ELECTRONIC SUPPORTING INFORMATION

For

Chemoselective Homologative Preparation of Trisubstituted Alkenyl Halides from Carbonyls and Carbenoids

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TABLE OF CONTENTS

Materials and methods

Melting Points were determined on a Reichert-Kofler hot-stage microscope and are uncorrected. Mass spectra were obtained on a Shimadzu QP 1000 instrument (EI, 70 eV) and on a Bruker maXis 4G instrument (ESI-TOF, HRMS). ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker Avance III 400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C, 40 MHz for ^{15}N, 376 MHz for ^{19}F) at 297 K using a, directly detecting broadband observe (BBFO) probe. The centre of the solvent signal was used as an internal standard which was related to TMS with δ 7.26 ppm (^{1}H in $CDCl_3$), δ 77.00 ppm (^{13}C in $CDCl_3$). ^{15}N spectra (gsHMBC) were referenced against neat, external nitromethane, ^{19}F NMR spectra by absolute referencing via *Ξ* ratio. Spin-spin coupling constants (*J*) are given in Hz.

In nearly all cases, full and unambiguous assignment of all resonances was performed by combined application of standard NMR techniques, such as APT, HSQC, HMBC, COSY and NOESY experiments.

All the reactions were carried out under inert atmosphere of argon. THF was distilled over Na/benzophenone. Chemicals were purchased from Sigma-Aldrich, Acros, Alfa Aesar and TCI Europe. Solutions were evaporated under reduced pressure with a rotary evaporator.

TLC was carried out on aluminium sheets precoated with silica gel 60F254 (Merchery-Nagel, Merk); the spots were visualised under UV light (λ = 254 nm).

General procedure

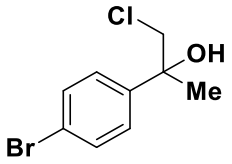
General Procedure 1

To a solution of carbonyl compound (aldehyde or ketone, 1 equiv) in dry THF (3 mL) cooled at -78 °C, the dihalomethane carbenoids precursor was added (1.5 equiv) under Argon atmosphere. After 10 min, MeLi-LiBr 2.2 M solution in diethyl ether (1.4 equiv) was added dropwise during a period of 15 min and, then the stirring was continued for additional 0.5 h. freshly distilled thionyl chloride (1.5 equiv) was added dropwise with good stirring at -78 °C during a period of 10 min. After the addition of thionyl chloride had been completed, the reaction mixture was stirred at rt for 30 min. The mixture was quenched with saturated (*aq.*) NH_4Cl (3 mL) and extracted with diethylether (3 mL). The organic layer was washed with saturated (*aq.*) NaCl (5 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure (bath: rt) to give the crude compound eventually purified as indicated below.

Characterization and spectral data of compounds

Compound 1b [1]

2-(4-Bromophenyl)-1-chloropropan-2-ol



By following the **General procedure 1**, starting from 1-(4-bromophenyl)ethanone (200 mg, 1.0 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.11 mL, 1.5 mmol, 1.5 equiv) , MeLi-LiBr 2.2 M solution in Et_2O (0.64 mL, 1.4 mmol, 1.4 equiv) and quenching the reaction with saturated (*aq.*) NH_4Cl (3 mL) and extracted with diethylether (3 mL), **compound 1b** was obtained in 90% yield (224 mg) as colorless oil after column chromatography on silica gel (*n*-hexane as eluent).

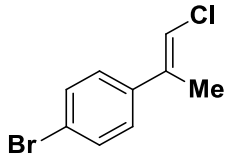
^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.50 (m, 2H, Ph H-3,5), 7.35 (m, 2H, Ph H-2,6), 3.76 (s, 2H, CH_2Cl), 2.63 (s, 1H, OH), 1.61 (s, 3H, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$) δ: 143.2 (Ph C-1), 131.5 (Ph C-3,5), 126.8 (Ph C-2,6), 121.6 (Ph C-4), 73.6 (COH), 55.0 (CH_2Cl), 27.3 (CH_3).

HRMS (ESI), *m/z*: calcd. for $C_9H_{11}BrClO^+$: 248.9676 $[M+H]^+$; found: 248.9680.

Compound 2

(4-bromo-1-[(1*E*)-1-chloro-1-propen-2-yl]benzene)



By following the **General procedure 1**, starting from 4'-bromoacetophenone (200 mg, 1.0 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.1 mL, 1.5 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.6 mL, 1.4 mmol, 1.4 equiv), thionyl chloride (0.1 mL, 1.5 mmol, 1.5 equiv), **compound 2** was obtained in 95% yield (220mg) as yellow oil after column chromatography on silica gel (*n*-hexane as eluent).

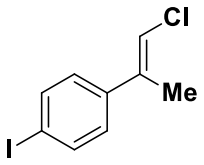
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46 (m, 2H, Ph H-3,5), 7.20 (m, 2H, Ph H-2,6), 6.33 (q, $^4J_{H,H}$ = 1.4 Hz, 1H, H-1), 2.17 (d, $^4J_{H,H}$ = 1.4 Hz, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.2 (C-2), 137.5 (Ph C-1), 131.6 (2C, Ph C-3,5), 127.5 (2C, Ph C-2,6), 121.8 (Ph C-4), 116.4 (C-1), 16.7 (C-3).

HRMS (ESI), *m/z*: calcd. for $C_9H_8BrClH^+$: 230.9571 $[M+H]^+$; found: 230.9573.

Compound 3

1-[(1*E*)-1-chloro-1-propan-2-yl]-4-iodobenzene



By following the **General procedure 1**, starting from 4-iodo-acetophenone (200 mg, 0.8 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.1 mL, 1.2 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.5 mL, 1.1 mmol, 1.4 equiv), thionyl chloride (0.1 mL, 1.2 mmol, 1.5 equiv), **compound 3** was obtained in 87% yield (198 mg) as oil after column chromatography on silica gel (*n*- hexane as eluent).

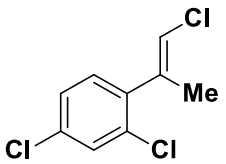
^{1}H NMR (400 MHz, $CDCl_3$) δ:7.66 (m, 2H, Ph H-3,5), 7.07 (m, 2H, Ph H-2,6), 6.33 (q, $^4J_{H,H}$ = 1.4 Hz, 1H, H-1), 2.17 (d, $^4J_{H,H}$ = 1.4 Hz, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.8 (Ph C-1), 137.6 (2C, Ph C-3,4), 127.7 (3C, Ph C-2,6, C-2), 116.4 (C-1), 93.2 (Ph C-4), 16.7 (CH_3).

HRMS (ESI), *m/z*: calcd. for $C_9H_8ClIH^+$: 278.9432 $[M+H]^+$; found: 278.9434.

Compound 4

2,4-dichloro-1-[(1*E*)-1-chloro-1-propen-2-yl]benzene



By following the **General procedure 1**, starting from 2',4'-dichloroacetophenone (200 mg, 1.1 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.1 mL, 1.6 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.7 mL, 1.5 mmol, 1.4 equiv), thionyl chloride (0.1 mL, 1.6 mmol, 1.5 equiv), **compound 4** was obtained in 92% yield (216 mg) as yellow oil after column chromatography on silica gel (*n*-hexane as eluent).

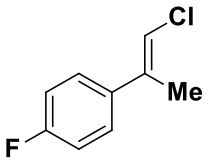
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (d, 1H, $^4J_{H,H}$ = 2.1 Hz, Ph H-3), 7.22 (dd, $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,H}$ = 2.1 Hz, 1H, Ph H-5), 7.10 (d, $^3J_{H,H}$ = 8.2 Hz, 1H, Ph H-6), 6.08 (q, $^4J_{H,H}$ = 1.5 Hz, 1H, H-1), 2.12 (d, $^4J_{H,H}$ = 1.5 Hz, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.6 (Ph C-1), 137.1 (C-2), 134.2 (Ph C-4), 133.4 (Ph C-2), 130.9 (Ph C-6), 129.7 (C-3), 127.1 (Ph C-5), 118.7 (C-1), 18.2 (CH_3).

HRMS (ESI), *m/z*: calcd. for $C_9H_7Cl_3H^+$: 220.9686 $[M+H]^+$; found: 220.9687.

Compound 5

1-[(1*E*)-1-chloro-1-propen-2-yl]-4-fluorobenzene



By following the **General procedure 1**, starting from 4-fluoro-acetophenone (200 mg, 1.45 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.2 mL, 2.17 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.9 mL, 2.03 mmol, 1.4 equiv), thionyl chloride (0.2 mL, 2.17 mmol, 1.5 equiv), **compound 5** was obtained in 89% yield (220 mg) as oil after column chromatography on silica gel (pentane as eluent).

^{1}H NMR (400 MHz, $CDCl_3$) δ:7.30 (m, 2H, Ph H-2,6), 7.03 (m, 2H, Ph H-3,5), 6.27 (q, $^{4}J_{H,H}$ = 1.4 Hz, 1H, H-1), 2.18 (d, $^{4}J_{H,H}$ = 1.4 Hz, 3H, CH_3).

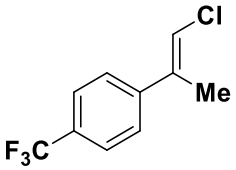
^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.4 (d, $^{1}J_{C,F}$ = 247.1 Hz, Ph C-4), 137.6 (C-2), 136.4 (d, $^{4}J_{C,F}$ = 3.4 Hz, Ph C-1), 127.5 (d, 2C, $^{3}J_{C,F}$ = 8.0, Ph C-2,6), 115.7 (d, $^{6}J_{C,F}$ = 1.5 Hz, C-1), 115.4 (d, 2C, $^{2}J_{C,F}$ = 21.5 Hz, Ph C-3,5), 17.0 (CH_3).

^{19}F NMR (376 MHz, $CDCl_3$) δ: -114.5 (m).

HRMS (ESI), *m/z*: calcd. for $C_9H_8ClFH^+$: 171.0371 $[M+H]^+$; found: 171.0373.

Compound 6

1-[(1*E*)-1-chloro-1-propen-2-yl]-4-(trifluoromethyl)benzene



By following the **General procedure 1**, starting from 1-[4-(trifluoromethyl)phenyl]ethanone (200 mg, 1.06 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.1 mL, 1.59 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.7 mL, 1.49 mmol, 1.4 equiv), thionyl chloride (0.1 mL, 1.59 mmol, 1.5 equiv), **compound 6** was obtained in 88% yield (206 mg) as oil after column chromatography on silica gel (pentane as eluent).

^{1}H NMR (400 MHz, $CDCl_3$) δ:7.60 (m, 2H, Ph H-3,5), 7.44 (m, 2H, Ph H-2,6), 6.40 (s, 1H, H-1), 2.22 (s, 3H, CH_3).

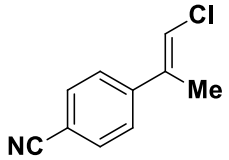
^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.7 (q, $^{5}J_{C,F}$ = 1.3 Hz, Ph C-1), 137.5 (C-1), 129.8 (q, $^{2}J_{C,F}$ = 32.6 Hz, Ph C-4), 126.2 (2C, Ph C-2,6), 125.5 (q, 2C, $^{3}J_{C,F}$ = 3.8 Hz, Ph C-3,5), 124.1 (q, $^{1}J_{C,F}$ = 270.1 Hz, CF_3), 117.8 (C-1), 16.8 (CH_3).

^{19}F NMR (376 MHz, $CDCl_3$) δ: -62.6 (s, CF_3).

HRMS (ESI), *m/z*: calcd. for $C_{10}H_8ClF_3H^+$: 221.0339 $[M+H]^+$; found: 221.0341.

Compound 7

4-[(1*E*)-1chloro-1-propen-2-ylbenzonitrile



By following the **General procedure 1**, starting from 4-acethylbenzonitrile (200 mg, 1.38 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.2 mL, 2.07 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.9 mL, 1.93 mmol, 1.4 equiv), thionyl chloride (0.2 mL, 2.07 mmol, 1.5 equiv), **compound 7** was obtained in 90% yield (220 mg) as oil after column chromatography on silica gel (chloroform/pentane 6:4 as eluent).

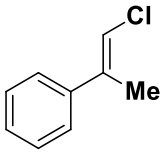
^{1}H NMR (400 MHz, $CDCl_3$) δ:7.63 (m, 2H, Ph H-3,5), 7.43 (m, 2H, Ph H-2,6), 6.45 (q, $^{4}J_{H,H}$ = 1.4 Hz, 1H, H-1), 2.21 (d, $^{4}J_{H,H}$ = 1.4 Hz, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.6 (Ph C-1), 137.2 (C-2), 132.4 (2C, Ph C-3,5), 126.5 (2C, Ph C-2,6), 118.9 (C-2), 118.6 (CN), 111.4 (Ph C-4), 16.6 (CH_3).

HRMS (ESI), *m/z*: calcd. for $C_{10}H_8ClNH^+$: 178.0418 $[M+H]^+$; found: 178.0418.

Compound 8[2]

[(1*E*)-1-chloro-1-propen-2-yl]benzene



By following the **General procedure 1**, starting from acetophenone (200 mg, 1.67 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.2 mL, 2.5 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (1.1 mL, 2.3 mmol, 1.4 equiv), thionyl chloride (0.2 mL, 2.5 mmol, 1.5 equiv), **compound 8** was obtained in 94% yield (239 mg) as yellow oil after column chromatography on silica gel (*n*-hexane as eluent).

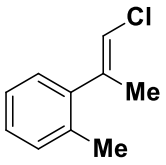
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 (m, 2H, Ph H-3,5), 7.33 (m, 2H, Ph H-2,6), 7.29 (m, 1H, Ph H-4), 6.32 (q, $^{4}J_{H,H}$ = 1.4 Hz, 1H, H-1), 2.20 (d, $^{4}J_{H,H}$ = 1.4 Hz, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.3 (C-2), 138.4 (Ph C-1), 128.5 (2C, Ph C-3,5), 127.8 (Ph C-4), 125.9 (2C, Ph C-2,6), 115.8 (C-1), 16.9 (CH_3).

HRMS (ESI), *m/z*: calcd. for $C_9H_9ClH^+$: 153.0466 $[M+H]^+$; found: 153.0466.

Compound 9

1-[(1*E*)-1-chloro-1-propen-2-yl]-2-methylbenzene



By following the **General procedure 1**, starting from 2'-methylacetophenone (200 mg, 1.5 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.2 mL, 2.2 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (1.0 mL, 2.1 mmol, 1.4 equiv), thionyl chloride (0.2 mL, 2.2 mmol, 1.5 equiv), **compound 9** was obtained in 85% yield (211 mg) as yellow oil after column chromatography on silica gel (*n*-hexane as eluent).

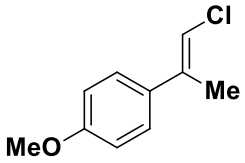
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.19 (m, 2H, Ph H-3,4), 7.15 (m, 1H, Ph H-5), 7.07 (m, 1H, Ph H-6), 5.96 (q, $^4J_{H,H}$ = 1.5 Hz, 1H, H-1), 2.28 (s, 3H, Ph CH_3), 2.08 (d, $^4J_{H,H}$ = 1.5 Hz, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.0 (Ph C-1), 139.6 (C-2), 135.3 (Ph C-2), 130.3 (Ph C-3), 128.4 (Ph C-6), 127.6 (Ph C-4), 125.7 (Ph C-5), 116.2 (C-1), 19.7 (Ph CH_3), 18.8 (CH_3).

HRMS (ESI), *m/z*: calcd. for $C_{10}H_{11}ClH^+$: 167.0622 $[M+H]^+$; found: 167.0624.

Compound 10

1-[(1*E*)-1-chloro-1-propen-2-yl]-4-methoxybenzene



By following the **General procedure 1**, starting from 4'-methoxyacetophenone (200 mg, 1.3 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.2 mL, 2.0 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.9 mL, 1.9 mmol, 1.4 equiv), thionyl chloride (0.2 mL, 2.0 mmol, 1.5 equiv), **compound 10** was obtained in 81% yield (197 mg) as yellow oil after column chromatography on silica gel (*n*-hexane as eluent).

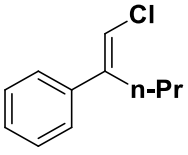
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (m, 2H, Ph H-2,6), 6.87 (m, 2H, Ph H-3,5), 6.25 (q, $^4J_{H,H}$ = 1.4 Hz, 1H, H-1), 3.81 (s, 3H, OCH_3), 2.17 (d, $^4J_{H,H}$ = 1.4 Hz, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.3 (Ph C-4), 137.9 (C-2), 132.8 (Ph C-1), 127.0 (2C, Ph C-2,6), 114.3 (C-1), 113.9 (2C, Ph C-3,5), 55.3 (OCH_3), 16.9 (CH_3).

HRMS (ESI), *m/z*: calcd. for $C_{10}H_{11}ClOH^+$: 183.0571 $[M+H]^+$; found: 183.0573.

Compound 11

[(1*E*)-1-chloro-1-penten-2-yl]benzene



By following the **General procedure 1**, starting from 1-phenylbutan-1-one (200 mg, 1.35 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.2 mL, 2.0 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.9 mL, 1.9 mmol, 1.4 equiv), thionyl chloride (0.2 mL, 2.0 mmol, 1.5 equiv), **compound 11** was obtained in 84% yield (205 mg) as yellow oil after column chromatography on silica gel (*n*-hexane as eluent).

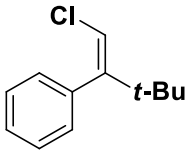
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32 (m, 2H, Ph H-3,5), 7.30 (m, 2H, Ph H-2,6), 7.29 (m, 1H, Ph H-4), 6.24 (m, 1H, H-1), 2.66 (m, 2H, H-3), 1.43 (m, 2H, H-4), 0.92 (t, $^3J_{H,H}$ = 7.4 Hz, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.4 (C-2), 139.7 (Ph C-1), 128.5 (2C, Ph C-3,5), 127.7 (Ph C-4), 126.6 (2C, Ph C-2,6), 115.6 (C-1), 32.5 (C-3), 20.7 (C-4), 13.7 (CH_3).

HRMS (ESI), *m/z*: calcd. for $C_{11}H_{13}ClH^+$: 181.0779 $[M+H]^+$; found: 181.0777.

Compound 12

[(1*Z*)-1-chloro-3,3-dimethyl-1-buten-2yl] benzene



By following the **General procedure 1**, starting from 2,2-dimethyl-1-phenylpropanone (200 mg, 1.23 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.1 mL, 1.85 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.8 mL, 1.73 mmol, 1.4 equiv), thionyl chloride (0.1 mL, 1.85 mmol, 1.5 equiv), **compound 12** was obtained in 91% yield (218 mg) as oil after column chromatography on silica gel (*n*- hexane as eluent).

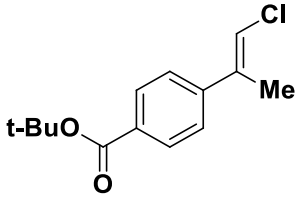
^{1}H NMR (400 MHz, $CDCl_3$) δ:7.39 (m, 2H, Ph H-3,5), 7.33 (m, 1H, Ph H-4), 7.07 (m, 2H, Ph H-2,6), 6.25 (s, 1H, H-1), 1.14 (s, 9H, $C(CH_3)_3$).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.8 (C-2), 138.1 (Ph C-1), 129.2 (2C, Ph C-2,6), 127.8 (2C, Ph C-3,5), 126.9 (Ph C-4), 114.2 (C-1), 37.0 ($C(CH_3)_3$), 29.2 (3C, $C(CH_3)_3$).

HRMS (ESI), *m/z*: calcd. for $C_{12}H_{15}ClNa^+$: 217.0755 $[M+Na]^+$; found: 217.0757.

Compound 13

2-methyl-2-propanyl-4-[(1*E*)-1-chloro-1-propen-2-yl]benzoate



By following the **General procedure 1**, starting from ter-butyl 4-acetylbenzoate (200 mg, 0.91 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.1 mL, 1.4 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.6 mL, 1.3 mmol, 1.4 equiv), thionyl chloride (0.1 mL, 1.4 mmol, 1.5 equiv), **compound 13** was obtained in 86% yield (197 mg) as oil after column chromatography on silica gel (chloroform/pentane 6:4 as eluent).

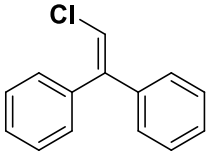
^{1}H NMR (400 MHz, $CDCl_3$) δ:7.95 (m, 2H, Ph H-3,5), 7.37 (m, 2H, Ph H-2,6), 6.41 (q, $^4J_{H,H}$ = 1.4 Hz, 1H, H-1), 2.09 (d, $^4J_{H,H}$ = 1.4 Hz, 3H, CH_3), 1.59 (s, 9H, $C(CH_3)_3$).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.4 (C=O), 144.1 (Ph C-1), 137.9 (C-2), 131.3 (Ph C-4), 129.7 (2C, Ph C-3,5), 125.6 (2C, Ph C-2,6), 117.5 (C-1), 81.1 ($C(CH_3)_3$), 28.2 [3C, $C(CH_3)_3$], 16.7 (CH_3).

HRMS (ESI), *m/z*: calcd. for $C_{14}H_{17}ClO_2H^+$: 253.0989 $[M+H]^+$; found: 253.0988.

Compound 14[2]

1,1'-(2-chloro-1,1-ethenediyl) dibenzene



By following the **General procedure 1**, starting from benzophenone (200 mg, 1.1 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.1 mL, 1.7 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.7 mL, 1.5 mmol, 1.4 equiv), thionyl chloride (0.1 mL, 1.7 mmol, 1.5 equiv), **compound 14** was obtained in 93% yield (219 mg) as yellow oil after column chromatography on silica gel (*n*-hexane as eluent).

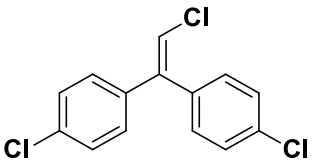
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41 (m, 2H, Ph H-3,5), 7.33 (m, 2H, Ph H-2,6), 7.31 (m, 4H, Ph H-4, H-3',4',5'), 7.22 (m, 2H, Ph H-2',6'), 6.60 (s, 1H, H-2).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.9 (C-1), 140.1 (Ph C-1'), 137.6 (Ph C-1), 129.8 (2C, Ph C-2,6), 128.4 (2C, Ph C-3',5'), 128.2 (2C, Ph C-3,5), 128.1 (Ph C-4'), 128.0 (Ph C-4), 127.7 (2C, Ph C-2',6'), 115.9 (C-2).

HRMS (ESI), *m/z*: calcd. for $C_{14}H_{11}ClH^+$: 215.0622 $[M+H]^+$; found: 215.0624.

Compound 15[3]

1,1'-(2-chloro-1,1-ethenediyl) bis (4-chlorobenzene)



By following the **General procedure 1**, starting from 4,4'-dichlorobenzophenone (200 mg, 0.8 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.1 mL, 1.2 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.5 mL, 1.1 mmol, 1.4 equiv), thionyl chloride (0.1 mL, 1.2 mmol, 1.5 equiv), **compound 15** was obtained in 89% yield (201 mg) as yellow oil after column chromatography on silica gel (heptane/acetone 95:5 as eluent).

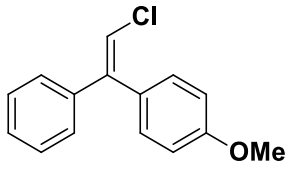
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38 (m, 2H, Ph H-3,5), 7.28 (m, 2H, Ph H-3',5'), 7.25 (m, 2H, Ph H-2,6), 7.12 (m, 2H, Ph H-2',6'), 6.59 (s, C-2).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.8 (C-1), 138.2 (Ph C-1'), 135.5 (Ph C-1), 134.3 (Ph C-4'), 134.2 (Ph C-4), 131.2 (2C, Ph C-2,6), 128.9 (2C, Ph C-1',6'), 128.7 (2C, Ph C-3',5'), 128.6 (2C, Ph C-3,5), 116.8 (C-2).

HRMS (ESI), *m/z*: calcd. for $C_{14}H_9Cl_3H^+$: 282.98426 $[M+H]^+$; found: 282.98428.

Compound 16[4a,b]

1-[(*Z*)-(2-chloro-1-phenylvinyl)-4-methoxybenzene



By following the **General procedure 1**, starting from 4-methoxybenzophenone (200 mg, 0.94 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.1 mL, 1.3 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.6 mL, 1.3 mmol, 1.5 equiv), thionyl chloride (0.1 mL, 1.4 mmol, 1.5 equiv), **compound 16** was obtained in 85% yield (196 mg) as yellow oil after column chromatography on silica gel (*n*-hexane as eluent).

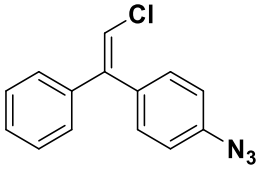
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30 (m, 3H, Ph H-3,4,5), 7.28 (m, 2H, Ph H-2',6'), 7.22 (m, 2H, Ph H-2,6), 6.93 (m, 2H, Ph H-3',5'), 6.52 (s, 1H, H-2), 3.85 (s, 3H, OCH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.2 (Ph C-4'), 143.4 (C-1), 140.6 (Ph H-1), 131.2 (2C, Ph C-2',6'), 129.8 (Ph C-1'), 128.4 (2C, Ph C-3,5), 128.0 (Ph C-4), 127.9 (2C, Ph C-2,6), 115.1 (C-2), 113.5 (2C, Ph C-3',5'), 55.2 (OCH_3).

HRMS (ESI), *m/z*: calcd. for $C_{15}H_{13}ClOH^+$: 245.0728 $[M+H]^+$; found: 245.0727.

Compound 17

1-[(2-chloro-1-(*Z*)-phenylvinyl)-4-azido] benzene



By following the **General procedure 1**, starting from 4-azidobenzophenone (200 mg, 0.9 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.1 mL, 1.3 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.6 mL, 1.3 mmol, 1.4 equiv), thionyl chloride (0.1 mL, 1.3 mmol, 1.5 equiv), **compound 17** was obtained in 94% yield (215 mg) as yellow oil after column chromatography on silica gel (*n*-hexane as eluent).

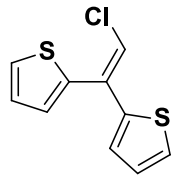
^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.34 (m, 5H, Ph H-2,3,4,5,6), 7.20 (m, 2H, Ph H-2',6'), 7.06 (m, 1H, Ph H-3´), 6.95 (m, Ph H-5´), 6.57 (s, 1H, H-2).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.0 (Ph C-4´), 140.0 (C-1), 136.9 (Ph C-1), 131.5 (2C, Ph C-2´,6´), 129.8 (2C, Ph C-3,5), 129.5 (Ph C-1´), 129.1 (Ph C-4), 128.5 (2C, Ph C-2,6), 118.8 (2C, Ph C-3´,5´), 116.1 (C-2).

HRMS (ESI), *m/z*: calcd. for $C_{14}H_{10}ClN_3Na^+$: 278.0461 $[M+Na]^+$; found: 278.0465.

Compound 18

2,2'-(2-chloro-1,1-ethenediyl) dithiophene



By following the **General procedure 1**, starting from di-3-thienyl ketone (200 mg, 1.0 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.1 mL, 1.5 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.7 mL, 1.4 mmol, 1.4 equiv), thionyl chloride (0.1 mL, 1.5 mmol, 1.5 equiv), **compound 18** was obtained in 86% yield (194 mg) as yellow oil after column chromatography on silica gel (heptane/acetone 95:5 as eluent).

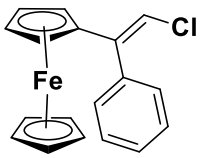
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 (dd, $^3J_{H,H}$ = 5.2 Hz, $^4J_{H,H}$ = 1.2 Hz, Th H-5), 7.30 (m, 2H, Th H-3,5'), 7.09 (dd, $^3J_{H,H}$ = 5.2 Hz, $^3J_{H,H}$ = 3.7 Hz, Th H-4), 7.06 (m, Th H-3'), 7.02 (dd, $^3J_{H,H}$ = 5.1 Hz, $^3J_{H,H}$ = 3.6 Hz, Th H-4'), 6.56 (s, H-2).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.0 (Th C-2'), 138.0 (Th C-2), 130.7 (C-1), 129.8 (Th C-3), 127.1 (Th C-5), 127.10 (2C, Th C-3',4'), 126.4 (Th C-4), 125.8 (Th C-5'), 115.7 (C-2).

HRMS (ESI), *m/z*: calcd. for $C_{10}H_7ClS_2H^+$: 226.9750 $[M+H]^+$; found: 226.9752.

Compound 19

3-[(*Z*)-2-chloro-1-phenylvinyl] ciclopentenyl (ciclopentyl) iron



By following the **General procedure 1**, starting from benzoylferrocene (200 mg, 0.7 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.1 mL, 1.0 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.4 mL, 1.0 mmol, 1.4 equiv), thionyl chloride (0.1 mL, 1.0 mmol, 1.5 equiv), **compound 19** was obtained in 84% yield (186 mg) as yellow oil after column chromatography on silica gel (heptane/acetone 9:1 as eluent).

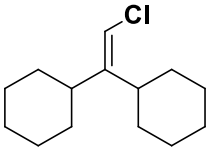
^{1}H NMR (400 MHz, $CDCl_3$) δ:7.45 (m, 2H, Ph H-3,5), 7.38 (m, Ph H-4), 7.34 (m, 2H, Ph H-2,6), 6.49 (s, 1H, H-2), 4.24 (s, 2H, Fc H-1,5), 4.19 (s, 2H, Fc H-2,4), 4.13 (s, 5H, Fc H-1,2,3,4,5).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.9 (C-1), 137.4 (Ph C-1), 129.0 (2C, Ph C-2,6), 128.1 (2C, Ph C-3,5), 127.6 (Ph C-4), 111.6 (C-2), 84.8 (Fc C-3), 69.5 (5C, Fc C-1,2,3,4,5), 68.9 (2C, Fc C-1,5), 66.6 (2C, Fc C-2,4).

HRMS (ESI), *m/z*: calcd. for $C_{18}H_{15}ClFeH^+$: 323.0284 $[M+H]^+$; found: 323.286.

Compound 20

1,1'-(2-chloro-1,1-ethenediyl)dicyclohexane



By following the **General procedure 1**, starting from dicyclohexylmethanone (200 mg, 1.0 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.1 mL, 1.5 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.7 mL, 1.4 mmol, 1.4 equiv), thionyl chloride (0.1 mL, 1.5 mmol, 1.5 equiv), **compound 20** was obtained in 90% yield (204 mg) as yellow oil after column chromatography on silica gel (*n*-hexane as eluent).

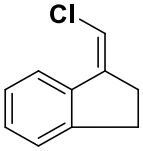
^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.76 (s, 1H, CHCl), 2.69 (m, 1H, H-1'), 1.98 (m, 1H, H-1), 1.76 (m, 2H, H-3',5'), 1.75 (m, 2H, H-3,5), 1.69 (m, 2H, H-2,6), 1.68 (m, 2H, H-4,4'), 1.54 (m, 2H, H-2',6'), 1.42 (m, 2H, H-2',6'), 1.31 (m, 2H, H-3',5'), 1.25 (m, 2H, H-3,5), 1.17 (m, 2H, H-4,4'), 1.12 (m, 2H, H-2,6).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.9 (C=C), 112.2 (CHCl), 41.0 (C-1), 40.7 (C-1'), 34.2 (2C, C-2,6), 29.7 (2C, C-2',6'), 27.0 (2C, C-3,5), 26.1 (2C, C-3',5'), 26.1 (C-4), 26.07 (C-4').

HRMS (ESI), *m/z*: calcd. for $C_{14}H_{23}ClH^+$: 227.1561 $[M+H]^+$; found: 227.151563.

Compound 21

(1*Z*)-1-chloromethylene)indane



By following the **General procedure 1**, starting from 1-indanone (200 mg, 1.5 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.2 mL, 2.3 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (1.0 mL, 2.1 mmol, 1.4 equiv), thionyl chloride (0.2 mL, 2.3 mmol, 1.5 equiv), **compound 21** was obtained in 93% yield (230 mg) as yellow oil after column chromatography on silica gel (*n*-hexane as eluent).

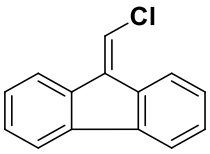
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39 (m, 1H, Ar H-7), 7.27 (m, 1H, Ar H-4), 7.23 (m, 1H, Ar H-5), 7.18 (m, 1H, Ar H-6), 6.52 (t, $^4J_{H,H}$ = 2.8 Hz, 1H, CHCl), 3.05-3.01 (m, 2H, H-3), 2.90-2.86 (m, 2H, H-2).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.9 (Ar C-3a), 145.4 (C-1), 138.9 (Ar C-7a), 128.5 (Ar C-5), 126.6 (Ar C-6), 125.6 (Ar C-4), 120.1 (Ar C-7), 108.7 (CHCl), 29.6 (C-3), 29.3 (C-2).

HRMS (ESI), *m/z*: calcd. for $C_{10}H_9ClH^+$: 165.0466 $[M+H]^+$; found: 165.0465.

Compound 22[5]

9-(chloromethylene)-9H-fluorene



By following the **General procedure 1**, starting from 9H-fluorenone (200 mg, 1.1 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.1 mL, 1.7 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.7 mL, 1.6 mmol, 1.4 equiv), thionyl chloride (0.1 mL, 1.7 mmol, 1.5 equiv), **compound 22** was obtained in 82% yield (193 mg) as yellow oil after column chromatography on silica gel (*n*-hexane as eluent).

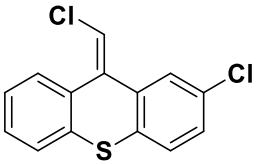
^{1}H NMR (400 MHz, C_6D_6) δ: 8.45 (m, 1H, Ar H-1), 7.41 (m, 1H, Ar H-4), 7.38 (m, 1H, Ar H-5), 7.13 (m, 1H, Ar H-3), 7.12 (m, 1H, Ar H-2), 7.10 (m, 1H, Ar H-6), 7.05 (m, 1H, Ar H-8), 6.99 (m, 1H, Ar H-7), 6.66 (s, 1H, CHCl).

^{13}C NMR (100 MHz, C_6D_6) δ: 141.5 (Ar C-4a), 139.4 (Ar C-4b), 138.0 (Ar C-8a), 137.1 (Ar C-9), 136.3 (Ar C-9a), 129.5 (Ar C-3), 128.7 (Ar C-6), 127.7 (Ar C-2), 127.3 (Ar C-7), 126.6 (Ar C-1), 120.4 (Ar C-8), 120.1 (Ar C-4), 117.6 (CHCl).

HRMS (ESI), *m/z*: calcd. for $C_{14}H_9ClH^+$: 213.0466 $[M+H]^+$; found: 213.0465.

