

Supporting Information

Reduction of titanocene dichloride with dysprosium: access to a stable titanocene(II) equivalent for phosphite-free Takeda carbonyl olefination.

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I. General

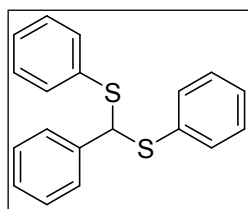
All reactions were conducted under an atmosphere of argon using standard Schlenk techniques and an argon-filled Jacomex BS531-type dry box. Tetrahydrofuran and diethylether were collected under argon from a PURSOLV MD-3 (Innovative Technologie Inc.) solvent purification unit. Titanocene dichloride was purchased from Strem Chemicals. Aldehydes, ketones and esters were purchased from Aldrich and used as received. Dysprosium ingot was purchased from Aldrich or Strem and, prior to use, freshly filed in a drybox under argon. ^1H , ^{13}C and ^{19}F NMR spectra were recorded in CDCl_3 , unless specified, on a 250 MHz Bruker Avance I spectrometer equipped with QNP probe and a 500 MHz Bruker Avance III spectrometer equipped with a BBFO+ probe. Chemical shifts are reported in delta (δ) units, expressed in parts per million (ppm). E/Z isomers of new compounds were determined by NOE experiments. High resolution ESI-MS spectra were recorded on a hybrid tandem quadrupole/time-of-flight (Q-TOF) instrument, equipped with a pneumatically assisted electrospray (Z-spray) ion source (Micromass, Manchester, UK) operated in positive mode. High resolution EI-MS spectra were obtained on a GCT-TOF mass spectrometer (Micromass, Manchester, UK) with EI source. EPR spectra were recorded with a Bruker ESP300e spectrometer (X-band) equipped with a Bruker E035M gaussmeter and an HP 5350B microwave frequency counter. Samples were prepared at a concentration of $2 \text{ mmol}\cdot\text{L}^{-1}$ in THF frozen solutions (150K, Bruker ER4111VY variable-temperature unit). The best resolution was obtained at $T = 150 \text{ K}$ by using the modulation amplitude 16.789 G, time constant 81.92 ms, conventional time 20.48 ms and sweep time 20.972 s.

II. Synthesis and analytical data of compounds 3a-g

General procedure for bis(arylsulfanes) 3a-g

A flask topped with a Dean-Stark apparatus was loaded with aldehyde (20 mmol), *p*-toluene sulfonic acid (0.5 mmol, 95 mg), thiophenol (50 mmol) and toluene (40 mL). The apparatus was set under argon and heated to 120°C for 15h. The reaction was quenched by addition of a 1N sodium hydroxide solution (15 mL). The aqueous layer was extracted with Et_2O (3 x 25 mL), the organic phases were combined, washed with brine, dried over MgSO_4 , and concentrated under vacuum. The dithioacetal was obtained without further purification.

(phenylmethylene)bis(phenylsulfane) (3a)¹



White solid, quantitative yield

^1H (600 MHz, CDCl_3)

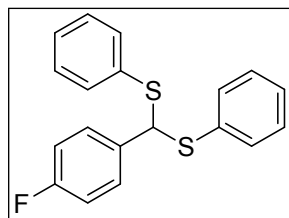
5.42 (s, 1H), 7.20-7.22 (m, 8H), 7.23-7.26 (m, 2H), 7.33-7.36 (m, 5H).

¹³C (150 MHz, CDCl₃)

60.5 (CH), 127.9 (CH), 128.0 (CH), 128.1 (CH), 128.6 (CH), 128.9 (CH), 132.6 (CH), 134.6 (C), 139.7 (C).

HRMS (EI) for C₁₉H₁₆S₂ : calc. (m/z) 308.0693 ; found (m/z) 308.0702.

((4-fluorophenyl)methylene)bis(phenylsulfane) (3b)



White solid, quantitative yield

¹H (500 MHz, CDCl₃)

5.39 (s, 1H), 6.90 (dd, J_{H-H} = 9.0 Hz, J_{H-H} = 9.0 Hz, 2H), 7.20-7.21 (m, 6H), 7.27-7.32 (m, 6H).

¹³C (125 MHz, CDCl₃)

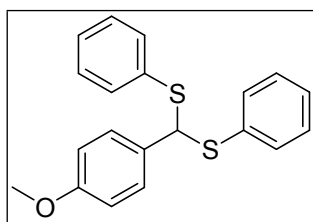
59.7 (CH), 115.4 (d, J_{F-C} = 21.6 Hz, CH), 128.1 (CH), 129.0 (CH), 129.7 (d, J_{F-C} = 8.3 Hz, CH), 132.8 (CH), 134.3 (C), 135.6 (d, J_{F-C} = 3.1 Hz, C), 162.3 (d, J_{F-C} = 245.8 Hz, C).

¹⁹F (470 MHz, CDCl₃)

-113.6

HRMS (EI) for C₁₉H₁₅FS₂ : calc. (m/z) 326.0599 ; found (m/z) 326.0597.

((4-methoxyphenyl)methylene)bis(phenylsulfane) (3c)²



White solid, quantitative yield

¹H (500 MHz, CDCl₃)

3.82 (s, 3H), 5.50 (s, 1H), 6.85 (d, J_{H-H} = 7.0 Hz, 2H), 7.29-7.30 (m, 6H), 7.37 (d, J_{H-H} = 7.0 Hz, 2H), 7.40-7.41 (m, 4H).

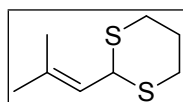
¹³C (125 MHz, CDCl₃)

55.3 (CH₃), 59.8 (CH), 113.9 (CH), 127.8 (CH), 128.9 (CH), 129.2 (CH), 131.7 (C), 132.4 (CH), 134.8 (C), 159.4 (C).

Elemental Analysis for C₂₀H₁₈OS₂ calc. C : 70.97, H : 5.96, S : 18.95 ; found C : 71.04, H : 5.44, S : 18.73.

2-(2-methylprop-1-enyl)-1,3-dithiane (3d)^{3,4}

A flask was loaded with aldehyde (5 mmol), 1,3-propanedithiol (5.5 mmol), iodine (0.5 mmol) and chloroform (20 mL). The solution was stirred for 30 minutes then the reaction was quenched with an addition of 1N sodium hydroxide solution (10 mL). The organic phase was separated and the aqueous layer was extracted with dichloromethane (3 x 25 mL). The organic phases were combined, washed with brine, dried over MgSO₄, and concentrated under vacuum. The dithiane was obtained without further purification.



Yellow oil, quantitative yield

¹H (500 MHz, CDCl₃)

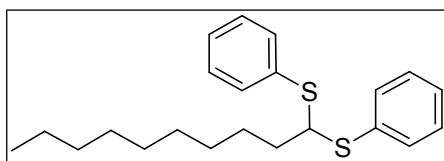
1.74 (s, 6H), 1.78-1.86 (m, 1H), 2.06-2.10 (m, 1H), 2.77-2.81 (m, 2H), 2.94 (dd, J_{H-H} = 13.0 Hz, J_{H-H} = 13.0 Hz, 2H), 4.86 (d, J_{H-H} = 10.0 Hz, 1H), 5.13 (d, J_{H-H} = 10.0 Hz, 1H).

¹³C (125 MHz, CDCl₃)

18.5 (CH₃), 25.1 (CH₂), 25.7 (CH₃), 30.7 (CH₂), 44.5 (CH), 121.3 (CH), 137.9 (C).

HRMS (EI) for C₈H₁₄S₂ : calc. (m/z) 174.0537 ; found (m/z) 174.0540.

decan-1,1-diylbis(phenylsulfane) (3e)



Yellow oil, quantitative yield

¹H (500 MHz, CDCl₃)

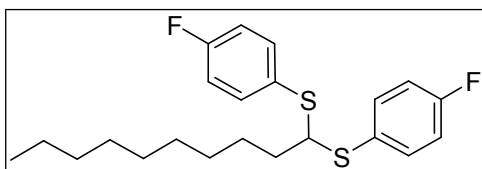
0.90 (t, J_{H-H} = 7.0 Hz, J_{H-H} = 7.0 Hz, 3H), 1.26-1.31 (m, 2H), 1.59-1.62 (m, 2H), 1.85 (q, J_{H-H} = 15.0 Hz, J_{H-H} = 7.0 Hz, 2H), 4.41 (t, J_{H-H} = 6.5 Hz, J_{H-H} = 6.5 Hz, 1H), 7.28-7.33 (m, 6H), 7.46-7.75 (m, 4H).

¹³C (125 MHz, CDCl₃)

14.3 (CH₃), 22.8 (CH₂), 27.2 (CH₂), 29.2 (CH₂), 29.4 (CH₂), 29.5 (CH₂), 29.6 (CH₂), 30.0 (CH₂), 36.0 (CH₂), 58.6 (CH), 127.7 (CH), 129.0 (CH), 132.8 (CH), 134.6 (C).

HRMS (EI) for C₂₂H₃₀S₂ : calc. (m/z) 358.1789 ; found (m/z) 358.1797.

decan-1,1-diylbis((4-fluorophenyl)sulfane) (3f)



Yellow oil, quantitative yield

¹H (500 MHz, CDCl₃)

0.88 (t, J_{H-H} = 7.0 Hz, J_{H-H} = 7.0 Hz, 3H), 1.24 (s, 10H), 1.28-1.31 (m, 2H), 1.54-1.58 (m, 2H), 1.76 (dd, J_{H-H} = 15.0 Hz, J_{H-H} = 7.0 Hz, 2H), 4.19 (t, J_{H-H} = 7.0 Hz, J_{H-H} = 7.0 Hz, 1H), 7.01 (dd, J_{H-H} = 8.5 Hz, J_{F-H} = 8.5 Hz, 4H), 7.43 (dd, J_{H-H} = 8.5 Hz, J_{F-H} = 5.0 Hz, 4H).

¹³C (125 MHz, CDCl₃)

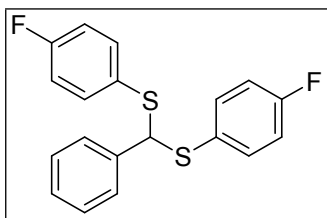
14.3 (CH₃), 22.8 (CH₂), 27.2 (CH₂), 29.1 (CH₂), 29.4 (CH₂), 29.5 (CH₂), 29.6 (CH₂), 32.0 (CH₂), 35.7 (CH₂), 60.5 (CH), 116.1 (d, J_{F-C} = 21.8 Hz, CH), 129.2 (d, J_{F-C} = 3.3 Hz, C), 135.9 (d, J_{F-C} = 8.3 Hz, CH), 162.9 (d, J_{F-C} = 246.9 Hz, C).

¹⁹F (235 MHz, CDCl₃)

-113.5

HRMS (EI) for C₂₂H₂₈F₂S₂ : calc. (m/z) 394.1600 ; found (m/z) 394.1577.

(phenylmethylene)bis((4-fluorophenyl)sulfane) (3g)



White solide, quantitative yield

¹H (500 MHz, CDCl₃)

5.23 (s, 1H), 6.92 (dd, J_{H-H} = 9.0 Hz, J_{F-H} = 9.0 Hz, 4H), 7.24-7.26 (m, 5H), 7.30 (dd, J_{H-H} = 9.0 Hz, J_{F-H} = 5.5 Hz, 4H).

¹³C (125 MHz, CDCl₃)

62.2 (CH), 116.1 (d, $J_{F-C} = 21.8$ Hz, CH), 127.9 (CH), 128.3 (CH), 128.6 (CH), 129.2 (d, $J_{F-C} = 3.4$ Hz, C), 135.9 (d, $J_{F-C} = 8.4$ Hz, CH), 139.4 (C), 163.0 (d, $J_{F-C} = 247.4$ Hz, C).

¹⁹F (470 MHz, CDCl₃)

-112.6

HRMS (EI) for C₁₉H₁₄F₂S₂ : calc. (m/z) 344.0505 ; found (m/z) 344.0517.

III. Synthesis and analytical data of compounds 5a-i.

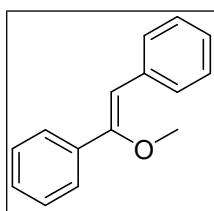
General procedure for the preparation of alkenes (5a-i).

A Schlenk tube was loaded with dichlorotitanocene (Cp₂TiCl₂) (370 mg, 1.5 mmol), dysprosium (244 mg, 1.5 mmol) and THF (5 mL) under an atmosphere of argon. The resulting mixture was stirred vigorously at room temperature until a deep green color appeared. After three hours, the dithioacetal (0.6 mmol) solubilized in THF (2 mL) was added to the reaction mixture. Twenty minutes later, the carbonyl compound (0.5 mmol) solubilized in THF (3 mL) was added dropwise. The solution was heated to 50°C for 90 minutes and the reaction was followed by TLC. At the end of the reaction petroleum ether was added to the cooled solution and the reaction mixture was filtered over celite (petroleum ether / ethyl acetate (80/20)). The solvent was concentrated under vacuum and the residue was purified by flash column chromatography (silica gel, petroleum ether) to give the corresponding alkene.

Procedure "All-in-one".

