Supporting Information

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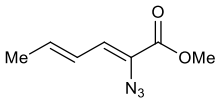
I. General experimental information

Dichloromethane, tetrahydrofuran, diethyl ether, toluene, and acetonitrile were dried by passage through columns of activated alumina. HPLC grade $CHCl_3$ was washed with 1 M NaOH and deionized H_2O, passed through a column of activated, basic Brockmann I Al_2O_3, and fractionally distilled from K_2CO_3 immediately prior to use. Irradiations were performed using a 1 W blue light-emitting diode (LED) strip (λ = 465-470 nm) purchased from Creative Lighting Solutions. Chromatography was performed with Purasil 60 Å silica gel (230–400 mesh). ^1H and ^{13}C NMR data for all previously uncharacterized compounds were obtained using Varian Inova-500 and Bruker-500 spectrometers and are referenced to TMS (0.00 ppm) or residual protio solvent signal. IR spectral data were obtained using a Bruker Vector 22 spectrometer (thin film on NaCl). Melting points were obtained using a Mel-Temp II (Laboratory Devices, Inc., USA) melting point apparatus. Mass spectrometry was performed with a Micromass LCT (electrospray ionization, time-of-flight analyzer or electron impact). These facilities are funded by the NSF (CHE-9974839, CHE-9304546) and the University of Wisconsin.

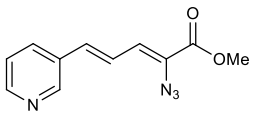
The catalyst complexes $Ru(dtbbpy)_3(PF_6)_2$[1] and $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF_6)$[2] were prepared according to literature procedures. Compounds **5a**, **5b**, **5c**, **5d**, and **8** were prepared as described by Seeberger,[3] and compound **5l** was prepared according to a procedure reported by Driver.[4] Compounds **12** and **13** were prepared according to Lemos[5] and Gilchrist[6], respectively.

II. Synthesis of cyclization substrates

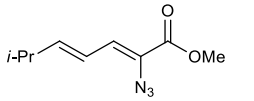


(2*Z*,4*E*)-Methyl 2-azidohexa-2,4-dienoate (1). Prepared using a modification of the procedure reported by Driver.[7] To a 100 mL round bottomed flask that had been flame-dried under high vacuum and purged with N_2 was added THF (14 mL) and hexamethyldisilazane (4.84 g, 30.0 mmol). The mixture was cooled to 0 °C after which *sec*-BuLi (24.0 mL of a 1.37 M solution in cyclohexane, 32.8 mmol) was added slowly. (Note: we found that use of *n*-BuLi led to formation of significant amounts of the butyl ester ((2*Z*,4*E*)-butyl 2-azidohexa-2,4-dienoate), and purification of the desired product away from the butyl ester derivative was very difficult). To ensure quantitative deprotonation, the reaction was stirred at 0 °C for an additional 10 min and thereafter cooled to –78 °C. After 10 min at –78 °C, a solution of freshly distilled crotonaldehyde (2.00 g, 28.5 mmol) in methyl azidoacetate (13.1 g, 114.1 mmol) was added dropwise over 1 h. Throughout the addition, a thick, dark sludge formed and continuous, vigorous stirring was required to achieve acceptable yields. Subsequently, the reaction was warmed to –10 °C and stirred until complete

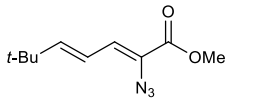
consumption of crotonaldehyde was observed (2 h). Thereafter, the mixture was warmed to rt and stirred for 2 h. At this time, the reaction was diluted with Et_2O (20 mL) and quenched via the slow addition of H_2O (20 mL). The organic layer was separated, and the aqueous layer was extracted with Et_2O (2 x 30 mL). The organic layers were combined and washed with H_2O (2 x 30 mL), brine (1 x 30 mL), dried over Na_2SO_4, filtered, and the volatiles were removed *in vacuo* to give a brown oil that was purified via flash column chromatography using a solvent gradient (99:1 to 24:1 hexanes:EtOAc) to afford the product (1.45 g, 8.66 mmol, 30% yield) as a pale yellow oil. Spectral data were in complete agreement with reported values.[7]



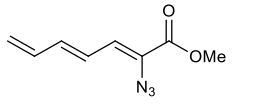
(2*Z*,4*E*)-Methyl 2-azido-5-(pyridin-3-yl)penta-2,4-dienoate (5e). Prepared according to the procedure of Seeberger.[3] A flame-dried 50 mL round bottomed flask under an atmosphere of N_2 was charged with *trans*-3-(3-pyridyl)acrolein (500 mg, 3.76 mmol), dry MeOH (5.3 mL), and methyl azidoacetate (1080 mg, 9.39 mmol). The solution was cooled to –15 °C, and after 10 min, a solution of NaOMe (freshly prepared from 216 mg Na (9.39 mmol) in 5.3 mL MeOH) was added dropwise over 20 min. The reaction was stirred at –15 °C for an additional 90 min, then slowly warmed to 4 °C and stirred for 12 h. Subsequently, the heterogeneous mixture was poured into ice-cold saturated aqueous NH_4Cl (15 mL). The resulting precipitate was isolated on a fritted funnel and washed with deionized H_2O until the filtrate came through clear. The beige solid was dissolved in CH_2Cl_2 and dried over Na_2SO_4. The organic solution was filtered, and the volatiles were removed *in vacuo* to give a residue that was purified by flash column chromatography using a solvent gradient (1:1 to 1:2 hexanes:EtOAc) to afford the title compound (455 mg, 1.98 mmol, 52% yield) as a pale yellow solid (mp = 99.7–100.4 °C). IR (neat) 2115, 1705, 1598, 1438, 1374, 1248, 971 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 8.66 (d, *J* = 1.8 Hz, 1H), 8.52 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.82 (app dt, *J* = 8.0, 1.8 Hz, 1H), 7.29 (dd, *J* = 8.1, 4.9 Hz, 1H), 7.22 (dd, *J* = 15.9, 11.2 Hz, 1H), 6.78 (d, *J* = 15.9 Hz, 1H), 6.74 (dd, *J* = 11.2, 0.9 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 163.4, 149.7, 149.2, 134.8, 133.1, 132.1, 126.7, 125.9, 124.1, 123.6, 52.8; HRMS (EI) calculated for $[C_{11}H_{10}N_4O_2]^+$ requires *m/z* 230.0804, found *m/z* 202.0737 ($[M-N_2]^+$, requires *m/z* 202.0742).



(2*Z*,4*E*)-Methyl 2-azido-6-methylhepta-2,4-dienoate (5f). Prepared in a similar manner to (2*Z*,4*E*)-methyl 2-azidohexa-2,4-dienoate **1** using (*E*)-4-methylpent-2-enal (980 mg, 10.0 mmol),[8] methyl azidoacetate (4.60 g, 40.0 mmol), hexamethyldisilazane (1.69 g, 10.5 mmol), *sec*-BuLi (8.38 mL of a 1.37 M solution in cyclohexane, 11.5 mmol), and THF (5.0 mL). Purified via flash column chromatography using a solvent gradient (99:1 to 24:1 hexanes:EtOAc) to afford the product (683 mg, 3.50 mmol, 35% yield) as a pale yellow oil. IR (neat) 2122, 1714, 1673, 1374, 1271, 1231 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 6.58 (d, *J* = 11.0 Hz, 1H), 6.39 (ddd, *J* = 15.4, 11.2, 1.4 Hz, 1H), 6.04 (ddd, *J* = 15.4, 6.8, 0.7 Hz, 1H), 3.84 (s, 3H), 2.44 (d of septets, *J* = 6.8, 1.3 Hz, 1H), 1.05 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 162.8, 149.6, 127.0, 122.8, 120.4, 51.5, 30.8, 20.8; HRMS (EI) calculated for $[C_9H_{13}N_3O_2]^+$ requires *m/z* 195.1008, found *m/z* 167.0941 ($[M-N_2]^+$, requires *m/z* 167.0946).

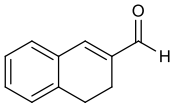


(2*Z*,4*E*)-Methyl 2-azido-6,6-dimethylhepta-2,4-dienoate (5g). Prepared in a similar manner to (2*Z*,4*E*)-methyl 2-azidohexa-2,4-dienoate **1** using (*E*)-4,4-dimethylpent-2-enal (650 mg, 5.79 mmol),[8] methyl azidoacetate (2.67 g, 23.2 mmol), hexamethyldisilazane (0.982 g, 6.08 mmol), *sec*-BuLi (4.86 mL of a 1.37 M solution in cyclohexane, 6.66 mmol), and THF (2.9 mL). Purified via flash column chromatography using a solvent gradient (99:1 to 24:1 hexanes:EtOAc) to afford the product (376 mg, 1.79 mmol, 31% yield) as a pale yellow oil. IR (neat) 2126, 1717, 1689, 1498, 1442, 1239 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 6.59 (dd, *J* = 11.0, 0.5 Hz, 1H), 6.36 (dd, *J* = 15.5, 10.9 Hz, 1H), 6.07 (dd, *J* = 15.5, 0.6 Hz, 1H), 3.84 (s, 3H), 1.07 (s, 9H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 162.8, 153.4, 127.3, 122.9, 118.3, 51.5, 33.2, 28.1; HRMS (EI) calculated for $[C_{10}H_{15}N_3O_2]$ requires *m/z* 209.1164, found *m/z* 209.1159.

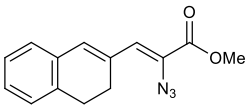


(2*Z*,4*E*)-Methyl 2-azidohepta-2,4,6-trienoate (5h). A flame-dried 50 mL round bottomed flask under an atmosphere of N_2 was charged with (*E*)-penta-2,4-dienal (600 mg, 7.31

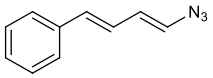
mmol),[9] dry MeOH (10.3 mL), and methyl azidoacetate (2103 mg, 18.3 mmol). The solution was cooled to –15 °C, and after 10 min, a solution of NaOMe (freshly prepared from 420 mg Na (18.3 mmol) in 10.3 mL MeOH) was added dropwise over 20 min. The reaction was stirred at –15 °C for an additional 90 min, then slowly warmed to 4 °C and stirred for 12 h. Subsequently, the heterogeneous mixture was poured into ice-cold saturated aqueous NH_4Cl (25 mL) and extracted with EtOAc (3 x 40 mL). The organic layer was dried over Na_2SO_4, filtered, and the volatiles were removed *in vacuo*. The resulting residue was purified via flash column chromatography (99:1 hexanes:EtOAc) to afford the trienyl azide (458 mg, 2.56 mmol, 35% yield) as a yellow oil that was used immediately. IR (neat) 2124, 1714, 1684, 1438, 1368, 1234 cm^{-1}. ^1H NMR: (499.8 MHz, C_6D_6) δ 6.56 (ddd, J = 14.9, 11.4, 0.5 Hz, 1H), 6.46 (d, J = 11.4 Hz, 1H), 6.19 (dtd, J = 17.0, 10.8, 0.5 Hz, 1H), 6.07 (ddd, J = 14.7, 10.9, 0.5 Hz, 1H), 5.07 (ddd, J = 16.9, 1.4 Hz, 1H), 4.99 (dd, J = 10.8, 1.3 Hz, 1H), 3.25 (s, 3H); ^{13}C NMR: (125.7 MHz, C_6D_6) δ 162.9, 139.3, 136.7, 126.6, 126.1, 125.9, 120.7, 51.7; HRMS (EI) calculated for $[C_8H_9N_3O_2]^+$ requires *m/z* 179.0695, found *m/z* 151.0628 ($[M-N_2]^+$, requires *m/z* 151.0633).



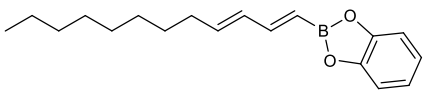
3,4-Dihydronaphthalene-2-carbaldehyde (S1). Prepared according to the procedure of Mock and Tsou.[10] To a 250 mL round bottomed flask that had been flame-dried under high vacuum and purged with N_2 was added distilled triethyl orthoformate (6.72 g, 45.4 mmol), which was then cooled to –30 °C. Subsequently, a solution of $BF_3{\cdot}Et_2O$ (7.73 g, 54.5 mmol) in CH_2Cl_2 (23 mL) was added dropwise over 20 min. The resulting slurry was stirred at –30 °C for an additional 5 min then warmed to 0 °C for 15 min. The solution was thereafter cooled to –78 °C and α-tetralone (3.32 g, 22.7 mmol) was added dropwise over 5 min followed by dropwise addition of diisopropylethylamine (8.80 g, 68.1 mmol) over 30 min. The reaction was then warmed to –20 °C and stirred for 30 min and slowly warmed to –10 °C over 90 min. Thereafter, the reaction was poured into saturated aqueous $NaHCO_3$ (250 mL) and CH_2Cl_2 (150 mL) was added followed by vigorous stirring for 10 min. The resulting layers were separated, and the organic layer was washed with cold, 0.5 M H_2SO_4 (1 x 50 mL) and cold H_2O (1 x 50 mL) and dried over Na_2SO_4. The organic layer was filtered, and the volatiles were removed *in vacuo* to afford a viscous, orange oil that was purified by Kugelrohr distillation (0.05 Torr, 200 °C glass oven temperature) to give 2-(diethoxymethyl)-3,4-dihydronaphthalen-1(2*H*)-one (5.24 g, 21.1 mmol, 93% yield) as a clear oil whose spectral data matched the reported literature values.[11] A dry 250 mL round bottomed flask equipped with an addition funnel was charged with 2-(diethoxymethyl)-3,4-dihydronaphthalen-1(2*H*)-one (3.20 g, 12.9 mmol) and EtOH (25 mL). The mixture was cooled to 0 °C, and then a solution of $NaBH_4$ (1.71 g, 45.1 mmol) in EtOH (55 mL) was added dropwise over 10 min. The reaction was heated to 80 °C and stirred for 30 min. Thereafter, the mixture was cooled to 0 °C and 6 M HCl was added dropwise over 20 min until H_2 evolution had ceased and the solution achieved a pH of 1. Subsequently, the reaction was heated to 80 °C and stirred for 4 h. At this time, the solution was cooled to rt and poured into brine (300 mL). EtOAc (150 mL) was added, and the organic layer was separated and washed with brine (1 x 50 mL), dried over Na_2SO_4, filtered, and the volatiles were removed *in vacuo* to afford a crude orange oil. Purification by flash-column chromatography on silica (9:1 hexanes:EtOAc) afforded the carbaldehyde (682 mg, 4.31 mmol, 33% yield over two steps) as a pale yellow oil. Spectral data were in complete agreement with previously reported values.[12]



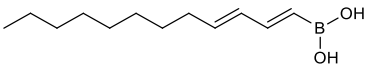
(*Z*)-Methyl 2-azido-3-(3,4-dihydronaphthalen-2-yl)acrylate (5i). Prepared in a similar manner to (2*Z*,4*E*)-methyl 2-azido-5-(pyridin-3-yl)penta-2,4-dienoate **5e** using 3,4-dihydronaphthalene-2-carbaldehyde **S1** (600 mg, 3.79 mmol), MeOH (5.3 mL), methyl azidoacetate (1091 mg, 9.49 mmol), and a solution of NaOMe (prepared from 218 mg Na (9.48 mmol) in 5.3 mL MeOH). The resulting residue was purified by flash-column chromatography using a solvent gradient (9:1 to 7:1 hexanes:EtOAc) to afford the title compound (534 mg, 2.09 mmol, 55% yield) as a pale yellow solid (mp = 62.6–64.0 °C). IR (neat) 2122, 1717, 1672, 1354, 1231 cm^{-1}. ^1H NMR: (499.8 MHz, $CDCl_3$) δ 7.14 (m, 4H), 6.88 (s, 1H), 6.66 (s, 1H), 3.88 (s, 3H), 2.85 (m, 2H), 2.80 (m, 2H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 164.3, 136.0, 135.0, 134.8, 133.8, 128.5, 127.8, 127.4, 126.7, 123.9, 52.9, 27.9, 25.6; HRMS (EI) calculated for $[C_{14}H_{13}N_3O_2]^+$ requires *m/z* 255.1003, found *m/z* 255.1002.



