

Electronic Supplementary Information

Copper-catalyzed synthesis of *gem*-diborylalkanes by B-H bond insertion of α -furyl boryl carbenes

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1. General Information

General. Unless otherwise noted, all reactions were carried out in a flame-dried, sealed Schlenk reaction tube under an atmosphere of nitrogen with magnetic stirring. The oil bath acts as heat source for reactions that require heating. Analytical thin-layer chromatography (TLC) was performed on glass plates coated with 0.25 mm 230-400 mesh silica gel containing a fluorescent indicator. Visualization was accomplished by exposure to a UV lamp. All the product in this article are compatible with standard silica gel chromatography. Column chromatography was performed on silica gel (200-300 mesh) using standard methods.

Structural Analysis. ^1H NMR and proton decoupled ^{13}C NMR and ^{11}B NMR spectra were recorded on Bruker Avance 500 MHz spectrometers at ambient temperature. NMR standards were used as follows: ^1H NMR spectroscopy: $\delta = 7.26$ ppm (CDCl_3). ^{13}C NMR spectroscopy: $\delta = 77.16$ ppm (CDCl_3); ^1H NMR spectroscopy: $\delta = 1.94$ ppm (CD_3CN). ^{13}C NMR spectroscopy: $\delta = 1.32$ ppm (CD_3CN); ^1H NMR spectroscopy: $\delta = 2.50$ ppm ($\text{DMSO-}d_6$). ^{13}C NMR spectroscopy: $\delta = 39.52$ ppm ($\text{DMSO-}d_6$). All ^{13}C NMR signals are singlets unless noted otherwise. High-resolution mass spectra were recorded on Thermo Fisher Scientific Ultimate 3000-Q-Exactive instrument or Advion Mass Expression CMS instrument. X-ray diffraction analysis was recorded on a XtaLAB Synergy X-ray single crystal diffractometer.

Materials. Solvents were distilled under nitrogen from calcium hydride or sodium/benzophenone. Reagents from commercial suppliers (*J&K*, Energy, Sigma-Aldrich, Alfa Aesar, Acros Organics, Strem Chemicals, TCI, Bidepharm) were used without further purification. Lewis base–borane adducts were commercially available from commercial suppliers (Energy Chemical *etc.*) or prepared according to literature procedures^[1]. Hydrosilanes, hydrogermanes and hydrostannanes are commercially available from commercial suppliers (Energy chemical, Bidepharm *etc.*)

2. Preparation and Characterization of BMIDA-Terminated Enynones

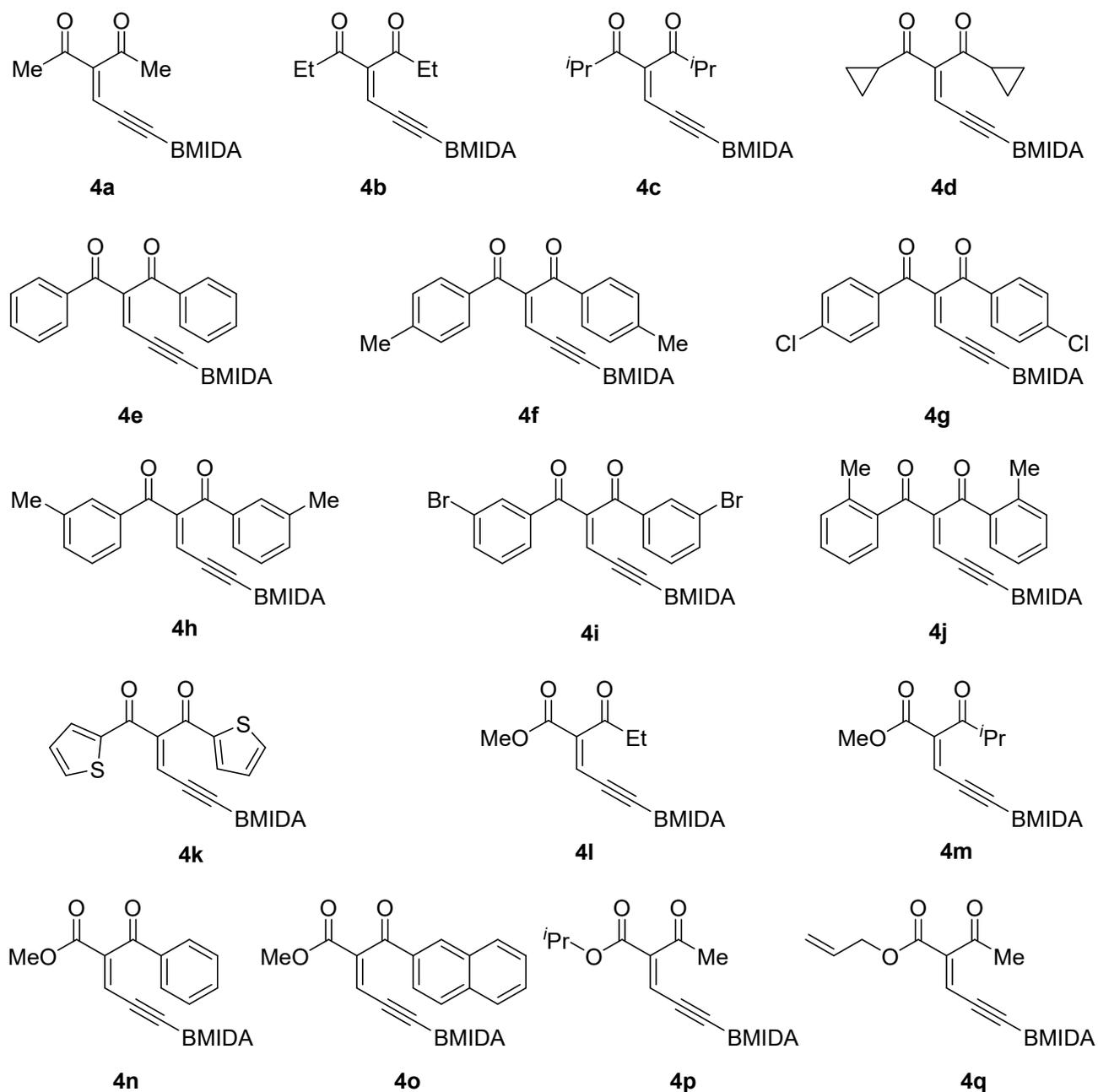
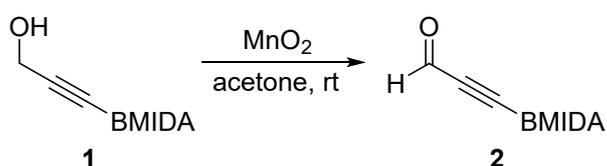


Figure S1. BMIDA-terminated enynones used in this work

2.1 Compound 1 prepared according to literature procedure^[2]

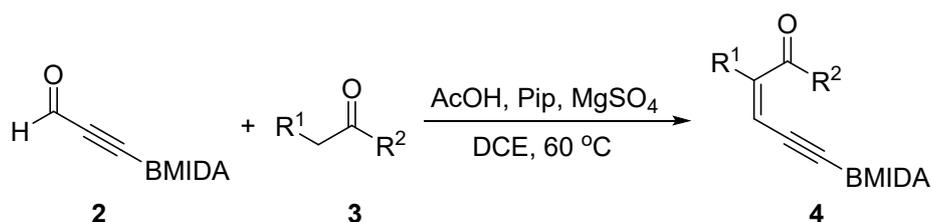
2.2 Synthetic procedure for compound 2



A pre-dried 50.0 mL Schlenk tube was charged with stirring bar, MnO_2 (434.7 mg, 5.0 mmol, 5.0 eq.), **1** (211.0 mg, 1.0 mmol, 1.0 eq.). Then, acetone (2.0 mL) was added and the mixture was stirred

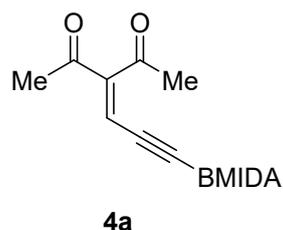
at room temperature for 2 h. The resulting mixture was filtered through celite and washed with acetone. Subsequently, the combined organic phases were concentrated and purified by flash column chromatography to give analytical compound **2**. White solid, m.p. 154-155 °C (125.4 mg, 60% yield). PE/EA = 1:3, $R_f = 0.20$. $^1\text{H NMR}$ (500 MHz, CD_3CN): δ 9.19 (s, 0.5 H), 4.06 (d, $J = 17.2$ Hz, 2H), 3.93 (d, $J = 17.2$ Hz, 2H), 3.07 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CD_3CN): δ 178.9, 168.4, 62.8, 49.1. $^{11}\text{B NMR}$ (160 MHz, CD_3CN) δ 6.1 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_8\text{H}_7\text{BNO}_5, \text{M} - \text{H}]^-$: 208.0417, found: 208.0415.

2.3 Synthetic procedure for compound 4

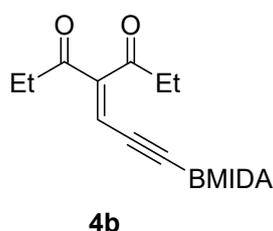


Under an argon atmosphere, to a solution of **2** (209.0 mg, 1.0 mmol, 1.0 eq.) in DCE (2.0 mL), AcOH (30.0 mg, 0.5 mmol, 0.5 eq.), piperidine (6.8 mg, 0.08 mmol, 0.08 eq.), MgSO_4 (24.1 mg, 0.2 mmol, 0.2 eq.) and **3** (2.5 mmol, 2.5 eq.) were successively added into a Schlenk tube at room temperature. The reaction mixture was stirred at 60 °C for 6 h. After the completion of the reaction, the reaction mixture was filtered through celite and the filter liquid was evaporated by rotary evaporation to give the residue. The resulting residue was purified by chromatography on silica gel (PE/EA) to give compound **4**.

2.4 Characterization of BMIDA-terminated enynones 4

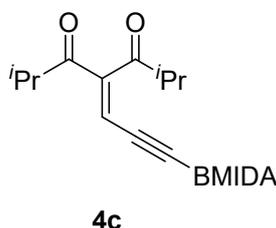


2-(4-Acetyl-5-oxohex-3-en-1-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4a). Yellow solid, m.p. 122-123 °C (174.6 mg, 60% yield). PE/EA = 1:3, $R_f = 0.20$. $^1\text{H NMR}$ (500 MHz, CD_3CN): δ 6.71 (s, 1H), 4.02 (d, $J = 17.2$ Hz, 2H), 3.87 (d, $J = 17.2$ Hz, 2H), 3.00 (s, 3H), 2.34 (s, 3H), 2.29 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CD_3CN): δ 202.5, 197.4, 168.5, 153.1, 121.4, 62.6, 48.9, 31.1, 26.9. $^{11}\text{B NMR}$ (160 MHz, CD_3CN) δ 6.2 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{13}\text{H}_{15}\text{BNO}_6, \text{M} + \text{H}]^+$: 292.0973, found: 292.0978.



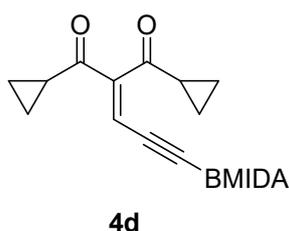
6-Methyl-2-(5-oxo-4-propionylhept-3-en-1-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (4b).

Yellow solid, m.p. 139-140 °C (175.5 mg, 55% yield). PE/EA = 1:2, $R_f = 0.20$. $^1\text{H NMR}$ (500 MHz, CD_3CN): δ 6.67 (s, 1H), 4.02 (d, $J = 17.2$ Hz, 2H), 3.85 (d, $J = 17.2$ Hz, 2H), 2.97 (s, 3H), 2.68-2.62 (m, 4H), 1.03-0.96 (m, 6H). $^{13}\text{C NMR}$ (125 MHz, CD_3CN): δ 206.1, 200.0, 168.6, 153.1, 119.9, 95.6, 62.6, 48.8, 37.1, 32.5, 8.1, 7.7. $^{11}\text{B NMR}$ (160 MHz, CD_3CN) δ 6.2 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{15}\text{H}_{19}\text{BNO}_6, \text{M} + \text{H}]^+$: 320.1300, found: 320.1299.



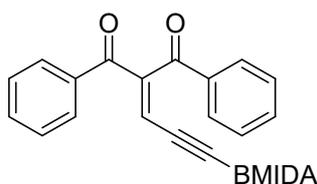
2-(4-Isobutyryl-6-methyl-5-oxohept-3-en-1-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4c).

Yellow solid, m.p. 201-202 °C (215.2 mg, 62% yield). PE/EA = 1:2, $R_f = 0.20$. $^1\text{H NMR}$ (500 MHz, CD_3CN): δ 6.73 (s, 1H), 4.02 (d, $J = 17.1$ Hz, 2H), 3.85 (d, $J = 17.1$ Hz, 2H), 3.21-3.15 (m, 1H), 2.99 (s, 3H), 2.95-2.89 (m, 1H), 1.08 (s, 6H), 1.07 (s, 6H). $^{13}\text{C NMR}$ (125 MHz, CD_3CN): δ 208.8, 204.3, 168.5, 152.3, 120.7, 62.6, 48.8, 36.3, 19.1, 17.9. $^{11}\text{B NMR}$ (160 MHz, CD_3CN) δ 6.2 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{17}\text{H}_{23}\text{BNO}_6, \text{M} + \text{H}]^+$: 348.1613, found: 348.1612.



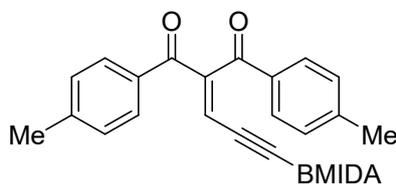
2-(4-(Cyclopropanecarbonyl)-5-cyclopropyl-5-oxopent-3-en-1-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4d).

White solid, m.p. 194-195 °C (205.9 mg, 60% yield). PE/EA = 1:3, $R_f = 0.20$. $^1\text{H NMR}$ (500 MHz, CD_3CN): δ 6.81 (s, 1H), 4.03 (d, $J = 17.2$ Hz, 2H), 3.87 (d, $J = 17.2$ Hz, 2H), 3.01 (s, 3H), 2.30-2.24 (m, 2H), 1.99-0.99 (m, 8H). $^{13}\text{C NMR}$ (125 MHz, CD_3CN): δ 204.9, 198.7, 168.6, 153.3, 120.3, 96.1, 62.5, 48.9, 23.1, 18.8, 13.1, 12.6. $^{11}\text{B NMR}$ (160 MHz, CD_3CN) δ 6.2 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{17}\text{H}_{19}\text{BNO}_6, \text{M} + \text{H}]^+$: 344.1300, found: 344.1295.



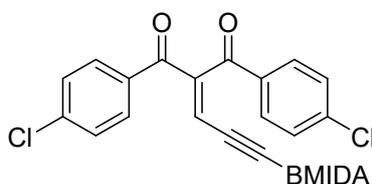
4e

2-(4-Benzoyl-5-oxo-5-phenylpent-3-en-1-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4e). Yellow solid, m.p. 85-86 °C (249.1 mg, 60% yield). PE/EA = 1:4, R_f = 0.20. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.91 (d, J = 7.5 Hz, 2H), 7.81 (d, J = 7.4 Hz, 2H), 7.58 (m, 2H), 7.46 (t, J = 7.8 Hz, 4H), 6.69 (s, 1H), 3.82 (d, J = 16.7 Hz, 2H), 3.52 (d, J = 16.7 Hz, 2H), 2.69 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 193.9, 192.8, 166.8, 150.1, 136.2, 135.9, 134.5, 133.6, 129.6, 129.2, 129.0, 123.5, 95.7, 61.4, 47.6. $^{11}\text{B NMR}$ (160 MHz, CDCl_3) δ 5.8 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{23}\text{H}_{19}\text{BNO}_6, \text{M} + \text{H}]^+$: 416.1300, found: 416.1293.



4f

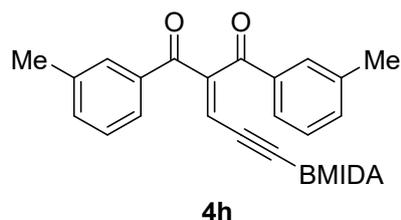
6-Methyl-2-(4-(4-methylbenzoyl)-5-oxo-5-(p-tolyl)pent-3-en-1-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (4f). Yellow solid, m.p. 88-89 °C (243.8 mg, 55% yield). PE/EA = 1:2, R_f = 0.20. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.78 (d, J = 8.1 Hz, 2H), 7.71 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 7.9 Hz, 4H), 6.63 (s, 1H), 3.86 (d, J = 16.9 Hz, 2H), 3.50 (d, J = 16.8 Hz, 2H), 2.67 (s, 3H), 2.38 (s, 3H), 2.35 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 193.6, 192.3, 167.4, 167.3, 150.4, 145.8, 144.6, 133.6, 133.4, 129.9, 129.8, 129.7, 129.6, 122.6, 95.7, 61.4, 47.6, 21.9, 21.8. $^{11}\text{B NMR}$ (160 MHz, CDCl_3) δ 6.6 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{25}\text{H}_{23}\text{BNO}_6, \text{M} + \text{H}]^+$: 444.1613, found: 444.1604.



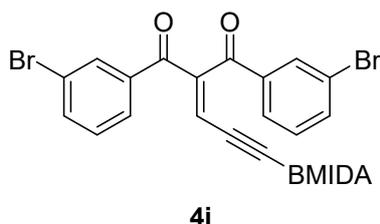
4g

2-(4-(4-Chlorobenzoyl)-5-(4-chlorophenyl)-5-oxopent-3-en-1-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4g). Yellow solid, m.p. 203-204 °C (242.0 mg, 50% yield). PE/EA = 3:2, R_f = 0.20. $^1\text{H NMR}$ (500 MHz, CD_3CN): δ 7.92 (d, J = 8.7 Hz, 2H), 7.77 (d, J = 8.5 Hz, 2H), 7.50 (t, J = 8.5 Hz, 4H), 6.79 (s, 1H), 3.93 (d, J = 17.2 Hz, 2H), 3.65 (d, J = 17.1 Hz, 2H), 2.64 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CD_3CN): δ 193.9, 193.1, 168.3, 149.2, 141.2, 140.0, 135.9, 135.3, 132.0, 131.9, 130.4, 130.0, 125.6, 95.4, 62.4, 48.4. $^{11}\text{B NMR}$ (160 MHz, CD_3CN) δ 6.1 (bs). **HRMS** (ESI, m/z)

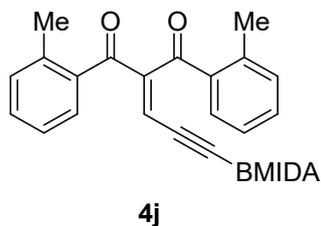
Calculated for $[C_{23}H_{17}BCl_2NO_6, M + H]^+$: 484.0521, found: 484.0519.



6-Methyl-2-(4-(3-methylbenzoyl)-5-oxo-5-(m-tolyl)pent-3-en-1-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (4h). Yellow solid, m.p. 85-86 °C (266.0 mg, 60% yield). PE/EA = 1:2, R_f = 0.20. 1H NMR (500 MHz, $CDCl_3$): δ 7.68 (t, J = 7.8 Hz, 2H), 7.59 (t, J = 7.3 Hz, 2H), 7.38 (d, J = 7.5 Hz, 2H), 7.33 (t, J = 7.9 Hz, 2H), 6.64 (s, 1H), 3.85 (d, J = 16.8 Hz, 2H), 3.49 (d, J = 16.7 Hz, 2H), 2.67 (s, 3H), 2.38 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 194.1, 193.1, 167.2, 150.3, 139.2, 139.0, 136.2, 135.9, 135.3, 134.3, 130.0, 129.0, 128.7, 126.9, 126.8, 123.2, 95.7, 61.4, 47.6, 21.4, 21.3. ^{11}B NMR (160 MHz, $CDCl_3$) δ 6.5 (bs). **HRMS** (ESI, m/z) Calculated for $[C_{25}H_{23}BNO_6, M + H]^+$: 444.1613, found: 444.1605.

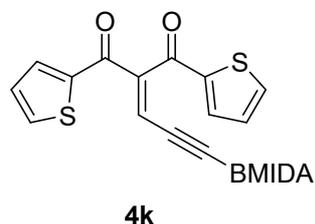


2-(4-(3-Bromobenzoyl)-5-(3-bromophenyl)-5-oxopent-3-en-1-yn-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4i). Yellow solid, m.p. 203-204 °C (286.5 mg, 50% yield). PE/EA = 1:1, R_f = 0.20. 1H NMR (500 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.91 (s, 1H), 7.76 (d, J = 7.8 Hz, 1H), 7.76 (dd, J = 7.9, 1.7 Hz, 3H), 7.35 (t, J = 7.7 Hz, 2H), 6.70 (s, 1H), 3.93 (d, J = 17.1 Hz, 2H), 3.61 (d, J = 17.0 Hz, 2H), 2.77 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.3, 191.3, 167.2, 148.6, 137.8, 137.6, 137.3, 136.5, 132.2, 132.1, 130.1, 130.5, 128.3, 128.1, 124.9, 123.3, 123.2, 95.2, 61.7, 47.9. ^{11}B NMR (160 MHz, $CDCl_3$) δ 5.9 (bs). **HRMS** (ESI, m/z) Calculated for $[C_{23}H_{17}BBr_2NO_6, M + H]^+$: 571.9510, found: 571.9510.

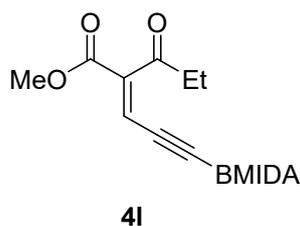


6-Methyl-2-(4-(2-methylbenzoyl)-5-oxo-5-(o-tolyl)pent-3-en-1-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (4j). Yellow solid, m.p. 85-86 °C (266.0 mg, 60% yield). PE/EA = 1:2, R_f = 0.20. 1H NMR (500 MHz, $CDCl_3$): δ 7.58 (d, J = 7.7 Hz, 1H), 7.40-7.31 (m, 3H), 7.25-7.17 (m, 4H), 6.56 (s, 1H), 3.84 (d, J = 16.7 Hz, 2H), 3.54 (d, J = 16.6 Hz, 2H), 2.77 (s, 3H), 2.45 (s, 3H), 2.29 (s, 3H). ^{13}C

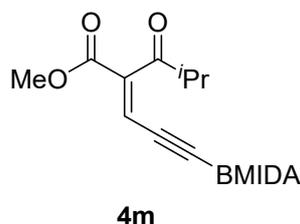
NMR (125 MHz, CDCl₃): δ 195.7, 195.4, 166.9, 166.8, 152.5, 139.7, 137.6, 136.7, 136.1, 132.7, 132.3, 131.5, 131.4, 130.8, 128.5, 126.1, 125.6, 124.1, 95.9, 61.4, 47.7, 21.1, 19.9. **¹¹B NMR** (160 MHz, CDCl₃) δ 6.6 (bs). **HRMS** (ESI, m/z) Calculated for [C₂₅H₂₃BNO₆, M + H]⁺: 444.1613, found: 444.1605.



6-Methyl-2-(5-oxo-5-(thiophen-2-yl)-4-(thiophene-2-carbonyl)pent-3-en-1-yn-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (4k). Yellow solid, m.p. 88-89 °C (256.4 mg, 60% yield). PE/EA = 1:2, R_f = 0.20. **¹H NMR** (500 MHz, CDCl₃): δ 7.80-7.67 (m, 4H), 7.13 (d, *J* = 3.1 Hz, 2H), 6.82 (s, 1H), 3.94 (d, *J* = 16.8 Hz, 2H), 3.67 (d, *J* = 16.8 Hz, 2H), 2.84 (s, 3H). **¹³C NMR** (125 MHz, CDCl₃): δ 185.5, 182.4, 167.2, 149.6, 143.0, 142.4, 136.7, 136.2, 136.1, 135.0, 129.3, 128.8, 122.3, 95.6, 61.6, 47.8. **¹¹B NMR** (160 MHz, CDCl₃) δ 5.5 (bs). **HRMS** (ESI, m/z) Calculated for [C₁₉H₁₄BNO₆S₂Na, M + Na]⁺: 450.0429, found: 450.0427.

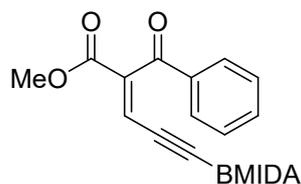


Methyl (E)-5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-2-propionylpent-2-en-4-ynoate (4l). Yellow solid, m.p. 110-111 °C (192.7 mg, 60% yield). PE/EA = 1:3, R_f = 0.20. **¹H NMR** (500 MHz, CD₃CN): δ 6.77 (s, 1H), 4.26-4.20 (m, 2H), 4.02 (d, *J* = 17.1 Hz, 2H), 3.87 (d, *J* = 17.1 Hz, 2H), 3.02 (s, 3H), 2.39 (s, 3H), 1.28-1.24 (m, 3H). **¹³C NMR** (125 MHz, CD₃CN): δ 200.0, 168.5, 164.4, 145.8, 122.3, 62.7, 62.6, 48.9, 30.6, 14.3. **¹¹B NMR** (160 MHz, CD₃CN) δ 6.1 (bs). **HRMS** (ESI, m/z) Calculated for [C₁₄H₁₇BNO₇, M + H]⁺: 322.1093, found: 322.1091.



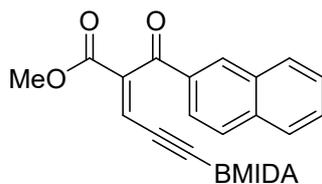
Methyl (E)-2-isobutyryl-5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)pent-2-en-4-ynoate (4m). Yellow solid, m.p. 110-111 °C (187.7 mg, 56% yield). PE/EA = 1:2, R_f = 0.20. **¹H NMR** (500 MHz, CD₃CN): δ 6.80 (s, 1H), 4.03 (d, *J* = 17.2 Hz, 2H), 3.86 (d, *J* = 17.1 Hz, 2H), 3.76 (s, 3H),

3.08-3.02 (m, 1H), 3.00 (s, 3H), 1.11 (s, 3H), 1.09 (s, 3H). ^{13}C NMR (125 MHz, CD_3CN): δ 206.6, 168.5, 165.0, 145.7, 122.4, 118.3, 62.6, 53.3, 48.9, 41.3, 18.0. ^{11}B NMR (160 MHz, CD_3CN) δ 6.2 (bs). HRMS (ESI, m/z) Calculated for $[\text{C}_{15}\text{H}_{19}\text{BNO}_7, \text{M} + \text{H}]^+$: 336.1249, found: 336.1249.



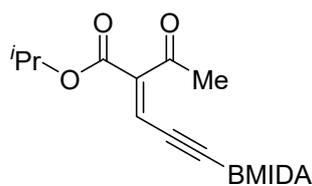
4n

Methyl (E)-2-benzoyl-5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)pent-2-en-4-ynoate (4n). Yellow solid, m.p. 129-130 °C (210.4 mg, 57% yield). PE/EA = 1:2, R_f = 0.20. ^1H NMR (500 MHz, CDCl_3): δ 7.89 (d, J = 7.5 Hz, 2H), 7.63 (t, J = 7.1 Hz, 1H), 7.58 (t, J = 7.3 Hz, 2H), 7.04 (s, 1H), 3.80 (d, J = 16.7 Hz, 2H), 3.76 (s, 3H), 3.44 (d, J = 16.7 Hz, 2H), 2.56 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 192.7, 167.0, 164.0, 143.2, 135.5, 134.7, 129.6, 129.3, 123.2, 95.3, 61.4, 47.5. ^{11}B NMR (160 MHz, CDCl_3) δ 6.1 (bs). HRMS (ESI, m/z) Calculated for $[\text{C}_{18}\text{H}_{17}\text{BNO}_7, \text{M} + \text{H}]^+$: 370.1093, found: 370.1089.



4o

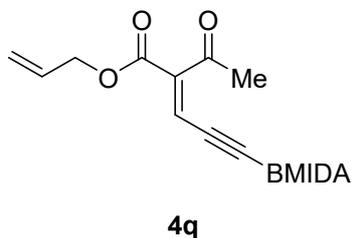
Methyl (E)-2-(2-naphthoyl)-5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)pent-2-en-4-ynoate (4o). Yellow solid, m.p. 203-204 °C (238.9 mg, 57% yield). PE/EA = 1:2, R_f = 0.20. ^1H NMR (500 MHz, CD_3CN): δ 8.50 (s, 1H), 8.05 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 9.2 Hz, 2H), 7.98 (d, J = 8.2 Hz, 1H), 7.70 (t, J = 7.1 Hz, 1H), 7.62 (t, J = 7.3 Hz, 1H), 7.13 (s, 1H), 3.78 (d, J = 17.1 Hz, 2H), 3.74 (s, 3H), 3.43 (d, J = 17.1 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (125 MHz, CD_3CN): δ 193.6, 168.1, 164.9, 143.9, 137.0, 133.8, 133.6, 133.5, 130.7, 130.4, 128.9, 128.3, 124.4, 123.7, 62.2, 53.4, 48.2. ^{11}B NMR (160 MHz, CD_3CN) δ 5.8 (bs). HRMS (ESI, m/z) Calculated for $[\text{C}_{22}\text{H}_{19}\text{BNO}_7, \text{M} + \text{H}]^+$: 420.1249, found: 420.1251.



4p

Isopropyl (E)-2-acetyl-5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)pent-2-en-4-ynoate (4p). Yellow solid, m.p. 57-58 °C (201.1 mg, 60% yield). PE/EA = 1:2, R_f = 0.20. ^1H NMR (500

MHz, CDCl₃): δ 6.73 (s, 1H), 5.13-5.04 (m, 1H), 4.12 (d, J = 17.1 Hz, 2H), 3.86 (d, J = 17.1 Hz, 2H), 3.12 (s, 3H), 2.39 (s, 3H), 1.28 (s, 3H), 1.26 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 198.9, 168.0, 163.1, 144.8, 122.7, 95.7, 69.9, 61.8, 48.2, 30.4, 25.8, 21.8. ¹¹B NMR (160 MHz, CDCl₃) δ 6.1 (bs). **HRMS** (ESI, m/z) Calculated for [C₁₅H₂₂BN₂O₇, M + NH₄]⁺: 353.1514, found: 353.1515.



Allyl (*E*)-2-acetyl-5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)pent-2-en-4-ynoate (4q). Yellow solid, m.p. 57-58 °C (199.9 mg, 60% yield). PE/EA = 1:2, R_f = 0.20. ¹H NMR (500 MHz, CDCl₃): δ 6.80 (s, 1H), 5.96-5.87 (m, 1H), 5.32 (d, J = 17.2 Hz, 1H), 5.26 (d, J = 10.4 Hz, 1H), 4.69 (d, J = 5.8 Hz, 2H), 4.10 (d, J = 16.9 Hz, 2H), 3.87 (d, J = 16.8 Hz, 2H), 3.13 (s, 3H), 2.41 (s, 3H). ¹³C NMR (125 MHz, CDCl₃): δ 198.6, 167.9, 163.3, 144.0, 131.3, 123.5, 119.4, 95.7, 66.5, 61.8, 48.2, 30.5, 25.8. ¹¹B NMR (160 MHz, CDCl₃) δ 6.2 (bs). **HRMS** (ESI, m/z) Calculated for [C₁₅H₁₇BNO₇, M + H]⁺: 334.1093, found: 334.1088.

3. Structure of Hydroboranes

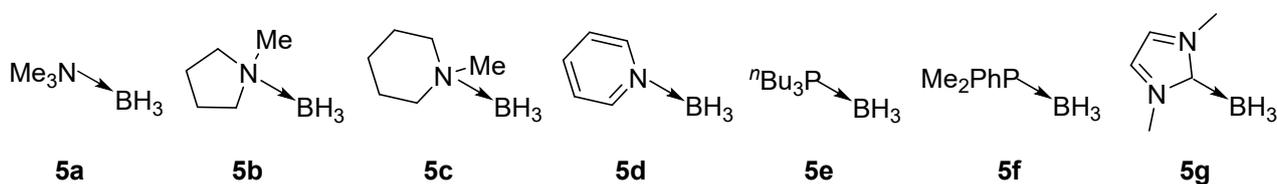
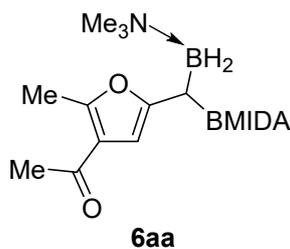


Figure S2. Structure of hydroboranes used in this work

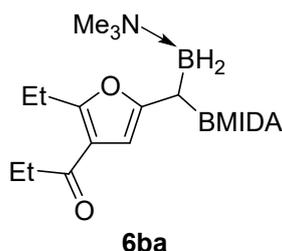
4. General Procedure for Copper-Catalyzed α -Furyl Boryl Carbene Insertion into B-H Bond

Enynones **4** (0.2 mmol, 1.0 eq.), CuCl (4.0 mg, 0.04 mmol, 0.2 eq.) and DCE (2.0 mL) were added to a pre-dried 10.0 mL Schlenk tube charged with stirring bar. After stirring the mixture at room temperature for 2 minutes, Lewis base-borane adducts **5** (0.8 mmol, 0.8 eq.) were injected into the Schlenk tube. The resulting mixture was stirred at 50 °C for 8 h. After reaching room temperature, the solvent was removed in vacuo, and the residue was transferred to a silica gel column and purified by flash chromatography with petroleum ether/ethyl acetate as eluent to give the analytical pure products **6**.

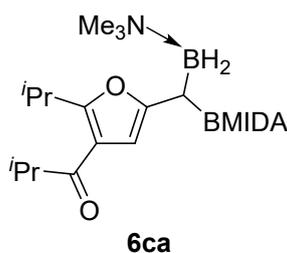
5. Product Characterization of Carbene B-H Bond Insertion Reactions



2-((4-Acetyl-5-methylfuran-2-yl)(trimethylamine-boraneyl)methyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (6aa). Light green solid, m.p. 197-198 °C (65.5 mg, 90% yield). EA, $R_f = 0.20$. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 6.11 (s, 1H), 3.77 (d, $J = 7.6$ Hz, 1H), 3.74 (d, $J = 7.7$ Hz, 1H), 3.57 (d, $J = 16.0$ Hz, 1H), 3.53 (d, $J = 16.7$ Hz, 1H), 2.96 (s, 3H), 2.49 (s, 3H), 2.46 (s, 9H), 2.33 (s, 3H), 1.57 (s, 1H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 174.0, 173.3, 140.9, 128.9, 127.4, 124.8, 60.4, 52.9, 52.8, 51.8, 43.6, 38.7, 37.8, 32.9, 29.8, 19.2, 15.8. $^{11}\text{B NMR}$ (160 MHz, CDCl_3) δ 14.8, -2.2 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{16}\text{H}_{26}\text{B}_2\text{N}_2\text{O}_6\text{Na}, \text{M} + \text{Na}]^+$: 387.1869, found: 387.1867.

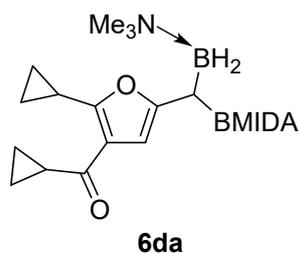


2-(Trimethylamine-boraneyl(5-ethyl-4-propionylfuran-2-yl)methyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (6ba). White solid, m.p. 86-87 °C (62.2 mg, 87% yield). PE/EA = 1:3, $R_f = 0.20$. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 6.07 (s, 1H), 3.79 (d, $J = 16.4$ Hz, 2H), 3.59 (d, $J = 16.4$ Hz, 1H), 3.57 (d, $J = 16.3$ Hz, 1H), 2.94 (s, 3H), 2.91-2.88 (m, 2H), 2.68-2.62 (m, 2H), 2.42 (s, 9H), 1.55 (d, $J = 6.7$ Hz, 1H), 1.13 (t, $J = 7.6$ Hz, 3H), 1.07 (t, $J = 7.3$ Hz, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 180.0, 168.5, 168.1, 161.6, 159.6, 121.1, 103.3, 63.0, 62.9, 52.1, 45.7, 34.5, 21.6, 19.5, 12.8, 8.0. $^{11}\text{B NMR}$ (160 MHz, CDCl_3) δ 14.6, -2.2 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{18}\text{H}_{30}\text{B}_2\text{N}_2\text{O}_6\text{Na}, \text{M} + \text{Na}]^+$: 415.2182, found: 415.2185.

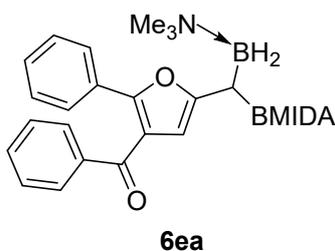


2-(Trimethylamine-boraneyl(4-isobutyryl-5-isopropylfuran-2-yl)methyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (6ca). White solid, m.p. 96-97 °C (79.8 mg, 95% yield). PE/EA = 1:2, $R_f =$

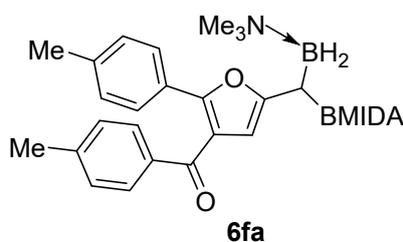
0.20. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 6.09 (s, 1H), 3.76 (d, $J = 2.9$ Hz, 1H), 3.73 (d, $J = 3.6$ Hz, 1H), 3.72-3.65 (m, 1H), 3.56 (d, $J = 16.5$ Hz, 1H), 3.40 (d, $J = 16.0$ Hz, 1H), 3.03-2.98 (m, 1H), 2.95 (s, 3H), 2.44 (s, 9H), 1.62 (d, $J = 6.8$ Hz, 1H), 1.18 (d, $J = 7.2$ Hz, 3H), 1.16 (d, $J = 7.2$ Hz, 3H), 1.09 (d, $J = 3.7$ Hz, 3H), 1.09 (d, $J = 3.7$ Hz, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 201.8, 168.2, 167.8, 163.6, 160.8, 119.3, 103.7, 63.0, 62.9, 52.1, 45.7, 38.4, 27.3, 21.3, 21.2, 18.9, 18.8. $^{11}\text{B NMR}$ (160 MHz, CDCl_3) δ 14.7, -2.8 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{20}\text{H}_{34}\text{B}_2\text{N}_2\text{O}_6\text{Na}, \text{M} + \text{Na}]^+$: 443.2495, found: 443.2496.



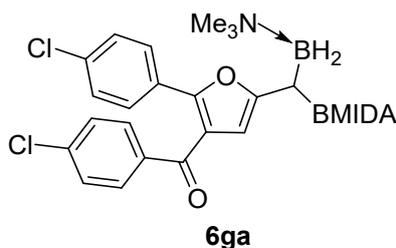
2-((4-(cyclopropanecarbonyl)-5-cyclopropylfuran-2-yl)(trimethylamine-boraneyl)methyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (6da). Green solid, m.p. 117-120 °C (68.2 mg, 82% yield). PE/EA = 1:4, $R_f = 0.20$. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 6.17 (s, 1H), 3.83 (d, $J = 7.0$ Hz, 1H), 3.80 (d, $J = 7.6$ Hz, 1H), 3.60 (d, $J = 16.1$ Hz, 1H), 3.38 (d, $J = 16.1$ Hz, 1H), 2.89 (s, 3H), 2.72-2.65 (m, 1H), 2.40 (s, 9H), 2.30-2.25 (m, 1H), 1.48 (d, $J = 6.5$ Hz, 1H), 1.06 (s, 2H), 0.94-0.84 (m, 6H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 197.2, 168.7, 168.3, 160.6, 158.6, 122.9, 103.7, 63.0, 62.8, 52.0, 45.6, 19.2, 11.1, 11.0, 9.7, 8.8, 8.6. $^{11}\text{B NMR}$ (160 MHz, CDCl_3) δ 14.7, -2.2 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{20}\text{H}_{30}\text{B}_2\text{N}_2\text{O}_6\text{Na}, \text{M} + \text{Na}]^+$: 439.2182, found: 439.2178.



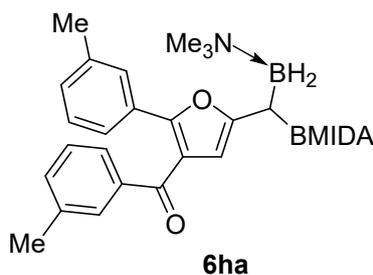
2-((4-benzoyl-5-phenylfuran-2-yl)(trimethylamine-boraneyl)methyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (6ea). Yellow solid, m.p. 115-116 °C (64.4 mg, 66% yield). PE/EA = 1:3, $R_f = 0.20$. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.80 (d, $J = 7.1$ Hz, 2H), 7.65 (d, $J = 7.3$ Hz, 2H), 7.49 (t, $J = 7.4$ Hz, 1H), 7.38 (t, $J = 7.8$ Hz, 2H), 7.25 (t, $J = 7.2$ Hz, 3H), 7.21 (t, $J = 7.2$ Hz, 1H), 6.23 (s, 1H), 3.73 (d, $J = 16.1$ Hz, 1H), 3.68 (d, $J = 16.6$ Hz, 1H), 3.65 (d, $J = 16.1$ Hz, 1H), 3.59 (d, $J = 16.5$ Hz, 1H), 3.03 (s, 3H), 2.51 (s, 9H), 1.75 (d, $J = 6.4$ Hz, 1H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 192.6, 168.0, 167.8, 152.7, 138.4, 132.8, 130.5, 129.8, 128.5, 128.4, 128.3, 126.8, 122.3, 108.4, 63.5, 63.2, 52.3, 46.2. $^{11}\text{B NMR}$ (160 MHz, CDCl_3) δ 14.6, -2.8 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{26}\text{H}_{30}\text{B}_2\text{N}_2\text{O}_6\text{Na}, \text{M} + \text{Na}]^+$: 511.2182, found: 511.2186.



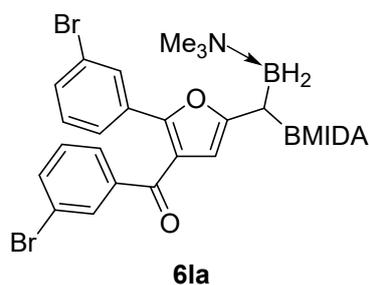
2-(Trimethylamine-boraneyl(4-(4-methylbenzoyl)-5-(p-tolyl)furan-2-yl)methyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (6fa). Yellow solid, m.p. 125-126 °C (74.3 mg, 72% yield). PE/EA = 1:3, $R_f = 0.20$. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.70 (d, $J = 8.1$ Hz, 2H), 7.56 (d, $J = 8.2$ Hz, 2H), 7.17 (d, $J = 8.0$ Hz, 2H), 7.06 (d, $J = 8.1$ Hz, 2H), 6.16 (s, 1H), 3.73 (t, $J = 16.9$ Hz, 2H), 3.58 (d, $J = 16.8$ Hz, 1H), 3.54 (d, $J = 16.2$ Hz, 1H), 2.97 (s, 3H), 2.47 (s, 9H), 2.37 (s, 3H), 2.29 (s, 3H), 1.69 (d, $J = 6.3$ Hz, 1H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 192.4, 168.4, 168.1, 162.6, 152.4, 143.5, 138.1, 135.9, 129.9, 129.1, 129.0, 127.8, 126.6, 121.8, 108.1, 63.2, 63.0, 52.2, 46.0, 21.7, 21.4, 19.9. $^{11}\text{B NMR}$ (160 MHz, CDCl_3) δ 14.1, -2.5 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{28}\text{H}_{34}\text{B}_2\text{N}_2\text{O}_6\text{Na}, \text{M} + \text{Na}]^+$: 539.2495, found: 539.2498.



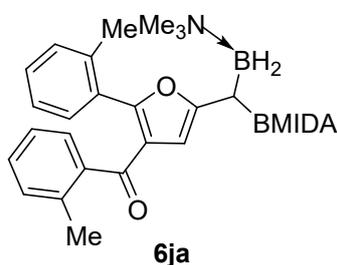
2-(Trimethylamine-boraneyl(4-(4-chlorobenzoyl)-5-(4-chlorophenyl)furan-2-yl)methyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (6ga). Yellow solid, m.p. 133-134 °C (69.1 mg, 62% yield). PE/EA = 1:1, $R_f = 0.20$. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.23 (d, $J = 8.5$ Hz, 2H), 7.63 (d, $J = 8.7$ Hz, 2H), 7.36 (d, $J = 8.5$ Hz, 2H), 7.25 (d, $J = 8.4$ Hz, 2H), 6.18 (s, 1H), 3.80 (d, $J = 11.4$ Hz, 1H), 3.77 (d, $J = 11.5$ Hz, 1H), 3.64 (d, $J = 9.7$ Hz, 1H), 3.61 (d, $J = 9.8$ Hz, 1H), 3.00 (s, 3H), 2.49 (s, 9H), 1.71 (d, $J = 6.1$ Hz, 1H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 191.1, 168.2, 168.0, 163.6, 151.6, 139.3, 136.7, 134.2, 131.2, 128.8, 128.7, 128.1, 122.2, 108.2, 63.5, 63.2, 52.2, 46.1, 19.9. $^{11}\text{B NMR}$ (160 MHz, CDCl_3) δ 14.1, -2.5 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{26}\text{H}_{28}\text{B}_2\text{Cl}_2\text{N}_2\text{O}_6\text{Na}, \text{M} + \text{Na}]^+$: 579.1403, found: 579.1403.



2-(Trimethylamine-borane(4-(3-methylbenzoyl)-5-(*m*-tolyl)furan-2-yl)methyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (6ha). Yellow solid, m.p. 114-115 °C (82.6 mg, 80% yield). PE/EA = 1:3, $R_f = 0.20$. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.60 (s, 1H), 7.55 (d, $J = 7.6$ Hz, 1H), 7.43 (d, $J = 7.0$ Hz, 2H), 7.28 (d, $J = 7.5$ Hz, 1H), 7.23 (m, 1H), 7.14 (m, 1H), 7.01 (d, $J = 7.4$ Hz, 1H), 6.20 (s, 1H), 3.73 (t, $J = 16.1$ Hz, 2H), 3.58 (d, $J = 16.5$ Hz, 2H), 3.00 (s, 3H), 2.49 (s, 9H), 2.32 (s, 3H), 2.25 (s, 3H), 1.73 (d, $J = 6.0$ Hz, 1H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 192.9, 168.2, 163.0, 152.3, 138.5, 138.1, 138.0, 133.4, 130.4, 130.2, 129.0, 128.3, 128.2, 127.5, 127.1, 124.0, 122.4, 108.2, 108.1, 63.4, 63.1, 52.2, 46.1, 21.5, 21.3, 20.0. $^{11}\text{B NMR}$ (160 MHz, CDCl_3) δ 14.6, -2.8 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{28}\text{H}_{34}\text{B}_2\text{N}_2\text{O}_6\text{Na}, \text{M} + \text{Na}]^+$: 539.2495, found: 539.2496.

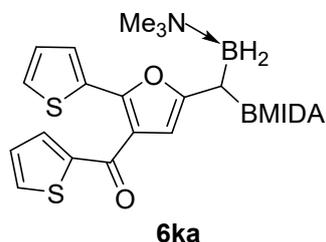


2-(Trimethylamine-borane(4-(3-bromobenzoyl)-5-(3-bromophenyl)furan-2-yl)methyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (6la). Yellow solid, m.p. 127-128 °C (62.0 mg, 48% yield). PE/EA = 1:2, $R_f = 0.20$. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.88 (s, 1H), 7.82 (s, 1H), 7.69 (d, $J = 7.7$ Hz, 1H), 7.67-7.55 (m, 2H), 7.50 (d, $J = 7.9$ Hz, 1H), 7.27 (t, $J = 7.9$ Hz, 1H), 7.15 (t, $J = 8.0$ Hz, 1H), 6.21 (s, 1H), 3.81-3.73 (m, 2H), 3.70-3.61 (m, 2H), 3.00 (s, 3H), 2.50 (s, 9H), 1.73 (d, $J = 5.1$ Hz, 1H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 190.7, 168.1, 168.0, 151.3, 140.2, 135.6, 132.6, 131.3, 130.2, 129.6, 122.6, 122.5, 122.4, 108.2, 63.5, 63.3, 52.2, 46.2, 19.9. $^{11}\text{B NMR}$ (160 MHz, CDCl_3) δ 14.1, -3.2 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{23}\text{H}_{16}\text{BBr}_2\text{NO}_6, \text{M} - \text{Me}_3\text{NBH}_2]^+$: 571.9516, found: 571.9518.

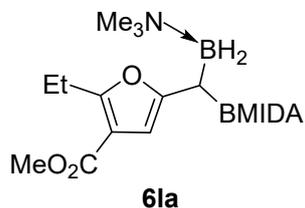


2-(Trimethylamine-borane(4-(2-methylbenzoyl)-5-(*o*-tolyl)furan-2-yl)methyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (6ja). Yellow solid, m.p. 117-118 °C (53.7 mg, 52% yield). PE/EA = 1:3, $R_f = 0.20$. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.13 (d, $J = 7.6$ Hz, 1H), 7.11-7.04 (m, 3H), 7.01 (d, $J = 7.7$ Hz, 1H), 6.99 (d, $J = 7.6$ Hz, 1H), 6.93-6.87 (m, 2H), 6.28 (s, 1H), 3.78-3.59 (m, 4H), 2.97 (s, 3H), 2.49 (s, 9H), 2.32 (s, 3H), 2.25 (s, 3H), 1.68 (d, $J = 5.7$ Hz, 1H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3):

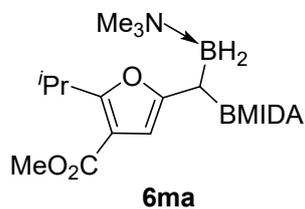
δ 193.9, 168.2, 168.1, 164.1, 156.0, 139.3, 137.3, 136.4, 130.8, 130.7, 130.4, 130.1, 130.0, 128.9, 128.6, 125.1, 125.0, 124.8, 105.2, 63.6, 63.2, 52.1, 46.3, 20.4, 20.0. **¹¹B NMR** (160 MHz, CDCl₃) δ 14.1, -3.6 (bs). **HRMS** (ESI, m/z) Calculated for [C₂₈H₃₄B₂N₂O₆Na, M + Na]⁺: 539.2495, found: 539.2498.



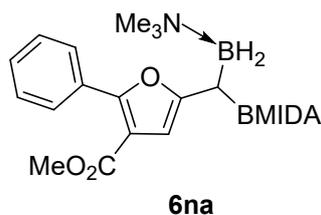
2-(Trimethylamine-boranyl(5-(thiophen-2-yl)-4-(thiophene-2-carbonyl)furan-2-yl)methyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (6ka). Yellow solid, m.p. 117-118 °C (76.0 mg, 76% yield). PE/EA = 1:2, R_f = 0.20. **¹H NMR** (500 MHz, CDCl₃): δ 7.84 (d, *J* = 3.6 Hz, 1H), 7.73 (d, *J* = 3.5 Hz, 1H), 7.63 (d, *J* = 4.8 Hz, 1H), 7.27 (d, *J* = 5.0 Hz, 1H), 7.13 (t, *J* = 4.6 Hz, 1H), 7.04 (t, *J* = 4.4 Hz, 1H), 6.45 (s, 1H), 3.76 (d, *J* = 11.7 Hz, 1H), 3.73 (d, *J* = 12.2 Hz, 1H), 3.67-3.61 (m, 2H), 3.08 (s, 3H), 2.50 (s, 9H), 1.75 (d, *J* = 6.6 Hz, 1H). **¹³C NMR** (125 MHz, CDCl₃): δ 182.2, 168.1, 167.8, 162.3, 149.1, 145.1, 133.7, 133.6, 132.7, 128.3, 127.9, 126.6, 126.4, 120.8, 107.3, 63.4, 63.2, 52.3, 46.2, 20.1. **¹¹B NMR** (160 MHz, CDCl₃) δ 15.9, -1.1 (bs). **HRMS** (ESI, m/z) Calculated for [C₂₂H₂₆B₂N₂O₆S₂Na, M + Na]⁺: 523.1310, found: 523.1314.



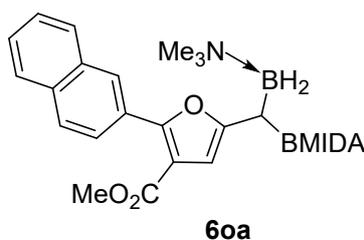
Methyl 5-(trimethylamine-boranyl(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)-2-ethylfuran-3-carboxylate (6la). Yellow solid, m.p. 103-104 °C (53.6 mg, 68% yield). PE/EA = 1:3, R_f = 0.20. **¹H NMR** (500 MHz, CDCl₃): δ 6.12 (s, 1H), 4.25-4.19 (m, 2H), 3.73 (t, *J* = 15.9 Hz, 2H), 3.56 (d, *J* = 6.1 Hz, 1H), 3.53 (d, *J* = 6.7 Hz, 1H), 2.97 (s, 3H), 2.48 (s, 3H), 2.45 (s, 9H), 1.57 (d, *J* = 5.9 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H). **¹³C NMR** (125 MHz, CDCl₃): δ 168.1, 168.0, 164.9, 161.7, 155.9, 114.1, 104.2, 63.3, 63.1, 60.0, 52.1, 46.0, 19.4, 14.5, 14.0. **¹¹B NMR** (160 MHz, CDCl₃) δ 14.7, -2.6 (bs). **HRMS** (ESI, m/z) Calculated for [C₁₇H₂₈B₂N₂O₇Na, M + Na]⁺: 417.1975, found: 417.1975.



