Electronic Supplementary Material (ESI) for ChemComm.

Alkene homologation via visible light promoted hydrophosphination using triphenylphosphonium triflate

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Content

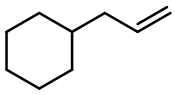
General methods

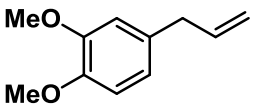
Hydrophosphination/Wittig reaction sequence was performed under an argon atmosphere in DURAN culture tubes with screw cap (catalog number 261351258). The reaction tube was irradiated with Hontiey 100W LED-matrix (450 nm wavelength), which was connected to a power supply (30V, 2A). During irradiation, the reaction tube was cooled with room temperature water (see ref. [1] for details).

THF was distilled from $LiAlH_4$ and stored under argon. Column chromatography was carried out employing silica gel (230–400 mesh). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography visualizing with UV and/or aq. $KMnO_4$ solution. High resolution mass spectra (HRMS) were measured using electrospray ionization (ESI) and time-of-flight (TOF) mass analyzer. The measurements were done in a positive ion mode (interface capillary voltage – 4500 V) or in a negative ion mode (3200 V); mass range from m/z 50 to m/z 3000.

Starting materials

4-Phenyl butene, 1-pentene, 1-hexene, 3,3-dimethyl-1-butene, cyclopentene were purchased from Acros Organics. Other alkenes and photocatalyst (naphthaloylidenebenzimidazol, NBI) were synthesized according to literature procedures:


Ref. [2]



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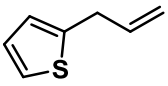

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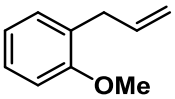

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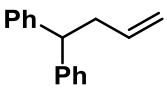
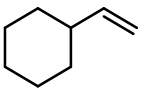
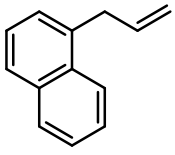
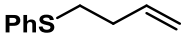


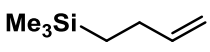
Ref. [6]


Ref. [7]

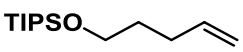

Ref. [8]



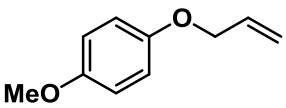
Ref. [9]



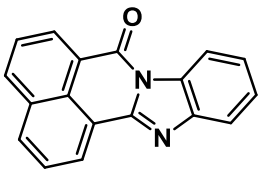
Ref. [10]



Ref. [11]

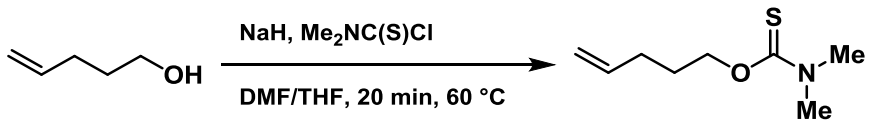


Ref. [12]



(NBI)
Ref. [13]

1-Dimethylthiocarbamoyloxypent-4-ene.



4-Penten-1-ol (10 mmol, 0.86 g) was added dropwise to a stirred suspension of NaH (10 mmol, 60% in paraffin oil) in DMF (2 mL), and after 15 min of stirring, THF (1 mL was added), the mixture was immersed in room temperature water bath and dimethylthiocarbamoyl chloride (10 mmol, 1.24 g) was added portionwise over 5 minutes. Then the bath was heated to 60 °C and the mixture was stirred at this temperature for 20 min. After cooling to room temperature, the reaction mixture was diluted with water (5 mL) and the product was extracted with petroleum ether (3×5 mL). The combined organic phases were filtered through Na_2SO_4, concentrated under vacuum, and the residue was purified by flash chromatography (hexanes/EtOAc, 6/1). Yield 1.22 g (70%). Colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.78 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.00 (dq, *J* = 17.2, 1.8 Hz, 1H), 4.94 (ddt, *J* = 10.1, 2.2, 1.3 Hz, 1H), 4.41 (t, *J* = 6.5 Hz, 2H), 3.32 (s, 3H), 3.07 (s, 3H), 2.12 (dtt, *J* = 7.9, 6.5, 1.5 Hz, 2H), 1.86 – 1.70 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 28.0, 30.1, 37.6, 42.5, 70.9, 115.1, 137.5, 188.2.

HRMS (ESI): calcd for $C_8H_{16}NOS$ 174.0947 $[M + H]^+$; found 174.0952.

Triphenylphosphonium triflate (6).

Triphenylphosphine (16.5 g, 63 mmol, 1.05 equiv) was dissolved in benzene (20 mL). The reaction flask was cooled with ice/water bath, and triflic acid (9.0 g, 60 mmol, 1 equiv) was added dropwise. The resulting solution was kept without stirring overnight in a refrigerator at 5 °C. The white crystals were filtered, washed twice with hexanes, and dried under vacuum (ca. 1 Torr) at 90 °C for one hour. Yield 24.3 g (98%). Colorless crystals. Mp 99–101 °C

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 – 7.72 (m, 9H) 7.72 – 7.58 (m, 6H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 135.5 (d, *J* = 3.1 Hz), 134.0 (d, *J* = 11.5 Hz), 130.6 (d, *J* = 13.4 Hz), 120.7 (q, *J* = 320.2 Hz), 115.8 (d, *J* = 86.3 Hz).

^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ 3.4.

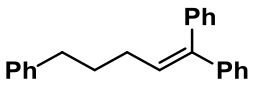
Calcd for $C_{19}H_{16}F_3O_3PS$ (412.36): C 55.34, H 3.91; found: C 55.38, H 3.99.

General procedure for hydrophosphination/Wittig reaction sequence.

In a screw capped reaction tube, a mixture of triphenylphosphonium triflate (548 mg, 1.33 mmol) and PPh_3 (13 mg, 0.05 mmol) was heated under vacuum (20 Torr) at 100 °C for 5 minutes. After cooling to room temperature, the mixture solidifies and THF (1.5 mL) was added. Then, alkene (1 mmol) and NBI (for **8a-h,j-m,o-v**, 8 mg, 0.03 mmol; for **8i,n**, 14 mg, 0.05 mmol;) was added. The tube was sealed and irradiated with blue-light LED-matrix (450 nm, 60W) (irradiation time: for **8a,g,o,p,u** – 16 h; for **8b-f,h,j-m,q-s,v** – 4 h, for **8i** – 24 h, for **8n** – 36 h). During irradiation, the reaction tube was cooled with room temperature water. Then, $(Me_3Si)_2NH$ (for **8a-e,g-u**, 70 μL, 0.33 mmol; for **8f,** 210 μL, 1.00 mmol) was added and the mixture was immersed in a cooling bath (–30 °C). *n*-BuLi (1.33 mmol, 530 μL of 2.5M hexane solution) was added dropwise with vigorous stirring [in case of **8v**, 1M solution of LiHMDS in THF (1.33 mmol, 1.33 mL) was used instead of addition of silazane and BuLi]. The dark-brown mixture was stirred for 10 min and a carbonyl compound [benzophenone (218 mg 1.2 mmol) or paraform (60 mg, 2 mmol)] was added. The mixture was stirred for 10 min at –30 °C, the colling bath was replaced by ice/water bath, and the temperature was allowed to raise to room temperature overnight. For the work-up, water (2 mL) was added, and the product was extracted with hexane (4 mL) and methyl *tert*-butyl ether (3×3 mL). The combined organic phases were filtered through Na_2SO_4, concentrated under vacuum, and the residue was purified by flash chromatography.

In case of products **8i**,**j**,**n** excess of PPh_3 was inseparable on column chromatography. For these compounds, the crude product was treated with MeI (1 eq) in CH_2Cl_2 (0.5 mL) for 3 hours, the solvent was evaporated, and the residue was purified by flash chromatography.

Pent-1-ene-1,1,5-triyltribenzene (8a).[14]



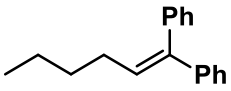
Yield 232 mg (78%). Colorless viscous oil.

Chromatography: hexanes/EtOAc, 30/1. R_f 0.57 (hexanes/EtOAc, 30/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.19 (m, 15H), 6.22 (t, *J* = 7.4 Hz, 1H), 2.71 (t, *J* = 7.5 Hz, 2H), 2.30 (q, *J* = 7.4 Hz, 2H), 1.88 (pent, *J* = 7.5, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 142.9, 142.5, 142.1, 140.3, 130.0, 129.7, 128.5, 128.4, 128.3, 128.2, 127.4, 127.0, 126.9, 125.8, 35.6, 31.8, 29.5.

Hex-1-ene-1,1-diyldibenzene (8b).[15]



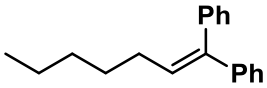
Yield 182 g (77%). Colorless viscous oil.

Chromatography: hexanes/EtOAc, 50/1. R_f 0.52 (hexanes/EtOAc, 50/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.51 – 7.22 (m, 10H), 6.18 (t, *J* = 7.5 Hz, 1H), 2.21 (dt, *J* = 7.3, 7.3 Hz, 2H), 1.62 – 1.32 (m, 4H), 0.95 (t, *J* = 7.2 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.0, 141.5, 140.4, 130.4, 130.0, 128.2, 128.1, 127.3, 126.9, 126.8, 32.3, 29.6, 22.4, 14.1.

Hept-1-ene-1,1-diyldibenzene (8c).[16]

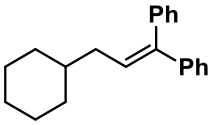


Yield 180 mg (72%). Colorless viscous oil. Chromatography: hexanes. R_f 0.40 (hexanes).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.16 (m, 10H), 6.12 (t, *J* = 7.5 Hz, 1H), 2.14 (q, *J* = 7.4 Hz, 2H), 1.47 (pent, *J* = 7.0 Hz, 2H), 1.37 – 1.22 (m, 4H), 0.95 – 0.85 (m, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.1, 141.6, 140.5, 130.4, 130.1, 128.23, 128.18, 127.3, 126.93, 126.86, 31.6, 29.88, 29.8, 22.7, 14.2.

(3-Cyclohexylprop-1-ene-1,1-diyl)dibenzene (8d).[17]

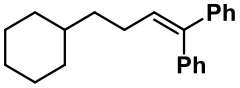


Yield 185 mg (67%). Colorless viscous oil. Chromatography: hexanes. R_f 0.44 (hexanes).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 – 7.19 (m, 10H), 6.19 (t, *J* = 7.5 Hz, 1H), 2.08 (t, *J* = 7.2 Hz, 2H), 1.89 – 1.63 (m, 5H), 1.56 – 1.39 (m, 1H), 1.39 – 1.13 (m, 3H), 1.05 – 0.86 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.1, 142.1, 140.6, 130.2, 129.2, 128.21, 128.18, 128.0, 126.9, 126.8, 38.9, 37.6, 33.4, 26.7, 26.5.

(4-Cyclohexylbut-1-ene-1,1-diyl)dibenzene (8e).



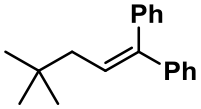
Chromatography: hexanes. R_f 0.19 (hexanes). Yield 209 mg (72%). Colorless viscous oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.20 (m, 10H), 6.14 (t, *J* = 7.5 Hz, 1H), 2.18 (q, *J* = 7.6 Hz, 2H), 1.80 – 1.59 (m, 5H), 1.40 (d, *J* = 6.8 Hz, 2H), 1.35 – 1.13 (m, 4H), 1.01 – 0.80 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.1, 141.4, 140.5, 130.7, 130.1, 128.22, 128.18, 127.3, 127.0, 126.8, 37.8, 37.4, 33.4, 27.3, 26.8, 26.5.

HRMS (ESI): calcd for $C_{22}H_{26}Ag$ 397.1080 [M + ^{107}Ag]$^+$; found 397.1075.

(4,4-Dimethylpent-1-ene-1,1-diyl)dibenzene (8f).[18]

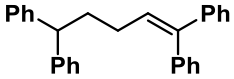


Yield 122 mg (49%). Colorless viscous oil. Chromatography: hexanes. R_f 0.25 (hexanes).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 – 7.21 (m, 10H), 6.28 (t, *J* = 7.6 Hz, 2H), 2.12 (d, *J* = 7.6 Hz, 2H), 1.00 (s, 9H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.3, 142.8, 140.6, 130.3, 128.2, 127.4, 127.3, 126.90, 126.86, 43.5, 31.8, 29.7.

