Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Photoinduced Generation of Ketyl Radicals and Application in C–C Coupling without External Photocatalyst

Yonggang Yan[a], Gang Li[a], Jiani Ma[a], Chao Wang[a], Jianliang Xiao[b] and Dong Xue*[a]

[a] Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, 710119, China, E-mail: xuedong_welcome@snnu.edu.cn

[b] Department of Chemistry, University of Liverpool, Liverpool, L69 7ZD, United Kingdom

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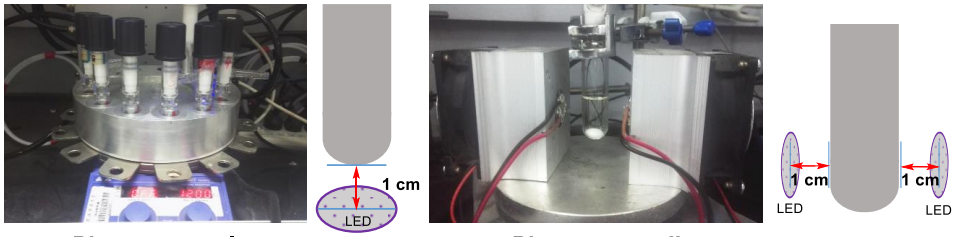
1. General Information

All reactions were performed with Schlenk-tube in the glovebox unless otherwise stated. Commercial reagents were used as purchased without further purification. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates and visualized by UV light (254 nm) or by staining with phosphomolybdic acid alcoholic solution or triketohydrindene alcoholic solution.

The general photochemical reactions were carried with 9 W purple LED (390-395 nm, composed of 3 LED units in series, LED Driver: XC-12W900-OS), the optical power up to 210 mw at 1 cm axis distance detected by Thorlabs' Optical Power Meter (PM100D, S120VC). The LED were purchased from Zhuhai UV Optoelectronics Co., LTD. (P/N: CUN96B1B).

^{1}H NMR spectra, ^{19}F NMR spectra and ^{13}C NMR spectra were recorded at 400 MHz, 376 MHz, 100 MHz on a Bruker 400 spectrometer. All chemical shifts in ^{1}HNMR spectra were given in parts per million (ppm) relative to the residual $CDCl_3$ (7.26 ppm) or DMSO-d_6 (2.50 ppm) as internal standards and coupling constants (J) were given in Hertz (Hz). ^{1}H NMR data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, br = broad), coupling constants, the number of protons (n) for a given resonance was indicated by nH. ^{19}F NMR chemical shifts were reported in ppm. ^{13}C NMR chemical shifts were reported in ppm relative to the central peak of $CDCl_3$ (77.16 ppm) or DMSO-d_6 (39.52 ppm) as internal standards. HRMS data were obtained by using ESI method. HRMS data were obtained by ESI or APCI method with Bruker mass spectrometer (MAXIS). EPR were recorded with Bruker E500 electron paramagnetic spectrometer. The ns-TA experiments were conducted using LP980 laser flash spectrometer (Edinburgh Instruments).



Photoreactor I
(WATTCAS parallel reactor)

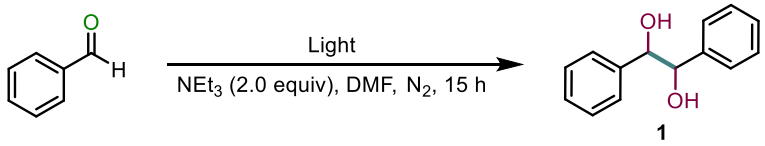
Photoreactor II
(9W pueple LED, 390-395 nm)

Figure S1. Pictures of photoreactor

2. Optimization of Reaction Condition

2.1 Optimization for pinacol coupling of benzaldehyde.

Table S1. Screening of light source (**Photoreactor I**)

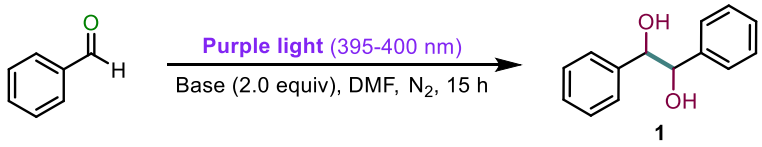


1

Entry	Light	Yield of **1**[a]
1	white LED	-
2	green LED (530 nm)	-
3	blue LED (460-465 nm)	-
4	purple LED (395-400 nm)	53%
5	UV LED (360-365 nm)	44%

Reaction conditions: Benzaldehyde (1.0 equiv, 0.4 mmol), NEt_3 (2.0 equiv, 0.8 mmol), DMF (4 mL), 3 W LED (**Photoreactor I**). a: NMR yields.

Table S2. Screening of base (**Photoreactor I**)

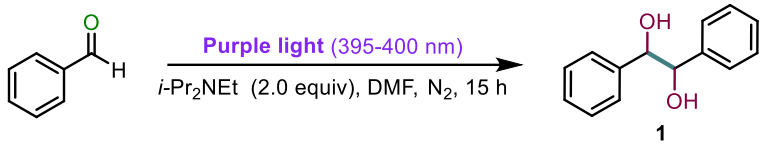


1

Entry	Base	Yield of **1**[a]
1	DABCO	21%
2	DBU	28%
3	*i*-Pr_2NEt	68%
4	Et_3N	53%
5	N,N-Dicyclohexylmethylamine	46%
6	N,N,N',N'-Tetramethylethylenediamine	25%

Reaction conditions: Benzaldehyde (1.0 equiv, 0.4 mmol), Base (2.0 equiv, 0.8 mmol), DMF (4 mL), 3 W purple LED (395-400 nm, **Photoreactor I**). a: NMR yields.

Table S3. Screening of solvent (**Photoreactor I**)

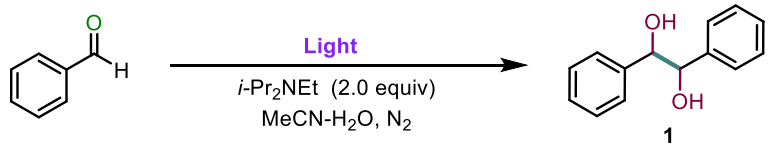


1

Entry	Solvent	Yield of **1**[a]
1	H_2O	46%
2	DCM	48%
3	MeCN	75%
4	THF	64%
5	DMSO	48%
6	EtOH	59%
7	*i*-PrOH	61%
8	DMF	68%
9	toluene	53%
10	MeCN-H_2O(3:1)	99%

Reaction conditions: Benzaldehyde (1.0 equiv, 0.4 mmol), *i*-Pr_2NEt (2.0 equiv, 0.8 mmol), Solvent (4 mL), 3 W purple LED (395-400 nm, **Photoreactor I**). a: NMR yields.

Table S4. Comparation between **Photoreactor I** and **Photoreactor II**



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Setup	Optical Power	Reaction Time	Yield of **1**[a]
Photoreactor I 3 W (395-400 nm)	~35 mw/cm^2	15 h	99%
Photoreactor II 9 W (390-395 nm)	~210 mw/cm^2	3 h	99%

Reaction conditions: Benzaldehyde (1.0 eq, 0.4 mmol), *i*-Pr_2NEt (2.0 eq, 0.8 mmol), MeCN/H_2O (3 mL, 1mL), a: NMR yields.

3. ns-TA Experiments and DFT Calculation

The ns-TA experiments were conducted using LP980 laser flash spectrometer (Edinburgh Instruments). A 355 nm laser pulse was used as the pump beam that generated from the third harmonic output of an Nd:YAG laser, the probe light source came from a 150 W xenon lamp. The sample solutions were prepared with an absorbance of 1 at 355 nm using a 1 cm quartz cuvette, and degassing with Ar before testing. The optimizated geometries and vibrational frequencies for aldehyde and

relevant intermediates were calculated using DFT under M062X/6-311G** level. UV−vis spectra were simulated by TD-DFT/M062X/6-311G** calculations. The solvation model based on density (SMD) in MeCN (ε = 35.688) was used to evaluate the solvent effect. All DFT calculations were conducted using Gaussian 16.

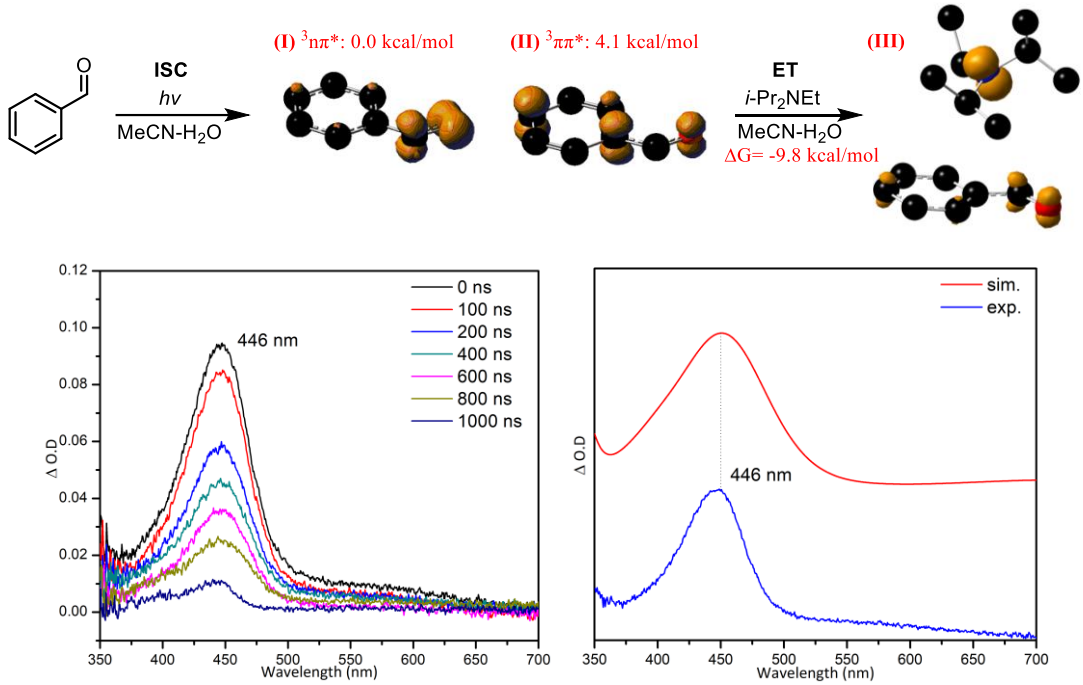


Figure S2. Left: ns-TA results acquired after 355 nm photoexcitation of benzaldehy with *i*-PrNEt in MeCN-H_2O. Right: comparision of UV-vis spectra of ketyl radical anion between experimental and simulated result.

Table S5. Cartesian coordinates and total energies for the optimized geometry of ketyl radical anion.

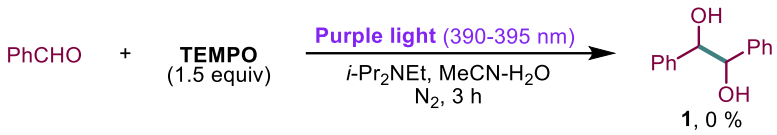
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.323177	-1.327712	0.000389
2	6	0	-0.042175	-1.103347	-0.000911
3	6	0	-0.571223	0.228873	-0.00084
4	6	0	0.380334	1.297638	-0.000441
5	6	0	1.737486	1.05332	0.000442
6	6	0	2.240458	-0.264866	0.000454
7	1	0	1.692153	-2.349731	0.000267
8	1	0	-0.737528	-1.935673	-0.000098
9	1	0	0.015261	2.321819	-0.000312
10	1	0	2.428748	1.891	0.000567
11	1	0	3.307597	-0.451465	-0.000854
12	6	0	-1.970253	0.481192	0.000374
13	8	0	-2.879682	-0.402089	0.000475
14	1	0	-2.255593	1.550175	-0.000171

Thermal correction to Gibbs Free Energy= 0.076094
Sum of electronic and thermal Free Energies= -345.540278
The number of imaginary frequencies: 0

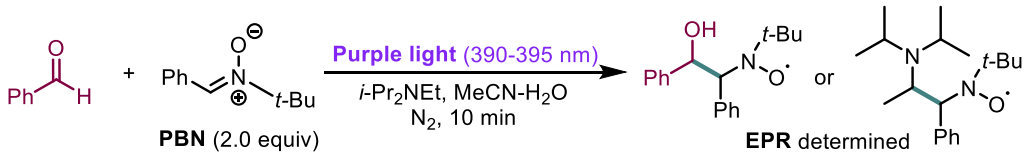
4. Control Experiments

4.1 Radical trapping experiments

To verify the photoinduced generation ketyl radical from benzaldehyde, experiments were performed by addition of radical trapping reagents such as TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl), PBN (*N*-*tert*-butyl-2-phenylnitrone) and 1,1-diphenylethene respectively.



In a glovebox, benzaldehyde (1.0 equiv, 0.4 mmol), *i*-Pr_2NEt (2.0 equiv, 0.8 mmol), TEMPO (1.5 equiv, 0.6 mmol) were placed into a 10 mL Schlenk-tube with a magnetic stir bar. Then degassed solvent H_2O (1 mL) and MeCN (3 mL) were added. The reaction mixture was placed in a stirrer and irradiated with 9 W pure LEDs. After 3 hours, the reaction mixture was washed with water and extracted with ethyl acetate (3 x 15 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtrated and concentrated under vacuum. No pinacol product was detected by TLC and HRMS.



The PBN (2.0 equiv, 0.8 mmol) was added in the above reaction instead of TEMPO, after irradiating for 10 minuntes, suitable volume of mixture was transferred to an oven-dried EPR tube. The EPR spectrum was recorded at room temperature.

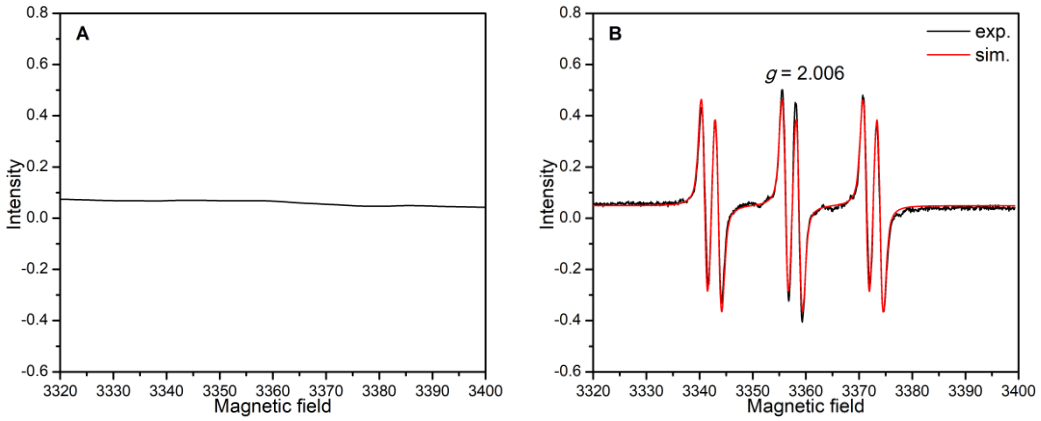
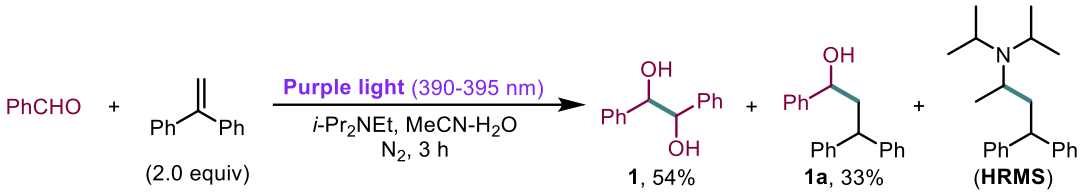
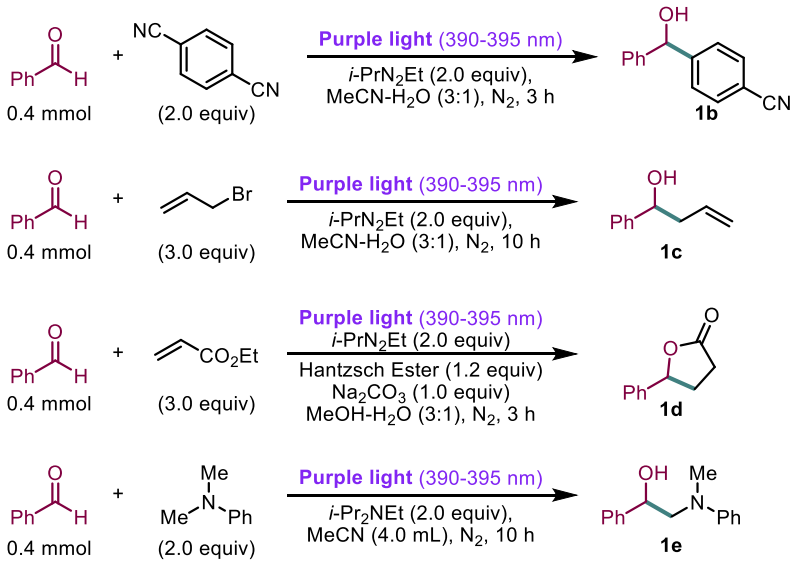


Figure S3. EPR spectrum of radical trapping with PBN. (A: no light; B: purple light irradiation)



The 1,1-diphenylethylene (2.0 equiv, 0.8 mmol) was added in the above reaction instead of TEMPO. After irradiation, the reaction mixture was firstly determined by HRMS, and then isolated to get the product **1** (54% yield) and **1a** (33% yield). The mass spectrum clearly shows a peak of the coupling product from *α*-amino radical and diphenylethylene, **HRMS** (**ESI**): m/z calcd for $C_{22}H_{32}N$ $[M+H]^+$: 310.2529, found: 310.2525.

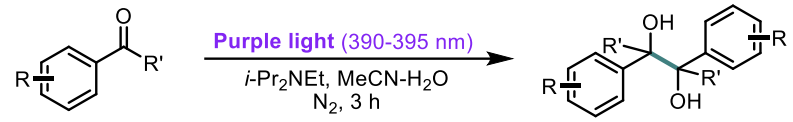
5. Application of Ketyl Radical in C-C Coupling



General procedure for ketyl readical coupling reactions (1b-1e): In the glovebox, the benzaldehyde (1.0 equiv, 0.4 mmol), *i*-Pr_2NEt (2.0 or 3.0 equiv), corresponding coupling partners and additives (if necessary) were placed into a 10 mL Schlenk-tube with a magnetic stir bar, respectively, then degassed solvent (4.0 mL) were added. The reaction mixture was placed in a stirrer and irradiated with 9 W pure LEDs (approximately 1 cm away from the tube, the optical power up to 210 mw, the mixture temperature ranging from 38 to 45 °C). After stirring for 3 hours or more, the mixture was washed with water and extracted with ethyl acetate (3 x 15 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtrated and concentrated under vacuum. The desired product was obtained by column chromatography.

6. General Procedure

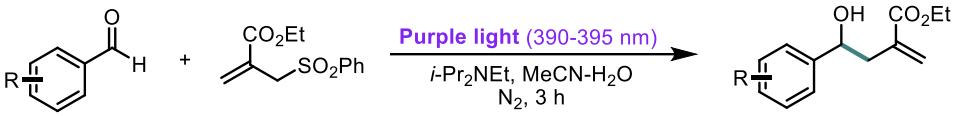
6.1 Standard procedure for pinacol coupling of aldehydes and ketones.



R'= H, aryl or alkyl

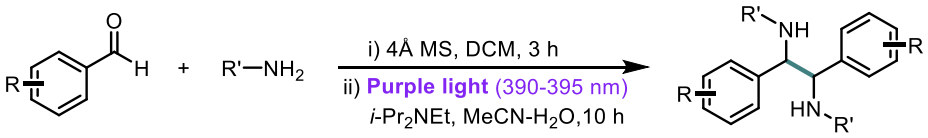
In the glovebox, the aldehydes or ketones (1.0 equiv, 0.4 mmol), *i*-Pr_2NEt (2.0 equiv, 0.8 mmol) were placed into a 10 mL Schlenk-tube with a magnetic stir bar. Then degassed solvent H_2O (1mL) and MeCN (3 mL) were added. The reaction mixture was placed in a stirrer and irradiated with 9 W pure LEDs (approximately 1 cm away from the tube, the optical power up to 210 mw, the mixture temperature ranging from 38 to 45 °C). After stirring for 3 hours or more, the reaction mixture was washed with water and extracted with ethyl acetate (3 x 15 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtrated and concentrated under vacuum. The desired product was obtained by column chromatography.

6.2 Standard procedure for photoinduced coupling of aldehydes with allyl sulfone.



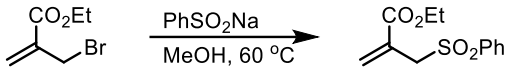
In the glovebox, the aldehyde (1.0 equiv, 0.4 mmol), allyl sulfone (3.0 equiv, 1.2 mmol), *i*-Pr_2NEt (2.0 equiv, 0.8 mmol) were placed into a 10 mL Schlenk-tube with a magnetic stir bar. Then degassed H_2O (1mL) and MeCN (3 mL) were added. The reaction mixture was placed in a stirrer and irradiated with 9 W purple LEDs (approximately 1 cm away from the tube, the optical power up to 210 mw, the mixture temperature ranging from 38 to 45 °C). After stirring for 3 hours, the reaction mixture was washed with water and extracted with ethyl acetate (3 x 15 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtrated and concentrated under vacuum. The desired product was obtained by column chromatography.

6.3 Standard procedure for the pinacol coupling of imines.



The aldehyde (1.0 equiv, 0.4 mmol), amine (1.0 equiv, 0.4 mmol), 4Å MS (200 mg) and DCM (2 mL) were added to a 10 mL Schlenk-tube with a magnetic stir bar. After stirring at room temperature for 3 h, the mixture was filtrated and concentrated, the crude product was transferred into the glovebox, redissolved in another 10 mL Schlenk-tube with MeCN (3 mL). Then, *i*-Pr_2NEt (2.0 equiv, 0.8 mmol) and H_2O (1 mL) were added. The reaction mixture was placed in a stirrer and irradiated with 9 W purple LEDs (approximately 1 cm away from the tube, the optical power up to 210 mw, the mixture temperature ranging from 38 to 45 °C). After stirring for 10 hours, the reaction mixture was washed with water and extracted with ethyl acetate (3 x 15 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtrated and concentrated under vacuum. The desired product was obtained by column chromatography, some of examples were directly filtrated and dried to get the desired racemize (*dl*) products.

6.4 Synthesis of allyl sulfone (ethyl 2-((phenylsulfonyl)methyl)acrylate) [1]



To a solution of ethyl 2-(bromomethyl) acrylate (1.99 g, 10.4 mmol) in dry methanol (25 mL) was added sodium phenylsulfinate (2.50 g, 15.2 mmol). After refluxing at 60 °C for 2.5 hours, the mixture was concentrated under reduced pressure, the obtained residue was dissolved in ethyl acetate and washed with water, brine, dried with Na_2SO_4, then purified by column chromatography (PE:EA = 2:1) to give the allyl sulfone as a colourless oil (1.95 g, 74% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 6.50 (s, 1H), 5.91 (s, 1H), 4.17 (s, 2H), 4.02 (q, *J* = 7.2 Hz, 2H), 1.17(t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.8, 138.4, 133.9, 133.4, 129.2, 129.1, 128.8, 61.5, 57.5, 14.0. **HRMS** (ESI) m/z calcd. for $C_{12}H_{14}NaO_4S$ $[M+Na]^+$: 277.0506, found: 277.0506.

7. Gram-Scale Procedure

7.1 Gram-scale procedure for pinacol coupling of aldehydes.

The corresponding aldehyde (15 mmol), *i*-Pr_2NEt (30 mmol,) were placed into a 100 mL Schlenk-tube with H_2O (15 mL) and MeCN (45 mL). The reaction mixture was bubbling with nitrogen for 10 minutes, then placed in a stirrer and surrounded by irradiation with pure LEDs for 12 hours. The desired products **1**, **3**, **11**, **20** were obtained by column chromatography in 98%, 98%, 86%, 94% yield.

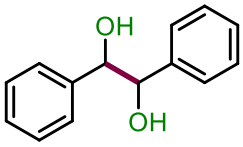
7.2 Gram-scale procedure for pinacol coupling of imines.

The corresponding aldehyde (20 mmol) and excess benzylamine (30 mmol) were directly added in a 100 mL Schlenk-tube with H_2O (15 mL) and MeCN (45 mL). The reaction mixture was bubbling with nitrogen for 10 minutes, then placed in a stirrer and surrounded by irradiation with pure LEDs for 12 hours. Large amounts of white solid appeared, the reaction mixture was filtrated and washed with *n*-hexane to obtain the racemic diamine **49**, **54**, **55** in 57 %, 55%, 36% yield.

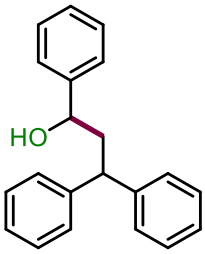
7.3 Gram-scale procedure for the reaction of benzaldehyde with allyl sulfone.

The corresponding aldehyde (1.0 equiv, 8 mmol), aulfone (3.0 equiv, 24 mmol), *i*-Pr_2NEt (2.0 equiv, 16 mmol,) were placed into a 100 mL Schlenk-tube with H_2O (15 mL) and MeCN (45 mL). The reaction mixture was bubbling with nitrogen for 10 minutes. Then placed in a stirrer and surrounded by irradiation with purple LED for 10 hours. The desired products **37, 47** were obtained by column chromatography in 85%, 87% yield.

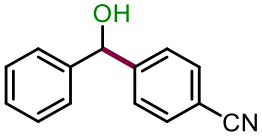
8. Characterization Data.



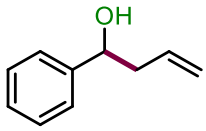
1,2-Diphenylethane-1,2-diol (1).[2] White solid, 42 mg, 98% yield, ***dl : meso*** = 1.7:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30-7.28 (m, 6H), 7.24-7.1 9 (m, 10H), 7.11-7.07 (m, 4H), 4.79 (s, 2H, *meso*), 4.64 (s, 2H, *dl*), 3.21 (s, 2H, *dl*), 2.54 (s, 2H, *meso*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.0, 139.8, 128.3, 128.2, 128.1, 128.0, 127.2, 127.1, 79.2, 78.1. **HRMS** (ESI) m/z calcd. for $C_{14}H_{14}NaO_2$ $[M+Na]^+$: 237.0886, found: 237.0887.



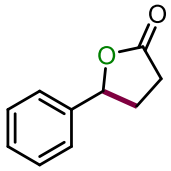
1,3,3-triphenylpropan-1-ol (1a).[3] Colorless oil, 33% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37-7.18 (m, 15H), 4.55-4.51 (m, 1H), 4.17 (dd, *J* = 8.9, 6.8 Hz, 1H), 2.58-2.43 (m, 2H), 1.80 (br, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.8, 144.3, 128.8, 128.7, 128.7, 128.2, 128.0, 127.9, 126.5, 126.4, 126.1, 72. 6, 47.8, 45.0. **HRMS (ESI)** m/z calcd. for $C_{21}H_{20}NaO$ $[M+Na]^+$: 311.1406, found: 311.1412.



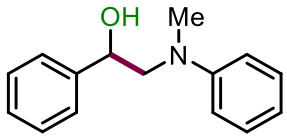
4-(hydroxy(phenyl)methyl)benzonitrile (1b).[4] White solid, 47 mg, 56% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.40-7.29 (m, 5H), 5.84 (s, 1H), 2.60 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 142.9, 132.4, 129.0, 128.4, 127.1, 126.8, 118.9, 111.2, 75.7. **HRMS** (ESI) m/z calcd. for $C_{14}H_{11}NNaO$ $[M+Na]^+$: 232.0733, found: 232.0730.



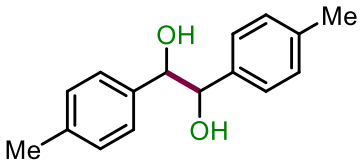
1-phenylbut-3-en-1-ol (1c).[5] Colourless oil, 34 mg, 57% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40-7.31 (m, 4H), 7.29-7.20 (m, 1H), 5.88-5.72 (m, 1H), 5.21-5.09 (m, 2H), 4.73 (t, *J* = 6.3 Hz, 1H), 2.61-2.45 (m, 2H), 2.07 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.0, 134.6, 128.6, 127.7, 126.0, 118.6, 73.4, 44.0. **HRMS** (ESI) m/z calcd. for $C_{10}H_{12}NaO$ $[M+Na]^+$: 171.0780, found: 171.0782.



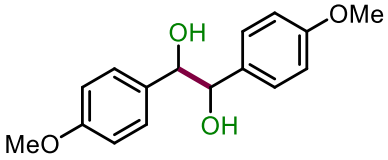
5-phenyldihydrofuran-2(3H)-one (1d).[6] Light yellow oil, 43 mg, 66% yield.**^{1} H NMR** (400 MHz, $CDCl_3$): δ 7.41-7.32 (m, 5H), 5.53-5.49 (m, 1H), 2.69-2.62 (m, 3H), 2.23-2.15 (m, 1H), **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.0, 139.5, 128.9, 128.5, 125.4, 81.3, 31.1, 29.0. **HRMS (ESI)** m/z calcd. for $C_{10}H_{10}NaO_2$ $[M+Na]^+$: 185.0573, found: 185.0579.



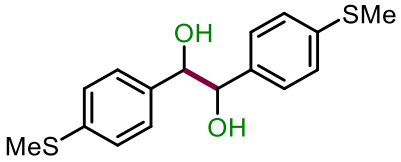
2-(methyl(phenyl)amino)-1-phenylethan-1-ol(1e).[7] Light brown oil, 40 mg, 44% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.34 (m, 4H), 7.33-7.22 (m, 3H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 4.99 (dd, *J* = 8.1, 4.1 Hz, 1H), 3.47 (qd, *J* = 14.7, 6.6 Hz, 2H), 2.94 (s, 3H), 2.52 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 142.1, 129.4, 128.7, 128.0, 126.0, 117.7, 113.4, 71.9, 62.2, 39.5. **HRMS** (ESI) m/z calcd. for $C_{15}H_{17}NNaO$ $[M+Na]^+$: 250.1202, found: 250.1206.



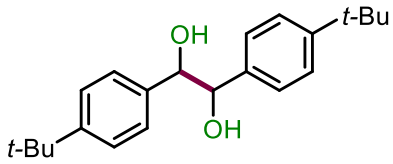
1,2-Di-*p*-tolylethane-1,2-diol (2).[8] White solid, 46 mg, 95% yield, ***dl* : *meso*** = 1.5:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 (dd, *J* = 13.5, 8.1 Hz, 8H, *dl*), 7.02 (dd, *J* = 14.0, 8.0 Hz, 8H, *meso*), 4.72 (s, 2H, *meso*), 4.63 (s, 2H, *dl*), 2.96 (s, 2H, *dl*), 2.35 (s, 6H, *meso*), 2.31 (s, 6H, *dl*), 2.24 (s, 2H, *meso*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.9, 137.6, 137.2, 137.1, 129.1, 128.9, 127.2, 127.0, 78.9, 78.1, 21.3, 21.3. **HRMS** (ESI) m/z calcd. for $C_{16}H_{18}NaO_2$ $[M+Na]^+$: 265.1199, found: 265.1193.



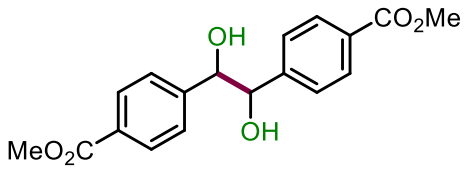
1,2-Bis(4-methoxyphenyl)ethane-1,2-diol (3).[2] White solid, 53 mg, 97% yield, ***dl* : *meso*** = 2:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.4 Hz, 4H, *meso*), 7.01 (d, *J* = 8.4 Hz, 4H, *dl*), 6.84 (d, *J* = 8.4 Hz, 4H, *meso*), 6.75 (d, *J* = 8.4 Hz, 4H, *dl*), 4.71 (s, 2H, *meso*), 4.59 (s, 2H, *dl*), 3.79 (s, 6H, *meso*), 3.75 (s, 6H, *dl*), 2.97 (s, 2H, *dl*), 2.24 (s, 2H, *meso*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.5, 159.3, 132.2, 132.1, 128.5, 128.3, 113.8, 113.6, 78.9, 77.9, 55.4, 55.3. **HRMS** (ESI) m/z calcd. for $C_{16}H_{18}NaO_4$ $[M+Na]^+$: 297.1097, found: 297.1091.



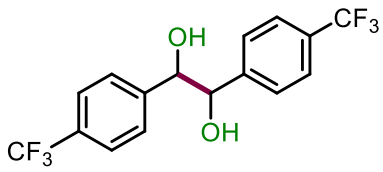
1,2-Bis(4-(methylthio)phenyl)ethane-1,2-diol (4). Pale yellow solid, 54 mg, 88% yield, ***dl* : *meso*** = 1:2.3. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.16 (dd, *J* = 15.2, 8.3 Hz, 8H, *dl*), 7.05 (dd, *J* = 13.6, 8.4 Hz, 8H, *meso*), 5.33 (s, 2H, *meso*), 5.20 (s, 2H, *dl*), 4.53 (s, 6H, *meso*), 4.50 (s, 6H, *dl*), 2.44 (s, 2H, *dl*), 2.41 (s, 2H, *meso*). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 140.1, 139.1, 136.0, 135.9, 128.0, 127.9, 125.2, 125.0, 77.0, 76.6, 14.9, 14.8. **HRMS** (ESI) m/z calcd. for $C_{16}H_{18}NaO_2S_2$ $[M+Na]^+$: 329.0640, found: 329.0632.



1,2-Bis(4-(tert-butyl)phenyl)ethane-1,2-diol (5).[2] White solid, 61 mg, 94% yield, ***dl : meso*** = 1:1.5. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.2 Hz, 4H, *dl*), 7.31 (d, *J* = 8.2 Hz, 4H, *meso*), 7.27 (d, *J* = 8.2 Hz, 4H, *dl*), 7.15 (d, *J* = 8.2 Hz, 4H, *meso*), 4.73 (s, 2H, *meso*), 4.70 (s, 2H, *dl*), 2.74 (s, 2H, *meso*), 2.03 (s, 2H, *dl*), 1.33 (s, 18H, *dl*), 1.30 (s, 18H, *meso*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.4, 150.9, 137.5, 137.4, 127.0, 126.6, 125.5, 125.2, 78.3, 78.2, 34.7, 34.6, 31.5, 31.4. **HRMS** (ESI) m/z calcd. for $C_{22}H_{30}NaO_2$ $[M+Na]^+$: 349.2138, found: 349.2138.

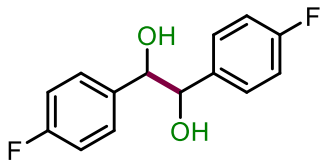


Dimethyl 4,4'-(1,2-dihydroxyethane-1,2-diyl)dibenzoate (6).[2] White solid, 61 mg, 92% yield, ***dl : meso*** = 1:1. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.84 (d, *J* = 8.0 Hz, 4H, *dl*), 7.77 (d, *J* = 8.0 Hz, 4H, *meso*), 7.36 (d, *J* = 8.0 Hz, 4H, *dl*), 7.24 (d, *J* =8.0 Hz, 4H, *meso*), 5.65 (s, 2H, *meso*), 5.54 (s, 2H, *dl*), 4.76 (s, 2H, *meso*), 4.69 (s, 2H, *dl*), 3.83 (s, 6H, *dl*), 3.81 (s, 6H, *meso*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.3, 166.2, 148.5, 147.7, 128.3, 128.2, 128.1, 128.0, 127.6, 127.4, 76.7, 76.5, 52.0, 51.9. **HRMS** (ESI) m/z calcd. for $C_{18}H_{18}NaO_6$ $[M+Na]^+$: 353.0996, found: 353.0991.

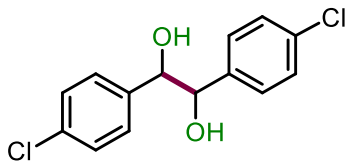


1,2-Bis(4-(trifluoromethyl)phenyl)ethane-1,2-diol (7).[8] White solid, 68 mg, 97% yield, ***dl : meso*** = 1.2:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55-7.46 (m, 8H), 7.24 (d, *J* = 8.1 Hz, 4H, *meso*), 7.18 (d, *J* = 8.1 Hz, 4H, *dl*), 4.91 (s, 2H, *meso*), 4.69 (s, 2H, *dl*), 3.19 (s, 2H, *dl*), 2.68(s, 2H, *meso*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.4, 143.3, 130.6 (q, *J* = 32.3 Hz), 130.4 (q, *J* = 32.3 Hz), 127.5, 125.4, 124.1 (q, *J* = 270.4 Hz), 124.1 (q, *J* = 270.4 Hz), 125.34 (q, *J* = 3.8 Hz), 125.18 (q, *J* = 3.8 Hz), 78.5, 77.3. **^{19}F NMR**

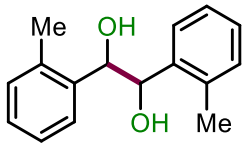
(376 MHz, $CDCl_3$) δ -62.57, -62.60. **HRMS** (ESI) m/z calcd. for $C_{16}H_{12}F_6NaO_2$ $[M+Na]^+$: 373.0634, found: 373.0629.



1,2-Bis(4-fluorophenyl)ethane-1,2-diol (8).[2] White solid, 48 mg, 96% yield, ***dl* : *meso*** = 1.4:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 (dd, *J* = 8.5, 5.5 Hz, 4H, *meso*), 7.04 (dd, *J* = 8.5, 5.5 Hz, 4H, *dl*), 7.00-6.95 (m, 4H, *meso*), 6.94-6.88 (m, 4H, *dl*), 4.81 (s, 2H, *meso*), 4.61 (s, 2H, *dl*), 2.97 (s, 2H, *dl*), 2.36 (s, 2H, *meso*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.8 (d, *J* = 8.2 Hz), 161.4 (d, *J* = 8.3 Hz), 135.5 (d, *J* = 3.1 Hz), 135.3 (d, *J* = 3.2 Hz), 128.8 (d, *J* = 8.0 Hz), 128.7 (d, *J* = 8.1 Hz), 115.3 (d, *J* = 1.2 Hz), 115.1 (d, *J* = 1.2 Hz), 78.9, 77.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.00, -114.05. **HRMS** (ESI) m/z calcd. for $C_{14}H_{12}F_2NaO_2$ $[M+Na]^+$: 273.0698, found: 273.0695.

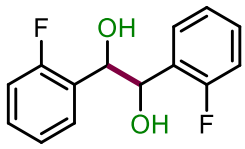


1,2-Bis(4-chlorophenyl)ethane-1,2-diol (9).[2] White solid, 54 mg, 96% yield, ***dl* : *meso*** = 1.5:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 6.7 Hz, 4H, *meso*), 7.18 (d, *J* = 6.7 Hz, 4H, *dl*), 7.02 (d, *J* = 6.7 Hz, 4H, *meso*), 6.94 (d, *J* = 6.7 Hz, 4H, *dl*), 4.74 (s, 2H, *meso*), 4.51 (s, 2H, *dl*), 3.27 (s, 2H, *dl*), 2.70(s, 2H, *meso*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.0, 137.9, 134.0, 133.9, 128.48, 128.44, 128.40, 78.6, 77.2. **HRMS** (ESI) m/z calcd. for $C_{14}H_{12}Cl_2NaO_2$ $[M+Na]^+$: 305.0107, found: 305.0105.

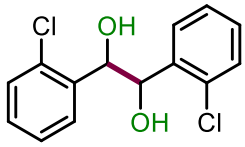


1,2-Di-*o*-tolylethane-1,2-diol (10).[2] White solid, 44 mg, 91% yield, ***dl* : *meso*** = 1.5:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.5 Hz, 2H, *dl*), 7.28 (d, *J* = 7.5 Hz, 2H, *meso*), 7.20-7.11 (m, 10H), 7.07 (d, *J* = 7.5 Hz, 2H, *meso*), 6.91 (d, *J* = 7.5 Hz, 2H, *dl*), 5.15 (s, 2H, *meso*), 4.90 (s, 2H, *dl*), 3.34 (s, 2H, *dl*), 2.57 (s, 2H, *meso*), 2.12 (s, 6H, *meso*),

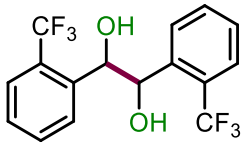
1.63 (s, 6H, *dl*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.2, 138.1, 136.1, 136.0, 130.2, 130.1, 127.7, 127.3, 126.9, 126.1, 126.0, 74.7, 73.3, 19.2, 18.8. **HRMS** (ESI) m/z calcd. for $C_{16}H_{18}NaO_2$ $[M+Na]^+$: 265.1199, found: 265.1197.



1,2-Bis(2-fluorophenyl)ethane-1,2-diol (11). White solid, 43 mg, 86% yield, ***dl : meso*** = 1.5:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44-7.42 (m, 2H), 7.24-7.18 (m, 6H), 7.09 (t, *J* = 7.5 Hz, 2H), 7.02 (t, *J* =7.5 Hz, 2H), 6.92-6.87 (m, 4H), 5.34 (s, 2H, *meso*), 5.12 (s, 2H, *dl*), 3.06 (s, 2H, *dl*), 2.83(s, 2H, *meso*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.2 (d, *J* = 245.9 Hz), 160.1 (d, *J* = 245.9 Hz), 129.7 (d, *J* = 8.4 Hz), 129.4 (d, *J* = 8.4 Hz), 128.6 (d, *J* = 4.3 Hz), 128.4 (d, *J* = 4.3 Hz), 127.0 (d, *J* = 12.8 Hz), 126.5 (d, *J* = 12.8 Hz), 124.2 (d, *J* = 3.4 Hz), 123.9 (d, *J* = 3.4 Hz), 115.3 (d, *J* = 22.3 Hz), 114.9 (d, *J* = 22.3 Hz), 72.0, 70.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.25, -118.62. **HRMS** (ESI) m/z calcd. for $C_{14}H_{12}F_2NaO_2$ $[M+Na]^+$: 273.0698, found: 273.0697.

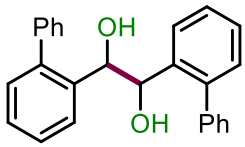


1,2-Bis(2-chlorophenyl)ethane-1,2-diol (12).[8] White solid, 52 mg, 92% yield, ***dl : meso*** = 1.1:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64-7.61 (m, 2H), 7.23-7.12 (m, 14H), 5.56 (s, 2H, *meso*), 5.32 (s, 2H, *dl*), 2.96 (s, 2H, *dl*), 2.91 (s, 2H, *meso*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.4, 136.5, 133.5, 132.7, 129.6, 129.3, 129.2, 129.0, 128.9, 128.8, 126.9, 126.5, 73.1, 72.2. **HRMS** (ESI) m/z calcd. for $C_{14}H_{12}Cl_2NaO_2$ $[M+Na]^+$: 305.0107, found: 305.0106.

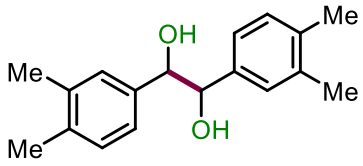


1,2-Bis(2-(trifluoromethyl)phenyl)ethane-1,2-diol (13). White solid, 65 mg, 93% yield, ***dl : meso*** = 1.7:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.8, 2H), 7.61-7.55 (m, 10H), 7.49 (t, *J* = 7.8, 2H), 7.38 (t, *J* = 7.8, 4H), 5.43 (s, 2H, *meso*), 5.36 (s, 2H, *dl*), 3.05 (s, 2H, *dl*), 2.54(s, 2H, *meso*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.9, 138.6, 132.2,

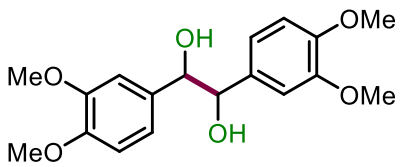
131.9, 129.7, 129.1, 128.7 (q, *J* = 30.0 Hz), 128.4, 128.3, 128.2 (q, *J* = 29.9 Hz), 125.9 (m), 125.5 (m), 122.9 (q, *J* = 2.6 Hz), 120.2 (q, *J* = 2.4 Hz), 72.3, 72.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.64, -57.65. **HRMS** (ESI) m/z calcd. for $C_{16}H_{12}F_6NaO_2$ $[M+Na]^+$: 373.0634, found: 373.0628.



1,2-Di([1,1'-biphenyl]-2-yl)ethane-1,2-diol (14). White solid, 69 mg, 94% yield, ***dl* : *meso*** = 1.5:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26-7.24 (m, 16H), 7.20-7.16 (m, 4H), 7.07-6.97 (m, 8H), 6.76 (br, 8H), 4.96 (s, 2H, *meso*), 4.91 (s, 2H, *dl*), 2.78 (br, 2H, *dl*), 2.28 (br, 2H, *meso*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.4, 142.0, 140.9, 140.7, 137.0, 136.7, 129.8, 129.7, 129.3, 129.2, 128.1, 128.0, 127.8, 127. 6, 127.5, 127.4 (3C), 127.0, 126.8, 74.5, 73.0. **HRMS** (ESI) m/z calcd. for $C_{26}H_{22}NaO_2$ $[M+Na]^+$: 389.1512, found: 389.1503.

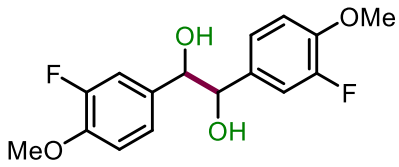


1,2-Bis(3,4-dimethylphenyl)ethane-1,2-diol (15).[9] White solid, 51 mg, 94% yield, ***dl* : *meso*** = 1.5:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.16-7.08 (m, 6H), 7.02-7.01 (m, 4H), 6.87 (d, *J* = 7.7 Hz, 2H), 4.65 (s, 2H, *meso*), 4.64 (s, 2H, *dl*), 2.83 (br, 2H), 2.27 (s, 12H, *dl*), 2.22 (s, 12H, *meso*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.9, 137.7, 136.8, 136.7, 136.4, 136.1, 129.8, 129.5, 128.5, 128.1, 124.8, 124.5, 78.5, 78.3, 19.9, 19.8, 19.7, 19.6. **HRMS** (ESI) m/z calcd. for $C_{18}H_{22}NaO_2$ $[M+Na]^+$: 293.1512, found: 293.1509.

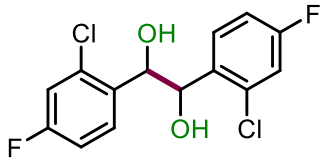


1,2-Bis(3,4-dimethoxyphenyl)ethane-1,2-diol (16).[10] White solid, 64 mg, 96% yield, ***dl* : *meso*** = 1:1.3. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 6.83-6.74 (m, 8H), 6.63-6.61 (m, 4H), 5.21 (s, 2H, *meso*), 5.04 (s, 2H, *dl*), 4.50 (S, 2H, *dl*), 4.46 (S, 2H, *meso*), 3.71 (s,

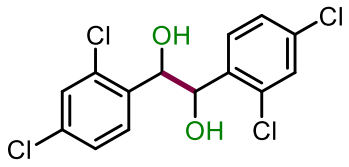
6H, *dl*), 3.68 (s, 6H, *meso*), 3.65 (s, 6H, *dl*), 3.58 (s, 6H, *meso*). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 147.9, 147.8, 147.6, 147.6, 135.8, 134.9, 119.6, 119.4, 111.3, 111.2, 110.9, 110.8, 77.6, 76.8, 55.5, 55.4, 55.3, 55.2. **HRMS** (ESI) m/z calcd. for $C_{18}H_{22}NaO_6$ $[M+Na]^+$: 357.1309, found: 357.1300.



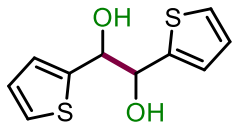
1,2-Bis(3-fluoro-4-methoxyphenyl)ethane-1,2-diol (17). White solid, 57 mg, 92% yield, ***dl : meso*** = 4.1:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.99 (d, *J* = 12.1 Hz, 2H), 6.92-6.87 (m, 4H), 6.81-6.72 (m, 6H), 4.71 (s, 2H, *meso*), 4.55 (s, 2H, *dl*), 3.87(s, 6H, *meso*), 3.84(s, 6H, *dl*), 2.93 (s, 2H, *dl*), 2.30 (s, 2H, *meso*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.1 (d, *J* = 245.9 Hz), 147.3 (d, *J* = 10.7 Hz), 132.8 (d, *J* = 5.8 Hz), 123.0 (d, *J* = 3.5 Hz), 114.7 (d, *J* = 18.9 Hz), 112.9 (d, *J* = 1.8 Hz), 78.3(2C), 56.3, 56.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -134.76, -134.87. **HRMS** (ESI) m/z calcd. for $C_{16}H_{16}F_2NaO_4$ $[M+Na]^+$: 333.0909, found: 333.0904.



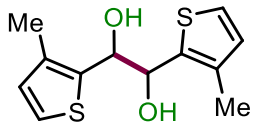
1,2-Bis(2-chloro-4-fluorophenyl)ethane-1,2-diol(18). White solid, 57 mg, 90% yield, ***dl : meso*** = 1.5:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 8.6, 6.2 Hz, 2H), 7.22 (dd, *J* = 8.6, 6.2 Hz, 2H), 7.00-6.93 (m, 6H), 6.90-6.86 (m, 2H), 5.53 (s, 2H, *meso*), 5.23 (s, 2H, *dl*), 2.84 (s, 2H, *dl*), 2.73 (s, 2H, *meso*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.2 (d, *J* = 250.4 Hz), 162.0 (d, *J* = 250.1 Hz), 133.9 (d, *J* = 10.2 Hz), 133.4 (d, *J* = 10.3 Hz), 133.2 (d, *J* = 3.5 Hz), 132.3 (d, *J* = 3.3 Hz), 130.6 (d, *J* = 8.9 Hz), 130.1 (d, *J* = 8.8 Hz), 116.8 (d, *J* = 24.7 Hz), 116.2 (d, *J* = 24.7 Hz), 114.4 (d, *J* = 21.0 Hz), 114.0 (d, *J* = 21.0 Hz), 73.0, 71.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.88, -112.30. **HRMS** (ESI) m/z calcd. for $C_{14}H_{10}Cl_2F_2NaO_2$ $[M+Na]^+$: 340.9918, found: 340.9911.



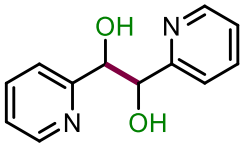
1,2-Bis(2,4-dichlorophenyl)ethane-1,2-diol (19). White solid, 58 mg, 83% yield, ***dl* : *meso*** = 1.1:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 7.7, 1.4 Hz, 2H), 7.29-7.10 (m, 10H), 5.56 (s, 2H, *meso*), 5.32 (s, 2H, *dl*), 2.99 (s, 2H, *dl*), 2.95 (s, 2H, *meso*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 135.7, 134.8, 134.6, 134.3, 133.9, 133.3, 130.2, 129.8, 129.3, 128.7, 127.4, 127.0, 72.8, 71.5. **HRMS** (ESI) m/z calcd. for $C_{14}H_{10}Cl_4NaO_2$ $[M+Na]^+$: 372.9327, found: 372.9322.



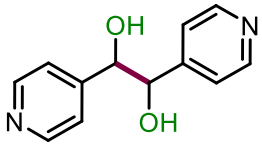
1,2-Di(thiophen-2-yl)ethane-1,2-diol (20).[9] Colorless oil, 42 mg, 93% yield, ***dl* : *meso*** = 2.3:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25-7.21 (m, 4H), 6.95-6.86 (m, 6H), 6.76 (d, *J* = 3.2 Hz, 2H), 5.07 (s, 2H, *meso*), 4.96 (s, 2H, *dl*), 3.53 (s, 2H, *dl*), 3.00 (s, 2H, *meso*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.0, 142.5, 126.7, 126.6, 126.1, 125.9, 125.8, 125.4, 74.9, 74.3. **HRMS** (ESI) m/z calcd. for $C_{10}H_{10}NaO_2S_2$ $[M+Na]^+$: 249.0014, found: 249.0013.



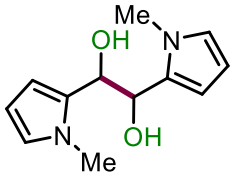
1,2-Bis(3-methylthiophen-2-yl)ethane-1,2-diol (21). Colorless oil, 42 mg, 83% yield, ***dl* : *meso*** = 1.3:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 4.9 Hz, 2H, *meso*), 7.14 (d, *J* = 4.9 Hz, 2H, *dl*), 6.79 (d, *J* = 4.9 Hz, 2H, *meso*), 6.66 (d, *J* = 4.9 Hz, 2H, *dl*), 5.19 (s, 2H, *meso*), 5.02 (s, 2H, *dl*), 3.16 (s, 2H, *dl*), 2.44 (s, 2H, *meso*), 2.16 (s, 6H, *meso*), 1.69 (s, 6H, *dl*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.5, 136.0, 135.8, 135.6, 130.0, 129.6, 124.7, 123.9, 73.9, 72.3, 14.0, 13.1. **HRMS** (ESI) m/z calcd. for $C_{12}H_{14}NaO_2S_2$ $[M+Na]^+$: 277.0327, found: 277.0319.



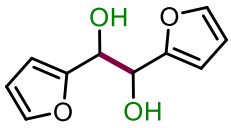
1,2-Di(pyridin-2-yl)ethane-1,2-diol (22).[11] Pale yellow solid, 29 mg, 67% yield, ***dl* : *meso*** = 1.1:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 4.1 Hz, 2H, *dl*), 8.41 (d, *J* = 4.1 Hz, 2H, *meso*), 7.68-7.61 (m, 4H), 7.47-7.42 (m, 4H), 7.20 (dd, *J* = 6.3, 5.6 Hz, 2H), 7.13 (dd, *J* = 6.3, 5.6 Hz, 2H), 5.39 (br, 4H), 5.14 (s, 2H, *meso*), 4.90 (s, 2H, *dl*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.7, 160.5, 147.9, 147.8, 137.0, 136.9, 122.7, 122.5, 122.1, 121.5, 75.4, 75.2. **HRMS** (ESI) m/z calcd. for $C_{12}H_{12}N_2NaO_2$ $[M+Na]^+$: 239.0791, found: 239.0787.



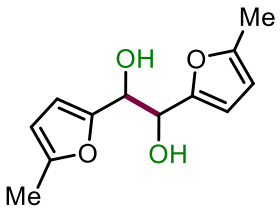
1,2-Di(pyridin-4-yl)ethane-1,2-diol (23).[9] Pale yellow solid, 36 mg, 83% yield, ***dl* : *meso*** = 2:1. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.44 (d, *J* = 5.6 Hz, 2H, *dl*), 8.40 (d, *J* = 5.6 Hz, 2H, *meso*), 7.23 (d, *J* = 5.6 Hz, 2H, *dl*), 7.19 (d, *J* = 5.6 Hz, 2H, *meso*), 5.68 (s, 4H, *dl* and *meso*), 4.76 (s, 2H, *meso*), 4.62 (s, 2H, *dl*). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 151.2, 150.8, 148.8, 148.6, 122.5, 122.2, 75.3, 75.1. **HRMS** (ESI) m/z calcd. for $C_{12}H_{12}N_2NaO_2$ $[M+Na]^+$: 239.0791, found: 239.0786.



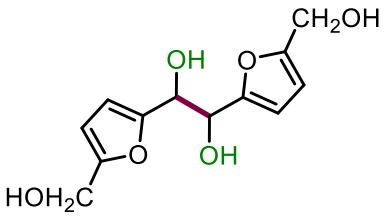
1,2-Bis(1-methyl-1H-pyrrol-2-yl)ethane-1,2-diol (24). White solid, 32 mg, 73% yield, ***dl* : *meso*** = 2.4:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.63 (s, 2 H, *meso*), 6.49 (s, 2 H, *dl*), 6.21-6.13 (m, 4H), 6.03 (s, 2H, *dl*), 4.95 (s, 2H, *meso*), 4.84 (s, 2H, *dl*), 3.60 (s, 6H, *meso*), 3.32 (s, 6H, *dl*), 2.75 (s, 2H, *dl*), 2.16 (s, 2H, *meso*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 131.5, 131.0, 123.8, 123.1, 107.354, 107.4, 107.3, 107.2, 70.4, 69.7, 34.2, 33.8. **HRMS** (ESI) m/z calcd. for $C_{12}H_{16}N_2NaO_2$ $[M+Na]^+$: 243.1104, found: 243.1100.



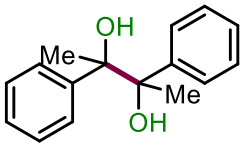
1,2-Di(furan-2-yl)ethane-1,2-diol (25).[9] White solid, 25 mg, 64% yield, ***dl* : *meso*** = 1.1:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 13.1 Hz, 4H), 6.33-6.25 (m, 8H), 5.01 (s, 2H, *meso*), 4.99 (s, 2H, *dl*), 3.02 (s, 2H, *dl*), 2.65 (s, 2H, *meso*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.9, 152.7, 142.6, 142.5, 110.5, 110.4, 108.4, 108.1, 70.2, 70.0. **HRMS** (ESI) m/z calcd. for $C_{10}H_{10}NaO_4$ $[M+Na]^+$: 217.0471, found: 217.0467.



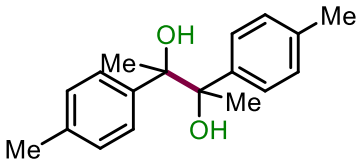
1,2-Bis(5-methylfuran-2-yl)ethane-1,2-diol (26).[2] White solid, 32 mg, 85% yield, ***dl* : *meso*** = 1.5:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.20 (d, *J* = 2.8 Hz, 2H, *meso*), 6.12 (d, *J* = 2.8 Hz, 2H, *dl*), 5.92 (d, *J* = 2.8 Hz, 2H, *meso*), 5.86 (d, *J* = 2.8 Hz, 2H, *dl*), 4.91 (s, 4H, *dl* and *meso*), 2.89 (s, 2H, *dl*), 2.43 (s, 2H, *meso*), 2.28 (s, 6H, *meso*), 2.25 (s, 6H, *dl*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.5, 152.2, 151.0, 150.9, 109.6, 108.9, 106.5, 106.3, 70.0, 69.9, 13.7, 13.6. **HRMS** (ESI) m/z calcd. for $C_{12}H_{14}NaO_4$ $[M+Na]^+$: 245.0784, found: 245.0779.



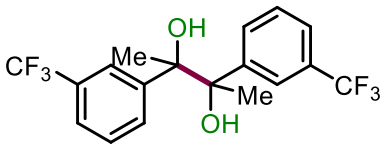
1,2-Bis(5-(hydroxymethyl)furan-2-yl)ethane-1,2-diol (27). Pale yellow solid, 44 mg, 87% yield, ***dl*** primary (the product was obtained without extraction). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 6.20 (d, *J* = 7.1 Hz, 4H), 5.34 (s, 2H), 5.15 (s, 2H), 4.66 (s, 2H), 4.37 (d, *J* = 4.5 Hz, 4H) **^{13}C NMR** (100 MHz, DMSO-d_6) δ 155.4, 154.0, 107.5, 107.4, 68.9, 55.9. **HRMS** (ESI) m/z calcd. for $C_{12}H_{14}NaO_6$ $[M+Na]^+$: 277.0683, found: 277.0687.



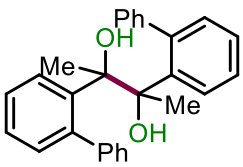
2,3-Diphenylbutane-2,3-diol (28).[2] White solid, 46 mg, 95% yield, ***dl : meso*** = 1.6:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24-7.17 (m, 20 H, *dl* and *meso*), 2.66 (s, 2H, *dl*), 2.35 (s, 2H, *meso*), 1.57 (s, 6H, *meso*), 1.49 (s, 6H, *dl*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.9, 143.6, 127.5, 127.4, 127.3, 127.2, 127.1, 127.0, 79.0, 78.7, 25.2, 25.0. **HRMS** (ESI) m/z calcd. for $C_{16}H_{18}NaO_2$ $[M+Na]^+$: 265.1199, found: 265.1193.



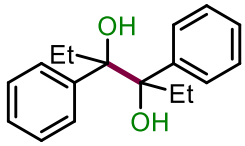
2,3-Di-*p*-tolylbutane-2,3-diol (29).[12] White solid, 50 mg, 93% yield, ***dl : meso*** = 1.2:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18-7.06 (m, 16 H, *dl* and *meso*), 2.66 (s, 2H, *dl*), 2.36 (s, 6H, *dl*), 2.34 (s, 6H, *meso*), 2.29 (s, 2H, *meso*), 1.56 (s, 6H, *meso*), 1.48 (s, 6H, *dl*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.0, 140.7, 136.6, 136.5, 128.1, 128.0, 127.4, 127.0, 78.9, 78.6, 25.3, 25.1, 21.1, 21.0. **HRMS** (ESI) m/z calcd. for $C_{18}H_{22}NaO_2$ $[M+Na]^+$: 293.1512, found: 293.1504.



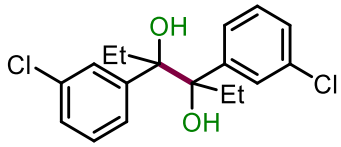
2,3-Bis(3-(trifluoromethyl)phenyl)butane-2,3-diol (30). White solid, 66 mg, 87% yield, ***dl : meso*** = 1.5:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53-7.31 (m, 16 H, *dl* and *meso*), 2.69 (s, 2H, *dl*), 2.52 (s, 2H, *meso*), 1.61 (s, 6H, *meso*), 1.54 (s, 6H, *dl*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.9, 145.5, 132.0, 131.6, 131.1 (q, *J* = 32.1Hz), 129.1, 129.0, 125.6 (q, *J* = 270.6 Hz), 125.5 (q, *J* = 3.8 Hz), 125.3 (q, *J* = 3.8 Hz), 80.0, 79.8, 26.2, 26.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.63, -62.70. **HRMS** (ESI) m/z calcd. for $C_{18}H_{16}F_6NaO_2$ $[M+Na]^+$: 401.0947, found: 401.0938.



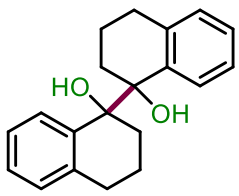
2,3-Di([1,1'-biphenyl]-2-yl)butane-2,3-diol (31). White solid, 71 mg, 90% yield, ***dl* : *meso*** = 1.7:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64-7.58 (m, 12H), 7.53-7.50 (m, 6H), 7.47-7.43 (m, 8 H), 7.40-7.32 (m, 10H), 2.66 (s, 2H, *dl*), 2.33 (s, 2H, *meso*), 1.66 (s, 6H, *meso*), 1.59 (s, 6H, *dl*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.1, 142.7, 140.8, 139.9, 128.9, 128.0, 127.6, 127.4, 127.23, 127.2, 126.1, 126.0, 79.0, 78.8, 25.4, 25.2. **HRMS** (ESI) m/z calcd. for $C_{28}H_{26}NaO_2$ $[M+Na]^+$: 417.18 25, found: 417.1825.



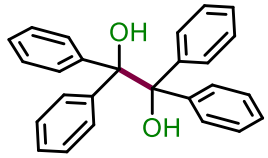
3,4-Diphenylhexane-3,4-diol (32).[2] White solid, 45 mg, 83% yield, ***dl* : *meso*** = 1.6:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24-7.15 (m, 20H, *dl* and *meso*), 2.61 (s, 2H, *dl*), 2.35 (dq, *J* = 14.7, 7.4 Hz, 2H), 2.08 (s, 2H, *meso*), 2.07 (dq, *J* = 14.7, 7.4, Hz, 2H), 1.70 (dq, *J* = 17.4, 7.4 Hz, 2H), 1.59 (dq, *J* = 14.7, 7.4 Hz, 2H), 0.61 (t, *J* = 7.3 Hz, 6H), 0.58 (t, *J* = 7.3 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.5, 140.5, 128.4, 127.8, 127.5, 127.2, 127.0, 126.8, 82.1, 82.0, 28.2, 27.8, 7.8, 7.7. **HRMS** (ESI) m/z calcd. for $C_{18}H_{22}NaO_2$ $[M+Na]^+$: 293.1512, found: 293.1504.



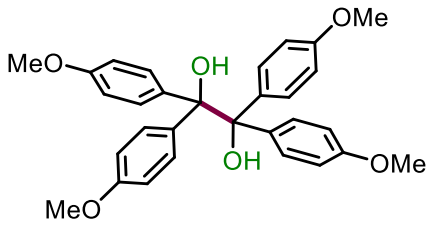
3,4-Bis(3-chlorophenyl)hexane-3,4-diol (33). White solid, 55 mg, 81% yield, ***dl* : *meso*** = 1.2:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.14 (m, 14 H, *dl* and *meso*), 6.94 (br, 2 H, *dl*), 2.62 (s, 2H, *dl*), 2.29 (dq, *J* = 14.6, 7.4 Hz, 2H), 2.13 (s, 2H, *meso*), 2.07 (dq, *J* = 14.6, 7.4 Hz, 2H), 1.64 (dq, *J* = 14.7, 7.4 Hz, 2H), 1.54 (dq, *J* = 14.7, 7.4 Hz, 2H), 0.62 (t, *J* = 7.1 Hz, 6H), 0.58 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.70, 142.53, 133.81, 133.64, 128.68, 128.6, 128.5, 128.2, 127.3, 127.1, 126.5, 126.0, 81.8, 81.7, 28.3, 27.7, 7.7, 7.5. **HRMS** (ESI) m/z calcd. for $C_{18}H_{20}Cl_2NaO_2$ $[M+Na]^+$: 361.0733, found: 361.0724.



