Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Nickel-Catalyzed Dynamic Kinetic Cross-Electrophile Coupling of Benzylic Alcohols and Alkenyl Triflates

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1. General Information

Reagents and solvents

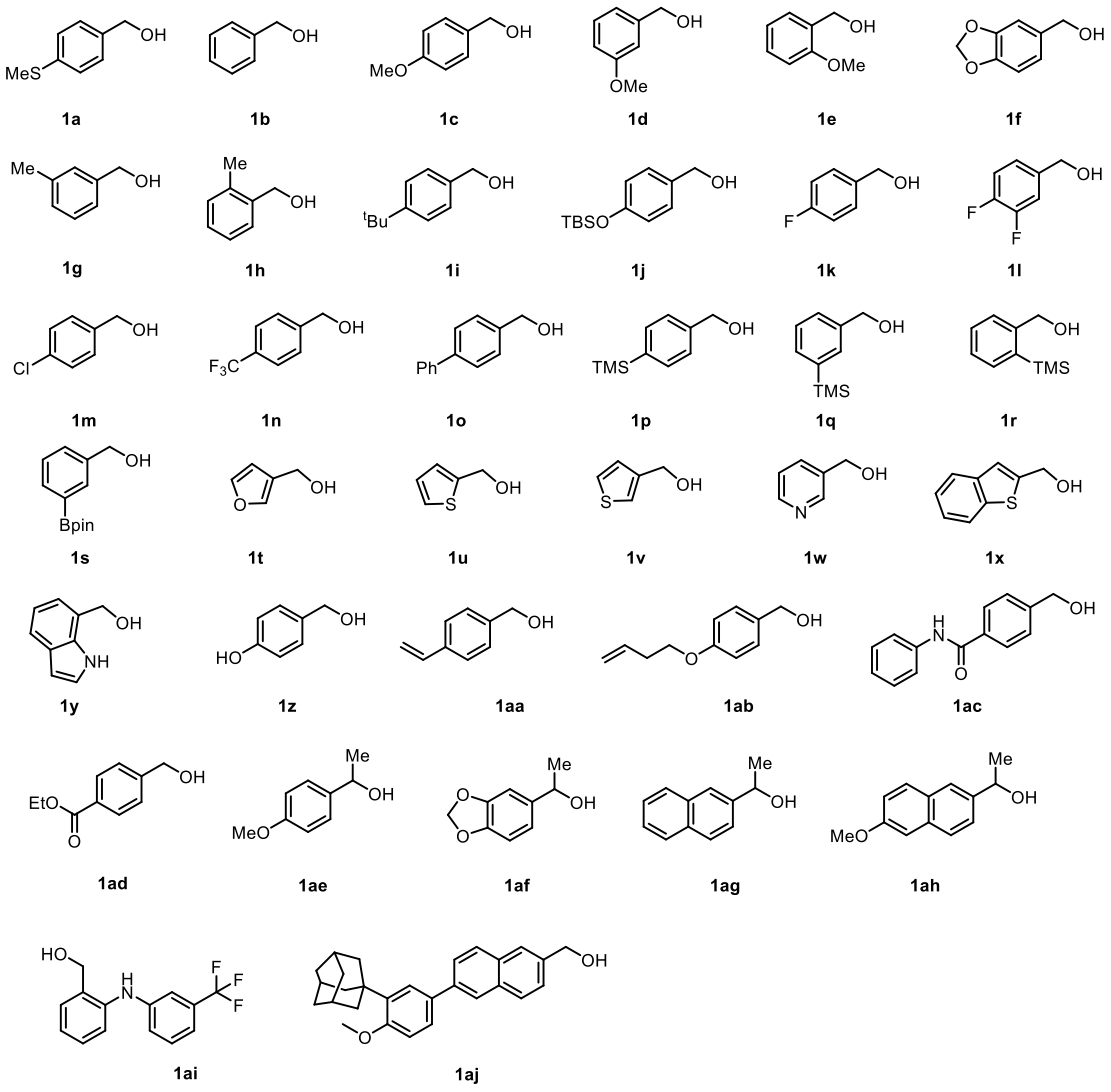
Unless otherwise stated, all chemicals used in the preparation of starting materials were commercially available and were used as received without further purification. All catalysts, reductants, ligands were purchased from Acros, Alfa Aesar, Aldrich, Ark Pharm, and Strem. Other chemicals were purchased from Adamas, TCI, and Energy chemicals, and were directly used without further purifications.

Anhydrous *N*, *N*-dimethylformamide (DMF), *N*, *N*-dimethylacetamide (DMA), Tetrahydrofuran (THF) were purified using a solvent-purification system by passing through activated alumina columns or molecular sieves. Other solvents were dried and purified according to the procedure from ‘‘Purification of Laboratory Chemicals’’.[1]

^{1}H and ^{13}C NMR spectra were collected on a Bruker AVANCE III 400MHz, JEOL JNM-ECS 400 MHz, BRUKER AVANCE NEO 600 MHz, and Agilent-NMR-Inova 600 MHz spectrometer at room temperature. All ^{1}H NMR spectra were reported in parts per million (ppm) downfield of tetramethylsilane (TMS) and were referenced to the signal of TMS (0 ppm). All ^{13}C NMR spectra were reported in ppm relative to residual $CHCl_3$ (77.16 ppm). Coupling constants, J, are reported in hertz (Hz). ^{19}F NMR spectra were also collected on Bruker AVANCE III 400 MHz spectrometers at room temperature. Melting points were determined on a microscopic apparatus. IR spectra were collected using Bruker-TENSOR 27 spectrometer and Agilent Technologies Cary 630 FTIR, and only major peaks were reported in cm^{-1}. HRMS was performed on Bruker Apex II FT-ICR mass instrument (ESI) and AB TripleTOF 5600plus Mass Spectrometry (ACPI). GC analysis was performed on Thermo Scientific TRACE 1300. GC-MS data were collected on Thermo Scientific TRACE DSQ GC-MS. Thin layer chromatography was carried out using XINNUO SGF 254 TLC plates. Flash chromatography was performed using XINNUO silica gel (200-300 mesh).

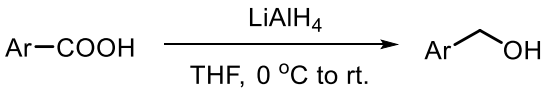
2. Synthesis of Substrates

2.1 Benzyl alcohols



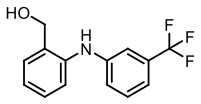
Benzyl alcohols： **1a-1o**, **1s-1aa** are commercially available. Compounds **1p**,[2] **1q**,[2] **1r**,[2] **1ab**,[3] **1ac**,[4] **1ad**,[5] **1ae**,[6] **1af**,[7] **1ag**,[8] **1ah**,[9] are known compounds, and they were synthesized according to the literature procedure. The preparation of new compounds and their characterization data are provided as follows.

General procedure A:[2]



To a solution of acid (10 mmol, 1.0 equiv) in THF (50 mL) was added $LiAlH_4$ (760 mg, 20 mmol, 2.0 equiv) at 0 ℃. The reaction solution was refluxed for two hours and then cooled down to room temperature. A solution of NaOH (10% in water) was added carefully until a white solid precipitated. The reaction mixture was extracted with EtOAc (30 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford corresponding benzyl alcohol.

(2-((3-(Trifluoromethyl)phenyl)amino)phenyl)methanol (1ai)



This compound was prepared from flufenamic acid (2.81 g, 10 mmol) according to General procedure A. It was purified by flash chromatography on silica gel (PE/EA = 3/1). 1.21 g, 45% yield, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37-7.31 (m, 2 H), 7.28-7.21 (m, 3 H), 7.19-7.17 (m, 1 H), 7.12 (d, *J* = 5.2 Hz, 1 H), 6.99-6.94 (m, 2 H), 4.70 (s, 2 H), 1.94 (s, 1 H).

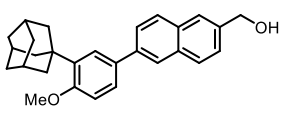
^{13}C NMR (150 MHz, $CDCl_3$): δ 143.9, 142.1, 131.9 (q, *J* = 19.0 Hz,) 130.0, 129.9, 129.5, 124.3 (q, *J* = 179.0 Hz), 121.8, 120.4, 118.0, 117.0 (q, *J* = 3.0 Hz), 117.0, 113.9 (q, *J* = 3.0 Hz), 64.6.

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.8.

IR (neat, cm^{-1}): 3528, 3439, 2937, 2363, 1619, 1588, 1496, 1428, 1338, 1124, 1070, 997, 867, 788, 699.

HRMS (ESI): $[M+H]^+$ calcd for $C_{14}H_{13}F_3NO$ 268.0944, found: 268.0941.

(6-(3-((1*R*,3*R*,5*S*)-adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)methanol (1aj)



This compound was prepared from adapalene (4.12 g, 10 mmol) according to General procedure A. It was purified by flash chromatography on silica gel (PE/EA = 5/1). 2.71 g, 68% yield, white solid, mp: 179-180 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.97 (s, 1 H), 7.87 (dd, *J* = 10.2, 8.4 Hz, 2 H), 7.80 (s, 1 H), 7.73 (dd, *J* = 8.4, 7.8 Hz, 1 H), 7.59 (d, *J* = 8.4 Hz, 1 H), 7.52 (dd, *J* = 8.4, 2.4 Hz,

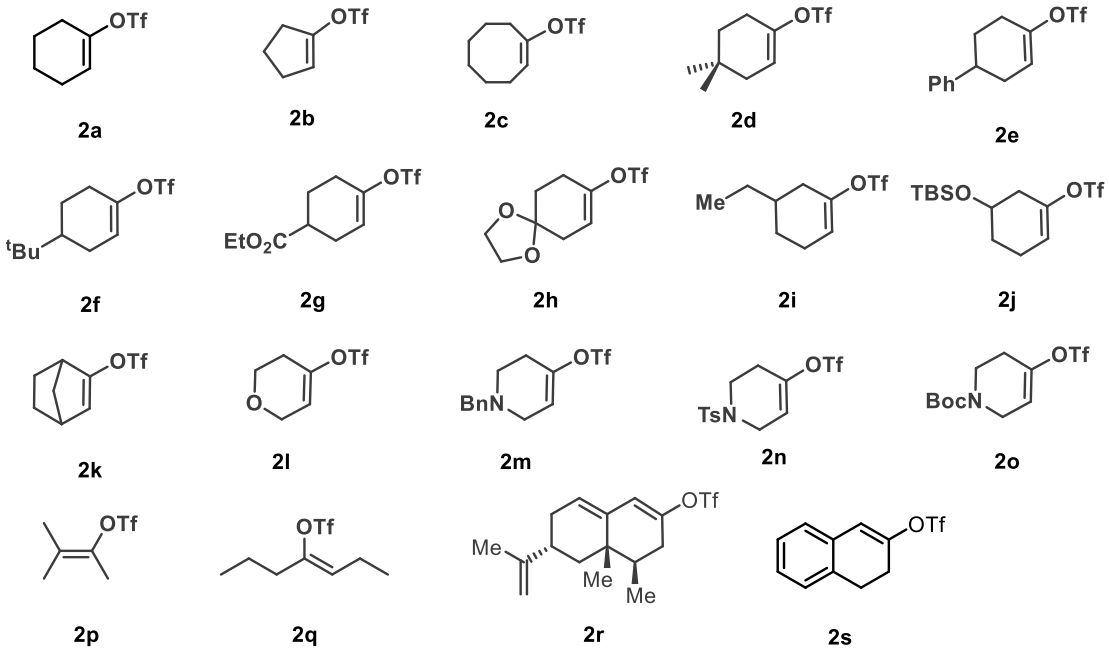
1 H), 7.48 (dd, *J* = 8.4, 1.2 Hz, 1 H), 7.25 (s, 1 H), 6.98 (d, *J* = 8.4 Hz, 1 H), 4.85 (s, 2 H), 3.89 (s, 3 H), 2.19 (d, *J* = 3.0 Hz, 6 H), 2.11-2.09 (m, 3 H), 1.81-1.89 (m, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 158.7, 139.2, 139.0, 138.1, 133.5, 133.2, 132.3, 128.7, 128.4, 126.2, 126.0, 125.7, 125.7, 125.4, 125.0, 112.2, 65.7, 55.3, 40.8, 37.3, 37.3, 29.3.

IR (neat, cm^{-1}): 3519, 2907, 2850, 1636, 1498, 1478, 1459, 1238, 1142, 1029, 882.

HRMS (ESI): $[M+Na]^+$ calcd for $C_{28}H_{30}NaO_2$ 421.2138, found: 421.2130.

2.2 Alkenyl Electrophiles



Alkenyl triflates 2a,[10] 2b,[10] 2c,[10] 2d,[11] 2e,[12] 2f,[10] 2g,[13] 2h,[10] 2i,[10] 2j,[10] 2k,[14] 2l,[10] 2m,[15] 2n,[10] 2o,[12] 2p,[16] 2q,[10] 2r,[16] 2s[17] are known compounds, and they were synthesized according to the literature procedure.

3. Optimization of Reaction Parameters

General Procedure B

The procedure was conducted in an argon-filled glove box. To a reaction tube equipped with a magnetic stir bar was charged with catalyst (10 mol%, 0.01 mmol), ligand (20 mol%, 0.02 mmol), reductant (3.0 equiv, 0.3 mmol), diethyl oxalate (DEO, 1.5 equiv, 0.15 mmol) and solvent (0.33 mL, 0.3M). Substrates **1a** (15.4 mg, 0.1 mmol) and **2a** (34.5 mg, 0.15 mmol) were then added. The reaction tube was sealed and removed from the glove box. The reaction mixture was stirred at 50 ℃ for 24 h. The reaction was quenched with water (10 mL), and the mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na_2SO_4. A 0.2 mL of solution was collected and diluted with ethyl acetate (1 mL). The yield of **3a** was determined by GC analysis versus the internal standard (dodecane).

Scheme S1. Reaction of 1a and 2a under the standard conditions for the arylation reactions

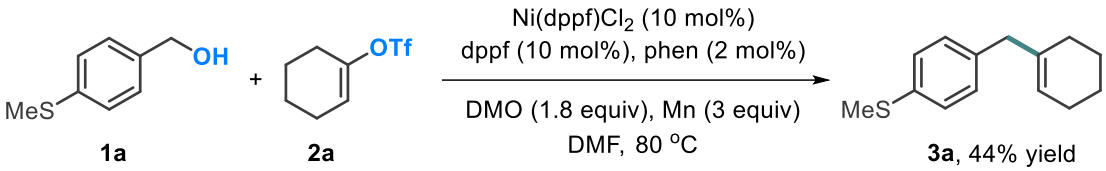
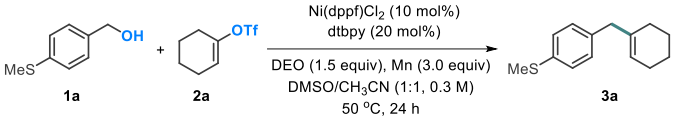


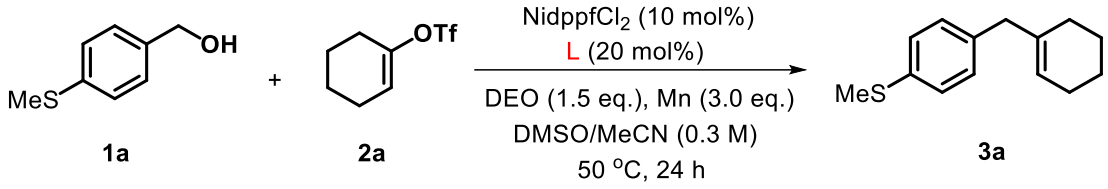
Table S1. Optimization of reaction conditions[a]



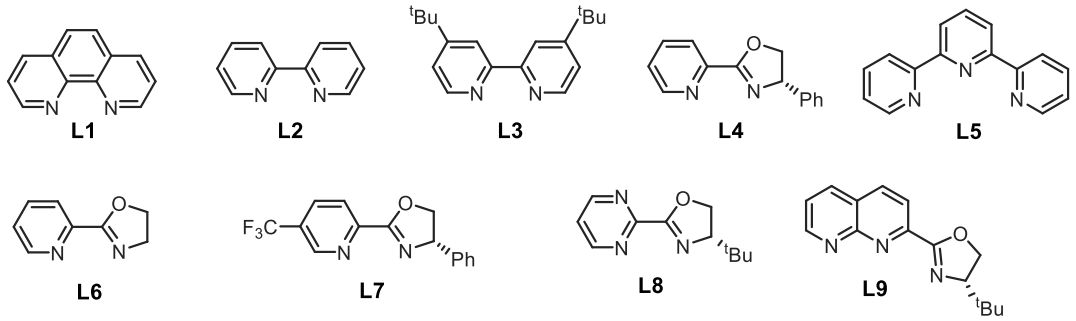
entry	change from standard conditions	**3a** (%)
1	none	98 (94)[b]
2	$NiCl_2$ instead of $Ni(dppf)Cl_2$	trace
3	$Ni(COD)_2$ instead of $Ni(dppf)Cl_2$	trace
4	No dtbpy	trace
5	$Ni(dppp)Cl_2$ instead of $Ni(dppf)Cl_2$	68
6	DMF	79
7	DMSO	43
8	CH_3CN	7
9	Zn instead of Mn	65
10	DMO instead of DEO	82
11	no DEO, Ni or Mn	0

[a]Reaction conditions: **1a** (0.1 mmol) and **2a** (0.15 mmol) were used; the yields were determined by NMR analysis using CH_2Br_2 as an internal standard; DEO: diethyl oxalate. [b]Isolated yield in parentheses is obtained from **1a** (0.2 mmol) and **2a** (0.3 mmol).

Table S2. Optimization of ligand for the reaction of 1a and 2a[a]

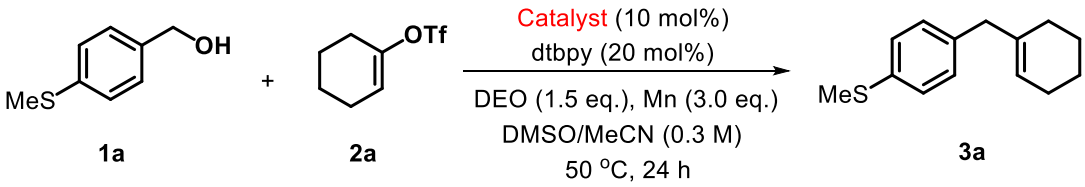


entry	ligand (mol%)	yield of **3a** (%)
1	L1	52
2	L2	78
3	L3	98(94)[b]
4	L4	24
5	L5	8
6	L6	18
7	L7	34
8	L8	26
9	L9	0



[a]**1a** (0.1 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), yields were determined by GC analysis with dodecane as an internal standard. [b]Isolated yield in parentheses is obtained from 1a (0.2 mmol) and 2a (0.3 mmol).

Table S3. Optimization of catalyst for the reaction of 1a and 2a

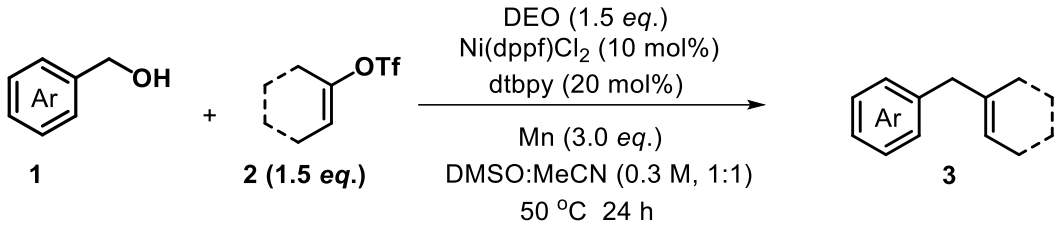


entry	catalyst	yield of **3a** (%)
1	$NiCl_2$	trace
2	$NiBr_2$	Trace
3	NiI_2	0
4	$NiBr_2$(diglyme)	12
5	$NiCl_2$(dme)	0
6	Ni(dppe)Cl_2	63
7 8	Ni(dppp)Cl_2	68
9	Ni(dppf)Cl_2	98
10	Ni(dtbpy)Cl_2 with no ligand	trace
11	Ni(dtbpy)Cl_2, dppf (10 mol%) instead of dtbpy	70
12	Ni(COD)$_2$	Trace
13	Ni(PMe$_3$)$_2$$Cl_2$	45
14	Ni(OTf)$_2$	0
15	$CoBr_2$	0
16	$CoCl_2$	0

[a]**1a** (0.1 mmol, 1.0 equiv), **2a** (0.15 mmol, 1.5 equiv), yields were determined by GC analysis with dodecane as an internal standard.

4. Nickel-catalyzed Cross-Electrophile Coupling of Benzyl Alcohols and Alkenyl Triflates

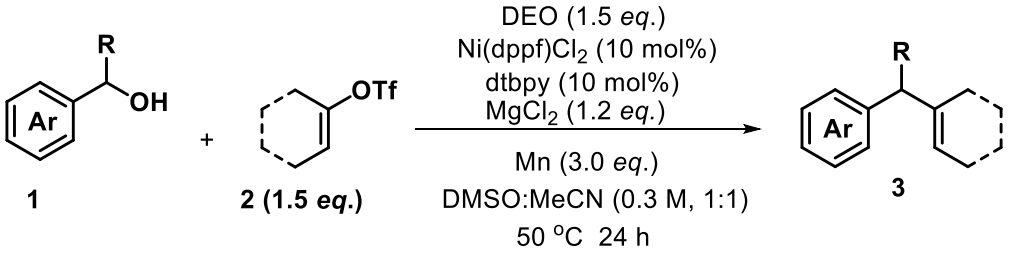
4.1 General procedure C



1 2 (1.5 *eq.*) 3

The procedure was conducted in an argon-filled glove box. To a reaction tube equipped with a magnetic stir bar was charged with Ni(dppf)Cl_2 (13.5 mg, 0.02 mmol), dtbpy (10.7 mg, 0.04 mmol), Mn (33 mg, 0.6 mmol), DEO (43.8 mg, 0.3 mmol) and DMSO/ MeCN (1:1, 0.66 mL, 0.3 M). Substrates **1** (0.2 mmol) and **2** (0.3 mmol) were then added. The reaction tube was sealed with a rubber septum, and removed from the glove box. The reaction mixture was stirred at 50 ℃ for 24 h. The reaction was quenched with water (10 mL), and the mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product **3**.

4.2 General procedure D



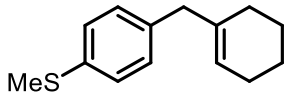
1 2 (1.5 *eq.*) 3

The procedure was conducted in an argon-filled glove box. To a reaction tube equipped with a magnetic stir bar was charged with Ni(dppf)Cl_2 (13.5 mg, 0.02 mmol), dtbpy (5.4 mg, 0.02 mmol), Mn (33 mg, 0.6 mmol), $MgCl_2$ (22.5 mg, 0.24 mmol), DEO (43.8 mg, 0.3 mmol) and DMSO/ MeCN (1:1, 0.66 mL, 0.3 M). Substrates **1** (0.2 mmol) and **2** (0.3 mmol) were then added. The reaction tube was sealed with a rubber septum, and removed from the glove box. The reaction mixture was stirred at 50 ℃ for 24 h. The

reaction was quenched with water (10 mL), and the mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product **3**.

4.2 Characterization Data of Products

(4-(Cyclohex-1-en-1-ylmethyl)phenyl)(methyl)sulfane (3a)



This compound was prepared according to General procedure C from the reaction of **1a** (30.8 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 41.1 mg, 94% yield. colorless oil.

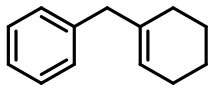
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.19 (d, *J* = 8.4 Hz, 2 H), 7.09 (d, *J* = 7.8 Hz, 2 H), 5.45 (s, 1 H), 3.20 (s, 2 H), 2.46 (s, 3 H), 2.02-2.00 (m, 2 H), 1.85-1.83 (m, 2 H), 1.59-1.51 (m, 4 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 137.7, 137.2, 135.4, 129.6, 127.1, 123.1, 44.3, 28.2, 25.5, 23.0, 22.5, 16.4.

IR (neat, cm^{-1}): 3038, 2922, 2857, 2835, 1668, 1638, 1600, 1493, 1437, 1403, 1288, 1094, 1018, 919, 805.

HRMS (ESI): $[M+H]^+$ calcd for $C_{14}H_{19}S$ 219.1202, found: 219.1211.

(Cyclohex-1-en-1-ylmethyl)benzene (3b)

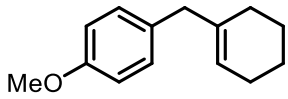


This compound was prepared according to General procedure C from the reaction of **1b** (21.6 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 19.3 mg, 56% yield, a colorless liquid. ^{1}H NMR and ^{13}C NMR data agree with those reported in ref. 18.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.23 (m, 2 H), 7.16 (d, *J* = 6.8 Hz, 3 H), 5.49-5.42 (m, 1 H), 3.23 (s, 2 H), 2.06-1.97 (m, 2 H), 1.85 (s, 2 H), 1.61-1.50 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.6, 137.4, 129.0, 128.3, 126.0, 123.1, 44.8, 28.2, 25.5, 23.1, 22.6.

1-(Cyclohex-1-en-1-ylmethyl)-4-methoxybenzene (3c)



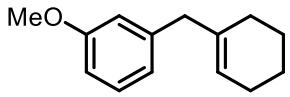
This compound was prepared according to General procedure C from the reaction of **1c** (27.6 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 34.4 mg, 85% yield, a colorless liquid. ^{1}H NMR and ^{13}C NMR data are consistent with

those reported in ref. 19.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (d, *J* = 8.4 Hz, 2 H), 6.81 (d, *J* = 8.5 Hz, 2 H), 5.43 (s, 1 H), 3.77 (s, 3 H), 3.17 (s, 2 H), 2.00 (d, *J* = 1.4 Hz, 2 H), 1.84 (s, 2 H), 1.60-1.49 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 137.7. 132.6, 129.9, 122.7, 113.7, 55.3, 43.9, 28.1, 25.5, 23.1, 22.6.

1-(Cyclohex-1-en-1-ylmethyl)-3-methoxybenzene (3d)



This compound was prepared according to General procedure C from the reaction of **1d** (27.6 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 31.6 mg, 78% yield. colorless oil.

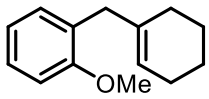
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21-7.16 (m, 1 H), 6.78-6.72 (m, 3 H), 5.47 (s, 1 H), 3.79 (s, 3 H), 3.21 (s, 2 H), 2.03-2.00 (m, 2 H), 1.87-1.84 (m, 2 H), 1.61-1.51 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 142.3, 137.1, 129.2, 123.2, 121.5, 114.8, 111.1, 55.2, 44.8, 28.1, 25.5, 23.1, 22.5.

IR (neat, cm^{-1}): 3047, 3000, 2928, 2857, 2836, 2365, 1726, 1601, 1454, 1437, 1282, 1258, 1154, 1053, 919, 768.

HRMS (ESI): $[M+H]^+$ calcd for $C_{14}H_{19}O$ 203.1430, found: 203.1424.

1-(Cyclohex-1-en-1-ylmethyl)-2-methoxybenzene (3e)



This compound was prepared according to General procedure C from the reaction of **1e** (27.6 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 32.4 mg, 80% yield. colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.17 (td, *J* = 8.0, 1.7 Hz, 1 H), 7.11 (dd, *J* = 7.4, 1.4 Hz, 1 H), 6.89 (td, *J* = 7.4, 0.8 Hz, 1 H), 6.85 (d, *J* = 8.2 Hz, 1 H), 5.39-5.38 (m, 1 H), 3.80 (s, 3 H), 3.25 (s, 2 H), 2.00-1.99 (m, 2 H), 1.93-1.90 (m, 2 H), 1.61-1.54 (m, 4 H).

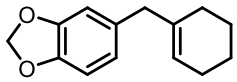
^{13}C NMR (150 MHz, $CDCl_3$): δ 157.8, 136.9, 130.2, 129.1, 127.1, 122.6, 120.5, 110.6, 55.6, 37.6, 28.5, 25.5, 23.2, 22.6.

IR (neat, cm^{-1}): 3066, 3025, 3000, 2924, 2836, 1728, 1640, 1588, 1463, 1493, 1290,

1243, 1174, 1075, 1051, 948, 751.

HRMS (ESI): $[M+H]^+$ calcd for $C_{14}H_{19}O$ 203.1430, found: 203.1424.

5-(Cyclohex-1-en-1-ylmethyl)benzo[d][1,3]dioxole (3f)



This compound was prepared according to General procedure C from the reaction of **1f** (30.8 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 50/1). 31.1 mg, 72% yield. colorless oil.

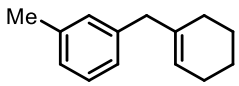
^{1}H NMR (600 MHz, $CDCl_3$): δ 6.72 (d, *J* = 7.8 Hz, 1 H), 6.67 (d, *J* = 1.2 Hz, 1 H), 6.62-6.61 (m, 1 H), 5.91 (s, 2 H), 5.46 (s, 1 H), 3.15 (s, 2 H), 2.02-2.01 (m, 2 H), 1.85-1.83 (m, 2 H), 1.59-1.53 (m, 4 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 147.6, 145.8, 137.48, 134.5, 123.1, 121.8, 109.4, 108.1, 100.86, 44.5, 28.1, 25.5, 23.1, 22.6.

IR (neat, cm^{-1}): 2928, 2859, 2838, 2376, 1504, 1442, 1359, 1245, 1187, 1042, 939, 867.

HRMS (ESI): $[M+H]^+$ calcd for $C_{14}H_{17}O_2$ 217.1223，found: 217.1227.

1-(Cyclohex-1-en-1-ylmethyl)-3-methylbenzene (3g)



This compound was prepared according to General procedure C from the reaction of **1g** (24.4 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 28.0 mg, 75% yield. colorless oil.

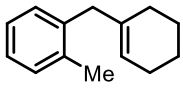
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.16 (t, *J* = 7.2 Hz, 1 H), 7.00-6.96 (m, 3 H), 5.45 (s, 1 H), 3.20 (s, 2 H), 2.32 (s, 3 H), 2.03-2.01 (m, 2 H), 1.87-1.84 (m, 2 H), 1.59-1.52 (m, 4 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 140.5, 137.8, 137.5, 129.9, 128.2, 126.7, 126.1, 122.9, 44.8, 28.2, 25.5, 23.1, 22.6, 21.6.

IR (neat, cm^{-1}): 3474, 3019, 2928, 2859, 2838, 1608, 1489, 1437, 1144, 1082, 785, 766, 703.

HRMS (APCI): $[M+H]^+$ calcd for $C_{14}H_{19}$ 187.1481, found: 187.1482.

1-(Cyclohex-1-en-1-ylmethyl)-2-methylbenzene (3h)



This compound was prepared according to General procedure C from the reaction of **1h** (24.4 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 24.9 mg, 67% yield. colorless oil.

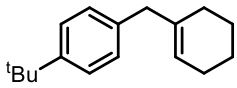
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.14-7.09 (m, 4 H), 5.27-5.25 (m, 1 H), 3.23 (s, 2 H), 2.26 (s, 3 H), 1.99-1.97 (m, 2 H), 1.91- 1.87 (m 2 H), 1.63-1.59 (m, 2 H), 1.57-1.52 (m, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 138.5, 137.0, 136.3, 130.1, 129.9, 126.1, 125.8, 122.7, 41.9, 28.8, 25.5, 23.2, 22.7, 19.6.

IR (neat, cm^{-1}): 3066, 3017, 2926, 2859, 2838, 1908, 1646, 1605, 1493, 1446, 1342, 1079, 1051, 949, 779.

HRMS (APCI): $[M+H]^+$ calcd for $C_{14}H_{19}$ 187.1481, found: 187.1486.

1-(Tert-butyl)-4-(cyclohex-1-en-1-ylmethyl)benzene (3i)



This compound was prepared according to General procedure C from the reaction of **1i** (32.8 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 29.6 mg, 65% yield. colorless oil.

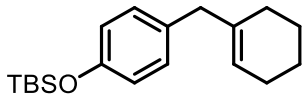
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.28 (m, 2 H), 7.11-7.09 (m, 2 H), 5.47-5.44 (m, 1 H), 3.21 (s, 2 H), 2.04-2.00 (m, 2 H), 2.00-1.85 (m, 2 H), 1.61-1.52 (m, 4 H), 1.31 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 148.7, 137.5, 128.6, 125.2, 122.9, 44.3, 34.5, 31.6, 28.3, 25.5, 23.1, 22.6.

IR (neat, cm^{-1}): 2961, 2926, 2857, 1634, 1515, 1413, 1364, 1269, 1202, 1131, 954, 818, 794.

HRMS (APCI): $[M+H]^+$ calcd for $C_{17}H_{25}$ 229.1951, found: 229.1955.

Tert-butyl(4-(cyclohex-1-en-1-ylmethyl)phenoxy)dimethylsilane (3j)



This compound was prepared according to General procedure C from the reaction of **1j** (47.6 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1).

41.7 mg, 69% yield. colorless oil.

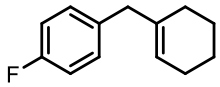
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.00 (d, *J* = 8.4 Hz, 2 H), 6.74 (d, *J* = 8.4 Hz, 2 H), 5.42 (s, 1 H), 3.16 (s, 2 H), 2.01-2.00 (m, 2 H), 1.84 (s, 2 H), 1.58-1.53 (m, 4 H), 0.98 (s, 9 H), 0.18 (s, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 153.8, 137.8, 133.2, 129.9, 122.6, 119.8, 44.0, 28.1, 25.8, 25.5, 23.1, 22.6, 18.3, -4.3.

IR (neat, cm^{-1}): 2930, 2959, 1609, 1508, 1466, 1265, 1096, 917, 836, 756.

HRMS (ESI): $[M+H]^+$ calcd for $C_{19}H_{31}OSi$: 303.2139, found: 303.2136.

1-(Cyclohex-1-en-1-ylmethyl)-4-fluorobenzene (3k)



This compound was prepared according to General procedure C from the reaction of **1k** (25.2 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 26.6 mg, 70% yield. colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13-7.09 (m, 2 H), 6.98-6.92 (m, 2 H), 5.45-5.43 (m, 1 H), 3.20 (s, 2 H), 2.03-1.99 (m, 2 H), 1.85-1.81 (m, 2 H), 1.61-1.50 (m, 4 H).

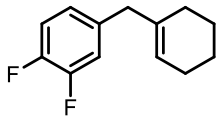
^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5 (d, *J* = 242 Hz), 137.3, 136.1 (d, *J* = 3.0 Hz), 130.3 (d, *J* = 7.0 Hz), 123.2, 115.0 (d, *J* = 21.0 Hz), 44.0, 28.1, 25.5, 23.0, 22.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ -117.86.

IR (neat, cm^{-1}): 3045, 3000, 2932, 2861, 2838, 1886, 1720, 1605, 1510, 1439, 1223, 1157, 1094, 1018, 855, 823.

HRMS (APCI): $[M+H]^+$ calcd for $C_{13}H_{16}F$ 191.1231, found: 191.1239.

4-(Cyclohex-1-en-1-ylmethyl)-1,2-difluorobenzene (3l)



This compound was prepared according to General procedure C from the reaction of **1l** (28.8 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 19.6 mg, 47% yield. colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.06-7.02 (m, 1 H), 6.98-6.95 (m, 1 H), 6.88-6.85 (m, 1 H), 5.47 (s, 1 H), 3.18 (s, 2 H), 2.04-2.01 (m, 2 H), 1.83-1.80 (m, 2 H), 1.60-1.53 (m, 4 H).

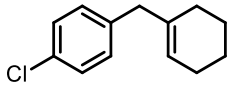
^{13}C NMR (150 MHz, $CDCl_3$): δ 150.1 (dd, *J* = 246.0, 13.5 Hz), 148.8 (dd, *J* = 244.5, 13.5 Hz), 137.5 (dd, J_1 = 4.5, 3.0 Hz), 136.5, 124.6 (dd, *J* = 6.0, 3.0 Hz), 123.8, 117.4 (d, *J* = 16.5 Hz), 116.7 (d, *J* = 16.5 Hz), 43.8, 27.9, 25.3, 22.8, 22.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ -138.78, -142.46.

IR (neat, cm^{-1}): 3047, 3002, 2930, 2861, 2838, 1608, 1519, 1437, 1176, 1280, 1038, 1135, 965, 874.

HRMS (APCI): $[M+H]^+$ calcd for $C_{13}H_{16}F_2$ 209.1136, found: 209.1141.

Chloro-4-(cyclohex-1-en-1-ylmethyl)benzene (3m)



This compound was prepared according to General procedure C from the reaction of **1m** (28.4 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 18.5 mg, 45% yield. colorless oil.

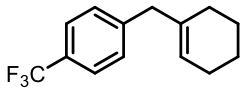
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.23 (d, *J* = 8.4 Hz, 2 H), 7.09 (d, *J* = 8.4 Hz, 2 H), 5.45 (s, 1 H), 3.19 (s, 2 H), 2.01 (s, 2 H), 1.83-1.81 (m, 2 H), 1.59-1.53 (m, 4 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 139.1, 137.0, 131.7, 130.4, 128.4, 123.5, 44.2, 28.2, 25.5, 23.1, 22.5.

IR (neat, cm^{-1}): 2935, 2866, 2371, 1720, 1657, 1493, 1407, 1375, 1279, 1092, 1015, 986, 807, 758.

HRMS (APCI): $[M+H]^+$ calcd for $C_{13}H_{16}Cl$ 207.0935, found: 207.0938.

1-(Cyclohex-1-en-1-ylmethyl)-4-(trifluoromethyl)benzene (3n)



This compound was prepared according to General procedure C from the reaction of **1n** (35.2 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 24.5 mg, 51% yield. colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.0 Hz, 2 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 5.48 (s, 1 H), 3.28 (s, 2 H), 2.05-2.01 (m, 2 H), 1.85-1.82 (m, 2 H), 1.60-1.53 (m, 4 H).

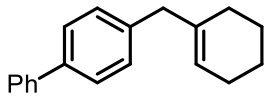
^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 136.5, 129.3, 128.4 (q, *J* = 32 Hz), 125.3 (q, *J* = 4 Hz), 124.6 (q, *J* = 271 Hz), 124.0, 44.6, 28.2, 25.5, 23.0, 22.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.26.

IR (neat, cm^{-1}): 3049, 3002, 2932, 2861, 2840, 1918, 1735, 1620, 1374, 1262, 1068, 920, 822.

HRMS (ACPI): $[M+H]^+$ calcd for $C_{14}H_{16}F_3$ 241.1199, found: 241.1189.

4-(Cyclohex-1-en-1-ylmethyl)-1,1'-biphenyl (3o)

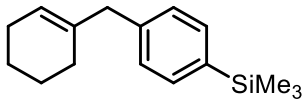


This compound was prepared according to General procedure C from the reaction of **1o** (36.8 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 45.7 mg, 92% yield. colorless oil. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 20.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.56 (m, 2 H), 7.51-7.49 (m, 2 H), 7.43-7.39 (m, 2 H), 7.33-7.29 (m, 1 H), 7.24 (d, *J* = 8.0 Hz, 2 H), 5.51-5.49 (m, 1 H), 3.27 (s, 2 H), 2.05-2.01 (m, 2 H), 1.91-1.87 (m, 2 H), 1.61-1.54 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3, 139.7, 138.9, 137.3, 129.4, 128.8, 127.1, 127.1, 123.2, 44.5, 28.3, 25.5, 23.1, 22.6.

(4-(Cyclohex-1-en-1-ylmethyl)phenyl)trimethylsilane (3p)



This compound was prepared according to General procedure C from the reaction of **1p** (36.0 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 22.9 mg, 47% yield. colorless oil.

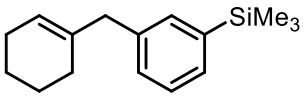
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.2 Hz, 1 H), 7.31 (s, 1 H), 7.27 (t, *J* = 7.4 Hz, 1 H), 7.16 (d, *J* = 7.8 Hz, 1 H), 5.46 (s, 1 H), 3.24 (s, 2 H), 2.02 (s, 2 H), 1.87 (s, 2 H), 1.59-1.54 (m, 4 H), 0.26 (s, 9 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 140.3, 139.7, 137.3, 134.1, 131.0, 129.5, 127.7, 123.1, 44.9, 28.3, 25.5, 23.1, 22.6, -0.9.

IR (neat, cm^{-1}): 3034, 3014, 2956, 2928, 2838, 1601, 1439, 1396, 1249, 1131, 1109, 837, 725.

HRMS (APCI): $[M+H]^+$ calcd for $C_{16}H_{25}Si$ 245.1720, found: 245.1727.

(3-(Cyclohex-1-en-1-ylmethyl)phenyl)trimethylsilane (3q)



This compound was prepared according to General procedure C from the reaction of **1q** (36.0 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 36.1 mg, 74% yield. colorless oil.

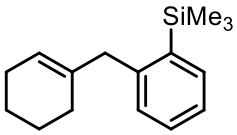
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34 (d, *J* = 7.2 Hz, 1 H), 7.30 (s, 1 H), 7.27 (t, *J* = 7.2 Hz, 1 H), 7.16 (d, *J* = 7.2 Hz, 1 H), 5.46 (s, 1 H), 3.24 (s, 2 H), 2.04-2.0 (m, 2 H), 1.88-1.85 (m, 2 H), 1.60-1.53 (m, 4 H), 0.26 (s, 9 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 140.3, 139.7, 137.3, 134.1, 131.0, 129.5, 127.7, 123.1, 44.9, 28.3, 25.5, 23.1, 22.6.

IR (neat, cm^{-1}): 3541, 3466, 3047, 2958, 2930, 2838, 1638, 1439, 1407, 1249, 1116, 919, 880, 839, 751, 708.

HRMS (APCI): $[M+H]^+$ calcd for $C_{16}H_{25}Si$ 245.1720, found: 245.1717.

(2-(Cyclohex-1-en-1-ylmethyl)phenyl)trimethylsilane (3r)



This compound was prepared according to General procedure C from the reaction of **1r** (36.0 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 19.5 mg, 40% yield. colorless oil.

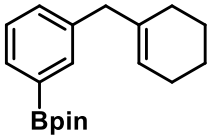
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.47 (m, 1 H), 7.32-7.28 (m, 1 H), 7.20-7.16 (m, 2 H), 5.24-5.21 (m, 1 H), 3.37 (s, 2 H), 2.02-1.98 (m, 2 H), 1.90-1.88 (s, 2 H), 1.64-1.57 (m, 4 H), 0.3 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 139.1, 137.6, 134.5, 129.2, 129.1, 125.3, 124.0, 44.3, 29.0, 25.5, 23.2, 22.7, 0.50.

IR (neat, cm^{-1}): 2922, 2857, 1625, 1590, 1459, 1439, 1249, 1122, 850, 727.

HRMS (APCI): $[M+H]^+$ calcd for $C_{16}H_{25}Si$ 245.1720, found: 245.1727.

2-(3-(Cyclohex-1-en-1-ylmethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3s)



This compound was prepared according to General procedure C from the reaction of **1s** (46.8 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA

= 100/1). 26.5 mg, 77% yield. colorless oil.

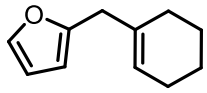
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65-7.63 (m, 1 H), 7.60 (s, 1 H), 7.31-7.26 (m, 2 H), 5.43 (s, 1 H), 3.24 (s, 2 H), 2.00 (s, 2 H), 1.85 (s, 2 H), 1.60-1.51 (m, 4 H), 1.35 (s, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 139.8, 137.4, 135.6, 132.5, 132.0, 127.8, 123.0, 83.9, 44.7, 31.3, 28.3, 25.5, 25.0, 23.1, 22.6.

IR (neat, cm^{-1}): 3055, 2982, 2924, 2859, 2838, 1608, 1425, 1388, 1321, 1271, 1146, 967, 889.

HRMS (ESI): $[M+Na]^+$ calcd for $C_{19}H_{27}BO_2Na$ 321.1996, found: 321.2022.

2-(Cyclohex-1-en-1-ylmethyl)furan (3t)



This compound was prepared according to General procedure C from the reaction of **1t** (19.6 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 23.7 mg, 73% yield. colorless oil.

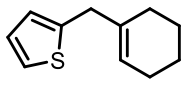
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (s, 1 H), 7.21 (s, 1 H), 6.24 (s, 1 H), 5.47 (s, 1 H), 3.03 (s, 2 H), 2.02-1.97 (m, 2 H), 1.92-1.88 (m, 2 H), 1.61-1.52 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7, 139.6, 136.6, 123.4, 122.4, 111.7, 33.6, 28.3, 25.4, 23.1, 22.6.

IR (neat, cm^{-1}): 2965, 2926, 2853, 1634, 1459, 1262, 1094, 1019, 798.

HRMS (ESI): $[M+H]^+$ calcd for $C_{11}H_{15}O$ 163.1117, found: 163.1110.

2-(Cyclohex-1-en-1-ylmethyl)thiophene (3u)



This compound was prepared according to General procedure C from the reaction of **1u** (22.8 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 21.4 mg, 60% yield. colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (dd, *J* = 5.2, 1.2 Hz, 1 H), 6.85 (dd, *J* = 5.2, 3.6 Hz, 1 H), 6.72-6.71 (m, 1 H), 5.48 (s, 1 H), 3.36 (s, 2 H), 1.97-1.94 (m, 2 H), 1.87-1.84 (m, 2 H), 1.54-1.47 (m, 4 H).

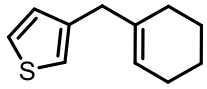
^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 136.9, 126.8, 125.1, 123.6, 123.4, 38.7, 28.0,

25.4, 23.1, 22.5.

IR (neat, cm^{-1}): 2928, 2861, 2837, 2374, 1832, 1655, 1439, 1290, 1265, 1038, 950, 801, 693.

HRMS (ESI): $[M+H]^+$ calcd for $C_{11}H_{15}S$ 179.0889, found: 179.0890.

3-(Cyclohex-1-en-1-ylmethyl)thiophene (3v)



This compound was prepared according to General procedure C from the reaction of **1v** (22.8 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 23.4 mg, 66% yield. colorless oil.

