Catalytic coupling of *N*-benzylic sulfonamides with silylated nucleophiles at room temperature

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Supporting information

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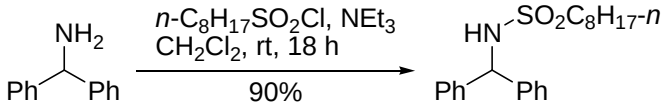
General information

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-300 FT (300 MHz and 75 MHz, respectively) using tetramethylsilane as internal reference, and chemical shifts (δ) and coupling constants (*J*) were expressed in ppm and Hz, respectively. IR spectra were recorded on a Perkin-Elmer 2000 FTIR spectrometer. High resolution mass spectra (HRMS) were recorded on a LC-TOF spectrometer (Micromass). Melting points are uncorrected. High pressure liquid chromatography (HPLC) analyses were performed on a Hewlett-Packard 1200 Series instrument equipped with an isostatic pump, using a Daicel Chiralpak OJ column (250 x 4.6 mm), and the UV detection was monitored at 230 nm.

Sulfonamide **1ae** was prepared as described below. Similarly, sulfonamides **1a**, **1ab-1ad**, **1f**, and **1i** were prepared by treatment of the corresponding amines with sulfonyl chloride and triethylamine in dichloromethane at room temperature. The rest of sulfonamides were prepared from the corresponding alcohols and primary sulfonamides according to a literature procedure.[1] Compounds **1af** and **1ag** were prepared by treatment of benzhydrylamine with PhCOCl and CbzCl, respectively, in the presence of triethylamine in dichloromethane at room temperature. The rest of chemicals and solvents were purchased from the Sinopharm Chemical Reagent Co., Meryer, Acros, and Alfa Aesar, and used as received.

Preparation of sulfonamide 1ae



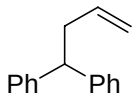
1ae

To a stirred solution of benzhydrylamine (549 mg, 3.0 mmol) in dichloromethane (30 mL) were added triethylamine (30.3 mg, 0.042 mL, 0.30 mmol) and octane-1-sulfonyl chloride (763 mg, 3.6 mmol). The resulting mixture was stirred at room temperature for 18 h. The reaction mixture was quenched with saturated aqueous sodium bicarbonate (30 mL), and extracted with dichloromethane (3 x 30 mL). The organic phase was dried over sodium sulfate, filtered, and concentrated. The residue was purified by silica gel column chromatography, eluting with petroleum ether/ethyl acetate (10:1), to give sulfonamide **1ae** (970 mg, 90 %) as a white solid. m.p. 71-72 ℃; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37-7.26 (m, 10H), 5.72 (d, *J* = 7.7 Hz, 1H), 5.25 (d, *J* = 7.7 Hz, 1H), 2.72-2.66 (m, 2H), 1.62-1.51 (m, 2H), 1.31-1.08 (m, 10H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.1, 128.9, 128.0, 127.5, 61.2, 53.9, 31.8, 29.0, 28.1, 23.4, 22.7, 14.2; IR (film): ν 3387, 3020, 2928, 1601, 1496, 1455 cm^{-1}; HRMS (EI) calcd. for $C_{15}H_{24}NO_2S$ (M-Ph): 282.1528. Found: 282.1533.

General procedure for the catalytic coupling of *N*-benzylic sulfonamides with allylic silanes (Table 2)

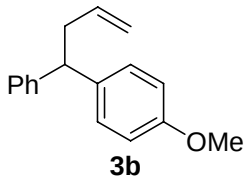
To a solution of sulfonamide **1** (0.20 mmol) in dichloromethane (0.30 mL) at room temperature were added an allylic silane (0.40 mmol) and Tf_2NH (5.6 mg, 10 mol %). The resulting mixture was stirred at room temperature until no further transformation was detected by TLC analysis. The mixture was purified by silica gel column chromatography, eluting with petroleum ether, to give product **3**.

Analytical data for the products shown in Table 2



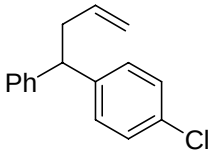
3a

3a,[2] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30-7.12 (m, 10H), 5.79-5.62 (m, 1H), 5.08-4.90 (m, 2H), 4.00 (t, *J* = 7.8 Hz, 1H), 2.83-2.76 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.6, 136.9, 128.5, 128.1, 126.3, 116.4, 51.3, 40.1.



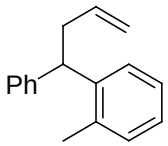
3b

3b,[2] white solid; m.p. 59-60℃; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30-7.11 (m, 7H), 6.85-6.78 (m, 2H), 5.79-5.63 (m, 1H), 5.07-4.91 (m, 2H), 3.95 (t, *J* = 7.8 Hz, 1H), 3.74 (s, 3H), 2.80-2.73 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.1, 145.1, 137.1, 136.8, 129.0, 128.5, 128.0, 126.2, 116.3, 113.9, 55.3, 50.5, 40.3.



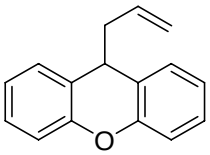
3c

3c,[2] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30-7.13 (m, 9H), 5.77-5.61 (m, 1H), 5.07-4.92 (m, 2H), 3.98 (t, *J* = 7.8 Hz, 1H), 2.82-2.73 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.7, 141.9, 136.5, 130.2, 129.5, 128.7, 128.0, 127.5, 126.5, 116.7, 50.7, 40.0.



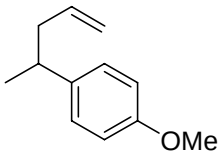
3d

3d,[3] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34-7.10 (m, 9H), 5.81-5.68 (m, 1H), 5.08-4.91 (m, 2H), 4.20 (t, *J* = 7.7 Hz, 1H), 2.81-2.73 (m, 2H), 2.25 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.2, 142.3, 137.1, 136.4, 130.6, 128.4, 127.0, 126.3, 126.1, 126.1, 116.4, 47.1, 40.5, 20.0.



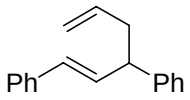
3e

3e,[4] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28-7.02 (m, 8H), 5.70-5.53 (m, 1H), 4.97-4.77 (m, 2H), 4.06 (t, *J* = 6.2 Hz, 1H), 2.51-2.46 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.3, 134.7, 128.9, 127.7, 123.1, 117.8, 116.4, 45.4, 39.5.



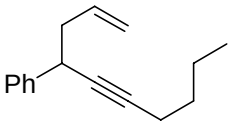
3f

3f,[3] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.12-7.08 (m, 2H), 6.86-6.80 (m, 2H), 5.78-5.62 (m, 1H), 5.01-4.91 (m, 2H), 3.78 (s, 3H), 2.80-2.68 (m, 1H), 2.40-2.20 (m, 2H), 1.22 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.9, 139.4, 137.5, 128.0, 115.9, 113.8, 55.4, 43.0, 39.1, 21.9.



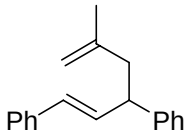
3g

3g,[5] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36-7.13 (m, 10H), 6.42-6.30 (m, 2H), 5.82-5.70 (m, 1H), 5.10-4.93 (m, 2H), 3.55-3.47 (m, 1H), 2.61-2.52 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.0, 137.6, 136.6, 133.6, 129.9, 128.6, 127.9, 127.2, 126.5, 126.3, 116.5, 49.1, 40.3.



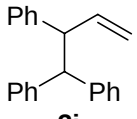
3h

3h,[6] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38-7.18 (m, 5H), 5.93-5.78 (m, 1H), 5.08-5.00 (m, 2H), 3.70-3.63 (m, 1H), 2.50-2.43 (m, 2H), 2.27-2.20 (m, 2H), 1.56-1.39 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.3, 136.0, 128.4, 127.6, 126.7, 116.7, 83.9, 81.2, 43.2, 38.2, 31.3, 22.1, 18.6, 13.7.



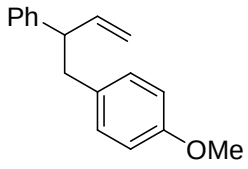
3i

3i,[5] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37-7.15 (m, 10H), 6.38-6.32 (m, 2H), 4.73 (s, 1H), 4.68 (s, 1H), 3.70-3.62 (m, 1H), 2.54 (d, J = 7.5 Hz, 2H), 1.72 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.2, 143.4, 137.7, 133.9, 129.6, 128.6, 127.8, 127.2, 126.4, 126.3, 112.7, 47.2, 44.5, 22.7.



3j

3j,[2] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38-6.93 (m, 15H), 5.98-5.84 (m, 1H), 4.91-4.80 (m, 2H), 4.31-4.26 (m, 1H), 4.20-4.11 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.6, 141.0, 128.8, 128.5, 128.5, 128.3, 128.2, 126.4, 126.2, 125.9, 116.0, 57.2, 54.5.

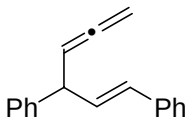


3k

3k, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30-7.11 (m, 5H), 6.96 (d *J* = 8.4 Hz, 2H), 6.75 (d *J* = 8.4 Hz, 2H), 6.08-5.96 (m, 1H), 5.03-4.91 (m, 2H), 3.76 (s, 3H), 3.56-3.48 (m, 1H), 2.98-2.92 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.9, 143.9, 141.6, 132.3, 130.2, 128.5, 128.0, 126.4, 114.8, 113.6, 55.3, 51.9, 41.5. IR (film): ν 3014, 2974, 1637, 1611, 1584, 1512, 1453 cm^{-1}; HRMS (EI) calcd. for $C_{17}H_{18}O$ (M): 238.1358. Found: 238.1363.

Catalytic coupling of sulfonamide 1g with propargylic silane 4a

To a solution of sulfonamide **1g** (72.6 mg, 0.20 mmol) in dichloromethane (0.30 mL) were added propargylic silane **4a** (44.9 mg, 0.060 mL, 0.40 mmol) and Tf_2NH (5.6 mg, 10 mol %). The resulting mixture was stirred at room temperature for 9 h. The mixture was purified by silica gel column chromatography, eluting with petroleum ether, to give allene **5a** (20.0 mg, 43%) as a colorless oil.

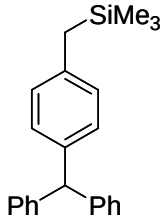


5a

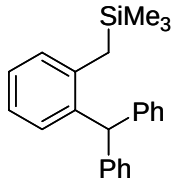
5a, colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38-7.16 (m, 10H), 6.46-6.40 (m, 2H), 5.49-5.41 (m, 1H), 4.82-4.78 (m, 2H), 4.28-4.19 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 208.6, 143.0, 137.4, 132.1, 130.5, 128.7,128.6, 128.1, 127.4, 126.8, 126.4, 93.4, 76.7, 48.1. IR (film): ν 3019, 1955, 1600, 1494, 1451 cm^{-1}; HRMS (EI) calcd. for $C_{18}H_{16}$ (M): 232.1252. Found: 232.1250.

Catalytic coupling of sulfonamide 1a with benzylic silane 6a

To a solution of sulfonamide **1a** (67.4 mg, 0.20 mmol) in dichloromethane (0.30 mL) were added benzyltrimethylsilane **6a** (39.4 mg, 0.046 mL, 0.24 mmol) and Tf_2NH (5.6 mg, 10 mol %). The resulting mixture was stirred at room temperature for 24 h. The mixture was purified by silica gel column chromatography, eluting with petroleum ether, to give a 97:3 mixture of regioisomers **7a** and **7b** (43.0 mg, 65%) as a colorless oil.



7a



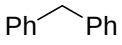
7b

7a, ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31-7.09 (m, 10H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 5.49 (s, 1H), 2.04 (s, 2H), -0.03 (s, 9H); Partial ^{1}H NMR for minor regioisomer **7b**, ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.62 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.5, 139.4, 138.5, 129.8, 129.6, 129.3, 128.4, 128.1, 126.3, 56.6, 26.7, -1.7; IR (film): ν 3025, 2954, 1599, 1508, 1494, 1450, 1416 cm^{-1}; HRMS (EI) calcd. for $C_{23}H_{26}Si$ (M): 330.1804. Found: 330.1793.

General procedure for the catalytic reduction of *N*-benzylic sulfonamides with triethylsilane (Table 3)

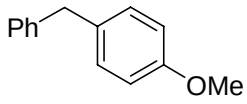
To a solution of sulfonamide **1** (0.20 mmol) in dichloromethane (0.30 mL) were added triethylsilane (27.9 mg, 0.039 mL, 0.24 mmol) and Tf_2NH (5.6 mg, 10 mol %). The resulting mixture was stirred at room temperature until no further transformation was detected by TLC analysis. The mixture was purified by silica gel column chromatography, eluting with petroleum ether, to give product **8**.