Pent-1-ene-1,1,5,5-tetrayltetrabenzene (8g). [19]



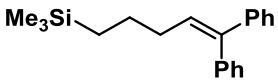
Yield 281 mg (75%). Colorless viscous oil.

Chromatography: hexanes/EtOAc, 30/1. R_f 0.48 (hexanes/EtOAc, 30/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.22 (m, 20H), 6.27 (t, *J* = 7.1 Hz, 1H), 4.05 (t, *J* = 7.3 Hz, 1H), 2.41 – 2.22 (m, 4H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 144.9, 142.9, 142.3, 140.1, 134.0, 133.7, 129.9, 129.4, 128.8, 128.7, 128.5, 128.23, 128.19, 127.96, 127.7, 127.3, 127.97, 126.94, 126.2, 50.9, 36.1, 28.3.

(5,5-Diphenylpent-4-en-1-yl)trimethylsilane (8h).[20]



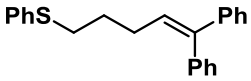
Yield 235 mg (80%). Colorless viscous oil.

Chromatography: hexanes. R_f 0.15 (hexanes).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 – 7.25 (m, 10H), 6.20 (t, *J* = 7.4 Hz, 1H), 2.25 (q, *J* = 7.4 Hz, 2H), 1.64 – 1.49 (m, 2H), 0.67 – 0.56 (m, 2H), 0.07 (s, 9H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.1, 141.8, 140.5, 130.3, 130.1, 128.24, 128.20, 127.4, 126.94, 126.88, 33.7, 24.6, 16.7, -1.5.

(5,5-Diphenylpent-4-en-1-yl)(phenyl)sulfane (8i).



Yield 152 mg (46%). Yellowish solid. Mp 30-31 °C.

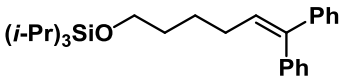
Chromatography: hexanes/EtOAc, 30/1. R_f 0.24 (hexanes/EtOAc, 30/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.14 (m, 15H), 6.11 (t, *J* = 7.5 Hz, 1H), 2.95 (d, *J* = 7.3 Hz, 2H), 2.31 (q, *J* = 7.5 Hz, 2H), 1.84 (p, *J* = 7.4 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 142.7, 142.6, 140.1, 136.7, 130.0, 129.2, 128.9, 128.5, 128.3, 128.2, 127.3, 127.10, 127.06, 125.9, 33.3, 29.6, 29.1.

HRMS (ESI): calcd for $C_{23}H_{23}S$ 331.1515 $[M + H]^+$; found 331.1511.

[(6,6-Diphenylhex-5-en-1-yl)oxy]triisopropylsilane (8j).



Yield 253 mg (62%). Colorless viscous oil.

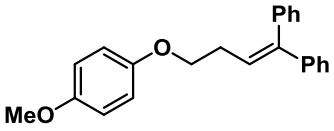
Chromatography: hexanes/EtOAc, from 100/1 to 30/1. R_f 0.64 (hexanes/EtOAc, 30/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.20 (m, 10H), 6.16 (t, *J* = 7.5 Hz, 1H), 3.71 (t, *J* = 5.8 Hz, 2H), 2.22 (q, *J* = 6.9 Hz, 2H), 1.67 – 1.53 (m, 4H), 1.16 – 1.08 (m, 20H).

^{13}C{^{1}H} NMR (76 MHz, $CDCl_3$) δ 143.0, 141.8, 140.4, 130.2, 130.1, 128.95, 128.89, 127.4, 127.0, 126.9, 63.3, 32.7, 29.7, 26.4, 18.2, 12.1.

HRMS (ESI): calcd for $C_{27}H_{41}OSi$ 409.2921 $[M + H]^+$; found 409.2910.

[4-(4-Methoxyphenoxy)but-1-ene-1,1-diyl]dibenzene (8k).



Compound **8k** and benzophenone are inseparable by colunm chromatography. The crude product was dissolved in MeOH (2 mL) and $NaBH_4$ (1.0 mmol, 38 mg) was added, and the mixture was srirred for two hours at room temperature. The mixture was worked-up (water/methyl *tert*-butyl ether), and the product was purified by flash column chromatography, hexanes/EtOAc, 15/1. R_f 0.25 (hexanes/EtOAc, 15/1).

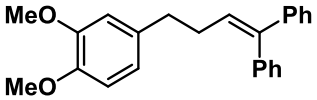
Yield 175 mg (53%). Colorless viscous oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 – 7.38 (m, 3H), 7.37 – 7.25 (m, 7H), 6.89 (s, 4H), 6.29 (t, *J* = 7.4 Hz, 1H), 4.05 (t, *J* = 6.8 Hz, 2H), 3.82 (s, 3H), 2.66 (q, *J* = 6.8 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 153.9, 153.1, 143.9, 142.5, 140.0, 130.0, 128.4, 128.2, 127.3, 127.2, 125.1, 115.6, 114.7, 68.2, 55.8, 30.2.

HRMS (ESI): calcd for $C_{23}H_{23}O_2$ 331.1693 $[M + H]^+$; found 331.1688.

[4-(3,4-Dimethoxyphenyl)but-1-ene-1,1-diyl]dibenzene (8l).



Yield 265 mg (77%). Colorless solid. Mp 65-66 °C.

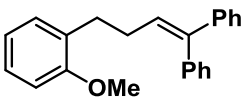
Chromatography: hexanes/EtOAc, 8/1. R_f 0.20 (hexanes/EtOAc, 8/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.21 (m, 8H), 7.20 – 7.05 (m, 2H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.73 (d, *J* = 8.5 Hz, 1H), 6.68 (s, 1H), 6.17 (t, *J* = 7.3 Hz, 1H), 3.90 (s, 3H), 3.86 (s, 3H), 2.76 (t, *J* = 7.5 Hz, 2H), 2.48 (q, *J* = 7.5 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 148.9, 147.3, 142.7, 142.4, 140.2, 134.4, 129.9, 128.9, 128.19, 128.16, 127.3, 127.0, 120.5, 112.0, 111.3, 56.0, 55.9, 35.8, 31.8.

HRMS (ESI): calcd for $C_{24}H_{25}O_2$ 345.1849 $[M + H]^+$; found 345.1844.

[4-(2-Methoxyphenyl)but-1-ene-1,1-diyl]dibenzene (8m).



Yield 223 mg (71%). Colorless viscous oil.

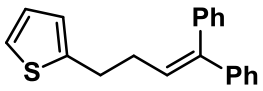
Chromatography: hexanes/EtOAc, 50/1. R_f 0.31 (hexanes/EtOAc, 50/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.17 (m, 13H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.30 (t, *J* = 7.6 Hz, 1H), 3.84 (s, 3H), 2.92 (t, *J* = 7.3 Hz, 2H) 2.56 (q, *J* = 7.4Hz, 2H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 157.6, 143.0, 141.9, 140.3, 130.2, 130.1, 130.0, 129.7, 128.1, 128.1, 127.3, 127.2, 126.8, 120.4, 110.3, 55.2, 30.7, 30.1.

HRMS (ESI): calcd for $C_{23}H_{22}O$ 315.1743 $[M + H]^+$; found 315.1739.

2-(4,4-Diphenylbut-3-en-1-yl)thiophene (8n).



Yield 157 mg (54%). Yellow viscous oil.

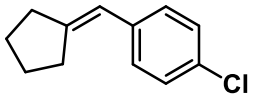
Chromatography: hexanes/EtOAc, 50/1. R_f 0.27 (hexanes/EtOAc, 50/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.18 (m, 12H), 7.02 (dd, *J* = 5.2, 3.4 Hz, 1H), 6.88 (d, *J* = 3.4 Hz, 1H), 6.25 (t, *J* = 7.4 Hz, 1H), 3.08 (t, *J* = 7.4 Hz, 2H), 2.63 (q, *J* = 7.4 Hz, 2H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 144.5, 142.8, 142.7, 140.1, 129.9, 128.29, 128.27, 128.2, 127.4, 127.10, 127.08, 126.8, 124.5, 123.2, 31.9, 30.2.

HRMS (ESI): calcd for $C_{20}H_{18}Ag$ 397.0175 $[M + {}^{107}Ag]^+$; found 397.0184.

1-Chloro-4-(cyclopentylidenemethyl)benzene (8o).[21]



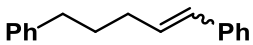
Yield 148 mg (77%). Colorless solid. Mp 26-27 °C.

Chromatography: hexanes. R_f 0.47 (hexanes).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 6.34 (pent, *J* = 2.4 Hz, 1H), 2.60 – 2.45 (m, 4H), 1.82 (pent, *J* = 6.6 Hz, 2H), 1.70 (pent, *J* = 7.0 Hz, 2H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 25.7, 27.3, 31.3, 36.1, 119.9, 128.4, 129.2, 131.2, 137.5, 148.1.

Pent-1-ene-1,5-diyldibenzene (8p).[22]



Yield 149 mg (67%). Colorless solid. Mixture of *E*/*Z*-isomers with 1/3 ratio.

Chromatography: from hexanes to hexanes/EtOAc, 30/1. R_f 0.31 (hexanes/EtOAc, 30/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ both isomers: 7.51 – 7.23 (m, 15H), 6.62 – 6.48 (m, 1H), 2.86 – 2.70 (m, 2H), 2.01 – 1.84 (m, 3H); major isomer: 5.81 (dt, *J* = 11.7, 7.3 Hz, 1H), 2.51 (qd, *J* = 7.4, 1.8 Hz, 2H); minor isomer: 6.36 (dt, *J* = 15.9, 6.7 Hz, 2H),2.38 (qd, *J* = 7.0, 1.3 Hz, 2H).

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ both isomers: 132.6, 130.6, 130.4, 129.4, 128.9, 128.60, 128.57, 128.43, 128.40, 128.2, 127.0, 126.6, 126.1, 125.8; major isomer: 142.4, 137.8, 35.6, 31.8, 28.2; minor isomer: 142.5, 137.9, 35.5, 32.7, 31.1.

(Hex-5-en-1-yloxy)triisopropylsilane (8q).[23]

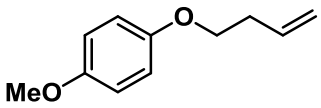
Yield 138 mg (54%). Colorless viscous oil.

Chromatography: hexanes/EtOAc100/1. R_f 0.33 (hexanes/EtOAc, 100/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.84 (ddt, *J* = 17.1, 10.1, 6.4 Hz, 1H), 5.03 (dq, *J* = 17.1, 1.6 Hz, 1H), 4.97 (ddt, *J* = 10.1, 2.3, 1.6 Hz, 1H), 3.71 (t, *J* = 6.4 Hz, 2H), 2.10 (qt, *J* = 7.1, 1.4 Hz, 2H), 1.67 – 1.40 (m, 4H), 1.13 – 1.05 (m, 21H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 139.2, 114.5, 63.4, 33.7, 32.6, 25.4, 18.2, 12.2.

1-(But-3-en-1-yloxy)-4-methoxybenzene (8r).[24]



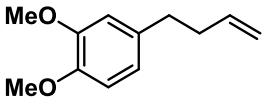
Yield 66 mg (37%). Colorless viscous oil.

Chromatography: hexanes/EtOAc, 30/1. R_f 0.19 (hexanes/EtOAc, 30/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.97 – 6.83 (m, 4H), 5.95 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.29 – 5.09 (m, 2H), 4.01 (t, *J* = 6.7 Hz, 2H), 3.80 (s, 3H), 2.56 (qt, *J* = 6.7, 1.4 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 153.9, 153.1, 134.6, 116.9, 115.6, 114.6, 67.9, 55.7, 33.8.

4-(But-3-en-1-yl)-1,2-dimethoxybenzene (8s). [25]



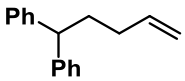
Yield mg (58%). Colorless viscous oil.