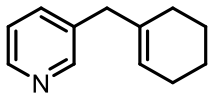
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (dd, *J* = 4.8, 2.8 Hz 1 H), 6.93-6.70 (m, 2 H), 5.46 (s, 1 H), 3.24 (s, 2 H), 2.03-1.99 (m, 2 H), 1.90-1.87 (m, 2 H), 1.63-1.55 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 137.0, 128.9, 125.1, 122.8, 121.0, 39.1, 28.3, 25.4, 23.1, 22.6.

IR (neat, cm^{-1}): 3047, 3000, 2930, 2859, 2836, 1638, 1437, 1388, 1295, 1239, 1129, 1045, 958, 855, 760.

HRMS (ESI): $[M+Na]^+$ calcd for $C_{11}H_{14}NaS$ 201.0708, found: 241.0726.

3-(Cyclohex-1-en-1-ylmethyl)pyridine (3w)



This compound was prepared according to General procedure C from the reaction of **1w** (21.8 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA =5/1). 23.5 mg, 68% yield. colorless oil.

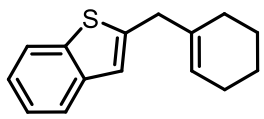
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (s, 2 H), 7.49 (d, *J* = 7.8 Hz, 1 H), 7.21 (dd, *J* = 7.8, 4.2 Hz, 1 H), 5.47 (s, 1 H), 3.23 (s, 2 H), 2.03-2.00 (s, 2 H), 1.86-1.83 (m, 2 H), 1.53-1.6 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 147.5, 136.3, 136.4, 135.8, 124.0, 123.3, 41.8, 30.7, 28.2 25.4, 22.9, 22.4.

IR (neat, cm^{-1}): 3084, 3049, 2928, 2859, 2837, 1726, 1575, 1422, 1342, 1265, 1077, 1027, 959, 716.

HRMS (ESI): $[M+H]^+$ calcd for $C_{12}H_{16}N$ 174.1277, found: 174.1290.

2-(Cyclohex-1-en-1-ylmethyl)benzo[b]thiophene (3x)



This compound was prepared according to General procedure C from the reaction of **1x** (32.8 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 31.9 mg, 70% yield. colorless oil.

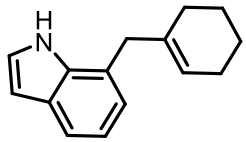
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.8 Hz, 1 H), 7.65 (d, *J* = 8.4 Hz, 1 H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 1 H), 7.00 (s, 1 H), 5.63 (s, 1H), 3.50 (s, 2 H), 2.06-2.04 (m, 2 H), 1.97-1.95 (m, 2 H), 1.62-1.55 (m, 4 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 145.3, 140.4, 139.9, 136.3, 124.1, 124.1, 123.5, 122.9, 122.3, 121.5, 39.7, 28.0, 25.4, 23.0, 22.4.

IR (neat, cm^{-1}): 3058, 3000, 2920, 2857, 2835, 2369, 1901, 1675, 1457, 1437, 1280, 1223, 1131, 1066, 969, 820, 745.

HRMS (ESI): $[M+H]^+$ calcd for $C_{15}H_{17}S$ 229.1045, found: 229.1055.

7-(Cyclohex-1-en-1-ylmethyl)-1H-indole (3y)



This compound was prepared according to General procedure C from the reaction of **1y** (29.4 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 10/1). 21.5 mg, 51% yield. colorless oil.

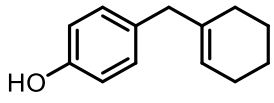
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (s, 1 H), 7.52 (d, *J* = 7.2 Hz, 1 H), 7.15 (t, *J* = 2.0 Hz, 1 H), 7.05 (t, *J* = 7.2 Hz, 1 H), 6.97 (d, *J* = 4.8 Hz, 1 H), 6.53 (dd, *J* = 2.0, 1.6 Hz, 1 H), 5.68 (s, 1 H), 3.53 (s, 2 H), 2.05 (s, 2 H), 1.85 (s, 2 H), 1.58-1.53 (m , 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.3, 135.6, 127.9, 123.9, 123.1, 122.9, 122.5, 119.9, 119.0, 102.7, 41.8, 28.1, 25.5, 22.9, 22.5.

IR (neat, cm^{-1}): 3435, 3055, 2926, 2857, 2837, 1638, 1489, 1277, 1213, 1165, 1105, 947, 846, 747.

HRMS (ESI): $[M+H]^+$ calcd for $C_{15}H_{18}N$ 212.1434, found: 212.1436.

4-(Cyclohex-1-en-1-ylmethyl)phenol (3z)



This compound was prepared according to General procedure C from the reaction of **1z** (24.8 mg, 0.2 mmol) and **2a** (69.0 mg,

0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 5/1). 20.7 mg, 55% yield. colorless oil.

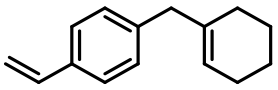
^{1}H NMR (600 MHz, $CDCl_3$): δ 6.96 (d, *J* = 8.4 Hz, 2 H), 6.67 (d, *J* = 8.4 Hz, 2 H), 5.36 (s, 1 H), 4.62 (s, 1 H), 3.09 (s, 2 H), 1.95-1.93 (m, 2 H), 1.78-1.76 (m, 2 H), 1.52-1.45 (m, 4 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 153.8, 137.7, 132.8, 130.1, 122.8, 115.1, 43.9, 28.1, 25.5 23.1, 22.6.

IR (neat, cm^{-1}): 2986, 2926, 2857, 2838, 1765, 1741, 1655, 1597, 1515, 1446, 1321, 1198, 1170, 1101, 1045, 824.

HRMS (ESI): $[M+H]^+$ calcd for $C_{13}H_{17}O$ 189.1274, found: 189.1275.

1-(Cyclohex-1-en-1-ylmethyl)-4-vinylbenzene (3aa)



This compound was prepared according to General procedure C from the reaction of **1aa** (26.8 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 11.9 mg, 30% yield. colorless oil.

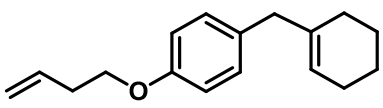
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33 (d, *J* = 8.4 Hz, 2 H), 7.13 (d, *J* = 7.8 Hz, 2 H), 6.70 (dd, *J* = 17.4, 10.8 Hz, 1 H), 5.71 (d, *J* = 18.0 Hz, 1 H), 5.47-5.45 (m, 1 H), 5.19 (d, *J* = 10.8 Hz, 1 H), 3.22 (s, 2 H), 2.03-2.00 (m, 2 H), 1.86-1.84 (m, 2 H), 1.59-1.53 (m, 4 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 140.4, 137.3, 136.9, 135.4, 129.2, 126.2, 123.2, 113.1, 44.5, 28.2, 25.5, 23.1, 22.5.

IR (neat, cm^{-1}): 2959, 2927, 2859, 2369, 2339, 1655, 1638, 1510, 1459, 1407, 1262, 1096, 904, 740.

HRMS (APCI): $[M+H]^+$ calcd for $C_{15}H_{19}$ 199.1481, found: 199.1482.

1-(But-3-en-1-yloxy)-4-(cyclohex-1-en-1-ylmethyl)benzene (3ab)



This compound was prepared according to General procedure C from the reaction of **1ab** (35.6 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 29.5 mg, 61% yield. colorless oil.

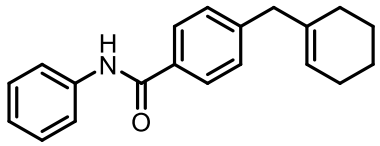
^{1}H NMR (400 MHz, $CDCl_3$)： 7.08-7.06 (m, 2 H), 6.83-6.79 (m, 2 H), 5.94-5.86 (m, 1 H), 5.43 (s, 1 H), 5.19-5.08 (m, 2 H), 4.01-3.97 (m, 2 H), 3.17 (s, 2 H), 2.56-2.51 (m, 2 H), 2.01-2.00 (m, 2 H), 1.84 (s, 2 H), 1.58-1.53 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): 157.3, 137.8, 134.7, 132.7, 129.9, 122.7, 117.1, 114.4, 67.3, 43.9, 33.9, 28.1, 25.5, 23.1, 22.6.

IR (neat, cm^{-1}): 3453, 2961, 2920, 1490, 1440, 1244, 1186, 1094, 1041, 934, 807.

HRMS (ESI): $[M+H]^+$ calcd for $C_{17}H_{23}O$ 243.1743, found: 243.1742

4-(Cyclohex-1-en-1-ylmethyl)-N-phenylbenzamide (3ac)



This compound was prepared according to General procedure C from the reaction of **1ac** (45.5 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 1/1). 30.3 mg, 52% yield. colorless oil.

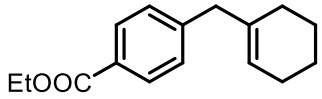
^{1}H NMR (600 MHz, $CDCl_3$)： δ 7.85 (s, 1H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.68-7.58 (m, 2H), 7.36 (dd, *J* = 8.6, 7.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.17-7.11 (m, 1H), 5.49-5.48 (m, 1H), 3.29 (s, 2H), 2.05-2.01 (m, 2H), 1.85-1.83 (m, 2H), 1.60-1.54 (m, 4H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 165.9, 145.1, 138.2, 136.6, 132.7, 129.4, 129.2, 127.1, 124.6, 123.9, 120.3, 44.7, 28.2, 25.5, 23.0, 22.4.

IR (neat, cm^{-1}): 3339, 3009, 1651, 1601, 1529, 1440, 1322, 1268, 918, 757.

HRMS (ESI): $[M+Na]^+$ calcd for $C_{20}H_{21}NNaO$ 314.1515, found: 314.1521.

Ethyl 4-(cyclohex-1-en-1-ylmethyl)benzoate (3ad)



This compound was prepared according to General procedure C from the reaction of **1ad** (36.0 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 20/1). 26.4 mg, 54% yield. colorless oil.

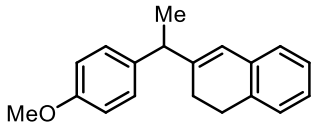
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* =8.0, 2 H), 7.16 (d, *J* =8.0, 2 H), 5.40 (s, 1 H), 4.29 (q, *J* = 7.2 Hz, 2 H), 3.21 (s, 2 H), 1.97-1.92 (m, 2 H), 1.77-1.73 (m, 2 H), 1.52-1.45 (m, 4 H), 1.38 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 146.1, 136.6, 129.6, 129.0, 128.4, 123.8, 60.9, 44.8, 28.2, 25.5, 23.0, 22.5, 14.5.

IR (neat, cm^{-1}): 2987, 2926, 2859, 2838, 2367, 2346, 1720, 1638, 1612, 1459, 1438, 1416, 1275, 1176, 1101, 1023, 918, 867, 752.

HRMS (ESI): $[M+H]^+$ calcd for $C_{16}H_{21}O_2$ 245.1536, found: 245.1535.

3-(1-(4-Methoxyphenyl)ethyl)-1,2-dihydronaphthalene (3ae)



This compound was prepared according to General procedure D from the reaction of **1ae** (30.4 mg, 0.2 mmol) and **2s** (83.4 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 200/1). 18.5 mg, 35% yield. colorless oil.

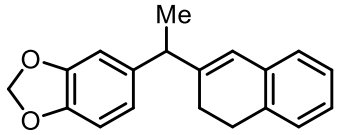
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18-7.14 (m, 3 H), 7.09-7.04 (m, 3 H), 6.84-6.82 (m, 2 H), 6.37 (s, 1 H), 3.78 (s, 3 H), 3.52 (q, *J* = 7.2 Hz, 1 H), 2.72-2.68 (m, 2 H), 2.11-2.06 (m, 2 H), 1.44 (d, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.1, 145.8, 137.1, 134.9, 134.8, 128.6, 127.2, 126.5, 126.4, 125.9, 121.6, 113.8, 55.3, 45.4, 28.5, 26.5, 19.9.

IR (neat, cm^{-1}): 2928, 2836, 2365, 1726, 1601, 1282, 1258, 1154, 1053, 919, 768.

HRMS (ESI): $[M+H]^+$ calcd for $C_{19}H_{21}O$ 265.1587, found: 265.1587.

5-(1-(3,4-Dihydronaphthalen-2-yl)ethyl)benzo[d][1,3]dioxole (3af)



This compound was prepared according to General procedure D from the reaction of **1af** (33.2 mg, 0.2 mmol) and **2s** (83.4 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 16.7 mg, 30% yield. colorless oil.

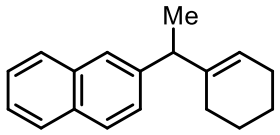
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.15-7.12 (m, 1 H), 7.09-7.04 (m, 3 H), 6.74-6.70 (m, 3 H), 6.37-6.36 (m, 1 H), 5.91 (s, 2 H), 3.50-3.46 (m, 1 H), 2.75-2.66 (m, 2 H), 2.14-2.06 (m, 2 H), 1.42 (d, *J* = 7.2 Hz, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 147.8, 146.0, 145.4, 139.2, 134.8, 134.8, 127.3, 126.5, 126.5, 125.9, 121.8, 120.6, 108.1, 100.9, 45.9, 28.5, 26.5, 19.9.

IR (neat, cm^{-1}): 2928, 2838, 2376, 1504, 1442, 1359, 1245, 1187, 1042, 939, 867.

HRMS (ESI): $[M+H]^+$ calcd for $C_{19}H_{19}O_2$ 279.1380, found: 279.1379.

2-(1-(Cyclohex-1-en-1-yl)ethyl)naphthalene (3ag)



This compound was prepared according to General procedure D from the reaction of **1ag** (34.4 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/0). 13.7 mg, 29% yield. colorless oil.

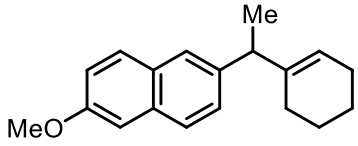
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.79-7.73 (m, 3 H), 7.62 (s, 1 H), 7.45-7.39 (m, 2 H), 7.35-7.33 (m, 1 H), 5.65-5.64 (m, 1 H), 3.47-3.43 (m, 1 H), 2.08-2.07 (m, 2 H), 1.84-1.74 (m, 2 H), 1.56-1.50 (m, 4 H), 1.42 (d, *J* = 7.2 Hz, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 143.6, 141.2, 133.6, 132.2, 127.7, 127.7, 127.6, 126.6, 125.8, 125.6, 125.2, 121.1, 46.7, 27.3, 25.5, 23.2, 22.8, 19.7.

IR (neat, cm^{-1}): 2961, 2857, 1634, 1413, 1269, 1202, 1131, 954, 818, 794.

HRMS (ESI): $[M+H]^+$ calcd for $C_{18}H_{21}$ 237.1638, found: 237.1638.

2-(1-(Cyclohex-1-en-1-yl)ethyl)-6-methoxynaphthalene (3ah)



This compound was prepared according to General procedure **D** from the reaction of **1ah** (40.4 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/0). 12.7 mg, 24% yield. colorless oil.

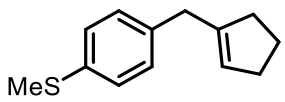
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.69-7.64 (m, 2 H), 7.55 (s, 1 H), 7.31-7.29 (m, 1 H), 7.12-7.10 (m, 2 H), 5.64-5.62 (m, 1 H), 3.90 (s, 3 H), 3.43-3.40 (m, 1 H), 2.08-2.06 (m, 2 H), 1.84-1.74 (m, 2 H), 1.54-1.51 (m, 4 H), 1.40 (d, *J* = 7.2 Hz, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 157.3, 141.4, 141.3, 133.2, 129.2, 129.1, 127.1, 126.6, 125.4, 120.9, 118.6, 105.7, 55.4, 46.5, 27.2, 25.5, 23.2, 22.8, 19.7.

IR (neat, cm^{-1}): 2987, 2838, 2367, 1720, 1612, 1459, 1275, 1176, 1023, 918, 867, 752.

HRMS (ESI): $[M+H]^+$ calcd for $C_{19}H_{23}O$ 267.1743, found: 267.1743.

(4-(Cyclopent-1-en-1-ylmethyl)phenyl)(methyl)sulfane (3ai)



This compound was prepared according to General procedure C from the reaction of **1a** (30.8 mg, 0.2 mmol) and **2b** (64.8 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 24.5 mg, 60% yield. colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21-7.18 (m, 2 H), 7.12-7.09 (m, 2 H), 5.33 (s, 1 H),

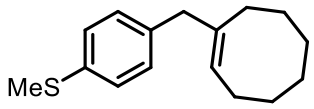
3.34 (s, 2 H), 2.47 (s, 3 H), 2.33-2.28 (m, 2 H), 2.21-2.26 (m, 2 H), 1.89-1.81 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 137.5, 135.4, 129.5, 127.1, 125.6, 37.5, 34.9, 32.6, 23.7, 16.5.

IR (neat, cm^{-1}): 2958, 2922, 2846, 1638, 1493, 1437, 1403, 1198, 1092, 1038, 969, 798

HRMS (ESI): $[M+H]^+$ calcd for $C_{13}H_{17}S$ 205.1045, found: 205.1052.

(*E*)-(4-(cyclooct-1-en-1-ylmethyl)phenyl)(methyl)sulfane (3aj)



This compound was prepared according to General procedure C from the reaction of **1a** (30.8 mg, 0.2 mmol) and **2c** (77.4 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 21.3 mg, 43% yield. colorless oil.

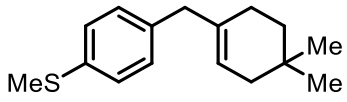
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.20-7.18 (m, 2 H), 7.12-7.10 (m, 2 H), 5.36 (t, *J* = 8.4 Hz, 1 H), 3.25 (s, 2 H), 2.47 (s, 3 H), 2.11-2.07 (m, 4 H), 1.48-1.39 (m, 8 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 140.2, 137.8, 135.4, 129.9, 129.9, 127.1, 126.1, 43.6, 30.2, 28.7, 28.6, 26.6, 26.5, 26.4, 16.5.

IR (neat, cm^{-1}): 3453, 2923, 2854, 1637, 1464, 1268, 1096, 917, 809, 755.

HRMS (ESI): $[M+H]^+$ calcd for $C_{16}H_{23}S$ 247.1515, found: 247.1495.

(4-((4,4-Dimethylcyclohex-1-en-1-yl)methyl)phenyl)(methyl)sulfane (3ak)



This compound was prepared according to General procedure C from the reaction of **1a** (30.8 mg, 0.2 mmol) and **2d** (77.5 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 38.4 mg, 78% yield. colorless oil.

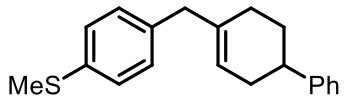
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20-7.18 (m, 2 H), 7.10-7.08 (m, 2 H), 5.39 (s, 1 H), 3.21 (s, 2 H), 2.47 (s, 3 H), 1.85-1.80 (m, 4 H), 1.31 (t, *J* = 6.0 Hz, 2 H), 0.87 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.8, 135.8, 135.4, 129.5, 127.0, 122.2, 43.9, 39.5, 35.8, 28.6, 28.3, 26.0, 16.4.

IR (neat, cm^{-1}): 3040, 3019, 2950, 2922, 2868, 2834, 1701, 1654, 1403, 1364, 1220, 1154, 967, 893.

HRMS (ESI): $[M+H]^+$ calcd for $C_{16}H_{23}S$ 247.1515, found: 247.1510.

Methyl(4-((1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)methyl)phenyl)sulfane (3al)



This compound was prepared according to General procedure C from the reaction of **1a** (30.8 mg, 0.2 mmol) and **2e** (91.8 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 48.3 mg, 82% yield. white solid, mp.: 57-58 ℃.

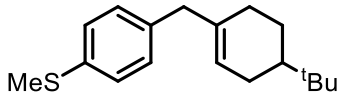
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33-7.27 (m, 2 H), 7.21-7.12 (m, 6 H), 5.54 (s, 1 H), 3.26 (s, 2 H), 2.76-2.71 (m, 1 H), 2.47 (s, 3 H), 2.33-2.29 (m, 1 H), 2.20-2.14 (m, 1 H), 2.10-1.89 (m, 3 H), 1.76-1.69 (m, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 147.3, 137.5, 137.3, 135.6, 129.6, 128.5, 127.2, 127.0, 126.1, 122.8, 43.9, 40.3, 33.8, 30.2, 28.9, 16.5.

IR (neat, cm^{-1}): 2918, 2836, 2344, 1638, 1493, 1437, 1247, 1211, 798, 757.

HRMS (ESI): $[M+H]^+$ calcd for $C_{20}H_{23}S$ 295.1515, found: 295.1503.

(4-((4-(Tert-butyl)cyclohex-1-en-1-yl)methyl)phenyl)(methyl)sulfane (3am)



This compound was prepared according to General procedure C from the reaction of **1a** (30.8 mg, 0.2 mmol) and **2f** (85.8 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 49.8 mg, 91% yield. colorless oil.

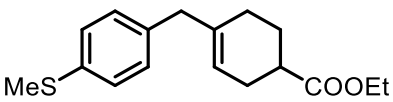
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.20-7.18 (m, 2 H), 7.10-7.08 (m, 2 H), 5.45 (s, 1 H), 3.20 (s, 2 H), 2.47 (s, 3 H), 2.06-2.01 (m, 1 H), 1.91-1.89 (m, 2 H), 1.82-1.75 (m, 2 H), 1.26-1.10 (m, 2 H), 0.85 (s, 9 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 137.8, 137.1, 135.4, 129.6, 127.1, 123.4, 44.2, 43.7, 32.3, 29.6, 27.4, 27.1, 24.4, 16.5.

IR (neat, cm^{-1}): 3081, 3019, 2959, 2367, 1638, 1493, 1437, 1403, 1366, 1247, 1232, 1094, 1018, 987, 913, 799.

GC-MS (EI) m/z (rel intensity, ion): 274.14 (100.00, M^+).

Ethyl 4-(4-(methylthio)benzyl)cyclohex-3-ene-1-carboxylate (3an)



This compound was prepared according to General procedure C from the reaction of **1a** (30.8 mg, 0.2

mmol) and **2g** (90.6 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 10/1). 45.3 mg, 78% yield. colorless oil.

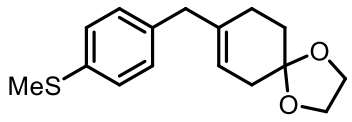
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20-7.17 (m, 2 H), 7.09-7.06 (m, 2 H), 5.45 (s, 1 H), 4.12 (q, *J* = 7.2 Hz, 2 H), 3.21 (s, 2 H), 2.51-2.44 (m, 4 H), 2.29-2.25 (m, 2 H), 1.98-1.91 (m, 3 H), 1.70-1.61 (m, 1 H), 1.24 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 176.0, 137.1, 136.9, 135.6, 129.5, 127.0, 121.3, 60.3, 43.7, 39.4, 27.8, 27.4, 25.5, 16.3, 14.3.

IR (neat, cm^{-1}): 3017, 2982, 2922, 2840, 2369, 1897, 1731, 1638, 1493, 1438, 1375, 1226, 1176, 1094, 971, 807.

HRMS (ESI): $[M+H]^+$ calcd for $C_{17}H_{23}O_2S$ 291.1413, found 291.1412.

8-(4-(Methylthio)benzyl)-1,4-dioxaspiro[4.5]dec-7-ene (3ao)



This compound was prepared according to General procedure C from the reaction of **1a** (30.8 mg, 0.2 mmol) and **2h** (86.4 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 30/1). 33.2 mg, 60% yield. colorless oil.

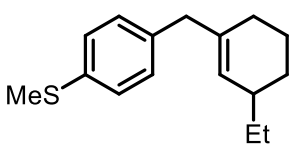
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.20-7.18 (m, 2 H), 7.11-7.09 (m, 2 H), 5.34 (s, 1 H), 3.98-3.95 (m, 4 H), 3.25 (s, 2 H), 2.47 (s, 3 H), 2.28 (s, 2 H), 2.13-2.10 (m, 2 H), 1.72 (t, *J* = 6.6 Hz, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 137.1, 136.9, 135.7, 129.6, 127.1, 120.4, 108.2, 64.5, 43.1, 35.9, 31.3, 27.4, 16.4.

IR (neat, cm^{-1}): 3075, 3019, 2954, 2920, 2838, 1726, 1638, 1492, 1433, 1377, 1359, 1340, 1115, 1060, 1012, 948, 840.

HRMS (ESI): $[M+Na]^+$ calcd for $C_{16}H_{20}NaO_2S$ 299.1076, found 299.1077.

(4-((3-Ethylcyclohex-1-en-1-yl)methyl)phenyl)(methyl)sulfane (3ap)



This compound was prepared according to General procedure C from the reaction of **1a** (30.8 mg, 0.2 mmol) and **2i** (77.4 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 30.5 mg, 62% yield. colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20-7.17 (m, 2 H), 7.11-7.08 (m, 2 H), 5.39 (s, 1 H),

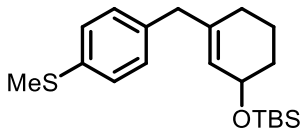
3.20 (s, 2 H), 2.47 (s, 3 H), 1.98-1.97 (m, 1 H), 1.82-1.65 (m, 4 H), 1.47-1.07 (m, 4 H), 0.91 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.8, 136.9, 135.4, 129.5, 128.4, 127.1, 44.3, 37.3, 29.4, 28.6, 28.3, 22.0, 16.4, 11.6.

IR (neat, cm^{-1}): 3463, 2961, 2924, 2859, 2876, 1638, 1493, 1418, 1144, 1094, 969, 887, 785.

HRMS (ESI): $[M+H]^+$ calcd for $C_{16}H_{23}S$ 247.1515, found 247.1513.

Tert-butyldimethyl((3-(4-(methylthio)benzyl)cyclohex-2-en-1-yl)oxy)silane (3aq)



This compound was prepared according to General procedure C from the reaction of **1a** (30.8 mg, 0.2 mmol) and **2j** (108.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 64.8 mg, 93% yield. colorless oil.

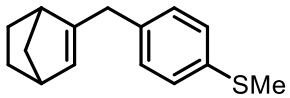
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.22-7.20 (m, 2 H), 7.13-7.11 (m, 2 H), 5.48 (s, 1 H), 4.29 (s, 1 H), 3.30-3.20 (m, 2 H), 2.49 (s, 3 H), 1.91-1.74 (m, 4 H), 1.55-1.46 (m, 2 H), 0.93 (s, 9 H), 0.11 (s, 3 H), 0.10 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 139.6, 137.0, 135.7, 129.6, 127.5, 127.1, 67.4, 43.8, 32.5, 27.9, 26.1, 20.0, 18.5, 16.4, -4.3, -4.4.

IR (neat, cm^{-1}): 2929.5, 2858.8, 1507.7, 1264.9, 916.9, 835.6, 755.4.

HRMS (ESI): $[M+H]^+$ calcd for $C_{20}H_{33}OSSi$ 349.2016, found: 349.2039.

(4-(Bicyclo[2.2.1]hept-2-en-2-ylmethyl)phenyl)(methyl)sulfane (3ar)



This compound was prepared according to General procedure C from the reaction of **1a** (30.8 mg, 0.2 mmol) and **2k** (72.6 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 23.5 mg, 51% yield. colorless oil.

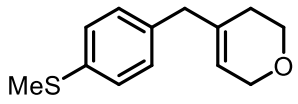
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.20-7.18 (m, 2 H), 7.10-7.09 (m, 2 H), 5.50 (s, 1 H), 3.37-3.30 (m, 2 H), 2.78 (m, 1 H), 2.63 (s, 1 H), 2.47 (s, 3 H), 1.64-1.54 (m, 2 H), 1.38-1.36 (m, 1 H), 1.08-1.03 (m, 2 H), 0.90-0.88 (m, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 148.7, 137.2, 135.4, 129.6, 129.6, 129.4, 127.1, 127.1, 48.7, 45.1, 42.4, 36.1, 26.9, 24.7, 16.4.

IR (neat, cm^{-1}): 2920, 2829, 2365, 1493, 1437, 1372, 1236, 1126, 1094, 1017, 852, 801.

HRMS (ESI): $[M+H]^+$ calcd for $C_{15}H_{19}S$ 231.1202, found: 231.1213.

4-(4-(Methylthio)benzyl)-3,6-dihydro-2H-pyran (3as)



This compound was prepared according to General procedure C from the reaction of **1a** (30.8 mg, 0.2 mmol) and **2l** (69.6 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 35.2 mg, 80% yield. colorless oil.

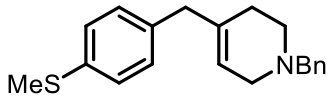
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.21-7.18 (m, 2 H), 7.11-7.08 (m, 2 H), 5.43 (tt, *J* = 2.8, 1.4 Hz, 1 H), 4.14-4.11 (m, 2 H), 3.74 (t, *J* = 5.2 Hz, 2 H), 3.26 (s, 2 H), 2.47 (s, 3 H), 2.00-1.97 (m, 2 H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 136.2, 136.0, 129.7, 127.1, 121.7, 65.6, 64.5, 43.2, 28.3, 16.3.

IR (neat, cm^{-1}): 3019, 2920, 2849, 2748, 2365, 2343, 1742, 1493, 1437, 1371, 1236, 1126, 1094, 1018, 852, 801.

HRMS (ESI): $[M+H]^+$ calcd for $C_{13}H_{17}OS$ 221.0995, found: 221.0998.

1-Benzyl-4-(4-(methylthio)benzyl)-1,2,3,6-tetrahydropyridine (3at)



This compound was prepared according to General procedure C from the reaction of **1a** (30.8 mg, 0.2 mmol) and **2m** (96.3 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 10/1). 58.7 mg, 95% yield, colorless oil.

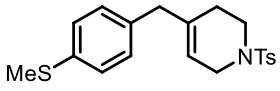
^{1}H NMR (600 MHz, CDCl$_3$): δ 7.34-7.30 (m, 4 H), 7.29-7.23 (m, 1 H), 7.19-7.18 (m, 2 H), 7.09-7.08 (m, 2 H), 5.36-5.35 (m, 1 H), 3.57 (s, 2 H), 3.23 (s, 2 H), 2.98 (s, 2 H), 2.52 (t, *J* = 6.0 Hz, 2 H), 2.46 (s, 3 H), 2.03 (s, 2 H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 138.4, 136.8, 135.9, 135.7, 129.8, 129.4, 128.3, 127.2, 127.1, 121.0, 62.8, 53.0, 50.0, 43.0, 29.0, 16.4.

IR (neat, cm^{-1}): 3027, 2924, 2799, 2751, 1638, 1495, 1437, 1455, 1264, 1094, 971, 805.

GC-MS (EI) m/z (rel intensity, ion): 309.13 (100.00, M^+).

4-(4-(Methylthio)benzyl)-1-tosyl-1,2,3,6-tetrahydropyridine (3au)



This compound was prepared according to General procedure C from the reaction of **1a** (30.8 mg, 0.2 mmol) and **2n** (115.6 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 10/1). 62.6 mg, 84% yield, white solid, mp.: 125-127 ℃

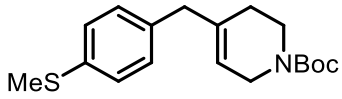
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.67-7.64 (m, 2 H), 7.32-7.29 (m, 2 H), 7.17-7.15 (m, 2 H), 7.01-6.99 (m, 2 H), 5.34 (s, 1 H), 3.57 (s, 2 H), 3.20 (s, 2 H), 3.13 (t, *J* = 6.0 Hz, 2 H), 2.46 (s, 3 H), 2.42 (s, 3 H), 2.06 (s, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 143.6, 136.2, 136.1, 135.8, 133.5, 129.7, 129.5, 127.8, 127.1, 118.3, 45.0, 43.0, 42.9, 28.1, 21.6, 16.3.

IR (neat, cm^{-1}): 2920, 2829, 2365, 1493, 1437, 1372, 1236, 1126, 1094, 1017, 852, 801.

HRMS (ESI): $[M+H]^+$ calcd for $C_{20}H_{24}NO_2S_2$ 374.1243, found: 374.1241.

Tert-butyl 4-(4-(methylthio)benzyl)-3,6-dihydropyridisne-1(2H)-carboxylate (3av)



This compound was prepared according to General procedure C from the reaction of **1a** (30.8 mg, 0.2 mmol) and **2o** (99.4 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 10/1). 58.7 mg, 92% yield, colorless oil.

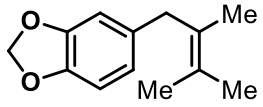
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20-7.18 (m, 2 H), 7.10-7.07 (m, 2 H), 5.37 (s, 1 H), 3.87 (s, 2 H), 3.44 (t, *J* = 5.6 Hz, 2 H), 3.26 (s, 2 H), 2.47 (s, 3 H), 1.98 (s, 2 H), 1.45 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.1, 136.3, 136.0, 129.6, 127.0, 79.6, 63.3, 43.3, 28.6, 28.2, 16.3, 14.1.

IR (neat, cm^{-1}): 3006, 2978, 2924, 2838, 1769, 1746, 1696, 1478, 1455, 1420, 1286, 1241, 1113, 1051, 988, 699.

HRMS (ESI): $[M+H]^+$ calcd for $C_{18}H_{26}NO_2S$ 320.1679, found: 320.1695.

5-(2,3-Dimethylbut-2-en-1-yl)-3a,7a-dihydrobenzo[d][1,3]dioxole (3aw)



This compound was prepared according to General procedure C from the reaction of **1f** (30.8 mg, 0.2 mmol) and **2p** (65.5 mg,

0.3 mmol), but $Ni(PCy_3)_2Cl_2$ (13.8 mg, 0.02 mmol) was used instead of $Ni(dppf)Cl_2$, 4,4'-Dimethyl-2,2'-bipyridyl (7.4 mg, 0.04 mmol) was used instead of dtbpy, and dppf (11 mg, 0.02mmol), $ZrCl_4$ (9.3 mg, 0.04 mmol) was used, conducted at 30 °C. It was purified by flash chromatography on silica gel (PE/EA = 100/1). 18.8 mg, 46% yield, colorless oil.

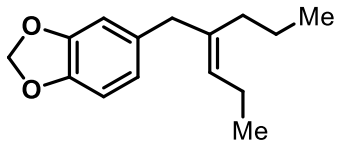
^{1}H NMR (600 MHz, $CDCl_3$): δ 6.71 (d, *J* = 7.8 Hz, 1 H), 6.63 (s, 1 H), 6.60 (d, *J* = 7.8 Hz, 1 H), 5.91 (s, 2 H), 3.30 (s, 2 H), 1.77 (s, 3 H), 1.72 (s, 3 H), 1.58 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 147.5, 134.9, 126.5, 125.8, 125.1, 121.2, 108.8, 108.0, 100.7, 39.7, 20.61, 20.6, 18.2.

IR (neat, cm^{-1}): 3517, 3447, 3362, 2926, 2858, 1656, 1598, 1495, 800, 732.

GC-MS (EI) m/z (rel intensity, ion): 204.09 (100.00, M^+).

(*E*)-5-(2-propylpent-2-en-1-yl)-3a,7a-dihydrobenzo[*d*] [1,3]dioxole (3ax)



This compound was prepared according to General procedure C from the reaction of **1f** (30.8 mg, 0.2 mmol) and **2q** (73.9 mg, 0.3 mmol), but $Ni(PCy_3)_2Cl_2$ (13.8 mg, 0.02 mmol) was used instead of $Ni(dppf)Cl_2$, 4,4'-Dimethyl-2,2'-bipyridyl (7.4 mg, 0.04 mmol) was used instead of dtbpy, and dppf (11 mg, 0.02 mmol), $ZrCl_4$ (9.3 mg, 0.04 mmol) was used, conducted at 30 °C. It was purified by flash chromatography on silica gel (PE/EA = 100/1). 24.2 mg, 52% yield. colorless oil.

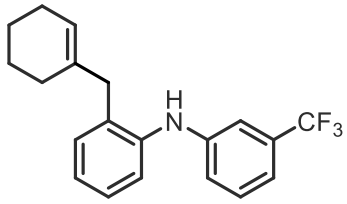
^{1}H NMR (600 MHz, $CDCl_3$): δ 6.77-6.55 (m, 3 H), 5.92 (s, 2 H), 5.20 (t, *J* = 7.2 Hz, 1 H), 3.19 (s, 2 H), 2.16-1.99 (m, 2 H), 1.92-1.88 (m, 2 H), 1.38-1.32 (m, 2 H), 0.96 (t, *J* = 7.4 Hz, 3 H), 0.86 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 147.6, 145.8, 138.1, 134.8, 129.4, 121.8, 109.4, 108.0, 100.8, 43.4, 31.5, 21.6, 21.3, 14.8, 14.2.

IR (neat, cm^{-1}): 3461, 2984, 1487, 1268, 1041, 932, 806, 756.

HRMS (ESI): $[M+Na]^+$ calcd for $C_{15}H_{20}NaO_2$ 255.1356, found: 255.1352.

2-(Cyclohex-1-en-1-ylmethyl)-N-(3-(trifluoromethyl)phenyl)aniline (4)



This compound was prepared according to General procedure C from the reaction of **1ak** (53.4 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 5/1). 35.7mg, 54% yield. colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.32-7.26 (m, 2 H), 7.21-7.19 (m, 2 H), 7.10 (s, 1 H), 7.07 (d, J = 7.7 Hz, 1 H), 7.04-6.99 (m, 2 H), 5.96 (s, 1 H), 5.48-5.47 (m, 1 H), 3.28 (s, 2 H), 2.05-2.00 (m, 2 H), 1.87 (s, 2 H), 1.63-1.54 (m, 4 H).

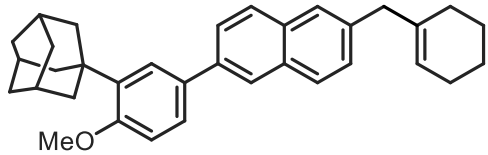
^{13}C NMR (150 MHz, $CDCl_3$): δ 144.9, 140.7, 136.5, 131.8 (q, J_{C-F} = 30 Hz), 131.7, 130.8, 129.9, 127.4, 124.3 (q, J_{C-F} = 271 Hz), 123.4, 123.1, 120.1, 119.4, 116.3 (q, J_{C-F} = 3 Hz), 41.6, 28.5, 25.4, 22.9, 22.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.8.

IR (neat, cm^{-1}): 3437, 3390, 3038, 2930, 2861, 2838, 1618, 1597, 1584, 1523, 1496, 1426, 1336, 1280, 1224, 1165, 1098, 997, 924, 865, 699.

HRMS (ESI): $[M+H]^+$ calcd for $C_{15}H_{23}O_2$ 332.1621, found: 332.1619.

(1R,3R,5S)-1-(5-(6-(cyclohex-1-en-1-ylmethyl)naphthalen-2-yl)-2-methoxyphenyl)adamantane (5)



This compound was prepared according to General procedure C from the reaction of **1al** (79.6 mg, 0.2 mmol) and **2a** (69.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 57.4 mg, 62% yield, white solid, mp.: 159-160 ℃.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.97-7.93 (m, 1 H), 7.80 (t, *J* = 8.0 Hz, 2 H), 7.69 (dd, *J* = 8.6, 1.8 Hz, 1 H), 7.60 (d, *J* = 1.6 Hz, 1 H), 7.58 (d, *J* = 2.2 Hz, 1 H), 7.51 (dd, *J* = 8.4, 2.2 Hz, 1 H), 7.33 (dd, *J* = 8.4, 1.6 Hz, 1 H), 6.97 (d, *J* = 8.4 Hz, 1 H), 5.54-5.51 (m, 1 H), 3.88 (s, 3 H), 3.40 (s, 2 H), 2.18 (d, *J* = 3.0 Hz, 6 H), 2.15-2.07 (m, 3 H), 2.06-2.02 (m, 2 H), 1.91-1.88 (m, 2 H), 1.80-1.79 (m, 6 H), 1.59-1.53 (m, 4 H).

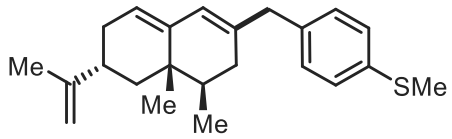
^{13}C NMR (150 MHz, $CDCl_3$): δ 158.6, 138.9, 138.4, 137.9, 137.4, 133.5, 132.5, 132.5,

128.2, 127.9, 126.9, 126.0, 125.8, 125.7, 124.9, 123.3, 112.2, 55.3, 45.0, 40.7, 37.3, 37.3, 29.3, 28.3, 25.5, 23.1, 22.6.

IR (neat, cm^{-1}): 3537, 3058, 2906, 2853, 1638, 1497, 1457, 1237, 1139, 882, 807, 740, 704.

HRMS (ESI): $[M+H]^+$ calcd for $C_{15}H_{23}O_2$ 463.2995, found: 463.2987.

(4-(((4R,4aS,6R)-4,4a-dimethyl-6-(prop-1-en-2-yl)-3,4,4a,5,6,7-hexahydronaphthalen-2-yl)methyl)phenyl)(methyl)sulfane (6)



This compound was prepared according to General procedure C from the reaction of **1a** (30.8 mg, 0.2 mmol) and **2r** (105.0 mg, 0.3 mmol). It was purified by flash chromatography on silica gel (PE/EA = 100/1). 50.1 mg, 74% yield. colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.20-7.16 (m, 2 H), 7.12-7.07 (m, 2 H), 5.81 (d, *J* = 2.2 Hz, 1 H), 5.41-5.40 (m, 1 H), 4.74-4.73 (m, 2 H), 3.27 (s, 2 H), 2.47 (s, 3 H), 2.26-2.21 (m, 1 H), 1.99-1.94 (m, 1 H), 1.86-1.82 (m, 1 H), 1.79-1.77 (m, 1 H), 1.75 (s, 3 H), 1.72-1.69 (m, 1 H), 1.53-1.46 (m, 1 H), 1.27-1.24 (m, 1 H), 1.16 (t, *J* = 12.7 Hz, 1 H), 0.85 (s, 3 H), 0.83 (d, *J* = 6.8 Hz, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 150.5, 142.5, 137.2, 136.6, 135.6, 129.5, 127.1, 125.6, 122.0, 108.7, 43.5, 40.2, 39.2, 37.5, 36.0, 35.2, 31.3, 20.8, 17.6, 16.3, 14.8.

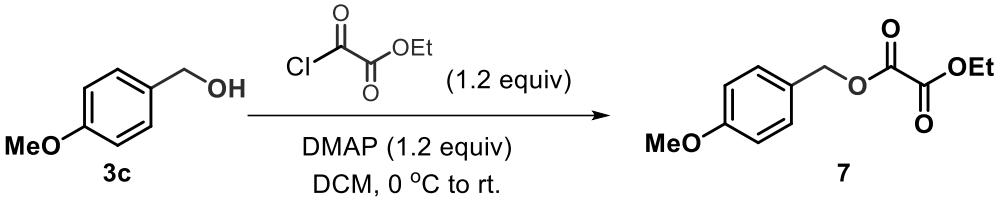
IR (neat, cm^{-1}): 3435, 2965, 2920, 2831, 1646, 1493, 1434, 1375, 1284, 1094, 1018, 967, 885, 801.

HRMS (ESI): $[M+H]^+$ calcd for $C_{15}H_{23}O_2$ 339.2141, found: 339.2143.

5. Mechanistic Investigation

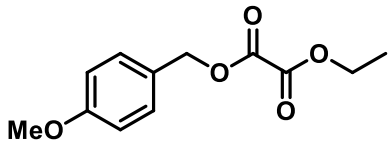
5.1 The effect of oxalate group on the coupling reaction

5.1.1 Preparation of benzylic oxalates 7



General procedure.[2] To a solution of DMAP (0.36 g, 3.0 mmol, 1.2 equiv.) in CH_2Cl_2 (10 mL) was dropwise added ethyl oxalyl monochloride (0.33 mL, 3.0 mmol, 1.2 equiv.) at 0 °C. The reaction mixture was stirred at room temperature for 5 min before slow addition of a solution of (4-methoxyphenyl)methanol (0.35 g, 2.5 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred for 10 min and then quenched with water (10 mL) and extracted with CH_2Cl_2 twice. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuum. The crude residue was purified by flash chromatography on silica gel to afford benzylic oxalates.

Ethyl (4-methoxybenzyl) oxalate (7)



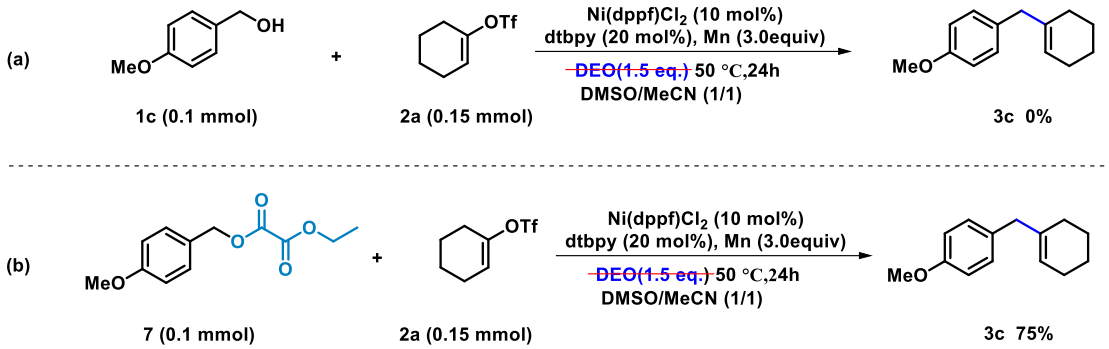
7 is a known compound. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 2.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.4 Hz, 2 H), 6.89 (m, d, *J* = 8.4 Hz, 2 H), 5.25 (s, 2 H), 4.32 (q, *J* = 7.2 Hz, 2 H), 3.81 (s, 3 H), 1.36 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 158.0, 157.9, 130.9, 126.5, 114.2, 68.6, 63.3, 55.4, 14.0.

