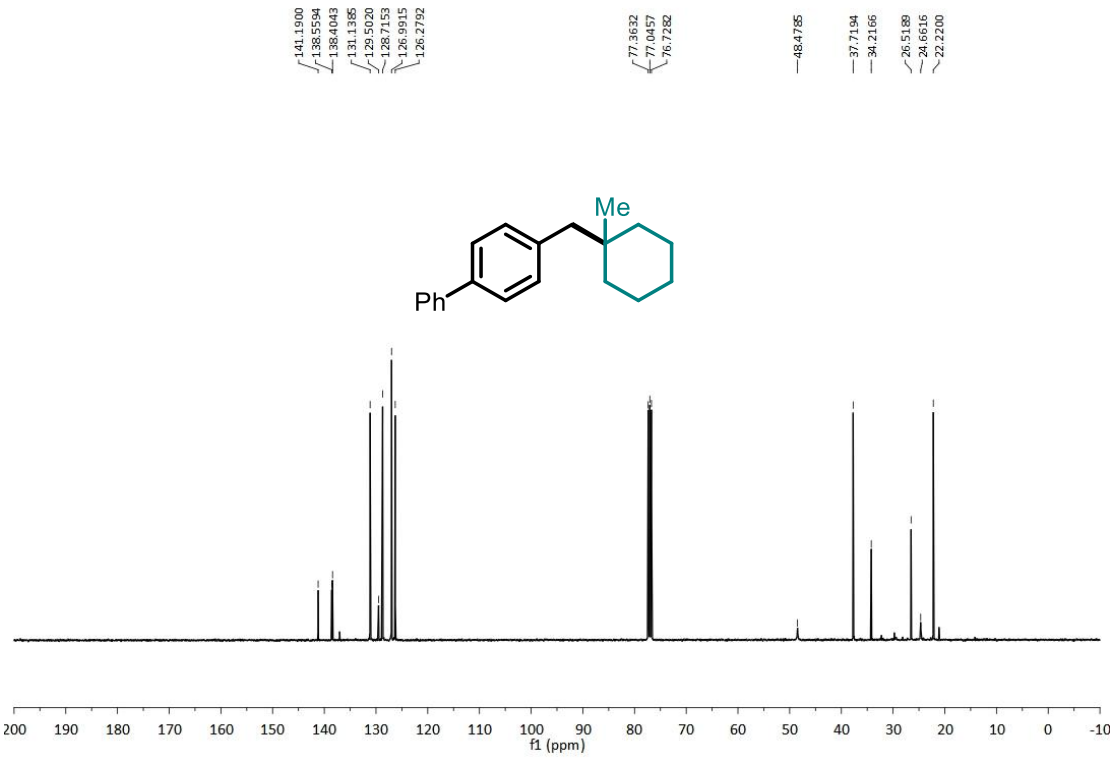
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **6**



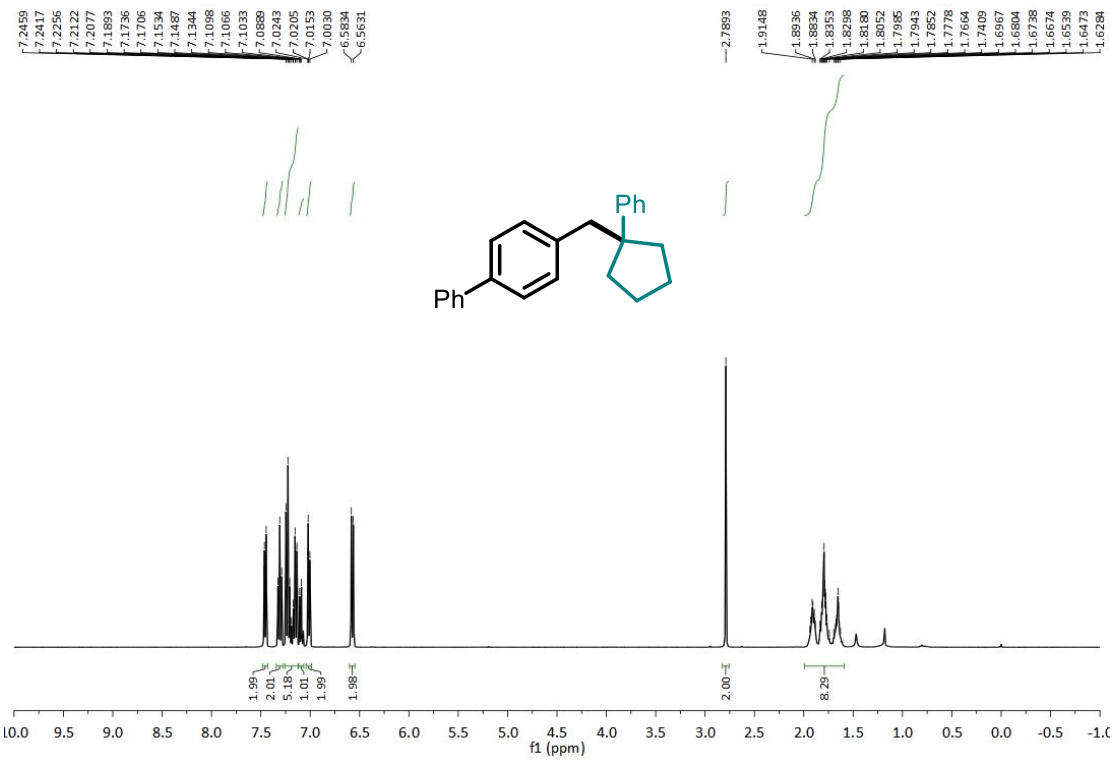
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **6**



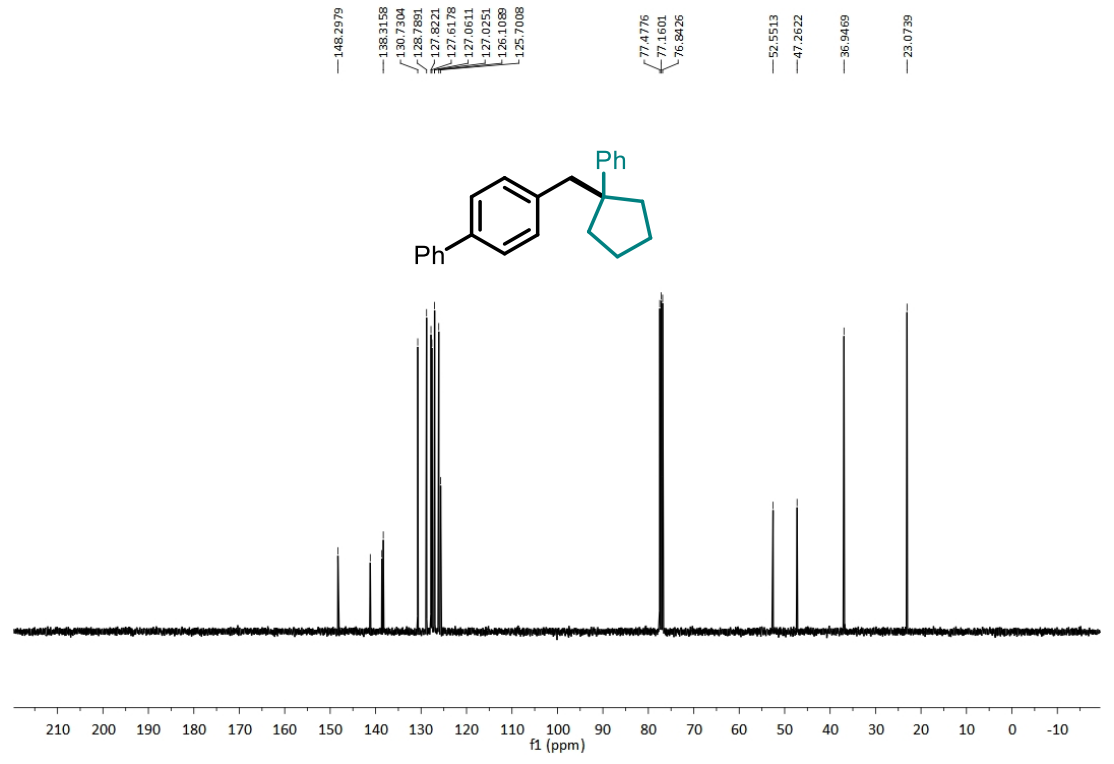
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **7**



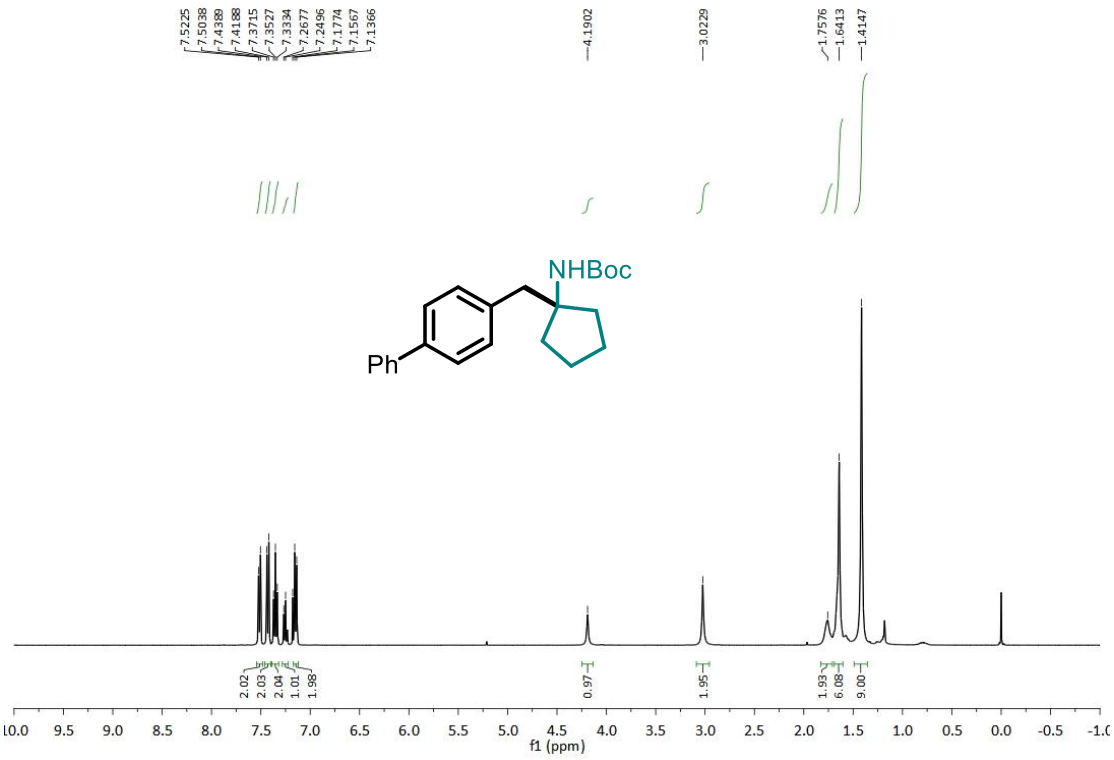
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **7**



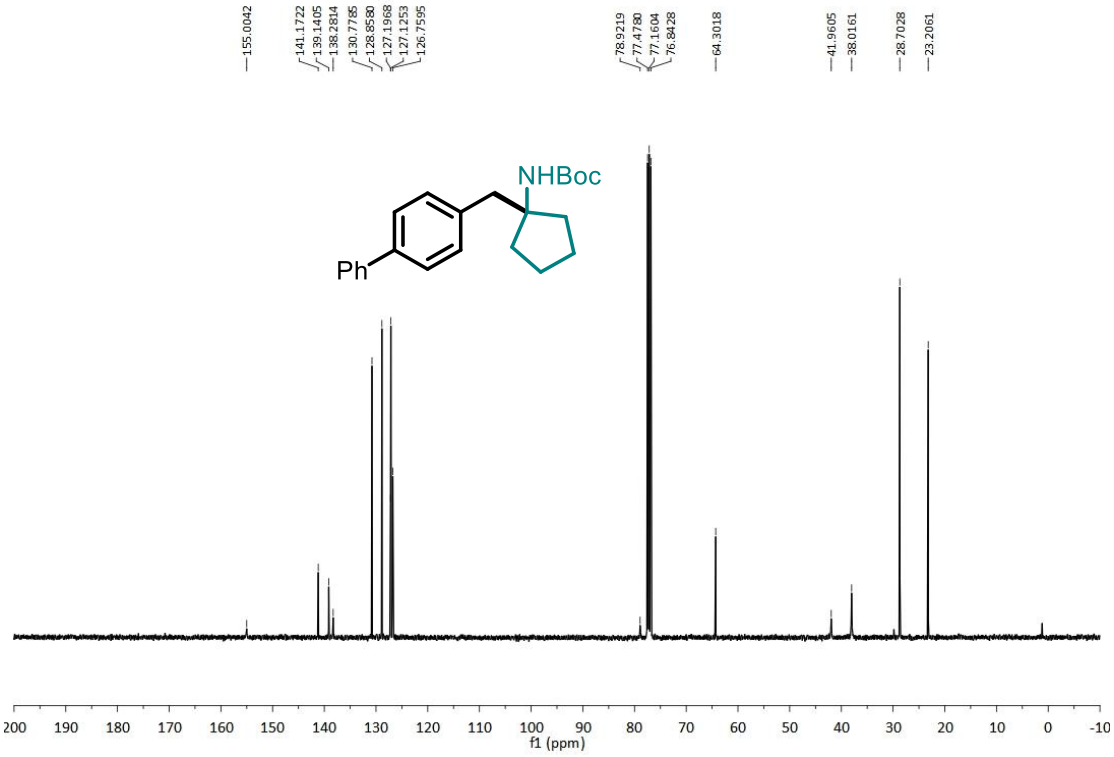
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **8**



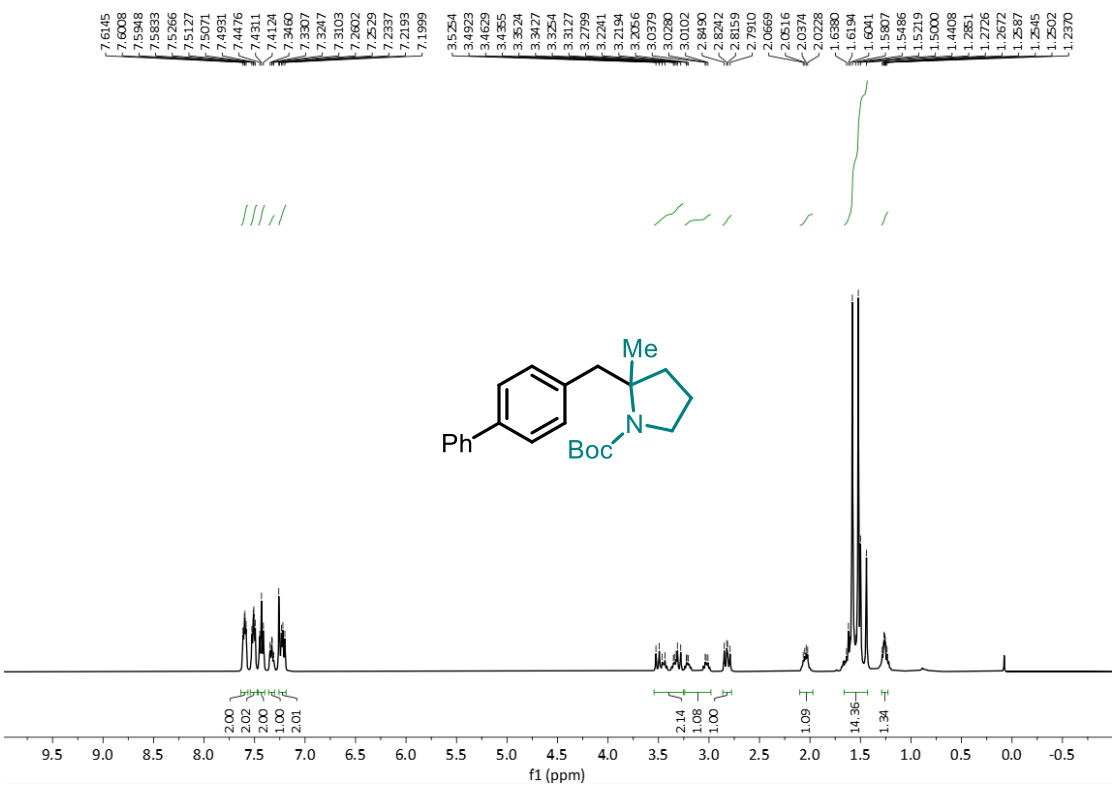
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **8**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **9**



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **9**



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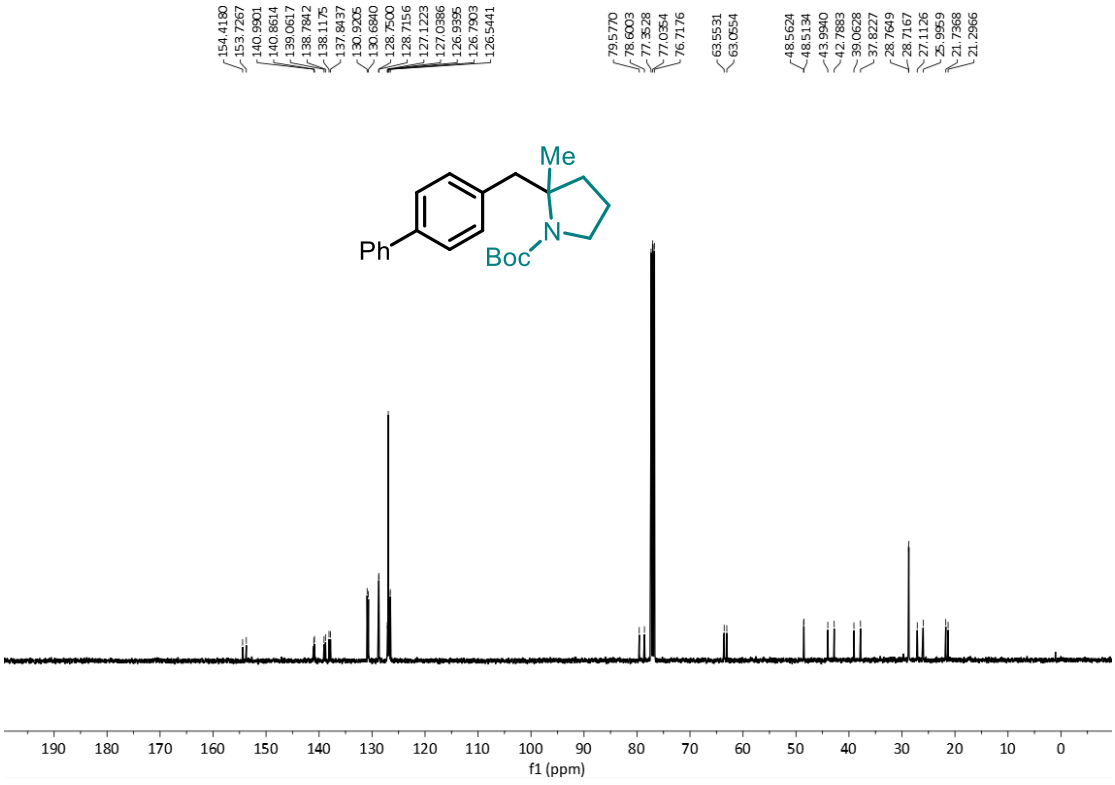
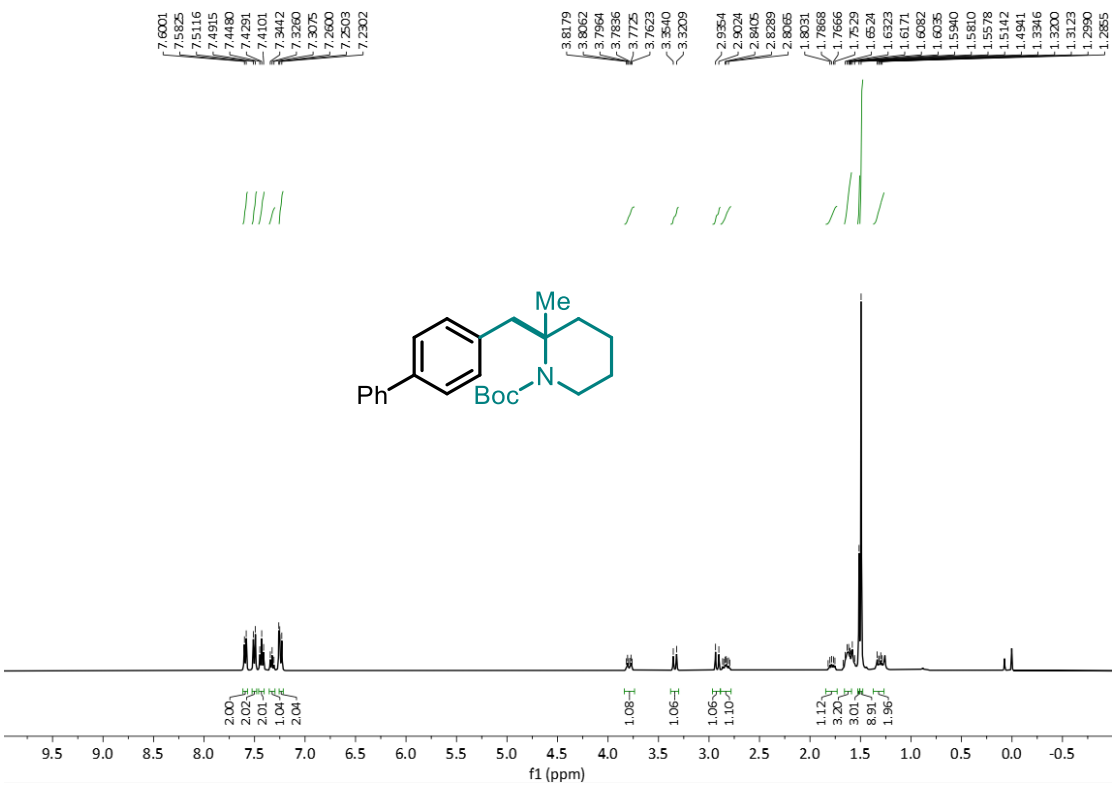
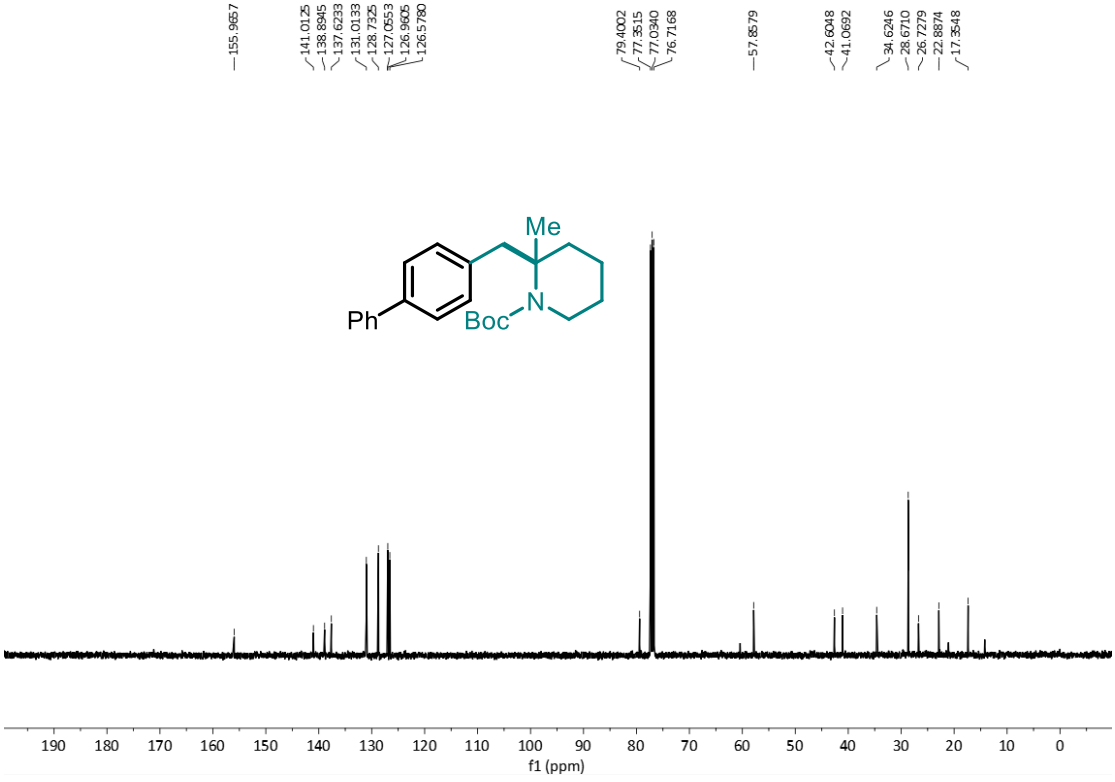


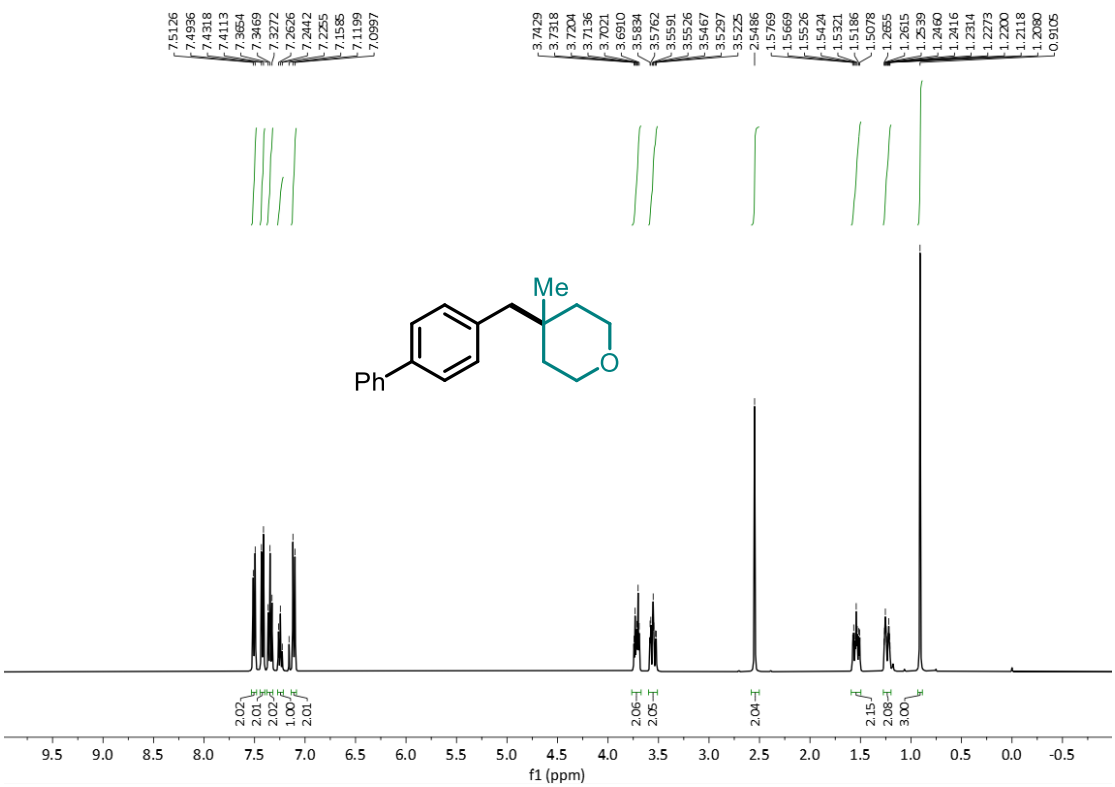
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **10**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **11**