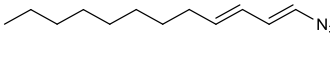
((1*E*,3*E*)-4-azidobuta-1,3-dien-1-yl)benzene (5j). Prepared according to the procedure of Guo.[13] A 25 mL round bottomed flask was charged with anhydrous $CuSO_4$ (42.5 mg, 0.267 mmol) and sodium azide (208 mg, 3.19 mmol). Then MeOH (8.0 mL) was added followed immediately by ((1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl)boronic acid (463 mg, 2.66 mmol).[14] The heterogeneous brown solution was vigorously stirred open to the atmosphere for 18 h. Thereafter, the volatiles were removed *in vacuo*, and the crude residue was dissolved in CH_2Cl_2 and filtered through a pad of silica (1:1 hexanes:EtOAc). The volatiles were removed *in vacuo* to give a dark yellow oil that was purified via flash column chromatography on silica (20:1 hexanes:EtOAc) to afford the product (163 mg, 0.95 mmol, 36% yield) as a pale yellow solid (mp = 51.4–53.1 °C). IR (neat) 2102, 1346, 1264, 976, 907 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.41-7.36 (m, 2H), 7.35-7.29 (m, 2H), 7.26-7.20 (m, 1H), 6.70 (ddd, *J* = 15.4, 10.9, 0.6 Hz, 1H), 6.49 (dd, *J* = 15.6, 0.7 Hz, 1H), 6.25 (dd, *J* = 13.3, 0.7 Hz, 1H), 6.12 (ddd, *J* = 13.2, 10.8, 0.8 Hz, 1H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 137.1, 131.5, 129.1, 128.7, 127.5, 126.1, 124.9, 120.7; HRMS (EI) calculated for $[C_{10}H_9N_3]^+$ requires *m/z* 171.0796, found *m/z* 143.0730 ($[M-N_2]^+$, requires *m/z* 143.0735).



2-((1*E*,3*E*)-Dodeca-1,3-dien-1-yl)benzo[*d*][1,3,2]dioxaborole (S2). To a 25 mL round bottomed flask with a stir bar that had been flame-dried under high vacuum and purged with N_2 was added (*E*)-dodec-3-en-1-yne (1.39 g, 8.46 mmol).[15,16] To the stirred compound was added freshly distilled catecholborane[17] (1.02 g, 8.46 mmol) over 5 min. Thereafter, the reaction was heated to 70 °C and stirred for 3 h, resulting in the formation of a dark brown oil. After cooling the mixture to rt, the crude oil was purified by Kugelrohr distillation at 0.05 Torr (impurity collected at 50–80 °C, product distilled at 132 °C) to afford the title compound (1.74 g, 6.12 mmol, 72% yield) as a clear oil. IR (neat) 2937, 2856, 2379, 2345, 1649, 1455, 1136, 1002 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 17.7, 10.4 Hz, 1H), 7.21 (app dd, *J* = 5.8, 3.3 Hz, 2H), 7.07 (app dd, *J* = 5.8, 3.3 Hz, 2H), 6.26 (dd, *J* = 15.2, 10.5 Hz, 1H), 6.06 (dt, *J* = 14.7, 7.1 Hz, 1H), 5.75 (d, *J* = 17.7 Hz, 1H), 2.17 (dt, *J* = 7.9, 7.7 Hz, 2H), 1.44 (tt, *J* = 7.9, 7.6 Hz, 2H), 1.29 (m, 10H), 0.89 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 152.9, 148.3, 142.0, 132.1, 122.5, 112.2, 32.8, 31.8, 29.4, 29.2, 29.2, 28.9, 22.7, 14.1; HRMS (EI) calculated for $[C_{18}H_{25}BO_2]^+$ requires *m/z* 284.1948, found *m/z* 284.1979.

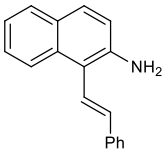


(1*E*,3*E*)-Dodeca-1,3-dien-1-ylboronic acid (S3). A 50 mL round bottomed flask was charged with 2-((1*E*,3*E*)-dodeca-1,3-dien-1-yl)benzo[*d*][1,3,2]dioxaborole **S2** (1.74 g, 6.12 mmol). Cold H_2O (29.2 mL) was added over 5 min, and the resulting heterogeneous mixture was vigorously stirred at rt for 2 h. The white precipitate that formed was isolated on a 15 mL medium fritted glass funnel, washed with copious H_2O, and air-dried for 15 min to afford the title compound (1.10 g, 5.25 mmol, 86% yield) as a white solid (mp = 88.3–90.2 °C). IR (neat) 2927, 2853, 2360, 2344, 1648, 1455, 1136, 1001 cm^{-1}. ^1H NMR: (500.2 MHz, $(CD_3)_2CO$) δ 6.95 (dd, *J* = 17.6, 10.3 Hz, 1H), 6.66 (s, 2H), 6.13 (ddd, *J* = 15.1, 10.3, 0.7 Hz, 1H), 5.84 (dt, *J* = 14.7, 7.2 Hz, 1H), 5.44 (d, *J* = 17.6 Hz, 1H), 2.11 (dtd, *J* = 7.7, 7.3, 1.1 Hz, 2H), 1.41 (tt, *J* = 7.9, 7.5 Hz, 2H), 1.30 (m, 10H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR: (125.8 MHz, $(CD_3)_2CO$) δ 149.3, 139.3, 134.6, 34.1, 33.5, 30.8, 30.7, 24.2, 15.2; HRMS (EI) calculated for $[C_{12}H_{23}BO_2]^+$ requires *m/z* 210.1791, found *m/z* 210.1779.

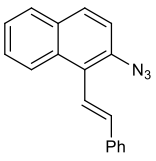


(1*E*,3*E*)-1-Azidododeca-1,3-diene (5k). A 25 mL round bottomed flask was charged with anhydrous $CuSO_4$ (76.6 mg, 0.480 mmol) and sodium azide (374 mg, 5.76 mmol). Then MeOH (14.4 mL) was added followed immediately by (1*E*,3*E*)-dodeca-1,3-dien-1-ylboronic acid **S3** (1009 mg, 4.80 mmol). The heterogeneous brown solution was stirred vigorously open to the atmosphere for 12 h. Thereafter, the volatiles were removed *in vacuo* and the crude residue was dissolved in CH_2Cl_2 and filtered through a pad of silica (1:1 hexanes:EtOAc). The volatiles were removed *in vacuo* and the residue was purified via flash column chromatography on silica (hexanes) to afford the title compound (318 mg, 1.53 mmol, 32% yield) as a pale yellow oil. IR (neat) 2102, 1651, 1611, 1457, 972 cm^{-1}. ^1H NMR: (499.8 MHz, C_6D_6) δ 5.85 (dd, *J* = 13.2, 11.0 Hz, 1H), 5.75 (ddt, *J* = 15.0, 10.8, 1.3 Hz, 1H), 5.45 (d, *J* = 13.2 Hz, 1H), 5.39 (dt, *J* = 14.6, 7.1 Hz, 1H), 1.96

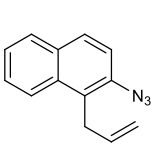
(dtd, J = 7.9, 7.3, 1.3 Hz, 2H), 1.27 (m, 12H), 0.91 (t, J = 6.9 Hz, 3H); ^{13}C NMR: (125.7 MHz, C_6D_6) δ 133.9, 126.7, 126.4, 120.6, 32.8, 32.0, 29.6, 29.4, 29.3, 29.3, 22.8, 14.1; HRMS (EI) calculated for $[C_{12}H_{21}N_3]^+$ requires *m/z* 207.1735, found *m/z* 179.1669 ($[M\text{-}N_2]^+$, requires *m/z* 179.1674).



(*E*)-1-Styrylnaphthalen-2-amine (S4). To a 100 mL round bottomed flask was added 1-bromonaphthalen-2-amine (500 mg, 2.25 mmol),[18] *trans*-2-phenylvinylboronic acid (500 mg, 3.38 mmol), K_2CO_3 (1245 mg, 9.01 mmol), and $Pd(PPh_3)_4$ (260 mg, 0.225 mmol). The system was equipped with a reflux condenser, evacuated, and purged with N_2 before adding toluene (23 mL), EtOH (9 mL), and H_2O (4.5 mL). The reaction was heated to 100 °C and refluxed for 72 h. Thereafter, the reaction was cooled to rt and diluted with H_2O (30 mL) and CH_2Cl_2 (30 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 30 mL). The combined organic layers were washed with H_2O (1 x 30 mL) and brine (1 x 30 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude residue was purified via flash column chromatography on silica using a solvent gradient (20:1 to 10:1 hexanes:EtOAc) to afford the title compound (359 mg, 1.46 mmol, 65% yield) as a bright yellow solid (mp = 74.9–76.5 °C). IR (neat) 3448, 3377, 3055, 3023, 2361, 2339, 1618, 1512, 1394, 1280, 1146 cm^{-1}. ^{1}H NMR: (500.0 MHz, $CDCl_3$) δ 7.92 (d, J = 8.6 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 8.6 Hz, 1H), 7.60 (m, 2H), 7.40 (m, 4H), 7.32 (tt, J = 7.2, 1.2 Hz, 1H), 7.25 (td, J = 8.1, 1.2 Hz, 1H), 7.00 (d, J = 8.8 Hz, 1H), 6.97 (d, J = 16.8 Hz, 1H), 4.13 (s, 2H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 141.5, 137.4, 135.2, 133.2, 128.8, 128.7, 128.3, 128.2, 127.8, 126.5, 126.3, 123.7, 123.4, 122.4, 118.4, 115.3; HRMS (EI) calculated for $[C_{18}H_{16}N_3]^+$ requires *m/z* 246.1278, found *m/z* 246.1282.



(*E*)-2-Azido-1-styrylnaphthalene (5m). To a 100 mL round bottomed flask was added (*E*)-1-styrylnaphthalen-2-amine (**S4**) (200 mg, 0.815 mmol) followed by H_2O (4.5 mL) and glacial AcOH (4.5 mL). The heterogeneous mixture was cooled to 0 °C and allowed to stir for 10 min before adding $NaNO_2$ (78.8 mg, 1.14 mmol) in a single portion. The resulting dark orange mixture was stirred at 0 °C for 1 h. Subsequently, NaN_3 (79.4 mg, 1.22 mmol) was added portionwise over 3 min and the resulting yellow solution was warmed to rt and stirred for 45 min. The reaction was diluted with H_2O (30 mL) and Et_2O (30 mL) and transferred to a 250 mL Erlenmeyer flask with a large stir bar. The solution was vigorously stirred while solid Na_2CO_3 was added until pH ~ 7. The organic layer was separated and the aqueous layer was extracted with Et_2O (2 x 30 mL). The organic layers were combined and washed with H_2O (2 x 20 mL) and brine (1 x 20 mL) before being dried over Na_2SO_4. The volatiles were removed *in vacuo* and the residue was purified via flash column chromatography on silica using a solvent gradient (50:1 to 25:1 hexanes:EtOAc) to afford the title compound (139 mg, 0.512 mmol, 63% yield) as an off-white solid (mp = 95.5–96.1 °C). IR (thin film) 3081, 3061, 2953, 2327, 2111, 2051, 1640, 1619, 1598, 1299 cm^{-1}. ^{1}H NMR: (500.0 MHz, $CDCl_3$) δ 8.21 (d, J = 8.7 Hz, 1H), 7.83 (d, J = 7.8 Hz, 1H), 7.82 (d, J = 8.7 Hz, 1H), 7.60 (d, J = 7.5 Hz, 2H), 7.51 (td, J = 6.9, 1.3 Hz, 1H), 7.43 (m, 4H), 7.37 (d, J = 8.8 Hz, 1H), 7.31 (tt, J = 7.1, 1.3 Hz, 1H), 7.04 (d, J = 16.8 Hz, 1H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 137.3, 136.4, 134.3, 132.5, 131.3, 129.1, 128.8, 128.5, 128.0, 127.1, 126.6, 125.3, 125.2, 125.1, 121.9, 117.2, HRMS (EI) calculated for $[C_{18}H_{13}N_3]^+$ requires *m/z* 271.1109, found *m/z* 243.1044 ($[M\text{-}N_2]^+$, requires *m/z* 243.1043).

