Exploring the benzylic *gem*-C(sp3)-Boron-Silicon and Boron-Tin Centers as a Synthetic Platform

Wei W. Chen,[a,b] Nahiane Pipaon Fernández,[a] Marta Díaz Baranda,[a,b] Anton Cunillera,[b] Laura G. Rodríguez,[a,b] Alexandr Shafir,[b,*] and Ana B. Cuenca.[a,*]

[a] Dept. of Organic and Pharmaceutical Chemistry, Institut Químic de Sarrià, URL, via Augusta 390, 08017 Barcelona

[b] Department of Biological Chemistry, IQAC-CSIC, Jordi Girona 20, 08034 Barcelona, Spain

Table of Contents

1. Materials and Methods

Reagents. All commercially acquired reagents were used as received unless indicated otherwise.

Reaction conditions. Most reactions requiring inert atmosphere were conducted under argon atmosphere using standard Schlenk line techniques. When indicated, reactions were conducted in septum-sealed screw-top tubes (Kimble®), so that the Ar atmosphere could be created by applying evacuate/refill cycles *via* a needle coupled to Schlenk line. All other reactions were performed employing standard organic synthesis protocols.

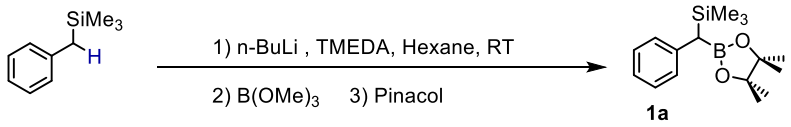
Chromatography. Thin layer chromatography (TLC) was performed using Merck aluminium-backed plates of TLC Silica gel 60 F254; the plates were revealed using UV light at 254 nm or by staining using potassium permanganate. Standard Flash Column chromatography was accomplished using silica gel (60 Å pore size, 230-400 µm mesh size). GC-LRMS measurements were recorded on an Agilent 6890 chromatograph equipped with an Agilent 5973 Network MS detector.

Gas Chromatography coupled to High Resolution Mass Spectrometry. Analyses were carried out at the IQAC Mass Spectrometry Facility, using a Thermo Scientific Trace 1310 Gas Chromatograph equipped with MS/MS Q Exactive GC Orbitrap

Nuclear Magnetic Resonance. Spectroscopic experiments for the characterization of compounds were carried out at the Servicio de Resonancia Magnética Nuclear of the IQAC-CSIC, as well as at the Structural Determination facility of the IQS, in both cases on a Varian Mercury 400 MHz (9.3950 T) instrument (400 MHz for ^{1}H and 101 MHz for ^{13}C). Additional spectra have also been acquired on a Bruker Avance NEO 400 MHz. The ^{1}H and ^{13}C chemical shifts (δ_H) are quoted in parts per million (ppm) and referenced to the appropriate NMR resonance, which for ^{1}H measurements would correspond to the residual *protio* component of the deuterated solvent. The ^{19}F signals are reported relative to $CFCl_3$ (0.00 ppm). The ^{11}B chemical shift are referenced relative to the external $BF_3{\cdot}Et_2O$ resonance at 0.0 ppm. 2D-NMR experiments COSY, HSQC and HMBC were used where necessary in assigning NMR spectra. Spin-spin coupling constants (*J*) are reported in Hertz (Hz).

Other. Infrared spectra were recorded on an Avatar 360 FT-IR spectrophotometer equipped with Smart *i*TR window and are reported in cm^{-1}.

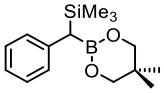
2. Synthesis of geminally substituted bis-metalloid substrates



1a

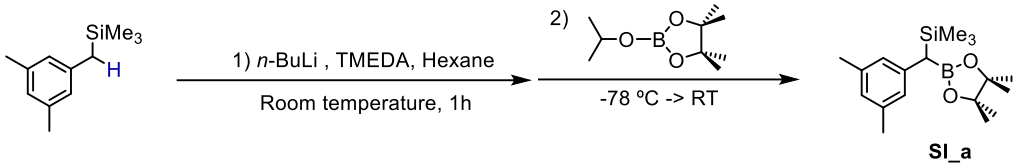
An oven-dried Schlenk tube equipped with a magnetic stirbar was purged with argon, and then charged with benzyltrimethylsilane (3.00 mmol, 493 mg, 0.571 mL), freshly distilled *N*,*N*,*N*',*N*' -tetramethylethylenediamine (TMEDA, 3.00 mmol, 349 mg, 0.45 mL) and dry hexane (3.60 mL). Then, *n*-BuLi (2.5 M in hexane, 1.2 mL, 3.00 mmol) was added dropwise into the tube and the resulting mixture was stirred vigorously at room temperature for 30 min. After that time, the flask was cooled to -78 °C in a dry ice/acetone bath, which led to the precipitation of a yellow solid. Next, while at this temperature, $B(OMe)_3$ (1.0 mL, 9.00 mmol) was added slowly via syringe and the resulting mixture was left to reach ambient temperature slowly during 1h (*inside the dry ice/acetone bath*). Once at RT, the resulting mixture was stirred for an additional 1h. Next, a saturated solution of NH_4Cl (~20 mL) was added and the mixture was stirred for 10 min. The organic layer was collected using a separatory funnel, and the aqueous layer was extracted with dichloromethane (2 x 20 mL). Combined organic phase was dried over $MgSO_4$ and filtered into a round bottom flask. Subsequently, pinacol (12.0 mmol, 1.42 g) was added and the mixture was stirred overnight. The solvent was evaporated and resulting residue purified by column chromatography: silica gel, 50:1 of hexanes/EtOAc (R_f = 0.27). White solid, 689 mg, yield: 79%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.13 (m, 4H), 7.03 (tt, *J* = 6.5, 1.9 Hz, 1H), 1.97 (s, 1H, C<u>H</u>Bpin), 1.26 (s, 6H), 1.24 (s, 6H), 0.00 (s, 9H, TMS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.98, 128.79, 127.95, 123.54, 83.20 (O<u>C</u>$(CH_3)_2$), 25.28 (diast. OC(<u>C</u>$H_3)_2$), 25.07 (diast. OC(<u>C</u>$H_3)_2$), -1.36 (TMS), *<u>C</u>-B was not observed by HSQCAD experiment*. ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.3 ppm. GC-HRMS (EI) *m/z* calcd for $C_{15}H_{24}BO_2Si$ $[M - CH_3]^+$ 275.1633, found: 275.1633.



(**1a'**) In a procedure analogous to that used to prepare the pinacolboronate **1a**, benzylsilane (5.00 mmol, 0.95 mL) was deprotonated using TMEDA (5.00 mmol, 0.74 mL) and *n*-BuLi (2.5M in hexane, 5.00 mmol, 2.0 mL), and then quenched with $B(OMe)_3$ (15.00 mmol, 1.70 mL). Following the initial workup, the intermediate boronic acid was esterified with 2,2-dimethylpropane-1,3-diol (20.00 mmol, 2.08 g) instead of pinacol. Column chromatography: silica gel, hexanes:EtOAc (50:1 -> 20:1); R_f = 0.21 in 50:1 hexanes:EtOAc. White solid, 712 mg. Yield: 52%.

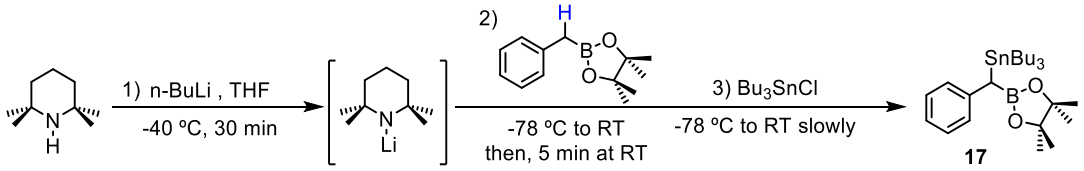
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.13 (m, 4H), 7.06 – 7.01 (m, 1H), 3.62 (s, 4H, 2xOC<u>H</u>$_2$), 1.86 (s, 1H, C<u>H</u>Si), 0.97 (s, 6H, 2xC<u>H</u>$_3$ neop.), 0.00 (s, 9H, TMS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.03, 128.81, 127.88, 123.40, 72.27 (O<u>C</u>H_2), 31.65 (C_q neop.), 30.07 (C-B, from HSQCAD experiment), 22.18 (<u>C</u>H_3 neop.), -1.13 (TMS). ^{11}B NMR (128 MHz, $CDCl_3$): δ 24.62 ppm. GC-HRMS (EI) *m/z* calcd for $C_{15}H_{25}BO_2Si$ $[M - CH_3]^+$ 276.1711, found: 276.1710.



An oven-dried Schlenk tube equipped with a magnetic stirbar was purged with argon, and then charged with (3,5-dimethylbenzyl)trimethylsilane (1.00 mmol, 192 mg), freshly distilled *N*,*N*,*N*',*N*' -tetramethylethylenediamine (TMEDA, 1.20 mmol, 179 µL) and dry hexane (1.2 mL). Then, *n*-BuLi (2.5 M in hexane, 0.48 mL, 1.20 mmol) was added dropwise into the tube and the resulting mixture was stirred vigorously at room temperature for 1h. After that time, the flask was cooled to -78 °C in a dry ice/acetone bath, which led to the precipitation of a yellow solid. Next, while at this temperature, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (372 mg, 408 µL, 2.00 mmol) was added dropwise and the resulting mixture was left to reach ambient temperature slowly during 1h (*inside the dry ice/acetone bath*). Once at RT, the resulting mixture was stirred for an additional 1h. The resulting mixture was diluted with Et_2O (10 mL) and treated with a saturated solution of NH_4Cl (~10 mL). The organic layer was collected using a separation funnel and the aqueous layer was extracted with Et_2O (2 x 10 mL). Combined organic phase was dried over $MgSO_4$, filtered. The solvent was removed under reduced pressure and the resulting residue was purified by column chromatography. Silica gel, hexanes:EtOAc (50:1) ; R_f = 0.18, 50:1 hexanes:EtOAc. Colorless oil, 122 mg, yield: 38%.

The isolated oil contained a small amount of an inseparable byproduct. Notwithstanding, the peaks of the desired product could be extracted from the mixture.

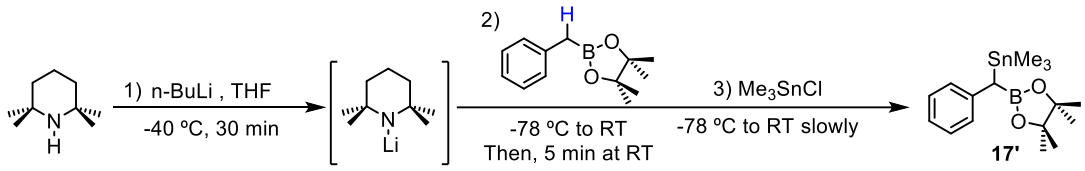
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (d, *J* = 1.6 Hz, 2H), 6.69 (s, 1H), 2.26 (s, 6H, 2xMe), 1.89 (s, 1H, C<u>H</u>Bpin), 1.26 (s, 6H, C(C<u>H</u>$_3$)$_2$), 1.24 (s, 6H, C(C<u>H</u>$_3$)$_2$), 0.00 (s, 9H, TMS). GC-LRMS (EI) *m/z* calcd for $C_{18}H_{31}BO_2Si$ $[M]^{+\cdot}$ 318, found: 318.



An oven-dried Schlenk tube equipped with a magnetic stirbar was charged with 2,2,6,6-tetramethylpiperidine (5.00 mmol, 706 mg, 0.844 ml) followed by THF (anh., 10.0 mL) under argon atmosphere. Subsequently, the flask was immersed in a dry ice/acetone bath with temperature adjusted to -40 °C. The solution was then treated with *n*-BuLi (2.5 M in hexane, 2.1 mL, 5.00 mmol) and the resulting mixture was stirred vigorously at -40 °C for 30 min. After that time, the flask was further cooled to -78 °C prior to the addition of benzyl boronate pinacol ester (5.00 mmol, 1.091 g, 1.11 mL,). At this point, the cold bath was removed and the resulting mixture was brought to room temperature and stirred at that temperature for 5 min. Afterwards, the flask was cooled again to -78 °C and Bu_3SnCl (2.44 mL, 9.00 mmol) was added dropwise. The resulting mixture was allowed to reach RT slowly during 2h (*inside the dry ice/acetone bath*). Once at RT, the resulting mixture was stirred for an additional 1h. Next, a saturated solution of Na_2CO_3 (~20 mL) was added and the mixture was stirred for 10 min. The organic layer was collected using a separation funnel and the aqueous layer was extracted with Et_2O (3 x 20 mL).

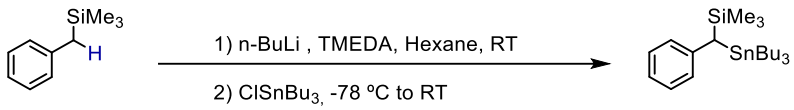
Combined organic phase was dried over $MgSO_4$, filtered. The solvent was removed under reduced pressure and the resulting residue was purified by column chromatography. Silica gel, hexanes:EtOAc (50:1 -> 20:1) ; R_f = 0.24 in 50:1 hexanes:EtOAc. Colorless oil, 2.52 g, yield: 99%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.11 (m, 4H), 6.99 – 6.89 (m, 1H), 2.31 (s, 1H, C<u>H</u>Bpin), 1.49 – 1.17 (m, 24H, 4 x Me + 6 x CH_2), 0.95 – 0.82 (m, 15H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.42, 128.07, 127.71, 122.53, 82.79 (O<u>C</u>$(CH_3)_2$), 29.00, 27.52, 25.32, 25.17, 19.78 (C-B, from HSQCAD experiment), 13.78, 10.32. ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.81 ppm. GC-HRMS (EI) *m/z* calcd for $C_{21}H_{36}BO_2Sn$ $[M - Bu]^+$ 451.1825, found: 451.1824.



An oven-dried Schlenk tube equipped with a magnetic stirbar was added 2,2,6,6-tetramethylpiperidine (3.00 mmol, 0.51 ml) followed by THF (anh., 6.0 mL) under argon atmosphere. Subsequently, the flask was immersed in a dry ice/acetone bath with temperature adjusted to -40 °C. The solution was then treated with *n*-BuLi (2.5 M in hexane, 1.26 mL, 3.15 mmol) and the resulting mixture was stirred vigorously at -40 °C for 30 min. After that time, the flask was further cooled to -78 °C prior to the addition of benzyl boronate pinacol ester (0.67 mL, 3.00 mmol). At this point, the cold bath was removed and the resulting mixture was brought to room temperature and stirred at that temperature for 5 min. Afterwards, the flask was cooled again to -78 °C and a solution of Bu_3SnCl (717 mg, 3.60 mmol) in 1.0 ml of dry THF was added dropwise. The resulting mixture was allowed to reach RT slowly during 2h (*inside the dry ice/acetone bath*). Once at RT, the resulting mixture was stirred for an additional 1h. Next, a saturated solution of NH_4Cl (~10 mL) was added and the mixture was stirred for 10 min. The organic layer was collected using a separation funnel and the aqueous layer was extracted with Et_2O (3 x 15 mL). Combined organic phase was dried over $MgSO_4$, filtered. The solvent was removed under reduced pressure and the resulting residue was purified by column chromatography. Silica gel, hexanes:EtOAc (50:1) ; R_f = 0.18, 50:1 hexanes:EtOAc. White solid, 647 mg, yield: 57%.

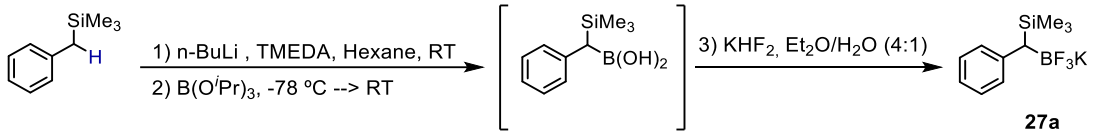
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.14 (m, 4H), 7.01 – 6.93 (m, 1H), 2.28 (s, 1H, C<u>H</u>Bpin), 1.27 (s, 6H, C(C<u>H</u>$_3)_2$), 1.25 (s, 6H, C(C<u>H</u>$_3)_2$), 0.09 (s, 9H, $SnMe_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.96, 128.16, 127.53, 122.76, 82.90 (O<u>C</u>$(CH_3)_2$), 20.91 (C_{sp3}-B, from HSQCAD experiment), 25.24 (pin Me), 25.17 (pin Me'), -8.93 ($SnMe_3$). ^{11}B NMR (128 MHz, $CDCl_3$): δ 32.98 ppm. GC-LRMS (EI) *m/z* calcd for $C_{16}H_{27}BO_2Sn$ $[M]^{+\cdot}$ 382, found: 382.



An oven-dried Schlenk tube equipped with a magnetic stirbar was purged with argon, and then charged with benzyltrimethylsilane (3.00 mmol, 493 mg, 0.571 mL), freshly distilled *N*,*N*,*N*',*N*' -tetramethylethylenediamine (TMEDA, 3.15 mmol, 0.47 mL) and dry hexane (3.60 mL). Then, *n*-BuLi (2.5 M in hexane, 1.26 mL, 3.15 mmol) was added dropwise into the tube and the resulting mixture was stirred vigorously at room temperature for 30 min. After that time, the flask was

cooled to -78 °C in a dry ice/acetone bath, which led to the precipitation of a yellow solid. Next, while at this temperature, Bu_3SnCl (2.44 mL, 9.00 mmol) was added slowly and the resulting mixture was left to reach ambient temperature slowly during 1h (*inside the dry ice/acetone bath*). Once at RT, the resulting mixture was stirred for an additional 1h. Next, a saturated solution of Na_2CO_3 (~10 mL) was added and the mixture was stirred for 10 min. The organic layer was collected using a separatory funnel, and the aqueous layer was extracted with Et_2O (3 x 15 mL). Combined organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel, eluting with hexanes (R_f = 0.94). Colorless oil, 1.11 g, yield: 82%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.09 (m, 2H), 6.96 – 6.92 (m, 1H), 6.91 – 6.87 (m, 2H), 1.83 (s, 1H, C<u>H</u>Si), 1.41 – 1.20 (m, 12H), 0.88 – 0.79 (m, 15H), 0.02 (s, 9H, TMS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.37, 128.30, 128.19, 122.62, 29.20 (<u>C</u>H$_2$), 27.57 (<u>C</u>H$_2$), 24.48 (<u>C</u>HSn), 13.77 (-CH$_2$<u>C</u>H$_3$), 10.77 (<u>C</u>H$_2$Sn), 0.25 (TMS). GC-HRMS (EI) *m/z* calcd for $C_{18}H_{33}SiSn$ [M – Bu]$^+$ 397.1368, found: 397.1365.



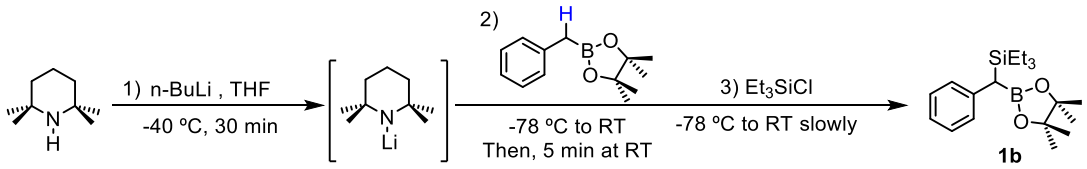
27a

An oven-dried Schlenk tube equipped with a magnetic stirbar was purged with argon, and then charged with benzyltrimethylsilane (10.0 mmol, 1.643 g, 1.90 mL), recently distilled *N*,*N*,*N*',*N*' -tetramethylethylenediamine (TMEDA, 10.5 mmol, 1.56 mL) and dry hexane (12.0 mL). Then, *n*-BuLi (2.5 M in hexane, 4.2 mL, 10.5 mmol) was added dropwise into the tube and the resulting mixture was stirred vigorously at room temperature for 30 min. After that time, the flask was cooled to -78 °C in a dry ice/acetone bath, which led to the precipitation of a yellow solid. Next, while at this temperature, $B(O^iPr)_3$ (40.0 mmol, 9.2 mL,) was added slowly and the resulting mixture was left to reach ambient temperature slowly during 2h (*inside the dry ice/acetone bath*). Once at RT, the resulting mixture was stirred for an additional 3h. Next, a saturated solution of NH_4Cl (~40 mL) was added and the mixture stirred for 10 min. The organic layer was collected using a separation funnel, and the aqueous layer was extracted with Et_2O (3 x 15 mL). Combined organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting residue containing the boronic acid intermediate (as free acid or anhydride) was dissolved in a mixture of 4:1 Et_2O/H_2O (25 mL) and cooled at 0 °C in an ice/water bath. Subsequently, solid KHF_2 (1.88 g, 24.0 mmol) was added in one portion and the mixture was stirred vigorously for 2h at 0 °C. The resulting white precipitated was filtered, washed with pentane (3 x 15 mL) and dried under high vacuum to afford a first crop of the product, 1.04 g.

A second crop was isolated from the mother liquors. Pentane (30 mL) was added to the filtrate leading to the precipitation of an addition portion of a white solid, which was isolated by filtration and washed with pentane (2 x 20 mL). Then, this 2nd crop of the white solid was dissolved in dry acetone (~6 mL) and transferred into a flask, concentrated under reduced pressure, and dried under high vacuum for 1h in order to remove H_2O, thus reducing the solubility of potential KHF_2 impurities. The white residue was again dissolved in dry acetone (2-3 mL) and decanted with the help of a Pasteur pipette. Solvent was evaporated under reduced

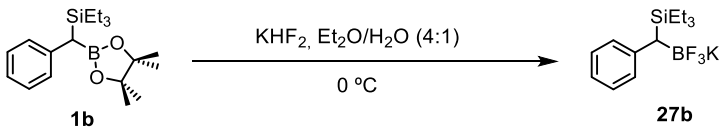
pressure and the resulting white solid was washed with pentane (2 x 15 mL) affording a white crystalline solid that was dried under high vacuum, 1.10 g of **27a**. Between the two crops, the reaction yielded 2.14 g of the product as a white crystalline solid, 79% yield.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.07 (pseudo dd, *J* = 8.2, 1.5 Hz, 2H), 7.04 – 6.98 (m, 2H), 6.85 – 6.79 (m, 1H), 1.26 (br q, *J* = 7.1 Hz, 1H, C<u>H</u>BF$_3$K), -0.11 (pseudo d, *J* = 0.5 Hz, 9H, TMS). ^{13}C NMR (126 MHz, Acetone-d_6) δ 149.56 (pseudo q, apparent *J* = 2.5 Hz), 129.85, 127.75, 122.10, -0.21 (pseudo d, *J* = 1.1 Hz). ^{19}F NMR (376 MHz, Acetone-d_6) δ -133.56 – -137.54 (isotopomeric pattern). ^{11}B NMR (128 MHz, Acetone-d_6): δ 1.18 (pseudo q, apparent *J* = 71.2 Hz).



An oven-dried Schlenk tube equipped with a magnetic stirbar was added 2,2,6,6-tetramethylpiperidine (2.10 mmol, 0.35 ml) followed by THF (anh., 4.0 mL) under argon atmosphere. Subsequently, the flask was immersed in a dry ice/acetone bath with temperature adjusted to -40 °C. The solution was then treated with *n*-BuLi (2.5 M in hexane, 0.84 mL, 2.10 mmol) and the resulting mixture was stirred vigorously at -40 °C for 30 min. After that time, the flask was further cooled to -78 °C prior to the addition of benzyl boronate pinacol ester (0.45 mL, 2.00 mmol). At this point, the cold bath was removed and the resulting mixture was brought to room temperature and stirred at that temperature for 5 min. Afterwards, the flask was cooled again to -78 °C and Et_3SiCl (0.41 mL, 2.40 mmol) was added dropwise. The resulting mixture was allowed to reach RT slowly during 1h (*inside the dry ice/acetone bath*). Once at RT, the resulting mixture was stirred for an additional 1h. Next, a saturated solution of NH_4Cl (~10 mL) was added and the mixture was stirred for 10 min. The organic layer was collected using a separation funnel and the aqueous layer was extracted with Et_2O (3 x 10 mL). Combined organic phase was dried over $MgSO_4$, filtered. The solvent was removed under reduced pressure and the resulting residue was purified by column chromatography. Silica gel, hexanes:EtOAc (50:1 -> 20:1) ; R_f = 0.33 in 50:1 hexanes:EtOAc. Pale yellow oil, 558 mg, yield: 84%.

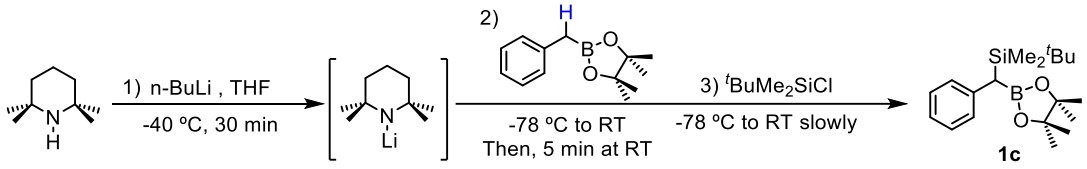
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.15 (m, 4H), 7.07 – 6.99 (m, 1H), 2.08 (s, 1H, C<u>H</u>Bpin), 1.26 (s, 6H, diast. Bpin), 1.23 (s, 6H, diast. Bpin), 0.91 (t, *J* = 7.9 Hz, 9H), 0.60 – 0.50 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.99, 128.98, 127.93, 123.48, 83.16 (O<u>C</u>(CH$_3$)$_2$), 25.37, 24.96, 21.82 (C-B, from HSQCAD experiment), 7.58, 3.54. ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.17 ppm. GC-LRMS (EI) *m/z* calcd for $C_{18}H_{30}BO_2Si$ $[M - Me]^+$ 317, found: 317.



A vial equipped with a magnetic stirbar was added the benzyltriethylsilyl boronate ester **x** (233 mg, 0.70 mmol) followed by a mixture of 4:1 Et_2O/H_2O (1.75 mL) and cooled at 0 °C in an ice/water bath. Then, solid KHF_2 (131 mg, 1.68 mmol) was added in one portion and the mixture

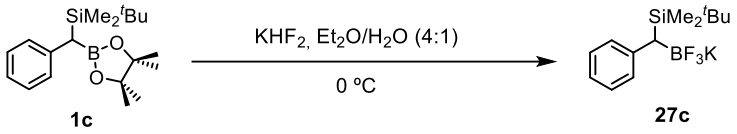
was stirred vigorously for 4h at 0 °C. The content was concentrated under reduced pressure by rotatory evaporator affording a white residue that was subsequently dried under high vacuum *via* Schlenk line during 1h. Dry acetone (2 mL) was added to the resulting residue, the vial was manually shaken, and solvent was filtrated into a new vial (This process was repeated 2 times more). The combined filtrate was concentrated under reduced pressure yielding a white solid. The solid residue was washed with pentane (~3 mL), centrifugated, and subsequently the pentane was decanted with the help of a Pasteur Pipette (Process repeated twice). The resulting residue was dried under high vacuum to afford 149 mg of the product .Yield: 68%.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.13 – 7.07 (m, 2H), 7.04 – 6.96 (m, 2H), 6.84 – 6.78 (m, 1H), 1.40 (q, *J* = 6.9 Hz, 1H, C<u>H</u>BF$_3$K), 0.85 (t, *J* = 7.9 Hz, 9H), 0.61 – 0.43 (m, 6H). ^{13}C NMR (126 MHz, Acetone-d_6) δ 149.75 (q, *J* = 2.7 Hz), 130.14, 127.69, 122.02, 8.22, 4.75. *<u>C</u>-B was not observed by HSQCAD experiment*. ^{19}F NMR (376 MHz, Acetone-d_6) δ -132.95 – -137.67 (m). ^{11}B NMR (128 MHz, Acetone-d_6): δ 4.76 (q, *J* = 64.0 Hz).



An oven-dried Schlenk tube equipped with a magnetic stirbar was added 2,2,6,6-tetramethylpiperidine (2.10 mmol, 0.35 ml) followed by THF (anh., 4.0 mL) under argon atmosphere. Subsequently, the flask was immersed in a dry ice/acetone bath with temperature adjusted to -40 °C. The solution was then treated with *n*-BuLi (2.5 M in hexane, 0.84 mL, 2.10 mmol) and the resulting mixture was stirred vigorously at -40 °C for 30 min. After that time, the flask was further cooled to -78 °C prior to the addition of benzyl boronate pinacol ester (0.45 mL, 2.00 mmol). At this point, the cold bath was removed and the resulting mixture was brought to room temperature and stirred at that temperature for 5 min. Afterwards, the flask was cooled again to -78 °C and ^{t}BuMe$_2$SiCl (0.42 mL, 2.40 mmol) was added dropwise. The resulting mixture was allowed to reach RT slowly during 1h (*inside the dry ice/acetone bath*). Once at RT, the resulting mixture was stirred for an additional 1h. Next, a saturated solution of NH_4Cl (~10 mL) was added and the mixture was stirred for 10 min. The organic layer was collected using a separation funnel and the aqueous layer was extracted with Et_2O (3 x 10 mL). Combined organic phase was dried over $MgSO_4$, filtered. The solvent was removed under reduced pressure and the resulting residue was purified by column chromatography. Silica gel, hexanes:EtOAc (100:1 -> 50:1) ; R_f = 0.29 in 50:1 hexanes:EtOAc. White solid, 397 mg, yield: 60%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.14 (m, 4H), 7.06 – 7.00 (m, 1H), 2.10 (s, 1H, C<u>H</u>Bpin), 1.23 (s, 6H, diast. Bpin), 1.21 (s, 6H, diast. Bpin), 0.79 (s, 9H, ^{t}Bu), 0.10 (s, 3H, Me), -0.11 (s, 3H, Me). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.44, 129.15, 127.95, 123.59, 83.25 (O<u>C</u>(CH$_3$)$_2$), 26.98 (C(<u>C</u>H$_3$)$_3$), 25.26 (Me, Bpin), 25.05 (Me, Bpin), 22.08 (C-B, from HSQCAD experiment), 18.09 (<u>C</u>(CH$_3$)$_3$), -4.98 (Me), -5.65 (Me). ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.57 ppm. GC-LRMS (EI) *m/z* calcd for $C_{18}H_{30}BO_2Si$ $[M - Me]^+$ 317, found: 317.

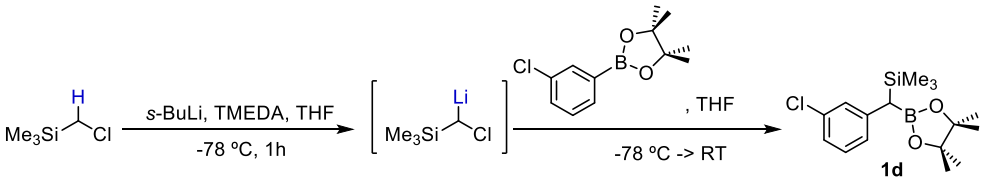


1c 27c

A vial equipped with a magnetic stirbar was added the benzyltriethylsilyl boronate ester **1c** (233 mg, 0.70 mmol) followed by a mixture of 4:1 Et_2O/H_2O (1.75 mL) and cooled at 0 °C in an ice/water bath. Then, solid KHF_2 (131 mg, 1.68 mmol) was added in one portion and the mixture was stirred vigorously for 4h at 0 °C. The content was concentrated under reduced pressure by rotatory evaporator affording a white residue that was subsequently dried under high vacuum *via* Schlenk line during 1h. Dry acetone (2 mL) was added to the resulting residue, the vial was manually shaken, and solvent was filtrated into a new vial (This process was repeated 2 times more). The combined filtrate was concentrated under reduced pressure yielding a white solid. The solid residue was washed with pentane (~3 mL), centrifugated, and subsequently the pentane was decanted with the help of a Pasteur Pipette (Process repeated twice). The resulting residue was dried under high vacuum. Yield: 188 mg, 86%.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.13 – 7.07 (m, 2H), 7.03 – 6.97 (m, 2H), 6.83 – 6.78 (m, 1H), 1.45 (q, *J* = 7.2 Hz, 1H, C<u>H</u>BF_3K), 0.72 (s, 9H, ^{t}Bu), 0.03 (pseudo d, *apparent J* = 0.8 Hz, 3H, Me), -0.11 (s, 3H, Me). ^{13}C NMR (126 MHz, Acetone-d_6) δ 150.51 (q, *J* = 2.5 Hz), 130.26, 127.69, 122.05, 27.82 (C(<u>C</u>$H_3)_3$), 18.74 (<u>C</u>$(CH_3)_3$), -3.91 (q, *J* = 1.9 Hz, diast. Me), -4.61 (q, *J* = 0.9 Hz, diast. Me). *<u>C</u>-B was not observed by HSQCAD experiment*. ^{19}F NMR (376 MHz, Acetone-d_6) δ -133.63 – -134.62 (m). ^{11}B NMR (128 MHz, Acetone-d_6): δ 4.83 (q, *J* = 62.4 Hz).

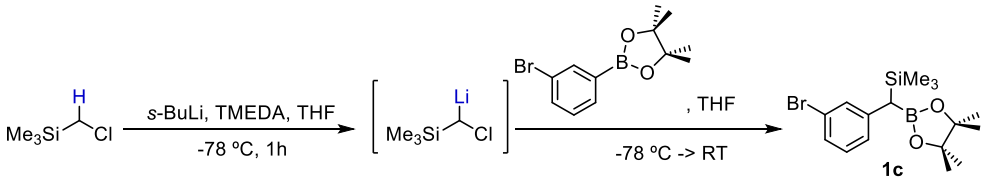
Synthesis of gem-silyl Bpin dimetalloid compounds by Matteson Homologation (Ref: D. Majumdar; D. S. Matteson, *J. Organometal. Chem.*, **1980**, *184*, C41-C43)



1d

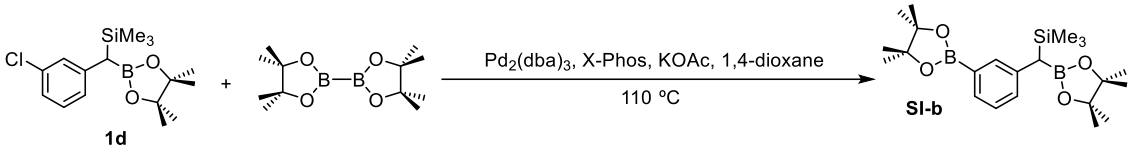
An oven-dried Schlenk tube equipped with a magnetic stirbar was charged with (chloromethyl)trimethylsilane (319 mg, 363 µL, 2.60 mmol), freshly distilled *N*,*N*,*N*',*N*' -tetramethylethylenediamine (TMEDA, 387 µL, 2.60 mmol) and anhydrous THF (6.0 mL) under argon atmosphere. Subsequently, the flask was cooled to -78 °C in a dry ice/acetone bath. The solution was then treated with a dropwise addition of *s*-BuLi (1.4 M in cyclohexane, 2.0 mL, 2.80 mmol) and the resulting mixture was stirred vigorously at -78 °C for 1h. After that time, a solution of 2-(3-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (477 mg, 2.00 mmol) in anhydrous THF (1.0 mL) was added dropwise. After 30 min of stirring at 78 °C, the content was allowed to reach room temperature as the bath warmed. The resulting mixture was diluted with Et_2O (10 mL) and treated with a saturated solution of NH_4Cl (~10 mL). The organic layer was collected using a separation funnel and the aqueous layer was extracted with Et_2O (3 x 15 mL). Combined organic phase was dried over $MgSO_4$, filtered. The solvent was removed under reduced pressure and the resulting residue was purified by column chromatography. Silica gel, hexanes:EtOAc (50:1 -> 20:1) ; R_f = 0.25, 50:1 hexanes:EtOAc. White solid, 535 mg, yield: 82%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, *J* = 1.9 Hz, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 7.06 – 6.98 (m, 2H), 1.95 (s, 1H, C<u>H</u>Bpin), 1.26 (s, 6H, C(C<u>H</u>$_3$)$_2$), 1.24 (s, 6H, C(C<u>H</u>$_3$)$_2$), 0.01 (s, 9H, TMS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.36, 133.72, 129.09, 128.55, 126.96, 123.77, 83.41 (O<u>C</u>(CH$_3$)$_2$), 25.27 (pin Me), 25.01 (pin Me'), -1.40. *(C_{sp3}-Bpin not observed due to the quadrupolar relaxation of the boron atom)*. ^{11}B NMR (128 MHz, $CDCl_3$): δ 32.67 ppm. GC-LRMS (EI) *m/z* calcd for $C_{16}H_{26}BClO_2Si$ $[M]^{+\cdot}$ 324, found: 324.



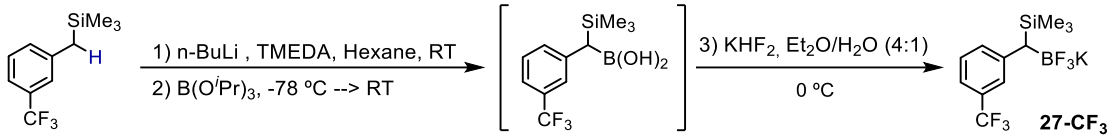
An oven-dried Schlenk tube equipped with a magnetic stirbar was charged with (chloromethyl)trimethylsilane (435 mg, 495 µL, 3.55 mmol), freshly distilled *N*,*N*,*N*',*N*' - tetramethylethylenediamine (TMEDA, 528 µL, 3.55 mmol) and anhydrous THF (9.0 mL) under argon atmosphere. Subsequently, the flask was cooled to -78 °C in a dry ice/acetone bath. The solution was then treated with a dropwise addition of *s*-BuLi (1.4 M in cyclohexane, 2.73 mL, 3.82 mmol) and the resulting mixture was stirred vigorously at -78 °C for 1h. After that time, a solution of 2-(3-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (773 mg, 2.73 mmol) in anhydrous THF (1.5 mL) was added dropwise. After 30 min of stirring at 78 °C, the content was allowed to reach room temperature as the bath warmed. The resulting mixture was diluted with Et_2O (15 mL) and treated with a saturated solution of NH_4Cl (~15 mL). The organic layer was collected using a separation funnel and the aqueous layer was extracted with Et_2O (3 x 15 mL). Combined organic phase was dried over $MgSO_4$, filtered. The solvent was removed under reduced pressure and the resulting residue was purified by column chromatography. Silica gel, hexanes:EtOAc (50:1) ; R_f = 0.22, 50:1 hexanes:EtOAc. White solid, 858 mg, yield: 85%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 1.9 Hz, 1H), 7.17 (dt, *J* = 7.6, 1.7 Hz, 1H), 7.13 – 7.02 (m, 2H), 1.94 (s, 1H, C<u>H</u>Bpin), 1.26 (s, 6H, C(C<u>H</u>$_3$)$_2$), 1.24 (s, 6H, C(C<u>H</u>$_3$)$_2$), 0.01 (s, 9H, TMS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.70, 131.45, 129.43, 127.37, 126.67, 122.14, 83.41 (O<u>C</u>(CH$_3$)$_2$), 26.45 (C_{sp3}-B, from HSQCAD experiment), 25.26 (pin Me), 25.00 (pin Me'), -1.41. ^{11}B NMR (128 MHz, $CDCl_3$): δ 32.63 ppm. GC-LRMS (EI) *m/z* calcd for $C_{16}H_{26}BBrO_2Si$ $[M]^{+\cdot}$ 368, found: 368.



An oven-dried Schlenk tube equipped with a magnetic stirbar was charged with the chloroarene **x** (195 mg, 0.60 mmol), $Pd_2(dba)_3$ (5.5 mg, 1% mol), 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (X-Phos, 11.4 mg, 4% mol), bis(pinacolato)diboron (456 mg, 1.80 mmol) and KOAc (177 mg, 1.80 mmol). The content was evacuated / backfilled with argon 3 times. Anhydrous 1,4-dioxane (2.0 mL) was added, the content was sealed and stirred at 110 °C for 6h. The resulting mixture was concentrated under reduced pressure and the resulting residue was purified by column chromatography. Silica gel, hexanes:EtOAc (20:1) ; R_f = 0.24, 20:1 hexanes:EtOAc. White solid, 216 mg, yield: 85%.

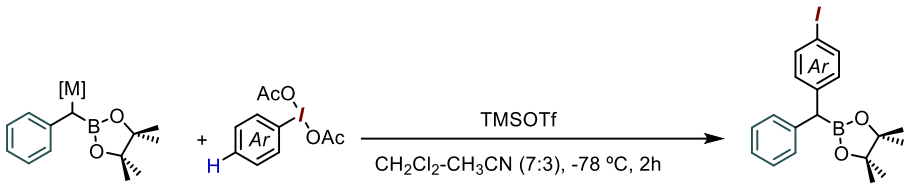
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dt, *J* = 7.2, 1.2 Hz, 1H), 7.44 (s, 1H), 7.41 (ddd, *J* = 7.8, 2.1, 1.3 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 2.00 (s, 1H, CHBpin), 1.33 (s, 12H, Ar-Bpin), 1.24 (s, 6H, CHBpin), 1.22 (s, 6H, CHBpin), 0.00 (s, 9H, TMS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.34, 135.43, 131.47, 130.12, 127.38, 83.62 ($OC(CH_3)_2$), 83.14 ($OC(CH_3)_2$), 25.96 (C_{sp3}-B, from HSQCAD experiment), 25.24 (pin Me), 25.04 (Ar-Bpin), 25.02 (Ar-Bpin), 25.00 (pin Me'), -1.25. *(C_{sp2}-Bpin not observed due to the quadrupolar relaxation of the boron atom)*. ^{11}B NMR (128 MHz, $CDCl_3$): δ br 30.98 ppm (The peak c*ontains both boron atoms*). GC-LRMS (EI) *m/z* calcd for $C_{22}H_{38}B_2O_4Si$ $[M]^{+\cdot}$ 416, found: 416.



An oven-dried Schlenk tube equipped with a magnetic stirbar was purged with argon, and then charged with trimethyl(3-(trifluoromethyl)benzyl)silane (1.00 mmol, 232 mg), recently distilled *N*,*N*,*N*',*N*' -tetramethylethylenediamine (TMEDA, 1.05 mmol, 0.16 mL) and dry hexane (1.20 mL). The content was cooled to 0 °C in an ice/water bath. Then, *n*-BuLi (2.5 M in hexane, 0.42 mL, 1.05 mmol) was added dropwise into the tube and the resulting mixture was stirred vigorously at 0 °C for 30 min. After that time, the flask was cooled to -78 °C in a dry ice/acetone bath, while at this temperature, $B(O^iPr)_3$ (9.2 mL, 40.0 mmol) was added slowly and the resulting mixture was left to reach ambient temperature slowly during 2h (*inside the dry ice/acetone bath*). Once at RT, the resulting mixture was stirred for an additional 3h. Next, a saturated solution of NH_4Cl (~40 mL) was added and the mixture stirred for 10 min. The organic layer was collected using a separation funnel, and the aqueous layer was extracted with Et_2O (3 x 15 mL). Combined organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting residue containing the free boronic acid was dissolved in a mixture of 4:1 Et_2O/H_2O (25 mL) and cooled at 0 °C in an ice/water bath. Subsequently, solid KHF_2 (1.88 g, 24.0 mmol) was added in one portion and the mixture was stirred vigorously for 2h at 0 °C. The resulting mixture was concentrated under reduced pressure leading to a white residue, and dried under high vacuum for 1h in order to remove H_2O, thus reducing the solubility of potential KHF_2 impurities. The white residue was dissolved in dry acetone (2-3 mL) and filtered through a Pasteur pipette plugged with a cotton ball and a layer of sand. The filtrate was evaporated under reduced pressure leading to a white residue. Subsequently, the residue is triturated with pentane (2-3 mL), centrifugated and decanted with the help of a Pasteur pipette (*This washing process was repeated twice).* The resulting white solid is dried under high vacuum affording 236 mg of product. Yield: 70%.

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.40 (s, 1H), 7.31 (d, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 7.7 Hz, 1H), 1.38 (q, *J* = 6.8 Hz, 1H, $CHBF_3K$), -0.10 (s, 9H, TMS). ^{13}C NMR (126 MHz, Acetone-d_6) δ 151.50 (q, *J* = 2.3 Hz), 133.59, 129.41 (q, *J* = 30.6 Hz), 128.13, 126.15 (q, *J* = 271.1 Hz), 126.09 (pseudo d, apparent *J* = 4.6 Hz), 118.56 (q, *J* = 4.1 Hz), 32.86 (C-B, from HSQCAD 2D experiment) -0.41 (d, *J* = 1.5 Hz, TMS). ^{19}F NMR (376 MHz, Acetone-d_6) δ -62.66 (s, CF_3), -134.68 – -135.75 (m, BF_3K). ^{11}B NMR (128 MHz, Acetone-d_6): δ 4.67 (pseudo q, apparent *J* = 74.2 Hz).

3. Iodane-guided C-H coupling reactions



[M] = $SiMe_3$, **1a**
SnR_3, **17 or 17'**

General procedure A. *Reactions were conducted under argon atmosphere and solvents were deoxygenated prior to use. The procedure 9described here is for a 0.2 mmol scale reaction*. A 15 mL reaction tube equipped with a stirbar and a screw-top septum cap was charged with the (diacetoxyiodo)arene (0.2 mmol) and benzyl *gem*-metalloid boronate (1.5 equiv.). Via a needle entry, the contents were evacuated and backfilled with argon 3 times. Next, the solvent medium CH_2Cl_2/CH_3CN (7:3, 1.4 mL total) was added, and the mixture was cooled at -78°C in a dry ice/acetone bath. At this temperature, TMSOTf (0.3 mmol, 67 mg, 54 µl) was added and the solution was allowed to stir for 2h at -78 °C. After this time, the reaction was allowed to reach room temperature and the solvent was removed by rotary evaporation. The product was isolated via silica gel flash column chromatography eluting with a hexanes:EtOAc mixture as indicated.

NMR comparison of the reactivity in an *iodane-guided C-H coupling* reaction between a benzyltributylstannyl boronate ester 17 and benzyltrimethylsilyl boronate ester 1a.

Following the general procedure A, TMSOTf (0.30 mmol, 54 µl) was added to a premixed solution of (diacetoxyiodo)benzene (0.15 mmol, 48 mg) and the corresponding *gem*-dimetalloid species (0.23 mmol, 1.5 equiv) in the CH_2Cl_2 – MeCN mixture (1.4 mL) at -78°C. The reaction mixture was stirred for 2h at -78°C. After that time, the reaction was warmed up to room temperature and an aliquot of each reaction was analyzed directly (without evaporation) by ^{1}H-NMR in $CDCl_3$ (Figure S**1**).

Run A: Using benzyltributylstannyl boronate ester **17** ^{1}H NMR analysis reveals a ratio of 2:1 between the C-H coupled product and the reduced iodobenzene. This translates to a conversion of 66% to the expected product.

Run B: Using benzyltrimethylsilyl boronate ester **1a** ^{1}H NMR analysis reveals a ratio of 1:4 between the coupled product and the reduced iodobenzene, which corresponds to a conversion of 20% to the expected product.

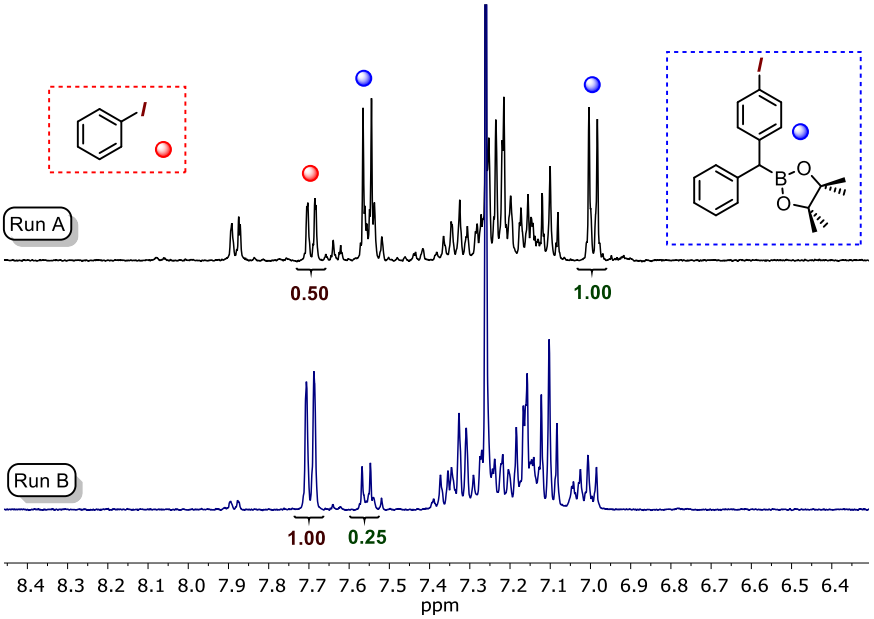
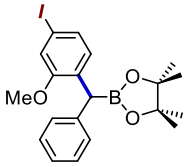


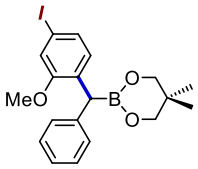
Figure S1. ^{1}H NMR spectra in $CDCl_3$ of crude reactions from "Run A" and "Run B".

Examples of iodane-guided C-Si arylation



(**6**) Following the general procedure A, TMSOTf (0.30 mmol, 54 µl) was added to a premixed solution of (3-methoxyphenyl)-λ^3-iodanediyl diacetate (0.2 mmol, 70 mg) and benzyltrimethylsilyl boronate ester **1a** (0.30 mmol, 87 mg) in CH_2Cl_2 – MeCN (1.4 mL total) at -78 °C. Column chromatography: silica gel, hexanes:EtOAc (50:1 -> 20:1) ; R_f = 0.11 in 50:1 hexanes:EtOAc. Colorless oil, 50 mg. Yield: 55%.

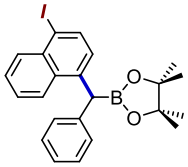
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 7.14 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.11 (d, *J* = 1.7 Hz, 1H), 6.57 (dd, *J* = 8.0, 0.9 Hz, 1H), 3.822 (s, 3H, OC$\underline{H}_3$) 3.816 (br s, 1H, C$\underline{H}$Bpin), 1.23 (s, 6H, C(C$\underline{H}_3$)$_2$), 1.19 (s, 6H, C(C$\underline{H}_3$)$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.28, 139.87, 132.10, 130.59, 130.13, 129.89, 128.67, 126.06, 118.98, 90.74 (C-***I***), 83.66 (O$\underline{C}$(CH$_3$)$_2$), 55.50 (O$\underline{C}$H$_3$), 33.45 (C-B, from HSQCAD experiment), 24.78 (pin Me), 24.68 (pin Me'). ^{11}B NMR (128 MHz, $CDCl_3$): δ 36.8 ppm. GC-LRMS (EI) *m/z* $C_{20}H_{24}BIO_3$ $[M]^{+\cdot}$ 450.



(**6'**) Following the general procedure A, TMSOTf (0.3 mmol, 54 µl) was added to a premixed solution of (3-methoxyphenyl)-λ^3-iodanediyl diacetate (0.2 mmol, 70 mg) and benzyltrimethylsilyl boronate ester **1a'** (0.30 mmol, 83 mg) in CH_2Cl_2 – MeCN (1.4 mL total) at -78 °C. Column chromatography: silica gel, hexanes:EtOAc (10:1); R_f = 0.12. Colorless oil, 69 mg. Yield: 79%. *This compound required rapid column chromatography due the instability of the –Bneop derivatives when in contact with silica gel.*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.25 – 7.12 (m, 5H), 6.61 (dd, *J* = 8.0, 0.9 Hz, 1H),

3.85 (s, 3H, OC<u>H</u>$_3$), 3.71 (br s, 1H, C<u>H</u>Bneop), 3.64 – 3.56 (m, 4H, OC<u>H</u>$_2$C), 0.93 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.37, 141.08, 132.94, 130.87, 129.94, 129.93, 128.59, 125.83, 119.23, 90.54 (C-***I***), 72.52 (O<u>C</u>H$_2$), 55.91 (O<u>C</u>H$_3$), 37.23 (<u>C</u>-B, from HSQCAD experiment), 31.87 (<u>C</u>(CH$_3$)$_2$), 21.98 (<u>C</u>H$_3$). GC-LRMS (EI) *m/z* $C_{19}H_{22}BIO_3$ $[M]^{+\cdot}$ 436.

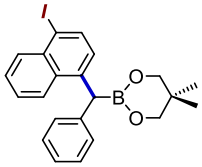


(**7**) Prepared using both the silyl and stannyl benzylic reagents.

*Via the silyl reagent **1a***. Following scale-down version of the general procedure A, TMSOTf (0.15 mmol, 27 µl) was added to a premixed solution of naphthalen-1-yl-λ^3-iodanediyl diacetate (0.10 mmol, 37 mg) and benzyltrimethylsilyl boronate ester **1a** (0.15 mmol, 44 mg) in CH_2Cl_2 – MeCN (0.7 mL total) at -78 °C. Column chromatography: silica gel, hexanes:EtOAc (50:1); R_f = 0.19. Colorless oil, 21 mg. Yield: 45%.

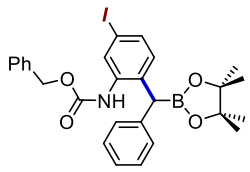
*Via the stannyl reagent **17***. Following a modification of the general procedure A, the reaction was scaled to 0.15 mmol. Thus, TMSOTf (0.225 mmol, 41 µl) was added to a premixed solution of naphthalen-1-yl-λ^3-iodanediyl diacetate (0.15 mmol, 56 mg) and benzyltributylstannyl boronate ester **12** (0.225 mmol, 114 mg) in CH_2Cl_2 – MeCN (1.0 mL total) at -78°C. Column chromatography: silica gel, hexanes:EtOAc (50:1); R_f = 0.19. Colorless oil, 43 mg. Yield: 61%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 8.5, 1.4 Hz, 1H), 8.05 (dd, *J* = 8.6, 1.2 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.58 – 7.46 (m, 2H), 7.32 – 7.24 (m, 4H), 7.23 – 7.17 (m, 1H), 7.05 (dd, *J* = 7.7, 0.7 Hz, 1H), 4.51 (s, 1H, C<u>H</u>Bpin), 1.22 (s, 6H, C(C<u>H</u>$_3$)$_2$), 1.20 (s, 6H, C(C<u>H</u>$_3$)$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.82, 139.85, 137.49, 134.56, 133.34, 133.18, 129.55, 128.71, 127.86, 127.35, 126.75, 126.06, 124.88, 97.86 (<u>C</u>-***I***), 84.16 (O<u>C</u>(CH$_3$)$_2$), 35.62 (<u>C</u>-B, from HSQCAD experiment), 24.79, 24.62. ^{11}B NMR (128 MHz, $CDCl_3$): δ 29.24 ppm. GC-HRMS (EI) *m/z* calcd for $C_{23}H_{24}BIO_2$ $[M]^{+\cdot}$ 470.0909, found: 470.0906.



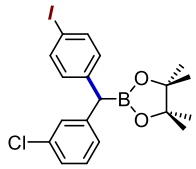
(**7'**) Following the general procedure A, TMSOTf (0.3 mmol, 54 µl) was added to a premixed solution of naphthalen-1-yl-λ^3-iodanediyl diacetate (0.20 mmol, 74 mg) and benzyltrimethylsilyl boronate ester **1a'** (0.30 mmol, 83 mg) in CH_2Cl_2 – MeCN (1.4 mL total) at -78°C. Column chromatography: silica gel, hexanes:EtOAc (10:1); R_f = 0.14. Colorless oil, 57 mg. Yield: 63%. This compound required rapid column chromatography due the instability of the –Bneop derivatives when in contact with silica gel.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.06 (m, 2H), 7.98 (d, *J* = 7.7 Hz, 1H), 7.58 – 7.46 (m, 2H), 7.31 – 7.26 (m, 3H), 7.22 – 7.12 (m, 2H), 7.02 (dd, *J* = 7.7, 0.7 Hz, 1H), 4.41 (s, 1H, C<u>H</u>Bneop), 3.68 – 3.55 (m, 4H, OC<u>H</u>$_2$C), 0.91 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.79, 140.83, 137.41, 134.53, 133.51, 133.19, 129.62, 128.63, 127.66, 127.26, 126.80, 125.89, 124.79, 97.55 (<u>C</u>-***I***), 72.53 (O<u>C</u>H$_2$), 39.62 (<u>C</u>-B, from HSQCAD experiment), 31.87 (<u>C</u>(CH$_3$)$_2$), 22.07 (<u>C</u>H$_3$). GC-MS (EI) *m/z* $C_{22}H_{22}BIO_2$ $[M]^{+\cdot}$ 456.



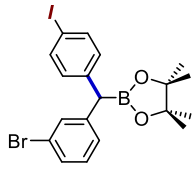
(**8**) Following a modification of the general procedure A, TMSOTf (0.15 mmol, 27 µl) was added to a premixed solution of (3-(((benzyloxy)carbonyl)amino)phenyl)-λ^3-iodanediyl diacetate (0.10 mmol, 47 mg) and benzyltrimethylsilyl boronate ester **1a** (0.15 mmol, 44 mg) in CH_2Cl_2 – MeCN (0.7 mL total) at -78°C. Column chromatography: silica gel, hexanes:EtOAc (10:1); R_f = 0.22. Colorless oil, 38 mg. Yield: 67%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (br s, 1H, NH), 7.41 – 7.30 (m, 6H), 7.29 – 7.23 (m, 2H), 7.21 – 7.15 (m, 4H), 6.90 (dd, *J* = 8.2, 0.5 Hz, 1H), 5.14 (pseudo doublet, 2H, apparent *J* = 1.1 Hz, diastereotopic OCH_2Ph), 3.86 (s, 1H, CHBpin), 1.21 (s, 6H, C(CH_3)$_2$), 1.21 (s, 6H, C(CH_3)$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.63 (C=O), 153.80, 139.22, 137.27, 136.37, 133.77, 132.03, 129.11, 128.84, 128.80, 128.64, 128.26, 128.15, 126.39, 91.55 (C-***I***), 84.55 (OC(CH$_3$)$_2$), 66.96 (OCH_2Ph), 35.27 (C-B, from HSQCAD experiment), 24.72, 24.65. ^{11}B NMR (128 MHz, $CDCl_3$): δ 27.12 ppm.



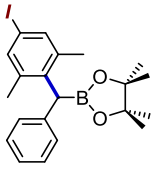
(**9**) Following the general procedure A, TMSOTf (0.20 mmol, 36 µl) was added to a premixed solution of PIDA (0.10 mmol, 32 mg) and ((3-chlorophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)trimethylsilane **1d** (0.15 mmol, 49 mg) in CH_2Cl_2 – MeCN (0.7 mL total) at -78 °C. Column chromatography: silica gel, hexanes:EtOAc (50:1 -> 20:1) ; R_f = 0.35 in 20:1 hexanes:EtOAc. Colorless oil, 28 mg. Yield: 62%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (pseudo d, *J* = 8.4 Hz, 2H), 7.25 – 7.08 (m, 4H), 7.00 (pseudo d, *J* = 8.4 Hz, 2H), 3.75 (s, 1H, CHBpin), 1.23 (s, 12H, 2xC(CH_3)$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.68, 141.18, 137.70, 134.39, 131.32, 129.81, 129.21, 127.34, 126.21, 91.38 (C-***I***), 84.23 (OC(CH$_3$)$_2$), 38.60 (C_{sp3}-B, from HSQCAD experiment), 24.73 (pin Me), 24.71 (pin Me'). ^{11}B NMR (128 MHz, $CDCl_3$): δ 32.5ppm. GC-LRMS (EI) *m/z* calcd for $C_{19}H_{21}BClIO_2$ $[M]^{+\cdot}$ 454, found: 454.



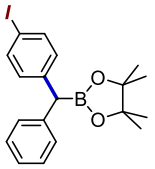
(**10**) Following the general procedure A, TMSOTf (0.20 mmol, 36 µl) was added to a premixed solution of PIDA (0.10 mmol, 32 mg) and ((3-bromophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)trimethylsilane **1e** (0.15 mmol, 55 mg) in CH_2Cl_2 – MeCN (0.7 mL total) at -78 °C. Column chromatography: silica gel, hexanes:EtOAc (50:1) ; R_f = 0.24 in 50:1 hexanes:EtOAc. Pale yellow solid, 29 mg. Yield: 57%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (pseudo d, *J* = 8.4 Hz, 1H), 7.37 (dt, *J* = 2.1, 1.0 Hz, 1H), 7.30 (dt, *J* = 7.1, 1.8 Hz, 1H), 7.19 – 7.09 (m, 2H), 6.99 (pseudo d, *J* = 8.0 Hz, 1H), 3.74 (s, 1H, CHBpin), 1.23 (s, 12H, 2xC(CH_3)$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.98, 141.16, 137.71, 132.12, 131.31, 130.13, 129.14, 127.80, 122.74, 91.40 (C-***I***), 84.24 (OC(CH$_3$)$_2$), 38.46 (C_{sp3}-B, from HSQCAD experiment), 24.73 (pin Me), 24.71 (pin Me'). ^{11}B NMR (128 MHz, $CDCl_3$): δ 32.9 ppm. GC-LRMS (EI) *m/z* calcd for $C_{19}H_{21}BBrIO_2$ $[M]^{+\cdot}$ 498, found: 498.



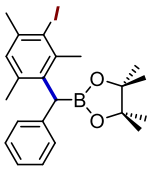
(**11**) Following a modification of the general procedure A, the reaction was scaled to 0.10 mmol, TMSOTf (0.15 mmol, 27 µl) was added to a premixed solution of (3,5-dimethylphenyl)-λ^3-iodanediyl diacetate (0.10 mmol, 35 mg) and benzyltrimethylsilyl boronate ester **1a** (0.15 mmol, 44 mg) in CH_2Cl_2 – MeCN (0.7 mL total) at -78°C. Column chromatography: silica gel, hexanes:EtOAc (50:1 to 20:1) ; R_f = 0.19 in 50:1 hexanes:EtOAc. Colorless oil, 38 mg. Yield: 85%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 2H), 7.24 – 7.18 (m, 2H), 7.15 – 7.08 (m, 3H), 4.15 (s, 1H, C<u>H</u>Bpin), 2.16 (s, 6H), 1.27 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.49, 140.04, 138.83, 137.21, 128.42, 128.18, 125.32, 91.43 (C-*I*), 83.84 (O<u>C</u>$(CH_3)_2$), 32.74 (C-B, from HSQCAD experiment), 25.04, 24.85, 21.02 (Ar-<u>C</u>H_3). ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.18 ppm. GC-HRMS (EI) *m/z* calcd for $C_{21}H_{26}BIO_2$ $[M]^{+\cdot}$ 448.1065, found: 448.1061; calcd for $C_{20}H_{23}BIO_2$ $[M - CH_3]^+$ 433.0830, found: 433.0828.



(**12**) Following a modification of the general procedure A, the reaction was scaled to 0.15 mmol, TMSOTf (0.3 mmol, 54 µl) was added to a premixed solution of PIDA (0.15 mmol, 48 mg) and benzyltributylstannyl boronate ester **x** (0.225 mmol, 114 mg) in CH_2Cl_2 – MeCN (1.0 mL total) at -78 °C. Column chromatography: silica gel, hexanes:EtOAc (50:1); R_f = 0.16. Colorless oil, 38 mg. Yield: 60%.

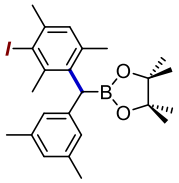
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (pseudo d, *J* = 8.4 Hz, 2H), 7.30 – 7.22 (m, 4H), 7.20 – 7.15 (m, 1H), 7.02 (pseudo d, *J* = 7.9 Hz, 2H), 3.80 (s, 1H, C<u>H</u>Bpin), 1.24 (s, 6H, C(C<u>H</u>$_3)_2$), 1.23 (s, 6H, C(C<u>H</u>$_3)_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.09, 141.51, 137.53, 131.34, 129.19, 128.65, 125.98, 91.00 (C-***I***), 84.02 (O<u>C</u>$(CH_3)_2$), 38.97 (C-B, from HSQCAD experiment), 24.74 (Me), 24.72 (Me'). ^{11}B NMR (128 MHz, $CDCl_3$): δ 27.79 ppm. GC-HRMS (EI) *m/z* calcd for $C_{19}H_{22}BIO_2$ $[M]^{+\cdot}$ 420.0752, found: 420.0755; calcd for $C_{18}H_{19}BIO_2$ $[M - CH_3]^+$ 405.0517, found: 405.0517.



(**13**) Following a modification of the general procedure A, the reaction was scaled to 0.10 mmol, TMSOTf (0.15 mmol, 27 µl) was added to a premixed solution of mesityl-λ^3-iodanediyl diacetate (0.10 mmol, 36 mg) and benzyltrimethylsilyl boronate ester **1a** (0.15 mmol, 44 mg) in CH_2Cl_2 – MeCN (0.7 mL total) at -78°C. Column chromatography: silica gel, hexanes:EtOAc (50:1 to 20:1) ; R_f = 0.19 in 50:1 hexanes:EtOAc. White solid, 39 mg. Yield: 85%.

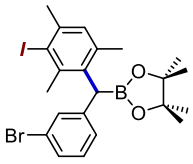
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 2H), 7.15 – 7.10 (m, 1H), 7.08 (pseudo dt, *J* = 8.1, 1.1 Hz, 2H), 7.00 (s, 1H), 4.27 (s, 1H, C<u>H</u>Bpin), 2.45 (s, 3H), 2.37 (s, 3H), 2.20 (s, 3H), 1.27 (s, 6H, C(C<u>H</u>$_3)_2$), 1.26 (s, 6H, C(C<u>H</u>$_3)_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.89, 140.63, 139.71, 137.23,

136.86, 129.85, 128.28, 128.13, 125.22, 108.03 (C-*I*), 83.86 (O<u>C</u>(CH$_3$)$_2$), 35.04 (C-B, from HSQCAD 2D experiment), 30.11 (Ar-<u>C</u>H$_3$), 28.95 (Ar-<u>C</u>H$_3$), 25.05, 24.86, 21.15 (Ar-<u>C</u>H$_3$). ^{11}B NMR (128 MHz, $CDCl_3$): δ 28.46 ppm. GC-HRMS (EI) *m/z* calcd for $C_{22}H_{28}BIO_2$ $[M]^{+\cdot}$ 462.1222, found: 462.1222; calcd for $C_{21}H_{25}BIO_2$ $[M - CH_3]^+$ 447.0987, found: 447.0982.



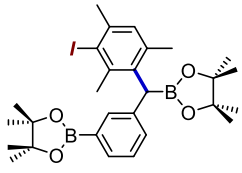
(**14**) Following the general procedure A, TMSOTf (0.20 mmol, 36 µl) was added to a premixed solution of mesityl-λ^3-iodanediyl diacetate (0.10 mmol, 36 mg) and ((3,5-dimethylphenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)trimethylsilane **SI-a** (0.15 mmol, 48 mg) in CH_2Cl_2 – MeCN (0.7 mL total) at -78 °C. Column chromatography: silica gel, hexanes:EtOAc (50:1) ; R_f = 0.37 in 20:1 hexanes:EtOAc. White solid, 35 mg. Yield: 71%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (s, 1H), 6.77 (d, *J* = 0.8 Hz, 1H), 6.66 (d, *J* = 0.8 Hz, 1H), 4.20 (s, 1H, C<u>H</u>Bpin), 2.46 (s, 3H, Me), 2.39 (s, 3H, Me), 2.24 (s, 6H, 2xMe), 2.20 (s, 3H, Me), 1.263 (s, 6H, (pin Me)), 1.260 (s, 6H, pin Me'). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.71, 140.68, 139.53, 137.34, 137.27, 136.88, 129.83, 127.07, 126.09, 108.04 (C-***I***), 83.77 (O<u>C</u>(CH$_3$)$_2$), 35.05 (C_{sp3}-B, from HSQCAD experiment), 30.12 (Ar-Me), 29.02 (Ar-Me), 25.08 (pin Me), 24.79 (pin Me'), 21.64 (Ar-Me), 21.21 (Ar-Me). ^{11}B NMR (128 MHz, $CDCl_3$): δ 34.0 ppm. GC-LRMS (EI) *m/z* calcd for $C_{24}H_{32}BIO_2$ $[M]^{+\cdot}$ 490, found: 490.



(**15**) Following the general procedure A, TMSOTf (0.20 mmol, 36 µl) was added to a premixed solution of mesityl-λ^3-iodanediyl diacetate (0.10 mmol, 36 mg) and ((3-bromophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)trimethylsilane **1e** (0.15 mmol, 55 mg) in CH_2Cl_2 – MeCN (0.7 mL total) at -78 °C. Column chromatography: silica gel, hexanes:EtOAc (50:1) ; R_f = 0.18 in 50:1 hexanes:EtOAc. White solid, 31 mg. Yield: 58%.

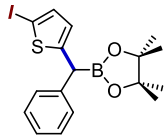
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 2H), 7.07 (t, *J* = 7.8 Hz, 1H), 7.02 – 6.94 (m, 2H), 4.21 (s, 1H, C<u>H</u>Bpin), 2.45 (s, 3H, Me), 2.35 (s, 3H, Me), 2.18 (s, 3H, Me), 1.27 (s, 6H, C(C<u>H</u>$_3$)$_2$), 1.26 (s, 6H, C(C<u>H</u>$_3$)$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.53, 140.49, 140.09, 137.12, 135.94, 131.32, 129.98, 129.63, 128.43, 126.90, 122.45, 108.09 (C-***I***), 84.07 (O<u>C</u>(CH$_3$)$_2$), 35 (C_{sp3}-B, from HSQCAD experiment), 30.13 (Ar-Me), 28.91 (Ar-Me), 25.03 (pin Me), 24.86 (pin Me'), 21.13 (Ar-Me). ^{11}B NMR (128 MHz, $CDCl_3$): δ 33.7 ppm. GC-LRMS (EI) *m/z* calcd for $C_{22}H_{27}BBrIO_2$ $[M]^{+\cdot}$ 540, found: 540.



(**16**) Following the general procedure A, TMSOTf (0.20 mmol, 36 µl) was added to a premixed solution of mesityl-λ^3-iodanediyl diacetate (0.10 mmol, 36 mg) and trimethyl((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methyl)silane **SI-b** (0.15 mmol, 62 mg) in CH_2Cl_2 – MeCN (0.7 mL total) at -78 °C. Column chromatography: silica gel, hexanes:EtOAc (20:1) ; R_f = 0.20 in 20:1 hexanes:EtOAc. Pale yellow solid,

37 mg. Yield: 63%.

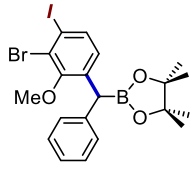
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 2.1, 1.0 Hz, 1H), 7.56 (pseudo dq, *apparent J* = 7.3, 1.1 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.98 (s, 1H), 6.91 (ddd, *J* = 7.8, 2.2, 1.2 Hz, 1H), 4.28 (s, 1H, C<u>H</u>Bpin), 2.45 (s, 3H, Me), 2.38 (s, 3H, Me), 2.18 (s, 3H, Me), 1.34 (s, 6H, C(C<u>H</u>$_3$)$_2$), 1.33 (s, 6H, C(C<u>H</u>$_3$)$_2$), 1.26 (s, 6H, C(C<u>H</u>$_3$)$_2$), 1.26 (s, 6H, C(C<u>H</u>$_3$)$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.70, 140.09, 139.67, 137.33, 136.58, 135.53, 131.64, 130.43, 129.91, 127.64, 108.05 (C-***I***), 83.87 (O<u>C</u>(CH$_3$)$_2$), 83.71 (O<u>C</u>(CH$_3$)$_2$), 35.45 (C_{sp3}-B, from HSQCAD experiment), 30.12 (Ar-Me), 29.08 (Ar-Me), 25.14 (pin Me), 25.08 (pin Me'), 24.93 (pin Me), 24.83 (pin Me'), 21.25 (Ar-Me). *(C_{sp2}-Bpin not observed due to the quadrupolar relaxation of the boron atom)*. ^{11}B NMR (128 MHz, $CDCl_3$): δ br 31.1 ppm (The peak c*ontains both boron atoms*). GC-LRMS (EI) *m/z* calcd for $C_{28}H_{39}B_2IO_4$ $[M]^{+\cdot}$ 588, found: 588.



(**20**) Following a modification of the general procedure A, the reaction was scaled to 0.15 mmol, TMSOTf (0.225 mmol, 41 µl) was added to a premixed solution of thiophen-2-yl-λ^3-iodanediyl diacetate (0.15 mmol, 49 mg) and benzyltributylstannyl trimethylsilane **17** (0.225 mmol, 114 mg) in CH_2Cl_2 – MeCN (1.4 mL total) at -78°C. Column chromatography: silica gel, hexanes:EtOAc (50:1) ; R_f = 0.61 in 20:1 hexanes:EtOAc. Yellow solid, 26 mg. Yield: 41%.

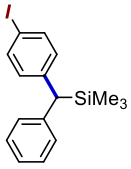
This compound required rapid column chromatography due to the instability when in contact with silica gel. In addition, the compound exhibit rapid decomposition even in solid state.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 4H), 7.22 – 7.17 (m, 1H), 7.06 (d, *J* = 3.6 Hz, 1H), 6.63 (dd, *J* = 3.5, 1.0 Hz, 1H), 3.99 (s, 1H, C<u>H</u>B), 1.243 (s, 6H, C(C<u>H</u>$_3$)$_2$), 1.238 (s, 6H, C(C<u>H</u>$_3$)$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.71, 141.27, 136.80, 128.71, 128.64, 127.29, 126.31, 84.31 (O<u>C</u>(CH$_3$)$_2$), 70.86 (C-***I***), 24.78, 24.66. GC-HRMS (EI) *m/z* calcd for $C_{16}H_{17}BIO_2S$ $[M - CH_3]^+$ 411.0082, found: 411.0082.



(**21**) Following the general procedure A, TMSOTf (0.15 mmol, 27 µl) was added to a premixed solution of (2-bromo-3-methoxyphenyl)-λ^3-iodanediyl diacetate (0.10 mmol, 43 mg) and trimethyl(phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)stannane **17'** (0.15 mmol, 57 mg) in CH_2Cl_2 – MeCN (0.7 mL total) at -78 °C. Column chromatography: silica gel, hexanes:EtOAc (50:1 -> 20:1) ; R_f = 0.09 in 50:1 hexanes:EtOAc. White solid, 27 mg. Yield: 51%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.3 Hz, 1H), 7.34 – 7.18 (m, 5H), 6.69 (dd, *J* = 8.3, 0.8 Hz, 1H), 3.95 (s, 1H, C<u>H</u>Bpin), 3.79 (s, 3H, OC<u>H</u>$_3$), 1.23 (s, 6H, C(C<u>H</u>$_3$)$_2$), 1.21 (s, 6H, C(C<u>H</u>$_3$)$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.62, 139.89, 138.67, 135.62, 130.44, 129.82, 128.77, 126.27, 124.90, 98.88 (C-***I***), 84.00 (O<u>C</u>(CH$_3$)$_2$), 60.38 (O<u>C</u>H$_3$), 33.57 (C_{sp3}-B, from HSQCAD experiment), 24.86 (pin Me), 24.66 (pin Me'). ^{11}B NMR (128 MHz, $CDCl_3$): δ 32.5ppm. GC-LRMS (EI) *m/z* calcd for $C_{20}H_{23}BBrIO_3$ $[M]^{+\cdot}$ 528, found: 528.

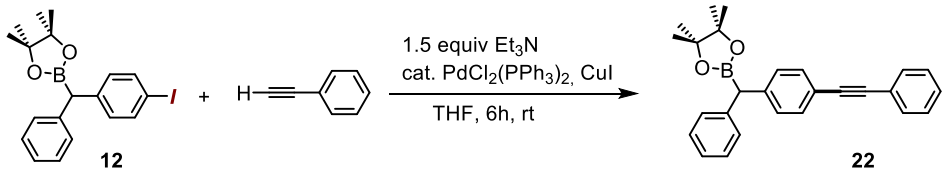


Following the general procedure A, TMSOTf (0.3 mmol, 54 µl) was added to a premixed solution of PIDA (0.2 mmol, 64 mg) and benzyltributylstannyl trimethylsilane **x** (0.30 mmol, 136 mg) in CH_2Cl_2 – MeCN (1.4 mL total) at -78°C. Column chromatography: silica gel, hexanes:EtOAc (1:0) ; R_f = 0.63 in 50:1 hexanes:EtOAc. White solid, 24 mg. Yield: 33%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (apparent double with *J* = 8.4 Hz, 2nd order effects 2H), 7.31 – 7.24 (m, 2H), 7.23 – 7.19 (m, 2H), 7.18 – 7.13 (m, 1H), 6.99 (apparent double with *J* = 8.4 Hz, 2nd order effects, 2H), 3.46 (s, 1H), 0.04 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.91, 142.36, 137.41, 130.82, 128.86, 128.56, 125.48, 90.10 (C-*I*), 45.76 (Ar-C<u>H</u>-Si), -1.62 (Si<u>Me</u>). GC-HRMS (EI) *m/z* calcd for $C_{15}H_{16}ISi$ $[M - CH_3]^+$ 351.0060, found: 351.0057.

4. Downstream structure diversification

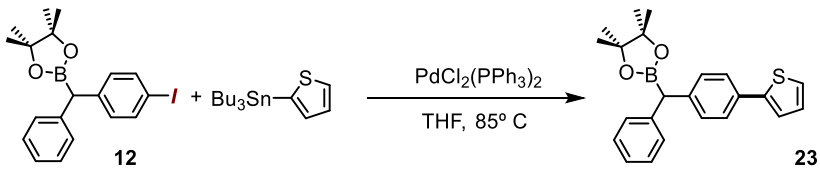
Sonogashira cross-coupling reaction



To an oven-dried GC vial equipped with a magnetic stirbar was added the iodoarene **12** (21 mg, 0.05 mmol), $PdCl_2(PPh_3)_2$ (1.4 mg, 4% mol) and CuI (0.8 mg, 8% mol). The flask was capped with a screw-top septum and then evacuated / backfilled with argon 3 times. THF (0.20 mL), Et_3N (11 µL, 0.075 mmol) and ethynylbenzene (6.0 µL, 0.055 mmol,) were added in this order. The resulting mixture was stirred at room temperature for 6h. After that time, the content was transferred into a separatory funnel and H_2O (5 mL) was added. The solution was extracted with Et_2O (3 x 5 mL). Combined organic phase was dried over $MgSO_4$, filtered and solvent evaporated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (hexanes:EtOAc = 20:1), R_f = 0.25. Prod. **22** was obtained as a pale-yellow solid (16 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.46 – 7.42 (m, 2H), 7.37 – 7.29 (m, 3H), 7.30 – 7.23 (m, 6H), 7.21 – 7.15 (m, 1H), 3.88 (s, 1H, C<u>H</u>BPin), 1.237 (s, 6H, diast 2xC<u>H</u>$_3$) overlapping with 1.233 (s, 6H, diast 2xC<u>H</u>$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.80, 141.64, 131.82, 131.70, 129.31, 129.26, 128.62, 128.44, 128.19, 125.93, 123.65, 120.55, 89.74 (<u>C</u>≡C), 89.02 (C≡<u>C</u>), 83.99 (O<u>C</u>$(CH_3)_2$), 39.51 (C-B, from HSQCAD 2D experiment), 24.74, 24.73. GC-HRMS (EI) *m/z* calcd for $C_{27}H_{27}BO_2$ $[M]^{+\cdot}$ 394.2099, found: 394.2097.

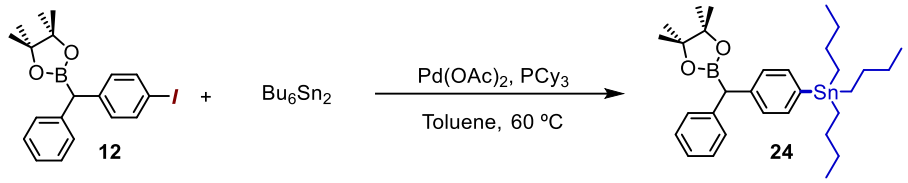
Stille cross-coupling reaction



An oven-dried GC vial equipped with a magnetic stirbar was charged with the iodoarene **12** (42 mg, 0.10 mmol) and $PdCl_2(PPh_3)_2$ (3.5 mg, 5% mol). The flask was evacuated and backfilled with argon 3 times. THF (0.4 mL) and 2-(tributylstannyl)thiophene (96 µL, 0.30 mmol) were added under argon atmosphere. The flask was sealed and the mixture stirred at 85 °C for 2h. After that, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (hexanes:EtOAc = 20:1), R_f = 0.31. Prod. **23** was obtained as a white solid (32 mg, 84%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.26 – 7.23 (m, 7H), 7.20 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.17 – 7.12 (m, 1H), 7.03 (dd, *J* = 5.1, 3.6 Hz, 1H), 3.85 (s, 1H, C<u>H</u>BPin), 1.22 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.69, 141.97, 141.72, 131.95, 129.71, 129.25, 128.60, 128.04, 126.15, 125.84, 124.42, 122.74, 83.95 (O<u>C</u>$(CH_3)_2$), 39.00 (C-B, from HSQCAD 2D experiment), 24.75 (two diastereotopic Me, appears as a poorly resolved set of 2 singlets). GC-HRMS (EI) *m/z* calcd for $C_{23}H_{25}BO_2S$ $[M]^{+\cdot}$ 376.1663, found: 376.1662.

Stannylation cross-coupling reaction

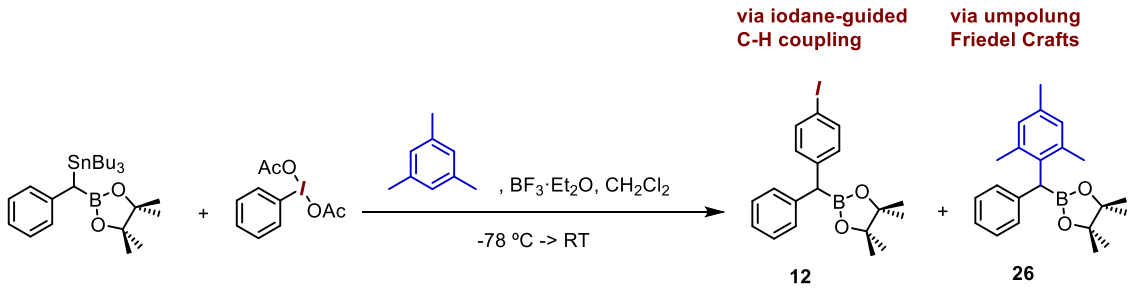


To an oven-dried GC vial equipped with a magnetic stirbar was added the iodoarene **12** (42 mg, 0.10 mmol), $Pd(OAc)_2$ (0.9 mg, 4% mol, 0.004 mmol) and tricyclohexylphosphine (2.2 mg, 8% mol, 0.008 mmol). The flask was capped with a screw-top septum and then evacuated / backfilled with argon 3 times. Dry toluene (previously degassed, 0.4 mL) was added, and the resulting mixture was stirred at 60 °C for 7h. After that time, the content was concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (hexanes:EtOAc = 40:1), R_f = 0.37 in 30:1 hexanes:EtOAc. Compound **24** was obtained as a colorless oil (30 mg, 52%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (pseudo d, apparent *J* = 8.0 Hz, 2H), 7.28 – 7.25 (m, 4H), 7.21 (pseudo d, apparent *J* = 8.0 Hz, 2H), 7.18 – 7.13 (m, 1H), 3.83 (s, 1H, C<u>H</u>BPin), 1.57 – 1.47 (m, 6H), 1.36 – 1.27 (m, 6H), 1.23 (s, 12H, Bpin), 1.05 – 0.98 (m, 6H), 0.88 (t, *J* = 7.3 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.25, 141.87, 138.43, 136.69, 129.34, 128.88, 128.49, 125.68, 83.83 (O<u>C</u>$(CH_3)_2$), 39.46 (C-B, from HSQCAD 2D experiment), 29.25, 27.54, 24.75 (diast. Me from pin), 24.74 (diast. Me from pin), 13.82, 9.67. ^{11}B NMR (128 MHz, $CDCl_3$): δ 32.30 ppm. GC-LRMS (EI) *m/z* calcd for $C_{27}H_{40}BO_2Sn$ $[M\text{-}Bu]^+$ 527, found: 527.

5. Mechanistic and synthetic assessment of the umpolung reactivity of 12.

Competition reaction between an iodane-guided rearrangement and Friedel-Craft (umpolung) arylation



A 15 mL reaction tube equipped with a stirbar was charged with the (diacetoxyiodo)benzene (32 mg, 0.10 mmol) and benzyl *gem*-tributylstannyl boronate **17** (51 mg, 0.10 mmol). The content was frozen at -78 °C in a dry CO_2/acetone bath and purged with argon via three evacuate / backfilled. While at this temperature, a mixture of dry CH_2Cl_2/CH_3CN (7:3, 0.7 mL total) was added, followed by the addition of mesitylene (14 µl, 0.10 mmol). Next, TMSOTf (0.20 mmol, 36 µl) was added and the solution was stirred for 2h at -78°C. After this time, the reaction was allowed to reach room temperature slowly (*inside the dry ice/acetone bath*), and, once at room temperature, was stirred for an additional 1 hour. Then, an aliquot of the crude reaction was diluted in $CDCl_3$ and analyzed by ^{1}H NMR as well as by GC-MS The analysis showed a mixture of **12** and **26** products in a ratio ~5:1 (See below, Figure S2).

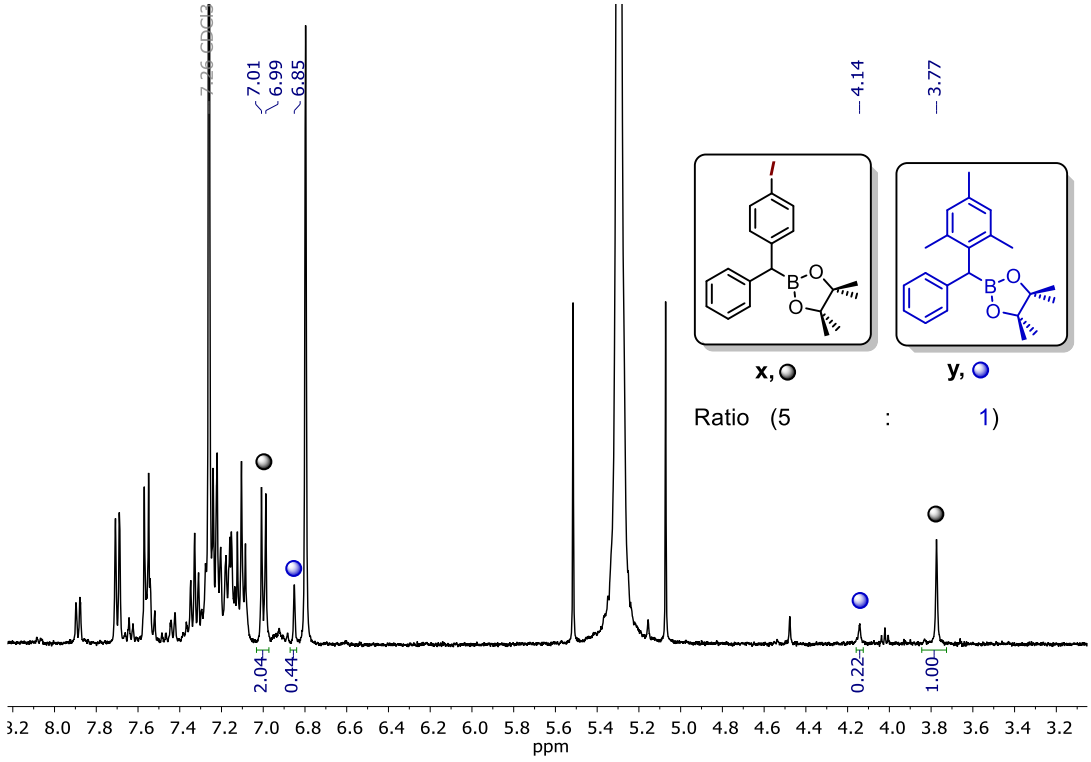
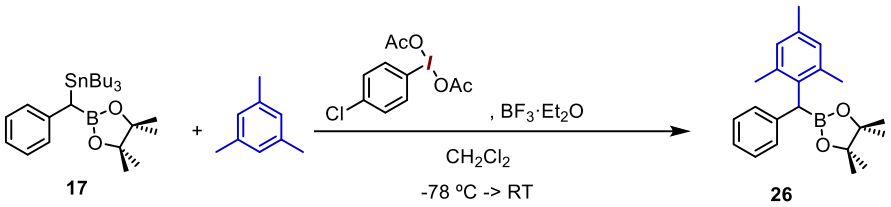


Figure S2. ^{1}H-NMR spectra in $CDCl_3$ of the crude competition experiment between $PhI(OAc)_2$ and mesitylene.

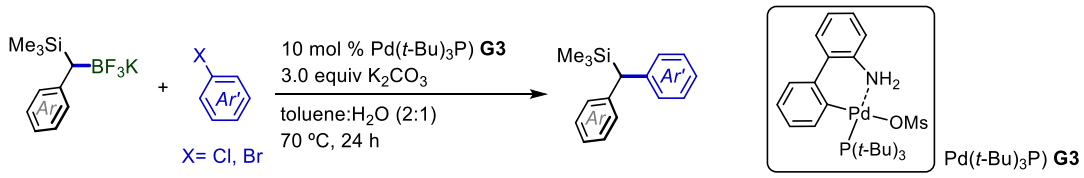
On-purpose umpolung arylation of 17 with mesitylene



A 15 mL reaction tube equipped with a stirbar was charged with the *p*-Cl-substituted λ^3-iodane (89 mg, 0.25 mmol) and benzyl *gem*-tributylstannyl boronate **17** (152 mg, 0.30 mmol). The content was frozen at -78°C in a dry CO_2/acetone bath and purged with argon via three evacuate / backfilled. Next, dry CH_2Cl_2 (1.75 mL) was added to the flask at -78°C, followed by the addition of mesitylene (104 µl, 0.75 mmol). At this temperature, $BF_3{\cdot}Et_2O$ (62 µL, 0.50 mmol) was added and the solution was stirred for 2h at -78°C, and then was allowed to reach room temperature slowly (*inside the dry ice/acetone bath*). Once at room temperature was stirred for an additional 1 hour. The solvent was evaporated under reduced pressure and resulting residue was purified by column chromatography on silica gel (hexanes:EtOAc = 50:1), R_f = 0.22. Prod. 20 was obtained as a white solid (46 mg, 55% based on the λ^3-iodane reagent).

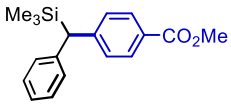
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 2H), 7.14 – 7.07 (m, 3H), 6.87 (s, 2H), 4.17 (s, 1H, C<u>H</u>BPin), 2.28 (s, 3H, *p*-Mes), 2.18 (s, 6H, *o*-Mes), 1.27 (s, 6H), 1.26 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.47, 137.37, 135.56, 135.12, 129.40, 128.47, 128.03, 125.01, 83.65 (O<u>C</u>$(CH_3)_2$), 33.20 (C-B, from HSQCAD 2D experiment), 25.06 (diast. OC(<u>C</u>$H_3)_2$), 24.87 (diast. OC(<u>C</u>$H_3)_2$), 21.34 (Mes *o*-CH_3), 21.04 (Mes *p*-<u>C</u>H_3). GC-HRMS (EI) *m/z* calcd for $C_{22}H_{29}BO_2$ $[M]^{+\cdot}$ 336.2255, found: 336.2253.

6. Pd-catalyzed arylation of the *gem*-silyl trifluoroborate salts



General procedure B: coupling using the *t*Bu$_3$P-Pd G3 catalyst.[1] *Reactions were conducted under argon atmosphere and solvents were deoxygenated prior to use; described here for a 0.2 mmol scale reaction*. A 15 mL reaction tube equipped with a stirbar and a screw-top septum cap was charged with the aryl halide (0.2 mmol, 1.0 equiv), the *gem*-silyl trifluoroborate precursor (0.4 mmol, 2.0 equiv), K_2CO_3 (0.60 mmol, 83 mg, 3.0 equiv) and the Pd-(*t*-Bu$_3$P) **G3** catalyst (0.02 mmol, 11 mg, 10 mol %). The tube was flushed with Ar, then toluene (deoxygenated, 0.4 mL) and water (deoxygenated, 0.2 mL) were added. The reaction was heated with stirring to 70 ºC for 2-18 h. Upon cooling to room temperature, the mixture was transferred to a small round bottom flask. A small of amount of silica gel was added and the solvent was evaporated. The resulting poweder was then used in flash column chromatography on silica gel eluting with a hexanes:EtOAc mixture as indicated. Alternatively, for larger scale reaction the crude reaction mixture was subjected to a workup with CH_2Cl_2 /H_2O and subsequent drying of the organic phase with $MgSO_4$. The residue was then purified by column chromatography.