Chromatography: hexanes/EtOAc, 15/1. R_f 0.21 (hexanes/EtOAc, 15/1).

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.85 – 6.72 (m, 3H), 5.89 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.07 (dq, *J* = 17.0, 1.7 Hz, 1H), 5.01 (ddt, *J* = 10.2, 2.2, 1.2 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 2.68 (dd, *J* = 9.0, 6.6 Hz, 2H), 2.45 – 2.32 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 148.8, 147.2, 138.1, 134.6, 120.2, 114.9, 111.8, 111.2, 55.9, 55.8, 35.7, 35.0.

Pent-4-ene-1,1-diyldibenzene (8t).[26]



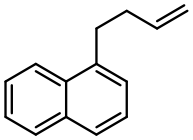
Yield 120 mg (54%). Colorless viscous oil.

Chromatography: hexanes. R_f 0.18 (hexanes).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.22 (m, 10H), 5.94 (ddt, *J* = 15.4, 10.6, 6.5 Hz, 1H), 5.14 – 5.05 (m, 2H), 4.04 (t, *J* = 7.7 Hz, 1H), 2.31 – 2.20 (m, 2H), 2.19 – 2.07 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 145.1, 138.5, 128.6, 128.0, 126.2, 115.0, 50.7, 34.9, 32.1.

1-(But-3-en-1-yl)naphthalene (8u).[27]



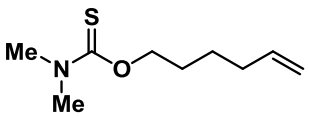
Yield 91 mg (50%). Colorless viscous oil.

Chromatography: hexanes, R_f 0.19 (hexanes).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.7 Hz, 1H), 7.94 (dd, *J* = 7.3, 2.0 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.64 – 7.52 (m, 2H), 7.54 – 7.43 (m, 1H), 7.42 (d, *J* = 1.4 Hz, 1H), 6.04 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.19 (dq, *J* = 17.0, 1.6 Hz, 1H), 5.12 (dq, *J* = 10.2, 1.6 Hz, 1H), 3.31 – 3.20 (m, 2H), 2.60 (tdt, *J* = 7.9, 6.5, 1.5 Hz, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 138.3, 138.0, 134.0, 131.9, 128.9, 126.7, 126.0, 125.8, 125.6, 125.5, 123.8, 115.0, 34.9, 32.5.

1-Dimethylthiocarbamoyloxyhex-5-ene (8v).



Yield 101 mg (54%). Colorless viscous oil.

Chromatography: hexanes/EtOAc, 20/1. R_f 0.25 (hexanes/EtOAc, 20/1).

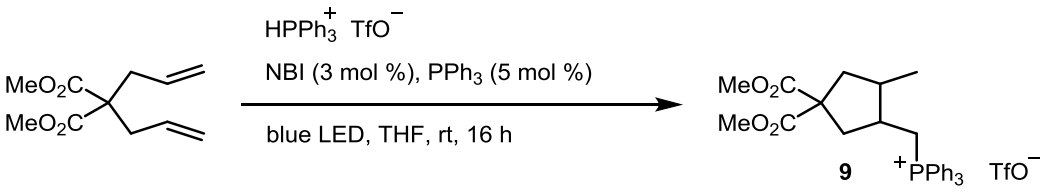
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.81 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.07 – 4.93 (m, 2H), 4.44 (t, *J* = 6.6 Hz, 2H), 3.36 (s, 3H), 3.11 (s, 3H), 2.10 (qt, *J* = 7.3, 1.4 Hz, 2H), 1.82 – 1.68 (m, 2H), 1.58 – 1.43 (m, 2H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 188.4, 138.4, 114.8, 71.5, 42.6, 37.7, 33.3, 28.2, 25.2.

HRMS (ESI): calcd for $C_9H_{18}NOS$ 188.1104 $[M + H]^+$; found 188.1110.

Reaction of 1,6-diene

{[4,4-Bis(methoxycarbonyl)-2-methylcyclopentyl]methyl}triphenylphosphonium trifluoromethanesulfonate (9).



In a screw capped reaction tube, a mixture of triphenylphosphonium triflate (548 mg, 1.33 mmol) and PPh_3 (13 mg, 0.05 mmol) was heated under vacuum (20 Torr) at 100 °C for 5 minutes. After cooling to room temperature, the mixture solidifies and THF (1.5 mL) was added. Then, 1,6-diene (212 mg, 1 mmol) and NBI (8 mg, 0.03 mmol) was added. The tube was sealed and irradiated with blue-light LED-matrix (450 nm, 60W) for 16 h. During irradiation, the reaction tube was cooled with room temperature water. For the work-up, triethylamine (0.5 mmol, 70µL) was added, the mixture was transferred to a silica gel column and eluted with EtOAc and then EtOAc/EtOH (4/1 v/v). Yellow glassy solid, 620 mg (purity ~80% based on NMR, yield 79%).

Mixture of isomers, ca. 5/1. Signals of major isomer are provided.

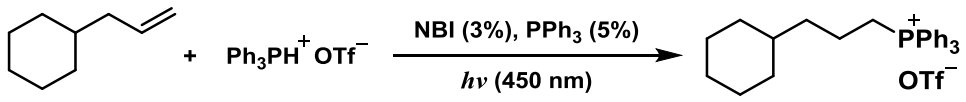
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 – 7.28 (m, 15H), 3.53 (s, 3H), 3.51 (s, 3H), 3.62 – 3.35 (m, 1H), 3.18 – 3.02 (m, 1H), 2.32 – 2.06 (m, 3H), 2.04 – 1.92 (m, 1H), 1.82 – 1.39 (m, 3H), 0.88 (d, *J* = 6.3 Hz, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 172.4, 172.0, 135.1 (d, *J* = 3.0 Hz), 133.3 (d, *J* = 10.0 Hz), 130.4 (d, *J* = 12.7 Hz), 120.7 (q, *J* = 321.2 Hz), 117.7 (d, *J* = 85.9 Hz), 58.1, 52.6 (d, *J* = 3.3 Hz), 40.1, 37.4 (d, *J* = 11.6 Hz), 36.8 (d, *J* = 4.3 Hz), 22.5 (d, *J* = 52.1 Hz), 14.6.

^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ: 24.3.

HRMS (ESI): calcd for $C_{29}H_{32}O_4P^+$ 475.2033 $[M]^+$; found 475.2026.

Quantum yield measurement

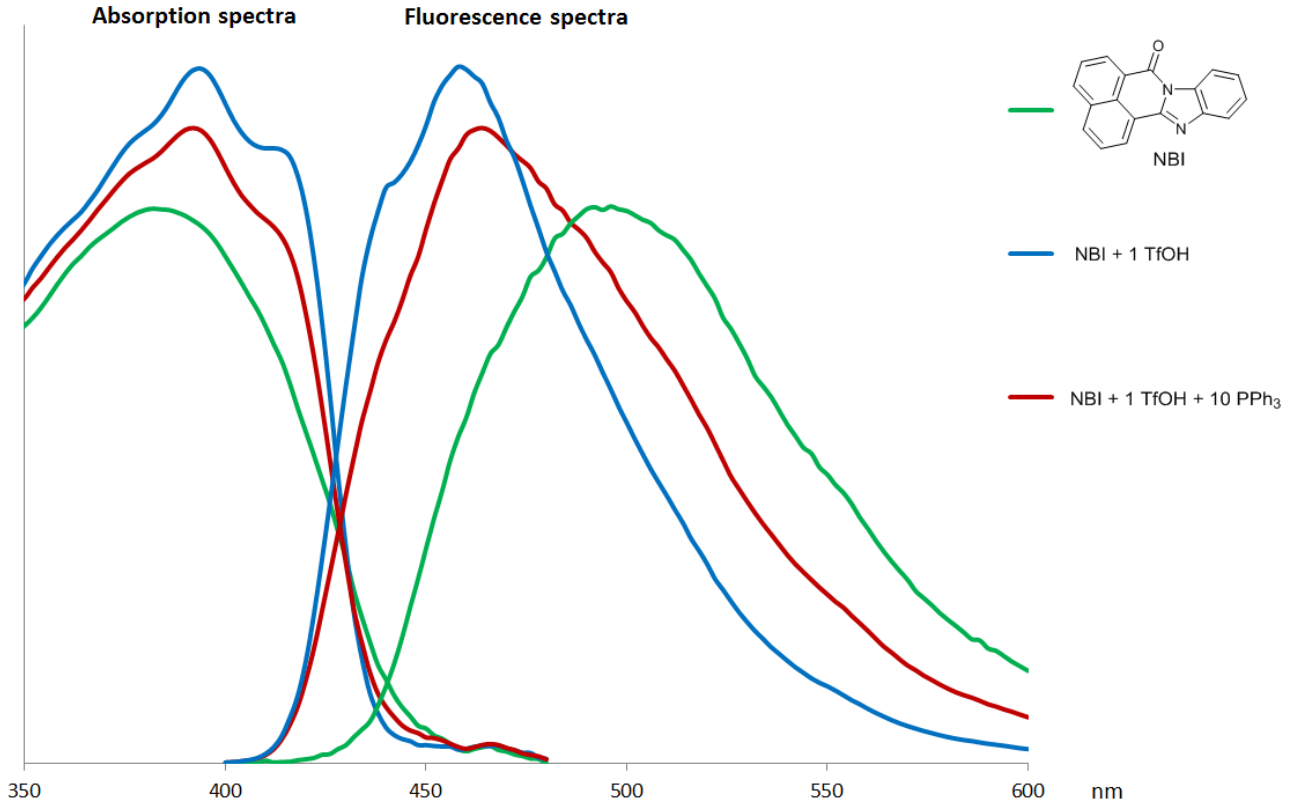


Quantum yield for the reaction of allylcyclohexane with Ph_3PHOTf was estimated using irradiation with 50 mW blue laser (450 nm). Photon flux of the laser was measured by standard ferrioxalate actinometry[28] – 12 μEs/min. A mixture of allylcyclohexane (1.0 mmol), Ph_3PHOTf (1.33 mmol), NBI (30 μmol) and *p*-xylene (0.33 mmol, internal standard) in THF (1.5 mL) was placed in a square quartz cuvette (10×10 mm). Light absorption coefficient of this mixture was determined by spectrophotometry to be 0.88 at 450 nm. After irradiation with the laser diode for 270 min GC analysis indicated that 15% of allylcyclohexane were consumed (150 μmol of the product formed). Using this parameters, quantum yield was calculated by the following equation:

$$\Phi = \frac{\text{moles of product formed}}{\text{absorbtion coefficient} \cdot \text{photon flux} \cdot \text{reaction time}} = \frac{150\ \mu\text{mol}}{0.88 \cdot 12\ \mu\text{Es}\cdot\text{min}^{-1} \cdot 270\ \text{min}} = 0.05$$

Spectroscopic studies

Figure 1S. Absorption spectra and fluorescence spectra. Spectra were recorded in dichloromethane at concentration of 10^{-5} m/L.