A Schlenk tube was loaded with dichlorotitanocene (Cp₂TiCl₂) (370 mg, 1.5 mmol), dysprosium (244 mg, 1.5 mmol), dithioacetal (0.6 mmol), carbonyl compound (0.5 mmol) and THF (10 mL) under an atmosphere of argon. The resulting mixture was stirred vigorously at room temperature until a deep green color appeared, which rapidly changed to purple. After four hours, petroleum ether was added to the solution and the reaction mixture was filtered over celite (petroleum ether / ethyl acetate (80/20)). The solvent was concentrated under vacuum and the residue was purified by flash column chromatography (silica gel, petroleum ether) to give the corresponding alkene.

1-methoxy-1,2-diphenylethene (5a)⁵



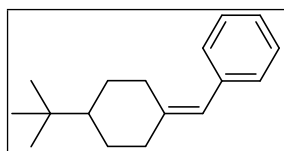
Colourless oil, 65% (Z / E : >95/5)

(Z)-isomer:

¹H (250 MHz, CDCl₃)

3.55 (s, 3H), 6.02 (s, 1H), 7.13-7.16 (m, 1H), 7.24-7.32 (m, 5H), 7.48 (dd, $J_{H-H} = 8.0$ Hz, $J_{H-H} = 1.5$ Hz, 2H), 7.63 (d, $J_{H-H} = 7.3$ Hz, 2H).

1-((4-tert-butylcyclohexylidene)methyl)benzene (5ba)⁶



Colourless oil, 57 %

¹H (250 MHz, CDCl₃)

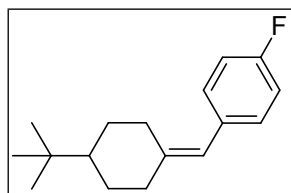
0.86 (s, 9H), 1.02-1.25 (m, 3H), 1.81-1.95 (m, 3H), 2.20 (dd, $J_{H-H} = 13.0$ Hz, $J_{H-H} = 13.0$ Hz, 1H), 2.39 (dd, $J_{H-H} = 13.3$ Hz, $J_{H-H} = 2.3$ Hz, 1H), 2.97 (dd, $J_{H-H} = 12.8$ Hz, $J_{H-H} = 2.0$ Hz, 1H), 6.22 (s, 1H), 7.17-7.23 (m, 3H), 7.27-7.33 (m, 2H).

¹³C (62.5 MHz, CDCl₃)

27.8 (CH₃), 28.7 (CH₂), 29.4 (CH₂), 29.4 (CH₂), 32.6 (C), 37.7 (CH₂), 48.4 (CH), 121.7 (CH), 125.9 (CH), 128.1 (CH), 129.1 (CH), 138.5 (C), 143.5 (C).

HRMS (EI) for C₁₇H₂₄ : calc. (m/z) 228.1878 ; found (m/z) 228.1887.

1-((4-tert-butylcyclohexylidene)methyl)-4-fluorobenzene (5bb)



Colourless oil, 57%

¹H (500 MHz, CDCl₃)

0.88 (s, 9H), 1.01-1.09 (m, 1H), 1.13-1.21 (m, 1H), 1.22-1.28 (m, 1H), 1.83-1.89 (m, 2H), 1.92-1.97 (m, 1H), 2.17-2.23 (m, 1H), 2.37-2.42 (m, 1H), 2.88-2.92 (m, 1H), 6.18 (s, 1H), 7.00 (dd, $J_{F-H} = 9.0$ Hz, $J_{H-H} = 8.5$ Hz, 2H), 7.16 (dd, $J_{H-H} = 8.5$ Hz, $J_{F-H} = 5.5$ Hz, 2H).

¹³C (125 MHz, CDCl₃)

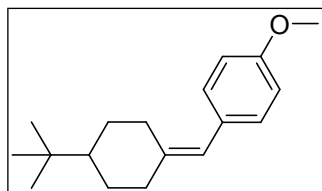
27.8 (CH₃), 28.6 (CH₂), 29.3 (CH₂), 32.6 (C), 37.6 (CH₂), 48.4 (CH₂), 114.9 (d, $J_{F-C} = 21.0$ Hz, CH), 120.7 (CH), 130.5 (d, $J_{F-C} = 7.6$ Hz, CH), 134.5 (d, $J_{F-C} = 3.3$ Hz, C), 143.5 (C), 161.2 (d, $J_{F-C} = 243.1$ Hz, C).

^{19}F (470 MHz, CDCl_3)

-116.9

HRMS (EI) for $\text{C}_{17}\text{H}_{23}\text{F}$: calc. (m/z) 246.1784 ; found (m/z) 246.1784.

1-((4-tert-butylcyclohexylidene)methyl)-4-methoxybenzene (5bc)



Colourless oil, 54%

^1H (500 MHz, CDCl_3)

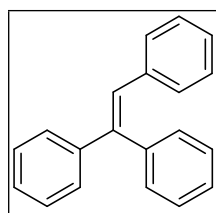
0.87 (s, 9H), 1.03-1.09 (m, 1H), 1.12-1.20 (m, 1H), 1.21-1.27 (m, 1H), 1.83-1.89 (m, 2H), 1.91-1.94 (m, 1H), 2.16-2.22 (m, 1H), 2.36-2.97 (m, 1H), 2.94-2.97 (m, 1H), 3.81 (s, 3H), 6.17 (s, 1H), 6.86 (d, $J_{\text{H-H}} = 9.0$ Hz, 2H), 7.15 (d, $J_{\text{H-H}} = 9.0$ Hz, 2H).

^{13}C (125 MHz, CDCl_3)

27.8 (CH_3), 28.6 (CH_2), 29.357 (CH_2), 29.375 (CH_2), 32.6 (C), 37.7 (CH_2), 48.4 (CH), 55.4 (CH_3), 113.6 (CH), 121.2 (CH), 130.1 (CH), 131.1 (C), 142.3 (C), 157.8 (C).

HRMS (EI) for $\text{C}_{18}\text{H}_{26}\text{O}$: calc. (m/z) 258.1984 ; found (m/z) 258.1988.

1,1,2-triphenylethene (5ca)⁷



Colourless oil, 64%

^1H (250 MHz, CDCl_3)

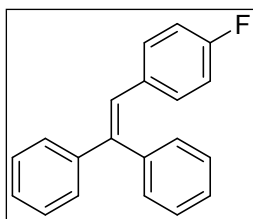
6.96 (s, 1H), 7.00-7.04 (m, 2H), 7.09-7.13 (m, 3H), 7.18-7.22 (m, 2H), 7.28-7.33 (m, 8H).

^{13}C (62.5 MHz, CDCl_3)

126.9 (CH), 127.5 (CH), 127.6 (CH), 127.7 (CH), 128.1 (CH), 128.3 (CH), 128.3 (CH), 128.8 (CH), 129.7 (CH), 130.5 (CH), 137.5 (C), 140.5 (C), 142.7 (C), 143.6 (C).

HRMS (EI) for $\text{C}_{20}\text{H}_{16}$: calc. (m/z) 256.1252 ; found (m/z) 256.1256.

1-(2-(4-fluorophenyl)-1-phenylvinyl)benzene (5cb)⁸



Colourless oil, 62%

¹H (500 MHz, CDCl₃)

6.84 (dd, $J_{\text{H-H}} = 9.0$ Hz, $J_{\text{F-H}} = 8.5$ Hz, 2H), 6.95 (s, 1H), 7.01 (dd, $J_{\text{H-H}} = 8.5$ Hz, $J_{\text{F-H}} = 5.5$ Hz, 2H), 7.21-7.23 (m, 2H), 7.31-7.37 (m, 8H).

¹³C (125 MHz, CDCl₃)

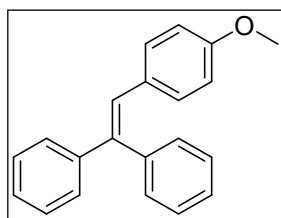
115.0 (d, $J_{\text{F-C}} = 21.3$ Hz, CH), 127.0 (CH), 127.7 (dd, $J_{\text{F-C}} = 3.4$ Hz, $J_{\text{F-C}} = 3.3$ Hz, CH), 128.4 (CH), 128.9 (CH), 130.5 (CH), 131.2 (d, $J_{\text{F-C}} = 7.8$ Hz, CH), 133.6 (d, $J_{\text{F-C}} = 3.3$ Hz, C), 140.3 (C), 142.6 (d, $J_{\text{F-C}} = 1.6$ Hz, C), 143.4 (C), 161.6 (d, $J_{\text{F-C}} = 245.6$ Hz, C).

¹⁹F (470 MHz, CDCl₃)

-114.7

HRMS (EI) for C₂₀H₁₅F : calc. (m/z) 274.1158 ; found (m/z) 274.1158.

1-(2-(4-methoxyphenyl)-1-phenylvinyl)benzene (5cc)⁹



Colourless oil, 60%

¹H (500 MHz, CDCl₃)

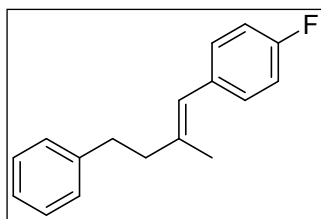
3.80 (s, 3H), 6.73 (d, $J_{\text{H-H}} = 3.8$ Hz, 2H), 6.98 (s, 1H), 7.02 (d, $J_{\text{H-H}} = 3.5$ Hz, 2H), 7.28-7.30 (m, 2H), 7.31-7.35 (m, 2H), 7.36-7.36 (m, 1H), 7.37-7.37 (m, 2H), 7.38-7.40 (m, 2H), 7.40-7.42 (m, 1H).

¹³C (125 MHz, CDCl₃)

55.3 (CH₃), 113.5 (CH), 127.3 (CH), 127.4 (CH), 127.5 (CH), 127.8 (CH), 128.3 (CH), 128.8 (CH), 130.2 (C), 130.5 (CH), 130.9 (CH), 140.7 (C), 140.8 (C), 143.7 (C), 158.5 (C).

HRMS (EI) for C₂₀H₁₅F : calc. (m/z) 286.1358 ; found (m/z) 286.1361.

1-fluoro-4-(2-methyl-4-phenylbut-1-enyl)benzene (5d)



Colourless oil, 53% (Z/E : 1 / 1)

(E)-isomer

¹H (500 MHz, CDCl₃)

1.88 (s, 3H), 2.47 (dd, $J_{H-H} = 8.0$ Hz, $J_{H-H} = 8.0$ Hz, 2H), 2.84 (dd, $J_{H-H} = 8.5$ Hz, $J_{H-H} = 7.5$ Hz, 2H), 6.21 (s, 1H), 7.00 (dd, $J_{H-H} = 9.0$ Hz, $J_{H-H} = 8.5$ Hz, 2H), 7.16 (dd, $J_{H-H} = 8.5$ Hz, $J_{H-H} = 5.5$ Hz, 2H), 7.21-7.23 (m, 3H), 7.31 (dd, $J_{H-H} = 8.0$ Hz, $J_{H-H} = 7.0$ Hz, 2H).

¹³C (125 MHz, CDCl₃)

18.0 (CH₃), 34.8 (CH₂), 42.6 (CH₂), 115.0 (d, $J_{F-C} = 21.1$ Hz, CH), 124.5 (CH), 126.0 (CH), 128.5 (d, $J_{F-C} = 12.8$ Hz, CH), 130.4 (d, $J_{F-C} = 7.6$ Hz, CH), 134.6 (d, $J_{F-C} = 3.3$ Hz, C), 138.3 (C), 142.1 (C), 161.3 (d, $J_{F-C} = 243.5$ Hz, C).

¹⁹F (470 MHz, CDCl₃)

-116.7

HRMS (EI) for C₁₇H₁₇F : calc. (m/z) 240.1314 ; found (m/z) 240.1320.

(Z)-isomer

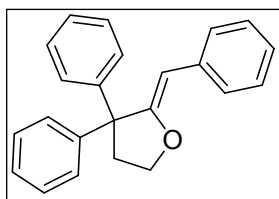
¹H (250 MHz, CDCl₃)

1.86 (s, 3H), 2.38-2.44 (m, 2H), 2.67-2.76 (m, 2H), 6.19 (s, 1H), 6.97 (dd, $J_{H-H} = 8.8$ Hz, $J_{H-H} = 8.8$ Hz, 2H), 7.13-7.22 (m, 7H).

¹⁹F (235 MHz, CDCl₃)

-117.1

(Z)-2-benzylidene-tetrahydro-3,3-diphenylfuran (5e)



White solid, 57% (Z / E : 1 / 0)

¹H (500 MHz, CDCl₃)

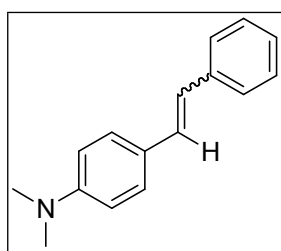
2.92 (t, $J_{H-H} = 6.5$ Hz, $J_{H-H} = 6.5$ Hz, 2H), 4.29 (t, $J_{H-H} = 6.5$ Hz, $J_{H-H} = 6.5$ Hz, 2H), 5.02 (s, 1H), 7.35-7.38 (m, 5H), 7.41 (s, 5H), 7.42 (s, 3H), 7.66-7.68 (m, 2H).

¹³C (125 MHz, CDCl₃)

40.4 (CH₂), 60.7 (C), 68.7 (CH₂), 102.4 (CH), 125.3 (CH), 127.0 (CH), 127.7 (CH), 128.3 (CH), 128.3 (CH), 128.9 (CH), 136.6 (C), 143.7 (C (x2)), 162.3 (C).

HRMS (EI) for C₂₃H₂₀O : calc. (m/z) 312.1514 ; found (m/z) 312.1523.

