Azide Trapping of Metallocarbenes: Generation of Reactive C-Acylimines and Domino Trapping with Nucleophiles

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Supporting Information: Experimental procedures, physical data and NMR spectra for compounds

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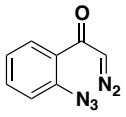
General Information

Reactions were carried out in oven (130 ºC) or flame-dried glassware under a positive argon atmosphere unless otherwise stated. Transfer of anhydrous reagents was accomplished with oven-dried syringes or cannulae. Solvents were distilled before use: acetonitrile (CH_3CN), dichloromethane (DCM) and dichloroethane (DCE) from calcium hydride, toluene (PhMe) from sodium metal, diethyl ether (Et_2O) and tetrahydrofuran (THF) from sodium metal/benzophenone ketyl. Microwave heating was carried out in a Biotage Initiator microwave reactor, using 2-5 mL microwave vials. Reaction temperature was determined through measurement of the vial surface temperature using an infrared sensor, then correction of internal temperature by the unit's processor using a proprietary algorithm. Thin layer chromatography was performed on glass plates pre-coated with 0.25 mm silica gel with fluorescent indicator UV_{254} (Rose Scientific). Flash chromatography columns were packed with 230-400 mesh silica gel (Silacycle). Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded at 300 MHz, 400 MHz, or 500 MHz and coupling constants (*J*) are reported in Hertz (Hz). Carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 100 MHz or 125 MHz. The chemical shifts are reported on

the δ scale (ppm) and referenced to the residual solvent peaks: $CDCl_3$ (7.26 ppm, ^1H; 77.06 ppm, ^{13}C), d_6-DMSO (2.49 ppm, ^1H; 39.5 ppm, ^{13}C) as internal standards.

Important safety precaution: While we did not observe any detonation during the preparation of ***6a-e*** *and their subsequent reactions with the catalyst and nucleophiles, and* ***6b-e*** *are amenable to gram-scale reactions, both azides and diazo groups are potentially explosive and must be handled with care, especially when the (C+O)/N ratio of the molecular formula is less than 3. In particular, for compound* ***6a*** *we recommend limiting the scale of its preparation to ≤ 250 mg, although the procedure given is at a larger scale. Compounds* ***6a-e*** *should be stored under argon at ≤ –20 °C and protected from exposure to light when not in use.*

Compound 6a:



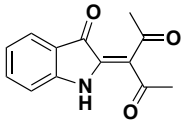
Dichloromethane (35 mL) was added to a reaction flask containing 2-azidobenzoic acid (1.35 g, 8.3 mmol) and the suspension was cooled to 0 °C. Addition of 2,6-lutidine (1.4 mL, 16 mmol) resulted in a homogeneous reaction mixture that was subsequently treated with oxalyl chloride (1.9 mL, 16.4 mmol). The reaction was allowed to stir at 0 °C, with gradual warming to room temperature overnight. Removal of the solvent provided a deep red solid that was immediately dissolved in Et_2O and cooled to -78 °C. Once cooled, the acid chloride solution was transferred via cannula into an ethereal solution of diazomethane (~5 equivalents, prepared from Diazald®) at -78 °C. The reaction was allowed to warm from -78 °C to room temperature overnight. Excess diazomethane was quenched by drop-wise addition of glacial acetic acid. The solution was subsequently washed with an equal volume of water (2x), 1 M NaOH (3x) and brine. The combined organic layers were then dried over $MgSO_4$, filtered and concentrated to provide yellow oil. Purification by flash chromatography, using a 9:1 mixture of hexanes:EtOAc, gave **6a** in 74 % yield. To prevent decomposition the product was stored under Ar in the freezer in a foil wrapped flask. Under these conditions the compound was stable over several months. *Inexperienced users should carry out this reaction at ~ ¼ scale.*

6a: bright yellow crystalline solid; (m.p. = 66-67 ºC), R_f = 0.5 (4:1 hexanes:EtOAc); IR (cast film) 3138, 2199, 2119, 1603, 1590, 1567, 1479, 1445, 1347, 1313, 1286 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.79 (br d, *J* = 6.3 Hz , 1H); 7.50 (ddd, *J* = 1.4, 7.0, 7.0 Hz, 1H), 7.26-7.19 (m, 2H), 6.18 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.9, 137.9, 132.8, 130.2, 129.3, 125.0, 118.9, 58.0; HRMS calc'd for $C_8H_5N_5ONa$ $[M + Na]^+$ 210.0386, found 210.0385.

General Procedure for the reaction of diazo-azide substrate 6a with external nucleophiles.

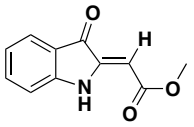
A solution of diazo-azide **6a** in toluene (0.04 M) was added via syringe pump over 1h to a solution of the nucleophile **8** (2 equiv, 0.04 M in toluene) and $Cu(hfacac)_2$ (10 mol %) at room temperature. These reactions were carried out using 50–70 mg (0.27–0.37 mmol) of **6a**. The reaction mixture turned dark brown over the course of the addition. Once the addition was complete, the reaction was monitored by TLC for consumption of the diazo-azide starting material. The reaction was typically complete within 15 minutes of the conclusion of the syringe pump addition. In most cases, the reaction mixture was washed with an equivalent volume of 0.5 M aqueous solution of K_2CO_3 and brine. The combined organic layers were then dried over $MgSO_4$, filtered, concentrated under reduced pressure and purified by flash chromatography. One exception, for the formation of **7f** using Danishefsky's diene (**8g**) as the nucleophile, gave better results by evaporating the crude reaction mixture followed by direct column chromatography.

Compound 7a



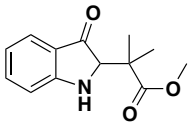
Isolated as bright red needles in 78 % yield; m.p. = 219-221 ºC; R_f = 0.36 (orange spot, 4:1 hexanes:EtOAc); IR (KBr pellet) 3302, 2924, 1715, 1683, 1638, 1615, 1573, 1465 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 10.21 (br s, 1H), 7.67-7.66 (m, 1H), 7.53 (ddd, *J* = 1.4, 7.4, 8.0 Hz, 1H), 7.04 (dt, *J* = 0.8, 7.4 Hz, 1H), 6.98-6.96 (m, 1H), 2.59 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.4, 197.6, 188.6, 152.9, 140.2, 137.7, 125.6, 122.6, 119.4, 116.8, 112.2, 32.3, 28.9; HRMS calc'd for $C_{13}H_{11}NO_3$ $[M]^+$ 229.0739, found 229.0714.

Compound 7b:



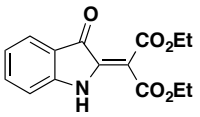
Isolated as orange/red needles in 96 % yield; m.p. = 183-185 ºC; R_f = 0.51 (orange spot, 7:3 hexanes:EtOAc); IR (cast film) 3362, 3057, 2997, 1720, 1662, 1606, 1468, 1309, 1209 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.85 (br s, 1H), 7.69 (br d, *J* = 7.4 Hz, 1H), 7.51 (app dt, *J* = 1.3, 7.7 Hz, 1H), 7.00 (app dt, *J* = 0.5, 7.5 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 5.89 (s, 1H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 186.8, 169.2, 152.8, 145.2, 137.4, 125.5, 121.6, 120.3, 111.6, 92.6, 51.8; HRMS calc'd for $C_{11}H_9NO_3$ $[M]^+$ 203.0582, found 203.0609. Anal. cal'd for $C_{11}H_9NO_3$: C: 65.02, H: 4.46, N: 6.89, found C: 65.04, H: 4.63 N: 6.62. Spectral data were consistent with previously reported values (Okuma, K.; Matsunaga, N.; Nagahora, N.; Shioji, K.; Yokomuri, Y. *Chem. Commun.* **2011**, 5822–5824; note that these authors reported an X-ray crystal structure for **7b** that confirmed the *Z*-geometry).

Compound 7c:



Isolated as a yellow oil in 93 % yield; R_f = 0.24 (yellow spot, 4:1 hexanes:EtOAc); IR (cast film) 3364, 2980, 2951, 1726, 1692, 1620, 1489, 1471 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.2 Hz, 1H), 7.47-7.43 (m, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 6.85-6.82 (m, 1H), 4.95 (br s, 1H), 4.04 (d, *J* = 3.0 Hz, 1H), 3.77 (s, 3H), 1.46 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.4, 176.9, 161.1, 137.0, 124.3, 122.6, 119.1, 112.5, 67.7, 52.3, 46.3, 20.9, 19.6; HRMS calc'd for $C_{13}H_{15}NO_3$ $[M]^+$ 233.1052, found 233.1045

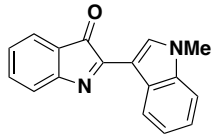
Compound 7d:



Isolated as red/orange needles in 83 % yield; m.p. = 118-120°C; R_f = 0.50 (orange spot, 3:7 EtOAc:hexanes); IR (cast film) 3379, 2982, 2935, 1730, 1688, 1690, 1609, 1482, 1283, 1195,

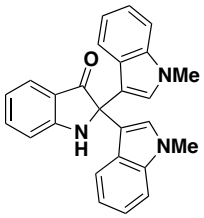
1145, 754 cm^{-1}; ^1H NMR (300MHz, $CDCl_3$) δ 9.17 (br s, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.48 (app t, *J* = 7.8 Hz, 1H), 6.98 (app t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 8.1 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.6, 166.1, 164.7, 152.2, 142.4, 137.5, 125.6, 122.1, 119.9, 111.8, 102.2, 62.0, 61.7, 14.1, 13.9; HRMS calc'd for $[C_{15}H_{15}NO_5 + Na]^+$ 312.0842, found 312.0837.

Compound 7e:



Isolated as purple solid with blue luster in 53 % yield; m.p. = 225-226 °C; R_f = 0.52 (purple spot, 3:7 EtOAc:hexanes); IR(cast film) 3051, 2924, 1719, 1610, 1558, 1457, 1368, 1291, 1157, 1141, 871, 771 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.61 (m, 1H), 8.42 (s, 1H), 7.51 (m, 2H), 7.39 (m, 4H), 7.13 (ddd, *J* = 0.8, 7.5, 7.5 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.1, 163.7, 158.2, 137.6, 137.0, 136.2, 127.1, 126.1, 124.5, 123.8, 123.5, 122.9, 122.5, 121.1, 109.8, 106.8, 33.6; HRMS calc'd for $[C_{17}H_{12}N_2O + H]^+$ 261.1022, found 261.1023.

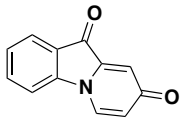
Bis(indole) adduct:



Upon extended stirring with N-methylindole **8f**, minor amounts of a 2:1 adduct was observed as an insoluble precipitate: isolated as light green crystals; m.p. > 250 °C (dec.), R_f = N.D. (3:7 EtOAc:hexanes; insoluble in variety of solvents, minimal solubility in cold DMSO); IR (microscope) 3420, 3048, 2941, 1696, 1619, 1547, 1537, 1332, 746 cm^{-1}; ^1H NMR (500 MHz, d_6-DMSO) δ 8.13 (s, 1H), 7.49 (m, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.08 (m, 2H), 7.08 (br s (buried in m), 2H), 6.92 (d, *J* = 8.5 Hz, 1H), 6.86 (ddd, *J* = 1.0, 7.5, 7.5 Hz, 2H), 6.71 (ddd, *J* = 0.5, 6.9, 6.9 Hz, 1H), 3.70 (s, 6H); ^{13}C NMR (125 MHz, d_6-DMSO) δ 201.5, 161.0, 138.0, 137.8, 128.7, 126.4, 125.0, 121.7, 121.1, 119.0, 118.1,

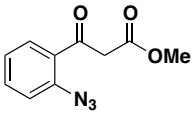
117.6, 113.5, 112.4, 110.3, 67.8, 32.8; HRMS cal'd for $[C_{26}H_{21}N_3O + Na]^+$ 414.1582, found 414.1575.

Compound 7f:



Isolated as a bright orange powder in 75 % yield; m.p. = 213-214 ºC; R_f = 0.18 (red spot, 9:1 EtOAc:MeOH); IR (KBr pellet) 3116, 3064, 1710, 1669, 1644, 1607, 1595, 1554, 1493, 1470, 1329, 1310 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.89 (app br d, *J* = 7.5 Hz, 2H), 7.75 (app dt, *J* = 1.3, 8.2 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.37 (dt, *J* = 0.6, 7.6 Hz, 1H), 7.00 (d, *J* = 2.0 Hz, 1H), 6.61 (dd, *J* = 2.0, 8.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.9, 180.6, 147.1, 139.4, 137.2, 130.5, 126.4, 126.2, 123.2, 118.9, 116.3, 110.4. HRMS calc'd for $C_{12}H_7NO_2$ $[M]^+$ 197.0477, found 197.0470.

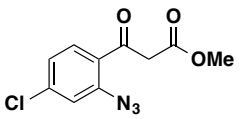
Compound 9a:



Dichloromethane (10 ml) was added to a conical flask containing 2-azidobenzoic acid (350 mg, 2.2 mmol) and the suspension was cooled to 0 °C before addition of methyl acetate (175 μL, 2.2 mmol) and trichloroacetyl chloride (290 μL, 2.6 mmol). This solution was slowly transferred *via* cannula to a suspension of NaH (60 % dispersion in oil, 105 mg, 2.6 mmol) in DCM (3 mL) at 0 ºC. After stirring at 0 ºC for 15 min the solution was cooled to -45 ºC before the addition of 1-methylimidazole (205 μL, 2.6 mmol). The solution was stirred for an additional 10 minutes at -45 ºC before slowly adding $TiCl_4$ (825 μL, 7.5 mmol) followed by NBu_3 (2 mL, 8.4 mmol). The dark red/brown solution was kept at -45 °C for 30 minutes before being warmed to 0 °C and subsequently quenched with water (10 mL). The organic layer was separated and the aqueous washed 3x with equal portions of Et_2O. The combined organic layers were washed with an equivalent volume of water and brine, dried over $MgSO_4$, filtered, and concentrated under

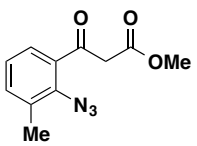
reduced pressure. The crude product was purified by flash chromatography (silica gel, 1:4 hexanes:EtOAc) to afford 322 mg (68 %) of **9a** as a pale yellow oil: R_f = 0.60 (7:3 hexanes:EtOAc); IR (cast film) 2953, 2128, 1746, 1680, 1650, 1627, 1480, 1449, 1289, 1254, 1203 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) *as a 4:1 mixture of keto:enol tautomers* δ(keto) 7.84 (ddd, *J* = 0.5, 1.6, 7.8 Hz, 1H), 7.59 (ddd, *J* = 1.7, 7.3, 8.1 Hz, 1H), 7.27-7.22 (m, 2H), 4.11 (s, 2H), 3.77 (s, 3H); δ(enol) 7.78 (dd, *J* = 1.6, 7.8 Hz, 1H), 7.48 (ddd, *J* = 1.6, 7.3, 8.1 Hz, 1H), 7.27-7.22 (m, 2H), 5.88 (s, 1H), 3.84 (s, 3H) *enol proton not detected*; ^{13}C NMR (125 MHz, $CDCl_3$) *as a mixture of keto:enol tautomers* δ 192.9, 173.4, 168.7, 168.1, 139.1, 137.9, 133.9, 131.6, 131.1, 129.9, 129.4, 125.7, 125.0, 124.8, 119.2, 119.1 92.6, 52.3, 51.6, 49.6; HRMS calc'd for $C_{10}H_9N_3O_3Na$ $[M + Na]^+$ 242.0536, found 242.0536.

Compound 9b:



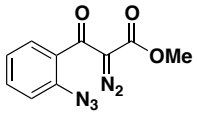
Compound **9b** was prepared analogously to the procedure described for Compound **9a**, using 2-azido-4-chlorobenzoic acid as the starting material in place of 2-azidobenzoic acid. Isolated as a yellow oil in 76 % yield: R_f = 0.70 (7:3 hexanes:EtOAc); IR (cast film) 2953, 2115, 1745, 1680, 1589, 1249, 807 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *as a 5:2 mixture of keto:enol tautomers* δ(keto) 7.66 (dd, *J* = 0.4, 8.4 Hz, 1H), 7.10-7.04 (m, 2H), 3.96 (s, 2H), 3.64 (s, 3H); δ(enol) 7.60(dd, *J* = 0.8, 8.0 Hz, 1H), 7.10-7.04 (m, 2H), 5.79 (s, 1H), 3.69 (s, 3H) *enol proton not detected*; ^{13}C NMR (125 MHz, $CDCl_3$) *as a mixture of keto:enol tautomers* δ 191.4, 173.2, 167.8, 167.0, 140.4, 139.8, 139.0, 137.2, 132.4, 130.9, 127.4, 125.3, 125.0, 123.7, 119.1(2x), 92.7, 52.2, 51.5, 49.3; HRMS calc'd for $C_{10}H_8{}^{35}ClN_3O_3Na$ $[M + Na]^+$ 276.0146, found 276.0144.

Compound 9c:



Compound **9c** was prepared analogously to the procedure described for Compound **9a**, using 2-azido-3-methylbenzoic acid as the starting material in place of 2-azidobenzoic acid. Isolated as a light yellow oil in 56 % yield: R_f = 0.63 (7:3 hexanes:EtOAc); IR (cast film) 2955, 2110, 1740, 1680, 1601, 1251, 807 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *3:1 mixture of keto:enol tautomers* δ(keto) 7.53 (br d, *J* = 7.9 Hz, 1H), 7.34-7.30 (m, 1H), 7.14 (app t, *J* = 7.5 Hz, 1H), 4.00 (s, 2H), 3.71 (s, 3H), 2.37 (br s, 3H); δ(enol) 7.33-7.30 (m, 1H), 7.22 (br d, *J* = 7.6 Hz 1H), 7.09 (app t, *J* = 7.7 Hz, 1H), 5.49 (s, 1H), 3.78 (s, 3H), 2.32 (s, 3H) *enol proton not detected*; ^{13}C NMR (125 MHz, $CDCl_3$) *as a mixture of keto:enol tautomers* δ 193.7, 173.0, 170.9, 167.7, 137.2, 135.9, 135.3, 133.7, 133.1, 132.9, 131.6, 128.7, 128.0, 127.7, 125.4, 92.2, 52.9, 52.4, 51.5, 48.4, 40.5, 18.1; HRMS calc'd for $C_{11}H_{11}N_3O_3Na$ $[M + Na]^+$ 256.0693, found: 256.0695

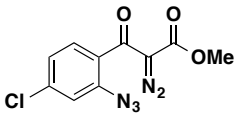
Compound 6b:



Triethylamine (715 μL, 5.1 mmol) was added to a stirred solution of ketoester **9a** (1.02 g, 4.65 mmol) in CH_3CN (19 ml). Tosyl azide (916 mg, 4.65 mmol) in CH_3CN (9 mL) was transferred *via* cannula into the flask and the reaction was left to stir overnight. Concentration under reduced pressure followed by purified *via* flash chromatography (silica gel, 17:3 hexanes:EtOAc) resulted in a quantitative yield of **6b** (1.14 g) as a pale yellow solid. To prevent decomposition the product was stored under Ar in the freezer in a foil wrapped flask. Under these conditions the compound was stable over several months.