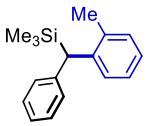
General procedure C: coupling using the RuPhos / Pd(Ac)$_2$ system.[2] A 15 mL reaction tube equipped with a stirbar and a screw-top septum cap was charged with the aryl halide (0.15 mmol, 1.0 equiv.), the *gem*-silyl trifluoroborate precursor (0.18 mmol, 1.2 equiv.), K_2CO_3 (0.45 mmol, 62 mg, 3.0 equiv), $Pd(OAc)_2$ (0.7 mg, 3.0 µmol, 2 mol%) and RuPhos (2.8 mg, 6.0 µmol, 4 mol%). The tube was flushed with Ar, then toluene (0.55 mL) and water (deoxygenated, 0.05 mL) were added. The reaction was heated with stirring to 75 °C for an indicated period of time. At this point, the workup was conducted as indicated in the General Procedure B..



(**29**). Following the general procedure B, methyl 4-chlorobenzoate (34 mg, 0.2 mmol) was allowed to react with the *gem*-Si-trifluoroborate salt **27a** (108 mg, 0.4 mmol) in the presence of Pd-(*t*-Bu$_3$P) **G3** catalyst (0.02 mmol, 11 mg, 10 mol %). Column chromatography: silica gel, eluent hexanes:EtOAc (50:1); R_f = 0.22. White solid, 59 mg. Yield: 99%.

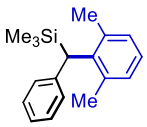
*The reaction was scaled to 2.00 mmol to give **29** as a white solid, 573 mg (Yield: 96%).*

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (pseudo d, *apparent J* = 8.5 Hz, 1H), 7.29 (pseudo d, *apparent J* = 8.1 Hz, 1H), 7.31 – 7.22 (m, 4H), 7.20 – 7.14 (m, 1H), 3.89 (s, 3H, OMe), 3.60 (s, 1H, SiC<u>H</u>), 0.04 (s, 9H, TMS). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.31 (C=O), 148.88, 142.01, 129.79, 129.06, 128.62, 128.47, 127.08, 125.62, 52.07 (O<u>C</u>H$_3$), 46.75 (Si<u>C</u>H), -1.62 (TMS). GC-HRMS (EI) *m/z* calcd for $C_{18}H_{22}O_2Si$ $[M]^{+\cdot}$ 298.1384, found: 298.1381.



(**30**). Following the general procedure B, 2-bromotoluene (34 mg, 24 µL, 0.2 mmol) was allowed to react with the *gem*-Si-trifluoroborate salt **27a** (108 mg, 0.4 mmol) in the presence of Pd-(*t*-Bu$_3$P) **G3** catalyst (0.02 mmol, 11 mg, 10 mol %). Column chromatography: silica gel, eluent: gradient from neat hexanes to hexane:EtOAc 50:1; R_f = 0.75 in 50:1 hexanes:EtOAc. Pale yellow oil, 50 mg. Yield: 98%.

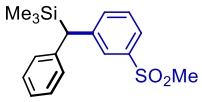
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.24 – 7.16 (m, 3H), 7.16 – 7.12 (m, 3H), 7.12 – 7.06 (m, 2H), 3.70 (s, 1H, C<u>H</u>SiMe$_3$), 2.25 (s, 3H), 0.08 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.72, 141.36, 137.23, 130.90, 129.73, 128.64, 128.22, 125.74, 125.65, 124.80, 41.38 (<u>C</u>HSiMe$_3$), 20.53 (Me), -1.22 (TMS). GC-MS (EI) *m/z* $C_{17}H_{22}Si$ $[M]^{+\cdot}$ 254.



(**31**) Following the general procedure B, 2,6-dibromotoluene (37 mg, 27 µL, 0.2 mmol) was allowed to react with the *gem*-Si-trifluoroborate salt **27a** (108 mg, 0.4 mmol) in the presence of Pd-(*t*-Bu$_3$P) **G3** catalyst (0.02 mmol, 11 mg, 10 mol %). Column chromatography: silica gel, eluent gradient from neat hexanes to hexane:EtOAc 50:1; R_f = 0.72 in 50:1 hexanes:EtOAc. Colorless oil, 35 mg. Yield: 65%.

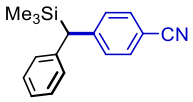
Evidence of hindered C-Xyl rotation by NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 2H), 7.16 – 7.08 (m, 3H), 7.03 (br s, 3H), 4.27 (s, 1H, C<u>H</u>SiMe$_3$), 2.33 (br s, 3H), 2.01 (br s, 3H), 0.16 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) (due to the fluxional behaviour, not all ^{13}C resonances could be

unequivocally located) δ 142.69, 140.23, 136.98 (br), 129.28, 128.29 (br), 128.19, 125.19, 124.78, 37.97 (CHSiMe$_3$), 22.24 (Me), 0.99 (TMS). GC-LRMS (EI) *m/z* $C_{18}H_{24}Si$ $[M]^{+\cdot}$ 268.



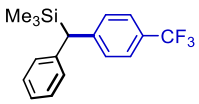
(**32**) Following the general procedure B, 1-bromo-3-(methylsulfonyl)benzene (47 mg, 0.2 mmol) was allowed to react with the *gem*-Si-trifluoroborate salt **27a** (108 mg, 0.4 mmol) in the presence of Pd-(*t*-Bu$_3$P) **G3** catalyst (0.02 mmol, 11 mg, 10 mol %). Column chromatography: silica gel, eluent hexanes:EtOAc (10:1 -> 4:1); R_f = 0.27 in 4:1 hexanes:EtOAc. Pale yellow solid, 63 mg. Yield: 99%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (t, *J* = 1.9 Hz, 1H), 7.71 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.53 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.26 – 7.21 (m, 2H), 7.21 – 7.16 (m, 1H), 3.63 (s, 1H, CHSi), 3.02 (s, 3H, SO_2Me), 0.05 (s, 9H, TMS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.21, 141.58, 140.64, 133.65, 129.42, 128.87, 128.77, 127.13, 125.83, 124.11, 46.38 (CHSi), 44.64 (SO_2Me), -1.72 (TMS). GC-LRMS (EI) *m/z* $C_{17}H_{22}O_2SSi$ $[M]^{+\cdot}$ 318.



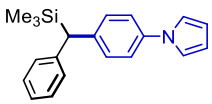
(**33**) Following the general procedure B, 4-chlorobenzonitrile (36 mg, 0.2 mmol) was allowed to react with the *gem*-Si-trifluoroborate salt **27a** (108 mg, 0.4 mmol) in the presence of Pd-(*t*-Bu$_3$P) **G3** catalyst (0.02 mmol, 11 mg, 10 mol %). Column chromatography: silica gel, eluent hexanes:EtOAc (50:1 -> 20:1); R_f = 0.36 in 20:1 hexanes:EtOAc. Colorless oil, 48 mg. Yield: 91%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (pseudo d, *J* = 8.6 Hz, 2H), 7.35 – 7.27 (m, 4H), 7.26 – 7.16 (m, 3H), 3.60 (s, 1H, CHSi), 0.05 (s, 9H, TMS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.17, 141.34, 132.22, 129.12, 128.98, 128.77, 125.94, 119.32, 108.80 (CN), 46.96 (CHSi), -1.67 (TMS). GC-LRMS (EI) *m/z* calcd for $C_{17}H_{19}NSi$ $[M]^{+\cdot}$ 265, found: 265.



(**34**) Following the general procedure B, 1-chloro-4-(trifluoromethyl)benzene (36 mg, 25 µL, 0.2 mmol) was allowed to react with the *gem*-Si-trifluoroborate salt **27a** (108 mg, 0.4 mmol) in the presence of Pd-(*t*-Bu$_3$P) **G3** catalyst (0.02 mmol, 11 mg, 10 mol %). Column chromatography: silica gel, eluent hexanes; R_f = 0.42. Colorless oil, 40 mg. Yield: 65%.

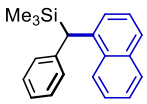
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.1 Hz, 2H), 7.35 – 7.27 (m, 4H), 7.26 – 7.22 (m, 2H), 7.21 – 7.15 (m, 1H), 3.60 (s, 1H, CHSi), 0.05 (s, 9H, TMS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.45, 141.98, 129.03, 128.73, 128.67, 127.43 (q, *J* = 32.3 Hz), 125.70, 125.34 (q, *J* = 3.8 Hz), 124.57 (q, *J* = 271.5 Hz, CF_3), 46.43 (CHSi), -1.64 (TMS). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.24. GC-LRMS (EI) *m/z* $C_{17}H_{19}F_3Si$ $[M]^{+\cdot}$ 308.



(**35**) Following the general procedure B, 1-(4-chlorophenyl)-1H-pyrrole (36 mg, 0.2 mmol) was allowed to react with the *gem*-Si-trifluoroborate salt **27a** (108 mg, 0.4 mmol) in the presence of Pd-(*t*-Bu$_3$P) **G3** catalyst (0.02 mmol, 11 mg, 10 mol %). Column

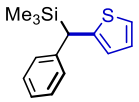
chromatography: silica gel, eluent hexanes:EtOAc (50:1); R_f = 0.26. White solid, 59 mg. Yield: 97%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 8H), 7.20 – 7.14 (m, 1H), 7.06 (pseudo t, *apparent J* = 2.2 Hz, 2H), 6.34 (pseudo t, *apparent J* = 2.2 Hz, 2H), 3.55 (s, 1H, CHSi), 0.08 (s, 9H, TMS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.79, 140.67, 138.29, 129.73, 128.84, 128.55, 125.39, 120.63, 119.43, 110.20, 45.60 (CHSi), -1.56 (TMS). GC-LRMS (EI) *m/z* $C_{20}H_{25}NSi$ $[M]^{+\cdot}$ 305.



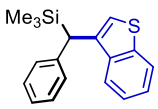
(**37**) Following the general procedure B, 1-chloronaphthalene (33 mg, 27 µL, 0.2 mmol) was allowed to react with the *gem*-Si-trifluoroborate salt **27a** (108 mg, 0.4 mmol) in the presence of Pd-(*t*-Bu_3P) **G3** catalyst (0.02 mmol, 11 mg, 10 mol %). Column chromatography: silica gel, eluent hexanes; R_f = 0.26. White solid, 57 mg. Yield: 99%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.09 (m, 1H), 7.85 – 7.79 (m, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.59 (dd, *J* = 7.2, 1.3 Hz, 1H), 7.47 (dd, *J* = 8.2, 7.2 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.25 – 7.18 (m, 4H), 7.10 – 7.05 (m, 1H), 4.33 (s, 1H, CHSi), 0.13 (s, 9H, TMS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.11, 138.96, 134.58, 133.10, 128.94, 128.45, 128.29, 127.30, 126.65, 125.93, 125.45, 125.20, 124.96, 124.39, 40.42 (CHSi), -1.04 (TMS). GC-LRMS (EI) *m/z* $C_{20}H_{22}Si$ $[M]^{+\cdot}$ 290.



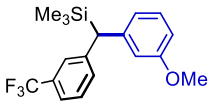
(**38**) Following the general procedure B, 2-bromothiophene (33 mg, 20 µL, 0.2 mmol) was allowed to react with the *gem*-Si-trifluoroborate salt **27a** (108 mg, 0.4 mmol) in the presence of Pd-(*t*-Bu_3P) **G3** catalyst (0.02 mmol, 11 mg, 10 mol %). Column chromatography: silica gel, eluent hexanes; R_f = 0.28. Colorless oil, 36 mg. Yield: 73%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.21 (m, 4H), 7.18 – 7.12 (m, 1H), 7.08 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.95 (dd, *J* = 5.2, 3.5 Hz, 1H), 6.89 (apparent doublet, *J* = 3.5 Hz, 1H), 3.78 (s, 1H, CHSi), 0.07 (s, 9H, TMS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.00, 142.53, 128.40, 128.08, 126.81, 125.33, 124.39, 122.67, 40.60 (CHSi), -1.97 (TMS). GC-LRMS (EI) *m/z* $C_{14}H_{18}SSi$ $[M]^{+\cdot}$ 246.



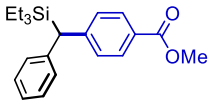
(**39**) Following the general procedure B, 3-bromobenzo[b]thiophene (43 mg, 26 µL, 0.2 mmol) was allowed to react with the *gem*-Si-trifluoroborate salt **27a** (108 mg, 0.4 mmol) in the presence of Pd-(*t*-Bu_3P) **G3** catalyst (0.02 mmol, 11 mg, 10 mol %). Column chromatography: silica gel, eluent hexanes:EtOAc (1:0 -> 50:1); R_f = 0.39 in 50:1 hexanes:EtOAc. Yellow oil, 52 mg. Yield: 88%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.81 (m, 1H), 7.70 – 7.63 (m, 1H), 7.35 (d, *J* = 0.7 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.26 – 7.18 (m, 4H), 7.13 – 7.07 (m, 1H), 3.90 (s, 1H, CHSi), 0.12 (s, 9H, TMS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.90, 140.04, 140.03, 136.66, 128.35, 128.17, 125.10, 124.27, 123.89, 122.80, 122.43, 121.99, 37.65 (CHSi), -1.52 (TMS). GC-LRMS (EI) *m/z* $C_{18}H_{20}SSi$ $[M]^{+\cdot}$ 296.



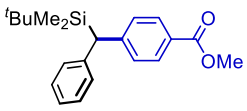
(**40**) Following a modification of the general procedure B, 3-bromoanisole (28 mg, 19 µL, 0.15 mmol) was allowed to react with the *gem*-Si-trifluoroborate salt **27-CF$_3$** (81 mg, 0.24 mmol) in the presence of K_2CO_3 (62 mg, 0.45 mmol, 3 equiv) and the Pd-(*t*-Bu_3P) **G3** catalyst (0.015 mmol, 8.6 mg, 10 mol %). Column chromatography: silica gel, eluent hexanes:EtOAc 20:1 R_f = 0.37. Colorless oil, 45 mg. Yield: 88%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 1.2, 0.6 Hz, 1H), 7.46 – 7.34 (m, 3H), 7.22 (ddd, *J* = 8.1, 7.6, 0.4 Hz, 1H), 6.83 (dddd, *J* = 7.7, 1.7, 0.9, 0.4 Hz, 1H), 6.80 – 6.76 (m, 1H), 6.73 (ddd, *J* = 8.2, 2.5, 0.9 Hz, 1H), 3.79 (s, 3H, OMe), 3.57 (s, 1H, C<u>H</u>SiMe$_3$), 0.06 (s, 9H, TMS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.81, 143.95, 143.63, 131.91 (q, *J* = 1.4 Hz), 130.69 (q, *J* = 31.7 Hz), 129.54, 128.83, 125.33 (q, *J* = 3.8 Hz), 124.42 (q, *J* = 272.3 Hz), 122.11 (q, *J* = 3.9 Hz), 121.38, 115.08, 110.54, 55.24 (O<u>C</u>H$_3$), 46.28 (<u>C</u>HSi), -1.64 (TMS). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.60 (s, CF_3). GC-LRMS (EI) *m/z* calcd for $C_{18}H_{21}FO_3Si$ $[M]^{+\cdot}$ 338, found: 338.



(**42**) Following a modification of the general procedure C, methyl 4-chlorobenzoate (17 mg, 0.10 mmol) was allowed to react with the *gem*-Si-trifluoroborate salt **27b** (34 mg, 0.11 mmol) in the presence of $Pd(OAc)_2$ (0.002 mmol, 0.5 mg, 2 mol %), 2-dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl (known as RuPhos ligand, 0.004 mmol, 1.8 mg, 4 mol %) and K_2CO_3 (0.30 mmol, 41 mg). Column chromatography: silica gel, eluent hexanes:EtOAc (40:1); R_f = 0.32 in 30:1 hexanes:EtOAc. Colorless oil, 28 mg. Yield: 82%.

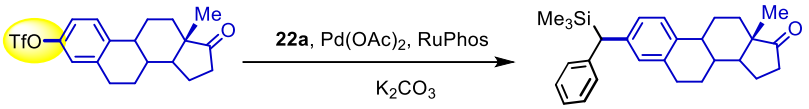
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (pseudo d, *apparent J* = 8.5 Hz, 2H), 7.32 (pseudo d, *apparent J* = 8.1 Hz, 2H), 7.29 – 7.25 (m, 4H), 7.20 – 7.13 (m, 1H), 3.89 (s, 3H, OMe), 3.74 (s, 1H, C<u>H</u>Si), 0.85 (t, *J* = 7.9 Hz, 9H), 0.65 – 0.56 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.31 (<u>C</u>=O), 148.95, 141.96, 129.78, 129.13, 128.59, 128.52, 127.02, 125.58, 52.06 (O<u>C</u>H$_3$), 43.68 (<u>C</u>HSi), 7.56, 3.49. GC-LRMS (EI) *m/z* calcd for $C_{21}H_{28}O_2Si$ $[M]^{+\cdot}$ 340, found: 340.



(**43**) Following a modification of the general procedure C, the reaction was scaled to 0.10 mmol, methyl 4-chlorobenzoate (17 mg, 0.10 mmol) was allowed to react with the *gem*-Si-trifluoroborate salt **27c** (34 mg, 0.11 mmol) in the presence of $Pd(OAc)_2$ catalyst (0.002 mmol, 0.5 mg, 2 mol %), 2-dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl (known as RuPhos ligand, 0.004 mmol, 1.8 mg, 4 mol %) and K_2CO_3 (0.30 mmol, 41 mg). Column chromatography: silica gel, eluent hexanes:EtOAc (40:1); R_f = 0.25 in 30:1 hexanes:EtOAc. Colorless oil, 24 mg. Yield: 71%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (pseudo d, *apparent J* = 8.5 Hz, 2H), 7.39 (pseudo d, *apparent J* = 8.3 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.29 – 7.24 (m, 2H), 7.19 – 7.12 (m, 1H), 3.88 (s, 3H, OMe), 3.68 (s, 1H, C<u>H</u>Si), 0.74 (s, 9H, ^{t}Bu), 0.05 (s, 3H, Me), 0.02 (s, 3H, Me). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.27 (<u>C</u>=O), 149.39, 142.62, 129.82, 129.23, 128.87, 128.62, 127.20, 125.71, 52.07 (O<u>C</u>H$_3$), 44.52 (<u>C</u>HSi), 27.21 (C(<u>C</u>H$_3$)$_3$), 18.04 (<u>C</u>(CH$_3$)$_3$), -5.62 (Me), -5.83 (Me). GC-LRMS (EI) *m/z* calcd for

$C_{21}H_{28}O_2Si$ $[M]^{+\cdot}$ 340, found: 340.



44

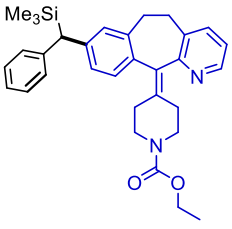
Following the general RuPhos-based procedure C, the Estrone-OTf precursor (60 mg, 0.15 mmol) was allowed to react with the *gem*-Si-trifluoroborate salt **27a** (49 mg, 0.18 mmol) in the presence of $Pd(OAc)_2$ (1.0 mg, 3 mol%), RuPhos (4.2 mg, 6 mol%) and K_2CO_3 (62 mg, 0.45 mmol). Reaction was conducted at 80 °C for 17h. Solvent was evaporated, residue absorbed onto silica gel and purified by column chromatography: hexane: gradient 40:1 to 10:1 EtOAc. Rf = 0.37 in 10:1 hexane:EtOAc. Colorless oil, slowly crystallizes into a white solid. Yield: 59 mg, 94%.

Similarly, the product could be accessed using the Estrone-Br precursor and employing the *t*Bu3P-Pd G3 system (94% yield).

Although the compound is likely a 1:1 mixture of diasteromers, the expected signal doubling is not readily evident in the 1H NMR spectrum. An exception is the estrone core Me resonance appearing as a poorly resolved doublet in 400 MHz spectrum. In contrast, extensive peak doubling is observed in the ^{13}C NMR spectrum of this compound, although at 400 MHz several of the very close peak separations are only observable when lowering the apodization exponential multiplier factor (i.e. line broadening) from 1.0 (default) to 0.0 (as per MestreNova processing)

^1H NMR (400 MHz, CD_2Cl_2) δ 7.28 – 7.16 (m, 5H), 7.16 – 7.07 (m, 1H), 7.07 – 6.99 (m, 1H), 6.98 – 6.93 (m, 1H), 3.44 (s, 1H), 2.92 – 2.82 (m; apear as dd, 2H), 2.49 – 2.36 (m, 2H), 2.27 (td, *J* = 12.1, 4.0 Hz, 1H), 2.16 – 1.96 (m, 3H), 1.94 – 1.85 (m, 1H), 1.67 – 1.38 (m, 6H), 0.89 (apparent d, at 400 MHz gives *J* = 1.8 Hz, 3H, C-Me), 0.03 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 221.0 (C=O), 143.82 (apparent d), 140.66 (splits into d at the value of *em*=0), 137.14 (splits into d at em=0), 136.89 (splits into d at em=0), 129.87, 129.70, 128.97, 128.60, 126.66, 126.52, 125.56 (splits into d at em=0), 125.31 (splits into d at em=0), 50.92, 48.28, 45.96, 45.92, 44.70, 44.67, 38.66, 38.63, 36.18, 32.10, 29.96, 29.88, 26.99, 26.15, 21.89, 14.11, -1.64. HRMS (ESI+), calcd for $C_{28}H_{37}OSi$ $(M+H)^+$: *m/z* 417.2608, found: 417.2606.



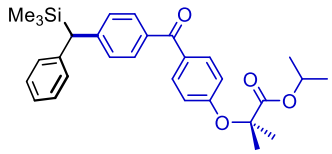
(**45**) Following the general RuPhos-based procedure C, the Ar-Cl substrate Loratadine (57 mg, 0.15 mmol) was allowed to react with the *gem*-Si-trifluoroborate salt **27a** (49 mg, 0.18 mmol) in the presence of $Pd(OAc)_2$ (0.7 mg, 2 mol%), RuPhos (2.8 mg, 4 mol%) and K_2CO_3 (62 mg, 0.45 mmol). Reaction was conducted at 75 °C for 15h. Column chromatography: silica gel, gradient 2:1 to 1:2 hexane:EtOAc; R_f = 0.31 in 1:2 Hexane:EtOAc. White solid, 72 mg. Yield: 94%.

The presence of the carbamate group caused some broadening to the NMR resonances. In solution, the two N-C rotamers are present in exactly a 1:1 ratio, causing some of the peaks to

appear as closely spaced doublets. This includes the benzylic CH and $SiMe_3$ in ^1H, as well as several of the peaks in ^{13}C. This phenomenon also led to a somewhat low s/n ratio in the ^{13}C spectrum even at 1k scans.

^1H NMR (400 MHz, $CDCl_3$) δ 8.38 (apparent dt, *J* = 4.7, 2.1 Hz, 1H), 7.42 (apparent ddd, *J* = 7.8, 3.9, 1.7 Hz, 1H), 7.30 – 7.17 (m, 4H), 7.17 – 7.00 (m, 4H), 6.99 (d, *J* = 6.1 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.79 (br s, 2H), 3.441 and 3.433 (two singlets, together appear as a doublet integrating for 1H, C<u>H</u>$SiMe_3$), 3.43 – 3.26 (m, 2H), 3.19 – 3.05 (m, 2H), 2.86 – 2.70 (m, 2H), 2.54 – 2.20 (m, 4H), 1.24 (t, *J* = 7.0 Hz, 3H), 0.014 and 0.006 (two singlets, together appear as a doublet integrating for 9H, $SiMe_3$).

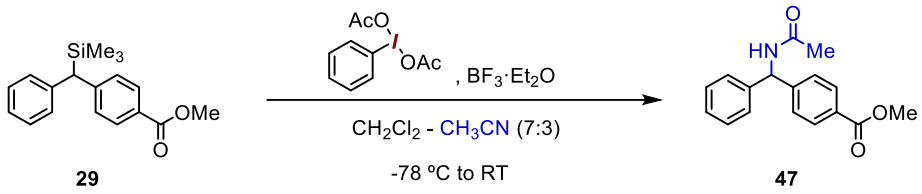
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.27 + 158.10 (pair), 155.65, 146.58 + 146.56 (pair), 142.97 + 142.95 (pair), 142.09 + 142.08 (pair), 137.45 + 137.38 (pair), 137.33 + 137.26 (pair), 136.48 + 136.45 (pair), 135.74 + 135.58 (possible pair), 135.34 + 135.31 (pair), 134.03 + 133.99 (pair), 129.61, 129.57, 129.50, 129.40, 128.86 + 128.81 (pair), 128.41 + 128.40 (pair), 126.33 + 126.18 (pair), 125.21 + 125.19 (pair), 122.14, 61.37, 46.03 + 45.91 (pair), 45.07 + 44.97 (pair), 32.31 + 32.26 (pair), 31.92 + 31.84 (pair), 30.86 + 30.66 (possible pair), 25.00, 14.83, -1.51 and -1.54 (pair, $SiMe_3$). HRMS (ESI+) calcd for $C_{32}H_{39}N_2O_2Si^+$ $(M+H)^+$: *m/z* 511.2775, found: 511.2793.



(**46**) Following a modification of the general procedure B, the reaction was run on the 0.09 mmol scale. The isopropyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (known as Fenofibrate, 33 mg, 0.09 mmol) was allowed to react with the *gem*-Si-trifluoroborate salt **27a** (49 mg, 0.18 mmol) in the presence of Pd-(*t*-Bu_3P) **G3** catalyst (0.009 mmol, 5 mg, 10 mol %). Column chromatography: silica gel, eluent hexanes:EtOAc (10:1); R_f = 0.20. White solid, 43 mg. Yield: 97%.

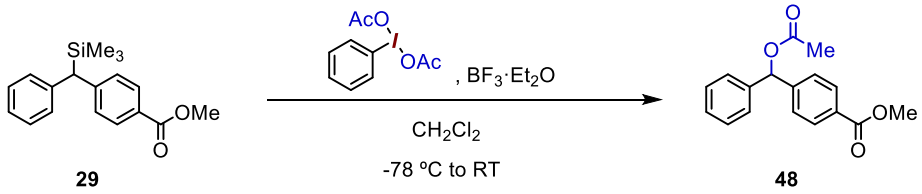
^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (pseudo d, *J* = 9.0 Hz, 2H), 7.68 (pseudo d, *J* = 8.5 Hz, 2H), 7.34 – 7.27 (m, 6H), 7.21 – 7.15 (m, 1H), 6.85 (pseudo d, *J* = 9.0 Hz, 2H), 5.08 (hept, *J* = 6.2 Hz, 1H, C<u>H</u>$(CH_3)_2$), 3.62 (s, 1H, C<u>H</u>Si), 1.65 (s, 6H, $(C\underline{H}_3)_2$-C-C=O), 1.20 (d, *J* = 6.3 Hz, 6H, CH$(C\underline{H}_3)_2$), 0.06 (s, 9H, TMS). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.37 (ketone <u>C</u>=O), 173.35 (<u>C</u>O_2CH), 159.45, 148.11, 142.12, 134.99, 132.05, 131.10, 130.25, 129.10, 128.63, 128.30, 125.63, 117.29, 79.48 (O<u>C</u>(CH_3)), 69.42 (O<u>C</u>H$(CH_3)_2$), 46.76 (<u>C</u>HSi), 25.53 (diast. OC(<u>C</u>H_3)), 25.51 (diast. OC(<u>C</u>H_3)), 21.67 (OCH(<u>C</u>$H_3)_2$), -1.58 (TMS). GC-LRMS (EI) *m/z* calcd for $C_{30}H_{36}O_4Si$ $[M]^{+\cdot}$ 488, found: 488.

7. Umpolung transformations



An oven-dried screw cap tube equipped with a magnetic stirbar was charged with the *bis*-aryl silane **29** (30 mg, 0.10 mmol) and (diacetoxyiodo)benzene (39 mg, 0.12 mmol). The flask was evacuated and backfilled with argon 3 times. A dry solvent mixture of CH_2Cl_2/CH_3CN (7:3, 0.7 mL total) was added, and the content was cooled to -78 °C in a dry ice/acetone bath. Then, $BF_3{\cdot}Et_2O$ (25 µL, 0.20 mmol) was added *via* syringe and the resulting mixture was allowed to reach room temperature slowly during 1h (*inside the dry ice/acetone bath*). Once at room temperature, stirring was continued for an additional 1 hour. The solvent was evaporated and the residue was purified by column chromatography on silica gel (DCM:MeOH = 40:1), R_f = 0.21.Yellow solid, 26 mg, 93%.

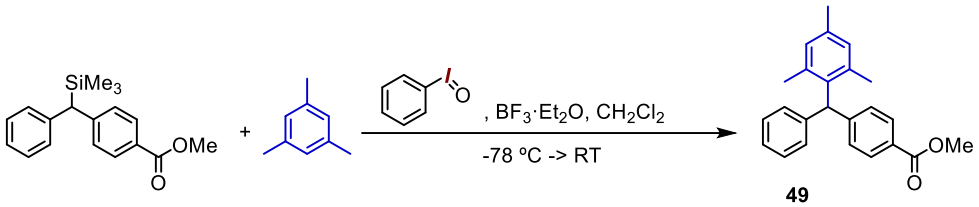
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (approximately a doublet, *J* = 8.5 Hz + 2nd order effects, 2H), 7.37 – 7.23 (m, 5H), 7.22 – 7.14 (m, 2H), 6.42 (d, *J* = 8.0 Hz, 1H, N<u>H</u>), 6.25 (d, *J* = 8.0 Hz, 1H, C<u>H</u>-N), 3.88 (s, 3H, OC<u>H</u>$_3$), 2.03 (s, 3H, C(O)C<u>H</u>$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.42 (N-<u>C</u>OCH$_3$), 166.89 (<u>C</u>O$_2$CH$_3$), 146.71, 140.98, 130.01, 129.31, 128.96, 127.93, 127.70, 127.38, 56.99 (<u>C</u>H-NH), 52.23 (O<u>C</u>H$_3$), 23.32 (C(O)<u>C</u>H$_3$).



An oven-dried screw cap tube equipped with a magnetic stirbar was charged with the *bis*-aryl silane **29** (30 mg, 0.10 mmol) and (diacetoxyiodo)benzene (39 mg, 0.12 mmol). The flask was evacuated and backfilled with argon 3 times. A dry CH_2Cl_2 (0.7 mL) was added, and the content was cooled at -78 °C in a dry ice/acetone. Then, $BF_3{\cdot}Et_2O$ (25 µL, 0.20 mmol) was added *via* syringe and the resulting mixture was allowed to reach room temperature slowly (*inside the dry ice/acetone bath*). Once at room temperature, stirring was allowed to continue for an additional 1 hour. The solvent was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel (hexanes:EtOAc = 10:1 -> 4:1), R_f = 0.26 (10:1 hexanes:EtOAc). Colorless oil (24 mg, 84%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (pseudo d, *J* = 8.5 Hz, 2H), 7.42 (pseudo d, *J* = 8.1 Hz, 2H), 7.37 – 7.28 (m, 5H), 6.90 (s, 1H, C<u>H</u>-O), 3.90 (s, 3H, OC<u>H</u>$_3$), 2.18 (s, 3H, C(O)C<u>H</u>$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.02 (O<u>C</u>OCH$_3$), 166.83 (<u>C</u>O$_2$CH$_3$), 145.27, 139.65, 129.98, 129.79, 128.79, 128.39, 127.38, 126.96, 76.57 (<u>C</u>H-O), 52.28 (O<u>C</u>H$_3$), 21.35 (CO<u>C</u>H$_3$).

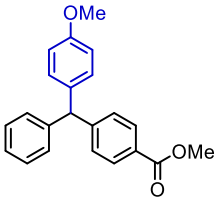
Synthesis of triarylmethanes



49

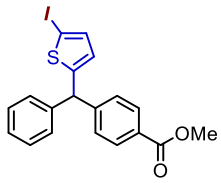
An oven-dried screw cap tube equipped with a magnetic stirbar was charged with the *bis*-aryl methylsilane **29** (30 mg, 0.1 mmol) and iodosyl benzene (26 mg, 0.12 mmol). The flask was evacuated and backfilled with argon 3 times. Dry dichloromethane (0.5 mL) was added, and the content was cooled to a temperature between -30 to -25 °C in a dry ice/acetone bath (temperature adjusted by controlled additions of dry ice). Then, $BF_3{\cdot}Et_2O$ (25 µL, 0.20 mmol) was added *via* syringe and the resulting mixture was stirred at this low temperature for 10 minutes. After that time, the content was cooled to -78 °C and mesitylene (139 µL, 1.0 mmol) was added under argon atmosphere. The flask was sealed and allowed to reach room temperature slowly (*inside the dry ice/acetone bath*). Once at room temperature, the mixture was stirred for an additional 1 hour. The solvent was evaporated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (hexanes:EtOAc = 50:1 -> 20:1), R_f = 0.41 (20:1 hexanes:EtOAc). White solid (28 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.89 (m, 2H), 7.32 – 7.26 (m, 2H), 7.26 – 7.20 (m, 1H), 7.20 – 7.15 (m, 2H), 7.11 – 7.07 (m, 2H), 6.87 (s, 2H), 6.02 (s, 1H, Ar-C<u>H</u>-Ar), 3.91 (s, 3H, OC<u>H</u>$_3$), 2.29 (s, 2H), 1.99 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.22 (<u>C</u>=O), 148.77, 141.47, 137.64, 136.51, 130.36, 129.60, 129.46, 129.39, 128.47, 127.99, 126.40, 52.15 (O<u>C</u>H$_3$), 51.29 (Ar-<u>C</u>H), 22.11, 20.95. GC-HRMS (EI) *m/z* calcd for $C_{24}H_{24}O_2$ $[M]^{+\cdot}$ 344.1771, found: 344.1769.



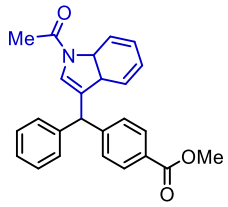
(**50**) Following the procedure used for the substituted triaryl-methane **49**, the *bis*-aryl methylsilane precursor **29** (15 mg, 0.05 mmol) was allowed to react with iodosylbenzene (22 mg, 0.10 mmol), $BF_3{\cdot}Et_2O$ (19 µL, 0.15 mmol) and anisole (27 µL, 0.25 mmol). Column chromatography: silica gel, eluent hexanes:EtOAc (20:1); R_f = 0.20. White solid, 15 mg. Yield: 88%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (pseudo d, *J* = 8.6 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.25 – 7.20 (m, 1H), 7.21 – 7.16 (m, 2H), 7.11 – 7.07 (m, 2H), 7.01 (pseudo dd, *J* = 8.9, 0.6 Hz, 2H), 6.84 (pseudo d, *J* = 8.8 Hz, 2H), 5.55 (s, 1H, Ar-CH), 3.90 (s, 3H, $CO_2C\underline{H}_3$), 3.79 (s, 3H, OC<u>H</u>$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.16 (<u>C</u>=O), 158.37, 149.79, 143.56, 135.37, 130.47, 129.76, 129.55, 129.45, 128.58, 128.35, 126.66, 113.97, 56.13 (Ar-<u>C</u>H), 55.38 (O<u>C</u>H$_3$), 52.18 ($CO_2\underline{C}H_3$). GC-HRMS (EI) *m/z* calcd for $C_{22}H_{20}O_3$ $[M]^{+\cdot}$ 332.1407, found: 332.1405.



(**51**) Following a modification of the procedure used for the synthesis of the substituted triaryl-methane **49**, the *bis*-aryl methylsilane precursor **29** (30 mg, 0.10 mmol) was allowed to react with iodosylbenzene (44 mg, 0.20 mmol), $BF_3{\cdot}Et_2O$ (38 µL, 0.30 mmol) and 2-iodothiophene (56 µL, 0.50 mmol). Column chromatography: silica gel, eluent hexanes:EtOAc (20:1) ; R_f = 0.30. White solid, 36 mg. Yield: 82%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.35 – 7.24 (m, 5H), 7.20 – 7.16 (m, 2H), 7.09 (d, *J* = 3.7 Hz, 1H), 6.37 (dd, *J* = 3.7, 1.1 Hz, 1H), 5.68 (s, 1H, Ar-C<u>H</u>), 3.90 (s, 3H, OC<u>H</u>$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.96 (<u>C</u>=O), 153.13, 148.30, 142.40, 136.77, 130.00, 129.04, 128.96, 128.87, 128.82, 128.42, 127.40, 72.60 (<u>C</u>-*I*), 52.32, 52.26. GC-HRMS (EI) *m/z* calcd for $C_{19}H_{15}IO_2S$ $[M]^{+\cdot}$ 433.9832, found: 433.9830.



(**52**) Following a modification of the procedure used for the synthesis of the substituted triaryl-methane **49**, at the same scale, the *bis*-aryl methylsilane precursor **29** (15 mg, 0.05 mmol) was allowed to react with iodosylbenzene (22 mg, 0.10 mmol), $BF_3{\cdot}Et_2O$ (19 µL, 0.15 mmol) and *N*-acetyl indole (40 mg, 0.25 mmol). Column chromatography: silica gel, eluent hexanes:EtOAc (10:1 -> 4:1) ; R_f = 0.33 in 4:1 hexanes:EtOAc. White solid, 12 mg. Yield: 63%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.27 (m, 6H), 7.23 – 7.19 (m, 2H), 7.17 – 7.09 (m, 2H), 6.74 (s, 1H, C<u>H</u>NAc), 5.64 (s, 1H, ArC<u>H</u>), 3.91 (s, 3H, OC<u>H</u>$_3$), 2.49 (s, 3H, COC<u>H</u>$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.56 (N-<u>C</u>OCH$_3$), 167.06 (<u>C</u>OOMe), 147.72, 141.60, 136.49, 130.06, 129.90, 129.11, 129.01, 128.90, 128.87, 127.20, 125.61, 125.56, 124.72, 123.69, 120.06, 116.80, 52.25 (O<u>C</u>H$_3$), 48.71 (Ar-<u>C</u>H), 24.12.

8. References

[1] Conditions adapted from: L. Li, S. Zhao, A. Joshi-Pangu, M. Diane and M. R. Biscoe, *J. Am. Chem. Soc*. 2014, **136**, 14027–14030.

[2] Catalytic conditions based on: S. D. Dreher, S.-E. Lim, D. L. Sandrock and G. A. Molander, *J. Org. Chem*. 2009, **74**, 3626–3631

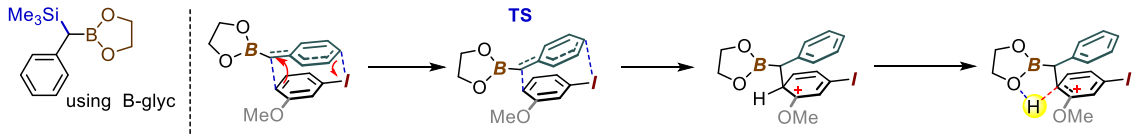
9. Computational details

All calculations were performed using Gaussian 09[3] by adapting a method described by Vasdev, Liang and co-workers for a series of iodine(III)-containing species.[4]

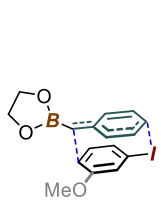
Geometry optimizations. All calculations were performed at the DFT level using the B3LYP functional with an ultrafine integration grid. The 6-31+G(d,p) basis set was used for C,H,O and S, while using for iodine the augmented LANL2DZ(dp) set described by Gilbert, Sunderlin and co-workers. [10] Empirical dispersion was applied using the D3 version of Grimme dispersion with Becke-Johnson damping (gd3BJ keyword).[5] All structures were fully optimized in dichloromethane using the SMD continuum model. Transition states were identified by having one imaginary frequency in the Hessian matrix. It was confirmed that transition states connect with the corresponding intermediates by means of application of the eigenvector corresponding to the imaginary frequency and subsequent optimization of the resulting structures. All energies collected in the text are Gibbs energies in solvent at 298 K.

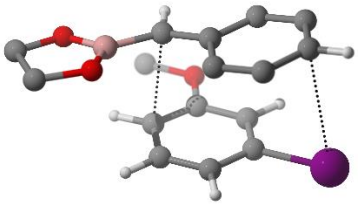
Single point energy calculations. Energy calculations were performed for the previously optimized structures using the PBE0 functional and the Aug-cc-pvtz basis set for C,H,O and S atoms and the DB-aug-cc-pVTZ for iodine. Calculations were performed in dichloromethane (SMD continuum model) and applying the D3 version of Grimme dispersion with Becke-Johnson damping (gd3BJ keyword).

Energy profile for the coupling between the *m*-iodoanisole core and the a-Bgly-benzyl fragment



Species: cationic PhI+ benzyl(Bgly)+ π adduct
Stoichiometry: $C_{16}H_{17}BIO_3$
Charge: 1 Multiplicity: 1





Coordinates (xyz)

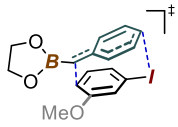
I	3.25680028	0.12479743	-0.60243879
C	1.26179978	0.75469327	-0.68511949
C	0.41335427	0.20107066	-1.67343582
C	0.80767233	1.71097913	0.21728324
C	-0.90327636	0.62269095	-1.72358312
H	0.79307052	-0.52224320	-2.38403318
C	-0.53757676	2.10572124	0.17367018
H	1.45862709	2.14774831	0.96465380
C	-1.41045272	1.53332217	-0.77823125
H	-1.56931070	0.22134681	-2.47950078
H	-2.43800494	1.86333158	-0.85400548
C	-1.88163955	-0.36440883	1.11191530
H	-2.06386355	0.41514593	1.84917079

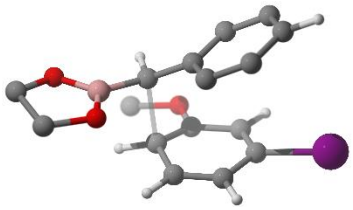
C	-0.66429660	-1.03219065	1.23189995
C	-0.27887650	-2.08296464	0.33513378
C	0.24652498	-0.65081803	2.27297605
C	0.93572837	-2.72403523	0.49644241
H	-0.96024418	-2.37293538	-0.45460375
C	1.45104654	-1.30104089	2.42519065
H	-0.03749469	0.15332667	2.94403751
C	1.80151560	-2.33116964	1.52916994
H	1.22880153	-3.51764184	-0.18131225
H	2.13623589	-1.01540976	3.21506743
H	2.75476562	-2.83610980	1.64666827
C	-4.39780864	-1.67557346	-1.41164054
C	-5.20214442	-0.59270779	-0.65342207
H	-4.19698398	-1.40357969	-2.45080161
H	-4.86830912	-2.65917727	-1.37806476
H	-5.60227184	0.17967329	-1.31238038
H	-6.01121637	-1.01200886	-0.05101992
B	-3.09271527	-0.71728695	0.18247081
O	-3.12607426	-1.74645672	-0.71310499
O	-4.24104430	0.01815627	0.24663280
O	-0.91578278	3.01329633	1.09760872
C	-2.26327735	3.51115542	1.07257987
H	-2.98270221	2.70362295	1.24025990
H	-2.32132134	4.23026389	1.88774319
H	-2.47287884	4.00892824	0.12112509

Imaginary frequencies: none

E(RPBE1PBE)=	-881.083456	Hartrees
Thermal correction to Gibbs Free Energy=	0.251811	
Sum of electronic and thermal Free Energies=	-880.831645	

Species: cationic transition state
Stoichiometry: $C_{16}H_{17}BIO_3$
Charge: 1 Multiplicity: 1





Coordinates (xyz)

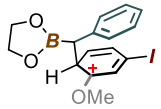
C	1.39857965	0.72564065	-0.69061560
C	0.53369971	0.20353413	-1.70215763
C	0.98392007	1.70357847	0.20409799
C	-0.77672700	0.58120859	-1.70088031
H	0.92057001	-0.48099122	-2.44624446
C	-0.35657734	2.10439569	0.19240390
H	1.66088164	2.15150479	0.92056974
C	-1.30703508	1.39544049	-0.63266150
H	-1.46417464	0.18455484	-2.43820291
H	-2.27098890	1.86215393	-0.80397448
I	3.34434957	-0.00247009	-0.57565686
C	-1.86209385	0.02179343	0.73196401
H	-2.09697988	0.72423370	1.53007912
C	-0.74828037	-0.85357767	1.07335114
C	-0.42563119	-1.99643620	0.30630229
C	0.04828240	-0.55155917	2.20301224
C	0.64966416	-2.80555614	0.66300530
H	-1.02544048	-2.24214247	-0.56153544
C	1.11809341	-1.36254641	2.55815648
H	-0.18540656	0.32868505	2.79502485
C	1.42646441	-2.48834742	1.78192487
H	0.88871843	-3.67839388	0.06463114

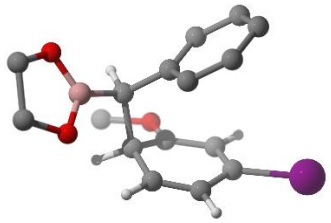
H	1.71912218	-1.11859036	3.42771550
H	2.26963252	-3.11619668	2.05158895
C	-4.54424617	-1.49249226	-1.49792434
C	-5.37287806	-0.75022642	-0.42600654
H	-4.60365495	-1.01819560	-2.48078166
H	-4.80575721	-2.54776029	-1.58623939
H	-6.07702348	-0.03269194	-0.84966746
H	-5.90430844	-1.43294136	0.24142815
B	-3.15728566	-0.49746621	0.00112851
O	-3.17144936	-1.38925321	-1.03226039
O	-4.38749181	-0.02842736	0.36065952
O	-0.69741812	3.05007700	1.05995215
C	-2.01143958	3.65344489	1.01457673
H	-1.98003846	4.44908601	1.75559617
H	-2.19997176	4.06922998	0.02196526
H	-2.78117560	2.92776222	1.28411332

Imaginary frequencies: one

E(RPBE1PBE)=	-881.085049	Hartrees
Thermal correction to Gibbs Free Energy=	0.251811	
Sum of electronic and thermal Free Energies=	-880.832653	

Species: cationic (Bgly)CH(Ph)-(H-*p*-I-anisole)
Stoichiometry: $C_{16}H_{17}BIO_3$
Charge: 1 Multiplicity: 1





Coordinates (xyz)

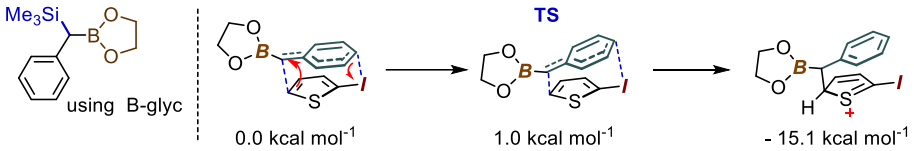
C	1.61721295	0.69253725	-0.57510877
C	0.74362767	0.39087919	-1.67791965
C	1.24732099	1.53939002	0.45800689
C	-0.54264590	0.80473889	-1.62534563
H	1.12077644	-0.17620020	-2.51968661
C	-0.05712882	2.04398244	0.47452933
H	1.93806312	1.83732691	1.23692947
C	-1.09443615	1.48126931	-0.42575221
H	-1.24284193	0.55697106	-2.41390089
H	-1.83801686	2.22972287	-0.70969238
I	3.50695817	-0.16273179	-0.56220969
C	-1.90825030	0.37758230	0.47589019
H	-2.23728153	0.91944178	1.36614675
C	-1.03982231	-0.77412249	0.93552187
C	-0.77683695	-1.87083970	0.10027011
C	-0.47118665	-0.75447265	2.21836664
C	0.04828609	-2.91234120	0.52939962
H	-1.21126118	-1.91068972	-0.89392364
C	0.35349483	-1.79358401	2.65076225
H	-0.67403067	0.08222068	2.88123074
C	0.62082844	-2.87354760	1.80337691
H	0.24380661	-3.75051522	-0.13206655
H	0.78667663	-1.75952179	3.64553277
H	1.26615004	-3.68058555	2.13587713
C	-4.71003156	-0.64768196	-1.89979039
C	-5.26649867	-1.06352021	-0.51983903
H	-5.25705809	0.18881957	-2.34165257
H	-4.66976643	-1.47369390	-2.61143495
H	-6.24976334	-0.63927173	-0.31076466
H	-5.30314890	-2.14833103	-0.39173008
B	-3.21570957	-0.11873201	-0.26687984

O	-3.35404702	-0.20332860	-1.62473223
O	-4.31302103	-0.52795371	0.43452312
O	-0.32953730	2.92446328	1.40718961
C	-1.58013982	3.66523060	1.42824792
H	-1.45854405	4.38431908	2.23432892
H	-1.71741161	4.17949133	0.47550933
H	-2.41650375	3.00049204	1.64126963

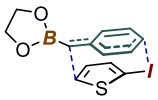
Imaginary frequencies: none

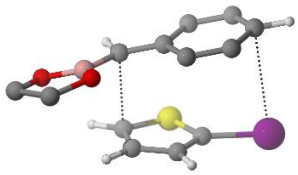
E(RPBE1PBE)= -881.094931 Hartrees
Thermal correction to Gibbs Free Energy= 0.25272
Sum of electronic and thermal Free Energies= -880.842211

Energy profile for the coupling between the 2-iodothiophene core and the a-Bgly-benzyl fragment



Species: cationic 2-I-Thip+ benzyl(Bgly)+ π adduct
Stoichiometry: $C_{13}H_{13}BIO_2S$
Charge: 1 Multiplicity: 1





Coordinates (xyz)

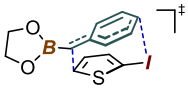
C	-1.07949500	-1.10655300	-0.12595900
C	-0.06425300	-1.26331200	-1.05689800
C	1.12517300	-1.73807700	-0.46404600
H	-0.17920400	-1.03598300	-2.10855600
C	1.02000800	-1.90540900	0.91271600
H	2.03072800	-1.95361600	-1.01726100
H	1.76101400	-2.31798500	1.58387800
I	-2.98481200	-0.41948500	-0.49676800
C	1.97596500	0.58454500	1.10045600
H	2.05526800	0.30792900	2.14995400
C	0.84942300	1.33372300	0.74979700
C	0.61003700	1.76103400	-0.59696100
C	-0.12251700	1.65965200	1.75132500
C	-0.52649000	2.48329200	-0.90849000
H	1.33798600	1.51617500	-1.36030100
C	-1.25121600	2.38437500	1.42882200
H	0.04946300	1.33361400	2.77159800
C	-1.46109300	2.78455600	0.09604900
H	-0.70795100	2.80302700	-1.92837900
H	-1.98292900	2.63049300	2.18980500
H	-2.35532700	3.34455500	-0.15780200
C	4.69379900	0.14127000	-1.51477000
C	5.29080000	-0.56637500	-0.27490700
H	4.45250000	-0.55382000	-2.32276200
H	5.33072900	0.93892900	-1.89972000
H	5.54925900	-1.60966800	-0.46332900
H	6.16005700	-0.04401400	0.13128300
B	3.23384000	0.26347500	0.22365400
O	3.45140300	0.72734400	-1.04241400
O	4.23431700	-0.52198900	0.71938800

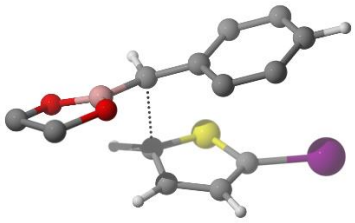
S	-0.58264900	-1.58771900	1.47771500

Imaginary frequencies: none

E(RPBE1PBE)=	-1087.344678	Hartrees
Thermal correction to Gibbs Free Energy=	0.186855	
Sum of electronic and thermal Free Energies=	-1087.157824	

Species: cationic transition state, 2-I-Thip+ benzyl(Bgly)+
Stoichiometry: $C_{13}H_{13}BIO_2S$
Charge: 1 Multiplicity: 1





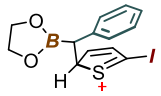
Coordinates (xyz)

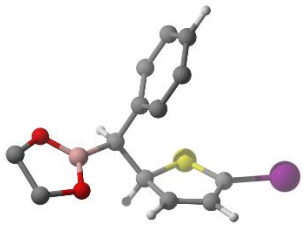
C	-1.13893946	-1.11989325	-0.15852628
C	-0.19619680	-1.24874537	-1.18926858
C	1.04661071	-1.64159931	-0.70401539
H	-0.42190754	-1.04257027	-2.22703648
C	1.10546779	-1.69719712	0.70918813
H	1.91556933	-1.80877501	-1.32935976
H	1.86516610	-2.21905846	1.27798970
I	-3.06051450	-0.43511884	-0.38875943
C	1.87326033	0.32782138	1.03195111
H	1.94840047	0.12807100	2.09943931
C	0.82414571	1.23862814	0.67273901
C	0.63602533	1.68645390	-0.66158377
C	-0.08663757	1.68291445	1.66839307
C	-0.41181984	2.54289064	-0.97781208
H	1.32391882	1.35940288	-1.43123018
C	-1.12639185	2.54033831	1.34877770
H	0.04133502	1.34150581	2.69074389
C	-1.29880474	2.96191526	0.02039908
H	-0.54838401	2.87573487	-2.00105070
H	-1.81331375	2.87460868	2.11862807
H	-2.12349346	3.62062173	-0.23226284
C	4.81597528	0.18241868	-1.36573690
C	5.34420686	-0.58539532	-0.13258074
H	4.65253333	-0.46765202	-2.22917062
H	5.45436813	1.01814117	-1.65545676
H	5.68520149	-1.59397964	-0.37098756
H	6.13801507	-0.04659835	0.39047068
B	3.22201483	0.13047617	0.25286949
O	3.52662740	0.70519119	-0.94735976
O	4.20097858	-0.67714469	0.75776565
S	-0.51015456	-1.56738806	1.38652452

Imaginary frequencies: one

E(RPBE1PBE)=	-1087.345806	Hartrees
Thermal correction to Gibbs Free Energy=	0.189645	
Sum of electronic and thermal Free Energies=	-1087.156161	

Species: cationic final (bora-)benzylation species of 2-iodothiophene
Stoichiometry: $C_{13}H_{13}BIO_2S$
Charge: 1 Multiplicity: 1





Coordinates (xyz)

C	-1.76381596	-0.75937473	0.01926619
C	-0.98808153	-1.29447855	-1.05507972
C	0.30107410	-1.52433431	-0.69058353
H	-1.40800142	-1.48443695	-2.03418294
C	0.65214222	-1.19151619	0.71367939
H	1.06518462	-1.93206403	-1.34308526
H	0.86466921	-2.12627996	1.25406586
I	-3.75061099	-0.28950215	-0.15579329
C	1.83387080	-0.20146856	0.91983028
H	1.96708707	-0.09155176	2.00073938
C	1.53700687	1.17246307	0.33171101
C	1.50994692	1.37560664	-1.05599382
C	1.27394310	2.25752506	1.17921366
C	1.20500196	2.63195163	-1.58524575
H	1.73661272	0.55599842	-1.73189937
C	0.97424854	3.51603367	0.65262020
H	1.29984143	2.11465869	2.25592647
C	0.93432630	3.70531841	-0.73187303
H	1.18740506	2.77201897	-2.66163610
H	0.77183235	4.34559847	1.32304502
H	0.70053471	4.68264989	-1.14246031
C	5.44267855	-0.92074793	0.00266928
C	4.70167533	-1.90598937	-0.92834617
H	5.89363070	-0.08757372	-0.54240618
H	6.20132711	-1.40521868	0.61927110
H	4.94393266	-1.76327345	-1.98246428
H	4.86501150	-2.95108334	-0.65392476
B	3.20319644	-0.75897150	0.34619104
O	4.40729533	-0.38588620	0.86788136
O	3.29432048	-1.60320445	-0.72812694
S	-0.91373106	-0.54651117	1.46349108

Imaginary frequencies: none

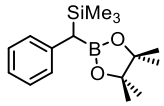
E(RPBE1PBE)=	-1087,370396	Hartrees
Thermal correction to Gibbs Free Energy=	0.188504	
Sum of electronic and thermal Free Energies=	-1087,181892	

[3] 9. Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

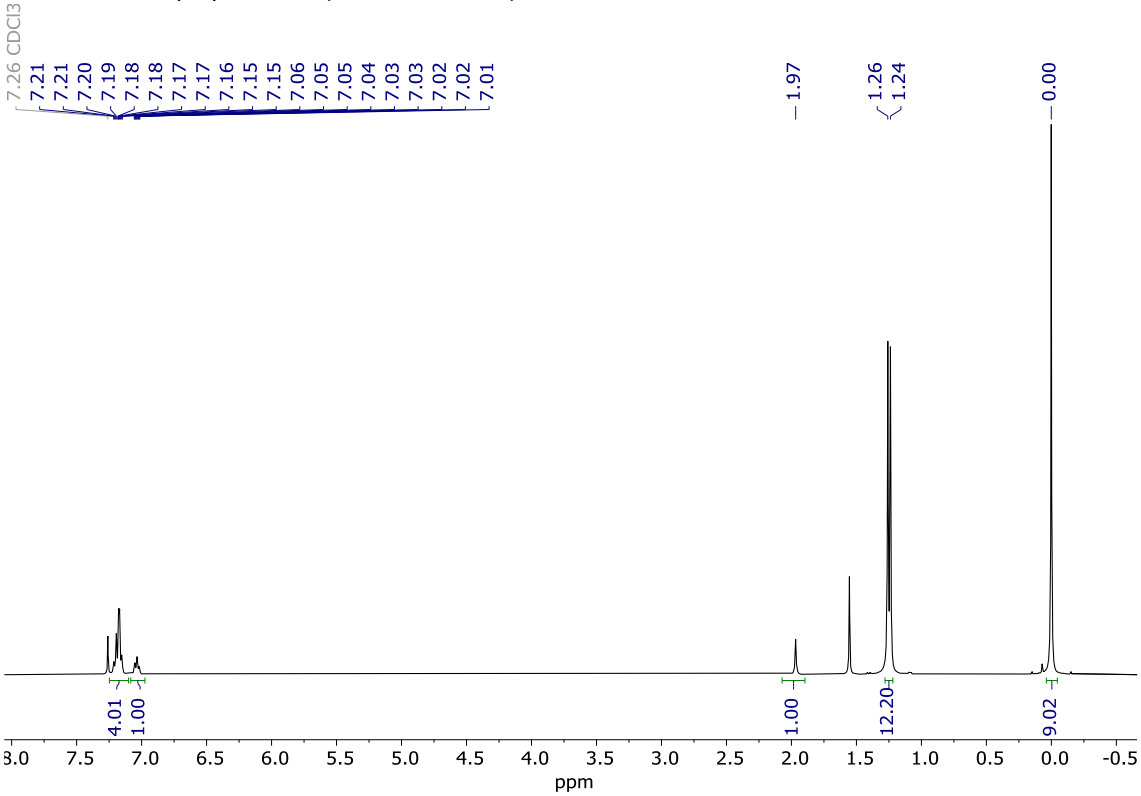
[4] B. H. Rotstein, L. Wang, R. Y. Liu, J. Patteson, E. E. Kwan, N. Vasdev, S. H. Liang, *Chem. Sci*., **2016**, *7*, 4407–4417.

[5] C. E. Check, T. O. Faust, J. M. Bailey, B. J. Wright, T. M. Gilbert, L. S. Sunderlin, *J. Phys. Chem. A* **2001,** *105,* 8111-8116.

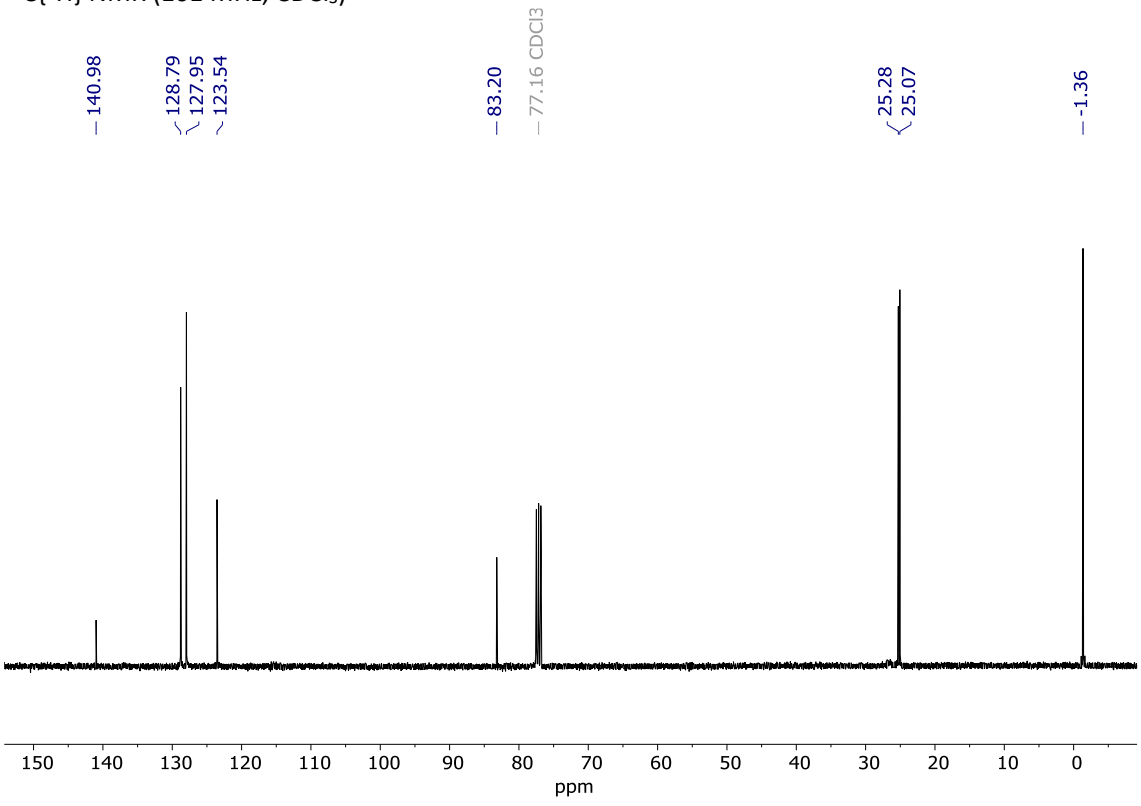
10. Characterization data



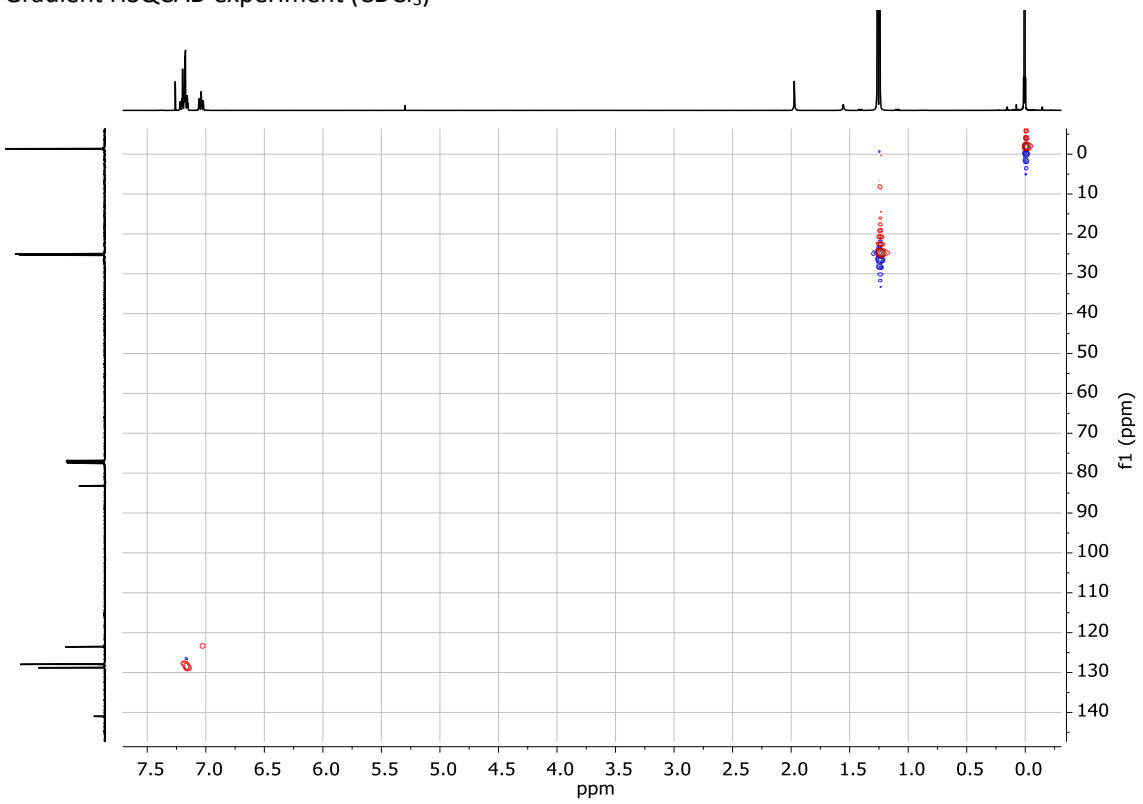
(**1a**) ^{1}H NMR (400 MHz, $CDCl_3$)



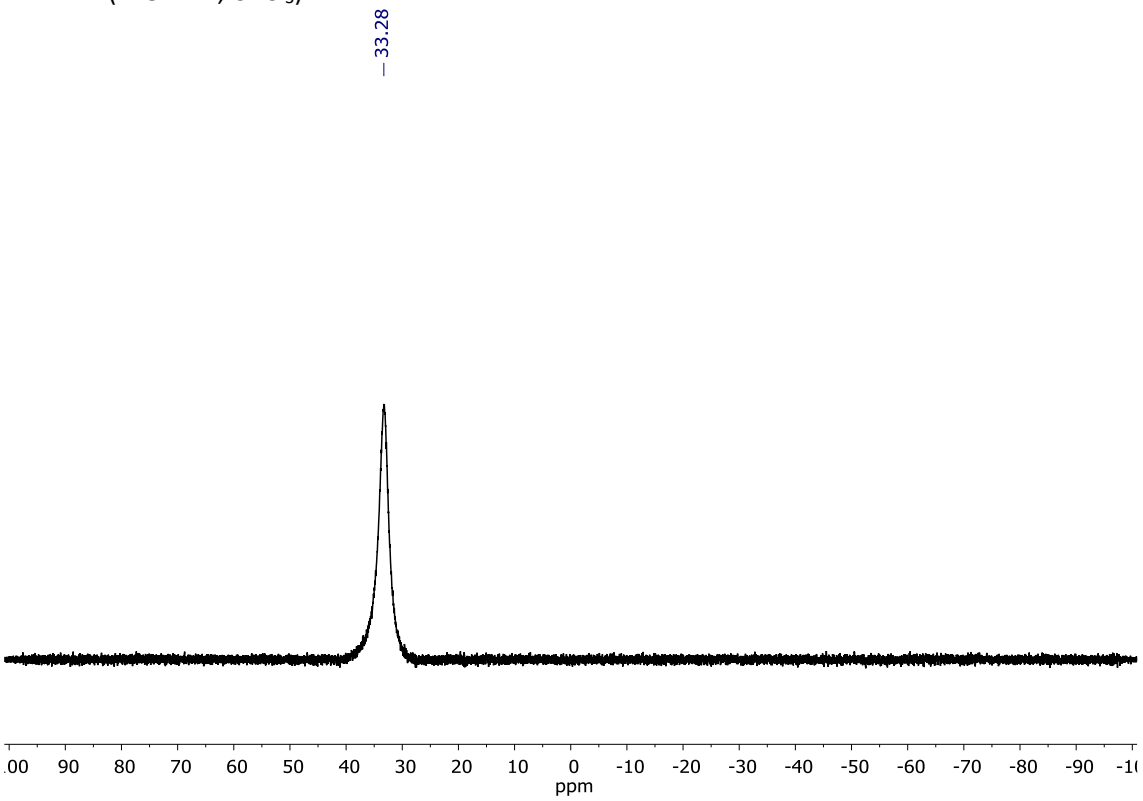
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

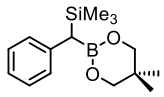


Gradient HSQCAD experiment ($CDCl_3$)

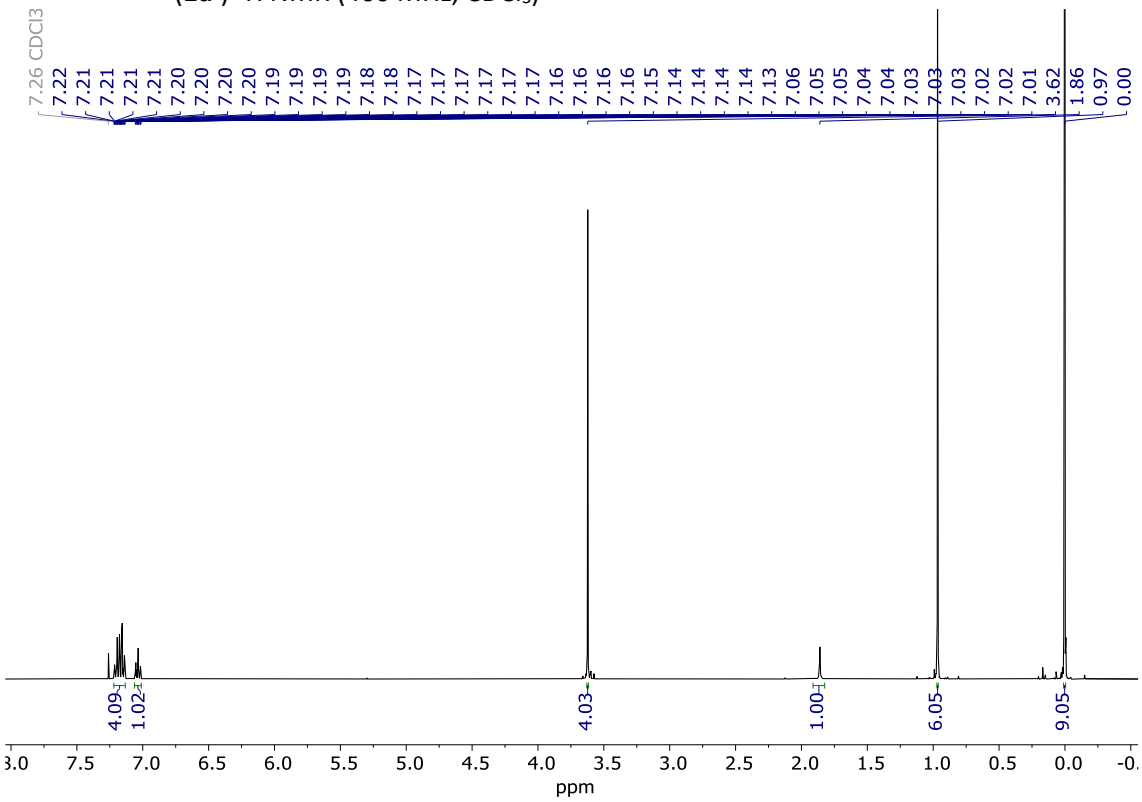


^{11}B NMR (128 MHz, $CDCl_3$)

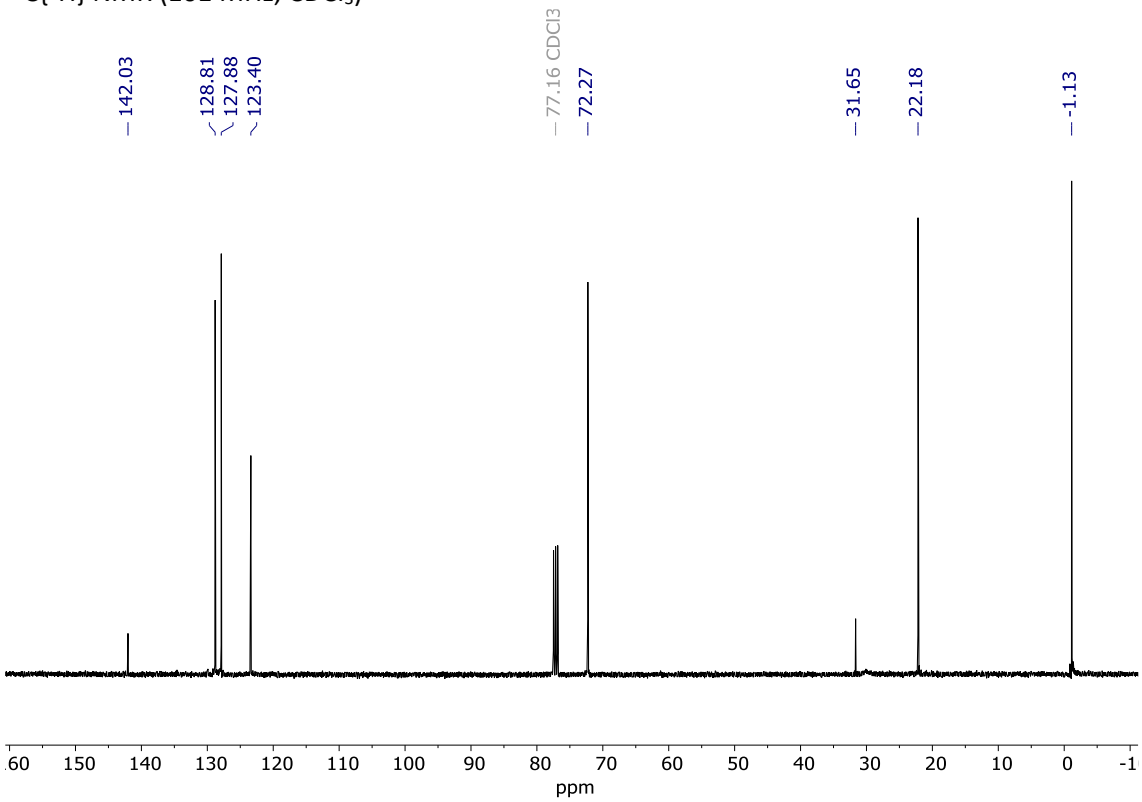




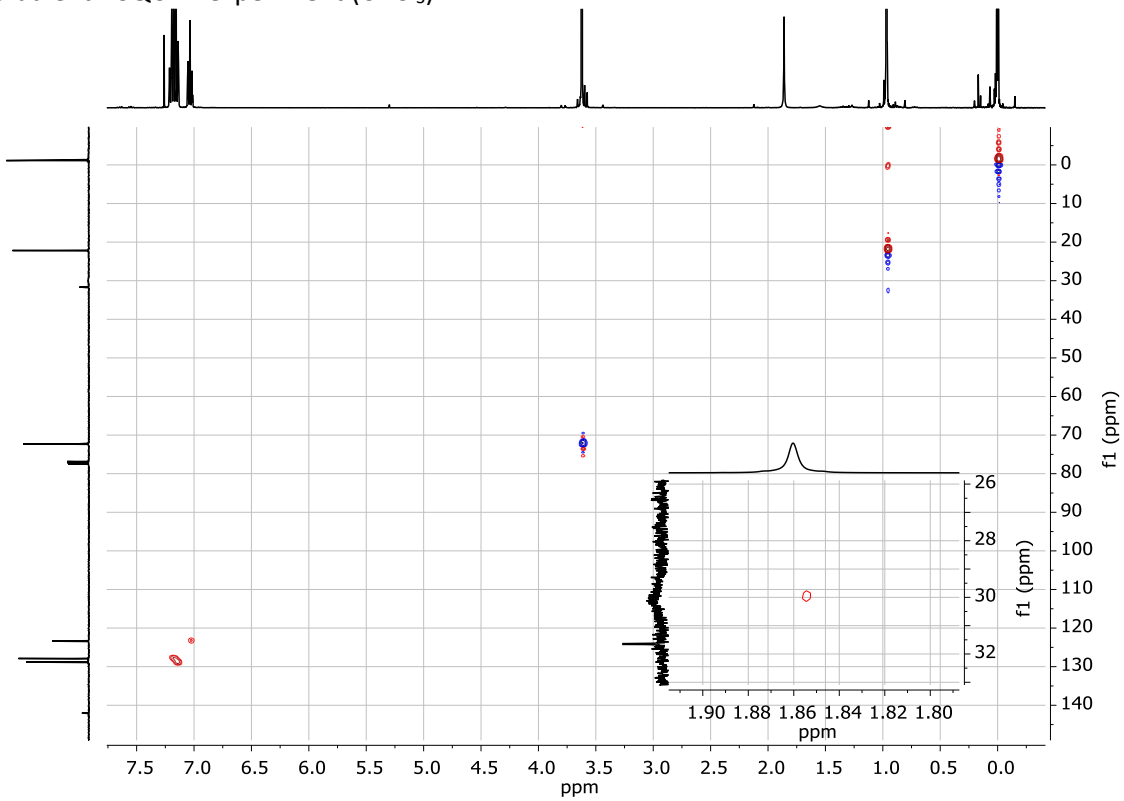
(**1a'**) ^{1}H NMR (400 MHz, $CDCl_3$)



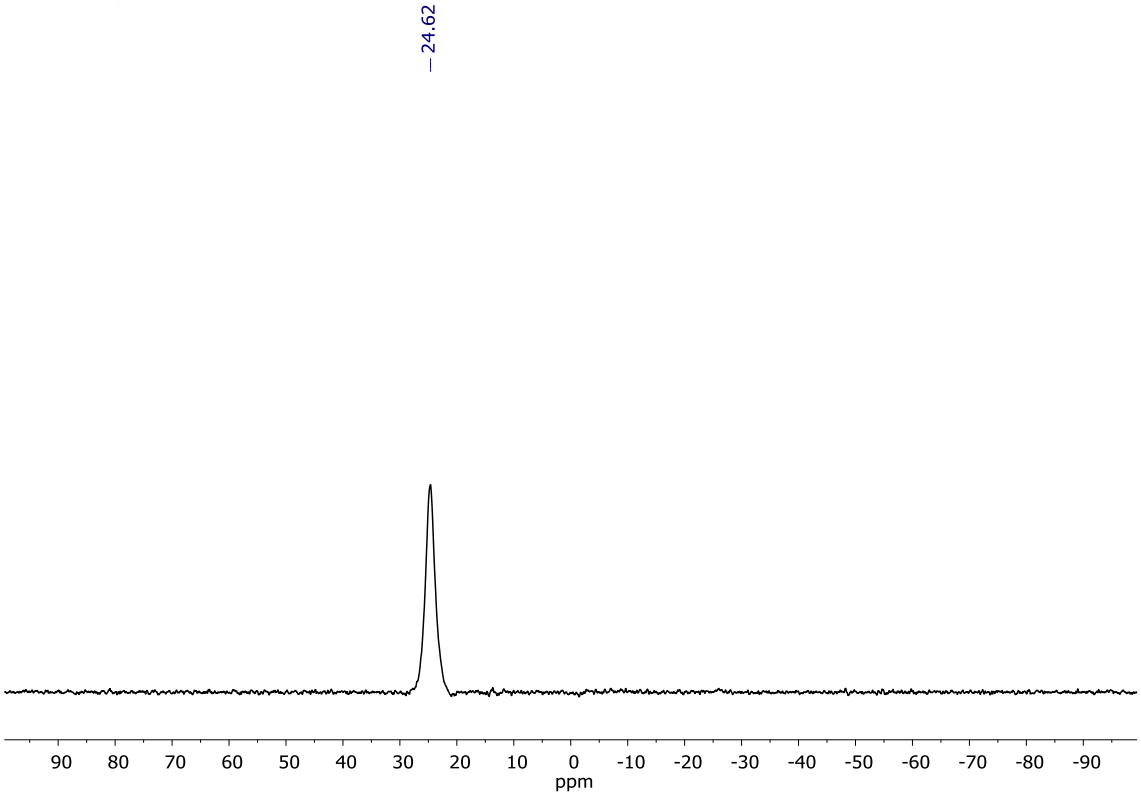
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

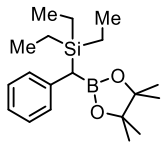


Gradient HSQCAD experiment ($CDCl_3$)

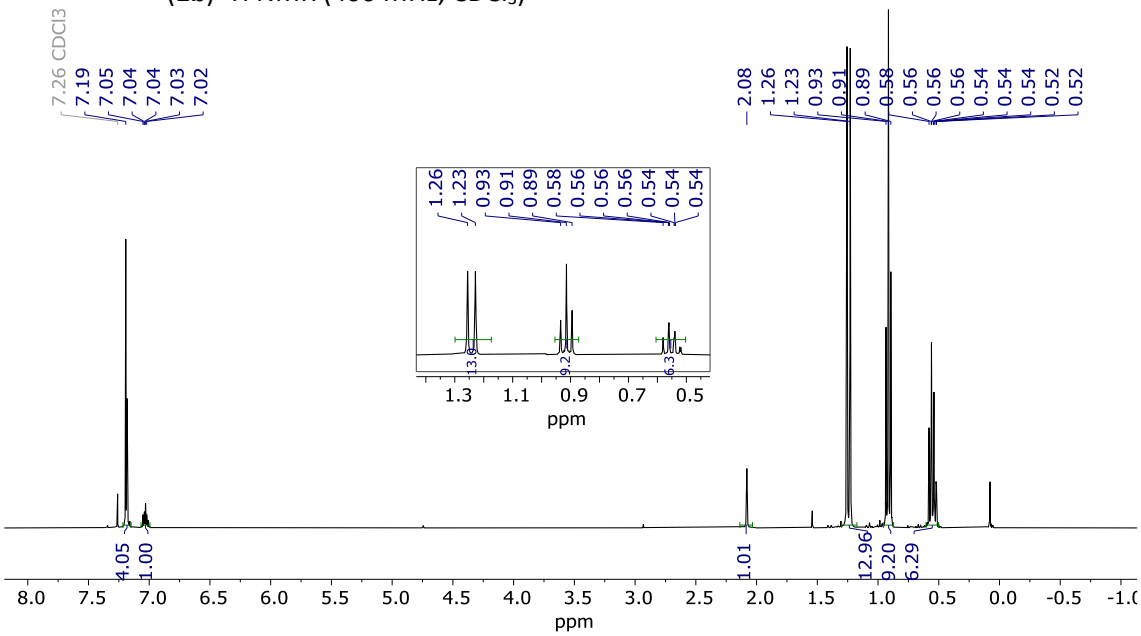


^{11}B NMR (128 MHz, $CDCl_3$)

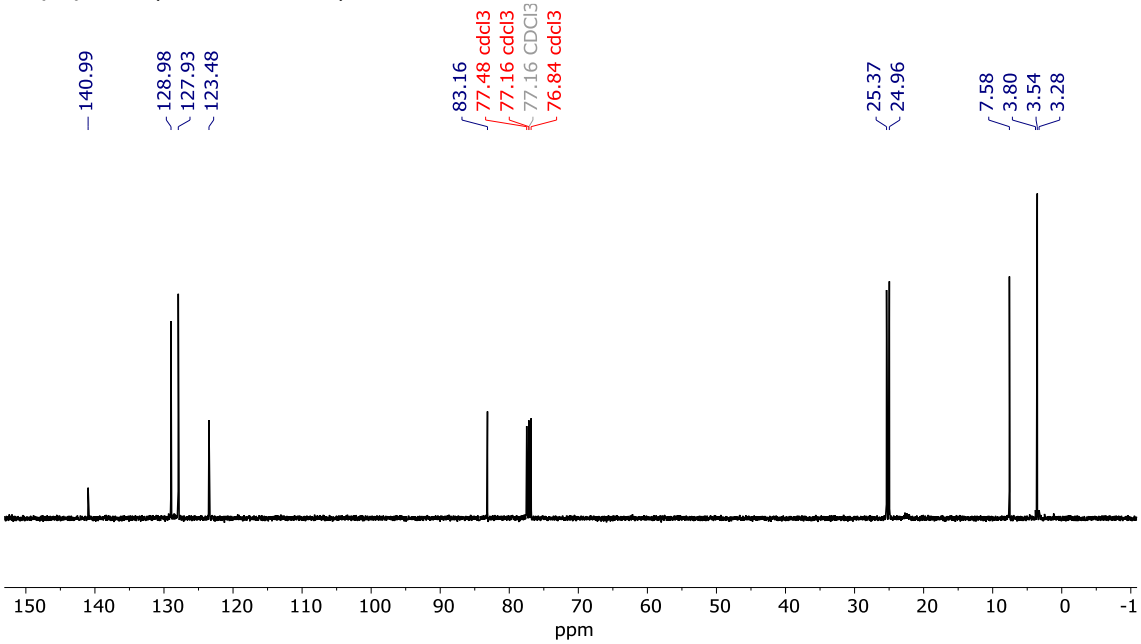




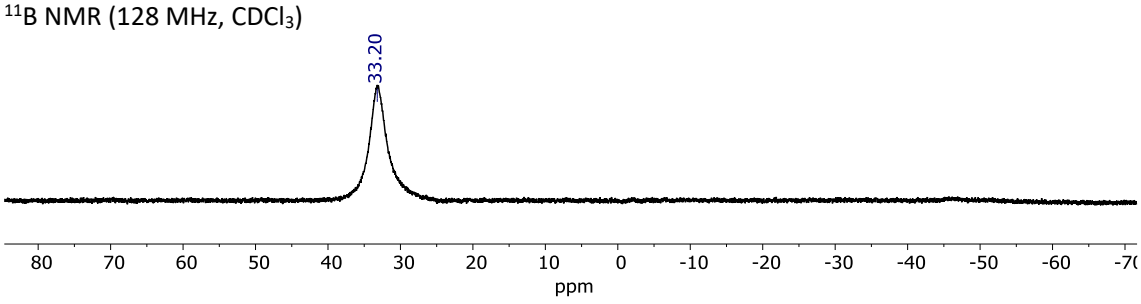
(**1b**) ^{1}H NMR (400 MHz, $CDCl_3$)

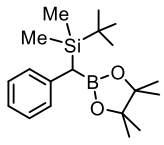


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

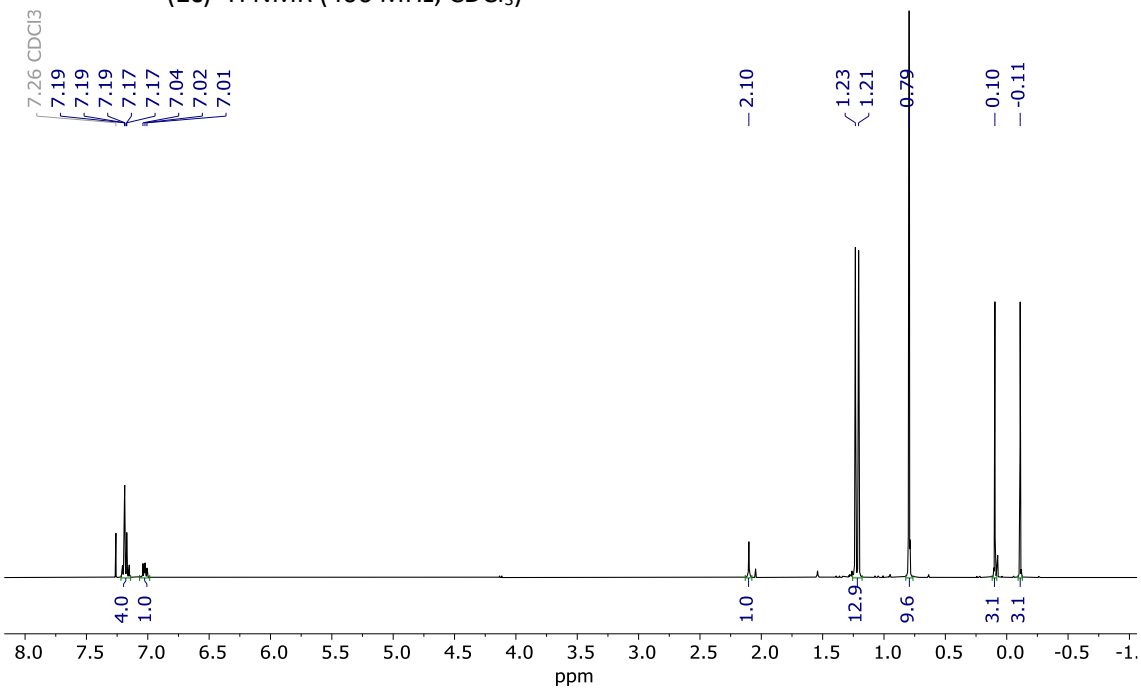


^{11}B NMR (128 MHz, $CDCl_3$)

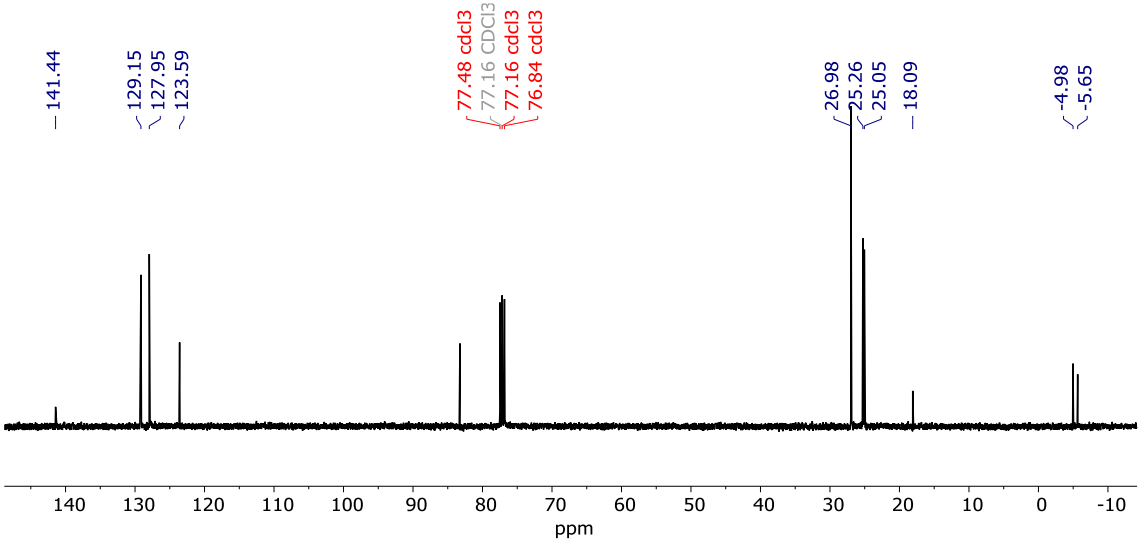




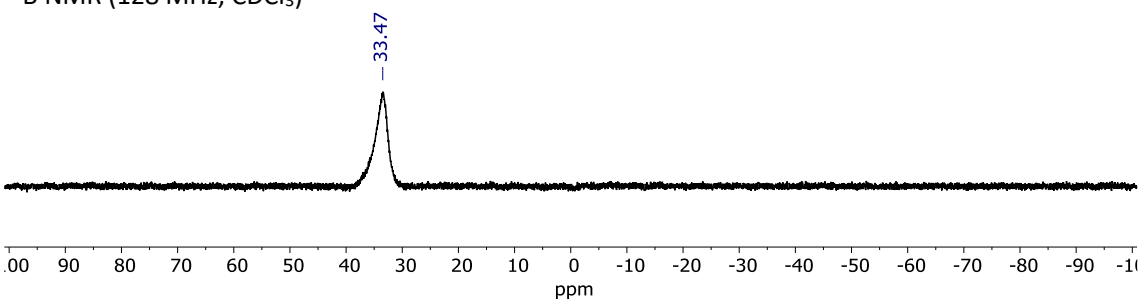
(**1c**) ^{1}H NMR (400 MHz, $CDCl_3$)

