

Palladium-catalyzed Dearomative Trimethylenemethane Cycloaddition Reactions

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1. Experimental Part

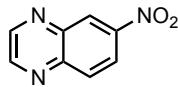
A. General Methods

Air and/or moisture sensitive reactions were carried out under an argon atmosphere in oven-dried glassware and with anhydrous solvents. All compounds were purchased from commercial sources unless otherwise noted and used without further purification. Solvents were freshly distilled (1,4-dioxane and toluene over sodium) or dried by passing through an alumina column. $\text{Pd}(\text{dba})_2$,¹ $\text{CpPd}(\eta^3\text{-C}_3\text{H}_5)$,² **L1**,³ **L3**,⁴ **L4**,³ and **L5**⁴ were prepared according to known literature procedures. **L2** is commercially available. TMM donors **1b**⁵ and **1c**⁶ have been prepared as previously described.

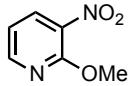
Thin layer chromatography was carried out on glass plates coated with silica gel SiO_2 60 F254 from Merck; visualization with a UV lamp (254 nm) or by staining with a *p*-anisaldehyde or potassium permanganate solution. Flash chromatography was performed with silica gel SiO_2 60 (0.040–0.063 μm , 230–400 mesh), technical solvents, and a head pressure of 0.2–0.4 bar. Melting points (m.p.) were measured on a Thomas Hoover capillary melting point apparatus in open capillaries and are uncorrected. Optical rotations ($[\alpha]^{20}_D$) were measured on a Jasco DIP-1000 digital polarimeter using 5 cm glass cells (1 mL) with a sodium 589 nm filter at ambient temperature and indicated concentrations in chloroform (c , g cm^{-3}). Proton (^1H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectroscopy was performed on a Mercury NMR instrument at 400 MHz (^1H) or 100 MHz (^{13}C) and on a Unity NMR spectrometer at 500 MHz (^1H) or 125 MHz (^{13}C). Chemical shifts are reported in ppm relative to the residual protiated solvent (CDCl_3 : $\delta_{\text{H}} = 7.26$ ppm, $\delta_{\text{C}} = 77.16$ ppm). All ^{13}C NMR spectra are proton decoupled. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet), and br (broad). Infrared spectroscopic (IR) data were recorded on sodium chloride plates neat or as thin films on a Perkin-Elmer Paragon 500 FT-IR spectrometer. Absorption bands are reported in wavenumbers ($\tilde{\nu}$, cm^{-1}) in the range of 4000–600 cm^{-1} . Chiral HPLC analysis was performed on an Agilent Technologies 1200 Series instrument using Chiralcel® columns (IA or IB) eluting with heptane/isopropanol mixtures, flow rates, and wavelengths (λ) as indicated. Retention times (t_{R}) for both enantiomers are reported in minutes. High-resolution mass spectrometry (HRMS) was measured on a Bruker micrOTOF-Q II electrospray ionization (ESI) mass spectrometer by the Vincent Coates Foundation Mass Spectrometry Laboratory at Stanford University. Mass peaks are reported in m/z units.

B. Nitroarene TMM Acceptors

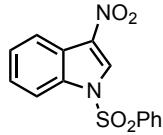
The following compounds were prepared according to known literature procedures:



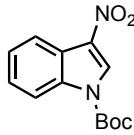
6-nitroquinoxaline,⁷



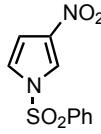
2-methoxy-3-nitropyridine,⁸



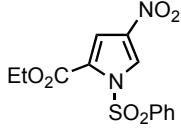
3-nitro-1-(phenylsulfonyl)-1H-indole,⁹



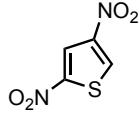
tert-butyl 3-nitro-1H-indole-1-carboxylate,¹⁰



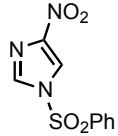
3-nitro-1-(phenylsulfonyl)-1H-pyrrole,¹¹



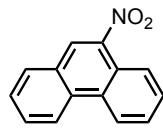
ethyl 4-nitro-1-(phenylsulfonyl)-1H-pyrrole-2-carboxylate,¹¹



2,4-dinitrothiophene,¹²



4-nitro-1-(phenylsulfonyl)-1H-imidazole,¹³ and

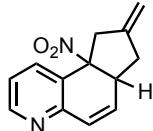


9-nitrophenanthrene.¹⁴

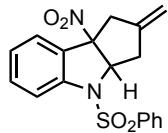
C. Dearomative TMM Cycloaddition Reactions and Functionalizations

General procedure for the dearomative cycloaddition reaction with nitroarenes. To an argon-purged, oven-dried vial containing the nitroarene (0.1 mmol), the ligand, and the palladium precatalyst, freshly distilled toluene (0.5 M, 0.2 mL) was added, and the vial was sealed. The solution was stirred at room temperature for 5 min prior to the addition of the TMM donor via microsyringe and then stirred at the indicated temperature for the stated time. The mixture was concentrated and directly purified by flash chromatography.

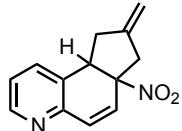
All cycloadducts were isolated as single regioisomers. In cases where diastereoselectivity (dr) was of concern, the dr was determined by analysis of the ¹H NMR spectra of the crude reaction mixture (after concentration and before purification by flash chromatography). The minor diastereoisomers were separated by flash chromatography and not isolated.



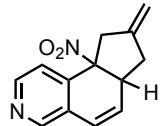
8-Methylene-9a-nitro-7,8,9,9a-tetrahydro-6aH-cyclopenta[f]quinolone (2). The reaction was performed with 5-nitroquinoline (17 mg, 0.100 mmol), **L2** (5.4 mg, 0.010 mmol), Pd(db₂) (2.9 mg, 0.005 mmol), and donor **1a** (32 mg, 0.170 mmol) at 25 °C for 15 h. Purification by flash chromatography (hexanes/Et₂O 3:1 to 2:1) gave the product (22 mg, 98%) as a colorless oil. Slow decomposition of the product was observed upon storage at room temperature. *R*_f = 0.38 (hexanes/Et₂O 1:2); ¹H NMR (400 MHz, CDCl₃): δ = 8.56 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.69–7.72 (m, 1H), 7.23 (dd, *J* = 8.0, 4.8 Hz, 1H), 6.67–6.70 (m, 1H), 6.30 (dd, *J* = 10.0, 4.4 Hz, 1H), 4.98 (p, *J* = 2.0 Hz, 1H), 4.93 (p, *J* = 2.1 Hz, 1H), 3.87–3.92 (m, 1H), 3.57–3.64 (m, 1H), 3.21–3.27 (m, 1H), 2.87–2.95 (m, 1H), 2.25–2.33 ppm (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 151.3, 150.6, 143.3, 134.8, 134.3, 128.0, 125.8, 123.0, 108.6, 96.4, 44.8, 44.5, 38.6 ppm; IR (thin film): $\tilde{\nu}$ = 3442, 2921, 1660, 1565, 1538, 1442, 1346, 1016, 885, 845, 796 cm⁻¹; HRMS (ESI⁺) calcd for [M+H]⁺ C₁₃H₁₃N₂O₂⁺ 229.0972, found 229.0977.



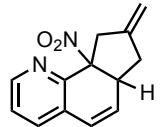
2-Methylene-8b-nitro-4-phenylsulfonyl-1, 2, 3, 3a, 4, 8b-hexahydrocyclopenta[b]indole (5). The reaction was performed with 3-nitro-1-(phenylsulfonyl)-1*H*-indole (30 mg, 0.100 mmol), **L2** (5.4 mg, 0.010 mmol), Pd(dba)₂ (2.9 mg, 0.005 mmol), and donor **1a** (32 mg, 0.170 mmol) at 25 °C for 22 h. Purification by flash chromatography (hexanes/EtOAc 9:1) gave the product (35 mg, quant) as an off white solid. M.p. = 156–157 °C; ¹H NMR (500 MHz, CDCl₃): δ = 7.73–7.78 (m, 3H), 7.56 (tt, *J* = 6.6, 1.2 Hz, 1H), 7.40–7.44 (m, 4H), 7.15 (dt, *J* = 7.8, 1.0 Hz, 1H), 5.28 (dd, *J* = 9.0, 4.6 Hz, 1H), 4.95 (t, *J* = 1.7 Hz, 1H), 4.88 (t, *J* = 1.7 Hz, 1H), 3.33 (d, *J* = 15.9 Hz, 1H), 3.23 (dd, *J* = 16.4, 9.0 Hz, 1H), 3.07 (d, *J* = 16.1 Hz, 1H), 2.72–2.78 ppm (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 142.8, 142.5, 136.7, 133.7, 132.0, 129.2, 128.2, 127.1, 125.6, 125.1, 115.9, 110.8, 98.9, 69.8, 44.7, 41.8 ppm; IR (neat); $\tilde{\nu}$ = 1546, 1358, 1171, 1093 cm⁻¹; chiral HPLC: Chiralcel® IA, heptane/isopropanol 95:5, 0.8 mL/min, λ = 254 nm, *t*_R = 12.326, *t*_R = 14.927, 66% ee; HRMS (ESI⁺) calcd for [M+Na]⁺ C₁₈H₁₆N₂NaO₄S⁺ 379.0723, found 379.0716.



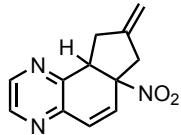
8-Methylene-9a-nitro-7,8,9,9a-tetrahydro-6a*H*-cyclopenta[f]quinolone (6). The reaction was performed with 6-nitroquinoline (17 mg, 0.100 mmol), **L2** (5.4 mg, 0.010 mmol), Pd(dba)₂ (2.9 mg, 0.005 mmol), and donor **1a** (32 mg, 0.170 mmol) at 25 °C for 2 h. Purification by flash chromatography (hexanes/EtOAc 3:2) gave the product (18 mg, 77%, purity 85%) as a white foam. Slow decomposition of the product was observed upon storage in the freezer. ¹H NMR (500 MHz, CDCl₃): δ = 8.48 (dd, *J* = 4.9, 1.6 Hz, 1H), 7.48–7.51 (m, 1H), 7.16 (dd, *J* = 7.6, 4.9 Hz, 1H), 6.97 (dd, *J* = 9.7, 0.5 Hz, 1H), 6.24 (dd, *J* = 9.8, 1.5 Hz, 1H), 4.98 (dt, *J* = 4.6, 2.2 Hz, 1H), 4.96 (dt, *J* = 4.3, 2.2 Hz, 1H), 4.21 (ddd, *J* = 11.0, 9.3, 1.6 Hz, 1H), 3.41 (dq, *J* = 16.8, 0.8 Hz, 1H), 3.12 (dd, *J* = 16.8, 0.8 Hz, 1H), 2.99 (ddq, *J* = 16.4, 9.2, 1.5 Hz, 1H), 2.34–2.37 ppm (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ = 148.6, 148.5, 143.1, 135.0, 134.2, 131.0, 128.6, 123.2, 108.5, 90.8, 46.4, 45.8, 41.0 ppm; IR (neat); $\tilde{\nu}$ = 3056, 2920, 1540, 1347 cm⁻¹; HRMS (ESI⁺) calcd for [M+H]⁺ C₁₃H₁₃N₂O₂⁺ 229.0972, found 229.0975.



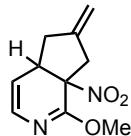
8-Methylene-9a-nitro-7,8,9,9a-tetrahydro-6aH-cyclopenta[f]isoquinoline (7). The reaction was performed with 5-nitroisoquinoline (17 mg, 0.100 mmol), **L2** (5.4 mg, 0.010 mmol), Pd(dba)₂ (2.9 mg, 0.005 mmol), and donor **1a** (32 mg, 0.170 mmol) at 25 °C for 15 h. Purification by flash chromatography (hexanes/Et₂O 3:1 to 1:1) gave the product (17 mg, 74%) as a colorless oil. *R*_f = 0.23 (hexanes/Et₂O 1:3); ¹H NMR (500 MHz, CDCl₃): δ = 8.54 (d, *J* = 5.1 Hz, 1H), 8.53 (s, 1H), 7.23 (d, *J* = 5.1 Hz, 1H), 6.53–6.55 (m, 1H), 6.08 (dd, *J* = 9.7, 4.2 Hz, 1H), 5.00 (p, *J* = 2.3 Hz, 1H), 4.95 (p, *J* = 2.3 Hz, 1H), 3.87–3.91 (m, 1H), 3.63 (d, *J* = 17.6 Hz, 1H), 3.10–3.14 (m, 1H), 2.84–2.90 (m, 1H), 2.30–2.35 ppm (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ = 150.0, 148.4, 143.2, 138.1, 131.9, 127.4, 122.6, 120.5, 108.7, 96.1, 44.8, 44.3, 38.3 ppm; IR (thin film): $\tilde{\nu}$ = 2998, 2880, 1640, 1565, 1521, 1469, 1397, 1367, 1333, 1267, 1364, 1049, 951, 880, 828, 786, 709 cm⁻¹; HRMS (ESI⁺) calcd for [M+H]⁺ C₁₃H₁₃N₂O₂⁺ 229.0972, found 229.0968.



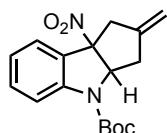
8-Methylene-9a-nitro-7,8,9,9a-tetrahydro-6aH-cyclopenta[h]quinolone (8). The reaction was performed with 8-nitroquinoline (17 mg, 0.100 mmol), **L2** (5.4 mg, 0.010 mmol), Pd(dba)₂ (2.9 mg, 0.005 mmol), and donor **1a** (32 mg, 0.170 mmol) at 25 °C for 15 h. Purification by flash chromatography (hexanes/Et₂O 1:1) gave the product (18 mg, 81%) as a colorless oil. *R*_f = 0.56 (hexanes/Et₂O 1:3); ¹H NMR (400 MHz, CDCl₃): δ = 8.50–8.52 (m, 1H), 7.47–7.50 (m, 1H), 7.28–7.31 (m, 1H), 6.45–6.48 (m, 1H), 6.09 (dd, *J* = 9.7, 4.8 Hz, 1H), 5.00 (p, *J* = 2.2 Hz, 1H), 4.93 (p, *J* = 2.3 Hz, 1H), 3.81–3.87 (m, 1H), 3.62–3.73 (m, 2H), 2.78–2.94 (m, 1H), 2.18–2.26 ppm (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ = 149.0, 148.7, 144.3, 134.5, 130.7, 128.5, 124.8, 124.6, 108.0, 96.8, 46.9, 42.7, 39.1 ppm; IR (thin film): $\tilde{\nu}$ = 3008, 2878, 1638, 1520, 1416, 1333, 1048, 875, 836, 808, 718 cm⁻¹; HRMS (ESI⁺) calcd for [M+H]⁺ C₁₃H₁₃N₂O₂⁺ 229.0972, found 229.0973.



8-Methylene-6a-nitro-7,8,9,9a-tetrahydro-6aH-cyclopenta[f]quinoxaline (9). The reaction was performed with 6-nitroquinoxaline (18 mg, 0.100 mmol), **L2** (5.4 mg, 0.010 mmol), Pd(dba)₂ (2.9 mg, 0.005 mmol), and donor **1a** (32 mg, 0.170 mmol) at 25 °C for 15 h. Purification by flash chromatography (hexanes/Et₂O 2:1) gave the product (14 mg, 61%) as a yellow oil. *R*_f = 0.31 (hexanes/Et₂O 1:2); ¹H NMR (400 MHz, CDCl₃): δ = 8.43 (dd, *J* = 2.6, 0.5 Hz, 1H), 8.38 (d, *J* = 2.6 Hz, 1H), 6.93 (d, *J* = 9.8 Hz, 1H), 6.38 (dd, *J* = 9.8, 1.2 Hz, 1H), 5.00 (dp, *J* = 6.8, 2.2 Hz, 2H), 4.41 (t, *J* = 9.7 Hz, 1H), 3.48 (dq, *J* = 16.7, 2.4 Hz, 1H), 3.16 (ddq, *J* = 16.6, 9.5, 1.8 Hz, 1H), 3.05–3.10 (m, 1H), 2.53–2.62 ppm (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ = 152.1, 144.4, 143.4, 143.3, 142.8, 132.4, 130.7, 109.2, 92.9, 48.2, 46.6, 39.2 ppm; IR (thin film): $\tilde{\nu}$ = 3010, 2882, 2812, 1640, 1521, 1400, 1364, 1328, 1243, 1164, 1127, 1051, 1001, 947, 881, 847, 817, 783, 731 cm⁻¹; HRMS (ESI⁺) calcd for [M+H]⁺ C₁₂H₁₂N₃O₂⁺ 230.0924, found 230.0929.

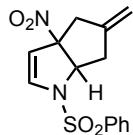


1-Methoxy-6-methylene-7a-nitro-5,6,7,7a-tetrahydro-4aH-cyclopenta[c]pyridine (10). The reaction was performed with 2-methoxy-3-nitropyridine (15 mg, 0.100 mmol), **L2** (5.4 mg, 0.010 mmol), Pd(dba)₂ (2.9 mg, 0.005 mmol), and donor **1a** (32 mg, 0.170 mmol) at 60 °C for 15 h. Purification by flash chromatography (hexanes/Et₂O 10:1) gave the product (14 mg, 68%) as a colorless oil. *R*_f = 0.39 (hexanes/Et₂O 3:1); ¹H NMR (500 MHz, CDCl₃): δ = 6.53 (dd, *J* = 7.2, 1.6 Hz, 1H), 5.37 (dd, *J* = 7.2, 4.5 Hz, 1H), 5.01 (p, *J* = 2.2 Hz, 1H), 4.97 (p, *J* = 2.1 Hz, 1H), 3.86 (s, 3H), 3.46–3.55 (m, 2H), 3.14–3.18 (m, 1H), 2.81 (ddq, *J* = 16.5, 8.8, 1.9 Hz, 1H), 2.21–2.27 ppm (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ = 158.6, 143.3, 132.1, 114.2, 108.5, 92.3, 54.8, 45.6, 41.2, 38.7 ppm; IR (thin film): $\tilde{\nu}$ = 2885, 2814, 1627, 1582, 1530, 1440, 1336, 1170, 1067, 687 cm⁻¹; HRMS (ESI⁺) calcd for [M+H]⁺ C₁₀H₁₃N₂O₃⁺ 209.0921, found 209.0924.

