Supporting Information

A Carbazolyl Dicyanobenzene Dye for the Photooxidation of Bis-Catecholato Silicates

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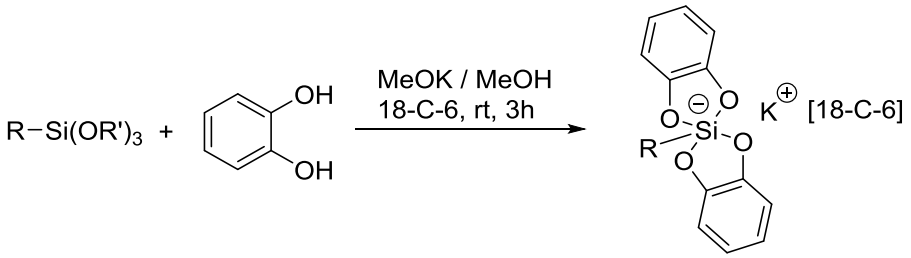
I. General informations

Unless otherwise noted, reactions were carried out under an argon atmosphere in oven-dried glassware. Methanol and toluene were distillated over CaH_2, THF and diethyl ether were distillated over sodium/benzophenone, triethylamine over potassium hydroxide. Catechol was purchased from commercial source and purified by crystallization from toluene followed by sublimation. Reagents and chemicals were purchased from commercial sources and used as received. Infrared (IR) spectra were recorded on a Bruker Tensor 27 (ATR diamond) spectrophotometer. Melting points were determined on a melting point apparatus SMP3 (Stuart scientific) and are uncorrected. ^{1}H, ^{19}F, ^{31}P and ^{13}C NMR spectra were recorded at room temperature at 400, 377, 162 and 100 MHz respectively, on a Bruker AVANCE 400 spectrometer. ^{29}Si NMR spectra were recorded at 119 MHz on a Bruker AVANCE III 600 spectrometer. Chemical shifts (δ) are reported in ppm and coupling constants (*J*) are given in Hertz (Hz). Abbreviations used for peak multiplicity are: s (singlet); bs (broad singlet); d (doublet); t (triplet); q (quartet); quint (quintet); sept (septet); m (multiplet). Thin layer chromatographies (TLC) were performed on Merck silica gel 60 F 254 and revealed with a UV lamp (λ = 254 nm) and $KMnO_4$ staining. Flash Column Chromatographies were conducted on silica Geduran® Si 60 Å (40 – 63 µm). High resolution mass spectrometries were performed on a microTOF (ESI).

II. General procedures

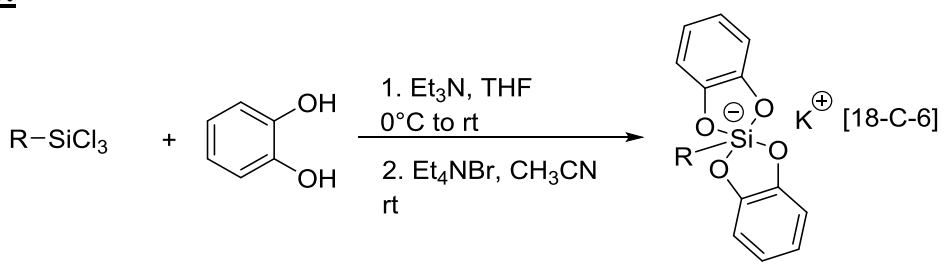
1. General procedure A for silicate synthesis

Method A:



To a stirred solution of catechol (2 eq.) in dry methanol (0.25 M) was added 18-C-6 (1 eq.). After dissolution of the crown ether, the trialkoxy organosilane (1 eq.) was added, followed by a solution of potassium methoxide in methanol (1 eq.). The reaction mixture was stirred for 3 hours and the solvent was removed under reduced pressure. The residue was dissolved in the minimum volume of acetone and diethyl ether was added until a cloudy solution was obtained (scrapping on the edge of the flask could be done to induce crystallization). The flask was placed at -20°C overnight. The crystals were collected by filtration, washed with cold diethyl ether and dried under vacuum to afford [18-C-6] silicate.

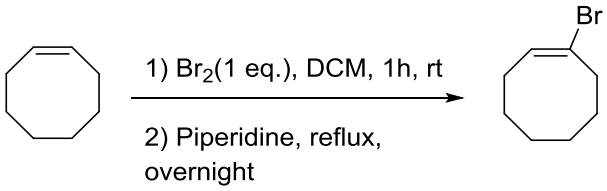
Method B:



To a stirred solution of catechol (2 eq.) in dry THF (0.1 M) was added triethylamine (4 eq.). The reaction mixture was cooled to 0°C with an ice bath and organotrichlorosilane (1 eq.) was added dropwise. The mixture was stirred for an hour at 0°C and an additional hour at room temperature. The triethylamine hydrochloride salt was filtered off and the filtrate was evaporated under reduced pressure. The residue was taken up in acetonitrile (0.3 M) and tetraethylammonium bromide (1 eq.) was added. The mixture was stirred for an hour and the solvent was evaporated under reduced pressure. The solid was taken up in water, filtered, washed with water and dried under high vacuum to afford tetraethylammonium silicate.

2. Synthesis of Alkenyl bromides

1-Bromocyclooctene (7a)

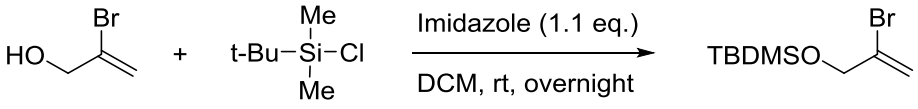


7a
37%

The compound **7a** has been synthesized following a previous reported procedure.[1] The spectroscopic data are in agreement with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.03 (t, *J* = 8.5, 1H), 2.63 – 2.59(m, 2H), 2.13 – 2.07 (m, 2H), 1.64 – 1.62 (m, 2H), 1.55 – 1.50 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 131.8, 125.0, 35.3, 30.0, 28.8, 27.6, 26.6, 25.6.

((2-Bromoallyl)oxy)(tert-butyl)dimethylsilane (7b)

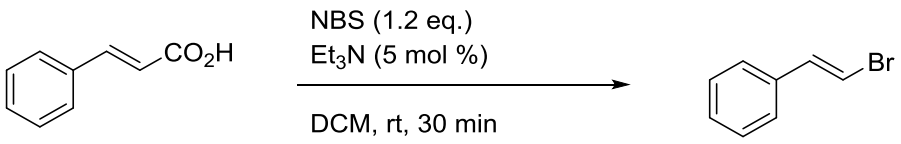


7b
99%

The compound **7b** has been synthesized following a previous reported procedure.[2] The spectroscopic data are in agreement with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.85 (d, *J* = 1.8 Hz, 1H), 5.43 (d, *J* = 1.6 Hz, 1H), 4.11 – 4.10 (m, 2H), 0.82 (s, 9H), 0.00 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 132.0, 114.8, 67.6, 25.9 (3 C), 18.5, -5.2 (2 C). **IR** (neat): 2958, 2854, 1637, 1463, 124, 1085, 838, 774 cm^{-1}.

(E)-(2-bromovinyl)benzene (7d)

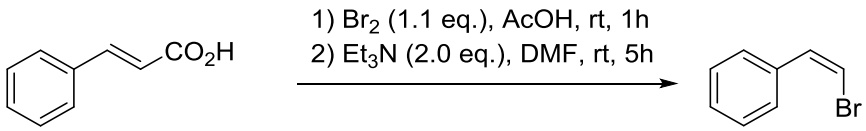


7d
55%

The compound **7d** has been synthesized following a previous reported procedure.[3] The spectroscopic data are in agreement with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.30 (m, 5H), 7.13 (d, *J* = 14.0 Hz, 1H), 6.79 (d, *J* = 14.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 137.3, 136.0, 128.9 (2 C), 128.4, 126.2 (2 C), 106.6.

(Z)-(2-bromovinyl)benzene (7d')

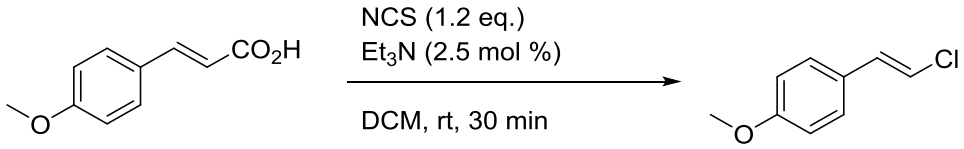


7d'
97%

The compound **7d'** has been synthesized following a previous reported procedure. [4] The spectroscopic data are in agreement with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 – 7.80 (m, 2H), 7.52 – 7.4 (m, 3H), 7.15 (d, *J* = 8.1 Hz, 1H), 6.52 (d, *J* = 8.1 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 137.3, 136.0, 128.9 (2 C), 128.4, 126.2 (2 C), 106.6.

(2-chlorovinyl)benzene (7e)



7e
27%

The compound **7f** has been synthesized following a previous reported procedure. [1] A mixture of isomer was obtained (ratio Z/E 5:95). The spectroscopic data are in agreement with those reported in the literature.[1]

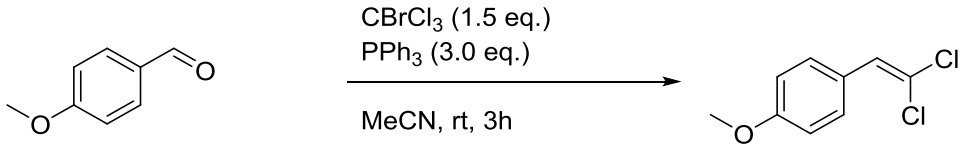
(E) isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (d, *J* = 8.6 Hz, 2H), 6.74 (d, *J* = 8.6 Hz, 2H), 6.65 (d, *J* = 13.6 Hz, 1H), 6.38 (d, *J* = 13.6 Hz, 1H), 3.69 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.7, 132.8, 127.7, 127.5 (2 C), 116.5, 114.3 (2 C), 55.4.

(Z) isomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.9 Hz, 2H), 6.45 (d, *J* = 8.1 Hz, 1H), 6.04 (d, *J* = 8.1 Hz, 1H), 3.71 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.5, 130.8 (2 C), 128.7, 127.0, 115.5, 113.8 (2 C), 55.4.

1-(2,2-dichlorovinyl)-4-methoxybenzene (7f)



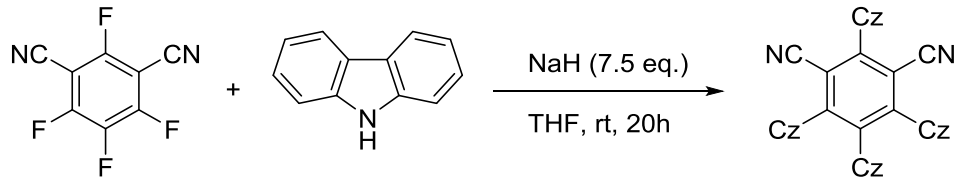
7f
56%

To a 250 mL round-bottom-flask was added the *para*-anisaldehyde (5 mmol, 0.607 mL) and 40 mL of MeCN. The reaction mixture was cooled with an ice bath to 0°C and $BrCCl_3$ (7.5 mmol, 0.740 mL) was added, followed by addition of a solution of triphenylphosphine (15 mmol, 3.95g) in the minimum of MeCN. The reaction mixture was stirred at room temperature for 3 hours and the solvent was removed under reduced pressure to afford the crude product. The residue was dissolved in 80 mL of pentane and the organic phase was washed with water (80 mL), brine (80 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue filtered on a pad of silica eluted with pentane, giving the pure material (559 mg, 55%).

The spectroscopic data are in agreement with those reported in the literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.79 (s, 1H), 3.83 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.7, 130.2 (2 C), 128.2, 126.1, 118.9, 114.0 (2 C), 55.4.

3. Synthesis of 4CzIPN



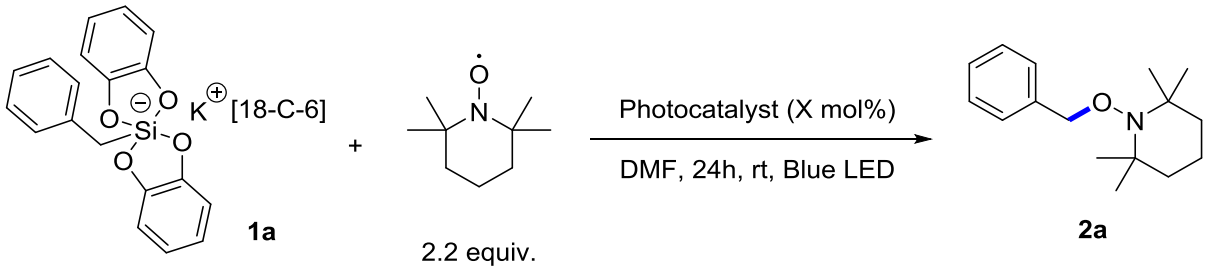
Cz-H **4CzIPN**
71%

The 4CzIPN has been synthesized following a previous reported procedure.[7] To a 100 mL round-bottom-flask was added NaH (60% in mineral oil) (7.5 eq., 15 mmol, 600 mg). THF (40 mL) was added followed by the slow addition of carbazole (5.0 eq., 10 mmol, 1.67 g). After 30 min of stirring at room temperature the tetrafluoroisophtalonitrile (1.0 eq., 2 mmol, 400 mg) was added and the mixture was stirred at room temperature for 20 hours. A yellow precipitate progressively appeared. Water (1 mL) was added to neutralize the excess of NaH and the mixture was evaporated to give a yellow solid. The solid was successively washed with water and ethanol. The crude product was dissolved in the minimum of DCM

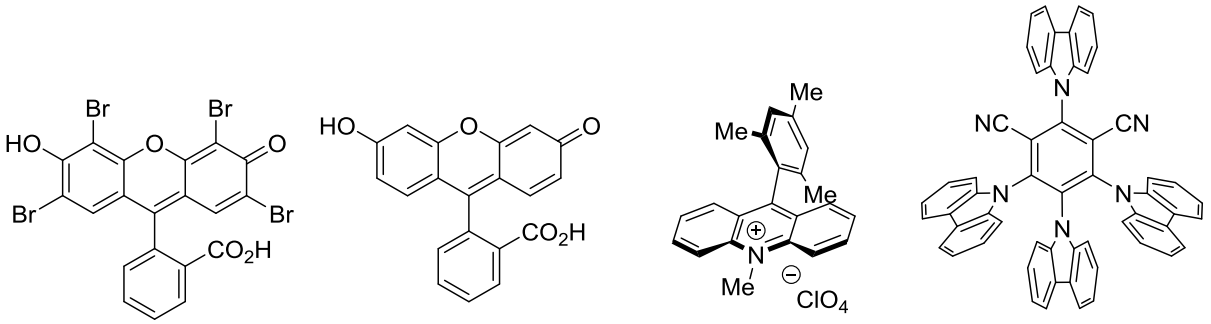
and crystallized by addition of pentane to give the pure **4CzIPN** (1.13g, 71% yield). The spectroscopic data are in agreement with those reported in the literature.[7]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (dt, *J* = 7.7, 1.0 Hz, 1H), 8.19 (d, *J* = 8.3 Hz, 1H), 7.87 – 7.84 (m, 2H), 7.76 – 7.72 (m, 3H), 7.55 – 7.44 (m, 3H), 7.12 (dtd, *J* = 17.9, 7.3, 1.3 Hz, 4H), 6.83 – 6.79 (m, 1H), 6.72 – 6.68 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.6, 144.8, 139.9, 138.5, 137.6, 136.4, 126.8, 125.4, 124.1, 123.6, 123.2, 122.8, 121.9, 121.3, 121.0, 120.5, 120.1, 119.4, 116.7, 112.2, 111.1, 110.9, 110.8.

4. Spin trapping experiments with TEMPO for screening of photocatalyst:



Organic photocatalysts screened

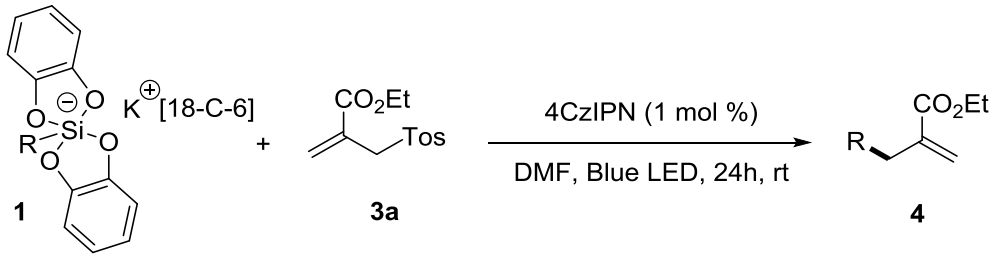


To a schlenk flask was added the potassium [18-Crown-6] bis(catecholato)-benzylsilicate **1a** (0.3 mmol), the appropriate photocatalyst (0.03 mmol) and TEMPO (0.66 mmol, 103 mg). The schlenk flask was sealed with a rubber septum, and evacuated / purged with vacuum / argon three times. Degassed DMF (3 mL) was introduced and the reaction mixture was irradiated with blue LED (477 nm) at room temperature for 24h under an argon atmosphere. The reaction mixture was diluted with diethyl ether (50 mL), washed with aqueous saturated Na_2CO_3 solution (2 times), brine (2 times), dried over $MgSO_4$ and evaporated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (pentane/Et_2O, 99/1) to afford **2a** as a colorless oil.

Table 1: Screening of organic photocatalyst in spin trapping experiments with TEMPO

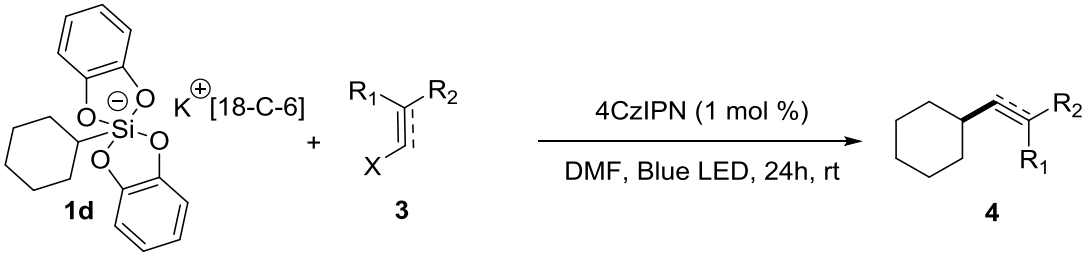
Entry	Photocatalyst used	Photocatalyst loading (% mol)	Isolated yield
1	Eosin Y	10	0
2	Fluorescein	10	0
3	Fukuzumi's catalyst	10	66
4	4CzIPN	10	92
5	**4CzIPN**	**1**	**94**

5. General procedure B for silicates additions on allylsulfone



To a schlenk flask was added the appropriate silicate (1 eq., 0.3 mmol), allyl sulfone **3a** (4 eq., 1.2 mmol, 322 mg) and 4CzIPN (1 mol %, 3 μmol, 2.4 mg). Degassed DMF was added (3 mL) and the reaction mixture was irradiated with blue LED (477 nm) at room temperature for 24h under an argon atmosphere. The reaction mixture was diluted with diethyl ether (50 mL), washed with saturated aqueous $NaHCO_3$ (2 times), brine (2 times), dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by flash column chromatography to afford the adduct **4**.

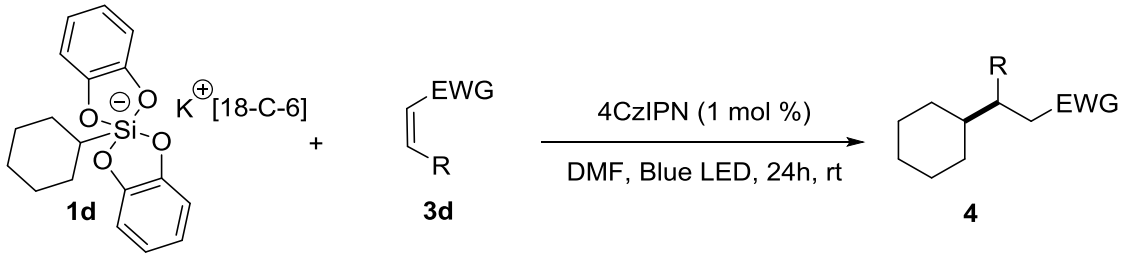
6. General procedure C for cyclohexylsilicate 1d vinylation and alkynylation reactions



To a schlenk flask was added potassium [18-C-6] bis(catecholato) cyclohexylsilicate **1d** (1 eq., 0.3 mmol, 189.3 mg), 4CzIPN (1 mol %, 3 μmol, 2.4 mg) and the desired acceptor

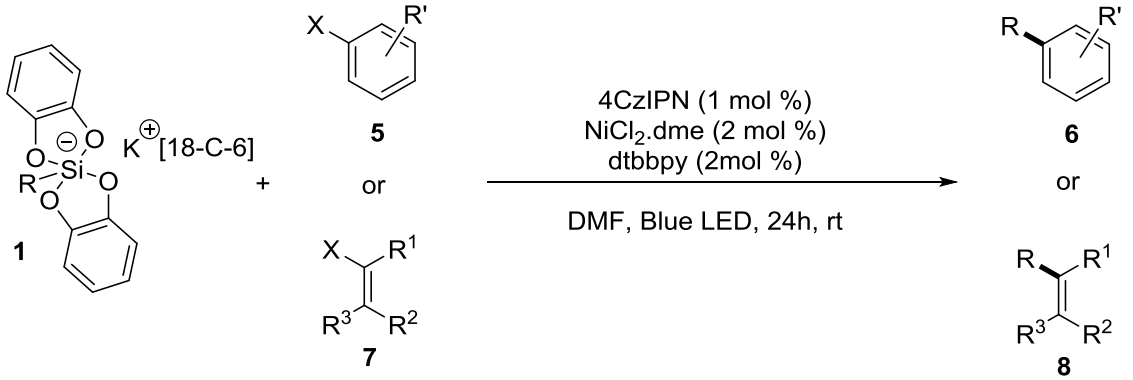
3 (4 eq., 1.2 mmol) (liquid alkenes were added with the solvent). Degassed DMF was added (3 mL). The reaction mixture was irradiated with blue LED (477 nm) for 24 hours. The reaction mixture was diluted with diethyl ether (50 mL), washed with saturated aqueous $NaHCO_3$ (2 times), brine (2 times), dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by flash column chromatography to afford the adduct **4**.

7. General procedure D for cyclohexylsilicate 1d addition into activated alkenes



To a schlenk flask was added potassium [18-C-6] bis(catecholato) cyclohexylsilicate **1d** (1 eq., 0.3 mmol, 189.3 mg), KH_2PO_4 (1.2 eq., 0.36 mmol, 49 mg), 4CzIPN (1 mol %, 3 µmol, 2.4 mg) and the desired alkene **3** (4 eq., 1.2 mmol) (liquid alkenes were added with the solvent). Degassed DMF was added (3 mL). The reaction mixture was irradiated with blue LED (477 nm) for 24 hours. The reaction mixture was diluted with diethyl ether (50 mL), washed with saturated aqueous $NaHCO_3$ (2 times), brine (2 times), dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by flash column chromatography to afford the 1,4 adduct **4**.

8. General procedure E for photoredox/nickel cross-coupling dual catalysis with aryl/heteroaryl halide or vinyl bromide



To a schlenk flask was added aryl, heteroaryl halide **5** or alkenyl halide **7** (1 eq., 0.3 mmol), appropriate silicate **1** (1.5 eq., 0.45 mmol), 4CzIPN (1 mol%, 3 µmol, 2.4 mg), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (2 mol %, 6 µmol, 1.6 mg). The schlenk flask was taken into

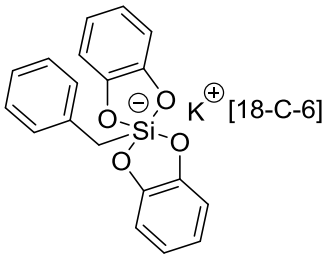
a glovebox and $NiCl_2$.dme (2 mol %, 6 µmol, 1.3 mg) was added. The schlenk flask was sealed with a rubber septum, removed from the glovebox, and evacuated / purged with vacuum / argon three times. Degassed DMF (3 mL) was introduced (followed by the aryl or heteroaryl halide if liquid) and the reaction mixture was irradiated with blue LEDs (477 nm) for 24 hours. The reaction mixture was diluted with diethyl ether (50 mL), washed with saturated $NaHCO_3$ (2 times), brine (2 times), dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the coupling adduct **6** or **8**.

9. Procedure for photoredox/nickel cross-coupling dual-catalysis scale up.

To a 100 mL schlenk flask was added 4'-bromoacetophenone **5a** (1 eq., 3 mmol, 597 mg), acetoxypropylsilicate **1g** (1.5 eq., 4.5 mmol, 2.92 g), 4CzIPN (1 mol%, 30 µmol, 23.7 mg) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (2 mol %, 60 µmol, 16.1 mg). The schlenk flask was taken into a glovebox and $NiCl_2$.dme (2 mol %, 60 µmol, 13.2 mg) was added. The schlenk flask was sealed with a rubber septum, removed from the glovebox, and evacuated / purged with vacuum / argon three times. Degassed DMF (30 mL) was introduced and the reaction mixture was irradiated with blue LEDs (477 nm) for 48 hours. The reaction mixture was diluted with diethyl ether (200 mL) and washed with saturated $NaHCO_3$. The aqueous phase was extracted with diethyl ether and the combined organic phases were washed with saturated $NaHCO_3$ (2 times), brine (2 times), dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the 4'-(acetoxypropyl)acetophenone **6ag** (503 mg, 76%).

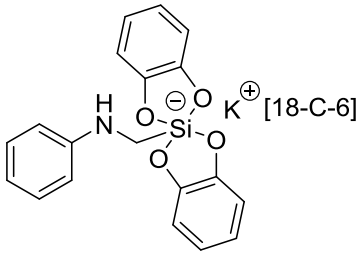
III. Compound characterizations

Potassium [18-Crown-6] bis(catecholato)-benzylsilicate (1a)



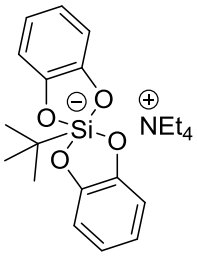
Silicate **1a** was synthesized as described. The spectroscopic data are in agreement with those reported in the literature.[8]

Potassium [18-Crown-6] bis(catecholato)-anilinomethylsilicate (1b)



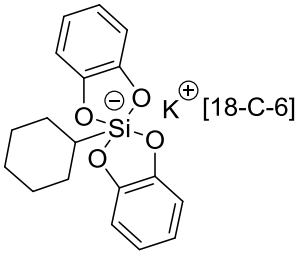
Silicate **1b** was synthesized as described. The spectroscopic data are in agreement with those reported in the literature.[8]

Tetraethylammonium bis(catecholato)-tertbutylsilicate (1c)



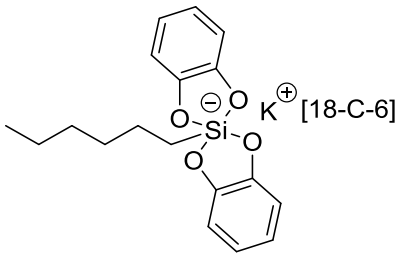
Silicate **1c** was synthesized as described. The spectroscopic data are in agreement with those reported in the literature.[8]

Potassium [18-Crown-6] bis(catecholato)-cyclohexylsilicate (1d)



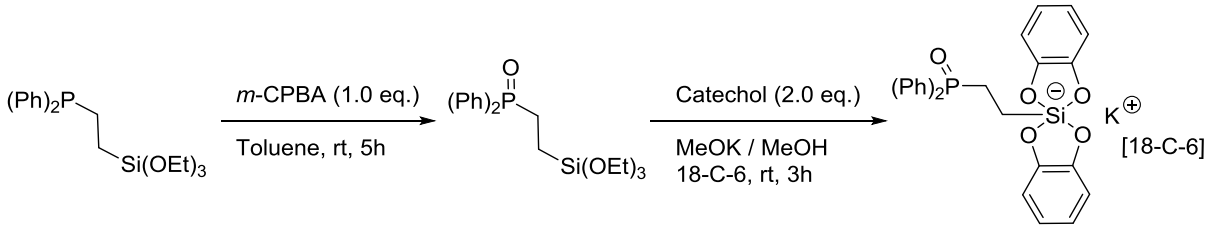
Silicate **1d** was synthesized as described. The spectroscopic data are in agreement with those reported in the literature.[8]

Potassium [18-Crown-6] bis(catecholato)-hexylsilicate (1e)



Silicate **1e** was synthesized as described. The spectroscopic data are in agreement with those reported in the literature.[8]

Potassium [18-Crown-6] bis(catecholato)-2-(diphenylphosphine oxide)ethylsilicate (1f)



a) Oxidation of diphenyl(2-(triethoxysilyl)ethyl)phosphine

The oxidation step has been realized according to a previous reported procedure.[10] To a stirred solution of diphenyl(2-(triethoxysilyl)ethyl)phosphine (6 mmol, 2.15 mL) in 50 mL of toluene was added, at 0°C, a solution of *m*-chloroperbenzoic acid (6 mmol, 1.04 g) in 15 mL of toluene. After complete addition, the reaction mixture was warmed to room temperature and stirred for 5h. The reaction mixture was quenched with 50 mL of aqueous saturated Na_2CO_3 solution. The organic phase was then washed with 50 mL of saturated Na_2CO_3 solution (2 times), 50 mL of brine and dried over $MgSO_4$. Toluene was removed under reduced pressure to give a white waxy solid. The crude material was dissolved in the minimum volume of DCM and crystallized by slow addition of pentane. The Diphenyl(2-(triethoxysilyl)ethyl)phosphine oxide was collected by filtration and washed with pentane (1.28 g, 54%).

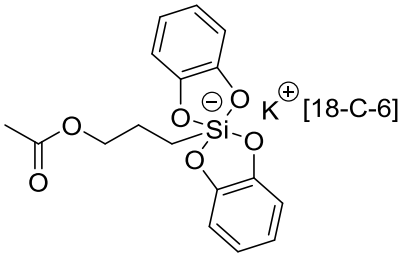
^{1}H NMR (400 MHz, Acetone-d6): δ 7.86 – 7.81 (m, 4H), 7.58 – 7.49 (m, 6H), 3.80 (q, *J* = 6.9 Hz, 6H), 2.34 – 2.27 (m, 2H), 1.17 (t, *J* = 6.9 Hz, 9H), 0.78 – 0.71 (m, 2H). **^{13}C NMR** (150 MHz, Acetone-d6): δ 135.37 (d, *J* = 95.1 Hz, 2 C), 132.4 (d, *J* = 2.5 Hz, 2 C), 131.8 (d, *J* = 9.1 Hz, 4 C), 129.6 (d, *J* = 11.1 Hz, 4 C), 59.2, 23.7 (d, *J* = 71.0 Hz), 18.9 (3 C), 2.13 (d, *J* = 6.4 Hz). **^{31}P NMR** (162 MHz, Acetone-d6): δ 29.92. **^{29}Si NMR** (119 MHz, Acetone-d6): δ -47.22 (d, *J* = 29.8 Hz). HRMS calc. for $[C_{20}H_{29}NaO_4PSi]^+$ 415.1465; found 415.1461. **M.p.** 72°C. **IR** (neat): 3053, 2973, 2924, 1482, 1167, 1064, 758, 748, 729, 692 cm-1.

b) Silicate synthesis

Following the general procedure A, with 2-(diphenylphosphine oxide)ethylsilane (2.5 mmol, 981 mg), catechol (5 mmol, 550.6 mg), 18-Crown-6 (2.5 mmol, 660 mg) and potassium methoxide (2.5 mmol, 700 μL of a 3.56 M solution in methanol) in 10 mL of dry methanol at room temperature. The crude product was purified according the general procedure to afford **1e** (1.41 g, 72%) as a white solid.

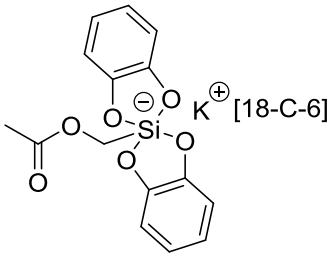
^{1}H NMR (400 MHz, Methanol-d4): δ 7.57 – 7.47 (m, 6H), 7.42 – 7.39 (m, 4H), 6.71 – 6.70 (m, 4H), 6.60 – 6.59 (m, 4H), 3.52 (s, 24H), 2.38 – 2.33 (m, 2H), 0.83 – 0.79 (m, 2H). **^{13}C NMR** (100 MHz, Methanol-d4): δ 150.8 (4 C), 133.3 (d, *J* = 97.5 Hz, 2 C), 133.0 (d, *J* = 2.6 Hz, 2 C), 131.8 (d, *J* = 9.3 Hz, 4 C), 129.8 (d, *J* = 11.6 Hz, 4 C), 119.6 (4 C), 111.7 (4 C), 71.2 (12 C), 25.1 (d, *J* = 70.4 Hz), 8.2 (d, *J* = 7.3 Hz, 2 C). **^{31}P NMR** (162 MHz, Methanol-d4): δ 40.12. **^{29}Si NMR** (119 MHz, Methanol-d4): δ -78.10 (d, *J* = 34.8 Hz). **HRMS** calc. for $[C_{26}H_{22}O_5PSi]^-$ 473.0980; found 473.0964. **M.p.** 229°C. **IR** (neat): 2990, 2895, 1482, 1238, 1103, 826, 734, 723 cm-1.

Potassium [18-Crown-6] bis(catecholato)-acetoxypropylsilicate (1g)



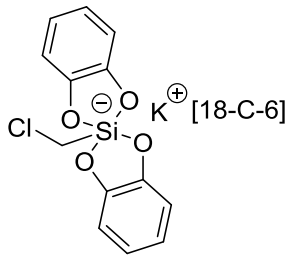
Silicate **1g** was synthesized as described. The spectroscopic data are in agreement with those reported in the literature.[9]

Potassium [18-Crown-6] bis(catecholato)-acetoxymethylsilicate (1h)



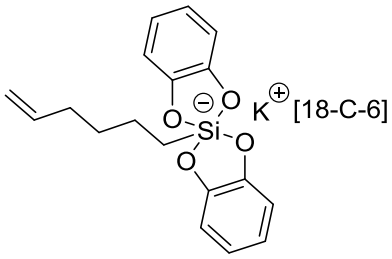
Silicate **1h** was synthesized as described. The spectroscopic data are in agreement with those reported in the literature.[9]

Potassium [18-Crown-6] bis(catecholato)-chloromethylsilicate (1i)



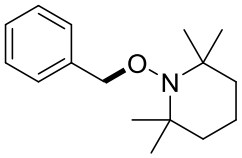
Silicate **1i** was synthesized as described. The spectroscopic data are in agreement with those reported in the literature.[8]

Potassium [18-Crown-6] bis(catecholato)-hex-5-enylsilicate (1j)



Silicate **1j** was synthesized as described. The spectroscopic data are in agreement with those reported in the literature.[8]

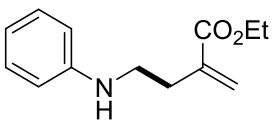
1-(Benzyloxy)-2,2,6,6-tetramethylpiperidine (2a)



Following procedure of spin-trapping experiments with **1a** (0.3 mmol, 192 mg). The crude product was purified by flash column chromatography (pentane/Et_2O, 99/1) to afford **2a** as a colorless oil. The spectroscopic data are in agreement with those reported in the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.26 (m, 5H), 4.85 (s, 2H), 1.58 – 1.50 (m, 5H), 1.38 – 1.35 (m, 1H), 1.28 (s, 6H), 1.21 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 138.6, 128.4 (2 C), 127.7 (2 C), 127.5, 79.0, 60.2 (2 C), 40.0 (2 C), 33.4 (2 C), 20.6 (2 C), 17.4.

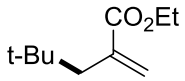
Ethyl 2-methylene-4-(phenylamino)butanoate (4ab)



Following general procedure B with **1b** (0.3 mmol, 196.2 mg). The crude product was purified by flash column chromatography (pentane/ethyl acetate, 95/5) to afford **4ab** as a colorless oil (62 mg, 93%). The spectroscopic data are in agreement with those reported in the literature.[8]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22 – 7.16 (m, 2H), 7.74 – 7.69 (m, 2H), 6.65 – 6.62 (m, 2H), 6.27 (d, *J* = 1.4 Hz, 1H), 6.54 (d, *J* = 1.3 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.68 (bs, 1H), 3.31 (d, *J* = 6.8 Hz, 2H), 2.64 (td, *J* = 6.8, 1.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 167.1, 148.0, 138.4, 129.3 (2 C), 126.7, 117.4, 112.9 (2 C), 61.0, 43.0, 32.1, 14.3.

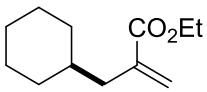
Ethyl 4,4-dimethyl-2-methylenepentanoate (4ac)



Following general procedure B with **1c** (0.3 mmol, 129.5 mg). The crude product was purified by flash column chromatography (pentane/ethyl acetate, 95/5) to afford **4ac** as a colorless oil (48 mg, 94%). The spectroscopic data are in agreement with those reported in the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.17 (d, *J* = 1.4 Hz, 1H), 5.44 – 5.44 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.28 (d, *J* = 0.8 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.88 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 168.2, 139.1, 126.8, 60.6, 53.4, 44.5, 31.5, 29.2 (3 C), 14.2.

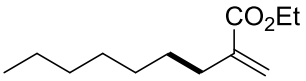
Ethyl 2-(cyclohexylmethyl)acrylate (4ad)



Following general procedure B with **1d** (0.3 mmol, 189.3 mg). The crude product was purified by flash column chromatography (pentane/diethyl ether, 95/5) to afford **4ad** as a colorless oil (52 mg, 88%). The spectroscopic data are in agreement with those reported in the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.13 (d, *J* = 1.8 Hz, 1H), 5.45 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.18 (dd, *J* = 7.1, 1.1 Hz, 2H), 1.72 – 1.61 (m, 5H), 1.46 – 1.41 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.23 – 1.08 (m, 3H), 0.92 – 0.85 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.7, 139.8, 125.6, 125.5, 60.6, 40.1, 36.8, 33.4, 33.2, 26.7, 26.4, 14.3.

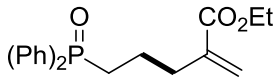
Ethyl 2-methylenenonanoate (4ae)



Following general procedure B with **1e** (0.3 mmol, 184.7 mg). The crude product was purified by flash column chromatography (pentane/diethyl ether, 95/5) to afford **4ae** as a colorless oil (34 mg, 57%). The spectroscopic data are in agreement with those reported in the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.11 (d, *J* = 1.5 Hz, 1H), 5.50 (q, *J* = 1.5 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.31 – 2.27 (m, 2H), 1.47 – 1.42 (m, 2H), 1.32 – 1.25 (m, 12H), 0.87 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.7, 141.3, 124.2, 60.7, 32.0, 32.0, 29.3, 29.2, 28.6, 22.8, 14.4, 14.2.