Compound 23

7-chloro-9-((*E*)chloromethylene)-9*H*-thioxanthene



By following the **General procedure 1**, starting from 2-chloro-9H-thioxanthen-9-one (200 mg, 0.8 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.1 mL, 1.2 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.5 mL, 1.1 mmol, 1.4 equiv), thionyl chloride (0.1 mL, 1.2 mmol, 1.5 equiv), **compound 23** was obtained in 89% yield (199 mg) as yellow oil after column chromatography on silica gel (*n*-hexane as eluent).

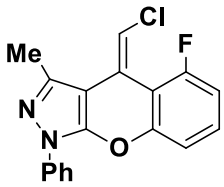
^{1}H NMR (400 MHz, C_6D_6) δ: 7.93 (m, 1H, H-1), 7.48-7.24 (m, 6H, H-2,3,4,5,6,8), 6.54 (s, 1H, CHCl).

^{13}C NMR (100 MHz, C_6D_6) δ: 136.5 (C-9), 135.7,135.67, 134.5, 132.8, 132.78, 132.5, 131.8, 131.75, 131.7, 130.7, 130.5, 129.3 (C-1), 129.0 (C-8´), 128.2, 128.0, 127.96, 127.7, 127.65, 127.2, 127.16, 126.6, 126.1, 126.07, 125.8, 125.6, 118.2 (CHCl), 118.1 (CHCl).

HRMS (ESI), *m/z*: calcd. for $C_{14}H_9Cl_2S^+$: 278.9802 $[M+H]^+$; found: 278.9807.

Compound 24

4-(*E*)-chloromethylene)-5-fluoro-3-methyl-1-phenyl-1,4-dihydrochromeno[2,3-c] pyrazole



By following the **General procedure 1**, starting from 4-(chloromethylene)-5-fluoro-3-methyl-1-phenyl-1,4-dihydrochromeno[2,3-c]pyrazole (200 mg, 0.68 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.1 mL, 1.0 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.4 mL, 1.0 mmol, 1.4 equiv), thionyl chloride (0.1 mL, 1.5 mmol, 1.5 equiv), **compound 24** was obtained in 84% yield (186 mg) as yellow oil after column chromatography on silica gel (*n*-hexane as eluent).

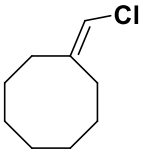
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (m, 2H, Ph H-2,6), 7.49 (m, 2H, Ph H-3,5), 7.33 (m, 1H, Ph H-4), 7.24 (m, 1H, Ar H-7), 7.03 (m, 1H, Ar H-8), 6.97 (m, 1H, Ar H-6), 6.68 (s, 1H, CHCl), 2.62 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.5 (d, $^{1}J_{C,F}$ = 250.1 Hz, Ar C-5), 152.0 (d, $^{3}J_{C,F}$ = 5.4 Hz, Ar C-8a), 148.0 (C-9a), 145.2 (Pyr C-3), 137.5 (Ph C-1), 129.2 (2C, Ph C-3,5), 128.5 (d, $^{3}J_{C,F}$ = 10.8 Hz, Ar C-7), 126.7 (Ph C-4), 121.9 (d, $^{3}J_{C,F}$ = 4.3 Hz, C-4), 121.2 (2C, Ph C-2,6), 113.2 (d, $^{5}J_{C,F}$ = 3.4 Hz, Ar C-8), 112.8 (d, $^{2}J_{C,F}$ = 17.1 Hz, Ar C-4a), 112.5 (d, $^{4}J_{C,F}$ = 18.1 Hz, CHCl), 112.4 (d, $^{2}J_{C,F}$ = 24.2 Hz, Ar C-6), 99.8 (Pyr C-3a), 18.1 (CH_3).

^{19}F NMR (376 MHz, $CDCl_3$) δ: -112.1 (dd,$^{1}J_{C,F}$ = 11.3 Hz, $^{3}J_{H,F}$ = 5.8 Hz, F).

HRMS (ESI), *m/z*: calcd. for $C_{18}H_{12}ClFN_2OH^+$: 327.0695 $[M+H]^+$; found: 327.0696.

Compound 25
(chlorometylene)cyclooctane



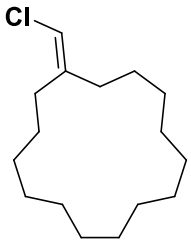
By following the **General procedure 1**, starting from cyclooctanone (200 mg, 1.6 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.2 mL, 2.4 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (1.0 mL, 2.2 mmol, 1.4 equiv), thionyl chloride (0.2 mL, 2.4 mmol, 1.5 equiv), **compound 25** was obtained in 92% yield (233 mg) as yellow oil after column chromatography on silica gel (*n*-hexane as eluent).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.82 (m, CHCl), 2.33 (m, 2H, H-2), 2.20 (m, 2H, H-8), 1.71 (m, 2H, H-3), 1.66 (m, 2H, H-7), 1.51-1.47 (m, 4H, H-4,5), 1.49 (m, 2H, H-6).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.4 (C-1), 111.7 (CHCl), 35.1 (C-8), 29.4 (C-2), 27.1 (C-6), 26.1 (C-4), 25.8 (C-5), 25.6 (C-3), 25.6 (C-7).

HRMS (ESI), *m/z*: calcd. for $C_9H_{15}ClH^+$: 159.0935 $[M+H]^+$; found: 159.0936.

Compound 26[6]
(cloromethyliden) cyclopentadecane



By following the **General procedure 1**, starting from cyclopentadecanone (200 mg, 0.89 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.1 mL, 1.3 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.6 mL, 1.3 mmol, 1.4 equiv), thionyl chloride (0.6 mL, 1.3 mmol, 1.5 equiv), **compound 26** was obtained in 83% yield (189 mg) as oil after column chromatography on silica gel (*n*- hexane as eluent).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 5,80 (s, 1H, CHCl), 2.20 (m, 2H, H-16), 2.07 (m, 2H, H-3), 1.50-1.26 (m, 24 H, H-4-15).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.3 (C-2), 112.1 (C-1), 35.4 (C-3), 30.2 (C-16), 27.6-25.7 (m, C4-16).

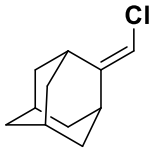
HRMS (ESI), *m/z*: calcd. for $C_{16}H_{29}ClH^+$: 257.2031 $[M+H]^+$; found: 257.2033.

Scale up of the reaction using 20 mmol of starting material

By following the **General procedure 1**, starting from cyclopentadecanone (4.5 g, 20 mmol, 1 equiv) in dry THF (30 mL), chloroiodomethane (2.2 mL, 30 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (12.7 mL, 28 mmol, 1.4 equiv), thionyl chloride (2.2 mL, 30 mmol, 1.5 equiv), **compound 26** was obtained in 87% yield (4.470 g) as yellow oil after column chromatography on silica gel (*n*- heptane as eluent). *Spectroscopic and spectrometric data match with those ones reported for the running reaction at 1.3 mmol scale.*

Compound 27

2-(chloromethylene)adamantane



By following the **General procedure 1**, starting from 2-adamantanone (200 mg, 1.3 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.2 mL, 2.0 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.9 mL, 1.9 mmol, 1.4 equiv), thionyl chloride (0.2 mL, 2.0 mmol, 1.5 equiv), **compound 27** was obtained in 90% yield (214 mg) as yellow oil after column chromatography on silica gel (*n*- heptane as eluent).

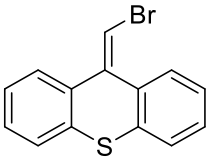
^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.75 (s, 1H, CHCl), 3.12 (m 1H, H-3), 2.49 (m, 1H, H-1), 1.97 (m, 2H, H-5,7), 1.89 (m, 2H, H-4,10), 1.88 (m, 2H, H-8,9), 1.83 (m, 2H, H-7), 1.75 (m, 4H, H-4,8,9,10).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.7 (C-2), 103.9 (CHCl), 39.3 (C-8,9), 38.0 (C-1), 37.9 (C-4,10), 36.8 (C-6), 31.8 (C-3), 28.2 (C-5,7).

HRMS (ESI), *m/z*: calcd. for $C_{11}H_{15}ClH^+$: 183.0935 $[M+H]^+$; found: 183.0937.

Compound 28

9-(bromomethylene)-9*H*-thioxanthene



By following the **General procedure 1**, starting from 9H-thioxanthen-9-one (200 mg, 0.9 mmol, 1 equiv) in dry THF (3 mL), dibromomethane (0.1 mL, 1.4 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.6 mL, 1.3 mmol, 1.4 equiv), thionyl chloride (0.1 mL, 1.4 mmol, 1.5 equiv), **compound 28** was obtained in 92% yield (239 mg) as yellow oil after column chromatography on silica gel (heptane/acetone 95:5 as eluent).

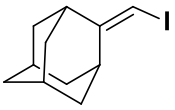
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.99 (m, 1H, Ph H-8), 7.48 (m, 1H, Ph H-5), 7.46 (m, 1H, Ph H-1), 7.42 (m, 1H, Ph H-4), 7.33 (m, 1H, Ph H-7), 7.30 (m, 1H, Ph H-6), 7.28 (m, 2H, Ph H-2,3), 6.69 (s, CHBr).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.3 (C-9), 135.9 (C-9a), 133.1 (C-10a), 132.0 (C-8a), 131.7 (C-4a), 129.1 (C-8), 128.0 (C-6), 127.7 (C-3), 127.0 (C-2), 126.7 (C-5), 126.0 (C-4), 125.7 (C-7), 125.7 (C-1), 106.3 (CHBr).

HRMS (ESI), *m/z*: calcd. for $C_{14}H_9BrSH^+$: 288.9681 $[M+H]^+$; found: 288.9686.

Compound 29[7]

2-(iodomethylene) adamantane



By following the **General procedure 1**, starting from 2-adamantanone (200 mg, 1.3 mmol, 1 equiv) in dry THF (3 mL), diiodomethane (0.2 mL, 2.0 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.9 mL, 1.9 mmol, 1.4 equiv), thionyl chloride (0.2 mL, 2.0 mmol, 1.5 equiv), **compound 29** was obtained in 87% yield (311 mg) as yellow oil after column chromatography on silica gel (*n*- heptane as eluent).

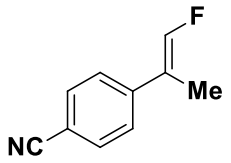
^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.75 (s, 1H, CHI), 3.12 (m, 1H, H-1), 2.49 (m, 1H, H-3), 1.97 (m, 2H, H-5,7), 1.89 (m, 2H, H-8,9), 1.88 (m, 2H, H-4,10), 1.84 (m, 2H, H-6), 1.76 (m, 4H, H-4,8,9,10).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 149.7 (C-2), 103.9 (CHI), 39.3 (2C, C-4,10), 38.0 (C-3), 37.9 (2C, C-8,9), 36.8 (C-6), 31.9 (C-1), 28.2 (2C, C-5,7).

HRMS (ESI), *m/z*: calcd. for $C_{11}H_{15}IH^+$: 275.0291 $[M+H]^+$; found: 275.0294.

Compound 30[8]

4-[(1*E*)-1-fluoro-1-propen-2-yl]benzonitrile



By following the **General procedure 1**, starting from 4-acetylbenzonitrile (200 mg, 1.4 mmol, 1 equiv) in dry THF/Et_2O (1:1 10 mL), fluoroiodomethane (0.1 mL, 2.1 mmol, 2 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.9 mL, 1.9 mmol, 1.4 equiv), thionyl chloride (0.2 mL, 2.1 mmol, 1.5 equiv), **compound 30** was obtained in 85% yield (192 mg) as yellow oil after column chromatography on silica inverse phase gel (Acetonitrile/water 8:2 as eluent).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.94 (m, 2H, Ph H-2,6), 6.53 (m, 2H, Ph H-3,5), 6.35 (d, $^2J_{H,F}$ = 83.5 Hz, CHF), 1.59 (d, $^4J_{H,H}$ = 3.8 Hz, 3H, CH_3).

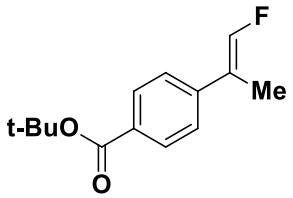
^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.8 (d, $^2J_{C,F}$ = 262.2 Hz, CHF), 141.6 (d, $^3J_{C,F}$ = 3.4 Hz, Ph C-4), 132.2 (2C, Ph C-2,6), 126.1(d, $^4J_{C,F}$ = 3.4 Hz, 2C, Ph C-3,5), 119.2 (d, $^2J_{C,F}$ = 11.0 Hz, C-2), 118.8 (CN), 111.5 (Ph, C-1), 11.4 (d, $^3J_{C,F}$ = 5.9 Hz, CH_3).

^{19}F NMR (376 MHz, $CDCl_3$) δ: -126.6 (dq, $^2J_{F,H}$ = 83.5 Hz, $^3J_{F,C}$ = 3.8 Hz, CHF).

HRMS (ESI), *m/z*: calcd. for $C_{10}H_8FNH^+$: 162.0714 $[M+H]^+$; found: 162.0716.

Compound 31

2-methyl-2-propanyl 4-[(1*E*)-1-fluoro-1-propen-2-yl]benzoate



By following the **General procedure 1**, starting from *ter*-butyl-4acetylbenzoate (200 mg, 0.9 mmol, 1 equiv) in dry THF/Et_2O (1:1 10 mL), fluoroiodomethane (0.1 mL, 1.4 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.6 mL, 1.3 mmol, 1.4 equiv), thionyl chloride (0.1 mL, 1.4 mmol, 1.5 equiv), **compound 31** was obtained in 93% yield (198 mg) as yellow oil after column chromatography on alumina gel grade I (*n*-heptane/acetone 99:1 as eluent).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.94 (m, 2H, Ph H-2,6), 7.34 (m, 2H, Ph H-3,5), 6.97 (qd, $^2J_{H,F}$ = 84.2 Hz, $^4J_{H,H}$ = 1.5 Hz, CHF), 2.05 (dd, $^4J_{H,F}$ = 3,8 Hz, $^4J_{H,H}$ = 1.5 Hz, 3H, CH_3), 1.59 (s, 9H, $C(CH_3)_3$).

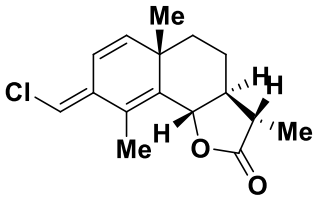
^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.5 (C=O), 146.9 (d, $^1J_{C,F}$ = 260.5 Hz, CHF), 141.7 (d, $^3J_{C,F}$ = 9.1 Hz, Ph C-4), 130.9 (Ph C-1), 129.7 (2C, Ph C-2,6), 125.5 (d, $^4J_{C,F}$ = 3.3 Hz, 2C, Ph C-3,5), 81.0 [$C(CH_3)_3$], 28.2 (3C, $C(CH_3)_3$), 12.0 (d, $^3J_{C,F}$ = 6.0 Hz, CH_3).

^{19}F NMR (376 MHz, $CDCl_3$) δ: -128.5 (dq, $^2J_{F,H}$ = 84.2 Hz, $^4J_{F,H}$ = 3.8 Hz, CHF).

HRMS (ESI), *m/z*: calcd. for $C_{14}H_{17}FO_2H^+$: 237.1285 $[M+H]^+$; found: 237.1287.

Compound 32

(3a*S*, 5a*S*,8*E*,9b*S*)-8-(chloromethylene)-3,5-a,9-trimethyl-3a,4,5,5a,8,9b-hexahydronaphto[1,2-b] furan-2(3*H*)-one



By following the **General procedure 1**, starting from santonin (200 mg, 0.8 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.1 mL, 1.2 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.5 mL, 1.1 mmol, 1.4 equiv), thionyl chloride (0.1 mL, 1.2 mmol, 1.5 equiv), **compound 32** was obtained in 90% yield (201 mg) as oil after column chromatography on silica gel (chloroform as eluent).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.67 (d, 1H, $^3J_{H,H}$ = 10.0 Hz, C_7H), 6.18 (m, 1H, CHCl), 5.72 (dd, 1H, $^3J_{H,H}$ = 10.0 Hz, $^4J_{H,H}$ = 1.6 Hz, C_6H), 4.81 (d, 1H, $^3J_{H,H}$ = 11.1 Hz, $C_{9b}H$), 2.33 (m, 1H, C_3H), 2.08 (d, 3H, $^5J_{H,H}$ = 1.3 Hz, C_9CH_3), 1.98 (m, 1H, C_4H_2), 1.81 (m, 1H, $C_{3a}H$), 1.69 (m, 1H, C_5H_2), 1.65 (m, 1H, C_4H_2), 1.54 (m, 1H, C_5H_2), 1.25 (d, 3H, $^3J_{H,H}$ = 7.0 Hz, C_3CH_3), 1.23 (s, 3H, $C_{5a}CH_3$).

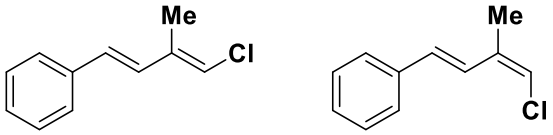
^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.1 (C=O), 139.8 (C-6), 135.2 (C-9a), 134.2 (C-8), 122.2 (C-9), 114.2 (CHCl), 82.4 (C-9b), 53.7 (C-3a), 41.1 (C-3), 40.9 (C-5a), 38.7 (C-5), 26.3 (C-5a CH_3), 24.1 (C-4), 13.5 (C-9 CH_3), 12.4 (C-3 CH_3).

HRMS (ESI), *m/z*: calcd. for $C_{16}H_{19}ClO_2H^+$: 279.1146 $[M+H]^+$; found: 279.1144.

Compound 33[9]

[(1*E*,3*E*)-4-chloro-3-methyl-1,3-butadien-1-yl]benzene

[(1*E*,3*Z*)-4-chloro-3-methyl-1,3-butadien-1-yl]benzene



major (E,E) 59% minor (E,Z) 41%

By following the **General procedure 1**, starting from 4-phenylbut-3-en-2-one (200 mg, 1.4 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.2 mL, 2.1 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.9 mL, 1.9 mmol, 1.4 equiv), thionyl chloride (0.2 mL, 2.1 mmol, 1.5 equiv), **compound 33** was obtained in 86% yield (215 mg) as yellow oil after column chromatography on silica gel (*n*-hexane as eluent).

Major:

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41 (m, 2H, Ph H-2,6), 7.37-7.22 (m, 3H, Ph H-3,4,5), 6.77 (d, 1H, $^3J_{H,H}$ = 16.0 Hz, H-2), 6.60 (d, 1H, $^3J_{H,H}$ = 16.0 Hz, H-1), 6.26 (m, 1H, H-4), 2.04 (d, 3H, $^4J_{H,H}$ = 1.3 Hz, CH_3).

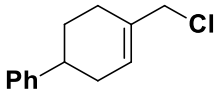
^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.1 (2C, Ph C-1, C-3), 128.7 (2C, Ph C-3,5), 128.6 (C-1), 128.5 (C-2), 127.7 (Ph C-4), 126.4 (2C, Ph C-2,6), 119.9 (C-4), 13.0 (CH_3).

Minor:
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50 (m, 2H, Ph H-2,6), 7.37-7.22 (m, 3H, Ph H-3,4,5), 7.38 (dd, 1H, $^{3}J_{H,H}$ = 16.2 $^{4}J_{H,H}$ = 0.8 Hz, H-2), 6.70 (d, 1H, $^{3}J_{H,H}$ = 16.2 Hz, H-1), 6.01 (m, 1H, H-4), 1.99 (d, 3H, $^{4}J_{H,H}$ = 1.5 Hz, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.9 (Ph C-1), 134.3 (C-3), 131.5 (C-1), 128.7 (2C, Ph C-3,5), 128.0 (Ph C-4), 126.8 (2C, Ph C-2,6), 124.0 (C-2), 116.0 (C-4), 18.2 (CH_3).

HRMS (ESI), *m/z*: calcd. for $C_{11}H_{11}ClH^+$: 179.0622 $[M+H]^+$; found: 179.0625.

Compound 34
[4-(chloromethyl)-3-cyclohexen-1-yl] benzene



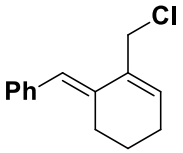
By following the **General procedure 1**, starting from 4-phenylcyclohexanone (200 mg, 1.2 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.1 mL, 1.7 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.7 mL, 1.6 mmol, 1.4 equiv), thionyl chloride (0.1 mL, 1.7 mmol, 1.5 equiv), **compound 34** was obtained in 84% yield (208 mg) as yellow oil after column chromatography on silica gel (*n*-hexane as eluent).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33 (m, 2H, Ph H-3,5), 7.24 (m, 2H, Ph H-2,6), 7.23 (m, 1H, Ph H-4), 5.92 (m, 1H, H-3), 4.07 (s, 2H, CH_2Cl), 2.80 (m, 1H, H-1), 2.38 (m, 1H, H-2), 2.30 (m, 2H, H-5), 2.22 (m, 1H, H-2), 2.04 (m, 1H, H-6), 1.82 (m, 1H, H-6).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 146.4 (Ph C-1), 134.3 (C-4), 128.4 (2C, Ph C-3,5), 127.1 (C-3), 126.8 (2C, Ph C-2,6), 126.2 (Ph C-4), 50.1 (CH_2Cl), 39.7 (C-1), 33.4 (C-2), 29.5 (C-6), 26.6 (C-5).

HRMS (ESI), *m/z*: calcd. for $C_{13}H_{15}ClH^+$: 207.0935 $[M+H]^+$; found: 207.0937.

Compound 35
(*E*)-[2-(chloromethyl)-2-cyclohexen-1-yl)methyl]benzene



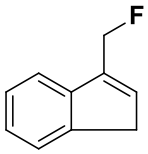
By following the **General procedure 1**, starting from 2-benzylidenecyclohexanone (200 mg, 1.1 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.1 mL, 1.6 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.7 mL, 1.5 mmol, 1.4 equiv), thionyl chloride (0.1 mL, 1.6 mmol, 1.5 equiv), **compound 35** was obtained in 92% yield (221 mg) as yellow oil after column chromatography on silica gel (*n*-hexane as eluent).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (m, 2H, Ph H-3,5), 7.31 (m, 2H, Ph H-2,6), 7.22 (m, 1H, Ph H-4), 6.66 (s, 1H, H-1), 6.18 (t, 1H, $^4J_{H,H}$ = 4.3 Hz, C_3H), 4.34 (s, 2H, CH_2Cl), 2.64 (m, 2H, C_6H_2), 2.26 (m, 2H, C_4H_2), 1.69 (m, 2H, C_5H_2).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.6 (Ph C-1), 134.6 (C-2), 134.3 (C-1), 134.0 (C-3), 129.4 (2C, Ph C-2,6), 128.0 (2C, Ph C-3,5), 126.4 (Ph C-4), 124.2 (C_1H), 46.3 (CH_2Cl), 27.0 (C_6H_2), 26.2 (C_4H_2), 22.5 (C_5H_2).

HRMS (ESI), *m/z*: calcd. for $C_{14}H_{15}ClH^+$: 219.0935 $[M+H]^+$; found: 219.0937.

Compound 36
(fluoromethyl)-3*H*-indene



By following the **General procedure 1**, starting from 1-indanone (200 mg, 1.5 mmol, 1 equiv) in dry THF/Et_2O (1:1 10 mL), fluoroiodomethane (0.2 mL, 2.3 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (1.0 mL, 2.1 mmol, 1.4 equiv), thionyl chloride (0.2 mL, 2.3 mmol, 1.5 equiv), **compound 36** was obtained in 81% yield (180 mg) as yellow oil after column chromatography on silica gel (*n*-hexane as eluent).

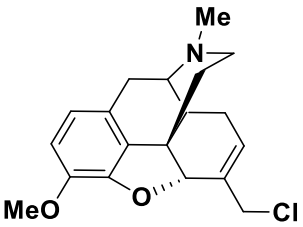
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50 (m, 1H, H-7), 7.46 (m, 1H, H-4), 7.33 (m, 1H, H-5), 7.25 (m, 1H, H-6), 6.58 (m, 1H, H-2), 5.43 (qd, 2H, $^4J_{H,F}$ = 47.3 Hz, $^4J_{H,H}$ = 1.4 Hz, CH_2F), 3.44 (m, 2H, H-1).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.1 (C-7a), 142.8 (d, $^3J_{C,F}$ = 2.0 Hz, C-3a), 139.9 (d, $^2J_{C,F}$ = 16.8 Hz, C-3), 132.8 (d, $^3J_{H,F}$ = 9.3 Hz, C-2), 126.3 (C-5), 125.3 (C-6), 124.0 (C-7), 119.6 (C-4), 79.3 (d, $^1J_{C,F}$ = 153.2 Hz, CHF), 38.1 (d, $^4J_{C,F}$ = 1.7 Hz, C-1).

^{19}F NMR (376 MHz, $CDCl_3$) δ: -216.8 (qt, $^2J_{H,F}$ = 47.3 Hz, $^4J_{H,F}$ = 6.2 Hz, CHF).

HRMS (ESI), *m/z*: calcd. for $C_{10}H_9FH^+$: 149.0761 $[M+H]^+$; found: 149.0763.

Compound 37
6-(chloromethylene)-3-methoxy-17-methyl-6,7-didehydro-4,5-epoxymorphinane



By following the **General procedure 1**, starting from hydrocodone (200 mg, 0.7 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.1 mL, 1.0 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.4 mL, 0.9 mmol, 1.4 equiv), thionyl chloride (0.1 mL, 1.0 mmol, 1.5 equiv), **compound 37** was obtained in 80% yield

(186 mg) as oil white solid after column chromatography on silica gel (dichloromethane/methanol 95:5 as eluent).

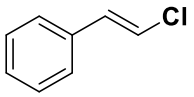
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.69 (d, 1H, $^3J_{H,H}$ = 8.2 Hz, C_2H), 6.62 (d, 1H, $^3J_{H,H}$ = 8.2 Hz, C_1H), 5.92 (d, 1H, $^3J_{H,H}$ = 5.5 Hz, C_7H), 5.13 (s, C_5H), 4.40 (dd, 1H, $^2J_{H,H}$ = 11.4 Hz, $^4J_{H,H}$ = 2.3 Hz, CH_2Cl), 3.95 (d, 1H, $^2J_{H,H}$ = 11.4 Hz, CH_2Cl), 3.85 (s, 3H, OCH_3), 3.15 (m, 1H, C_9H), 3.03 (d, 1H, $^2J_{H,H}$ = 18.6 Hz, $C_{10}H_2$), 2.58 (m, 1H, $C_{16}H_2$), 2.44 (m, 1H, $C_{14}H$), 2.43 (s, 3H, NCH_3), 2.41 (m, 1H, $C_{10}H$), 2.29 (m, 1H, $C_{16}H$), 2.03 (m, 1H, C_8H), 1.99 (m, 1H, $C_{15}H$), 1.82 (m, 1H, $C_{15}H$), 1.55 (m, 1H, C_8H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.6 (C-4), 143.2 (C-3), 132.4 (C-6), 131.7 (C-7), 129.4 (C-12), 127.0 (C-11), 118.8 (C-1), 113.6 (C-2), 86.3 (C-5), 59.0 (C-9), 56.5 (OCH_3), 46.8 (C-16), 46.5 (CH_2Cl), 43.1 (NCH_3), 41.2 (C-13), 38.4 (C-14), 35.3 (C-15), 24.9 (C-8), 20.8 (C-10).

HRMS (ESI), *m/z*: calcd. for $C_{19}H_{22}ClNO_2Na^+$: 354.1231 $[M+Na]^+$; found: 354.1234.

Compound 38[10]

[(*E*)-2-chloro-vinyl] benzene



By following the **General procedure 1**, starting from benzaldehyde (200 mg, 1.9 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.2 mL, 2.8 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (1.2 mL, 2.6 mmol, 1.4 equiv), thionyl chloride (0.2 mL, 2.8 mmol, 1.5 equiv), **compound 38** was obtained in 93% yield (245 mg) as oil after column chromatography on silica gel (*n*- hexane as eluent).

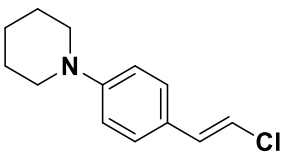
^{1}H NMR (400 MHz, $CDCl_3$) δ:7.32 (m, 2H, Ph H-3,5), 7.31 (m, 2H, Ph H-2,6), 7.29 (m, 1H, Ph H-4), 6.83 (d, 1H, $^3J_{H,H}$ = 13.7 Hz, H-1), 6.65 (d, 1H, $^3J_{H,H}$ = 13.7 Hz, H-2).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 134.9 (Ph C-1), 133.3 (C-1), 128.8 (2C, Ph C-3,5), 128.1 (Ph C-4), 126.1 (2C, Ph C-2,6), 118.7 (C-2).

HRMS (ESI), *m/z*: calcd. for $C_8H_7ClNa^+$: 161.0123 $[M+Na]^+$; found: 161.0125.

Compound 39

1-4-[(*E*)-2chlorovinyl] phenyl piperidine



By following the **General procedure 1**, starting from 4-(piperidin-1-yl)benzaldehyde (200 mg, 1.1 mmol, 1.0 equiv) in dry THF (3 mL), iodochloromethane (0.1 mL, 1.6 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl

ether (0.7 mL, 1.5 mmol, 1.4 equiv), thionyl chloride (0.1 mL, 1.6 mmol, 1.5 equiv), **compound 39** was obtained in 87% yield (212 mg) as oil after column chromatography on silica gel (*n*- hexane as eluent).

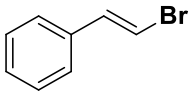
^{1}H NMR (400 MHz, $CDCl_3$) δ:7.18 (m, 2H, Ph H-3,5), 6.86 (m, 2H, Ph H-2,6), 6.73 (d, 1H, $^3J_{H,H}$ = 13.6 Hz, H-1), 6.46 (d, 1H, $^3J_{H,H}$ = 13.6 Hz, H-2), 3.18 (m, 2H, Pip H-6), 1.70 (m, 6H, Pip H-2,3,5), 1.59 (m, 2H, Pip H-4).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.7 (Ph C-1), 132.9 (C-1), 127.0 (2C, Ph C-3,5), 125.4 (Ph C-4), 115.9 (2C, Ph C-2,6), 115.2 (C-2), 50.0 (2C, Pip C-2,6), 25.6 (2C, Pip C-3,5), 24.3 (Pip C-4).

HRMS (ESI), *m/z*: calcd. for $C_{13}H_{16}ClNNa^+$: 244.0863 $[M+Na]^+$; found: 244.0865.

Compound 40[11]

[(*E*)-2-bromo-vinyl] benzene



By following the **General procedure 1**, starting from benzaldehyde (200 mg, 1.9 mmol, 1 equiv) in dry THF (3 mL), dibromomethane (0.2 mL, 2.8 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (1.2 mL, 2.6 mmol, 1.4 equiv), thionyl chloride (0.2 mL, 2.8 mmol, 1.5 equiv), **compound 40** was obtained in 91% yield (317 mg) as oil after column chromatography on silica gel (*n*- hexane as eluent).

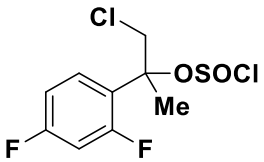
^{1}H NMR (400 MHz, $CDCl_3$) δ:7.31 (m, 4H, Ph H-2,3,5,6), 7.29 (m, 1H, Ph H-4), 7.11 (d, 1H, $^3J_{H,H}$ = 14.0 Hz, H-1), 6.77 (d, 1H, $^3J_{H,H}$ = 14.0 Hz, H-2).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.2 (C-1), 135.9 (Ph C-1), 128.8 (2C, Ph C-3,5), 128.3 (Ph C-4), 126.1 (2C, Ph C-2,6), 106.5 (C-2).

HRMS (ESI), *m/z*: calcd. for $C_8H_7BrNa^+$: 204.9623 $[M+Na]^+$; found: 204.9625.

Compound 41

1-chloro-2-(2,4-difluorophenyl)-2-propanylsulfurochloridoite



By following the **General procedure 1**, starting from 2',4'-difluoroacetophenone (200 mg, 1.3 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.2 mL, 1.9 mmol, 1,5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.8 mL, 1.8 mmol, 1.4 equiv), thionyl chloride (0.2 mL, 1.9 mmol, 1.5 equiv). The reaction was quenched with water (3 mL) and extracted with diethylether (3 mL). The organic layer was washed with saturated (*aq.*) NaCl (5 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced

pressure (bath: rt) to give the **compound 41** was obtained in 74 % yield (278 mg) as yellow oil after column chromatography on silica gel (*n*-hexane as eluent).

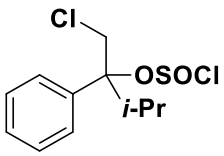
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (m, 1H, Ph H-6), 6.89 (m, 1H, Ph H-5), 6.85 (m, 1H, Ph H-3), 4.32 (d, 1H, ^2J = 11.3 Hz, H-1), 4.01 (dd, 1H, ^2J = 11.3, ^4J = 0.8 Hz, H-1), 2.10 (d, 3H, ^4J = 0.7 Hz, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 163.1 (dd, ^1J = 251.3, ^3J =12.4 Hz, Ph C-4), 160.6 (dd, ^1J = 253.5, ^3J = 12.4 Hz, Ph C-2), 130.1 (dd, ^3J = 9.66, ^4J = 4.7 Hz, Ph C-6), 120.2 (Ph C-1), 111.0 (dd, ^2J = 20.9, ^4J = 3.6 Hz, Ph C-5), 105.1 (dd, ^2J = 27.5, ^2J = 25.6 Hz, Ph C-3), 68.0 (d, ^3J = 3.4 Hz, C-2), 52.7 (d, ^4J = 6.7 Hz, C-1), 29.0 (d, ^4J = 2.9 Hz, CH_3).

HRMS (ESI), *m/z*: calcd. for $C_9H_9Cl_2F_2O_2S^+$: 288.9663 $[M+H]^+$; found: 288.9665.

Compound 42

1-chloro-3-methyl-2-phenyl-2-butanyl sulfurochloridoite



By following the **General procedure 1**, starting from Isobutyrophenone (200 mg, 1.4 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.2 mL, 2.0 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.9 mL, 1.9 mmol, 1.4 equiv), thionyl chloride (0.2 mL, 2.0 mmol, 1.5 equiv). The reaction was quenched with water (3 mL) and extracted with diethylether (3 mL). The organic layer was washed with saturated (*aq.*) NaCl (5 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure (bath: rt) to give the **compound 42** was obtained in 66% yield (260 mg) as yellow oil after column chromatography on silica gel (*n*-hexane as eluent).

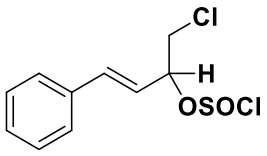
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (m, 2H, Ph H-2,6), 7.37 (m, 2H, Ph H-3,5), 7.31 (m, 1H, Ph H-4), 4.14-3.97 (AB-System, 2H, $^2J_{AB}$ = 11.4 Hz, H-1), 2.70 (m, 1H, H-3), 1.14 (d, 3H, ^4J = 6.5 Hz, CH_3), 0.91 (d, 3H, ^4J = 6.6 Hz, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.9 (Ph C-1), 128.0 (2C, Ph C-3,5), 127.8 (Ph C-4), 127.4 (2C, Ph C-2,6), 81.7 (C-2), 53.1 (C-1), 35.5 (C-3), 18.3 (CH_3), 17.3 (CH_3).