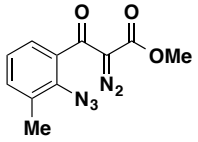
6b: m.p. = 76-78 ºC; R_f = 0.54 (7:3 hexanes:EtOAc); IR (cast film) 2956, 2132, 1729, 1700, 1633, 1597, 1486, 1446, 1438, 1334, 1316, 1287 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.54-7.52 (m, 1H), 7.34 (dd, *J* = 1.5, 7.8 Hz, 1H), 7.28-7.21 (m, 2H), 3.79 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.7, 160.9, 137.7, 137.5, 131.9, 130.3, 128.4, 124.8, 118.3, 52.3; HRMS calc'd for $C_{10}H_7N_5O_3$ $[M]^+$ 245.0549, found 245.0549.

Compound 6d:



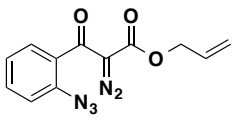
Compound **6d** was prepared analogously to the procedure described for Compound **6b**, using compound **9b** as the starting material in place of Compound **9a**. Isolated as a light orange oil in 94 % yield: R_f = 0.65 (7:3 hexanes:EtOAc); IR (cast film) 2956, 2113, 1729, 1633, 1591, 1318, 907 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25-7.23 (m, 1H), 7.17-7.15 (m, 2H), 3.76 (s, 3H); ^{13}C NMR (125MHz, $CDCl_3$) δ 184.6, 160.7, 139.2, 137.8, 129.7, 128.7, 125.1, 118.6, 52.4 (diazoketone ^{13}C signal was not detected due to broadening); HRMS calc'd for $C_{10}H_6{}^{35}ClN_5O_3Na$ $[M + Na]^+$ 302.0051, found: 302.0054.

Compound 6e:



Compound **6e** was prepared analogously to the procedure described for Compound **6b**, using compound **9c** as the starting material in place of Compound **9a**. Isolated as yellow oil in 88 % yield: R_f = 0.59 (7:3 hexanes:EtOAc); IR (cast film) 2956, 2122, 1725, 1630, 1455, 1306, 1200, 1126, 750 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31-7.29 (m, 1H), 7.18-7.16 (m, 2H), 3.79 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.2, 160.8, 135.5, 133.7, 132.5, 132.4, 126.1, 125.4, 52.4, 17.9 (diazoketone ^{13}C signal was not detected due to broadening); HRMS calc'd for $C_{11}H_9N_5O_3Na$ $[M+Na]^+$ 282.0598, found: 282.0598.

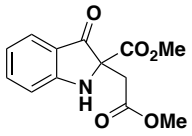
Preparation of **Compound 6c:**



Dichloromethane (10 ml/ 350 mg acid) was added to a conical flask containing 2-azido benzoic acid (1.0-1.2 g, 6.3-7.5 mmol) and the suspension was cooled to 0 °C before addition of allyl acetate (1.0 equiv) and trichloroacetyl chloride (1.2 equiv). This solution was slowly transferred via cannula to a suspension of NaH (1.2 equiv) in DCM (3 mL/350 mg acid) at 0 ºC. After stirring at 0 ºC for 15 min the solution was cooled to -45 ºC before the addition of 1-methylimidazole (1.2 equiv). The solution was stirred for an additional 10 minutes at -45 ºC before slowly adding $TiCl_4$ (3.4 equiv) followed by NBu_3 (4.0 equiv). The dark red/brown solution was kept at -45 °C for 30 minutes before being warmed to 0 °C and subsequently quenched with water (10 mL/ 350 mg acid). The organic layer was separated and the aqueous washed 3x with equal portions of DCM. The combined organic layers were washed with an equivalent volume of water and brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was partially purified by flash chromatography to afford orange oil whose R_f was about 0.7 (7:3 hexanes:EtOAc). The orange oil was concentrated and added to a stirred solution of triethylamine (1.2 equiv) in CH_3CN (20 mL/1.2 equiv). Tosyl azide (1.0 equiv) in CH_3CN (9 mL/1.0 equiv) was transferred via cannula into the flask and the reaction was left to stir overnight. Concentration under reduced pressure followed by purification via flash chromatography (silica gel, 8:2 hexanes:EtOAc→7:3 hexanes:EtOAc slowly added in gradient) furnished **6c** as a yellow oil in 46 % yield (from starting 2-azidobenzoic acid).

6c: R_f = 0.59 (7:3 hexanes:EtOAc); IR (cast film) 2956, 2122, 1725, 1630, 1455, 1306, 1200, 1126, 750 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.45 (ddd, *J* = 1.7, 8.0, 8.0 Hz, 1H), 7.31 (ddd, *J* = 0.6, 1.7, 8.0 Hz, 1H), 7.18-7.16 (m, 2H), 5.80 (app tdd, *J* = 5.8, 10.4, 17.2 Hz 1H), 5.22 (app tdd, *J* = 1.5, 1.5, 17.2 Hz, 1H), 5.21 (app tdd, *J* = 1.3, 1.3, 10.4 Hz, 1H), 4.62-4.60 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$,) δ 185.6, 160.2, 137.7, 131.9, 131.3, 130.4, 128.5, 124.7, 119.0, 118.3, 65.9 (diazoketone ^{13}C signal was not observed due to broadening); HRMS calc'd for $C_{12}H_9N_5O_3Na$ $[M+Na]^+$ 294.0598, found: 294.0594.

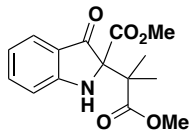
Representative procedure for reaction of 6b-e with nucleophiles: Compound 7g:



A solution of diazo-azide **6b** in toluene (0.04 N) was added to a solution of 1-methoxy-1-trimethoxysiloxyethene **8a** (2 equiv, 0.04 N in toluene) and $Cu(hfacac)_2$ (10 mol %) at reflux *via* syringe pump over 1h. The reaction mixture turned dark brown over the course of the addition. Once the addition was complete, the reaction was monitored by TLC for consumption of the diazo-azide starting material. Upon consumption of **6b**, the reaction mixture was cooled to room temperature and then washed with an equivalent volume of 0.5 M aqueous solution of K_2CO_3 and brine. The combined organic layers were then dried over $MgSO_4$, filtered, concentrated under reduced pressure and purified by flash chromatography (silica gel, 4:1 hexanes:EtOAc) to yield 89 % of **7g** as a yellow oil: R_f = 0.3 (yellow spot, 7:3 hexanes:EtOAc); IR (cast film) 3377, 2955, 1743, 1617, 1488, 1469, 1214 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.60 (br d, *J* = 7.8 Hz, 1H), 7.52-7.48 (m, 1H), 6.97 (dd, *J* = 0.7, 7.5 Hz, 1H), 6.91-6.88 (m, 1H), 5.61 (br s, 1H), 3.74 (s, 3H), 3.72 (s, 3H), 3.55 (d, *J* = 17.4 Hz, 1H), 2.57 (d, *J* = 17.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.0, 171.5, 167.8, 161.8, 138.0, 125.4, 120.3, 119.2, 113.3, 71.5, 53.6, 52.2, 39.6; HRMS calc'd for $C_{13}H_{13}NO_5$ $[M]^+$ 263.0794, found: 263.0794.

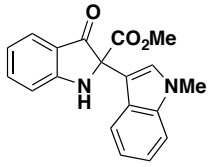
Similar procedures were followed in the preparation of **7h-p**. These reactions were carried out using 250 mg (0.92 mmol) of **6b**. Reactions with **6c**-**e** were run at a similar scale.

Compound 7h:



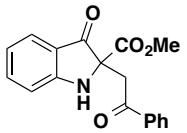
Isolated as a yellow oil in 48 % yield: R_f = 0.38 (yellow spot, 7:3 hexanes:EtOAc); IR (cast film) 3373, 2994, 2954, 1743, 1617, 1488, 1471, 1281, 1252, 1196, 1149 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.60 (br d, *J* = 7.7 Hz, 1H), 7.49 (ddd, *J* = 1.3, 7.1, 7.7 Hz, 1H), 6.95 (br d, *J* = 8.3 Hz, 1H), 6.88 (dt, *J* = 0.8, 7.4 Hz, 1H), 5.90 (s, 1H), 3.76 (s, 3H), 3.67 (s, 3H), 1.59 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.8, 176.5, 168.4, 160.9, 137.6, 124.9, 121.3, 119.9, 112.8, 75.4, 53.3, 52.4, 49.6, 21.0, 20.1; HRMS calc'd for $C_{15}H_{17}NO_5$ $[M]^+$ 291.1107, found 291.1106.

Compound 7i:



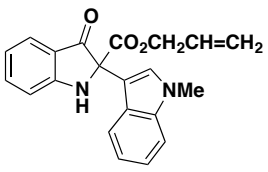
Isolated as a yellow solid in 72 % yield: m.p. = 80–81 °C; R_f = 0.31 (yellow spot, 7:3 hexanes:EtOAc); IR (cast film) 3366, 3051, 1744, 1702, 1616, 1485, 1293, 742 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.56 (app dt, *J* = 1.0, 8.0 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.30 (s, 1H), 7.26 (app dt, *J* = 0.5, 8.0 Hz, 1H), 7.14 (app dt, *J* = 0.5, 7.5 Hz, 1H), 7.02 (d, *J* = 8.5 Hz, 1H), 6.96 (app t, *J* = 8.0 Hz, 1H), 5.77 (br s, 1H), 3.84 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.2, 169.1, 161.0, 137.9, 137.4, 128.0 126.0, 125.4, 122.3, 120.4, 120.0, 119.9, 119.5, 113.6, 109.8, 109.8, 72.4, 53.8, 32.9; HRMS calc'd for $C_{19}H_{17}N_2O_3$ $[M + H]^+$ 321.1234, found: 321.1233.

Compound 7j:



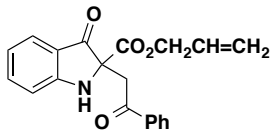
Isolated as a yellow oil in 71 % yield: R_f = 0.48 (yellow spot, 7:3 hexanes:EtOAc); IR (cast film) 3379, 2953, 2919, 1745, 1702, 1619, 1487, 1221, 753 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.67-7.62 (m, 2H), 7.56-7.50 (m, 3H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.93 (app t, *J* = 8.0 Hz, 1H), 5.81 (br s, 1H), 4.37 (d, *J* = 18.0 Hz, 1H), 3.77 (s, 3H), 3.22 (d, *J* = 18.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.7, 195.0, 168.1, 162.0, 138.1, 135.8, 133.9, 128.8, 128.3, 125.4, 120.1 119.1, 113.2, 71.9, 53.6, 44.8; HRMS calc'd for $C_{18}H_{16}NO_4$ $[M + H]^+$ 310.1074, found: 310.1074

Compound 7k:



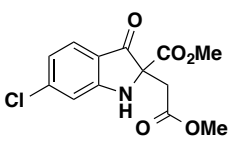
Isolated as yellow powder in 63% yield: m.p. 92 °C (dec.); R_f = 0.43 (yellow spot, 7:3 hexanes:EtOAc); IR (cast film) 3371, 3051, 2919, 1742, 1703, 1615, 1485, 1225, 743 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.72 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.52 (ddd, *J* = 1.3, 7.1, 8.3 Hz, 1H), 7.32-7.30 (m, 2H), 7.26 (ddd, *J* = 1.1, 7.0, 8.2 Hz, 1H), 7.12 (ddd, *J* = 1.1, 7.0, 8.0 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 1H), 6.94 (app t, *J* = 7.8 Hz, 1H), 5.88 (app tdd, *J* = 5.6, 10.5, 17.2 Hz, 1H), 5.83 (br s, 1H), 5.29 (app tdd, *J* = 1.5, 1.5, 17.2 Hz, 1H), 5.22 (app tdd, *J* = 1.2, 1.2, 10.4 Hz, 1H), 4.76 (app tdd, *J* = 1.5, 5.5, 13.5 Hz, 1H), 4.71 (app tdd, *J* = 1.5, 5.5, 13.5 Hz, 1H), 3.73 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 194.7, 168.3, 161.0, 137.8, 137.4, 131.2, 128.1, 126.0, 125.4, 122.2, 120.2, 119.9(2x), 119.8, 119.1, 113.5, 109.8, 109.7, 72.5, 67.1, 32.9; HRMS calc'd for $C_{21}H_{19}N_2O_3$ $[M + H]^+$ 347.1390, found: 347.1393.

Compound 7l:



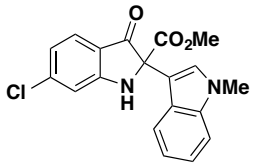
Isolated as yellow oil in 52 % yield: R_f = 0.55 (yellow spot, 7:3 hexanes:EtOAc); IR (cast film) 3379, 2918, 1744, 1702, 1619, 1487, 1220, 753 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.01-7.99 (m, 2H), 7.66 (br d, *J* = 7.7 Hz, 1H), 7.63 (m, 1H) 7.53-7.50 (m, 3H), 7.00 (d, *J* = 8.5 Hz, 1H), 6.92 (app t, *J* = 8.0 Hz, 1H), 5.85 (app tdd, *J* = 5.5, 10.5, 17.2 Hz, 1H), 5.85 (buried br s, 1H), 5.28 (app tdd, *J* = 1.5, 1.5, 17.2 Hz, 1H), 5.20 (app tdd, *J* = 1.3, 1.3, 10.5 Hz, 1H), 4.68 (app tdd, *J* = 1.0, 5.5, 13.0 Hz, 1H), 4.63 (app tdd, *J* = 1.0, 5.5, 13.0 Hz, 1H), 4.40 (d, *J* = 18.2 Hz, 1H), 3.22 (d, *J* = 18.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.6, 195.0, 167.3, 162.0, 138.0, 135.9, 133.9, 131.3, 128.8, 128.2, 125.4, 120.0, 119.1, 118.6, 113.2, 72.0, 66.9, 44.8; HRMS calc'd for $C_{20}H_{18}NO_4$ $[M + H]^+$ 336.1230, found: 336.1230.

Compound 7m:



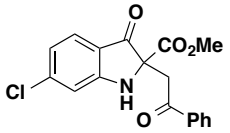
Isolated as a light yellow oil in 73 % yield: R_f = 0.40 (yellow spot, 7:3 hexanes:EtOAc); IR (cast film) 3368, 2955, 1746, 1716, 1612, 1438, 1214, 922 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 1.9 Hz, 1H), 6.90 (dd, *J* = 1.6, 8.2 Hz, 1H), 5.72 (br s, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.58 (d, *J* = 18.0 Hz, 1H), 2.62 (d, *J* = 18.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.6, 171.4, 167.5, 161.9, 144.7, 126.4, 121.2, 117.7, 113.1, 71.9, 53.8, 52.3, 39.5; HRMS calc'd for $C_{13}H_{13}{}^{35}ClNO_5$ $[M + H]^+$ 298.0477, found: 298.0474

Compound 7n:



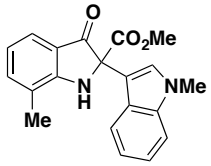
Isolated as bright yellow crystals in 76 % yield: m.p. = 194-195°C; R_f = 0.35 (yellow spot, 7:3 hexanes:EtOAc); IR (cast film) 3364, 3052, 2952, 1746, 1711, 1610, 1242, 741 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.52 (ddd, *J* = 1.0, 1.8, 8.0 Hz, 1H), 7.31 (ddd, *J* = 1.1, 1.8, 8.3 Hz, 1H), 7.26-7.22 (m, 2H), 7.10 (ddd, *J* = 1.1, 7.0, 8.1 Hz, 1H), 6.99 (dd, *J* = 0.5, 1.7 Hz, 1H), 6.89 (dd, *J* = 1.7, 8.3 Hz, 1H) 5.80 (br s, 1H), 3.81 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.3, 168.6, 161.1, 144.5, 137.3, 128.0, 126.4, 125.8, 122.3, 121.1, 120.1, 119.3, 118.1, 113.3, 109.8, 109.3, 72.7, 53.9, 32.9; HRMS calc'd for $C_{19}H_{16}{}^{35}ClN_2O_3$ $[M + H]^+$ 355.0844, found: 355.0846

Compound 7o:



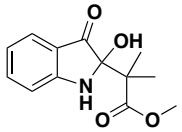
Isolated as light yellow oil in 76 % yield: R_f = 0.43 (yellow spot, 7:3 hexanes:EtOAc); IR (cast film) 3394, 2955, 1747, 1709, 1612, 1221, 787 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 8.00 (dd, *J* = 1.0, 8.3 Hz, 2H), 7.65 (app dt, *J* = 1.3, 7.3 Hz, 1H), 7.59 (dd, *J* = 0.6, 8.4 Hz, 1H), 7.54-7.41 (m, 2H), 7.00 (dd, *J* = 0.5, 1.7 Hz, 1H), 6.90 (dd, *J* = 1.7, 8.3 Hz, 1H), 5.87 (br s, 1H), 4.37 (d, *J* = 18.0 Hz, 1H), 3.77 (s, 3H), 3.22 (d, *J* = 18.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 197.5, 193.5, 167.7, 162.1, 144.7, 135.7, 134.0, 128.8, 128.3, 126.3, 120.9, 117.5, 113.0, 72.3, 53.7, 44.6; HRMS calc'd for $C_{18}H_{15}{}^{35}ClNO_4$ $[M + H]^+$ 344.0684, found: 344.0686

Compound 7p:



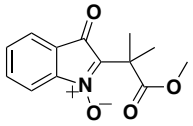
Isolated as yellow powder in 68 % yield: m.p. = 170-171 °C; R_f = 0.35 (yellow spot, 7:3 hexanes:EtOAc); IR(cast film) 3359, 3055, 2950, 1746, 1705, 1608, 1460, 1241, 743 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.55-7.33 (m, 2H), 7.31-7.19 (m, 4H), 7.07 (app t, *J* = 7.9 Hz, 1H), 6.84 (app t, *J* = 7.3 Hz, 1H), 5.58 (br s, 1H), 3.77 (s, 3H), 3.72 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.2, 169.2, 160.2, 137.9, 137.4, 128.1, 126.1, 122.8, 122.7, 122.2, 120.5, 119.9, 119.5, 119.5, 110.0, 109.8, 72.5, 53.8, 32.9, 15.8; HRMS calc'd for $C_{20}H_{19}N_2O_3$ $[M + H]^+$ 335.1396, found: 335.1388

Compound 10:



Isolated as a yellow oil; R_f = 0.33 (7:3 hexanes:EtOAc); IR (cast film) 3373, 2990, 2952, 1710, 1619, 1487, 1472 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 6.83 (t, *J* = 7.2 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 5.05 (br s, 1H), 4.91 (br s, 1H), 3.79 (s, 3H), 1.30 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.2, 177.9, 160.3, 138.0, 125.1, 120.0, 119.9, 112.4, 89.4, 52.7, 47.6, 21.1, 18.8; HRMS calc'd for $C_{13}H_{15}NO_4$ $[M]^+$ 249.1001, found 249.1000.