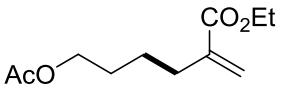
Ethyl 5-(diphenylphosphoryl)-2-methylenepentanoate (4af)



Following general procedure B with **1f** (0.3 mmol, 233.1 mg). The crude product was purified by flash column chromatography (pentane/ethyl acetate, 80/20) to afford **4af** as a colorless oil (48 mg, 46%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 – 7.69 (m, 4H), 7.52 – 7.42 (m, 6H), 6.14 (d, *J* = 1.3 Hz, 1H), 5.49 (d, *J* = 1.3 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.42 – 2.38 (m, 2H), 2.29 – 2.22 (m, 2H), 1.84 – 1.80 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.0, 139.7, 133.1 (d, *J* = 98.2 Hz, 2 C), 131.8 (d, *J* = 2.7 Hz, 2 C), 130.9 (d, *J* = 9.2 Hz, 4 C), 128.7 (d, *J* = 11.6 Hz, 4 C), 125.6, 60.8, 32.9 (d, *J* = 15.3 Hz), 29.2 (d, *J* = 72.2 Hz), 20.5 (d, *J* = 3.4 Hz), 14.3. **^{31}P NMR** (162 MHz, $CDCl_3$): δ 32.2. **IR** (neat): 3120, 2944, 1903, 1710, 1629, 1437, 1176, 1105, 717, 694 cm^{-1}. **HRMS** calc. for $[C_{20}H_{23}NaO_3P]^+$ 365.1277; found 365.1268, for $[(C_{20}H_{23}O_3P)_2Na]^+$ 707.2662; found 707.2366 .

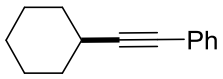
Ethyl 5-(diphenylphosphoryl)-2-methylenepentanoate (4ag)



Following general procedure B with **1g** (0.3 mmol, 194.6 mg). The crude product was purified by flash column chromatography (pentane/diethyl ether, 90/10) to afford **4ag** as a colorless oil (24 mg, 37%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.15 (d, *J* = 1.5 Hz, 1H), 5.52 (d, *J* = 1.4 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 4.07 (t, *J* = 6.5 Hz, 2H), 2.35 – 2.31 (m, 2H), 2.04 (s, 3H), 1.69 – 1.62 (m, 2H), 1.58 – 1.50 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.3, 167.3, 140.6, 124.8, 64.4, 60.8, 31.6, 28.3, 25.0, 21.1, 14.4. **IR** (neat): 2995, 2949, 1741, 1710, 1630, 1368, 1234, 1187, 1146, 1028, 944, 813 cm^{-1}. **HRMS** calc. for $[C_{11}H_{18}NaO_4]^+$ 237.1097; found 237.1097.

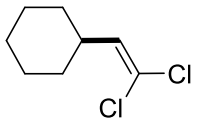
(Cyclohexylethynyl)benzene (4bd)



Following general procedure C with 1-phenyl-2-p-toluenesulfonylethyne **3b** (1.2 mmol, 307.6 mg). The crude product was purified by flash column chromatography (pentane) to afford **4bd** as a colorless oil (44 mg, 78%). The spectroscopic data are in agreement with those reported in the literature.[8]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42 – 7.39 (m, 2H), 7.31 – 7.24 (m, 3H), 2.64 – 2.55 (m, 1H), 1.92 – 1.85 (m, 2H), 1.79 – 1.74 (m, 2H), 1.58 – 1.52 (m, 3H), 1.40 – 1.33 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 131.7 (2 C), 128.3 (2 C), 127.5, 124.3, 94.6, 80.7, 32.9, 29.8, 26.1 (2 C), 25.1 (2 C).

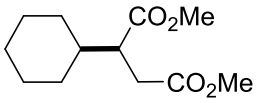
(2,2-Dichlorovinyl)cyclohexane (4cd)



Following general procedure C with trichloroethylene **3c** (1.2 mmol, 108 μL). The crude product was purified by flash column chromatography (pentane) to afford **4cd** as a colorless oil (39 mg, 70%). The spectroscopic data are in agreement with those reported in the literature.[8]

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.70 (d, *J* = 9.2 Hz, 1H), 2.43 – 2.32 (m, 1H), 1.77 – 1.62 (m, 5H), 1.37 – 1.04 (m, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 135.2, 118.7, 39.3, 31.8 (2 C), 25.9, 25.7 (2 C).

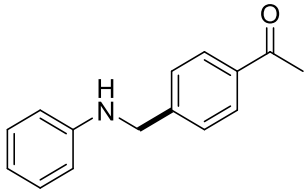
Dimethyl 2-cyclohexylsuccinate (4dd)



Following general procedure D with dimethyl maleate **3d** (1.2 mmol, 150 μL). The crude product was purified by flash column chromatography (pentane/ethyl acetate, 95/5) to afford **4dd** as a colorless oil (84 mg, 78%). The spectroscopic data are in agreement with those reported in the literature.[8]

^{1}H NMR (300 MHz, $CDCl_3$): δ 3.67 (s, 3 H), 3.64 (s, 3 H), 2.76 – 2.65 (m, 2 H), 2.48 – 2.38 (m, 1 H), 1.74 – 1.85 (m, 6 H), 1.29 – 0.97 (m, 5 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 175.0, 173.0, 51.80, 51.6, 47.1, 40.03, 33.3, 30.7, 30.2, 29.8, 26.4, 26.2.

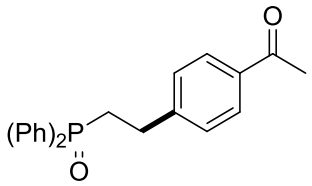
4'-(Anilinomethyl)acetophenone (6ab)



Following general procedure E with anilinomethylsilicate **1b** (0.45 mmol, 294 mg) and 4'-bromoacetophenone **5a** (0.3 mmol, 60 mg). The crude product was purified by flash column chromatography (pentane/diethyl ether, 80/20) to afford **6ab** as a colorless oil (53 mg, 78 %). The spectroscopic data are in agreement with those reported in the literature.[9]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.21 – 7.15 (m, 2H), 6.76 – 6.72 (m, 1H), 6.63 – 6.60 (m, 2H), 4.42 (s, 2H), 4.19 (s, 1H), 2.60 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.8, 147.8, 145.4, 136.3, 129.4 (2 C), 128.8 (2 C), 127.4 (2 C), 117.9, 113.0 (2 C), 48.0, 26.7.

1-(3-(2-(Diphenylphosphoryl)ethyl)phenyl)ethan-1-one (6af)

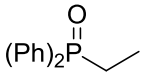


Following general procedure F with 2-(diphenylphosphine oxide)ethylsilicate **1f** (0.45 mmol, 350 mg) and 4'-bromoacetophenone **5a** (0.3 mmol, 60 mg). The crude product was purified by flash column chromatography (dichloromethane/ethyl acetate, 60/40 to 40/60)) to

afford **6af** contaminated with 15% of ethyldiphenylphosphine oxide as a white solid (79 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.77 – 7.72 (m, 4H), 7.53 – 7.43 (m, 6H), 7.23 (d, *J* = 8.3 Hz, 2H), 3.06 – 2.87 (m, 2H), 2.60 – 2.54 (m, 2H), 2.53 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.7, 146.8 (d, *J* = 14.6 Hz), 135.5, 132.6 (d, *J* = 98.8 Hz, 2 C), 132.0 (d, *J* = 2.7 Hz, 2 C), 130.8 (d, *J* = 9.2 Hz, 4 C), 128.8 (d, *J* = 11.2 Hz, 4 C), 128.8 (2 C), 128.4 (2 C), 31.5 (d, *J* = 69.8 Hz), 27.7 (d, *J* = 3.0 Hz), 26.6. **^{31}P NMR** (162 MHz, $CDCl_3$): 31.11. **IR** (neat): 3015, 2895, 2257, 1904, 1674, 1601, 1437, 1264, 1174, 1111, 747, 725 cm^{-1}. **HRMS** calc. for $[C_{22}H_{21}NaO_2P]^+$ 371.1171; found 371.1159.

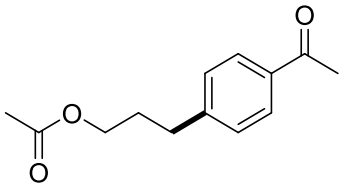
Ethyldiphenylphosphine oxide



Ethyldiphenylphosphine oxide has been obtained as a contaminant of **6af**. The spectroscopic data are in agreement with those reported in the literature.[11]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 – 7.69 (m, 4H), 7.51 – 7.41 (m, 6H), 2.30 – 2.21 (m, 2H), 1.21 – 1.13 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 132.9 (d, *J* = 97.8 Hz, 2 C), 131.7 (d, *J* = 2.7 Hz, 2 C), 130.9 (d, *J* = 9.0 Hz, 4 C), 128.7 (d, *J* = 11.6 Hz, 4 C), 22.7 (d, *J* = 72.9 Hz), 5.7 (d, *J* = 5.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$): 34.09. **HRMS** calc. for $[C_{14}H_{15}NaOP]^+$ 253.0753; found 253.0755.

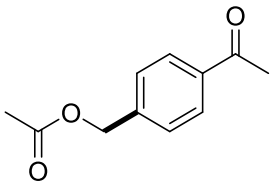
4'-(Acetoxypropyl)acetophenone (6ag)



Following general procedure E with acetoxypropylsilicate **1ge** (0.45 mmol, 292 mg) and 4'-bromoacetophenone **5a** (0.3 mmol, 60 mg). The crude product was purified by flash column chromatography (pentane/diethyl ether, 80/20) to afford **6ag** as a colorless oil (55 mg, 83%). The spectroscopic data are in agreement with those reported in the literature.[9]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 4.08 (t, *J* = 6.5 Hz, 2H), 2.76 – 2.72 (m, 2H), 2.57 (s, 3H), 2.04 (s, 3H), 2.00 – 1.93 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.9, 171.2, 147.1, 135.4, 128.8, 128.7, 63.7, 32.4, 30.0, 26.7, 21.1.

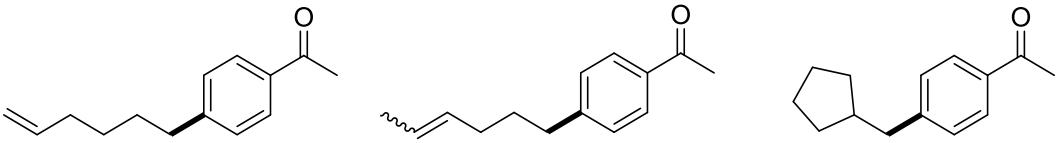
4'-(Acetoxymethyl)acetophenone (6ah)



Following general procedure F with acetoxymethylsilicate **1h** (0.45 mmol, 279 mg) and 4'-bromoacetophenone **5a** (0.3 mmol, 60 mg). The crude product was purified by flash column chromatography (pentane/diethyl ether, 90/10) to afford **6ah** as a colorless oil (51 mg, 88%). The spectroscopic data are in agreement with those reported in the literature.[9]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 5.15 (s, 2H), 2.60 (s, 3H), 2.12 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.6, 170.8, 141.3, 137.0, 128.7 (2 C), 128.0 (2 C), 65.6, 26.8, 21.0.

4'-(Acetoxymethyl)acetophenone (6aj), 1-(4-(hex-4-en-1-yl)phenyl)ethan-1-one (6aj') and 1-(4-(cyclopentylmethyl)phenyl)ethan-1-one (6aj'')



6aj **6aj'** **6aj''**

Following general procedure F with hex-5-enylsilicate **1j** (0.45 mmol, 279 mg) and 4'-bromoacetophenone **5a** (0.3 mmol, 60 mg). The crude product was purified by flash column chromatography (pentane/diethyl ether, 90/10) to afford a mixture of **6aj**, **6aj'g** and **6aj''** in a ratio of 10:13:77 as a colorless oil (51 mg, 88%). The spectroscopic data are in agreement with those reported in the literature.[9]

Compound 6aj

^{1}H NMR (400 MHz, C_6D_6): δ 7.80 (d, *J* = 8.3 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 5.72 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.03 – 4.96 (m, 2H), 2.15 (s, 3H), 1.98 – 1.83 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.2, 138.8, 114.8.

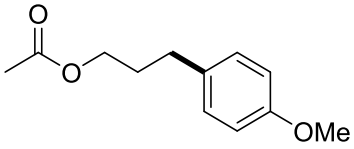
Compound 6aj'

^{1}H NMR (400 MHz, C_6D_6): δ 5.54 – 5.35 (m, 2H), 1.97 – 1.85 (m, 2H), 1.45 – 1.39 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.2, 130.3, 124.6, 12.9.

Compound 6aj''

^{1}H NMR (400 MHz, C_6D_6): δ 7.80 (d, *J* = 8.3 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 2.40 (d, *J* = 7.5 Hz, 2H), 2.16 (s, 3H), 1.94 – 1.83 (m, 1H), 1.61 – 1.38 (m, 5H), 1.08 – 0.99 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 196.2, 147.7, 135.7, 129.1, 128.7, 42.2, 42.0, 32.7, 26.2, 25.2. **HRMS** calc. for $[C_{14}H_{18}NaO_2]^+$ 225.1250; found 225.1247.

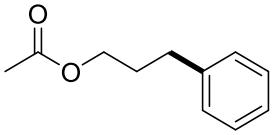
3-(4-Methoxyphenyl)propyl acetate (6bg)



Following general procedure F with acetoxypropylsilicate **1g** (0.45 mmol, 292 mg) and 4-iodoanisole **5b** (0.3 mmol, 70 mg). The crude product was purified by flash column chromatography (pentane/diethyl ether, 90/10) to afford **6bg** as a colorless oil (34 mg, 54%). The spectroscopic data are in agreement with those reported in the literature.[9]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 4.08 (t, *J* = 6.6 Hz, 2H), 3.79 (s, 3H), 2.65 – 2.61 (m, 2H), 2.05 (s, 3H), 1.96 – 1.89 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.3, 158.1, 133.4, 129.4 (2 C), 114.0 (2 C), 64.0, 55.4, 31.4, 30.6, 21.1.

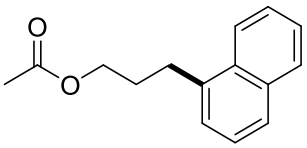
3-Phenylpropyl acetate (6cg)



Following general procedure F with acetoxypropylsilicate **1g** (0.45 mmol, 292 mg) and bromobenzene **5c** (0.3 mmol, 32 µl). The crude product was purified by flash column chromatography (pentane/diethyl ether, 95/5) to afford **6cg** as a colorless oil (41 mg, 76%). The spectroscopic data are in agreement with those reported in the literature.[12]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 – 7.23 (m, 2H), 7.20 – 7.15 (m, 2H), 4.07 (t, *J* = 6.5 Hz, 2H), 2.70 – 2.65 (m, 2H), 2.04 (s, 3H), 2.03 – 1.90 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.2, 141.3, 128.5 (2C), 128.5 (2C), 126.1, 63.9, 32.3, 30.3, 21.1.

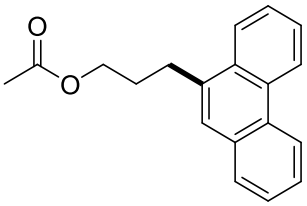
3-(Naphthalen-1-yl)propyl acetate (6dg)



Following general procedure F with acetoxypropylsilicate **1g** (0.45 mmol, 292 mg) and 1-bromonaphthalene **5d** (0.3 mmol, 42 µl). The crude product was purified by flash column chromatography (pentane/diethyl ether, 95/5) to afford **6dg** as a colorless oil (43 mg, 63%). The spectroscopic data are in agreement with those reported in the literature.[13]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.87 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.74 – 7.72 (m, 1H), 7.55 – 7.46 (m, 2H), 7.42 – 7.39 (m, 1H), 7.34 – 7.32 (m, 1H), 4.17 (t, *J* = 6.5 Hz, 2H), 3.18 – 3.15 (m, 2H), 2.14 – 2.07 (m, 2H), 2.09 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.2, 137.2, 133.9, 131.8, 128.8, 126.9, 126.1, 125.9, 125.5, 125.5, 123.6, 64.1, 29.5, 29.3, 21.0. **IR** (neat): 2052, 2953, 1930, 1733, 1592, 1360, 1234, 1040, 738 cm^{-1}. **HRMS** calc. for $[C_{15}H_{16}NaO_2]^+$ 251.1043; found 251.1041.

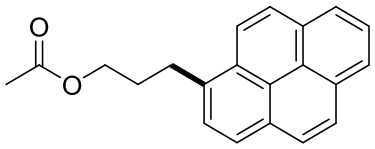
3-(Phenanthren-9-yl)propyl acetate (6eg)



Following general procedure F with acetoxypropylsilicate **1g** (0.45 mmol, 292 mg) and 9-bromophenanthrene **5e** (0.3 mmol, 77 mg). The crude product was purified by flash column chromatography (pentane/diethyl ether, 95/5) to afford **6eg** as a colorless oil (38 mg, 45%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 – 8.74 (m, 1H), 8.68 – 8.65 (m, 1H), 8.11 – 8.07 (m, 1H), 7.85 – 7.82 (m, 1H), 7.70 – 7.56 (m, 5H), 4.23 (t, *J* = 6.5 Hz, 2H), 3.23 – 3.19 (m, 2H), 2.20 – 2.14 (m, 2H), 2.10 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.3, 135.5, 131.9, 131.28, 130.9, 129.9, 128.2, 126.8, 126.8, 126.4, 126.4, 126.3, 124.3, 123.5, 122.6, 64.3, 29.9, 29.1, 21.2.**IR** (neat): 2917, 1957, 1929, 1722, 1245, 1067, 1031, 755, 736 cm^{-1}. **HRMS** calc. for $[C_{19}H_{18}NaO_2]^+$ 301.1199; found 301.1195.

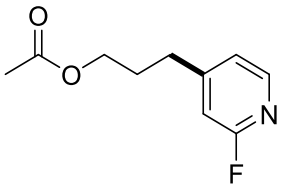
3-(Pyren-1-yl)propyl acetate (6fg)



Following general procedure F with acetoxypropylsilicate **1g** (0.45 mmol, 292 mg) and 9-bromophenanthrene **5f** (0.3 mmol, 84.3 mg). The crude product was purified by flash column chromatography (pentane/diethyl ether, 95/5) to afford **6fg** as a colorless oil (58 mg, 64%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.26 (d, *J* = 9.2 Hz, 1H), 8.18 – 8.16 (m, 2H), 8.12 (d, *J* = 9.2 Hz, 2H), 8.05 – 8.02 (m, 2H), 8.00 (t, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 4.21 (t, *J* = 6.4 Hz, 2H), 3.45 – 3.42 (m, 2H), 2.23 – 2.19 (m, 2H), 2.11 (s, 3H). **^{13}C** NMR (150 MHz, CDCl3) δ 171.3, 135.5, 131.6, 131.0, 130.1, 128.8, 127.6, 127.6, 127.3, 126.9, 126.0, 125.3, 125.1, 125.1, 125.0, 124.9, 123.2, 64.1, 30.6, 29.9, 21.2. **IR** (neat): 3140, 2953, 2895, 1728, 1361, 1238, 1036, 836, 769, 708 cm^{-1}. **HRMS** calc. for $[C_{21}H_{18}NaO_2]^+$ 325.1199; found 325.1209.

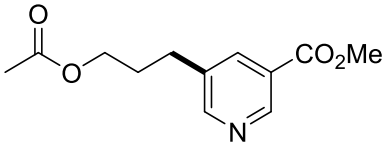
3-(2-Fluoropyridin-4-yl)propyl acetate (6gg)



Following general procedure F with acetoxypropylsilicate **1g** (0.45 mmol, 292 mg) and 4-bromo-2-fluoropyridine **5g** (0.3 mmol, 31 µl). The crude product was purified by flash column chromatography (pentane/EtOAc, 80/20) to afford **6gg** as a colorless oil (43 mg, 73%). The spectroscopic data are in agreement with those reported in the literature.[9]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 5.1 Hz, 1H), 7.01 – 6.99 (m, 1H), 6.75 (m, 1H), 4.09 (t, *J* = 6.4 Hz, 2H), 2.74 – 2.70 (m, 2H), 2.04 (s, 3H), 2.01 – 1.94 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.1, 164.3 (d, *J* = 238.6 Hz), 156.4 (d, *J* = 7.7 Hz), 147.6 (d, *J* = 15.3 Hz), 121.7 (d, *J* = 3.9 Hz), 109.2 (d, *J* = 36.9 Hz), 63.4, 31.6 (d, *J* = 3.0 Hz), 29.0, 21.0. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -68.81.

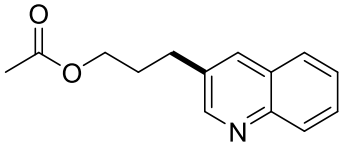
Methyl 5-(3-acetoxypropyl)nicotinate (6hg)



Following general procedure F with acetoxypropylsilicate **1g** (0.45 mmol, 292 mg) and methyl 5-bromonicotinate **5h** (0.3 mmol, 65 mg). The crude product was purified by flash column chromatography (pentane/diethyl ether, 40/60) to afford **6gh** as a colorless oil (39 mg, 54%). The spectroscopic data are in agreement with those reported in the literature.[9]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.05 (d, *J* = 2.0 Hz, 1H), 8.60 (d, *J* = 2.2 Hz, 1H), 8.11 (dd, *J* = 2.2, 2.0 Hz, 1H), 4.09 (t, *J* = 6.4 Hz, 2H), 3.93 (s, 3H), 2.77 – 2.73 (m, 2H), 2.04 (s, 3H), 2.01 – 1.94 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.1, 166.0, 153.7, 148.8, 136.8, 136.5, 125.9, 63.4, 25.5, 29.8, 29.3, 21.0.

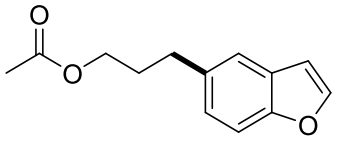
3-(Quinolin-3-yl)propyl acetate (6ig)



Following general procedure F with acetoxypropylsilicate **1g** (0.45 mmol, 292 mg) and 4-bromoquinoline **5i** (0.3 mmol, 41 µl). The crude product was purified by flash column chromatography (pentane/diethyl ether, 90/10) to afford **6ig** as a colorless oil (31 mg, 45%). The spectroscopic data are in agreement with those reported in the literature.[9]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (d, *J* = 2.3 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 1H), 7.92 (d, *J* = 3.2 Hz, 1H), 7.75 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.65 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.51 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 4.14 (t, *J* = 6.4 Hz, 2H), 2.90 – 2.86 (m, 2H), 2.09 – 2.02 (m, 2H), 2.05 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.1, 151.9, 147.1, 134.4, 133.9, 129.3, 128.9, 128.2, 127.4, 126.8, 63.6, 30.0, 29.7, 21.0.

3-(Benzofuran-5-yl)propyl acetate (6jg)

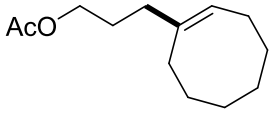


Following general procedure F with acetoxypropylsilicate **1j** (0.45 mmol, 292 mg) and 5-bromobenzofuran **5j** (0.3 mmol, 38 µl). The crude product was purified by flash column

chromatography (pentane/diethyl ether, 90/10) to afford **6jg** as a colorless oil (31 mg, 45%). The spectroscopic data are in agreement with those reported in the literature.[9]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 2.2 Hz, 1H), 7.48 – 7.34 (m, 2H), 7.12 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.71 (dd, *J* = 2.2, 1.0 Hz, 1H), 4.11 (t, *J* = 6.6 Hz, 2H), 2.80 – 2.77 (m, 2H), 2.06 (s, 3H), 2.03 – 1.96 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.3, 153.8, 145.3, 135.8, 127.7, 125.0, 120.6, 111.3, 106.5.

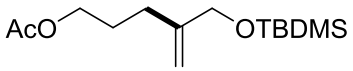
(E)-3-(Cyclooct-1-en-1-yl)propyl acetate (8ag)



Following general procedure F with acetoxypropylsilicate **1g** (0.45 mmol, 292 mg) and (E)-1-bromocyclooct-1-ene **7a** (0.3 mmol, 44 µl). The crude product was purified by flash column chromatography (pentane/diethyl ether, 95/5) to afford **8ag** as a colorless oil (29 mg, 46%). The spectroscopic data are in agreement with those reported in the literature.[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.34 (t, *J* = 8.1 Hz, 1H), 4.05 (t, *J* = 6.7 Hz, 2H), 2.15 – 2.12 (m, 2H), 2.09 – 2.01 (m, 4H), 2.04 (s, 3H), 1.78 – 1.70 (m, 2H), 1.53 – 1.43 (m, 8H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.3, 139.6, 124.5, 64.6, 33.7, 30.1, 29.0, 28.9, 27.1, 26.7, 26.4, 26.4, 21.2.

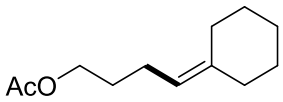
4-(((*tert*-butyldimethylsilyl)oxy)methyl)pent-4-en-1-yl acetate (8bg)



Following general procedure F with acetoxypropylsilicate **1g** (0.45 mmol, 292 mg) and ((2-bromoallyl)oxy)(*tert*-butyl)dimethylsilane **7b** (0.3 mmol, 68 µl). The crude product was purified by flash column chromatography (pentane/diethyl ether, 95/5) to afford **8bg** as a colorless oil (46 mg, 56%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.05 (dt, *J* = 1.6, 0.8 Hz, 1H), 4.83 (t, *J* = 1.5 Hz, 1H), 4.10 – 4.05 (m, 4H), 2.11 – 2.06 (m, 2H), 2.04 (s, 3H), 1.84 – 1.74 (m, 2H), 0.91 (s, 9H), 0.07 (s, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 171.3, 147.6, 109.3, 66.0, 64.3, 29.1, 26.9, 26.1 (3 C), 21.1, 18.5, -5.2 (2 C). **IR** (neat): 2972, 2945, 2885, 2852, 1740, 1653, 1465, 1361, 1237, 1116, 1078, 1039, 839, 773 cm^{-1}. **HRMS** calc. for $[C_{14}H_{28}NaSiO_3]^+$ 295.1700; found 295.1710.

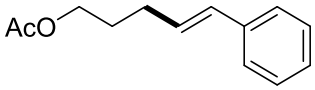
Cyclohexylidenebutyl acetate (8cg)



Following general procedure F with acetoxypropylsilicate **1g** (0.45 mmol, 292 mg) and bromomethylenecyclohexane **7c** (0.3 mmol, 40 µl). The crude product was purified by flash column chromatography (pentane/diethyl ether, 95/5) to afford **8cg** as a colorless oil (32 mg, 55%). The spectroscopic data are in agreement with those reported in the literature.[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.09 – 4.93 (m, 1H), 4.04 (t, *J* = 6.8 Hz, 2H), 2.12 – 2.03 (m, 6H), 2.04 (s, 3H), 1.65 (p, *J* = 6.8 Hz, 2H), 1.56 – 1.45 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.2, 140.8, 119.7, 64.0, 37.2, 28.9, 28.7, 28.6, 27.8, 26.90, 23.3, 21.

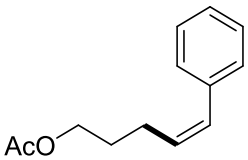
(E)-5-Phenylpent-4-en-1-yl acetate (8dg)



Following general procedure F with acetoxypropylsilicate **1g** (0.45 mmol, 292 mg) and (E)-(2-bromovinyl)benzene **7e** (0.3 mmol, 39 µl). The crude product was purified by flash column chromatography (pentane/diethyl ether, 90/10) to afford **8dg** as a colorless oil (46 mg, 75%). The spectroscopic data are in agreement with those reported in the literature.[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.31 (m, 4H), 7.28 – 7.23 (m, 1H), 6.50 – 6.44 (m, 1H), 6.25 (dt, *J* = 15.8, 6.8 Hz, 1H), 4.18 (t, *J* = 6.6 Hz, 2H), 2.39 – 2.31 (m, 2H), 2.11 (s, 3H), 1.92 – 1.83 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.2, 137.7, 130.8, 129.5, 128.6 (2C), 127.2, 126.1 (2C), 64.1, 29.5, 28.5, 21.1.

(Z)-5-Phenylpent-4-en-1-yl acetate (8d'g)

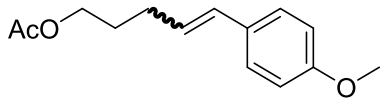


Following general procedure F with acetoxypropylsilicate **1g** (0.45 mmol, 292 mg) and (Z)-(2-bromovinyl)benzene **7d'** (0.3 mmol, 39 µl). The crude product was purified by flash column chromatography (pentane/diethyl ether, 90/10) to afford **8d'g** as a colorless oil (39 mg, 65%). The spectroscopic data are in agreement with those reported in the literature.[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.36 (m, 2H), 7.34 – 7.26 (m, 3H), 6.53 – 6.51 (m, 1H), 5.70 (dt, *J* = 11.5, 7.3 Hz, 1H), 4.13 (t, *J* = 6.6 Hz, 2H), 2.46 (qd, *J* = 7.4, 1.8 Hz, 2H),

2.05 (s, 3H), 1.87 – 1.80 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.2, 137.5, 131.4, 130.0, 128.8 (2 C), 128.3 (2 C), 126.8, 64.0, 28.9, 25.1, 21.0.

(E)-5-Phenylpent-4-en-1-yl acetate (8eg)



Following general procedure F with acetoxypropylsilicate **1g** (0.45 mmol, 292 mg) and (E)-1-(2-chlorovinyl)-4-methoxybenzene **7e** (0.3 mmol, 50.6 mg). The crude product was purified by flash column chromatography (pentane/diethyl ether, 90/10) to afford **8eg** as a colorless oil (46 mg, 65%, Z/E:8/92). The spectroscopic data are in agreement with those reported in the literature.[1]

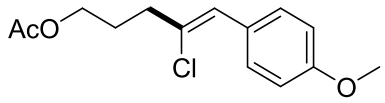
(E) isomer:

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.35 (d, *J* = 15.8 Hz, 1H), 6.05 (dt, *J* = 15.8, 7.1 Hz, 1H), 4.12 (t, *J* = 6.6 Hz, 2H), 3.80 (s, 3H), 2.26 (qd, *J* = 7.1, 1.5 Hz, 1H), 2.05 (s, 3H), 1.82 – 1.78 (m, 2H). **^{13}C NMR** (151 MHz, CDCl3) δ 171.3, 158.9, 130.5, 130.2, 127.2, 127.2 (2 C), 114.0 (2 C), 64.1, 554, 29.5, 28.6, 21.1.

(Z) isomer:

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.21 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.39 (d, *J* = 11.7 Hz, 1H), 5.54 (dt, *J* = 11.6, 7.3 Hz, 1H), 4.08 (t, *J* = 6.6 Hz, 2H), 3.81 (s, 3H), 2.40 (qd, *J* = 7.3, 1.9 Hz, 2H), 2.01 (s, 3H), 1.80 – 1.76 (m, 2H). **^{13}C NMR** (151 MHz, CDCl3) δ 171.2, 158.4, 130.1, 130.0, 129.8, 129.4 (2 C), 113.7 (2 C), 64.0, 55.4, 29.0, 25.1, 21.0.

(E)-5-Phenylpent-4-en-1-yl acetate (8fg)



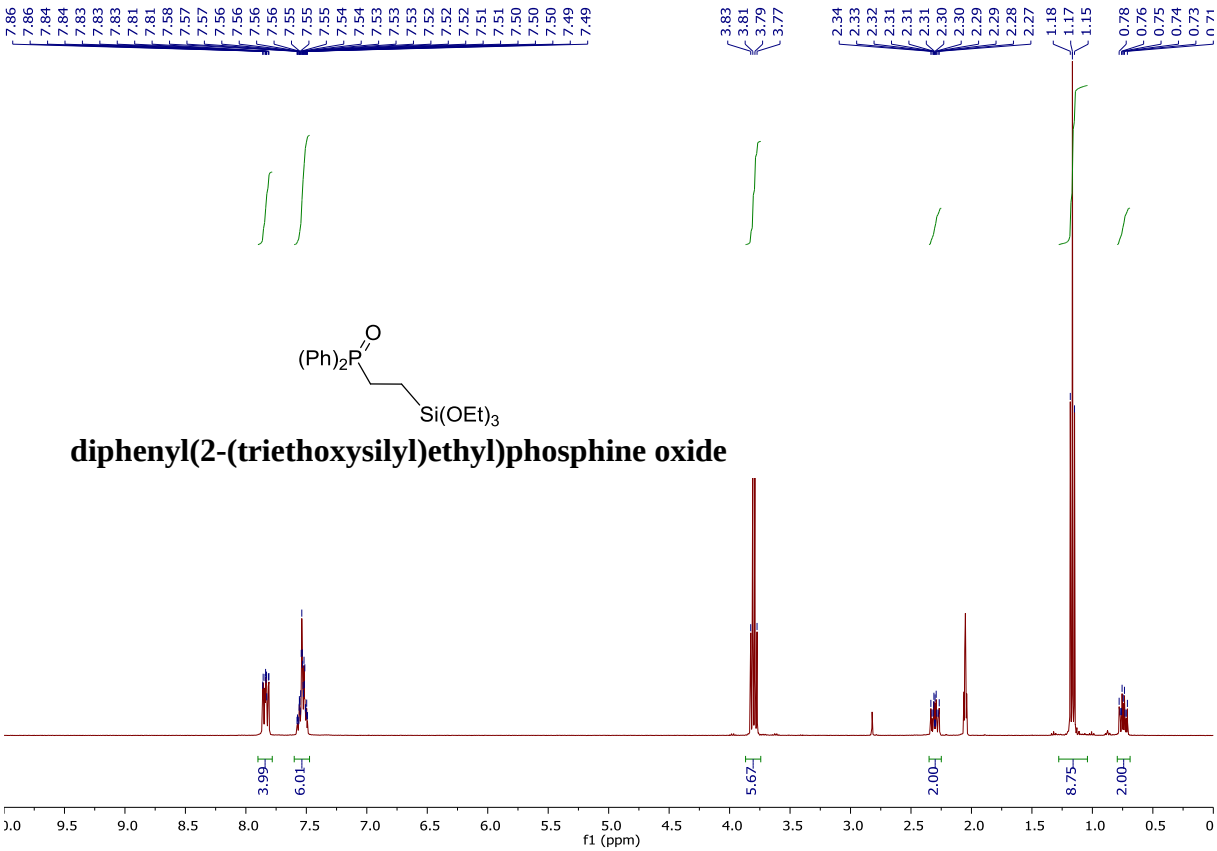
Following general procedure F with acetoxypropylsilicate **1f** (0.45 mmol, 292 mg) and (E)-1-(2-chlorovinyl)-4-methoxybenzene **7g** (0.3 mmol, 61 mg). The crude product was purified by flash column chromatography (pentane/diethyl ether, 90/10) to afford **8fg** as a colorless oil (44 mg, 54%). Geometry of the double bond determined by NOESY experiment.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 6.43 (s, 1H), 4.14 (t, *J* = 6.4 Hz, 2H), 3.82 (s, 3H), 2.55 (td, *J* = 7.3, 0.9 Hz, 2H), 2.06 (s, 3H), 2.04 – 1.98 (m, 2H). **^{13}C NMR** (100 MHz, CDCl3) δ 171.2, 159.1, 131.6, 130.4 (2 C), 127.6, 124.7, 113.7 (2 C), 63.4, 55.4, 37.8, 26.9, 21.1. **IR** (neat): 2948, 2846, 1734, 1605, 1508, 1361,

1240, 1175, 1032, 819, 609 cm^{-1}. **HRMS** calc. for $[C_{14}H_{17}ClNaO_3]^+$ 291.0758; found 291.0763.