HRMS (ESI), *m/z*: calcd. for $C_{11}H_{15}Cl_2O_2S^+$: 281.0164 $[M+H]^+$; found: 281.0169.

Compound 43

(3E)-1-chloro-4-phenyl-3-buten-2-yl sulfurochloridoite



By following the **General procedure 1**, starting from cinnamaldehyde (200 mg, 1.5mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.2 mL, 2.3 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (1.0 mL, 2.1 mmol, 1.4 equiv), thionyl chloride (0.2 mL, 2.3 mmol, 1.5 equiv). The reaction was quenched with water (3 mL) and extracted with diethylether (3 mL). The organic layer was washed with saturated (*aq.*) NaCl (5 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure (bath: rt) to give the **compound 43** was obtained in 71% yield (282 mg) as yellow oil after column chromatography on silica gel (*n*-hexane as eluent).

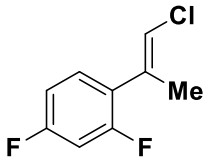
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42 (m, 2H, Ph H-2,6), 7.35 (m, 2H, Ph H-3,5), 7.31 (m, 1H, Ph H-4), 6.73 (d, 1H, ^3J = 15.7 Hz, H-4), 6.21 (dd, 1H, ^3J = 15.7, ^4J = 8.8 Hz, H-3), 4.70 (m, 1H, H-2), 3.88 (dd, 1H, ^2J = 11.2, ^3J= 5.5 Hz, H-1), 3.78 (dd, 1H, ^2J = 11.2, ^4J= 8.0 Hz, H-1).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 135.4 (Ph C-1), 135.0 (C-4), 128.7 (2C, Ph C-3,5), 128.6 (Ph C-4), 126.9 (2C, Ph C-2,6), 125.9 (C-3), 61.1 (C-2), 47.8 (C-1).

HRMS (ESI), *m/z*: calcd. for $C_{10}H_{11}Cl_2O_2S^+$: 264.9851 $[M+H]^+$; found: 264.9855.

Compound 44

(*E*)-1-(1-chloroprop-1-en-2-yl)-2,4-difluorobenzene



By following the **General procedure 1**, starting from 2',4'-difluoroacetophenone (200 mg, 1.3 mmol, 1 equiv) in dry THF (3 mL), chloroiodomethane (0.1 mL, 1.9 mmol, 1.5 equiv), MeLi-LiBr 2.2 M solution in diethyl ether (0.8 mL, 1.8 mmol, 1.4 equiv), thionyl chloride (0.1 mL, 1.9 mmol, 1.5 equiv), **compound 44** was obtained as a mixture of two separable isomers consisting in ***(E)*-44** (47% yield, 115 mg, yellow oil) and ***(Z)*-44** (37% yield, 91 mg, yellow oil) after column chromatography on silica gel (*n*-hexane as eluent) ***(Z)*** R_f 0.8, ***(E)*** R_f 0.77

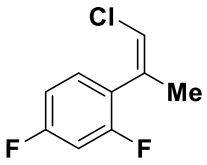
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.17 (dd, 1H, ^3J = 8.7, ^3J =6.4 Hz, Ph H-3), 6.83 (m, 2H, Ph H-5,6), 6.23 (s, 1H, H-1), 2.15 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.4 (dd, ^1J = 244.9, ^3J =11.6 Hz, Ph C-4), 159.4 (dd, ^1J = 250.8, ^3J = 8.0 Hz, Ph C-2), 133.5 (C-2), 130.2 (dd, ^3J = 9.2, ^3J = 5.4 Hz, Ph C-6), 124.6 (d, ^2J = 20.1, Ph C-1), 118.6 (C-2), 111.3 (dd, ^2J = 21.1, ^4J = 3.8 Hz, Ph C-5), 104.4 (t, ^2J = 26.0 Hz, Ph C-3), 17.7 (d, ^4J = 2.9Hz, CH_3).

^{19}F NMR (376 MHz, $CDCl_3$) δ: -110.7 (p, ^4J = 8.0 Hz, F1), -110.4 (q, ^4J = 8.9 Hz, F2).

HRMS (ESI), *m/z*: calcd. for $C_9H_7ClF_2H^+$: 189.0283 $[M+H]^+$; found: 189.0285.

(*Z*)-1-(1-chloroprop-1-en-2-yl)-2,4-difluorobenzene



^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.20 (m, 1H, Ph H-3), 6.87 (m, 2H, Ph H-5,6), 6.19 (s, 1H, H-1), 2.06 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.5 (dd, ^1J = 248.8, ^3J =11.1 Hz, Ph C-4), 159.4 (dd, ^1J = 249.4, ^3J = 12.4 Hz, Ph C-2), 133.3 (C-2), 130.9 (dd, ^3J = 8.9, ^3J = 4.5 Hz, Ph C-6), 122.6 (Ph C-1), 115.9 (C-2), 111.2 (dd, ^2J = 21.3, ^4J = 3.7 Hz, Ph C-5), 104.2 (t, ^2J = 25.6 Hz, Ph C-3), 22.5 (d, ^4J = 2.0 Hz, CH_3).

^{19}F NMR (376 MHz, $CDCl_3$) δ: -110.6 (p, ^4J = 8.0 Hz, F1), -110.1 (q, ^4J = 8.5 Hz, F2).

HRMS (ESI), *m/z*: calcd. for $C_9H_7ClF_2H^+$: 189.0283 $[M+H]^+$; found: 189.0289.

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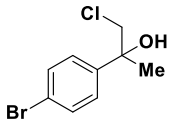
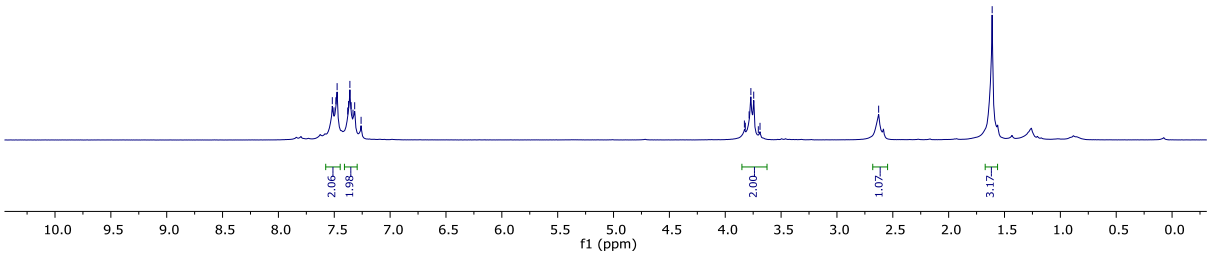
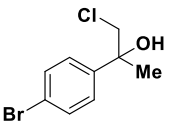
Copies of NMR spectra

Compound 1b

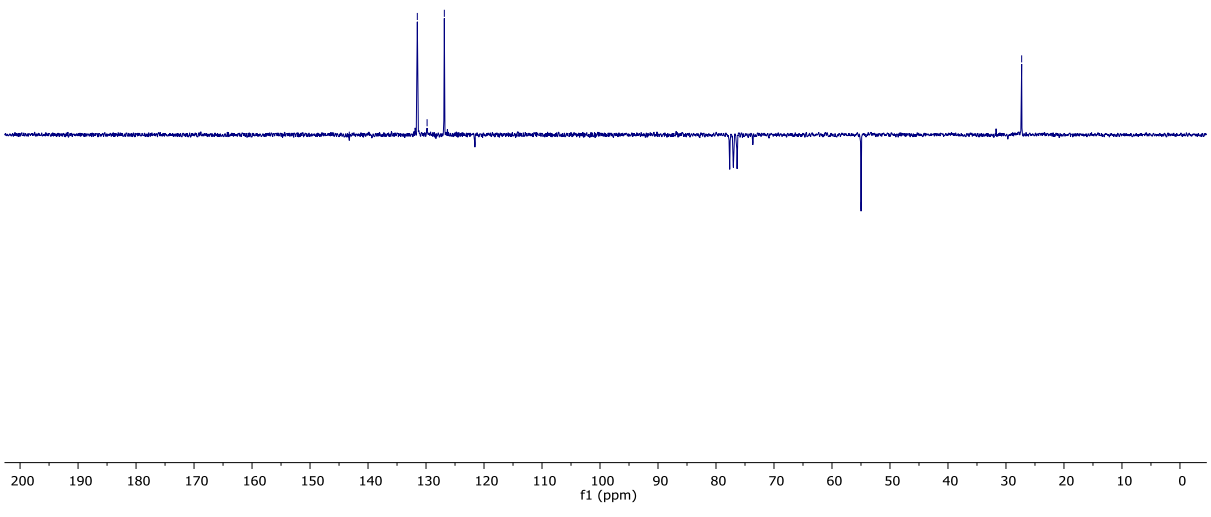


(^{1}H NMR, $CDCl_3$, 200 MHz)

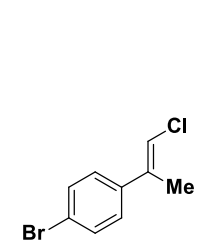




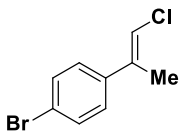
(^{13}C NMR, $CDCl_3$, 50 MHz)



Compound 2

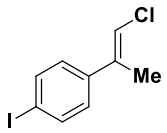


^{1}H NMR, 400 MHz, $CDCl_3$

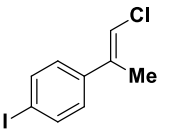


^{13}C NMR, 100 MHz, $CDCl_3$

Compound 3

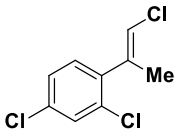


^{1}H NMR, 400 MHz, $CDCl_3$

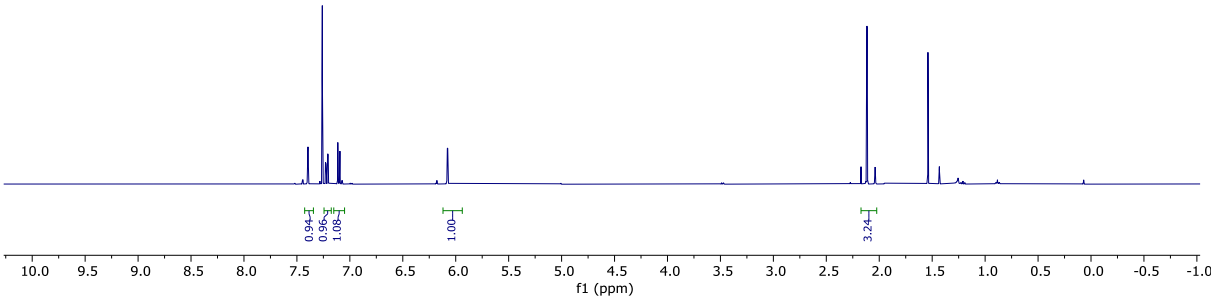


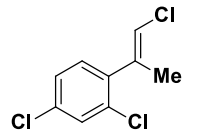
^{13}C NMR, 100 MHz, $CDCl_3$

Compound 4

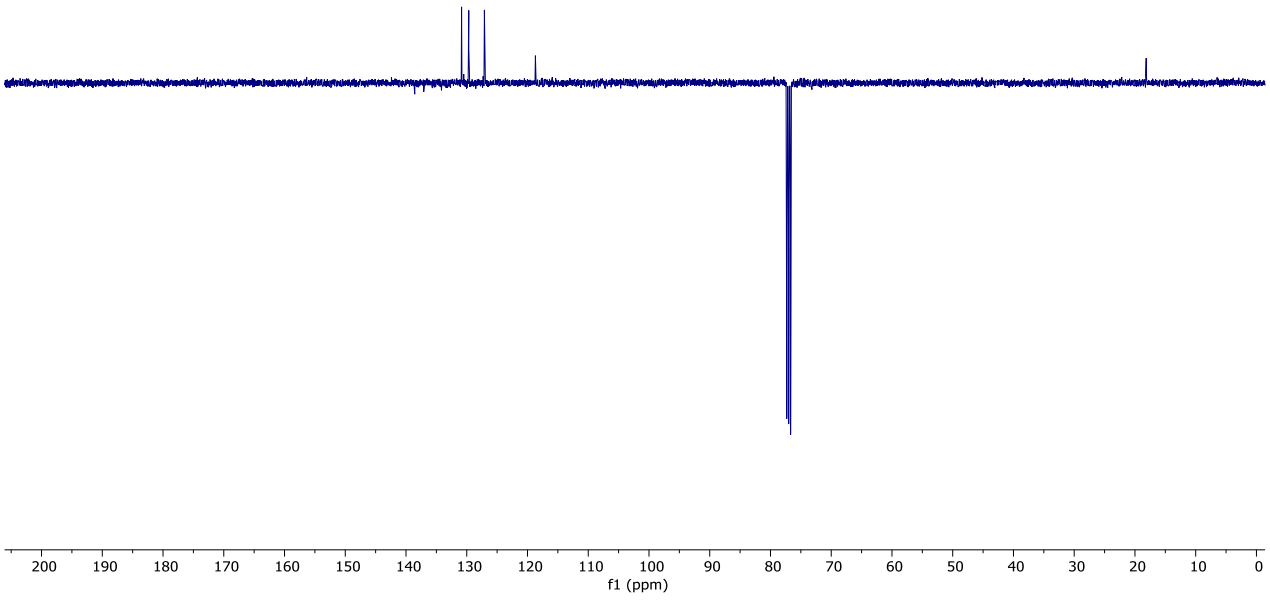


^{1}H NMR, 400 MHz, $CDCl_3$

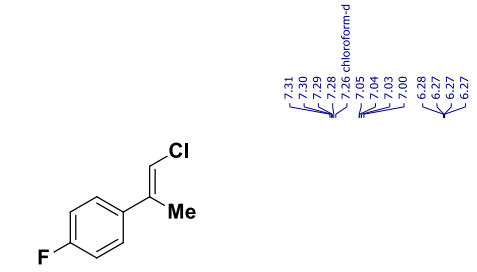




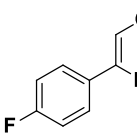
^{13}C NMR, 100 MHz, $CDCl_3$



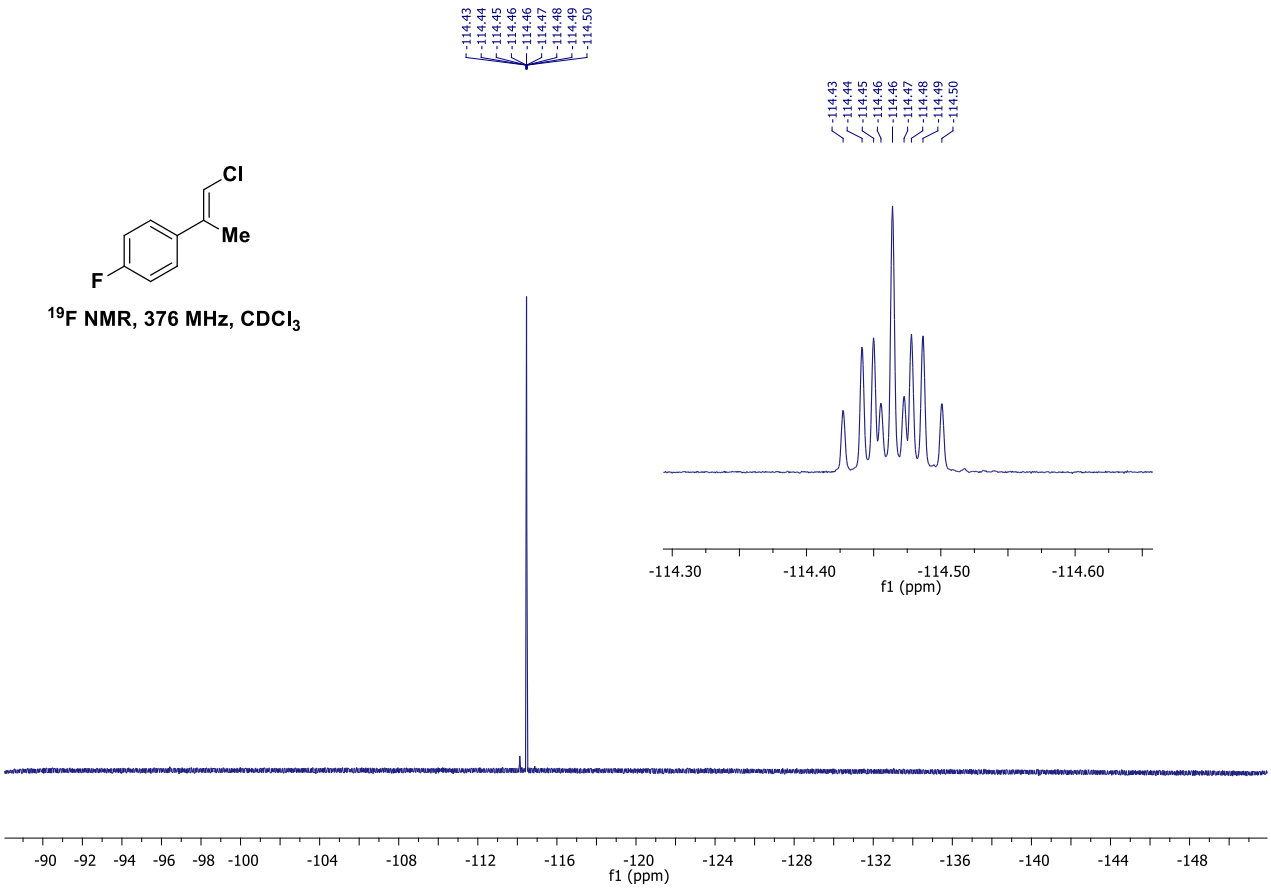
Compound 5



^{1}H NMR, 400 MHz, $CDCl_3$

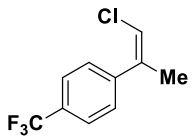


^{13}C NMR, 100 MHz, $CDCl_3$

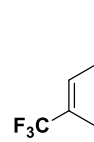


^{19}F NMR, 376 MHz, $CDCl_3$

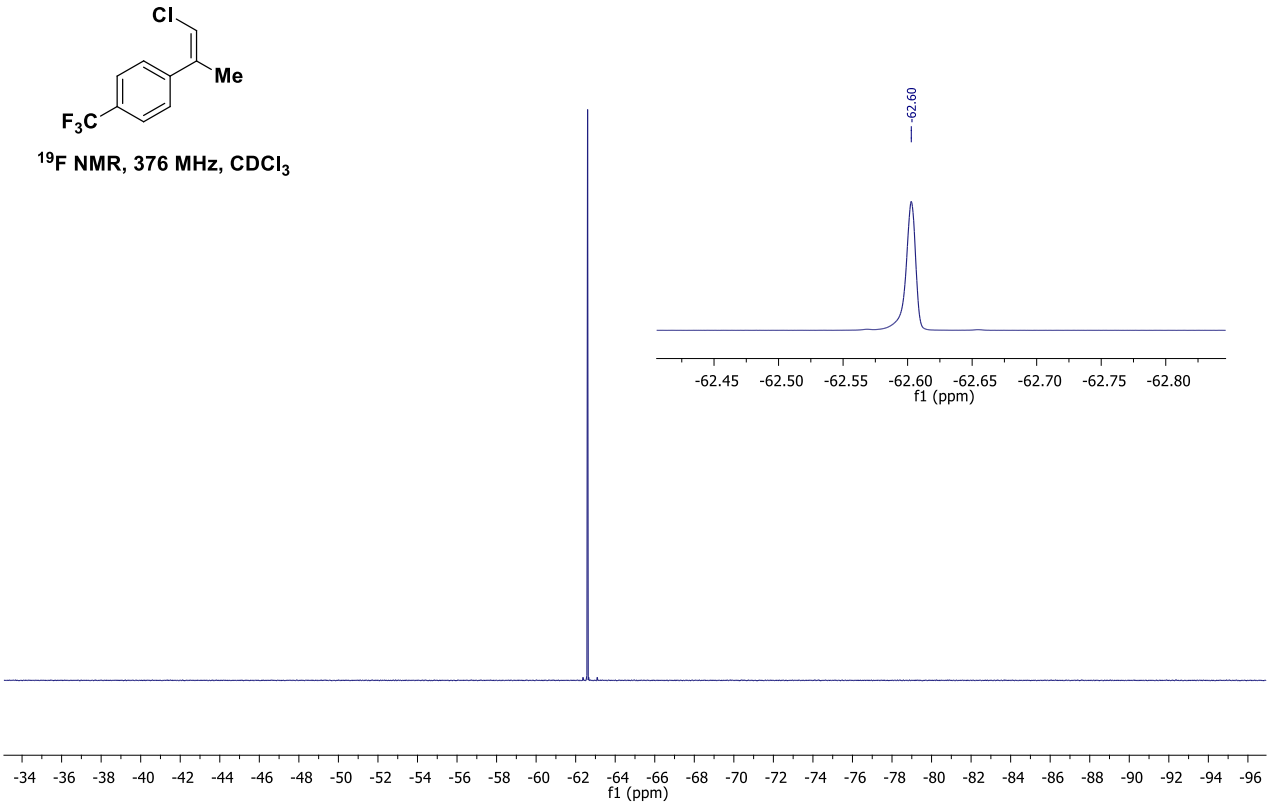
Compound 6



^{1}H NMR, 400 MHz, $CDCl_3$

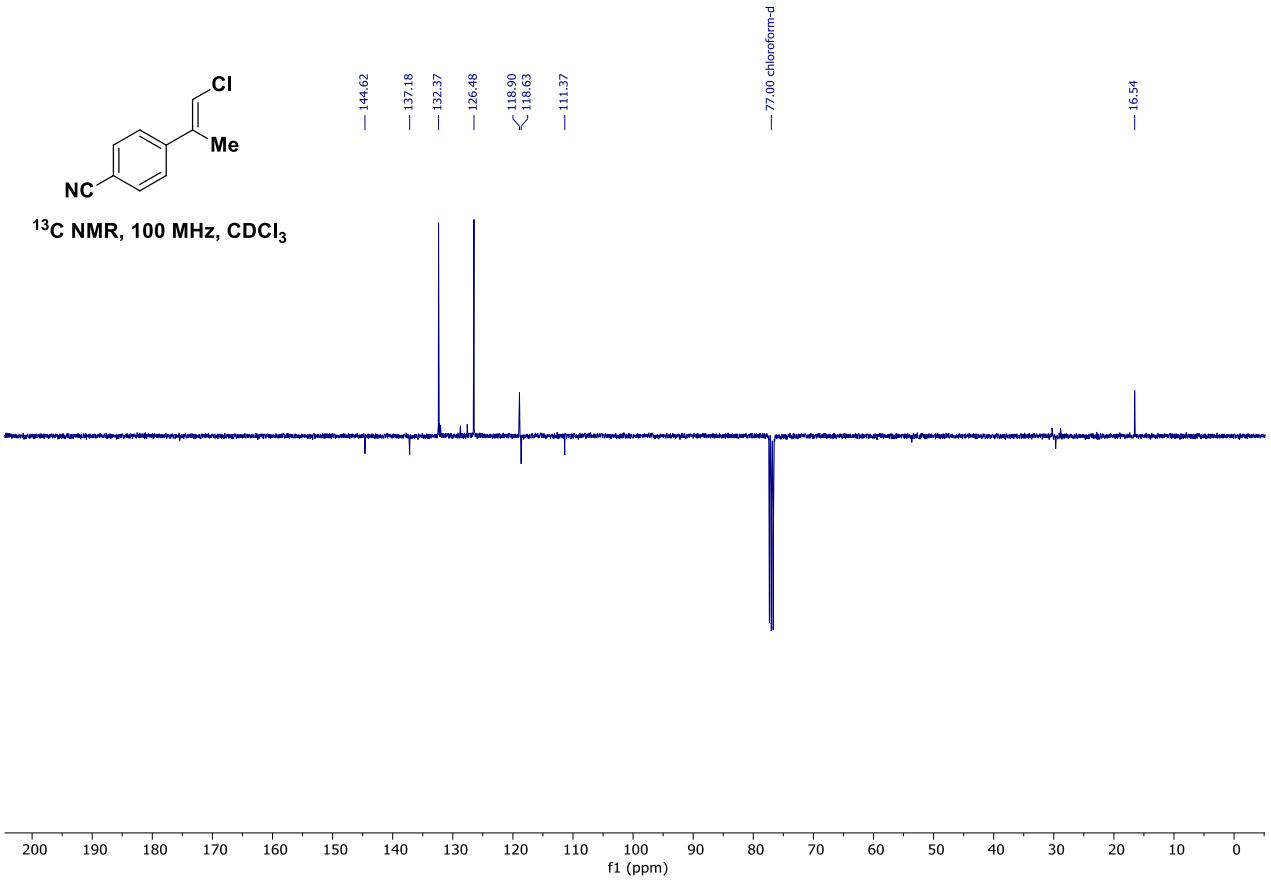


^{13}C NMR, 100 MHz, $CDCl_3$


Cl
Me
F3C
19F NMR, 376 MHz, CDCl3
-62.60
-62.60
-62.45 -62.50 -62.55 -62.60 -62.65 -62.70 -62.75 -62.80
f1 (ppm)
-34 -36 -38 -40 -42 -44 -46 -48 -50 -52 -54 -56 -58 -60 -62 -64 -66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90 -92 -94 -96
f1 (ppm)