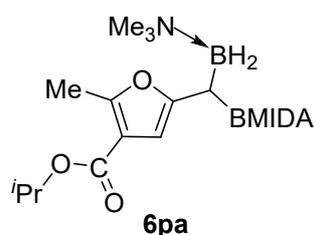
Methyl 5-(trimethylamine-boraneyl(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)-2-isopropylfuran-3-carboxylate (6ma). White solid, m.p. 99-100 °C (37.5 mg, 46% yield). PE/EA = 1:2, $R_f = 0.20$. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 6.06 (d, $J = 2.0$ Hz, 1H), 3.80-3.75 (m, 2H), 3.73 (s, 3H), 3.69-3.62 (m, 1H), 3.57 (d, $J = 16.5$ Hz, 1H), 3.44 (dd, $J = 16.0, 3.9$ Hz, 1H), 2.94 (s, 3H), 2.42 (s, 9H), 1.59 (d, $J = 6.3$ Hz, 1H), 1.18 (t, $J = 7.5$ Hz, 6H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 168.3, 168.1, 164.5, 161.6, 155.6, 114.5, 104.2, 67.3, 63.2, 63.1, 52.1, 46.0, 22.2, 19.4, 14.0. $^{11}\text{B NMR}$ (160 MHz, CDCl_3) δ 14.3, -2.5 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{18}\text{H}_{30}\text{B}_2\text{N}_2\text{O}_7\text{Na}, \text{M} + \text{Na}]^+$: 431.2132, found: 431.2132.



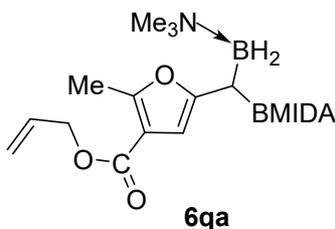
Methyl 5-(trimethylamine-boraneyl(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)-2-phenylfuran-3-carboxylate (6na). Yellow solid, m.p. 79-80 °C (57.5 mg, 65% yield). PE/EA = 1:2, $R_f = 0.20$. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.95 (d, $J = 7.6$ Hz, 2H), 7.34 (t, $J = 7.5$ Hz, 2H), 7.31 (t, $J = 7.4$ Hz, 1H), 6.35 (s, 1H), 3.78 (s, 3H), 3.70 (d, $J = 16.3$ Hz, 1H), 3.66 (d, $J = 7.2$ Hz, 1H), 3.60 (d, $J = 15.9$ Hz, 1H), 3.55 (d, $J = 16.5$ Hz, 1H), 2.97 (s, 3H), 2.48 (s, 9H), 1.71 (d, $J = 6.3$ Hz, 1H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 168.0, 167.9, 164.8, 163.0, 154.0, 130.4, 128.6, 128.3, 127.7, 114.7, 107.1, 63.4, 63.2, 52.2, 51.6, 46.2, 19.7. $^{11}\text{B NMR}$ (160 MHz, CDCl_3) δ 13.9, -3.1 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{21}\text{H}_{28}\text{B}_2\text{N}_2\text{O}_7\text{Na}, \text{M} + \text{Na}]^+$: 465.1975, found: 465.1975.



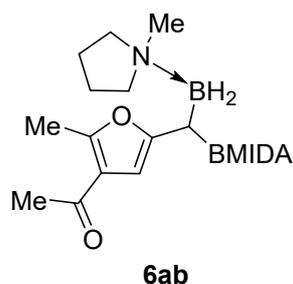
Methyl 5-(trimethylamine-boraneyl(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)-2-(naphthalen-2-yl)furan-3-carboxylate (6oa). Yellow solid, m.p. 135-136 °C (52.2 mg, 53% yield). PE/EA = 1:2, $R_f = 0.20$. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 8.52 (s, 1H), 8.05 (dd, $J = 8.6, 1.6$ Hz, 1H), 7.93-7.89 (m, 1H), 7.83 (d, $J = 8.8$ Hz, 1H), 7.82-7.79 (m, 1H), 7.50-7.44 (m, 2H), 6.41 (s, 1H), 3.82 (s, 3H), 3.67-3.61 (m, 3H), 3.52 (d, $J = 16.5$ Hz, 1H), 2.96 (s, 3H), 2.50 (s, 9H), 1.74 (d, $J = 6.0$ Hz, 1H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 168.0, 167.8, 164.9, 163.3, 154.1, 133.2, 133.1, 128.9, 127.8, 127.7, 127.6, 127.2, 126.7, 126.4, 125.3, 115.0, 107.4, 63.5, 63.2, 52.2, 51.6, 46.2, 19.9. $^{11}\text{B NMR}$ (160 MHz, CDCl_3) δ 14.4, -2.4 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{25}\text{H}_{30}\text{B}_2\text{N}_2\text{O}_7\text{Na}, \text{M} + \text{Na}]^+$: 515.2131, found: 515.2136.



Isopropyl 5-(trimethylamine-boranyl(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)-2-methylfuran-3-carboxylate (6pa). White solid, m.p. 94-95 °C (57.9 mg, 71% yield). PE/EA = 1:3, R_f = 0.20. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 6.10 (s, 1H), 5.13-5.04 (m, 1H), 3.77 (d, J = 11.2 Hz, 1H), 3.74 (d, J = 11.6 Hz, 1H), 3.56 (d, J = 8.7 Hz, 1H), 3.53 (d, J = 8.1 Hz, 1H), 2.97 (s, 3H), 2.46 (s, 3H), 2.45 (s, 9H), 1.55 (d, J = 6.0 Hz, 1H), 1.29 (s, 3H), 1.27 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 168.0, 167.8, 164.9, 163.3, 154.1, 133.2, 133.1, 128.9, 127.8, 127.7, 127.6, 127.2, 126.7, 126.4, 125.3, 115.0, 107.4, 63.5, 63.2, 52.2, 51.6, 46.2, 19.9. $^{11}\text{B NMR}$ (160 MHz, CDCl_3) δ 15.5, -2.3 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{18}\text{H}_{30}\text{B}_2\text{N}_2\text{O}_7\text{Na}, \text{M} + \text{Na}]^+$: 431.2131, found: 431.2130.

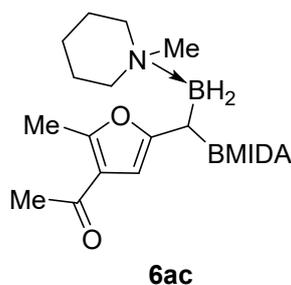


Allyl 5-(tributylamine-boranyl(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)-2-methylfuran-3-carboxylate (6qa). White solid, m.p. 89-90 °C (52.0 mg, 64% yield). PE/EA = 1:2, R_f = 0.20. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 6.13 (s, 1H), 6.01-5.93 (m, 1H), 5.34 (dd, J = 17.2, 1.4 Hz, 1H), 5.23 (dd, J = 10.5, 1.1 Hz, 1H), 4.67 (dd, J = 5.5, 0.8 Hz, 2H), 3.76 (d, J = 13.0 Hz, 1H), 3.73 (d, J = 13.2 Hz, 1H), 3.57 (d, J = 6.8 Hz, 1H), 3.53 (d, J = 7.5 Hz, 1H), 2.97 (s, 3H), 2.49 (s, 3H), 2.45 (s, 9H), 1.57 (d, J = 6.0 Hz, 1H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 168.2, 168.0, 164.5, 161.9, 156.2, 132.7, 118.0, 113.8, 104.1, 64.7, 63.4, 63.1, 52.1, 46.1, 19.3, 14.0. $^{11}\text{B NMR}$ (160 MHz, CDCl_3) δ 14.5, -2.3 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{18}\text{H}_{28}\text{B}_2\text{N}_2\text{O}_7\text{Na}, \text{M} + \text{Na}]^+$: 429.1975, found: 429.1973.

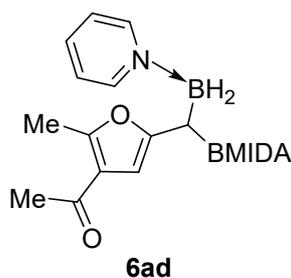


2-((4-Acetyl-5-methylfuran-2-yl)(1-methylpyrrolidine-boranyl)methyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (6ab). White solid, m.p. 95-96 °C (60.1 mg, 77% yield). PE/EA = 1:5, R_f

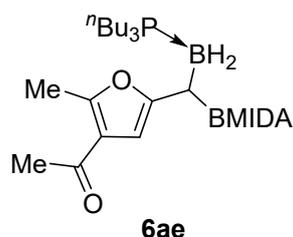
= 0.20. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 6.10 (s, 1H), 3.77 (d, $J = 9.2$ Hz, 1H), 3.74 (d, $J = 9.4$ Hz, 1H), 3.59 (d, $J = 16.6$ Hz, 1H), 3.54 (d, $J = 16.3$ Hz, 1H), 3.15-3.10 (m, 1H), 2.97 (s, 3H), 2.96-2.89 (m, 1H), 2.80-2.74 (m, 1H), 2.57-2.52 (m, 1H), 2.49 (s, 3H), 2.44 (s, 3H), 2.32 (s, 3H), 1.98-1.86 (m, 4H), 1.58 (d, $J = 6.1$ Hz, 1H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 195.0, 168.2, 168.0, 162.1, 154.8, 122.8, 103.8, 63.3, 63.1, 61.6, 61.0, 47.7, 46.0, 29.3, 22.8, 22.2, 19.5, 14.6. $^{11}\text{B NMR}$ (160 MHz, CDCl_3) δ 14.5, -3.9 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{18}\text{H}_{28}\text{B}_2\text{N}_2\text{O}_6\text{Na}, \text{M} + \text{Na}]^+$: 413.2025, found: 413.2024.



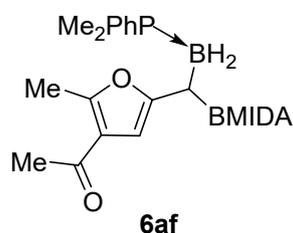
2-((4-Acetyl-5-methylfuran-2-yl)(1-methylpiperidine-boranyl)methyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (6ac). White solid, m.p. 98-99 °C (60.6 mg, 75% yield). PE/EA = 1:6, $R_f = 0.20$. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 6.09 (s, 1H), 3.77 (d, $J = 8.9$ Hz, 1H), 3.74 (d, $J = 9.4$ Hz, 1H), 3.57 (d, $J = 11.9$ Hz, 1H), 3.54 (d, $J = 11.4$ Hz, 1H), 2.97 (s, 3H), 2.89-2.77 (m, 2H), 2.74-2.66 (m, 1H), 2.58-2.52 (m, 1H), 2.48 (s, 3H), 2.39 (s, 3H), 2.32 (s, 3H), 1.74-1.69 (m, 1H), 1.66-1.53 (s, 5H), 1.45-1.38 (m, 1H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 195.0, 168.2, 168.1, 162.3, 154.8, 122.7, 103.8, 63.4, 63.2, 58.3, 58.2, 46.1, 46.0, 29.3, 20.2, 14.6. $^{11}\text{B NMR}$ (160 MHz, CDCl_3) δ 14.7, -2.4 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{19}\text{H}_{30}\text{B}_2\text{N}_2\text{O}_6\text{Na}, \text{M} + \text{Na}]^+$: 427.2182, found: 427.2184.



2-((4-Acetyl-5-methylfuran-2-yl)(pyridine-boranyl)methyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (6ad). Green solid, m.p. 139-140 °C (26.9 mg, 35% yield). PE/EA = 1:4, $R_f = 0.20$. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 8.44 (d, $J = 5.4$ Hz, 2H), 7.94 (t, $J = 7.7$ Hz, 1H), 7.47 (t, $J = 7.1$ Hz, 2H), 5.87 (s, 1H), 3.78-3.71 (m, 3H), 3.42 (d, $J = 16.0$ Hz, 1H), 2.98 (s, 3H), 2.37 (s, 3H), 2.28 (s, 3H), 1.71 (s, 1H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 195.1, 168.1, 167.7, 160.8, 154.9, 147.4, 139.9, 125.2, 122.5, 103.1, 62.7, 62.6, 45.6, 14.4. $^{11}\text{B NMR}$ (160 MHz, CDCl_3) δ 20.1, -11.5 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{18}\text{H}_{22}\text{B}_2\text{N}_2\text{O}_6\text{Na}, \text{M} + \text{Na}]^+$: 407.1556, found: 407.1557.



2-((4-Acetyl-5-methylfuran-2-yl)(tributylphosphane-boraneyl)methyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (6ae). White solid, m.p. 47-48 °C (58.8 mg, 58% yield). PE/EA = 1:5, R_f = 0.20. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 6.07 (s, 1H), 3.73 (d, J = 13.2 Hz, 3H), 3.59 (d, J = 15.9 Hz, 1H), 3.02 (s, 3H), 2.49 (s, 3H), 2.32 (s, 3H), 1.45-1.29 (m, 18H), 0.88 (t, J = 6.6 Hz, 10H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 194.9, 168.0, 167.7, 162.0, 161.9, 154.4, 122.7, 103.5, 63.2, 63.0, 45.4, 29.3, 24.6, 24.5, 21.0, 20.7, 14.5, 13.7. $^{11}\text{B NMR}$ (160 MHz, CDCl_3) δ 14.6, -29.0 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{25}\text{H}_{44}\text{B}_2\text{NO}_6\text{PNa}, \text{M} + \text{Na}]^+$: 531.2984, found: 530.2986.



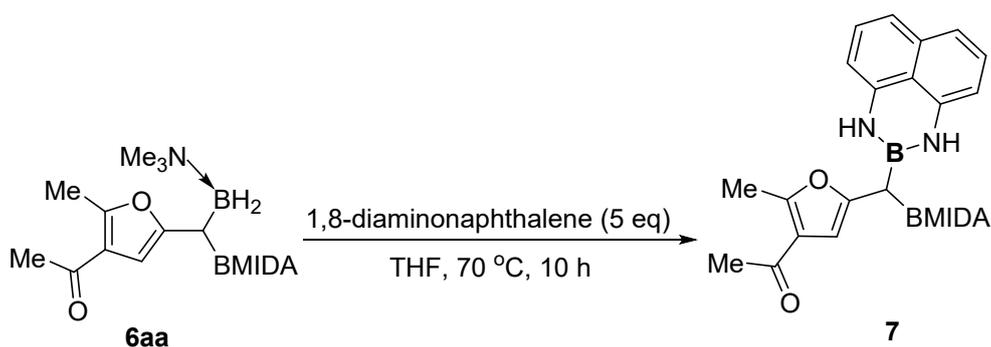
2-((4-Acetyl-5-methylfuran-2-yl)(dimethyl(phenyl)phosphane-boraneyl)methyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (6af). White solid, m.p. 77-78 °C (45.2 mg, 51% yield). PE/EA = 1:5, R_f = 0.20. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.48 (t, J = 8.6 Hz, 2H), 7.44-7.36 (m, 3H), 5.88 (s, 1H), 3.78-3.70 (m, 3H), 3.49 (d, J = 16.1 Hz, 1H), 2.96 (s, 3H), 2.34 (s, 3H), 2.22 (s, 3H), 1.60-1.56 (m, 1H), 1.45 (d, J = 10.2 Hz, 3H), 1.40 (d, J = 10.3 Hz, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 194.9, 168.1, 167.8, 161.0, 160.9, 154.4, 130.6, 130.5, 128.8, 128.7, 122.4, 103.8, 63.0, 62.9, 45.3, 29.2, 14.4, 11.0, 10.8, 10.5, 10.2. $^{11}\text{B NMR}$ (160 MHz, CDCl_3) δ 14.8, -24.9 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{21}\text{H}_{28}\text{B}_2\text{NO}_6\text{PNa}, \text{M} + \text{Na}]^+$: 466.1732, found: 466.1731.

6. Large-scale Experiments and Synthetic Transformations

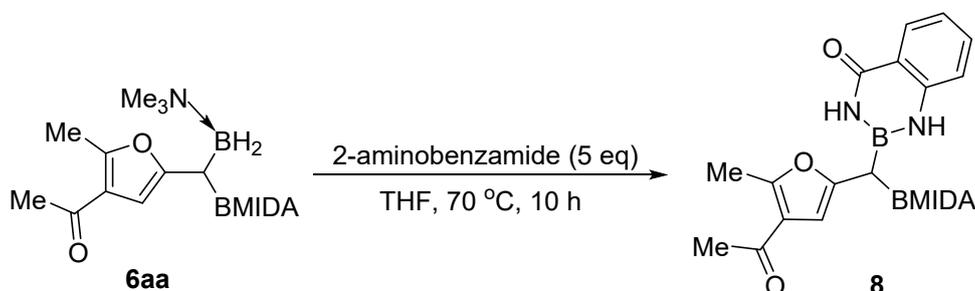
(a) 10-Fold Scale Experiment

Under argon atmosphere, a pre-dried 10.0 mL Schlenk tube was charged with stirring bar, CuCl (39.6 mg, 0.4 mmol, 0.2 eq.). Then 10.0 mL DCE solution of **4a** (582.1 mg, 2.0 mmol, 1.0 eq.) and borane adduct **5a** (583.6 mg, 8.0 mmol, 4 eq.) was injected into the Schlenk tube in one portion. The resulting mixture was stirred at 50 °C for 16 h. The product was purified by flash chromatography on silica gel to give the analytical pure product **6aa** (626.1 mg, 86% yield).

(b) Synthetic transformation of product **6aa**

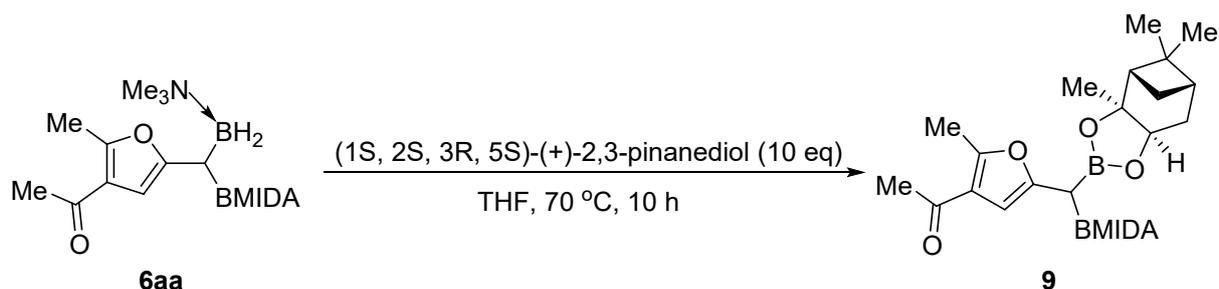


Under argon atmosphere, **6aa** (36.4 mg, 0.1 mmol, 1.0 eq.), 1,8-diaminonaphthalene (79.1 mg, 0.5 mmol, 5.0 eq.), and THF (1.0 mL) were introduced to a Schlenk tube and stirred at 70 °C for 10 h. Then the resulting mixture was filtered through funnel and washed the crude product with DCM. The solvent was removed in vacuo to give product **7** (purple solid, m.p. 212-213 °C, 26.6 mg, 58% yield). $^1\text{H NMR}$ (500 MHz, DMSO- d_6): δ 7.30 (s, 2H), 7.04 (s, 2H), 6.88 (d, $J = 6.7$ Hz, 2H), 6.48 (d, $J = 5.9$ Hz, 2H), 6.43 (s, 1H), 4.34 (d, $J = 17.1$ Hz, 1H), 4.19 (d, $J = 16.9$ Hz, 1H), 4.01 (d, $J = 17.0$ Hz, 1H), 3.62 (d, $J = 16.8$ Hz, 1H), 2.84 (s, 3H), 2.46 (s, 3H), 2.33 (s, 3H), 2.20 (s, 1H). $^{13}\text{C NMR}$ (125 MHz, DMSO- d_6): δ 193.8, 168.8, 168.5, 154.9, 154.1, 141.9, 135.9, 127.6, 122.4, 119.2, 116.2, 105.4, 104.9, 62.3, 62.1, 46.1, 29.2, 14.0. $^{11}\text{B NMR}$ (160 MHz, DMSO- d_6) δ 22.1, 9.2 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{24}\text{H}_{24}\text{BN}_3\text{O}_6, \text{M} + \text{H}]^+$: 460.1846, found: 460.1848.

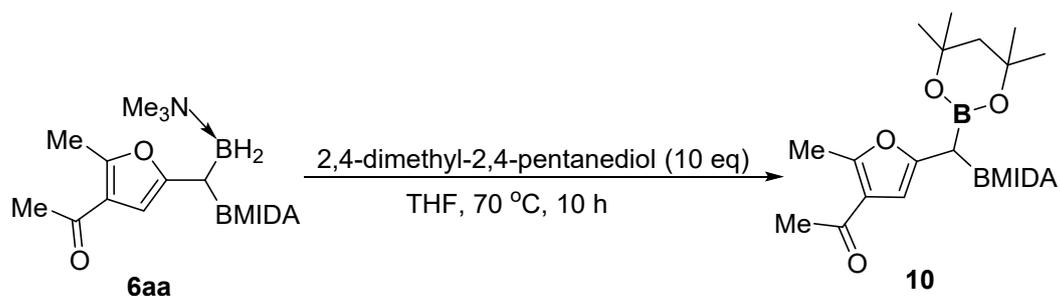


A pre-dried 10.0 mL Schlenk tube was charged with stirring bar, **6aa** (36.4 mg, 0.1 mmol, 1.0 eq.), 2-aminobenzamide (68.1 mg, 0.5 mmol, 5.0 eq.). Then, THF (1.0 mL) was added and the reaction mixture was stirred at 70 °C for 10 h. Subsequently, solvent was removed by rotary evaporation instrument and the residue was transferred to a column and purified by flash chromatography on silica

gel (PE/EA = 1:1, $R_f = 0.20$) to give the analytical pure product **8** (white solid, m.p. 259-260 °C, 34.1 mg, 78% yield). $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$): δ 8.63 (s, 1H), 8.43 (s, 1H), 7.95 (d, $J = 7.3$ Hz, 1H), 7.51 (d, $J = 6.7$ Hz, 1H), 7.41 (d, $J = 7.5$ Hz, 1H), 7.06 (m, 1H), 6.48 (s, 1H), 4.35 (d, $J = 17.1$, 1H), 4.22 (d, $J = 17.0$ Hz, 1H), 4.02 (d, $J = 17.2$ Hz, 1H), 3.68 (d, $J = 17.0$ Hz, 1H), 2.85 (s, 3H), 2.45 (s, 4H), 2.33 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, $\text{DMSO-}d_6$): δ 193.8, 168.6, 168.5, 165.4, 155.1, 153.3, 145.2, 133.3, 127.8, 122.4, 120.7, 118.3, 118.1, 105.5, 62.3, 62.1, 46.3, 29.1, 18.1, 14.0. $^{11}\text{B NMR}$ (160 MHz, $\text{DMSO-}d_6$) δ 20.8, 12.1 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{20}\text{H}_{22}\text{B}_2\text{N}_3\text{O}_7, \text{M} + \text{H}]^+$: 438.1639, found: 438.1636.

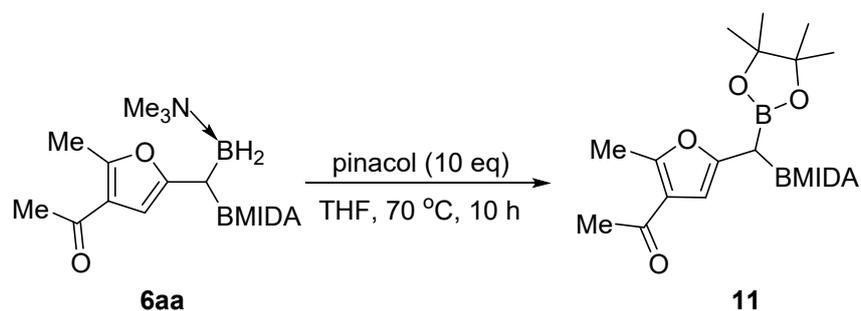


A pre-dried 10.0 mL Schlenk tube was charged with stirring bar, **6aa** (36.4 mg, 0.1 mmol, 1.0 eq.), (1S, 2S, 3R, 5S)-(+)-2,3-pinanediol (170.3 mg, 1.0 mmol, 10.0 eq.). Then, THF (1.0 mL) was added and the reaction mixture was stirred at 70 °C for 10 h. Subsequently, solvent was removed by rotary evaporation instrument and the residue was transferred to a column and purified by flash chromatography on silica gel (PE/EA = 1:4, $R_f = 0.20$) to give the analytical pure product **9** (white solid, m.p. 113-114 °C, 41.9 mg, 89% yield). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 6.27 (d, $J = 3.7$ Hz, 1H), 4.36-4.29 (m, 1H), 3.91 (d, $J = 8.1$ Hz, 1H), 3.88 (d, $J = 7.7$ Hz, 1H), 3.73 (q, $J = 5.3$ Hz, 1H), 3.58 (q, $J = 8.8$ Hz, 1H), 2.97 (d, $J = 9.2$ Hz, 3H), 2.48 (s, 3H), 2.33 (s, 3H), 2.33-2.28 (m, 1H), 2.46-2.17 (m, 2H), 2.03 (q, $J = 5.0$ Hz, 1H), 1.89 (s, 1H), 1.85-1.80 (m, 1H), 1.37 (d, $J = 5.4$ Hz, 3H), 1.27 (d, $J = 2.8$ Hz, 3H), 1.18 (q, $J = 11.1$ Hz, 1H), 0.82 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 194.7, 167.5, 167.4, 167.3, 167.2, 155.9, 152.3, 152.2, 122.8, 106.4, 86.4, 86.5, 63.1, 63.0, 62.9, 51.3, 51.2, 46.3, 39.5, 39.4, 38.3, 35.5, 35.4, 29.3, 28.7, 28.6, 27.1, 26.4, 24.1, 14.4. $^{11}\text{B NMR}$ (160 MHz, CDCl_3) δ 22.4, 12.1 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{23}\text{H}_{32}\text{B}_2\text{NO}_8, \text{M} + \text{H}]^+$: 427.2309, found: 427.2300.

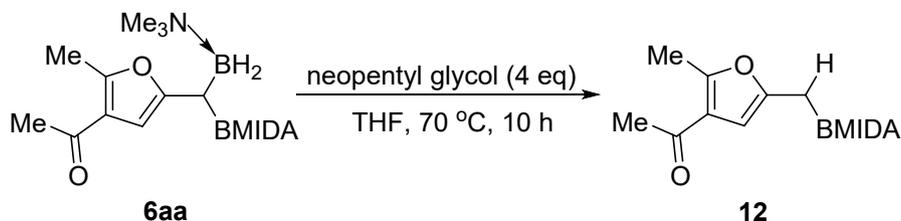


A pre-dried 10.0 mL Schlenk tube was charged with stirring bar, **6aa** (36.4 mg, 0.1 mmol, 1.0 eq.),

2,4-dimethyl-2,4-pentanediol (132.2 mg, 1.0 mmol, 10.0 eq.). Then, THF (1.0 mL) was added and the reaction mixture was stirred at 70 °C for 10 h. Subsequently, solvent was removed by rotary evaporation instrument and the residue was transferred to a column and purified by flash chromatography on silica gel (PE/EA = 1:3, R_f = 0.20) to give the analytical pure product **10** (white solid, m.p. 79-80 °C, 40.3 mg, 93% yield). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 6.23 (s, 1H), 3.87 (d, J = 5.1 Hz, 1H), 3.85 (d, J = 5.0 Hz, 1H), 3.68 (d, J = 16.7 Hz, 1H), 3.63 (d, J = 16.6, 1H), 2.94 (s, 3H), 2.46 (s, 3H), 2.32 (s, 3H), 2.03 (s, 1H), 1.82 (s, 2H), 1.32 (d, J = 6.3 Hz, 12H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 194.9, 167.6, 167.5, 155.4, 153.8, 155.9, 122.7, 105.9, 71.6, 63.2, 63.1, 48.7, 46.5, 31.7, 31.6, 29.3, 19.2, 14.4. $^{11}\text{B NMR}$ (160 MHz, CDCl_3) δ 18.5, 12.3 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{20}\text{H}_{30}\text{B}_2\text{NO}_8, \text{M} + \text{H}]^+$: 434.2152, found: 434.2147.

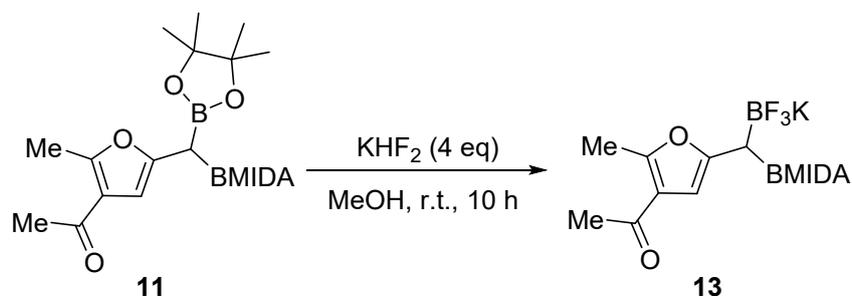


A pre-dried 10.0 mL Schlenk tube was charged with stirring bar, **6aa** (36.4 mg, 0.1 mmol, 1.0 eq.), pinacol (118.2 mg, 1 mmol, 10.0 eq.). Then, THF (1.0 mL) was added and the reaction mixture was stirred at 70 °C for 10 h. Subsequently, solvent was removed by rotary evaporation instrument and the residue was transferred to a column and purified by flash chromatography on silica gel (PE/EA = 1:4, R_f = 0.20) to give the analytical pure product **11** (white solid, m.p. 159-160 °C, 36.9 mg, 88% yield). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 6.26 (s, 1H), 3.90 (dd, J = 16.9, 3.2 Hz, 2H), 3.72 (d, J = 16.8 Hz, 1H), 3.64 (d, J = 16.5 Hz, 1H), 2.97 (s, 3H), 2.47 (s, 3H), 2.33 (s, 3H), 2.17 (s, 1H), 1.24 (d, J = 2.4 Hz, 12H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 194.7, 167.6, 167.3, 155.9, 152.3, 122.8, 106.4, 84.2, 63.1, 63.0, 46.4, 29.3, 24.8, 24.7, 15.0, 14.4. $^{11}\text{B NMR}$ (160 MHz, CDCl_3) δ 22.5, 22.1 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{19}\text{H}_{28}\text{B}_2\text{NO}_8, \text{M} + \text{H}]^+$: 420.1996, found: 420.1991.

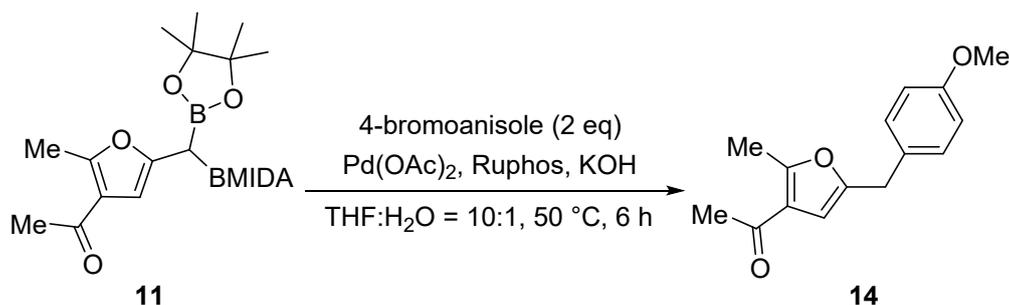


A pre-dried 10.0 mL Schlenk tube was charged with stirring bar, **6aa** (36.4 mg, 0.1 mmol, 1.0 eq.), neopentyl glycol (41.7 mg, 0.4 mmol, 4.0 eq.). Then, THF (1.0 mL) was added and the reaction mixture was stirred at 70 °C for 10 h. Subsequently, solvent was removed by rotary evaporation instrument and the residue was transferred to a column and purified by flash chromatography on silica

gel (PE/EA = 5:1, R_f = 0.20) to give the analytical pure product **12** (white solid, m.p. 176-177 °C, 17.0 mg, 58% yield). $^1\text{H NMR}$ (500 MHz, CD_3CN): δ 6.24 (s, 1H), 3.98 (d, J = 17.0 Hz, 2H), 3.75 (d, J = 17.0 Hz, 2H), 2.93 (s, 3H), 2.47 (s, 3H), 2.32 (s, 3H), 2.13 (s, 2H). $^{13}\text{C NMR}$ (125 MHz, CD_3CN): δ 195.0, 168.9, 156.8, 153.3, 123.3, 106.9, 63.2, 47.0, 29.5, 14.4. $^{11}\text{B NMR}$ (160 MHz, CD_3CN) δ 11.7 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{13}\text{H}_{20}\text{BN}_2\text{O}_6, \text{M} + \text{NH}_4]^+$: 311.1409, found: 311.1417.

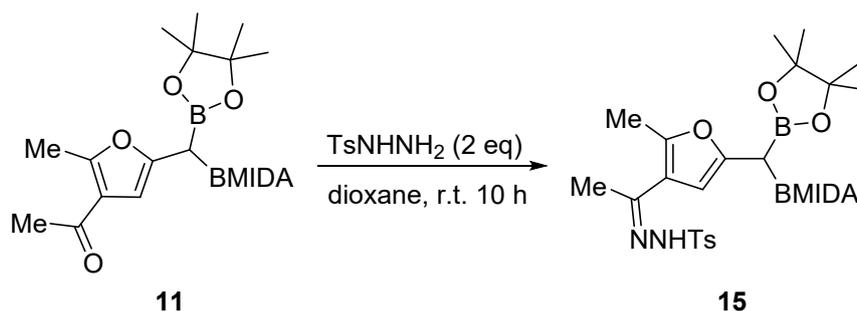


Under argon atmosphere, **11** (41.9 mg, 0.1 mmol, 1.0 eq.), aq KHF_2 solution (4.5 M solution, 4.0 eq.), and THF (1.0 mL) were introduced to a Schlenk tube and stirred at r.t for 10 h. Then the resulting mixture was filtered through funnel and washed the crude product with DCM. The solvent was removed in vacuo to give product **13** (white solid, m.p. 191-192 °C, 37.9 mg, 95% yield). $^1\text{H NMR}$ (500 MHz, $\text{DMSO}-d_6$): δ 5.87 (s, 1H), 4.02 (d, J = 16.9 Hz, 1H), 3.93 (d, J = 16.3 Hz, 1H), 3.82 (d, J = 16.3 Hz, 1H), 3.69 (d, J = 16.9 Hz, 1H), 2.92 (s, 3H), 2.41 (s, 3H), 2.23 (s, 3H), 1.21 (d, J = 5.3 Hz, 1H). $^{13}\text{C NMR}$ (125 MHz, $\text{DMSO}-d_6$): δ 193.8, 169.4, 169.0, 161.6, 152.5, 122.2, 101.9, 62.1, 61.6, 29.0, 14.2. $^{11}\text{B NMR}$ (160 MHz, CD_3CN) δ 4.9, 0.6 (bs). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{13}\text{H}_{15}\text{B}_2\text{F}_2\text{NO}_6, \text{M} - \text{K}]^+$: 360.1038, found: 360.1034.



A pre-dried 10.0 mL Schlenk tube was charged with stirring bar, **11** (41.9 mg, 0.1 mmol, 1.0 eq.), $\text{Pd}(\text{OAc})_2$ (4.5 mg, 0.02 mmol, 0.1 eq.), Ruphos (18.7 mg, 0.04 mmol, 0.2 eq.), 4-bromoanisole (37.4 mg, 0.2 mmol, 2.0 eq.). Then, the solution (THF: H_2O = 10:1, 1.0 mL) was added and the reaction mixture was stirred at 50 °C for 6 h. Subsequently, solvent was removed by rotary evaporation instrument and the residue was transferred to a column and purified by flash chromatography on silica gel (PE/EA = 10:1, R_f = 0.20) to give the analytical pure product **14** (yellow oil, 15.4 mg, 63% yield). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.15 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 6.16 (s, 1H), 3.84 (s, 2H), 3.80 (s, 3H), 2.53 (s, 3H), 2.34 (s, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 194.4, 158.6, 157.6,

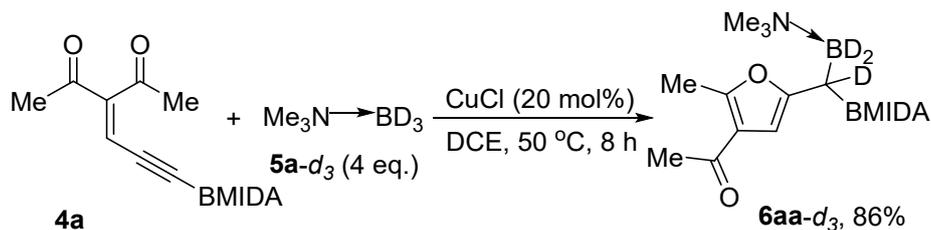
129.8, 129.5, 122.2, 114.2, 106.7, 55.4, 33.5, 29.2, 14.5. **HRMS** (ESI, m/z) Calculated for $[C_{15}H_{17}O_3, M + H]^+$: 245.1172, found: 245.1166.



A pre-dried 10.0 mL Schlenk tube was charged with stirring bar, **69** (41.9 mg, 0.1 mmol, 1.0 eq.), TsNHNH₂ (37.2 mg, 0.2 mmol, 2 eq.). Then, the dioxane (1.0 mL) was added and the reaction mixture was stirred at rt for 8 h. Then the resulting mixture was filtered through funnel and washed the crude product with DCM. The solvent was removed in vacuo to give product **72** (white solid, m.p. 205-206 °C, 43.5 mg, 74% yield). **¹H NMR** (500 MHz, CD₃CN): δ 8.25 (s, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 5.98 (s, 1H), 3.94 (d, *J* = 11.5 Hz, 1H), 3.90 (d, *J* = 11.2 Hz, 1H), 3.81 (d, *J* = 17.0 Hz, 1H), 3.57 (d, *J* = 17.0 Hz, 1H), 2.90 (s, 3H), 2.40 (s, 3H), 2.21 (s, 3H), 2.18 (s, 1H), 2.00 (s, 3H), 1.21 (d, *J* = 3.5 Hz, 12H). **¹³C NMR** (125 MHz, CD₃CN): δ 169.1, 168.8, 153.7, 152.3, 149.6, 145.2, 136.9, 130.5, 129.1, 120.9, 106.2, 84.5, 63.7, 63.6, 47.2, 25.0, 24.9, 21.6, 16.1, 14.4. **¹¹B NMR** (160 MHz, CD₃CN) δ 33.7, 12.1 (bs). **HRMS** (ESI, m/z) Calculated for $[C_{26}H_{36}B_2N_3O_9S, M + H]^+$: 588.2353, found: 588.2351.

7. Control Experiments

(a) Deuterium-labelling experiment



A pre-dried 10.0 mL Schlenk tube was charged with stirring bar, CuCl (4.0 mg, 0.02 mmol, 0.2 eq.), **4a** (58.2 mg, 0.2 mmol, 1.0 eq.). Then, DCE (2.0 mL) was added and the mixture was stirred at room temperature. The solution added successively with **5a-d₃** (60.8 mg, 0.8 mmol, 4.0 eq.). Then, the reaction mixture was stirred at 50 °C for 8 h. Subsequently, solvent was removed by rotary evaporation instrument and the residue was transferred to a column and purified by flash chromatography on silica gel (EA, $R_f = 0.20$) to give the analytical pure product **6aa-d₃** (light green solid, m.p. 110-111 °C, 63.1 mg, 86% yield, **Figure S3**). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 6.08 (s, 1H), 3.82 (d, $J = 6.1$ Hz, 1H), 3.78 (d, $J = 6.6$ Hz, 1H), 3.61 (d, $J = 16.7$ Hz, 1H), 3.47 (d, $J = 16.2$ Hz, 1H), 2.96 (s, 3H), 2.47 (s, 3H), 2.43 (s, 9H), 2.31 (s, 3H). **HRMS** (ESI, m/z) Calculated for $[\text{C}_{16}\text{H}_{24}\text{D}_3\text{B}_2\text{N}_2\text{O}_6, \text{M} + \text{H}]^+$: 368.2238, found: 368.2238.

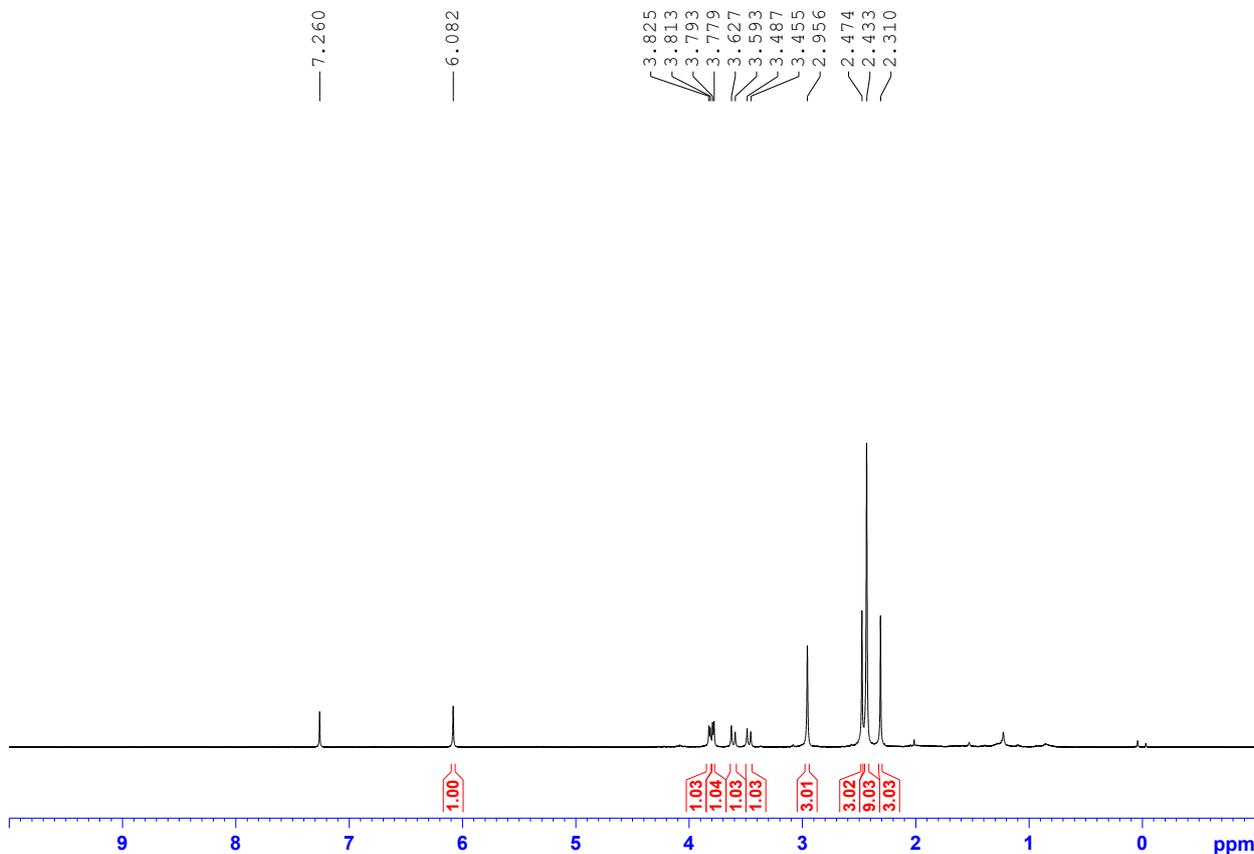
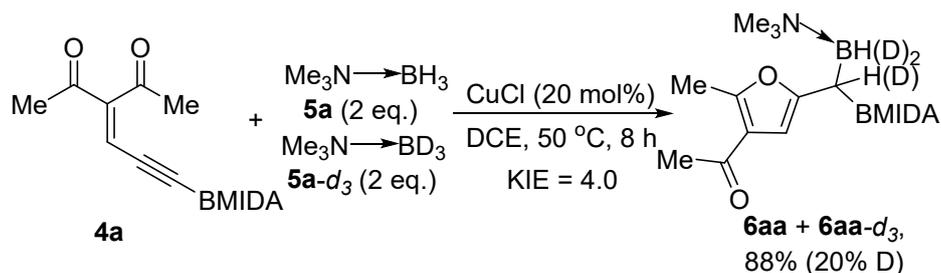


Figure S3. $^1\text{H NMR}$ spectrum of **9-d₃**

(b) Kinetic isotopic effect experiment



A pre-dried 10.0 mL Schlenk tube was charged with stirring bar, CuCl (4.0 mg, 0.02 mmol, 0.2 eq.), **4a** (58.2 mg, 0.2 mmol, 1.0 eq.). Then, DCE (2.0 mL) was added and the mixture was stirred at room temperature. The solution added successively with **5a** (29.2 mg, 0.4 mmol, 2.0 eq.), **5a-d₃** (30.4 mg, 0.4 mmol, 2.0 eq.). Then, the reaction mixture was stirred at 50 °C for 8 h. Subsequently, solvent was removed by rotary evaporation instrument and the residue was transferred to a column and purified by flash chromatography on silica gel (EA, $R_f = 0.20$) to give the mixture product **6aa** and **6aa-d₃** (light green solid, 64.7 mg, 88% yield, 20%D, **Figure S4**). **¹H NMR** (500 MHz, CDCl_3): δ 6.07 (s, 1H), 3.82 (d, $J = 7.3$ Hz, 1H), 3.79 (d, $J = 7.4$ Hz, 1H), 3.61 (d, $J = 16.8$ Hz, 1H), 3.46 (d, $J = 16.7$ Hz, 1H), 2.95 (s, 3H), 2.47 (s, 3H), 2.43 (s, 9H), 2.30 (s, 3H), 1.54 (d, $J = 6.1$ Hz, 0.8H).

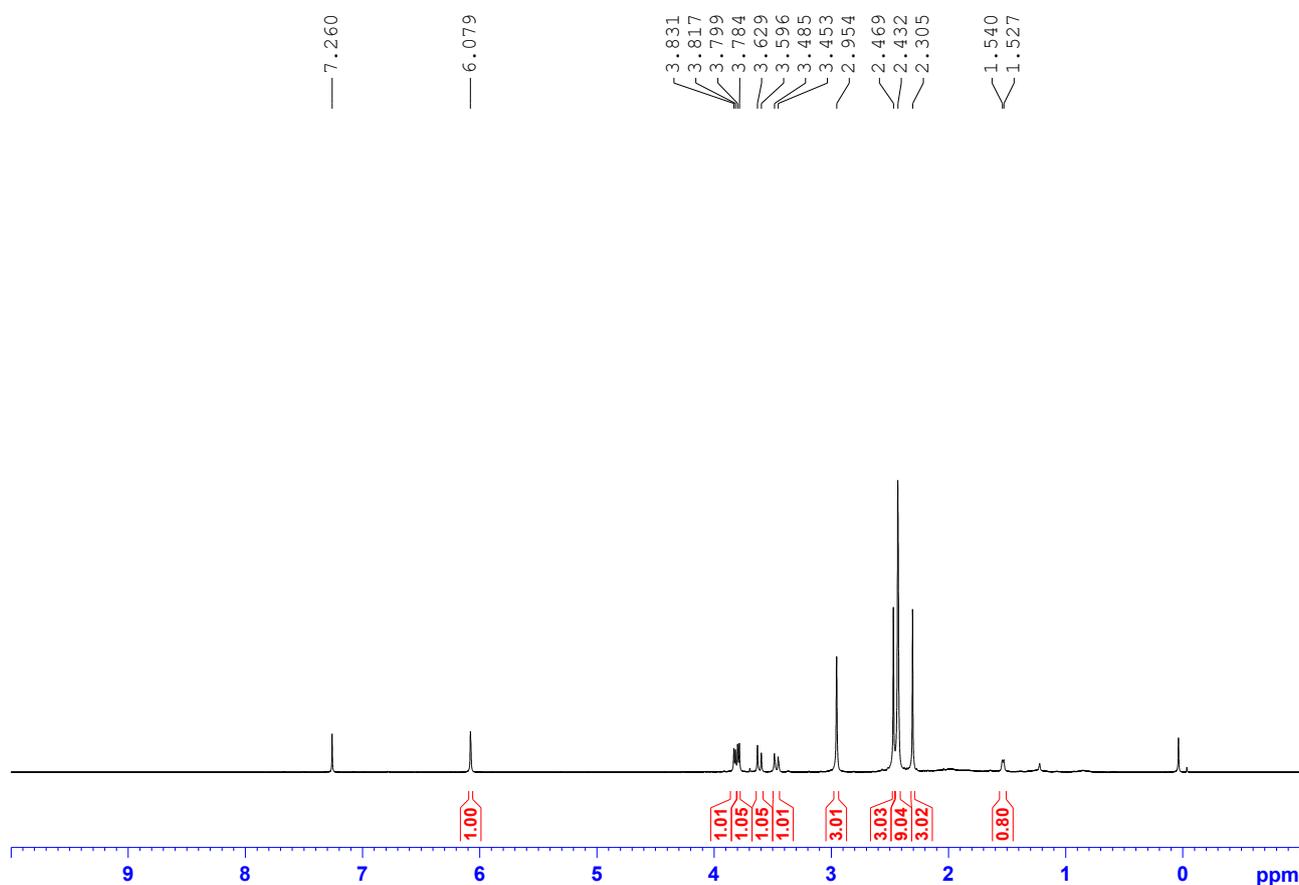
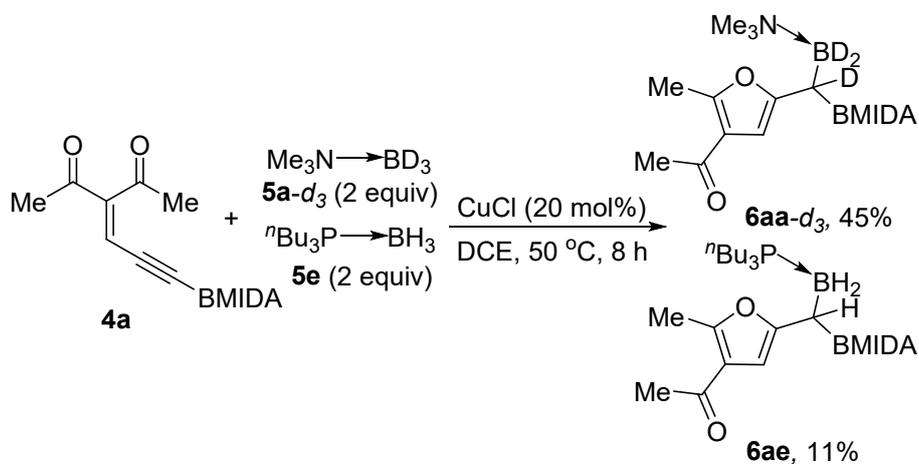


Figure S4. ¹H NMR spectrum of **9** and **9-d₃**

(c) Exchange experiment



A pre-dried 10.0 mL Schlenk tube was charged with stirring bar, CuCl (4.0 mg, 0.02 mmol, 0.2 eq.), **4a** (58.2 mg, 0.2 mmol, 1.0 eq.). Then, DCE (2.0 mL) was added and the mixture was stirred at room temperature. The solution added successively with **5a-d₃** (30.4 mg, 0.4 mmol, 2.0 eq.) and **5e** (87.7 mg, 0.4 mmol, 2.0 eq.). Then, the reaction mixture was stirred at 50 °C for 8 h. Subsequently, solvent was removed by rotary evaporation instrument and the residue was transferred to a column and purified by flash chromatography on silica gel (EA, $R_f = 0.20$) to give the product **6aa-d₃** (33.1 mg, 45% yield) and **6ae** (10.7 mg, 11% yield).

8. DFT Calculation

1.1 Computational details

All calculations were carried out by using the Gaussian 16 suite of computational programs.^[3] The obtained transition states were fully optimized at the DFT level using the B3LYP-D3(0)^[4] functional. The standard def2-TZVP^[5] basis set was applied for all atoms. Frequencies were analytically computed at the same level of theory to get the thermodynamic corrections and to confirm whether the structures are the corresponding transition states (only one imaginary frequency). All energies were reported in kcal/mol. The most stabilized conformation was reported herein, when several different conformations were obtained. Visualization was completed using CLYview20 software.^[6]

1.2 Results and discussion

The calculations indicated that the initial coordination of CuCl catalyst with **4a** generates chelation complex **INT1**. Then, the carbonyl group of **INT1** was released by coordination of the Cu center to another molecule of **4a**. The released carbonyl group subsequently attacks the Cu-activated alkyne moiety via **TS1** to give electrophilic Cu-carbene species **INT2**. This step requires an energy barrier of 9.19 kcal/mol. After that, **INT2** interacts with amine-borane adduct $\text{Me}_3\text{N}\cdot\text{BH}_3$ **5a** via a three-membered-ring concerted transition state **B-TS2** to give product **6aa** and release the CuCl catalyst associated with a molecule of **4a**. The energy barrier for this step is 16.99 kcal/mol.

The calculations showed that the energy barrier for the B–H bond insertion step (**INT2-B-TS2-6**) is 7.8 kcal/mol higher than that for the generation of carbene species (**INT1-TS1-INT2**). These results indicate that the B–H insertion rather than the copper carbene formation is the rate-limiting step, which is in line with the results of KIE experiments (**Figures S5 and S6**).