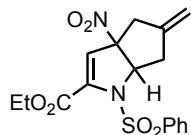


tert-Butyl-2-methylene-8b-nitro-1,3,3a,8b-tetrahydrocyclopenta[b]indole-4-(2H)-carboxylate (11). The reaction was performed with *tert*-butyl 3-nitro-1*H*-indole-1-carboxylate (26 mg, 0.100 mmol), **L2**

(5.4 mg, 0.010 mmol), Pd(dba)₂ (2.9 mg, 0.005 mmol), and donor **1a** (32 mg, 0.170 mmol) at 25 °C for 1 h. Purification by flash chromatography (hexanes/EtOAc 9:1) gave the product (31 mg, quant) as a colorless oil. ¹H NMR (500 MHz, CDCl₃): δ = 7.89–7.94 (br, 1H), 7.46–7.49 (m, 1 H), 7.37 (t, J = 7.5 Hz, 1H), 7.07 (t, J = 7.5 Hz, 1H), 5.35–5.41 (br, 1H), 4.89 (s, 2H), 3.48 (d, J = 15.7 Hz, 1H), 3.05–3.25 (m, 2H), 2.48 (d, J = 16.1 Hz, 1H), 1.59 ppm (s, 9H); ¹³C NMR (125 MHz, CDCl₃): δ = 143.6, 131.7, 125.0, 123.2, 115.4, 110.3, 81.8, 81.7, 67.7, 45.1, 41.0, 40.98, 28.3 ppm; IR (neat): $\tilde{\nu}$ = 1710, 1646, 1389, 1166 cm⁻¹; HRMS (ESI⁺) calcd for [M+Na]⁺ C₁₇H₂₀N₂NaO₄⁺ 339.1315, found 339.1310.

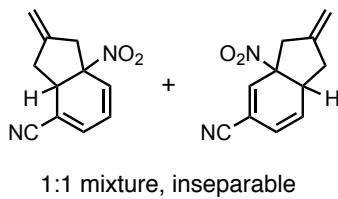


5-Methylene-3a-nitro-1-phenylsulfonyl-1,3a,4,5,6,6a-hexahydrocyclopenta[b]pyrrole (12). The reaction was performed with 3-nitro-1-(phenylsulfonyl)-1*H*-pyrrole (25 mg, 0.100 mmol), **L2** (5.4 mg, 0.010 mmol), Pd(dba)₂ (2.9 mg, 0.005 mmol), and donor **1a** (32 mg, 0.170 mmol) at 25 °C for 17 h. Purification by flash chromatography (hexanes/EtOAc) gave the product (28 mg, 92%) as an orange oil. ¹H NMR (500 MHz, CDCl₃): δ = 7.75–7.79 (m, 2H), 7.62–7.66 (m, 1H), 7.52–7.56 (m, 2H), 6.70 (d, J = 4.0 Hz, 1H), 5.31 (d, J = 4.0 Hz, 1H), 5.02 (s, 1H), 4.95 (s, 1H), 4.67 (dd, J = 8.5, 3.3 Hz, 1H), 3.01–3.08 (m, 2H), 2.80 (d, J = 15.7 Hz, 1H), 2.70–2.74 ppm (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ = 143.4, 136.3, 135.7, 133.8, 129.4, 127.3, 111.0, 109.9, 103.2, 67.4, 44.3, 40.9 ppm; IR (neat): $\tilde{\nu}$ = 3104, 2921, 1544, 1359, 1171 cm⁻¹; HRMS (ESI⁺) calcd for [M+Na]⁺ C₁₄H₁₄N₂NaO₄S⁺ 329.0566, found 329.0561.

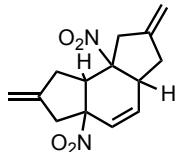


Ethyl 5-methylene-3a-nitro-1-(phenylsulfonyl)-1,3a,4,5,6,6a-hexahydrocyclopenta[b]pyrrole-2-carboxylate (13). The reaction was performed with ethyl 4-nitro-1-(phenylsulfonyl)-1*H*-pyrrole-2-carboxylate (32 mg, 0.100 mmol), **L2** (5.4 mg, 0.010 mmol), Pd(dba)₂ (2.9 mg, 0.005 mmol), and donor **1a** (32 mg, 0.170 mmol) at 25 °C for 17 h. Purification by flash chromatography (hexanes/EtOAc) gave the product (32 mg, 85%) as a pale yellow oil. ¹H NMR (500 MHz, CDCl₃): δ = 7.78 (dd, J = 8.3, 1.0 Hz, 2H), 7.64–7.67 (m, 1H), 7.53 (t, J = 7.8 Hz, 2H), 5.88 (s, 1H), 5.03 (t, J = 1.6 Hz, 1H), 4.94 (t, J = 1.5 Hz, 1H), 4.89 (dd, J = 9.1, 4.5 Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H), 3.11 (dd, J = 16.2, 9.1 Hz, 1H), 2.98 (d, J = 15.9 Hz, 1H), 2.80 (d, J = 15.9 Hz, 1H), 2.65 (ddd, J = 16.3, 4.3, 1.2 Hz, 1H), 1.38 ppm (d, J = 14.3 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ = 160.7, 142.3, 141.5, 135.1, 134.1, 129.4, 127.9,

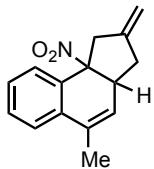
117.7, 111.2, 99.9, 69.0, 62.6, 44.4, 40.9, 14.0 ppm; IR (neat): $\tilde{\nu}$ = 3059, 1714, 1525, 1347, 1156 cm^{-1} ; HRMS (ESI $^+$) calcd for $[M-\text{HNO}_2]^+$ $\text{C}_{17}\text{H}_{18}\text{NO}_4\text{S}^+$ 332.0951, found 332.0947.



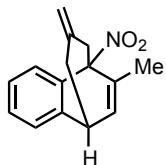
2-Methylene-7a-nitro-2,3,3a,7a-tetrahydro-1H-indene-4-carbonitrile and 2-methylene-3a-nitro-2,3,3a,7a-tetrahydro-1H-indene-5-carbonitrile (16). The reaction was performed with 3-nitrobenzonitrile (15 mg, 0.100 mmol), **L2** (5.4 mg, 0.010 mmol), $\text{Pd}(\text{dba})_2$ (2.9 mg, 0.005 mmol), and donor **1a** (32 mg, 0.170 mmol) at 25 $^\circ\text{C}$ for 15 h. Purification by preparative TLC (hexanes/EtOAc 4:1) gave the product (14 mg, 67%, 1:1 mixture of regioisomers) as a pale yellow oil. ^1H NMR (500 MHz, CDCl_3): δ = 5.72 (dd, J = 9.8, 2.9 Hz), 5.41 (ddd, J = 9.8, 2.5, 1.3 Hz), 4.88–5.02 (m), 3.61–3.63 (m), 3.38–3.45 (m), 3.05–3.13 (m), 2.92–2.98 (m), 2.75 (dt, J = 16.0, 1.3 Hz), 2.44–2.50 (m), 2.33–2.37 (m), 2.15–2.21 ppm (m); ^{13}C NMR (125 MHz, CDCl_3): δ = 143.6, 142.9, 133.6, 122.8, 121.8, 109.87, 109.67, 98.7, 46.3, 42.8, 40.0, 37.6, 36.9, 36.5, 33.5 ppm; IR (neat): $\tilde{\nu}$ = 2877, 2326, 1517, 1406 cm^{-1} .



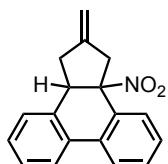
2,7-Dimethylene-3a,8a-dinitro-1,2,3,3a,5a,6,7,8,8a,8b-decahydro-as-indacene (17). The reaction was performed with 1,3-dinitrobenzene (17 mg, 0.100 mmol), **L2** (5.4 mg, 0.010 mmol), $\text{Pd}(\text{dba})_2$ (2.9 mg, 0.005 mmol), and donor **1a** (45 mg, 0.240 mmol) at 25 $^\circ\text{C}$ for 15 h. Purification by flash chromatography (hexanes/EtOAc) gave the product (23 mg, 84%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ = 5.87–5.95 (m, 2H), 4.89–4.97 (m, 4H), 4.10–4.15 (m, 1H), 3.64–3.68 (m, 1H), 3.22–3.28 (m, 1H), 2.88–3.02 (m, 3H), 2.61–2.69 (m, 1H), 2.50–2.57 (m, 1H), 2.37–2.42 (m, 1H), 2.23–2.32 ppm (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ = 143.4, 141.6, 135.2, 122.6, 109.9, 109.8, 98.0, 91.4, 48.3, 45.4, 42.3, 38.0, 36.2, 34.0 ppm; IR (neat): $\tilde{\nu}$ = 2921, 1663, 1539 cm^{-1} ; HRMS (ESI $^+$) calcd for $[M+\text{H}]^+$ $\text{C}_{14}\text{H}_{17}\text{N}_2\text{O}_4^+$ 277.1183, found 277.1186.



5-Methyl-2-methylene-9b-nitro-2,3,3a,9b-tetrahydro-1H-cyclopenta[a]naphthalene (18b). The reaction was performed with 4-methyl-1-nitronaphthalene (19 mg, 0.100 mmol), **L2** (5.4 mg, 0.010 mmol), Pd(dba)₂ (2.9 mg, 0.005 mmol), and donor **1a** (32 mg, 0.170 mmol) at 25 °C for 15 h. Purification by flash chromatography (hexanes/EtOAc) gave the product (19 mg, 80%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃): δ = 7.32–7.44 (m, 4H), 5.81 (dt, *J* = 2.9, 1.4 Hz, 1H), 4.96 (dt, *J* = 3.5, 2.0 Hz, 2H), 3.78–3.83 (m, 1H), 3.60–3.64 (m, 1H), 3.23 (dd, *J* = 17.4, 1.7 Hz, 1H), 2.79–2.85 (m, 1H), 2.26–2.32 (m, 1H), 2.12 ppm (t, *J* = 1.6 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ = 144.5, 133.8, 130.5, 129.6, 128.0, 126.4, 124.2, 107.7, 97.4, 44.6, 44.4, 38.4, 19.5 ppm; IR (neat): $\tilde{\nu}$ = 3072, 2921, 1539, 1351 cm⁻¹; HRMS (ESI⁺) calcd for [M+H]⁺ C₁₅H₁₆NO₂⁺ 242.1175, found 242.1173.

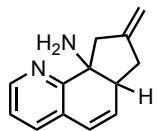


11-Methyl-7-methylene-5-nitro-6,7,8,9-tetrahydro-5H-5,9-ethenobenzo[7]annulene (19b). The reaction was performed with 2-methyl-1-nitronaphthalene (19 mg, 0.100 mmol), **L2** (5.4 mg, 0.010 mmol), Pd(dba)₂ (2.9 mg, 0.005 mmol), and donor **1a** (32 mg, 0.170 mmol) at 25 °C for 15 h. Purification by flash chromatography (hexanes/EtOAc) gave the product (20 mg, 81%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃): δ = 7.17–7.27 (m, 4H), 6.90–6.91 (m, 1H), 6.25 (dq, *J* = 6.7, 1.5 Hz, 1H), 4.65 (s, 1H), 4.60 (s, 1H), 3.64 (ddd, *J* = 6.9, 4.2, 3.0 Hz, 1H), 3.01 (q, *J* = 16.5 Hz, 2H), 2.36–2.39 (m, 1H), 2.29 (dd, *J* = 14.2, 4.5 Hz, 1H), 1.86 ppm (d, *J* = 1.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ = 141.1, 139.3, 138.1, 137.3, 129.1, 127.7, 126.5, 124.9, 122.0, 118.0, 94.5, 41.3, 39.0, 37.1, 16.9 ppm; IR (neat): $\tilde{\nu}$ = 2895, 1521, 1335, 888 cm⁻¹; HRMS (ESI⁺) calcd for [M+H]⁺ C₁₅H₁₆NO₂⁺ 242.1175, found 242.1173.



2-Methylene-3a-nitro-2,3,3a,11b-tetrahydro-1H-cyclopenta[1]phenanthrene (20). The reaction was performed with 9-nitrophenanthrene (22 mg, 0.100 mmol), **L2** (5.4 mg, 0.010 mmol), Pd(dba)₂ (2.9 mg,

0.005 mmol), and donor **1a** (32 mg, 0.170 mmol) at 25 °C for 15 h. Purification by flash chromatography (hexanes/EtOAc) gave the product (26 mg, 92%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃): δ = 7.91–7.93 (m, 1H), 7.83 (dd, J = 7.8, 0.4 Hz, 1H), 7.66 (dd, J = 7.8, 1.3 Hz, 1H), 7.47–7.50 (m, 1H), 7.40 (td, J = 7.6, 1.2 Hz, 1H), 7.24–7.35 (m, 3H), 4.94–4.96 (m, 1H), 4.80–4.82 (m, 1H), 4.15 (dd, J = 11.9, 8.8 Hz, 1H), 3.62–3.65 (m, 1H), 3.58 (dq, J = 16.5, 2.5 Hz, 1H), 2.85–2.90 (m, 1H), 2.12–2.19 ppm (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ = 143.2, 134.4, 134.1, 130.61, 130.47, 129.0, 128.54, 128.47, 128.45, 128.37, 128.0, 124.28, 124.24, 108.4, 92.8, 48.4, 44.8, 39.5 ppm; IR (neat): $\tilde{\nu}$ = 3072, 2922, 1540, 1349 cm⁻¹; HRMS (ESI⁺) for the corresponding amine calcd [M+H]⁺ C₁₈H₁₈N⁺ 248.1434, found 248.1434.

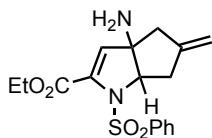


8-Methylene-7,8,9,9a-tetrahydro-6aH-cyclopenta[*h*]quinolin-9a-amine (21). A suspension of the cycloadduct (0.35 g, 0.15 mmol) in methanol (2.0 mL) and concentrated HCl (0.25 mL) was carefully treated with zinc dust (0.40 g, 6.13 mmol) at 0 °C. The suspension was stirred at 0 °C for 10 min and warmed to 25 °C. A saturated aqueous NaHCO₃ solution was slowly added. The mixture was filtered through celite, eluting with EtOAc. The filtrate was dried over Na₂SO₄, filtered, and evaporated. Purification by flash chromatography (CH₂Cl₂/methanol 20:1) gave the product (0.29 g, 96%) as a yellow oil. R_f = 0.14 (CH₂Cl₂/methanol 10:1); ¹H NMR (400 MHz, CDCl₃): δ = 8.41 (dd, J = 5.3, 1.5 Hz, 1H), 7.66 (dd, J = 7.7, 1.5 Hz, 1H), 7.48 (dd, J = 7.8, 5.3 Hz, 1H), 6.45 (dd, J = 9.8, 2.8 Hz, 1H), 5.93 (dd, J = 9.8, 2.3 Hz, 1H), 5.18 (br s, 2H), 3.31–3.38 (m, 2H), 3.07–3.14 (m, 1H), 2.92–2.97 (m, 2H), 2.71–2.78 ppm (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 155.6, 145.6, 143.4, 137.1, 136.2, 128.9, 125.4, 123.5, 111.4, 64.8, 48.4, 45.2, 36.9 ppm; IR (thin film): $\tilde{\nu}$ = 3417, 2883, 1616, 1558, 1427, 1359, 1145, 1106, 1041, 898, 813, 766, 723, 638 cm⁻¹; HRMS (ESI⁺) calcd for [M+H]⁺ C₁₃H₁₅N₂⁺ 199.1230, found 199.1232.

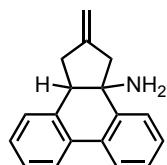


2-Methylene-4-(phenylsulfonyl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-8b-amine (22). A suspension of the cycloadduct (50 mg, 0.14 mmol) in methanol (1.4 mL) and concentrated HCl (0.3 mL) was carefully treated with zinc dust (376 mg, 5.61 mmol) at 0 °C. The suspension was stirred at 0 °C for 5 min and warmed to 25 °C. A saturated aqueous NaHCO₃ solution was slowly added. The mixture was

filtered through celite, eluting with EtOAc. The filtrate was dried over MgSO_4 , filtered, and evaporated. Purification by flash chromatography ($\text{CH}_2\text{Cl}_2/\text{methanol}$ 95:5) gave the product (48 mg, quant) as a white solid. ^1H NMR (400 MHz, CDCl_3): δ = 7.74–7.77 (m, 2H), 7.67–7.69 (m, 1H), 7.51–7.56 (m, 1H), 7.40–7.45 (m, 2H), 7.25–7.30 (m, 1H), 7.18 (ddd, J = 7.6, 1.4, 0.6 Hz, 1H), 7.10 (td, J = 7.4, 1.0 Hz, 1H), 4.74–4.79 (m, 2H), 4.12 (dd, J = 8.6, 3.9 Hz, 1H), 3.05–3.12 (m, 1H), 2.66 (ddd, J = 15.6, 5.0, 1.4 Hz, 2H), 2.53–2.56 (m, 1H), 1.16 ppm (s, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ = 146.4, 140.8, 137.8, 137.3, 133.3, 129.2, 129.0, 127.1, 125.0, 123.8, 116.1, 108.4, 75.3, 68.7, 47.3, 41.6 ppm; IR (neat): $\tilde{\nu}$ = 3072, 2922, 1599, 1461, 1353, 1168, 1092 cm^{-1} ; HRMS (ESI $^+$) calcd for $[M+\text{H}]^+$ $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_2\text{S}^+$ 327.1162, found 327.1163.

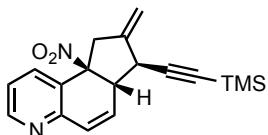


Ethyl 3a-amino-5-methylene-1-(phenylsulfonyl)-1,3a,4,5,6,6a-hexahydrocyclopenta[b]pyrrole-2-carboxylate (23). A suspension of the cycloadduct (20 mg, 0.05 mmol) in methanol (1.0 mL) and concentrated HCl (0.1 mL) was carefully treated with zinc dust (140 mg, 2.11 mmol) at 0 °C. The suspension was stirred at 0 °C for 15 min and warmed to 25 °C. A saturated aqueous NaHCO_3 solution was slowly added. The mixture was filtered through celite, eluting with EtOAc. The filtrate was dried over Na_2SO_4 , filtered, and evaporated. Purification by flash chromatography ($\text{CH}_2\text{Cl}_2/\text{methanol}$ 10:1) gave the product (18 mg, 98%) as a pale yellow oil. R_f = 0.61 ($\text{CH}_2\text{Cl}_2/\text{methanol}$ 10:1); ^1H NMR (400 MHz, CDCl_3): δ = 7.88–7.90 (m, 2H), 7.62–7.65 (m, 1H), 7.56–7.59 (m, 2H), 5.75 (s, 1H), 4.86 (br s, 1H), 4.79 (br s, 1H), 4.29–4.35 (m, 2H), 3.97 (dd, J = 9.1, 4.3 Hz, 1H), 2.91–2.98 (m, 1H), 2.46–2.53 (m, 2H), 2.32–2.36 (m, 1H), 1.46 (br s, 2H), 1.35 ppm (dt, J = 7.2, 0.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ = 162.1, 145.8, 136.5, 136.3, 136.3, 133.6, 129.4, 129.2, 128.3, 108.8, 72.9, 70.5, 62.1, 45.4, 41.1, 14.2 ppm; IR (thin film): $\tilde{\nu}$ = 2880, 2811, 1708, 1604, 1426, 1341, 1291, 1244, 1152, 1116, 1078, 1011, 881, 748, 726, 681 cm^{-1} ; HRMS (ESI $^+$) calcd for $[M+\text{Na}]^+$ $\text{C}_{17}\text{H}_{20}\text{N}_2\text{NaO}_4\text{S}^+$ 371.1036, found 371.1032.