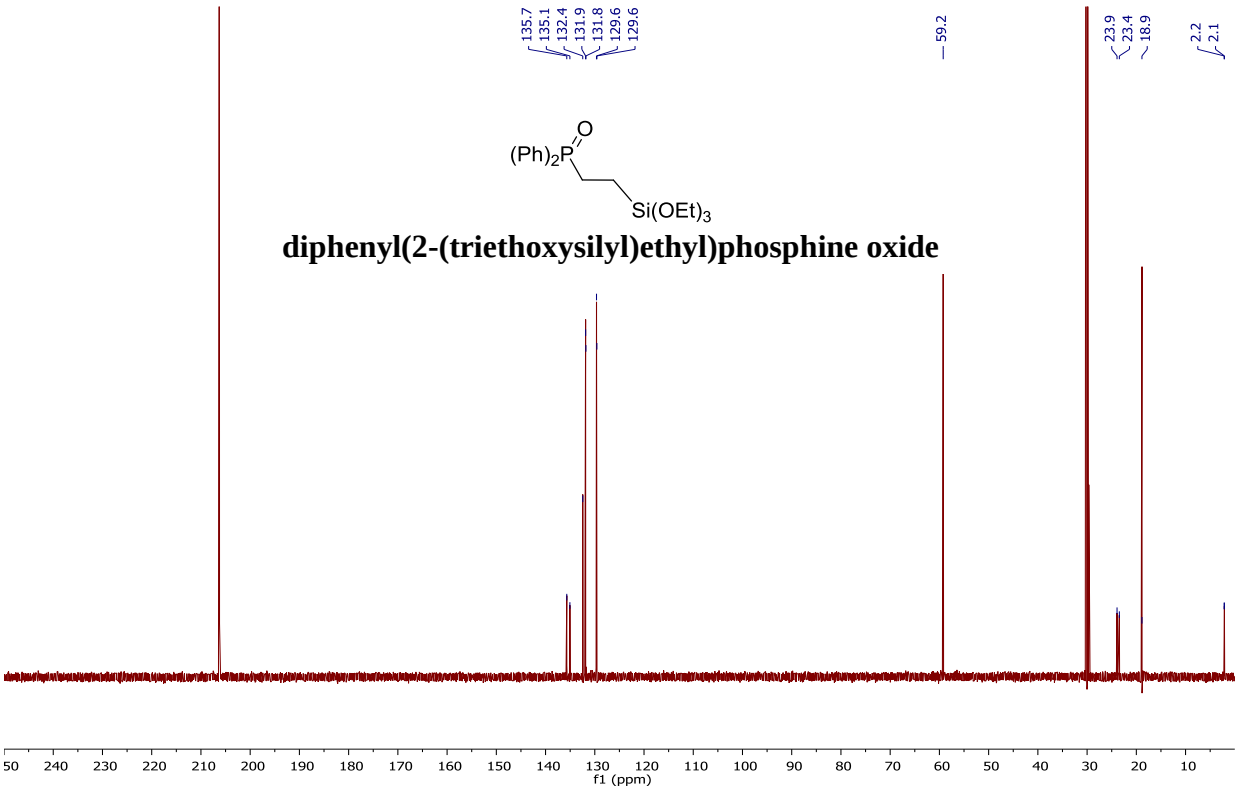
IV. ^{1}H, ^{13}C, ^{19}F, ^{29}Si and ^{31}P NMR spectra

^{1}H spectrum of diphenyl(2-(triethoxysilyl)ethyl)phosphine oxide



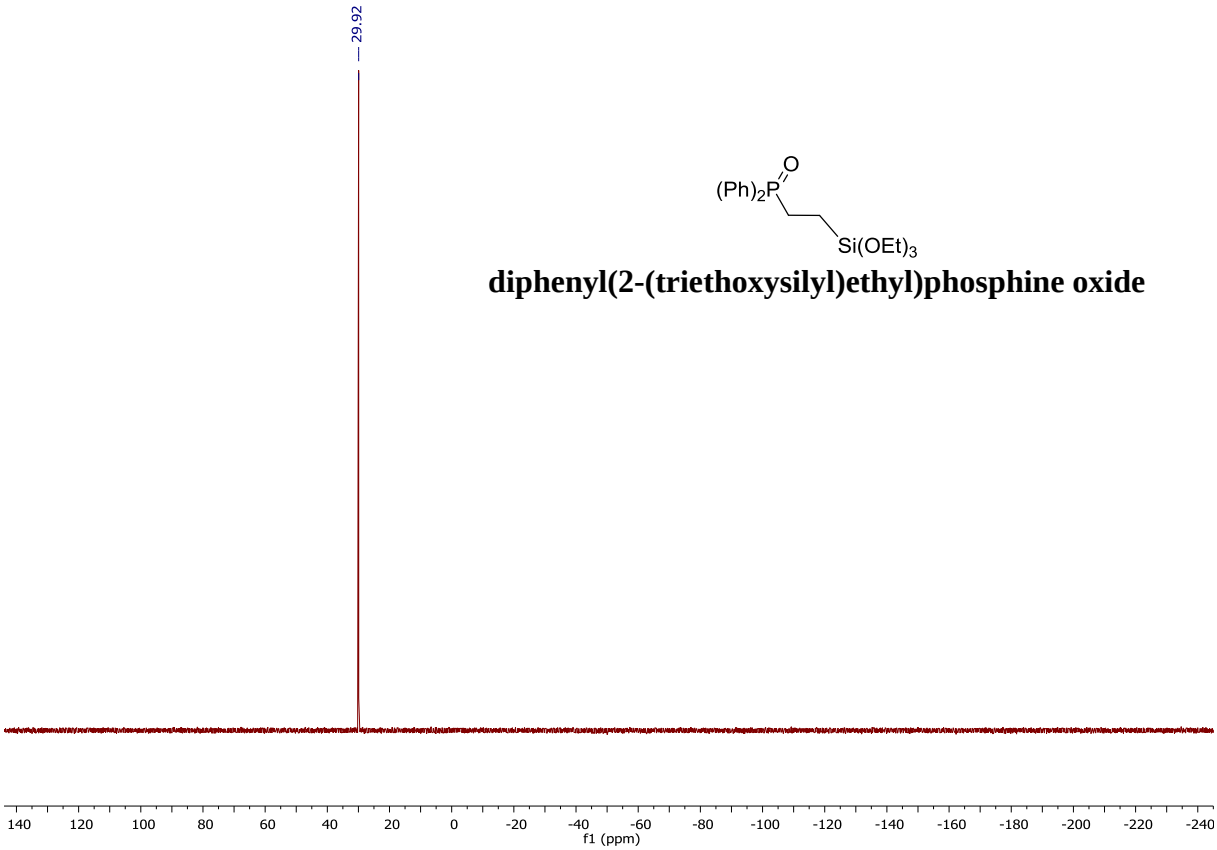
diphenyl(2-(triethoxysilyl)ethyl)phosphine oxide

^{13}C spectrum of diphenyl(2-(triethoxysilyl)ethyl)phosphine oxide



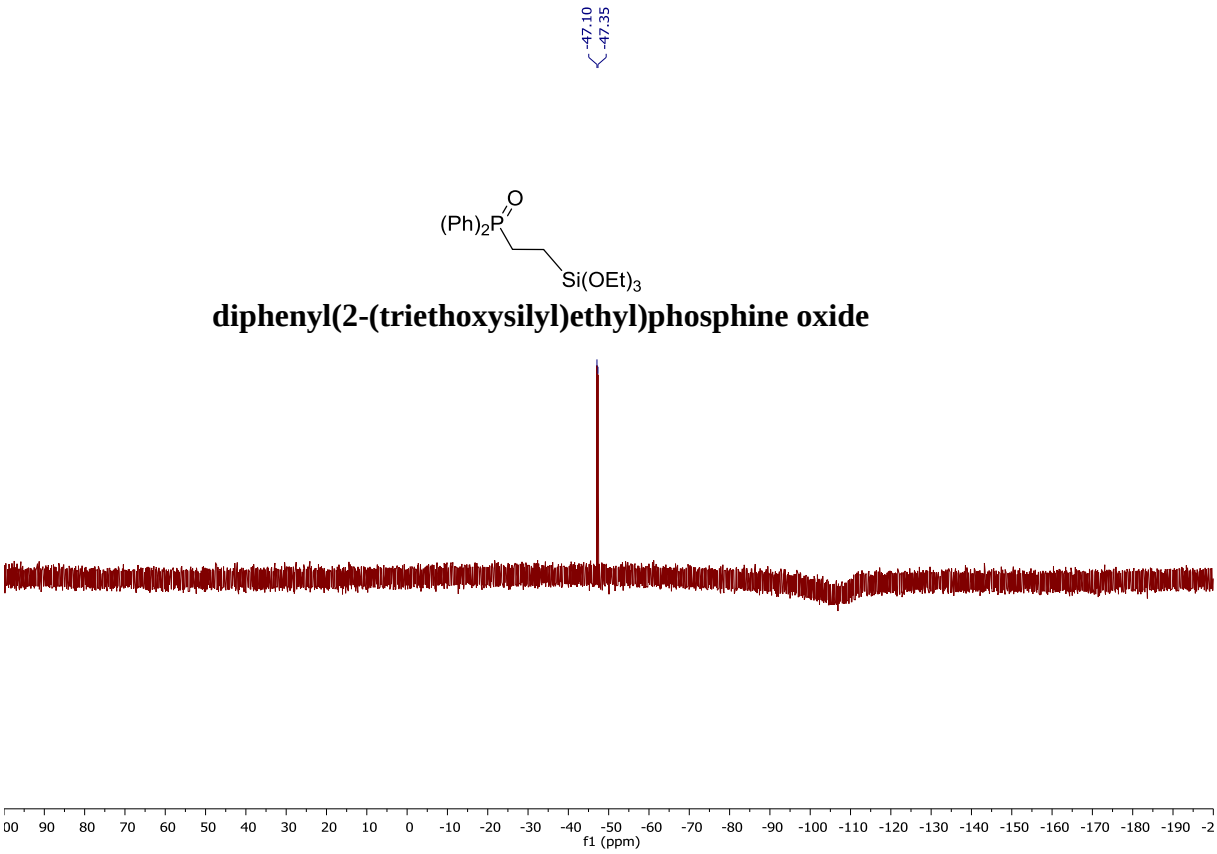
diphenyl(2-(triethoxysilyl)ethyl)phosphine oxide

^{31}P spectrum of diphenyl(2-(triethoxysilyl)ethyl)phosphine oxide



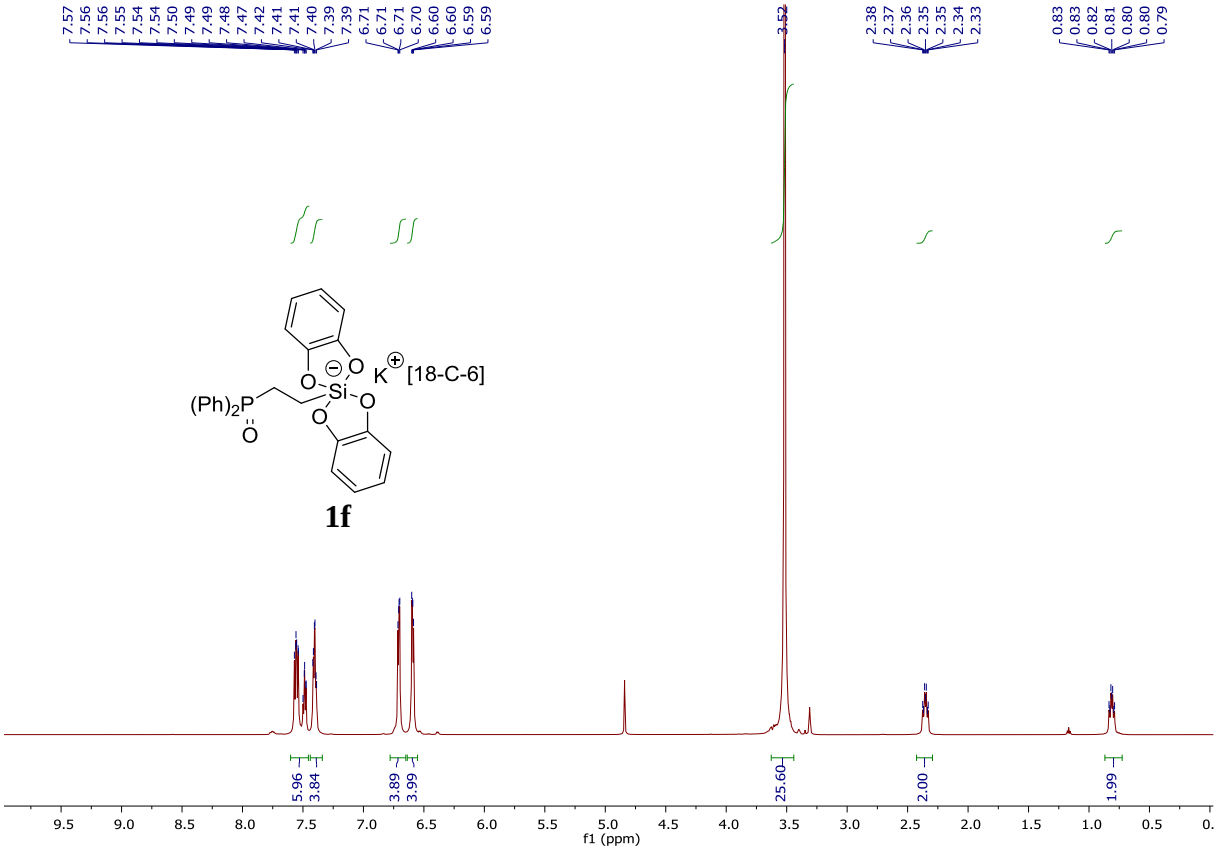
diphenyl(2-(triethoxysilyl)ethyl)phosphine oxide

^{29}Si spectrum of diphenyl(2-(triethoxysilyl)ethyl)phosphine oxide



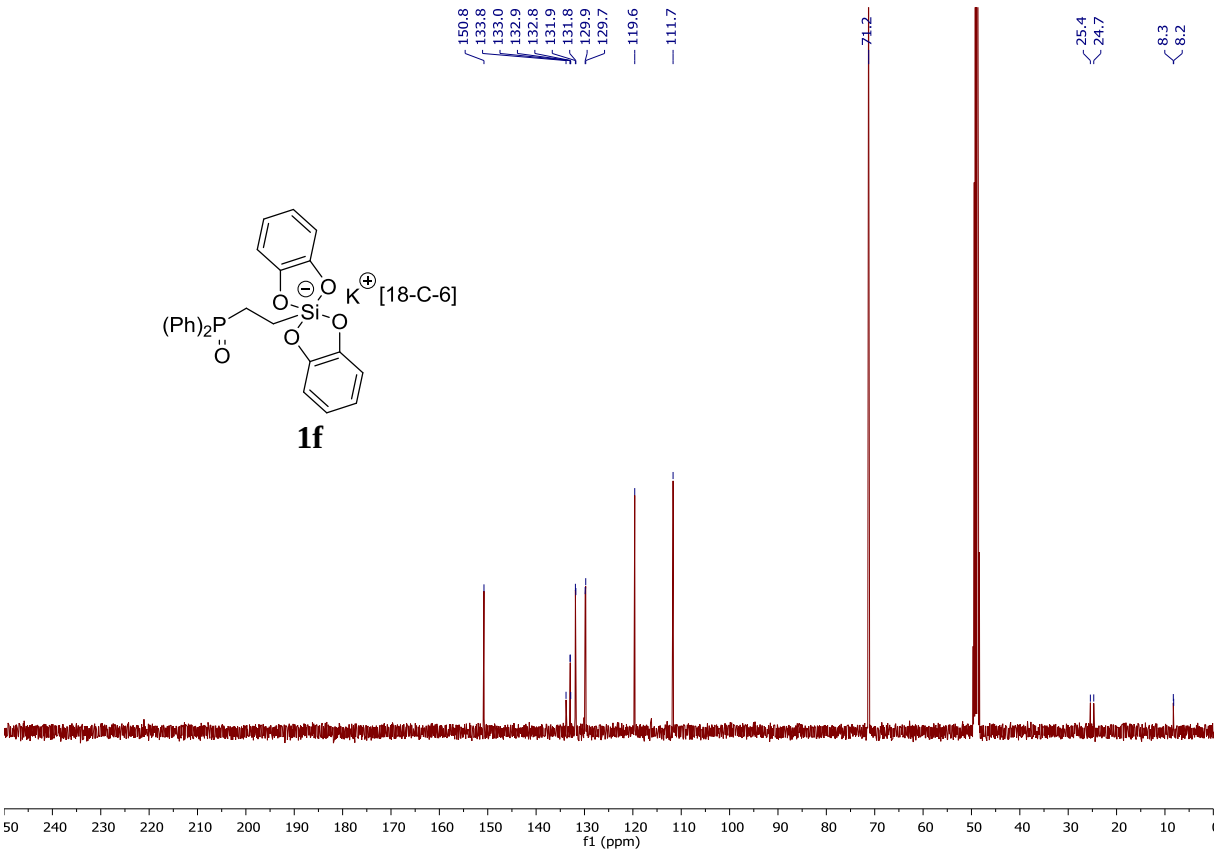
diphenyl(2-(triethoxysilyl)ethyl)phosphine oxide