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **11**



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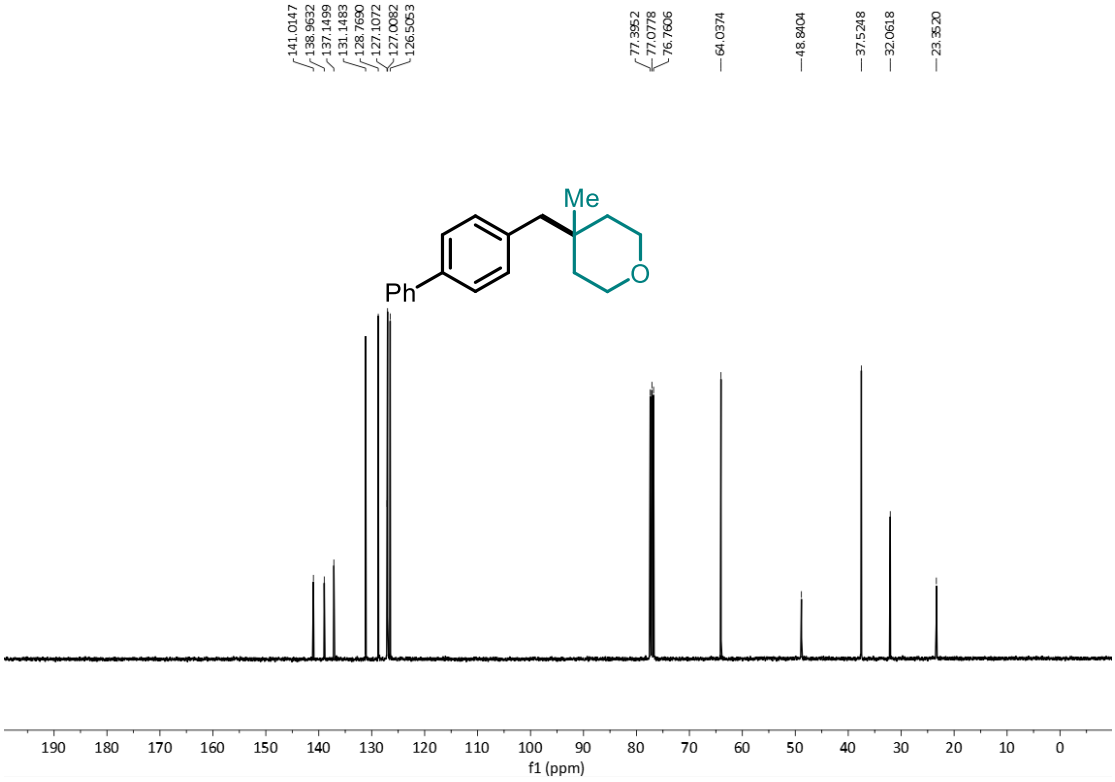

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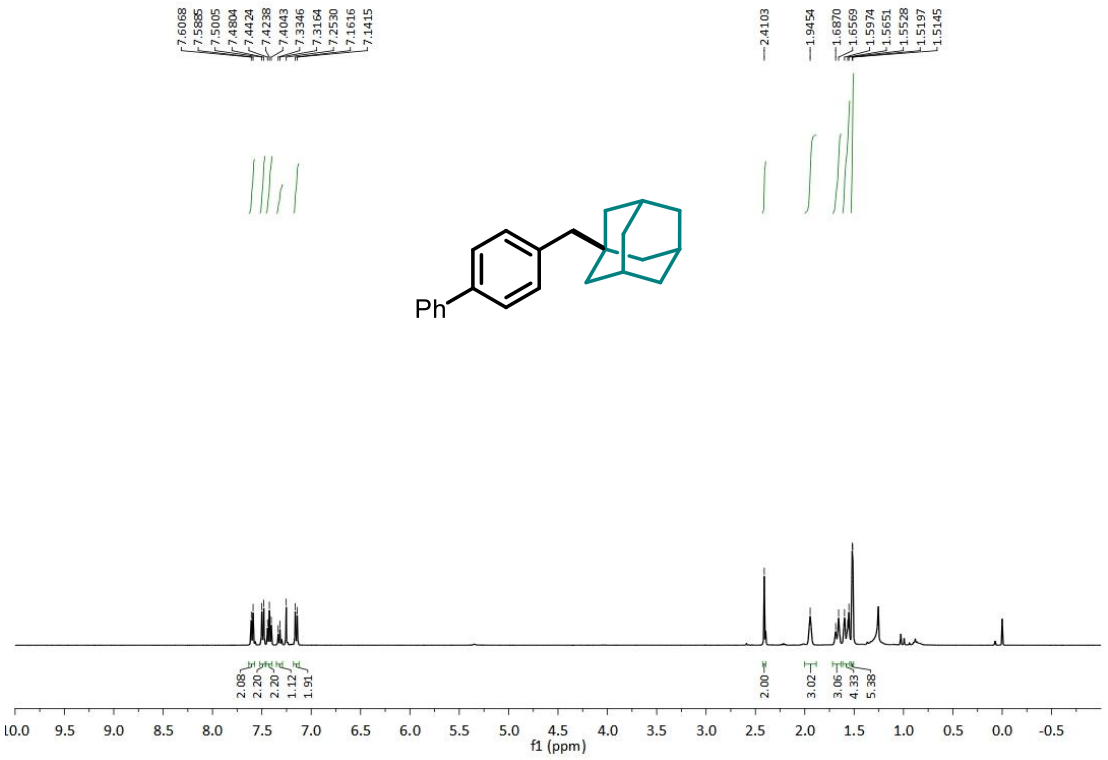
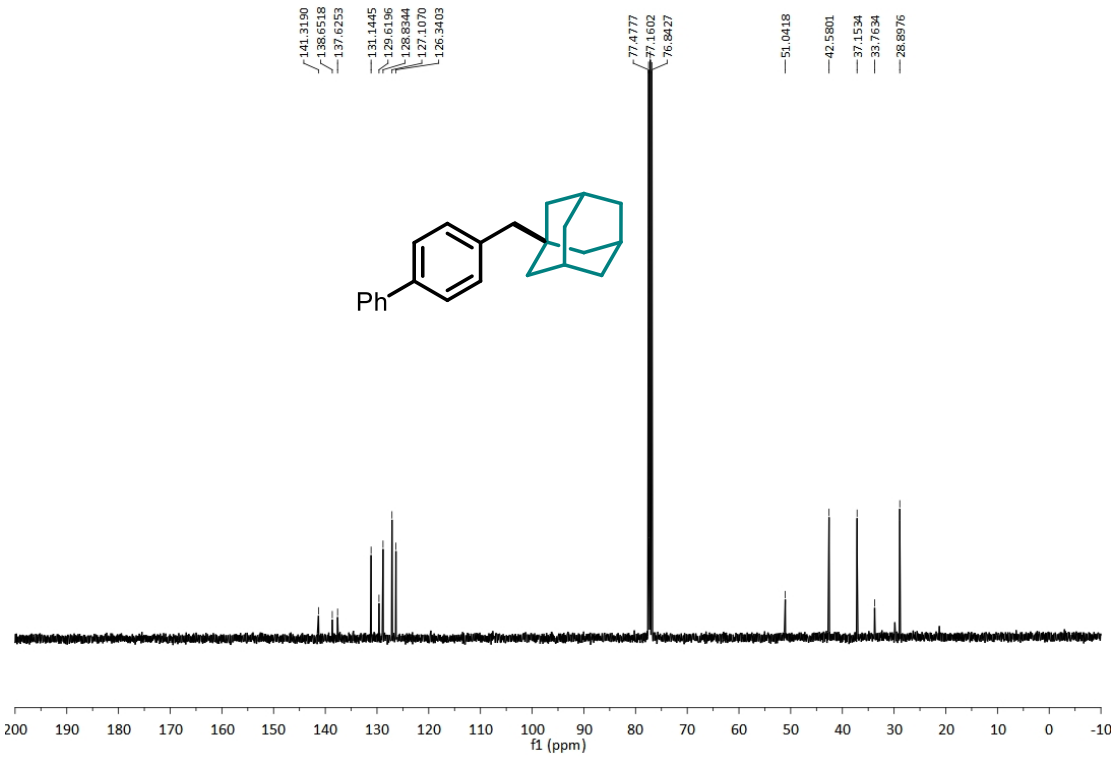
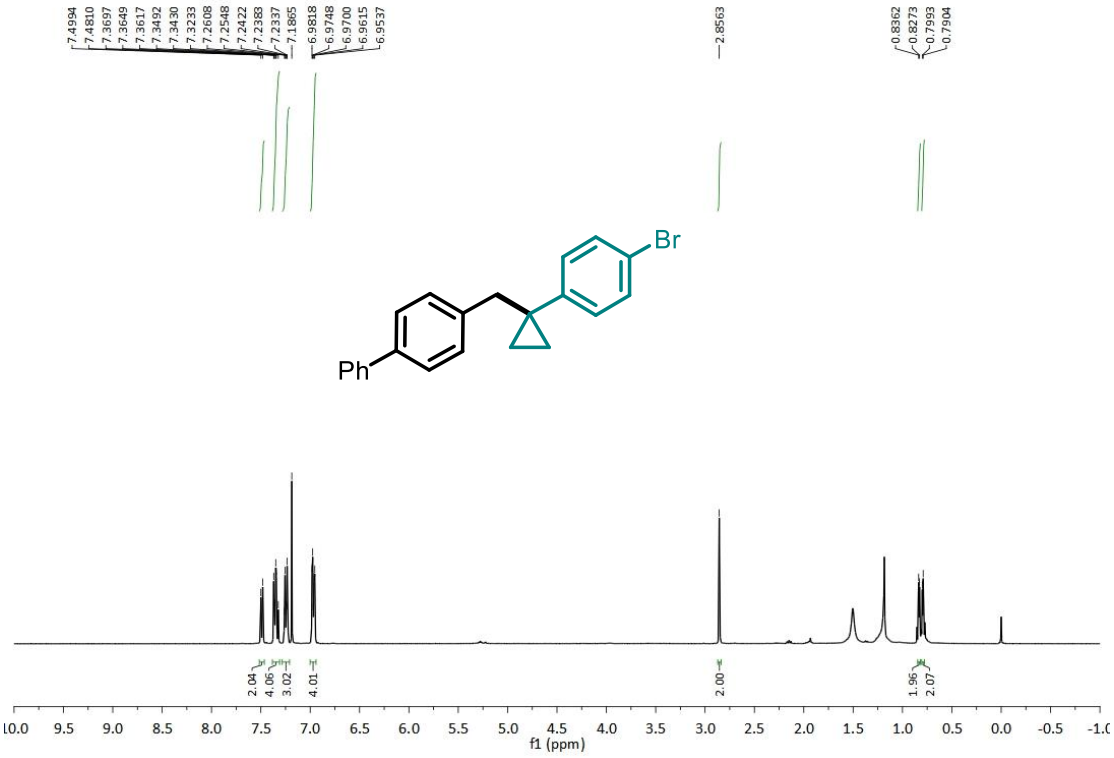


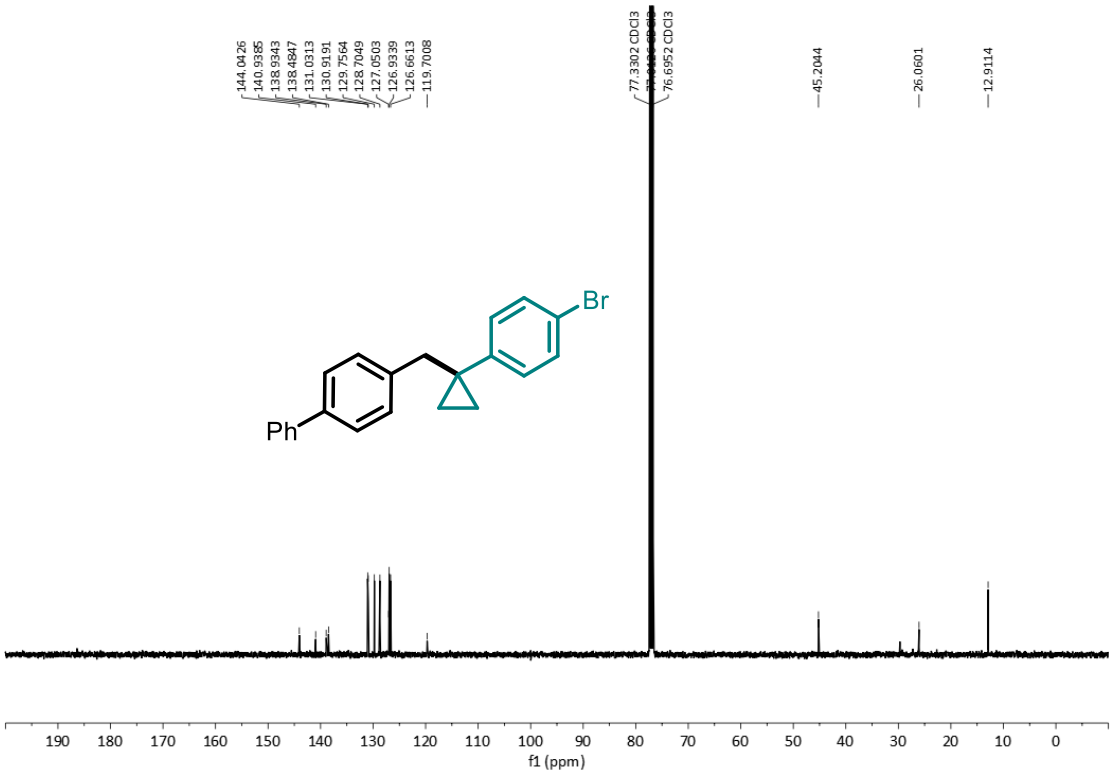
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **13**



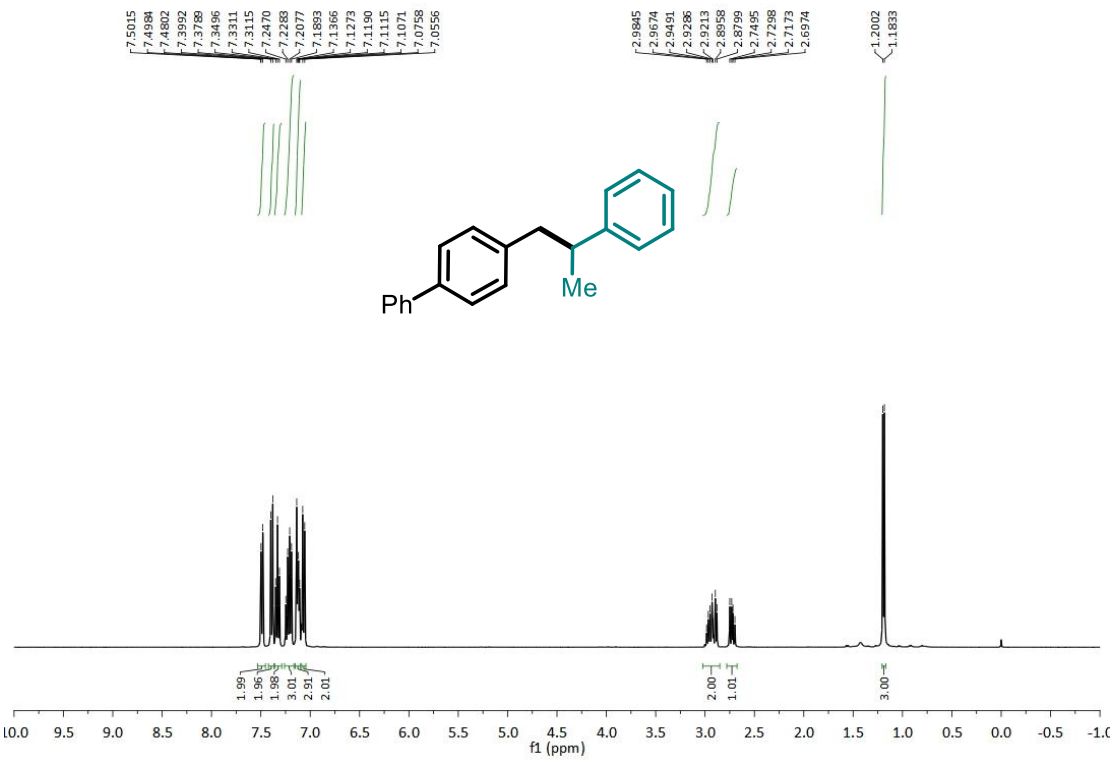
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **13**



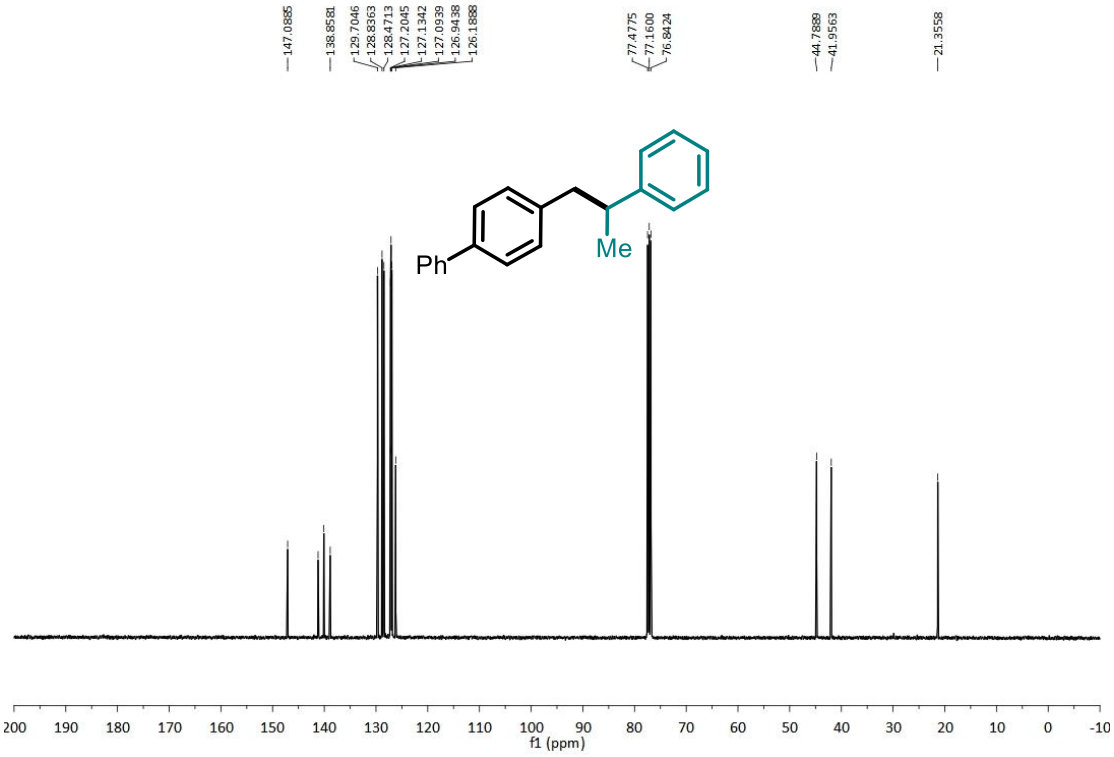
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **14**



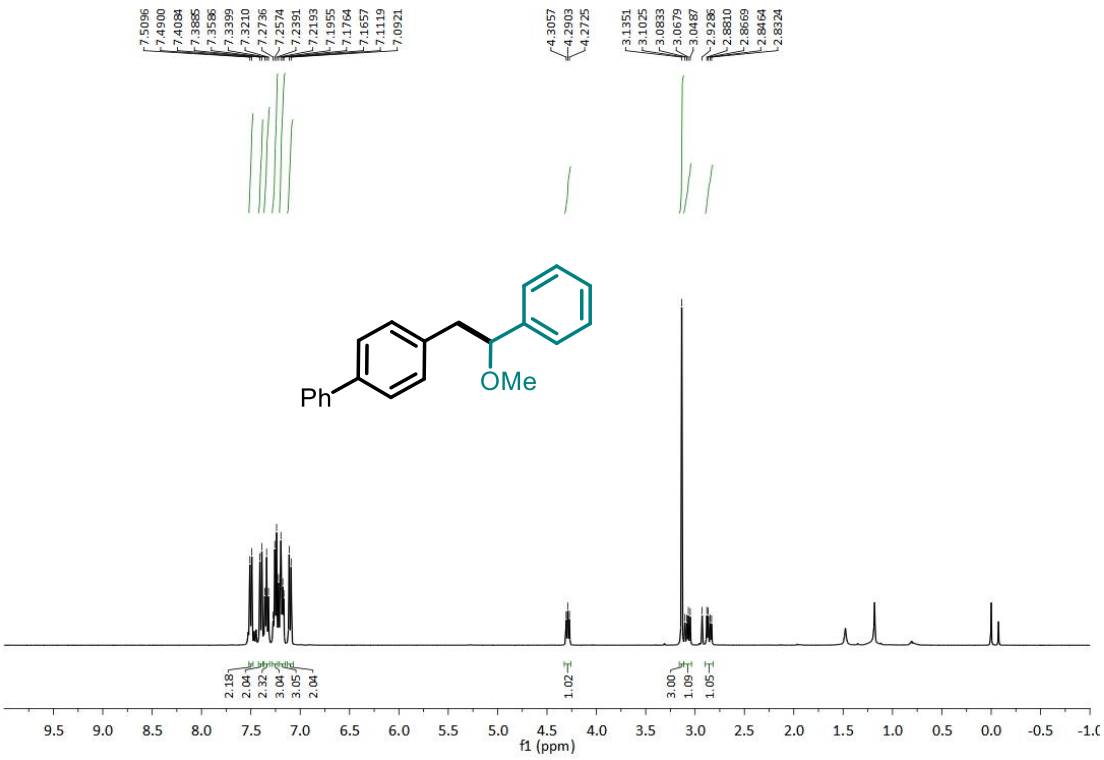
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **14**



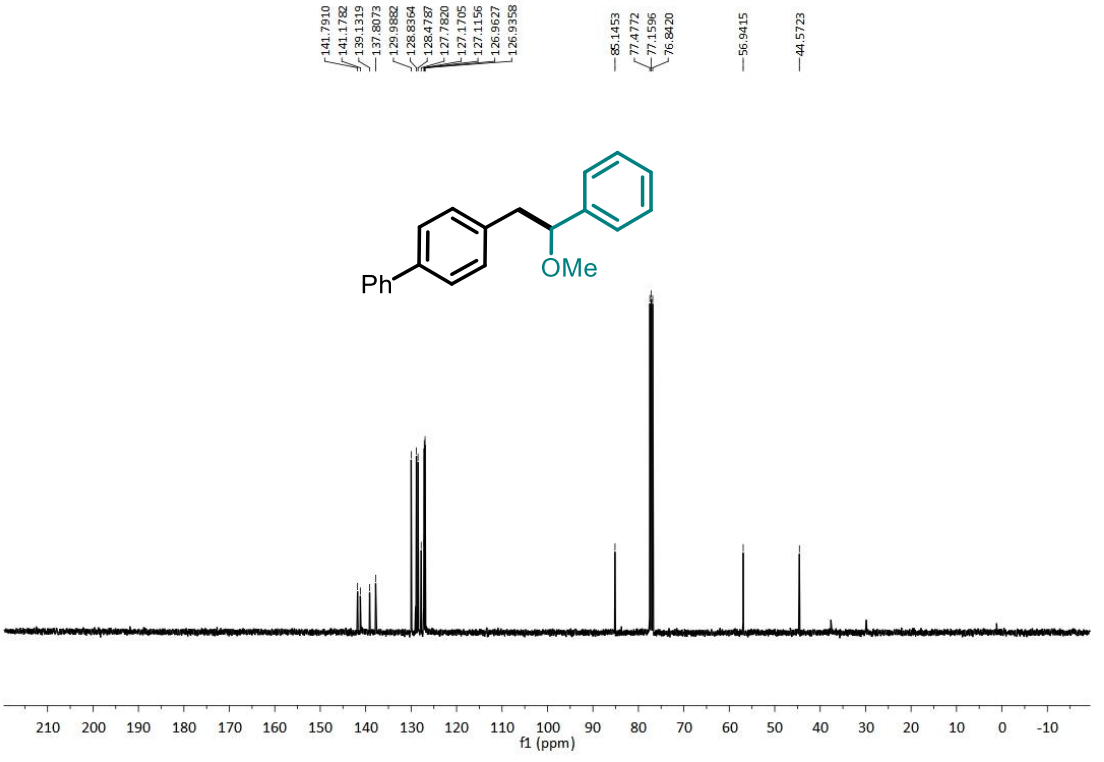
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **15**



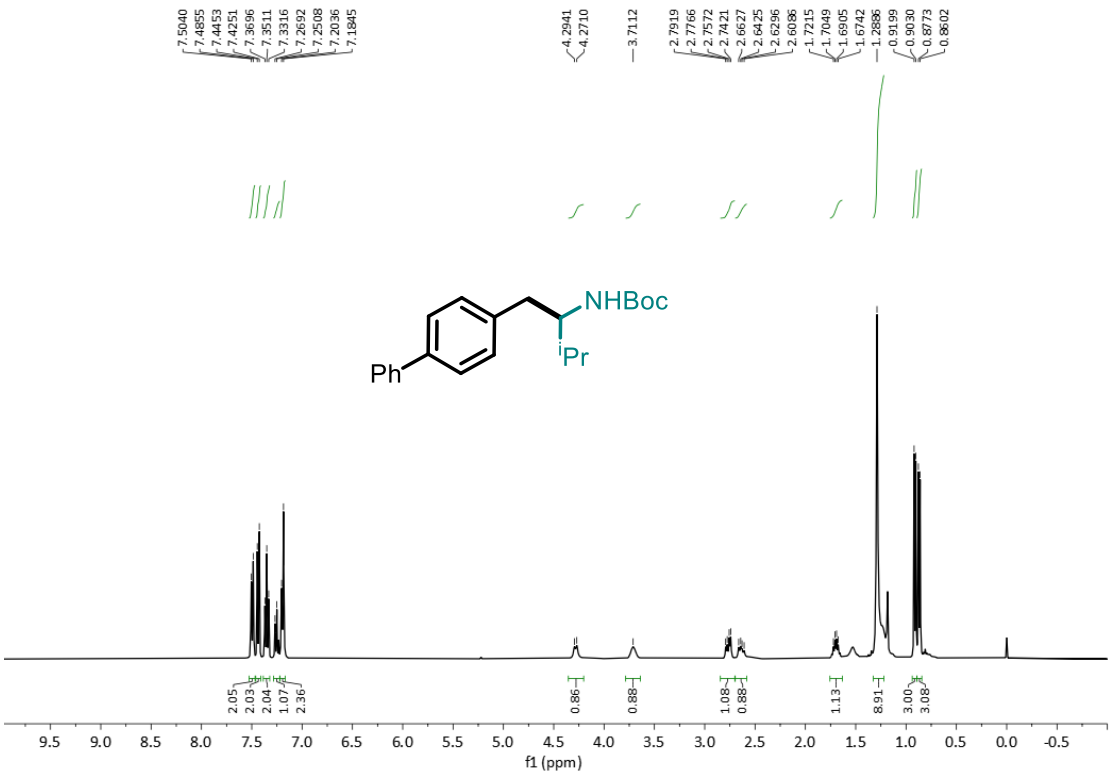
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **15**