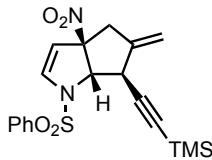
2-Methylene-2,3,3a,11b-tetrahydro-1H-cyclopenta[1]phenanthren-3a-amine (24). A suspension of the cycloadduct (35 mg, 0.13 mmol) in methanol (2.0 mL) and concentrated HCl (0.2 mL) was carefully treated with zinc dust (330 mg, 5.00 mmol) at 0 °C. The suspension was stirred at 0 °C for 10 min and

warmed to 25 °C. A saturated aqueous NaHCO₃ solution was slowly added. The mixture was filtered through celite, eluting with EtOAc. The filtrate was dried over Na₂SO₄, filtered, and evaporated. Purification by flash chromatography (CH₂Cl₂/methanol 100:0 to 60:1) gave the product (31 mg, quant) as a colorless oil. *R*_f = 0.14 (CH₂Cl₂/methanol 10:1); ¹H NMR (500 MHz, CDCl₃): δ = 7.85 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.37–7.40 (m, 1H), 7.32–7.35 (m, 2H), 7.21–7.24 (m, 2H), 4.88 (br s, 1H), 4.71 (br s, 1H), 3.50–3.54 (m, 1H), 3.38 (d, *J* = 16.3 Hz, 1H), 2.97 (d, *J* = 16.3 Hz, 1H), 2.73 (dd, *J* = 17.1, 8.6 Hz, 1H), 1.98–2.05 ppm (m, 1H), NH₂ hidden in noise; ¹³C NMR (100 MHz, CDCl₃): δ = 146.9, 136.1, 132.4, 131.8, 129.9, 128.8, 128.2, 128.1, 127.7, 126.6, 124.3, 124.2, 106.7, 60.4, 52.3, 46.4, 39.8 ppm; IR (thin film): $\tilde{\nu}$ = 3289, 2881, 1696, 1636, 1578, 1502, 1468, 1431, 1354, 1314, 1247, 1151, 1016, 872, 748, 724, 692 cm⁻¹; HRMS (ESI⁺) calcd for [M+H]⁺ C₁₈H₁₈N⁺ 248.1434, found 248.1434.

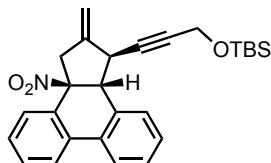


8-Methylene-9a-nitro-7-((trimethylsilyl)ethynyl)-7,8,9,9a-tetrahydro-6aH-cyclopental[f]quinolone (25).

The reaction was performed with 5-nitroquinoline (17 mg, 0.100 mmol), **L4** (4.2 mg, 0.006 mmol), CpPd(η^3 -C₃H₅) (1.1 mg, 0.005 mmol), and donor **1c** (48 mg, 0.170 mmol) at 25 °C for 15 h. Purification by flash chromatography (hexanes/Et₂O 2:1) gave the product (25 mg, 77%) as a white solid. The diastereomeric ratio (4:1 dr) was determined from the crude ¹H NMR before purification using the signals at δ = 5.30 ppm (dt; major) and δ = 5.14 ppm (dt; minor). *R*_f = 0.29 (hexanes/Et₂O 1:2); m.p. 101–102 °C; [α]²⁰_D = +265.92 (*c* 1.02 CHCl₃, 95% ee); ¹H NMR (400 MHz, CDCl₃): δ = 8.59 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.82–7.85 (m, 1H), 7.24–7.28 (m, 1H), 6.78–6.80 (m, 1H), 6.56 (dd, *J* = 10.0, 5.3 Hz, 1H), 5.30 (dt, *J* = 2.5, 2.0 Hz, 1H), 5.14 (dt, *J* = 2.7, 2.0 Hz, 1H), 3.73–3.79 (m, 2H), 3.34–3.39 (m, 1H), 3.09–3.14 (m, 1H), 0.21 ppm (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ = 151.1, 142.4, 136.1, 131.8, 128.5, 125.8, 123.2, 110.1, 102.8, 92.8, 89.9, 50.4, 44.3, 44.1, -0.2 ppm; IR (thin film): $\tilde{\nu}$ = 3020, 2917, 2883, 2141, 1543, 1525, 1425, 1326, 1283, 1231, 1053, 1017, 886, 831, 800, 748, 723, 677 cm⁻¹; chiral HPLC: Chiralcel® IA, heptane/isopropanol 98:2, 0.8 mL/min, λ = 220 nm, *t*_R = 12.091 (major), *t*_R = 15.560 (minor); HRMS (ESI⁺) calcd for [M+H]⁺ C₁₈H₂₁N₂O₂Si⁺ 325.1367, found 325.1367.

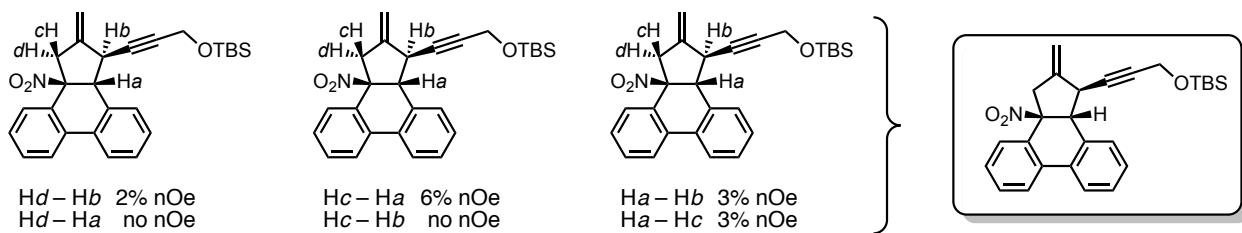


(3aR,6S,6aS)-5-Methylene-3a-nitro-1-(phenylsulfonyl)-6-((trimethylsilyl)ethynyl)-1,3a,4,5,6,6a-hexahydrocyclopenta[b]pyrrole (26). The reaction was performed with 3-nitro-1-(phenylsulfonyl)-1*H*-pyrrole (25 mg, 0.100 mmol), **L4** (4.2 mg, 0.006 mmol), CpPd(η^3 -C₃H₅) (1.1 mg, 0.005 mmol), and TMS alkyne donor (48 mg, 0.170 mmol) at 25 °C for 15 h. Purification by flash chromatography (hexanes/Et₂O 10:1) gave the product (22 mg, 55%) as a colorless oil. The diastereomeric ratio (5:1 dr) was determined from the crude ¹H NMR before purification using the signals at δ = 8.01–8.04 ppm (m; minor) and δ = 7.80–7.82 ppm (m; major). R_f = 0.42 (hexanes/Et₂O 1:1); $[\alpha]^{20}_D$ = -199.50 (*c* 0.10 CHCl₃, 90% ee); ¹H NMR (500 MHz, CDCl₃): δ = 7.80–7.82 (m, 2H), 7.64–7.68 (m, 1H), 7.54–7.57 (m, 2H), 6.71 (d, *J* = 4.0 Hz, 1H), 5.35 (d, *J* = 4.0 Hz, 1H), 5.28–5.39 (m, 1H), 5.06–5.08 (m, 1H), 4.65 (d, *J* = 5.0 Hz, 1H), 3.55–3.57 (m, 1H), 3.27 (d, *J* = 16.0 Hz, 1H), 2.79 (d, *J* = 16.0 Hz, 1H), 0.23 (s, 9H); ¹³C NMR (125 MHz, CDCl₃): δ = 142.8, 136.6, 135.6, 134.1, 129.6, 127.8, 112.6, 110.7, 102.0, 90.9, 85.8, 73.0, 45.5, 42.6, 0.1 ppm; IR (thin film): $\tilde{\nu}$ = 2919, 2882, 2812, 2145, 1648, 1588, 1527, 1428, 1349, 1235, 1157, 1078, 1023, 835, 790, 748, 715, 678 cm⁻¹; chiral HPLC: Chiralcel® IB, heptane/isopropanol 99:1, 0.8 mL/min, λ = 220 nm, t_R = 15.587 (minor), t_R = 18.351 (major); HRMS (ESI⁺) calcd for [M+H]⁺ C₁₉H₂₃N₂O₄SSi⁺ 403.1142, found 403.1130.



tert-Butyldimethyl((3-(2-methylene-3a-nitro-2,3,3a,11b-tetrahydro-1*H*-cyclopenta[1]phenanthren-1-yl)prop-2-yn-1-yl)oxy)silane (27). The reaction was performed with 9-nitrophenanthrene (22 mg, 0.100 mmol), **L5** (5.3 mg, 0.006 mmol), CpPd(η^3 -C₃H₅) (1.1 mg, 0.005 mmol), and alkyne donor (60 mg, 0.170 mmol) at 25 °C for 15 h. Purification by flash chromatography (hexanes/Et₂O 15:1) gave the product (33.5 mg, 75%) as a colorless oil. The diastereomeric ratio (5:1 dr) was determined from the crude ¹H NMR before purification using the signals at δ = 4.06 ppm (d; major) and δ = 3.97 ppm (dt; minor). R_f = 0.52 (hexanes/Et₂O 2:1); $[\alpha]^{20}_D$ = +132.25 (*c* 1.74 CHCl₃, 85% ee); ¹H NMR (400 MHz, CDCl₃): δ = 7.95 (d, *J* = 7.8 Hz, 1H), 7.87 (d, *J* = 8.3 Hz, 1H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.51–7.55 (m, 1H), 7.39–7.47 (m, 3H), 7.31–7.35 (m, 1H), 5.22–5.24 (m, 1H), 5.14–5.16 (m, 1H), 4.36 (d, *J* = 1.9 Hz, 2H), 4.07 (d, *J* = 12.1 Hz, 1H), 3.78–3.82 (m, 1H), 3.68 (dq, *J* = 17.0, 2.8 Hz, 1H), 3.09–3.14 (m, 1H), 0.91 (s, 9H), 0.10 ppm (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ = 134.1, 132.1, 130.9, 130.6, 129.8,

129.3, 128.7, 128.7, 128.6, 128.3, 124.5, 124.2, 110.5, 91.0, 83.2, 82.7, 54.2, 52.0, 43.4, 42.5, 26.0, 18.4, -5.0, -5.0 ppm; IR (thin film): $\tilde{\nu}$ = 3028, 2913, 2889, 2817, 1523, 1435, 1331, 1237, 1340, 1066, 825, 768, 734 cm⁻¹; chiral HPLC: Chiralcel® IB, heptane/isopropanol 99:1, 0.8 mL/min, λ = 220 nm, t_R = 9.831 (major), t_R = 12.814 (minor); HRMS (ESI⁺) calcd for [M+H]⁺ C₂₇H₃₂NO₃Si⁺ 446.2146, found 446.2150.

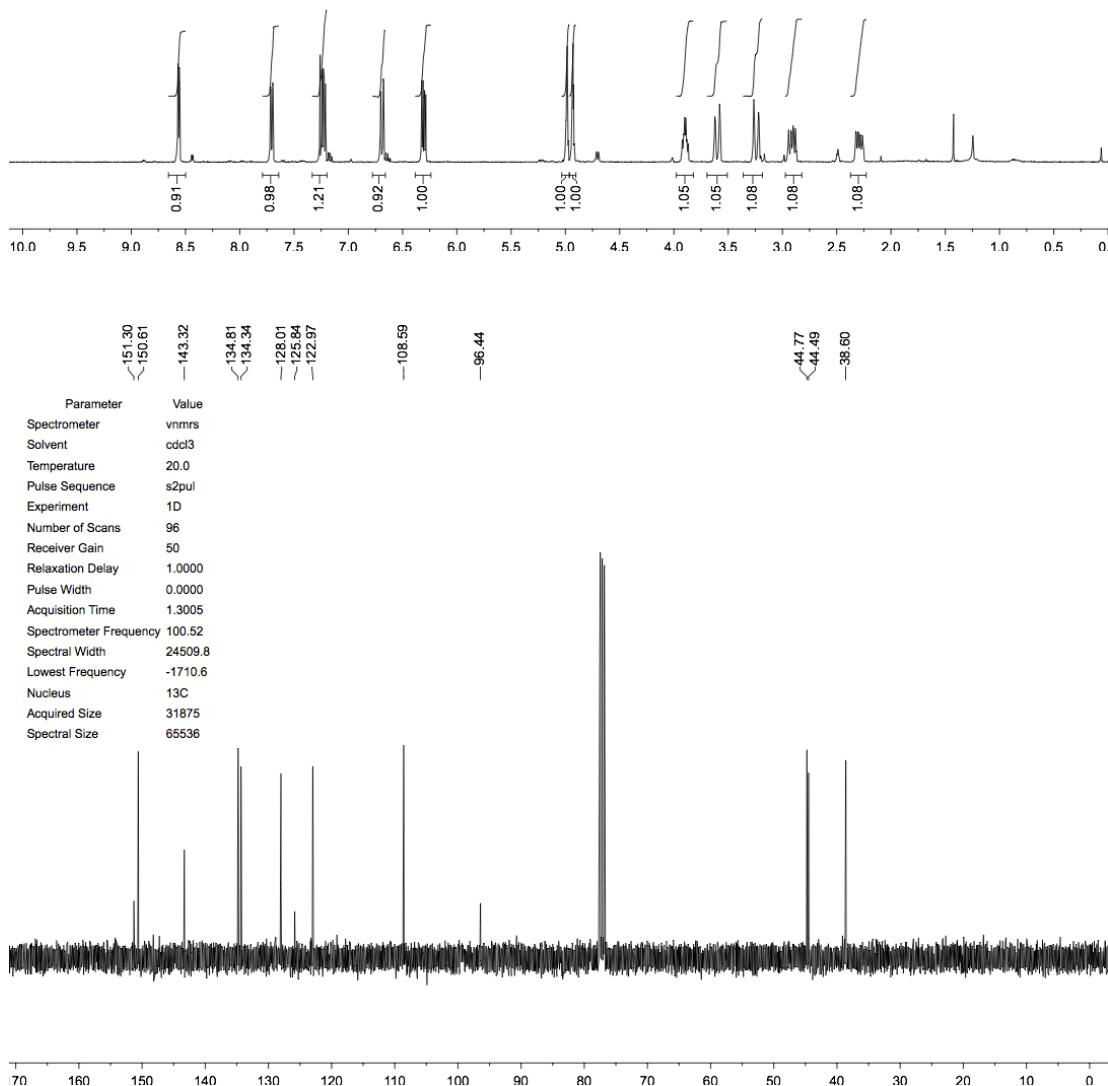
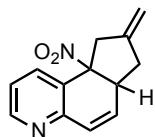


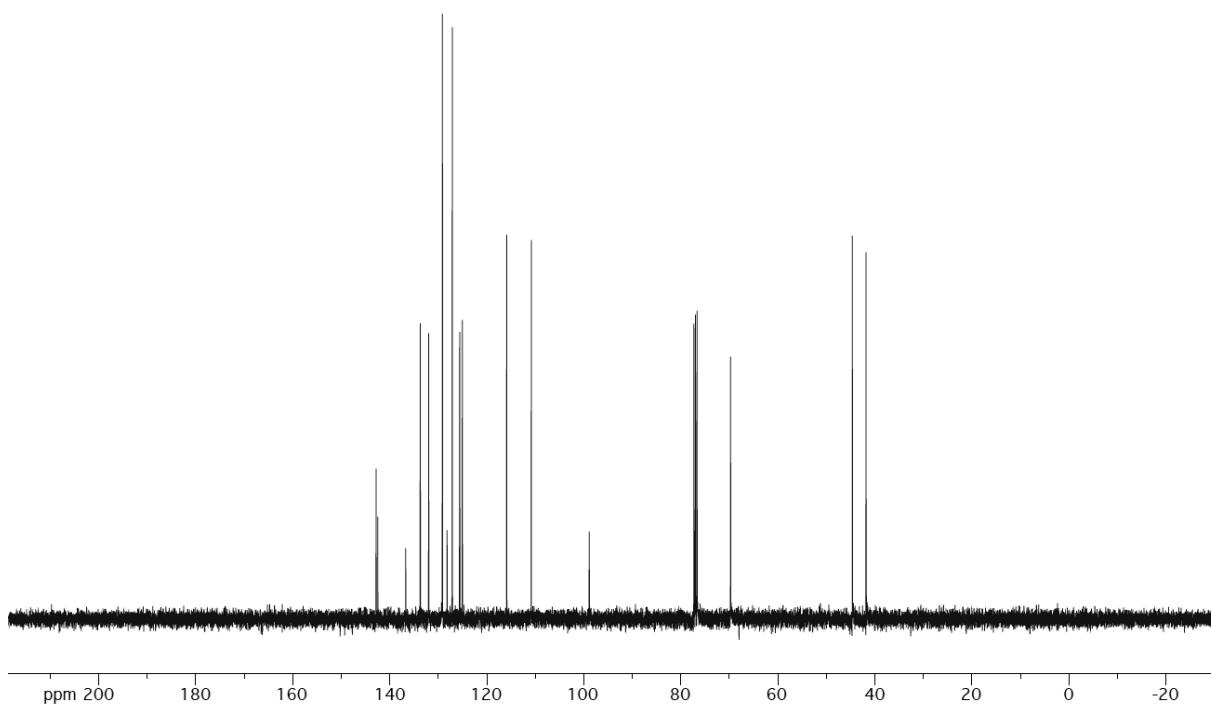
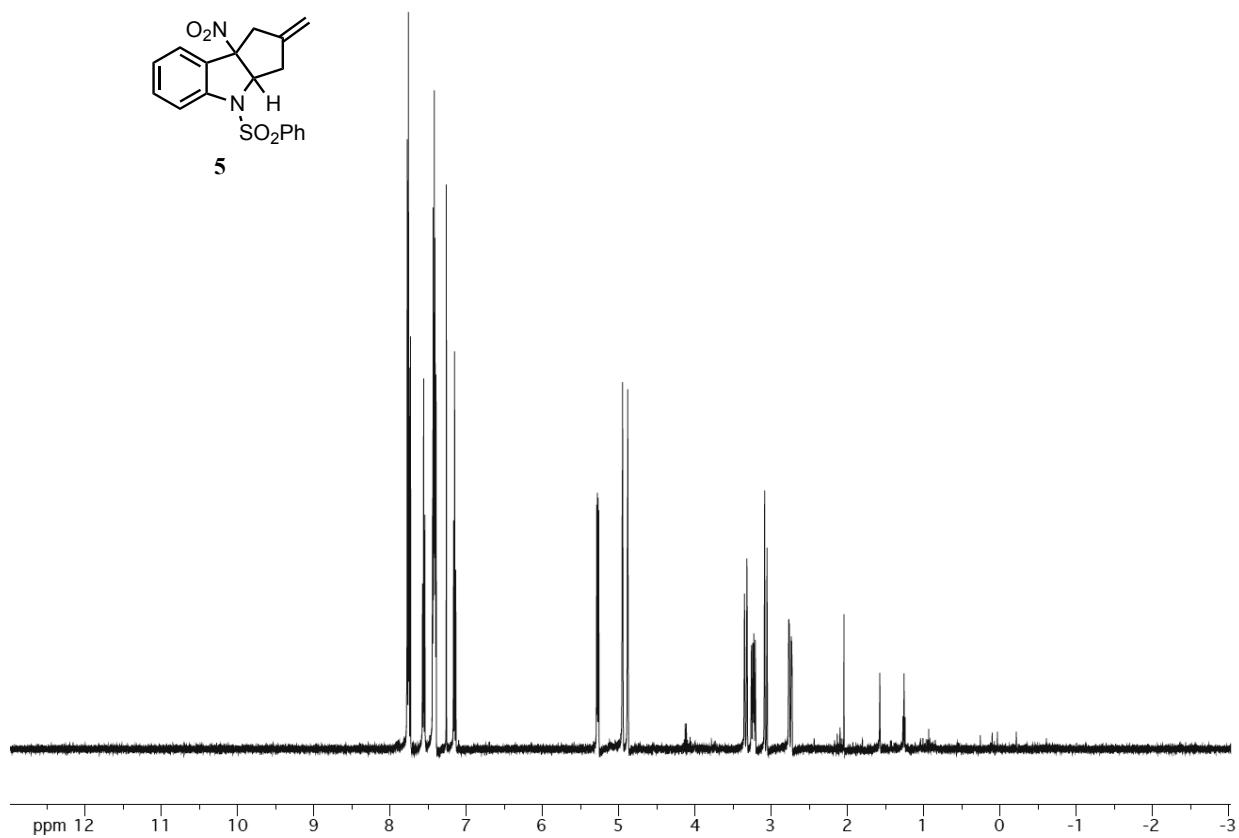
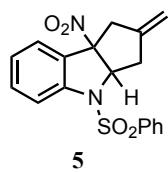
2. References