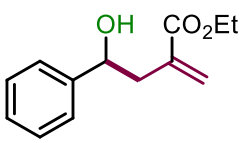
3,3',4,4'-Tetrahydro-[1,1'-binaphthalene]-1,1'(2H,2'H)-diol (34). White solid, 48 mg, 82% yield, ***dl* : *meso*** = 1.8:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.6 Hz, 2H), 7.25-7.17 (m, 4H), 7.09 (d, *J* = 7.6 Hz, 2H), 3.18 (s, 2H), 2.72-2.68 (m, 2H), 2.59-2.50 (m, 2H), 1.67-1.58 (m, 6H), 1.30-1.23 (m, 2H). **^{13}C NMR of (*dl*)-34** (100 MHz, $CDCl_3$) δ 140.7, 138.5, 129.2, 129.0, 127.3, 126.5, 77.3, 36.6, 31.3, 20.2. **^{1}H NMR of (*meso*)-34** (400 MHz, $CDCl_3$) δ 7.17-7.14 (m, 2 H), 7.03-6.94 (m, 6H), 2.64 (s, 2H), 2.61-2.60 (m, 2H), 2.22-2.16 (m, 2H), 2.14-2.04 (m, 2H), 1.70-1.64 (m, 2H), 1.60-1.51 (m, 2H). **^{13}C NMR of (*meso*)-34** (100 MHz, $CDCl_3$) δ 140.2, 139.3, 128.4, 128.3, 127.3, 125.7, 78.3, 35.6, 31.0, 20.5, **HRMS** (ESI) m/z calcd. for $C_{20}H_{22}NaO_2$ $[M+Na]^+$: 317.1512, found: 317.1509.



1,1,2,2-Tetraphenylethane-1,2-diol (35).[2] White solid, 63 mg, 86% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30-7.28 (m, 8 H), 7.16-7.15 (m, 12H), 3.02 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.3, 128.7, 127.4, 127.1, 83.2. **HRMS** (ESI) m/z calcd. for $C_{26}H_{22}NaO_2$ $[M+Na]^+$: 389.1512, found: 389.1507.

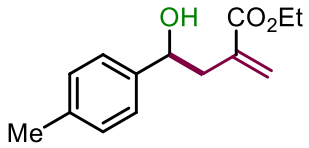


1,1,2,2-Tetrakis(4-methoxyphenyl)ethane-1,2-diol (36).[13] White solid, 83 mg, 85% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.8 Hz, 8 H), 6.68 (d, *J* = 8.8 Hz, 8 H), 3.76 (s, 2H), 3.73 (s, 12H), 2.93 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.4, 159.7, 138.2, 137.9, 131.3, 129.2, 115.3, 113.9, 84.2, 76.7, 56.7, 56.6. **HRMS** (ESI) m/z calcd. for $C_{30}H_{30}NaO_6$ $[M+Na]^+$: 509.1935, found: 509.1929.

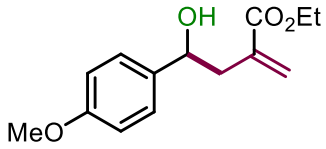


Ethyl-4-hydroxy-2-methylene-4-phenylbutanoate (37). Colorless oil, 71 mg, 81%

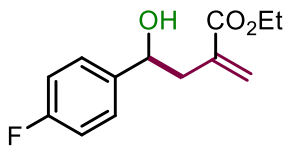
yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36-7.23 (m, 5H), 6.21 (d, *J* = 0.7 Hz, 1H), 5.57 (d, *J* = 0.7 Hz, 1H), 4.86 (dt, *J* = 8.1, 4.0 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 3.05 (d, J = 3.0 Hz, 1H), 2.92 (s, 1H), 2.77 (dd, *J* = 14.0, 3.8 Hz, 1H), 2.65 (dd, *J* = 14.0, 8.4 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.8, 144.1, 137.2, 128.4, 128.2, 127.5, 125.8, 73.2, 61.1, 42.5, 14.2. **HRMS** (ESI) m/z calcd. for $C_{13}H_{16}NaO_3$ $[M+Na]^+$: 243.0992, found: 243.0988.



Ethyl-4-hydroxy-2-methylene-4-(*p*-tolyl)butanoate (38).[14] Colorless oil, 74 mg, 79% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 7.6 Hz, 2H), 7.13 (d, *J* = 7.6 Hz, 2H), 6.21 (s, 1H), 5.57 (s, 1H), 4.82 (m, 1H), 4.20 (q, *J* = 7.0 Hz, 2H), 2.82 (s, 1H), 2.74 (dd, *J* = 14.0, 3.8 Hz, 1H), 2.65 (dd, *J* = 13.7, 8.4 Hz, 1H), 2.32 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.8, 141.1, 137.3, 137.1, 129.1, 128.1, 125.8, 73.0, 61.1, 42.5, 21.2, 14.2. **HRMS** (ESI) m/z calcd. for $C_{14}H_{18}NaO_3$ $[M+Na]^+$: 257.1148, found: 257.1148.

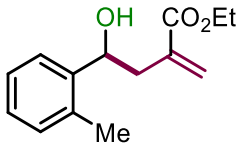


Ethyl-4-hydroxy-4-(4-methoxyphenyl)-2-methylenebutanoate (39).[15] Colorless oil, 74 mg, 74% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 6.22 (s, 1H), 5.58 (s, 1H), 4.83 (m, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 2.75 (dd, *J* = 14.0, 3.9 Hz, 1H), 2.67 (dd, *J* = 14.2, 8.3 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.8, 159.1, 137.4, 136.3, 128.1, 127.1, 113.9, 72.9, 61.1, 55.4, 42.6, 14.3. **HRMS** (ESI) m/z calcd. for $C_{14}H_{18}NaO_4$ $[M+Na]^+$: 273.1097, found: 273.1098.

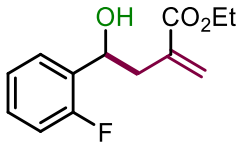


Ethyl-4-(4-fluorophenyl)-4-hydroxy-2-methylenebutanoate (40).[15] Colorless oil, 73 mg, 77% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.29 (m, 2H), 7.03-6.98 (m, 2H),

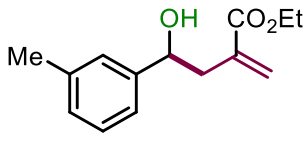
6.22 (d, *J* = 0.7 Hz 1H), 5.56 (s, 1H), 4.85 (dt, *J* = 8.1, 4.0 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.05 (d, *J* = 3.0 Hz, 1H), 2.74 (dd, *J* = 14.0, 4.2 Hz, 1H), 2.63 (dd, *J* = 14.0, 8.2 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.8, 162.2 (d, *J* = 245.0 Hz), 139.8 (d, *J* = 245.0 Hz), 137.0, 128.4, 127.5 (d, *J* = 8.0 Hz), 115.2 (d, *J* = 21.3 Hz), 72.6, 61.2, 42.7, 14.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.36. **HRMS** (ESI) m/z calcd. for $C_{13}H_{15}FNaO_3$ $[M+Na]^+$: 261.0897, found: 261.0895.



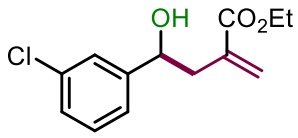
Ethyl-4-hydroxy-2-methylene-4-(o-tolyl)butanoate (41). Colorless oil, 71 mg, 76% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.6 Hz, 1H), 7.21-7.11 (m, 3H), 6.26 (s, 1H), 5.64 (s, 1H), 5.08 (dt, *J* = 5.8, 3.0 Hz, 1H), 4.22 (q, *J* = 6.9 Hz, 2H), 2.75 (dd, *J* = 14.0, 2.9 Hz, 1H), 2.67 (d, *J* = 2.8 Hz, 1H), 2.54 (dd, *J* = 14.0, 9.0 Hz, 1H), 2.36 (s, 3H) 1.31 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 142.3, 134.4, 130.4, 128.4, 127.3, 126.3, 125.1, 69.4, 61.1, 41.5, 19.1, 14.3. **HRMS** (ESI) m/z calcd. for $C_{14}H_{18}NaO_3$ $[M+Na]^+$: 257.1148, found: 257.1148.



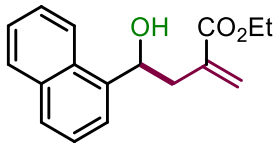
Ethyl-4-(2-fluorophenyl)-4-hydroxy-2-methylenebutanoate (42). Colorless oil, 78 mg, 82% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (t, *J* = 7.5 Hz, 1H), 7.24-7.19 (m, 1H), 7.14-7.10 (m, 1H), 7.01-6.97 (m, 1H), 6.20 (s, 1H), 5.55 (s, 1H), 5.18 (m, 1H), 4.21 (q, *J* = 7.0 Hz, 2H), 3.34 (d, *J* = 4.0 Hz, 1H), 2.80 (dd, *J* = 14.0, 4.2 Hz, 1H), 2.74 (dd, *J* = 14.0, 7.9 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.1, 159.73 (d, *J* = 245.3 Hz), 137.0, 131.0 (d, *J* = 13.2 Hz), 128.8 (d, *J* = 8.2 Hz), 128.4, 127.4 (d, *J* = 4.6 Hz), 124.2 (d, *J* = 3.4 Hz), 115.1 (d, *J* = 21.7 Hz), 67.7, 67.6, 61.3, 41.1, 14.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -119.21. **HRMS** (ESI) m/z calcd. for $C_{13}H_{15}FNaO_3$ $[M+Na]^+$: 261.0897, found: 261.0899.



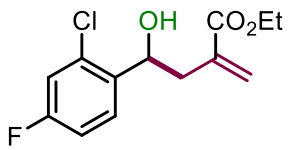
Ethyl-4-hydroxy-2-methylene-4-(m-tolyl)butanoate (43). Colorless oil, 71 mg, 76% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25-7.13 (m, 3H), 7.07 (d, *J* = 7.3 Hz, 1H), 6.23 (s, 1H), 5.6 (s, 1H), 4.83 (m, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.77 (dd, *J* = 13.8, 3.8 Hz, 1H), 2.65 (dd, *J* = 14.0, 8.6 Hz, 1H), 2.34 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.8, 144.1, 138.1, 137.4, 128.4, 128.3, 128.1, 126.5, 122. 9, 73.2, 61.1, 42.6, 21.5, 14.3. **HRMS** (ESI) m/z calcd. for $C_{14}H_{18}NaO_3$ $[M+Na]^+$: 257.1148, found: 257.1147.



Ethyl-4-(3-chlorophenyl)-4-hydroxy-2-methylenebutanoate (44). Colorless oil, 75 mg, 74% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.27-7.21 (m, 3H), 6.24 (s, 1H), 5.59 (s, 1H), 4.85 (m, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.06 (d, *J* = 3.4 Hz 1H), 2.77 (dd, *J* = 14.0, 3.8 Hz, 1H), 2.62 (dd, *J* = 14.0, 8.4 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 146.2, 136.9, 134.4, 129.7, 128.6, 127.6, 126.0, 124.0, 72.7, 61.3, 42.7, 14.3. **HRMS** (ESI) m/z calcd. for $C_{13}H_{15}ClNaO_3$ $[M+Na]^+$: 277.0602, found: 277.0599.

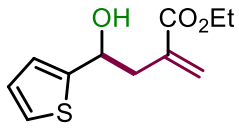


Ethyl-4-hydroxy-2-methylene-4-(naphthalen-1-yl)butanoate (45).[14] Colorless oil, 82 mg, 76% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 4H), 7.50-7.46 (m, 3H), 6.24 (s, 1H), 5.60 (s, 1H), 5.05 (m, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.04 (d, *J* = 3.2 Hz, 1H), 2.88 (dd, *J* = 14.0, 4.0 Hz, 1H), 2.75 (dd, *J* = 14.0, 8.4 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.9, 141.5, 137.2, 133.4, 133.0, 128.3, 128.2, 128.1, 127.8, 126.2, 125.9, 124.5, 124.1, 73.3, 61.2, 42.5, 14.2. **HRMS** (ESI) m/z calcd. for $C_{17}H_{18}NaO_3$ $[M+Na]^+$: 293.1148, found: 293.1149.

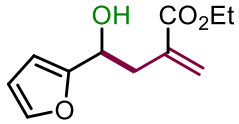


Ethyl-4-(2-chloro-4-fluorophenyl)-4-hydroxy-2-methylenebutanoate (46).

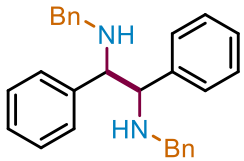
Colorless oil, 78 mg, 72% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56-7.52 (m, 1H), 7.06-6.95 (m, 2H), 6.22 (s, 1H), 5.58 (s, 1H), 5.19 (m, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.63 (s, 1H), 2.79 (dd, *J* = 14.1, 3.2 Hz, 1H), 2.61 (dd, *J* = 14.1, 8.6 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.5, 161.6 (d, *J* = 248.7 Hz), 137.4 (d, *J* = 3.4 Hz), 137.0, 132.2 (d, *J* = 10.2 Hz), 128.8, 128.6 (d, *J* = 8.7 Hz), 116.6 (d, *J* = 24.7 Hz), 114.2 (d, *J* = 20.8 Hz), 69.8, 61.5, 40.7, 14.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.69. **HRMS** (ESI) m/z calcd. for $C_{13}H_{14}ClFNaO_3$ $[M+Na]^+$: 295.0508, found: 295.0507.



Ethyl-4-hydroxy-2-methylene-4-(thiophen-2-yl)butanoate (47).[14] Colorless oil, 78 mg, 86% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23-7.21 (m, 1H), 6.95-9.94 (m, 2H), 6.25 (s, 1H), 5.63 (s, 1H), 5.13 (dt, *J* = 8.2, 4.1 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.07 (d, *J* = 4.0 Hz, 1H), 2.87 (dd, *J* = 14.0, 4.6 Hz, 1H), 2.79 (dd, *J* = 14.0, 8.2 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 148.1, 136.7, 128.6, 126.7, 124.5, 123.6, 69.3, 61.2, 42.6, 14.2. **HRMS** (ESI) m/z calcd. for $C_{11}H_{14}NaO_3S$ $[M+Na]^+$: 249.0556, found: 249.0557.

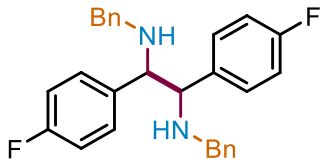


Ethyl-4-(furan-2-yl)-4-hydroxy-2-methylenebutanoate (48).[14] Colorless oil, 61 mg, 73% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (m, 1H), 6.32-6.31 (m, 1H), 6.25 (m, 2H), 5.64 (s, 1H), 4.90 (dt, *J* = 8.4, 5.0 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.90 (dd, *J* = 14.1, 4.9 Hz, 1H), 2.82 (dd, *J* = 14.0, 8.0 Hz, 1H), 2.77 (d, *J* = 5.0 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.7, 156.1, 142.0, 136.7, 128.4, 110.2, 106.2, 67.1, 61.2, 38.9, 14.3. **HRMS** (ESI) m/z calcd. for $C_{11}H_{14}NaO_4$ $[M+Na]^+$: 233.0784, found: 233.0782.

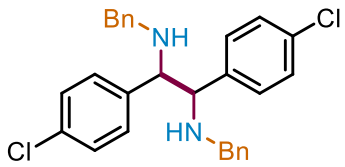


N,N-dibenzyl-1,2-diphenylethane-1,2-diamine (49).[2] White solid, 70 mg, 89% yield,

dl : meso = 1.6:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.12(m, 32H), 7.04 (dd, *J* = 7.7, 1.8 Hz, 4H, *meso*), 6.97-6.96 (m, 4H, *dl*), 3.75 (s, 2H, *dl*), 3.71 (s, 2H, *meso*), 3.66 (d, *J* =13.3 Hz, 2H, *meso*), 3.53 (d, *J* = 13.7 Hz, 2H, *dl*), 3.49 (d, *J* = 13.3 Hz, 2H, *meso*), 3.30 (d, *J* = 13.7 Hz, *dl*), 1.92 (br, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.3, 141.0, 140.8, 140.5, 128.7, 128.5, 128.4, 128.3, 128.2, 128.11, 128.10, 128.0, 127.8, 127.0, 126.9, 126.8, 68.5, 67.3, 51.5, 51.1. **HRMS** (ESI) m/z calcd. for $C_{28}H_{28}N_2Na$ $[M+Na]^+$: 415.2145, found: 415.2140.

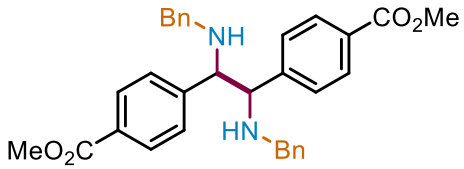


N,N-dibenzyl-1,2-bis(4-fluorophenyl)ethane-1,2-diamine (50).[2] White solid, 65 mg, 76% yield, ***dl : meso*** = 1.5:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.17 (m, 20H), 7.01-6.94 (m, 12H), 6.86-6.82(m, 4H), 3.70 (s, 2H, *dl*), 3.64(d, *J* =13.3 Hz, 2H, *meso*), 3.63 (s, 2H, *meso*), 3.54 (d, *J* = 13.6 Hz, 2H, *dl*), 3.47 (d, *J* =13.3 Hz, 2H, *meso*), 3.29 (d, *J* = 13.6 Hz, 2H, *dl*), 1.89 (br, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.5 (d, *J* = 245.6 Hz), 162.0 (d, *J* = 245.0 Hz), 140.5, 140.2, 136.8 (d, *J* = 2.9 Hz), 136.3 (d, *J* =3.0 Hz), 130.1 (d, *J* = 7.9 Hz), 129.5 (d, *J* = 8.0 Hz), 128.5, 128.4, 128.2, 128.0, 127.1, 127.0, 115.3 (d, *J* = 21.2 Hz), 115.0 (d, *J* =21.2 Hz), 67.9, 66.5, 51.4, 51.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.89, -115.62. **HRMS** (ESI) m/z calcd. for $C_{28}H_{26}F_2N_2Na$ $[M+Na]^+$: 451.1956, found: 451.1955.

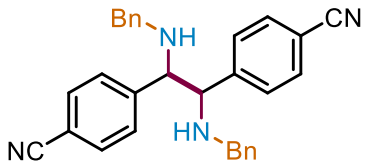


N,N-Dibenzyl-1,2-bis(4-chlorophenyl)ethane-1,2-diamine (51).[16] White solid, 65 mg, 71% yield, ***dl : meso*** = 1.8:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.13 (m, 28H), 7.01 (d, *J* = 6.7 Hz, 4H), 6.95 (d, *J* =8.3 Hz, 4H), 3.71 (s, 2H, *dl*), 3.65 (d, *J* = 13.3 Hz, 2H, *meso*), 3.63 (s, 2H, *meso*), 3.54 (d, *J* = 13.6 Hz, 2H, *dl*), 3.46 (d, *J* =13.3 Hz, 2H, *meso*), 3.30 (d, *J* = 13.6 Hz, 2H, *dl*), 1.87 (br, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.2, 140.0, 139.5, 139.0, 133.4, 132.9, 130.0, 129.4, 128.6, 128.5, 128.4, 128.2, 128.0, 127.1, 127.0, 67.7, 66.4, 51.3, 51.1. **HRMS** (ESI) m/z calcd. for $C_{28}H_{26}Cl_2N_2Na$ $[M+Na]^+$:

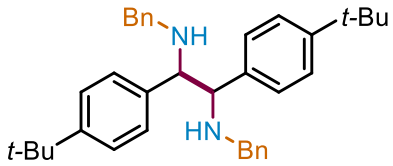
483.1365, found: 483.1360.



Dimethyl 4,4'-(1,2-bis(benzylamino)ethane-1,2-diyl)dibenzoate (52).[17] White solid, 85 mg, 84% yield, ***dl : meso*** = 1.2:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 4H, *dl*), 7.82 (d, *J* = 8.2 Hz, 4H, *meso*), 7.28-7.19 (m, 20H), 7.09 (d, *J* = 8.1 Hz, 4H, *dl*), 7.01 (d, *J* =6.6 Hz, 4H, *meso*), 3.90 (s, 6H, *dl*), 3.87 (s, 2H, *dl*), 3.85 (s, 6H, *meso*), 3.76 (s, 2H, *meso*), 3.63 (d, *J* =13.2 Hz, 2H, *meso*), 3.56 (d, *J* = 13.6 Hz, 2H, *dl*), 3.47 (d, *J* = 13.2 Hz, 2H, *meso*), 3.32 (d, *J* = 13.6 Hz, 2H, *dl*), 2.10 (br, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.0, 166.9, 146.4, 145.9, 140.1, 139.9, 129.6, 129.5, 128.6, 128.5, 128.4, 128.1, 128.0, 127.9, 127.1, 127.0, 68.1, 66.7, 52.1, 52.0, 51.4, 51.1. **HRMS** (ESI) m/z calcd. for $C_{32}H_{32}N_2NaO_4$ $[M+Na]^+$: 531.2254, found: 531.2250.

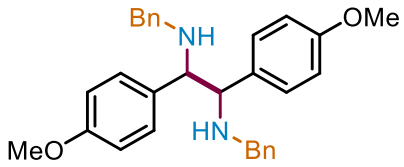


4,4'-(1,2-Bis(benzylamino)ethane-1,2-diyl)dibenzonitrile (53).[2] White solid, 80mg, 90% yield, ***dl : meso*** = 1.2:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 6.7 Hz, 4H, *dl*), 7.47 (d, *J* = 6.7 Hz, 4H, *meso*), 7.31-7.19 (m, 20H), 7.13 (d, *J* = 6.7 Hz, 4H, *dl*), 7.05 (d, *J* = 8.3 Hz, 4H, *meso*), 3.88 (s, 2H, *dl*), 3.72 (s, 2H, *meso*), 3.64 (d, *J* = 13.3 Hz, 2H, *meso*), 3.59 (d, *J* = 13.6 Hz, 2H, *dl*), 3.47 (d, *J* =13.3 Hz, 2H, *meso*), 3.35 (d, *J* = 13.6 Hz, 2H, *dl*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.5, 145.7, 139.6, 139.5, 132.1, 129.3, 128.7, 128.6, 128.1, 128.0, 127.3, 118.8, 118.7, 111.7, 111.4, 67.9, 66.4, 51.4, 51.2. **HRMS** (ESI) m/z calcd. for $C_{30}H_{26}N_4Na$ $[M+Na]^+$: 465.2050, found: 465.2050.

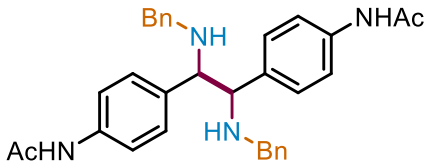


N,N-Dibenzyl-1,2-bis(4-(tert-butyl)phenyl)ethane-1,2-diamine (54). White solid obtained by filtration, 61 mg, 61% yield, ***dl*** primary. **^{1}H - NMR** (400 MHz, $CDCl_3$) δ

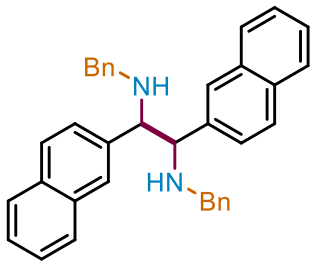
7.35-7.16 (m, 14H), 6.93-6.91 (m, 4H), 3.66 (s, 2H), 3.52 (d, *J* = 13.9 Hz, 2H), 3.28 (d, *J* = 13.9 Hz, 2H), 1.72 (br, 2H), 1.35 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.6, 140.7, 138.1, 128.3, 128.2, 127.9, 126.7, 125.4, 67.1, 51.0, 34.7, 31.6. **HRMS** (ESI) m/z calcd. for $C_{36}H_{44}N_2Na$ $[M+Na]^+$: 527.3397, found: 527.3388.



N,N-Dibenzyl-1,2-bis(4-methoxyphenyl)ethane-1,2-diamine (55).[2] White solid obtained by filtration, 40 mg, 44% yield, ***dl*** primary. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24-7.16 (m, 10H), 6.97 (d, *J* = 6.7 Hz, 4H), 6.87 (d, *J* = 8.6 Hz, 4H), 3.82 (s, 6H), 3.65 (s, 2H), 3.52 (d, *J* = 13.8 Hz, 2H), 3.27 (d, *J* = 13.8 Hz, 2H), 1.68 (br, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.2, 140.5, 132.9, 129.7, 128.3, 128.0, 126.8, 113.9, 66.7, 55.4, 51.0. **HRMS** (ESI) m/z calcd. for $C_{30}H_{32}N_2NaO_2$ $[M+Na]^+$: 475.2356, found: 475.2350.

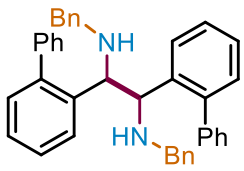


N,N'-((1,2-Bis(benzylamino)ethane-1,2-diyl)bis(4,1-phenylene))diacetamide (56).[2] White solid obtained by filtration, 67 mg, 66% yield, ***dl*** primary. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 9.87 (s, 2H), 7.47 (d, *J* = 6.7 Hz, 4H), 7.24-7.06 (m, 14H), 3.67 (s, 2H), 3.47 (d, *J* = 13.6 Hz, 2H), 3.28 (d, *J* = 13.6 Hz, 2H), 2.15 (br, 2H), 2.03 (s, 6H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 168.1, 140.6, 138.1, 135.7, 128.4, 128.0, 127.6, 126.5, 118.4, 66.1, 50.3, 24.0. **HRMS** (ESI) m/z calcd. for $C_{32}H_{34}N_4NaO_2$ $[M+Na]^+$: 529.2574, found: 529.2568.

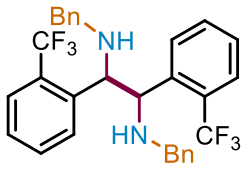


N,N-Dibenzyl-1,2-di(naphthalen-2-yl)ethane-1,2-diamine (57).[2] White solid

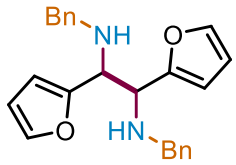
obtained by filtration, 80 mg, 81% yield, ***dl*** primary. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90-7.81 (m, 8H), 7.55-7.51 (m, 6H), 7.17-7.15 (m, 6H), 6.90 (d, *J* = 3.2 Hz, 4H), 4.02 (*s*, 2H), 3.54 (d, *J* = 13.8 Hz, 2H), 3.30 (d, *J* = 13.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.2, 138.5, 133.5, 133.4, 128.6, 128.5, 128.3, 128.1, 128.0, 127.9, 126.8, 126.2, 126.1, 126.0, 67.1, 51.0. **HRMS** (ESI) m/z calcd. for $C_{36}H_{32}N_2Na$ $[M+Na]^+$: 515.2458, found: 515.2449.



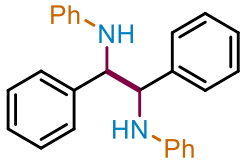
1,2-Di([1,1'-biphenyl]-2-yl)-N,N-dibenzylethane-1,2-diamine (58). White solid, 81 mg, 74% yield, ***dl : meso*** = 1.4:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38-7.00 (m, 52H), 6.75-6.45 (br, 4H), 4.16 (s, 2H, *dl*), 4.16 (s, 2H, *meso*), 3.70 (d, *J* = 13.0 Hz, 2H, *meso*), 3.66 (d, *J* = 13.0 Hz, 2H, *meso*), 3.57 (d, *J* = 13.7 Hz, 2H, *dl*), 3.38 (d, *J* = 13.7 Hz, 2H, *dl*), 2.24 (br, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.7, 143.2, 141.4, 141.3, 141.1, 138.9, 138.1, 129.8, 129.7, 129.4, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.5, 127.2, 126.8, 126.7, 126.6, 126.5, 126.5, 126.3, 63.7, 60.7, 51.4, 50.9. **HRMS** (ESI) m/z calcd. for $C_{40}H_{36}N_2Na$ $[M+Na]^+$: 567.2771, found: 567.2764.



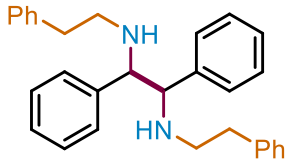
N,N-Dibenzyl-1,2-bis(2-(trifluoromethyl)phenyl)ethane-1,2-diamine (59). White solid, 75 mg, 71% yield, ***dl : meso*** = 1:1.2. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.8 Hz, 2H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.54-7.47 (m, 6H), 7.36-7.16 (m, 20H), 7.08 (d, *J* = 7.8 Hz, 4H), 4.48 (s, 2H, *dl*), 4.42 (s, 2H, *meso*), 3.61 (d, *J* = 12.5 Hz, 2H, *meso*), 3.63-3.40 (m, 6H), 2.09 (br, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.2 (q, *J* = 9.8 Hz), 140.7 (q, *J* = 2.1 Hz), 132.4 (q, *J* = 3.1 Hz), 132.1 (q, *J* = 7.7 Hz), 130.0 (m), 129.0 (m), 128.5, 128.3, 128.2, 127.7, 127.5, 127.4, 127.1, 126.8, 125.5, 123.2 (m), 123.0 (m), 62.6, 62.4, 51.6, 51.3. **HRMS** (ESI) m/z calcd. for $C_{30}H_{26}F_6N_2Na$ $[M+Na]^+$: 551.1892, found: 551.1883.



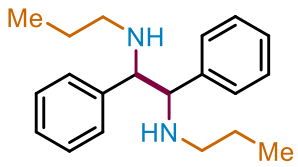
N, N-Dibenzyl-1,2-di(furan-2-yl)ethane-1,2-diamine (60). White solid, 47 mg, 63% yield, ***dl*** primary. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36-7.15 (m, 12H), 6.32 (m, 2H), 6.13 (d, *J* = 2.8 Hz, 2H), 4.04 (s, 2H), 3.71 (d, *J* = 13.5 Hz, 2H), 3.49 (d, *J* = 13.5 Hz, 2H), 1.94 (br, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.1, 142.1, 140.2, 128.4, 128.2, 127.0, 110.1, 108.6, 58.9, 51.2. **HRMS** (ESI) m/z calcd. for $C_{24}H_{24}N_2NaO_2$ $[M+Na]^+$: 395.1730, found: 395.1726



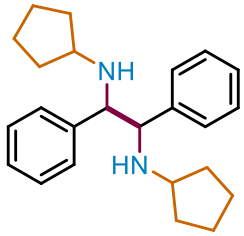
N,N,1,2-Tetraphenylethane-1,2-diamine (61).[18] White solid, 45 mg, 62% yield, ***dl* : *meso*** = 1:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22-6.94 (m, 28H), 6.67-6.34 (m, 4H), 6.52-6.49 (m, 8H), 4.96 (br, 2H, meso), 4.55 (br, 2CH, 4NH). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.2, 146.6, 140.1, 138.4, 129.4, 129.2, 128.5, 128.4, 127.7, 127.5, 118.2, 118.0, 114.2, 113.9, 64.1, 62.1. **HRMS** (ESI) m/z calcd. for $C_{26}H_{24}N_2$ Na $[M+ Na]^+$: 387.1832, found: 387.1830.



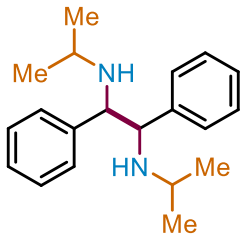
N,N-Diphenethyl-1,2-diphenylethane-1,2-diamine (62). Yellowish brown solid, 49 mg, 58% yield, ***meso*** primary. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25-6.94 (m, 20H), 3.72 (s, 2H), 2.57-2.45 (m, 8H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.97, 140.14, 128.66, 128.41, 127.62, 126.00, 68.54, 48.68, 36.15. HRMS (ESI) m/z calcd. for $C_{30}H_{33}N_2$ $[M+H]^+$: 421.2638, found: 421.2646.



1,2-Diphenyl-N,N-dipropylethane-1,2-diamine (63).[19] White solid, 41 mg, 69% yield, ***dl : meso*** = 1:6.6. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.02 (m, 20H), 3.73 (s, 2H, *meso*), 3.61 (s, 2H, *dl*), 2.41-2.33 (m, 4H, *dl*), 2.27-2.16 (m, 4H, *meso*), 1.47-1.38 (m, 4H, *dl*), 1.30-1.23 (m, 4H, *meso*), 0.85 (t, *J* = 7.4 Hz, 6H, *dl*), 0.67 (t, *J* = 7.4 Hz, 6H, *meso*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.0, 141.6, 128.5, 128.4, 128.0, 127.9, 127.6, 126.8, 69.5, 68.7, 49.8, 49.4, 23.4, 22.9, 11.9, 11.6. **HRMS** (ESI) m/z calcd. for $C_{20}H_{29}N_2$ $[M+H]^+$: 297.2325, found: 297.2324.

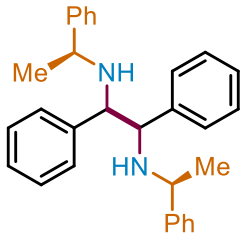


N,N-Dicyclopentyl-1,2-diphenylethane-1,2-diamine (64).[20] White solid, 54 mg, 78% yield, ***dl : meso*** = 1:1.7. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32-7.03 (m, 20H), 3.80 (s, 2H, *meso*), 3.64 (s, 2H, *dl*), 2.81 (t, *J* = 6.1 Hz, 2H, *dl*), 2.67 (t, *J* = 6.1 Hz, 2H, *meso*), 1.69-1.01 (m, 32H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.3, 141.7, 128.6, 128.3, 128.1, 127.8, 127.5, 126.7, 67.9, 67.1, 57.4, 57.1, 34.2, 33.8, 32.4, 32.1, 23.8, 23.7, 23.6, 23.5. **HRMS** (ESI) m/z calcd. for $C_{24}H_{33}N_2$ $[M+H]^+$: 349.2638, found: 349.2645.



N,N-Diisopropyl-1,2-diphenylethane-1,2-diamine (65).[20] White solid, 49 mg, 83% yield, ***dl : meso*** = 1:1.6. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27-7.00 (m, 20H), 3.90 (s, 2H, *meso*), 3.71 (s, 2H, *dl*), 2.53 (q, *J* = 6.1 Hz, 2H, *dl*), 2.46 (q, *J* = 6.1 Hz, 2H, *meso*), 1.00-0.91 (m, 12H, *dl*), 0.90-0.75 (m, 12H, *meso*). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.4, 141.5, 128.4, 128.1, 128.0, 127.8, 127.2, 126.7, 66.8, 65.6, 46.1, 45.5, 24.6, 24.3, 22.2,

22.0. HRMS (ESI) m/z calcd. for $C_{20}H_{29}N_2$ $[M+H]^+$: 297.2325, found: 297.2329.



1,2-Diphenyl-N,N-bis((S)-1-phenylethyl)ethane-1,2-diamine (66).[21,22] White solid, 70 mg, 83% yield, ***dl : meso*** = 2.6:1. **^{1}H NMR of (R, S + S, S)-66** (400 MHz, $CDCl_3$) δ 7.28-6.88(m, 40H), 3.87 (s, 2H, S, S), 3.73 (d, *J* = 6.8 Hz, 2H, R, S), 3.58 (q, *J* = 6.6 Hz, 2H, S, S), 3.57 (d, *J* = 6.8 Hz, 2H, R, S), 3.37 (q, *J* = 6.7 Hz, 2H, R, S), 3.27 (q, *J* = 6.7 Hz, 2H, R, S), 1.77 (br, 4H), 1.29 (d, *J* = 6.5 Hz, 6H, S, S), 1.16 (d, *J* = 6.7 Hz, 3H, R, S), 1.07 (d, *J* = 6.5 Hz, 3H, R, S). **^{13}C NMR of (R, S + S, S)-66** (100 MHz, $CDCl_3$) δ 146.7, 146.1, 145.6, 141.7, 141.6, 141.0, 128.6, 128.5, 128.3, 128.2, 128.1, 127.9, 127.4, 127.3, 126.86, 126.82, 126.76, 126.64, 126.60, 66.5, 65.7, 64.2, 54.9, 54.8, 54.5, 24.7, 22.6, 22.1. **^{1}H NMR of (R, R)-66** (400 MHz, $CDCl_3$) δ 7.27-6.91 (m, 20H), 3.42 (q, *J* = 6.6 Hz, 2H), 3.37 (s, 2H), 2.02 (br, 2H), 1.25 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR of (R, R)-66** (100 MHz, $CDCl_3$) δ 145.7, 141.8, 128.5, 128.1, 128.0, 126.8, 126.7, 65.9, 55.2, 25.4. **HRMS** (ESI) m/z calcd. for $C_{30}H_{33}N_2$ $[M+H]^+$: 421.2638, found: 421.2639.

9. References

[1] J. Zhang, Y. Li, F. Zhang, C. Hu and Y. Chen, *Angew. Chem., Int. Ed*., 2016, **55**, 1872–1875.

[2] M. Nakajima, E. Fava, S. Loescher, Z. Jiang and M. Rueping, *Angew. Chem., Int. Ed.,* 2015, **54**, 8828–8832.

[3] Y.-X. Liao, C.-H. Xing, P. He and Q.-S. Hu, *Org. Lett*., 2008, **10**, 2509–2512.

[4] S. Zhang, L. Li, J. Li, J. Shi, K. Xu, W. Gao, L. Zong, G. Li and M. Findlater, *Angew. Chem., Int. Ed.,* 2021, **60**, 7275–7282.

[5] A. L. Berger, K. Donabauer and B. König, *Chem. Sci.,* 2018, **9**, 7230–7235.

[6] T. Duhamel and K. Muñiz, *Chem. Commun*., 2019, **55**, 933–936.

[7] N. C. Mamillapalli and G. Sekar, *RSC Adv.,* 2014, **4**, 61077–61085.

[8] K. Li, Q. Wan, C. Yang, X.-Y. Chang, K.-H. Low and C.-M. Che, *Angew. Chem., Int. Ed.,* 2018, **57**, 14129–14133.

[9] C. Liu, R. Li, W. Zhou, Y. Liang, Y. Shi, R-L. Li, Y. Ling, Y. Yu, J. Li and B. Zhang, *ACS Catal.,* 2021, **11**, 8958–8967.

[10] Y.-B. Huang, Z. Yang, J.-J. Dai, Q.-X. Guo and Y. Fu, *RSC Adv.,* 2012, **2**, 11211–11214.

[11] A. Caron, É. Morin and S. K. Collins, *ACS Catal.,* 2019, **9**, 9458–9464.

[12] H. Ito and A. Sudo, *Results Chem.,* 2021, **3**, 100123.

[13] J. Jo, S. Kim, J.-H. Choi and W.-J. Chung*, Chem. Commun.*, 2021, **57**, 1360–1363.

[14] L. Qi and Y. Chen, *Angew Chem., Int. Ed.,* 2016, **55**, 13312–13315.

[15] D. Liu, J. Zhang and Y. Chen*, Synlett,* 2021, **32**, 356–361.

[16] S. Okamoto, R. Ariki, H. Tsujioka and A. Sudo, *J. Org. Chem.,* 2017, **82**, 9731–9736.

[17] H. Wang, J.-P. Qu and Y.-B. Kang, *Org. Lett.,* 2021, **23**, 2900–2903.

[18] L. Leng and J. M. Ready, *ACS Catal*., 2020, **10**, 13196–13201.

[19] M. P. Dutta, B. Baruah, A. Boruah, D. Prajapati and J. S. Sandhu, *Synlett,* 1998, **8**, 857–858.

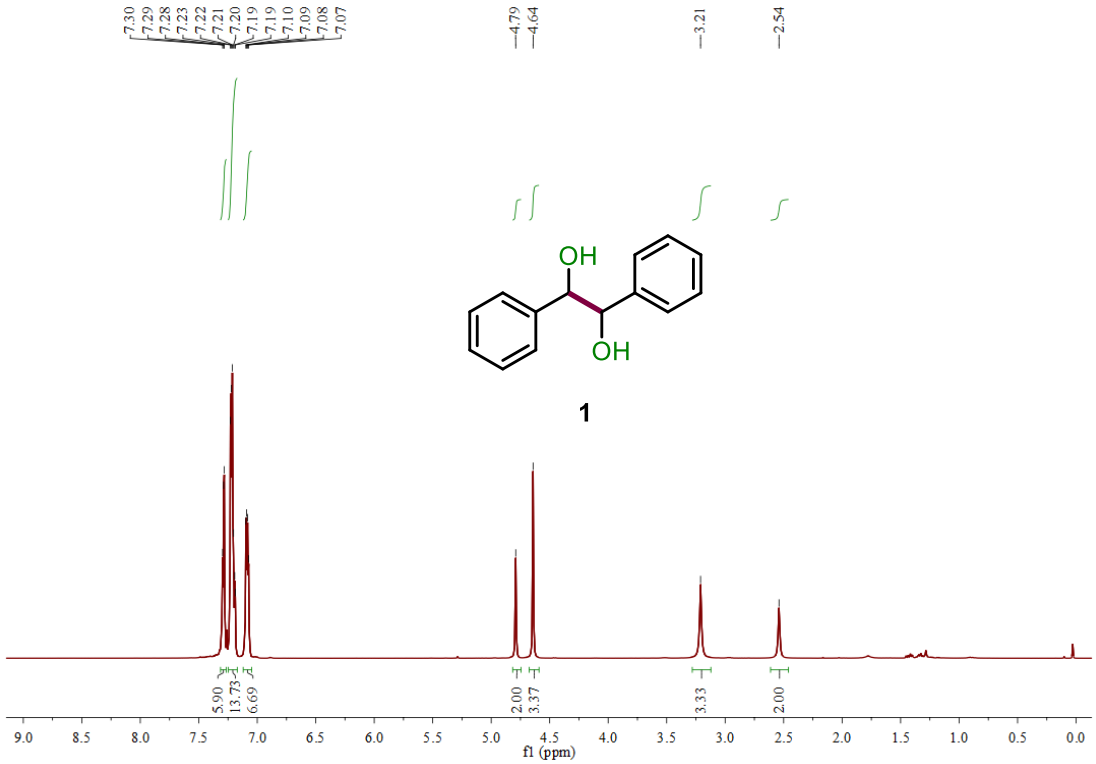
[20] P.-Q. Huang, Q.-W. Lang, A.-E Wang and J.-F. Zheng, *Chem. Commun.,* 2015, **51**, 1096–1099.

[21] K. Bambridge, M. J. Begley and N. S. Simpkins, *Tetrahedron Lett.,* 1994, **35** 3391–3394.

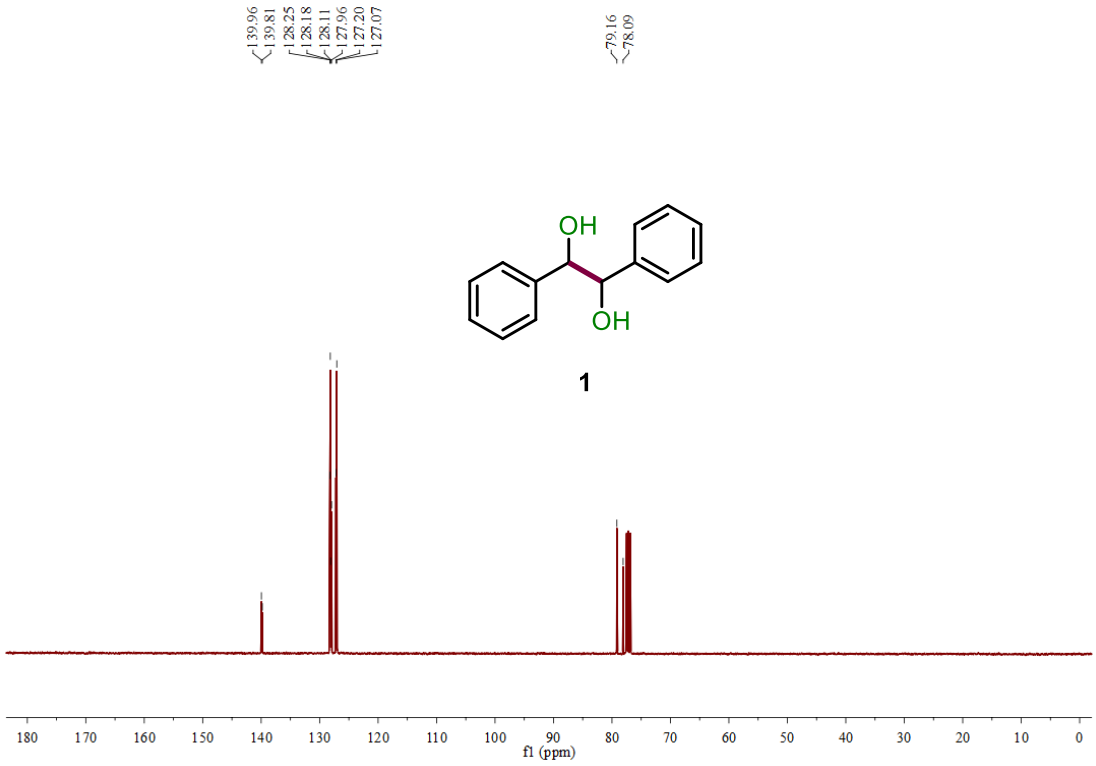
[22] G. Martelli, S. Mori and D. Savoia, *Tetrahedron,* 2000, **56**, 8367–8374.

10. Copies of NMR Spectra.

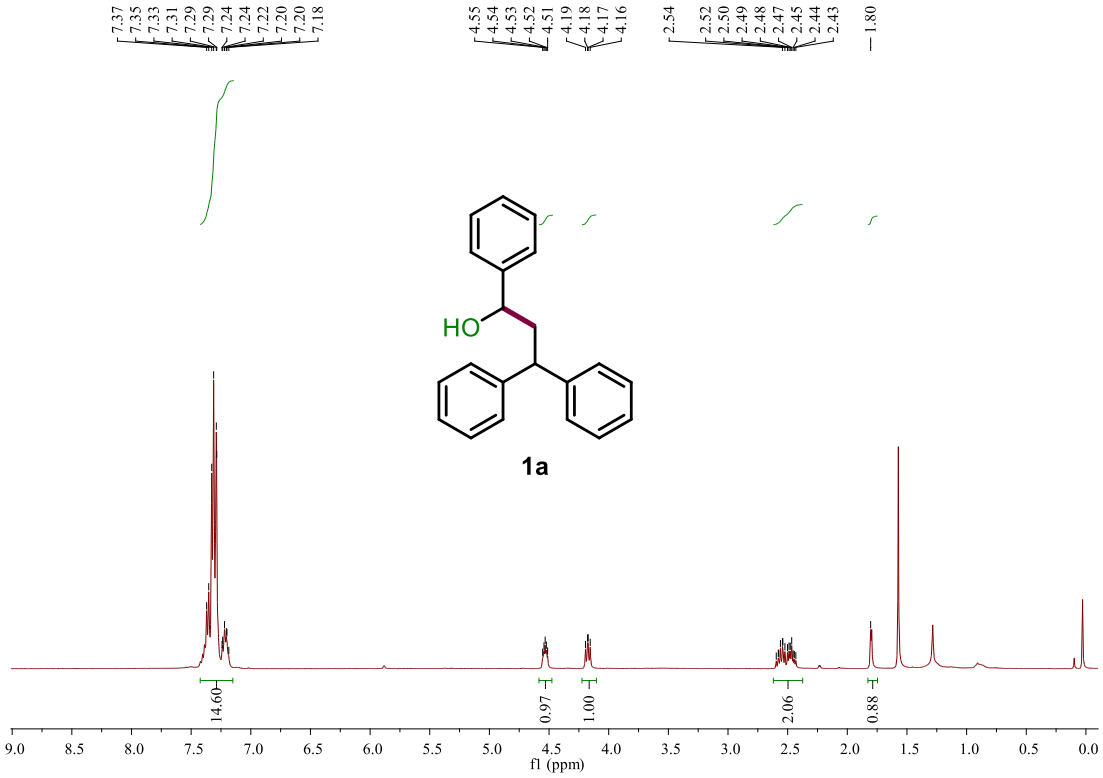
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 1



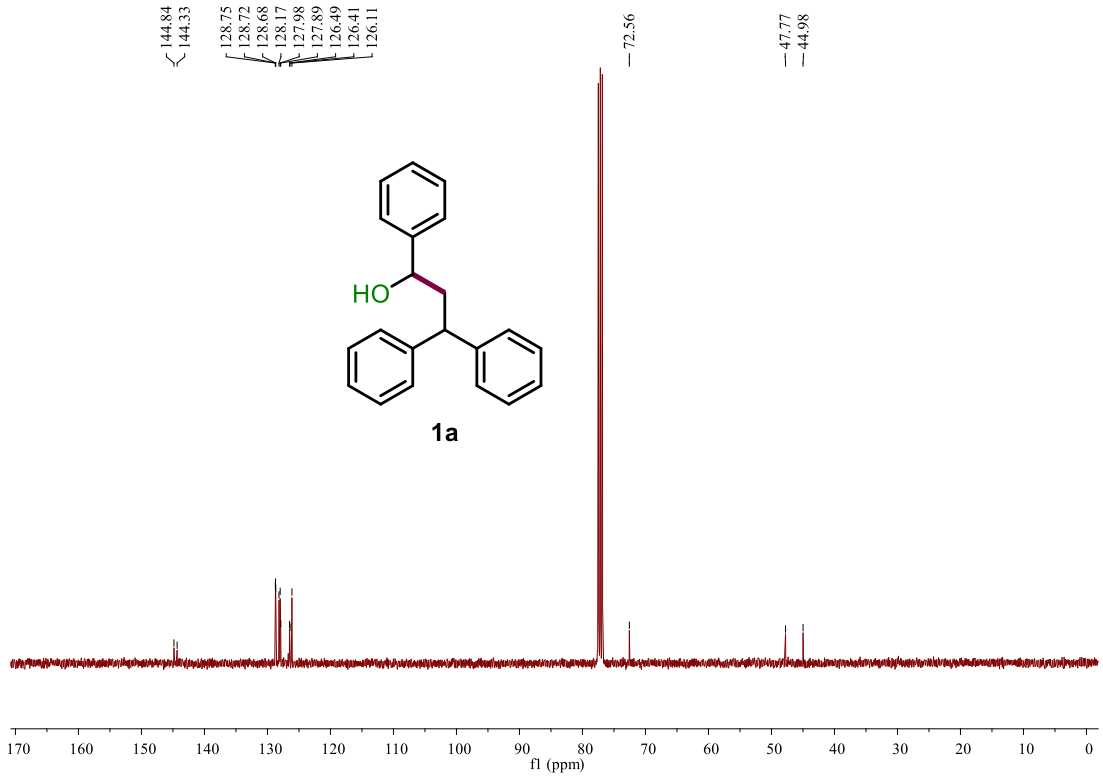
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 1



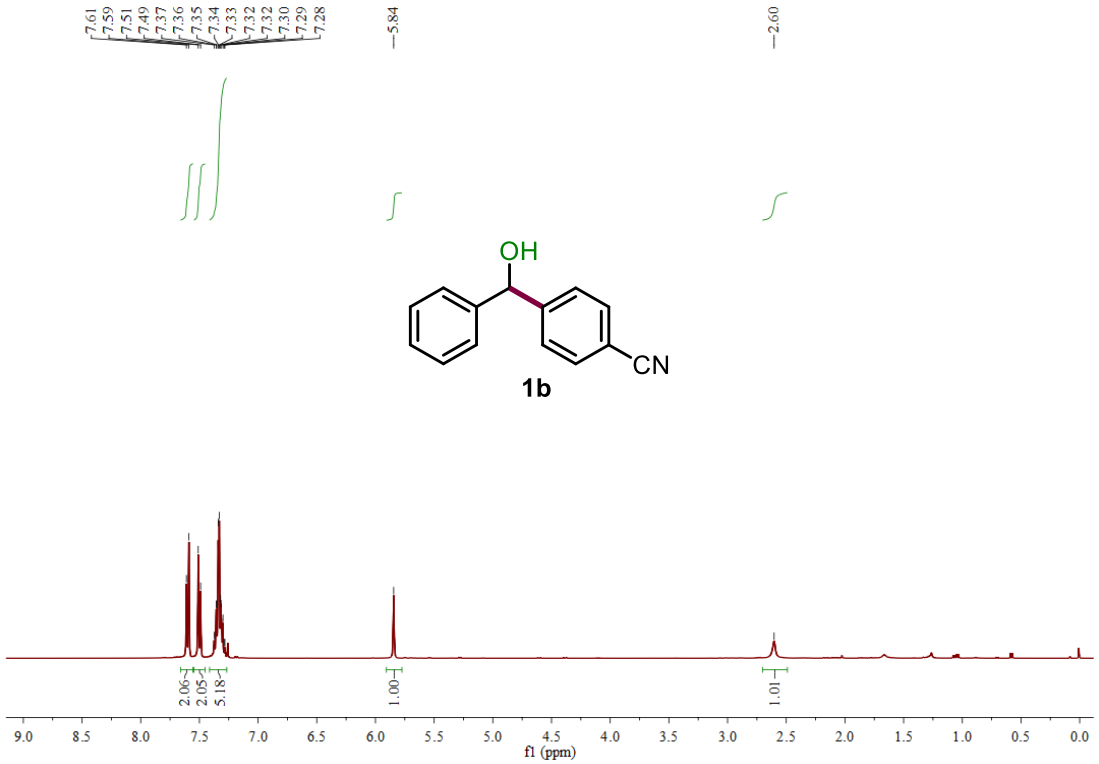
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 1a



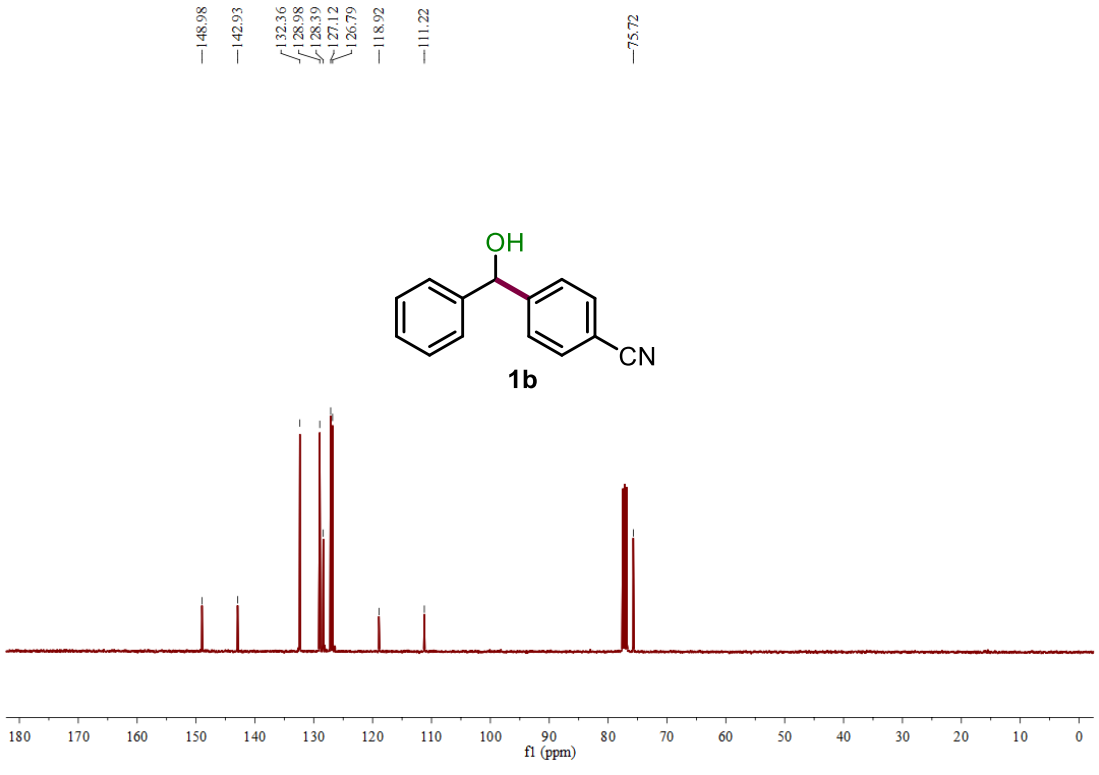
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 1a



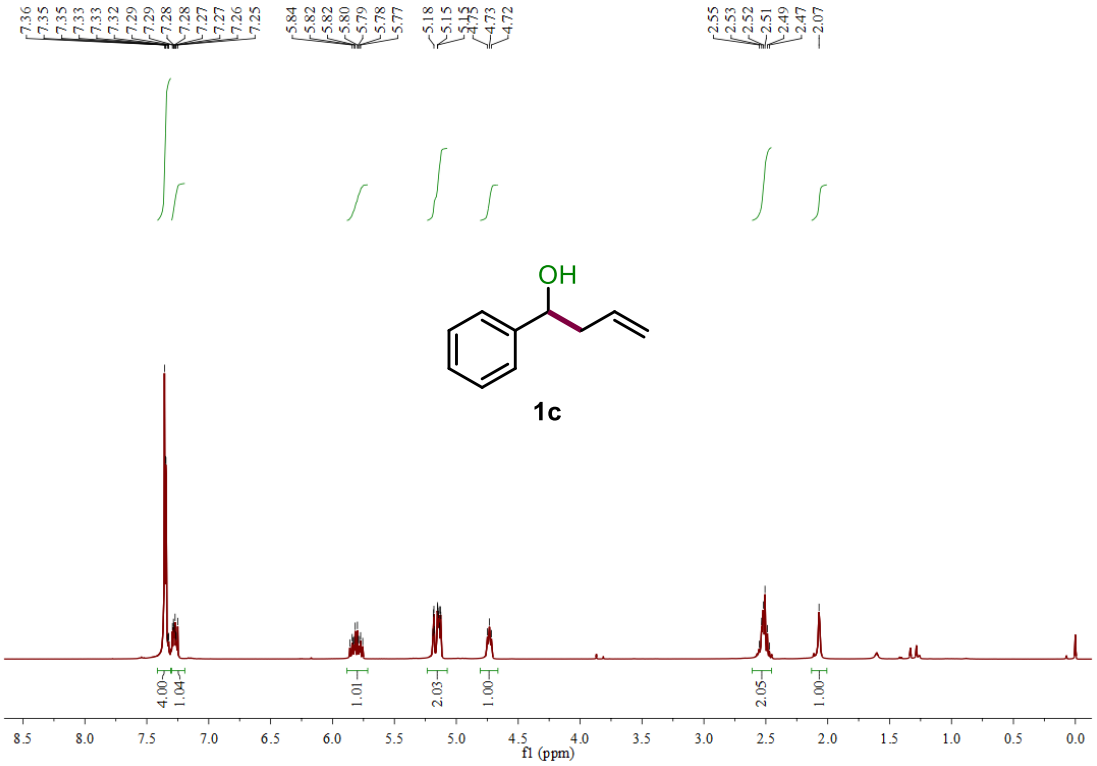
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 1b



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 1b



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



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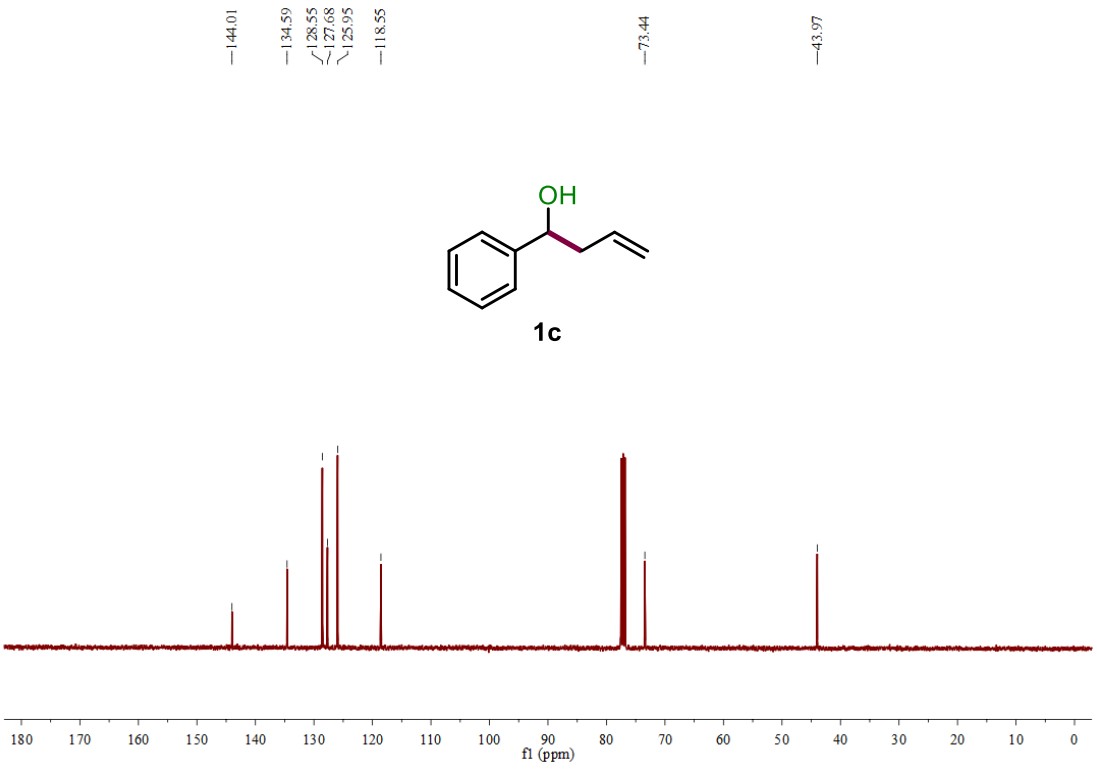

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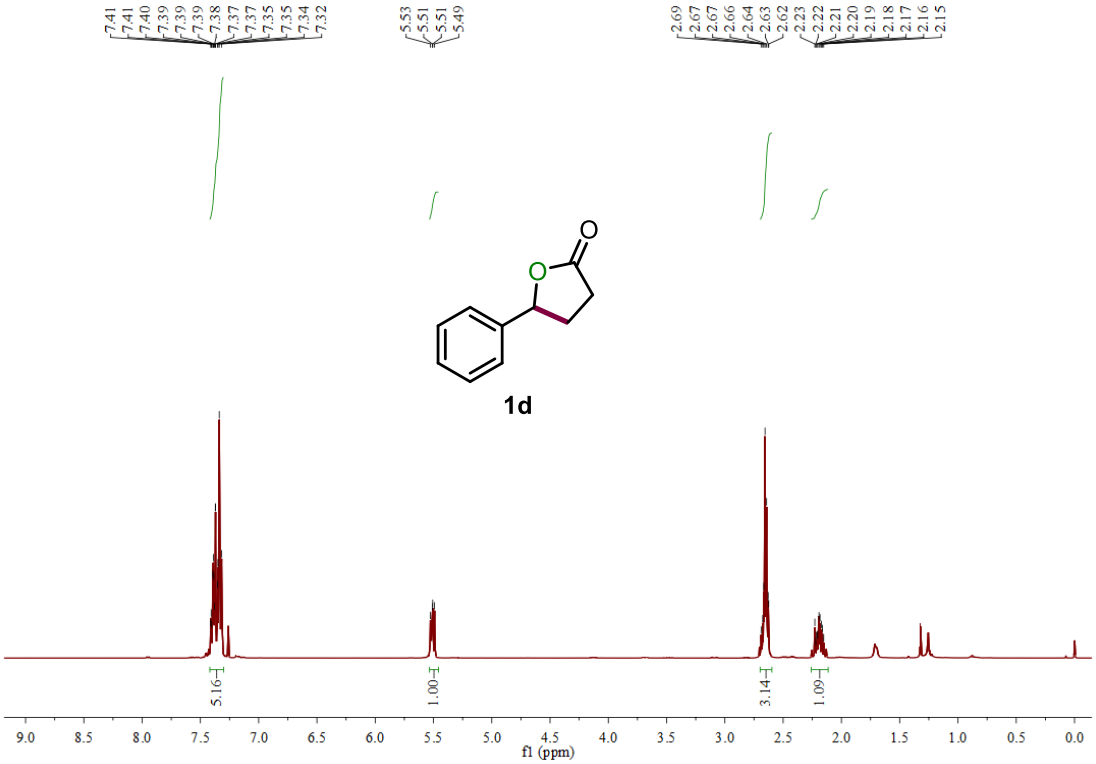
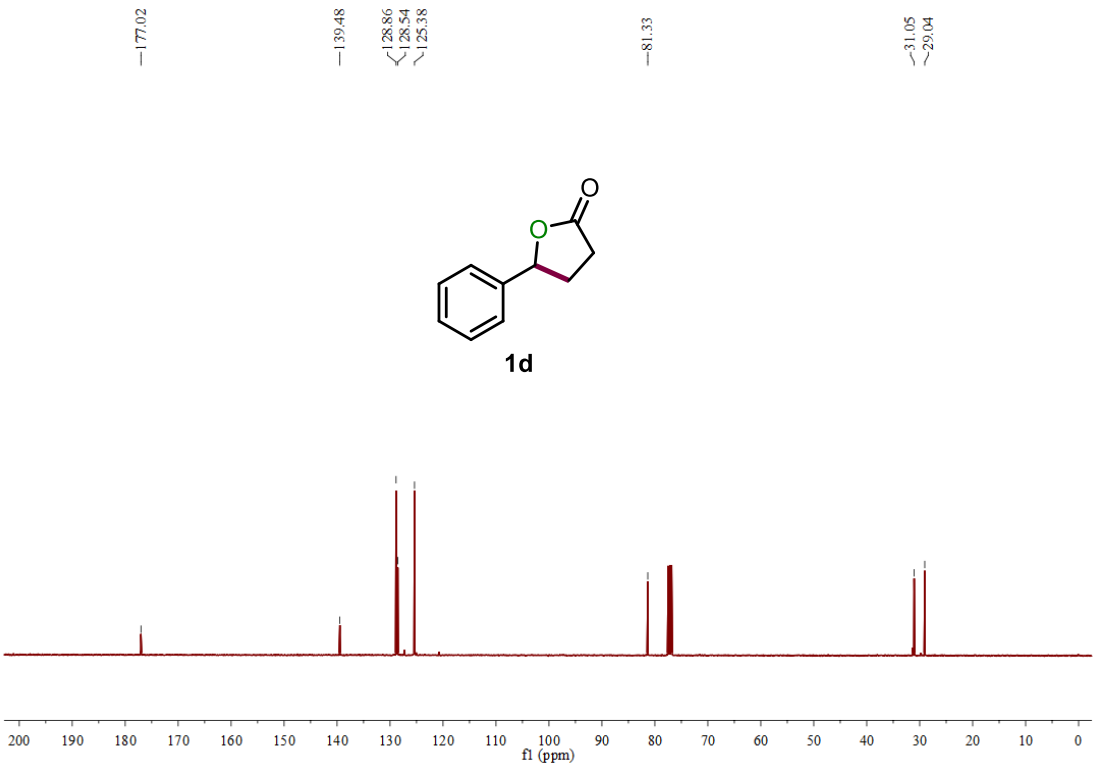
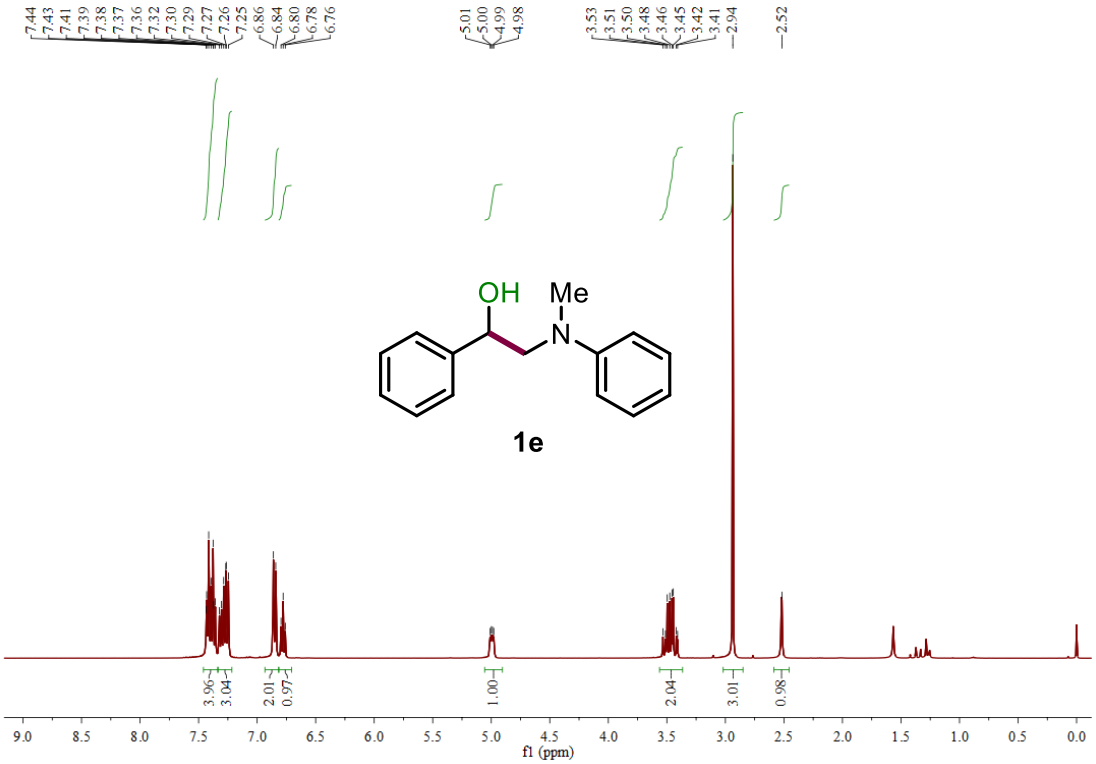