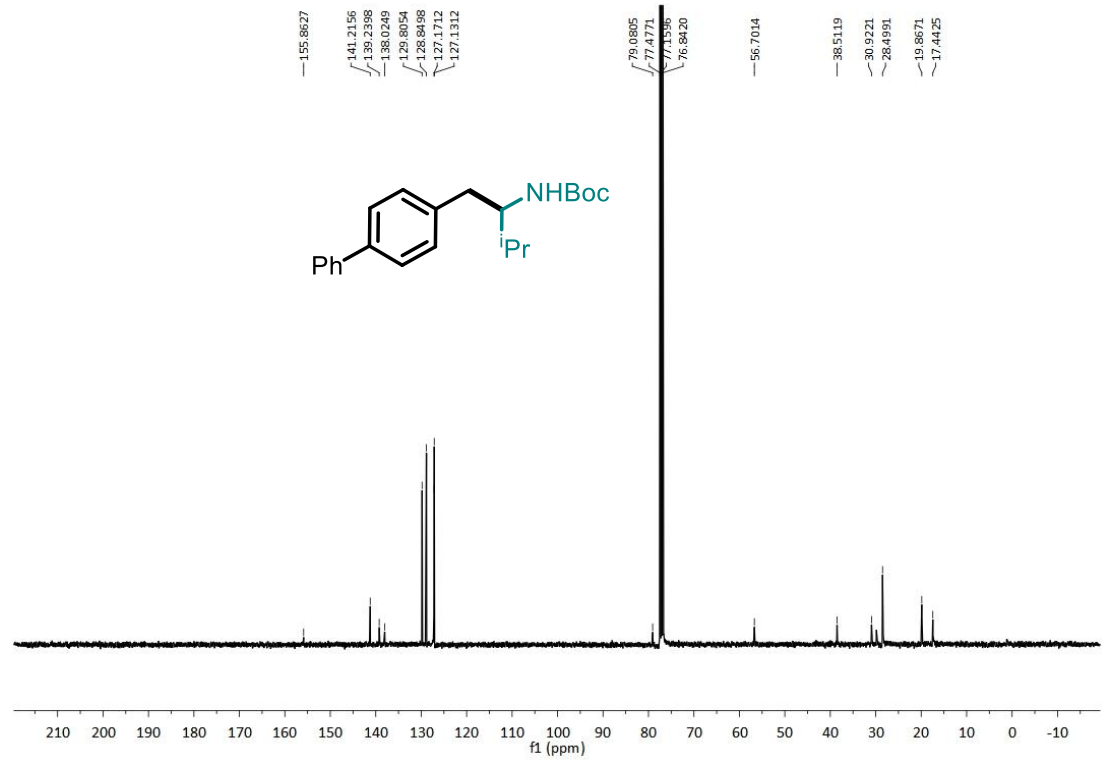
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **16**



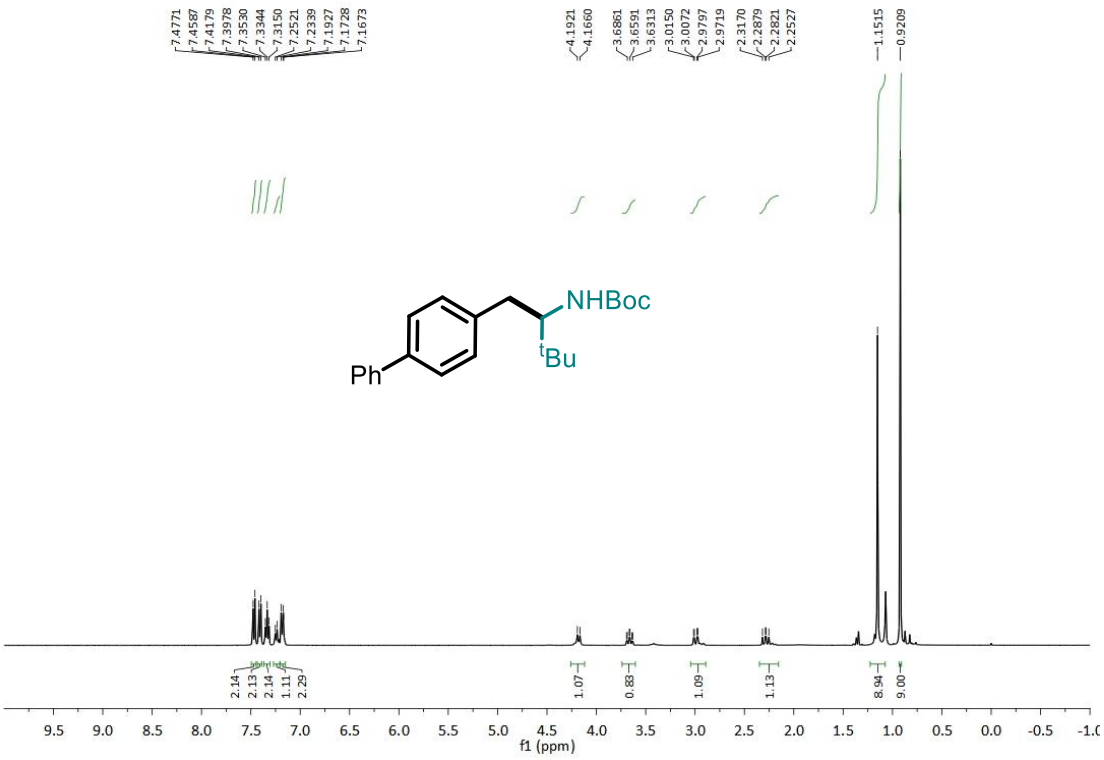
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **16**



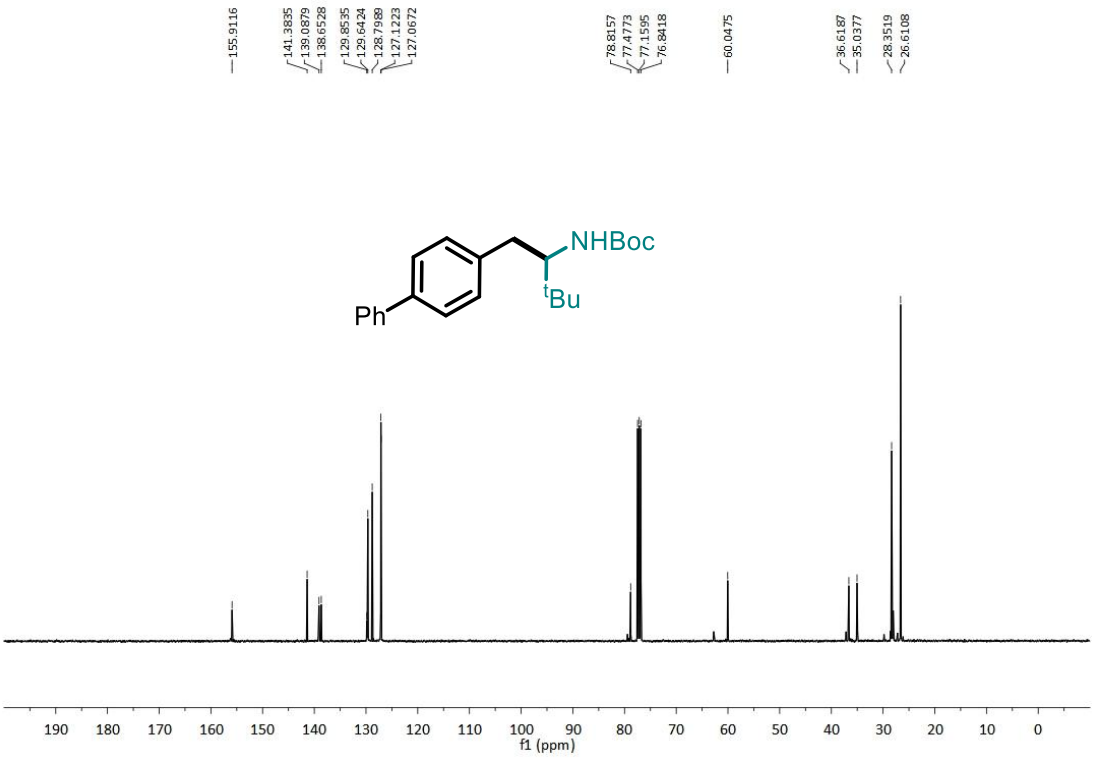
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **17**



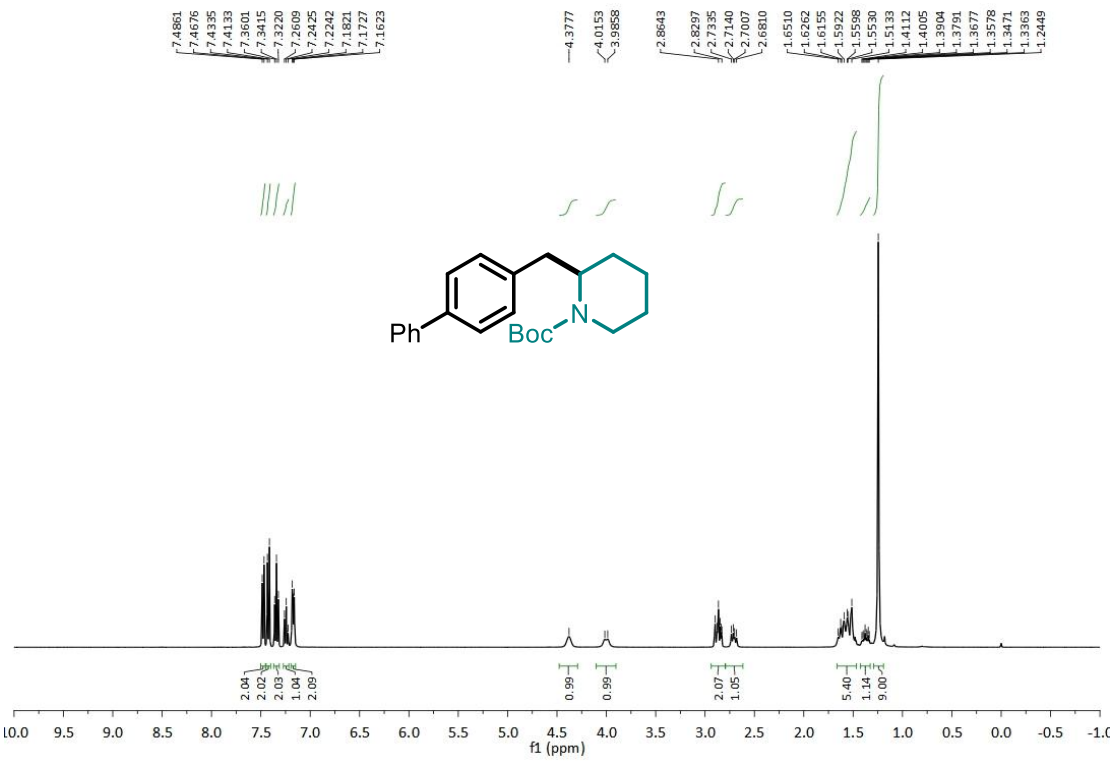
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **17**



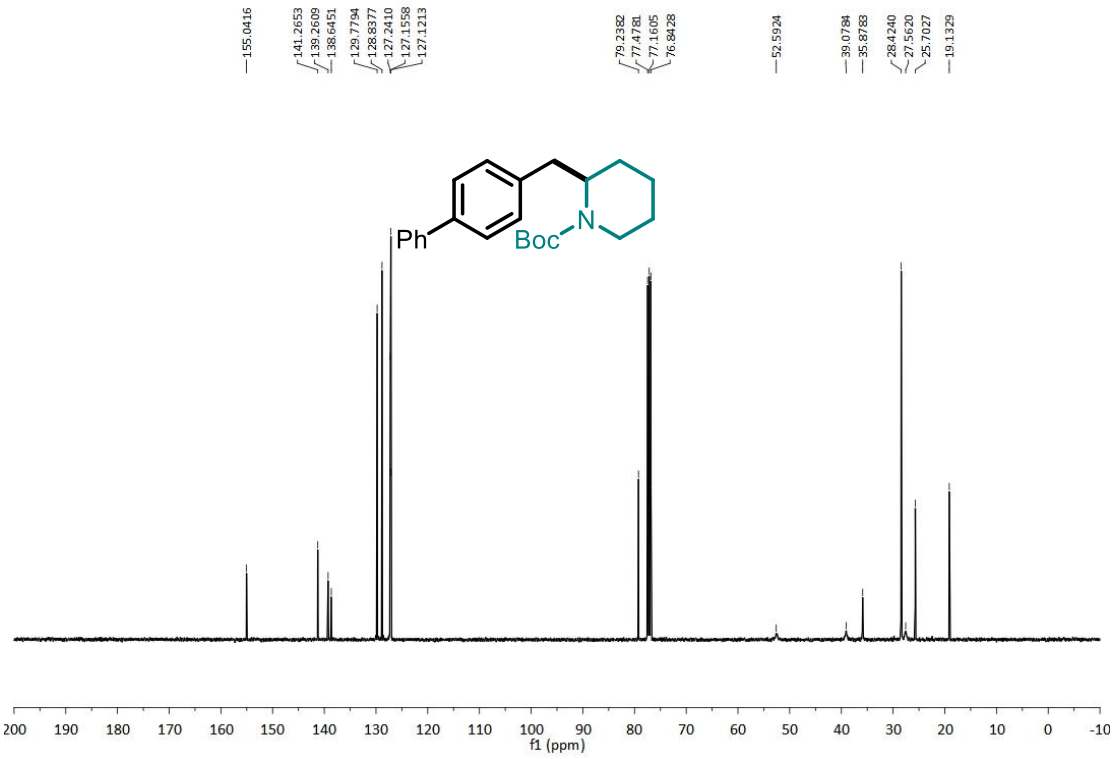
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **18**



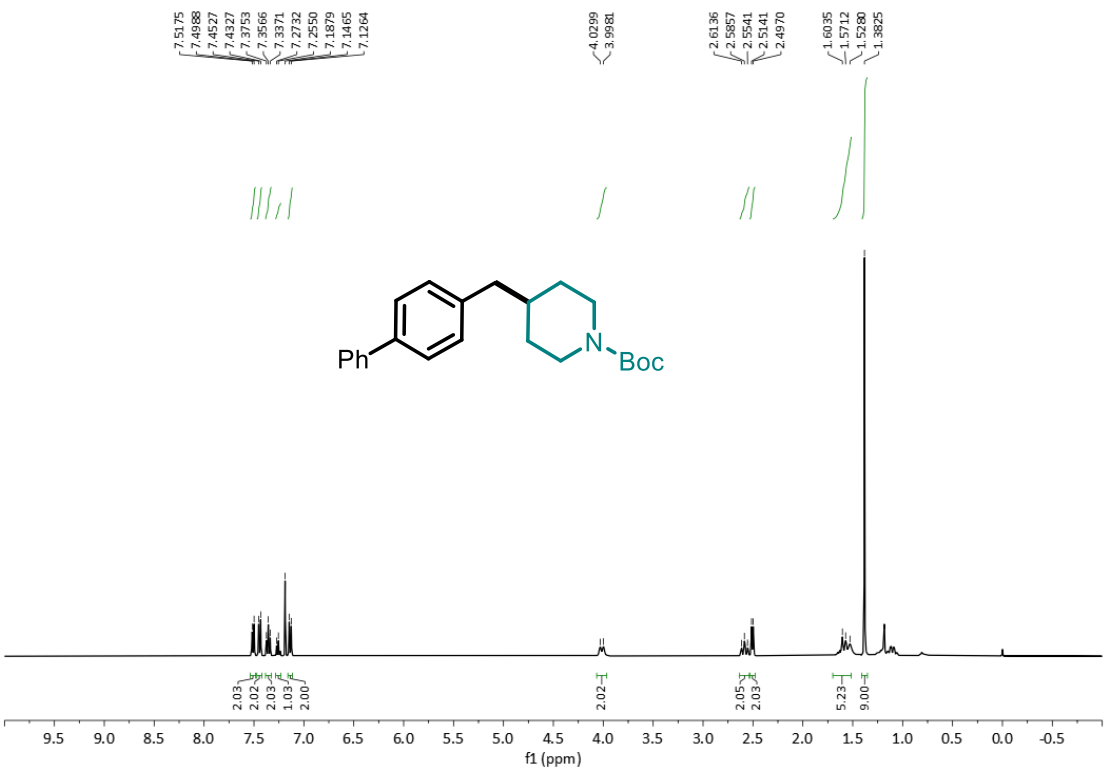
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **18**



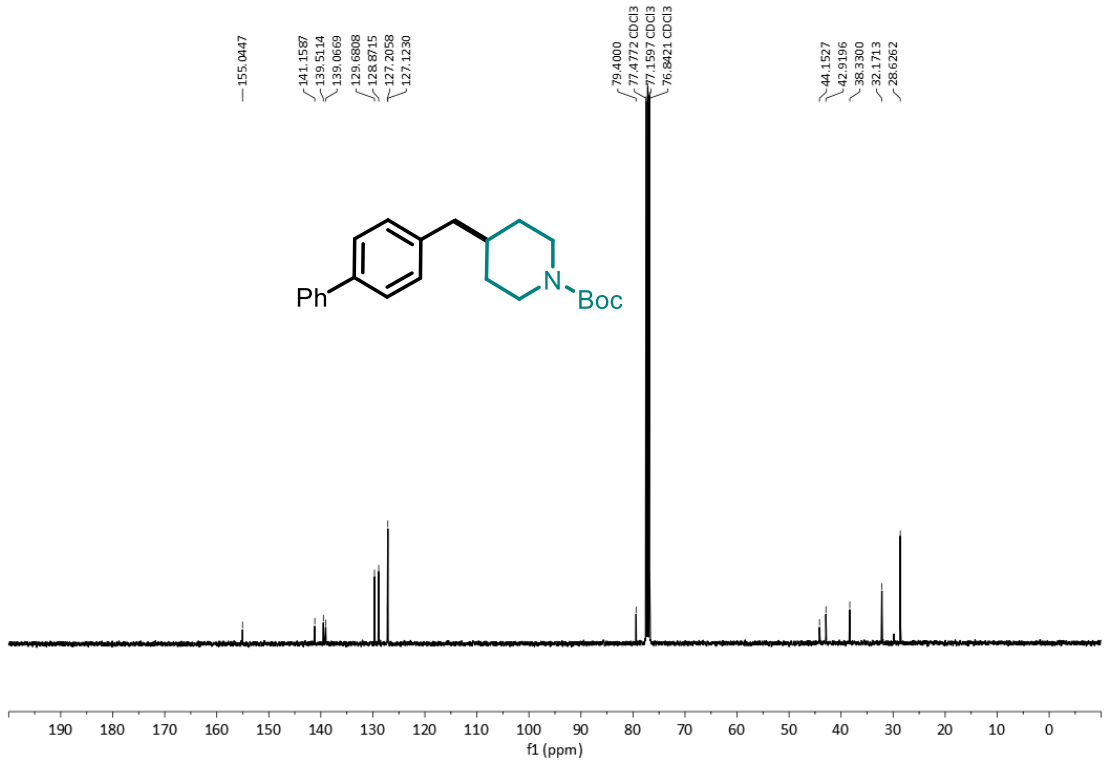
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **19**



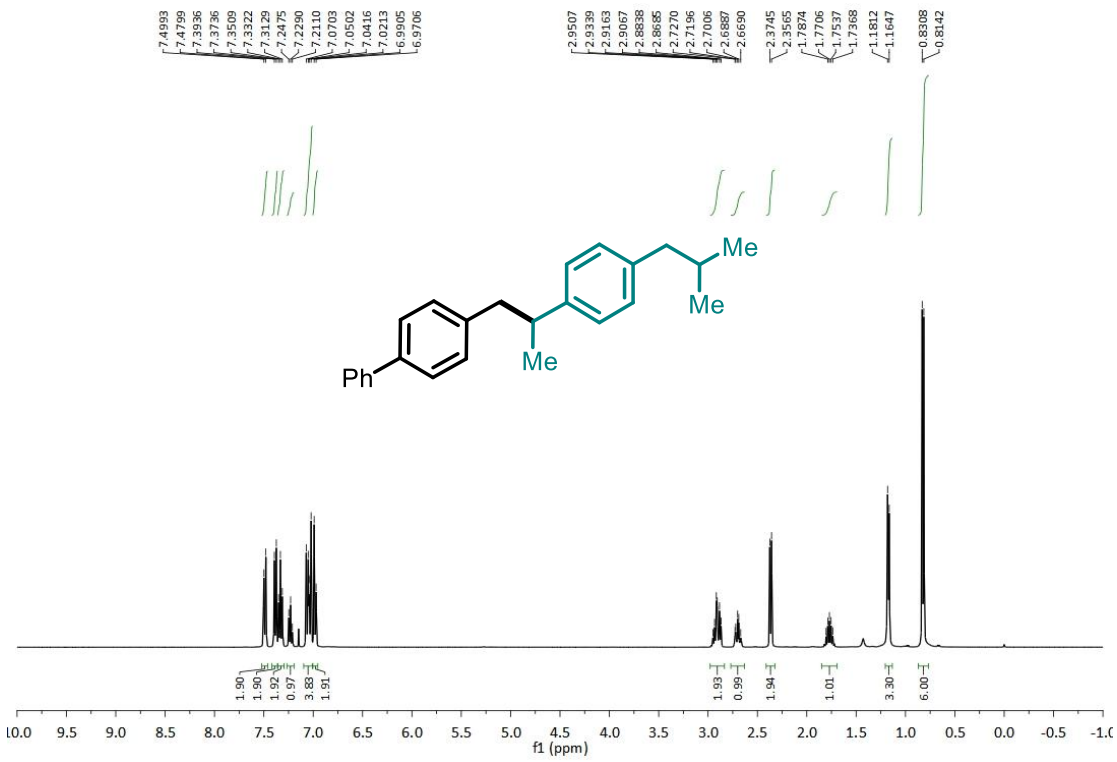
^{13}C NMR (100 MHz, CDC_{l3}) spectrum of compound **19**



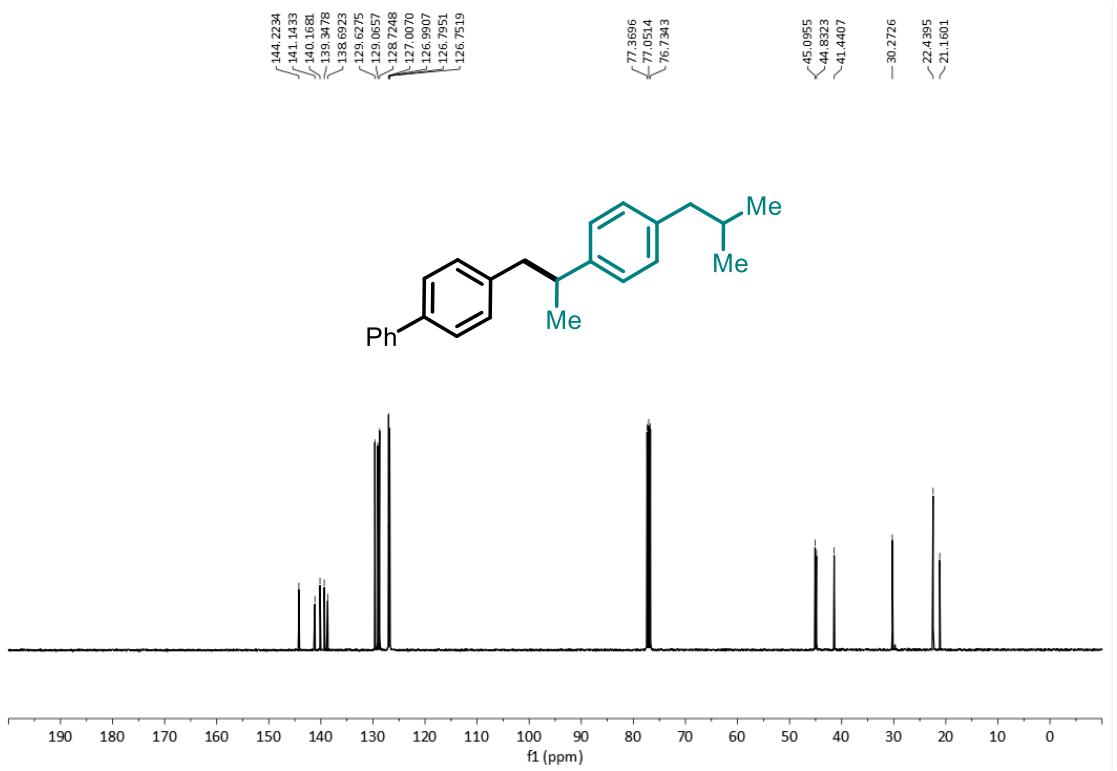
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **20**



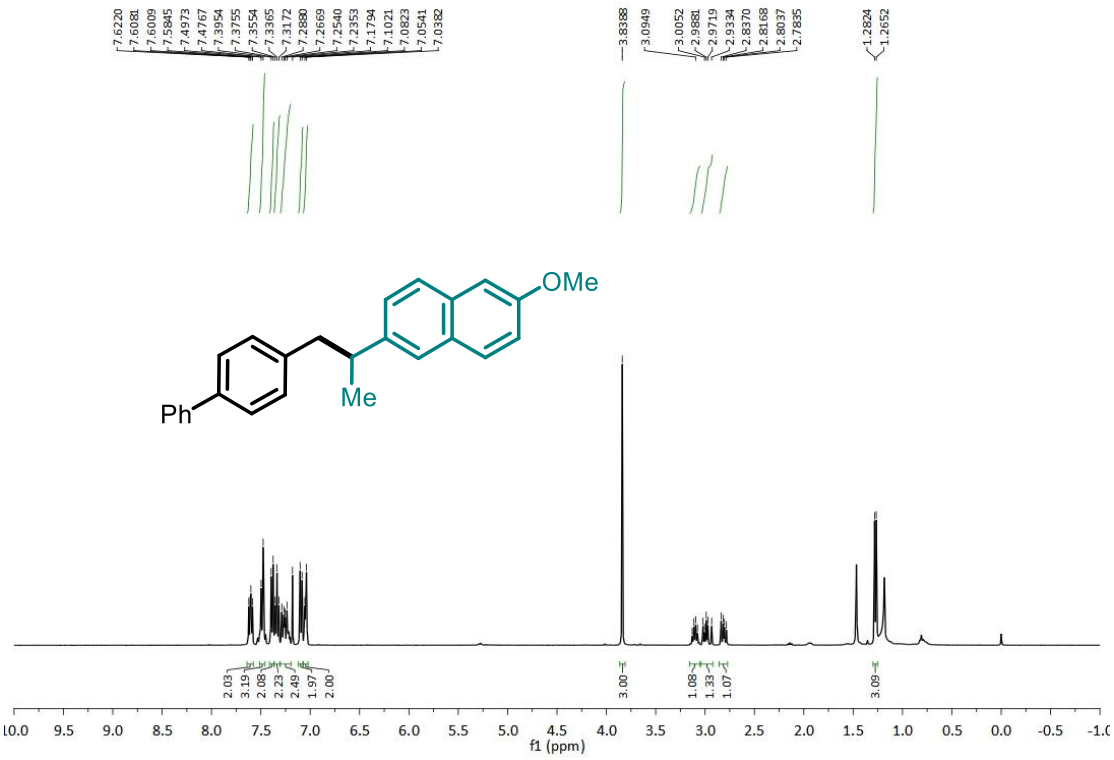
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **20**