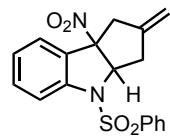
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3. NMR Spectra and HPLC Data

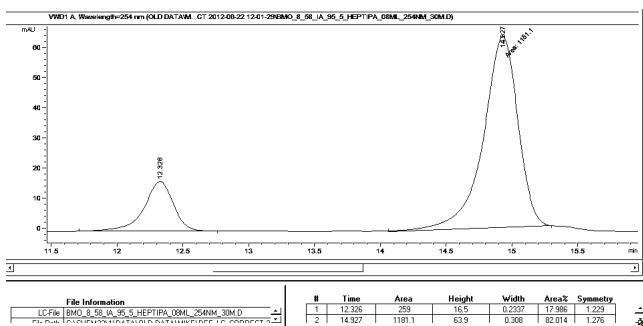
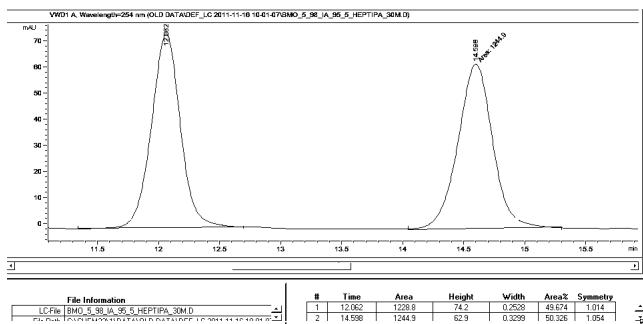
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Experiment	1D
Number of Scans	16
Receiver Gain	20
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	4.0001
Spectrometer Frequency	399.74
Spectral Width	5605.4
Lowest Frequency	-798.9
Nucleus	1H
Acquired Size	22422
Spectral Size	65536

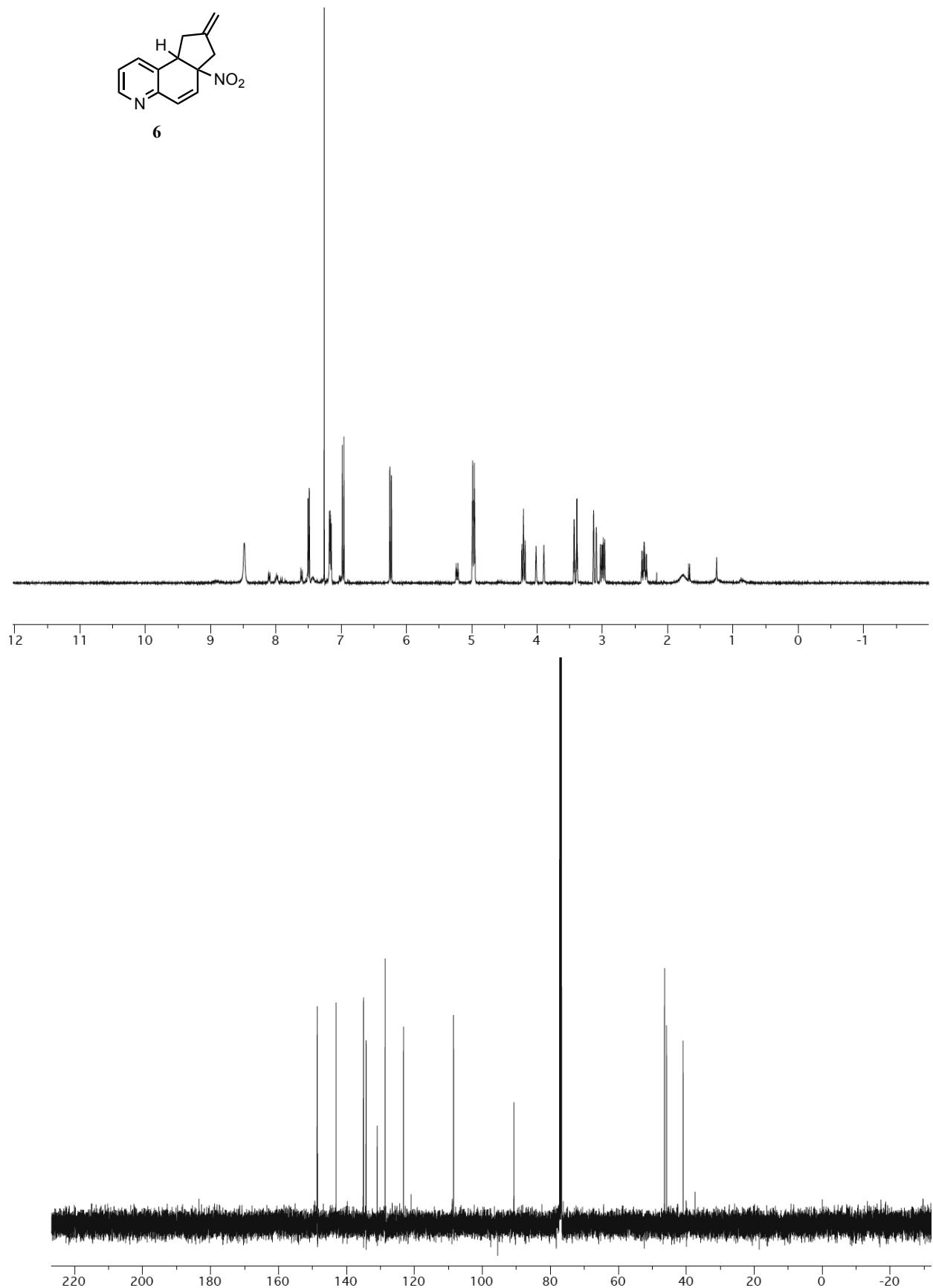
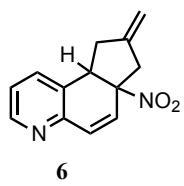




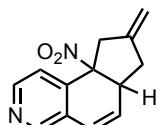


66% ee

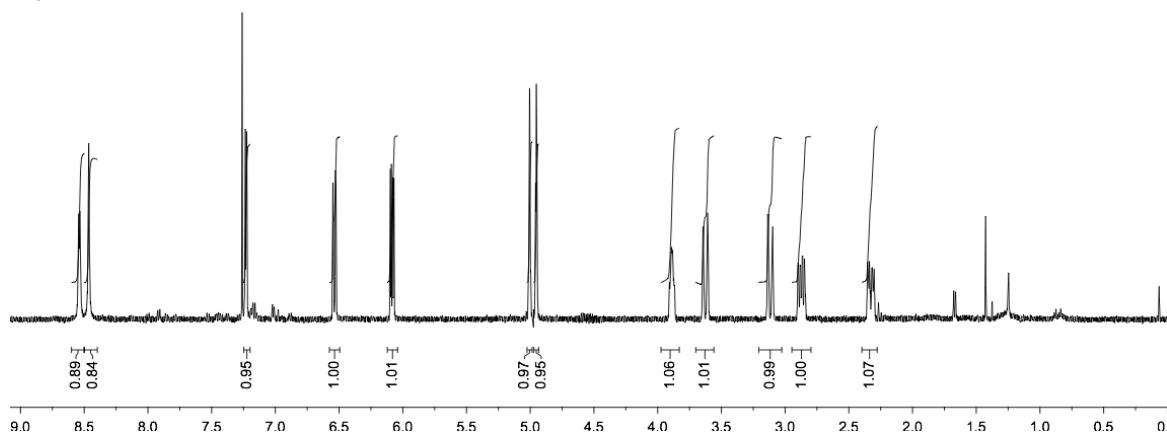




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Experiment	1D
Number of Scans	1
Receiver Gain	40
Relaxation Delay	0.0000
Pulse Width	0.0000
Acquisition Time	4.0000
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Spectral Width	8000.0
Lowest Frequency	-1514.2
Nucleus	1H
Acquired Size	32000
Spectral Size	65536

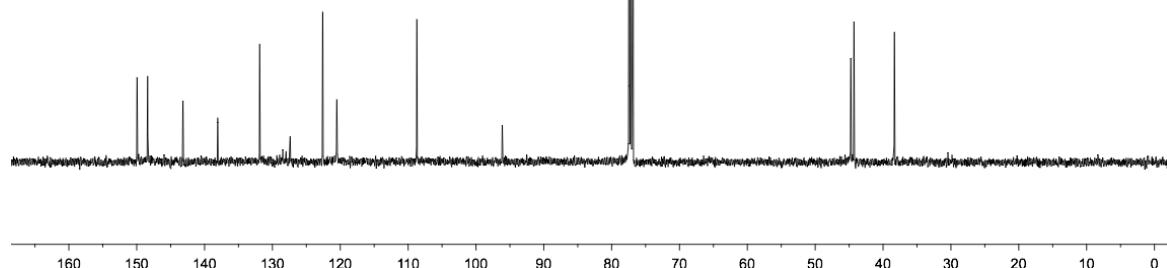


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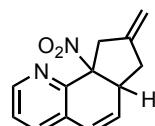


149.95
148.38
143.18
138.05
131.88
127.38
122.59
120.51
-108.71
-96.12
-44.76
-44.29
-38.33

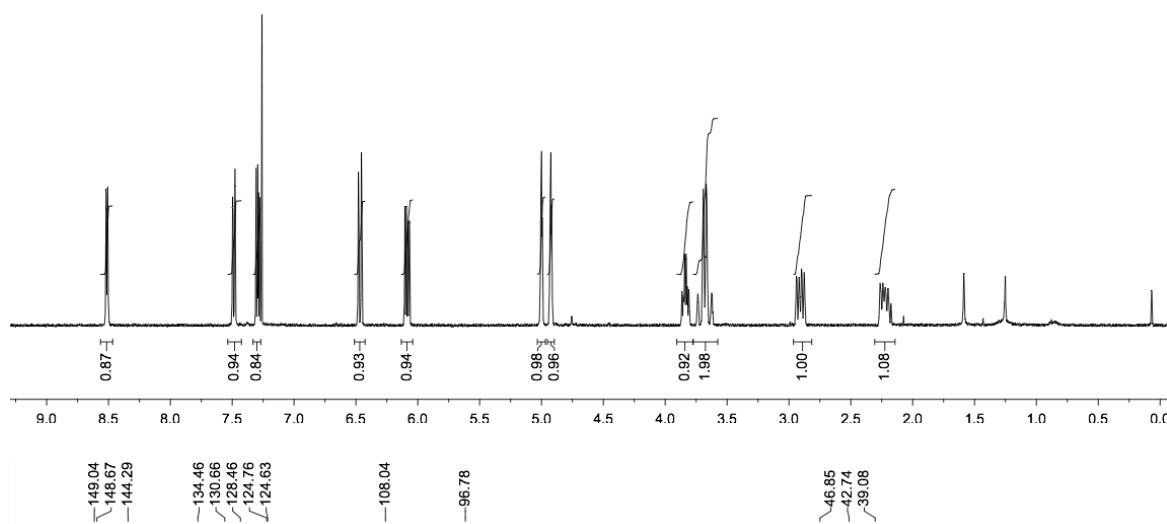
Parameter	Value
Spectrometer	inova
Solvent	CDCl ₃
Temperature	29.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	404
Receiver Gain	54
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	1.5001
Spectrometer Frequency	125.67
Spectral Width	33003.3
Lowest Frequency	-4478.2
Nucleus	13C
Acquired Size	49508
Spectral Size	131072



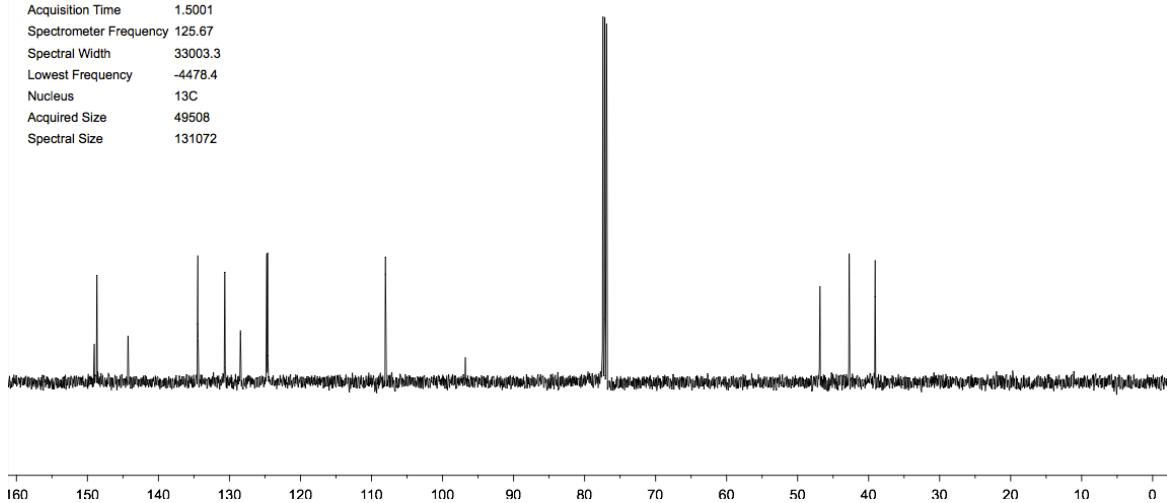
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Solvent	cdcl3
Temperature	20.0
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Pulse Width	0.0000
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Lowest Frequency	-798.3
Nucleus	1H
Acquired Size	22422
Spectral Size	65536



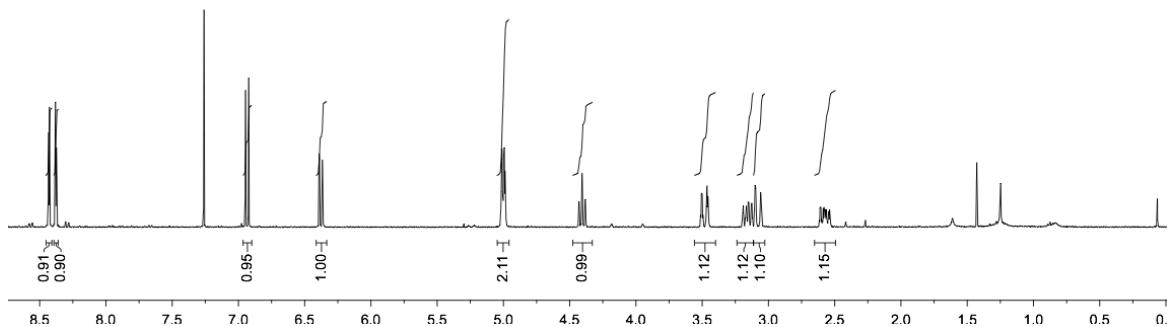
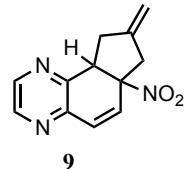
8



Parameter	Value
Spectrometer	inova
Solvent	CDCl3
Temperature	29.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	136
Receiver Gain	54
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	1.5001
Spectrometer Frequency	125.67
Spectral Width	33003.3
Lowest Frequency	-4478.4
Nucleus	13C
Acquired Size	49508
Spectral Size	131072



Parameter	Value
Spectrometer	mercury
Solvent	CDCl ₃
Temperature	29.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	30
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	4.0020
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Spectral Width	4997.5
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Nucleus	1H
Acquired Size	20000
Spectral Size	65536

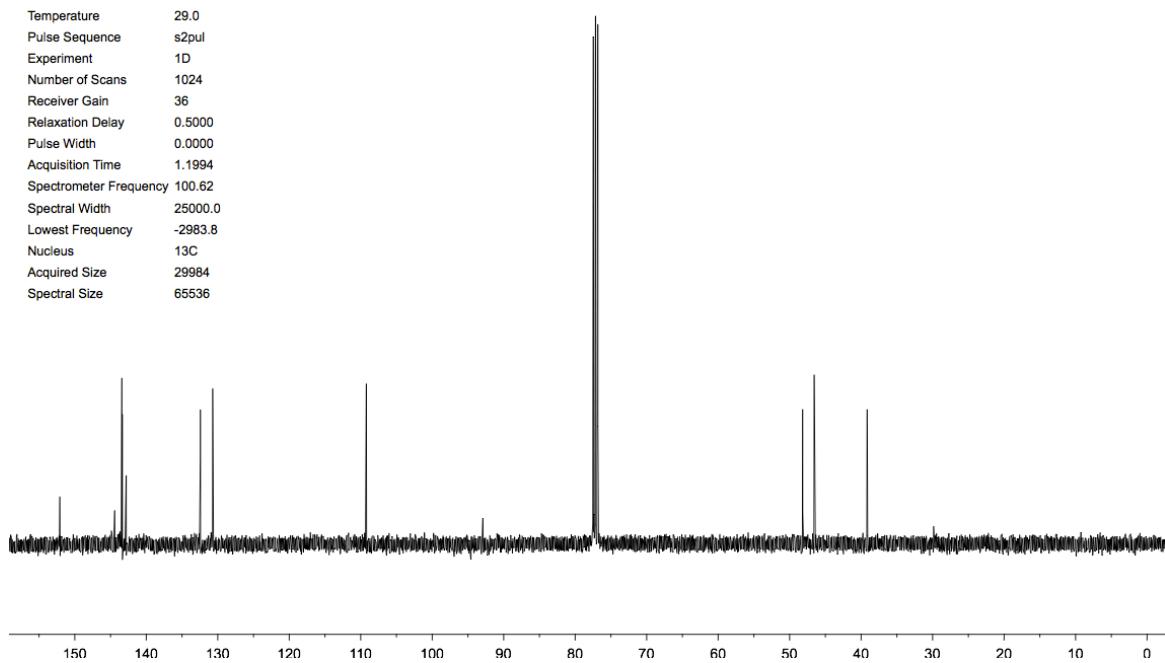


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—143.42
—143.35
—142.81
—132.43
—130.71