^{1}H spectrum of 1f



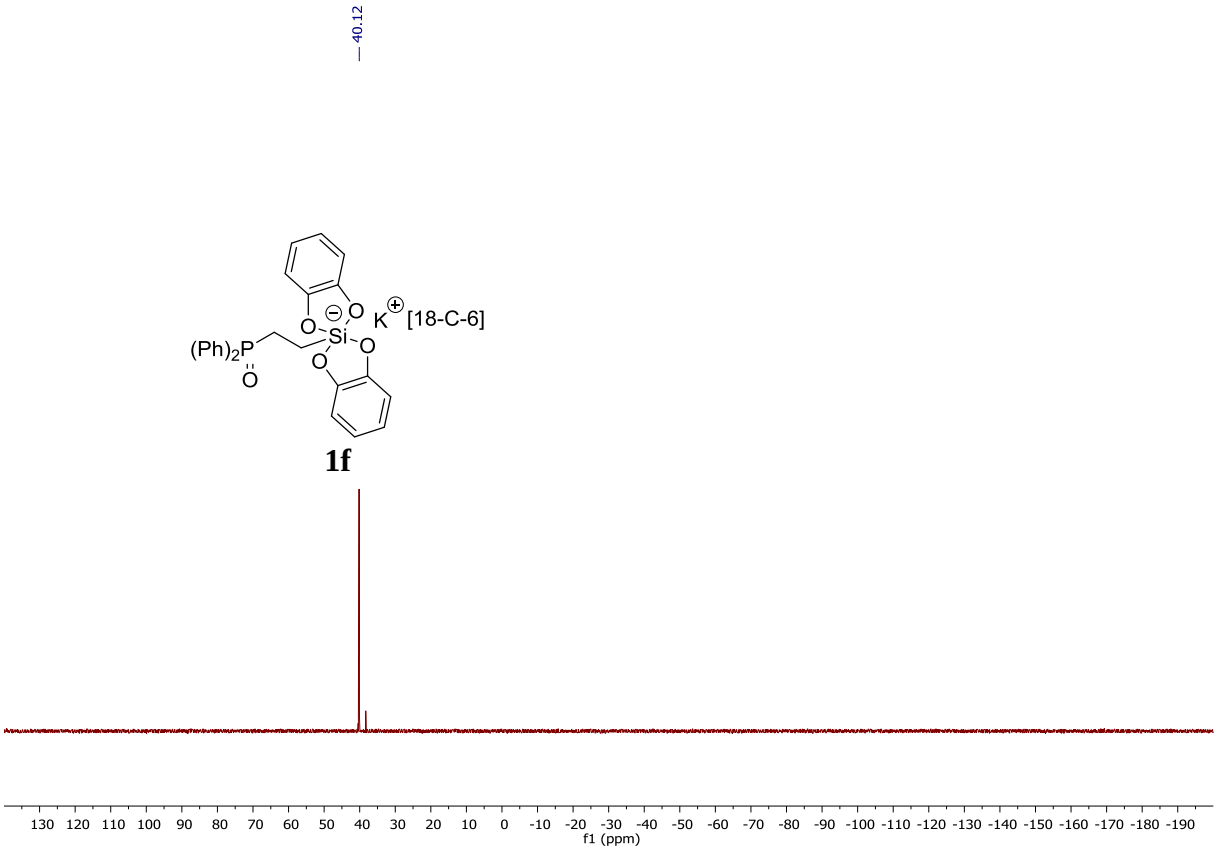
1f

^{13}C spectrum of 1f



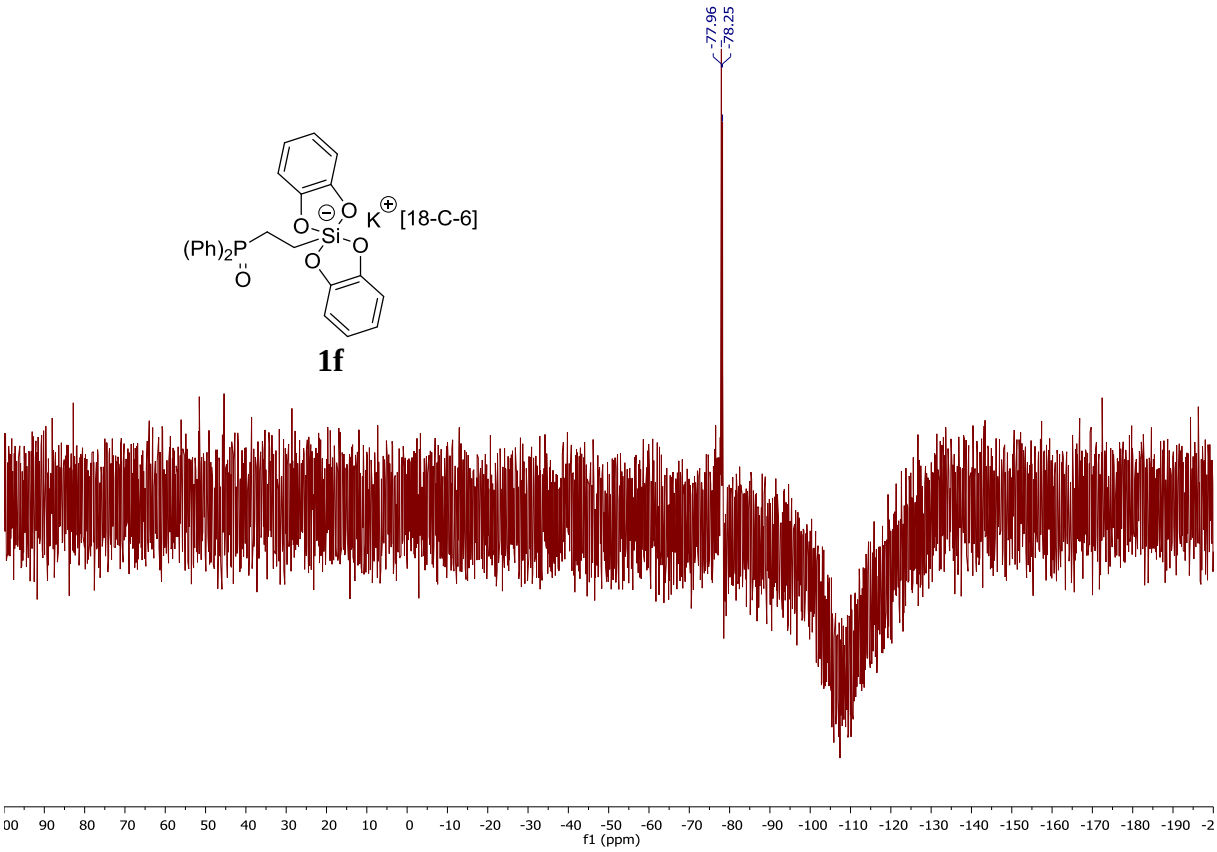
1f

^{31}P spectrum of 1f



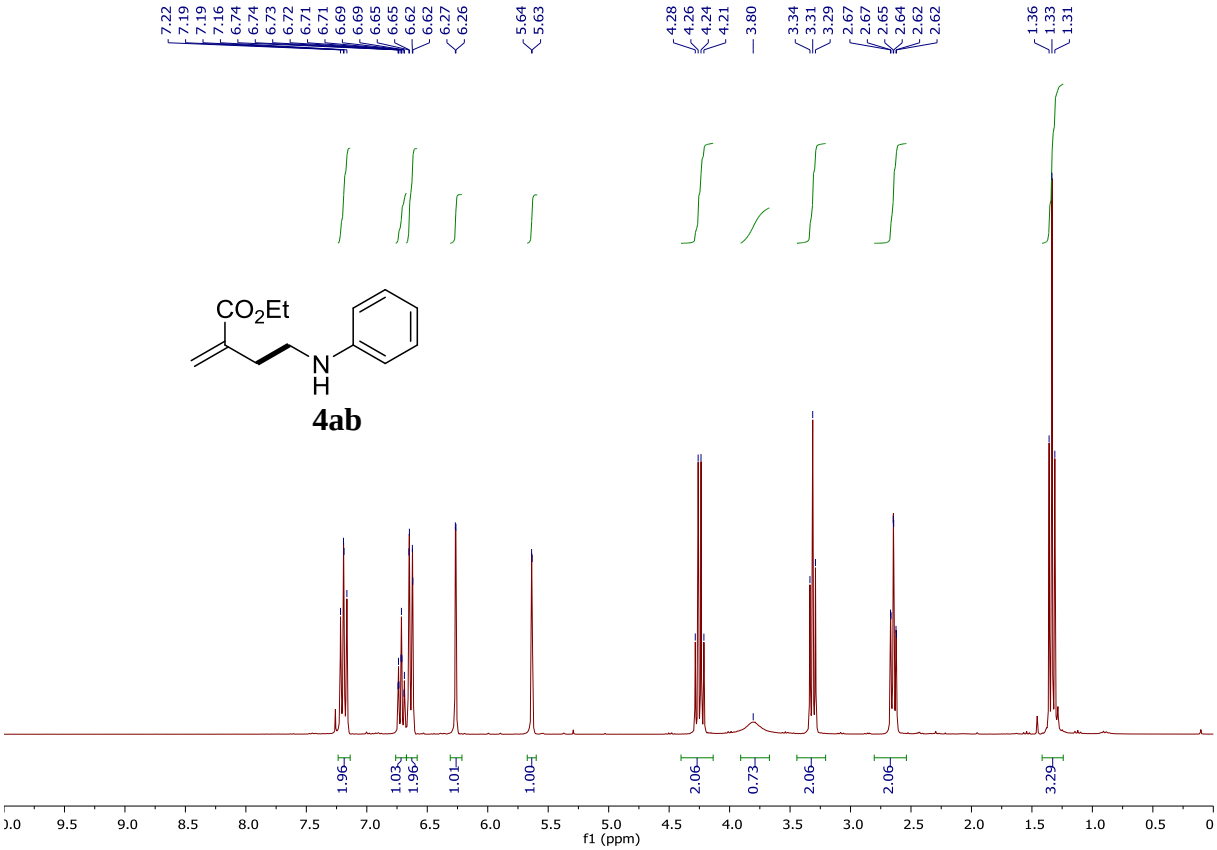
1f

^{29}Si spectrum of 1f

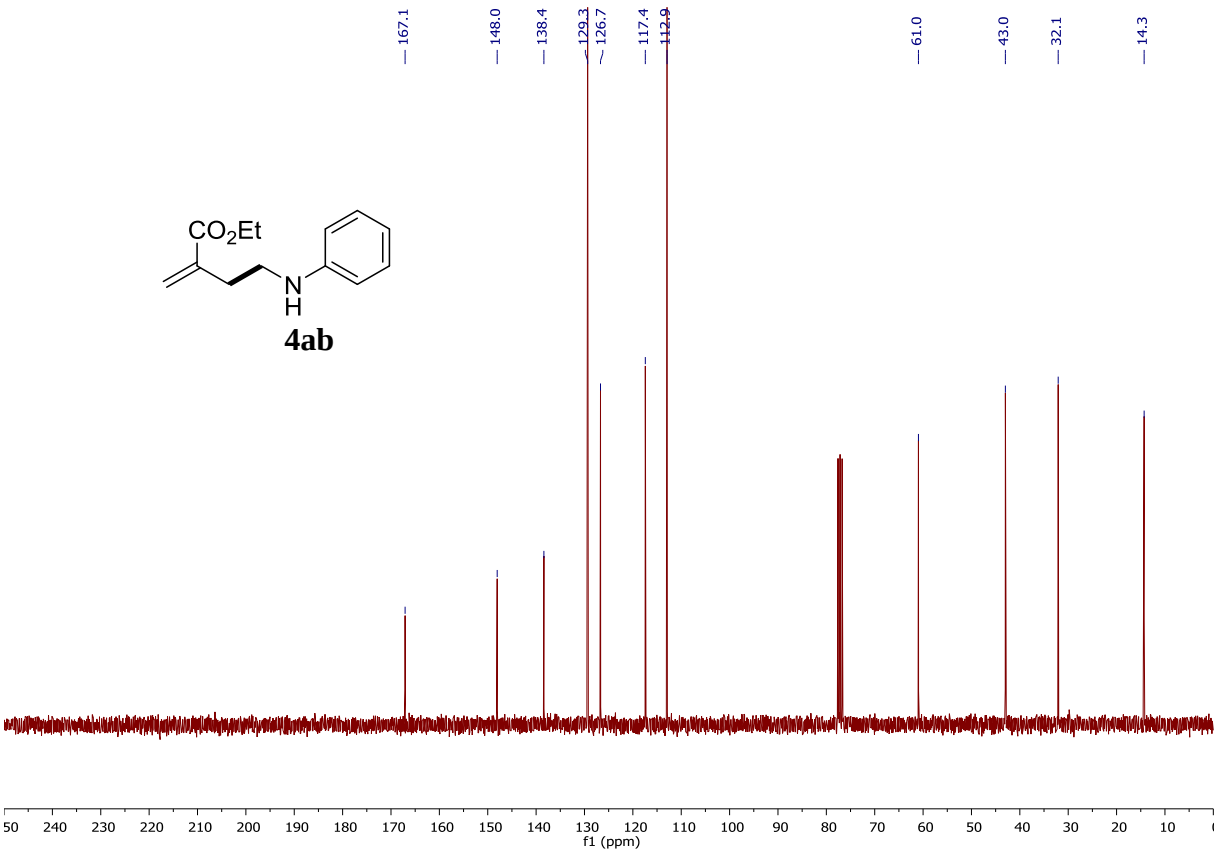


1f

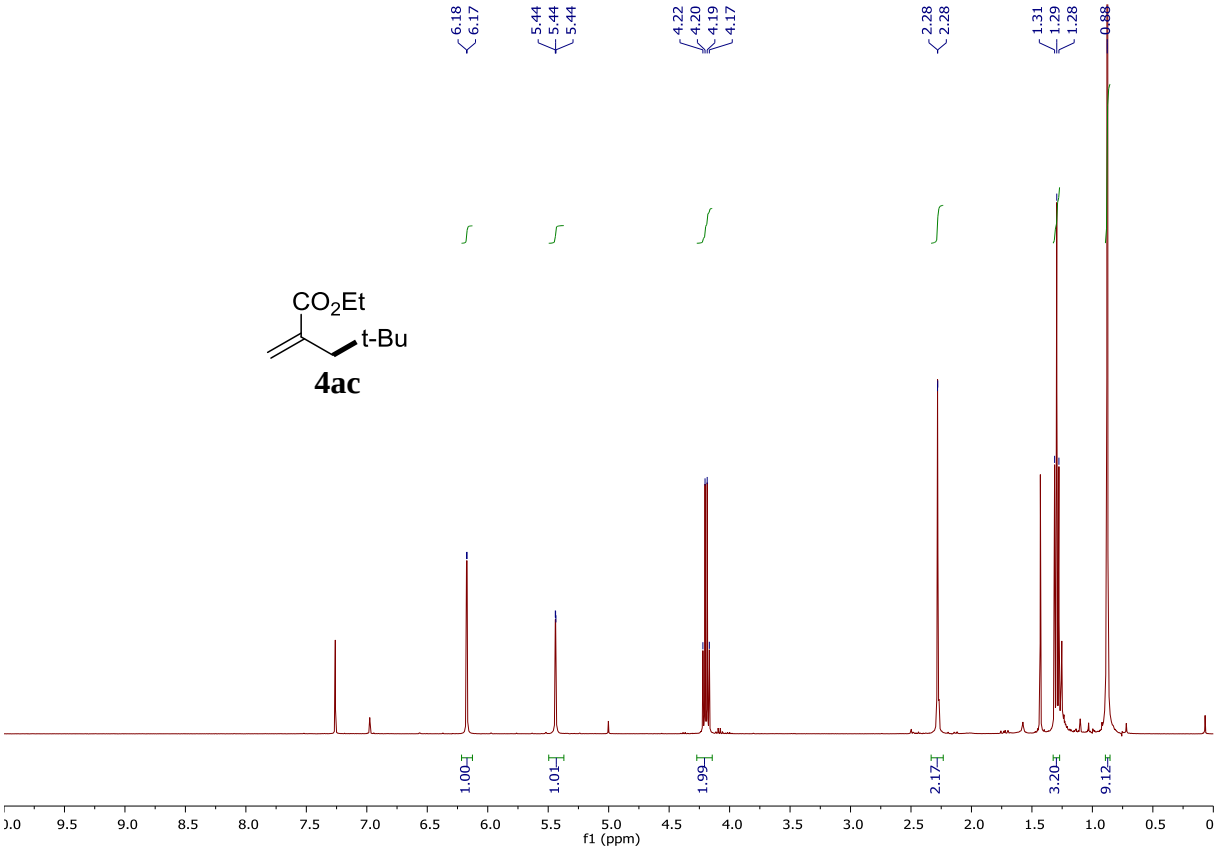
^{1}H spectrum of 4ab



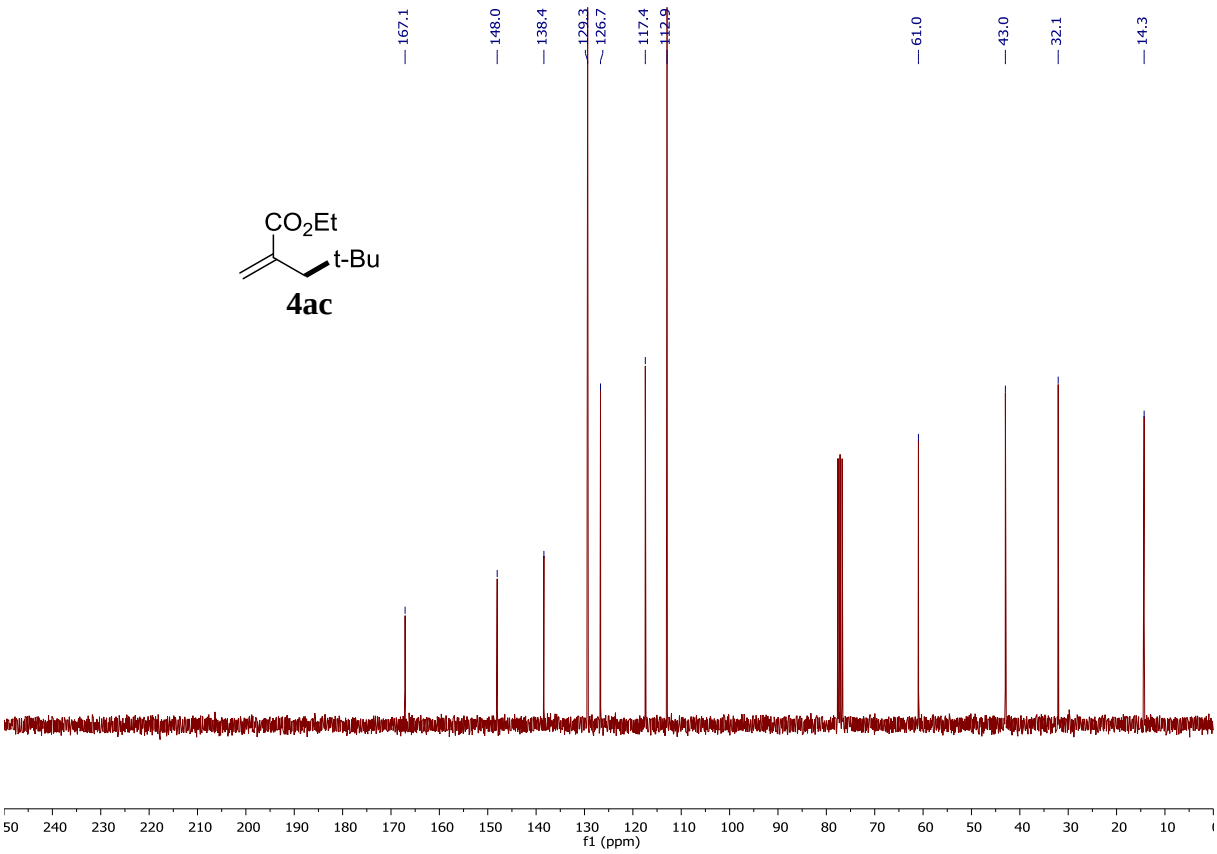
^{13}C spectrum of 4ab



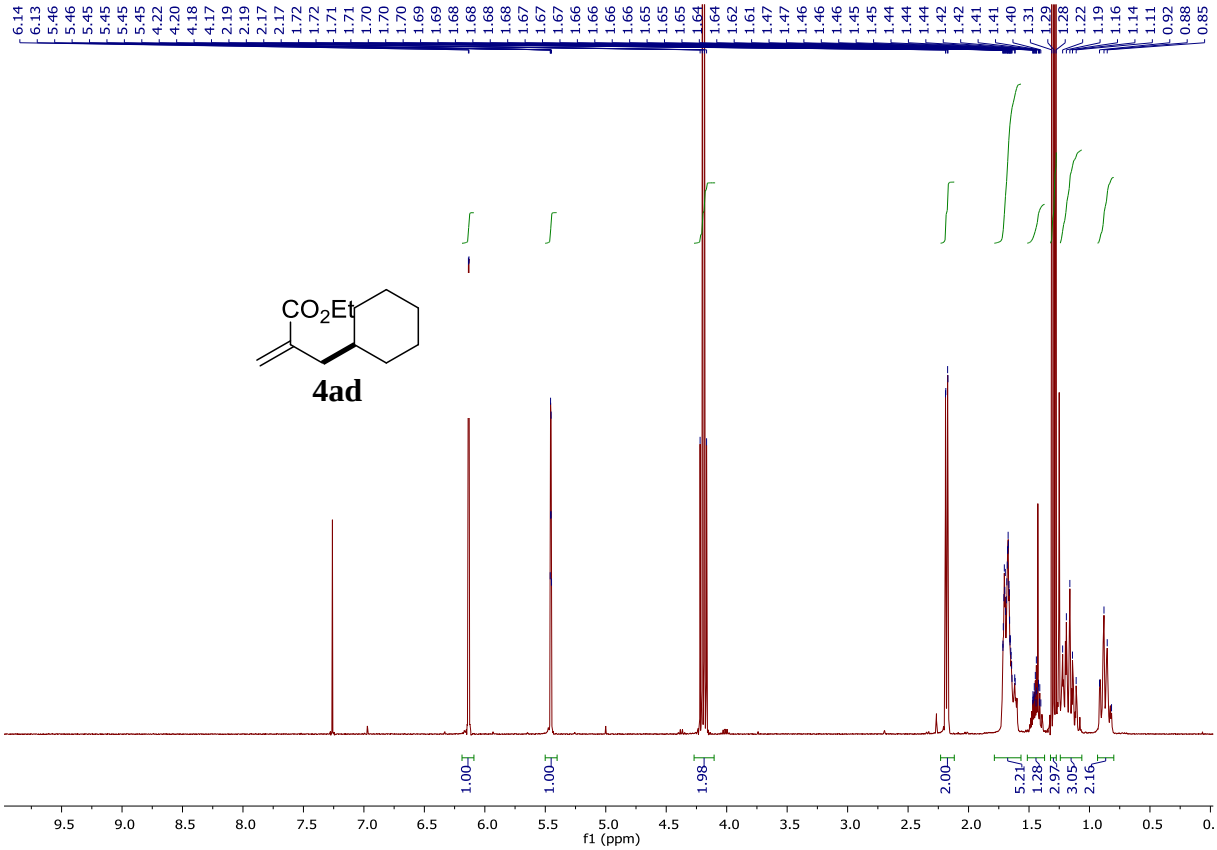
^{1}H spectrum of 4ac



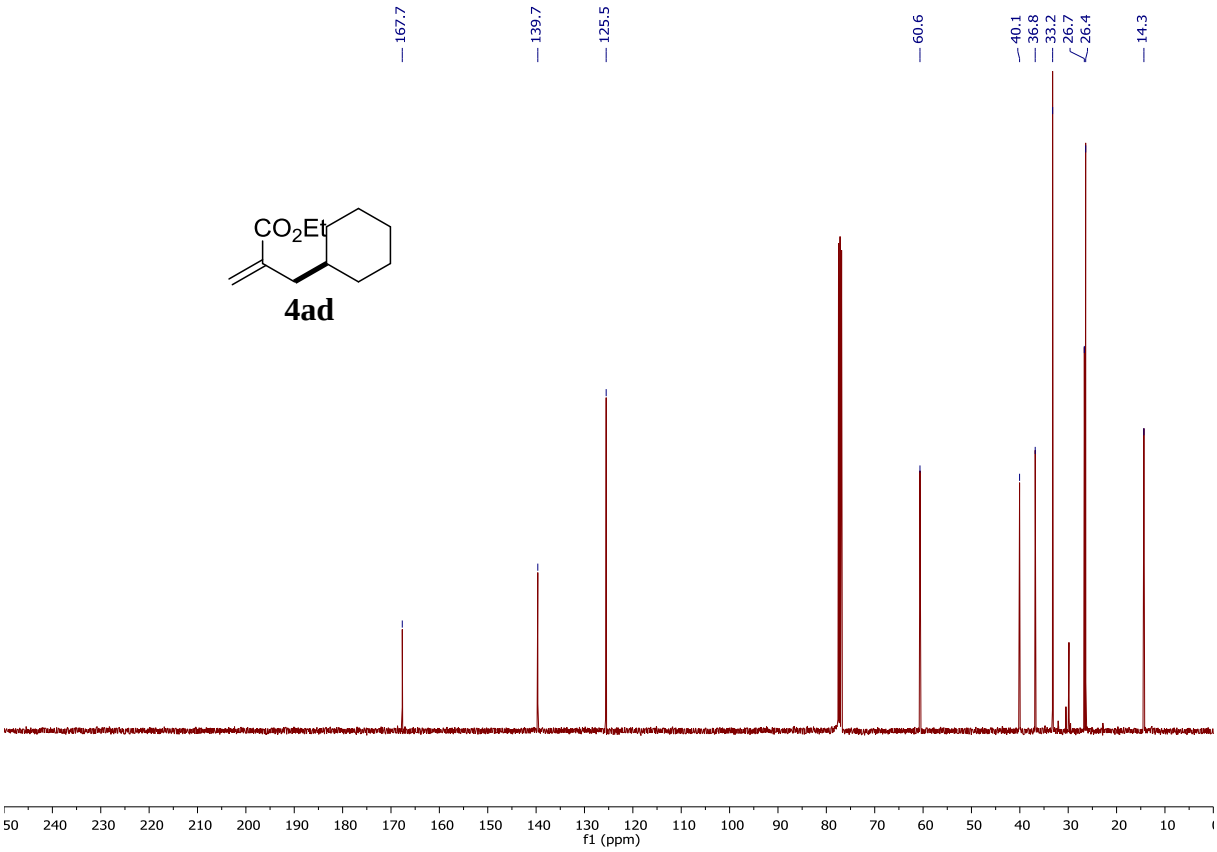
^{13}C spectrum of 4ac



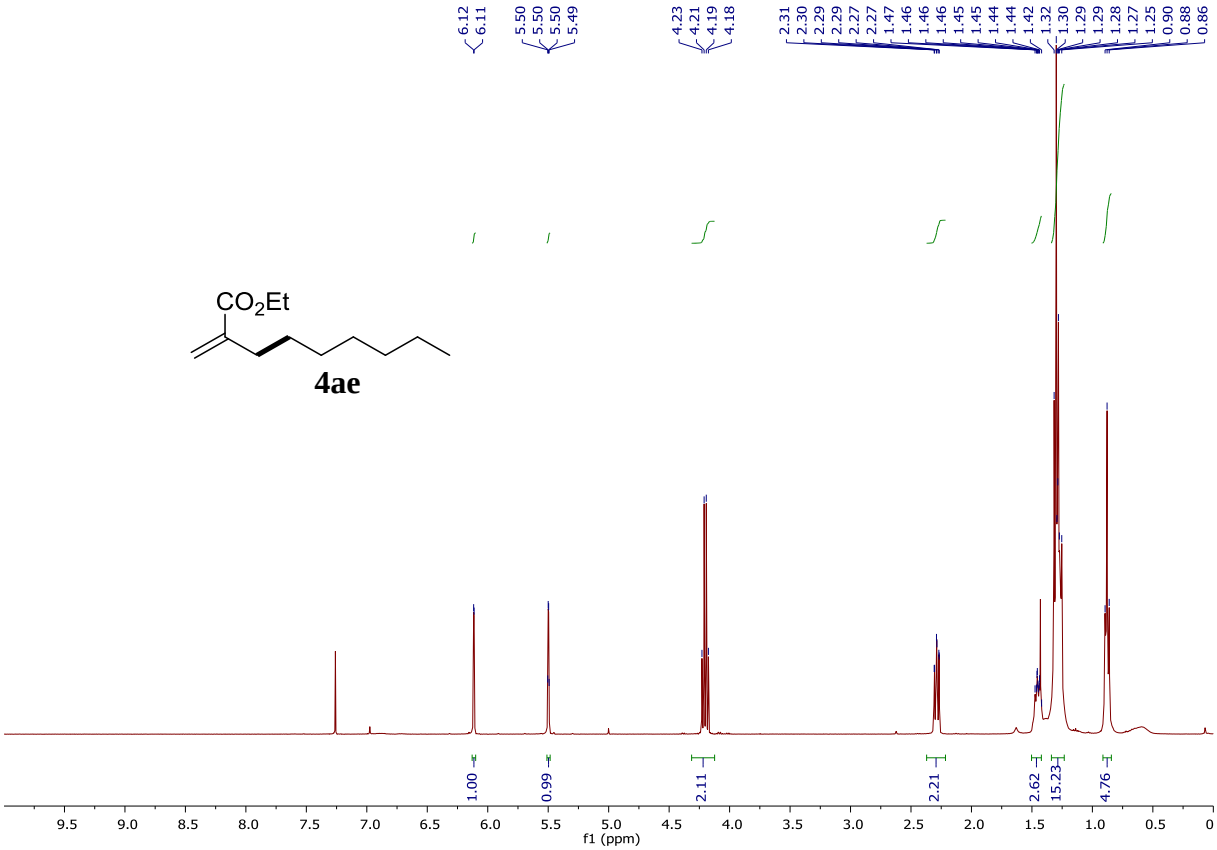
^{1}H spectrum of 4ad



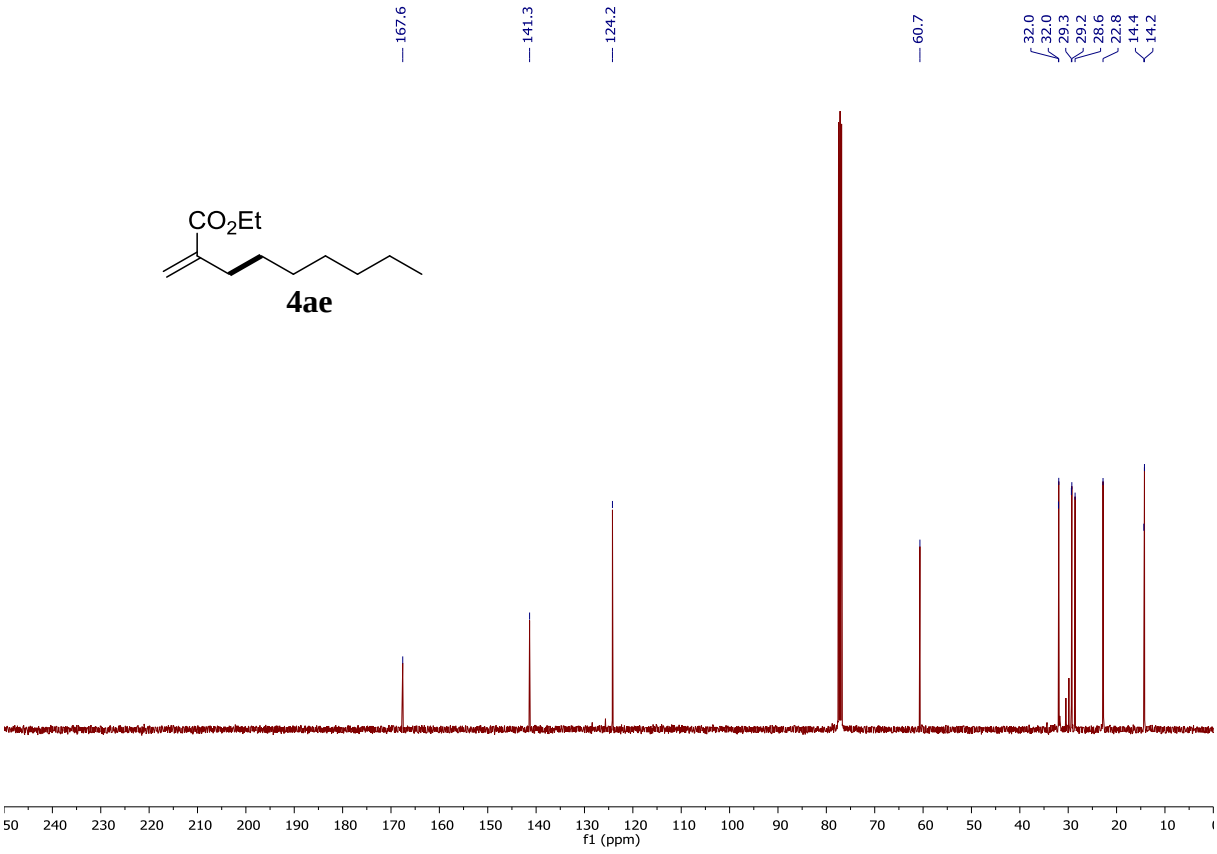
^{13}C spectrum of 4ad



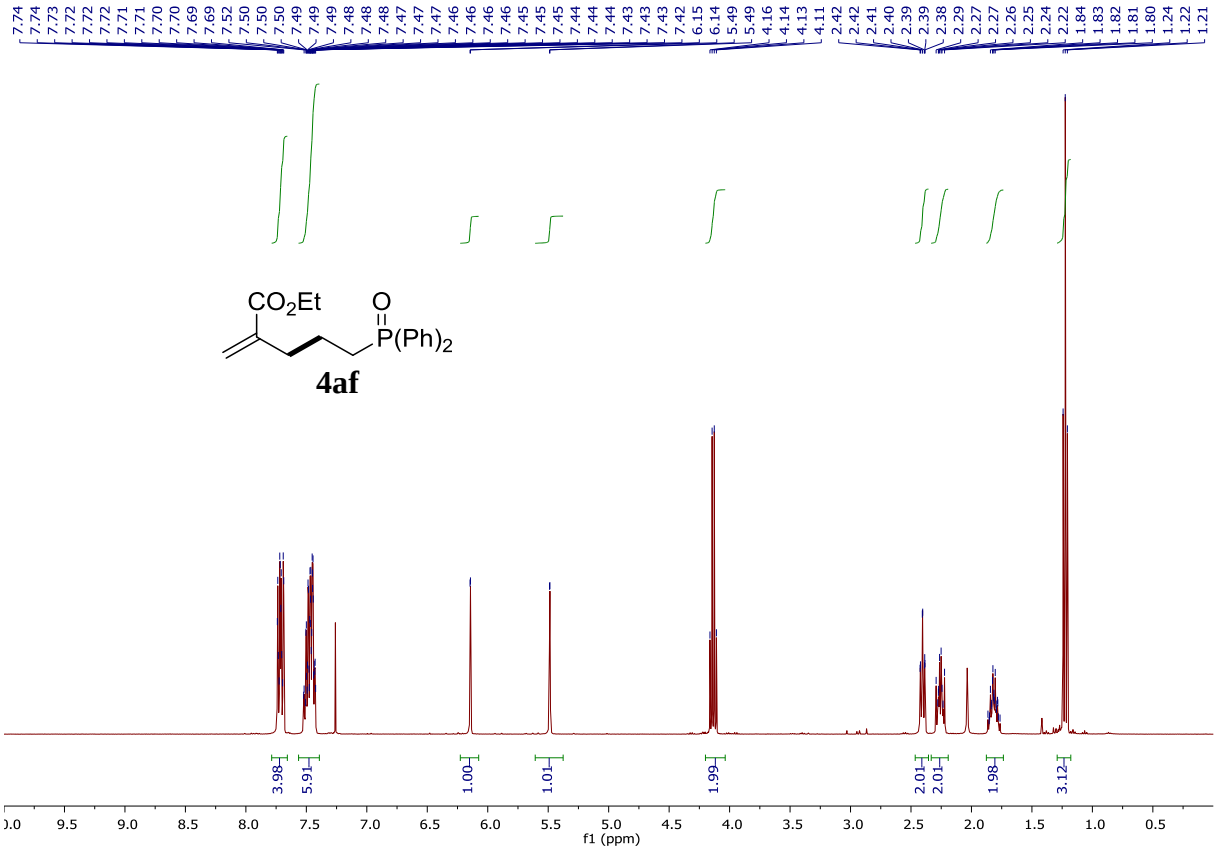
^{1}H spectrum of 4ae



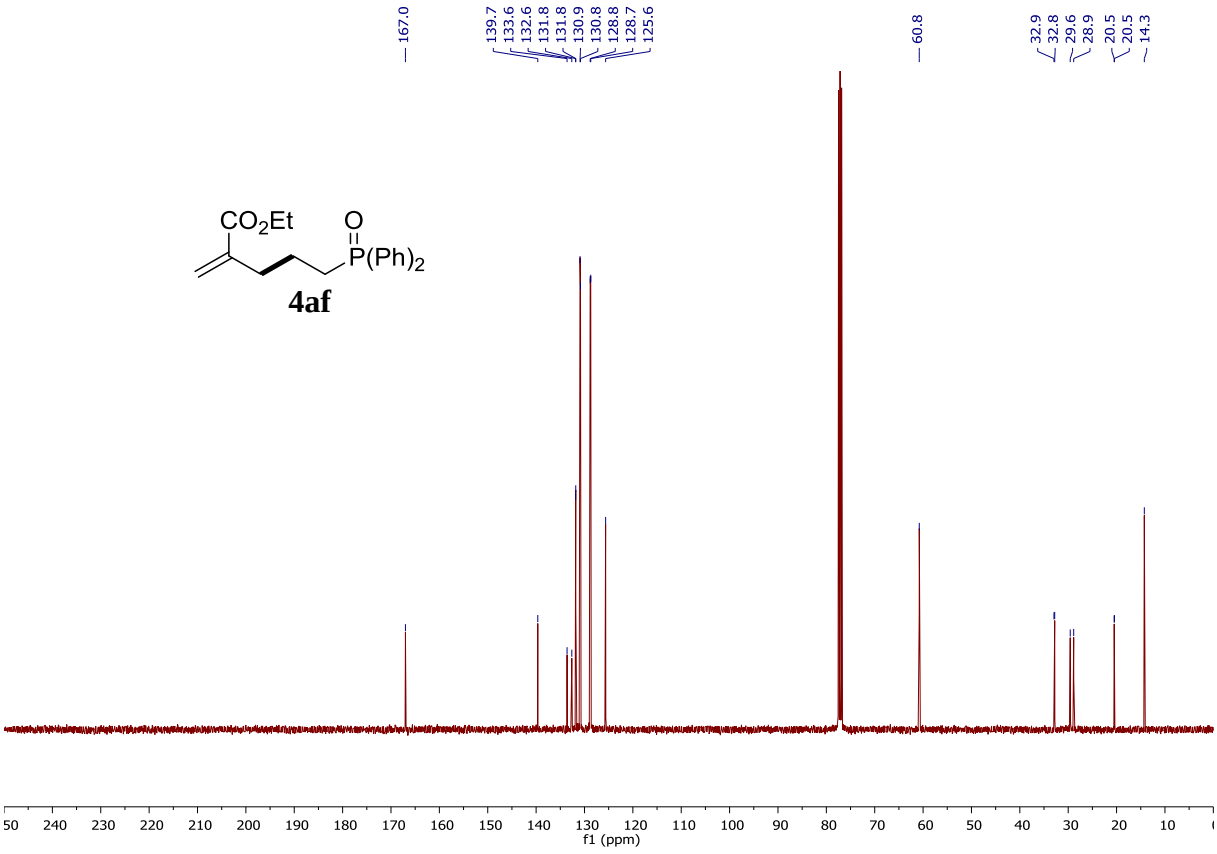
^{13}C spectrum of 4ae



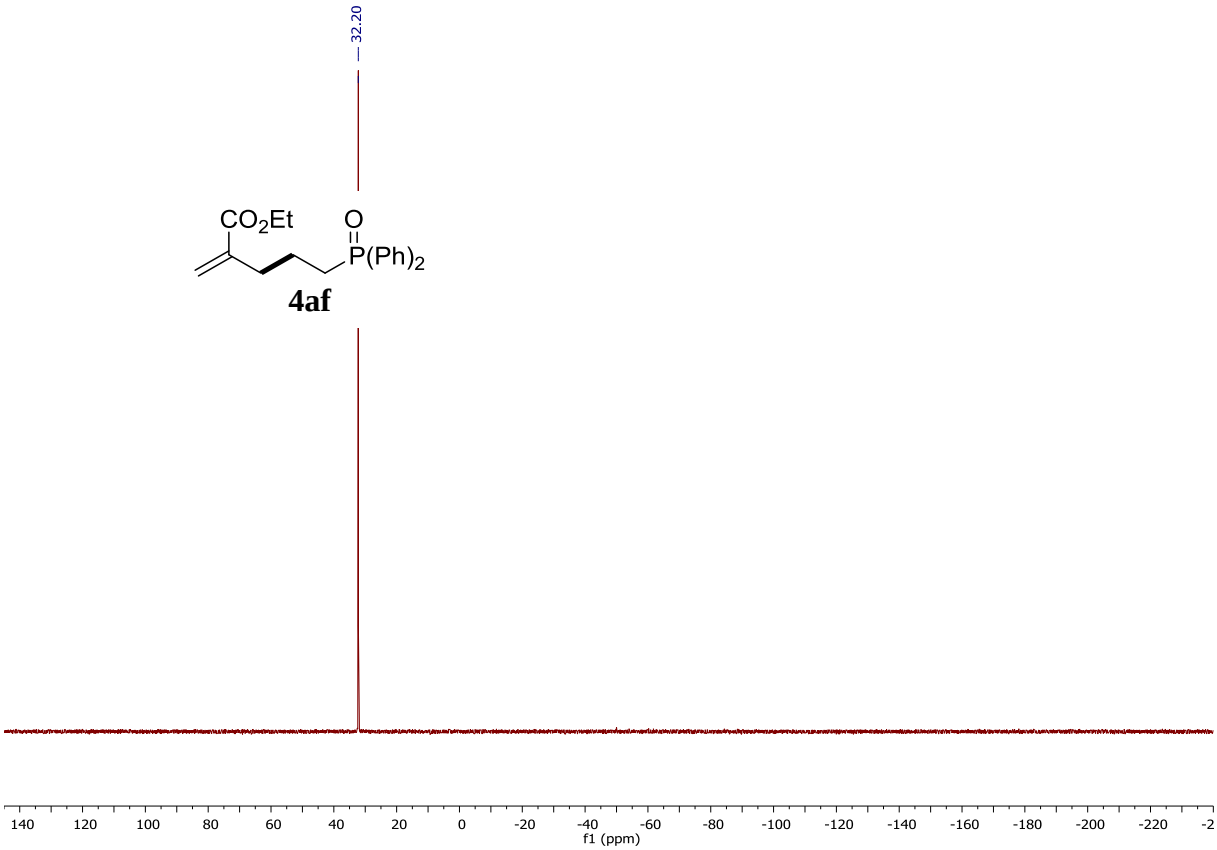
^{1}H spectrum of 4af



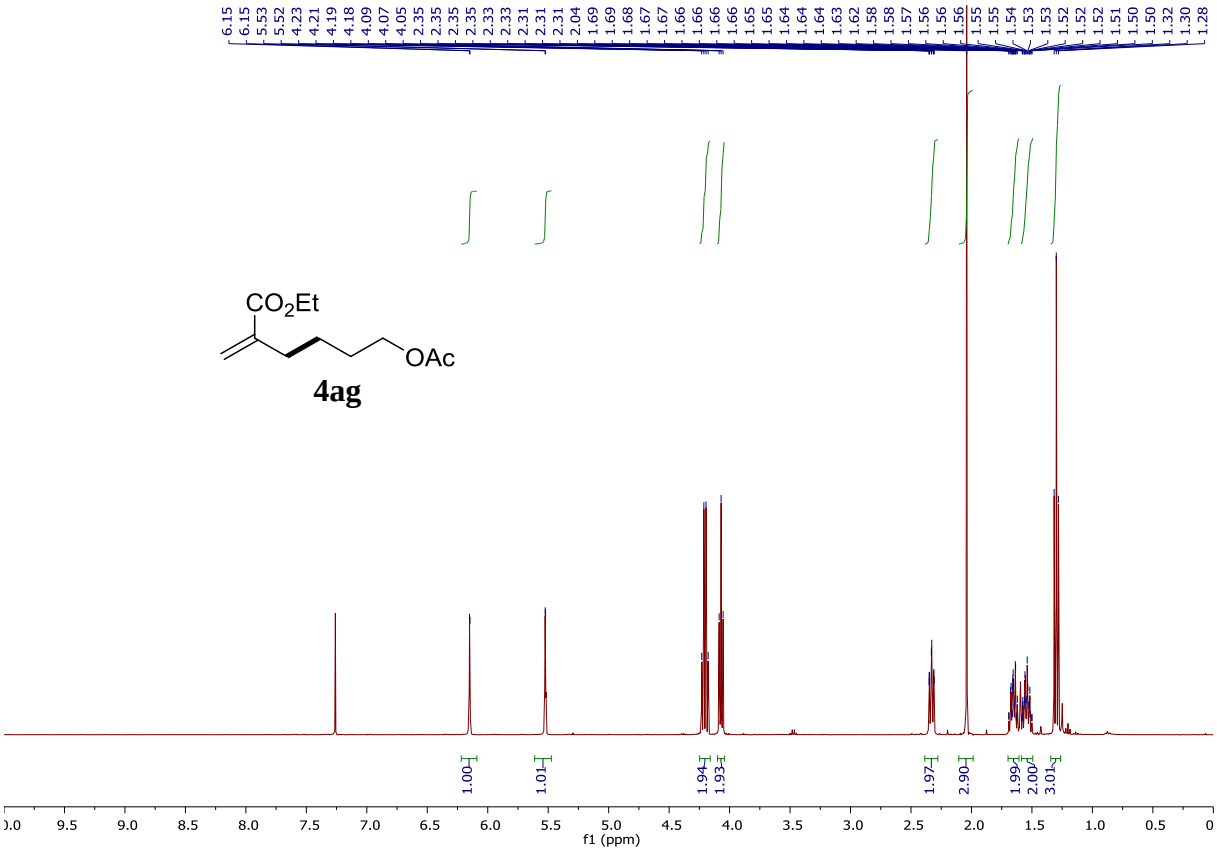