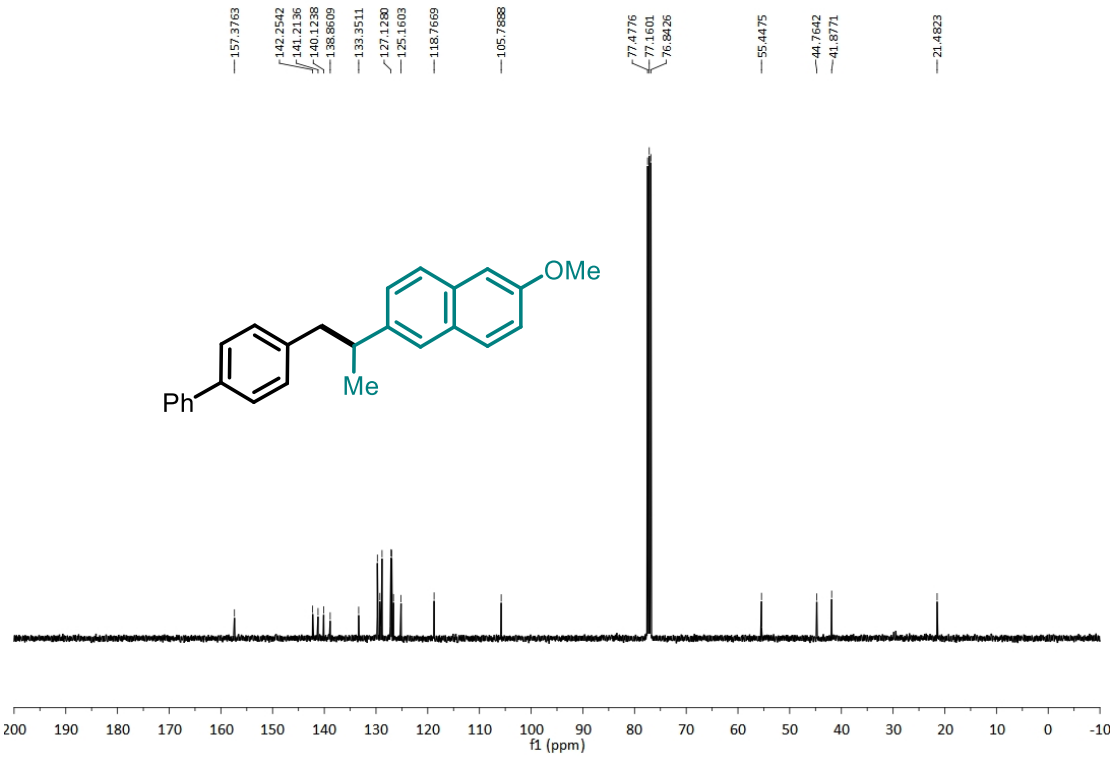
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **21**



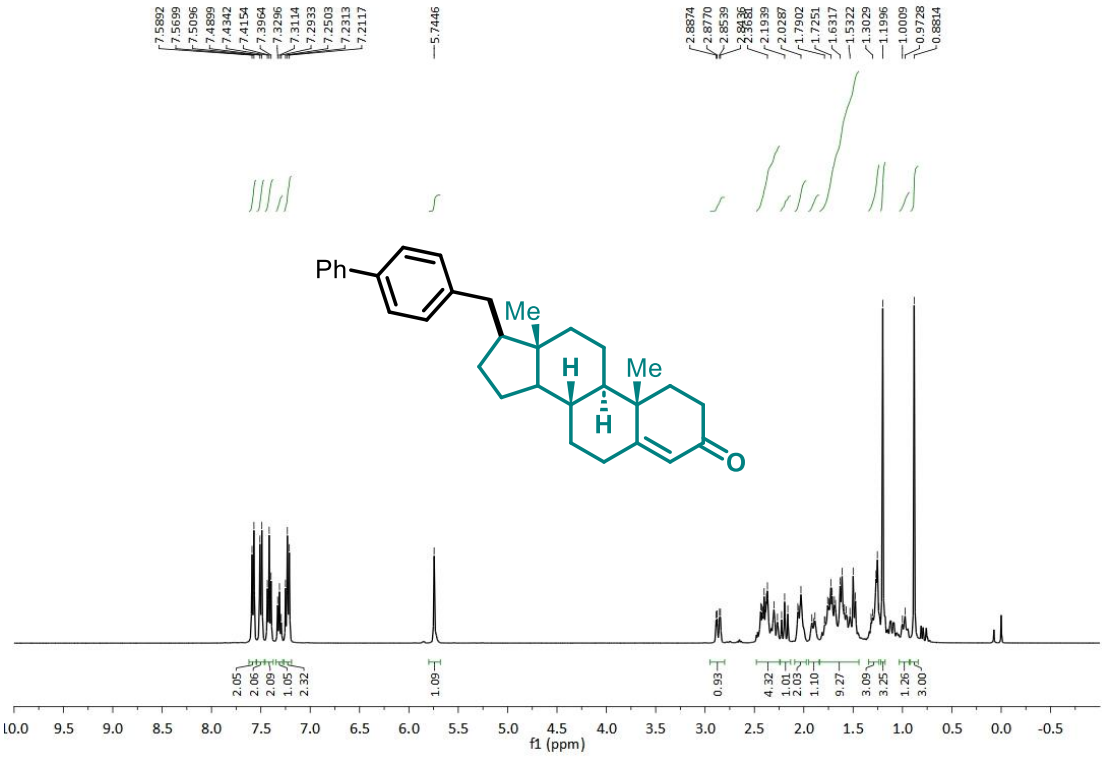
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **21**



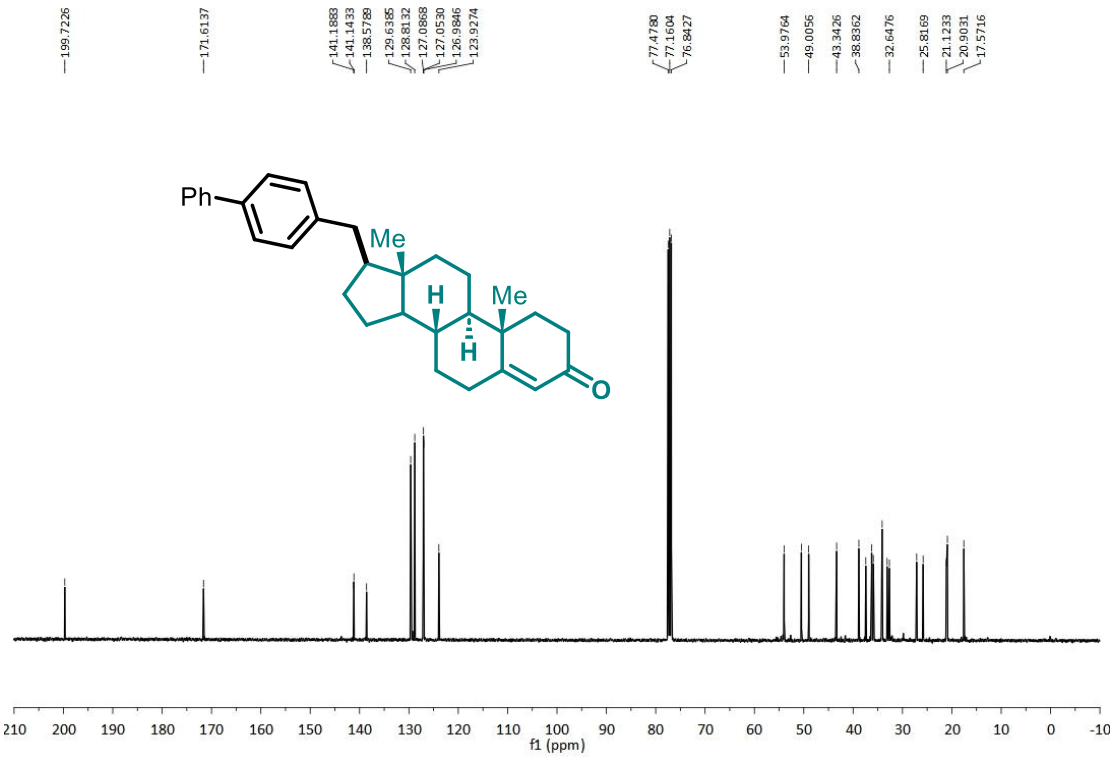
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **22**



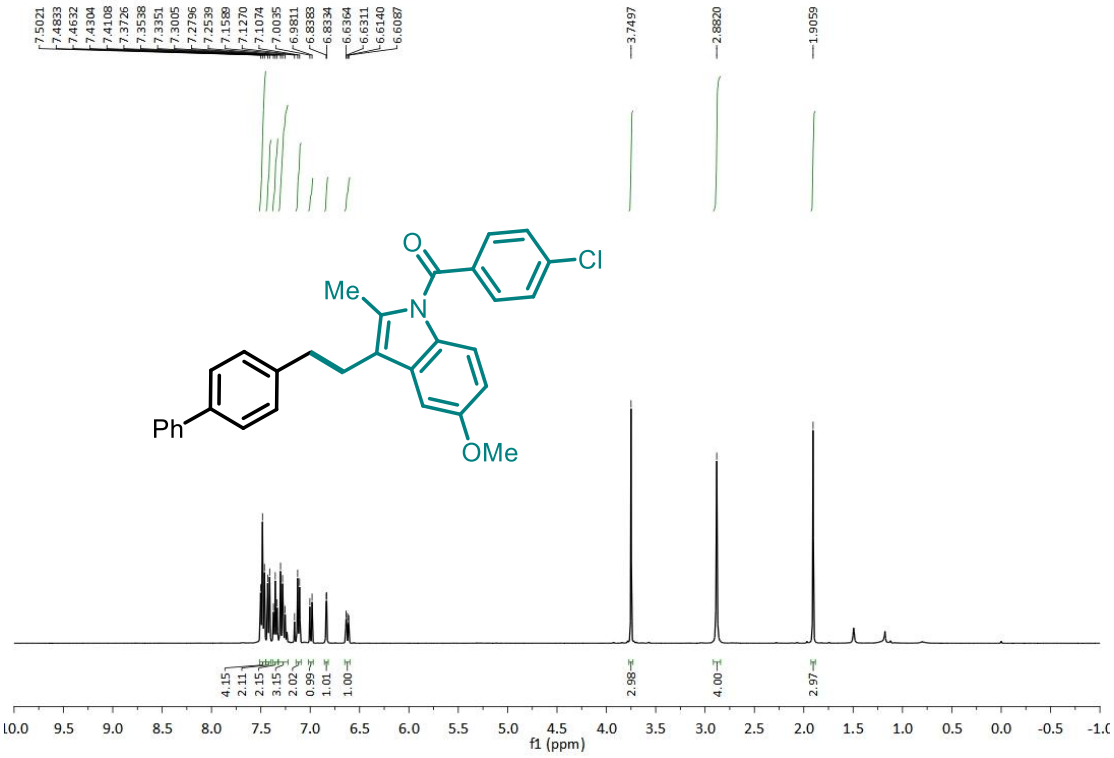
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **22**



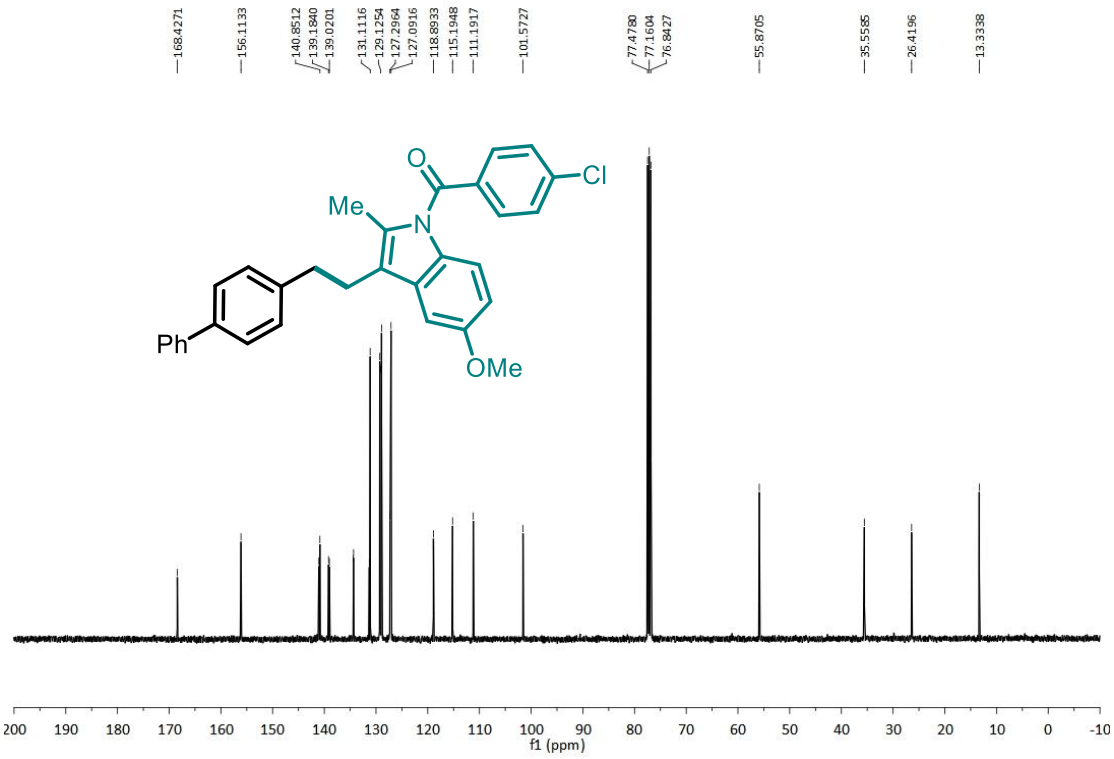
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **23**



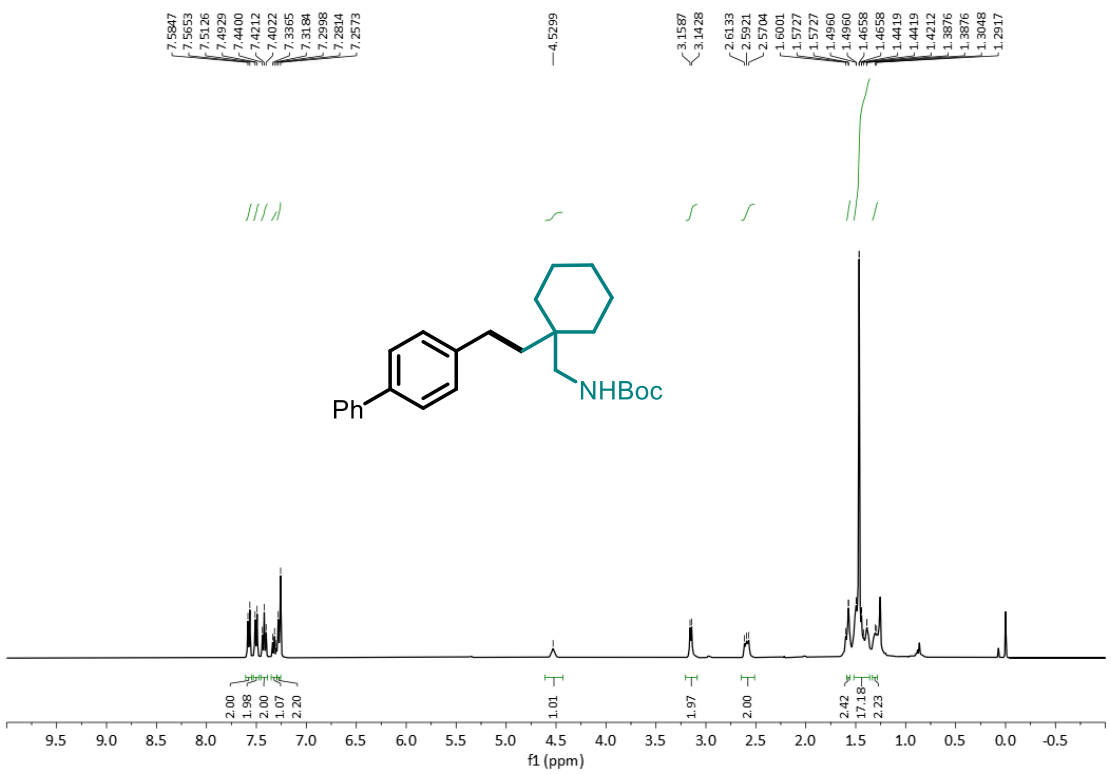
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **23**



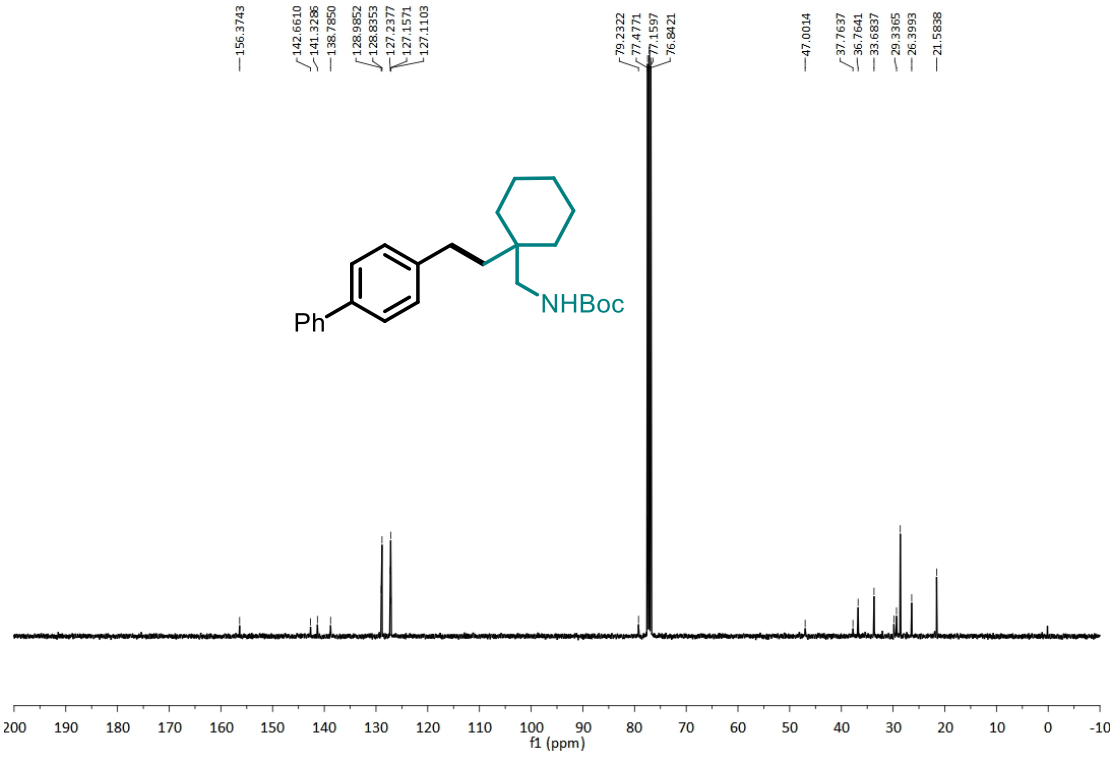
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **24**



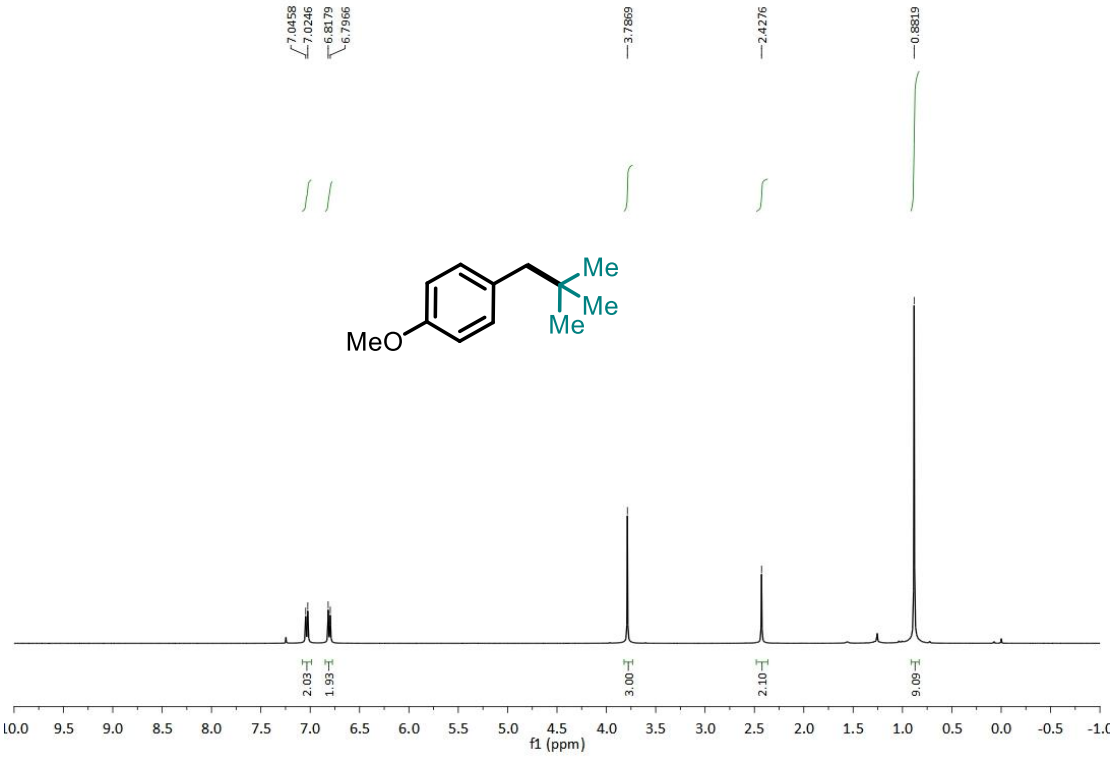
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **24**



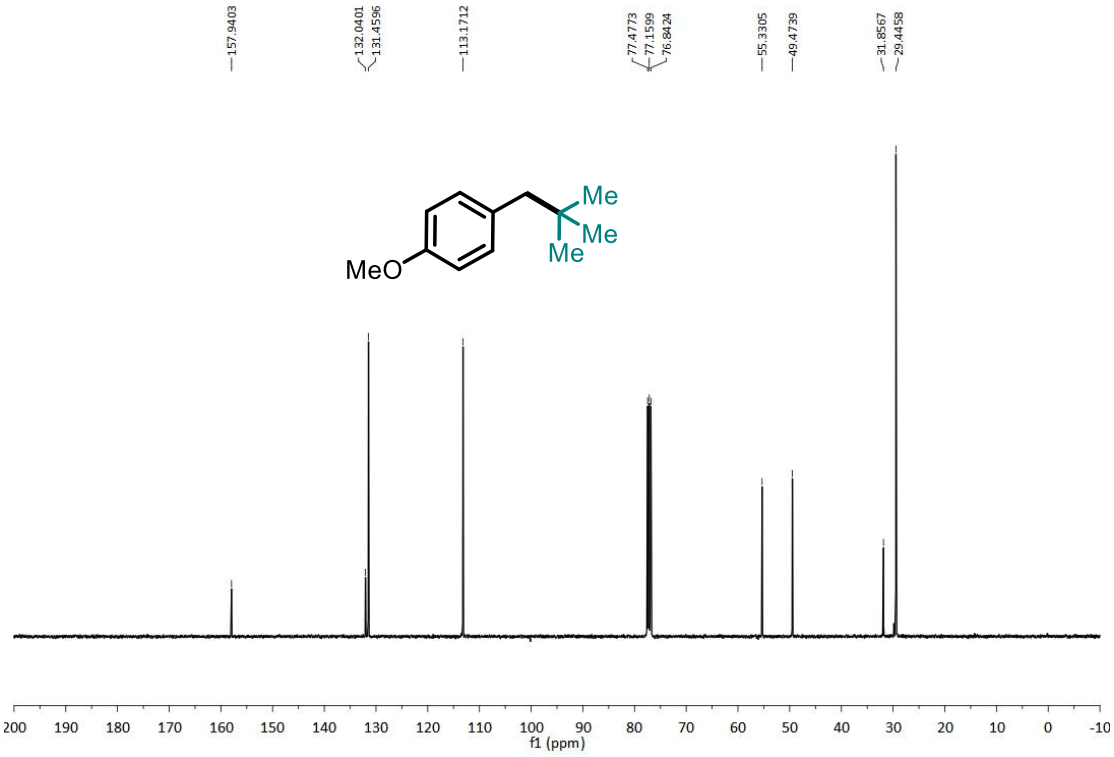
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **25**



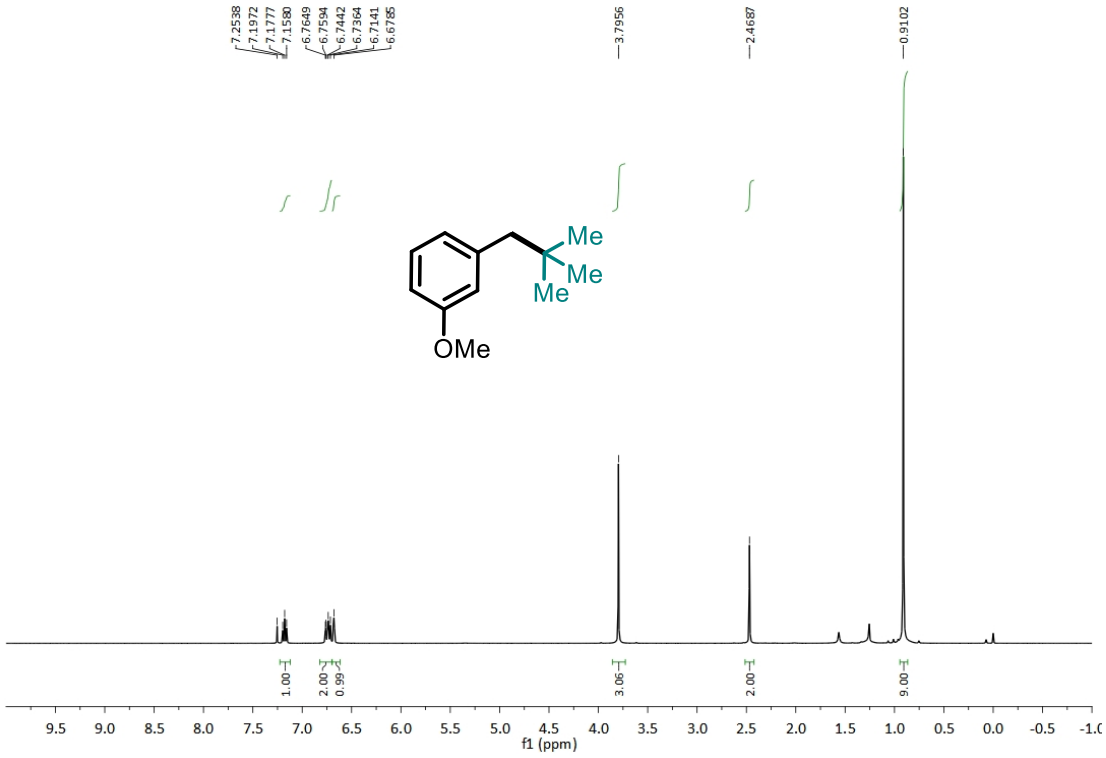
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **25**