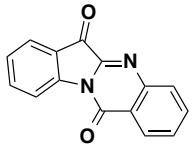
Compound 11:



Isolated as a yellow oil; R_f = 0.64 (7:3 hexanes:EtOAc); IR (cast film) 2993, 2953, 1766, 1644, 1608, 1475, 1465 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.19 (br d, *J* = 8.4 Hz, 1H), 7.82-7.78 (m,

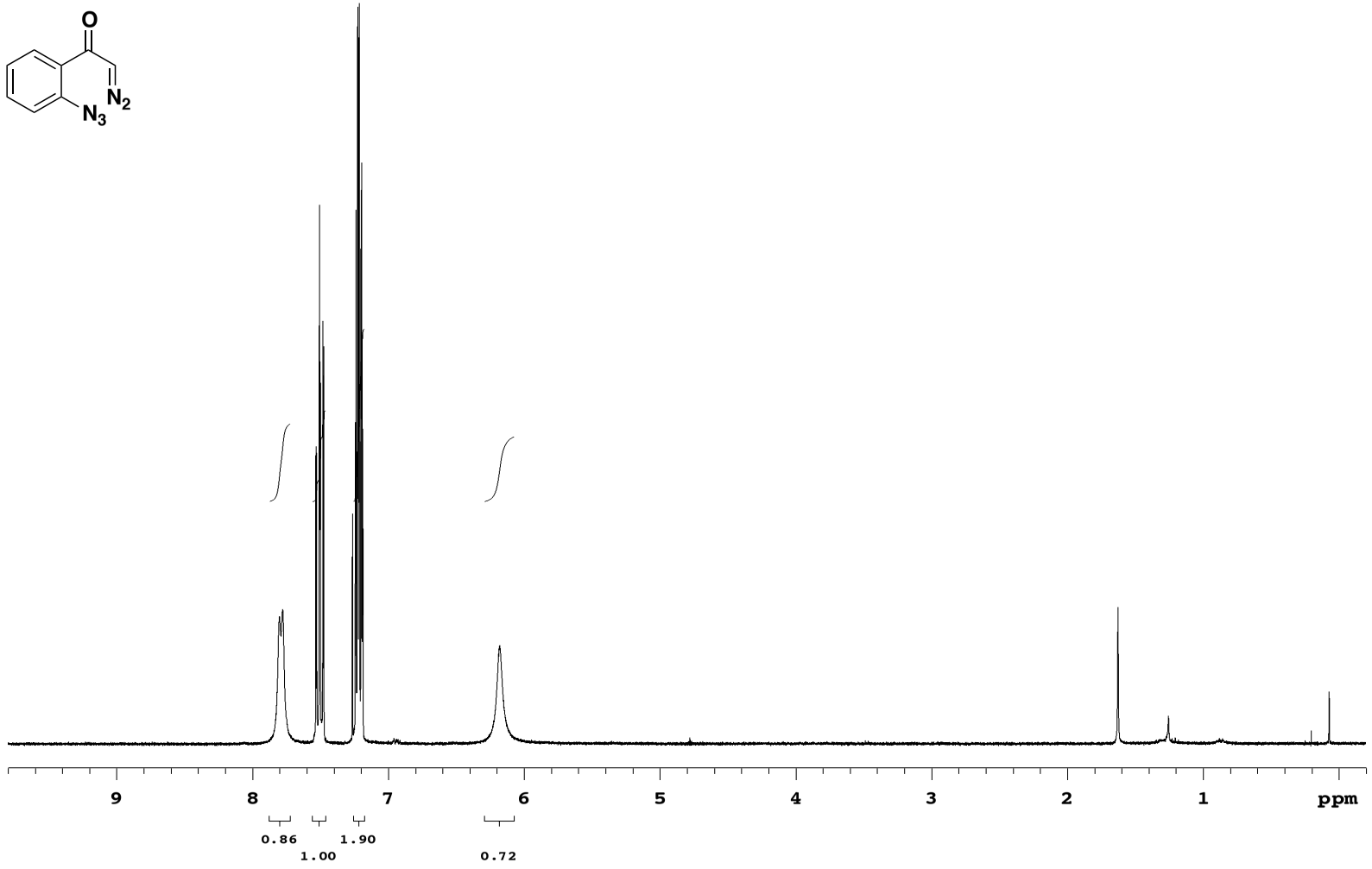
1H), 7.61 (br d, J = 8.1 Hz, 1H), 7.54-7.50 (m, 1H), 3.73 (s, 3H), 1.65 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.4, 162.8, 159.3, 146.1, 136.4, 128.6, 128.4, 127.2, 117.0, 52.8, 49.3, 23.5 (x2); HRMS calc'd for $C_{13}H_{13}NO_4$ $[M]^+$ 247.0845, found 247.0844.

Tryptanthrin 13:

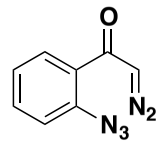


Anthranilic acid (2.0 equiv) in toluene (20 mL) solution was added with thionyl chloride (2.0 equiv) and the solution was heated at reflux for 2 h. The reaction mixture was allowed to cool to rt then a toluene solution of $Cu(hfacac)_2$ (0.1 equiv) was added and stirred for 30 mins. The solution was then allowed to warm to 40 – 50 °C before a toluene solution of **6a** (49 mg, 0.26 mmol, 1.0 equiv, 0.04 M) was added via syringe pump over 1 h and then stirred for an additional 6 h. The reaction mixture was allowed to cool and was washed with equivalent volume of 1.0 M aq K_2CO_3 and brine. The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford black crude material. The mixture was dissolved in small amount of DCM and purified by column chromatography using (silica gel; 20%→30→40% EtOAc in hexane gradient elution to furnish 40 mg (62 %) of **13** as a fibrous yellow solid (minimal solubility in $CHCl_3$ and DMSO): m.p. 262-264 °C; R_f = 0.72 (yellow spot, 1:1 EtOAc:hexanes); IR(cast film) 2920, 1735, 1694, 1468, 1316, 775, 757 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65 (d, J = 8.1 Hz, 1H), 8.46 (d, J = 7.2 Hz, 1H), 8.05 (d, J = 8.1 Hz, 1H), 7.78-7.94 (m, 3H), 7.69 (app t, J = 7.5 Hz, 1H) 7.44 (app t, J = 7.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 182.6, 158.2, 146.7, 146.4, 144.4, 138.3, 135.2, 130.8, 130.3, 127.6, 127.2, 125.4, 123.8, 122.0, 118.0; HRMS calc'd for $C_{15}H_8O_2N_2$ $[M]^+$ 248.0586, found 248.0585.

Compound 6a

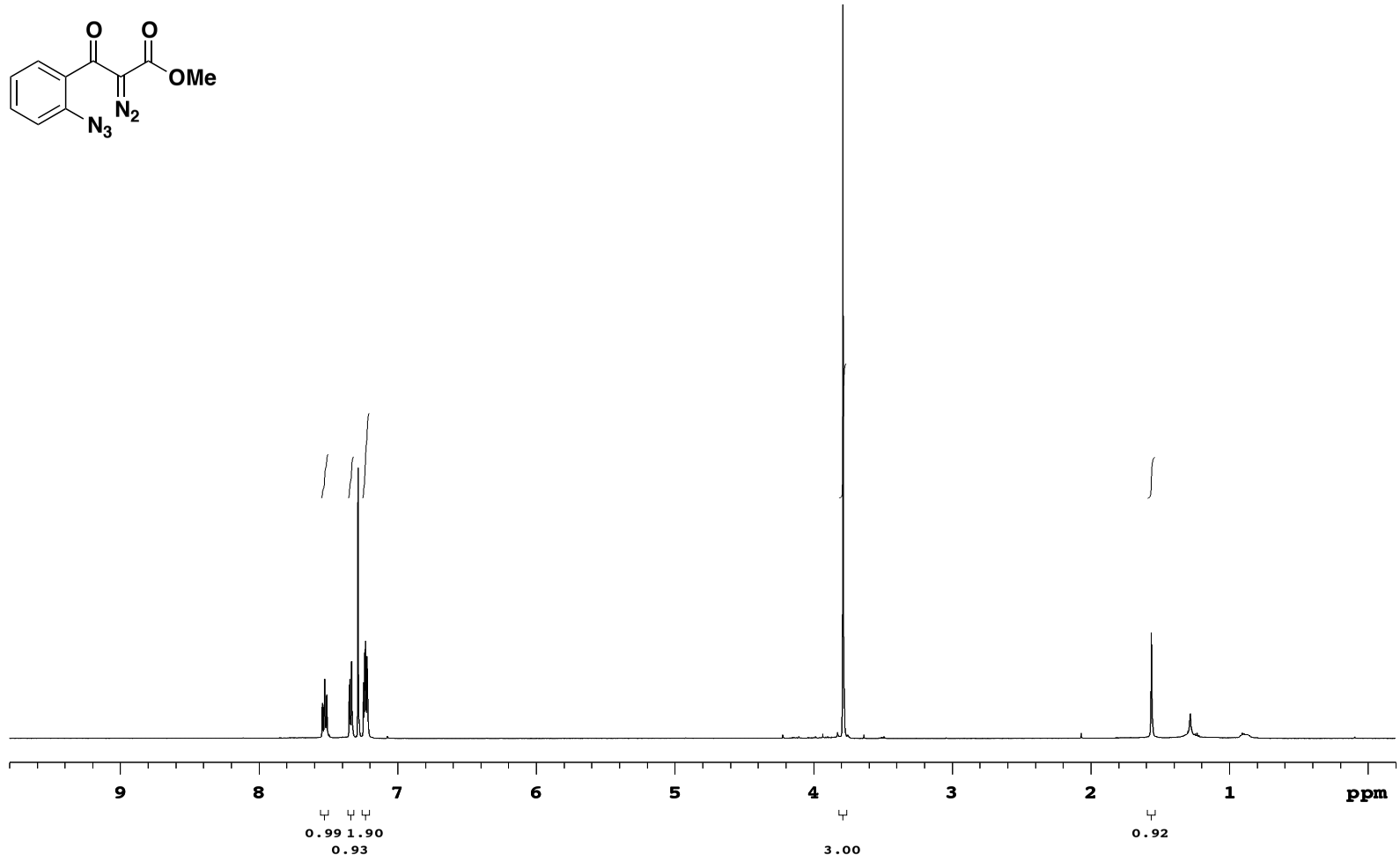


Compound 6a

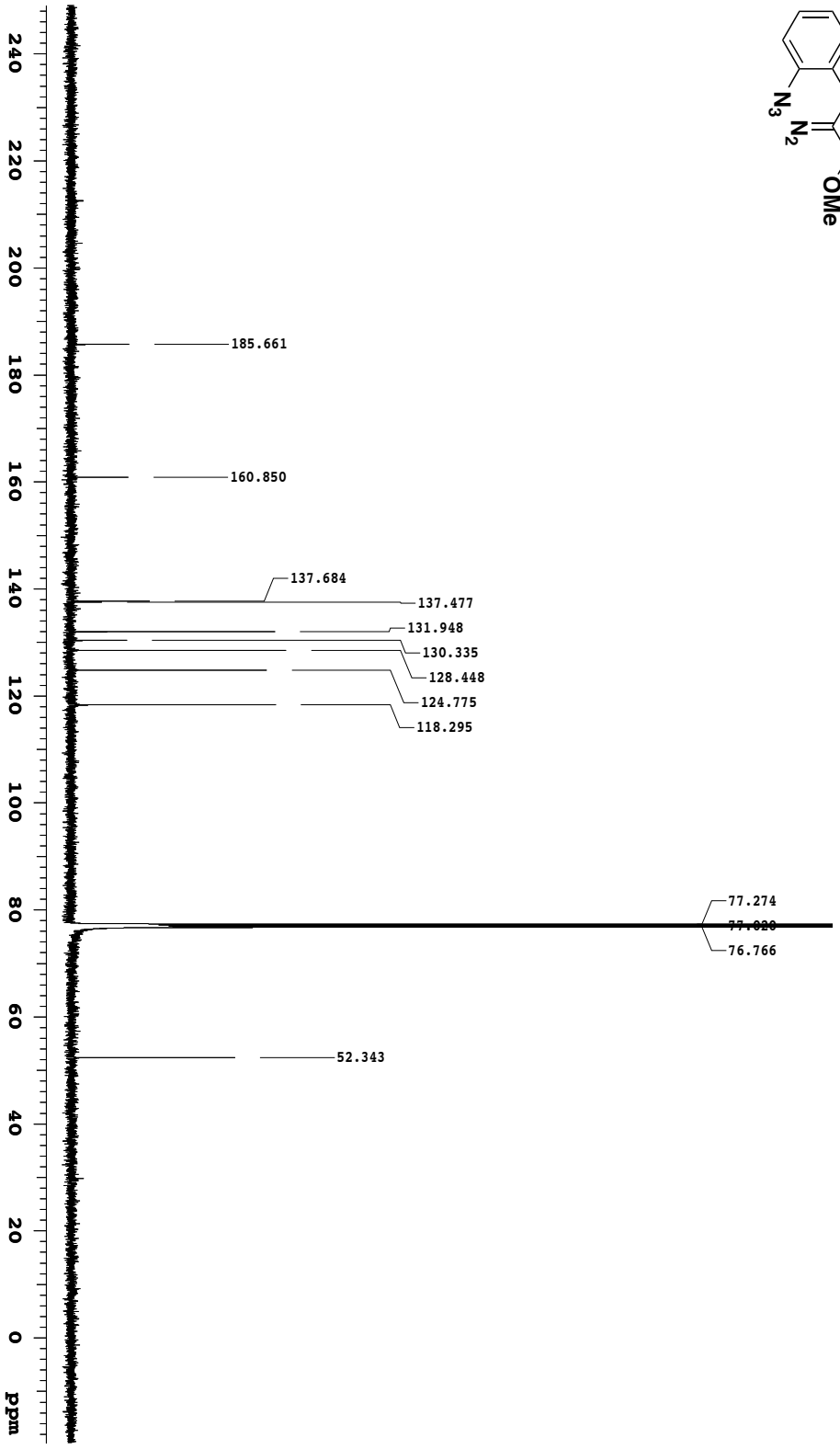

O
N2
N3

184.939
137.928
132.793
130.195
129.324
124.952
118.949
77.330
77.075
76.821
57.957
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