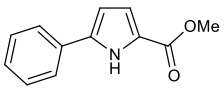


1-Allyl-2-azidonaphthalene (15). To a flame-dried 25 mL round bottomed flask was added 1-bromonaphthalen-2-amine (290 mg, 1.31 mmol).[18] The flask was equipped with a reflux condenser and the system was evacuated and purged with N_2 before adding DMF (3.3 mL), allyltributylstannane (519 mg, 1.56 mmol), and $Pd(PPh_3)_4$ (151 mg, 0.131 mmol). The mixture was heated to 85 °C and stirred for 40 h. Thereafter, the reaction was cooled to rt and diluted with H_2O (5 mL) and Et_2O (10 mL). The organic layer was separated, and the aqueous layer was extracted with Et_2O (4 x 5 mL). The combined organic layers were washed with H_2O (4 x 5 mL) and subsequently dried over Na_2SO_4. The volatiles were removed *in vacuo* and the residue was purified via flash column chromatography on silica (9:1 hexanes:EtOAc) to afford 1-allylnaphthalen-2-amine (176 mg, 0.960 mmol, 73% yield) as a pale yellow oil. To a

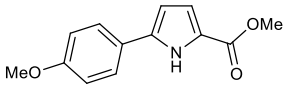
100 mL round bottomed flask was added 1-allylnaphthalen-2-amine (171 mg, 0.933 mmol) followed by H_2O (5.2 mL) and glacial AcOH (5.2 mL). The heterogeneous mixture was cooled to 0 °C and allowed to stir for 10 min before adding $NaNO_2$ (90.1 mg, 1.31 mmol) in a single portion. The resulting dark orange mixture was stirred at 0 °C for 1 h. Subsequently, NaN_3 (91 mg, 1.40 mmol) was added portionwise over 3 min and the resulting yellow solution was warmed to rt and stirred for 1 h. The reaction was diluted with H_2O (30 mL) and Et_2O (30 mL) and transferred to a 250 mL Erlenmeyer flask with a large stir bar. The solution was vigorously stirred while solid Na_2CO_3 was added until pH ~ 7. The organic layer was separated and the aqueous layer was extracted with Et_2O (2 x 30 mL). The organic layers were combined and washed with H_2O (2 x 20 mL) and brine (1 x 20 mL) before being dried over Na_2SO_4. The volatiles were removed *in vacuo* and the residue was purified via flash column chromatography on silica (50:1 hexanes:EtOAc) to afford the title compound (151 mg, 0.722 mmol, 77% yield) as a pale yellow oil. IR (thin film) 3081, 3061, 2953, 2327, 2111, 2051, 1640, 1619, 1598, 1299 cm^{-1}. ^1H NMR: (500.0 MHz, $CDCl_3$) δ 7.94 (d, J = 8.6 Hz, 1H), 7.81 (m, 2H), 7.52 (td, J = 6.8, 1.2 Hz, 1H), 7.43 (t, J = 7.8 Hz, 1H), 7.35 (d, J = 8.7 Hz, 1H), 6.00 (ddt, J = 17.3, 10.6, 6.2 Hz, 1H), 5.02 (dd, J = 10.3, 1.6 Hz, 1H), 4.96 (dd, J = 17.3, 1.6 Hz, 1H), 3.82 (d, J = 6.0 Hz, 2H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 135.9, 134.6, 132.9, 131.2, 128.7, 128.7, 127.0, 125.2, 125.0, 124.2, 116.9, 115.7, 30.7, HRMS (EI) calculated for $[C_{13}H_{11}N_3]^+$ requires *m/z* 209.0948, found *m/z* 209.0944.

III. Cyclizations of vinyl and aryl azides

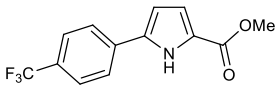
General procedure for visible light sensitization of azides: To an oven-dried 25 mL Schlenk tube with a stir bar was added the azide (0.75 mmol, 1 equiv.), $Ru(dtbbpy)_3(PF_6)_2$ or $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF_6)$ (0.0075 mmol, 0.01 equiv.), and freshly distilled $CHCl_3$ (7.5 mL, 0.1 M). The solution was submitted to three freeze-pump-thaw cycles, purged with N_2, and irradiated at rt with a 1 W blue light-emitting diode (LED) strip (λ = 465–470 nm). Upon completion of the reaction, the mixture was concentrated *in vacuo*, and the crude residue was purified by flash column chromatography to afford the pure pyrrole.



Methyl 5-phenyl-1*H*-pyrrole-2-carboxylate (6a) (Table 2, entry 1). Experiment 1: Prepared according to the General Procedure using 172 mg (0.75 mmol) of (2*Z*,4*E*)-methyl 2-azido-5-phenylpenta-2,4-dienoate **5a**,[7] 9.0 mg (0.0075 mmol) of $Ru(dtbbpy)_3(PF_6)_2$, 7.5 mL of chloroform, and an irradiation time of 3 h. Purified by flash column chromatography on silica using a solvent gradient (7:1 to 5:1 hexanes:EtOAc) to afford 148 mg (0.74 mmol, 98% yield) of the pyrrole as a white solid. Experiment 2: 172 mg (0.75 mmol) of dienyl azide, 9.2 mg (0.0077 mmol) of $Ru(dtbbpy)_3(PF_6)_2$, and 7.5 mL of chloroform. Isolated 150 mg (0.75 mmol, 99% yield). All spectral data were in complete agreement with previously reported values.[7]

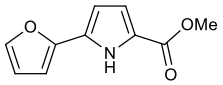


Methyl 5-(4-methoxyphenyl)-1*H*-pyrrole-2-carboxylate (6b) (Table 2, entry 2). Experiment 1: Prepared according to the General Procedure using 195 mg (0.75 mmol) of (2*Z*,4*E*)-methyl 2-azido-5-(4-methoxyphenyl)penta-2,4-dienoate **5b**,[7] 9.1 mg (0.0076 mmol) of $Ru(dtbbpy)_3(PF_6)_2$, 7.5 mL of chloroform, and an irradiation time of 4 h. Purified by flash column chromatography on silica using a solvent gradient (4:1 to 3:1 hexanes:EtOAc) to afford 171 mg (0.74 mmol, 98% yield) of the pyrrole as a white solid. Experiment 2: 194 mg (0.75 mmol) of dienyl azide, 9.0 mg (0.0075 mmol) of $Ru(dtbbpy)_3(PF_6)_2$, and 7.5 mL of chloroform. Isolated 172 mg (0.74 mmol, 99% yield). All spectral data were in complete agreement with previously reported values.[7]

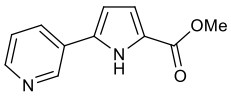


Methyl 5-(4-(trifluoromethyl)phenyl)-1*H*-pyrrole-2-carboxylate (6c) (Table 2, entry 3). Experiment 1: Prepared according to the General Procedure using 224 mg (0.75 mmol) of (2*Z*,4*E*)-methyl 2-azido-5-(4-(trifluoromethyl)phenyl)penta-2,4-dienoate **5c**,[7] 9.0 mg (0.0075 mmol) of $Ru(dtbbpy)_3(PF_6)_2$, 7.5 mL of chloroform, and an irradiation time of 2.5 h. Purified by flash column chromatography on silica using a solvent gradient (8:1 to 6:1 hexanes:EtOAc) to afford 194 mg (0.72 mmol, 96% yield) of the pyrrole as a white solid. Experiment 2: 223 mg (0.75 mmol) of dienyl azide, 9.1 mg

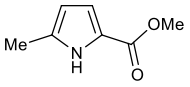
(0.0076 mmol) of $Ru(dtbbpy)_3(PF_6)_2$, and 7.5 mL of chloroform. Isolated 190 mg (0.71 mmol, 95% yield). All spectral data were in complete agreement with previously reported values.[7]



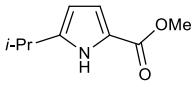
Methyl 5-(furan-2-yl)-1*H*-pyrrole-2-carboxylate (6d) (Table 2, entry 4). Experiment 1: Prepared according to the General Procedure using 164 mg (0.75 mmol) of (2*Z*,4*E*)-methyl 2-azido-5-(furan-2-yl)penta-2,4-dienoate **5d**,[7] 9.1 mg (0.0076 mmol) of $Ru(dtbbpy)_3(PF_6)_2$, 7.5 mL of chloroform, and an irradiation time of 4 h. Purified by flash column chromatography on silica using a solvent gradient (4:1 to 3:1 hexanes:EtOAc) to afford 142 mg (0.74 mmol, 99% yield) of the pyrrole as a white solid. Experiment 2: 164 mg (0.75 mmol) of dienyl azide, 9.0 mg (0.0075 mmol) of $Ru(dtbbpy)_3(PF_6)_2$, and 7.5 mL of chloroform. Isolated 138 mg (0.72 mmol, 96% yield). All spectral data were in complete agreement with previously reported values.[7]



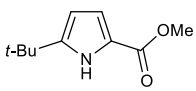
Methyl 5-(pyridin-3-yl)-1*H*-pyrrole-2-carboxylate (6e) (Table 2, entry 5). Experiment 1: Prepared according to the General Procedure using 173 mg (0.75 mmol) of (2*Z*,4*E*)-methyl 2-azido-5-(pyridin-3-yl)penta-2,4-dienoate **5e**, 9.2 mg (0.0077 mmol) of $Ru(dtbbpy)_3(PF_6)_2$, 7.5 mL of chloroform, and an irradiation time of 3 h. Purified by flash column chromatography on silica using a solvent gradient (1:1 to 1:2 hexanes:EtOAc) to afford 132 mg (0.65 mmol, 87% yield) of the pyrrole as a white solid (mp = 147.9–149.4 °C). Experiment 2: 173 mg (0.75 mmol) of dienyl azide, 9.0 mg (0.0075 mmol) of $Ru(dtbbpy)_3(PF_6)_2$, and 7.5 mL of chloroform. Isolated 132 mg (0.65 mmol, 86% yield). IR (neat) 3321, 2952, 1689, 1645, 1436, 1283, 1156 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 9.96 (m, 1H), 8.93 (dd, *J* = 2.2, 0.7 Hz, 1H), 8.55 (dd, *J* = 4.8, 1.8 Hz, 1H), 7.89 (app dtd, *J* = 8.0, 2.2, 1.7 Hz, 1H), 7.34 (ddd, *J* = 8.0, 4.9, 0.7 Hz, 1H), 6.99 (dd, *J* = 3.9, 2.5 Hz, 1H), 6.60 (dd, *J* = 3.8, 2.7 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 161.8, 148.6, 146.4, 133.7, 132.0, 127.5, 124.1, 123.6, 117.0, 108.9, 51.8; HRMS (EI) calculated for $[C_{11}H_{10}N_2O_2]^+$ requires *m/z* 202.0742, found *m/z* 202.0740.



Methyl 5-methyl-1*H*-pyrrole-2-carboxylate (2) (Table 2, entry 6). Experiment 1: Prepared according to the General Procedure using 126 mg (0.75 mmol) of (2*Z*,4*E*)-methyl 2-azidohexa-2,4-dienoate **1**, 9.0 mg (0.0075 mmol) of $Ru(dtbbpy)_3(PF_6)_2$, 7.5 mL of chloroform, and an irradiation time of 8 h. Purified by flash column chromatography on silica using a solvent gradient (9:1 to 7:1 hexanes:EtOAc) to afford 96 mg (0.69 mmol, 92% yield) of the pyrrole as a white solid. Experiment 2: 126 mg (0.75 mmol) of dienyl azide, 9.0 mg (0.0075 mmol) of $Ru(dtbbpy)_3(PF_6)_2$, and 7.5 mL of chloroform. Isolated 99 mg (0.71 mmol, 95% yield). All spectral data were in complete agreement with previously reported values.[7,19]

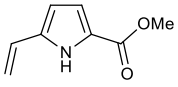


Methyl 5-isopropyl-1*H*-pyrrole-2-carboxylate (6f) (Table 2, entry 7). Experiment 1: Prepared according to the General Procedure using 146 mg (0.75 mmol) of (2*Z*,4*E*)-methyl 2-azido-6-methylhepta-2,4-dienoate **5f**, 9.0 mg (0.0075 mmol) of $Ru(dtbbpy)_3(PF_6)_2$, 7.5 mL of chloroform, and an irradiation time of 11 h. Purified by flash column chromatography on silica using a solvent gradient (9:1 to 7:1 hexanes:EtOAc) to afford 111 mg (0.66 mmol, 89% yield) of the pyrrole as a white solid (mp = 59.8–61.8 °C). Experiment 2: 147 mg (0.75 mmol) of dienyl azide, 9.0 mg (0.0075 mmol) of $Ru(dtbbpy)_3(PF_6)_2$, and 7.5 mL of chloroform. Isolated 112 mg (0.67 mmol, 89% yield). IR (neat) 3311, 2956, 1682, 1496, 1221, 1158 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 9.10 (br s, 1H), 6.83 (dd, *J* = 3.6, 2.5 Hz, 1H), 5.98 (m, 1H), 3.83 (s, 3H), 2.96 (septet, *J* = 6.8 Hz, 1H), 1.28 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 161.9, 144.8, 120.8, 115.9, 106.1, 51.3, 27.4, 22.3; HRMS (EI) calculated for $[C_9H_{13}NO_2]^+$ requires *m/z* 167.0946, found *m/z* 167.0938.

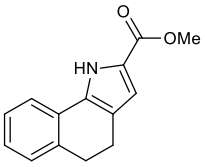


Methyl 5-(*tert*-butyl)-1*H*-pyrrole-2-carboxylate (6g) (Table 2, entry 8). Experiment 1: Prepared according to the General Procedure using 157 mg (0.75 mmol) of (2*Z*,4*E*)-methyl 2-azido-6,6-dimethylhepta-2,4-dienoate **5g**, 9.0 mg (0.0075 mmol) of $Ru(dtbbpy)_3(PF_6)_2$, 7.5 mL of chloroform, and an irradiation time of 14 h. Purified by flash column chromatography on silica using a solvent gradient (9:1 to 7:1 hexanes:EtOAc) to afford 115 mg (0.63 mmol, 85% yield) of the pyrrole as a white solid (mp = 125.0–126.8 °C). Experiment 2: 157 mg (0.75 mmol) of dienyl azide, 9.0 mg (0.0075 mmol) of $Ru(dtbbpy)_3(PF_6)_2$,

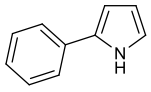
and 7.5 mL of chloroform. Isolated 119 mg (0.66 mmol, 88% yield). IR (neat) 3333, 2952, 1689, 1492, 1274, 1171 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 8.98 (br s, 1H), 6.82 (dd, J = 3.7, 2.5 Hz, 1H), 6.00 (dd, J = 3.7, 2.7 Hz, 1H), 3.83 (s, 3H), 1.32 (s, 9H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 161.9, 147.8, 120.8, 115.7, 105.7, 51.4, 31.8, 30.3; HRMS (EI) calculated for $[C_{10}H_{15}NO_2]^+$ requires *m/z* 181.1103, found *m/z* 181.1100.