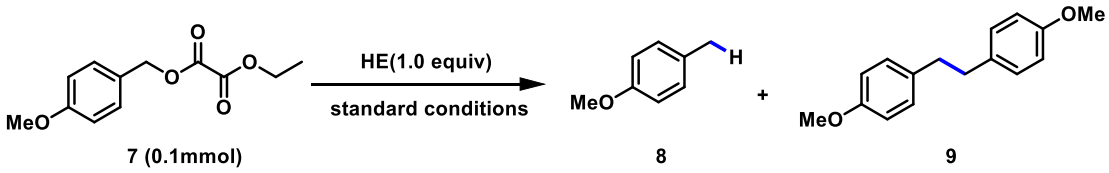
5.1.2 Effect of the oxalate group

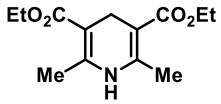
Scheme S2. Effect of the oxalate group



These reactions were conducted according to the General procedure C. DEO was not used in the reactions. **7** was used instead of alcohol **1c** in the reaction in Scheme S2b. The yields were isolated yields.

5.2 Radical trapping experiments





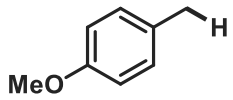
Hantzsch Ester(HE)

conditions	8	9
without HE	5%	47%
with HE	20%	34%

General procedure for reaction without HE: The reaction was conducted in an argon-filled glove box. To a reaction tube equipped with a magnetic stir bar was added Ni(dppf)Cl_2 (6.8 mg, 0.01 mmol), dtbpy (5.4 mg, 0.02 mmol), Mn (16.5 mg, 0.3 mmol), **7** (23.8 mg, 0.1 mmol) and DMSO/ MeCN (1:1, 0.33 mL, 0.3 M). It was then sealed and removed from the glove box. The reaction mixture was stirred at 50 ℃ for 24 h. The reaction was quenched with water (10 mL), and the mixture was extracted with ethyl acetate (3 ×10 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na_2SO_4. A 0.2 mL of solution was collected and diluted with ethyl acetate (1 mL). The yields of **8** and **9** were determined by GC Analysis using dodecane as internal standard.

General procedure for reaction of 7 in the presence of HE: The reaction was conducted in an argon-filled glove box. To a reaction tube equipped with a magnetic stir bar was added Ni(dppf)Cl_2 (6.8 mg, 0.01 mmol), dtbpy (5.4 mg, 0.02 mmol), Mn (16.5 mg, 0.3 mmol), hantzsch ester (25.3 mg, 0.1 mmol), **7** (23.8 mg, 0.1 mmol) and DMSO/ MeCN (1:1, 0.33 mL, 0.3 M). It was then sealed and removed from the glove box. The reaction mixture was stirred at 50 ℃ for 24 h. The reaction was quenched with water (10 mL), and the mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na_2SO_4. A 0.2 mL of solution was collected and diluted with ethyl acetate (1 mL). The yields of **8** and **9** were determined by GC Analysis using dodecane as internal standard.

4-Methylanisole (8)

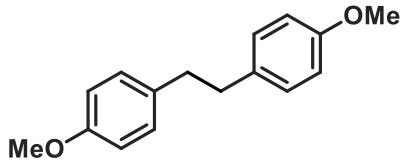


8 is a known compound. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 2.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.08 (d, *J* = 8.5 Hz, 2 H), 6.80 (d, *J* = 8.5 Hz, 2 H), 3.77 (s, 3 H), 2.28 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 157.6, 130.0, 130.0, 113.8, 55.4, 20.6.

1,2-Bis(4-methoxyphenyl)ethane (9)



9 is a known compound. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 2.

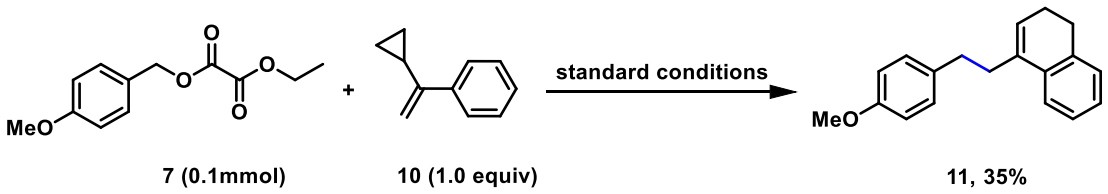
^{1}H NMR (600 MHz, CDCl3): δ 7.00 (d, *J* = 8.6 Hz, 4 H), 6.74 (d, *J* = 8.6 Hz, 4 H), 3.71 (s, 6 H), 2.75 (s, 4 H).

^{13}C NMR (150 MHz, CDCl3): δ 157.9, 134.1, 129.5, 113.8, 55.4, 37.4.

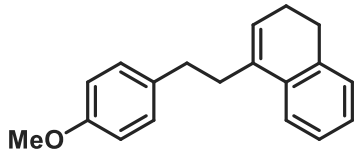
5.3 Radical clock experiments

General procedure. The procedure was conducted in an argon-filled glove box. To a reaction tube equipped with a magnetic stir bar was charged with Ni(dppf)Cl_2 (6.8 mg, 0.01 mmol), dtbpy (5.4 mg, 0.02 mmol), and Mn (16.5 mg, 0.3 mmol). The solution of

7 (22.4 mg, 0.1 mmol) and **10** (14.4 mg, 0.1 mmol) in DMSO/MeCN (1:1, 0.33 mL, 0.3 M) was then added. It was then removed from the glove box, and the reaction mixture was stirred at 50 ℃ for 24 h. The reaction was quenched with water (10 mL), and the mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na_2SO_4. The yield of **11** was determined by ^{1}H NMR analysis with CH_2Br_2 as an internal standard.



4-(4-Methoxyphenethyl)-1,2-dihydronaphthalene (11)



11 is a known compound. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 2.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31 (d, *J* = 7.6 Hz, 1 H), 7.23-7.20 (m, 1 H), 7.16-7.15 (m, 2 H), 7.12 (d, *J* = 8.4 Hz), 6.84 (d, *J* = 8.6 Hz, 2 H), 5.83 (t, *J* = 4.6 Hz, 1 H), 3.80 (s, 3 H), 2.80-2.77 (m, 2 H), 2.74-2.69 (m, 4 H), 2.24-2.21 (m, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 157.9, 137.0, 136.0, 134.9, 134.5, 129.5, 127.8, 126.7, 126.5, 125.4, 122.7, 113.8, 55.4, 35.2, 34.1, 28.6, 23.2.

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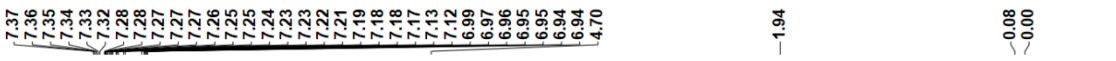
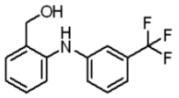
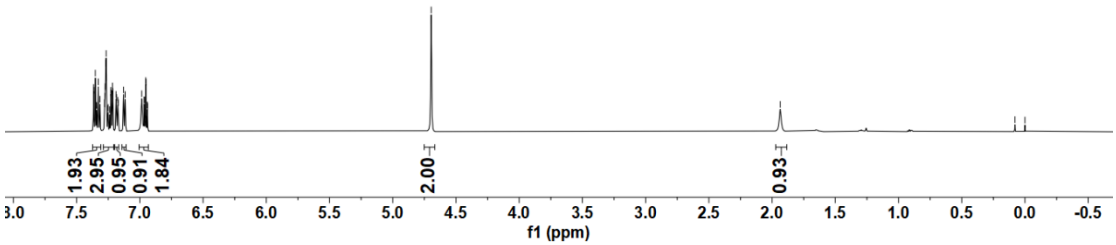
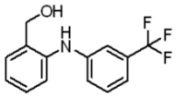
7. Copies of NMR Spectra

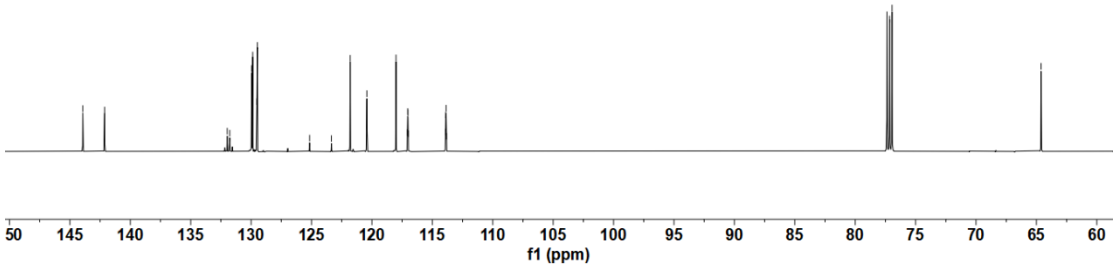
1ai, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)



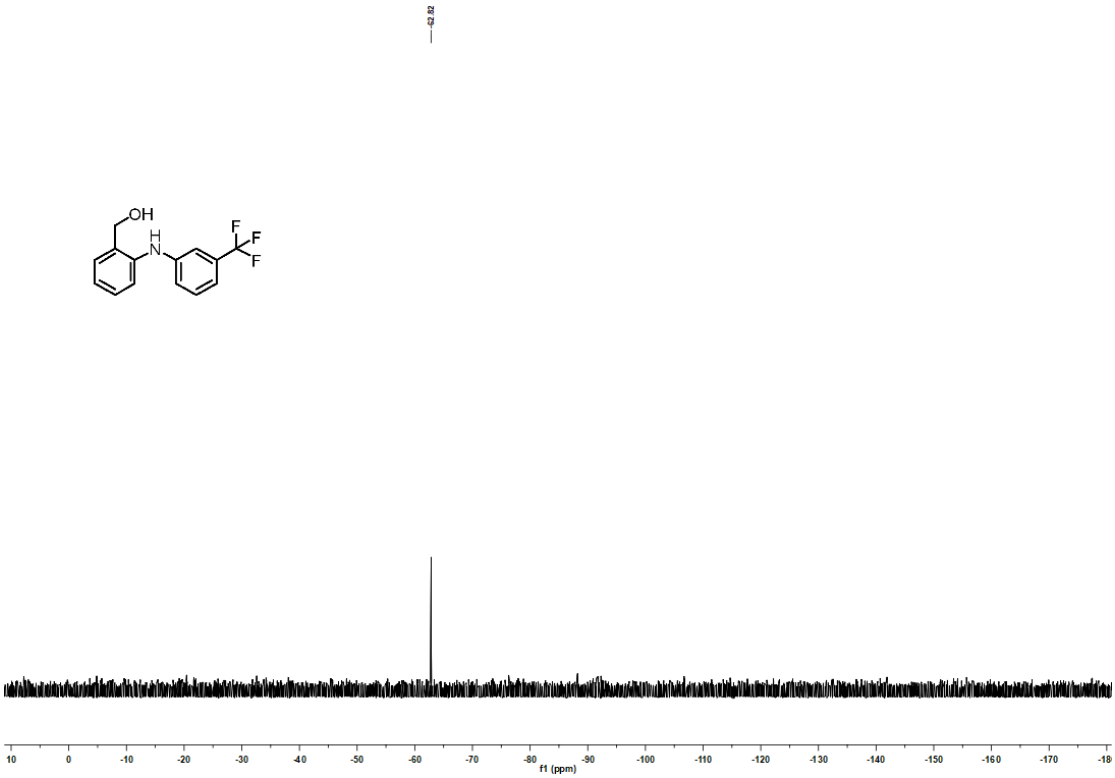




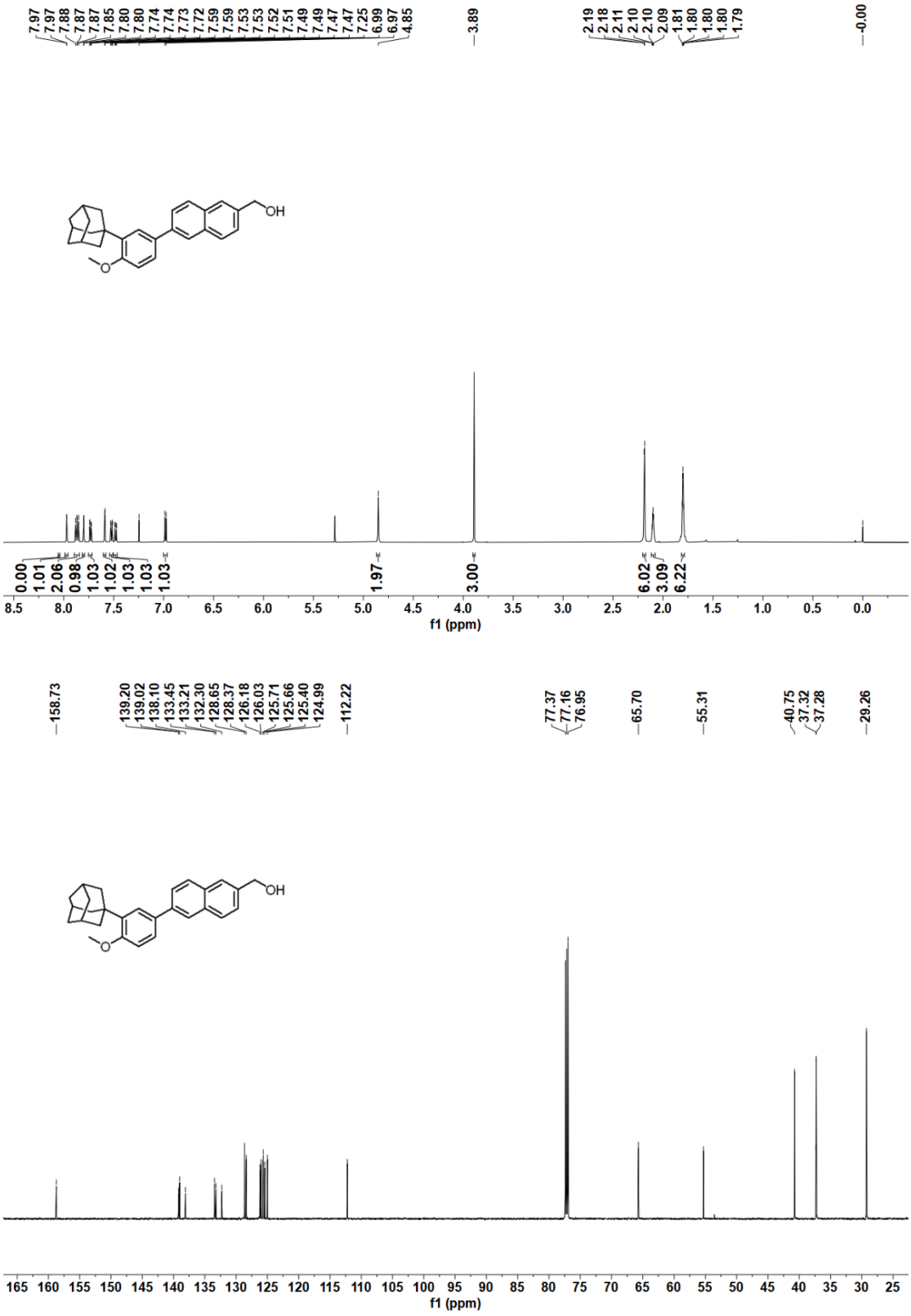




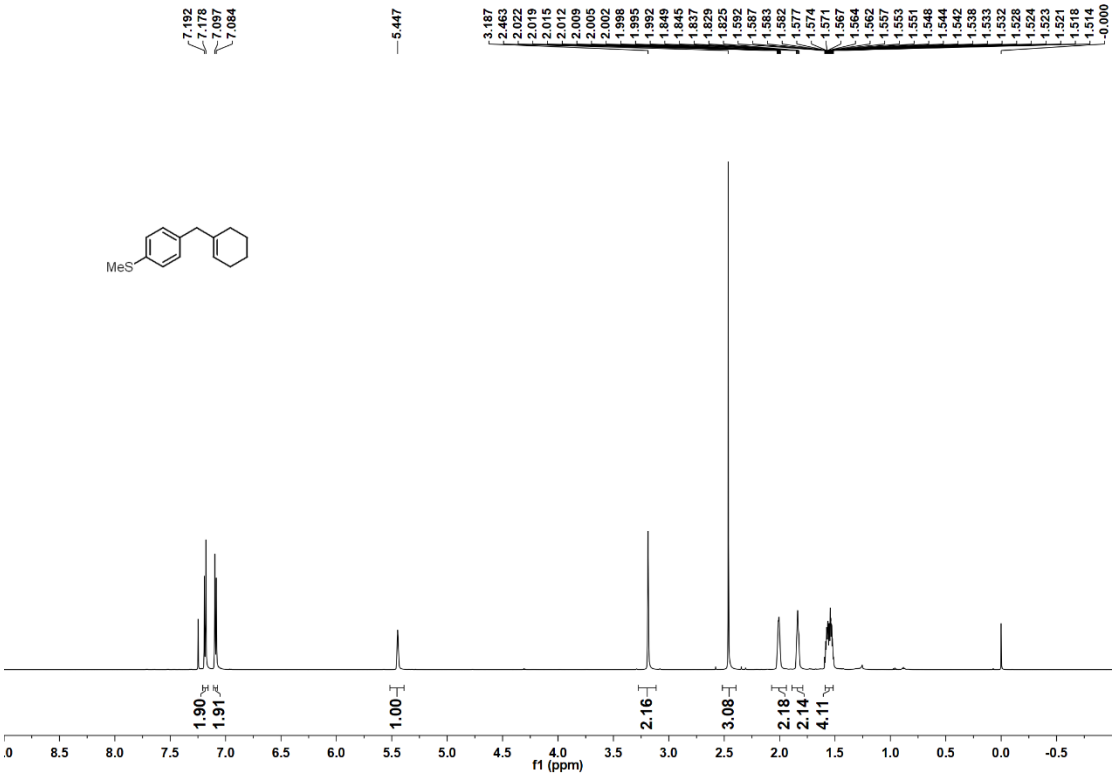
1ai, ^{19}F NMR (600 MHz, $CDCl_3$)

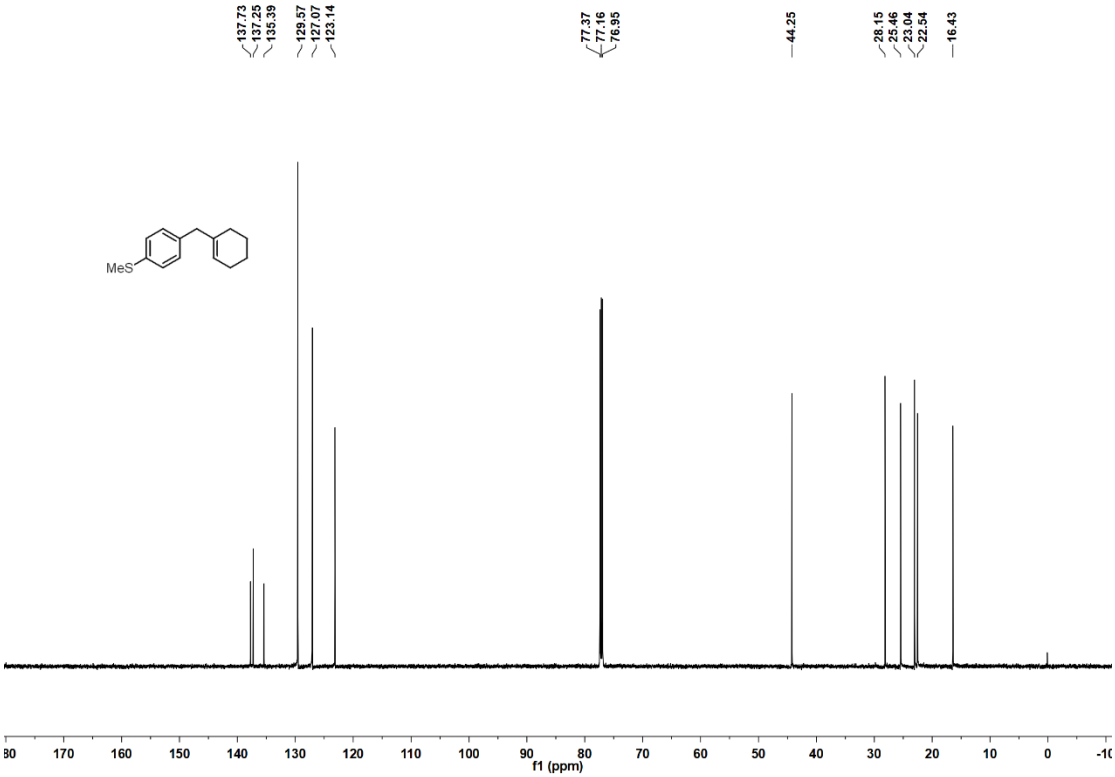


1aj, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

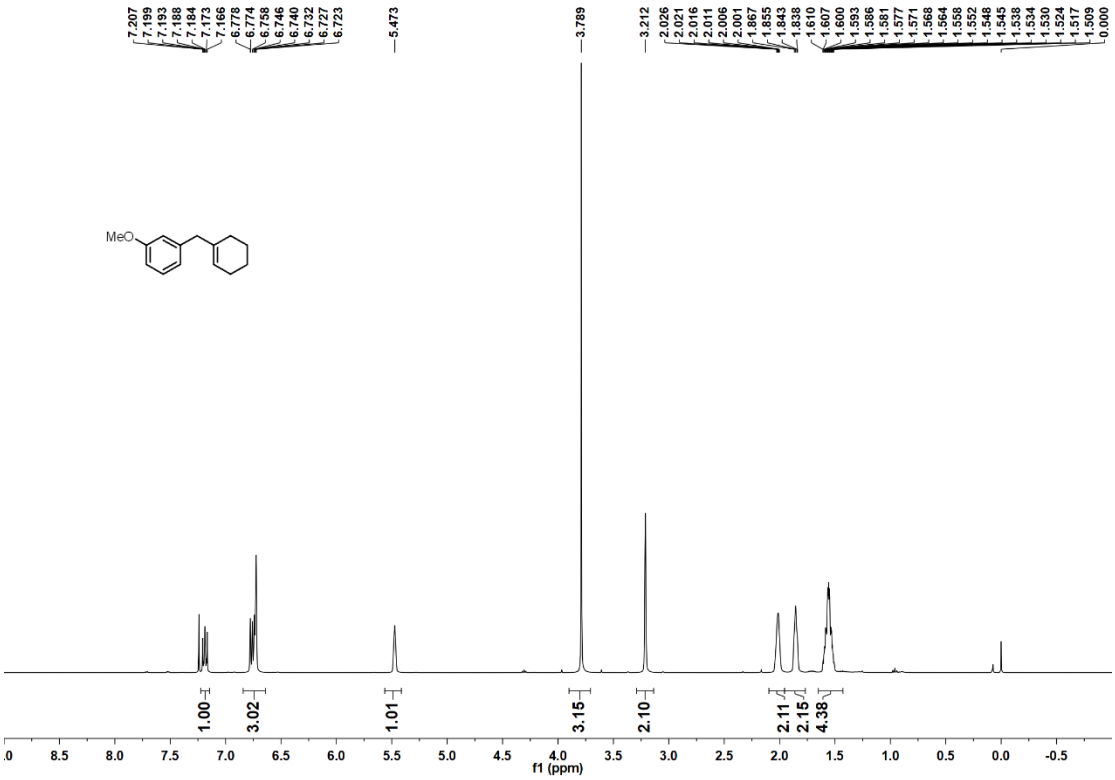


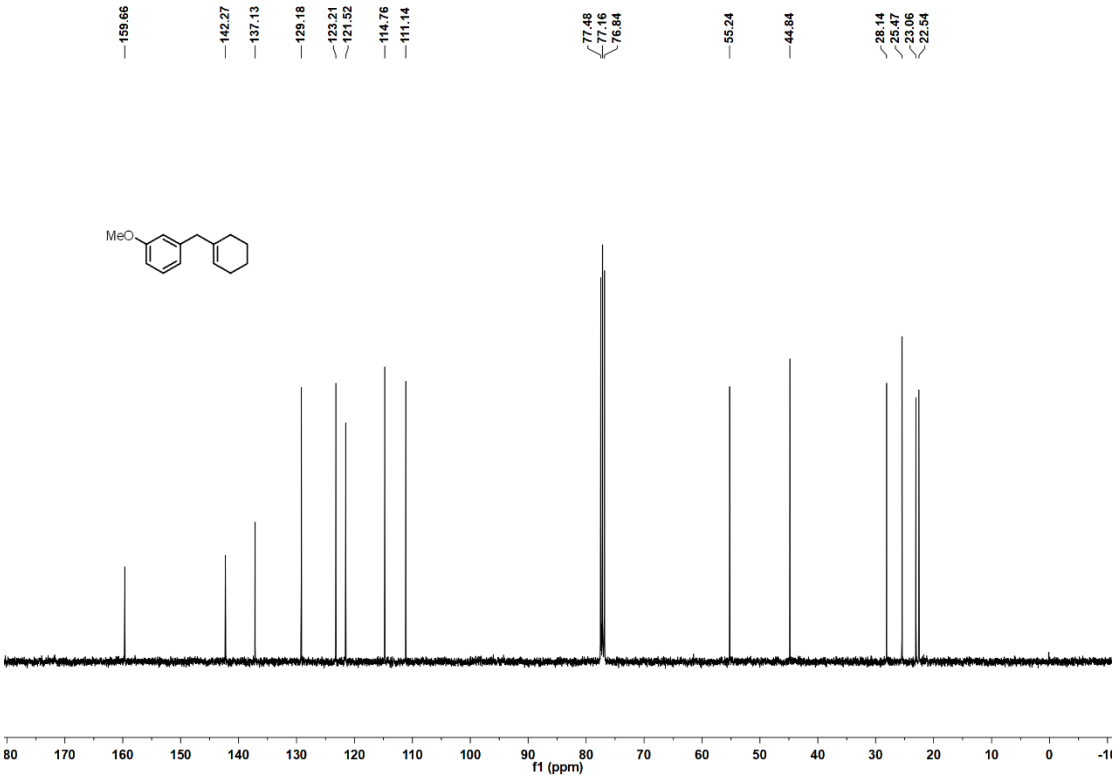
3a, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)



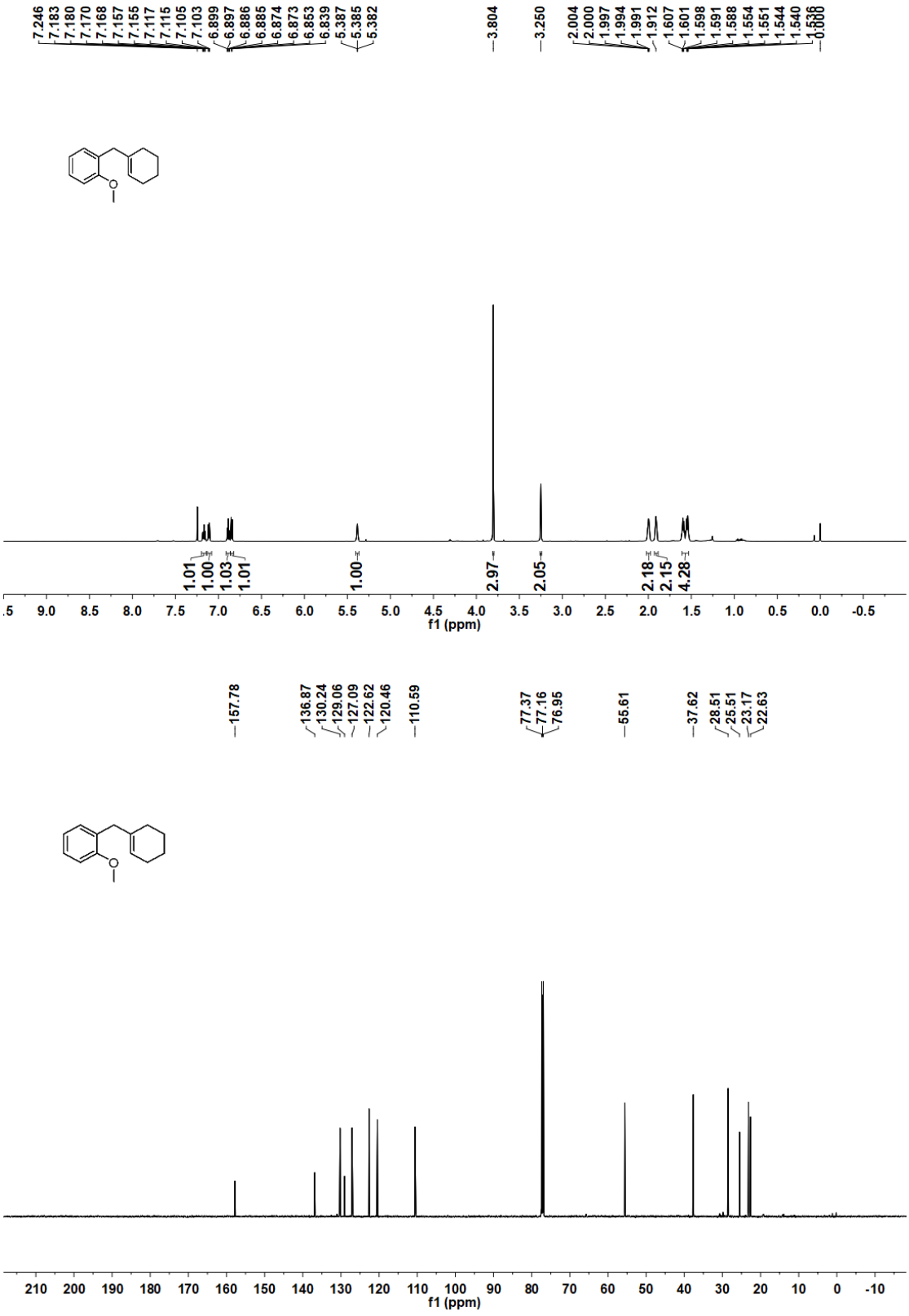


3d, ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)

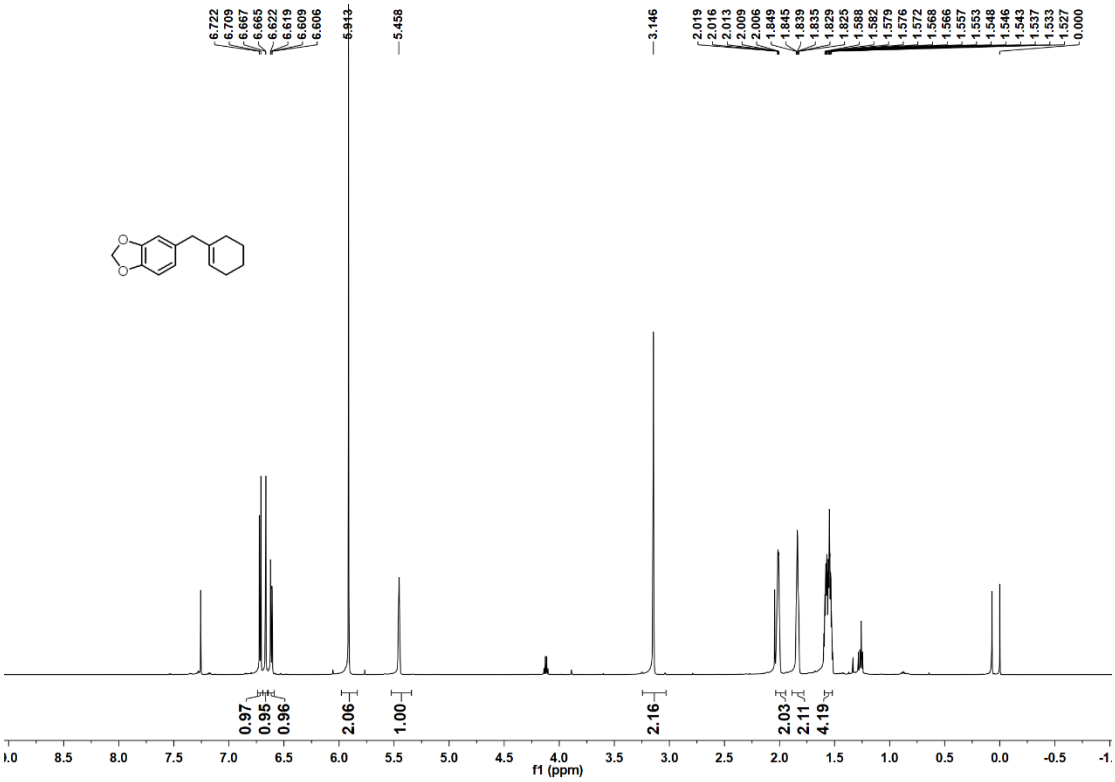


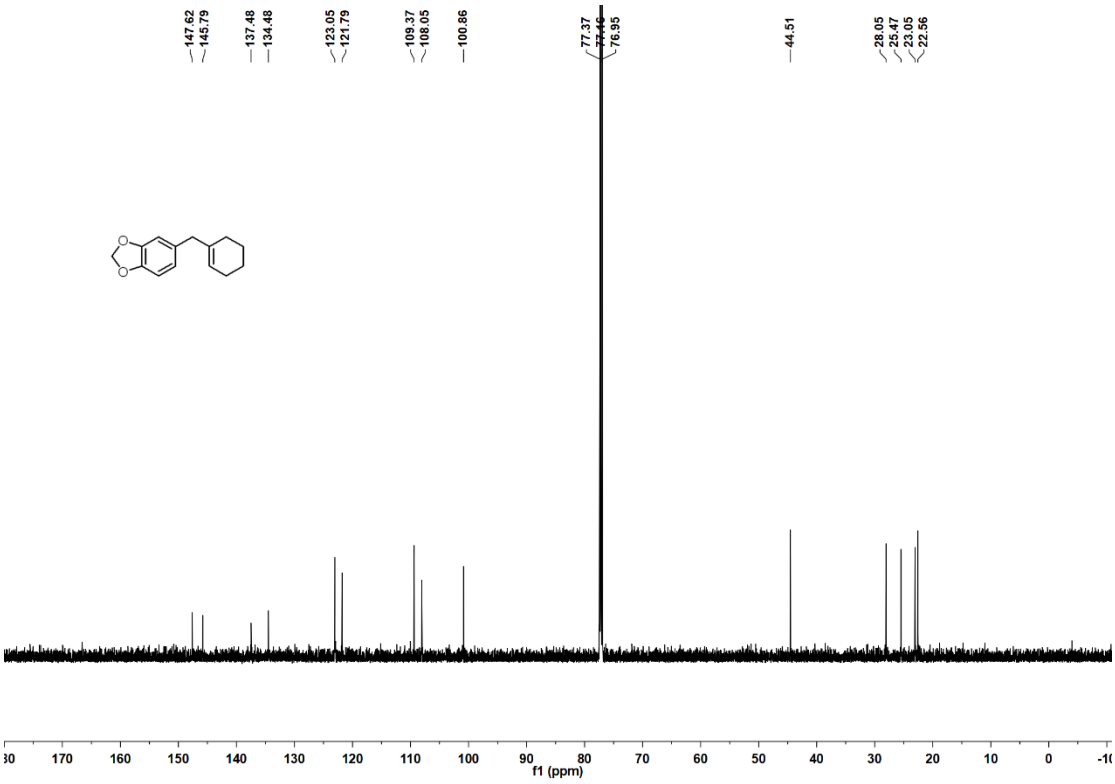


3e, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13} C NMR (150 MHz, $CDCl_3$)

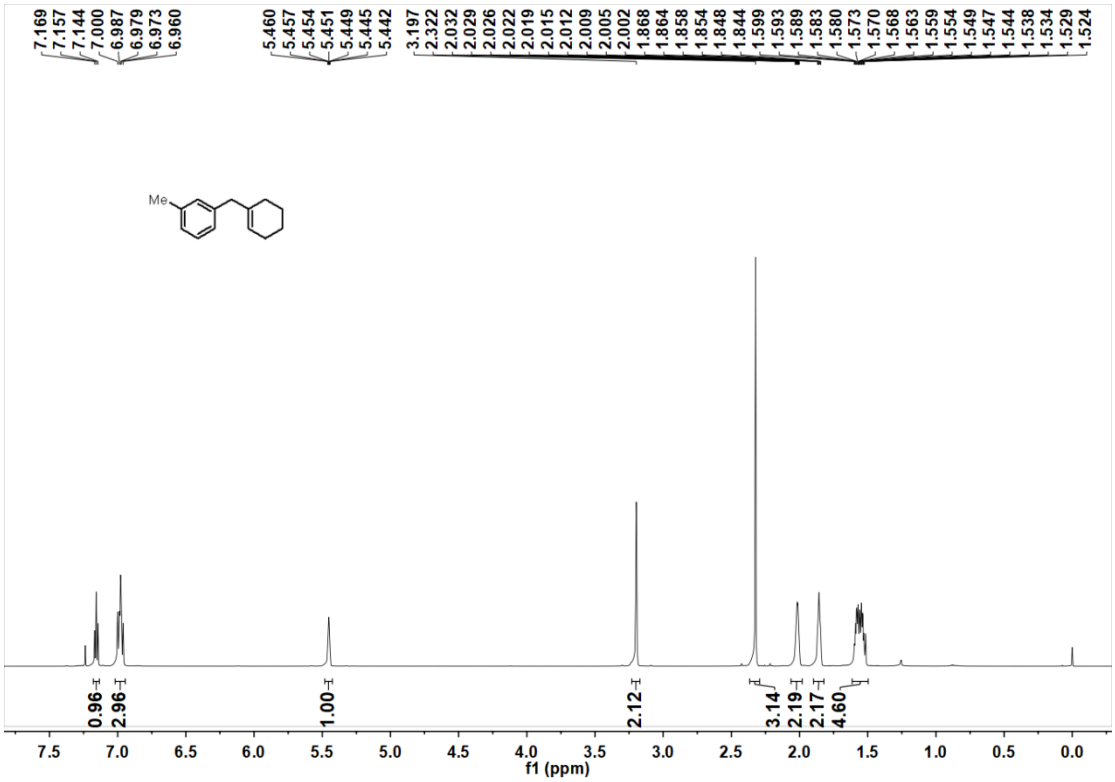


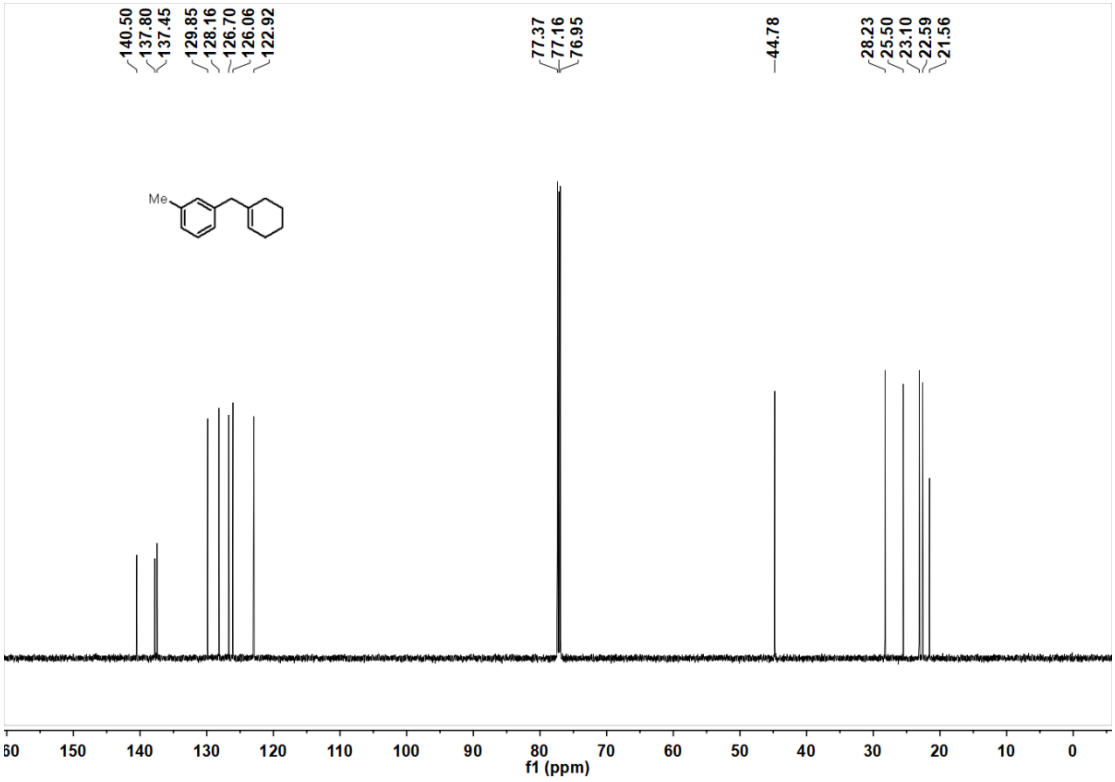
3f, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)



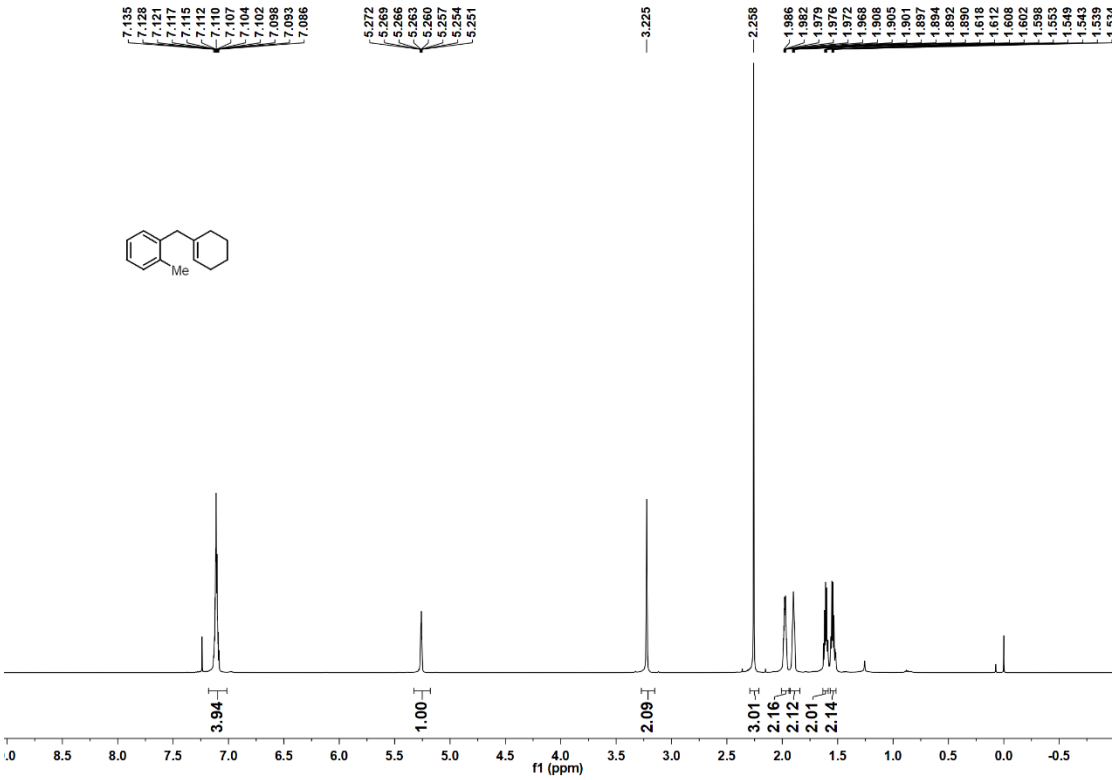


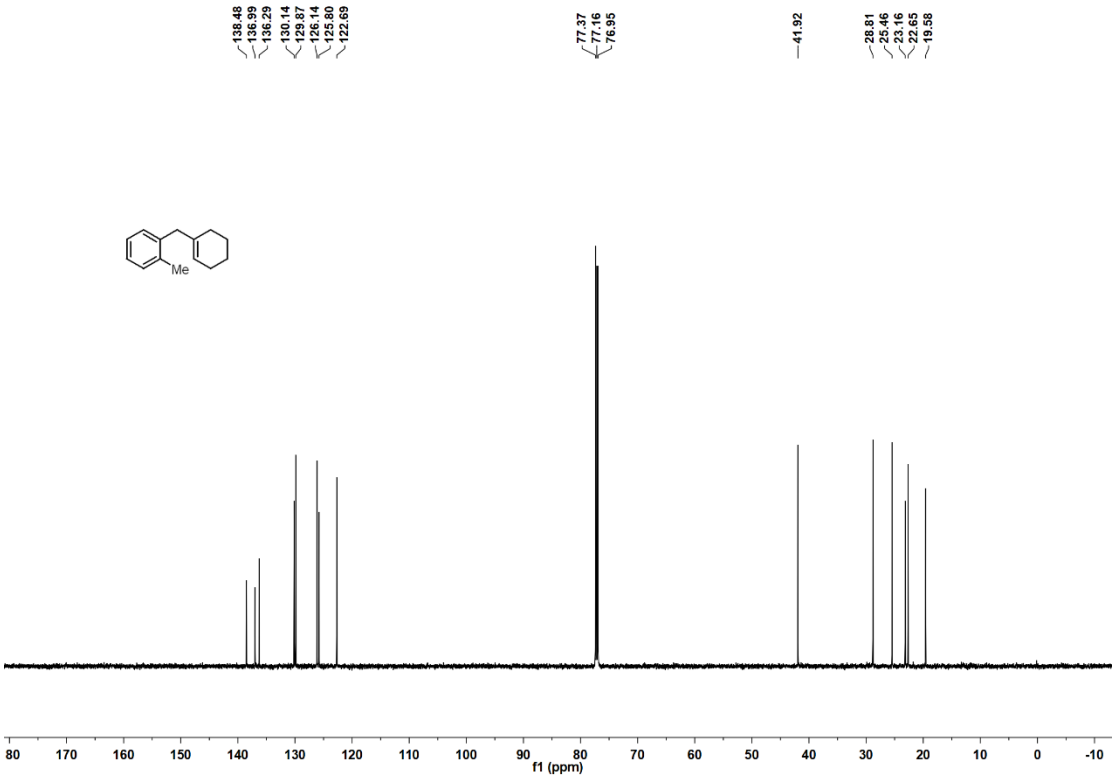
3g, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)