Compound 6b

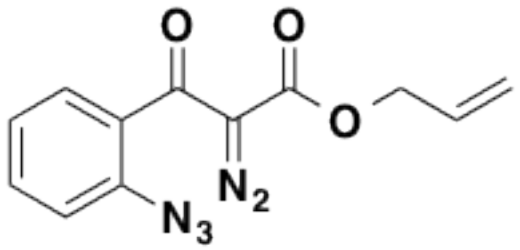


Compound 6b

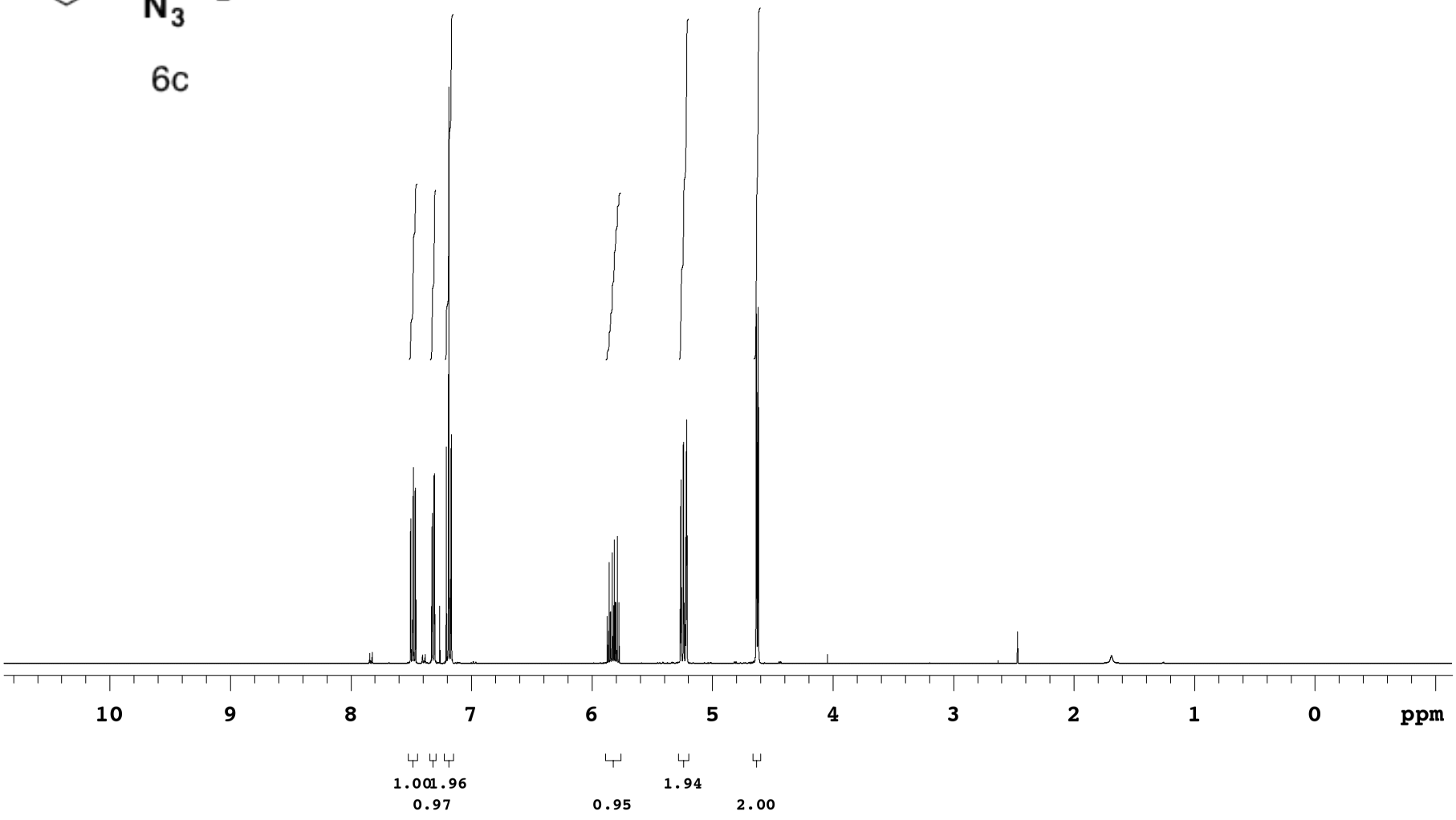

185.661
160.850
137.684
137.477
131.948
130.335
128.448
124.775
118.295
77.274
77.020
76.766
52.343
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

BA 03-02-XX(DIAZO AZIDE WITH ALLYL SIDE CHAIN) CDCl3 1H

Pulse Sequence: s2pul

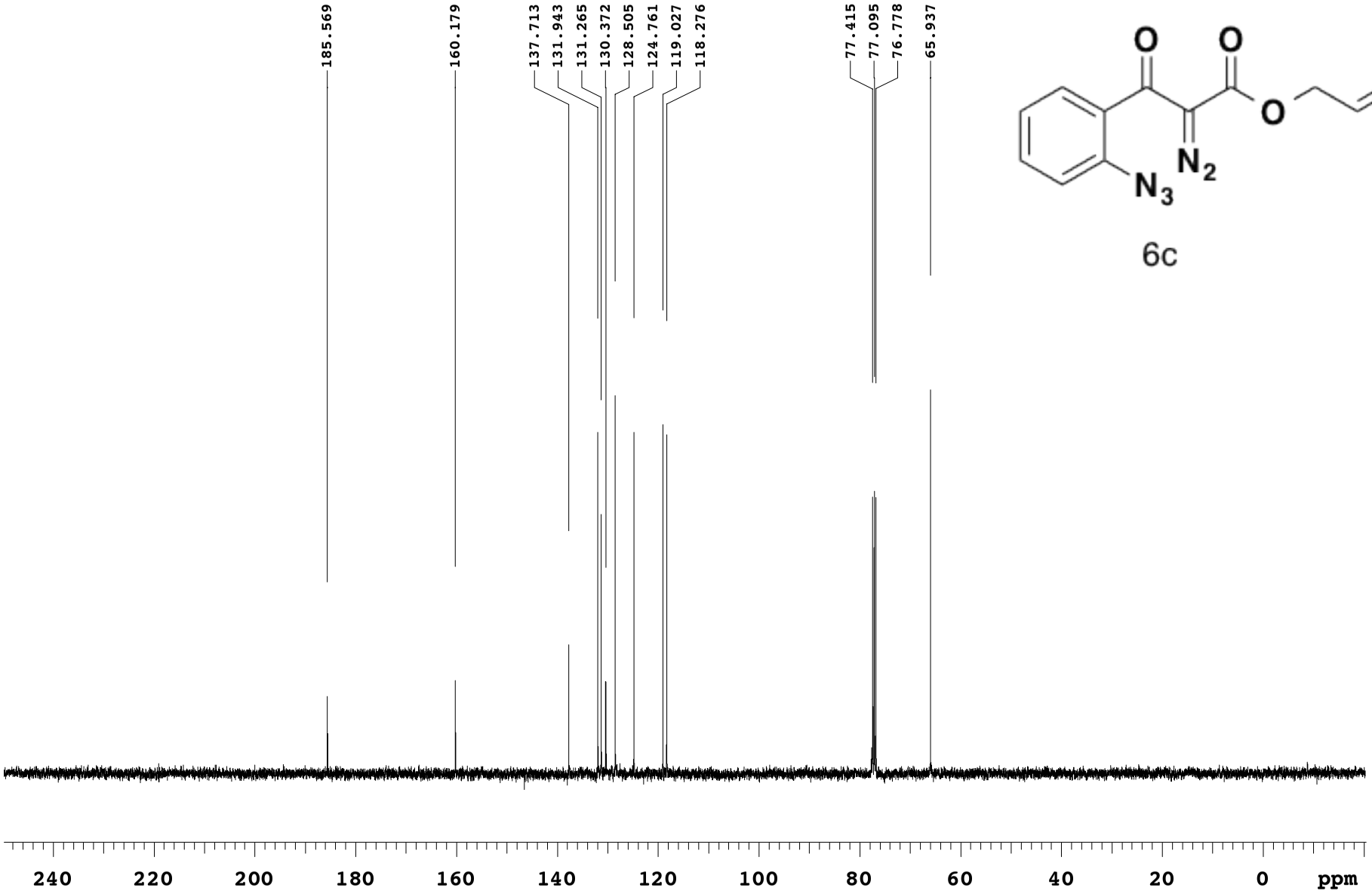


6c



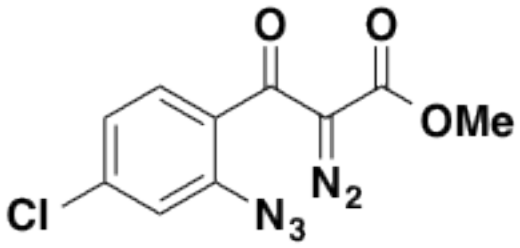
BA 03-02-XX(DIAZO AZIDE WITH ALLYL SIDE CHAIN) CDCl3 13C

Pulse Sequence: s2pul

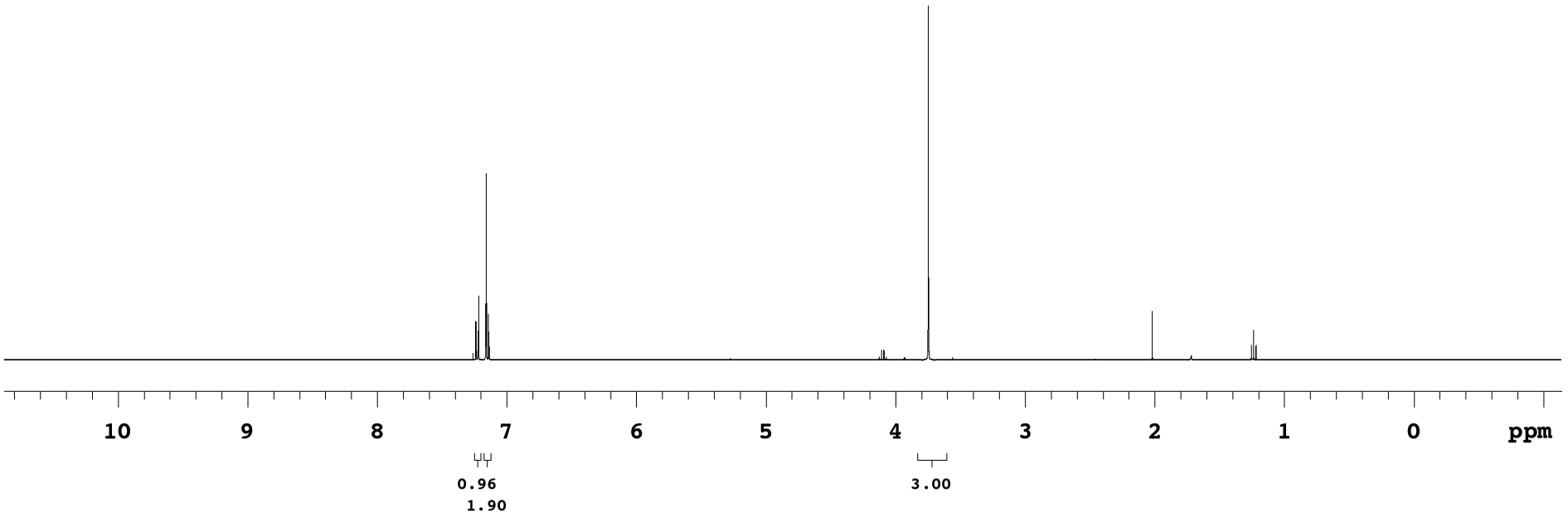


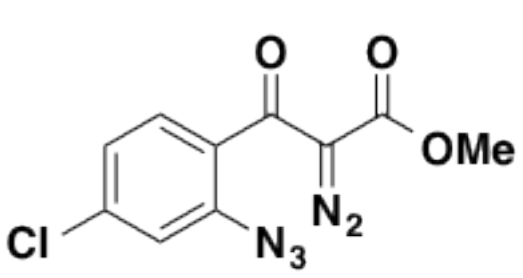
Chloro diazo azide CDCl3 1H

Pulse Sequence: s2pul



6d



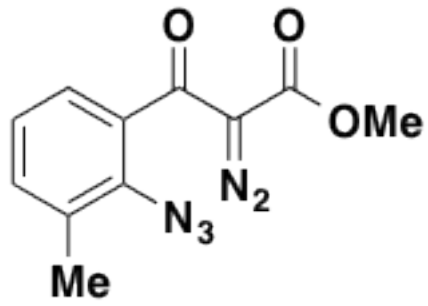

O
O
OMe
N2
Cl
N3

6d

184.584
160.684
139.166
137.752
129.655
128.703
125.075
118.559
77.425
77.105
76.788
52.353
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

Bren+Jordan, BA_03-43_Methyl_diazo_azide

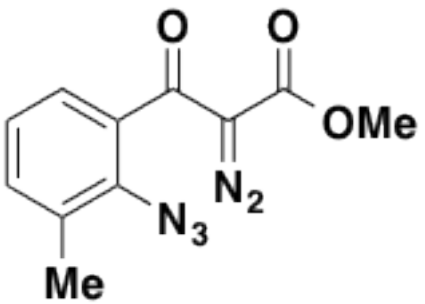
Pulse Sequence: PRESAT



6e

Bren+Jordan, BA_03-43_Methyl_diazo_azide

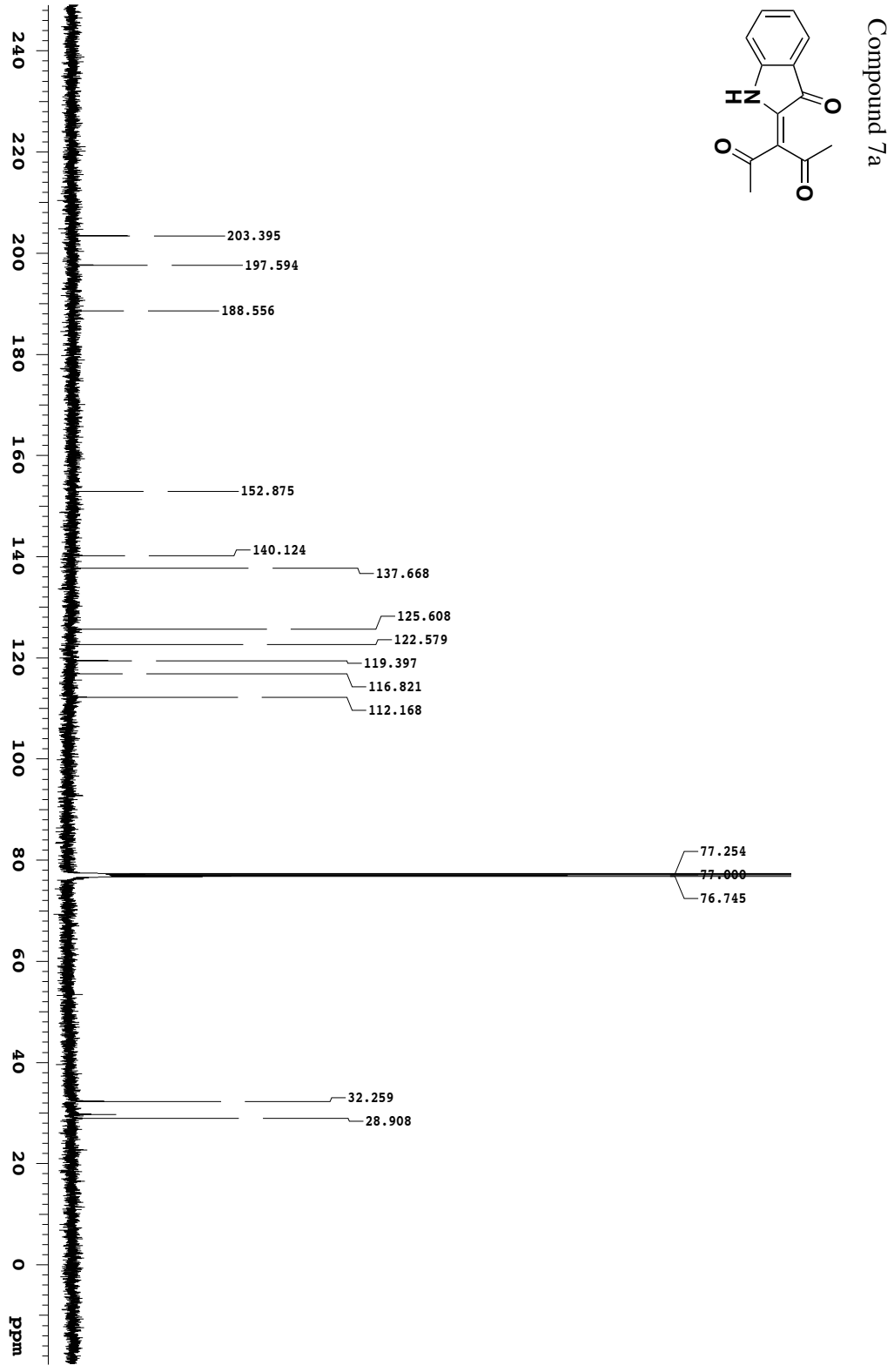
Pulse Sequence: s2pul



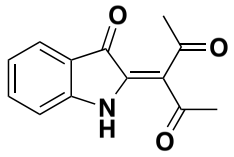
6e

186.171
160.839
135.518
133.701
132.497
132.439
126.129
125.404
77.282
77.028
76.910
76.896
76.774
52.378
17.887

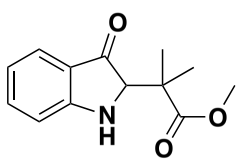
240 220 200 180 160 140 120 100 80 60 40 20 ppm


Compound 7a
O
N
H
O
O
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm
203.395
197.594
188.556
152.875
140.124
137.668
125.608
122.579
119.397
116.821
112.168
77.254
77.000
76.745
32.259
28.908