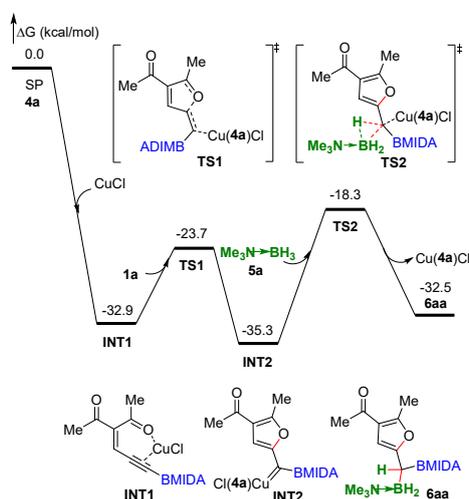


Figure S5. The calculated potential energy surface

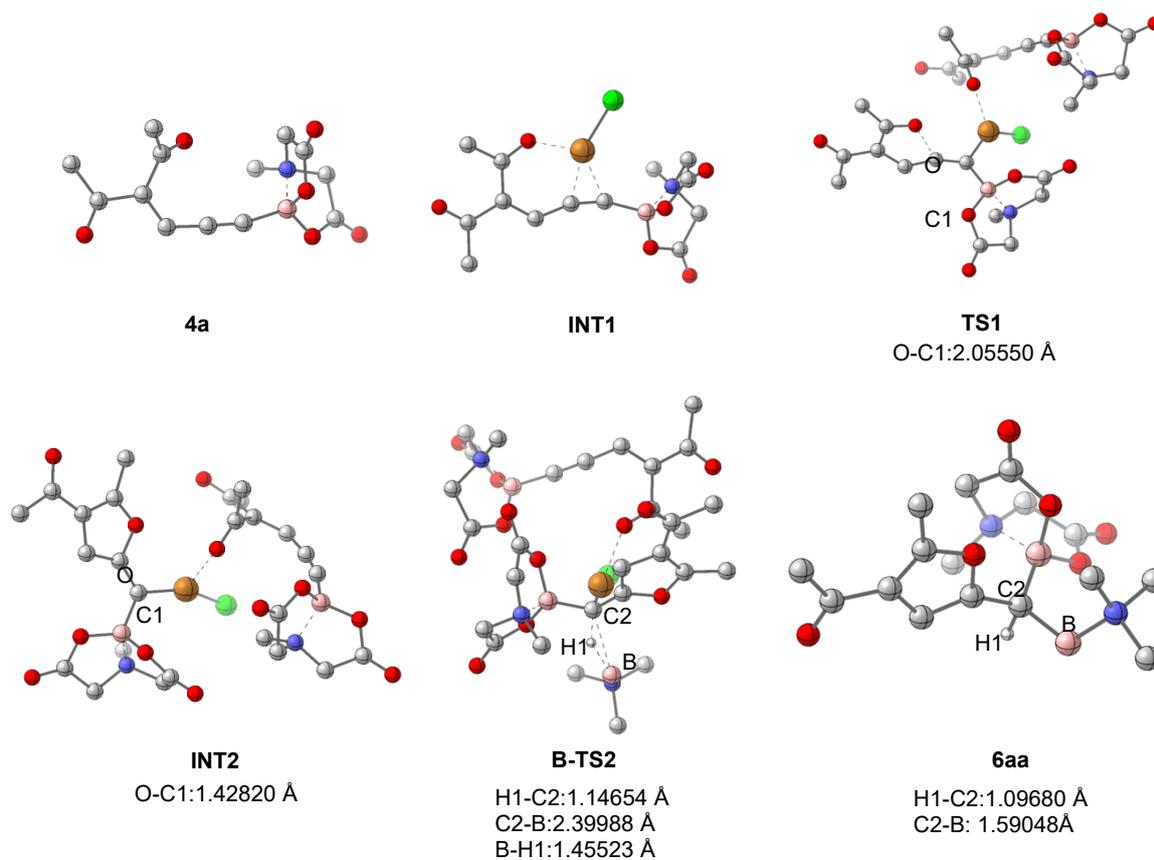


Figure S6. Geometric structures of selected transition states and intermediates

1.3 The calculated energies

Table S3 The calculated energies

	Ec [a]	G [b]	Imaginary frequency
4a	0.212613	-1035.054759	/
Me₃N-BH₃	0.125971	-201.107768	/
CuCl	-0.022459	-2100.857509	/
INT1	0.211129	-3135.964703	/
TS1	0.445076	-4171.004815	-145.30
INT2	0.447910	-4171.023333	/
B-TS2	0.598808	-4372.104031	-170.97
6aa	0.371560	-1236.214277	/

^aThermal correction to Gibbs Free Energy

^bSum of electronic and thermal Free Energies

Cartesian coordinates

4a

C	3.04195700	-0.49024900	-0.14560200
C	2.18359400	-1.37963500	-0.69610600
C	0.79561300	-1.19711400	-0.79110100
O	1.60576900	0.87352000	1.15547700
C	2.53230000	0.82042000	0.37023800
C	3.15027900	2.09486700	-0.16515300
C	4.49871700	-0.85688600	-0.09603300
C	5.43116300	0.02009300	0.70991100
O	4.90965100	-1.85255900	-0.65275600
H	2.61428700	-2.28928500	-1.10607700
H	3.73472700	2.57313800	0.62353500
H	3.78830500	1.92903700	-1.03128800
H	2.34025800	2.77436200	-0.43113200
H	5.69485900	0.90948300	0.13302700
H	4.96912700	0.35520900	1.64063900
H	6.34119300	-0.53571300	0.92255700
C	-0.39782100	-0.99857200	-0.83534600
B	-1.85025400	-0.46106600	-0.68582100
O	-2.08017800	0.77382900	-1.45373700
O	-2.91822900	-1.43335300	-0.81632000
C	-1.94177300	1.89562700	-0.74796600
C	-3.91828200	-1.24297800	0.04544800
C	-1.72866200	1.56407600	0.73039100
O	-1.96737400	3.00768200	-1.19051800
C	-3.57920700	-0.08483400	0.98909300
O	-4.93678700	-1.86709900	0.08702100
H	-0.66874700	1.67245300	0.96339700

N	-2.10855000	0.13652200	0.87228200
H	-2.31062500	2.21777800	1.37682100
H	-3.87606700	-0.30591200	2.01129300
H	-4.11819400	0.79814200	0.64658700
C	-1.37043800	-0.56838000	1.95142900
H	-0.30350900	-0.45271900	1.78506400
H	-1.64812300	-0.14672800	2.91790000
H	-1.63382400	-1.62434200	1.92225200

Me₃N-BH₃

B	1.65923800	-0.00059000	-0.00077900
H	1.98170900	0.14068600	-1.15880100
H	1.98199700	-1.07405900	0.45584300
H	1.98289100	0.93163600	0.70014000
N	0.00388700	-0.00002300	0.00001100
C	-0.49232700	-1.11790000	-0.84053000
H	-1.58523700	-1.13366500	-0.85132600
H	-0.11318300	-0.99106100	-1.85155000
H	-0.11204800	-2.05384300	-0.43872200
C	-0.49090000	-0.16892200	1.38884500
H	-0.11018800	0.64716900	1.99804000
H	-1.58379300	-0.17058200	1.40895100
H	-0.11119400	-1.10779300	1.78427100
C	-0.49136200	1.28731200	-0.54763800
H	-0.11100100	2.09907900	0.06748000
H	-0.11155800	1.40694000	-1.55931900
H	-1.58425900	1.30566800	-0.55525600

CuCl

Cu	0.00000000	0.00000000	0.77325400
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Cl	0.00000000	0.00000000	-1.31908000
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INT1

C	-2.16794100	1.31184000	-0.12561700
C	-3.38862700	0.71589400	-0.09707500
C	-4.61079600	1.58638600	-0.02417900
C	-4.52312700	3.02965600	-0.47570700
O	-5.64984900	1.14327800	0.41727800
C	-3.54511600	-0.76990200	-0.10222100
C	-0.89236600	0.71430500	-0.09102100
O	-2.60190900	-1.51908300	0.14672600
C	0.34327600	0.56908000	-0.09403900
C	-4.86053700	-1.39511400	-0.46344300
H	-5.36135500	-0.85569400	-1.26662600
H	-5.52770400	-1.35072000	0.39841000
H	-4.68153900	-2.43162100	-0.73971800
H	-4.02919500	3.12616000	-1.44359700
H	-3.96046800	3.62454800	0.24826600
H	-5.53321000	3.42787100	-0.53085800
H	-2.12872300	2.39501500	-0.16932900
Cl	0.51464700	-3.07286000	0.71680700
Cu	-0.55593500	-1.22824200	0.23752800
B	1.87765000	0.85839700	-0.35528500
O	2.29227900	0.40438200	-1.67777300
O	2.19866500	2.24986400	-0.06939800
C	3.05759300	-0.69969600	-1.67077200
C	3.41136000	2.40853700	0.46871000
C	3.29993700	-1.14969200	-0.23424800
O	3.47602200	-1.24939300	-2.64449900
C	4.06203300	1.04089100	0.67038800

O	3.92149200	3.45334900	0.74376700
H	2.60259100	-1.95993800	-0.00248200
N	2.95673600	0.03454600	0.60250400
H	4.32277400	-1.48360600	-0.07692900
H	4.59840400	0.98624300	1.61395700
H	4.76438200	0.87677800	-0.14663500
C	2.48286600	-0.31287000	1.96932600
H	1.66416500	-1.02263700	1.89368100
H	3.30074700	-0.76204900	2.53196100
H	2.15192200	0.59838200	2.46533600

TS1

C	-4.06746600	0.12528100	-1.04418200
C	-4.66944800	-1.08700900	-1.16829800
C	-5.94951900	-1.31673400	-1.87709600
C	-6.62013400	-0.13282200	-2.54030600
O	-6.44571100	-2.42590300	-1.92528400
C	-3.87905900	-2.13668000	-0.48920600
C	-2.85467900	0.27487500	-0.36822700
O	-2.83757600	-1.73952500	0.04043000
C	-1.85498000	0.91154200	0.07620800
C	-4.27256100	-3.57224800	-0.42076800
H	-4.38929400	-3.96697000	-1.43155700
H	-5.25817500	-3.66300700	0.03823500
H	-3.52111000	-4.12590800	0.13571600
H	-5.96517800	0.31582800	-3.29052500
H	-6.85869100	0.64139200	-1.80741700
H	-7.53608600	-0.47322100	-3.01636300
H	-4.47327500	1.04436500	-1.45128000
Cu	-0.39363100	-0.13762400	0.88874500

Cl	0.72637500	-0.07192800	2.79453900
O	-1.34567400	-4.41594000	1.15467700
C	-0.35322800	-3.98620300	1.71597000
C	0.70478200	-3.30840800	0.92570000
H	2.22930700	-3.39865100	2.37984300
C	-0.18292400	-4.07768100	3.21199700
C	1.95272000	-3.08493300	1.38045000
C	0.32065300	-2.81676800	-0.44419000
O	0.09820200	-1.63040800	-0.61975800
C	0.23721700	-3.81130900	-1.55252700
H	-0.47689900	-4.58657900	-1.26607700
H	1.21183500	-4.29134200	-1.67570900
H	-0.06107800	-3.32613000	-2.47908900
H	-0.01758000	-3.08048900	3.62674000
H	0.68076000	-4.69417600	3.47138100
H	-1.07813300	-4.52266500	3.63947900
C	2.93104400	-2.43350400	0.60481400
C	3.68125600	-1.80677600	-0.10785400
B	4.42669600	-0.78467800	-1.02194000
O	5.89011100	-0.88402900	-1.04121200
O	3.84292400	-0.69752100	-2.34957600
C	6.53056800	0.07032600	-0.37223000
C	3.65831200	0.54922800	-2.78653400
C	5.52288500	1.04009700	0.24799800
O	7.71720100	0.16124900	-0.24243500
C	4.07164400	1.55397200	-1.71142900
O	3.24461500	0.85319600	-3.86627400
H	5.42023300	0.79266700	1.30452200
N	4.23248100	0.78494400	-0.43720400
H	5.84661500	2.07444200	0.15923100

H	3.33435500	2.34698300	-1.60473200
H	5.02498000	1.99015400	-2.00824000
C	3.05925900	0.97858800	0.45494400
H	3.13832900	0.32887200	1.31870000
H	3.00363300	2.02093100	0.75747200
H	2.15683900	0.70813200	-0.08944200
B	-1.69477200	2.49540700	-0.01655200
O	-0.49430000	2.92319100	-0.75110000
O	-2.90373300	3.18549100	-0.46486200
C	0.50116600	3.33804500	0.02257300
C	-3.14713700	4.32459200	0.18250400
C	0.07731300	3.32310200	1.48809400
O	1.59366300	3.65672800	-0.36296400
C	-2.07100400	4.55150300	1.24353300
O	-4.06018400	5.06739500	-0.02843100
H	0.47905200	2.42067800	1.95802000
N	-1.40564400	3.23026500	1.46069800
H	0.43032600	4.20100300	2.02474100
H	-2.49332300	4.94654600	2.16373500
H	-1.35368200	5.27005500	0.84729700
C	-1.97715000	2.53608900	2.64644300
H	-1.50598400	1.56257100	2.75144300
H	-1.79312100	3.13329100	3.53915500
H	-3.04867300	2.41660600	2.49599500

INT2

C	-3.88387700	-0.17610500	-1.11583300
C	-4.32648100	-1.45621700	-1.42184800
C	-5.42602700	-1.87275900	-2.31900200
C	-6.18739800	-0.78181700	-3.03100100

O	-5.68963900	-3.04996400	-2.46530100
C	-3.49941600	-2.33622600	-0.68881800
C	-2.79983700	-0.26696300	-0.22498100
O	-2.61602400	-1.66457400	0.00445800
C	-1.94616200	0.61211800	0.36486400
C	-3.48450900	-3.80685600	-0.60057200
H	-3.30784700	-4.22634700	-1.59372800
H	-4.47096800	-4.16714800	-0.30385800
H	-2.71887000	-4.13239600	0.09959800
H	-5.51253800	-0.19673700	-3.66072300
H	-6.63402300	-0.09257900	-2.31018000
H	-6.96619900	-1.22762300	-3.64432200
H	-4.27254300	0.76046400	-1.47814000
Cu	-0.45031300	-0.00205300	1.37525900
Cl	0.93492400	0.06752900	3.05847200
O	-0.88524000	-4.02112100	1.61615000
C	0.17831300	-3.68654700	2.11471600
C	1.22365500	-3.09598300	1.25099600
H	2.82908600	-3.12844000	2.62685400
C	0.43371400	-3.80181500	3.59444500
C	2.49447800	-2.86451300	1.63099500
C	0.77194900	-2.66696800	-0.12482000
O	0.40575300	-1.52325000	-0.30918600
C	0.81104600	-3.68824500	-1.21601600
H	0.22257000	-4.55664700	-0.91106500
H	1.84351100	-4.02059200	-1.35268000
H	0.43305300	-3.26773600	-2.14535000
H	0.61121500	-2.80329300	4.00245300
H	1.31637700	-4.41071300	3.80052600
H	-0.43472100	-4.25204700	4.06911200

C	3.39702800	-2.22066300	0.76151700
C	4.00446400	-1.57135500	-0.05936200
B	4.44241600	-0.53112300	-1.13719700
O	5.88106000	-0.28850600	-1.27416800
O	3.77284300	-0.75540800	-2.40918300
C	6.30941900	0.86810900	-0.77548300
C	3.24849100	0.34344700	-2.95414300
C	5.13564600	1.64702100	-0.17934100
O	7.44430800	1.24914100	-0.76414000
C	3.49690600	1.55043000	-2.05128200
O	2.68087300	0.39290800	-4.00579400
H	5.15789900	1.51934500	0.90292800
N	3.90756500	1.01268300	-0.71639200
H	5.19270100	2.70840900	-0.40910100
H	2.61628100	2.18396700	-1.97019000
H	4.31117300	2.12978300	-2.48623500
C	2.77169700	1.05490300	0.24460200
H	3.04778600	0.55863100	1.16767700
H	2.50568100	2.09130100	0.43289200
H	1.92379800	0.52517100	-0.18478700
B	-2.11189600	2.16768400	0.09376900
O	-1.03420400	2.65915600	-0.79791600
O	-3.43067000	2.65536400	-0.31426600
C	-0.02862000	3.24834000	-0.16793900
C	-3.74426300	3.85655400	0.16949400
C	-0.34358400	3.40158300	1.31962600
O	1.00153700	3.60215700	-0.67703500
C	-2.62468800	4.34966400	1.08348400
O	-4.74308900	4.46800500	-0.07313100
H	0.19644200	2.63057100	1.87481300

N	-1.80311000	3.15142100	1.43343800
H	-0.05724800	4.38201200	1.69502400
H	-3.01948500	4.84243300	1.96820600
H	-2.02382900	5.06448200	0.52170700
C	-2.21049000	2.60410000	2.75458100
H	-1.63056500	1.71022900	2.96789200
H	-2.03662300	3.35159600	3.52848100
H	-3.26934300	2.35322200	2.71629300

B-TS2

C	-3.16083100	1.61032000	-1.81993300
C	-2.31375000	0.46005900	-1.96059300
C	-2.44672700	-0.30105200	-0.84553800
O	-3.40328100	0.30718700	-0.03417100
C	-3.81288000	1.45718200	-0.62372400
C	-4.80658500	2.25621200	0.14033100
C	-3.19962800	2.70992700	-2.79058900
C	-3.97659300	3.96284200	-2.45026300
O	-2.58678600	2.62176100	-3.84264700
H	-1.63511300	0.32167200	-2.77972600
H	-4.37624400	3.21069700	0.45126600
H	-5.70057000	2.46813800	-0.44800200
H	-5.10318200	1.70637000	1.03236000
H	-5.03514400	3.73611100	-2.30529300
H	-3.60491300	4.40164900	-1.52116500
H	-3.86939900	4.67610900	-3.26444800
C	-1.66704600	-1.38686300	-0.26282000
Cu	-0.81529100	-0.63434200	1.39437500
Cl	-0.11291400	-0.34256900	3.43880600
B	-3.21807300	-2.95940200	0.67571800

H	-2.27285800	-2.36025000	-0.25448000
H	-4.17321600	-2.27057100	0.55613700
H	-3.08385000	-3.92845600	-0.01189800
N	-2.89010500	-3.31457700	2.17370300
C	-3.21771800	-2.19928100	3.12154400
H	-3.04461800	-2.53936000	4.14139400
H	-2.56676800	-1.35349100	2.92151100
H	-4.25931100	-1.92059100	2.98208500
C	-3.81965300	-4.45804500	2.46966000
H	-3.53852600	-5.31720100	1.86665000
H	-3.74088900	-4.70688200	3.52690700
H	-4.84196400	-4.16360200	2.23880400
C	-1.48057300	-3.78698200	2.40030600
H	-1.23385800	-4.54553900	1.66276200
H	-0.80214800	-2.94613200	2.29688500
H	-1.41109700	-4.19227400	3.40902300
O	-2.17339400	4.98084900	0.56019800
C	-0.96875500	5.06895500	0.73697900
C	-0.17344500	3.83853300	0.95792100
H	1.70116500	4.76263700	0.74430700
C	-0.28170700	6.41630100	0.68583000
C	1.17714400	3.82149700	0.87956300
C	-0.93201700	2.55966100	1.17605400
O	-0.67626100	1.59713400	0.48308900
C	-1.89435200	2.48744600	2.32416300
H	-2.64300100	1.72590600	2.11812600
H	-2.35787100	3.44479200	2.54604800
H	-1.31491800	2.13897000	3.18604100
H	0.37705000	6.47648000	-0.18362600
H	0.32596300	6.58732300	1.57611800

H	-1.04204900	7.18914200	0.60363800
C	2.00004200	2.68007700	0.92606700
C	2.73644300	1.71958600	0.89010000
B	-0.36023900	-1.95897900	-0.92877700
O	0.65735700	-0.95752100	-1.27586100
O	0.11060100	-3.12466200	-0.17837200
C	0.98161200	-0.80668500	-2.53645000
C	0.46264900	-4.19934600	-0.86417000
C	0.13974000	-1.70437500	-3.43670800
O	1.82989200	-0.05698800	-2.95526900
C	0.47412200	-3.88507200	-2.35178400
O	0.72309800	-5.26967600	-0.38702400
H	-0.65174800	-1.10655300	-3.88582300
N	-0.43938200	-2.72604000	-2.54515100
H	0.74167700	-2.13384900	-4.23560600
H	0.18129700	-4.74292400	-2.95379200
H	1.49677200	-3.59624900	-2.59593900
C	-1.79978900	-3.15229100	-2.93051500
H	-2.46353800	-2.29120100	-2.89676300
H	-1.79521900	-3.58654000	-3.93193700
H	-2.15264600	-3.89597500	-2.21867300
B	3.70566500	0.51704500	0.68063700
O	4.73964600	0.36441500	1.71009800
O	3.06104000	-0.74790500	0.36049700
C	5.96803500	0.71129400	1.34937600
C	3.57666100	-1.39168900	-0.66830400
C	5.97009700	1.21081200	-0.09634500
O	6.94448800	0.67306900	2.04216000
C	4.73858800	-0.60515300	-1.26950000
O	3.21487800	-2.45704000	-1.09347000

H	5.99976800	2.29990300	-0.07468800
N	4.68556500	0.77238200	-0.69462900
H	6.83503900	0.84851800	-0.64754300
H	4.66094900	-0.58496300	-2.35307000
H	5.66646100	-1.09923500	-0.98296000
C	4.15300900	1.74356300	-1.68880400
H	4.03294500	2.70788800	-1.20449100
H	4.85278900	1.82457700	-2.52164900
H	3.18966500	1.38926600	-2.04536200

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C	-3.10196500	-0.01419400	0.49546200
C	-1.99839500	-0.05574100	1.42216200
C	-0.88222900	0.32673900	0.75643000
O	-1.24426400	0.60624200	-0.55187200
C	-2.57976400	0.39701300	-0.70435200
C	-3.09182300	0.66309500	-2.07407000
C	-4.48005300	-0.36885700	0.86730100
C	-5.59569100	-0.20338400	-0.14480300
O	-4.72190600	-0.79309500	1.98356400
H	-2.07251800	-0.33259700	2.45966900
H	-3.93763000	0.02601700	-2.31923200
H	-3.41327500	1.70333300	-2.18587800
H	-2.29621500	0.47755000	-2.79667800
H	-5.57950400	0.78774200	-0.60070700
H	-5.48691900	-0.93686800	-0.94787400
H	-6.54794000	-0.36695900	0.35450000
C	0.55299200	0.43609200	1.11775500
B	1.07551100	1.97361900	1.46018600
H	0.61369000	0.02374700	2.13228000

H	0.15990700	2.60353500	1.93891300
H	2.03538000	1.93017900	2.19279200
N	1.60228600	2.94710300	0.20923700
C	0.61181800	3.03292600	-0.89566400
H	0.92910300	3.78326200	-1.62349600
H	0.52924900	2.06601800	-1.37879800
H	-0.35430600	3.30746700	-0.47880100
C	1.78384700	4.30298200	0.79627200
H	2.48036000	4.23646500	1.62850000
H	2.17373200	4.98642500	0.03879500
H	0.82741900	4.66347900	1.16456600
C	2.91452600	2.50545000	-0.34133500
H	3.61477600	2.37717600	0.47925400
H	2.79659800	1.56259800	-0.86052400
H	3.28946000	3.25367900	-1.04326300
B	1.48373200	-0.48755500	0.21762200
O	1.39276300	-0.25197300	-1.25622100
O	2.87779400	-0.56177800	0.64946200
C	0.60587300	-1.09089000	-1.91339700
C	3.45173400	-1.74294000	0.45357300
C	0.17824200	-2.23663300	-0.99409100
O	0.26230200	-0.98327800	-3.05828200
C	2.42451900	-2.74599000	-0.07562700
O	4.60424800	-2.00636300	0.64690500
H	-0.84709900	-2.05627900	-0.67180100
N	1.08014900	-2.15220500	0.17852800
H	0.23182300	-3.19964800	-1.49895700
H	2.53678200	-3.71670100	0.40166600
H	2.58809500	-2.86136200	-1.14659400
C	0.49359100	-2.69342200	1.42642700

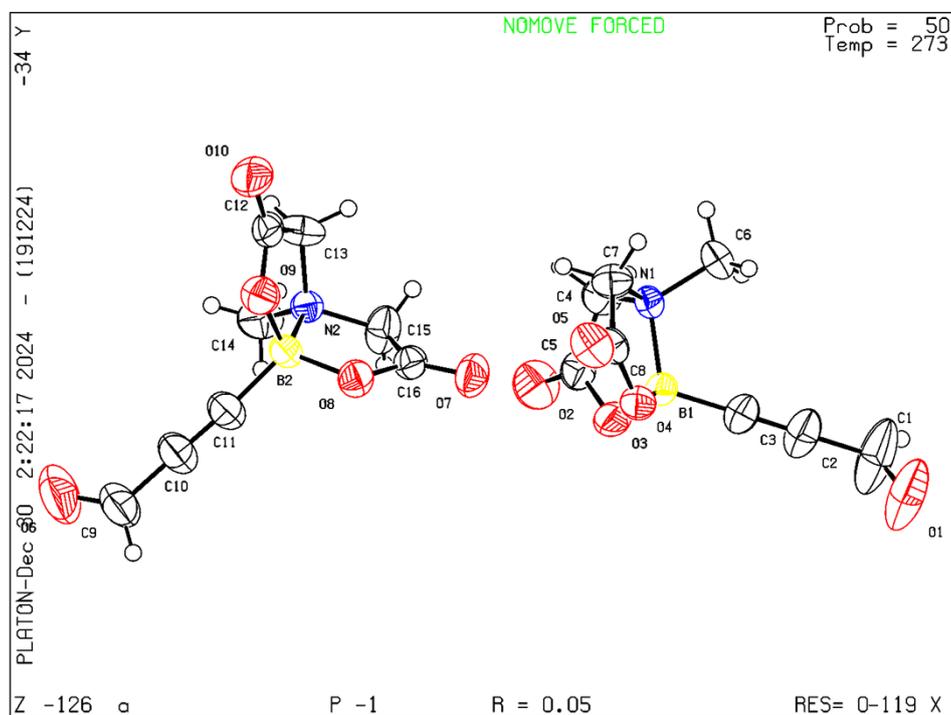
H	-0.44363900	-2.18459700	1.62948600
H	0.32148900	-3.76546800	1.32197100
H	1.18709200	-2.51431300	2.24610400

9. References

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10. Crystal Data and Structure Refinement

(a) ORTEP drawing of **2** (thermal ellipsoids set at 50% probability). Recrystallization from *n*-hexane/acetone afforded the single crystal suitable for X-ray diffraction analysis.



Bond precision: C-C = 0.0034 Å Wavelength=1.54178
 Cell: a=6.8267 (1) b=11.0677 (2) c=13.3937 (2)
 alpha=106.294 (1) beta=90.195 (1) gamma=97.336 (1)
 Temperature: 273 K

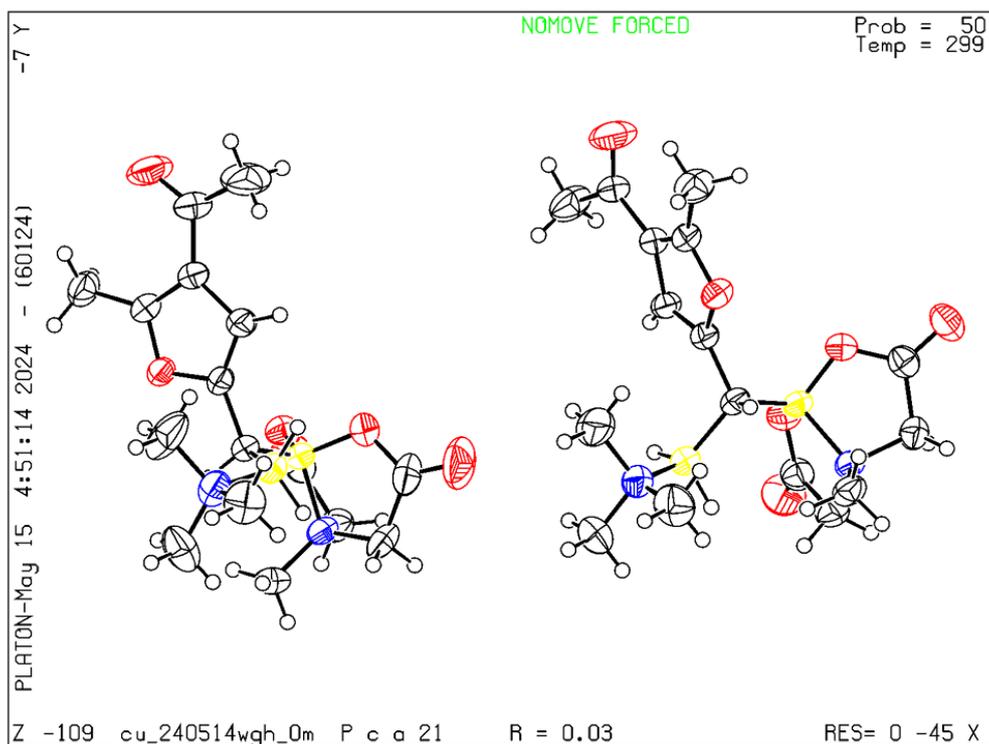
	Calculated	Reported
Volume	962.56 (3)	962.56 (3)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C8 H8 B N O5	C8 H8 B N O5
Sum formula	C8 H8 B N O5	C8 H8 B N O5
Mr	208.96	208.96
Dx, g cm ⁻³	1.442	1.442
Z	4	4
Mu (mm ⁻¹)	1.022	1.022
F000	432.0	432.0
F000'	433.66	
h, k, lmax	8, 13, 16	8, 13, 16
Nref	3536	3419
Tmin, Tmax	0.832, 0.903	0.402, 0.753
Tmin'	0.815	

Correction method= # Reported T Limits: Tmin=0.402 Tmax=0.753
 AbsCorr = MULTI-SCAN

Data completeness= 0.967 Theta (max)= 68.434

R(reflections)= 0.0548 (3187) wR2(reflections)=
 S = 1.035 Npar= 273 0.1480 (3419)

(b) ORTEP drawing of **6aa** (thermal ellipsoids set at 50% probability). Recrystallization from *n*-hexane/acetone afforded the single crystal suitable for X-ray diffraction analysis.



Bond precision: C-C = 0.0034 Å

Wavelength=1.54184

Cell: a=10.95800

b=13.20000

c=26.66000

alpha=90

beta=90

gamma=90

Temperature: 299 K

	Calculated	Reported
Volume	3856.252	3856
Space group	P c a 21	P c a 21
Hall group	P 2c -2ac	P 2c -2ac
Moiety formula	C16 H26 B2 N2 O6	C16 H26 B2 N2 O6
Sum formula	C16 H26 B2 N2 O6	C16 H26 B2 N2 O6
Mr	364.01	364.01
Dx, g cm ⁻³	1.254	1.254
Z	8	8
Mu (mm ⁻¹)	0.769	0.769
F000	1552.0	1552.0
F000'	1557.07	
h, k, lmax	13, 15, 32	13, 15, 32
Nref	7073 [3622]	6820
Tmin, Tmax	0.871, 0.926	0.423, 0.753
Tmin'	0.857	

Correction method= # Reported T Limits: Tmin=0.423 Tmax=0.753

AbsCorr = MULTI-SCAN

Data completeness= 1.88/0.96

Theta (max)= 68.347

R(reflections)= 0.0332 (6434)

wR2(reflections)=
0.0922 (6820)

S = 1.036

Npar= 499

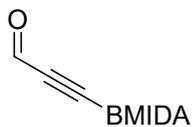
11. NMR Spectra

— 9.196

4.080
4.046
3.955
3.921

— 3.076

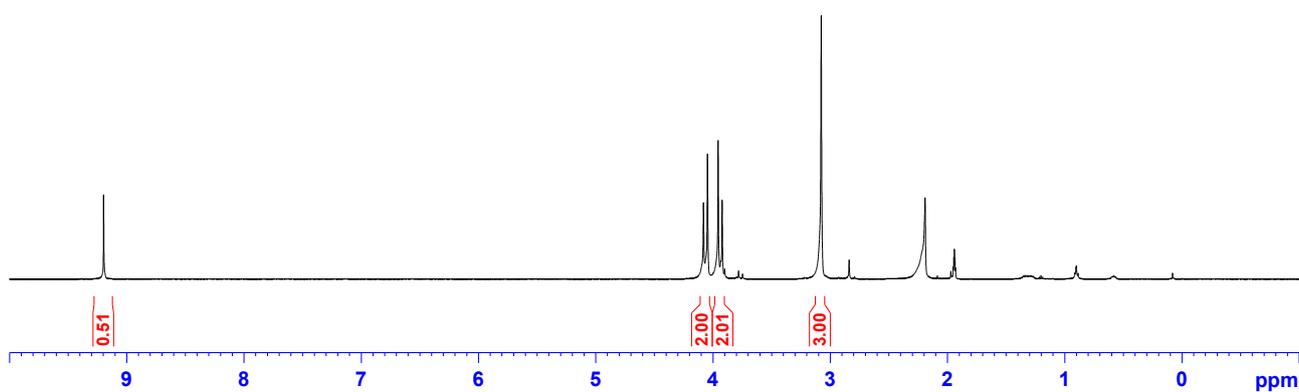
1.950
1.945
1.940
1.935
1.930



BMIDA

2

¹H NMR (500 MHz, CD₃CN)



— 178.99

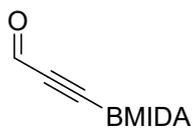
— 168.46

— 118.36

— 62.81

— 49.12

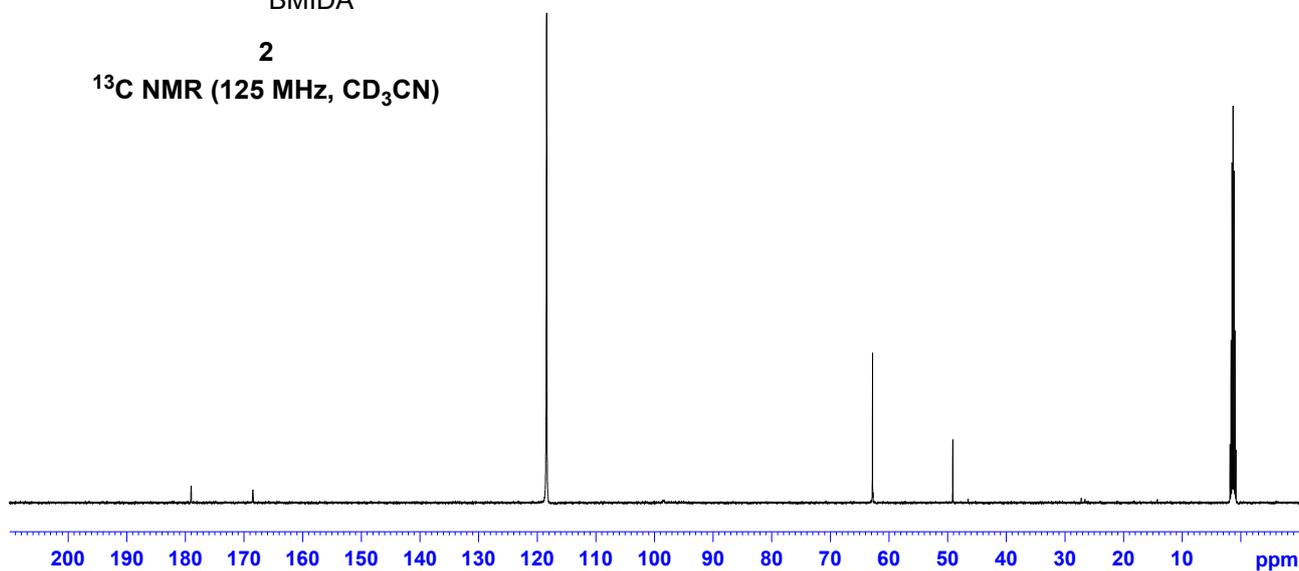
1.82
1.65
1.49
1.32
1.16
0.99

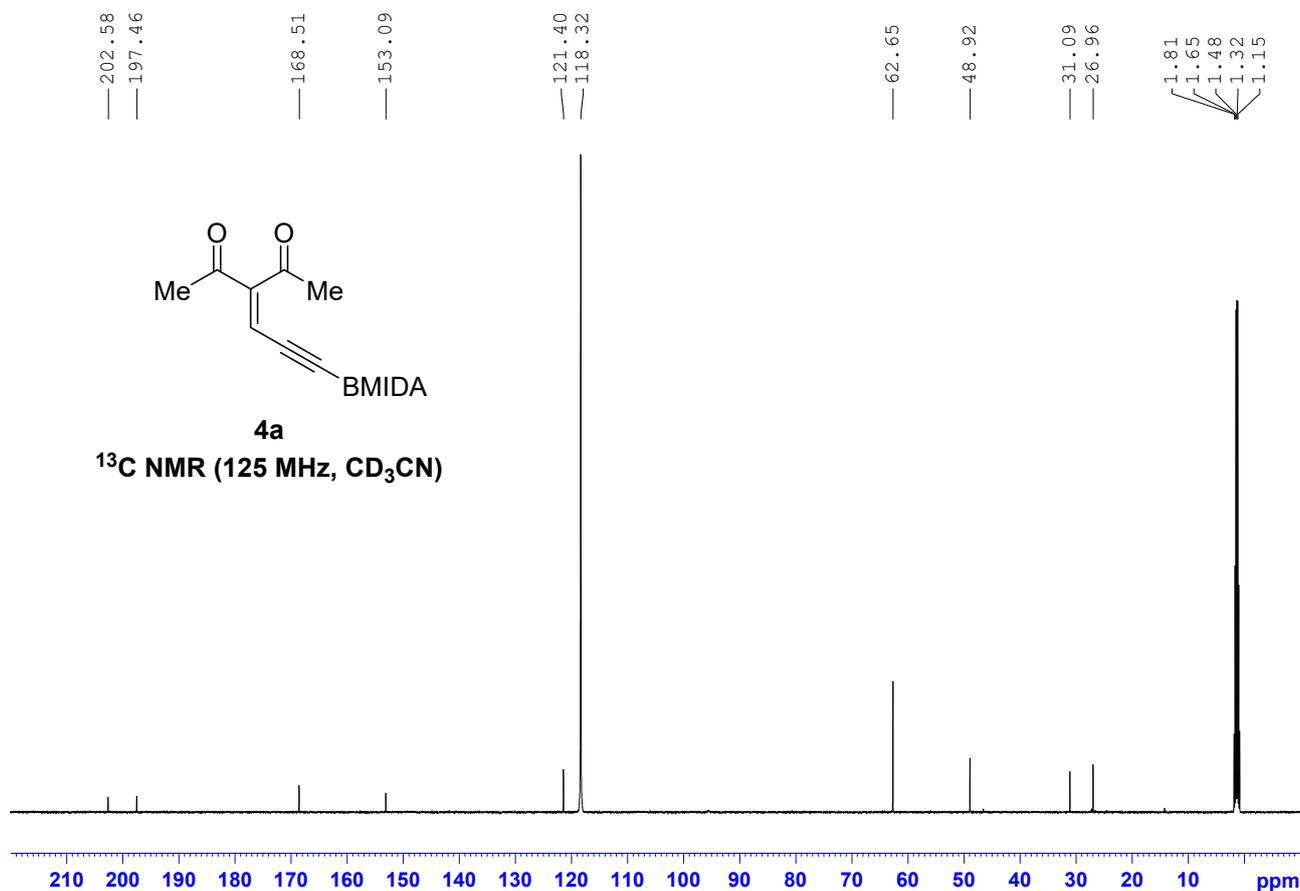
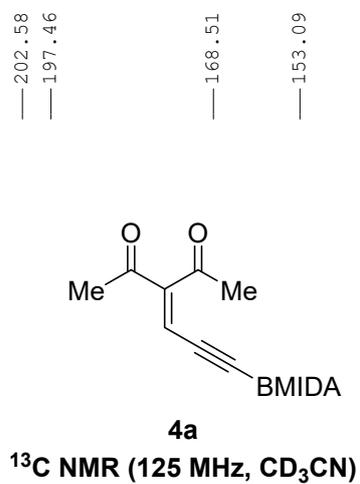
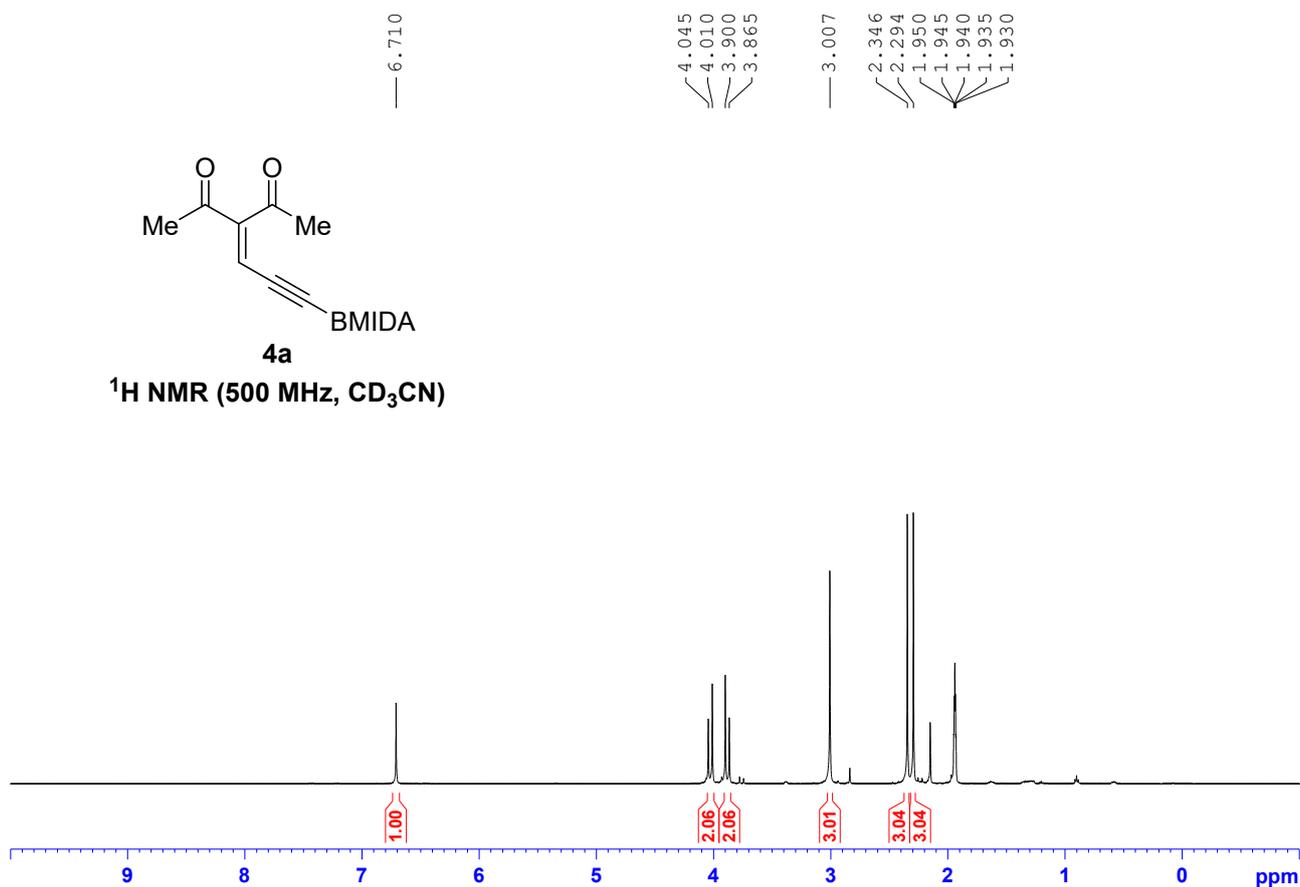
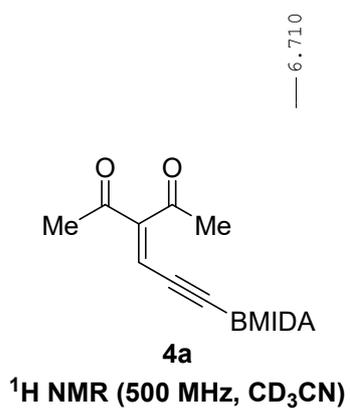


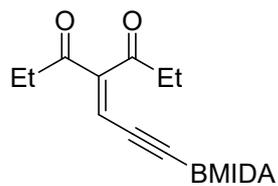
BMIDA

2

¹³C NMR (125 MHz, CD₃CN)

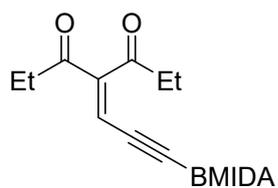
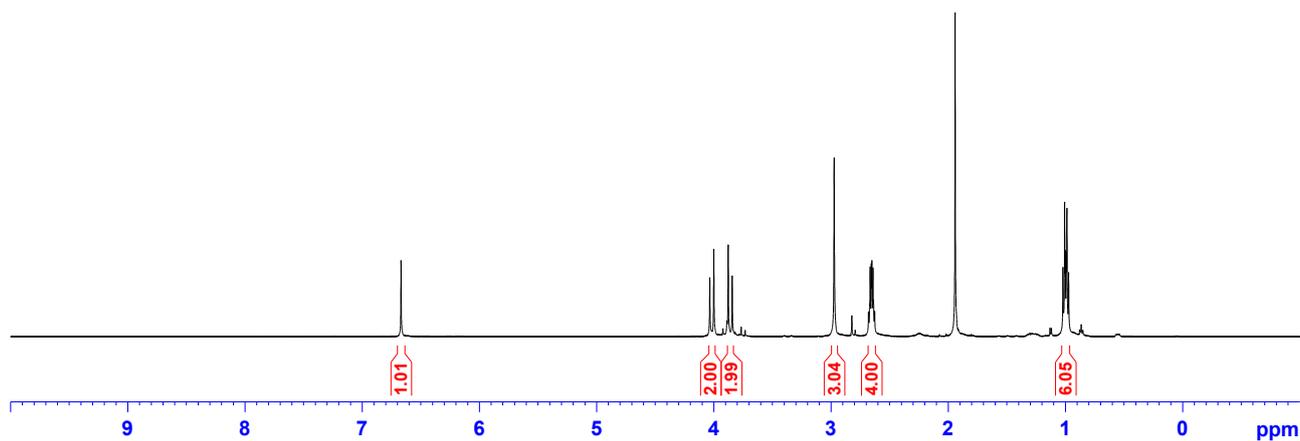






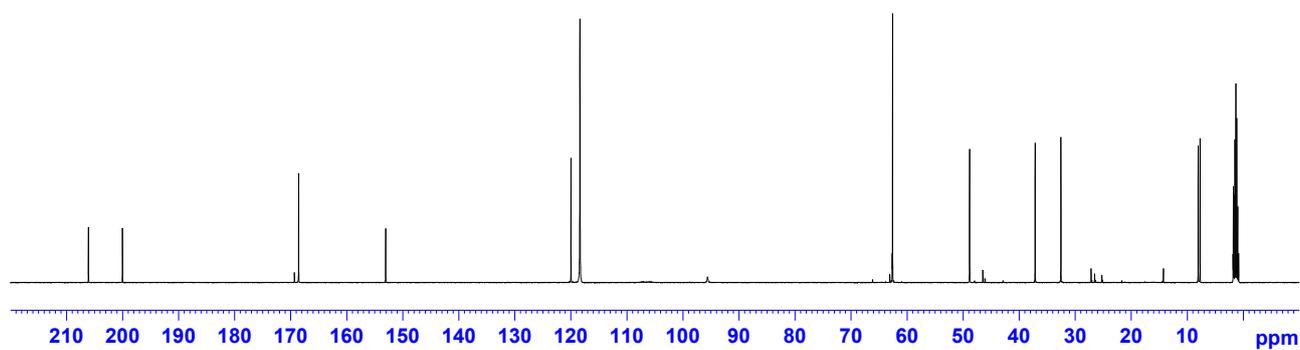
4b

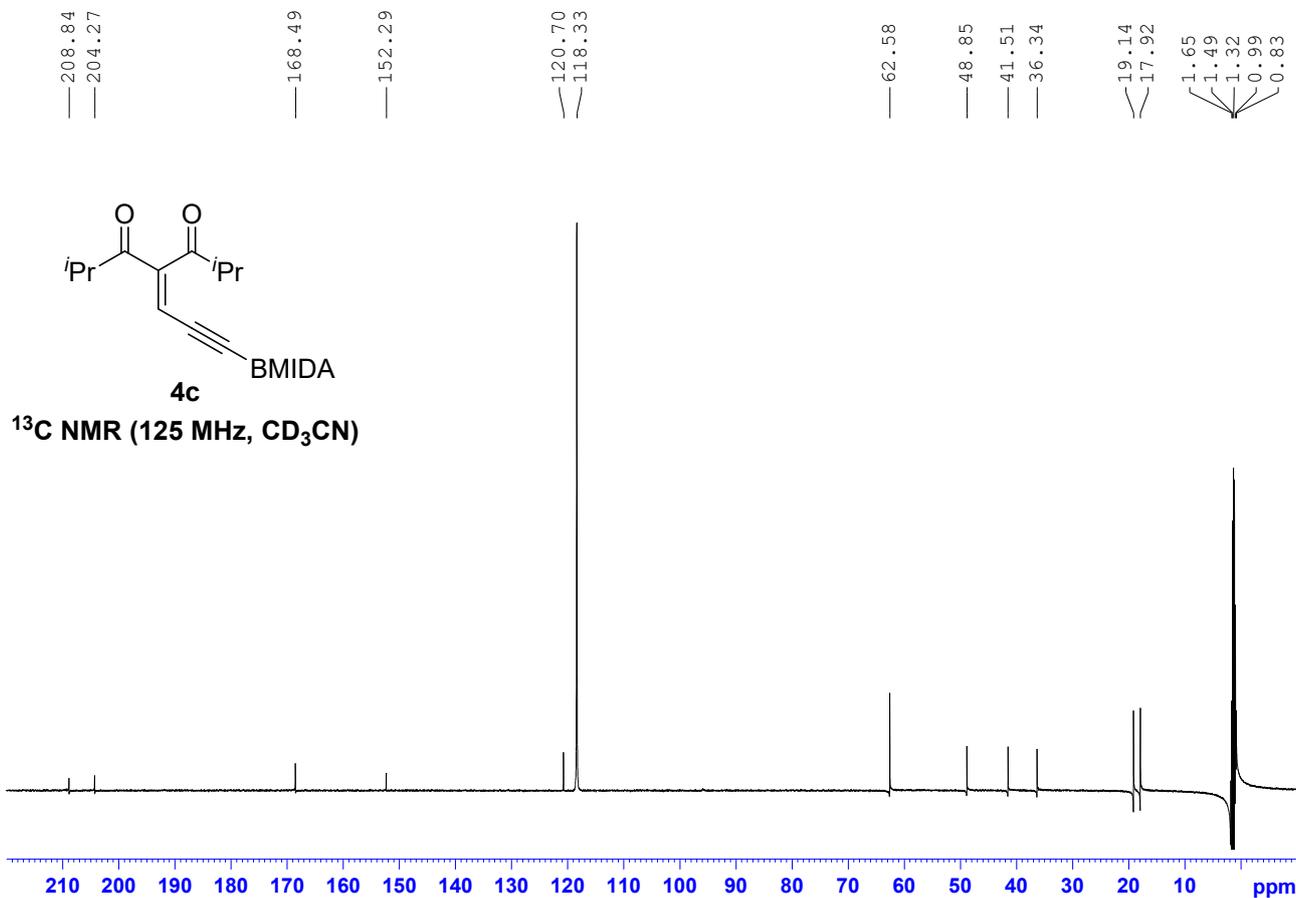
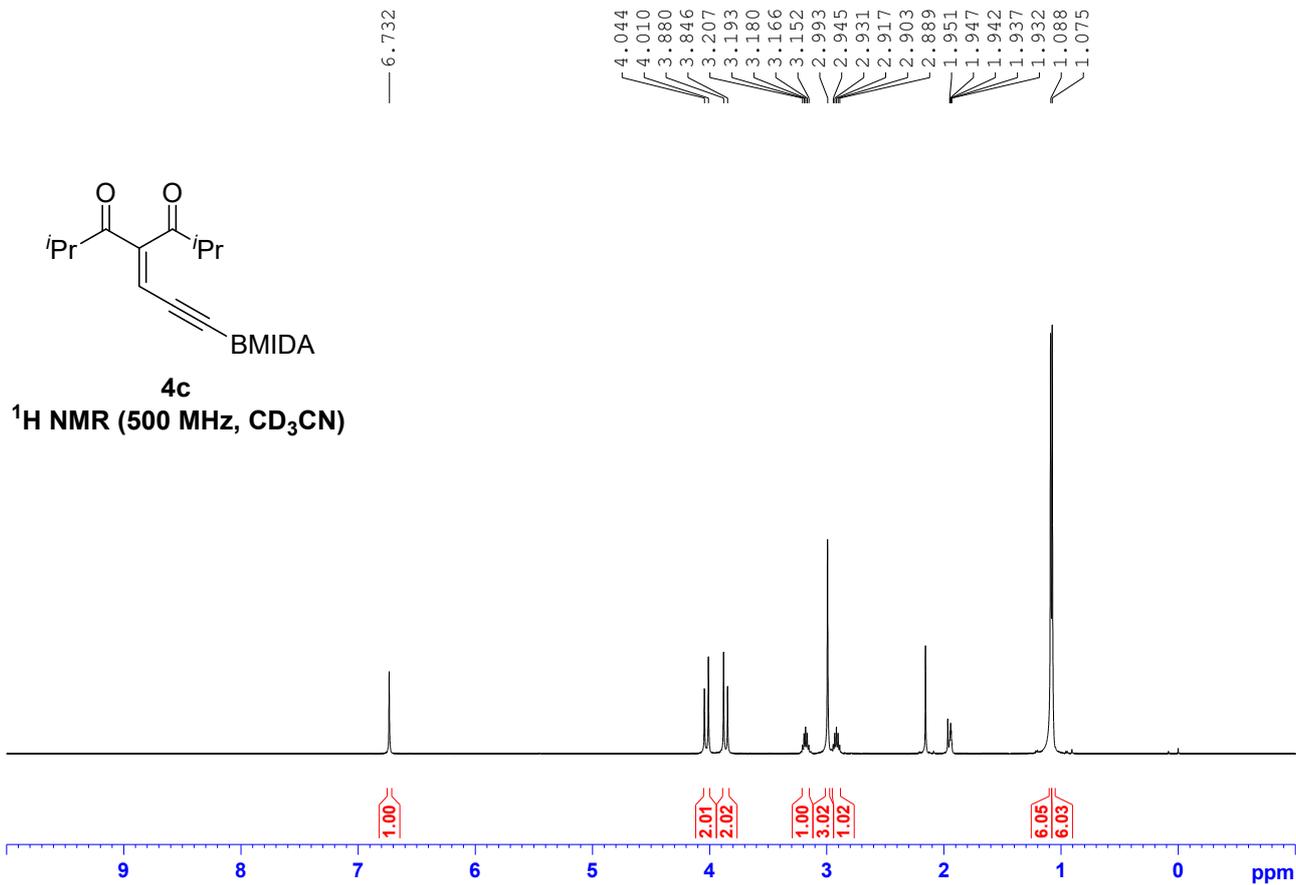
¹H NMR (500 MHz, CD₃CN)