1-[4-N,N-(dimethylamino)phenyl]-2-phenylethene (5f)¹⁰



White solid, 45% (Z / E : 1 / 4.5)

(E)-isomer

¹H (250 MHz, CDCl₃)

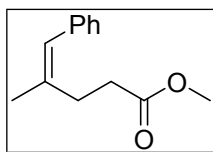
2.99 (s, 6H), 6.75 (d, $J_{H-H} = 8.8$ Hz, 2H), 6.92 (m, 1H), 7.05 (m, 1H), 7.20 (m, 1H), 7.33 (m, 2H), 7.42 (m, 2H), 7.48 (m, 2H).

(Z)-isomer

¹H (250 MHz, CDCl₃)

2.92 (s, 6H), 6.40 (m, 1H), 6.48 (m, 1H), 6.55-6.57 (m, 2H), 7.14-7.18 (m, 3H), 7.22-7.25 (m, 2H), 7.31-7.33 (m, 2H).

Methyl 4-methyl-5-phenylpent-4-enoate (5g)



White solid, 56% (Z / E : 3 / 2)

(Z)-isomer

¹H (500 MHz, CDCl₃)

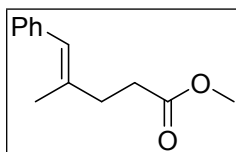
1.87 (d, $J_{H-H} = 0.5$ Hz, 3H), 2.50-2.52 (m, 2H), 2.54-2.56 (m, 2H), 3.70 (s, 3H), 6.30 (s, 1H), 7.22 (d, $J_{H-H} = 7.5$ Hz, 3H), 7.30-7.33 (m, 2H).

¹³C (125 MHz, CDCl₃)

17.8 (CH₃), 33.1 (CH₂), 35.7 (CH₂), 51.7 (CH₃), 125.8 (CH), 128.3 (CH), 128.7 (CH), 129.0 (CH), 137.2 (C), 138.3 (C), 173.8 (C).

HRMS (EI) for C₁₃H₁₆O₂ : calc. (m/z) 204.1150 ; found (m/z) 204.1152.

(E)-isomer



¹H (500 MHz, CDCl₃)

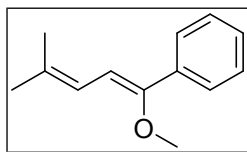
1.89 (d, $J_{H-H} = 1.0$ Hz, 3H), 2.46-2.50 (m, 2H), 2.57-2.60 (m, 2H), 3.65 (s, 3H), 6.34 (s, 1H), 7.19 (d, $J_{H-H} = 7.5$ Hz, 3H), 7.30-7.33 (m, 2H).

¹³C (125 MHz, CDCl₃)

23.7 (CH₃), 28.0 (CH₂), 32.8 (CH₂), 51.7 (CH₃), 126.3 (CH), 127.2 (CH), 128.3 (CH), 137.0 (C), 138.1 (C), 173.8 (C).

HRMS (EI) for C₁₃H₁₆O₂ : calc. (m/z) 204.1150 ; found (m/z) 204.1152.

1-(1-methoxy-4-methylpenta-1,3-dienyl)benzene (5h)¹¹



Colourless oil, 68% (Z / E : 4 / 1)

(Z)-isomer

¹H (250 MHz, CDCl₃)

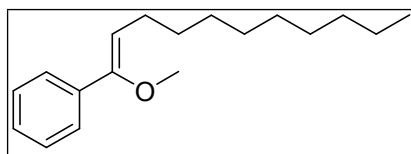
1.81 (s, 3H), 1.87 (s, 3H), 3.60 (s, 3H), 6.16 (d, $J_{H-H} = 11.3$ Hz, 1H), 6.29-6.37 (m, 1H), 7.22-7.57 (m, 5H).

(E)-isomer

¹H (250 MHz, CDCl₃)

1.72 (s, 3H), 1.78 (s, 3H), 3.72 (s, 3H), 5.67 (d, $J_{H-H} = 11.0$ Hz, 1H), 5.85-5.92 (m, 1H), 7.22-7.57 (m, 5H).

1-(1-methoxyundec-1-enyl)benzene (5i)



Colourless oil, 31% (Z / E : 7 / 1)

(Z)-isomer

¹H (500 MHz, C₆D₆)

0.91 (t, $J_{H-H} = 7.0$ Hz, $J_{H-H} = 7.0$ Hz, 3H), 1.28-1.30 (m, 10H), 1.35-1.41 (m, 2H), 1.43-1.49 (m, 2H), 2.39 (q, $J_{H-H} = 15.0$ Hz, $J_{H-H} = 7.5$ Hz, 2H), 3.34 (s, 1H), 5.32 (t, $J_{H-H} = 7.5$ Hz, $J_{H-H} = 7.5$ Hz, 1H), 7.15-7.18 (m, 3H), 7.47-7.49 (m, 2H).

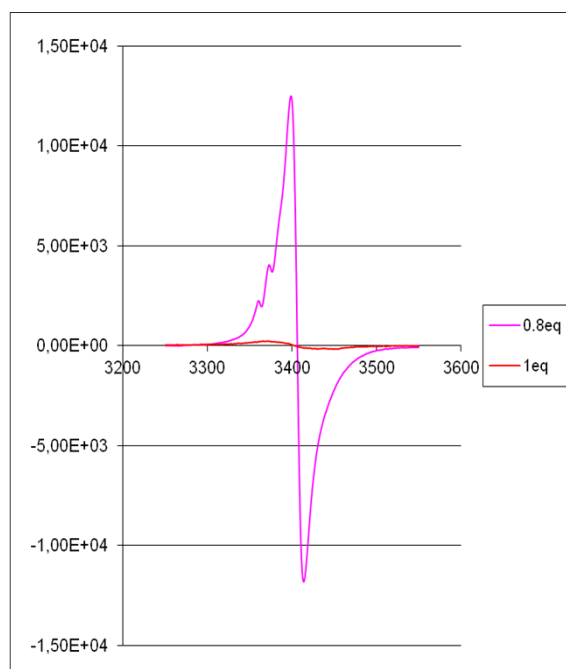
¹³C (125 MHz, C₆D₆)

14.4 (CH₃), 23.1 (CH₂), 26.1 (CH₂), 29.8 (CH₂), 29.9 (CH₂), 30.1 (CH₂), 30.1 (CH₂), 30.4 (CH₂), 35.4 (CH₂), 58.2 (CH₃), 114.9 (CH), 126.4 (CH), 127.9 (CH), 128.7 (CH), 136.8 (C), 155.6 (C).

HRMS (EI) for C₁₈H₂₈O : calc. (m/z) 260.2140 ; found (m/z) 260.2134.

IV. Optimisation studies with Dy

A Schlenk tube was loaded with dichlorotitanocene (Cp_2TiCl_2) (370 mg, 1.5 mmol), dysprosium (1.2 or 1.5 mmol) and THF (5 mL) under an atmosphere of argon. The resulting mixture was stirred vigorously at room temperature until a deep green color appeared. After three hours, the agitation was stopped and the solution was diluted with THF to a concentration of 2 mmol/L. An EPR tube was loaded under argon with 0.5 mL of the solution and measured at 150K.



Comparison of EPR spectra with 1.2 mmol Dy (0.8 equiv., pink line) and 1.5 mmol Dy (1.0 equiv., red line): The concentration of Ti(III) present in solution is 50 times less with 1.0 equiv. Dy compared to 0.8 equiv. Dy.

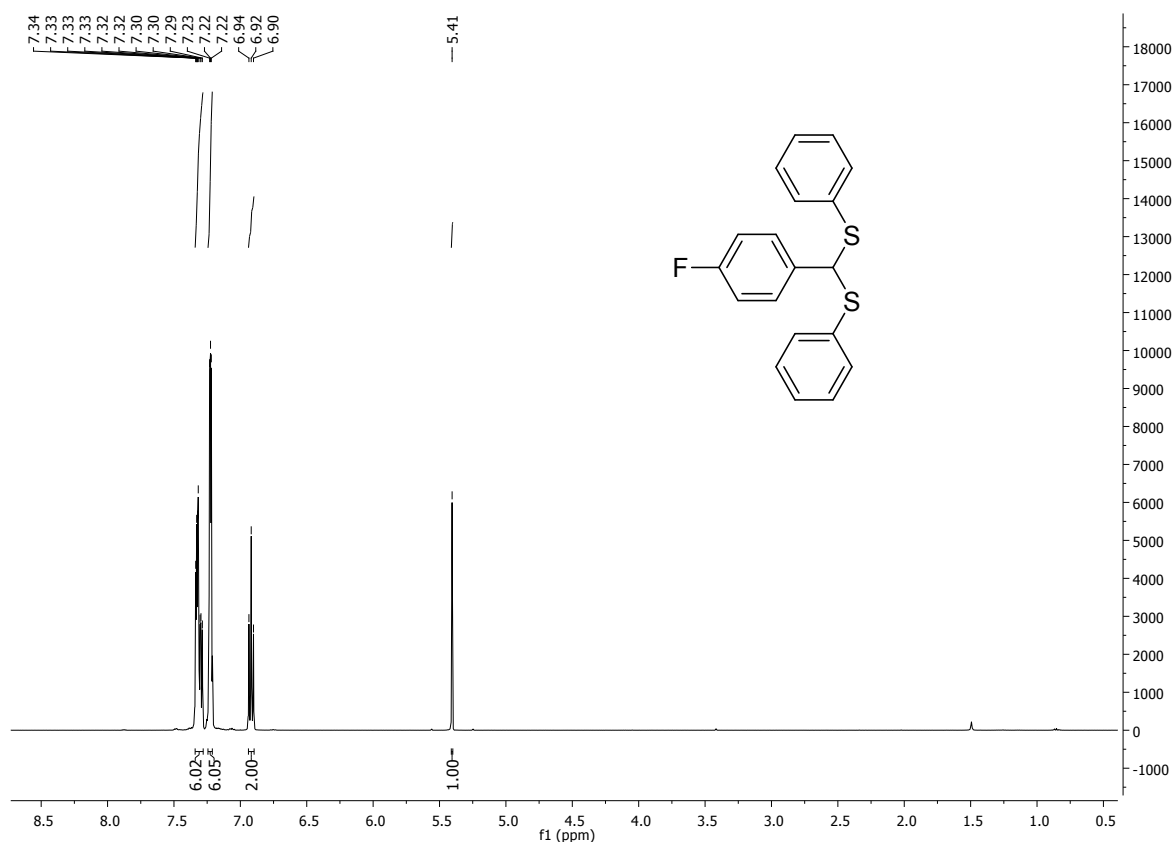
V. References

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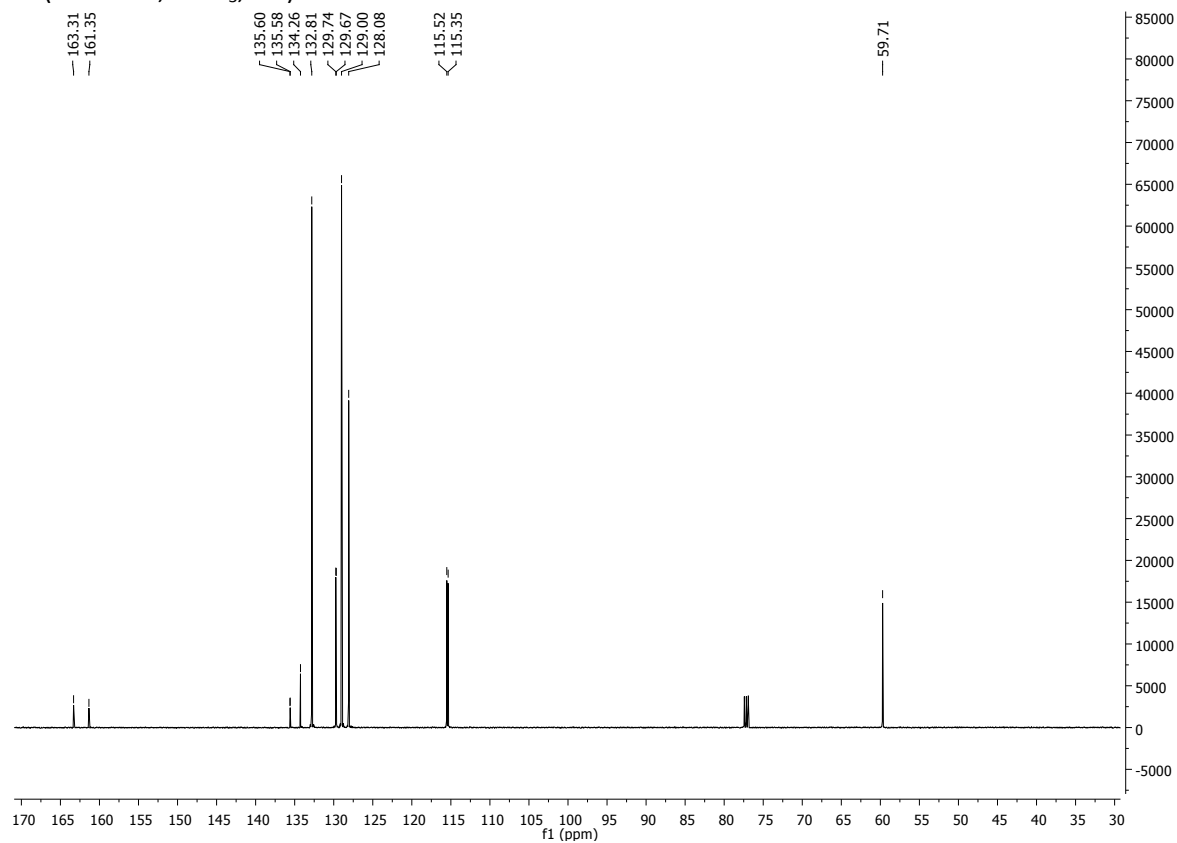
VI. ^1H , ^{13}C and ^{19}F NMR spectra for compounds **3b**, **3e-g**, **5bb**, **5bc**, **5d**, **5e**, **5g**, **5i**.