^{13}C spectrum of 4af



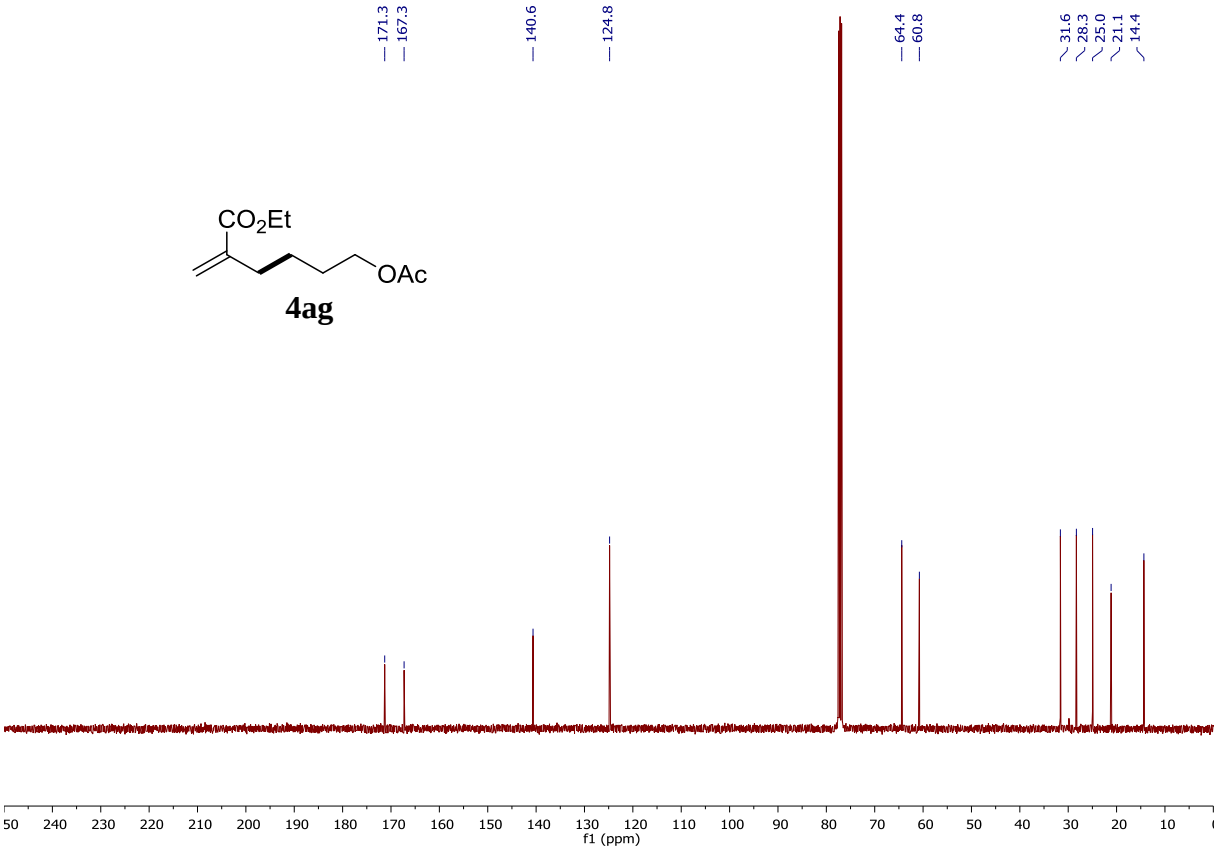
^{31}P spectrum of 4af



^{1}H spectrum of 4ag

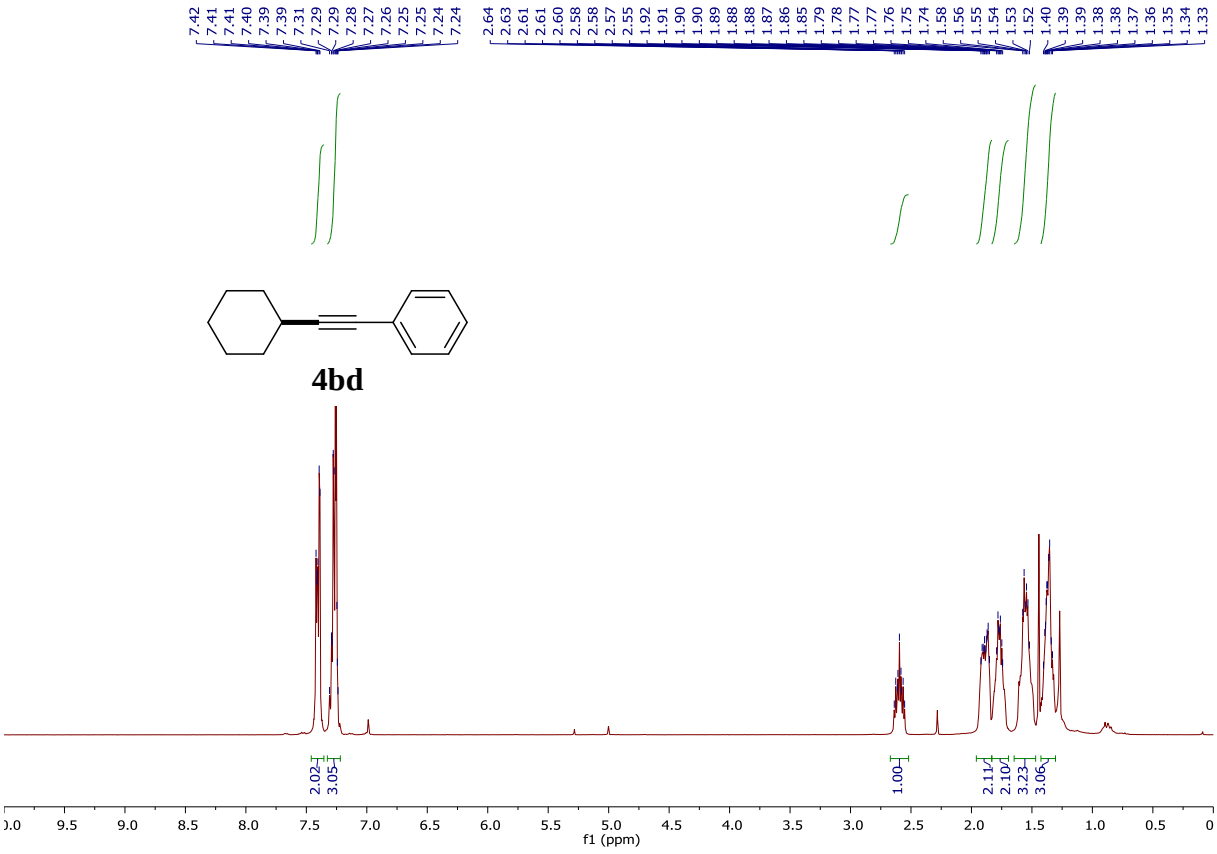


^{13}C spectrum of 4ag



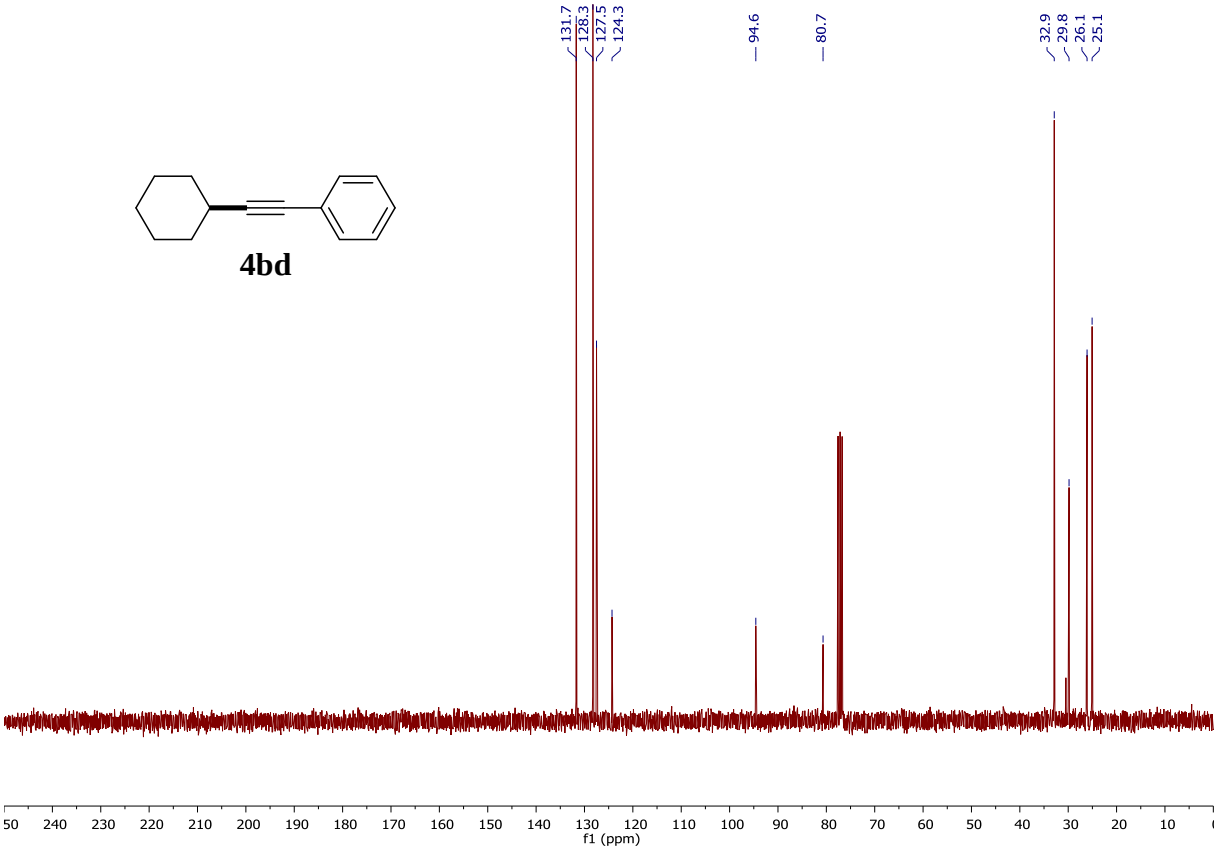
4ag

^{1}H spectrum of 4bd



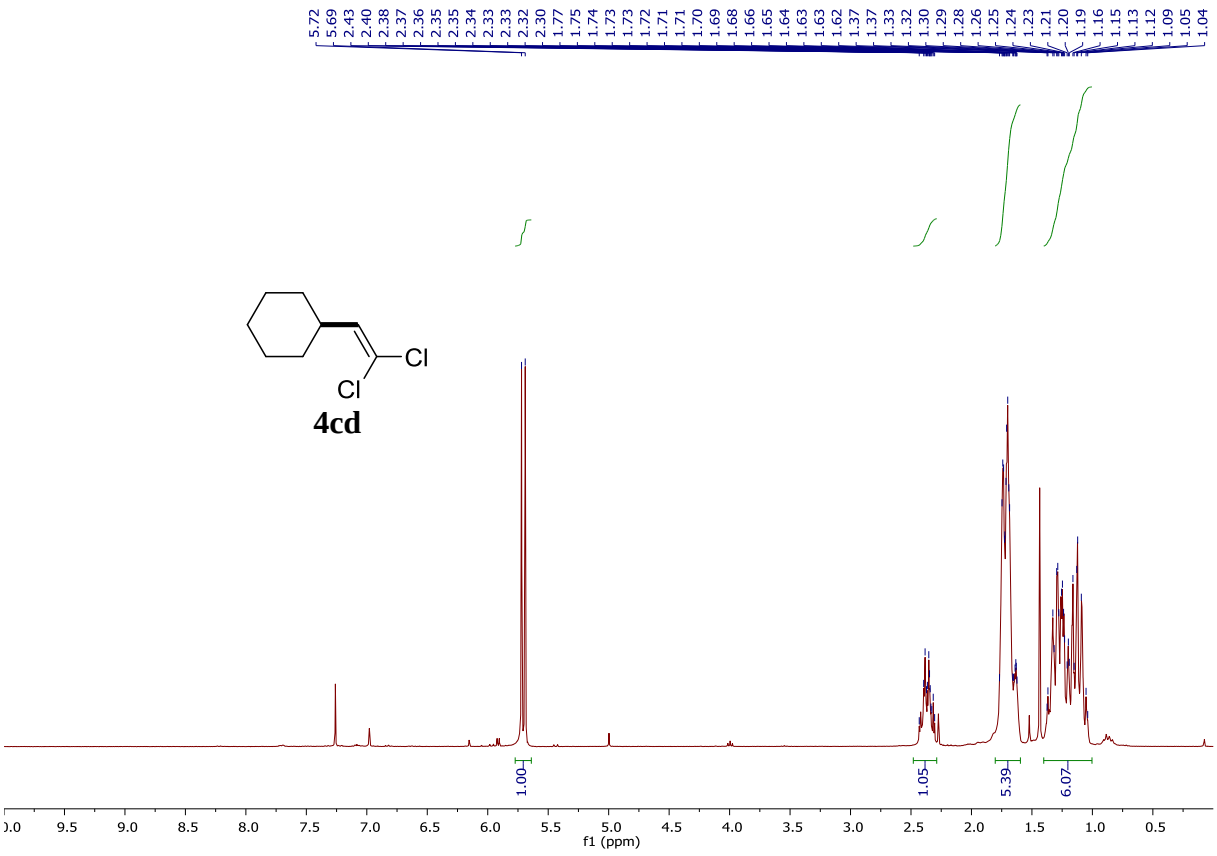
4bd

^{13}C spectrum of 4bd



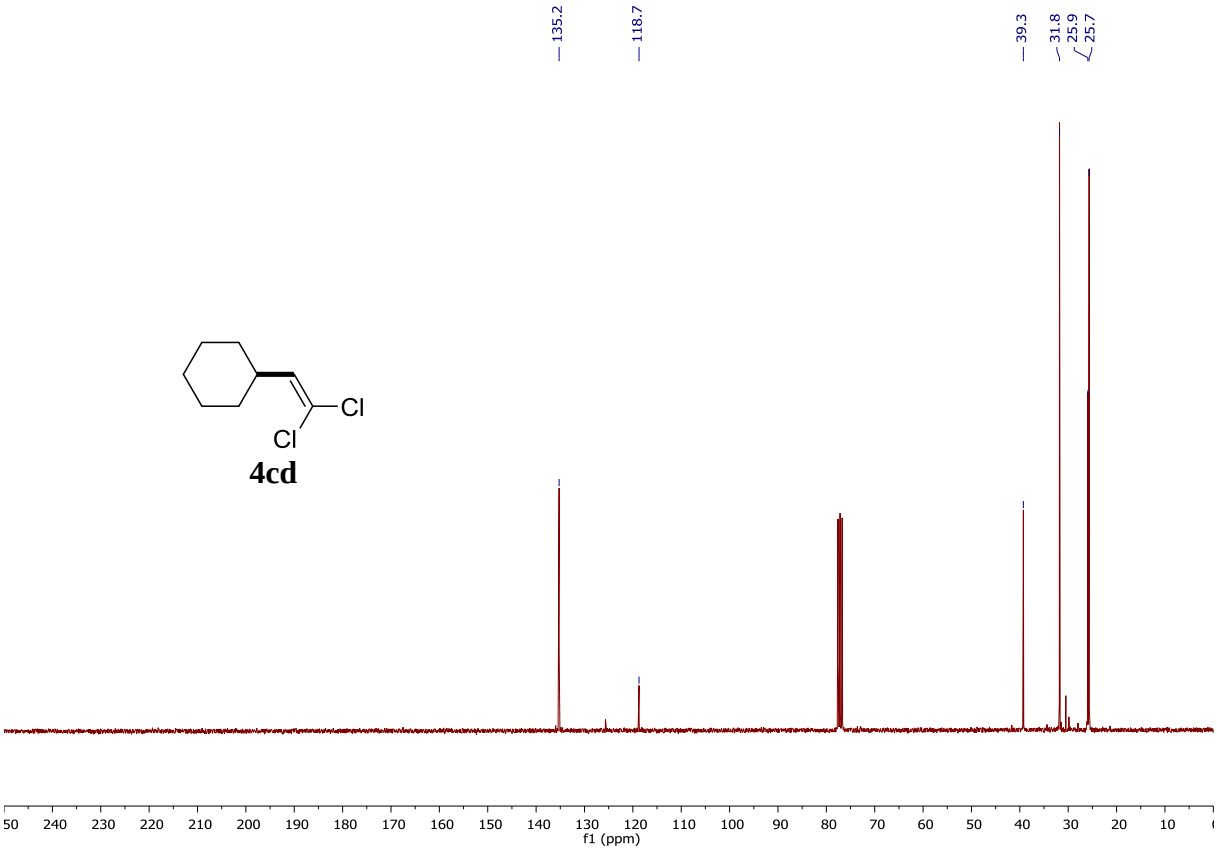
4bd

^{1}H spectrum of 4cd

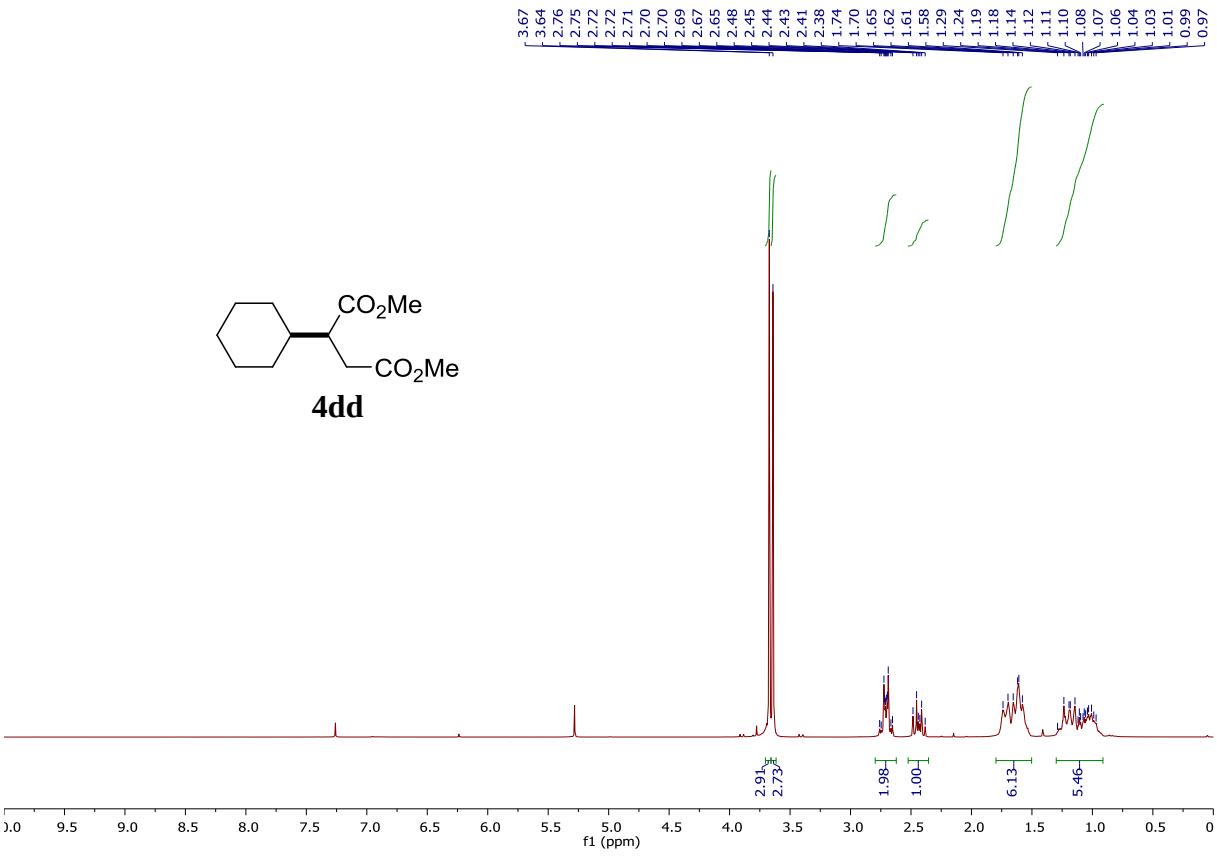


4cd

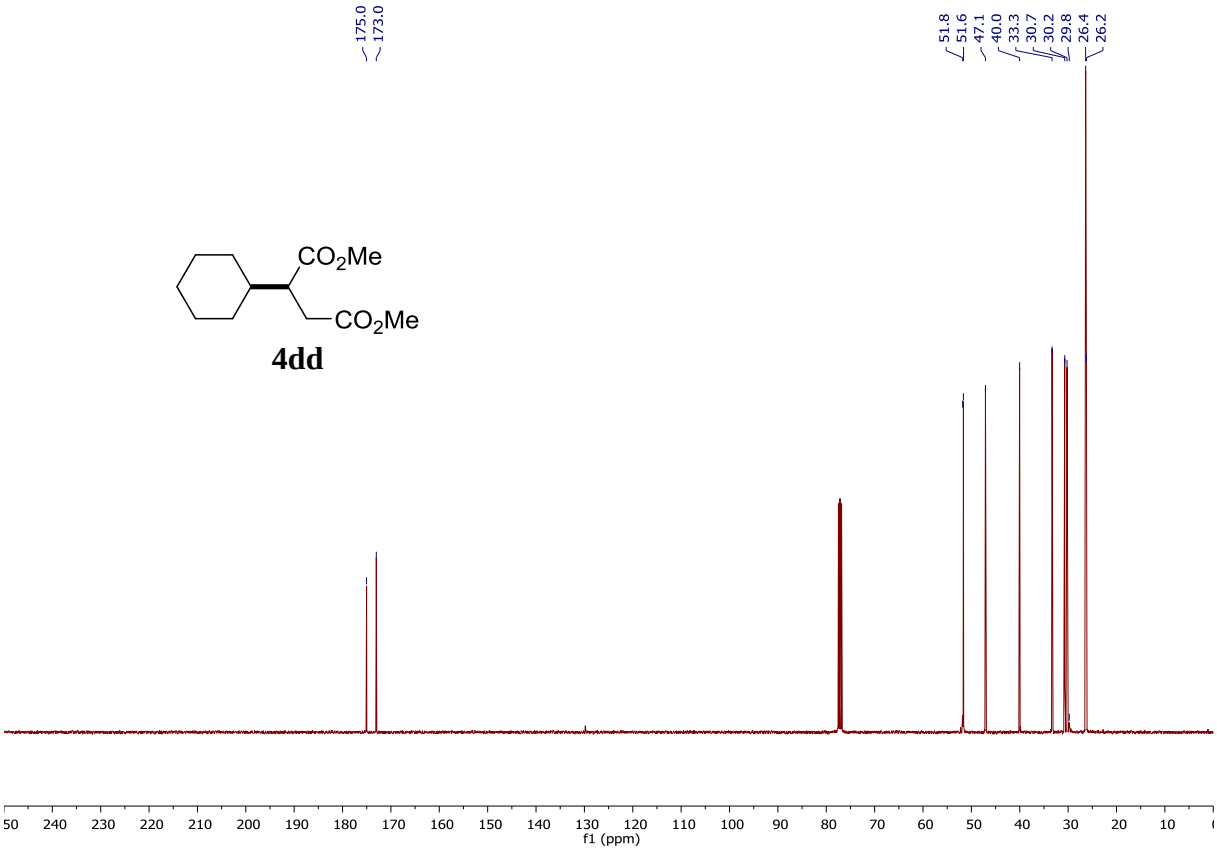
^{13}C spectrum of 4cd



^{1}H spectrum of 4dd

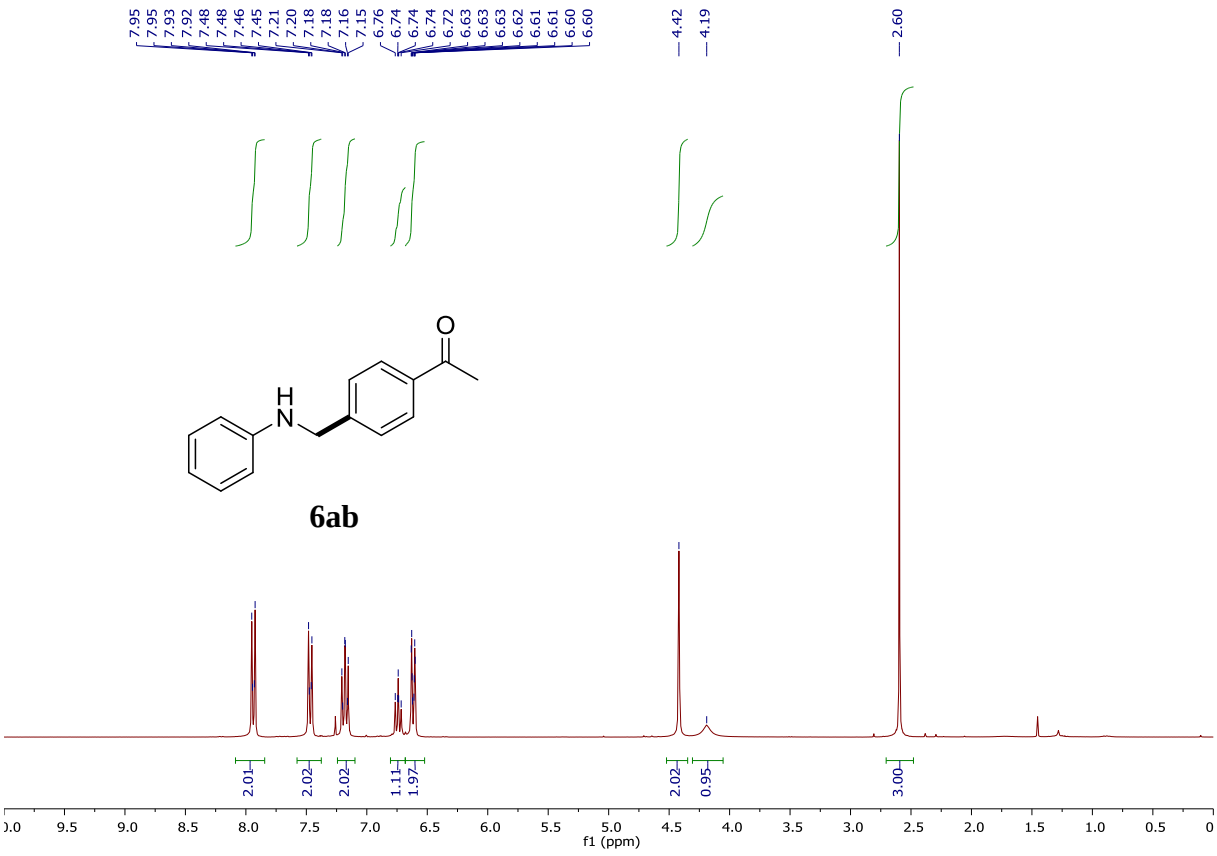


^{13}C spectrum of 4dd



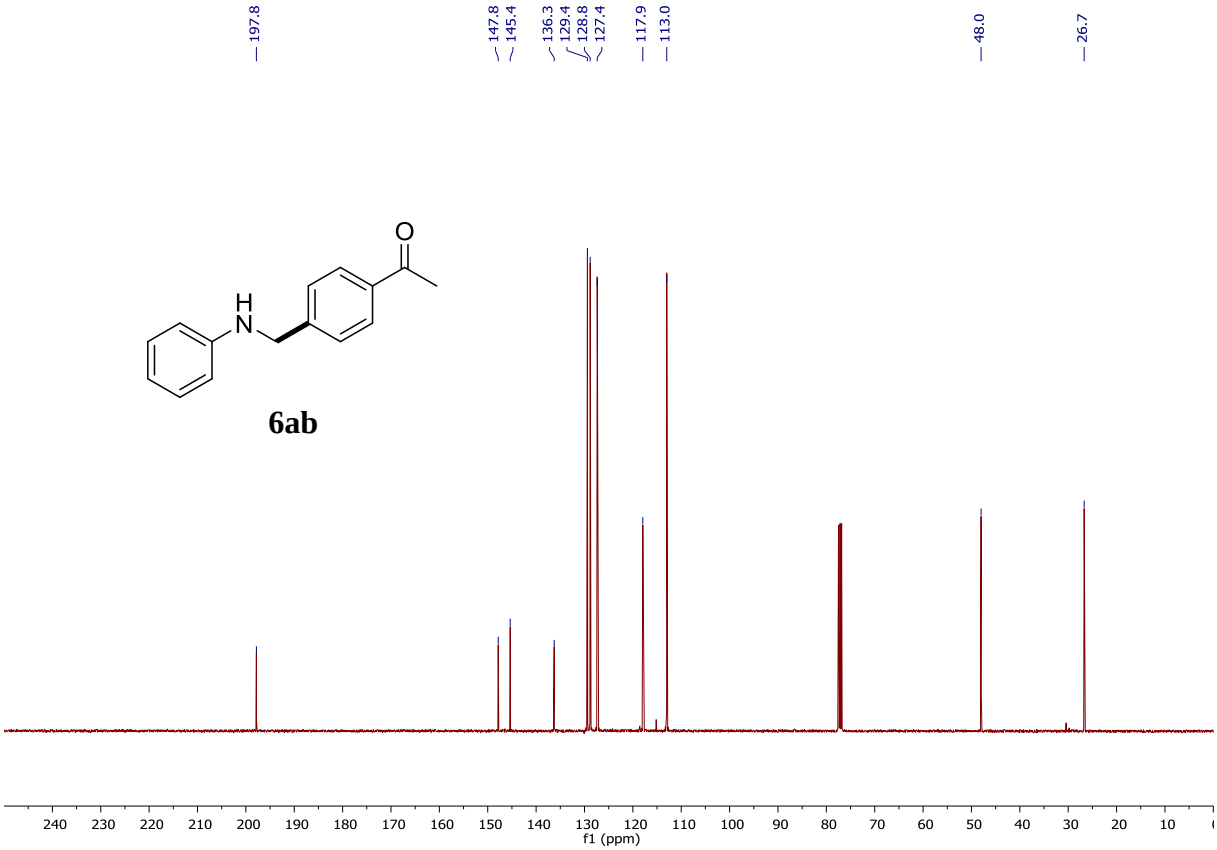
4dd

^{1}H spectrum of 6ab



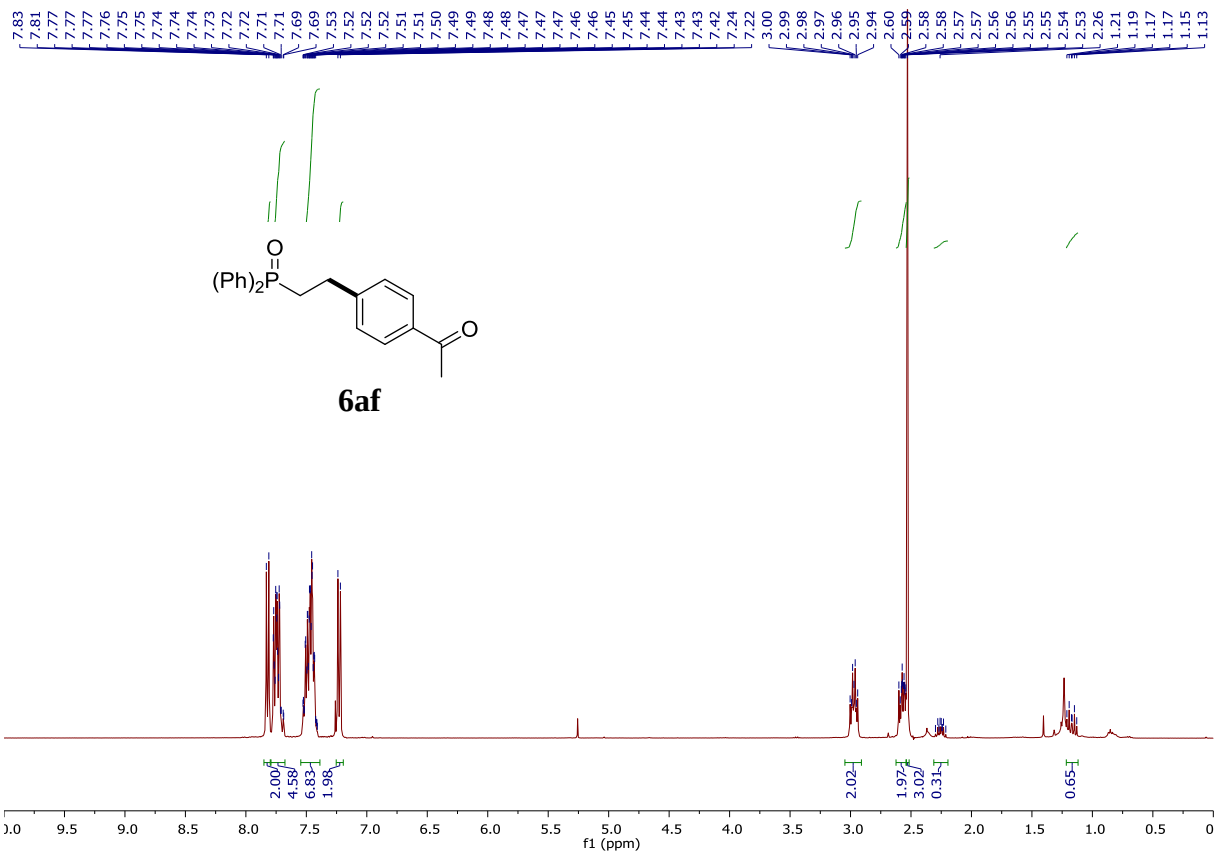
6ab

^{13}C spectrum of 6ab



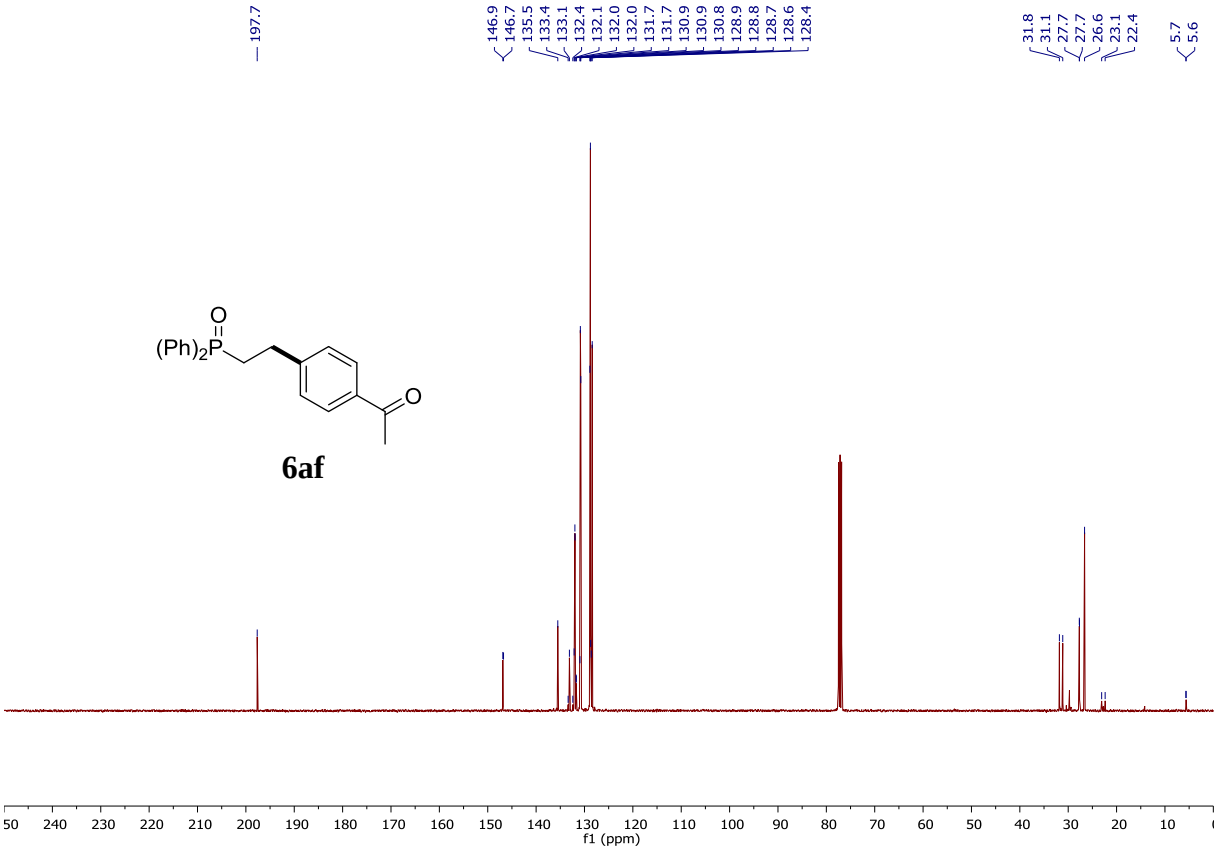
6ab

^{1}H spectrum of 6af

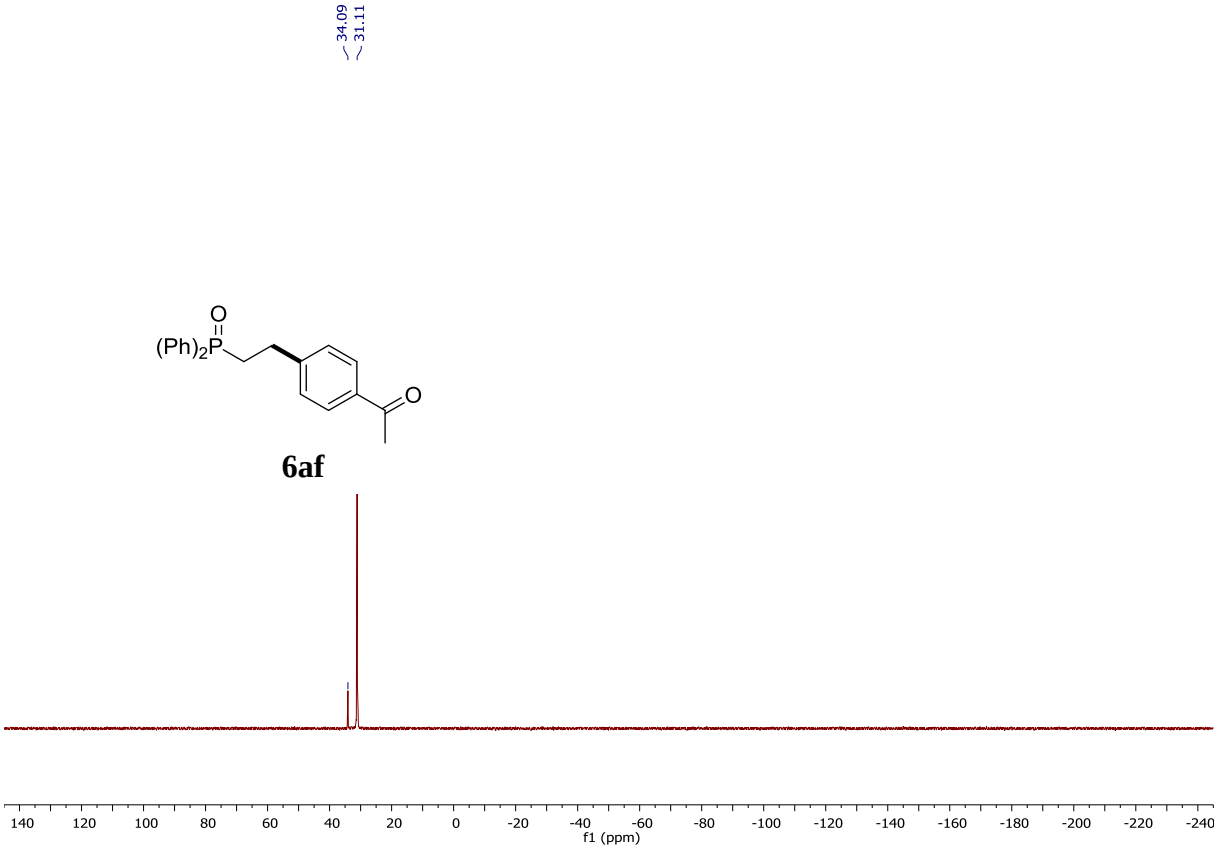


6af

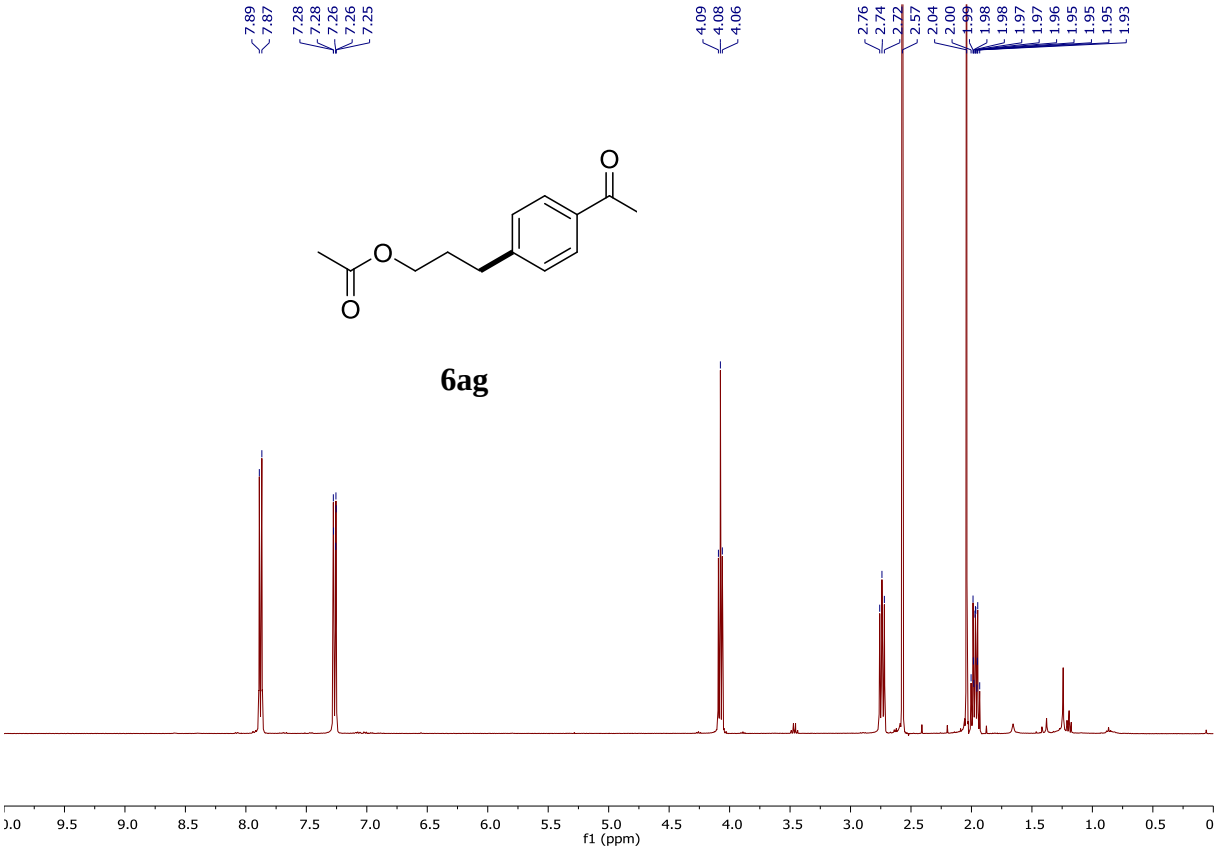
^{13}C spectrum of 6af