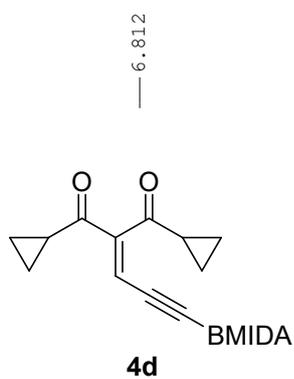


4b

¹³C NMR (125 MHz, CD₃CN)

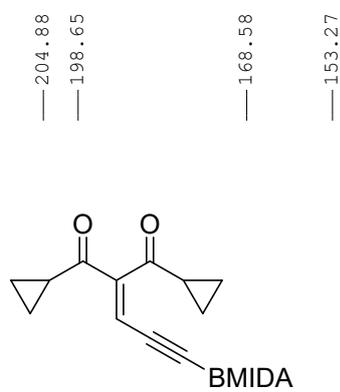
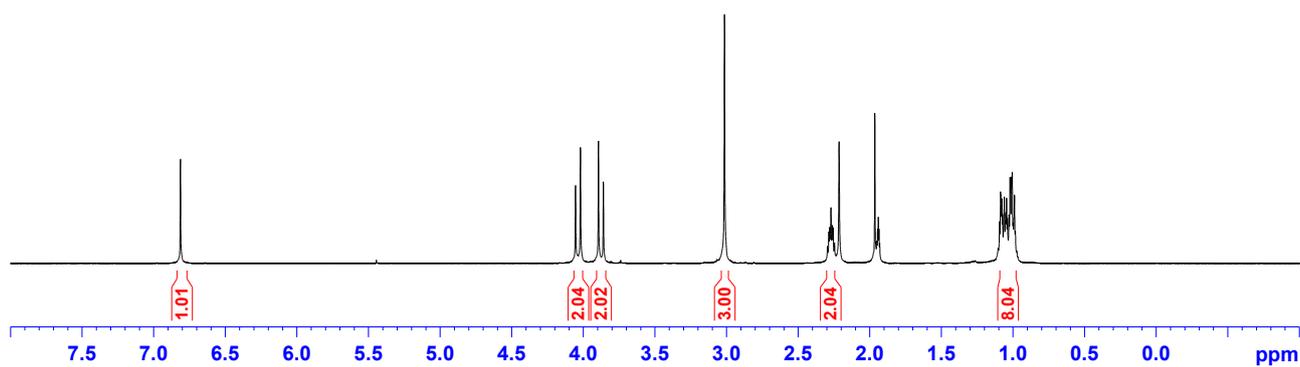




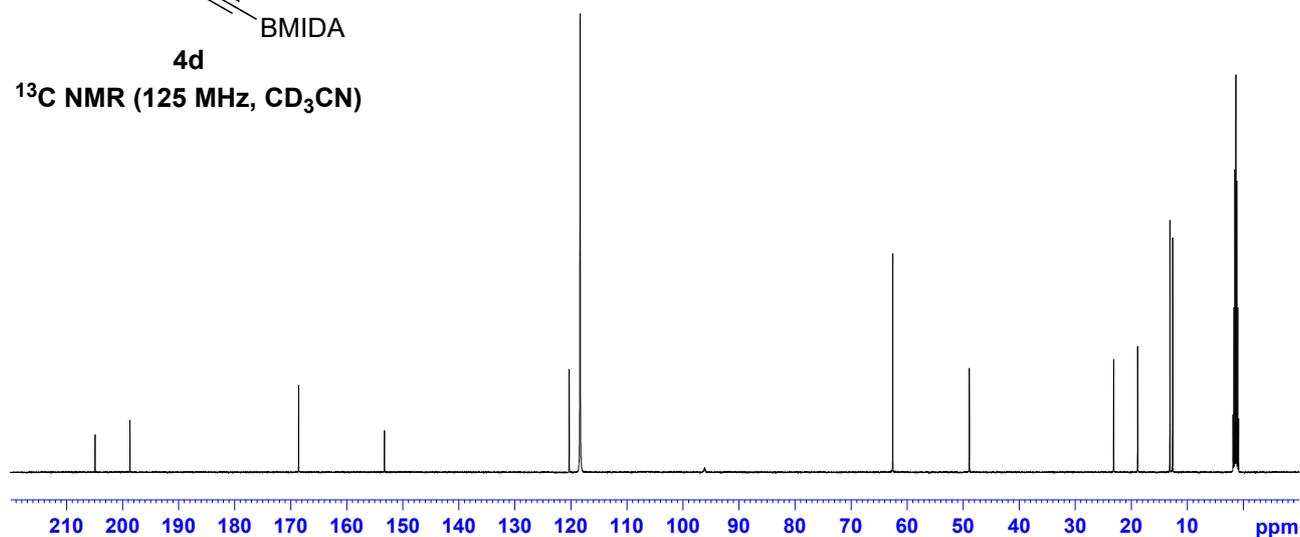


$^1\text{H NMR}$ (500 MHz, CD_3CN)

4.054
4.020
3.894
3.860
3.014
2.295
2.285
2.280
2.271
2.261
2.255
2.246
1.093
1.086
1.084
1.077
1.072
1.060
1.053
1.049
1.044
1.038
1.027
1.020
1.017
1.010
1.004
0.998
0.989
0.983



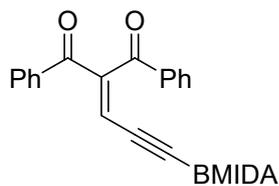
$^{13}\text{C NMR}$ (125 MHz, CD_3CN)



7.916
7.902
7.820
7.805
7.600
7.588
7.572
7.482
7.467
7.452
7.264
6.688

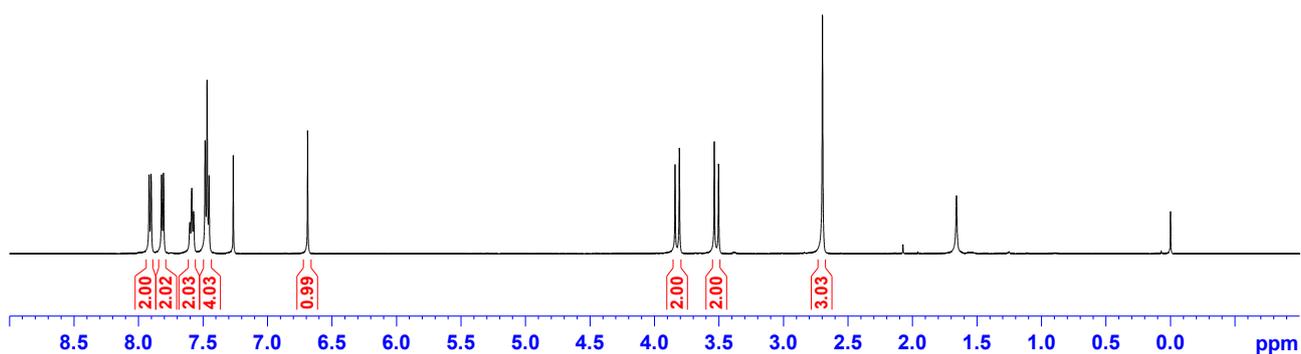
3.841
3.807
3.537
3.503

2.698



4e

¹H NMR (500 MHz, CDCl₃)



193.95
192.83

166.83

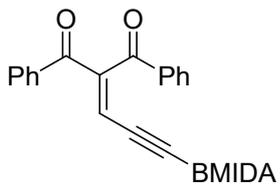
150.08
136.21
135.93
134.52
133.62
129.64
129.60
129.23
128.95
123.49

95.66

77.42
77.16
76.91

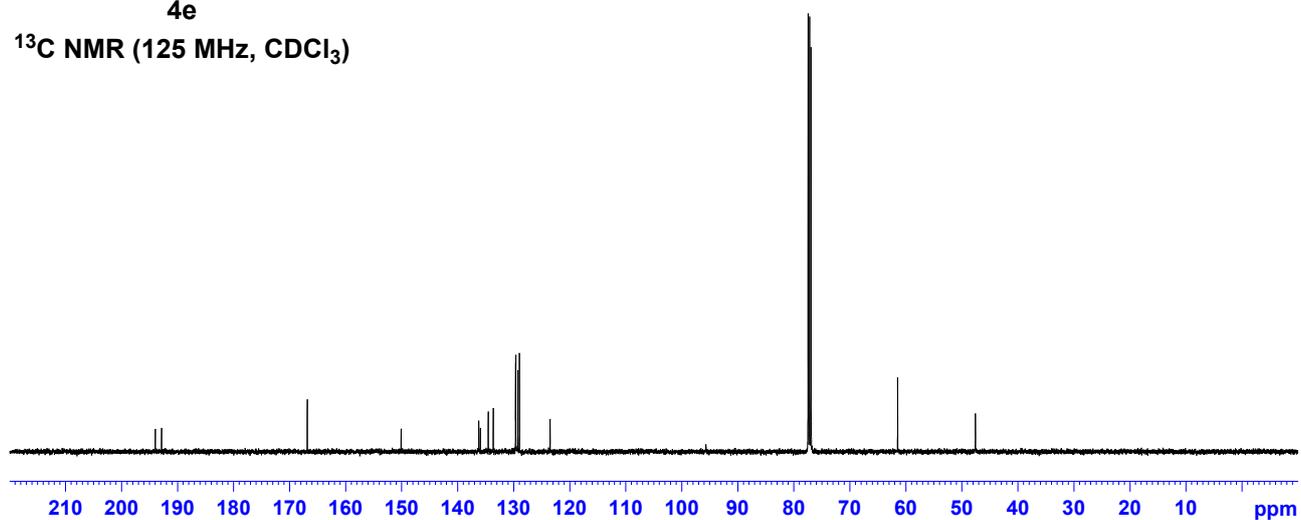
61.44

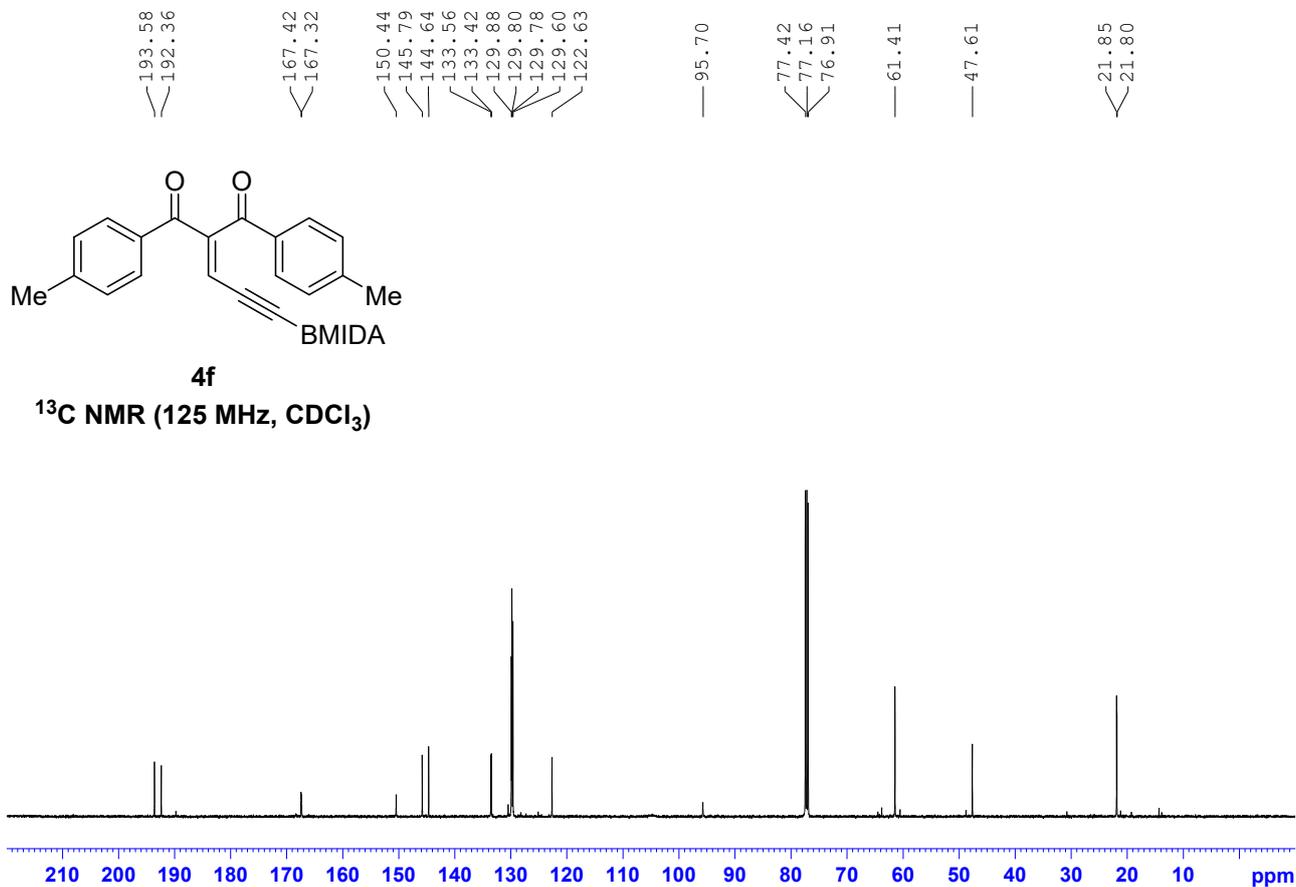
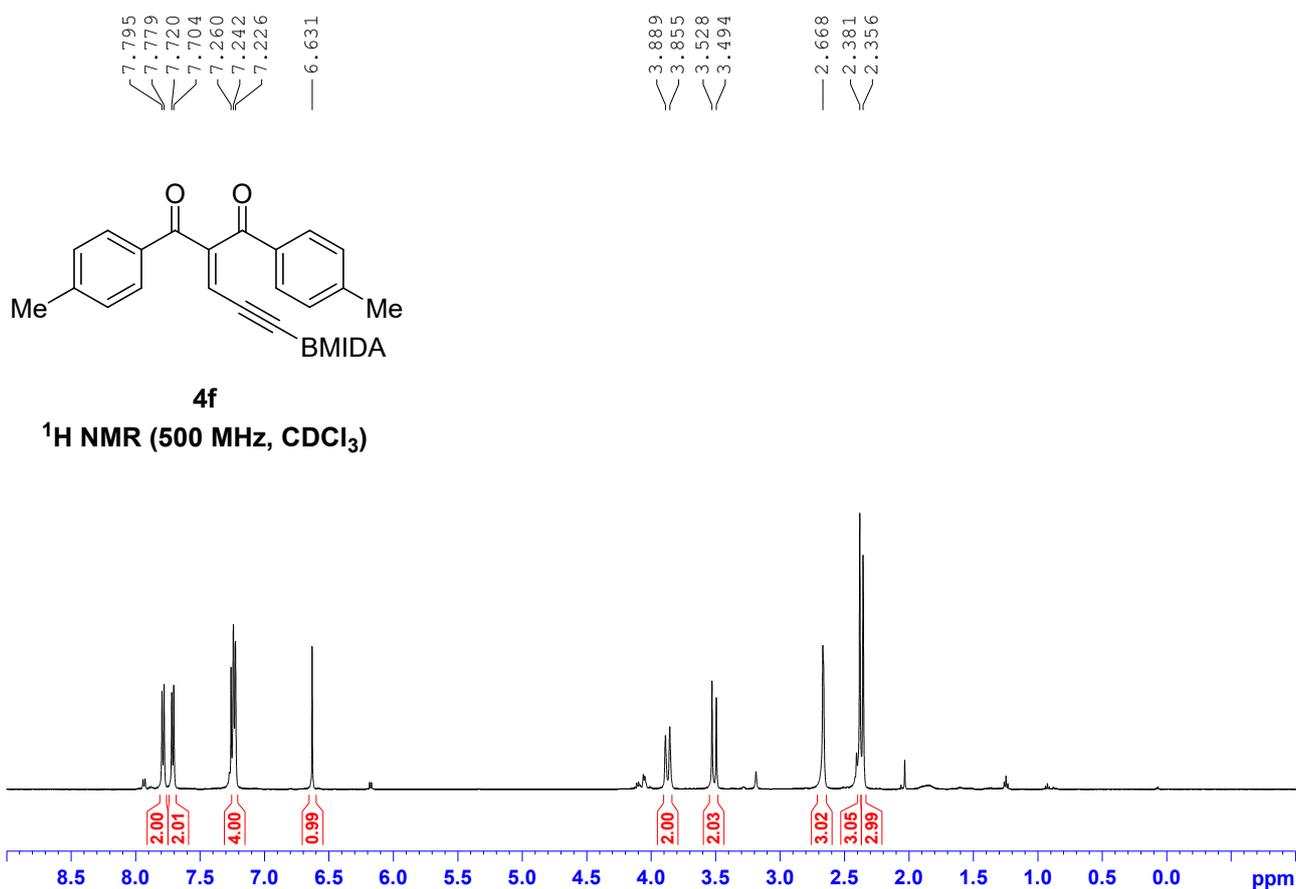
47.55

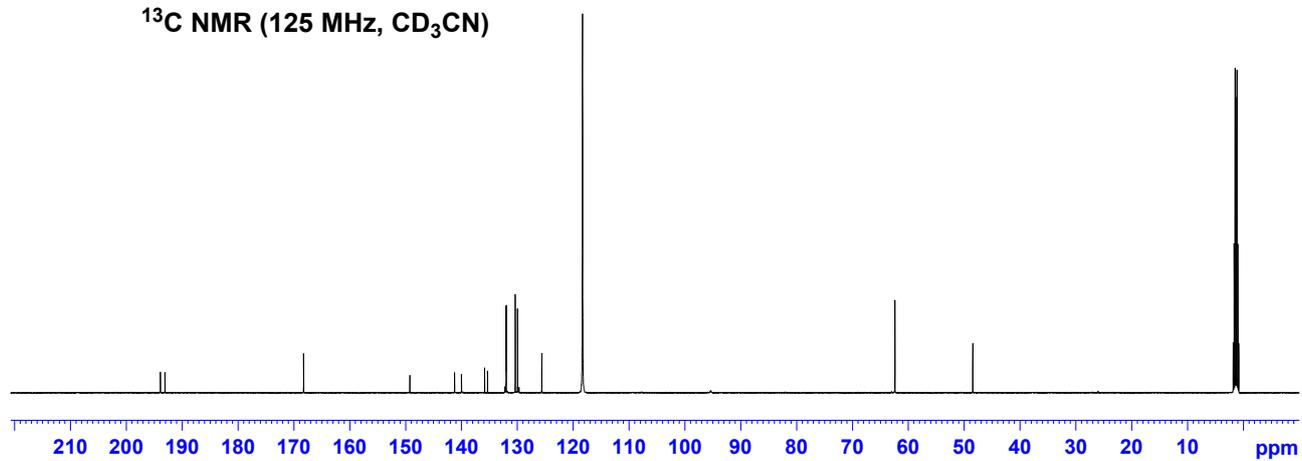
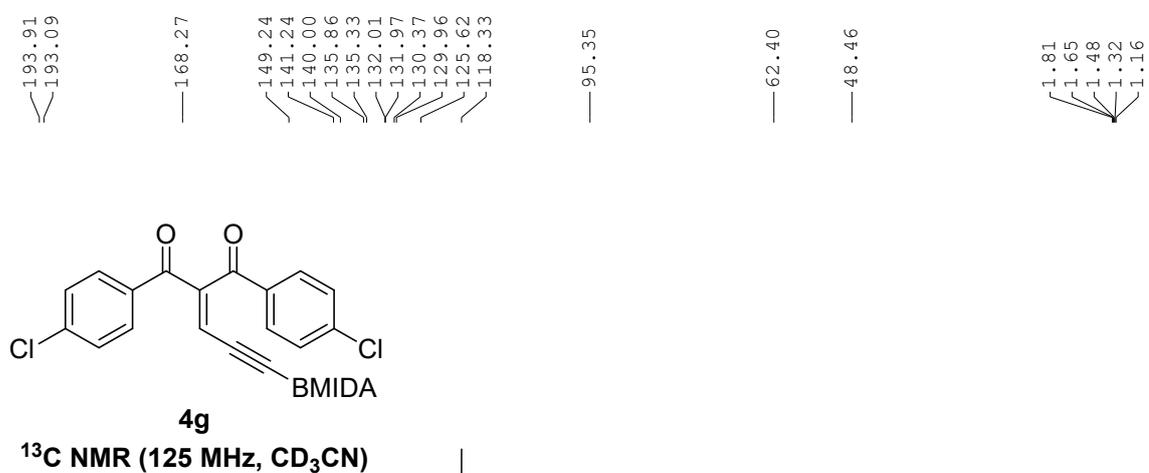
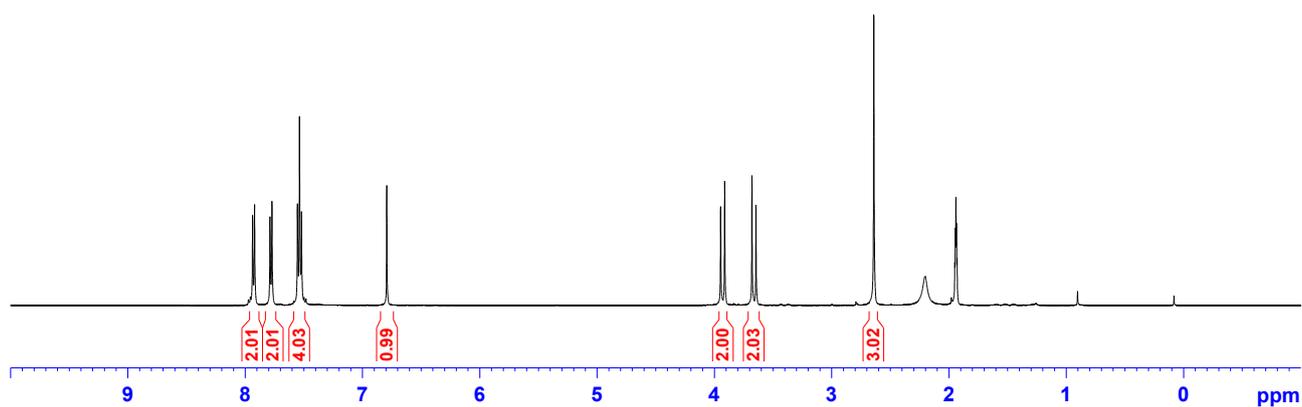
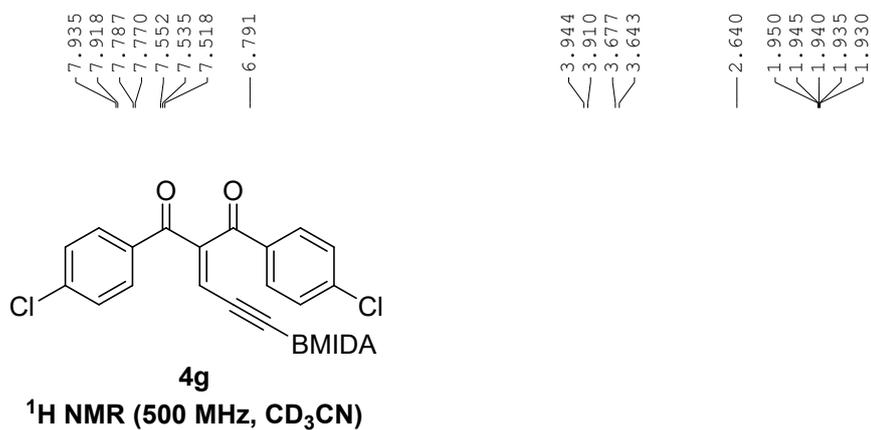


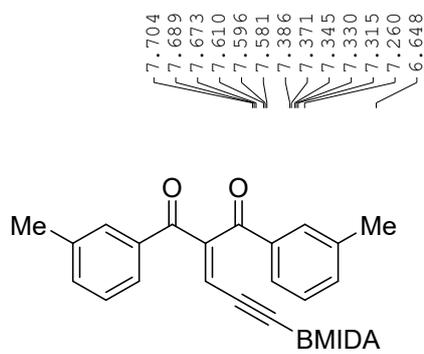
4e

¹³C NMR (125 MHz, CDCl₃)



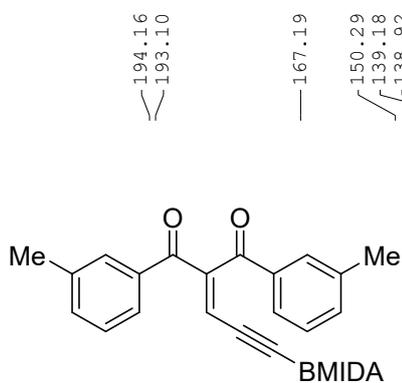
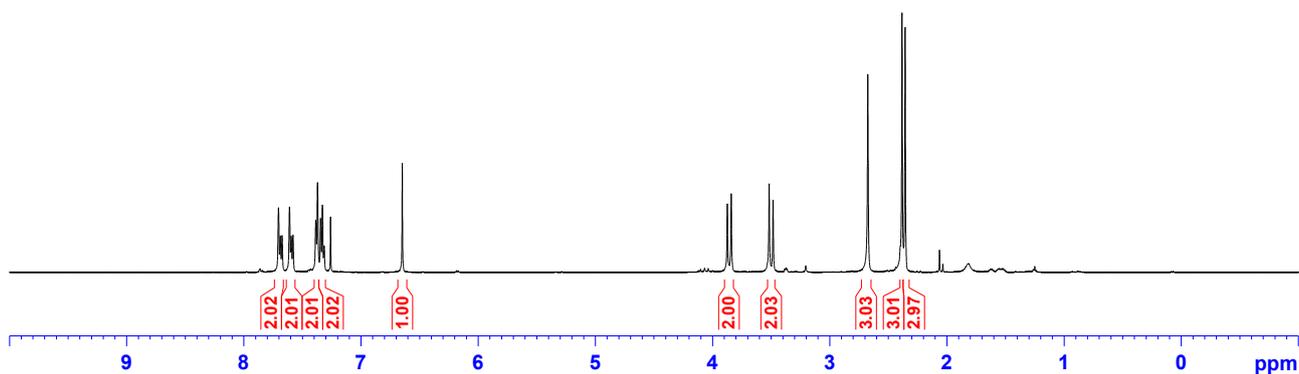






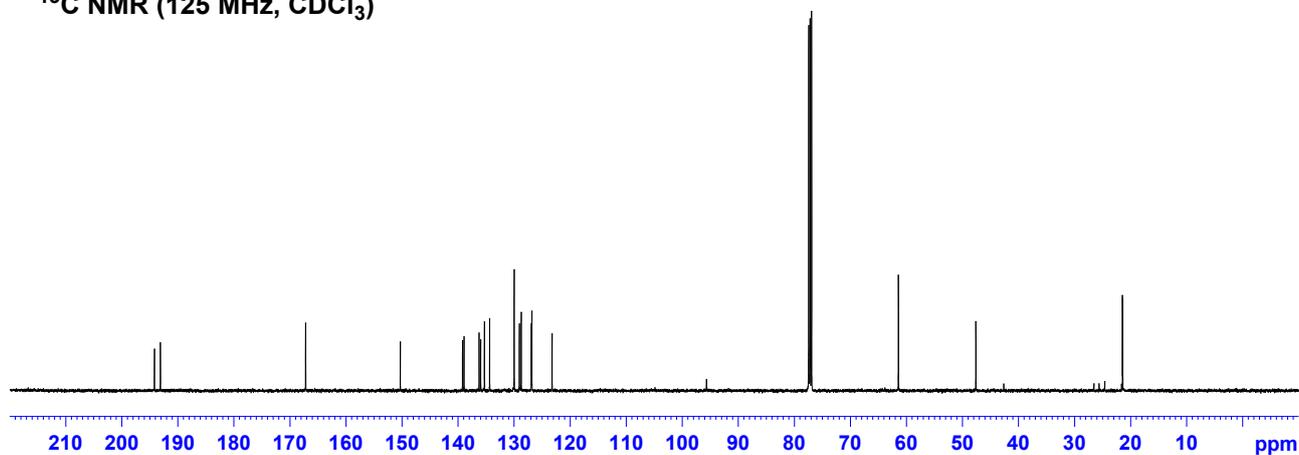
4h

$^1\text{H NMR}$ (500 MHz, CDCl_3)



4h

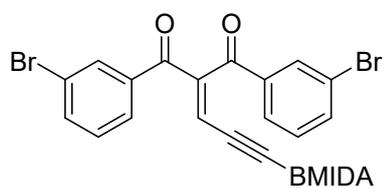
$^{13}\text{C NMR}$ (125 MHz, CDCl_3)



7.986
7.909
7.770
7.755
7.706
7.703
7.690
7.687
7.355
7.340
7.324
7.260
6.710

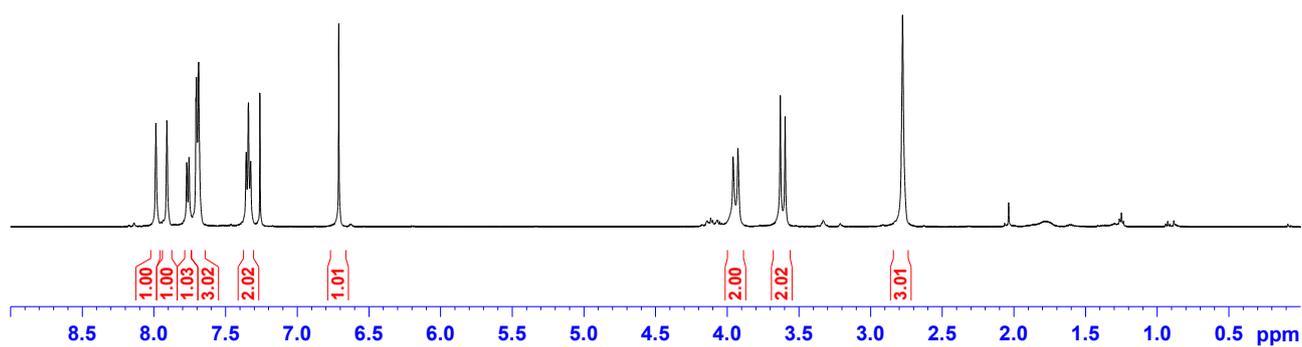
3.958
3.924
3.628
3.595

2.775



4i

¹H NMR (500 MHz, CDCl₃)



192.32
191.33

167.23

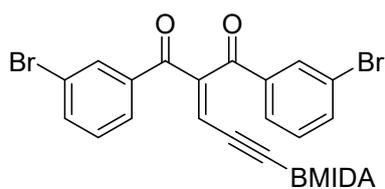
148.63
137.79
137.60
137.28
136.53
132.25
132.09
130.94
130.52
128.29
128.10
124.87
123.33
123.28

95.18

77.41
77.16
76.91

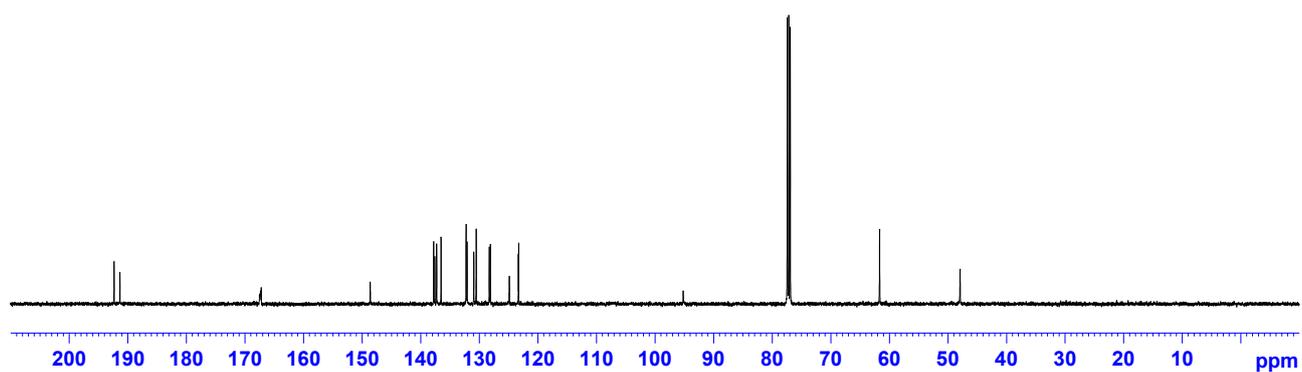
61.65

47.91



4i

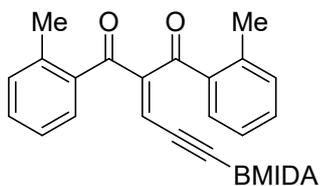
¹³C NMR (125 MHz, CDCl₃)



7.590
7.574
7.384
7.368
7.349
7.333
7.319
7.260
7.251
7.236
7.226
7.209
7.191
7.176
6.559

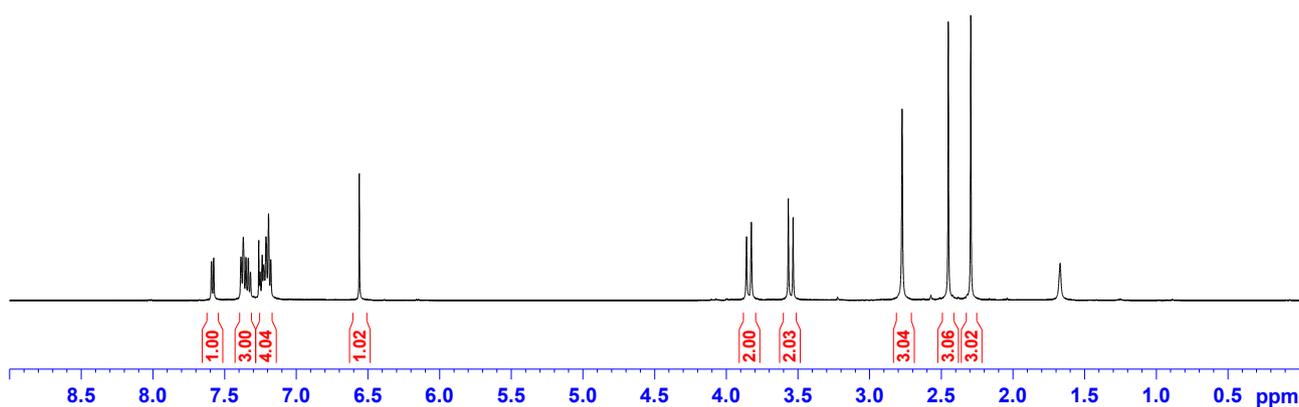
3.856
3.823
3.567
3.533

2.773
2.450
2.293



4j

¹H NMR (500 MHz, CDCl₃)



195.72
195.45

166.91
166.86

152.54
139.70
137.59
136.79
136.08
132.75
132.29
131.58
131.42
130.81
128.47
126.08
125.58
124.11

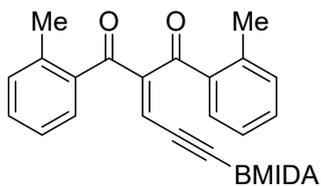
95.85

77.41
77.16
76.90

61.48

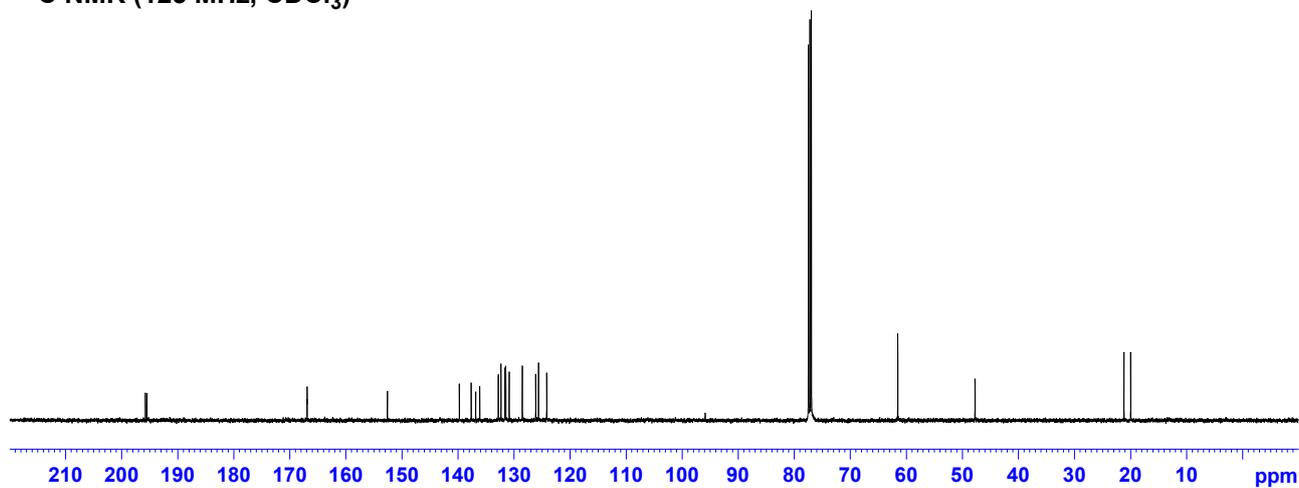
47.69

21.11
19.92



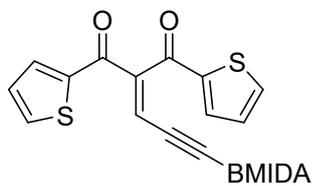
4j

¹³C NMR (125 MHz, CDCl₃)



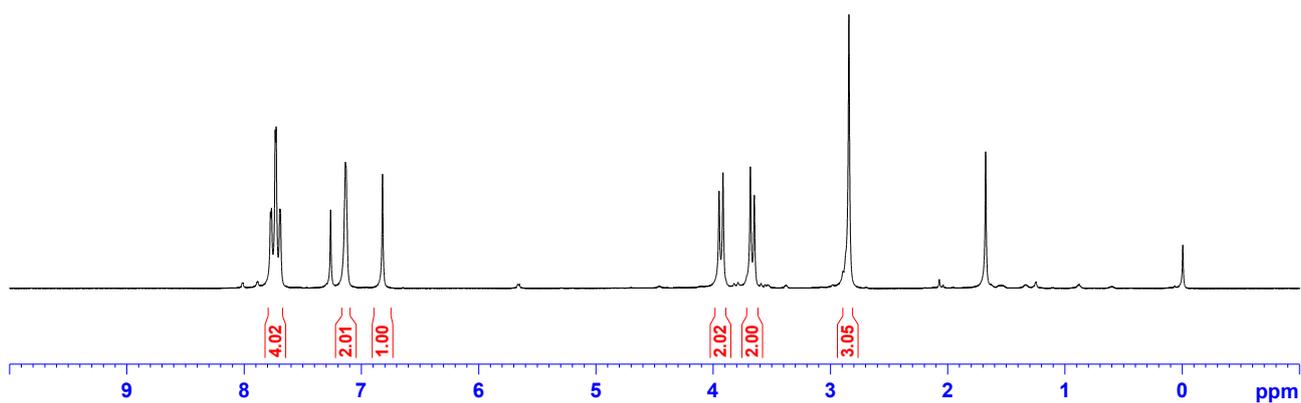
7.773
7.764
7.732
7.725
7.694
7.688
7.260
7.134
7.128
6.817

3.949
3.916
3.682
3.649
— 2.842



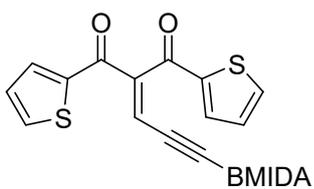
4k

¹H NMR (500 MHz, CDCl₃)



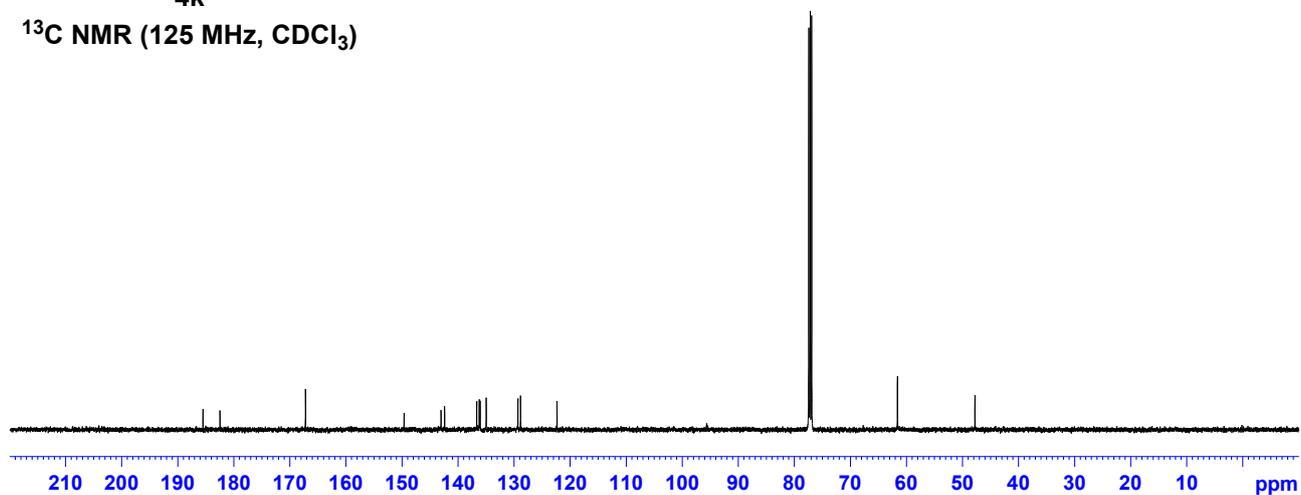
185.49
182.47
— 167.21
149.62
143.03
142.39
136.66
136.20
136.05
134.96
129.31
128.84
122.34

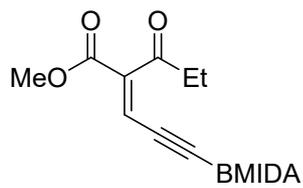
— 95.60
77.41
77.16
76.90
— 61.59
— 47.77



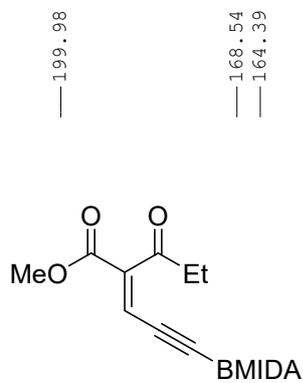
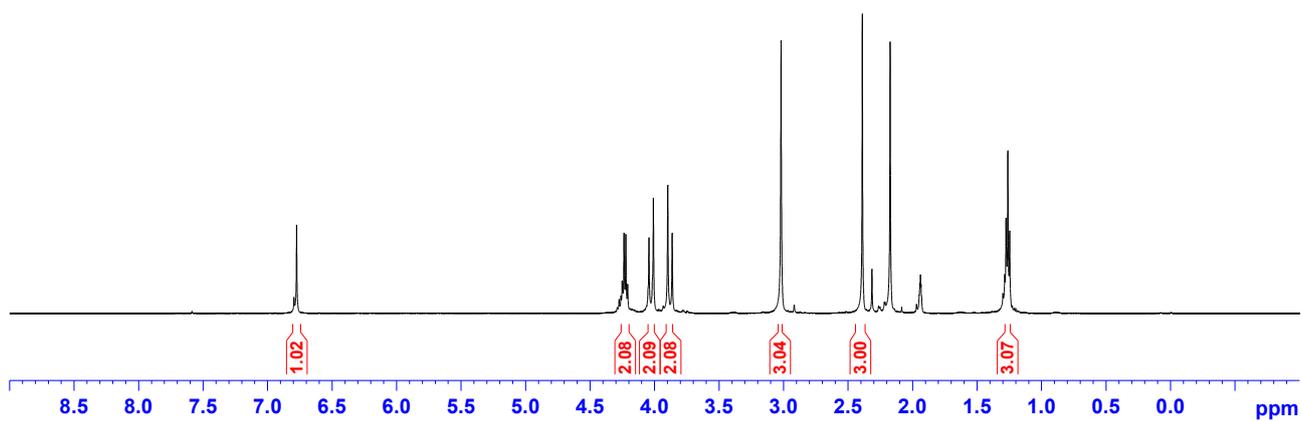
4k

¹³C NMR (125 MHz, CDCl₃)

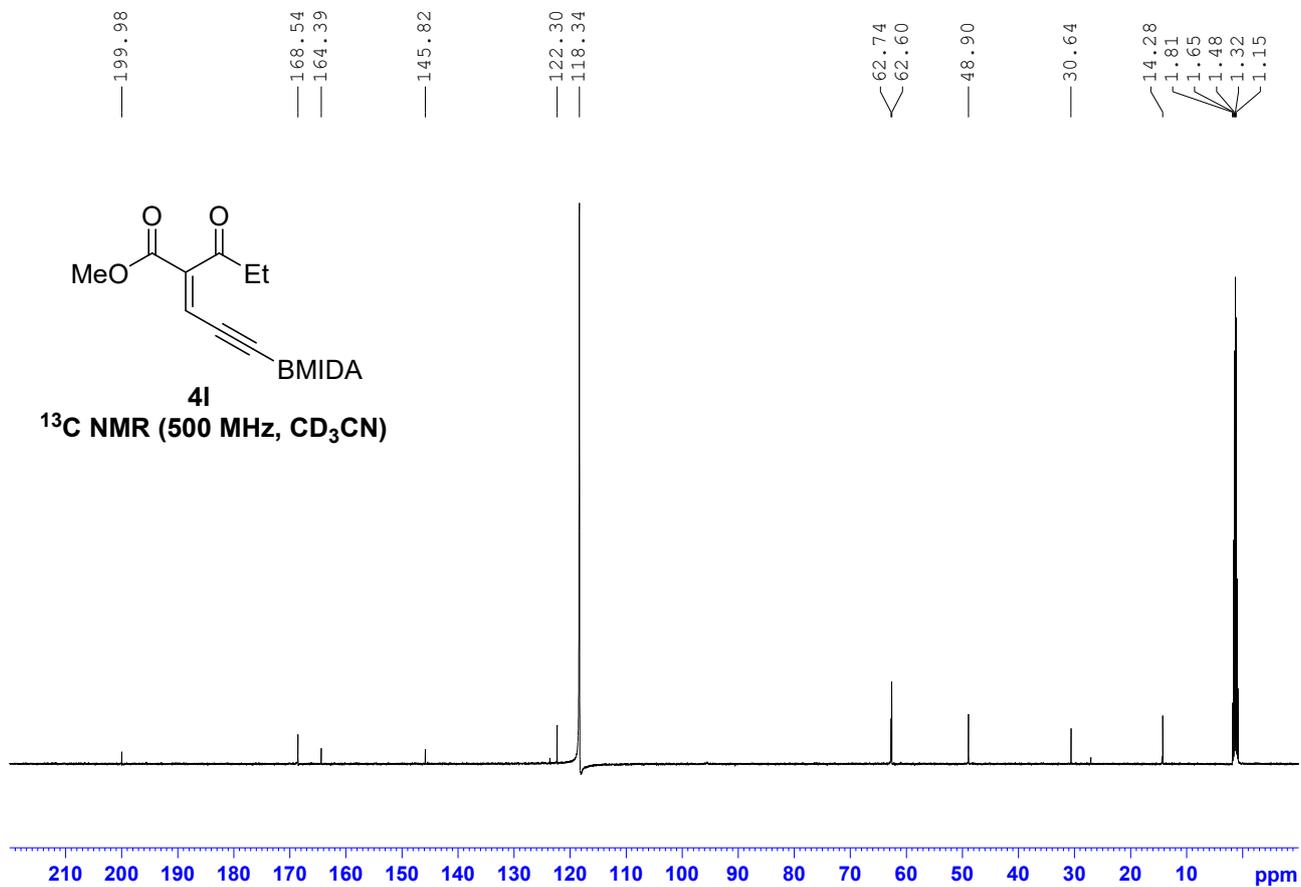


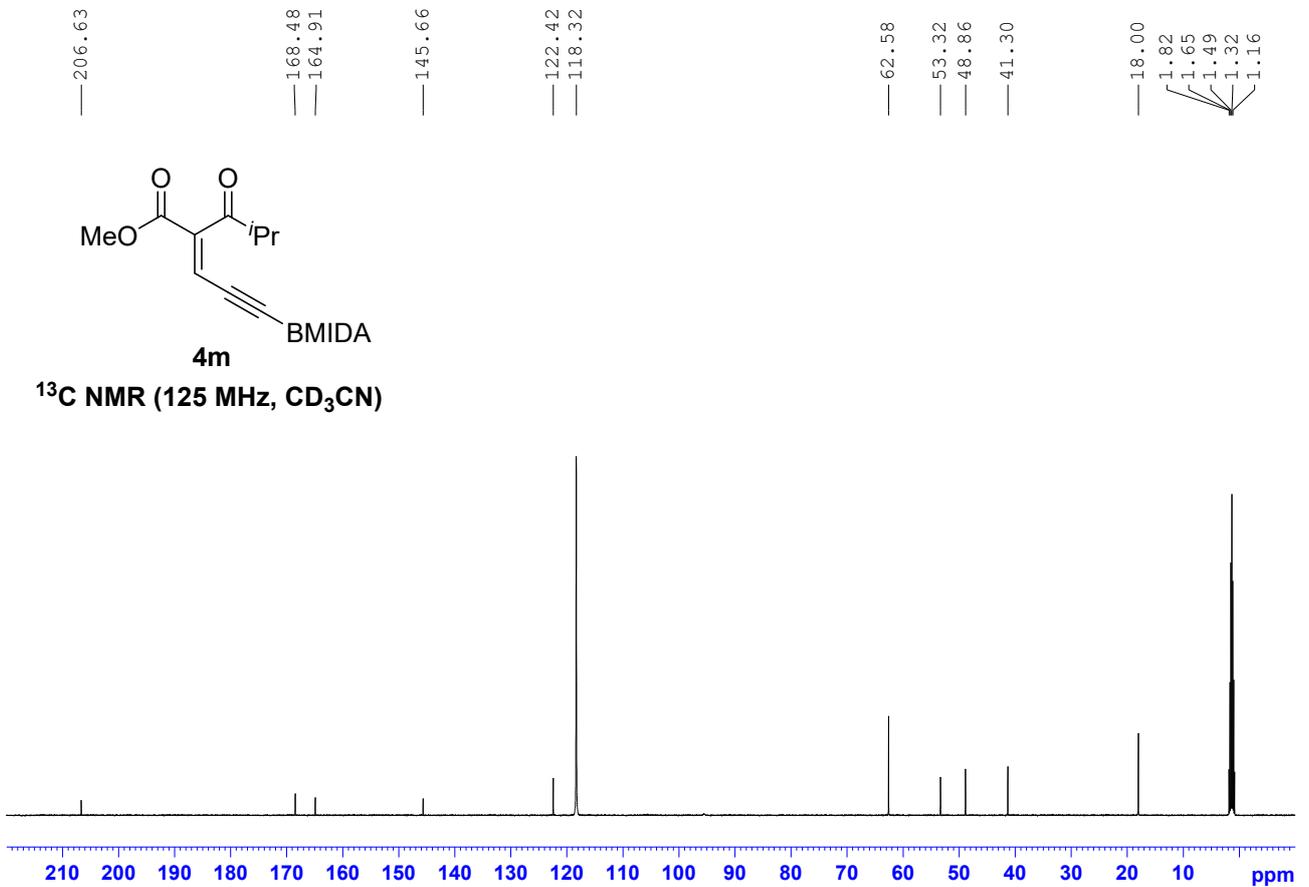
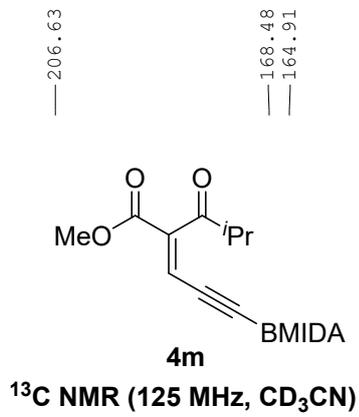
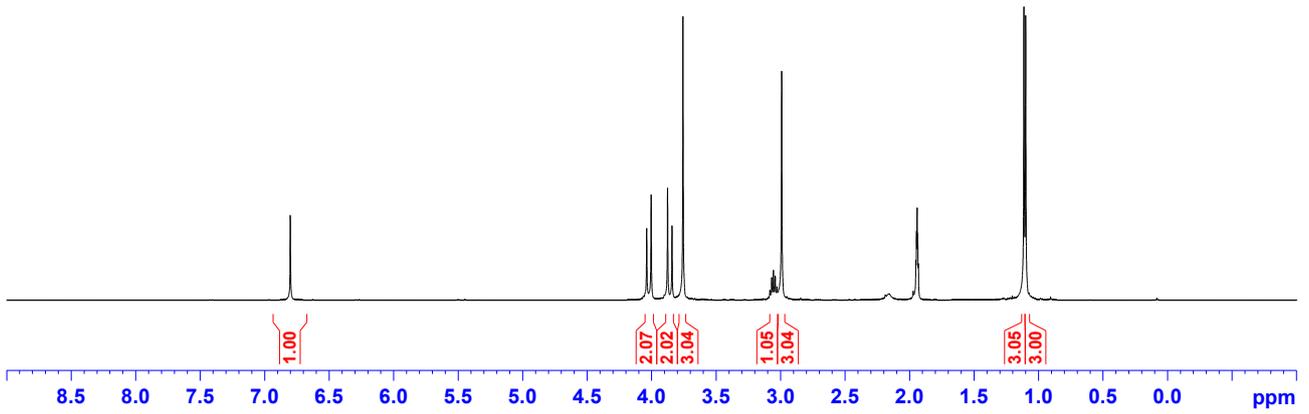
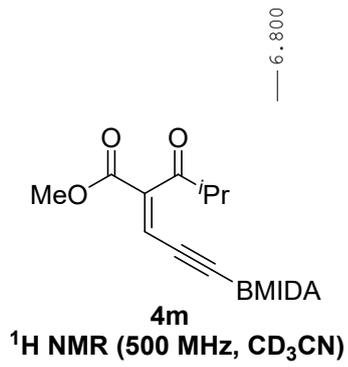