3b

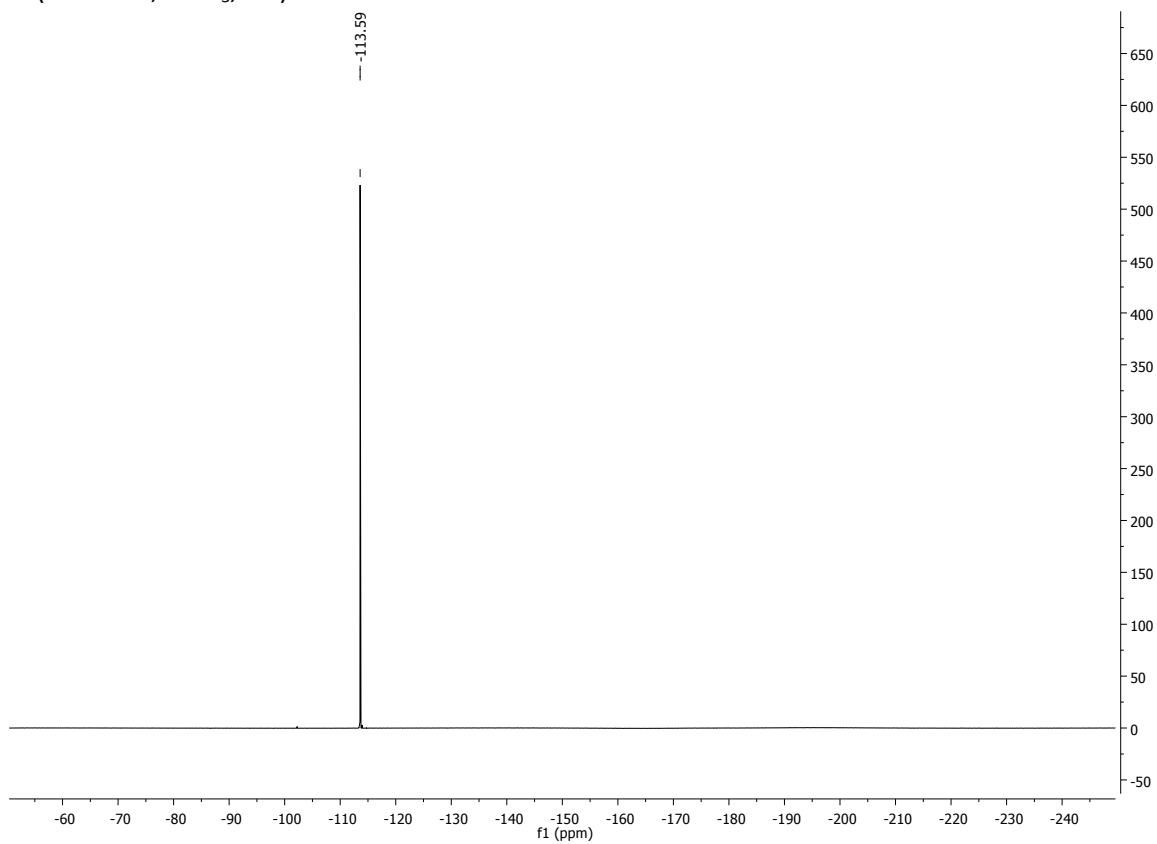
^1H (500 MHz, CDCl_3 , r.t.)



^{13}C (125 MHz, CDCl_3 , r.t.)



^{19}F (470 MHz, CDCl_3 , r.t.)

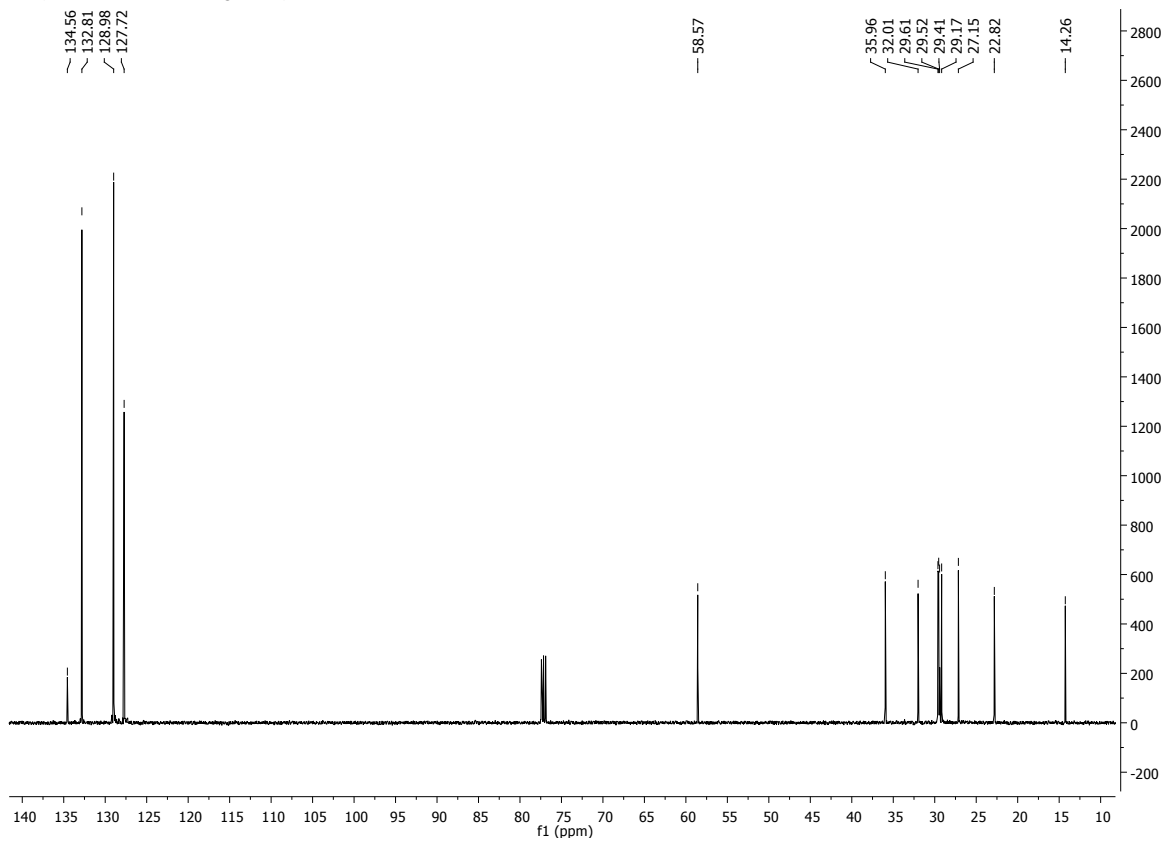


3e

^1H (500 MHz, CDCl_3 , r.t.)



^{13}C (125 MHz, CDCl_3 , r.t.)

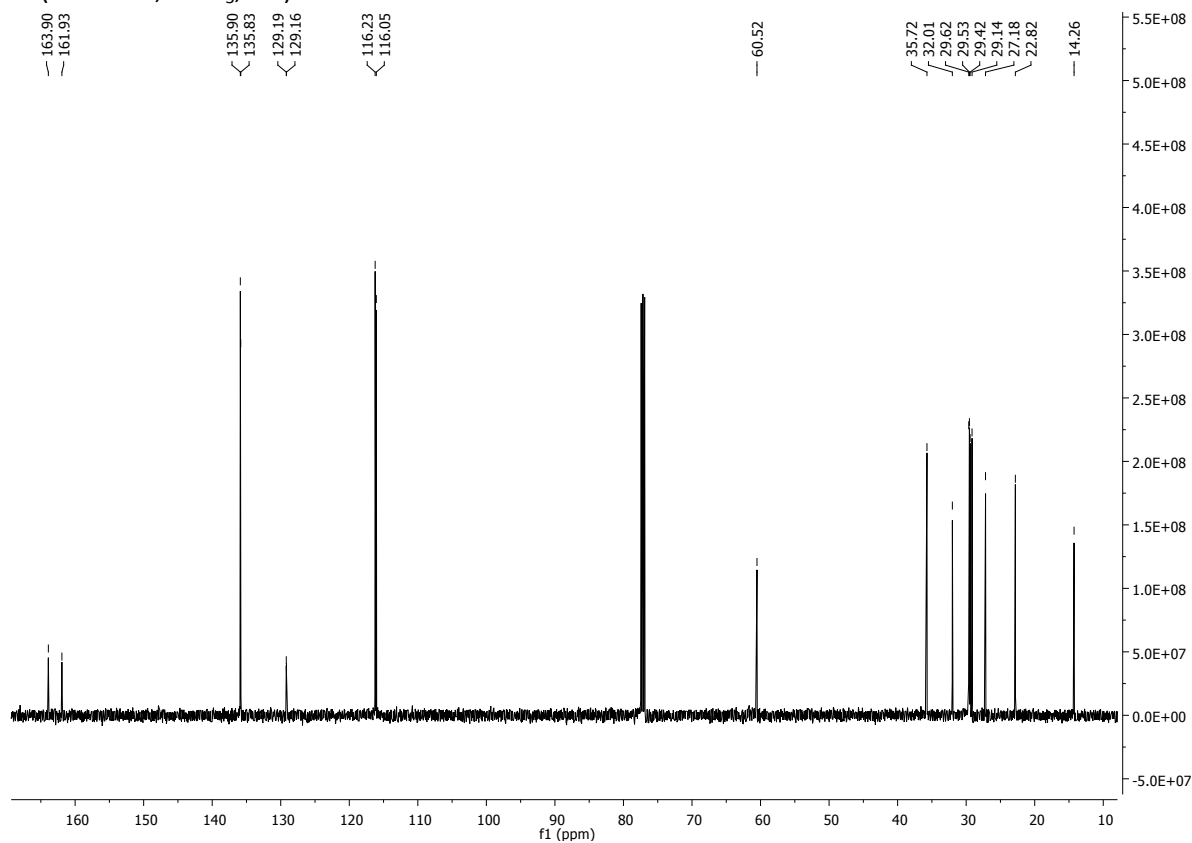


3f

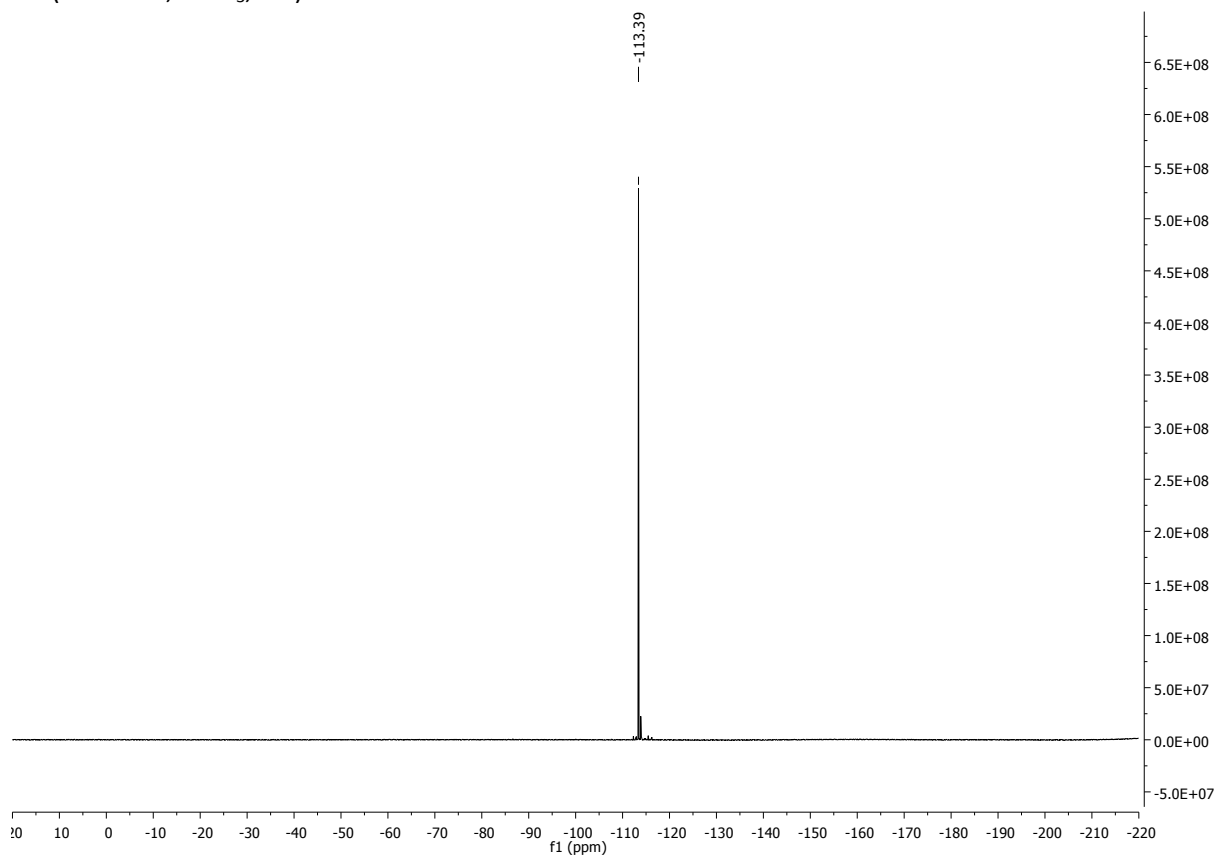
^1H (500 MHz, CDCl_3 , r.t.)