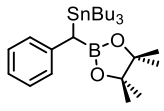


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

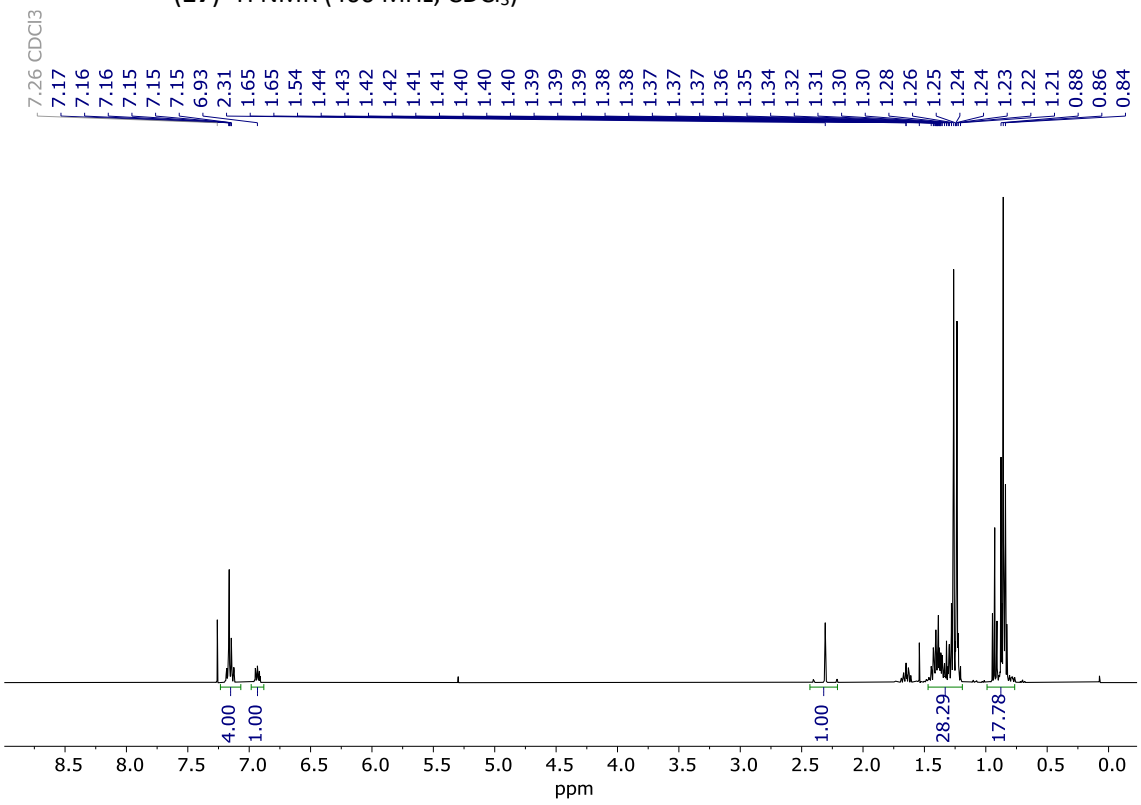


^{11}B NMR (128 MHz, $CDCl_3$)

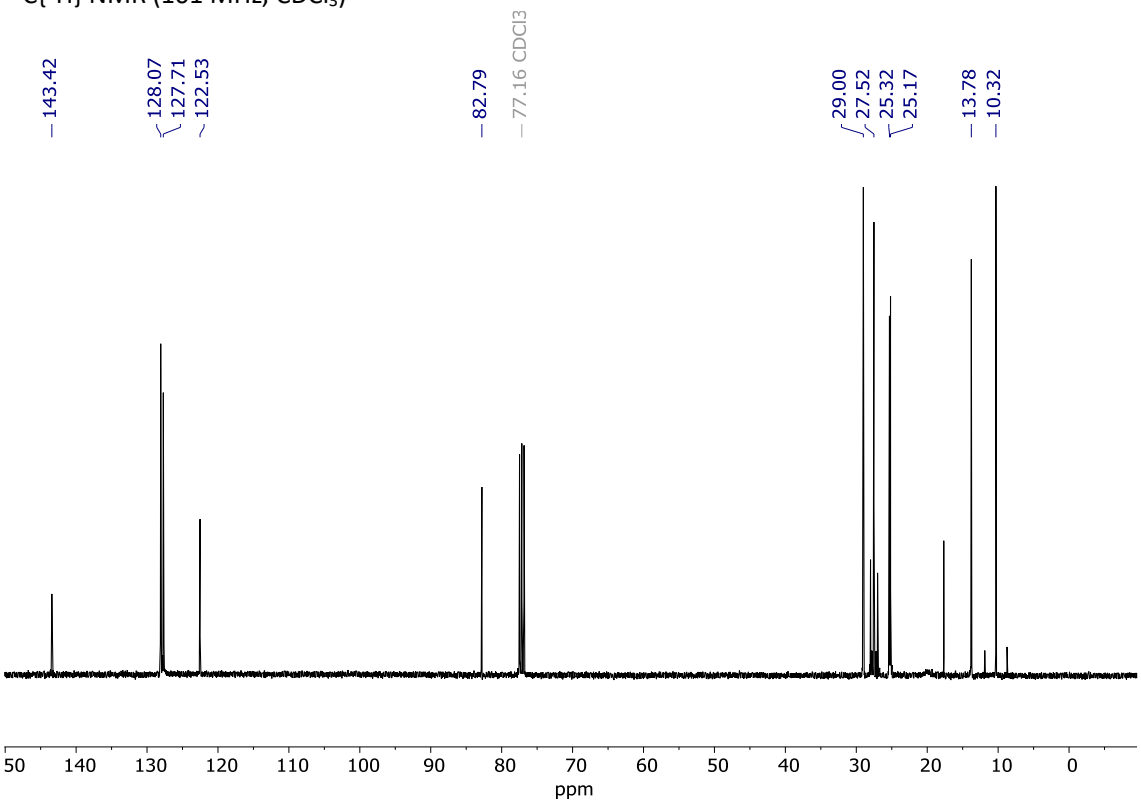




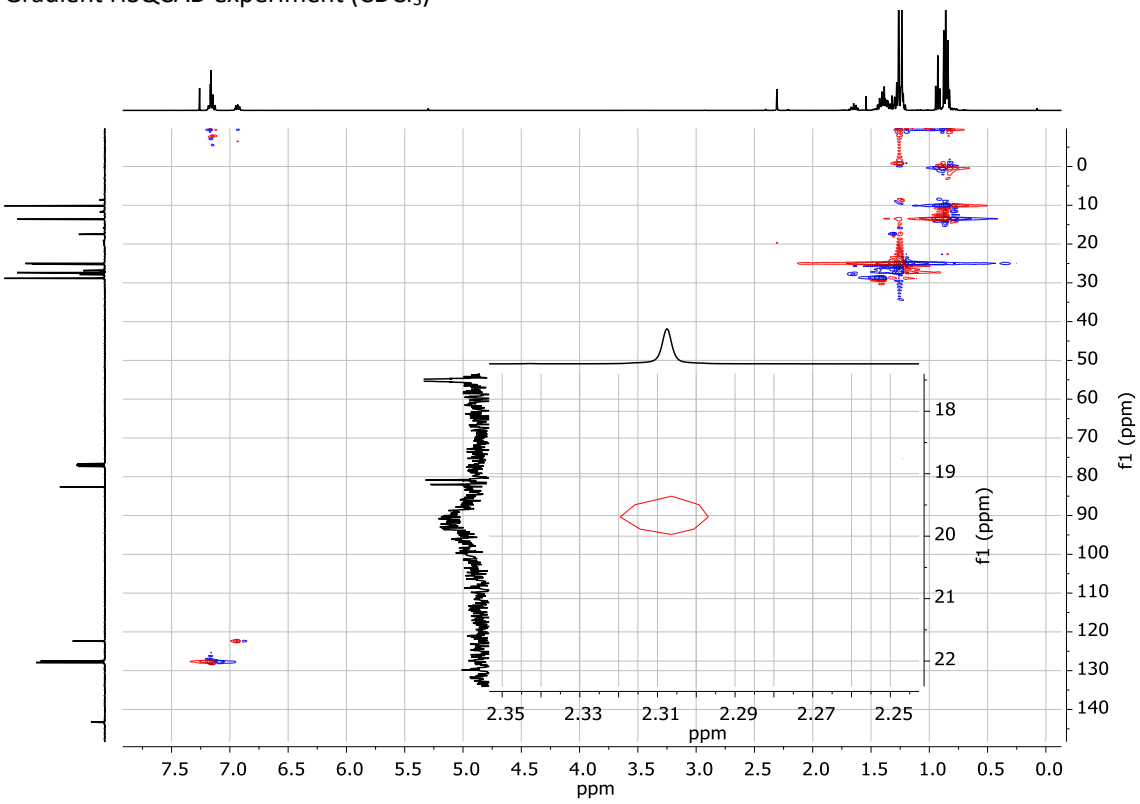
(**17**) ^{1}H NMR (400 MHz, $CDCl_3$)



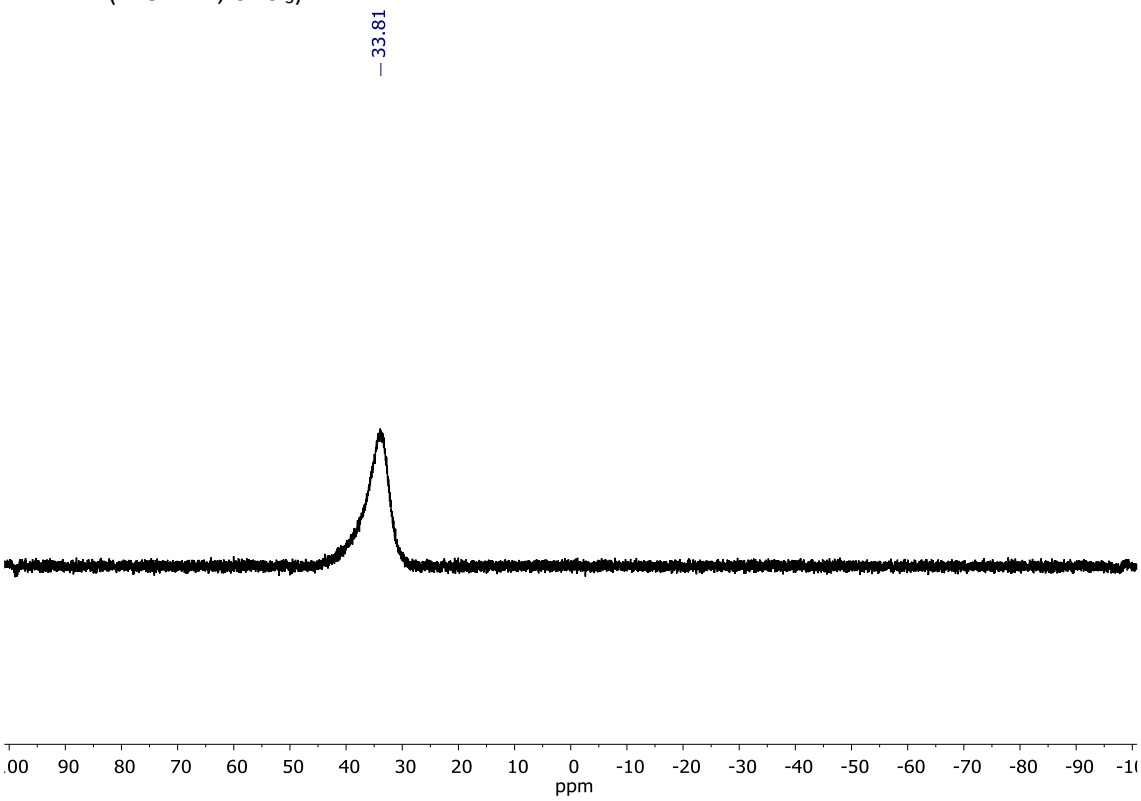
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

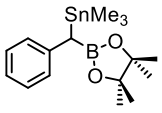


Gradient HSQCAD experiment ($CDCl_3$)

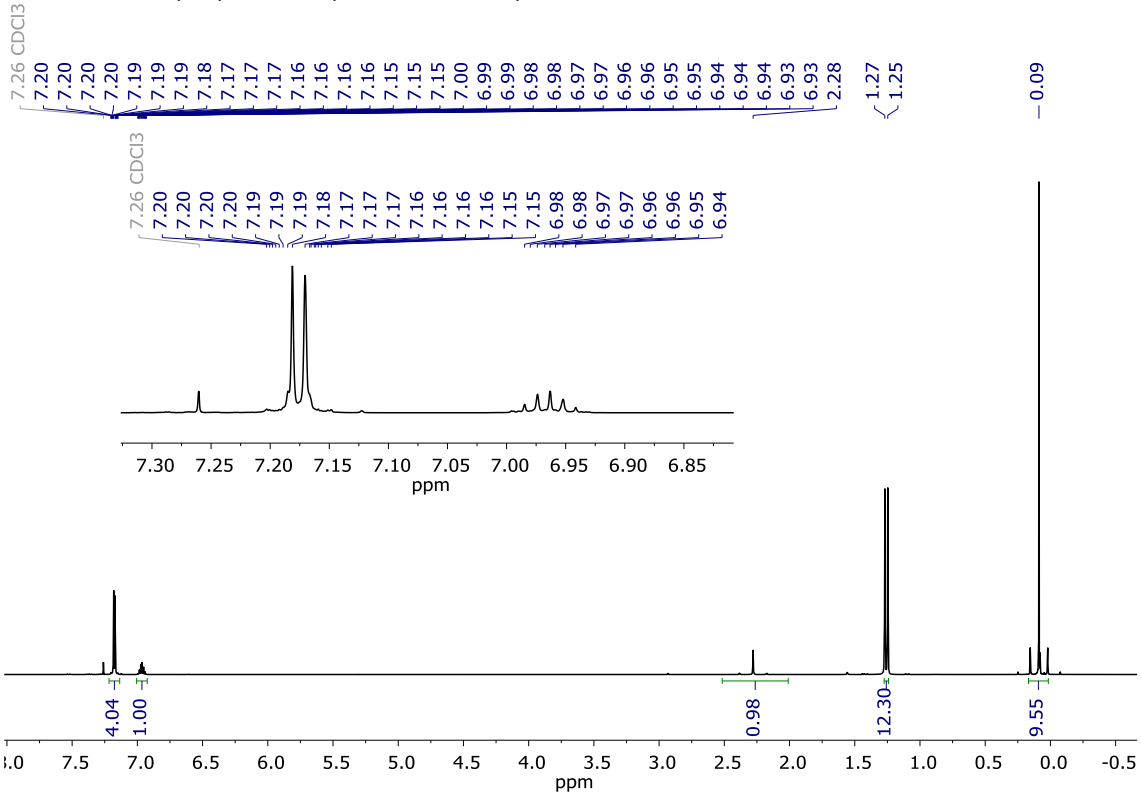


^{11}B NMR (128 MHz, $CDCl_3$)

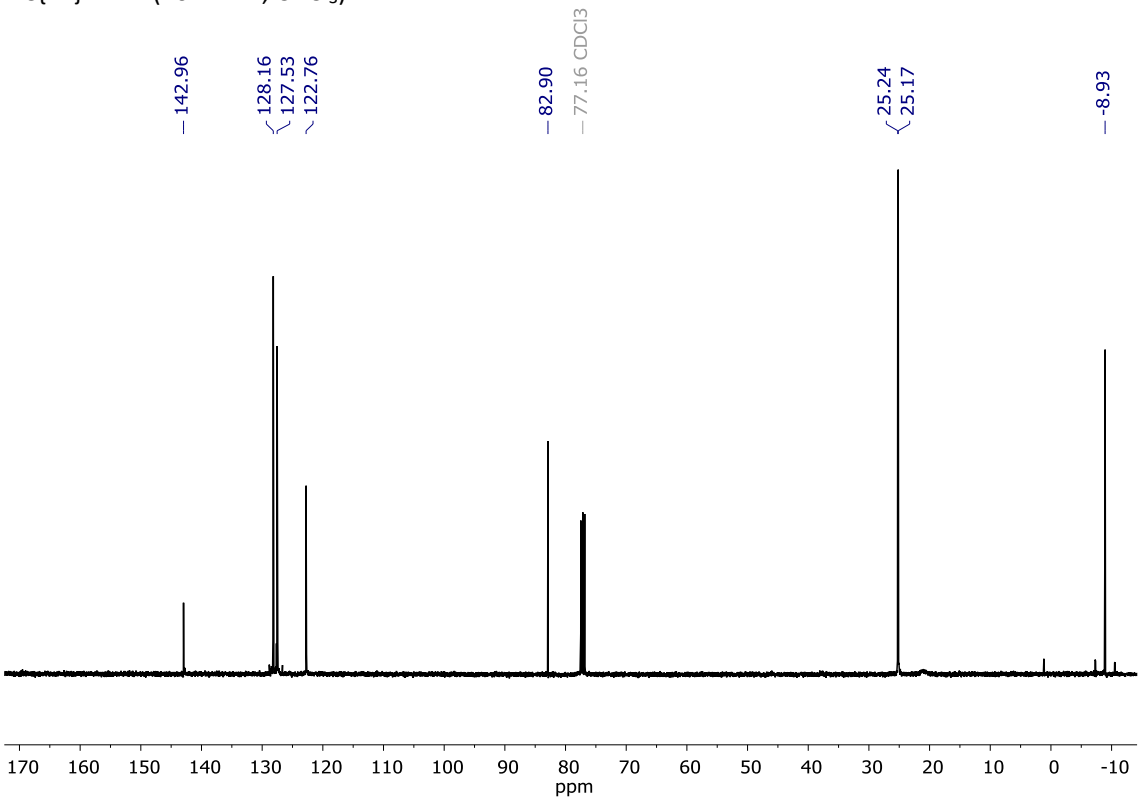




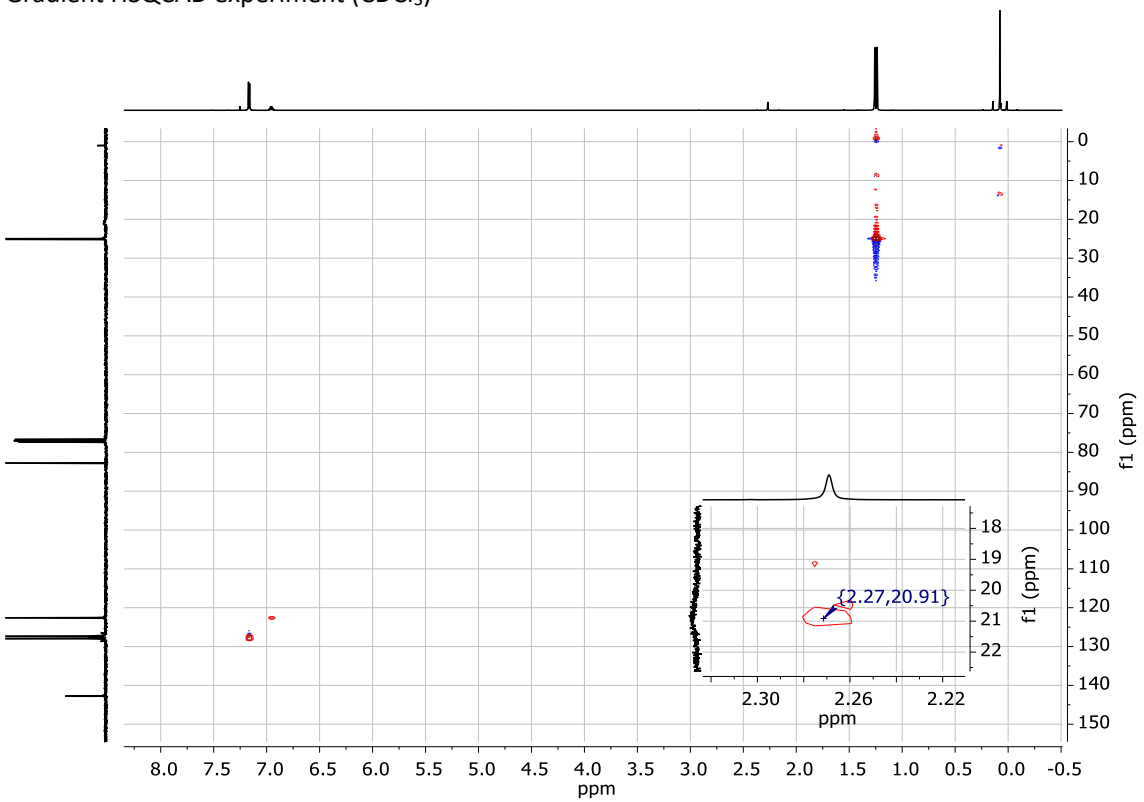
(**17'**) ^{1}H NMR (400 MHz, $CDCl_3$)



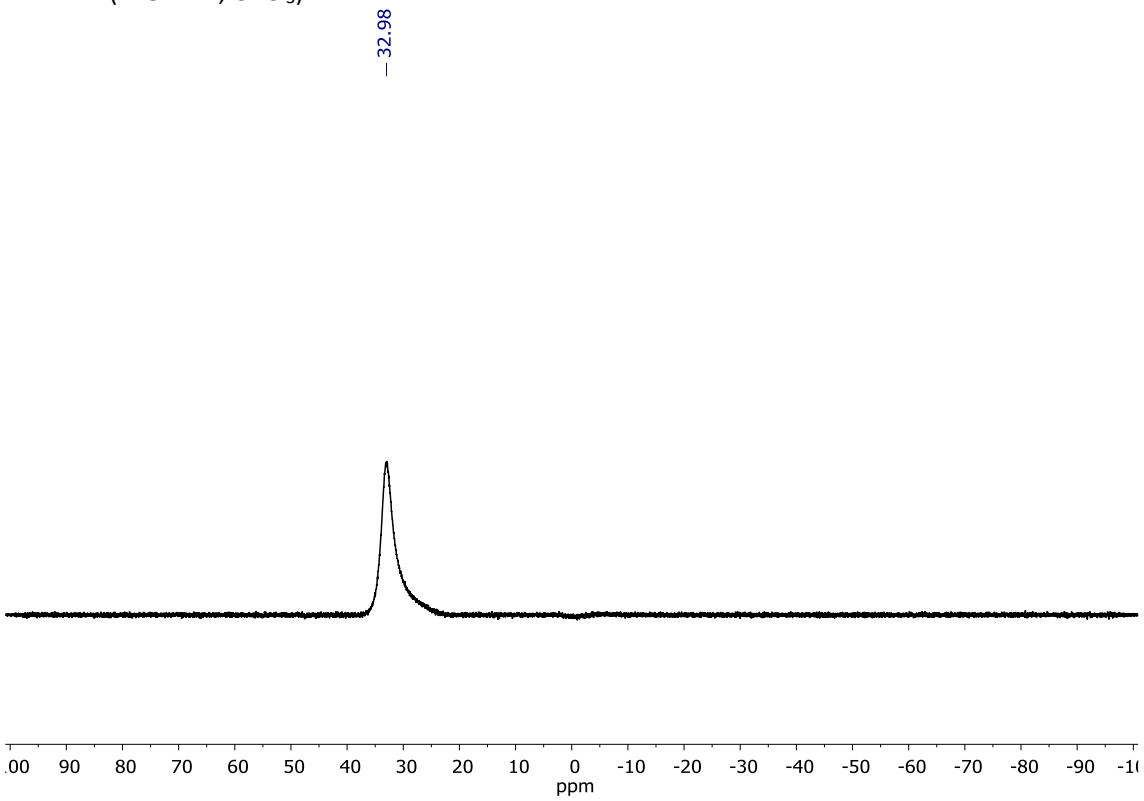
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

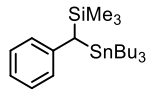


Gradient HSQCAD experiment ($CDCl_3$)

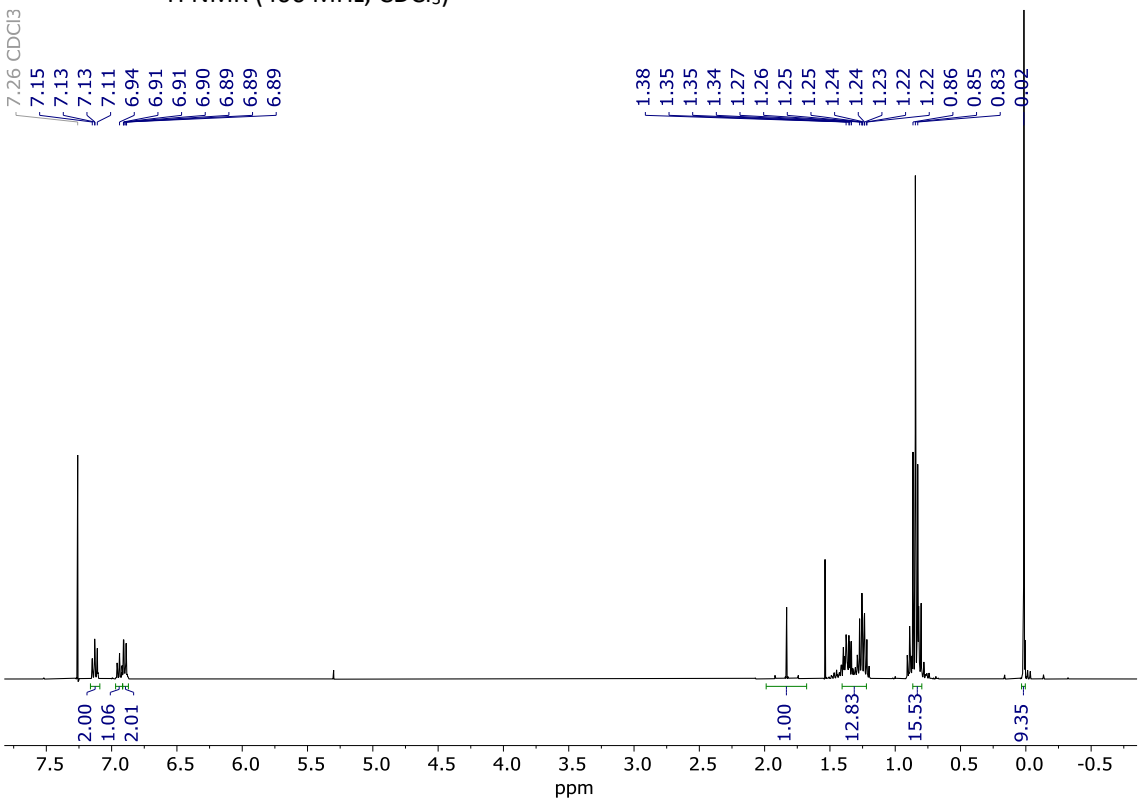


^{11}B NMR (128 MHz, $CDCl_3$)

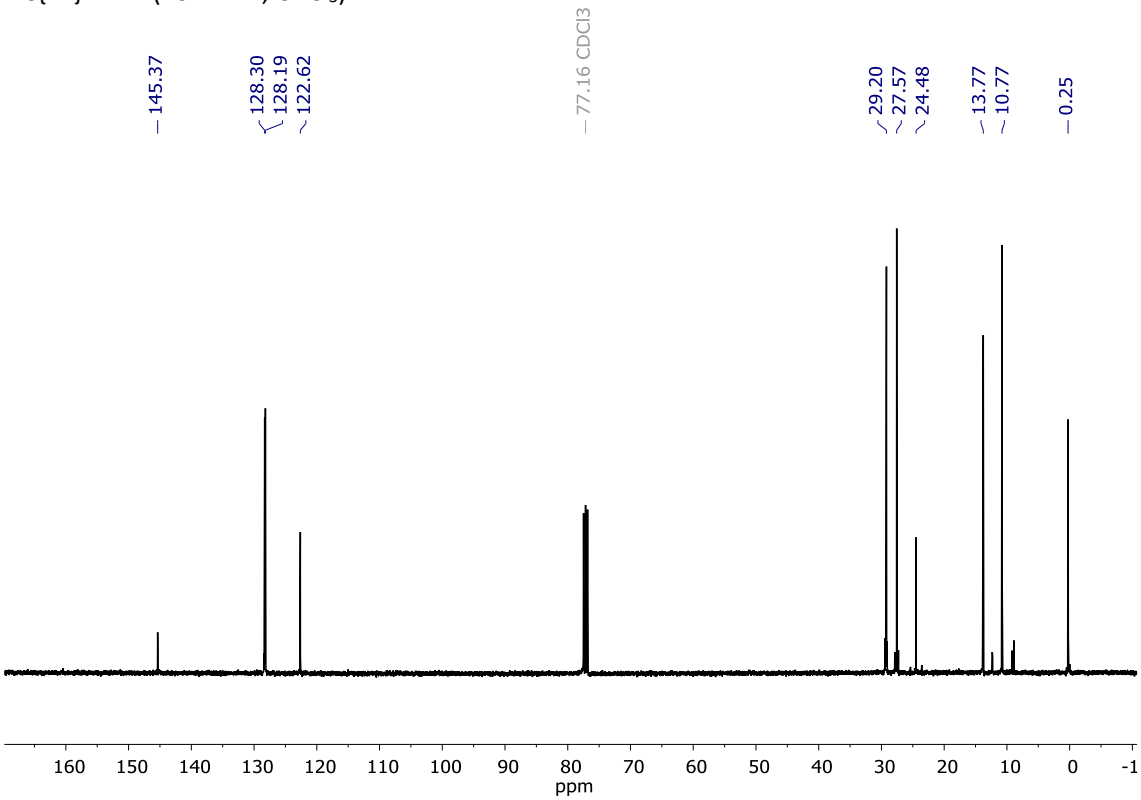




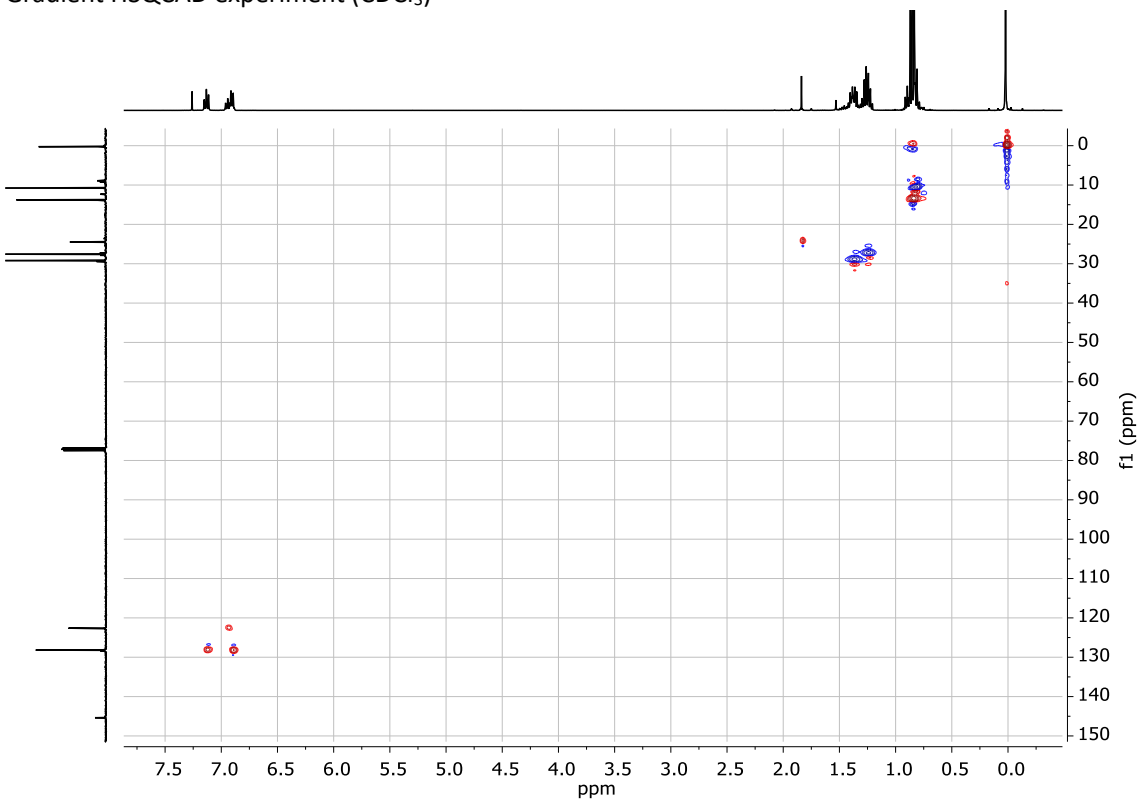
^{1}H NMR (400 MHz, $CDCl_3$)



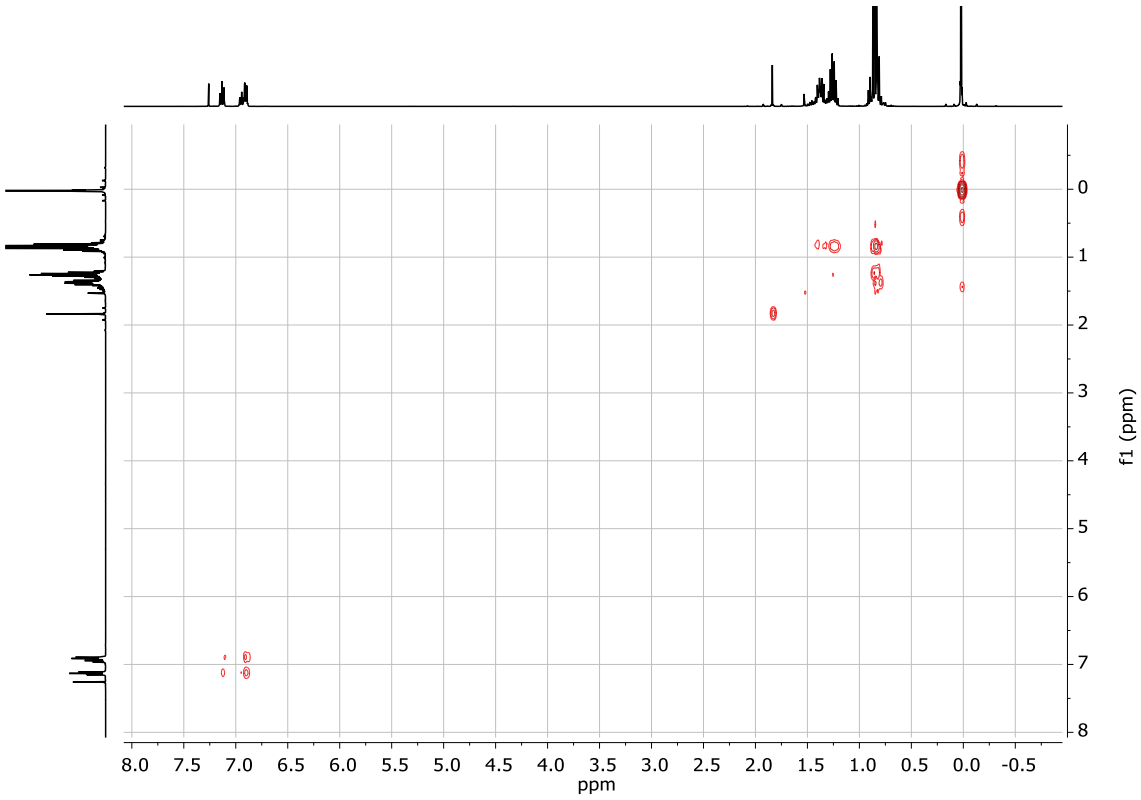
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

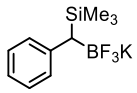


Gradient HSQCAD experiment ($CDCl_3$)

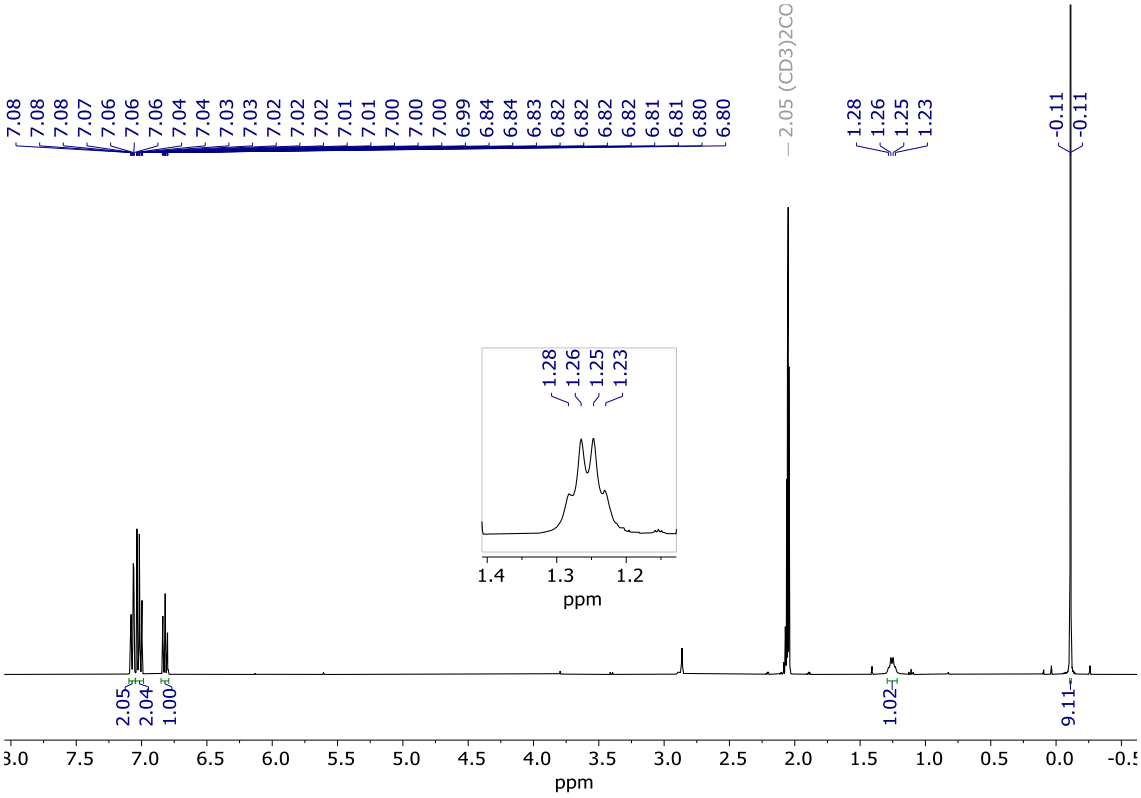


^1H COSY experiment ($CDCl_3$)

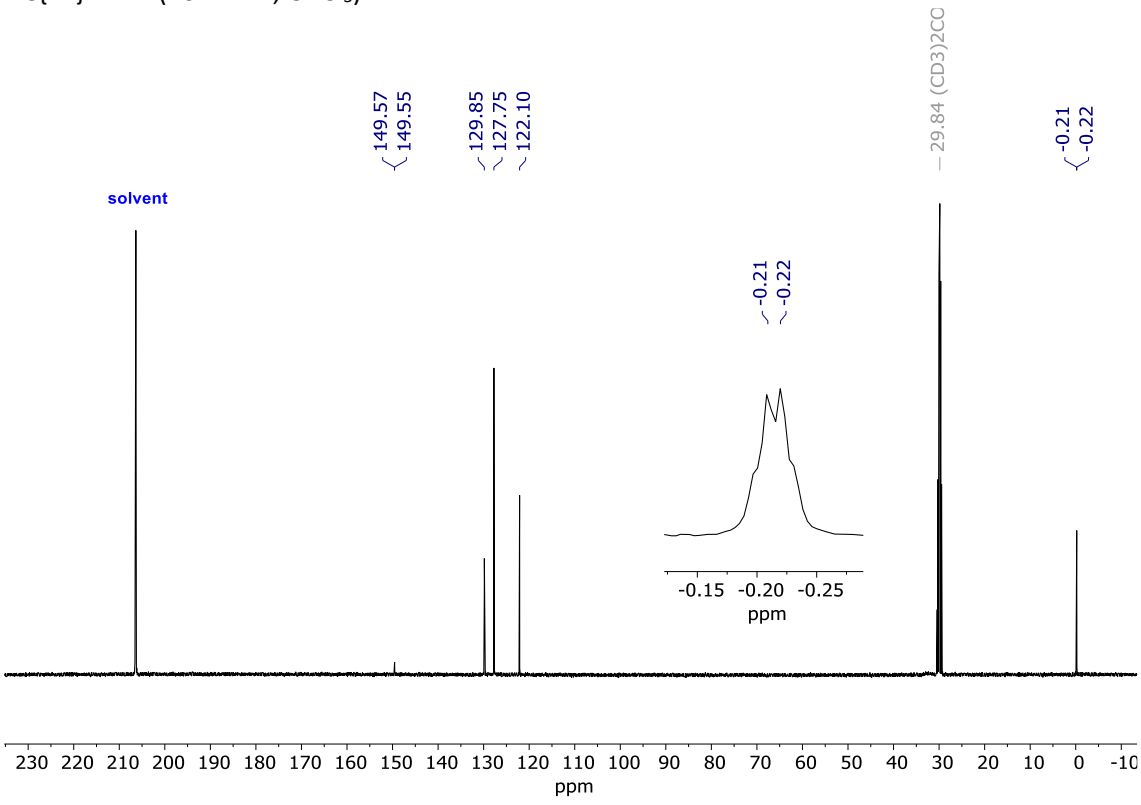




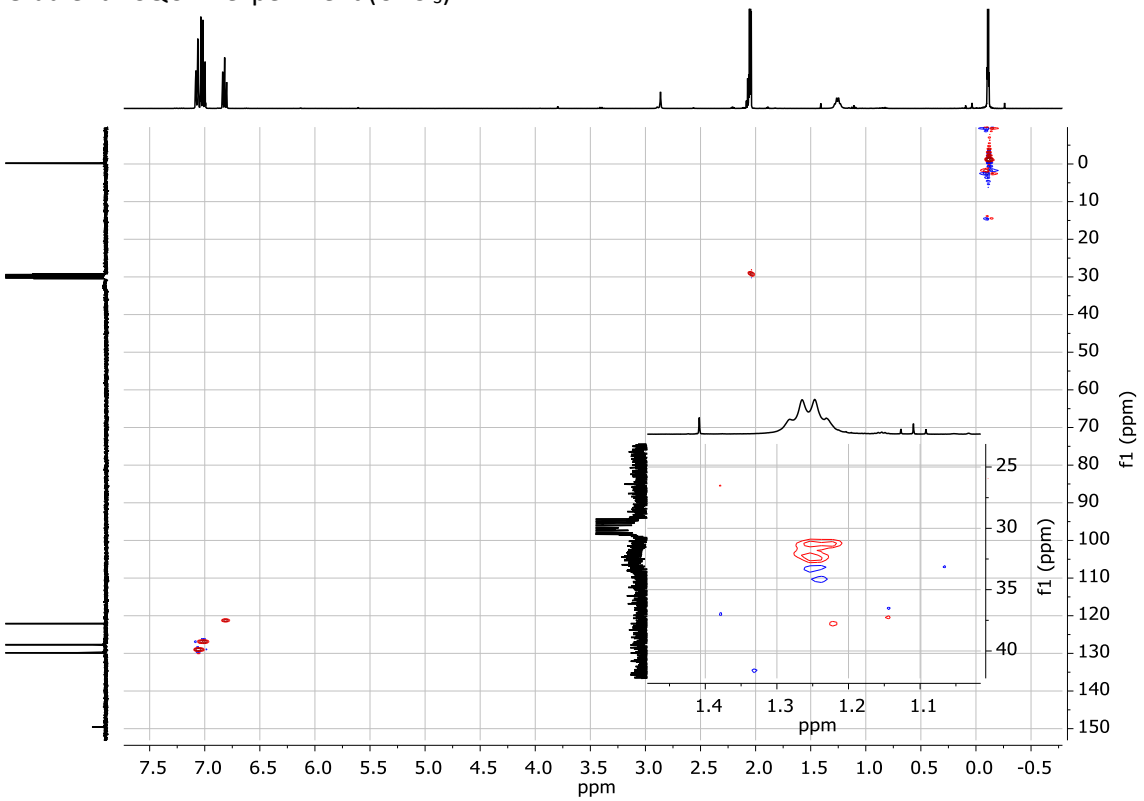
(**27a**) ^{1}H NMR (400 MHz, $CDCl_3$)



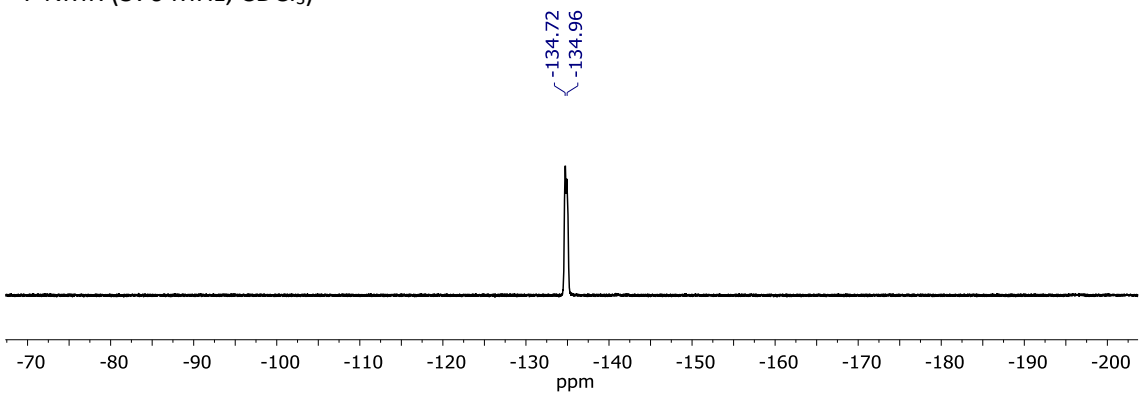
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



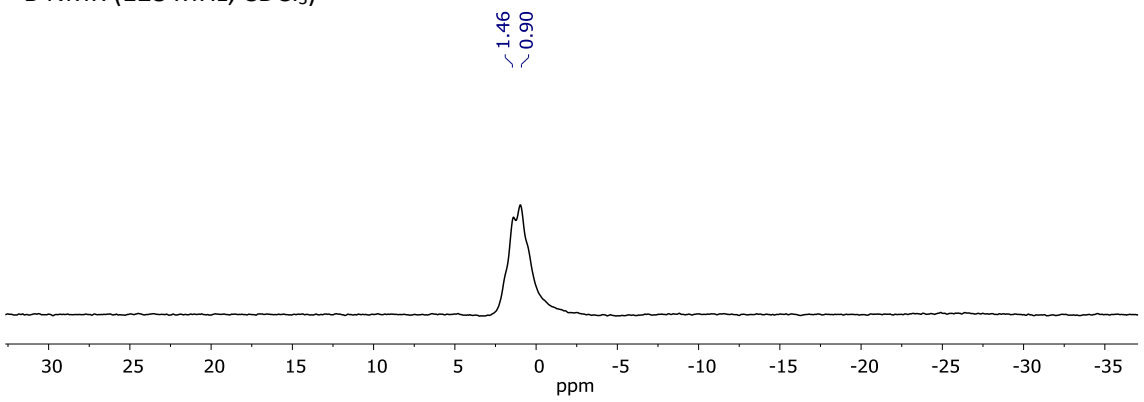
Gradient HSQCAD experiment ($CDCl_3$)

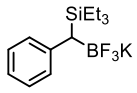


^{19}F NMR (376 MHz, $CDCl_3$)

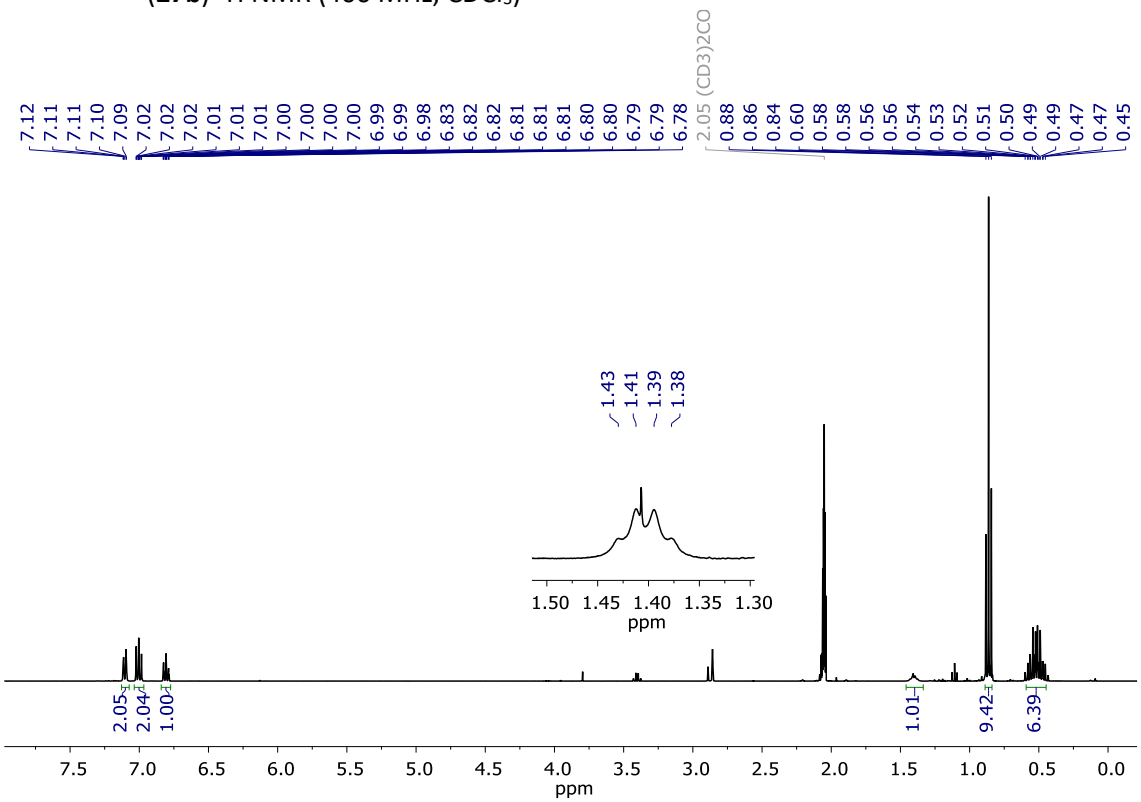


^{11}B NMR (128 MHz, $CDCl_3$)

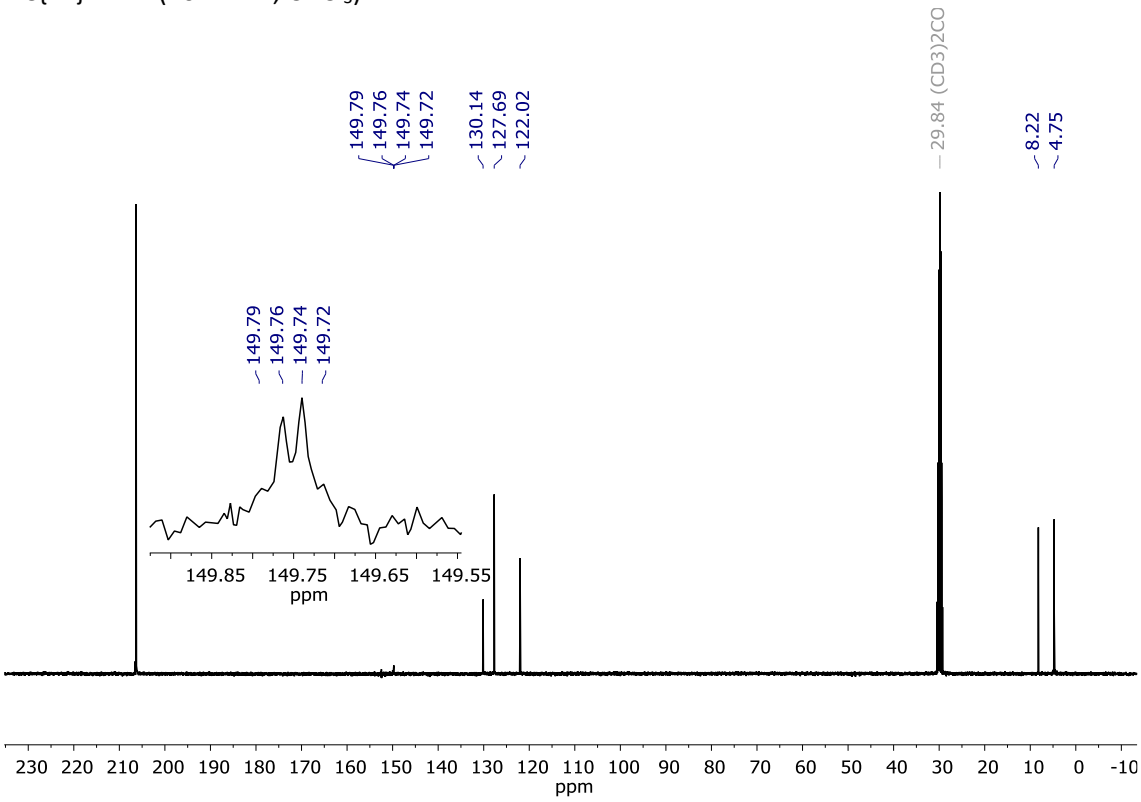




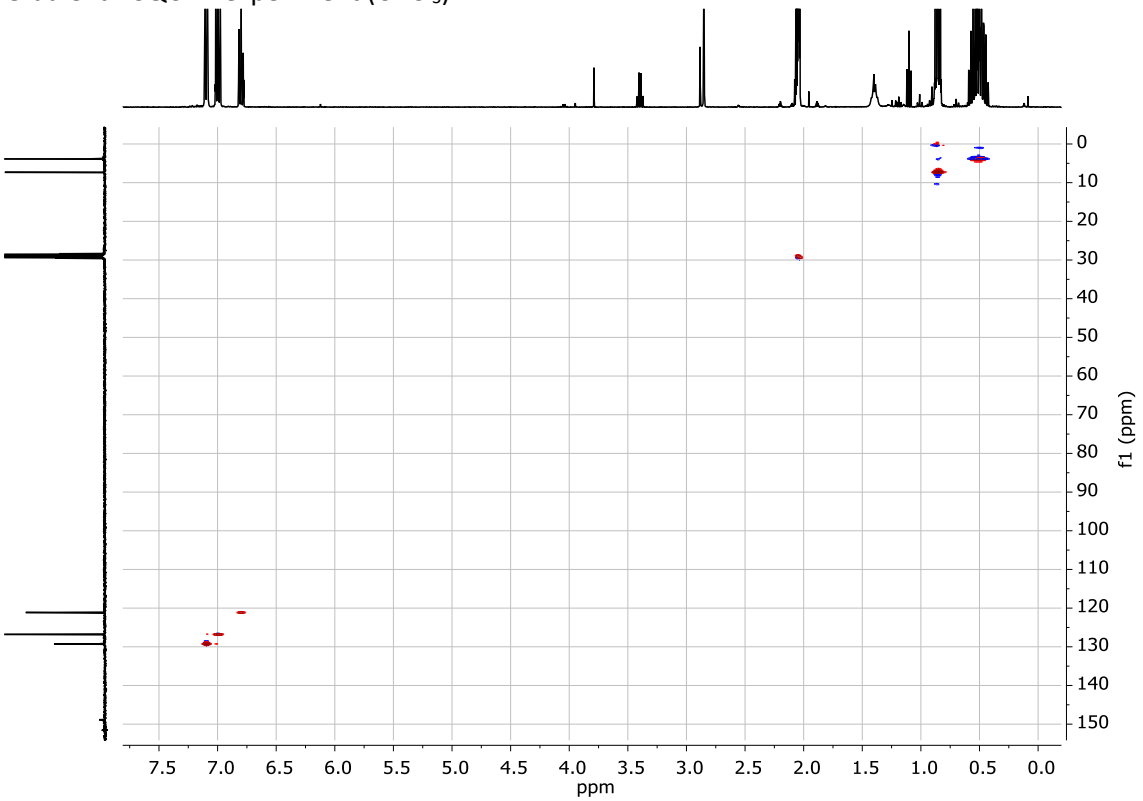
(**27b**) ^{1}H NMR (400 MHz, $CDCl_3$)



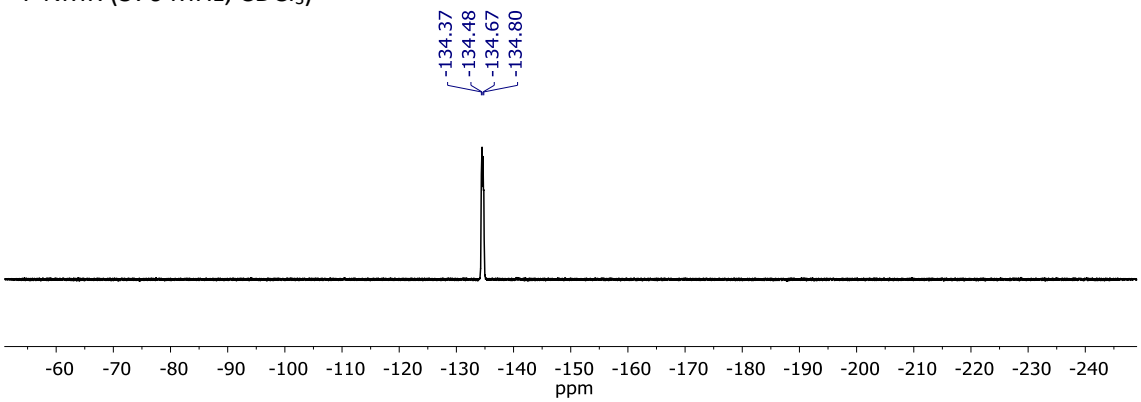
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



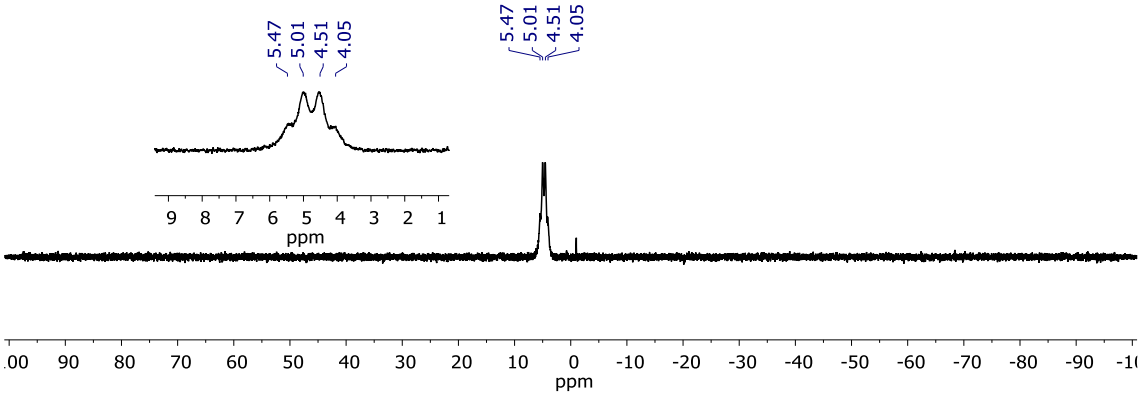
Gradient HSQCAD experiment ($CDCl_3$)

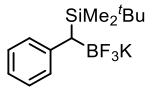


^{19}F NMR (376 MHz, $CDCl_3$)

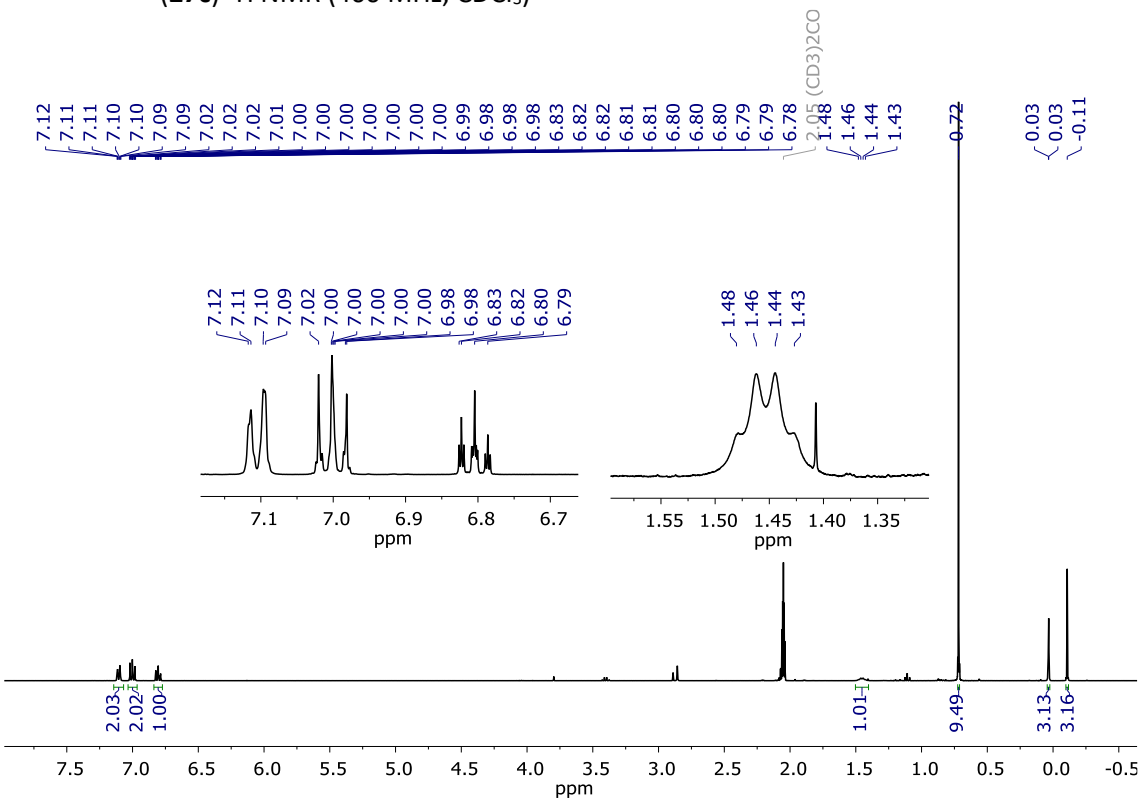


^{11}B NMR (128 MHz, $CDCl_3$)

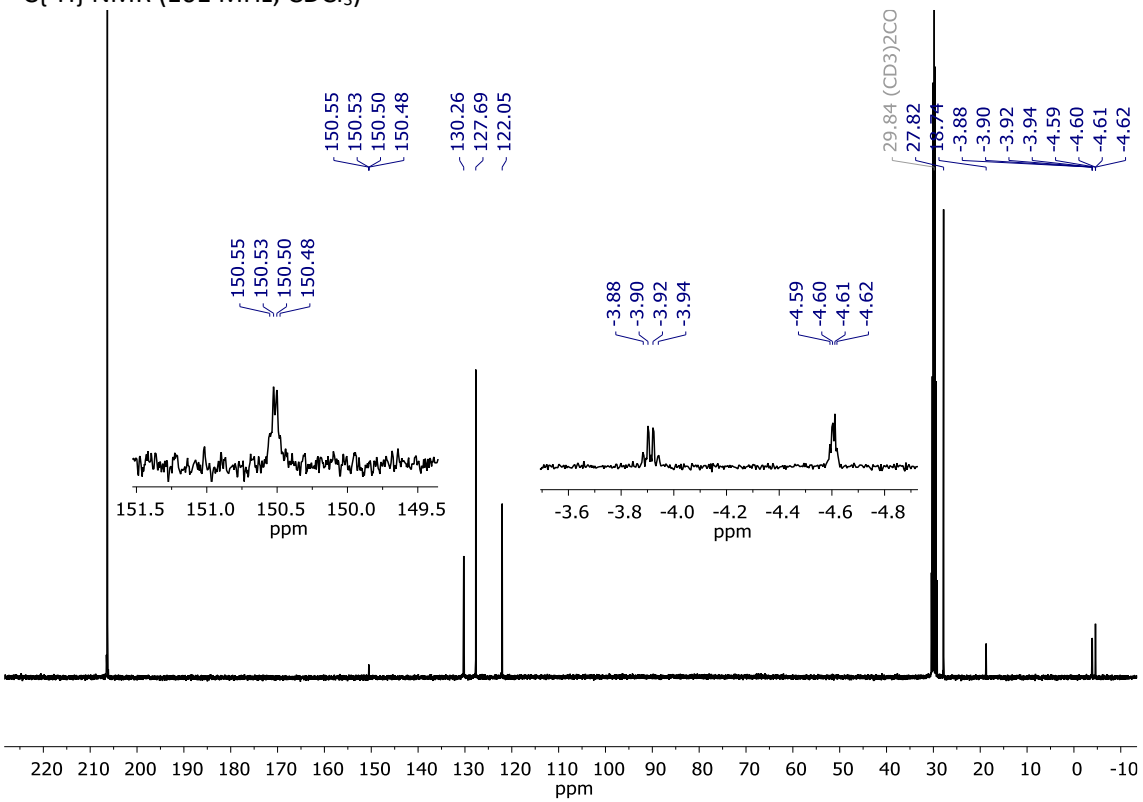




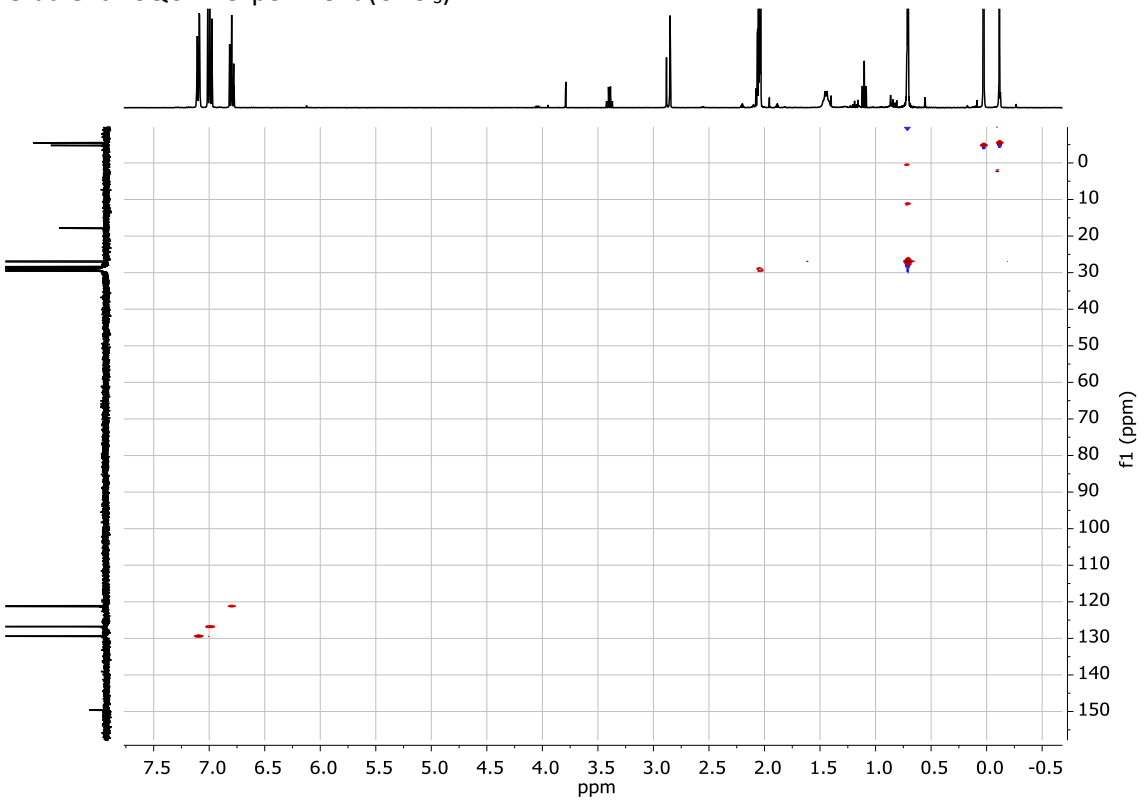
(**27c**) ^{1}H NMR (400 MHz, $CDCl_3$)



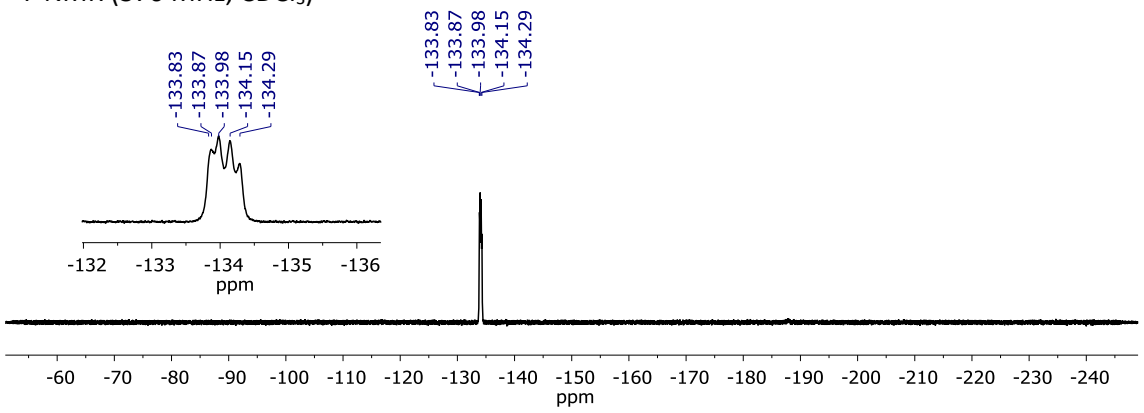
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



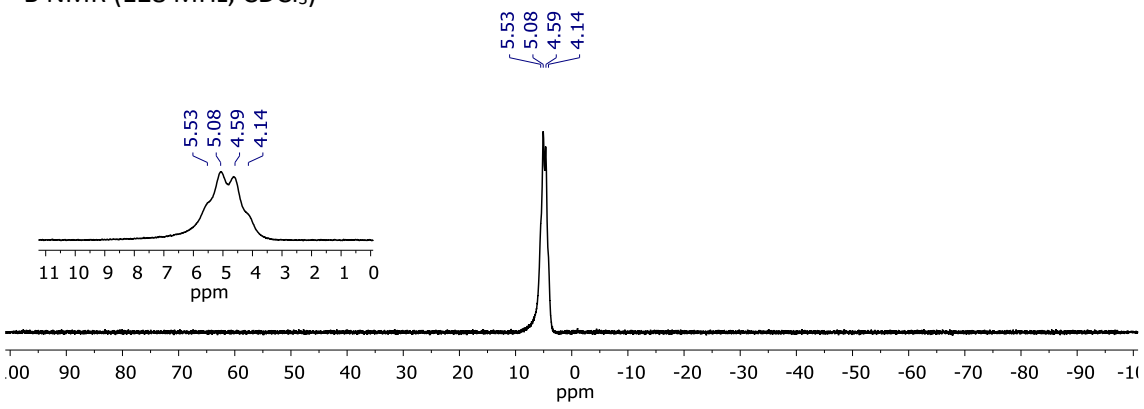
Gradient HSQCAD experiment ($CDCl_3$)

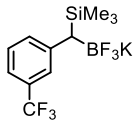


^{19}F NMR (376 MHz, $CDCl_3$)

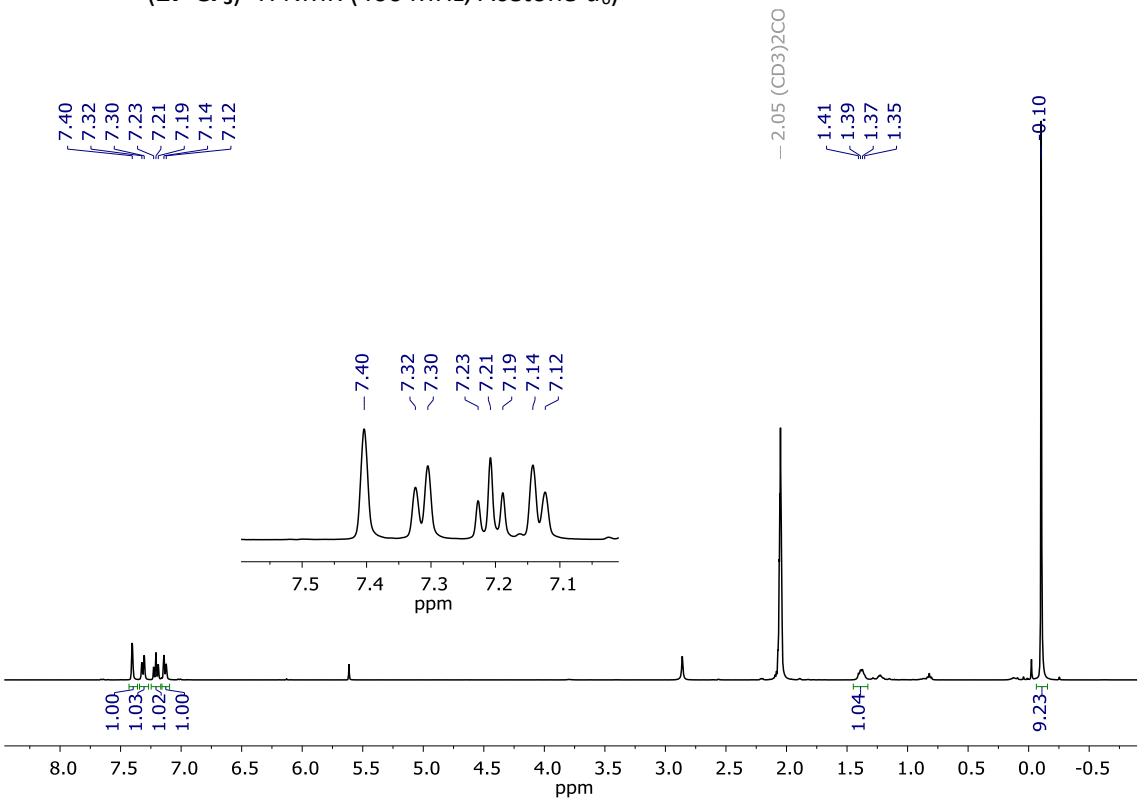


^{11}B NMR (128 MHz, $CDCl_3$)

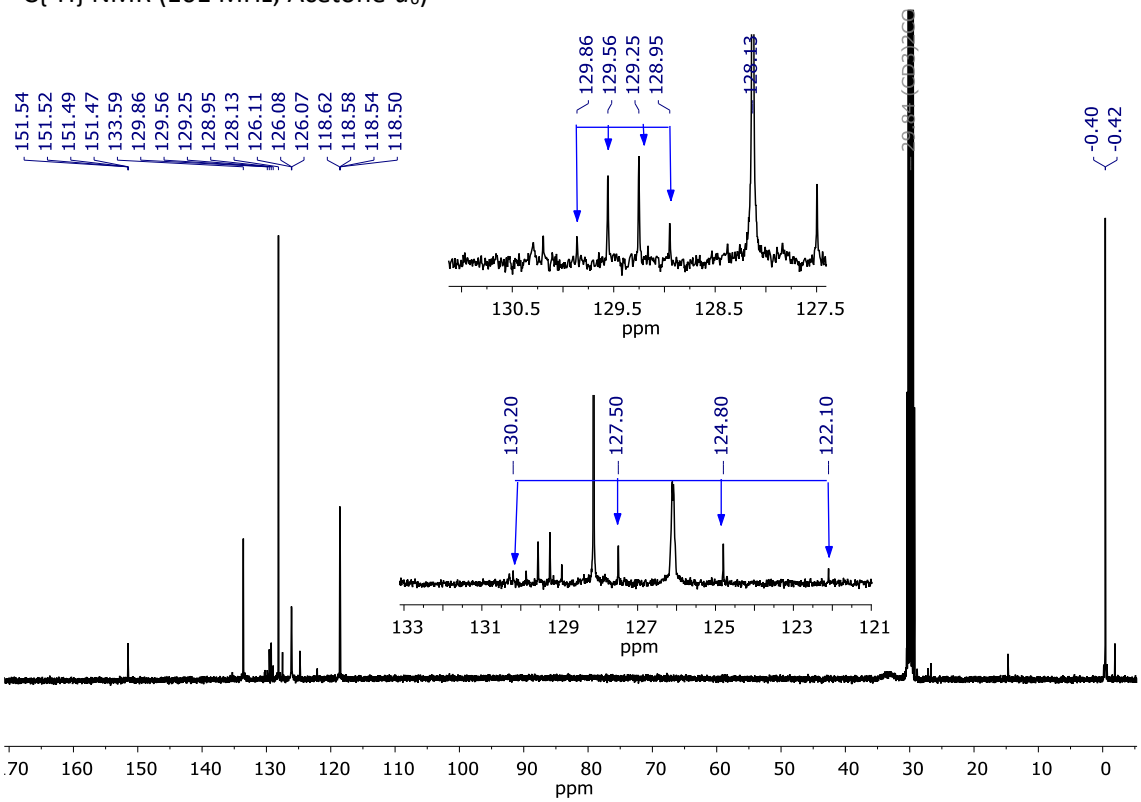




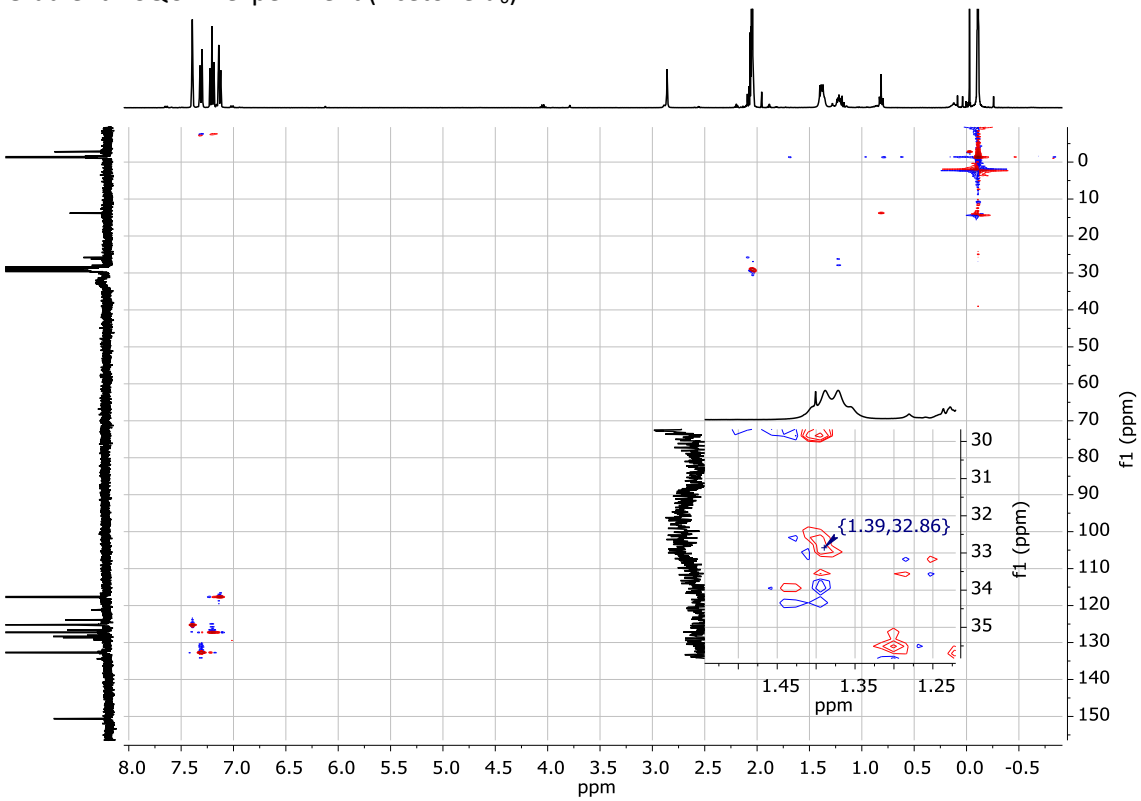
(**27-CF$_3$**) ^{1}H NMR (400 MHz, Acetone-d_6)



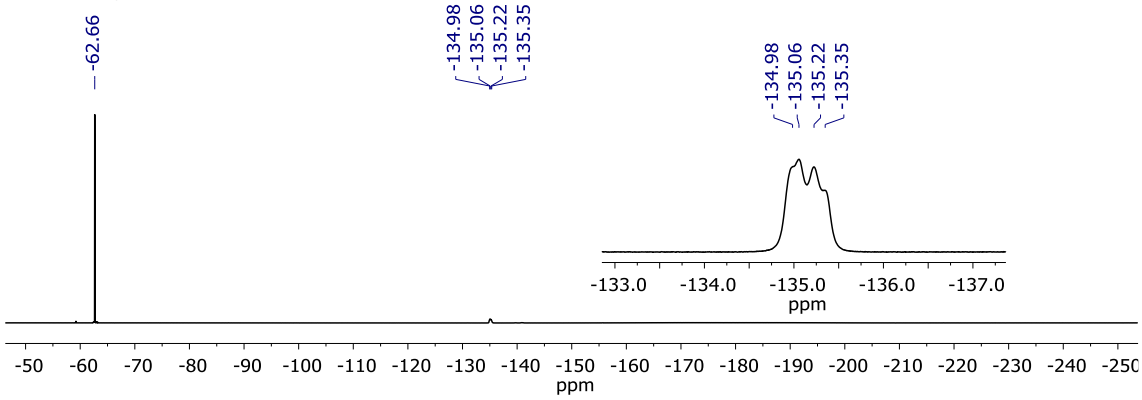
^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6)



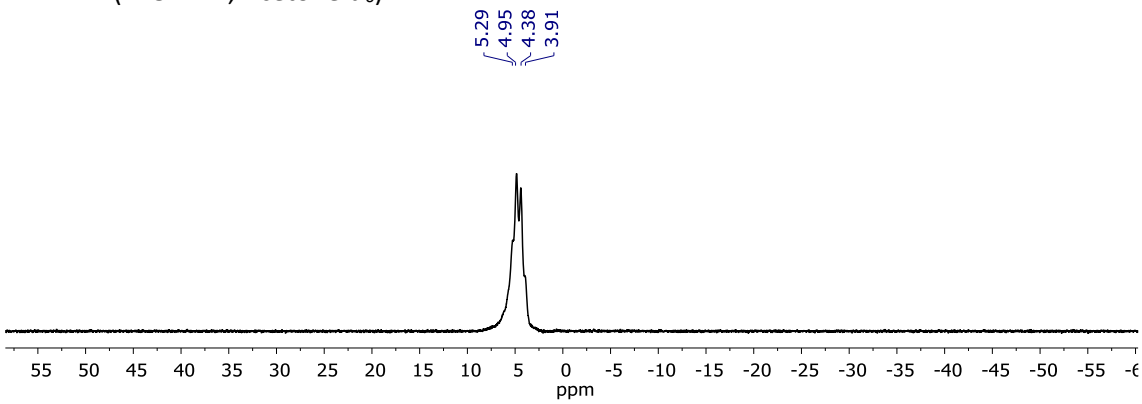
Gradient HSQCAD experiment (Acetone-d_6)

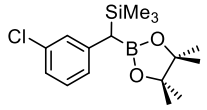


^{19}F NMR (376 MHz, Acetone-d_6

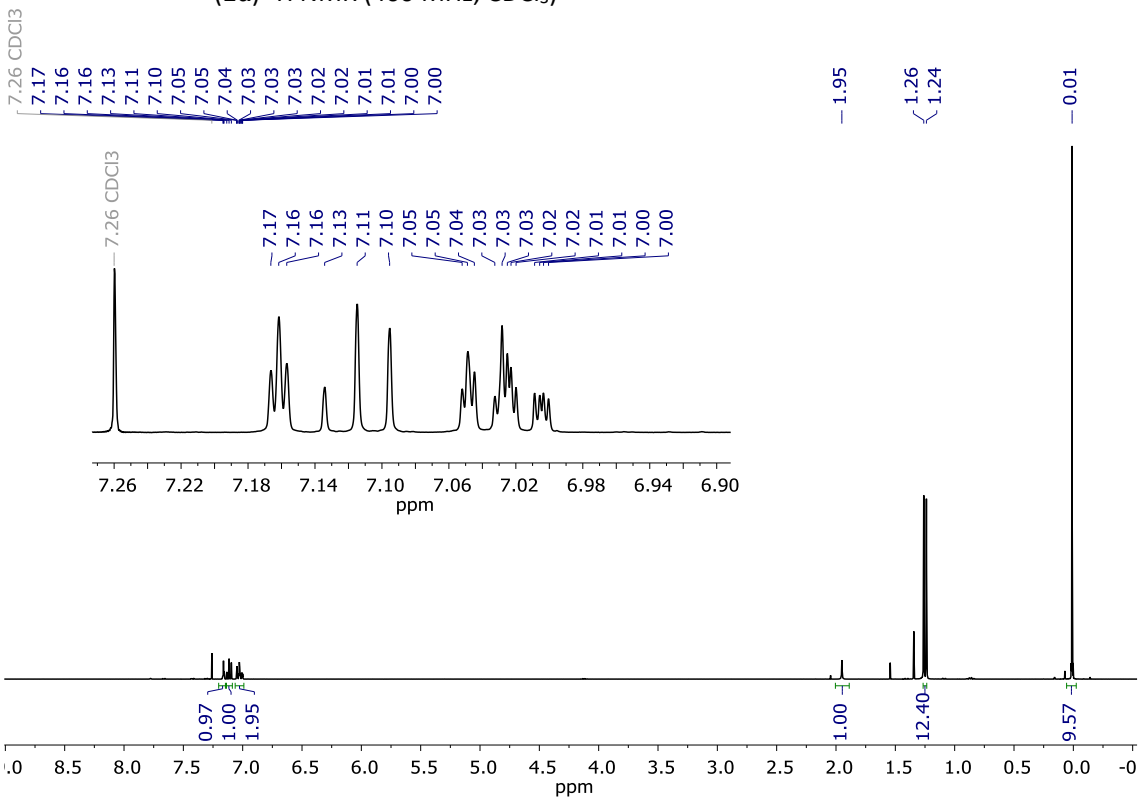


^{11}B NMR (128 MHz, Acetone-d_6)

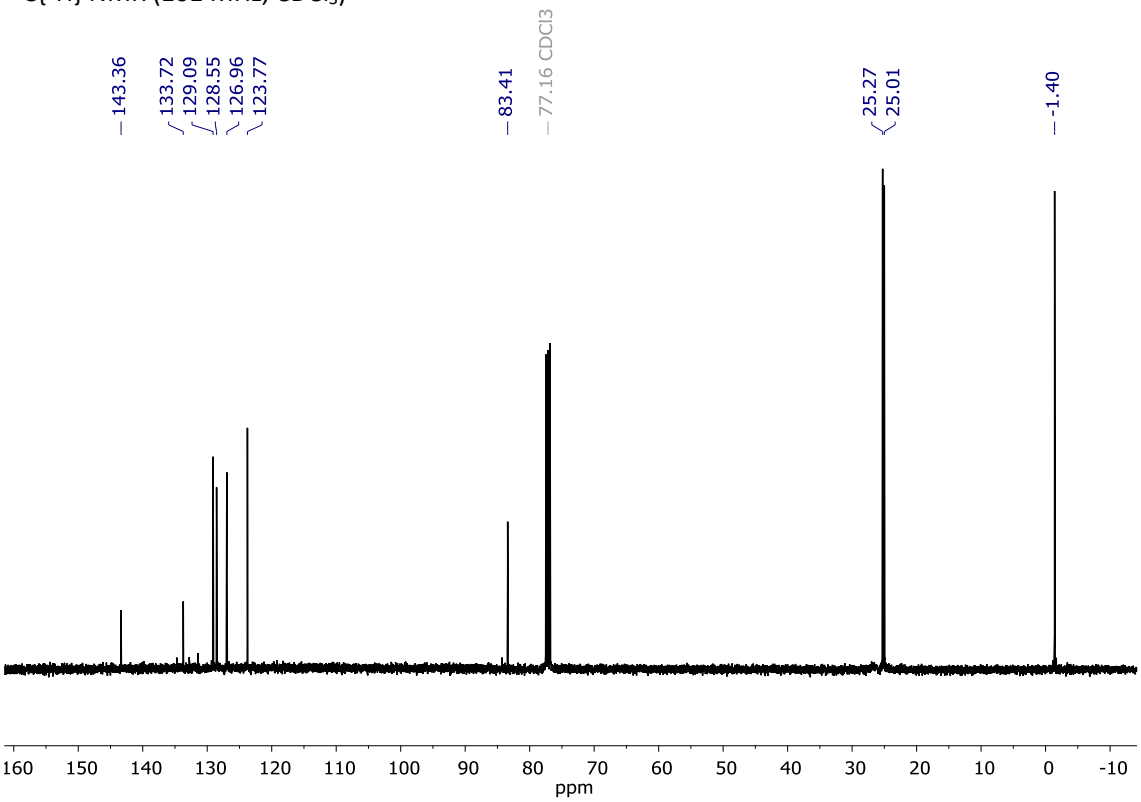




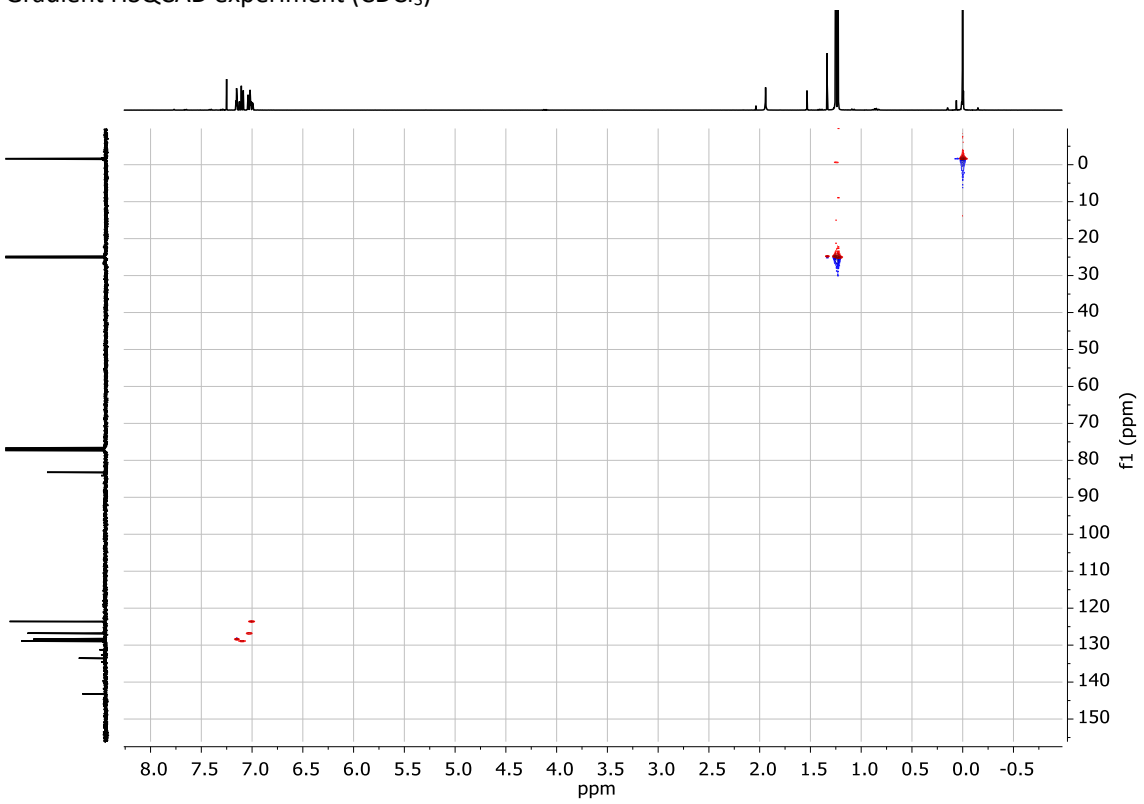
(**1d**) ^{1}H NMR (400 MHz, $CDCl_3$)



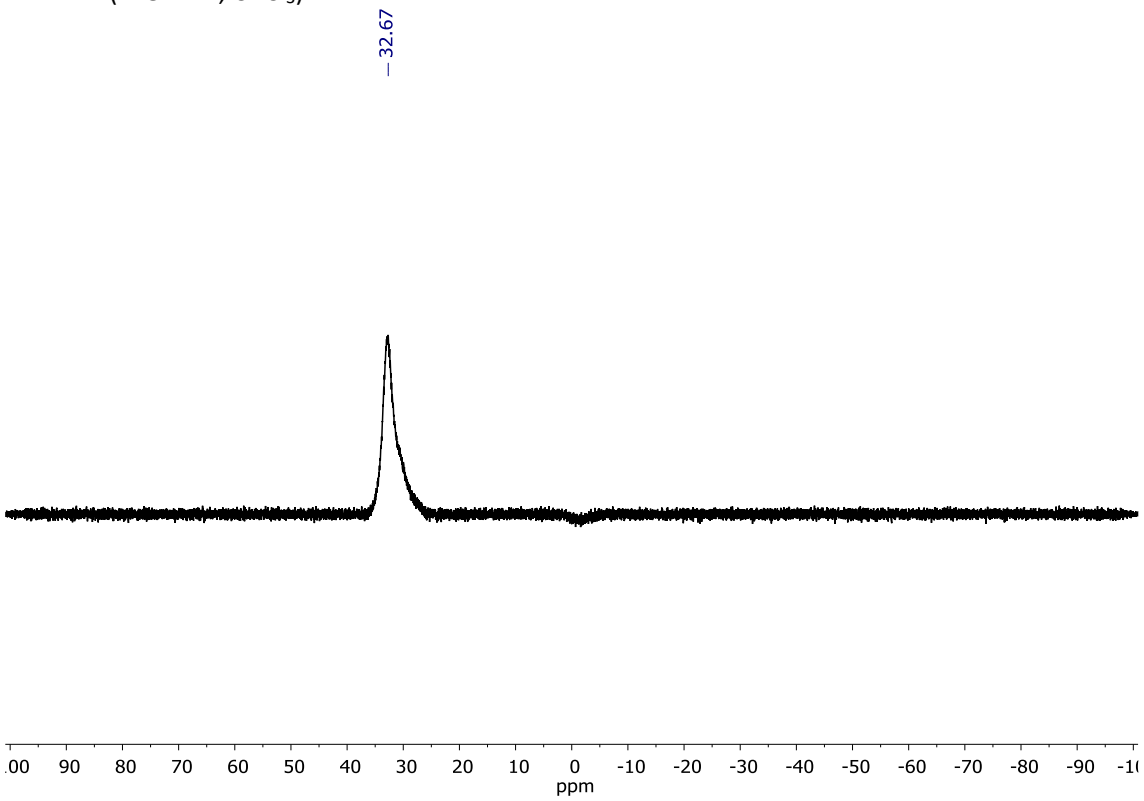
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