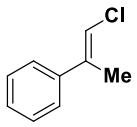
Compound 7

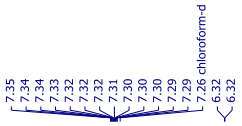
^{1}H NMR, 400 MHz, $CDCl_3$



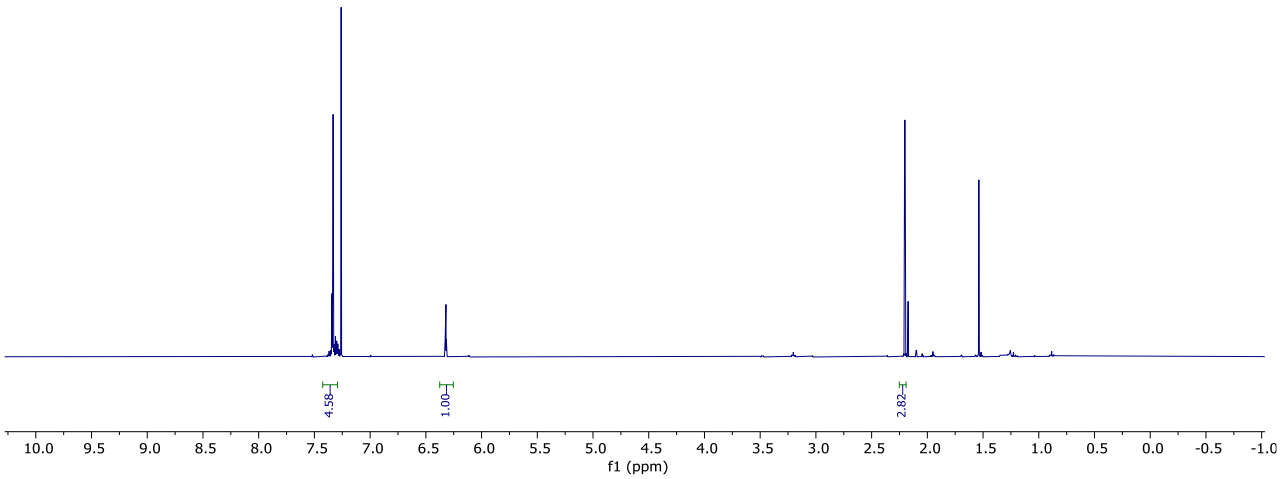
^{13}C NMR, 100 MHz, $CDCl_3$

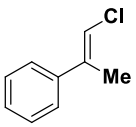
Compound 8



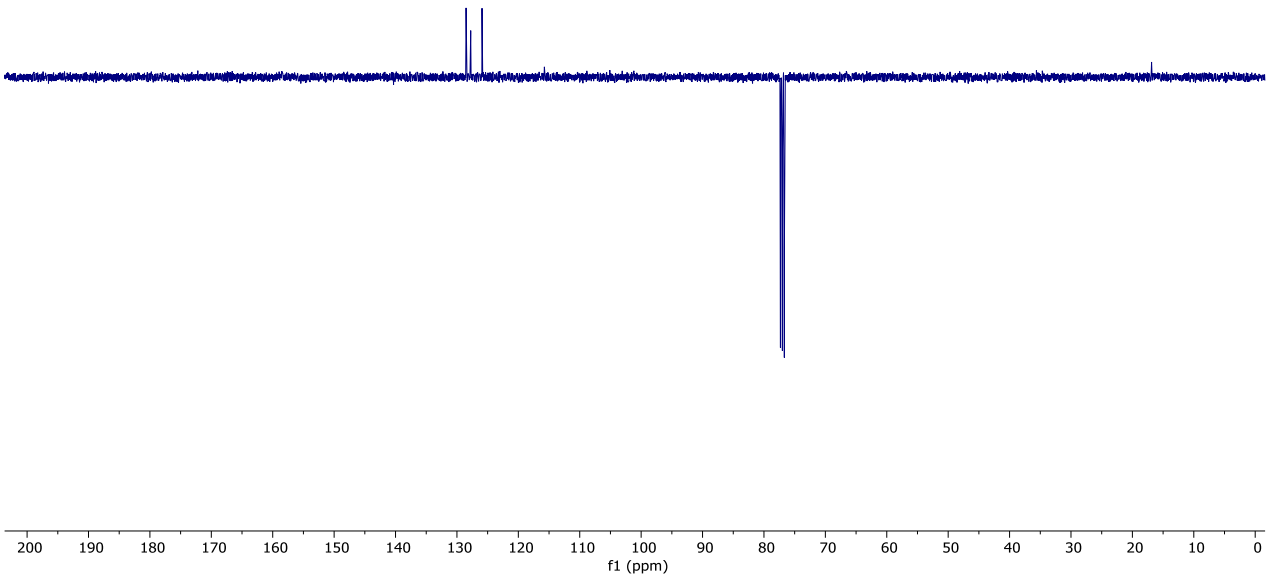


^{1}H NMR, 400 MHz, $CDCl_3$

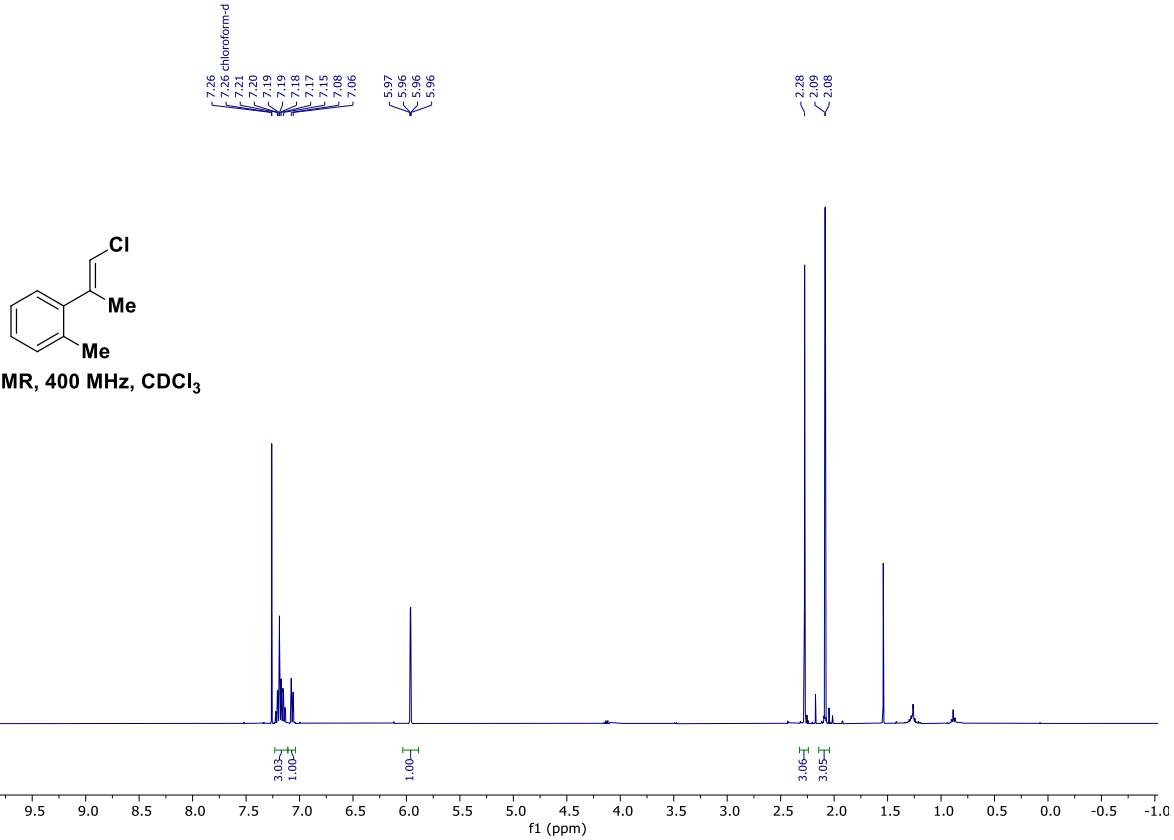




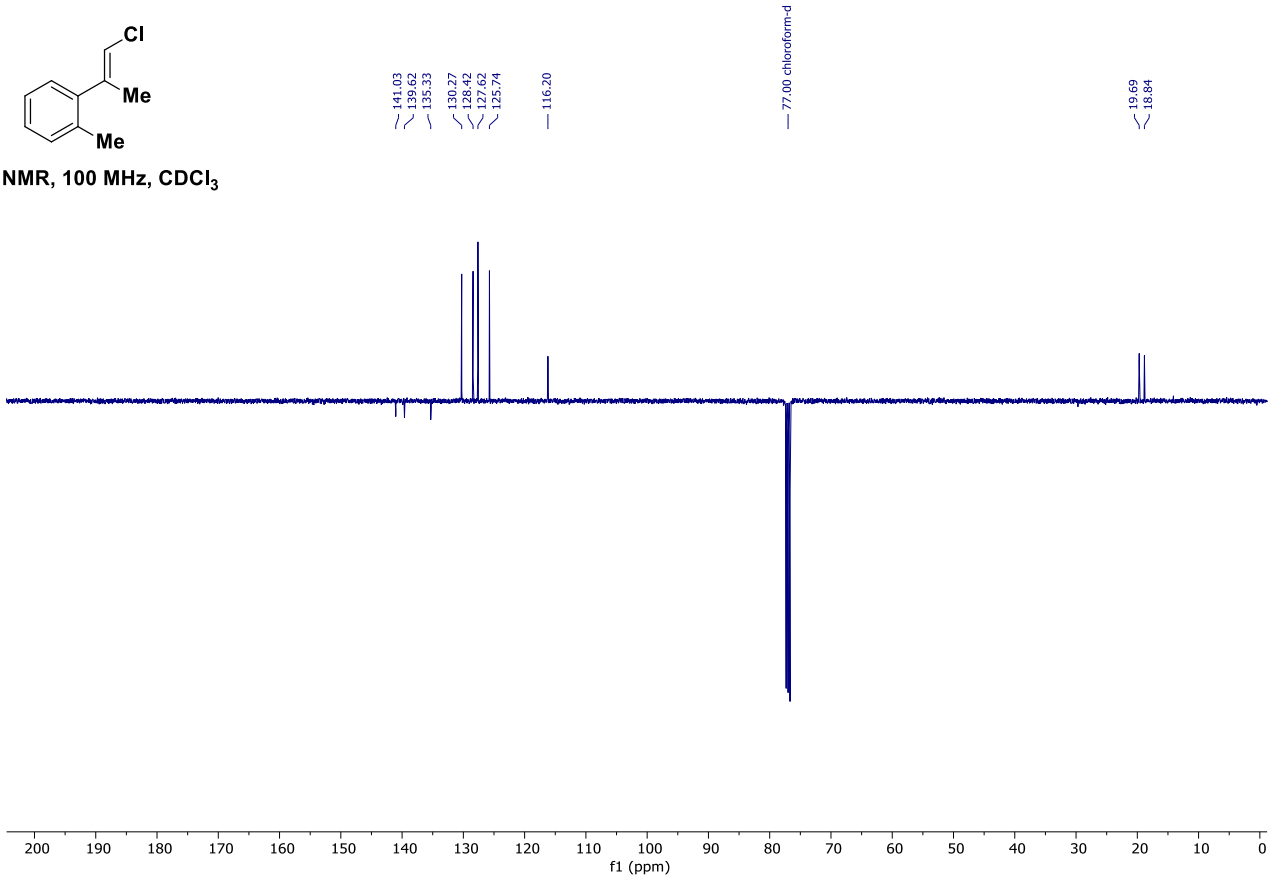
^{13}C NMR, 100 MHz, $CDCl_3$



Compound 9

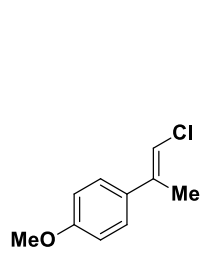


^{1}H NMR, 400 MHz, $CDCl_3$

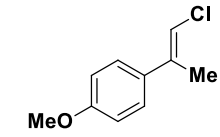


^{13}C NMR, 100 MHz, $CDCl_3$

Compound 10

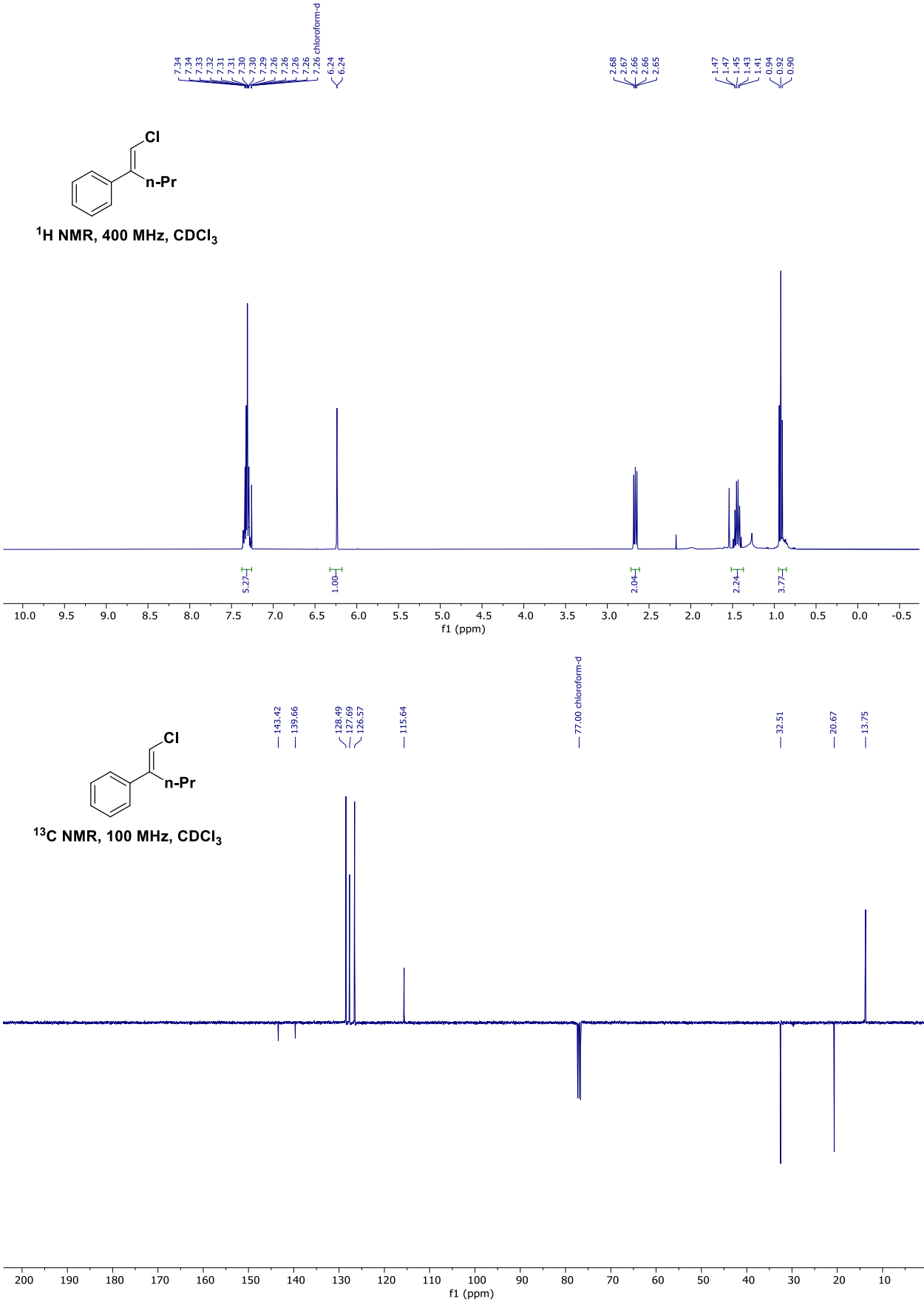


^{1}H NMR, 400 MHz, $CDCl_3$

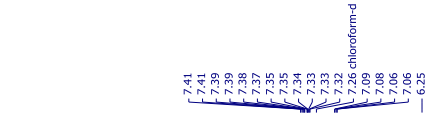


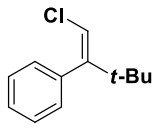
^{13}C NMR, 100 MHz, $CDCl_3$

Compound 11

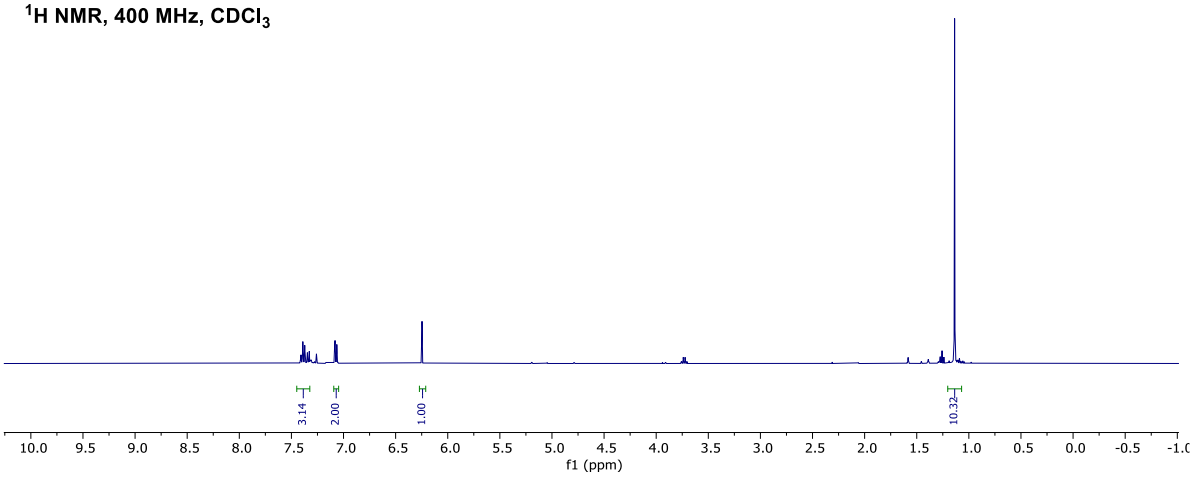

7.34
7.34
7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.26
7.26
7.26
7.26 chloroform-d
6.24
6.24
2.68
2.67
2.66
2.66
2.65
1.47
1.47
1.45
1.43
1.41
0.94
0.92
0.90
Cl
n-Pr
1H NMR, 400 MHz, CDCl3
5.27
1.00
2.04
2.24
3.77
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
143.42
139.66
128.49
127.69
126.57
115.64
77.00 chloroform-d
32.51
20.67
13.75
Cl
n-Pr
13C NMR, 100 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