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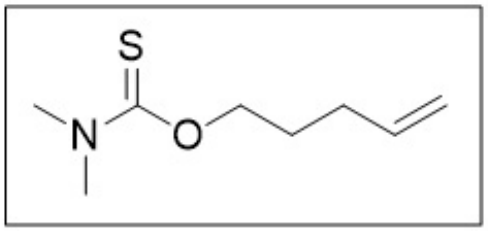
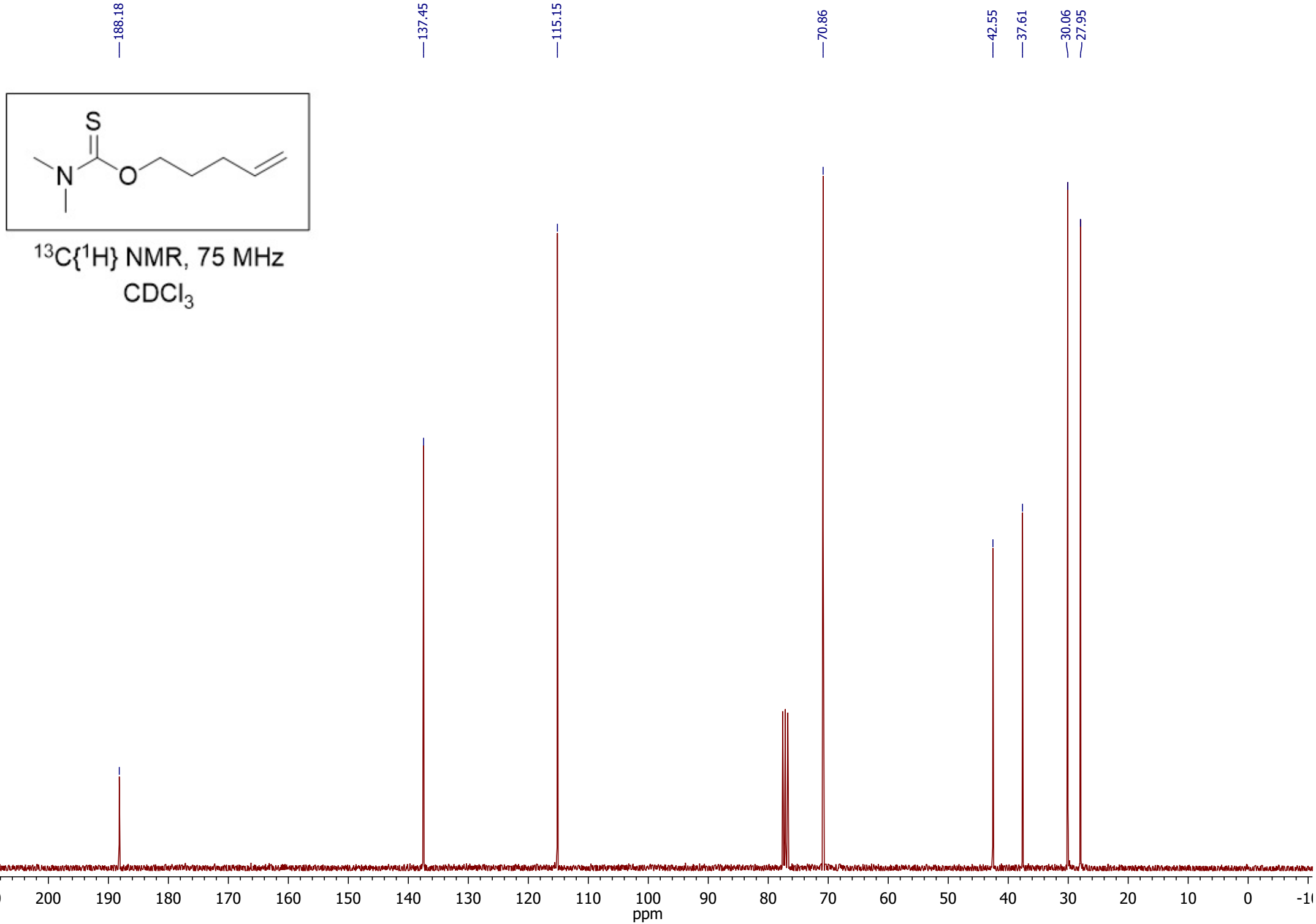


^{1}H NMR, 300 MHz

$CDCl_3$

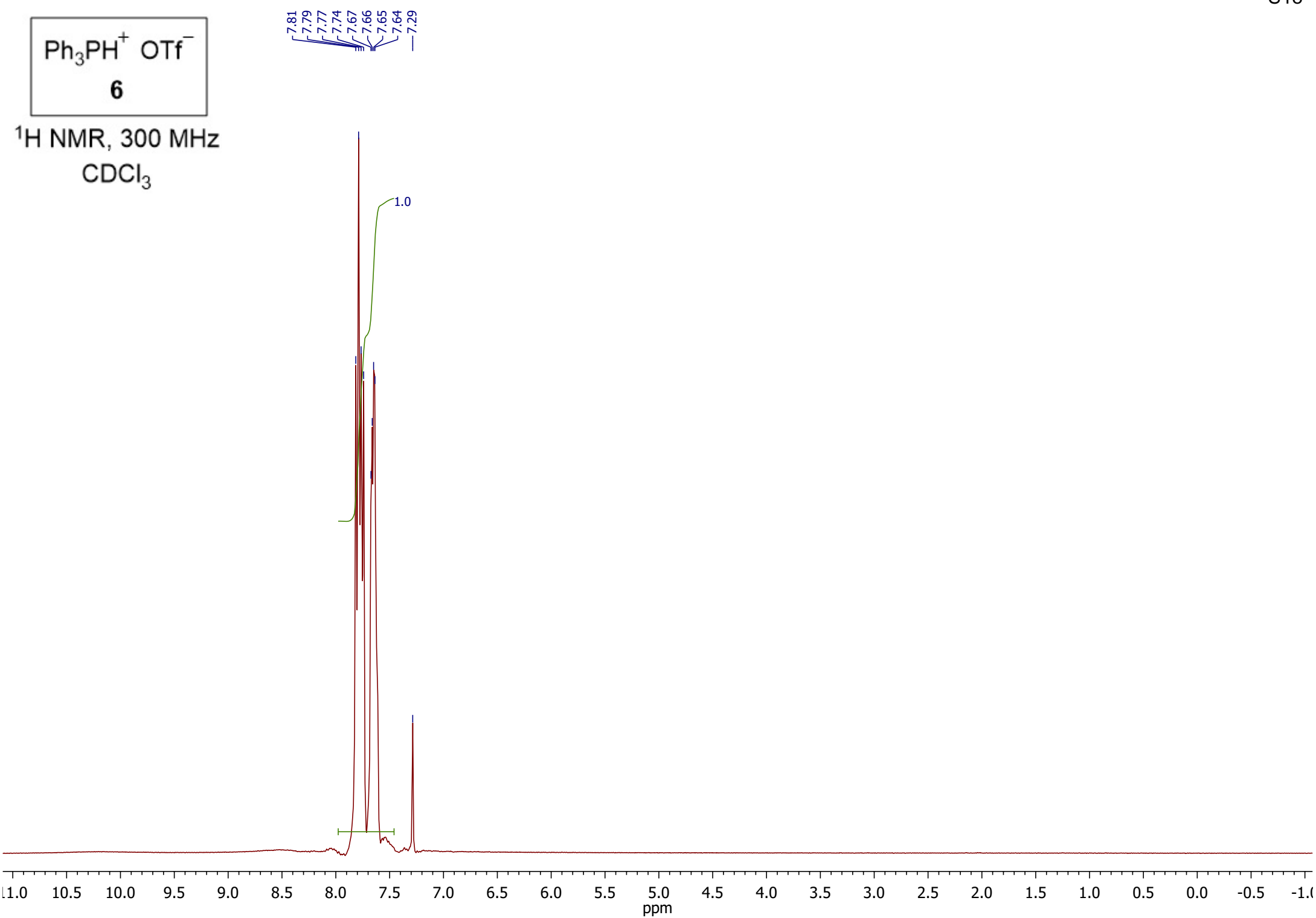

188.18
137.45
115.15
70.86
42.55
37.61
30.06
27.95
S
N
O
$^{13}C\{^{1}H\}$ NMR, 75 MHz
$CDCl_3$
ppm