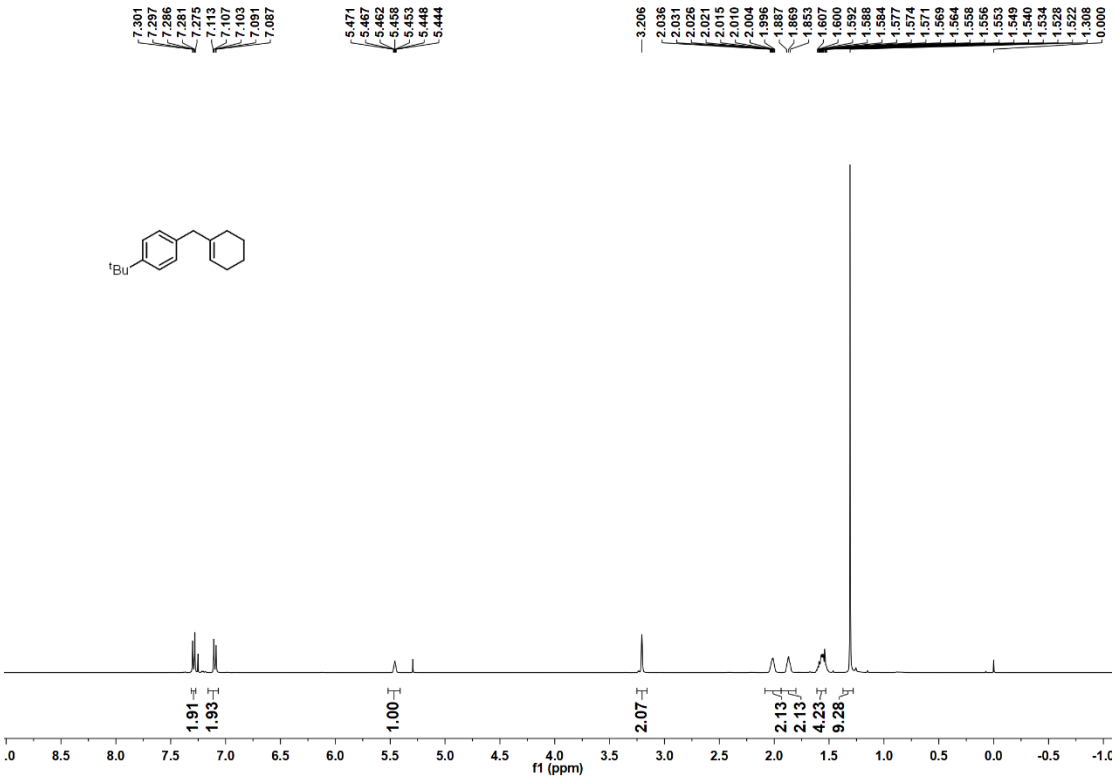


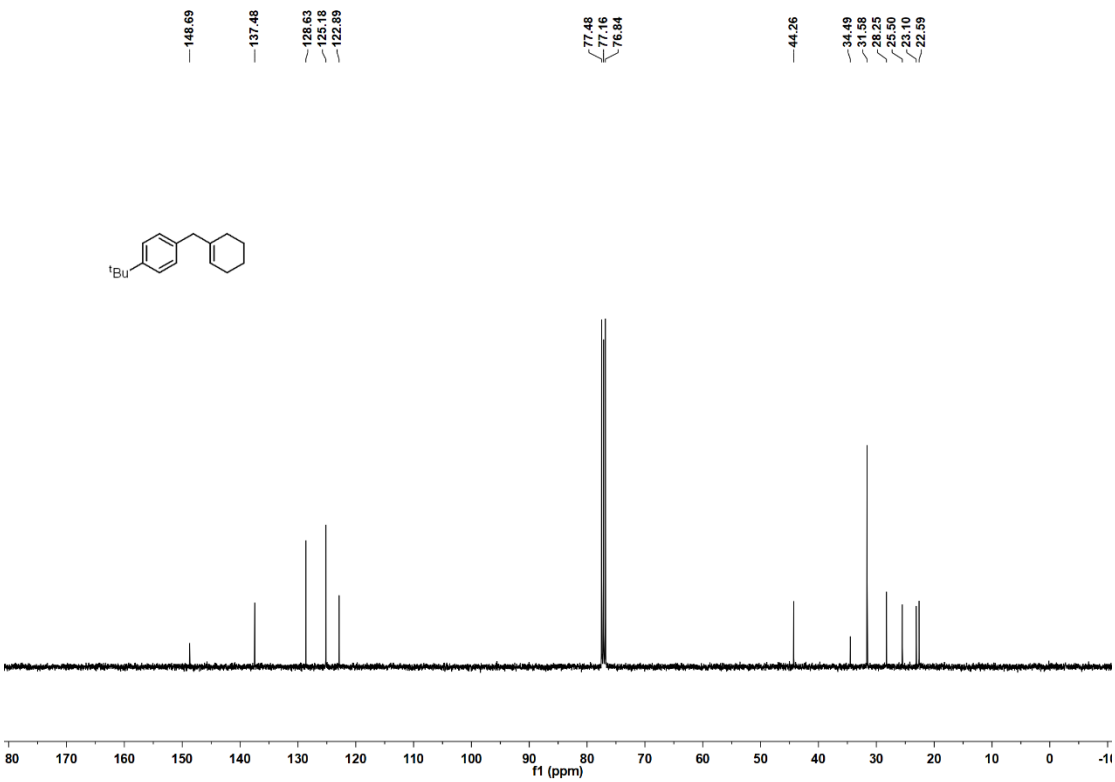
3h, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)



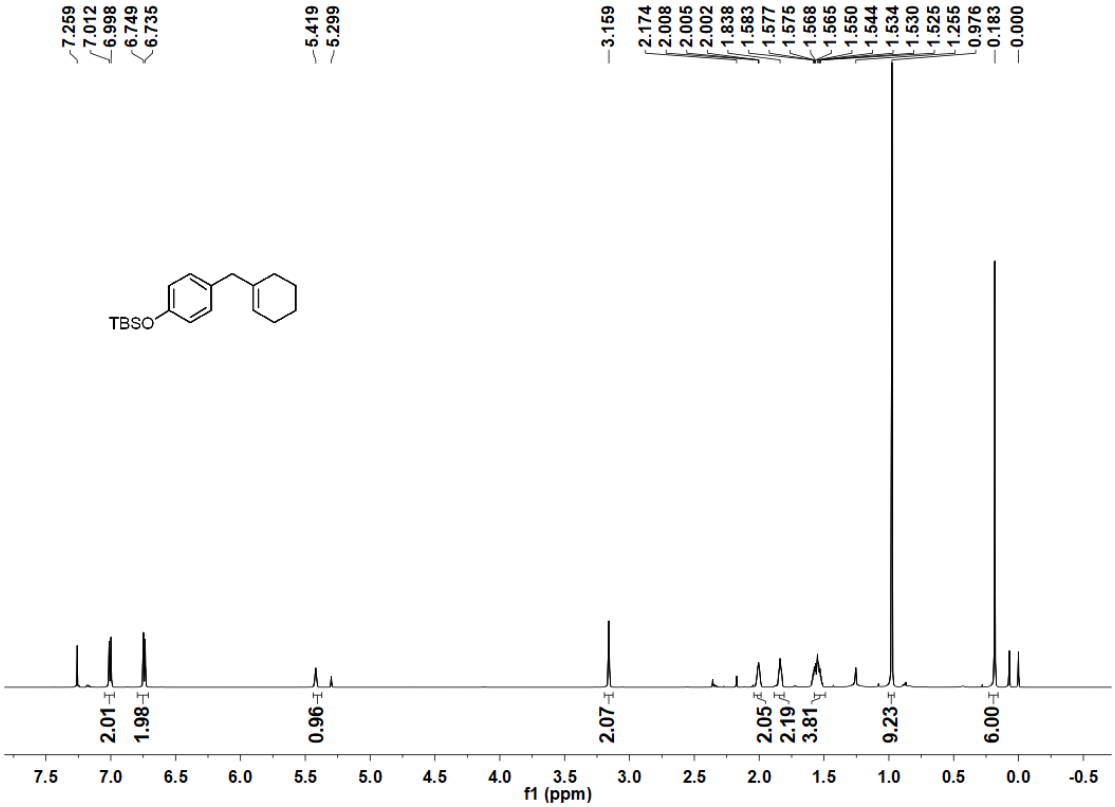


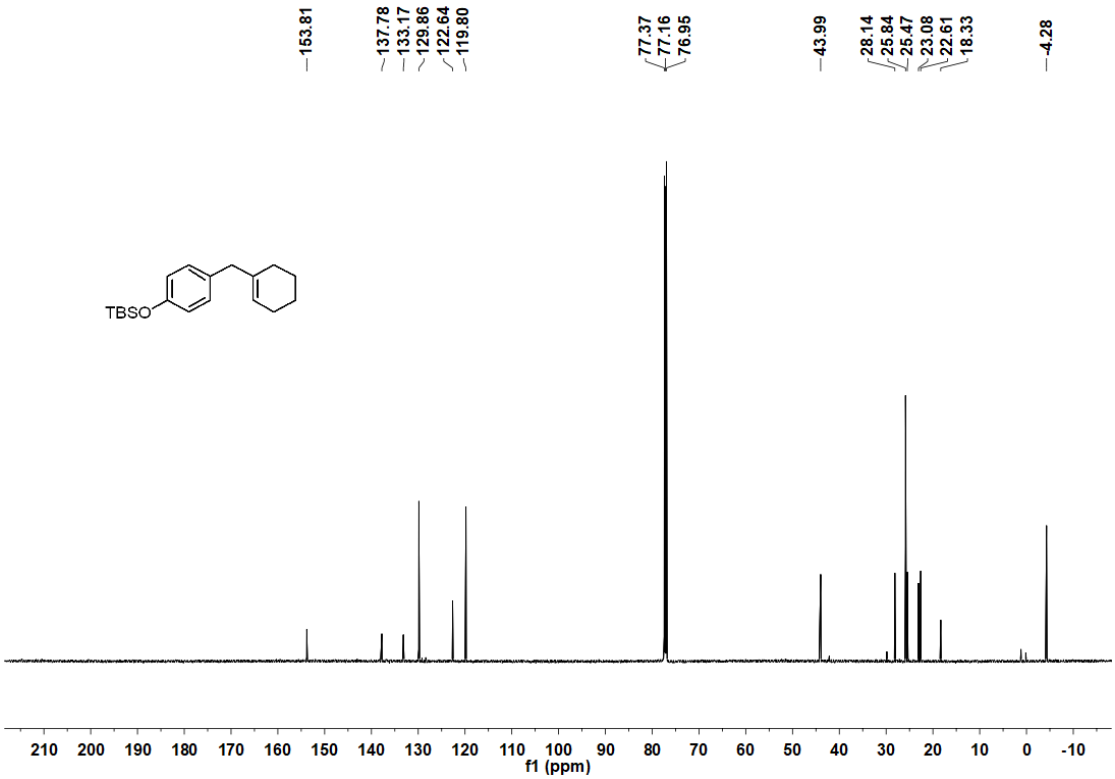
3i, ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)



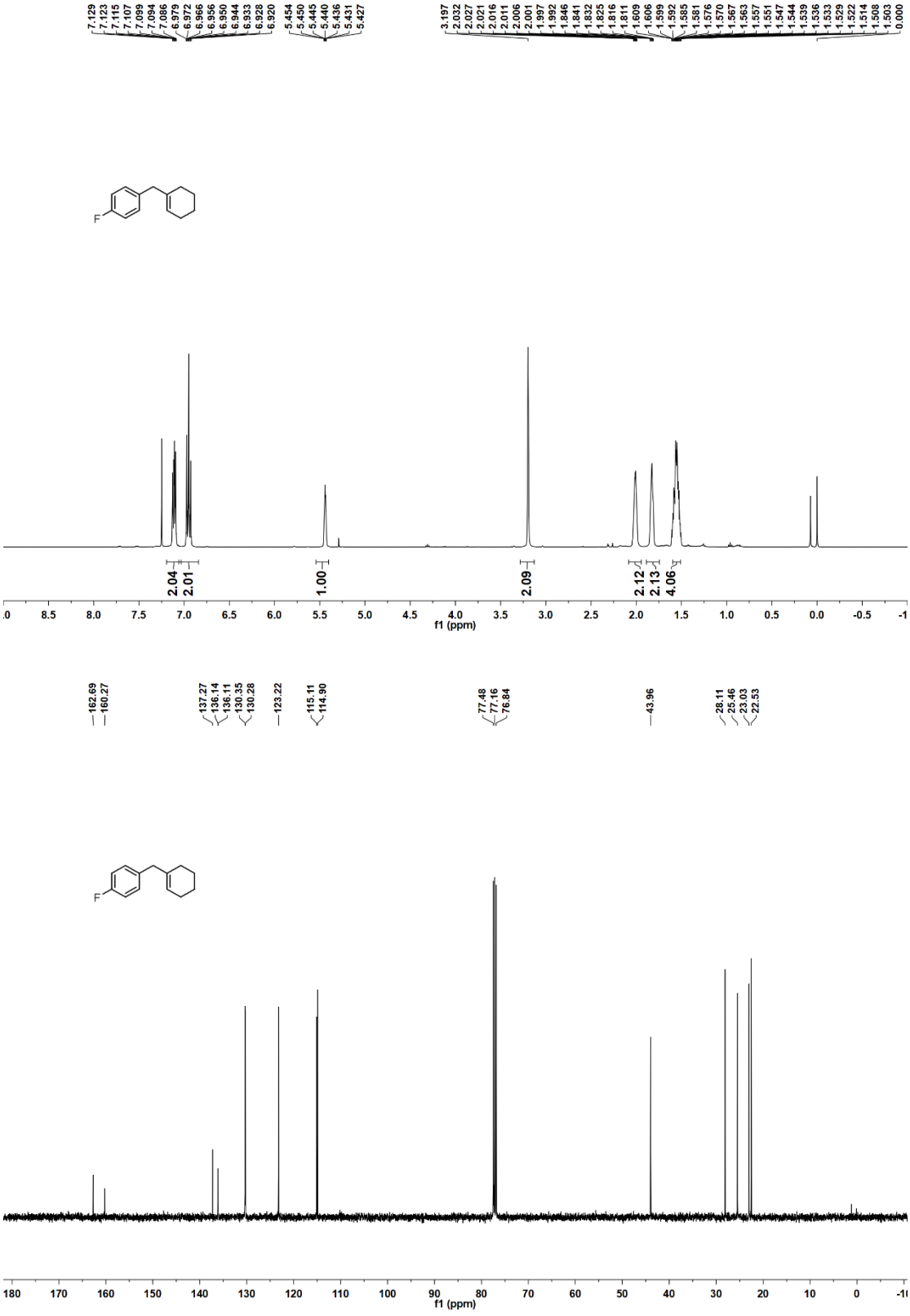


3j, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

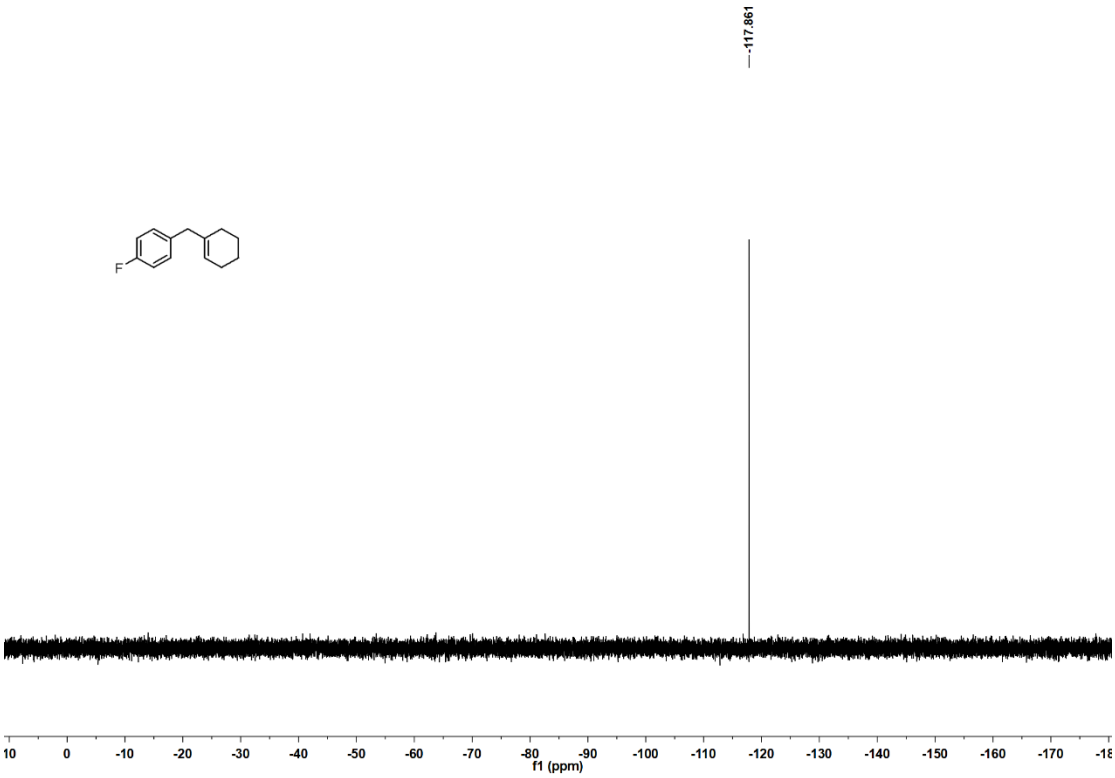




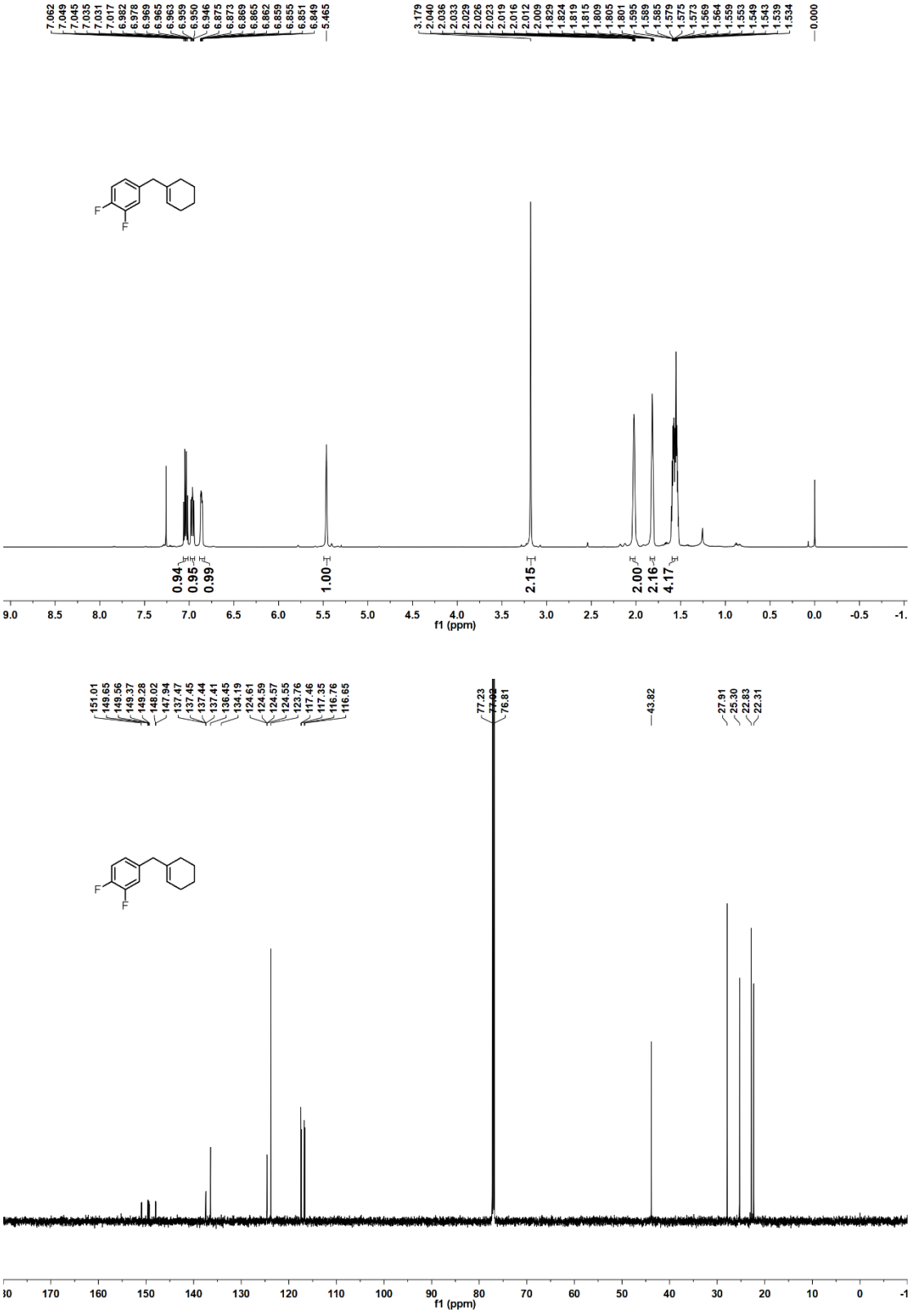
3k, ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)



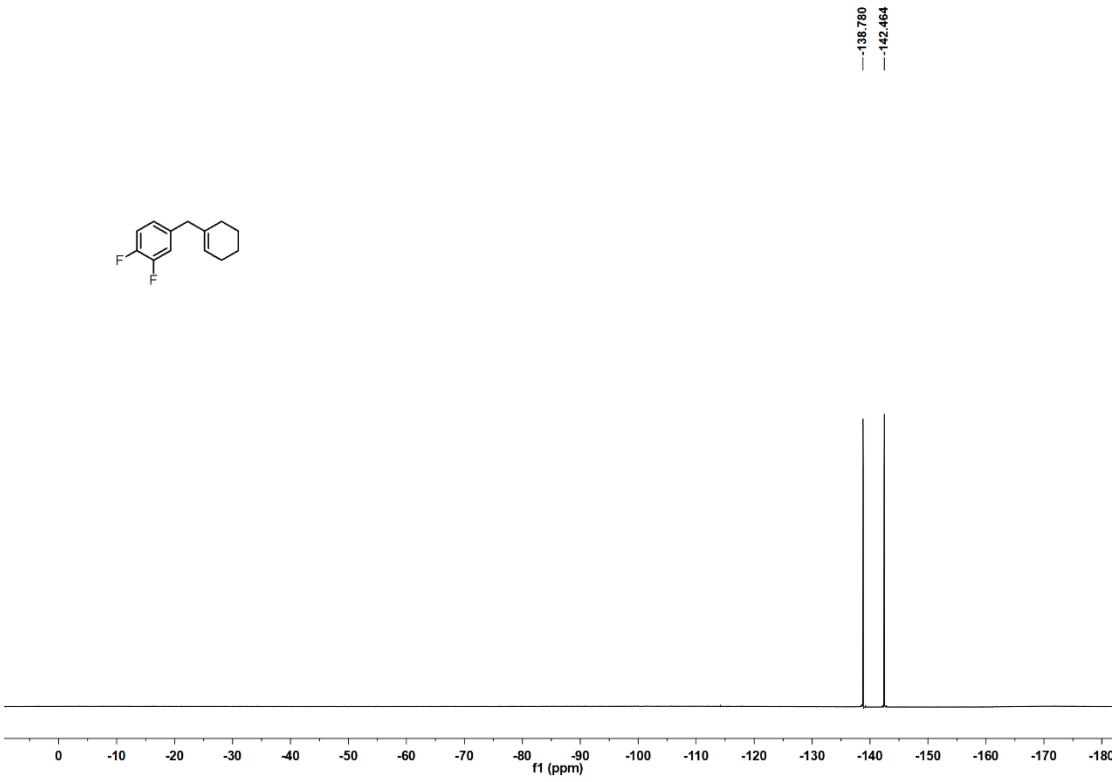
3k, ^{19}F NMR (376 MHz, $CDCl_3$)



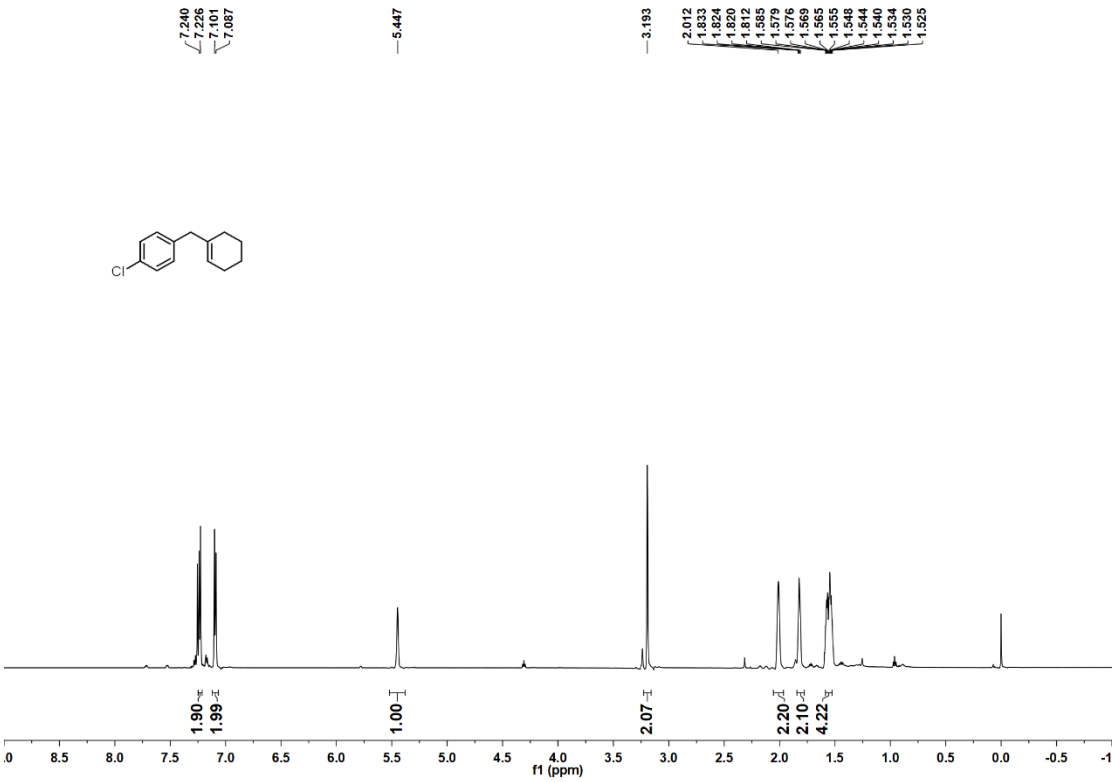
3l, ^{1}H NMR (600 MHz, $CDCl_3$), ^{13}C NMR (150 MHz, $CDCl_3$)

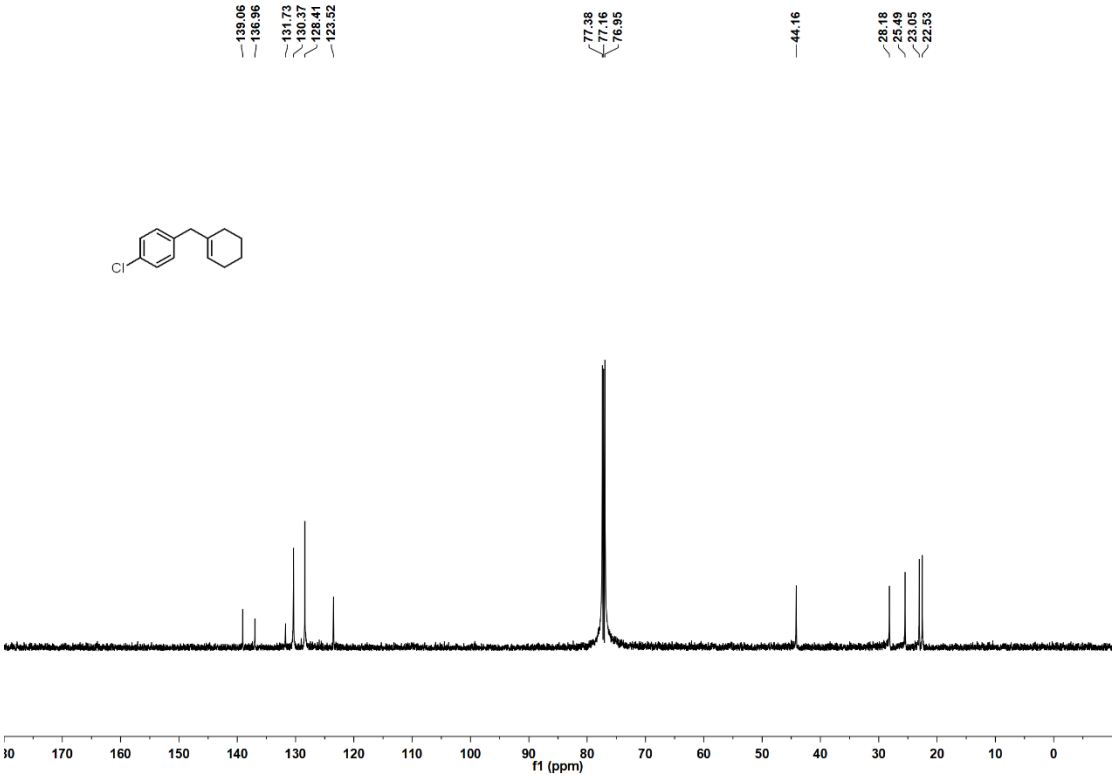


3l, ^{19}F NMR (376 MHz, $CDCl_3$)

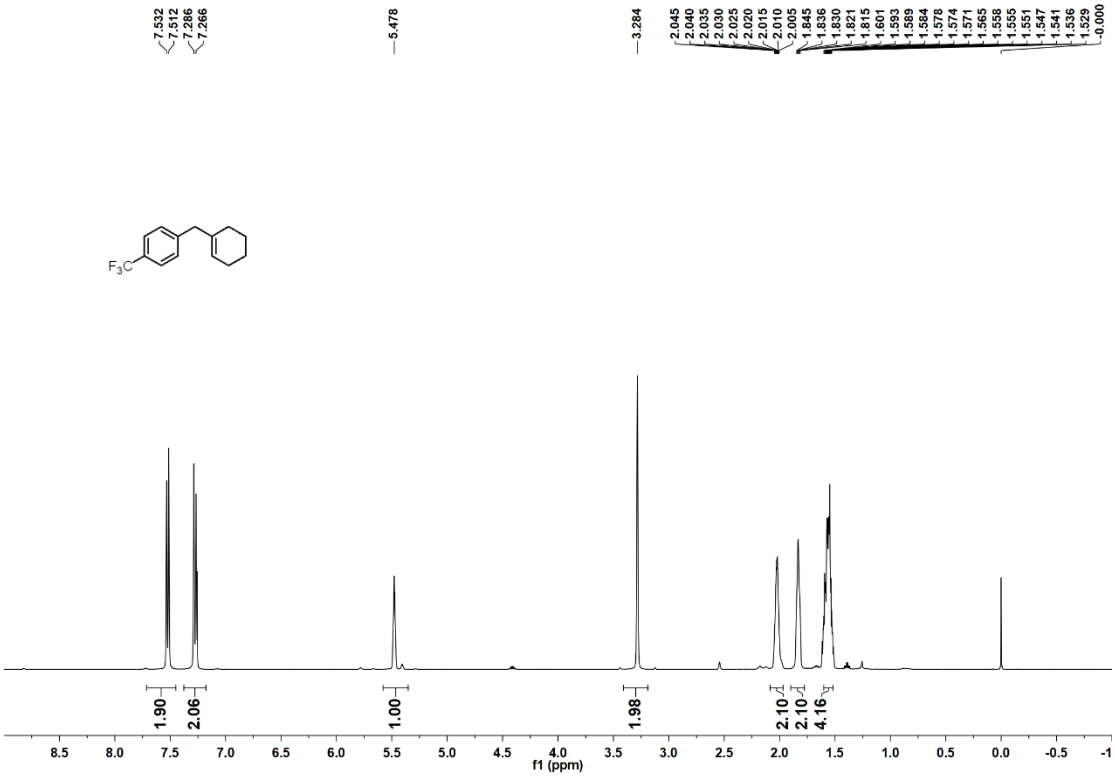


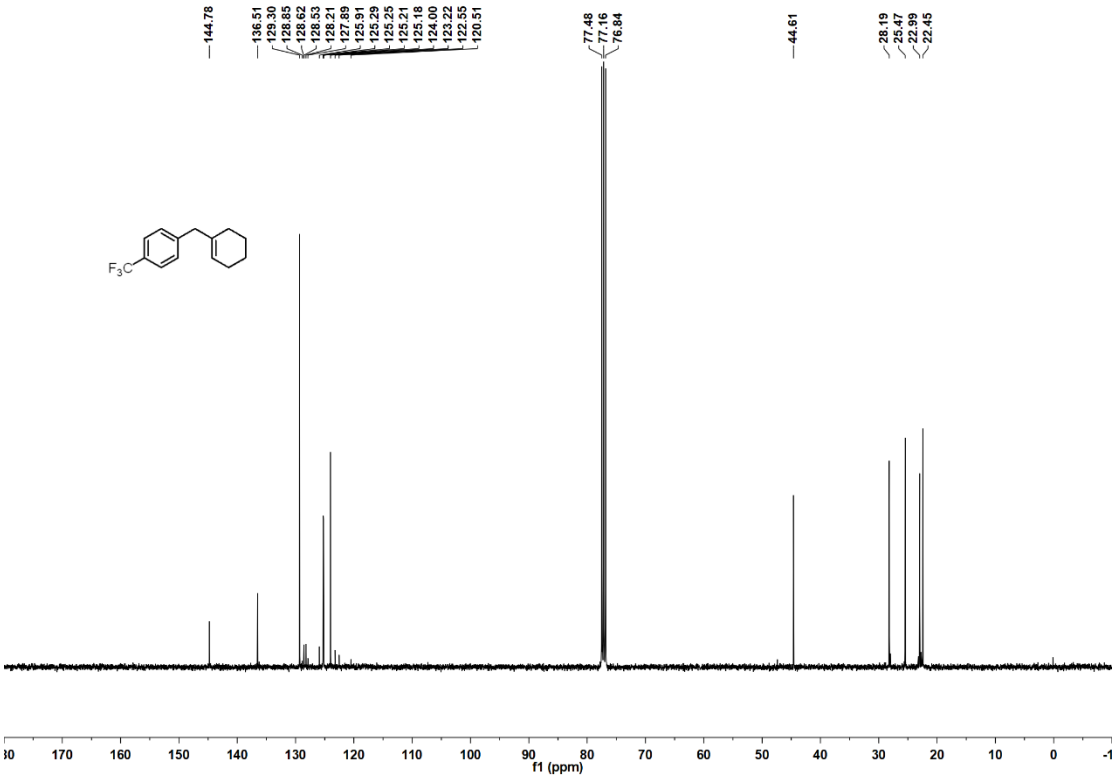
3m, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)



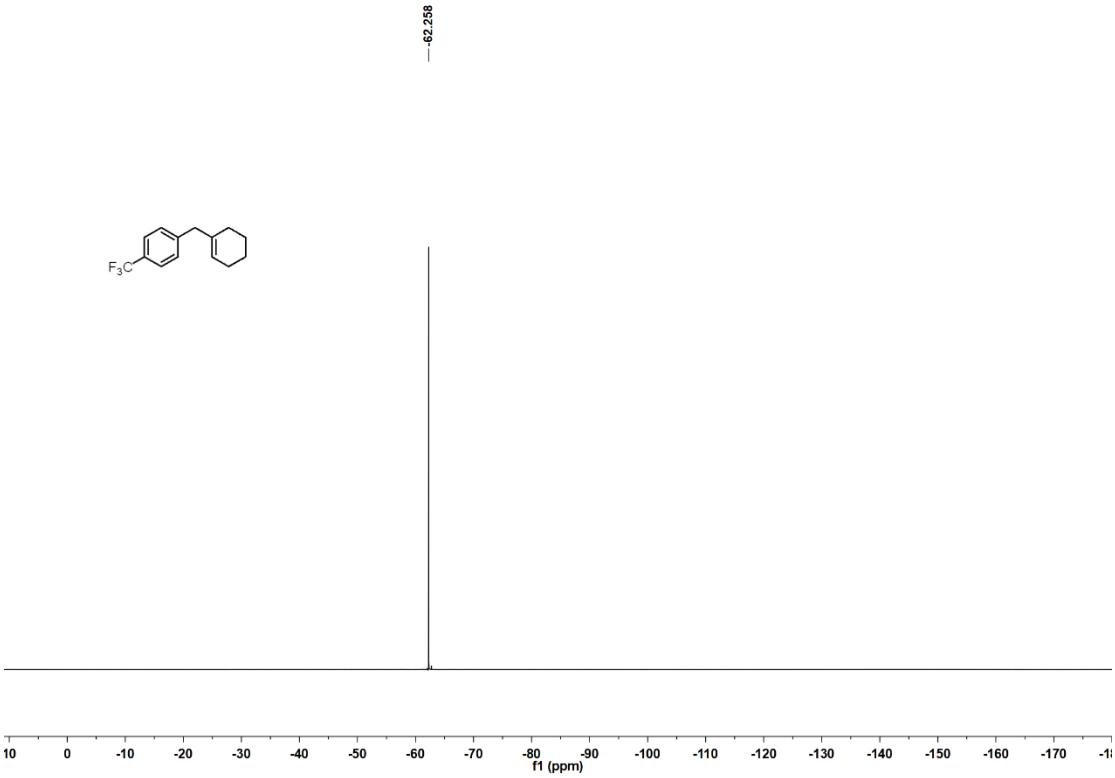


3n, ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)

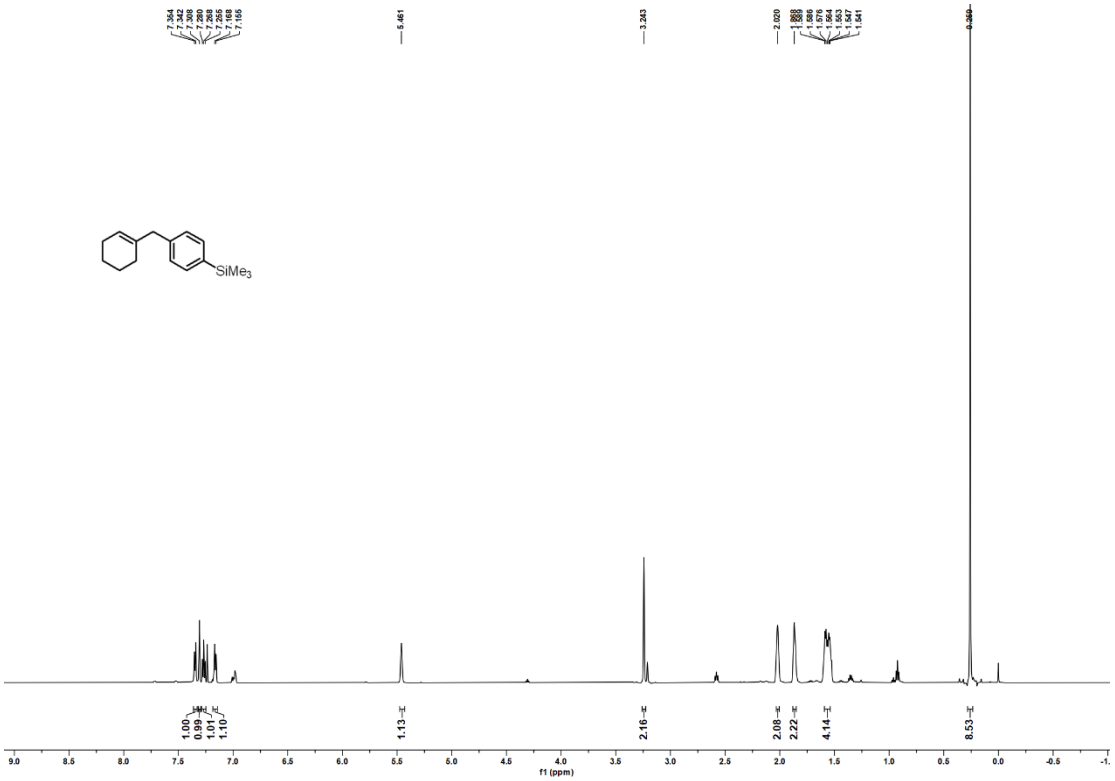


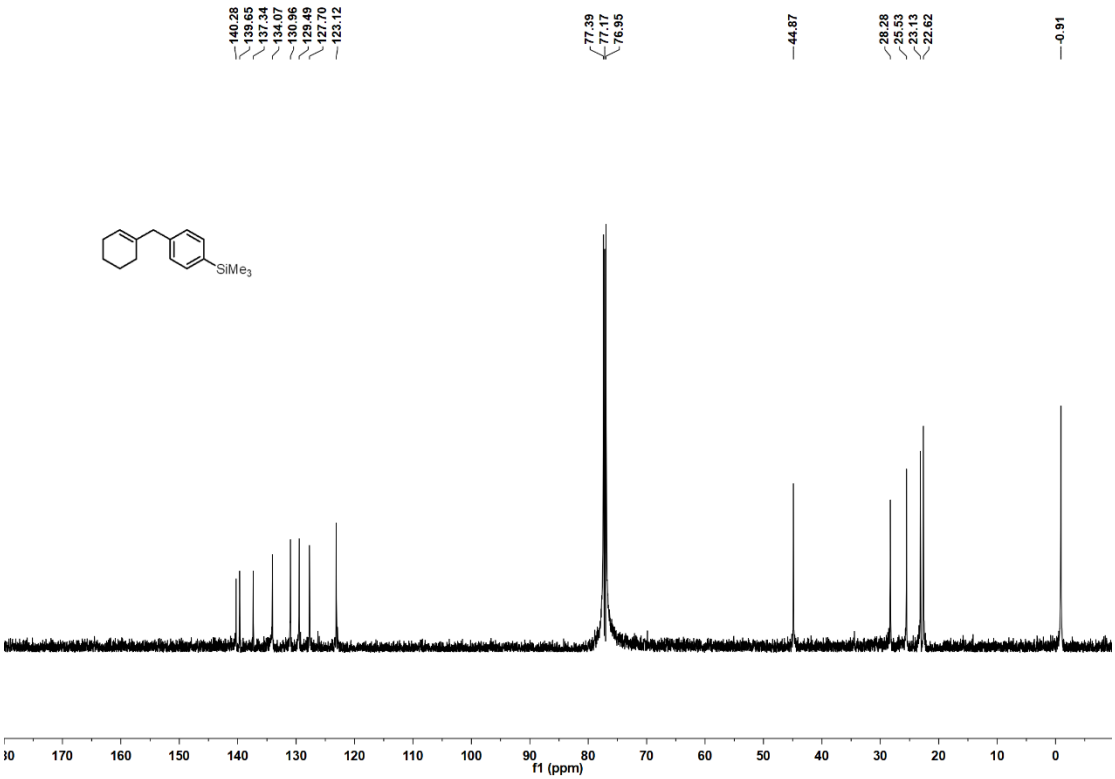


3n, ^{19}F NMR (376 MHz, $CDCl_3$)

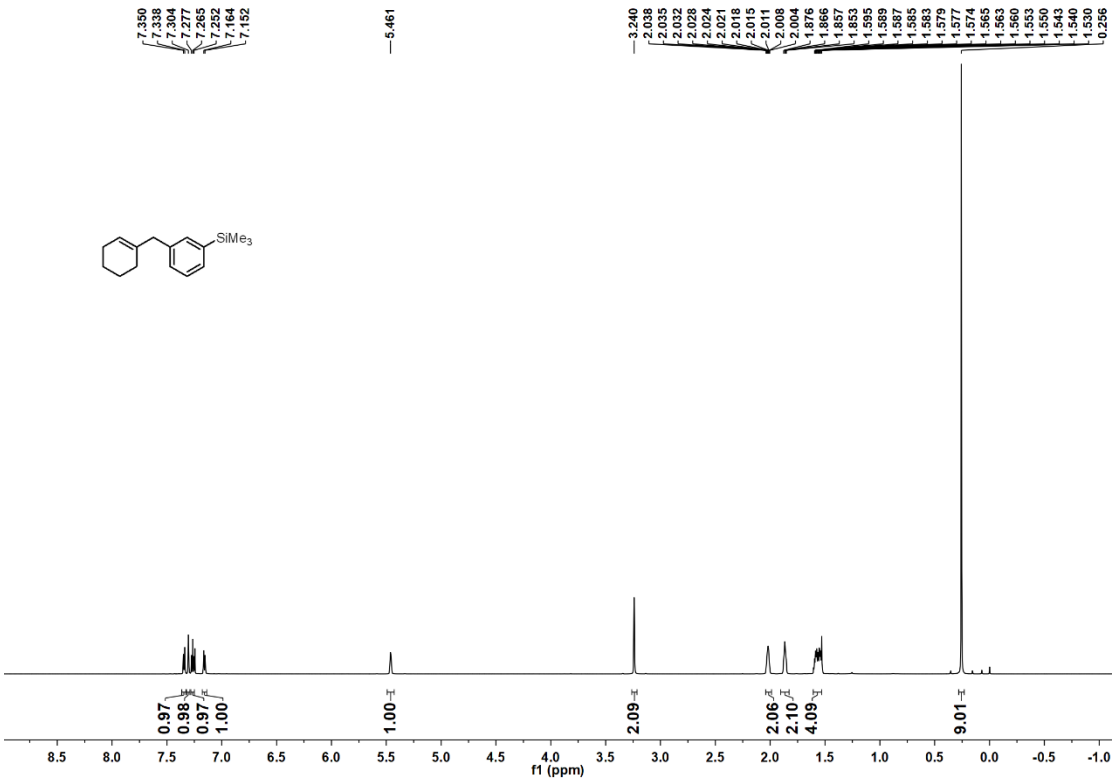


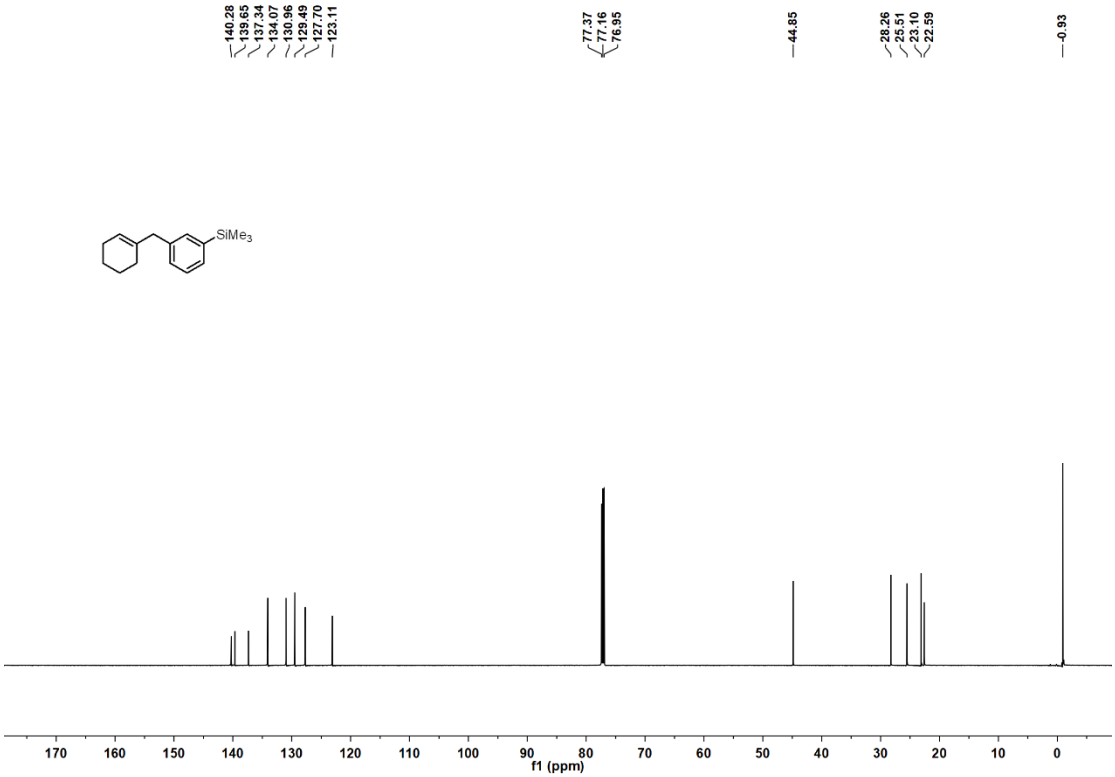
3p, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)