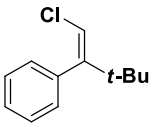
Compound 12



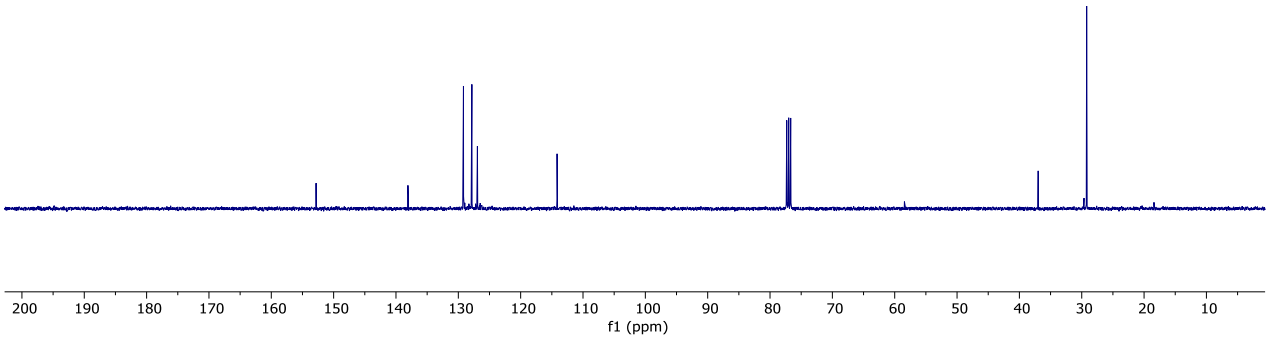


^{1}H NMR, 400 MHz, $CDCl_3$

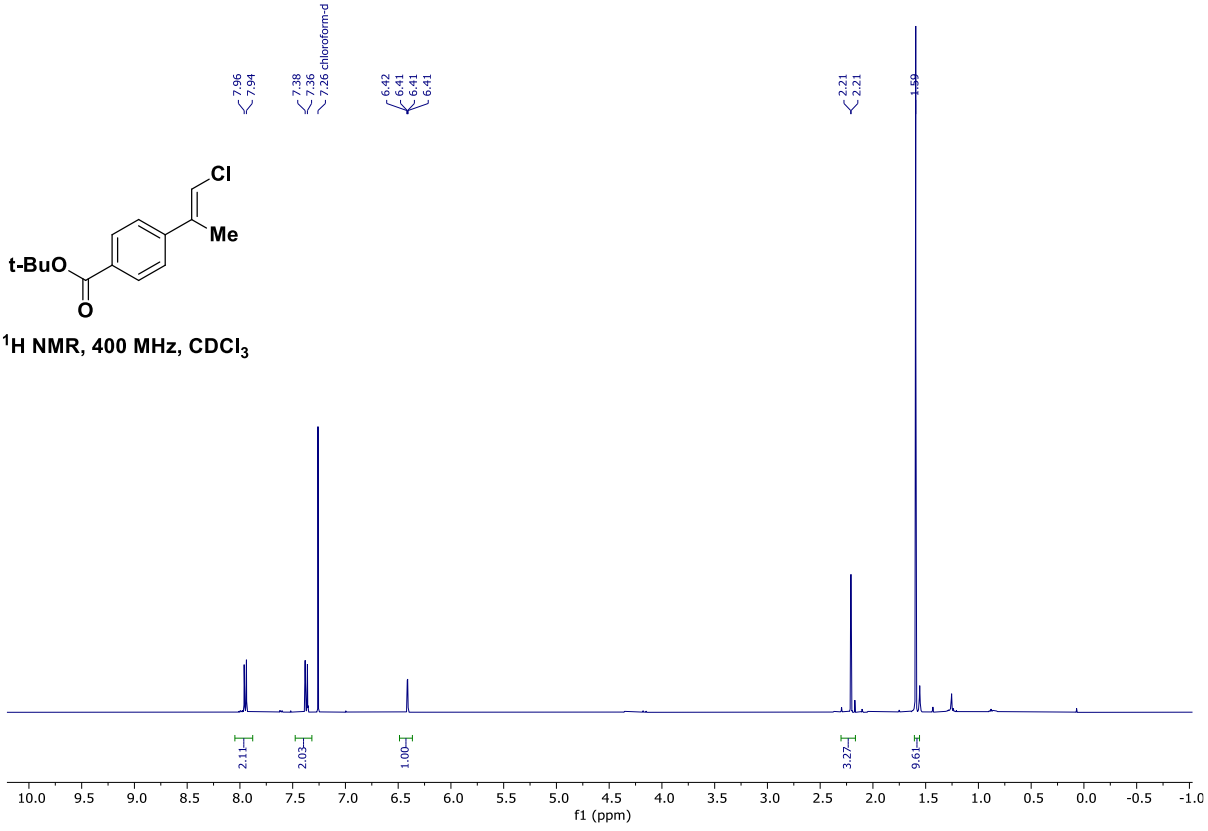




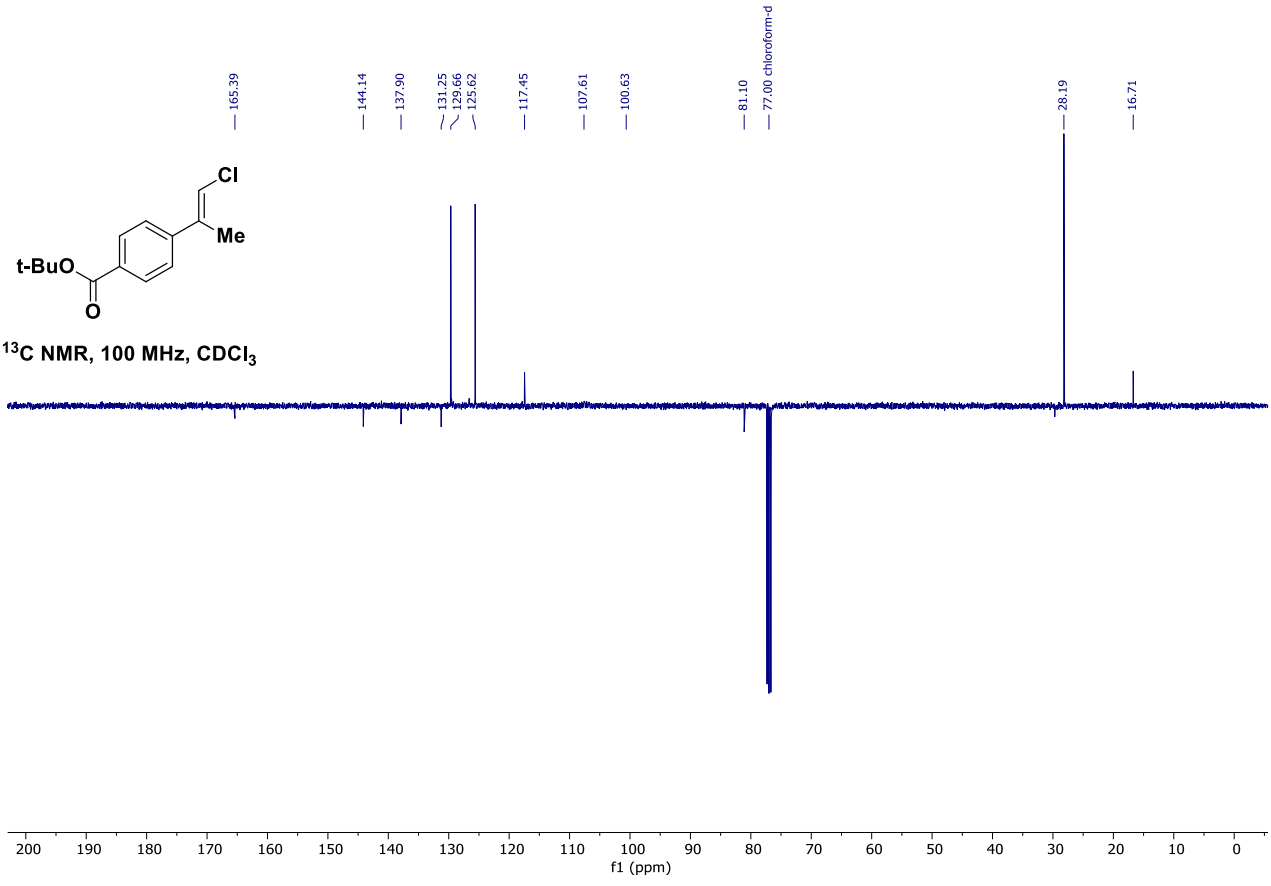
^{13}C NMR, 100 MHz, $CDCl_3$



Compound 13

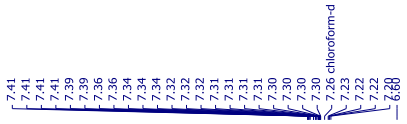


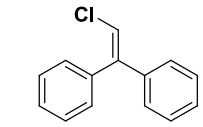
^{1}H NMR, 400 MHz, $CDCl_3$



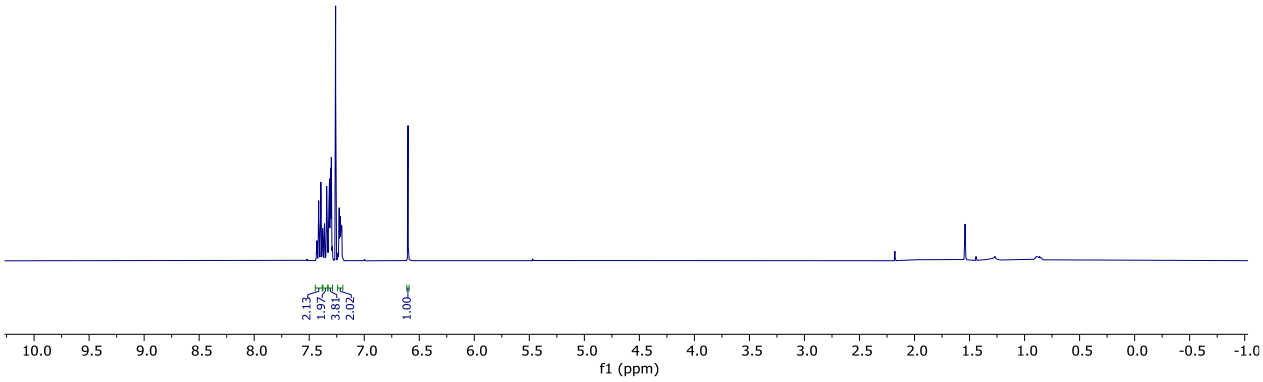
^{13}C NMR, 100 MHz, $CDCl_3$

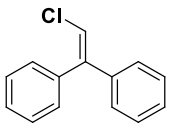
Compound 14



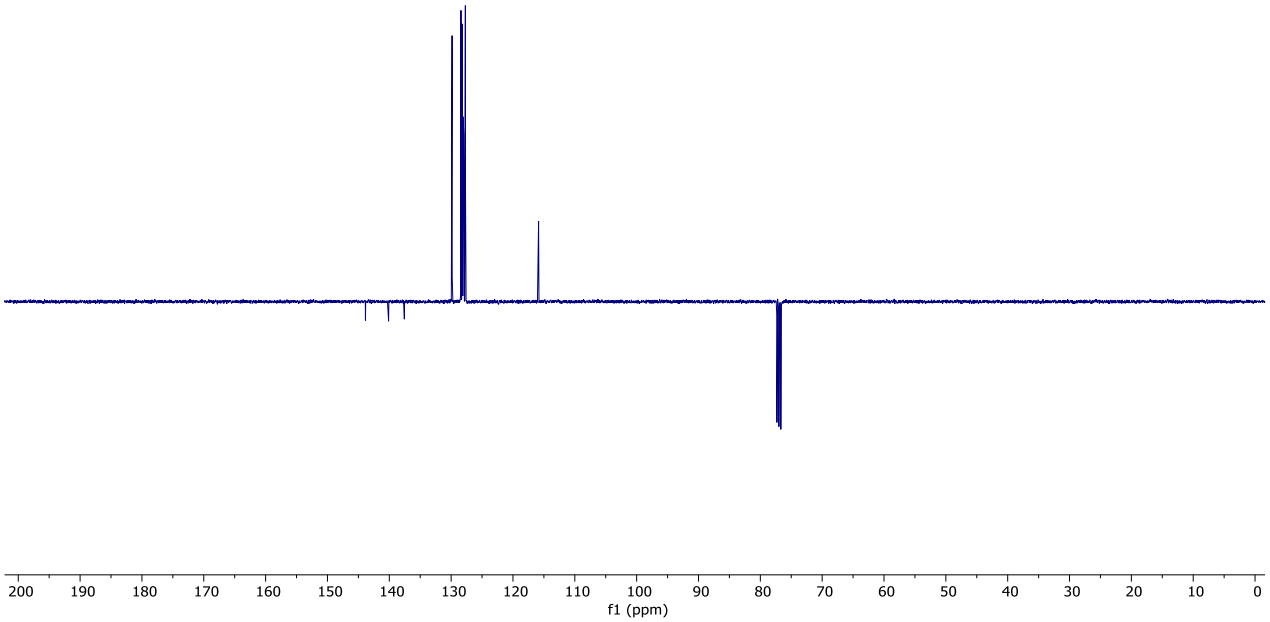


^{1}H NMR, 400 MHz, $CDCl_3$

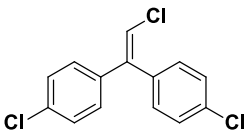




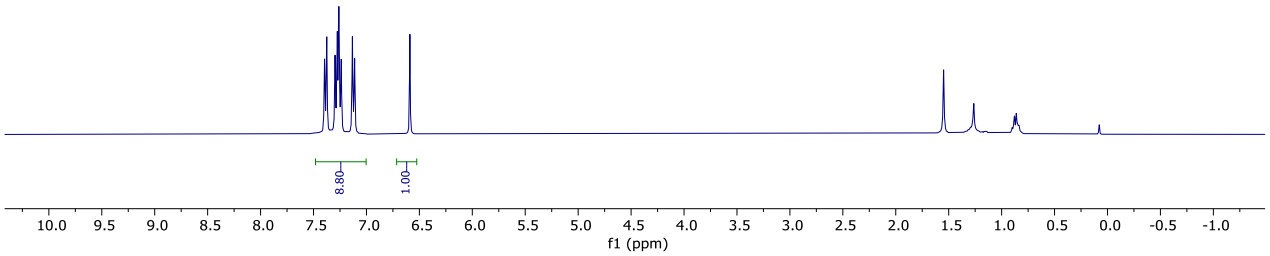
^{13}C NMR, 100 MHz, $CDCl_3$

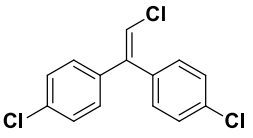


Compound 15

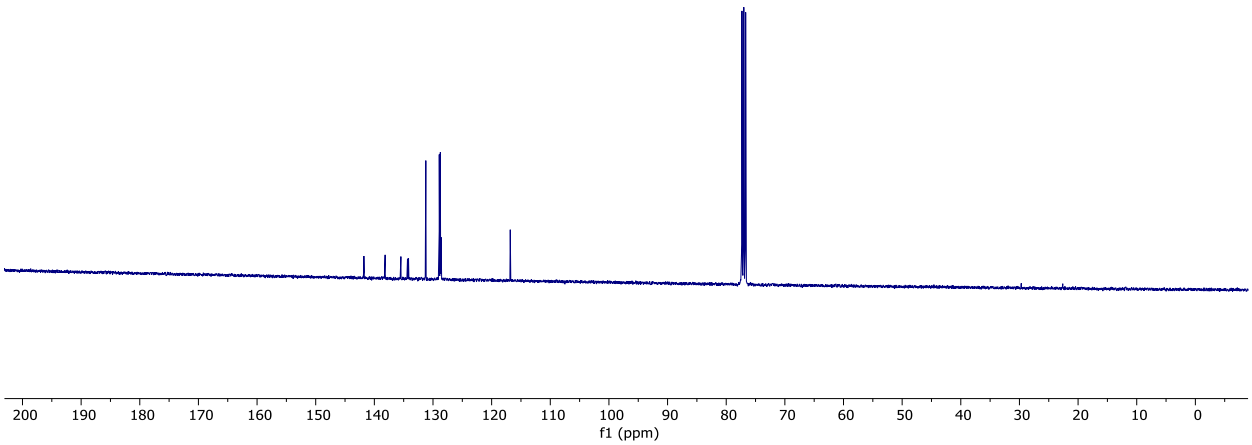


^{1}H NMR, 400 MHz, $CDCl_3$

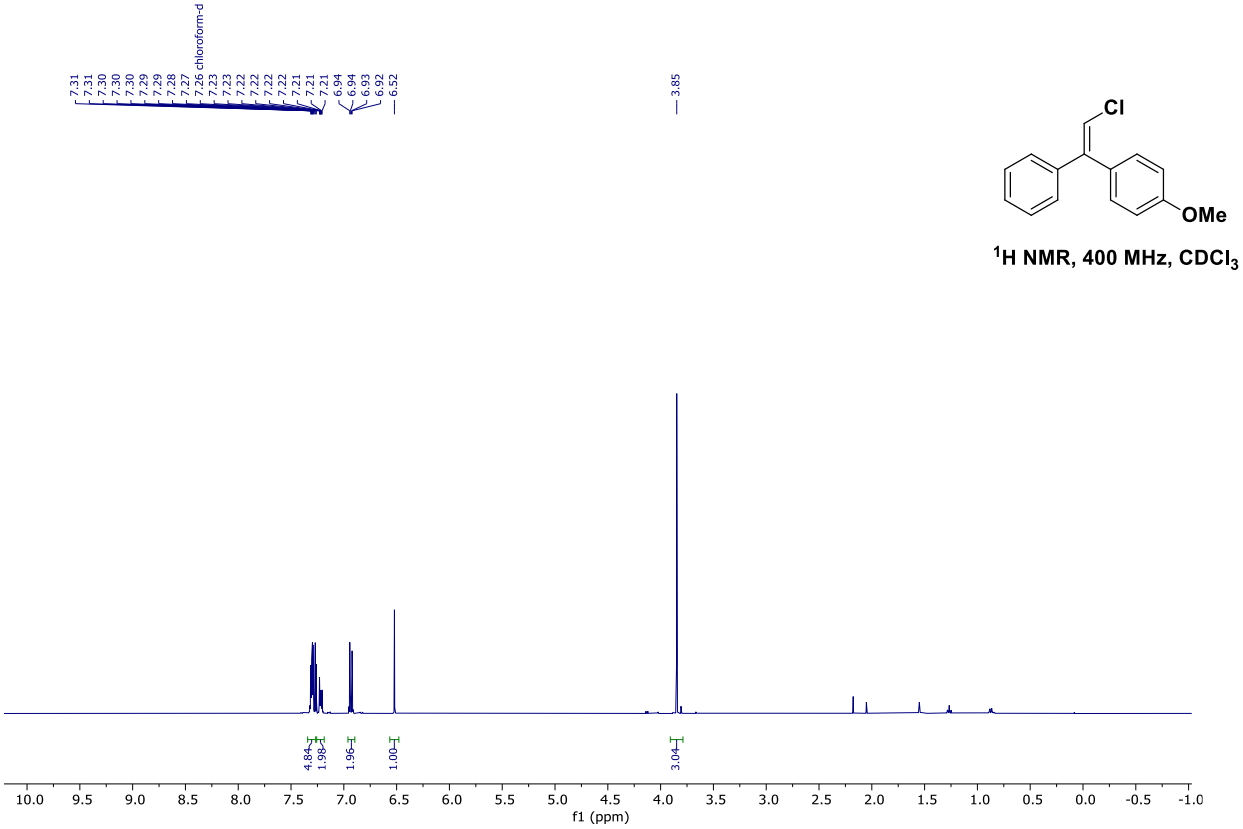




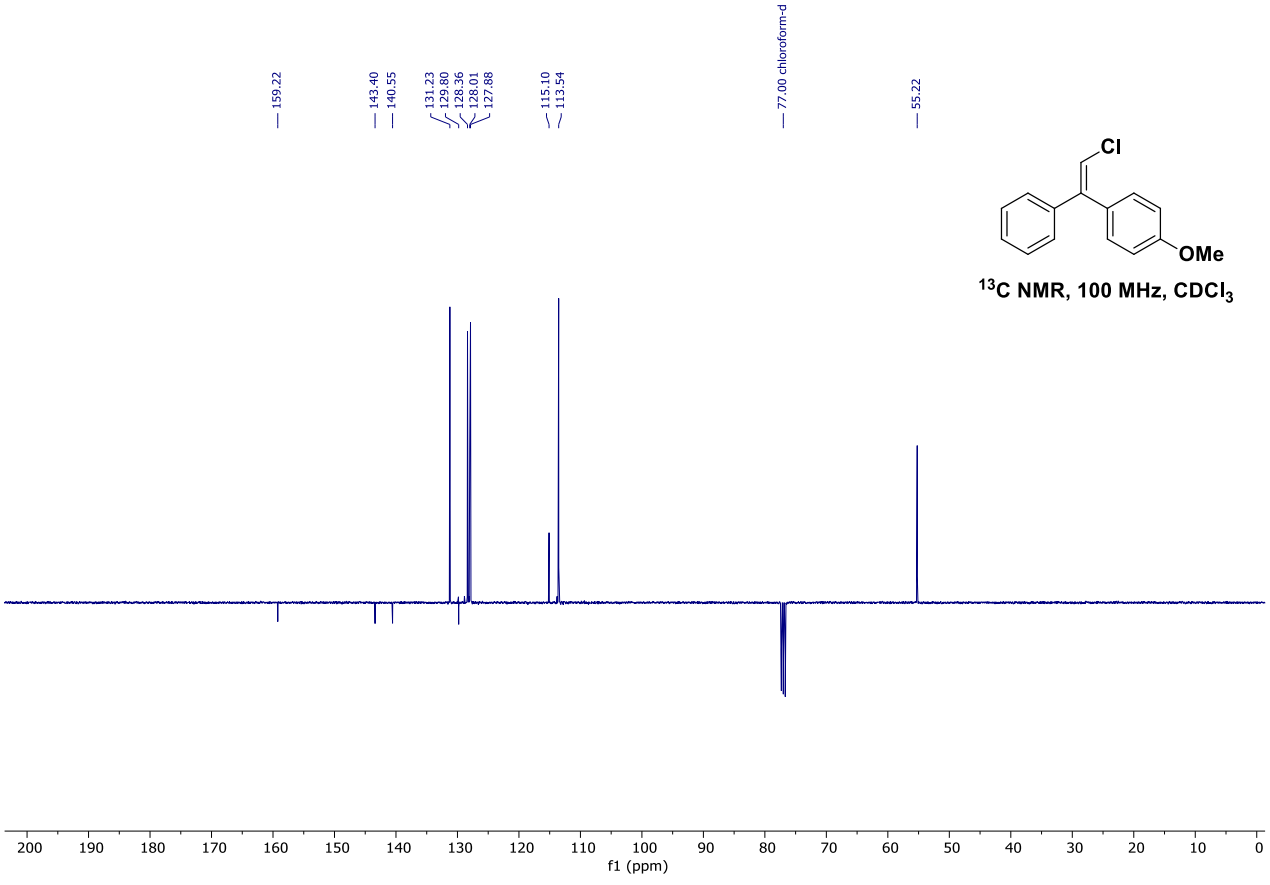
^{13}C NMR, 100 MHz, $CDCl_3$



Compound 16

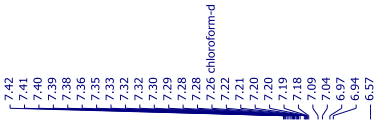


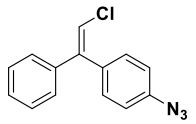
^{1}H NMR, 400 MHz, $CDCl_3$



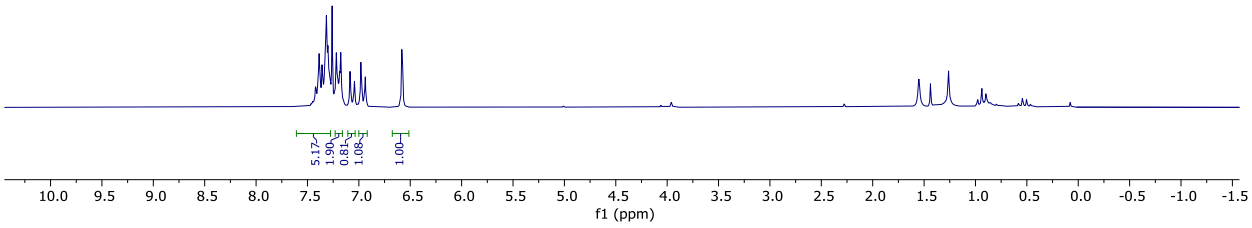
^{13}C NMR, 100 MHz, $CDCl_3$

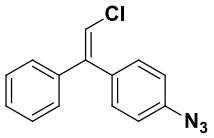
Compound 17



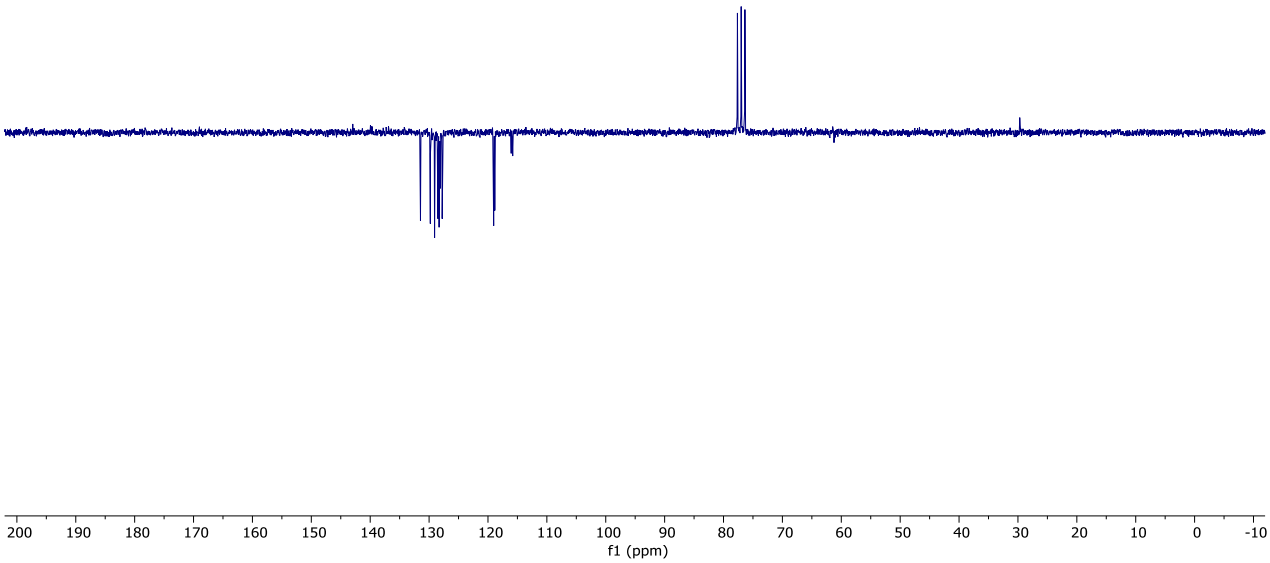


^{1}H NMR, 200 MHz, $CDCl_3$

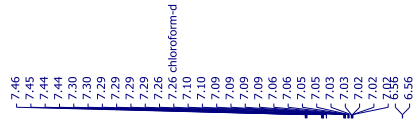


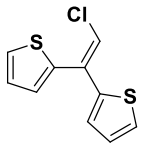


^{13}C NMR, 100 MHz, $CDCl_3$

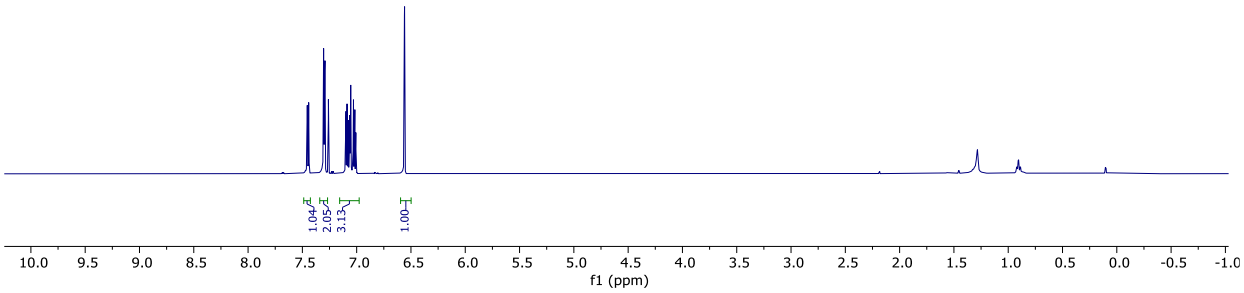


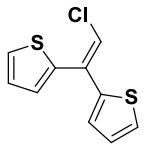
Compound 18



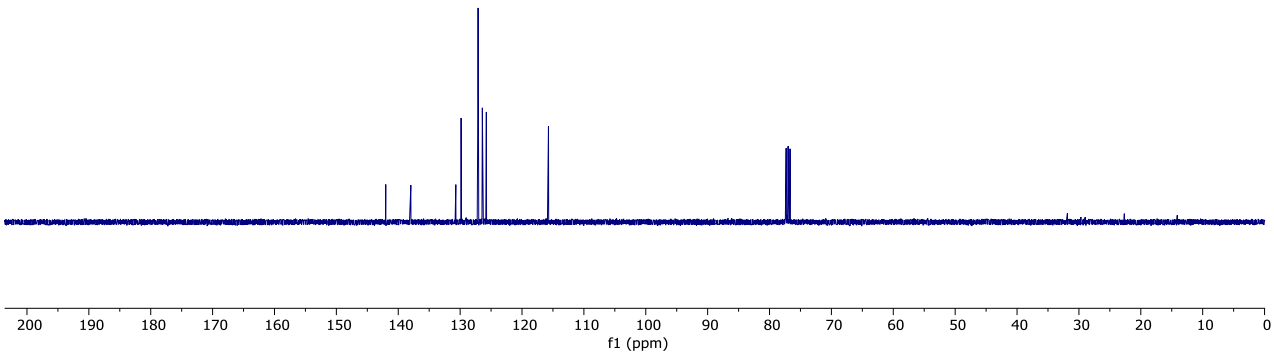


^{1}H NMR, 400 MHz, $CDCl_3$

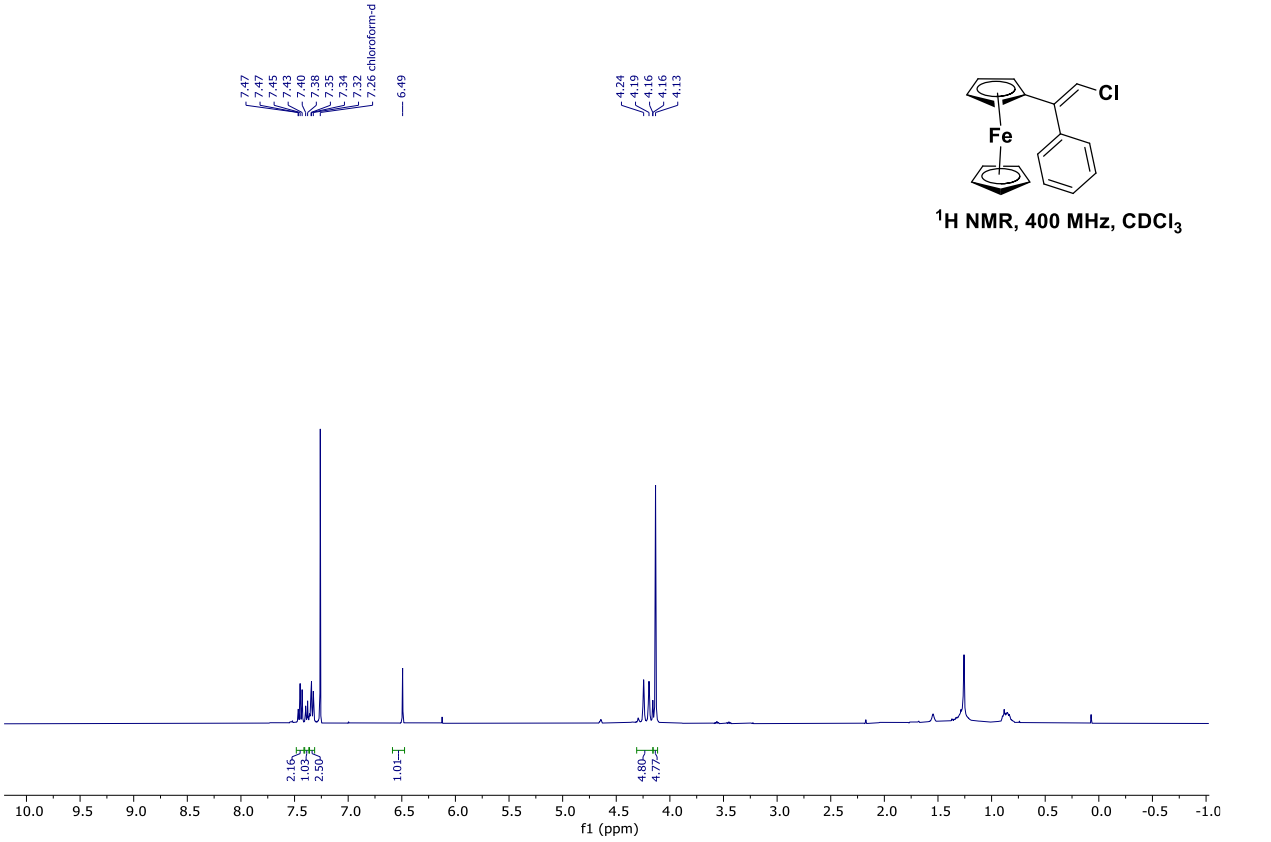




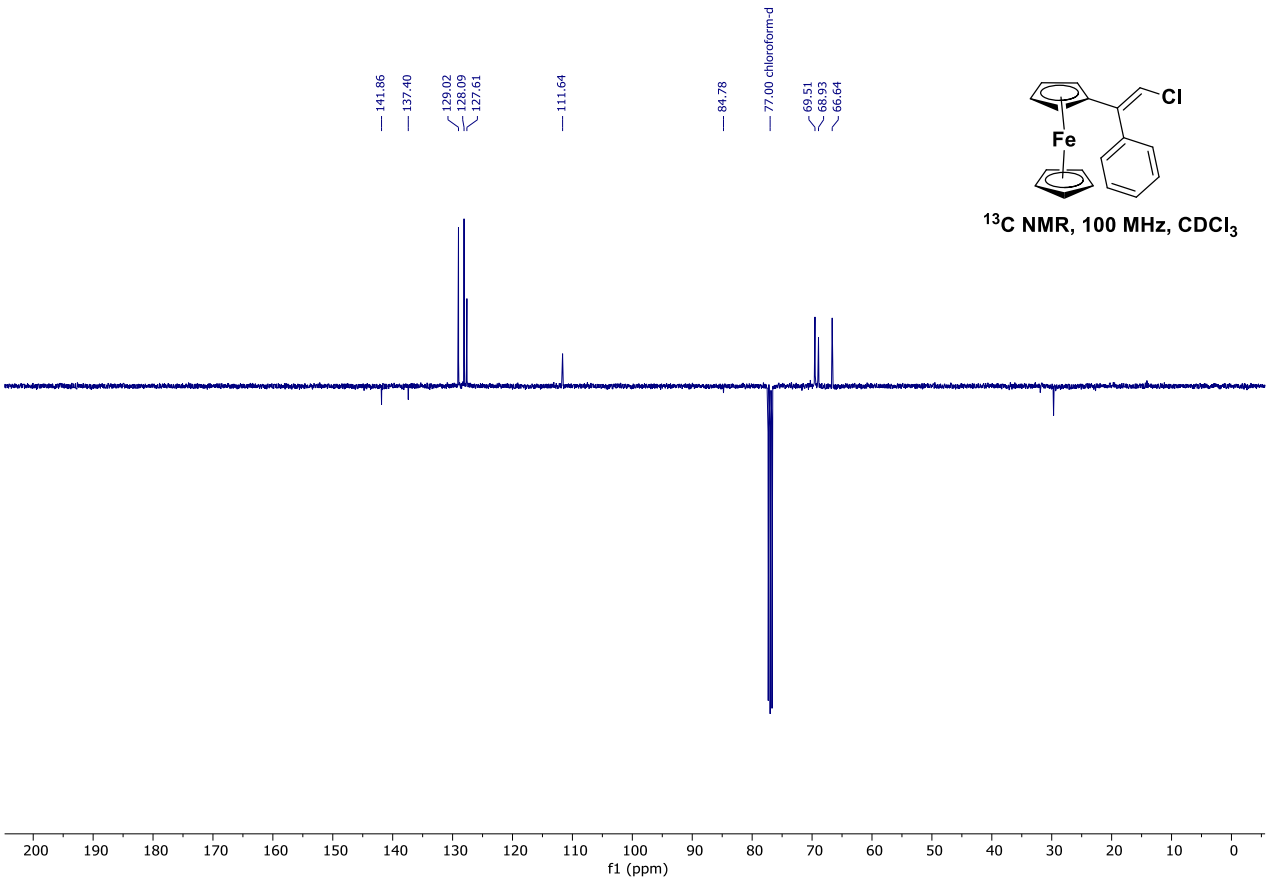
^{13}C NMR, 100 MHz, $CDCl_3$



Compound 19

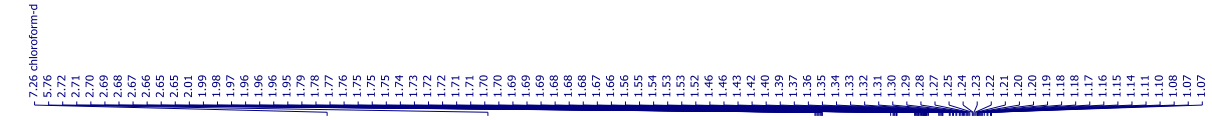


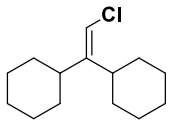
^{1}H NMR, 400 MHz, $CDCl_3$



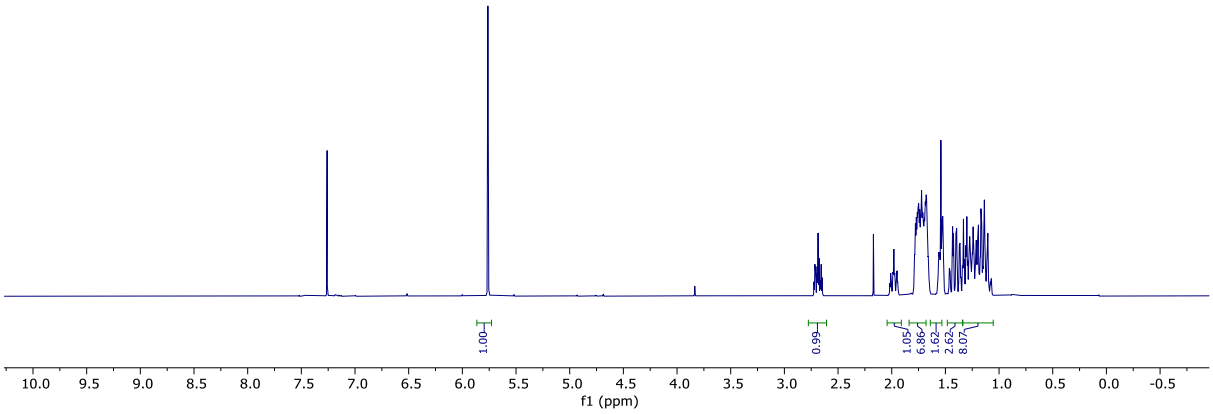
^{13}C NMR, 100 MHz, $CDCl_3$

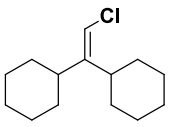
Compound 20





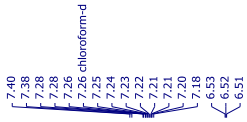
^{1}H NMR, 400 MHz, $CDCl_3$

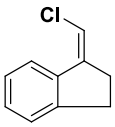




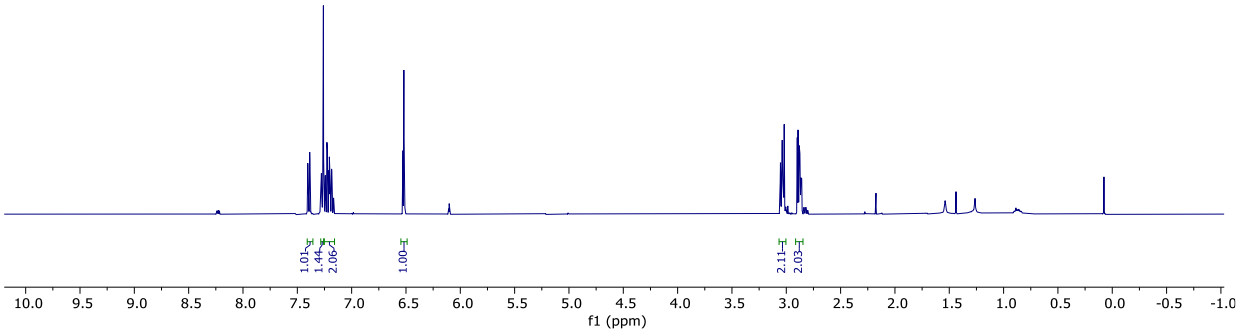
^{13}C NMR, 100 MHz, $CDCl_3$

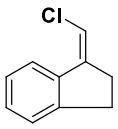
Compound 21



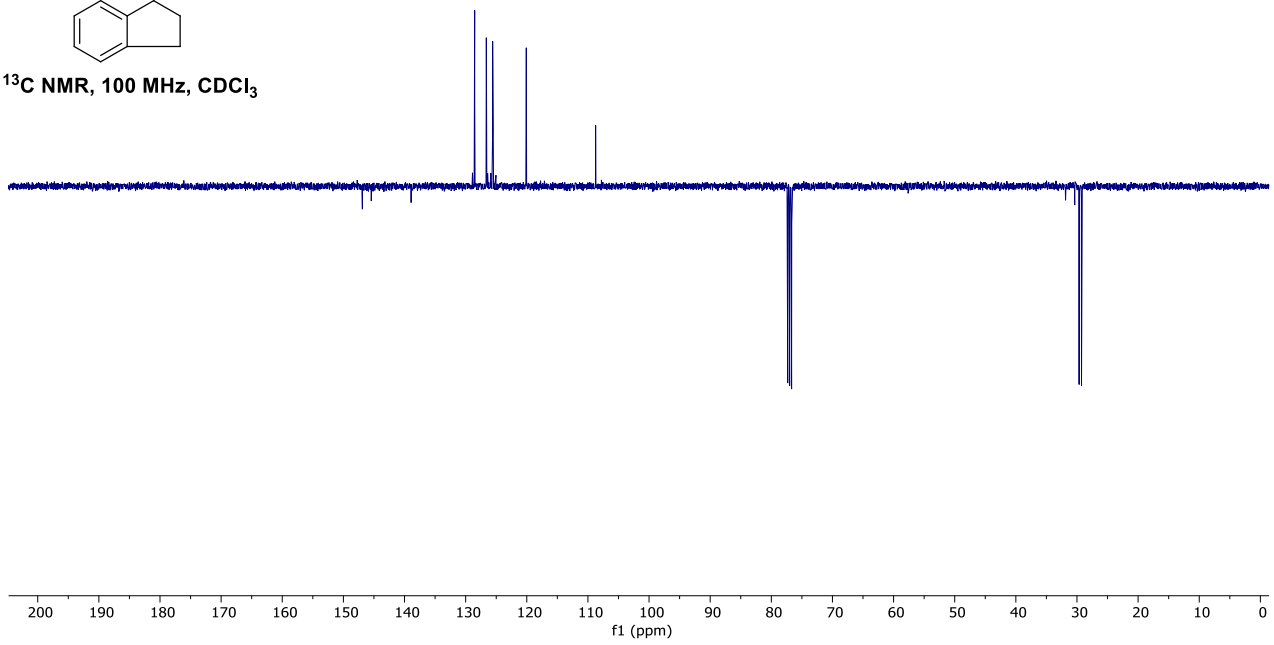