Ph_3PH^+ OTf^-

6

^1H NMR, 300 MHz

$CDCl_3$

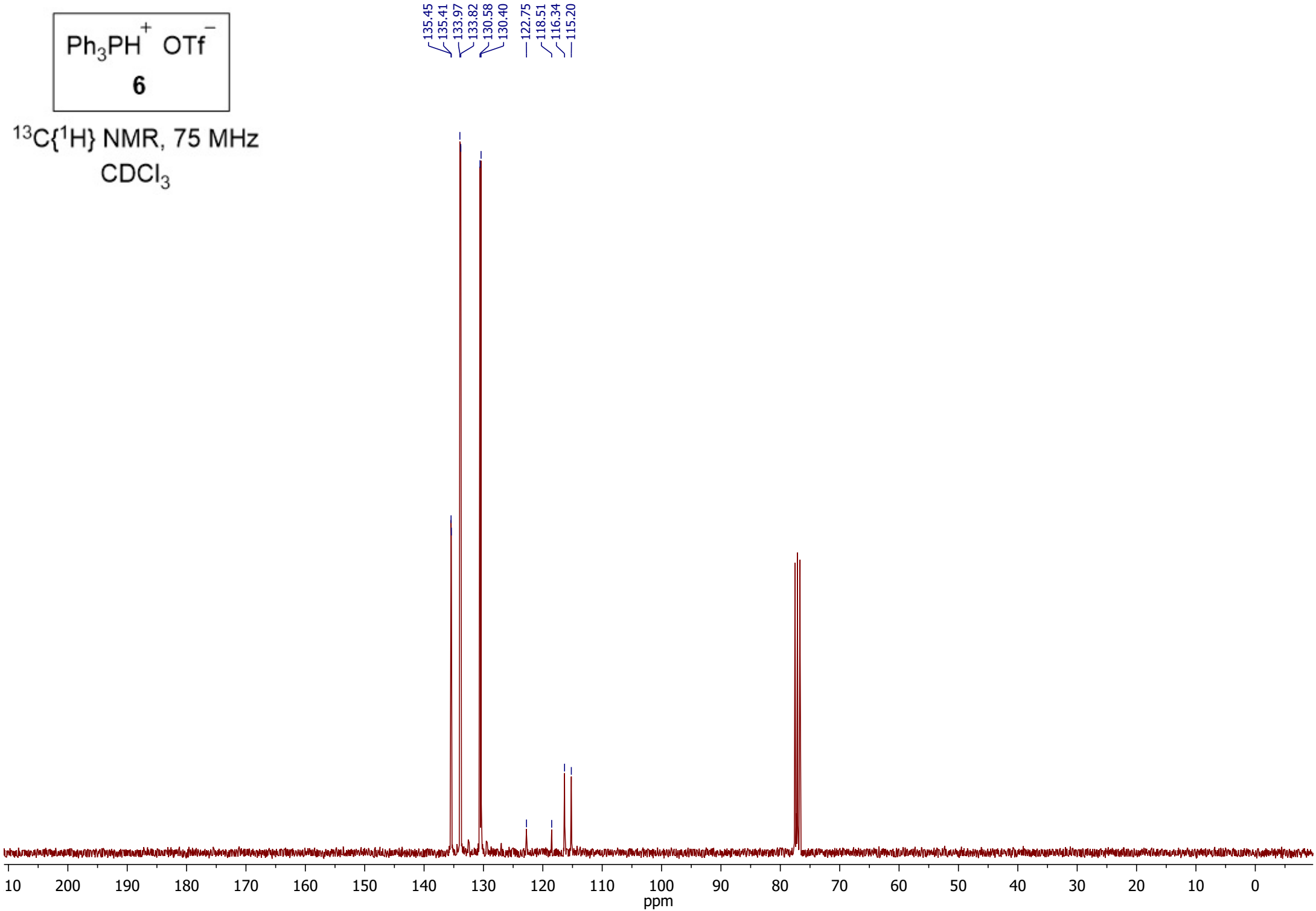


$Ph_3PH^+ \ OTf^-$

6

$^{13}C\{^1H\}$ NMR, 75 MHz

$CDCl_3$

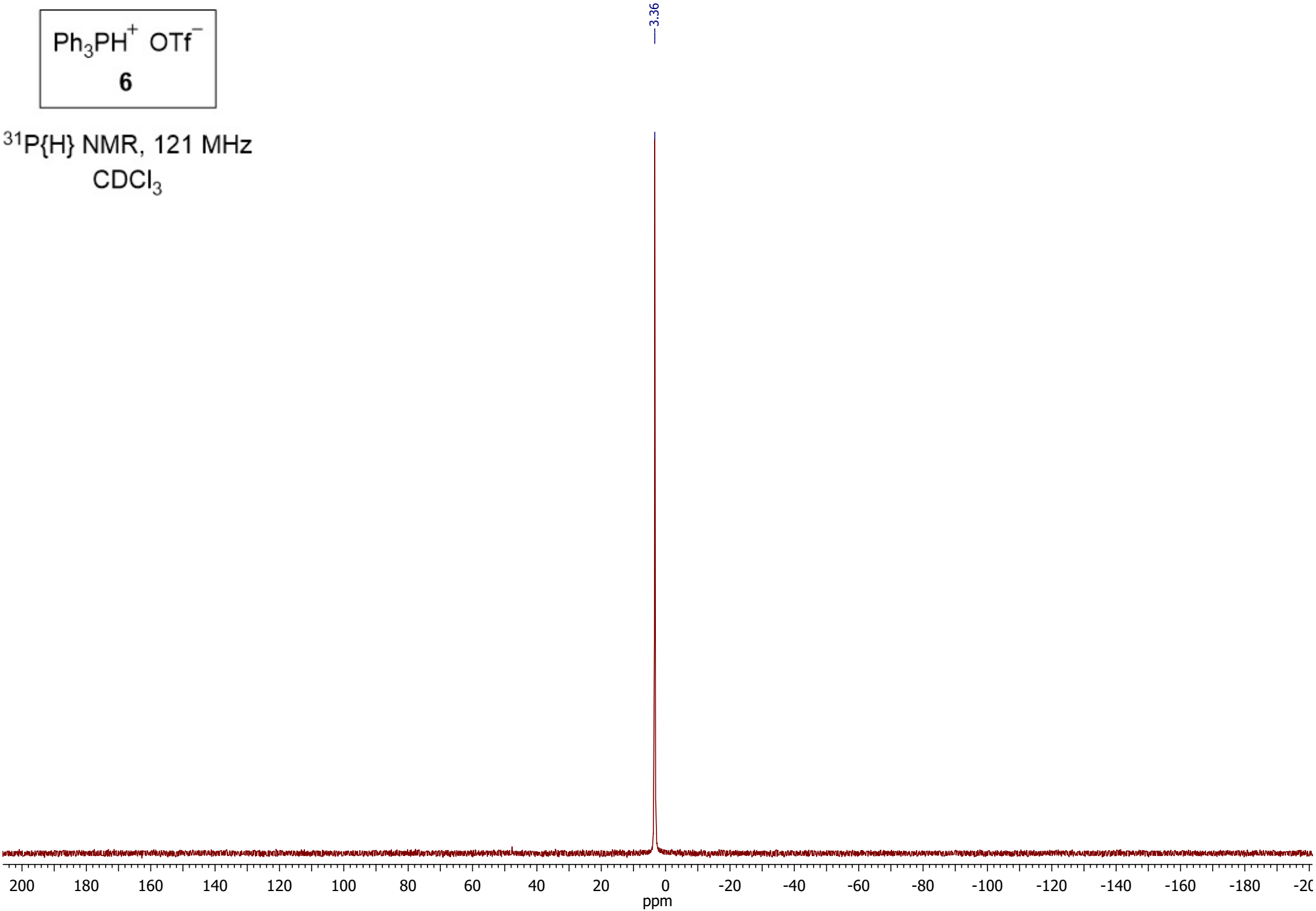


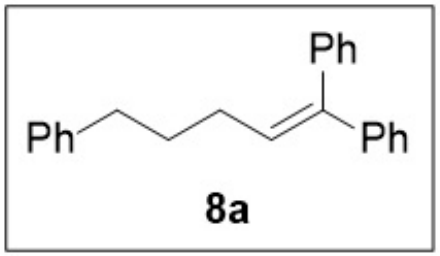
Ph_3PH^+ OTf^-

6

$^{31}P\{H\}$ NMR, 121 MHz

$CDCl_3$

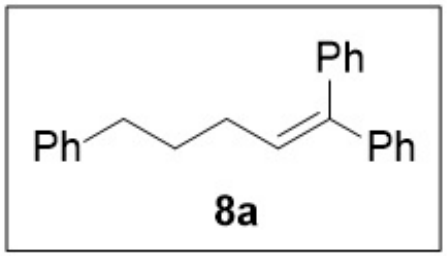




8a

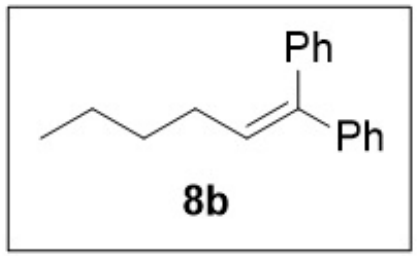
^{1}H NMR, 300 MHz

$CDCl_3$



$^{13}C\{^{1}H\}$ NMR, 75 MHz

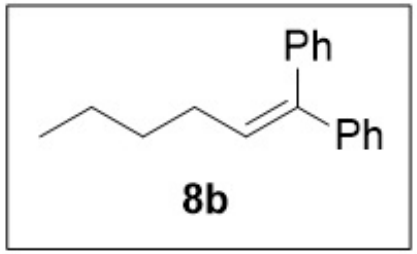
$CDCl_3$



8b

^{1}H NMR, 300 MHz

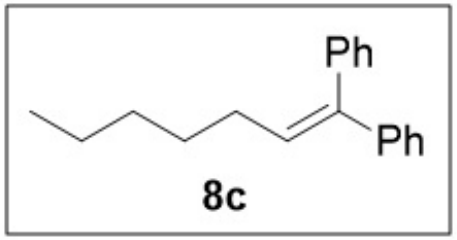
$CDCl_3$



8b

$^{13}C\{^{1}H\}$ NMR, 75 MHz

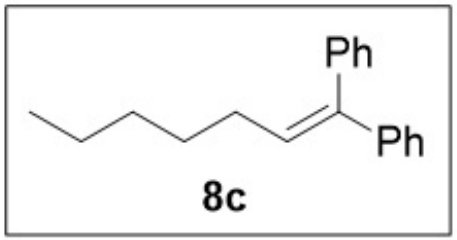
$CDCl_3$



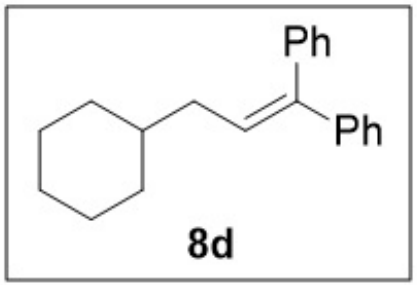
8c

^{1}H NMR, 300 MHz

$CDCl_3$

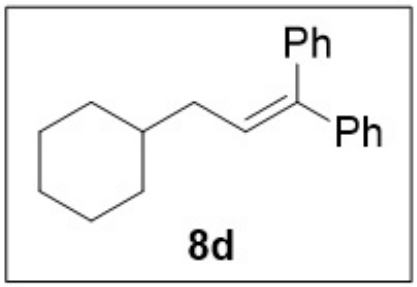


$^{13}C\{^{1}H\}$ NMR, 75 MHz
$CDCl_3$



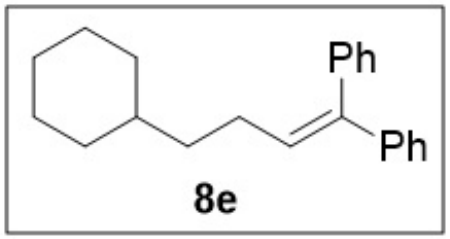
^{1}H NMR, 300 MHz

$CDCl_3$



$^{13}C\{^{1}H\}$ NMR, 75 MHz

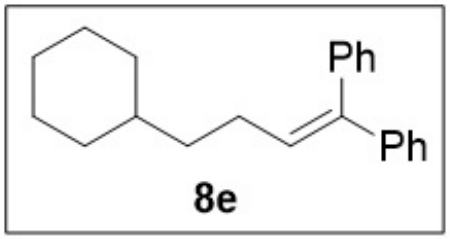
$CDCl_3$



8e

^{1}H NMR, 300 MHz

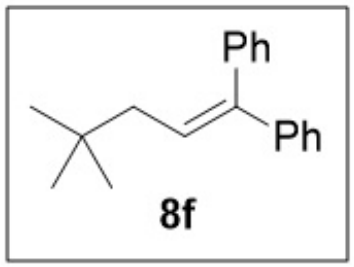
$CDCl_3$



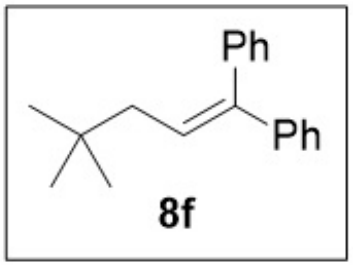
8e

$^{13}C\{^{1}H\}$ NMR, 75 MHz

$CDCl_3$

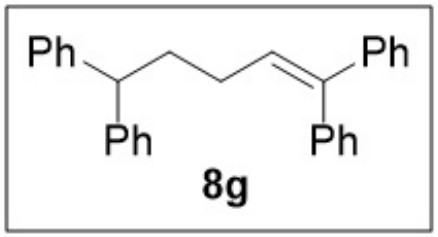


^{1}H NMR, 300 MHz
$CDCl_3$



$^{13}C\{^{1}H\}$ NMR, 75 MHz

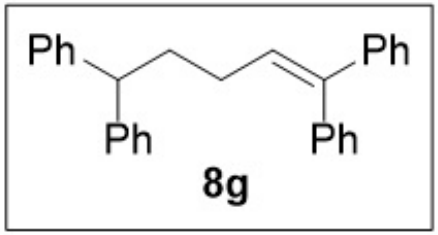
$CDCl_3$



8g