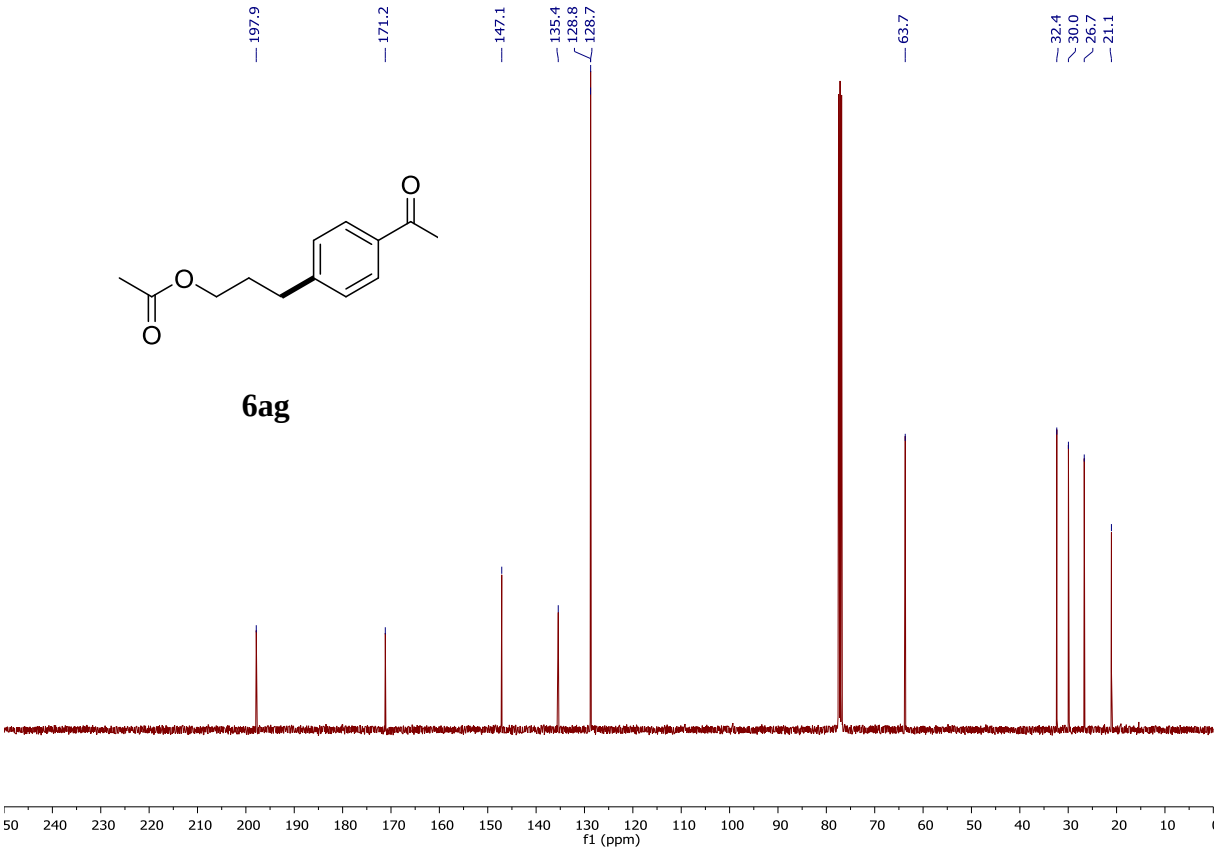
^{31}P spectrum of 6af



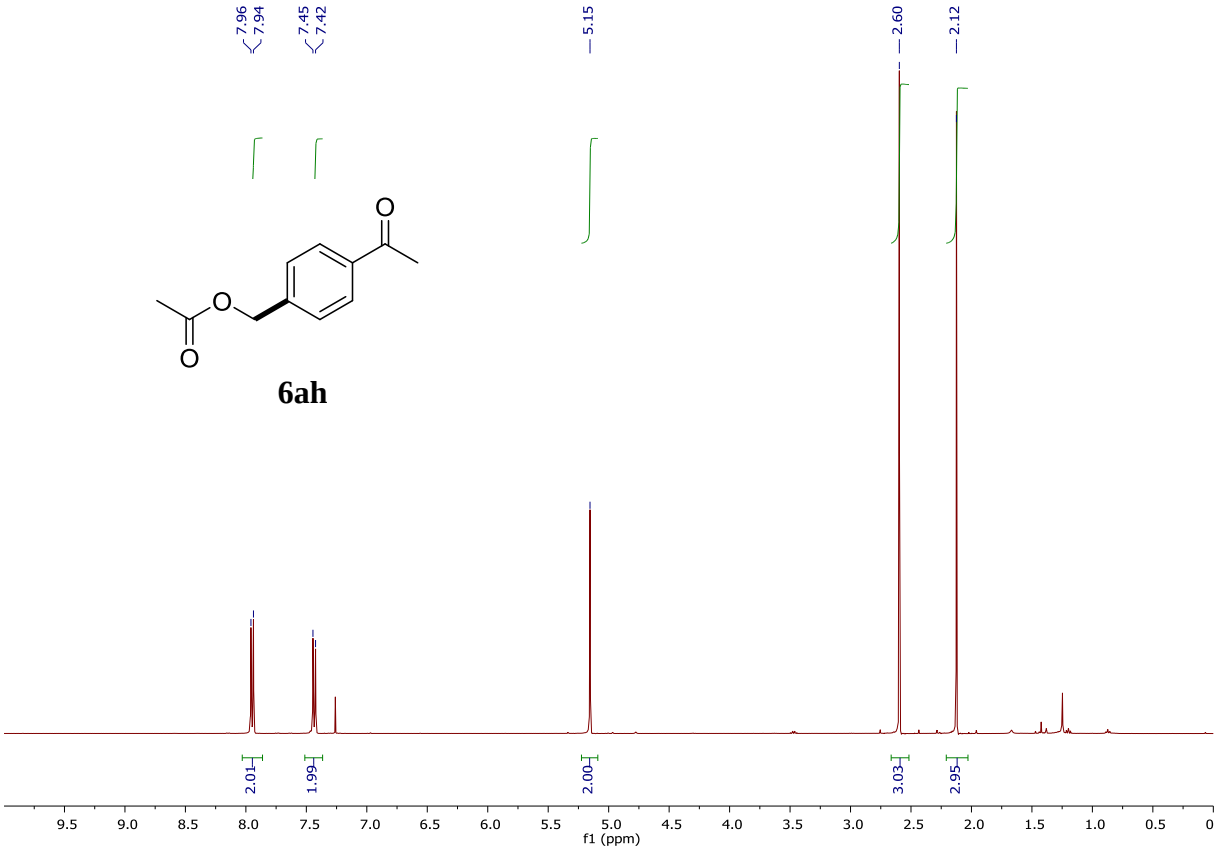
^{1}H spectrum of 6ag



^{13}C spectrum of 6ag

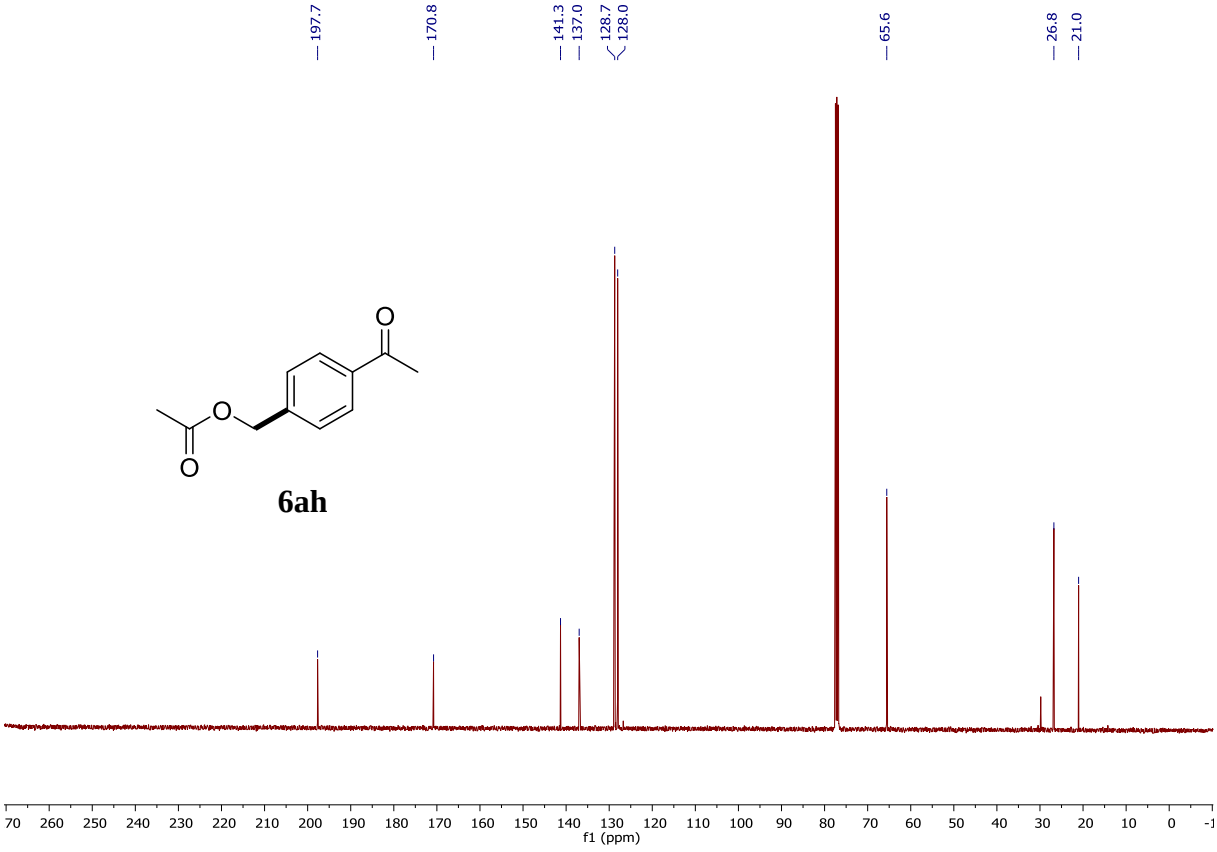


^{1}H spectrum of 6ah



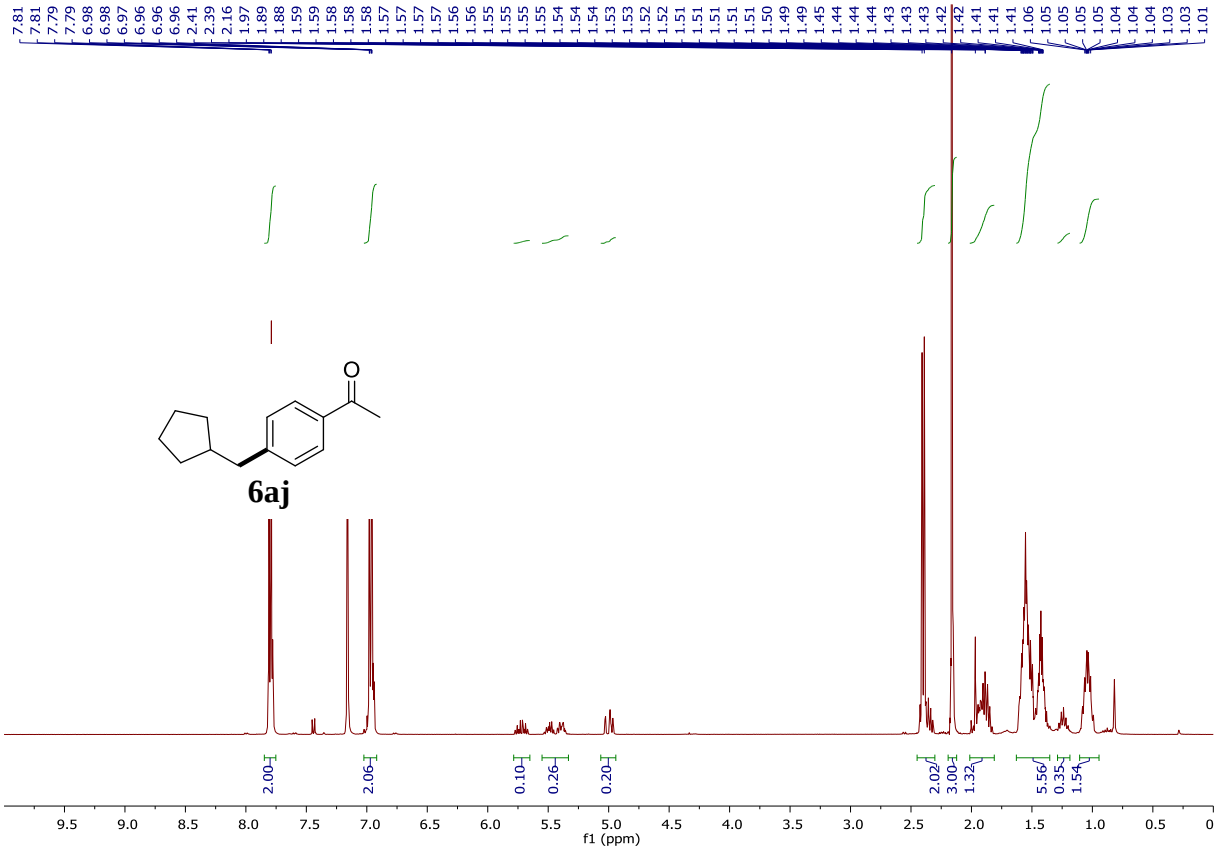
6ah

^{13}C spectrum of 6ah

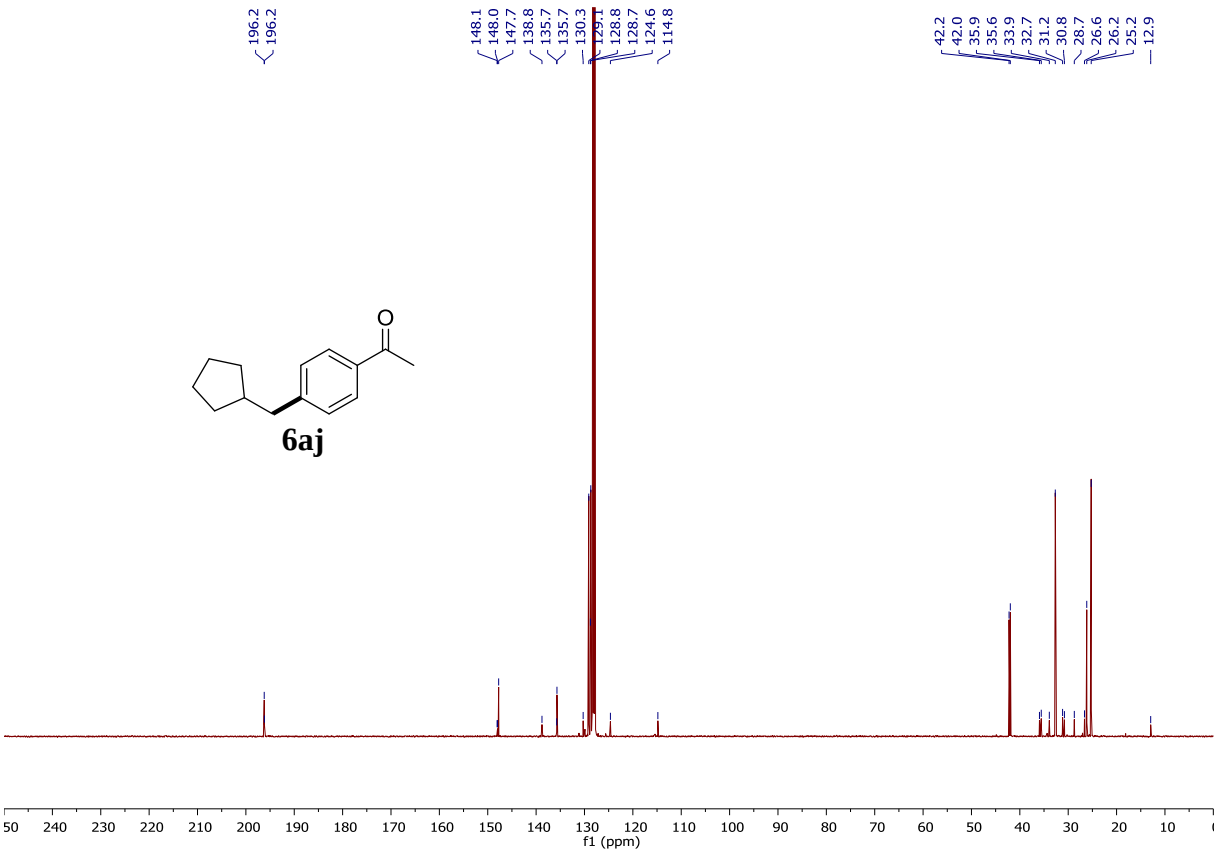


6ah

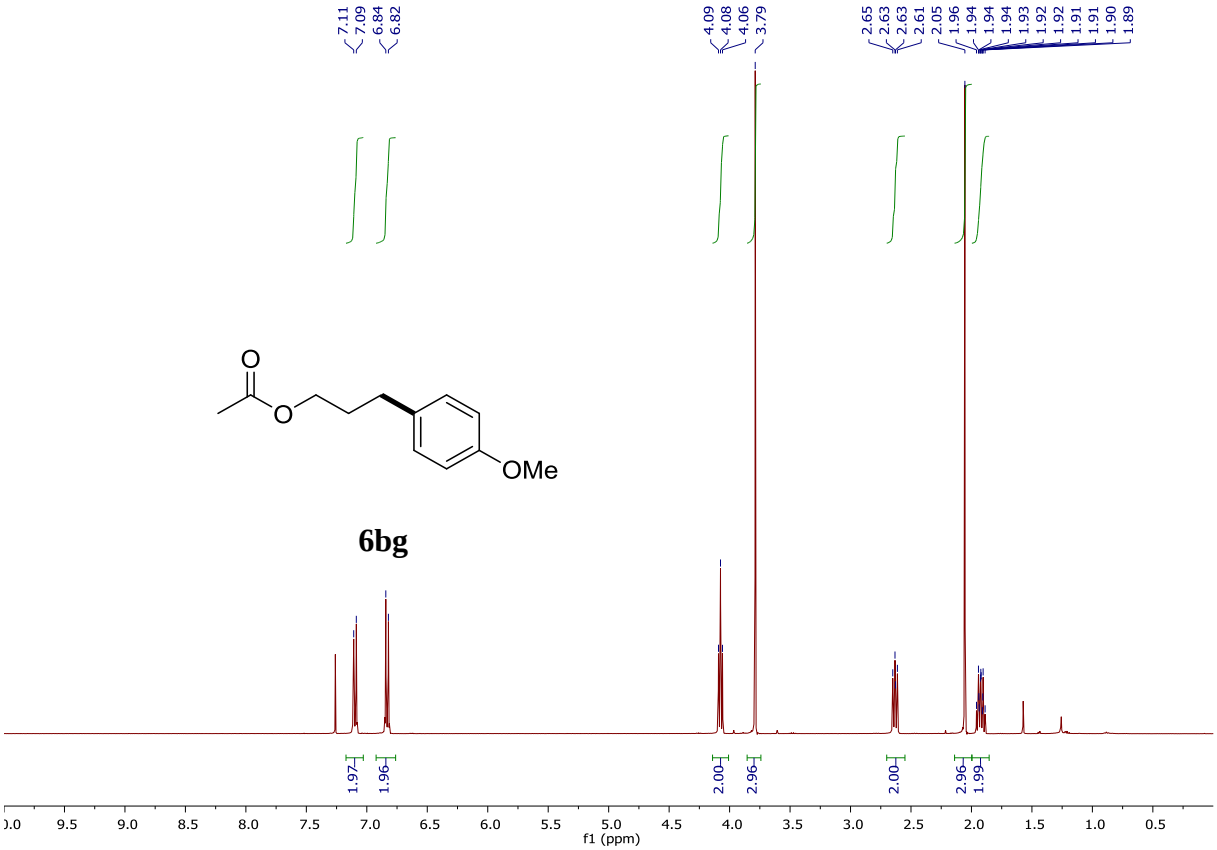
^{1}H spectrum of 6aj



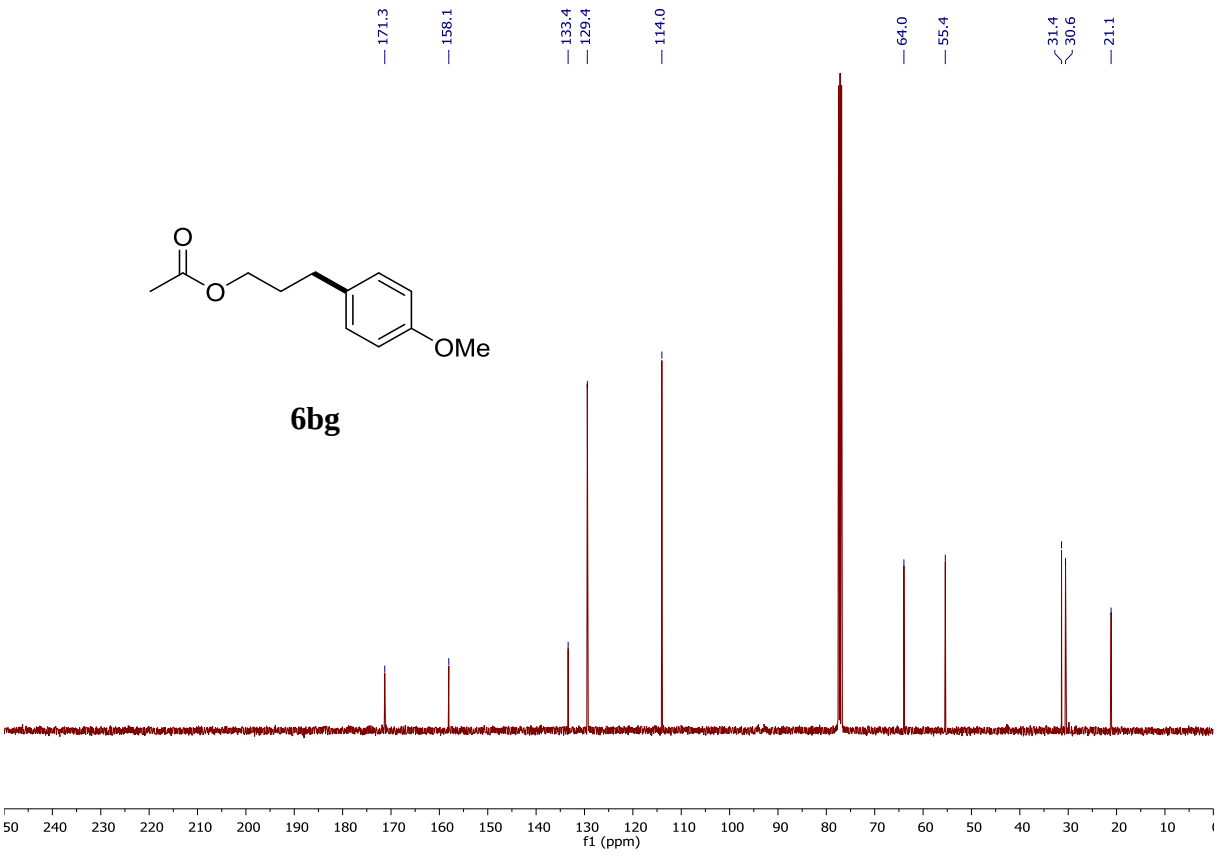
^{13}C spectrum of 6aj



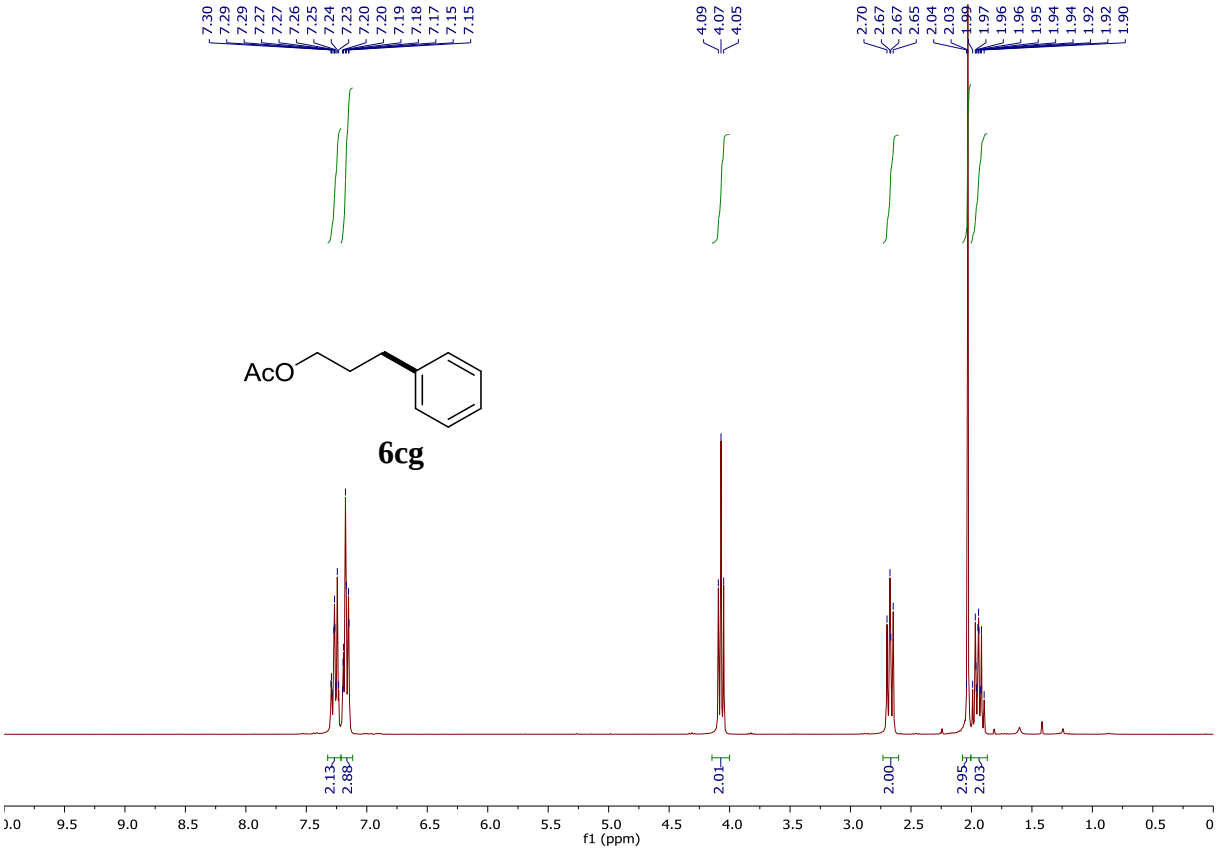
^{1}H spectrum of 6bg



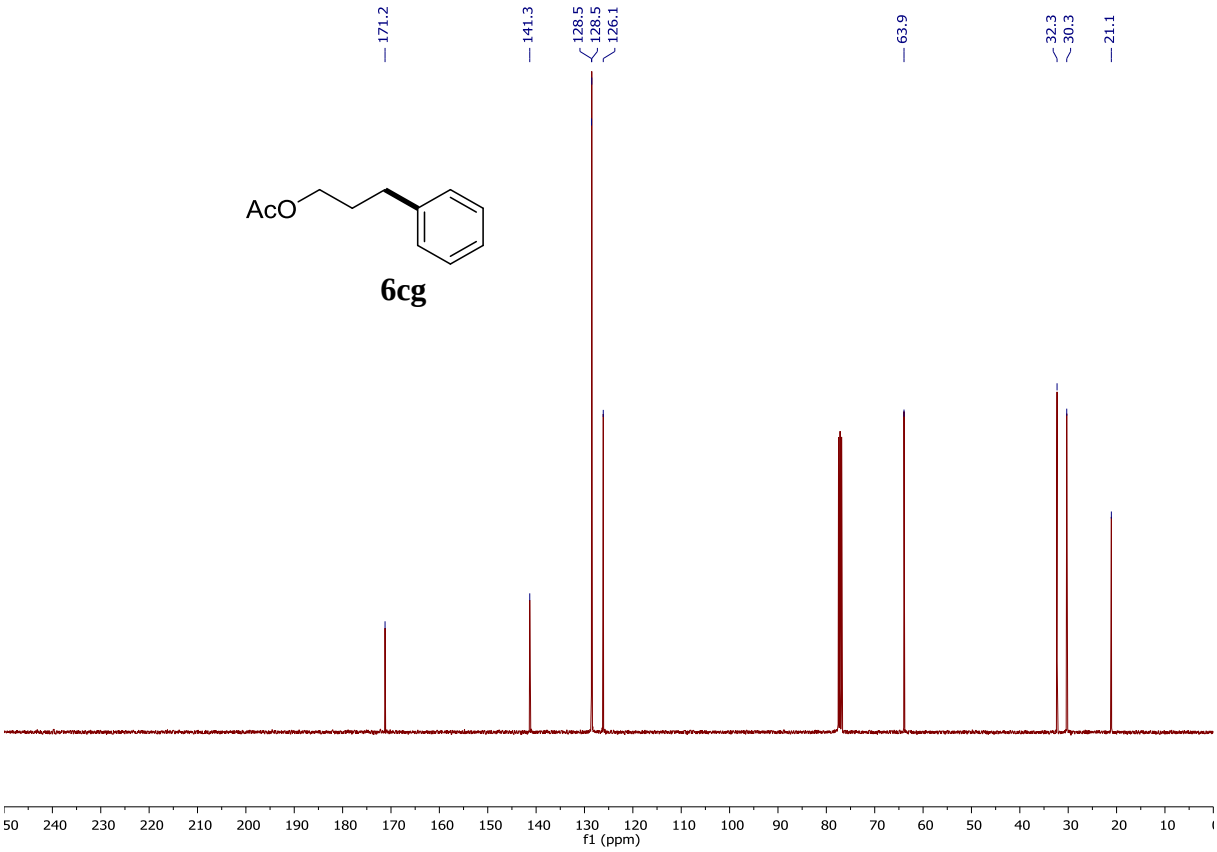
^{13}C spectrum of 6bg



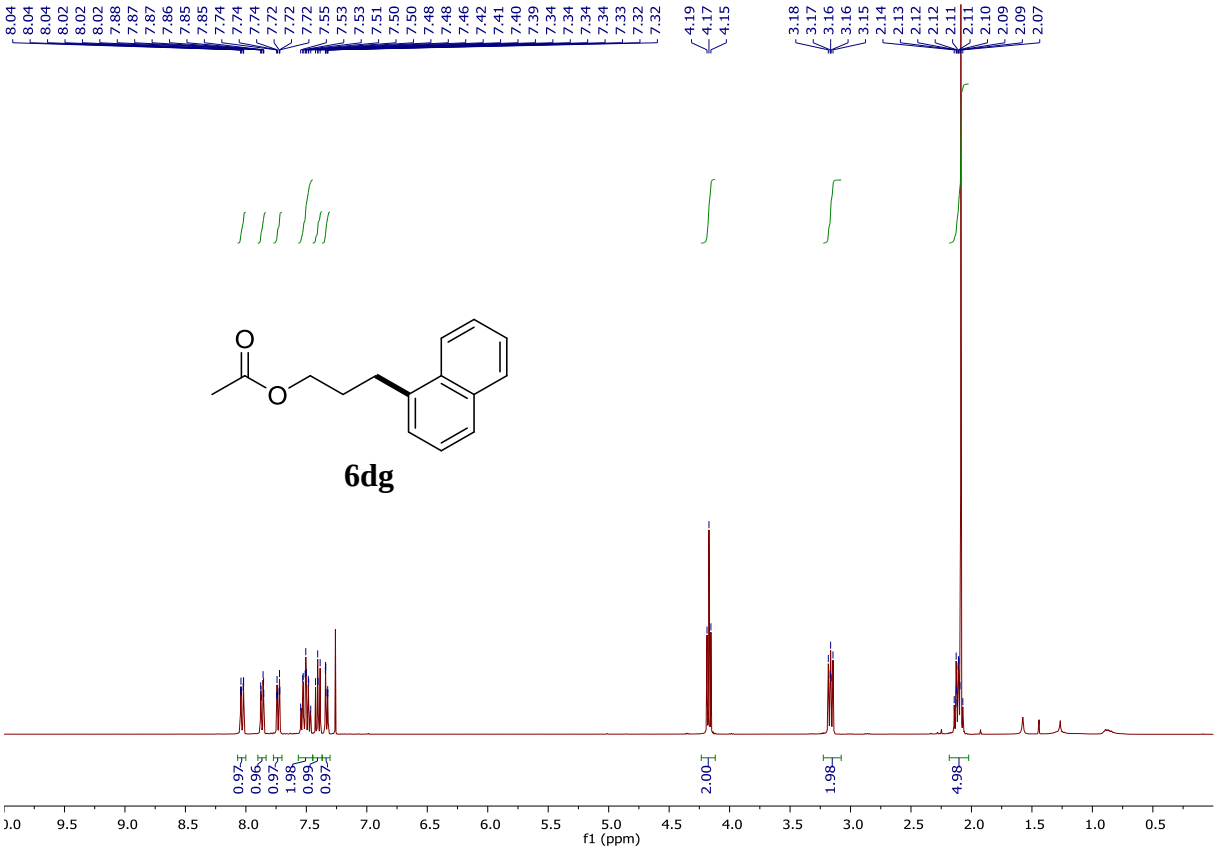
^{1}H spectrum of 6cg



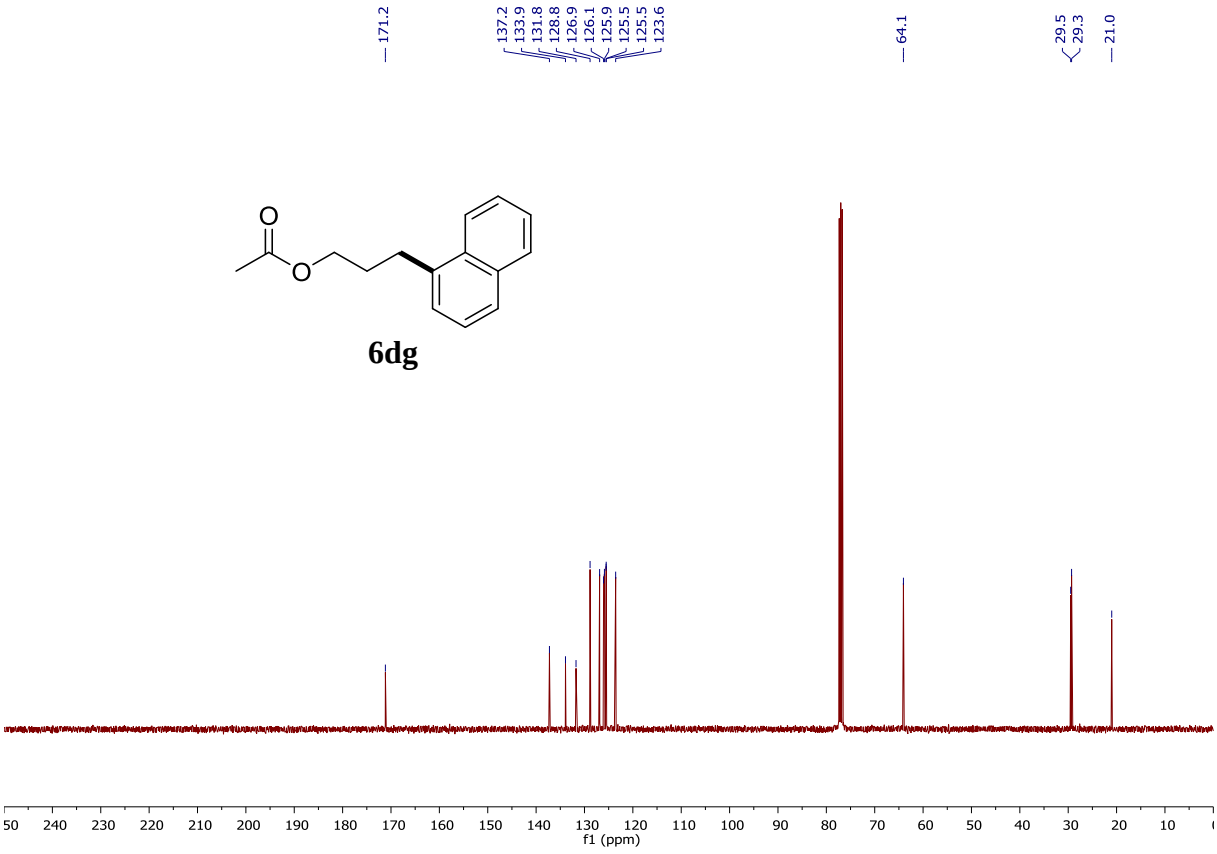
^{13}C spectrum of 6cg



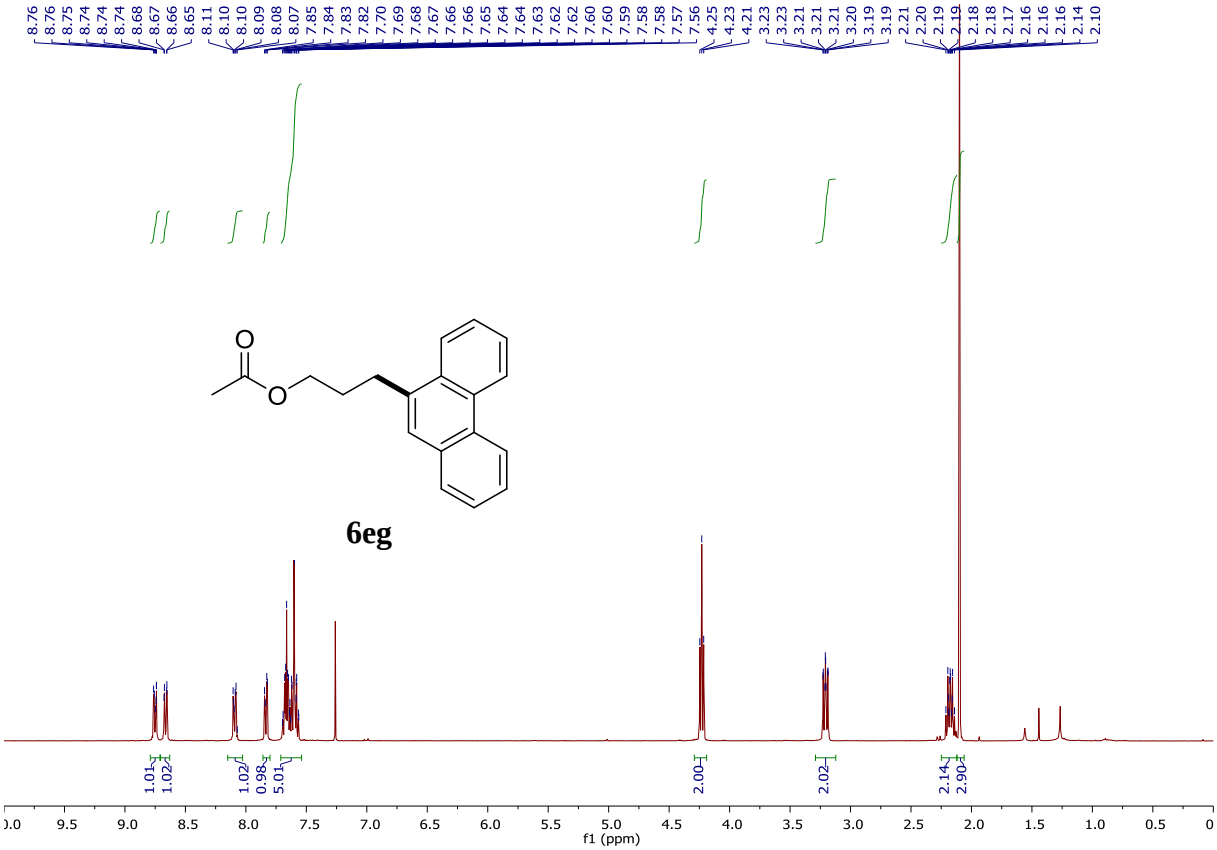
^{1}H spectrum of 6dg



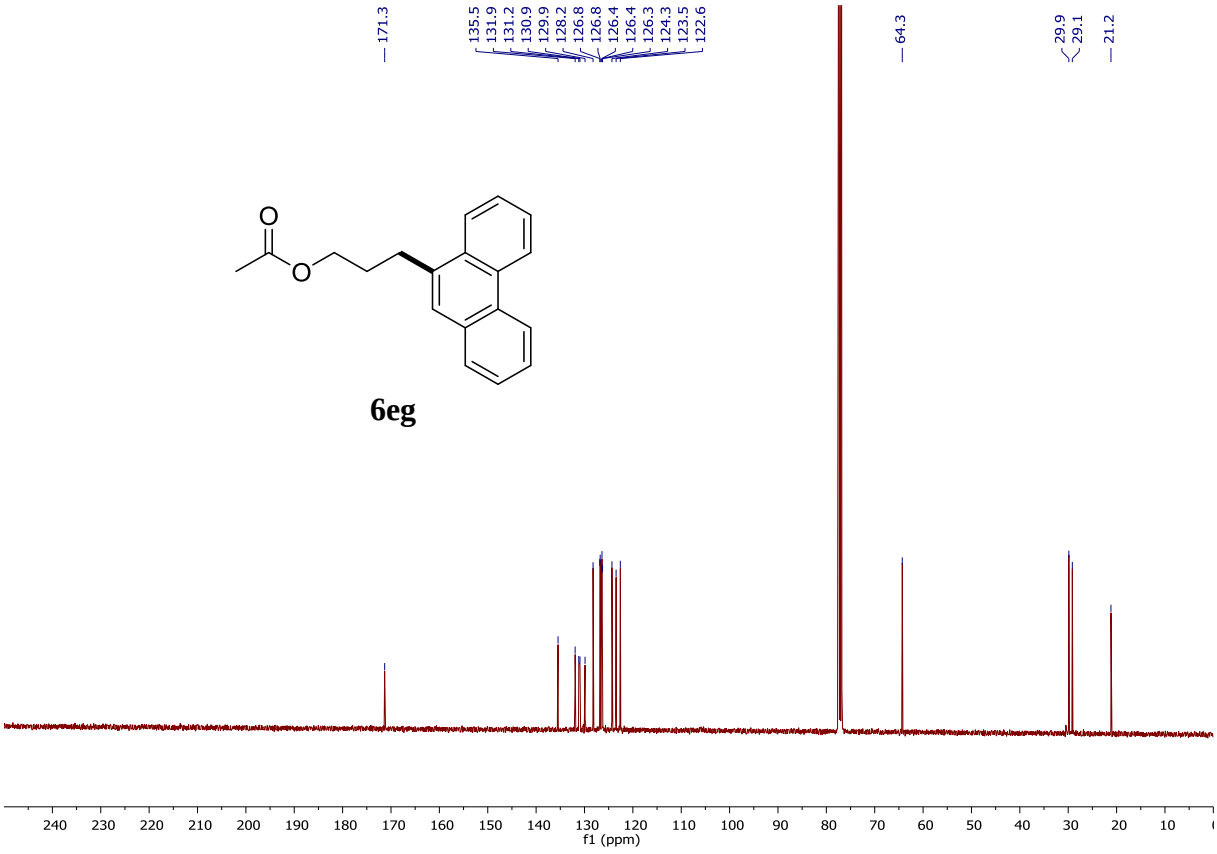
^{13}C spectrum of 6dg



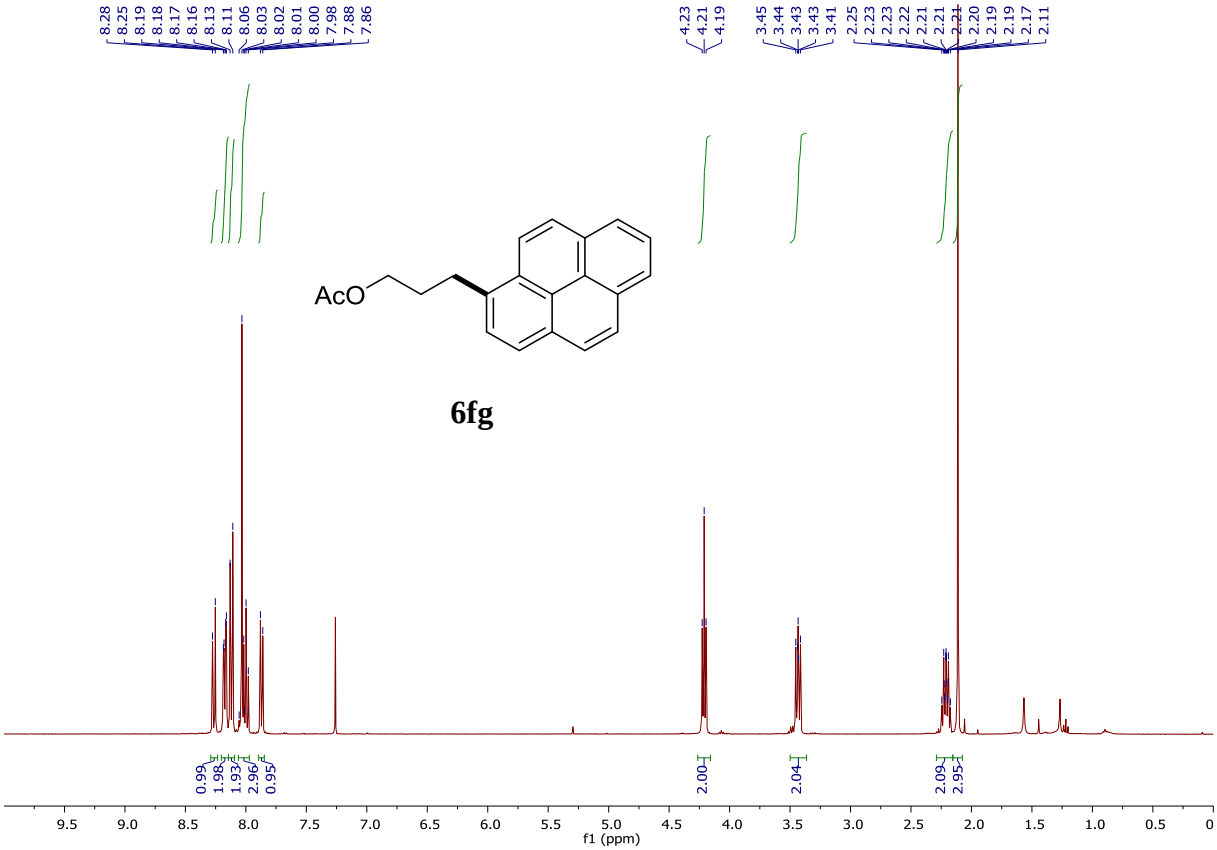