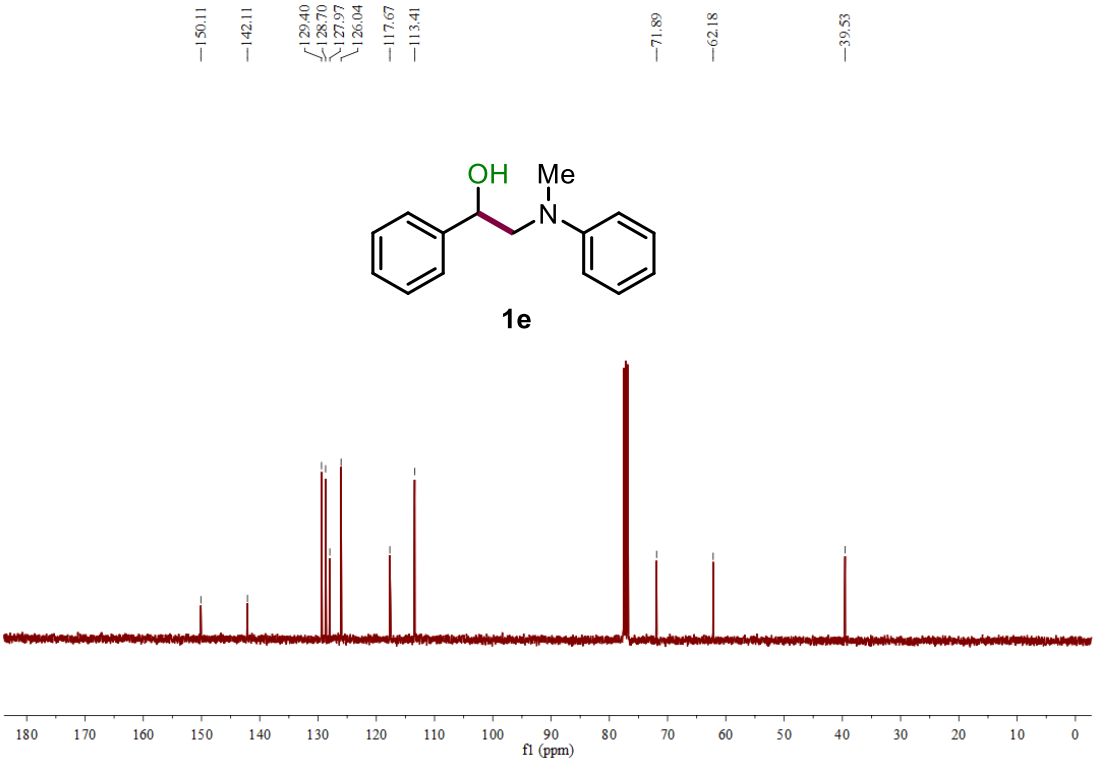
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 1d



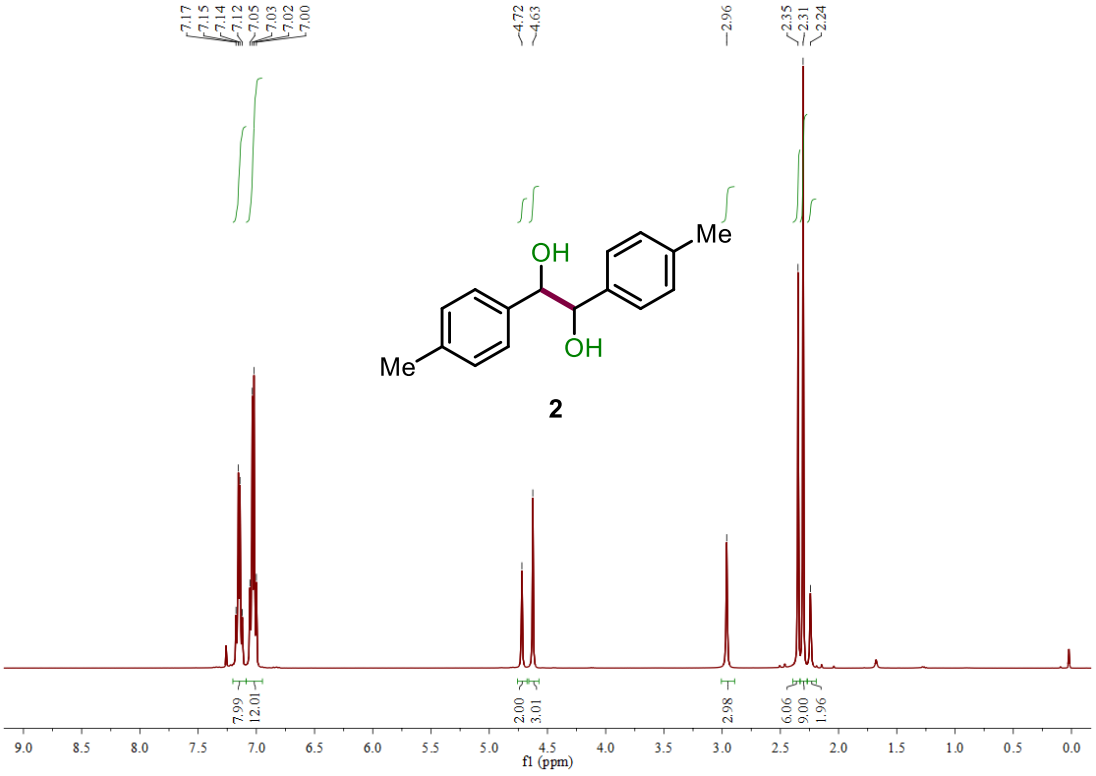
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 1e



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 1e

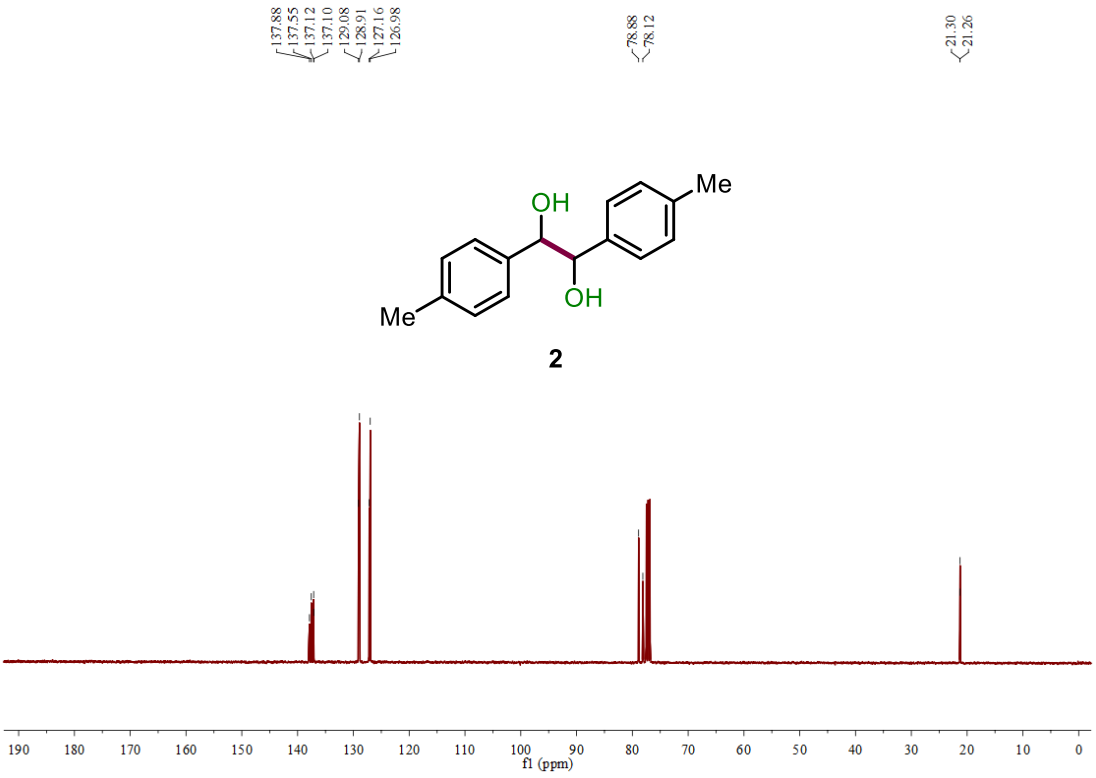


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 2



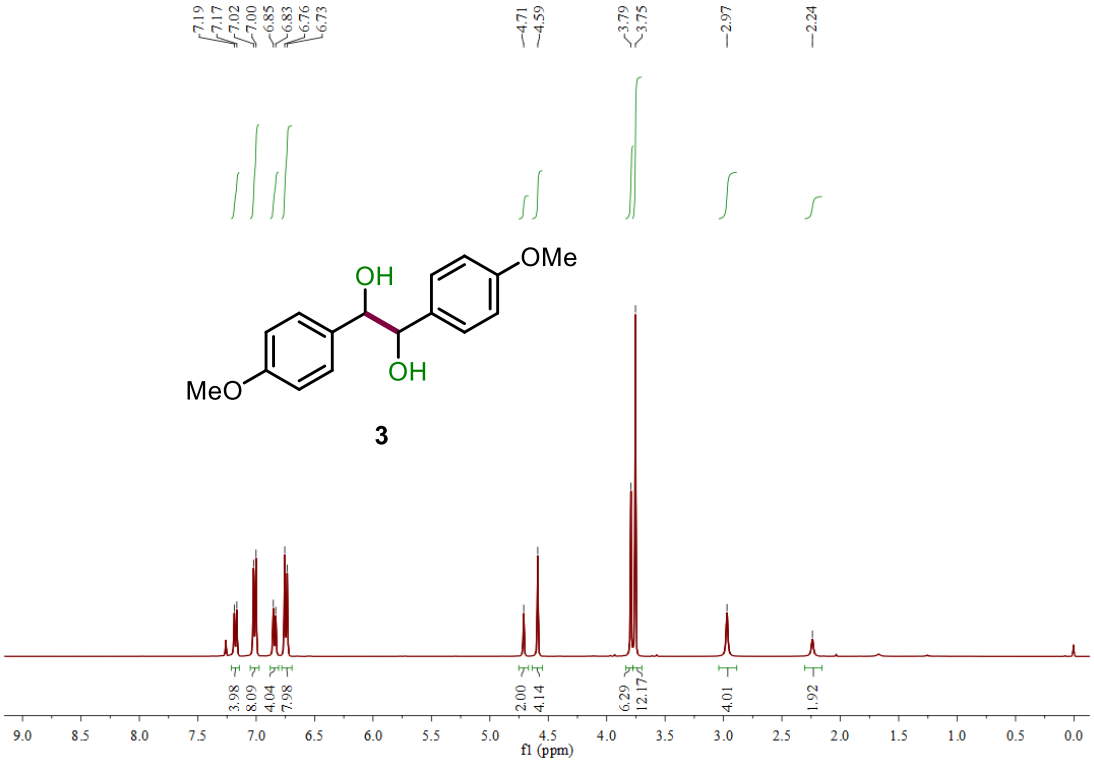
2

^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 2



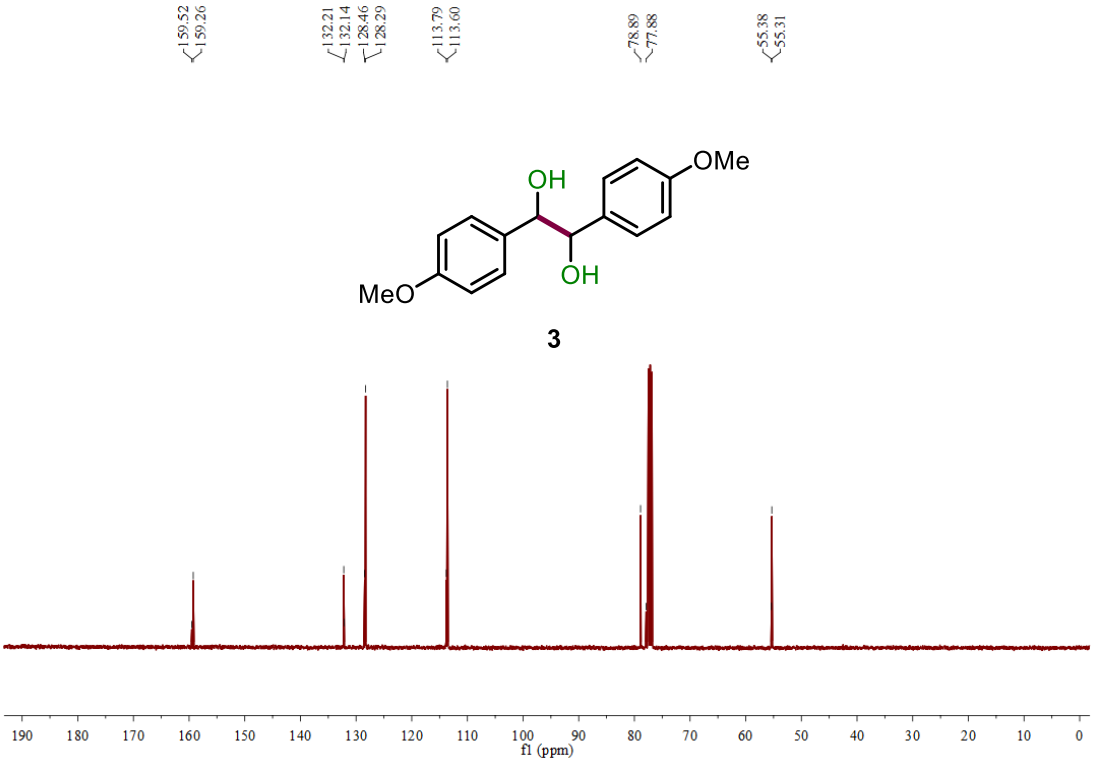
2

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



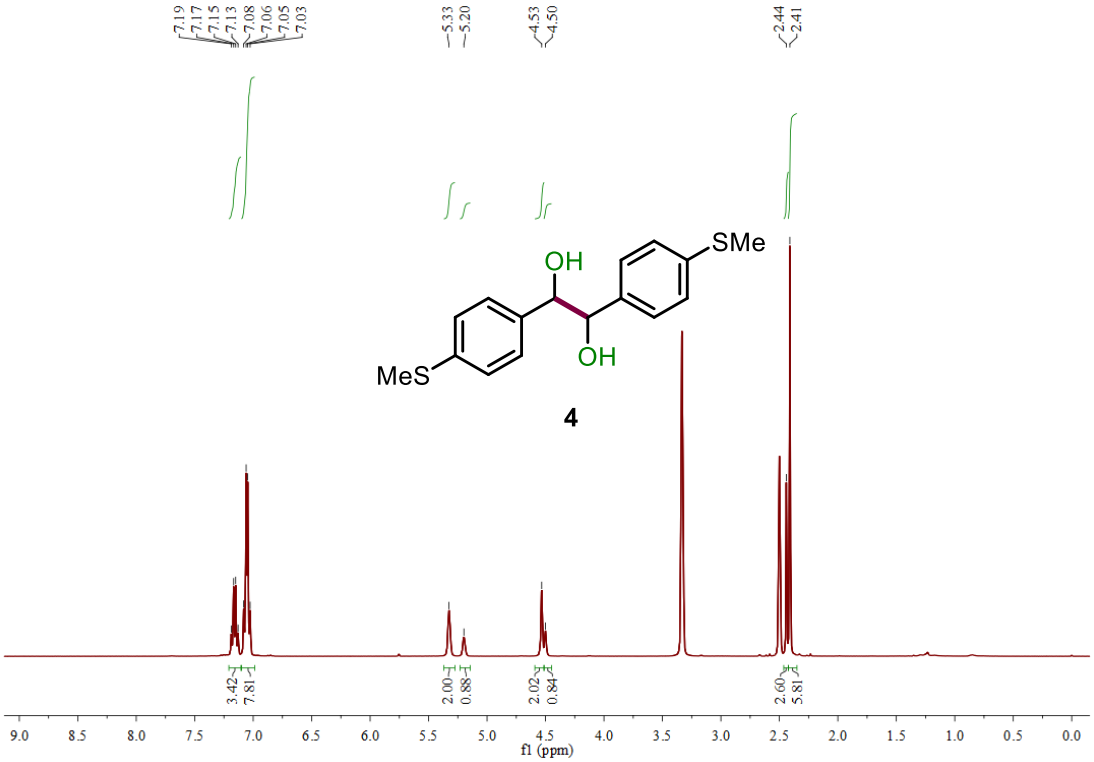
3

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

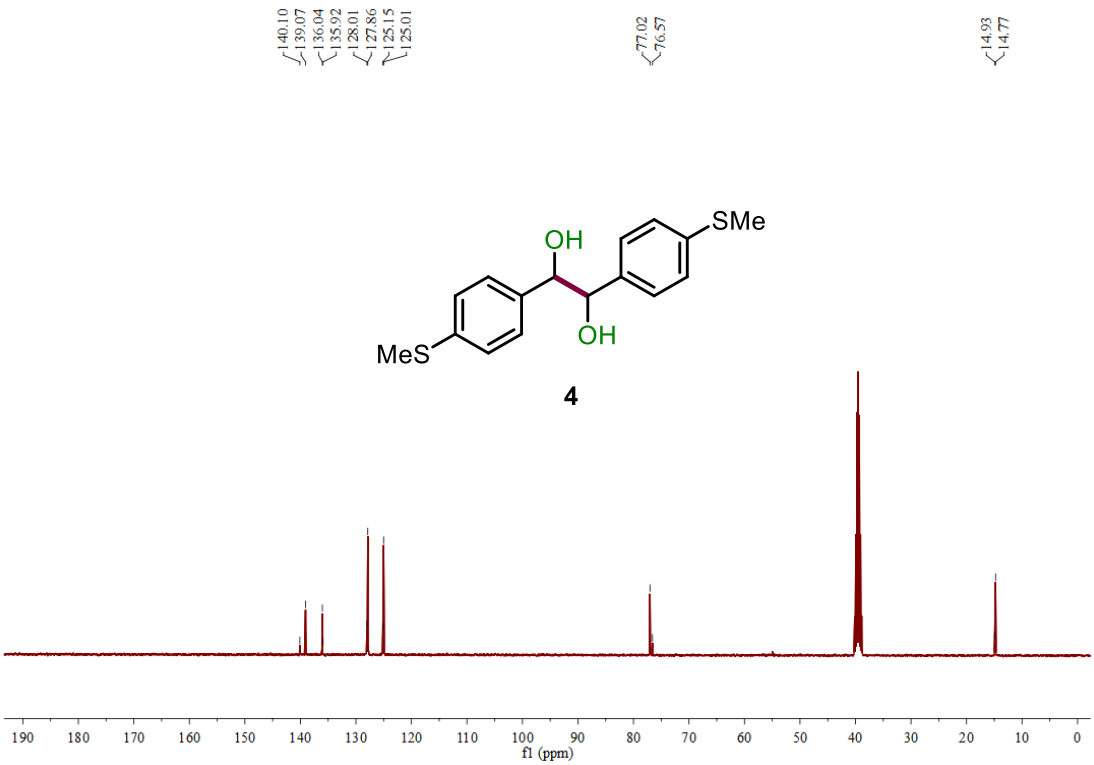


3

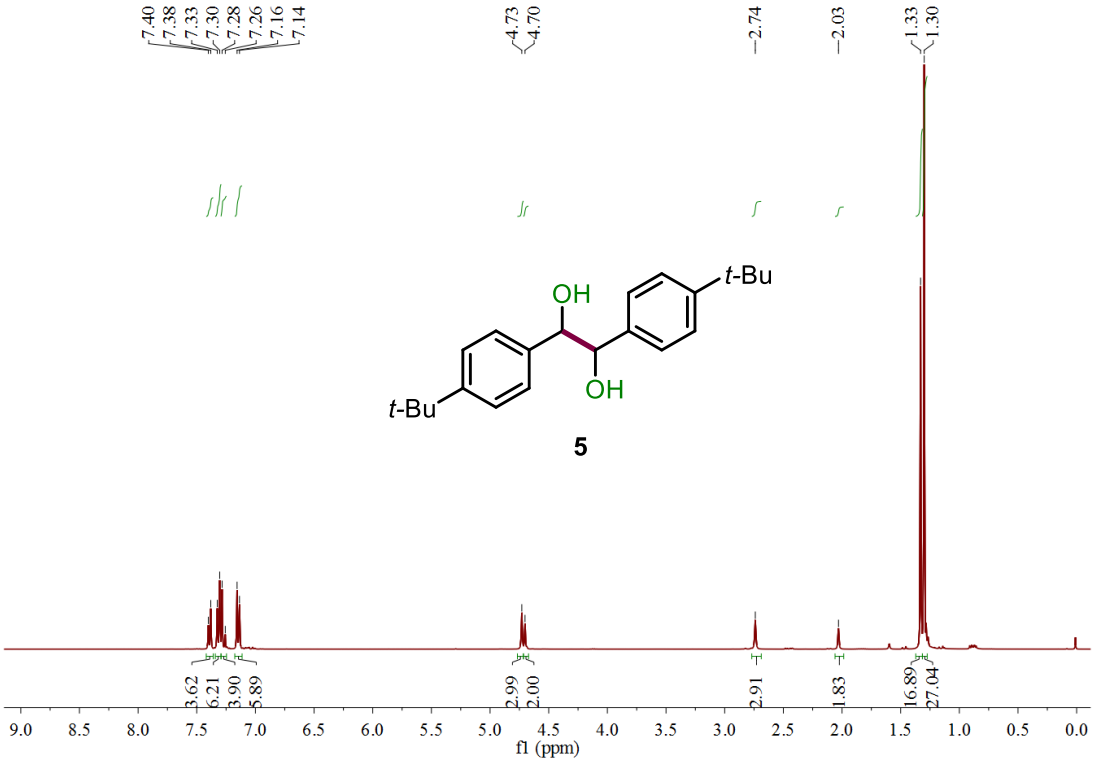
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 4



^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 4

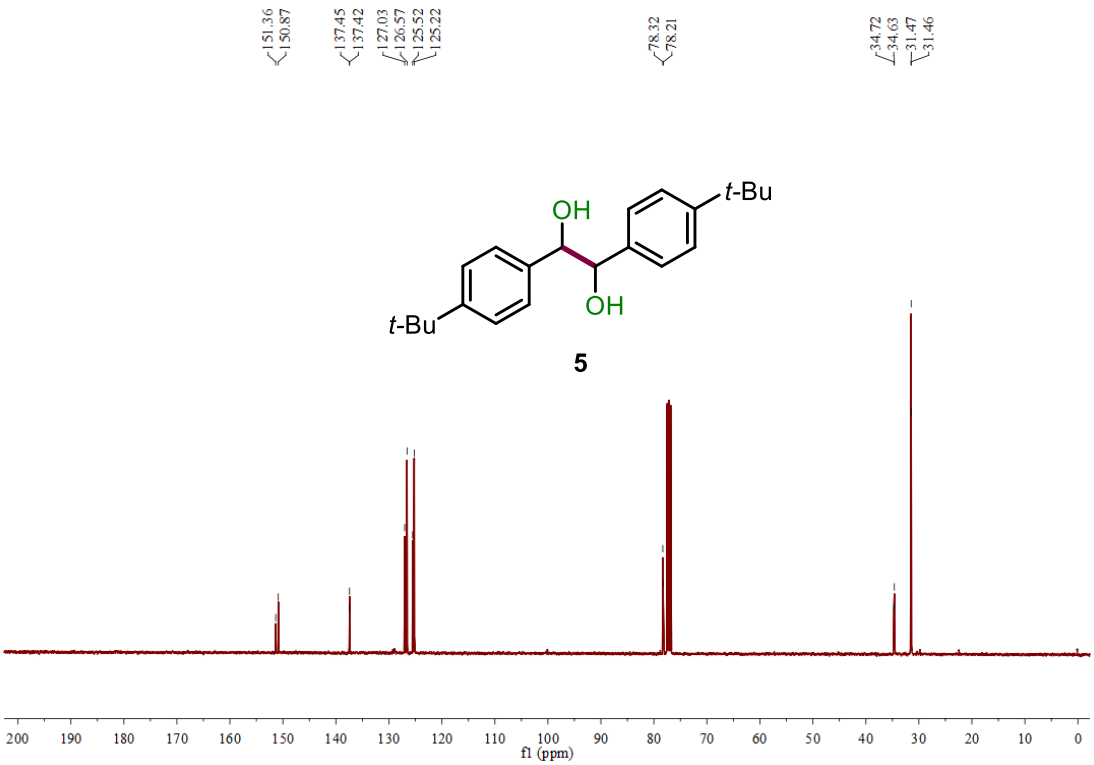


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5



5

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



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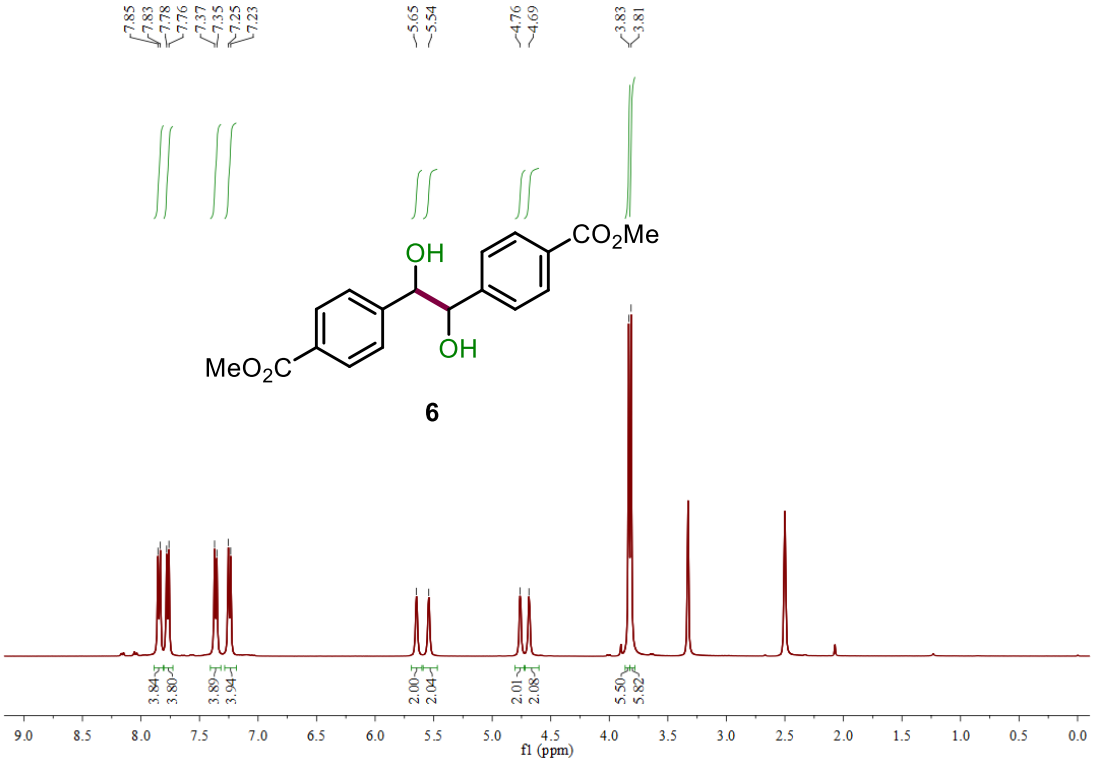
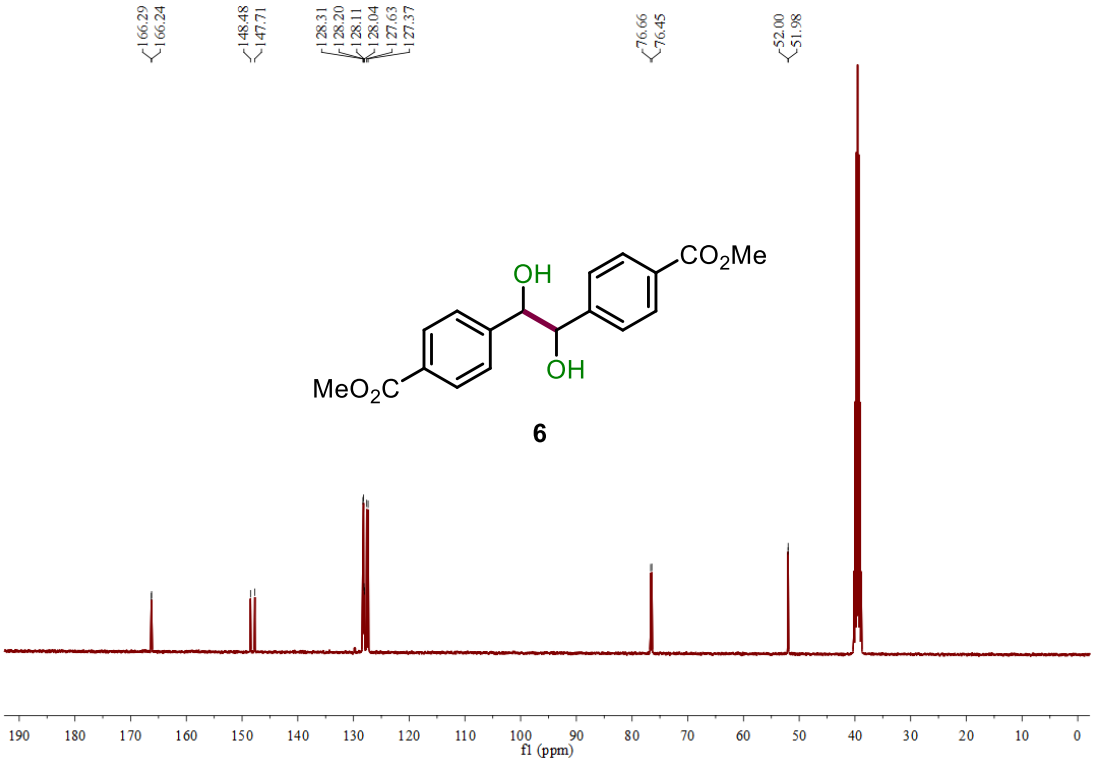
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 6



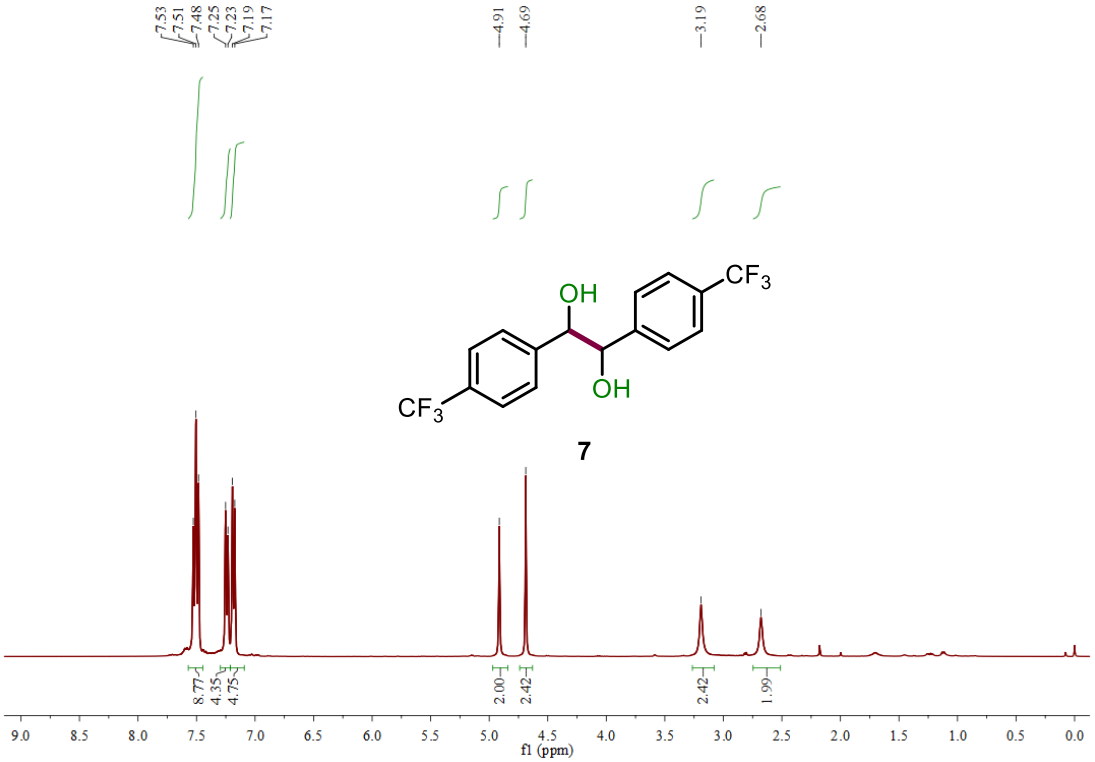
6

^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 6

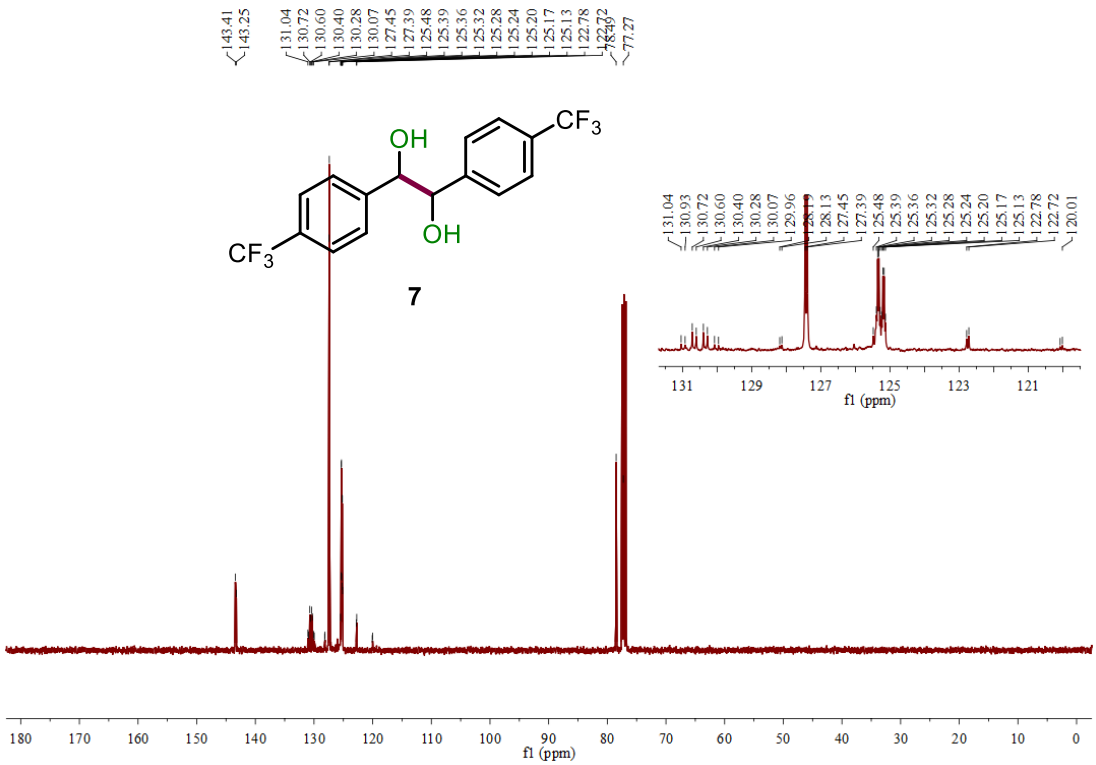


6

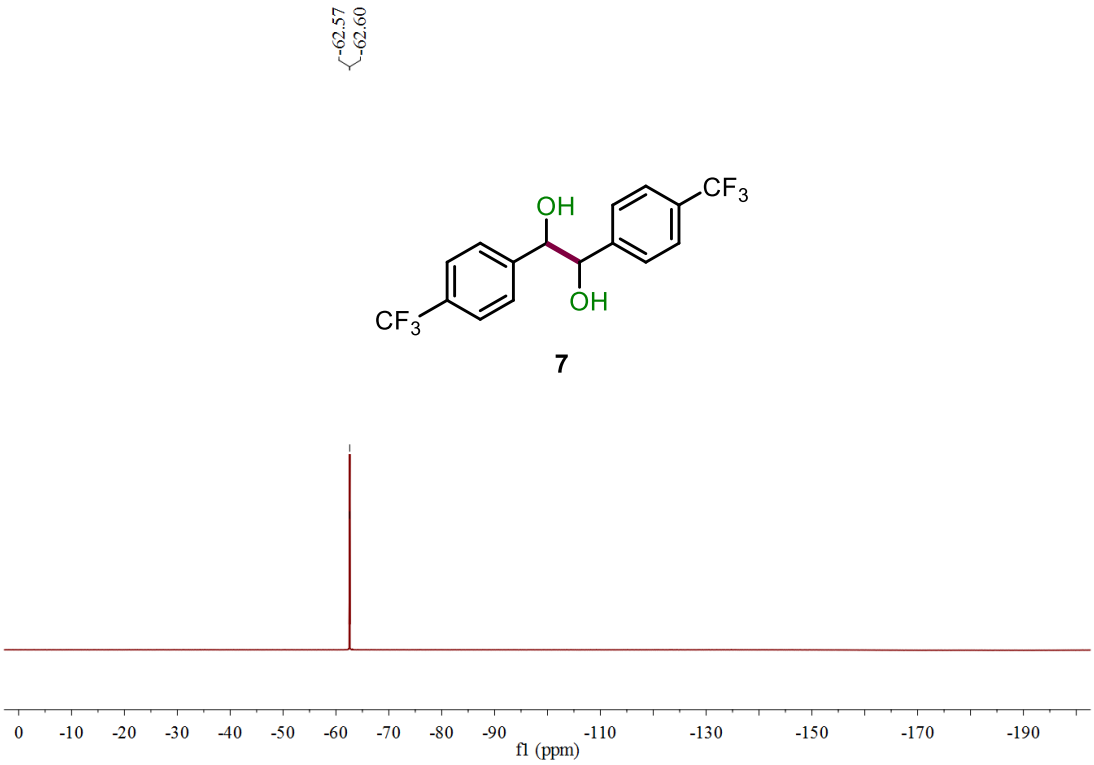
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 7



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

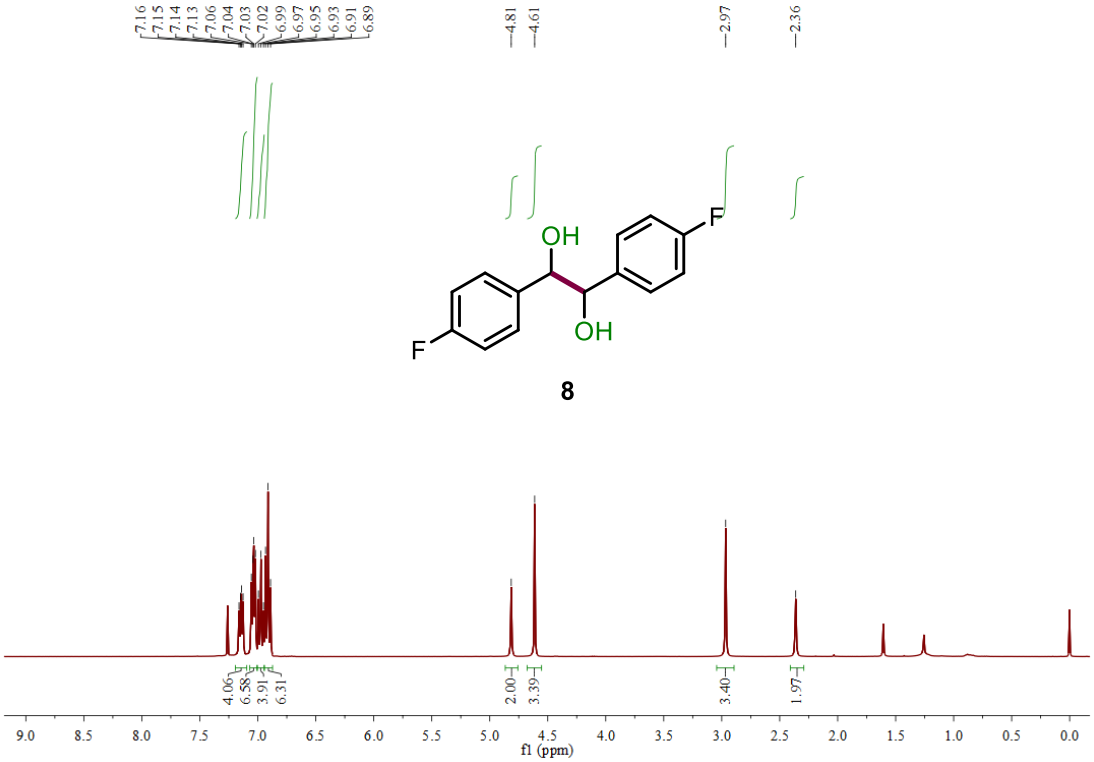


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound 7



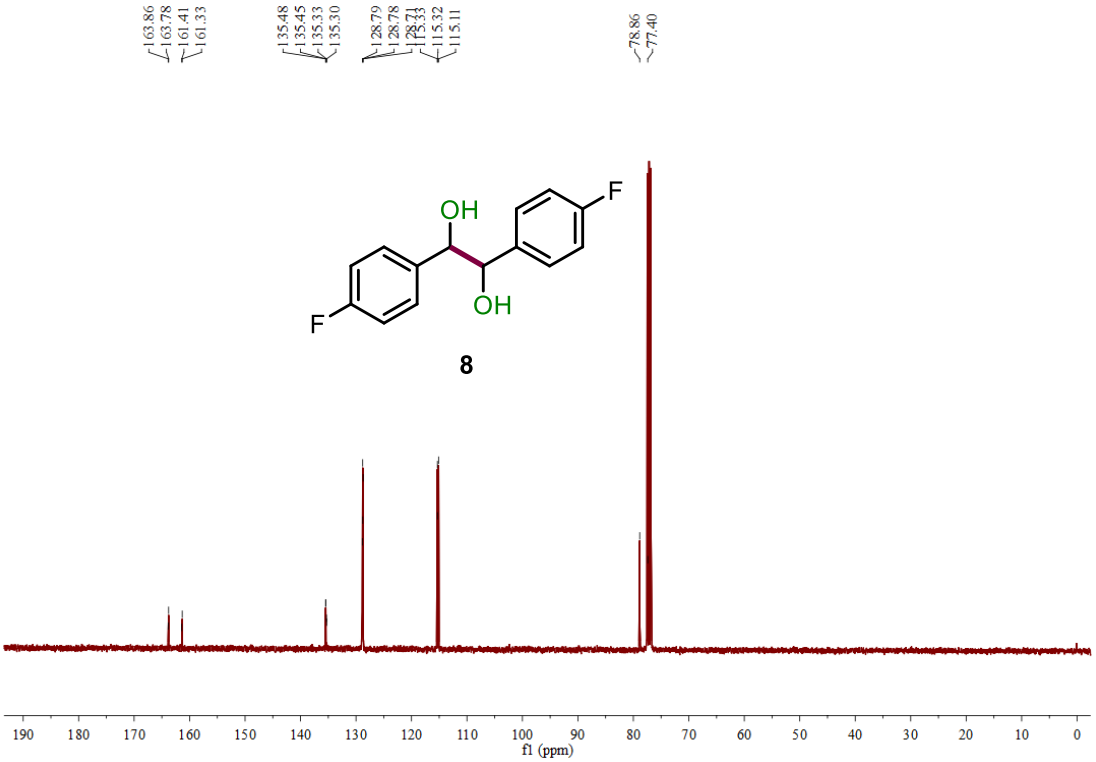
7

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



8

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



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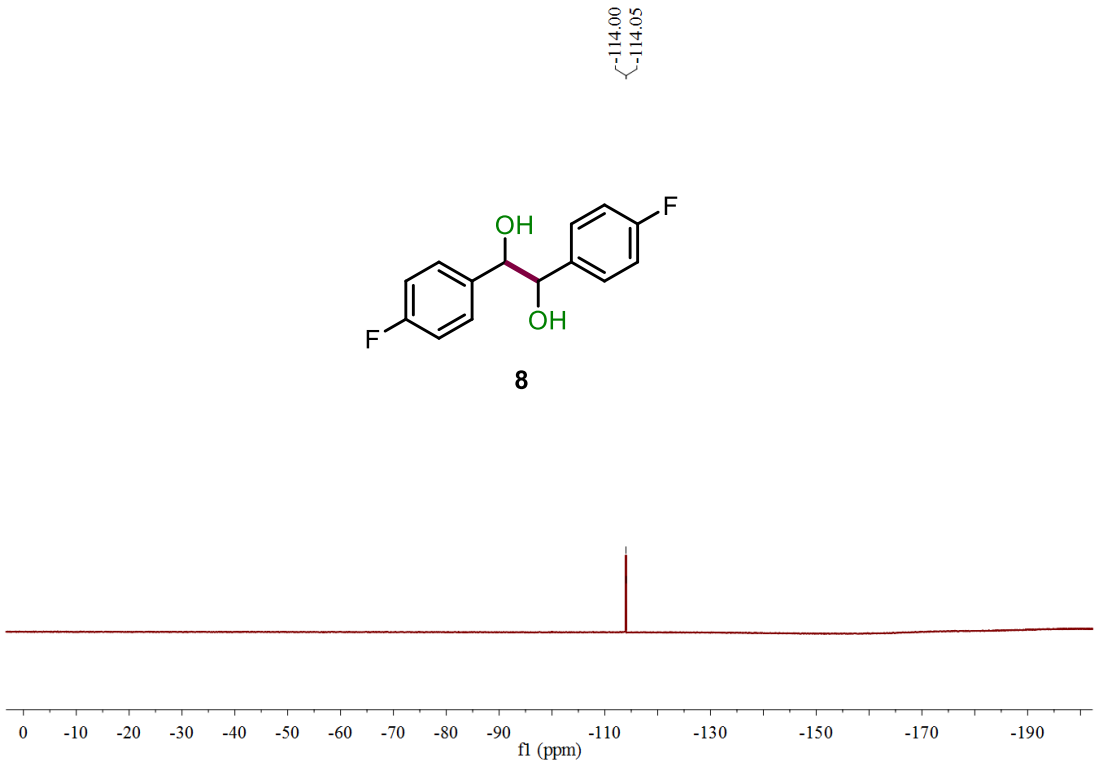
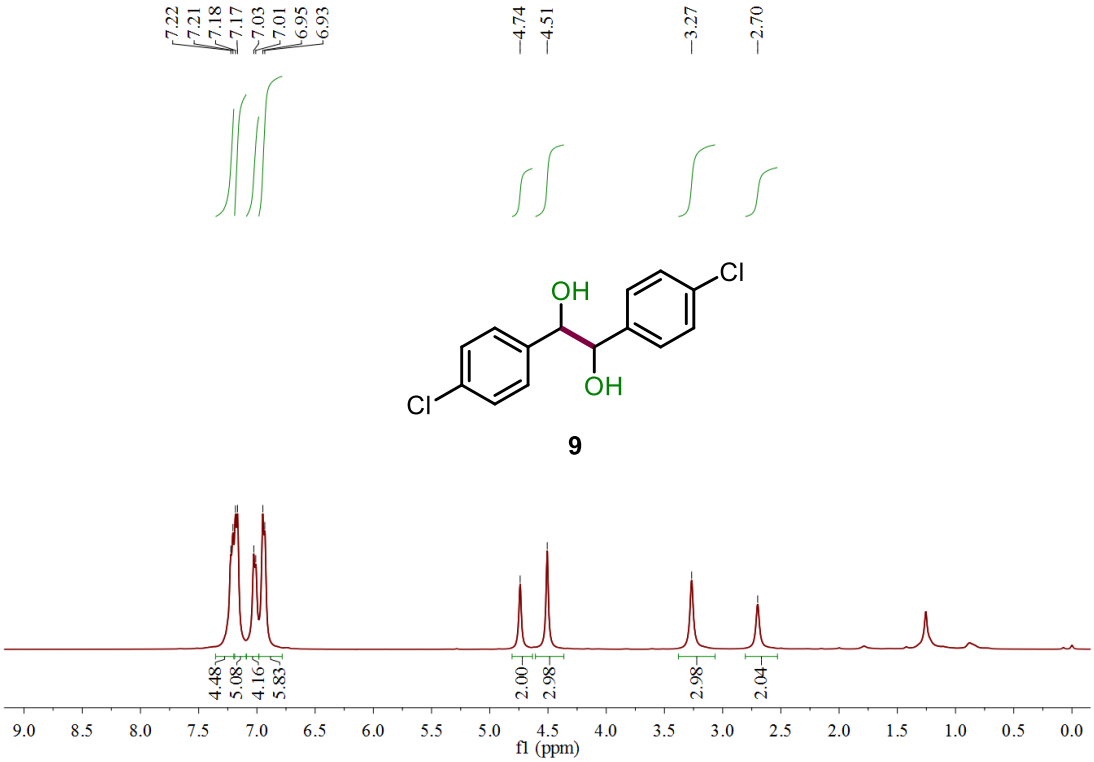
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound 8



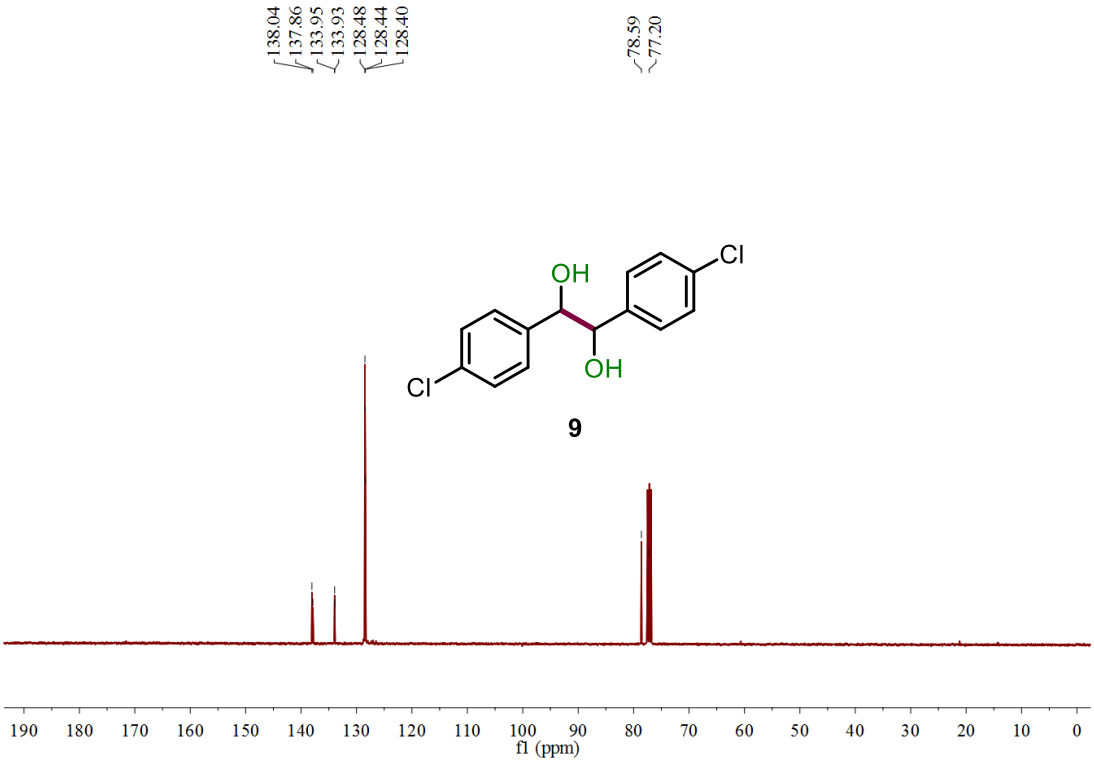
8

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



9

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



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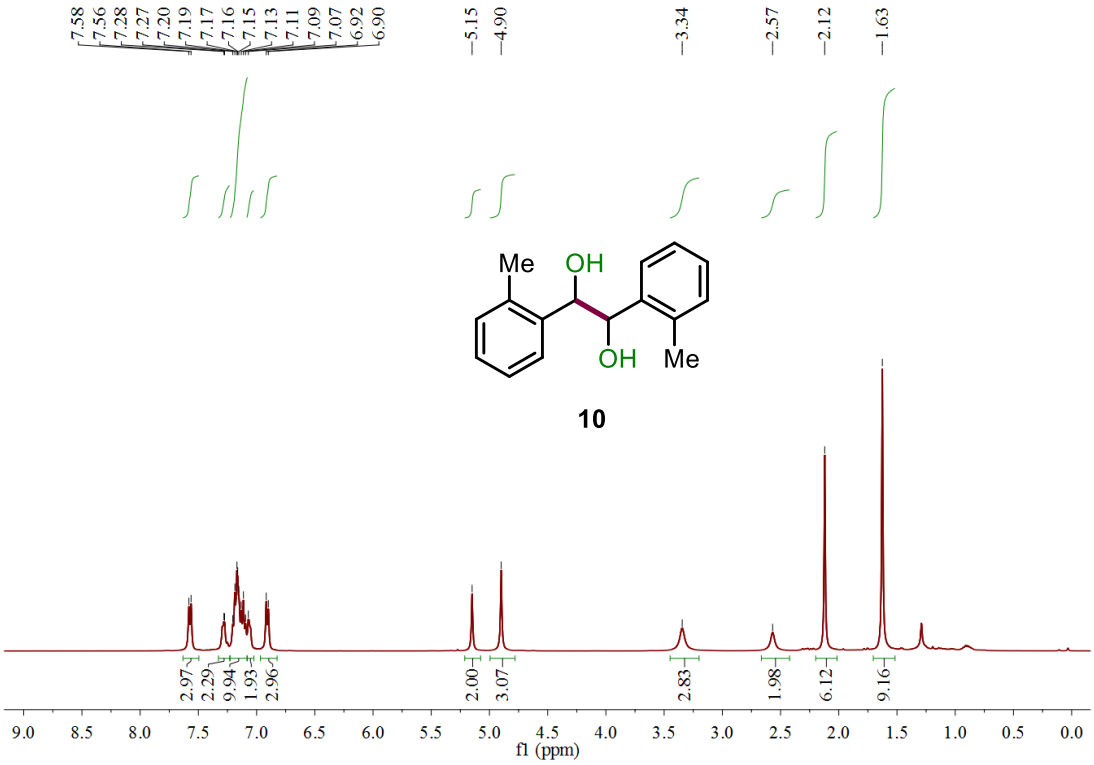
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 10



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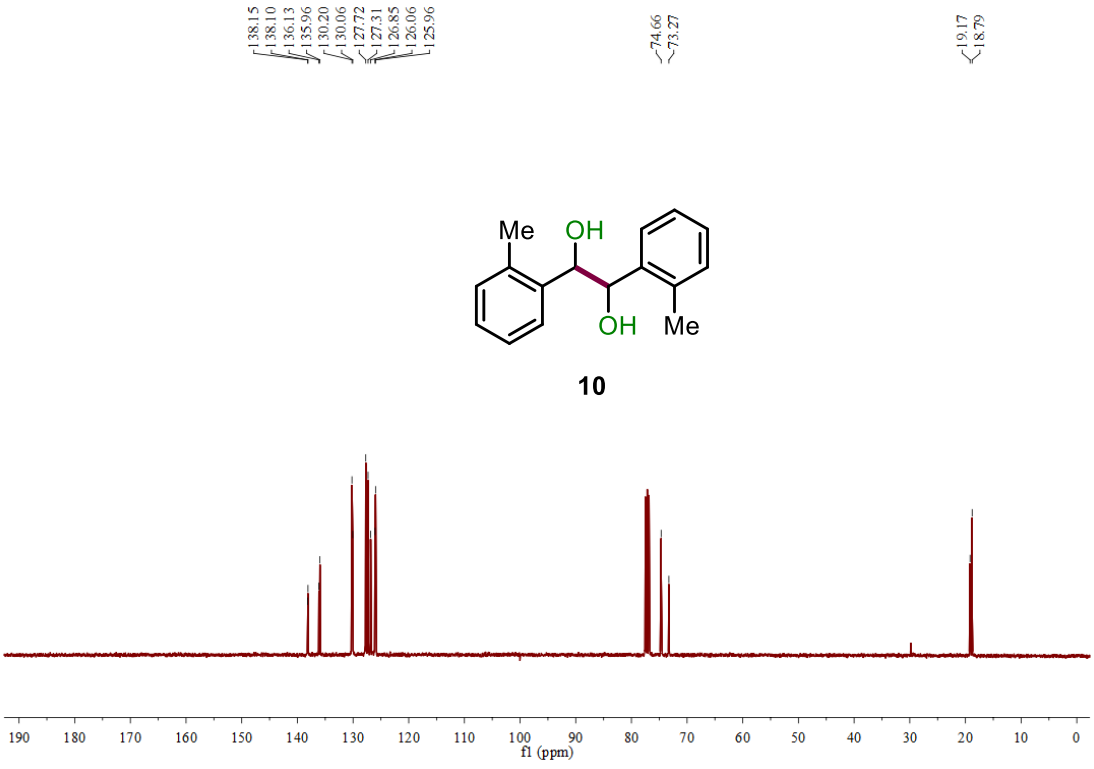
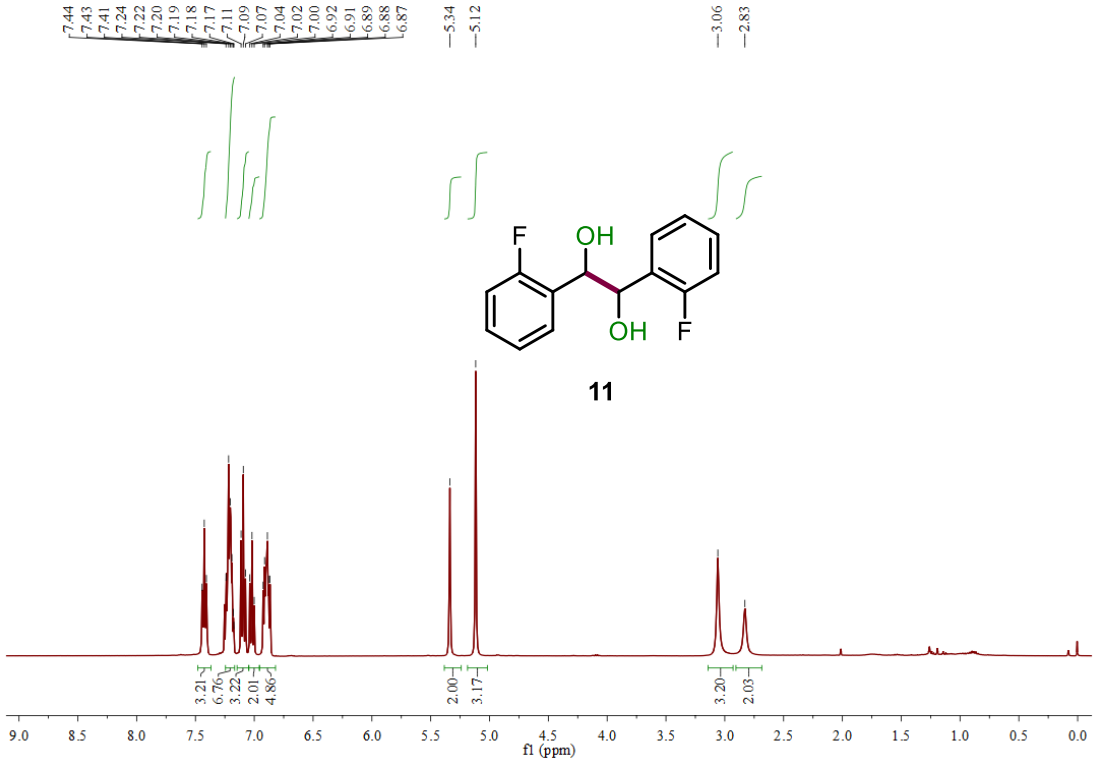
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 10

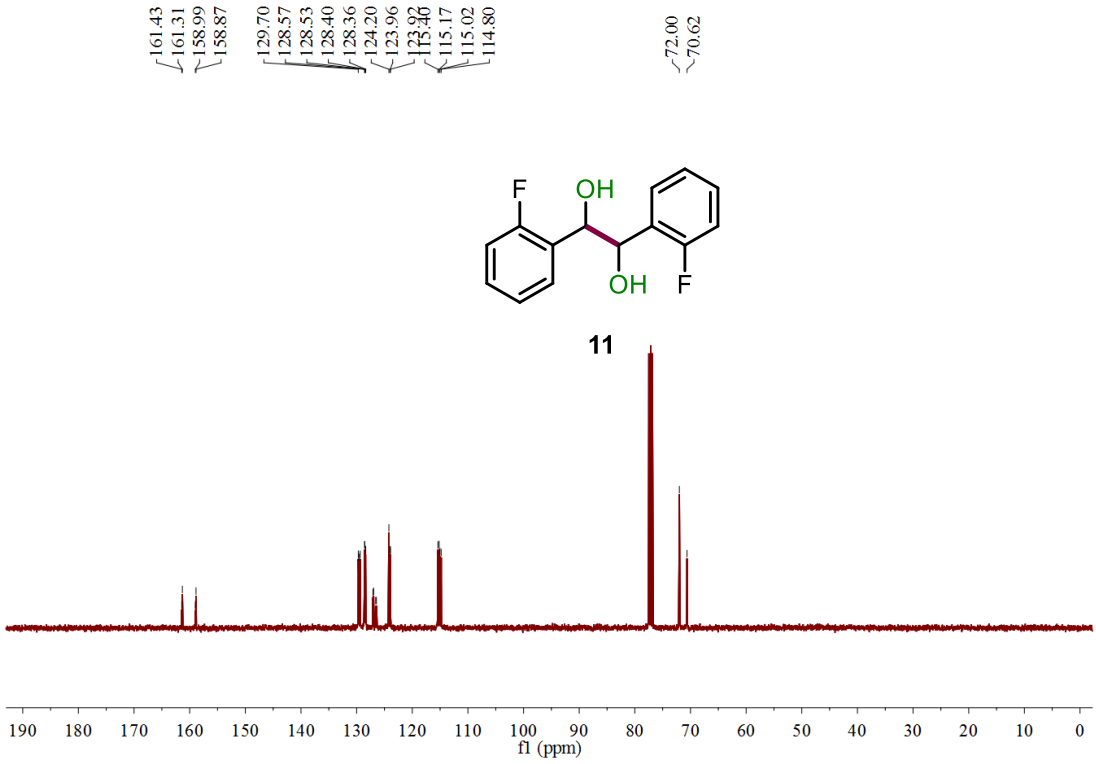


10

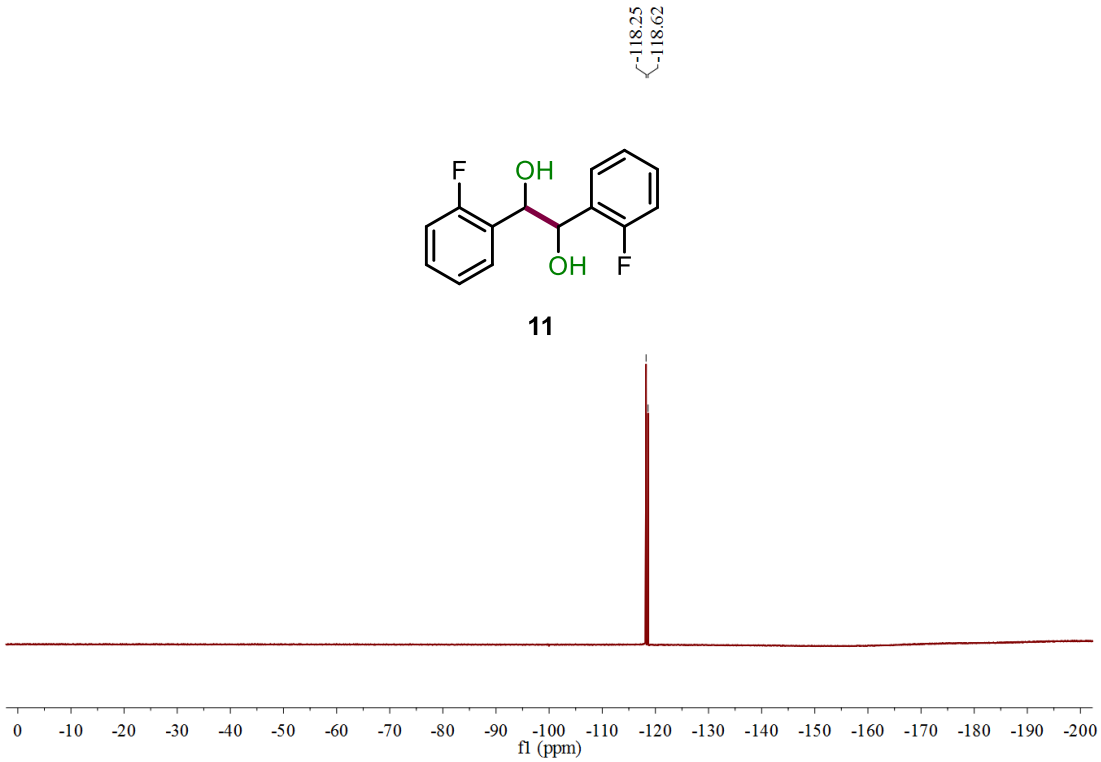
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 11