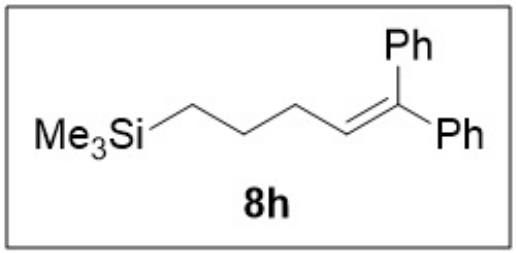
^{1}H NMR, 300 MHz

$CDCl_3$



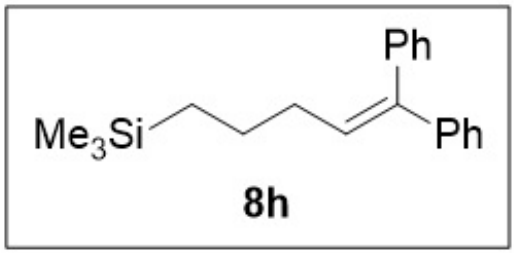
$^{13}C\{^{1}H\}$ NMR, 75 MHz

$CDCl_3$



8h

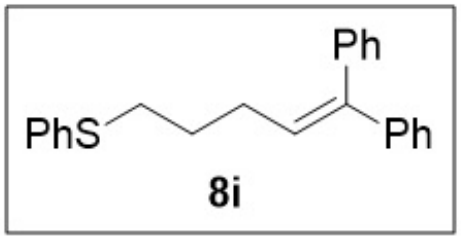
^{1}H NMR, 300 MHz
$CDCl_3$



8h

$^{13}C\{^{1}H\}$ NMR, 75 MHz

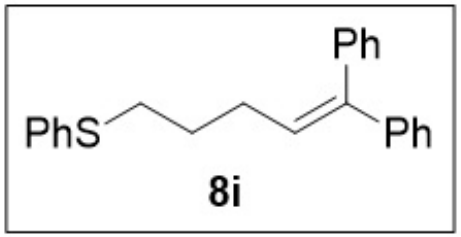
$CDCl_3$



8i

^{1}H NMR, 300 MHz

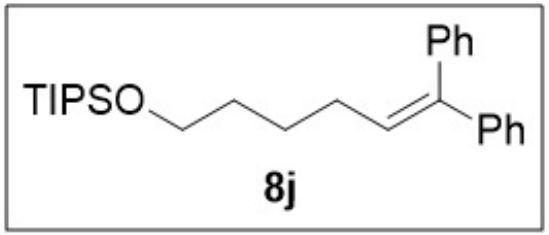
$CDCl_3$



8i

$^{13}C\{^{1}H\}$ NMR, 75 MHz

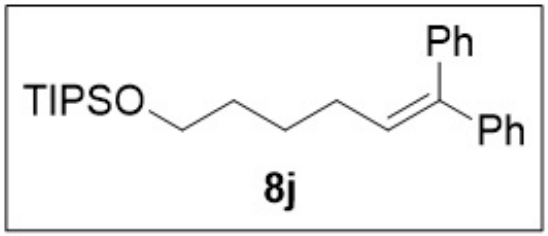
$CDCl_3$



8j

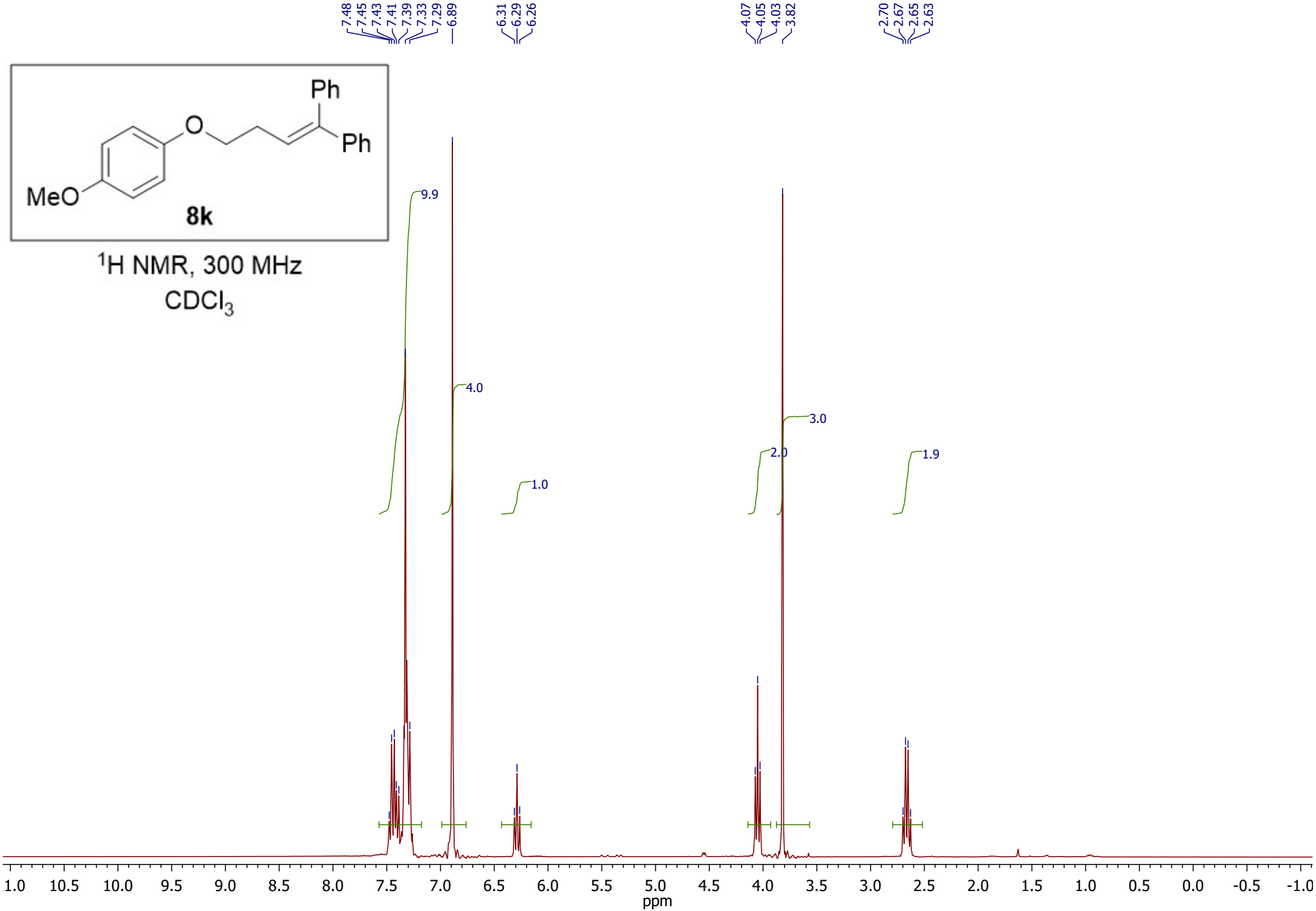
^{1}H NMR, 300 MHz

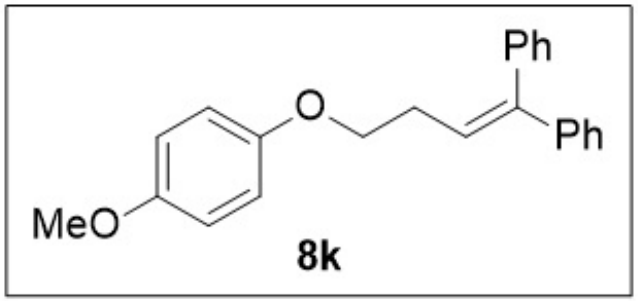
$CDCl_3$



$^{13}C\{^{1}H\}$ NMR, 75 MHz

$CDCl_3$

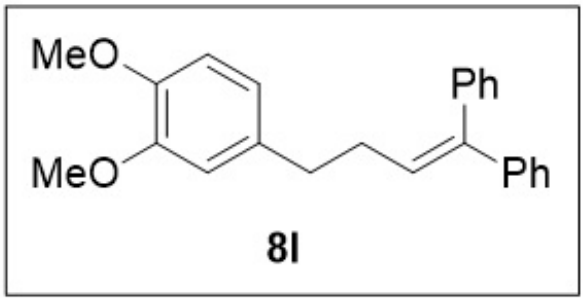

7.48
7.45
7.43
7.41
7.39
7.33
7.29
6.89
6.31
6.29
6.26
4.07
4.05
4.03
3.82
2.70
2.67
2.65
2.63
Ph
O
Ph
MeO
8k
1H NMR, 300 MHz
CDCl3
9.9
4.0
1.0
3.0
2.0
1.9
ppm



8k

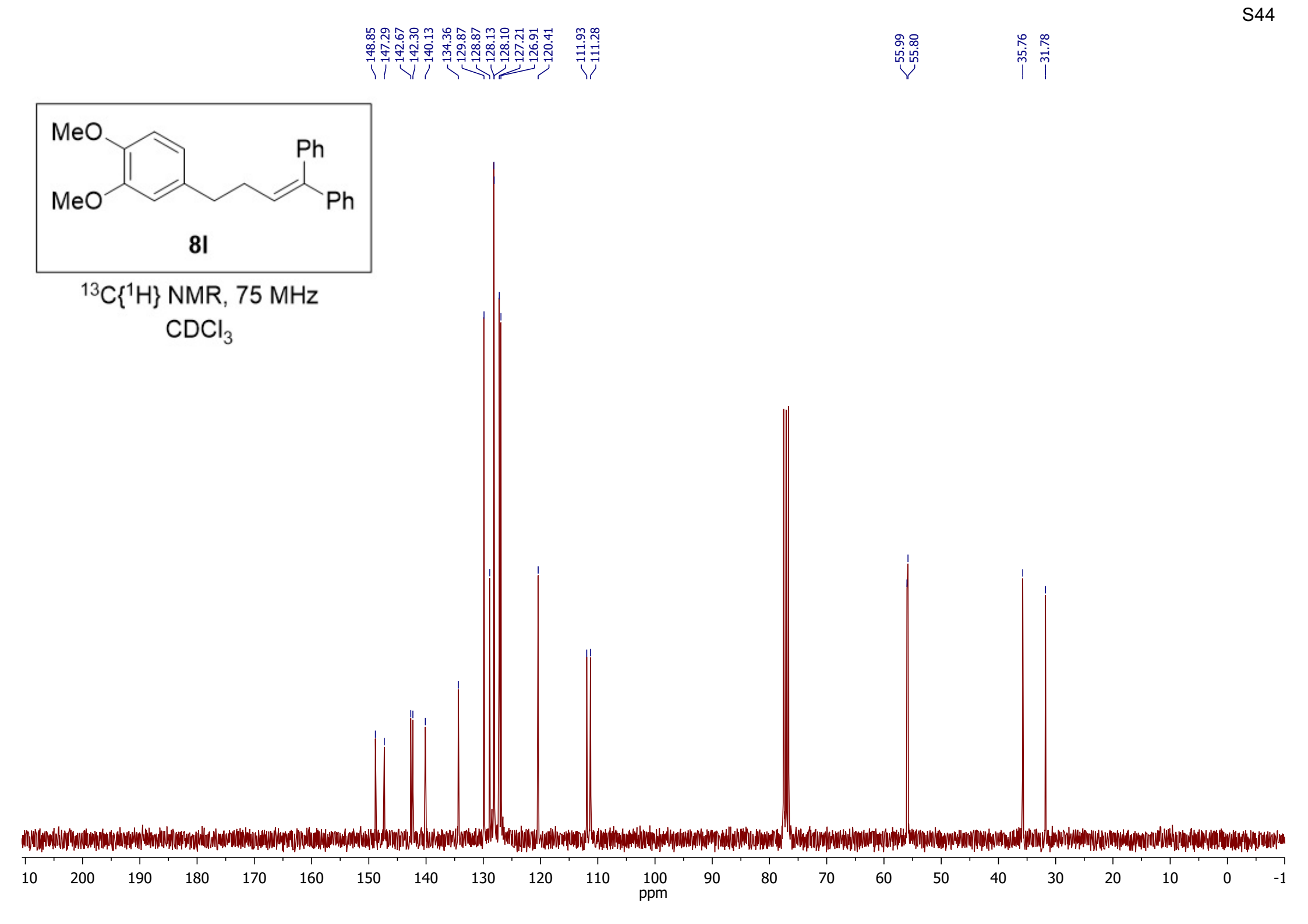
$^{13}C\{^{1}H\}$ NMR, 75 MHz

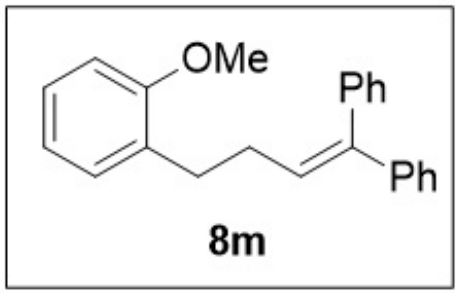
$CDCl_3$



8l

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

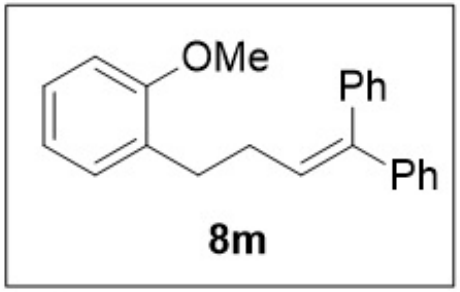

148.85
147.29
142.67
142.30
140.13
134.36
129.87
128.87
128.13
128.10
127.21
126.91
120.41
111.93
111.28
55.99
55.80
35.76
31.78
MeO
MeO
Ph
Ph
8l
13C{1H} NMR, 75 MHz
CDCl3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
ppm