^{1}H spectrum of 6eg



^{13}C spectrum of 6eg

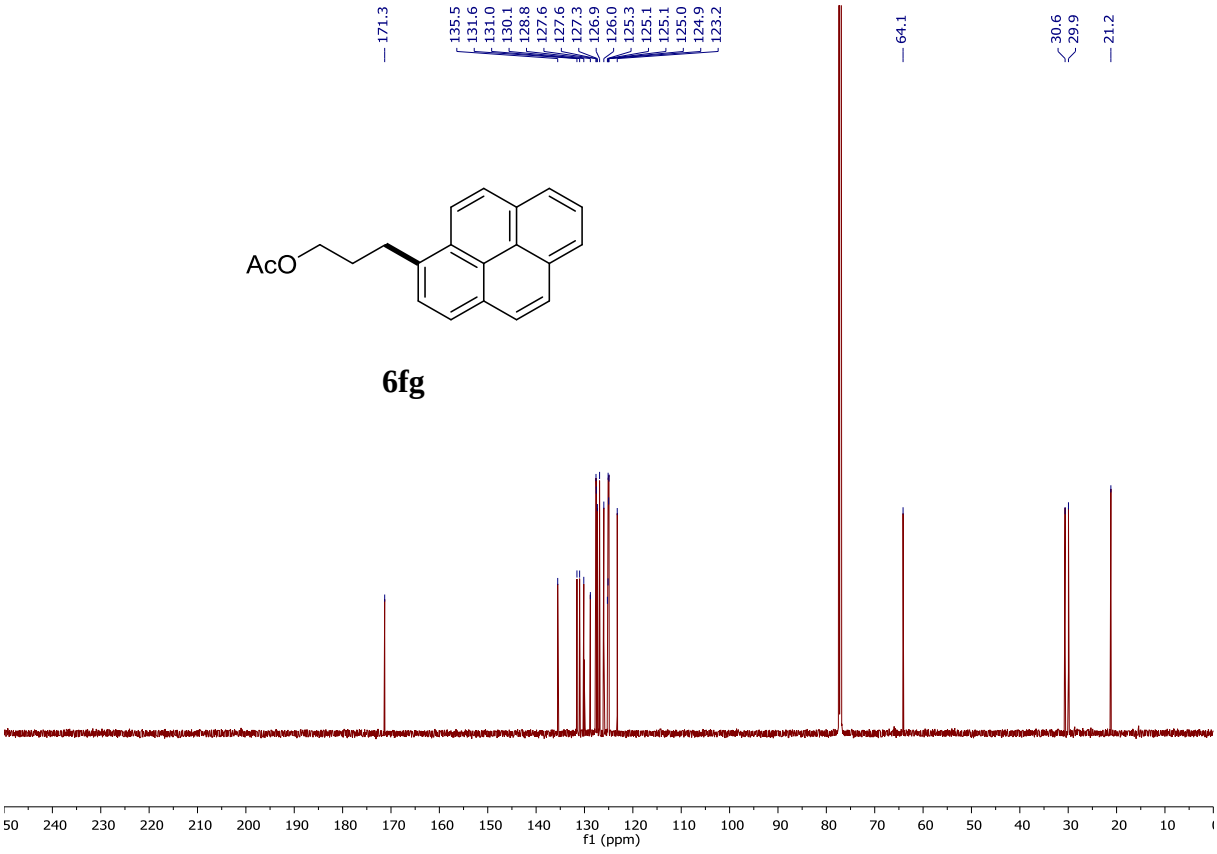


^{1}H spectrum of 6fg



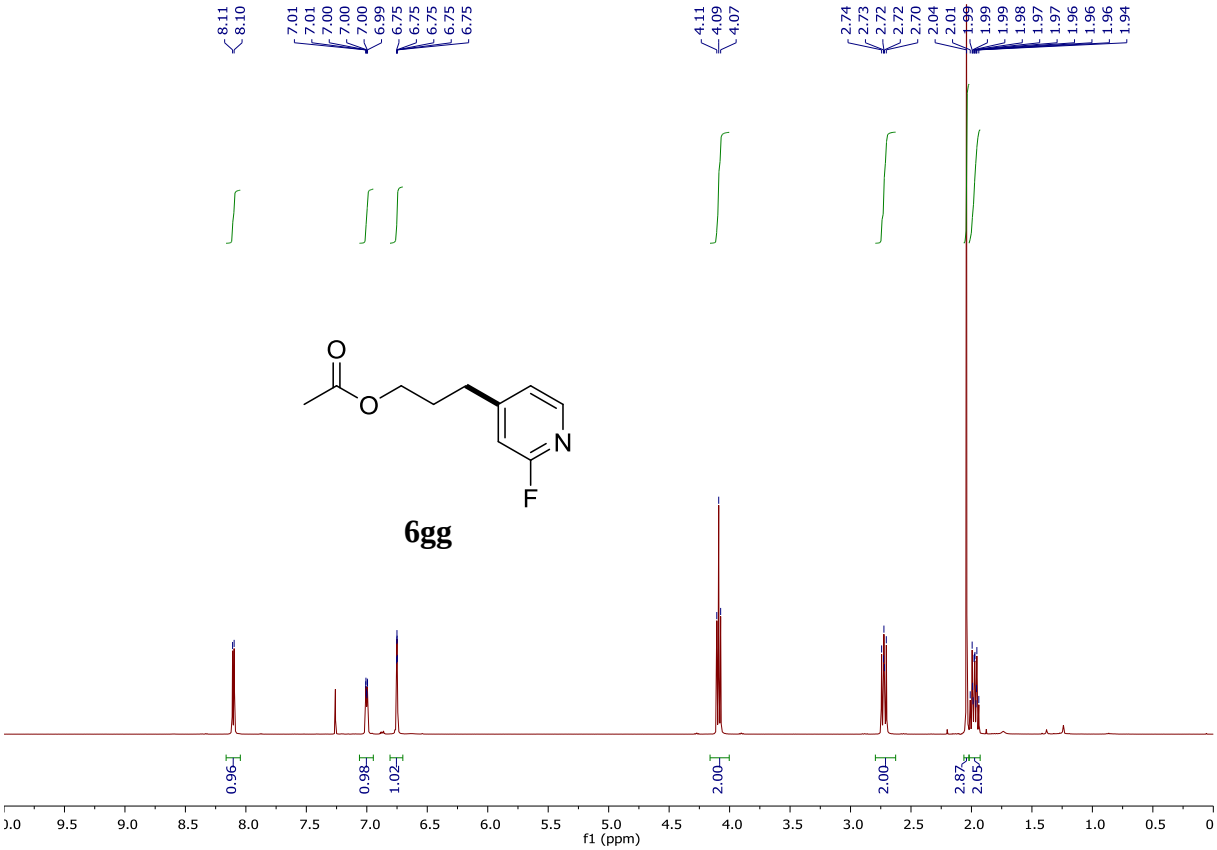
6fg

^{13}C spectrum of 6fg

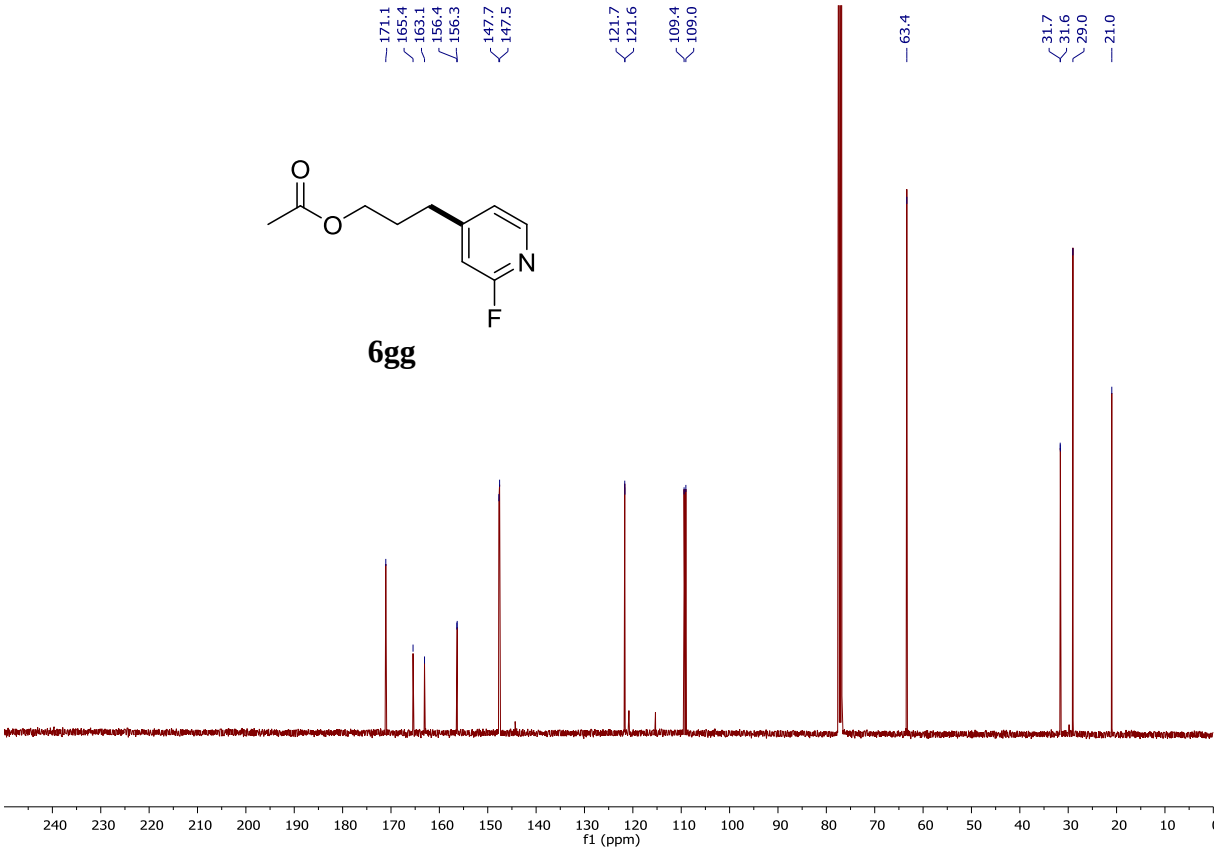


6fg

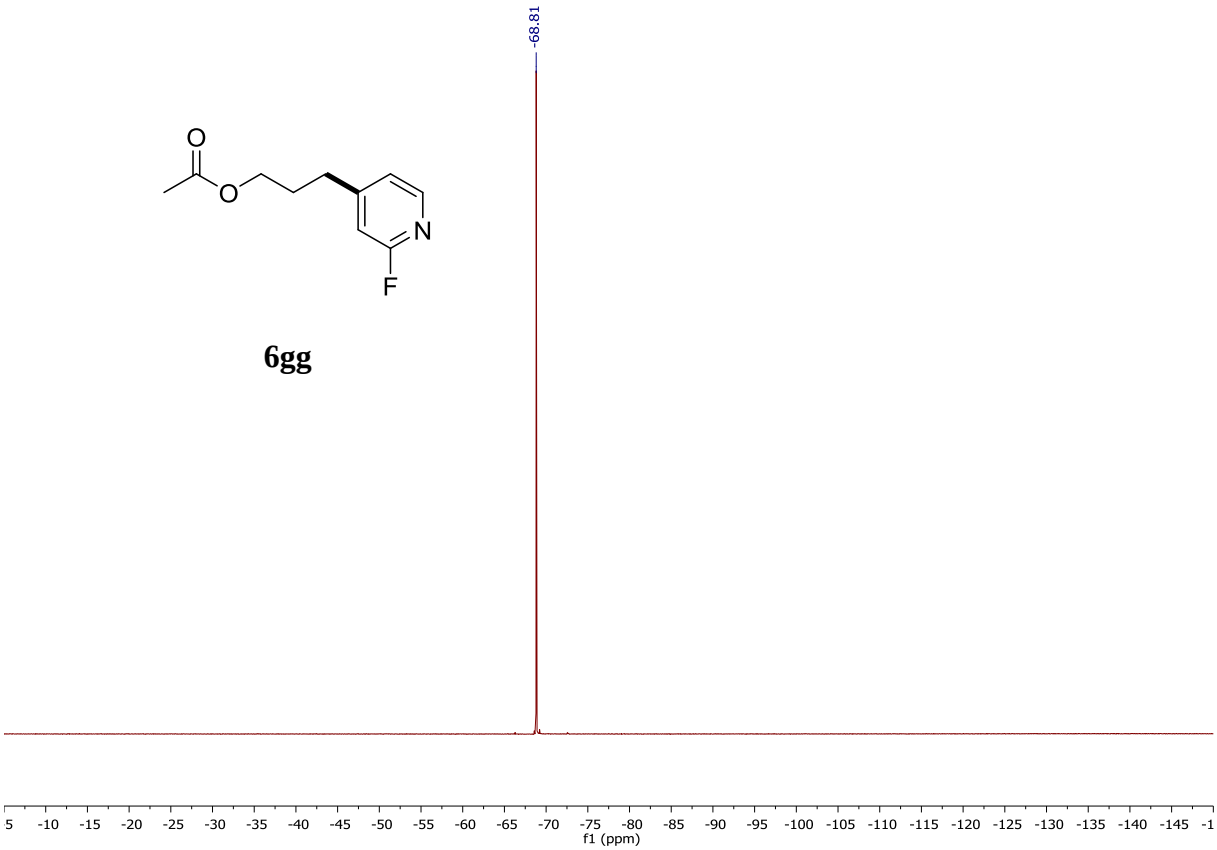
^{1}H spectrum of 6gg



^{13}C spectrum of 6gg

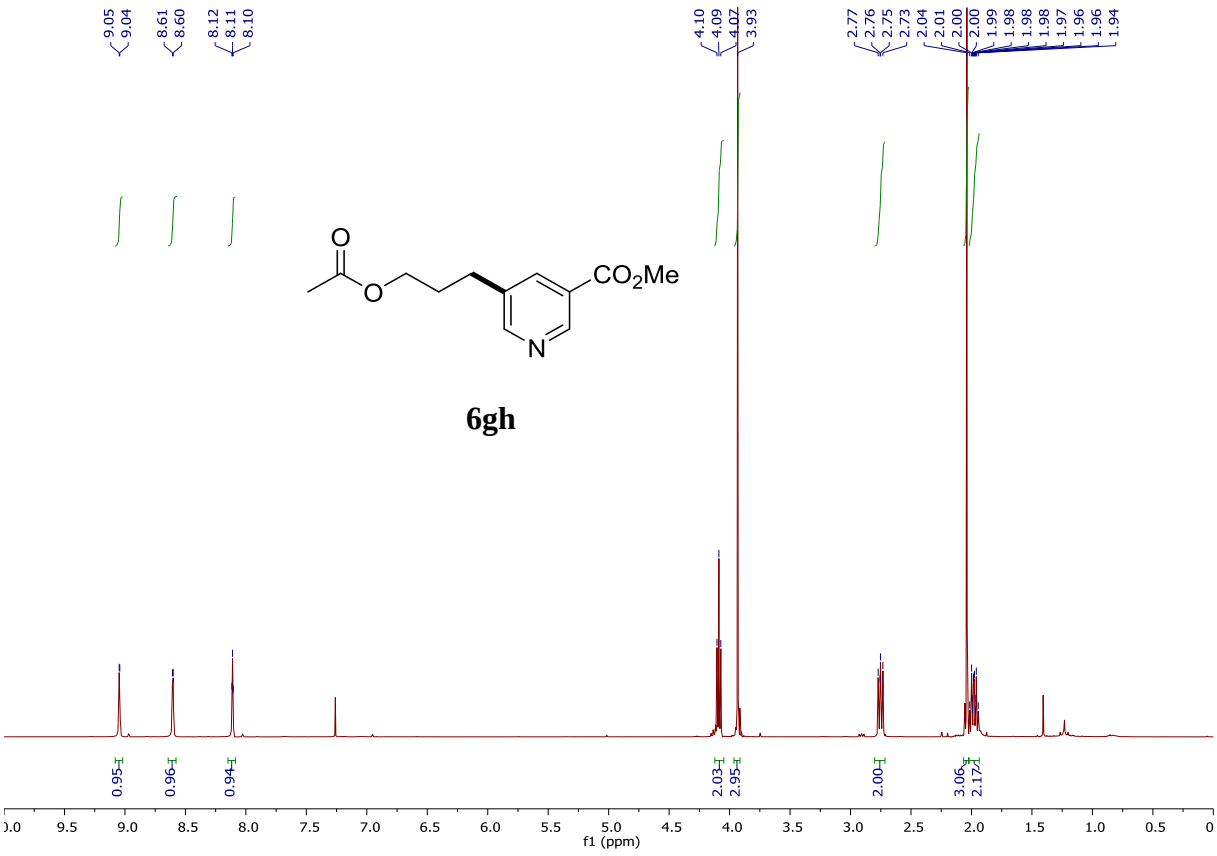


^{19}F spectrum of 6gg



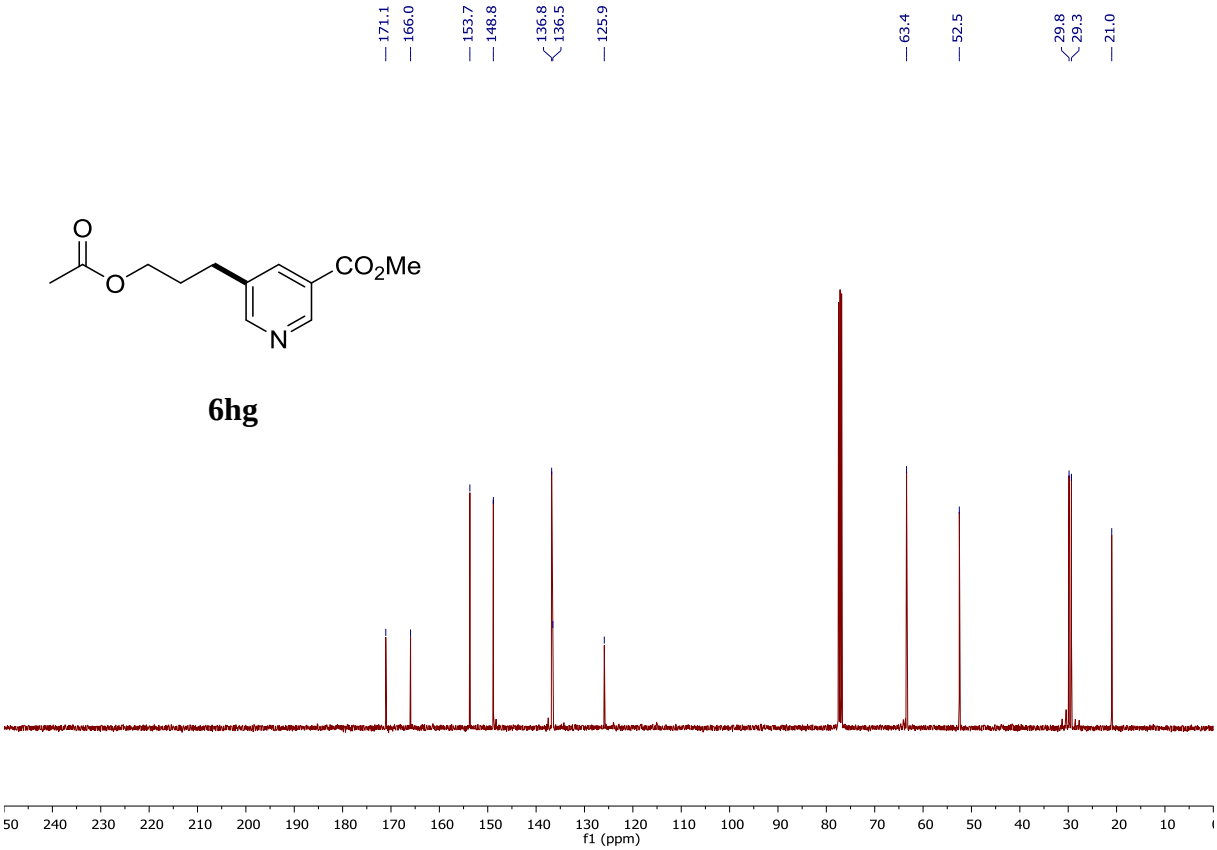
6gg

^{1}H spectrum of 6hg



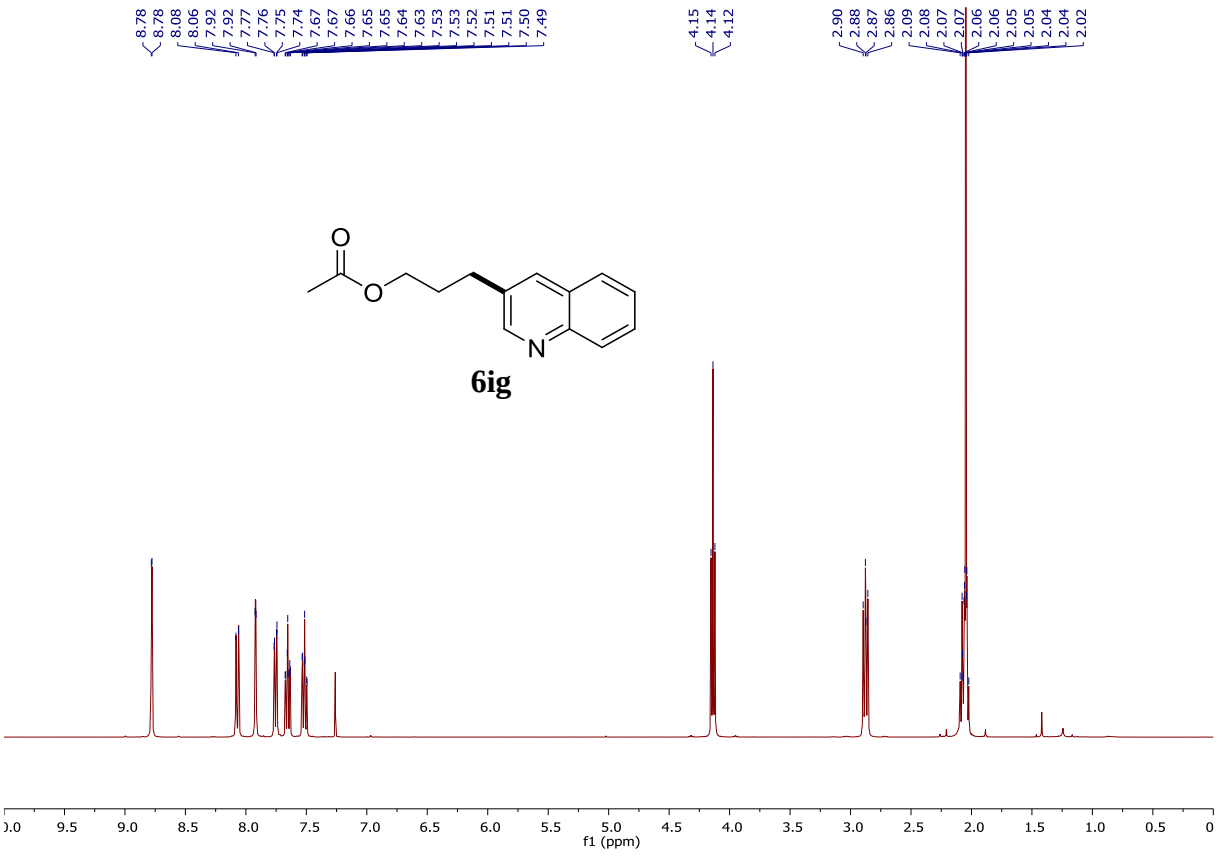
6gh

^{13}C spectrum of 6hg



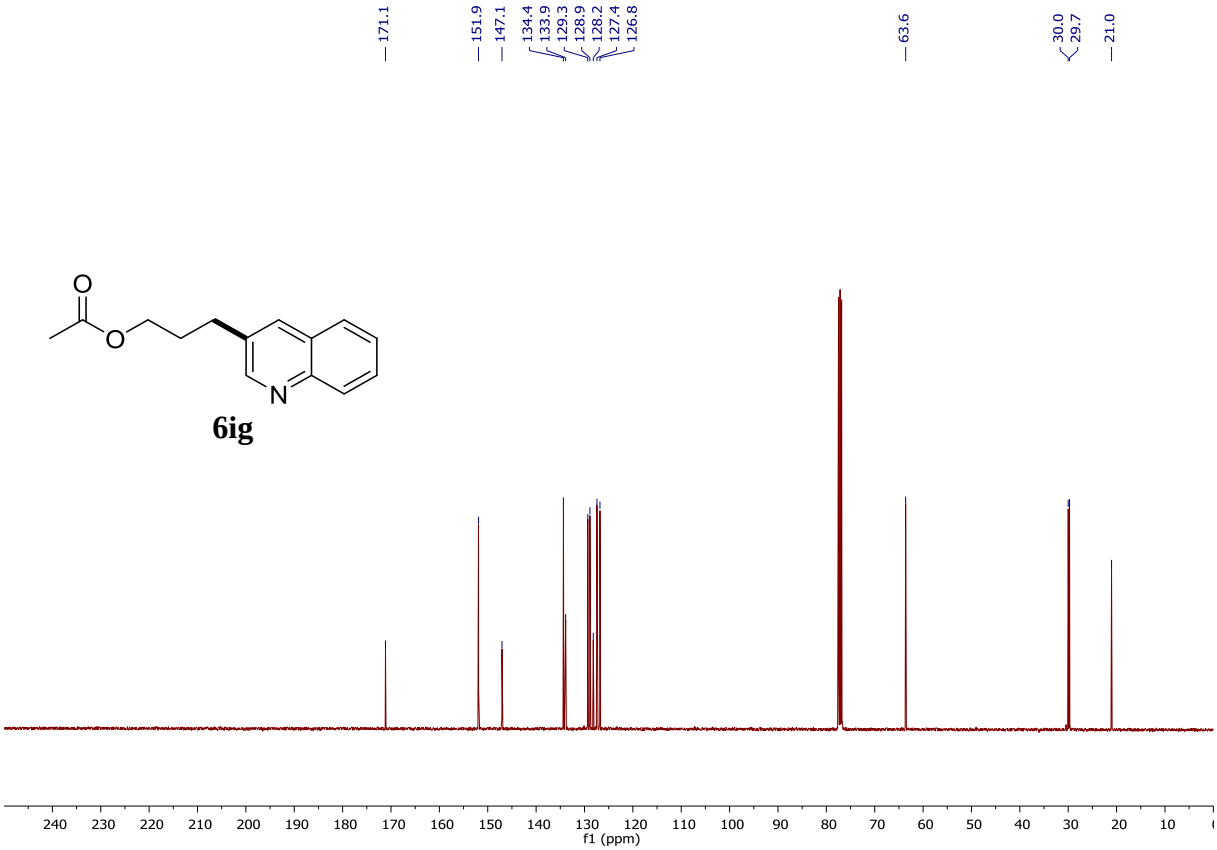
6hg

^{1}H spectrum of 6ig

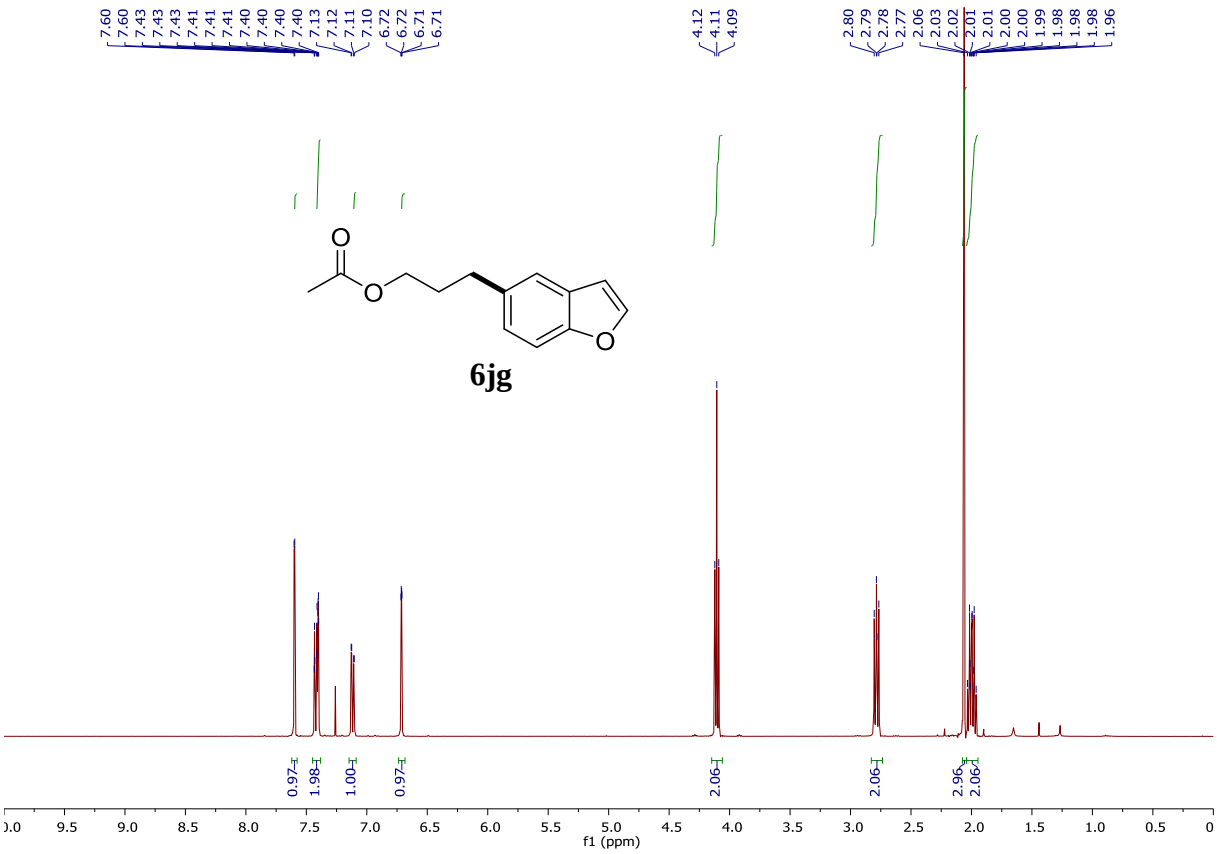


6ig

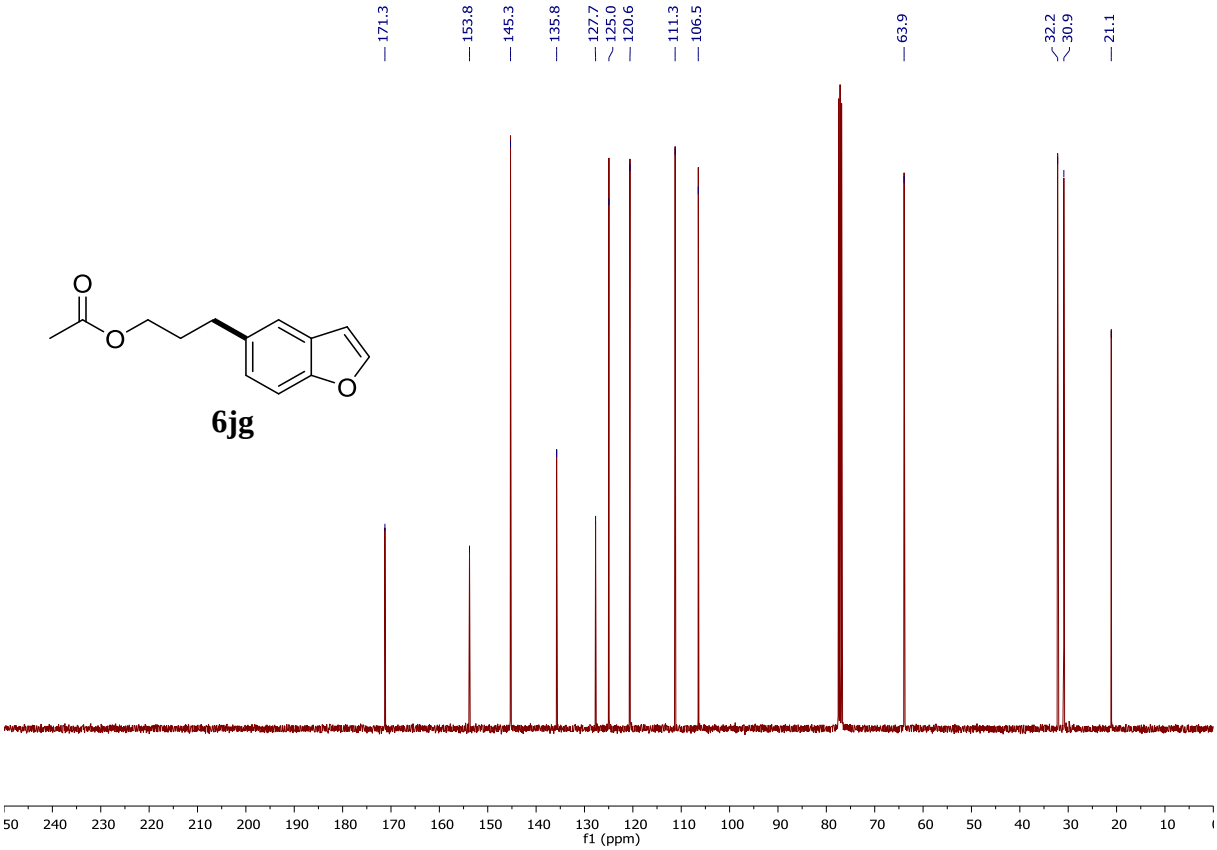
^{13}C spectrum of 6ig



^{1}H spectrum of 6jg

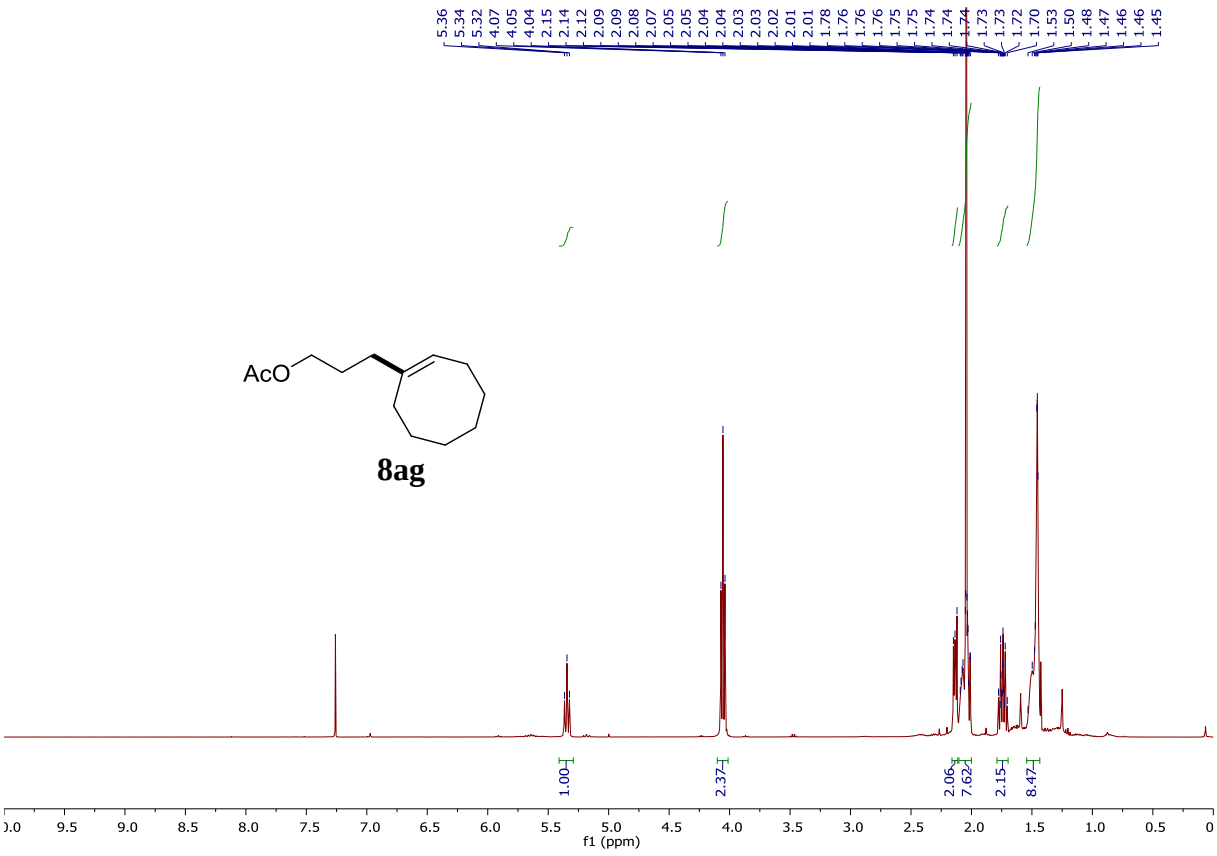


^{13}C spectrum of 6jg



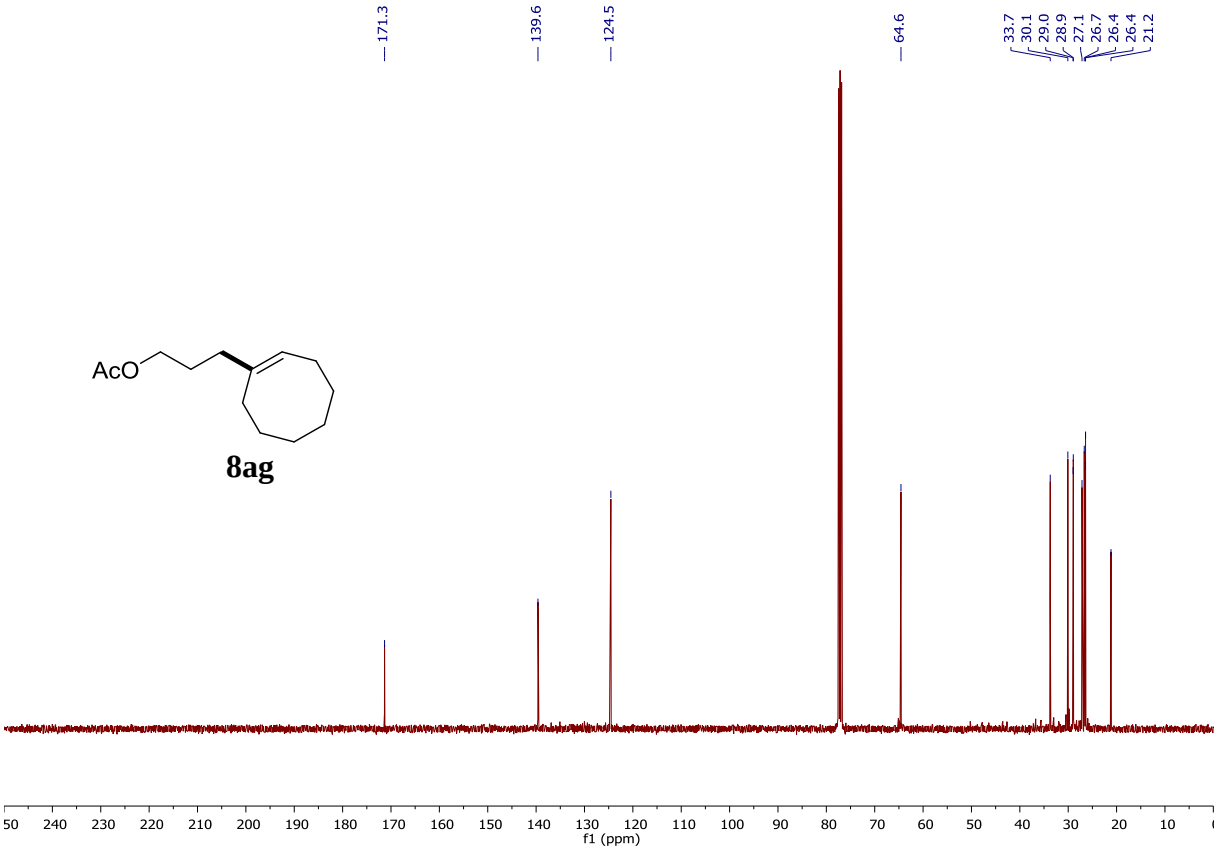
6jg

^{1}H spectrum of 8ag



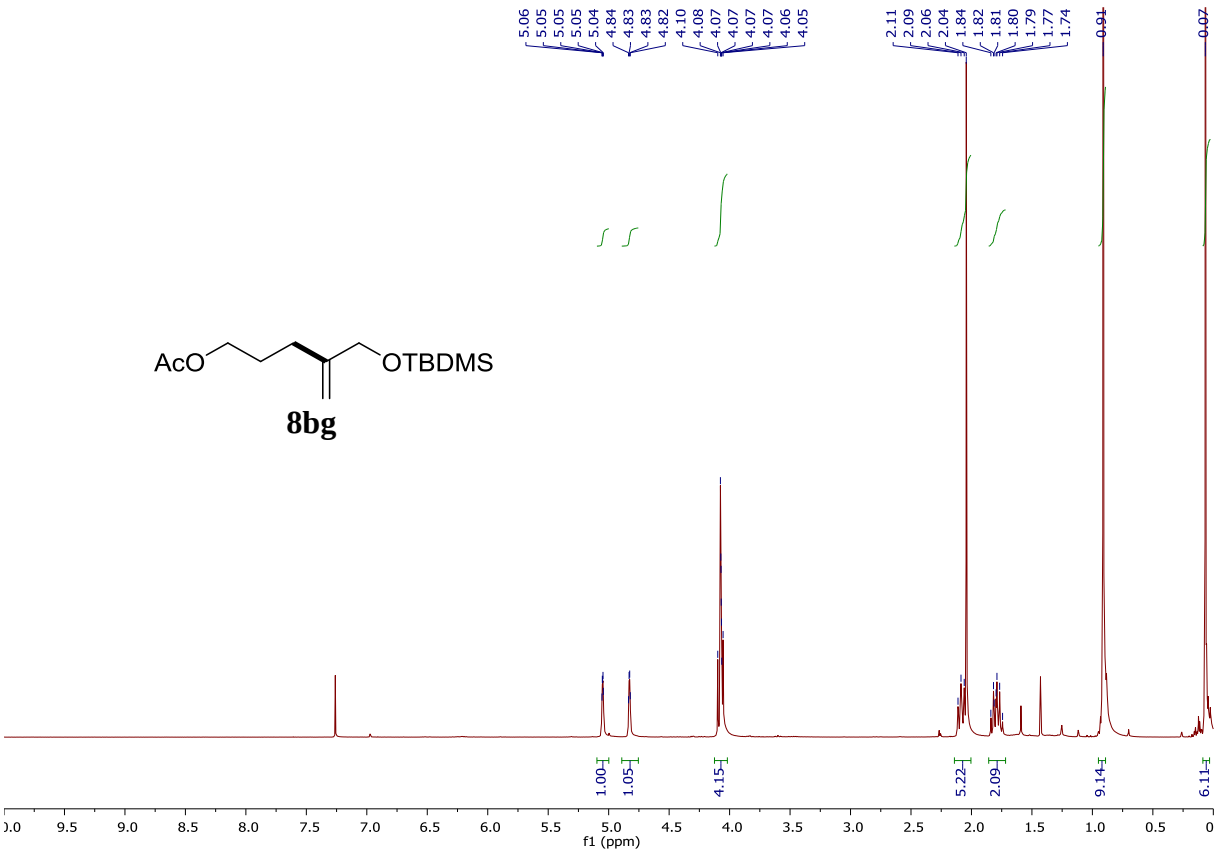
8ag