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

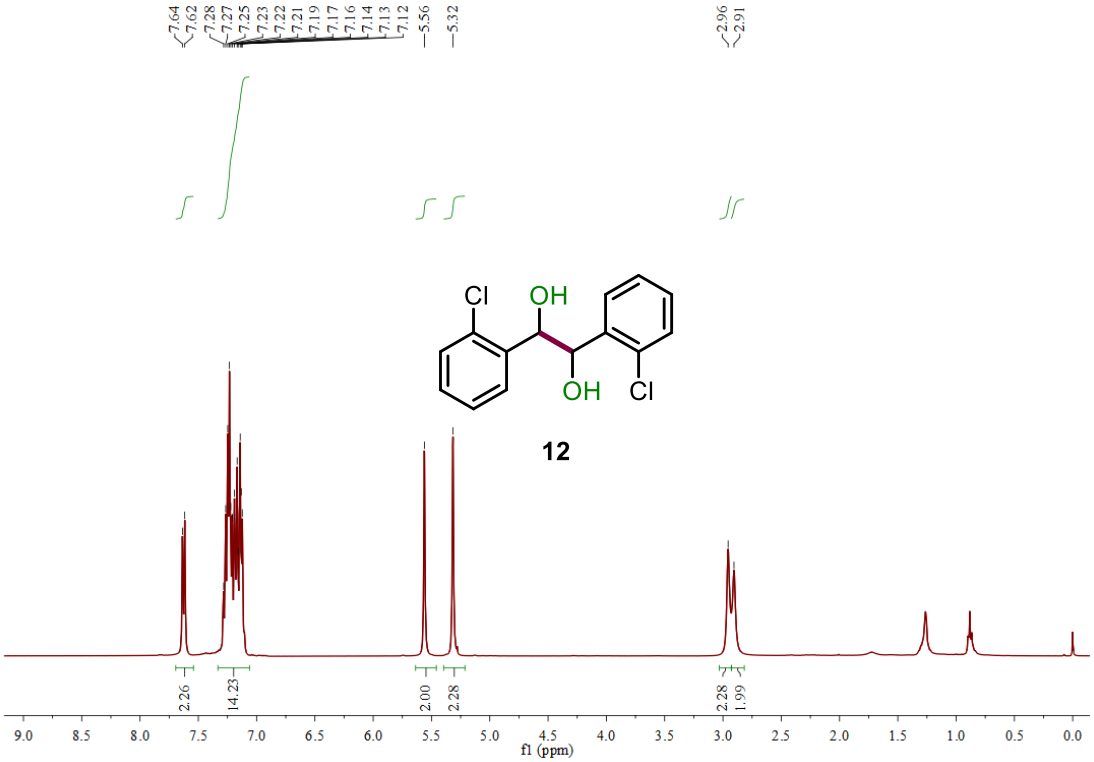


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound 11



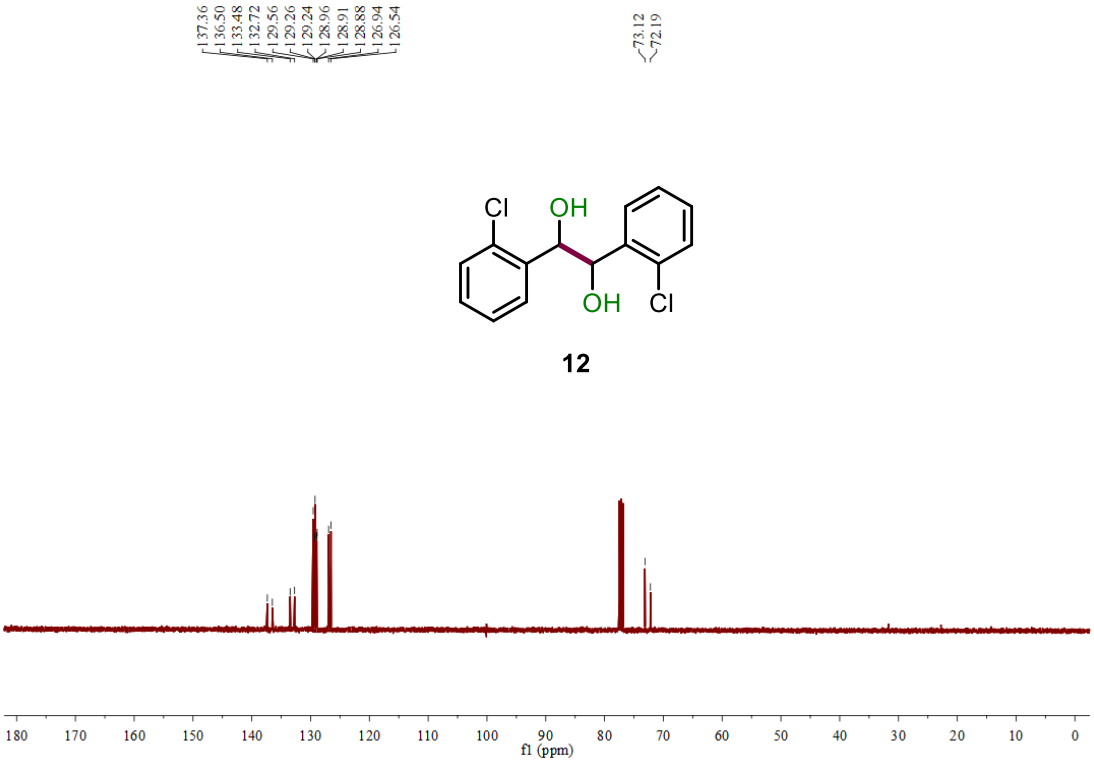
11

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 12



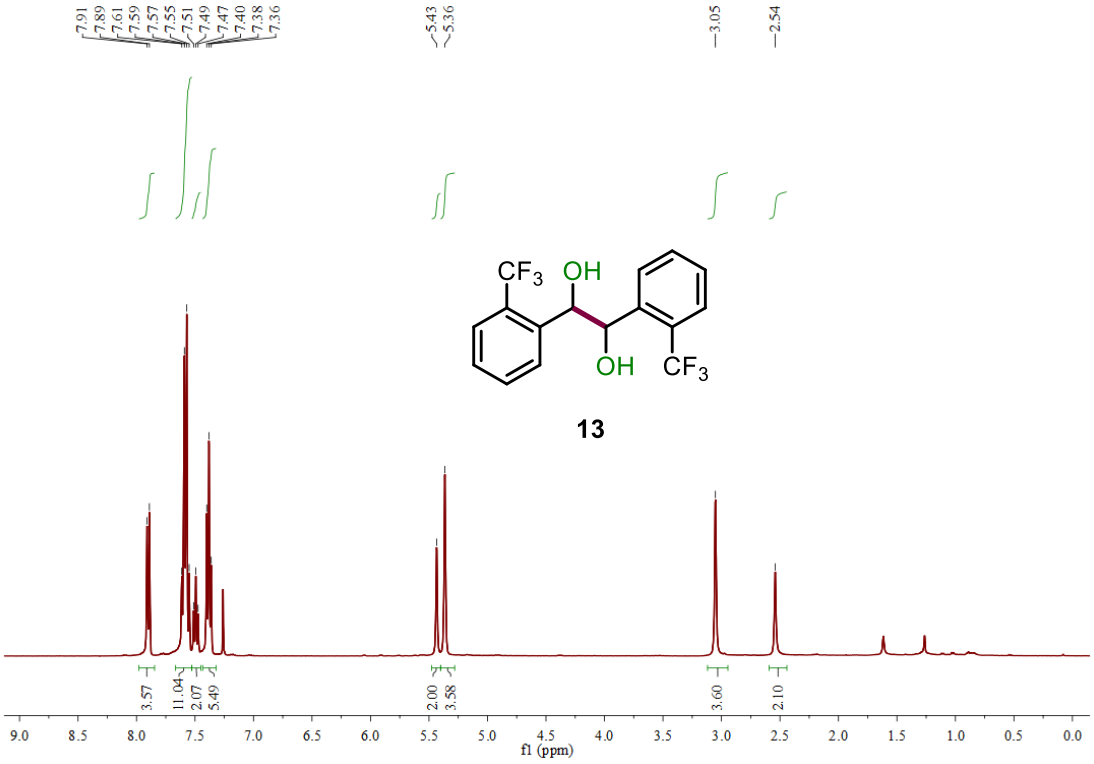
12

^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 12



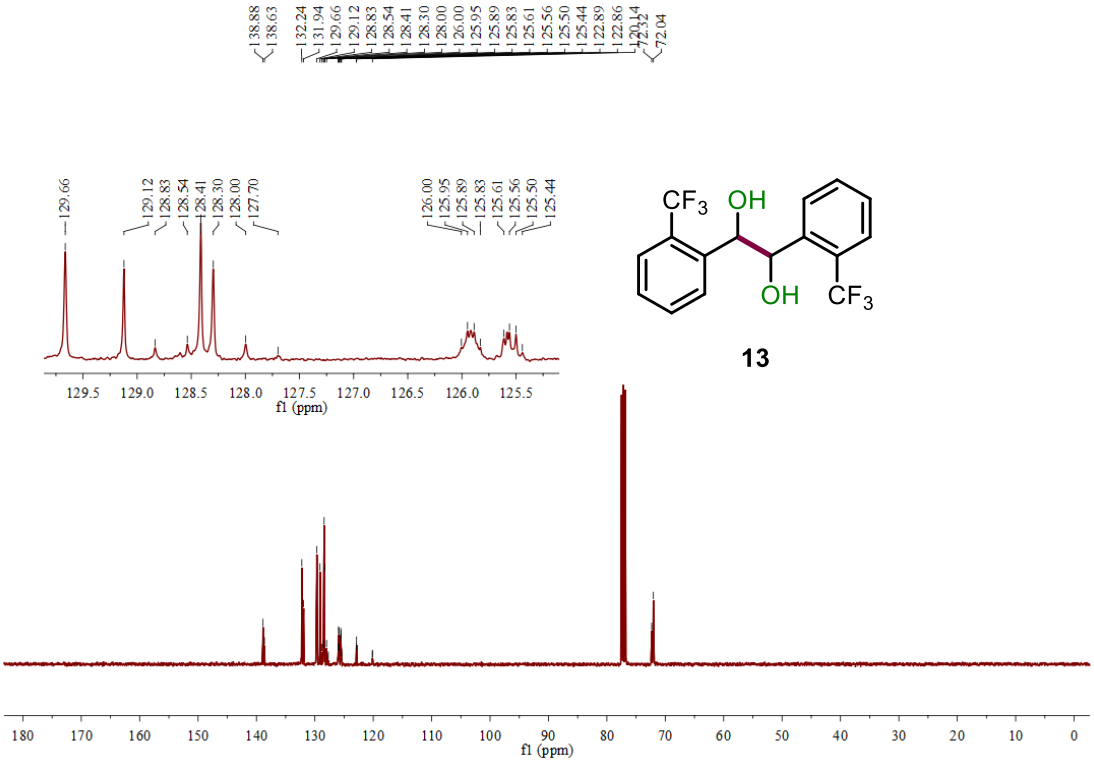
12

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



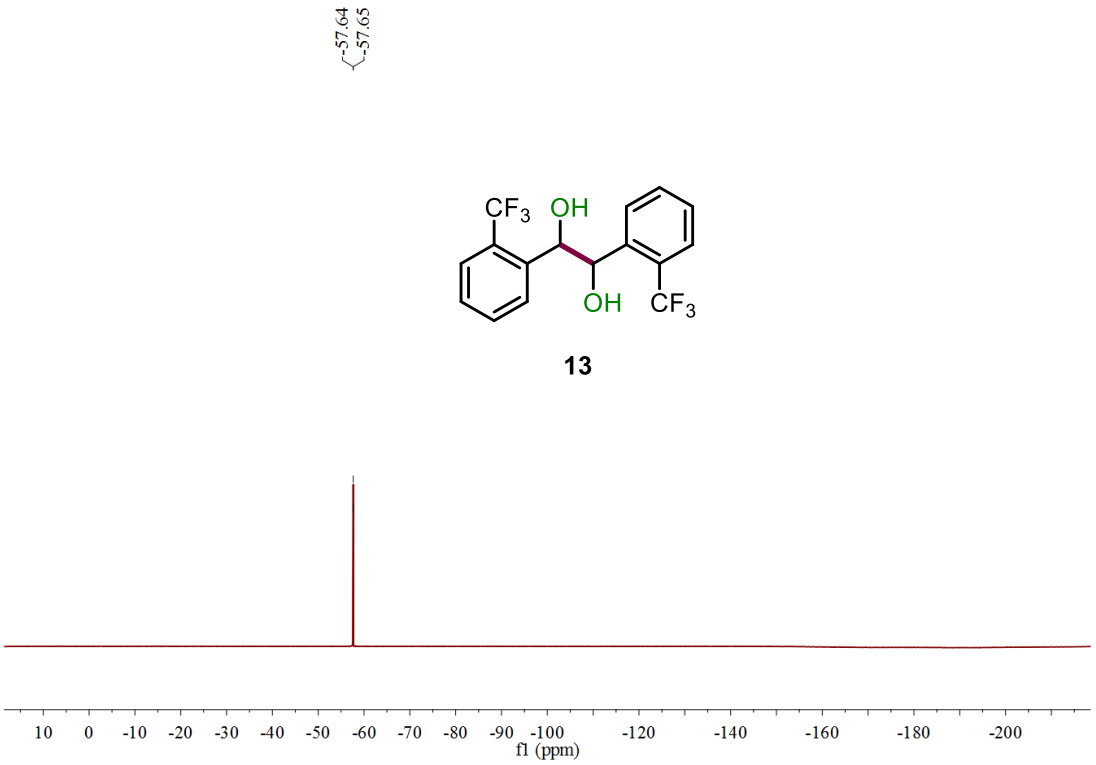
13

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



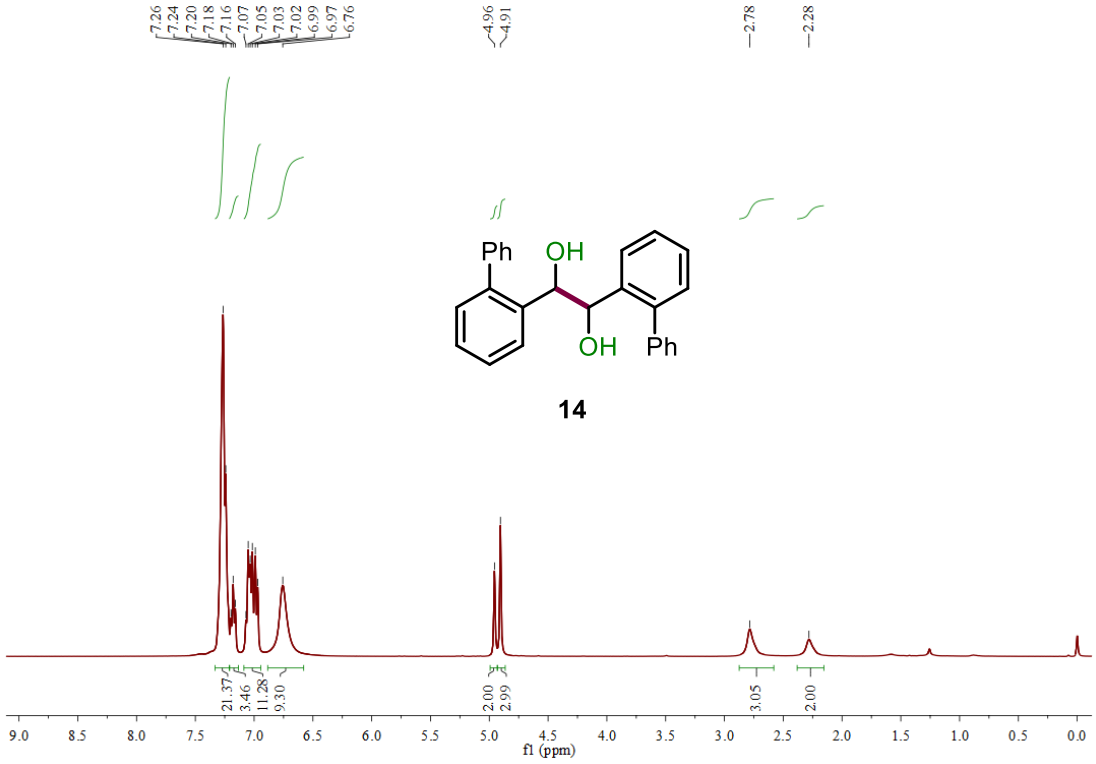
13

^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound 13



13

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



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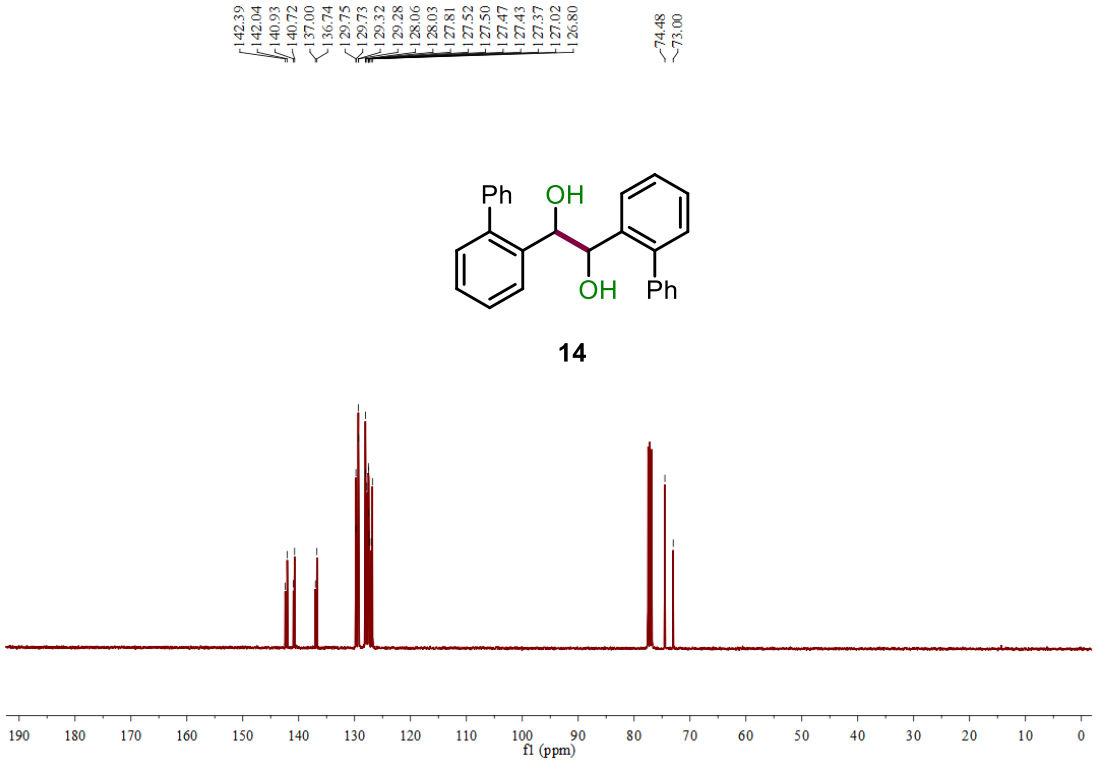
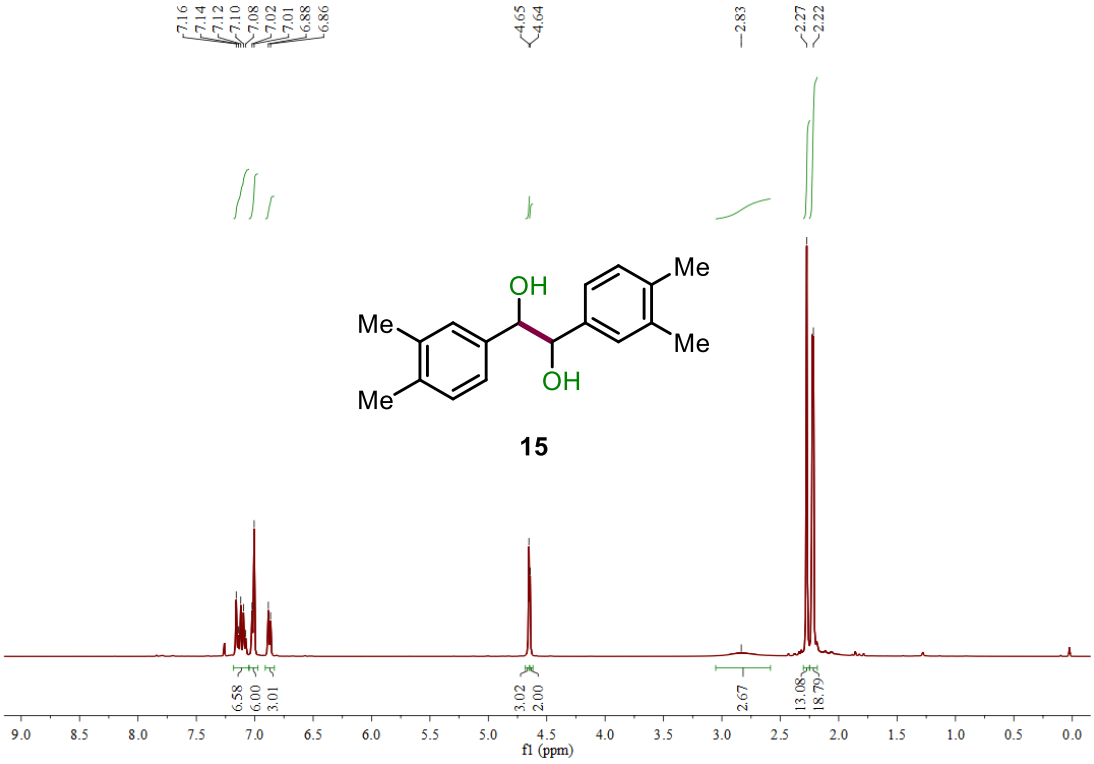
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 14



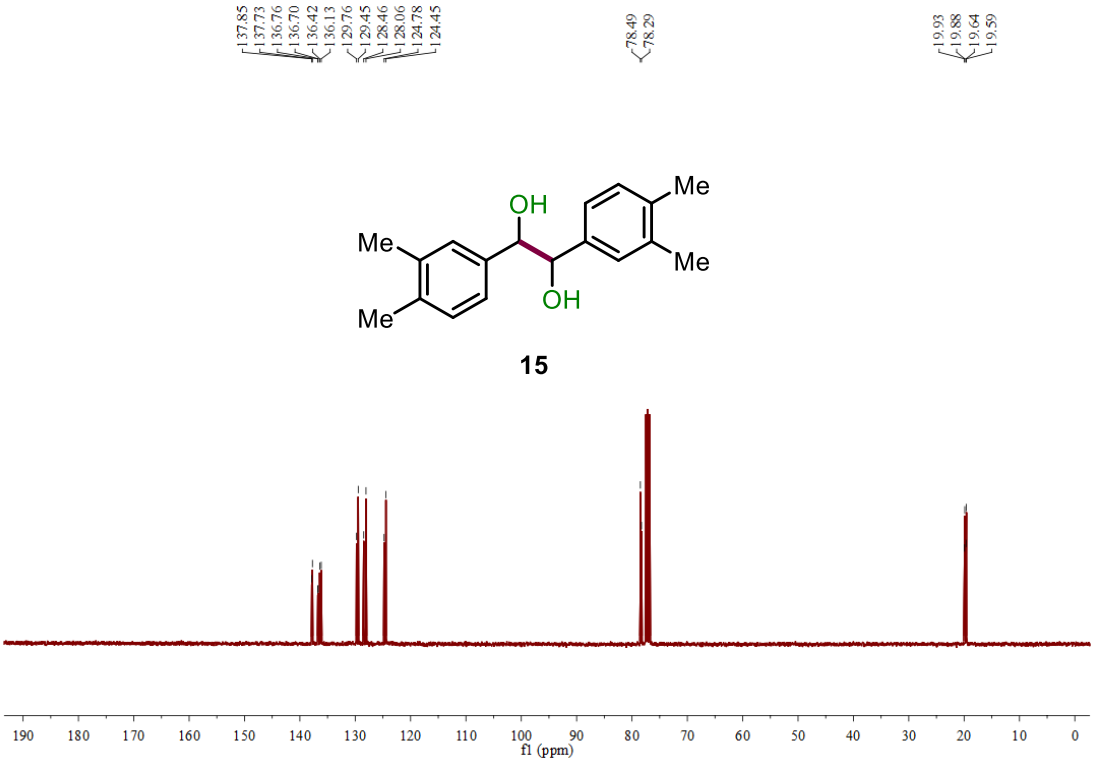
14

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



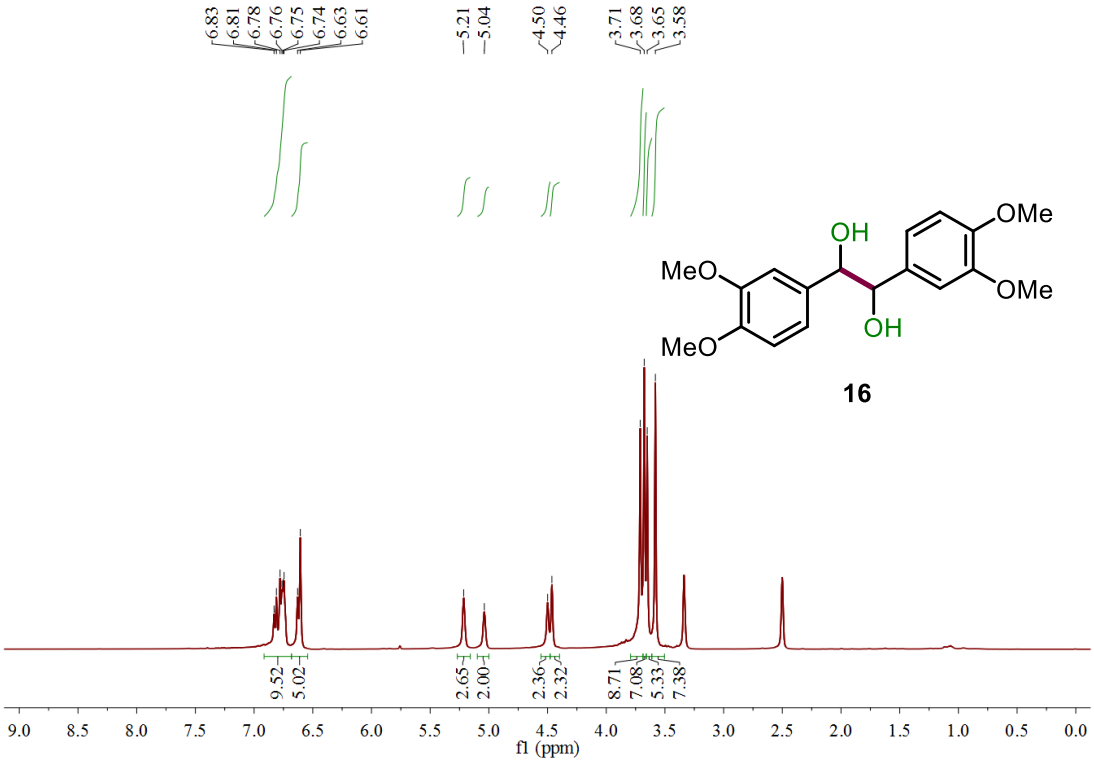
15

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

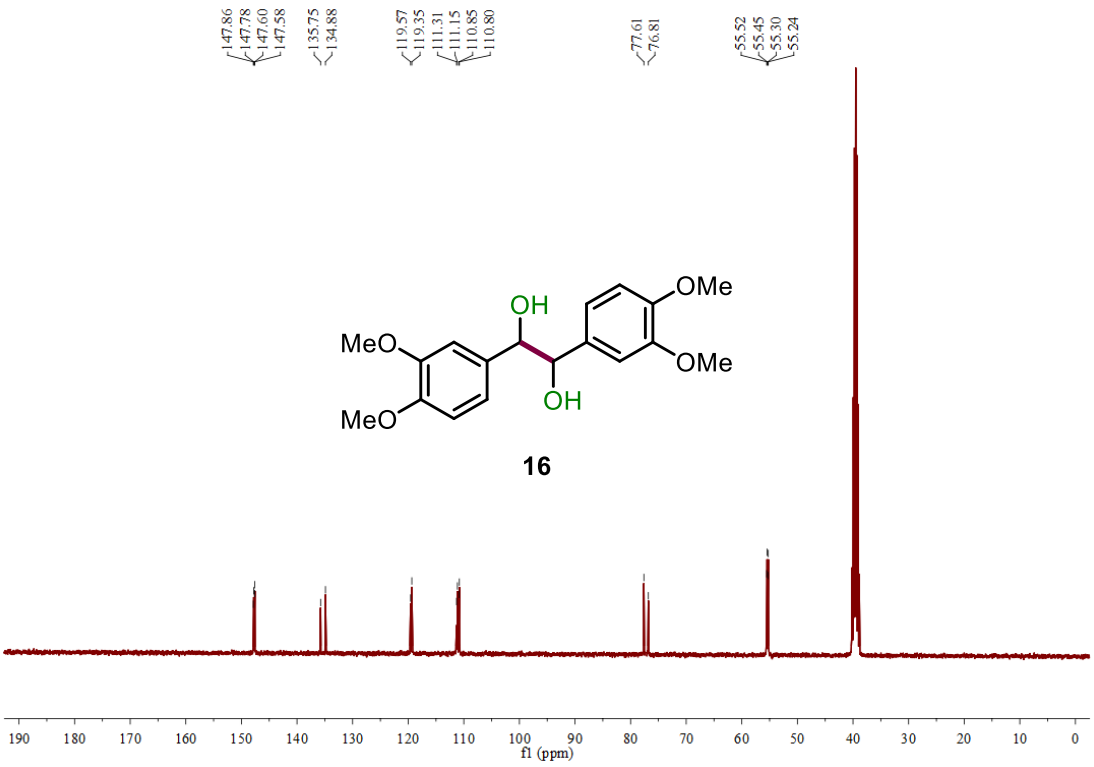


15

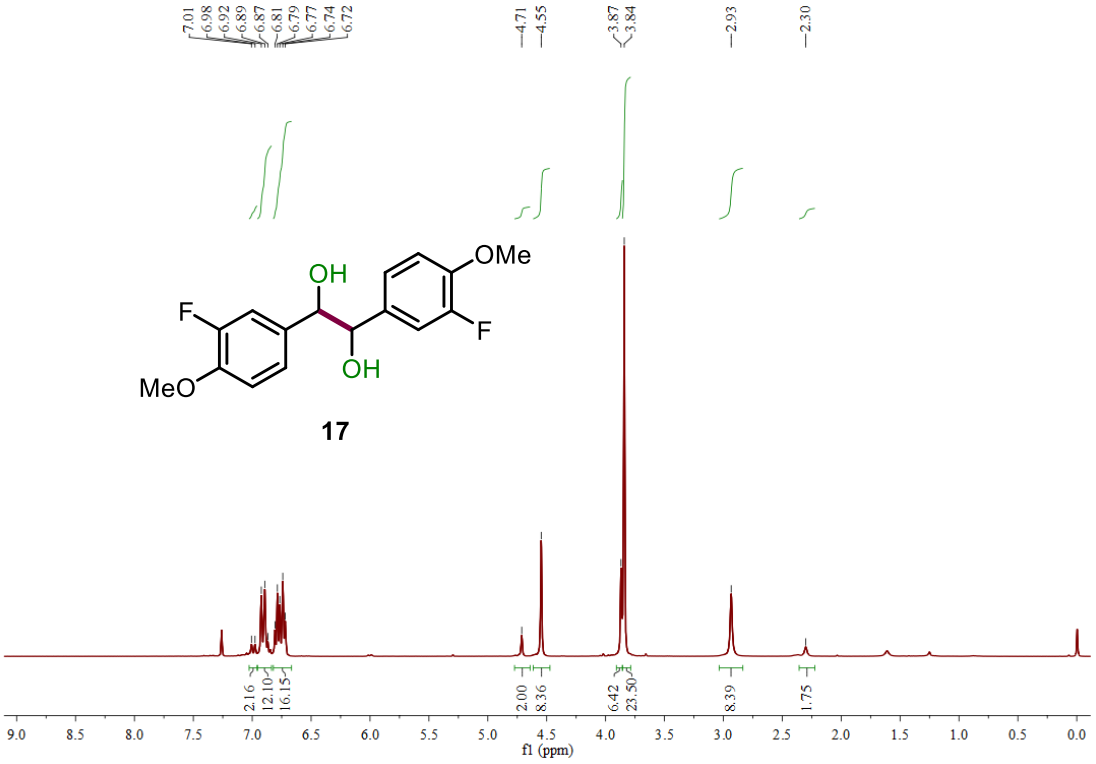
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 16



^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 16

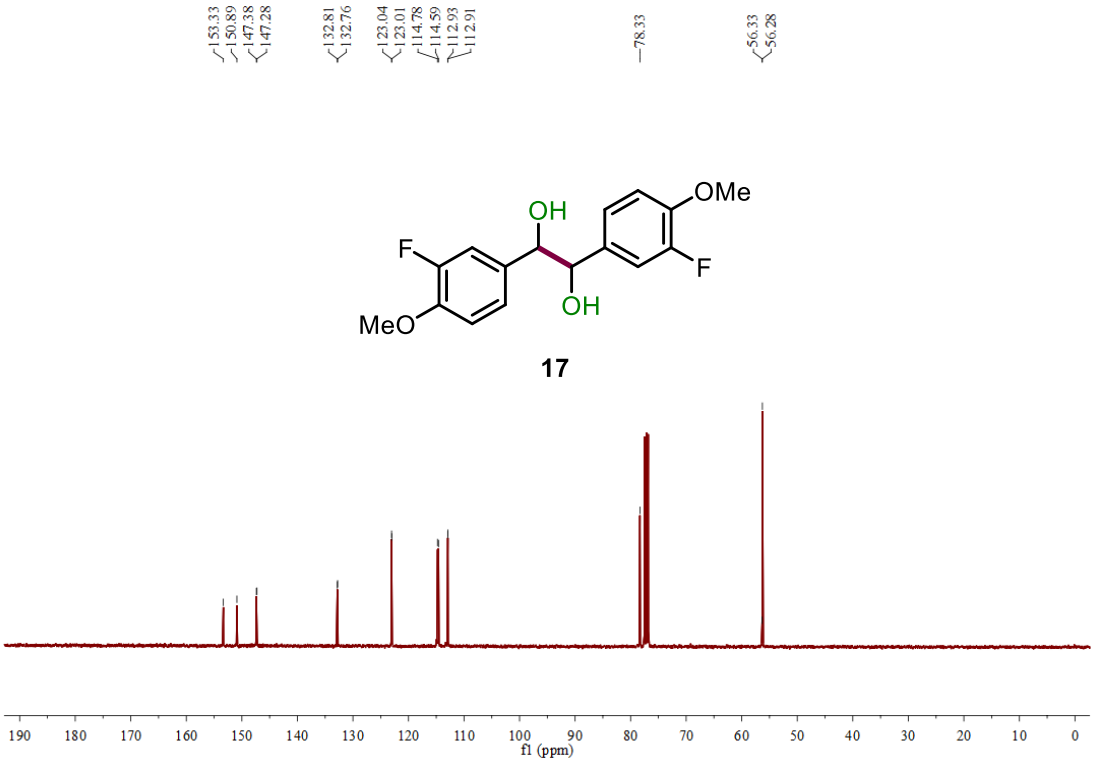


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 17



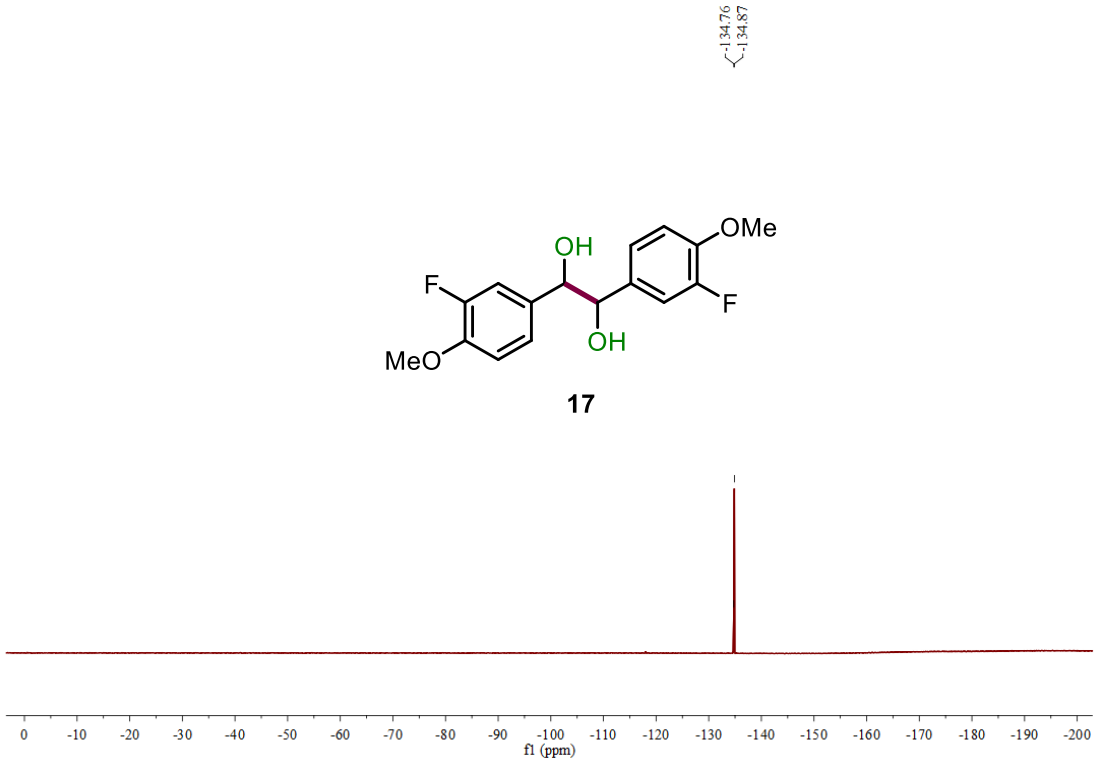
17

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



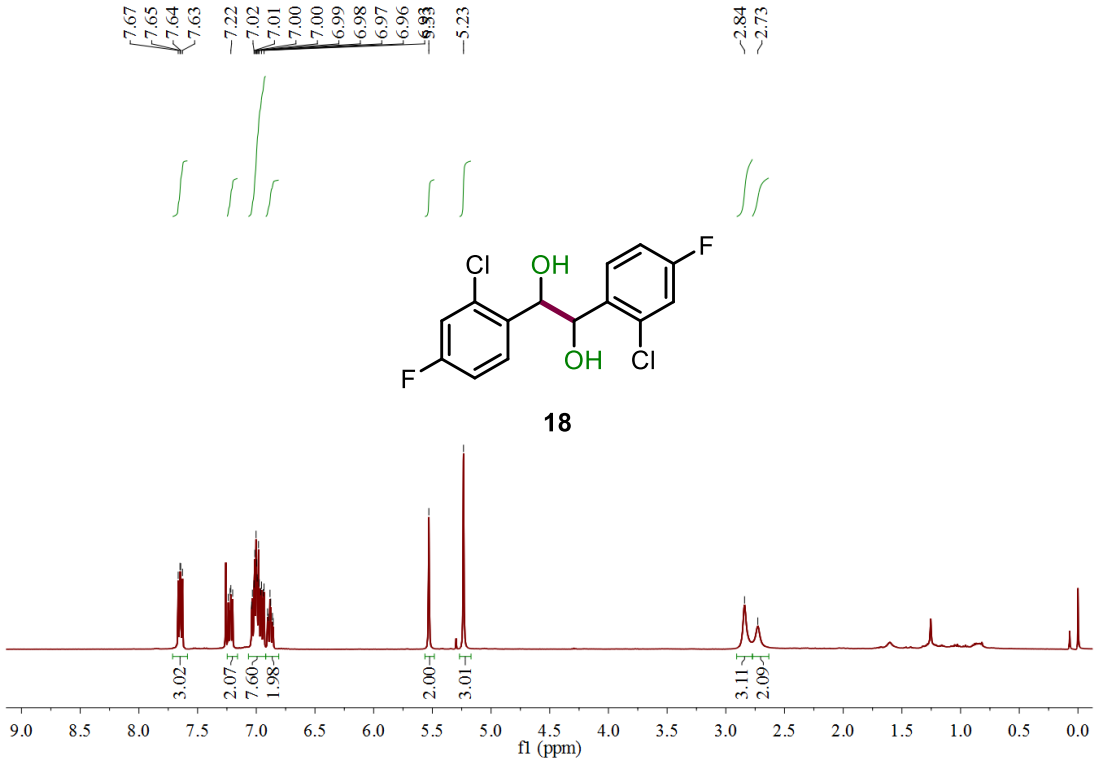
17

^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound 17

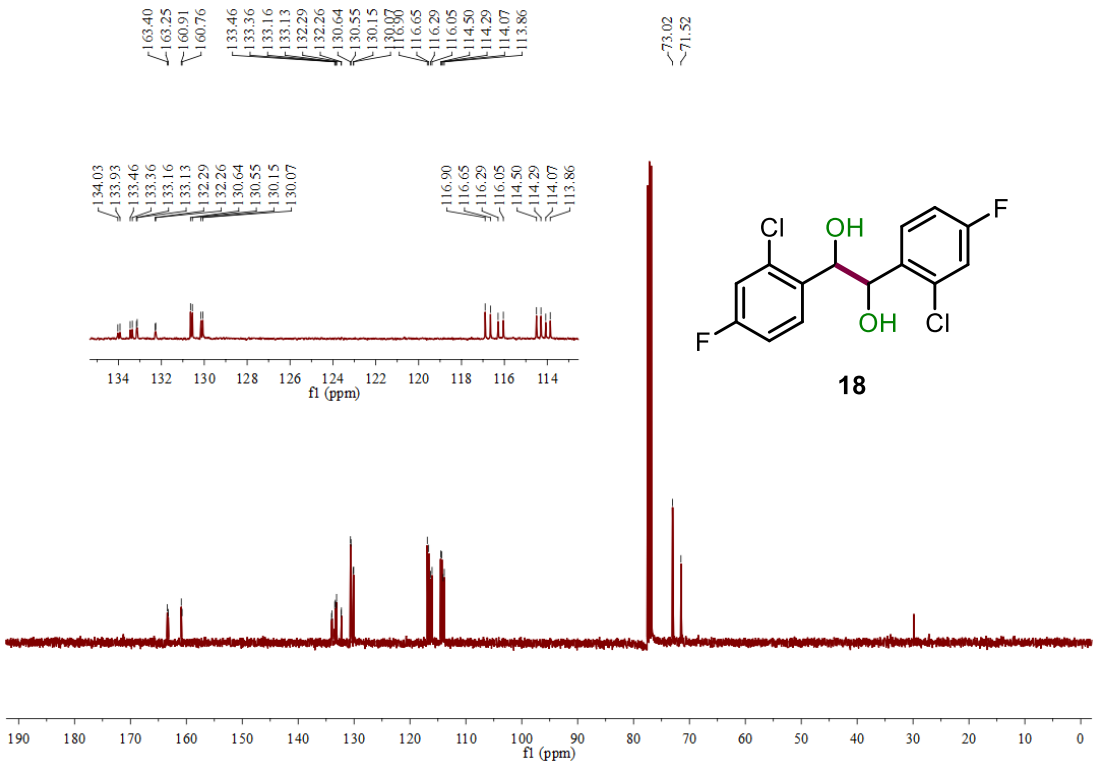


17

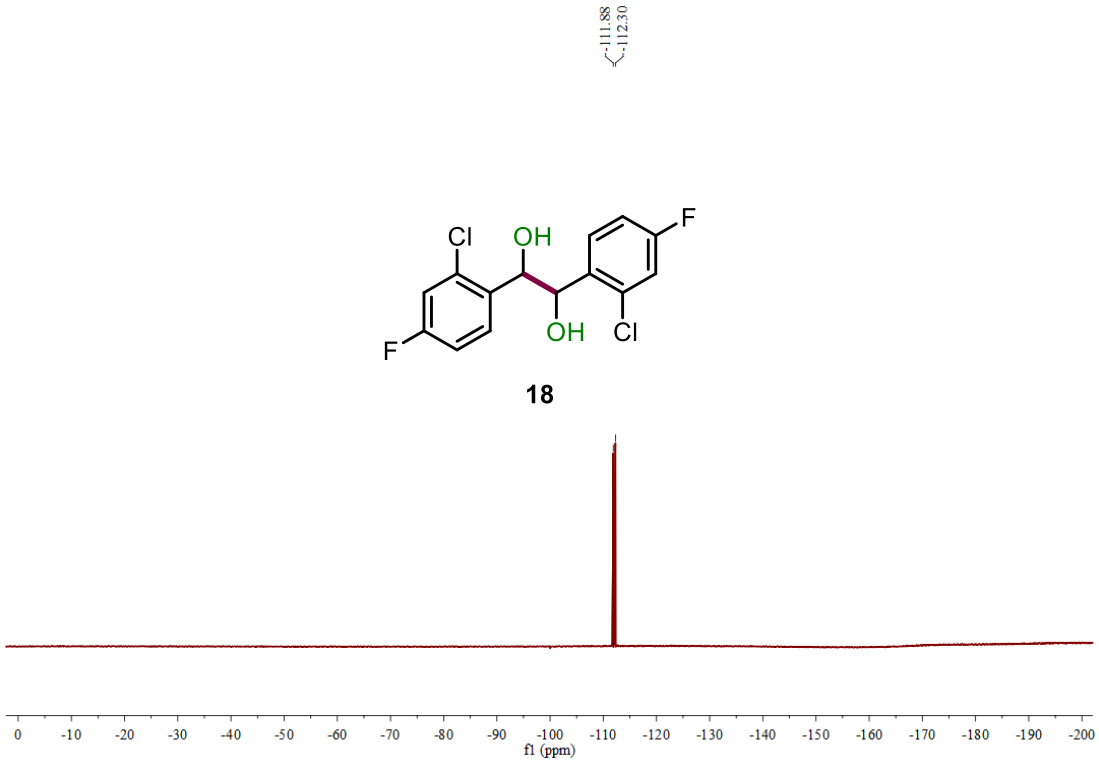
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 18



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

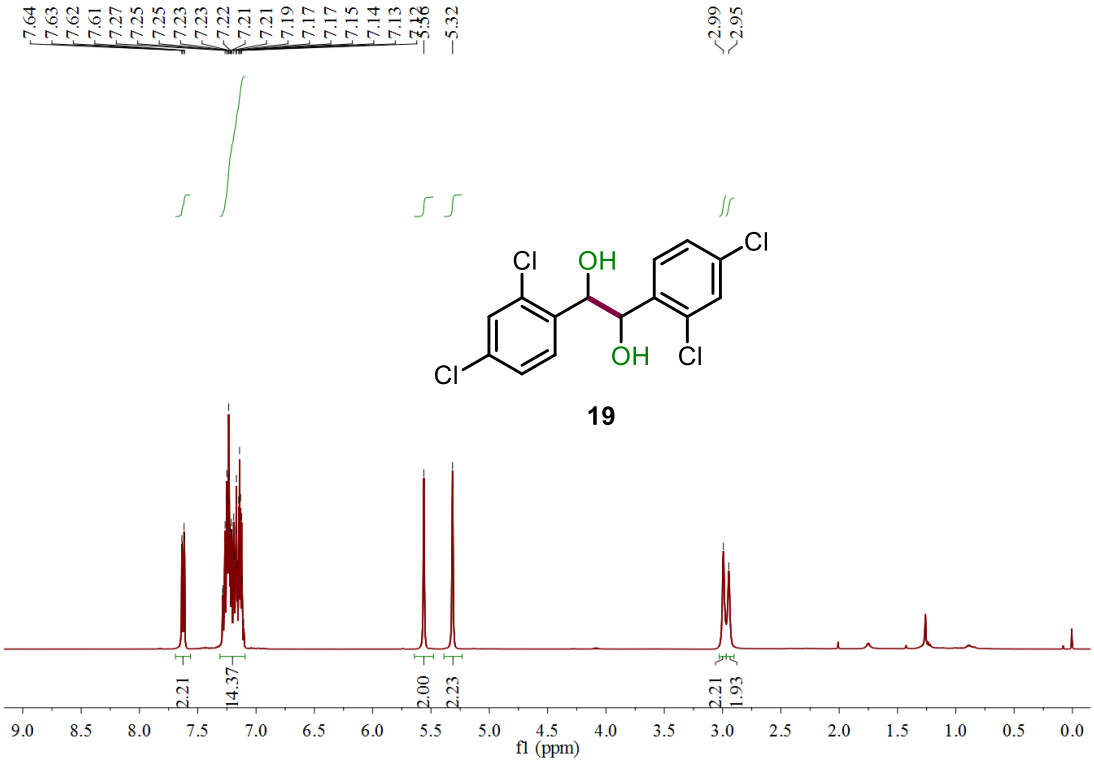


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound 18

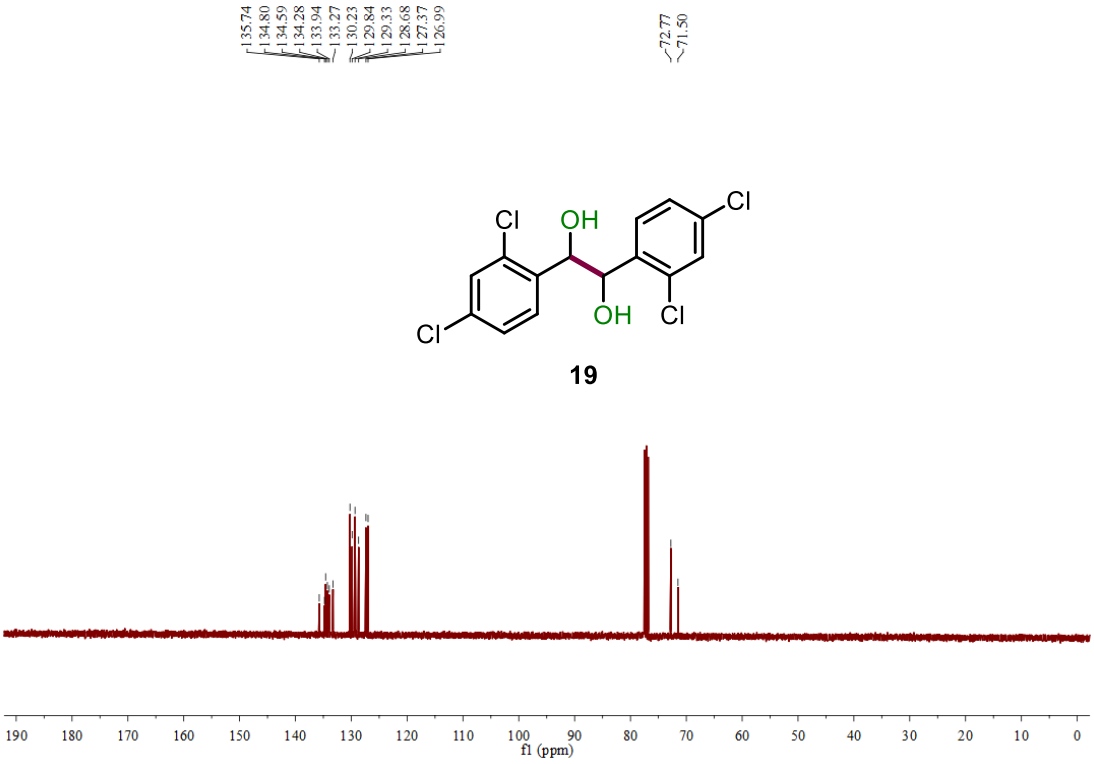


18

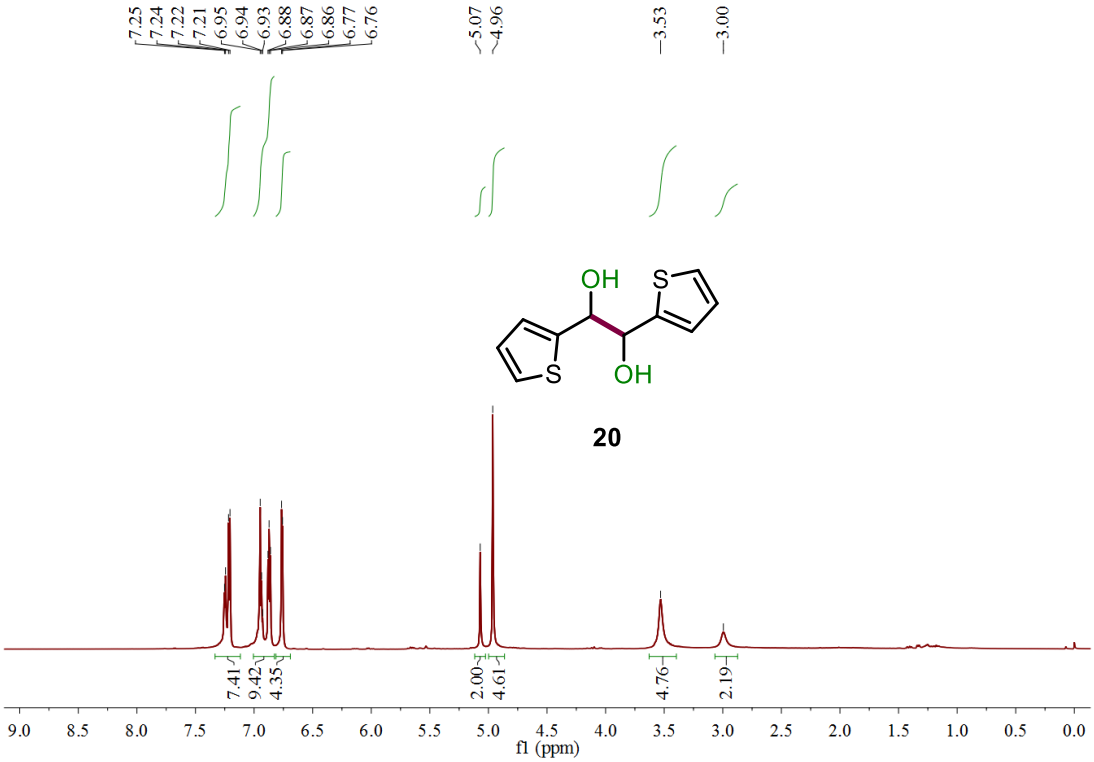
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 19



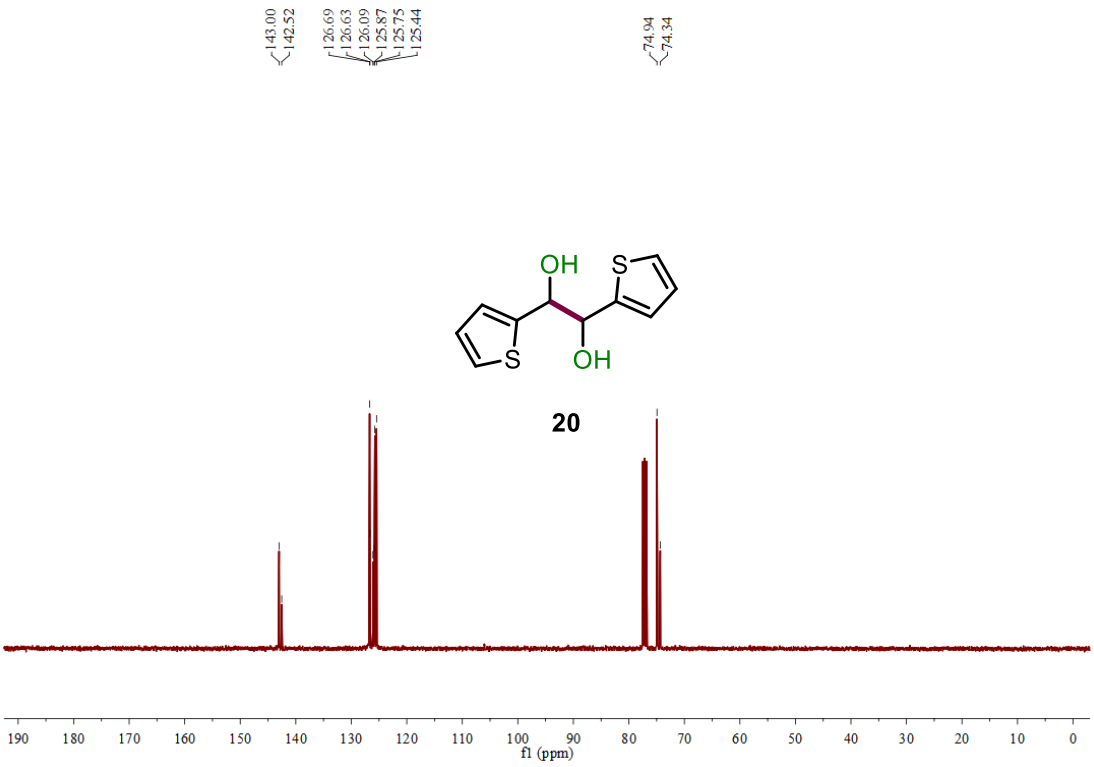
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 19



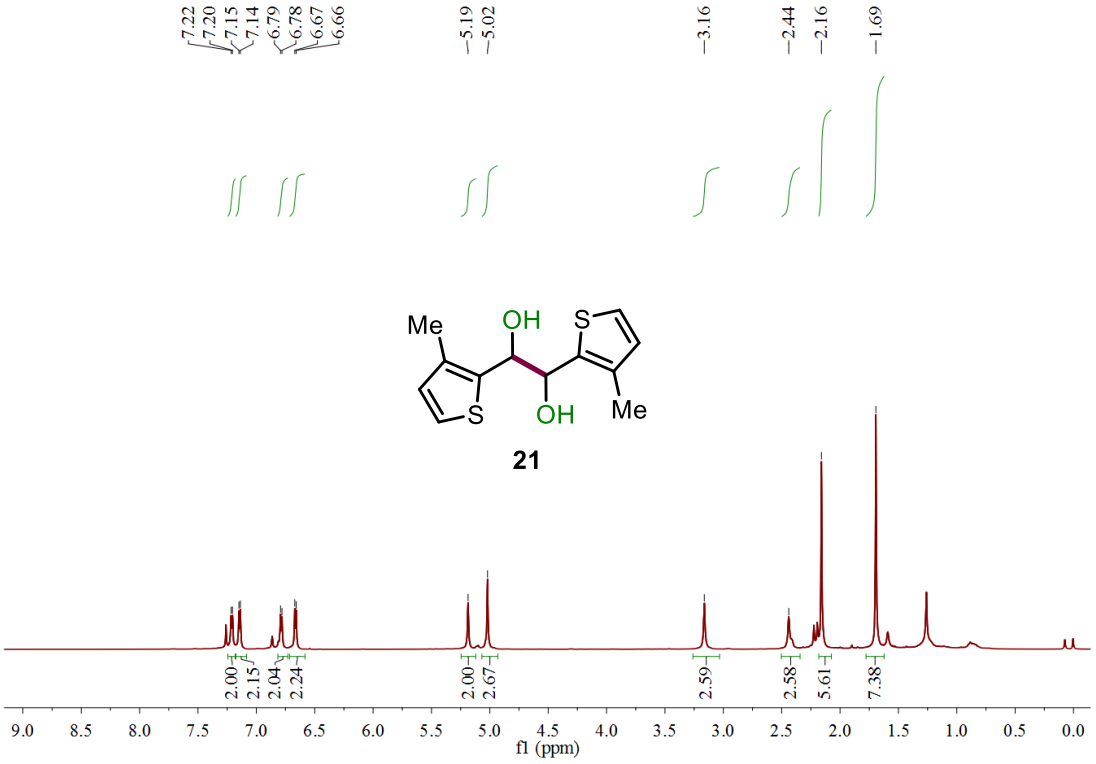
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 20