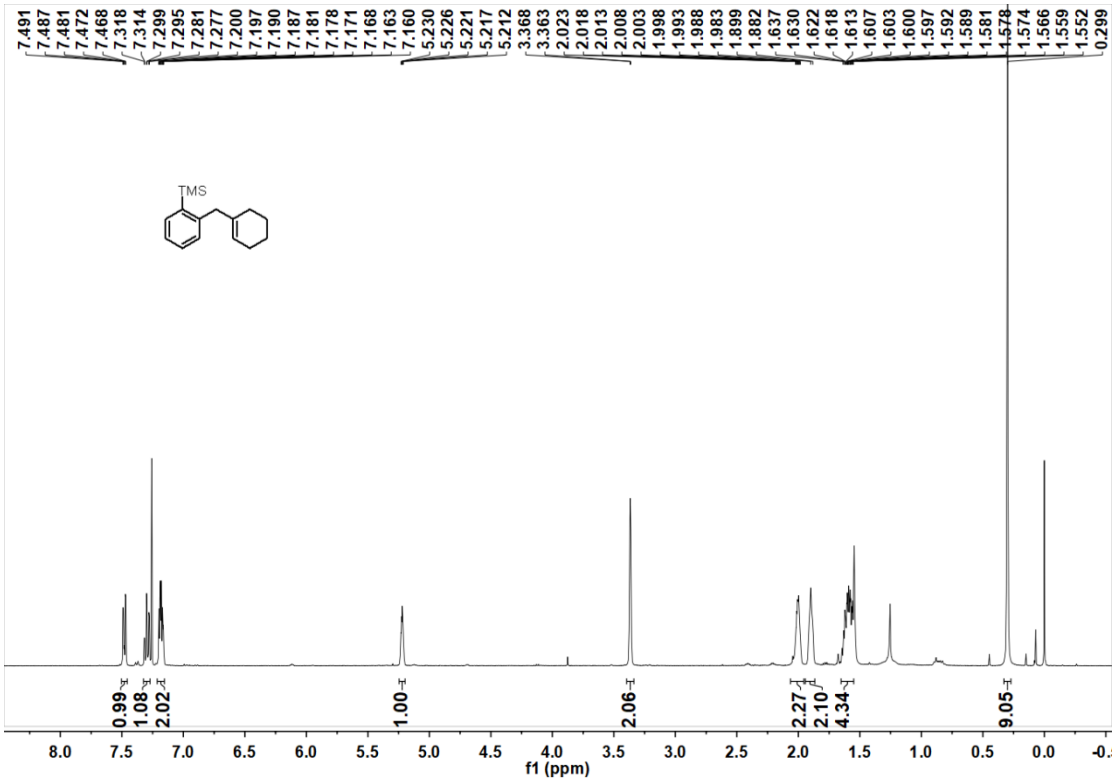


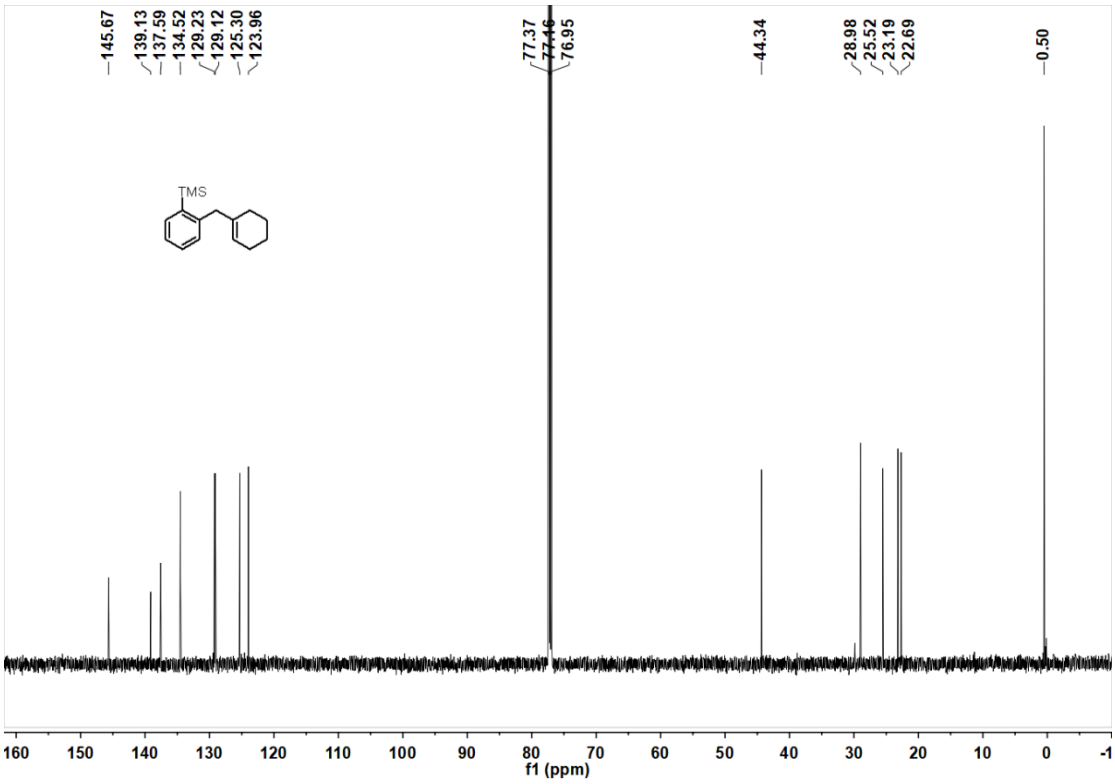
3q, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)



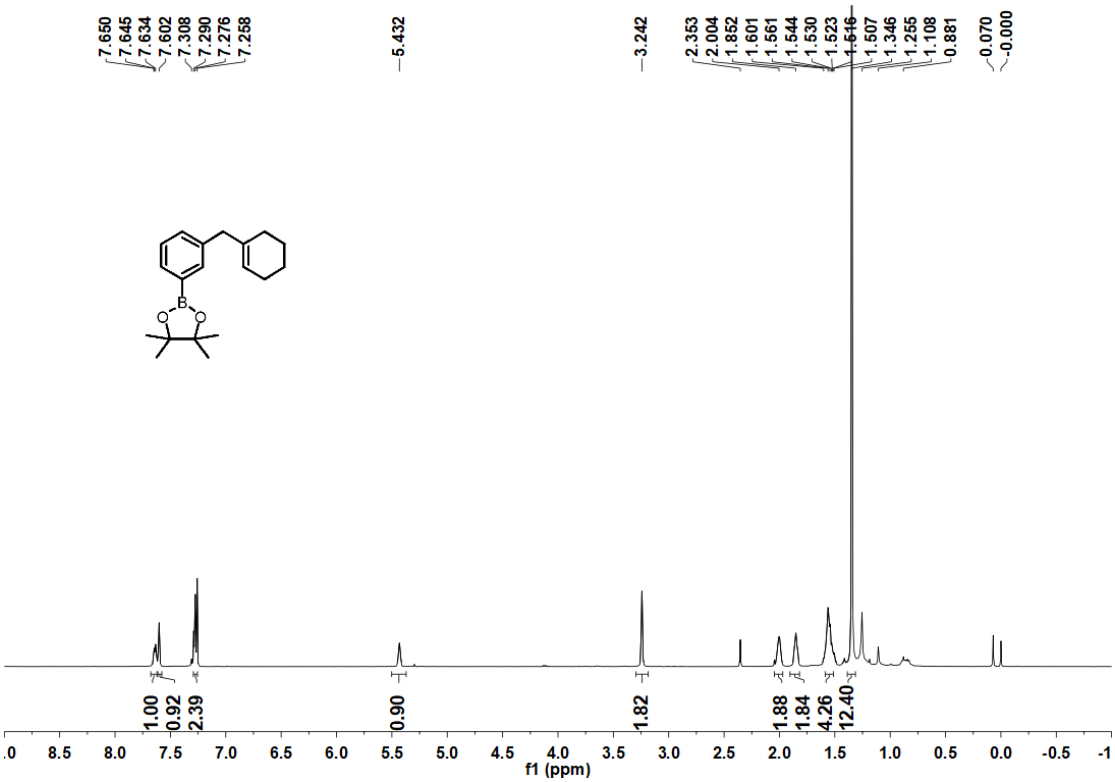


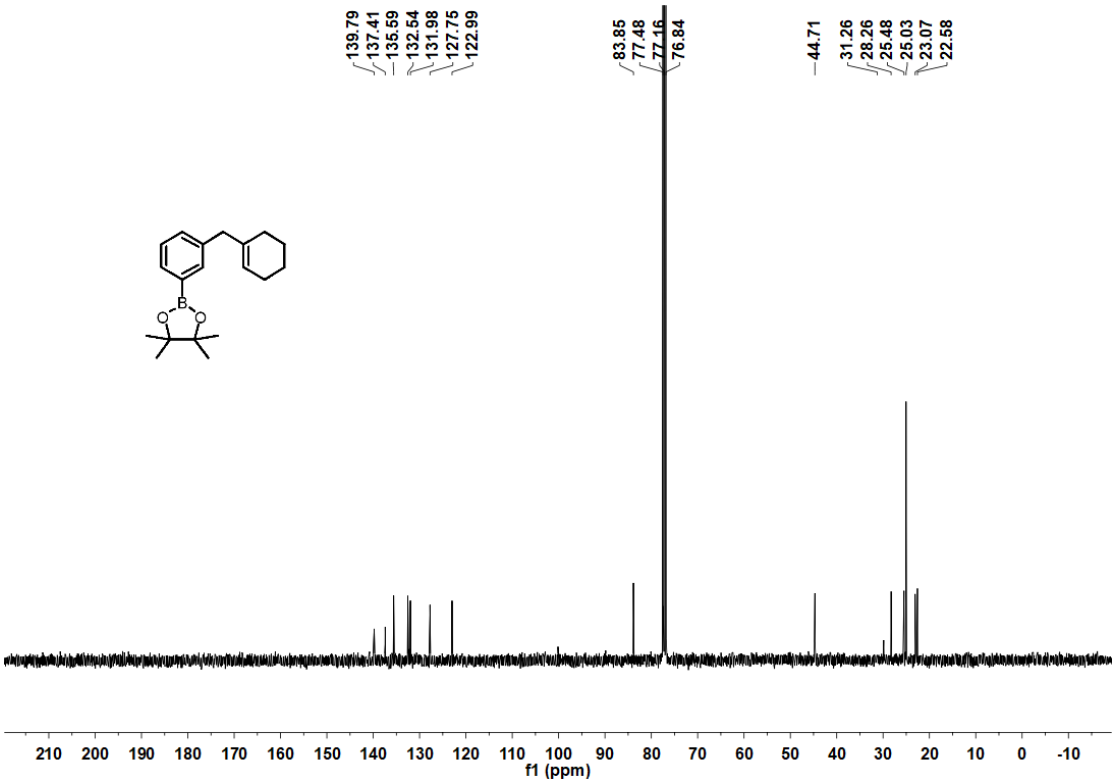
3r, ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)



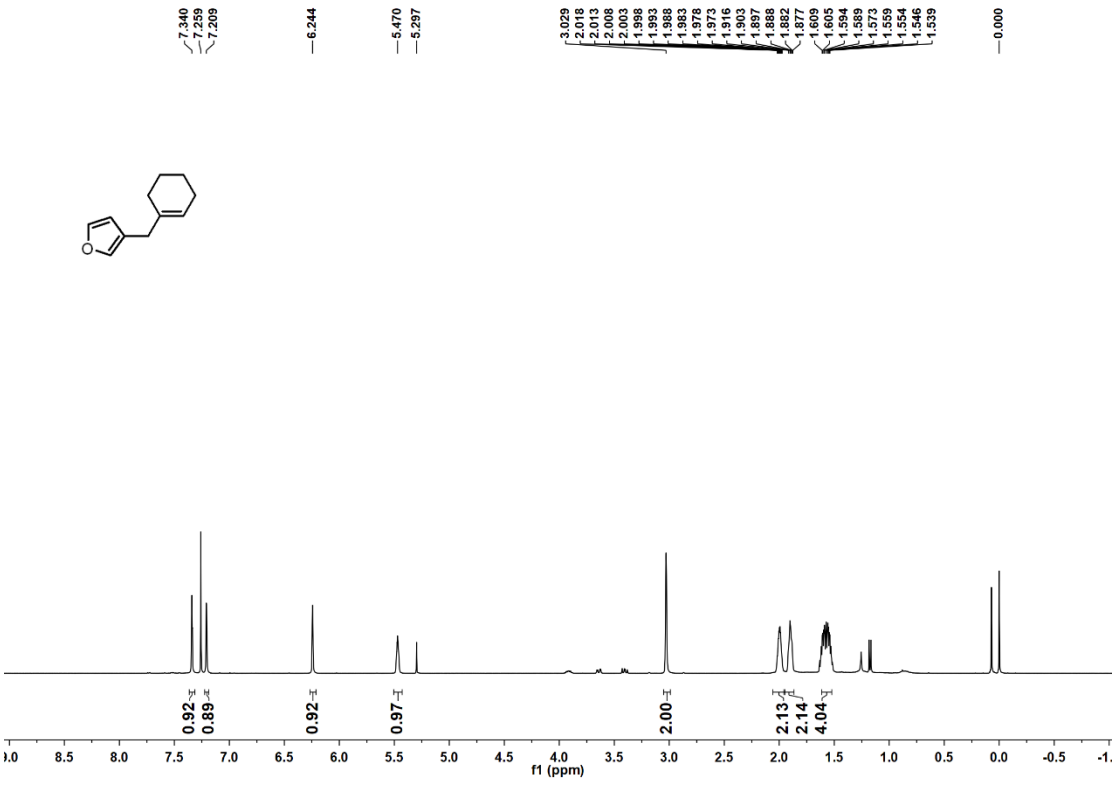


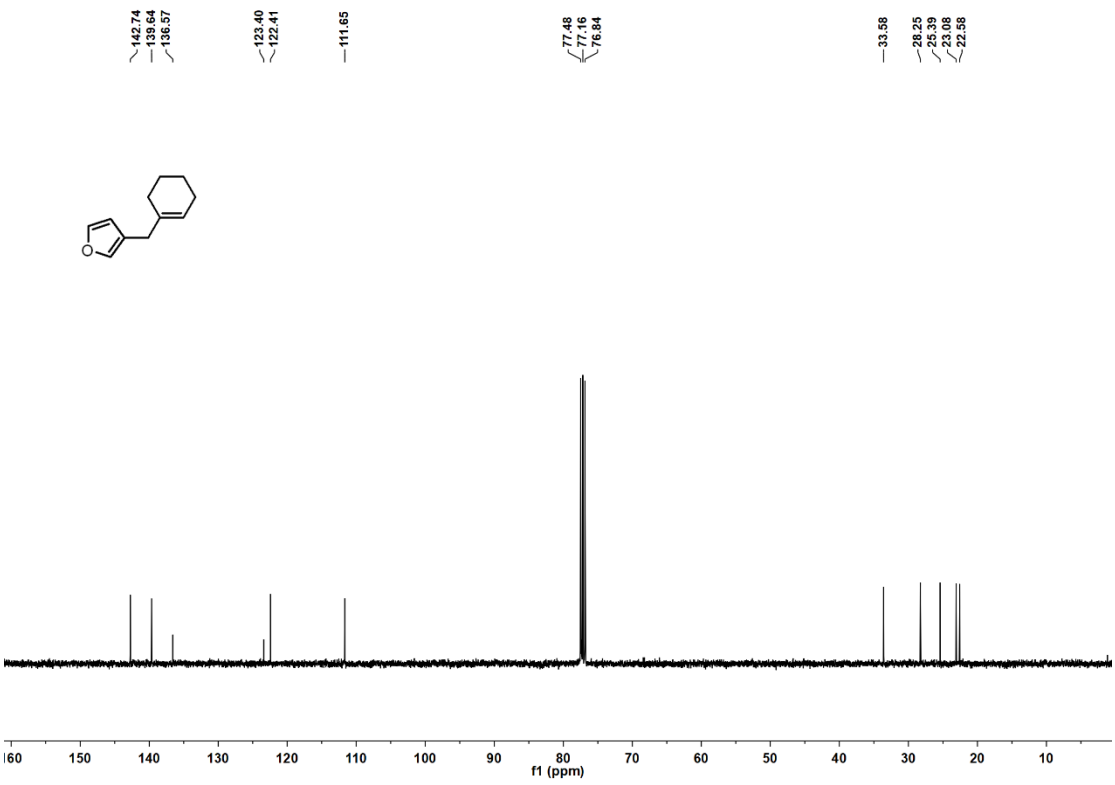
3s, ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)



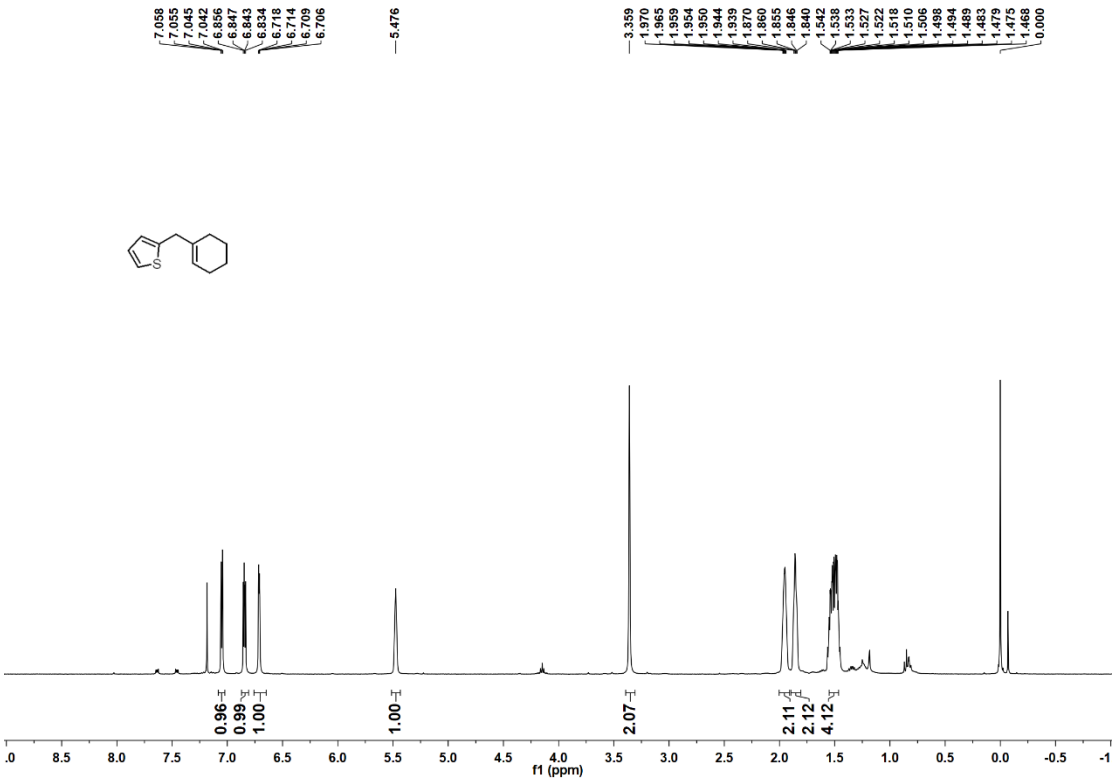


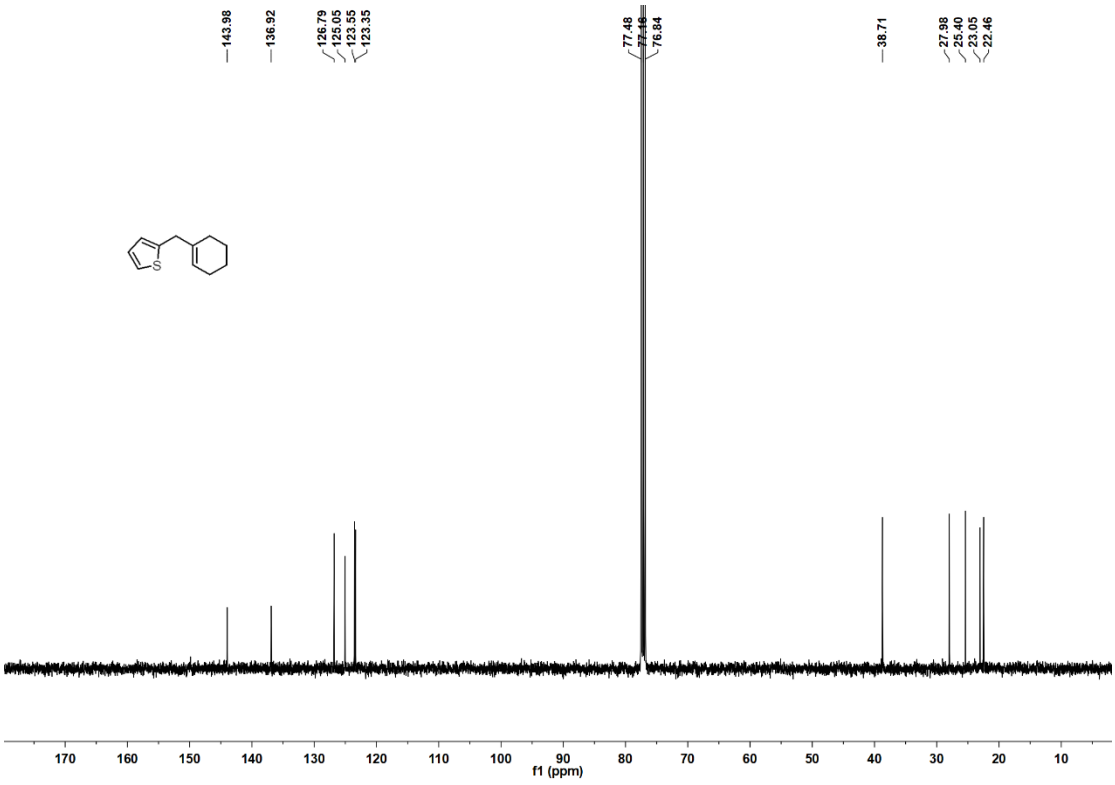
3t, ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)



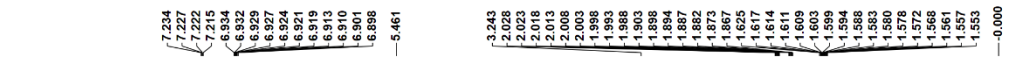


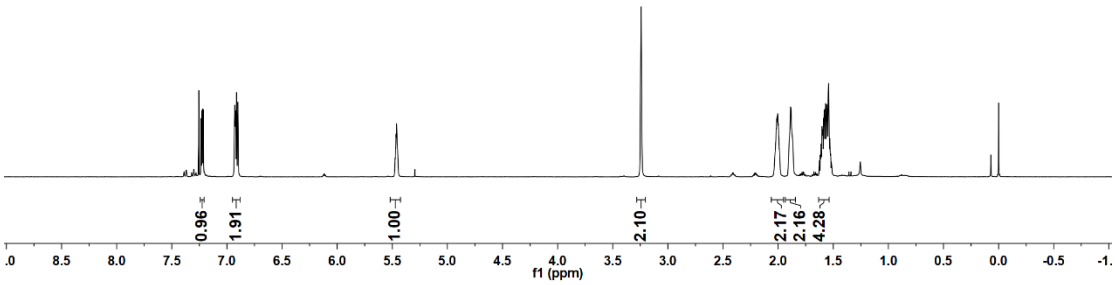
3u, ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)

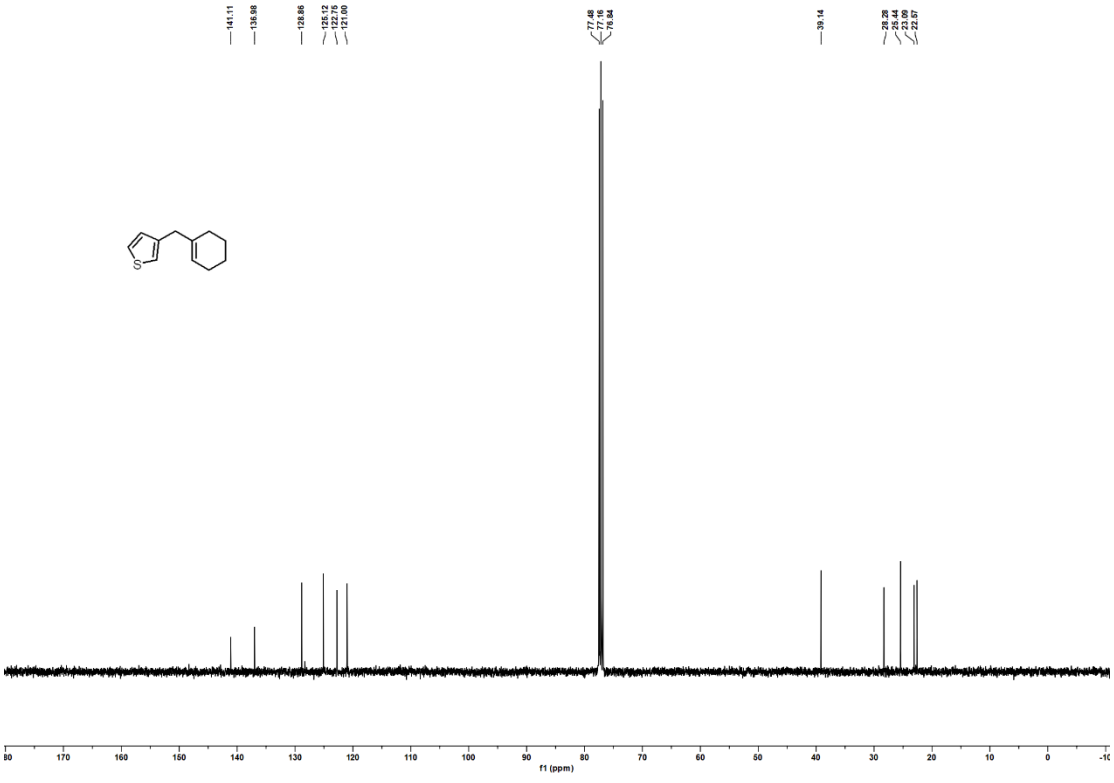




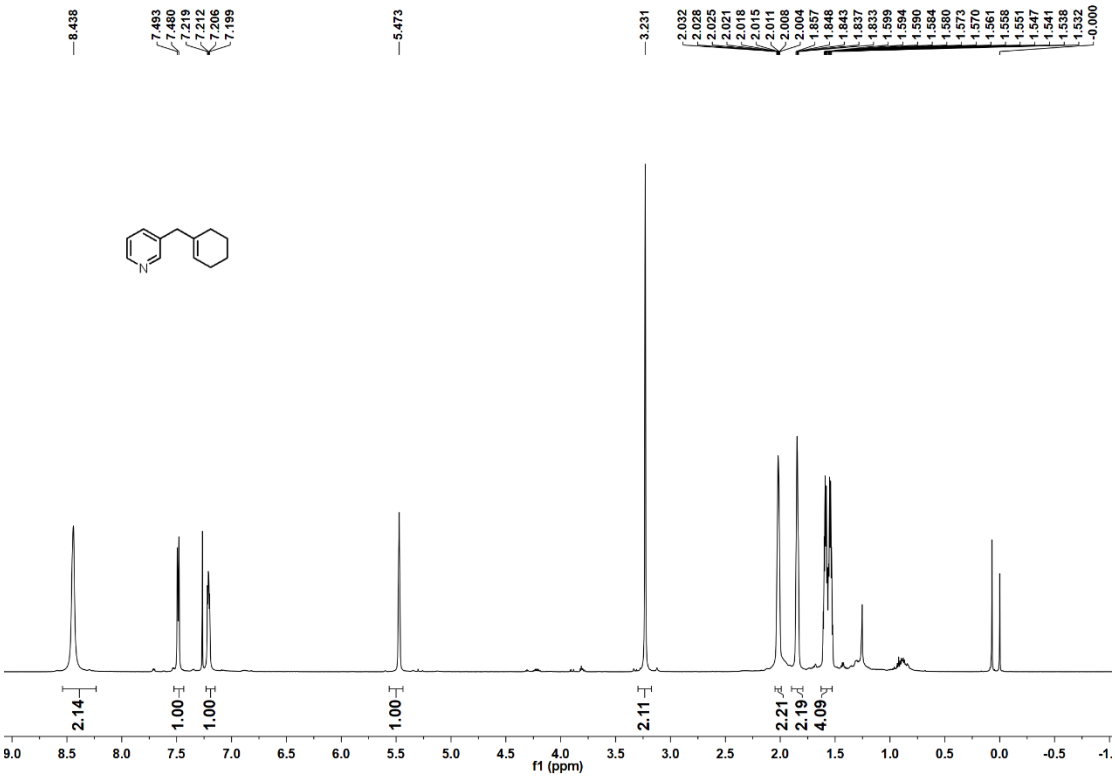
3v, ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)

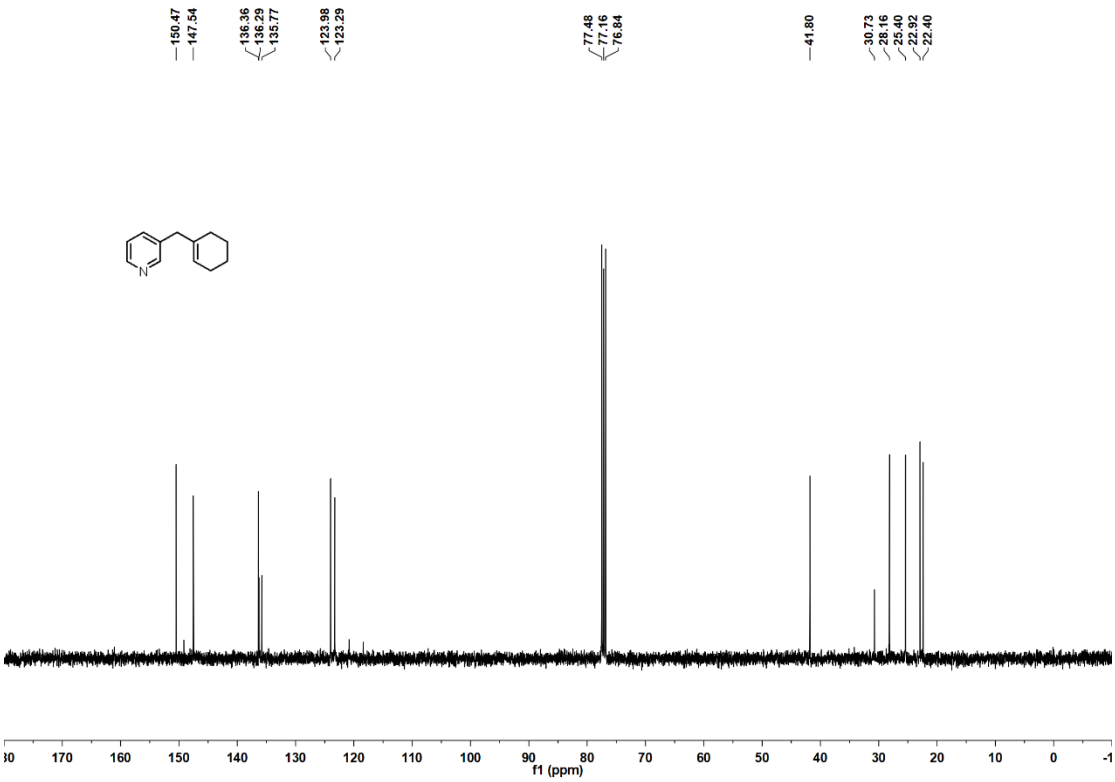




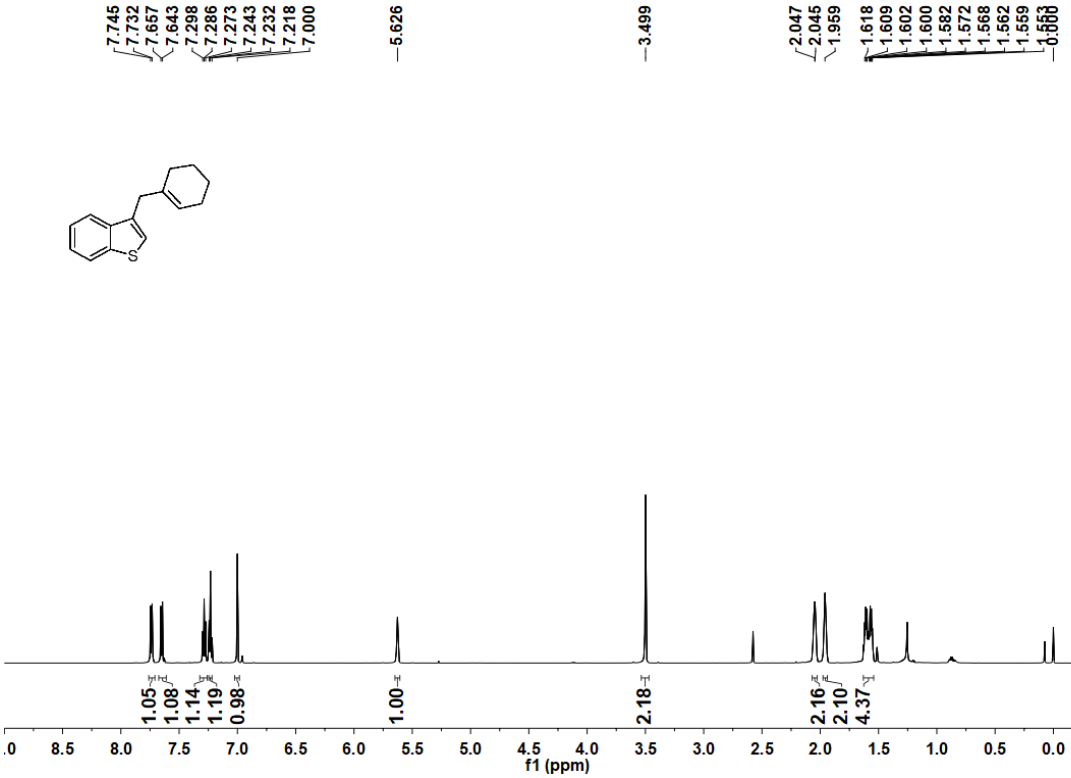


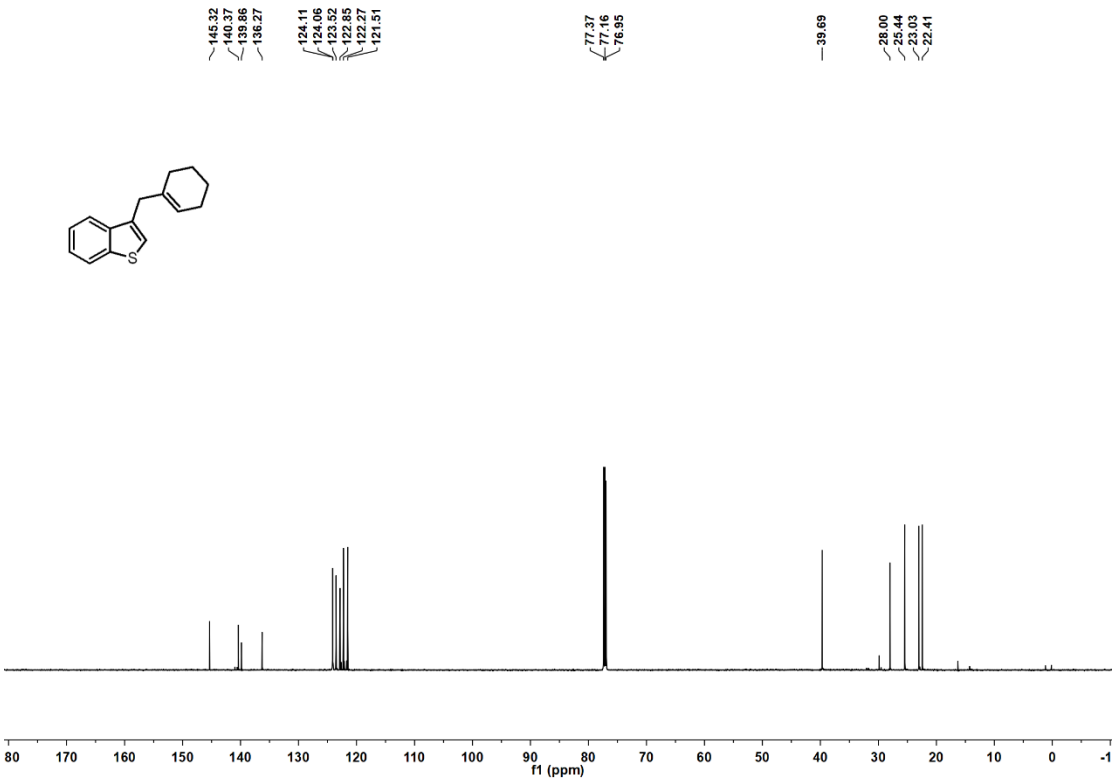
3w, ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)



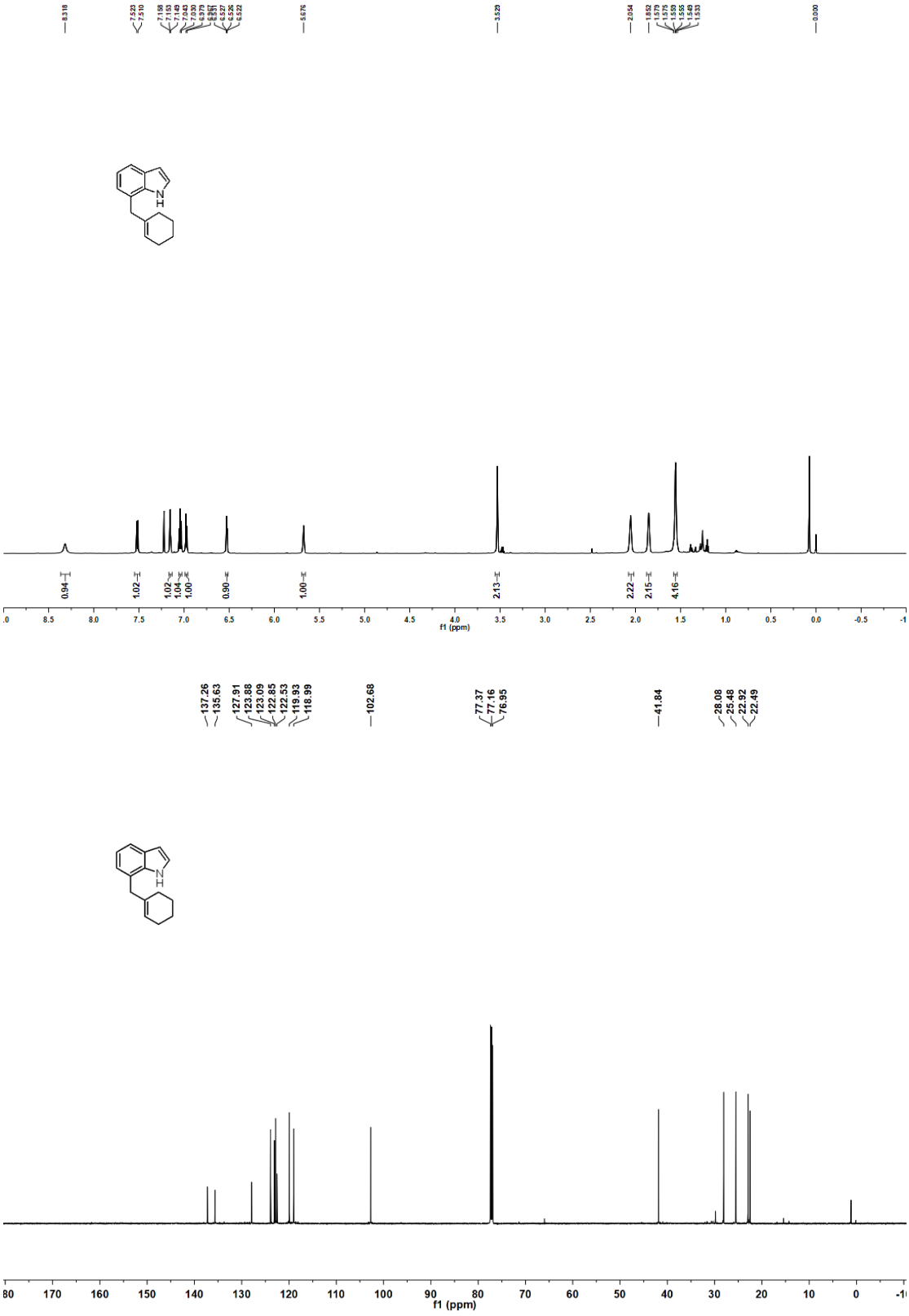


3x, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

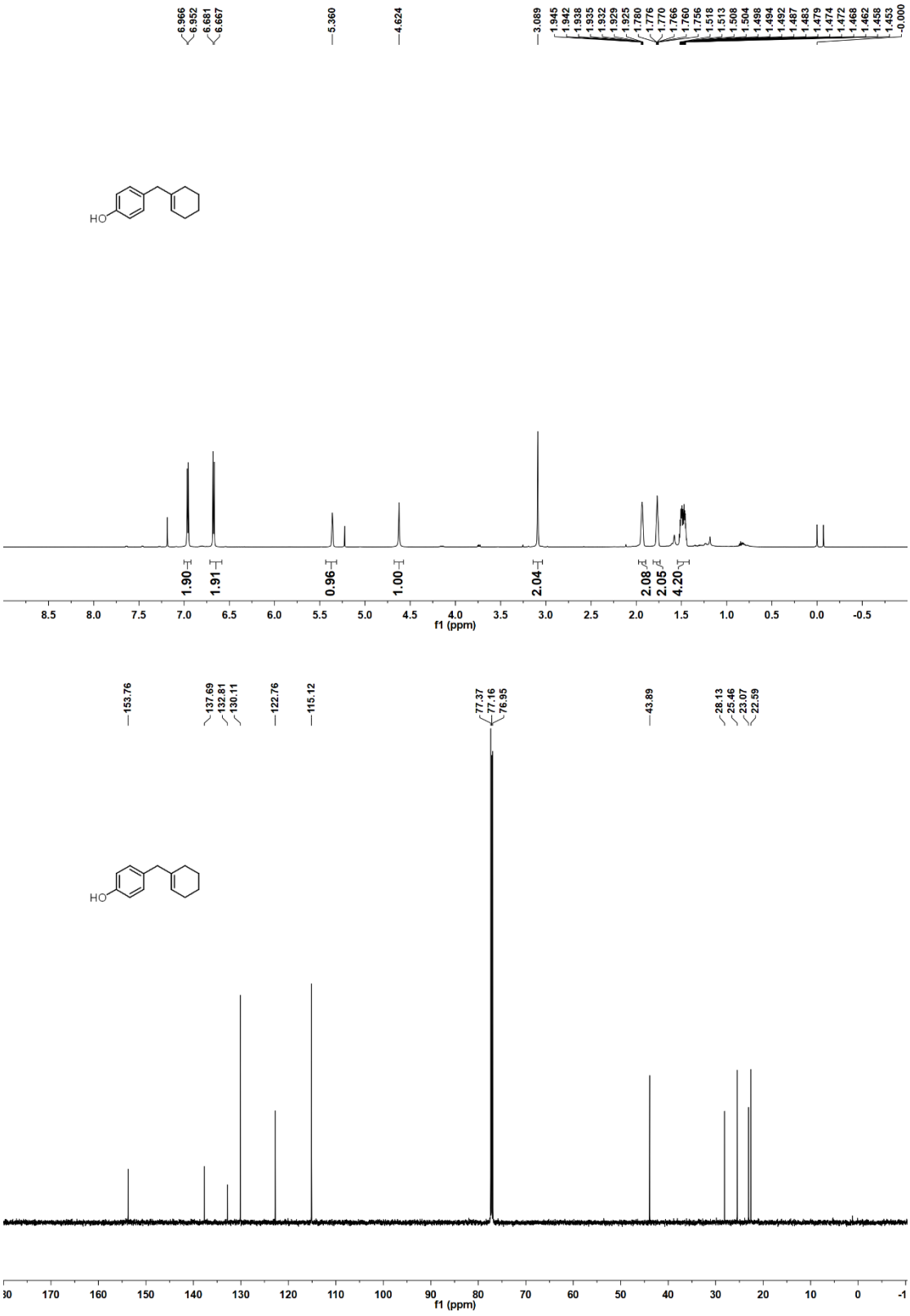




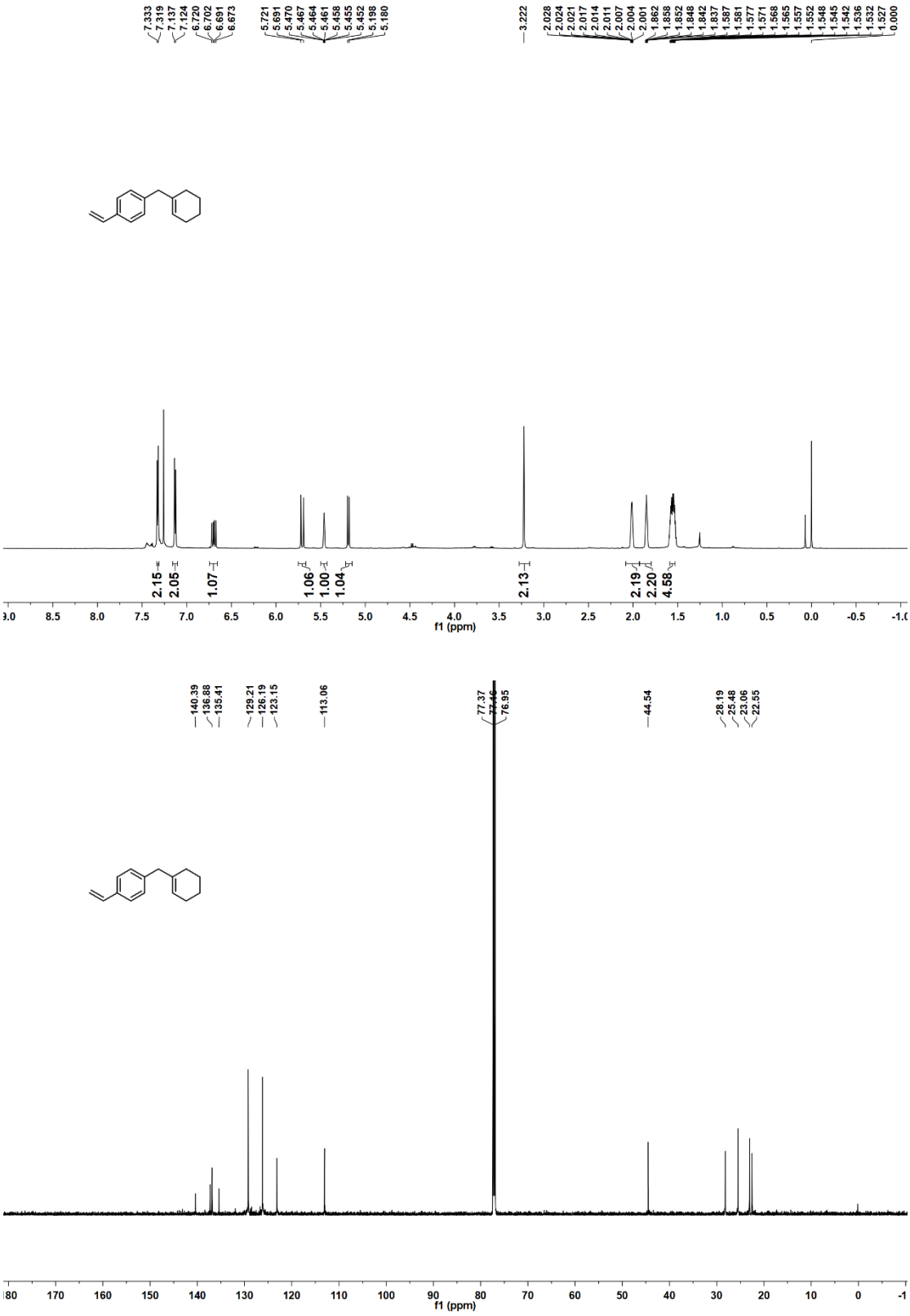
3y, ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)