^{13}C (125 MHz, CDCl_3 , r.t.)

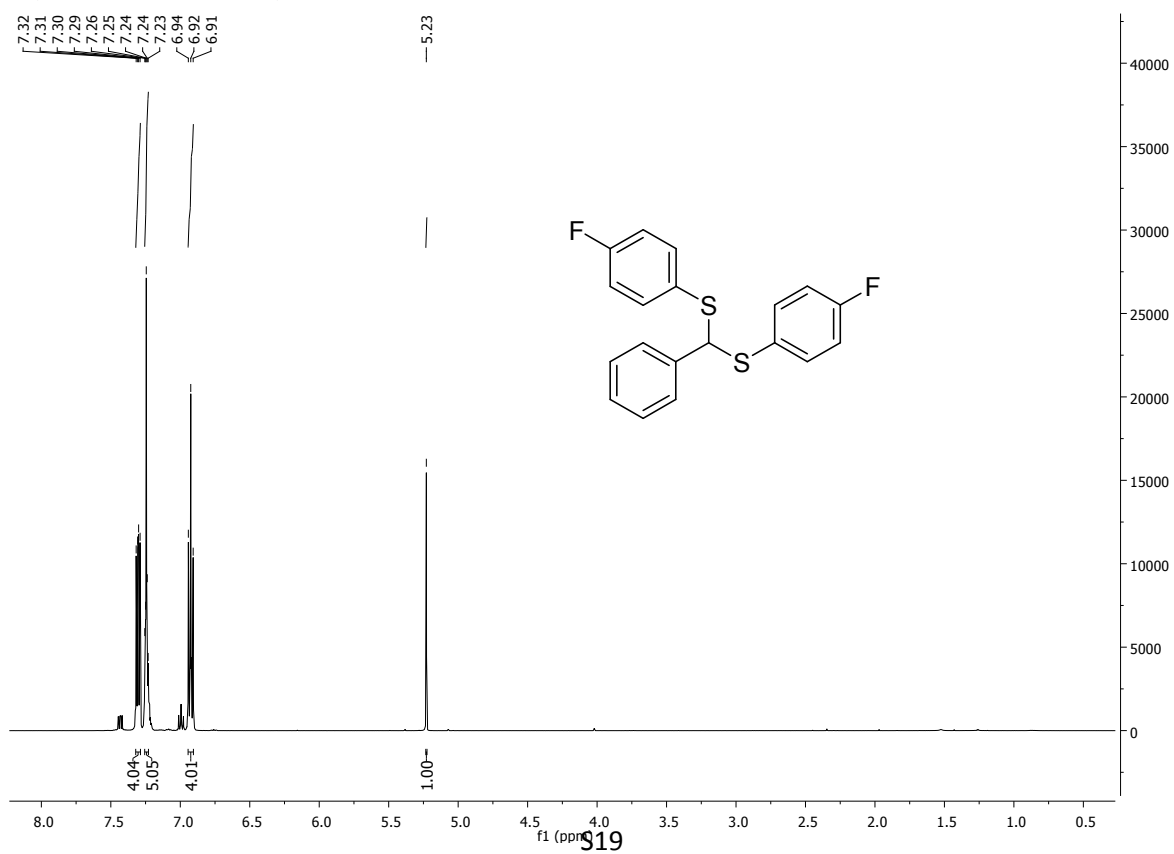


^{19}F (235 MHz, CDCl_3 , r.t.)

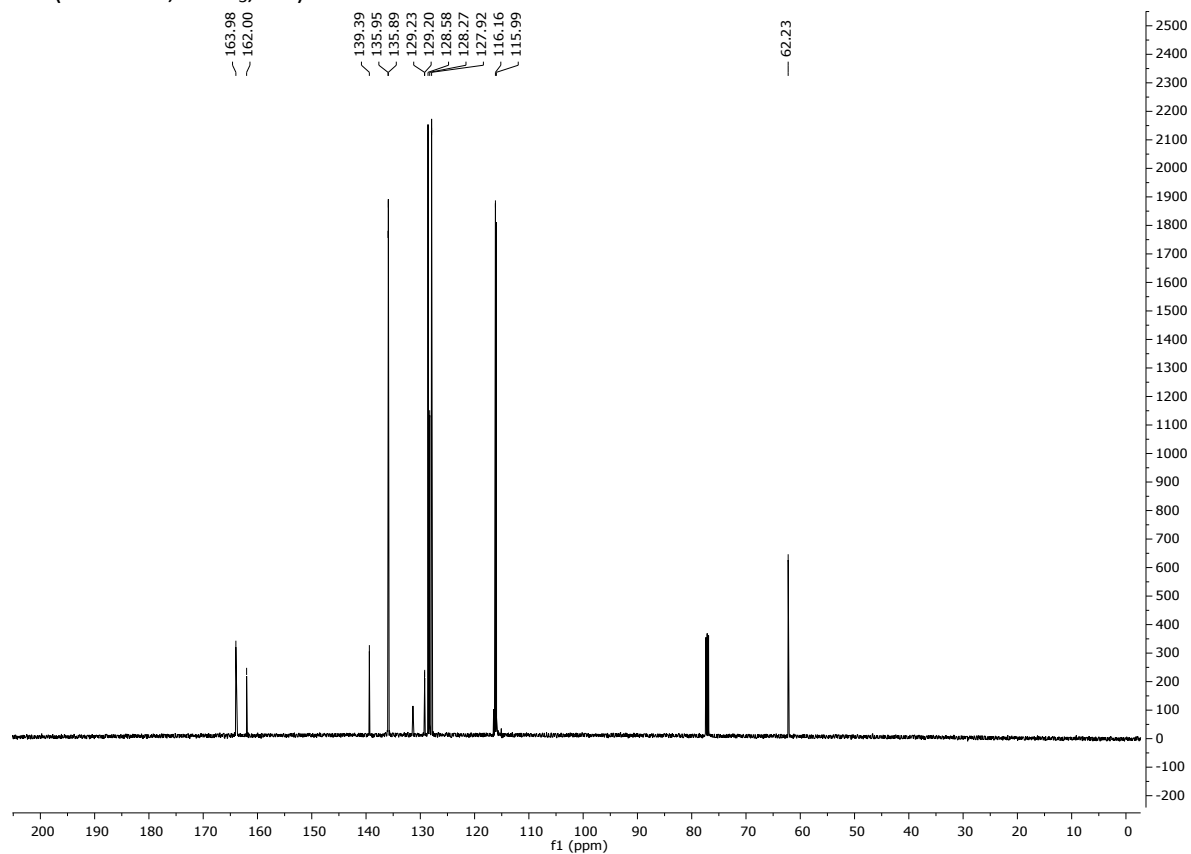


3g

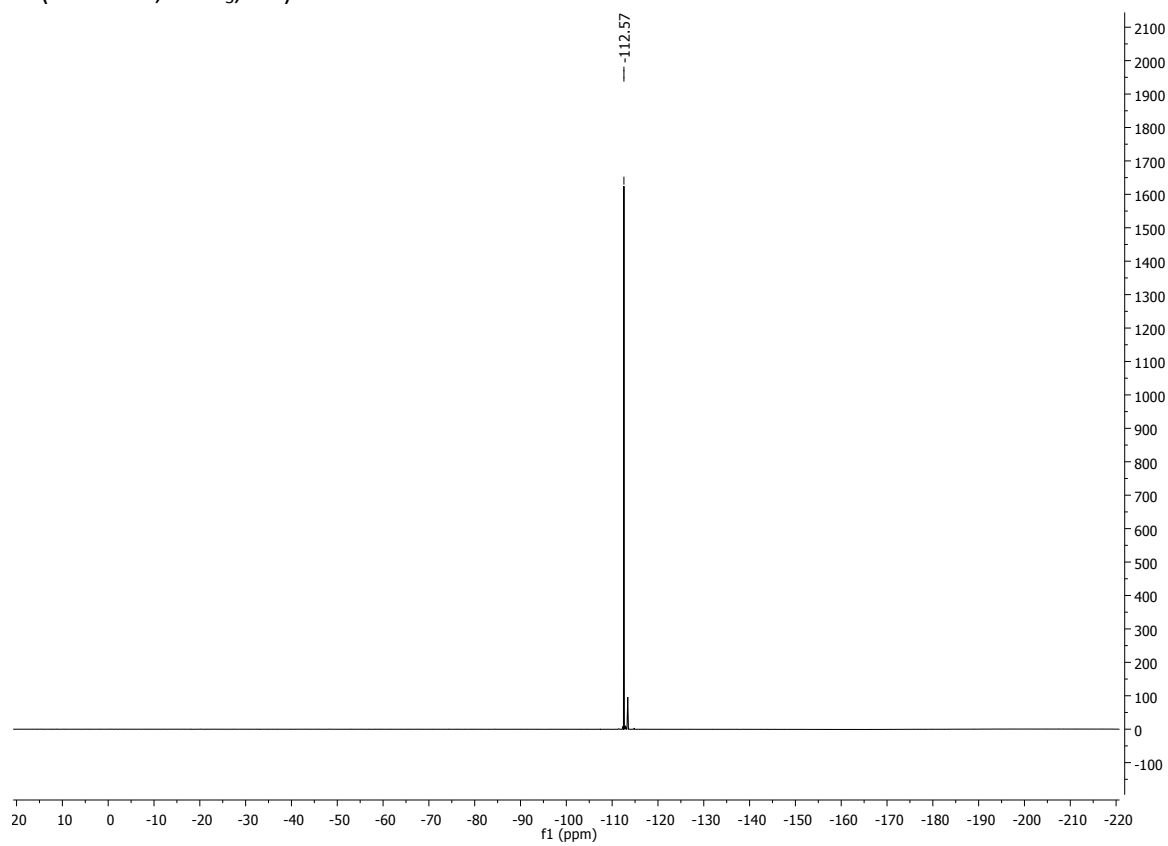
^1H (500 MHz, CDCl_3 , r.t.)



^{13}C (125 MHz, CDCl_3 , r.t.)

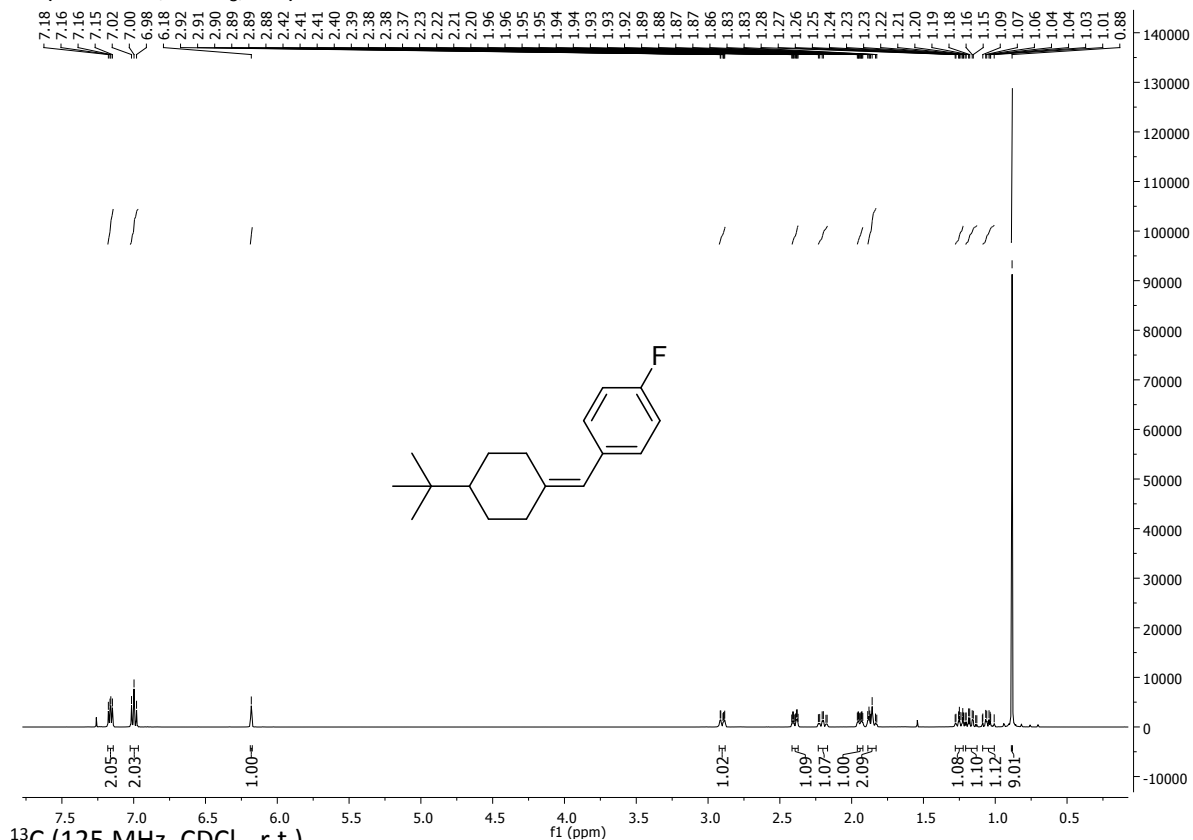


^{19}F (470 MHz, CDCl_3 , r.t.)