Analytical data for the products shown in Table 3



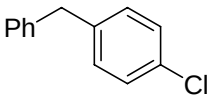
8a

8a,[7] Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29-7.14 (m, 10H), 3.96 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.2, 129.1, 128.6, 126.2, 42.1.



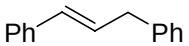
8b

8b,[7] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29-7.14 (m, 5H), 7.09 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.4 Hz, 2H), 3.91 (s, 2H), 3.76 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.1, 141.7, 133.4, 130.0, 128.9, 128.6, 126.1, 114.0, 55.4, 41.2.



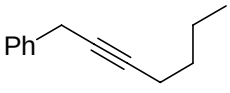
8c

8c,[7] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31-7.07 (m, 9H), 3.93 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.7, 139.7, 132.1, 130.4, 129.0, 128.7, 126.4, 41.4.



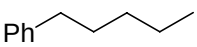
8d

8d,[8] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38-7.15 (m, 10H), 6.50-6.30 (m, 2H), 3.54 (d, J = 6.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.3, 137.6, 131.2, 129.4, 128.8, 128.6, 127.2, 126.3, 39.5.



8e

8e,[9] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38-7.19 (m, 5H), 3.58 (s, 2H), 2.27-2.19 (m, 2H), 1.58-1.38 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.8, 128.5, 128.0, 126.5, 82.8, 77.4, 31.3, 25.3, 22.1, 18.7, 13.8.



8f

8f,[10] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30-7.15 (m, 5H), 2.60 (t, J = 7.8 Hz, 2H), 1.68-1.57

(m, 2H), 1.39-1.27 (m, 4H), 0.89 (t, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.1, 128.5, 128.4, 125.7, 36.1, 31.7, 31.3, 22.7, 14.2.

Reaction of sulfonamide 1f with allylic silane 2a

This reaction was performed according to the general procedure for the catalytic coupling of *N*-benzylic sulfonamides with allylic silanes, and the ee of product **3f** was determined to be 3% by HPLC analysis (Chiralpak OJ column, IPA/*n*-Hex = 1:99, flow rate = 0.50 mL/min, t_{minor} = 12.5 min, t_{major} = 14.0 min).

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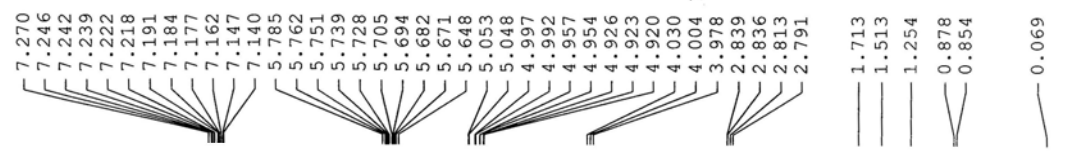
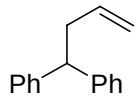
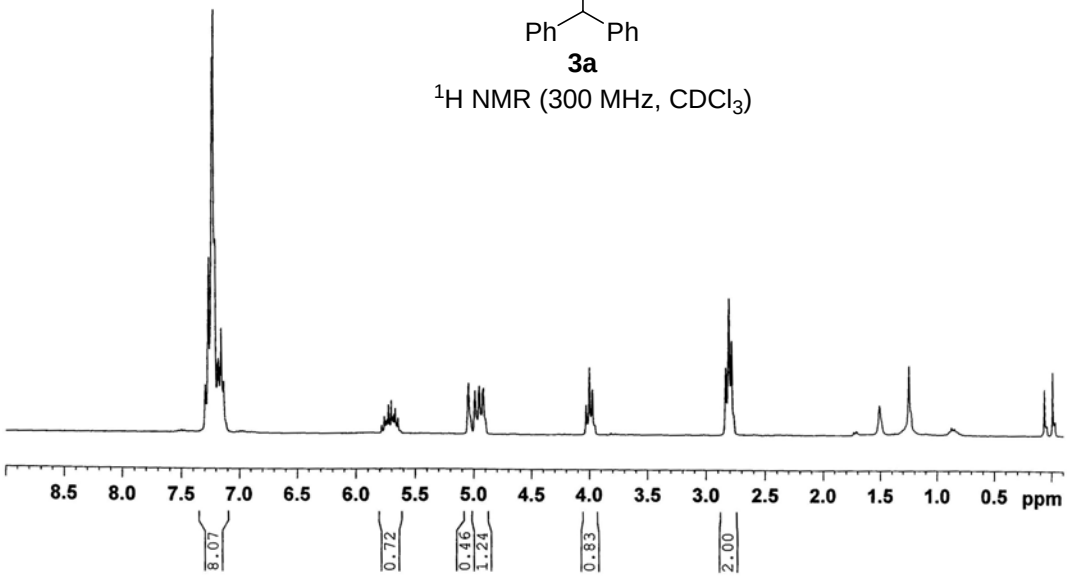
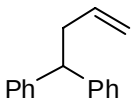




3a

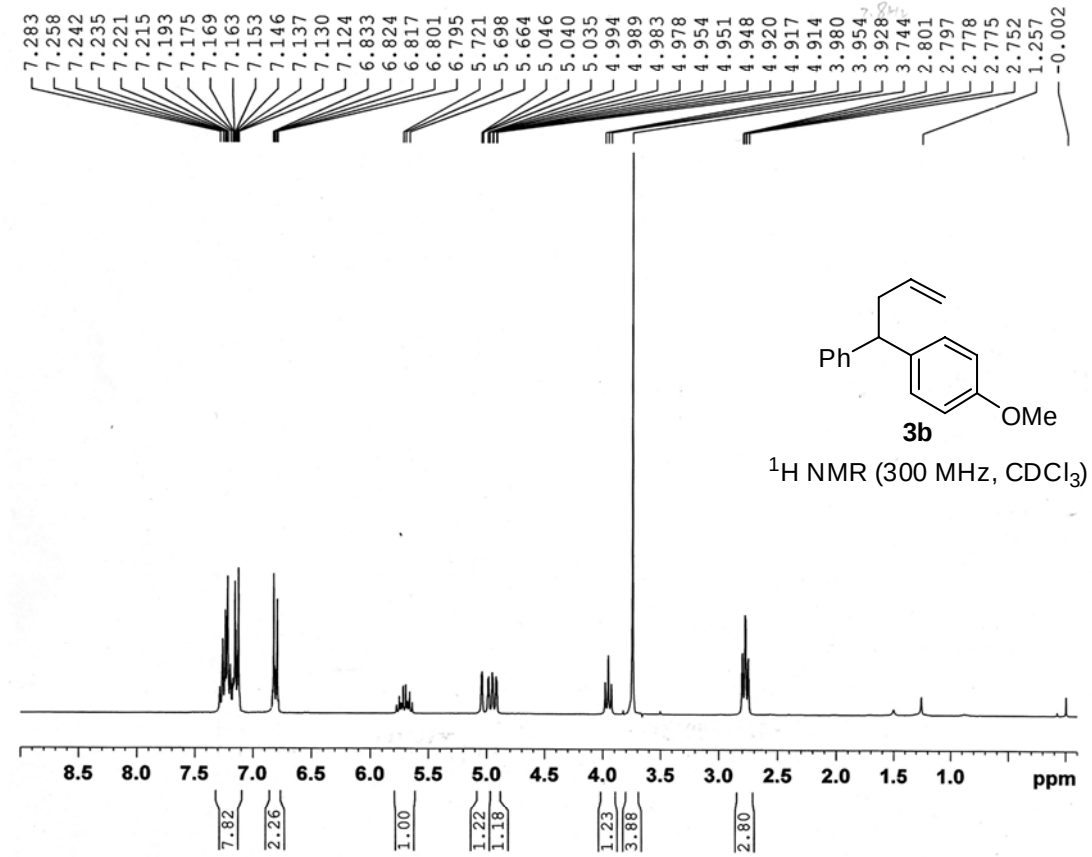
^{1}H NMR (300 MHz, $CDCl_3$)





3a

^{13}C NMR (75 MHz, $CDCl_3$)



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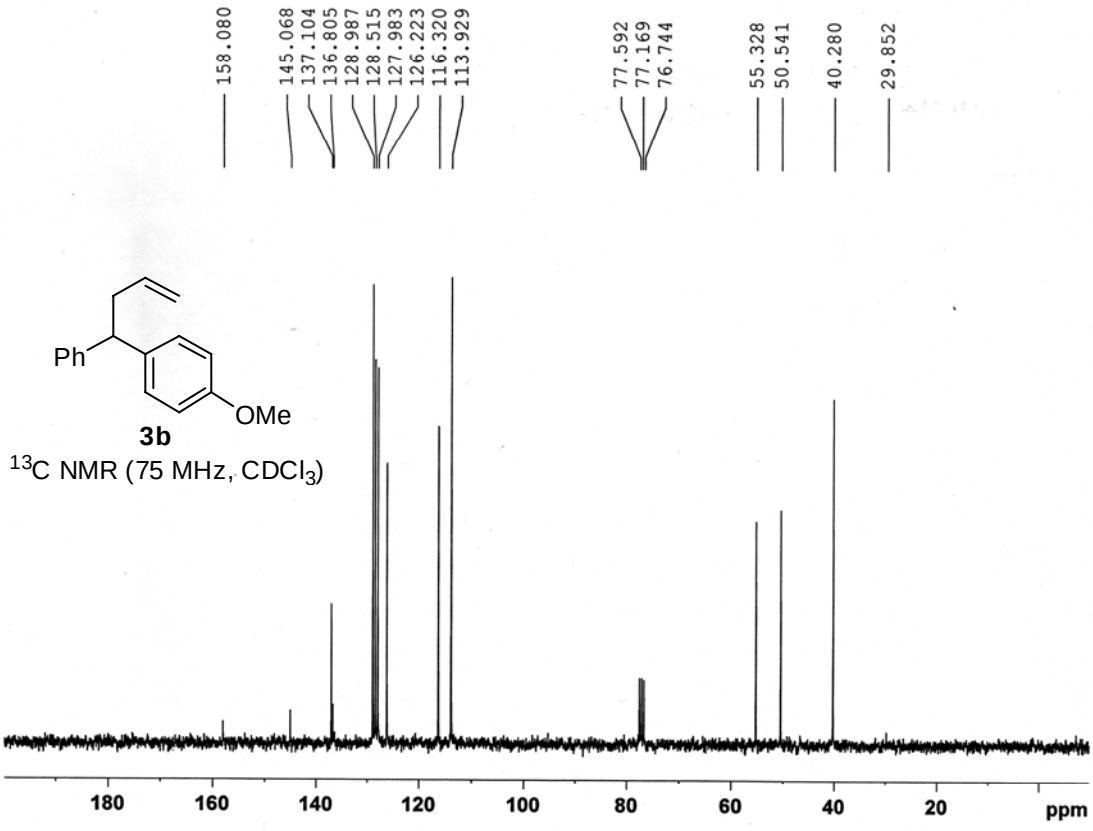

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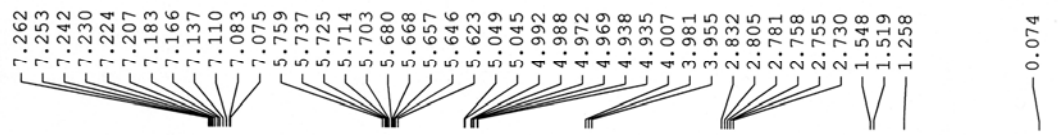
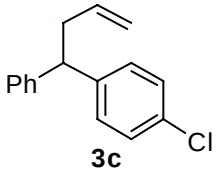
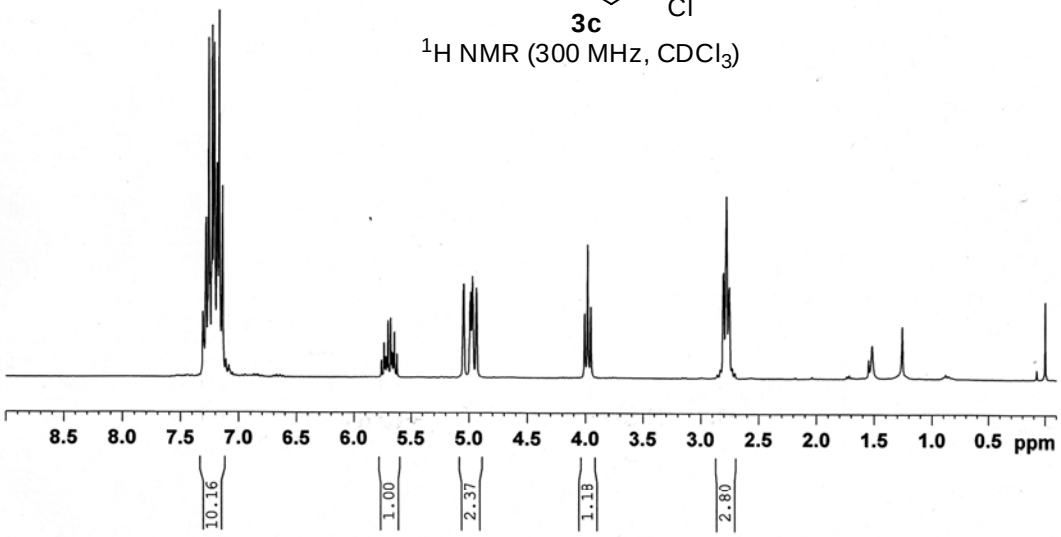
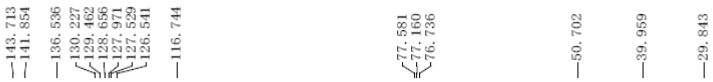