8m

^{1}H NMR, 300 MHz

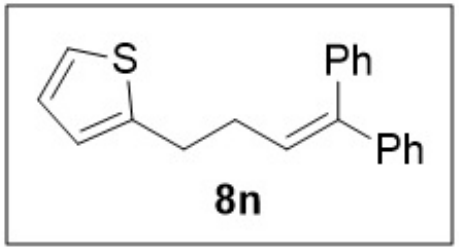
$CDCl_3$



8m

^{1}H NMR, 300 MHz

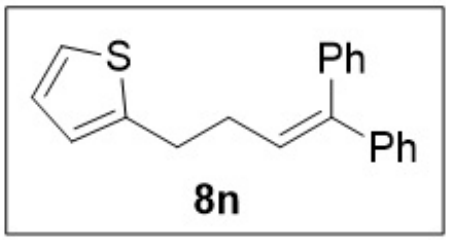
$CDCl_3$



8n

^{1}H NMR, 300 MHz

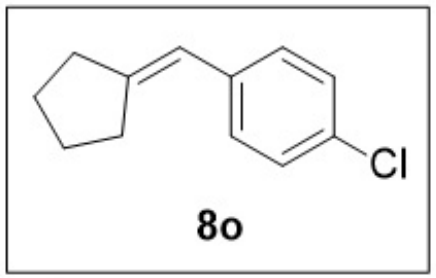
$CDCl_3$



8n

$^{13}C\{^{1}H\}$ NMR, 75 MHz

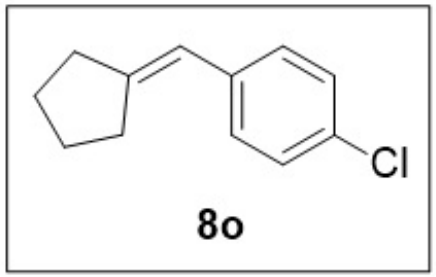
$CDCl_3$



8o

^{1}H NMR, 300 MHz

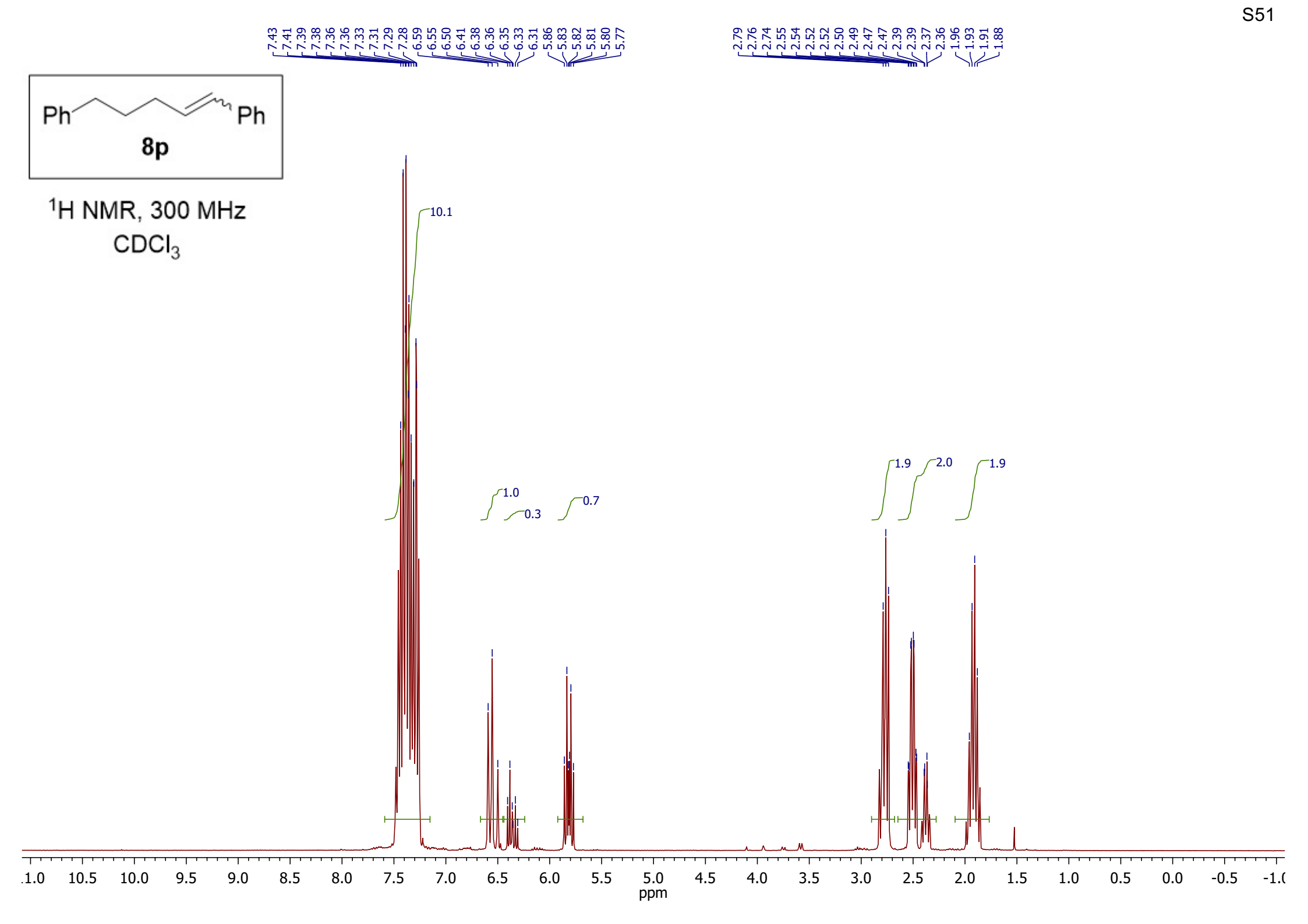
$CDCl_3$

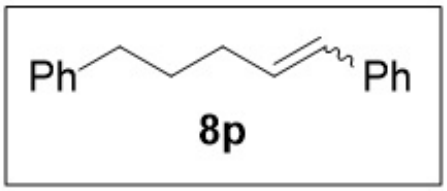


8o

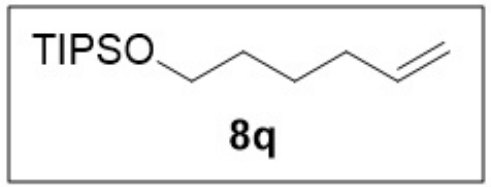
$^{13}C\{^{1}H\}$ NMR, 75 MHz

$CDCl_3$


7.43
7.41
7.39
7.38
7.36
7.36
7.33
7.31
7.29
7.28
6.59
6.55
6.50
6.41
6.38
6.36
6.35
6.33
6.31
5.86
5.83
5.82
5.81
5.80
5.77
2.79
2.76
2.74
2.55
2.54
2.52
2.52
2.50
2.49
2.47
2.47
2.39
2.39
2.37
2.36
1.96
1.93
1.91
1.88
Ph
Ph
8p
1H NMR, 300 MHz
CDCl3
10.1
1.0
0.3
0.7
1.9
2.0
1.9
ppm



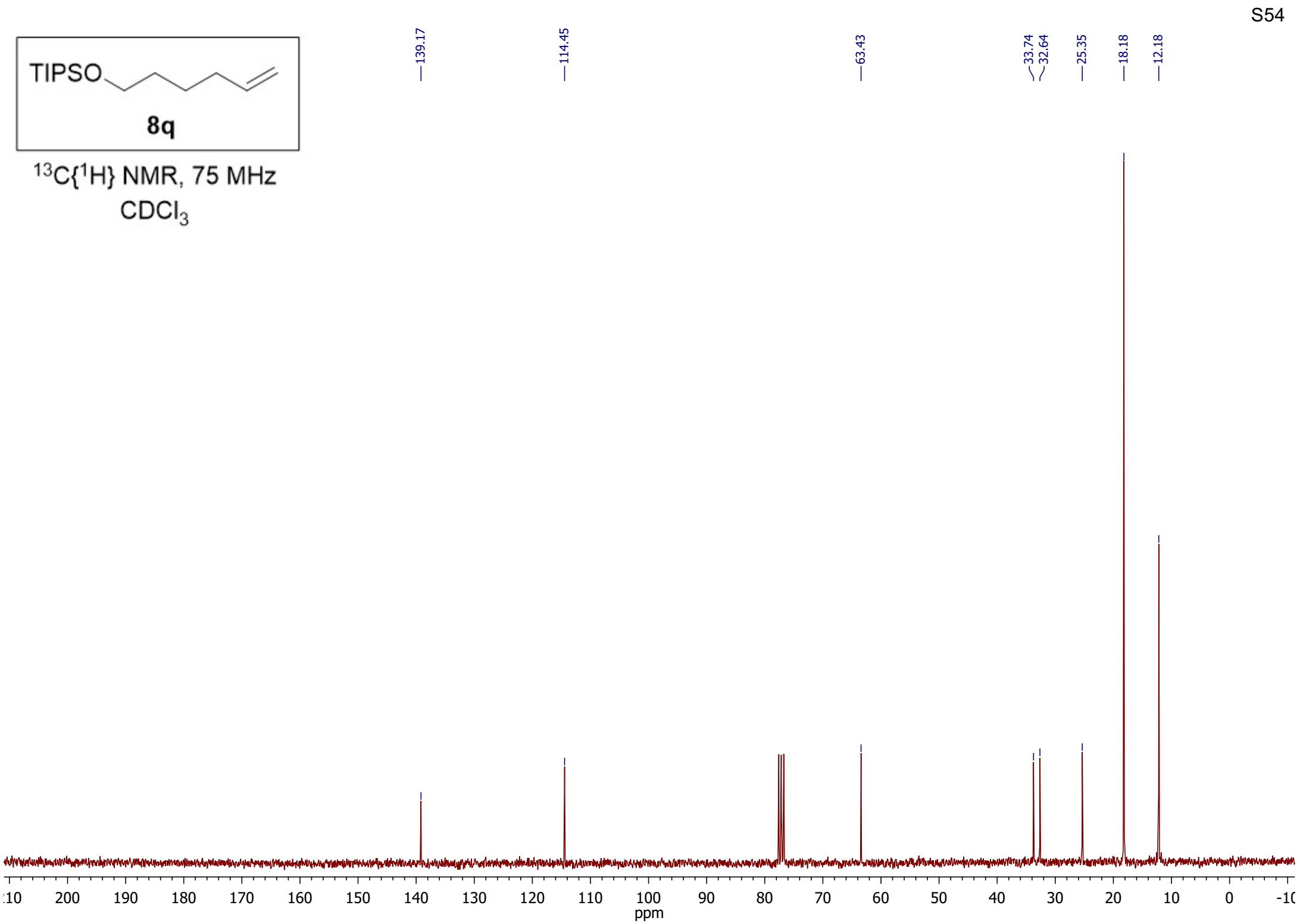
$^{13}C\{^{1}H\}$ NMR, 75 MHz
$CDCl_3$

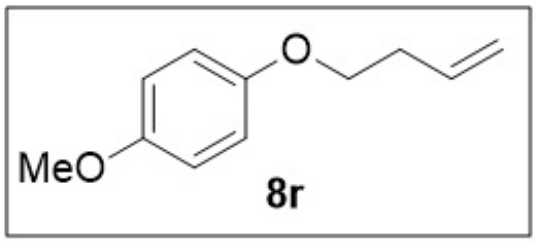


8q

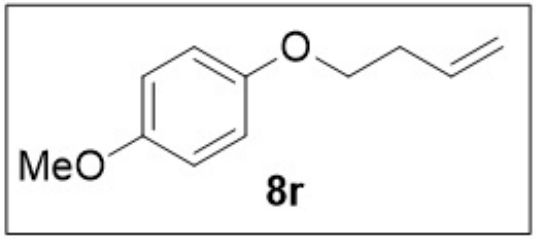
^{1}H NMR, 300 MHz

$CDCl_3$


TIPSO
8q
$^{13}C\{^{1}H\}$ NMR, 75 MHz
$CDCl_3$
139.17
114.45
63.43
33.74
32.64
25.35
18.18
12.18
ppm