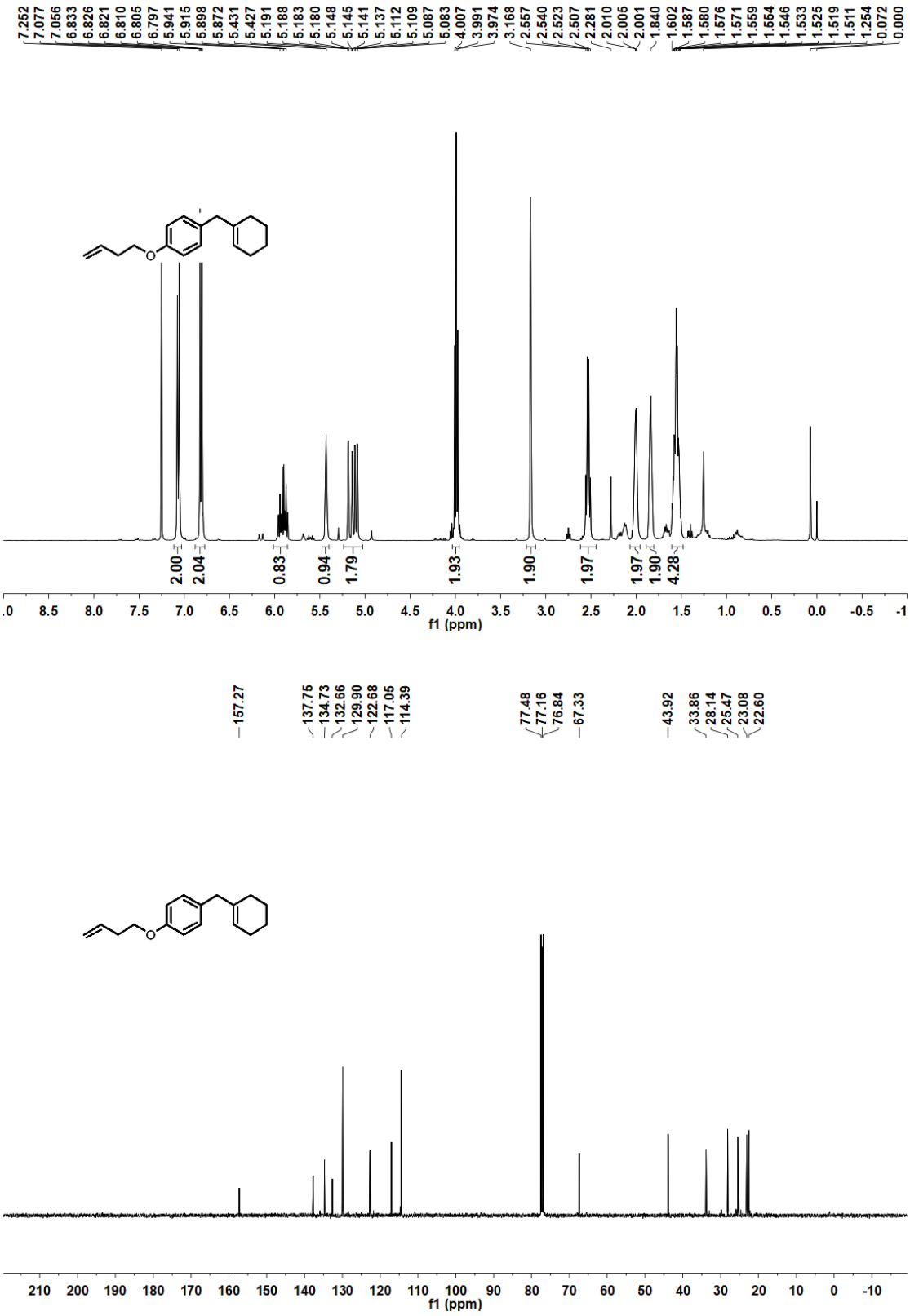
3z, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)



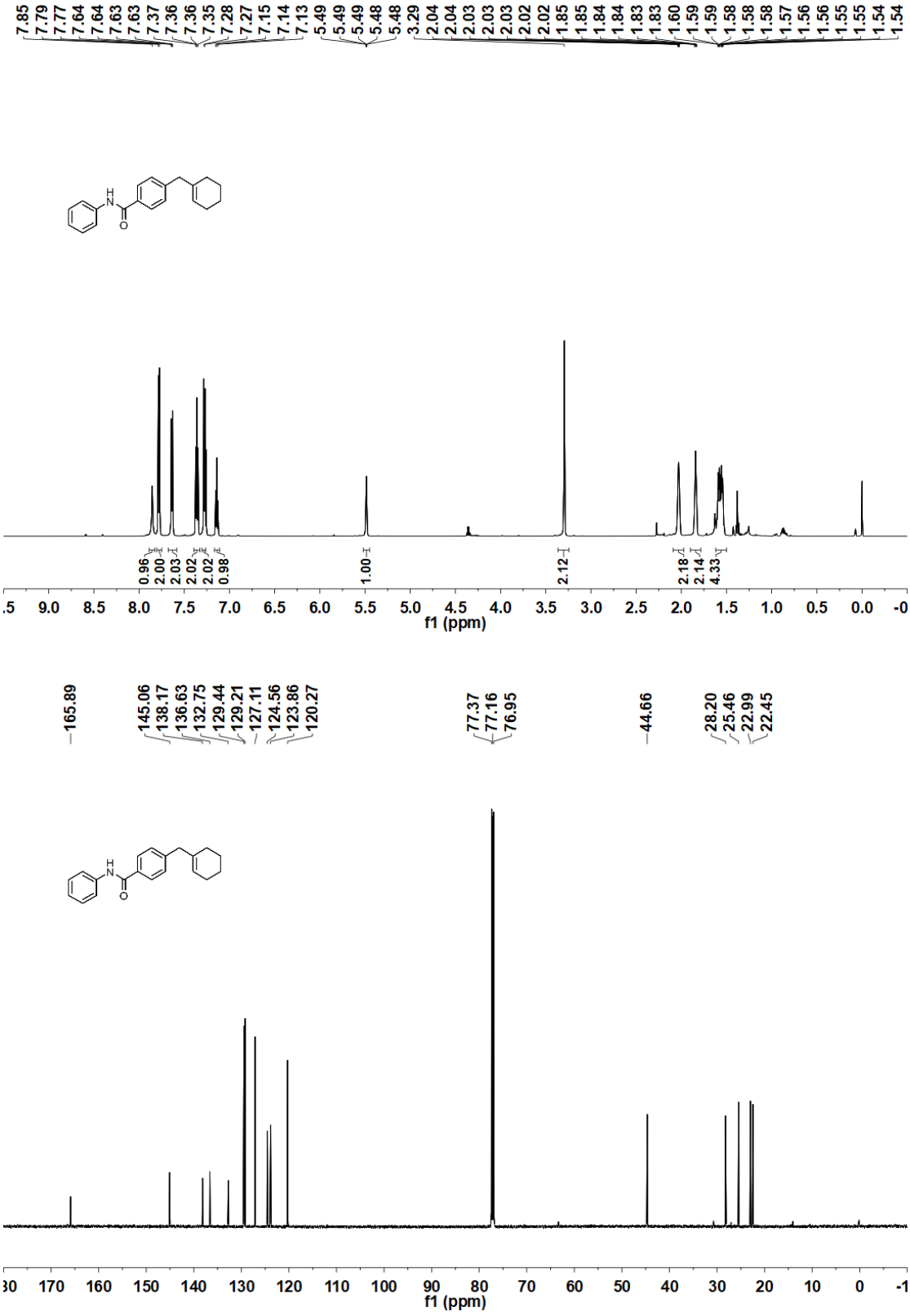
3aa, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)



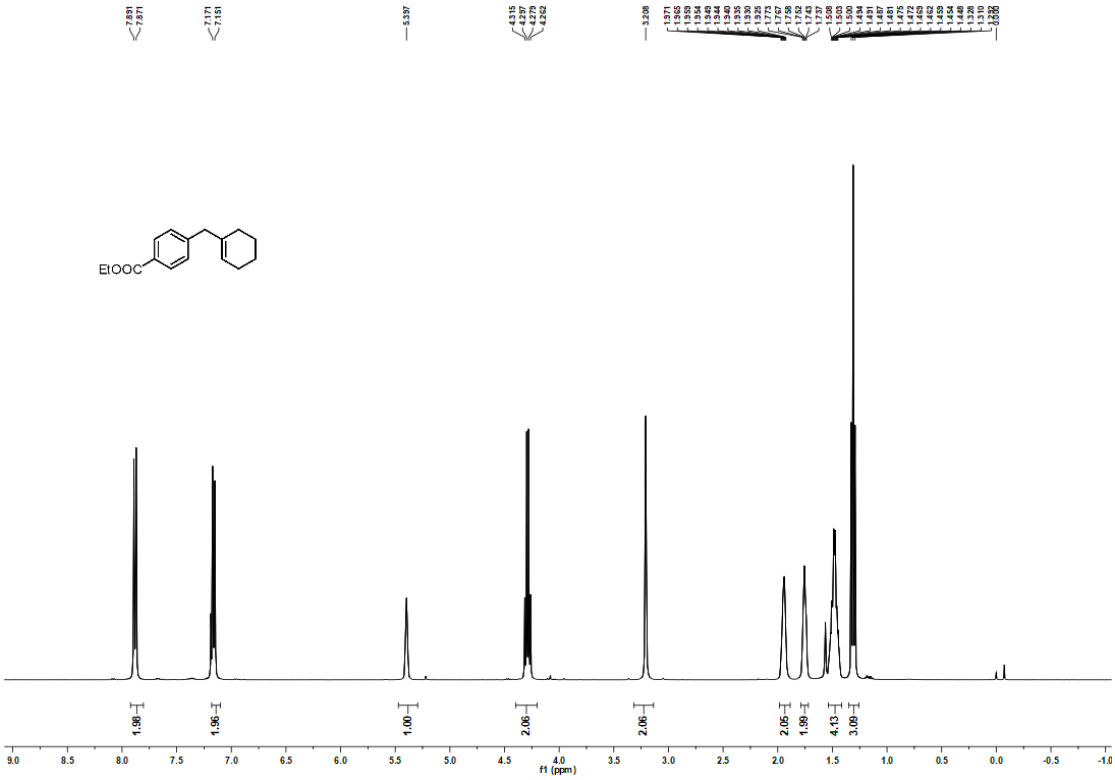
3ab, ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)

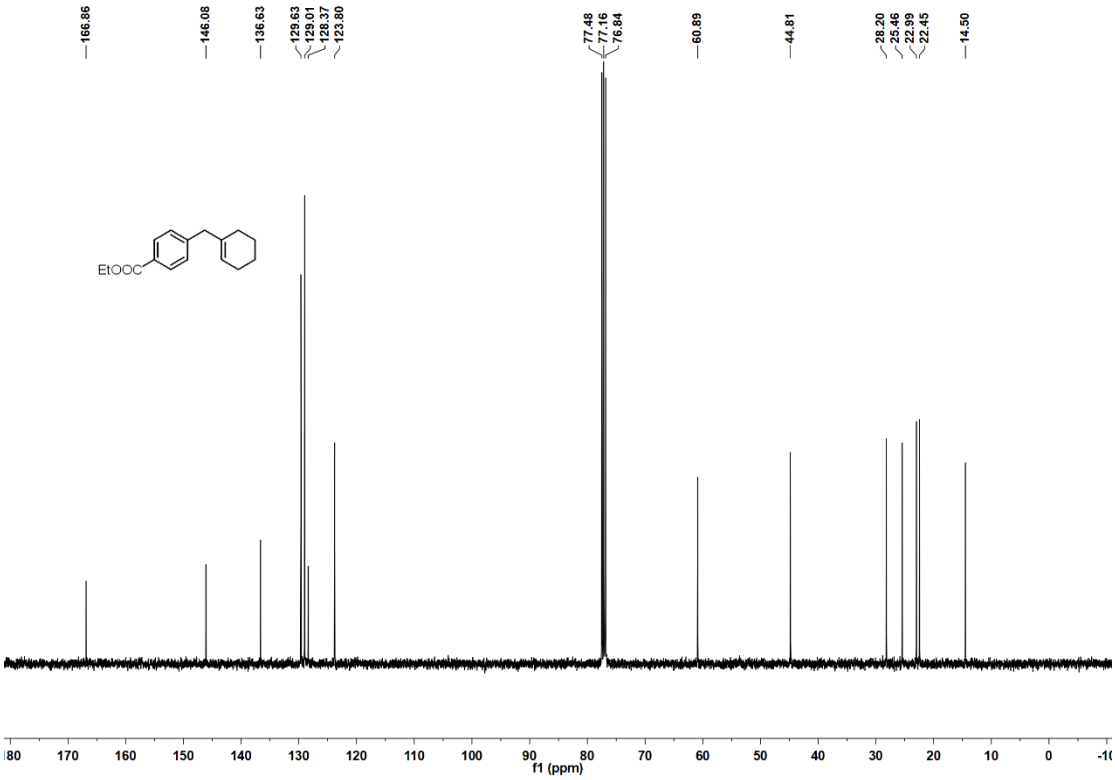


3ac, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

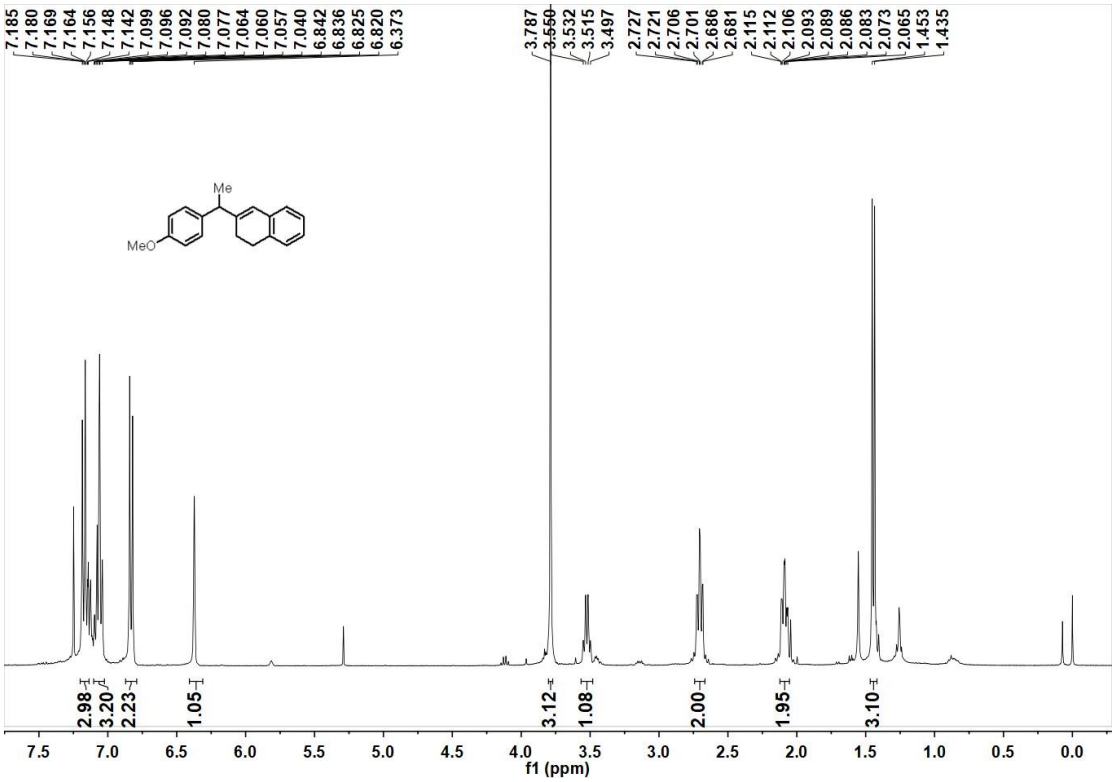


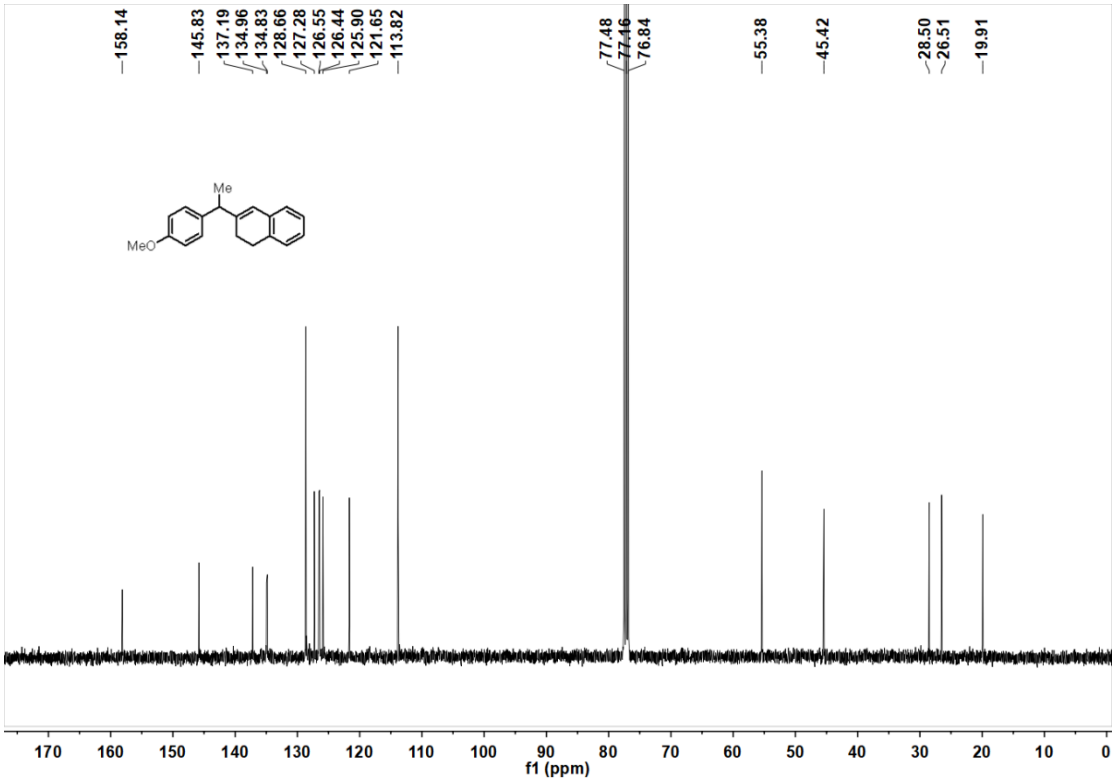
3ad, ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)



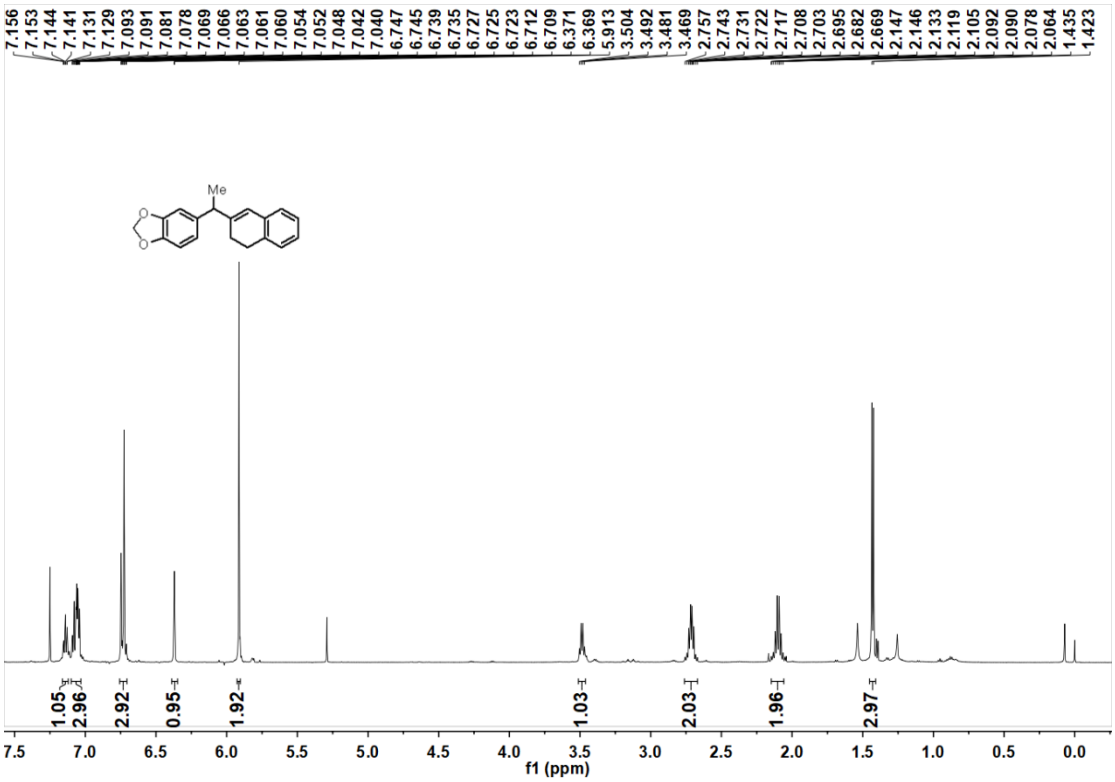


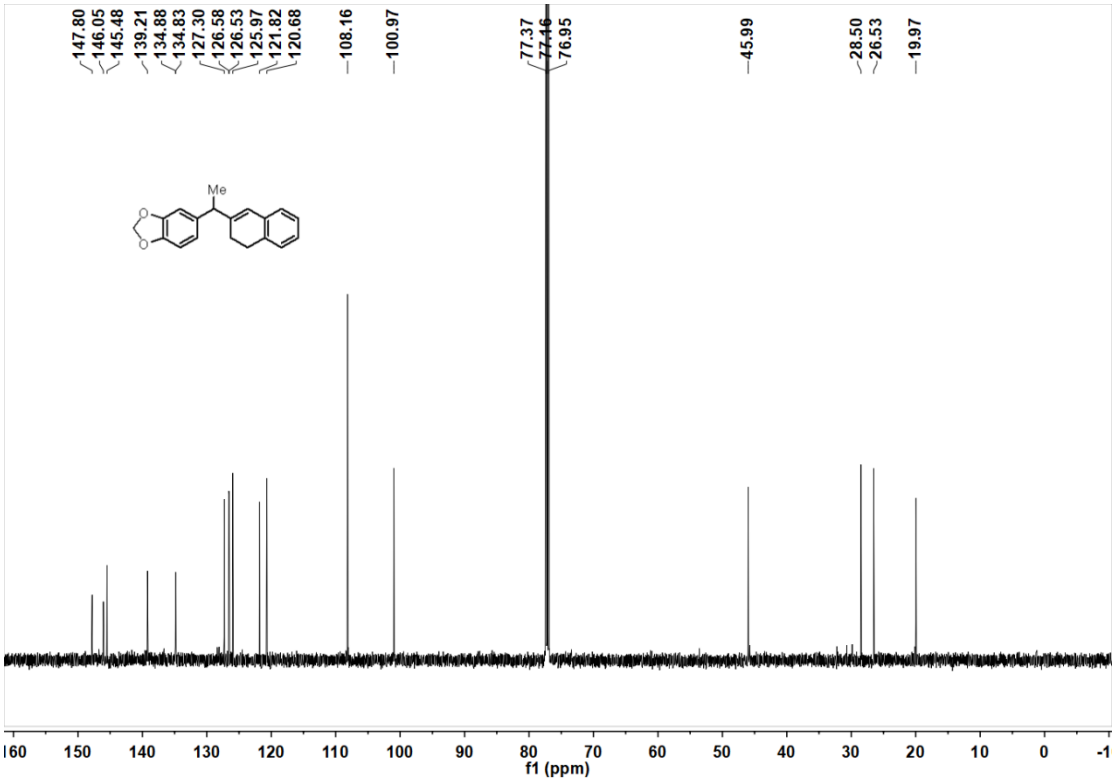
3ae, ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)



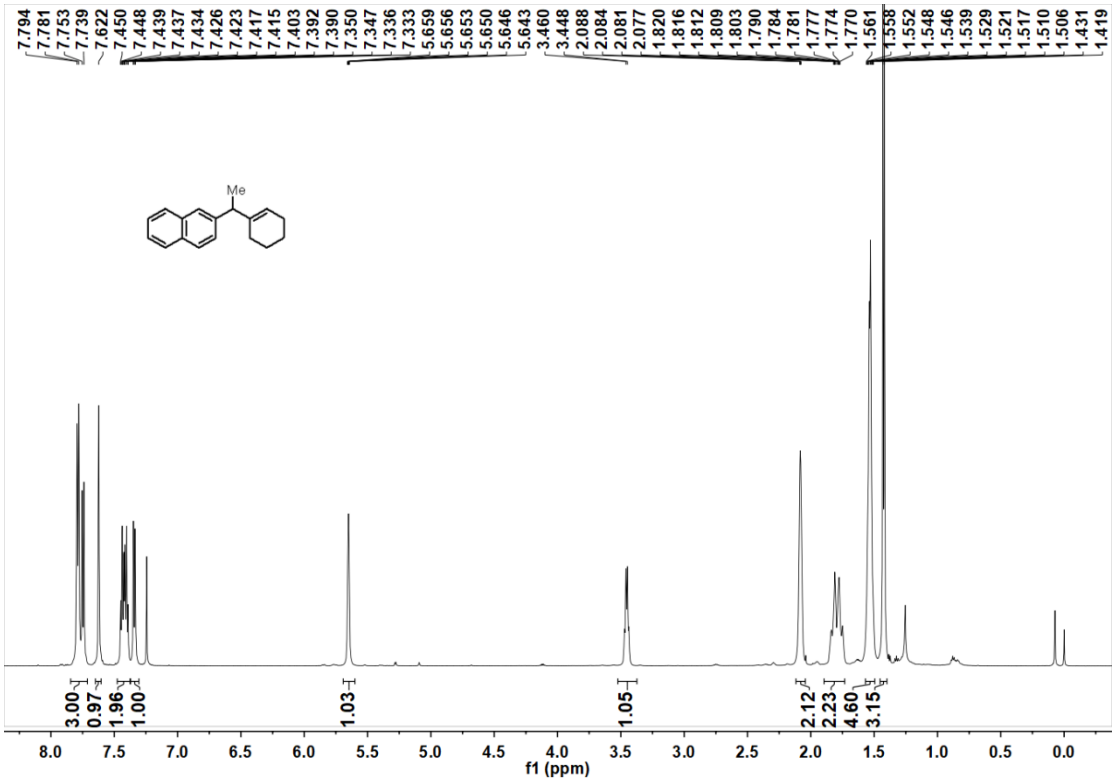


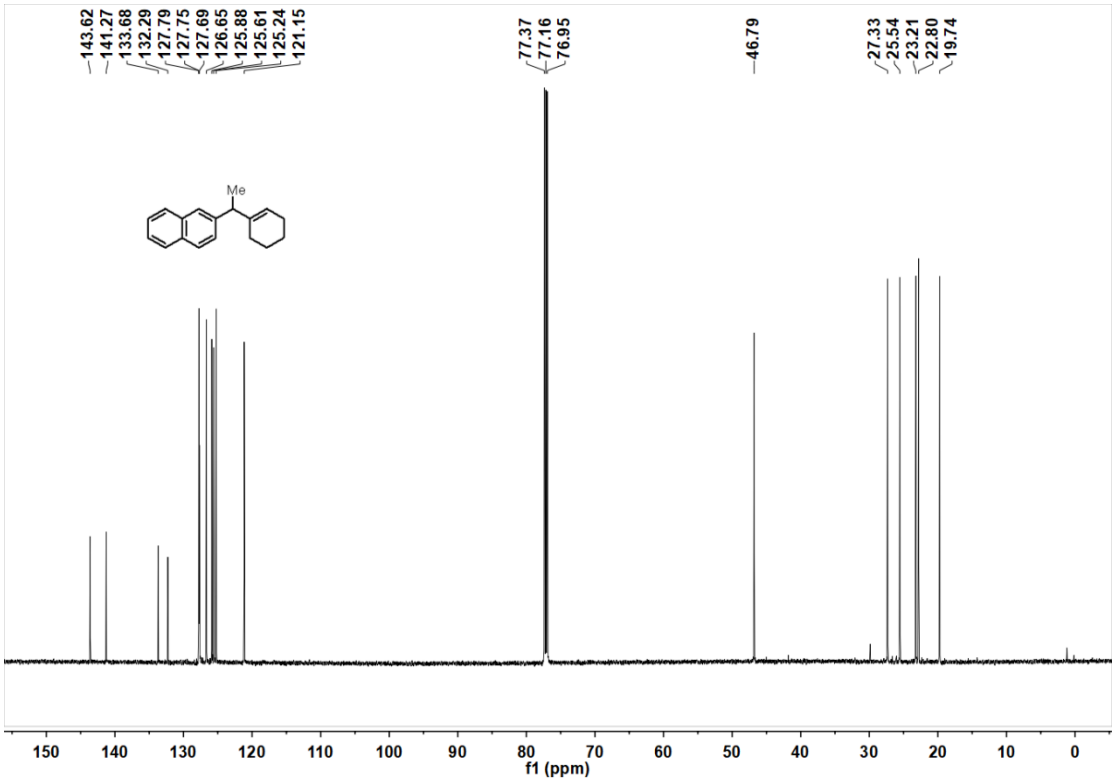
3af, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)



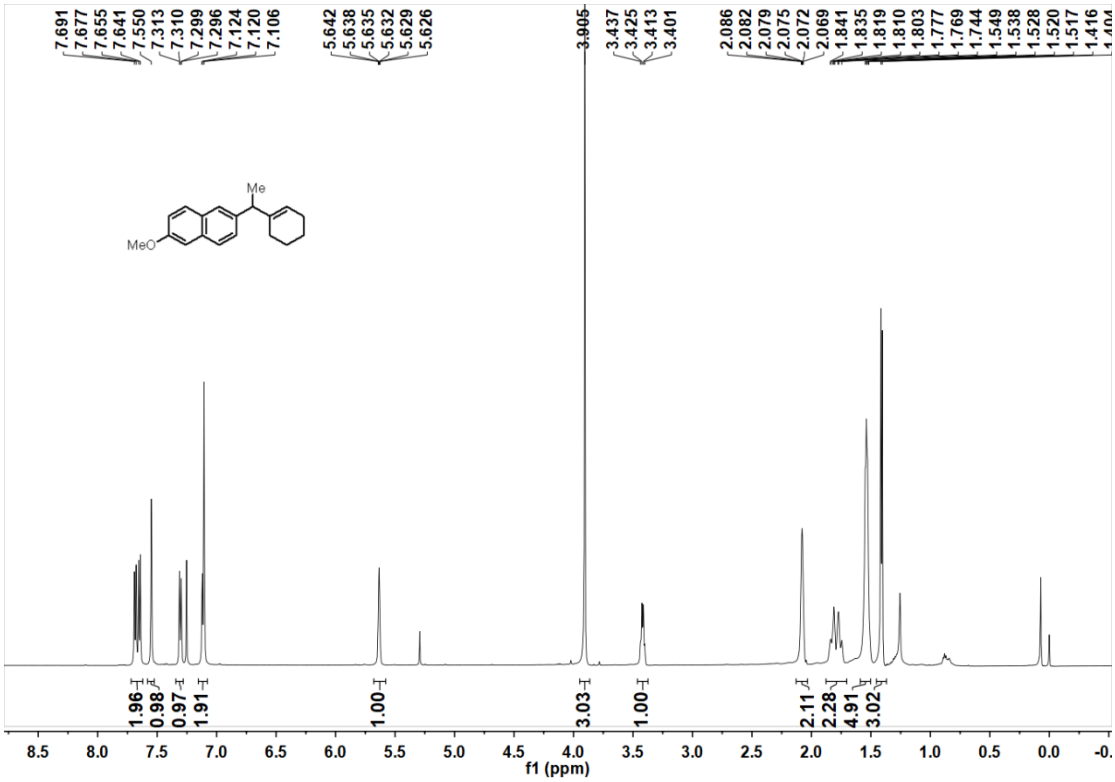


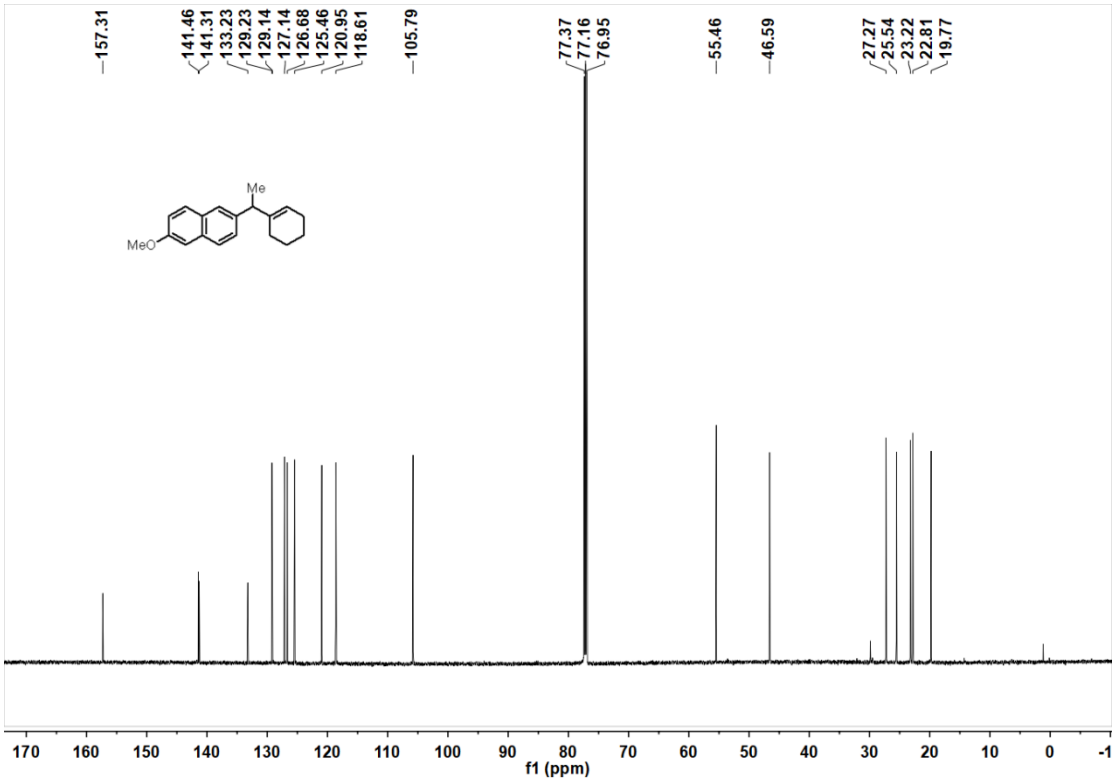
3ag, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)



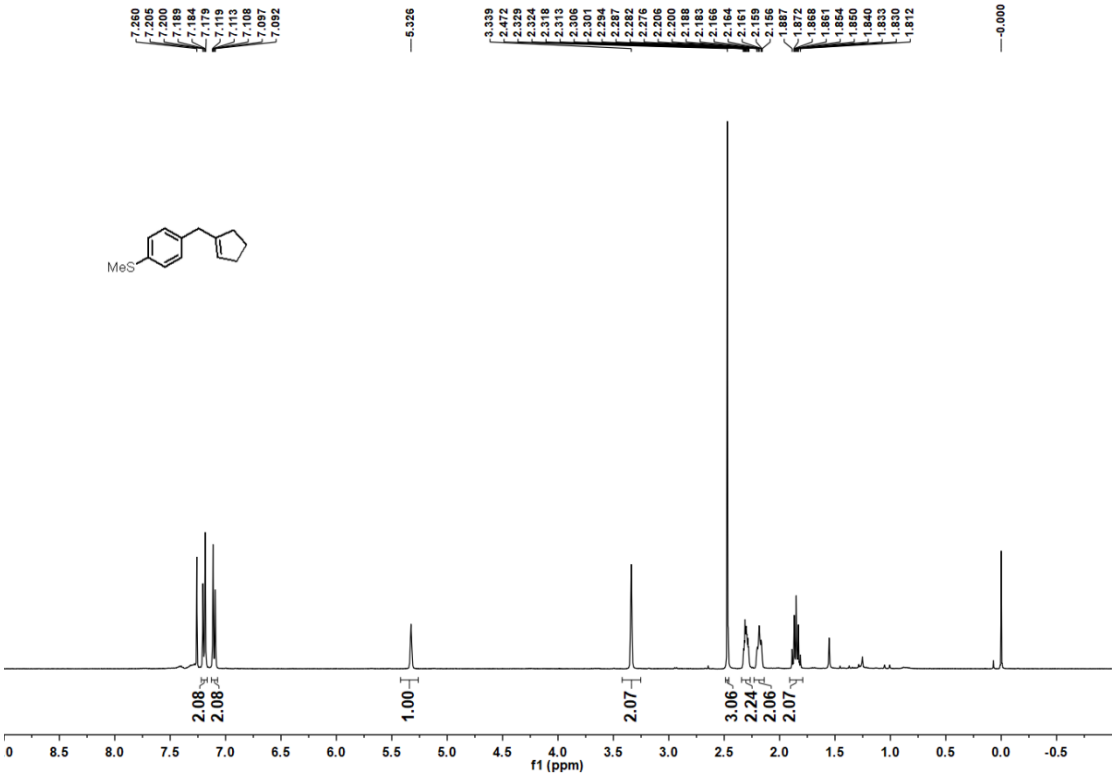


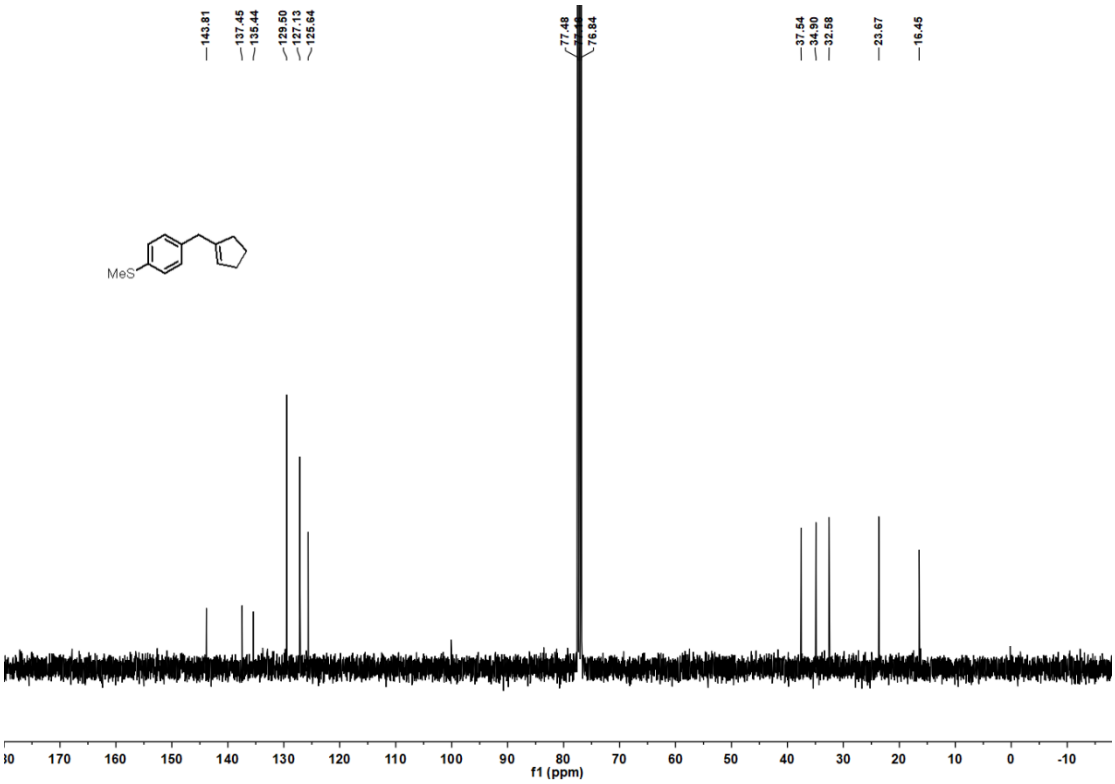
3ah, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)