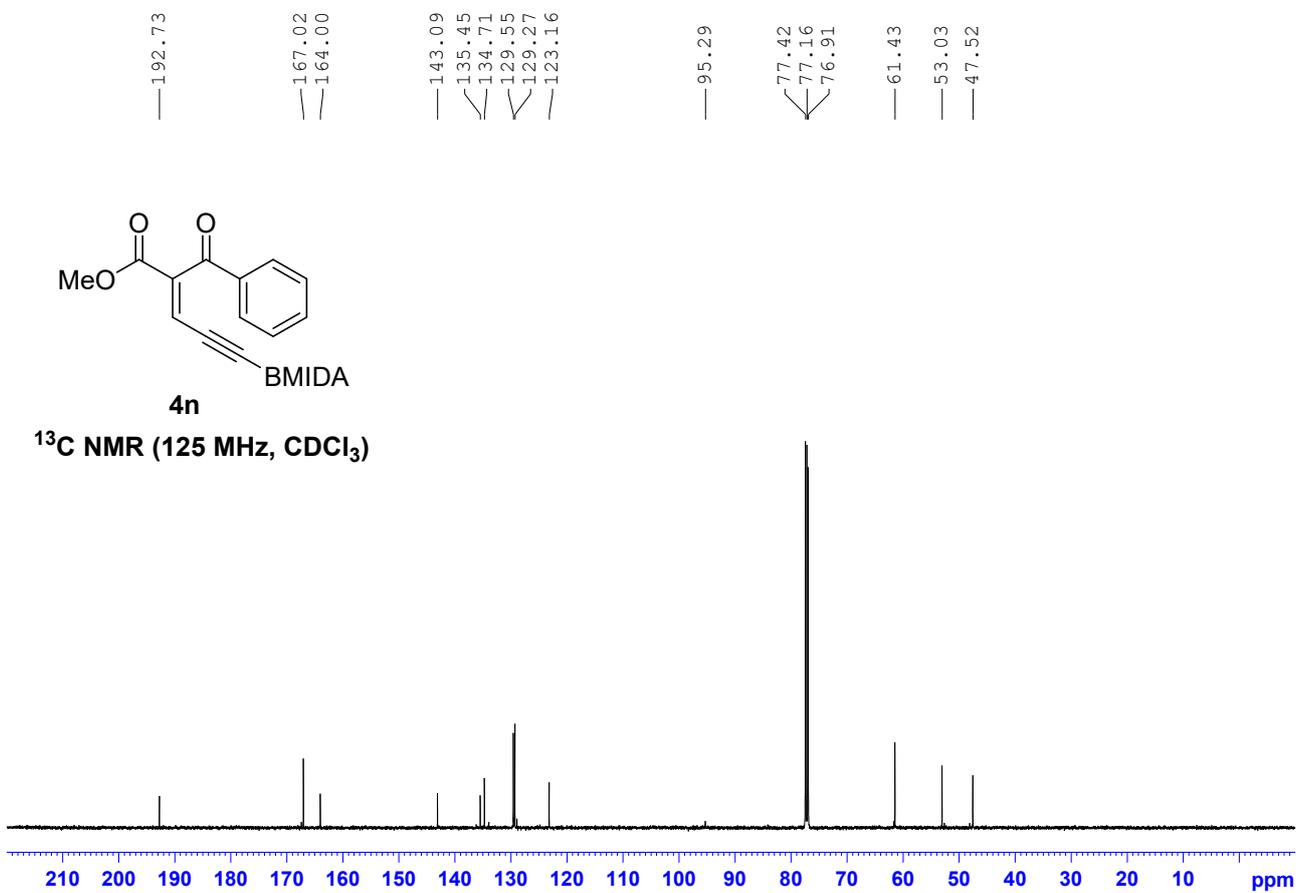
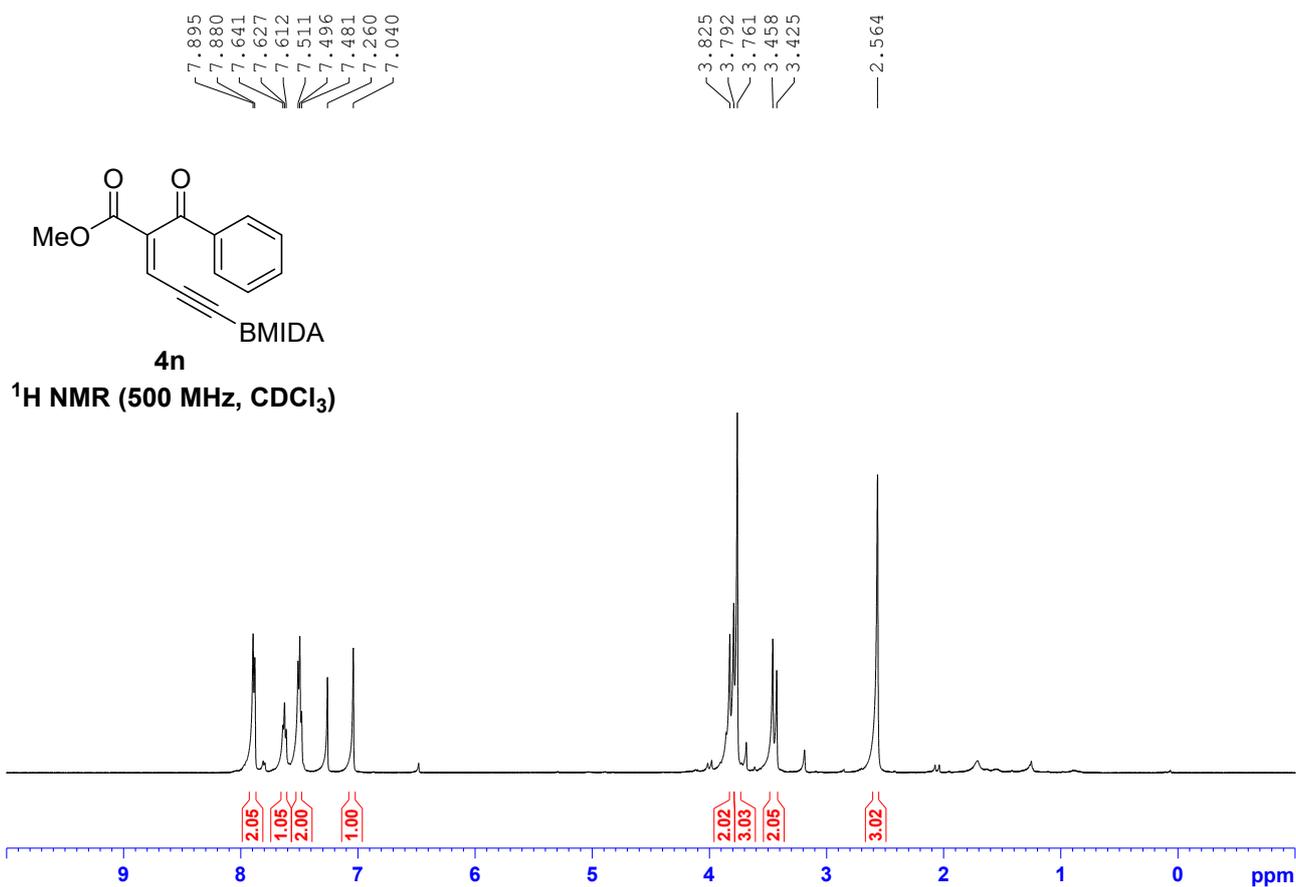
¹H NMR (500 MHz, CD₃CN)

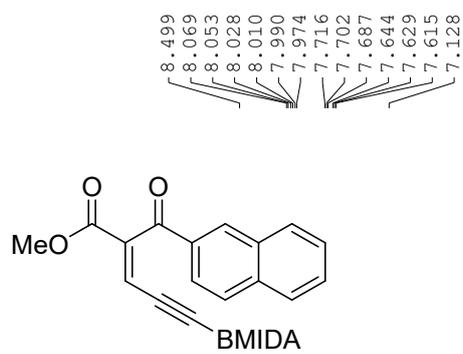


¹³C NMR (500 MHz, CD₃CN)

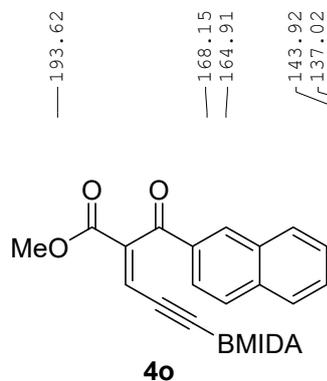
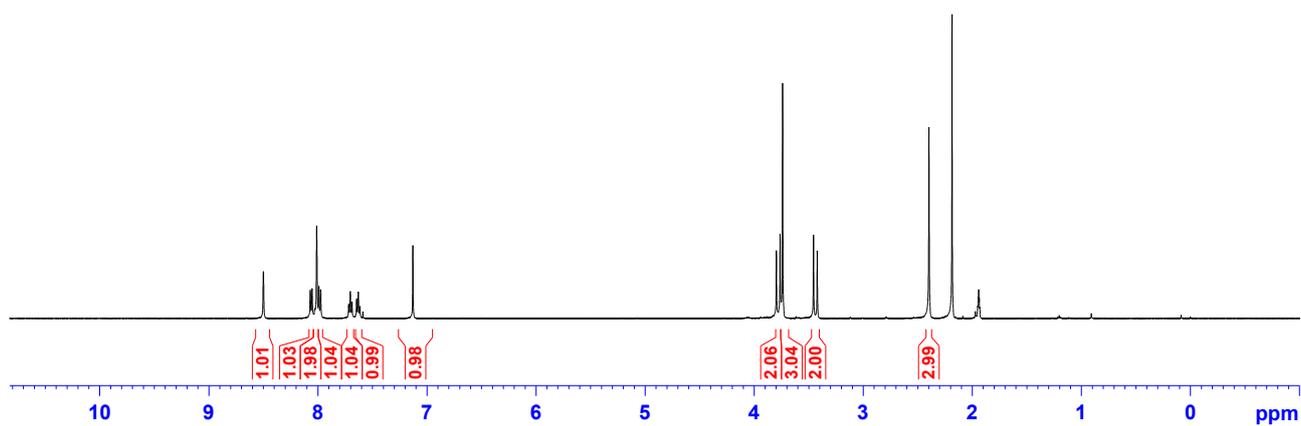




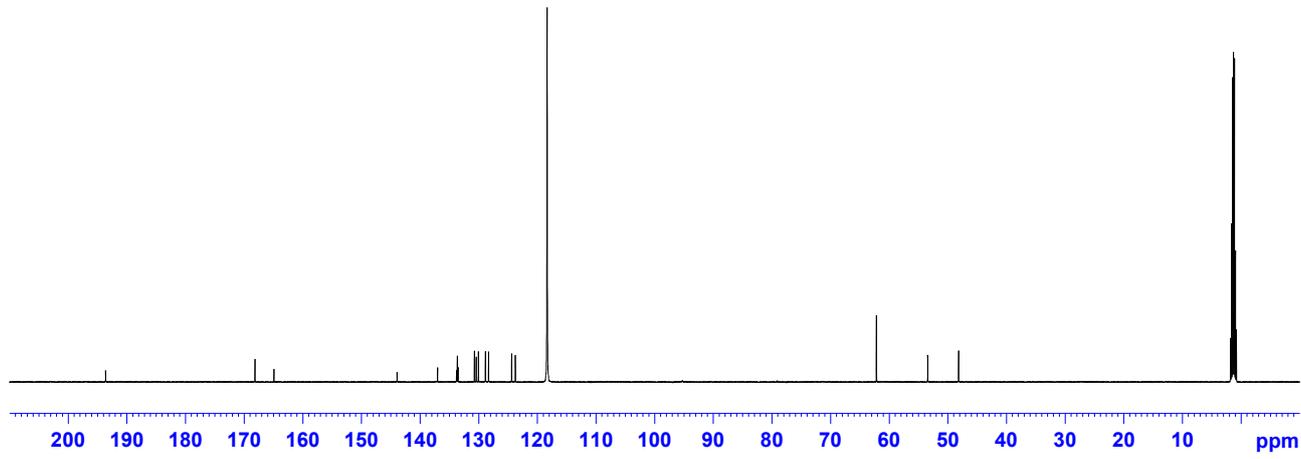


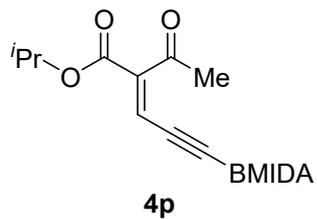


¹H NMR (500 MHz, CD₃CN)

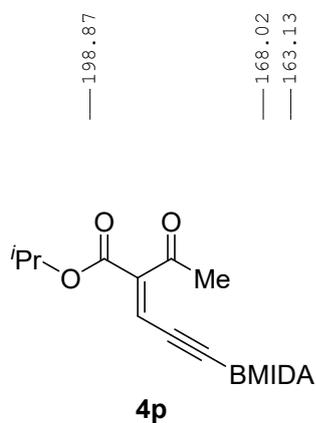
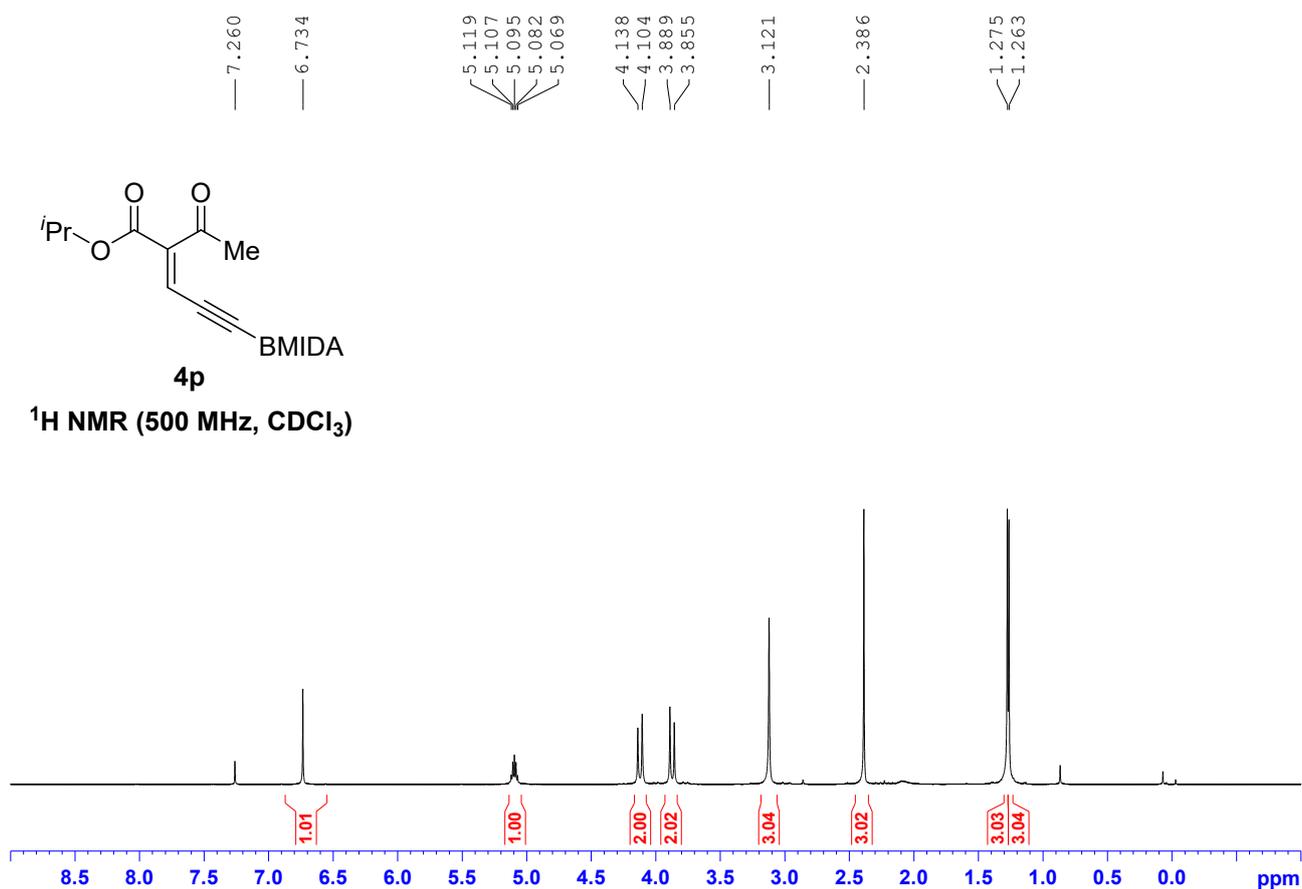


¹³C NMR (125 MHz, CD₃CN)

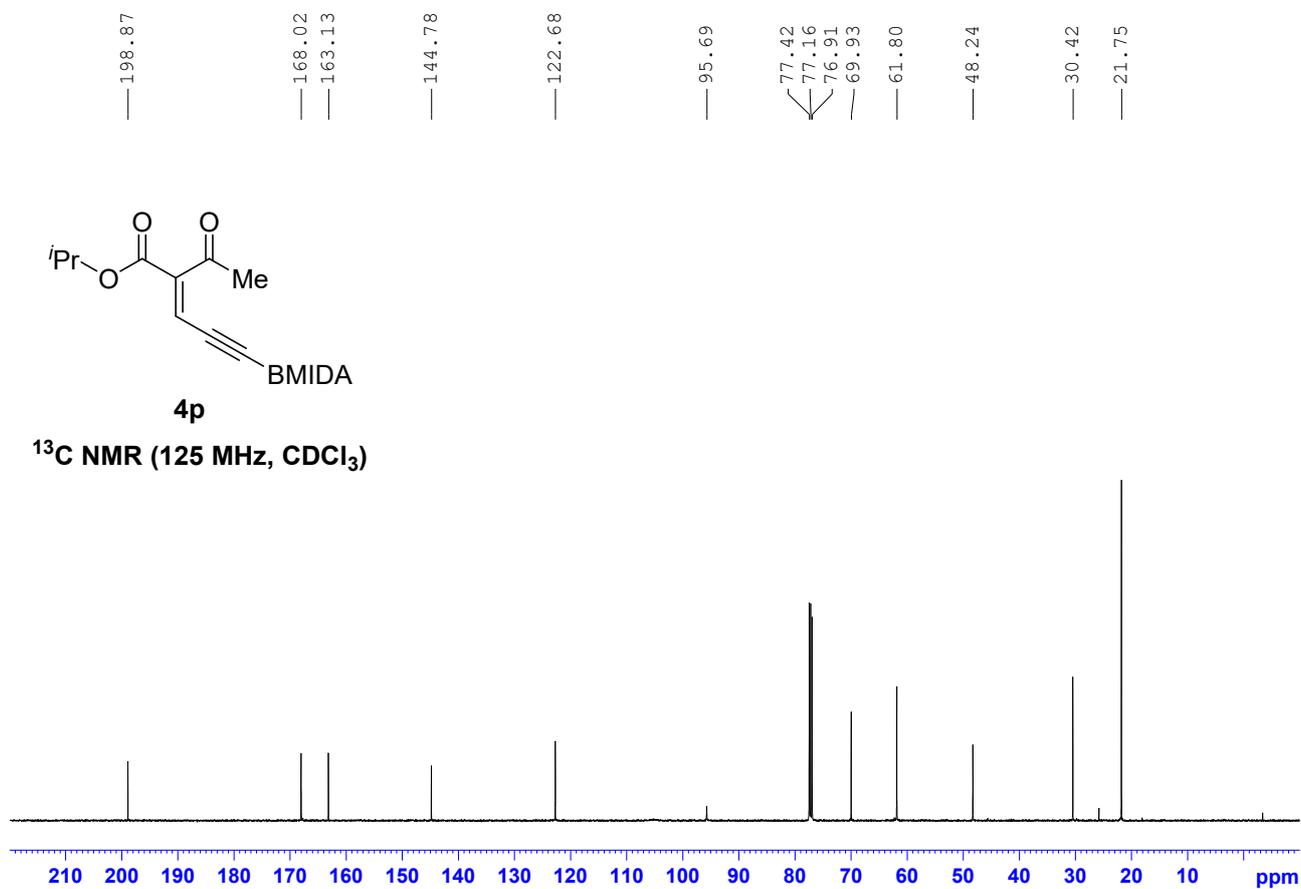


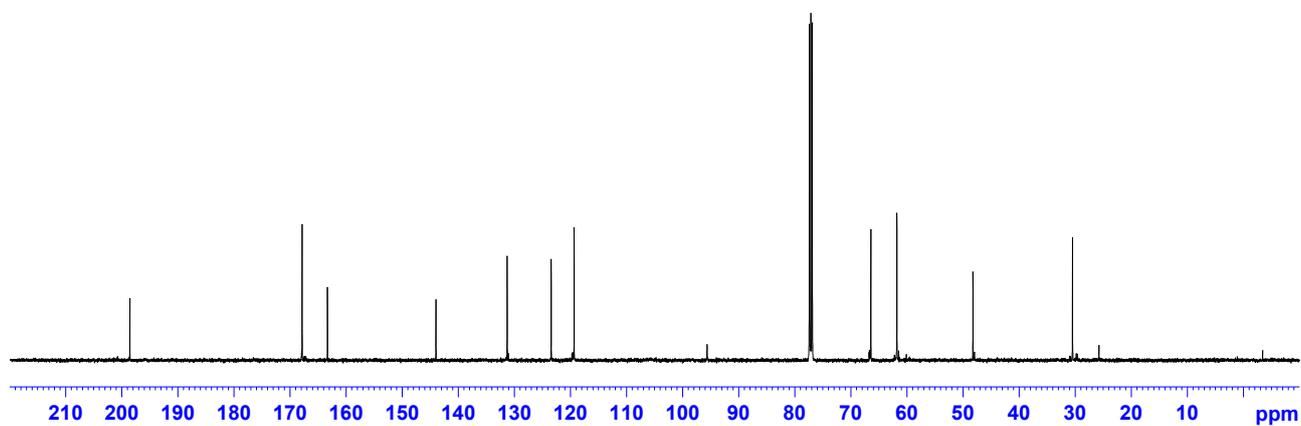
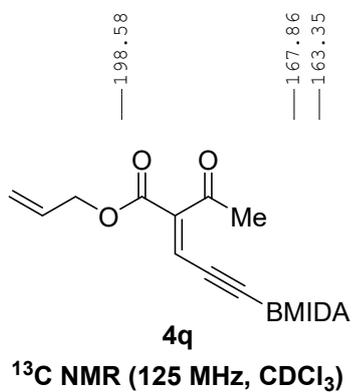
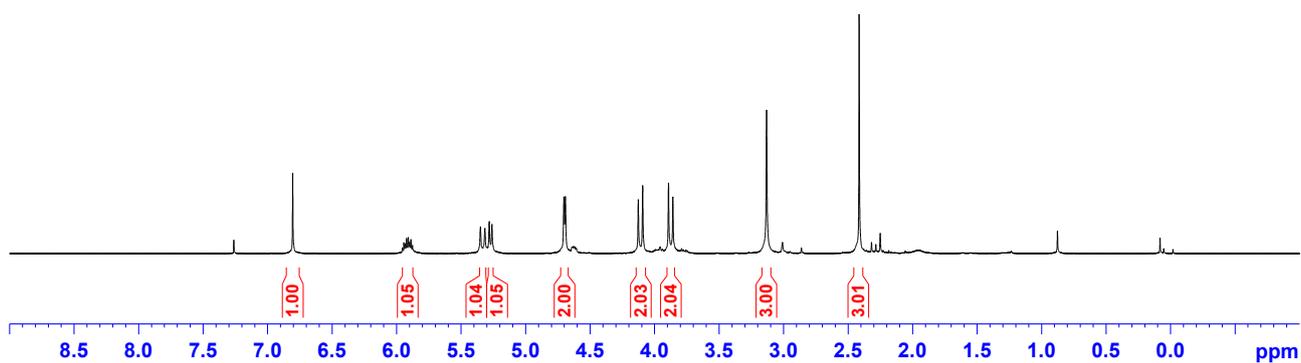
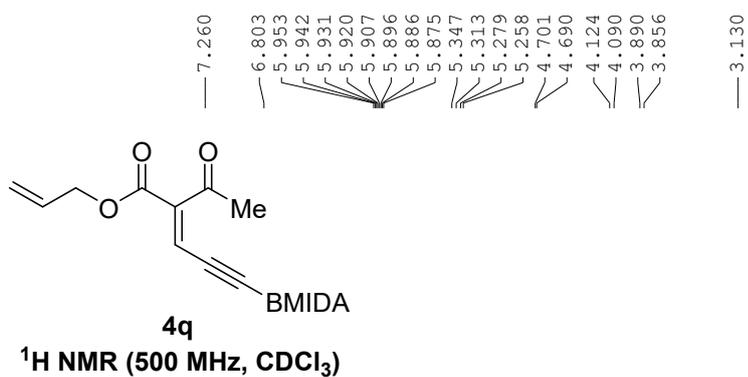


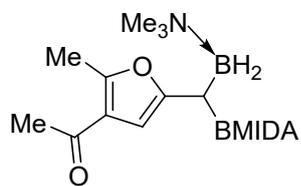
¹H NMR (500 MHz, CDCl₃)



¹³C NMR (125 MHz, CDCl₃)

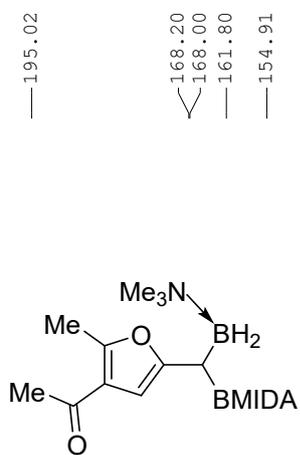
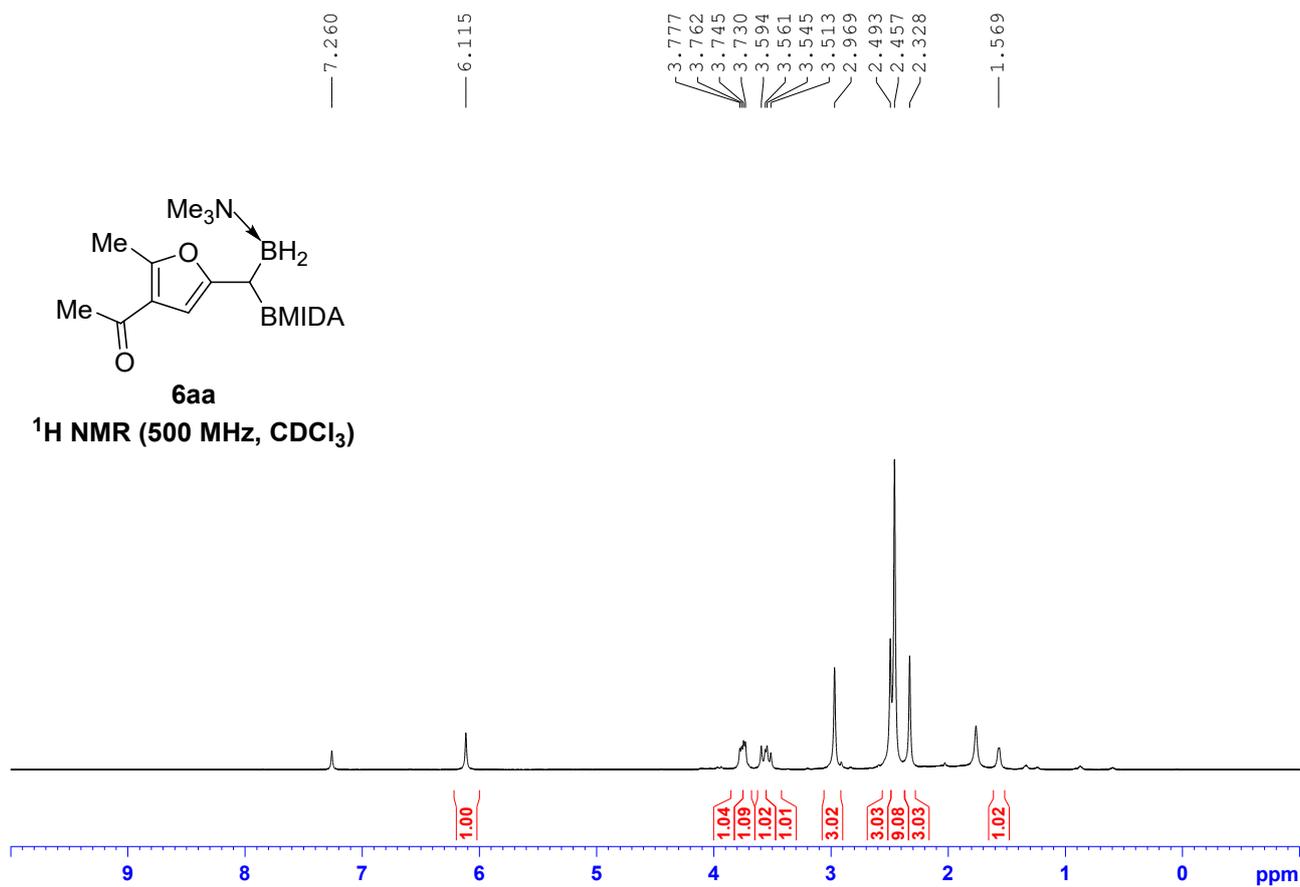






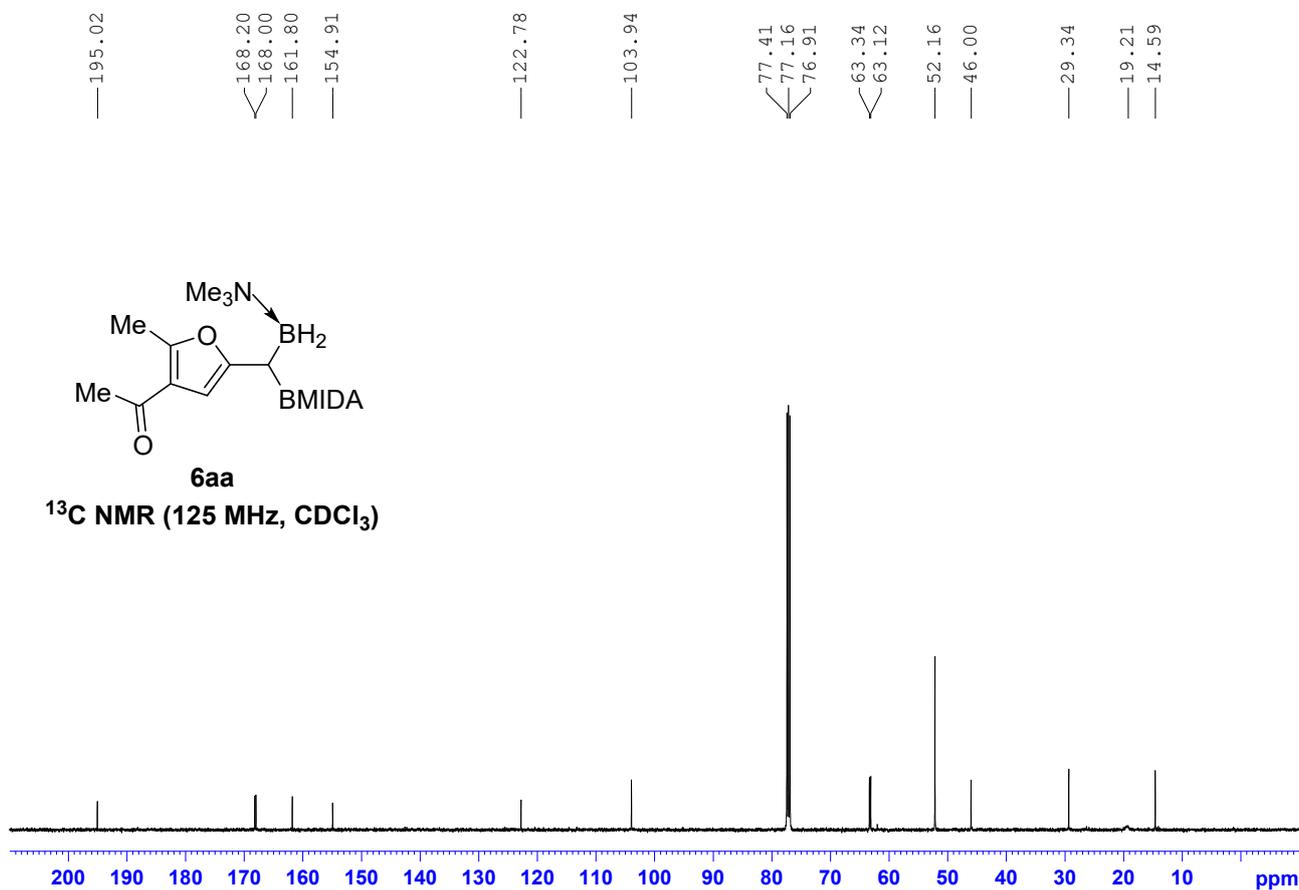
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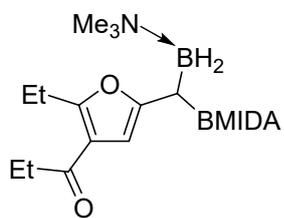
¹H NMR (500 MHz, CDCl₃)



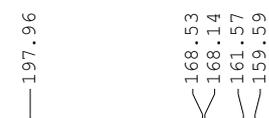
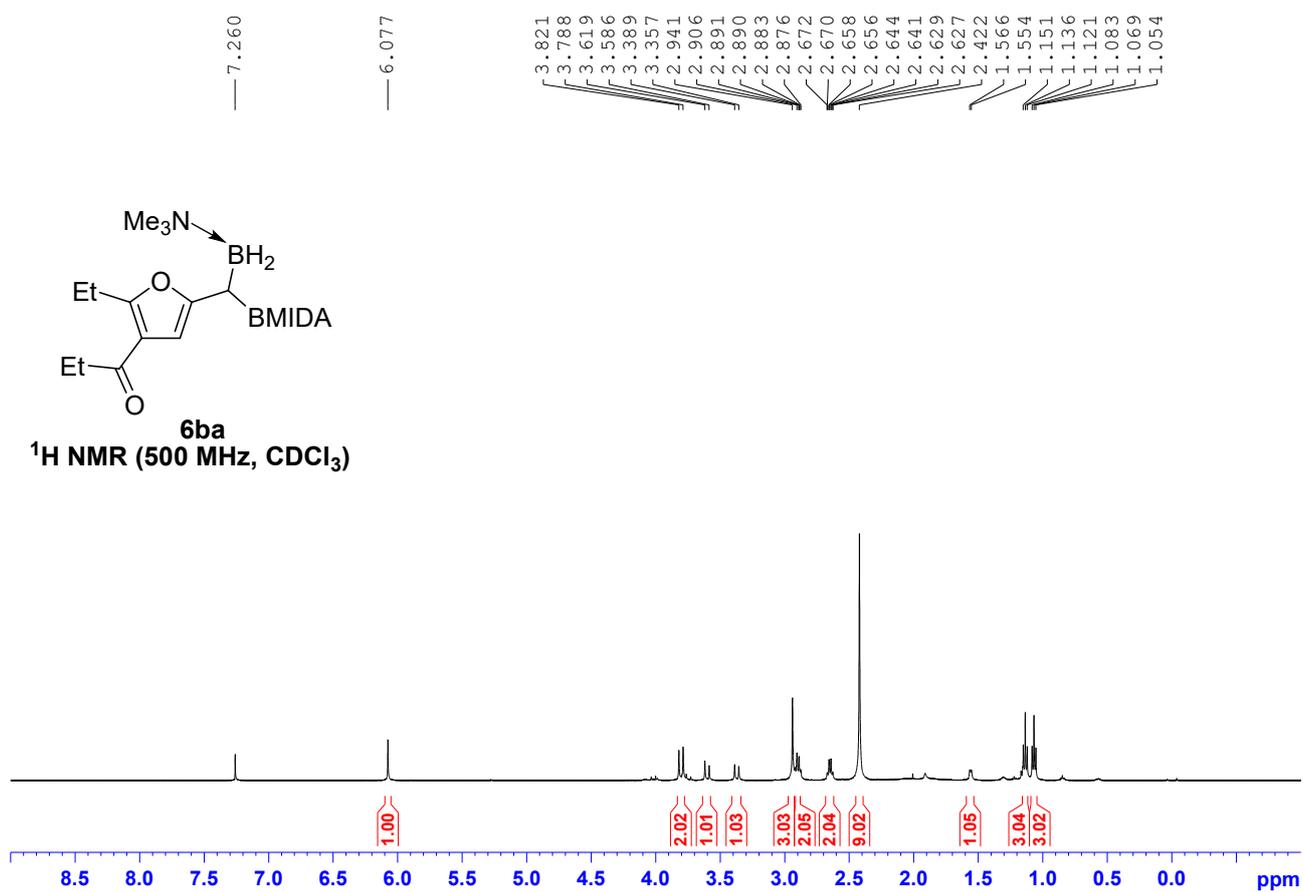
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¹³C NMR (125 MHz, CDCl₃)

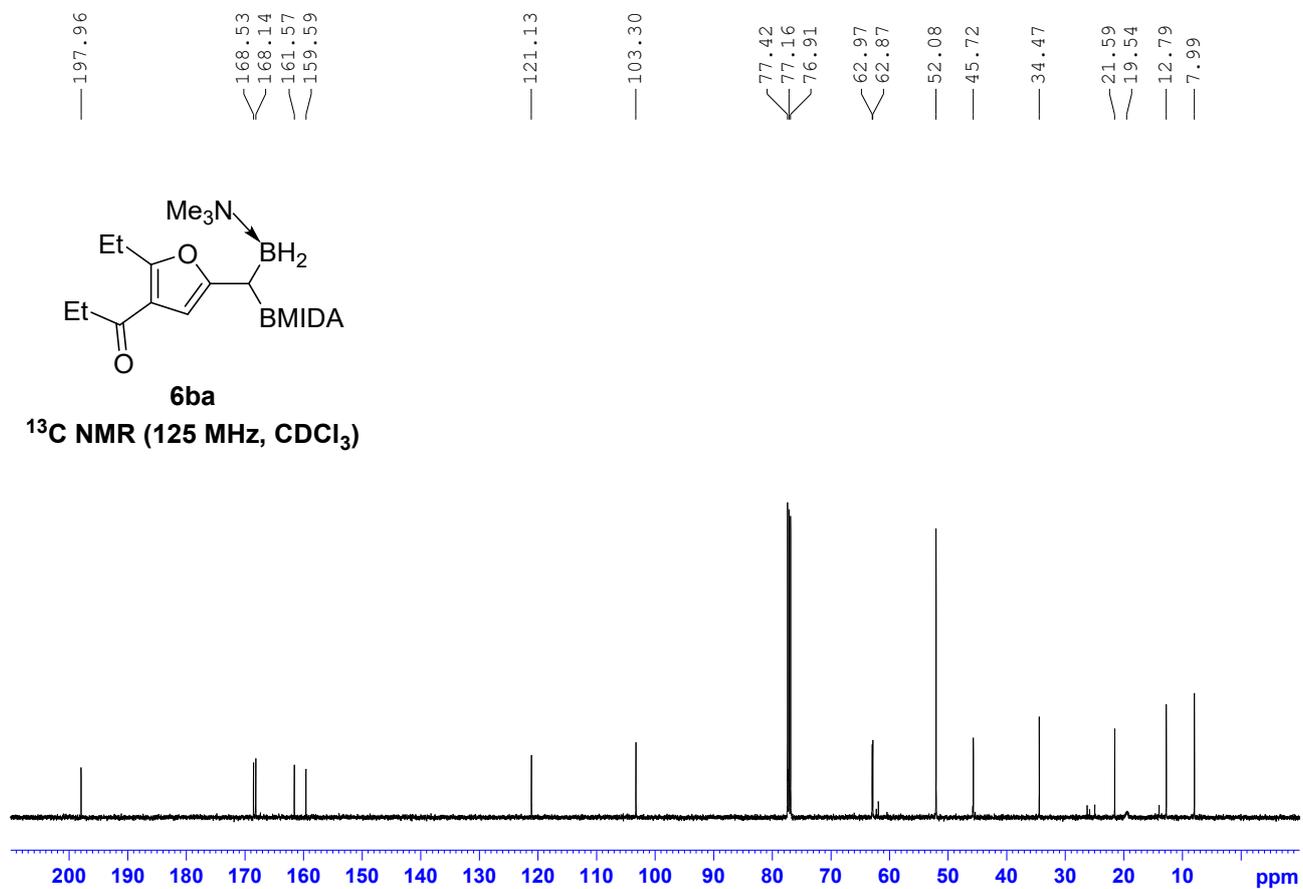


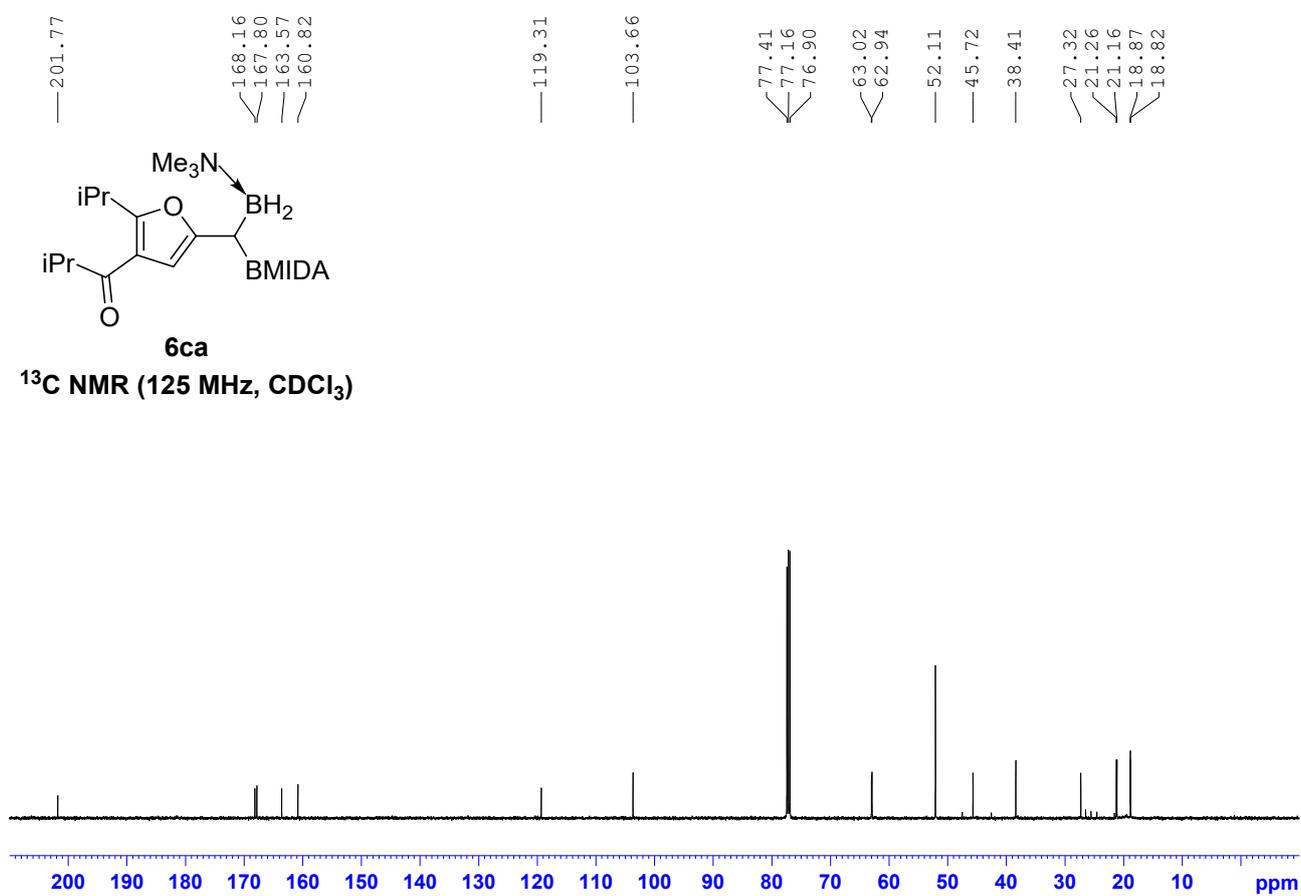
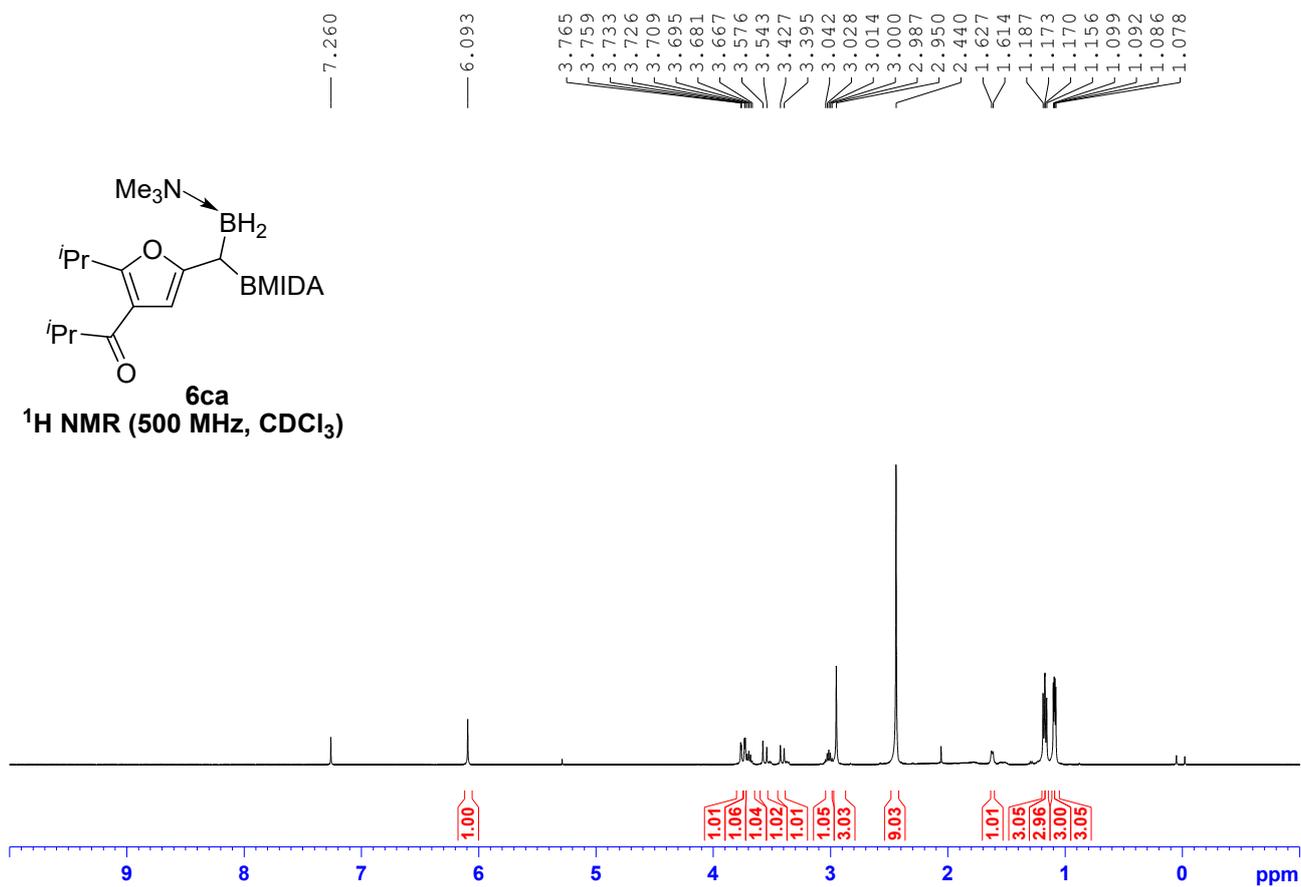


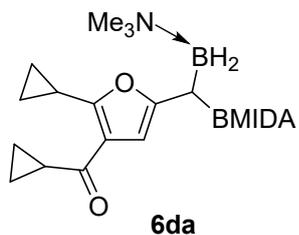
6ba
 $^1\text{H NMR}$ (500 MHz, CDCl_3)



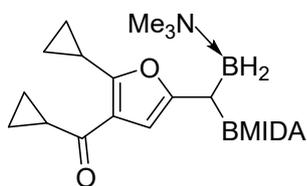
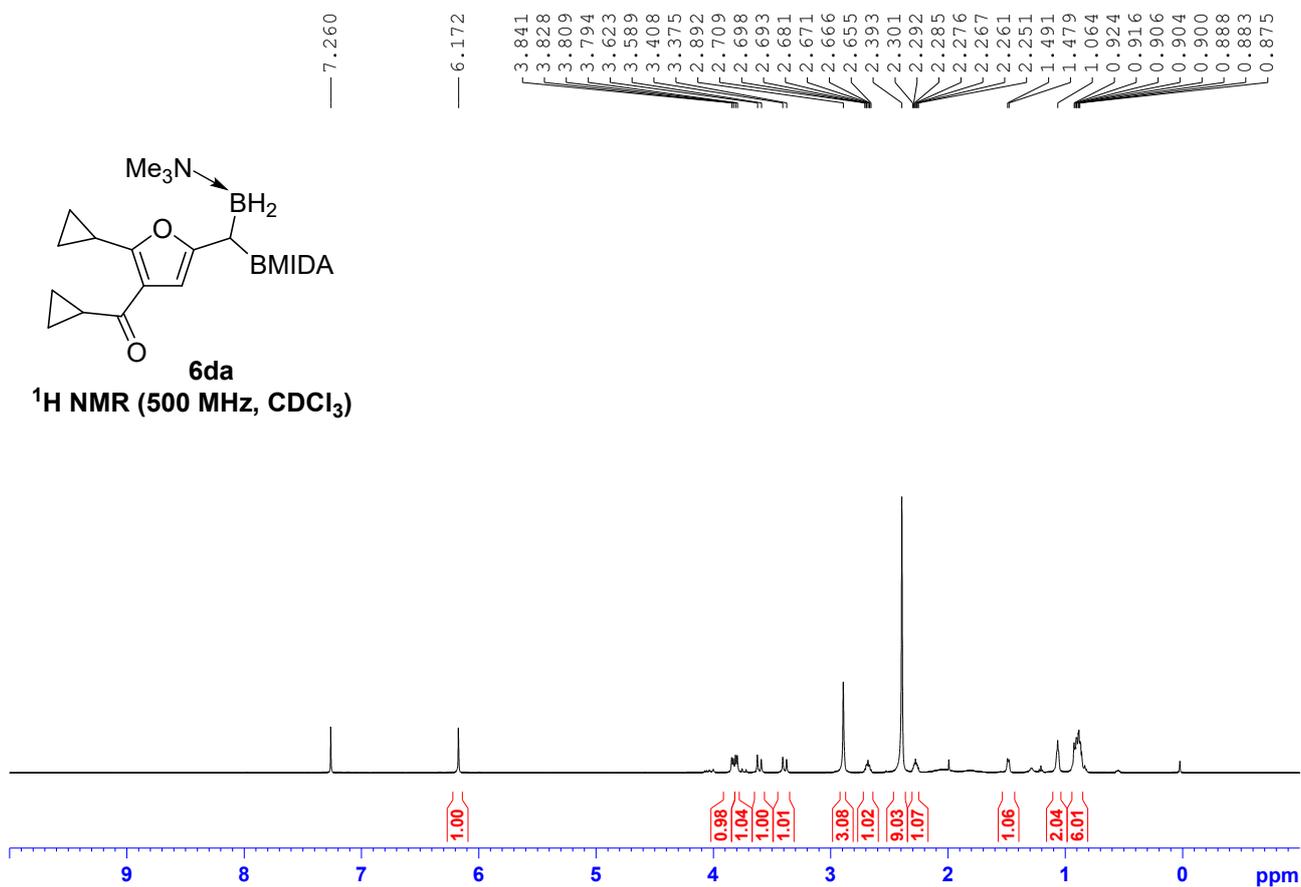
6ba
 $^{13}\text{C NMR}$ (125 MHz, CDCl_3)