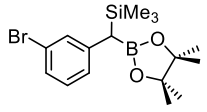


Gradient HSQCAD experiment ($CDCl_3$)

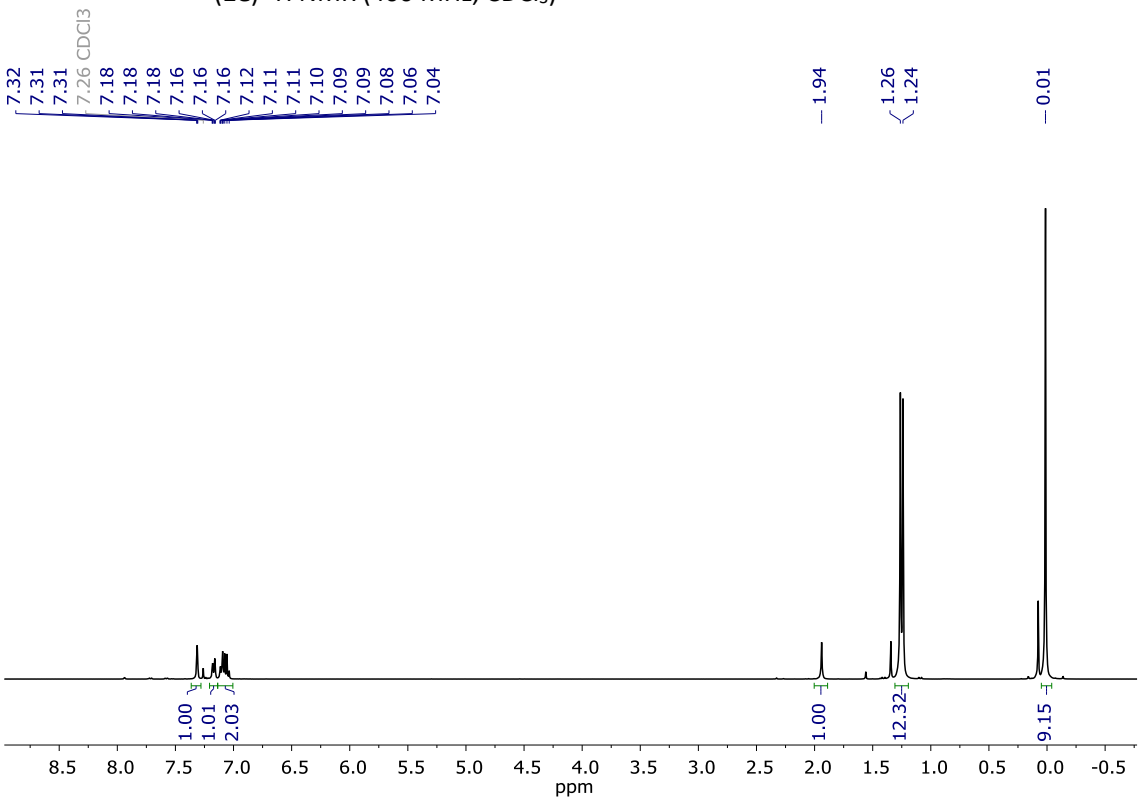


^{11}B NMR (128 MHz, $CDCl_3$)

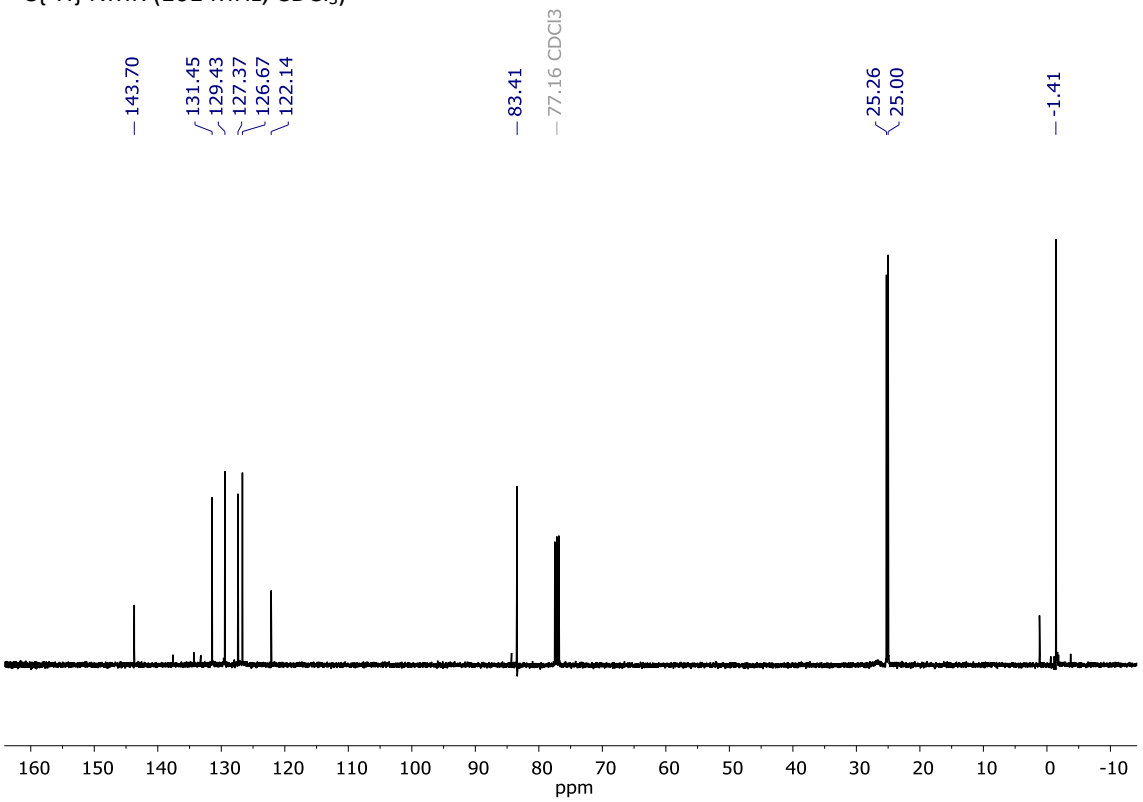




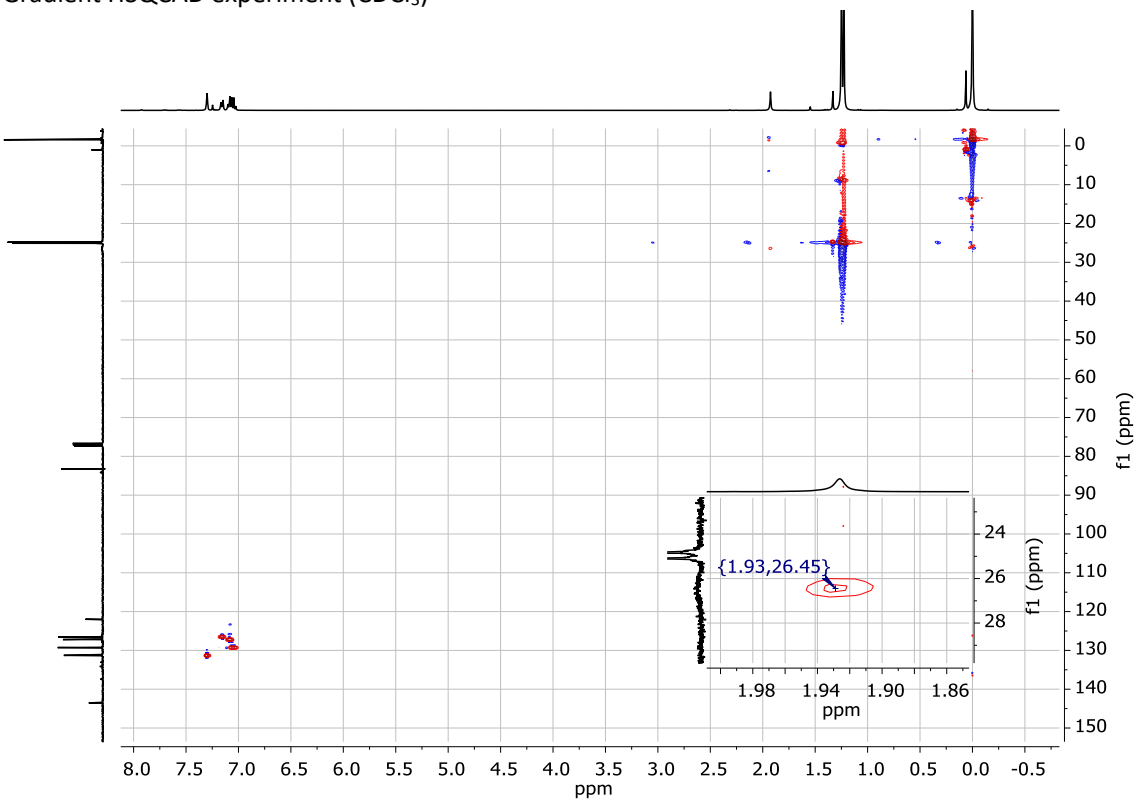
(**1e**) ^{1}H NMR (400 MHz, $CDCl_3$)



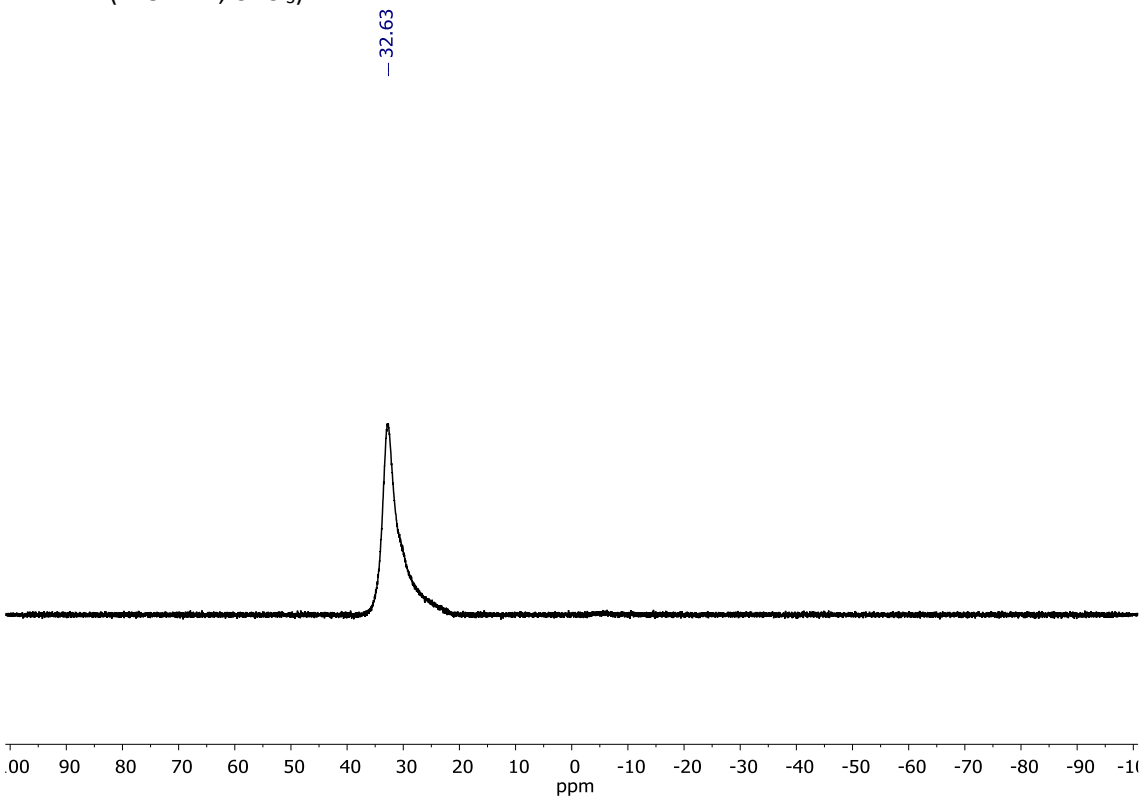
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

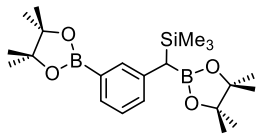


Gradient HSQCAD experiment ($CDCl_3$)

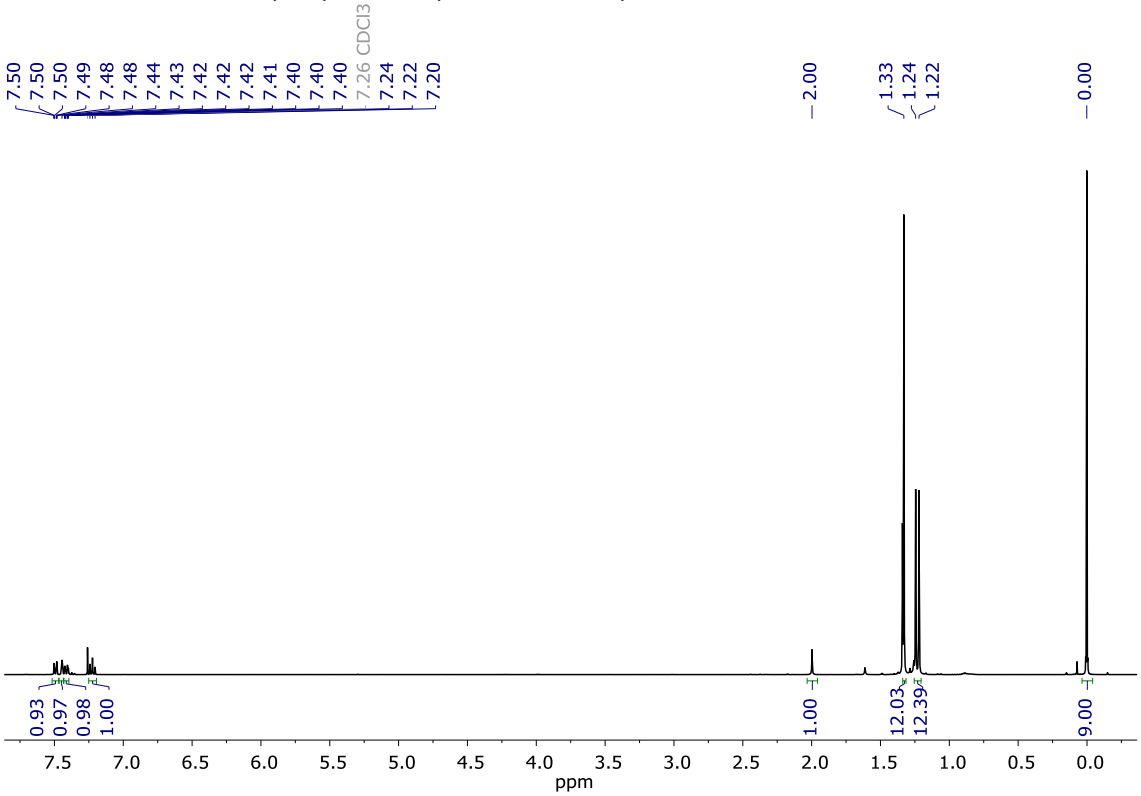


^{11}B NMR (128 MHz, $CDCl_3$)

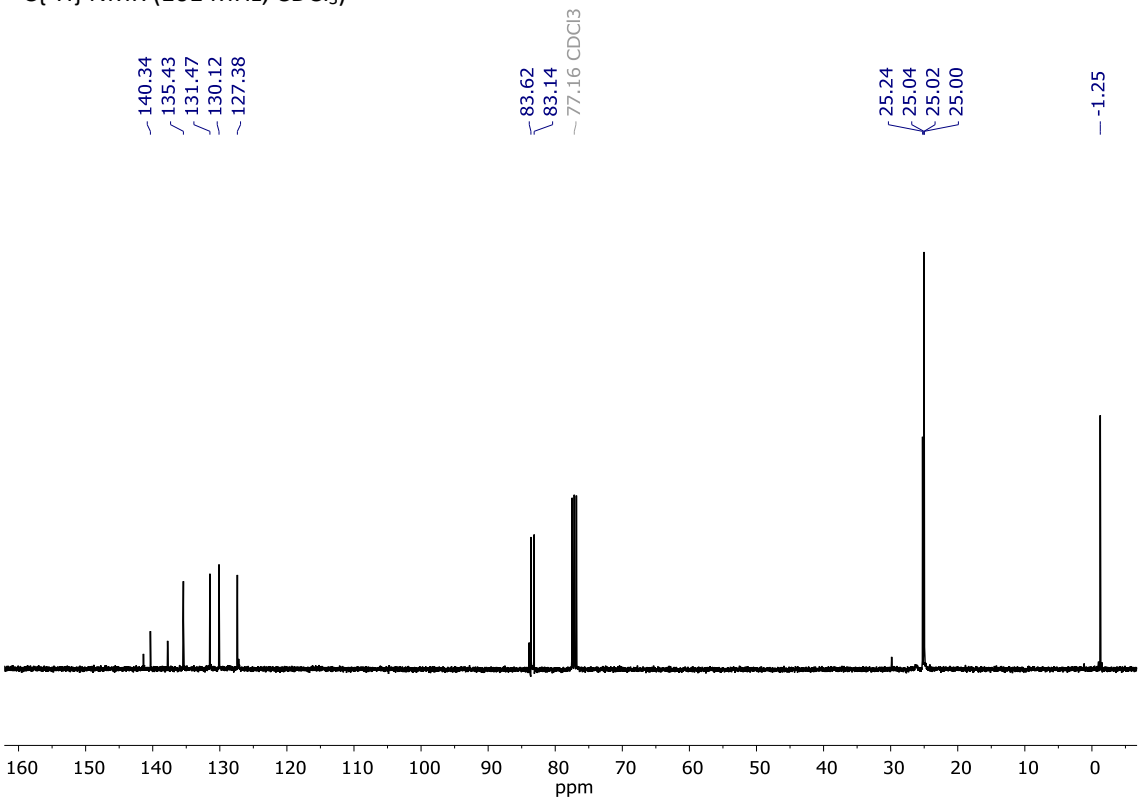




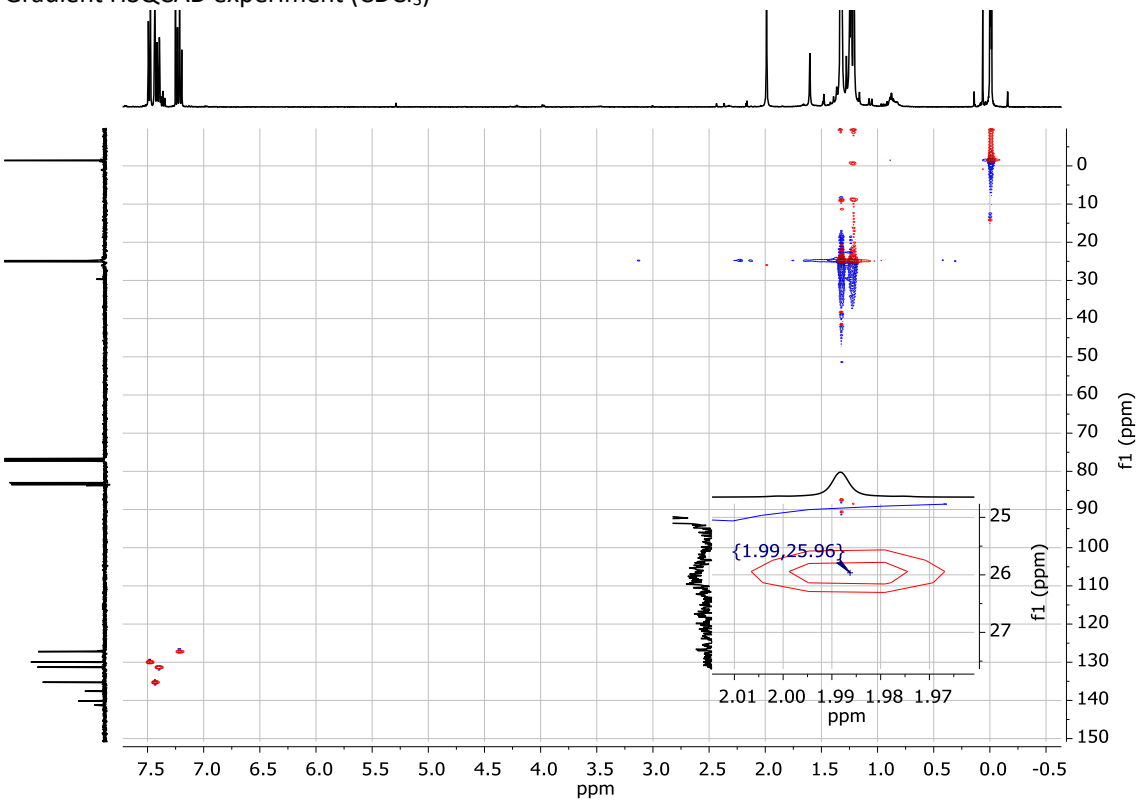
(**SI-b**) ^{1}H NMR (400 MHz, $CDCl_3$)



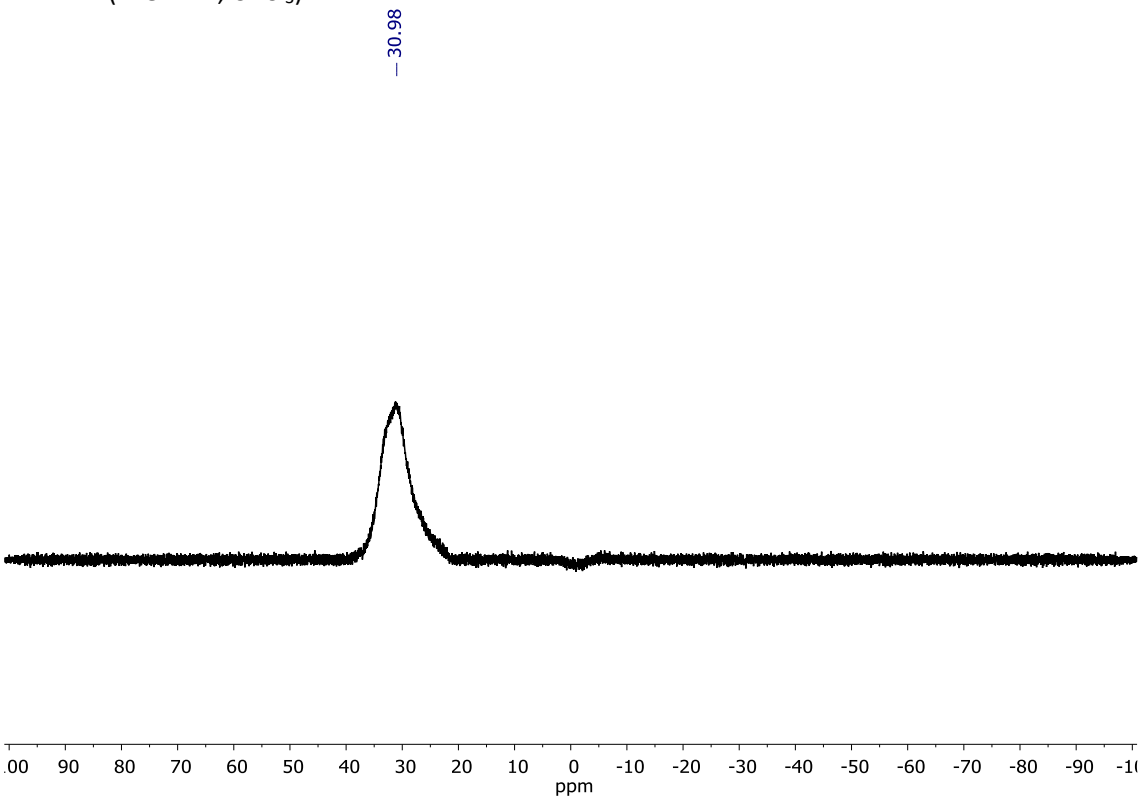
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

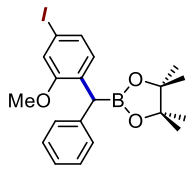


Gradient HSQCAD experiment ($CDCl_3$)

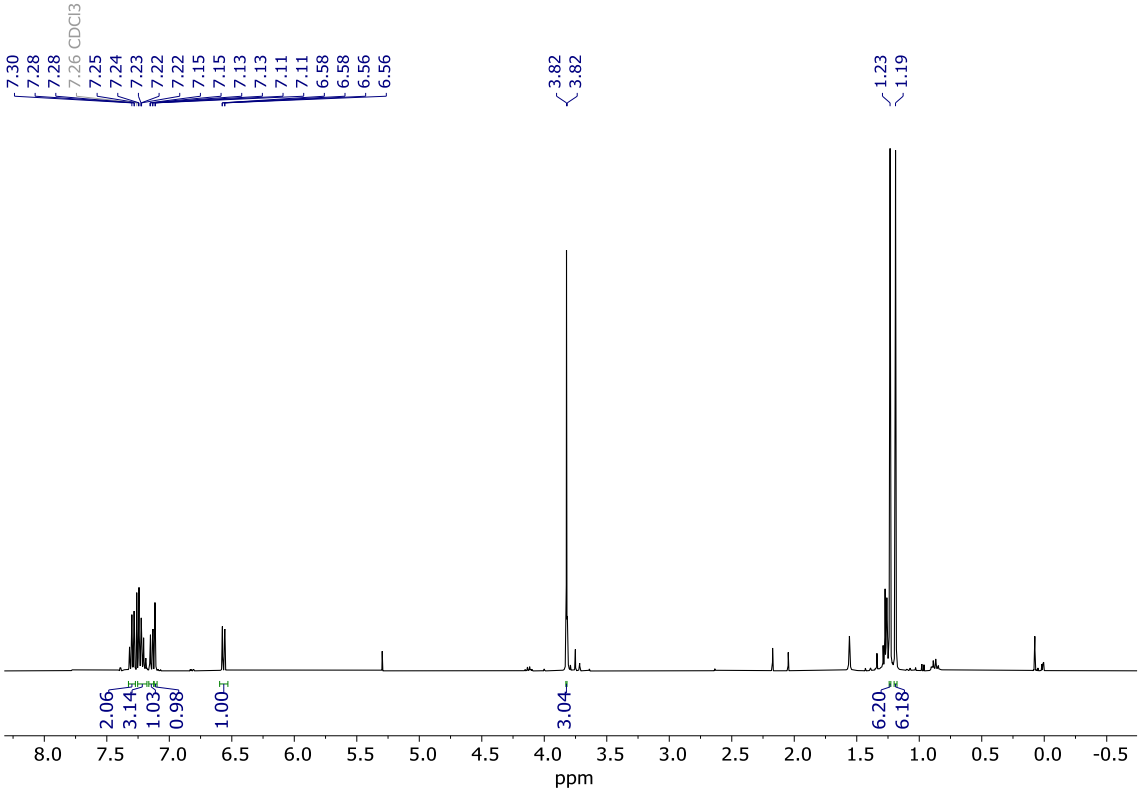


^{11}B NMR (128 MHz, $CDCl_3$)

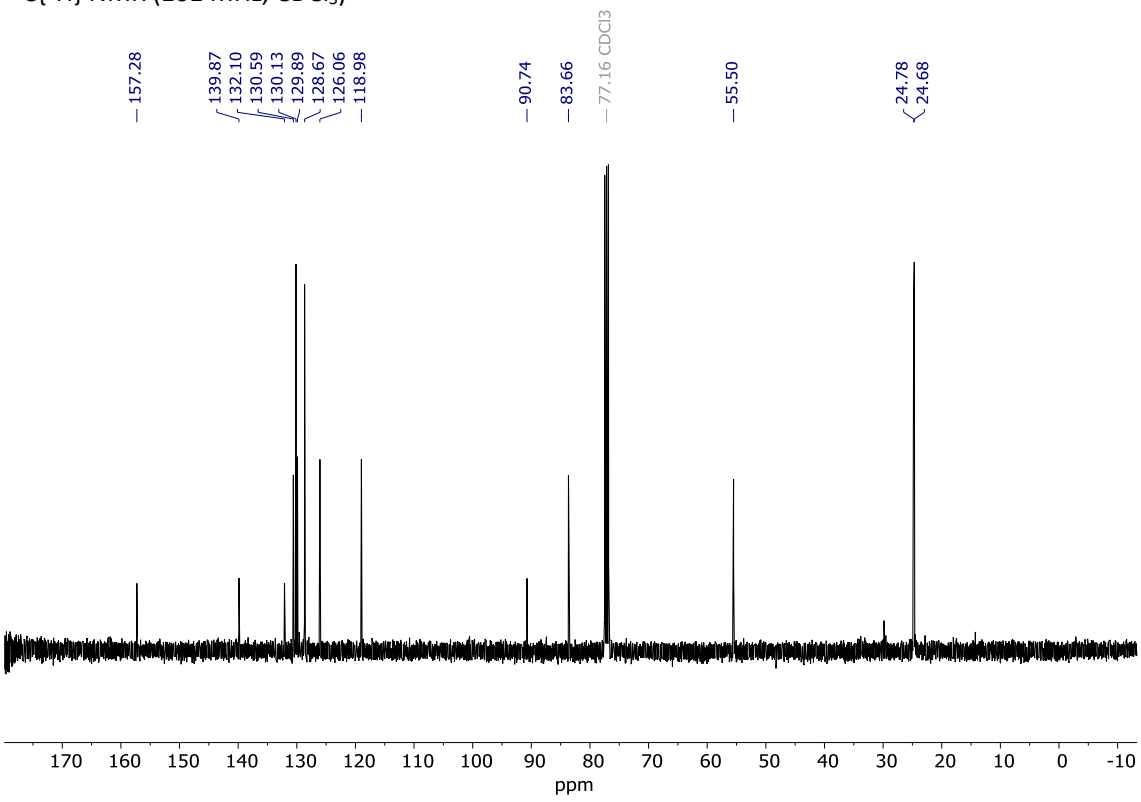




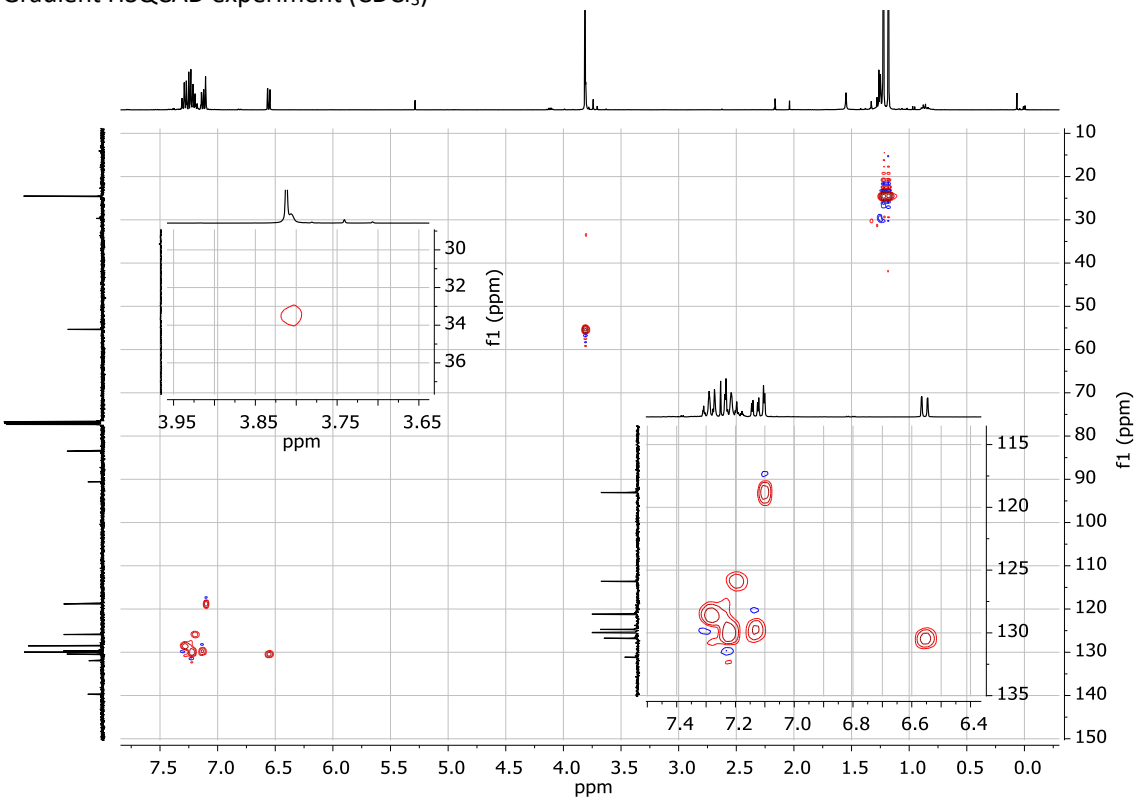
(**6**) ^{1}H NMR (400 MHz, $CDCl_3$)



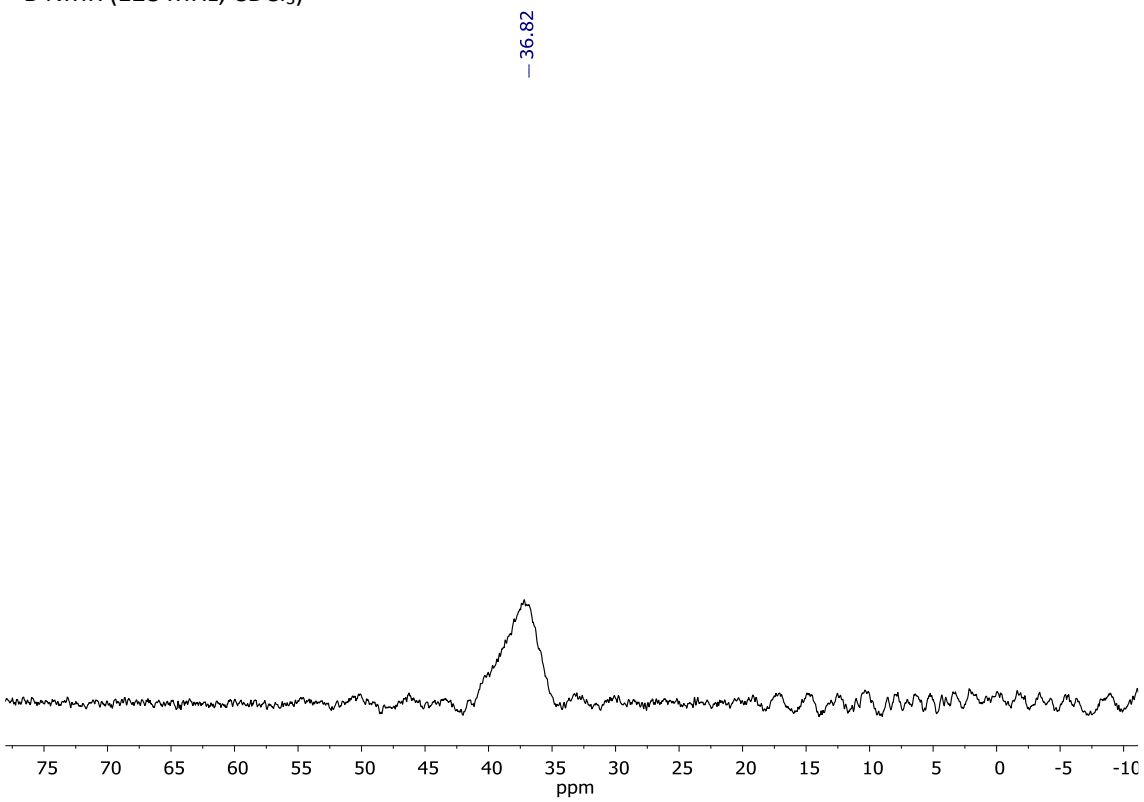
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

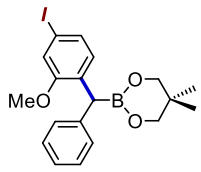


Gradient HSQCAD experiment ($CDCl_3$)



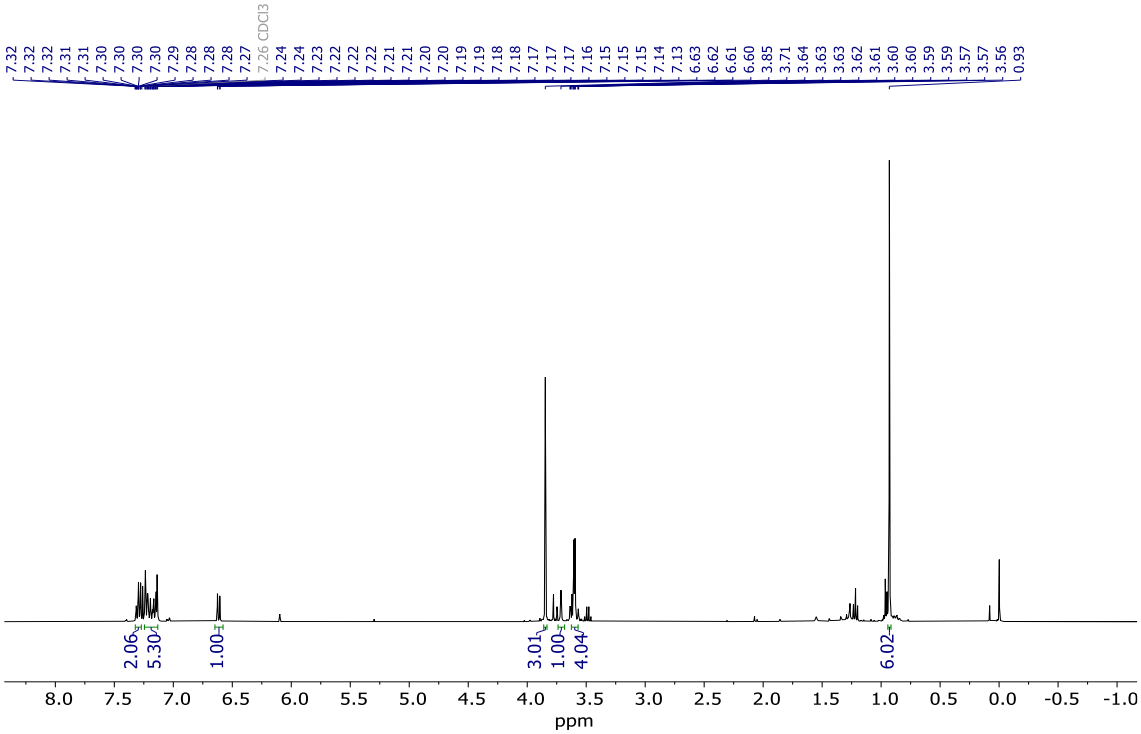
^{11}B NMR (128 MHz, $CDCl_3$)



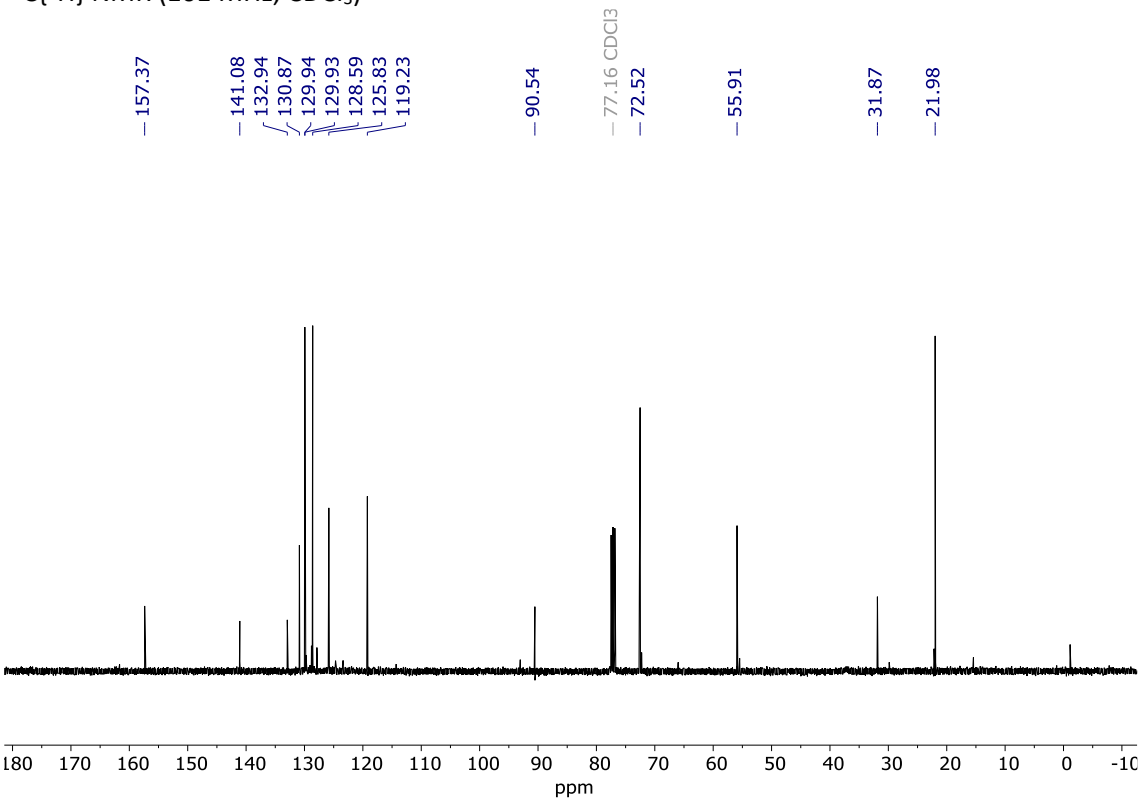


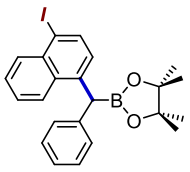
(**6'**) ^{1}H NMR (400 MHz, $CDCl_3$)

Impurities observed in the spectrum are due to the inherent instability of this class of C(sp3)-Bp derivatives, and in particular of those with a Bnep fragment, on column chromatography.

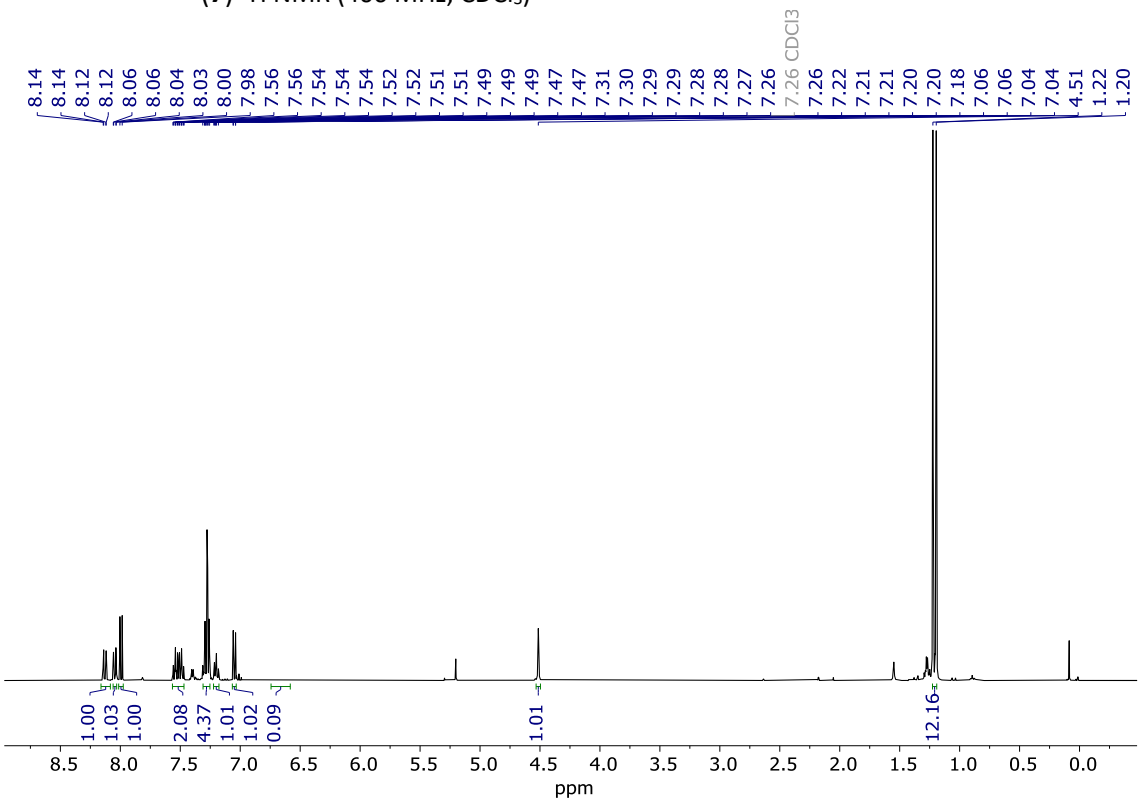


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

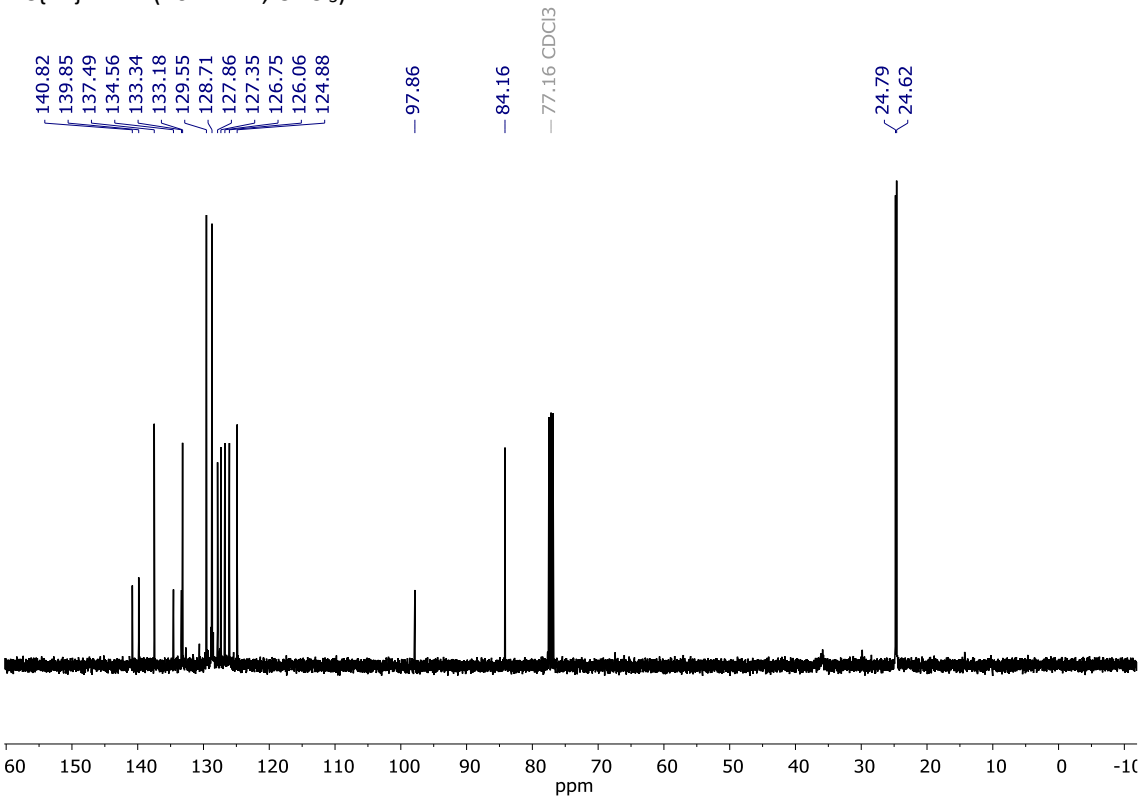




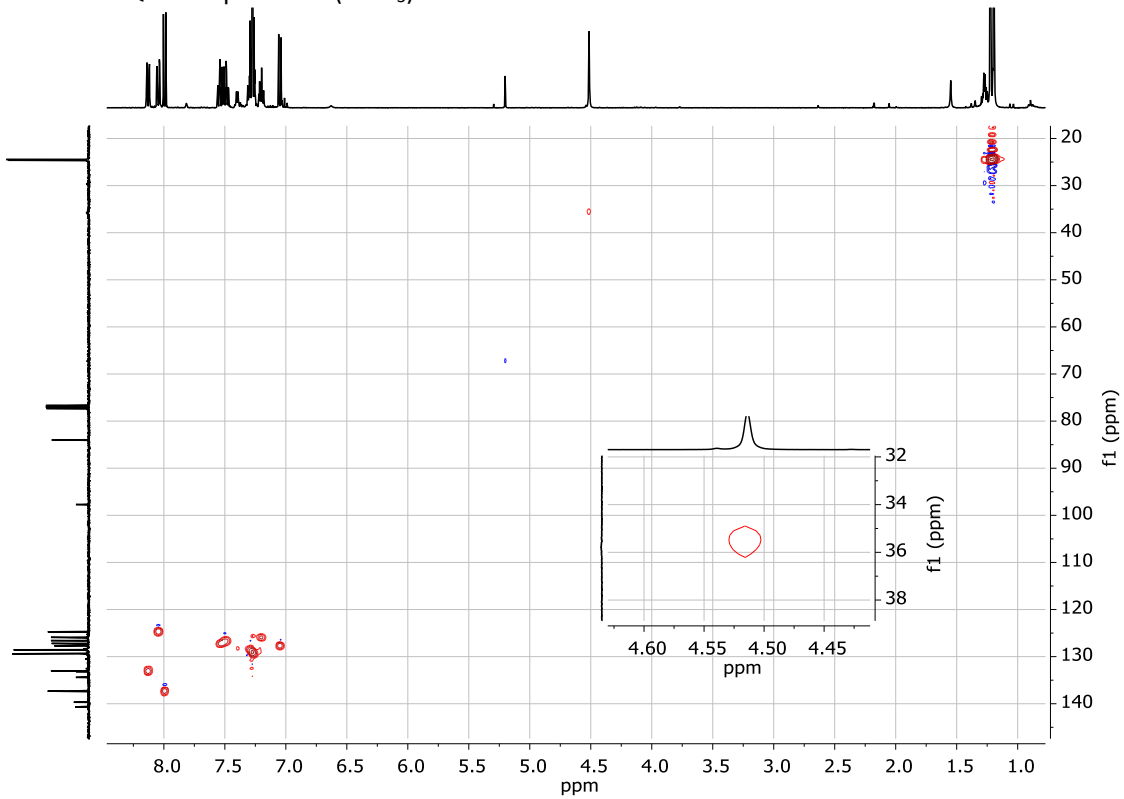
(**7**) ^{1}H NMR (400 MHz, $CDCl_3$)



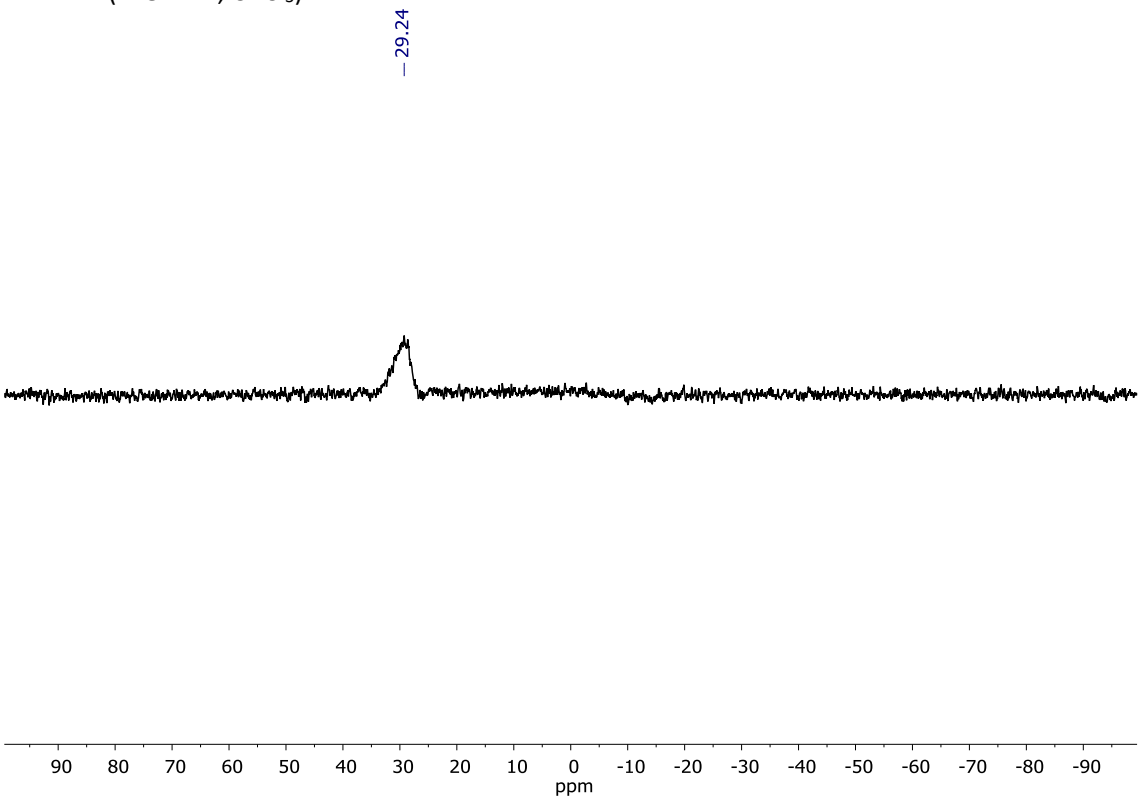
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

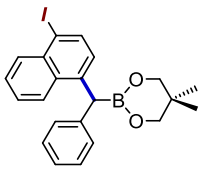


Gradient HSQCAD experiment ($CDCl_3$)

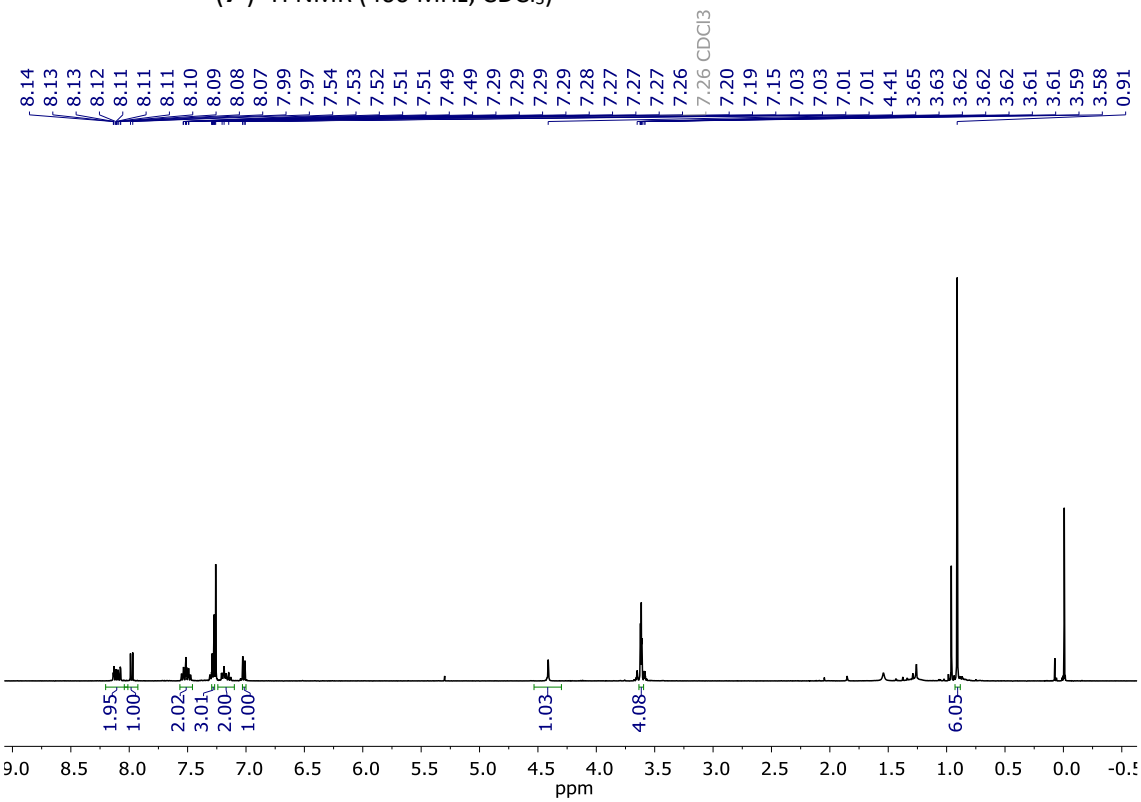


^{11}B NMR (128 MHz, $CDCl_3$)

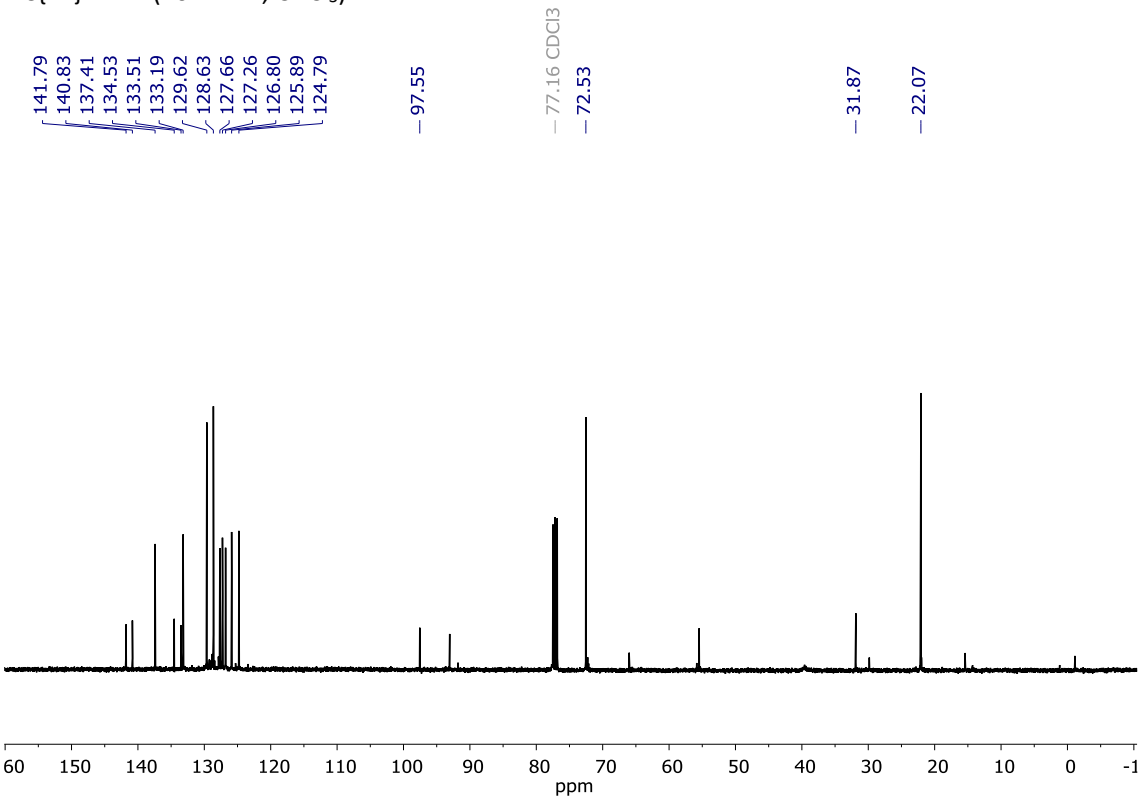


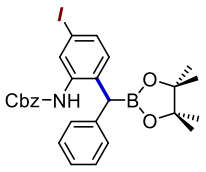


(**7'**) ^{1}H NMR (400 MHz, $CDCl_3$)

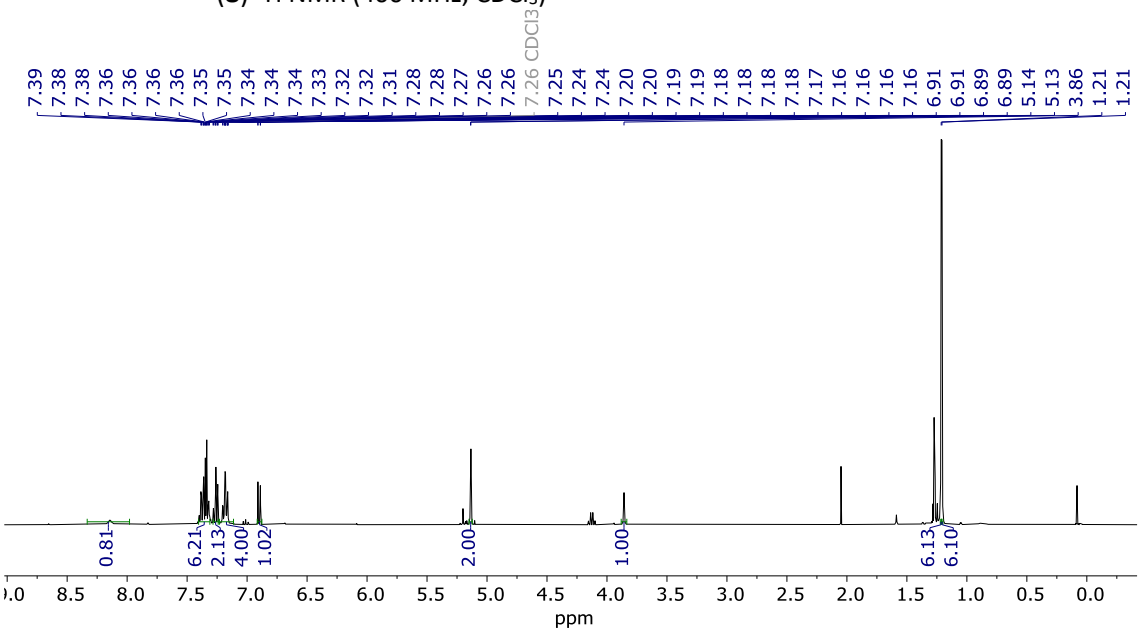


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

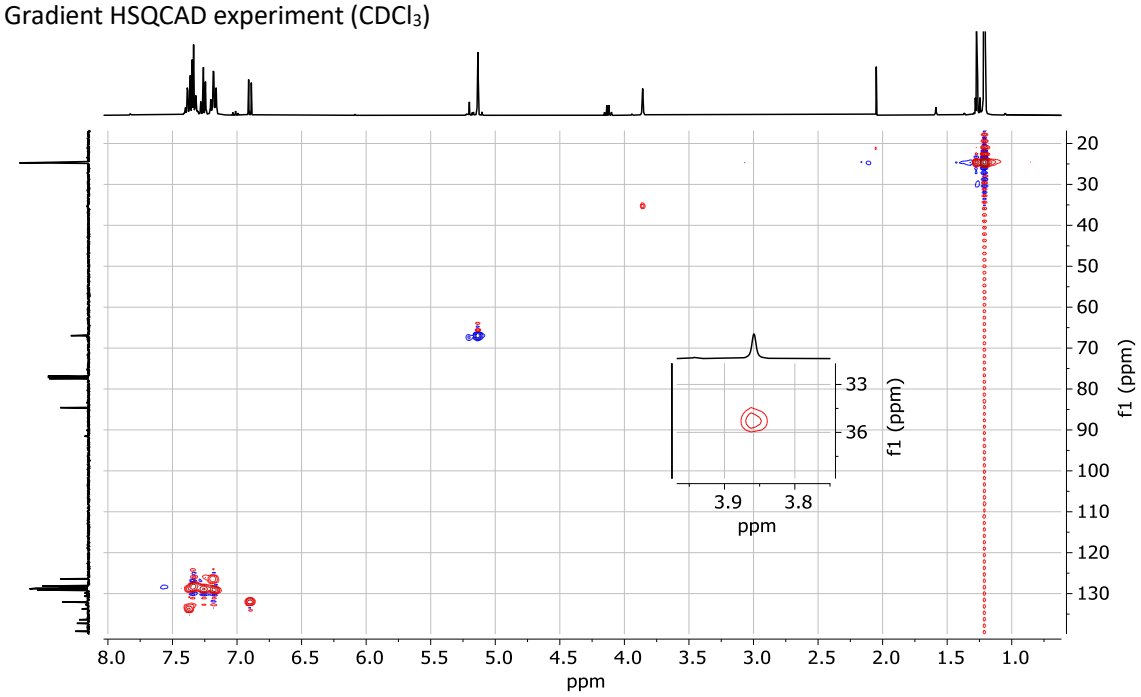




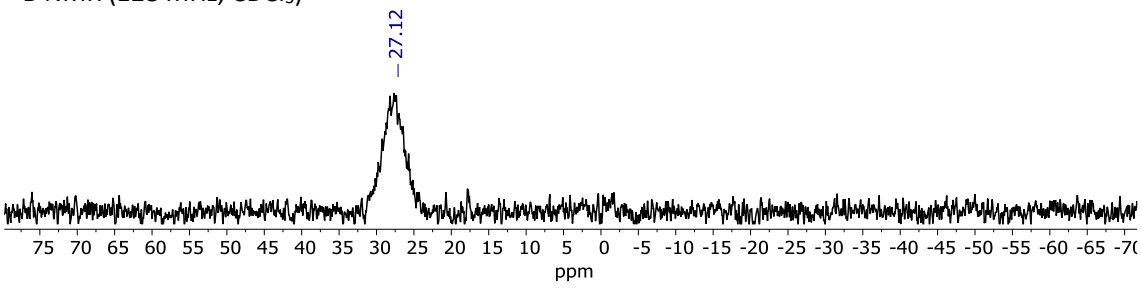
(**8**) ^{1}H NMR (400 MHz, $CDCl_3$)

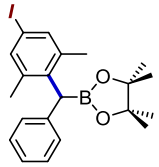


Gradient HSQCAD experiment ($CDCl_3$)

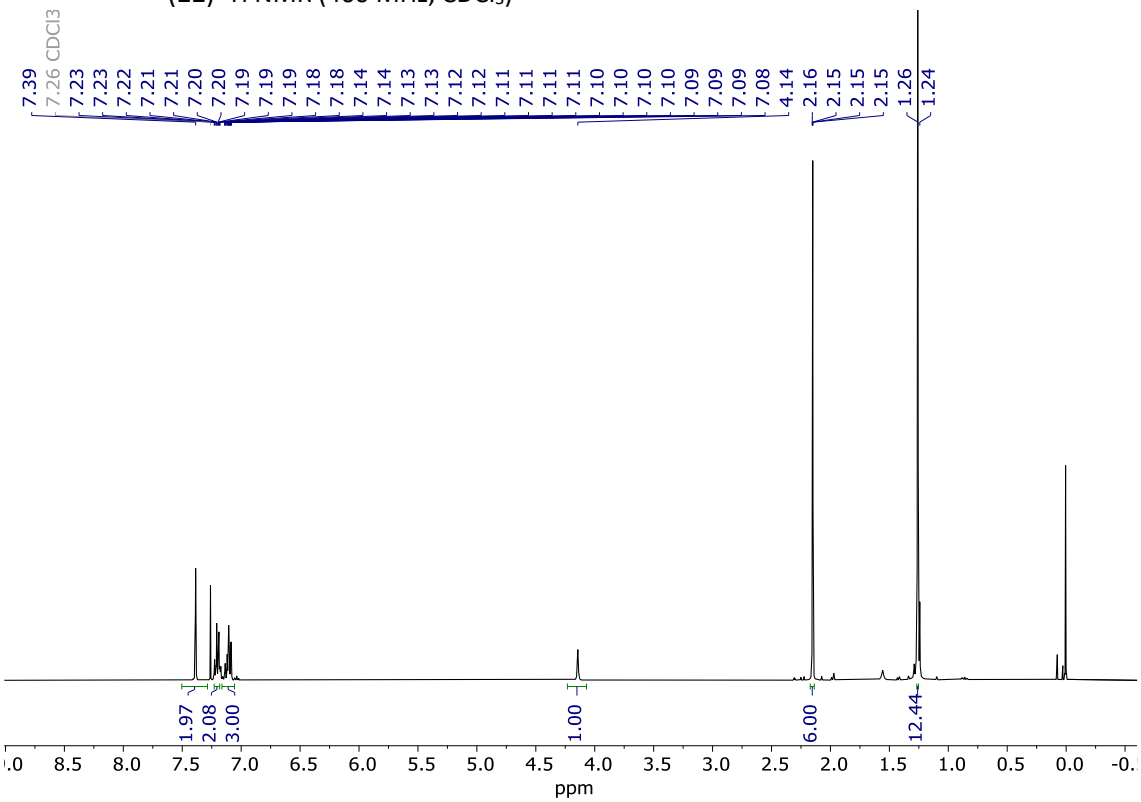


^{11}B NMR (128 MHz, $CDCl_3$)

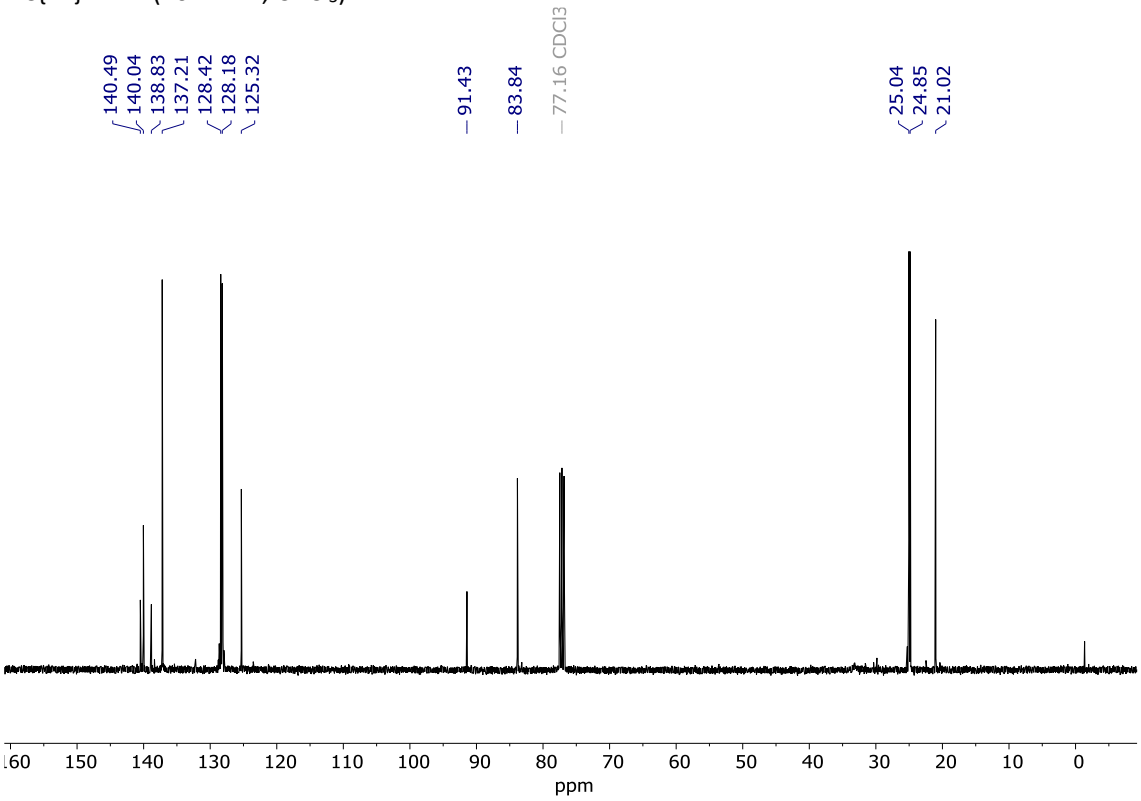




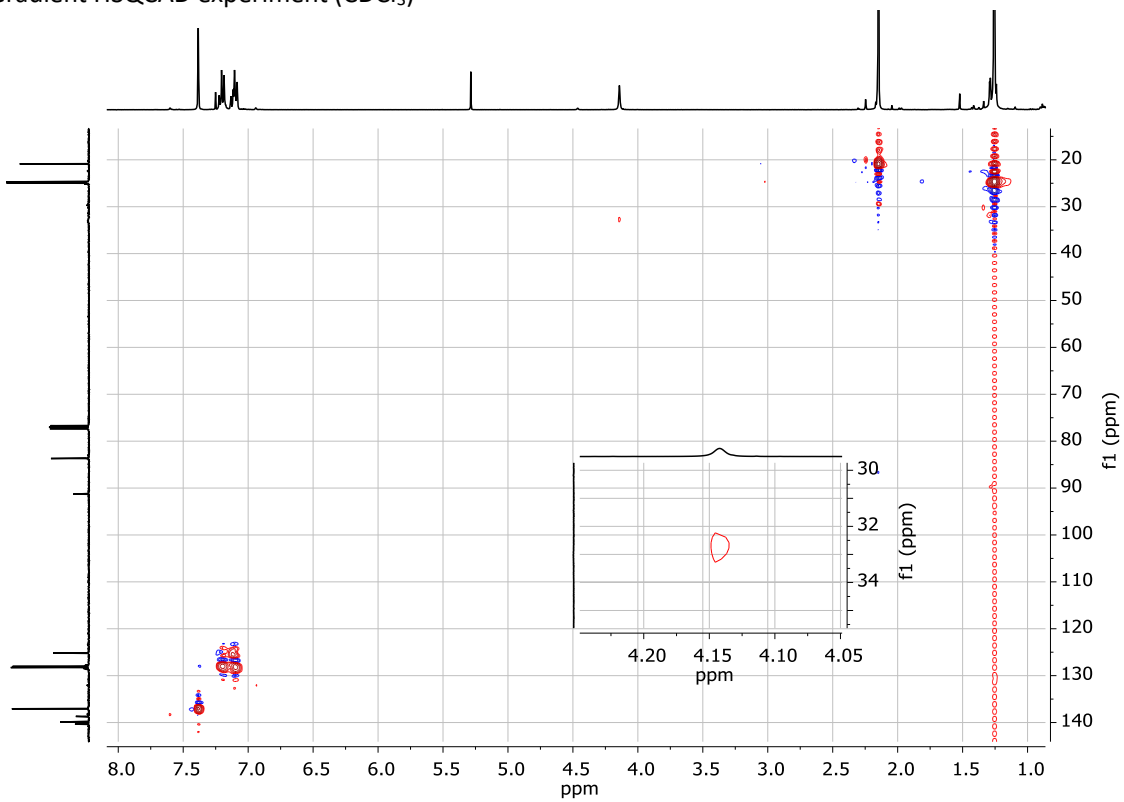
(**11**) ^{1}H NMR (400 MHz, $CDCl_3$)



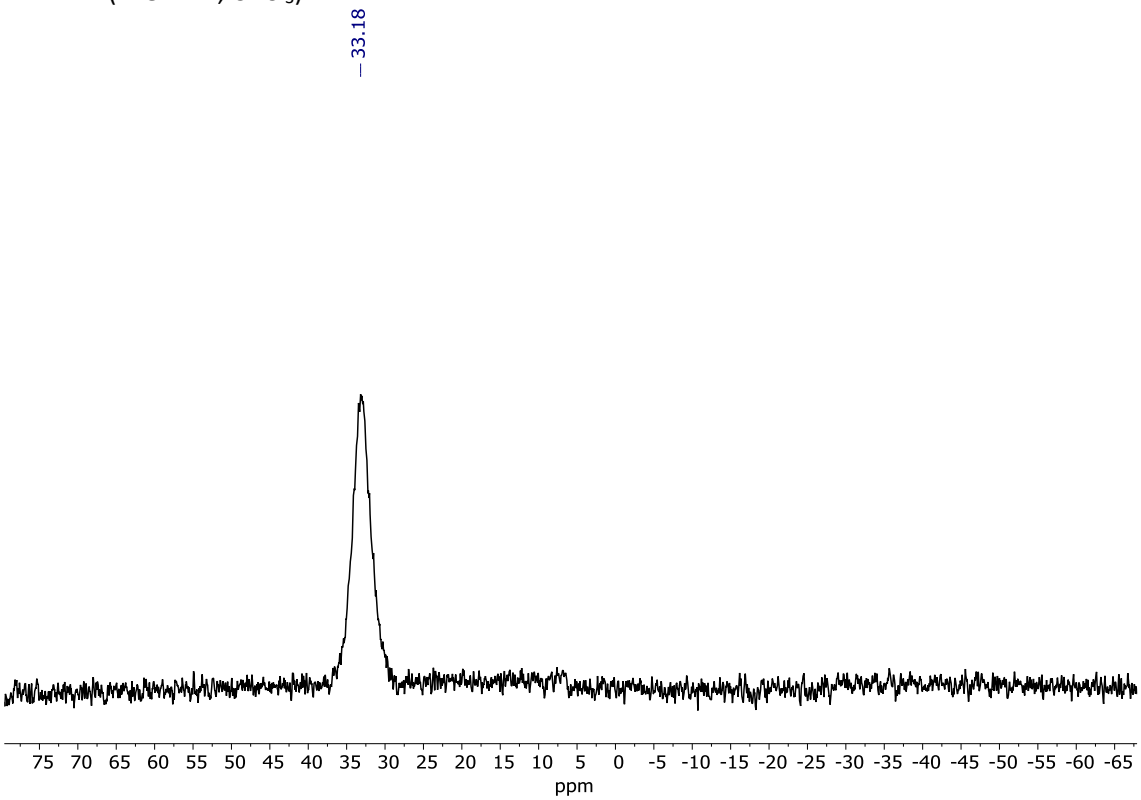
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

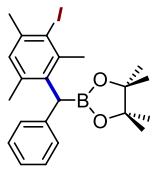


Gradient HSQCAD experiment ($CDCl_3$)

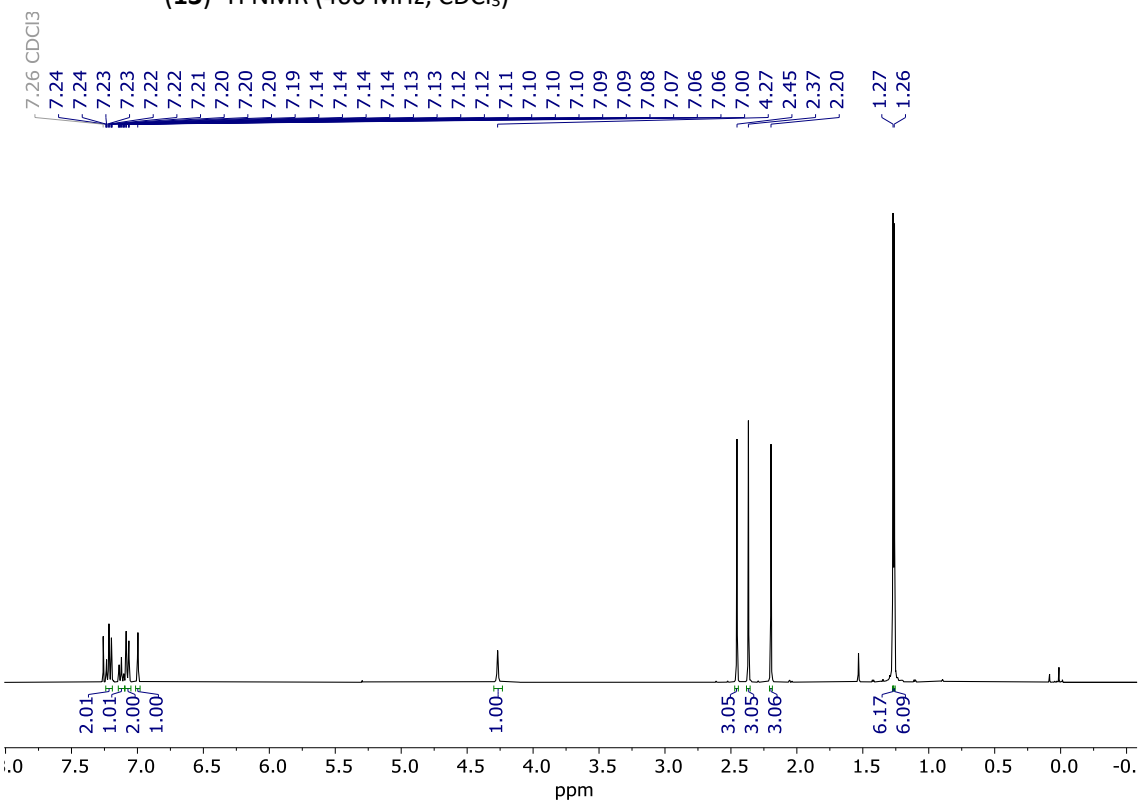


^{11}B NMR (128 MHz, $CDCl_3$)

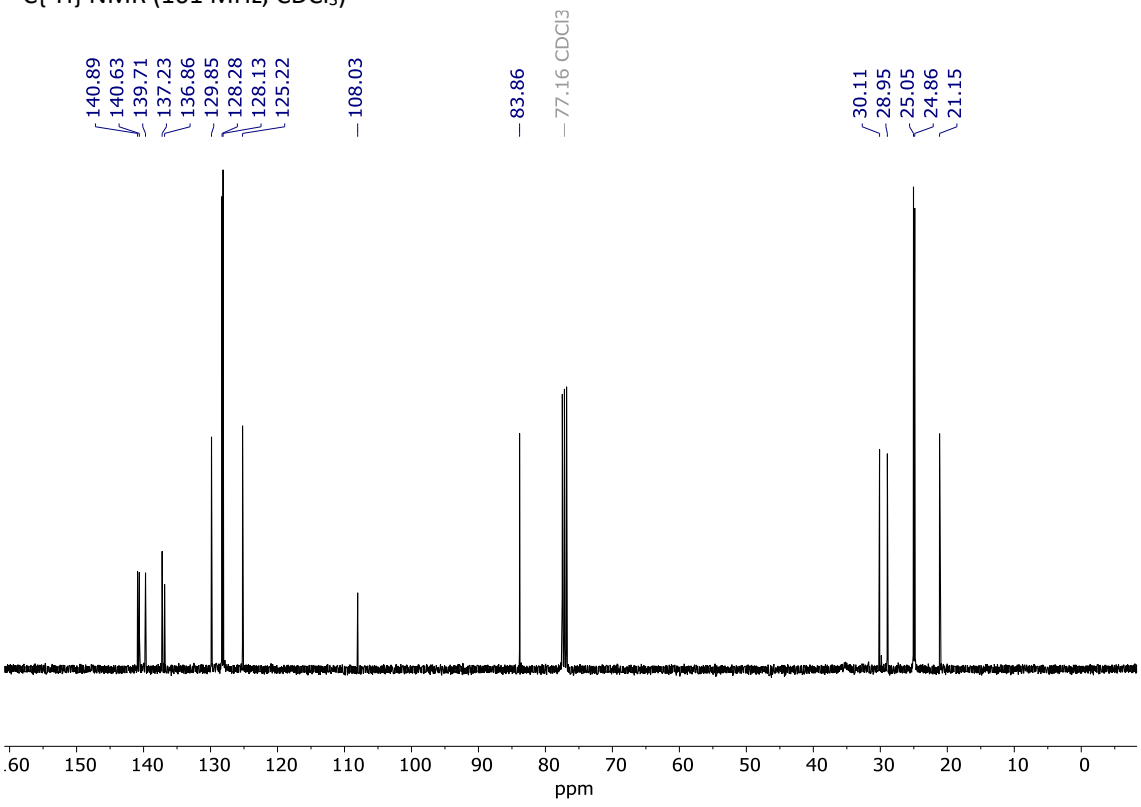




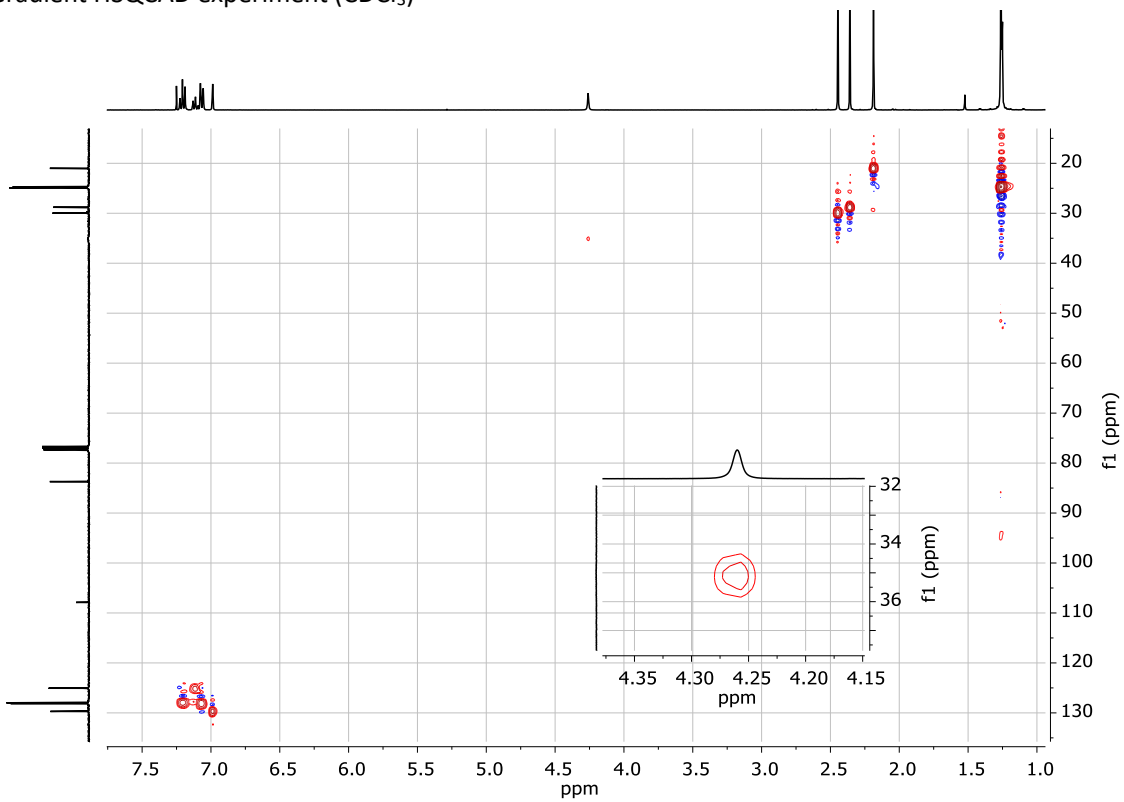
(**13**) ^{1}H NMR (400 MHz, $CDCl_3$)



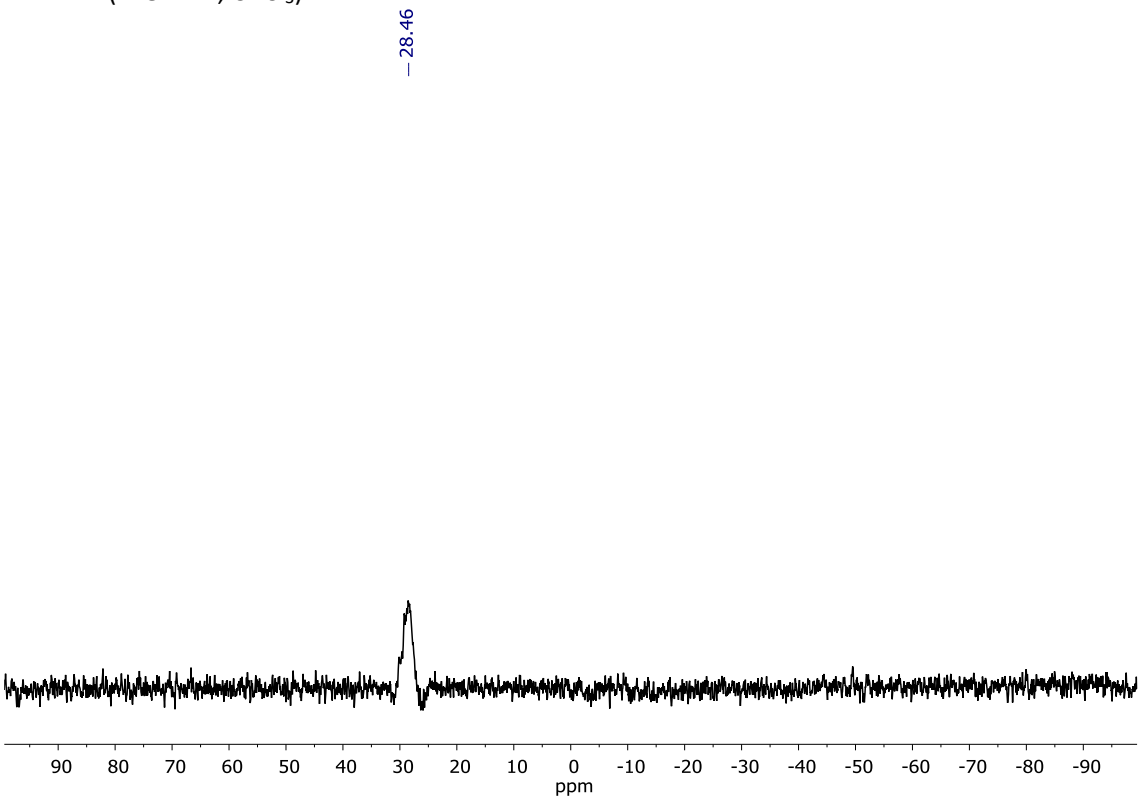
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

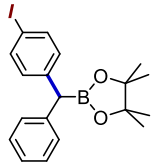


Gradient HSQCAD experiment ($CDCl_3$)

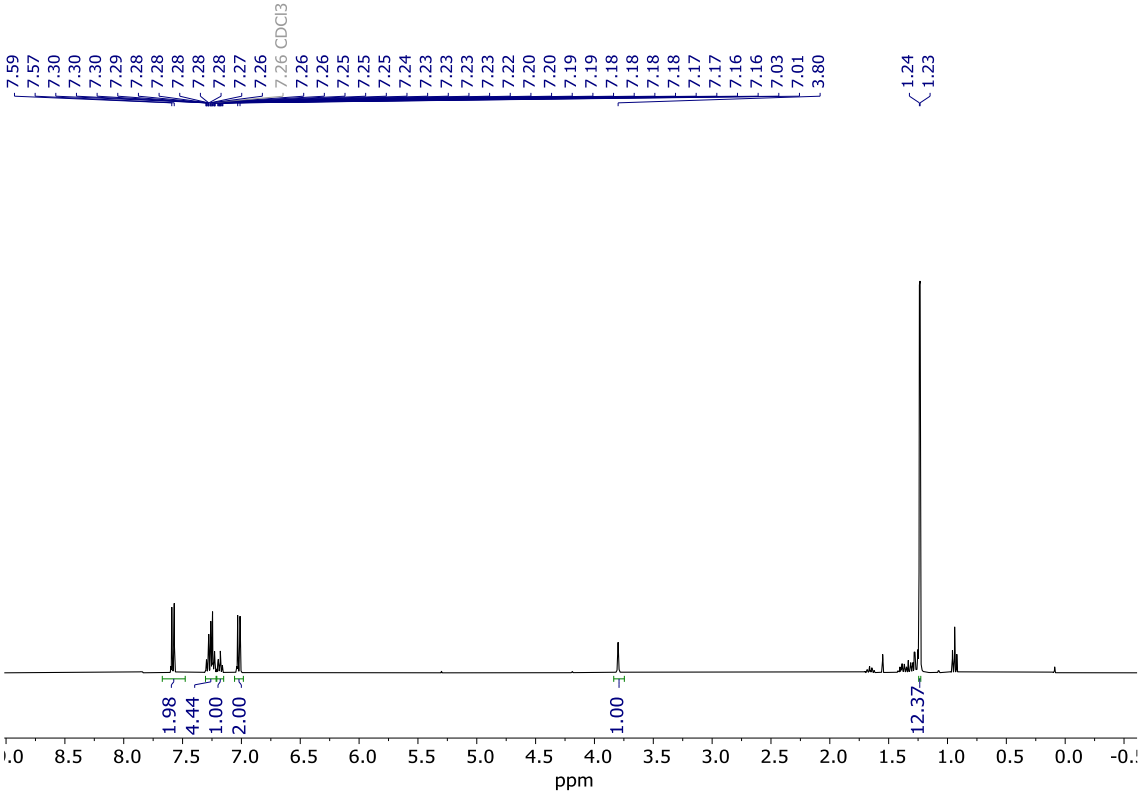


^{11}B NMR (128 MHz, $CDCl_3$)