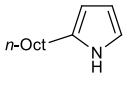
Methyl 5-vinyl-1*H*-pyrrole-2-carboxylate (6h) (Table 2, entry 9). Experiment 1: Prepared according to the General Procedure using 134 mg (0.75 mmol) of (2*Z*,4*E*)-methyl 2-azidohepta-2,4,6-trienoate **5h**, 9.1 mg (0.0076 mmol) of $Ru(dtbbpy)_3(PF_6)_2$, 7.5 mL of chloroform, and an irradiation time of 2 h. Purified by flash column chromatography on silica using a solvent gradient (8:1 to 7:1 hexanes:EtOAc) to afford 99 mg (0.65 mmol, 87% yield) of the pyrrole as a white solid (mp = 100.3–101.4 °C). Experiment 2: 134 mg (0.75 mmol) of dienyl azide, 9.1 mg (0.0076 mmol) of $Ru(dtbbpy)_3(PF_6)_2$, and 7.5 mL of chloroform. Isolated 102 mg (0.67 mmol, 90% yield). IR (neat) 3285, 1682, 1483, 1439, 1331, 1257, 1149, 1052 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$) δ 9.26 (m, 1H), 6.86 (dd, J = 3.8, 2.4 Hz, 1H), 6.55 (dd, J = 17.8, 11.2 Hz, 1H), 6.27 (dd, J = 3.7, 2.7 Hz, 1H), 5.57 (d, J = 17.9 Hz, 1H), 5.22 (d, J = 11.4 Hz, 1H), 3.86 (s, 1H); ^{13}C NMR: (125.8 MHz, $CDCl_3$) δ 161.6, 135.3, 126.3, 122.5, 116.3, 113.1, 109.7, 51.5; HRMS (EI) calculated for $[C_8H_9NO_2]^+$ requires *m/z* 151.0633, found *m/z* 151.0628.



Methyl 4,5-dihydro-1*H*-benzo[*g*]indole-2-carboxylate (6i) (Table 2, entry 10). Experiment 1: Prepared according to the General Procedure using 191 mg (0.75 mmol) of (*Z*)-methyl 2-azido-3-(3,4-dihydronaphthalen-2-yl)acrylate **5i**, 9.1 mg (0.0076 mmol) of $Ru(dtbbpy)_3(PF_6)_2$, 7.5 mL of chloroform, and an irradiation time of 4 h. Purified by flash column chromatography on silica using a solvent gradient (6:1 to 4:1 hexanes:EtOAc) to afford 164 mg (0.72 mmol, 96% yield) of the pyrrole as a white solid (mp = 145.3–147.0 °C). Experiment 2: 191 mg (0.75 mmol) of dienyl azide, 9.0 mg (0.0075 mmol) of $Ru(dtbbpy)_3(PF_6)_2$, and 7.5 mL of chloroform. Isolated 165 mg (0.73 mmol, 97% yield). IR (neat) 3303, 2844, 1686, 1448, 1300, 766 cm^{-1}. ^1H NMR: (499.8 MHz, $CDCl_3$) δ 9.75 (br s, 1H), 7.47 (m, 1H), 7.19 (m, 3H), 6.78 (d, J = 2.2 Hz, 1H), 3.90 (s, 3H), 2.94 (t, J = 7.1 Hz, 1H), 2.75 (t, J = 7.1 Hz, 1H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 162.2, 136.4, 133.0, 128.6, 128.1, 127.0, 126.7, 121.9, 121.8, 120.4, 114.4, 51.7, 29.8, 21.5; HRMS (EI) calculated for $[C_{14}H_{13}NO_2]^+$ requires *m/z* 227.0946, found *m/z* 227.0950.

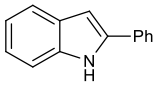


2-Phenyl-1*H*-pyrrole (6j) (Table 2, entry 11). Experiment 1: Prepared according to the General Procedure using 129 mg (0.75 mmol) of ((1*E*,3*E*)-4-azidobuta-1,3-dien-1-yl)benzene **5j**, 9.1 mg (0.0076 mmol) of $Ru(dtbbpy)_3(PF_6)_2$, 7.5 mL of chloroform, and an irradiation time of 3 h. Purified by flash column chromatography on silica using a solvent gradient (7:1 to 6:1 hexanes:EtOAc) to afford 100 mg (0.70 mmol, 93% yield) of the pyrrole as a white solid. Experiment 2: 128 mg (0.75 mmol) of dienyl azide, 9.0 mg (0.0075 mmol) of $Ru(dtbbpy)_3(PF_6)_2$, and 7.5 mL of chloroform. Isolated 97 mg (0.68 mmol, 90% yield). All spectral data were in complete agreement with a sample of commercially available material.

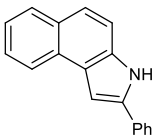


2-Octyl-1*H*-pyrrole (6k) (Table 2, entries 12-13). Experiment 1: Prepared according to the General Procedure using 156 mg (0.75 mmol) of (1*E*,3*E*)-1-azidododeca-1,3-diene **5k**, 9.0 mg (0.0075 mmol) of $Ru(dtbbpy)_3(PF_6)_2$, 7.5 mL of chloroform, and an irradiation time of 36 h. Purified by flash column chromatography on silica using a solvent gradient (10:1 to 8:1 hexanes:EtOAc) to afford 61 mg (0.34 mmol, 45% yield) of the pyrrole as a clear oil that turned yellow upon standing. Experiment 2: 156 mg (0.75 mmol) of dienyl azide, 9.2 mg (0.0077 mmol) of $Ru(dtbbpy)_3(PF_6)_2$, and 7.5 mL of chloroform. Isolated 66 mg (0.37 mmol, 49% yield). Experiment 3: Prepared according to the General Procedure using 156 mg (0.75 mmol) of (1*E*,3*E*)-1-azidododeca-1,3-diene **5k**, 8.4 mg (0.0075 mmol) of $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF_6)$, 7.5 mL of chloroform, and an irradiation time of 12 h. Purified by flash column chromatography on silica using a solvent gradient (10:1 to 8:1 hexanes:EtOAc) to afford 91 mg (0.51 mmol, 68% yield) of the pyrrole. Experiment 4: 156 mg (0.75 mmol) of dienyl azide, 8.3 mg (0.0074 mmol) of $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF_6)$, and 7.5 mL of chloroform. Isolated 95 mg (0.53 mmol, 71% yield). IR (neat) 3383, 2952, 2931, 2856, 1567, 1467, 1093 cm^{-1}. ^1H NMR: (500.2 MHz, $CDCl_3$)

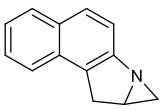
δ 7.89 (br s, 1H), 6.66 (dd, *J* = 2.7, 1.6 Hz, 1H), 6.13 (app dt, *J* = 3.0, 2.6 Hz, 1H), 5.91 (m, 1H), 2.59 (m, 2H), 1.62 (tt, *J* = 7.9, 6.7 Hz, 2H), 1.30 (m, 10H), 0.88 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 133.0, 116.0, 108.3, 104.9, 32.0, 29.8, 29.5, 29.5, 29.3, 27.8, 22.8, 14.2; HRMS (EI) calculated for $[C_{12}H_{21}N]^+$ requires *m/z* 179.1674, found *m/z* 179.1669.



2-Phenyl-1*H*-indole (6l) (Table 2, entry 14). Experiment 1: Prepared according to the General Procedure using 166 mg (0.75 mmol) of (*E*)-1-azido-2-styrylbenzene **5l**, 9.0 mg (0.0075 mmol) of $Ru(dtbbpy)_3(PF_6)_2$, 7.5 mL of chloroform, and an irradiation time of 20 h. Purified by flash column chromatography on silica (20:1 hexanes:EtOAc) to afford 107 mg (0.55 mmol, 74% yield) of the pyrrole as a white solid. Experiment 2: 166 mg (0.75 mmol) of dienyl azide, 9.0 mg (0.0075 mmol) of $Ru(dtbbpy)_3(PF_6)_2$, and 7.5 mL of chloroform. Isolated 110 mg (0.57 mmol, 76% yield). All spectral data were in complete agreement with previously reported values.[2]

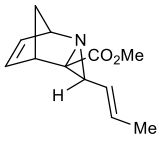


2-Phenyl-3*H*-benzo[*e*]indole (6m) (Table 2, entry 15). Experiment 1: Prepared according to the General Procedure using 204 mg (0.75 mmol) of (*E*)-2-azido-1-styrylnaphthalene **5m**, 9.1 mg (0.0076 mmol) of $Ru(dtbbpy)_3(PF_6)_2$, 7.5 mL of chloroform, and an irradiation time of 6 h. Purified by flash column chromatography on silica (9:1 hexanes:EtOAc) to afford 169 mg (0.69 mmol, 93% yield) of the pyrrole as a white solid (mp = 136.6–137.1 °C). Experiment 2: 204 mg (0.75 mmol) of dienyl azide, 9.0 mg (0.0075 mmol) of $Ru(dtbbpy)_3(PF_6)_2$, and 7.5 mL of chloroform. Isolated 167 mg (0.69 mmol, 92% yield). IR (neat) 3427, 3048, 1621, 1603, 1484, 1455, 1333, 1181, 1026 cm^{-1}. ^{1}H NMR: (500.0 MHz, $CDCl_3$) δ 8.65 (br s, 1H), 8.27 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.72 (m, 2H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.56 (m, 2H), 7.47 (m, 2H), 7.43 (td, *J* = 6.9, 1.0 Hz, 1H), 7.38 (d, *J* = 1.9 Hz, 1H), 7.32 (tt, *J* = 7.2, 1.2 Hz, 1H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 136.1, 133.2, 132.5, 129.4, 129.1, 128.6, 128.1, 127.4, 125.9, 124.9, 124.3, 123.6, 123.4, 123.0, 112.5, 99.3; HRMS (EI) calculated for $[C_{18}H_{14}N]^+$ requires *m/z* 244.1121, found *m/z* 244.1116.



8a,9-Dihydro-8*H*-azirino[1,2-*a*]benzo[*e*]indole (16). Prepared according to the General Procedure using 103 mg (0.49 mmol) of 1-allyl-2-azidonaphthalene (**15**), 5.5 mg (0.0049 mmol) of $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF_6)$, 4.9 mL of chloroform, and an irradiation time of 5 h. Purified by flash column chromatography on silica (3:2 hexanes:EtOAc) to afford 71 mg (0.39 mmol, 81% yield) of the aziridine as an off-white solid (mp = 78.4–80.8 °C). IR (neat) 3060, 3024, 2988, 2904, 2850, 1625, 1586, 1517, 1460, 1257, 1157 cm^{-1}. ^{1}H NMR: (500.0 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.3 Hz, 1H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.49 (d, *J* = 8.6 Hz, 1H), 7.47 (m, 1H), 7.39 (m, 1H), 3.69 (d, *J* = 16.8 Hz, 1H), 3.56 (dd, *J* = 16.8, 7.4 Hz, 1H), 3.18 (m, 1H), 2.46 (d, *J* = 5.3 Hz, 1H), 1.41 (d, *J* = 3.9 Hz, 1H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 155.7, 131.5, 131.3, 130.0, 128.6, 128.0, 126.3, 124.4, 123.5, 119.5, 41.2, 39.4, 31.7; HRMS (EI) calculated for $[C_{13}H_{11}N]^+$ requires *m/z* 181.0886, found *m/z* 181.0884.

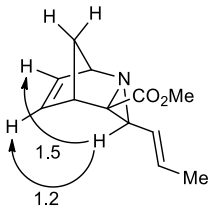
IV. Azirine trapping experiments

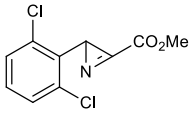


Methyl 3-((*E*)-prop-1-en-1-yl)-2-azatricyclo[3.2.1.0^{2,4}]oct-6-ene-4-carboxylate (7). To an oven-dried 25 mL Schlenk tube with a stir bar was added 41.8 mg (0.25 mmol) of (2*Z*,4*E*)-methyl 2-azidohexa-2,4-dienoate **1**, 16.5 mg (0.25 mmol) of freshly cracked cyclopentadiene, 3.0 mg (0.0025 mmol) of $Ru(dtbbpy)_3(PF_6)_2$, and 2.5 mL of CH_3CN. The solution was submitted to three freeze-pump-thaw cycles, purged with N_2, and irradiated at rt with a 1 W blue light-emitting diode (LED) strip (λ = 465–470 nm) for 150 min. Thereafter, the reaction was diluted with 1:1 hexanes:EtOAc (1 mL) and eluted through a short silica plug. The volatiles were removed *in vacuo*, and the residue was purified via flash column chromatography on silica (3:2 hexanes:EtOAc) to afford the title compound (36.1 mg, 0.176 mmol, 71% yield) as a clear oil. IR (neat) 3060, 3024, 2988, 2904, 2850, 1625, 1586, 1517, 1460, 1257, 1157 cm^{-1}. ^{1}H NMR: (500.0 MHz, $CDCl_3$) δ 6.19 (dd, *J* = 5.4, 2.4 Hz, 1H), 5.73 (m, 1H), 5.72 (dq, *J* = 16.0, 6.6 Hz, 1H), 5.47 (ddq, *J* = 16.0, 8.0, 1.6

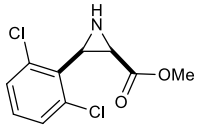
Hz, 1H), 4.20 (s, 1H), 3.78 (s, 3H), 3.53 (s, 1H), 2.09 (d, J = 8.1 Hz, 1H), 2.02 (dt, J = 8.1, 1.8 Hz, 1H), 1.69 (d, J = 8.1 Hz, 1H), 1.67 (dd, J = 6.6, 1.5 Hz, 1H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 172.3, 132.6, 130.4, 128.6, 126.3, 66.8, 58.9, 54.6, 52.4, 49.6, 47.4, 18.0; HRMS (EI) calculated for $[C_{12}H_{16}NO_2]^+$ requires *m/z* 206.1176, found *m/z* 206.1173.

The relative stereochemistry of **7** was determined using NOESY1D spectra – Varian's standard NOESY1D Chempack sequence was used with a typical setup as follows: mix=0.7·T1(shortest) ~ 1 s, d1=3·T1(longest) ~ 12 s, nt=16, ss=-2, selective pulse using a seduce shape. The numbers shown are % enhancements measured as ratios of integrals, normalized by number of protons involved, of the enhanced to selected protons.