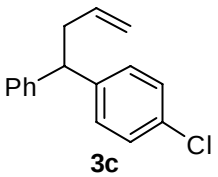


3c

^{1}H NMR (300 MHz, $CDCl_3$)

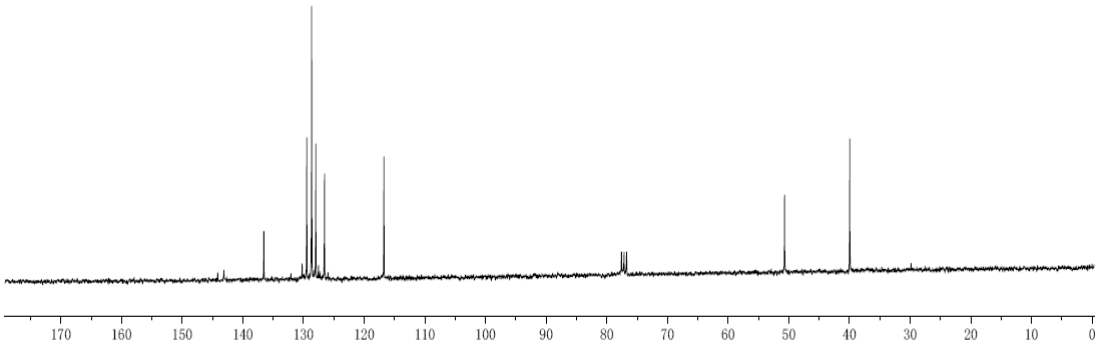


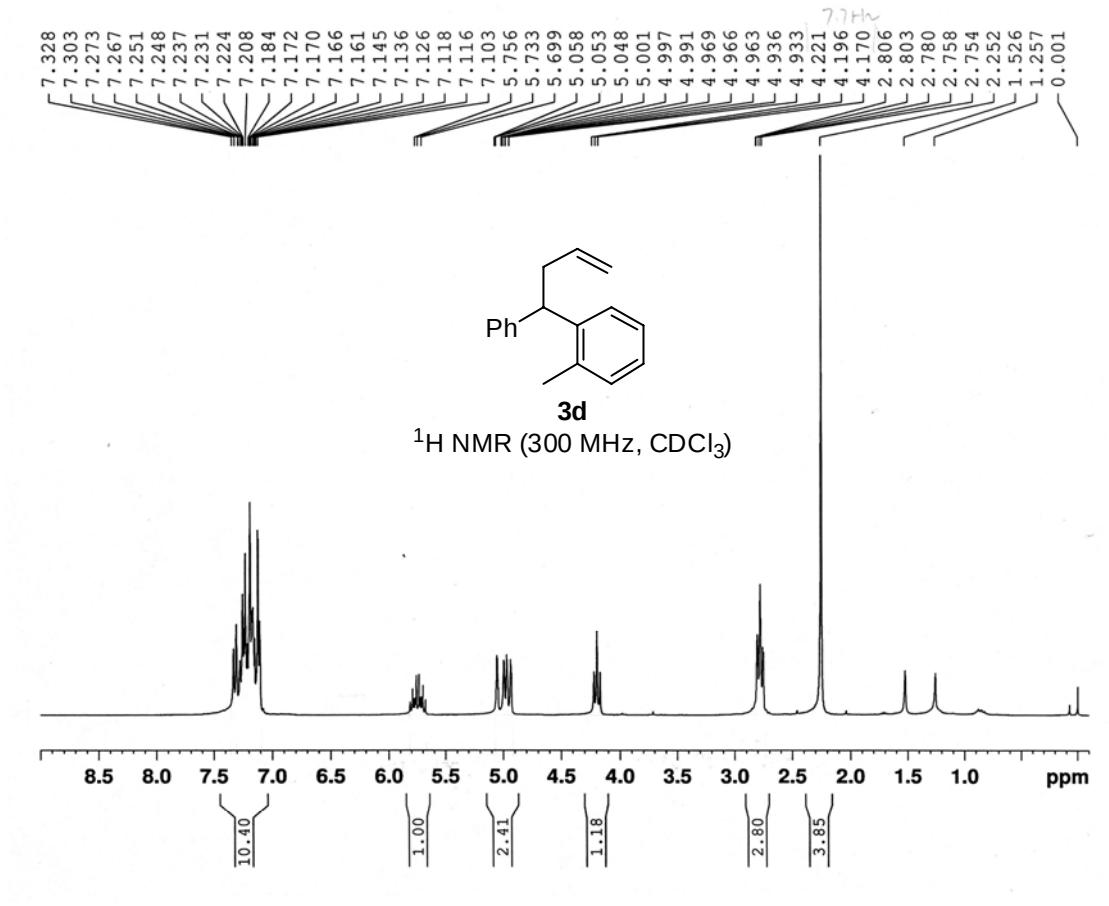




3c

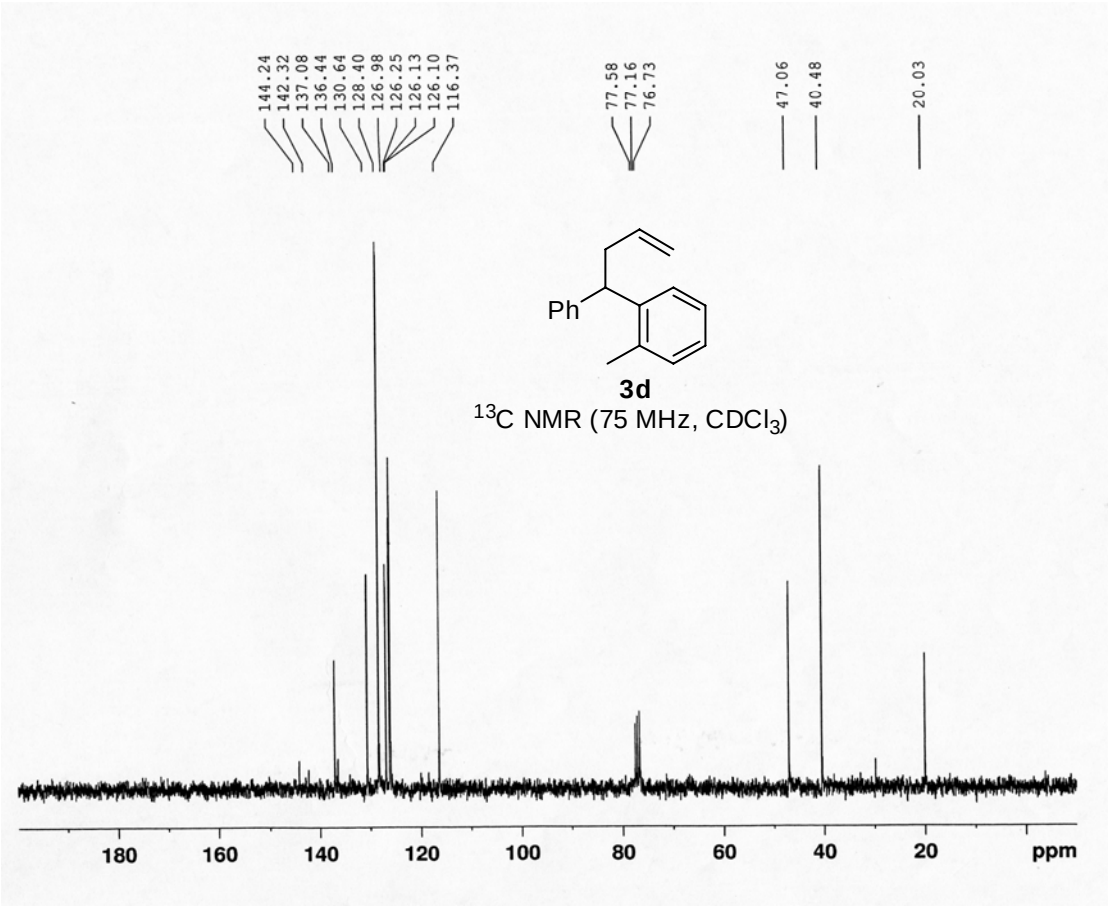
^{13}C NMR (75 MHz, $CDCl_3$)





3d

^{1}H NMR (300 MHz, $CDCl_3$)



3d

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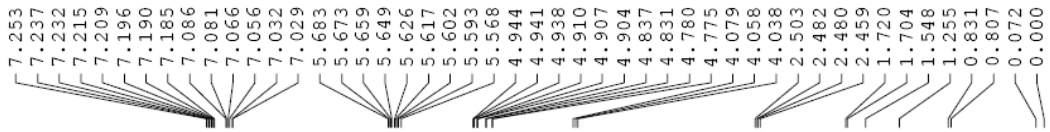
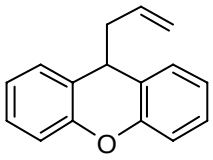
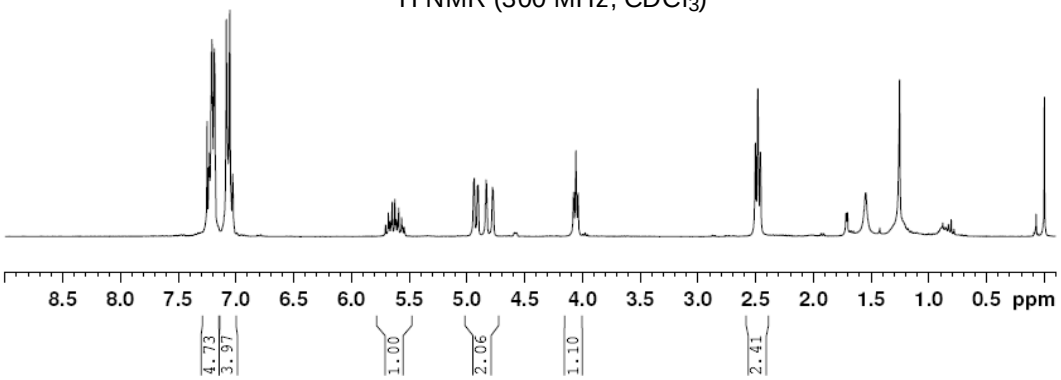
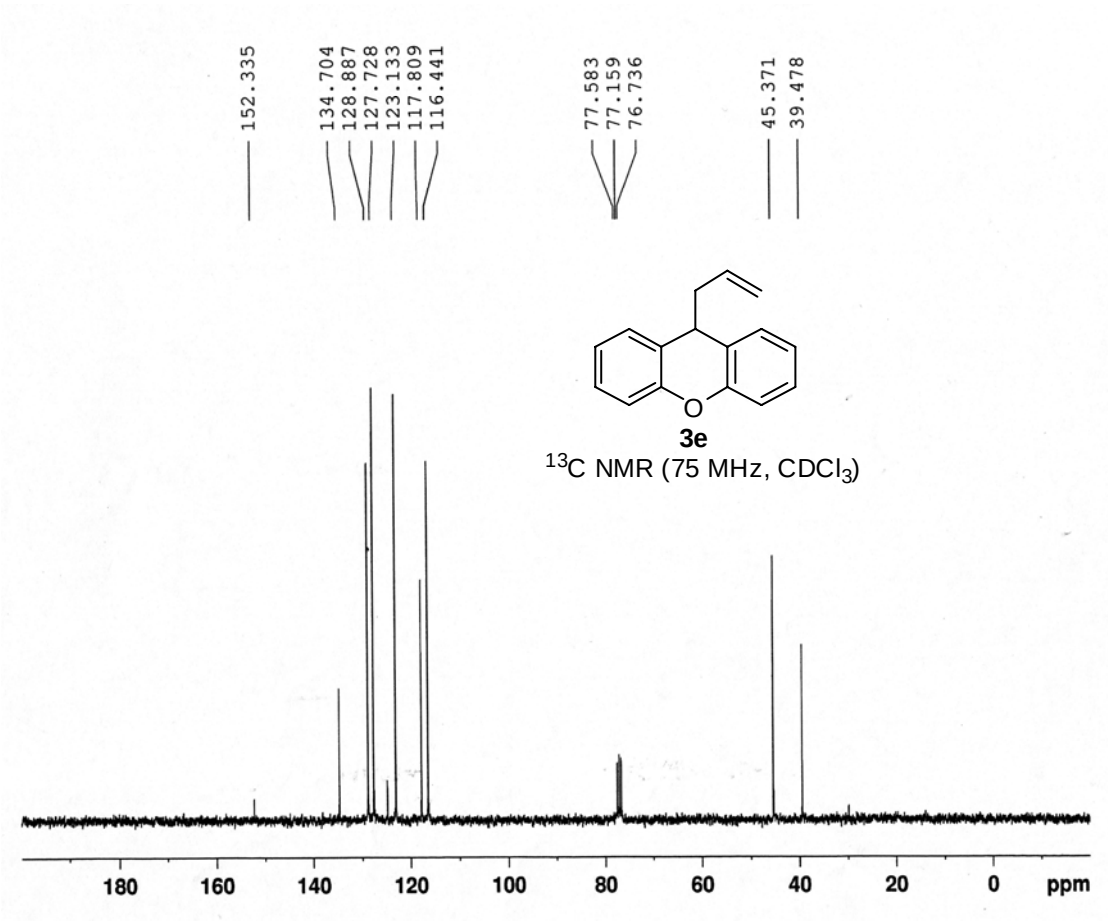