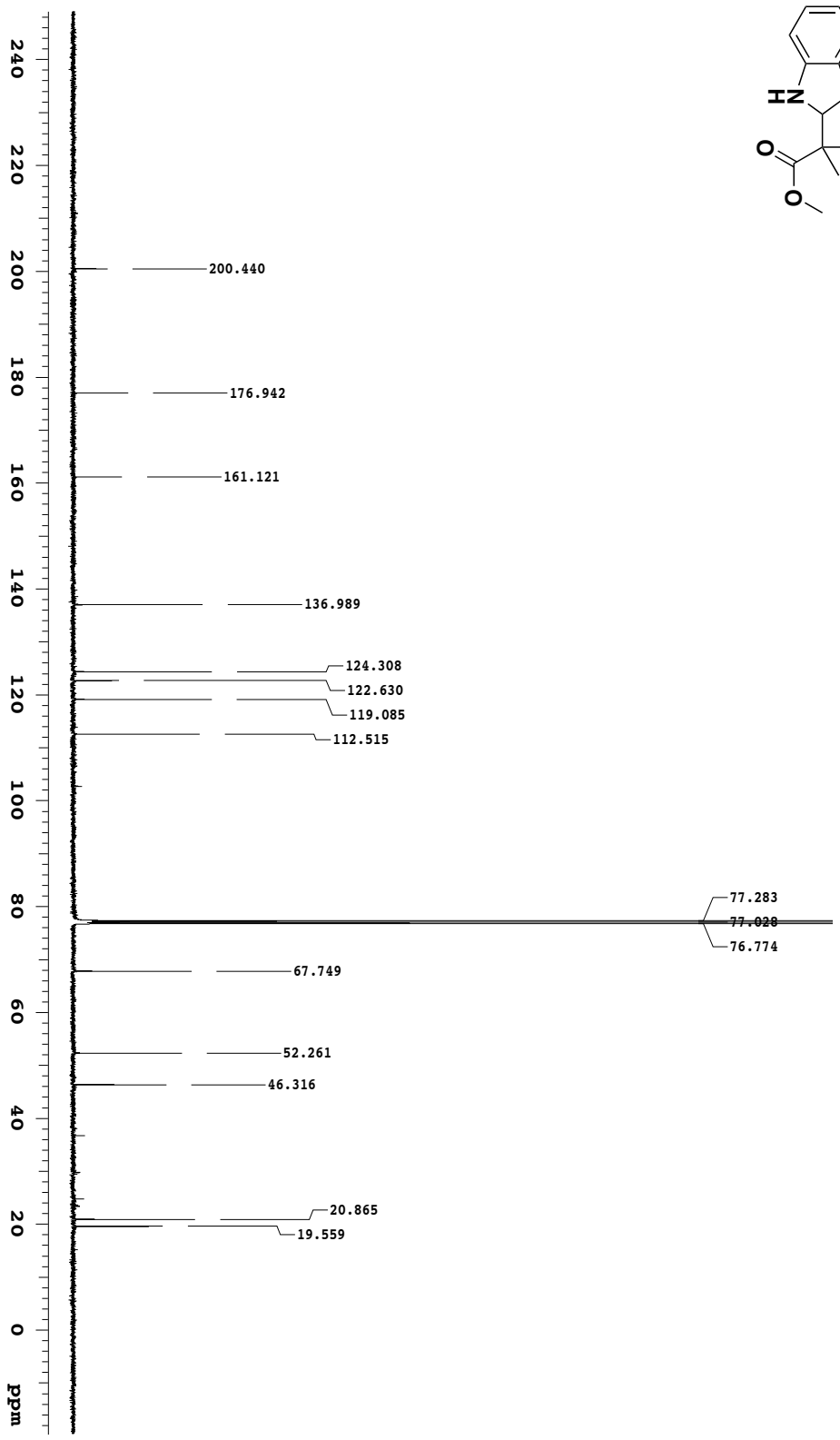
Compound 7a



Compound 7c

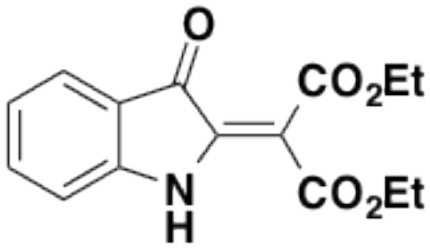


Compound 7c

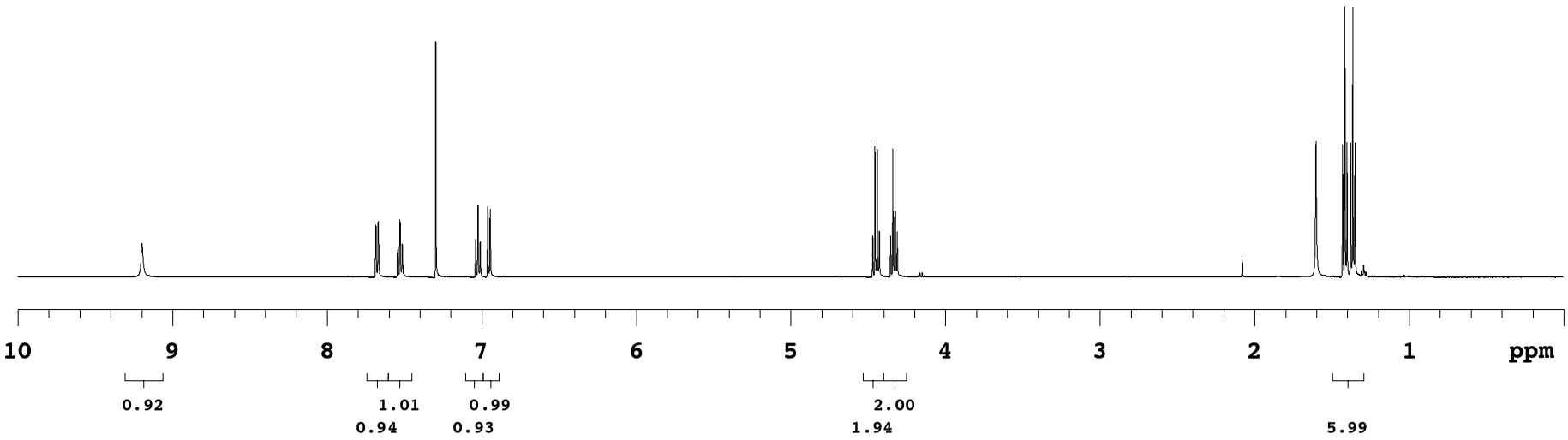

200.440
176.942
161.121
136.989
124.308
122.630
119.085
112.515
77.283
77.028
76.774
67.749
52.261
46.316
20.865
19.559
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

DEBM TRAP

Pulse Sequence: PRESAT

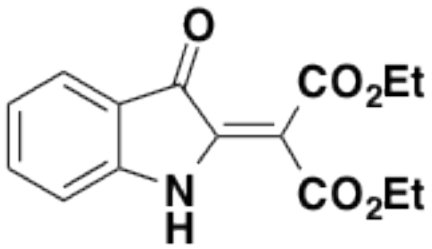


7d



DEBM Trap

Pulse Sequence: s2pul



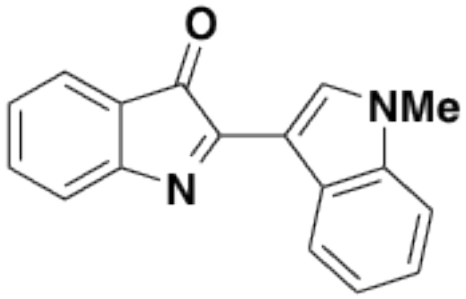
7d

185.689
166.159
164.702
152.209
142.512
137.571
125.685
122.151
119.956
111.863
102.305
77.286
77.234
77.032
76.778
62.057
61.711
14.102
13.893

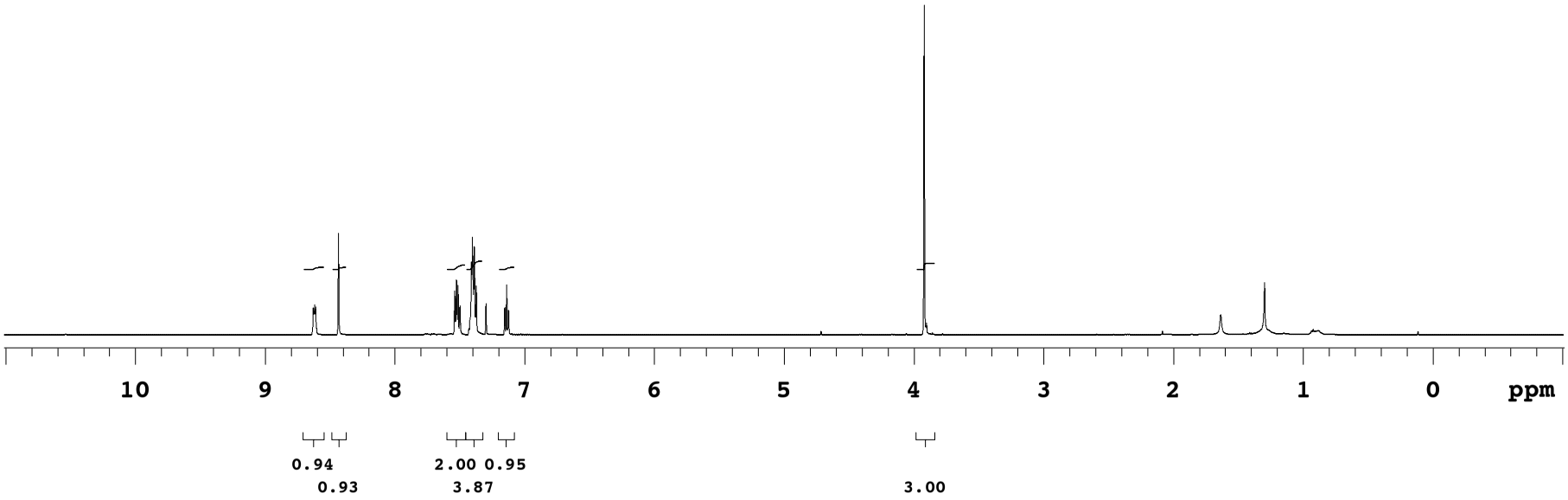
240 220 200 180 160 140 120 100 80 60 40 20 ppm

BA N-METHYLINDOLE TRAP CDCl3_1H

Pulse Sequence: PRESAT

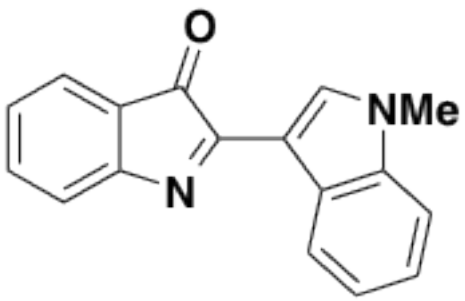


7e



N-methylindoletrap 13C_CDCl3

Pulse Sequence: s2pul



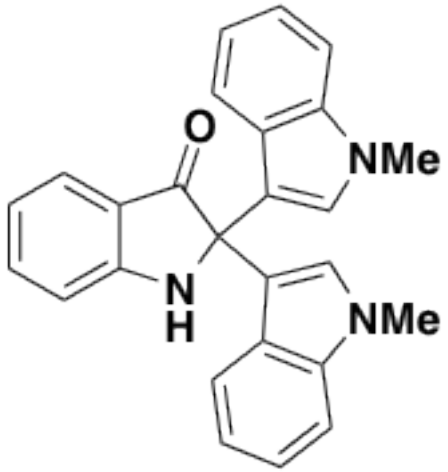
7e

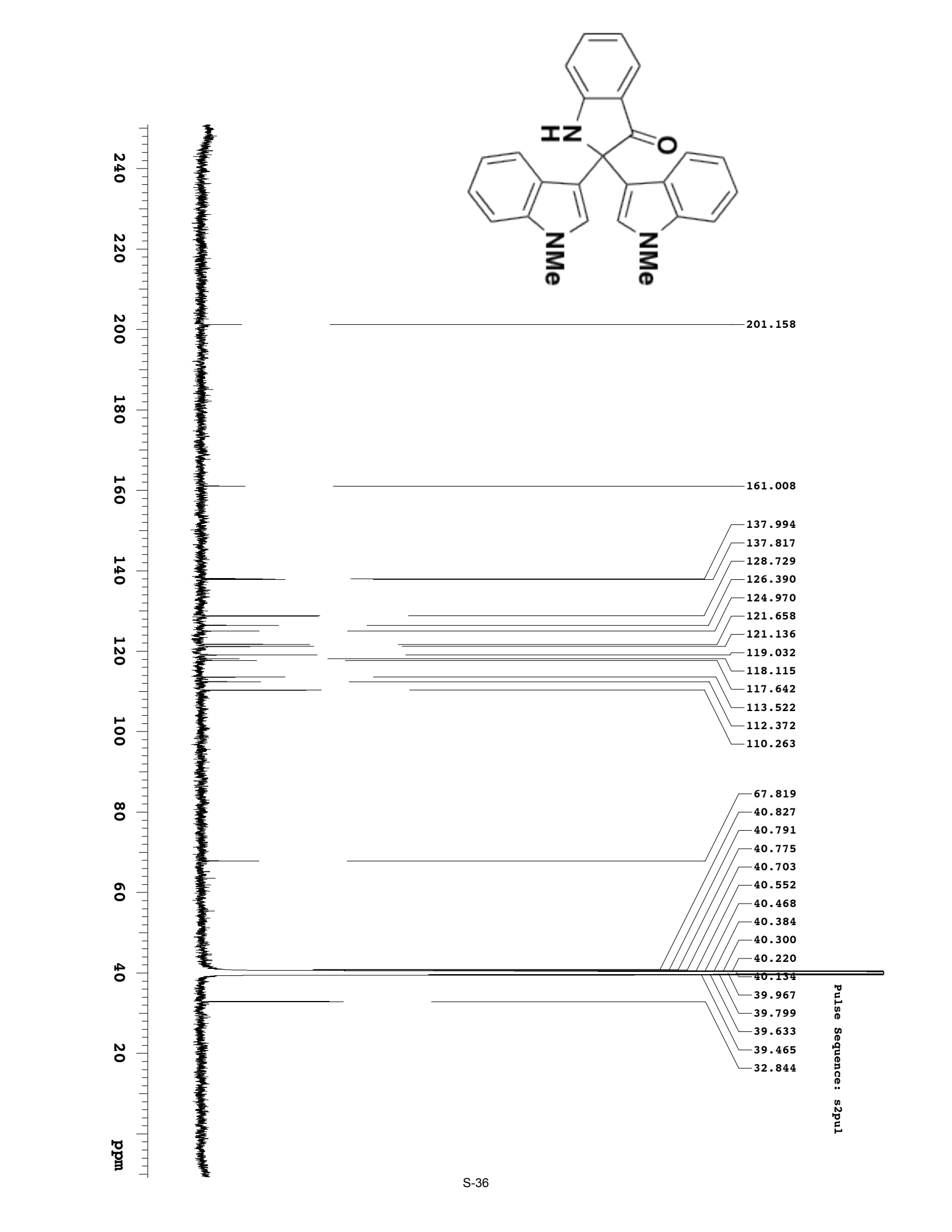
196.070
163.706
158.237
137.641
137.020
136.161
127.093
126.093
124.509
123.790
123.529
122.948
122.478
121.080
109.844
106.763
77.300
77.045
76.791
33.648