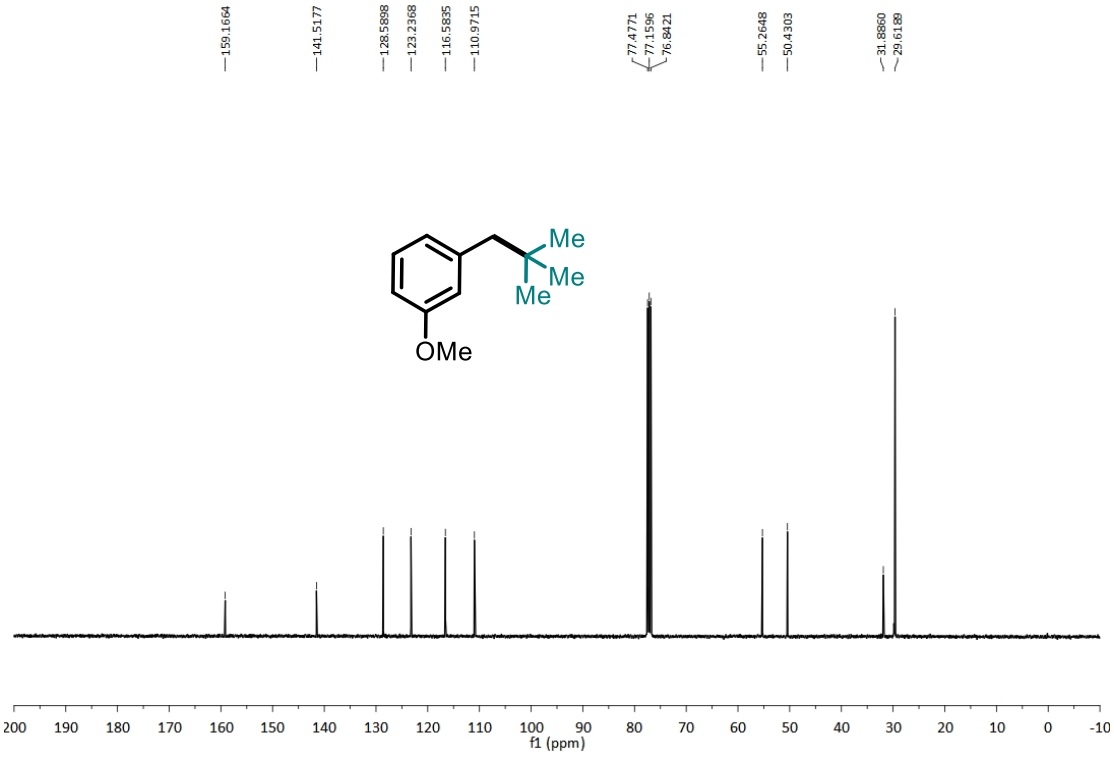
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **26**



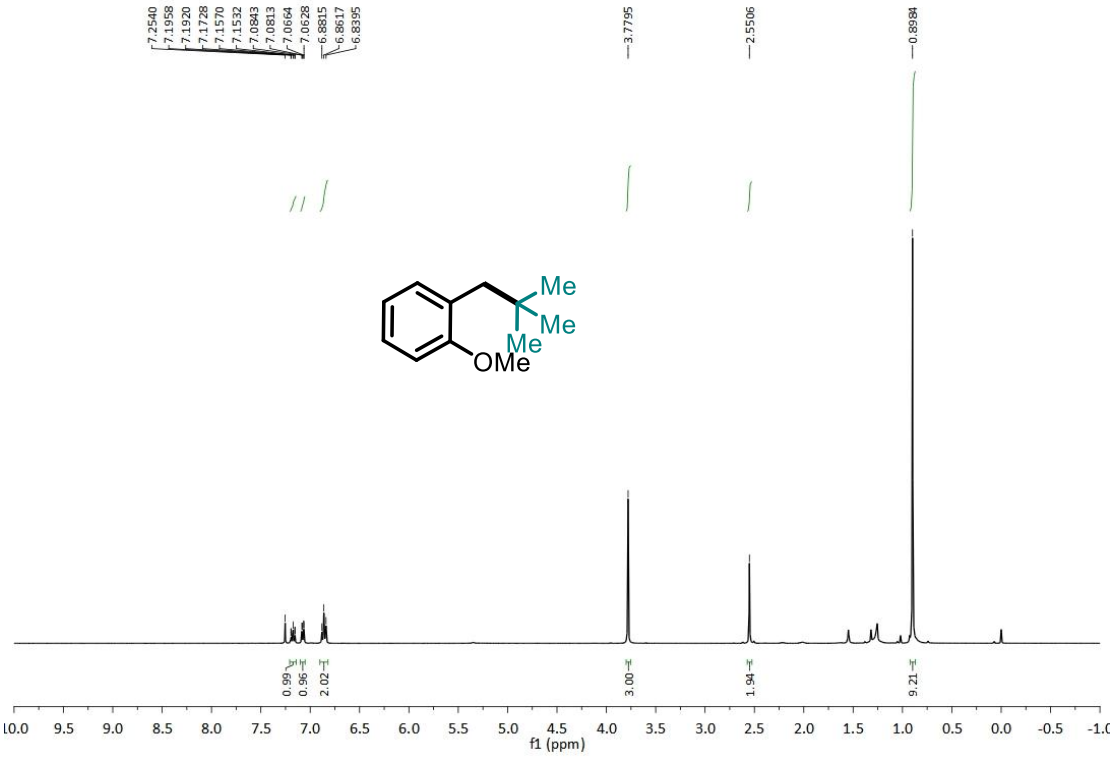
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **26**



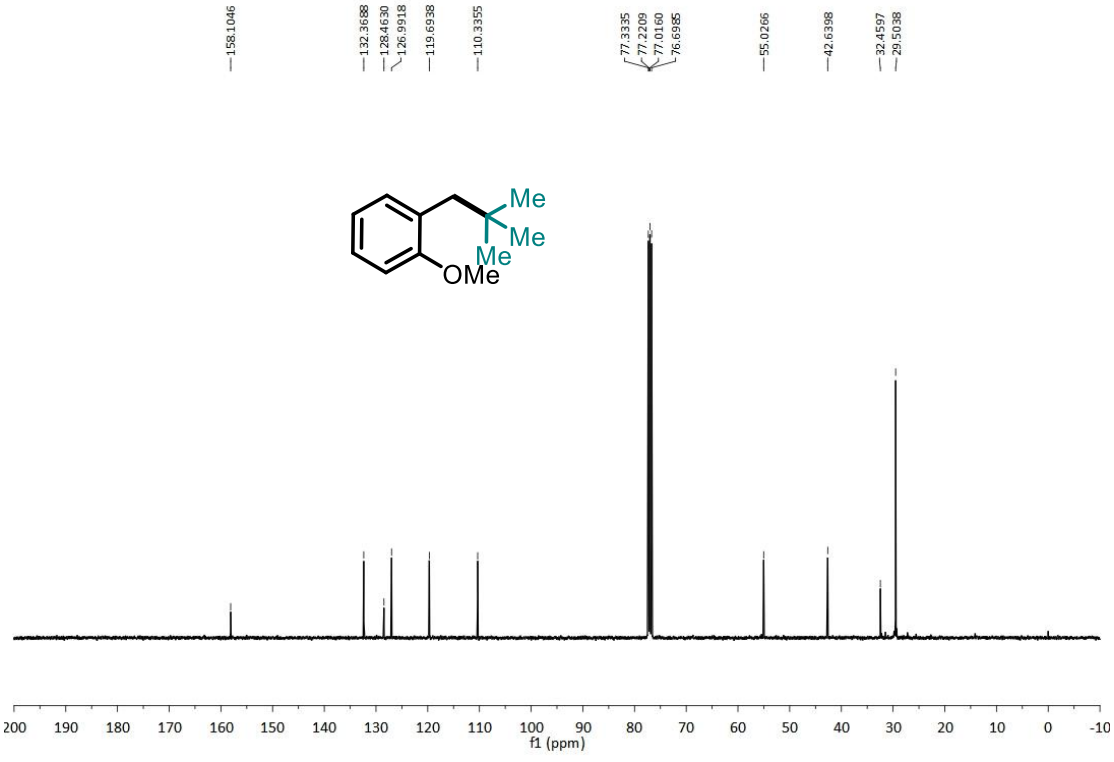
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **27**



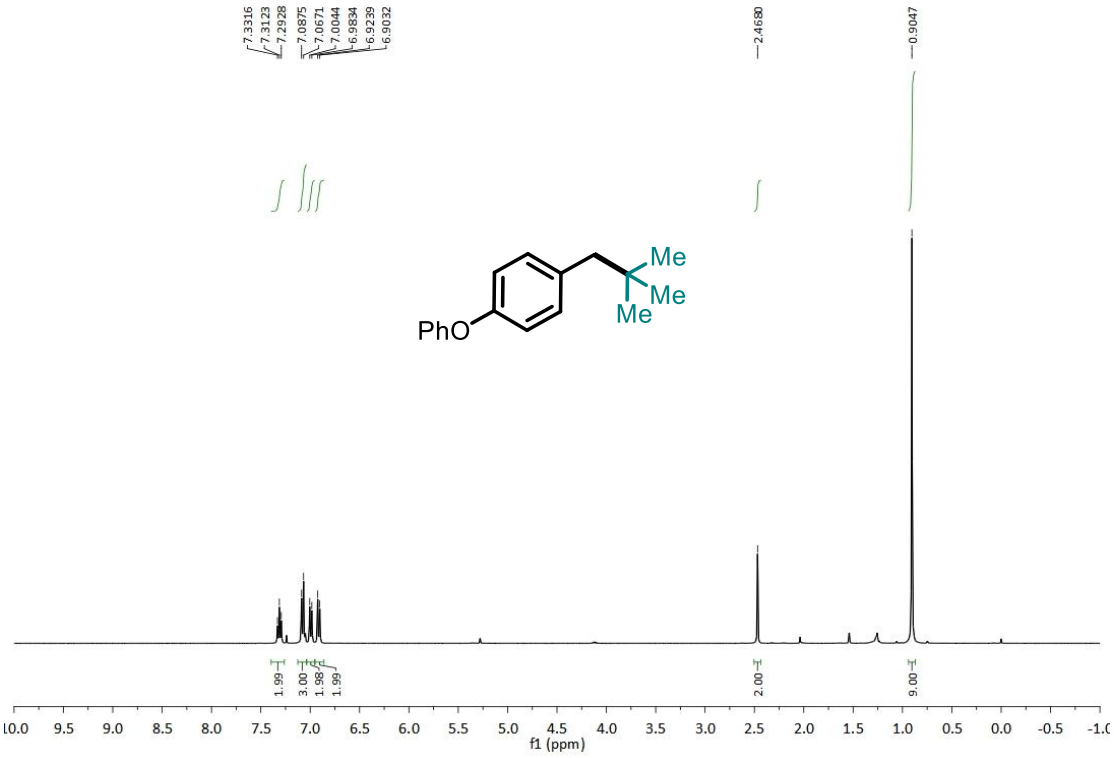
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **27**



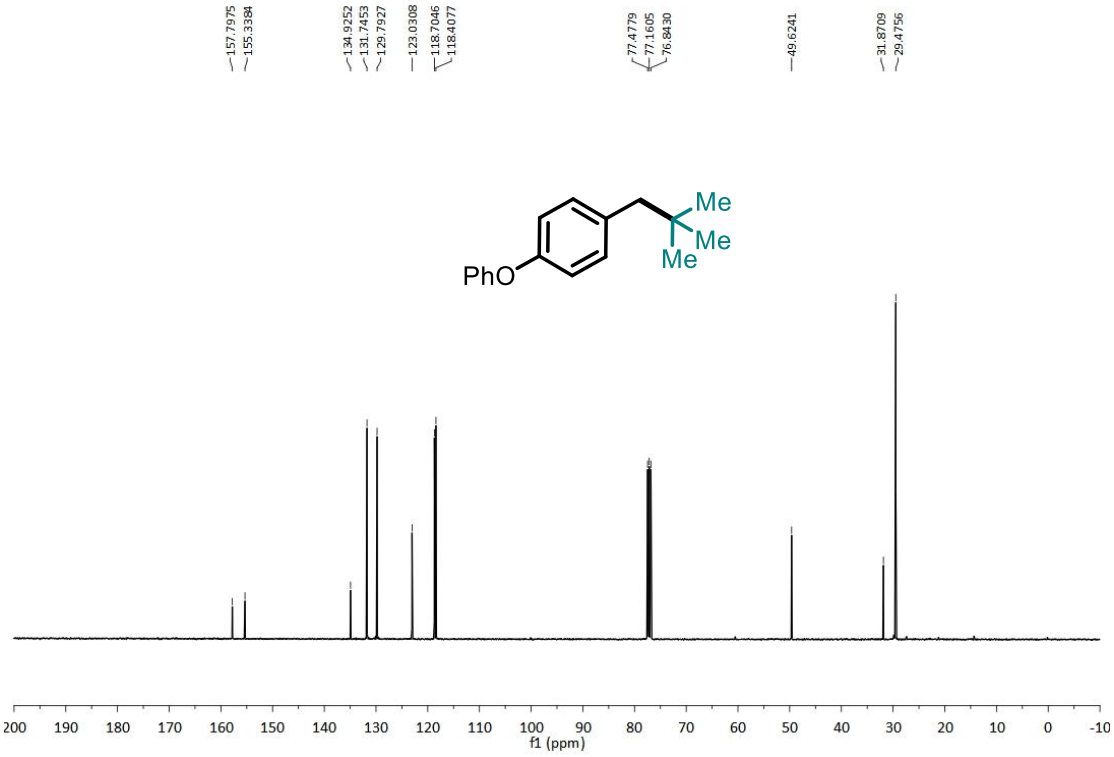
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **28**



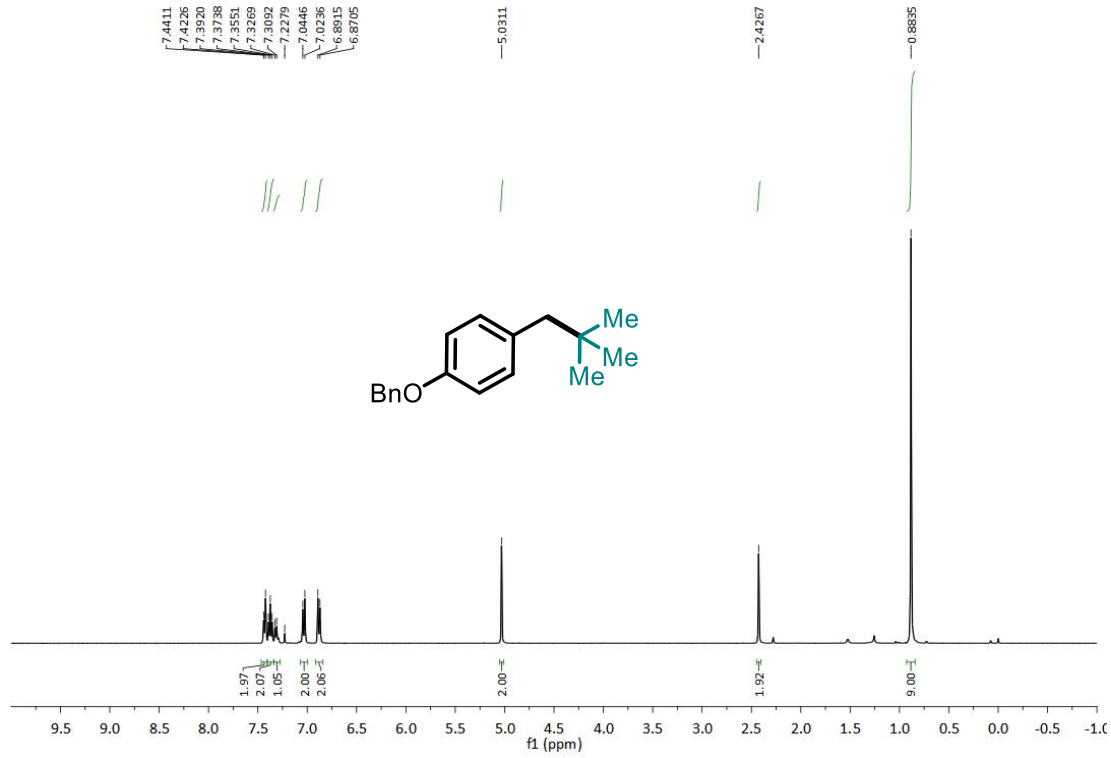
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **28**



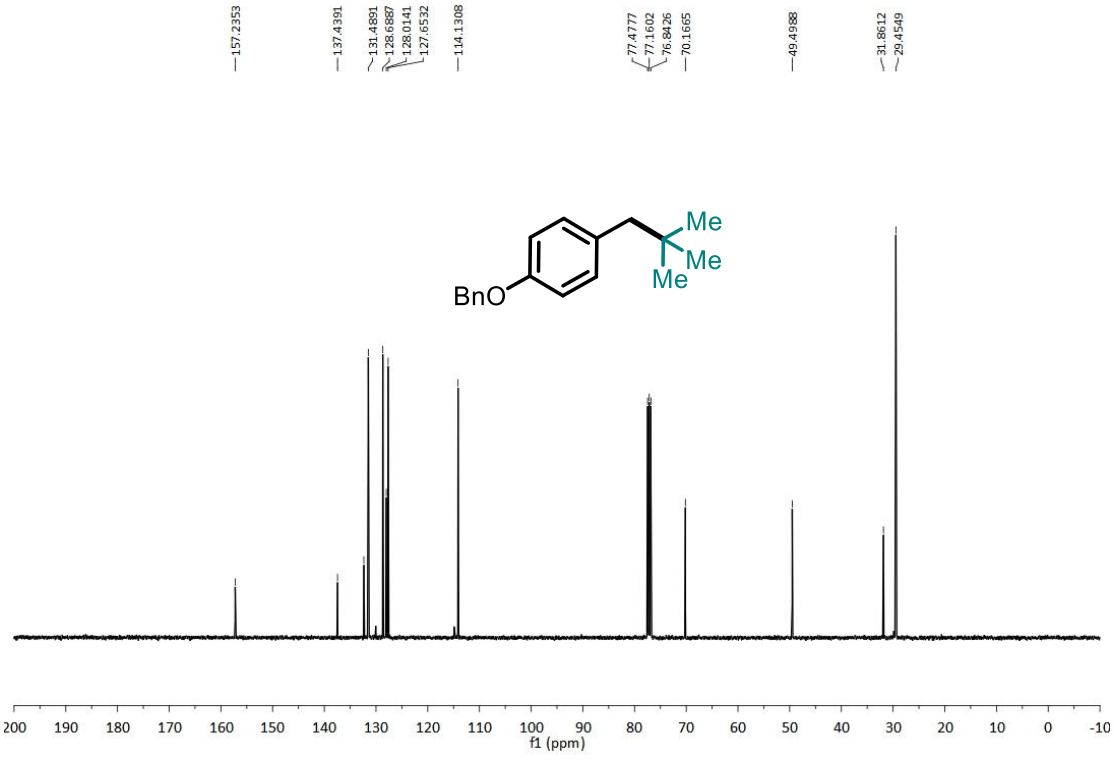
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **29**



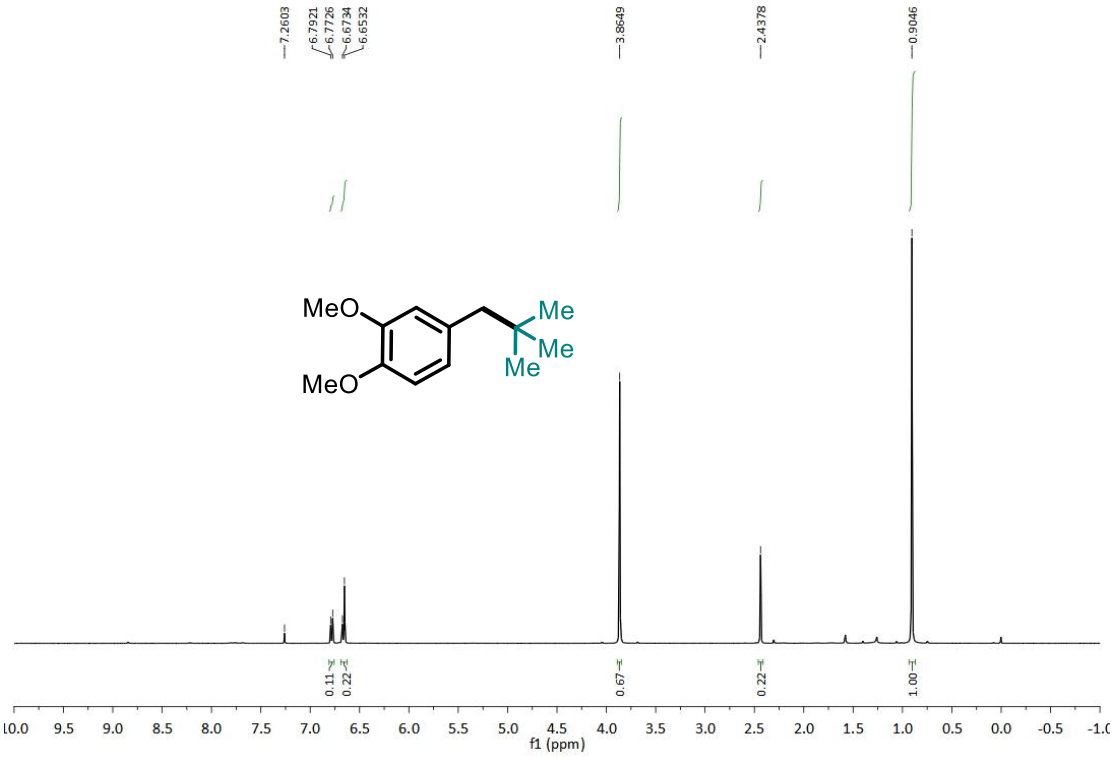
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **29**



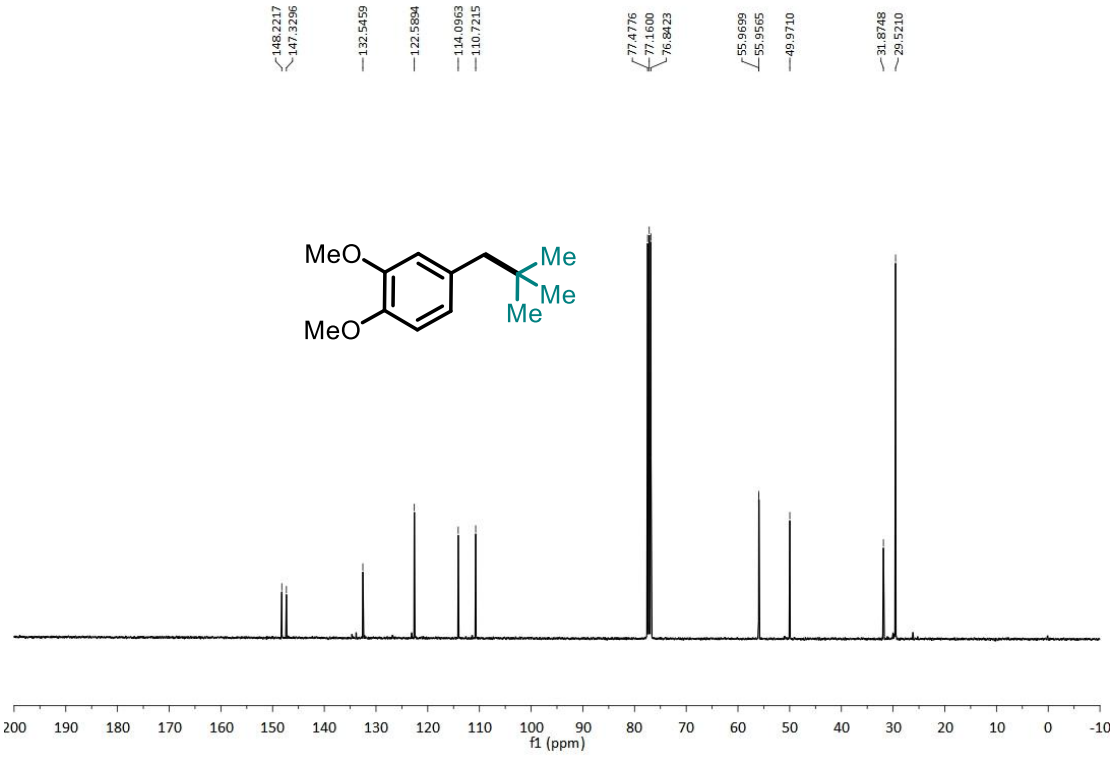
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **30**



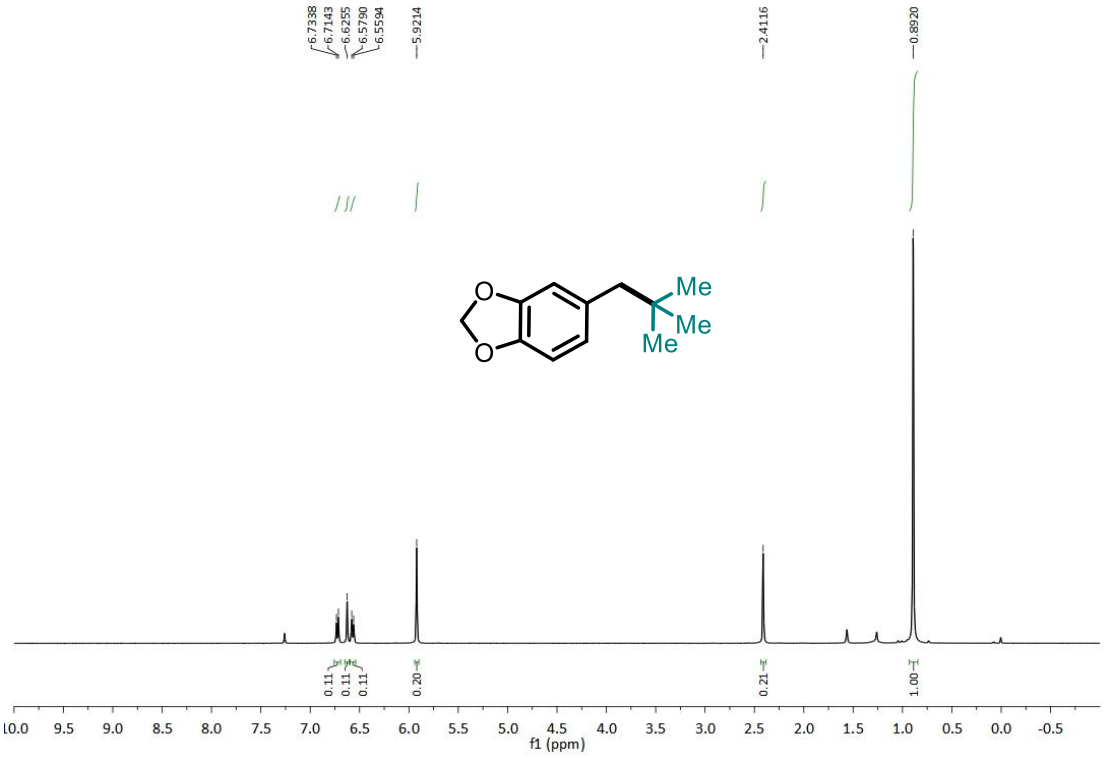
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **30**



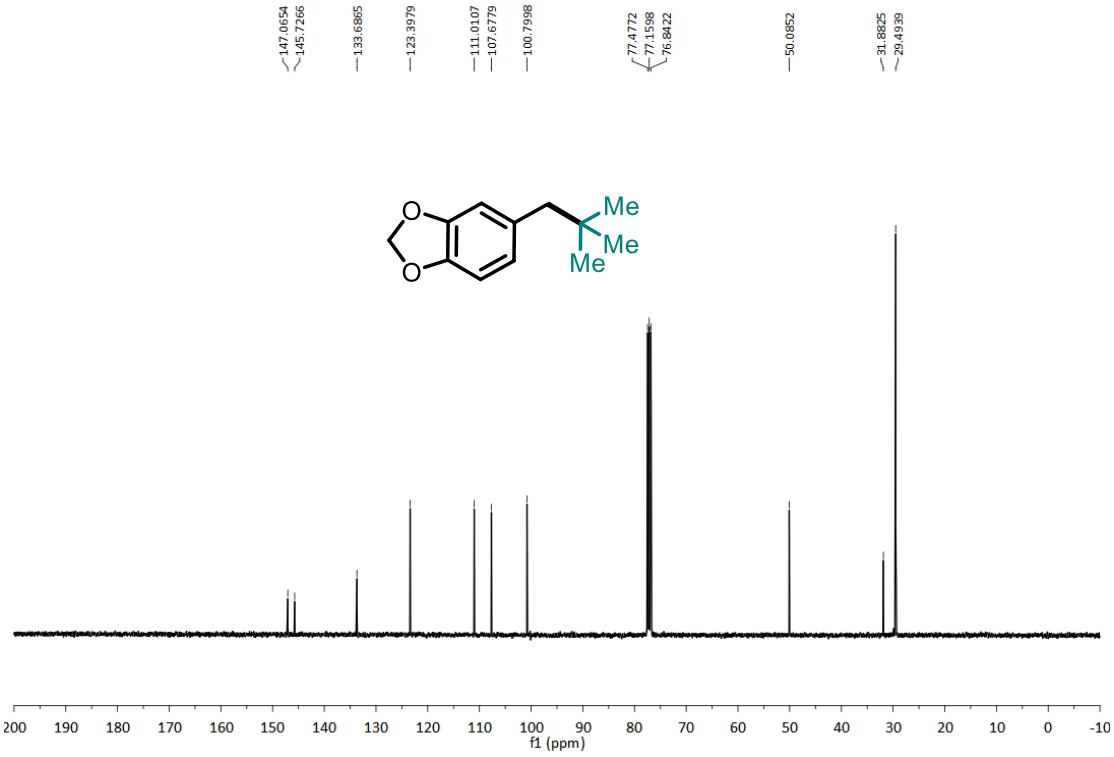
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **30**