3e

^{1}H NMR (300 MHz, $CDCl_3$)





3e

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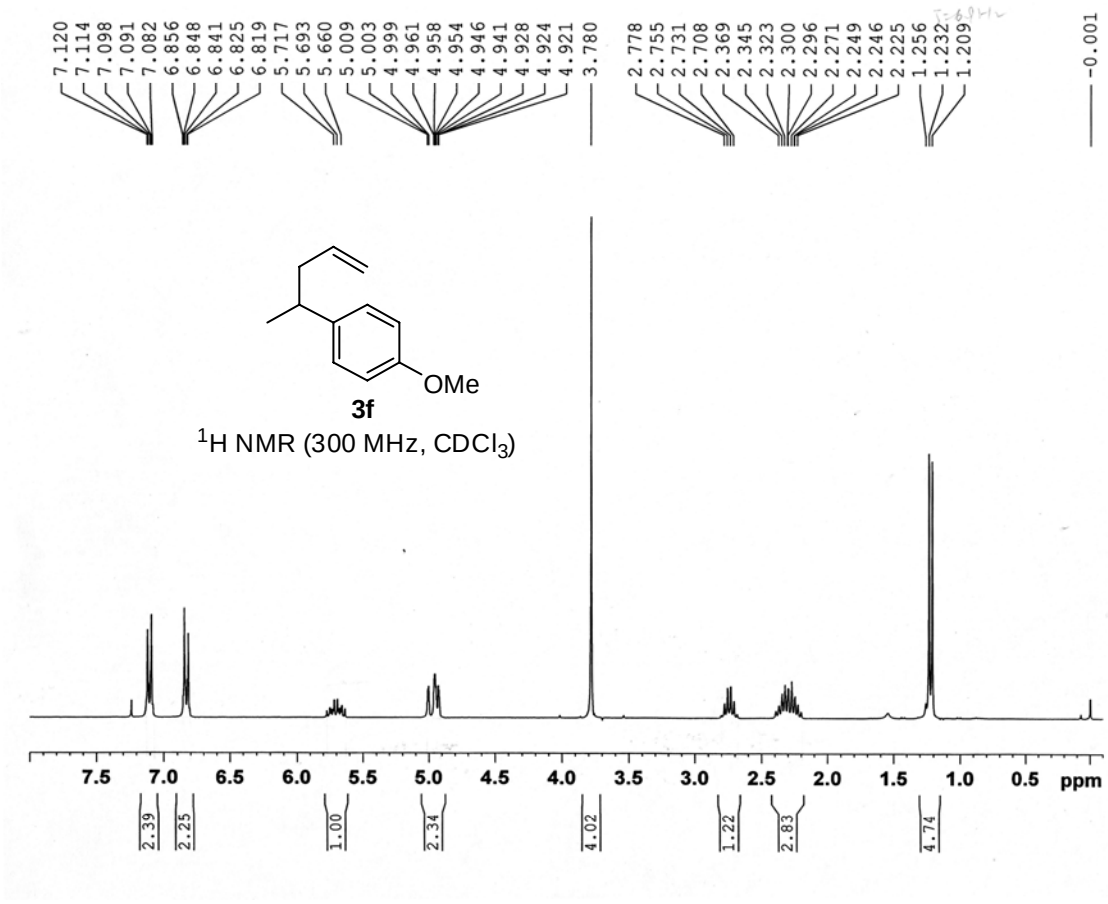

3f

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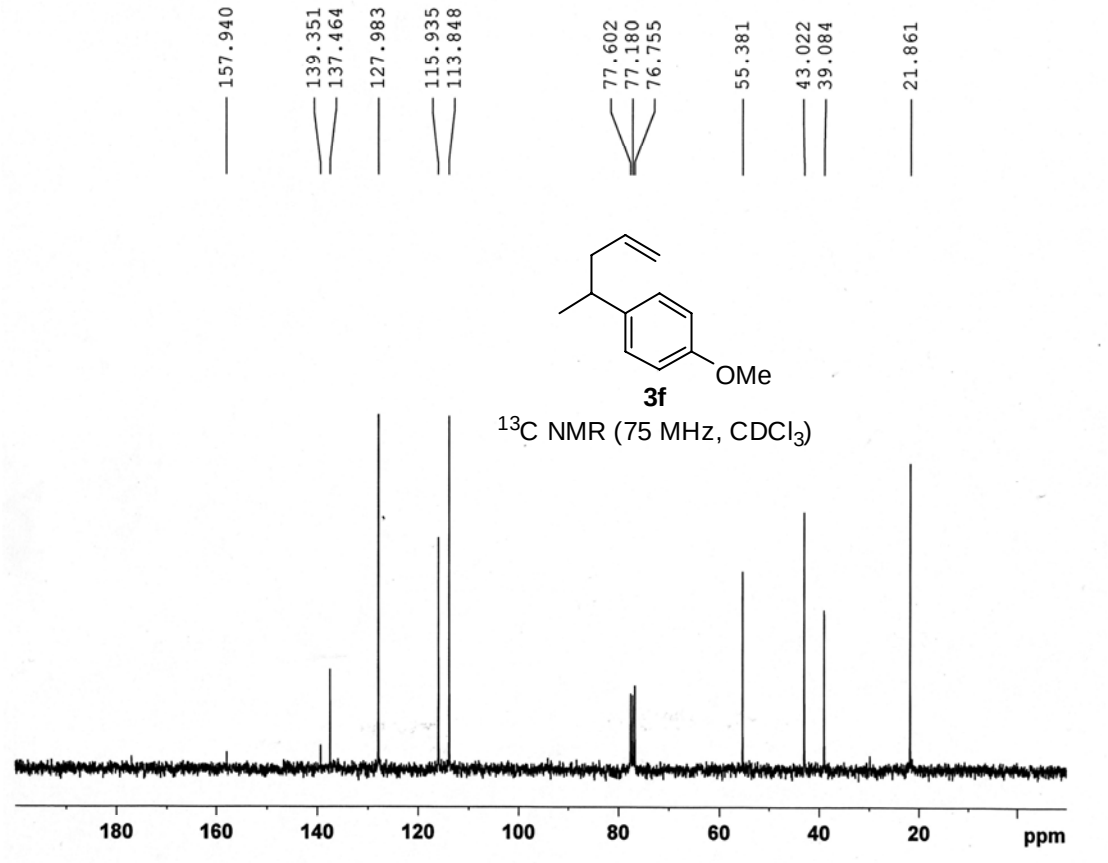
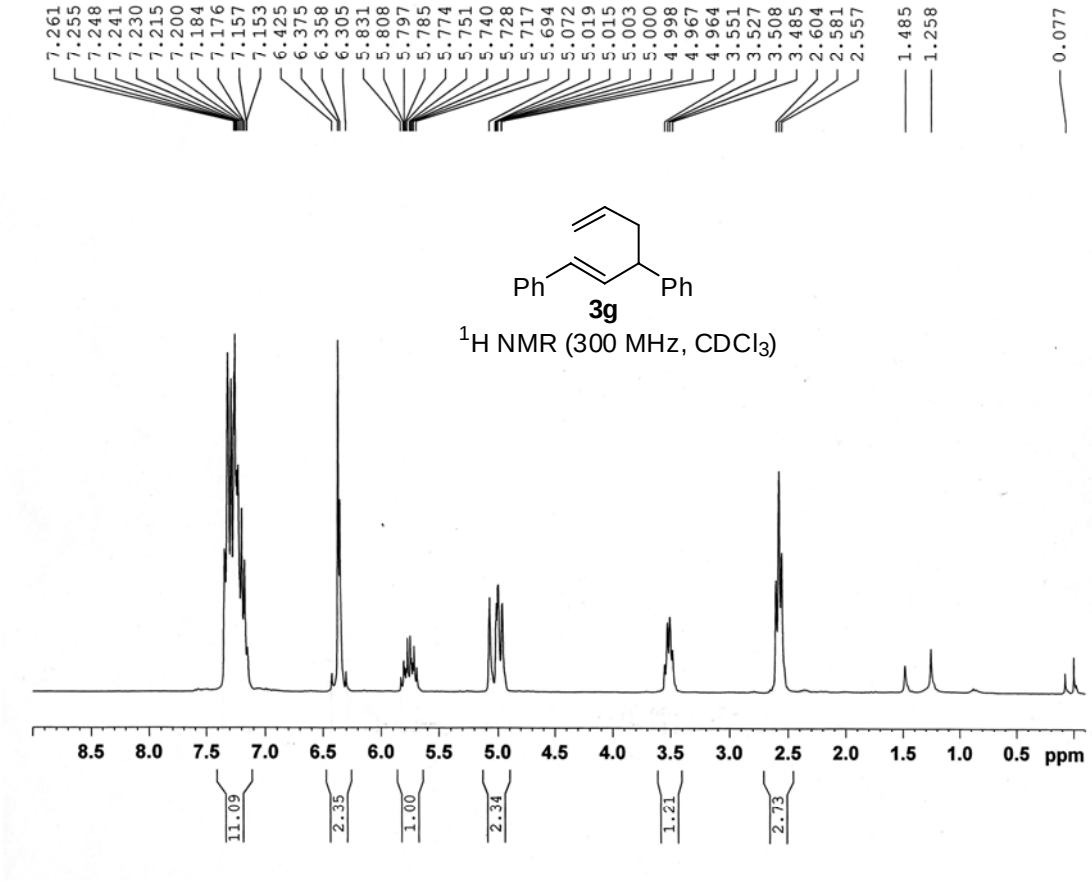


3f

^{13}C NMR (75 MHz, $CDCl_3$)