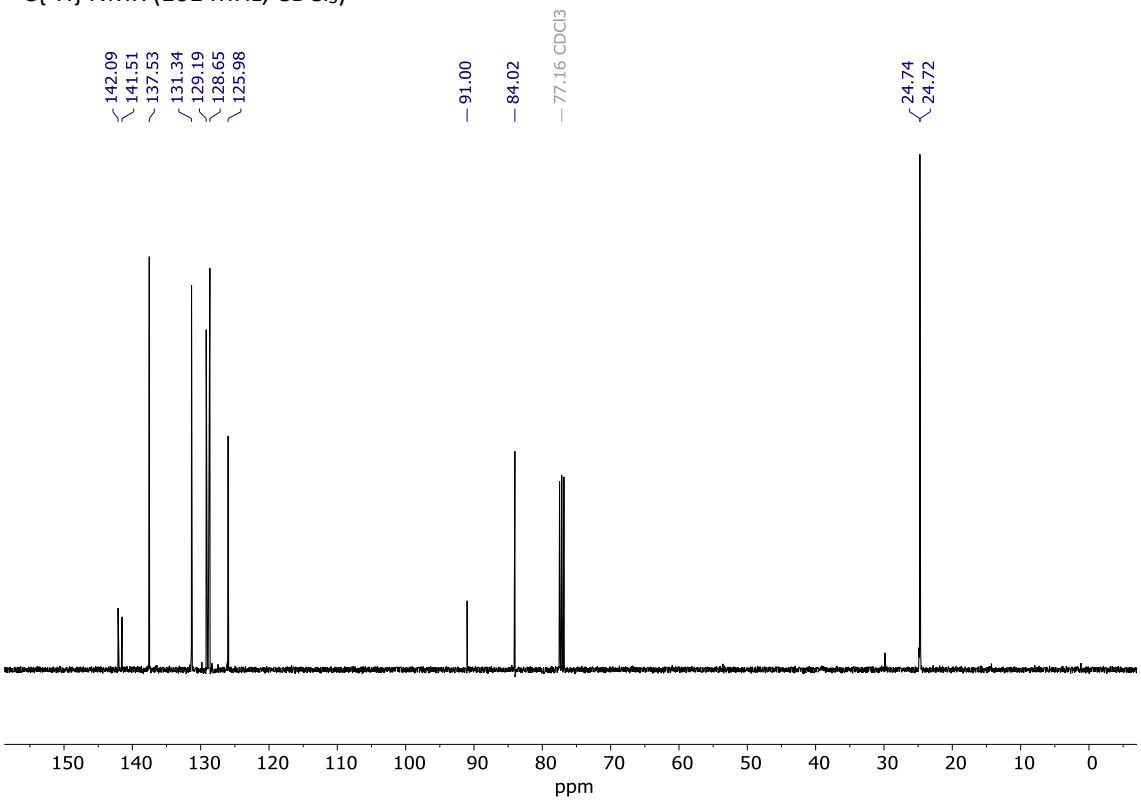




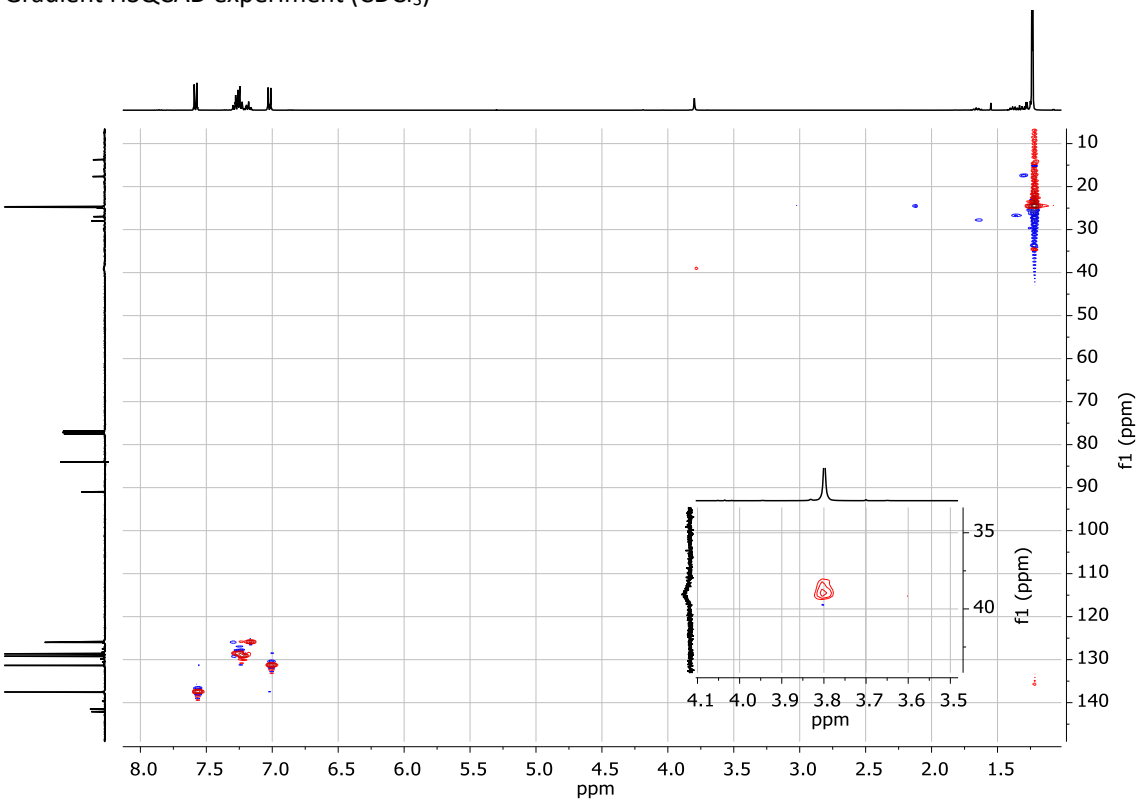
(**12**) ^{1}H NMR (400 MHz, $CDCl_3$)



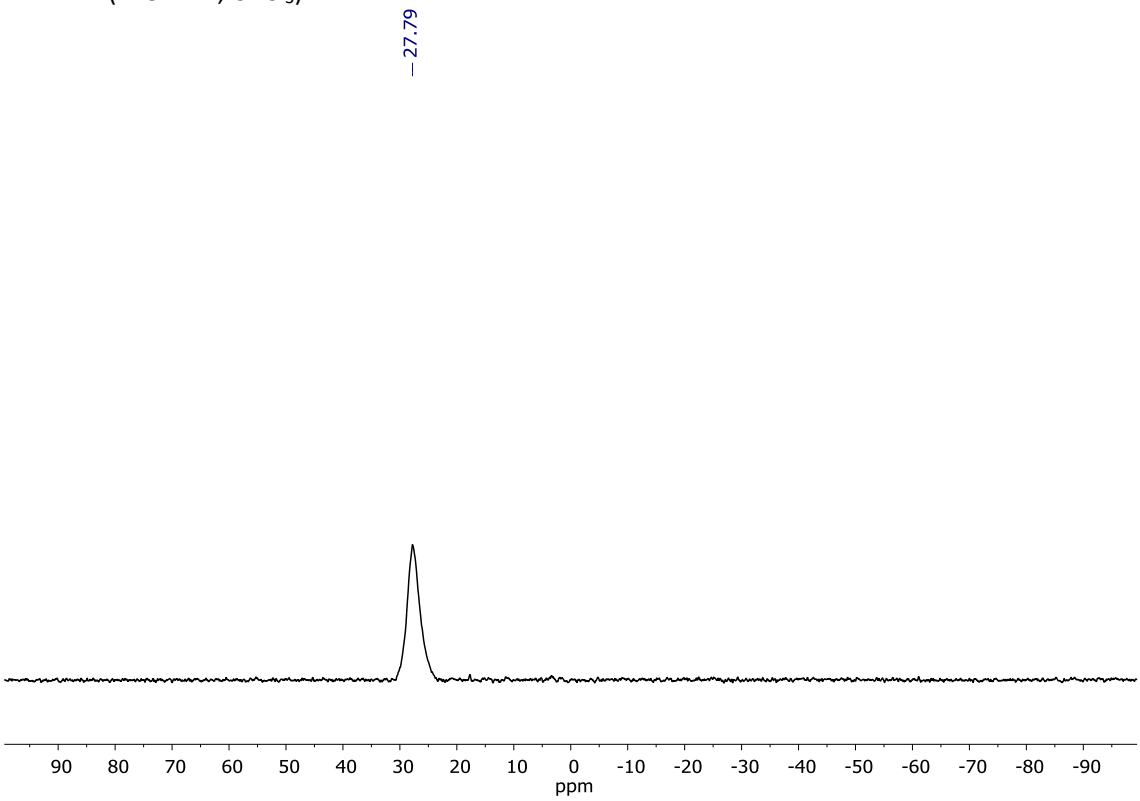
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

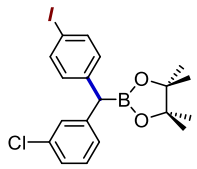


Gradient HSQCAD experiment ($CDCl_3$)

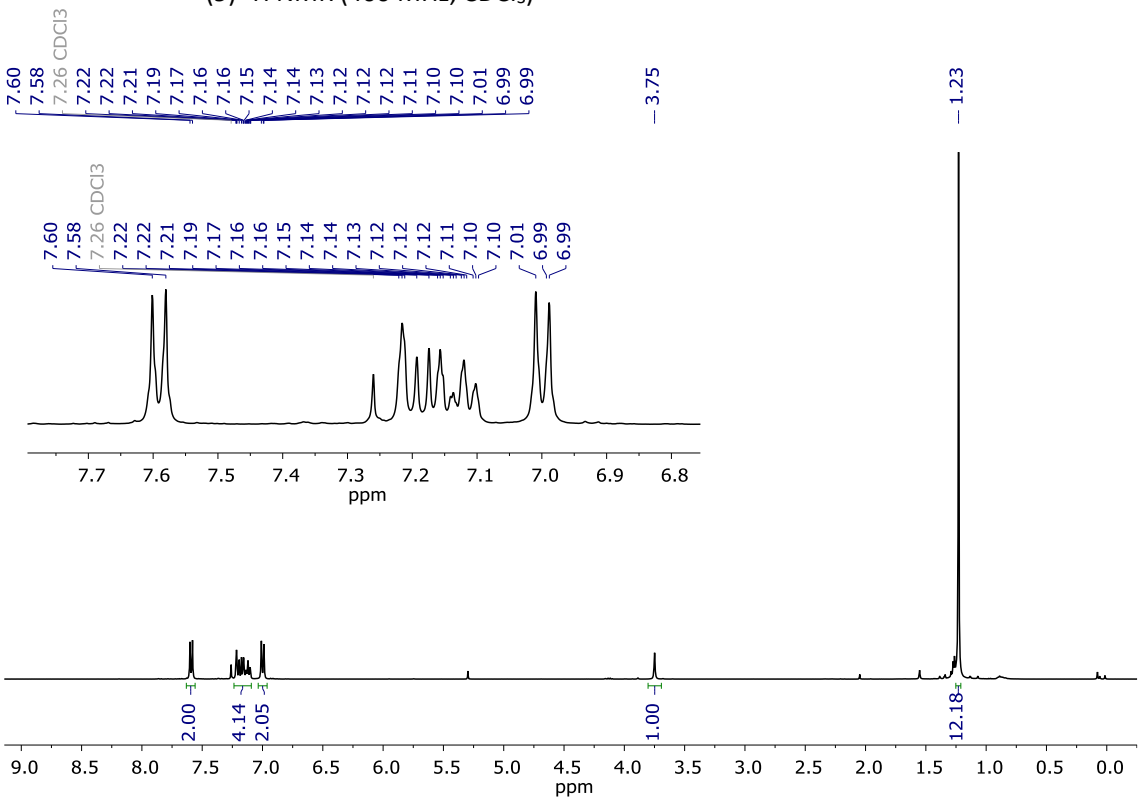


^{11}B NMR (128 MHz, $CDCl_3$)

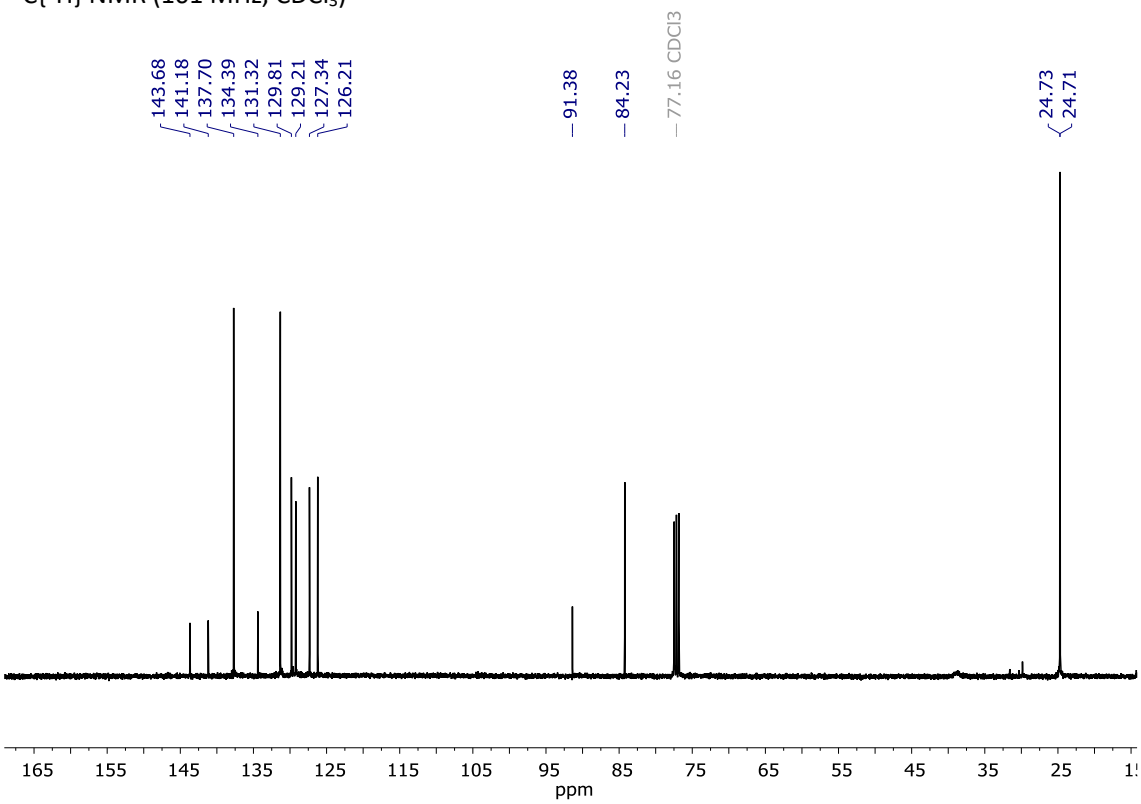




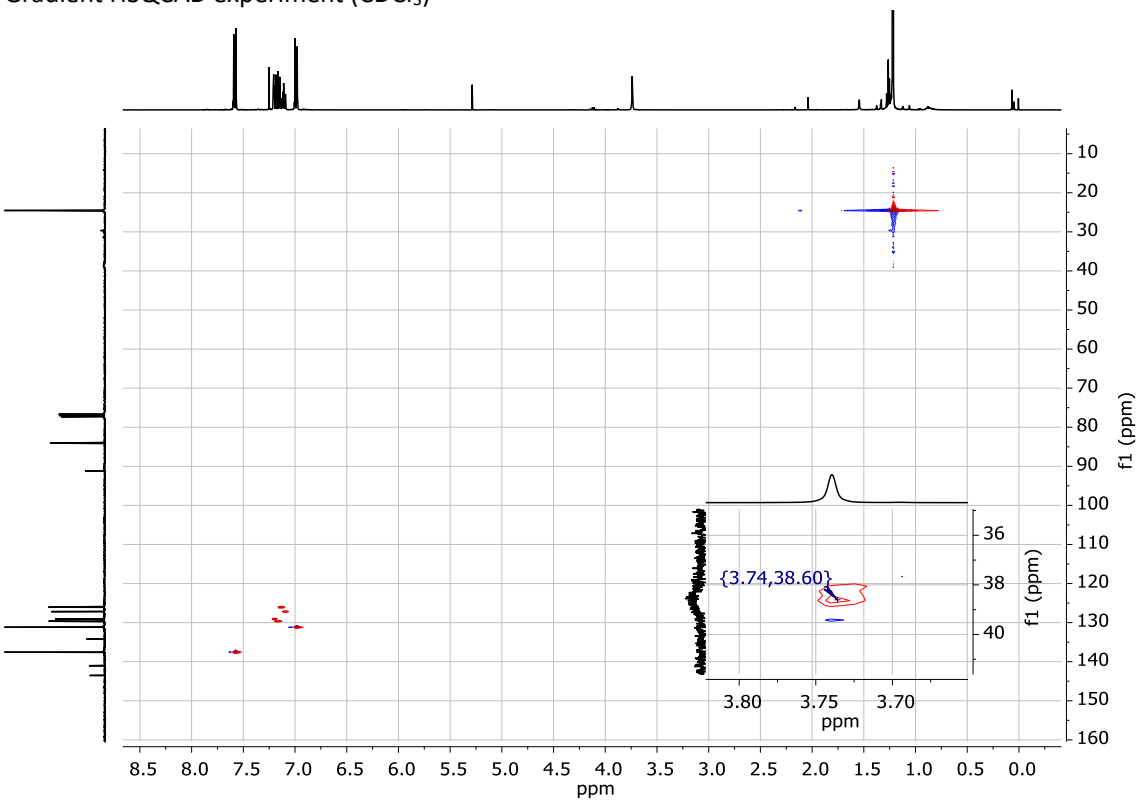
(**9**) ^{1}H NMR (400 MHz, $CDCl_3$)



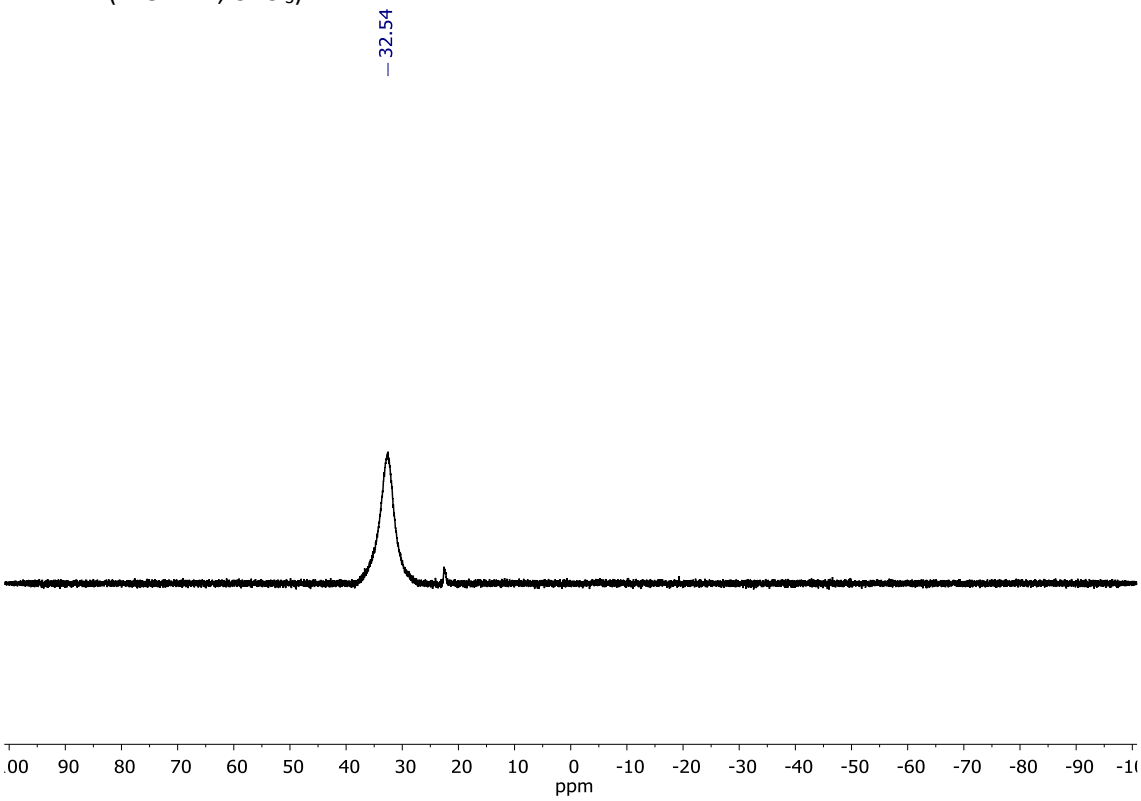
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

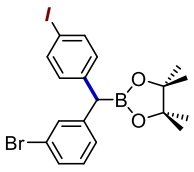


Gradient HSQCAD experiment ($CDCl_3$)

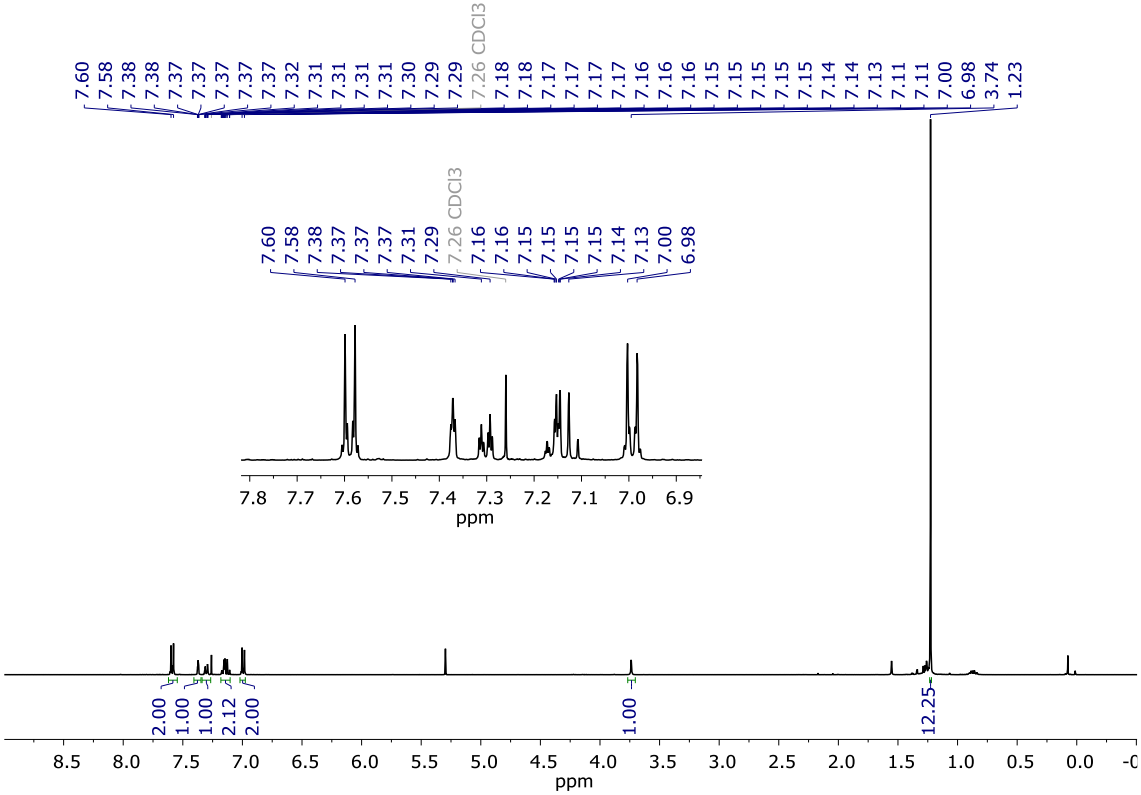


^{11}B NMR (128 MHz, $CDCl_3$)

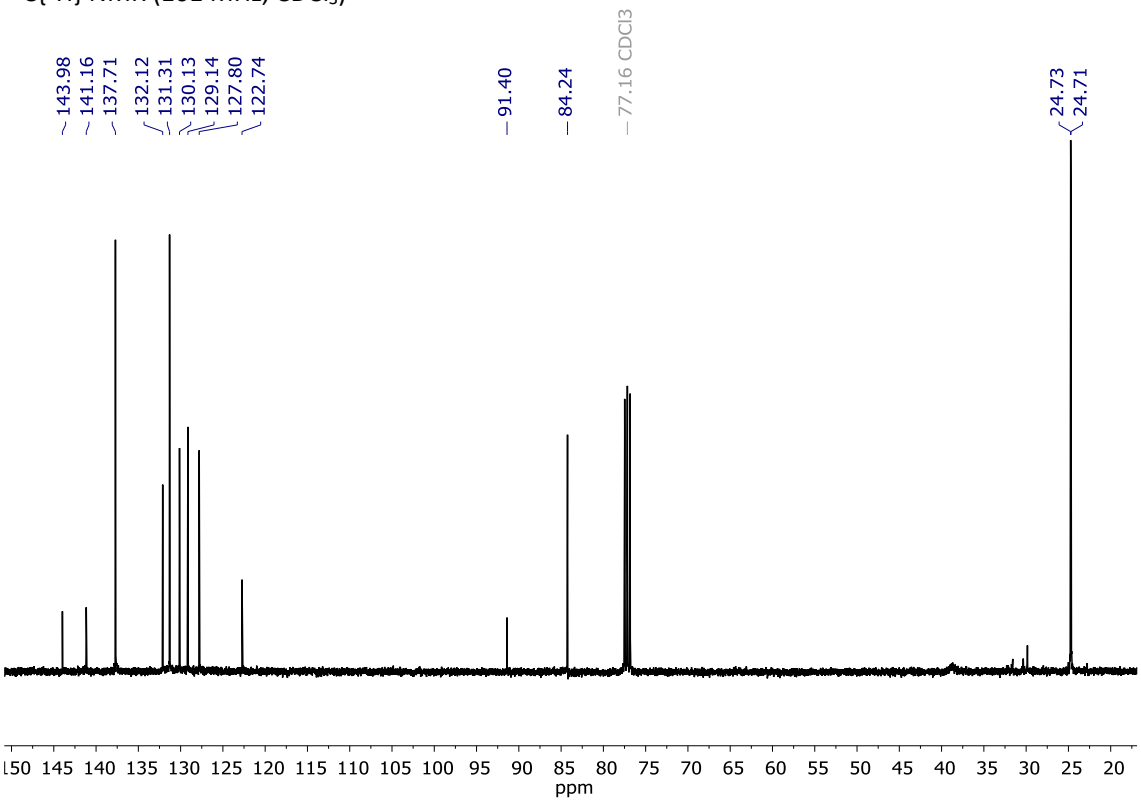




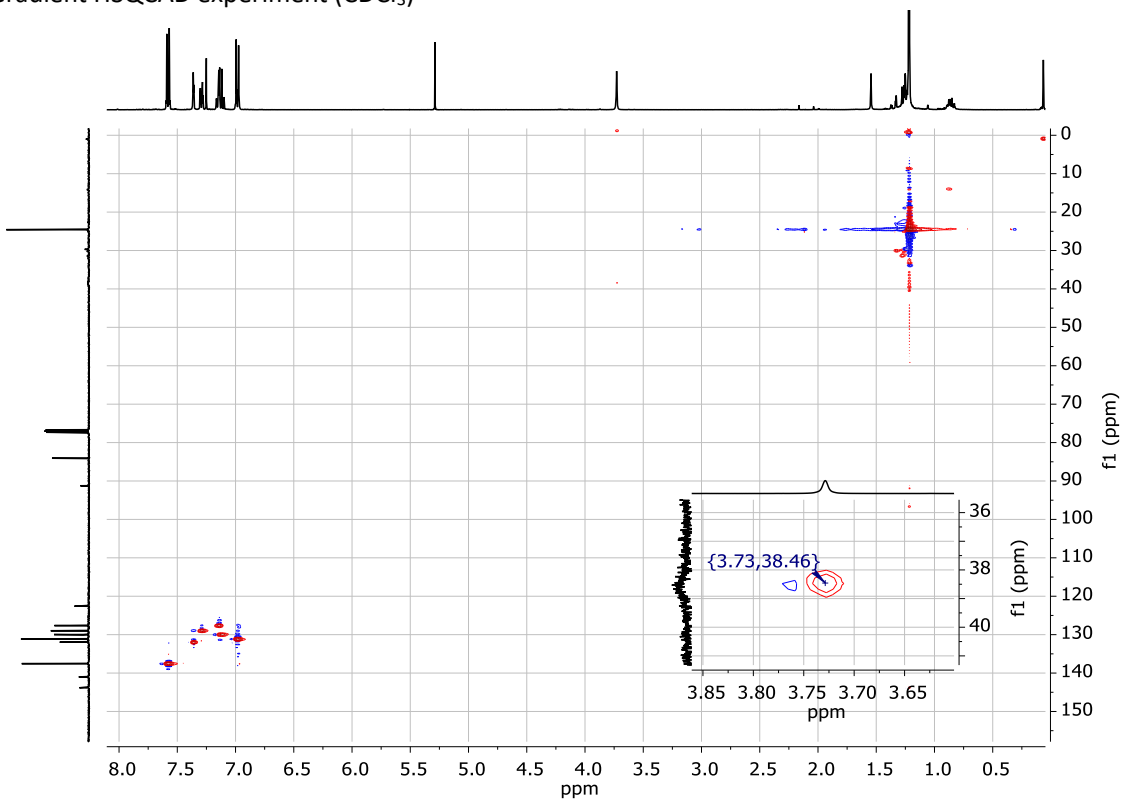
(**10**) ^{1}H NMR (400 MHz, $CDCl_3$)



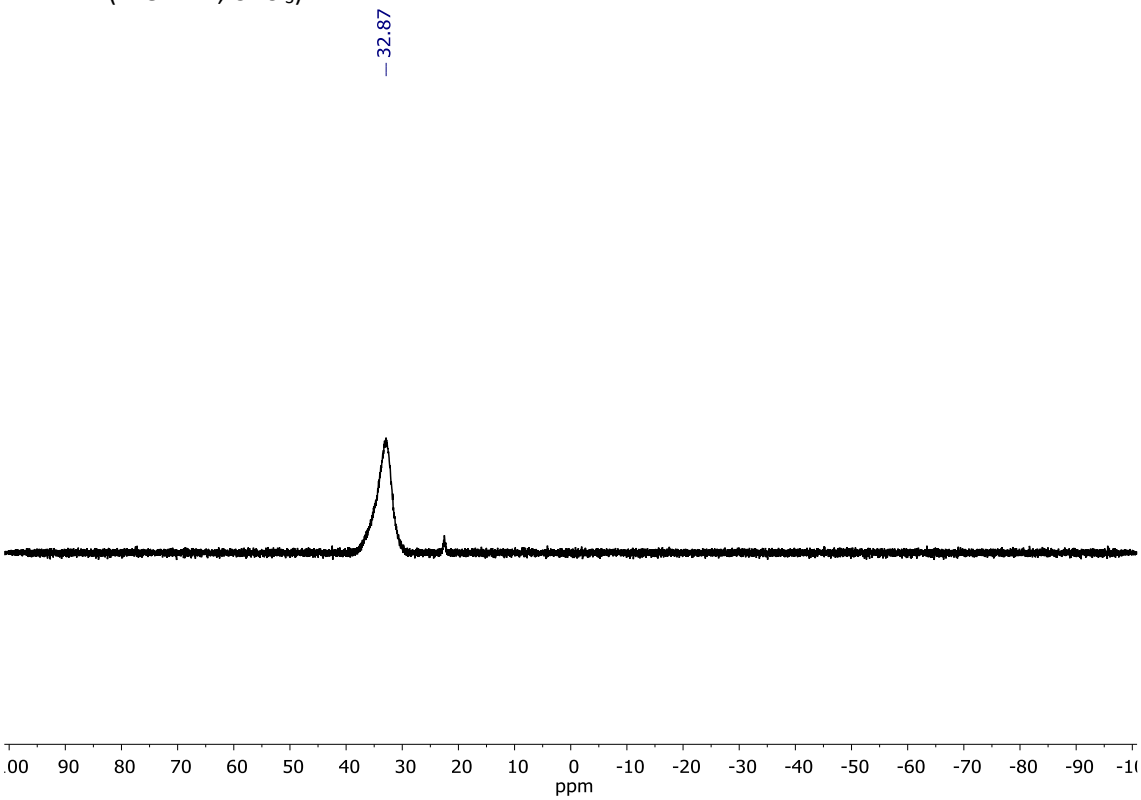
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

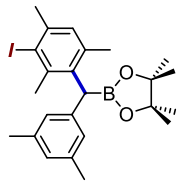


Gradient HSQCAD experiment ($CDCl_3$)

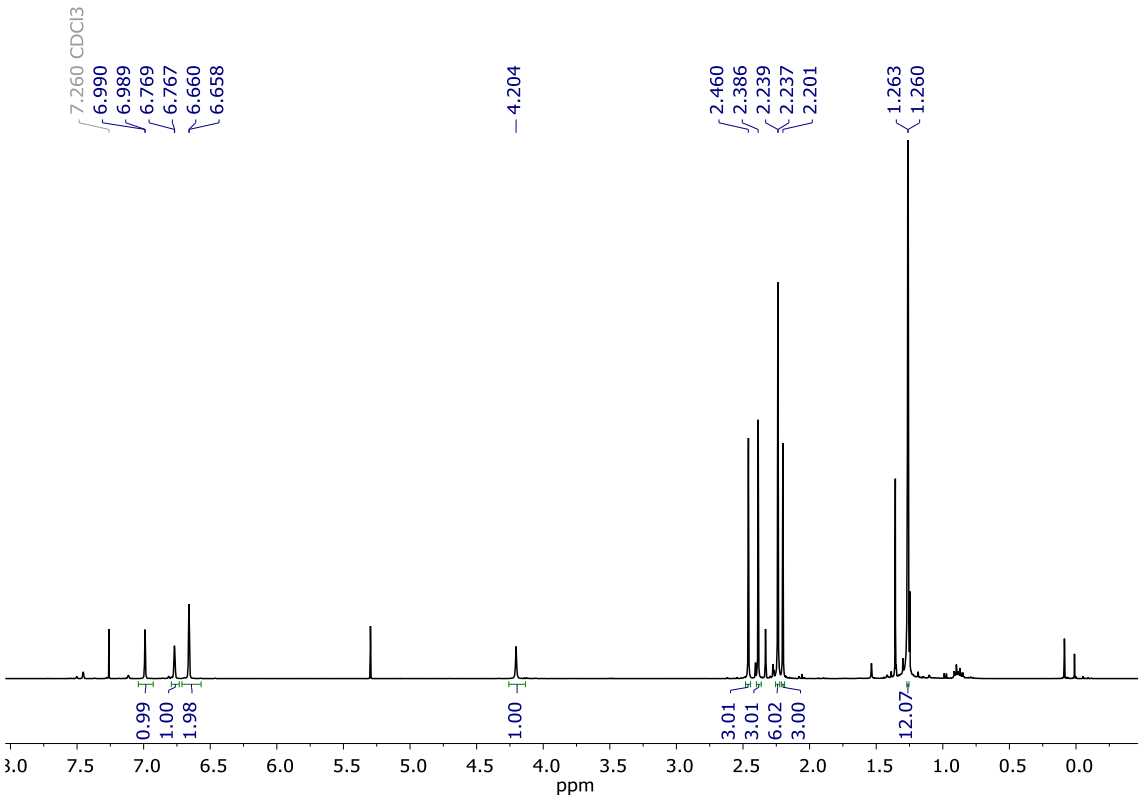


^{11}B NMR (128 MHz, $CDCl_3$)

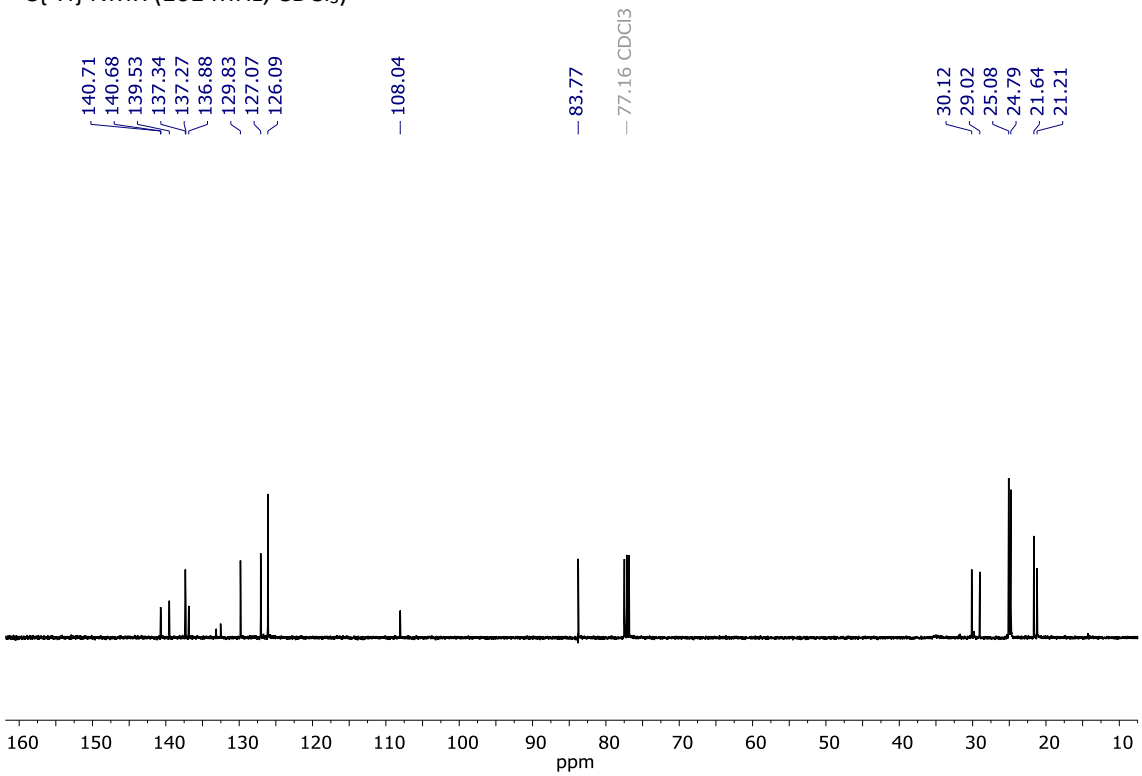




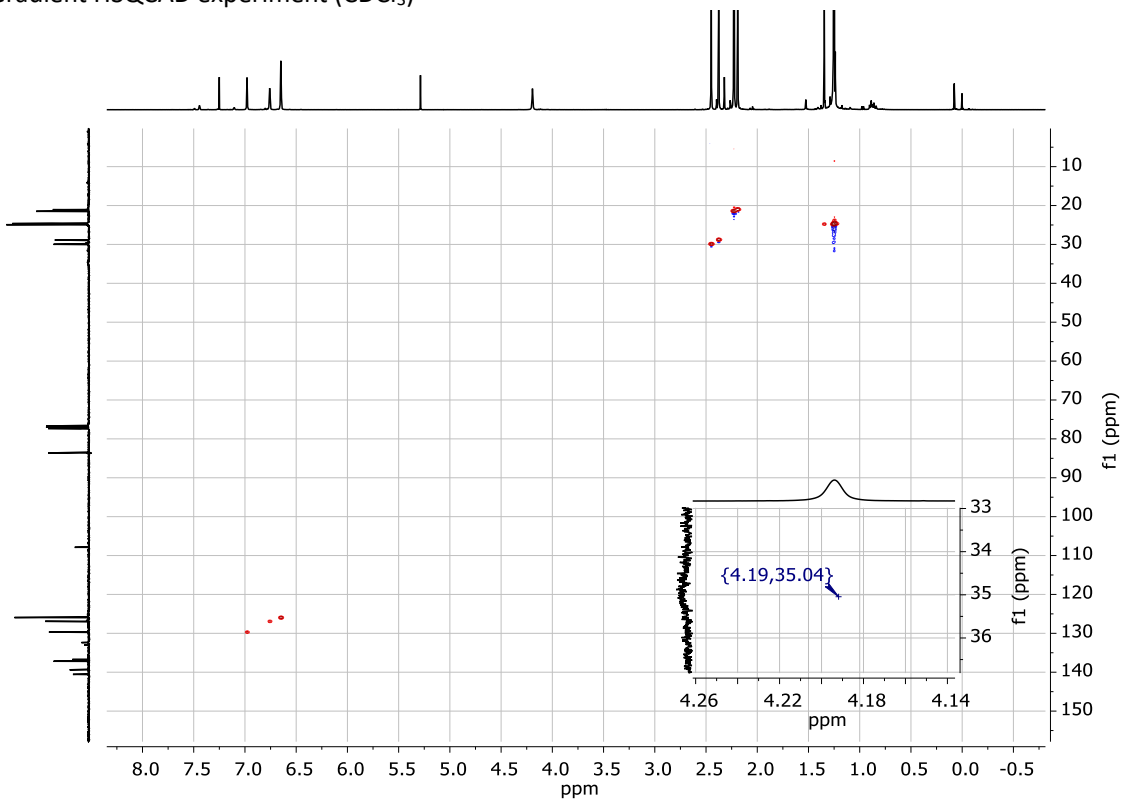
(**14**) ^{1}H NMR (400 MHz, $CDCl_3$)



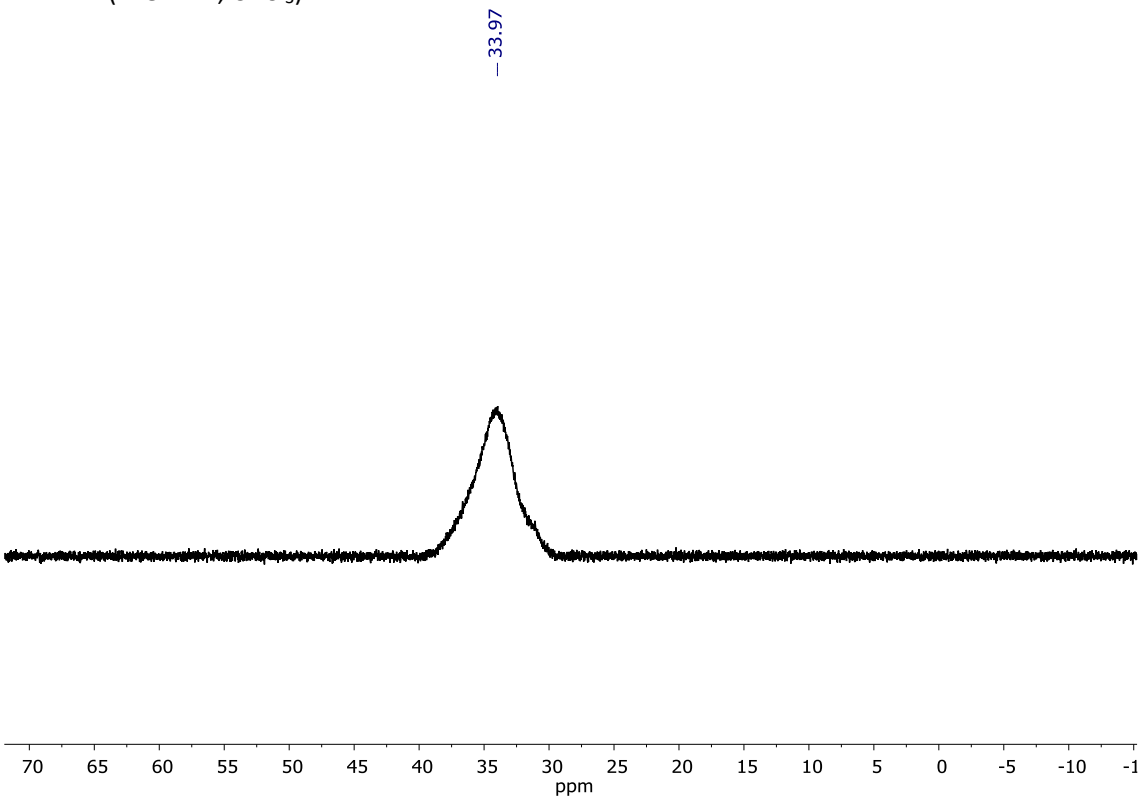
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

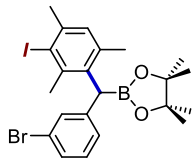


Gradient HSQCAD experiment ($CDCl_3$)

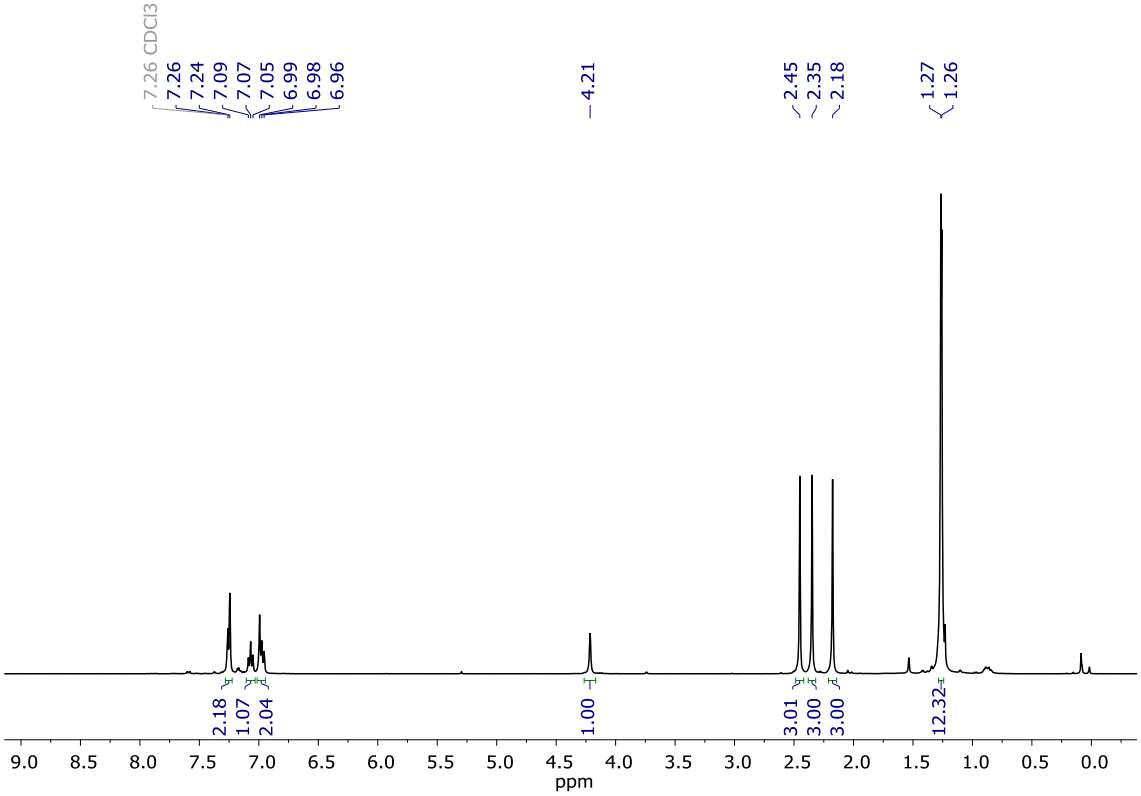


^{11}B NMR (128 MHz, $CDCl_3$)

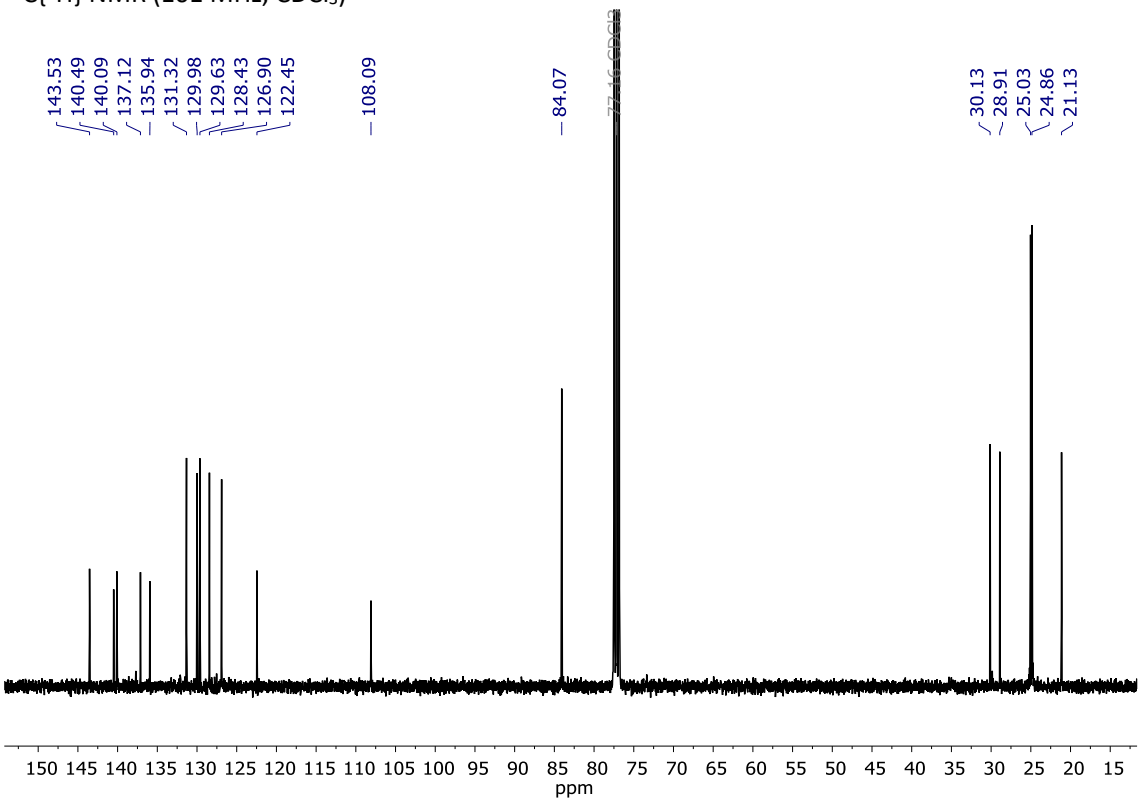




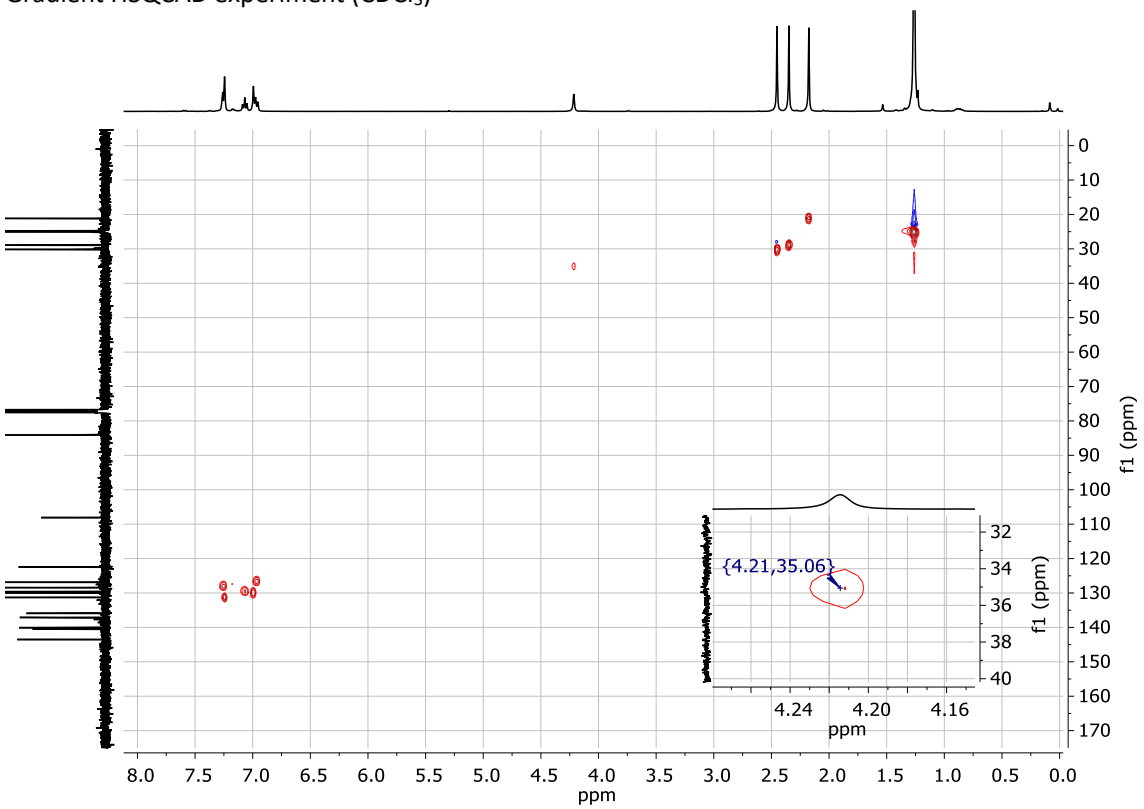
(**15**) ^{1}H NMR (400 MHz, $CDCl_3$)



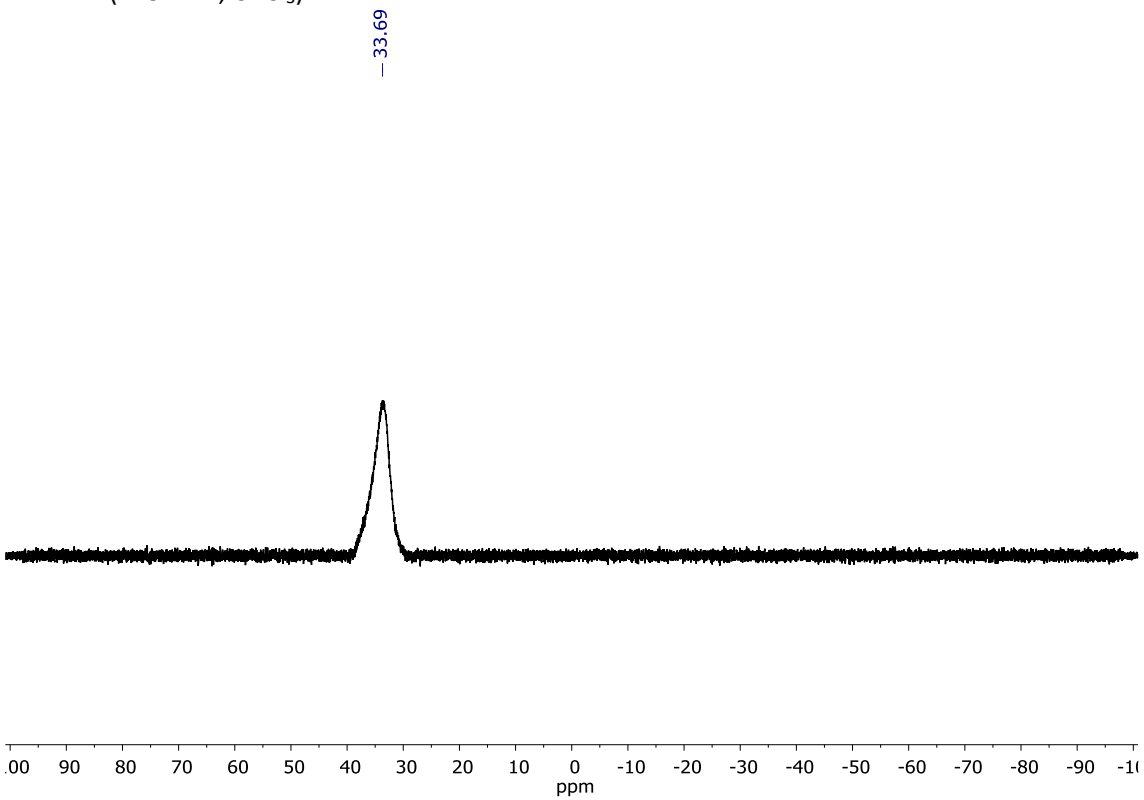
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

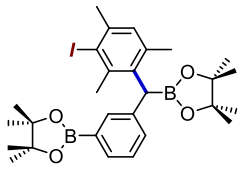


Gradient HSQCAD experiment ($CDCl_3$)

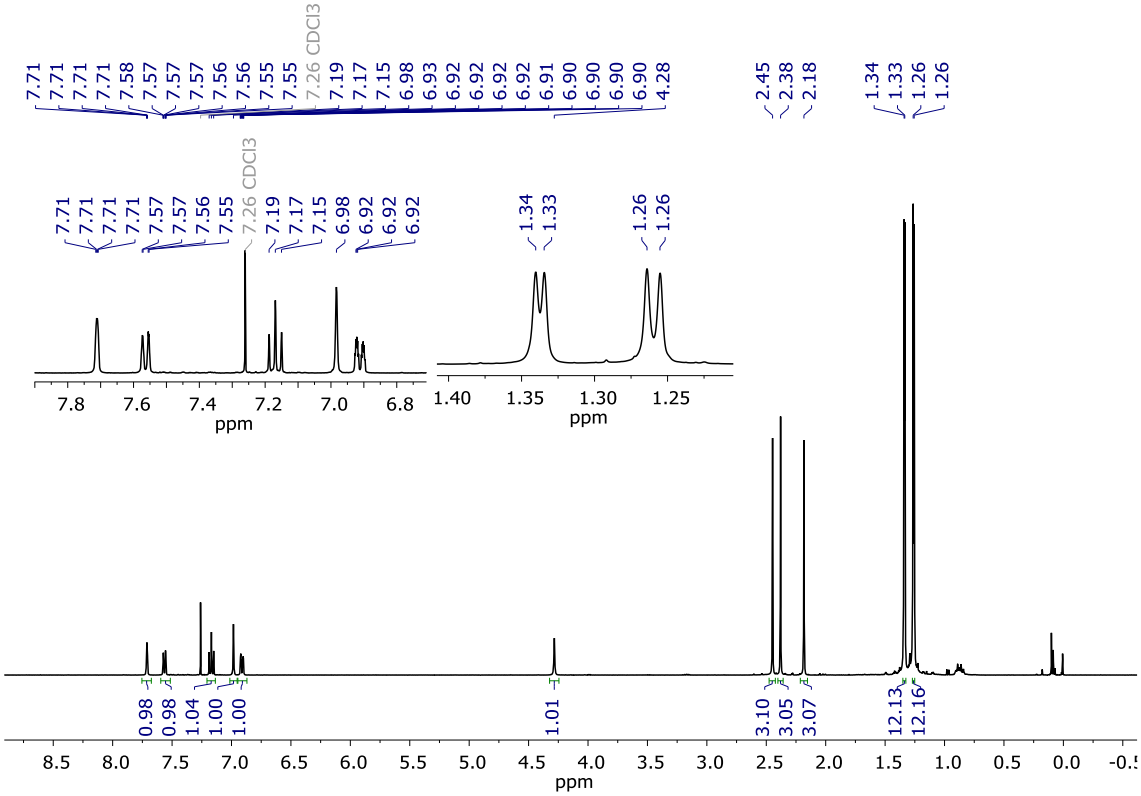


^{11}B NMR (128 MHz, $CDCl_3$)

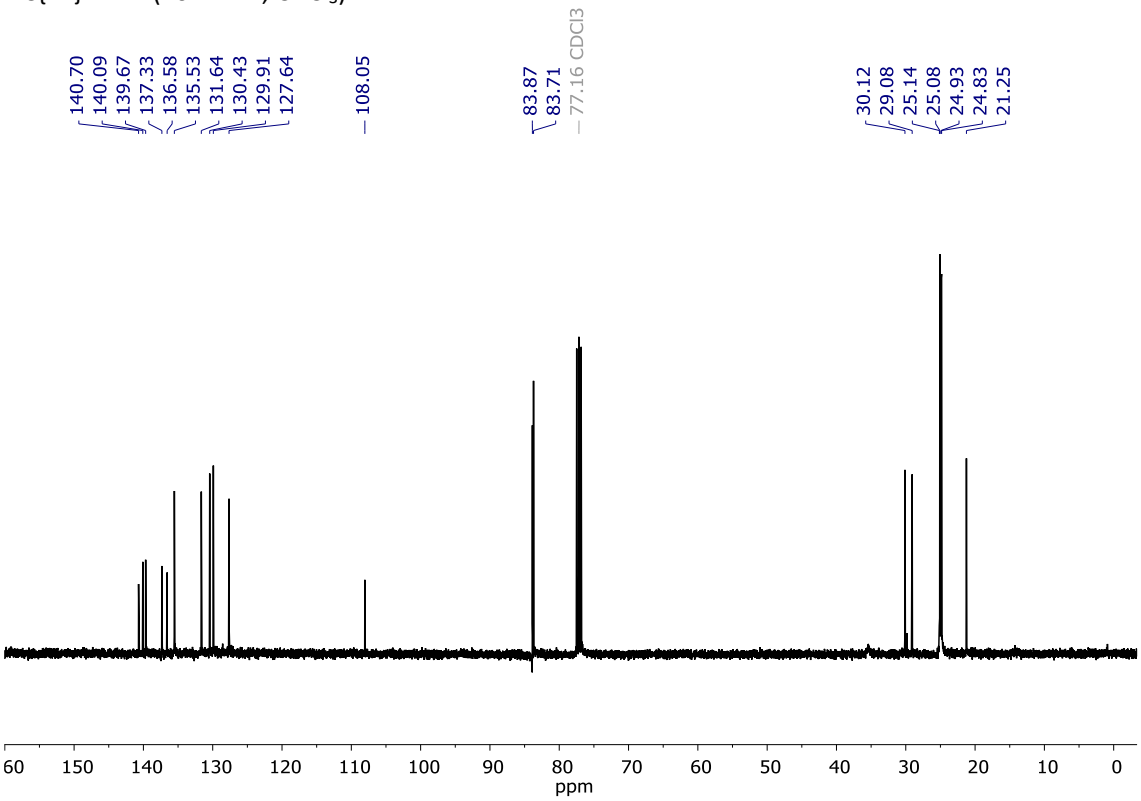




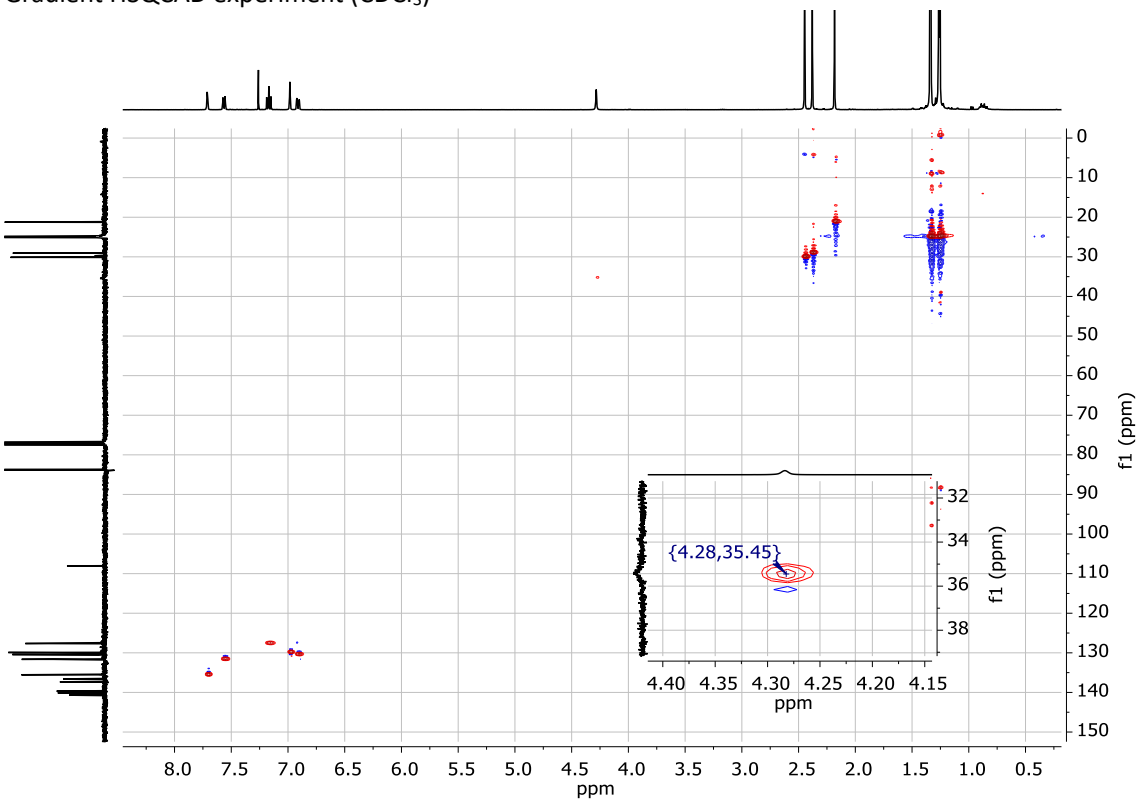
(**16**) ^{1}H NMR (400 MHz, $CDCl_3$)



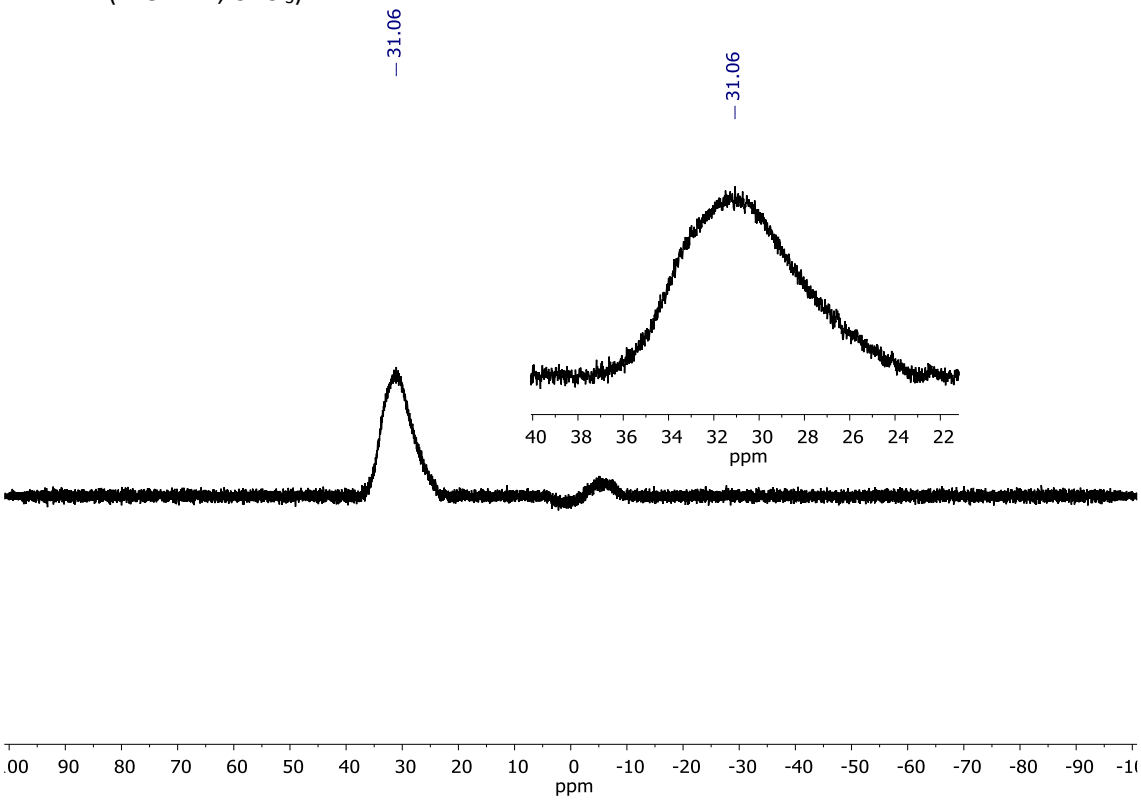
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

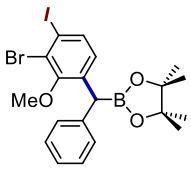


Gradient HSQCAD experiment ($CDCl_3$)

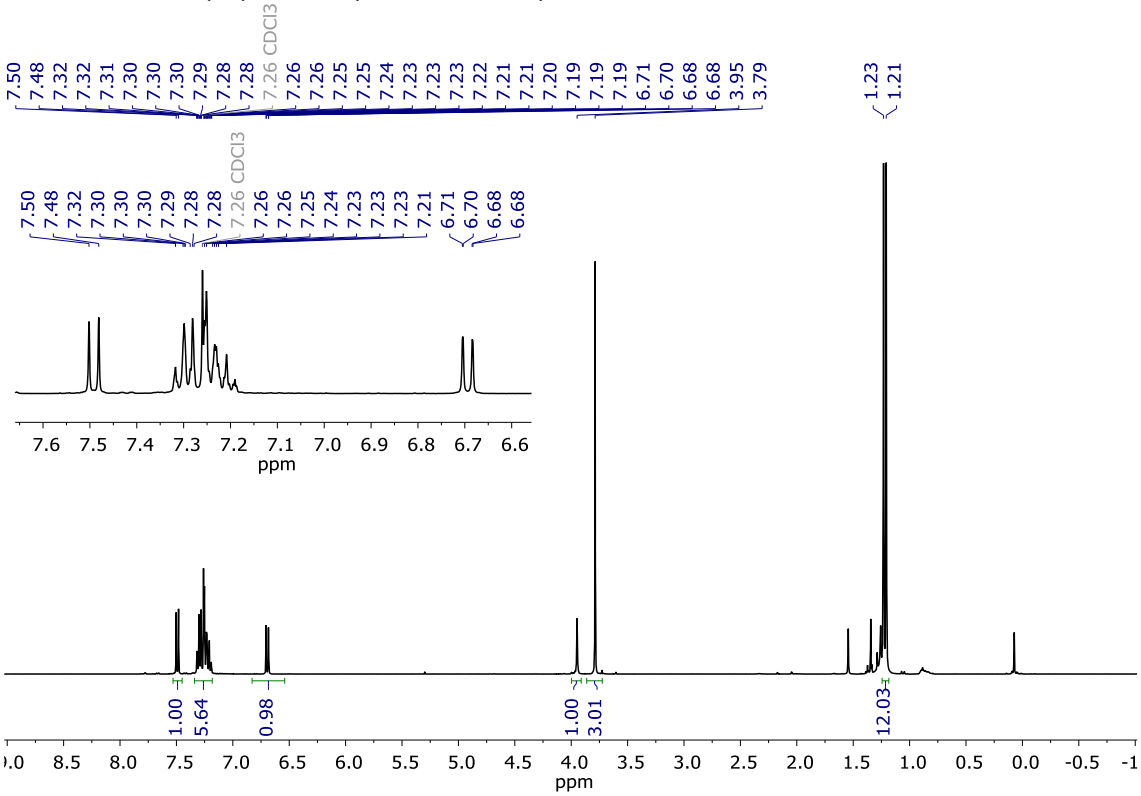


^{11}B NMR (128 MHz, $CDCl_3$)

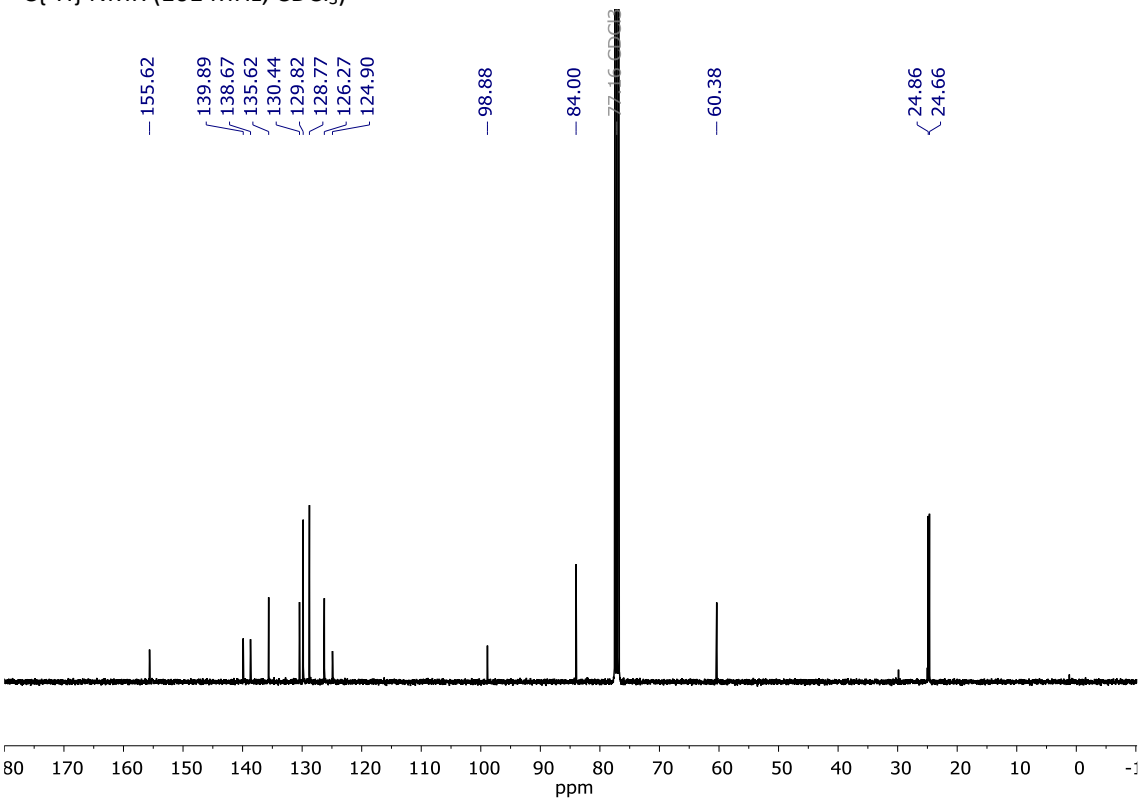




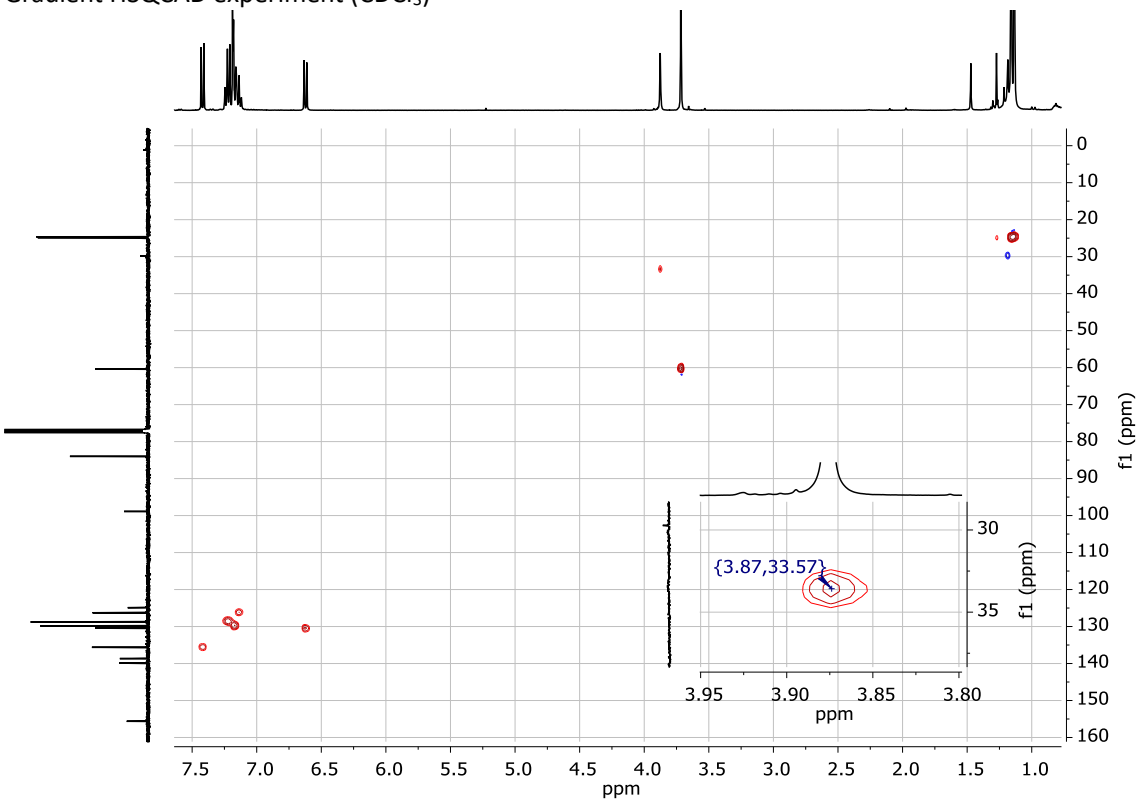
(**21**) ^{1}H NMR (400 MHz, $CDCl_3$)



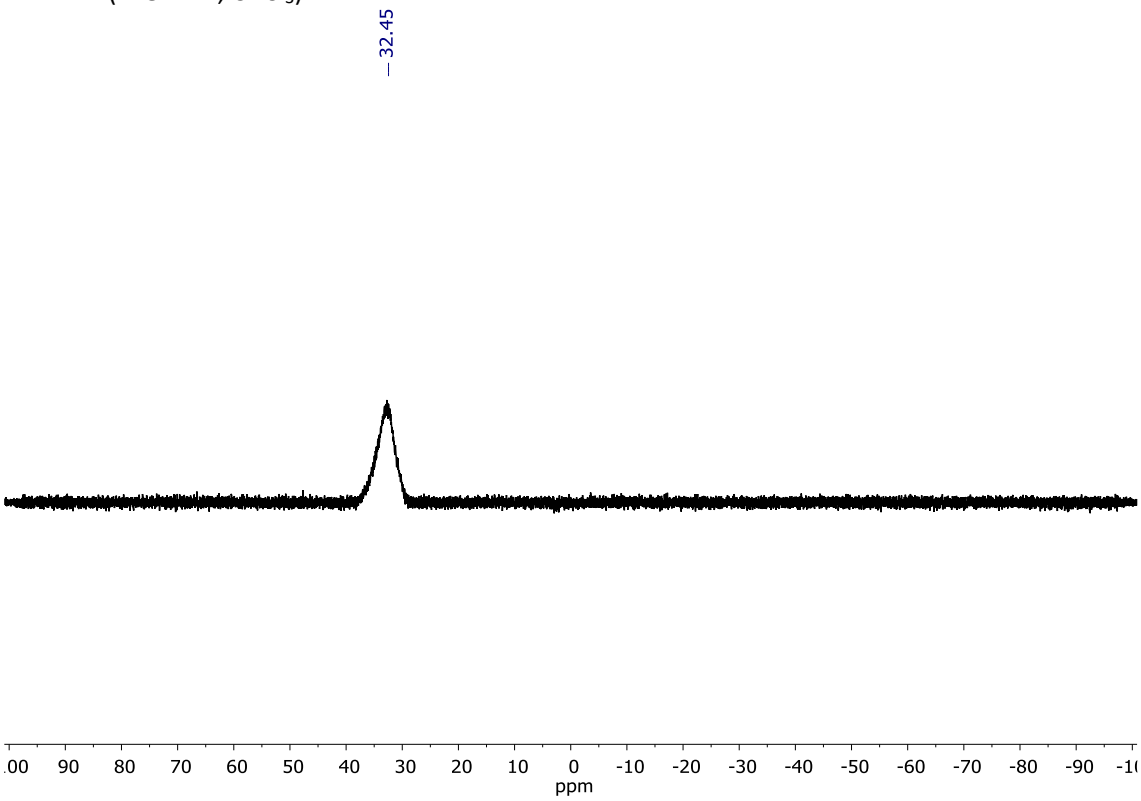
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

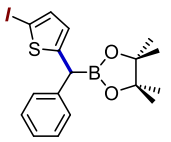


Gradient HSQCAD experiment ($CDCl_3$)

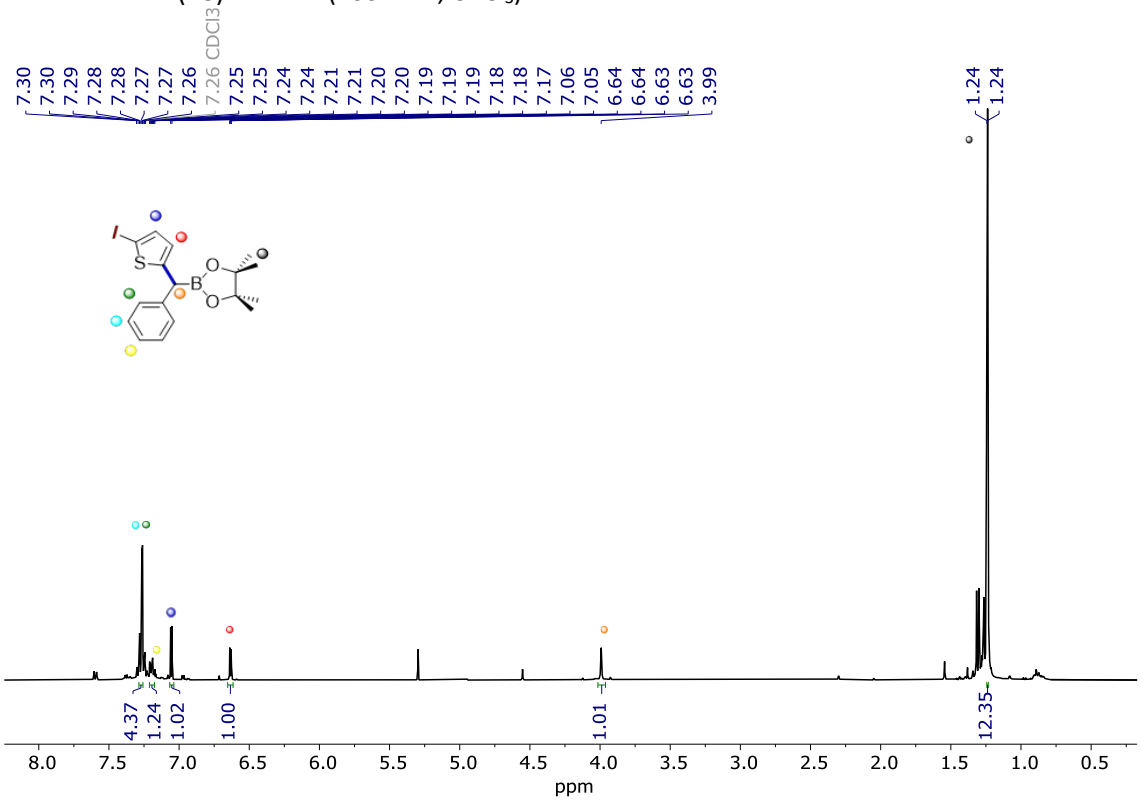


^{11}B NMR (128 MHz, $CDCl_3$)

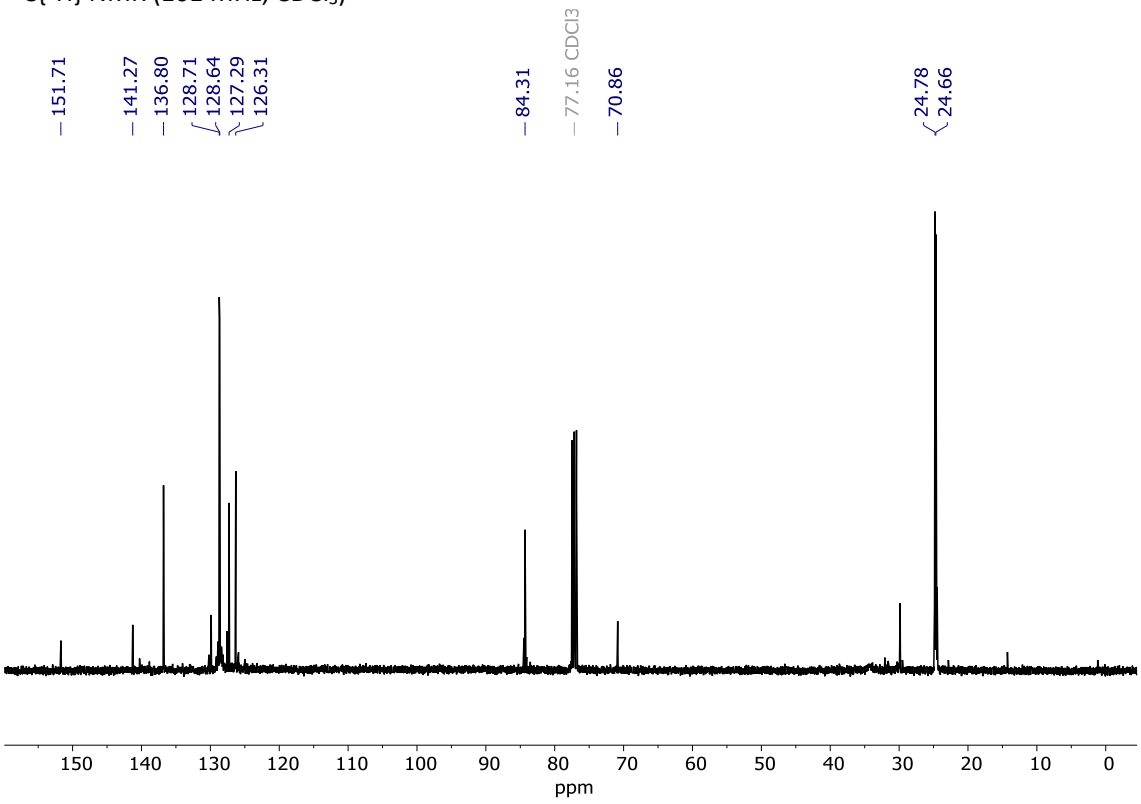




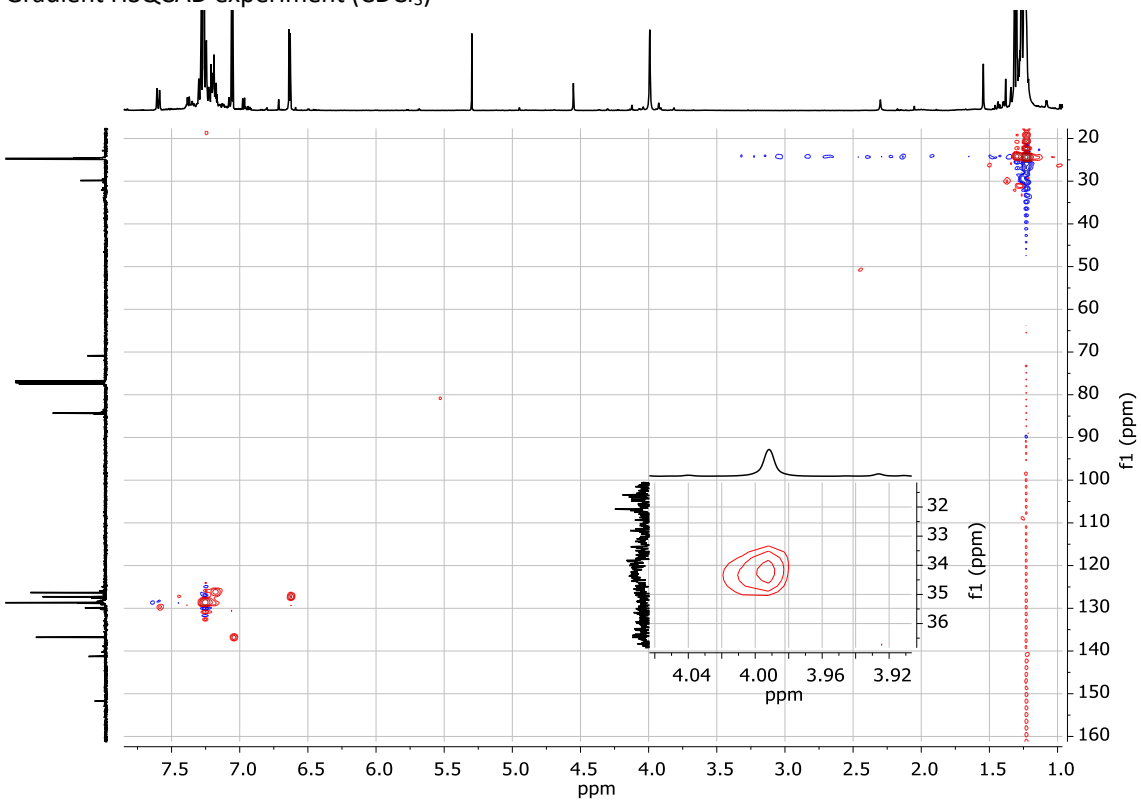
(**20**) ^{1}H NMR (400 MHz, $CDCl_3$)



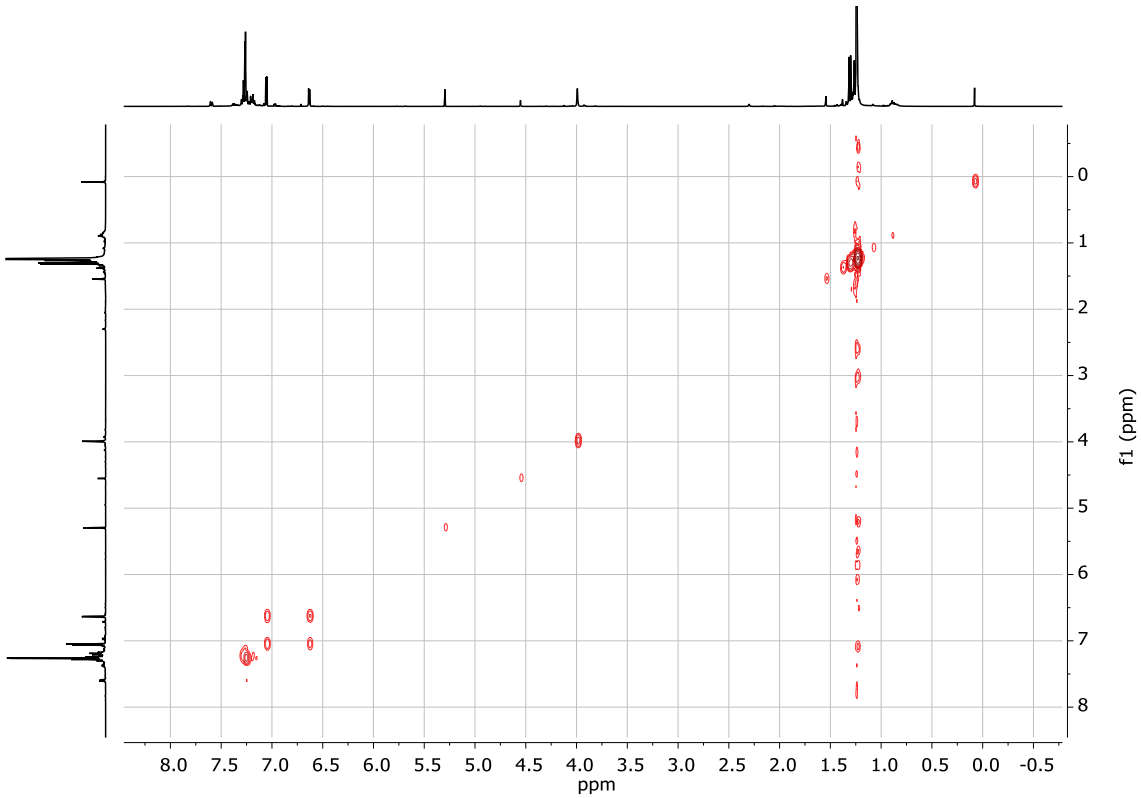
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

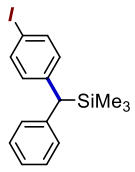


Gradient HSQCAD experiment ($CDCl_3$)