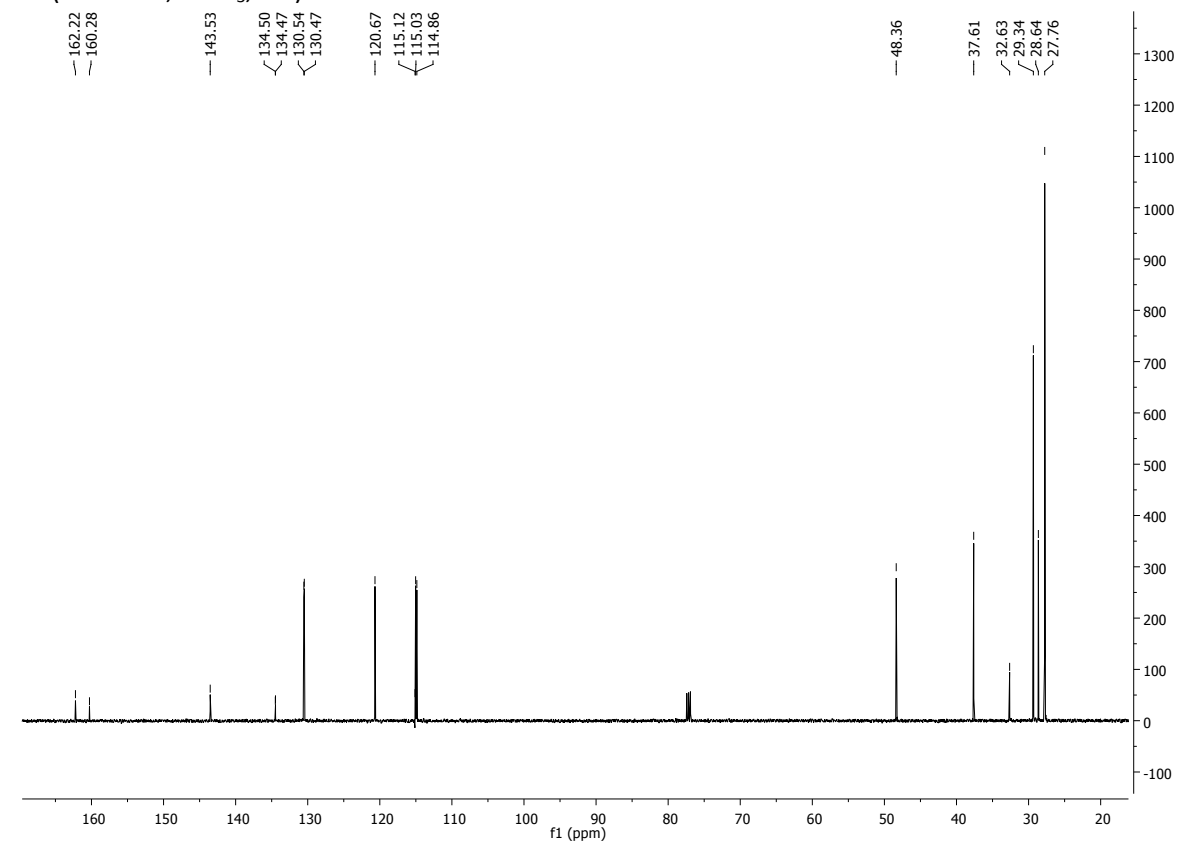


5bb

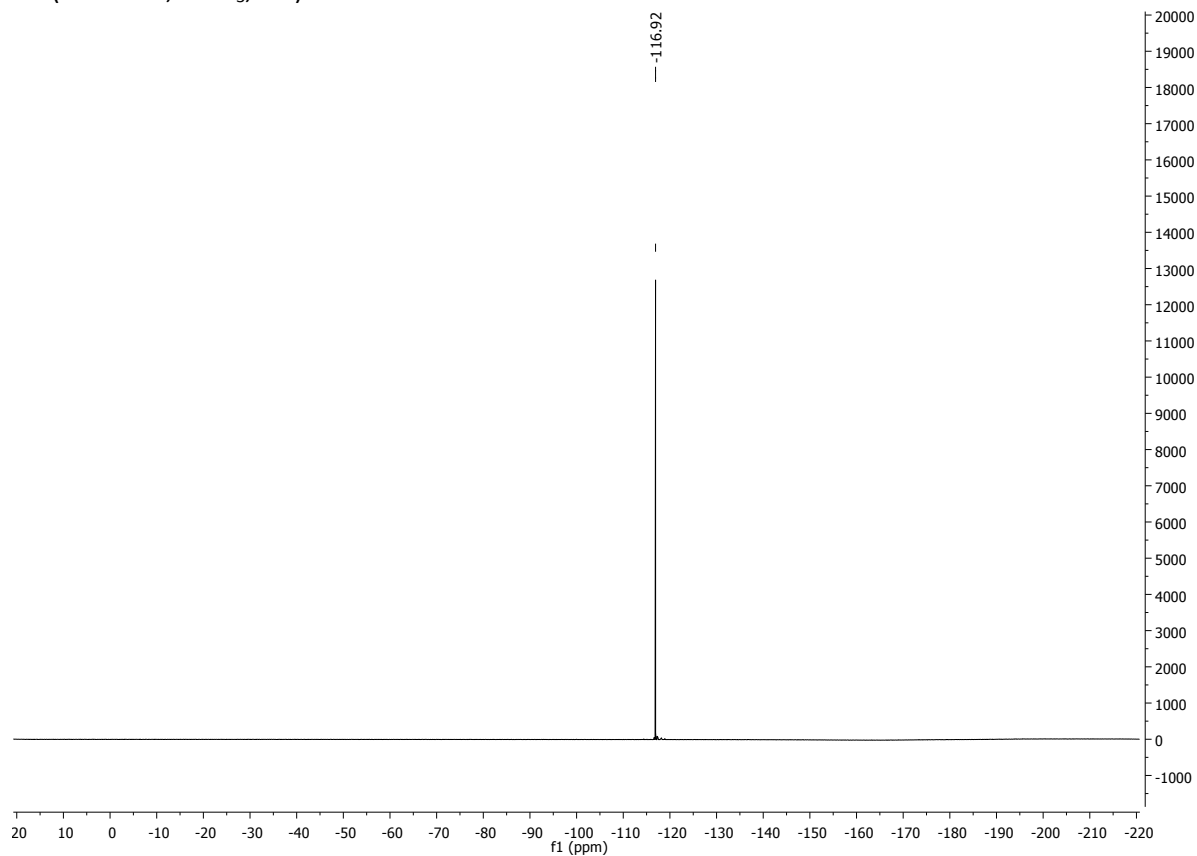
¹H (500 MHz, CDCl₃, r.t.)



¹³C (125 MHz, CDCl₃, r.t.)

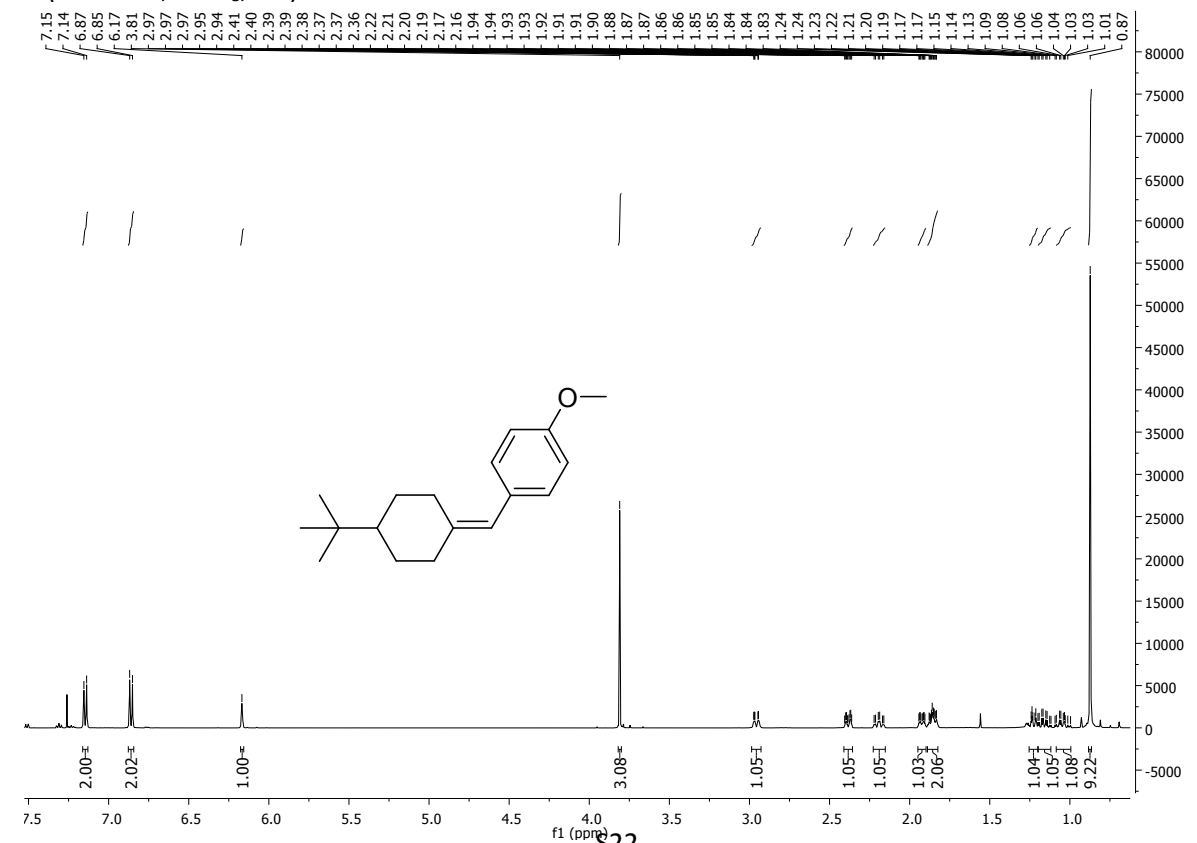


^{19}F (470 MHz, CDCl_3 , r.t.)

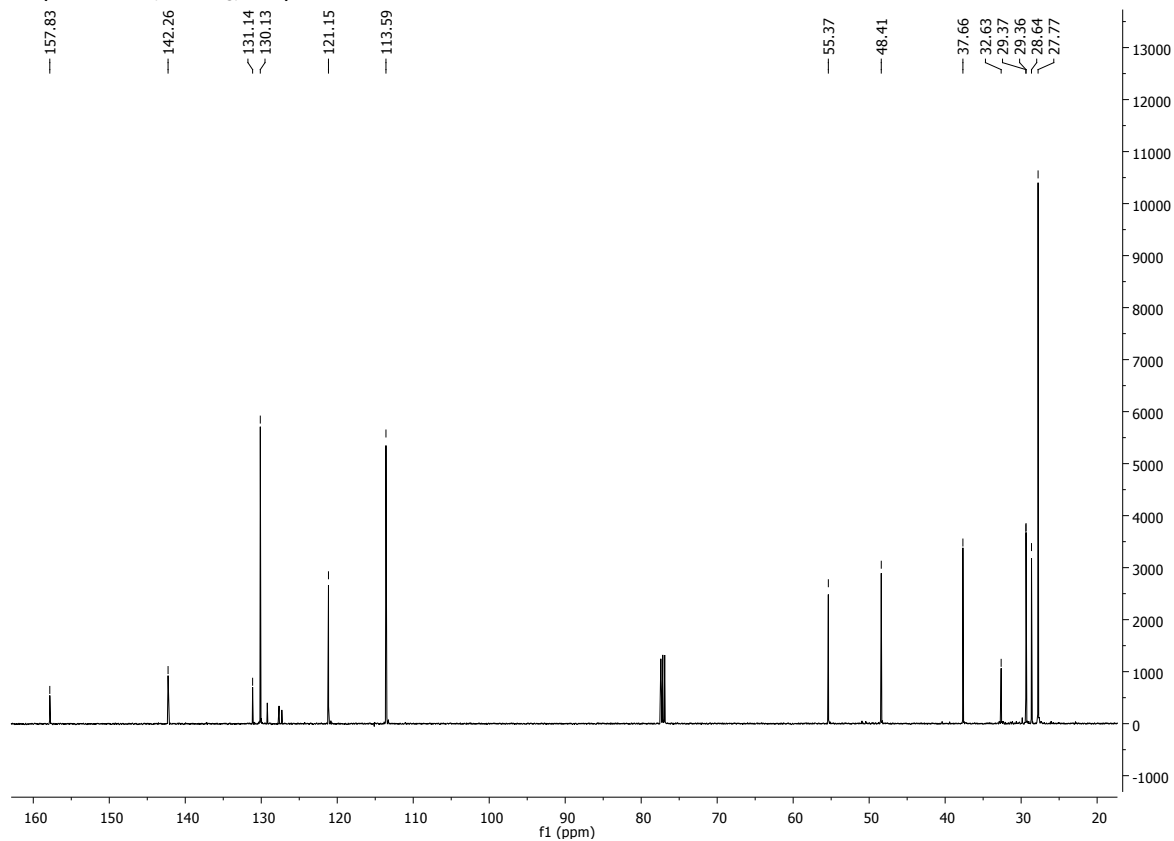


5bc

^1H (500 MHz, CDCl_3 , r.t.)