^{1}H NMR, 400 MHz, $CDCl_3$

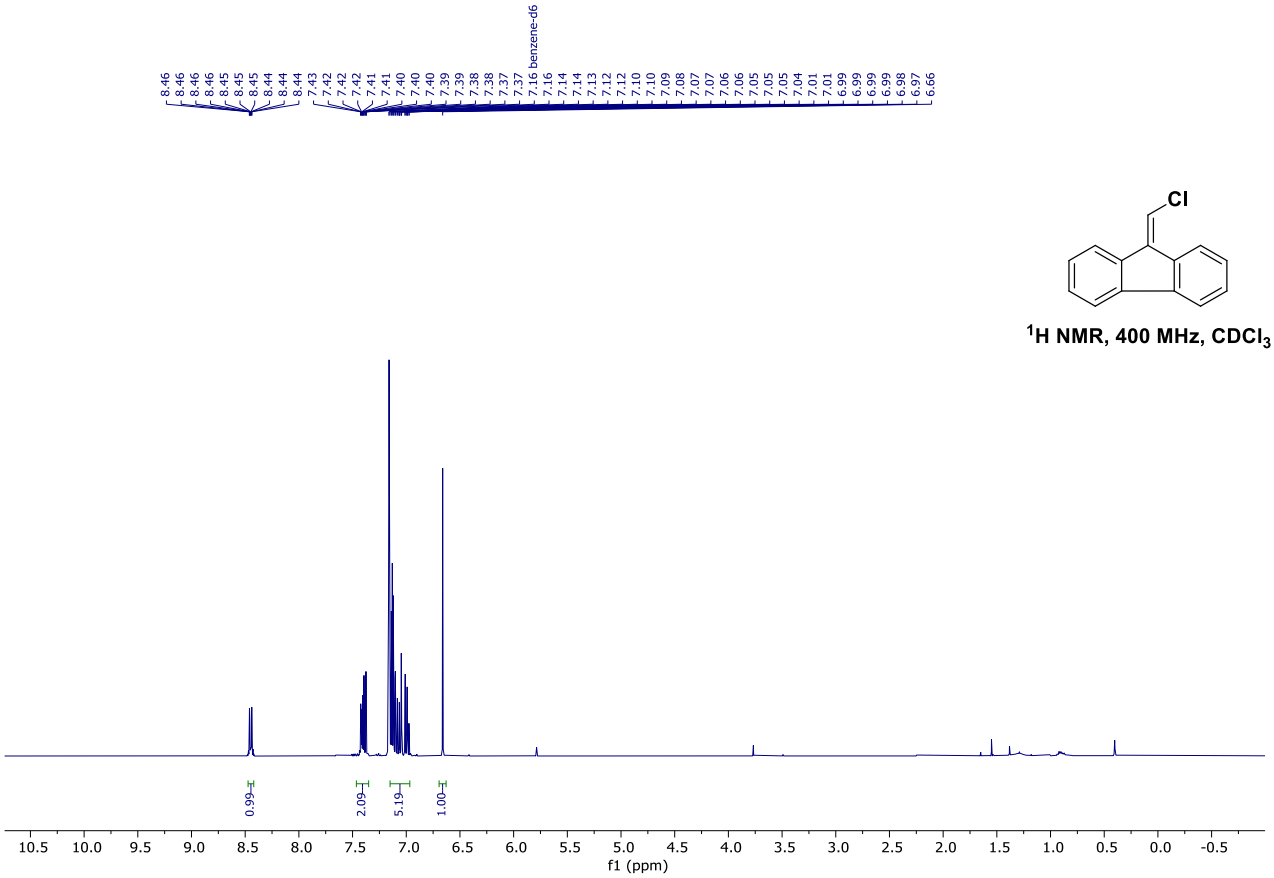




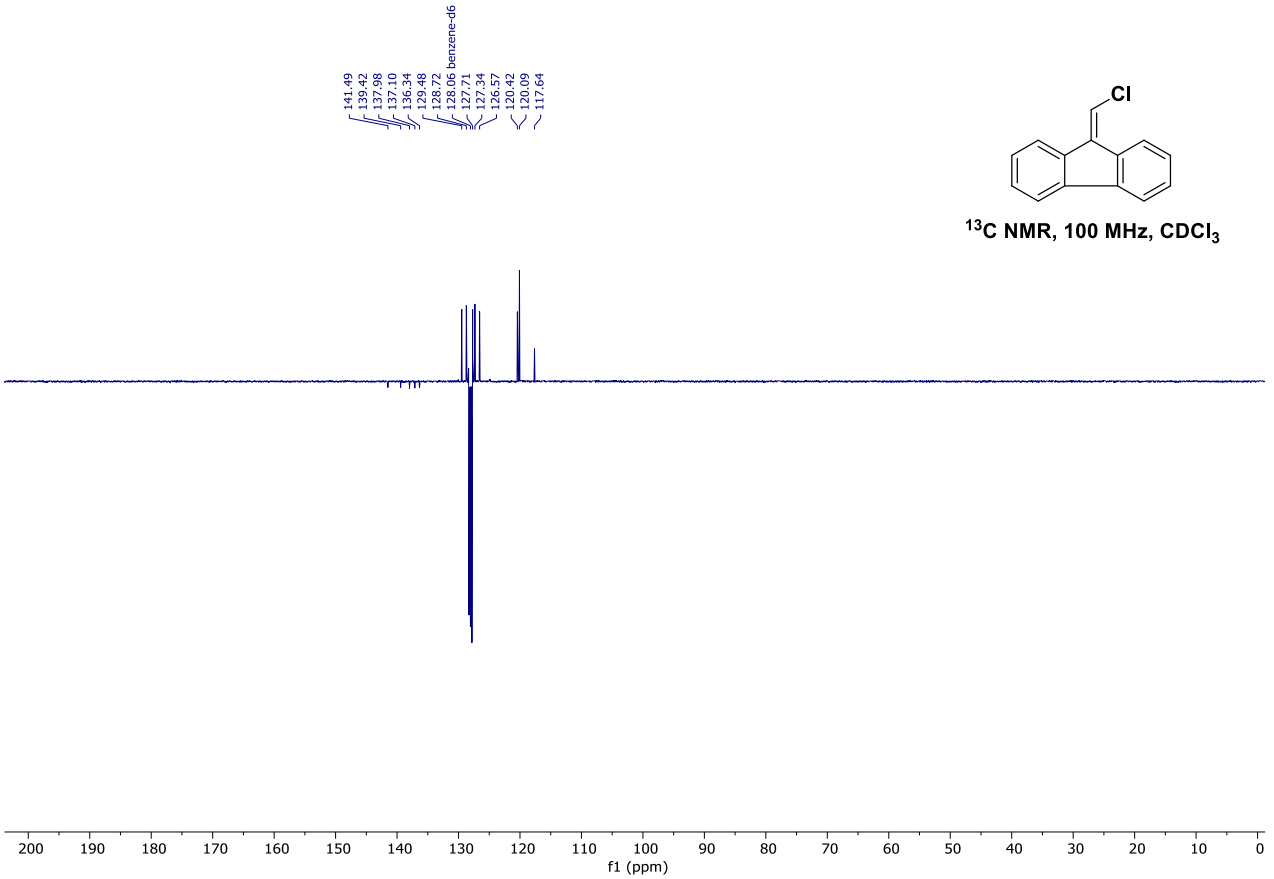
^{13}C NMR, 100 MHz, $CDCl_3$



Compound 22

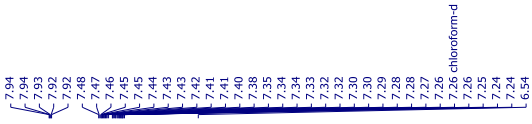


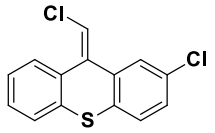
^{1}H NMR, 400 MHz, $CDCl_3$



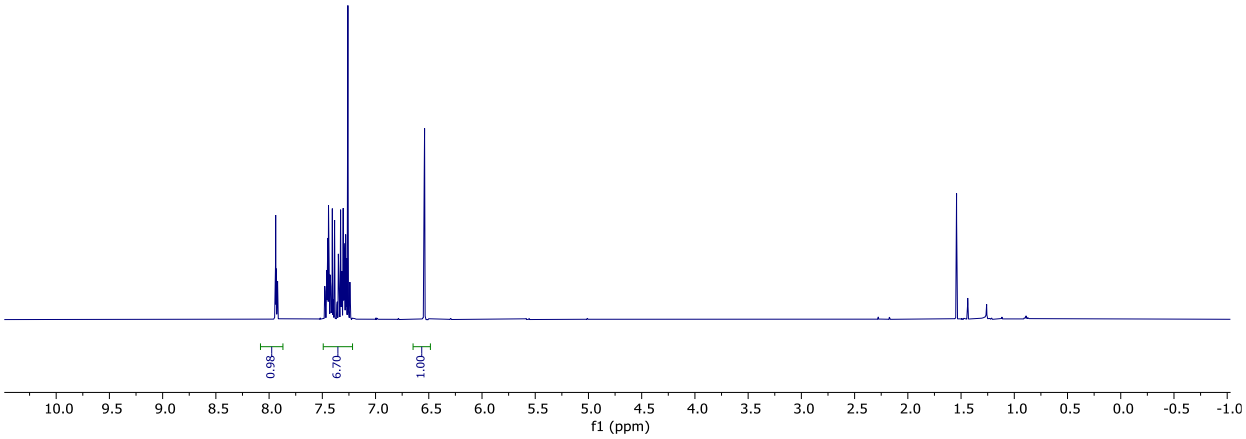
^{13}C NMR, 100 MHz, $CDCl_3$

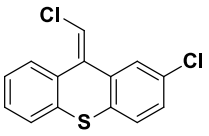
Compound 23



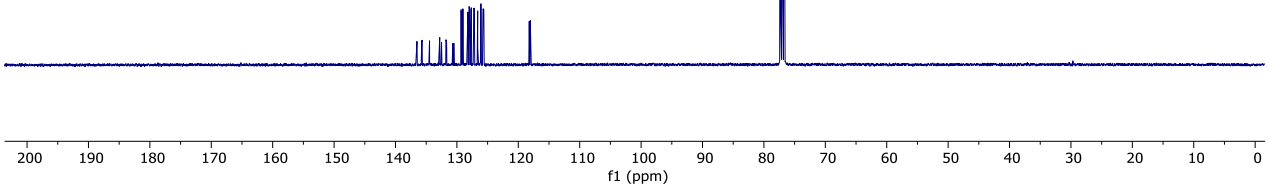


^{1}H NMR, 400 MHz, $CDCl_3$

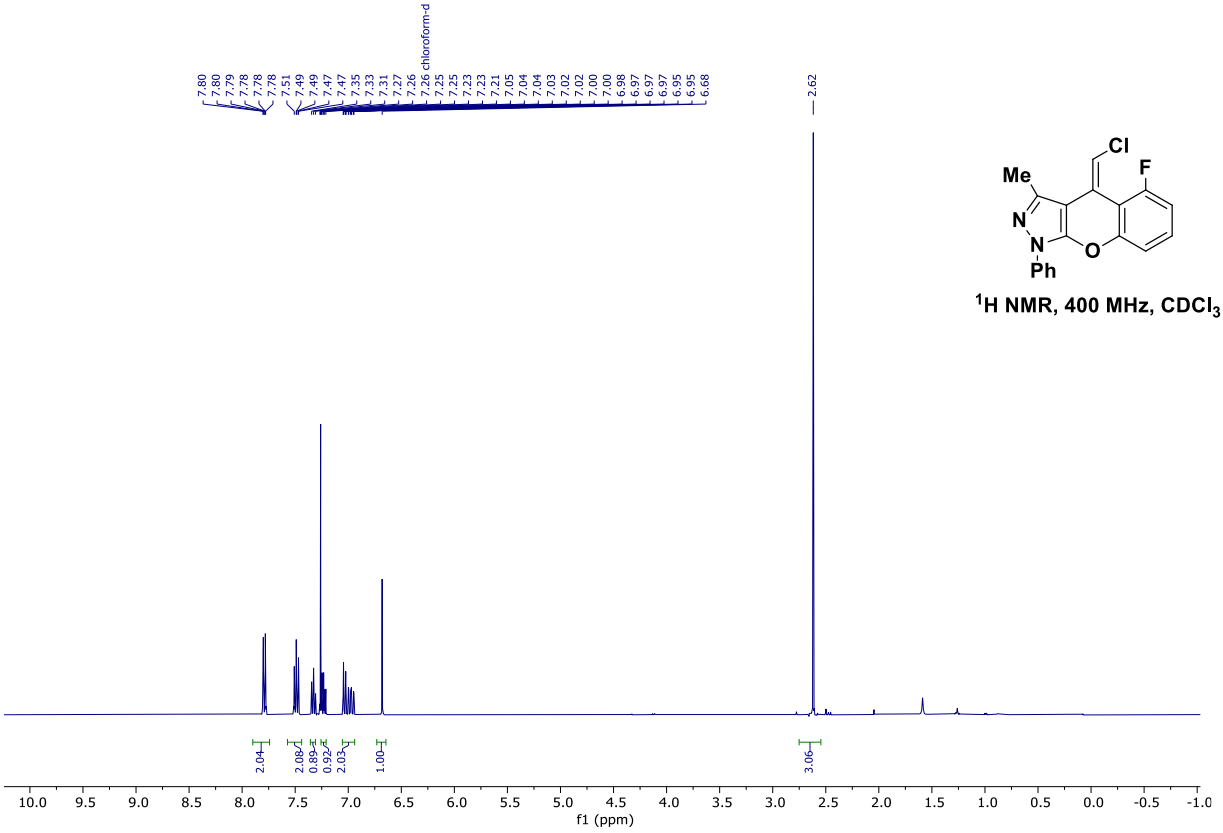




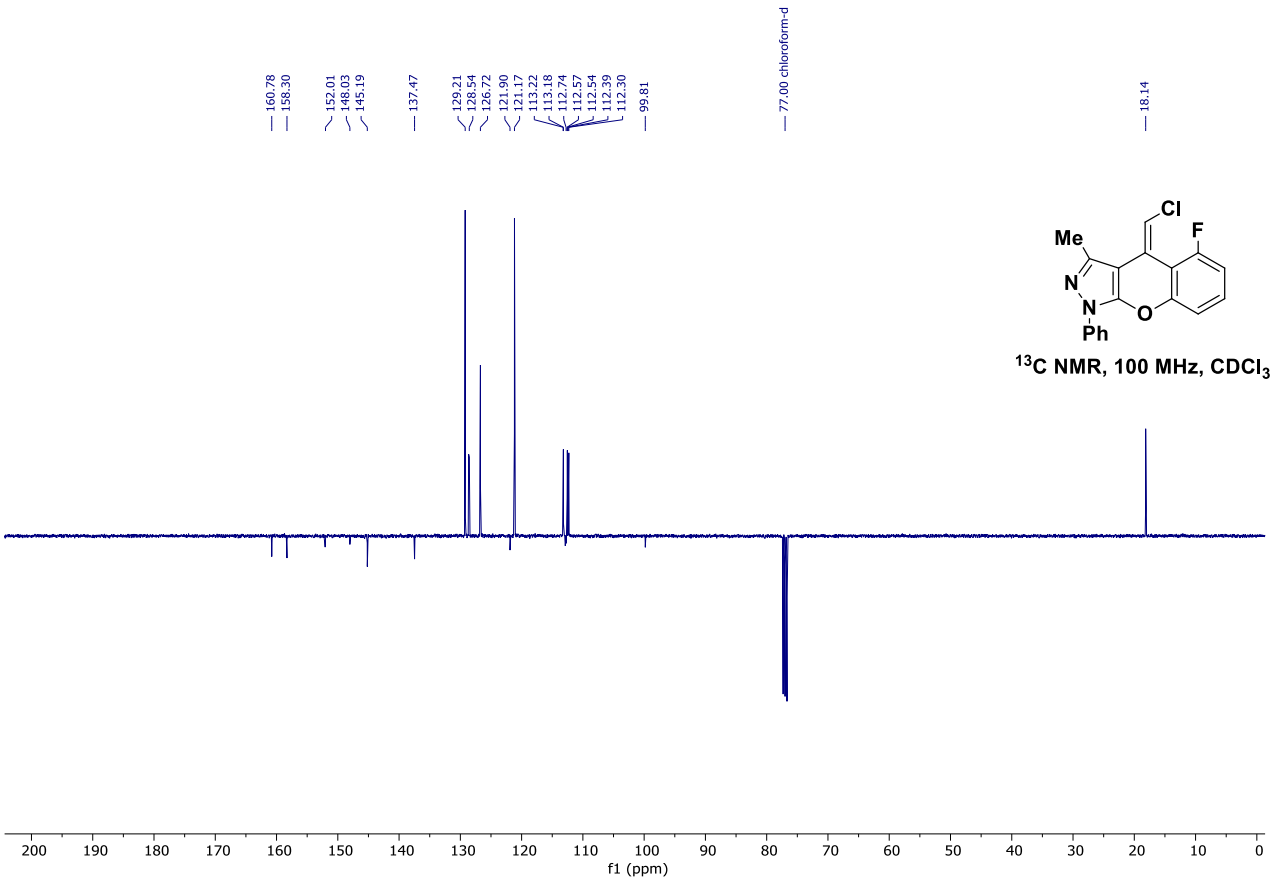
^{13}C NMR, 100 MHz, $CDCl_3$



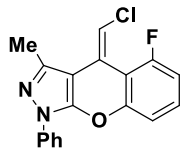
Compound 24



^{1}H NMR, 400 MHz, $CDCl_3$

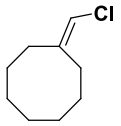


^{13}C NMR, 100 MHz, $CDCl_3$

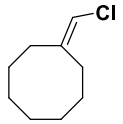


^{19}F NMR, 376 MHz, $CDCl_3$

Compound 25

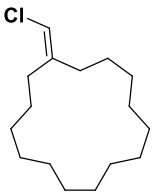


^{1}H NMR, 400 MHz, $CDCl_3$

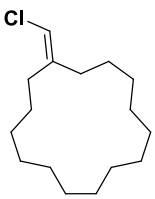


^{13}C NMR, 100 MHz, $CDCl_3$

Compound 26

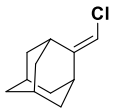


^{1}H NMR, 400 MHz, $CDCl_3$

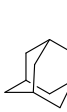


^{13}C NMR, 100 MHz, $CDCl_3$

Compound 27

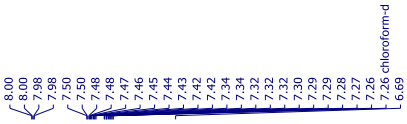


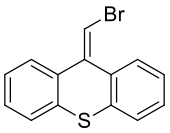
^{1}H NMR, 400 MHz, $CDCl_3$



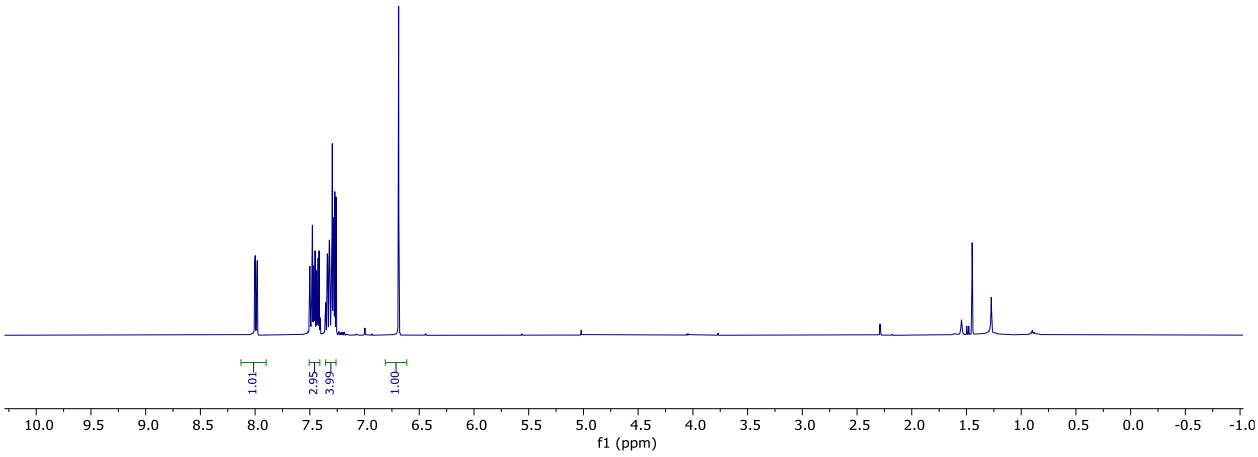
^{13}C NMR, 100 MHz, $CDCl_3$

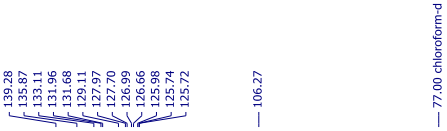
Compound 28

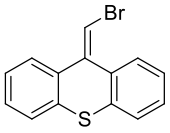




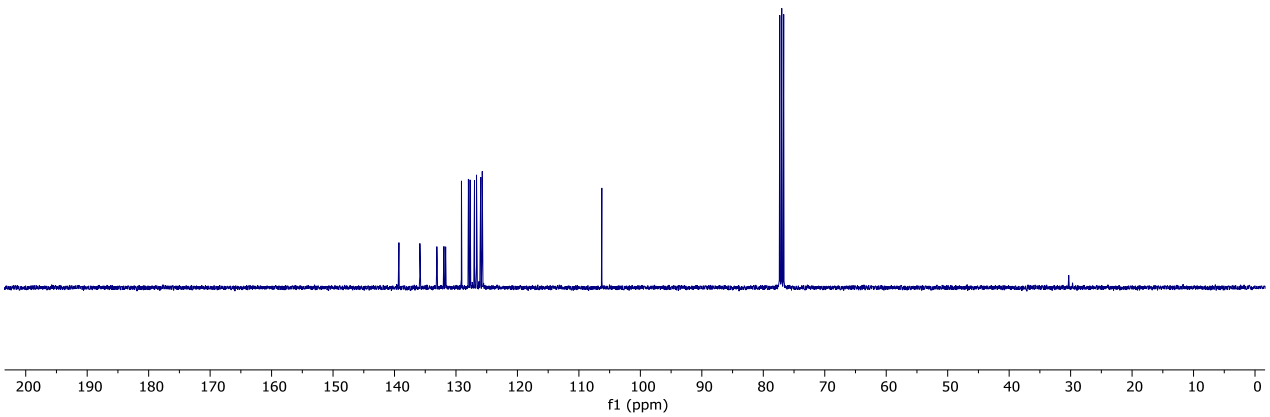
^{1}H NMR, 400 MHz, $CDCl_3$



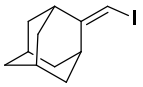




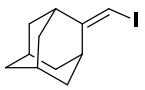
^{13}C NMR, 100 MHz, $CDCl_3$



Compound 29

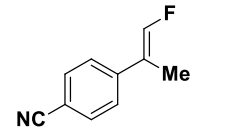


^{1}H NMR, 400 MHz, $CDCl_3$

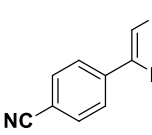


^{13}C NMR, 100 MHz, $CDCl_3$

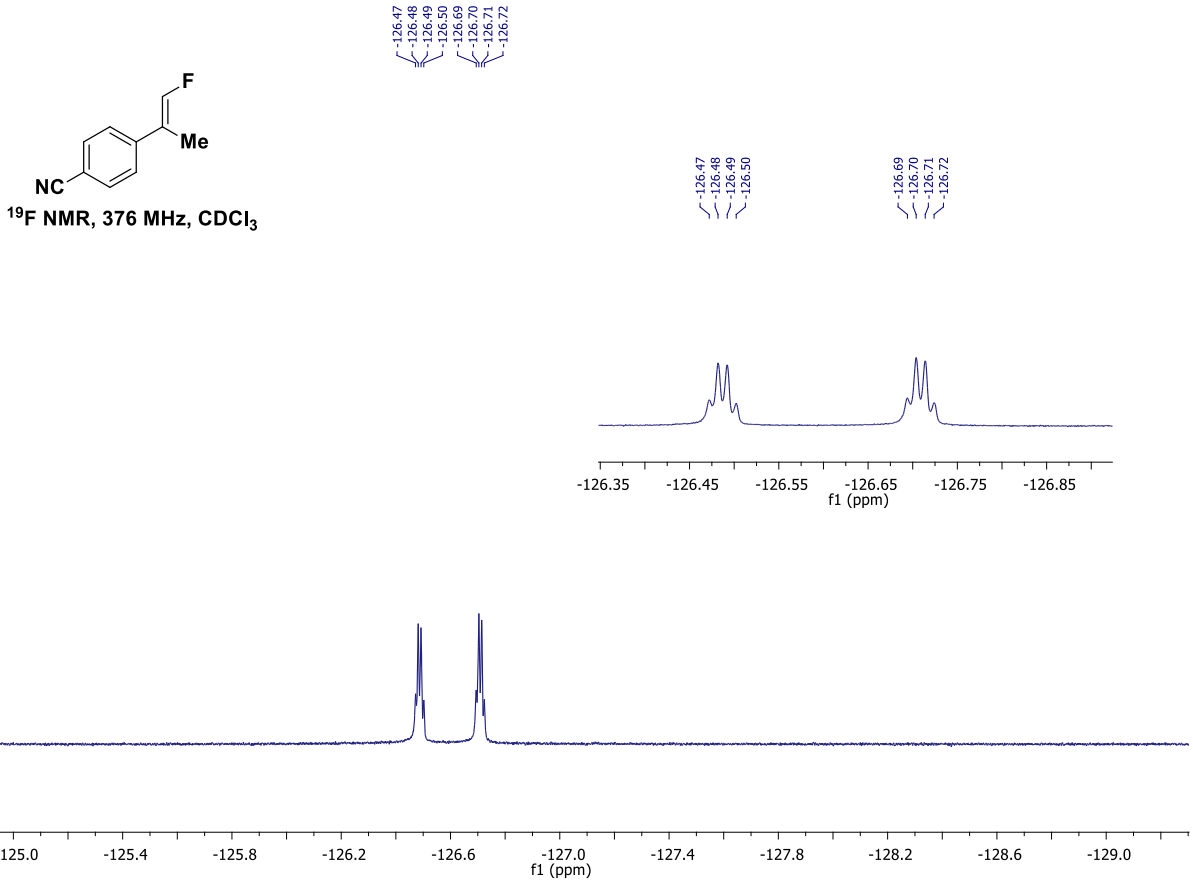
Compound 30



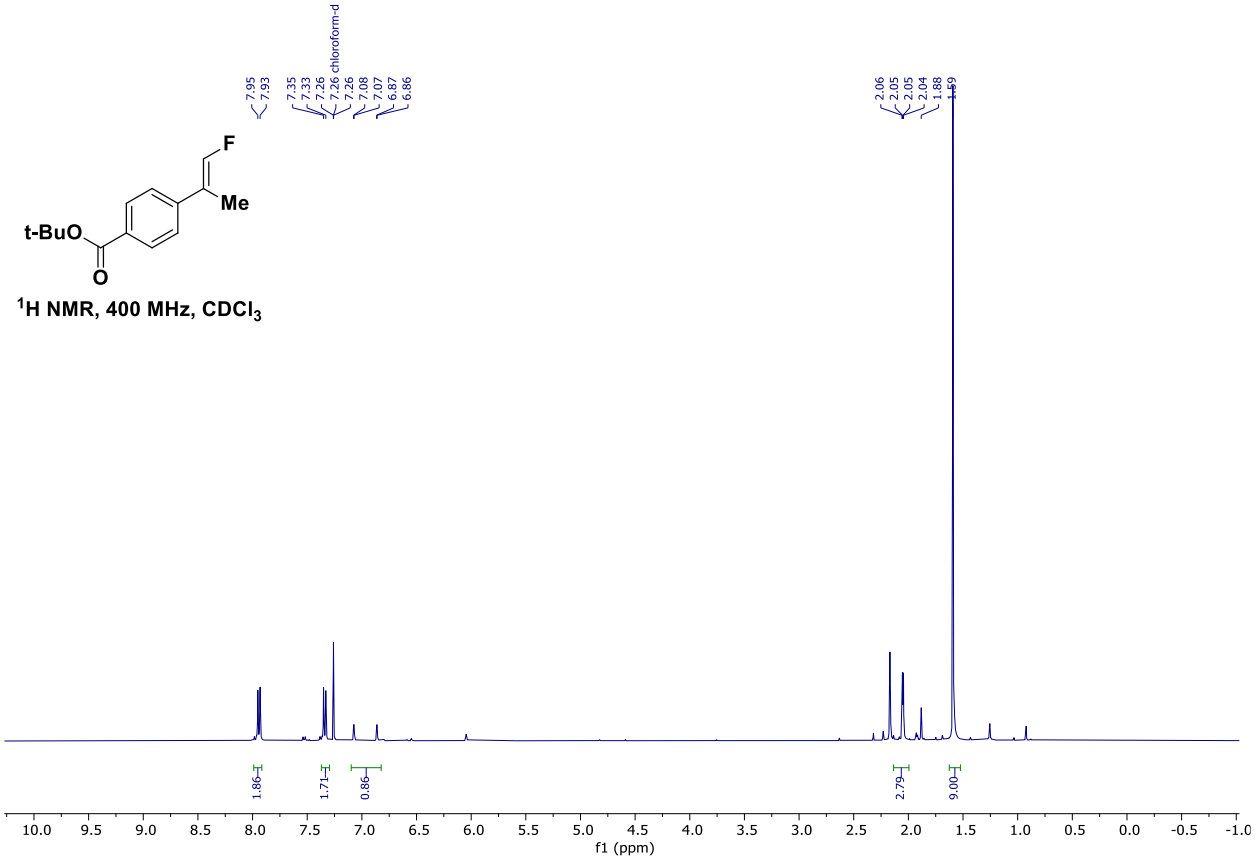
^{1}H NMR, 400 MHz, $CDCl_3$



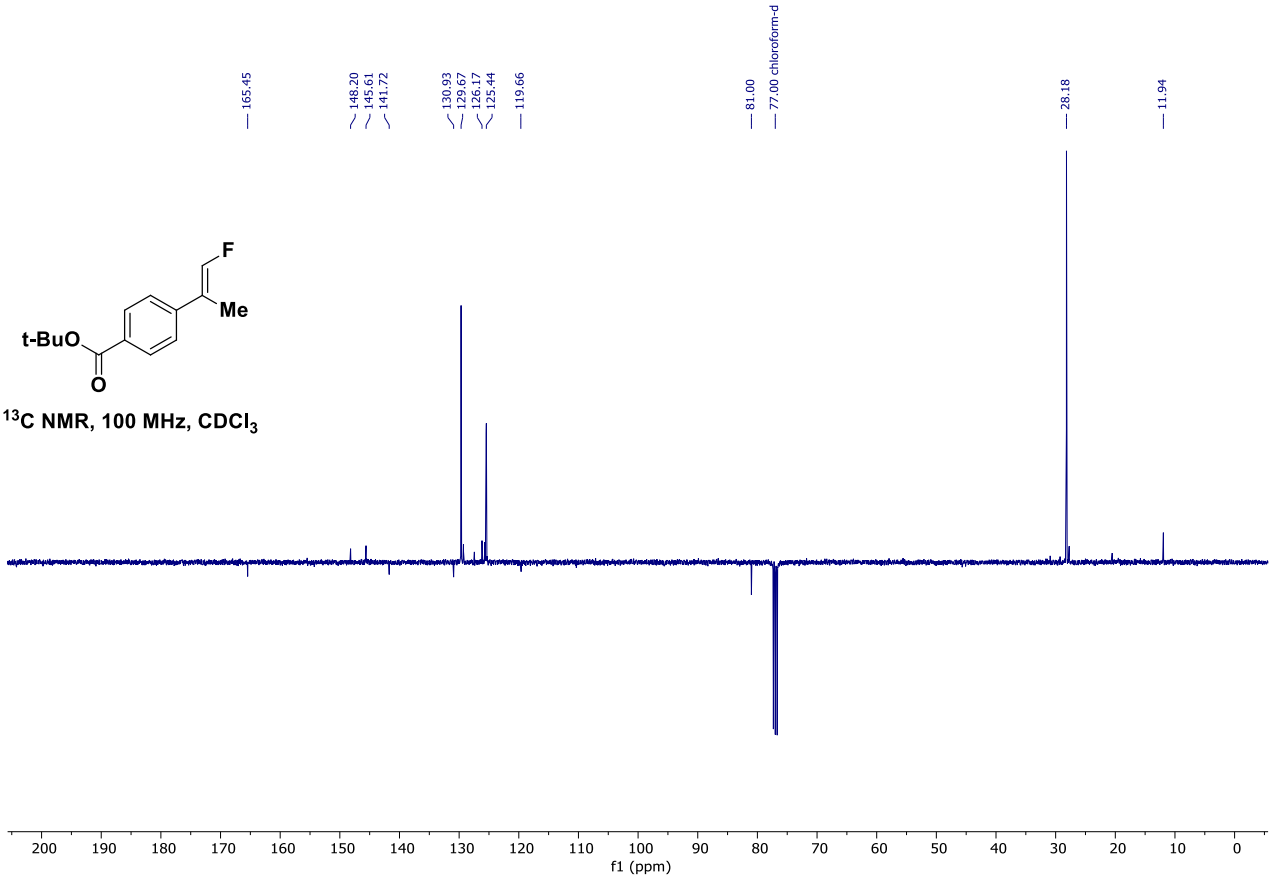
^{13}C NMR, 100 MHz, $CDCl_3$


-126.47
-126.48
-126.49
-126.50
-126.69
-126.70
-126.71
-126.72
F
Me
NC
^{19}F NMR, 376 MHz, CDCl$_3$
-126.35
-126.45
-126.55
-126.65
-126.75
-126.85
f1 (ppm)
-125.0
-125.4
-125.8
-126.2
-126.6
-127.0
-127.4
-127.8
-128.2
-128.6
-129.0
f1 (ppm)