240 220 200 180 160 140 120 100 80 60 40 20 ppm

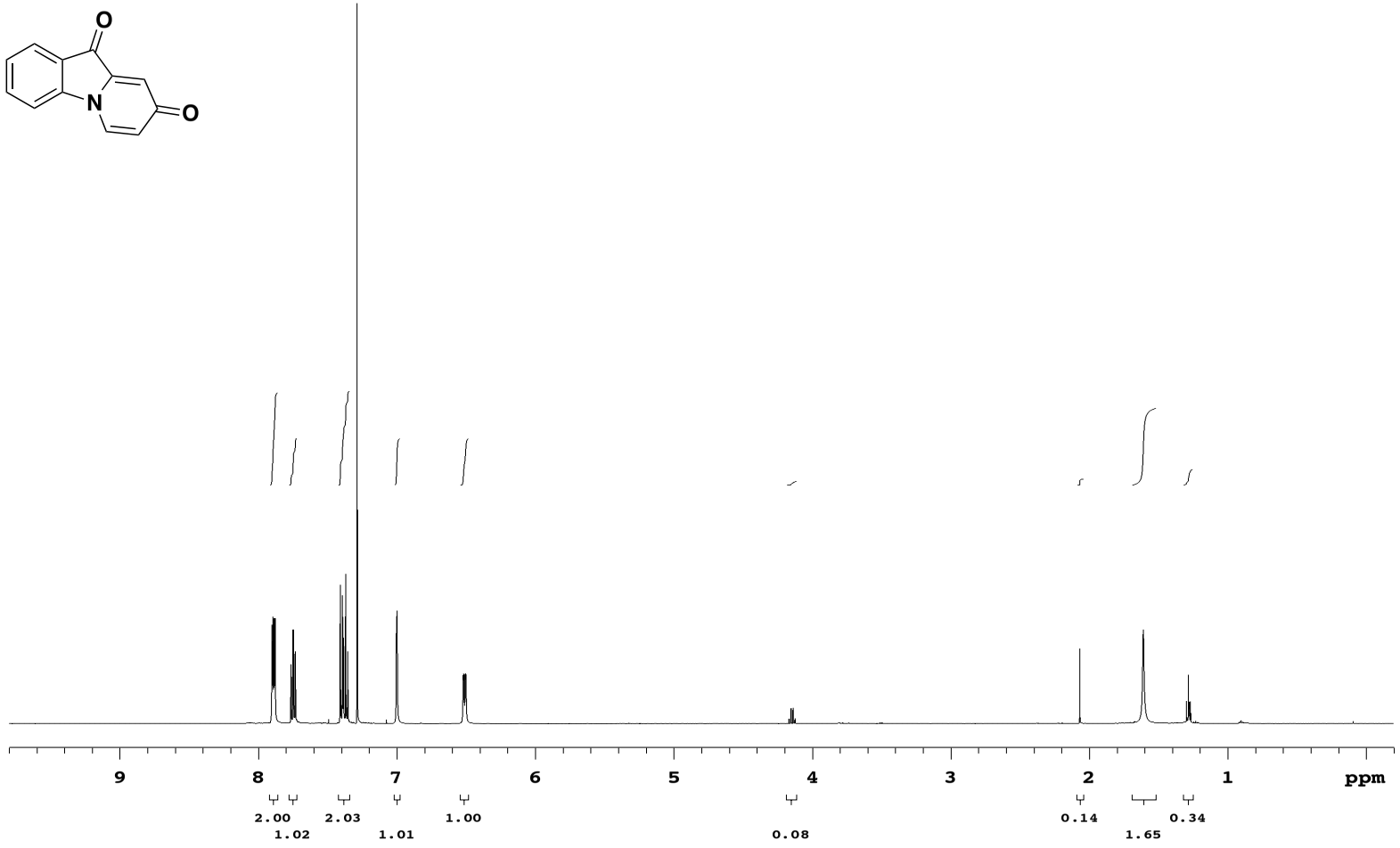
N-Methyl indole 2:1 adduct

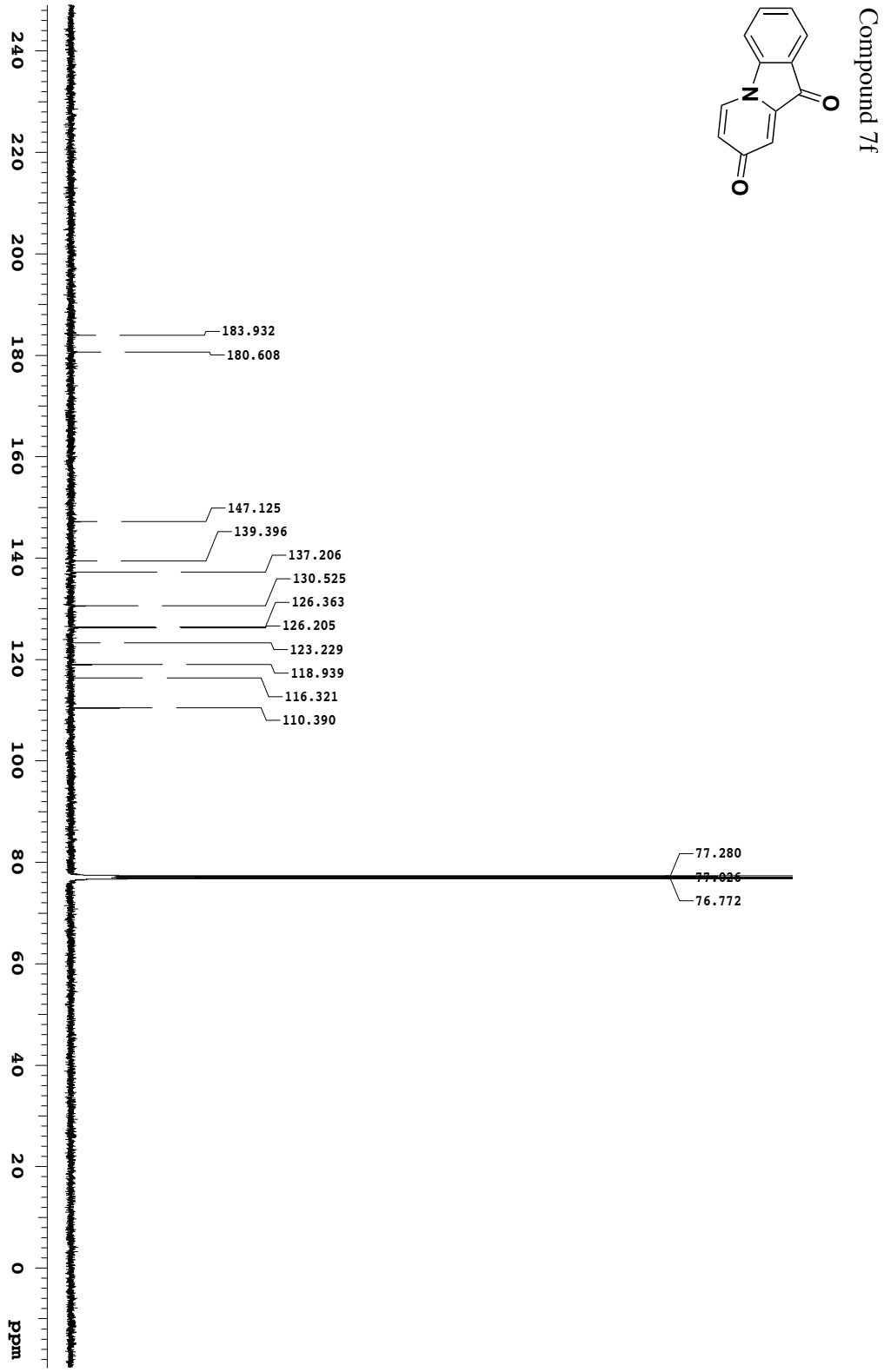
Pulse Sequence: PRESAT



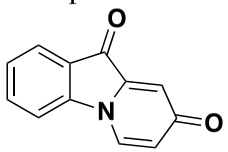

NMe
NMe
H
N
O
201.158
161.008
137.994
137.817
128.729
126.390
124.970
121.658
121.136
119.032
118.115
117.642
113.522
112.372
110.263
67.819
40.827
40.791
40.775
40.703
40.552
40.468
40.384
40.300
40.220
40.134
39.967
39.799
39.633
39.465
32.844
Pulse Sequence: s2pul
240
220
200
180
160
140
120
100
80
60
40
20
ppm

Compound 7f



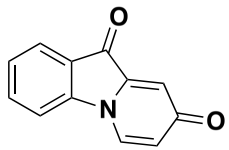

Compound 7f
O
N
O
183.932
180.608
147.125
139.396
137.206
130.525
126.363
126.205
123.229
118.939
116.321
110.390
77.280
77.026
76.772
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

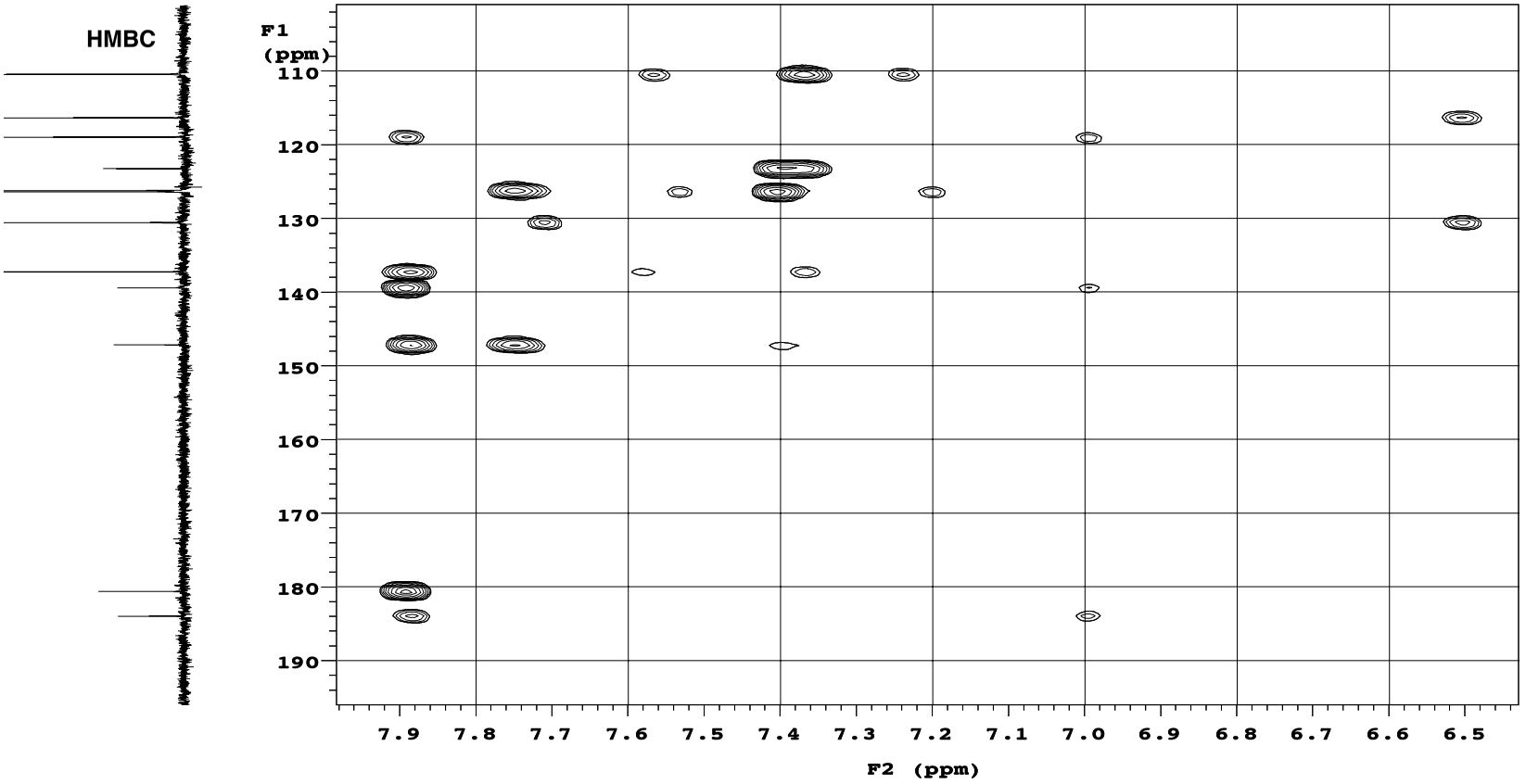
Compound 7f



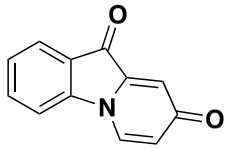
COSY

Compound 7f

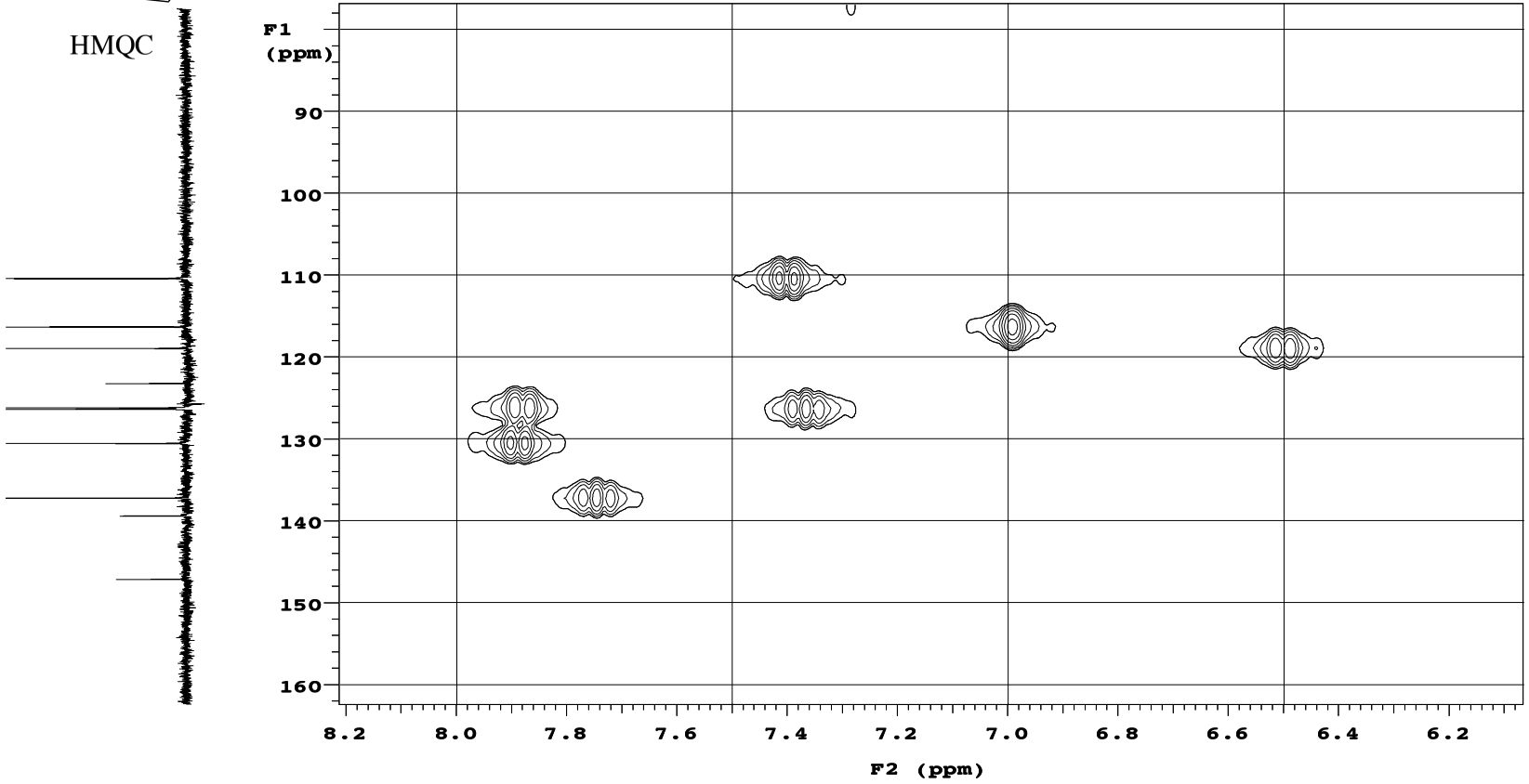

O
N
O


HMBC
F1
(ppm)
110
120
130
140
150
160
170
180
190
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
F2 (ppm)

Compound 7f



HMQC

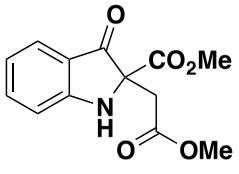


Compound 7g

O
N
H
O
CO2Me
OMe

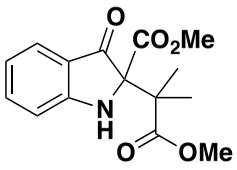
7.603
7.587
7.518
7.516
7.504
7.501
7.499
7.487
7.485
7.254
6.981
6.979
6.978
6.964
6.963
6.908
6.906
6.893
6.892
6.878
6.876
5.611
3.744
3.719
3.567
3.532
2.586
2.551
1.00
1.14
1.08
1.12
1.04
3.37
3.37
1.20
1.15
ppm

Compound 7g


O
CO2Me
N
H
O
OMe

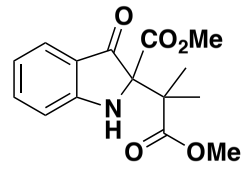
194.024
171.525
167.839
161.770
138.003
125.390
120.304
119.193
113.274
77.259
77.001
76.748
71.528
53.639
52.213
39.648
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

Compound 7h


O
CO2Me
N
H
O
OMe

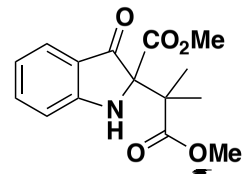
9
8
7
6
5
4
3
2
1
ppm
1.00
1.03
0.99
1.02
0.97
3.09
3.10
3.14
3.44

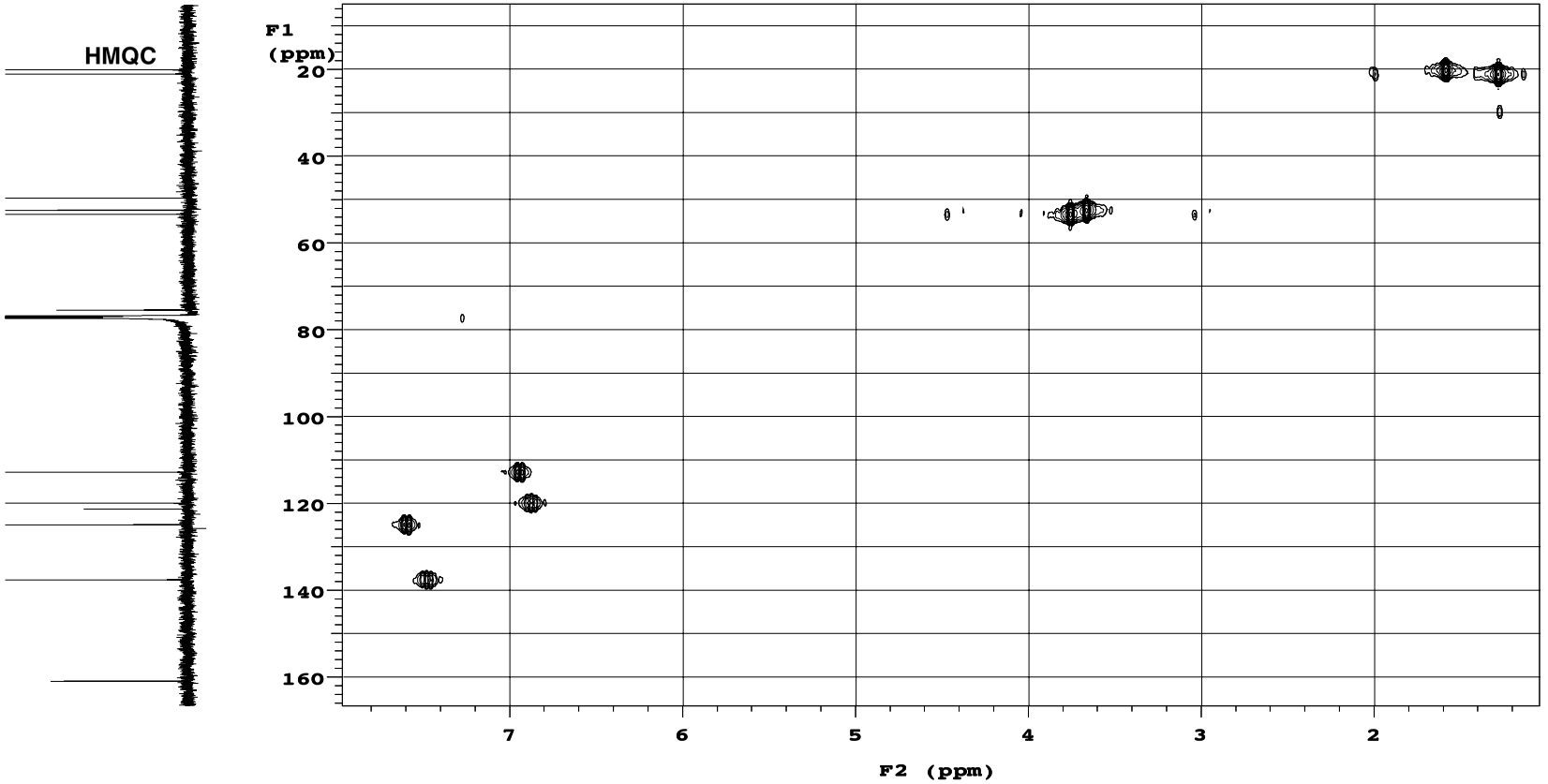
Compound 7h


O
CO2Me
N
H
O
OMe

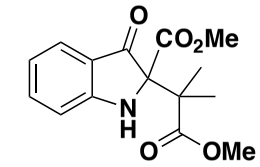
194.846
176.464
168.425
160.924
137.586
124.884
121.285
119.895
112.777
77.270
77.018
76.764
75.406
53.345
52.404
49.613
21.035
20.053
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

Compound 7h


O
CO2Me
N
H
O
OMe


HMQC
F1
(ppm)
20
40
60
80
100
120
140
160
7
6
5
4
3
2
F2 (ppm)

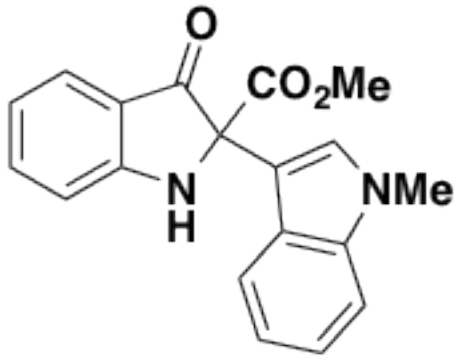
Compound 7h


O
CO2Me
N
H
O
OMe

HMBC
F1
(ppm)
40
60
80
100
120
140
160
180
200
220
7
6
5
4
3
2
1
F2 (ppm)