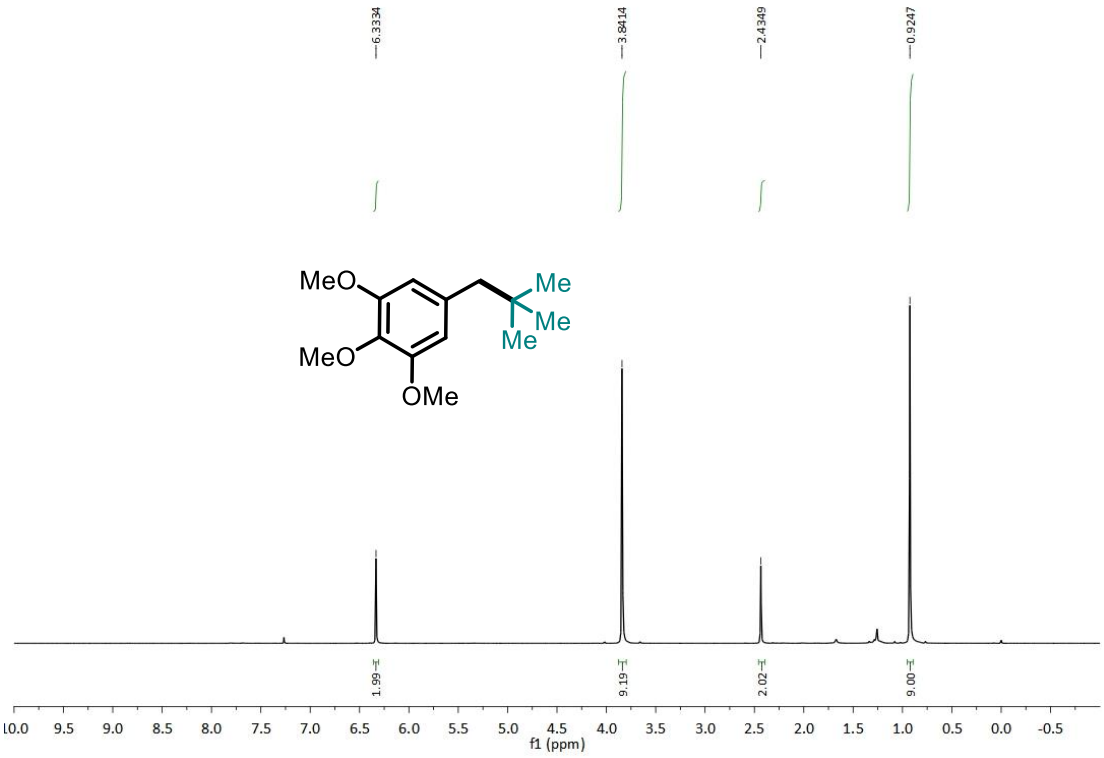
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **31**



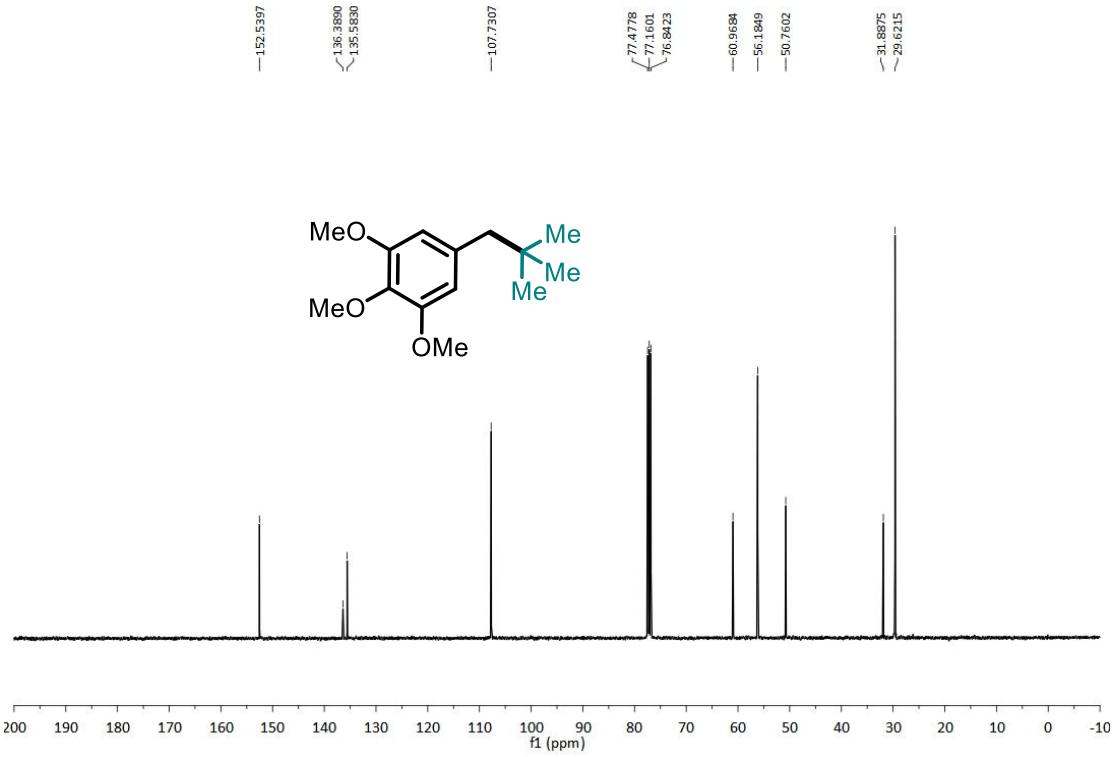
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **32**



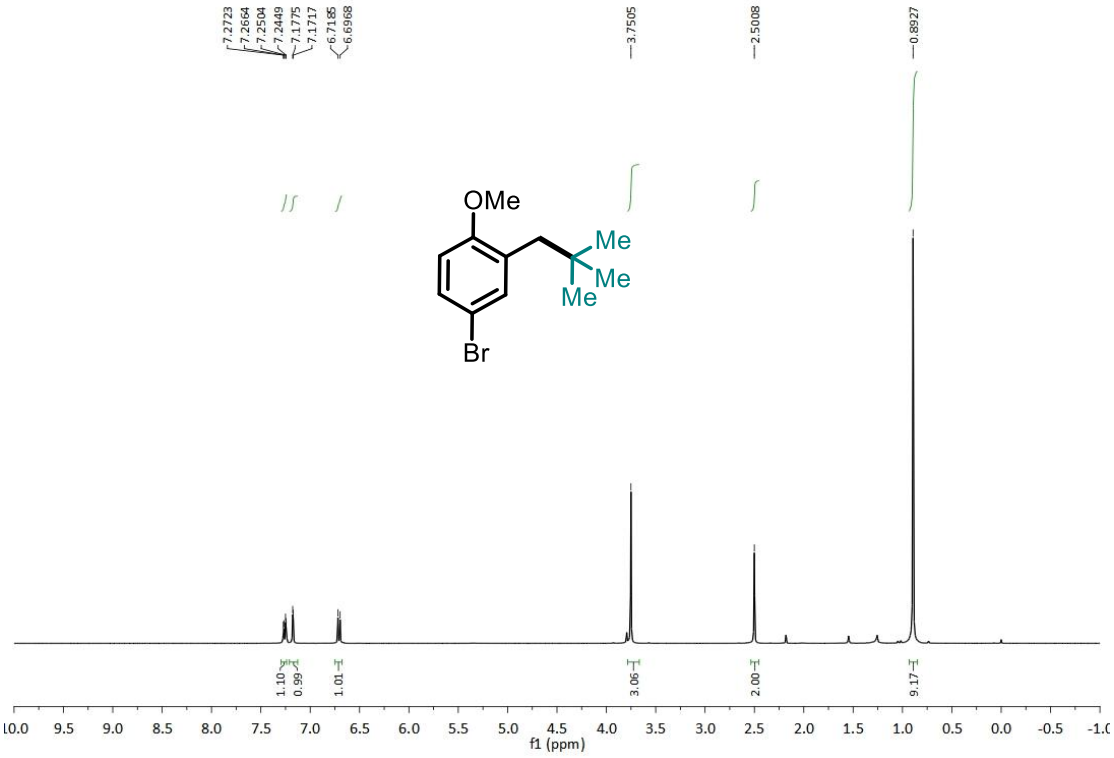
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **32**



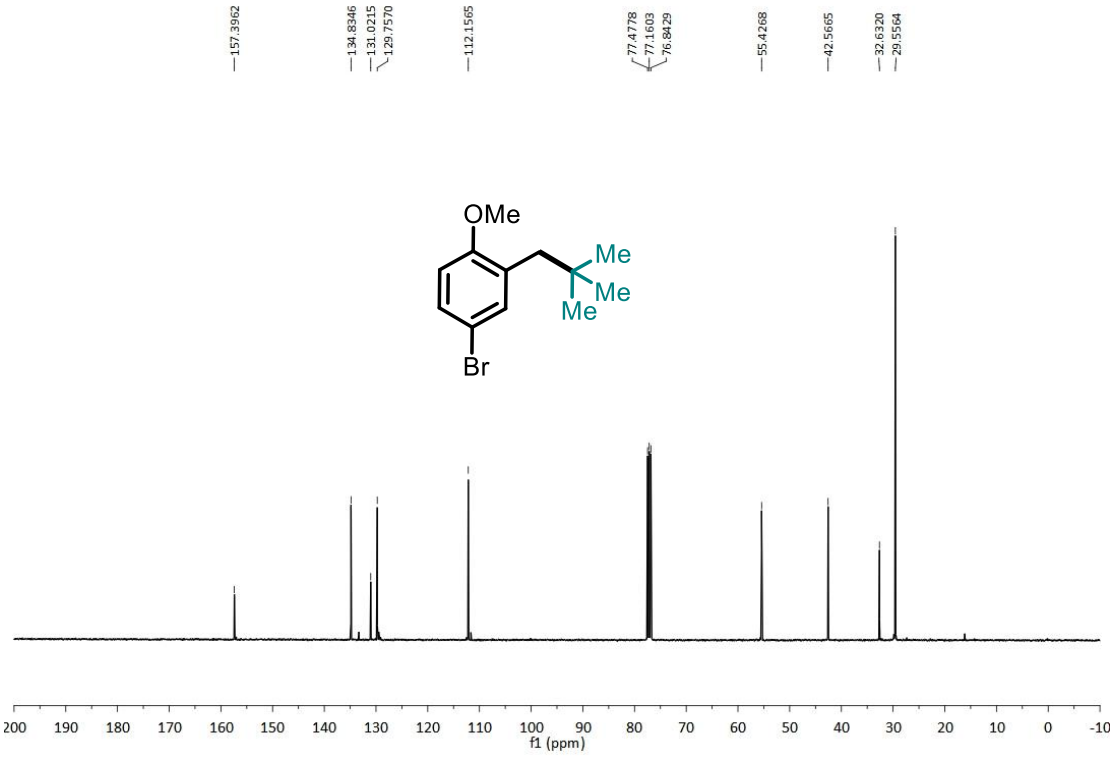
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **33**



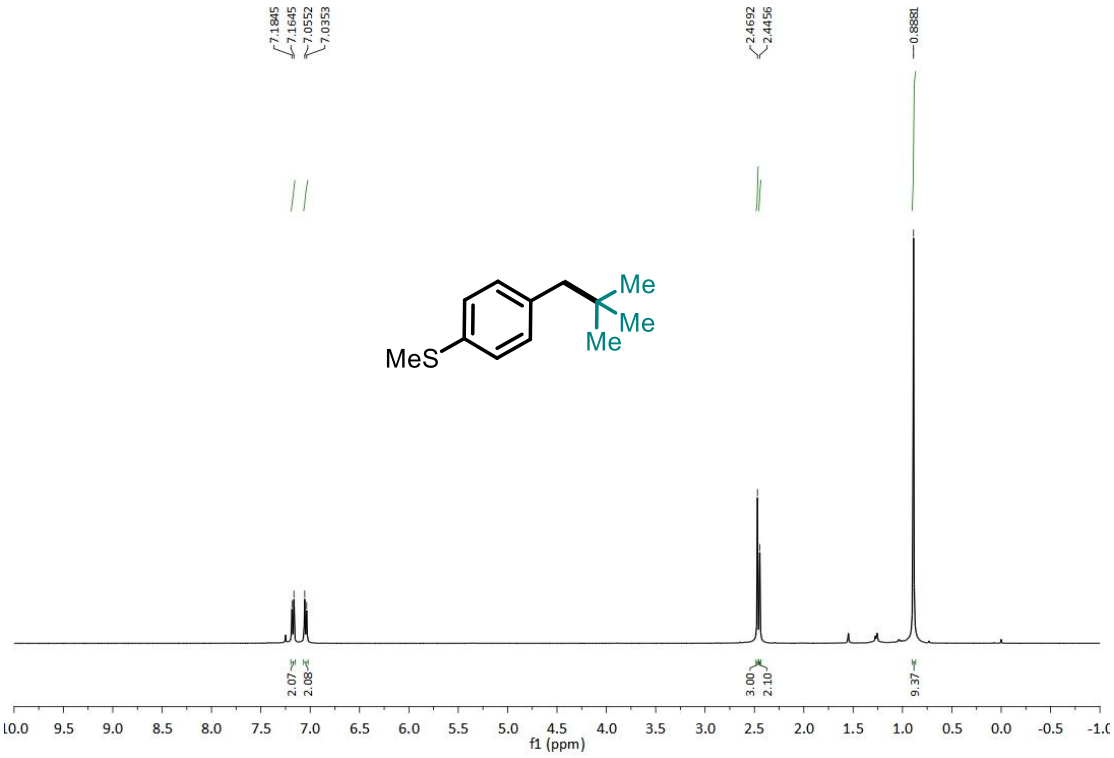
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **33**



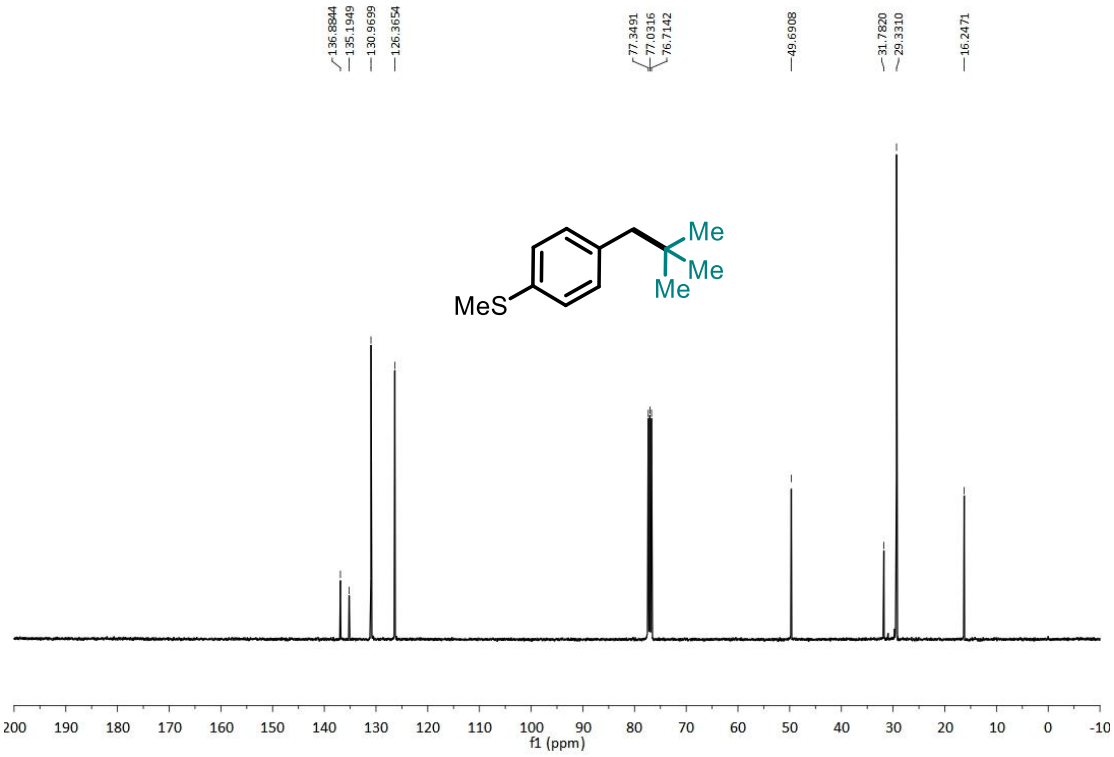
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **34**



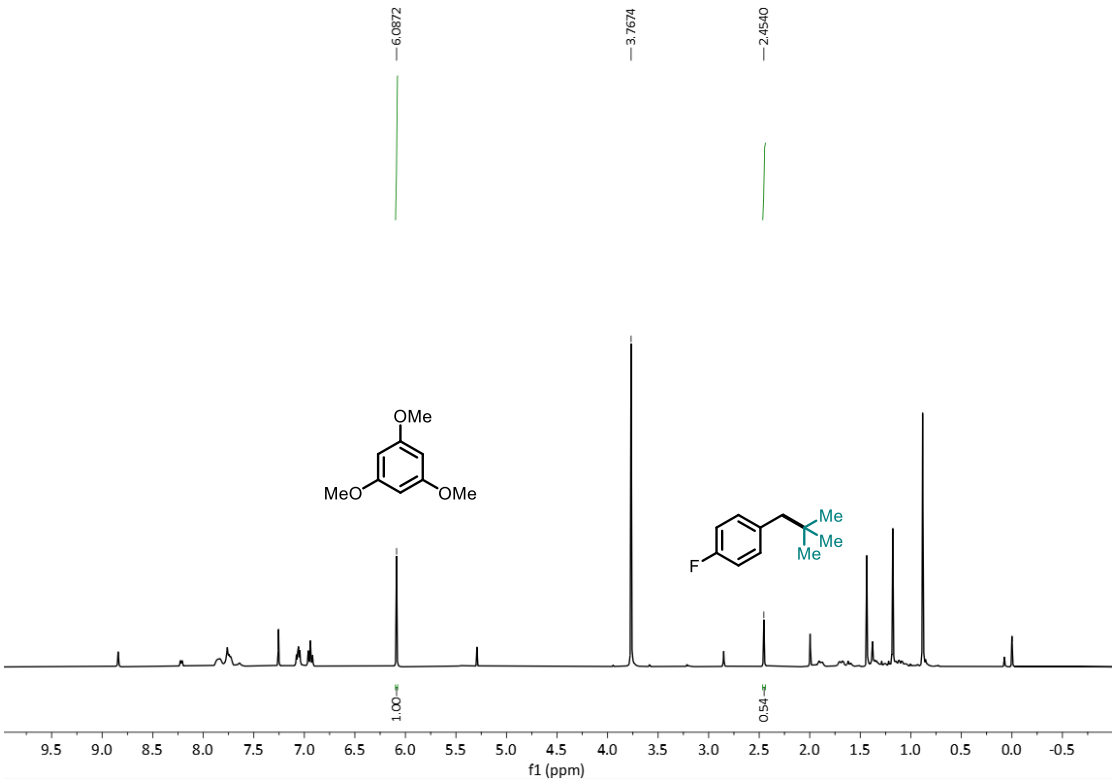
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **34**



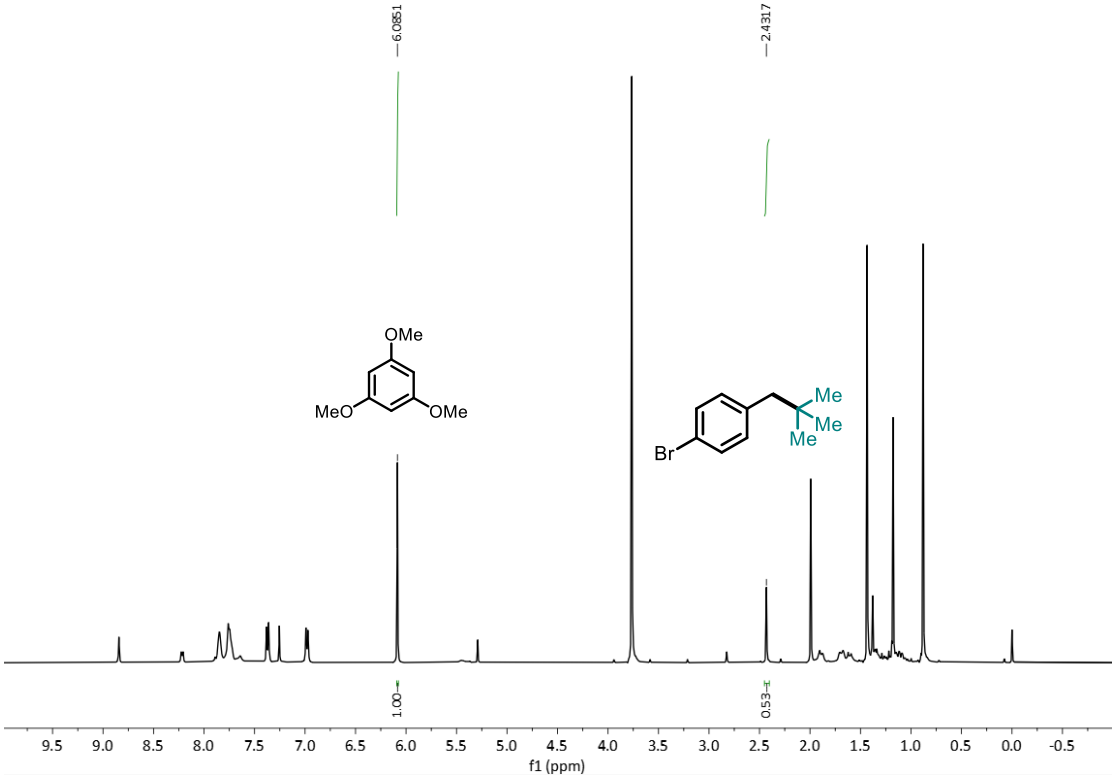
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **35**



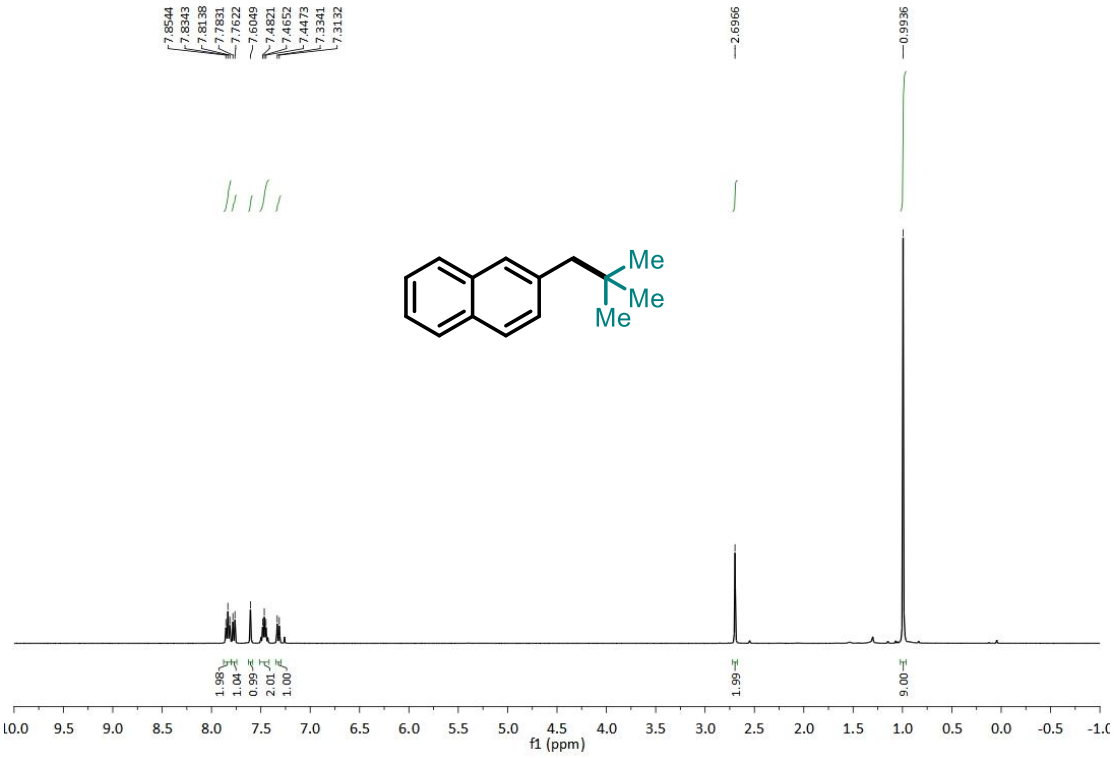
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **35**



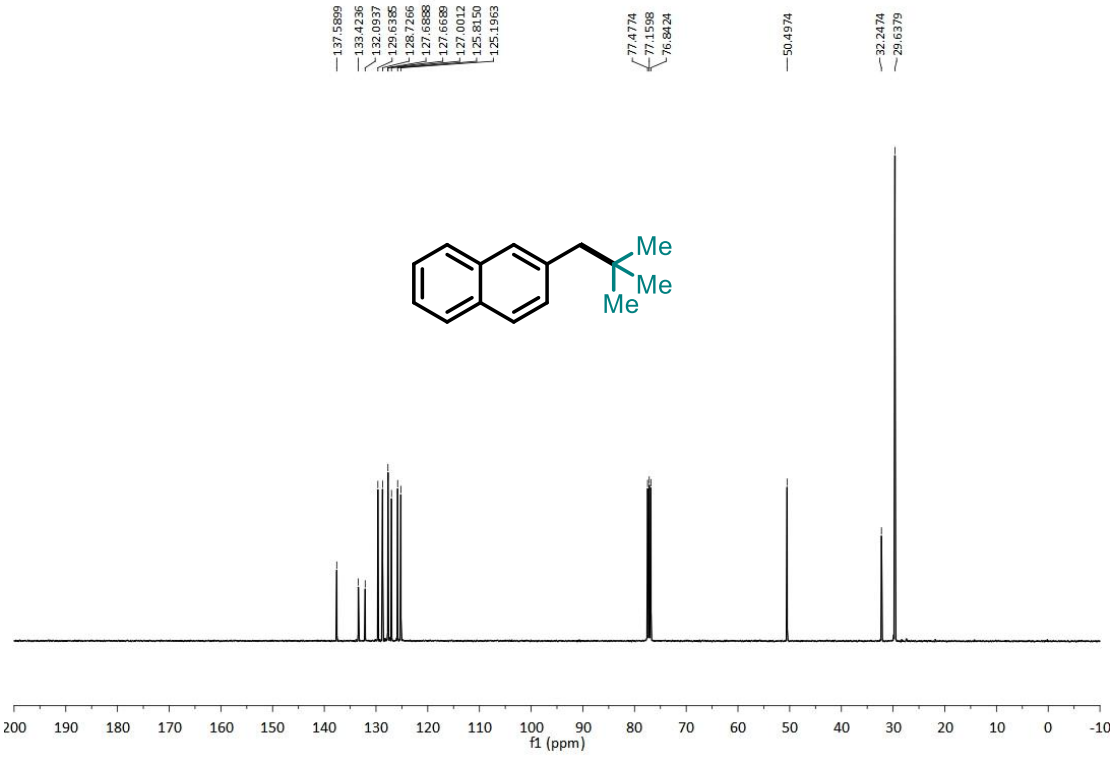
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **36**