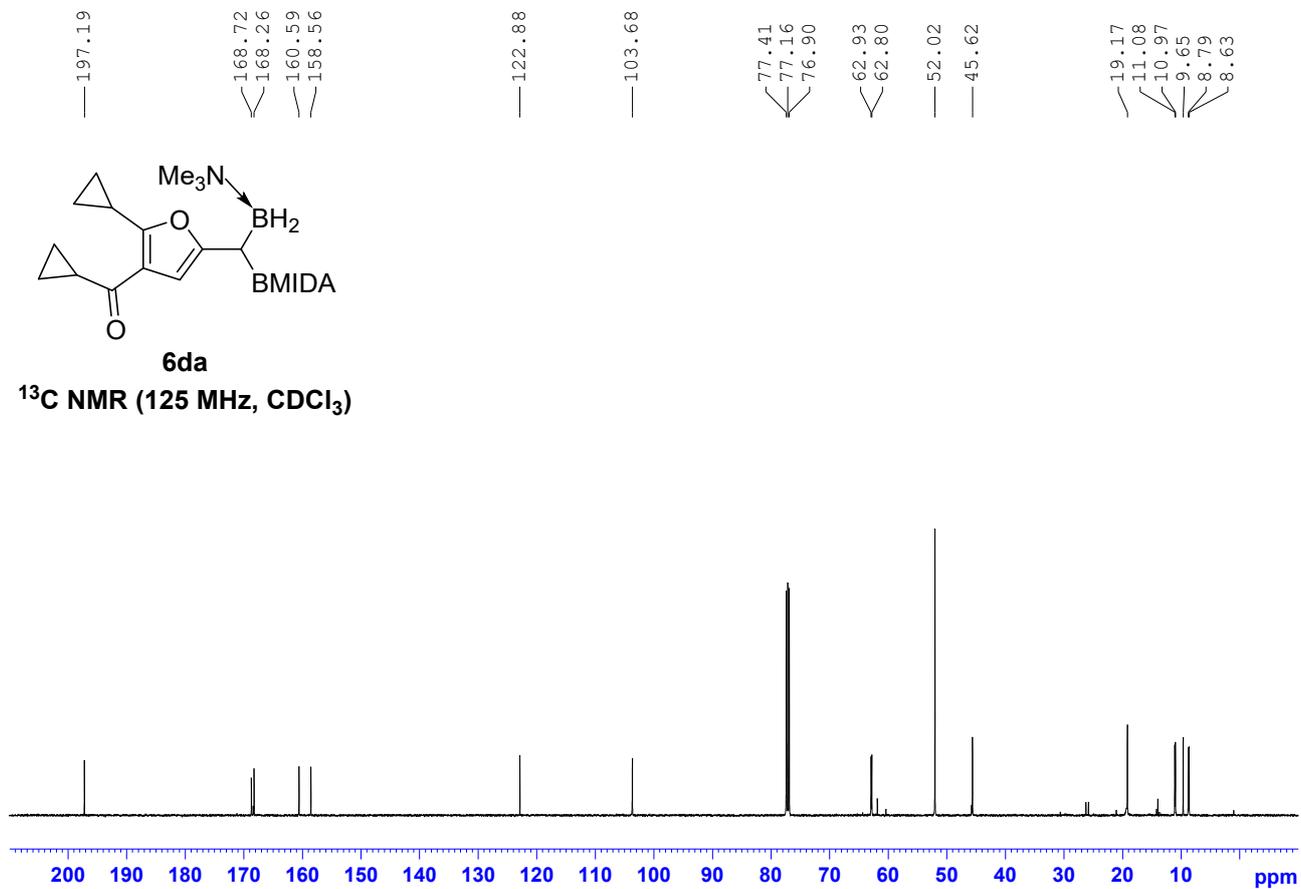


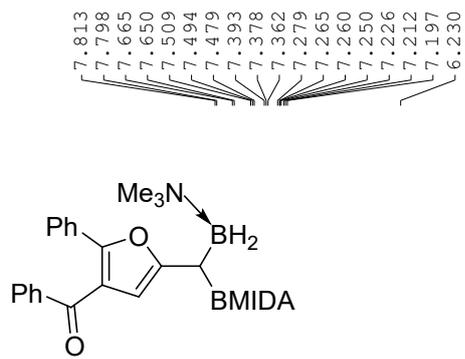


¹H NMR (500 MHz, CDCl₃)



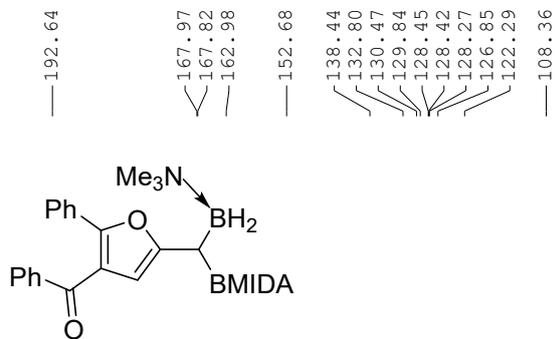
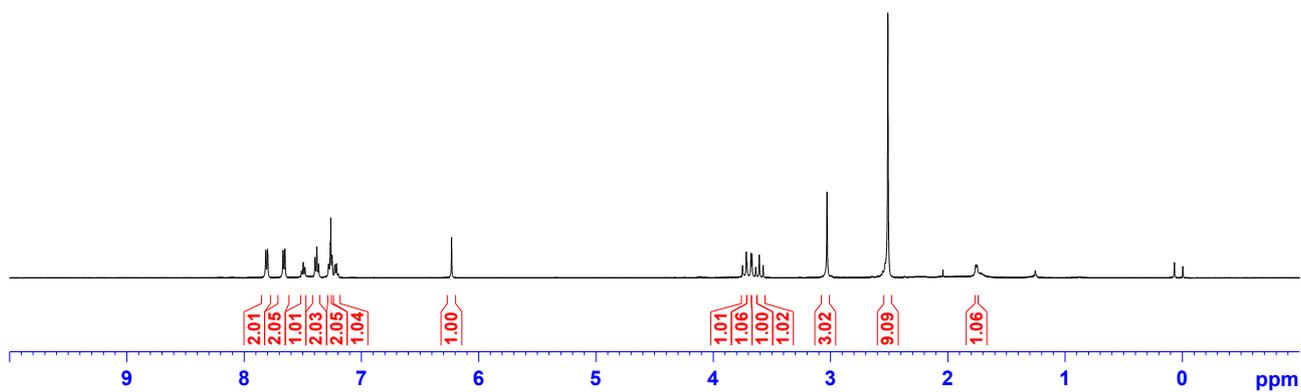
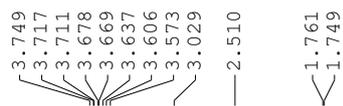
¹³C NMR (125 MHz, CDCl₃)





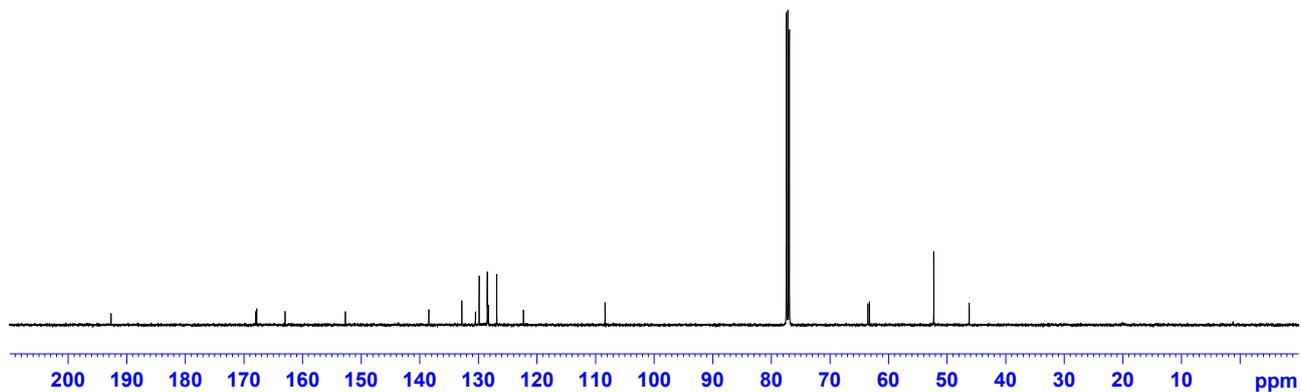
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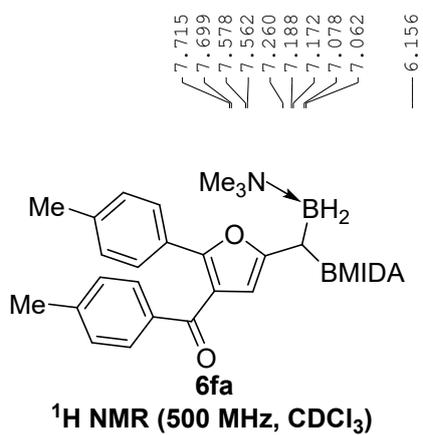
¹H NMR (500 MHz, CDCl₃)



6ea

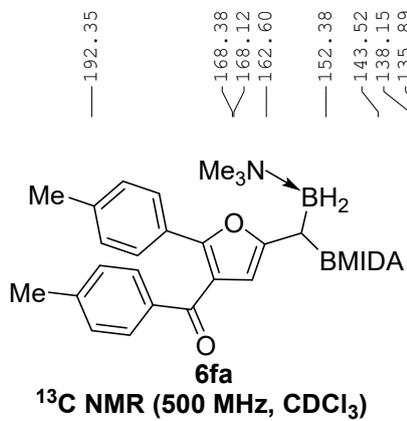
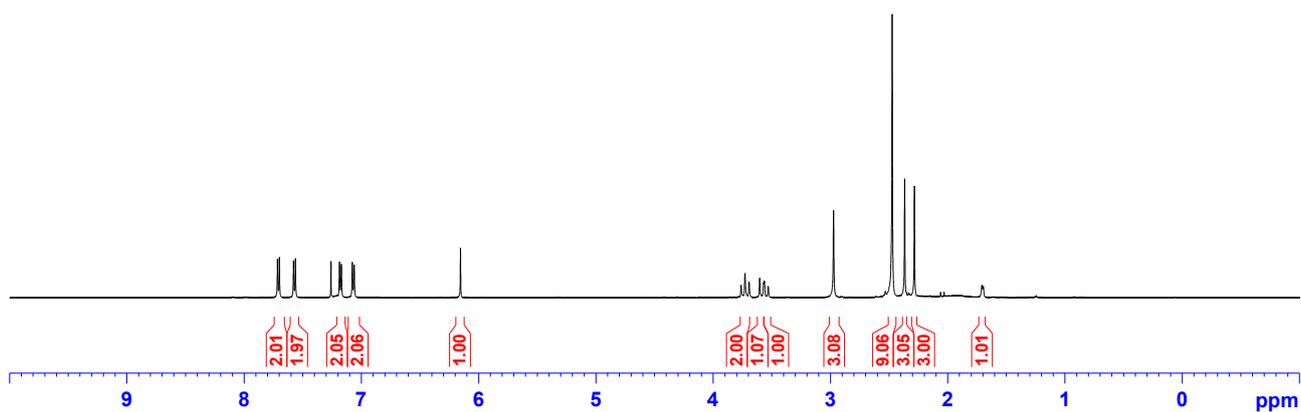
¹³C NMR (125 MHz, CDCl₃)





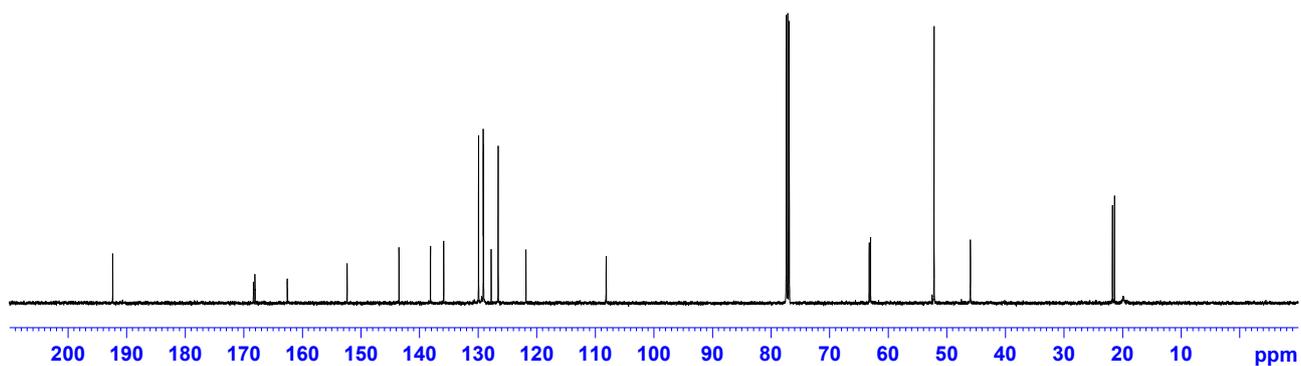
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 7.699
 7.578
 7.562
 7.260
 7.188
 7.172
 7.078
 7.062
 — 6.156

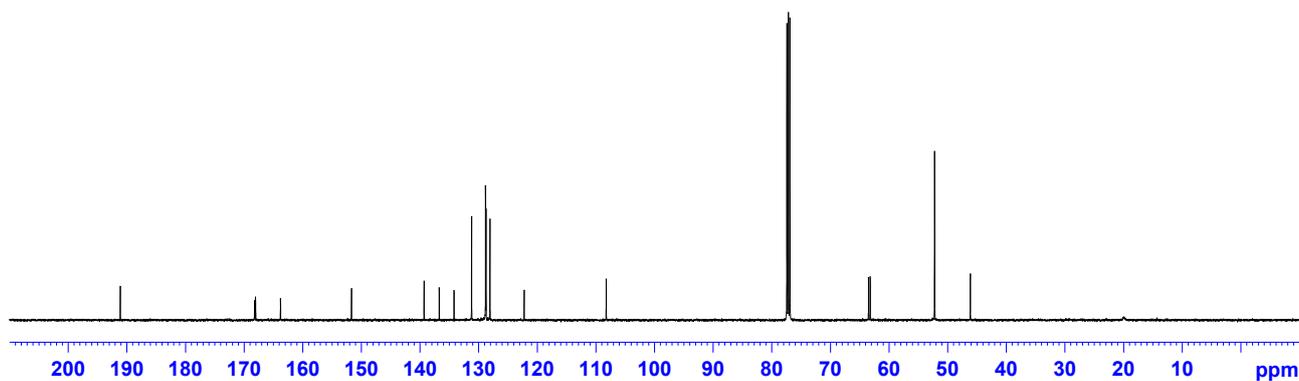
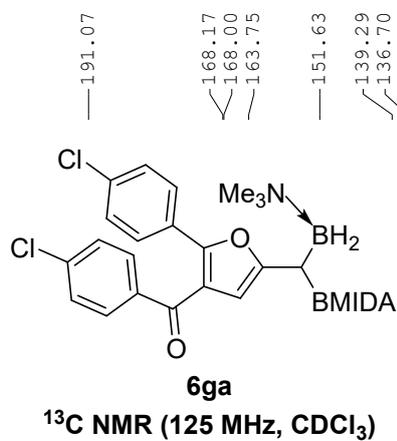
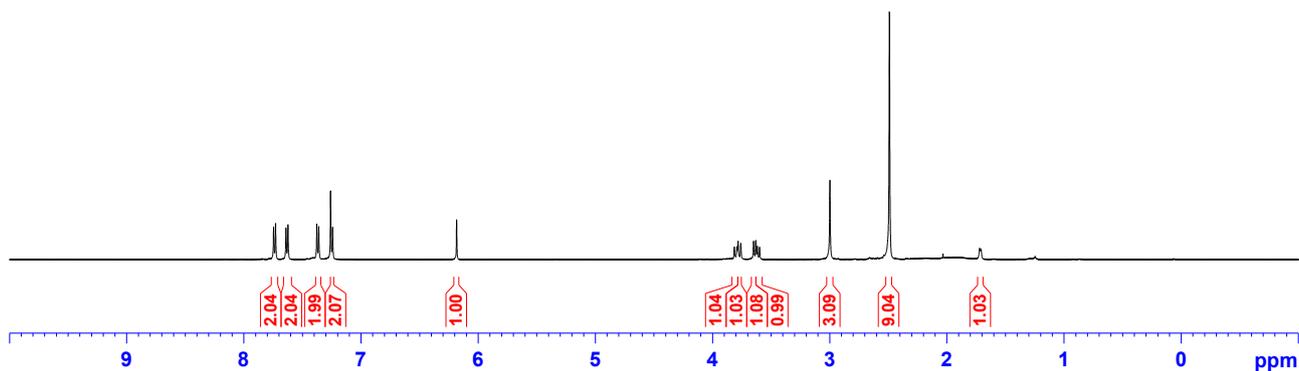
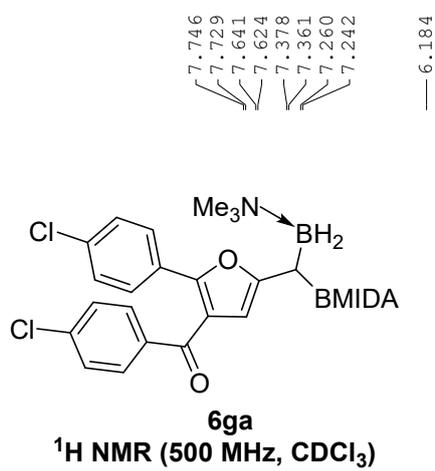
3.764
 3.730
 3.696
 3.604
 3.571
 3.565
 3.532
 2.974
 2.475
 2.368
 2.285
 1.710
 1.697



192.35
 168.38
 168.12
 162.60
 152.38
 143.52
 138.15
 135.89
 129.94
 129.12
 129.09
 127.78
 126.59
 121.85
 108.13

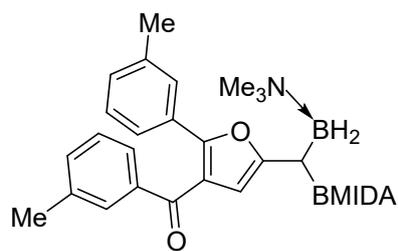
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 77.16
 76.91
 63.24
 63.03
 52.18
 45.98
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 21.36
 19.88





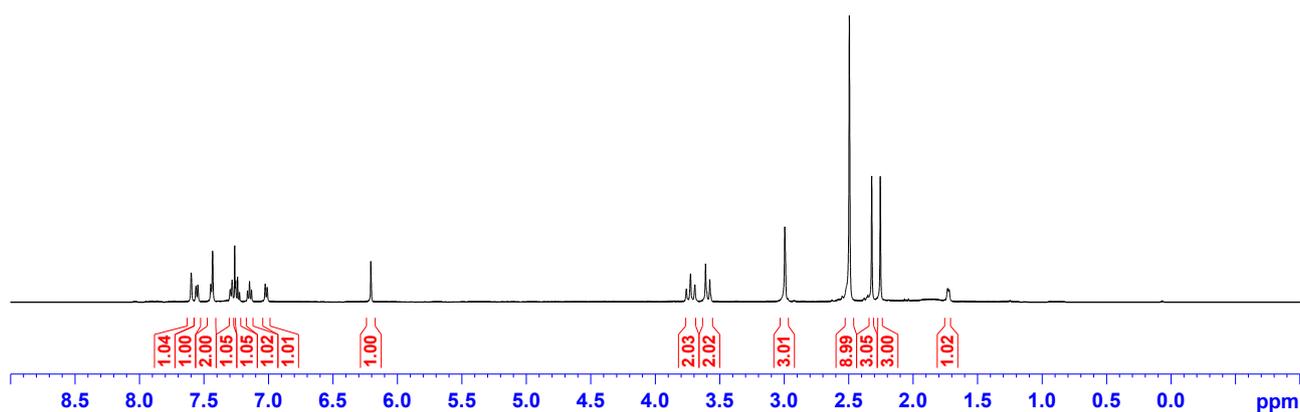
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7.561
7.545
7.445
7.431
7.295
7.280
7.260
7.253
7.238
7.223
7.161
7.145
7.129
7.023
7.008
6.206

3.758
3.726
3.692
3.609
3.576
— 2.995
— 2.494
— 2.320
— 2.254
— 1.732
— 1.720



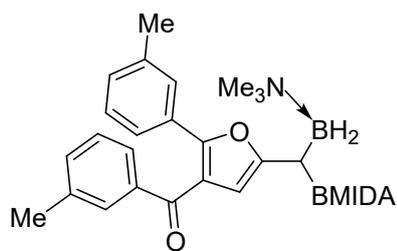
6ha

¹H NMR (500 MHz, CDCl₃)



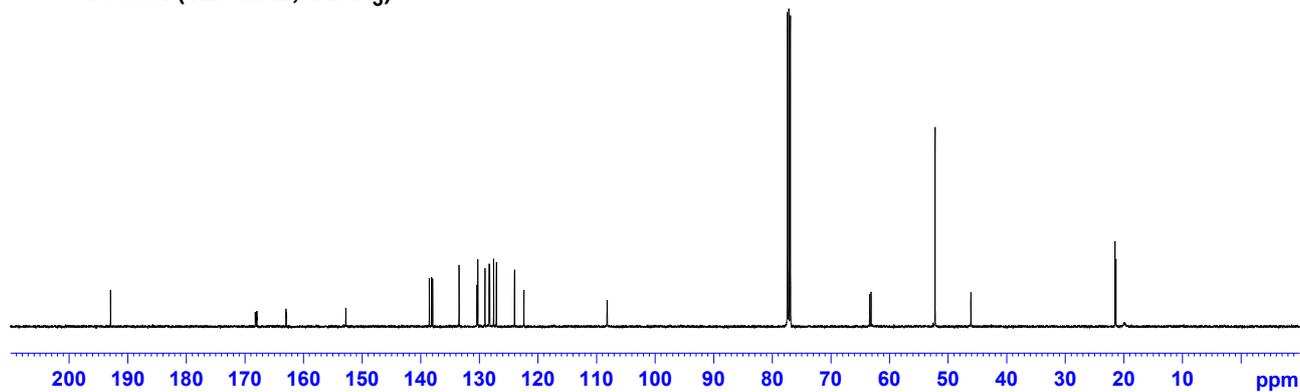
— 192.90
— 168.22
— 163.00
152.77
138.53
138.13
137.96
133.44
130.41
130.24
129.02
128.31
128.21
127.55
127.07
123.98
122.38
108.18
108.15

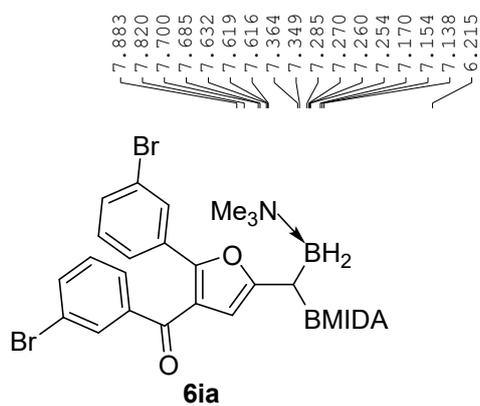
77.41
77.16
76.91
63.36
63.13
— 52.21
— 46.09
21.50
21.34
19.89



6ha

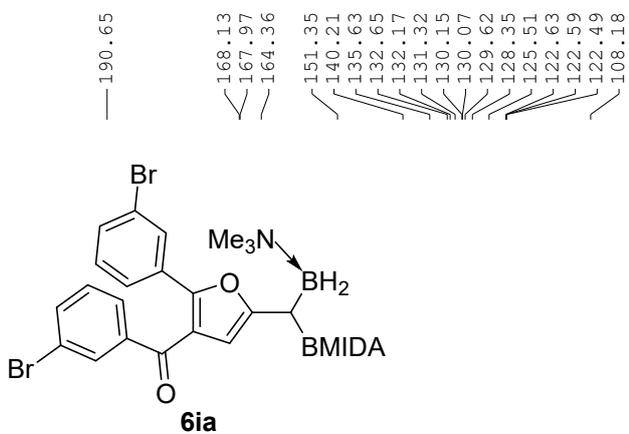
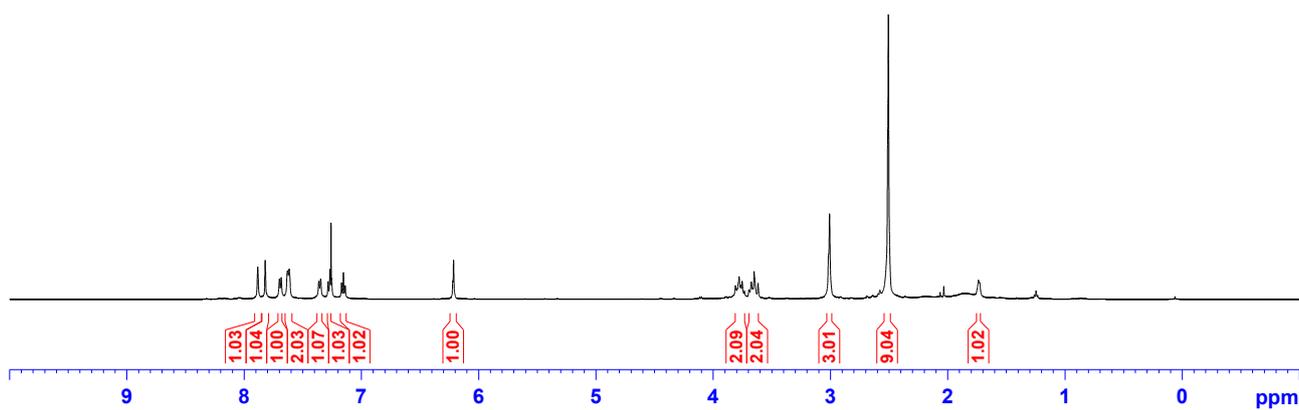
¹³C NMR (125 MHz, CDCl₃)





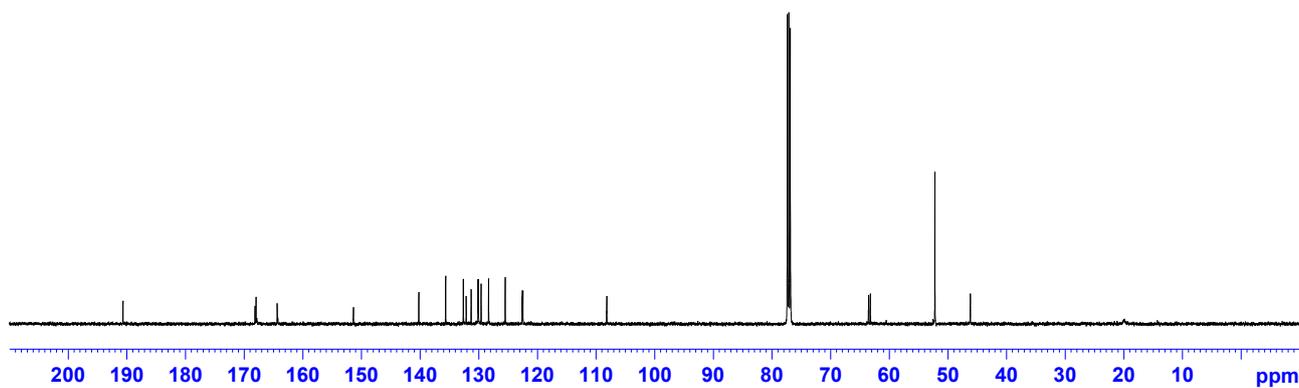
¹H NMR (500 MHz, CDCl₃)

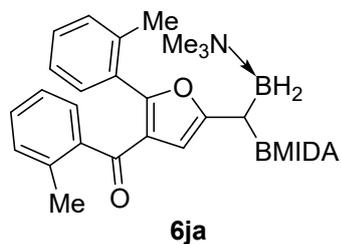
7.883, 7.820, 7.700, 7.685, 7.632, 7.619, 7.616, 7.364, 7.349, 7.285, 7.270, 7.260, 7.254, 7.170, 7.154, 7.138, 6.215
 3.812, 3.780, 3.766, 3.755, 3.735, 3.697, 3.676, 3.665, 3.652, 3.619, 3.009, 2.507
 1.739, 1.729



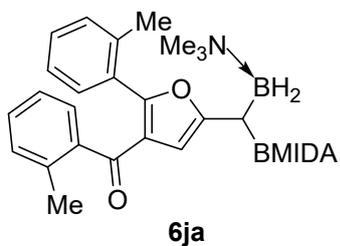
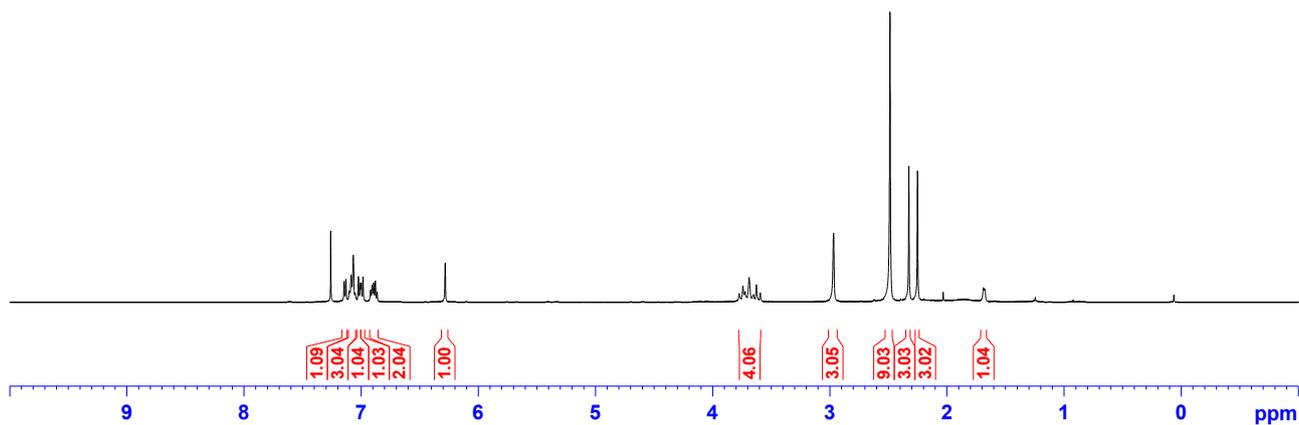
¹H NMR (500 MHz, CDCl₃)

190.65, 168.13, 167.97, 164.36, 151.35, 140.21, 135.63, 132.65, 132.17, 131.32, 130.15, 130.07, 129.62, 128.35, 125.51, 122.63, 122.59, 122.49, 108.18, 77.42, 77.16, 76.91, 63.54, 63.25, 52.24, 46.19, 19.93

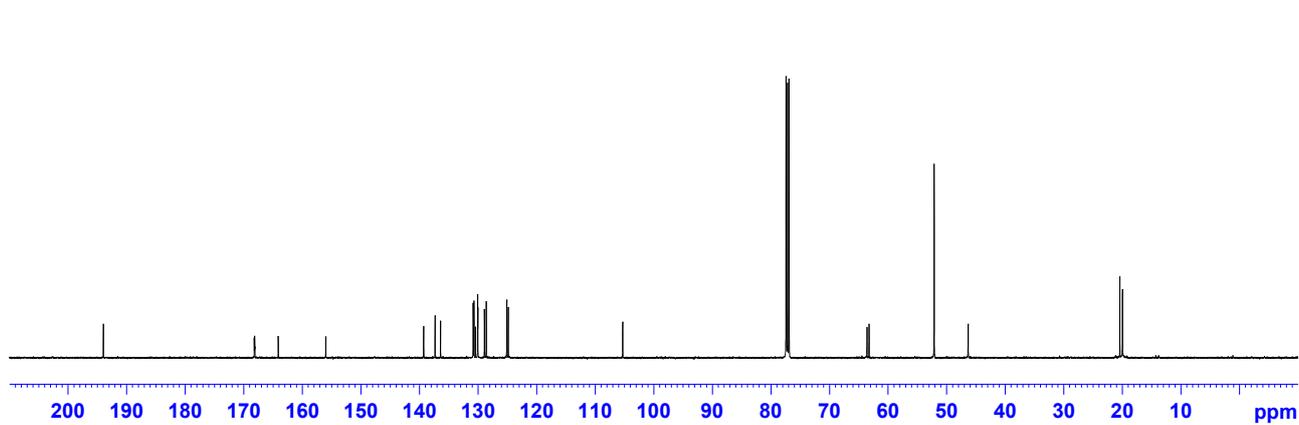


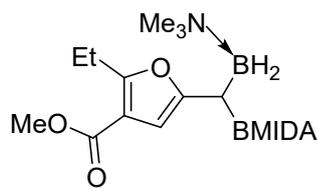


¹H NMR (500 MHz, CDCl₃)



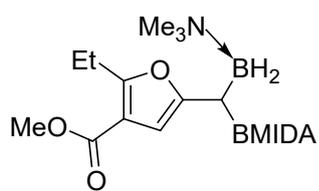
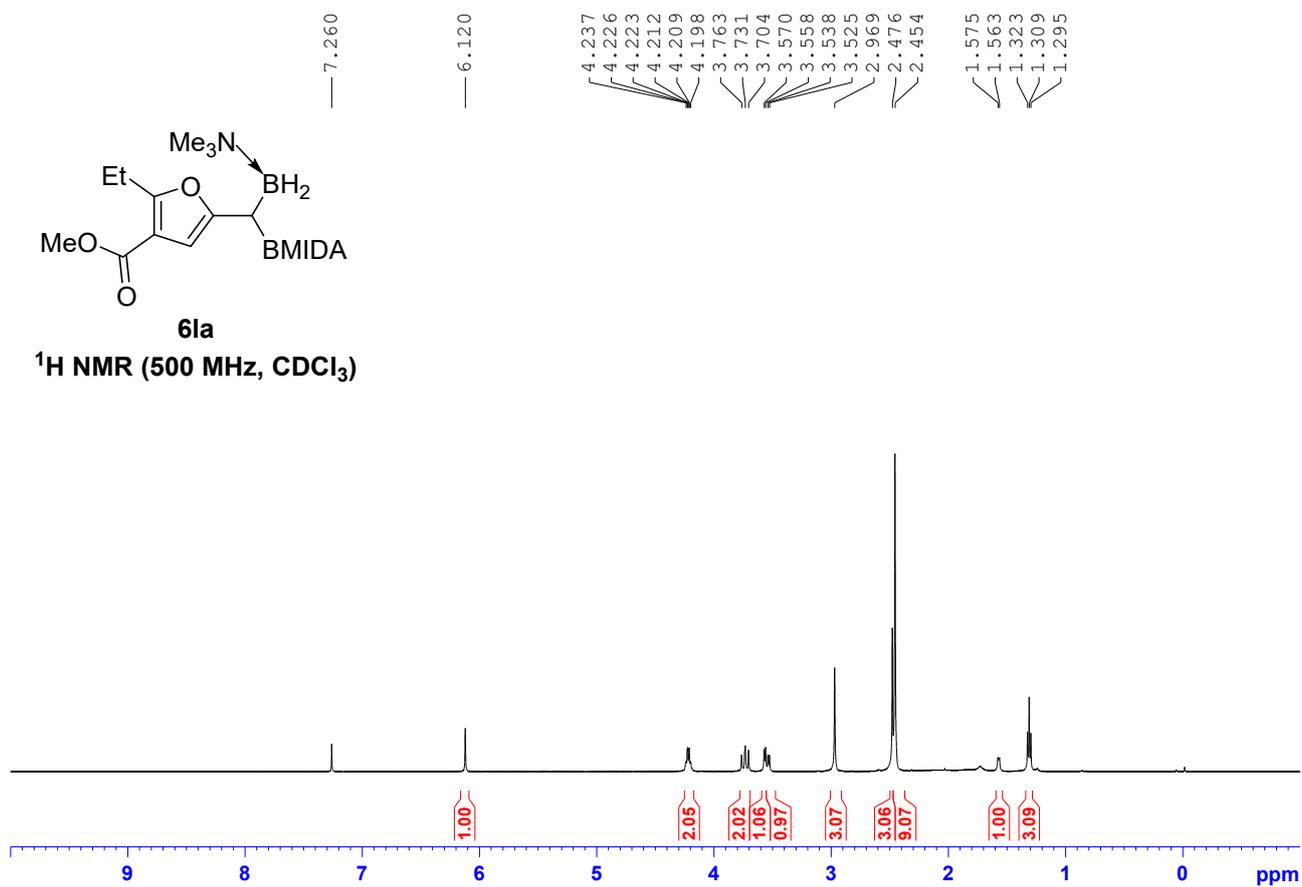
¹³C NMR (125 MHz, CDCl₃)





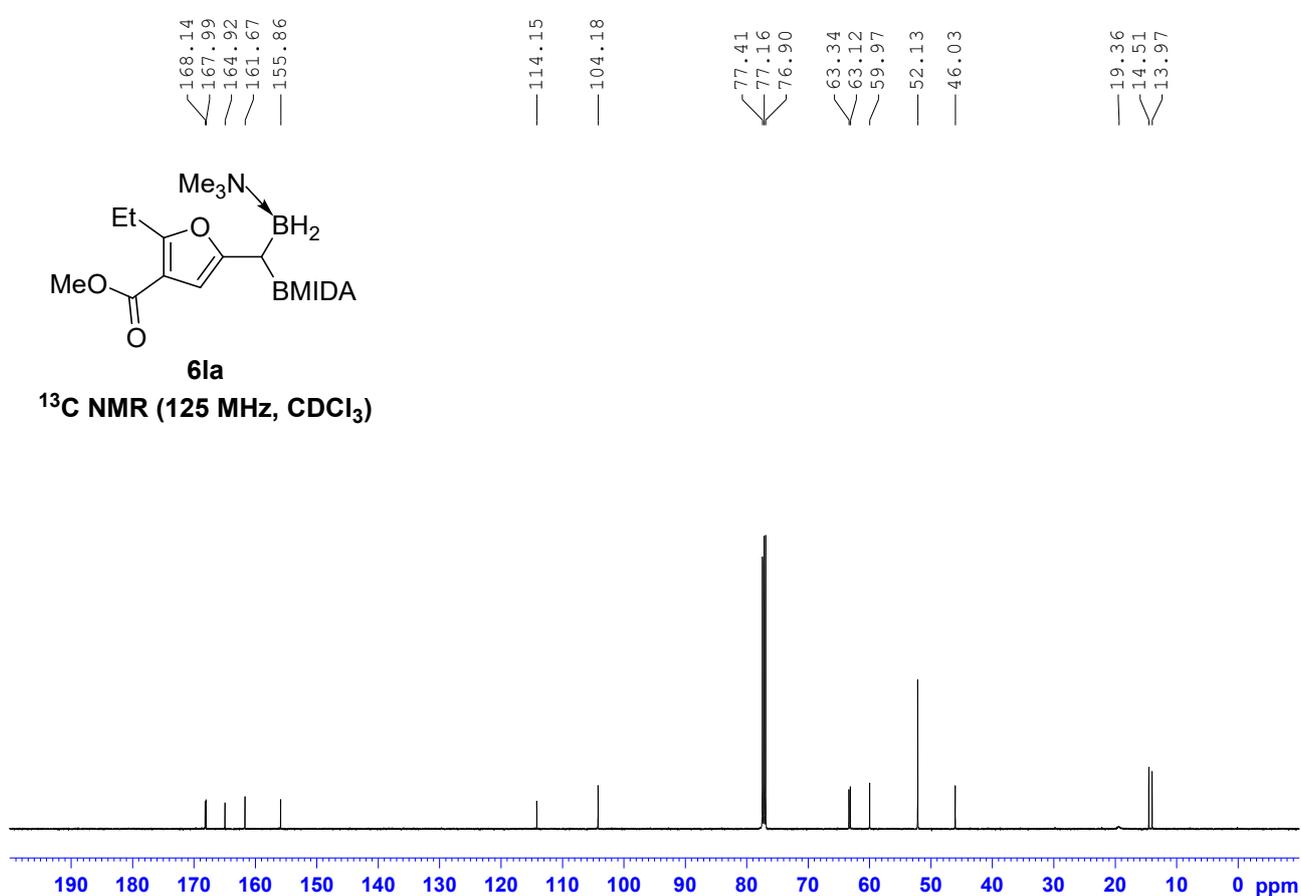
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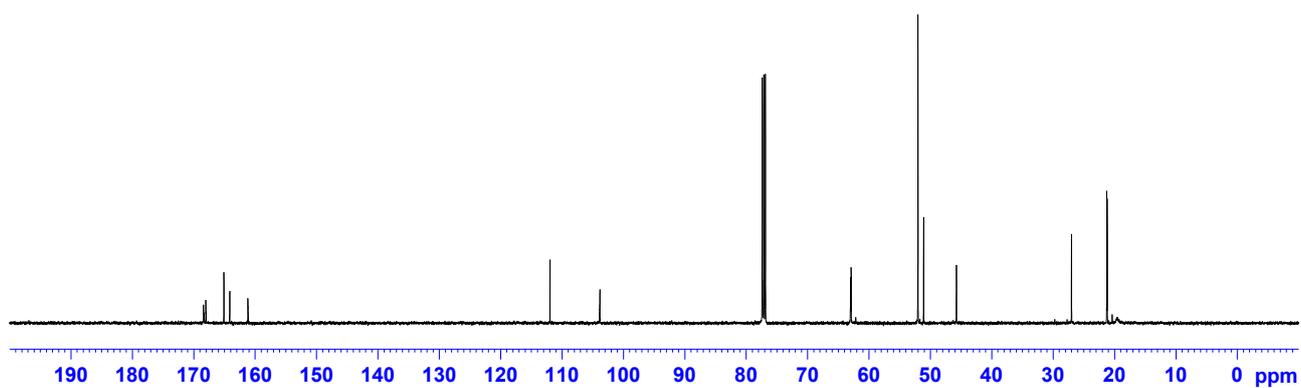
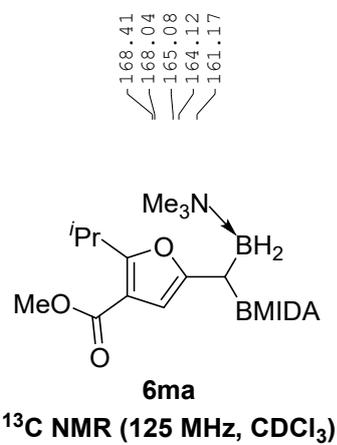
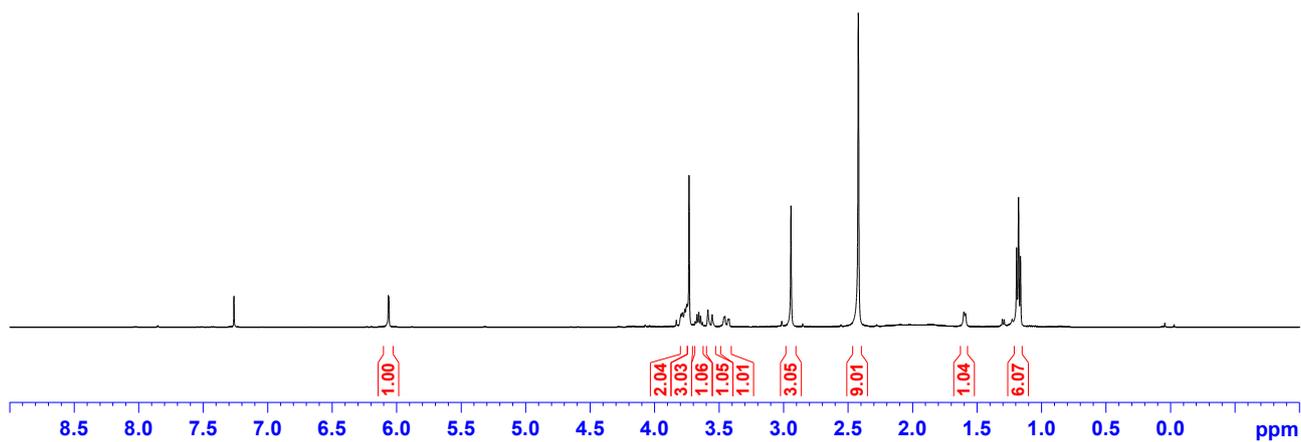
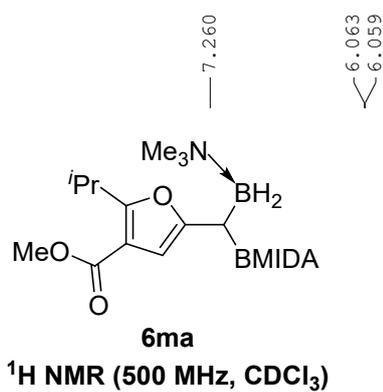
¹H NMR (500 MHz, CDCl₃)

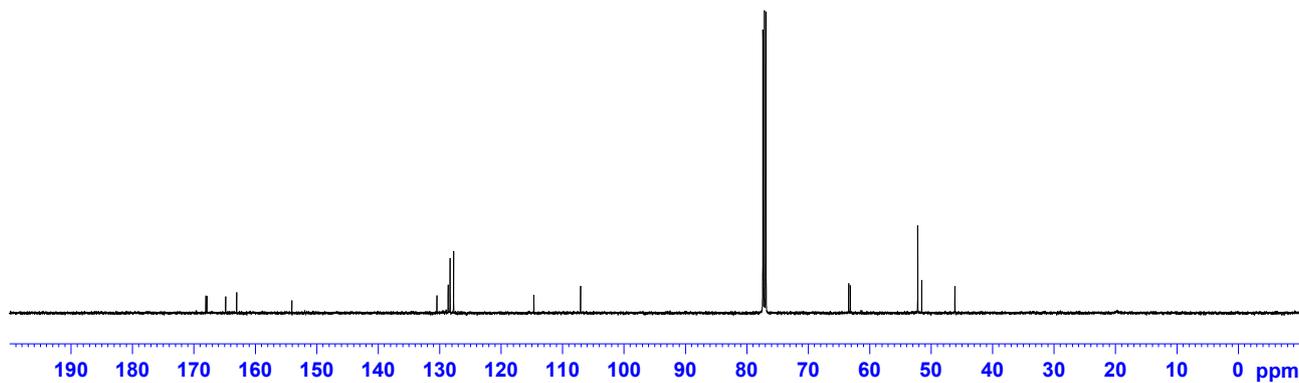
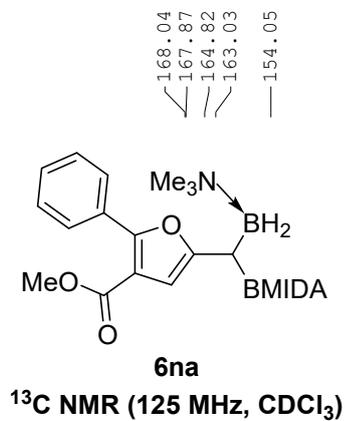
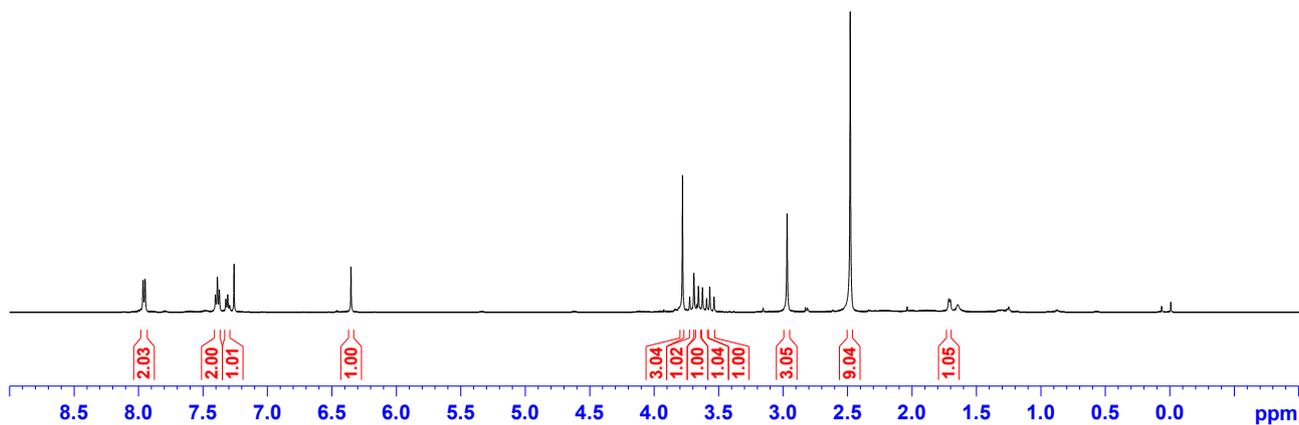
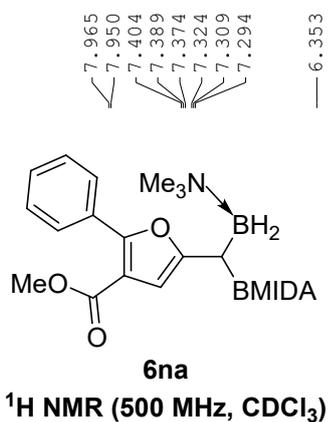


6la

¹³C NMR (125 MHz, CDCl₃)

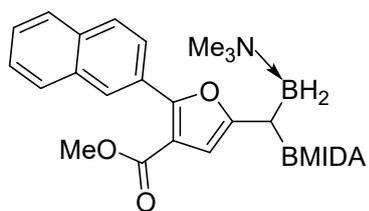






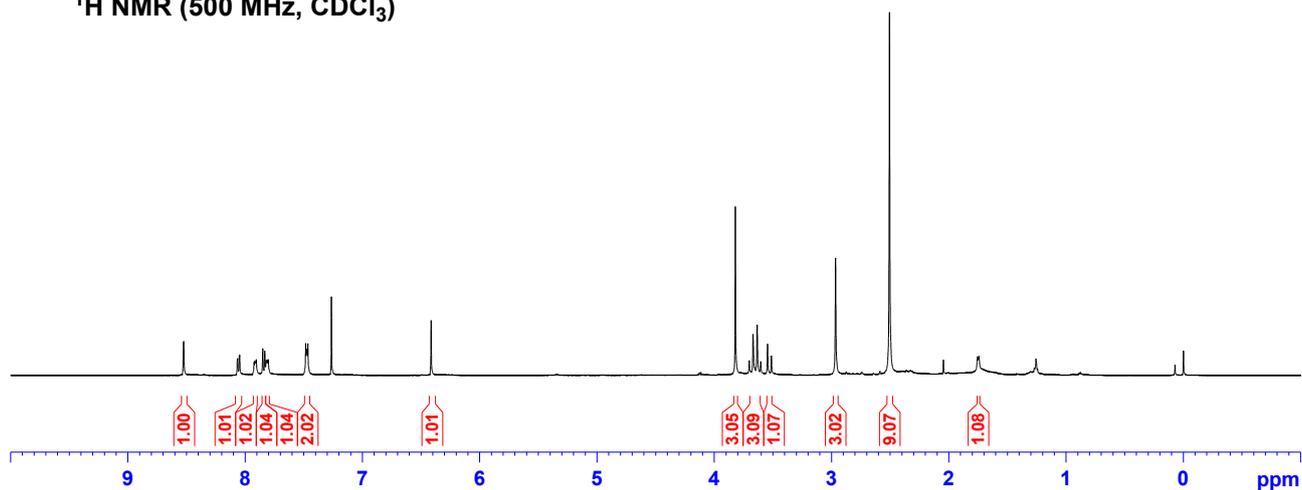
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8.049
8.046
7.923
7.916
7.905
7.849
7.832
7.821
7.809
7.802
7.483
7.476
7.470
7.465
7.264