BA H1 1H

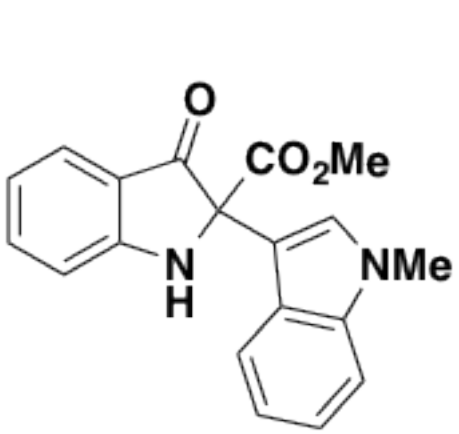
Pulse Sequence: PRESAT



7i

BA H1

Pulse Sequence: s2pul



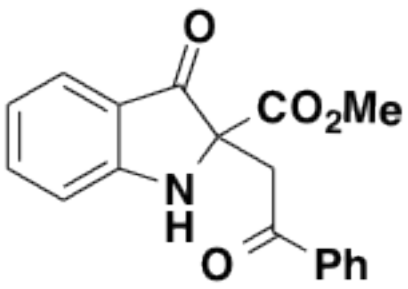
7i

194.863
169.083
161.031
137.933
137.383
128.050
125.995
125.408
122.255
120.320
119.972
119.818
119.527
113.596
109.822
109.782
77.353
77.100
76.844
72.391
53.778
32.920

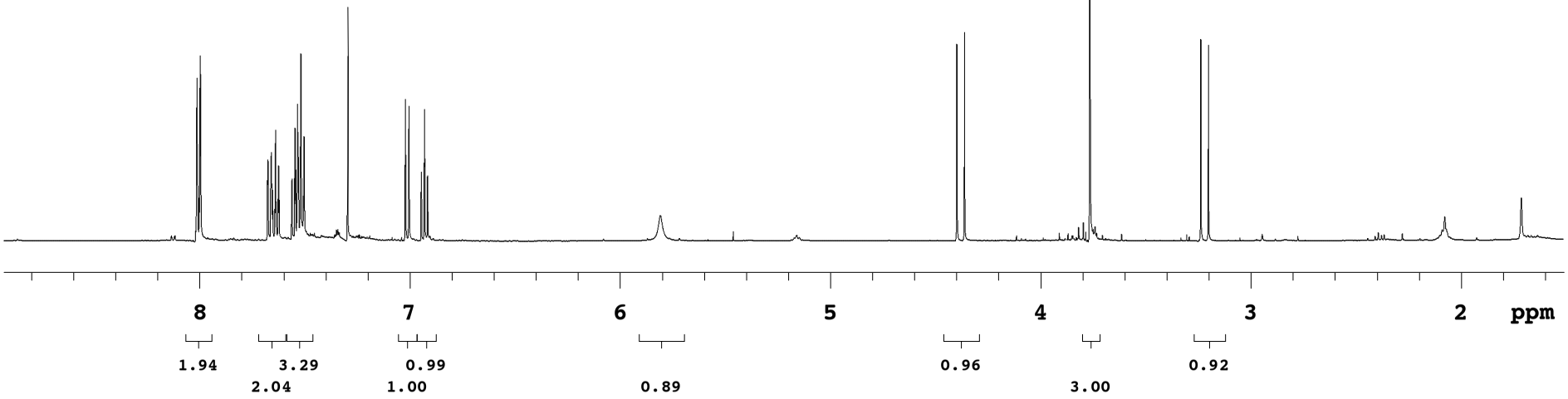
240 220 200 180 160 140 120 100 80 60 40 20 ppm

BA PHENYLSILYLENOLETHER TRAP ON SIMPLE DIAZO AZIDE

Pulse Sequence: PRESAT

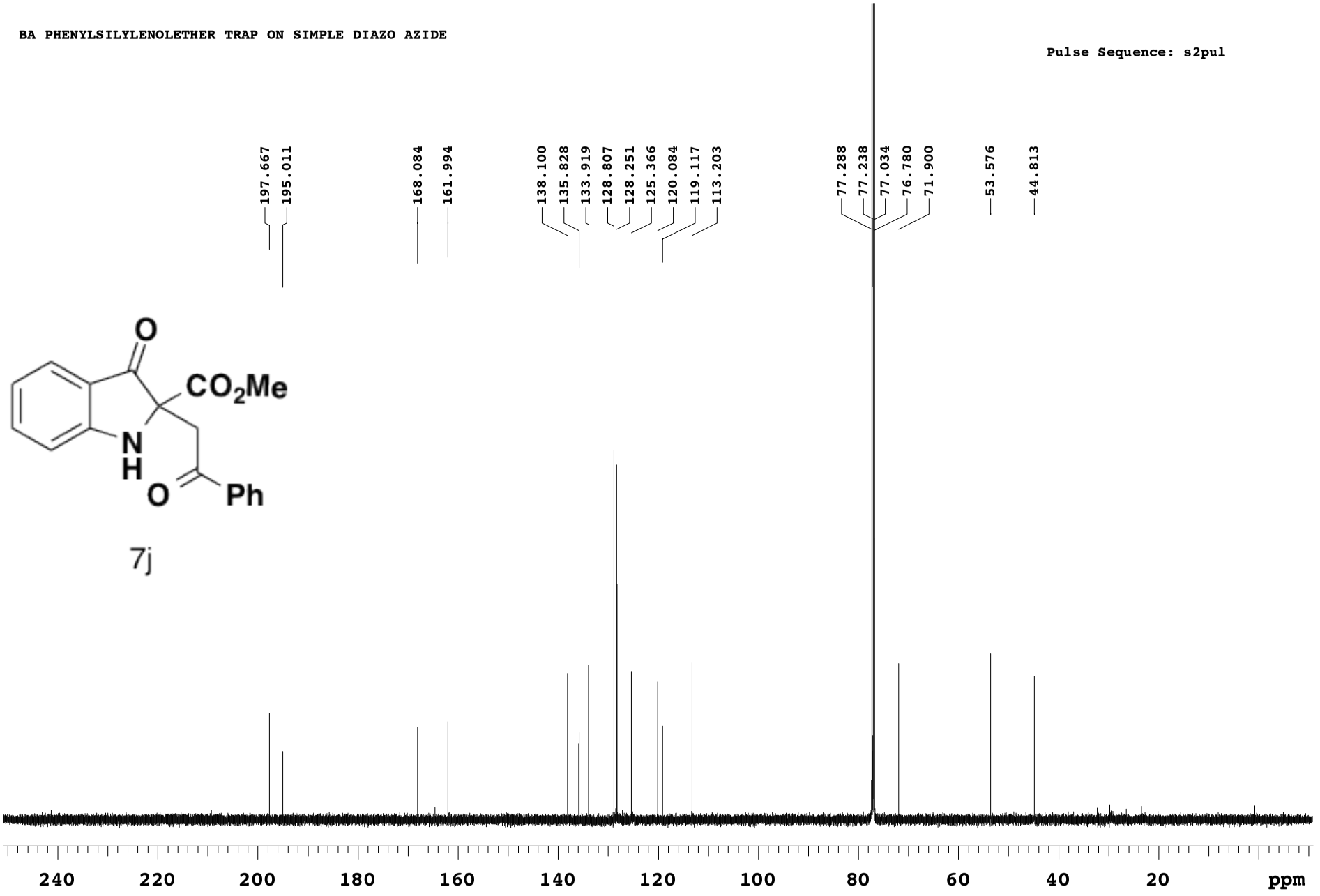


7j



BA PHENYLSILYLENOLETHER TRAP ON SIMPLE DIAZO AZIDE

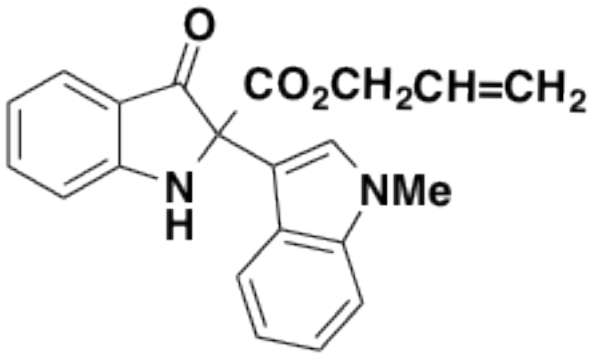
Pulse Sequence: s2pul



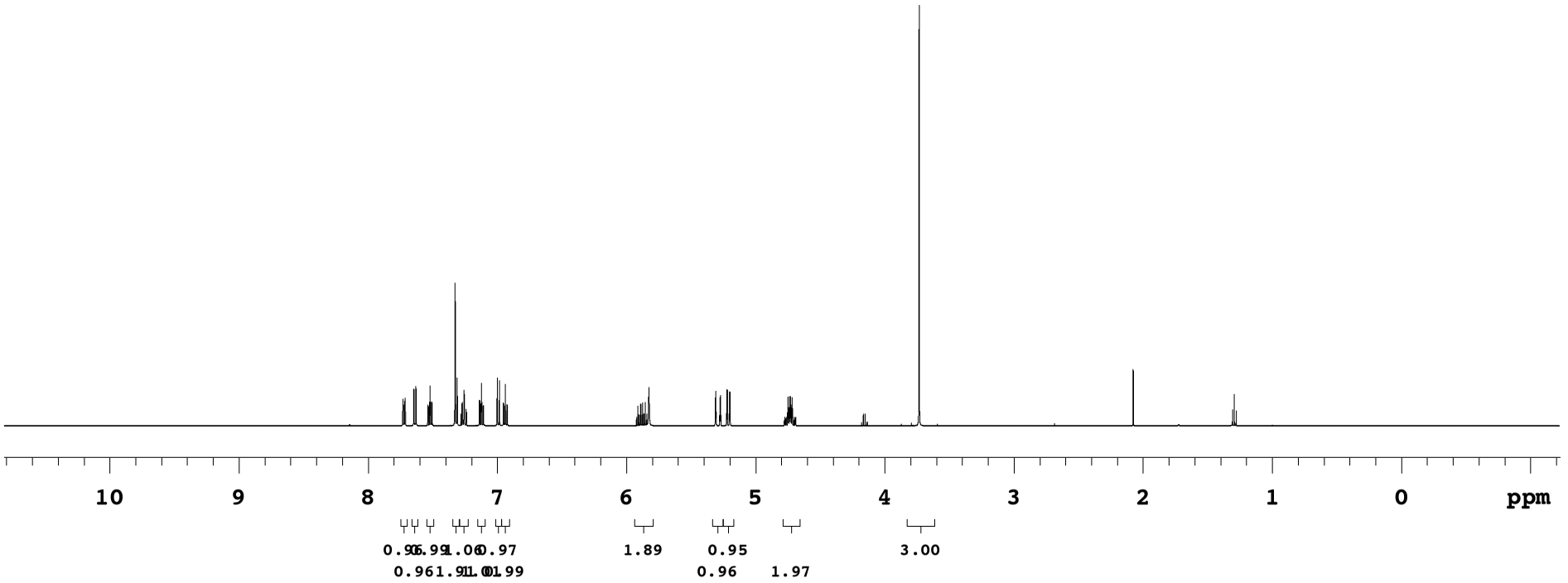
7j

BA ALL1H

Pulse Sequence: s2pul



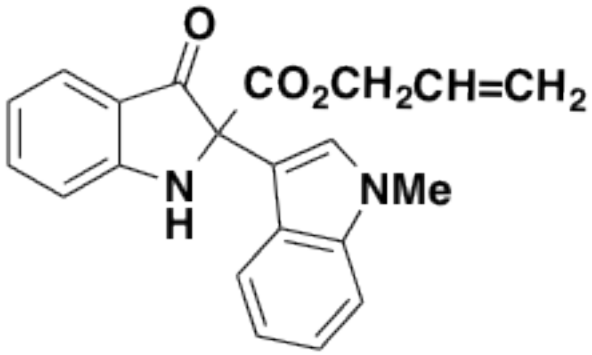
7k



ALL1

Pulse Sequence: s2pul

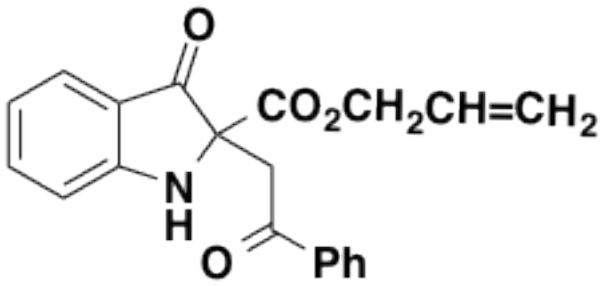
194.776
168.260
161.015
137.843
137.371
131.221
128.140
125.985
125.400
122.196
120.228
119.874
119.785
119.050
113.523
109.771
109.720
77.379
77.123
76.868
72.501
67.128
32.891