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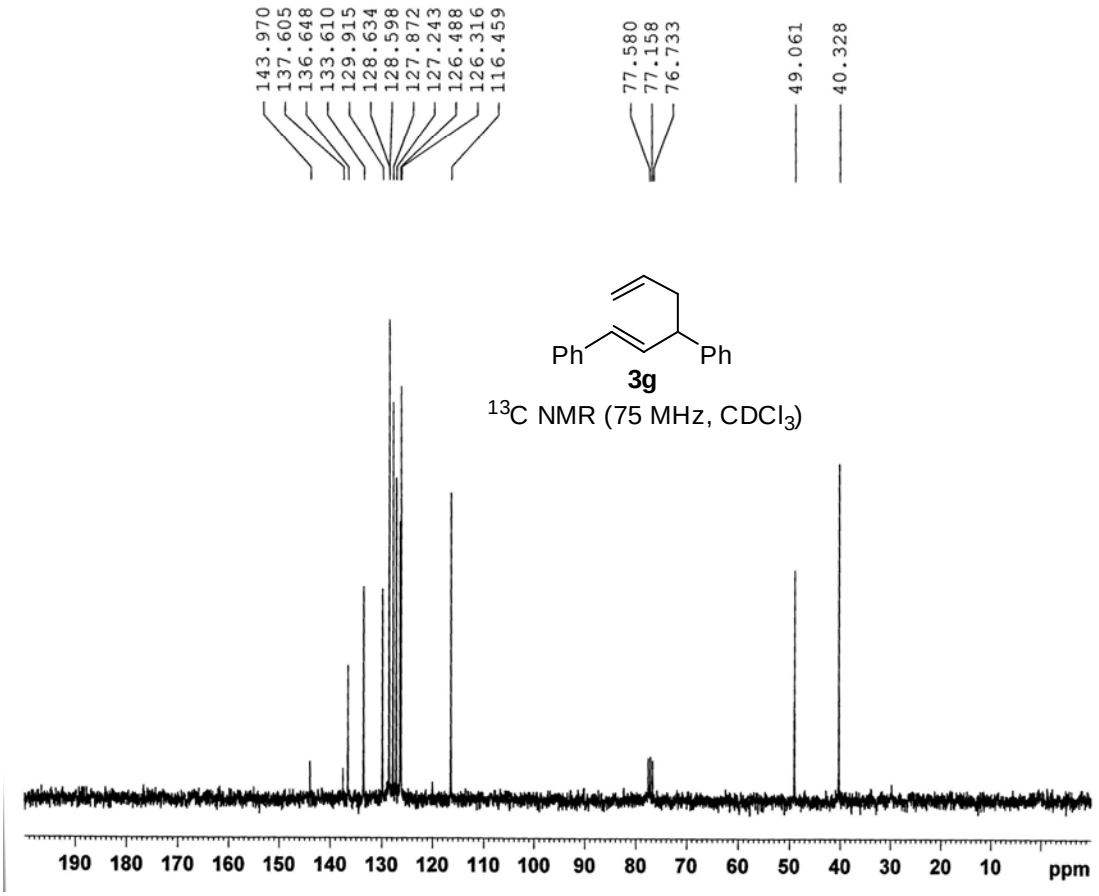

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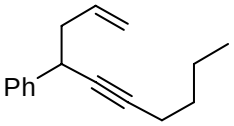

3h

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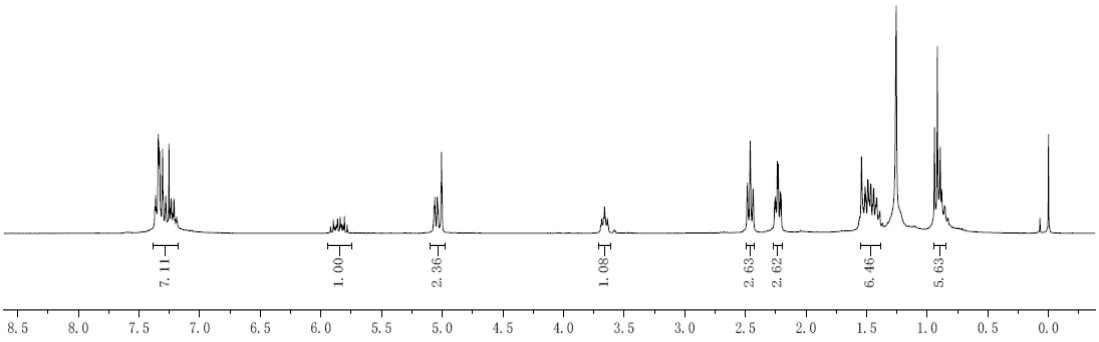

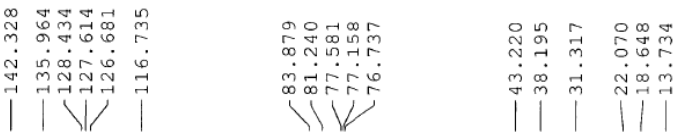

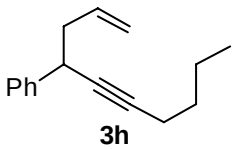

3h

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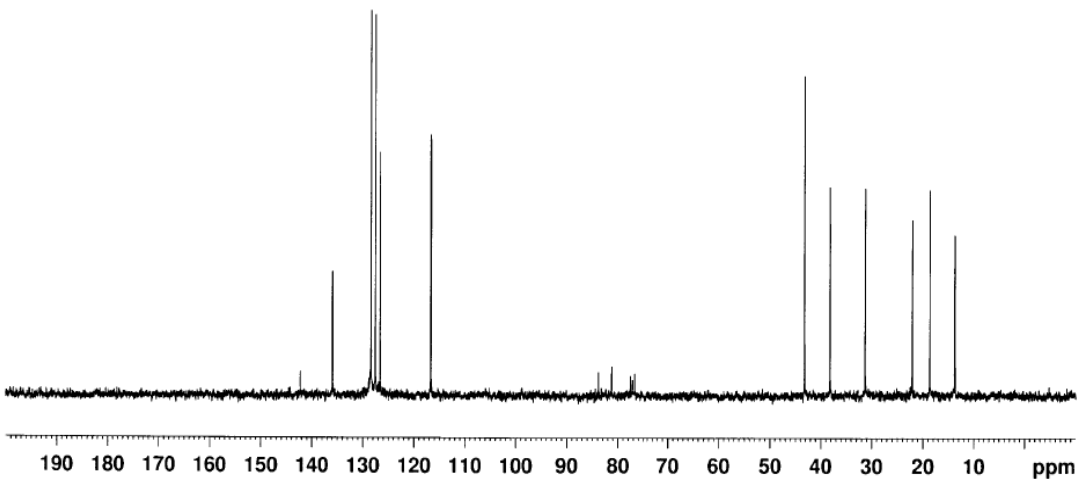

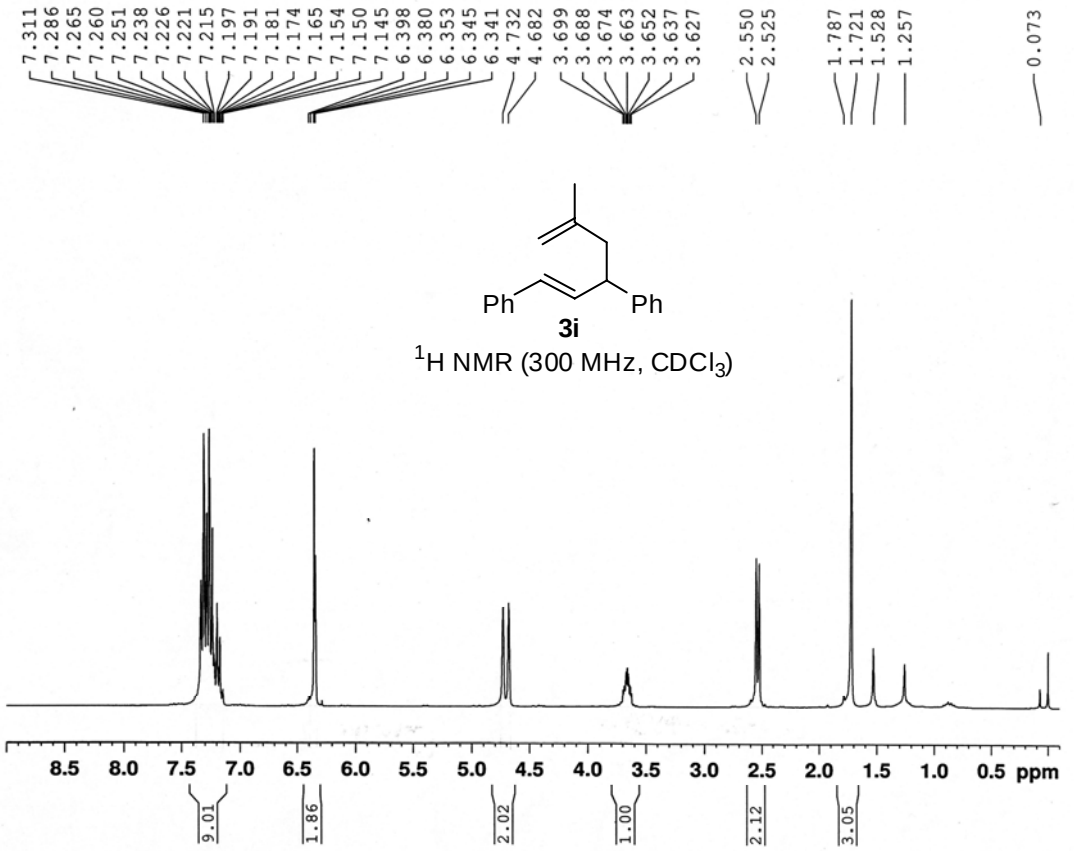

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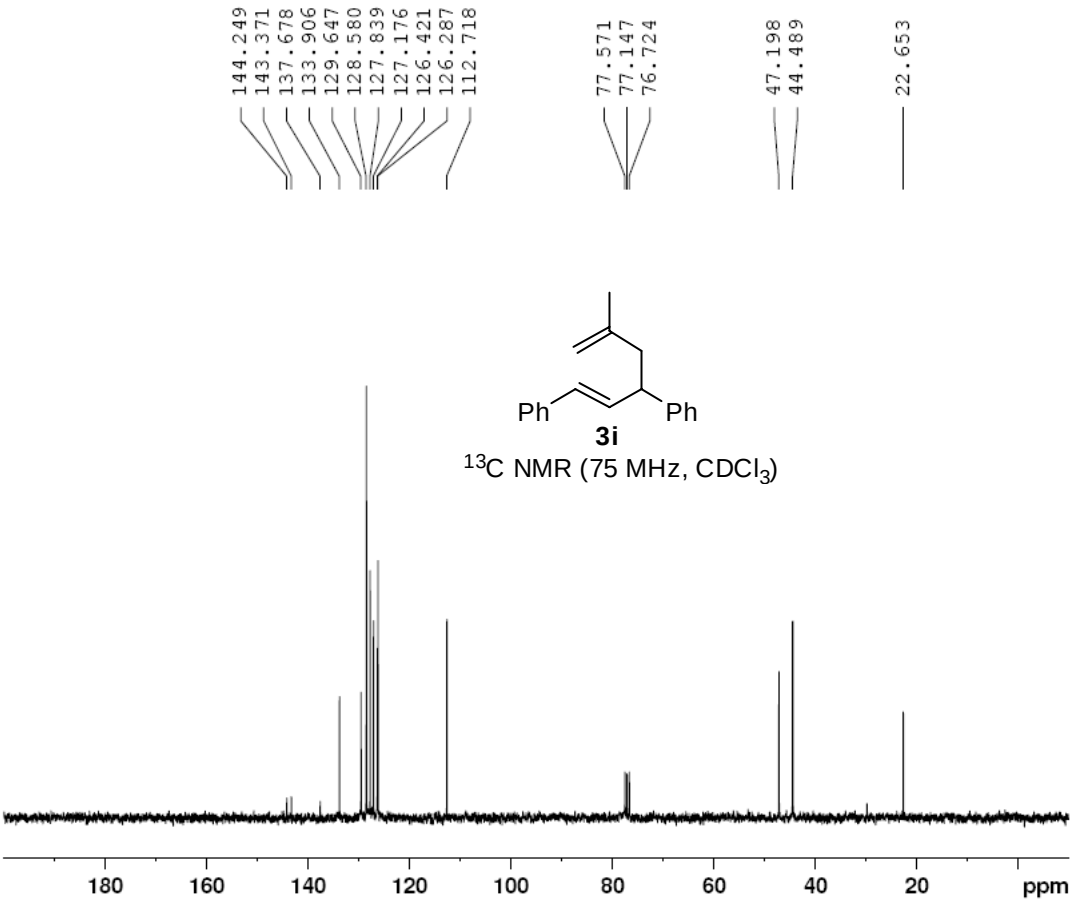