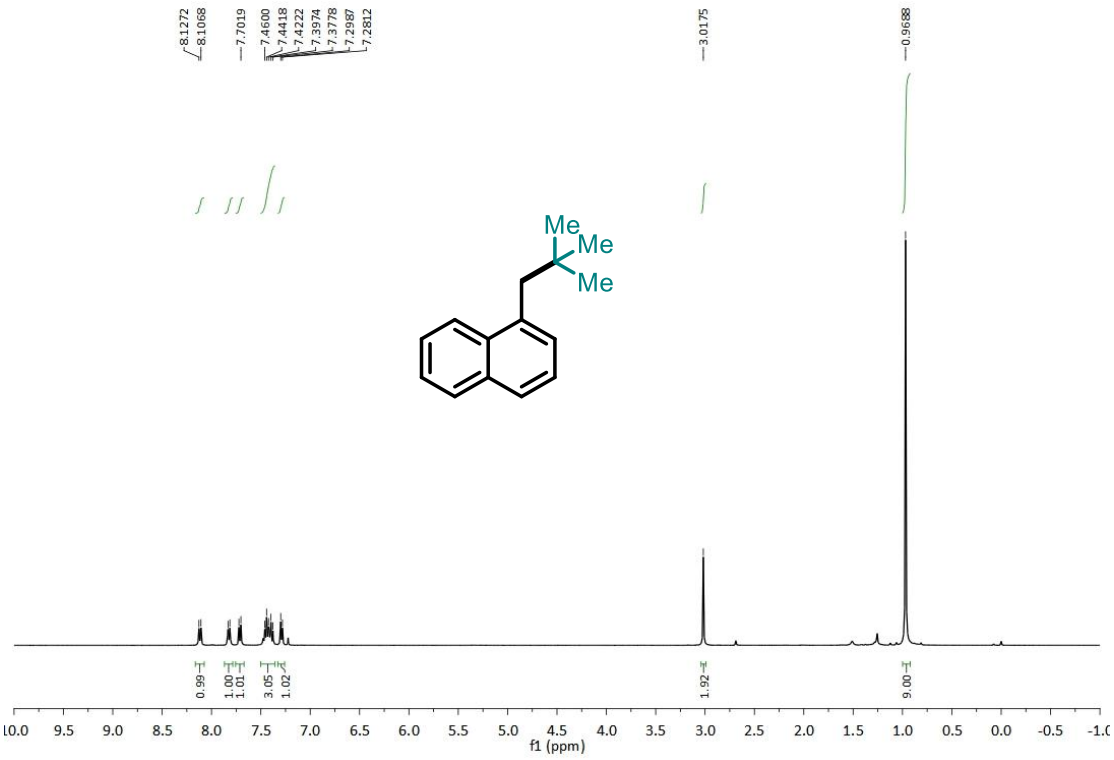
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **37**



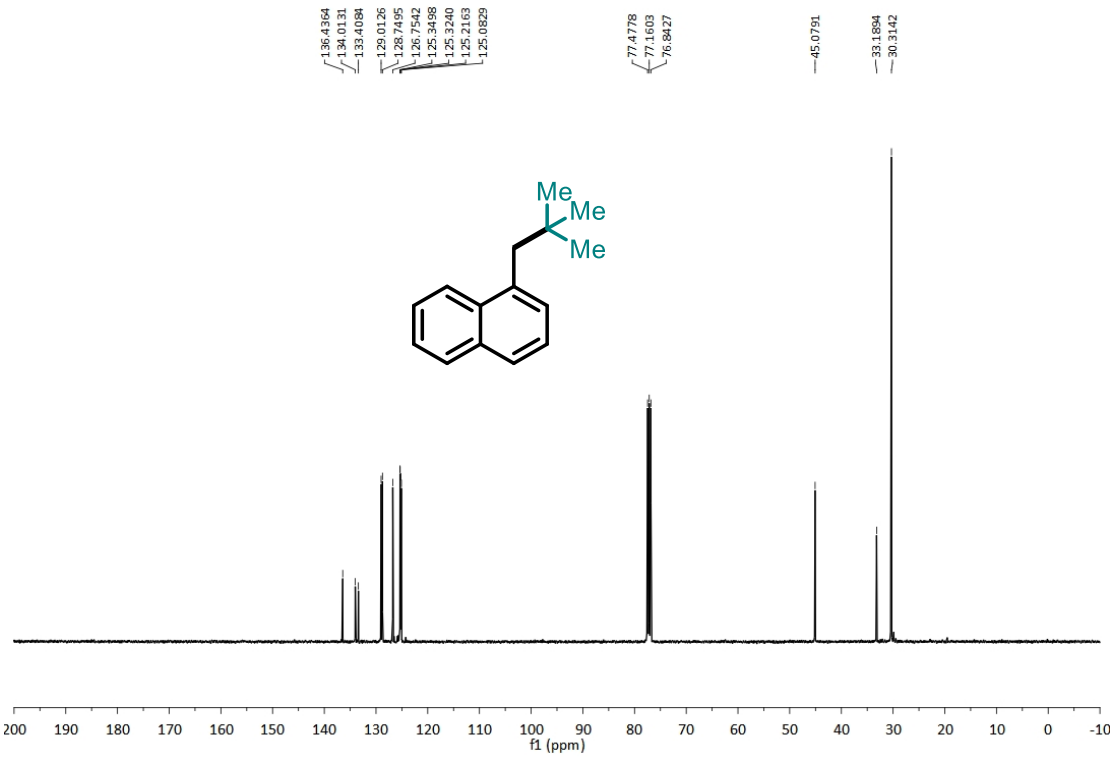
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **38**



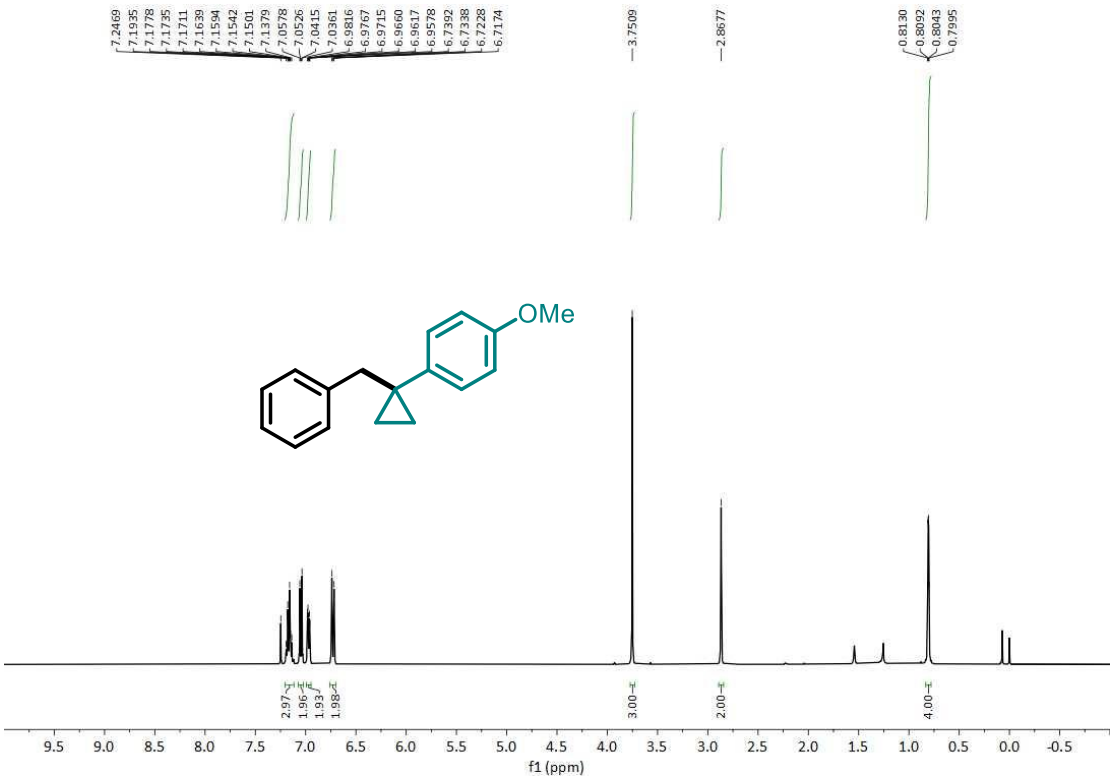
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **38**



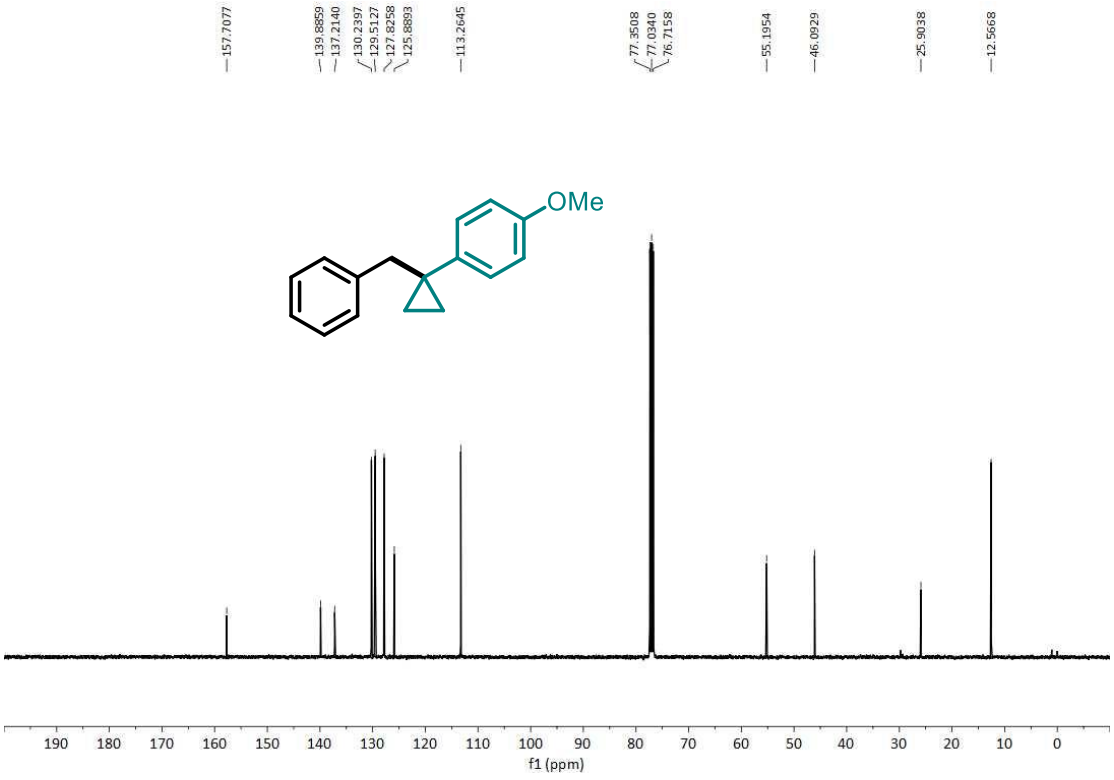
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **39**



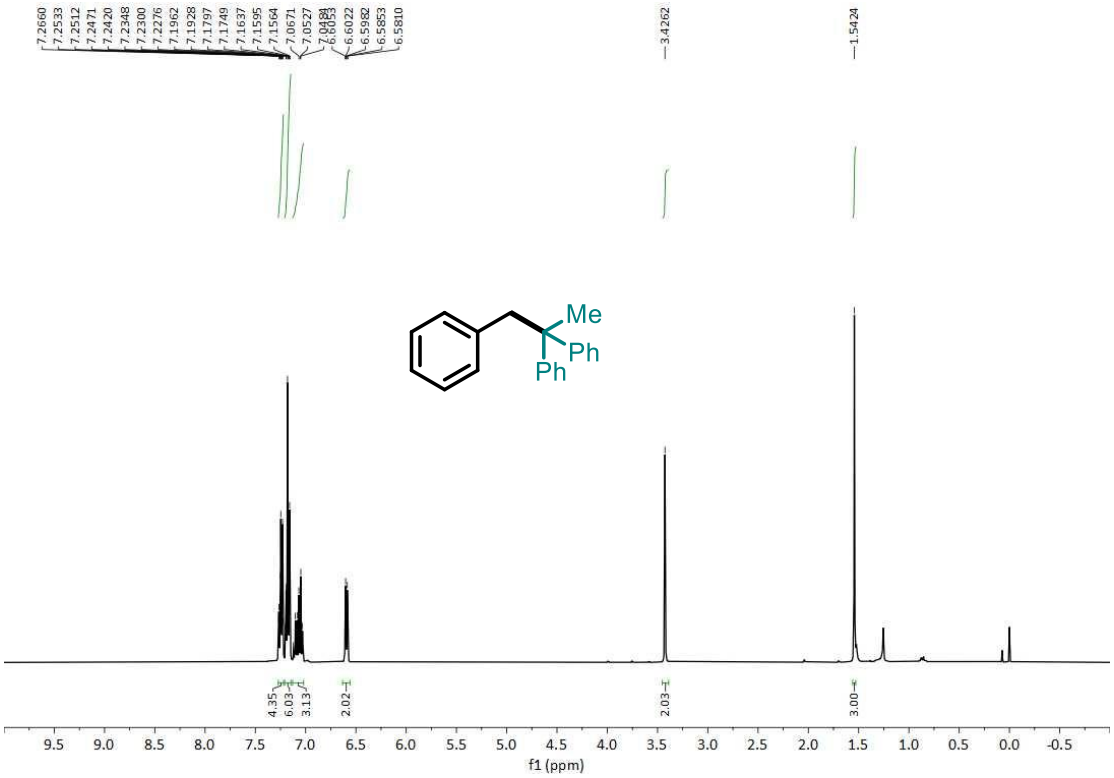
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **39**



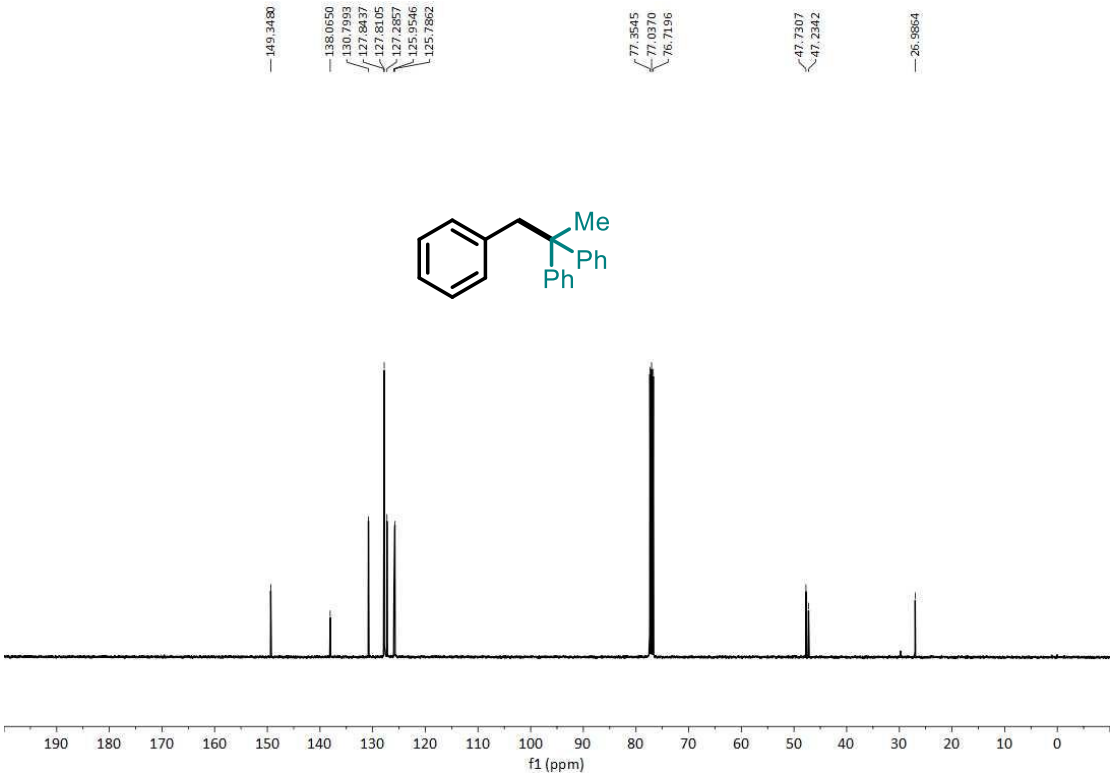
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **40**



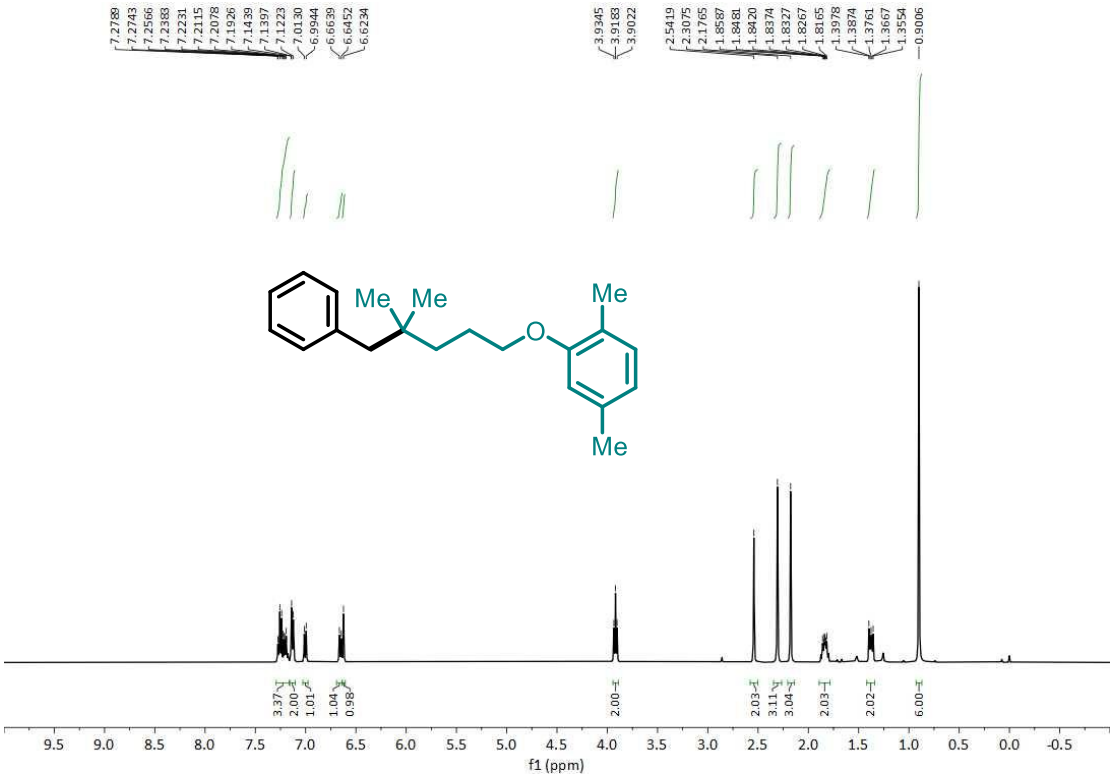
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **40**



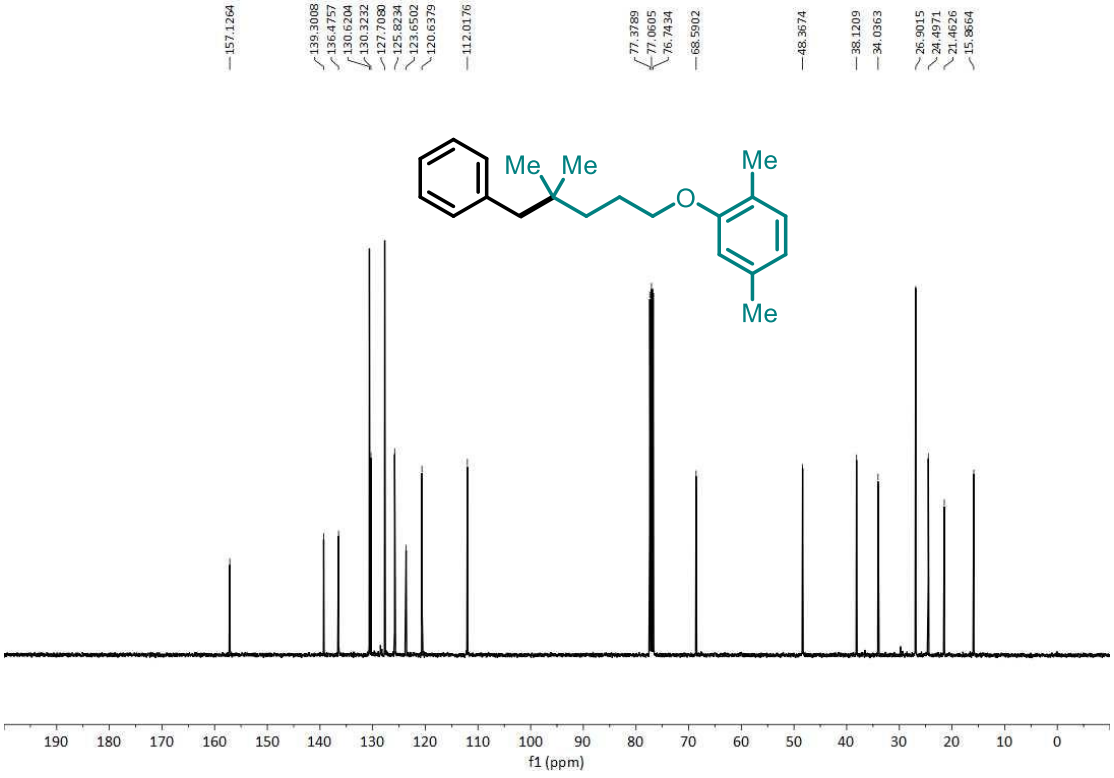
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **41**



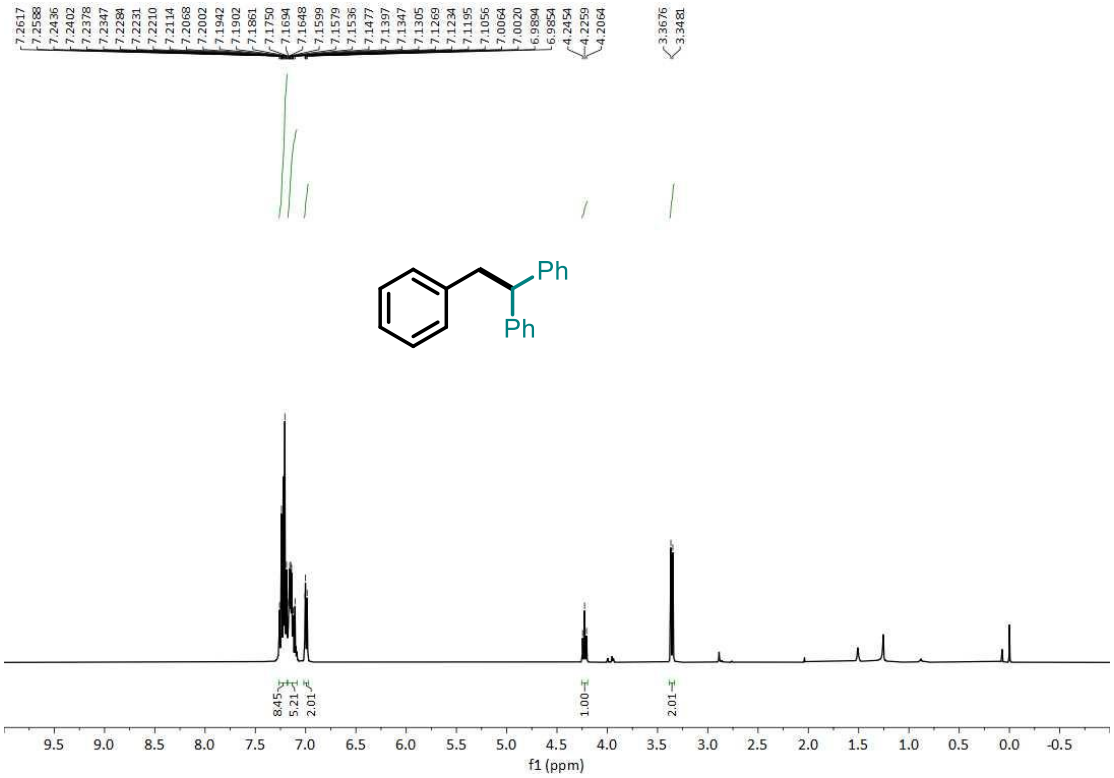
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **41**



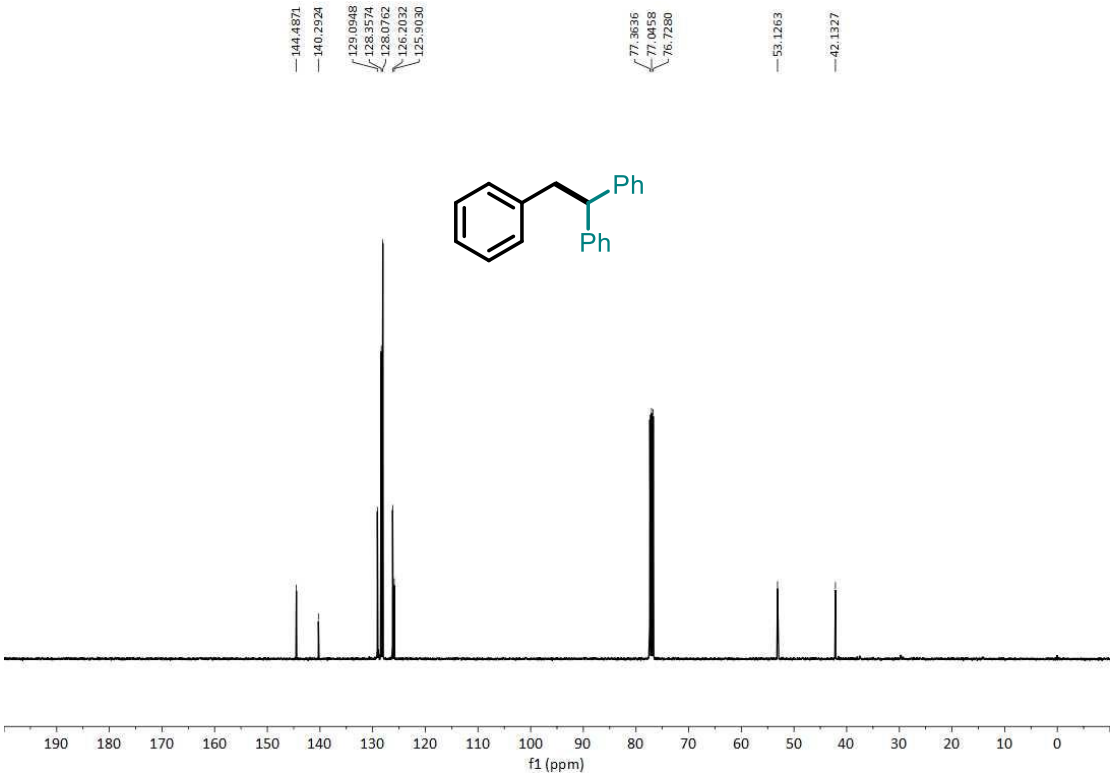
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **43**