3.819
3.701
3.669
3.633
3.603
3.545
3.512
2.965
— 2.505
—
1.754
1.742



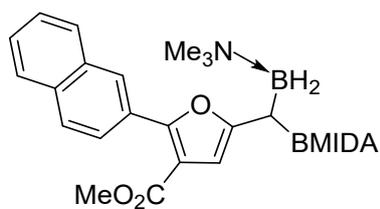
6oa

$^1\text{H NMR}$ (500 MHz, CDCl_3)



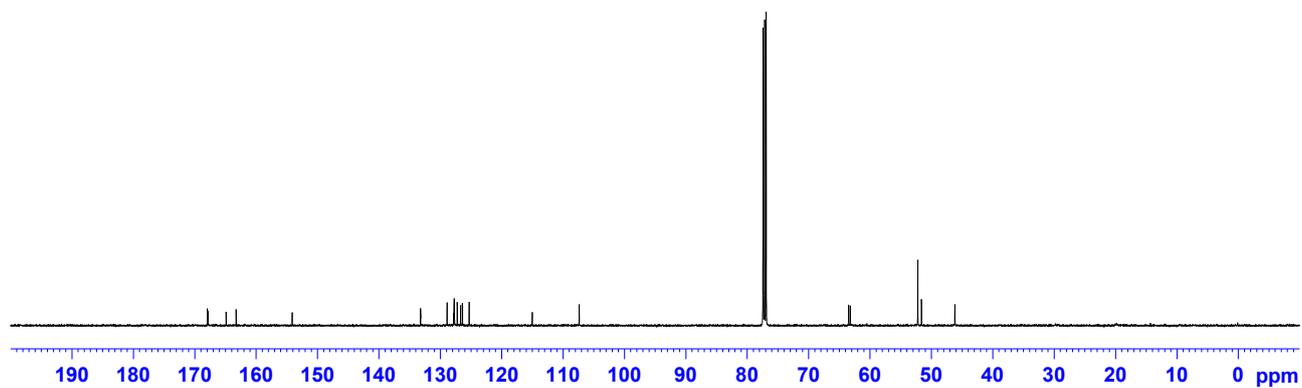
167.92
167.80
164.88
163.25
— 154.12
133.23
133.20
128.88
127.82
127.73
127.68
127.23
126.68
126.38
125.28
115.01
107.37

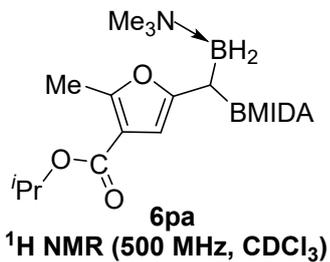
77.41
77.16
76.90
63.50
63.23
52.23
51.63
46.19
— 19.86



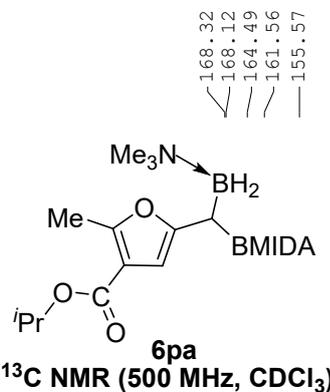
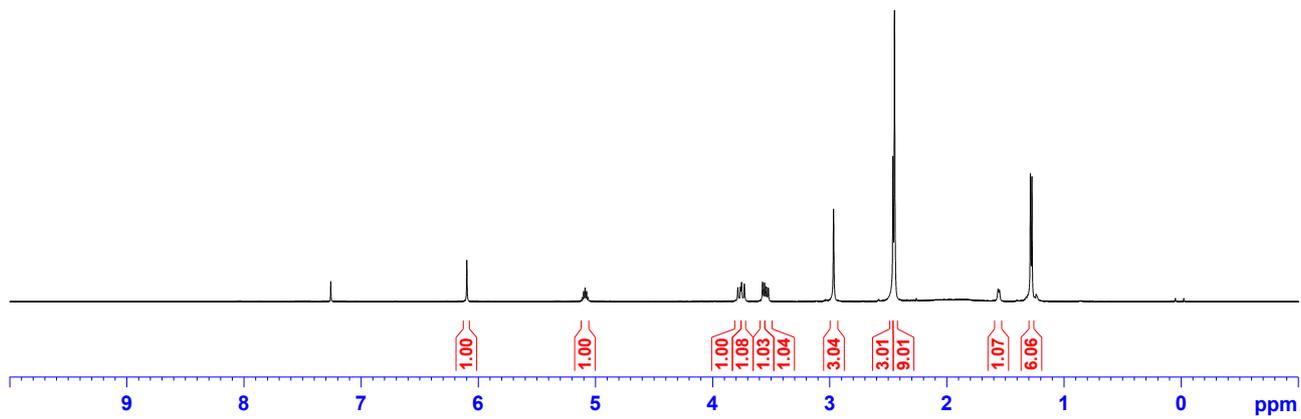
6oa

$^{13}\text{C NMR}$ (125 MHz, CDCl_3)

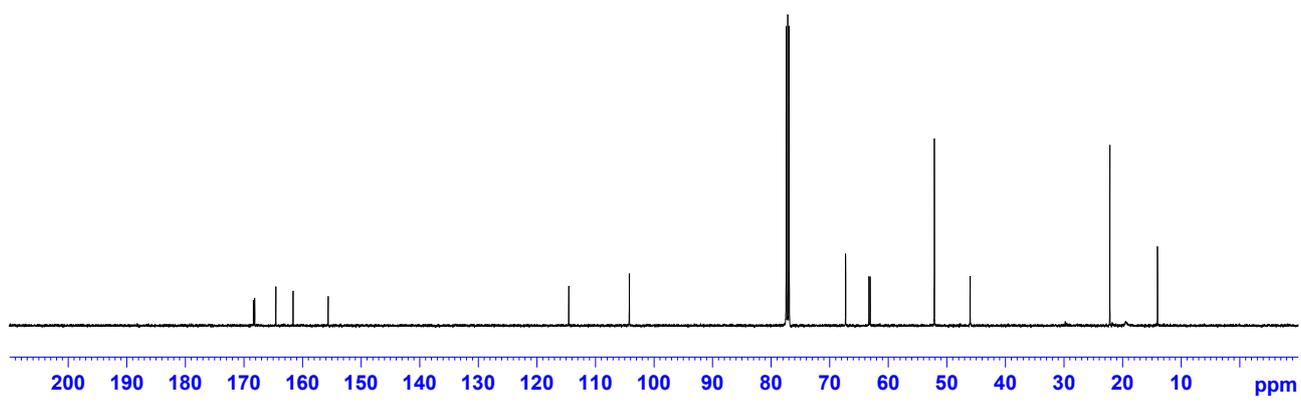


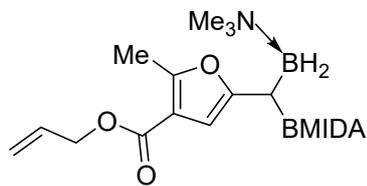


— 7.260
 — 6.098
 { 5.113
 { 5.101
 { 5.088
 { 5.076
 { 5.063
 { 3.785
 { 3.762
 { 3.752
 { 3.729
 { 3.573
 { 3.556
 { 3.540
 { 3.524
 { 2.967
 { 2.461
 { 2.447
 { 1.563
 { 1.551
 { 1.287
 { 1.274



{ 168.32
 { 168.12
 { 164.49
 { 161.56
 { 155.57
 — 114.53
 — 104.20
 { 77.41
 { 77.16
 { 76.91
 { 67.28
 { 63.29
 { 63.09
 — 52.13
 — 46.01
 { 22.17
 { 19.45
 { 14.03

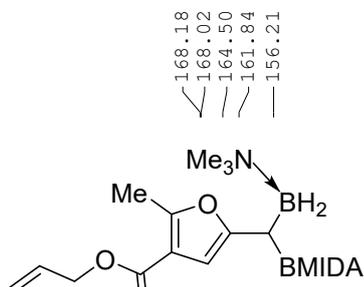
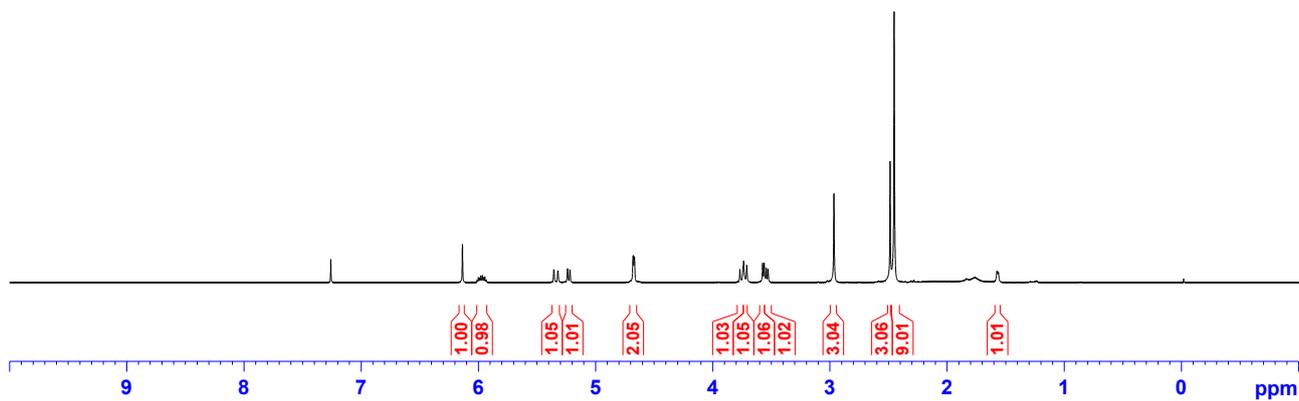




6qa

¹H NMR (500 MHz, CDCl₃)

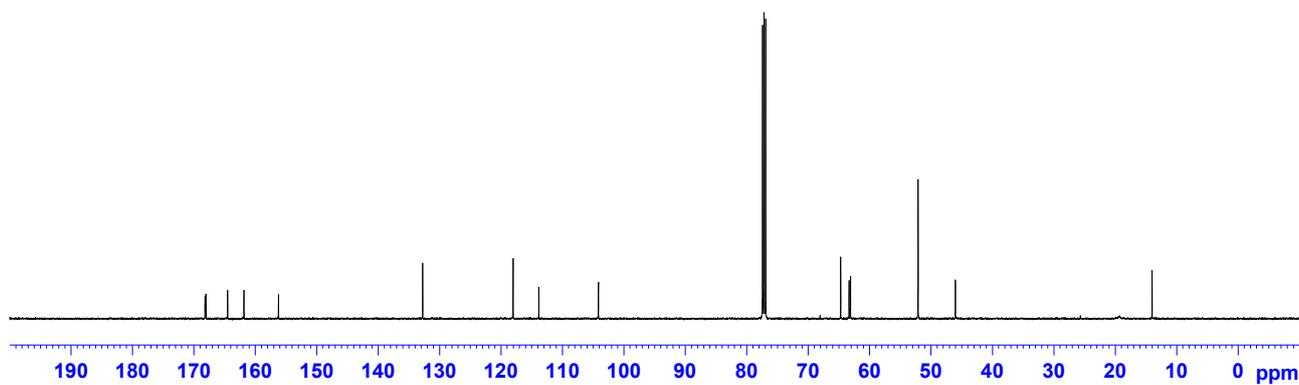
7.260
6.137
6.012
6.001
5.990
5.980
5.966
5.956
5.946
5.934
5.358
5.355
5.323
5.321
5.241
5.239
5.220
5.218
4.680
4.670
4.669
3.769
3.743
3.737
3.710
3.575
3.561
3.543
3.528
2.967
2.487
2.453
1.576
1.564

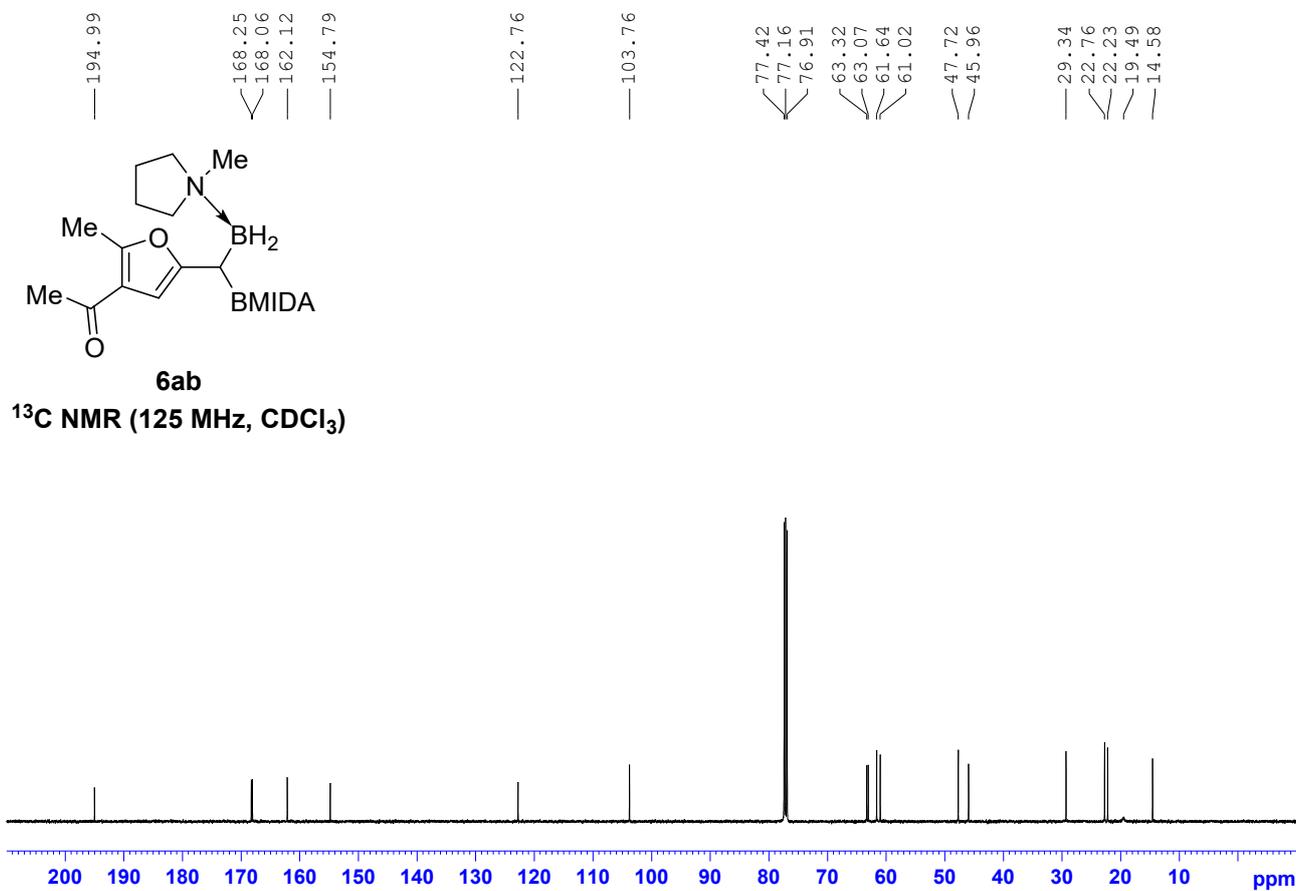
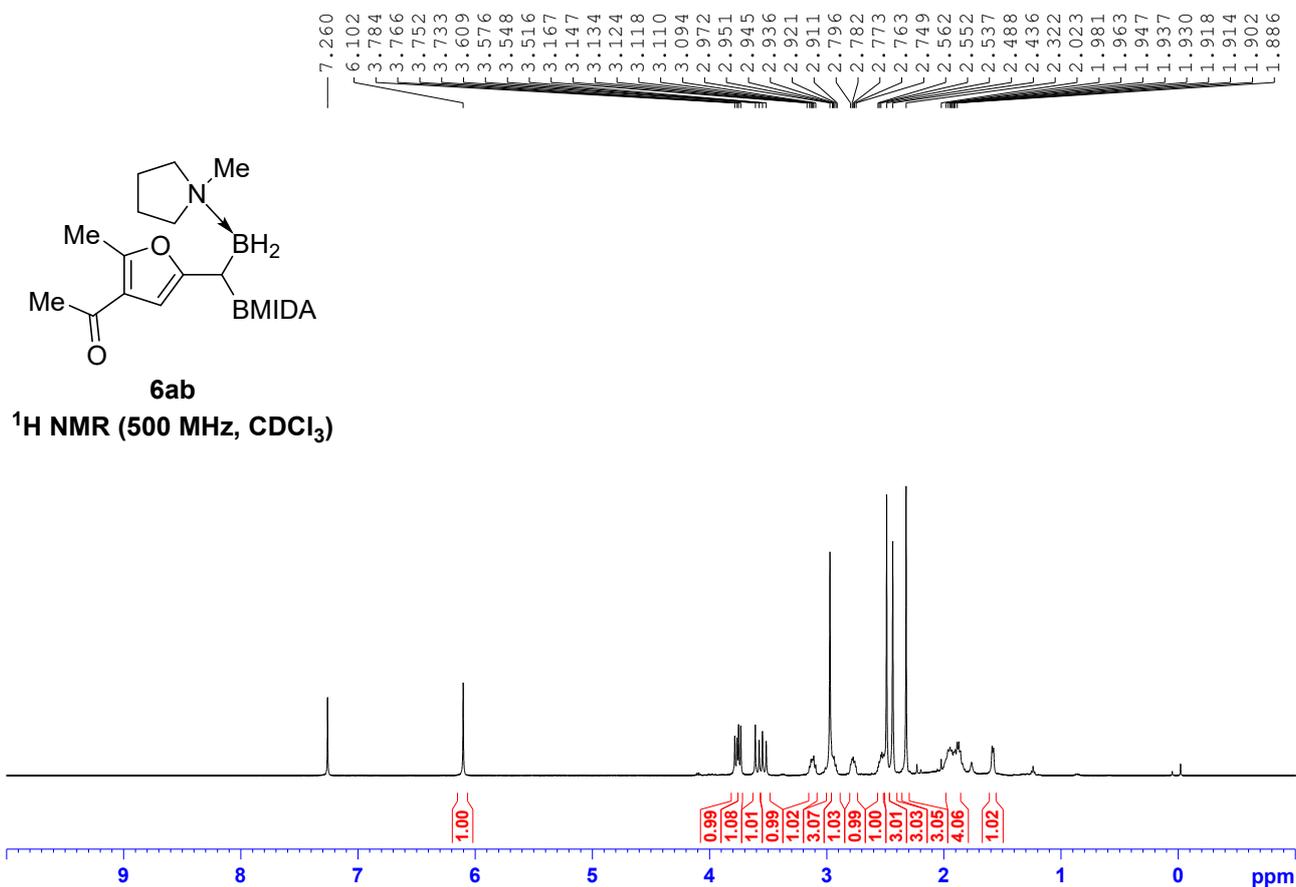


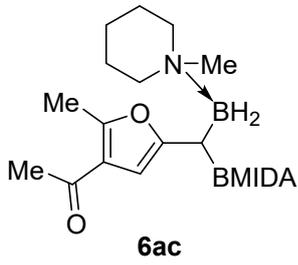
6qa

¹³C NMR (125 MHz, CDCl₃)

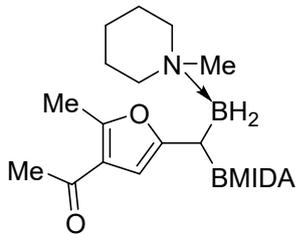
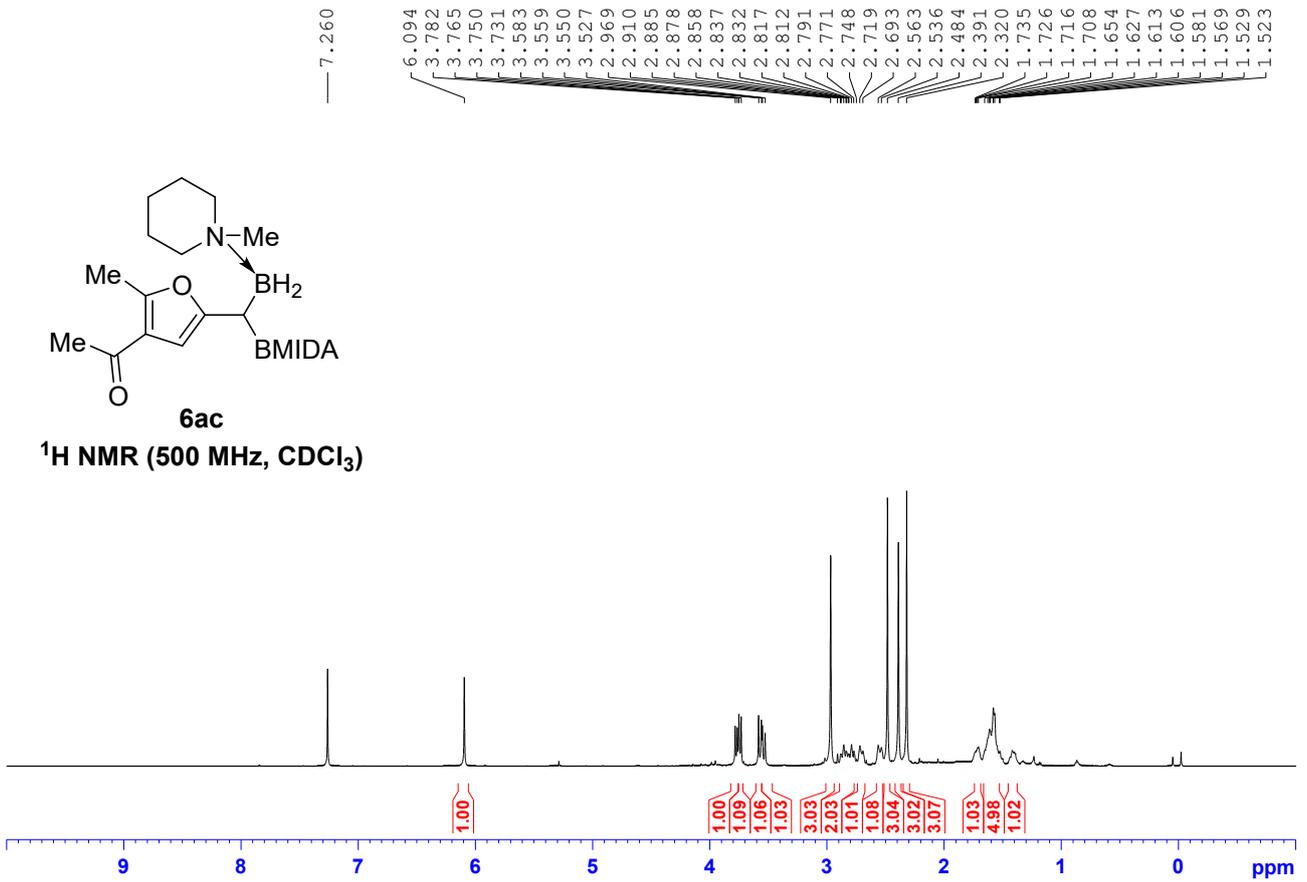
168.18
168.02
164.50
161.84
156.21
132.74
118.01
113.84
104.13
77.41
77.16
76.90
64.73
63.35
63.13
52.13
46.05
19.34
14.03



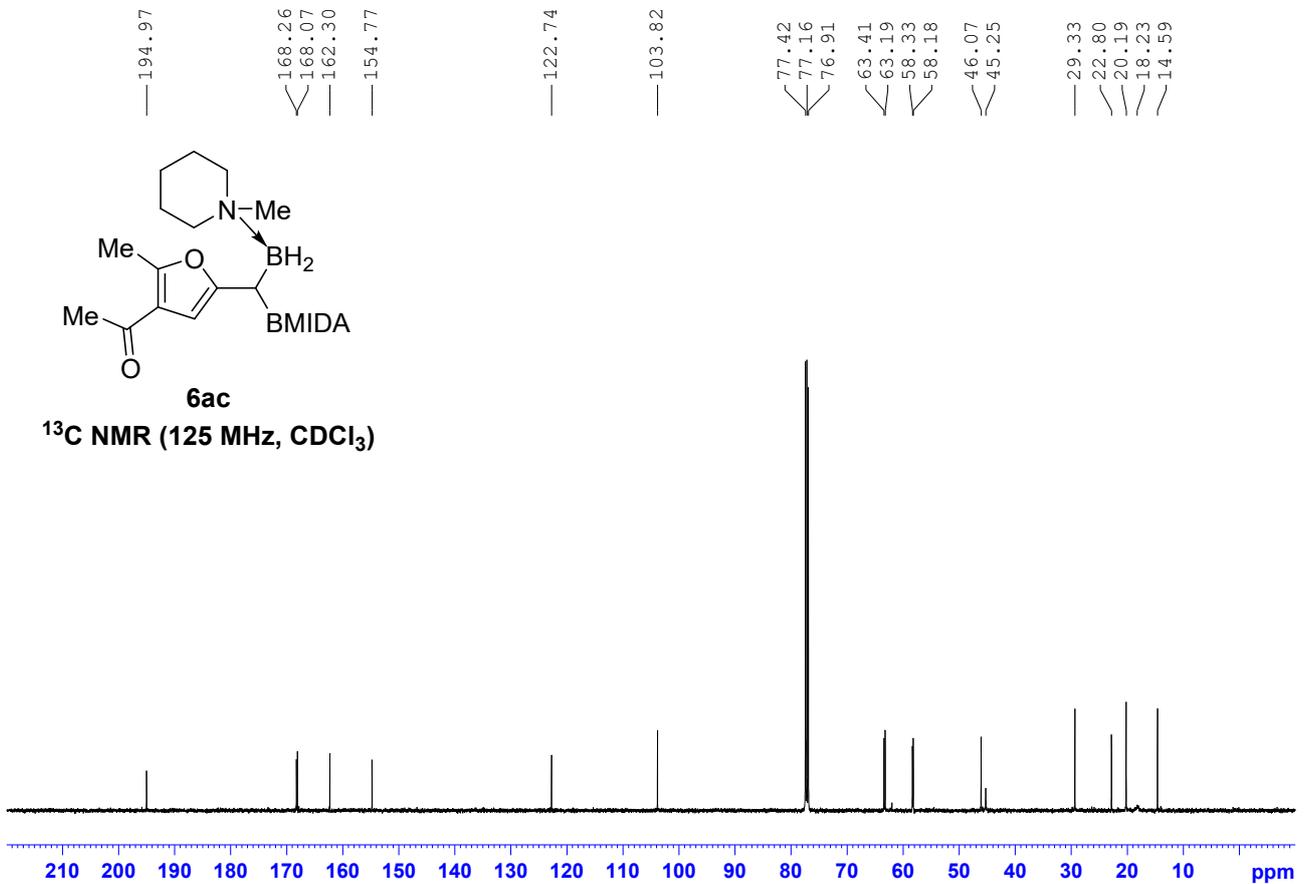


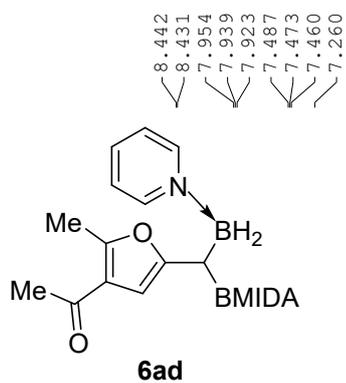


¹H NMR (500 MHz, CDCl₃)

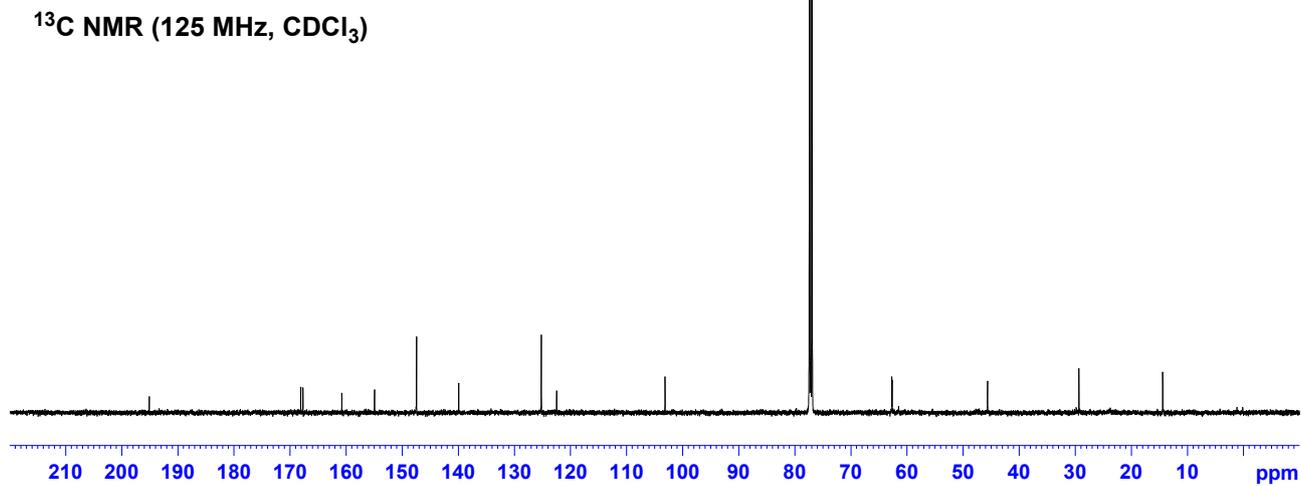
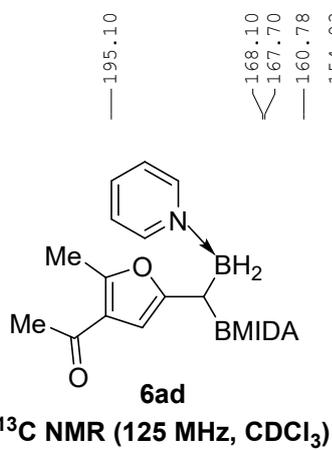
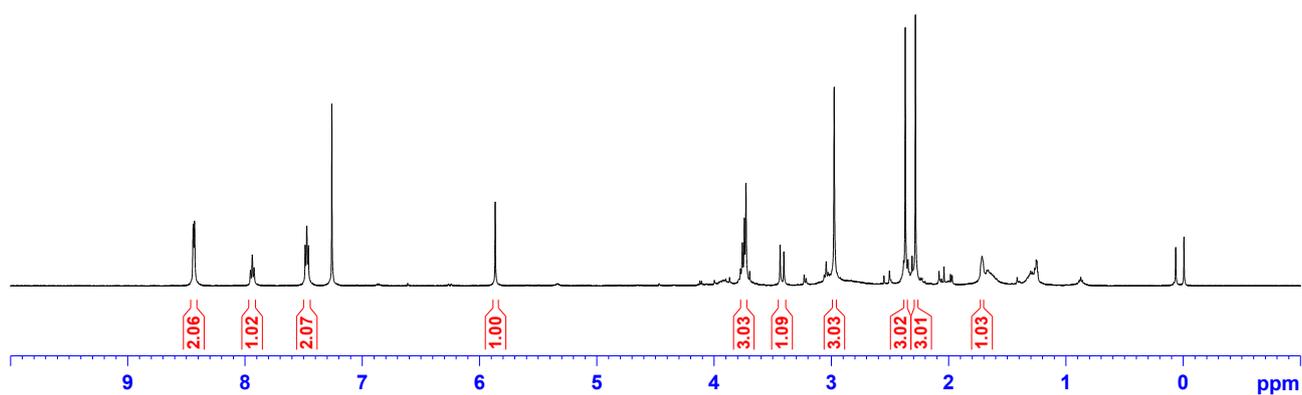


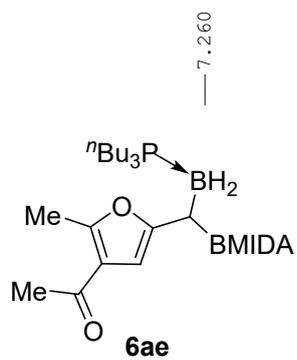
¹³C NMR (125 MHz, CDCl₃)



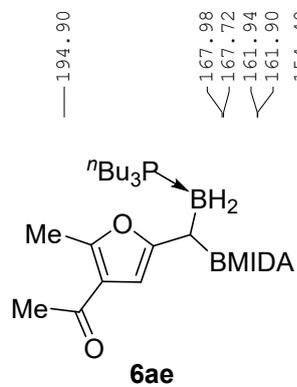
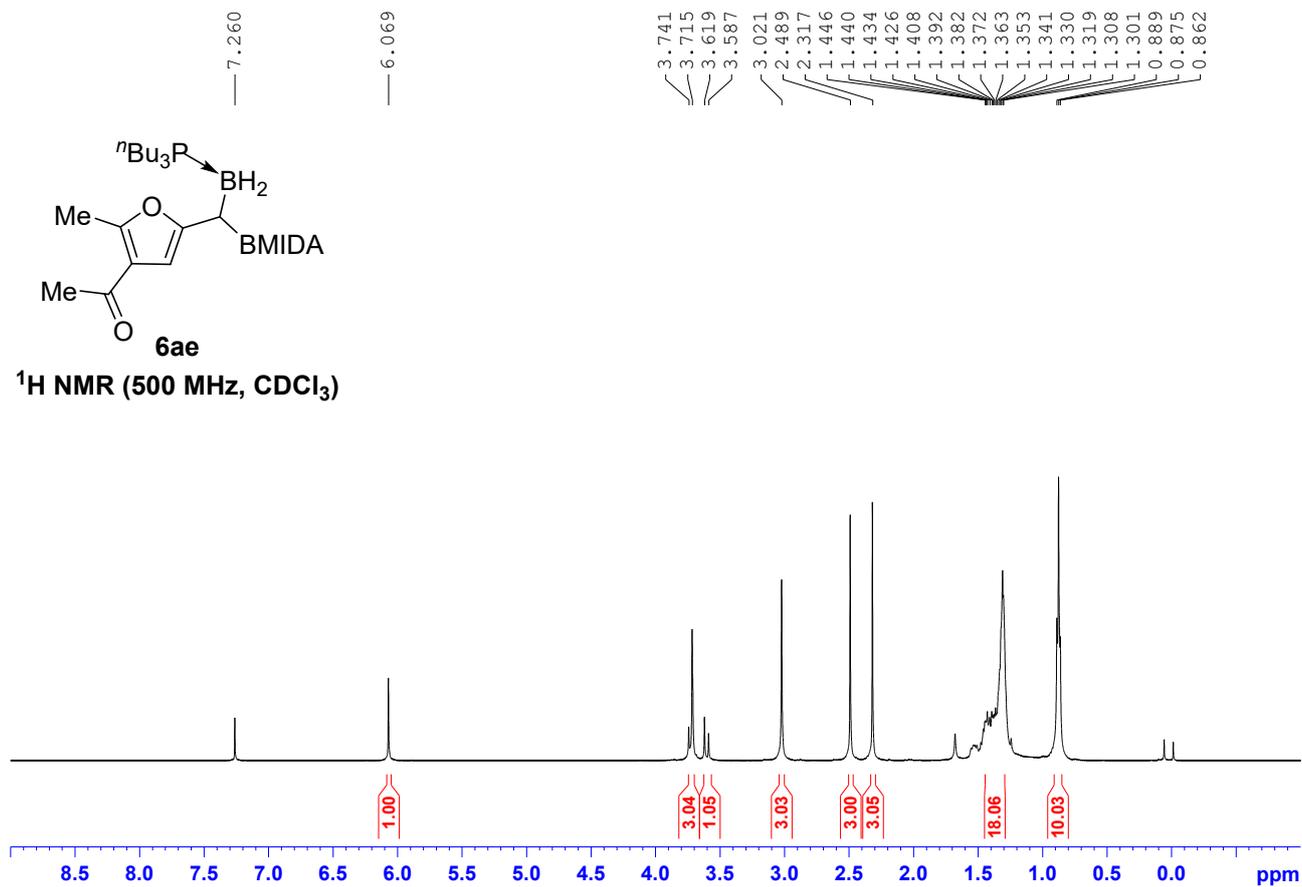


$^1\text{H NMR}$ (500 MHz, CDCl_3)

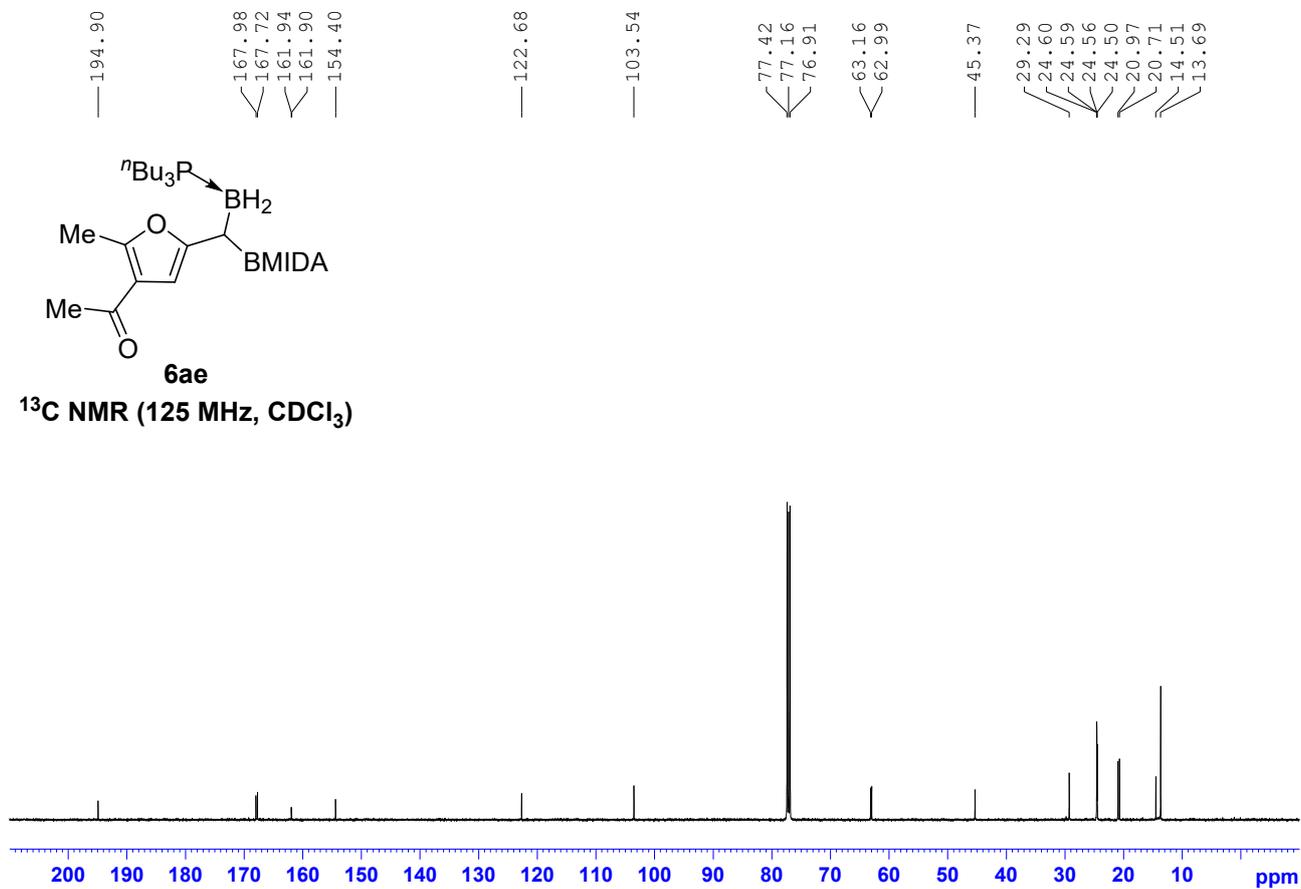


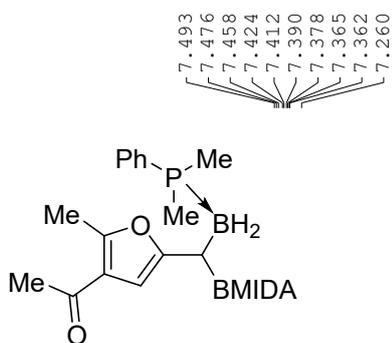


^1H NMR (500 MHz, CDCl_3)



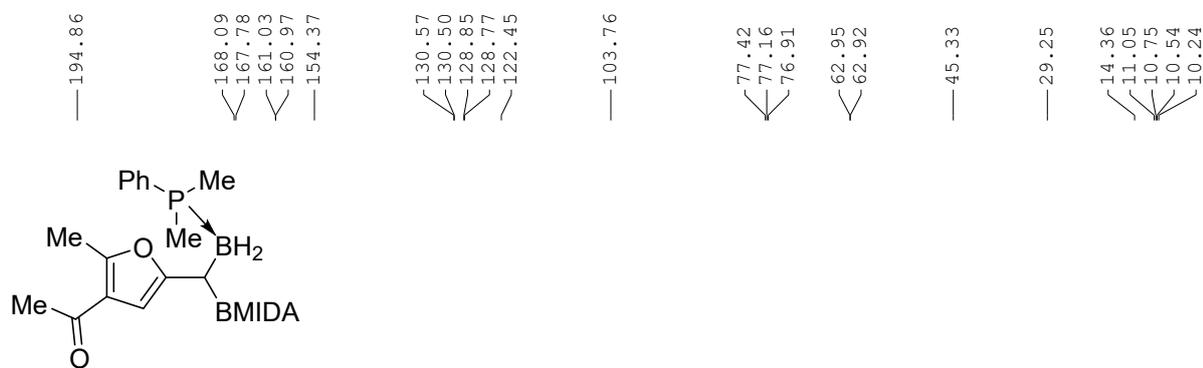
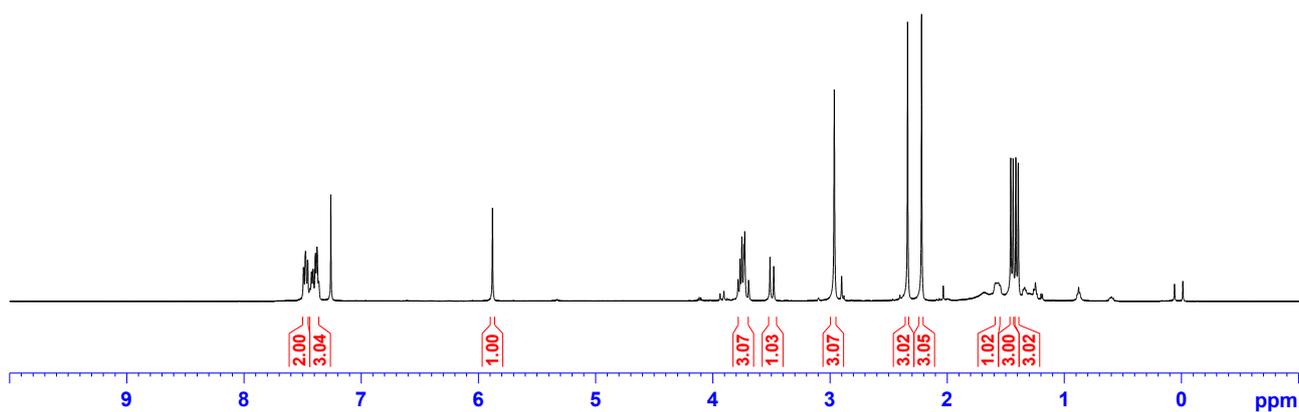
^{13}C NMR (125 MHz, CDCl_3)





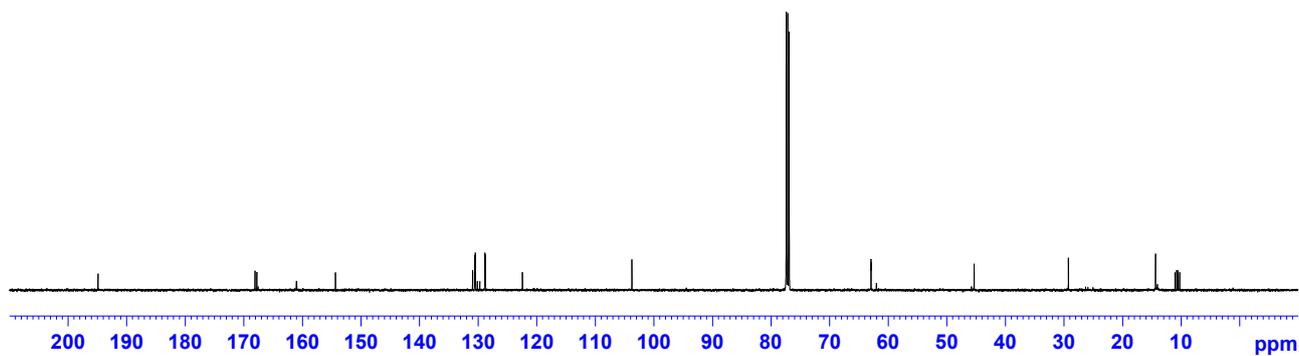
6af

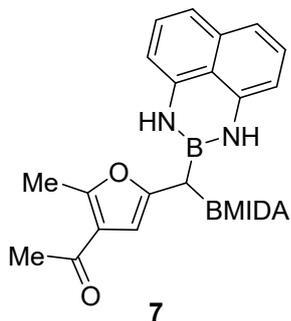
^1H NMR (500 MHz, CDCl_3)



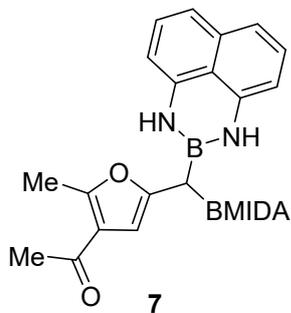
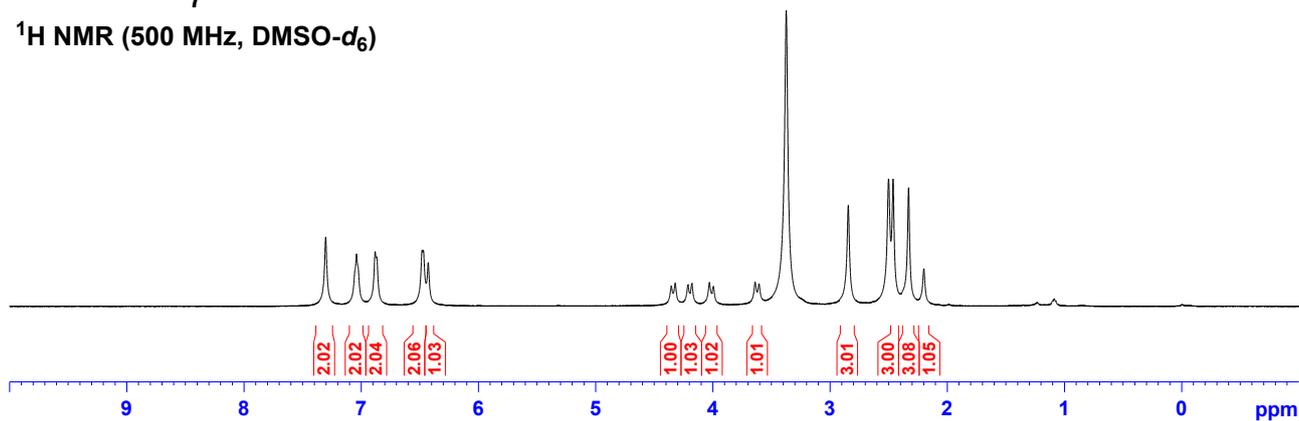
6af

^{13}C NMR (125 MHz, CDCl_3)

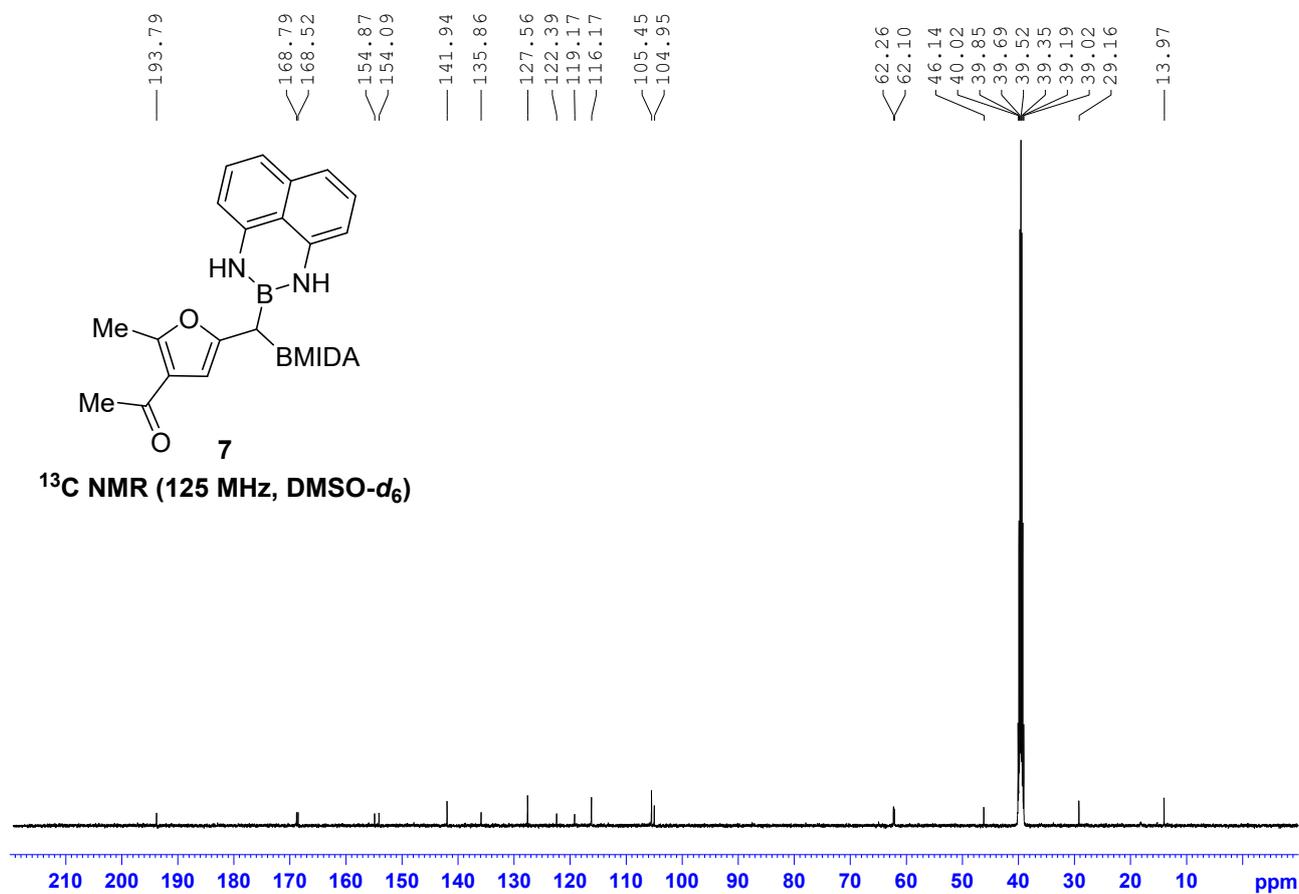


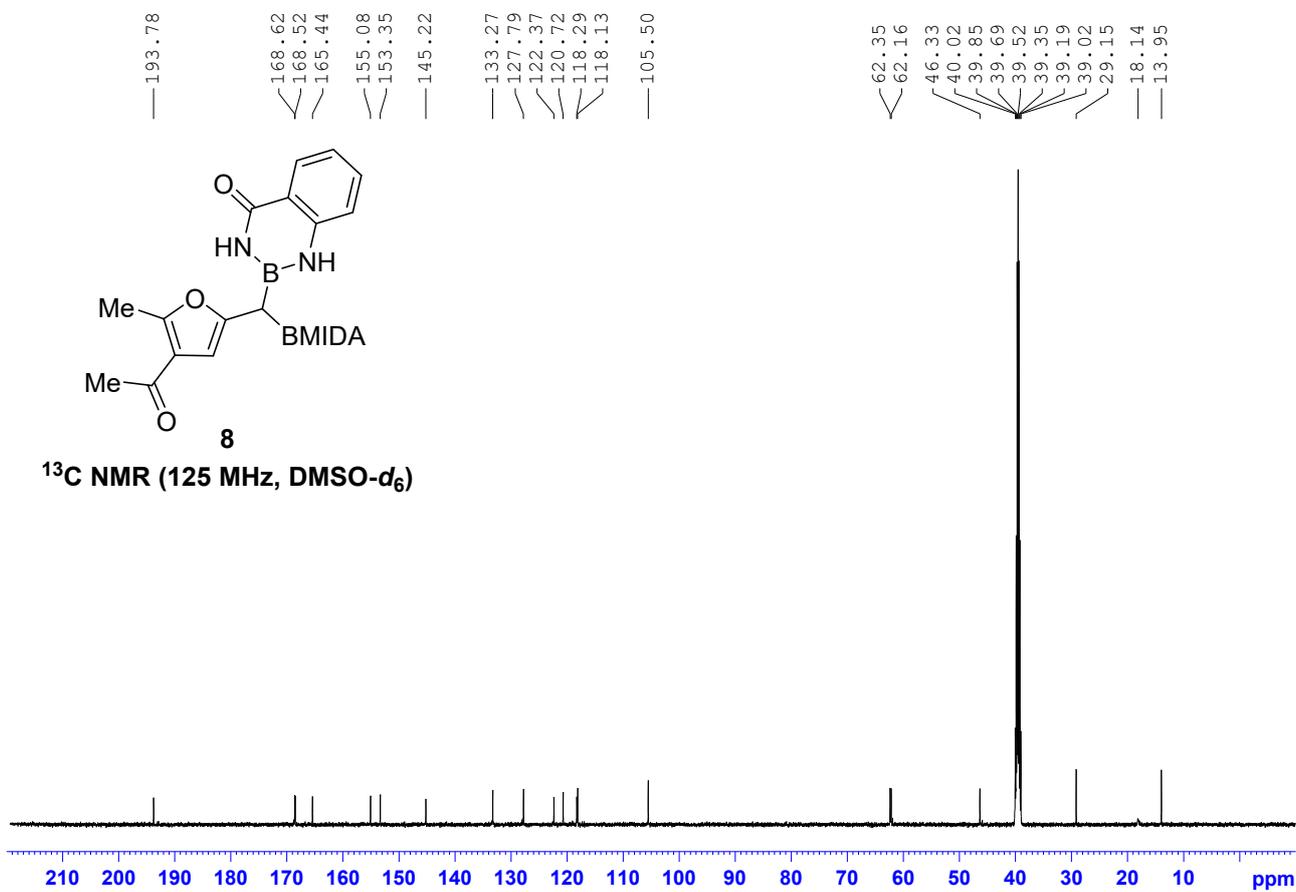
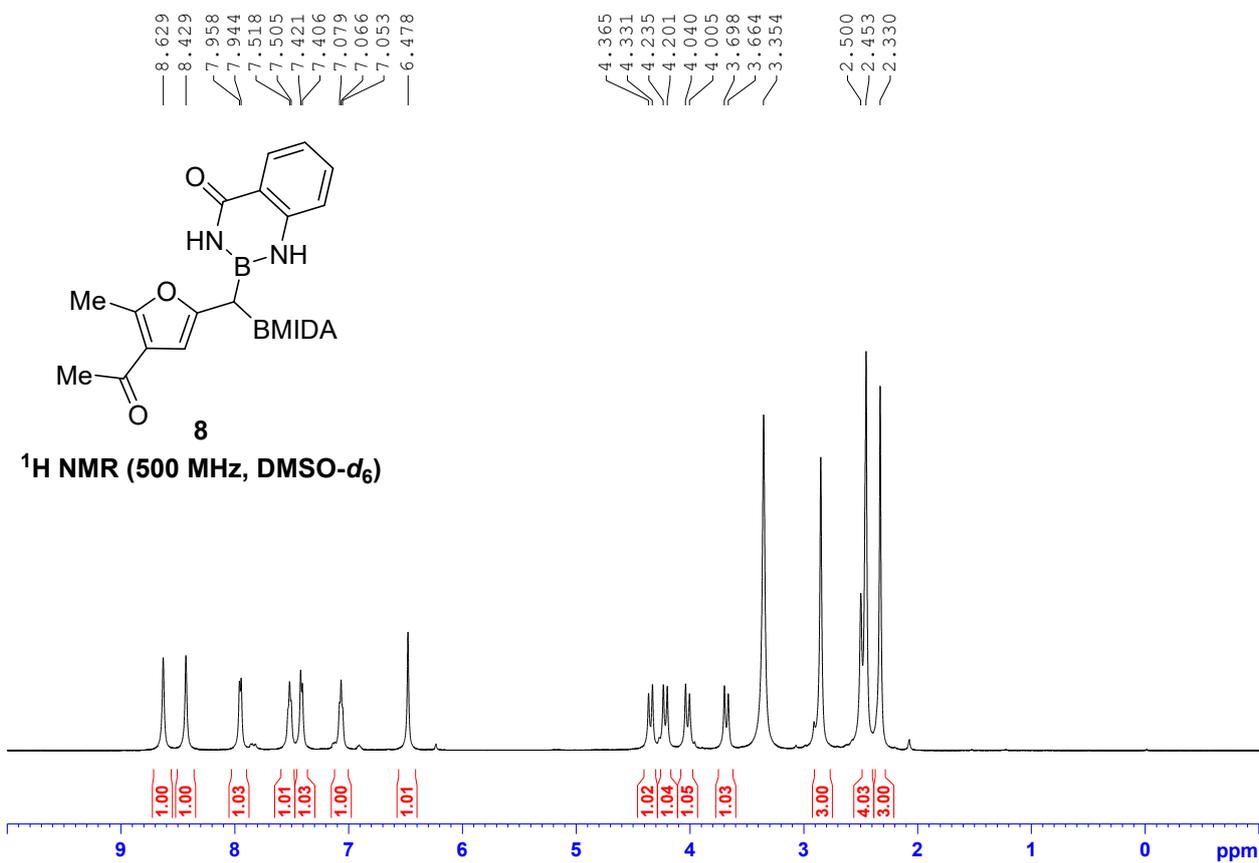