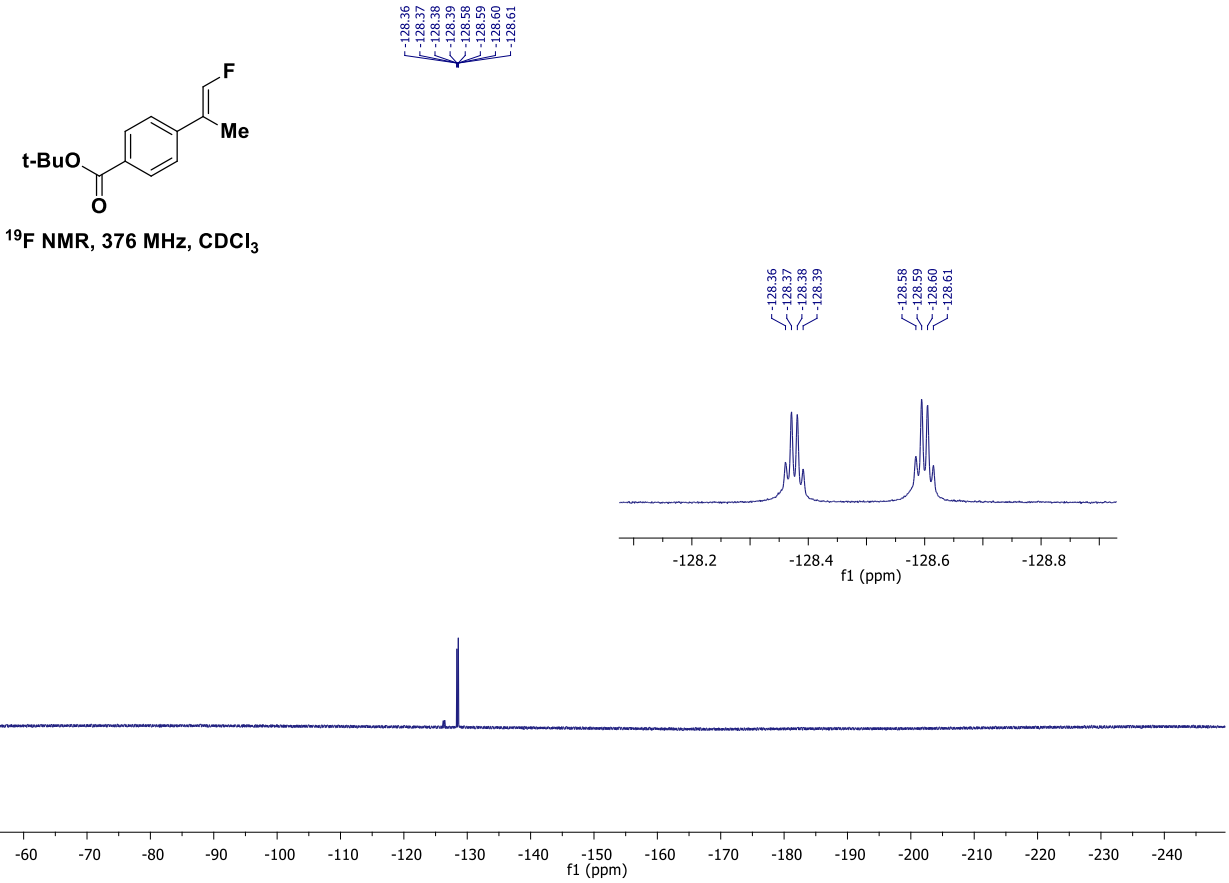
Compound 31



^{1}H NMR, 400 MHz, $CDCl_3$

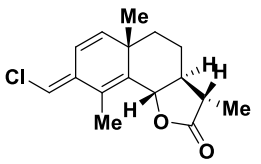


^{13}C NMR, 100 MHz, $CDCl_3$

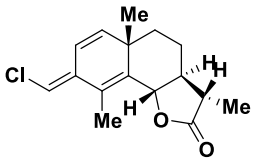


^{19}F NMR, 376 MHz, $CDCl_3$

Compound 32

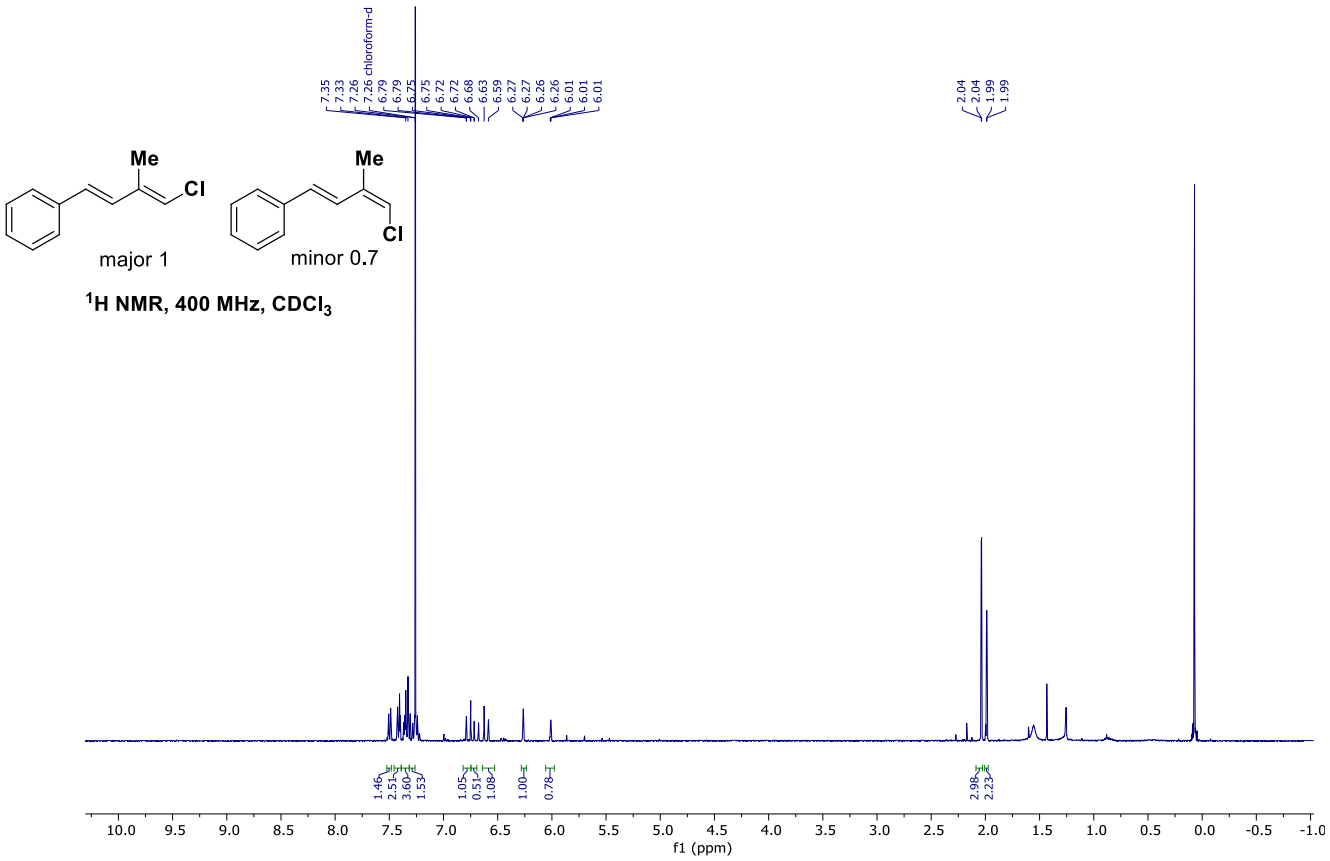


^{1}H NMR, 400 MHz, $CDCl_3$

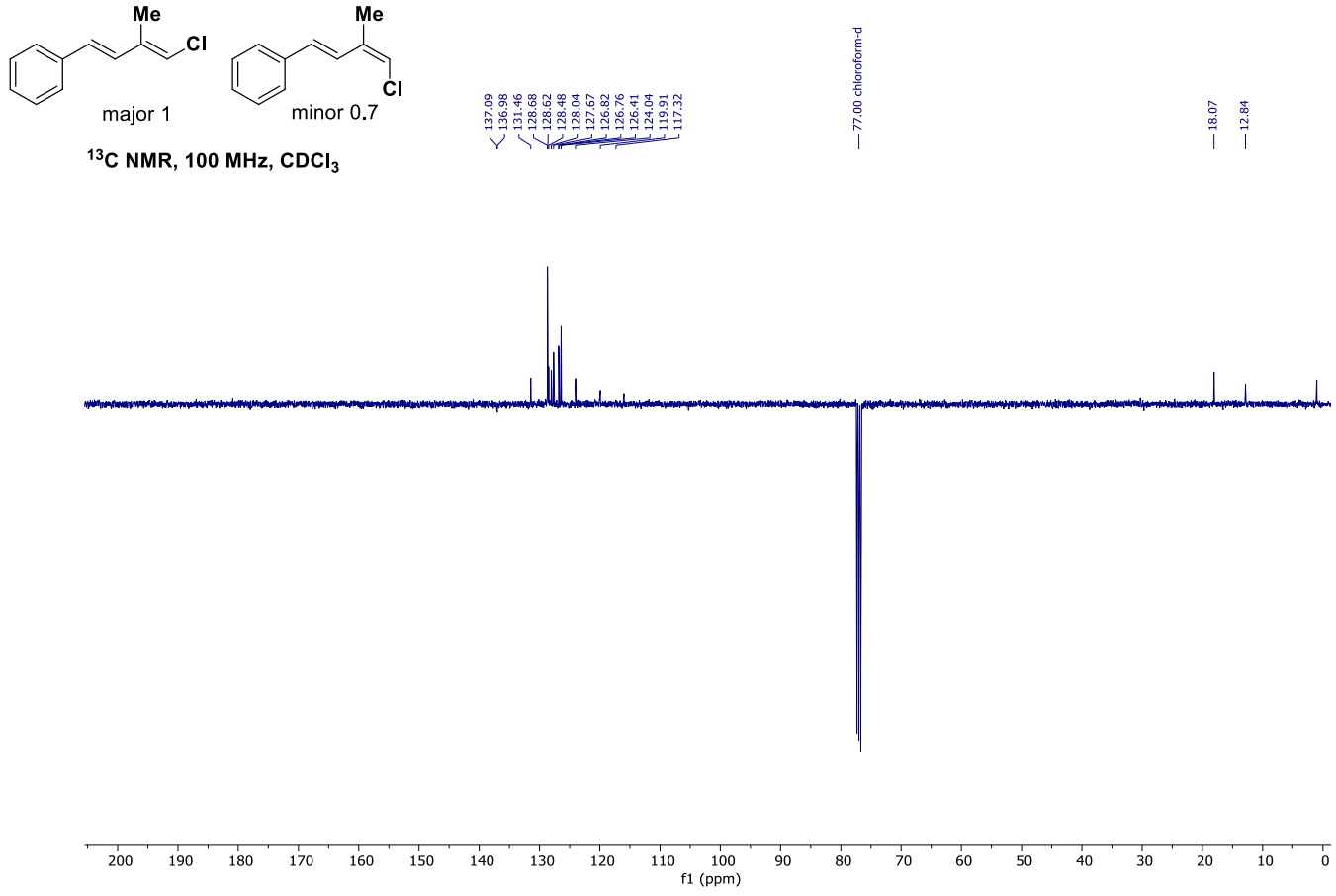


^{13}C NMR, 100 MHz, $CDCl_3$

Compound 33

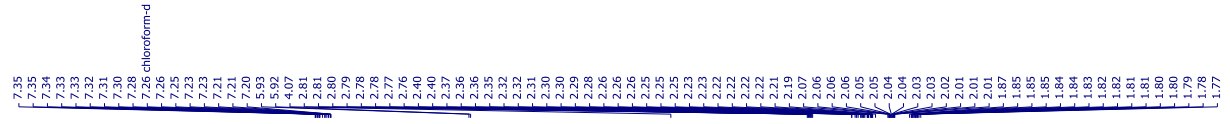


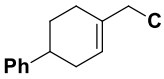
^{1}H NMR, 400 MHz, $CDCl_3$



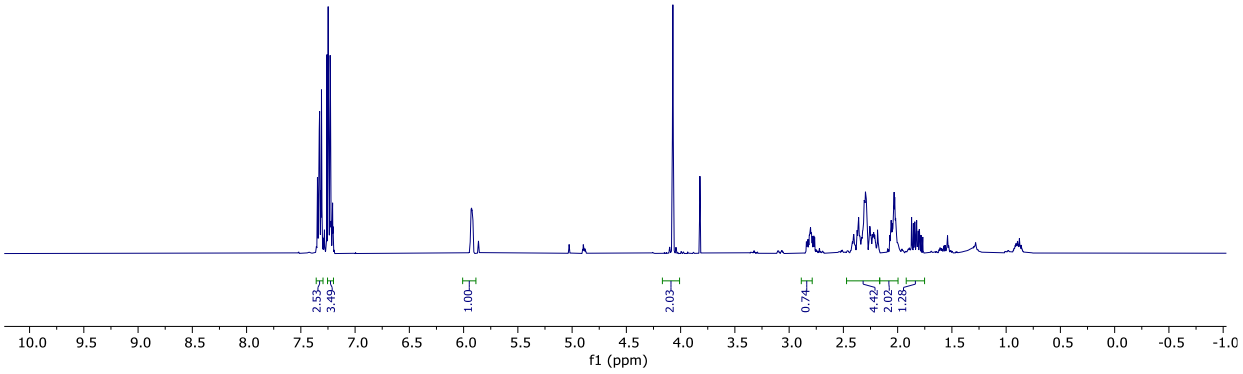
^{13}C NMR, 100 MHz, $CDCl_3$

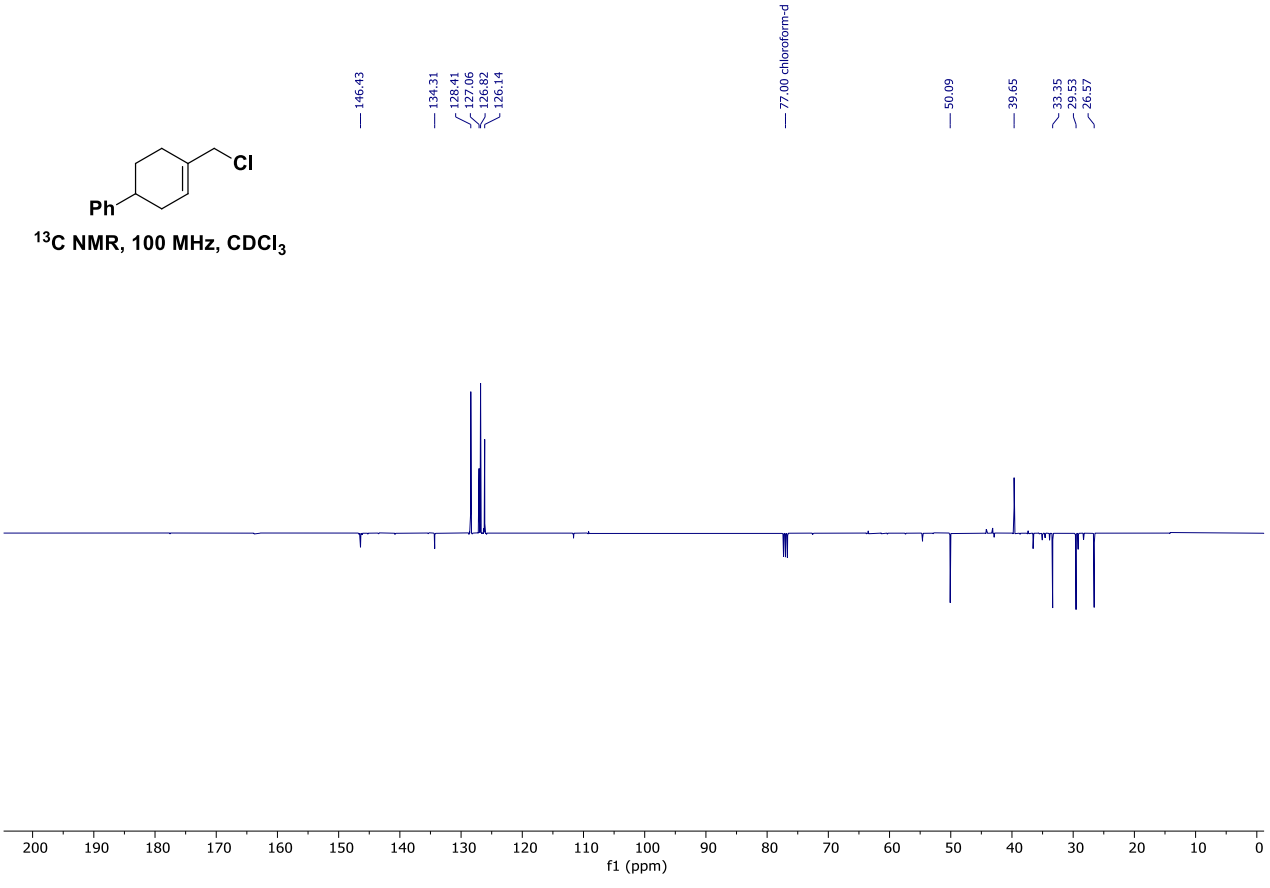
Compound 34





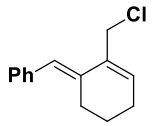
^{1}H NMR, 400 MHz, $CDCl_3$



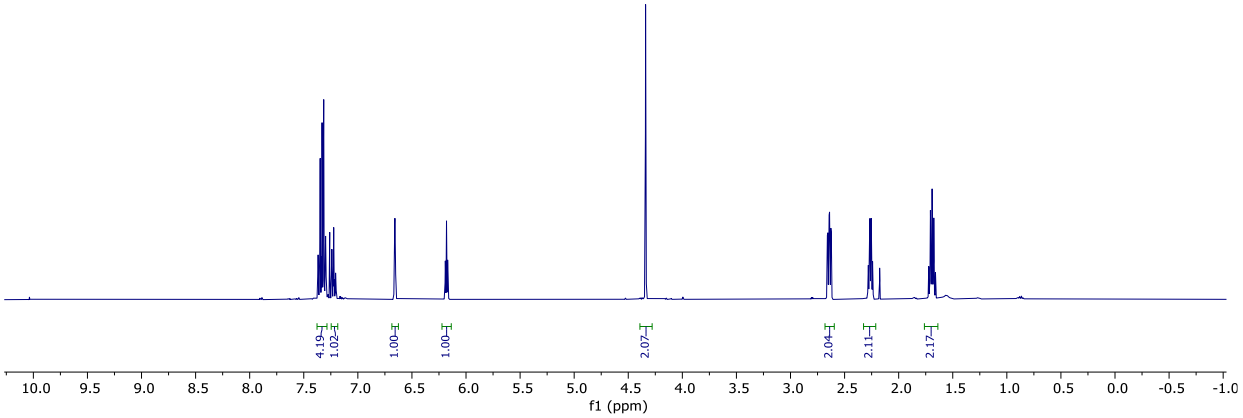


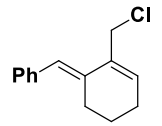
^{13}C NMR, 100 MHz, $CDCl_3$

Compound 35



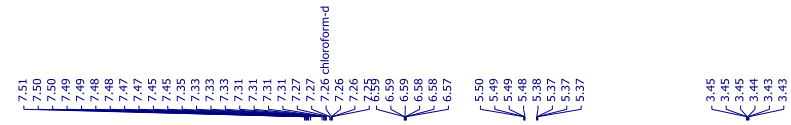
^{1}H NMR, 400 MHz, $CDCl_3$

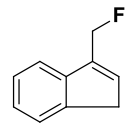




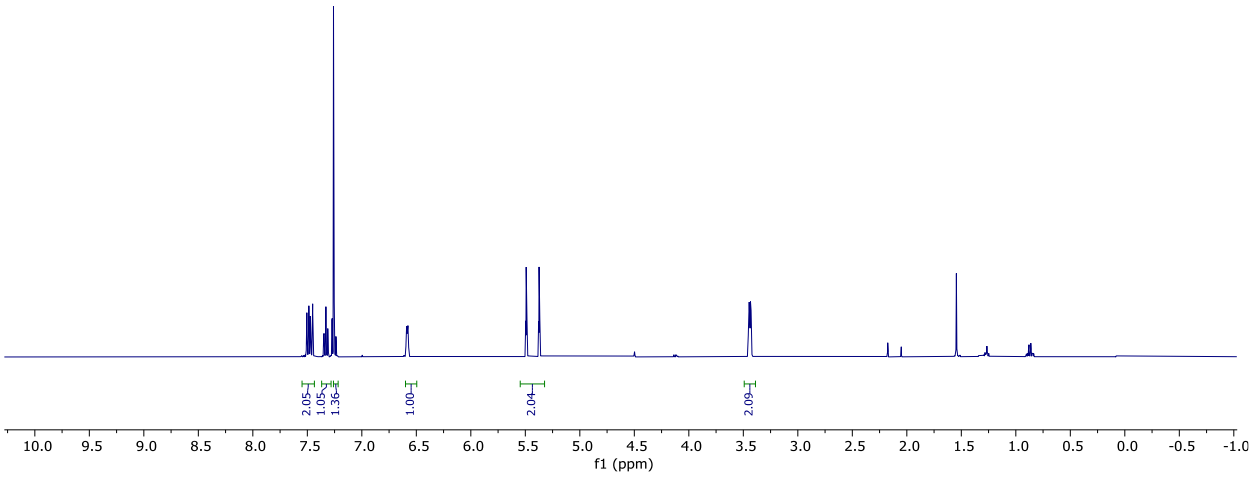
^{13}C NMR, 100 MHz, $CDCl_3$

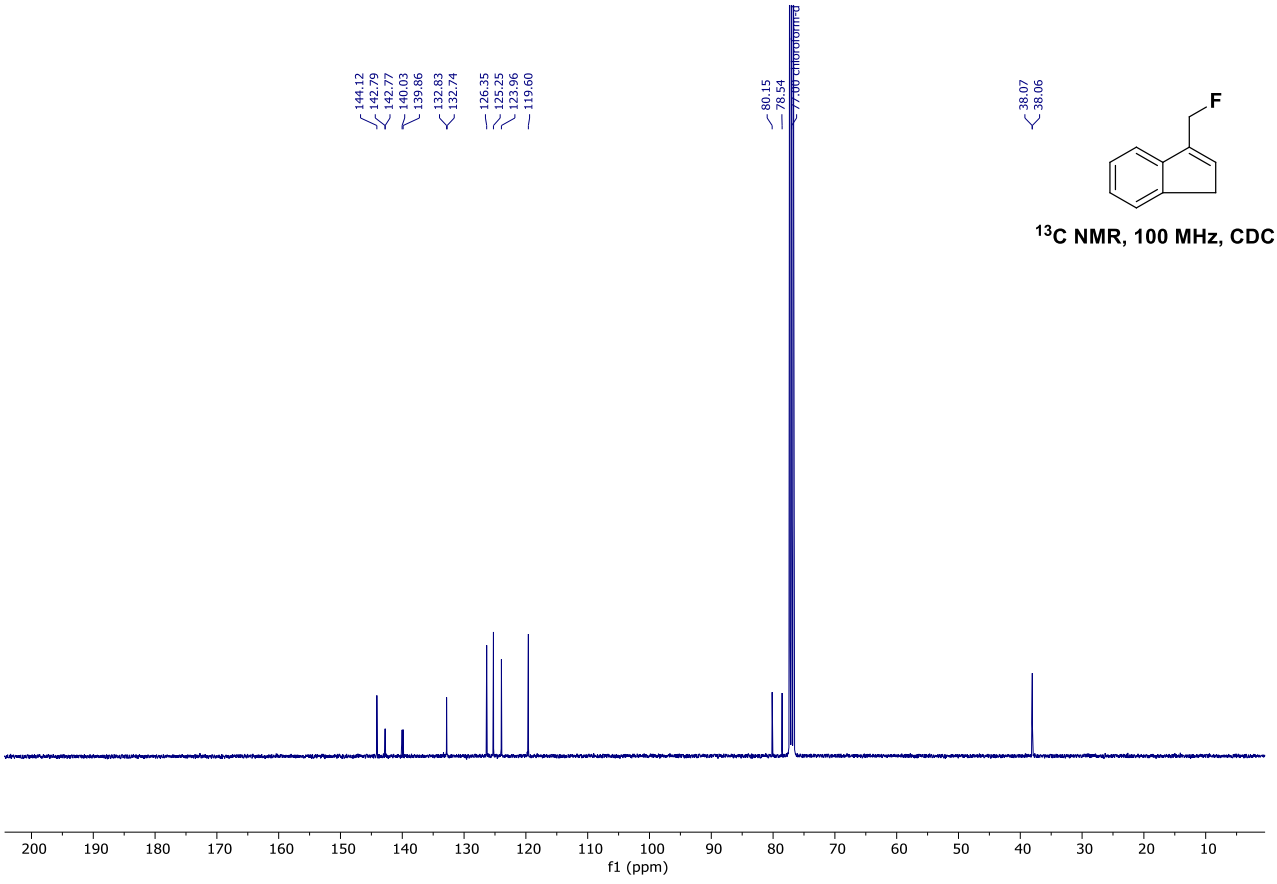
Compound 36



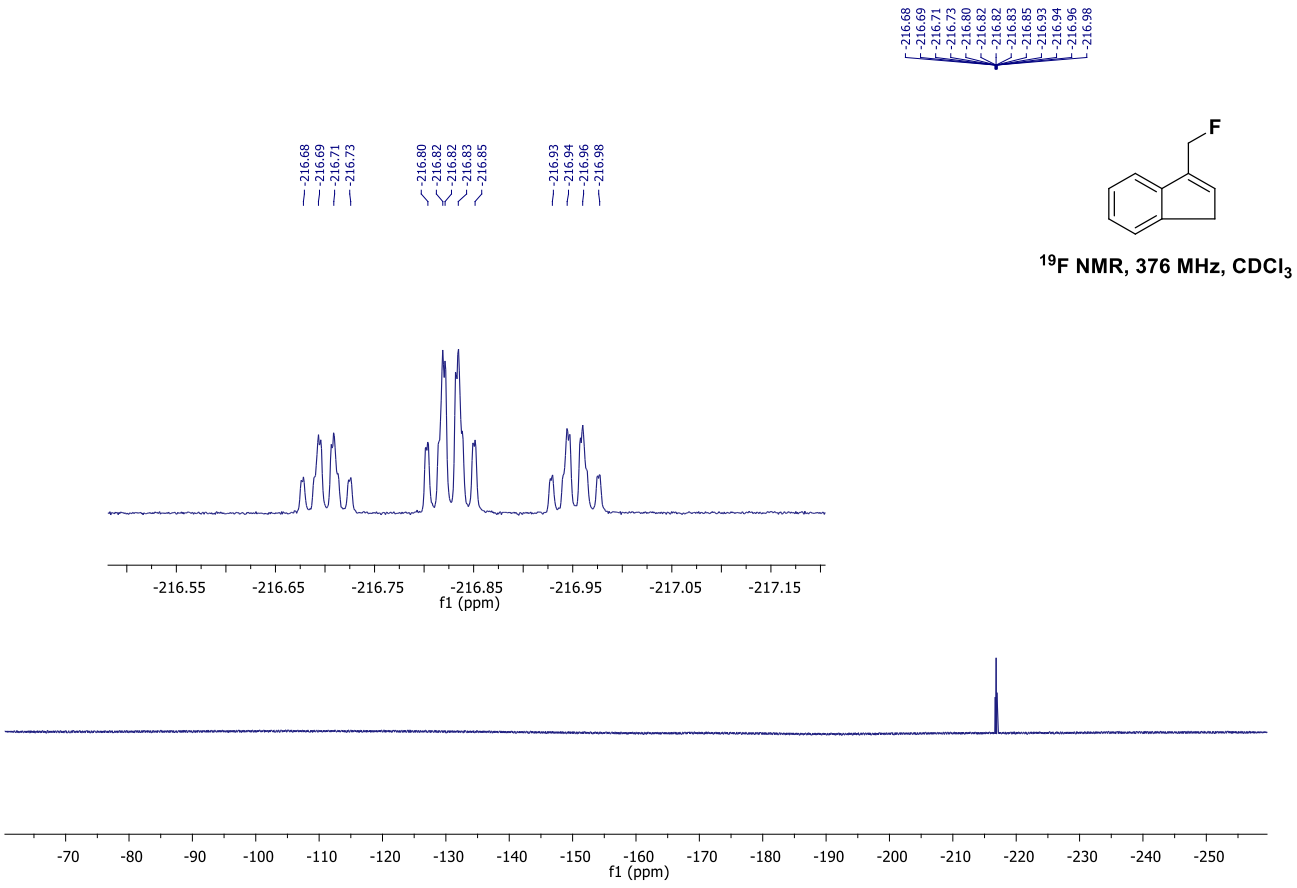


^{1}H NMR, 400 MHz, $CDCl_3$



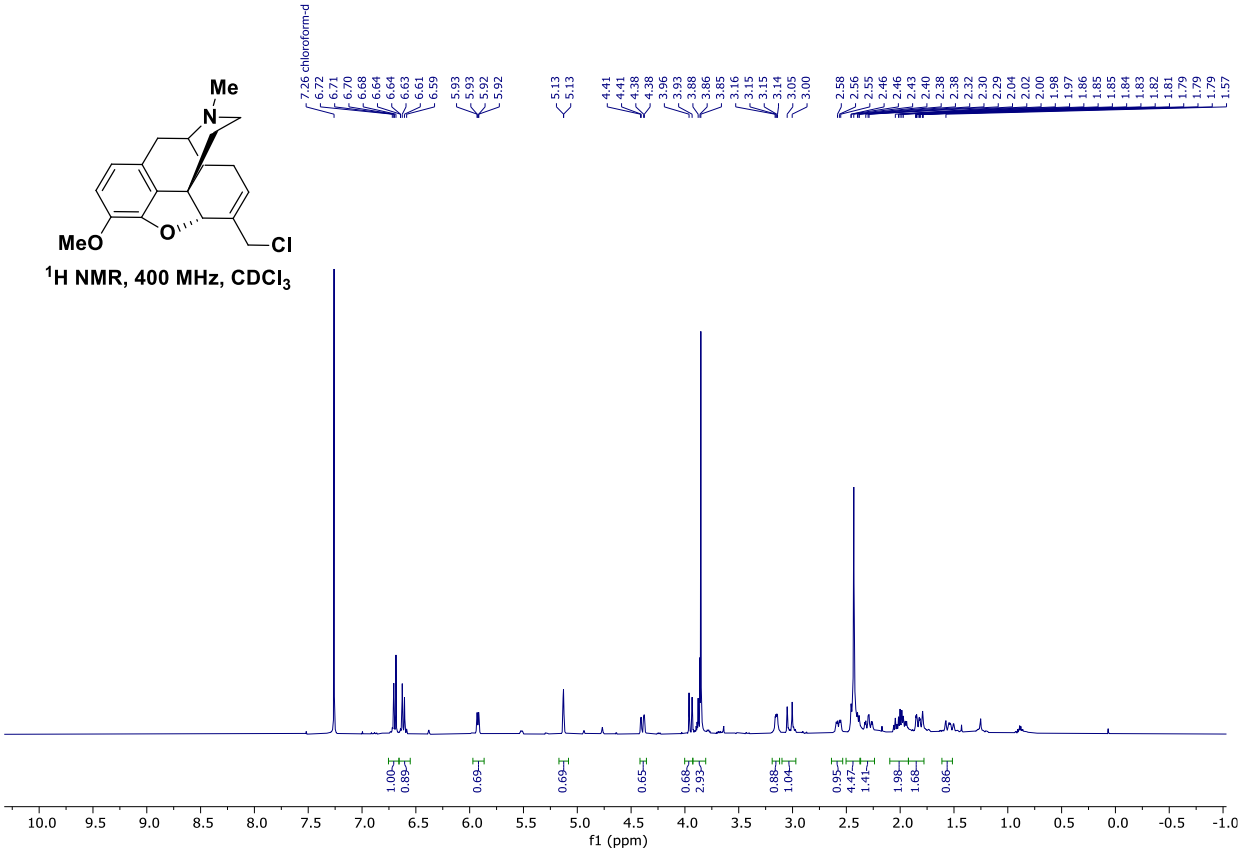


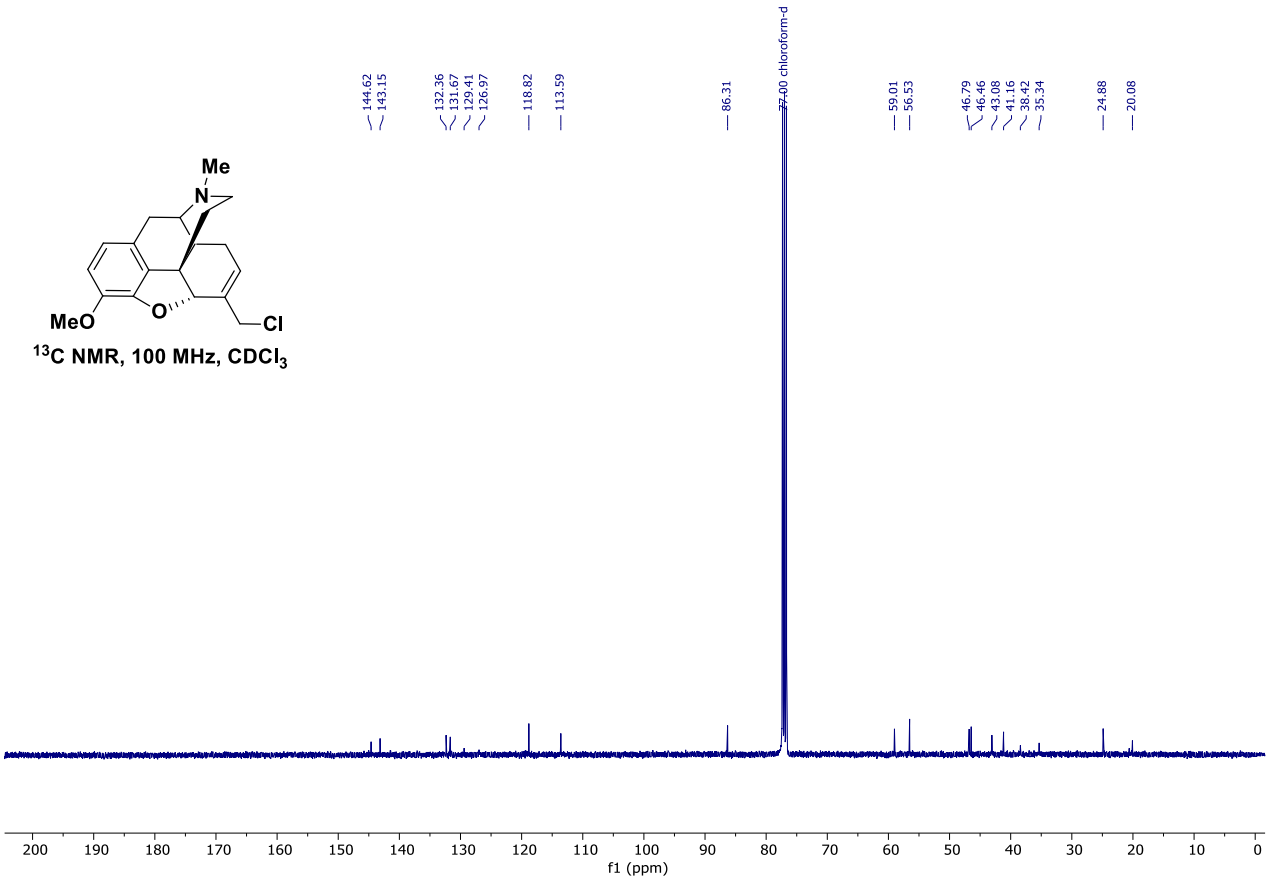
^{13}C NMR, 100 MHz, $CDCl_3$



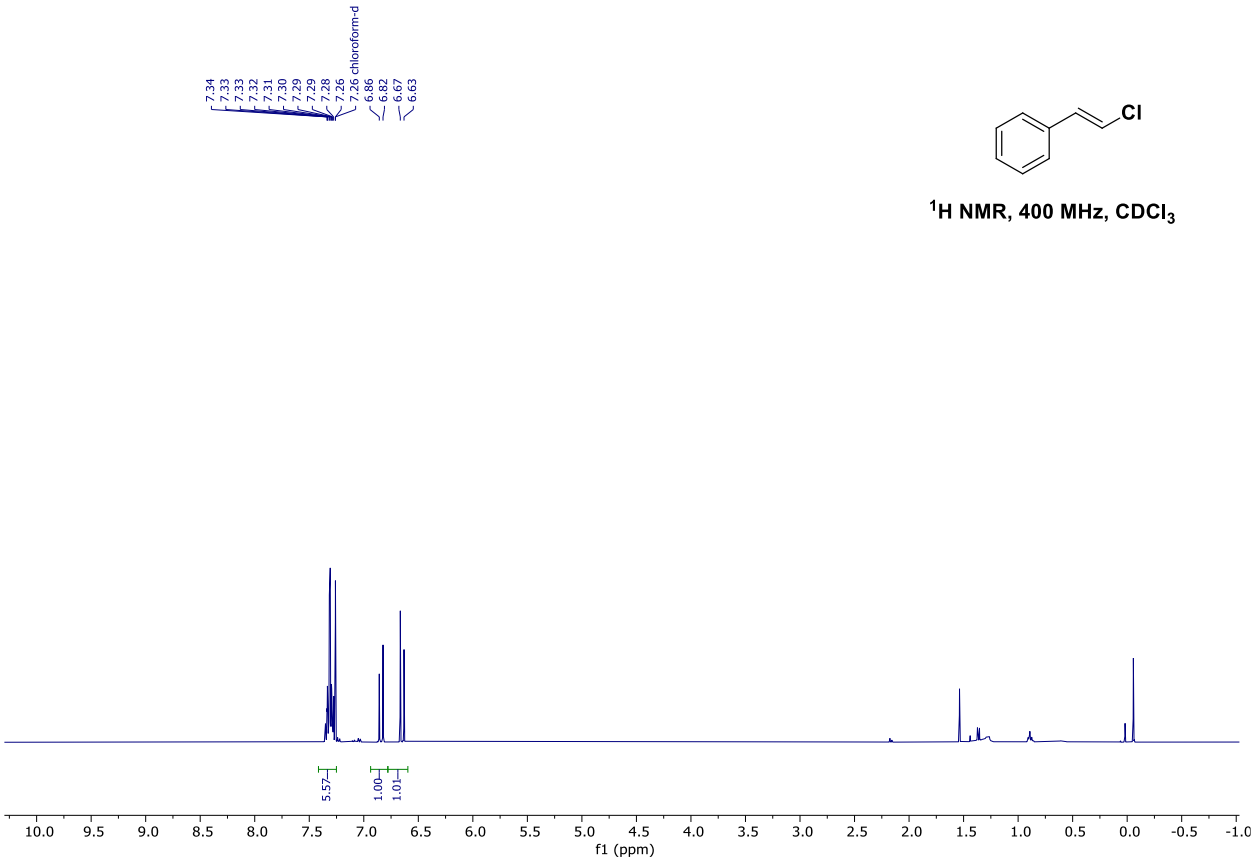
^{19}F NMR, 376 MHz, $CDCl_3$

Compound 37

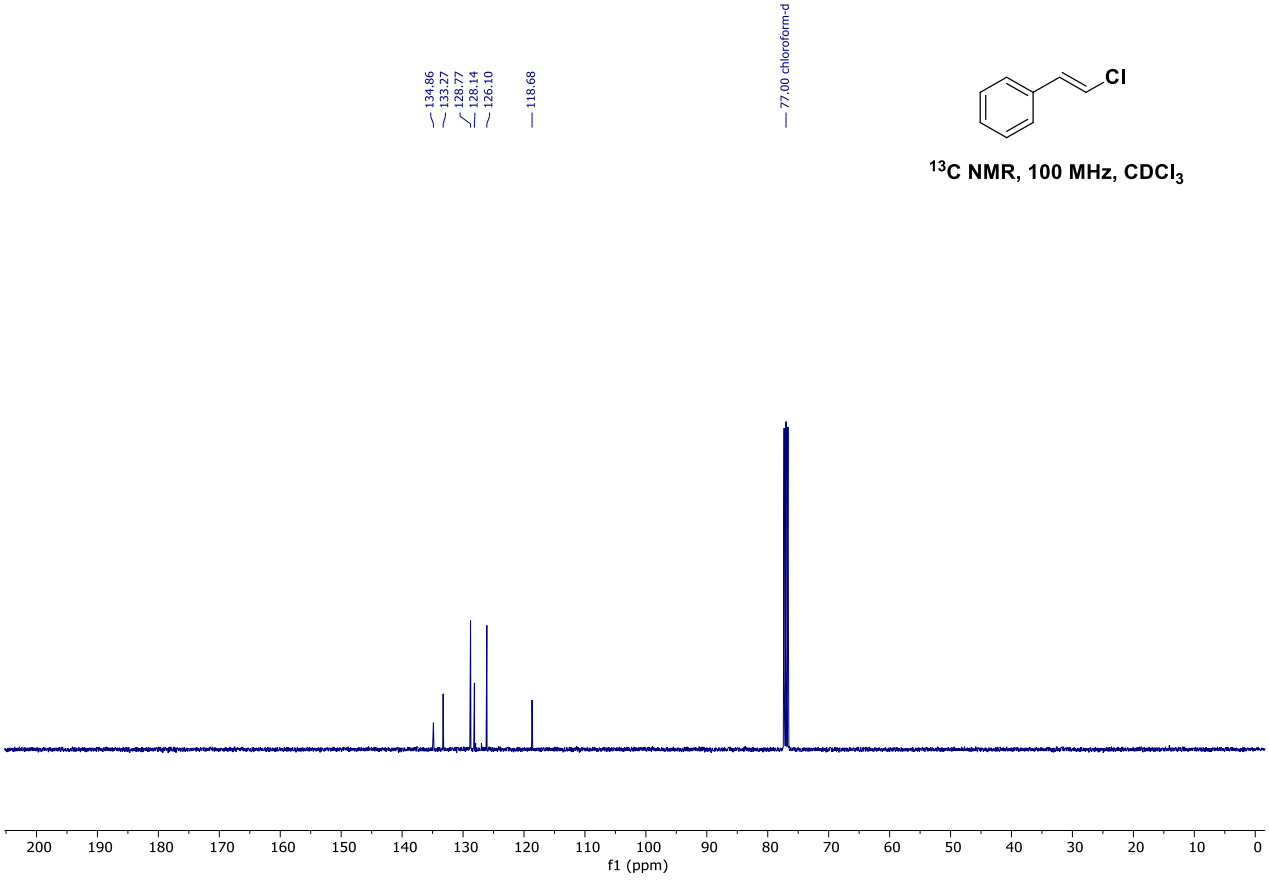




Compound 38

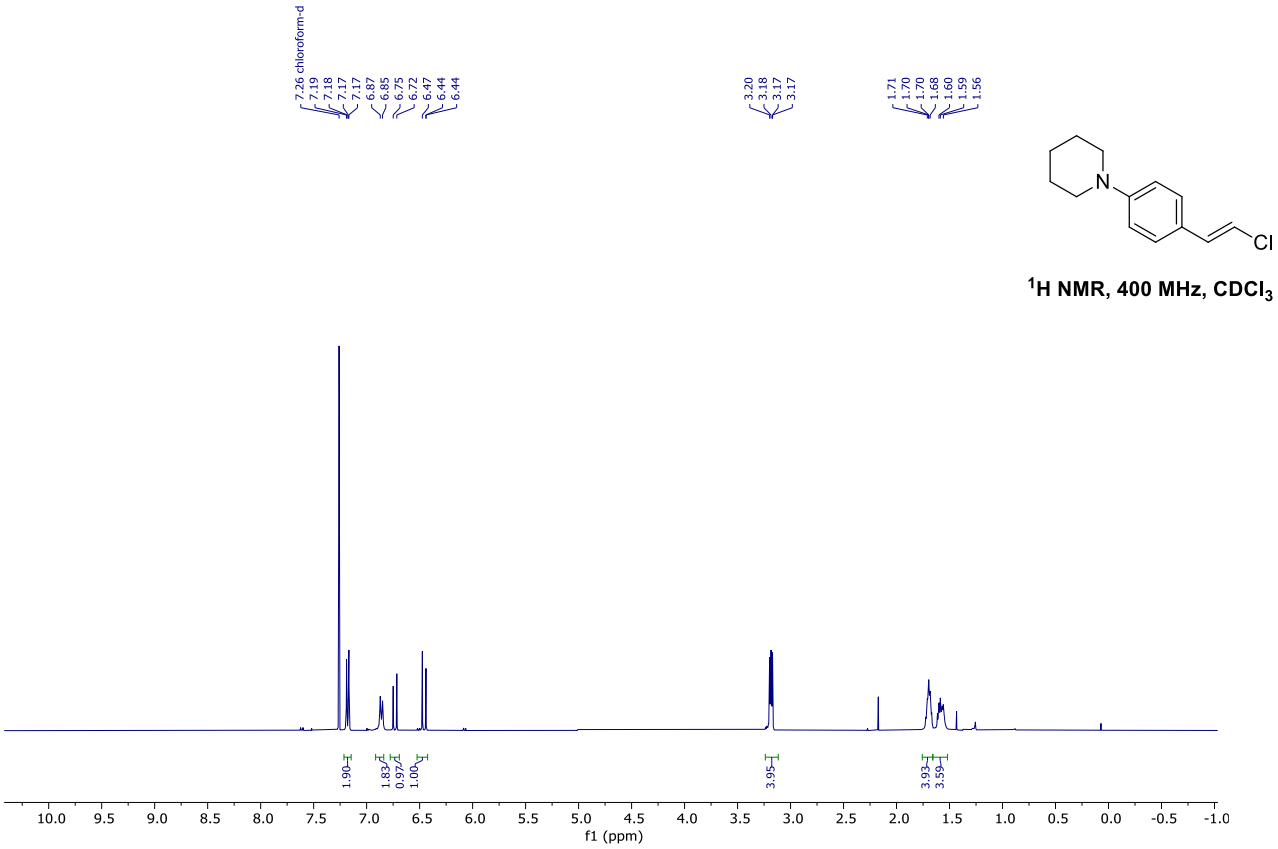


^{1}H NMR, 400 MHz, $CDCl_3$

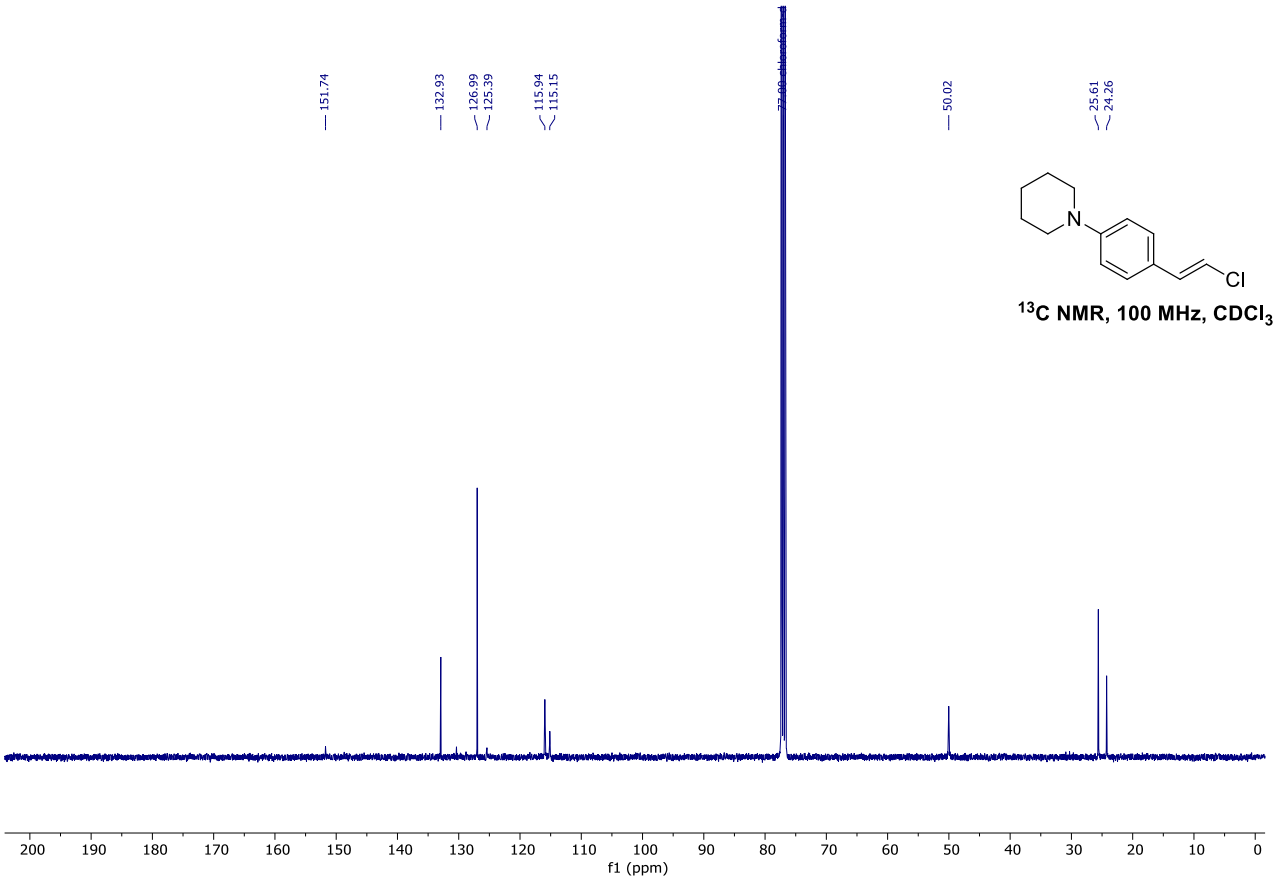


^{13}C NMR, 100 MHz, $CDCl_3$

Compound 39

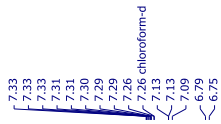


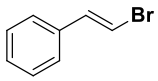
^{1}H NMR, 400 MHz, $CDCl_3$



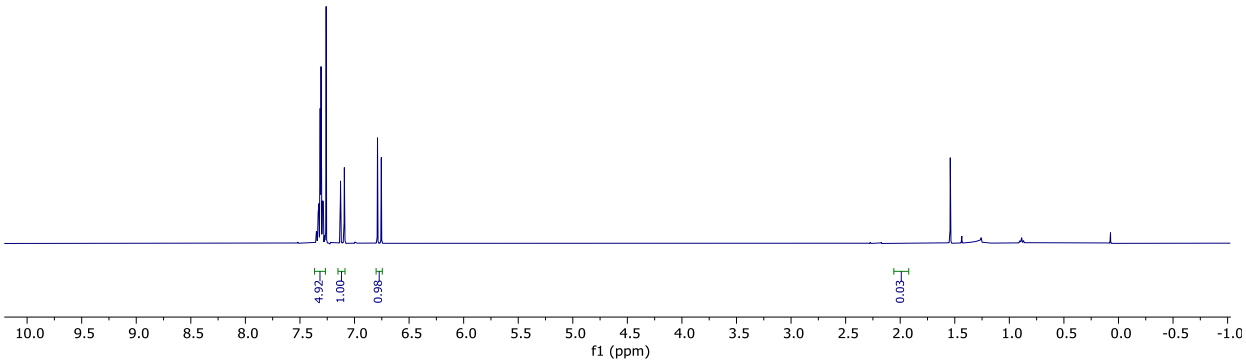
^{13}C NMR, 100 MHz, $CDCl_3$

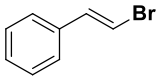
Compound 40