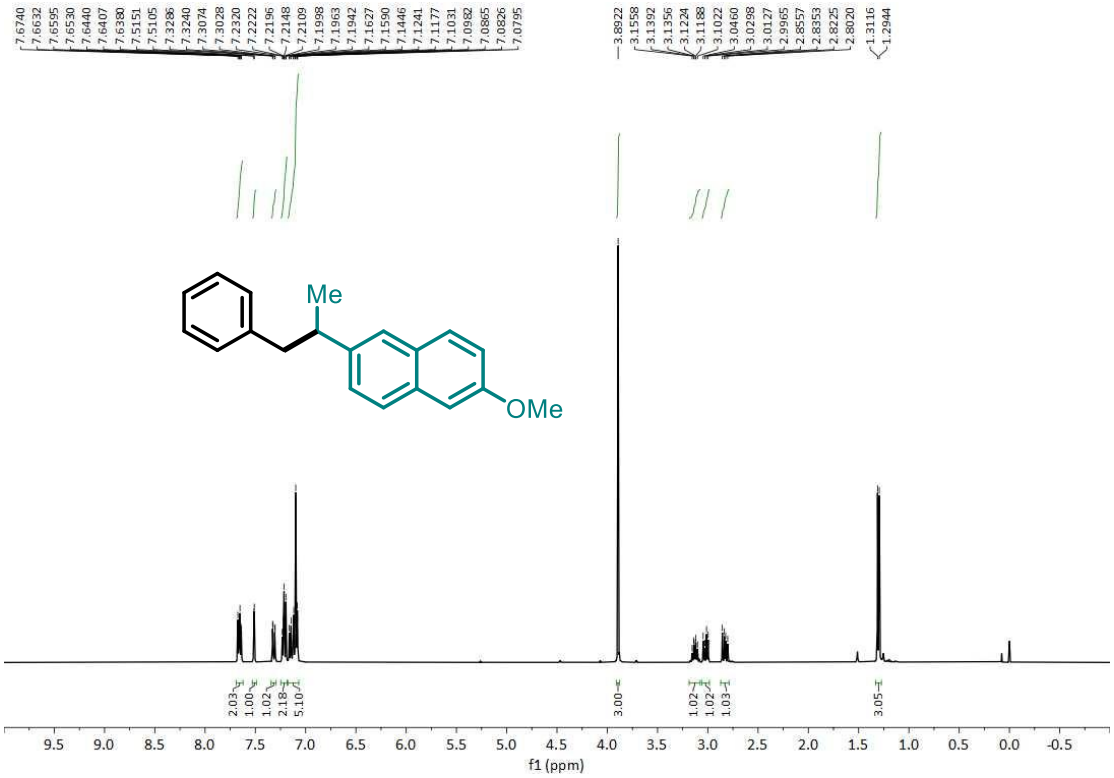
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **43**



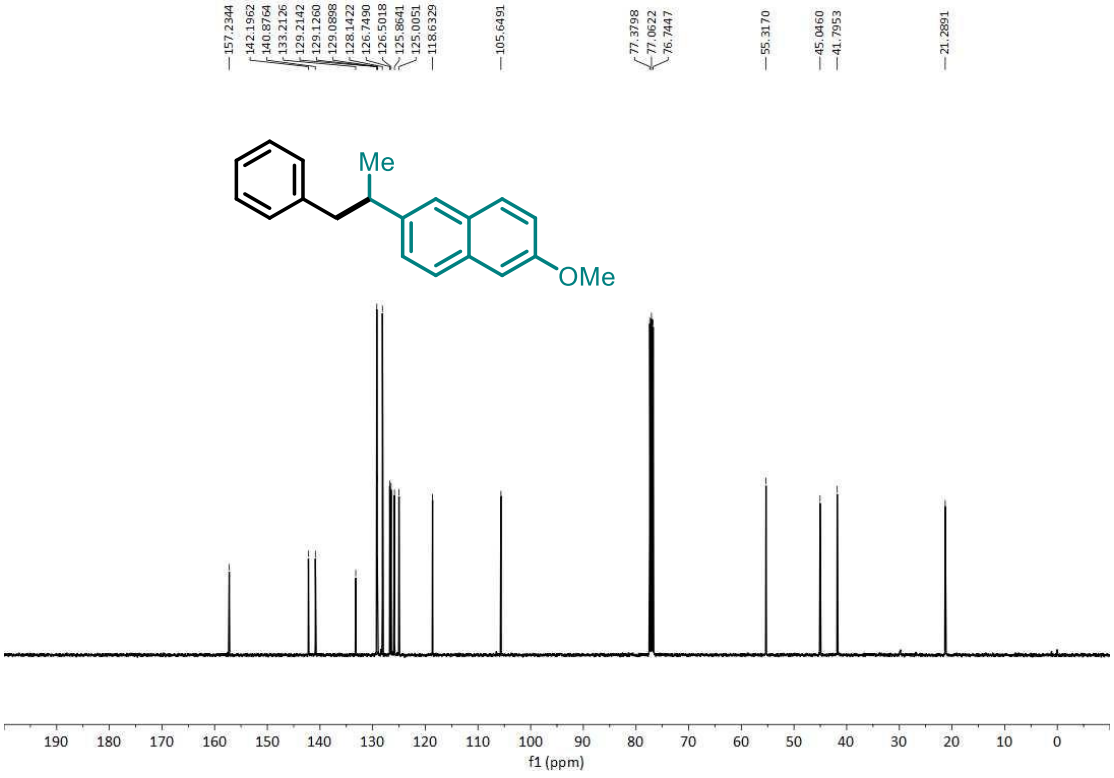
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **44**



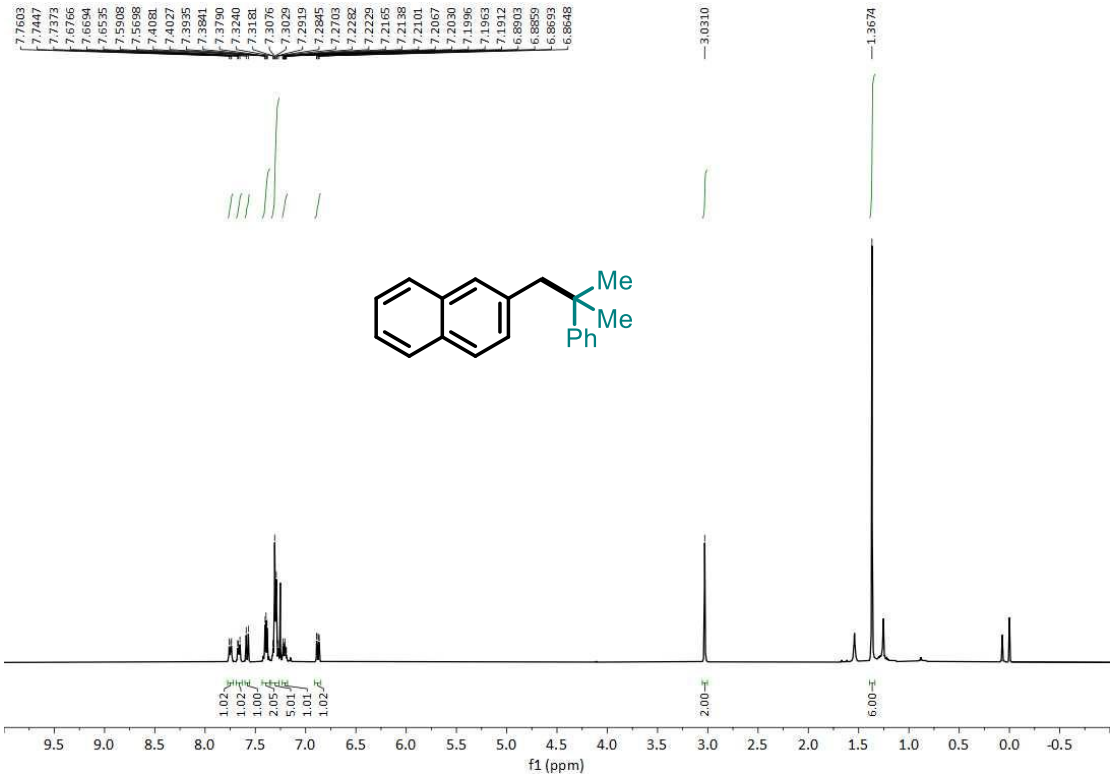
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **44**



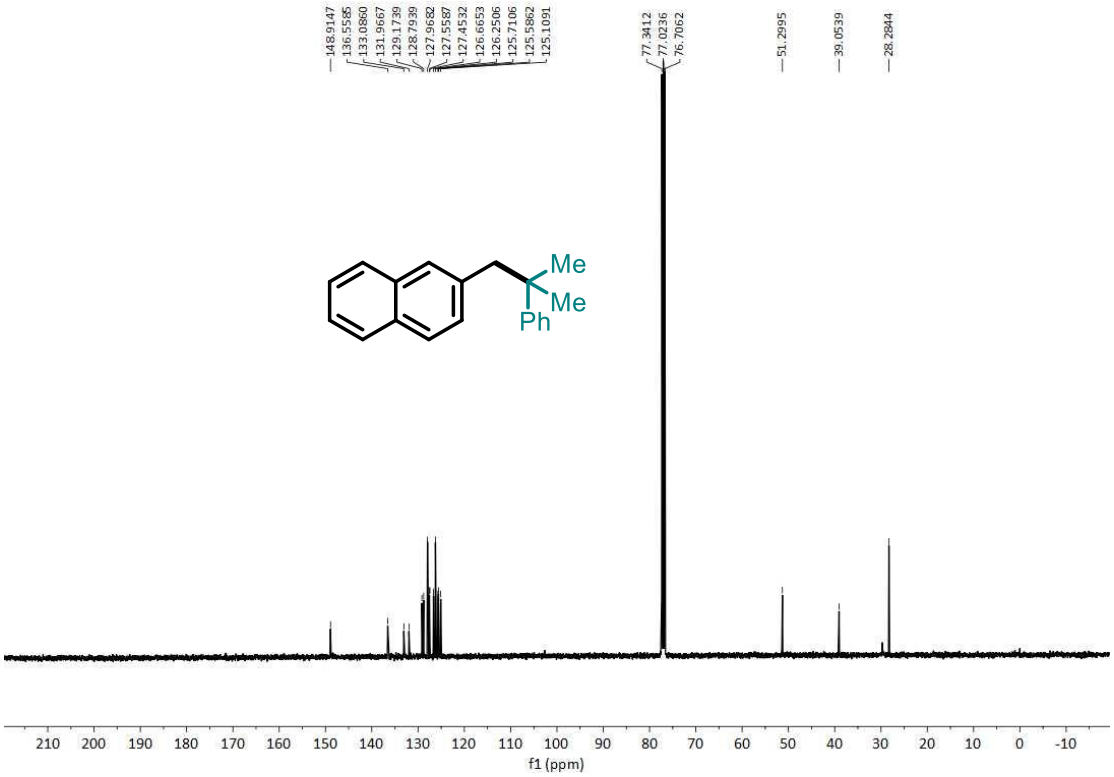
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **45**



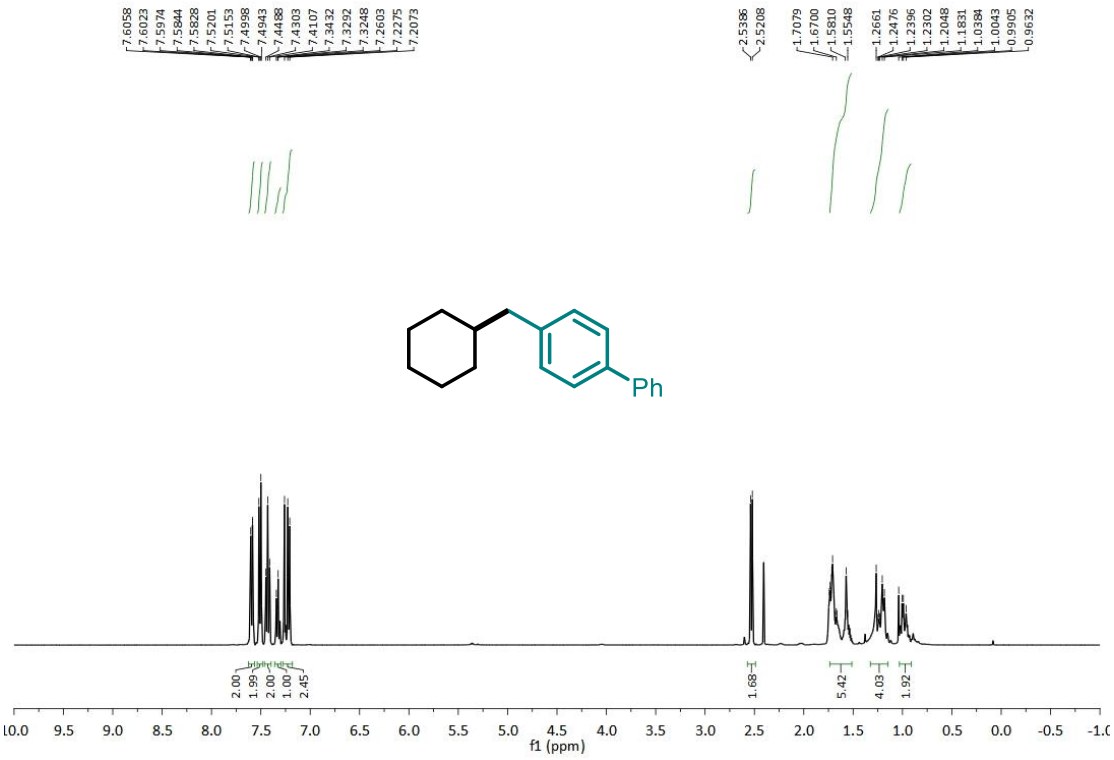
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **45**



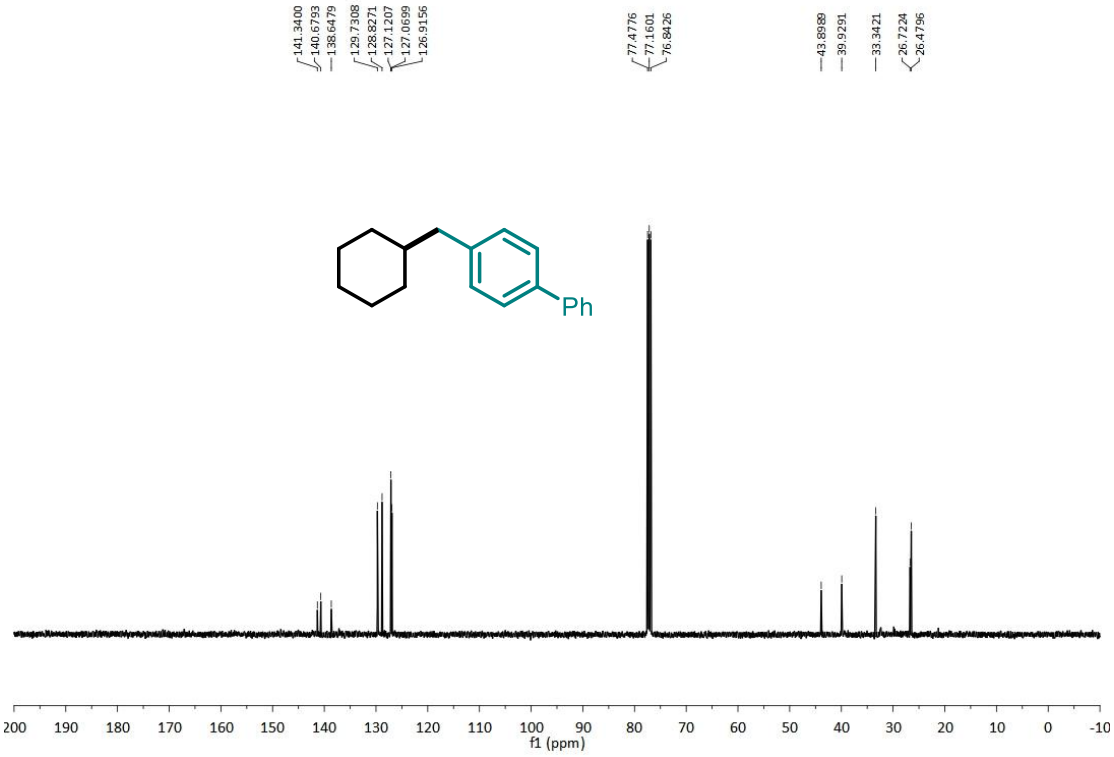
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **46**



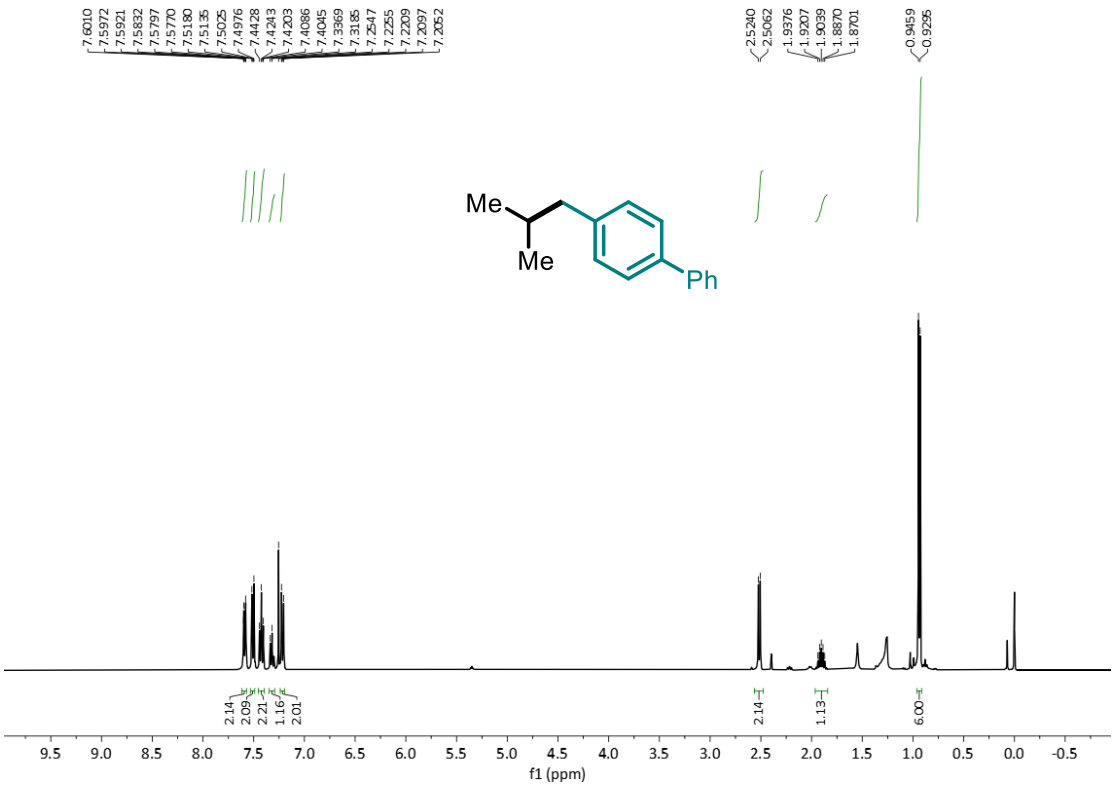
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **46**



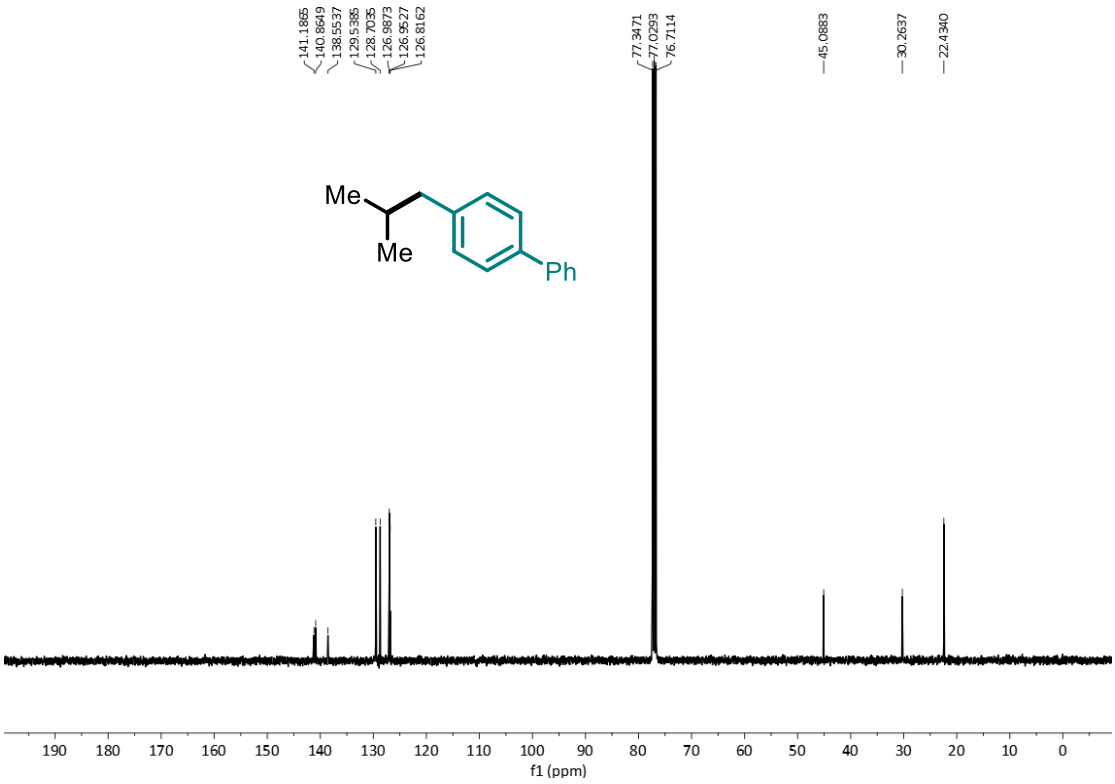
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **47**



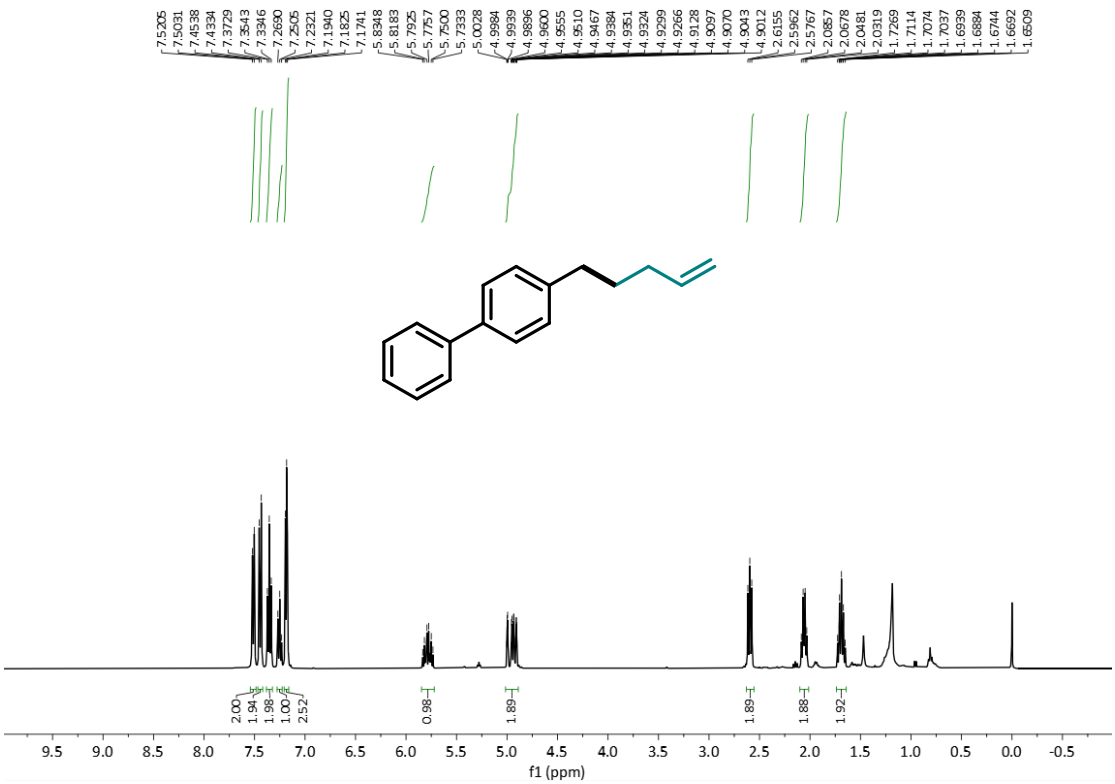
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **47**



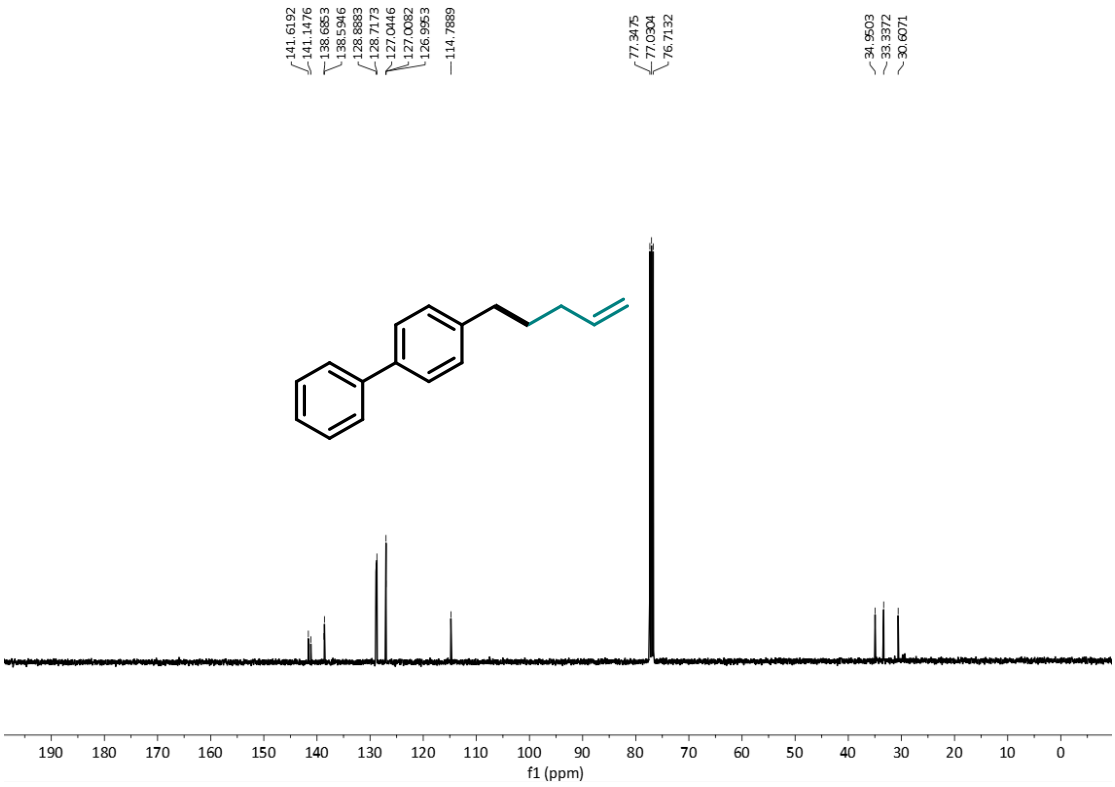
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **48**



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **48**



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **61**



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **61**