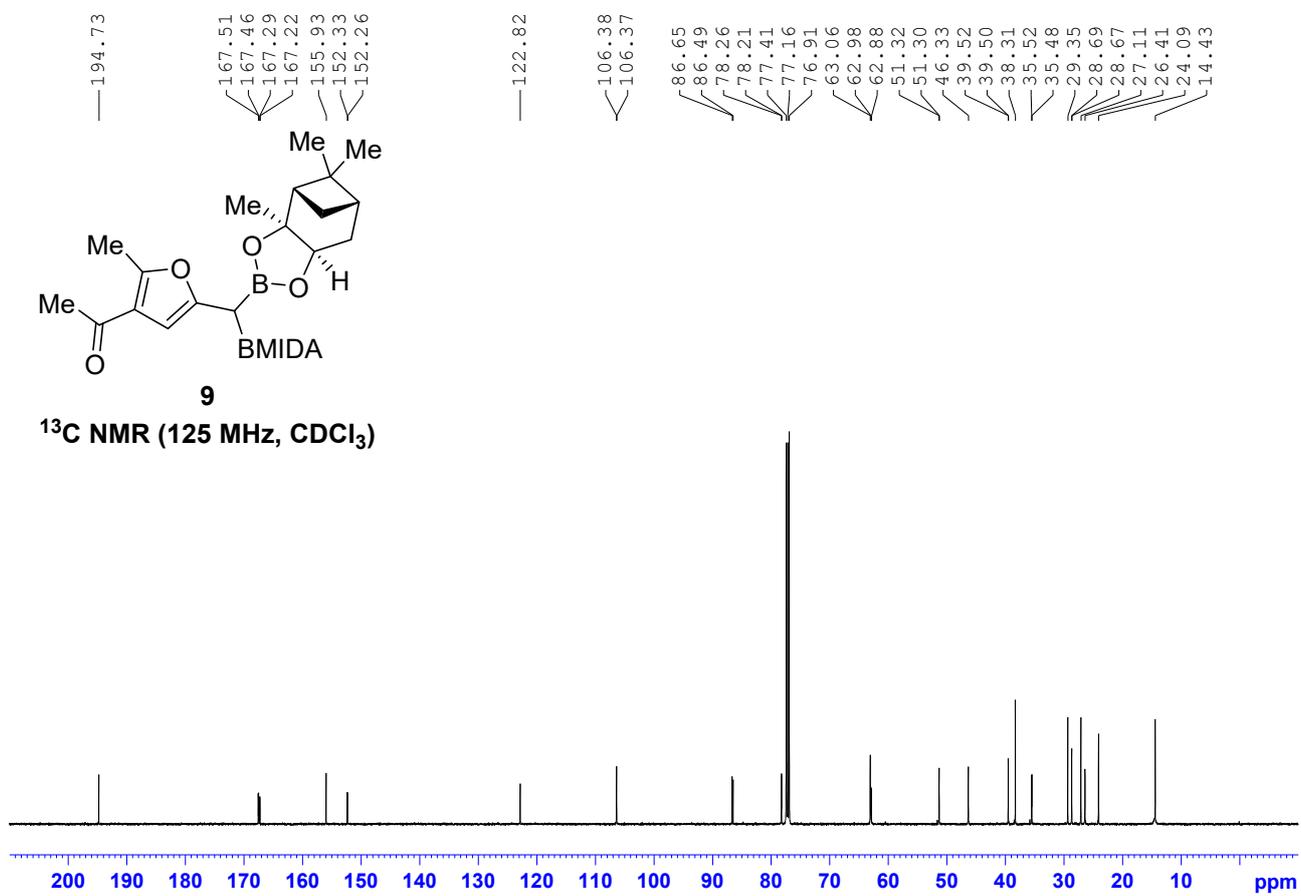
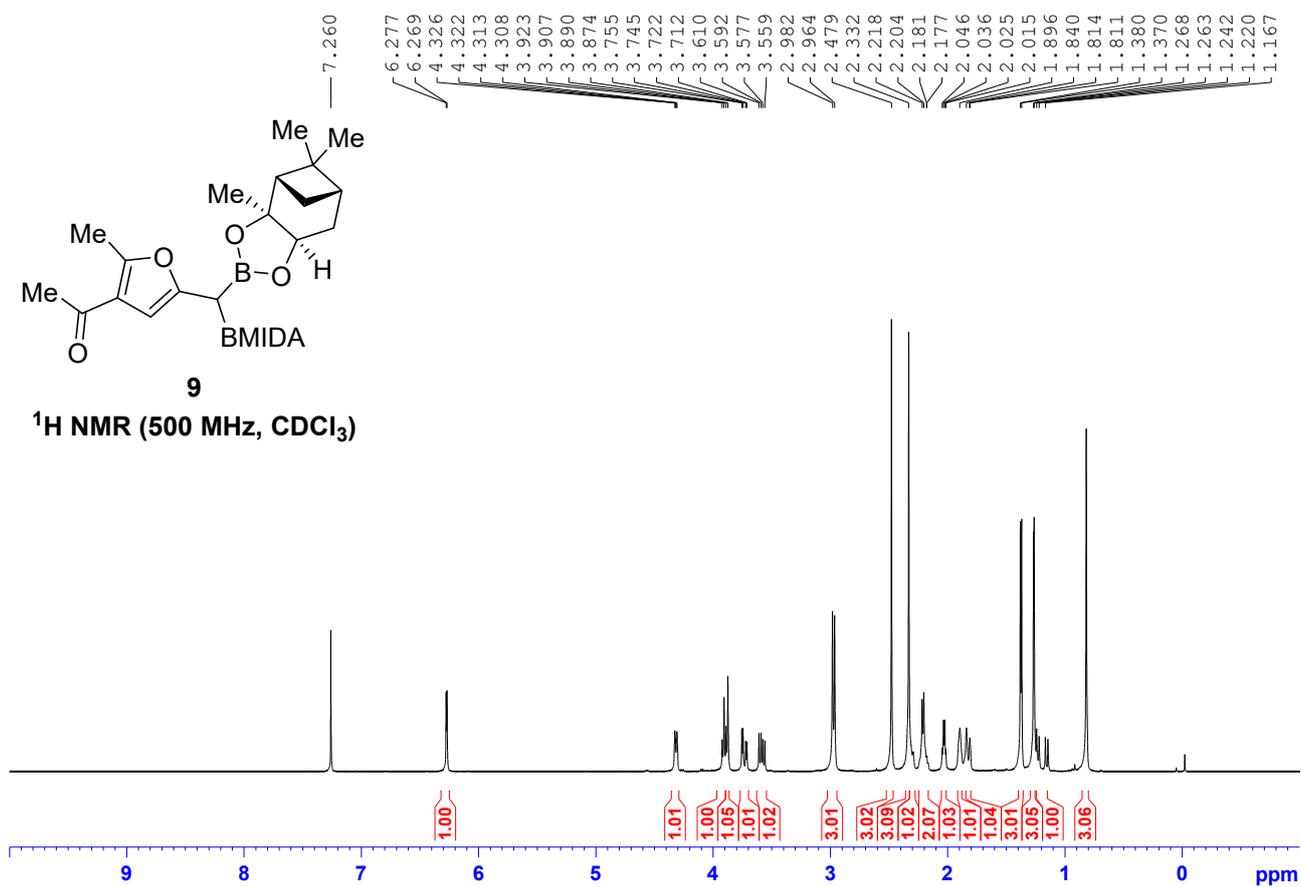
$^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$)

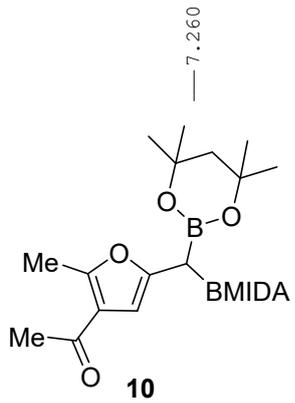


$^{13}\text{C NMR}$ (125 MHz, $\text{DMSO-}d_6$)

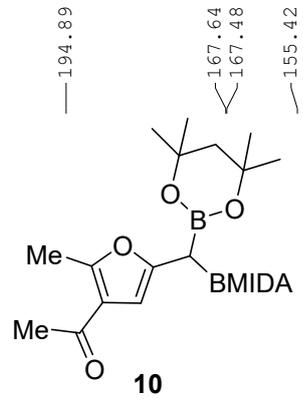
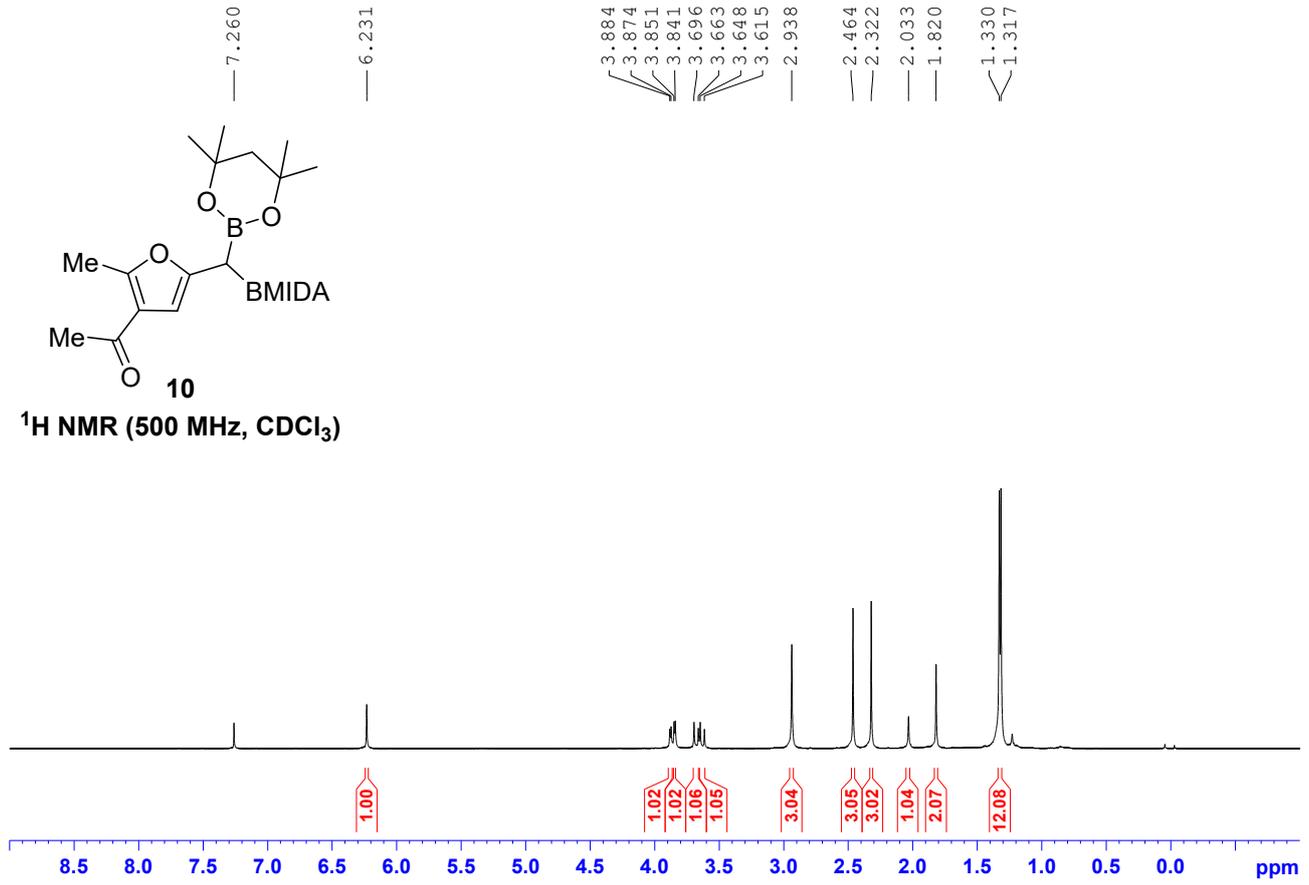




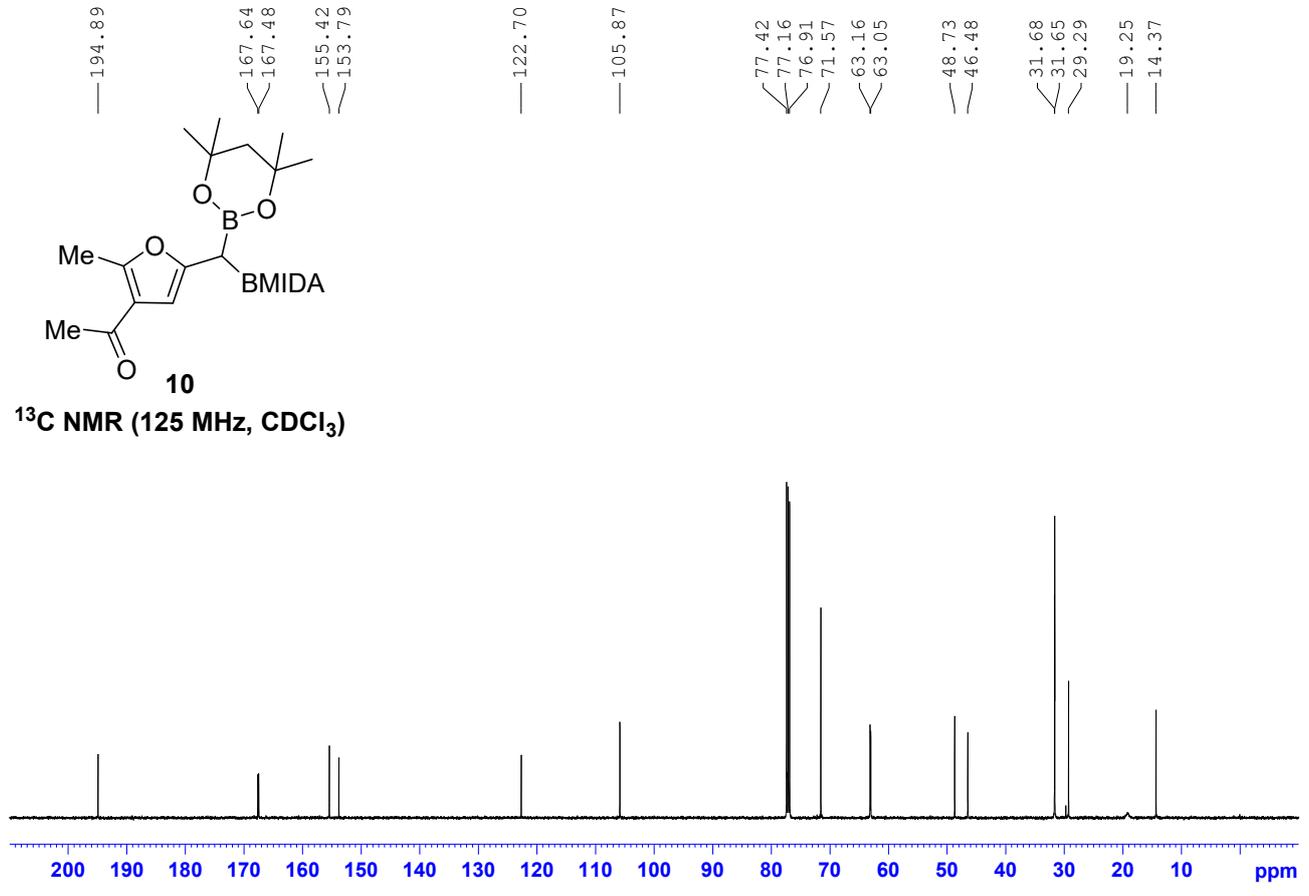


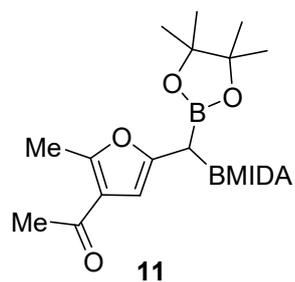


¹H NMR (500 MHz, CDCl₃)

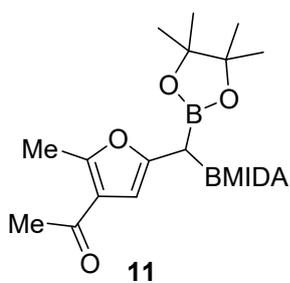
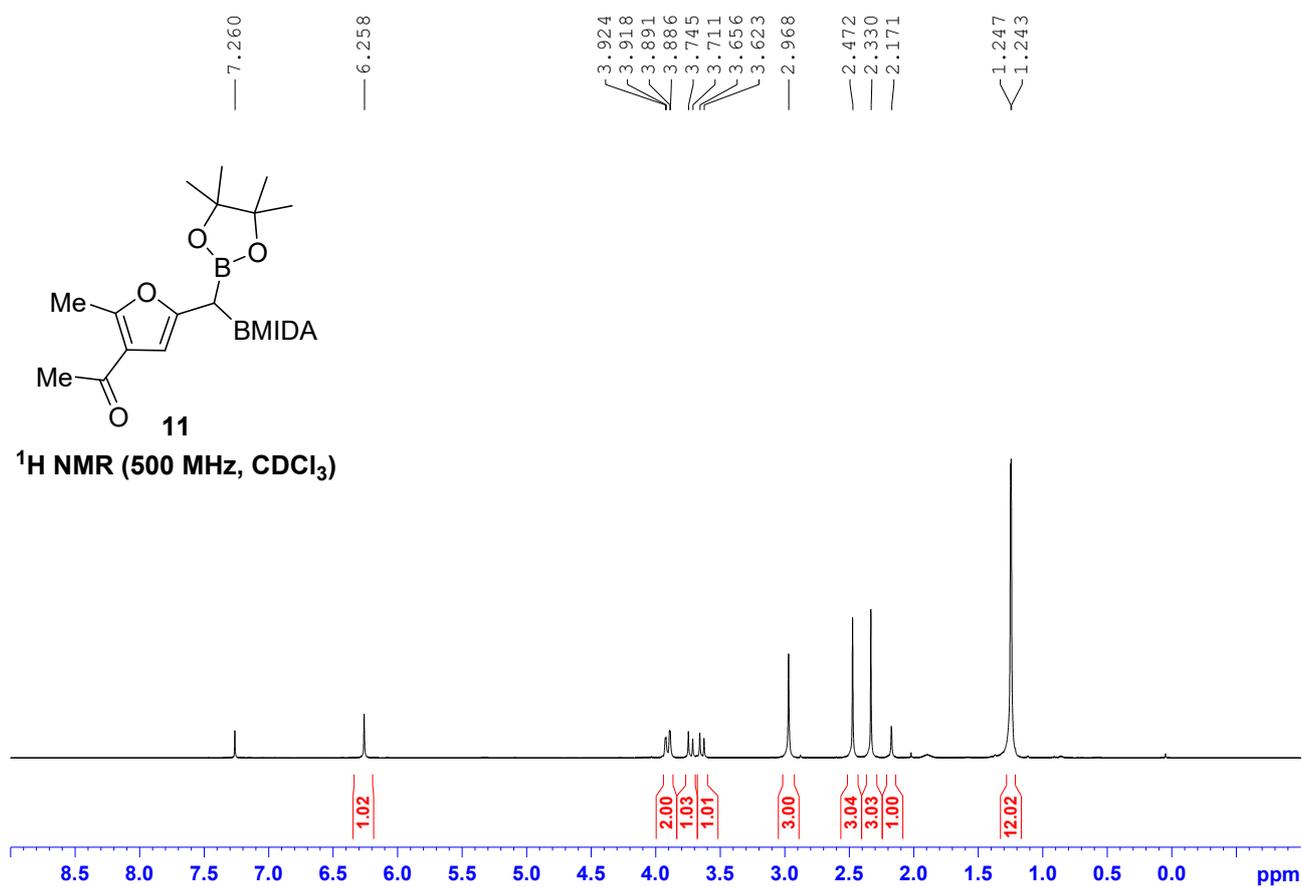


¹³C NMR (125 MHz, CDCl₃)

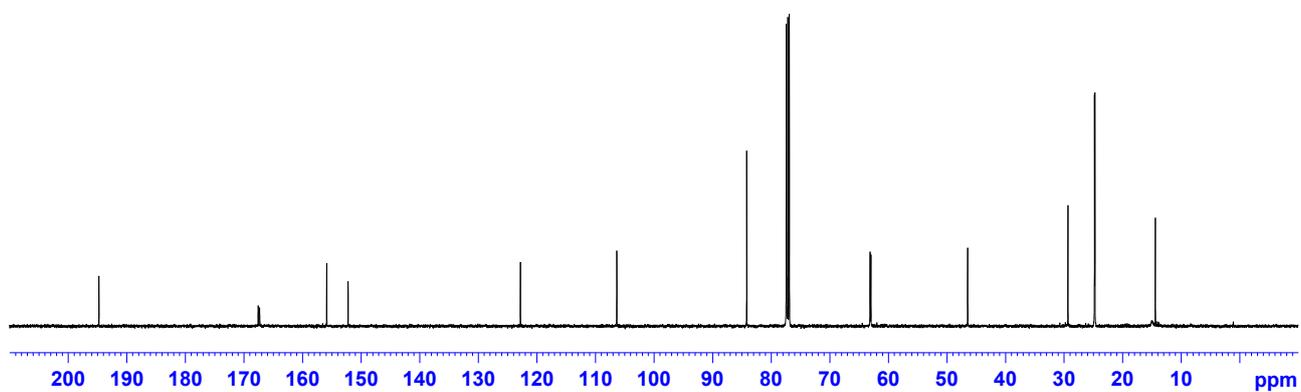


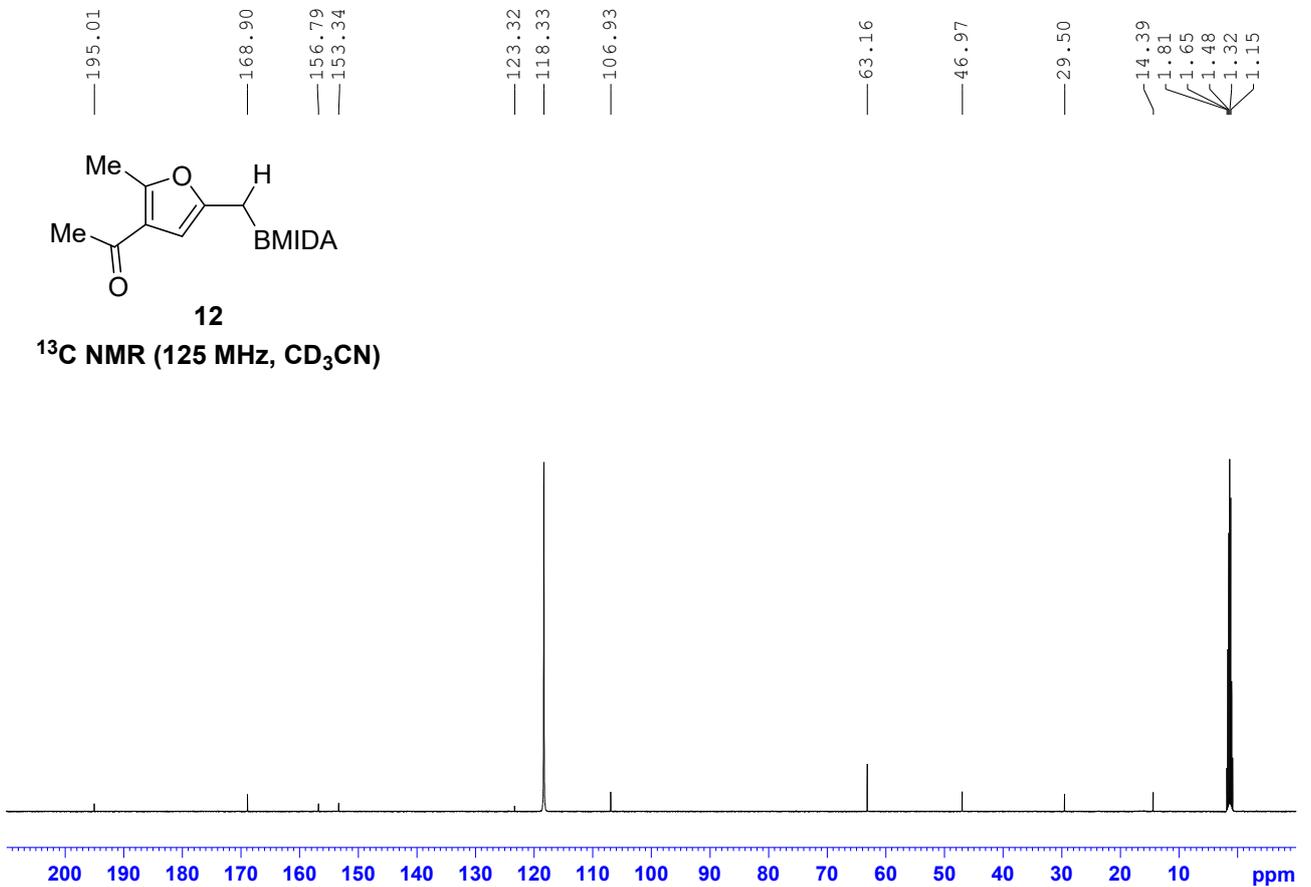
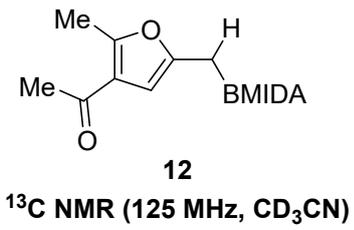
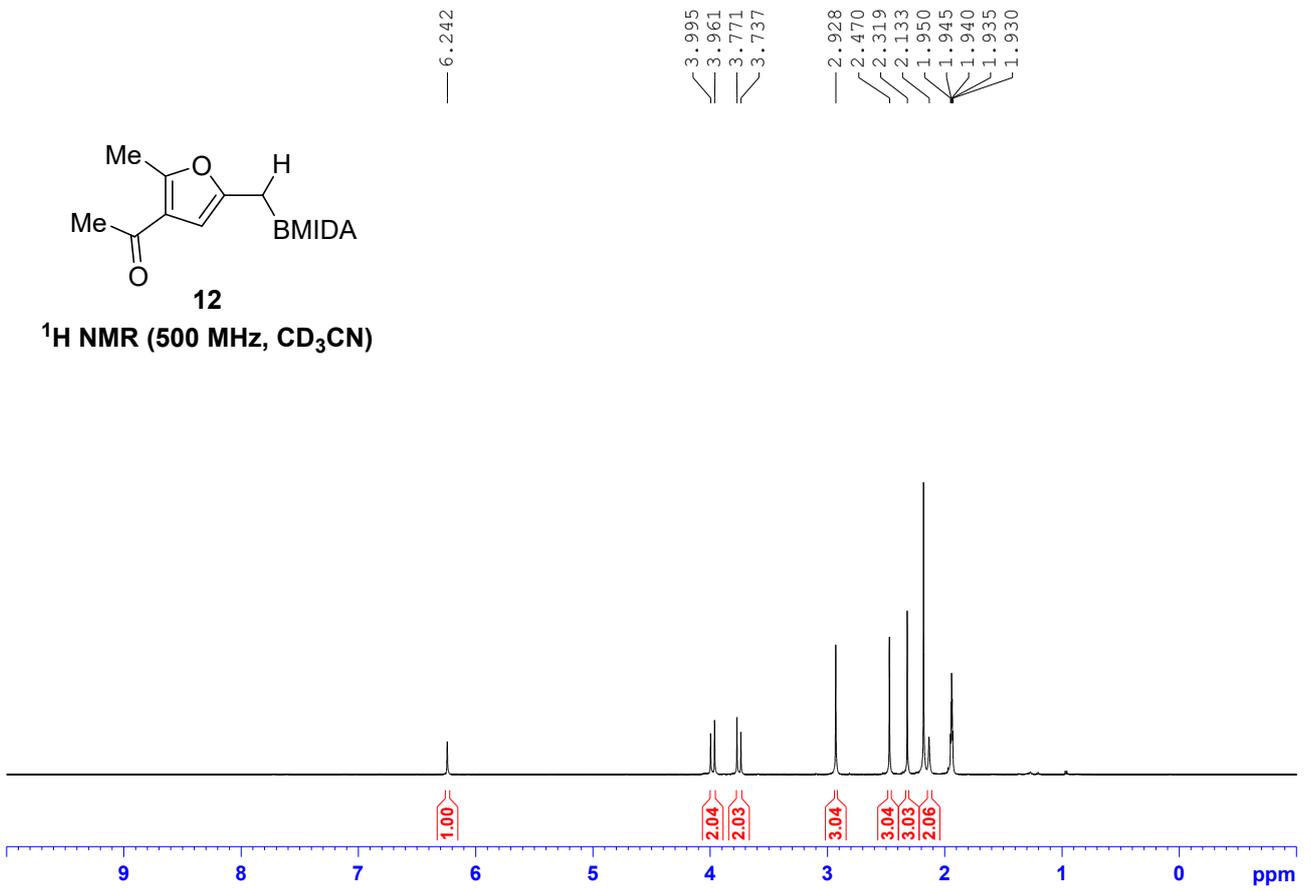
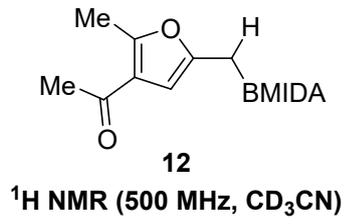


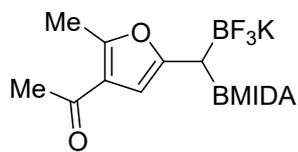
$^1\text{H NMR}$ (500 MHz, CDCl_3)



$^{13}\text{C NMR}$ (125 MHz, CDCl_3)

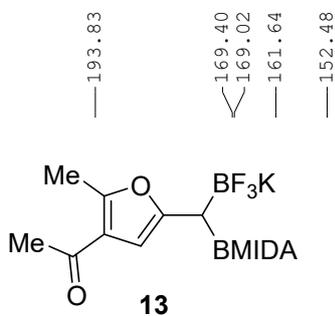
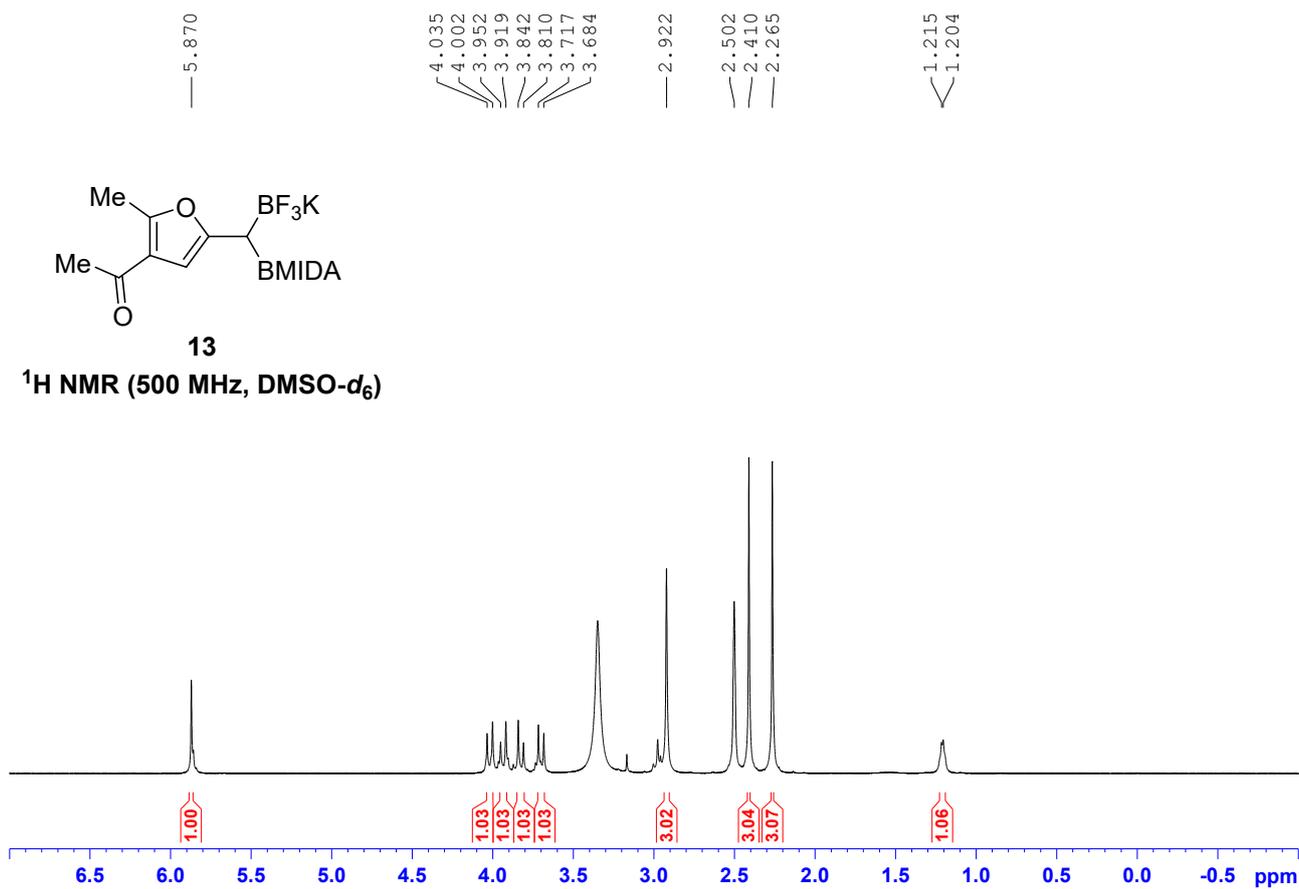






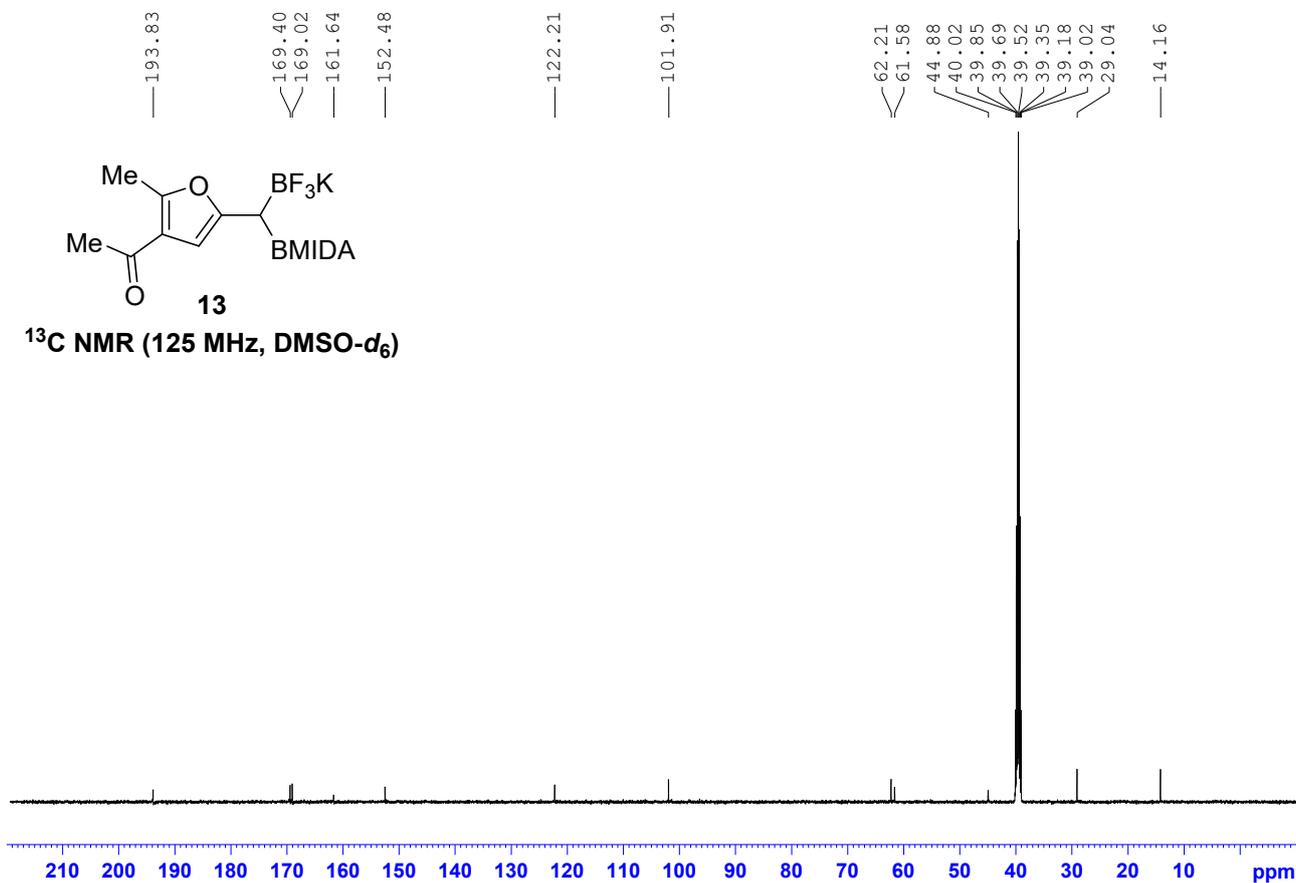
13

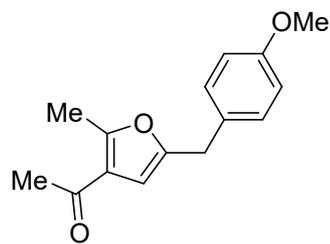
¹H NMR (500 MHz, DMSO-d₆)



13

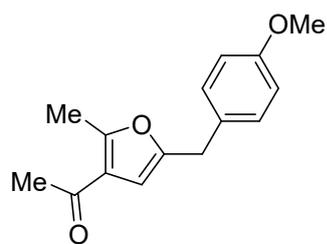
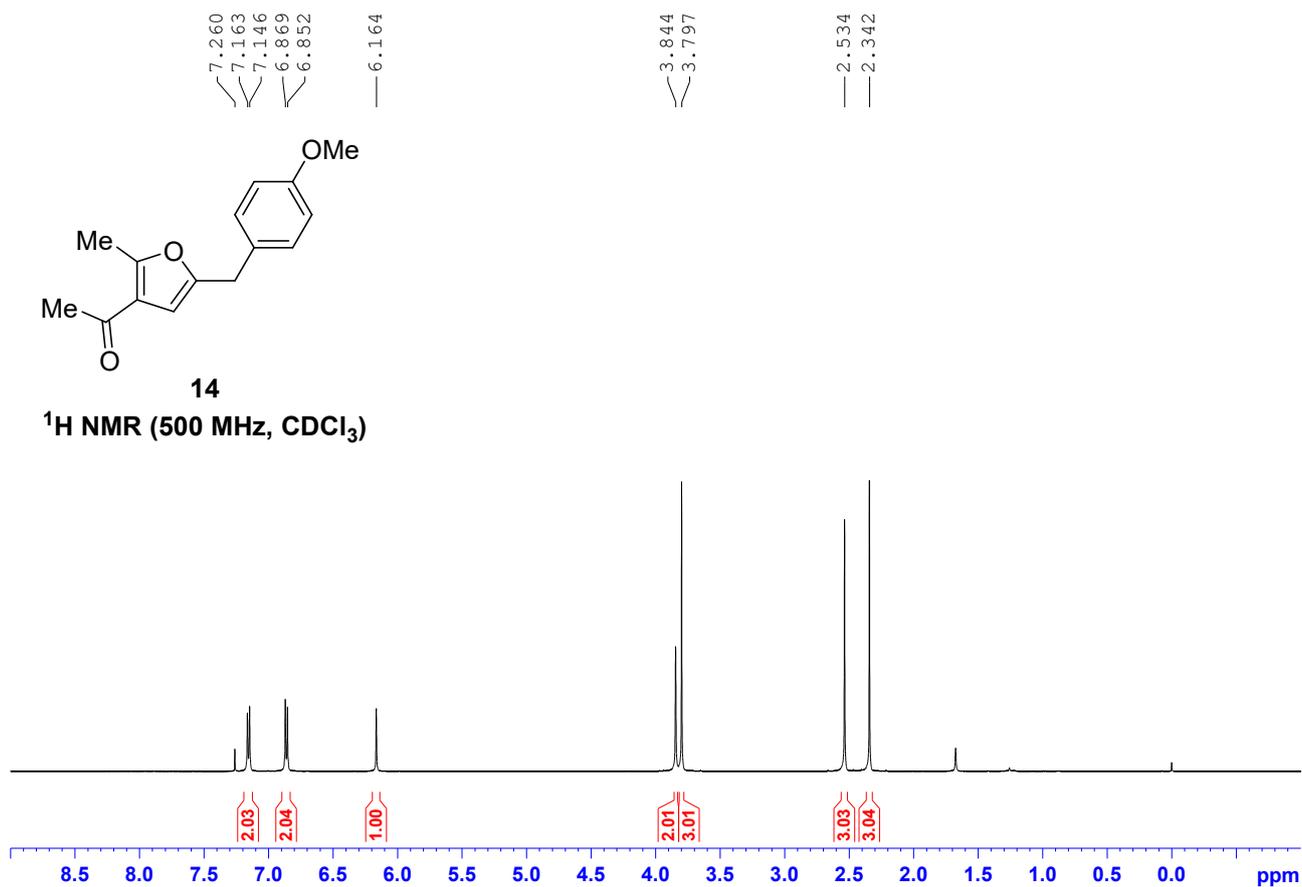
¹³C NMR (125 MHz, DMSO-d₆)





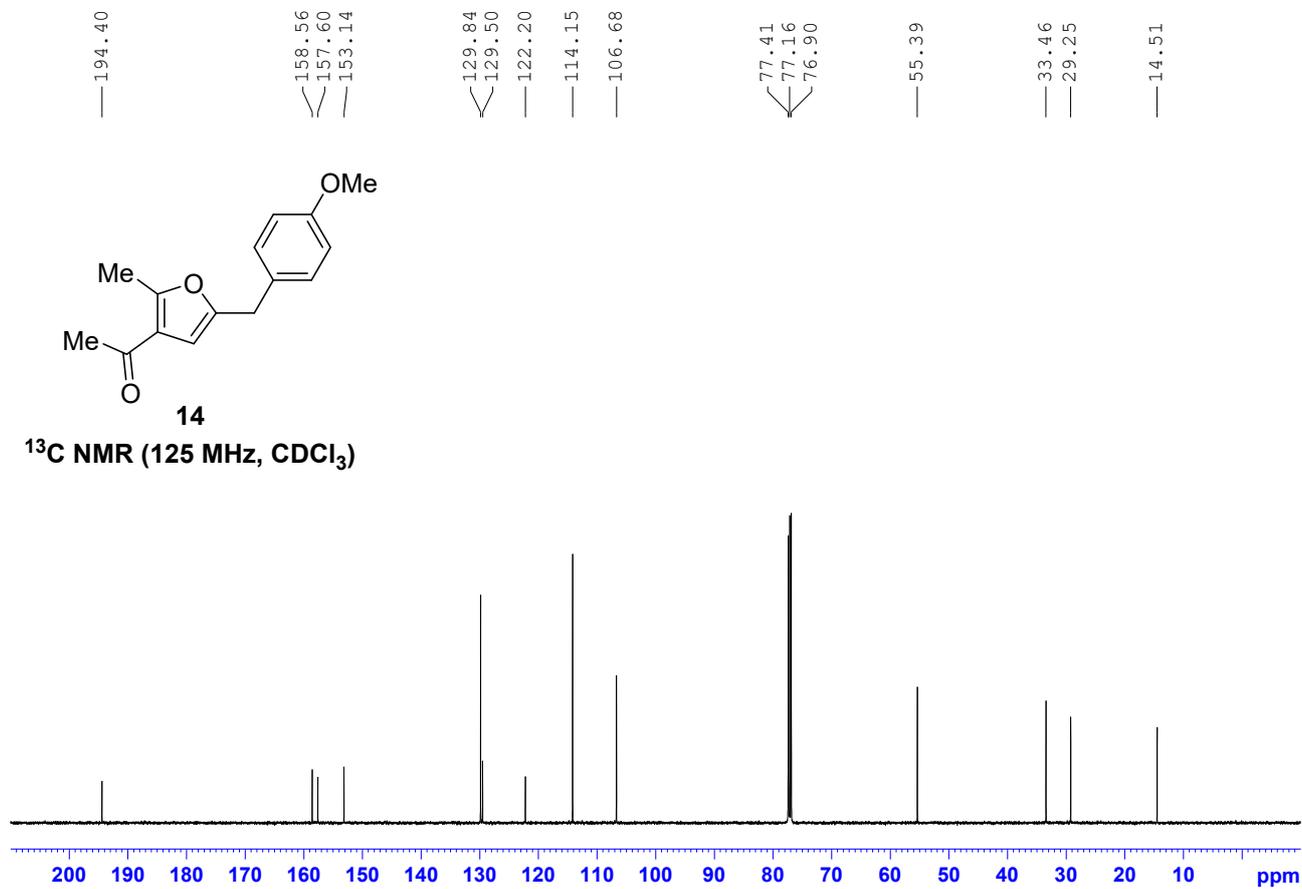
14

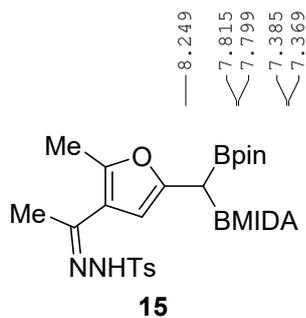
¹H NMR (500 MHz, CDCl₃)



14

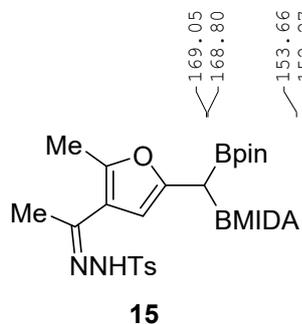
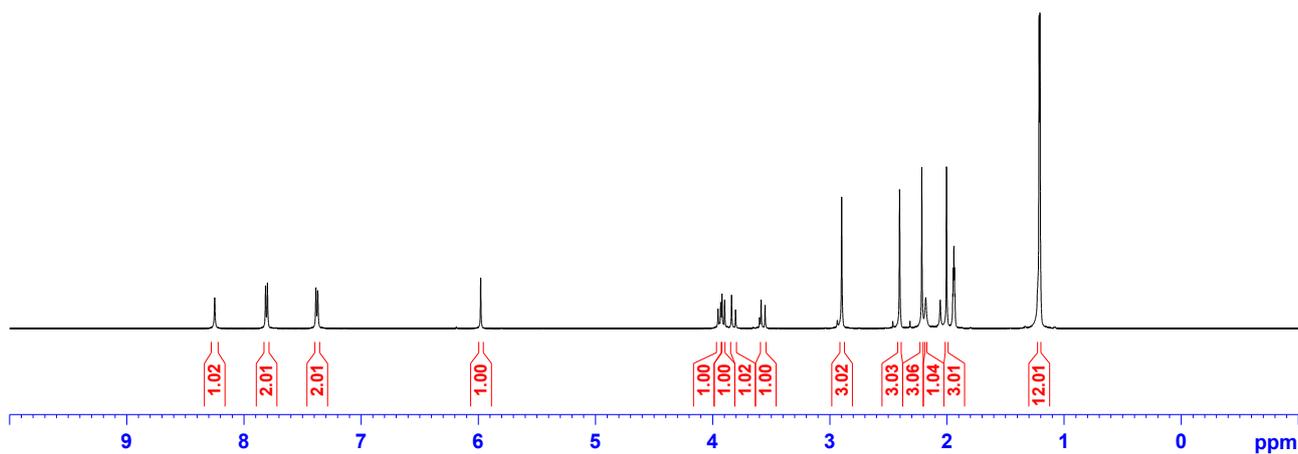
¹³C NMR (125 MHz, CDCl₃)





^1H NMR (500 MHz, CD_3CN)

8.249
 7.815
 7.799
 7.385
 7.369
 5.979
 3.953
 3.930
 3.919
 3.897
 3.837
 3.803
 3.586
 3.552
 2.898
 2.403
 2.214
 2.180
 2.003
 1.950
 1.945
 1.940
 1.935
 1.930
 1.214
 1.207



^{13}C NMR (125 MHz, CD_3CN)

169.05
 168.80
 153.66
 152.27
 149.62
 145.19
 136.91
 130.45
 129.06
 120.90
 118.32
 106.16
 84.53
 63.70
 63.67
 47.18
 24.99
 24.94
 21.57
 16.15
 14.38
 1.81
 1.65
 1.48
 1.32
 1.15