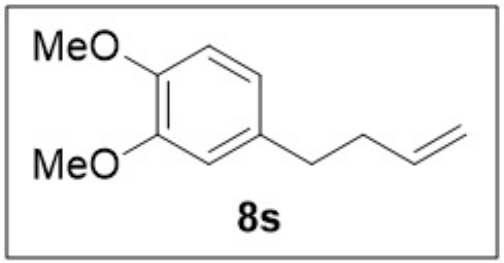
^{1}H NMR, 300 MHz
$CDCl_3$



8r

$^{13}C\{^{1}H\}$ NMR, 75 MHz

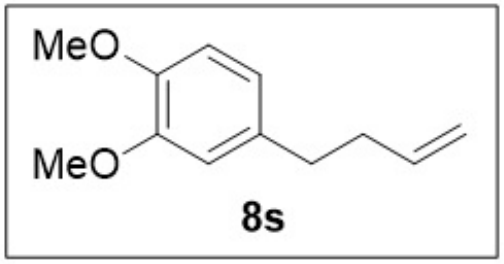
$CDCl_3$



8s

^{1}H NMR, 300 MHz

$CDCl_3$



8s

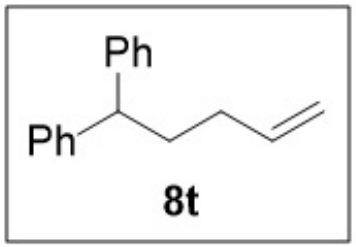
$^{13}C\{^{1}H\}$ NMR, 75 MHz

$CDCl_3$

148.80
147.21
138.15
134.56
120.22
114.90
111.85
111.24
55.92
55.82
35.72
34.99

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

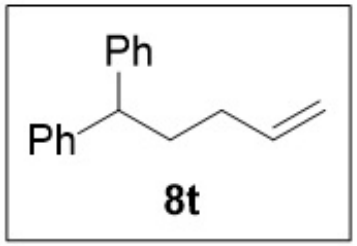
ppm



8t

^{1}H NMR, 300 MHz

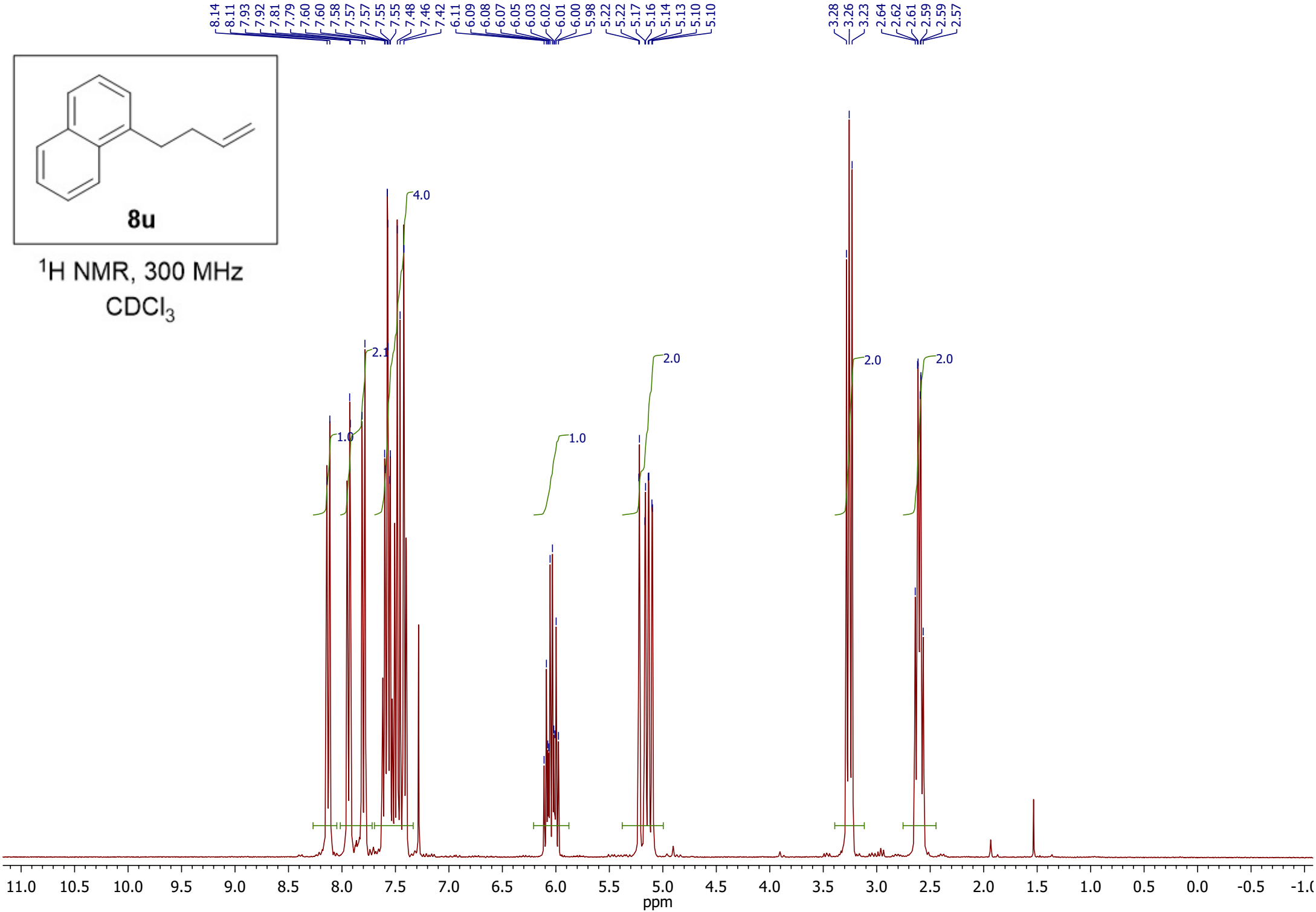
$CDCl_3$

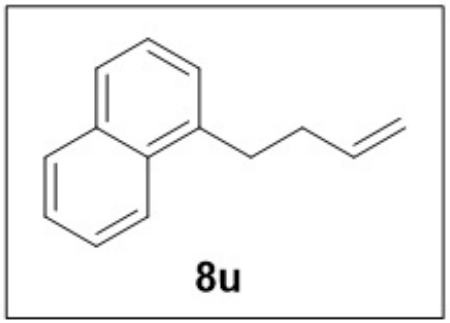


8t

$^{13}C\{^{1}H\}$ NMR, 75 MHz

$CDCl_3$

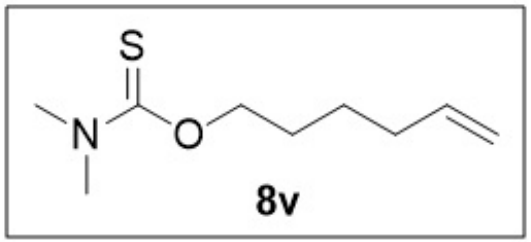

8.14
8.11
7.93
7.92
7.81
7.79
7.60
7.60
7.58
7.57
7.57
7.55
7.55
7.48
7.46
7.42
6.11
6.09
6.08
6.07
6.05
6.03
6.02
6.01
6.00
5.98
5.22
5.22
5.17
5.16
5.14
5.13
5.10
5.10
3.28
3.26
3.23
2.64
2.62
2.61
2.59
2.59
2.57
8u
1H NMR, 300 MHz
CDCl3
4.0
2.1
1.0
1.0
2.0
2.0
2.0
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
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
0.5
0.0
-0.5
-1.0
ppm



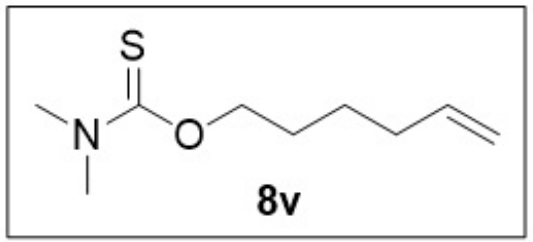
8u

$^{13}C\{^{1}H\}$ NMR, 75 MHz

$CDCl_3$

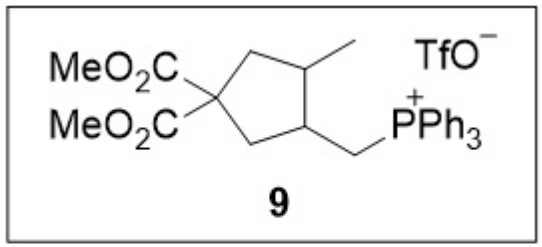


^{1}H NMR, 300 MHz
$CDCl_3$



$^{13}C\{H\}$ NMR, 75 MHz

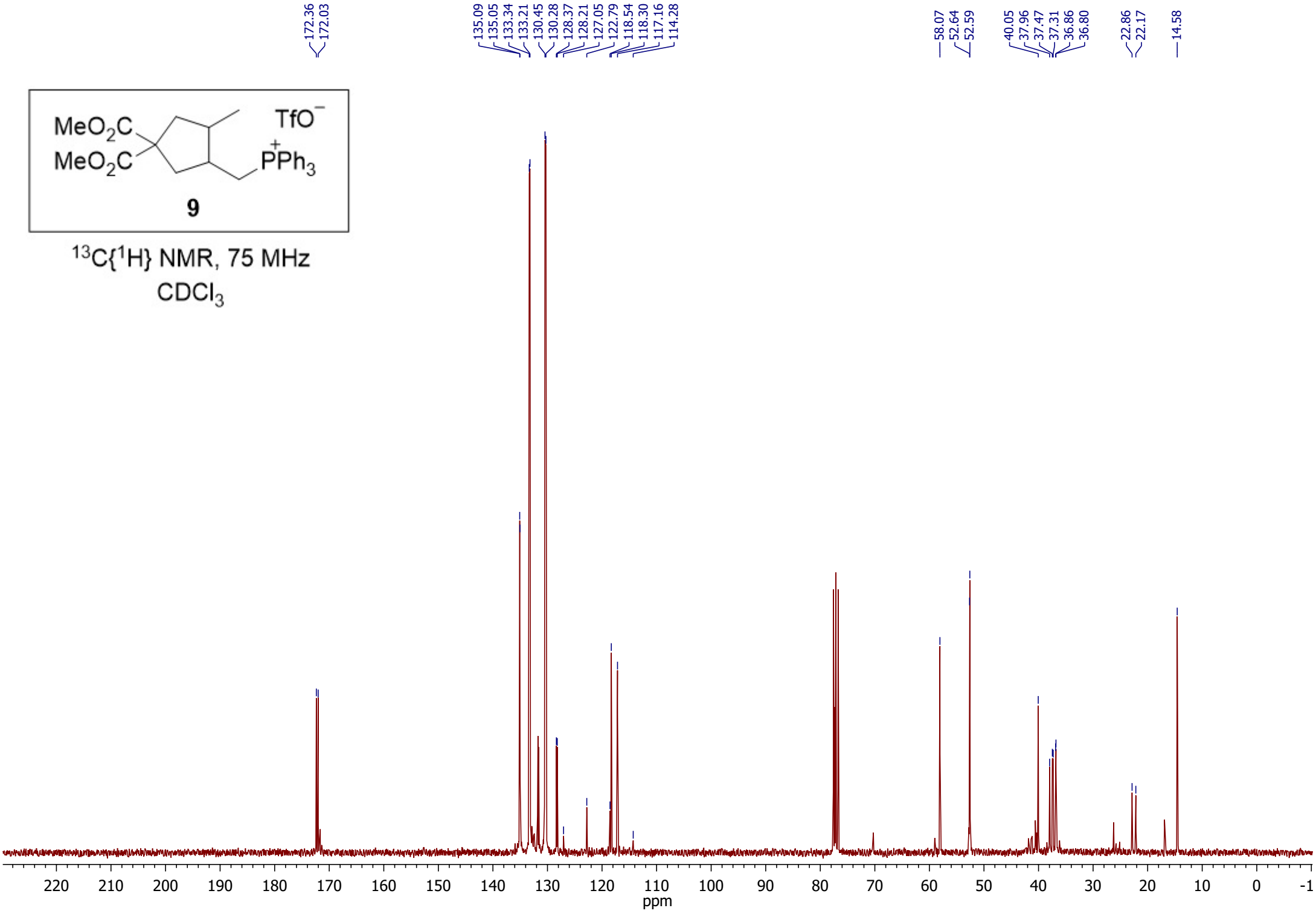
$CDCl_3$

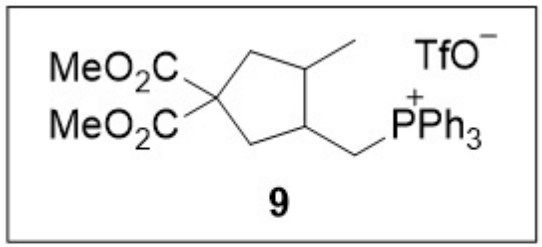


9

^{1}H NMR, 300 MHz

$CDCl_3$


172.36
172.03
135.09
135.05
133.34
133.21
130.45
130.28
128.37
128.21
127.05
122.79
118.54
118.30
117.16
114.28
58.07
52.64
52.59
40.05
37.96
37.47
37.31
36.86
36.80
22.86
22.17
14.58
MeO2C
MeO2C
TfO−
+PPh3
9
13C{1H} NMR, 75 MHz
CDCl3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
ppm



9

$^{31}P\{^{1}H\}$ NMR, 121 MHz
$CDCl_3$