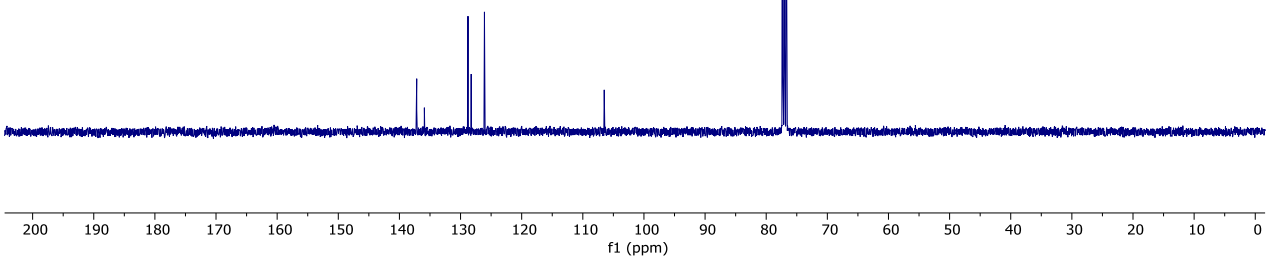


^{1}H NMR, 400 MHz, $CDCl_3$

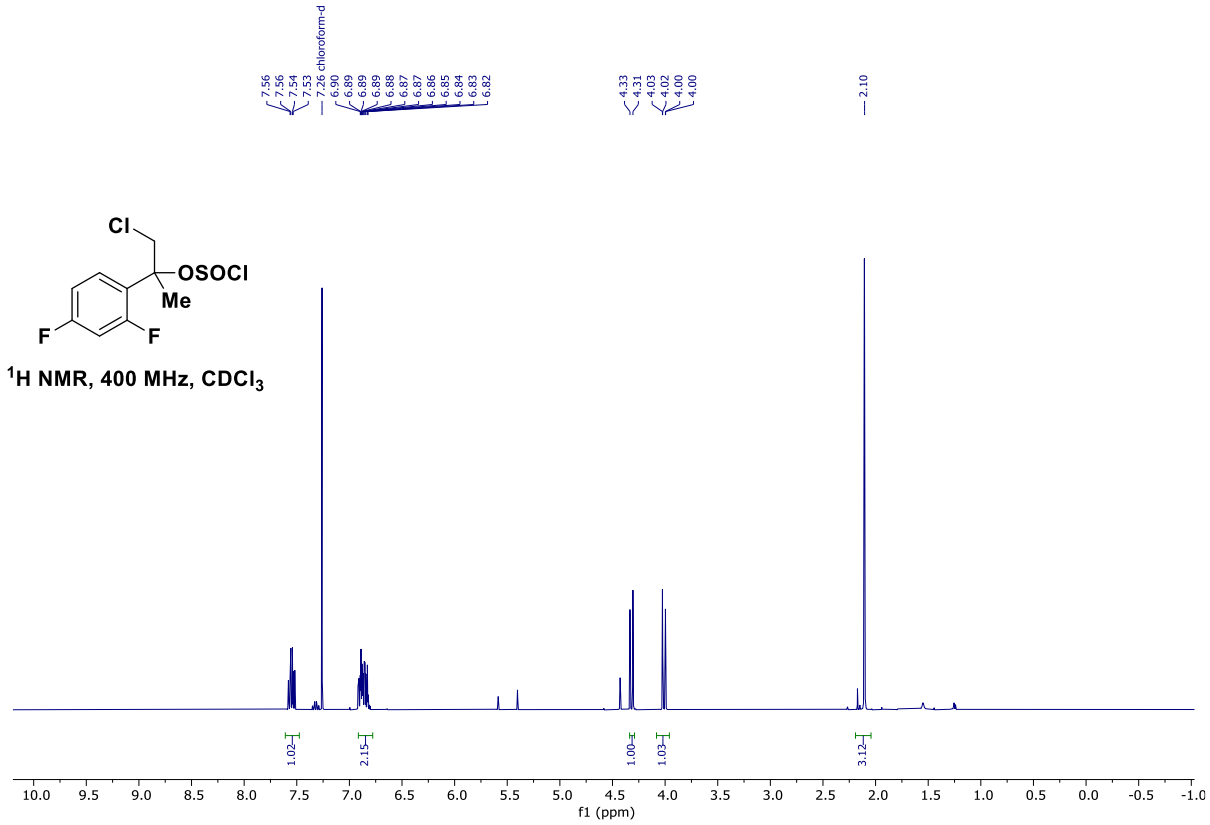


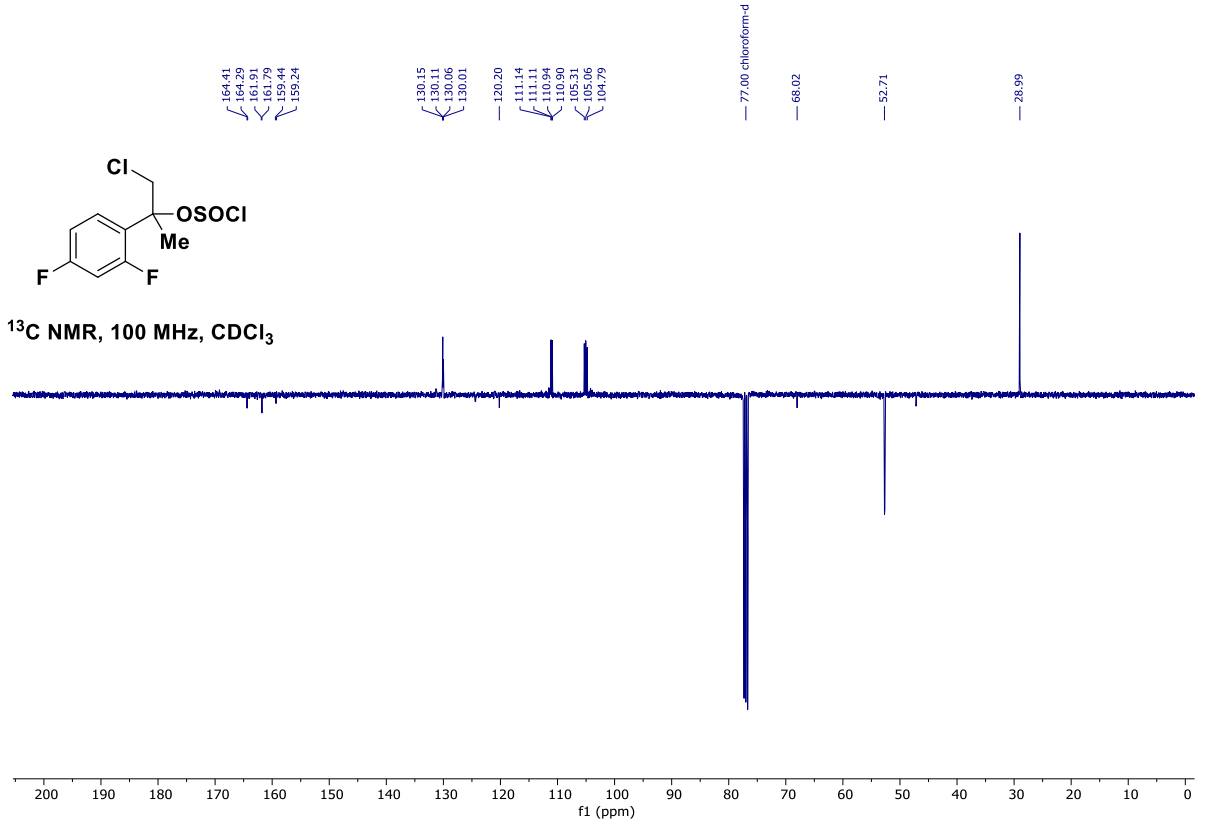


^{13}C NMR, 100 MHz, $CDCl_3$

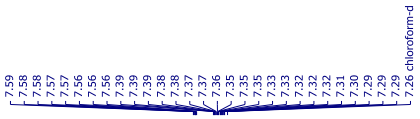


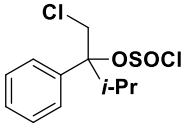
Compound 41


Cl
OSOCl
Me
F
F
1H NMR, 400 MHz, CDCl3
7.56
7.56
7.54
7.53
7.26 chloroform-d
6.90
6.89
6.89
6.89
6.88
6.87
6.87
6.86
6.85
6.84
6.83
6.82
4.33
4.31
4.03
4.02
4.00
4.00
2.10
1.02
2.15
1.00
1.03
3.12
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
f1 (ppm)

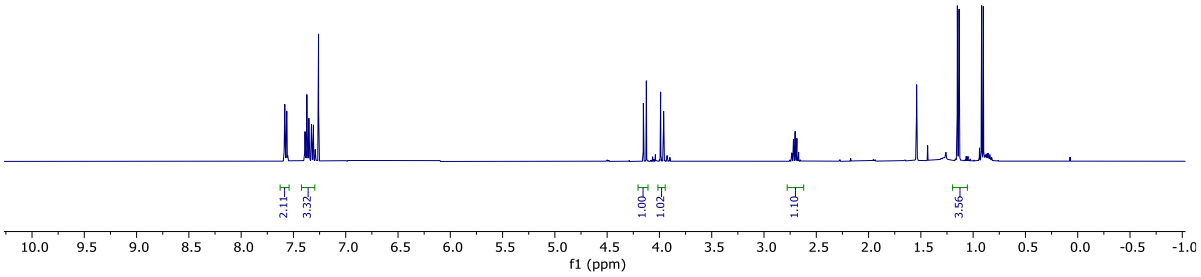

Cl
OSOCl
Me
F
F
13C NMR, 100 MHz, CDCl3
164.41
164.29
161.91
161.79
159.44
159.24
130.15
130.11
130.06
130.01
120.20
111.14
111.11
110.94
110.90
105.31
105.06
104.79
77.00 chloroform-d
68.02
52.71
28.99
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

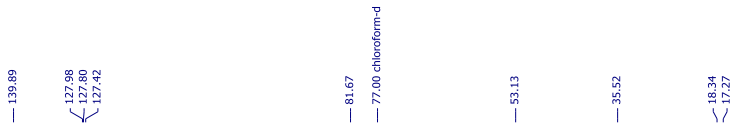
Compound 42

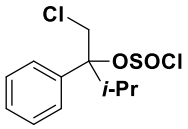




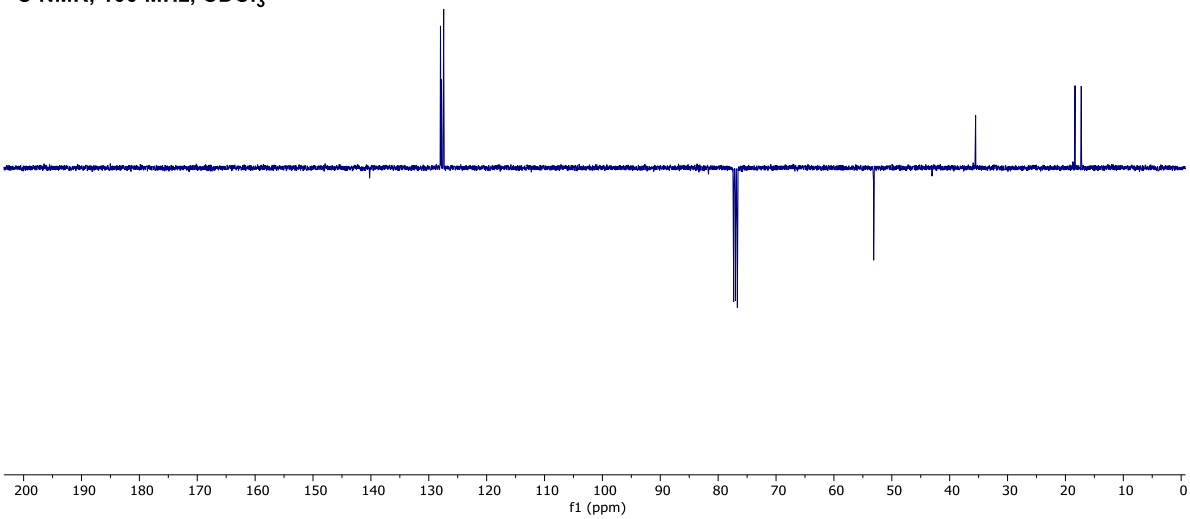
^{1}H NMR, 400 MHz, $CDCl_3$



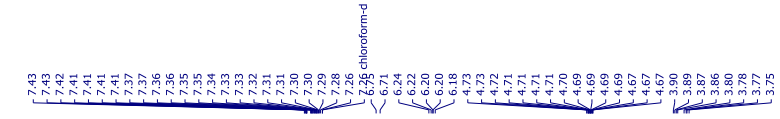


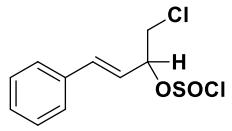


^{13}C NMR, 100 MHz, $CDCl_3$

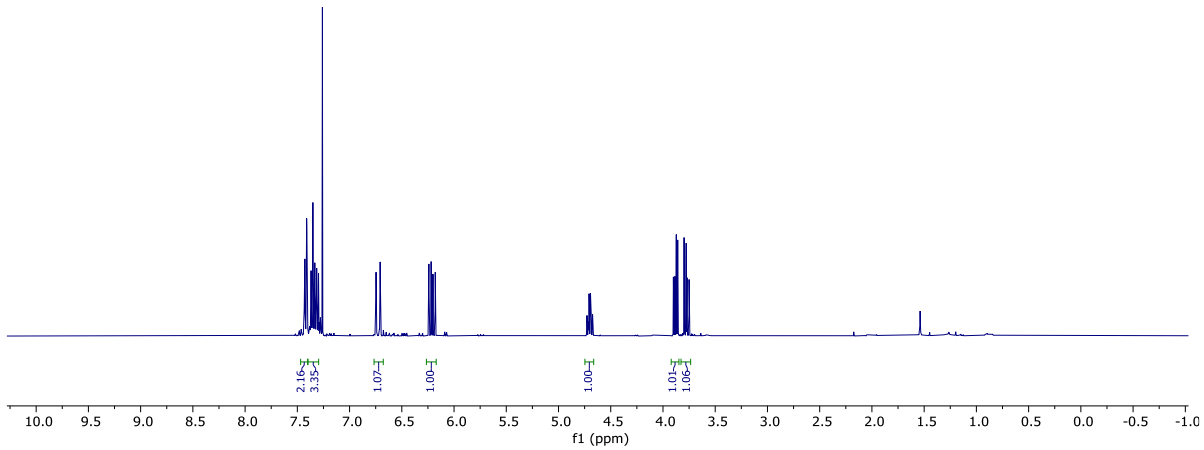


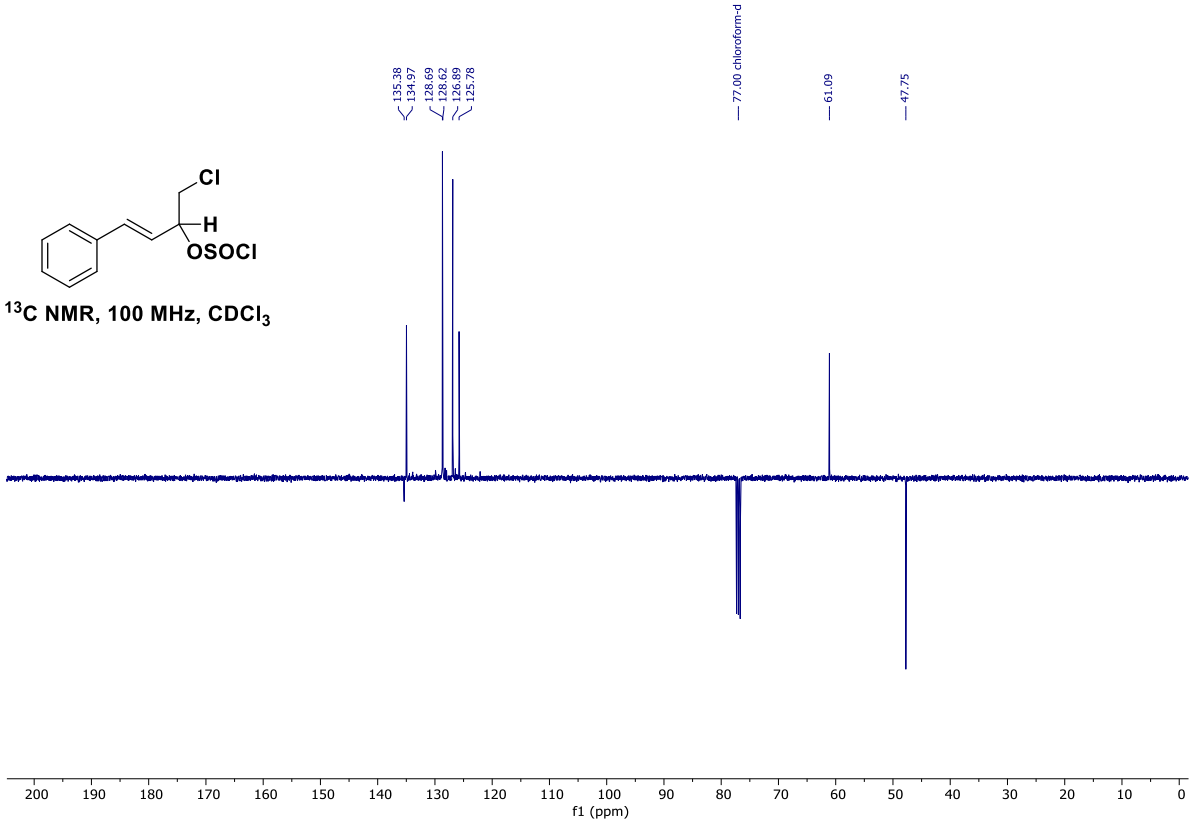
Compound 43





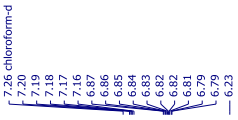
^{1}H NMR, 400 MHz, $CDCl_3$

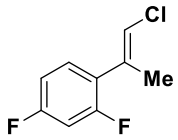




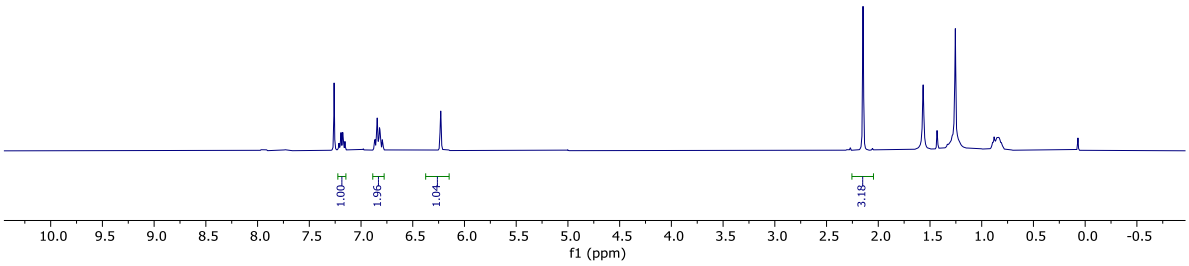
^{13}C NMR, 100 MHz, $CDCl_3$

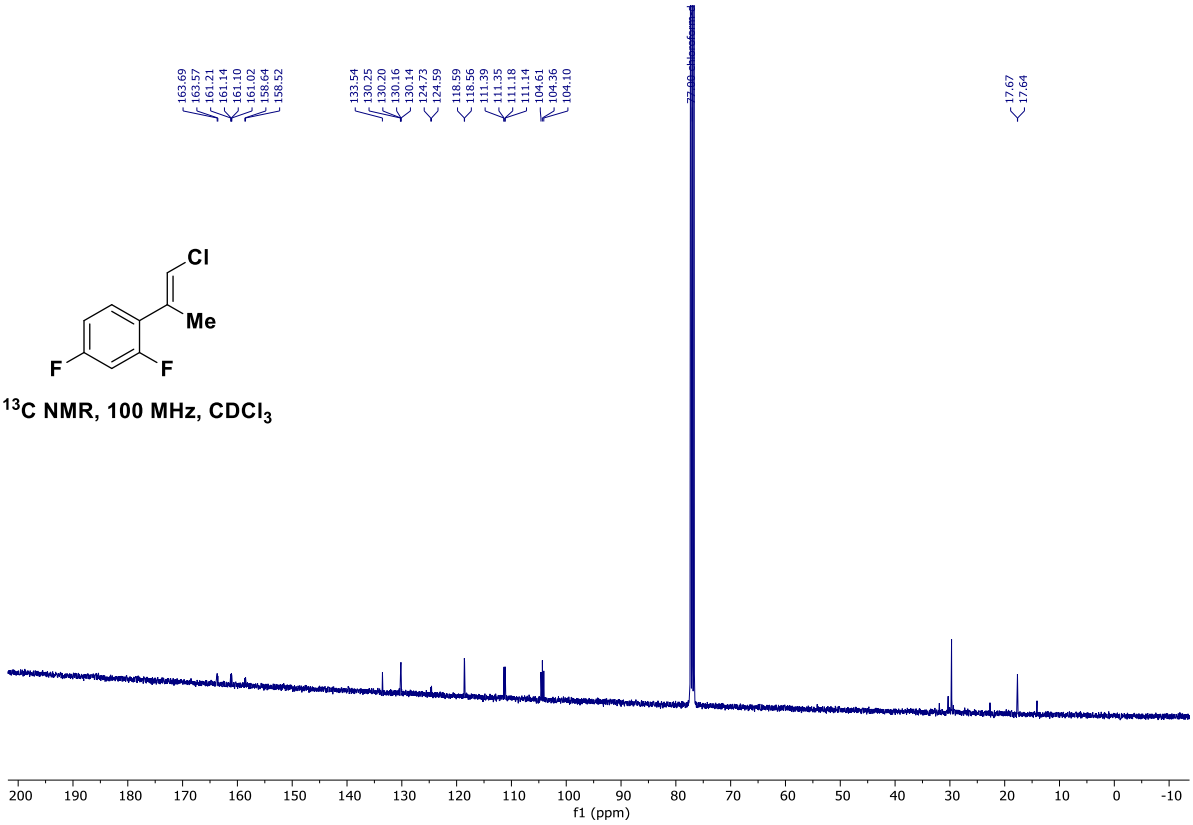
Compound (*E*)-44



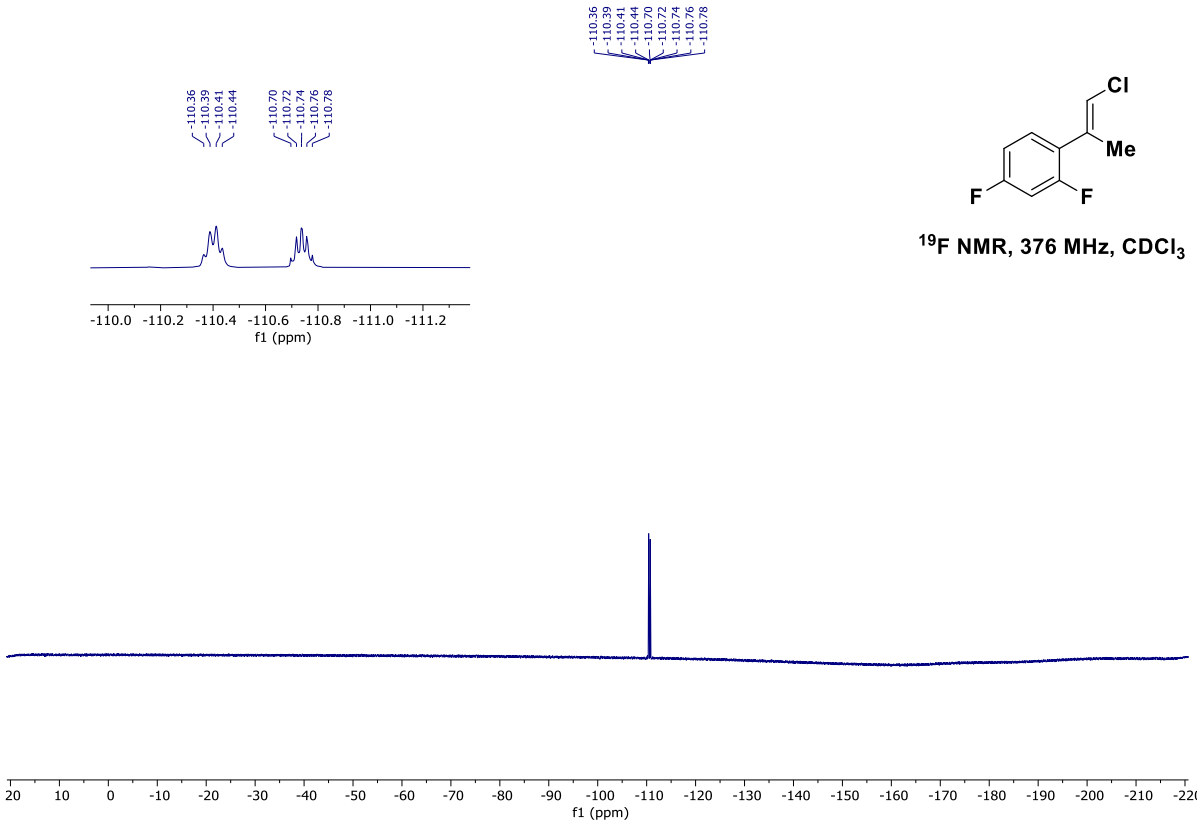


^{1}H NMR, 400 MHz, $CDCl_3$



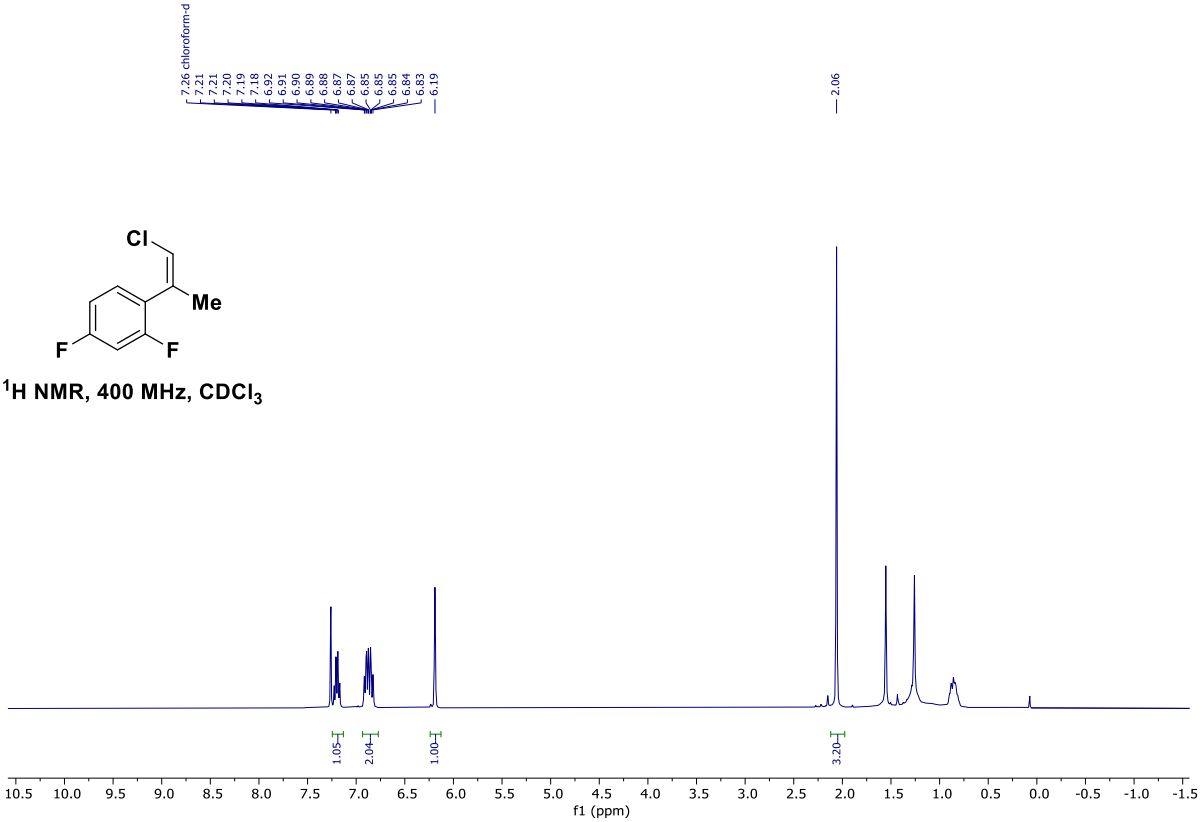


^{13}C NMR, 100 MHz, $CDCl_3$

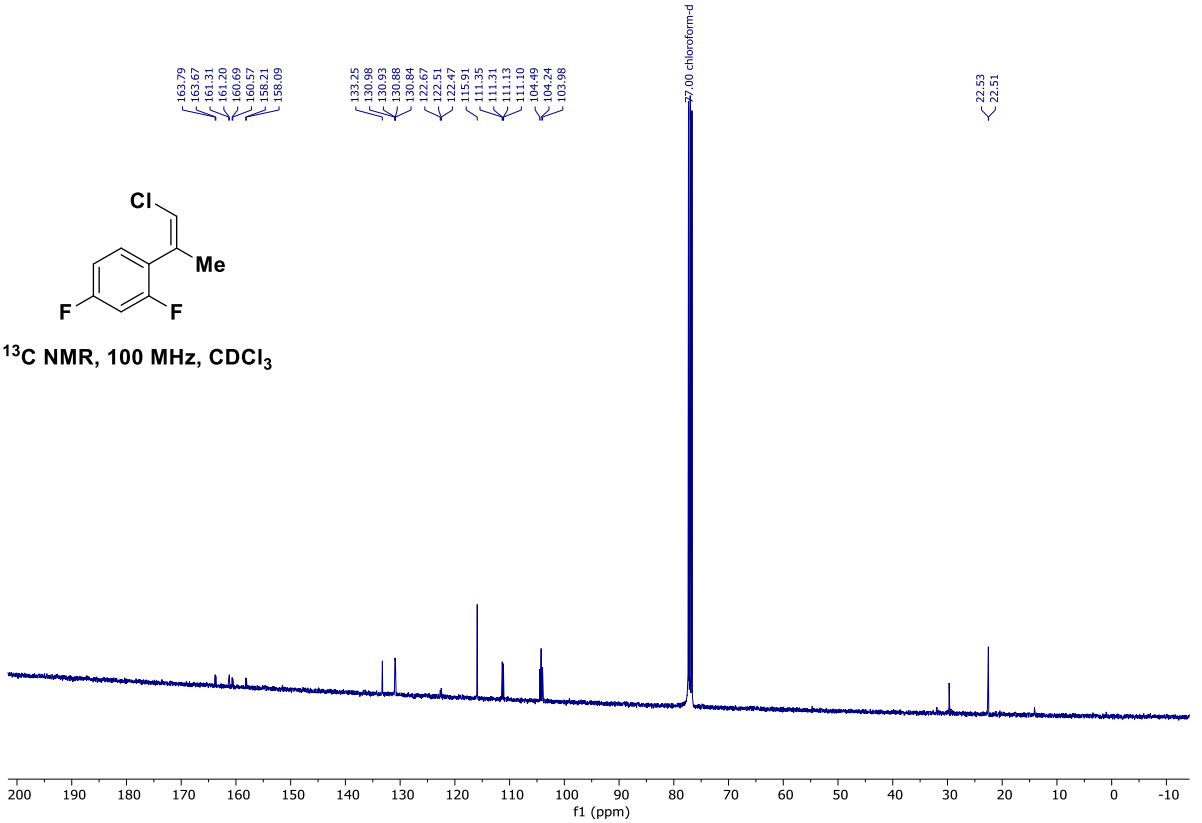


^{19}F NMR, 376 MHz, $CDCl_3$

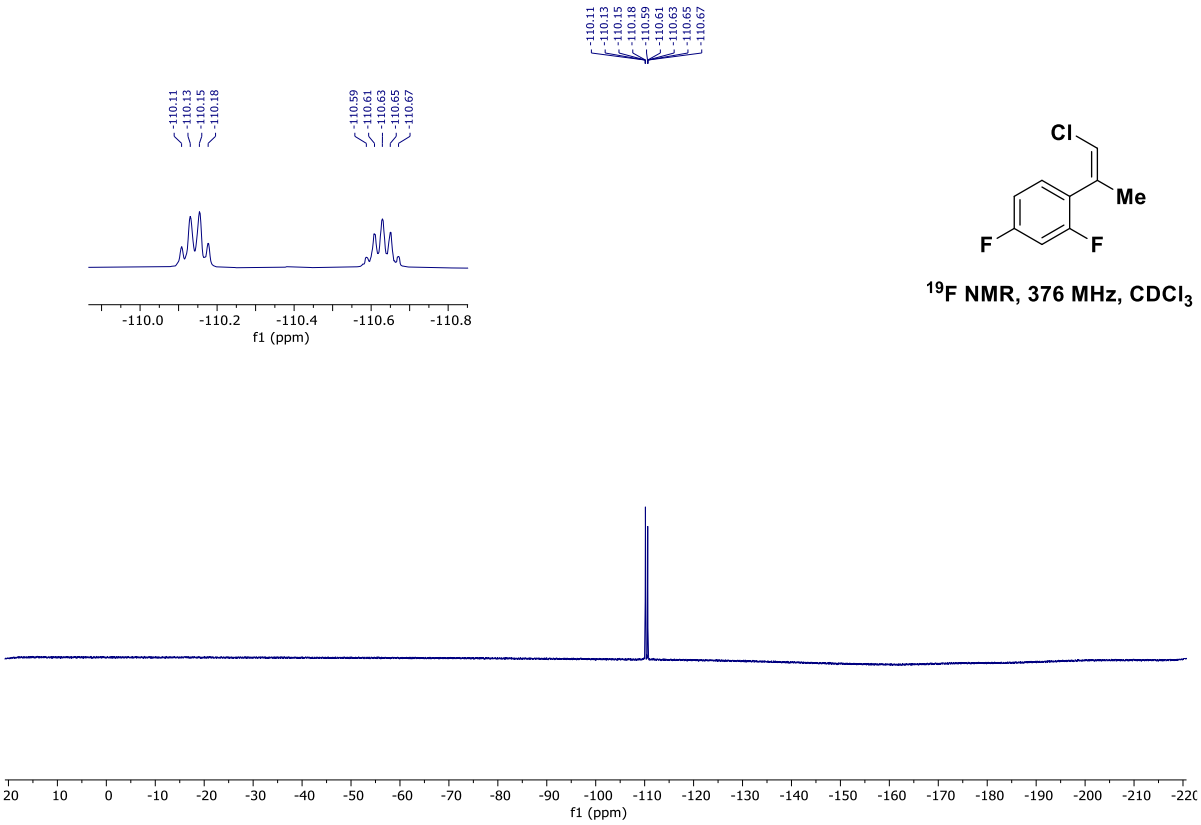
Compound (*Z*)-44



^{1}H NMR, 400 MHz, $CDCl_3$



^{13}C NMR, 100 MHz, $CDCl_3$



^{19}F NMR, 376 MHz, $CDCl_3$