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

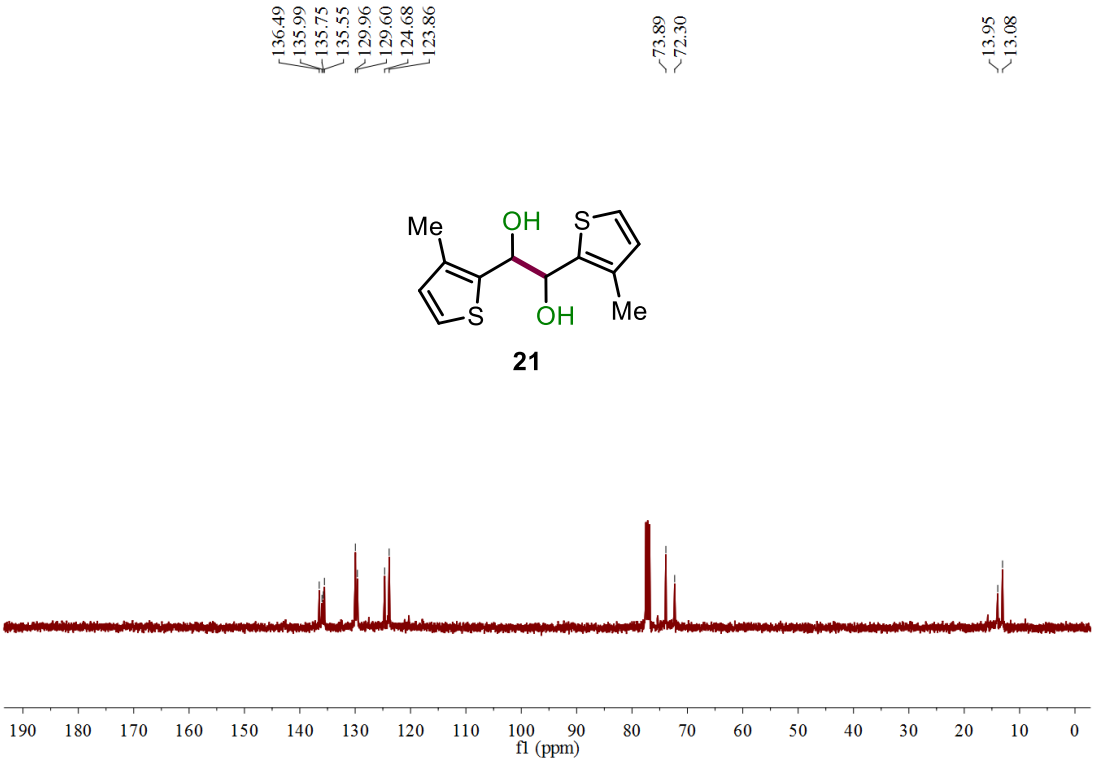


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 21



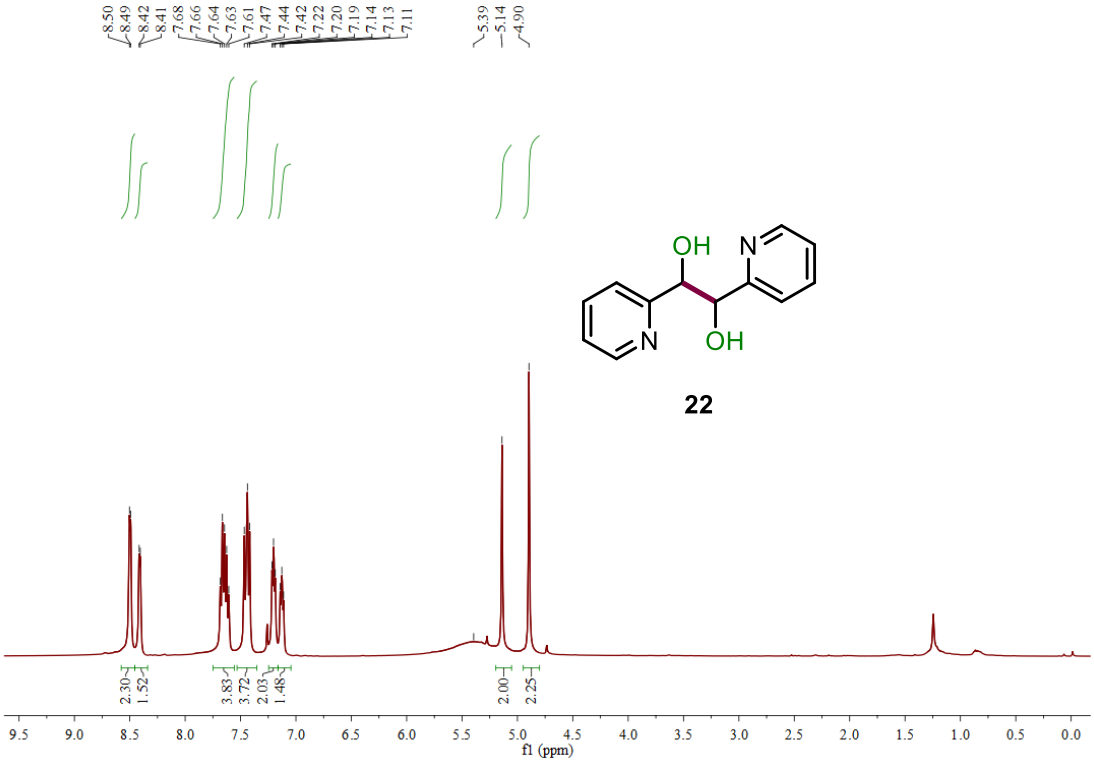
21

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



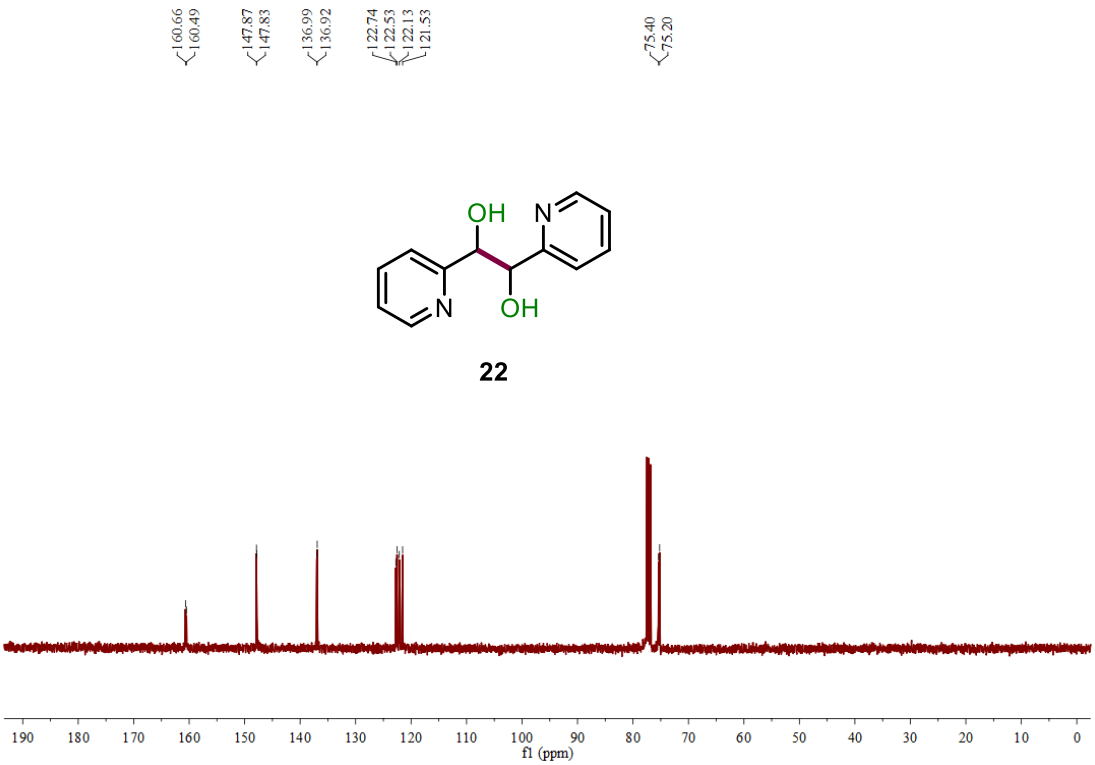
21

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



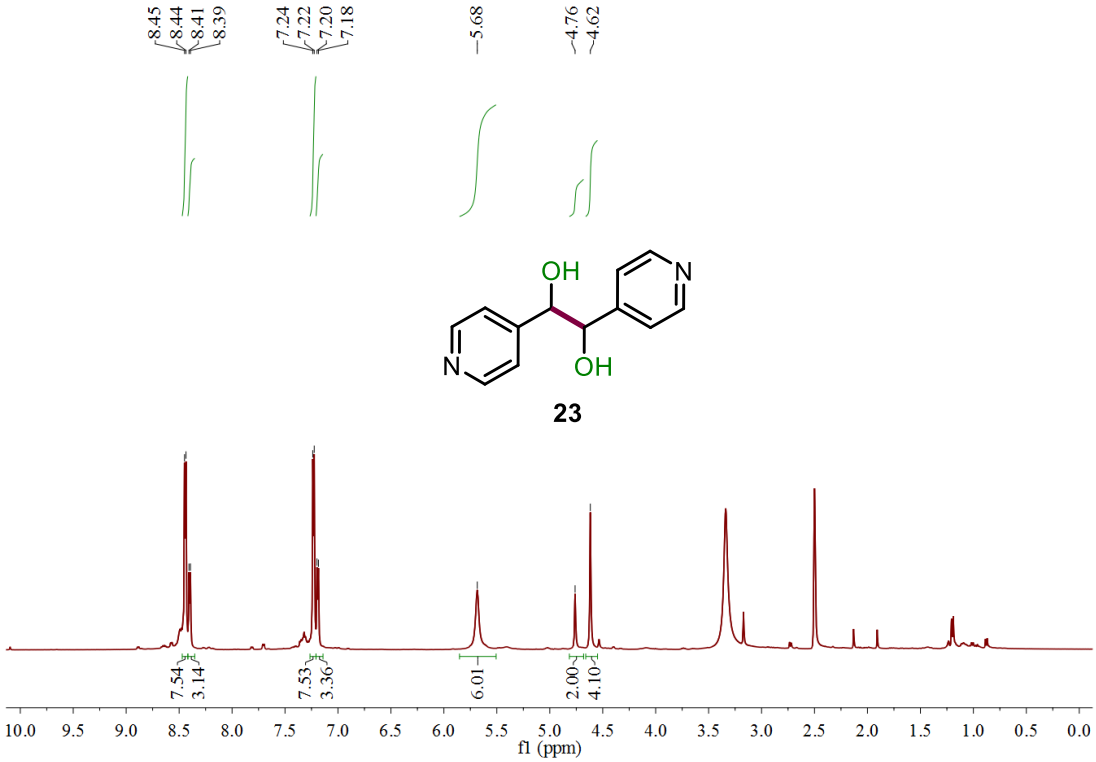
22

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



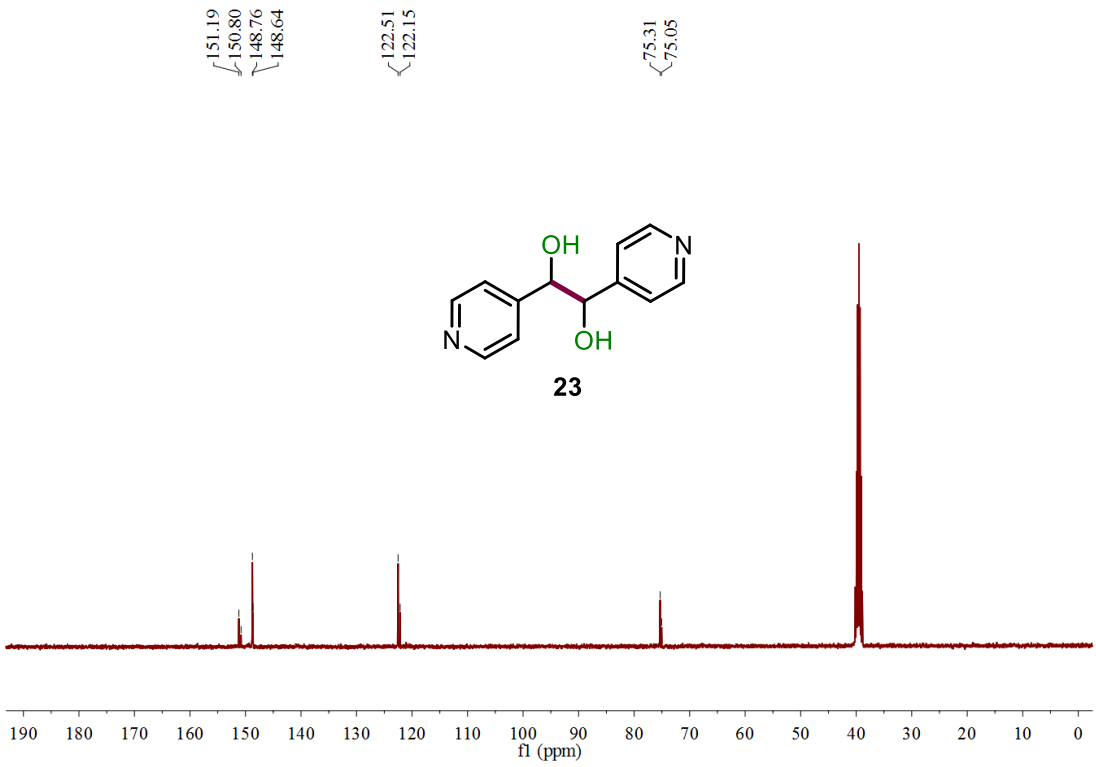
22

^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 23



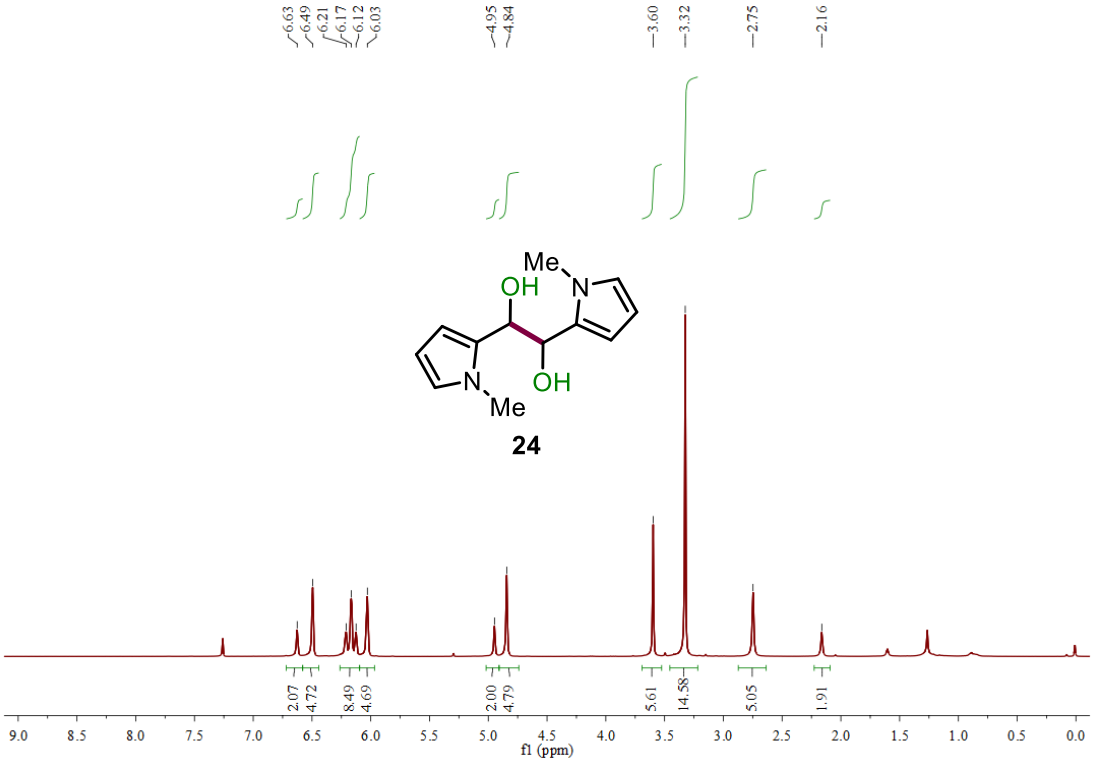
23

^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 23



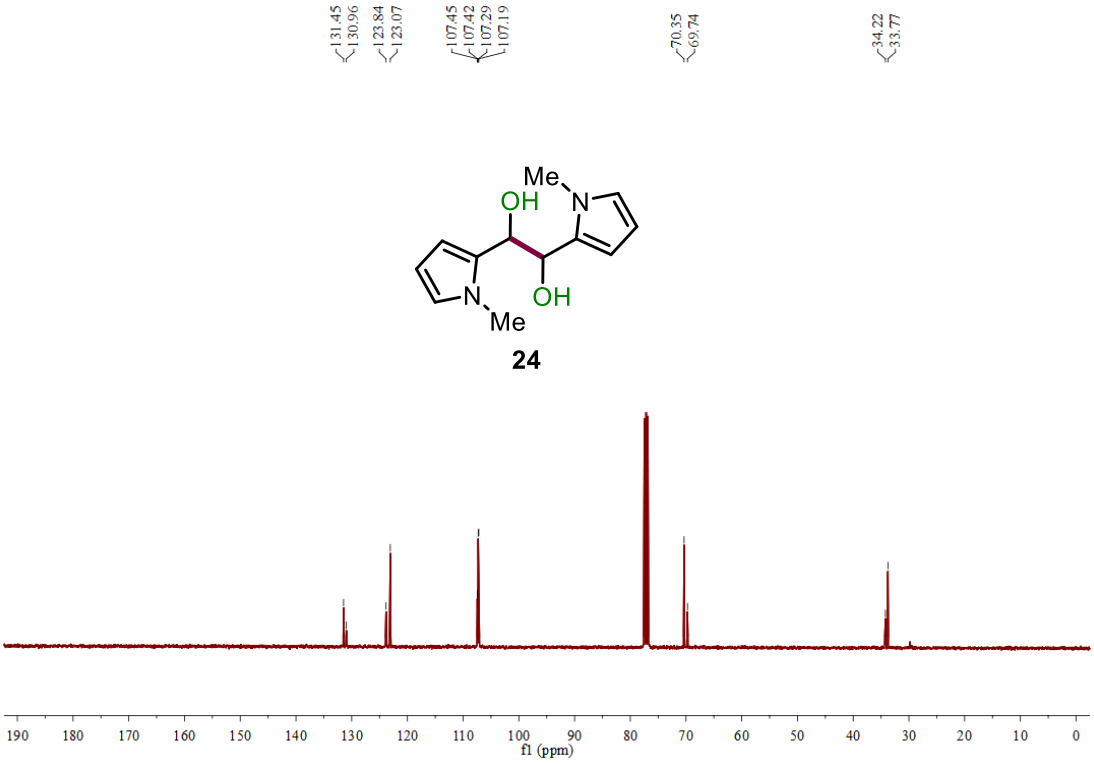
23

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



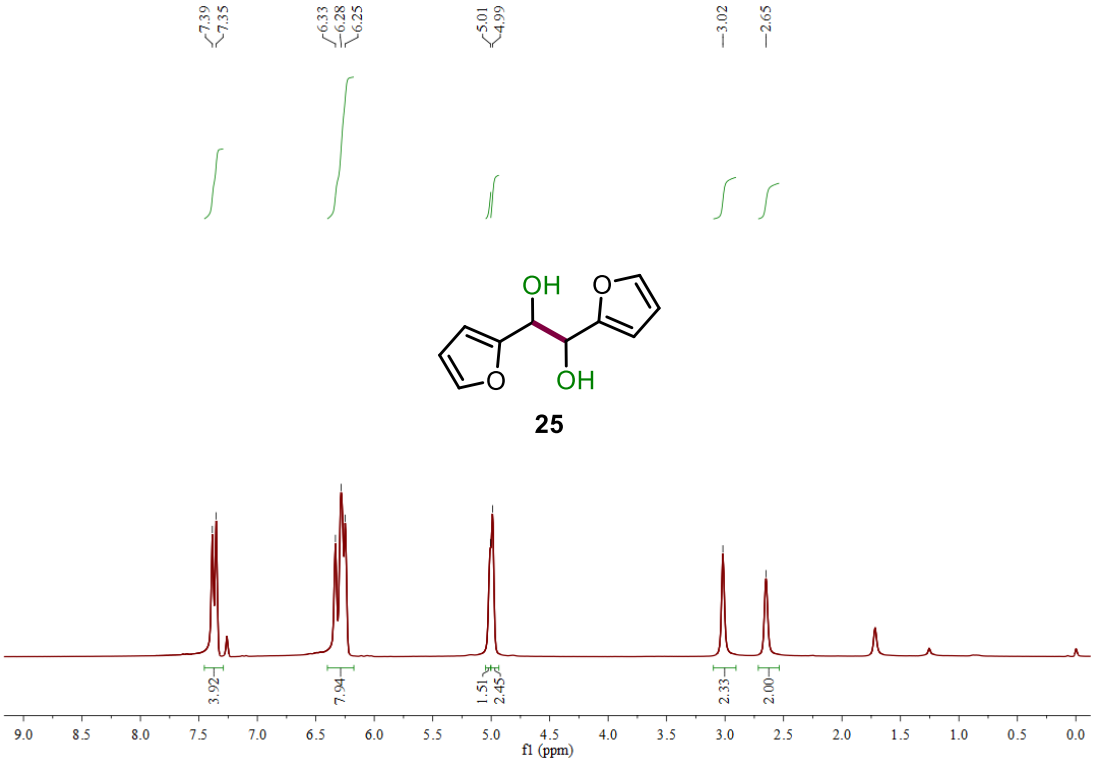
24

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



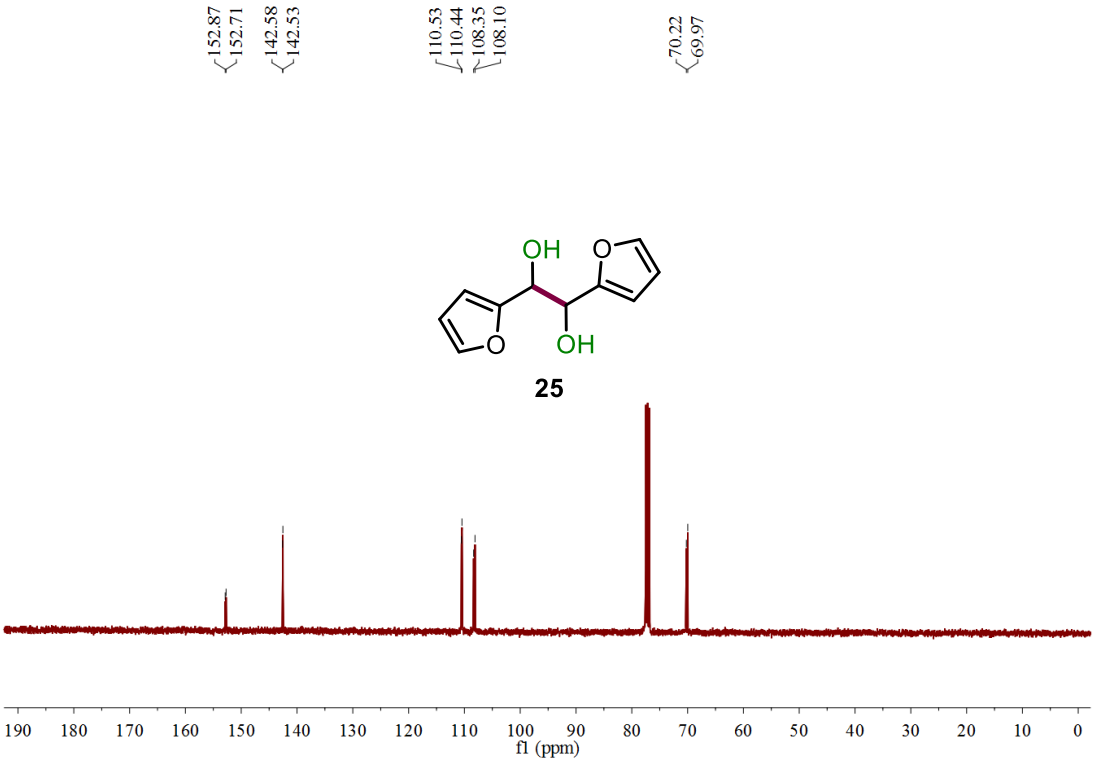
24

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



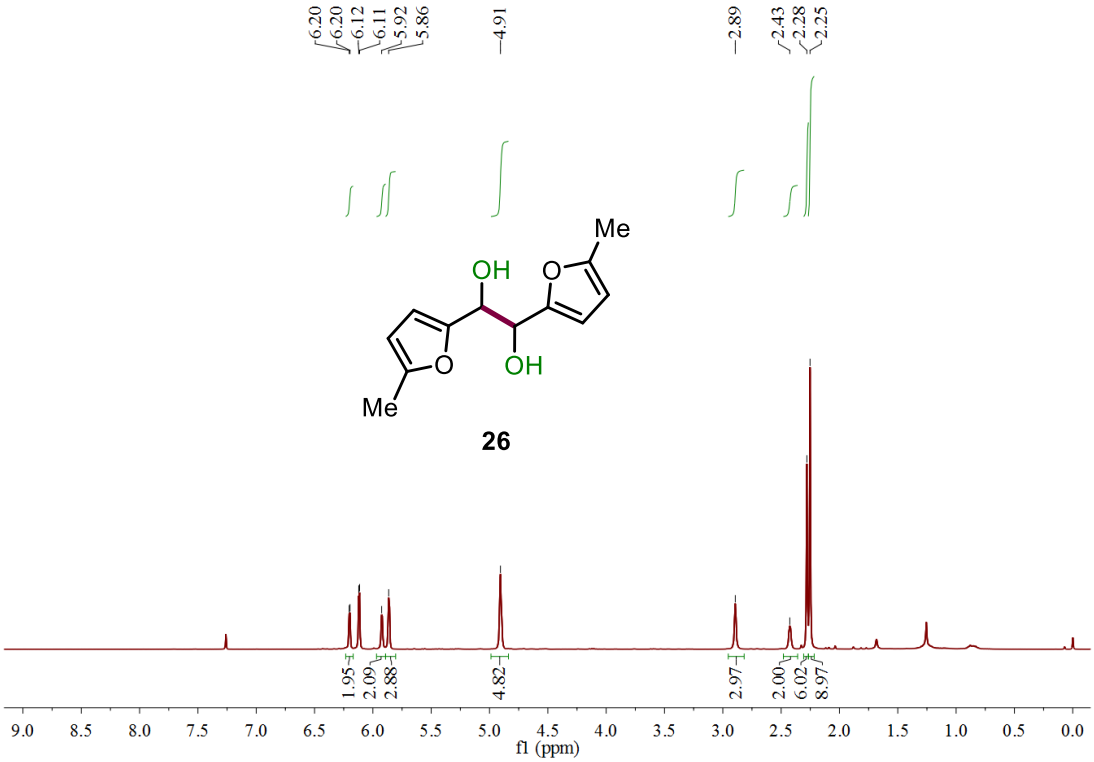
25

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



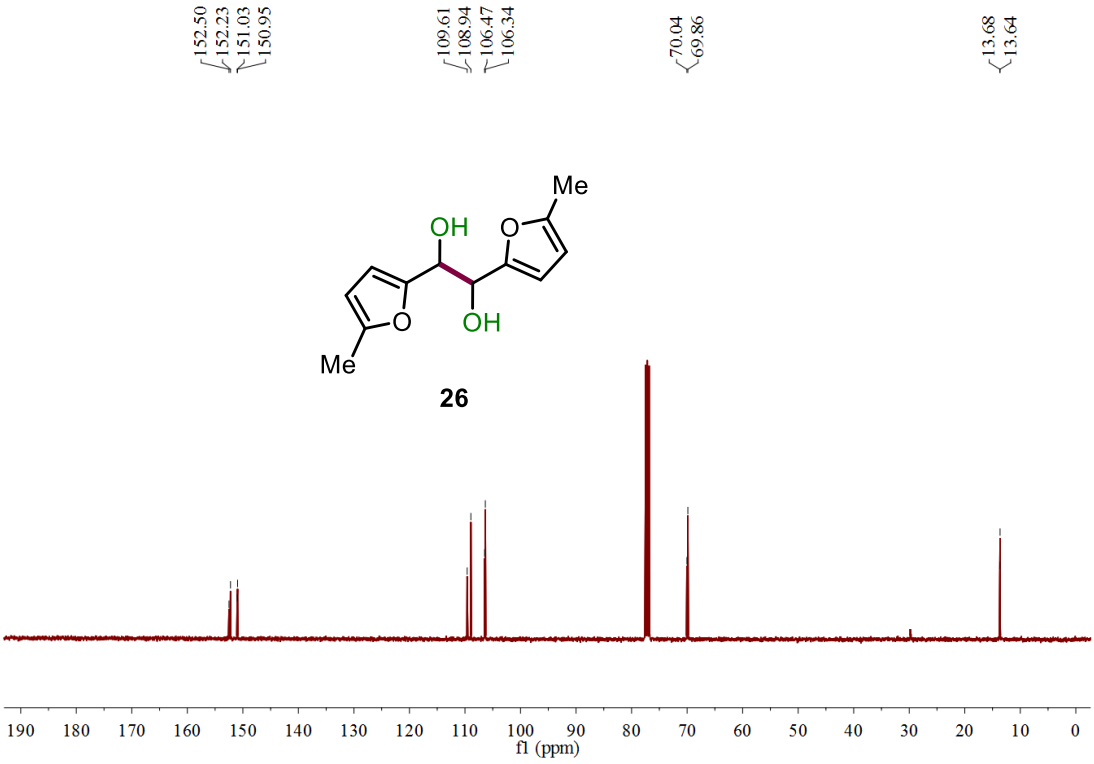
25

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



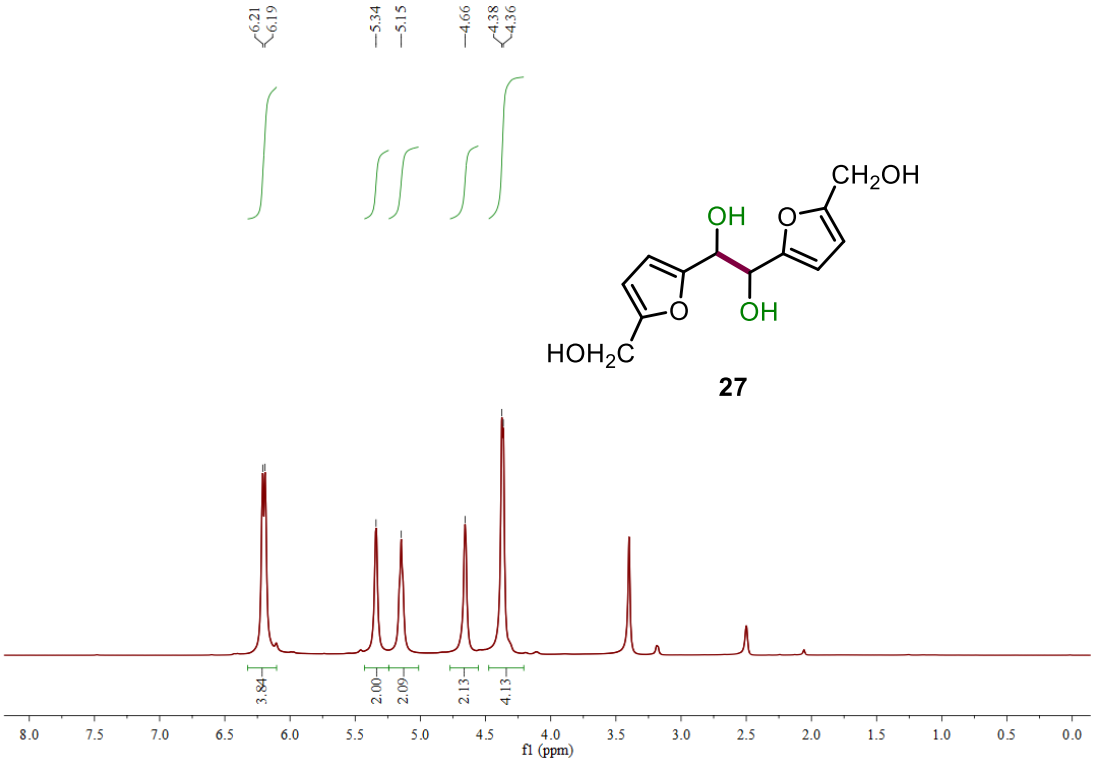
26

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



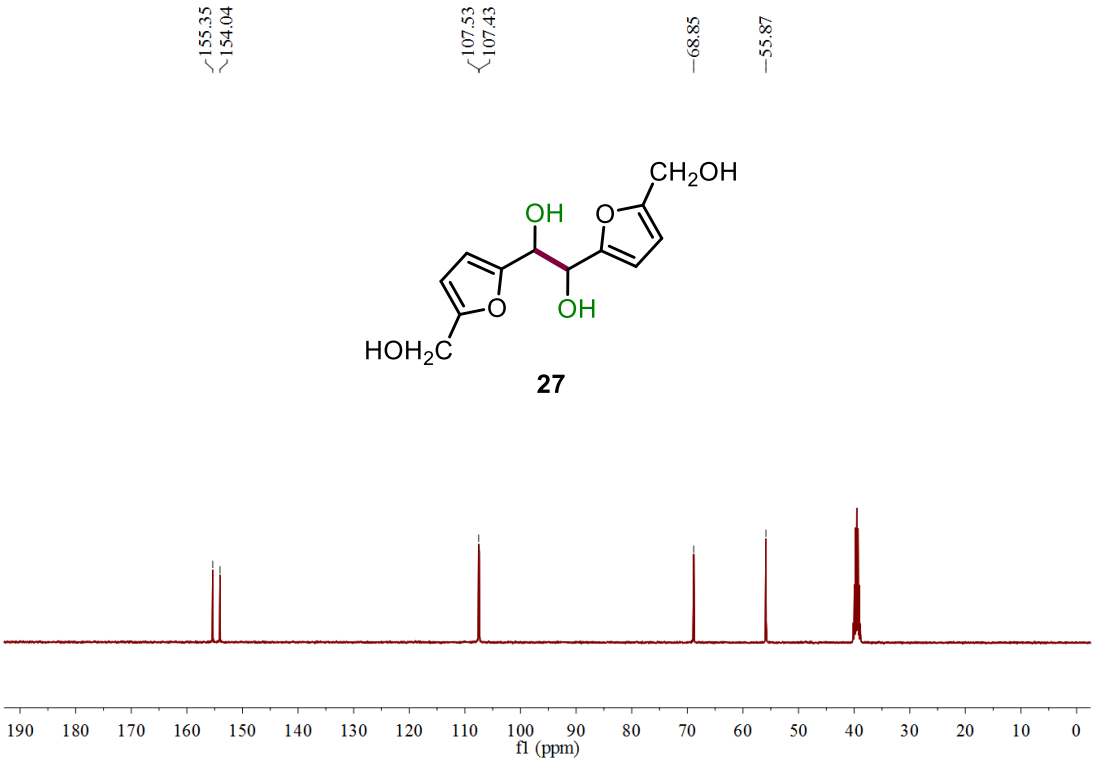
26

^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 27



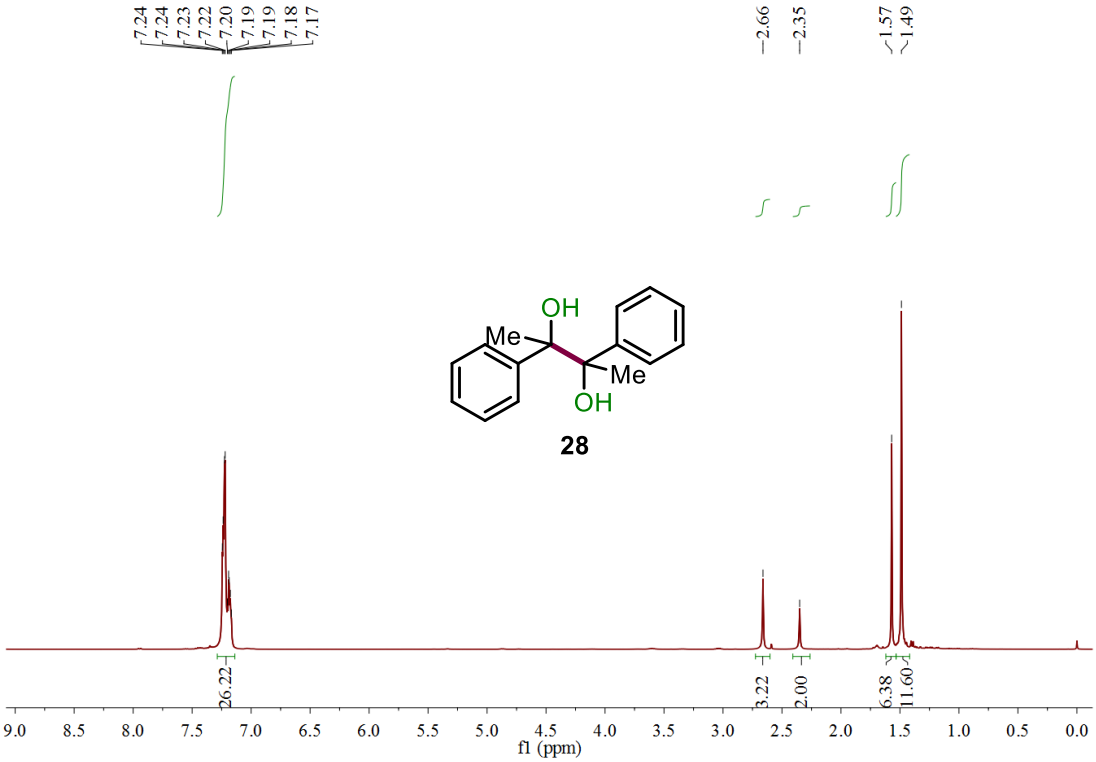
27

^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 27



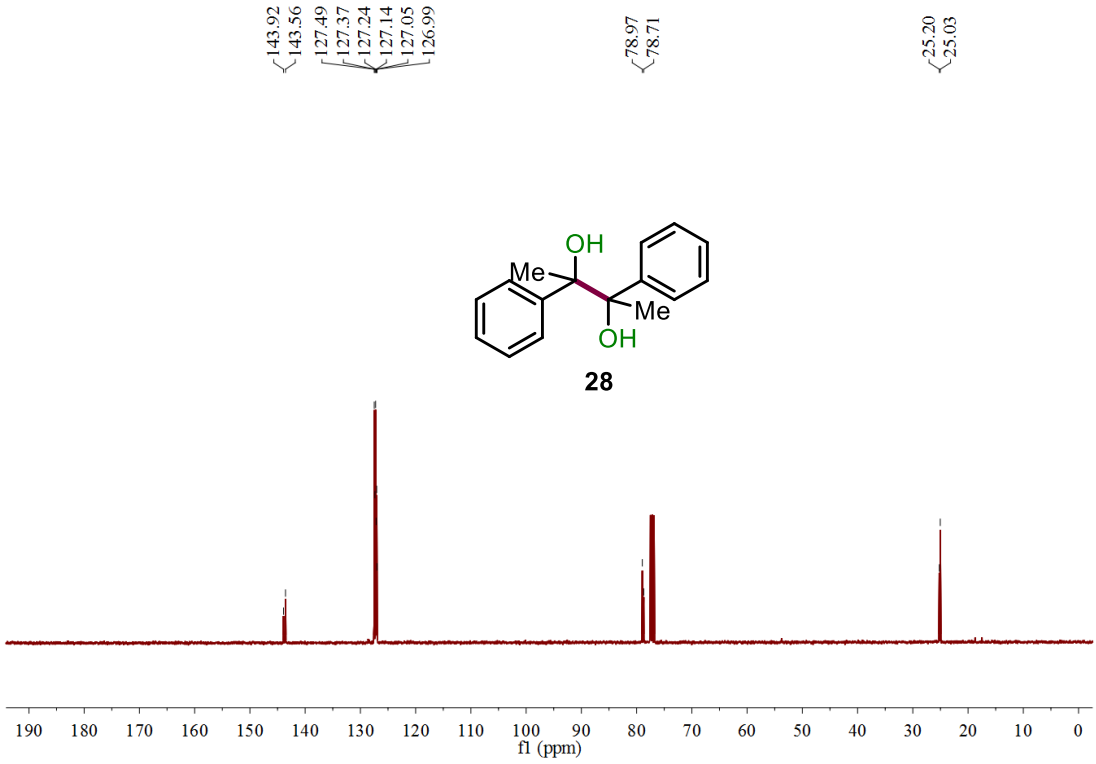
27

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



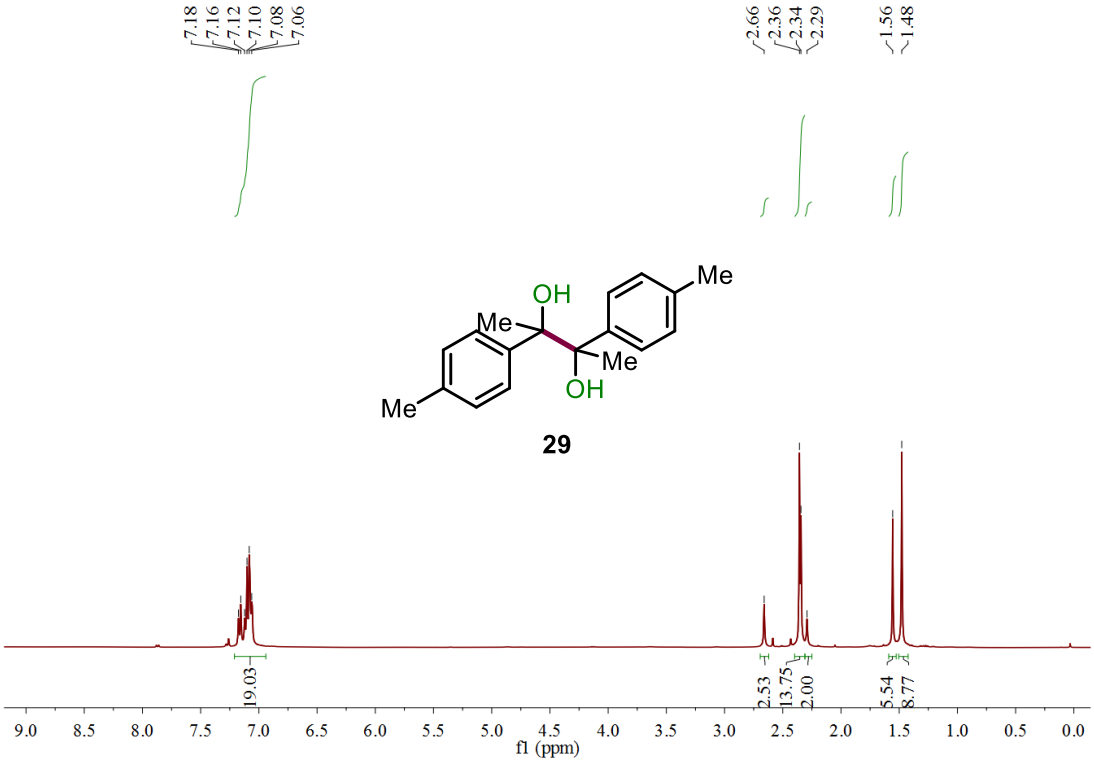
28

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



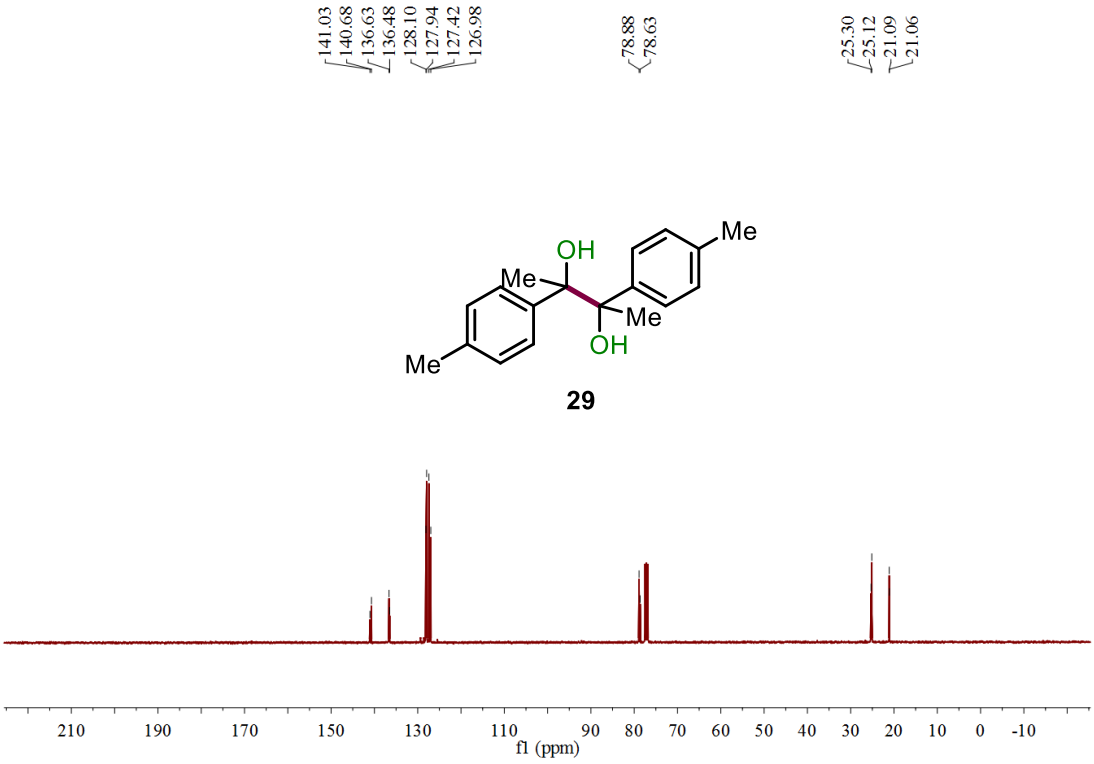
28

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



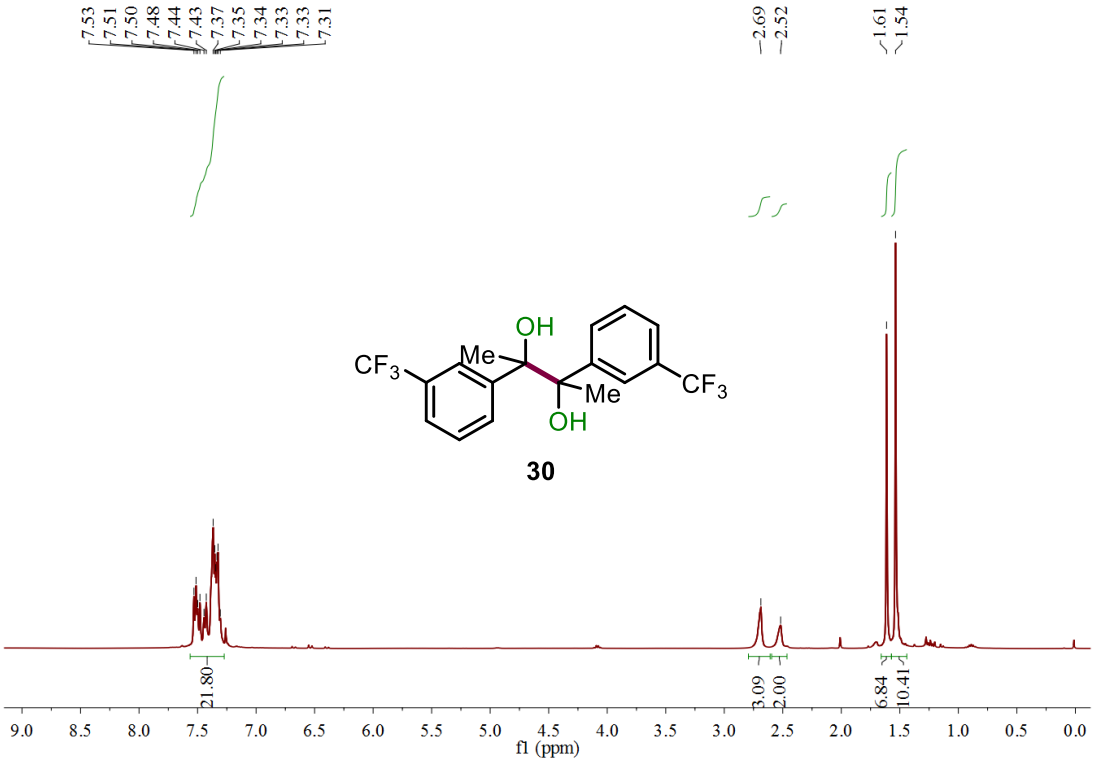
29

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



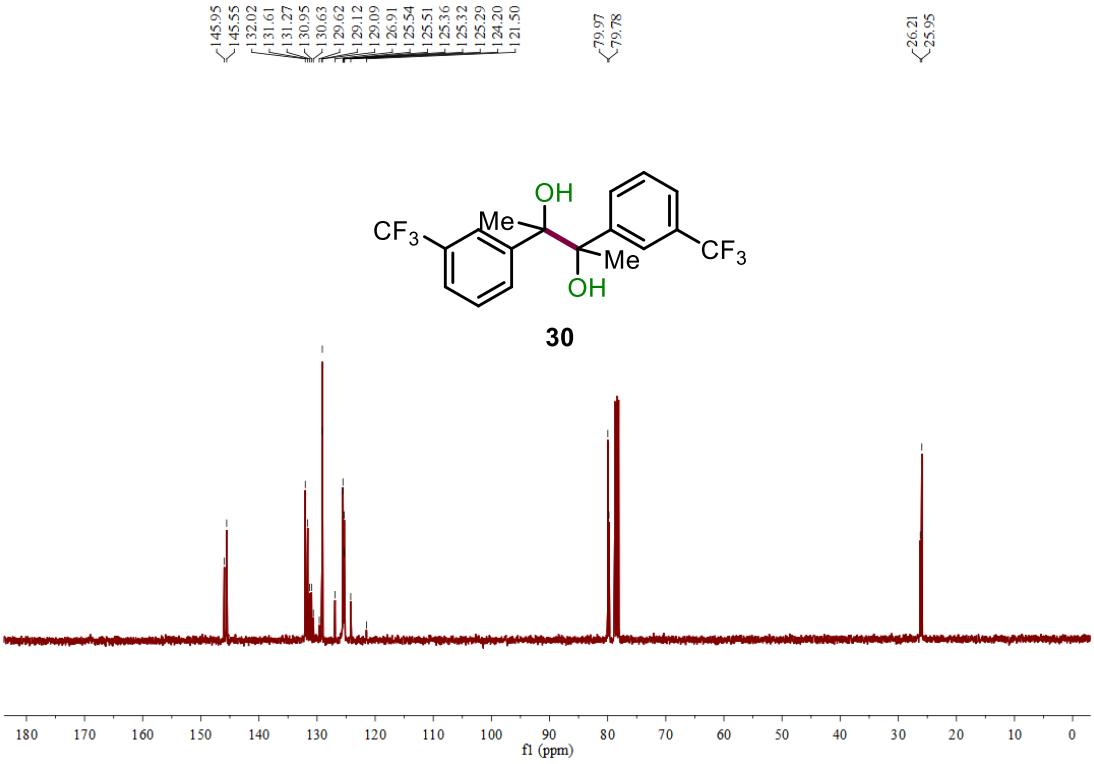
29

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



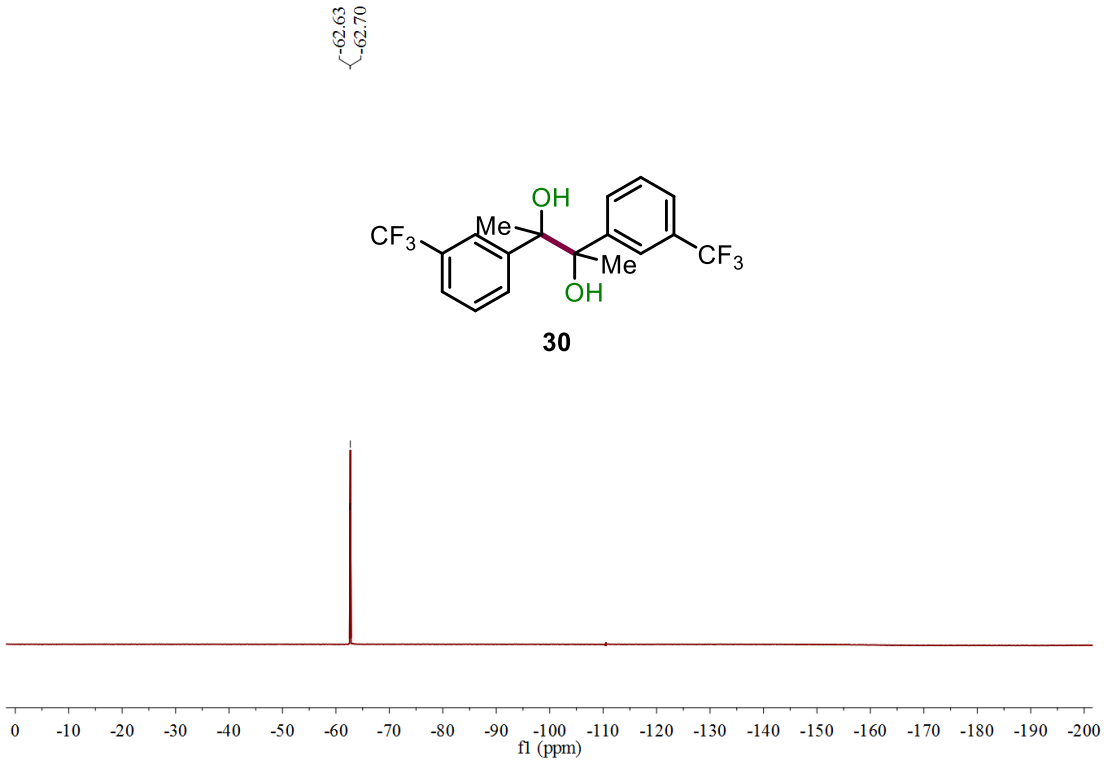
30

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



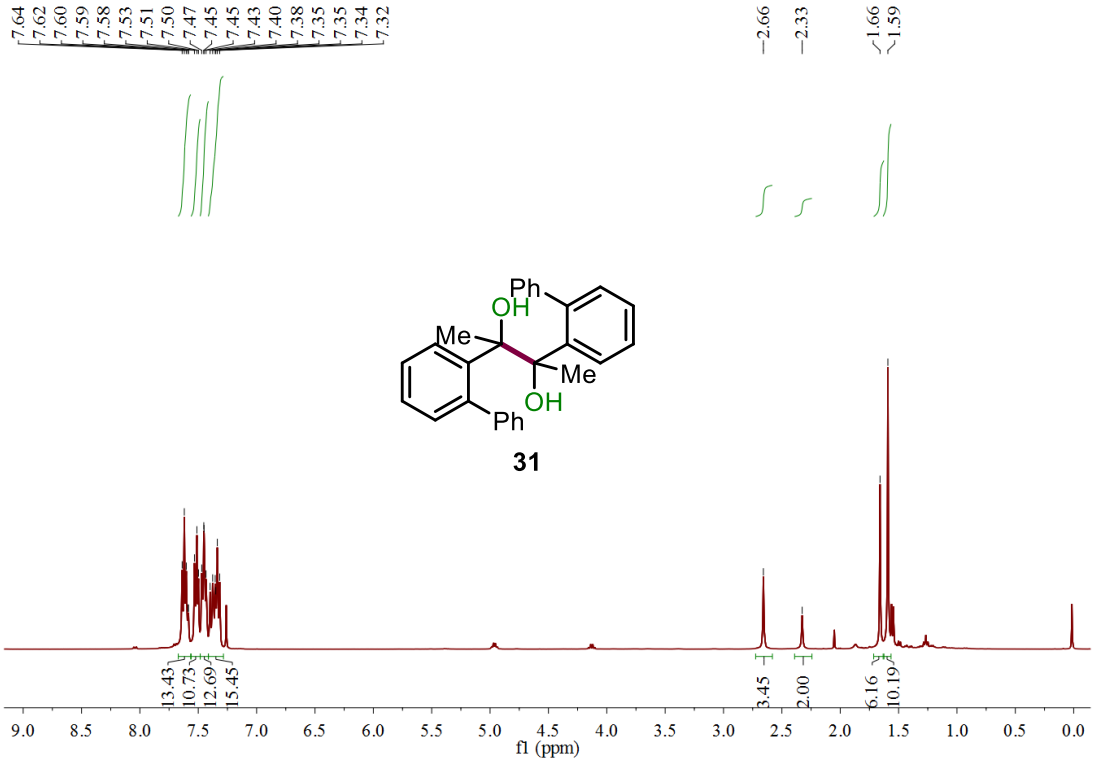
30

^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound 30

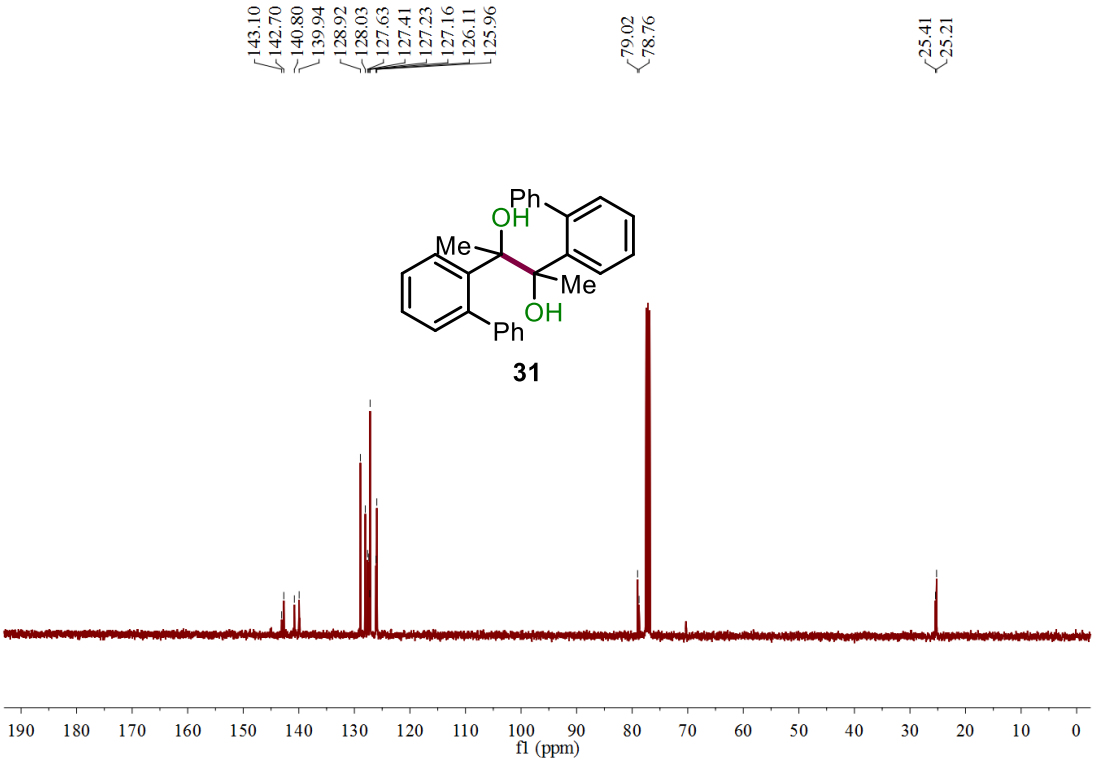


30

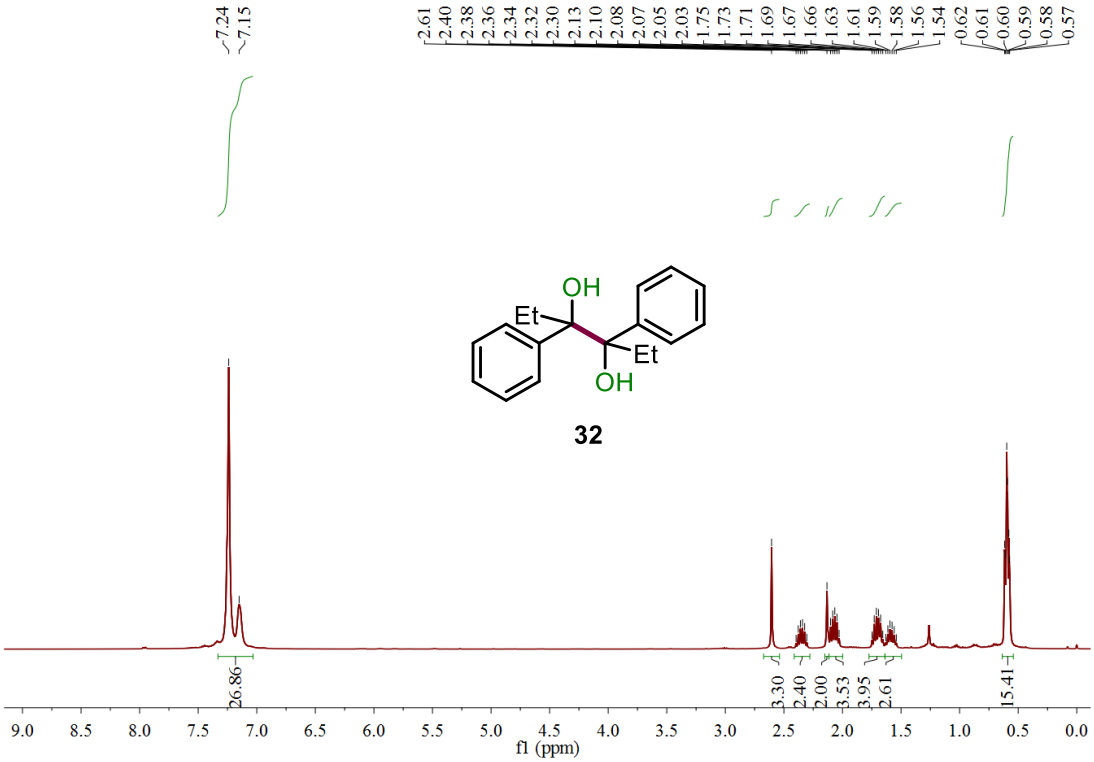
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 31



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

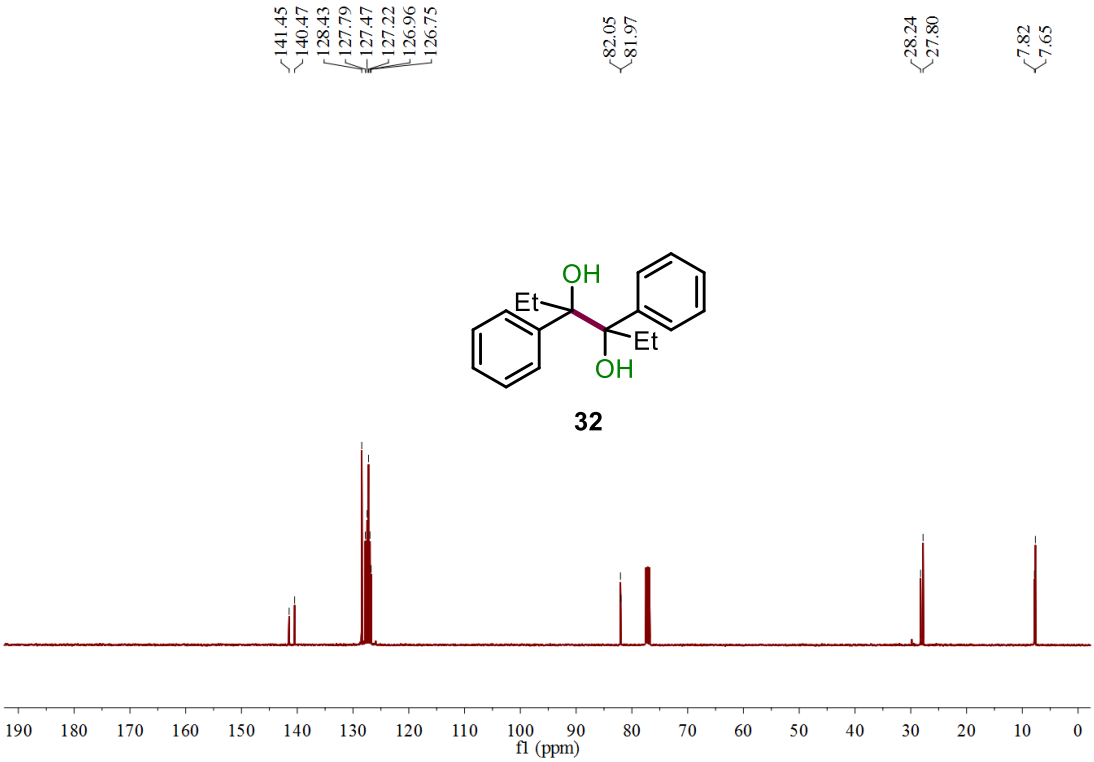


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 32



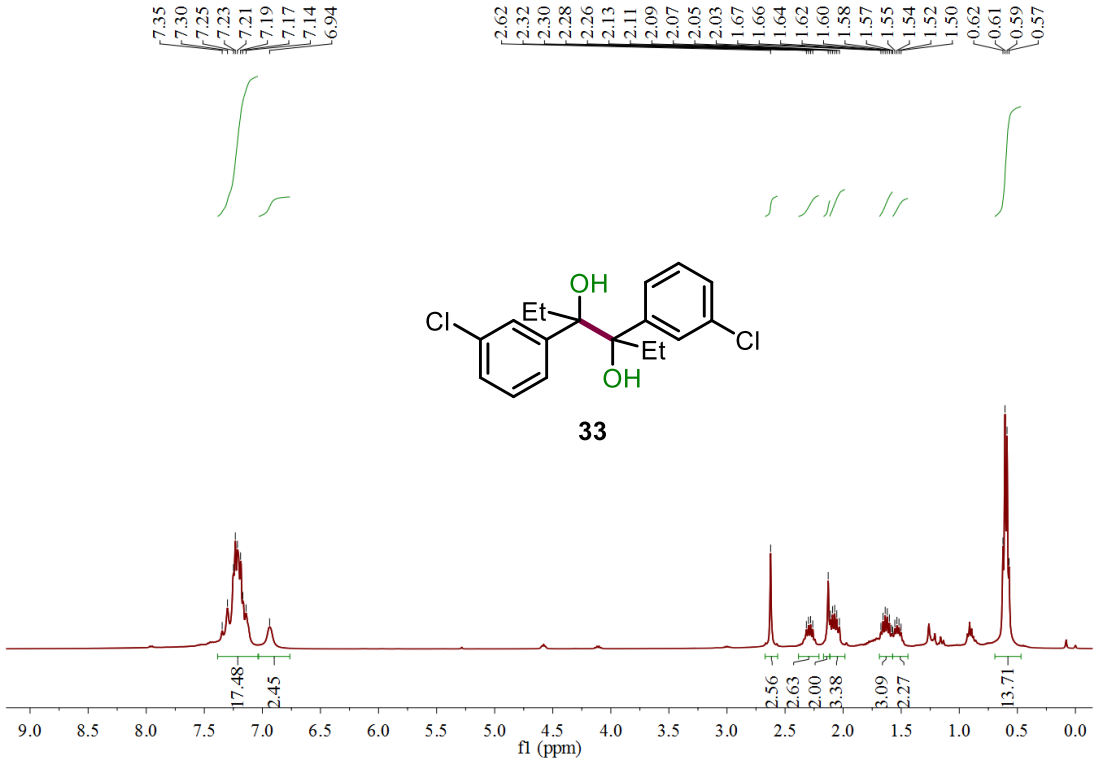
32

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



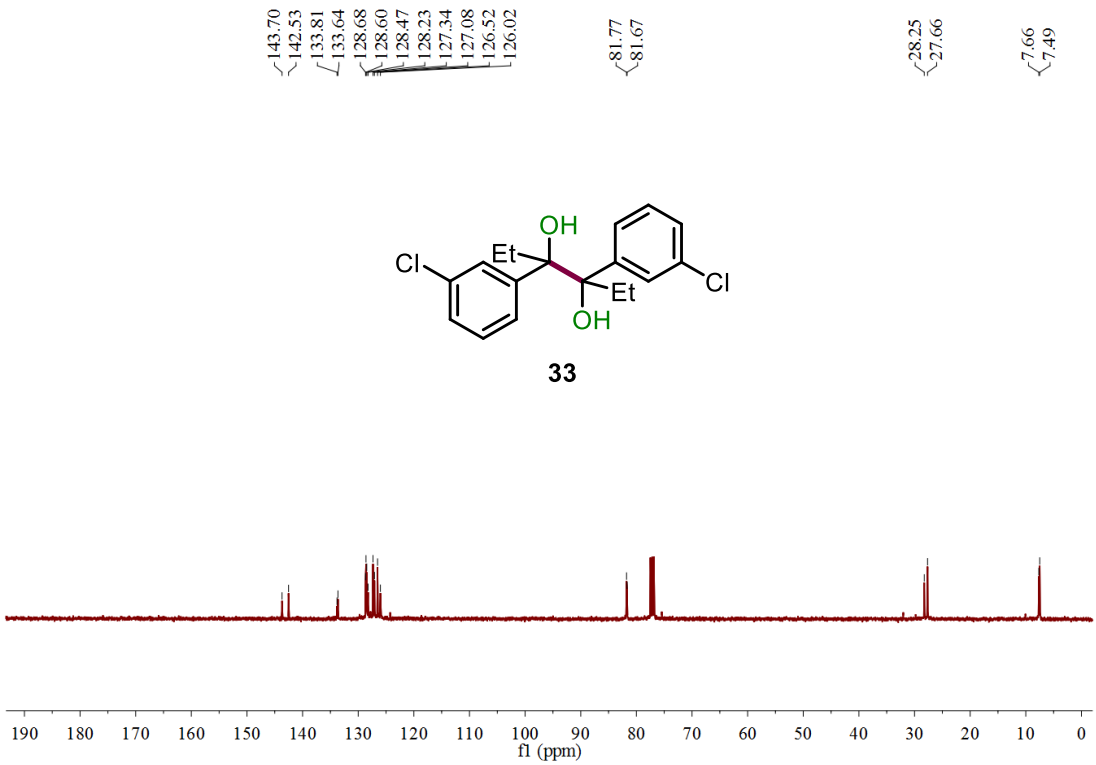
32

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



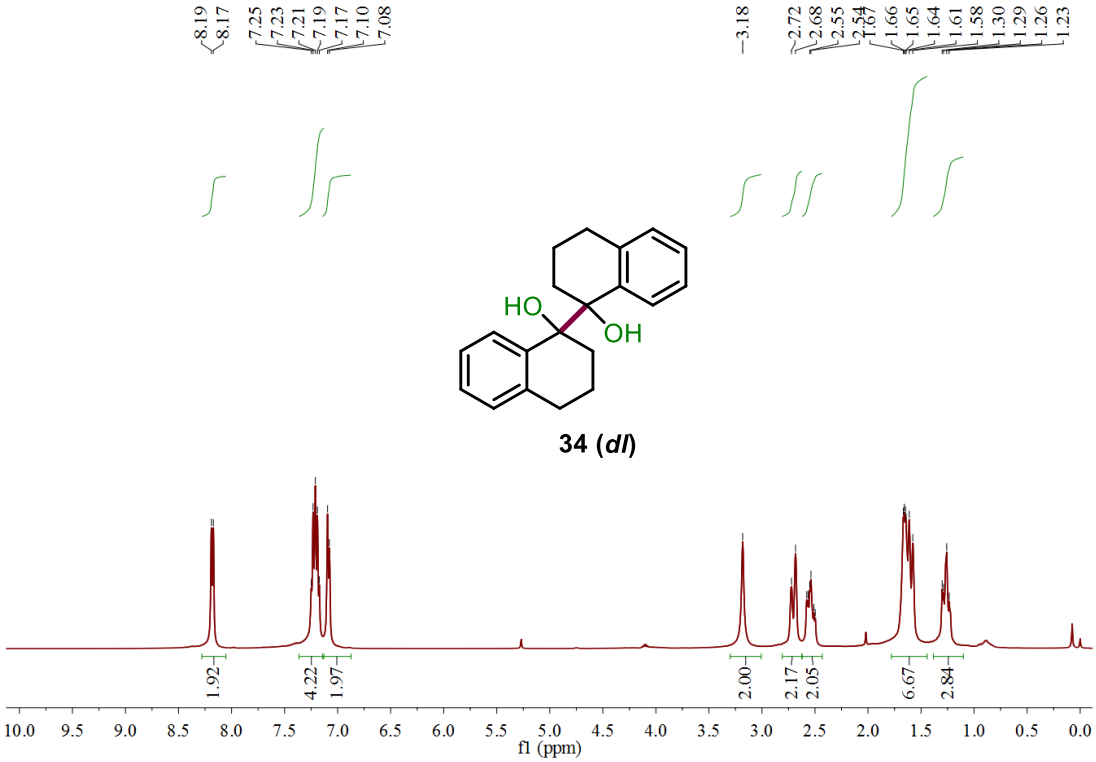
33

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



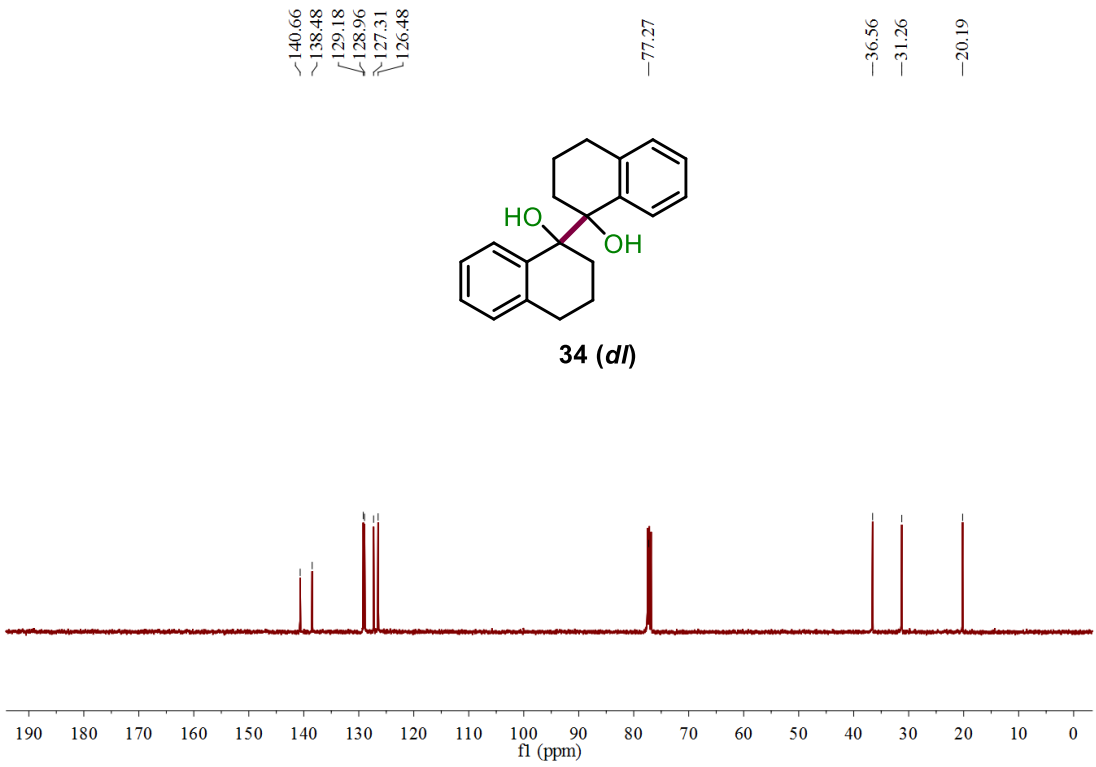
33

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



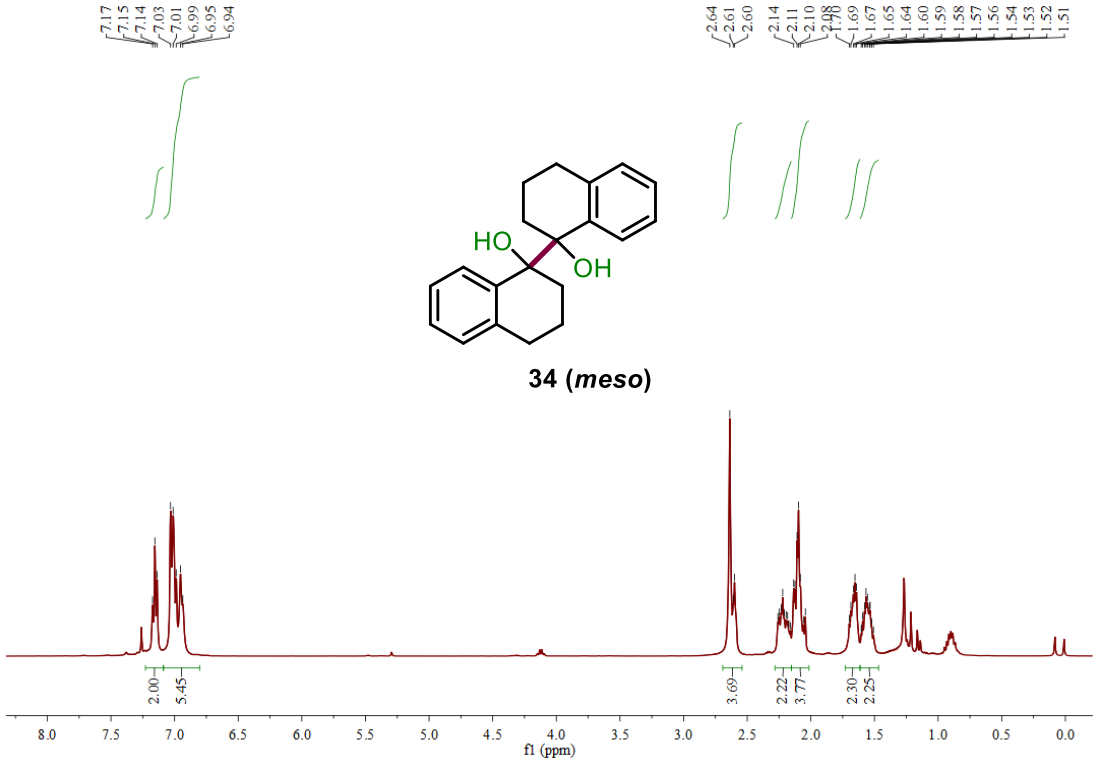
34 (*dl*)