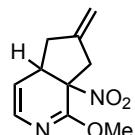
—109.22
—92.91

—48.18
—46.57
—39.16

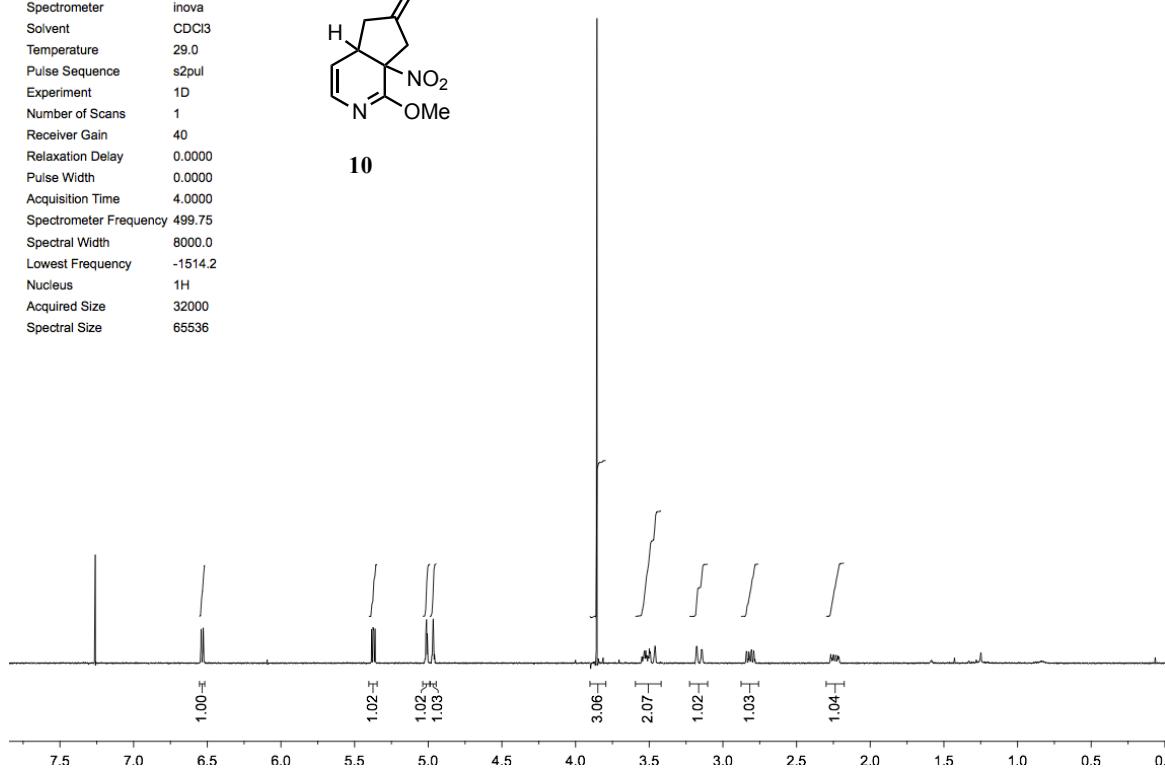
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Pulse Width	0.0000
Acquisition Time	1.1994
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Lowest Frequency	-2983.8
Nucleus	13C
Acquired Size	29984
Spectral Size	65536



Parameter	Value
Spectrometer	inova
Solvent	CDCl ₃
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Pulse Sequence	s2pul
Experiment	1D
Number of Scans	1
Receiver Gain	40
Relaxation Delay	0.0000
Pulse Width	0.0000
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Spectral Width	8000.0
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Nucleus	1H
Acquired Size	32000
Spectral Size	65536

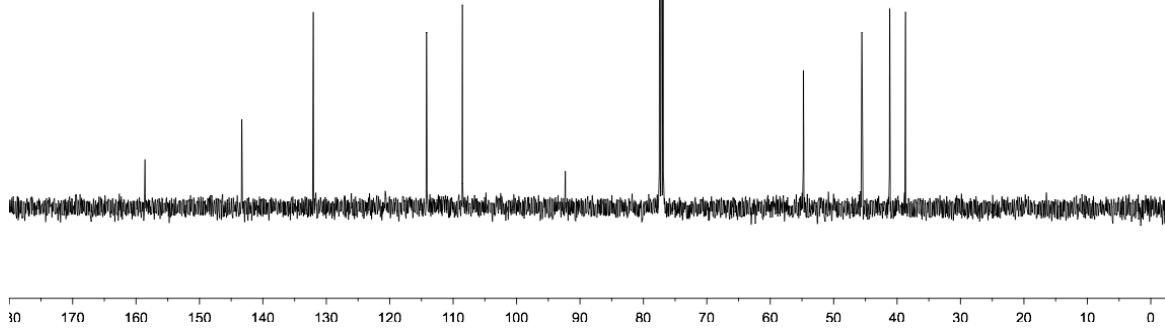


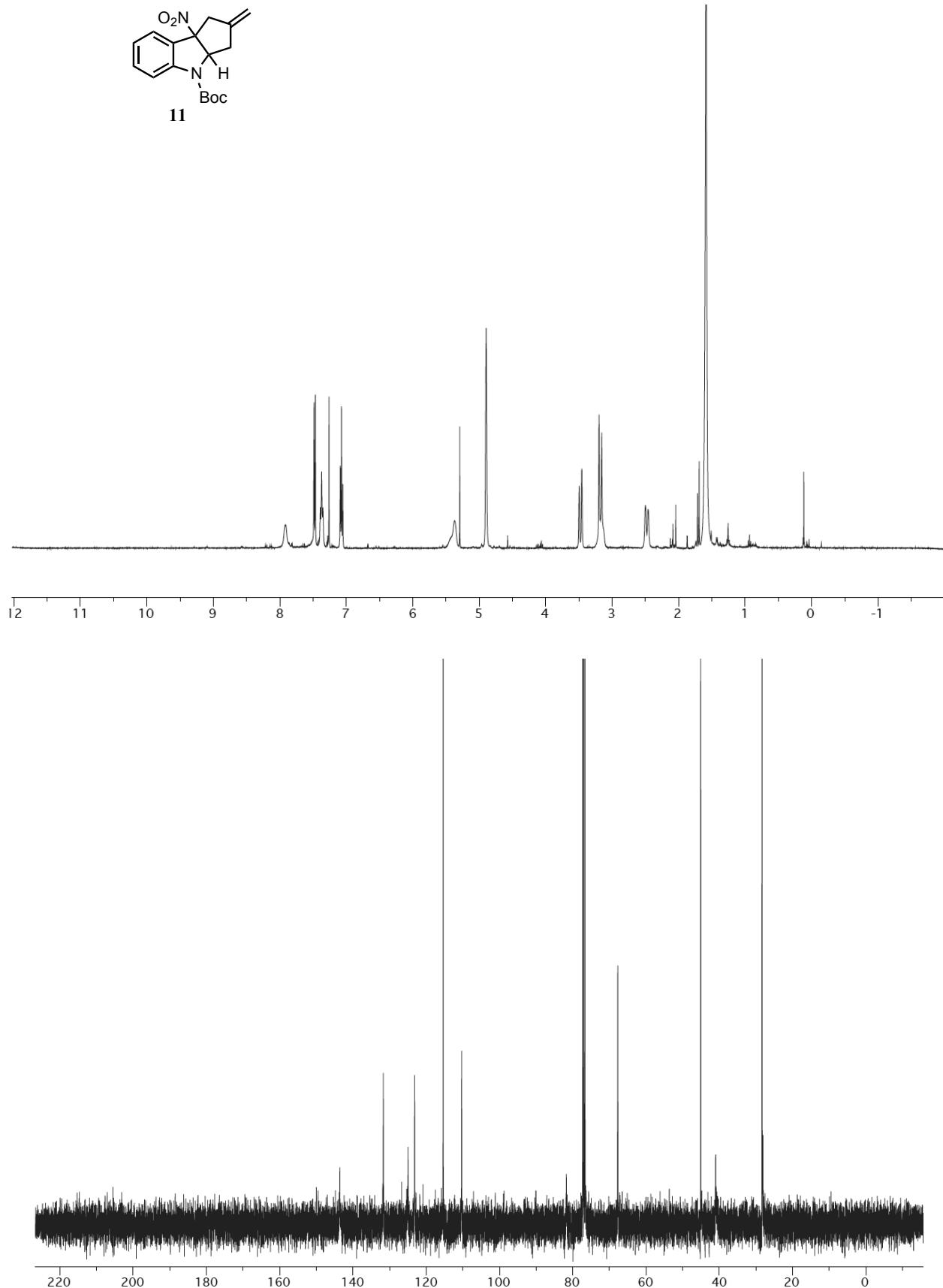
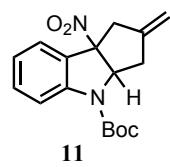
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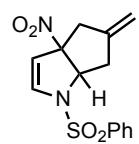


—158.59 —143.33 —132.05 —114.19 —108.54 —92.31 —54.77
 ~45.56 ~41.17 ~38.67

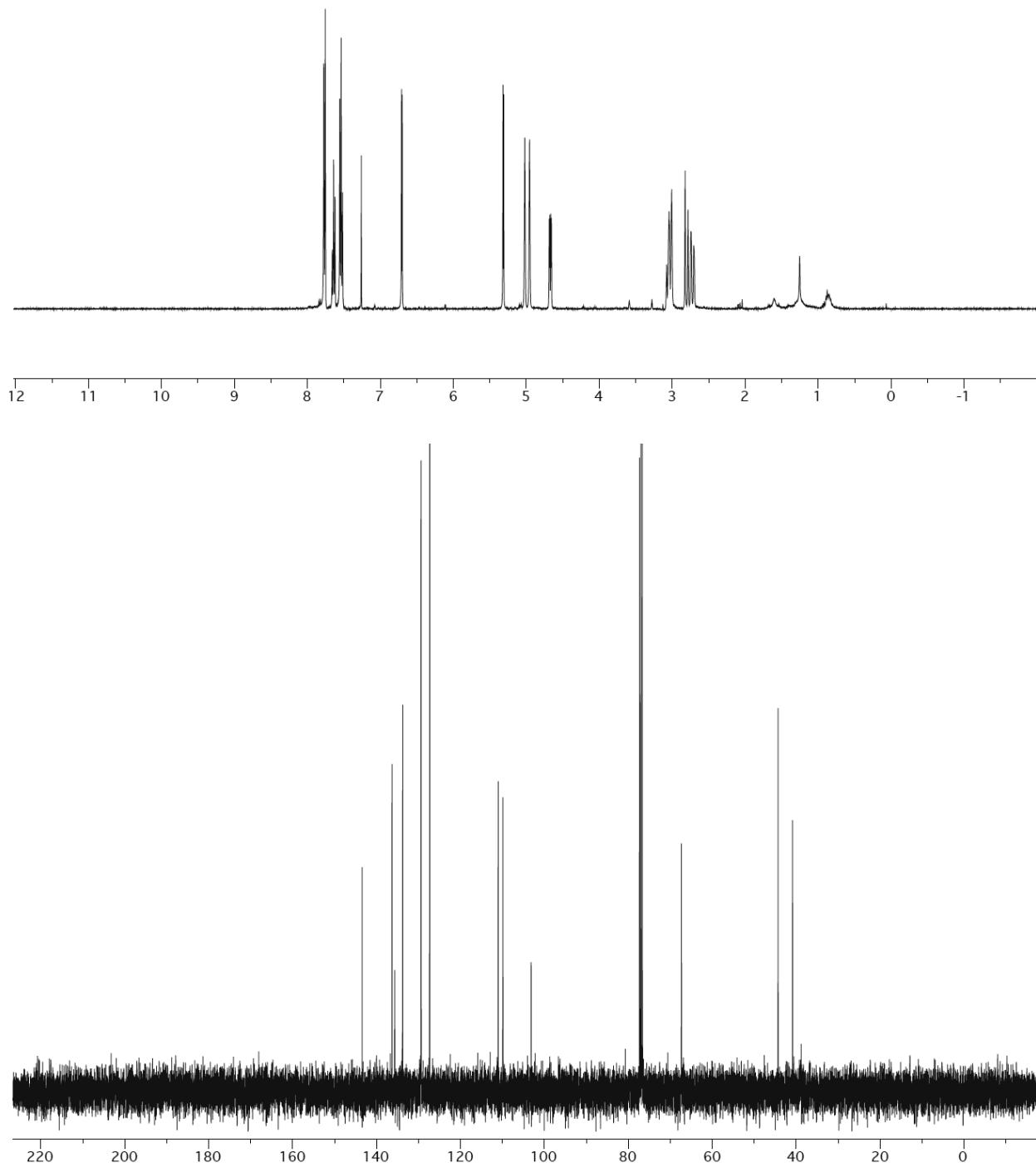
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Solvent	CDCl ₃
Temperature	29.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	168
Receiver Gain	54
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	1.5001
Spectrometer Frequency	125.67
Spectral Width	33003.3
Lowest Frequency	-4477.2
Nucleus	13C
Acquired Size	49508
Spectral Size	131072

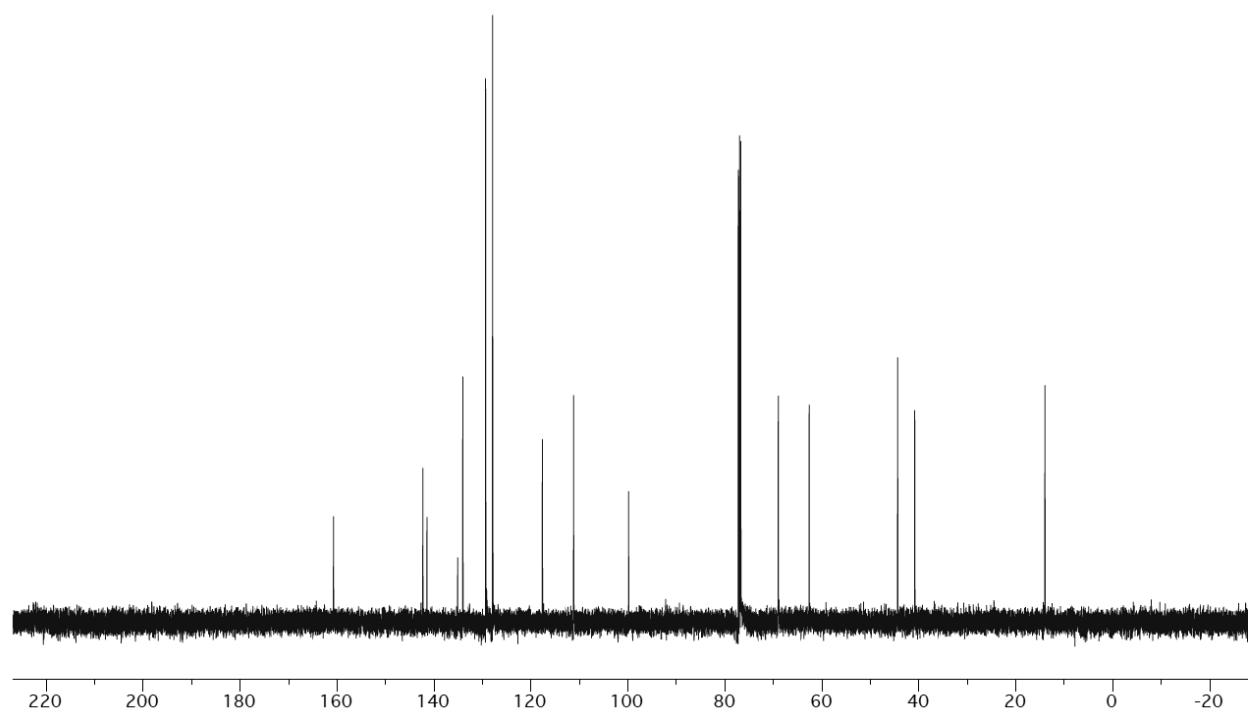
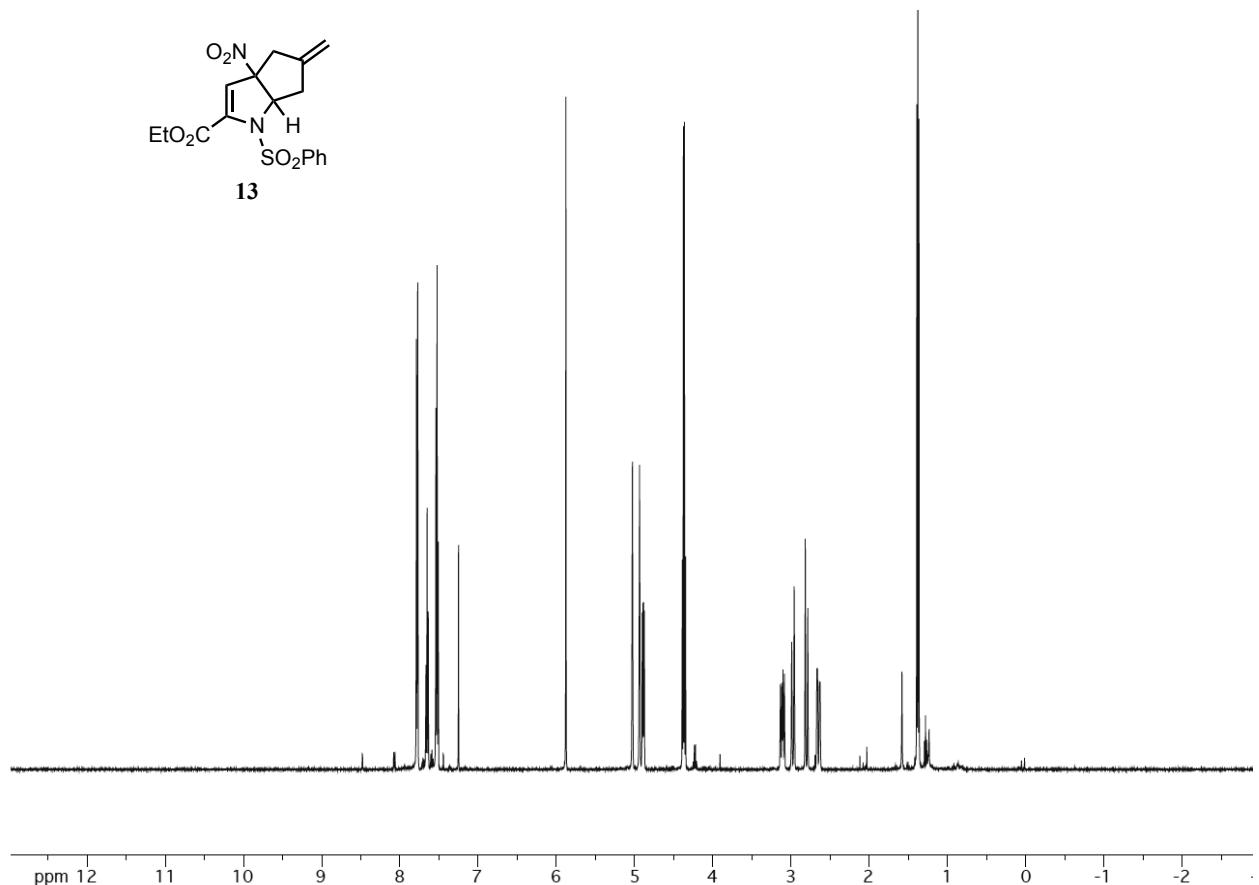
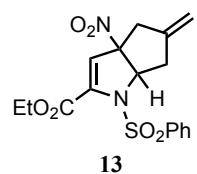