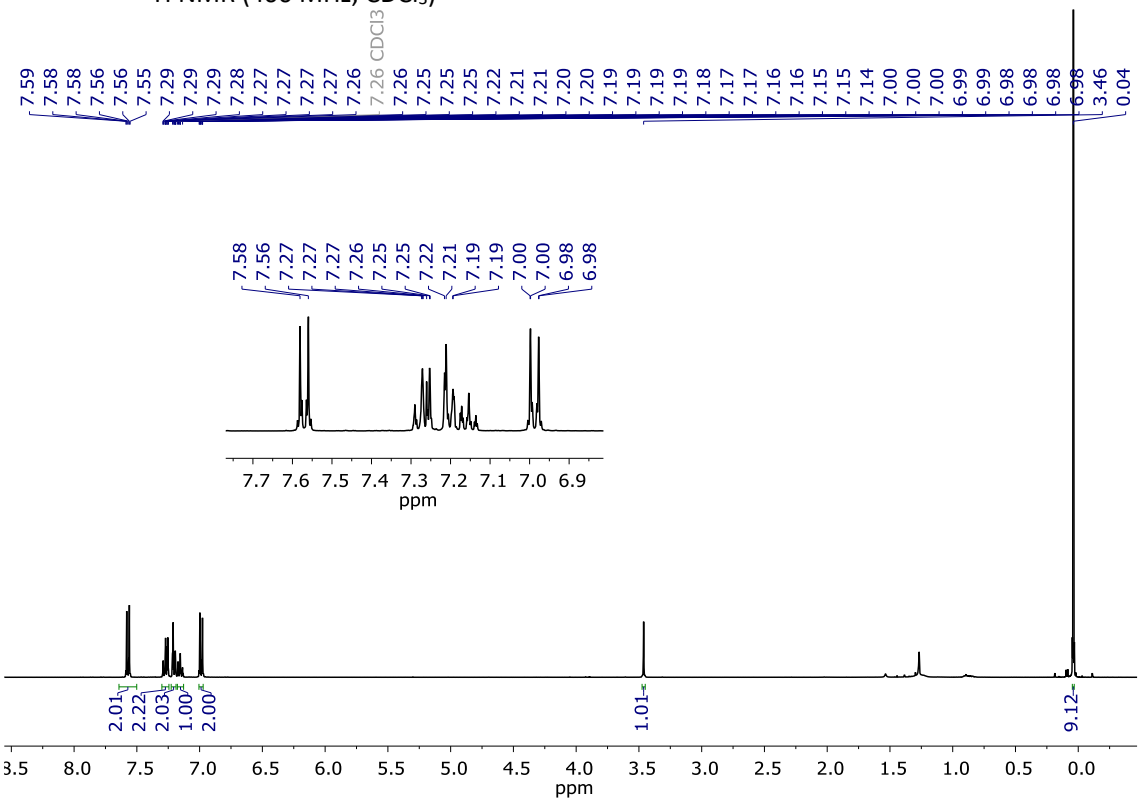


^1H COSY experiment ($CDCl_3$)

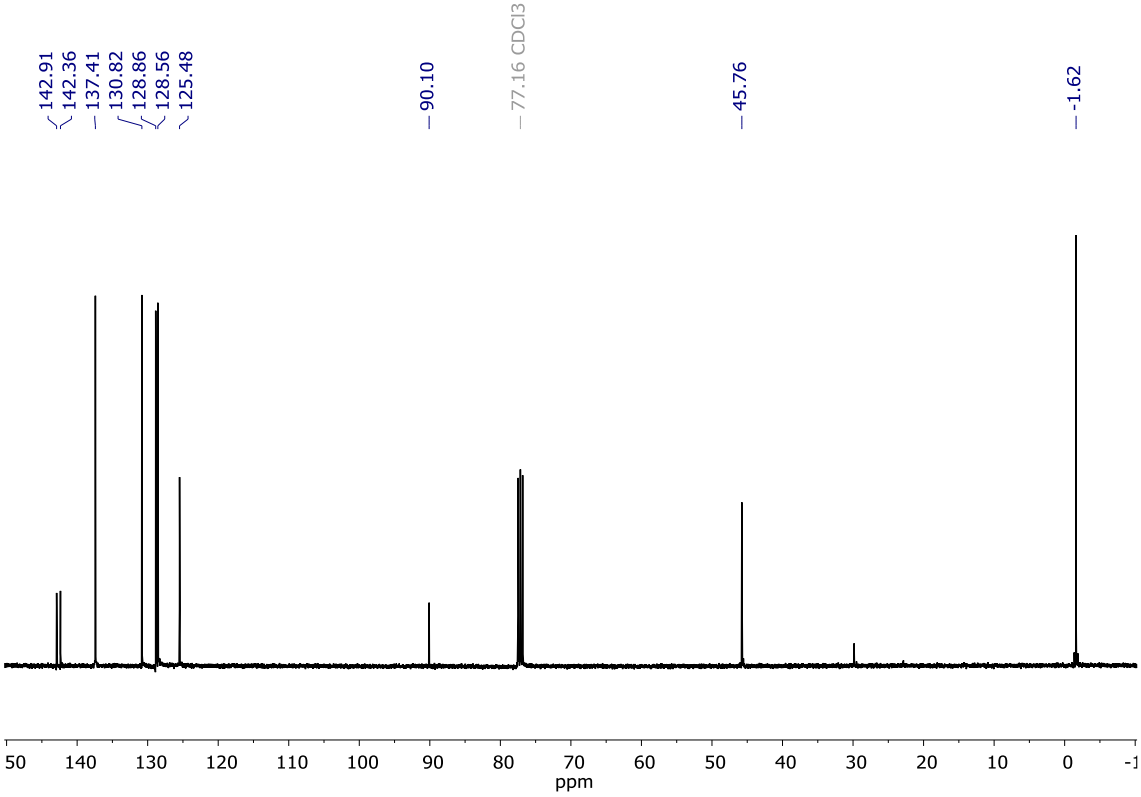


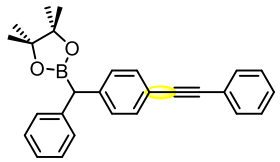


^{1}H NMR (400 MHz, $CDCl_3$)

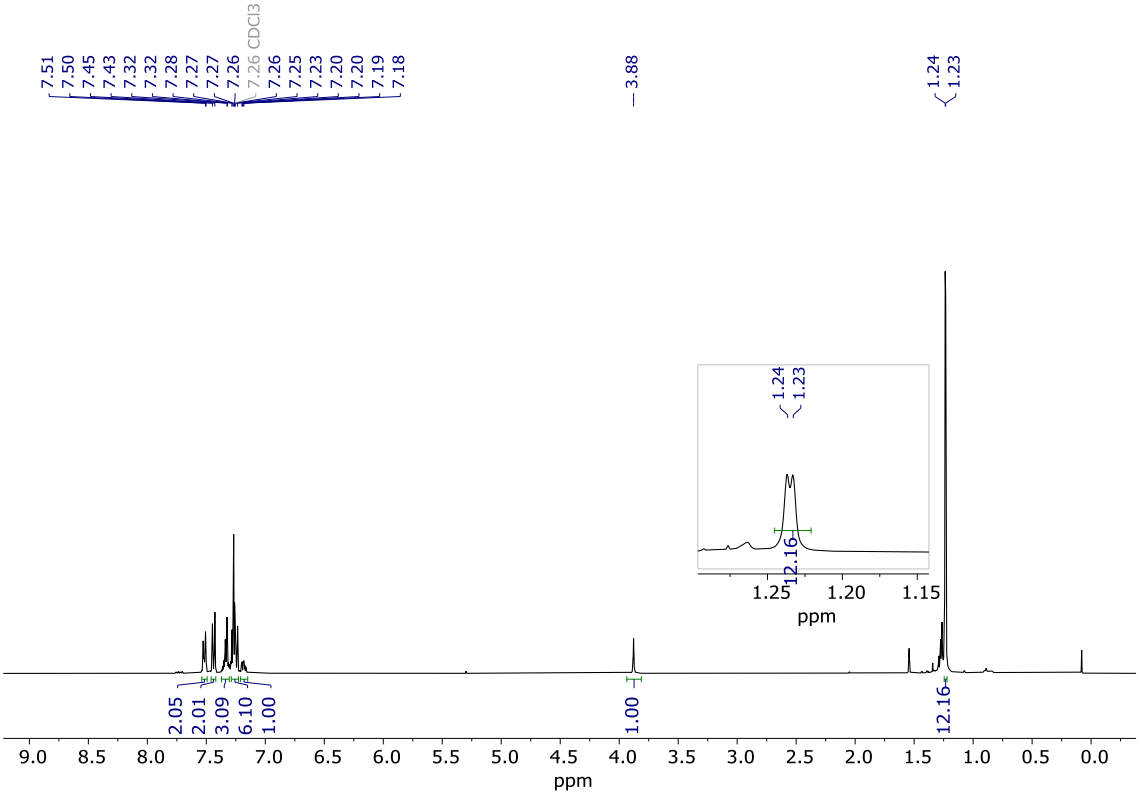


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

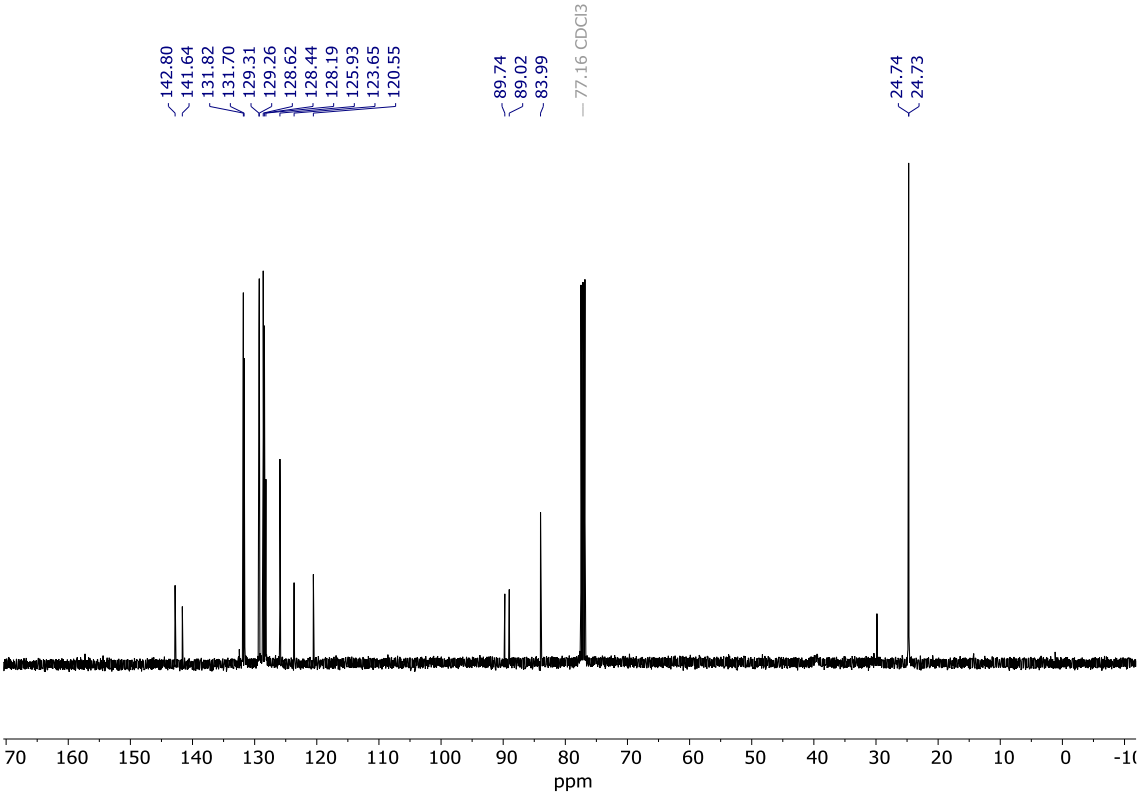




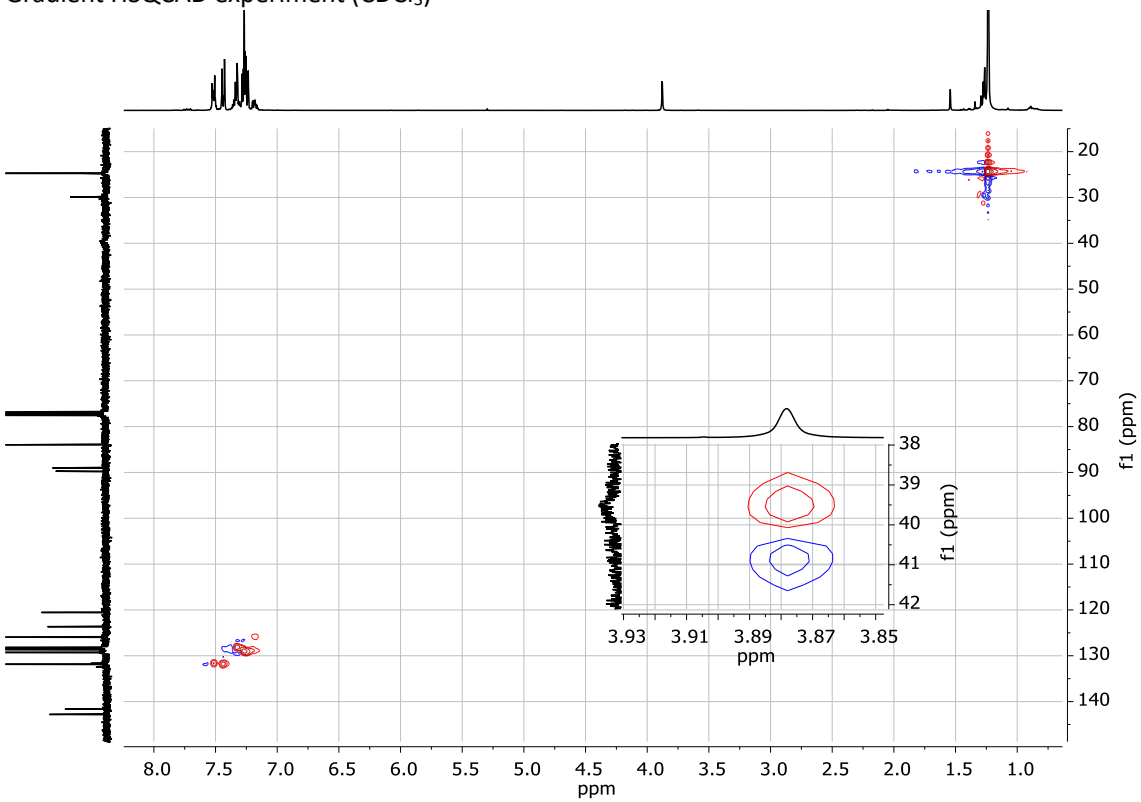
(**22**) ^{1}H NMR (400 MHz, $CDCl_3$)



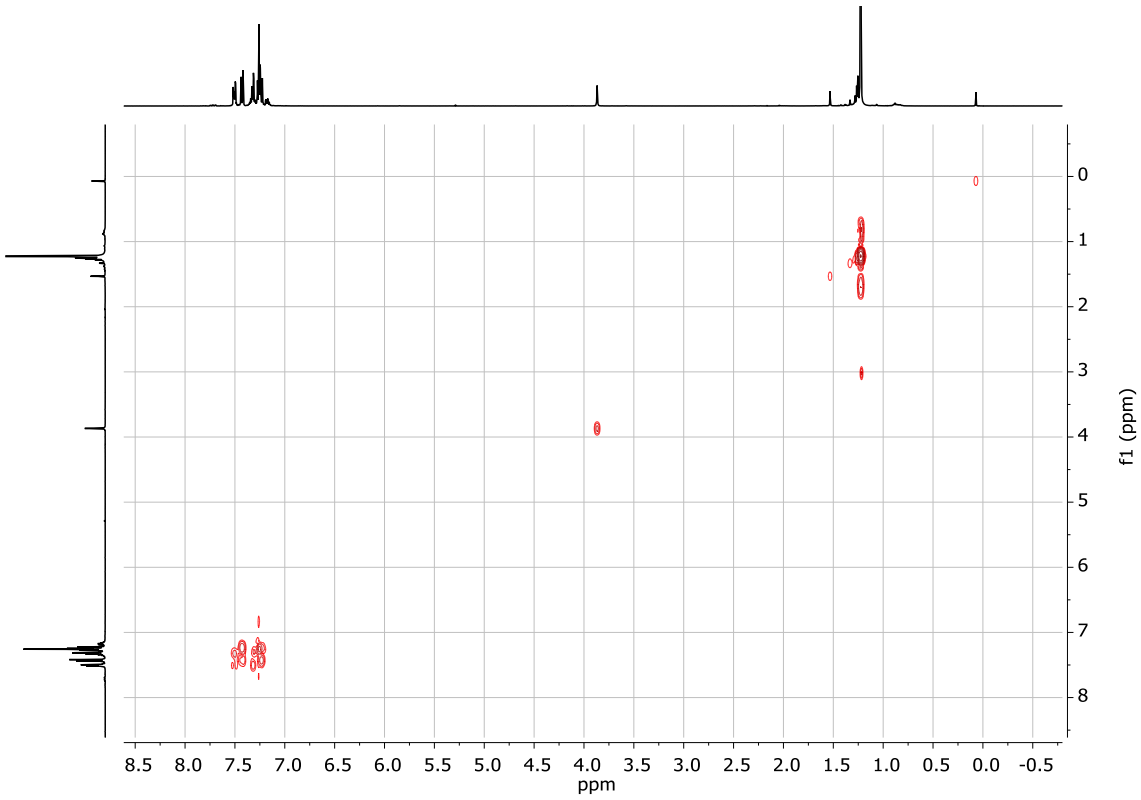
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

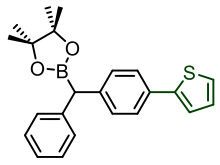


Gradient HSQCAD experiment ($CDCl_3$)

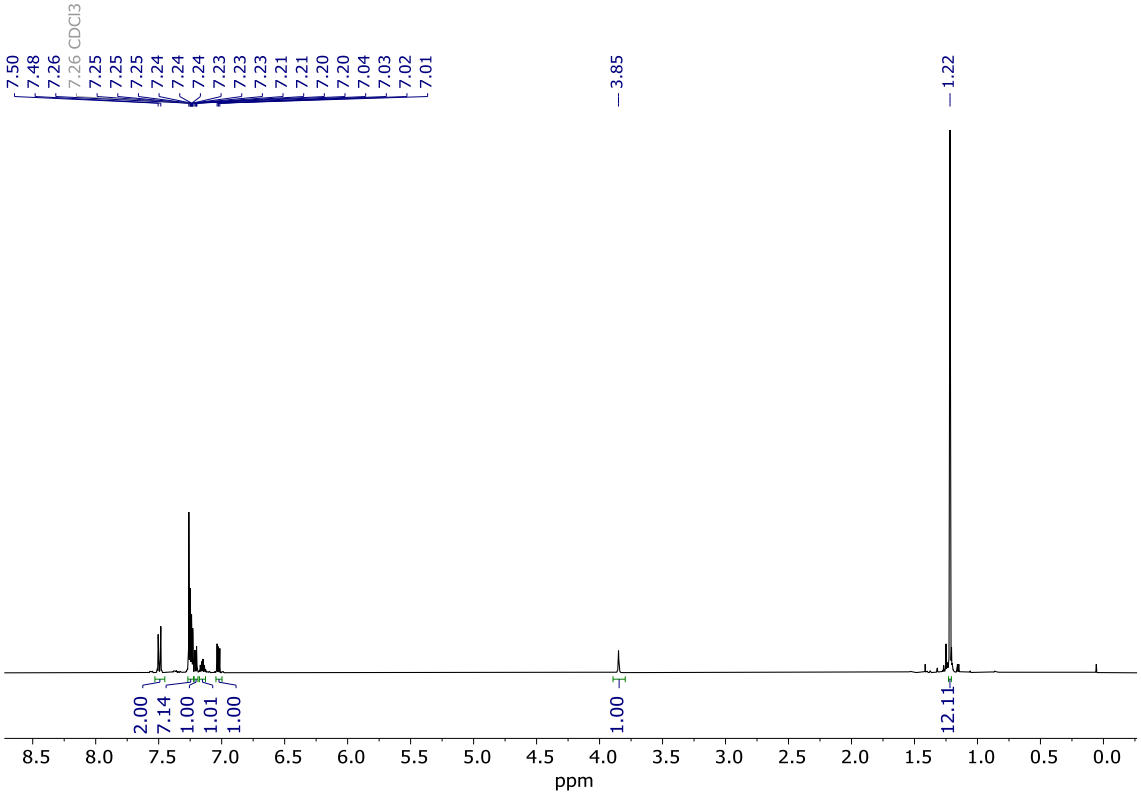


^1H COSY experiment ($CDCl_3$)

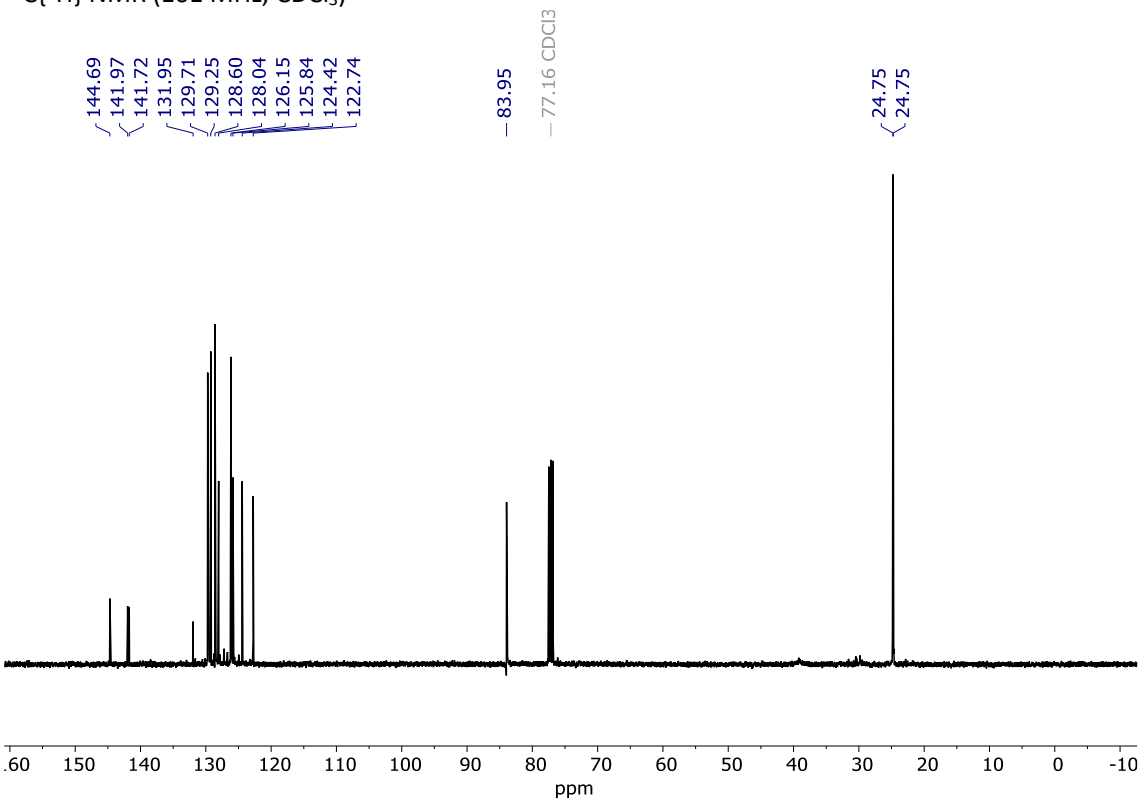




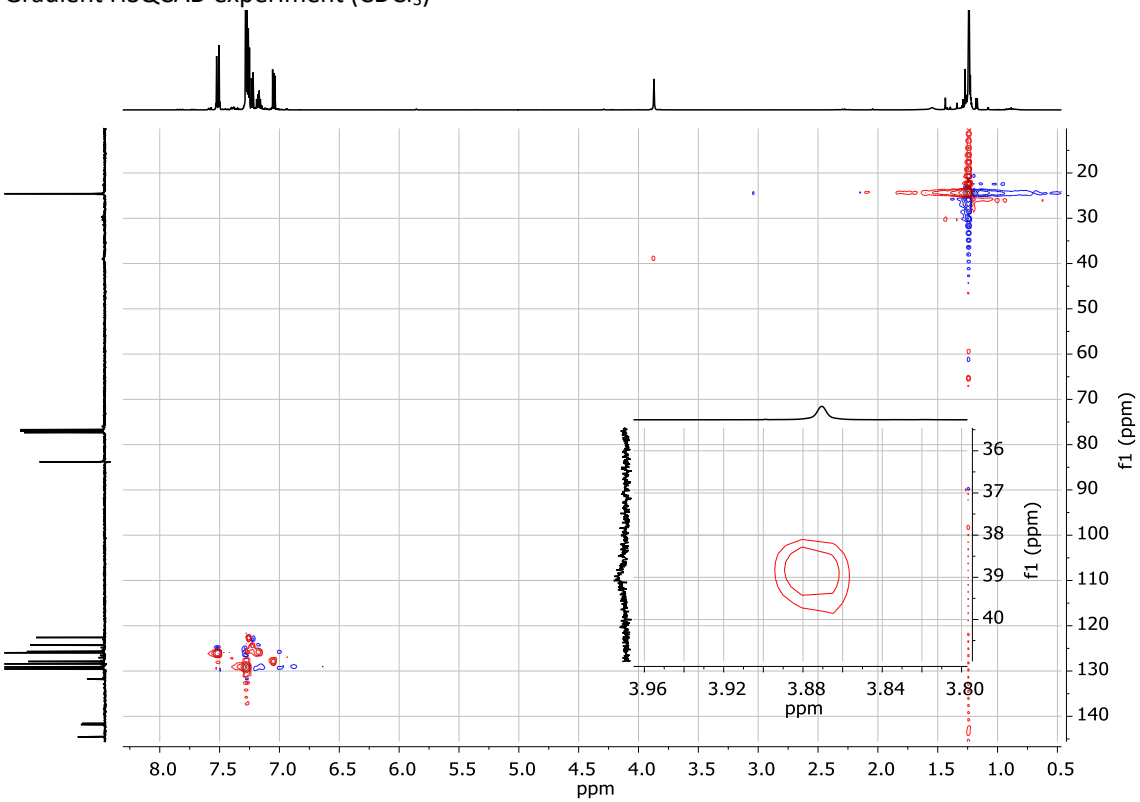
(**23**) ^{1}H NMR (400 MHz, $CDCl_3$)



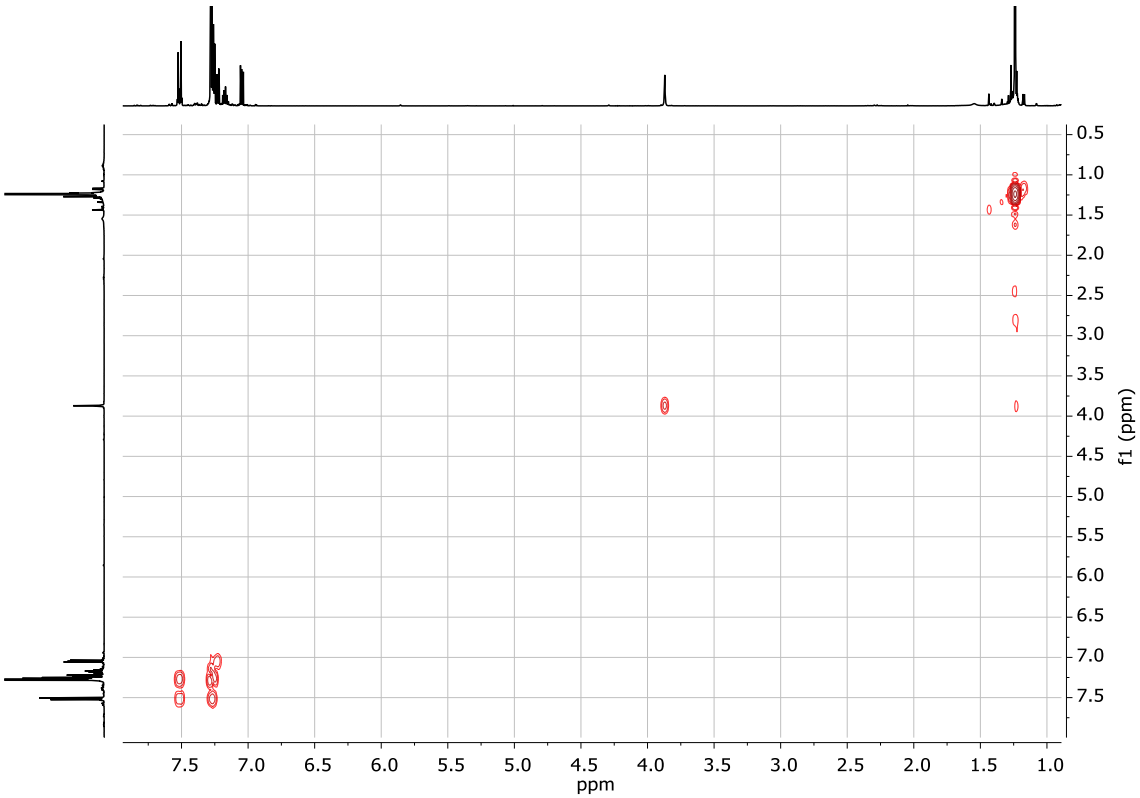
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

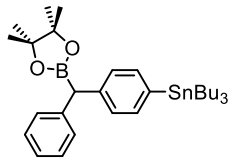


Gradient HSQCAD experiment ($CDCl_3$)

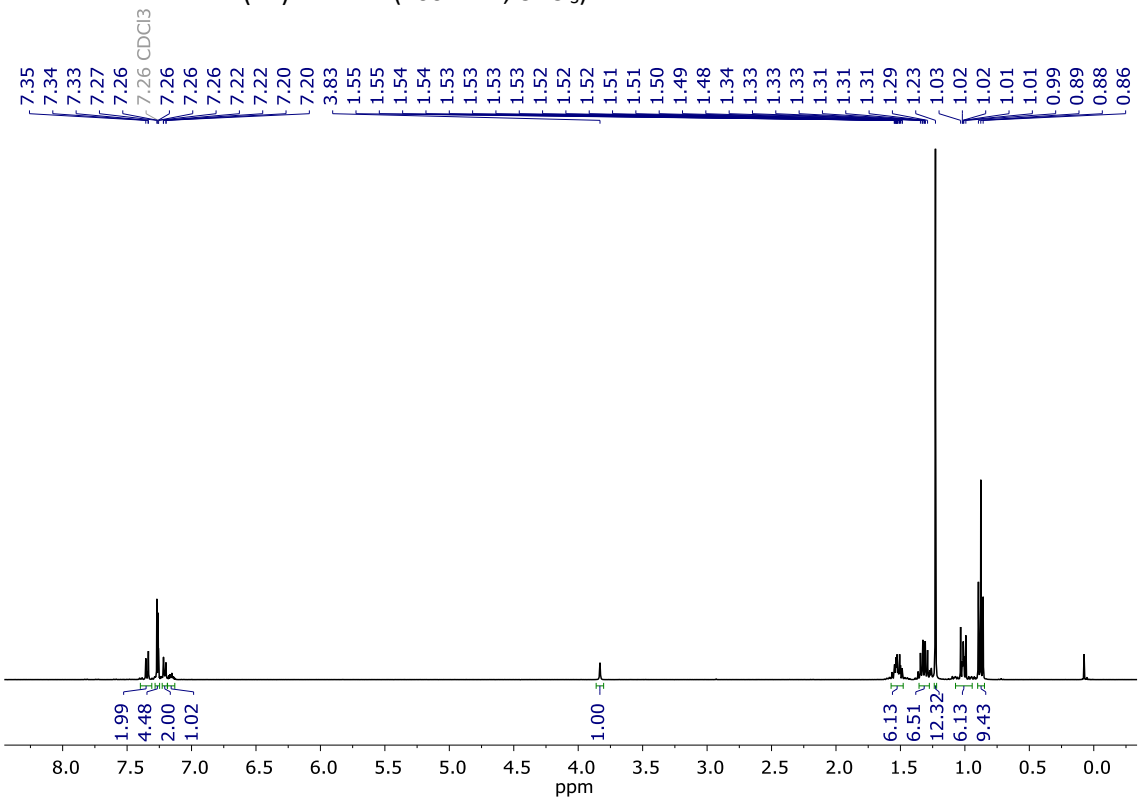


^1H COSY experiment ($CDCl_3$)

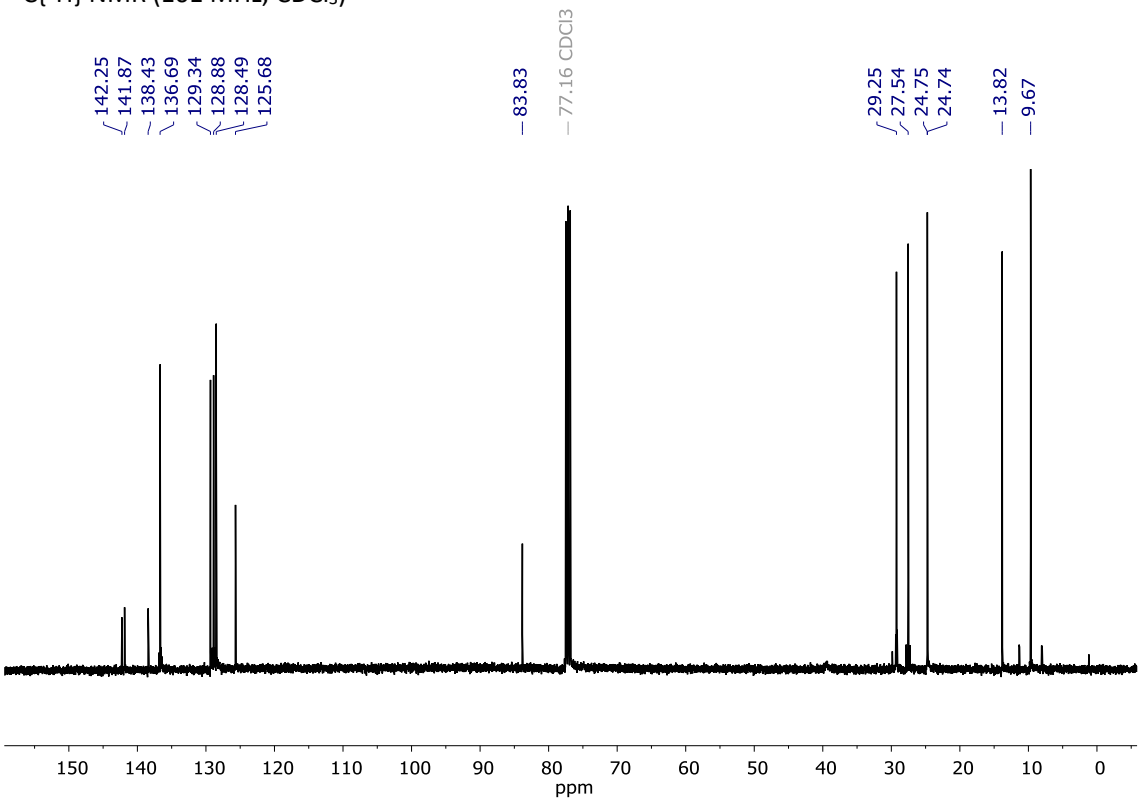




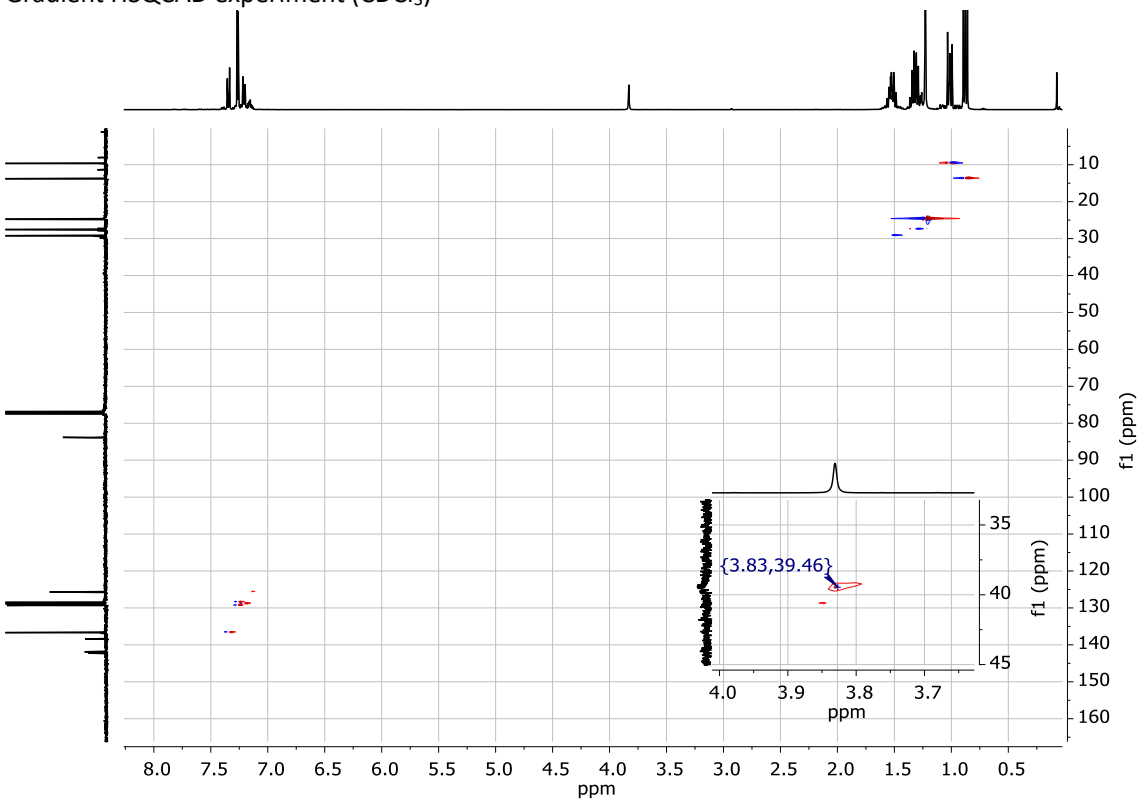
(**24**) ^{1}H NMR (400 MHz, $CDCl_3$)



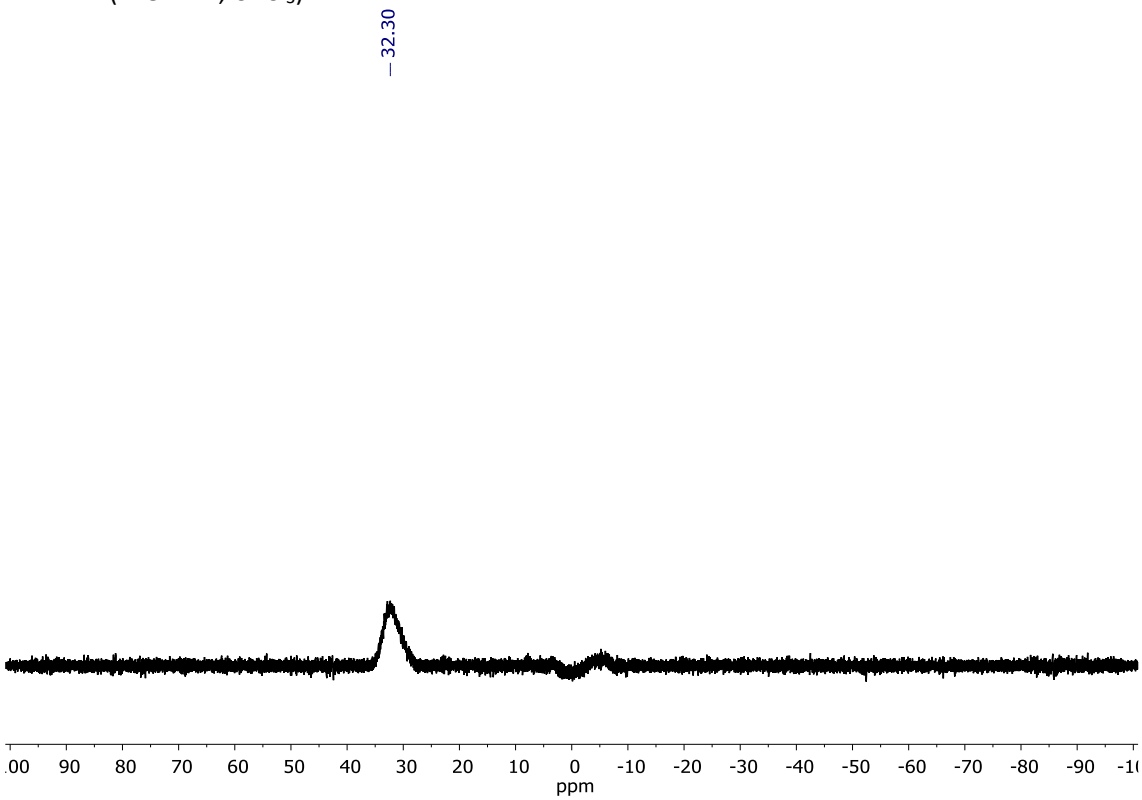
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

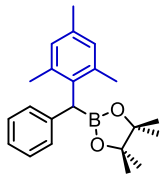


Gradient HSQCAD experiment ($CDCl_3$)

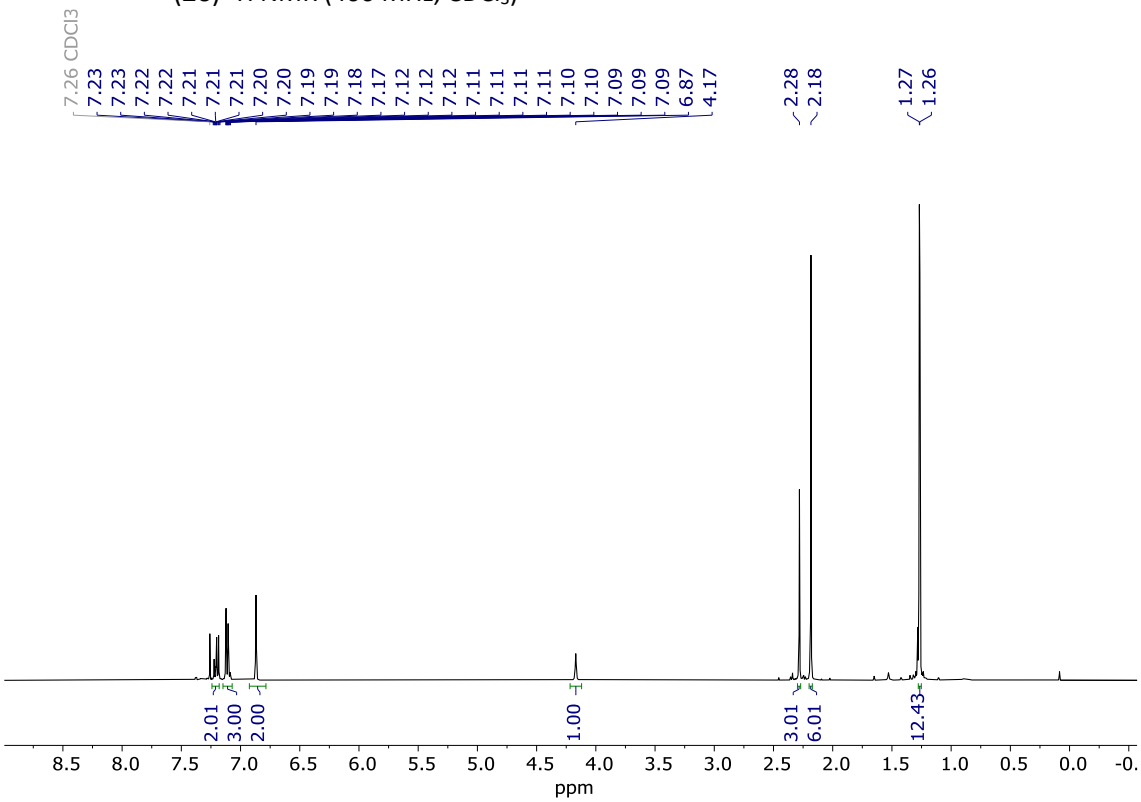


^{11}B NMR (128 MHz, $CDCl_3$)

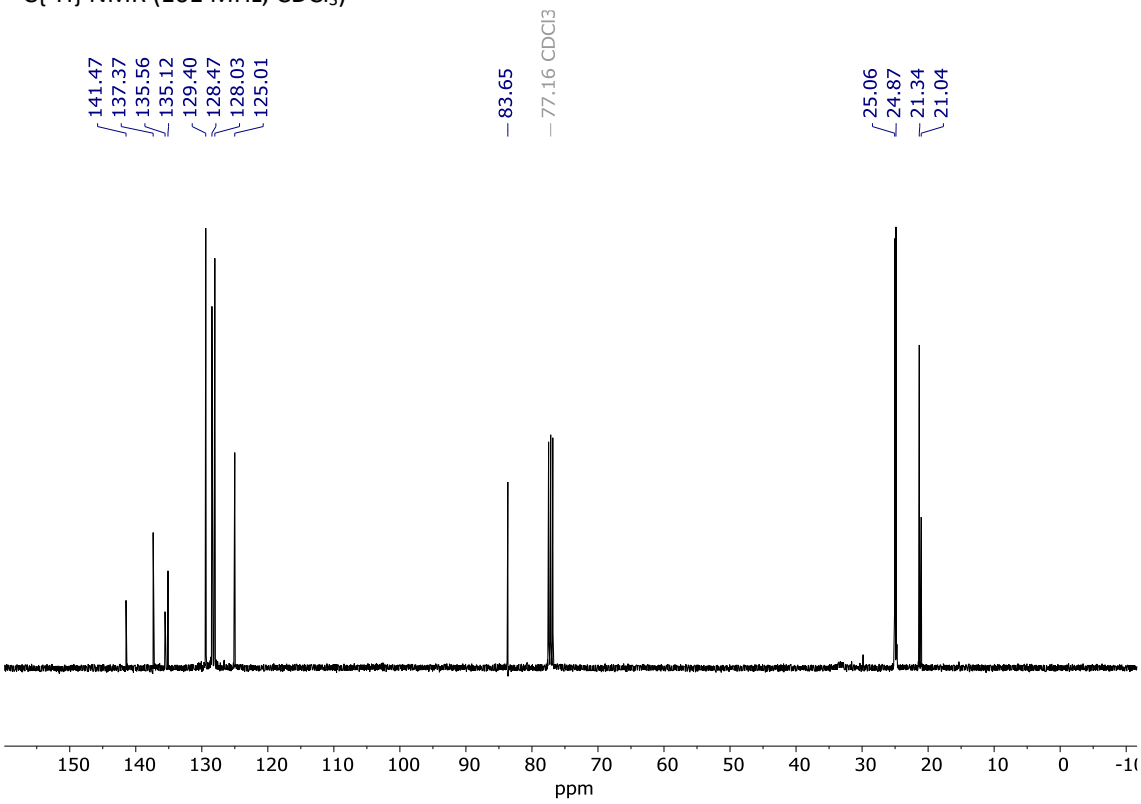




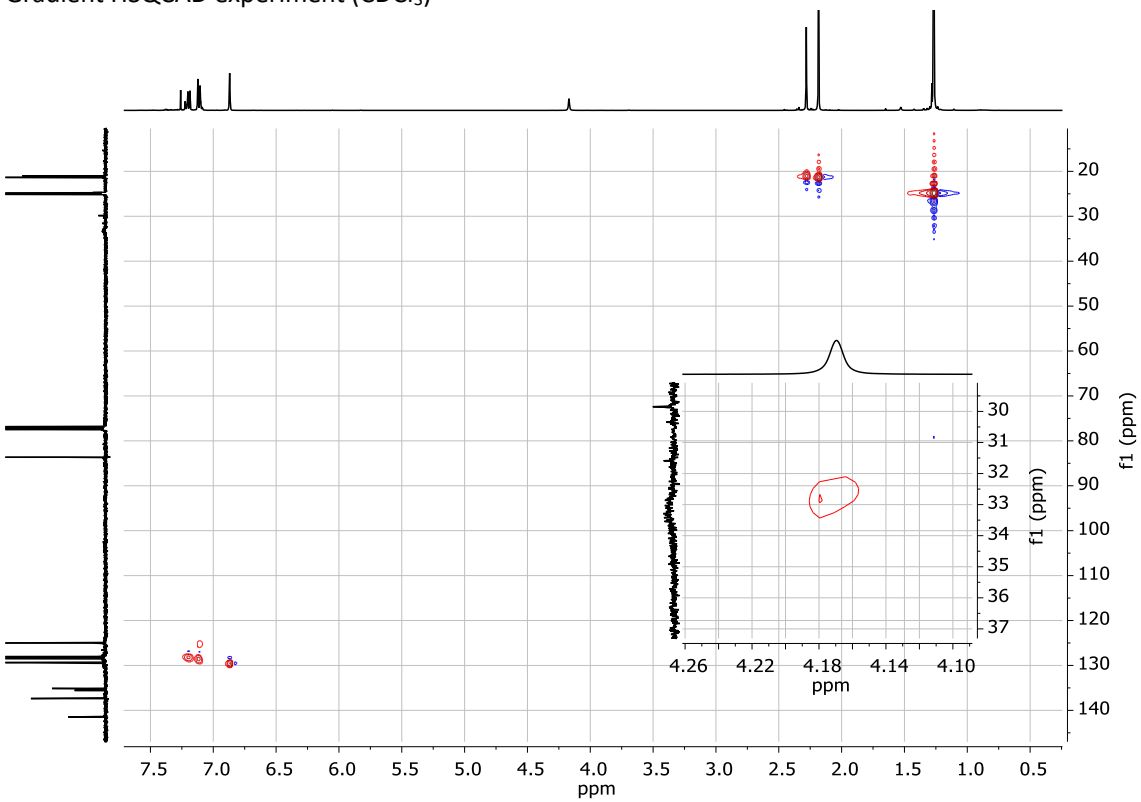
(**26**) ^{1}H NMR (400 MHz, $CDCl_3$)



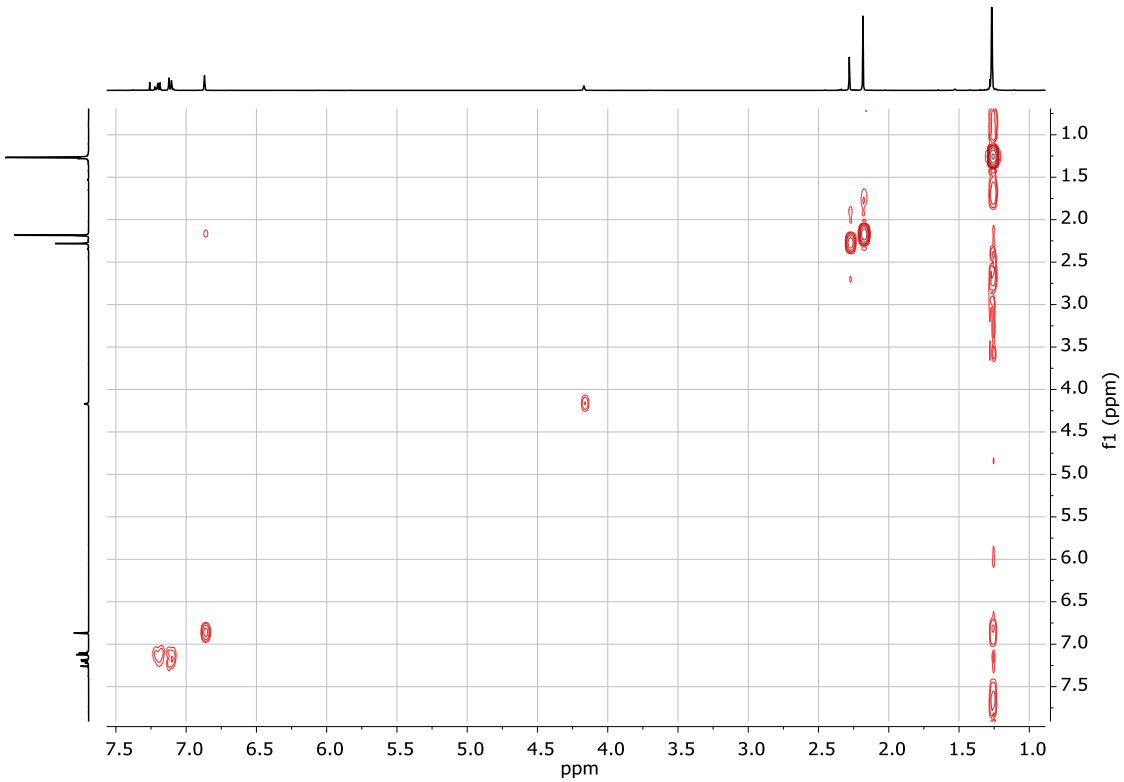
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

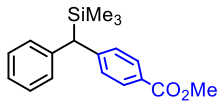


Gradient HSQCAD experiment ($CDCl_3$)

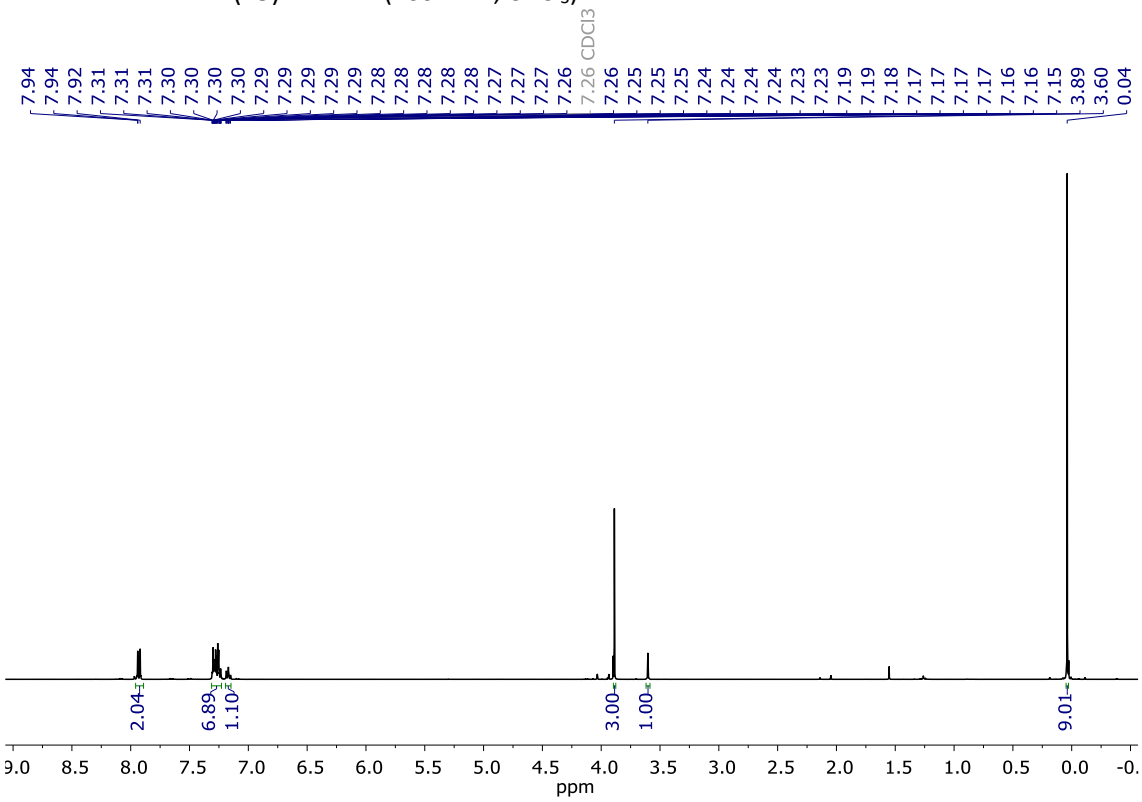


^1H COSY experiment ($CDCl_3$)

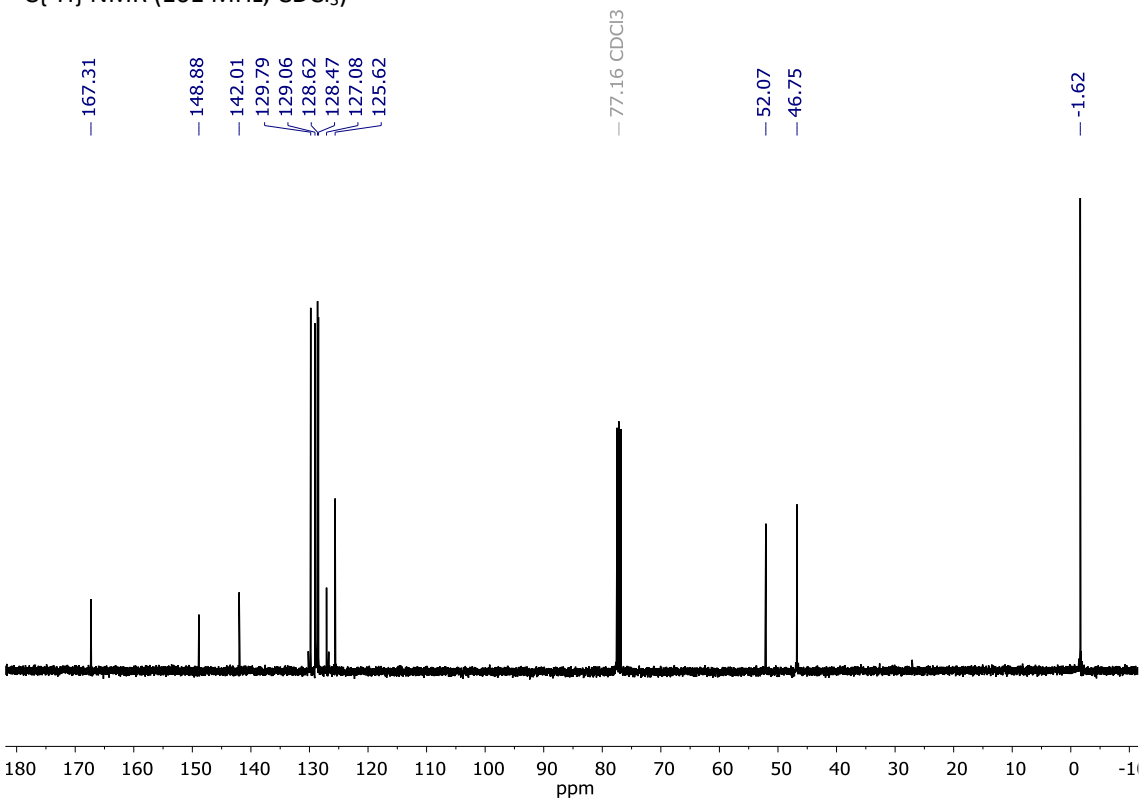




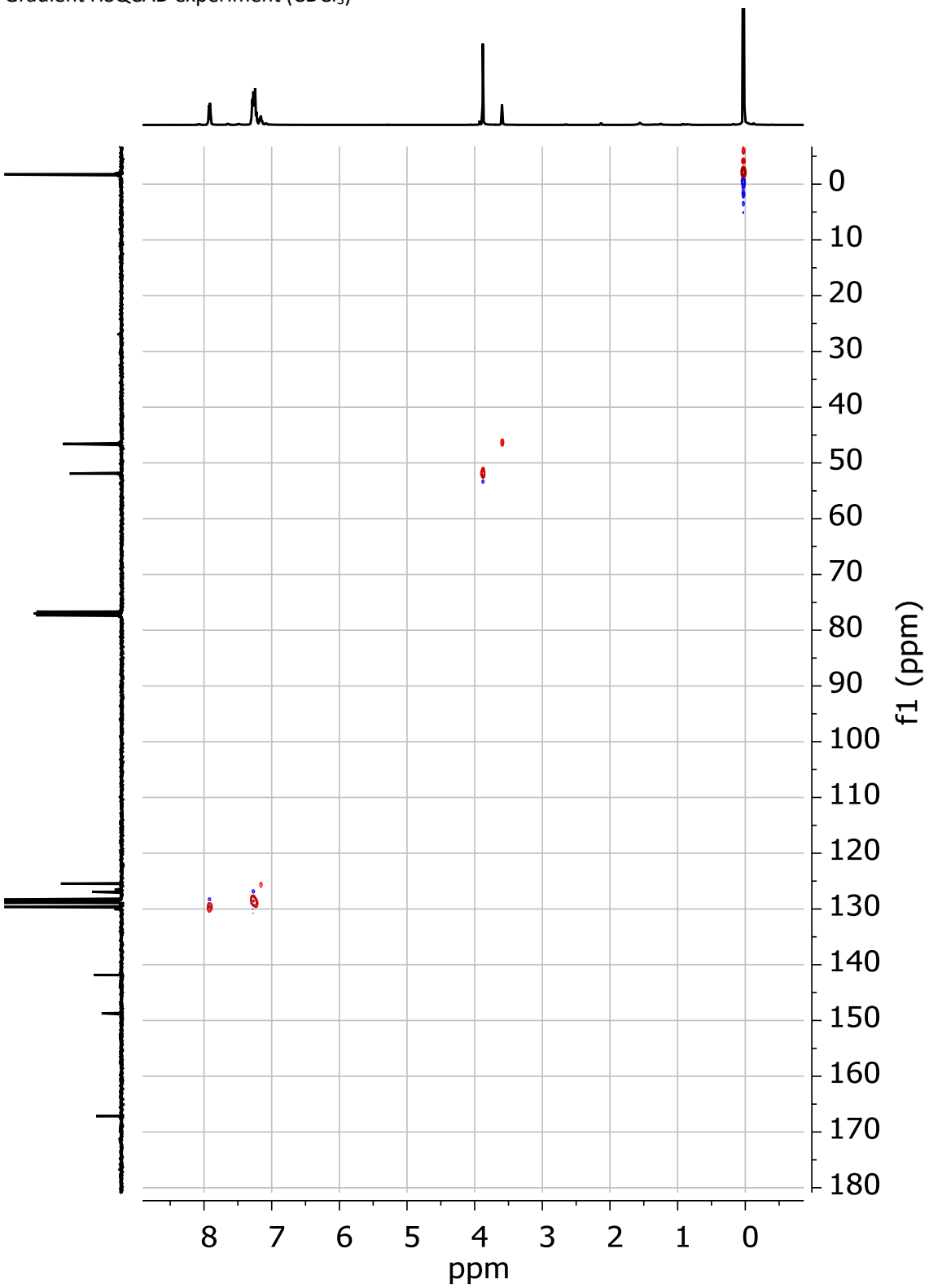
(**29**) ^{1}H NMR (400 MHz, $CDCl_3$)

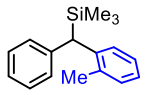


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

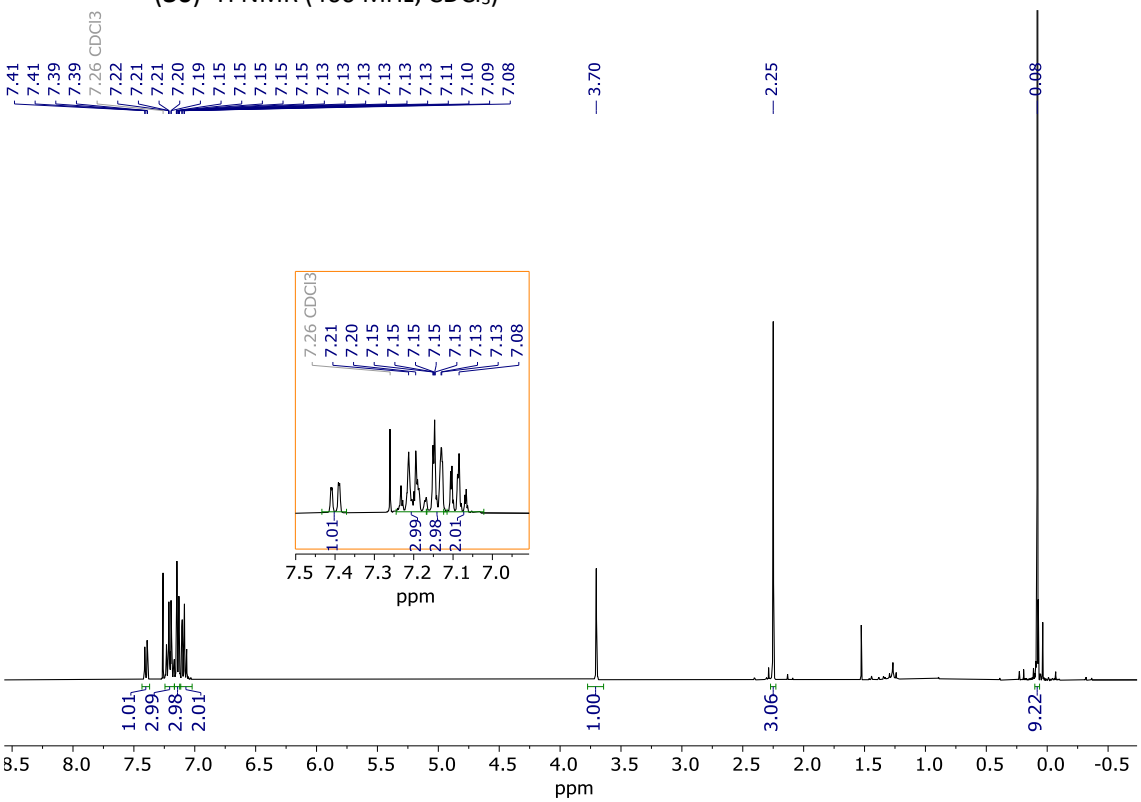


Gradient HSQCAD experiment ($CDCl_3$)

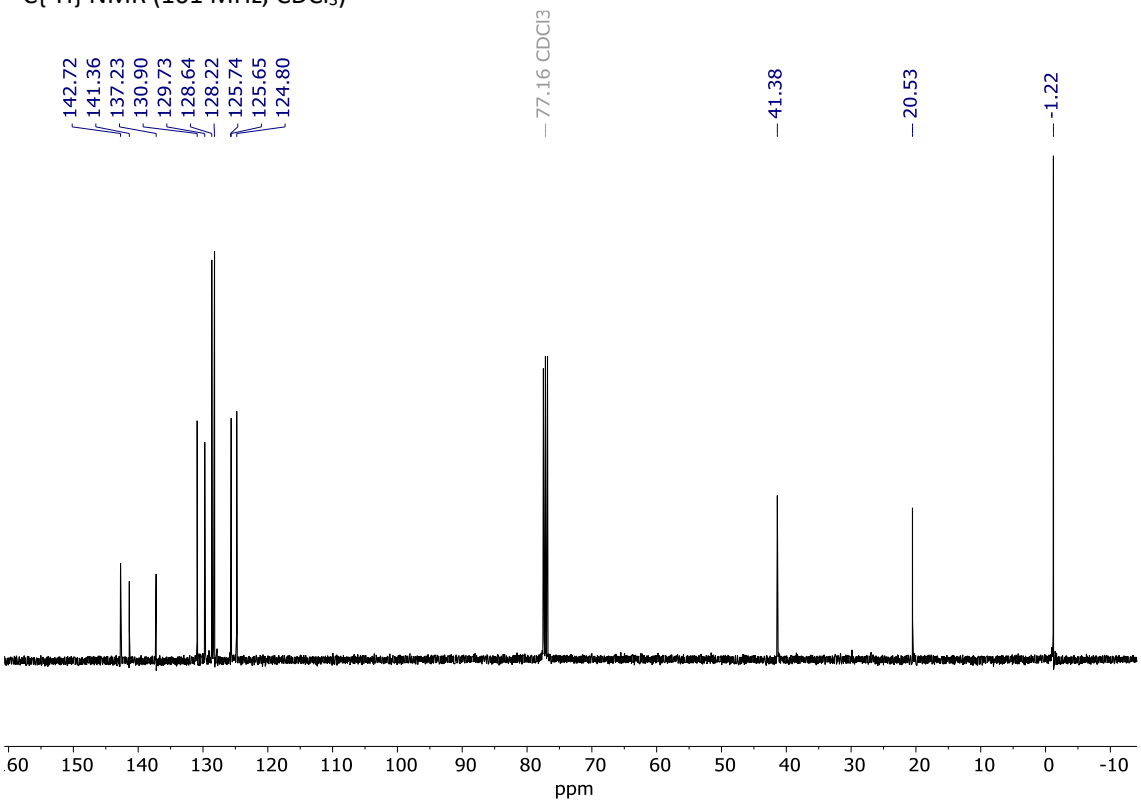




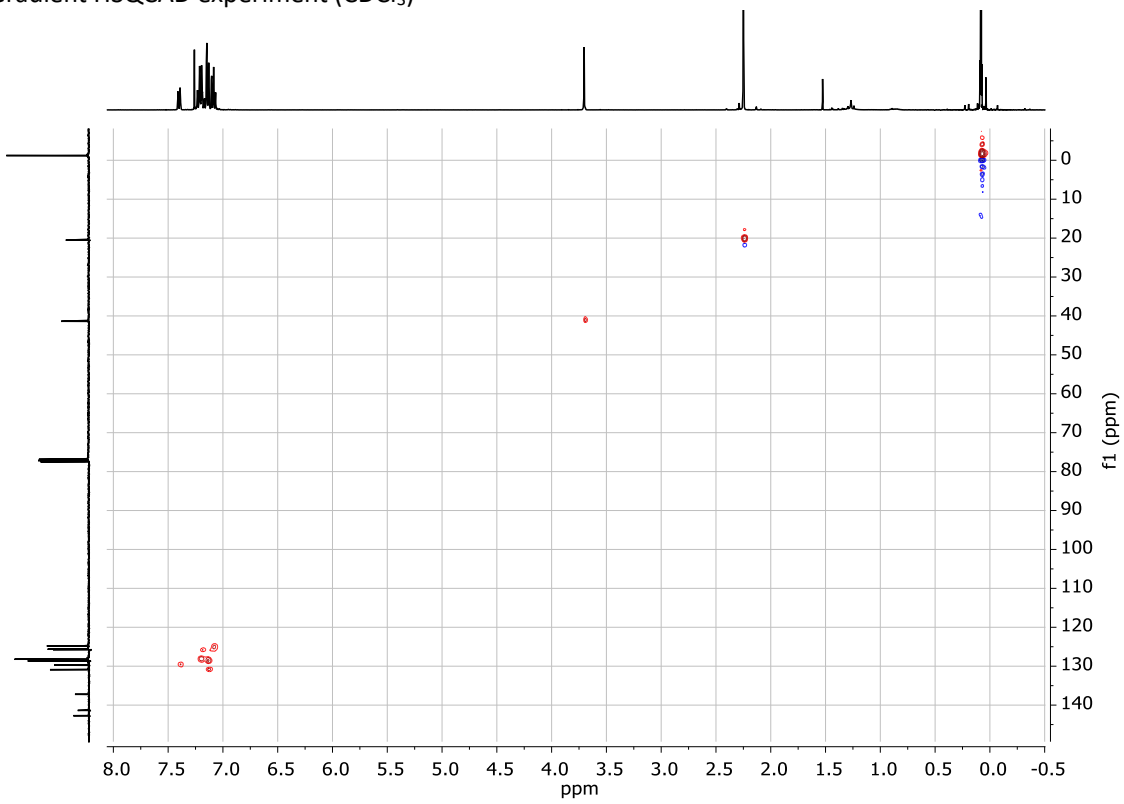
(**30**) ^{1}H NMR (400 MHz, $CDCl_3$)



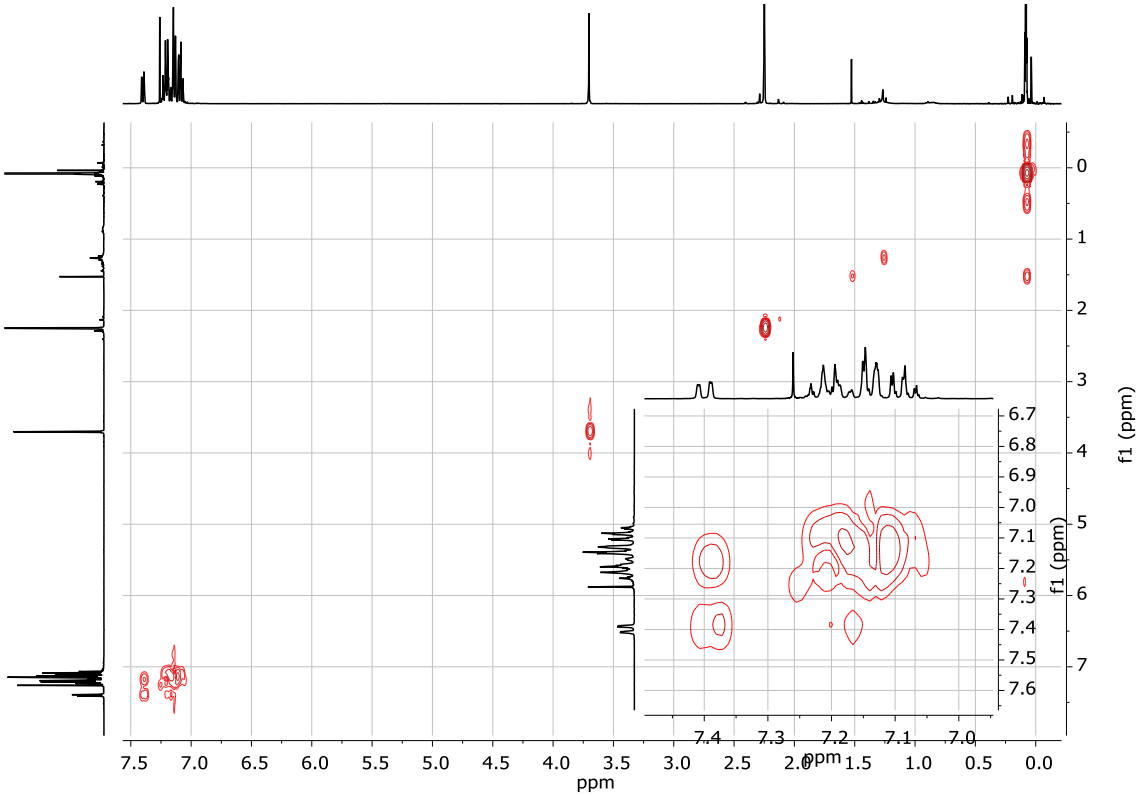
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

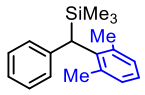


Gradient HSQCAD experiment ($CDCl_3$)

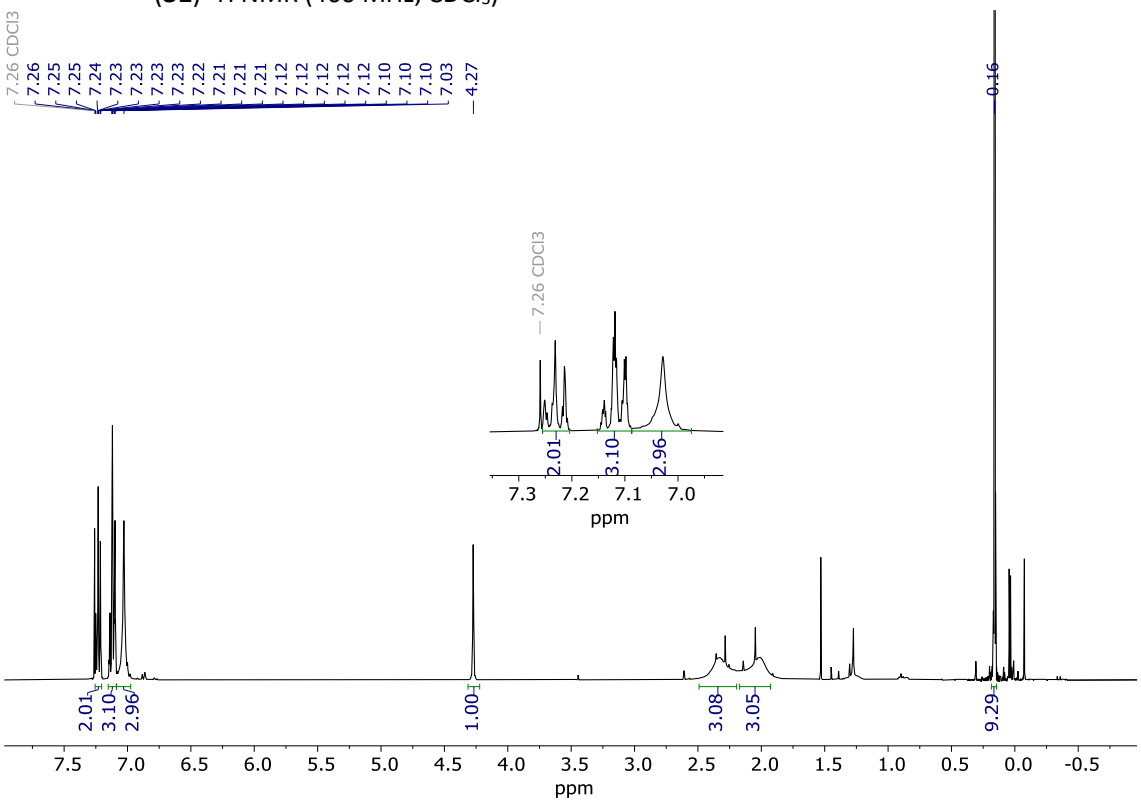


^1H COSY experiment ($CDCl_3$)

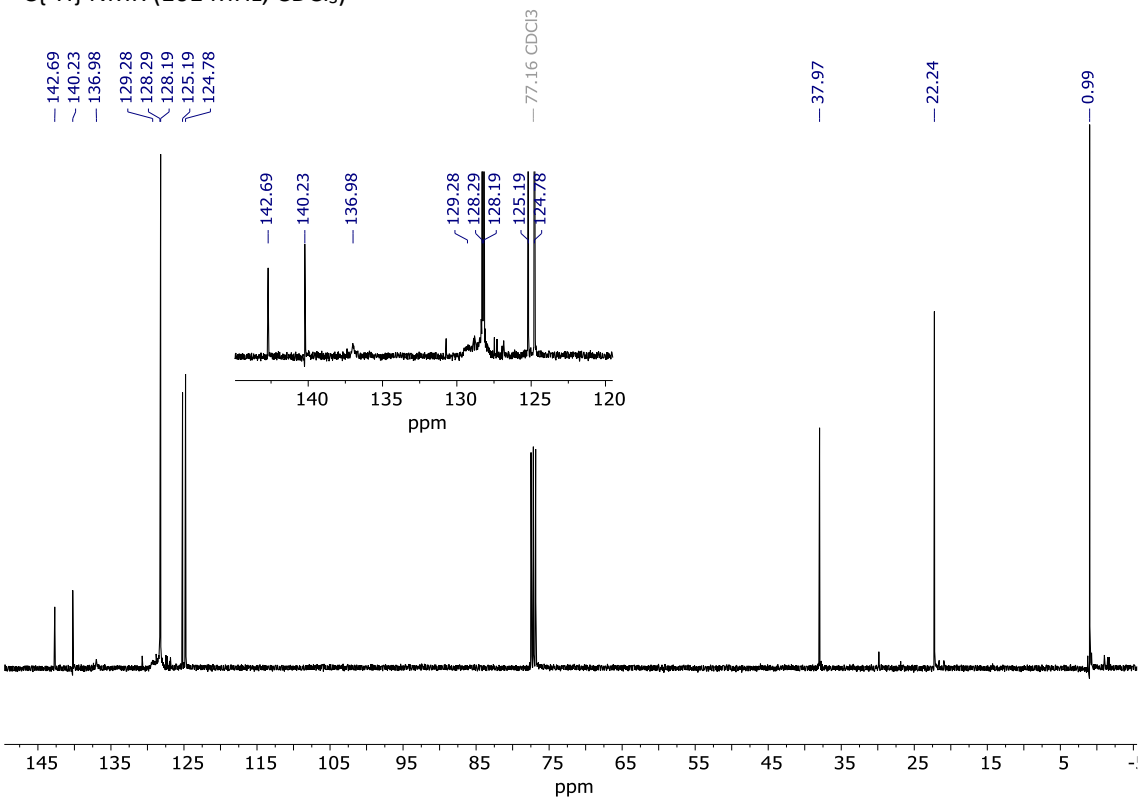




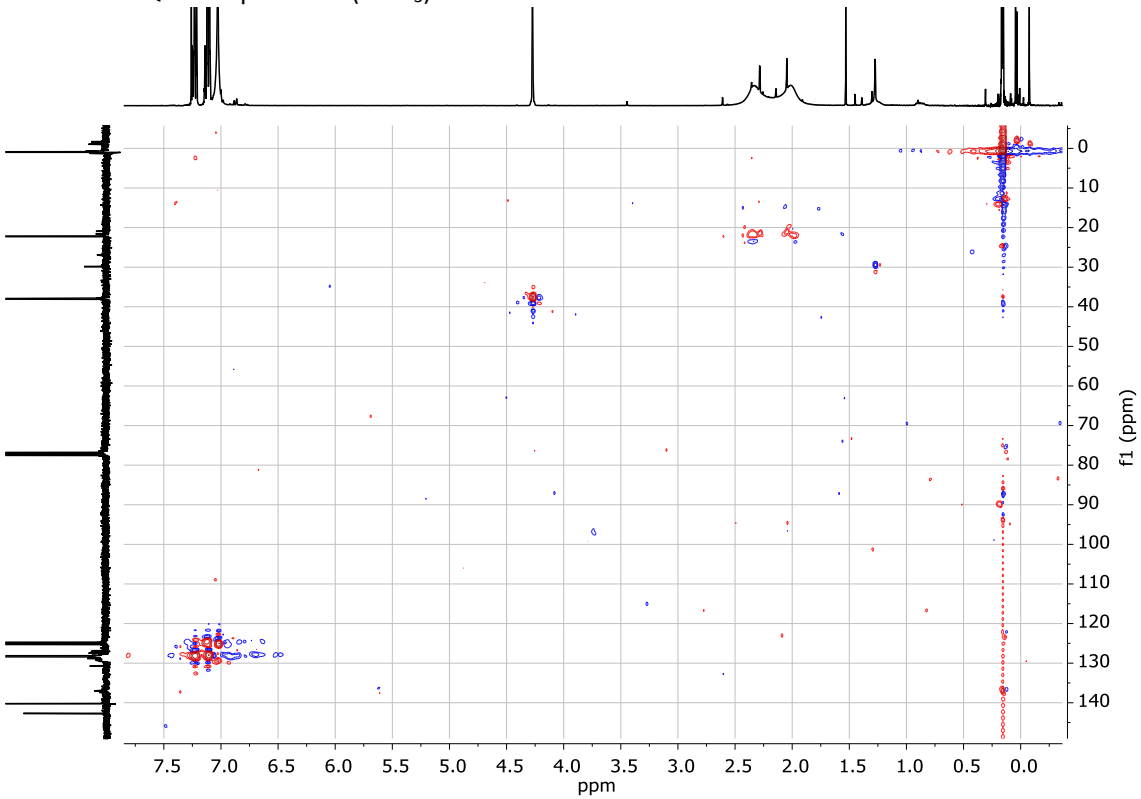
(**31**) ^{1}H NMR (400 MHz, $CDCl_3$)



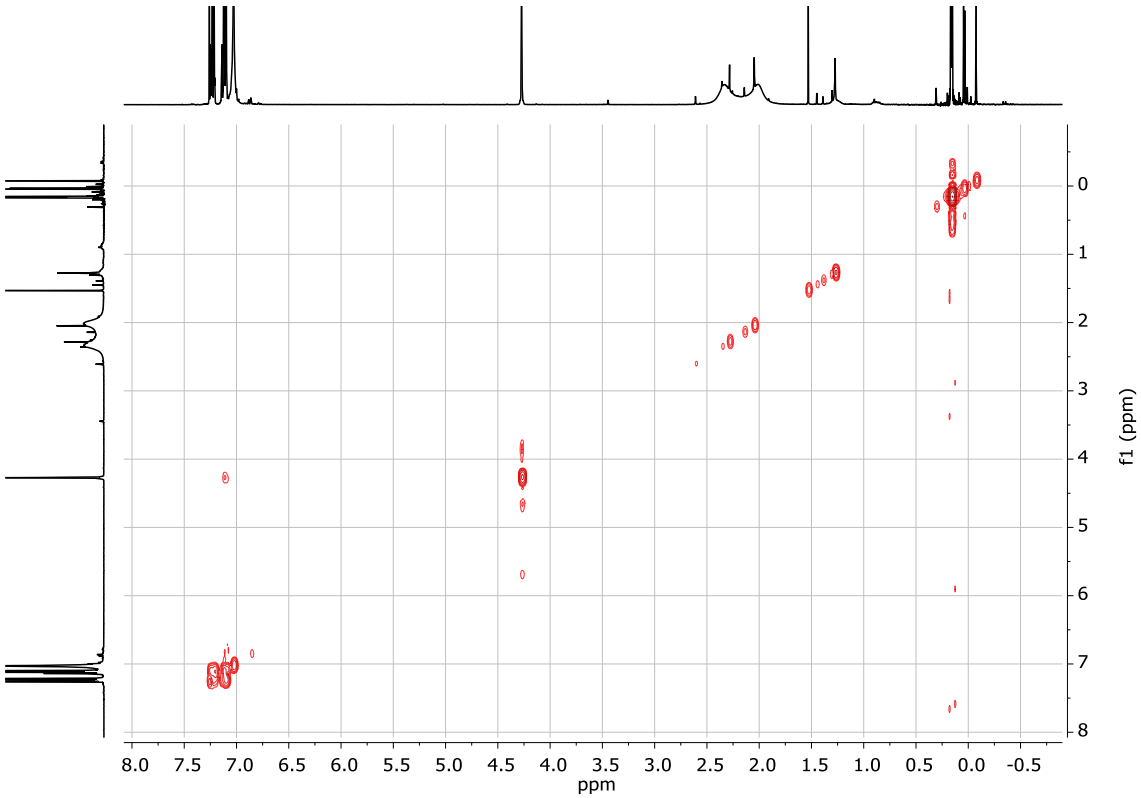
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

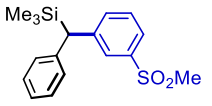


Gradient HSQCAD experiment ($CDCl_3$)

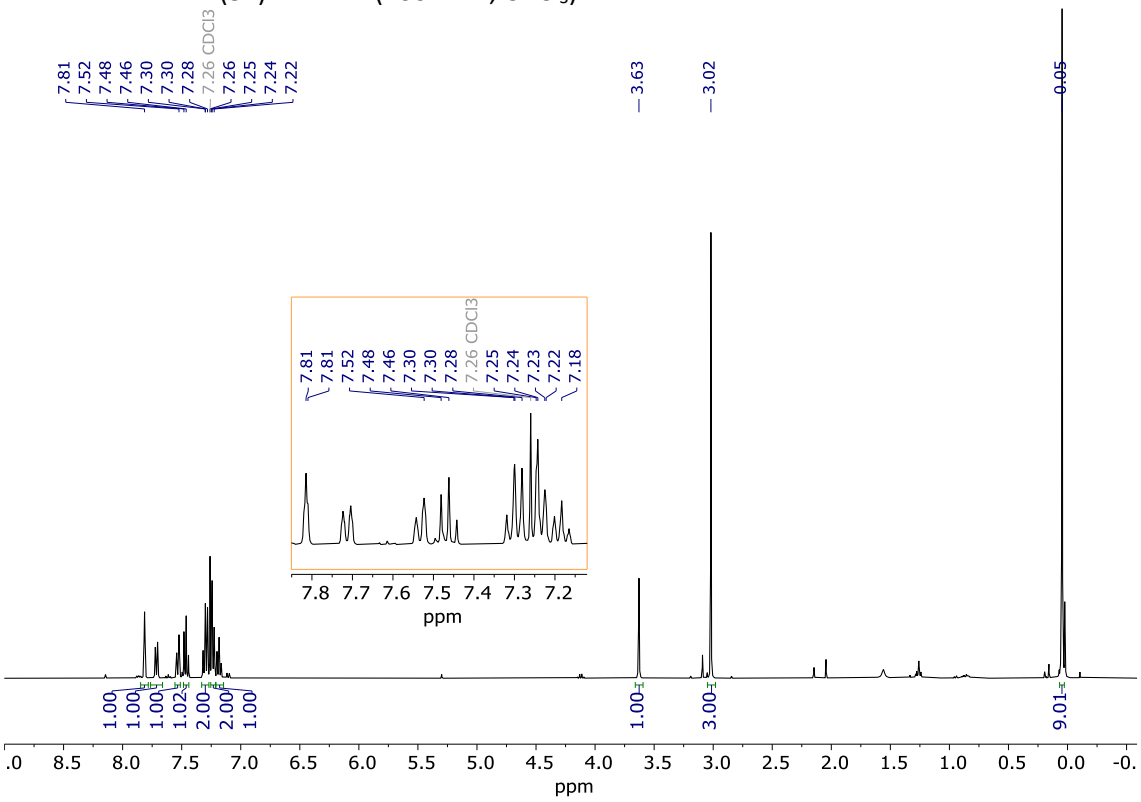


^1H COSY experiment ($CDCl_3$)

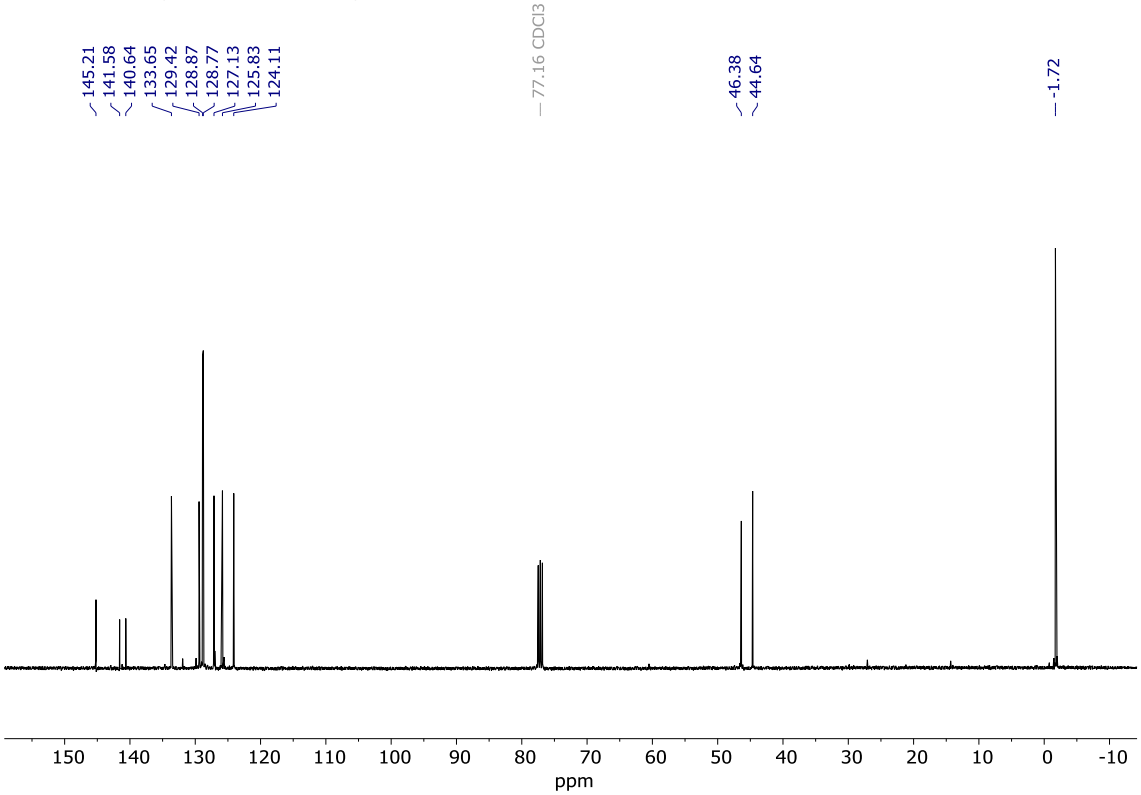




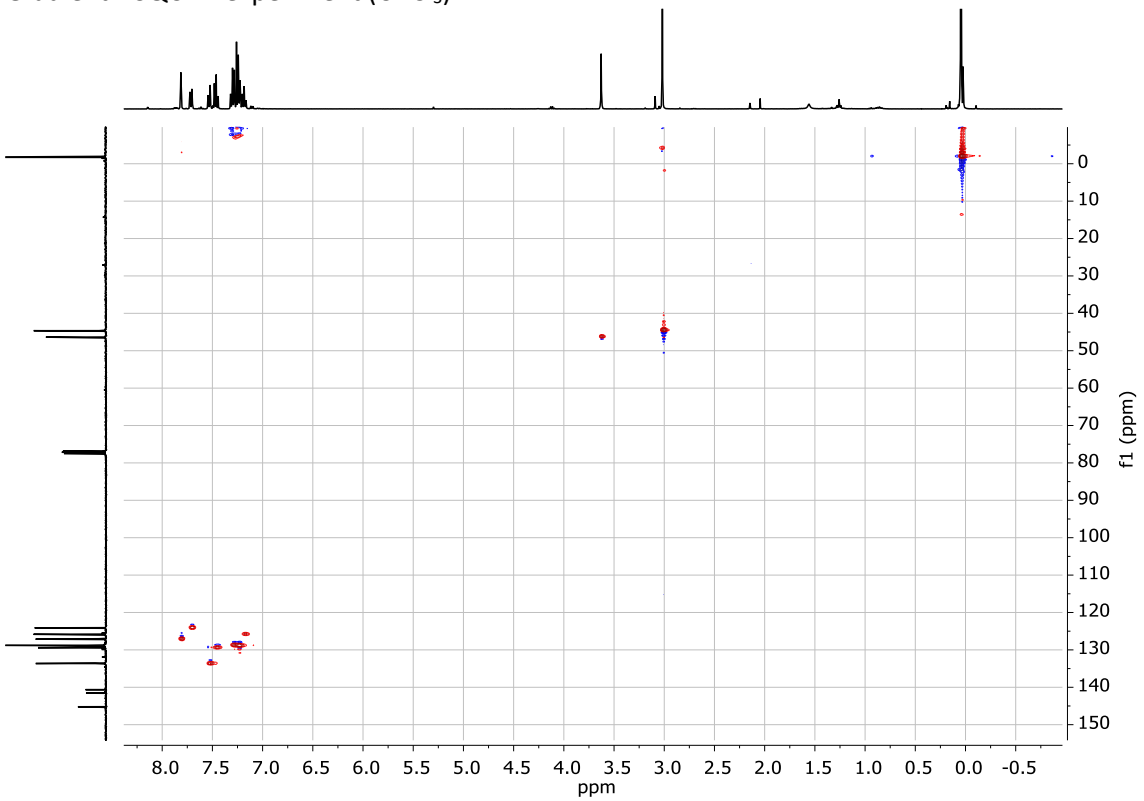
(**32**) ^{1}H NMR (400 MHz, $CDCl_3$)