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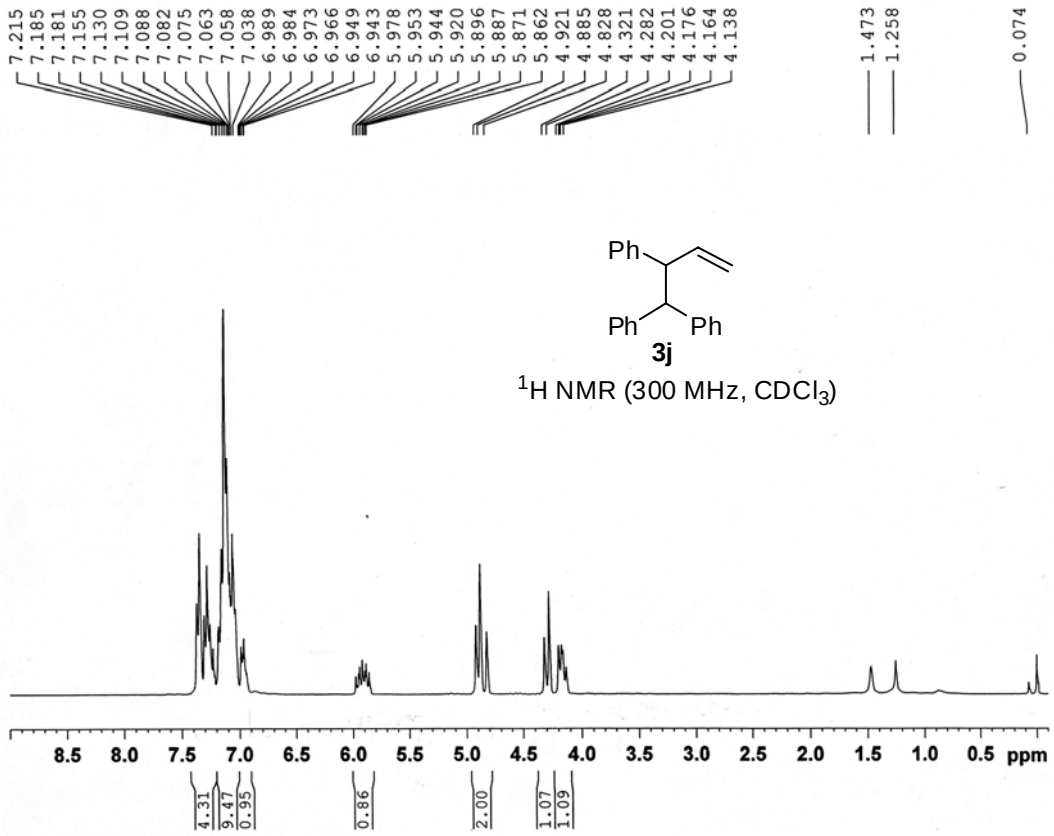

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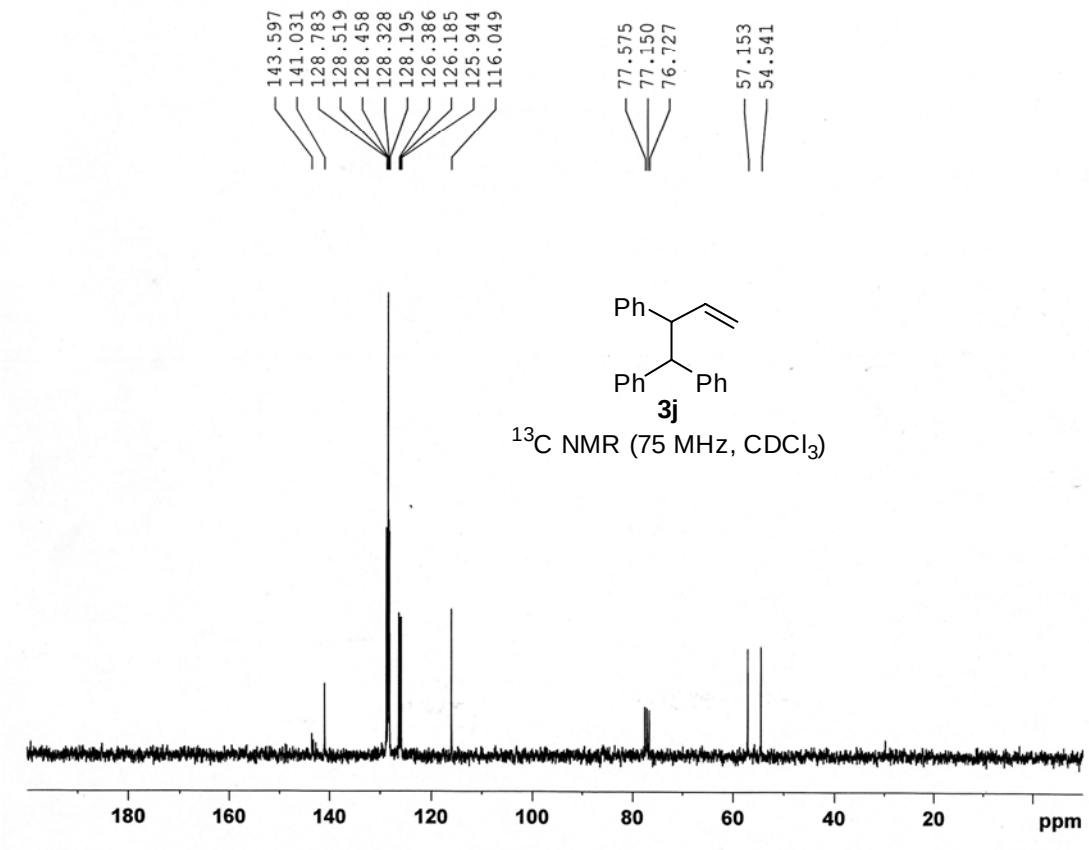

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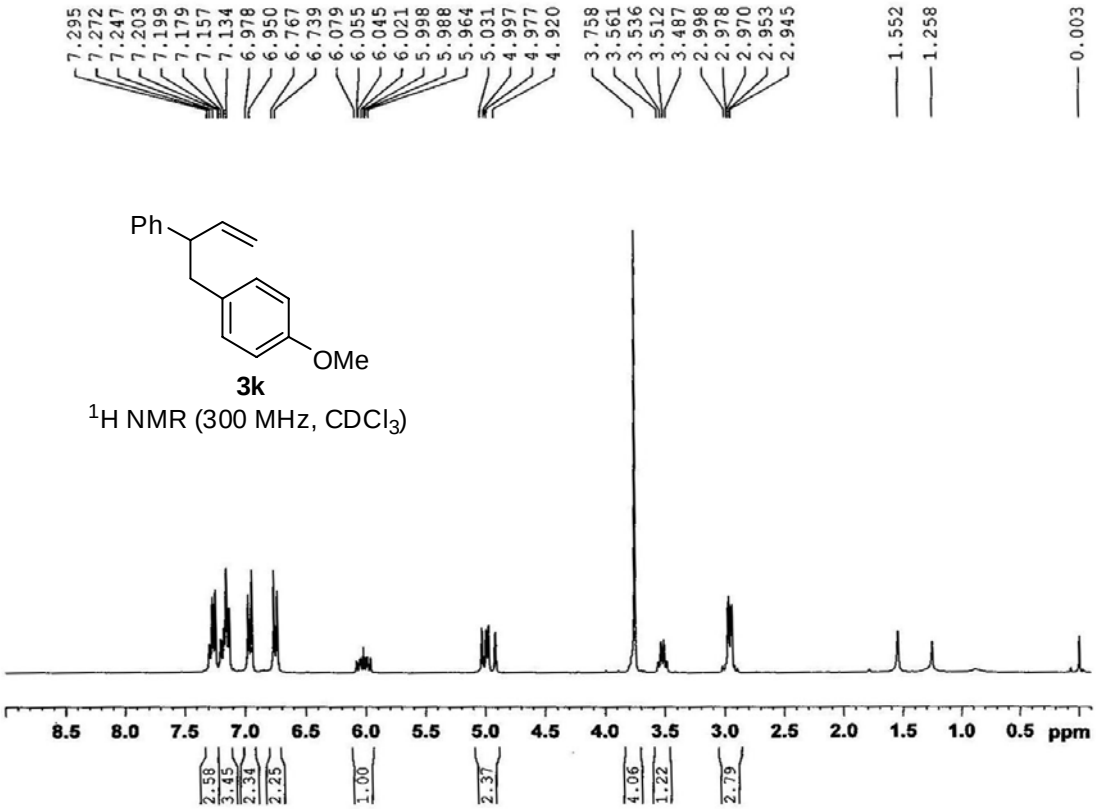

3k

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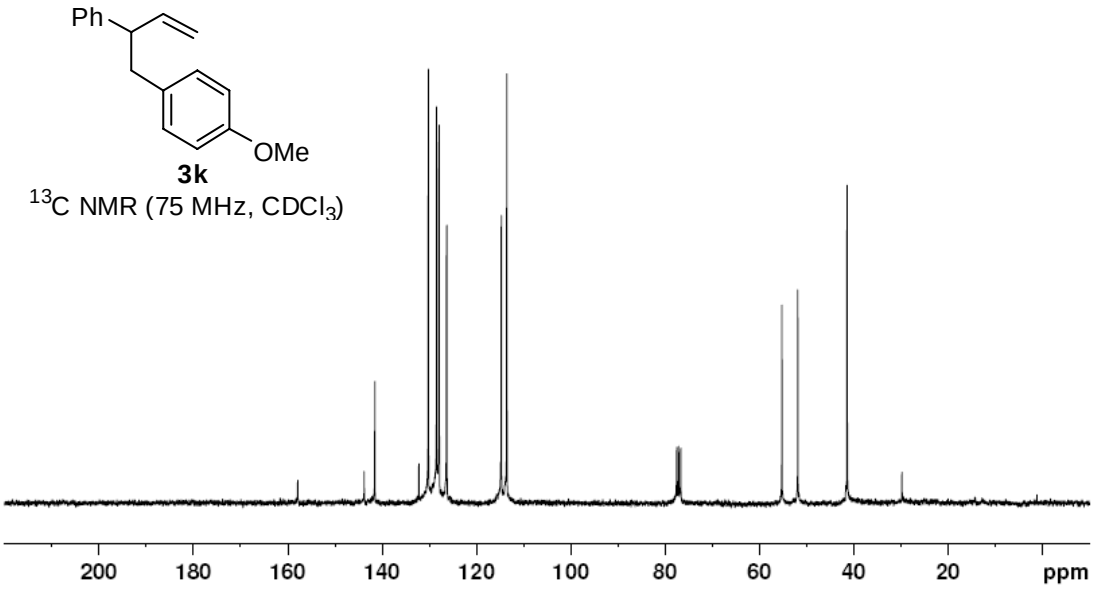
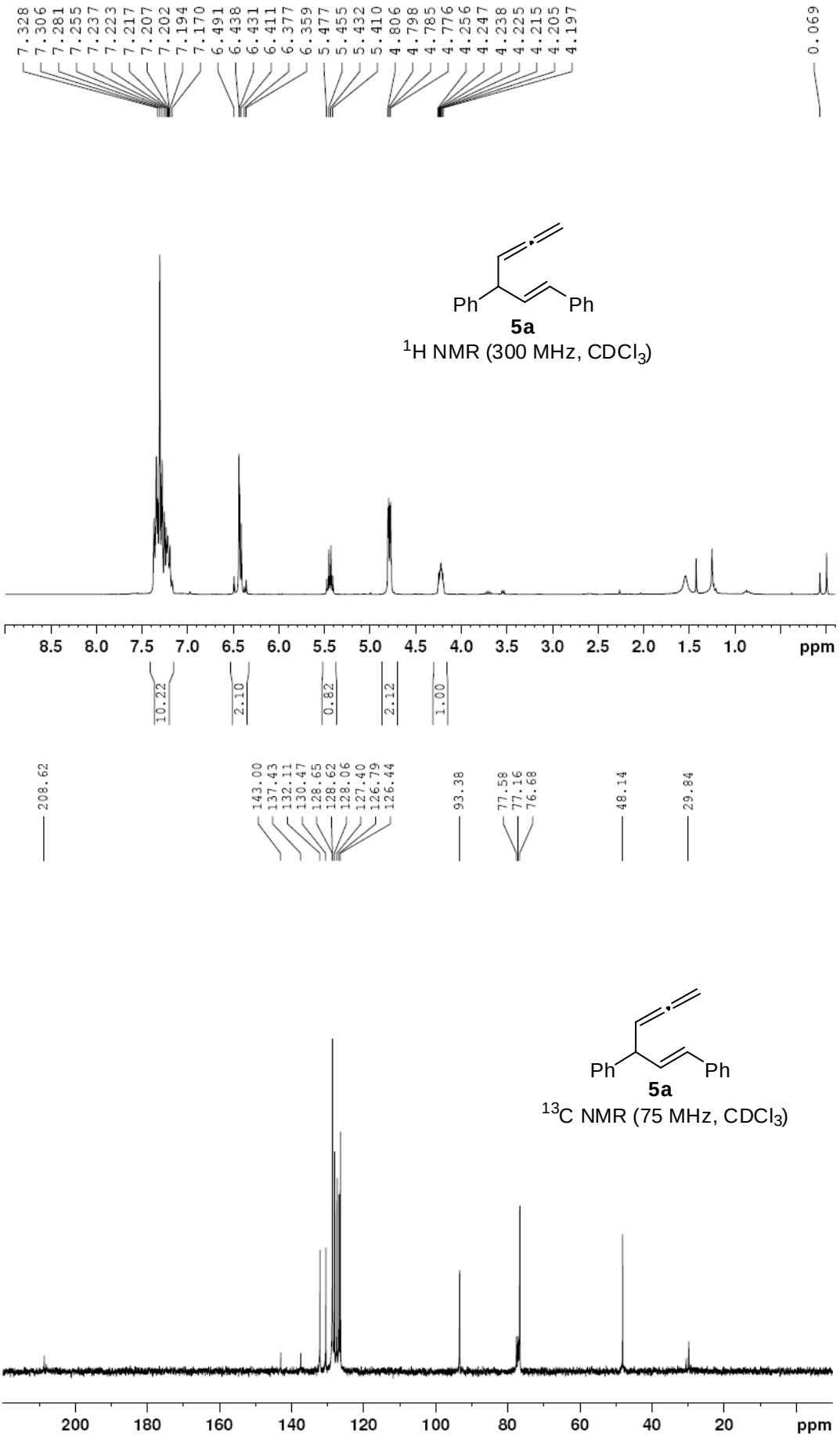