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



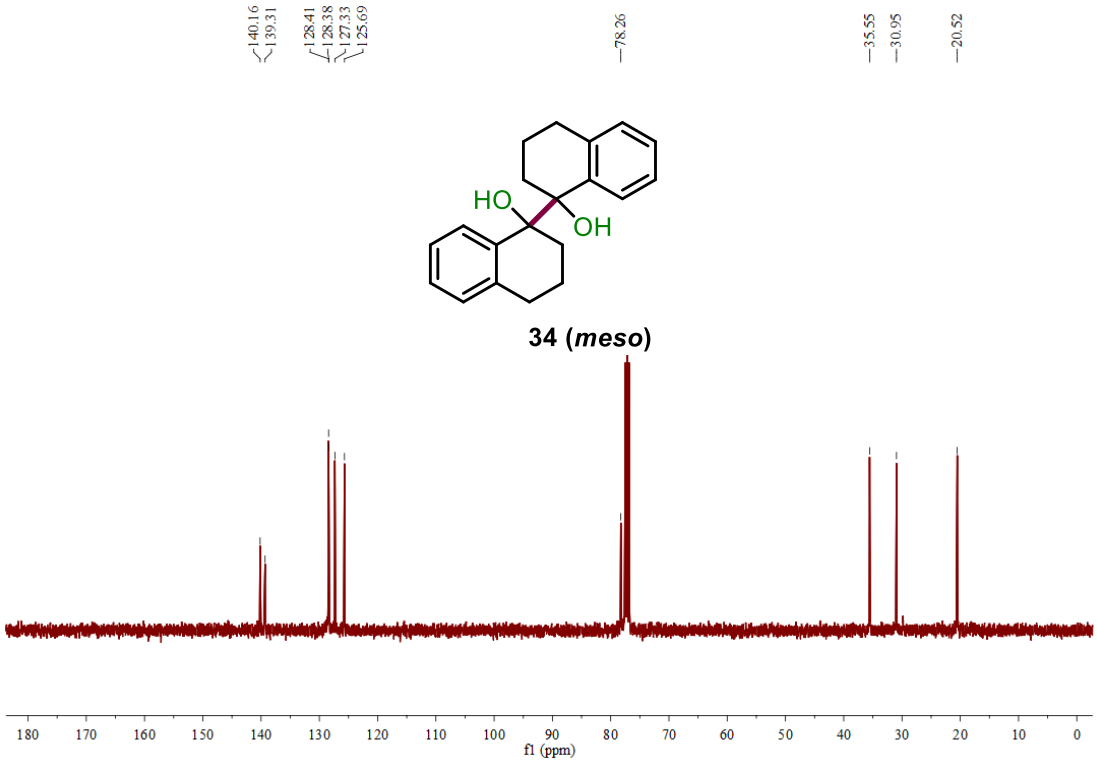
34 (*dl*)

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



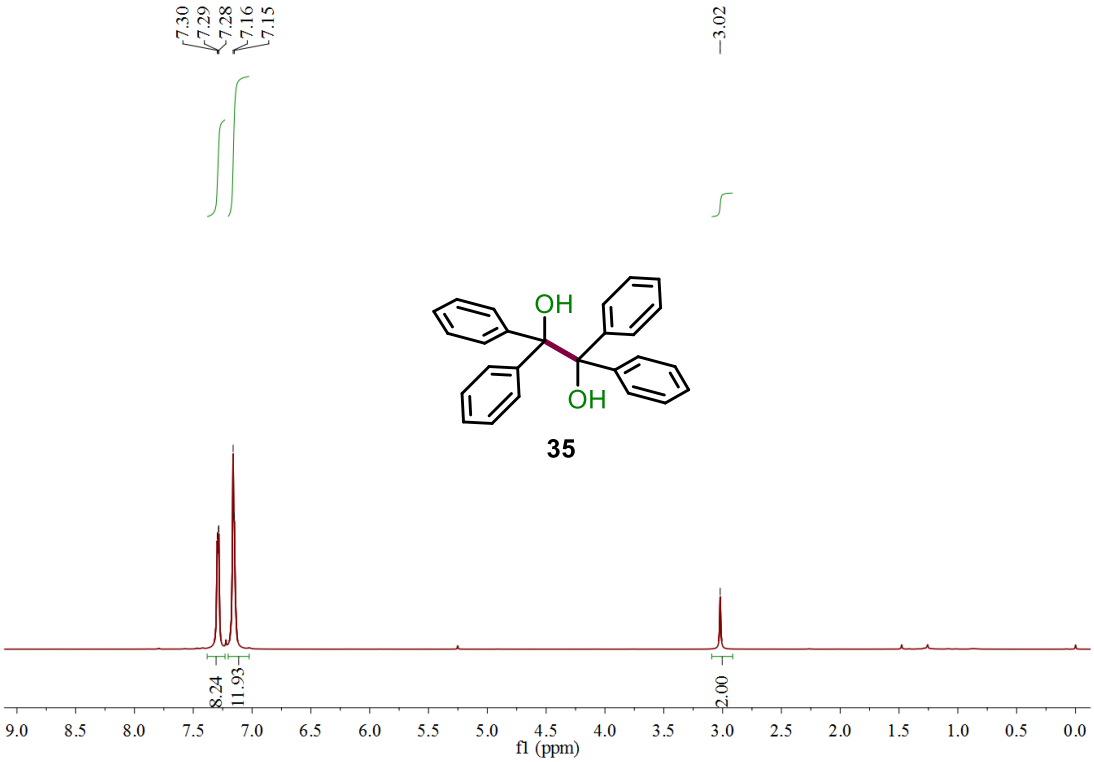
34 (*meso*)

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

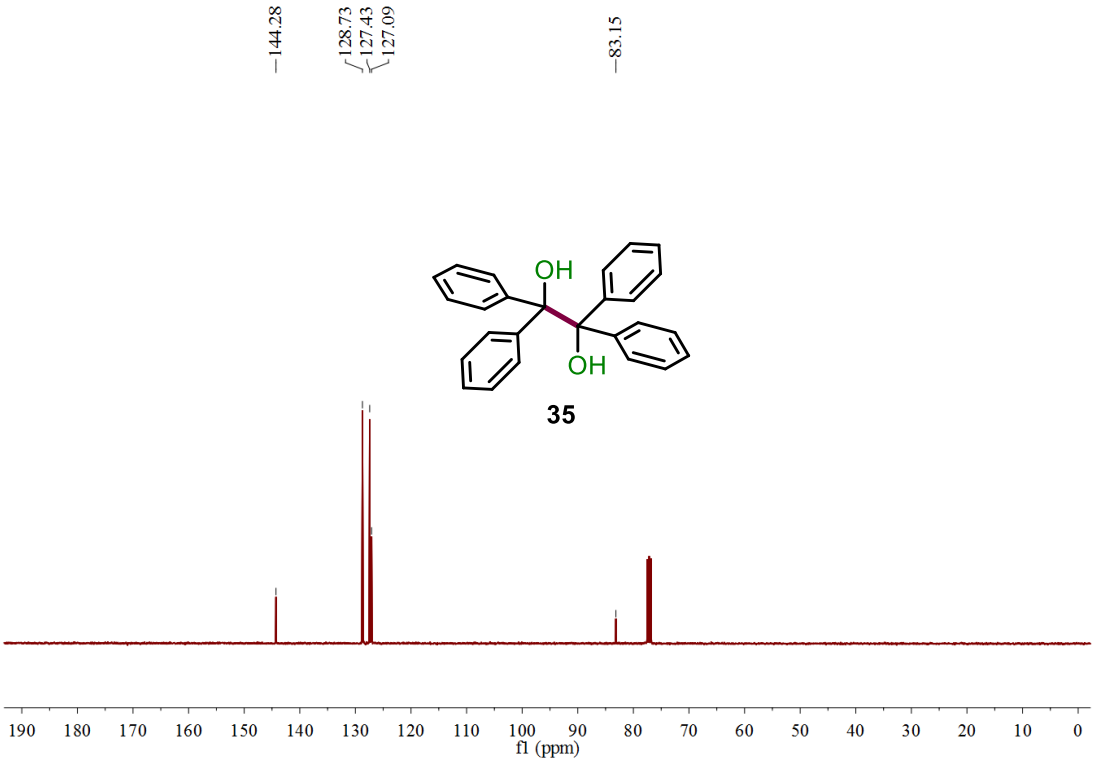


34 (*meso*)

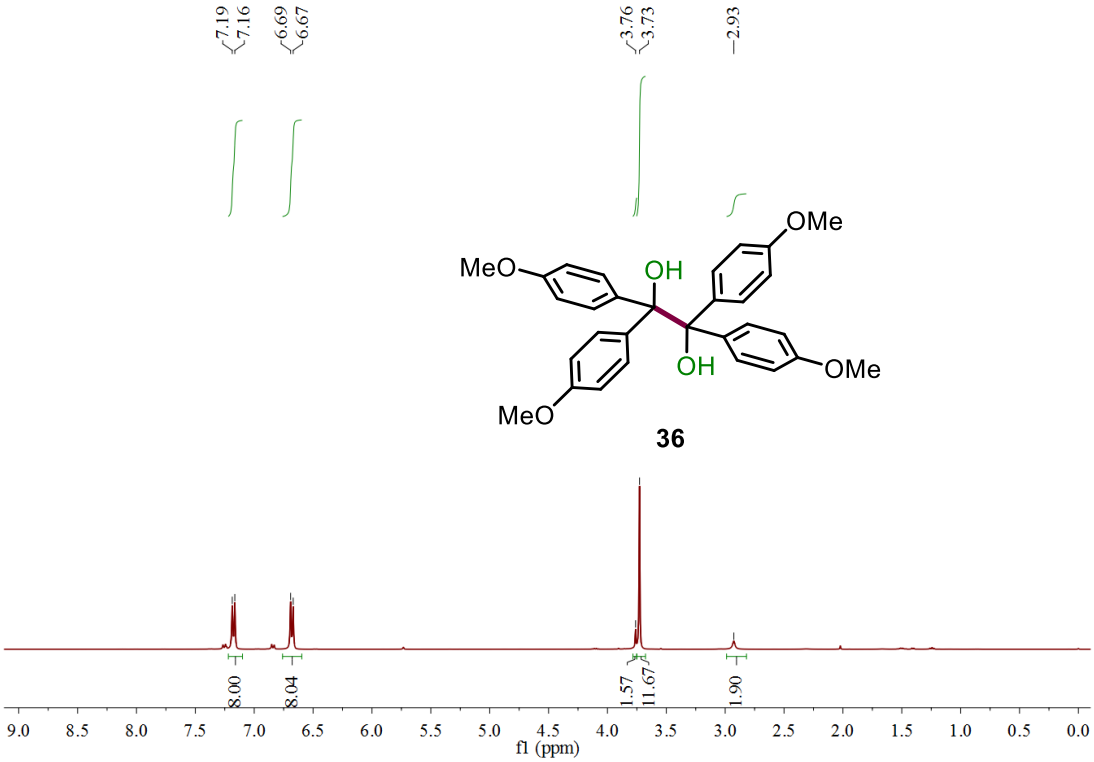
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 35



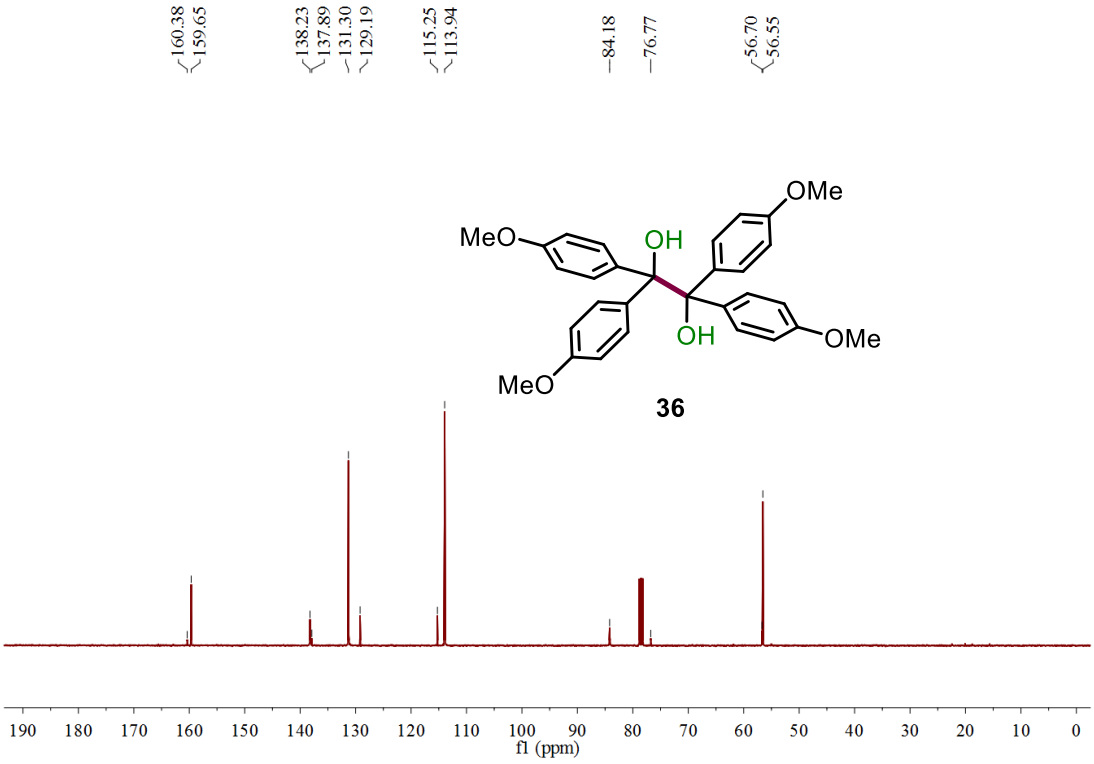
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 35



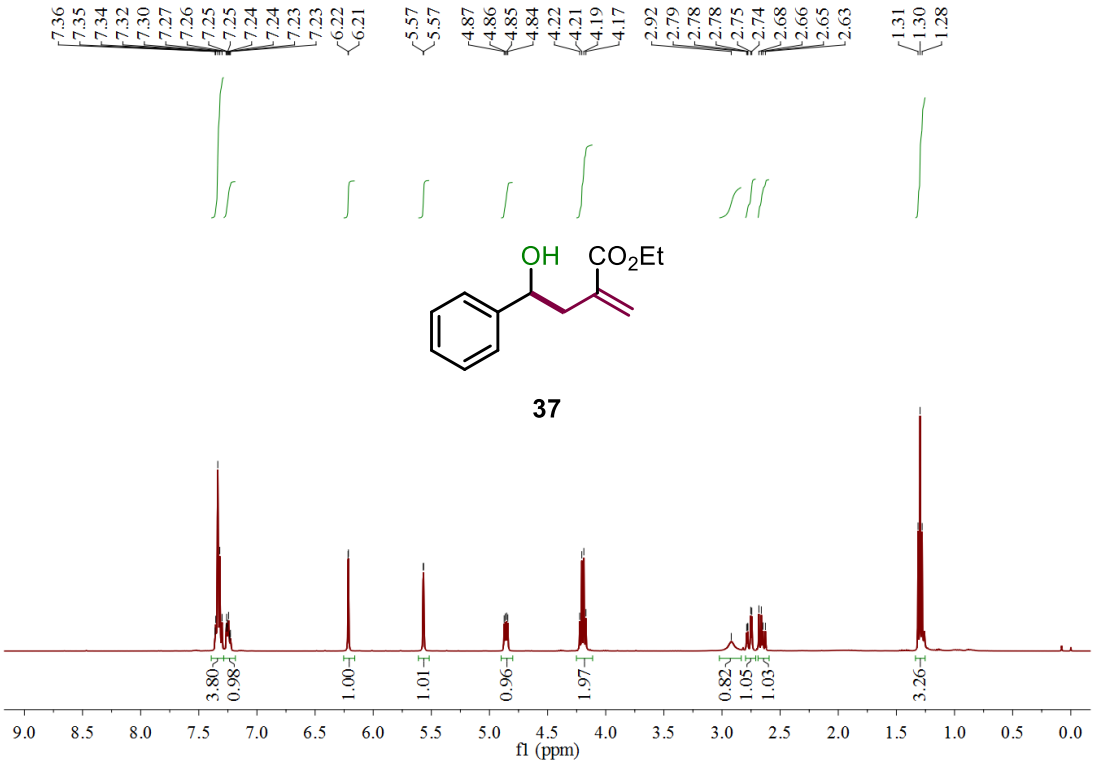
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 36



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 36

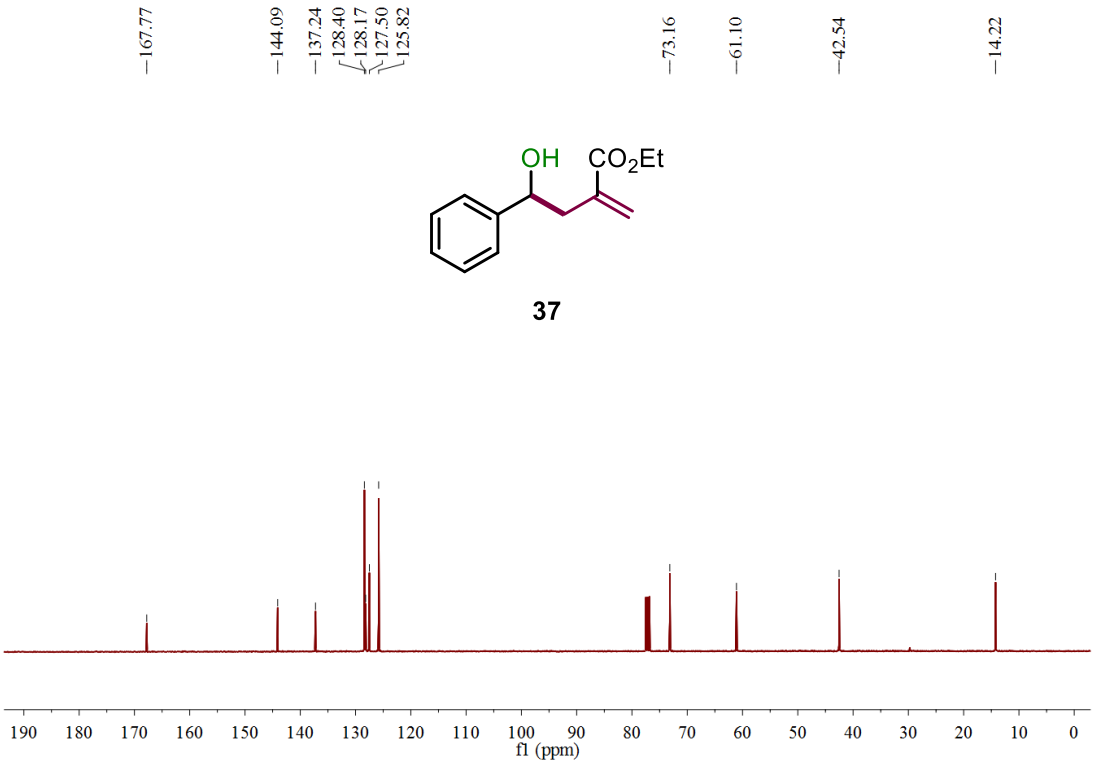


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 37



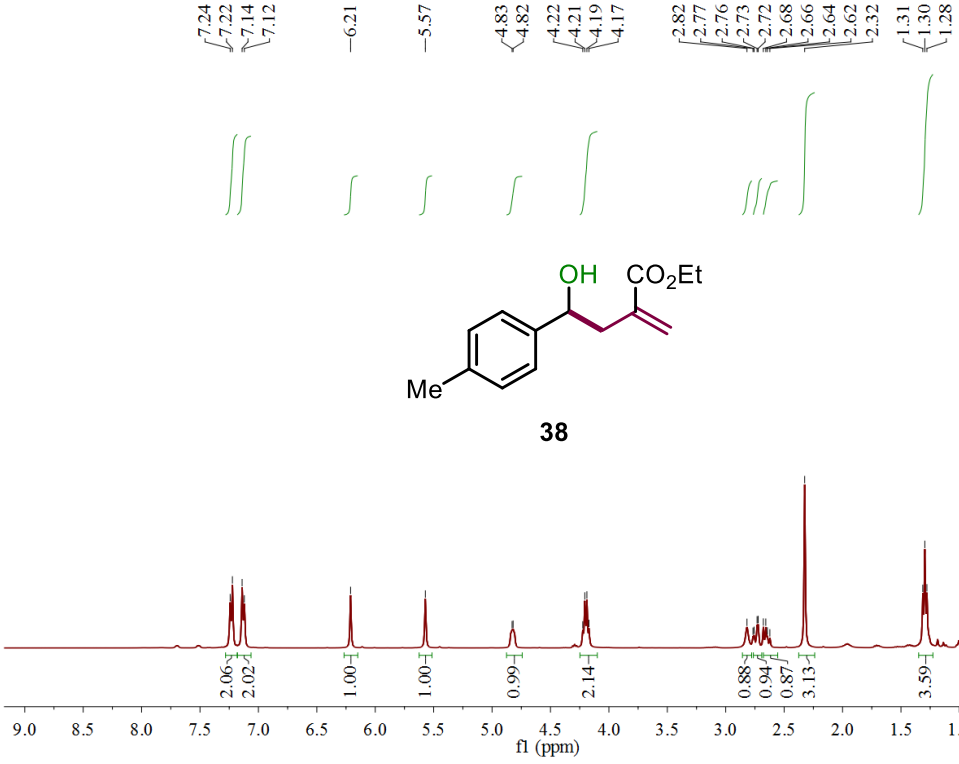
37

^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 37



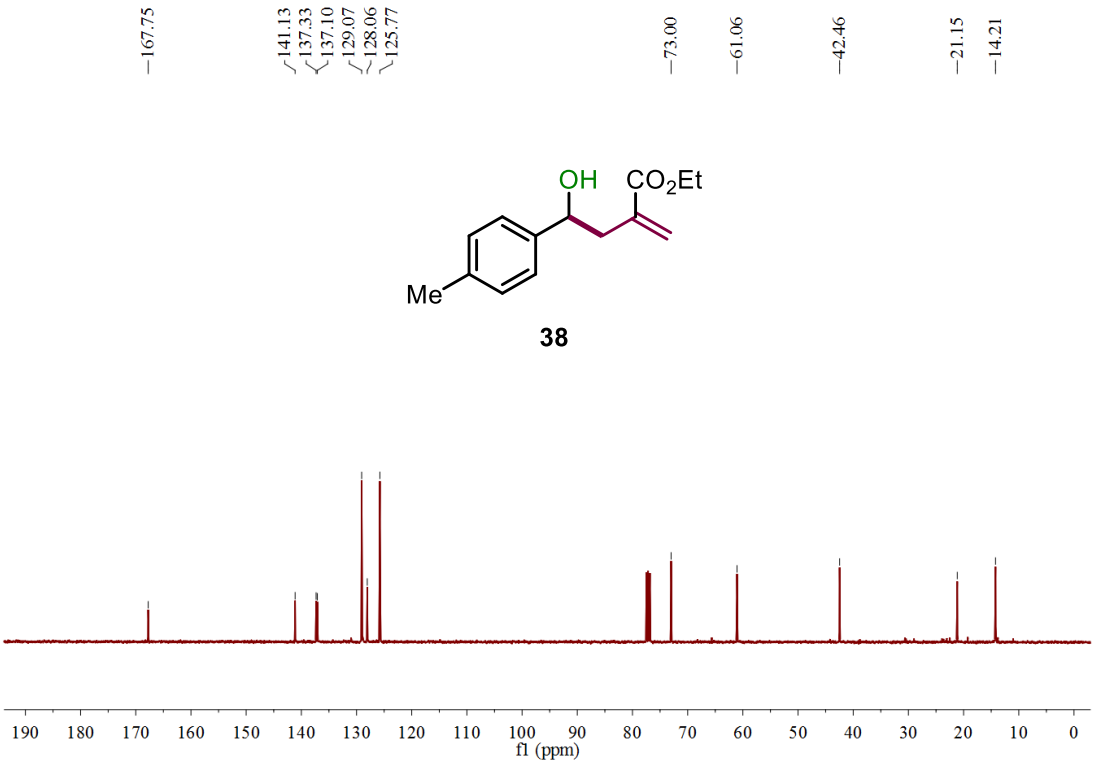
37

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



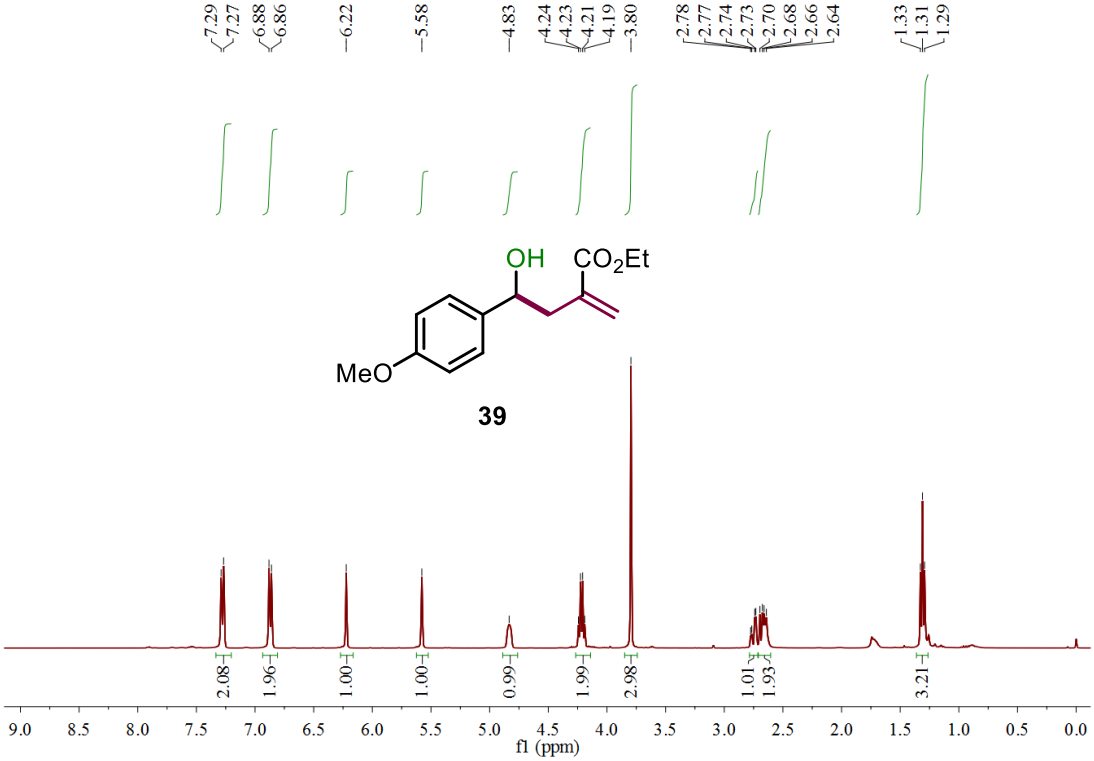
38

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

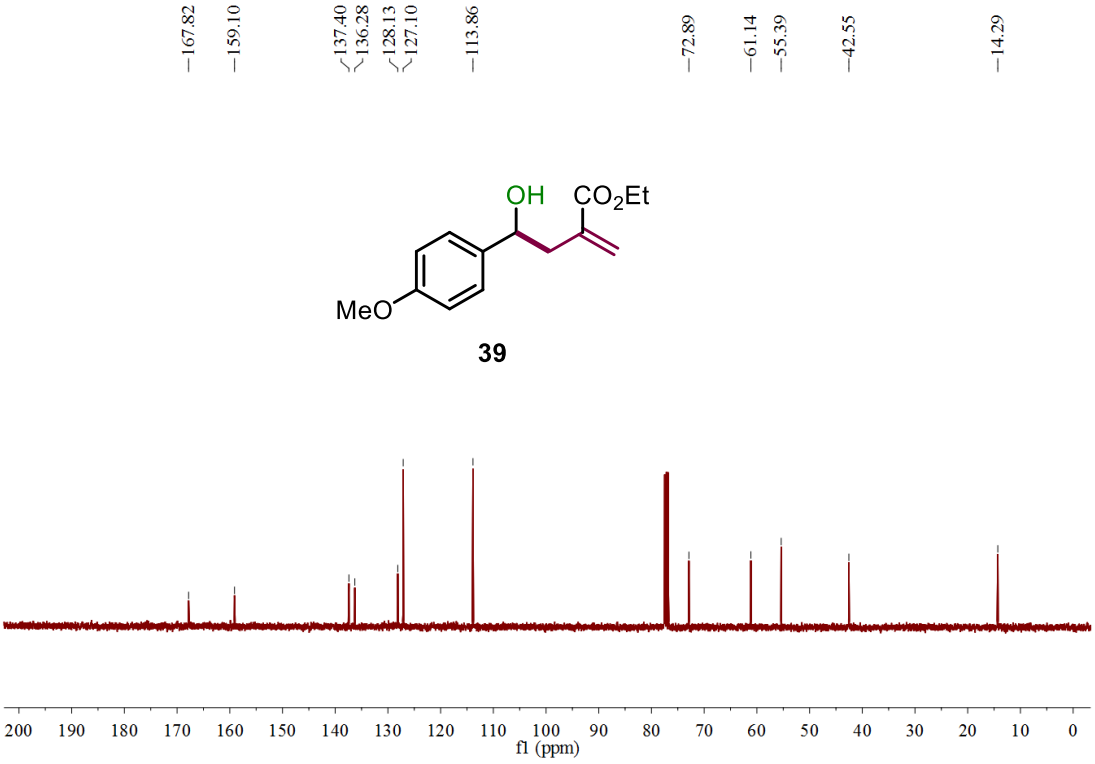


38

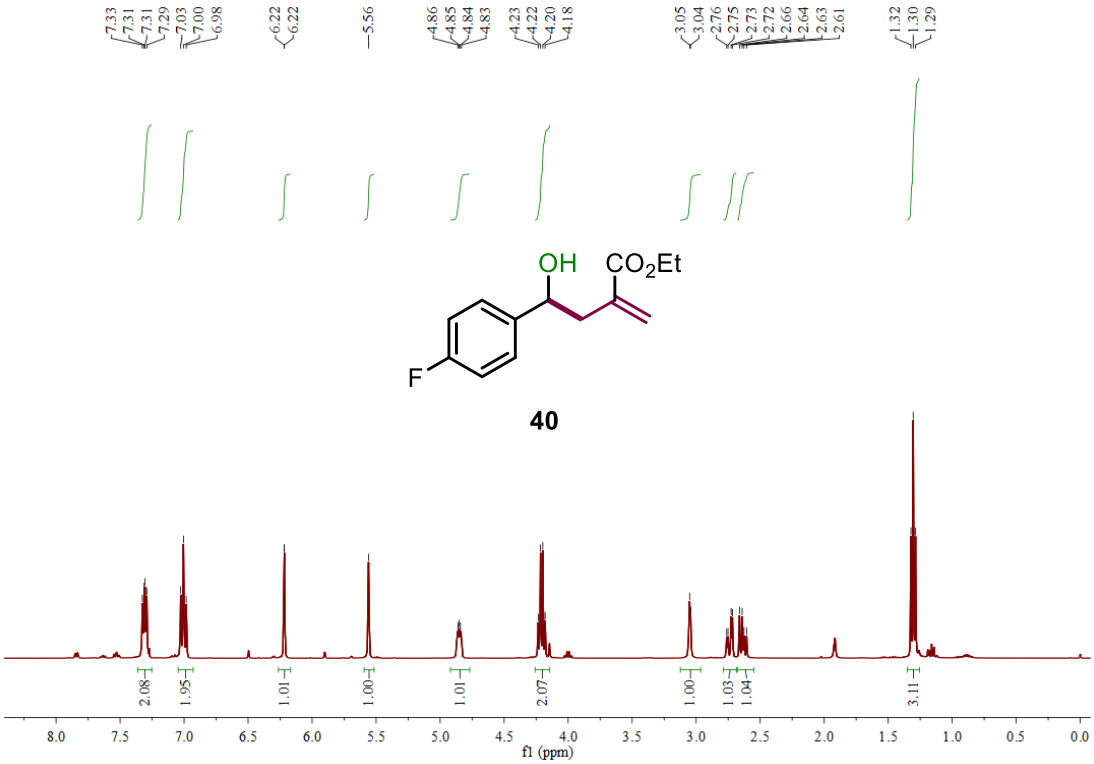
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 39



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

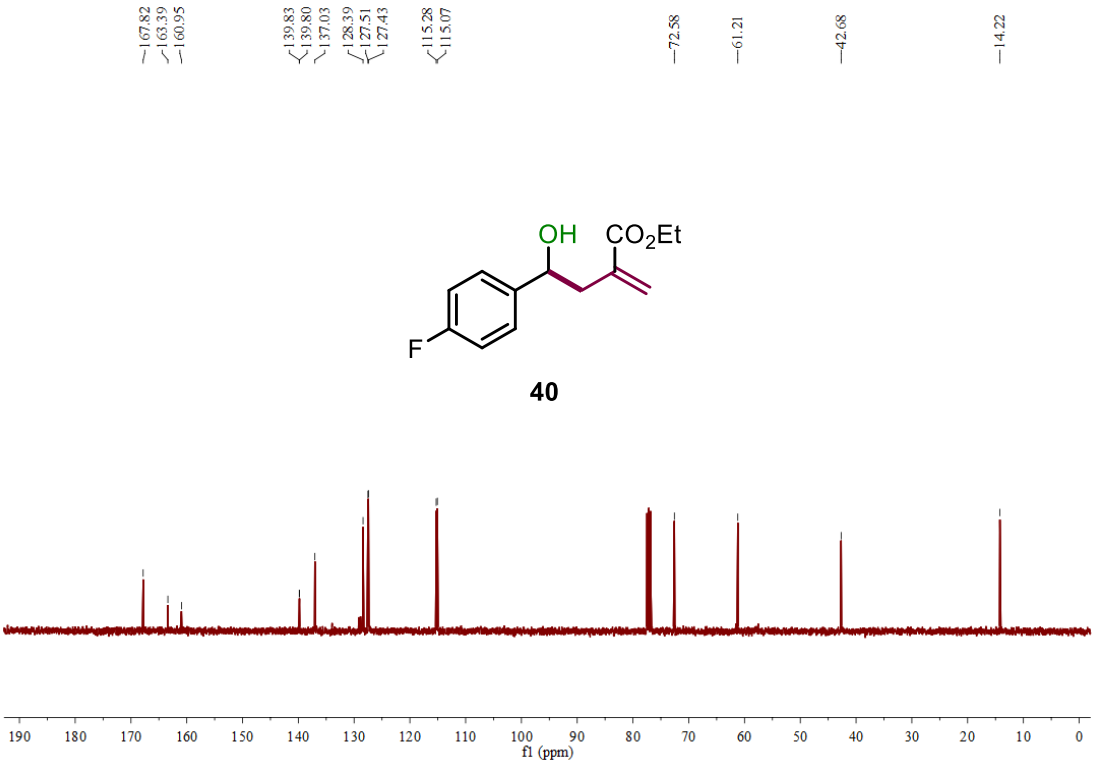


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 40



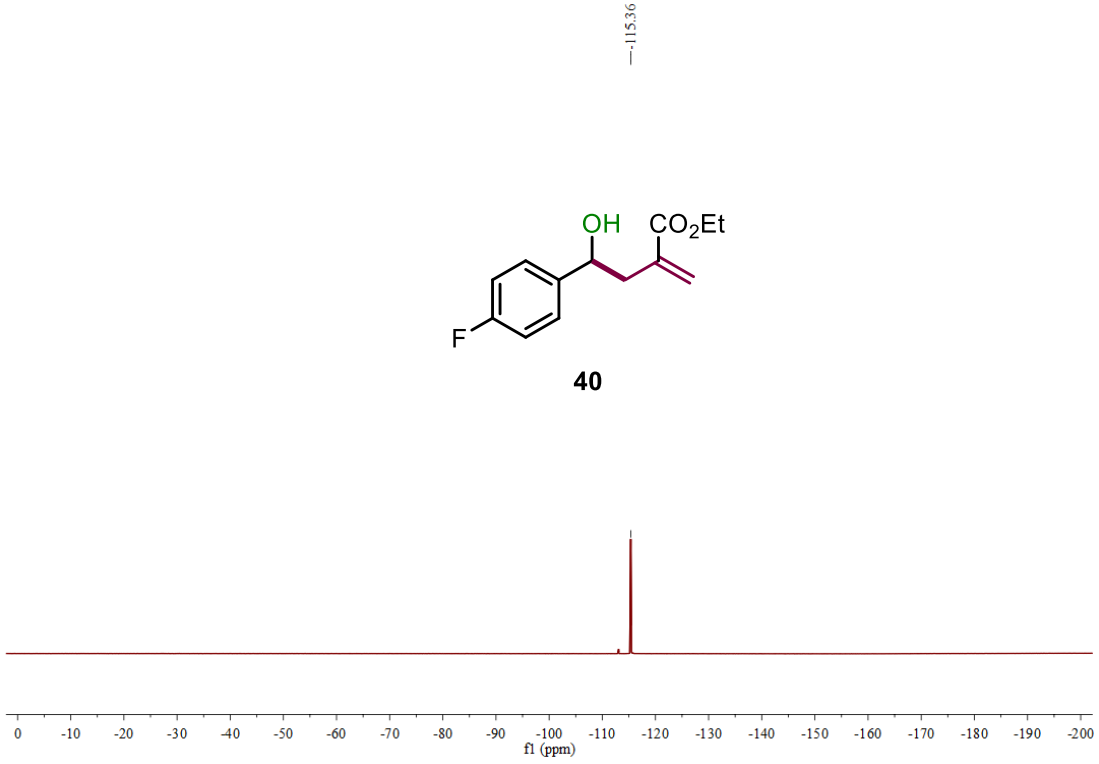
40

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



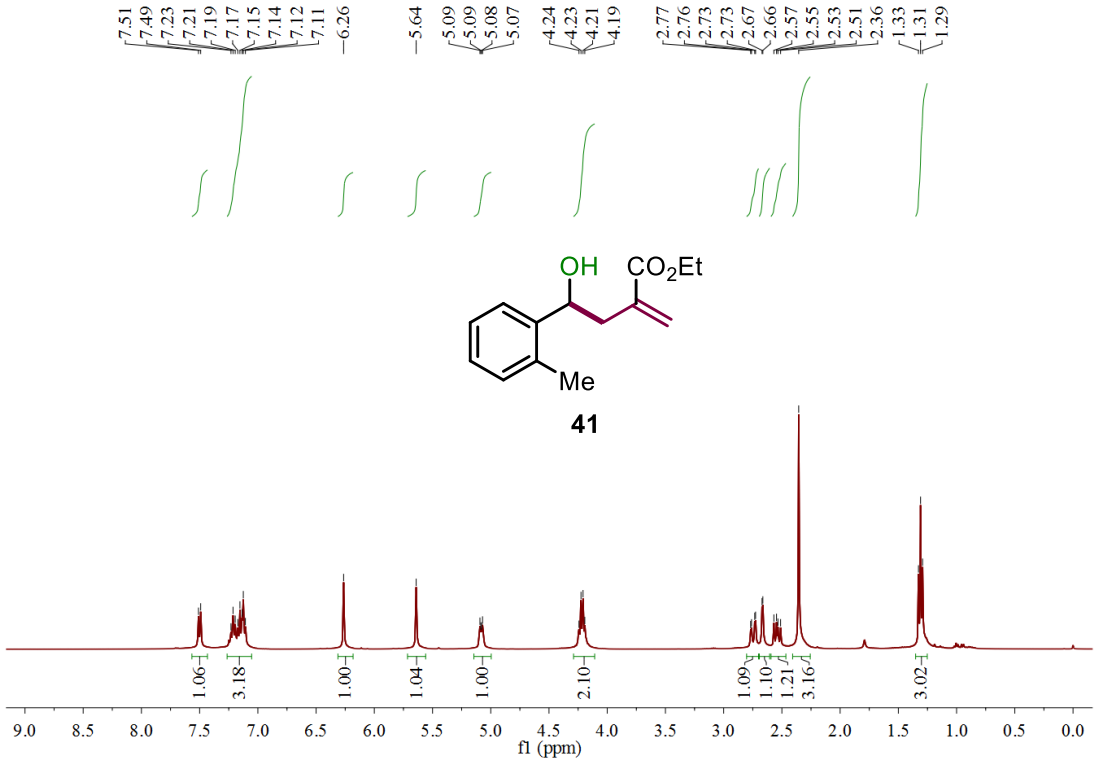
40

^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound 40

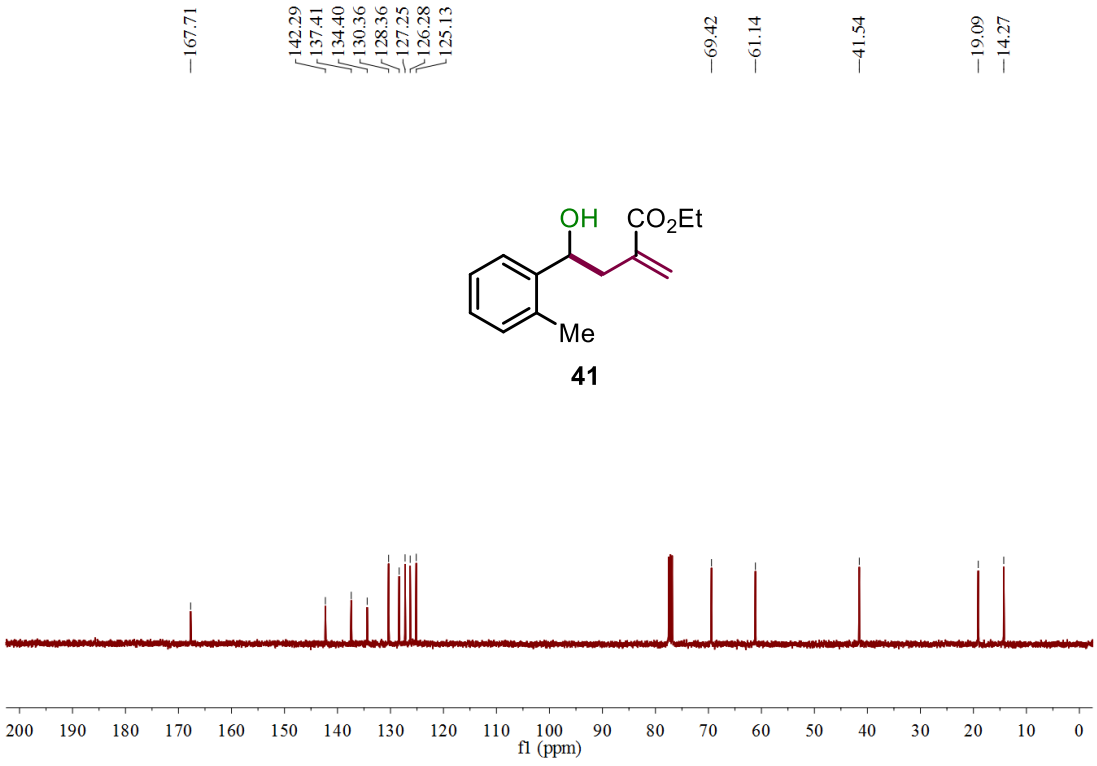


40

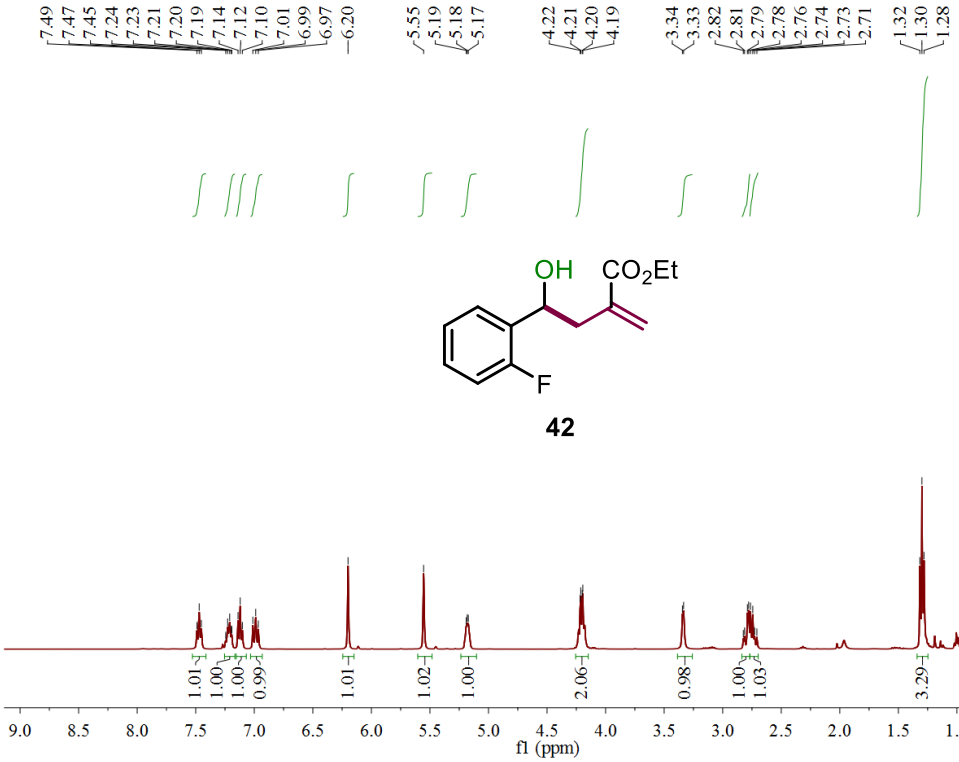
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 41