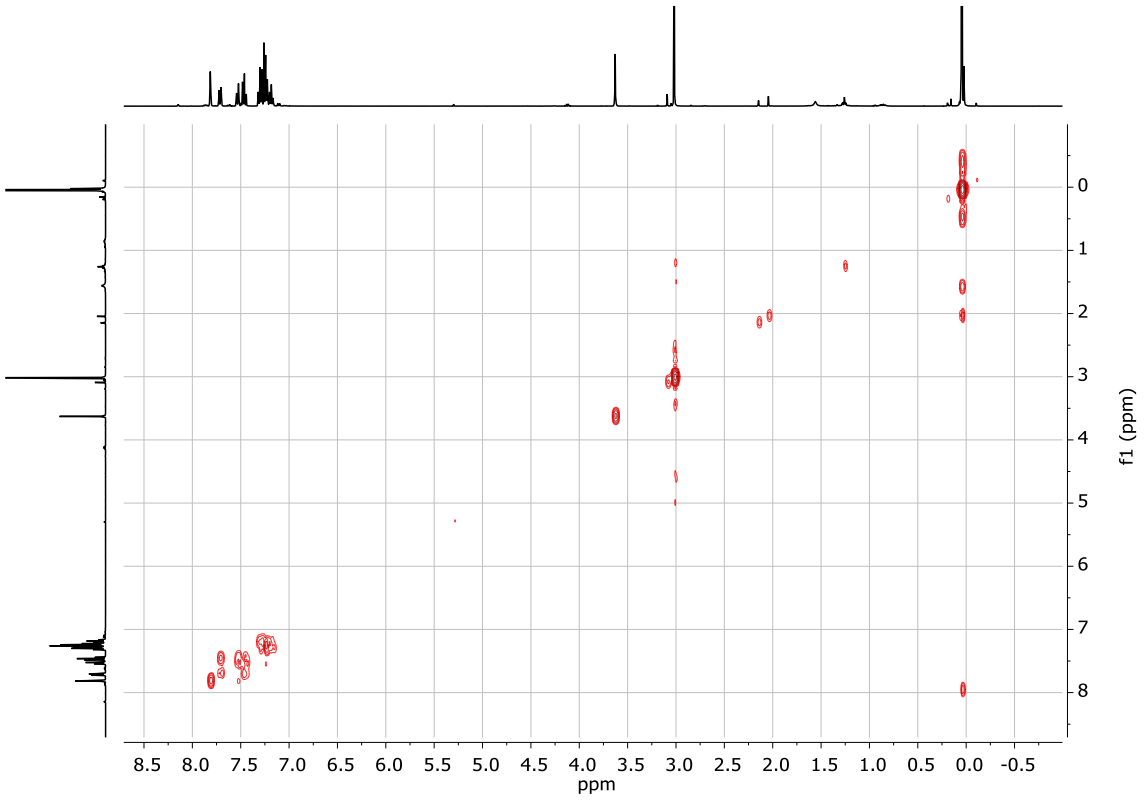
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

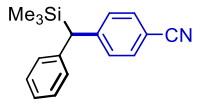


Gradient HSQCAD experiment ($CDCl_3$)

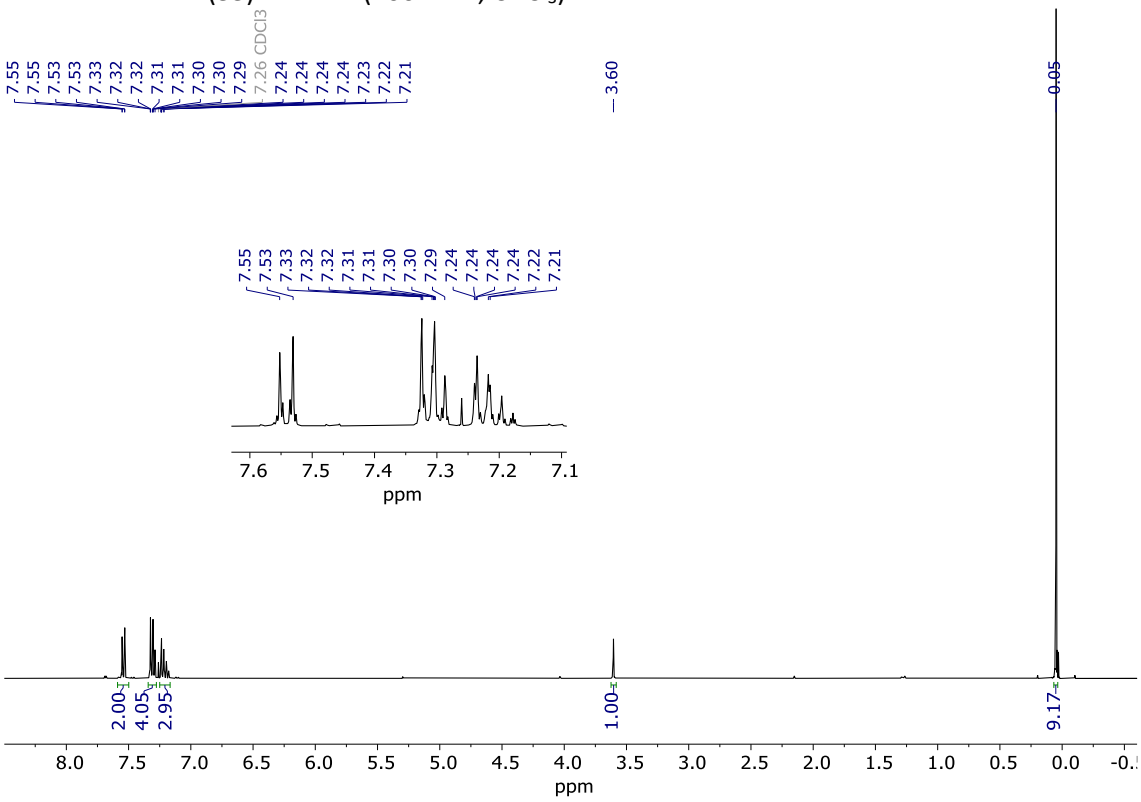


^1H COSY experiment ($CDCl_3$)

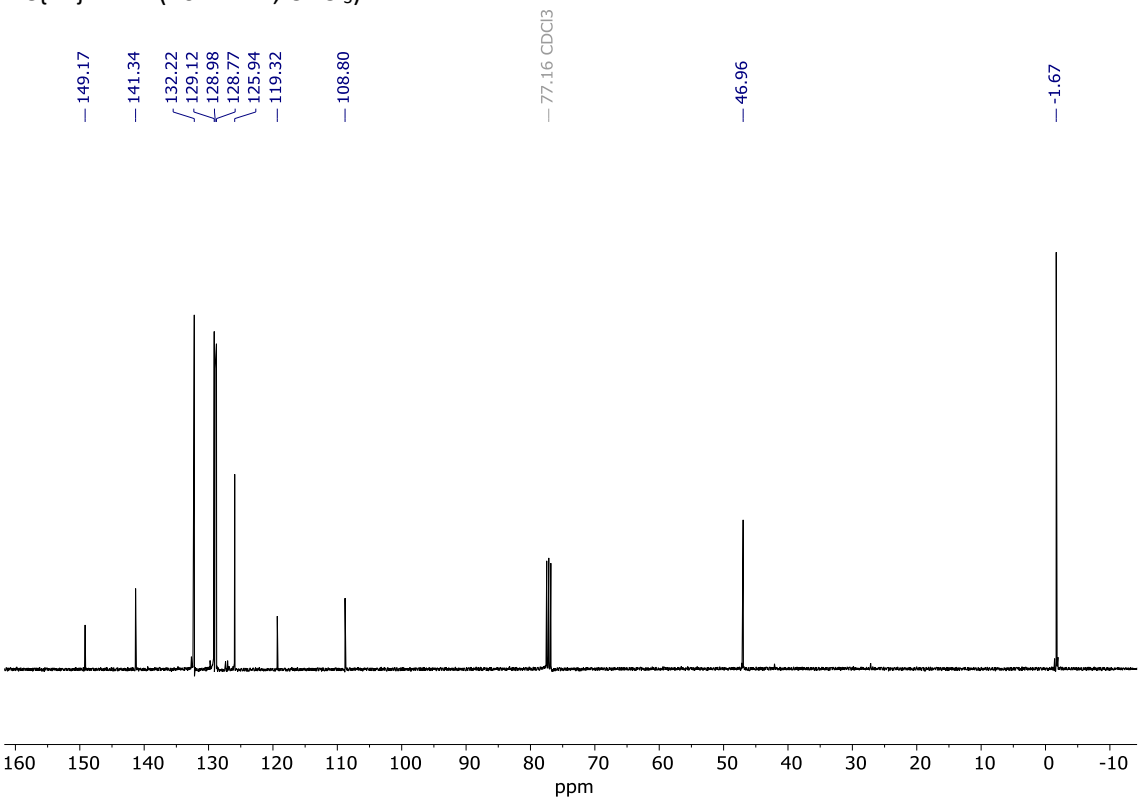


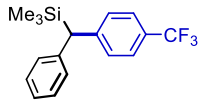


(**33**) ^{1}H NMR (400 MHz, $CDCl_3$)

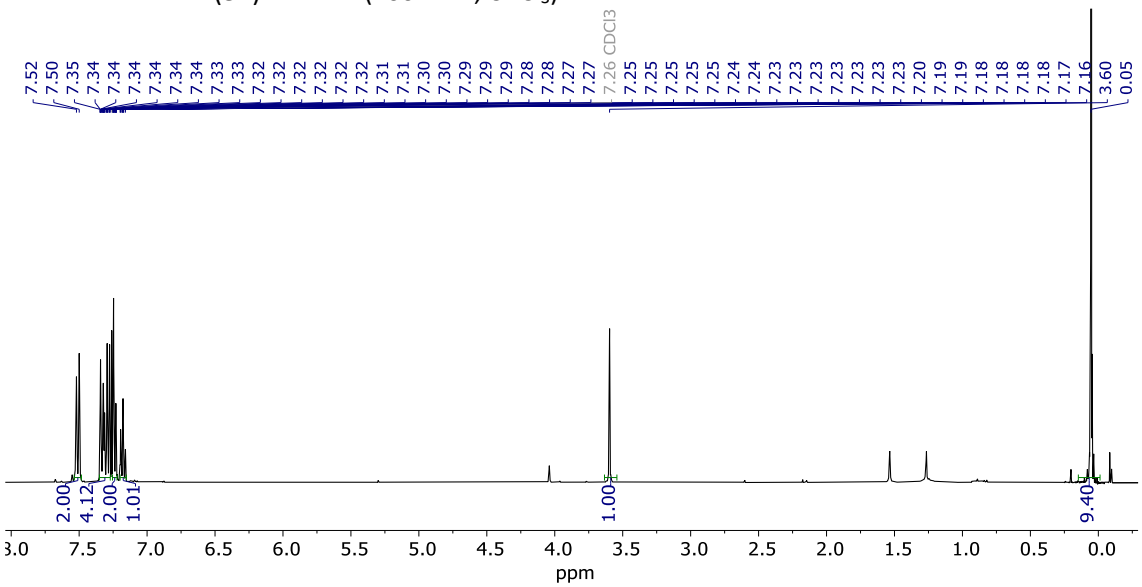


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

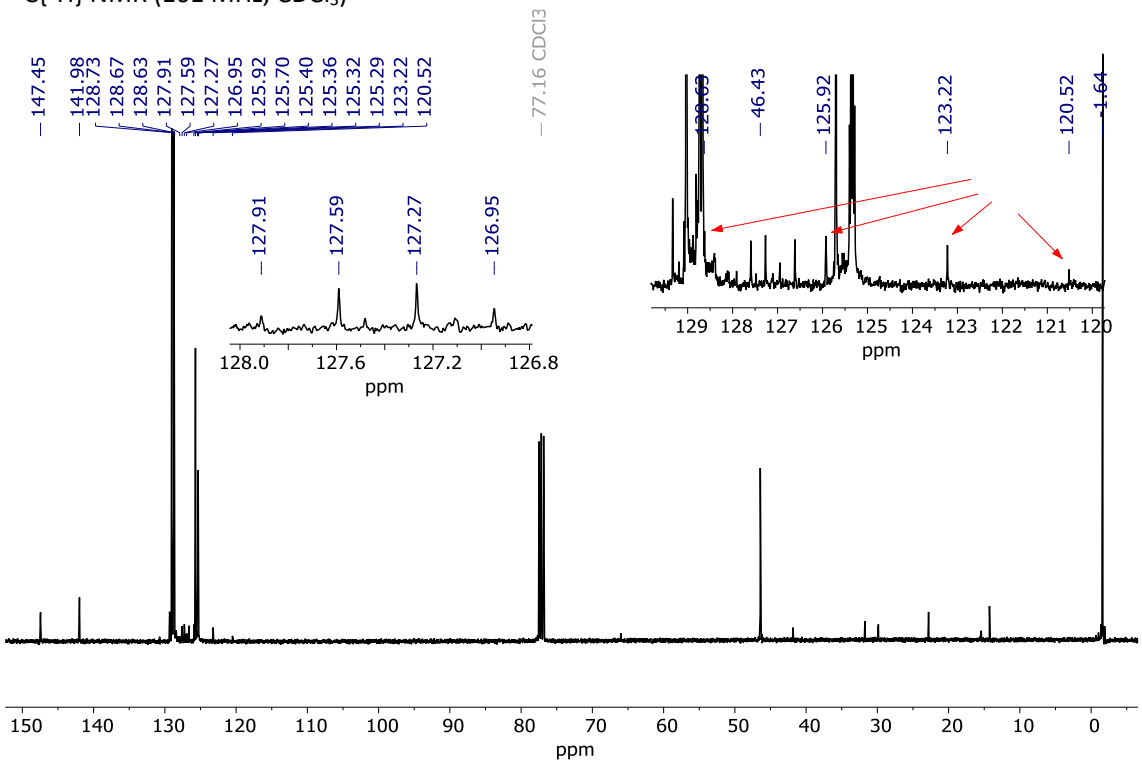




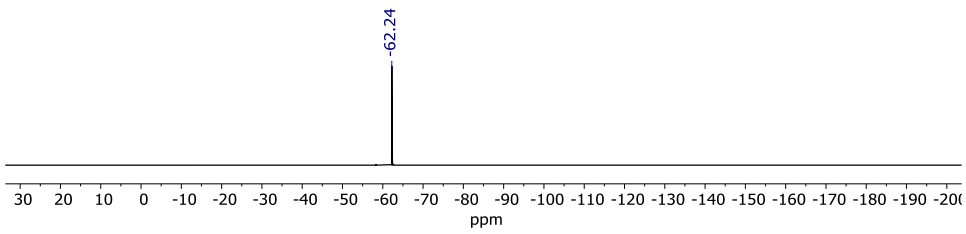
(**34**) ^{1}H NMR (400 MHz, $CDCl_3$)

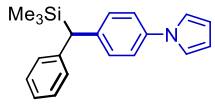


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

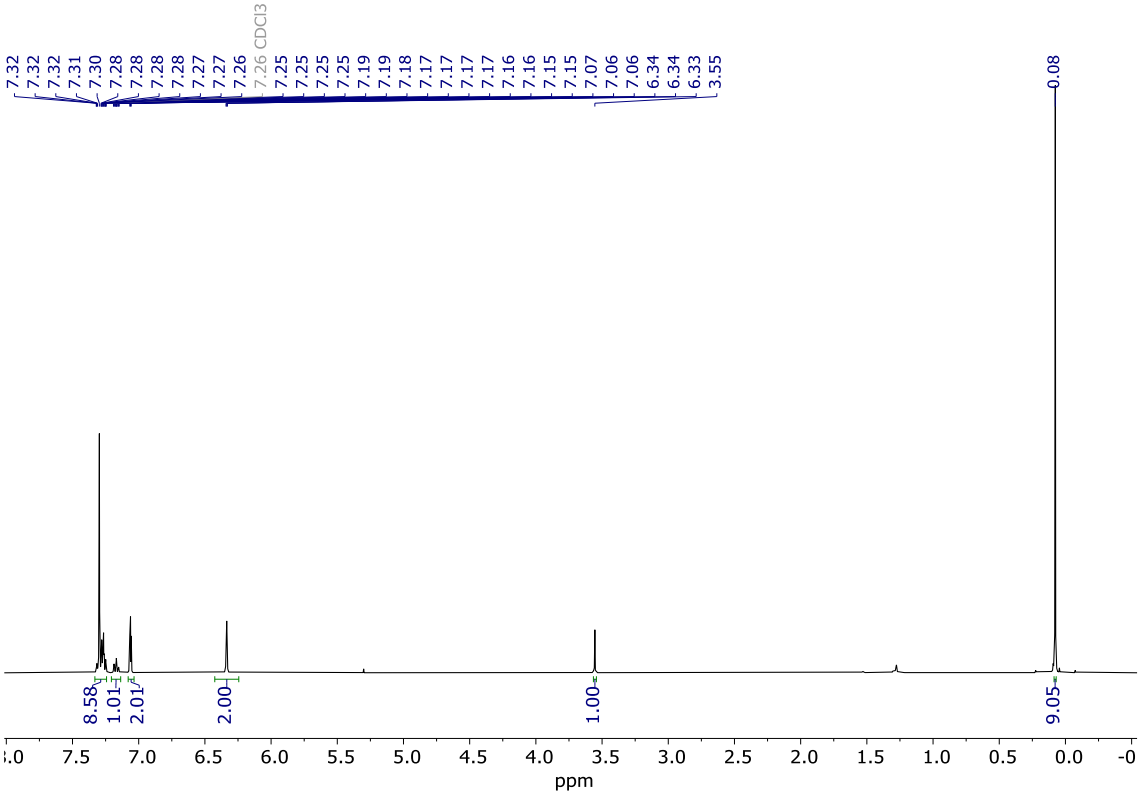


^{19}F NMR (471 MHz, $CDCl_3$)

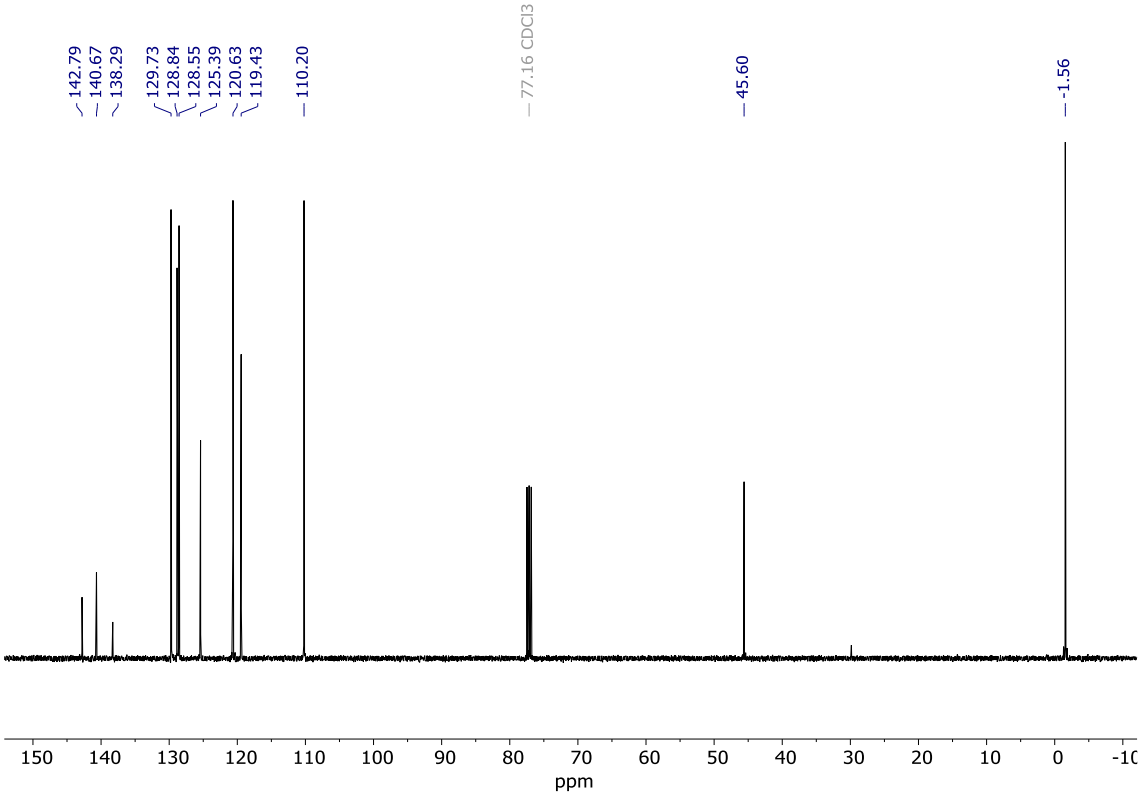




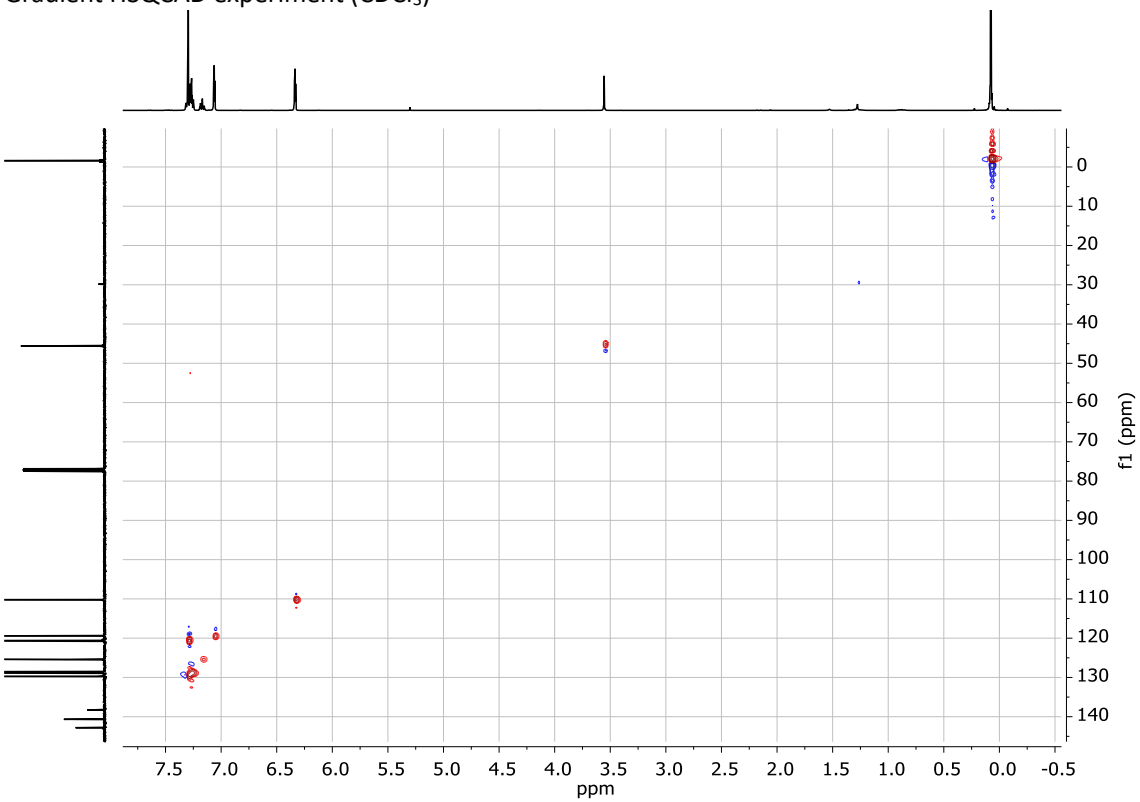
(**35**) ^{1}H NMR (400 MHz, $CDCl_3$)



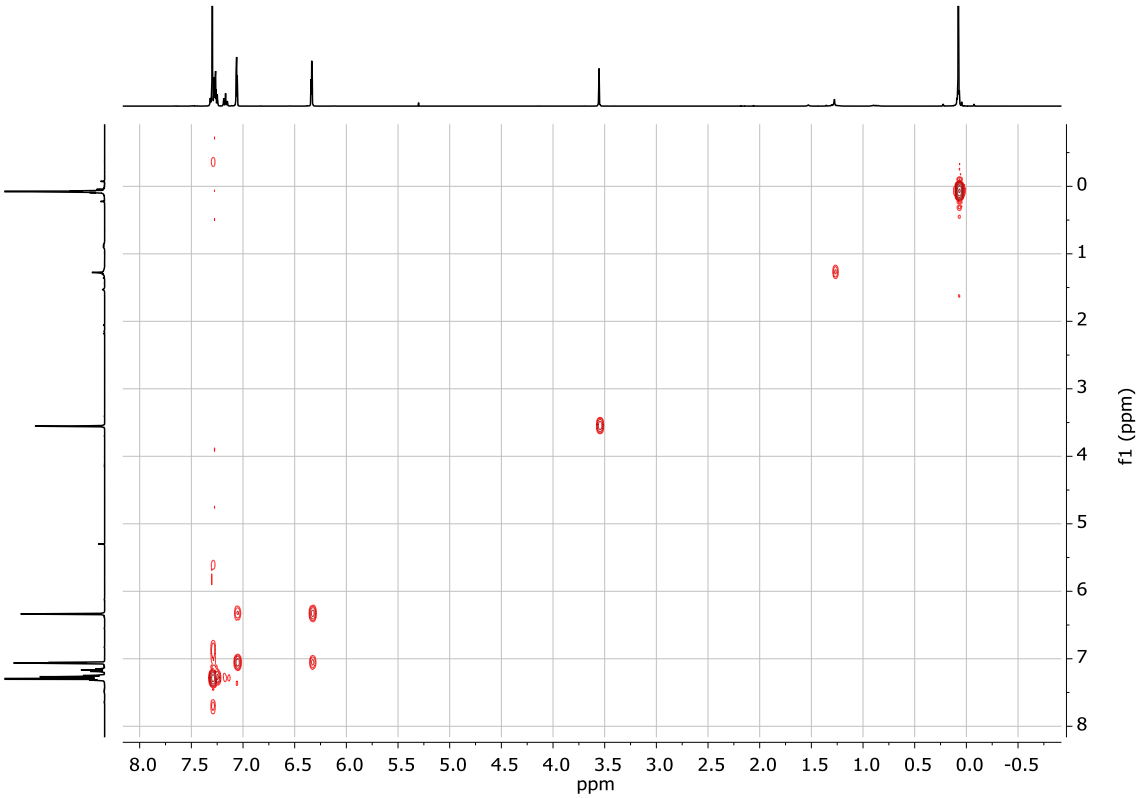
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

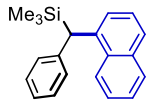


Gradient HSQCAD experiment ($CDCl_3$)

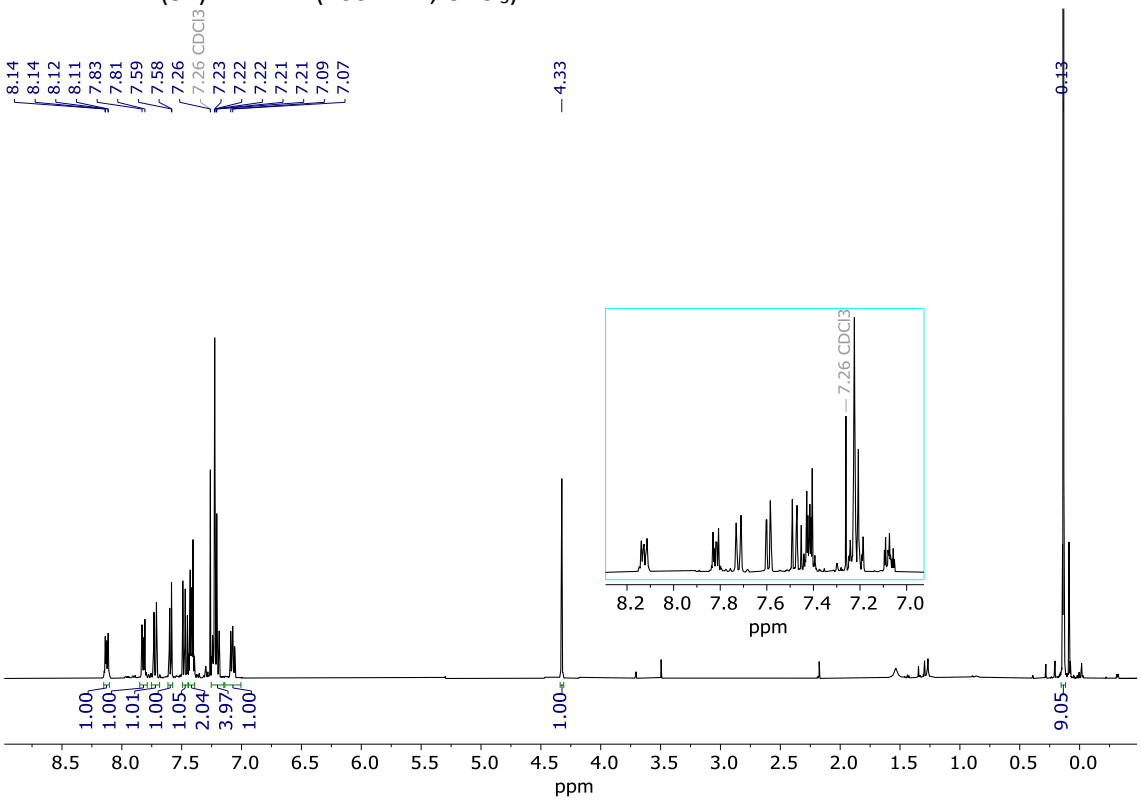


^1H COSY experiment ($CDCl_3$)

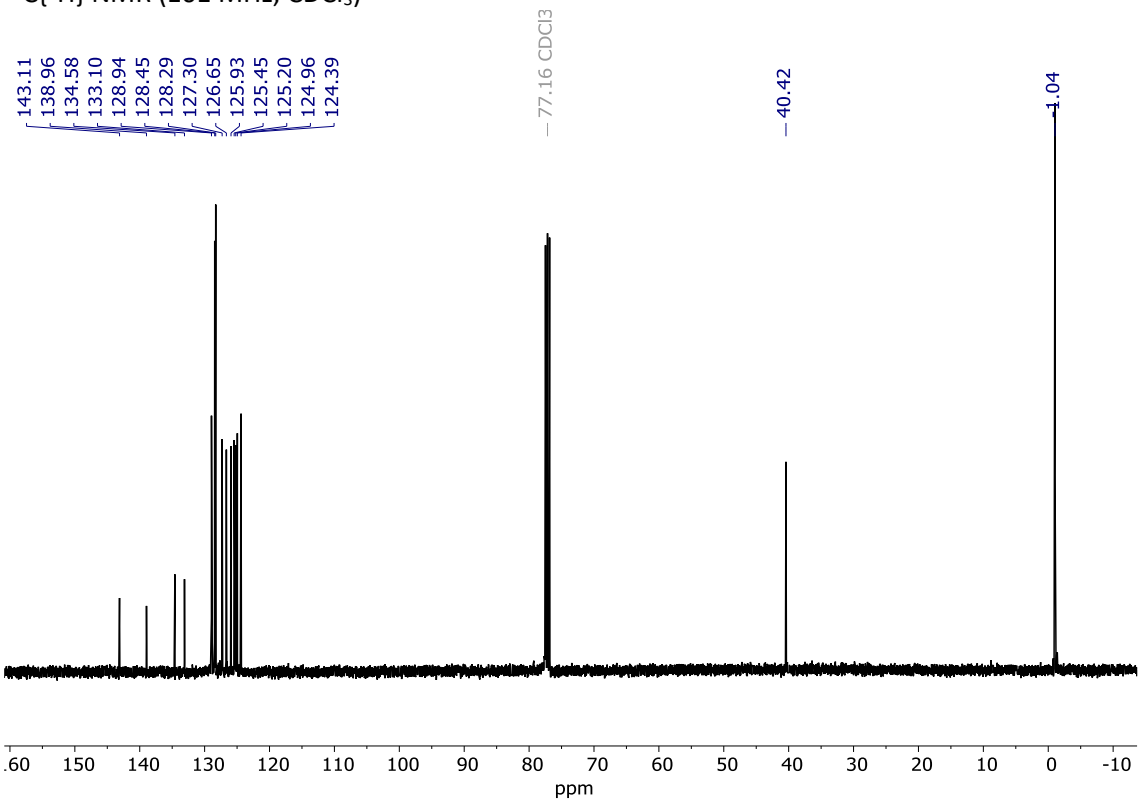




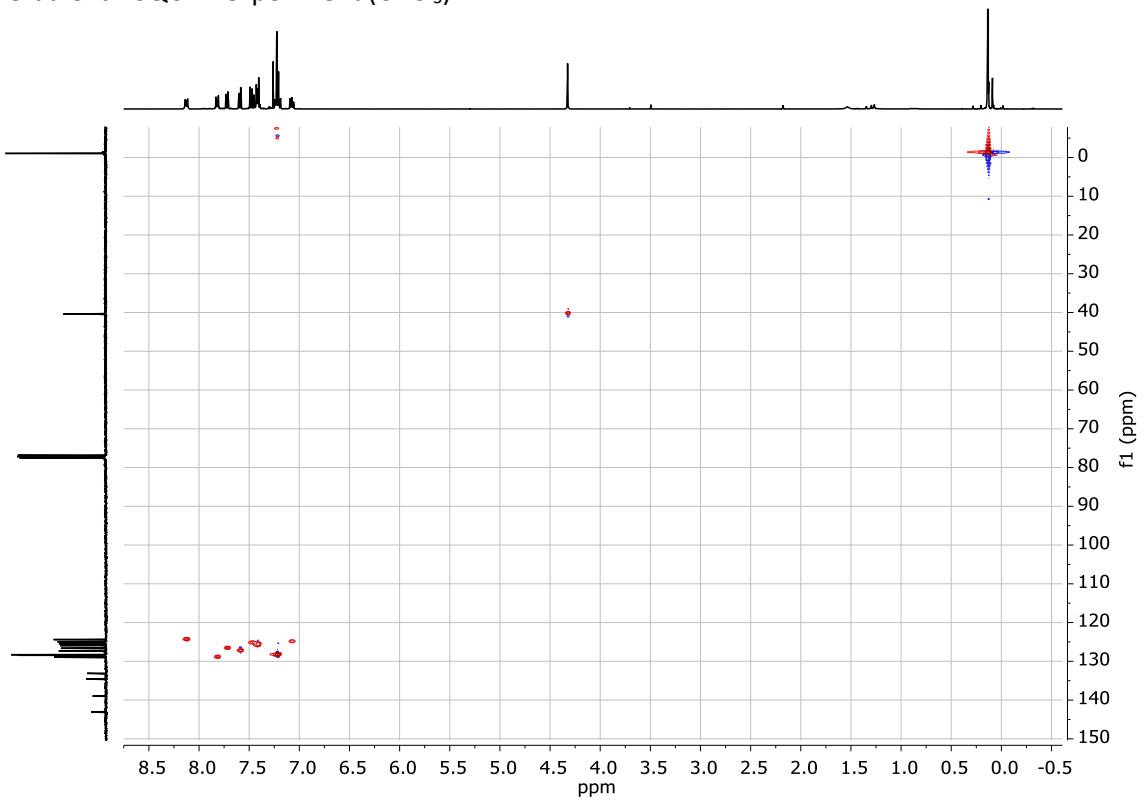
(**37**) ^{1}H NMR (400 MHz, $CDCl_3$)



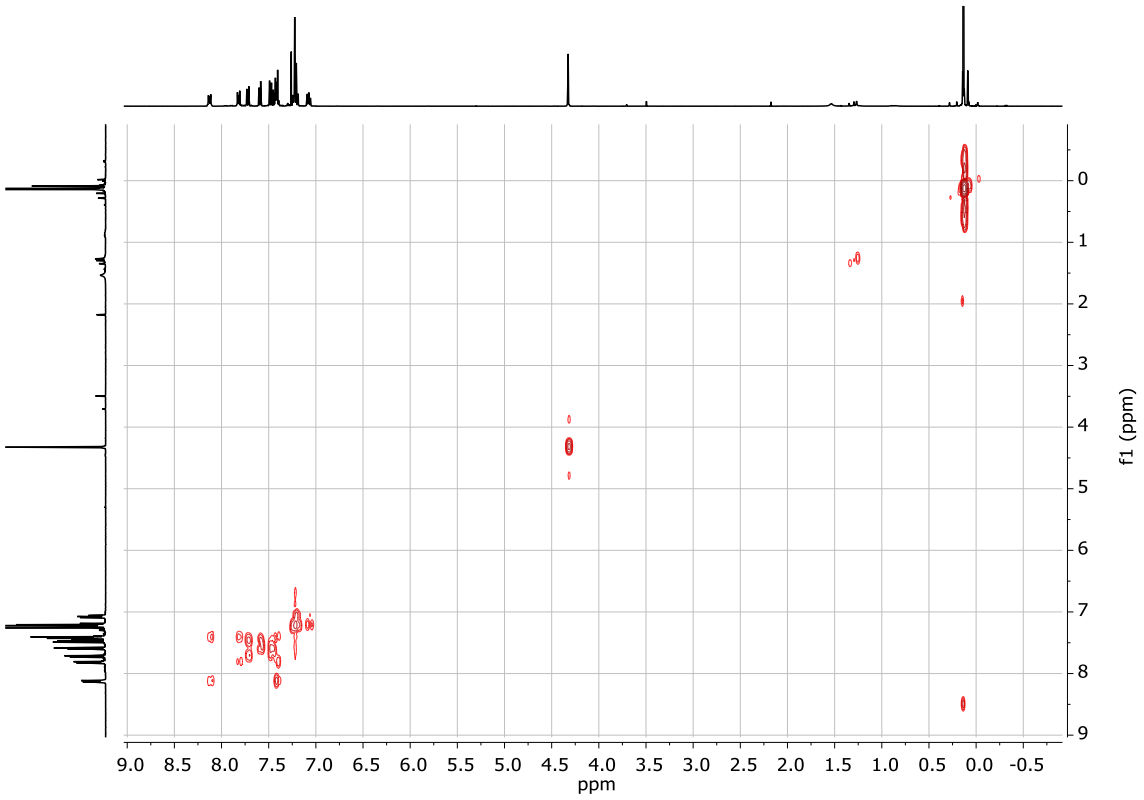
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

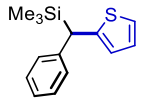


Gradient HSQCAD experiment ($CDCl_3$)

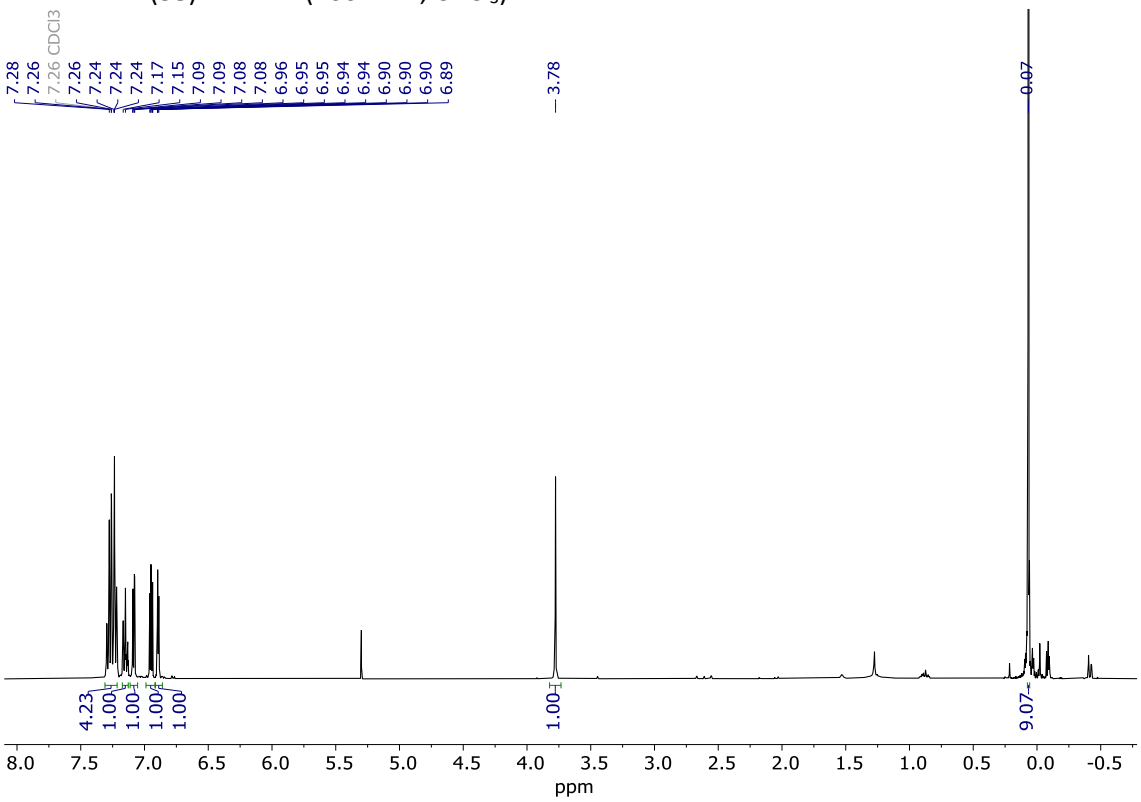


^1H COSY experiment ($CDCl_3$)

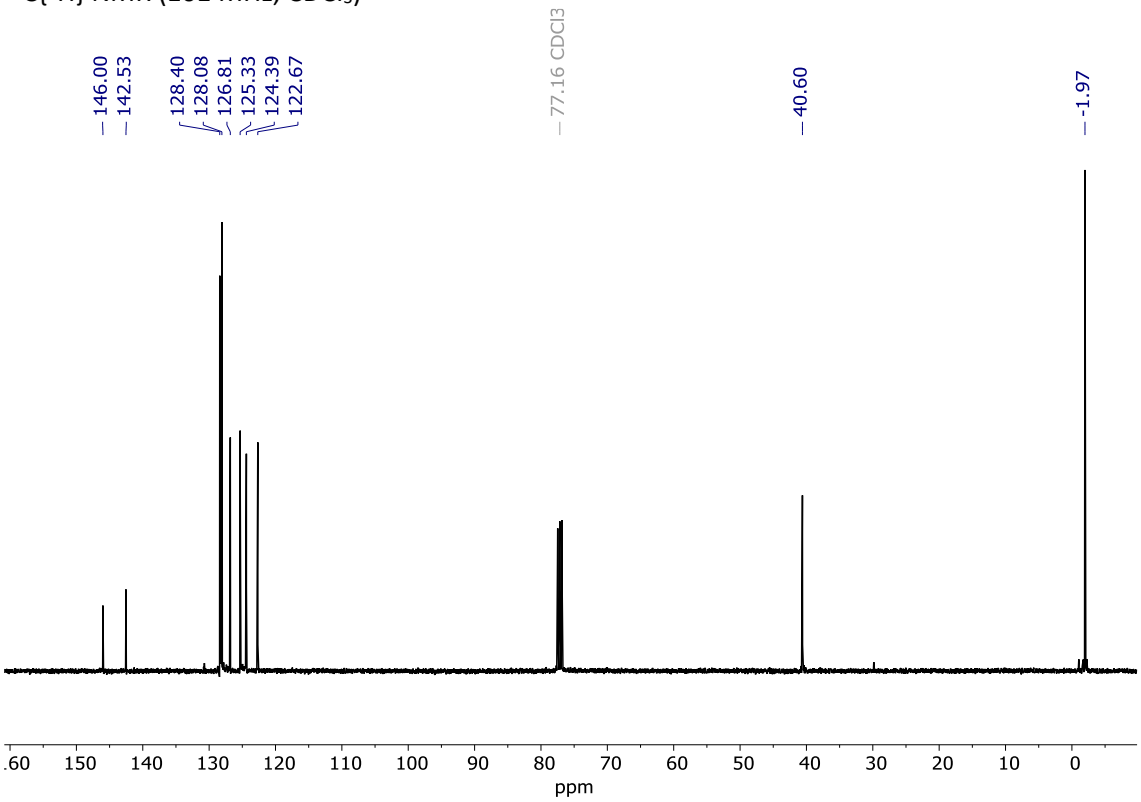




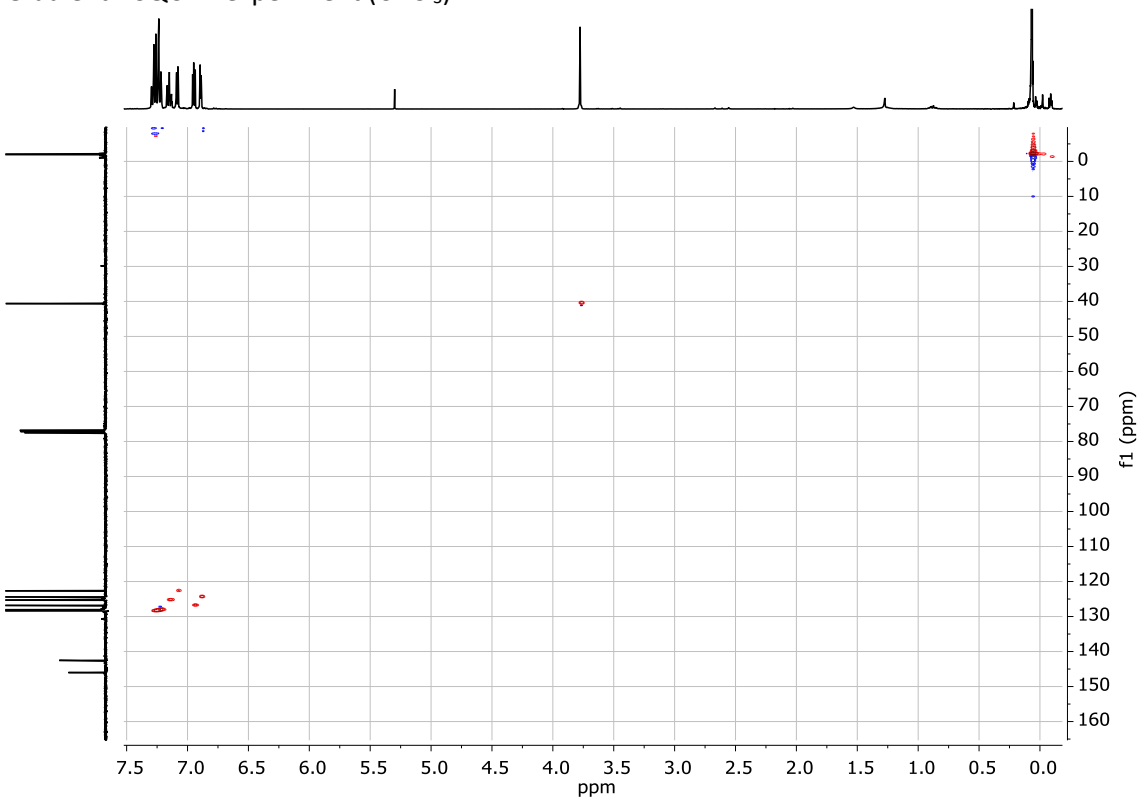
(**38**) ^{1}H NMR (400 MHz, $CDCl_3$)



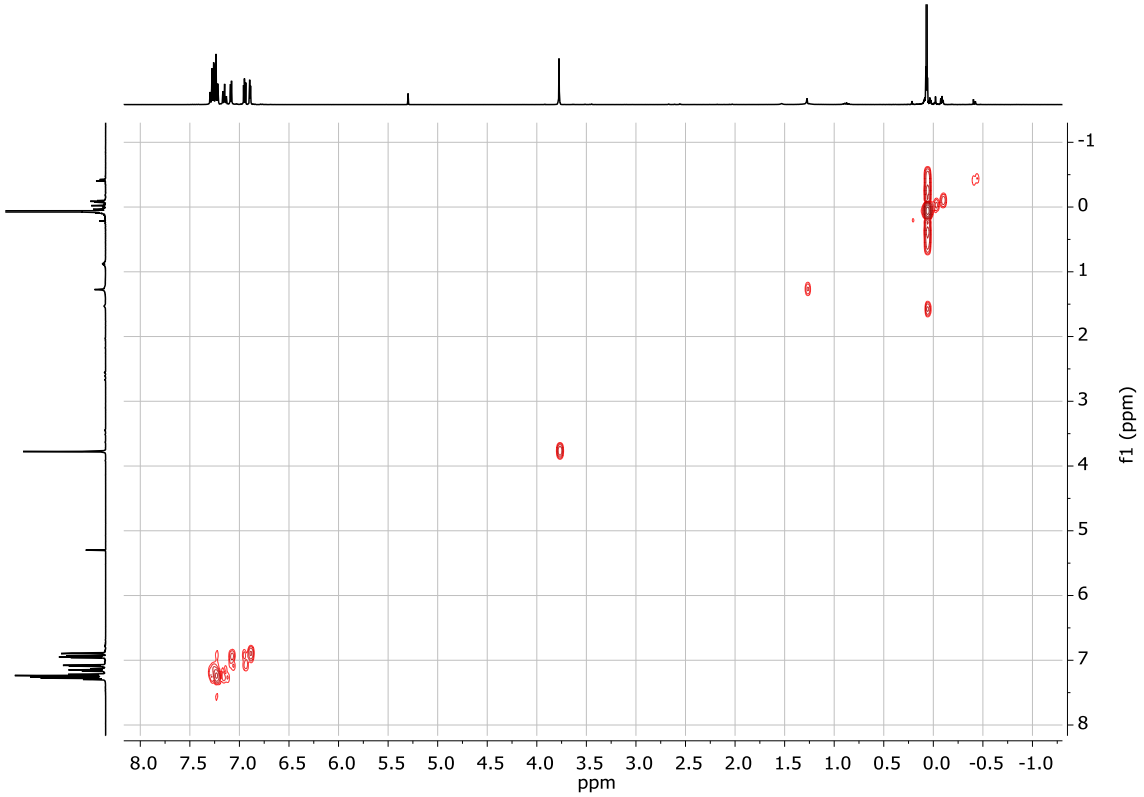
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

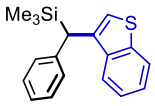


Gradient HSQCAD experiment ($CDCl_3$)

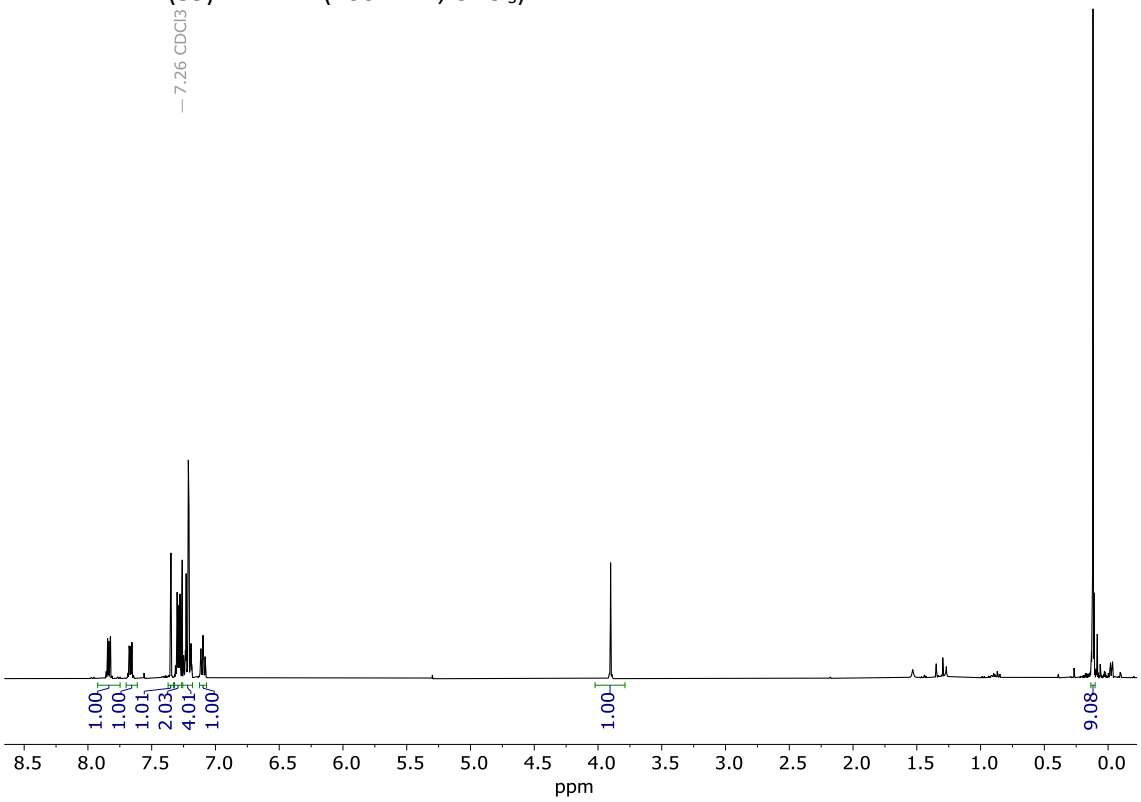


^1H COSY experiment ($CDCl_3$)

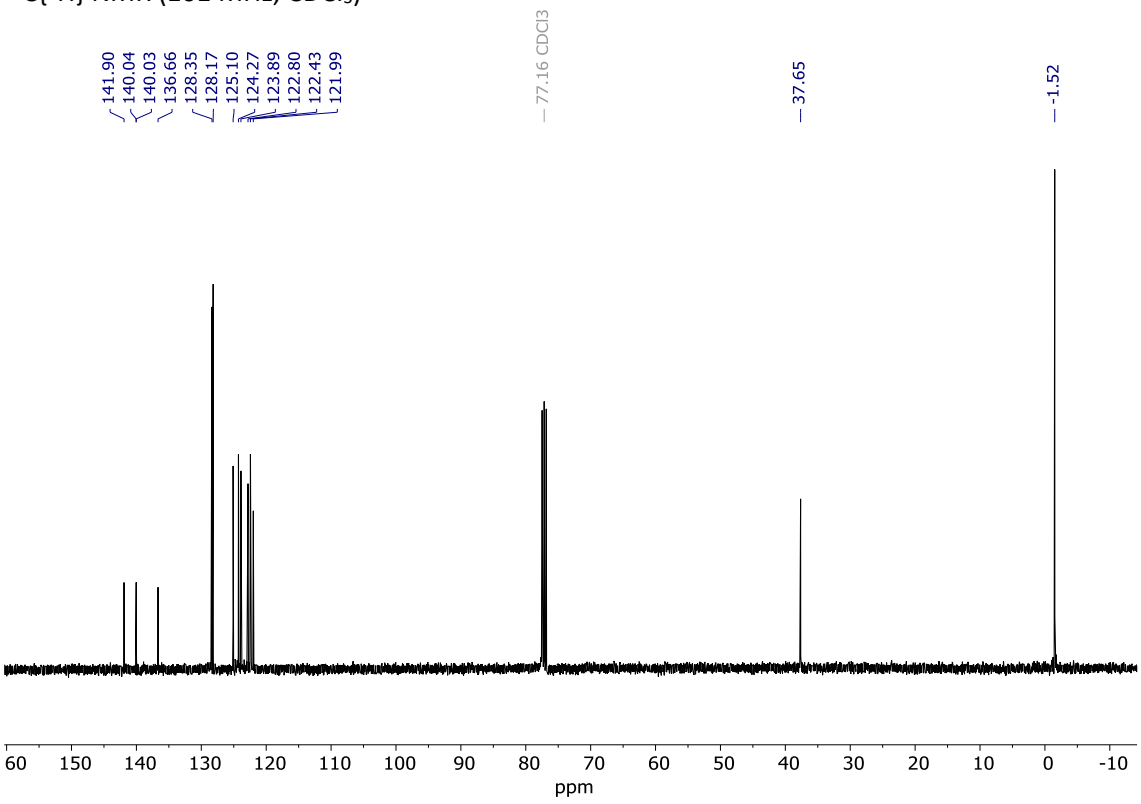




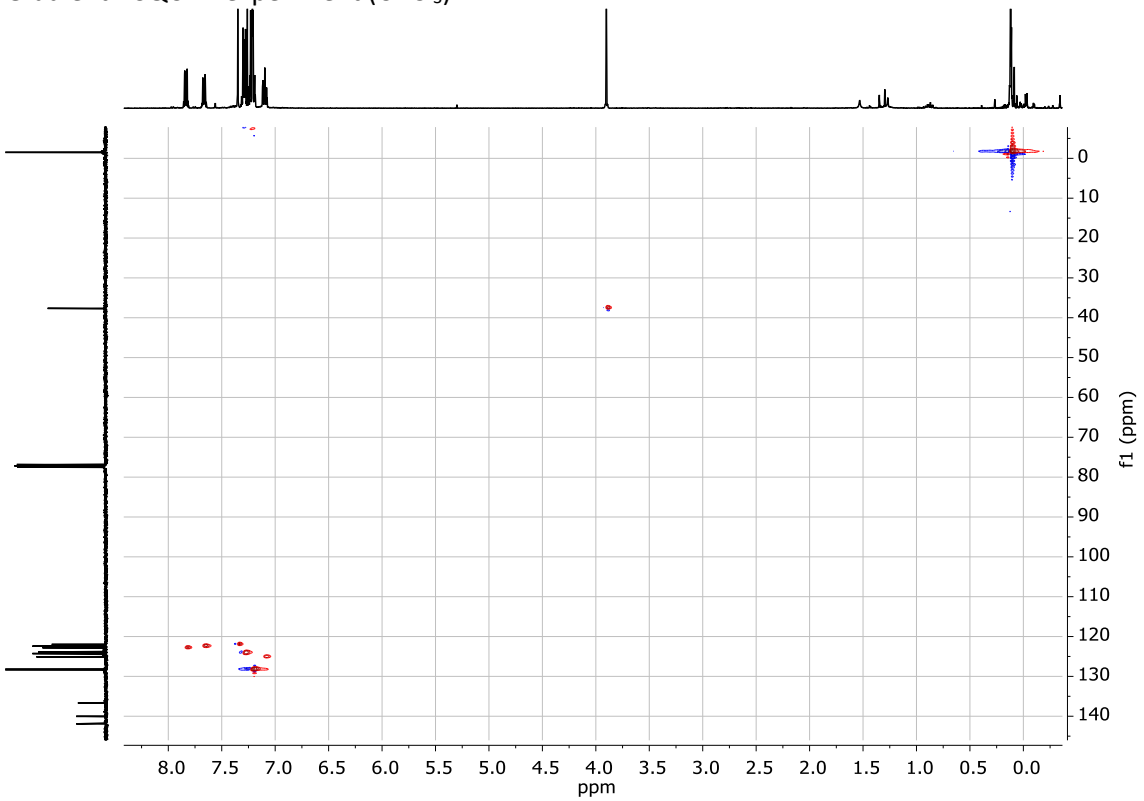
(**39**) ^{1}H NMR (400 MHz, $CDCl_3$)



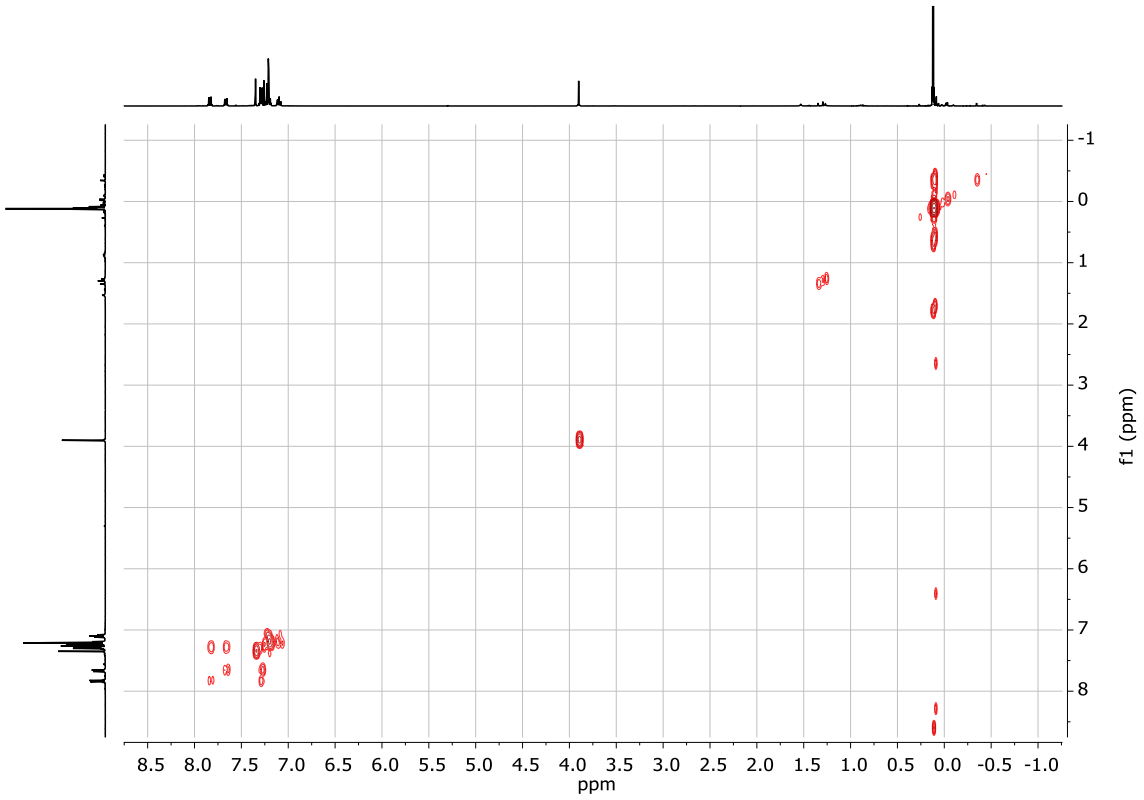
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

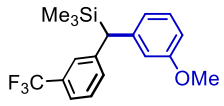


Gradient HSQCAD experiment ($CDCl_3$)

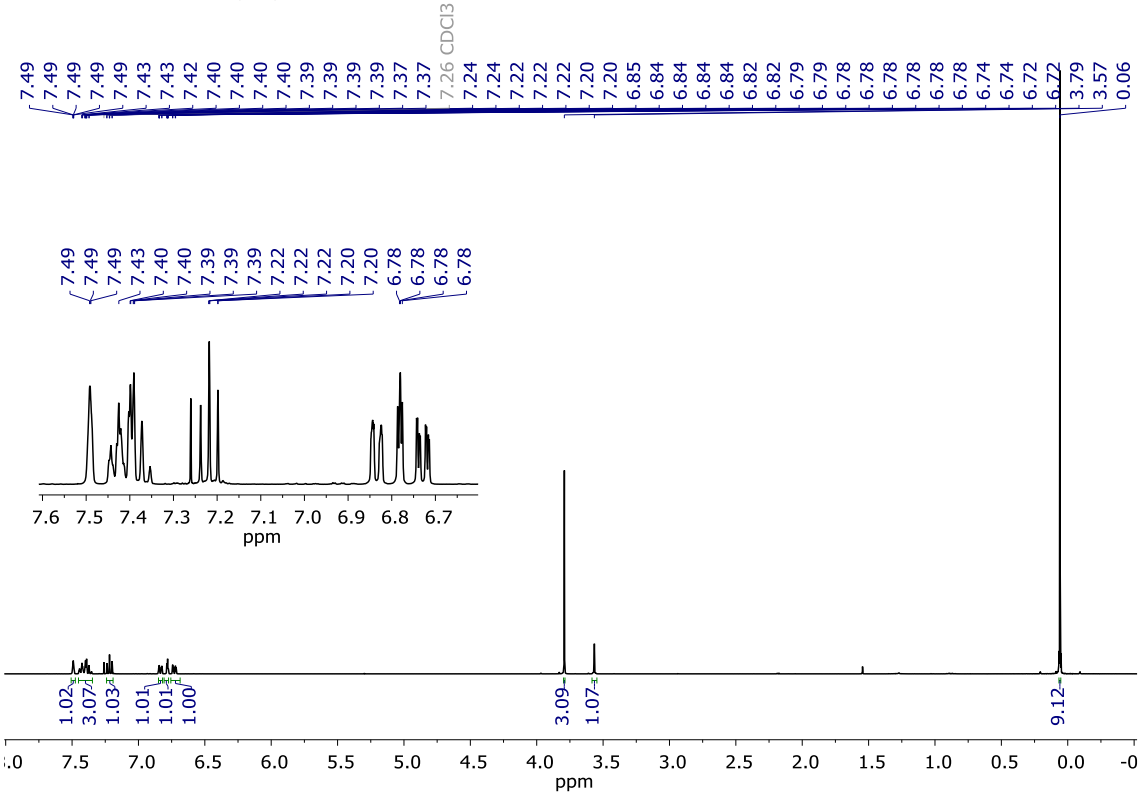


^1H COSY experiment ($CDCl_3$)

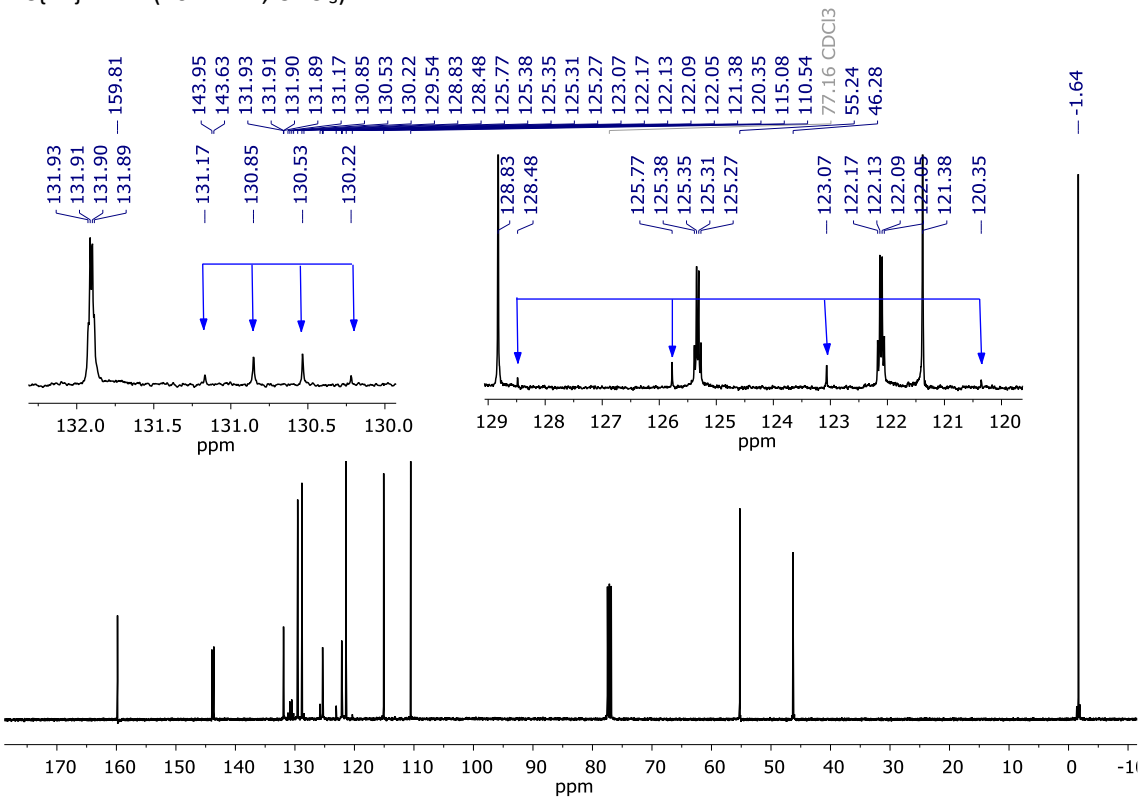




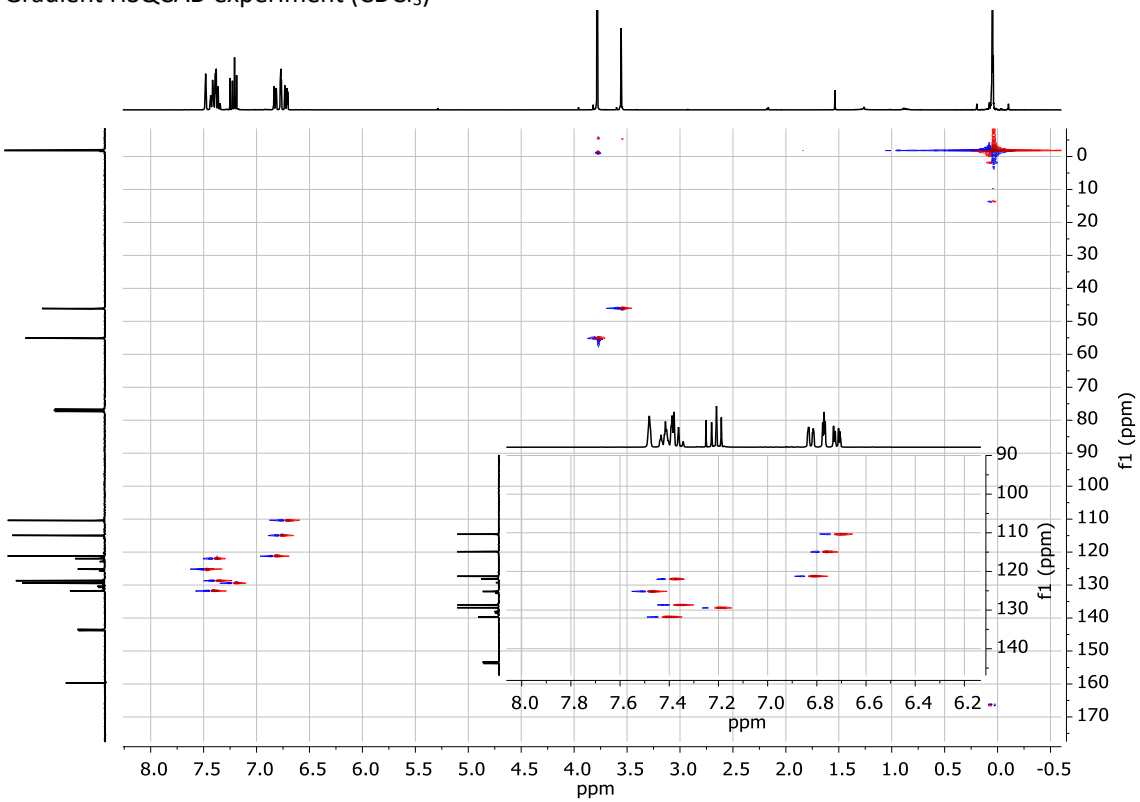
(**40**) ^{1}H NMR (400 MHz, $CDCl_3$)



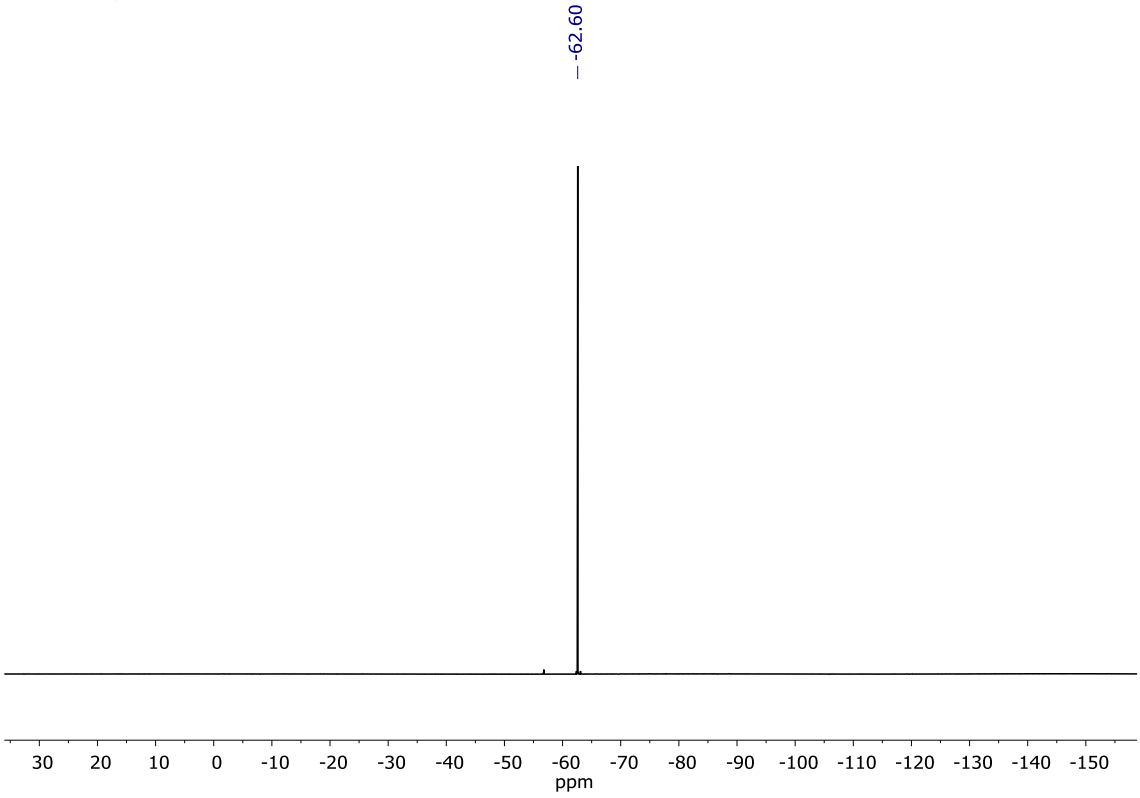
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

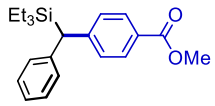


Gradient HSQCAD experiment ($CDCl_3$)

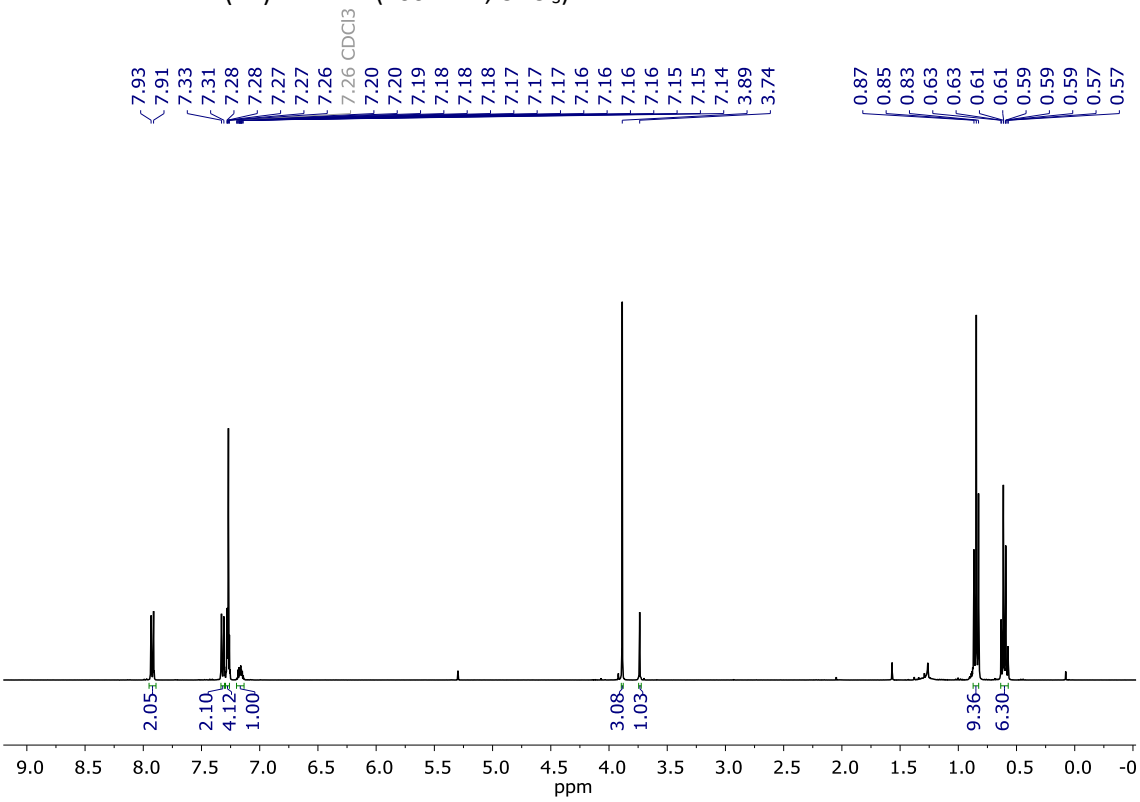


^{19}F NMR (376 MHz, $CDCl_3$)

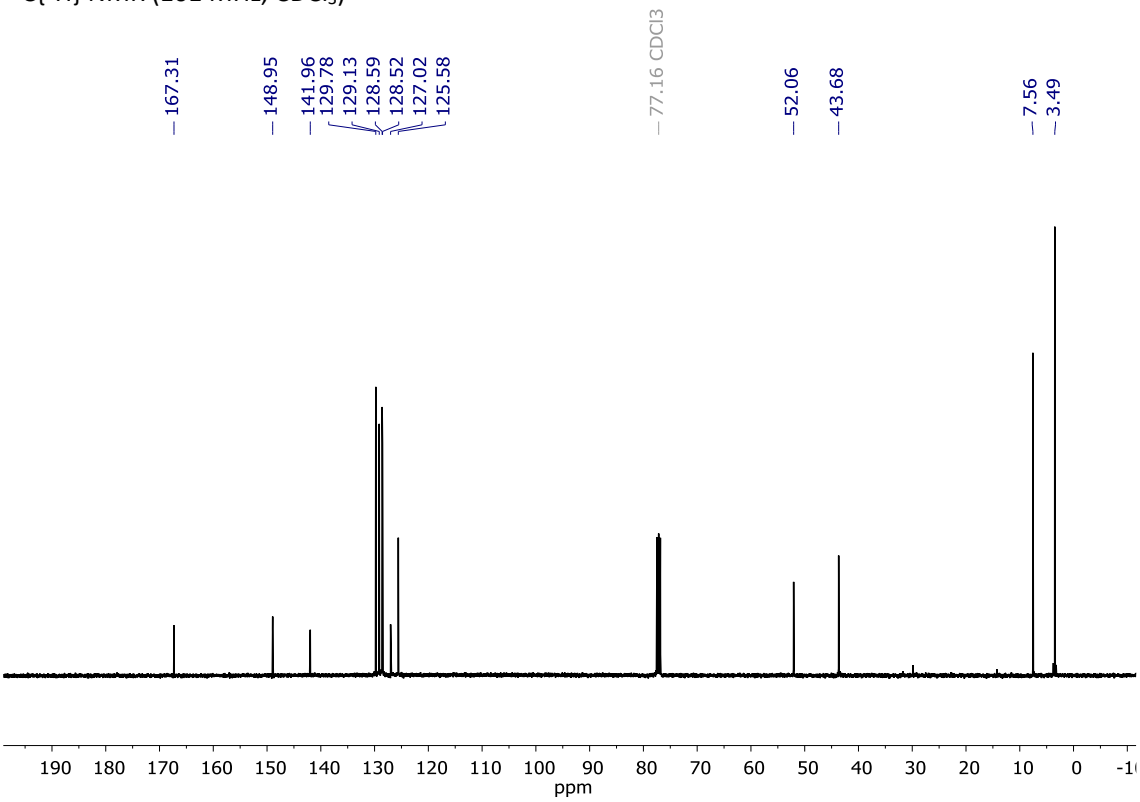




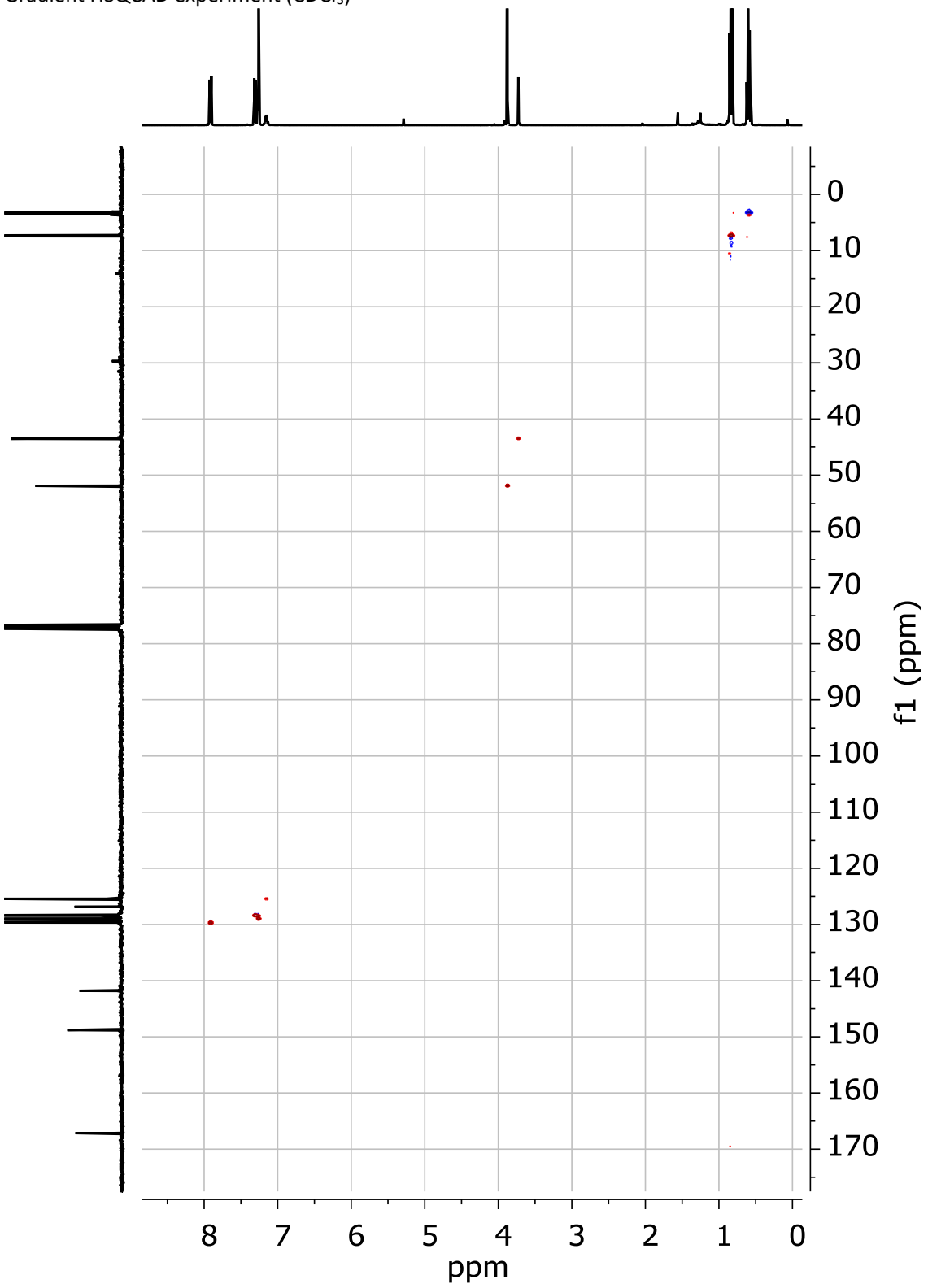
(**42**) ^{1}H NMR (400 MHz, $CDCl_3$)

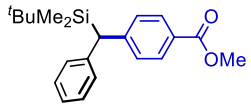


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

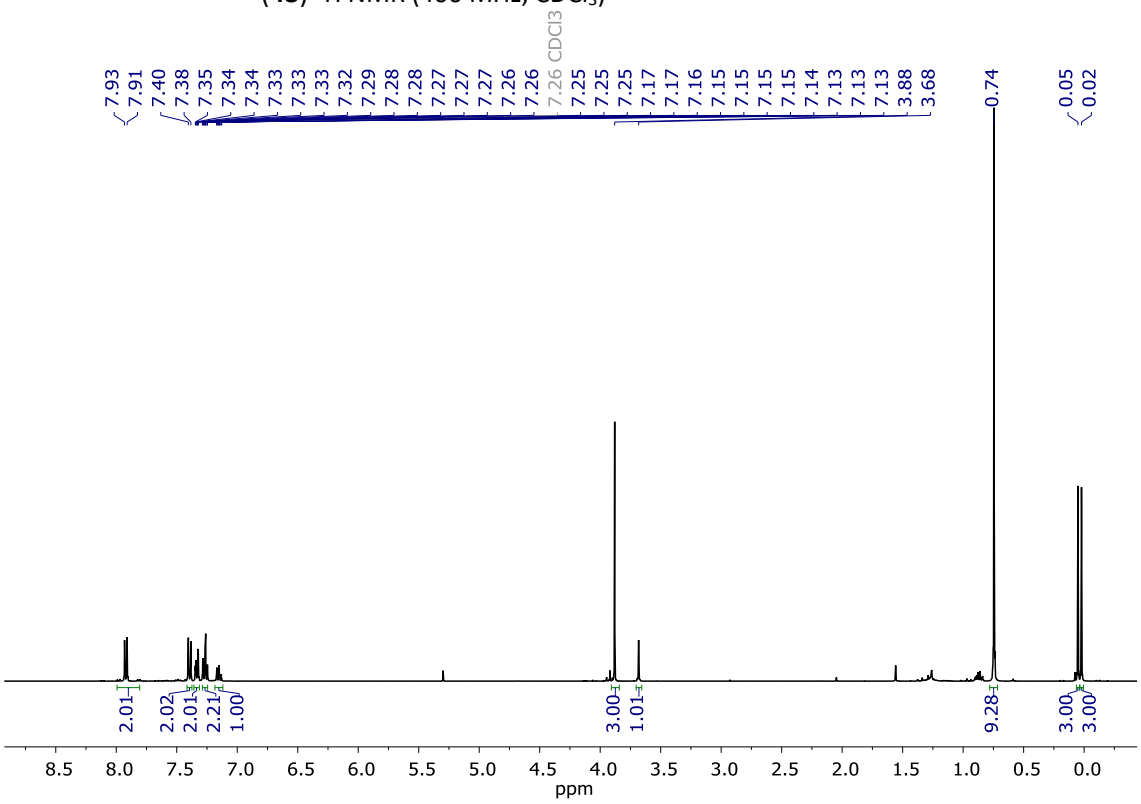


Gradient HSQCAD experiment ($CDCl_3$)

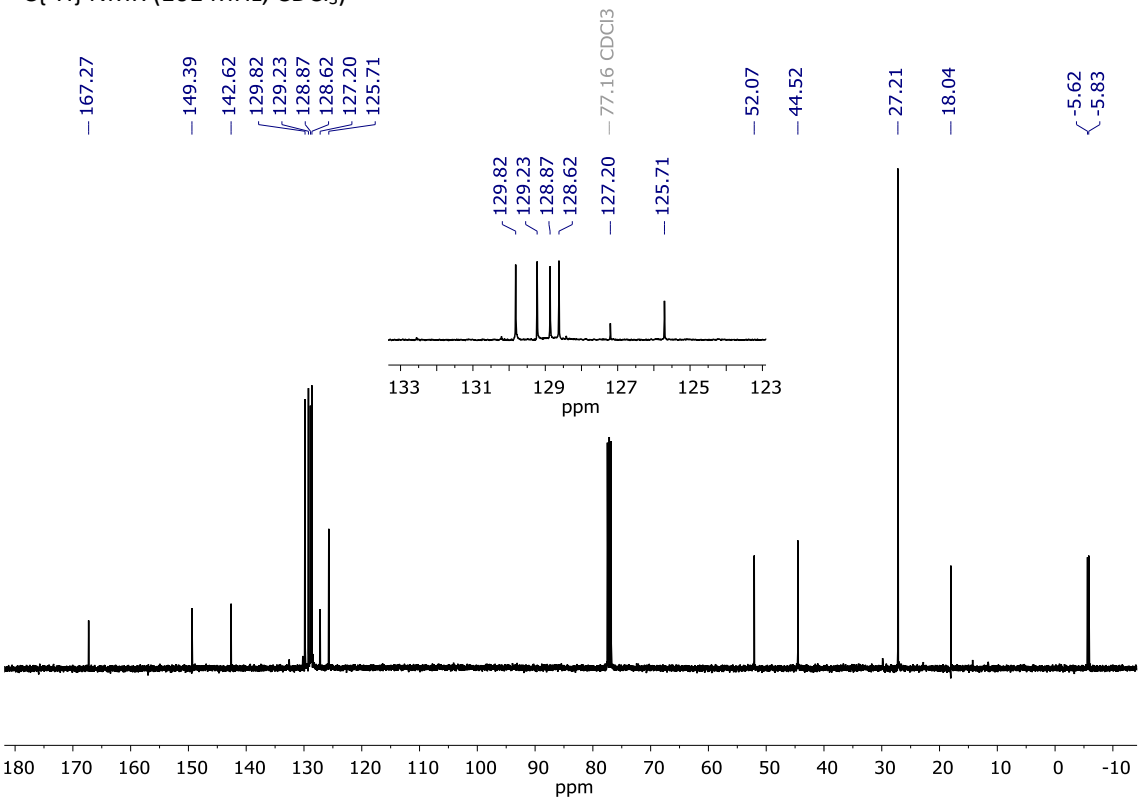




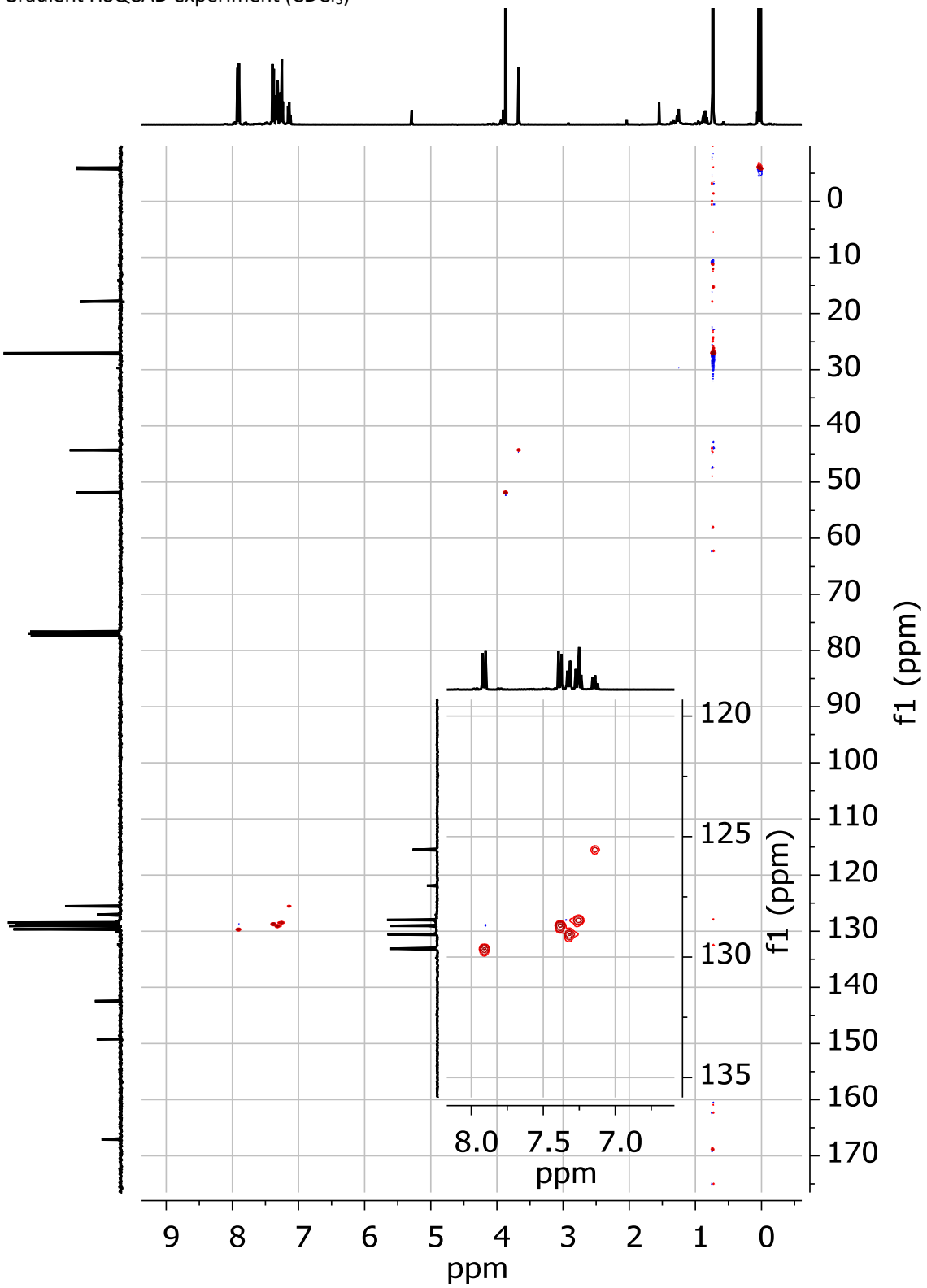
(**43**) ^{1}H NMR (400 MHz, $CDCl_3$)