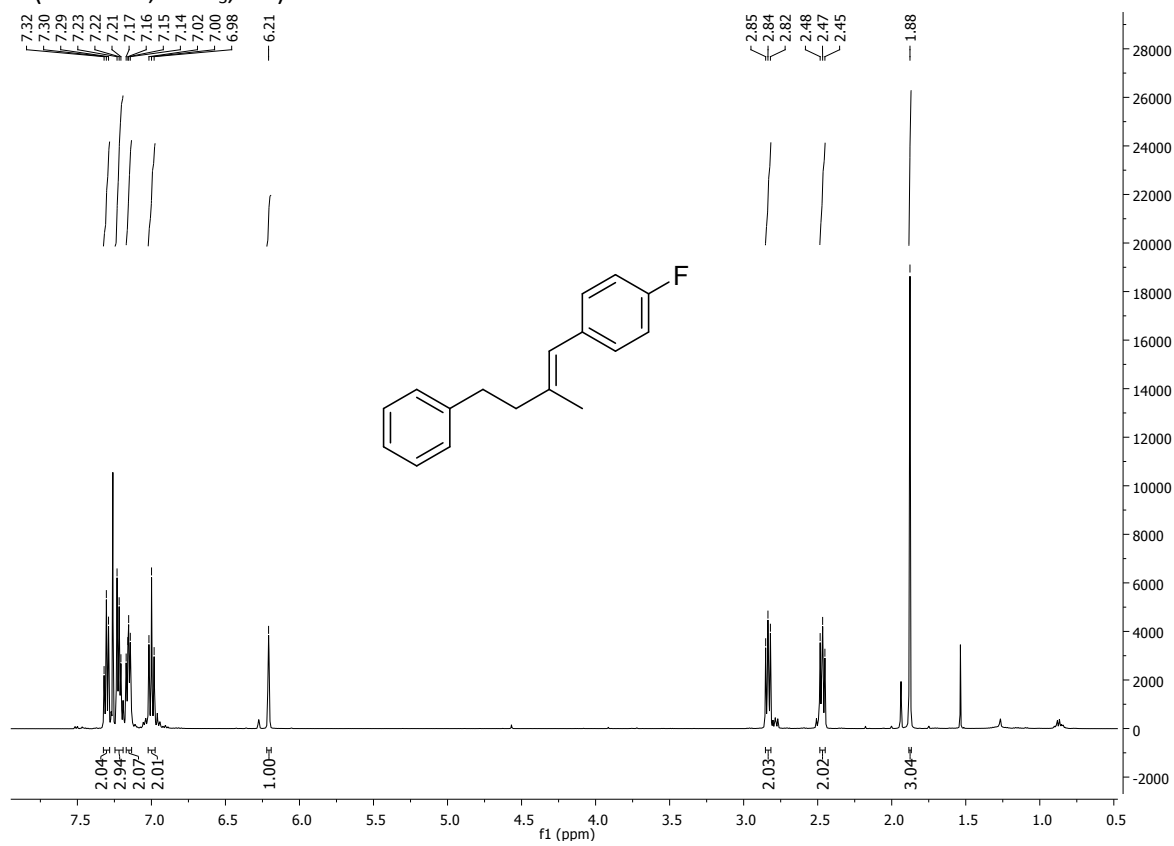


¹³C (125 MHz, CDCl₃, r.t.)



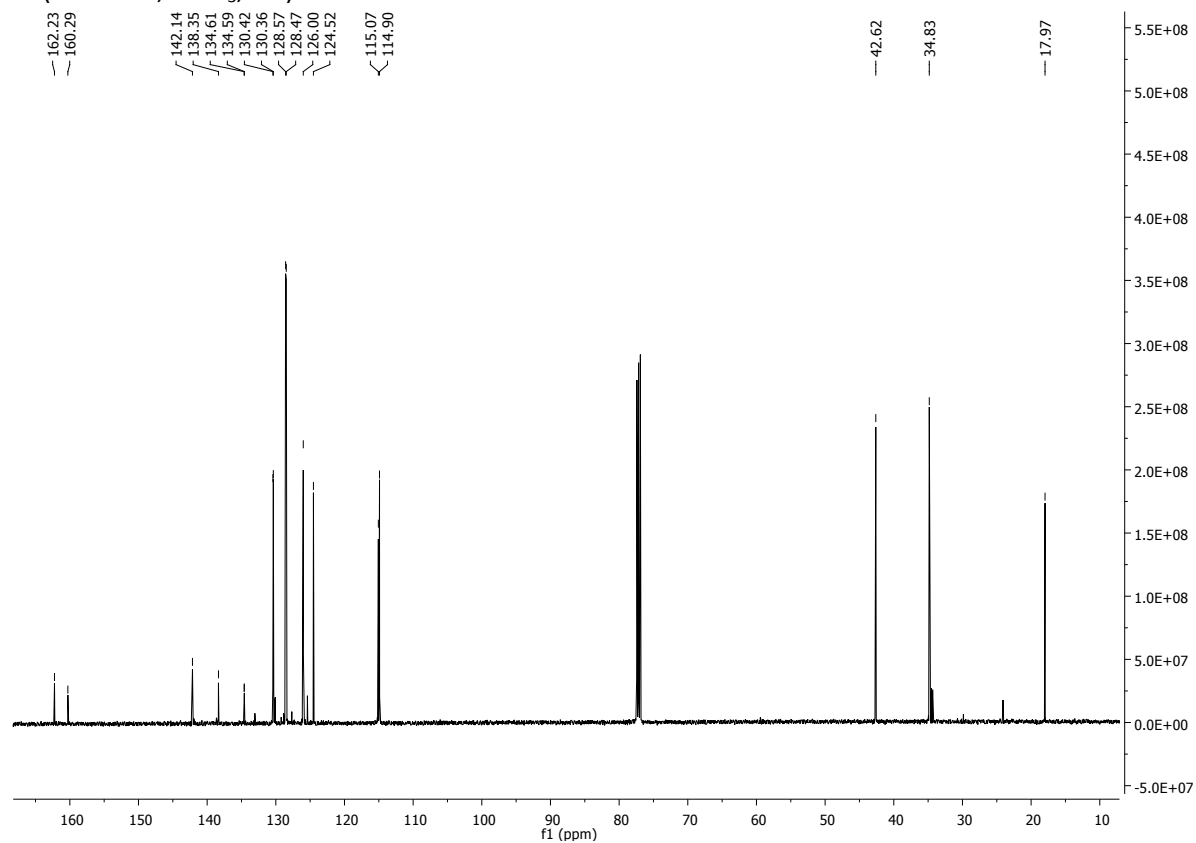
5d

¹H (500 MHz, CDCl₃, r.t.)

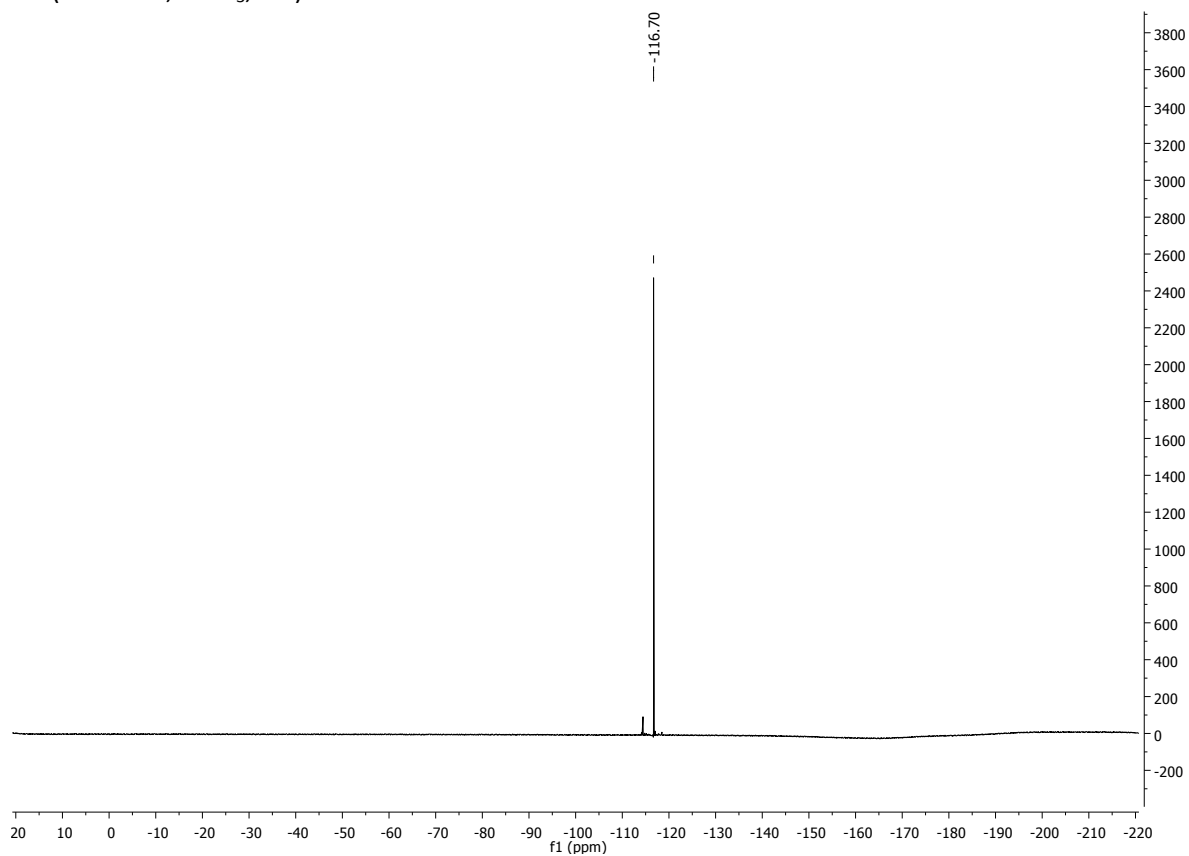


S23

¹³C (125 MHz, CDCl₃, r.t.)

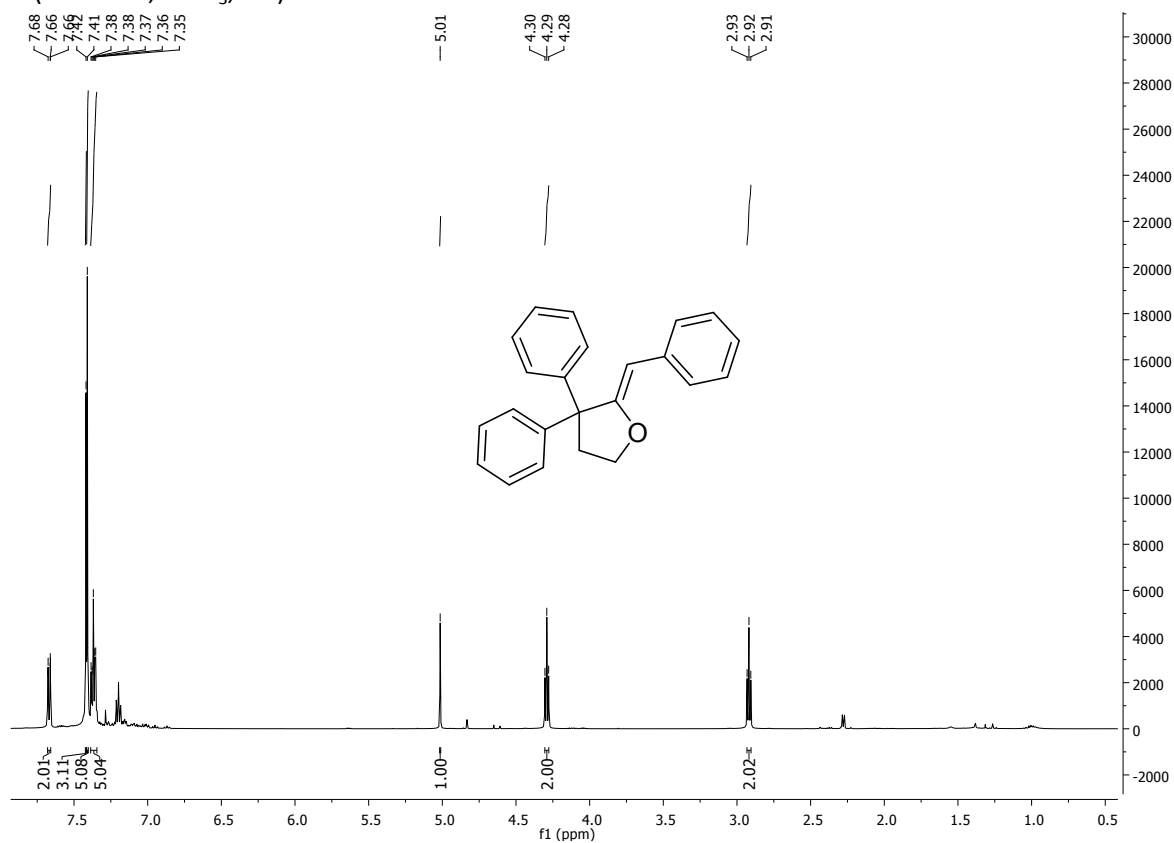


¹⁹F (470 MHz, CDCl₃, r.t.)