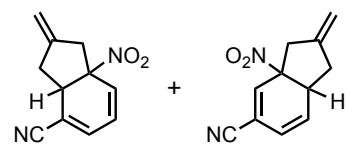




12

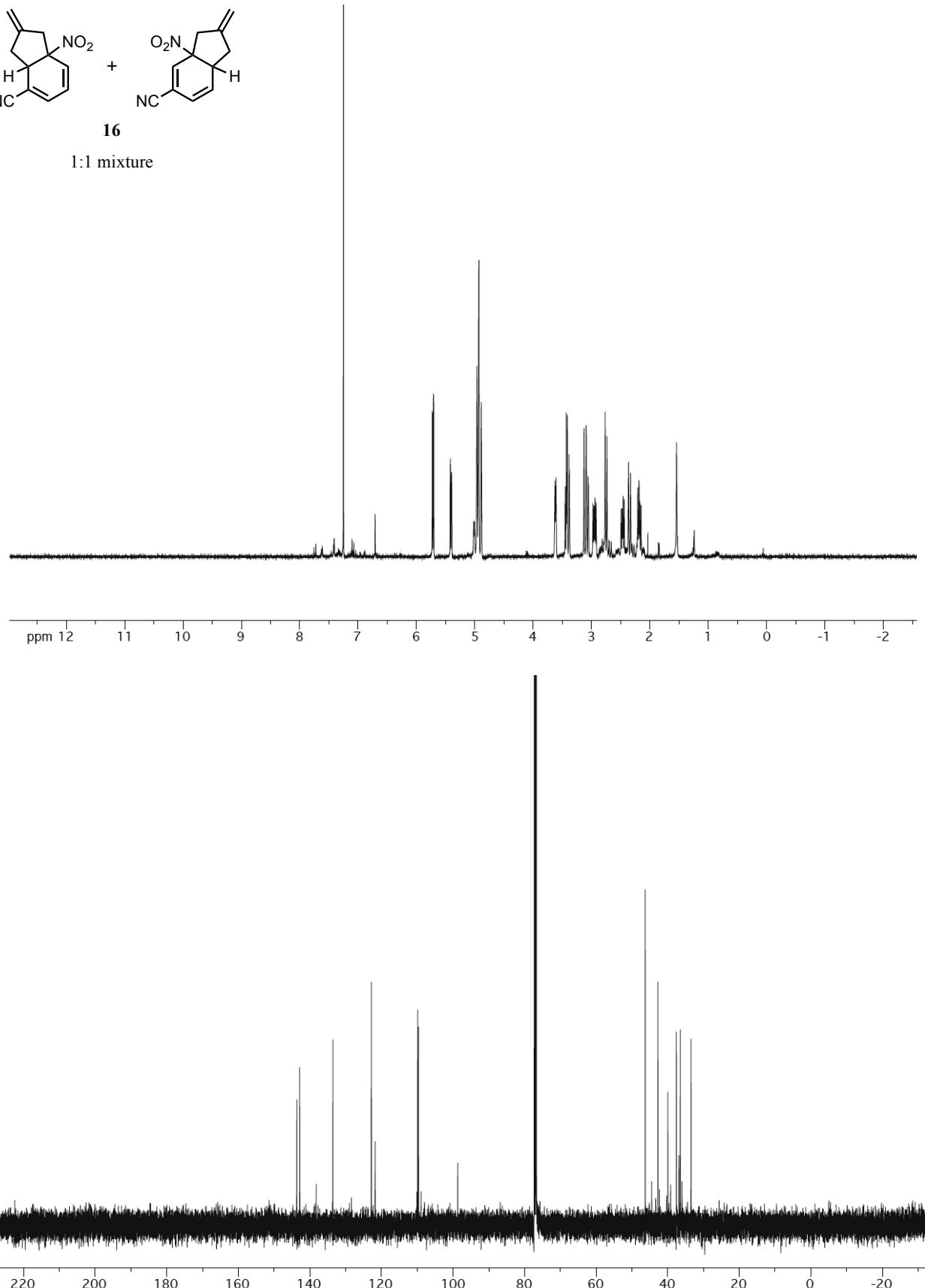


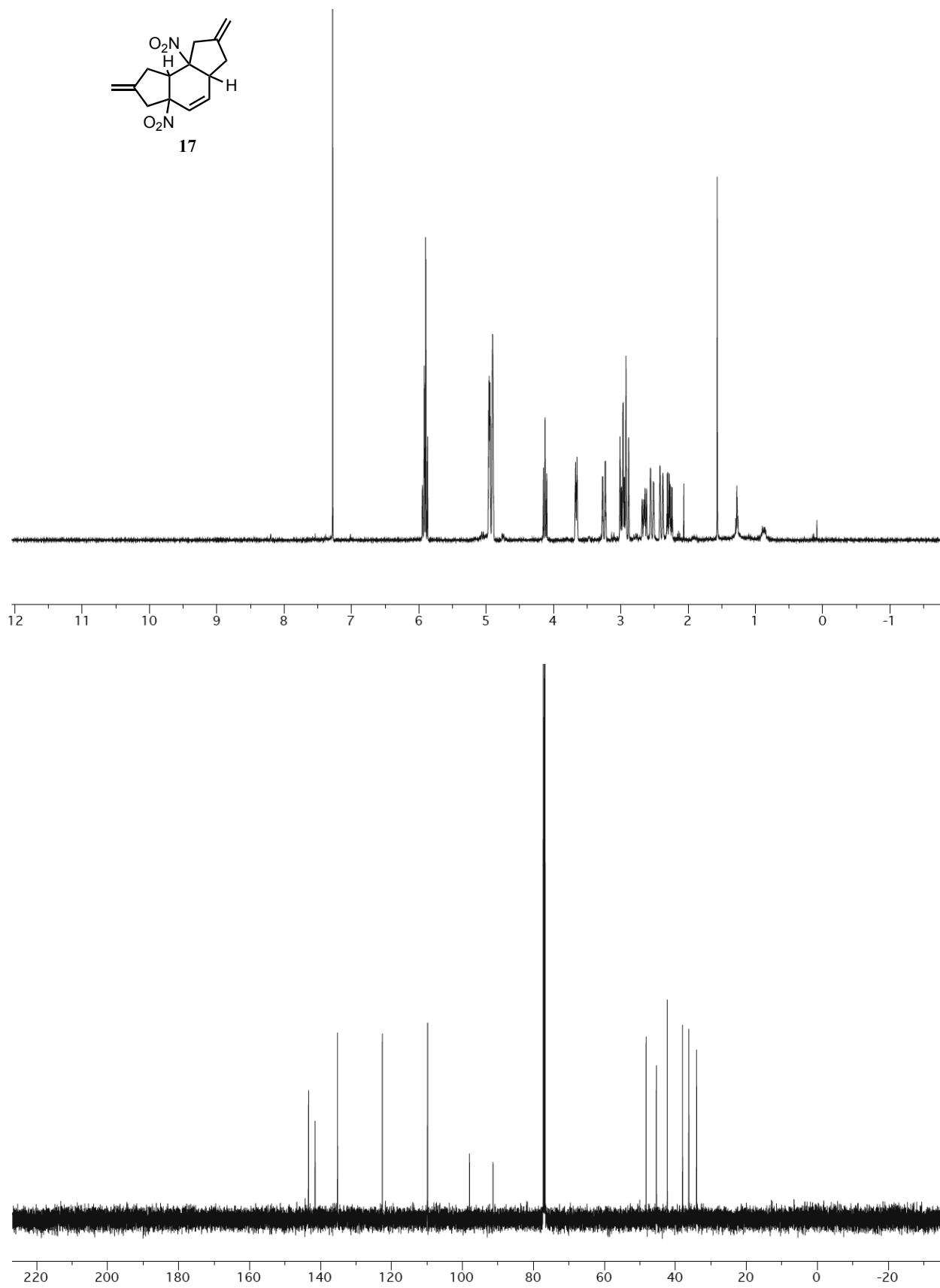
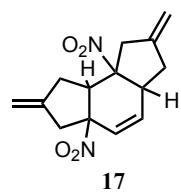


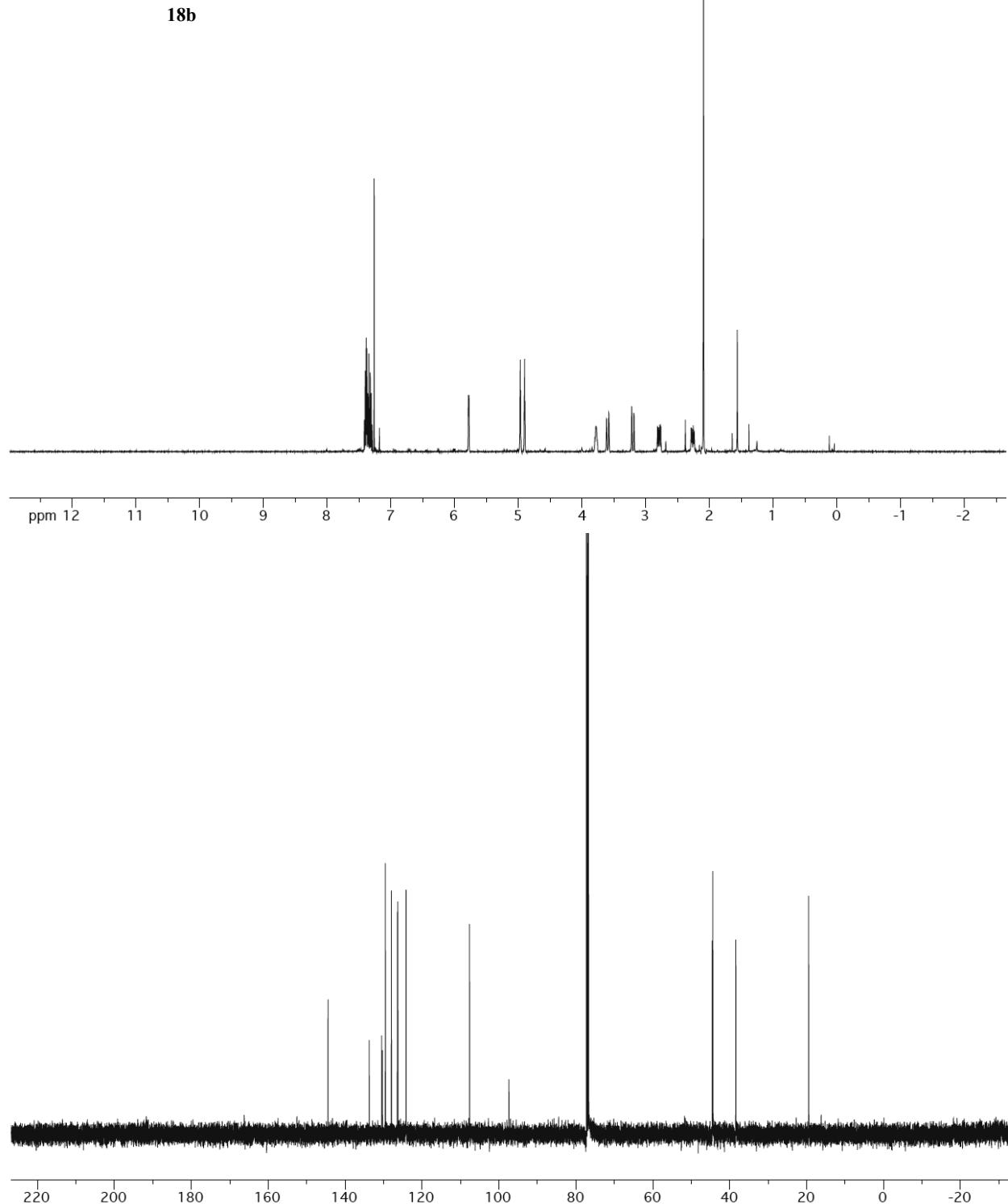
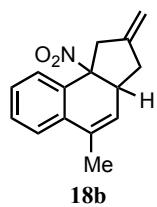


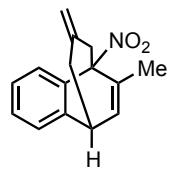
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1:1 mixture