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

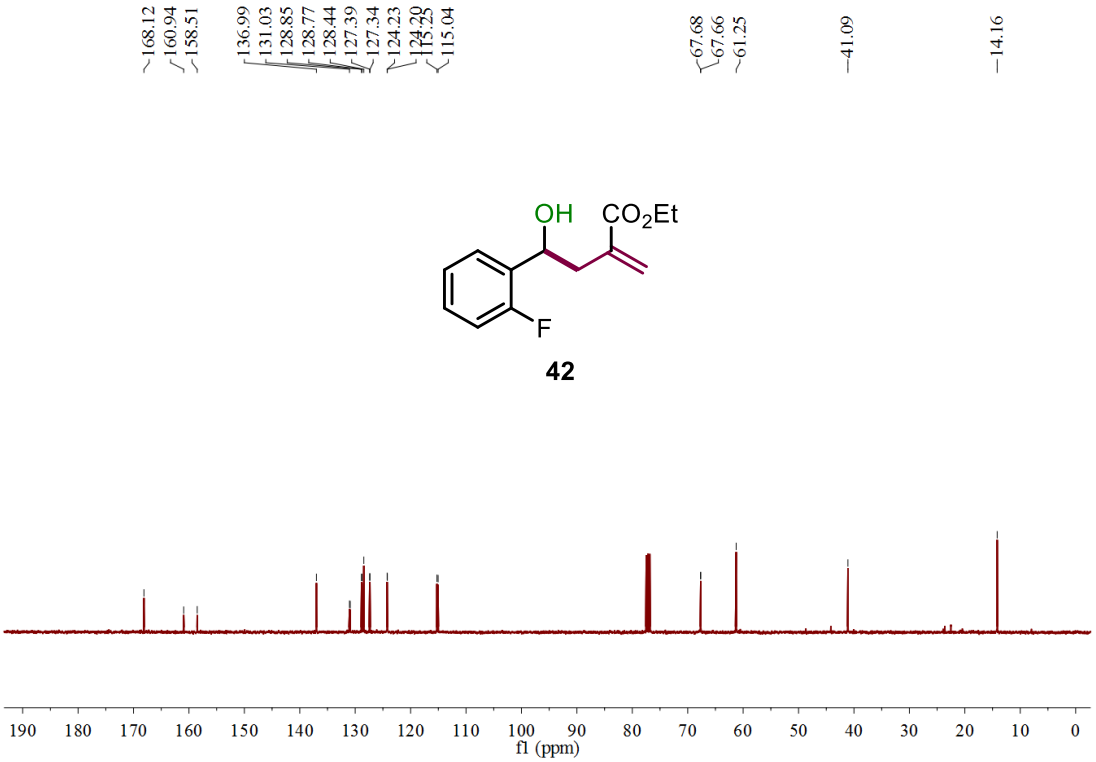


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 42



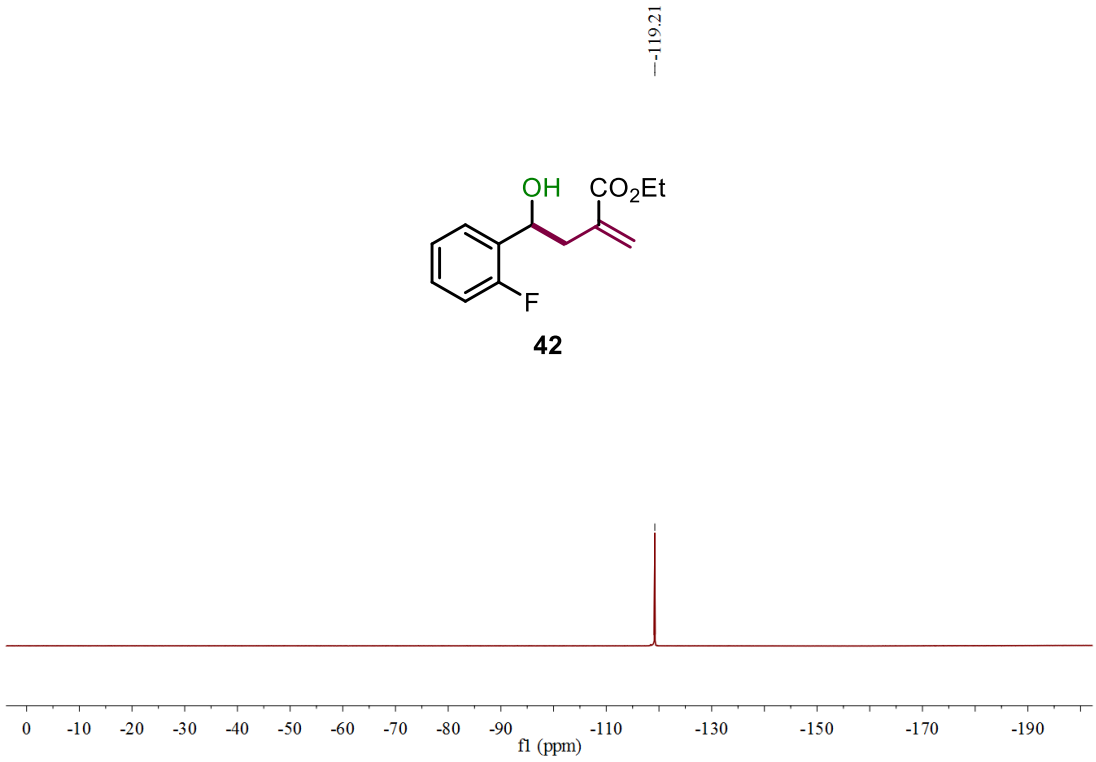
42

^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 42



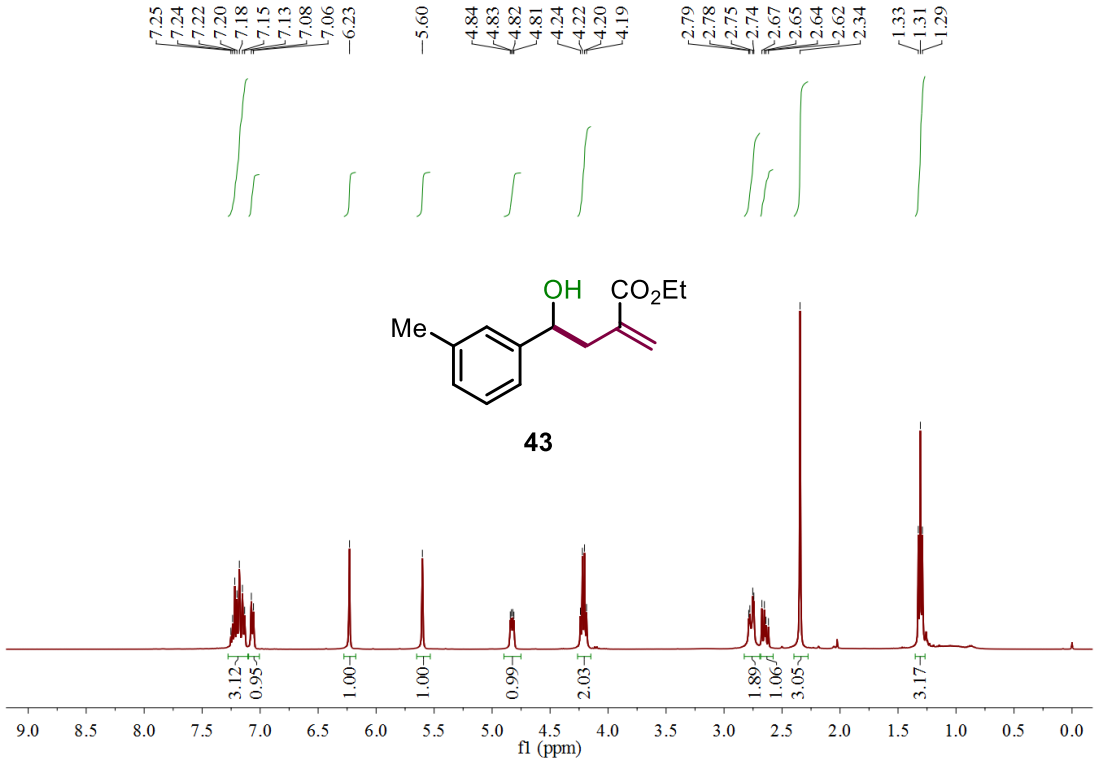
42

^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound 42



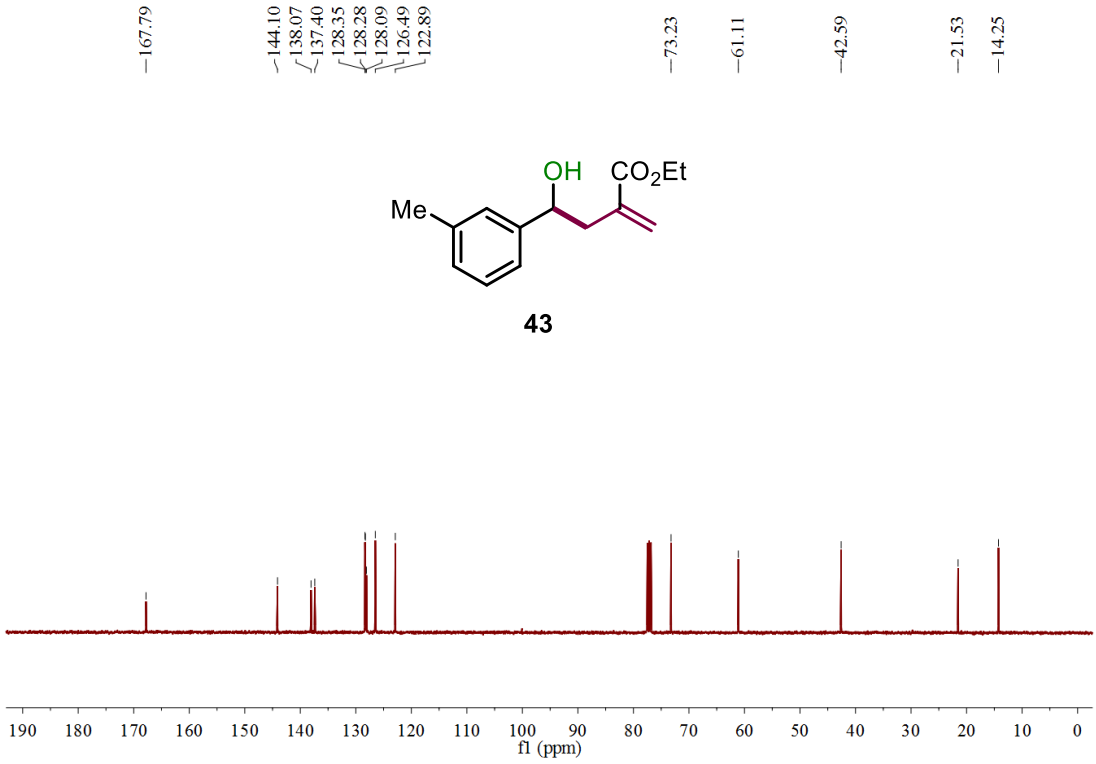
42

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



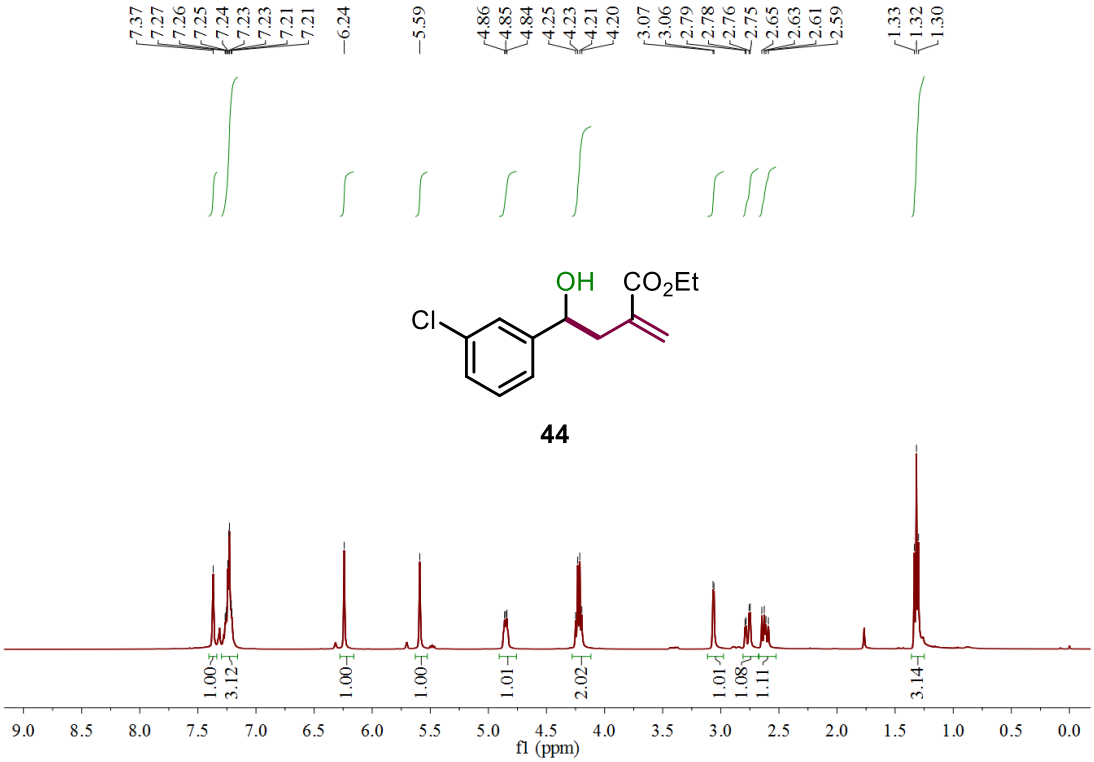
43

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



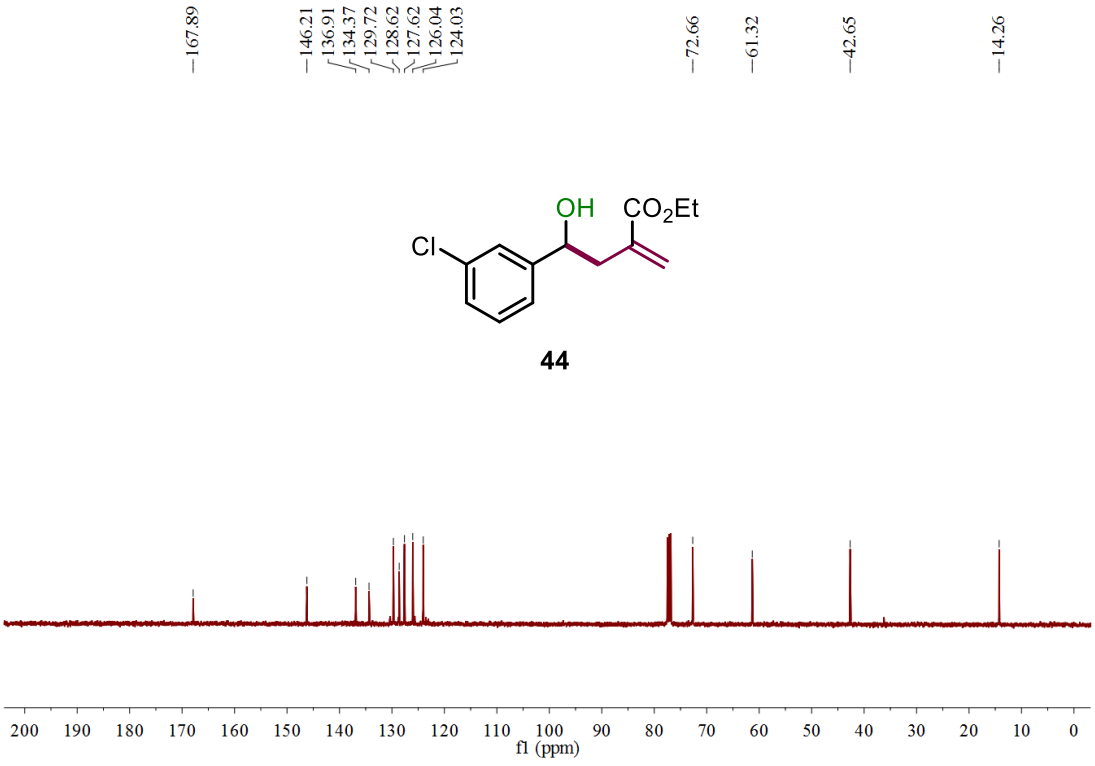
43

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



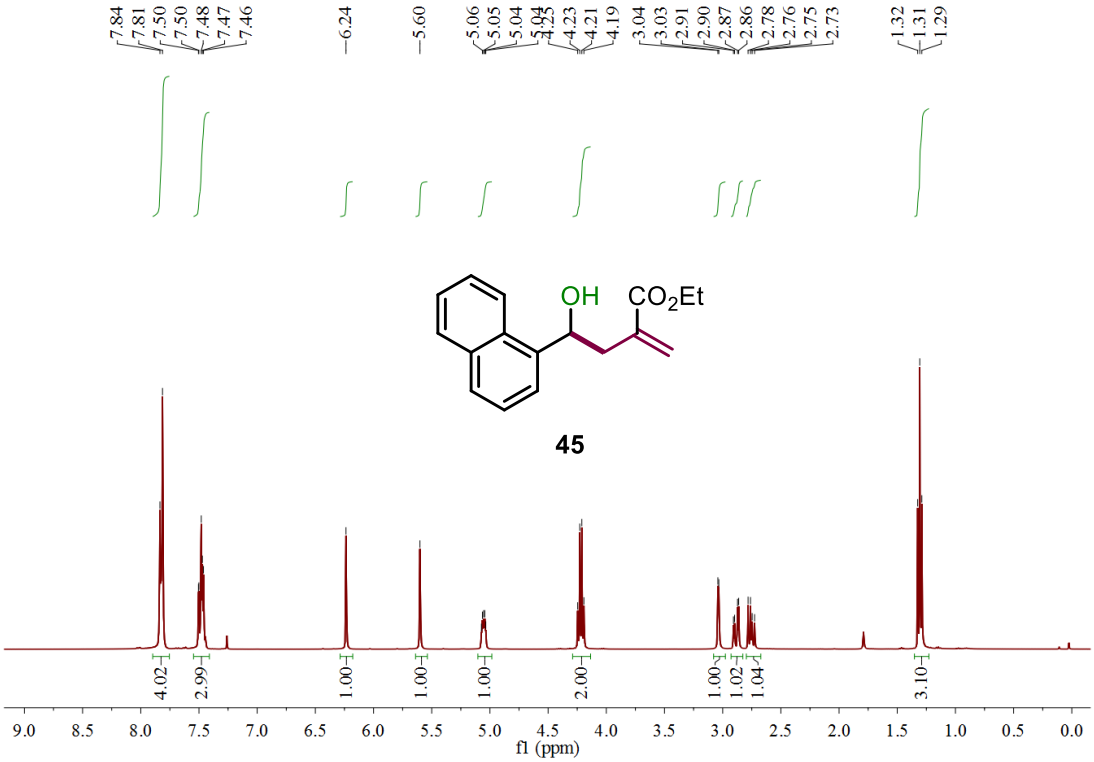
44

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



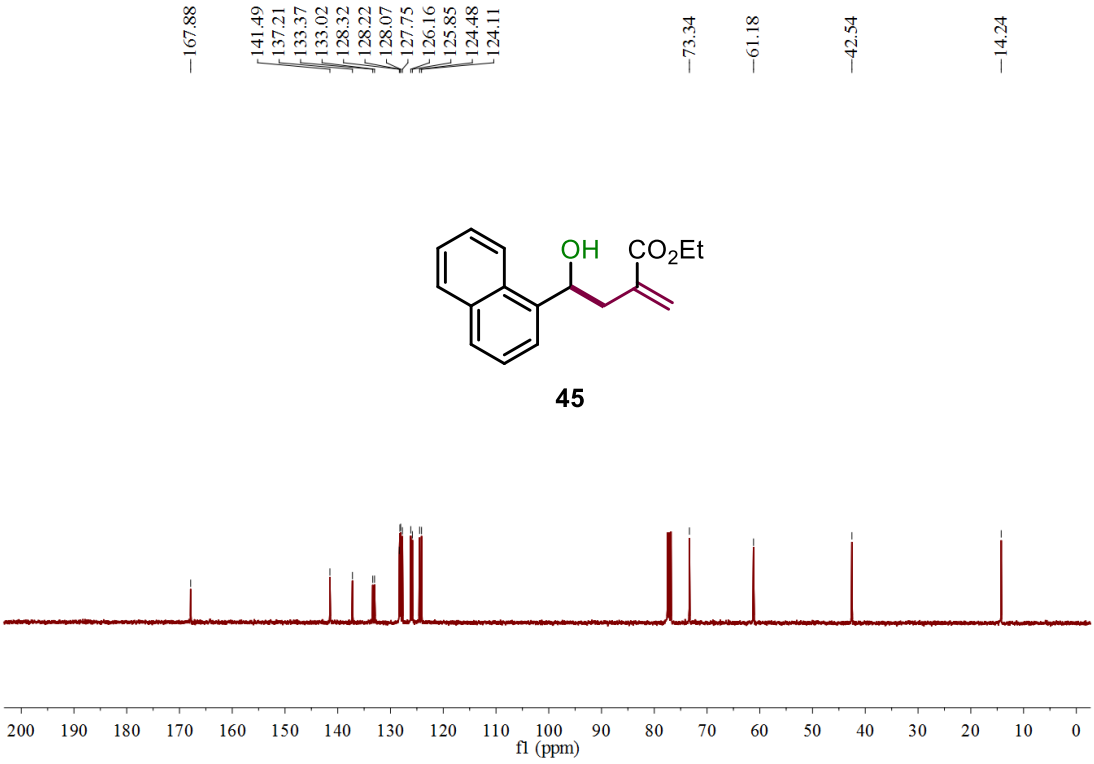
44

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



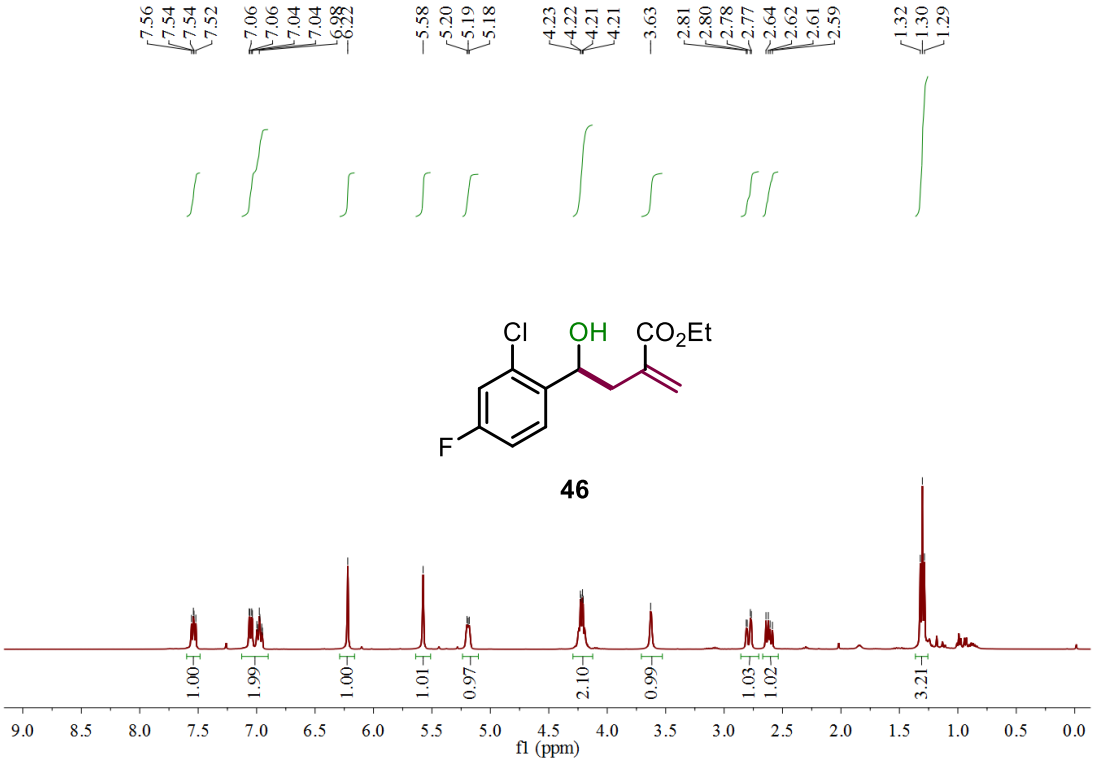
45

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



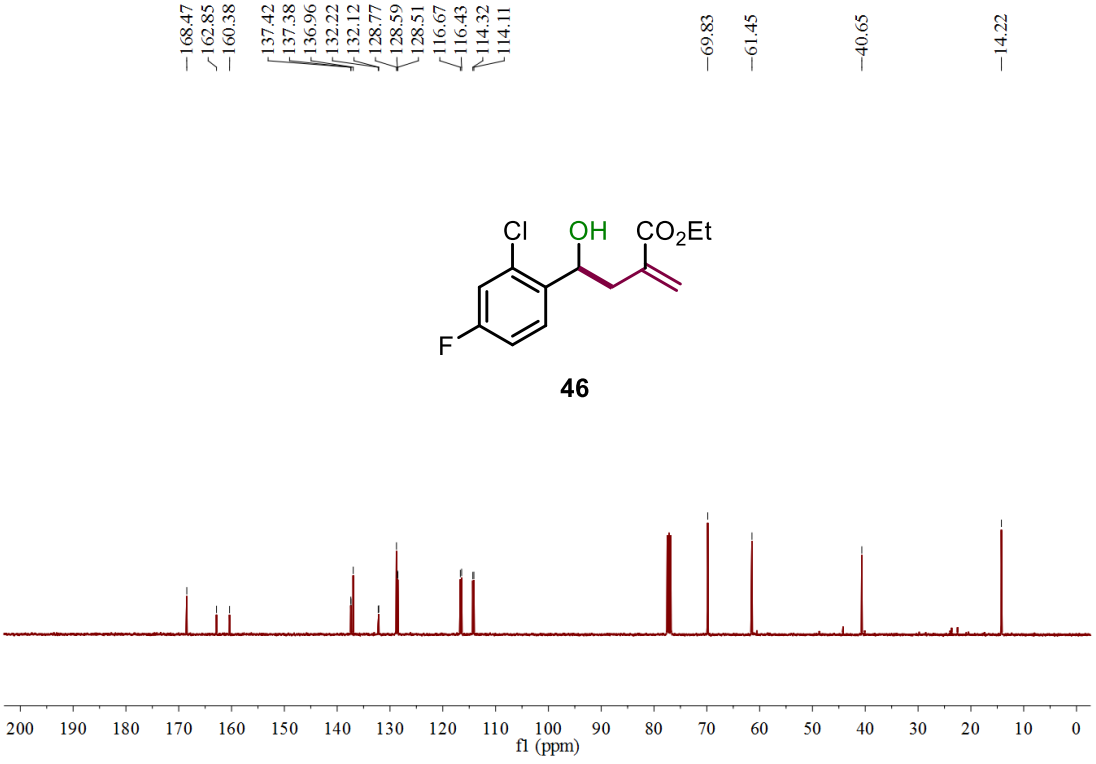
45

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



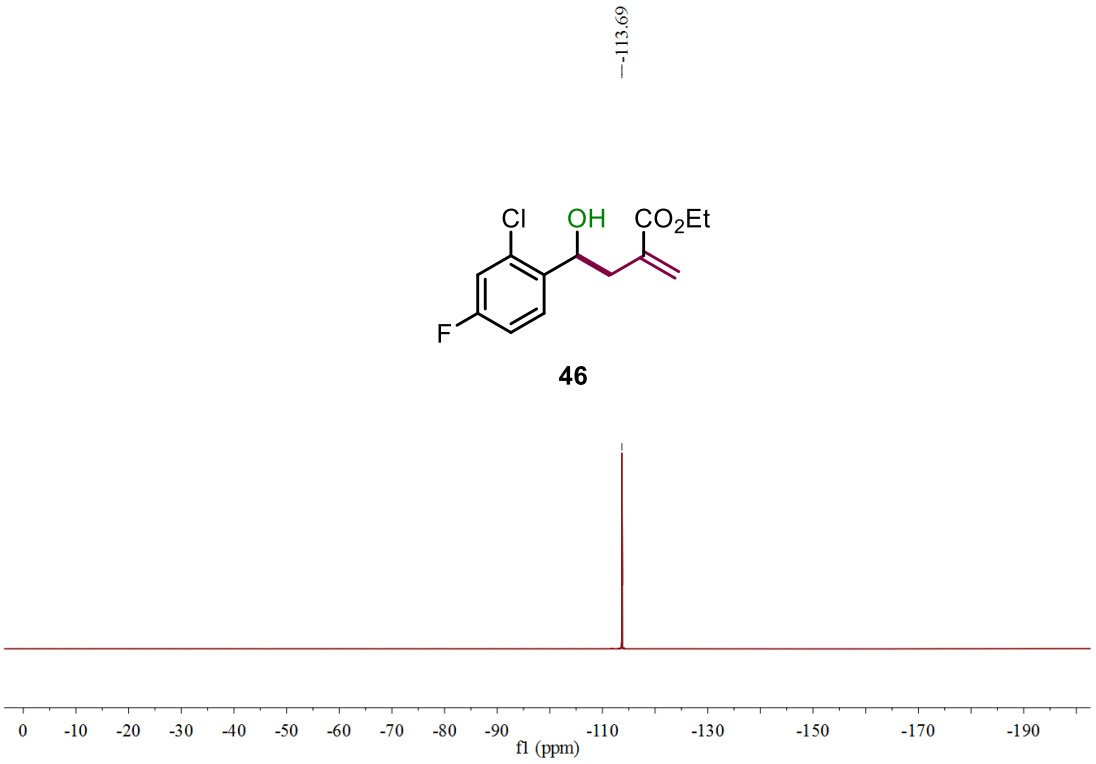
46

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



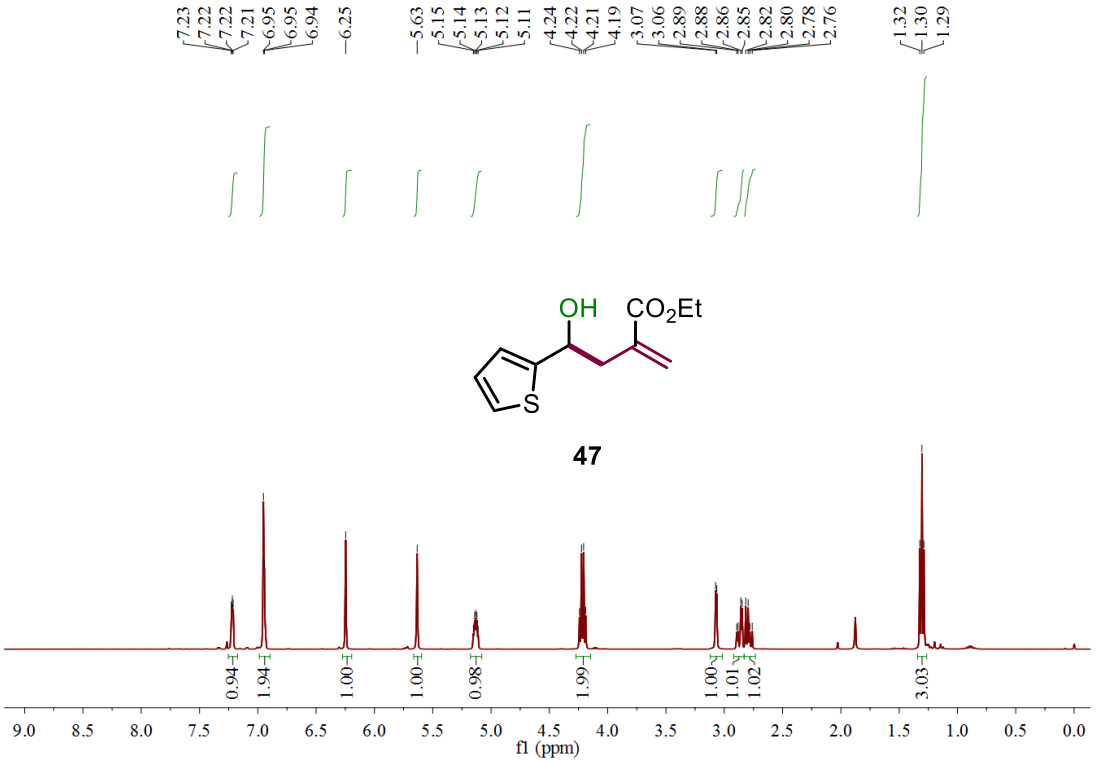
46

^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound 46



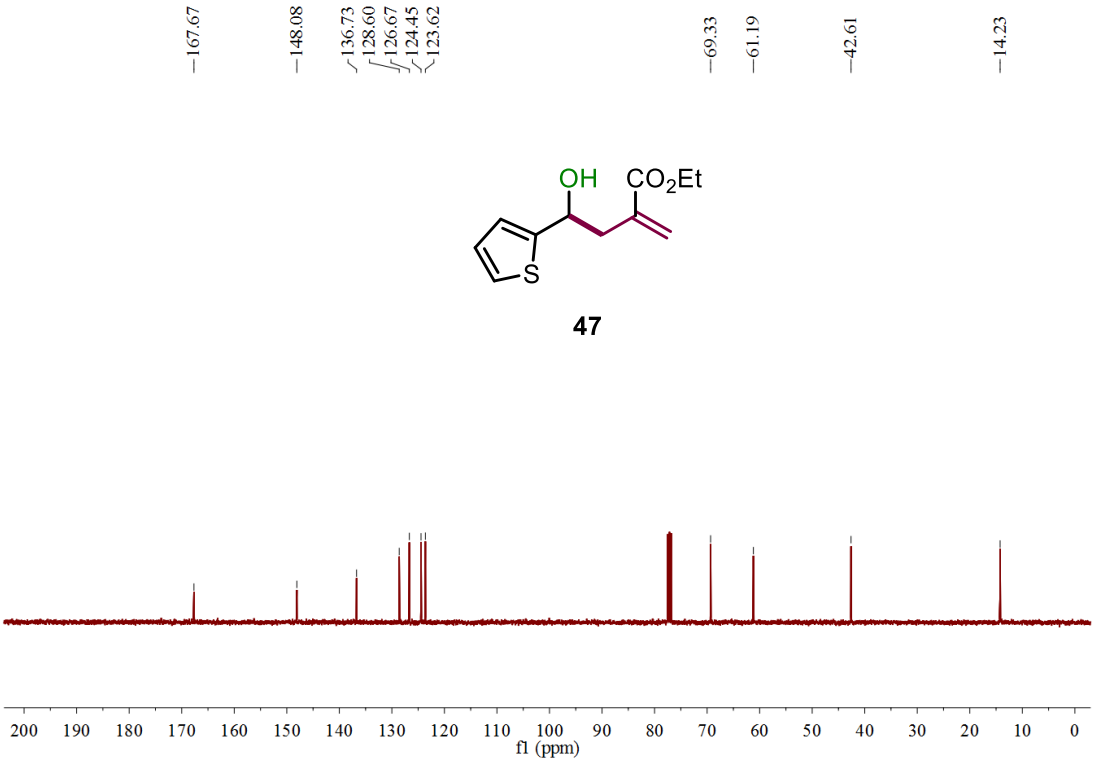
46

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



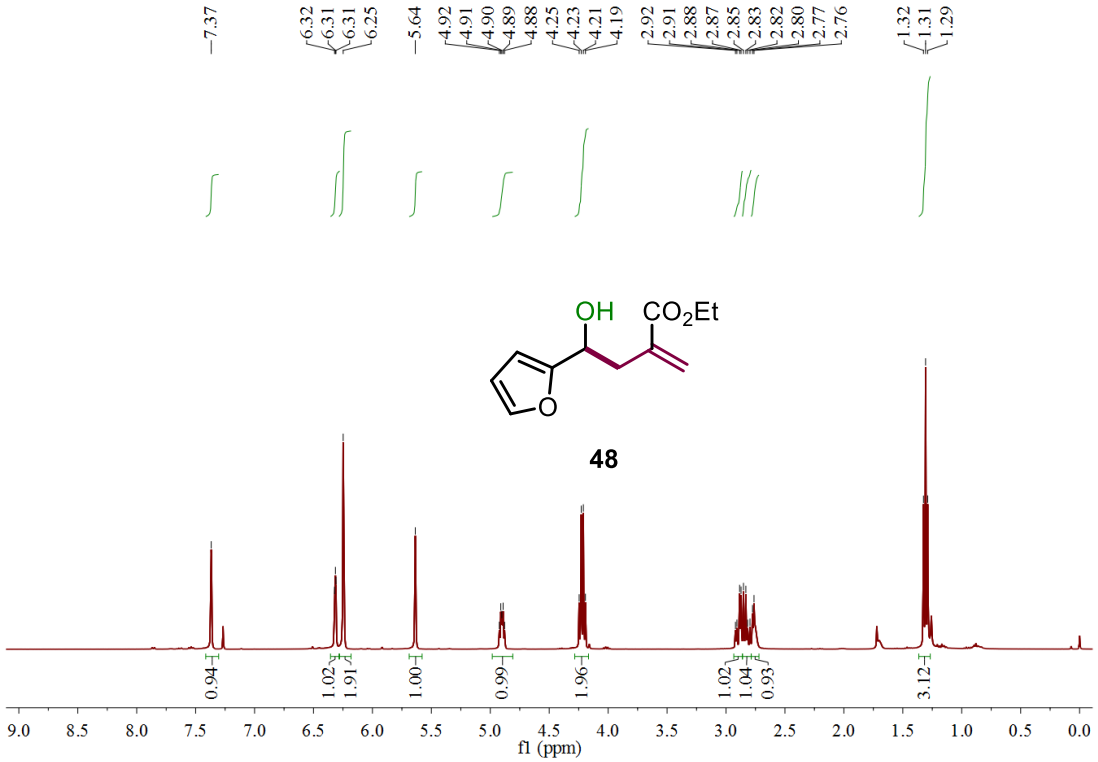
47

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

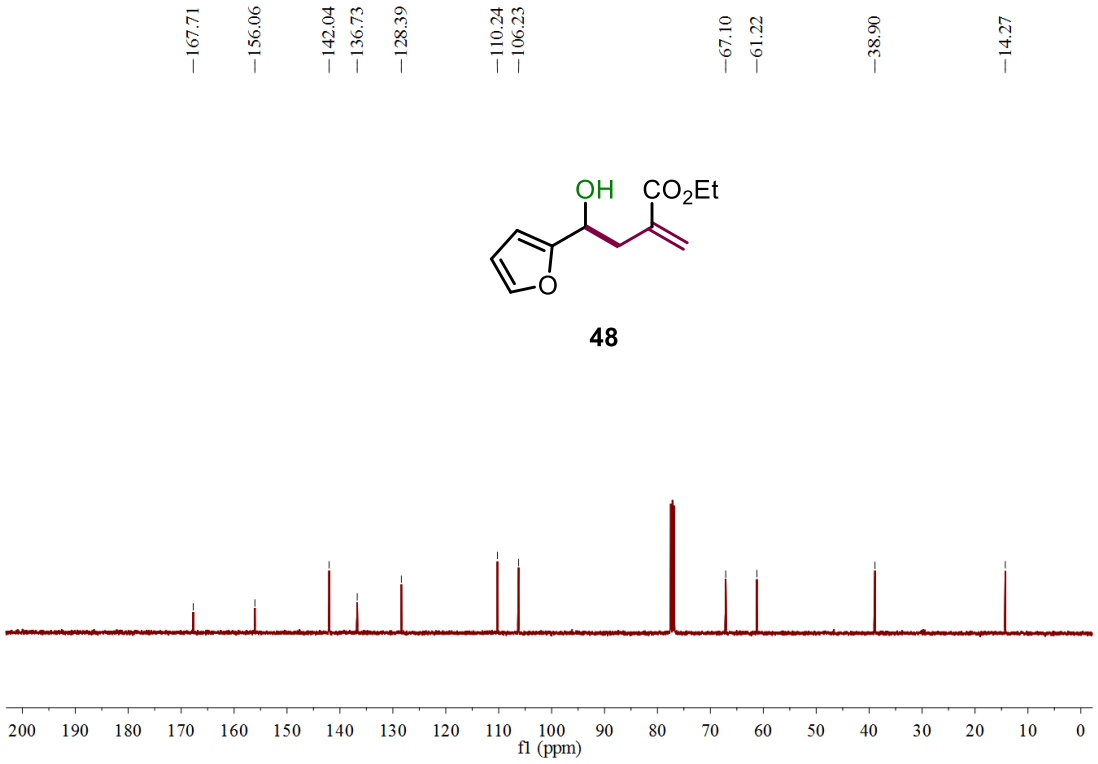


47

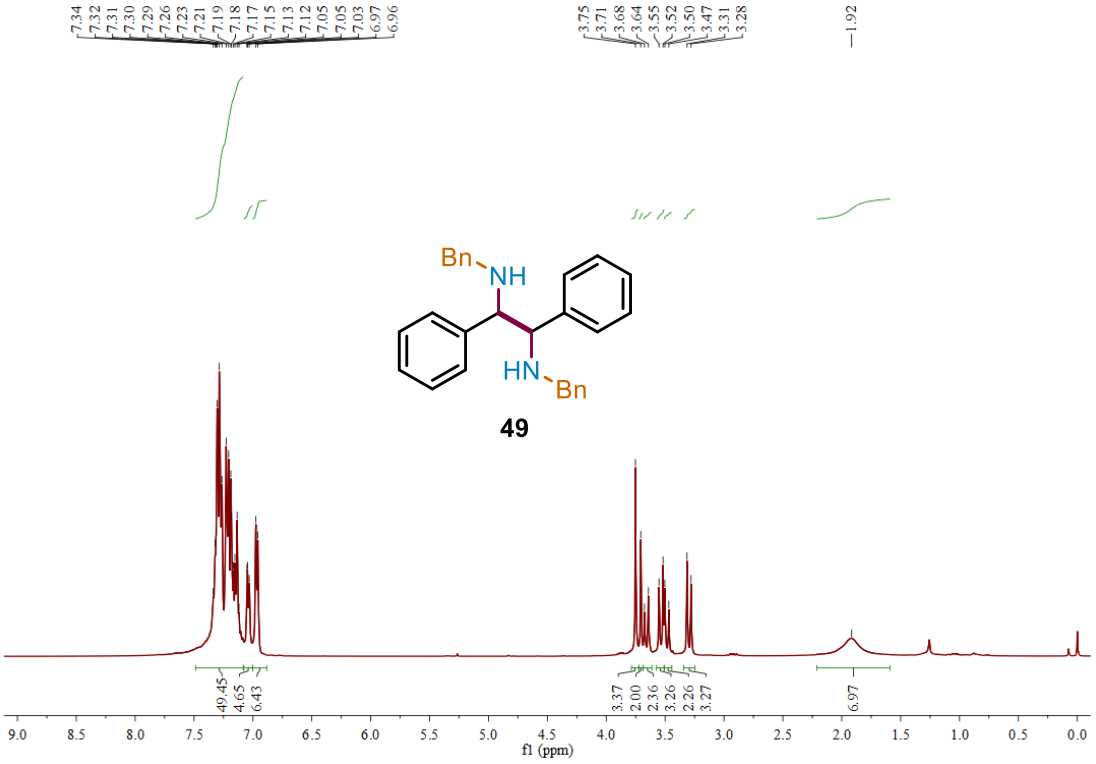
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 48



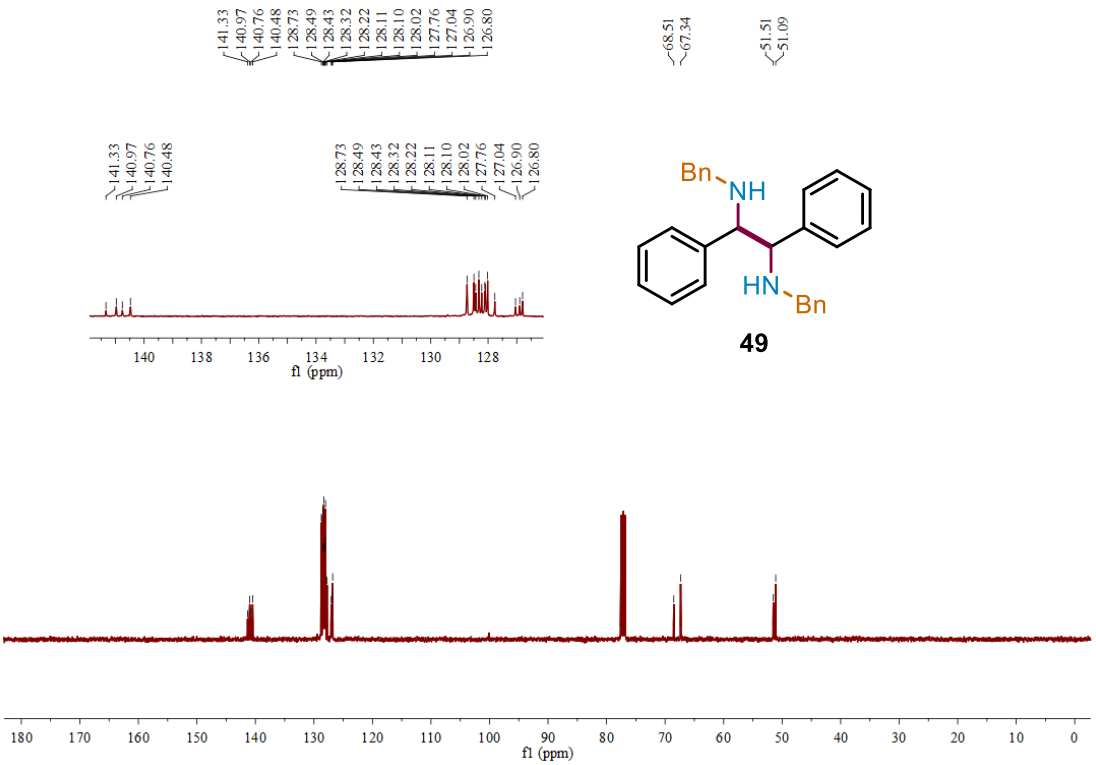
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 48



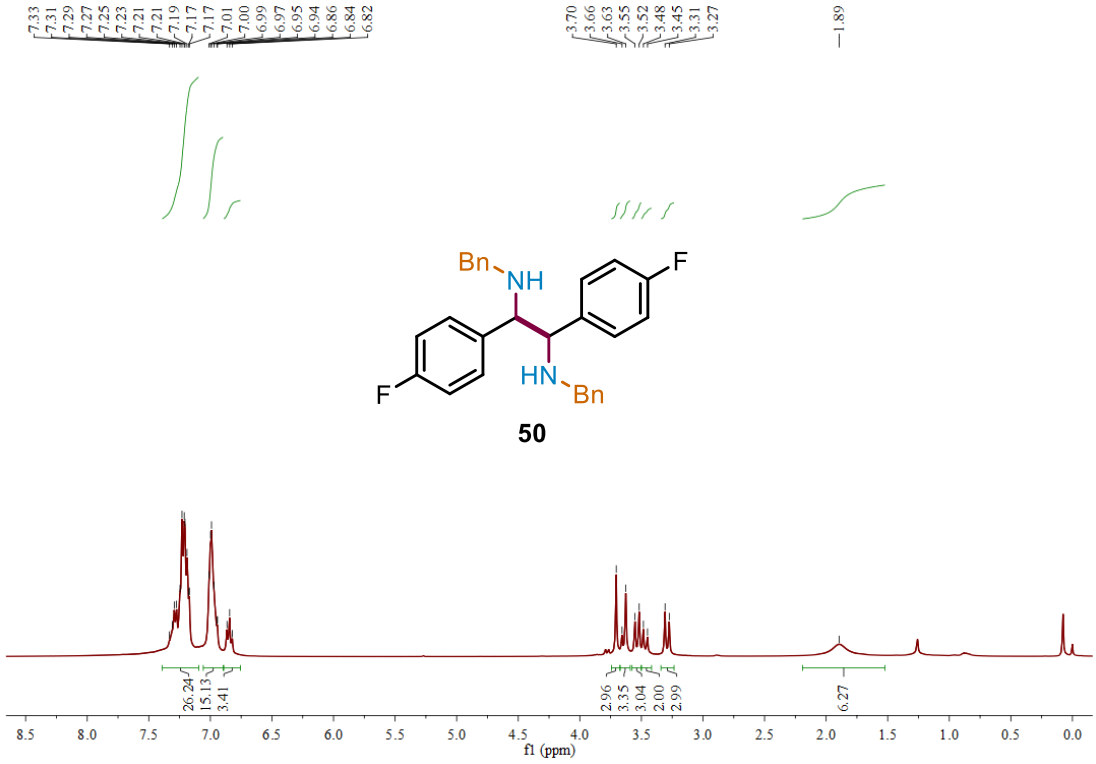
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 49



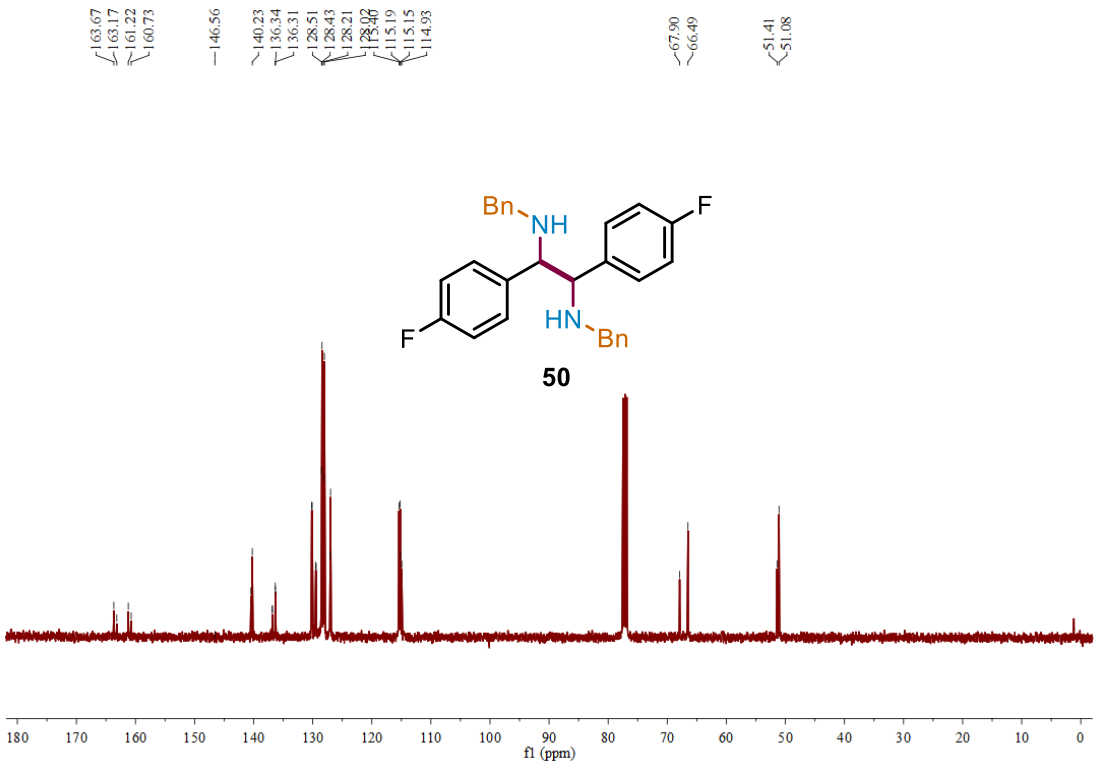
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 49



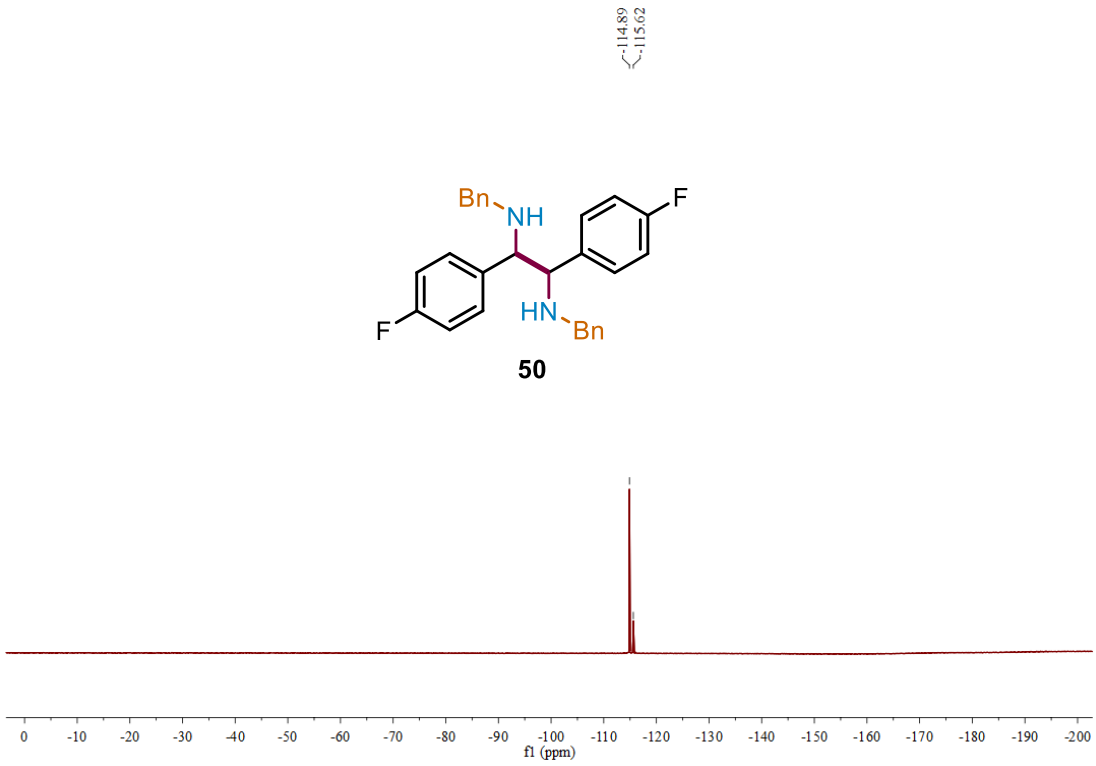
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 50



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 50

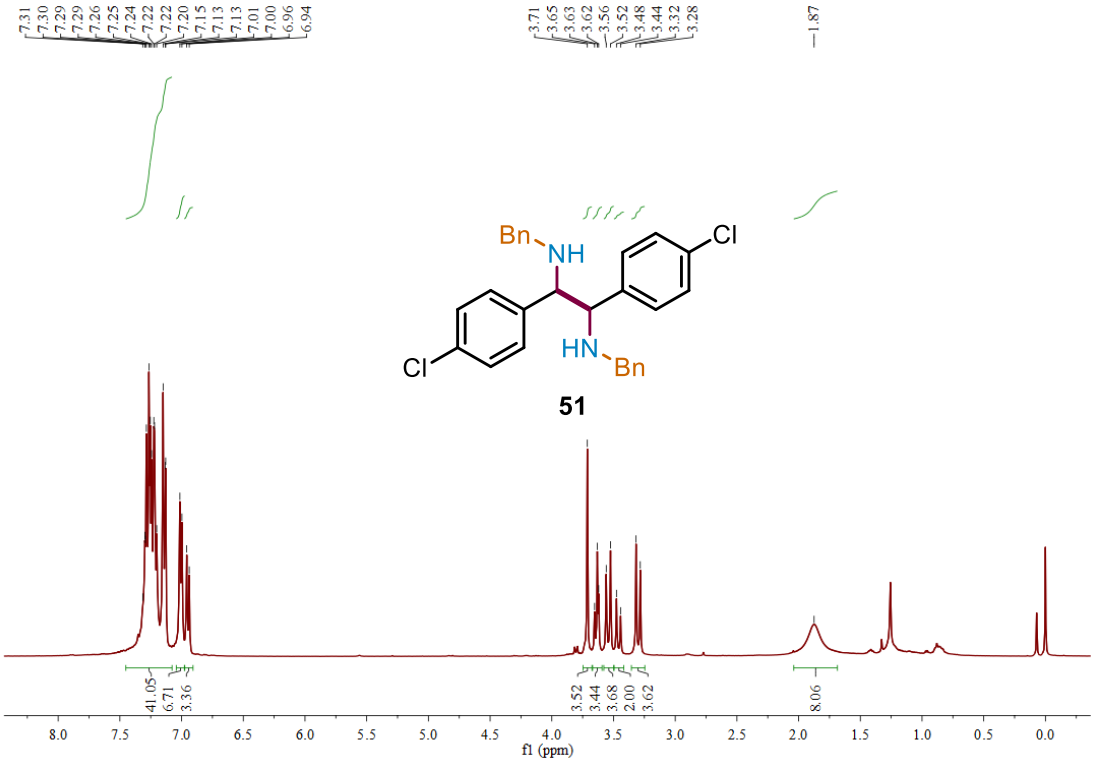


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound 50

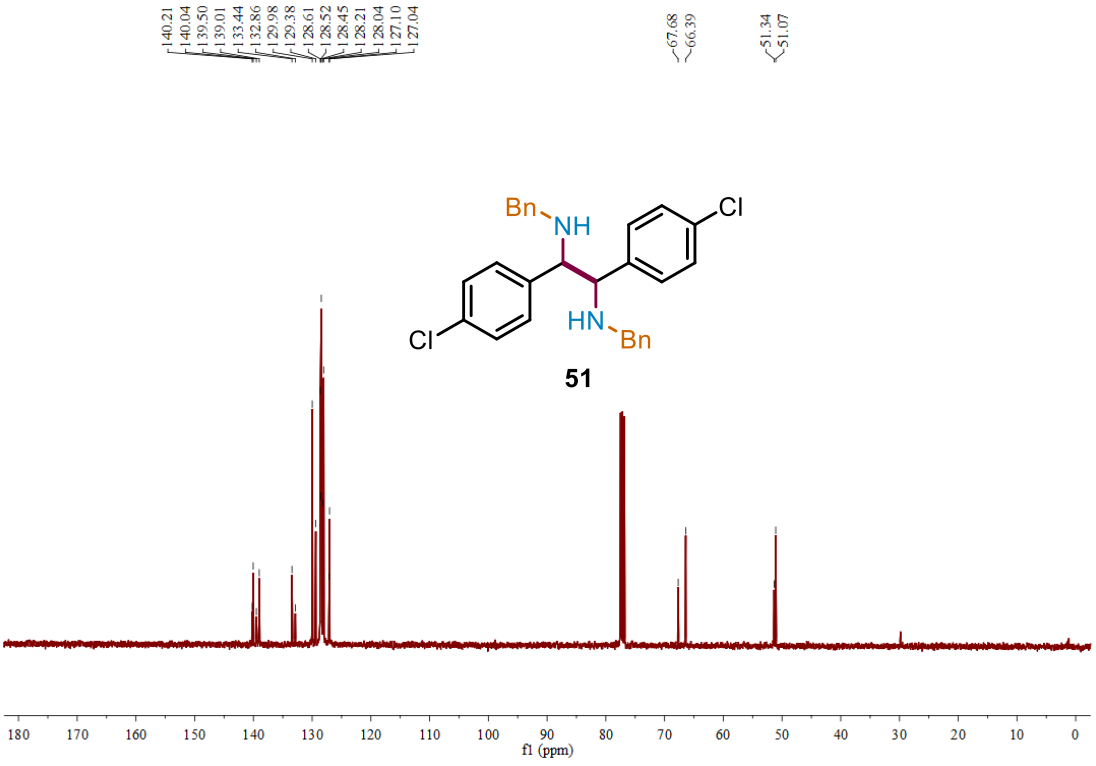


50

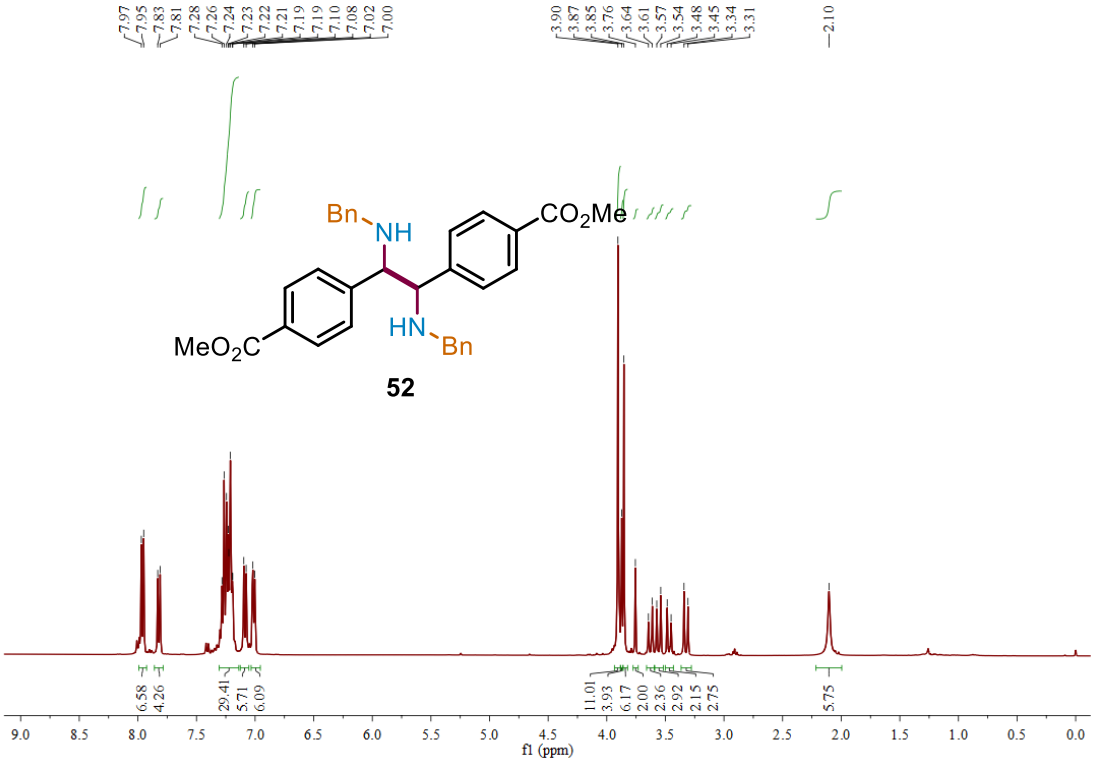
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 51



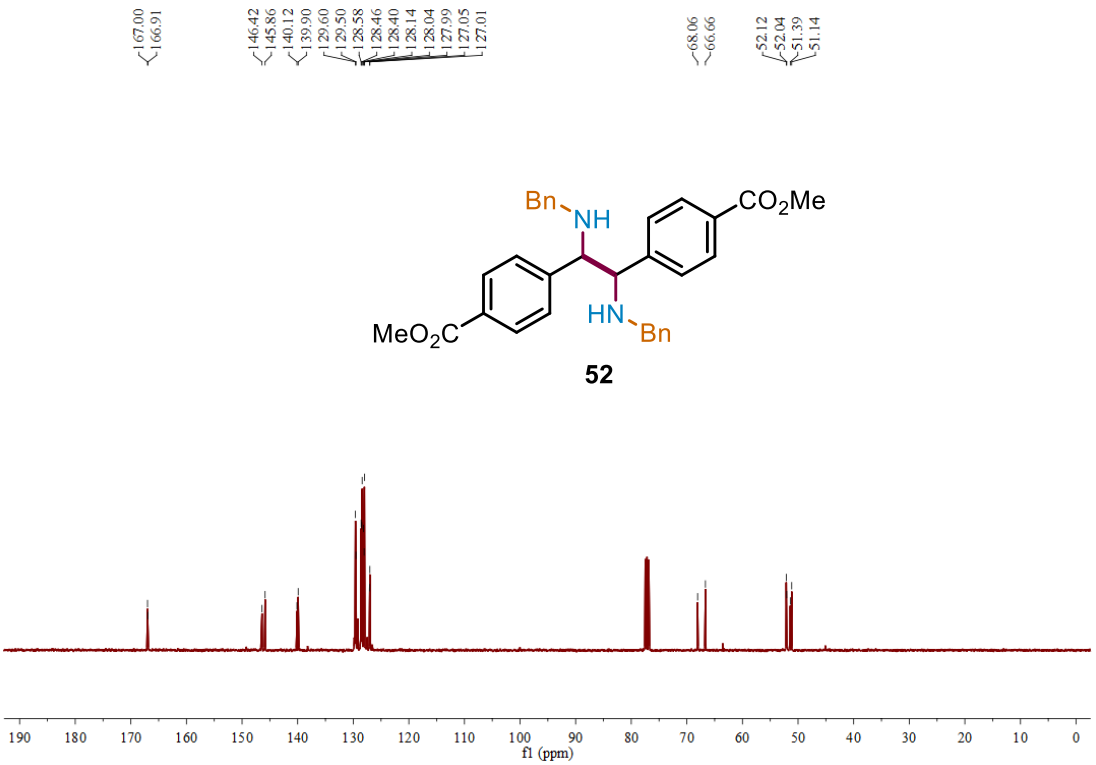
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 51



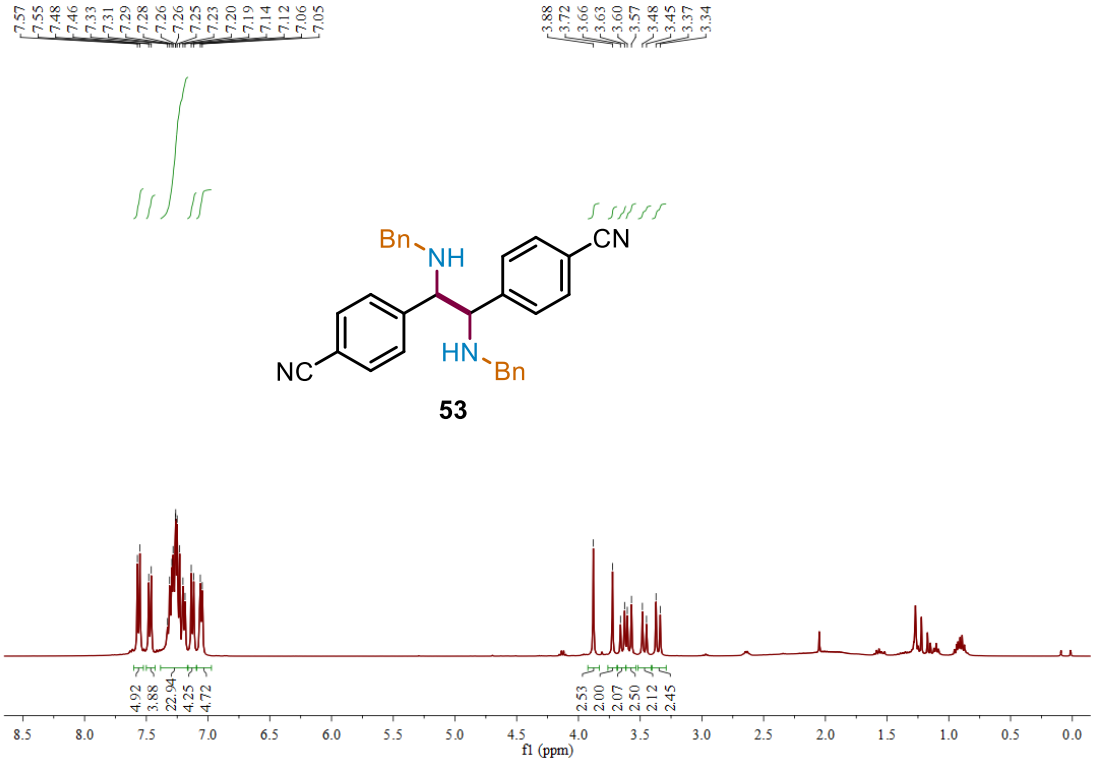
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 52



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 52

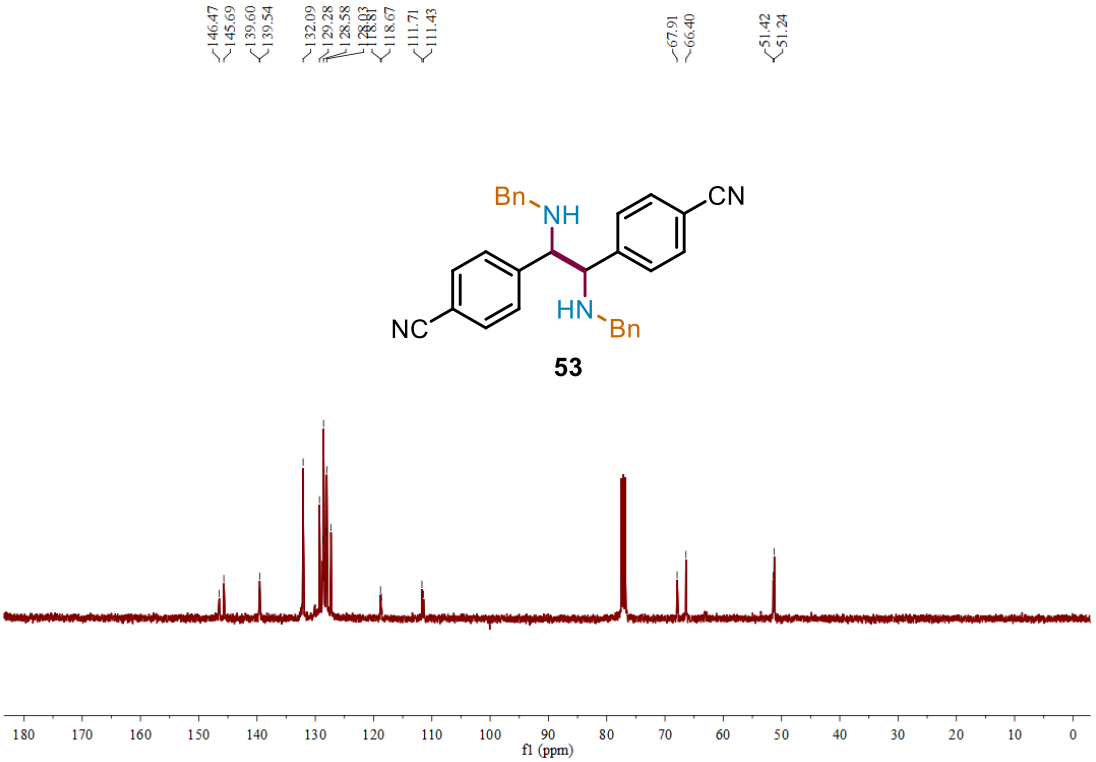


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 53



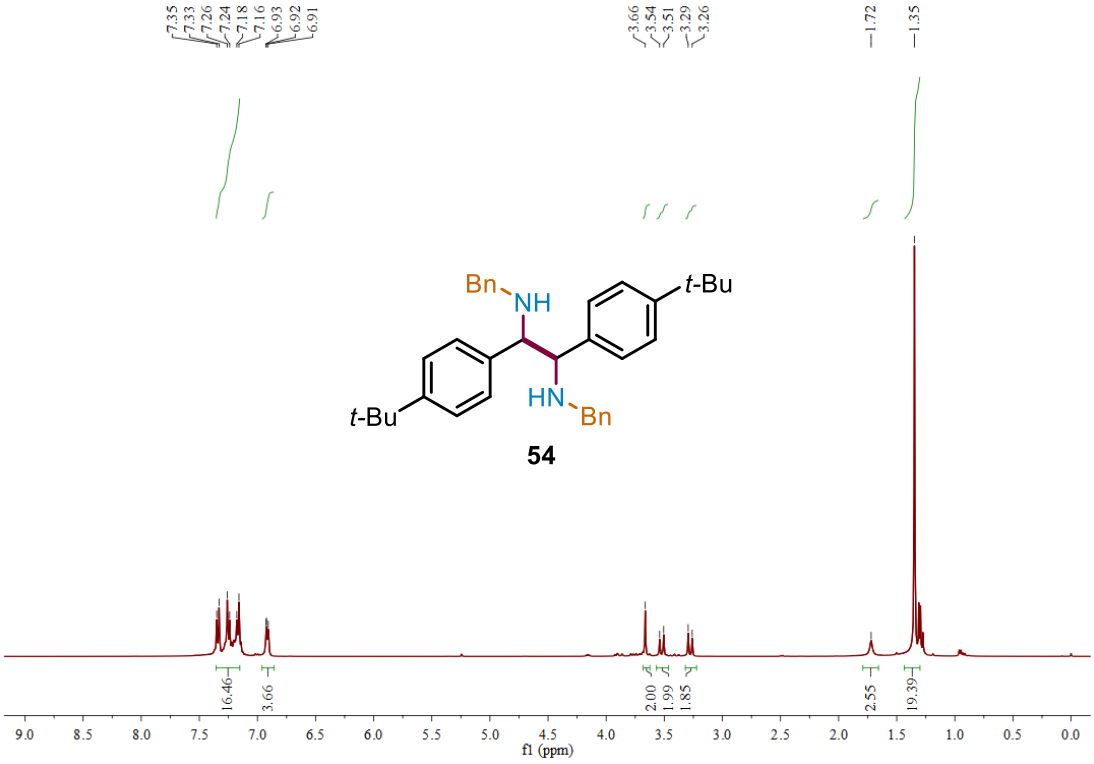
53

^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 53



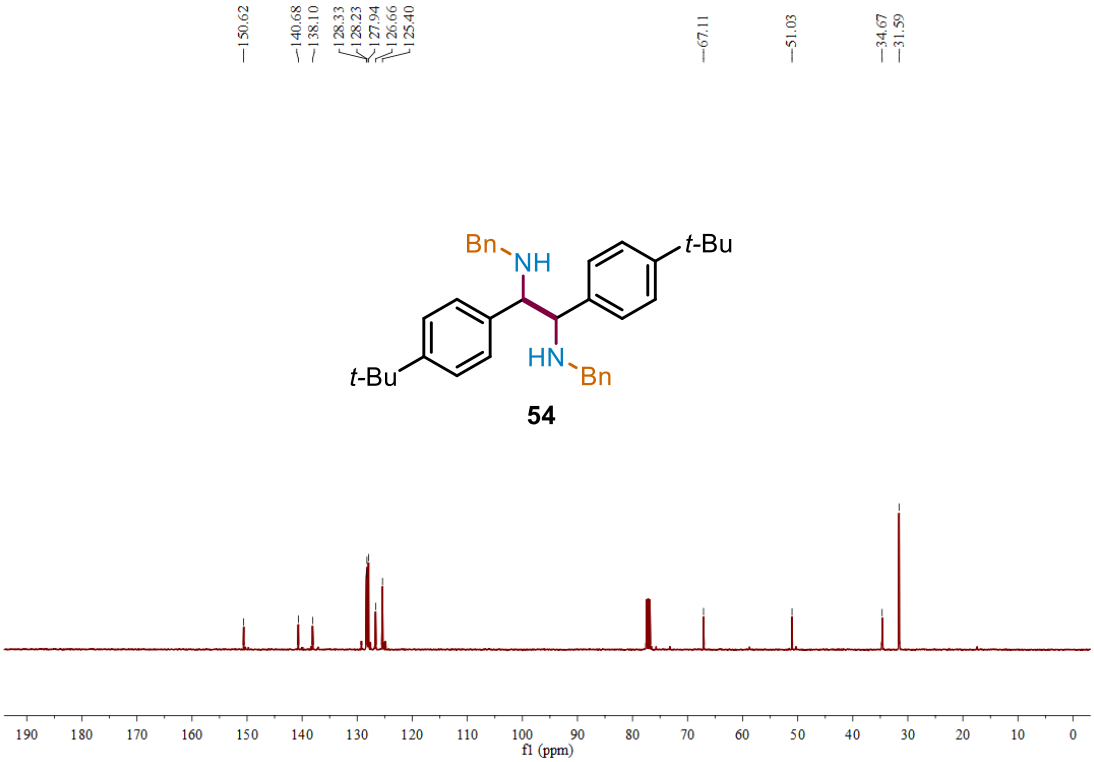
53

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 54



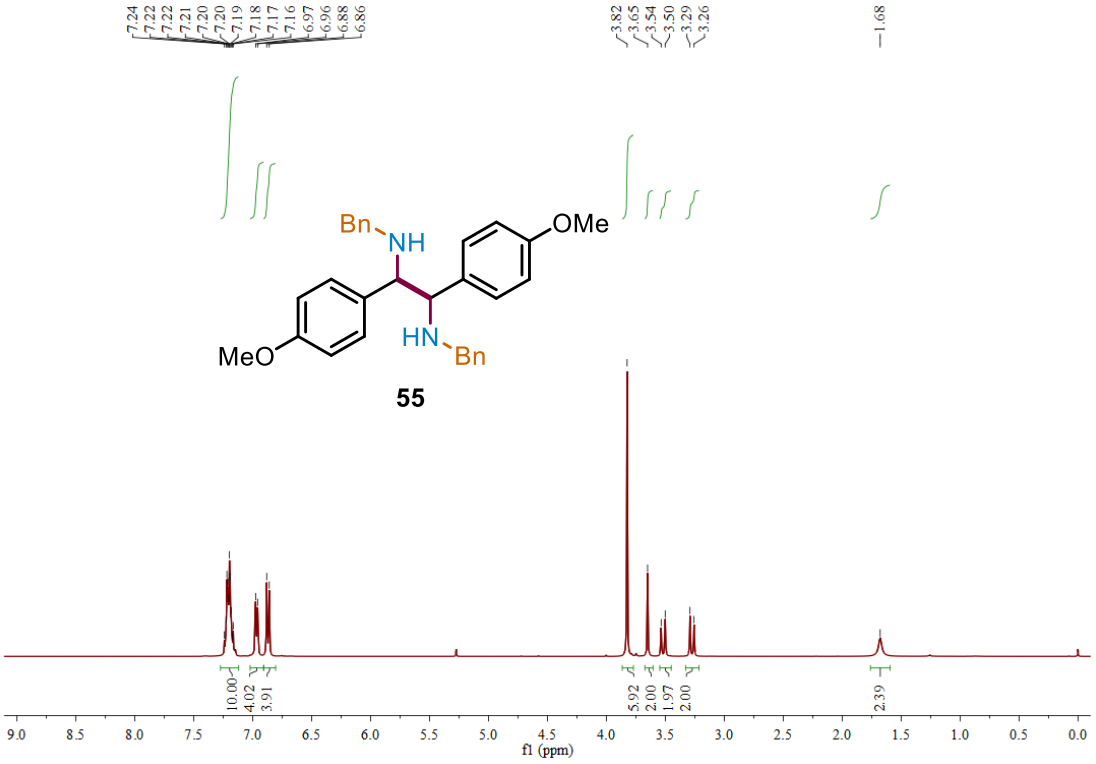
54

^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 54

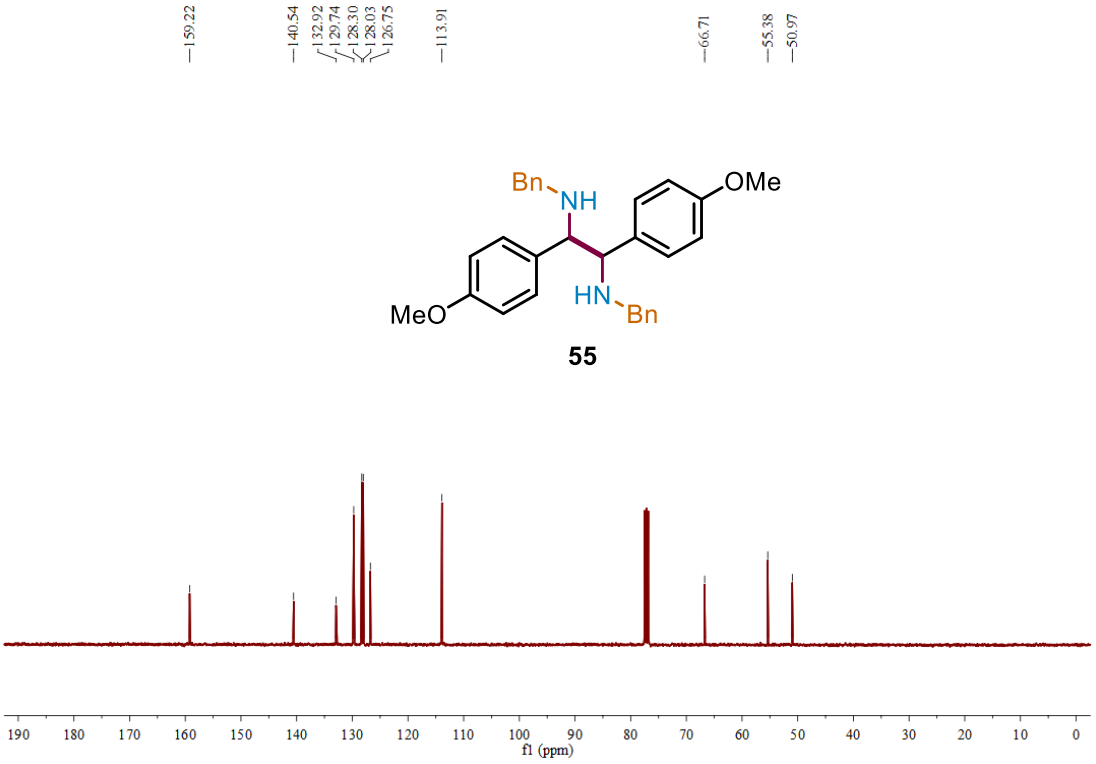


54

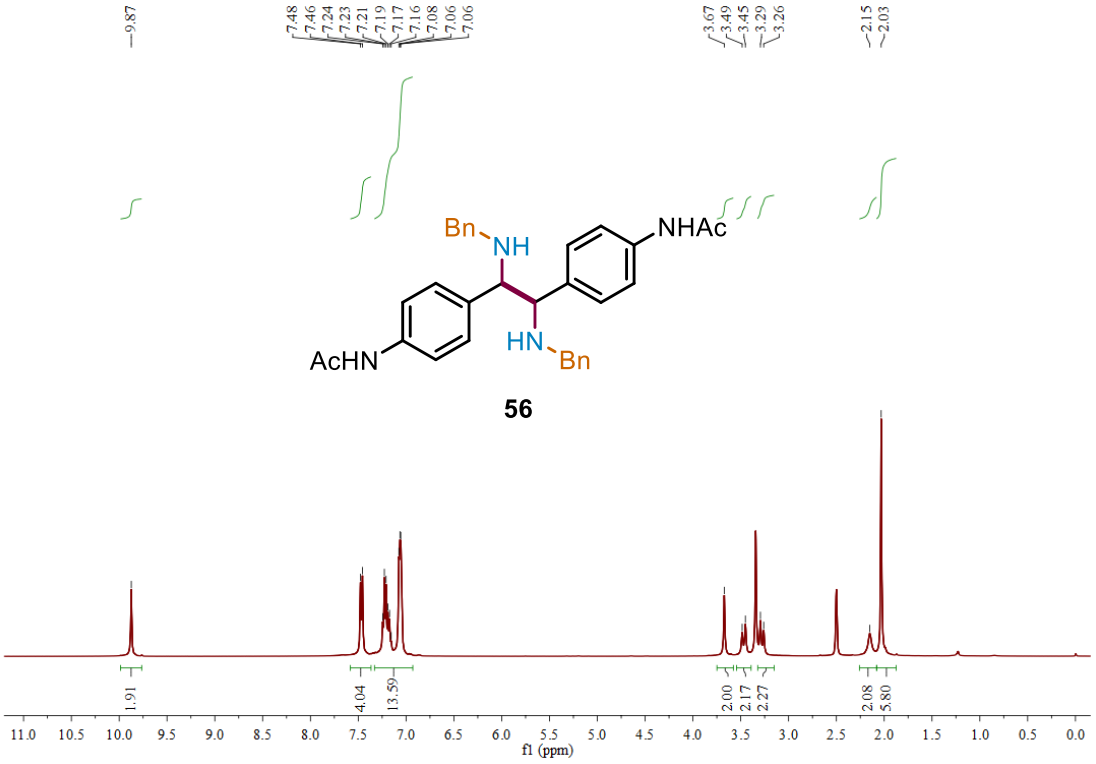
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 55