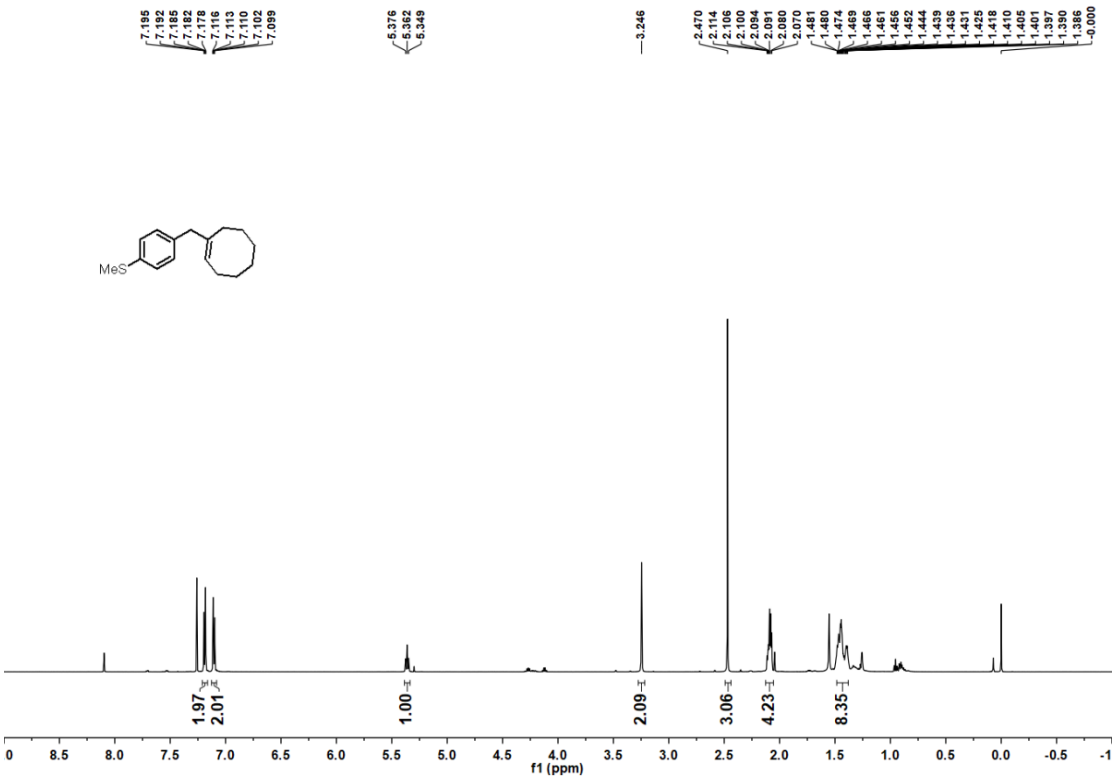


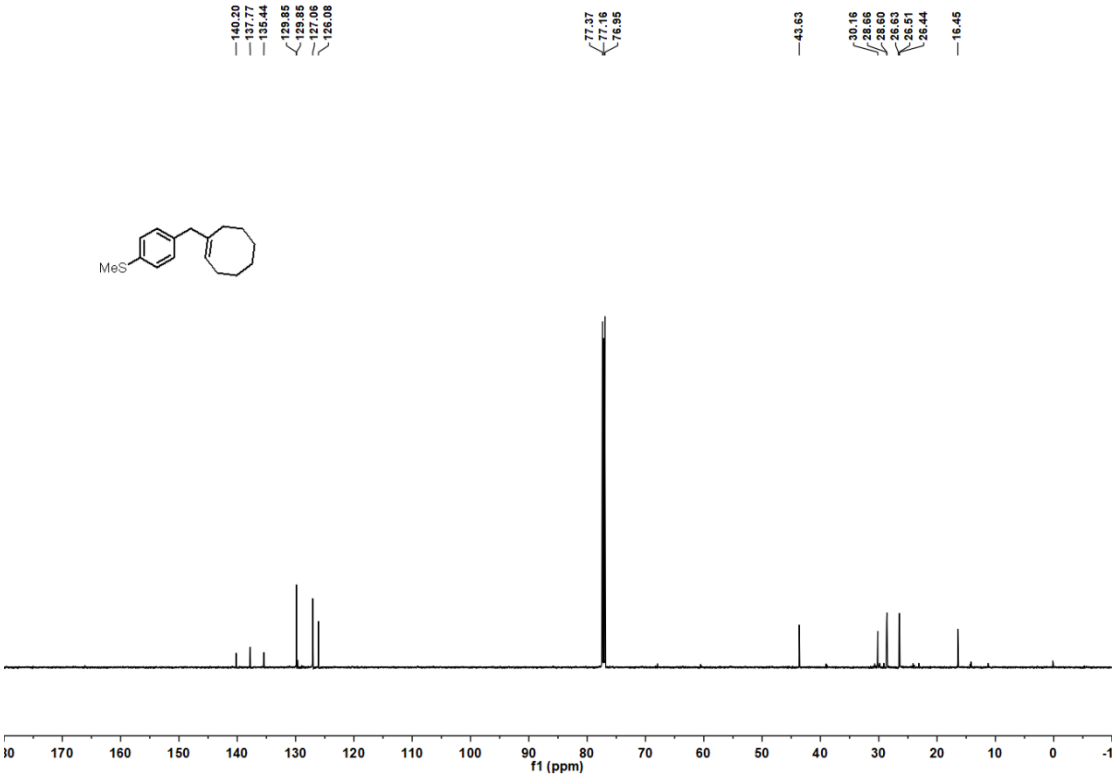
3ai, ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)



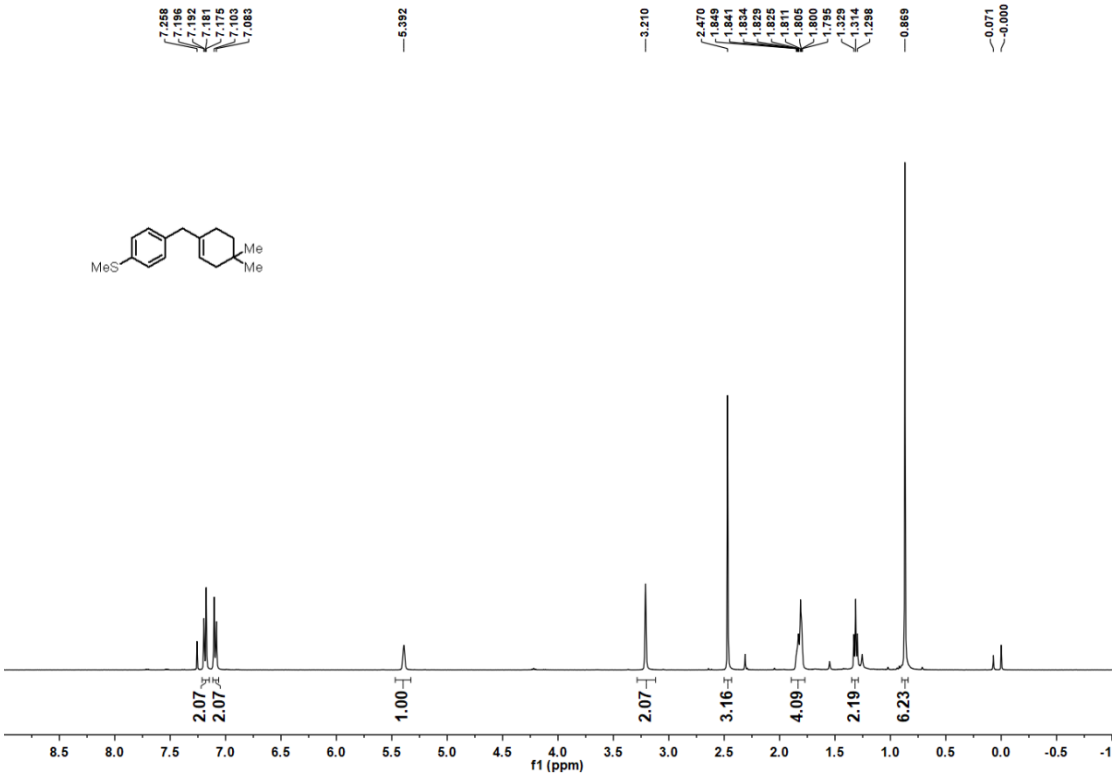


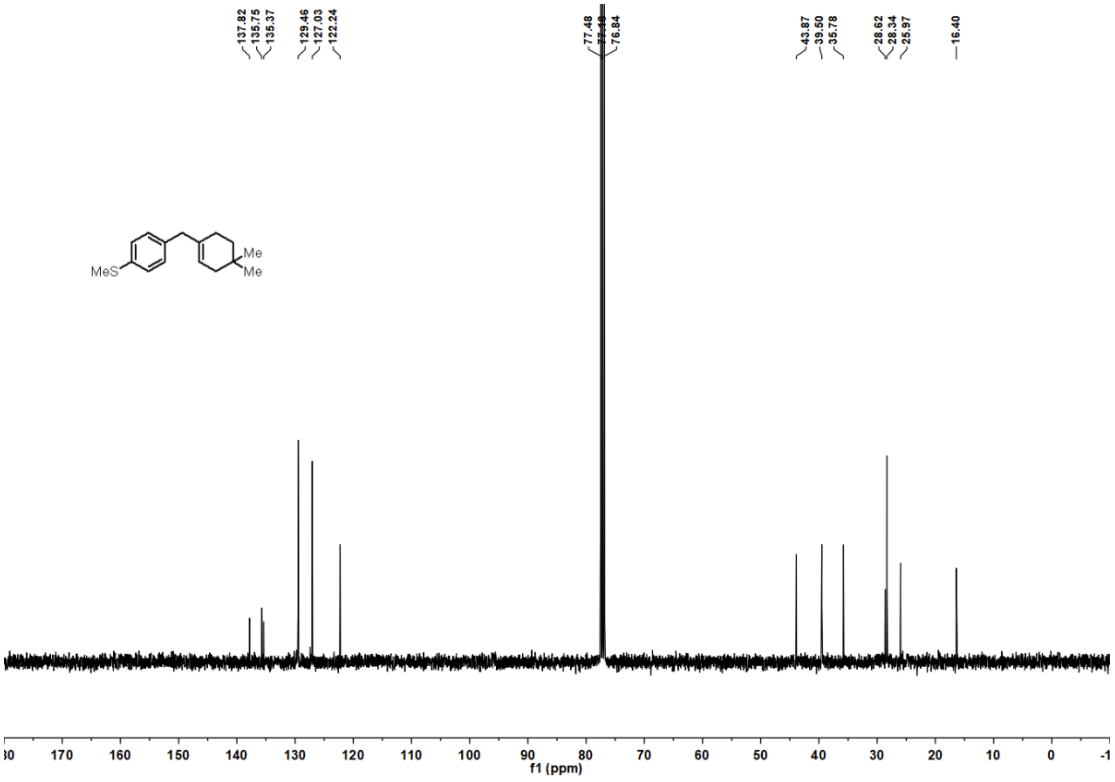
3aj, ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)



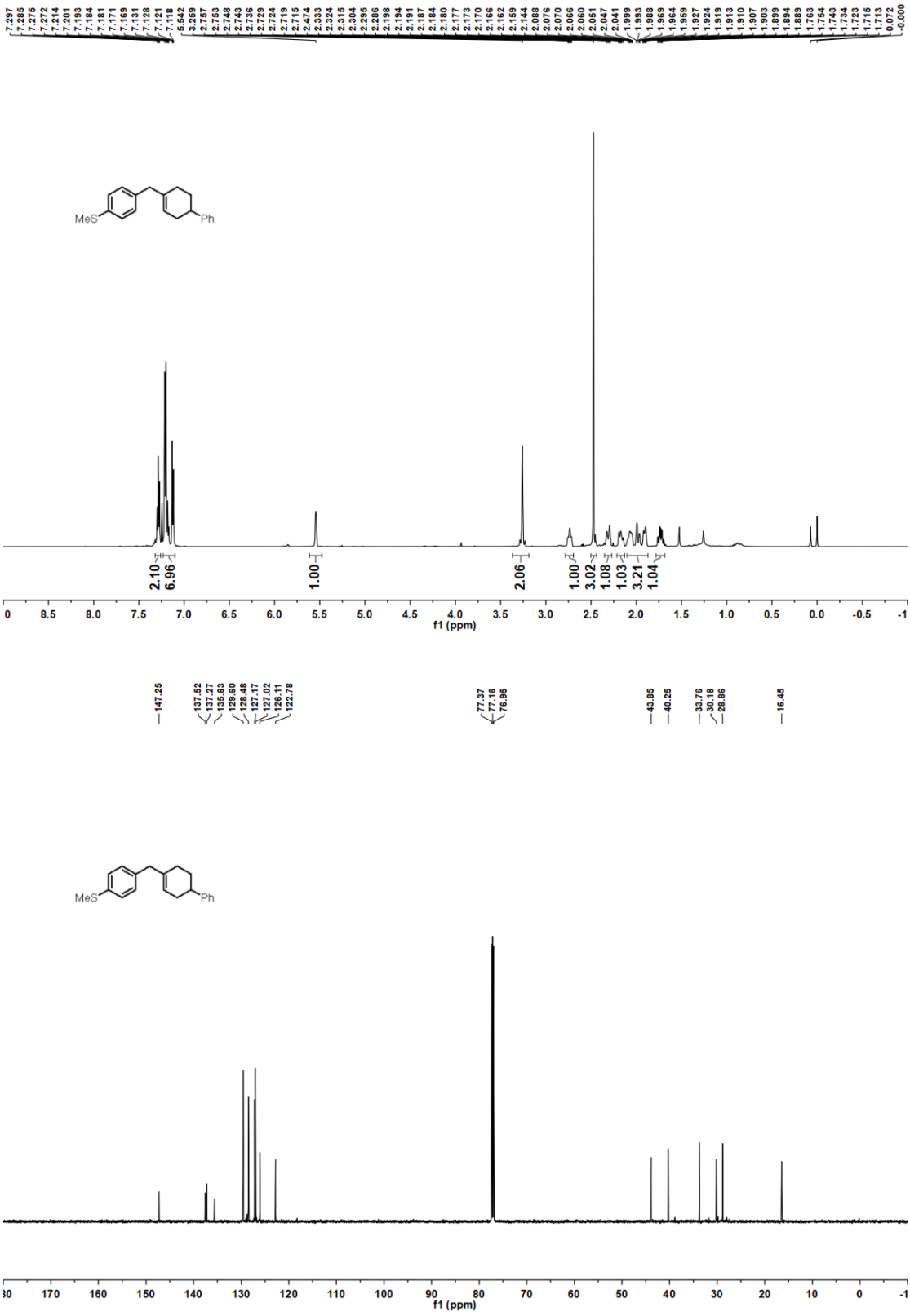


3ak, ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)

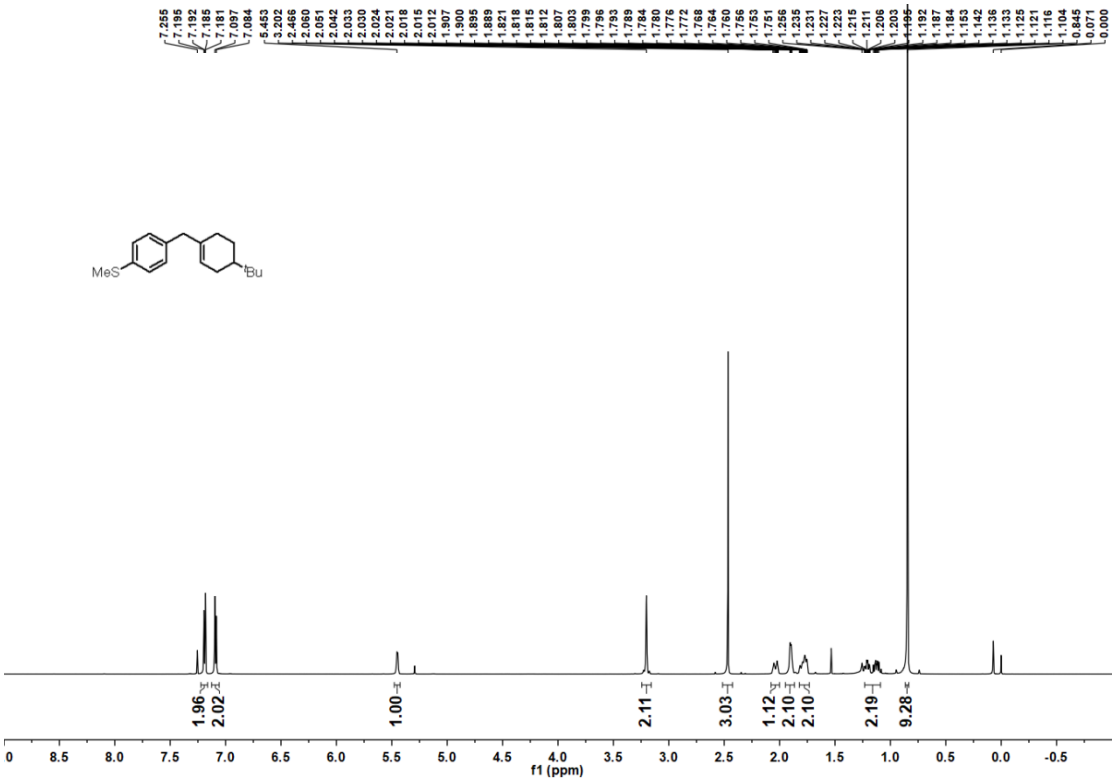


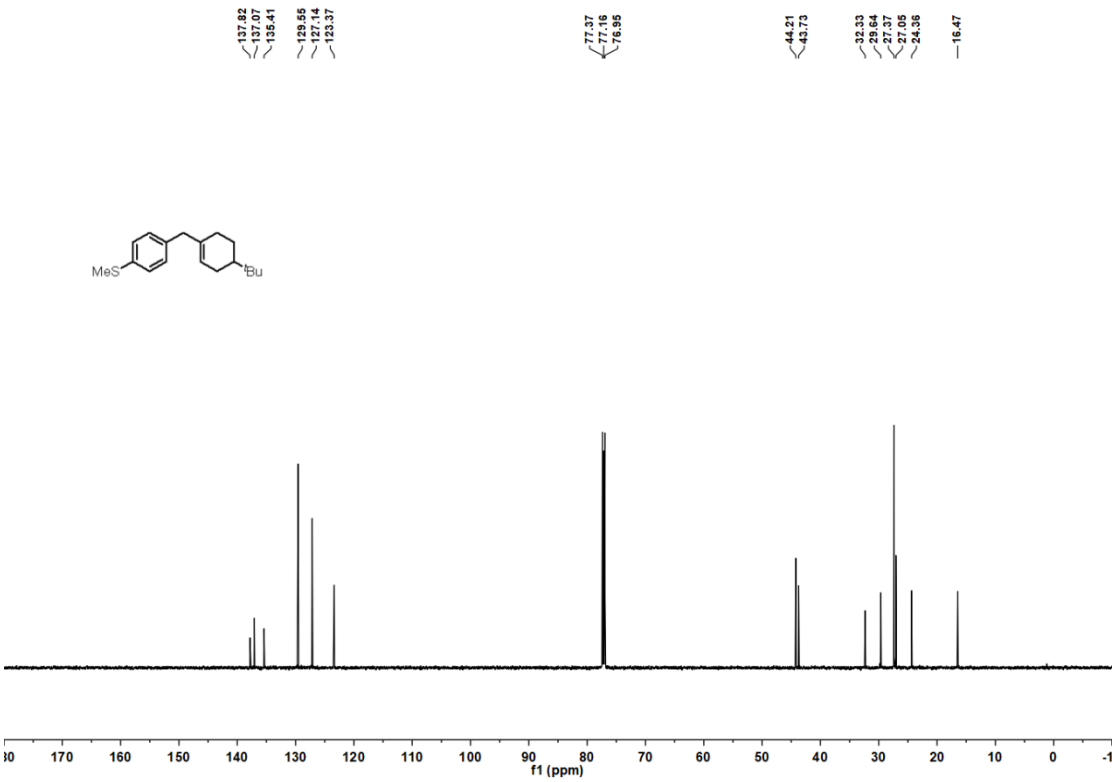


3al, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

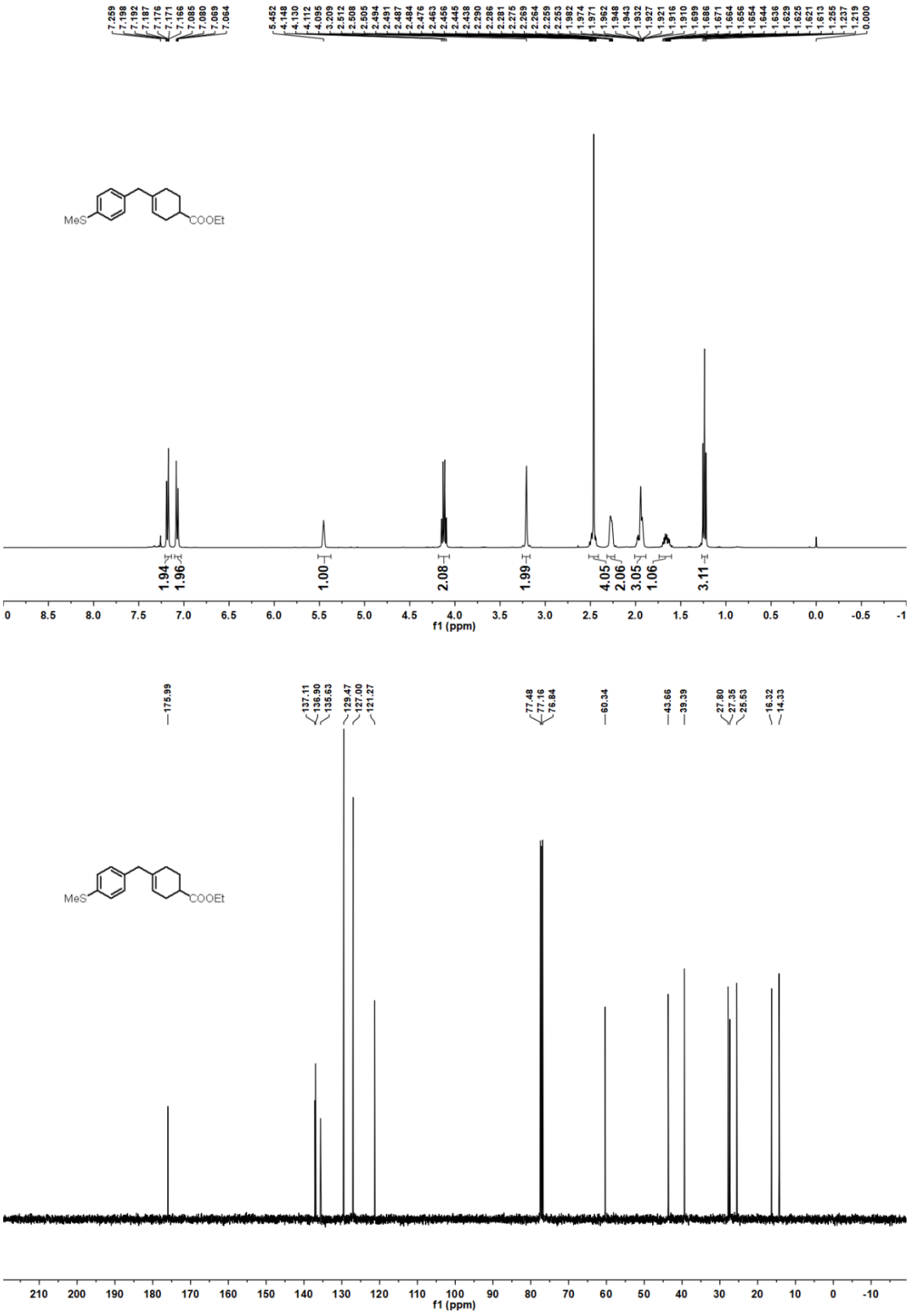


3am, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

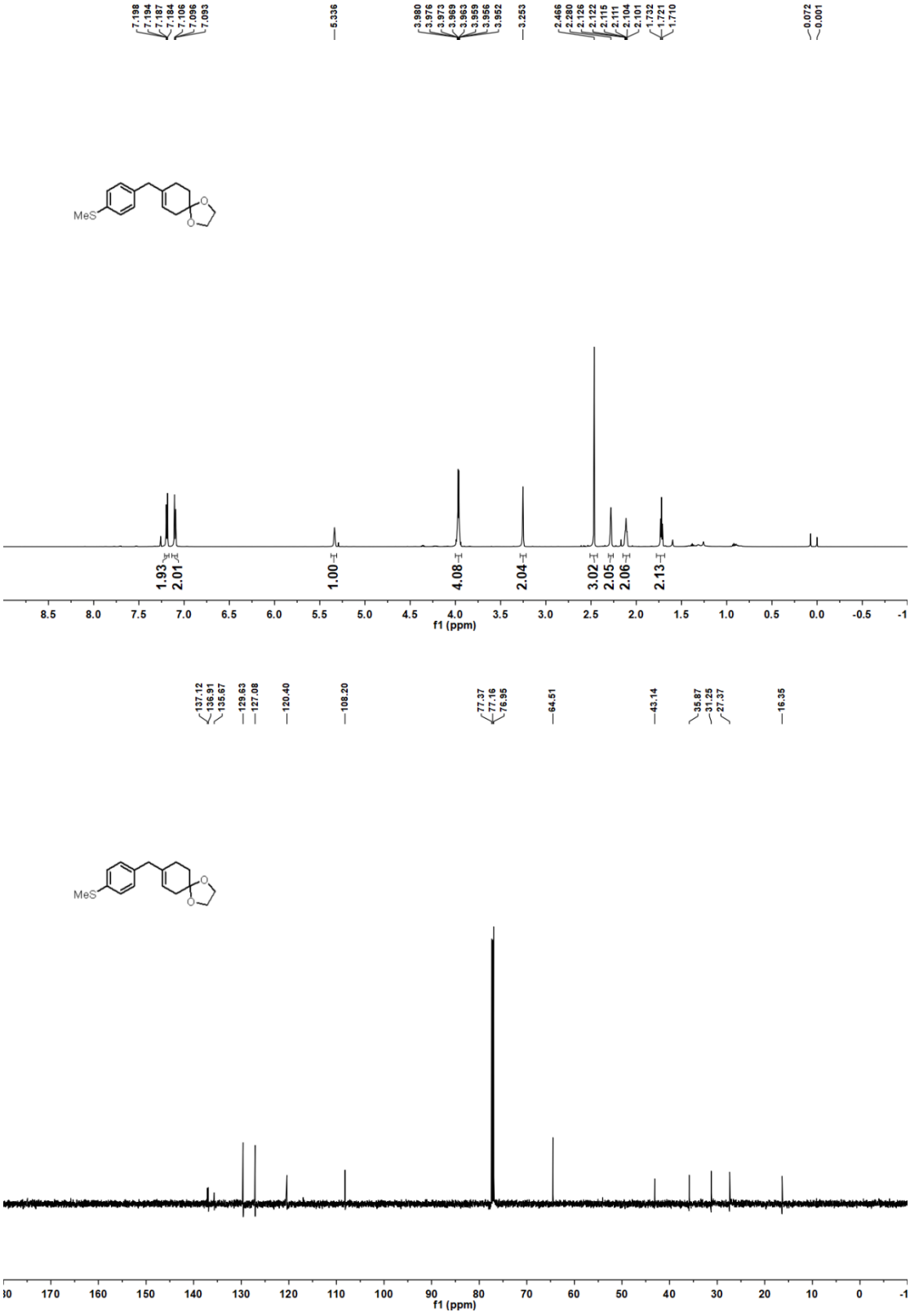




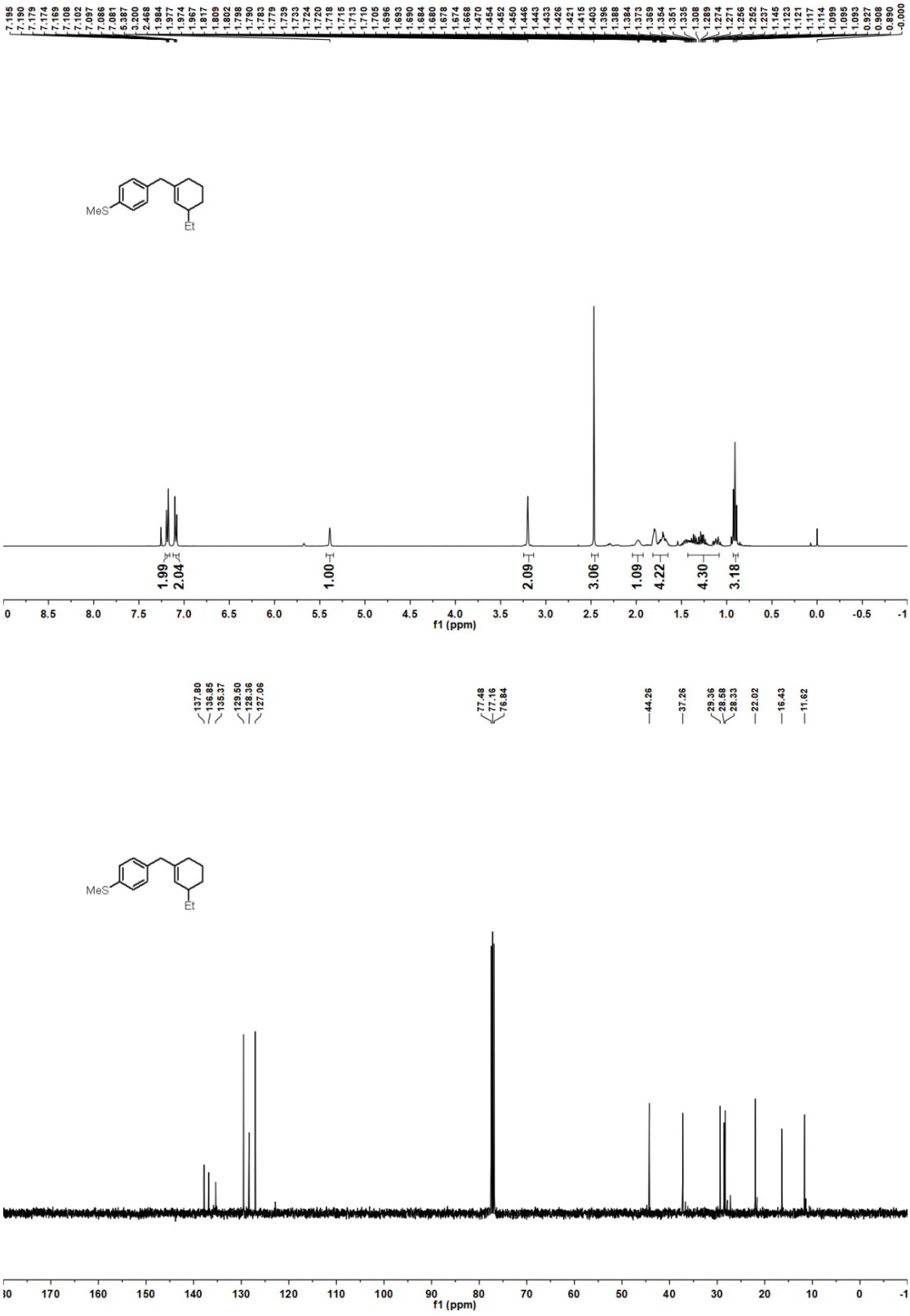
3an, ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)



3ao, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

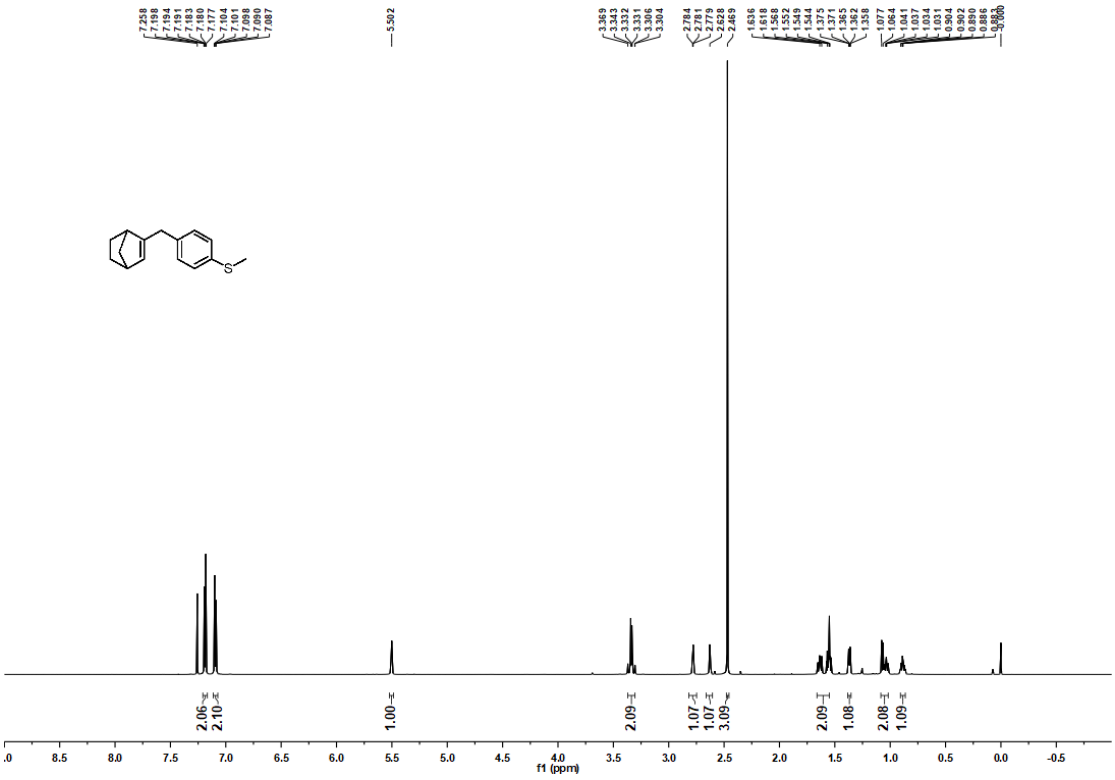


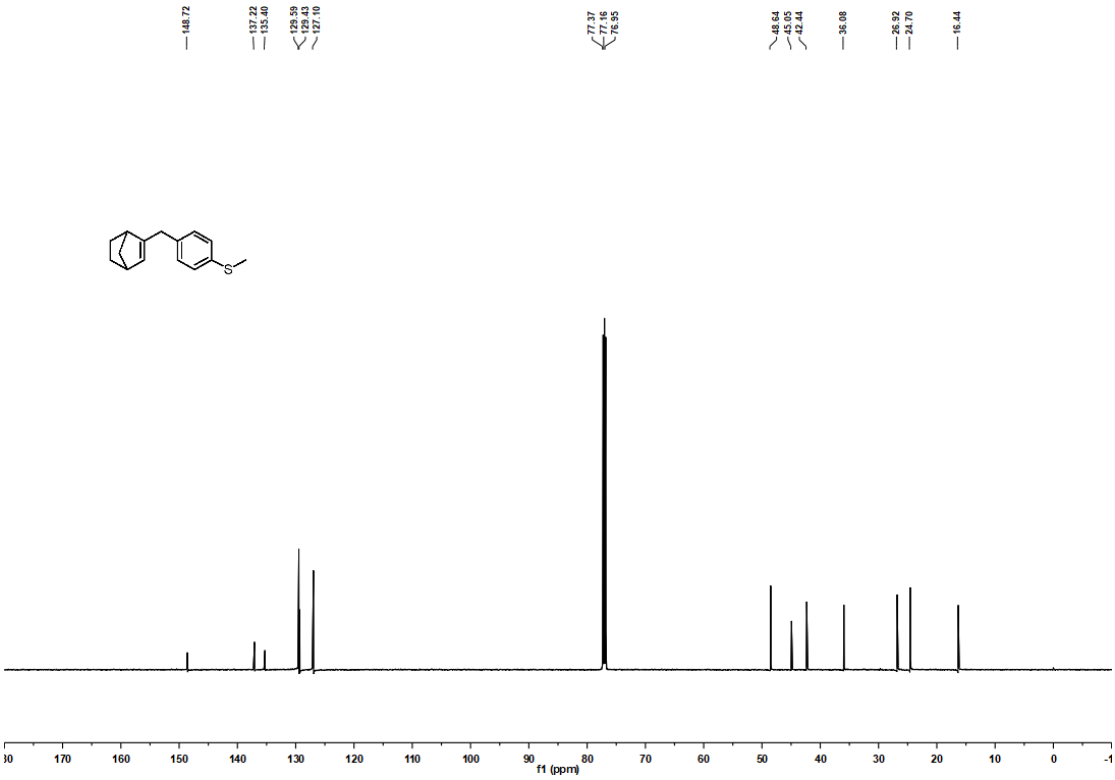
3ap, ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)



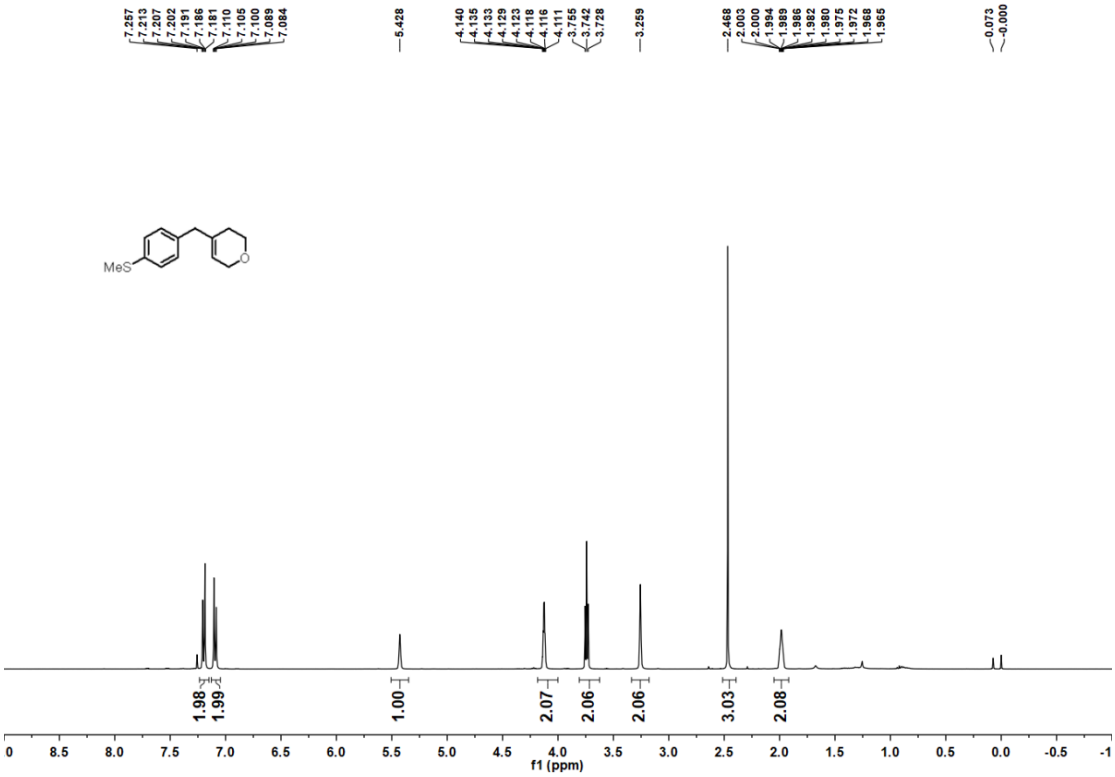
3aq, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

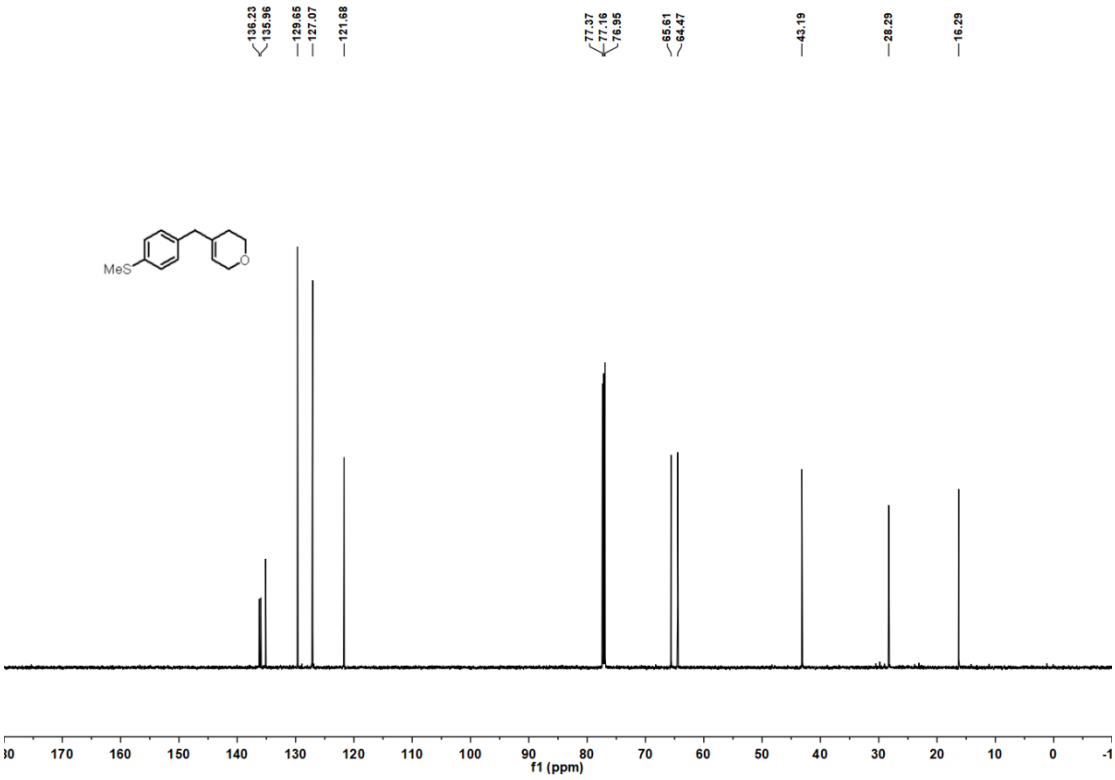
3ar, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)



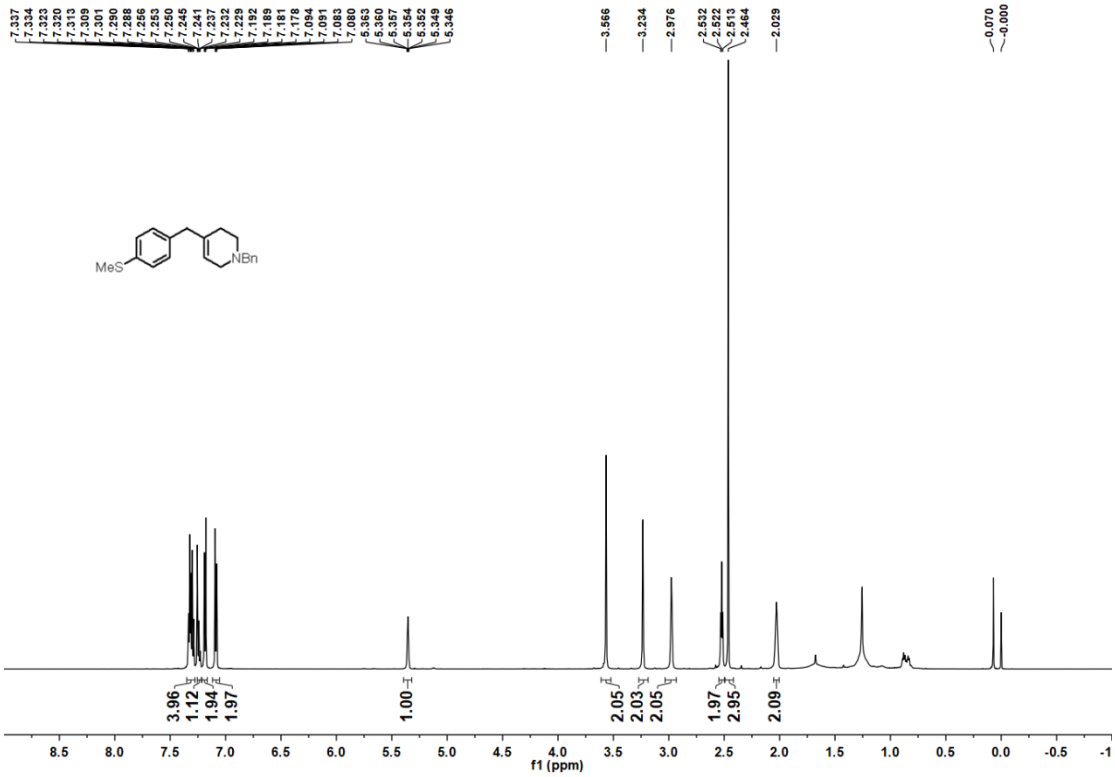


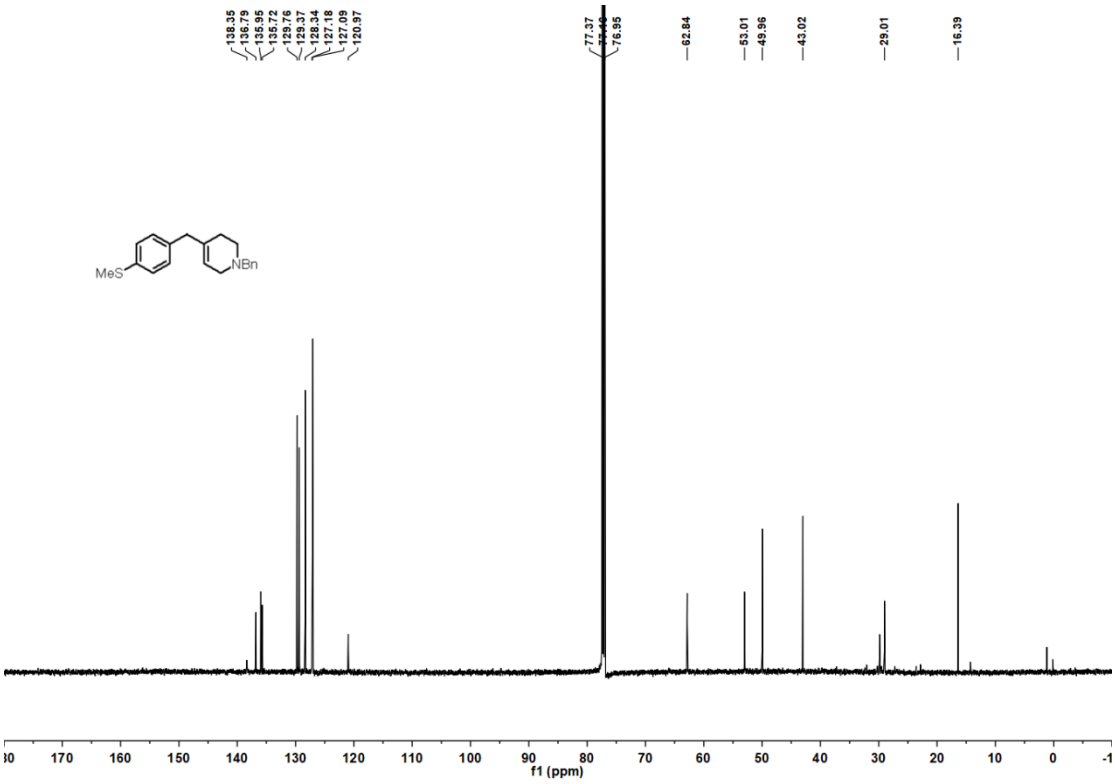
3as, ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)