3k

^{13}C NMR (75 MHz, $CDCl_3$)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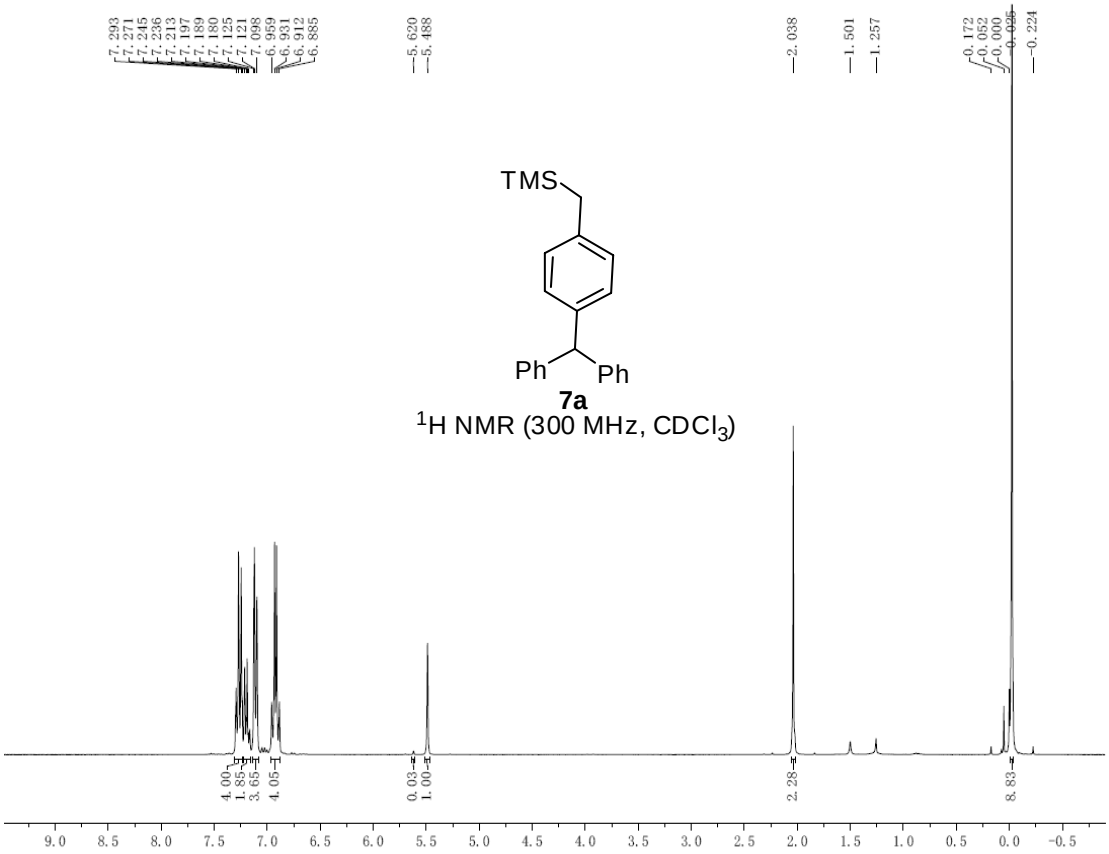
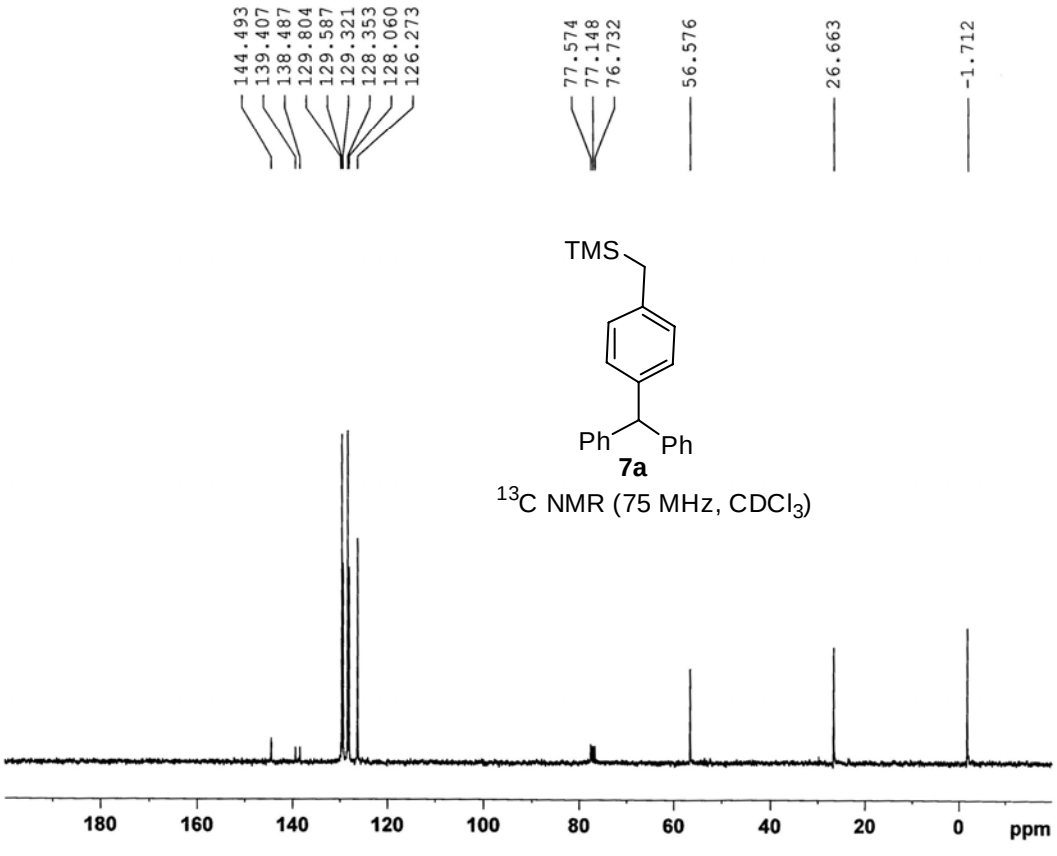
7.306
7.281
7.255
7.237
7.223
7.217
7.207
7.202
7.194
7.170
6.491
6.438
6.431
6.411
6.377
6.359
5.477
5.455
5.432
5.410
4.806
4.798
4.785
4.776
4.256
4.247
4.238
4.225
4.215
4.205
4.197
0.069
Ph
Ph
5a
1H NMR (300 MHz, CDCl3)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
10.22
2.10
0.82
2.12
1.00
208.62
143.00
137.43
132.11
130.47
128.65
128.62
128.06
127.40
126.79
126.44
93.38
77.58
77.16
76.68
48.14
29.84
Ph
Ph
5a
13C NMR (75 MHz, CDCl3)
200 180 160 140 120 100 80 60 40 20 ppm



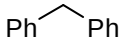
7a

^{1}H NMR (300 MHz, $CDCl_3$)



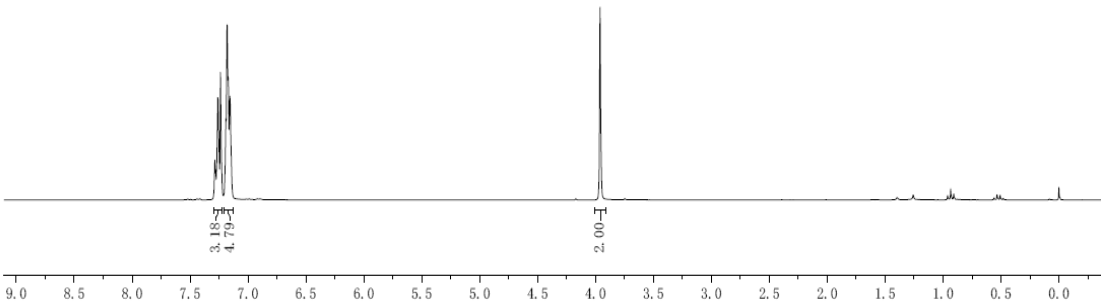
7a

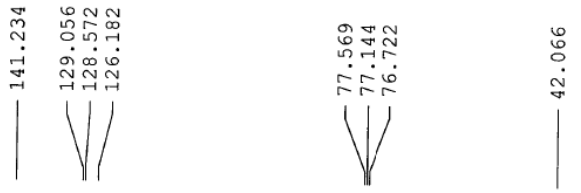
^{13}C NMR (75 MHz, $CDCl_3$)

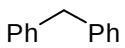


8a

^{1}H NMR (300 MHz, $CDCl_3$)