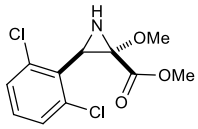




Methyl 2-(2,6-dichlorophenyl)-2*H*-azirine-3-carboxylate (9). Prepared according to the General Procedure using 204 mg (0.75 mmol) of vinyl azide **8**, 8.4 mg (0.0049 mmol) of $[Ir(dF(CF_3)ppy)_2(dtbbpy)](PF_6)$, 7.5 mL of chloroform, and an irradiation time of 8 h. Thereafter, the volatiles were removed *in vacuo* and the resulting residue was recrystallized from benzene/hexanes to afford 165 mg (0.68 mmol, 90% yield) of the azirine as an off-white solid. All spectral data were in complete agreement with previously reported values.[20]

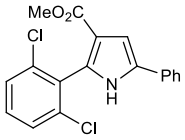


Methyl 3-(2,6-dichlorophenyl)aziridine-2-carboxylate (10). To a flame-dried 24 mL vial was added methyl 2-(2,6-dichlorophenyl)-2*H*-azirine-3-carboxylate **9** (120 mg, 0.492 mmol). The system was evacuated and purged with N_2 three times before adding CH_2Cl_2 (4.9 mL). The homogenous solution was cooled to –78 °C and subsequently a solution of Bu_4NBH_4 (127 mg, 0.492 mmol) in CH_2Cl_2 (4.9 mL) was added dropwise over 5 min. The reaction was stirred for an additional 30 min, after which ^{1}H NMR showed no remaining azirine. The reaction was warmed to 0 °C and H_2O (5 mL) was added to quench the reaction. The organic layer was separated and further extracted with H_2O (2 x 5 mL), washed with brine (1 x 5 mL), dried over Na_2SO_4, filtered, and the volatiles were removed *in vacuo* to afford 198 mg of a viscous yellow oil. The residue was dissolved in CH_2Cl_2 (2 mL) and eluted through a short plug of silica gel (4:1 hexanes:EtOAc). The volatiles were removed *in vacuo* and the resulting residue was purified via flash column chromatography on silica (5:1 hexanes:EtOAc) to afford the title compound (72 mg, 0.293 mmol, 58% yield) as a clear oil as a single diastereomer. IR (neat) 3282, 1723, 1546, 1132, 798 cm^{-1}. ^{1}H NMR: (500.0 MHz, $CDCl_3$) δ 7.29 (d, J = 8.0 Hz, 2H), 7.17 (t, J = 8.0 Hz, 1H), 3.65 (s, 3H), 3.27 (br s, 1H), 3.10 (br s, 1H), 2.02 (br s, 1H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 171.1, 136.0, 131.5, 129.4, 128.4, 52.6, 39.1, 36.9; HRMS (EI) calculated for $[C_{10}H_9Cl_2NO_2]^+$ requires *m/z* 245.0010, found *m/z* 245.0008. The relative stereochemistry was determined by performing a D_2O shake – the broad singlets at δ 3.27 and δ 3.10 resolved to δ 3.27 (dd, J = 9.6, 5.8 Hz, 1H), 3.10 (dd, J = 7.8, 5.8 Hz, 1H). The ^3J = 5.8 Hz coupling is consistent with a *cis* relationship of the aziridine ring protons.



Methyl 3-(2,6-dichlorophenyl)-2-methoxyaziridine-2-carboxylate (11). To a flame-dried 12 mL vial was added a solution of NaOMe (freshly prepared from 5.7 mg Na (0.25 mmol) in 1.23 mL MeOH). The solution was cooled to 0 °C and then THF (1.23 mL) was added. The solution was stirred for 5 min before adding methyl 2-(2,6-dichlorophenyl)-2*H*-azirine-3-carboxylate **9** (30 mg, 0.123 mmol) in a single portion. The reaction immediately turned light yellow and was stirred for 10 min, at which

time TLC analysis indicated complete consumption of the azirine. The reaction was quenched with H_2O (5 mL) and extracted into EtOAc (2 x 25 mL). The organic layers were combined and washed with brine (1 x 25 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give a clear residue that was purified was purified via flash column chromatography using a solvent gradient (4:1 to 2:1 hexanes:EtOAc) to afford the title product (31 mg, 0.11 mmol, 91% yield) as a clear oil as a single diastereomer. IR (neat) 3277, 1740, 1533, 1121, 777 cm^{-1}. ^1H NMR: (500.0 MHz, $CDCl_3$) δ 7.29 (d, J = 8.0 Hz, 2H), 7.17 (t, J = 8.0 Hz, 1H), 3.71 (s, 3H), 3.57 (s, 3H) 3.47 (d, J = 9.8 Hz, 1H), 2.61 (d, J = 9.7 Hz, 1H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 169.6, 135.6, 130.8, 129.5, 128.5, 73.9, 54.8, 53.3, 46.8; HRMS (EI) calculated for $[C_{11}H_{12}Cl_2NO_3]^+$ requires *m/z* 276.0189, found *m/z* 276.0194.



Methyl 2-(2,6-dichlorophenyl)-5-phenyl-1H-pyrrole-3-carboxylate (14). To a flame-dried 12 mL vial under N_2 was added methyl 2-(2,6-dichlorophenyl)-2*H*-azirine-3-carboxylate **9** (100 mg, 0.41 mmol) and 1-phenyl-2-(triphenyl-phosphanylidene)-ethanone (156 mg, 0.41 mmol) followed by CH_2Cl_2 (2.0 mL). The reaction was stirred at rt for 24 h after which the mixture was directly purified via flash column chromatography using a solvent gradient (5:1 to 2:1 hexanes:EtOAc) to afford the title product (82 mg, 0.24 mmol, 58% yield) as a white solid (mp = 161.6–163.1 °C). IR (neat) 3319, 2962, 1689, 1645, 1436, 1137 cm^{-1}. ^1H NMR: (500.0 MHz, $CDCl_3$) δ 8.54 (br s, 1H), 7.53 (d, J = 7.3 Hz, 2H), 7.42 (m, 4H), 7.30 (m, 2H), 7.04 (d, J = 3.0 Hz, 1H), 3.71 (s, 3H); ^{13}C NMR: (125.7 MHz, $CDCl_3$) δ 164.4, 136.6, 132.6, 131.4, 131.1, 131.0, 130.6, 129.1, 127.9, 127.3, 124.1, 116.3, 107.4, 51.2; HRMS (EI) calculated for $[C_{18}H_{14}Cl_2NO_2]^+$ requires *m/z* 346.0397, found *m/z* 346.0409.

V. References

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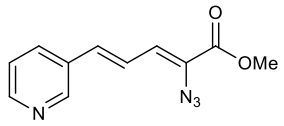
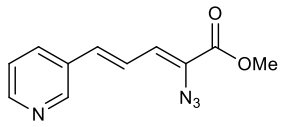
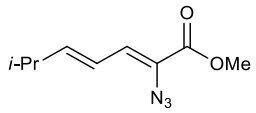
(2*Z*,4*E*)-methyl 2-azido-5-(pyridin-3-yl)penta-2,4-dienoate (**5e**)
^{1}H NMR (500.2 MHz, $CDCl_3$)



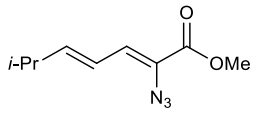
(2*Z*,4*E*)-methyl 2-azido-5-(pyridin-3-yl)penta-2,4-dienoate (**5e**)
^{13}C NMR (125.8 MHz, $CDCl_3$)



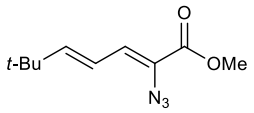
(2*Z*,4*E*)-methyl 2-azido-6-methylhepta-2,4-dienoate (**5f**)
^{1}H NMR (500.2 MHz, $CDCl_3$)



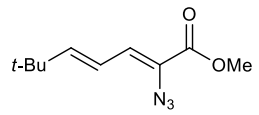
(2*Z*,4*E*)-methyl 2-azido-6-methylhepta-2,4-dienoate (**5f**)
^{13}C NMR (125.8 MHz, $CDCl_3$)



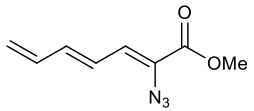
(2*Z*,4*E*)-methyl 2-azido-6,6-dimethylhepta-2,4-dienoate (**5g**)
^{1}H NMR (500.2 MHz, $CDCl_3$)



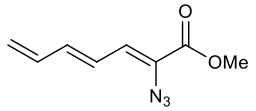
(2*Z*,4*E*)-methyl 2-azido-6,6-dimethylhepta-2,4-dienoate (**5g**)
^{13}C NMR (125.8 MHz, $CDCl_3$)



(2*Z*,4*E*)-methyl 2-azidohepta-2,4,6-trienoate (**5h**)
^{1}H NMR (499.8 MHz, C_6D_6)

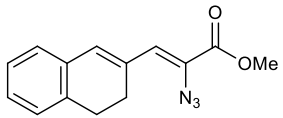


(2*Z*,4*E*)-methyl 2-azidohepta-2,4,6-trienoate (**5h**)
^{13}C NMR (125.7 MHz, C_6D_6)

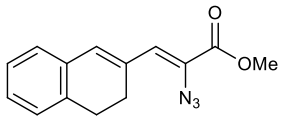


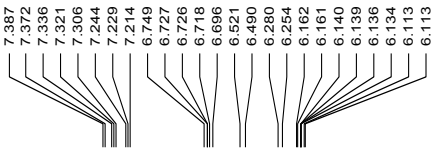
(*Z*)-methyl 2-azido-3-(3,4-dihydronaphthalen-2-yl)acrylate (**5i**)

^{1}H NMR (499.8 MHz, $CDCl_3$)

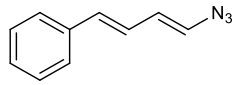


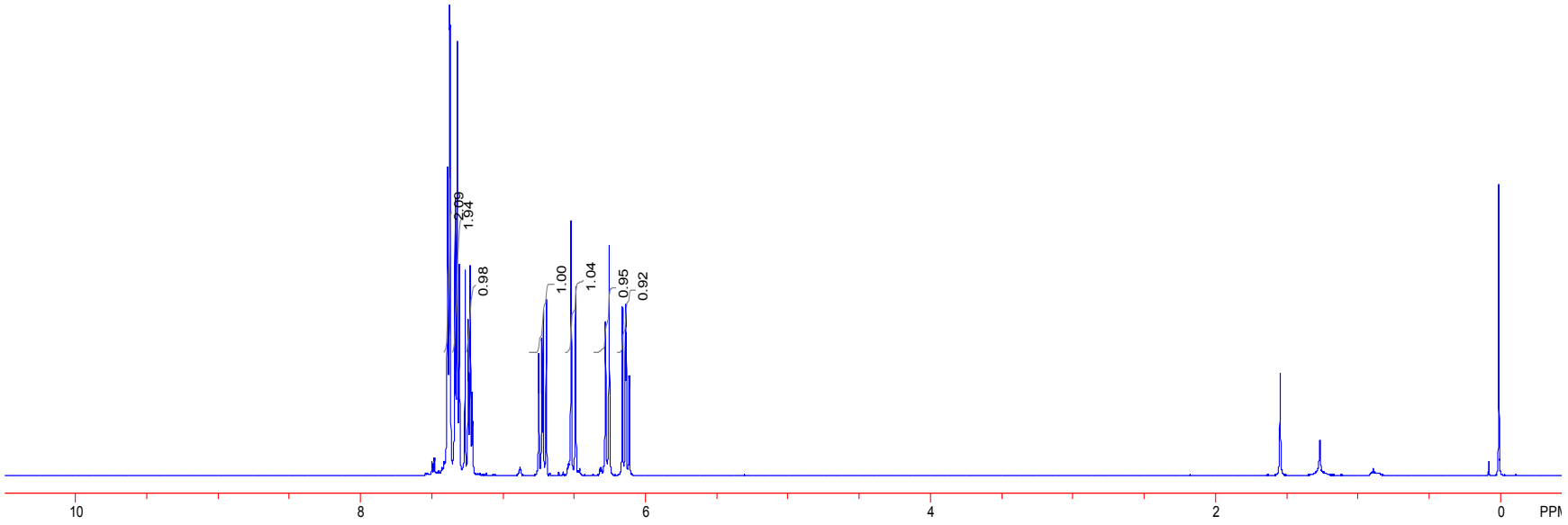
(*Z*)-methyl 2-azido-3-(3,4-dihydronaphthalen-2-yl)acrylate (**5i**)
^{13}C NMR (125.7 MHz, $CDCl_3$)