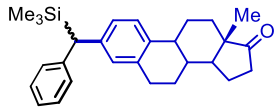


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

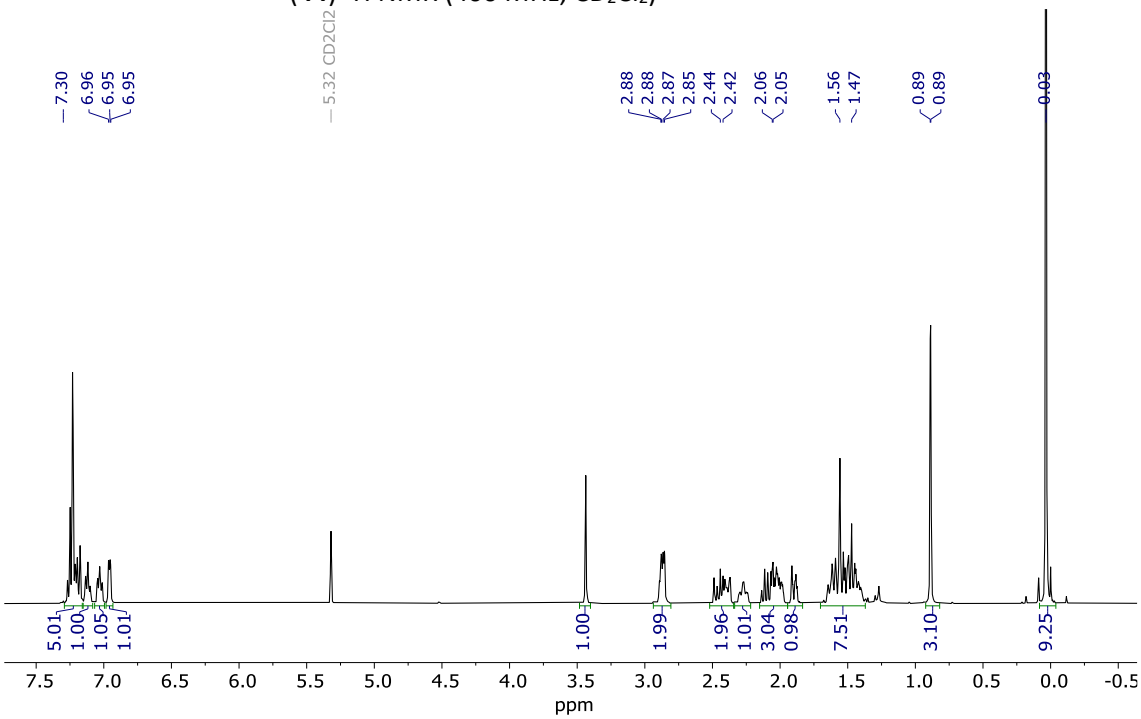


Gradient HSQCAD experiment ($CDCl_3$)

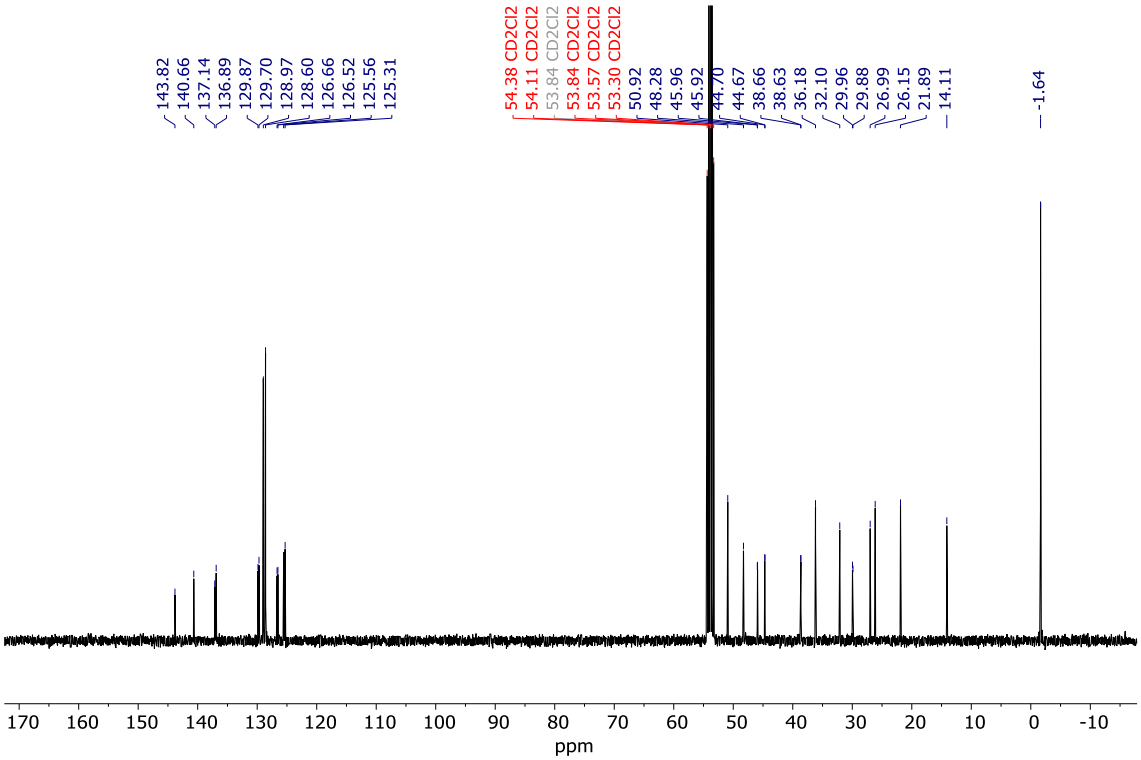


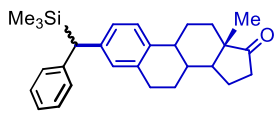


(**44**) ^{1}H NMR (400 MHz, CD_2Cl_2)

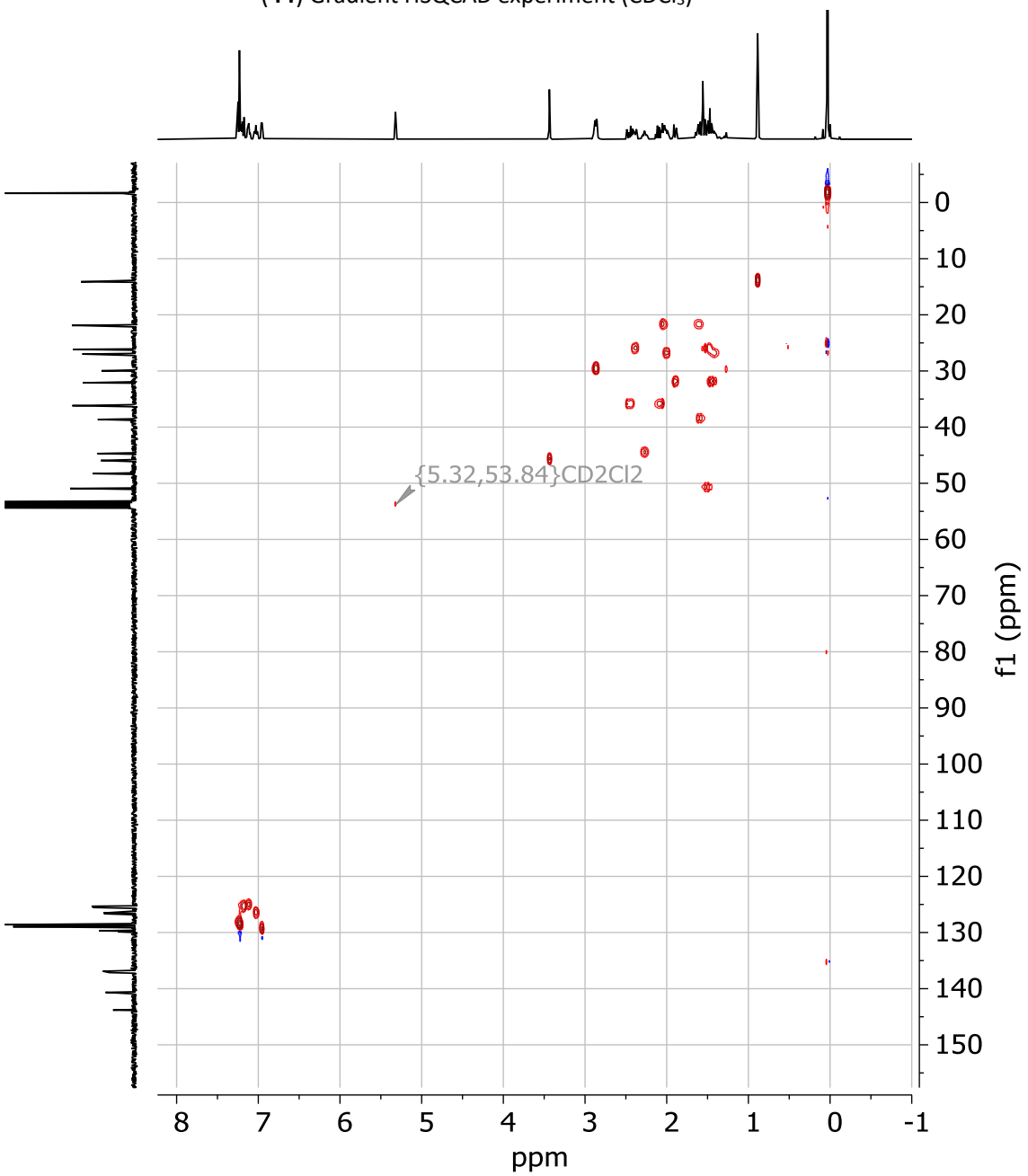


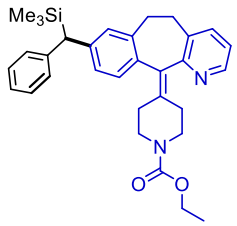
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)



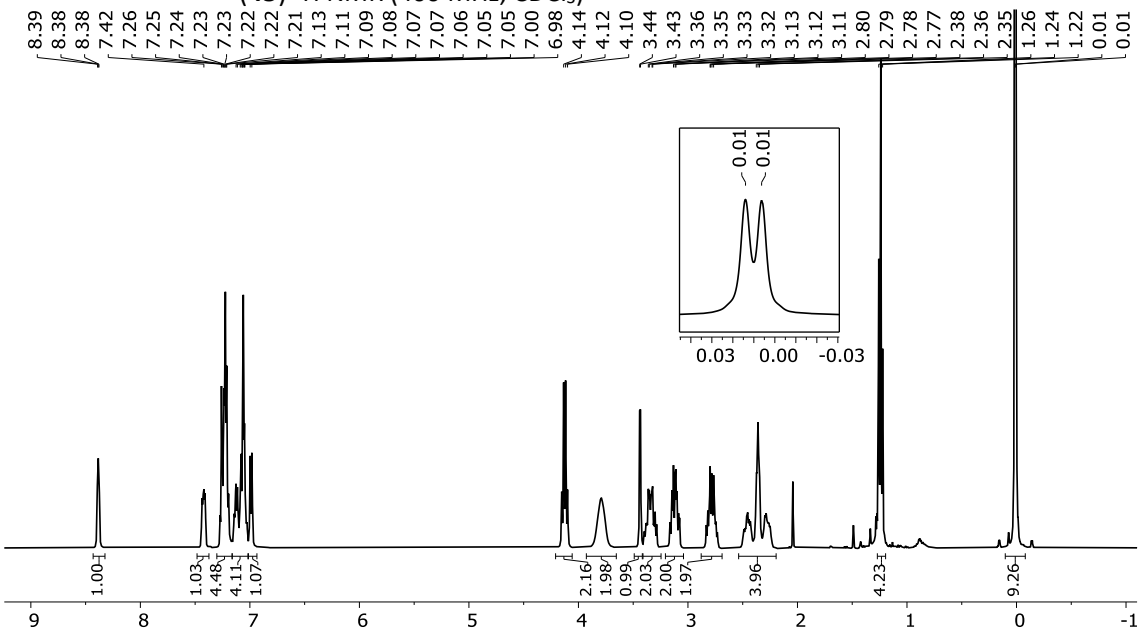


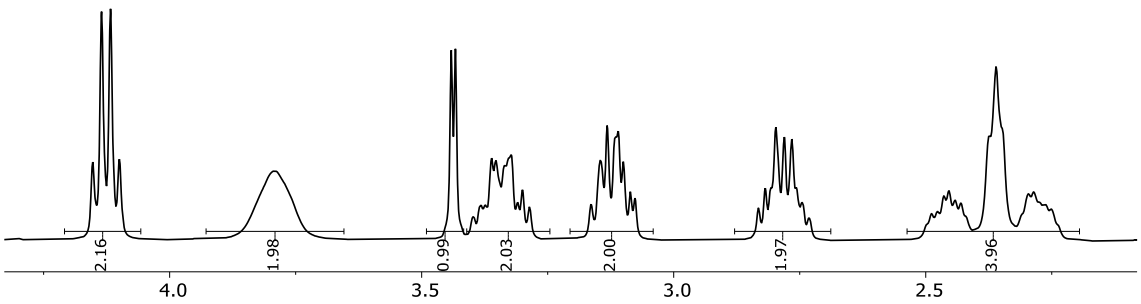
(**44**) Gradient HSQCAD experiment ($CDCl_3$)



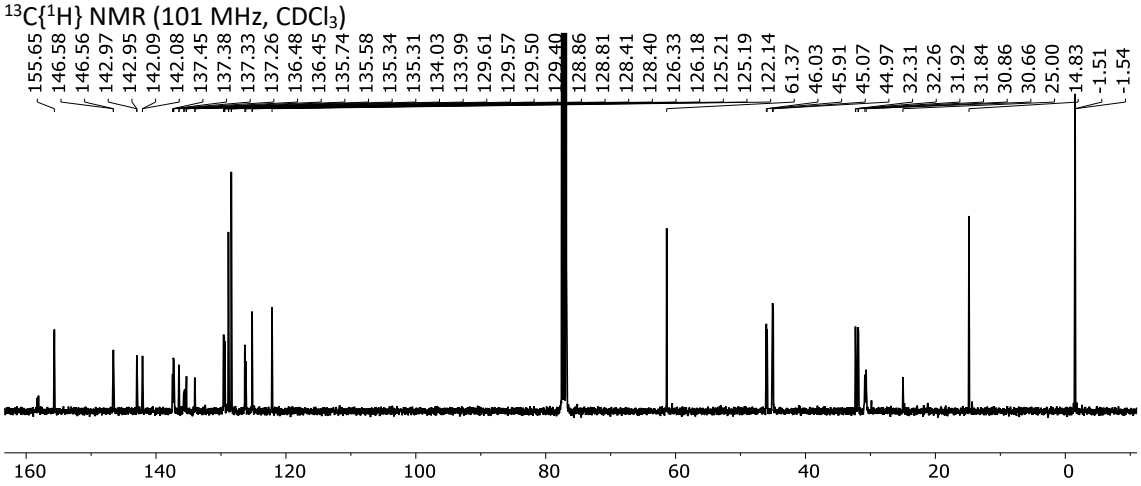


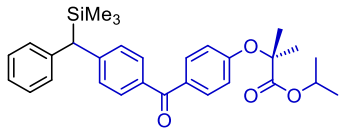
(**45**) ^{1}H NMR (400 MHz, $CDCl_3$)



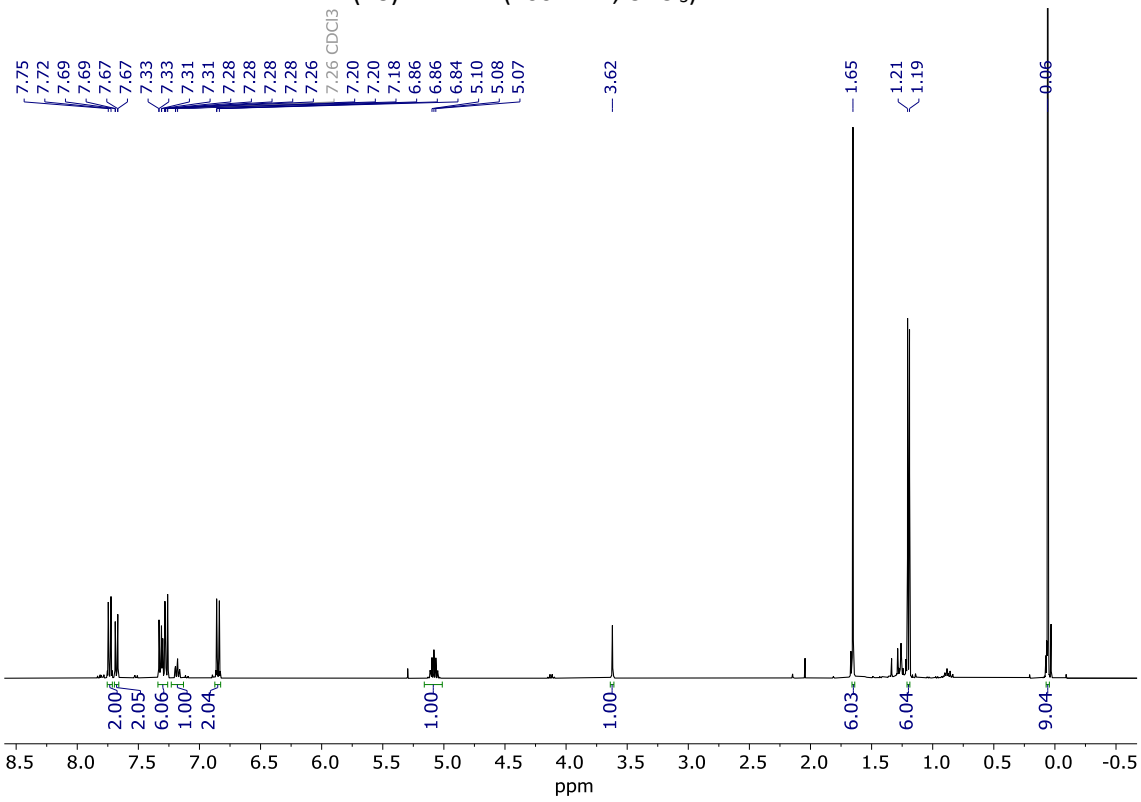


$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

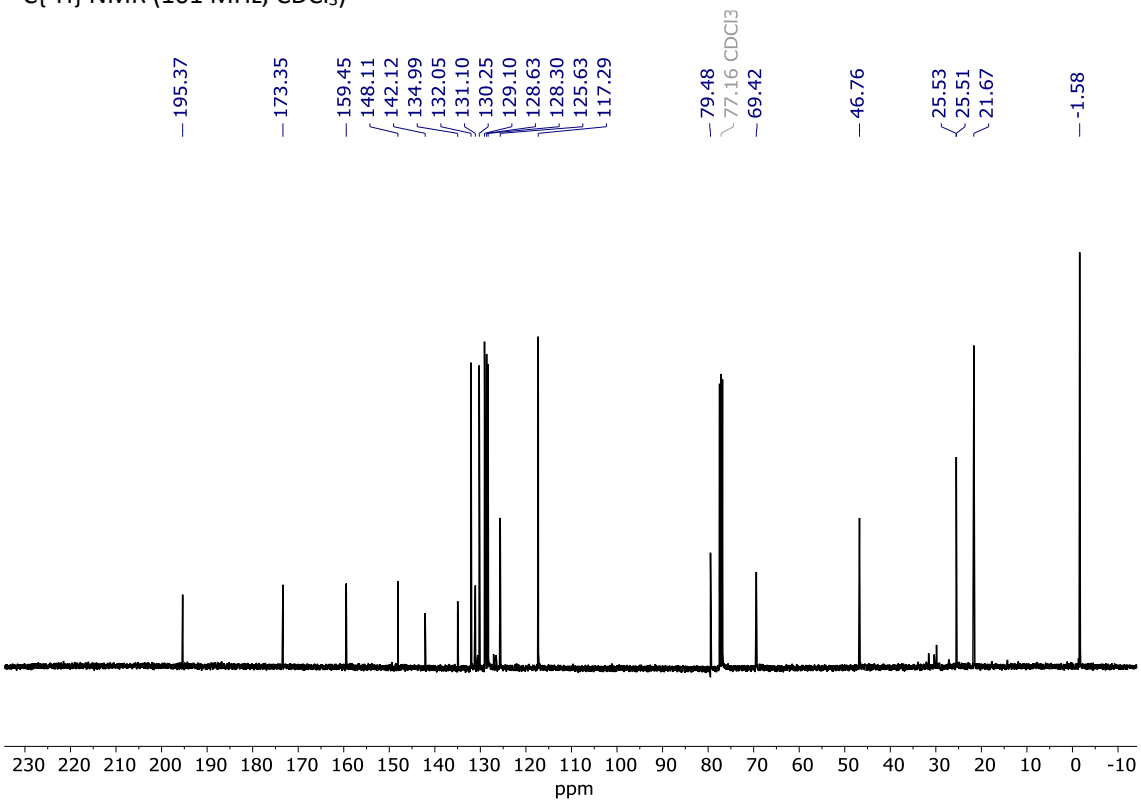




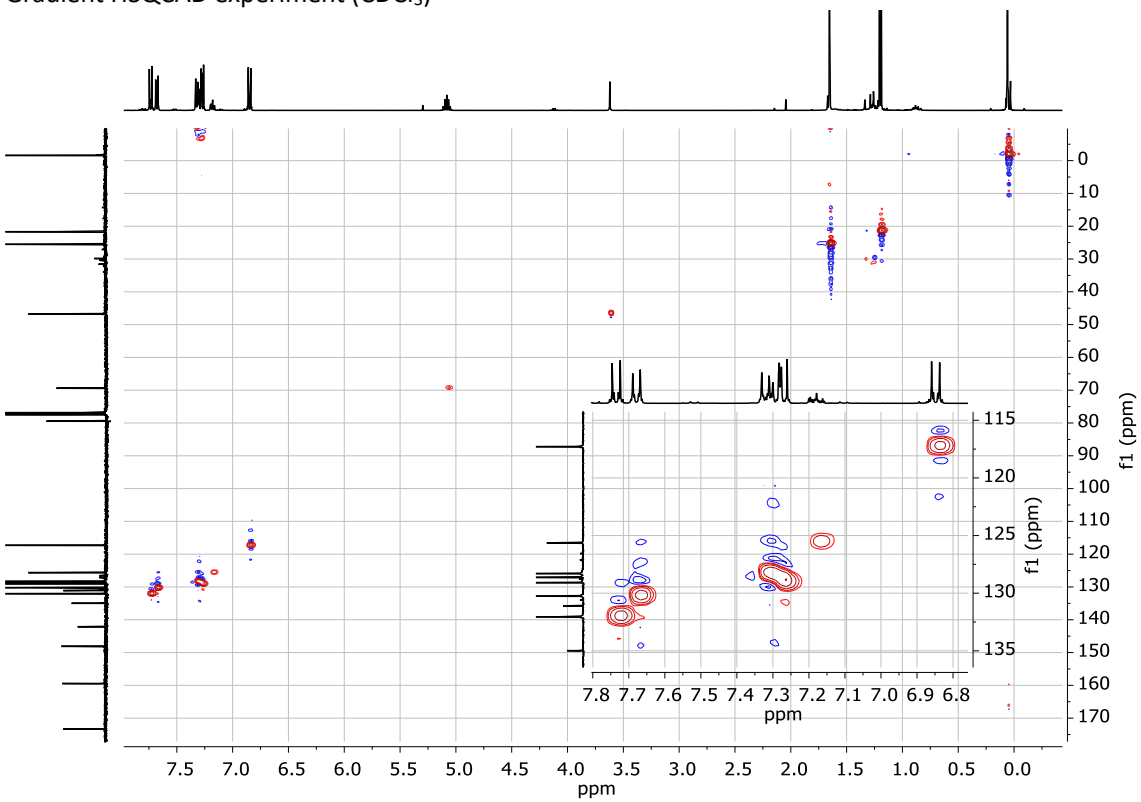
(**46**) ^{1}H NMR (400 MHz, $CDCl_3$)



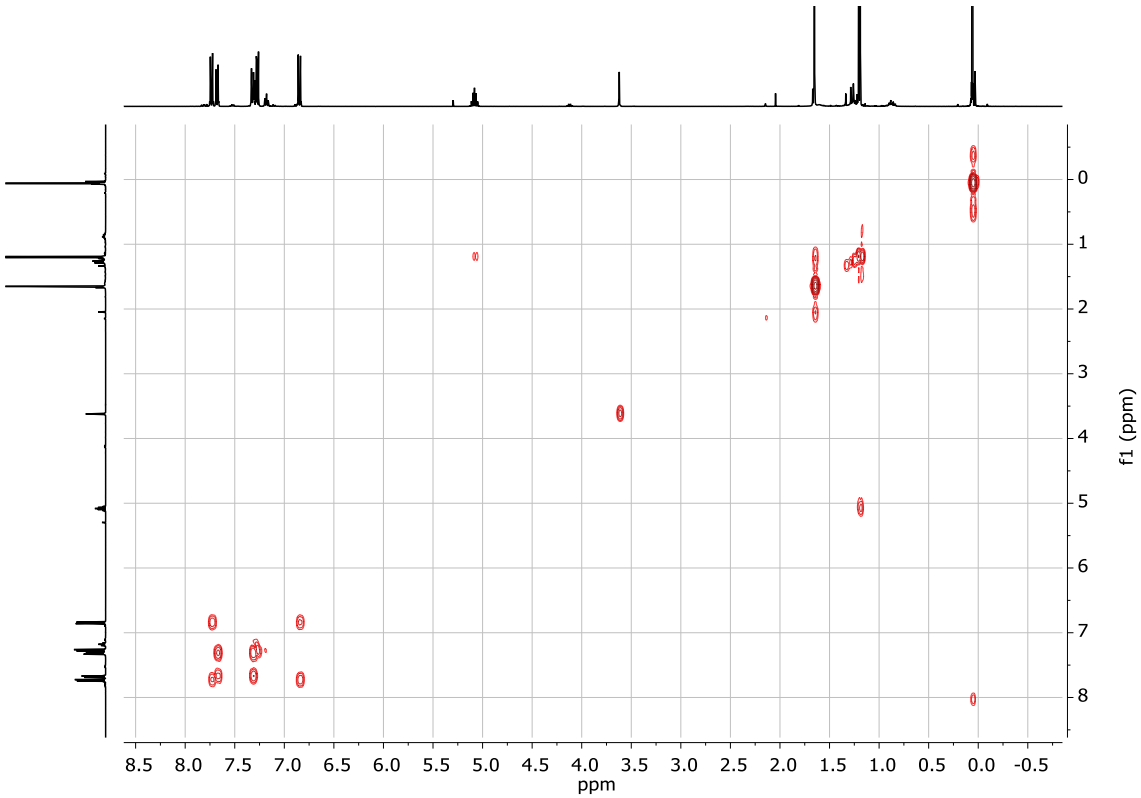
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

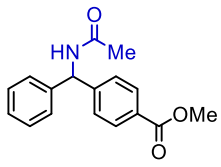


Gradient HSQCAD experiment ($CDCl_3$)

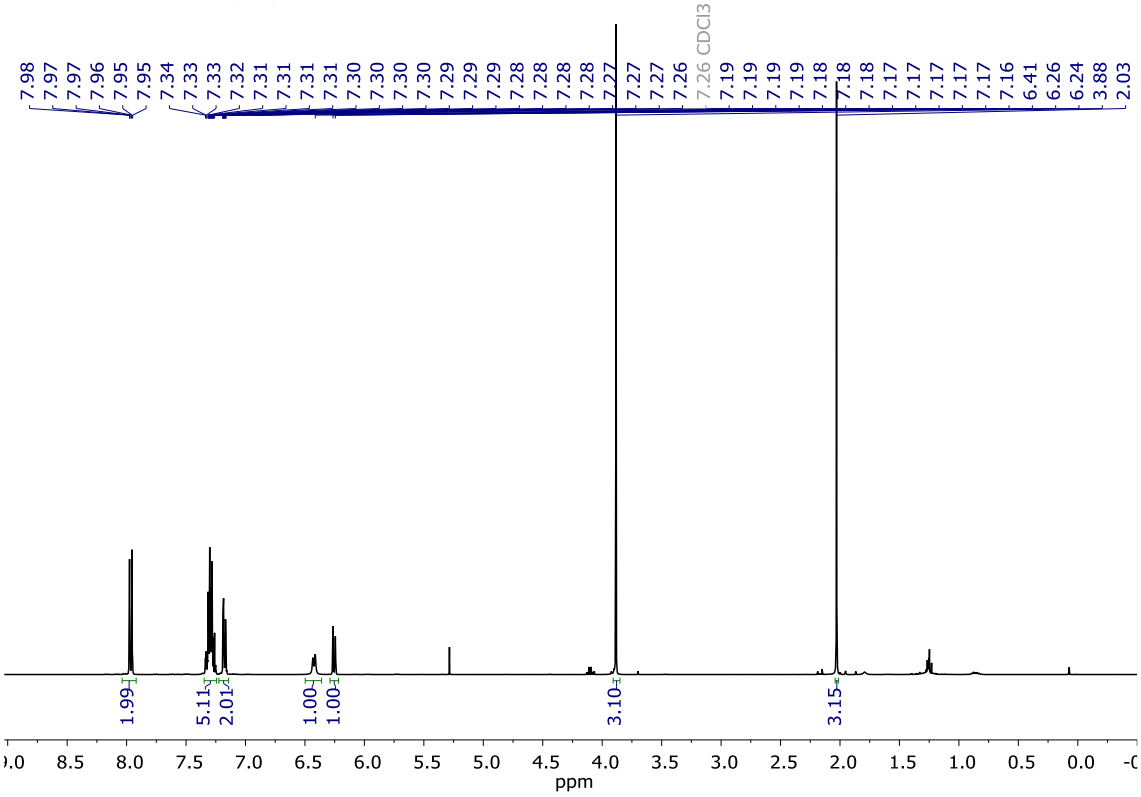


^1H COSY experiment ($CDCl_3$)

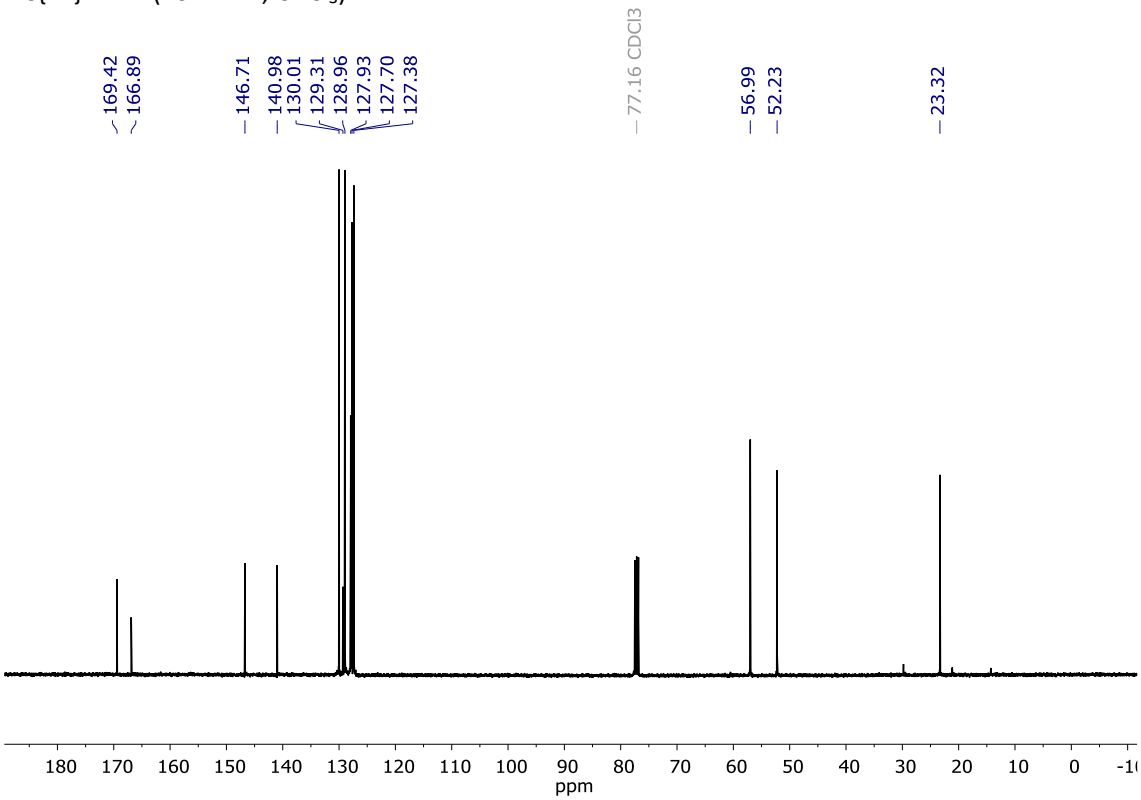




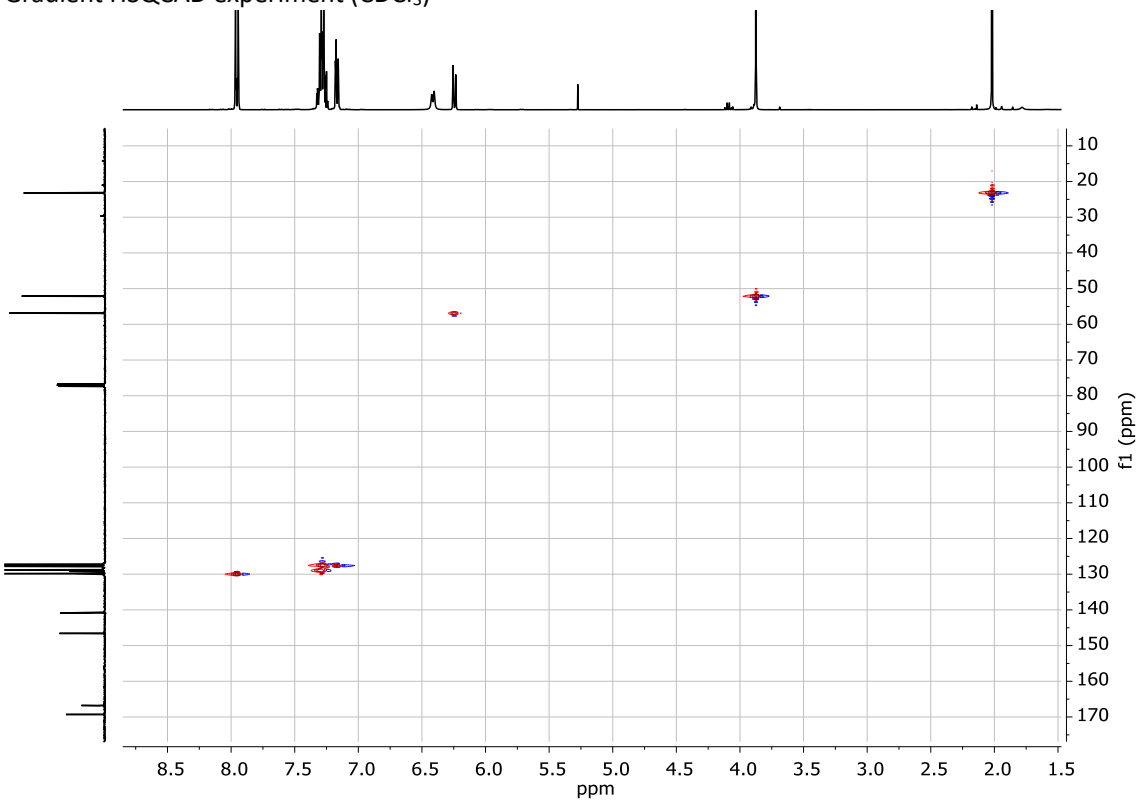
(**47**) ^{1}H NMR (400 MHz, $CDCl_3$)



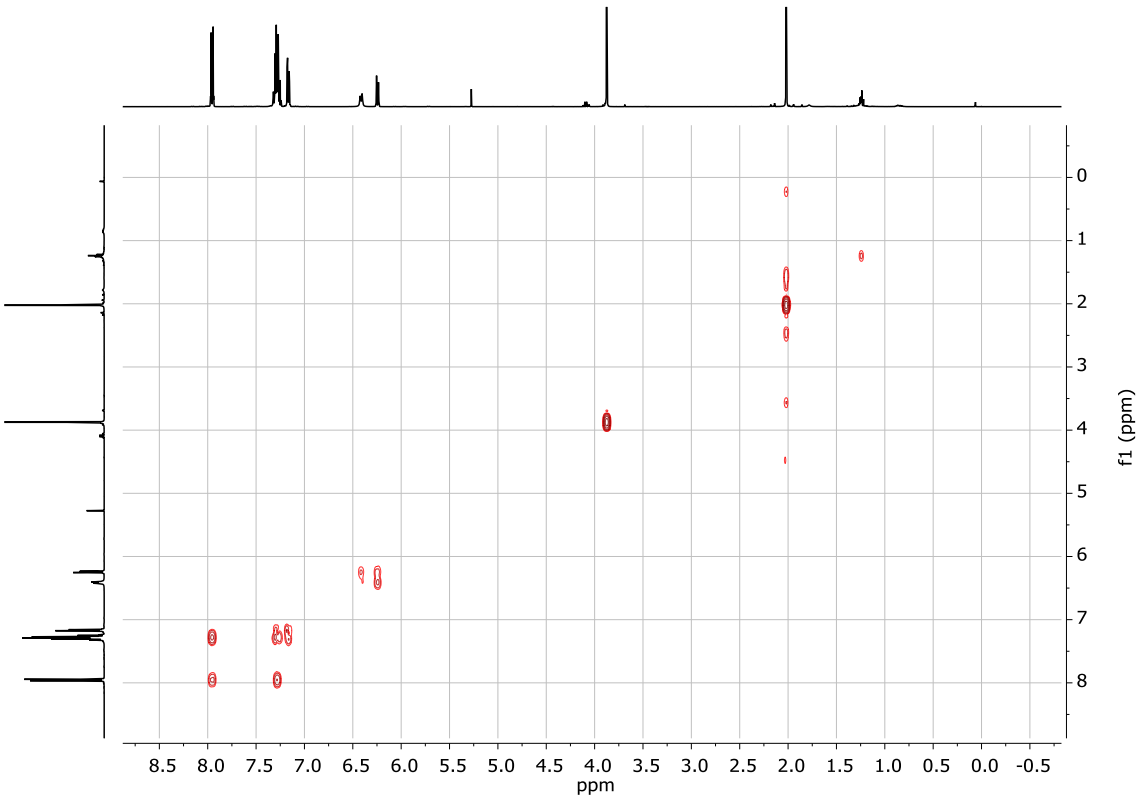
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

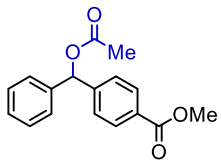


Gradient HSQCAD experiment ($CDCl_3$)

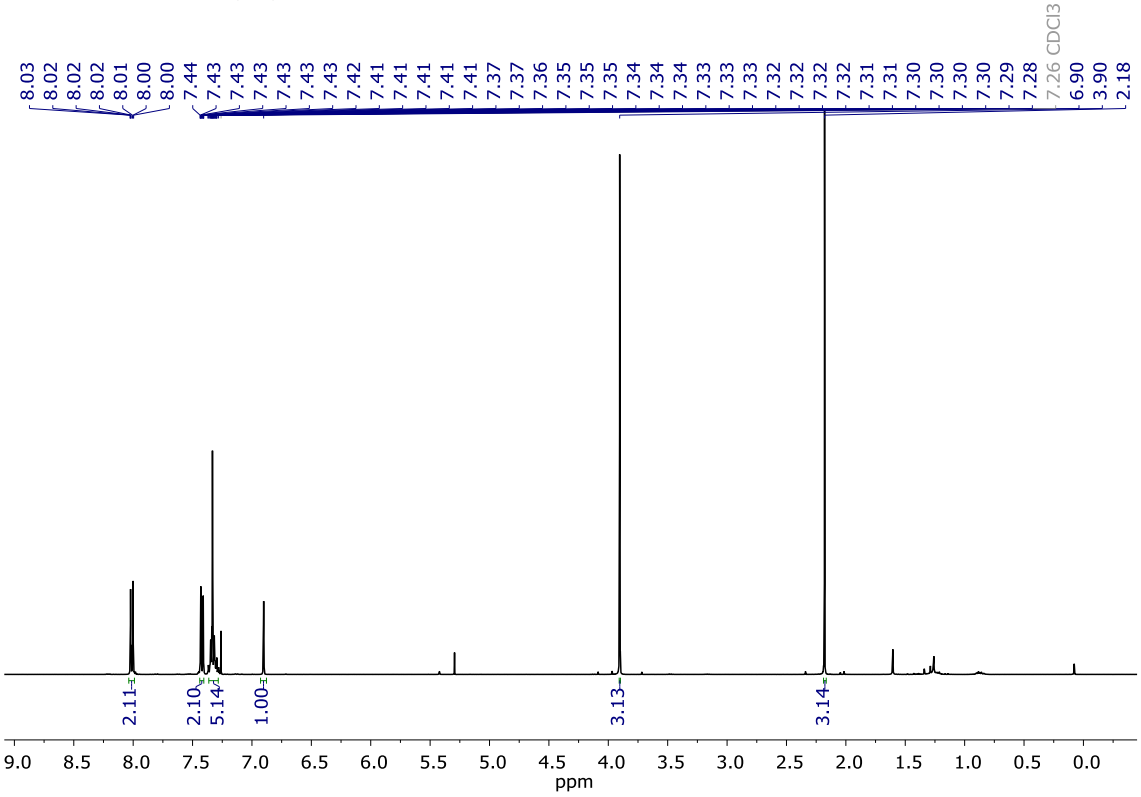


^1H COSY experiment ($CDCl_3$)

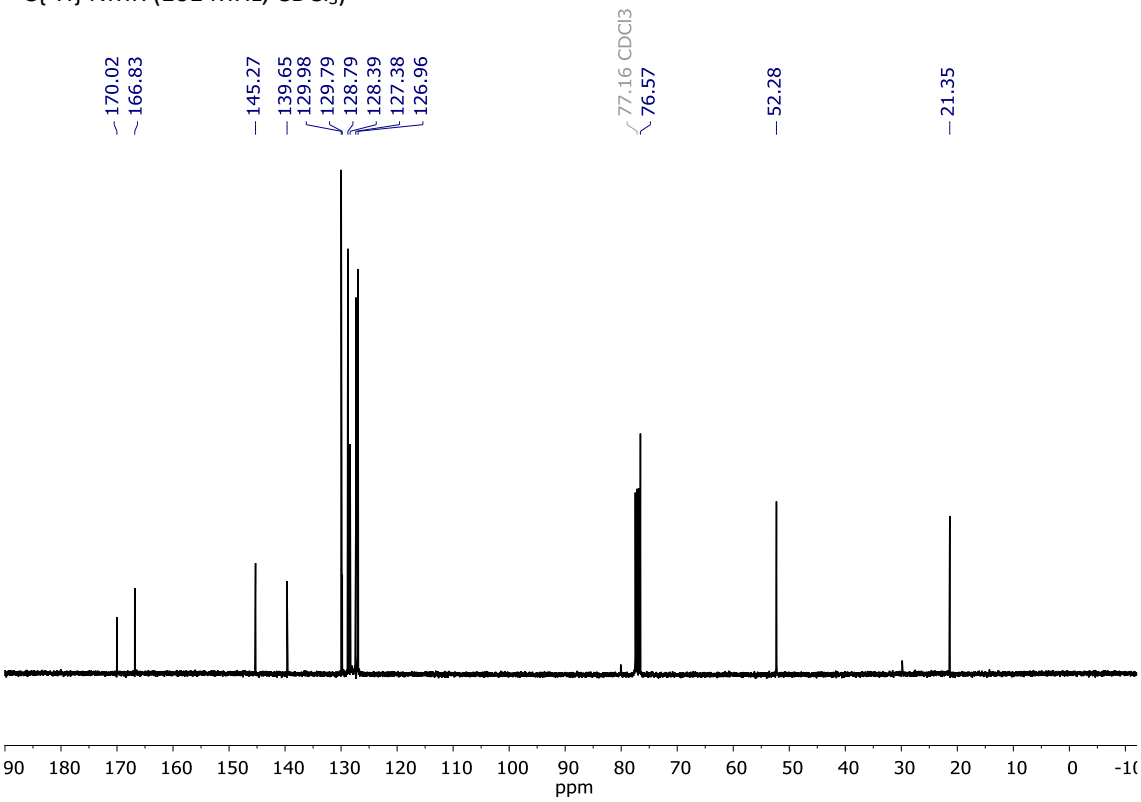




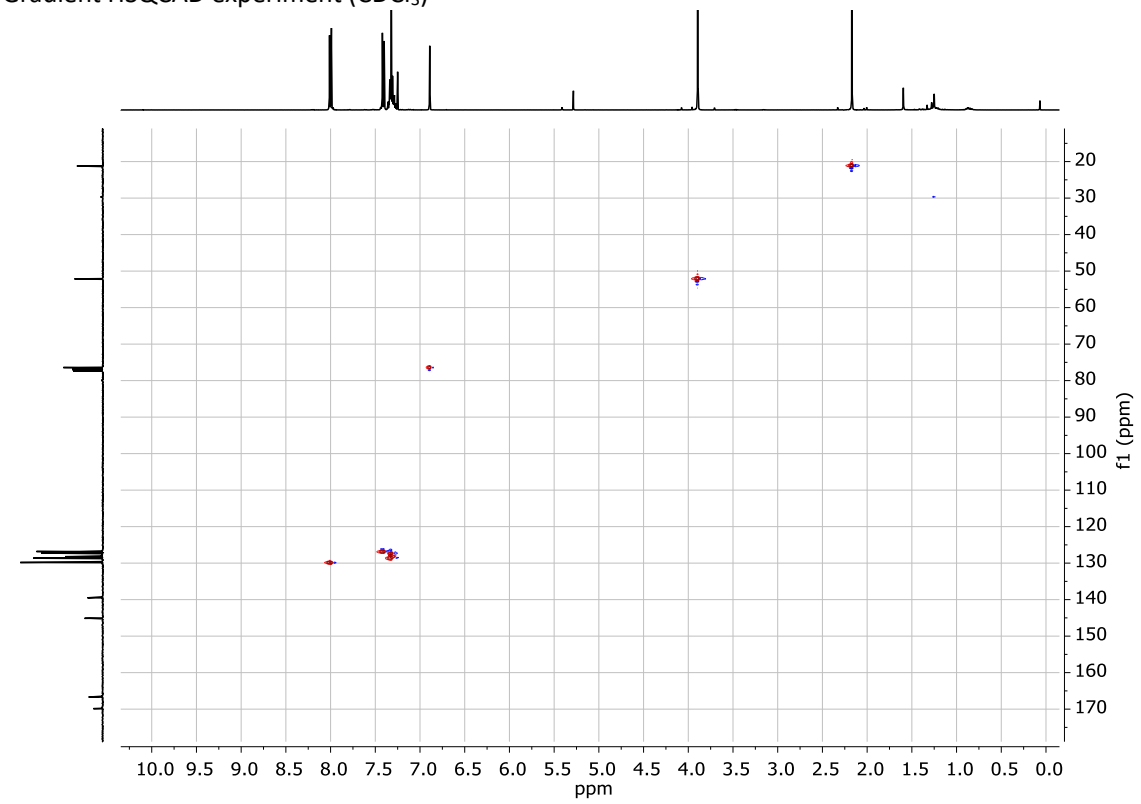
(**48**) ^{1}H NMR (400 MHz, $CDCl_3$)



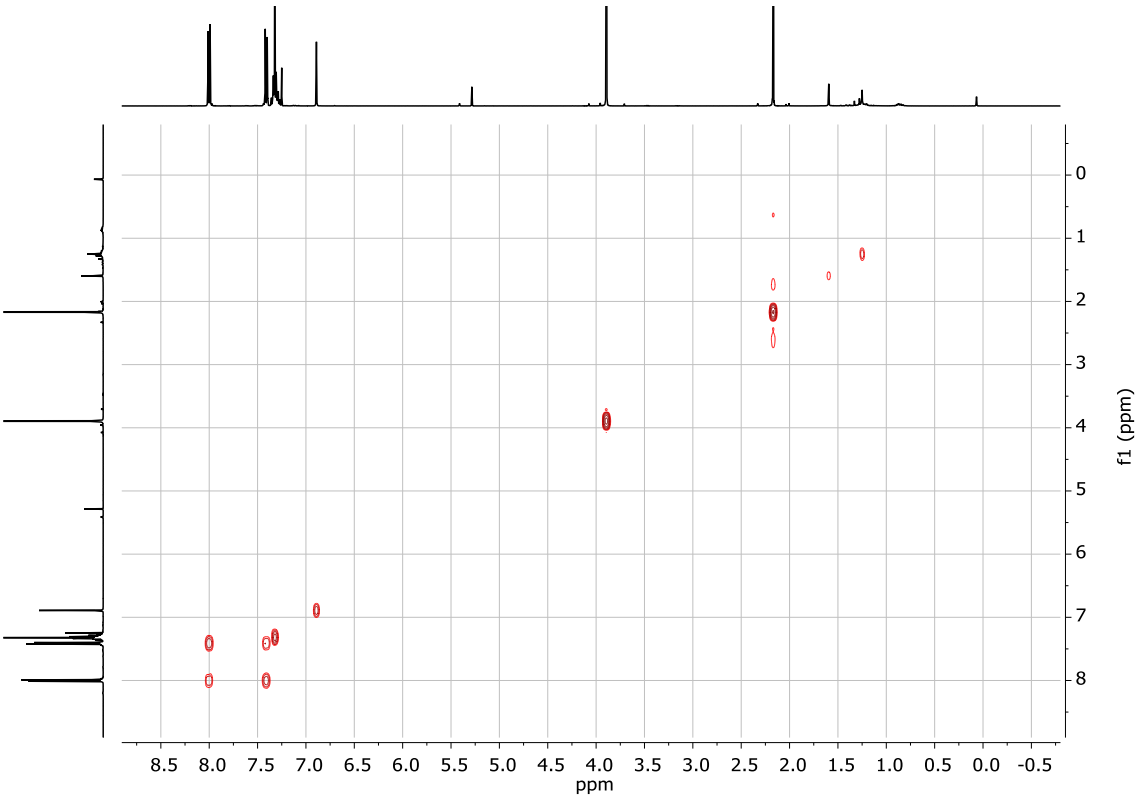
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

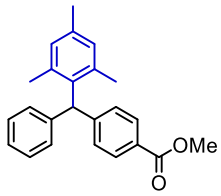


Gradient HSQCAD experiment ($CDCl_3$)

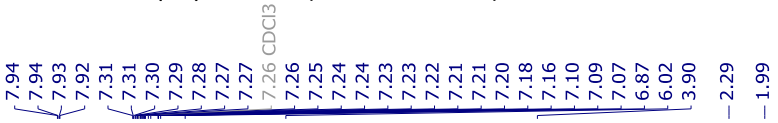


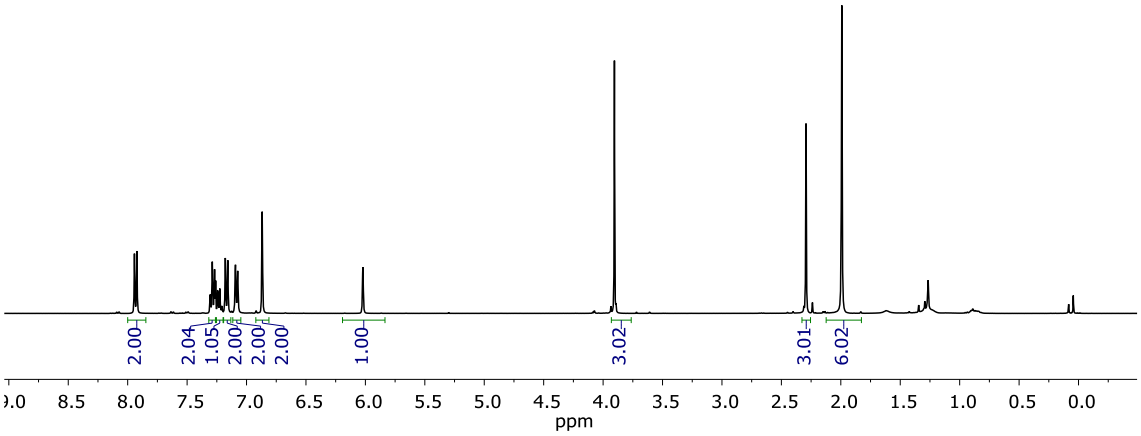
^1H COSY experiment ($CDCl_3$)



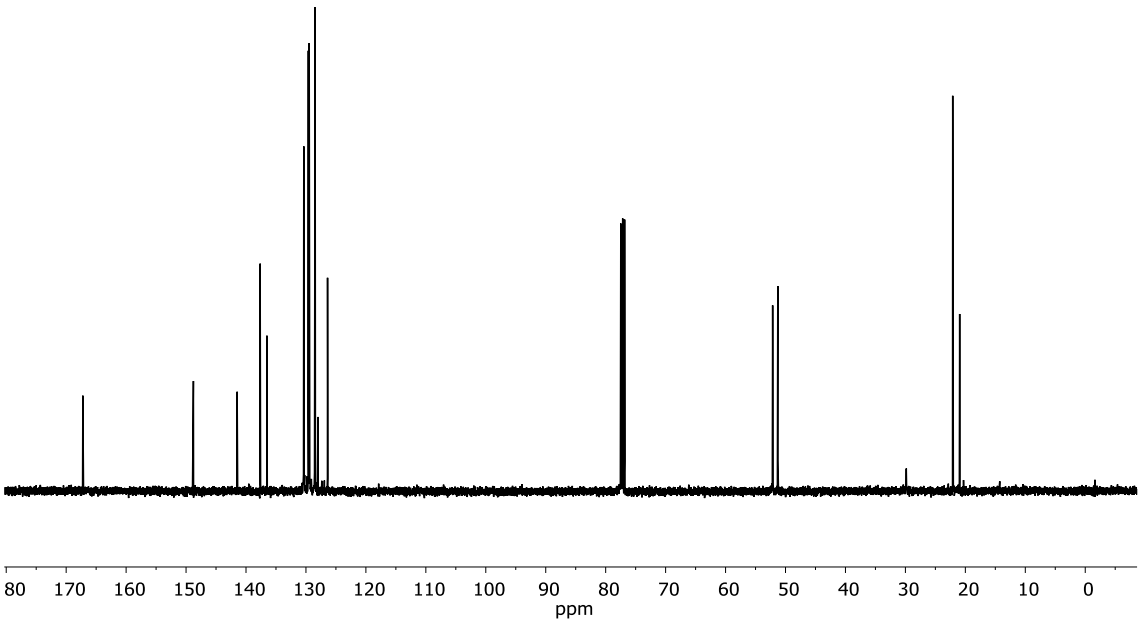


(**49**) ^{1}H NMR (400 MHz, $CDCl_3$)

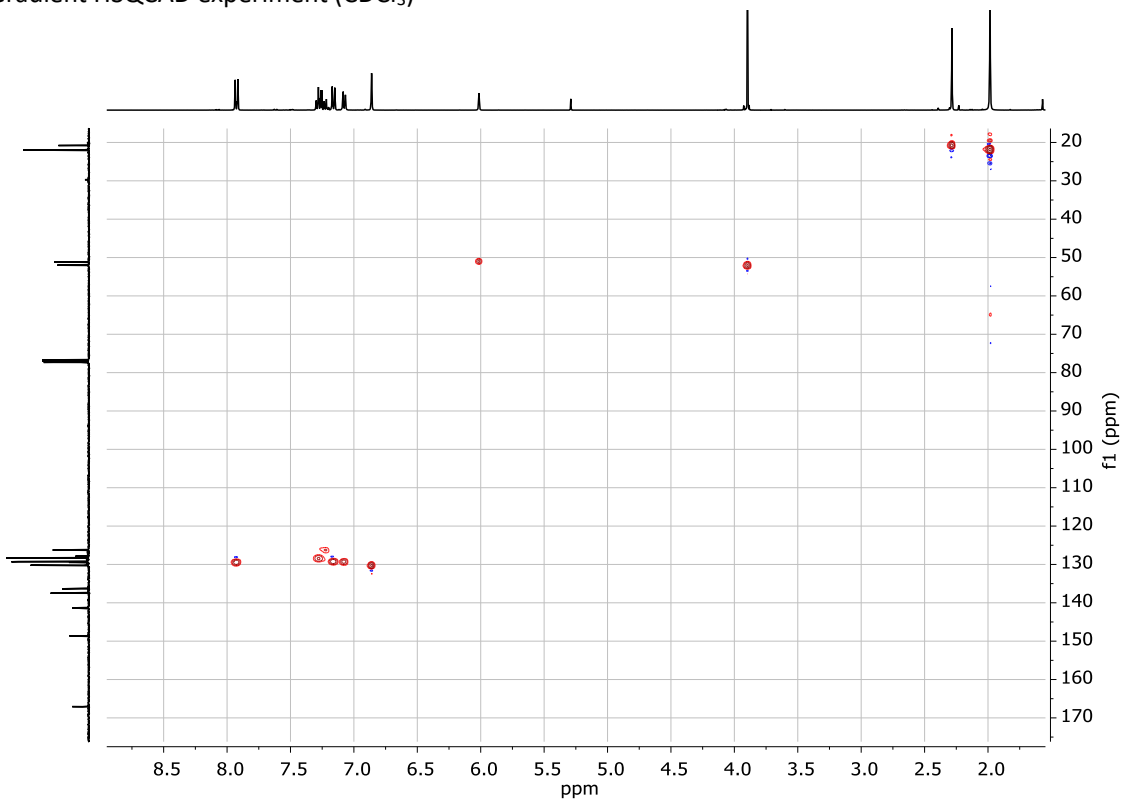




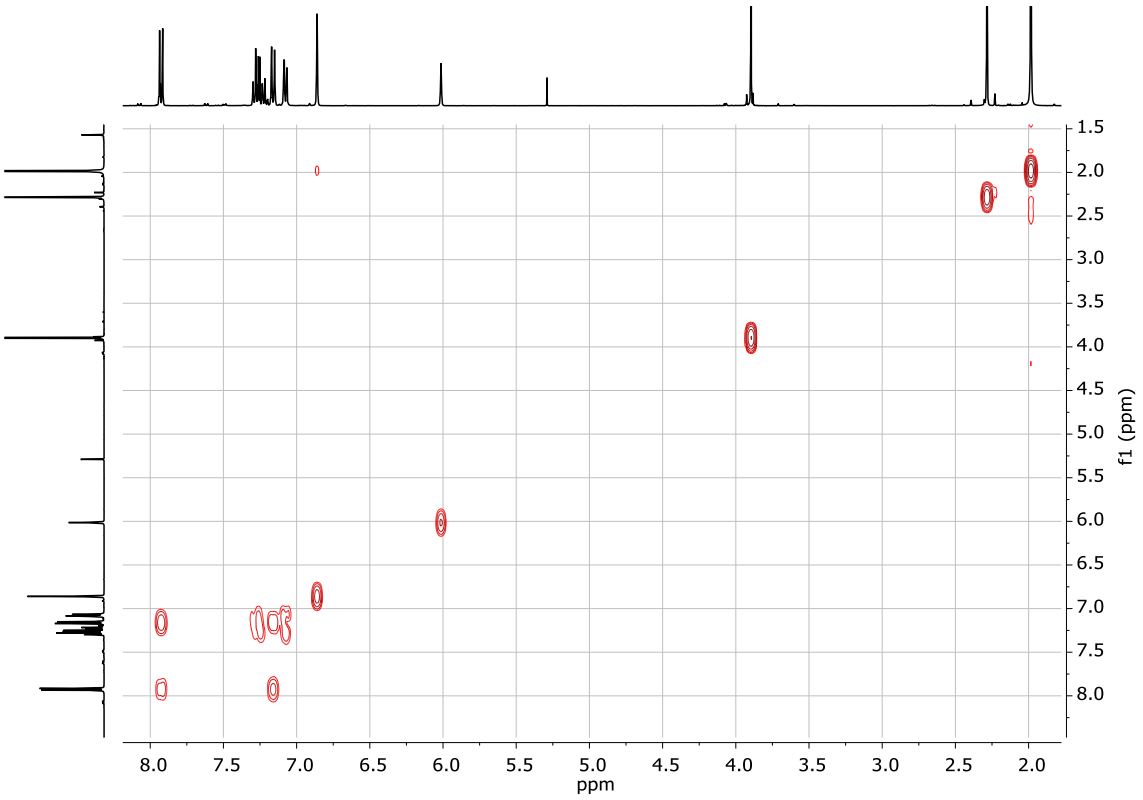
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

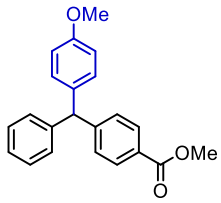


Gradient HSQCAD experiment ($CDCl_3$)

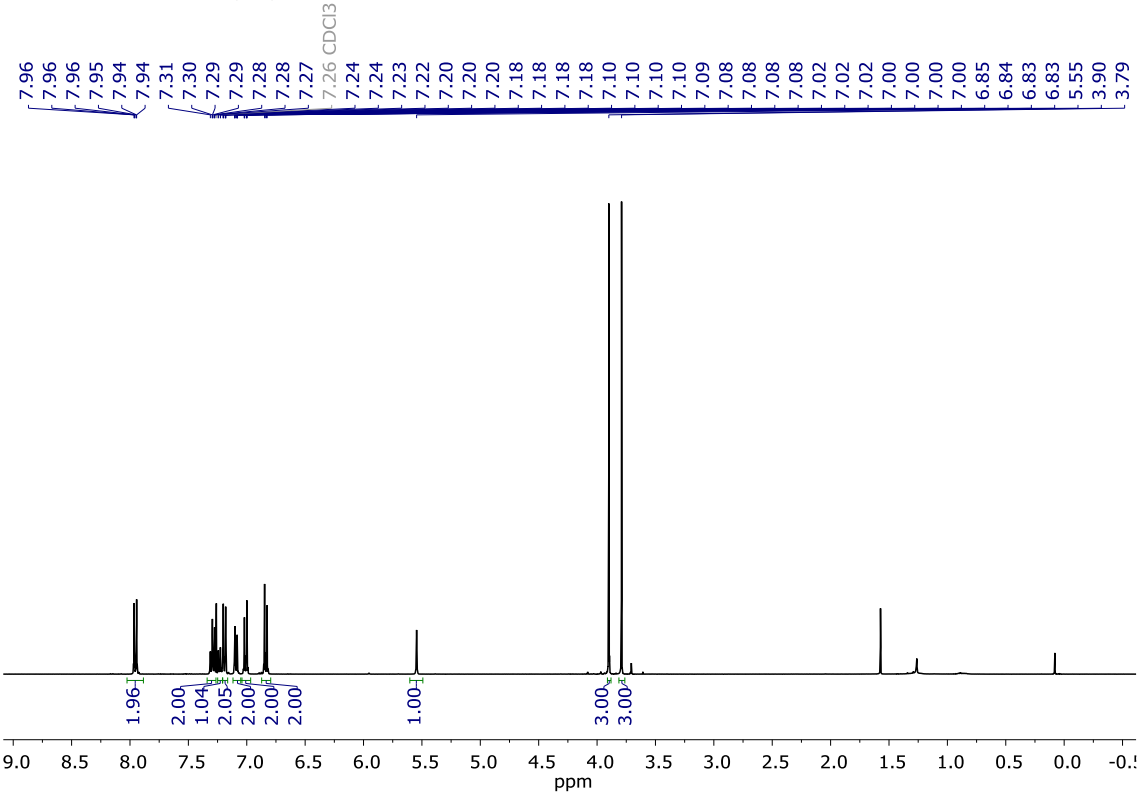


^1H COSY experiment ($CDCl_3$)

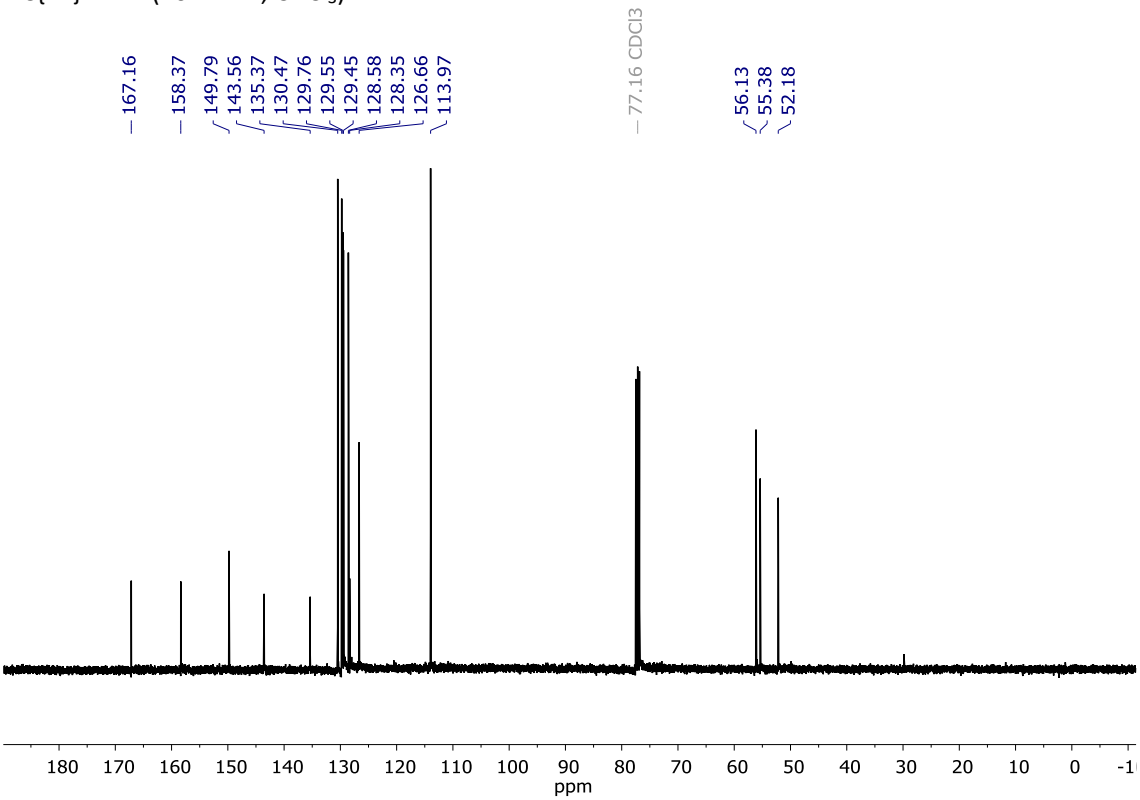




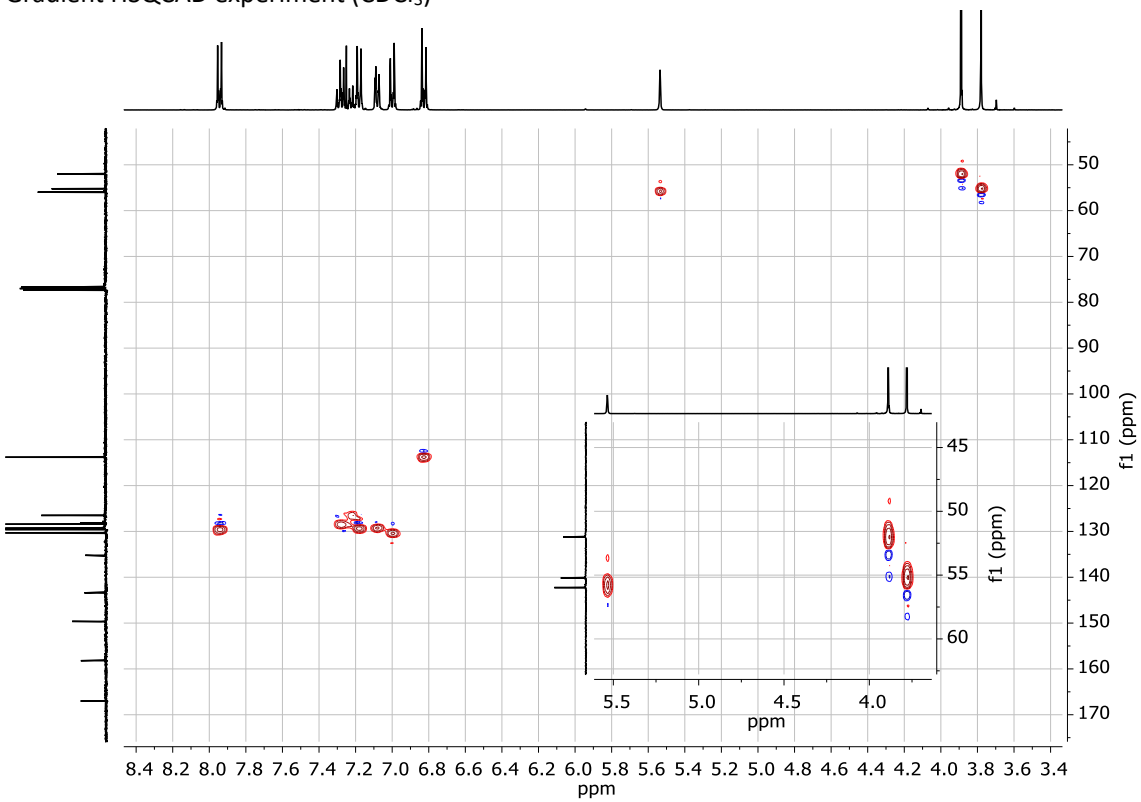
(**50**) ^{1}H NMR (400 MHz, $CDCl_3$)



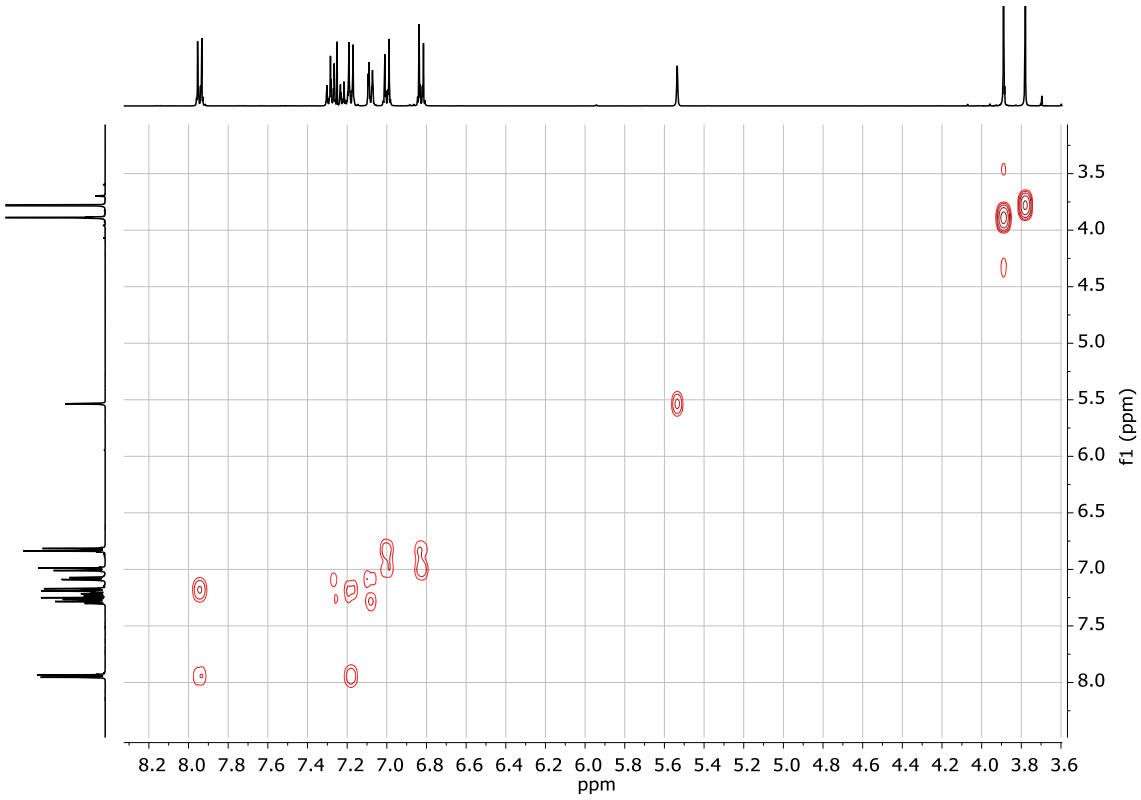
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

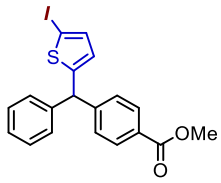


Gradient HSQCAD experiment ($CDCl_3$)

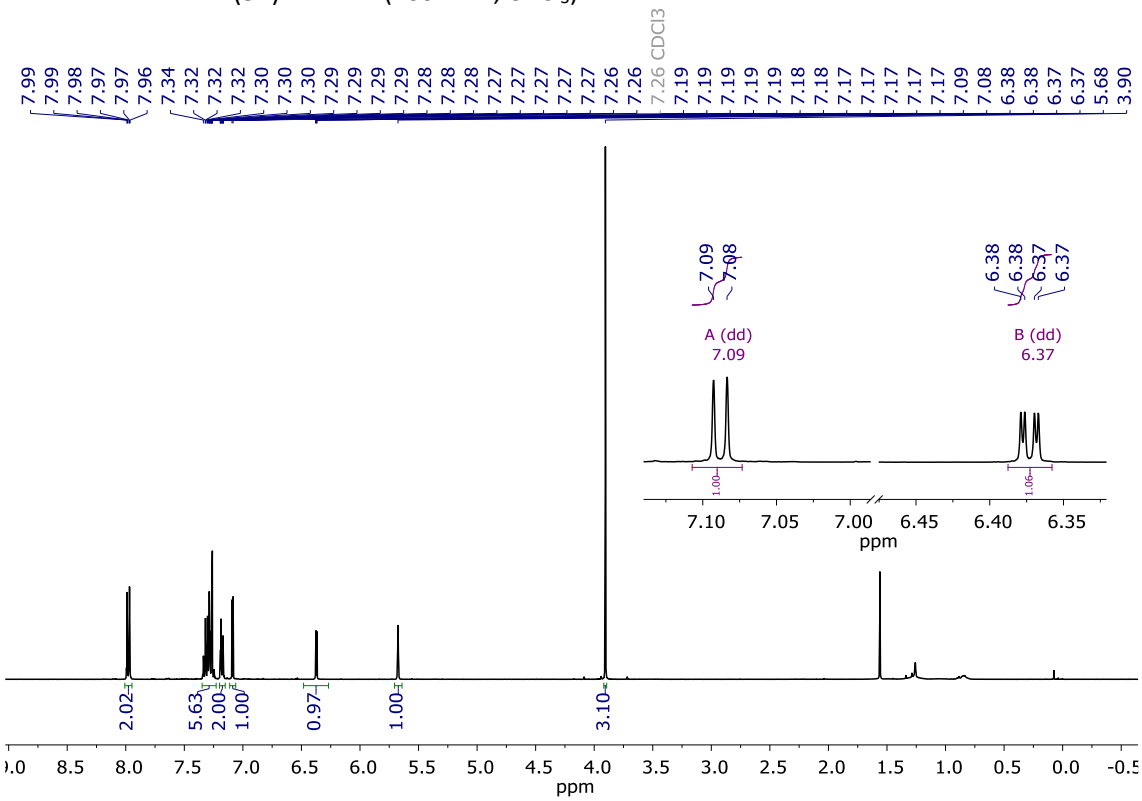


^1H COSY experiment ($CDCl_3$)

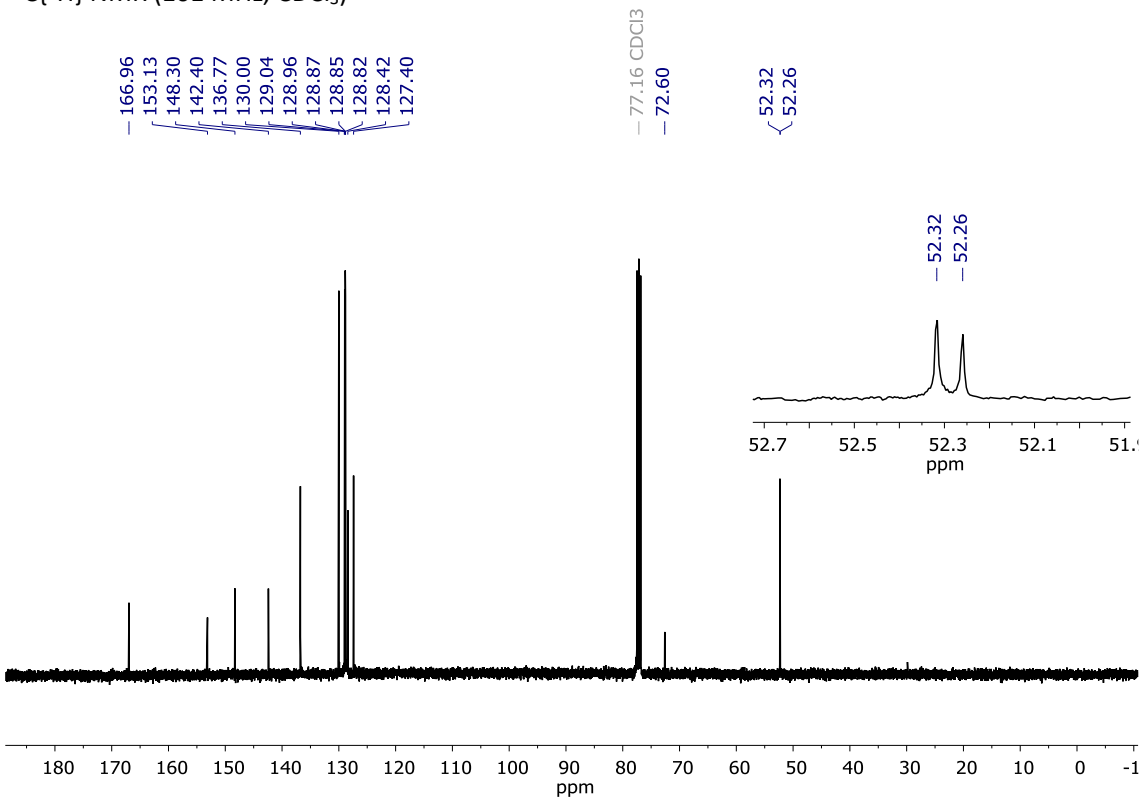




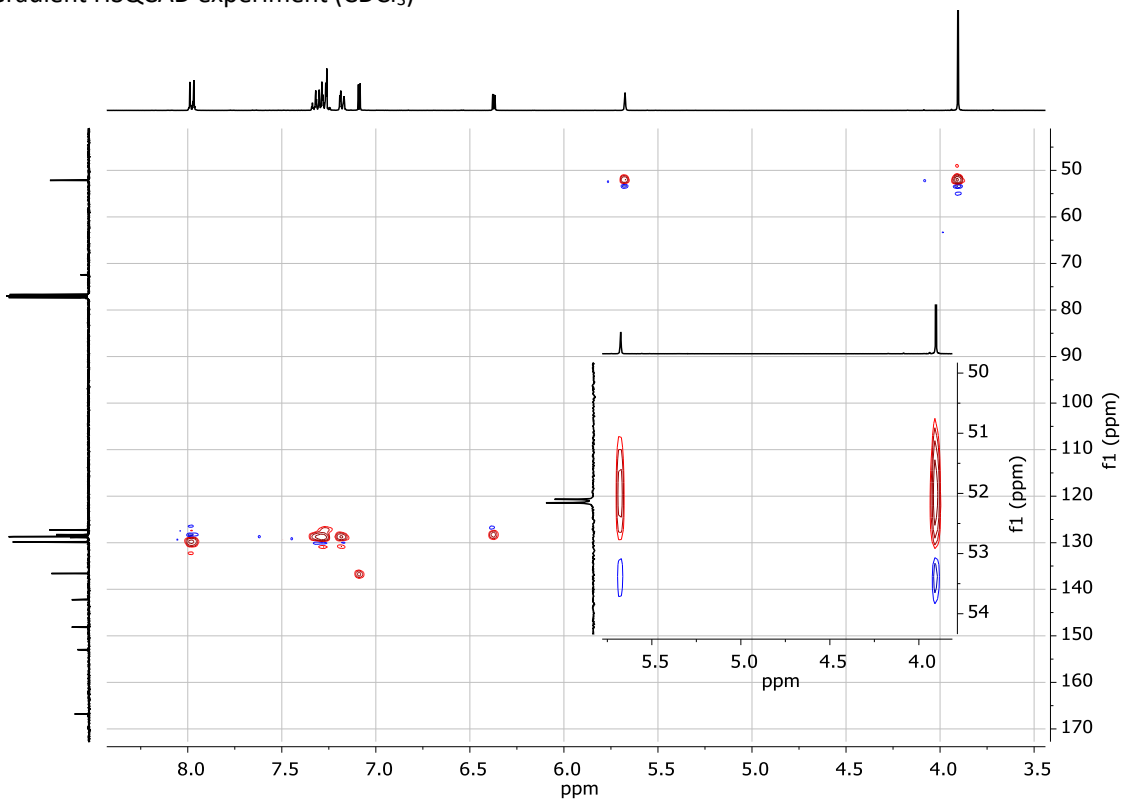
(**51**) ^{1}H NMR (400 MHz, $CDCl_3$)



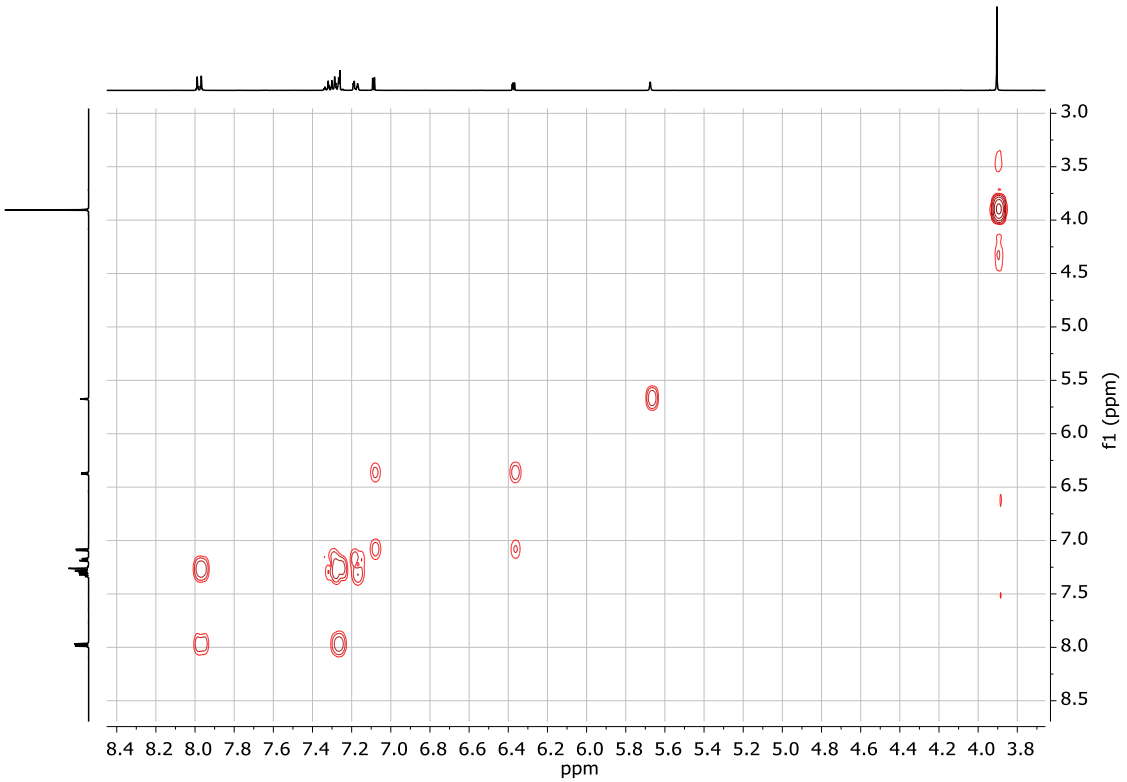
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

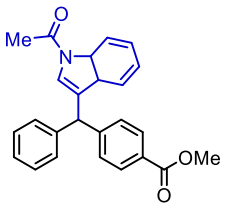


Gradient HSQCAD experiment ($CDCl_3$)

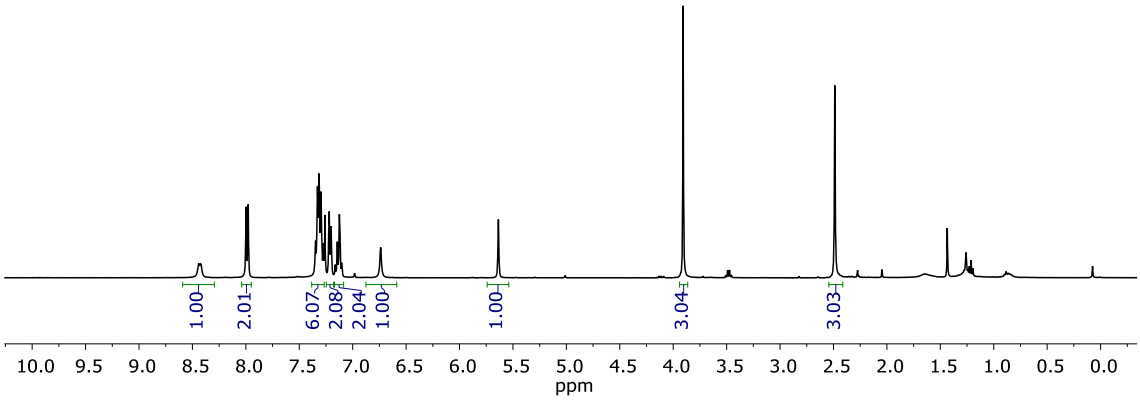


^1H COSY experiment ($CDCl_3$)

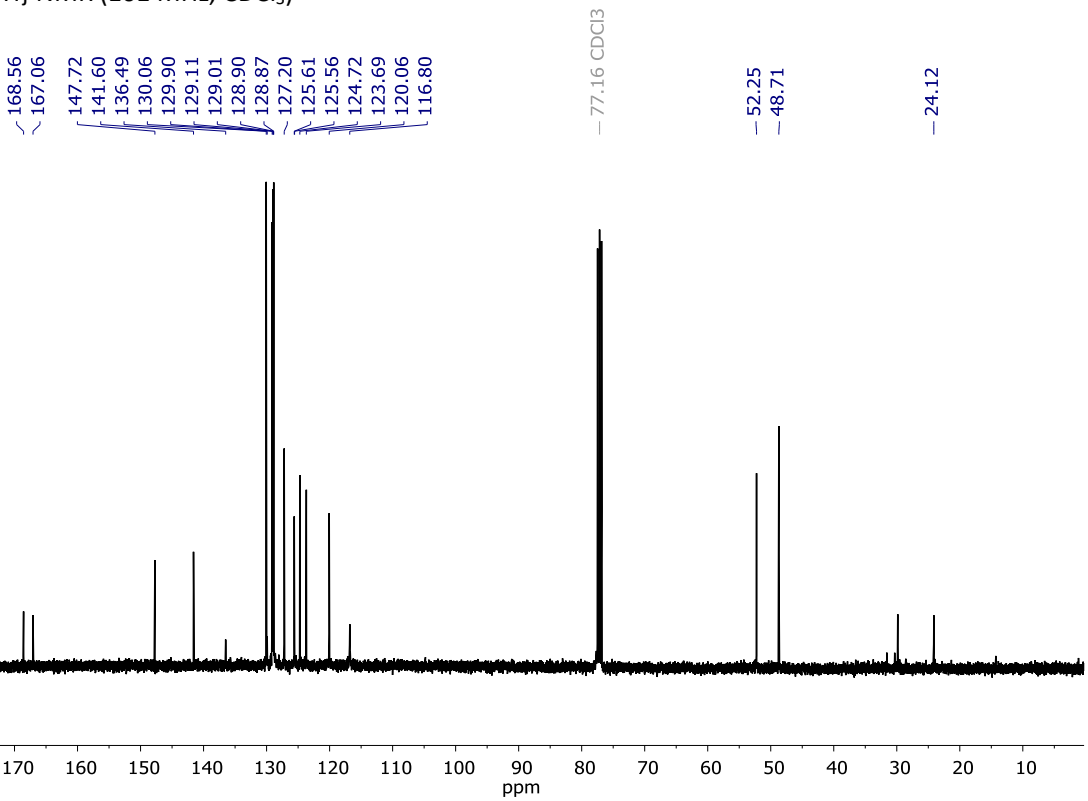




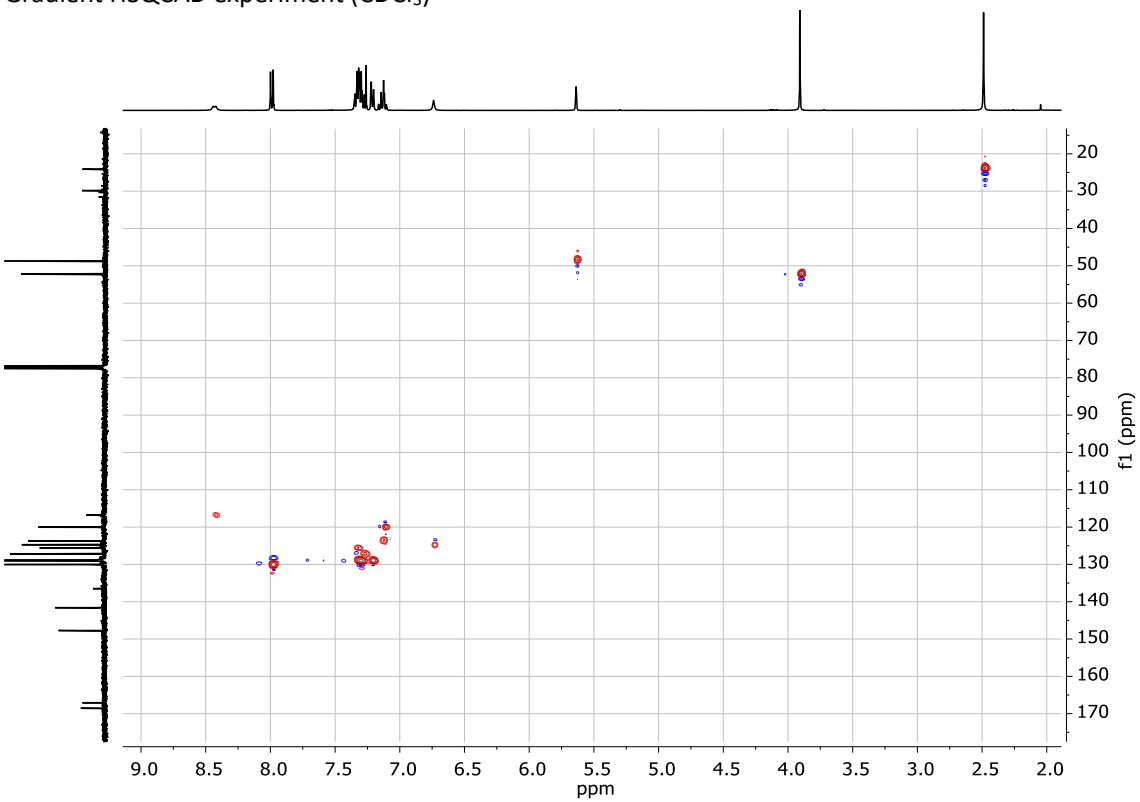
(**52**) ^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



Gradient HSQCAD experiment ($CDCl_3$)



^1H COSY experiment ($CDCl_3$)