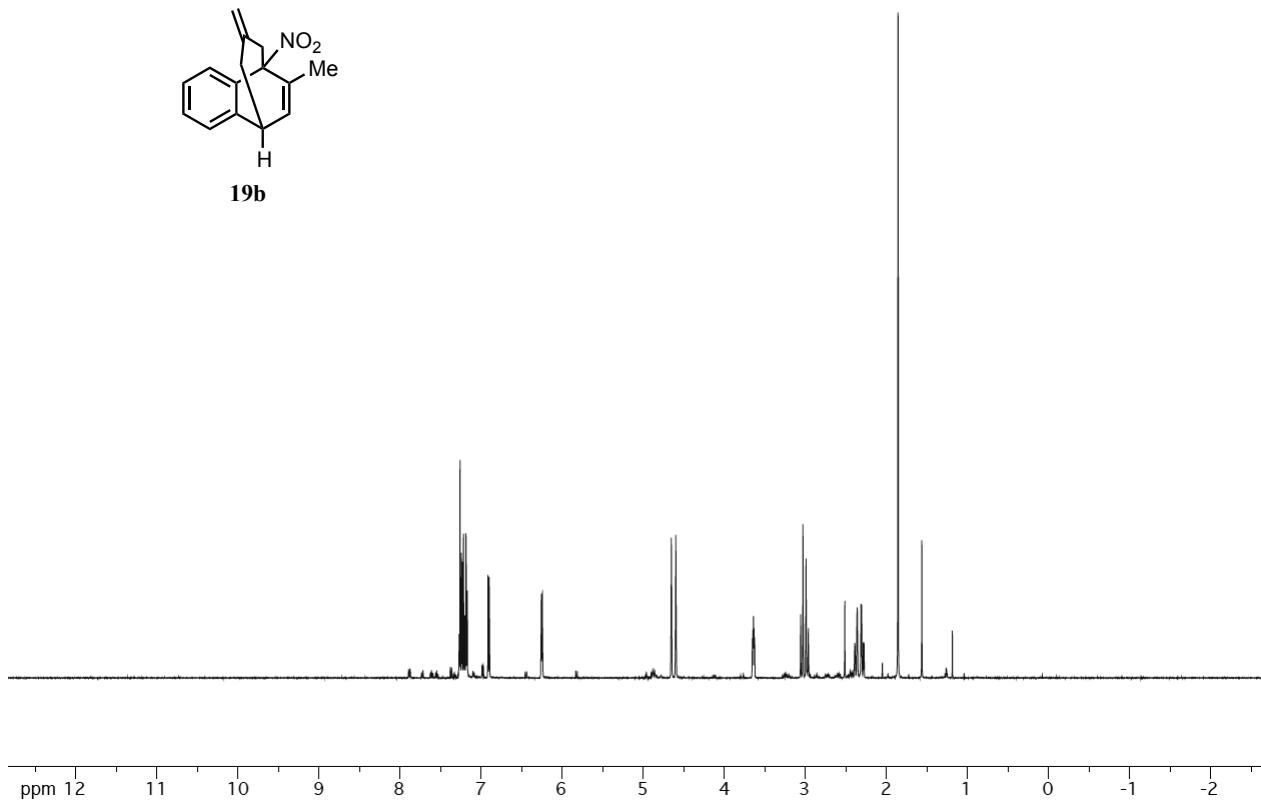






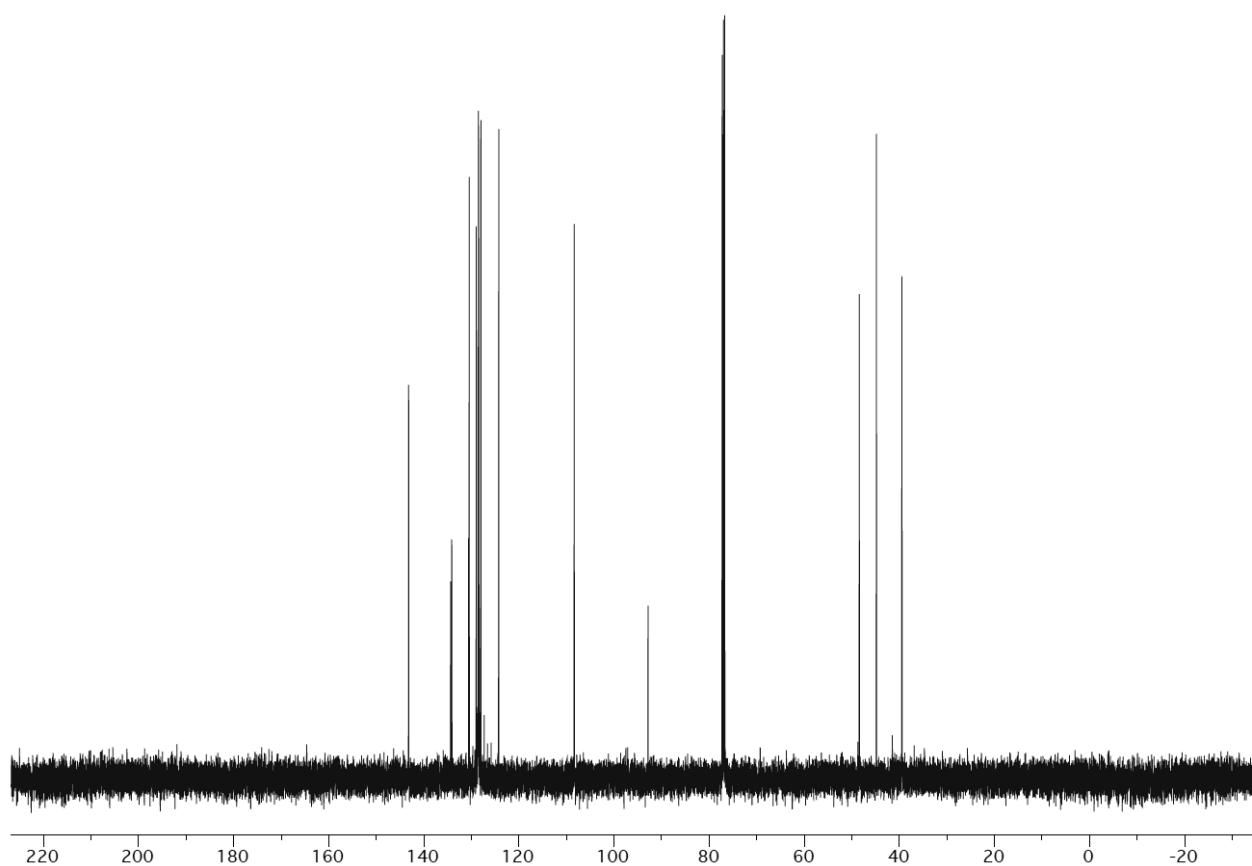
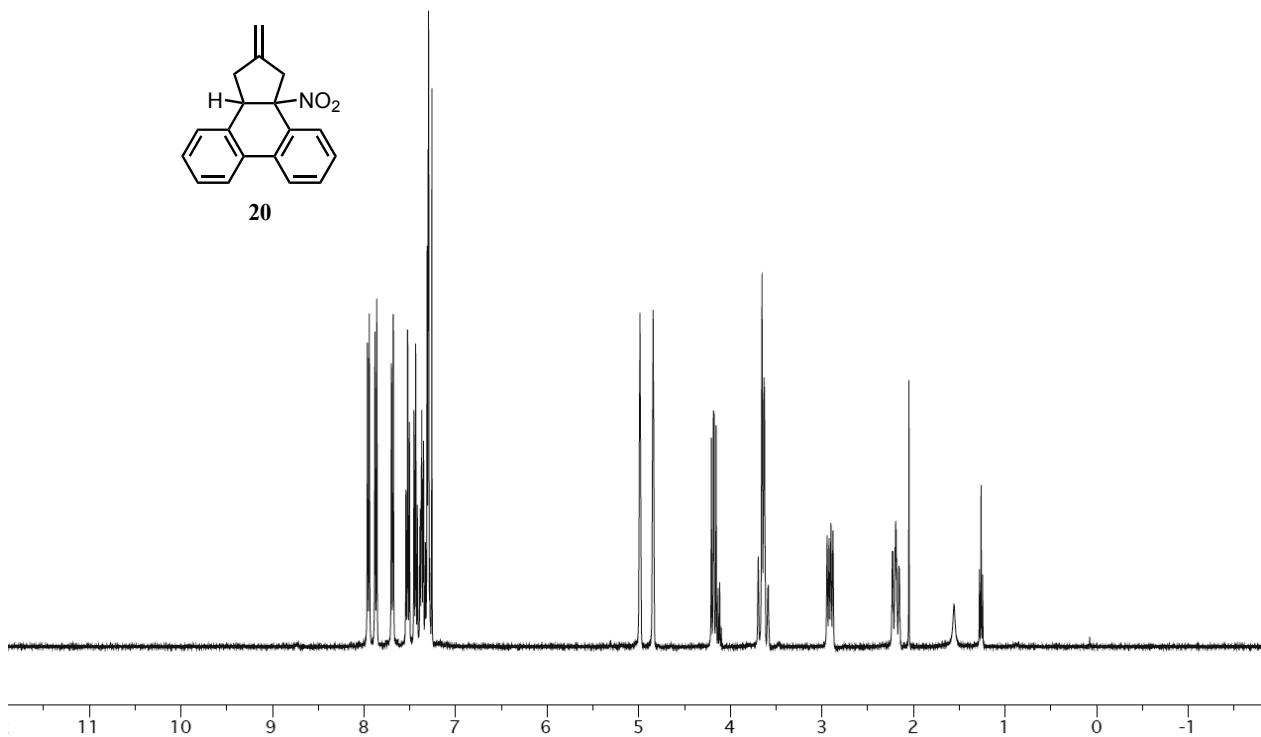
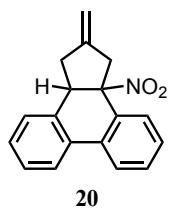


19b

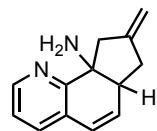


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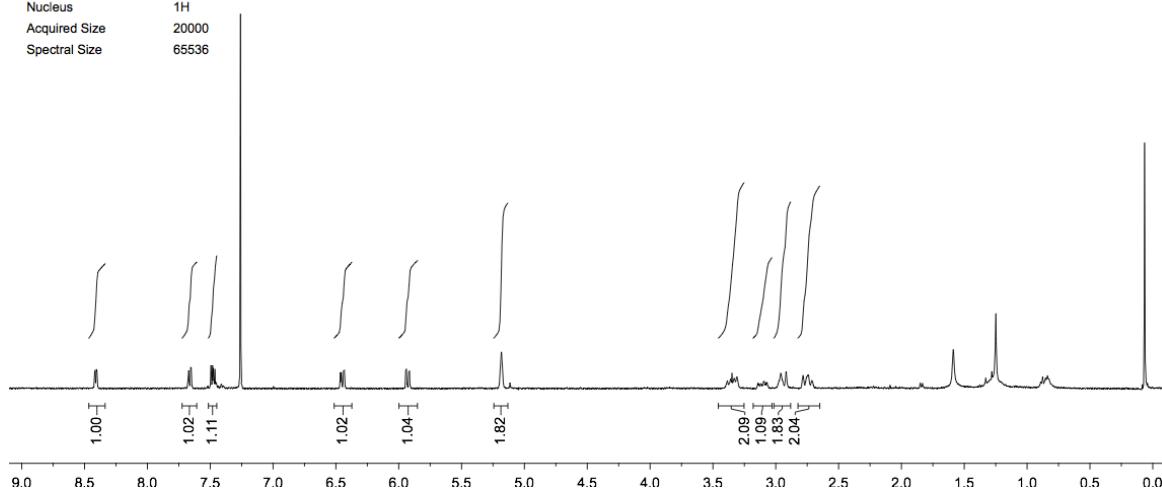
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Parameter	Value
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Solvent	CDCl ₃
Temperature	29.0
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Experiment	1D
Number of Scans	0
Receiver Gain	30
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	4.0020
Spectrometer Frequency	400.11
Spectral Width	4997.5
Lowest Frequency	-479.6
Nucleus	1H
Acquired Size	20000
Spectral Size	65536



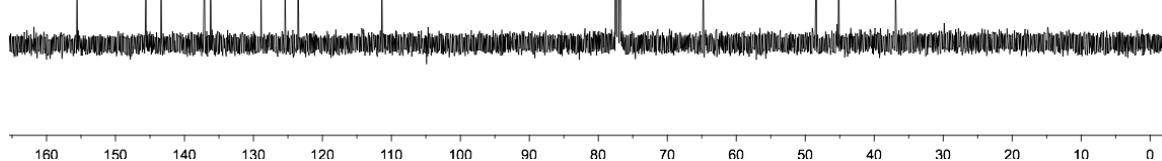
21

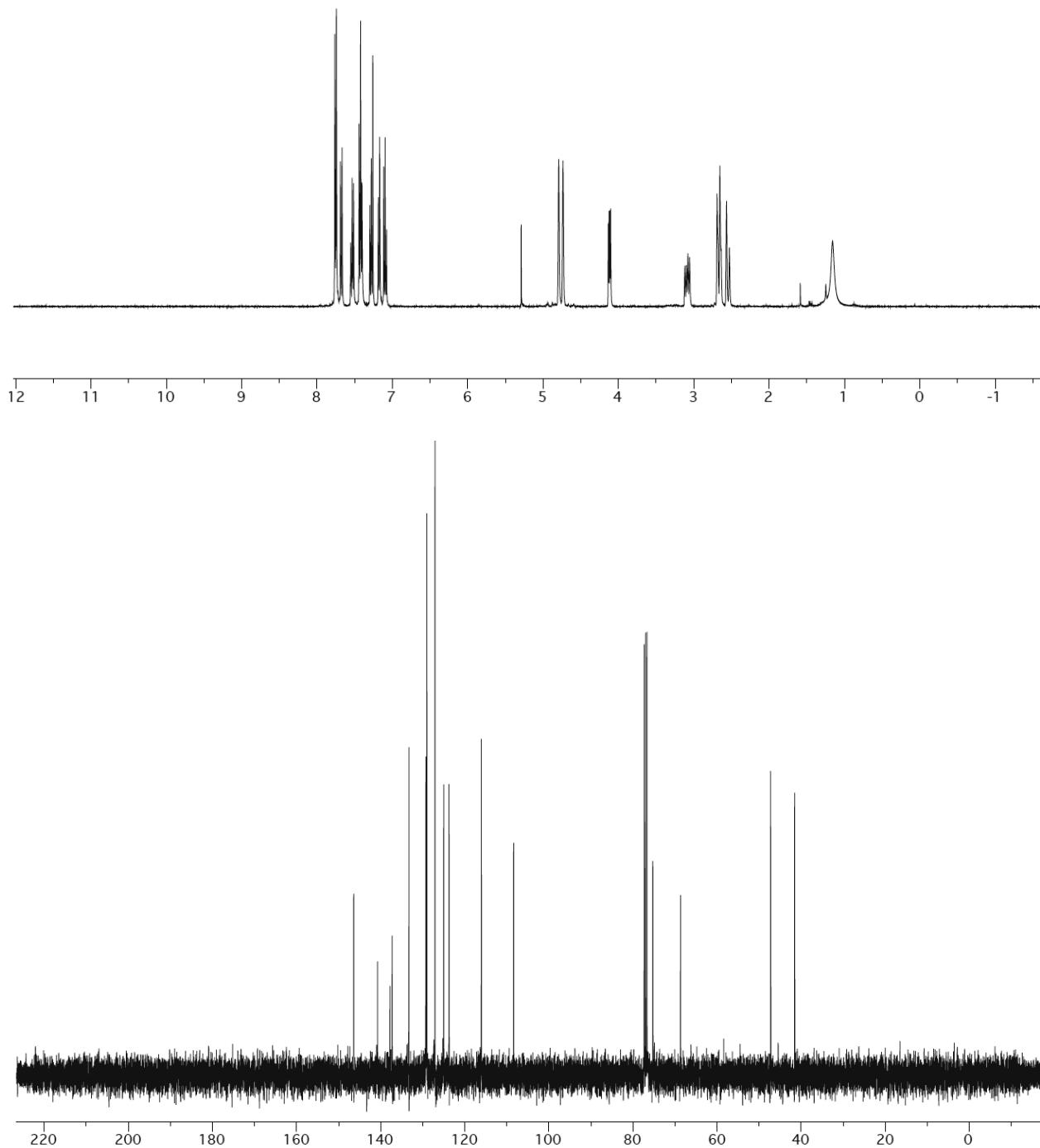
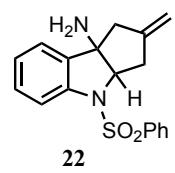


—155.58
—145.59
—143.39
—137.14
—136.22
—128.91
—125.38
—123.54
—111.39

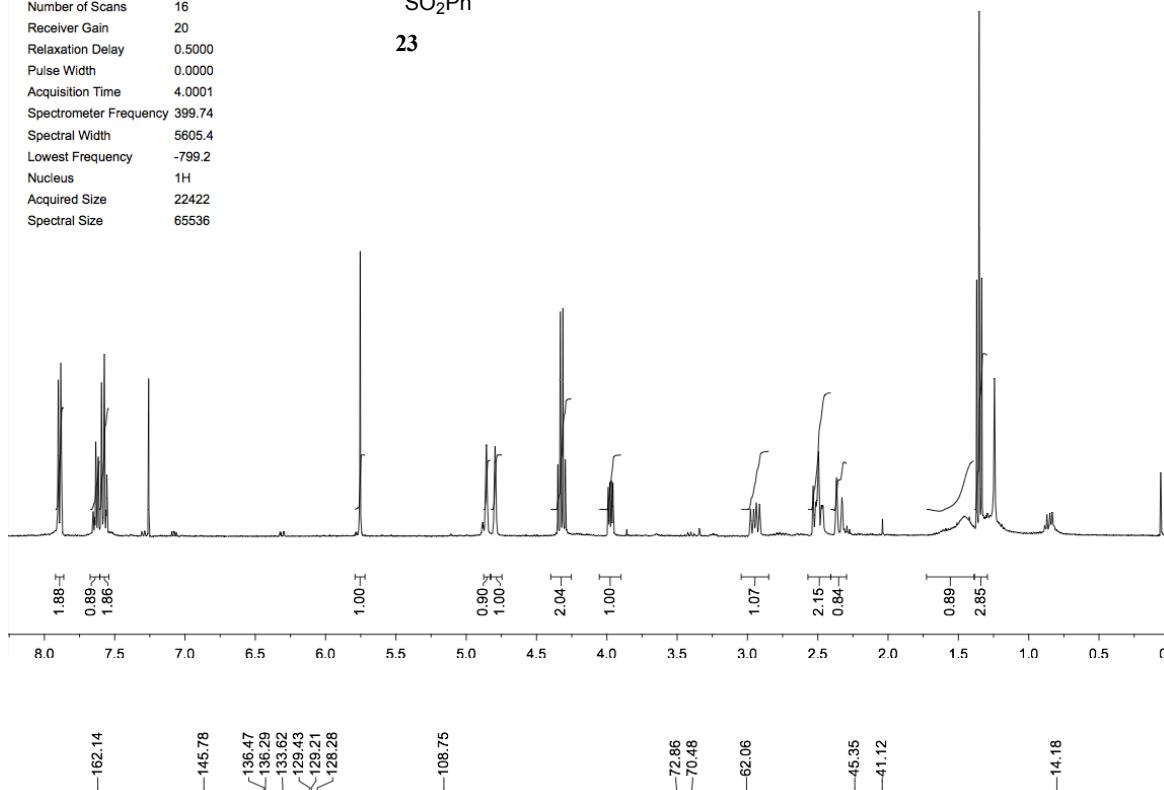
Parameter	Value
Spectrometer	vnmr
Solvent	cdcl ₃
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	448
Receiver Gain	50
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.3005
Spectrometer Frequency	100.52
Spectral Width	24509.8
Lowest Frequency	-1709.7
Nucleus	13C
Acquired Size	31875
Spectral Size	65536

—64.81
—48.40
—45.15
—36.89

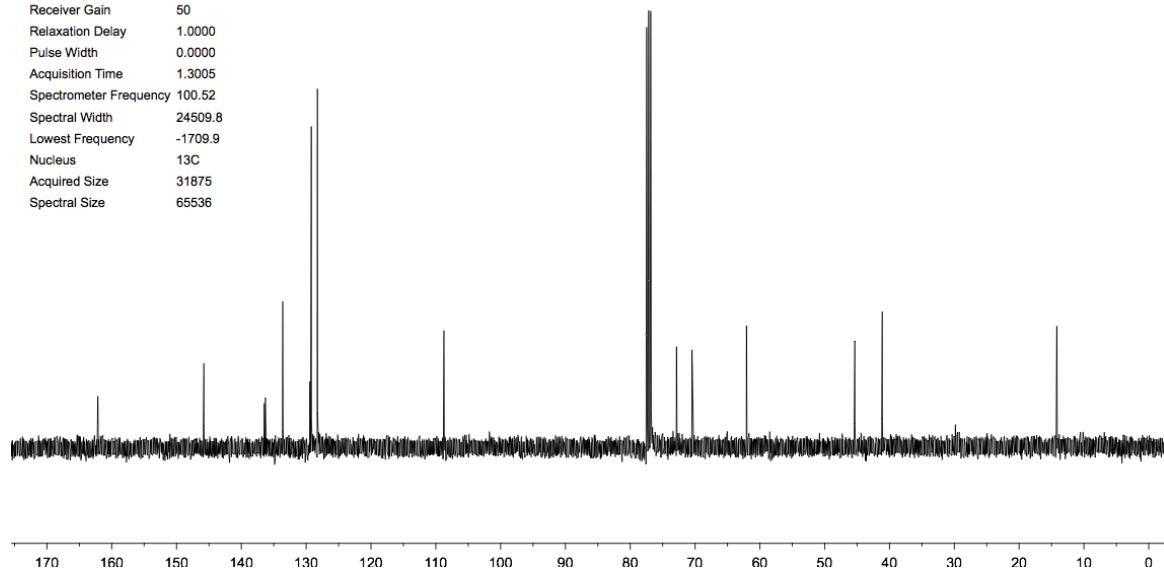




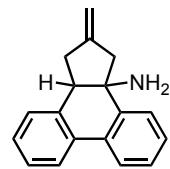
Parameter	Value
Spectrometer	vnmr
Solvent	cdcl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	20
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	4.0001
Spectrometer Frequency	399.74
Spectral Width	5605.4
Lowest Frequency	-799.2
Nucleus	1H
Acquired Size	22422
Spectral Size	65536



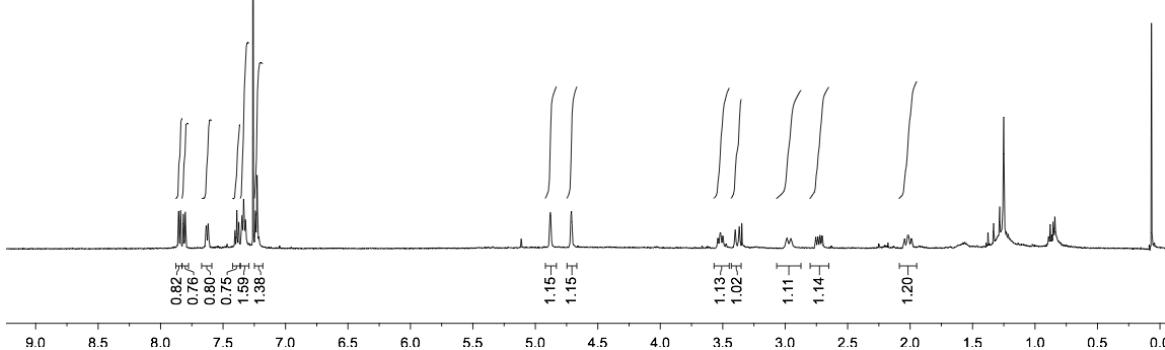
Parameter	Value
Spectrometer	vnmr
Solvent	cdcl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	252
Receiver Gain	50
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.3005
Spectrometer Frequency	100.52
Spectral Width	24509.8
Lowest Frequency	-1709.9
Nucleus	13C
Acquired Size	31875
Spectral Size	65536