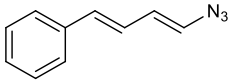


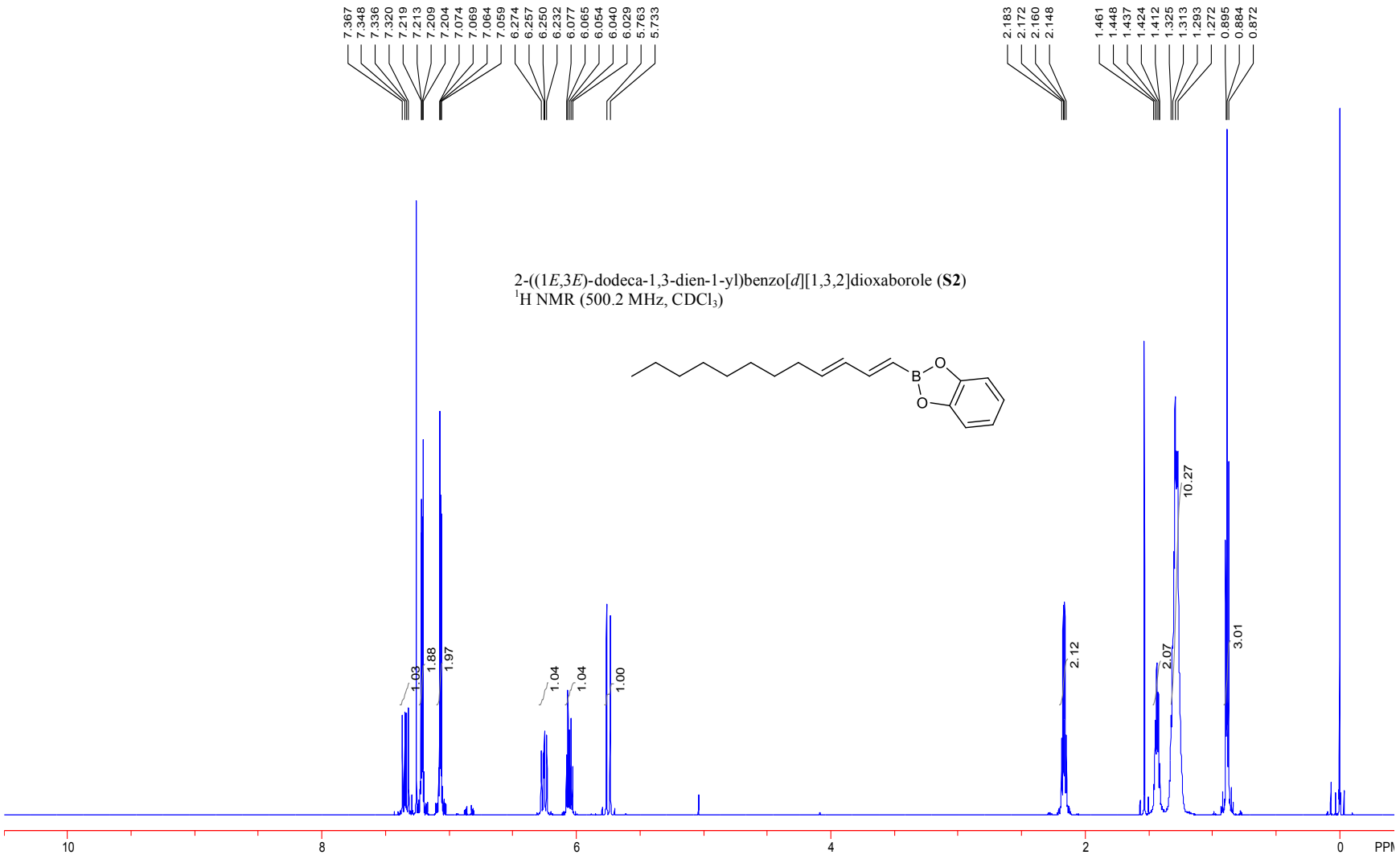
((1*E*,3*E*)-4-azidobuta-1,3-dien-1-yl)benzene (**5j**)
^{1}H NMR (500.2 MHz, $CDCl_3$)



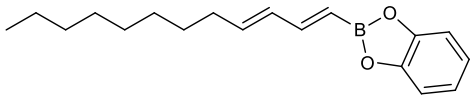


((1*E*,3*E*)-4-azidobuta-1,3-dien-1-yl)benzene (**5j**)
^{13}C NMR (125.8 MHz, $CDCl_3$)

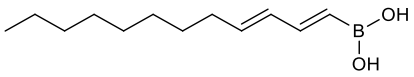



7.367
7.348
7.336
7.320
7.219
7.213
7.209
7.204
7.074
7.069
7.064
7.059
6.274
6.257
6.250
6.232
6.077
6.065
6.054
6.040
6.029
5.763
5.733
2.183
2.172
2.160
2.148
1.461
1.448
1.437
1.424
1.412
1.325
1.313
1.293
1.272
0.895
0.884
0.872
2-((1E,3E)-dodeca-1,3-dien-1-yl)benzo[d][1,3,2]dioxaborole (S2)
1H NMR (500.2 MHz, CDCl3)
B
O
O
1.03
1.88
1.97
1.04
1.04
1.00
2.12
2.07
10.27
3.01
10
8
6
4
2
0
PPM

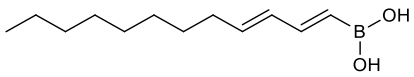
2-((1*E*,3*E*)-dodeca-1,3-dien-1-yl)benzo[*d*][1,3,2]dioxaborole (**S2**)
^{13}C NMR (125.8 MHz, $CDCl_3$)



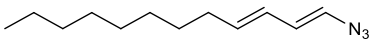
(1*E*,3*E*)-dodeca-1,3-dien-1-ylboronic acid (**S3**)
^{1}H NMR (500.2 MHz, $(CD_3)_2CO$)

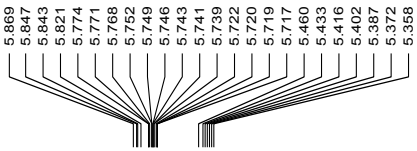


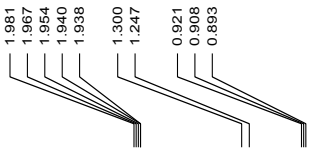
(1*E*,3*E*)-dodeca-1,3-dien-1-ylboronic acid (**S3**)
^{13}C NMR (125.8 MHz, $(CD_3)_2CO$



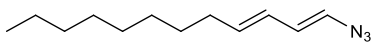
(1*E*,3*E*)-1-azidododeca-1,3-diene (**5k**)
^{1}H NMR (499.8 MHz, C_6D_6)



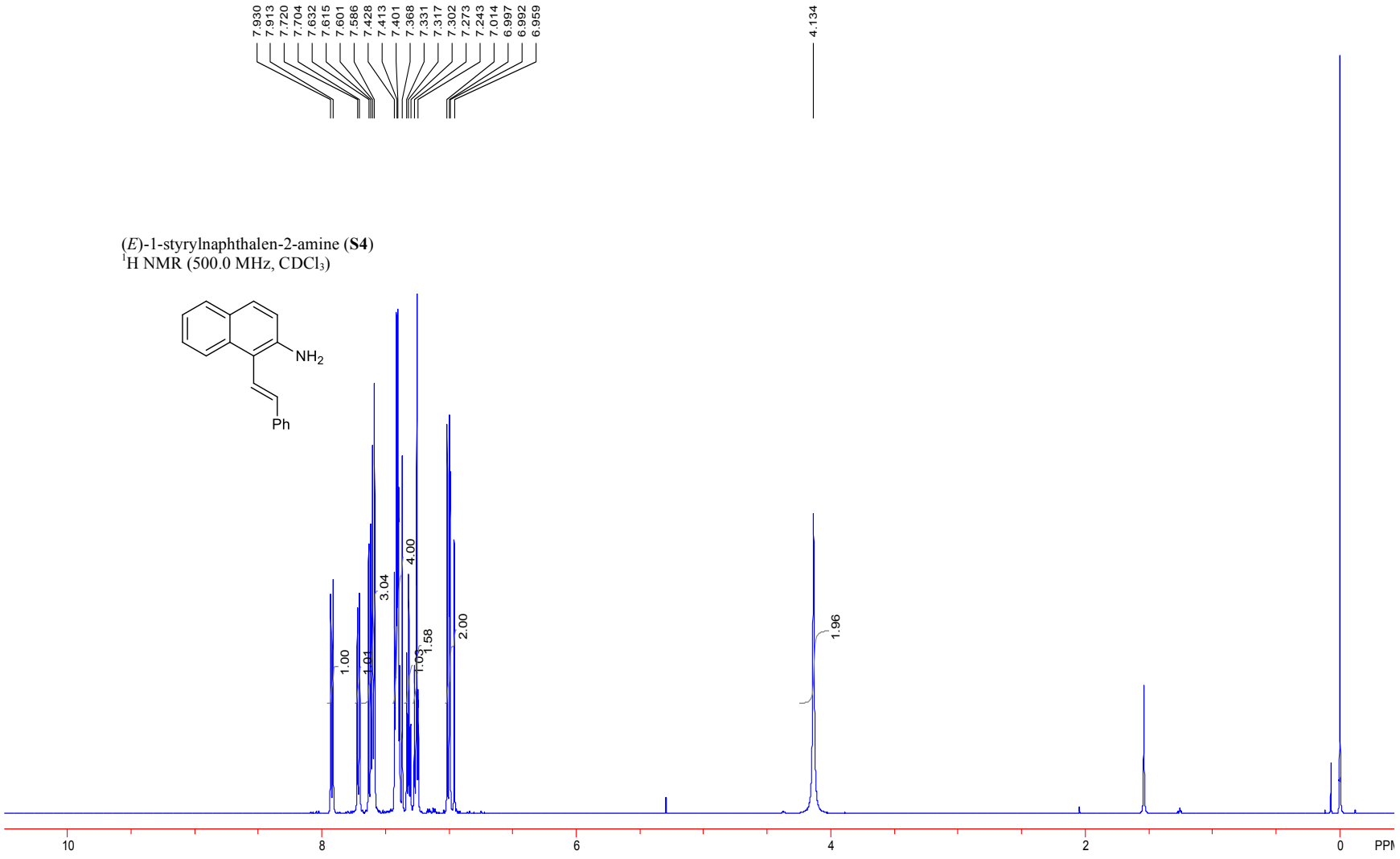




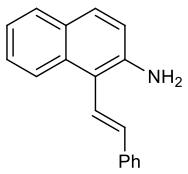
(1*E*,3*E*)-1-azidododeca-1,3-diene (**5k**)
^{13}C NMR (125.7 MHz, C_6D_6)

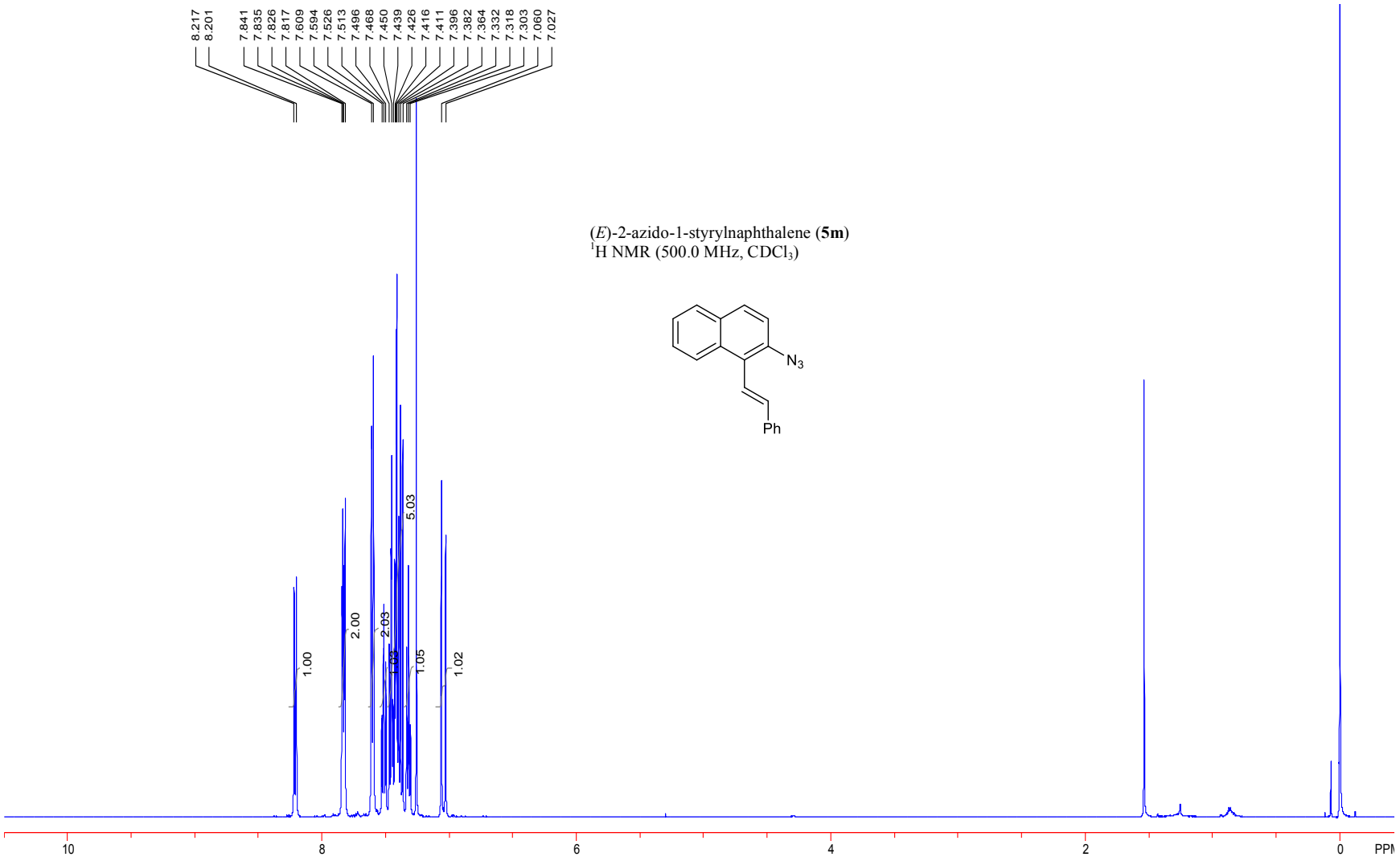


(*E*)-1-styrylnaphthalen-2-amine (**S4**)
^{1}H NMR (500.0 MHz, $CDCl_3$)



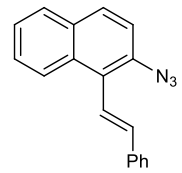
(*E*)-1-styrylnaphthalen-2-amine (**S4**)
^{13}C NMR (125.7 MHz, $CDCl_3$)



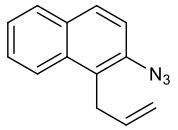


(*E*)-2-azido-1-styrylnaphthalene (**5m**)
^{1}H NMR (500.0 MHz, $CDCl_3$)

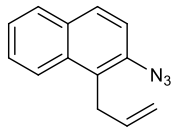
(*E*)-2-azido-1-styrylnaphthalene (**5m**)
^{13}C NMR (125.7 MHz, $CDCl_3$)

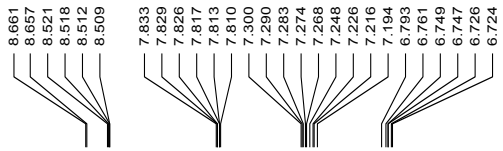


1-allyl-2-azidonaphthalene (**15**)
^{1}H NMR (500.0 MHz, $CDCl_3$)

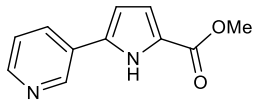


1-allyl-2-azidonaphthalene (**15**)
^{13}C NMR (125.7 MHz, $CDCl_3$)

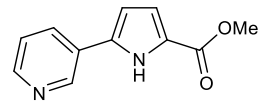




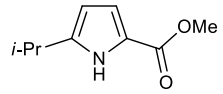
Methyl 5-(pyridin-3-yl)-1*H*-pyrrole-2-carboxylate (**6e**)
^{1}H NMR (500.2 MHz, $CDCl_3$)



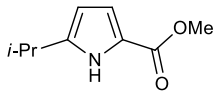
Methyl 5-(pyridin-3-yl)-1*H*-pyrrole-2-carboxylate (**6e**)
^{13}C NMR (125.8 MHz, $CDCl_3$)