^{13}C spectrum of 8ag



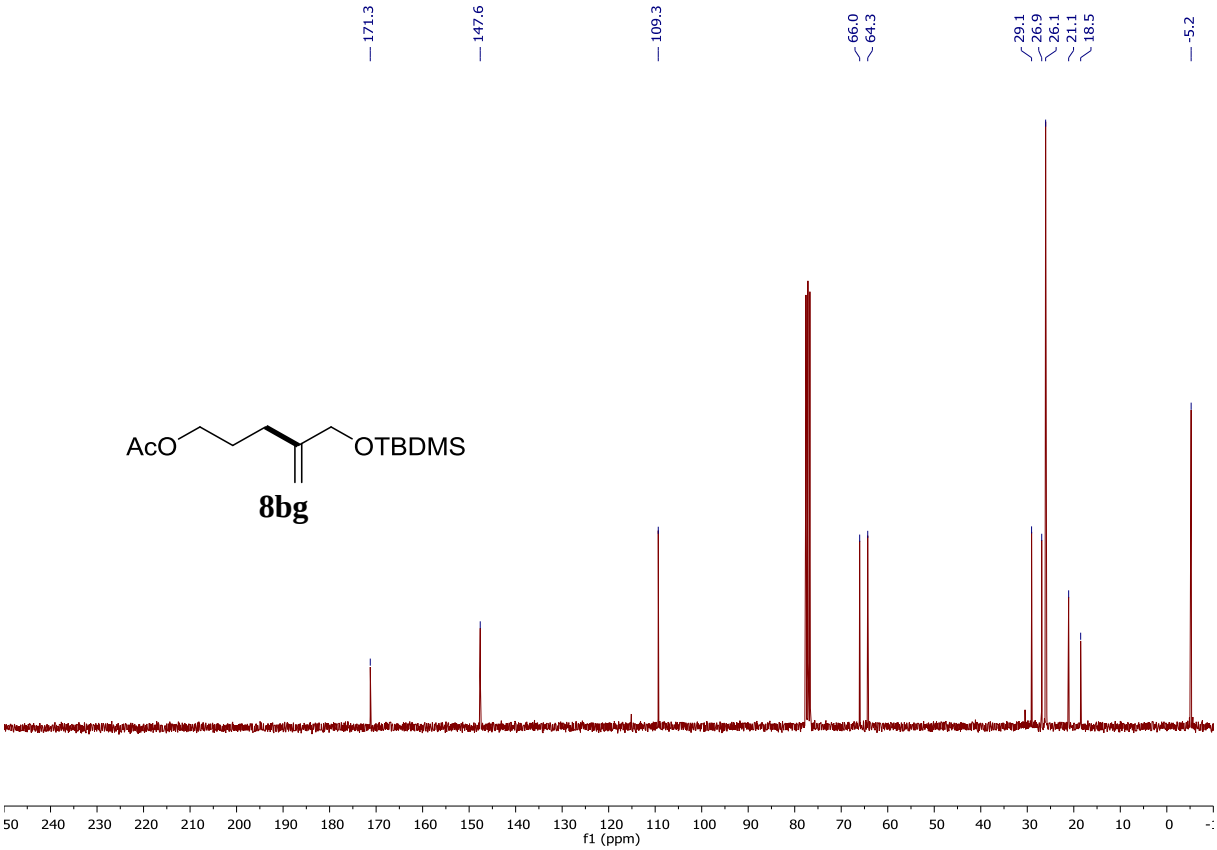
8ag

^{1}H spectrum of 8bg

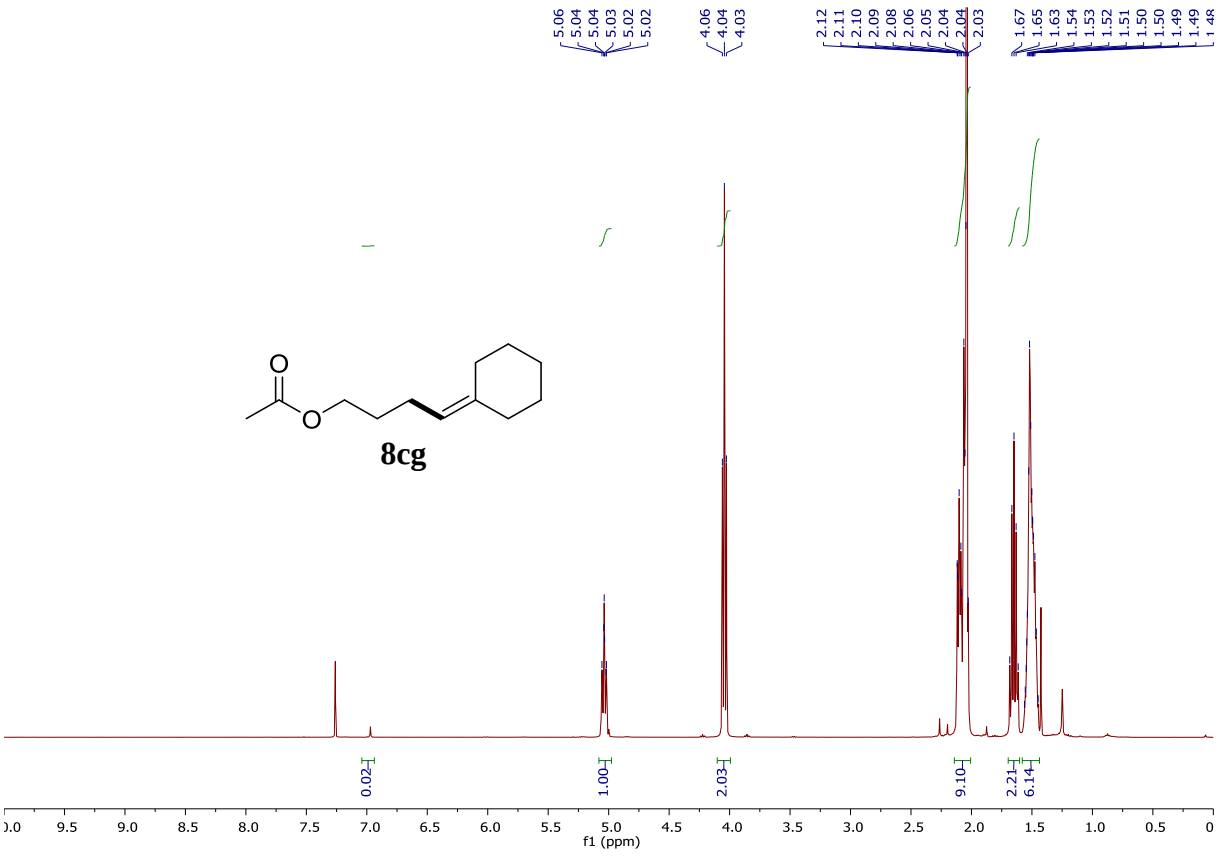


8bg

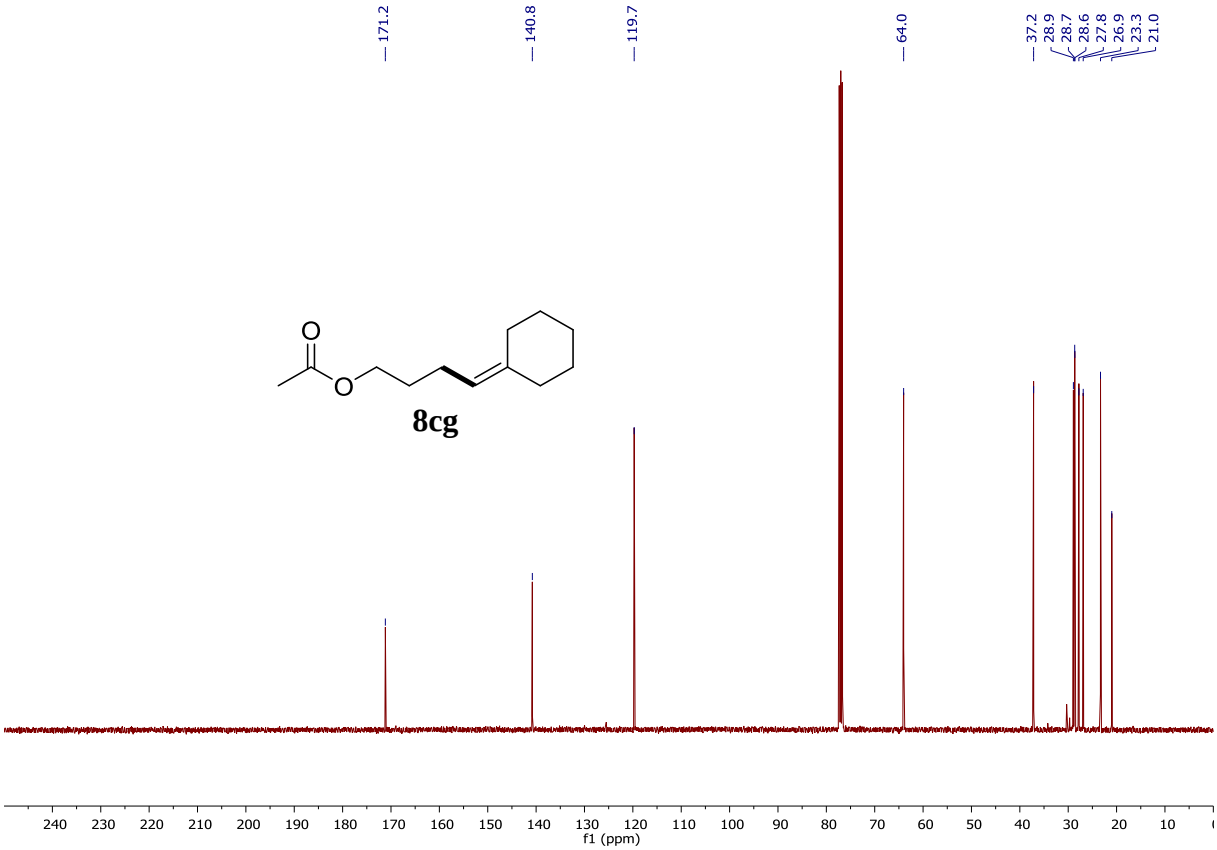
^{13}C spectrum of 8bg



^{1}H spectrum of 8cg

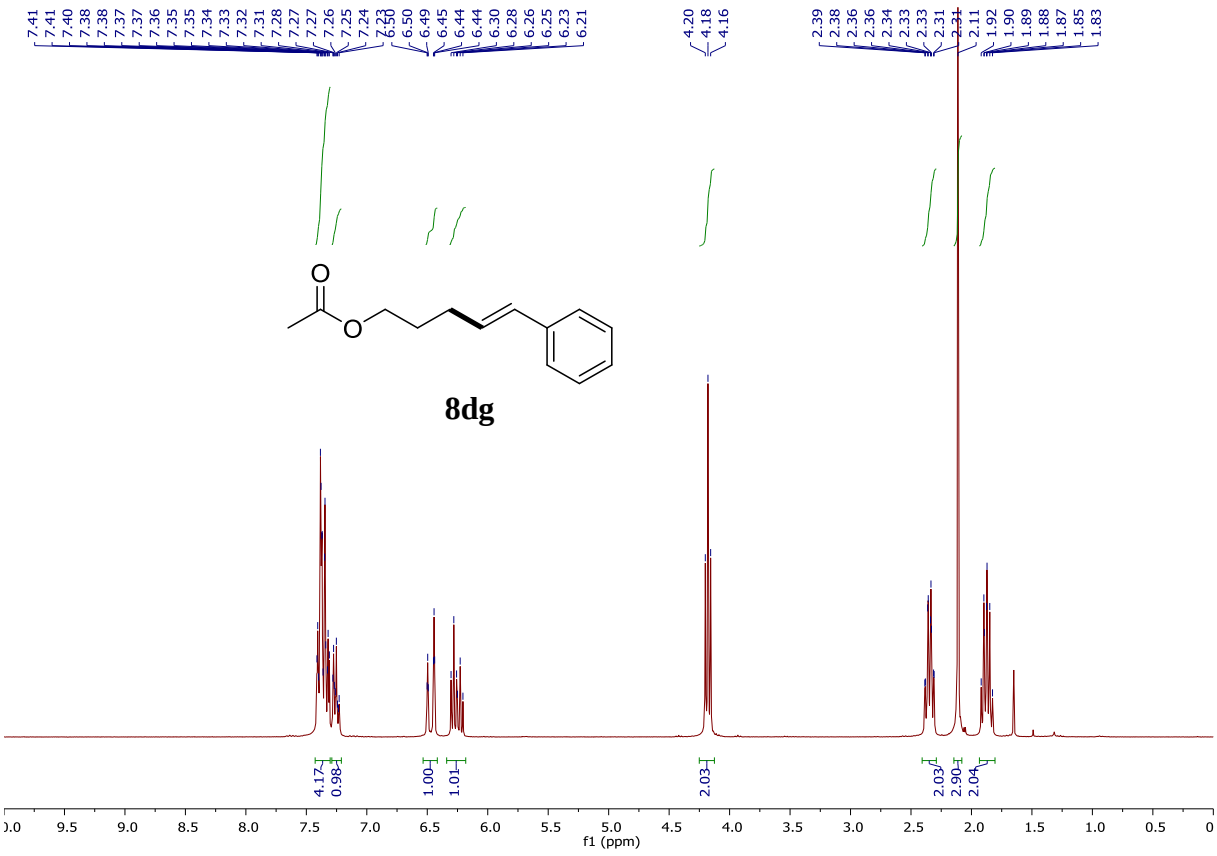


^{13}C spectrum of 8cg



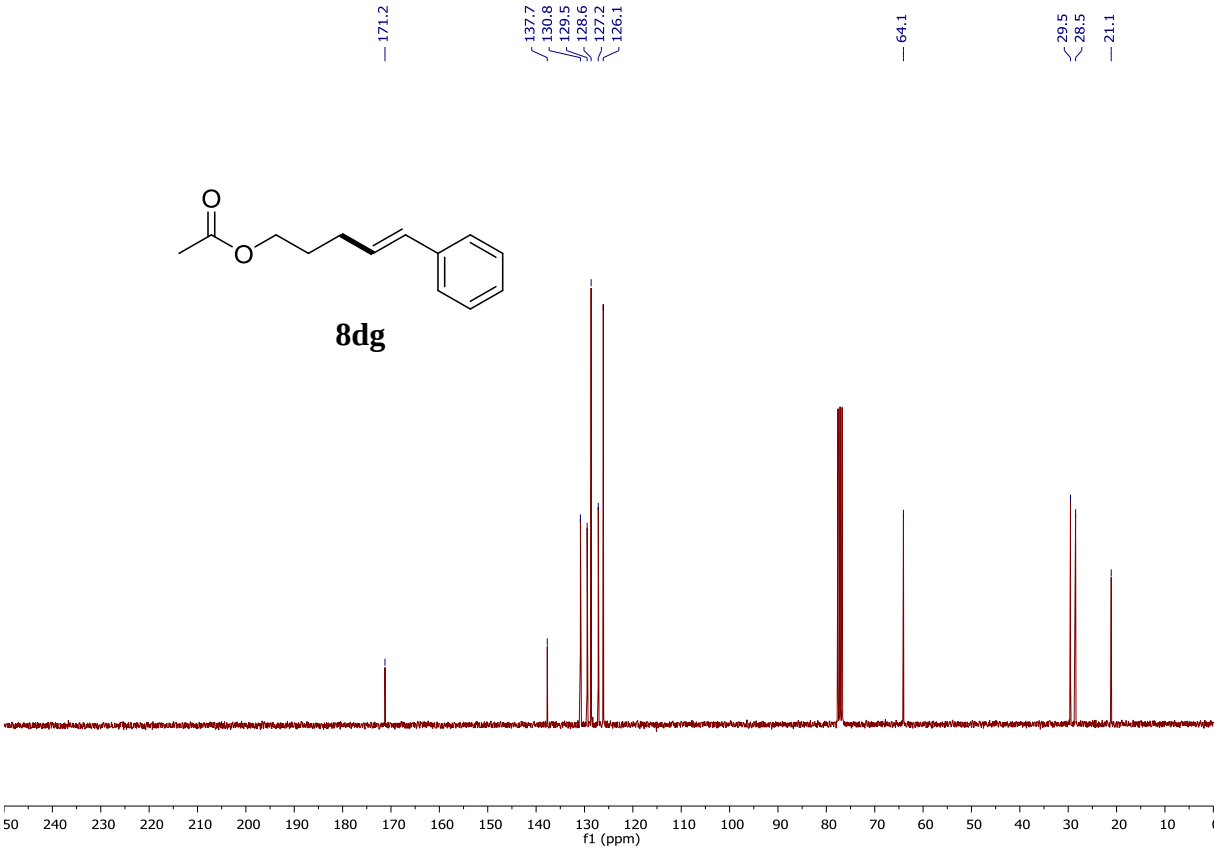
8cg

^{1}H spectrum of 8dg

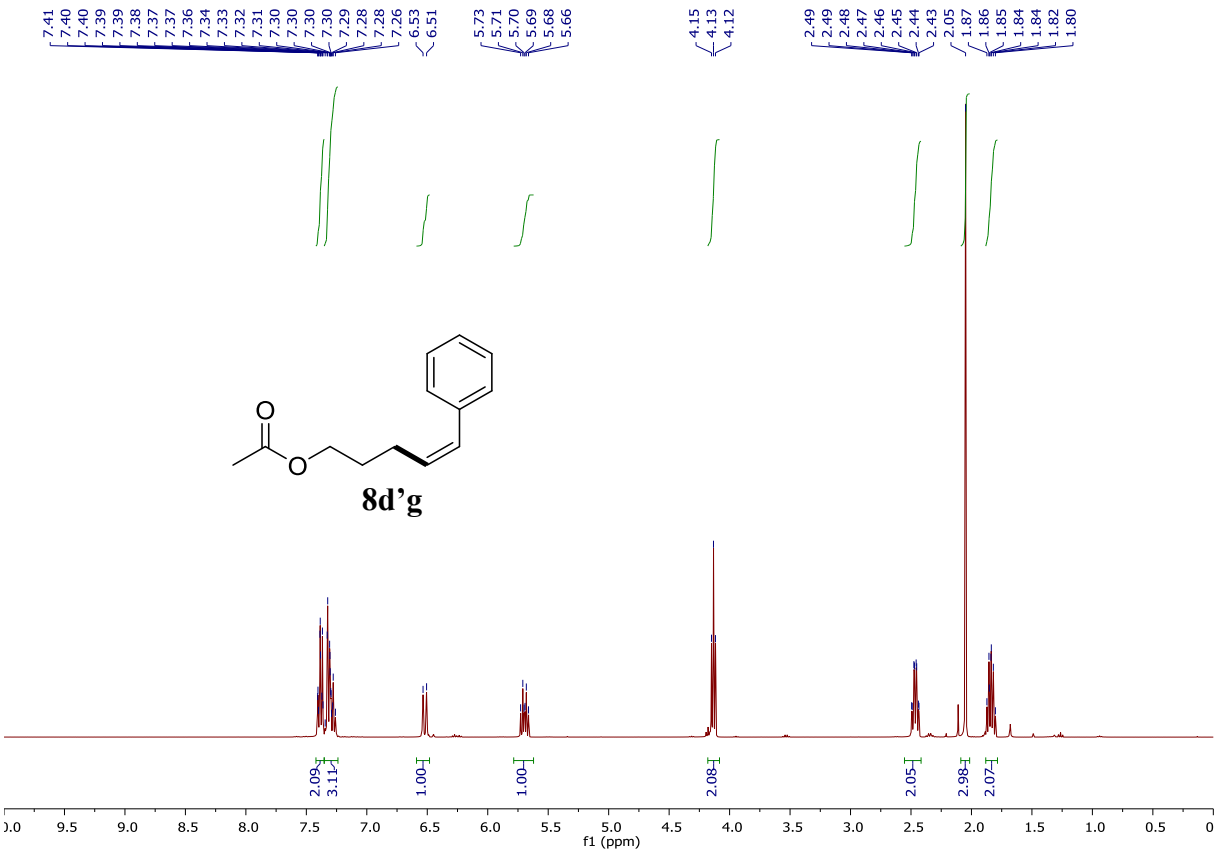


8dg

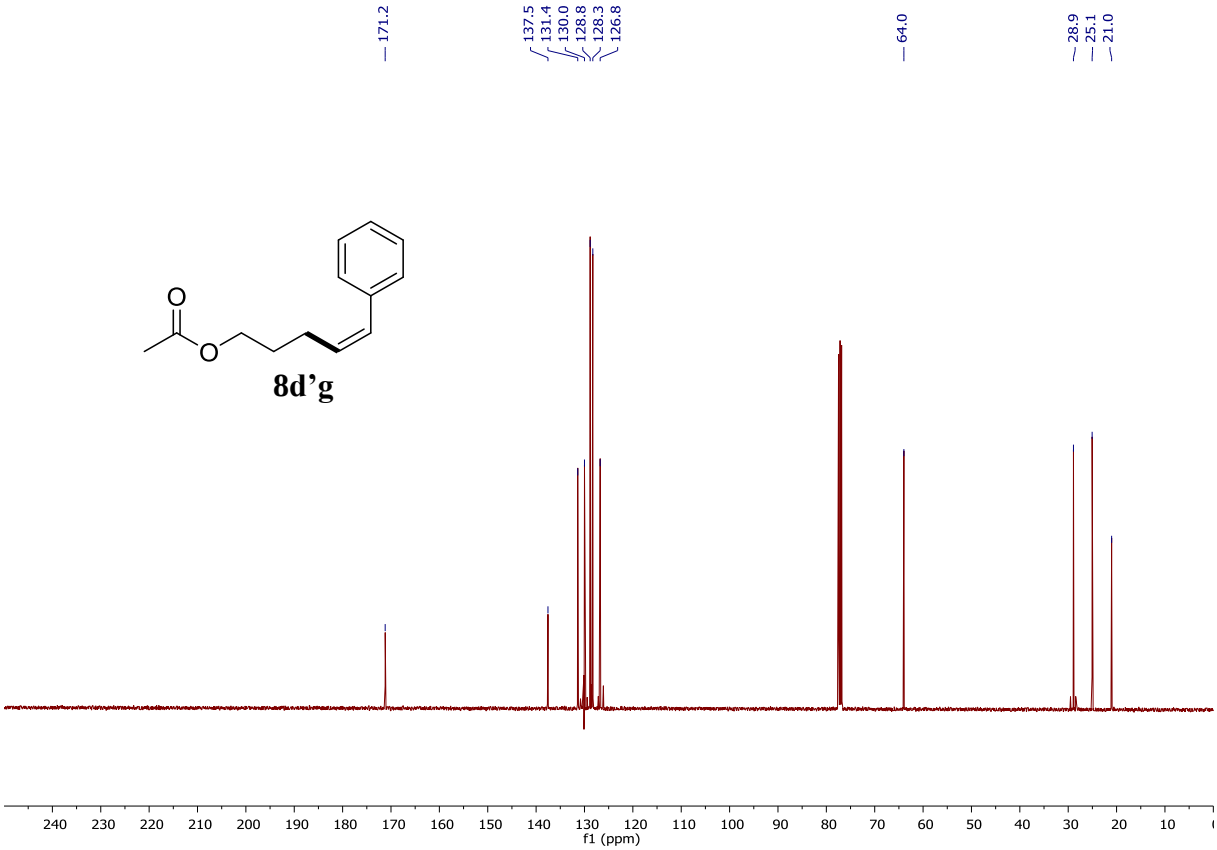
^{13}C spectrum of dg



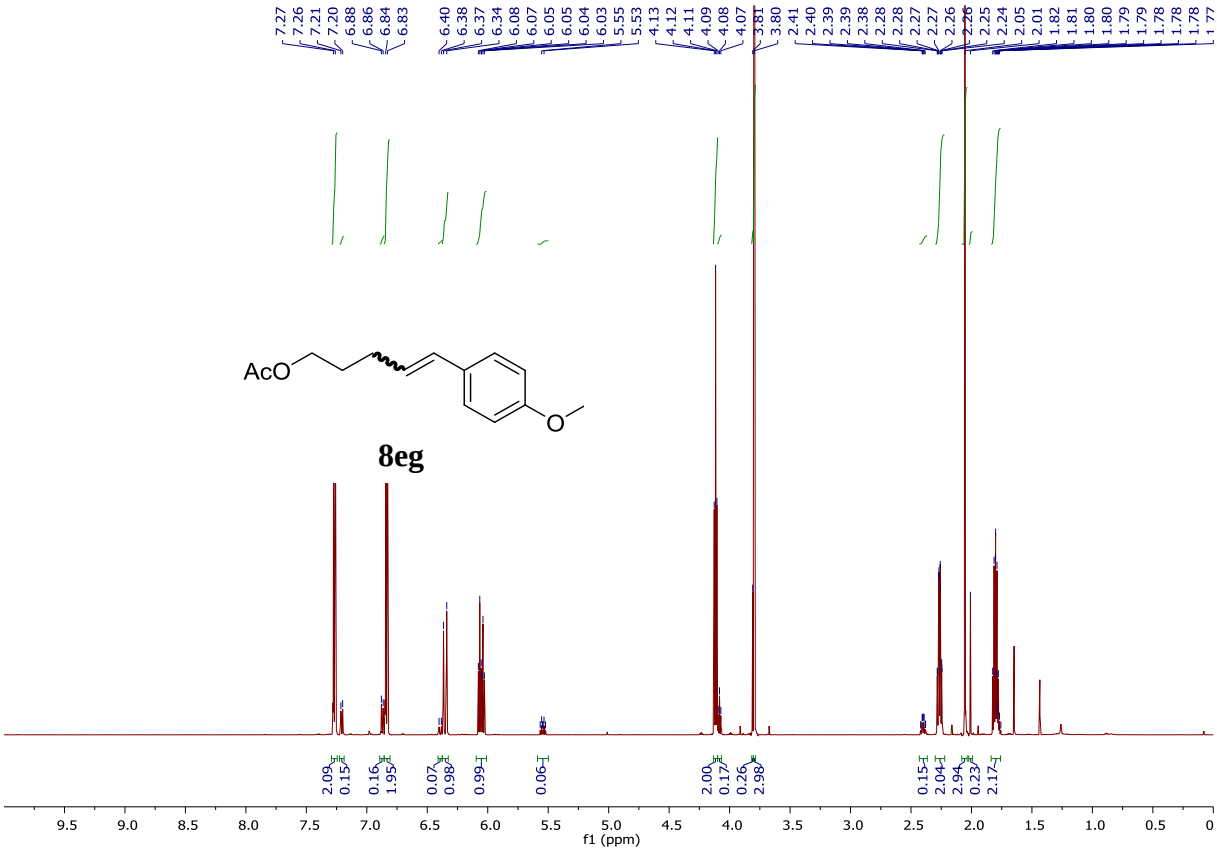
^{1}H spectrum of 8d'g



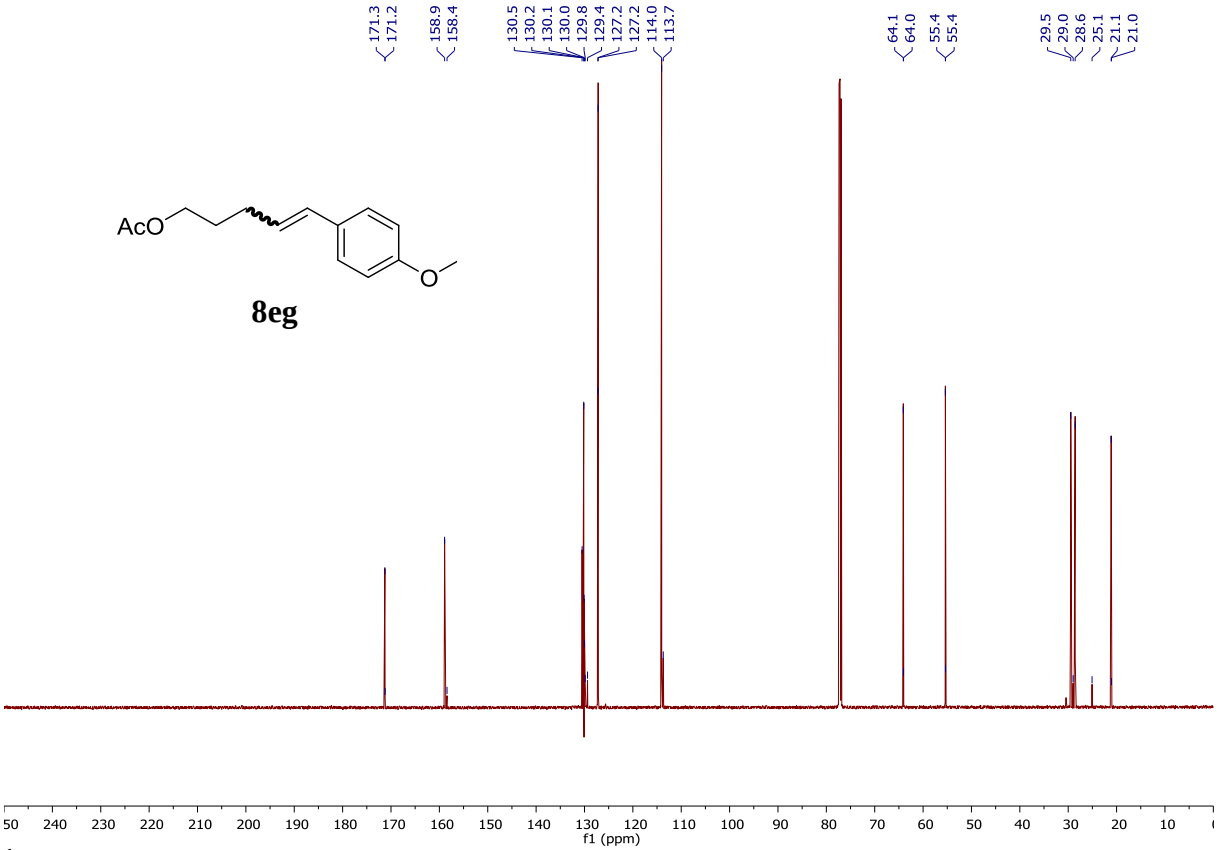
^{13}C spectrum of 8d'g



^{1}H spectrum of 8eg

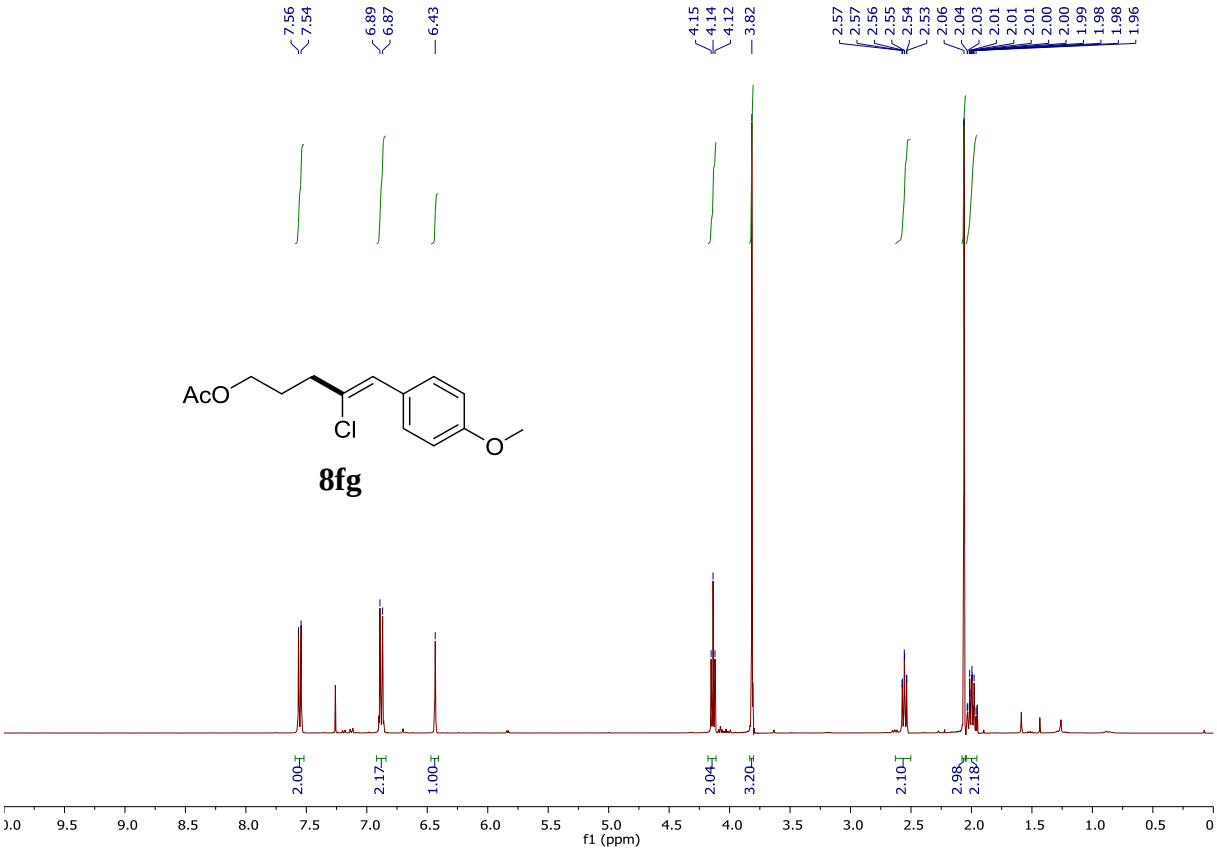


^{13}C spectrum of 8eg



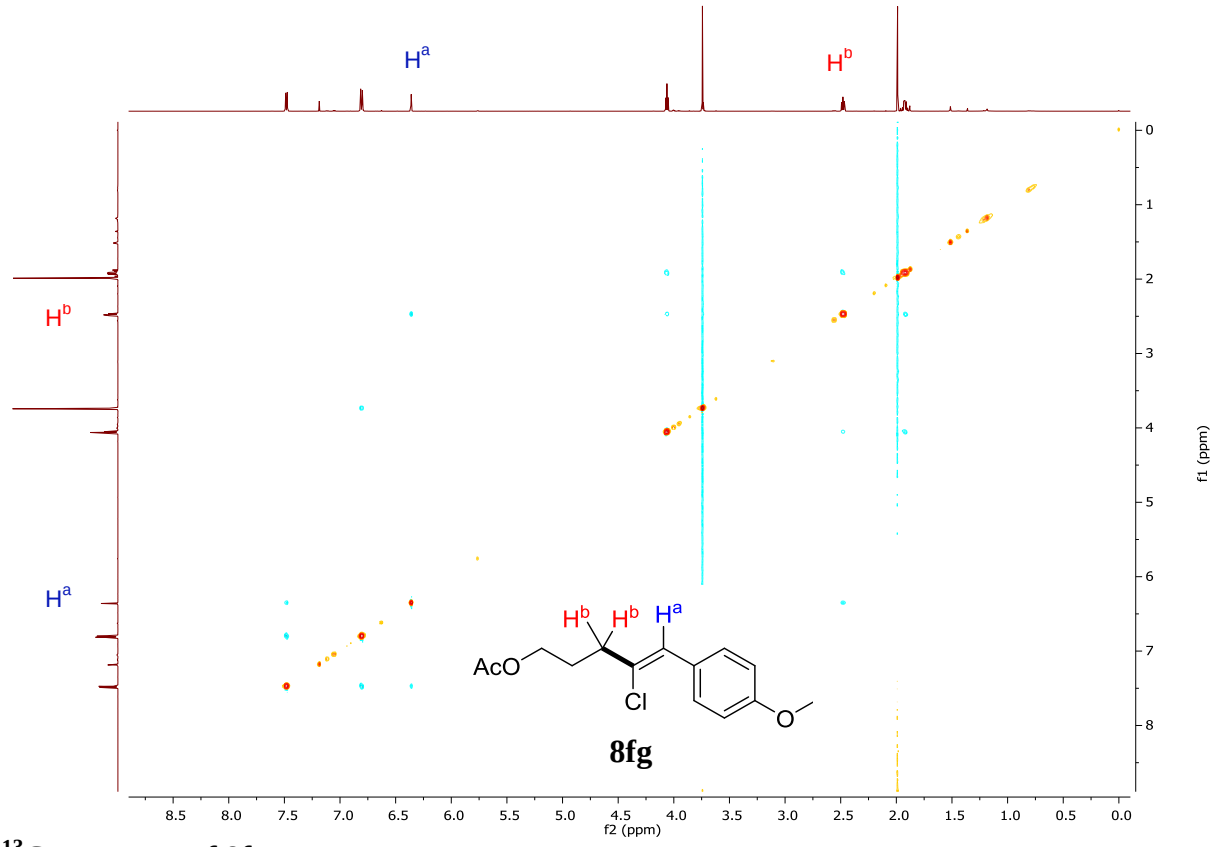
8eg

^{1}H spectrum of 8fg

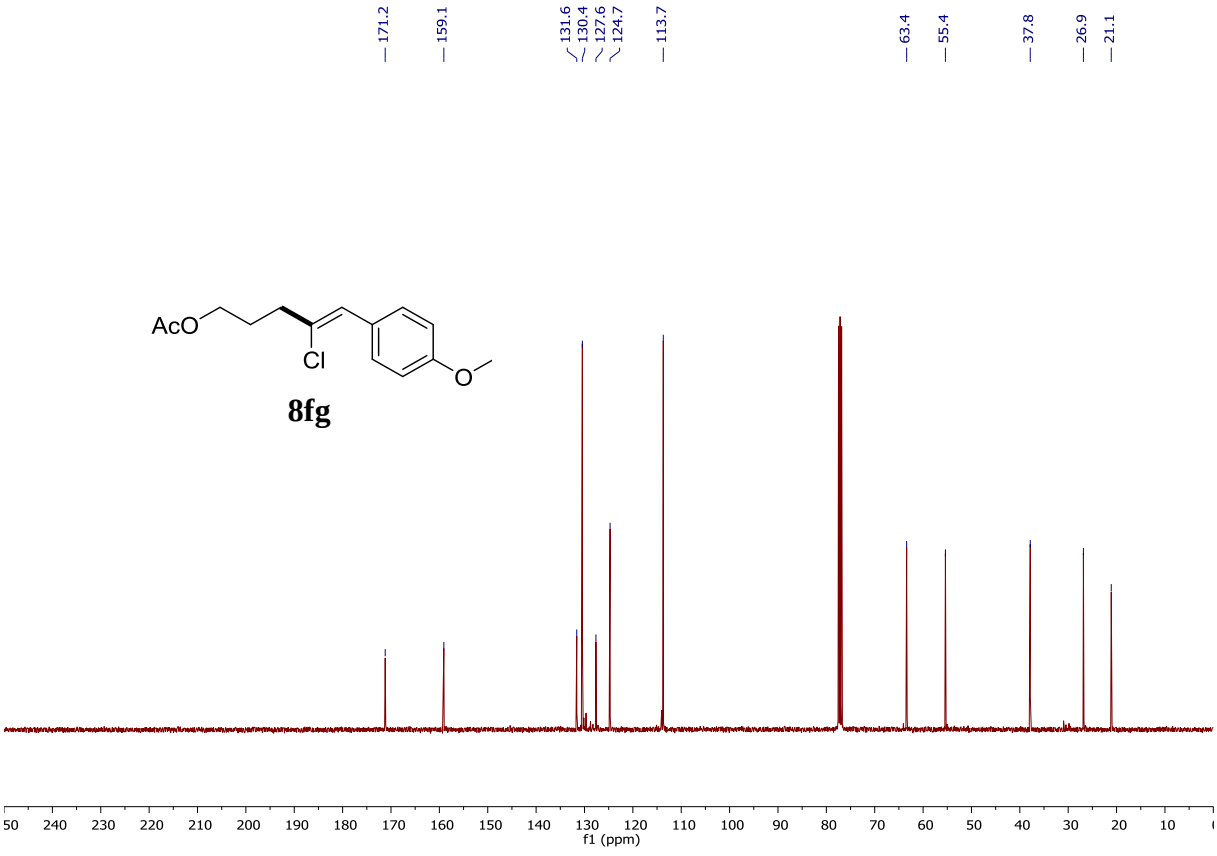


8fg

NOESY of 8fg



^{13}C spectrum of 8fg



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