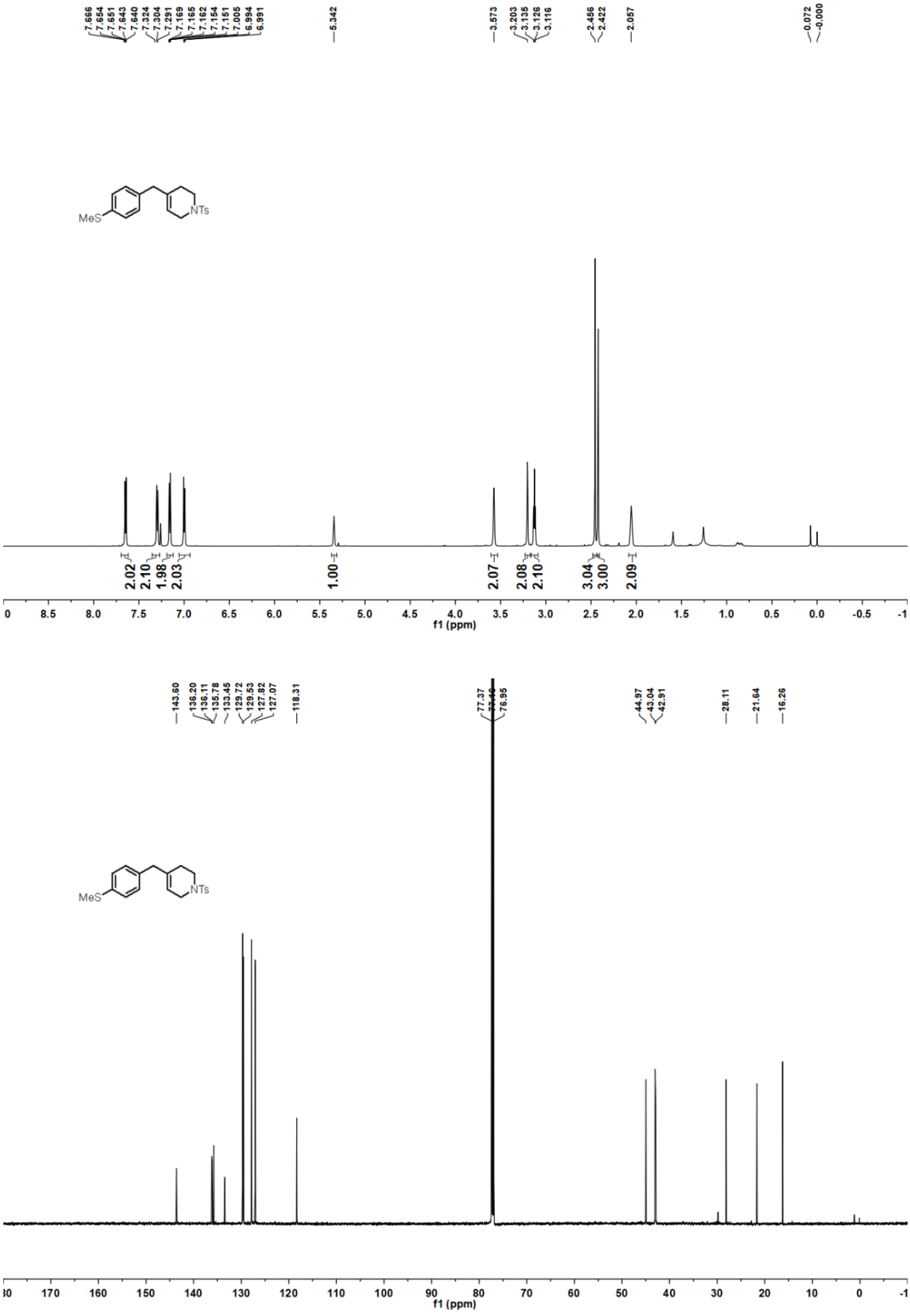


3at, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

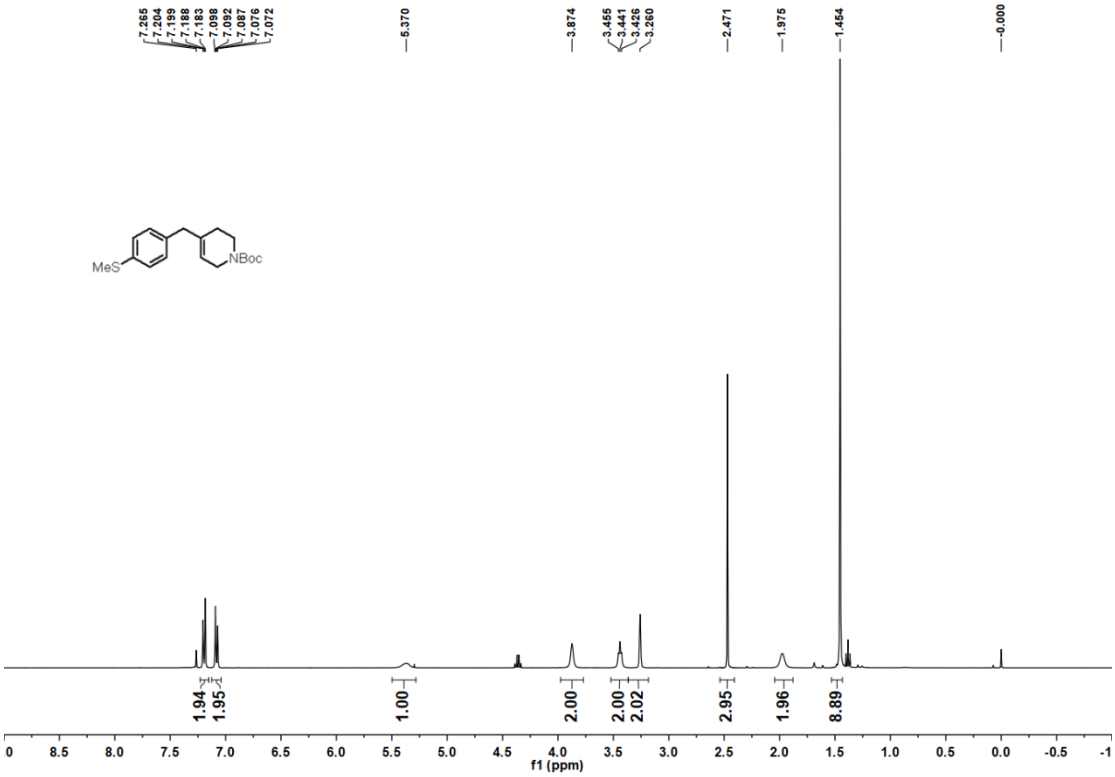


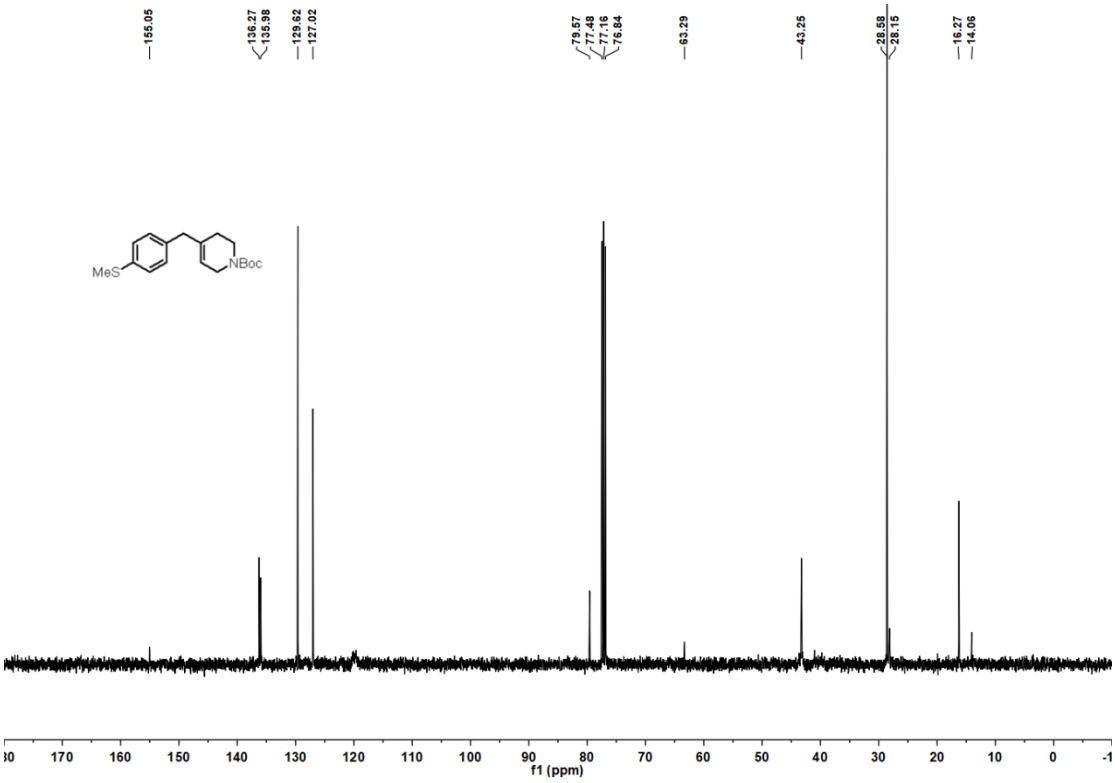


3au, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

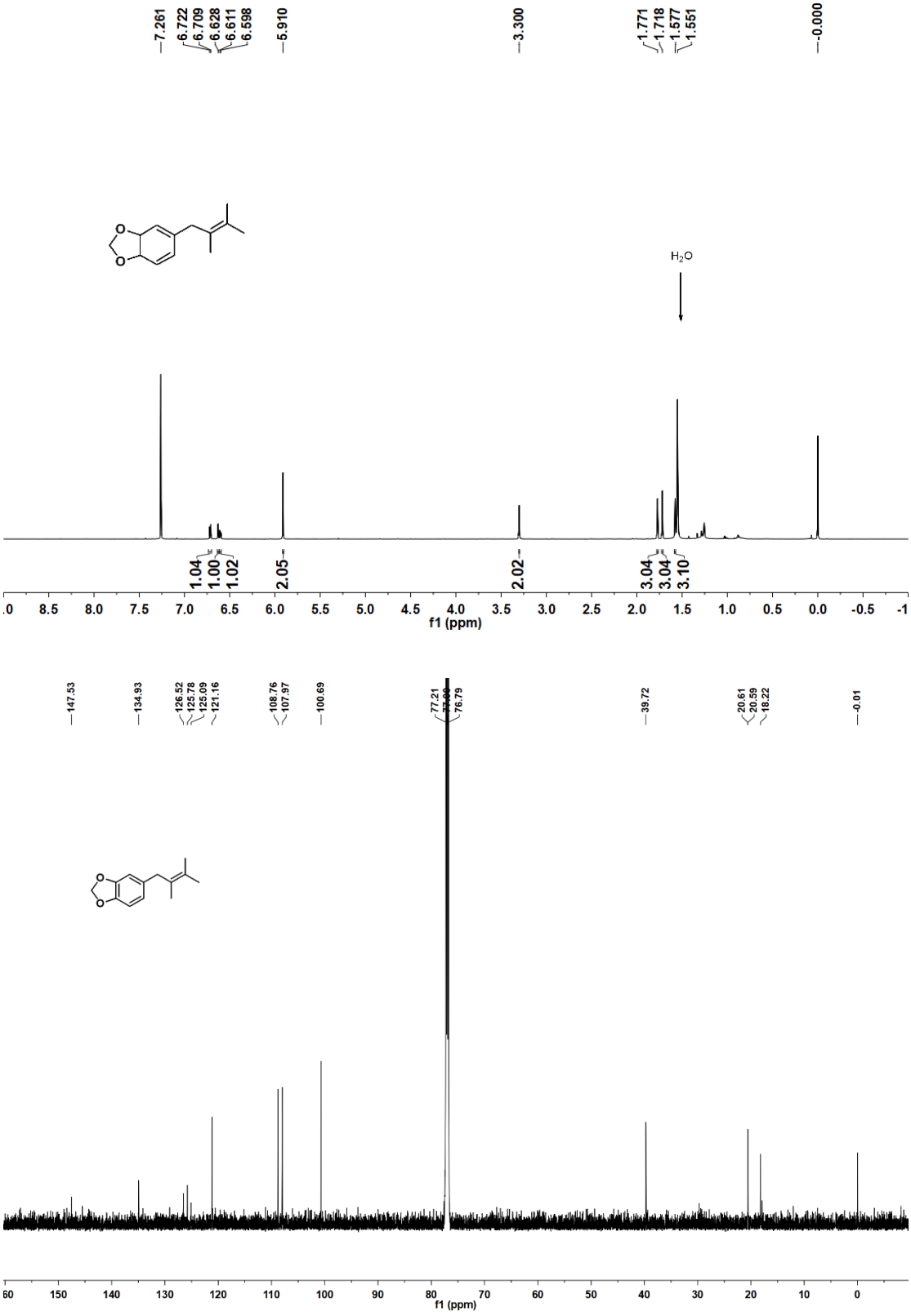


3av, ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)

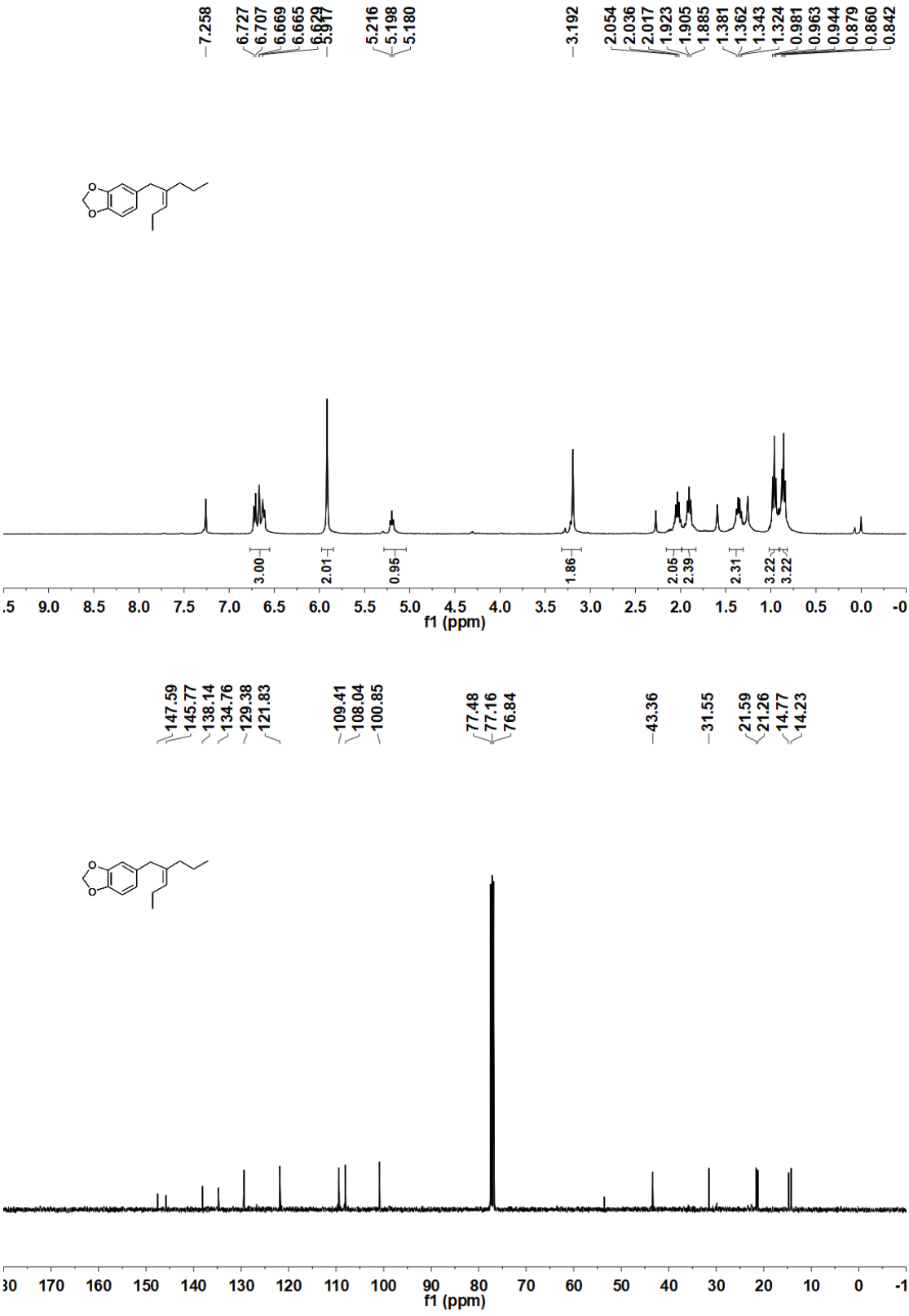




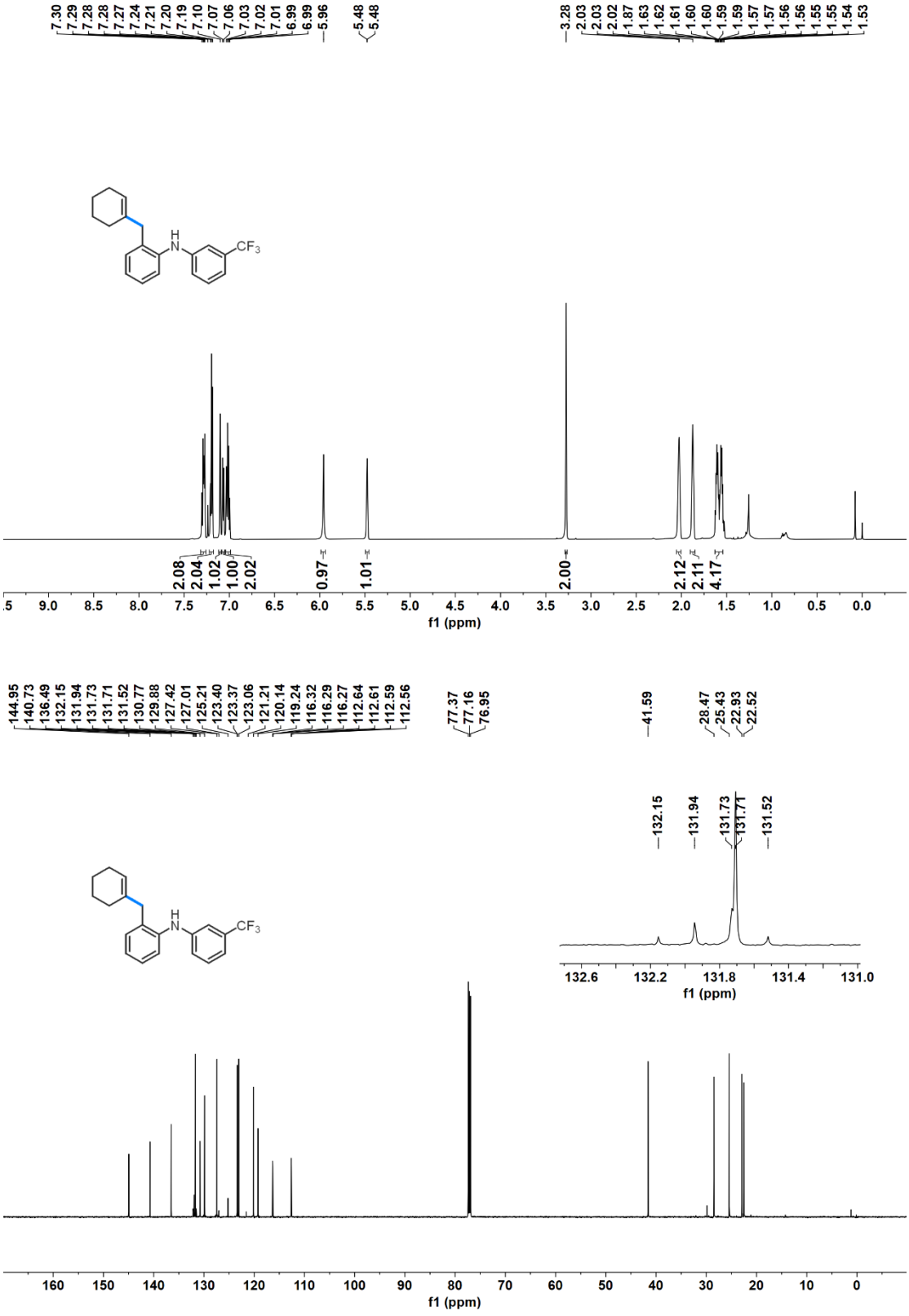
3aw, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)



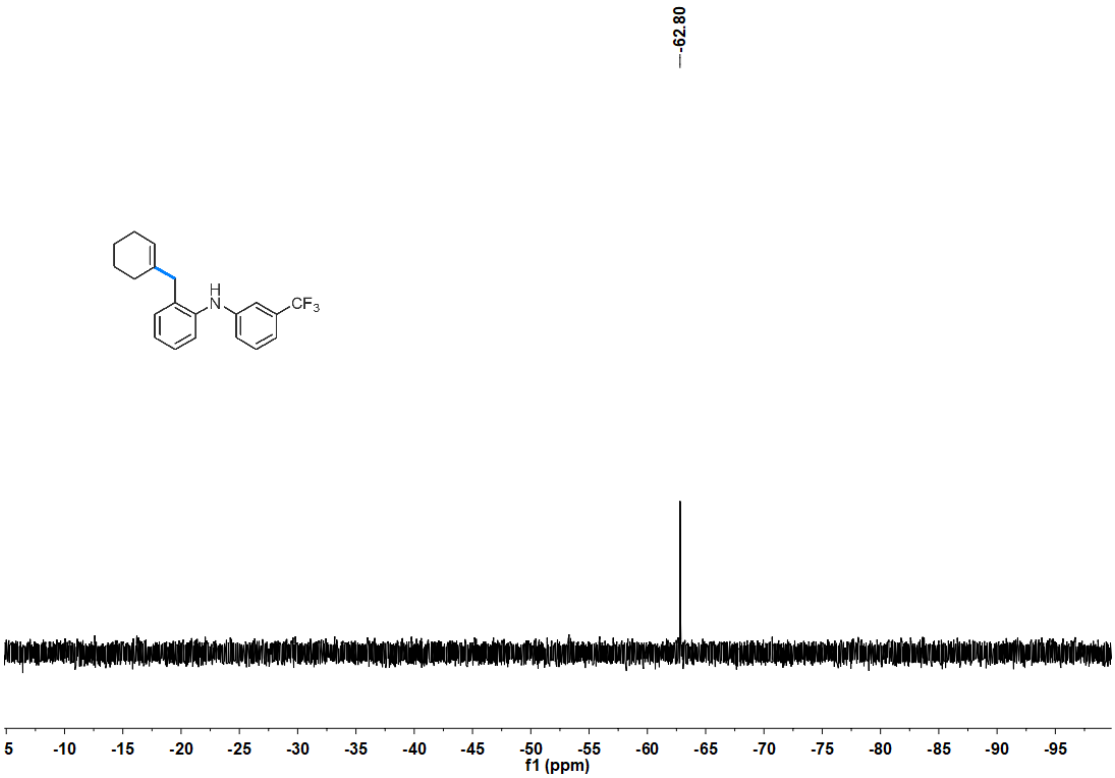
3ax, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)



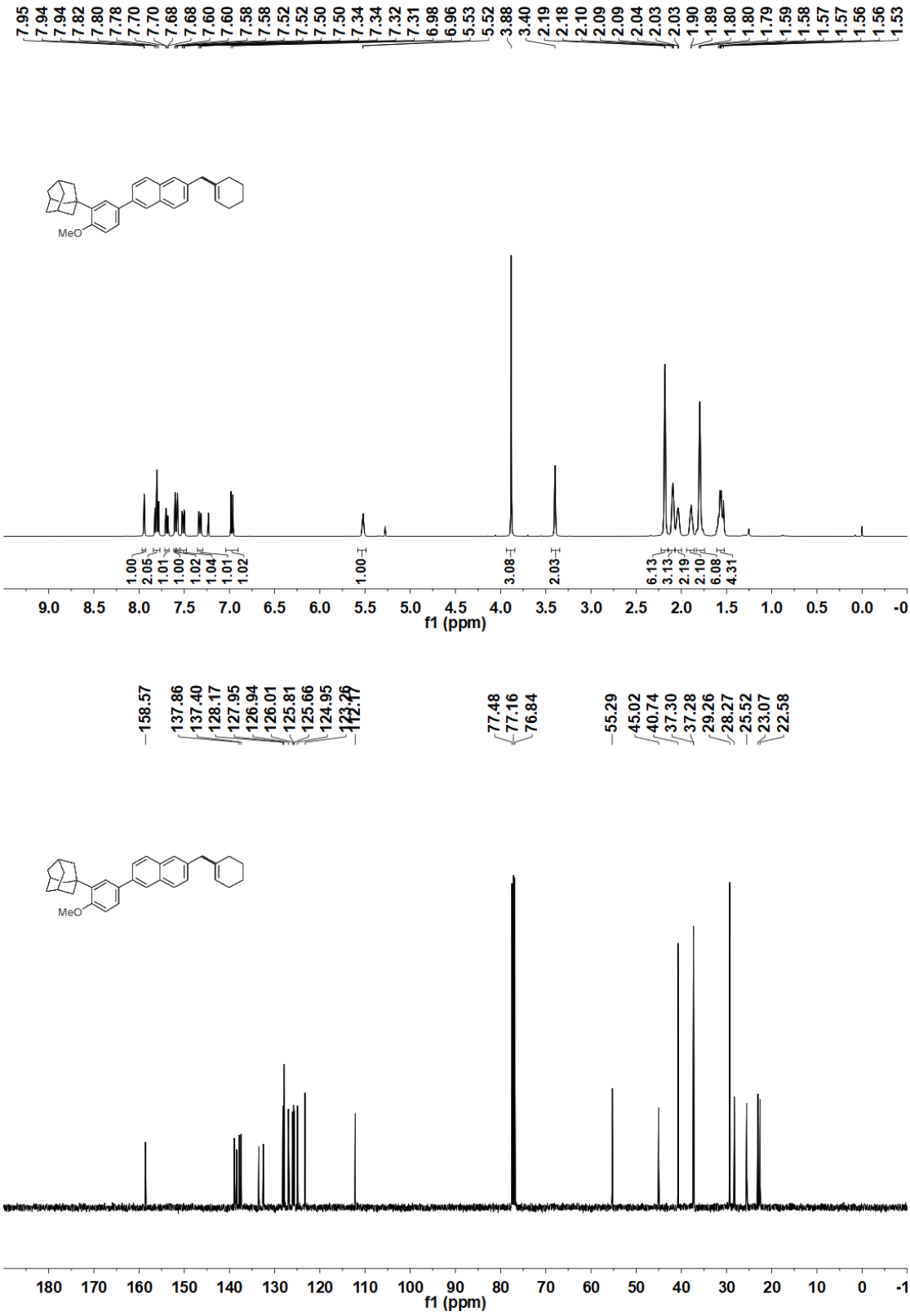
4, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)



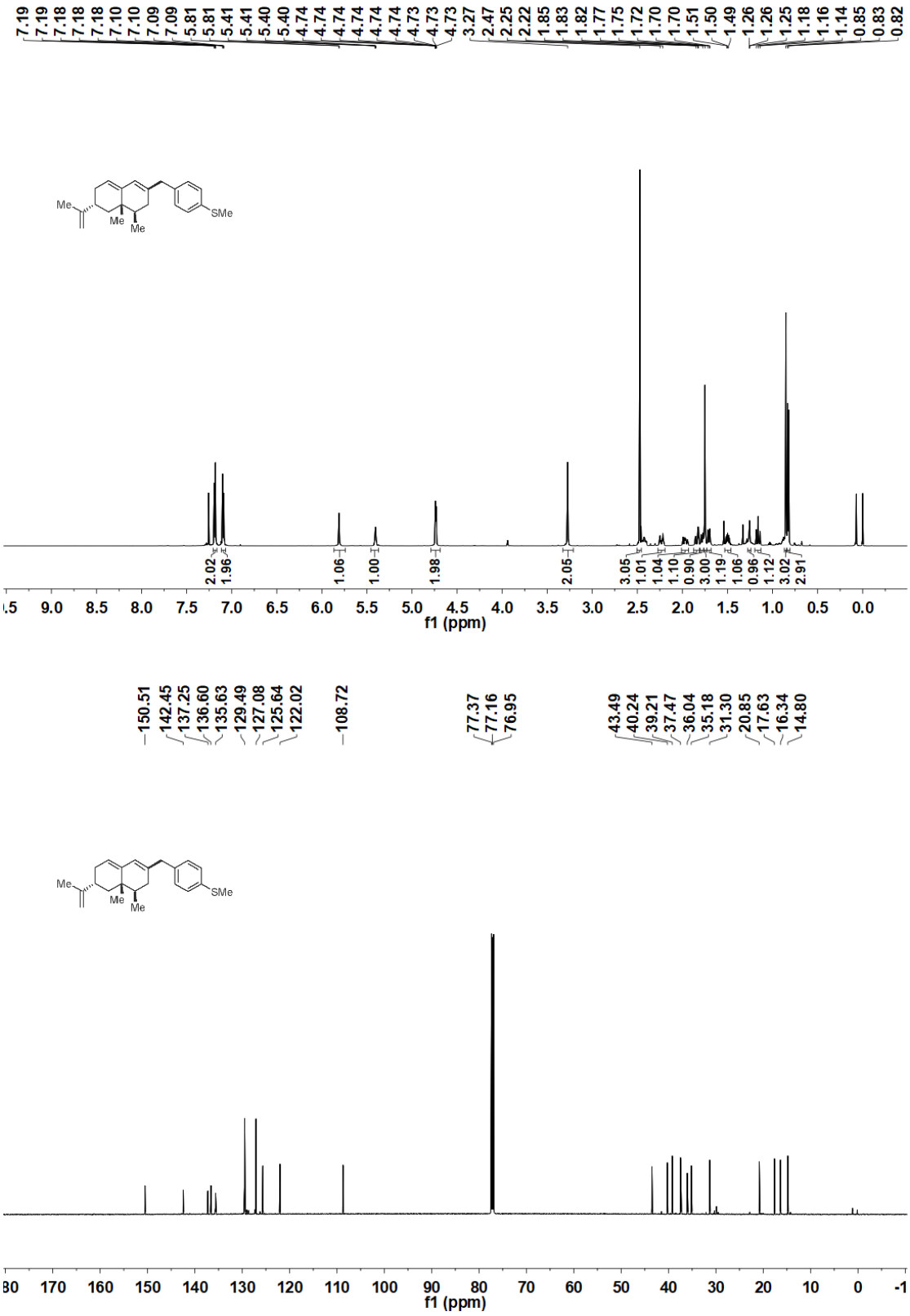
4, ^{19}F NMR (376 MHz, $CDCl_3$)



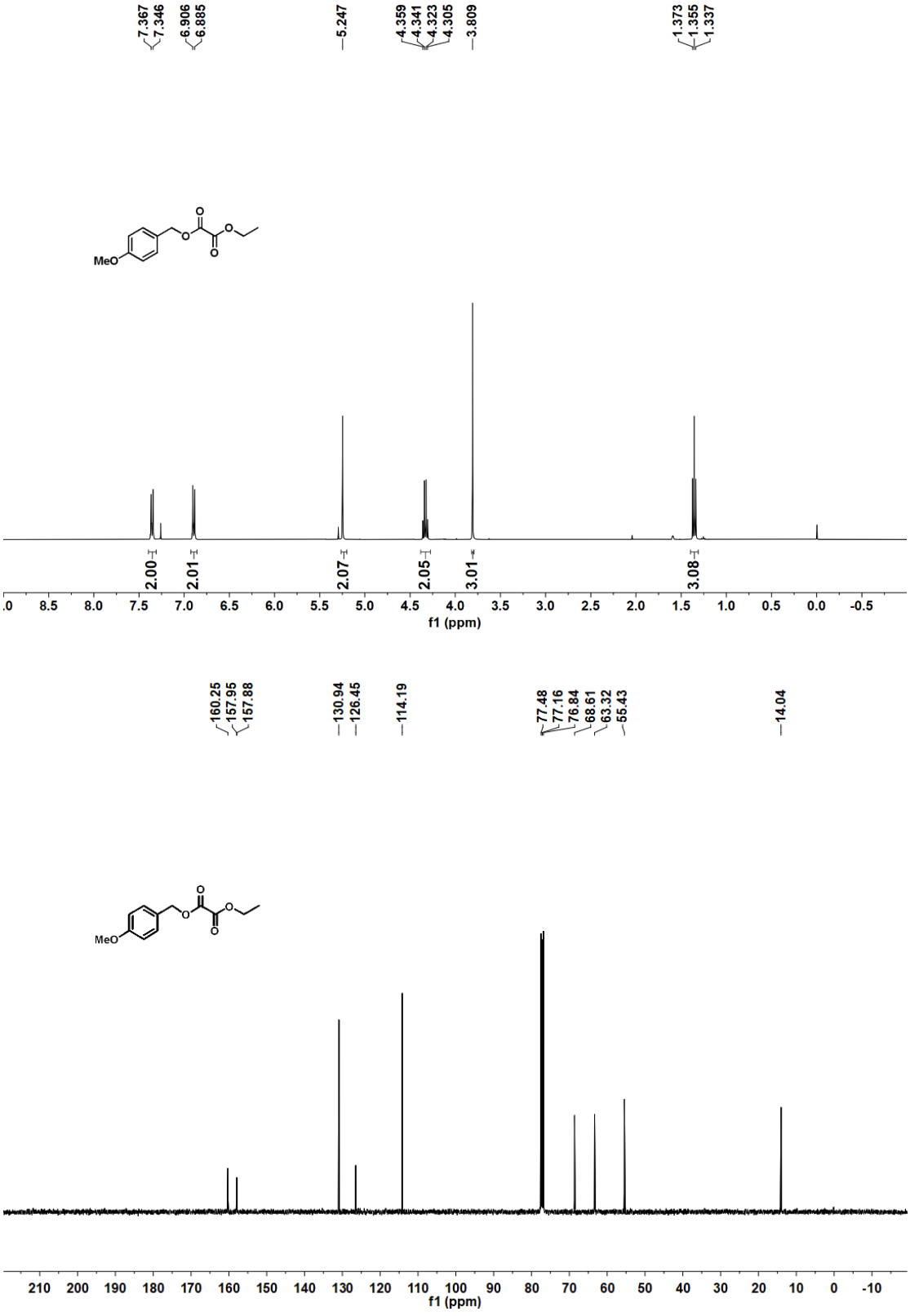
5, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)



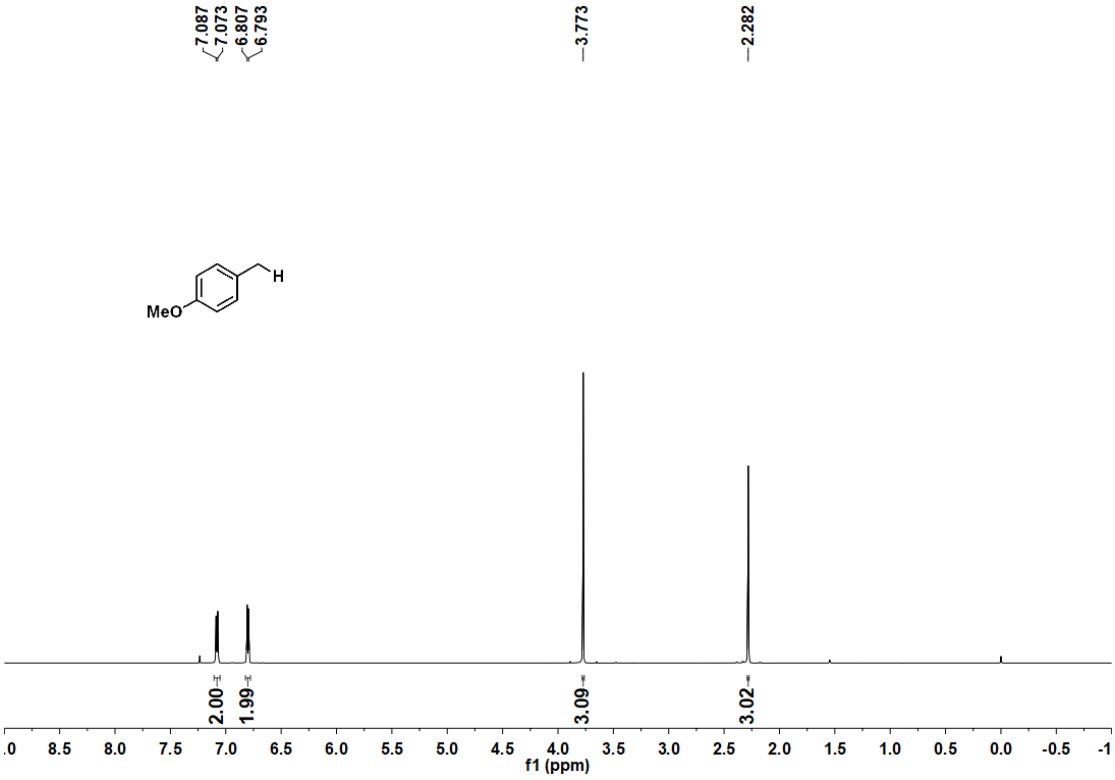
6, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)

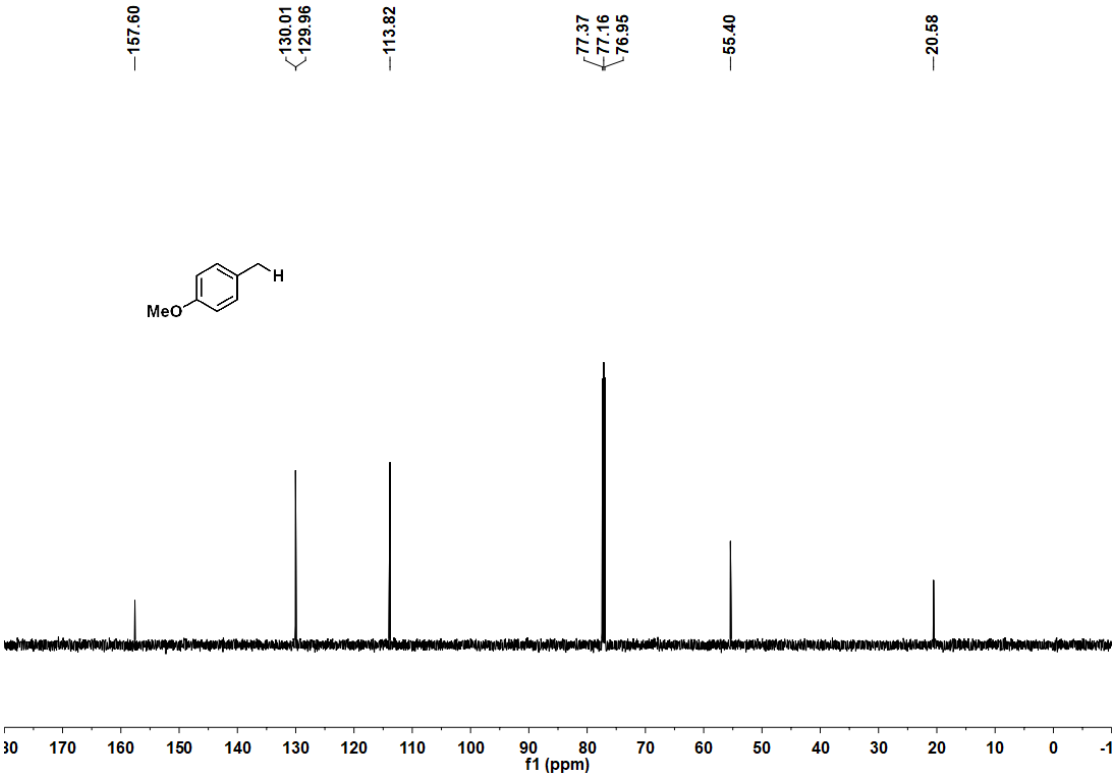


7, ^{1}H NMR (400 MHz, $CDCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$)

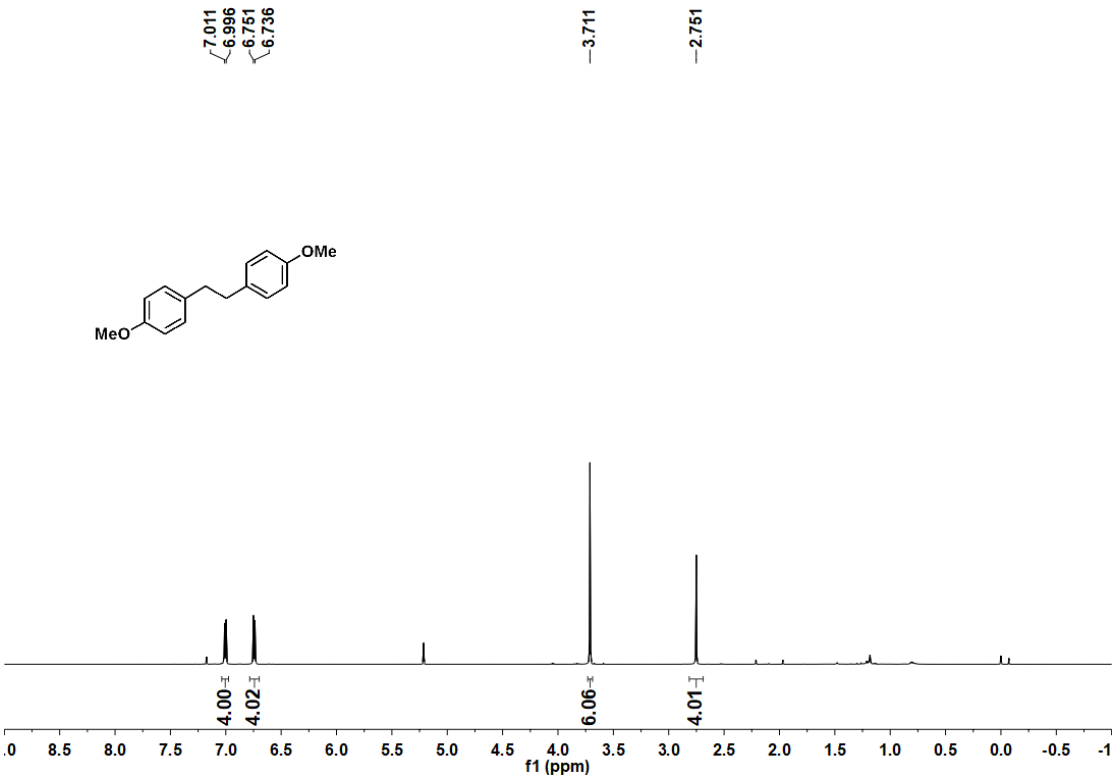


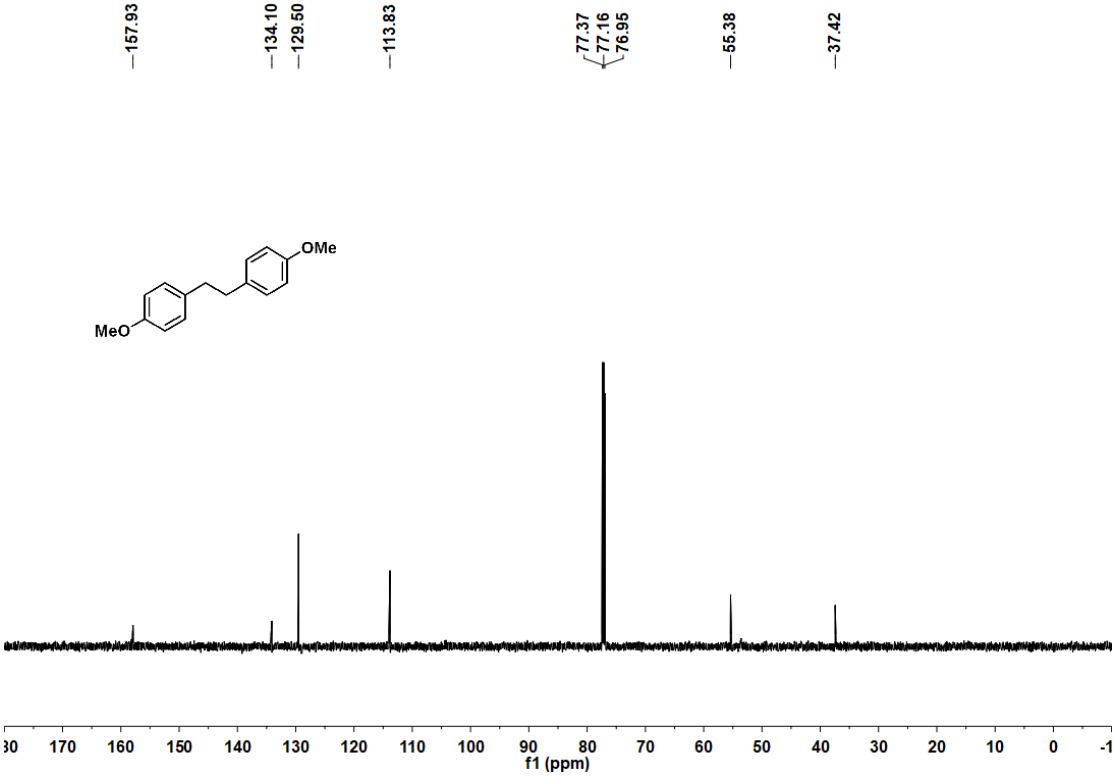
8, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)





9, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)





11, ^{1}H NMR (600 MHz, $CDCl_3$); ^{13}C NMR (150 MHz, $CDCl_3$)