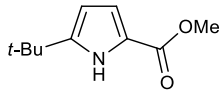
Methyl 5-isopropyl-1*H*-pyrrole-2-carboxylate (**6f**)
^{1}H NMR (500.2 MHz, $CDCl_3$)



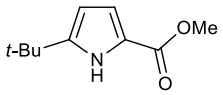
Methyl 5-isopropyl-1*H*-pyrrole-2-carboxylate (**6f**)
^{13}C NMR (125.8 MHz, $CDCl_3$)



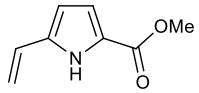
Methyl 5-(*tert*-butyl)-1*H*-pyrrole-2-carboxylate (**6g**)
^{1}H NMR (500.2 MHz, $CDCl_3$)



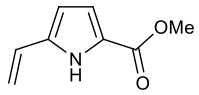
Methyl 5-(*tert*-butyl)-1*H*-pyrrole-2-carboxylate (**6g**)
^{13}C NMR (125.8 MHz, $CDCl_3$)



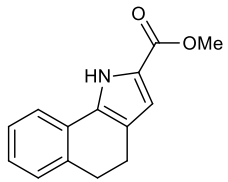
Methyl 5-vinyl-1*H*-pyrrole-2-carboxylate (**6h**)
^{1}H NMR (500.2 MHz, $CDCl_3$)



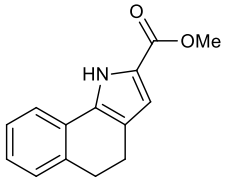
Methyl 5-vinyl-1*H*-pyrrole-2-carboxylate (**6h**)
^{13}C NMR (125.8 MHz, $CDCl_3$)

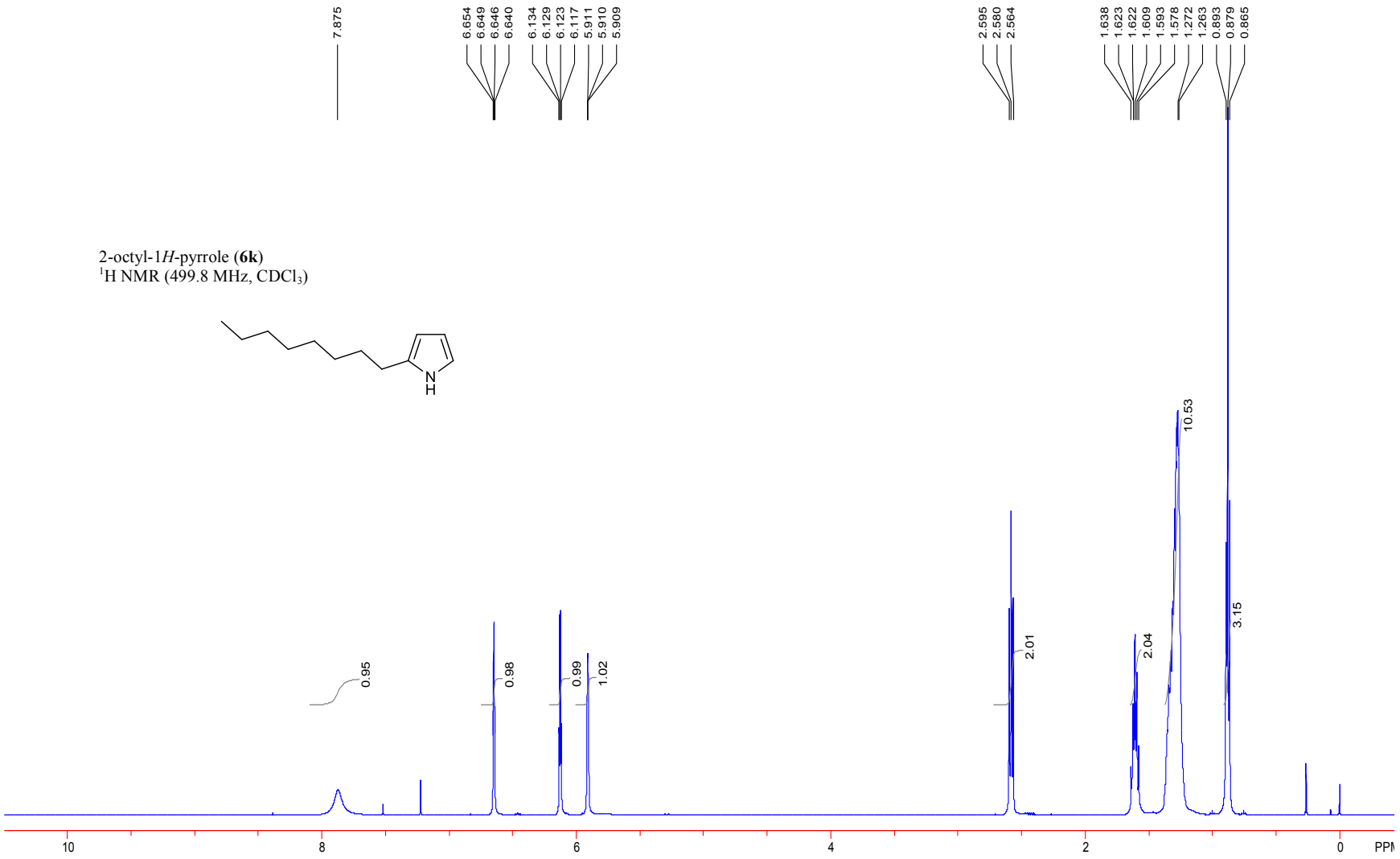


Methyl 4,5-dihydro-1*H*-benzo[*g*]indole-2-carboxylate (**6i**)
^{1}H NMR (500.2 MHz, $CDCl_3$)



Methyl 4,5-dihydro-1*H*-benzo[*g*]indole-2-carboxylate (**6i**)
^{13}C NMR (125.7 MHz, $CDCl_3$)

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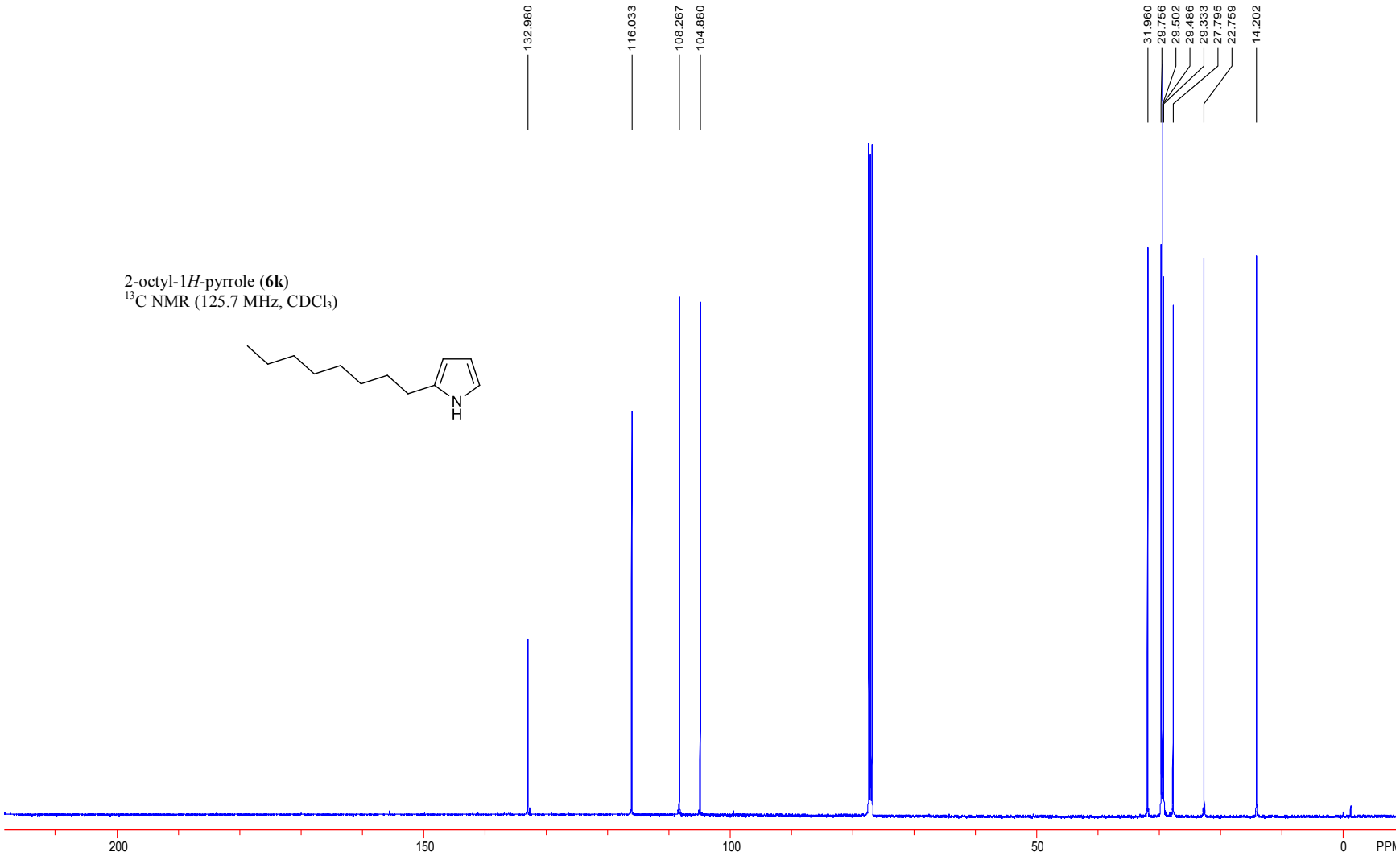
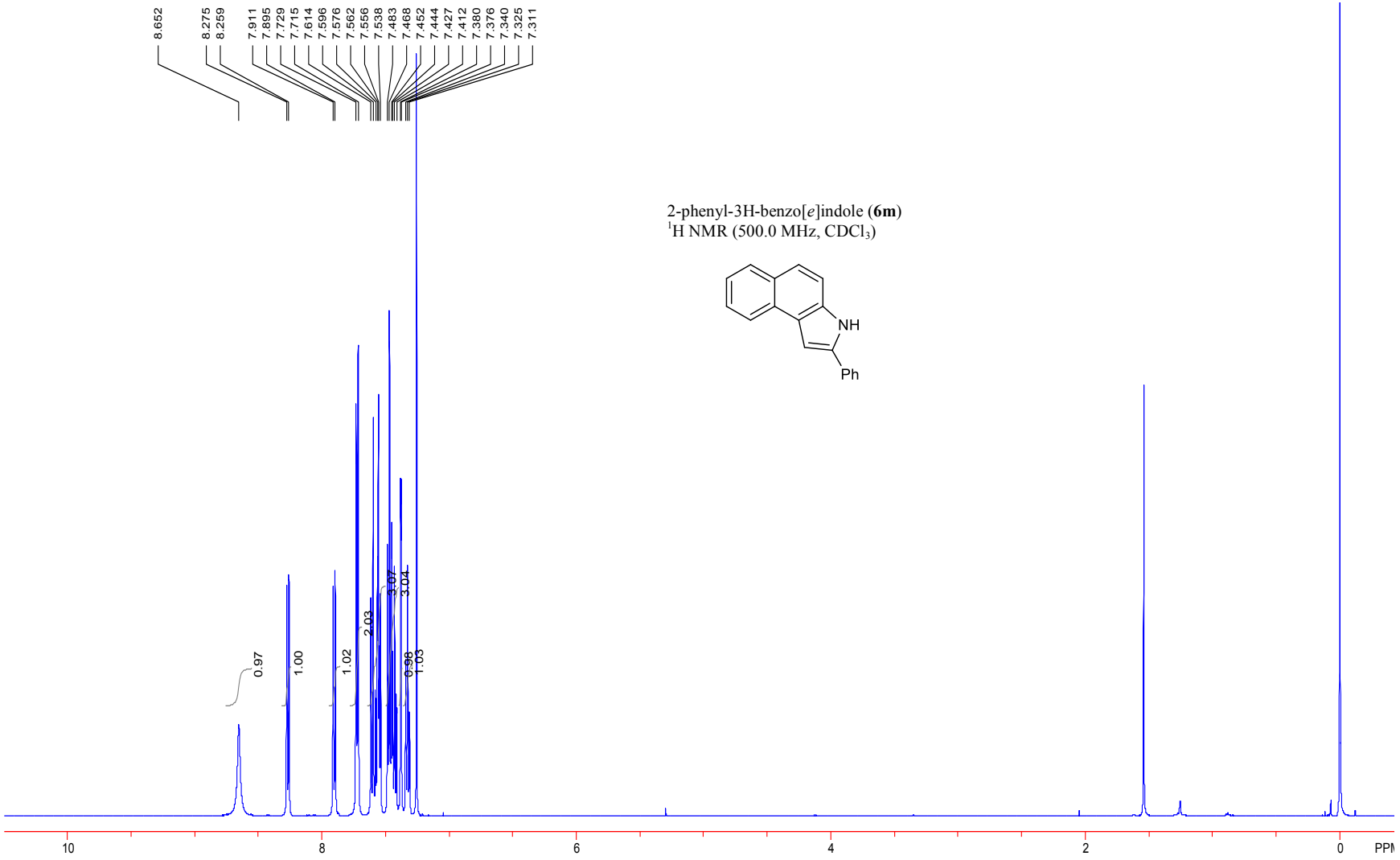
6.649
6.646
6.640
6.134
6.129
6.123
6.117
5.911
5.910
5.909
2.595
2.580
2.564
1.638
1.623
1.622
1.609
1.593
1.578
1.272
1.263
0.893
0.879
0.865
2-octyl-1H-pyrrole (6k)
1H NMR (499.8 MHz, CDCl3)
N
H
0.95
0.98
0.99
1.02
2.01
2.04
10.53
3.15
10
8
6
4
2
0
PPM

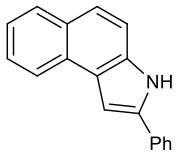

132.980
116.033
108.267
104.880
31.960
29.756
29.502
29.486
29.333
27.795
22.759
14.202
2-octyl-1*H*-pyrrole (**6k**)
^{13}C NMR (125.7 MHz, $CDCl_3$)
N
H
200
150
100
50
0
PPM