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 55

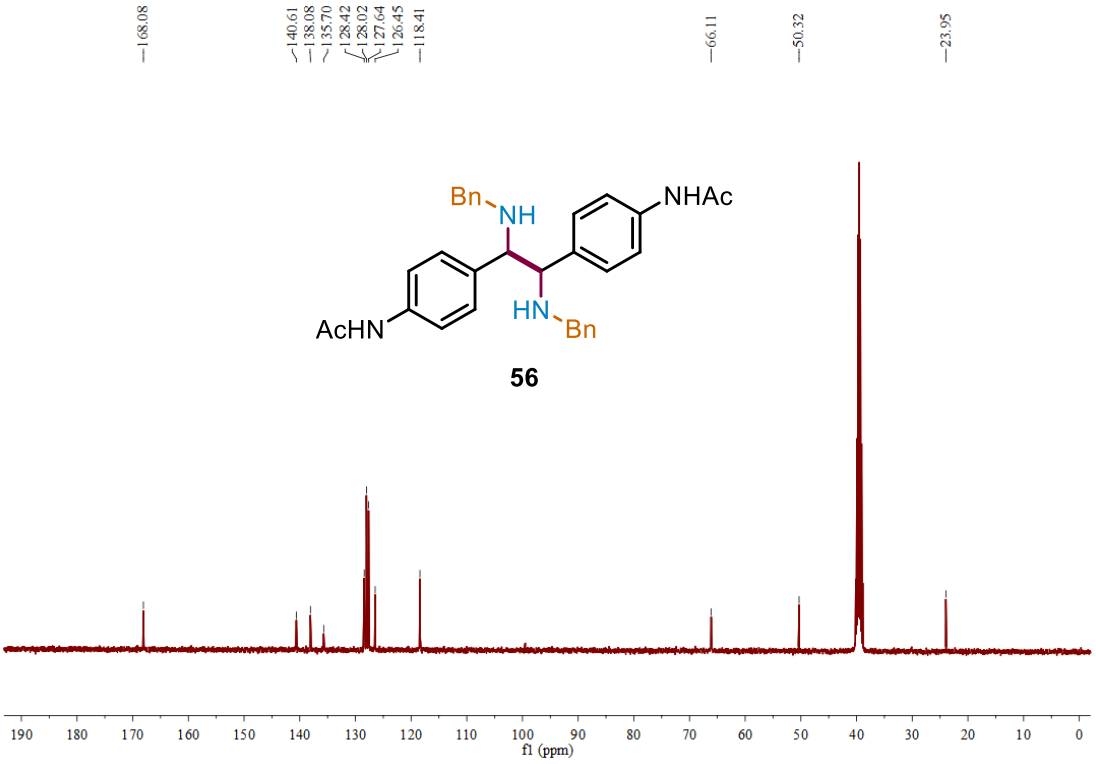


^{1}H NMR (400 MHz, DMSO-d_6) spectrum of compound 56



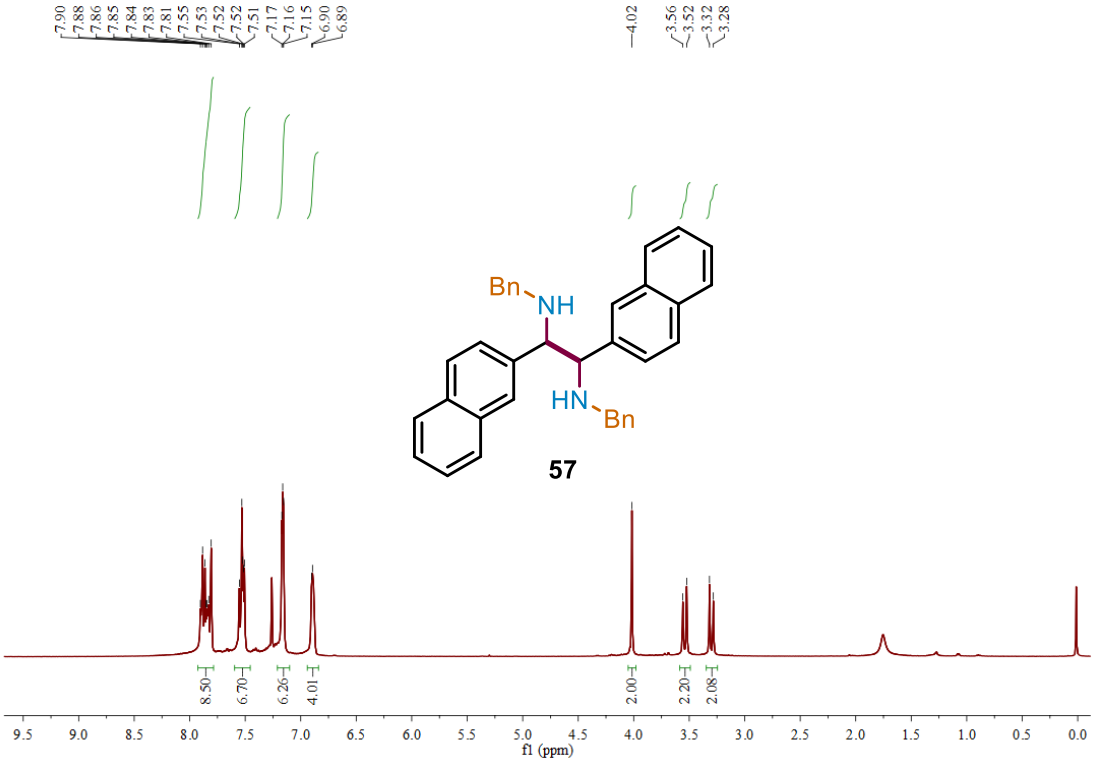
56

^{13}C NMR (100 MHz, DMSO-d_6) spectrum of compound 56

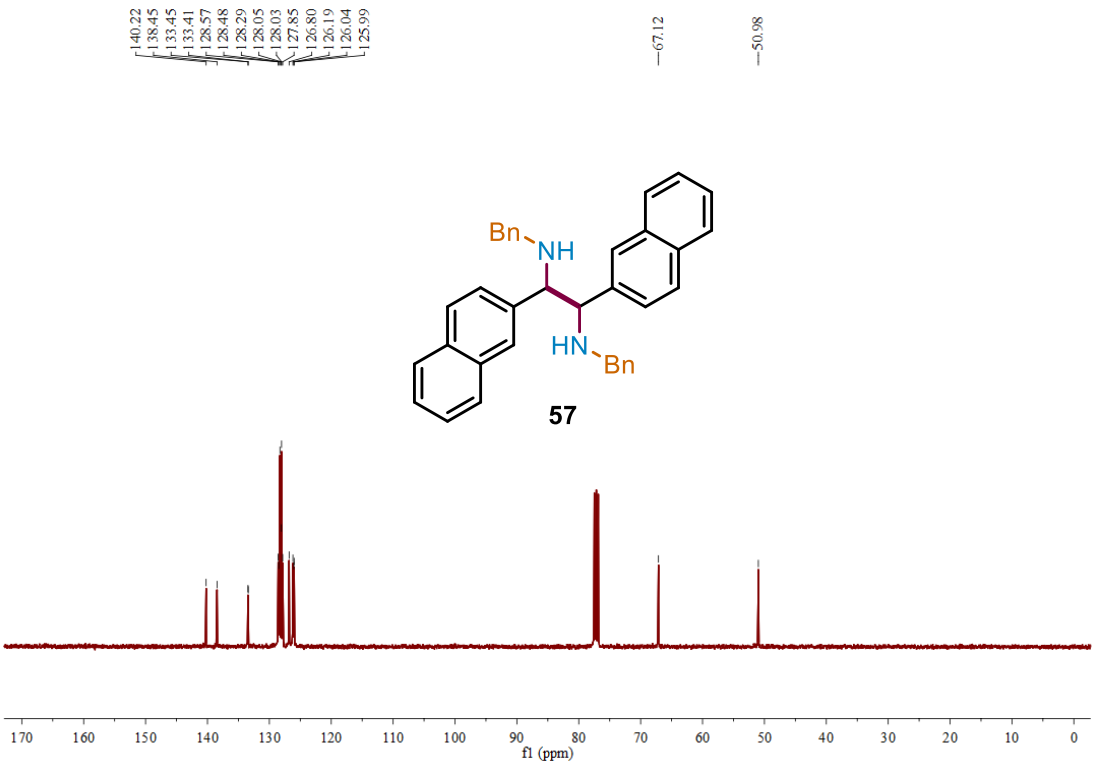


56

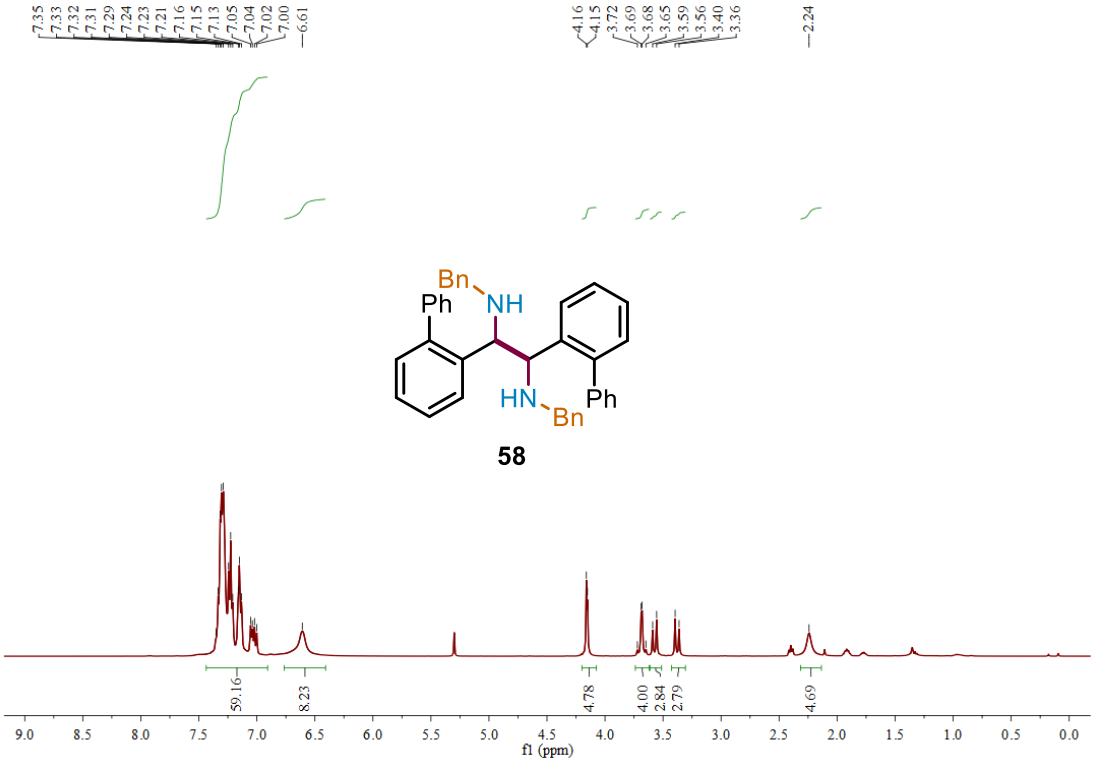
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 57



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 57

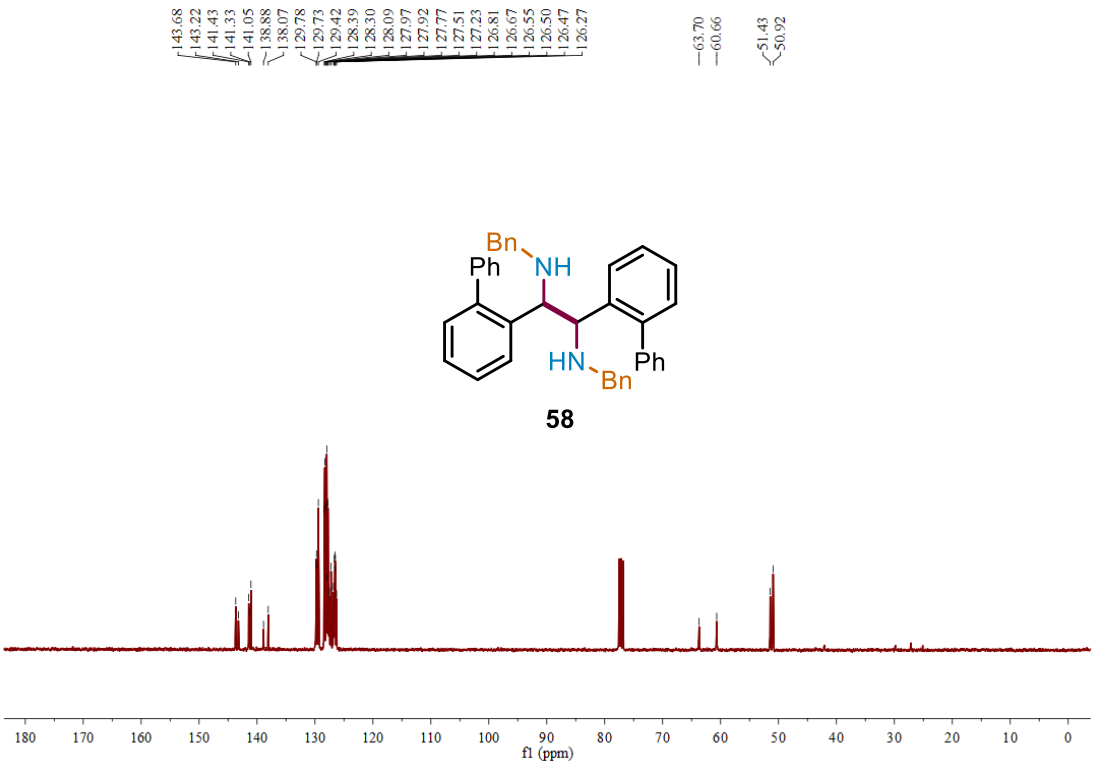


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 58



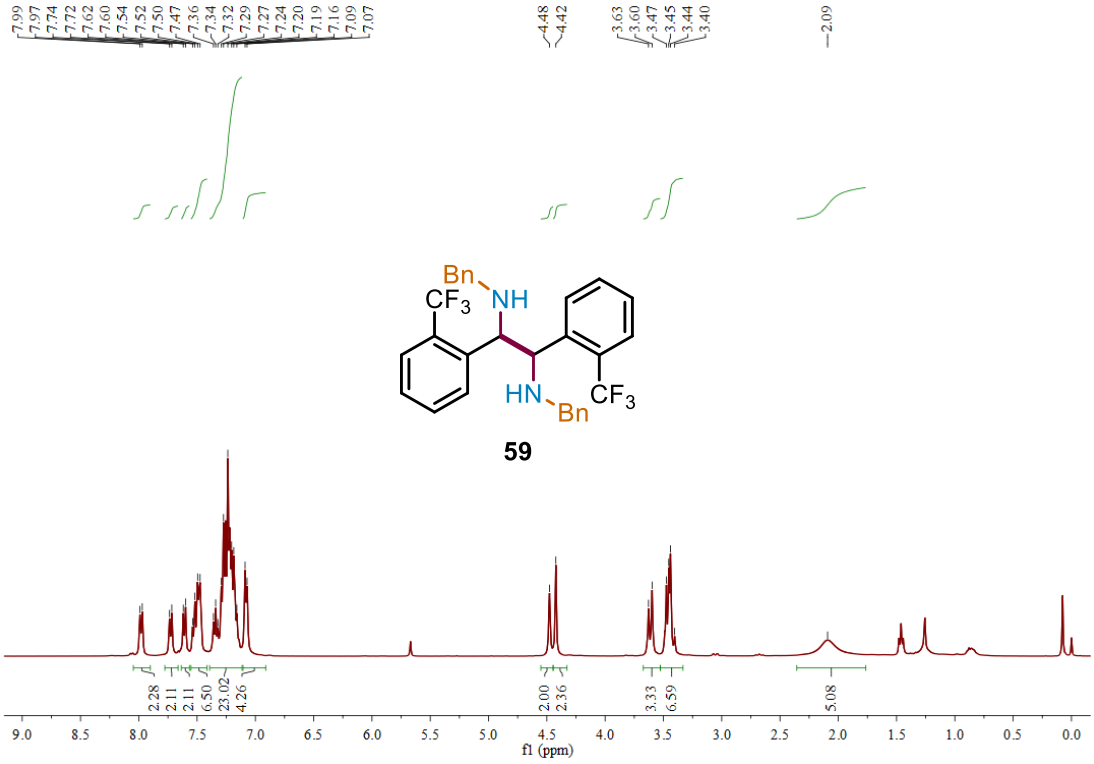
58

^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 58

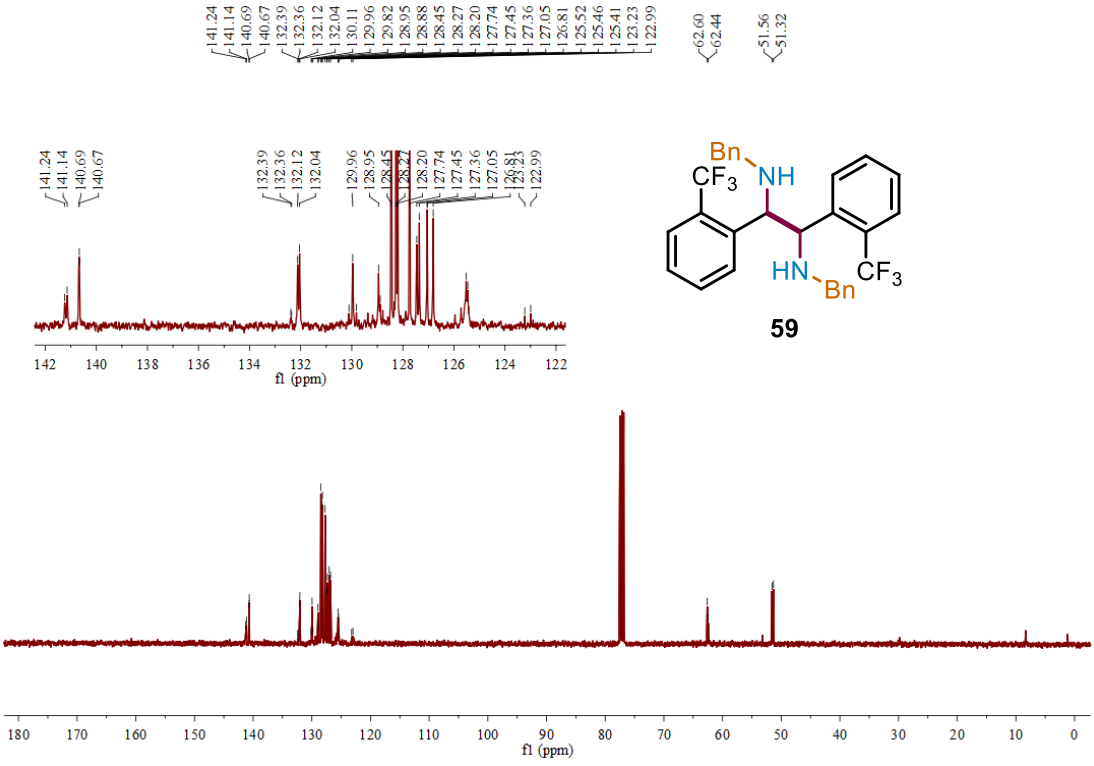


58

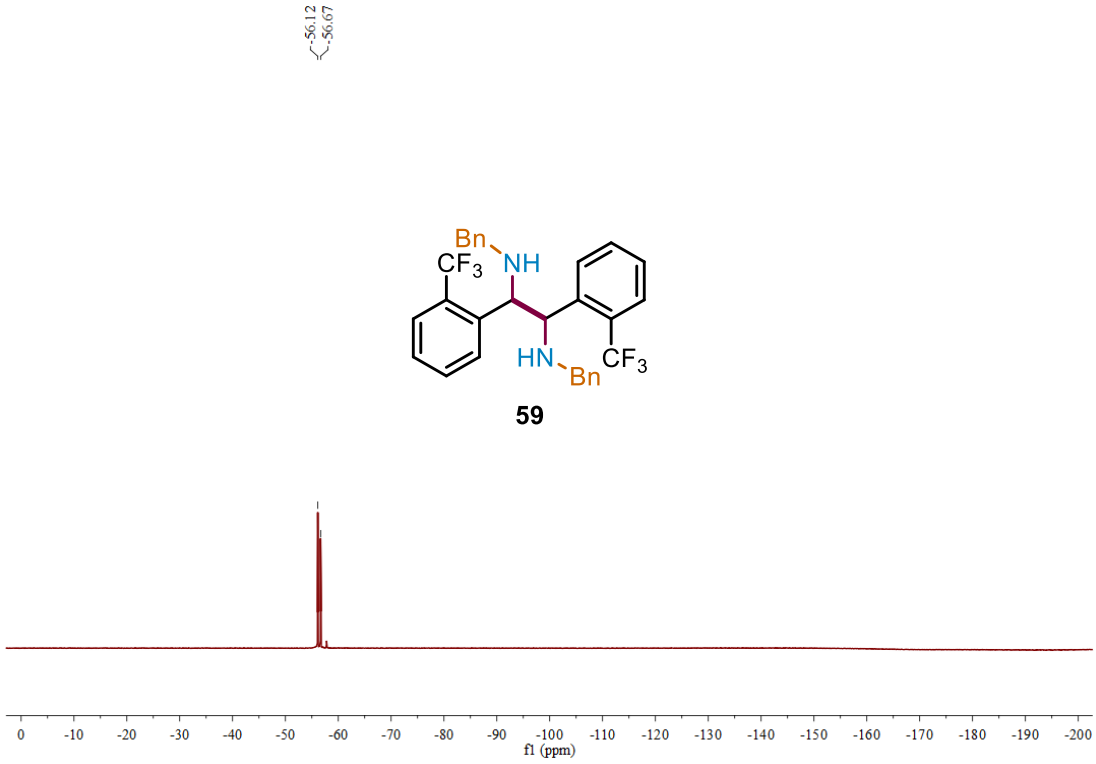
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 59



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 59

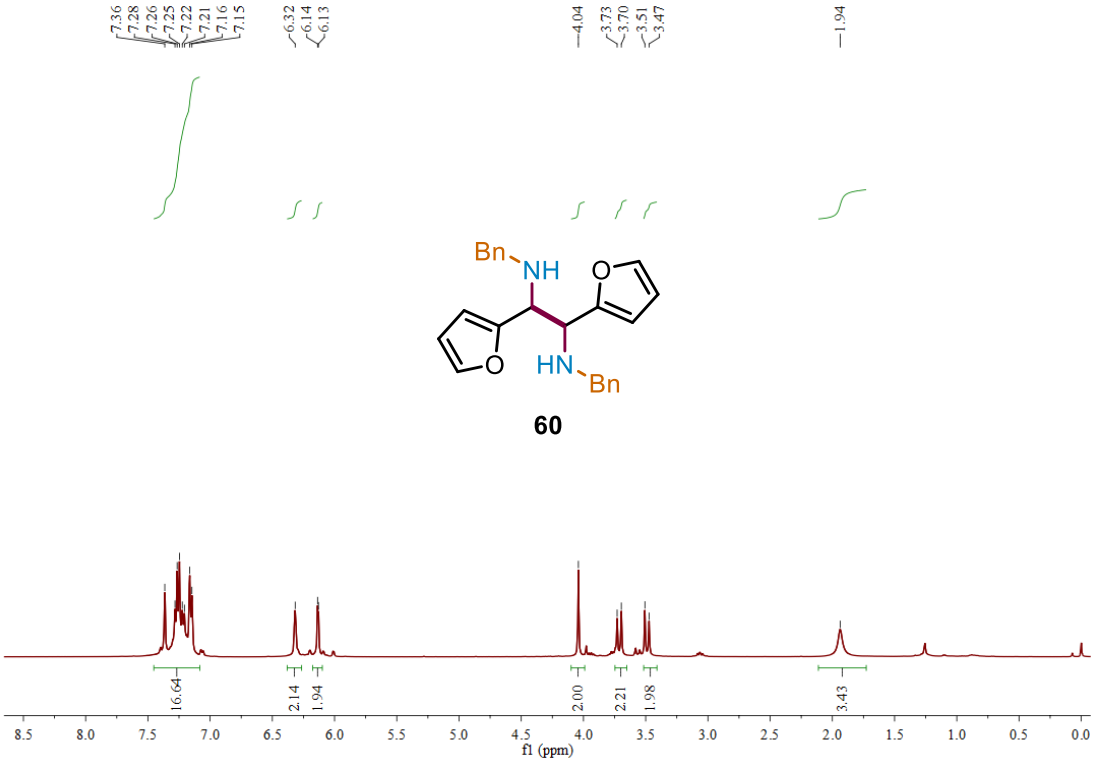


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound 59



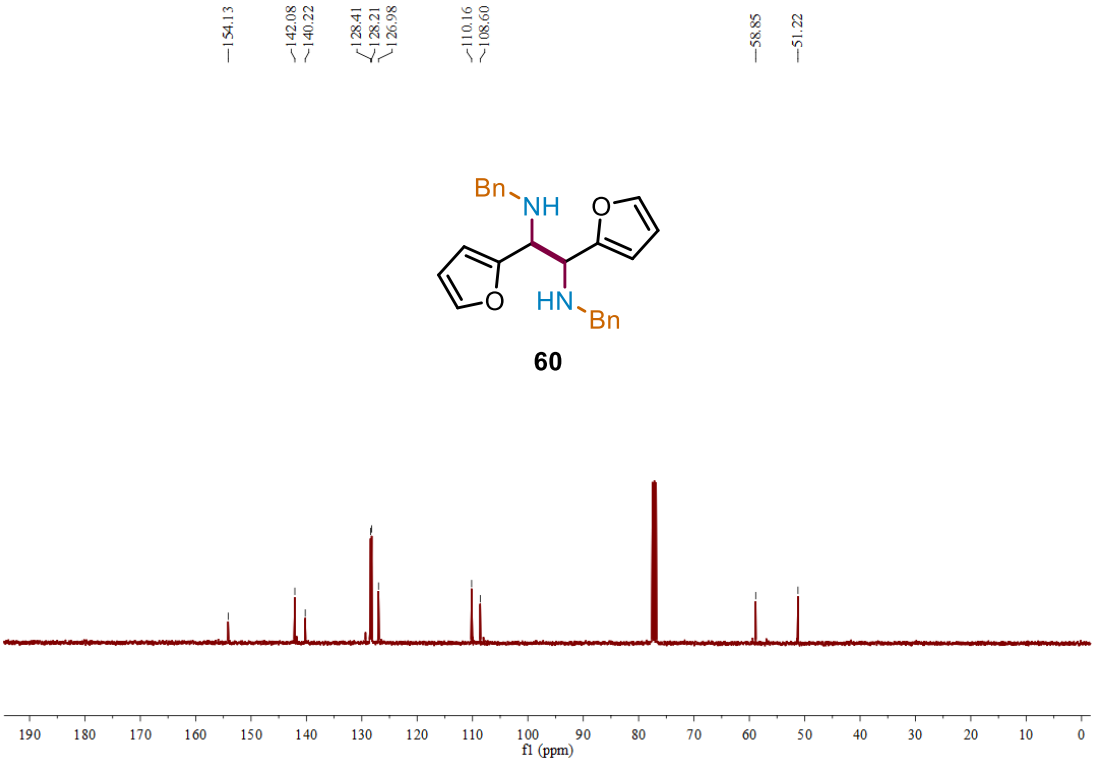
59

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 60



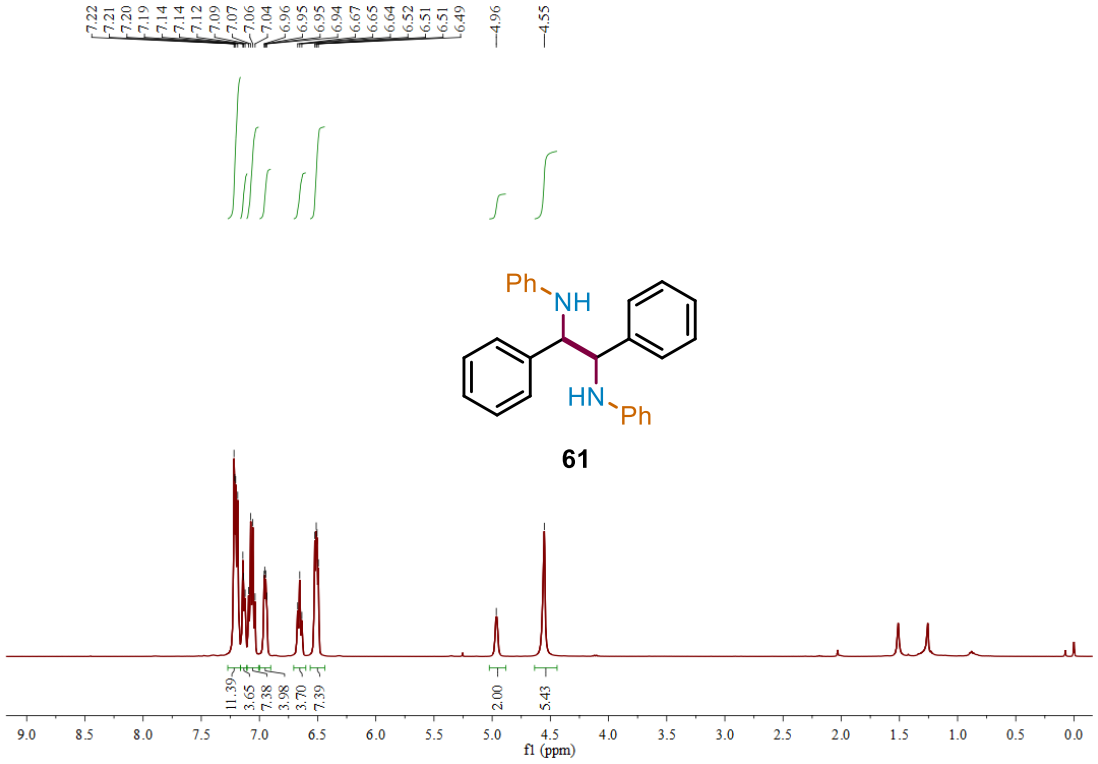
60

^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 60



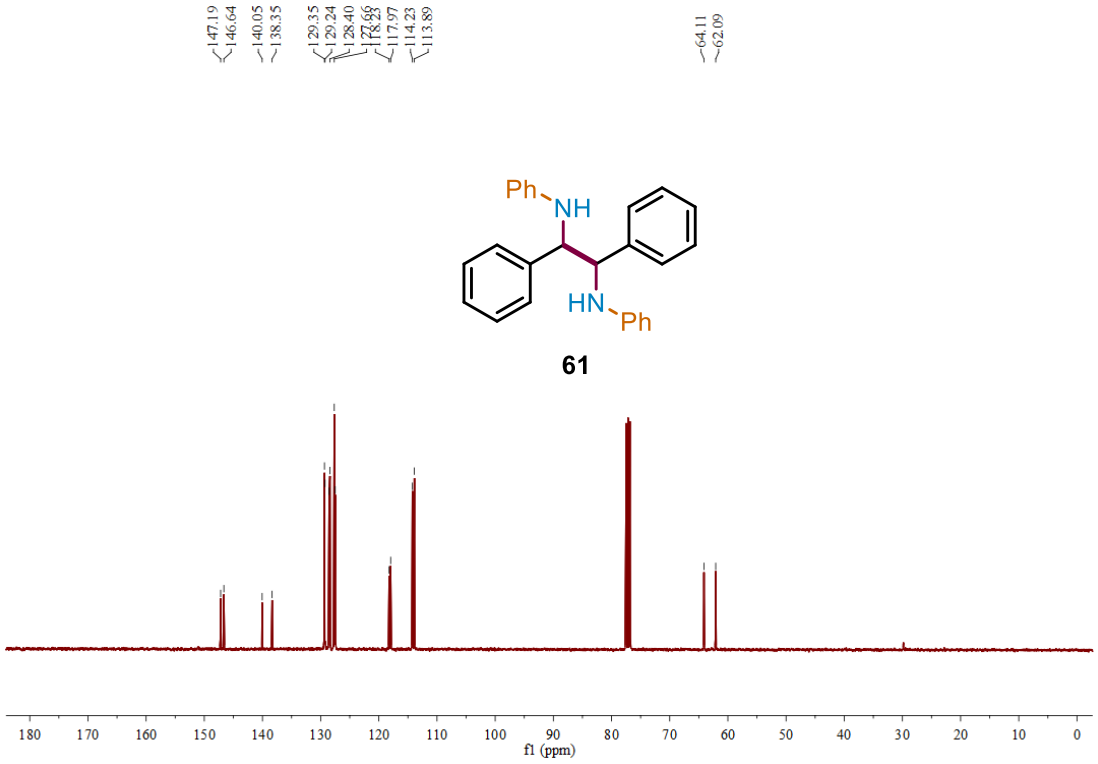
60

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



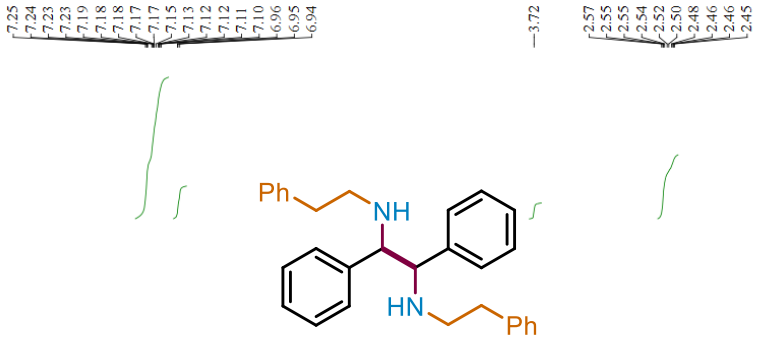
61

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

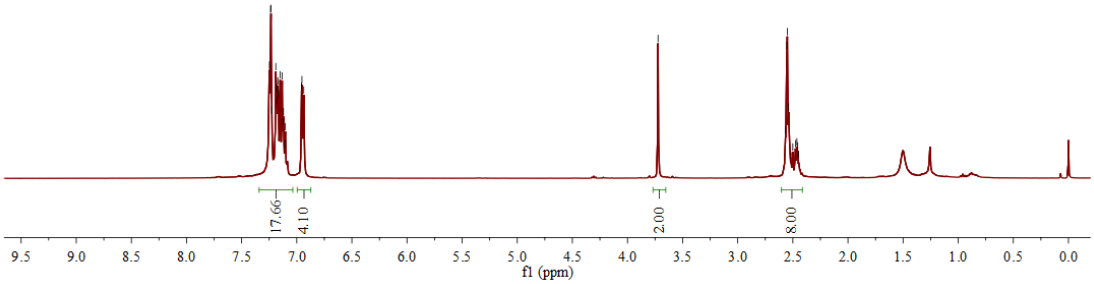


61

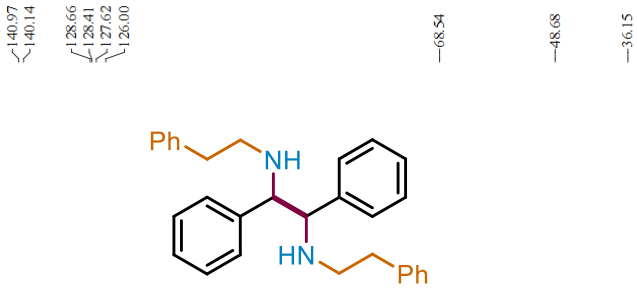
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 62



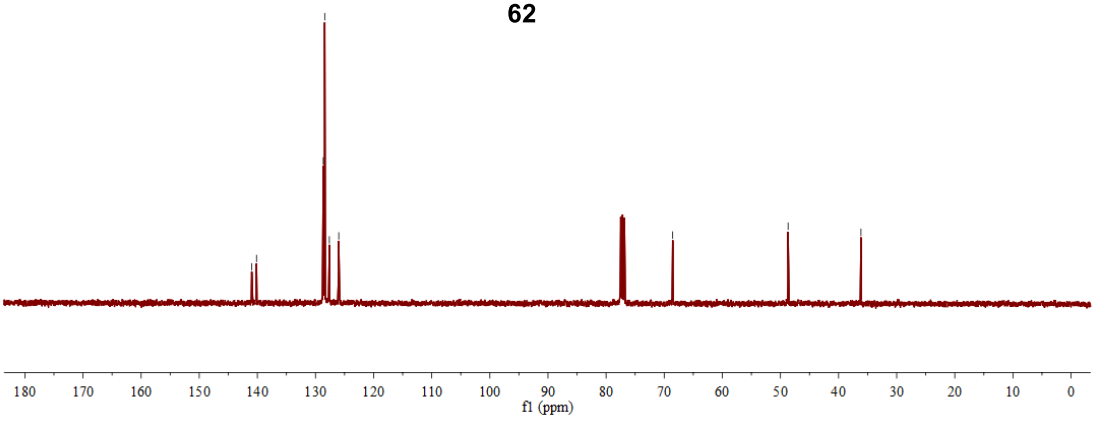
62



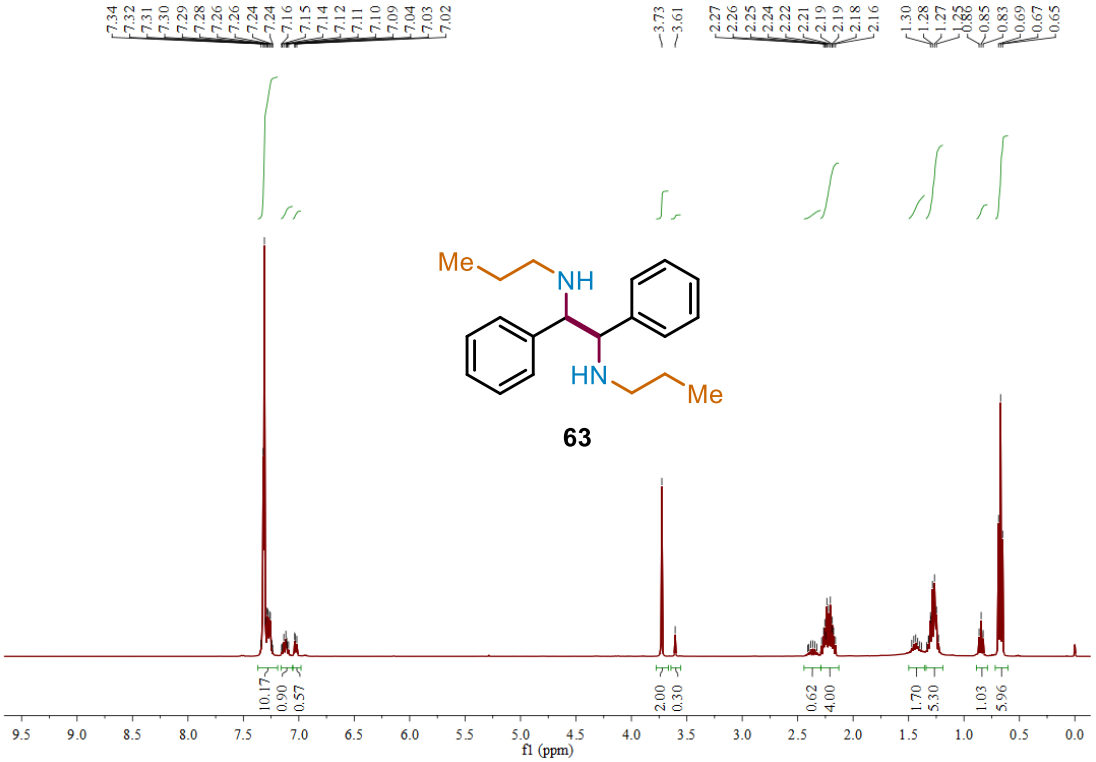
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 62



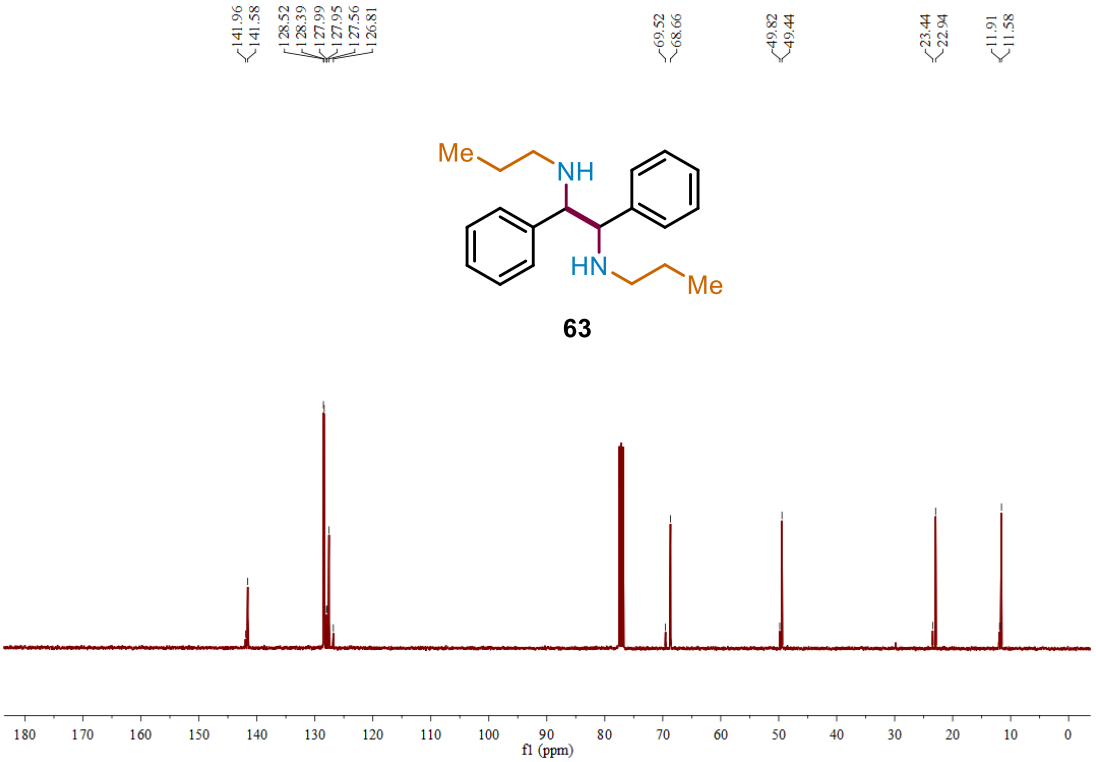
62



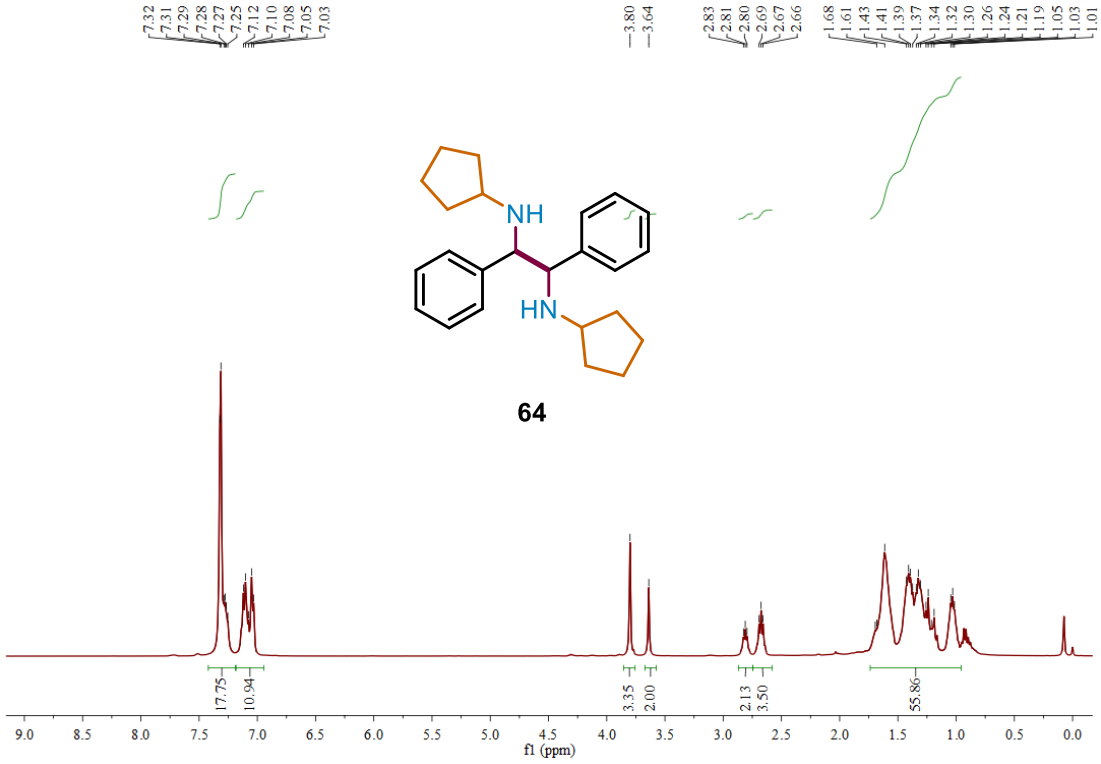
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 63



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 63

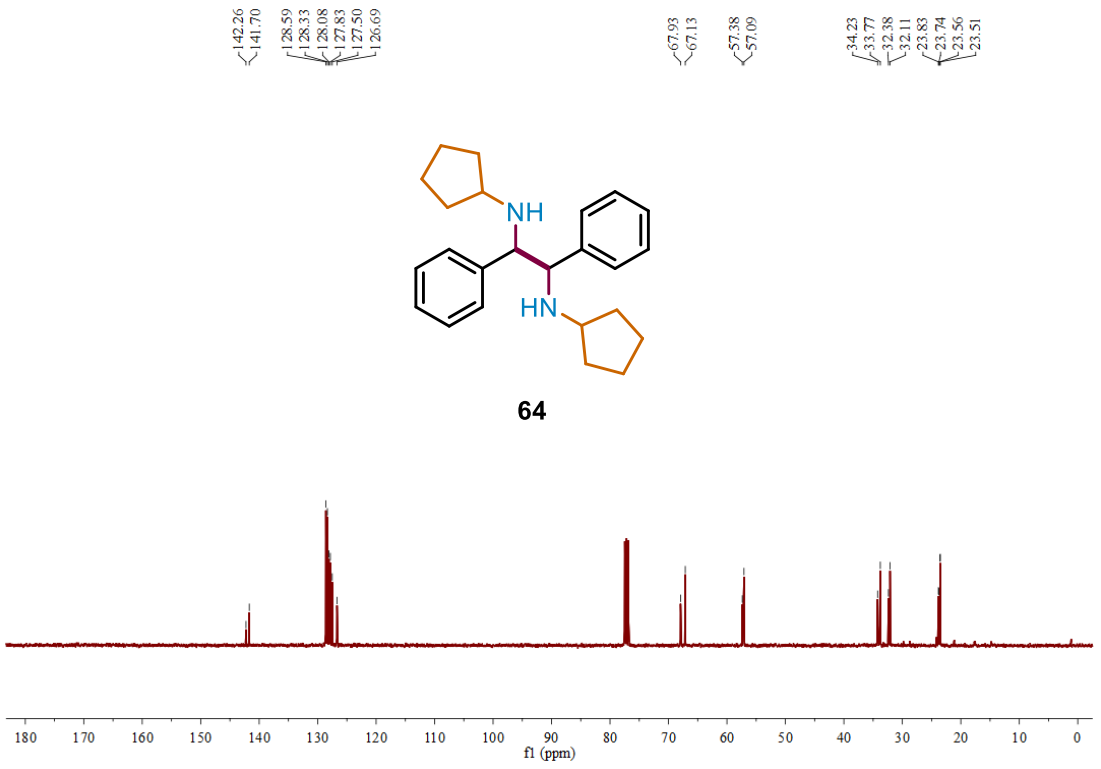


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 64



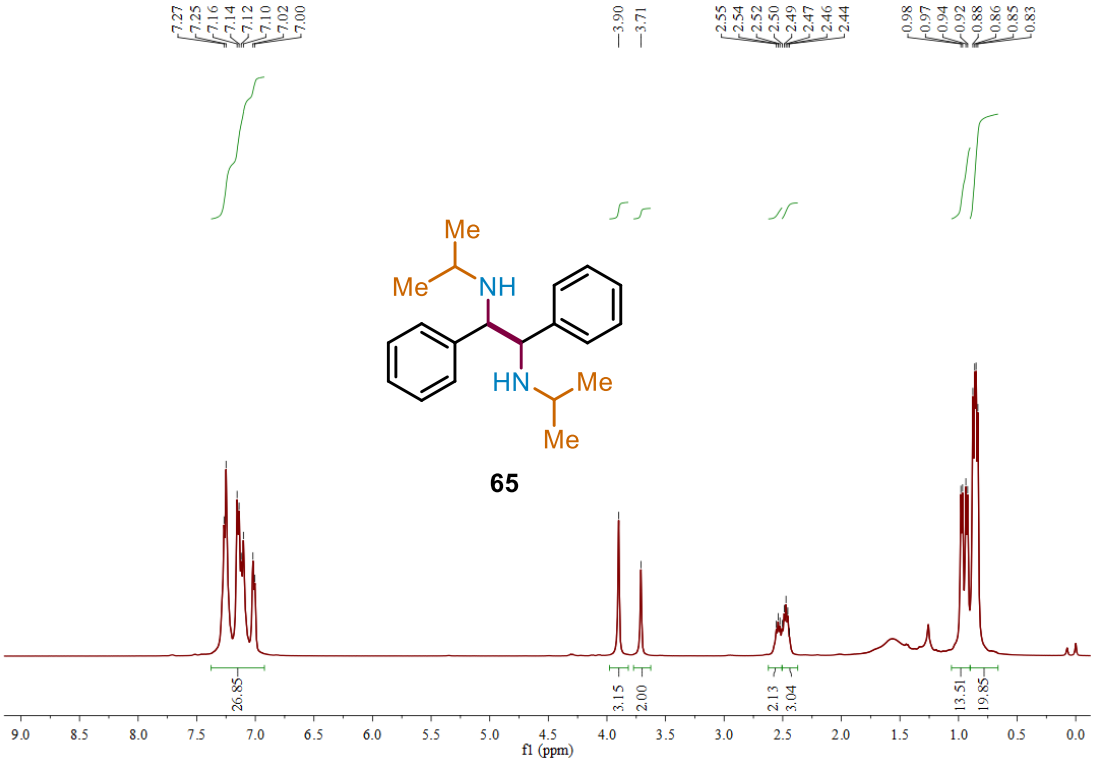
64

^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 64



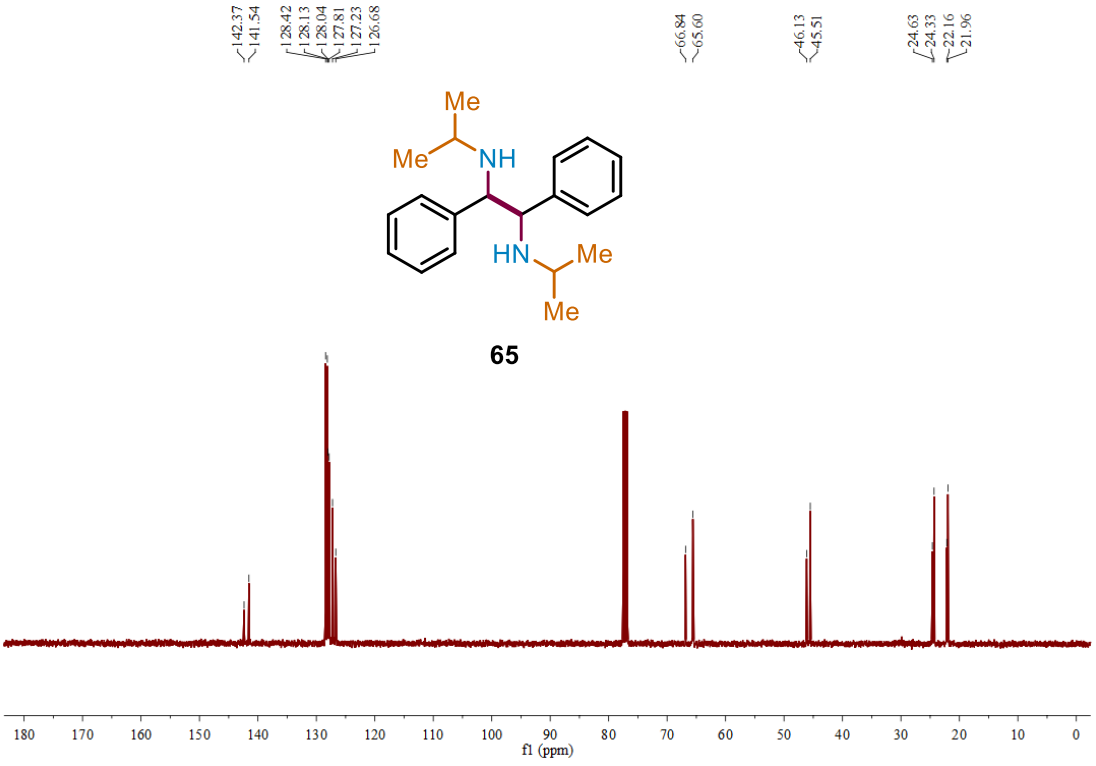
64

^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 65



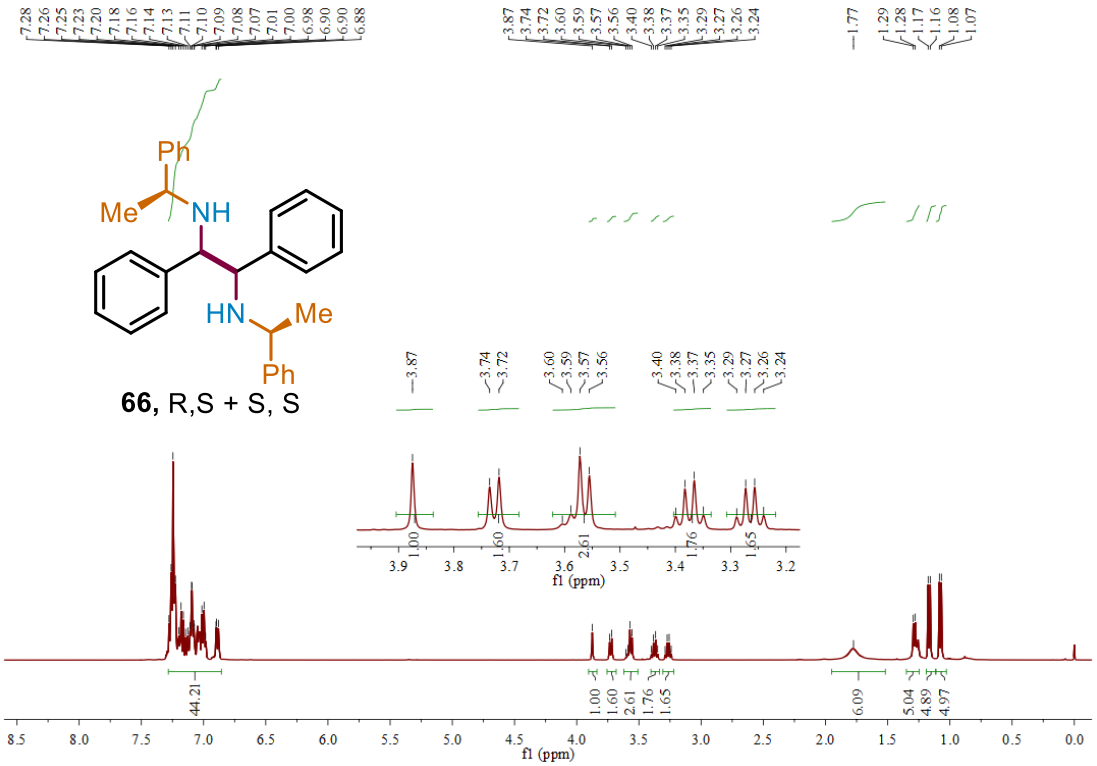
65

^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 65

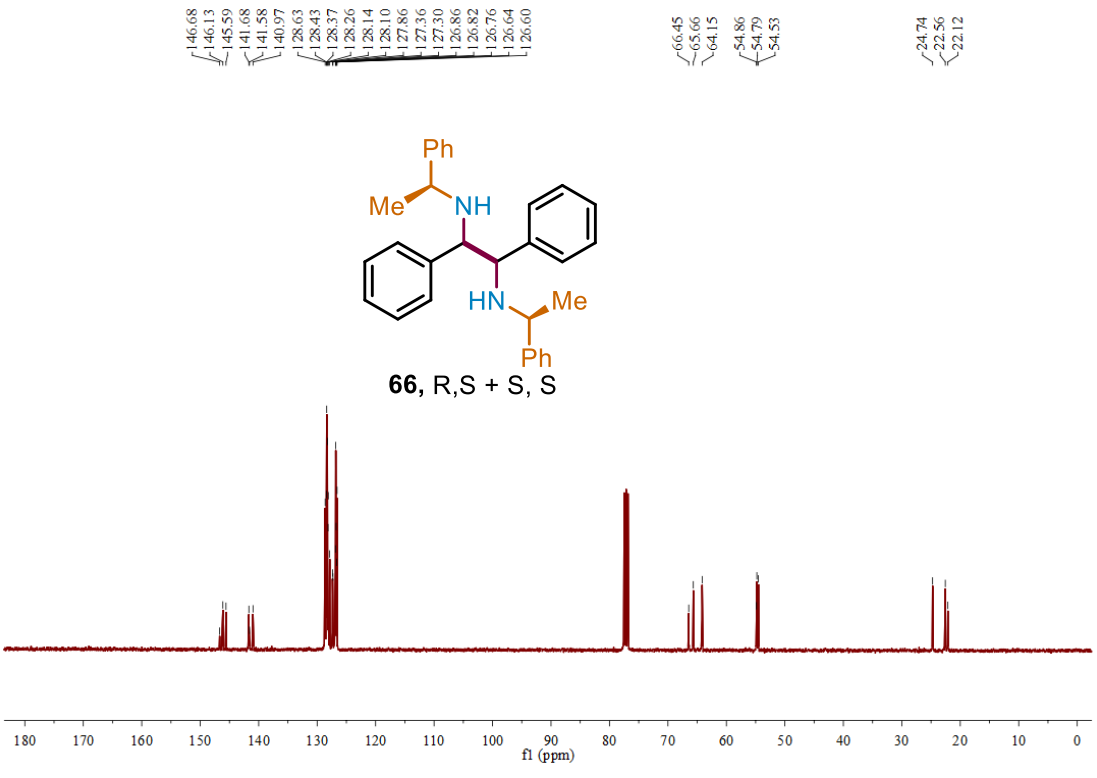


65

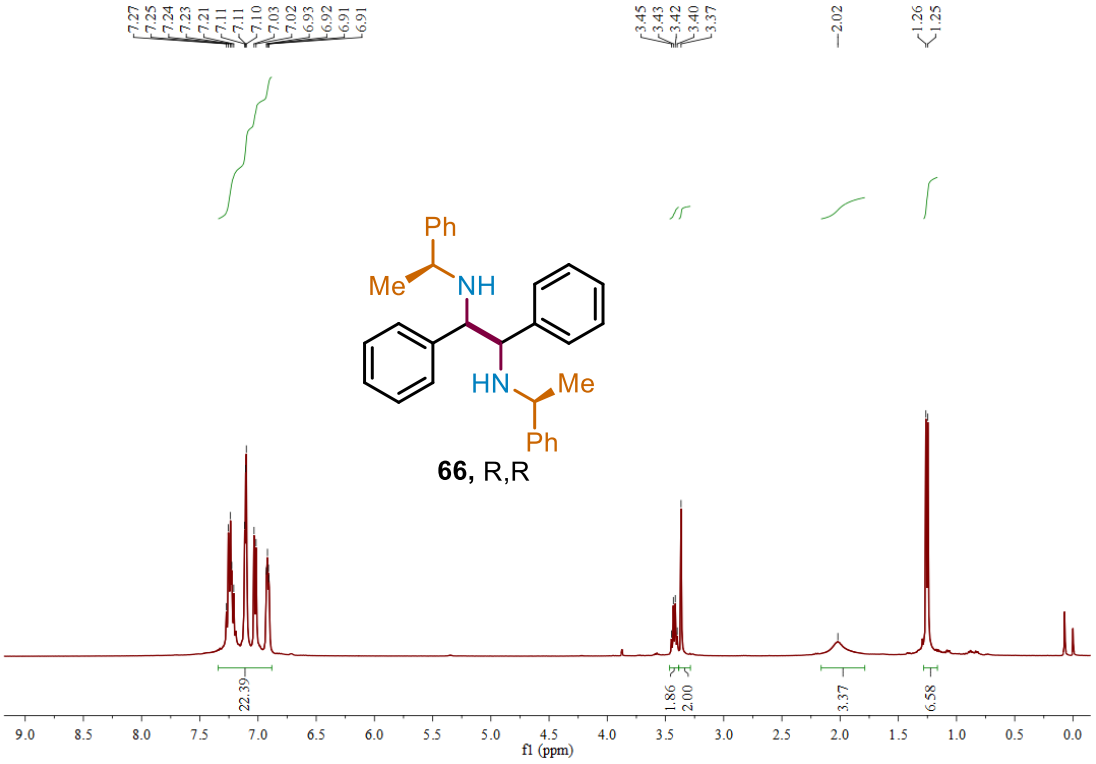
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound (R, S + S, S)-66



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound (R, S + S, S)-66



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound (R, R)-66



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound (R, R)-66