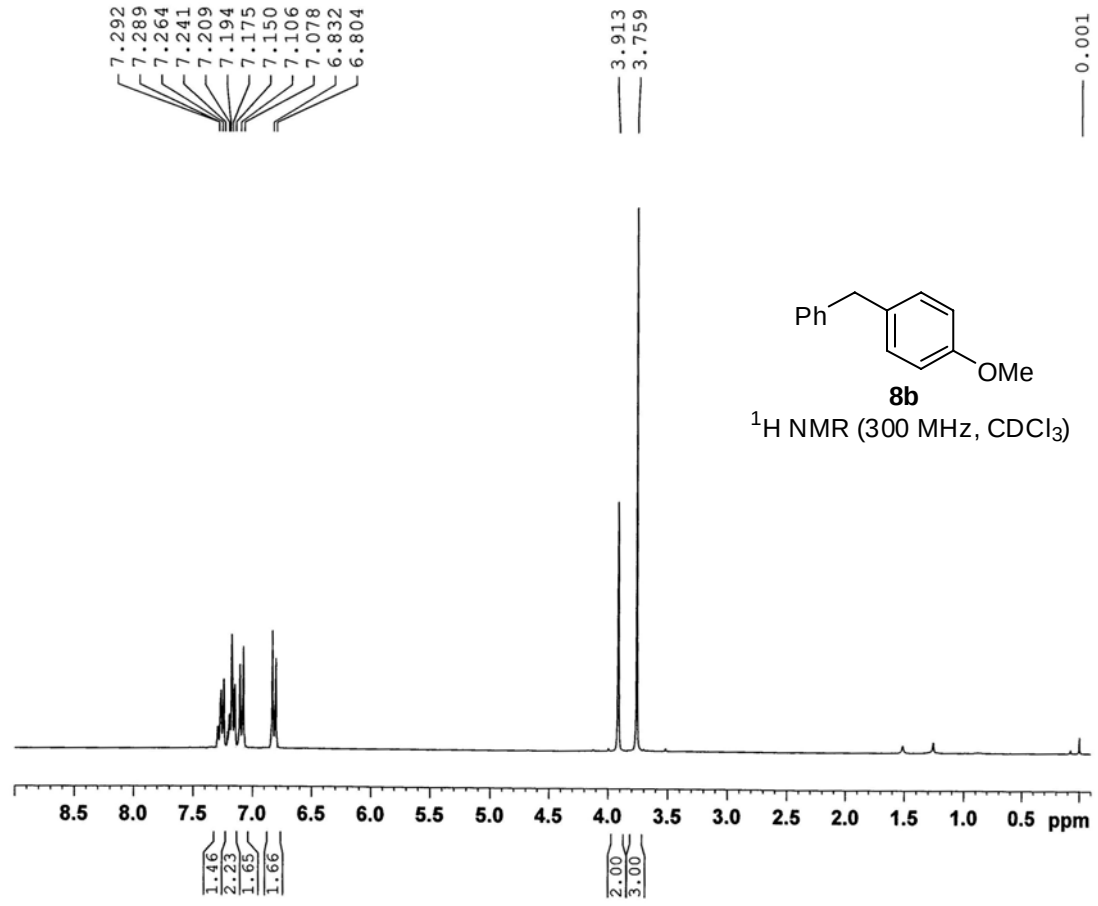






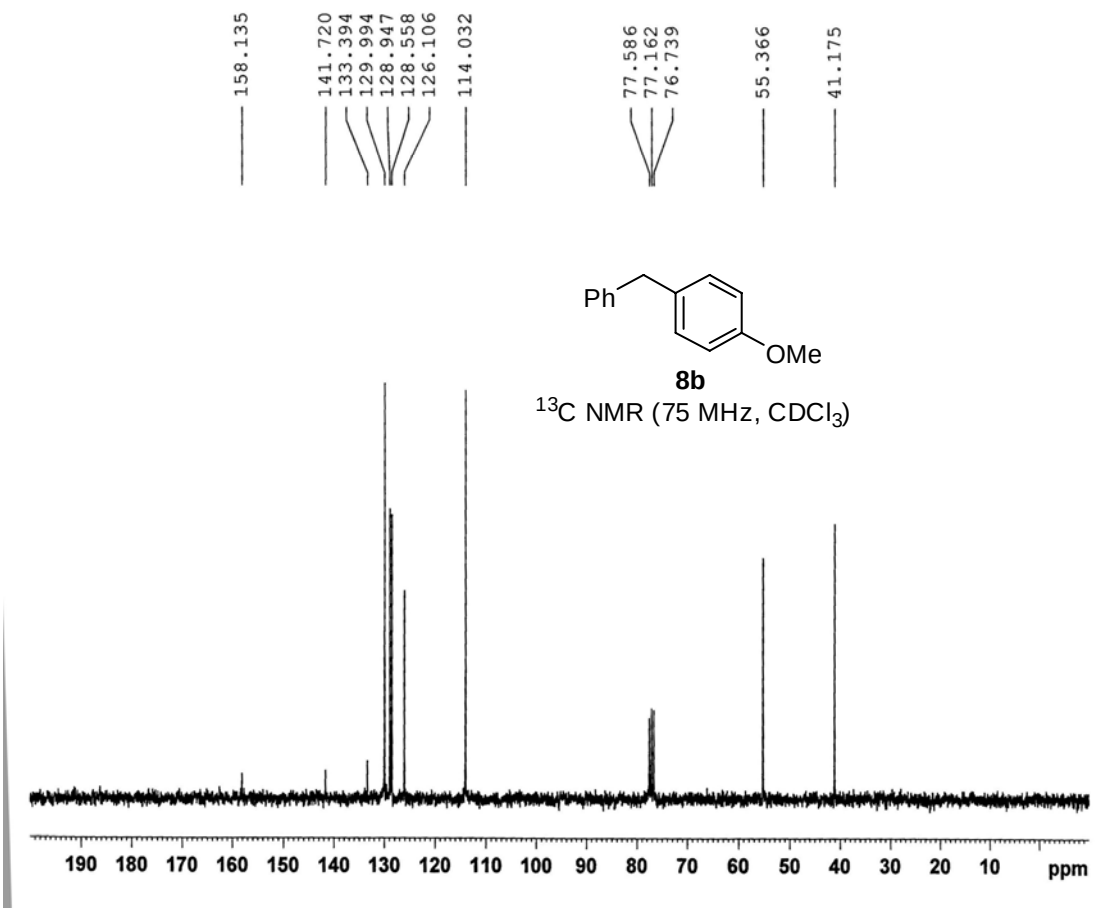
8a

^{13}C NMR (75 MHz, $CDCl_3$)



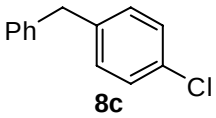
8b

^{1}H NMR (300 MHz, $CDCl_3$)



8b

^{13}C NMR (75 MHz, $CDCl_3$)



8c

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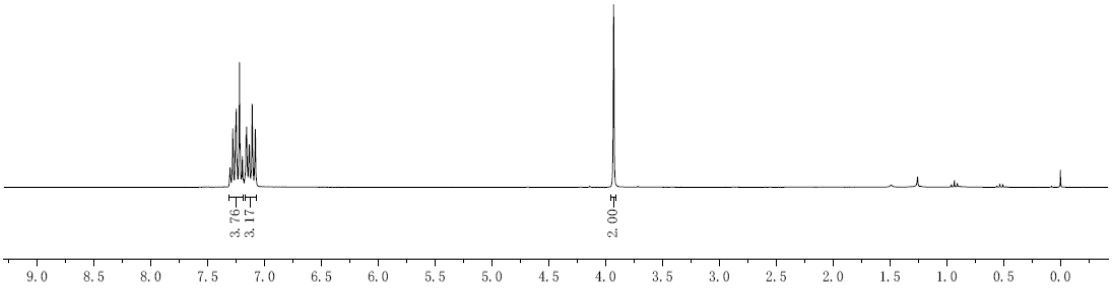
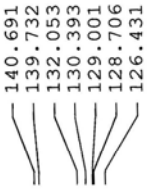
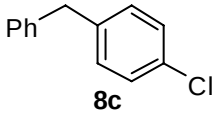
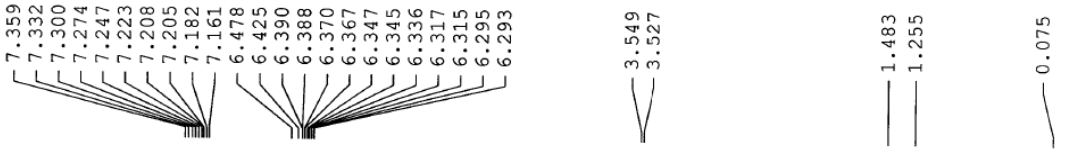


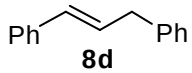




8c

^{13}C NMR (75 MHz, $CDCl_3$)





8d

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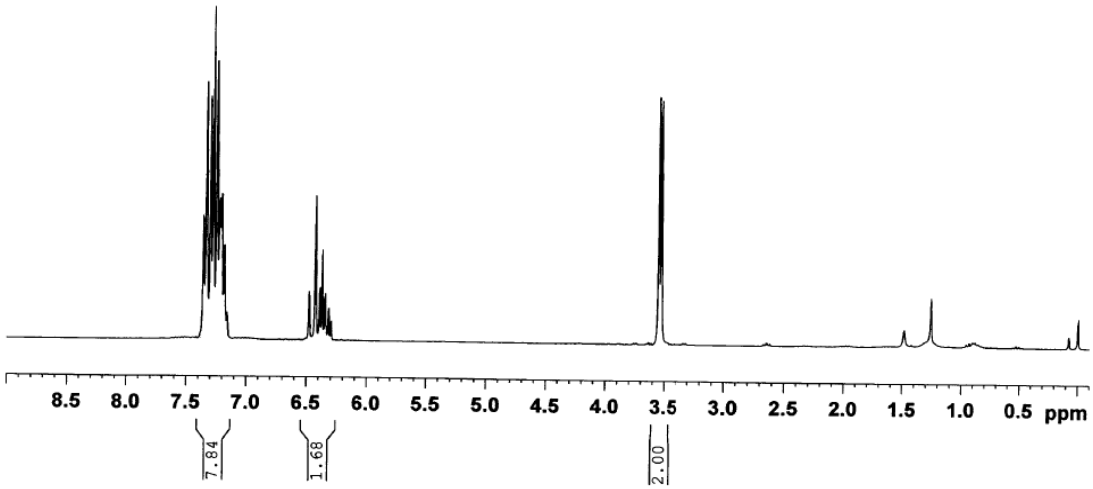

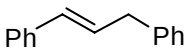

8d

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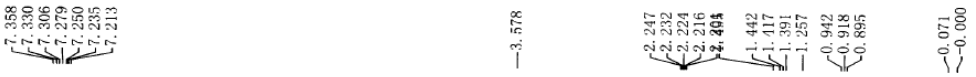
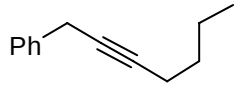
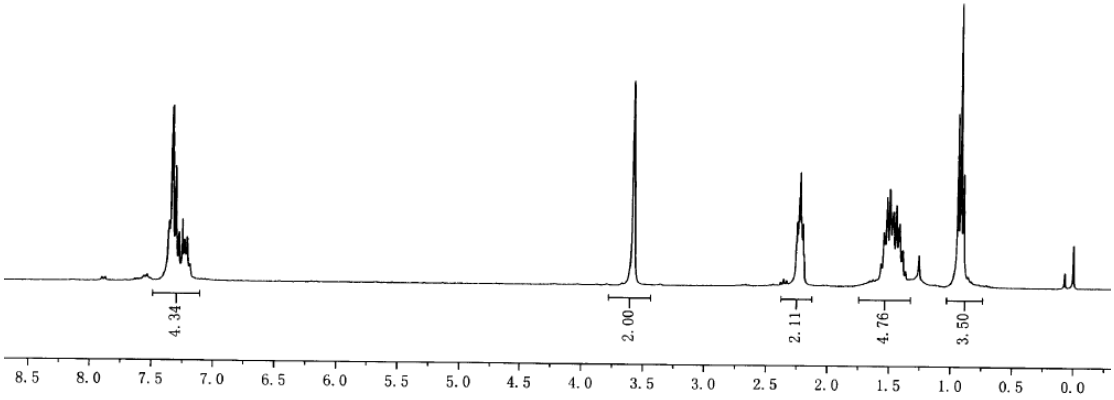
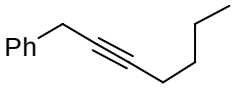




8e

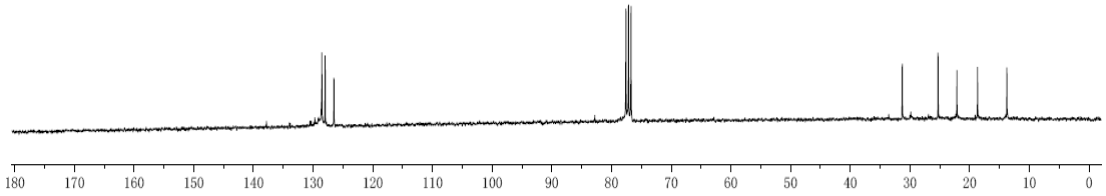
^{1}H NMR (300 MHz, $CDCl_3$)

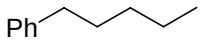




8e

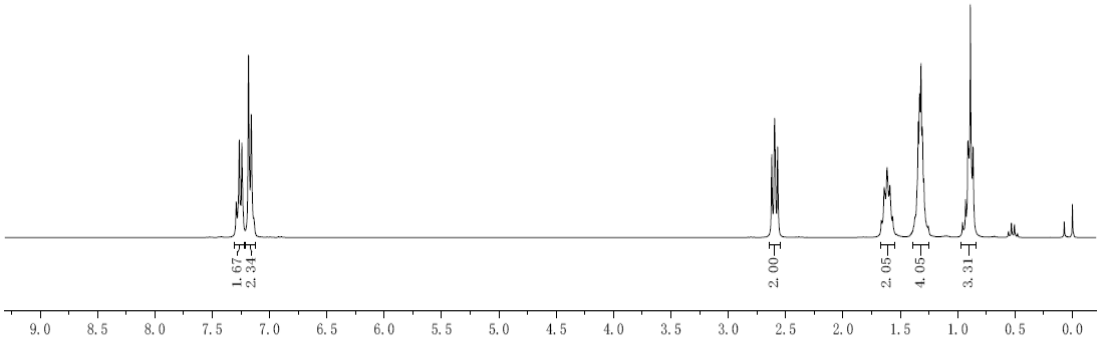
^{13}C NMR (75 MHz, $CDCl_3$)

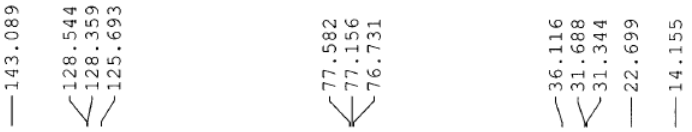


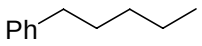


8f

^{1}H NMR (300 MHz, $CDCl_3$)







8f

^{13}C NMR (75 MHz, $CDCl_3$)