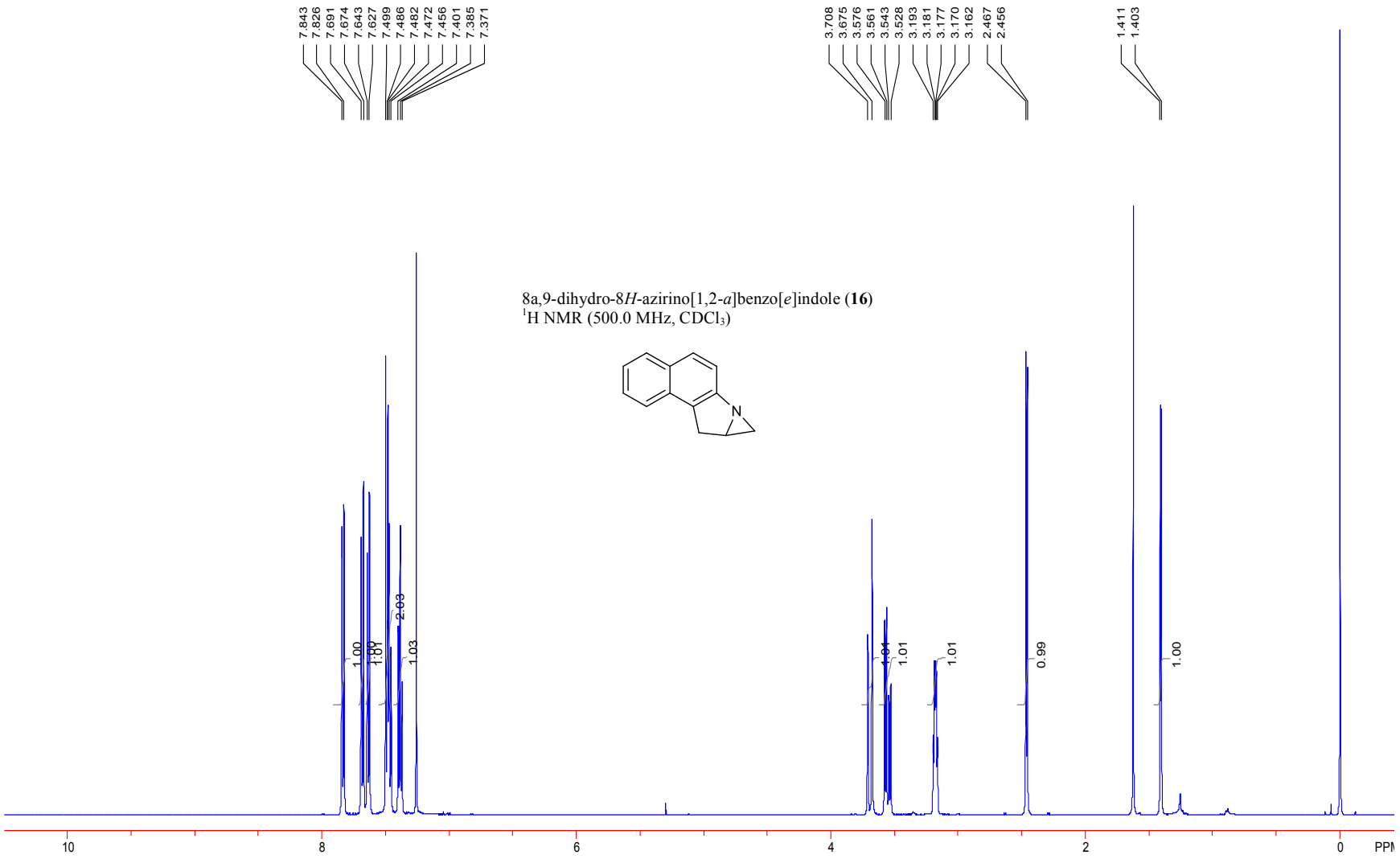


2-phenyl-3H-benzo[*e*]indole (**6m**)

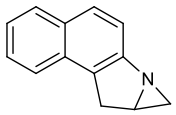
^{1}H NMR (500.0 MHz, $CDCl_3$)

2-phenyl-3H-benzo[*e*]indole (**6m**)
^{13}C NMR (125.7 MHz, $CDCl_3$)

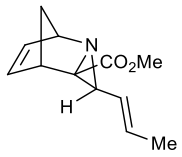



7.843
7.826
7.691
7.674
7.643
7.627
7.499
7.486
7.482
7.472
7.456
7.401
7.385
7.371
3.708
3.675
3.576
3.561
3.543
3.528
3.193
3.181
3.177
3.170
3.162
2.467
2.456
1.411
1.403
8a,9-dihydro-8H-azirino[1,2-a]benzo[e]indole (16)
1H NMR (500.0 MHz, CDCl3)
N
1.00
1.80
2.03
1.03
1.01
1.01
1.01
0.99
1.00
10
8
6
4
2
0
PPM

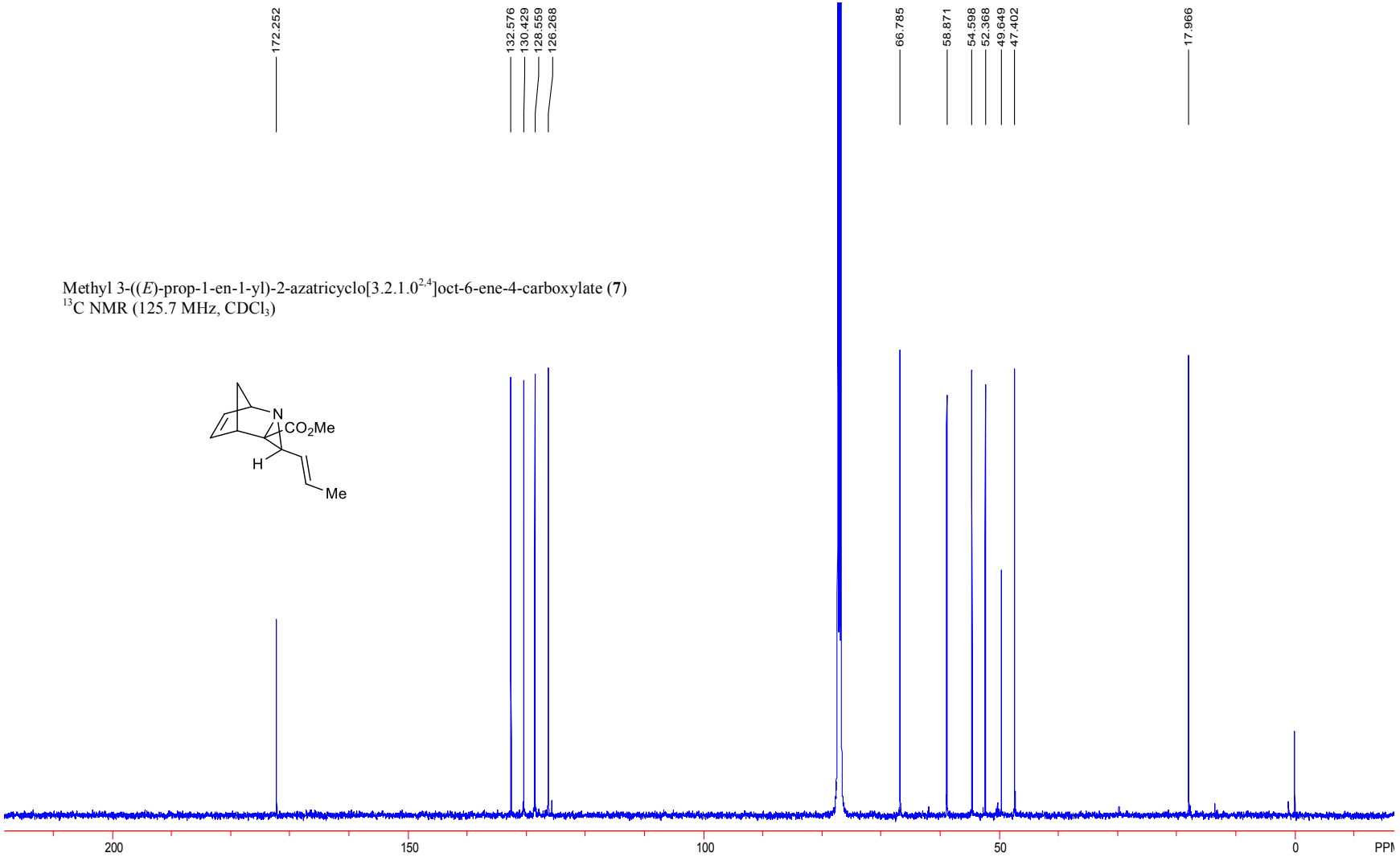
8a,9-dihydro-8*H*-azirino[1,2-*a*]benzo[*e*]indole (**16**)
^{13}C NMR (125.7 MHz, $CDCl_3$)



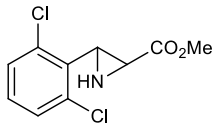
Methyl 3-((*E*)-prop-1-en-1-yl)-2-azatricyclo[3.2.1.0^{2,4}]oct-6-ene-4-carboxylate (**7**)
^{1}H NMR (500.0 MHz, $CDCl_3$)



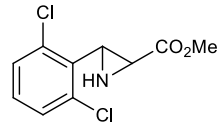
Methyl 3-((*E*)-prop-1-en-1-yl)-2-azatricyclo[3.2.1.0^{2,4}]oct-6-ene-4-carboxylate (**7**)
^{13}C NMR (125.7 MHz, $CDCl_3$)



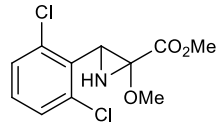
Methyl 3-(2,6-dichlorophenyl)aziridine-2-carboxylate (**10**)
^{1}H NMR (500.0 MHz, $CDCl_3$)



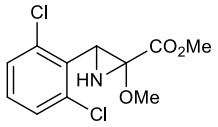
Methyl 3-(2,6-dichlorophenyl)aziridine-2-carboxylate (**10**)
^{13}C NMR (125.7MHz, $CDCl_3$)

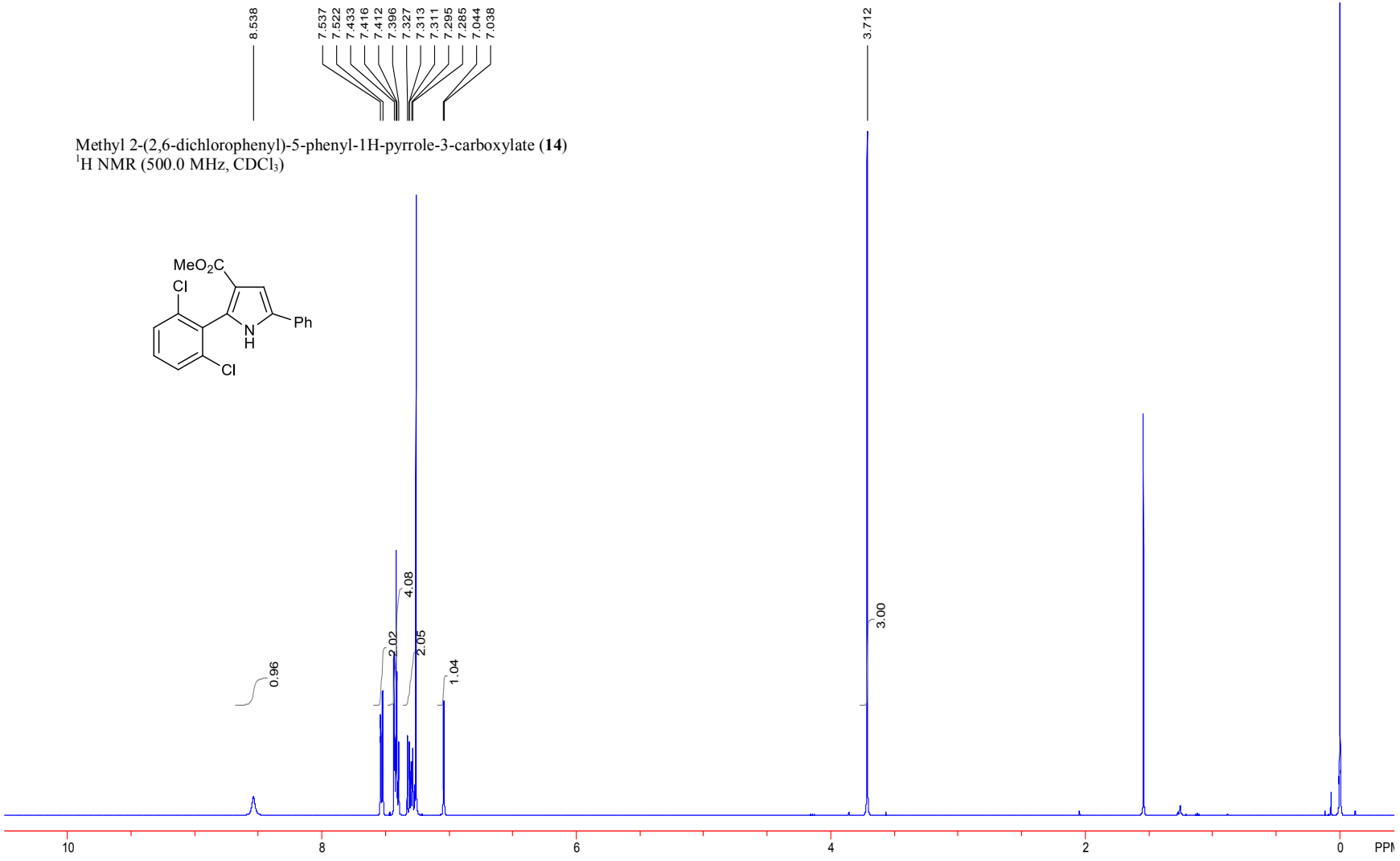


Methyl 3-(2,6-dichlorophenyl)-2-methoxyaziridine-2-carboxylate (**11**)
^{1}H NMR (500.0 MHz, $CDCl_3$)



Methyl 3-(2,6-dichlorophenyl)-2-methoxyaziridine-2-carboxylate (**11**)
^{13}C NMR (125.7 MHz, $CDCl_3$)





Methyl 2-(2,6-dichlorophenyl)-5-phenyl-1H-pyrrole-3-carboxylate (**14**)
^{1}H NMR (500.0 MHz, $CDCl_3$)

Methyl 2-(2,6-dichlorophenyl)-5-phenyl-1H-pyrrole-3-carboxylate (**14**)
^{13}C NMR (125.7 MHz, $CDCl_3$)