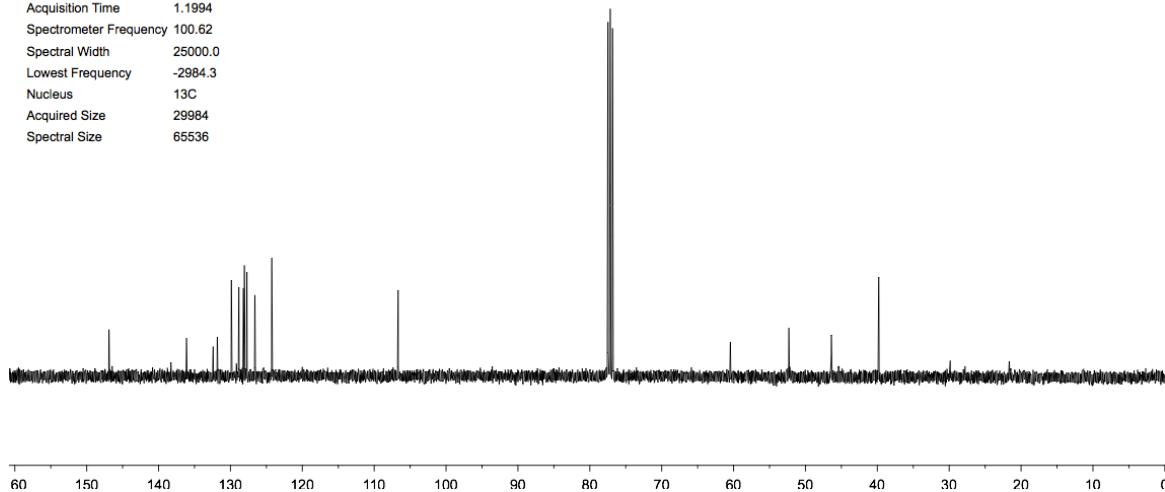
Parameter	Value
Spectrometer	inova
Solvent	CDCl ₃
Temperature	29.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	36
Receiver Gain	40
Relaxation Delay	0.0000
Pulse Width	0.0000
Acquisition Time	4.0000
Spectrometer Frequency	499.75
Spectral Width	8000.0
Lowest Frequency	-1514.2
Nucleus	1H
Acquired Size	32000
Spectral Size	65536



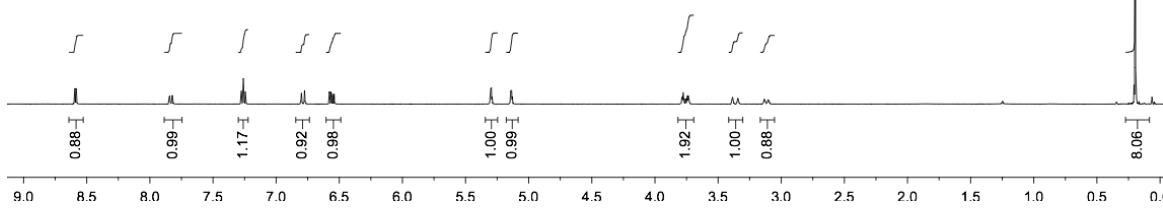
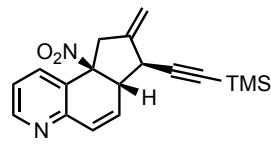
24



Parameter	Value
Spectrometer	mercury
Solvent	CDCl ₃
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	720
Receiver Gain	36
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	1.1994
Spectrometer Frequency	100.62
Spectral Width	25000.0
Lowest Frequency	-2984.3
Nucleus	13C
Acquired Size	29984
Spectral Size	65536



Parameter	Value
Spectrometer	mercury
Solvent	CDCl ₃
Temperature	29.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	0
Receiver Gain	30
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	4.0020
Spectrometer Frequency	400.11
Spectral Width	4997.5
Lowest Frequency	-479.6
Nucleus	1H
Acquired Size	20000
Spectral Size	65536

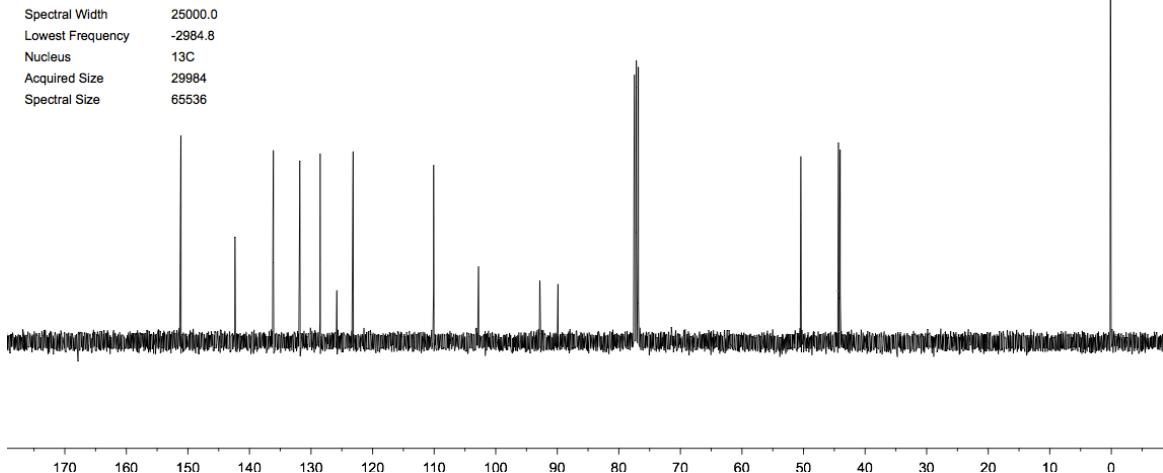


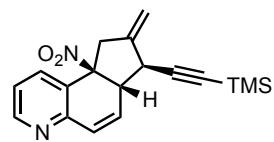
—151.14
—142.35
—136.12
—131.83
—128.52
—125.82
—123.17
—110.08
—102.80
—92.84
—89.89

—50.44
—44.33
—44.06

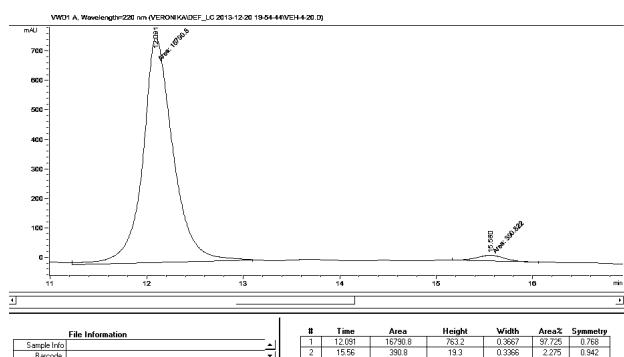
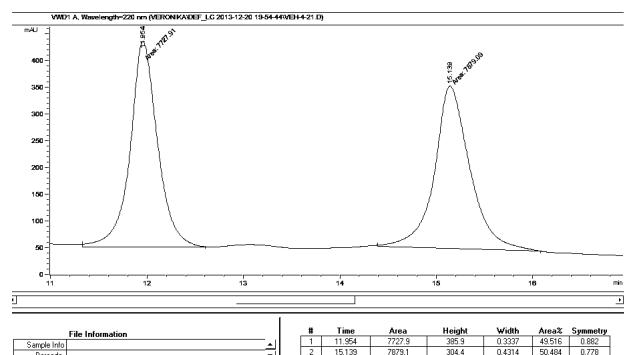
—0.15

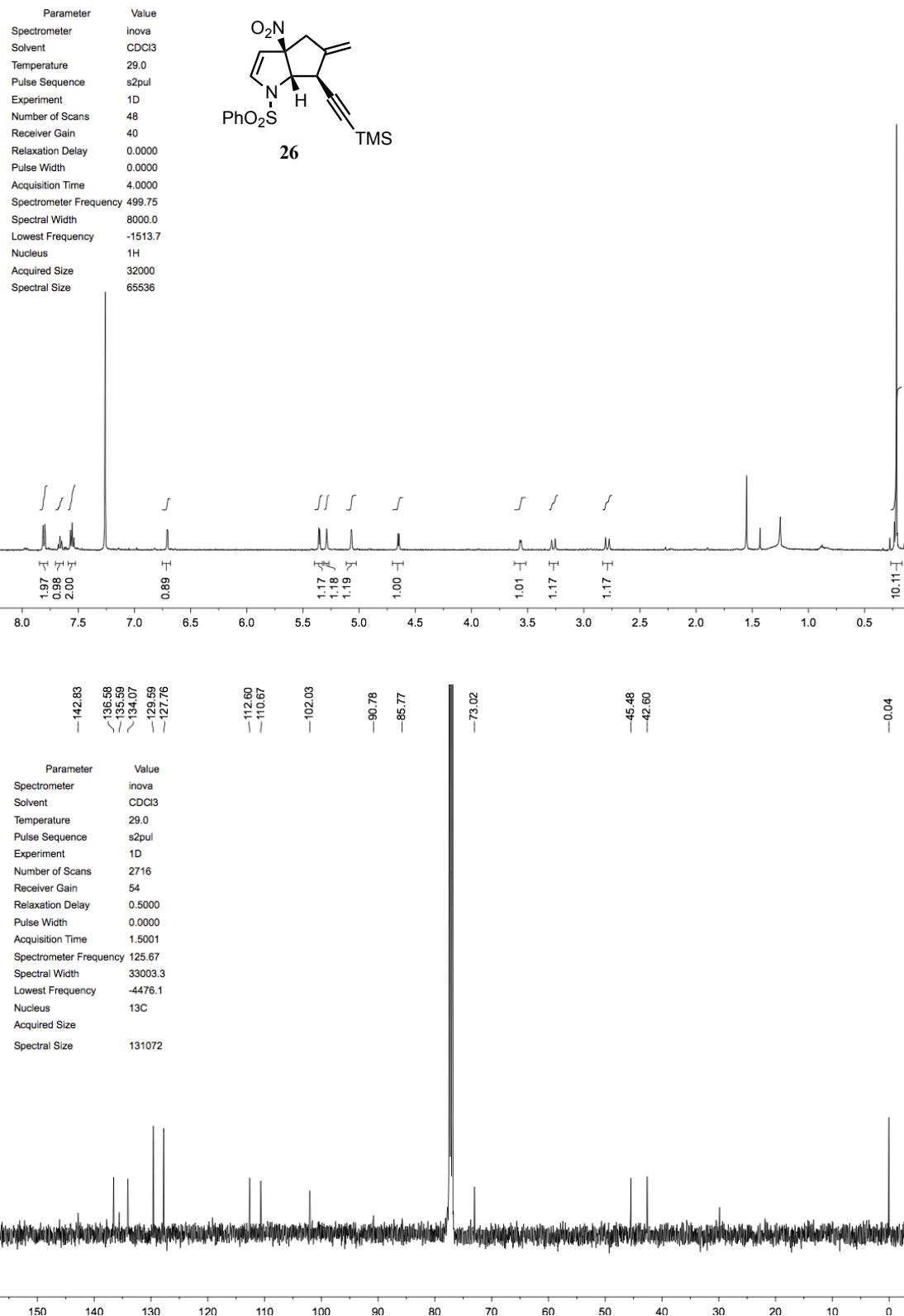
Parameter	Value
Spectrometer	mercury
Solvent	CDCl ₃
Temperature	29.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	0
Receiver Gain	36
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	1.1994
Spectrometer Frequency	100.62
Spectral Width	25000.0
Lowest Frequency	-2984.8
Nucleus	13C
Acquired Size	29984
Spectral Size	65536

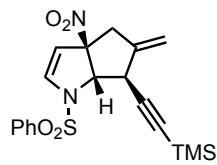




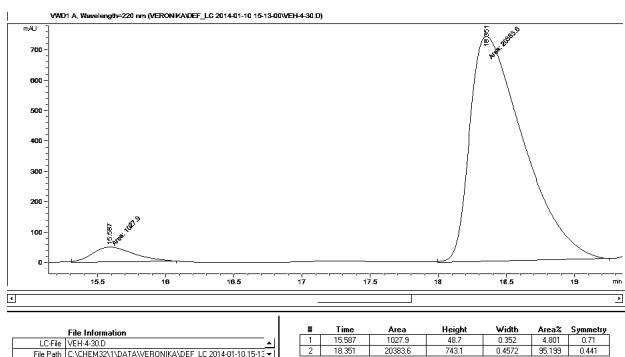
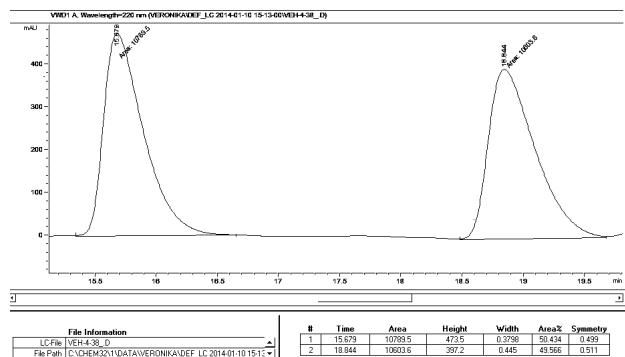
95% ee



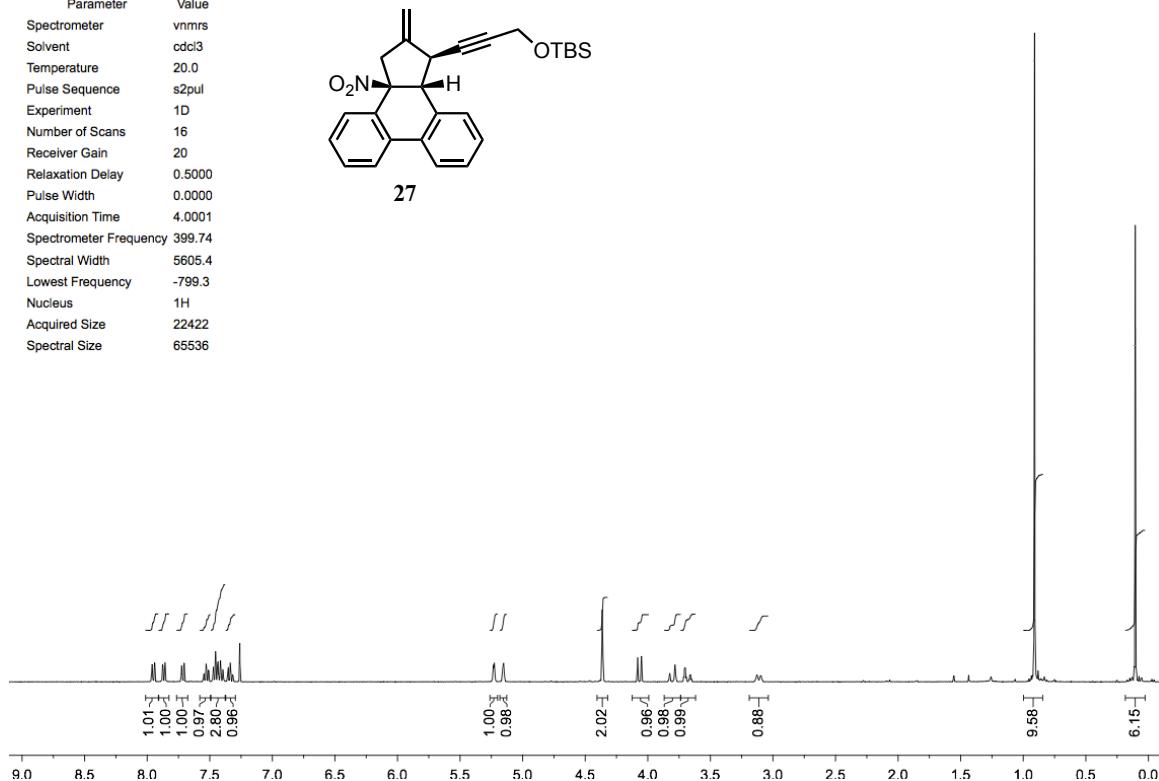
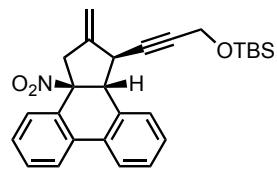




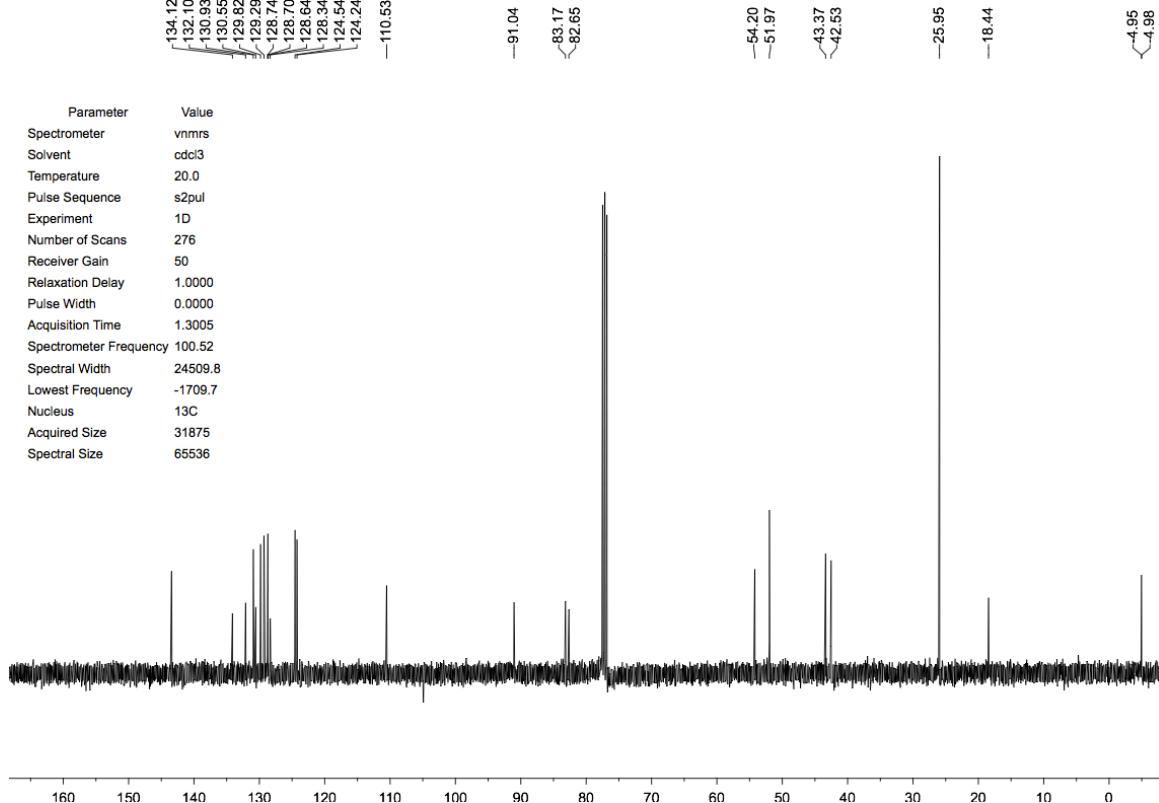
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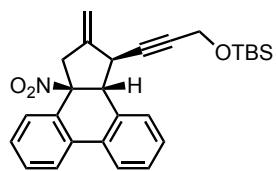


Parameter	Value
Spectrometer	vnmr
Solvent	cdcl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	16
Receiver Gain	20
Relaxation Delay	0.5000
Pulse Width	0.0000
Acquisition Time	4.0001
Spectrometer Frequency	399.74
Spectral Width	5605.4
Lowest Frequency	-799.3
Nucleus	1H
Acquired Size	22422
Spectral Size	65536



Parameter	Value
Spectrometer	vnmr
Solvent	cdcl3
Temperature	20.0
Pulse Sequence	s2pul
Experiment	1D
Number of Scans	276
Receiver Gain	50
Relaxation Delay	1.0000
Pulse Width	0.0000
Acquisition Time	1.3005
Spectrometer Frequency	100.52
Spectral Width	24509.8
Lowest Frequency	-1709.7
Nucleus	13C
Acquired Size	31875
Spectral Size	65536





85% ee