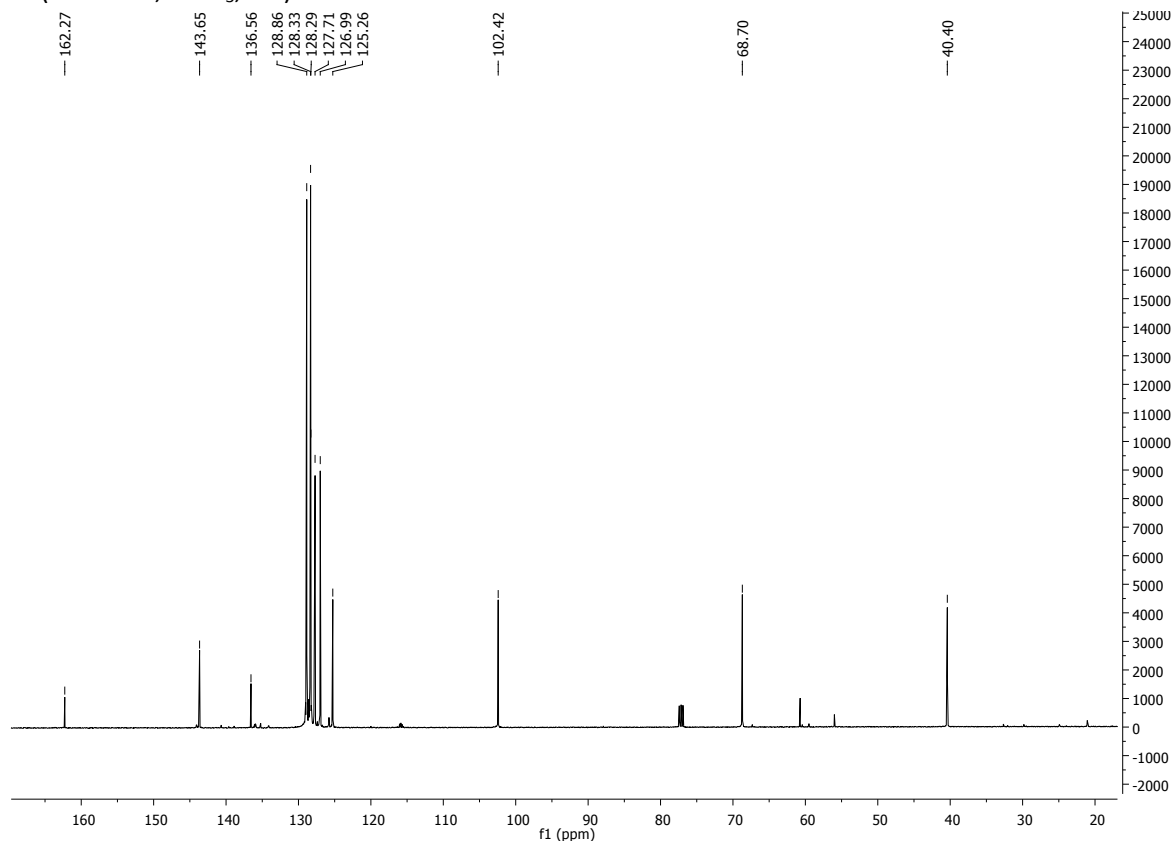


5e

^1H (500 MHz, CDCl_3 , r.t.)

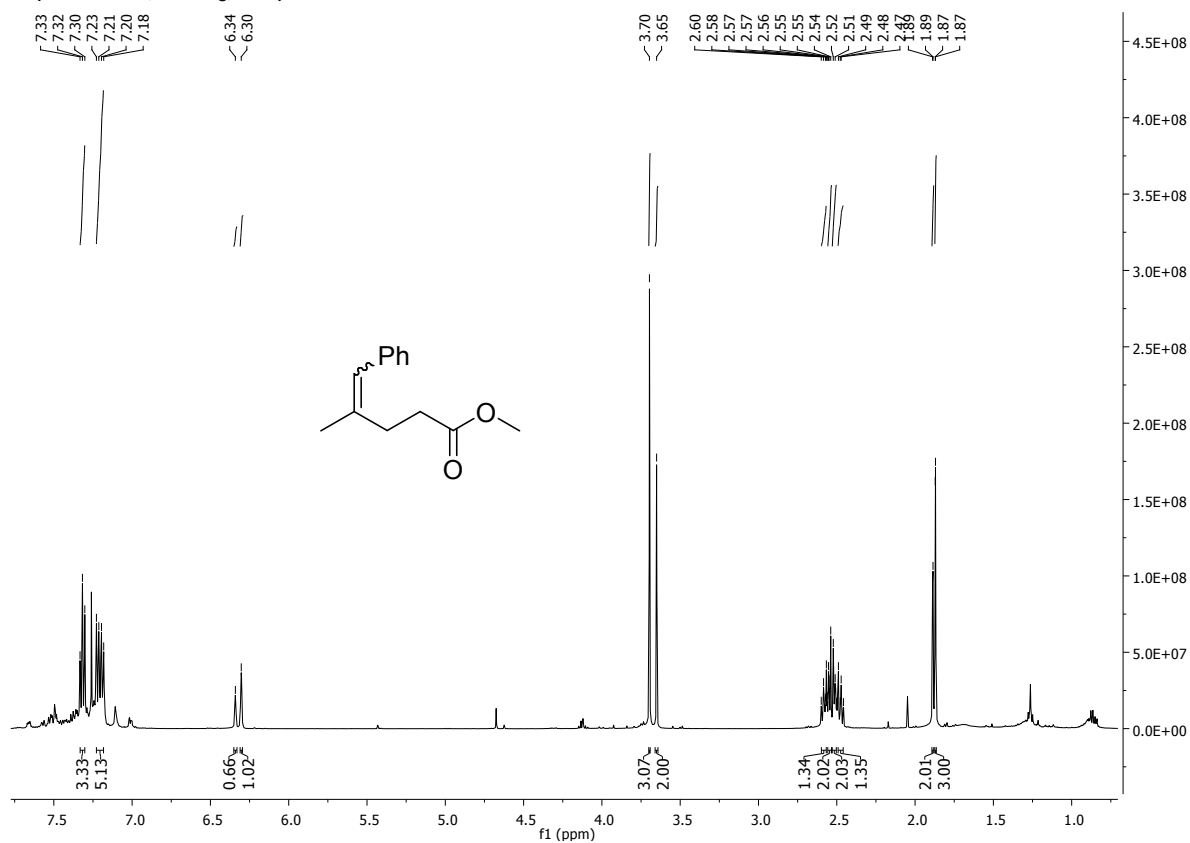


^{13}C (125 MHz, CDCl_3 , r.t.)

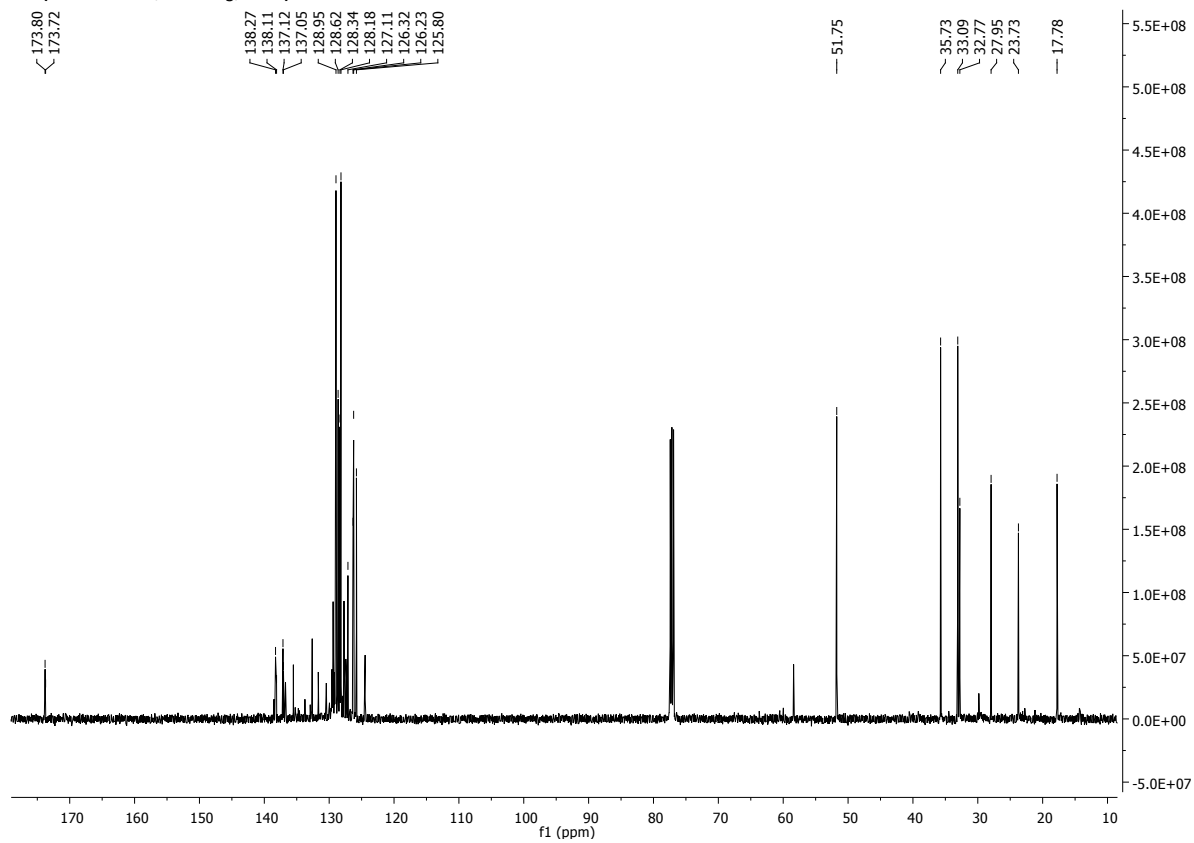


5g

^1H (500 MHz, CDCl_3 , r.t.)

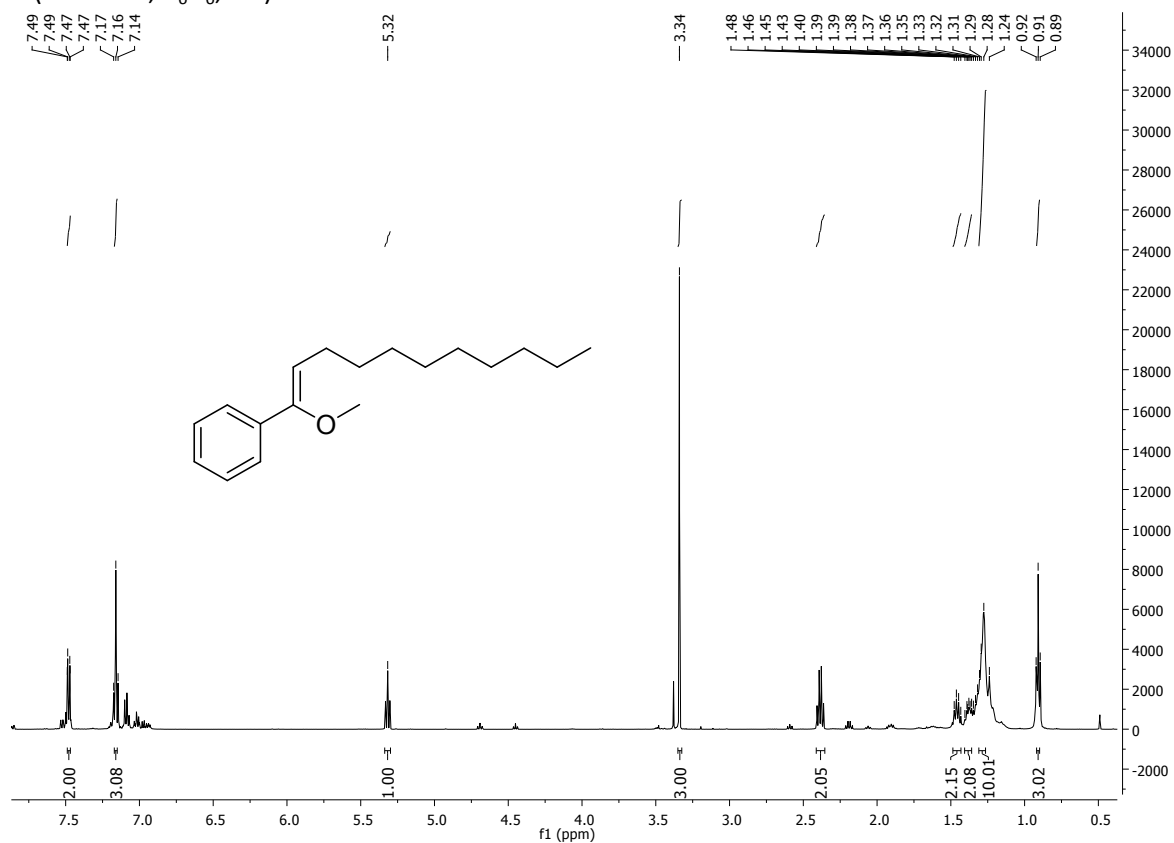


^{13}C (125 MHz, CDCl_3 , r.t.)



5j

^1H (500 MHz, C_6D_6 , r.t.)



^{13}C (125 MHz, C_6D_6 , r.t.)