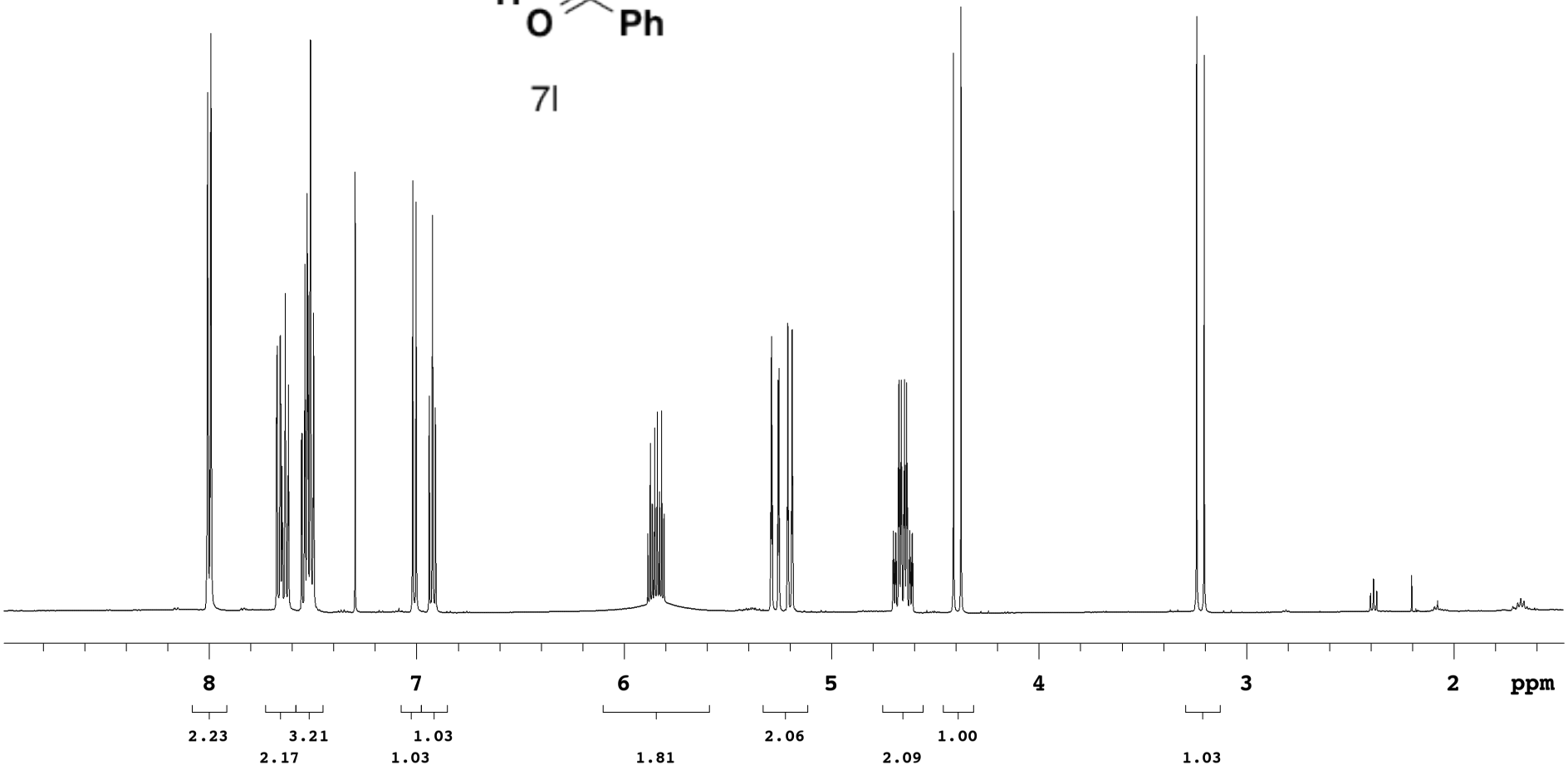
7k

PHENYLSILYLENOLETHER TRAP ON ALLYL DIAZOAZIDE

Pulse Sequence: PRESAT

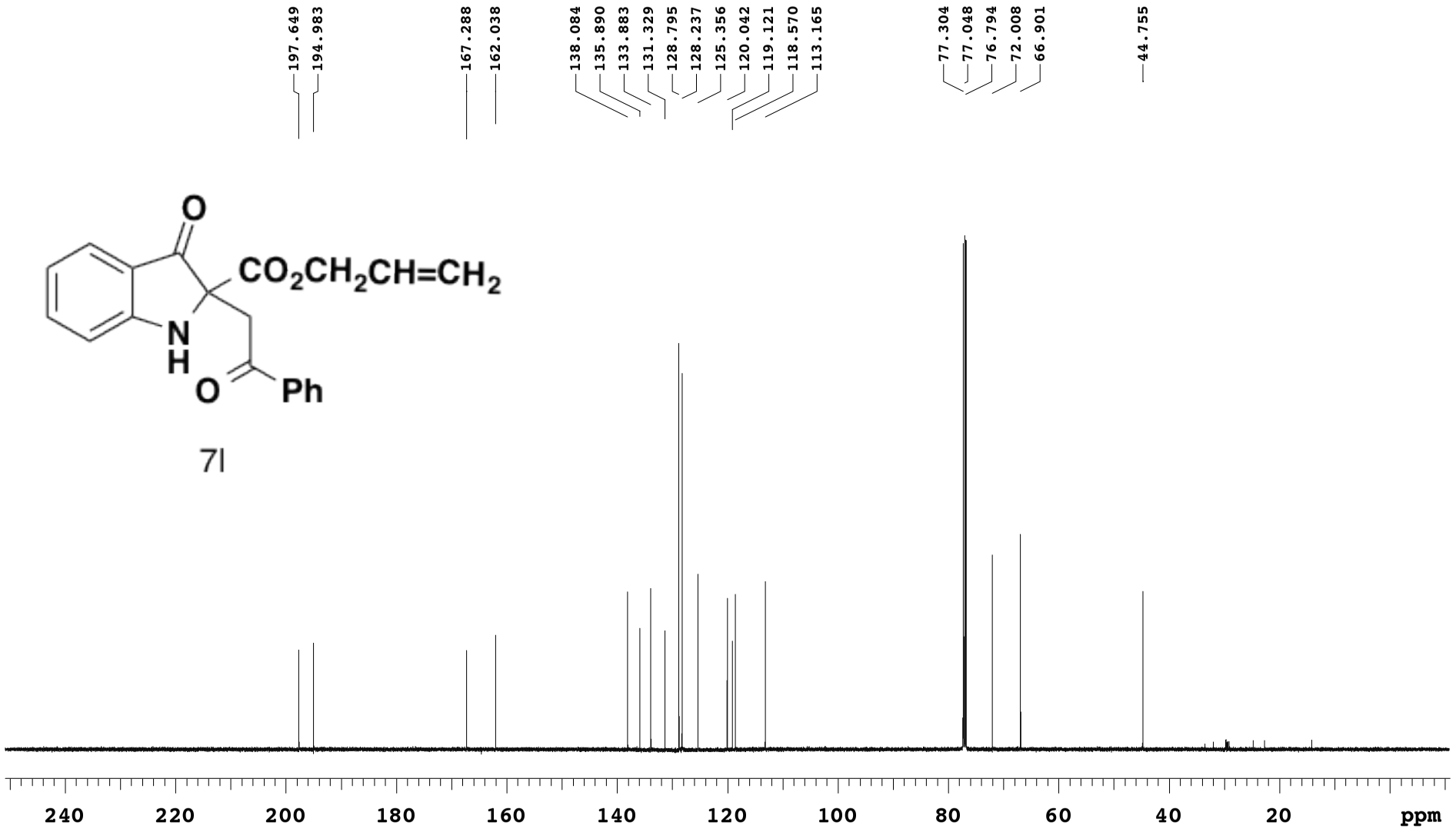


7l



BA PHENYLSILYLENOLETHER TRAP OF ALLYL DIAZOAZIDE

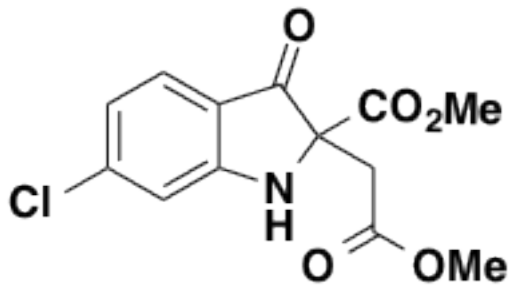
Pulse Sequence: s2pul



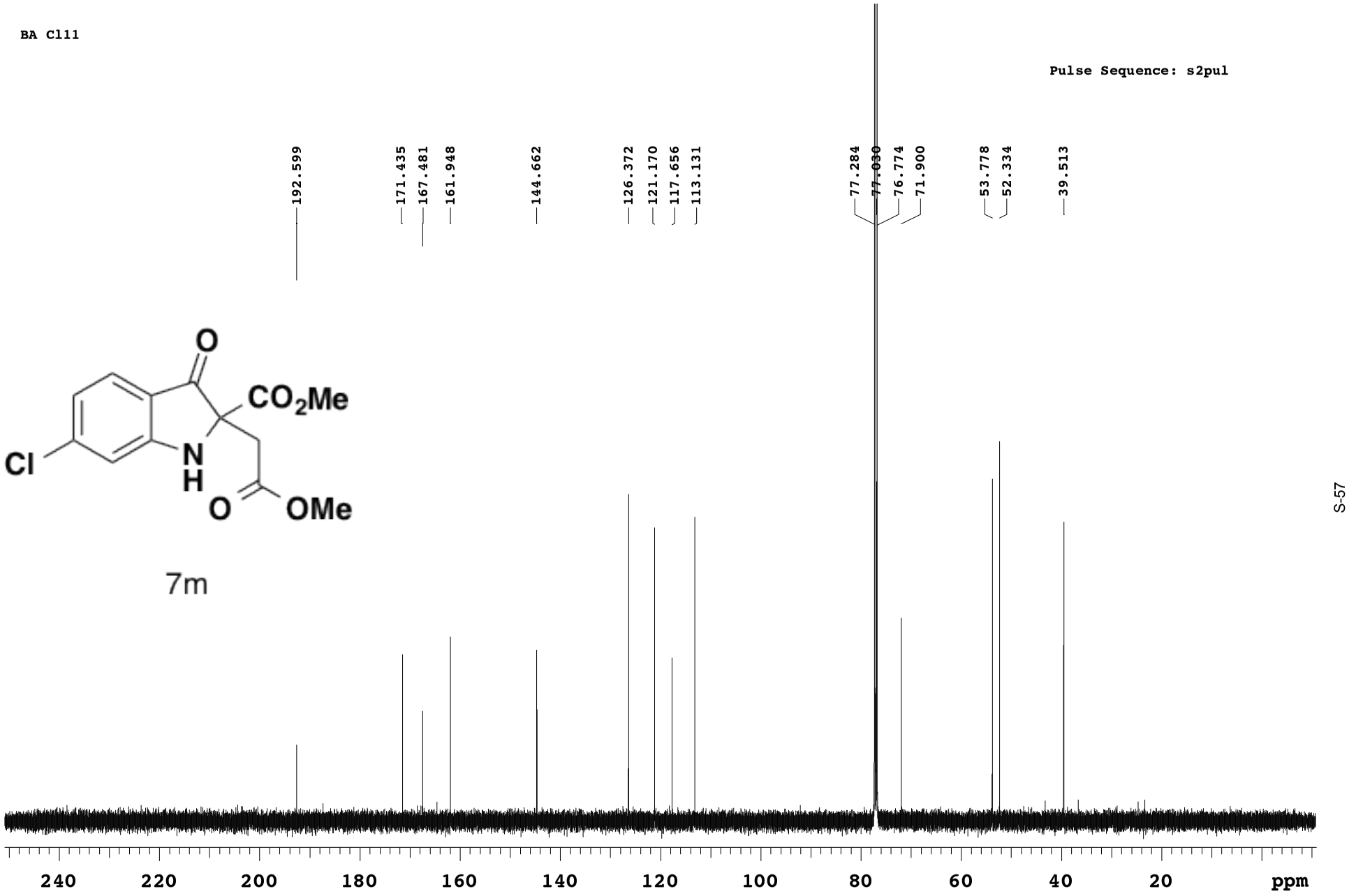
7l

BA C111

Pulse Sequence: PRESAT

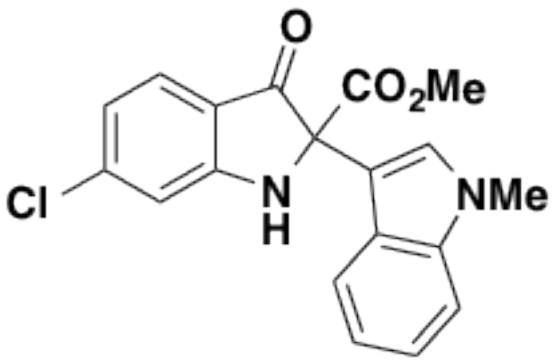


7m

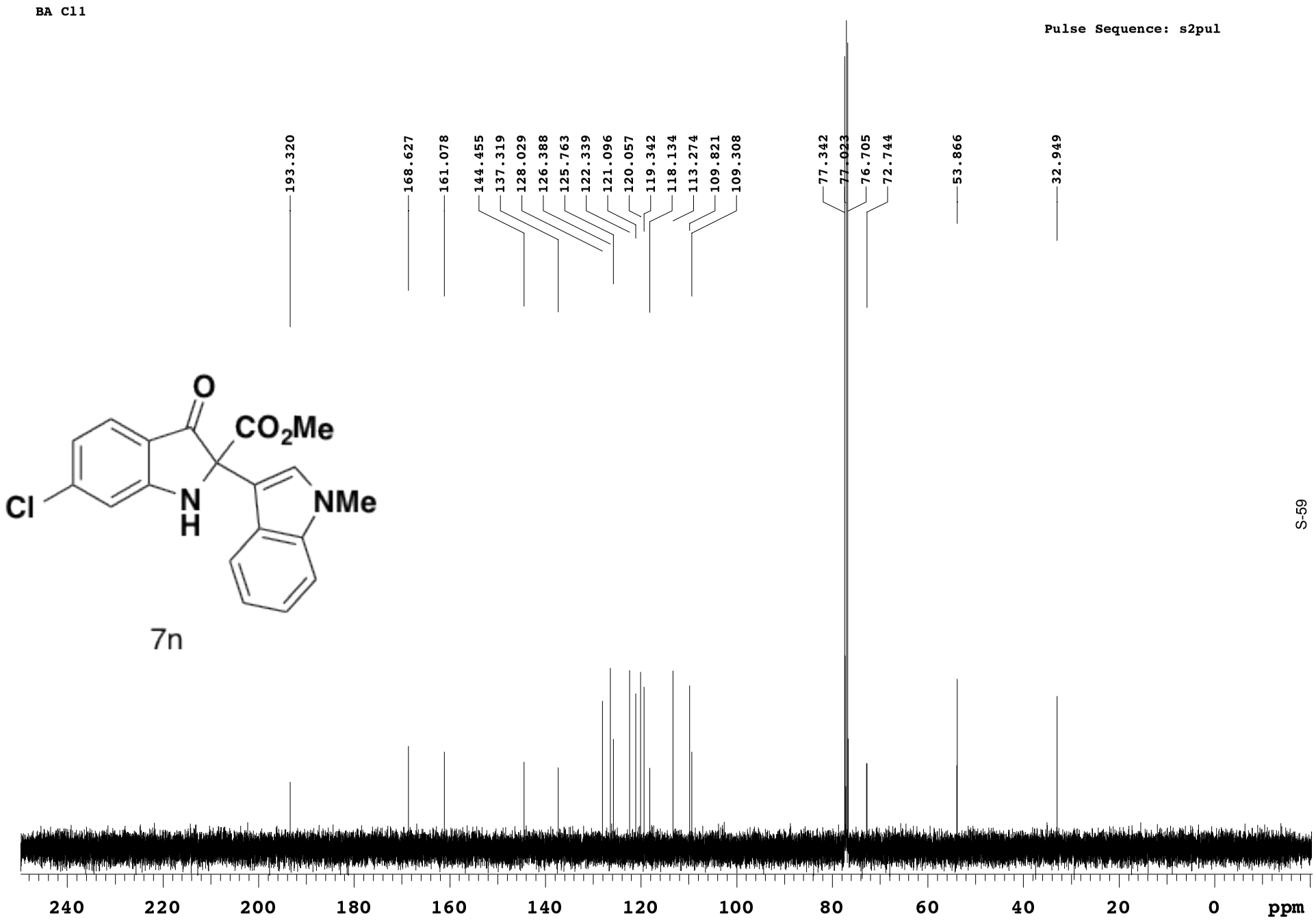

BA Cl11
Pulse Sequence: s2pul
192.599
171.435
167.481
161.948
144.662
126.372
121.170
117.656
113.131
77.284
77.030
76.774
71.900
53.778
52.334
39.513
O
CO2Me
Cl
N
H
O
OMe
7m
240
220
200
180
160
140
120
100
80
60
40
20
ppm

BA C11

Pulse Sequence: s2pul

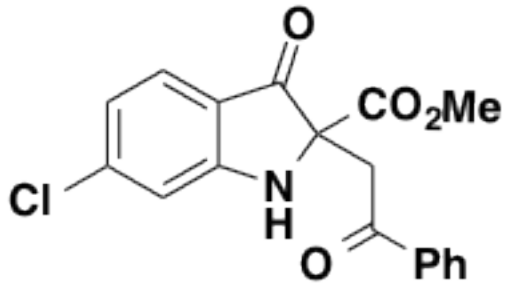


7n


BA Cl1
Pulse Sequence: s2pul
193.320
168.627
161.078
144.455
137.319
128.029
126.388
125.763
122.339
121.096
120.057
119.342
118.134
113.274
109.821
109.308
77.342
77.023
76.705
72.744
53.866
32.949
O
CO2Me
Cl
N
H
NMe
7n
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

Phenylsilylenol ether trap on chlorodiazoazide

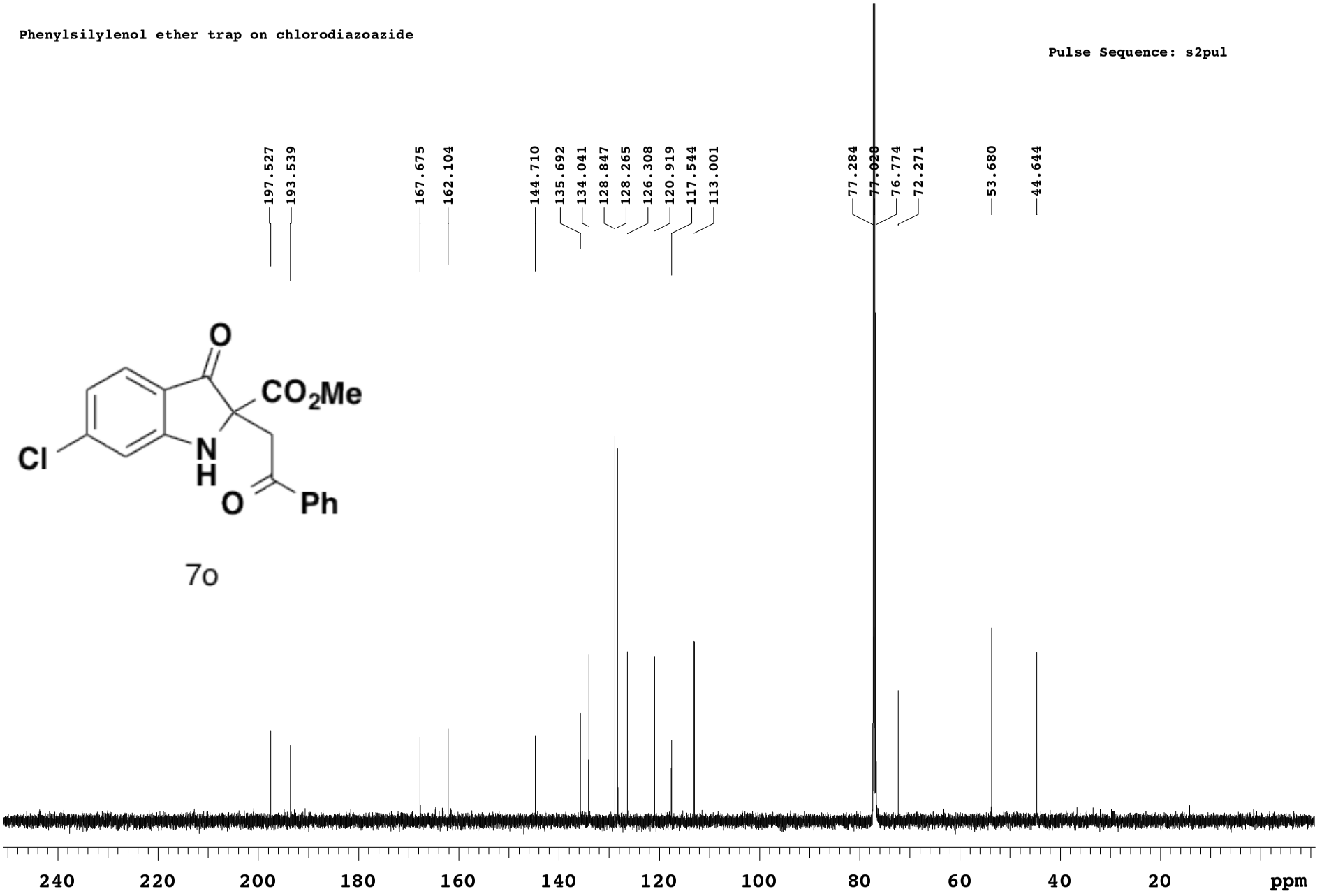
Pulse Sequence: PRESAT



7o

Phenylsilylenol ether trap on chlorodiazoazide

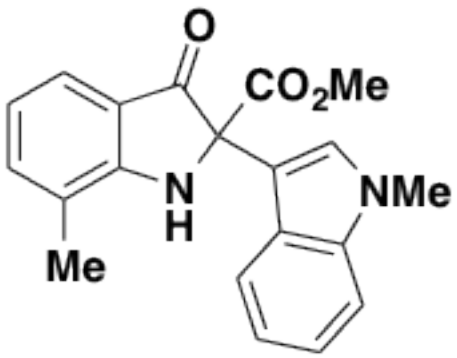
Pulse Sequence: s2pul



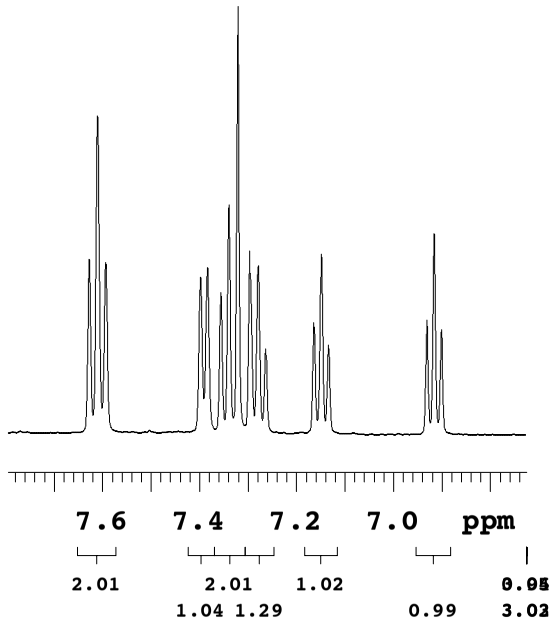
7o

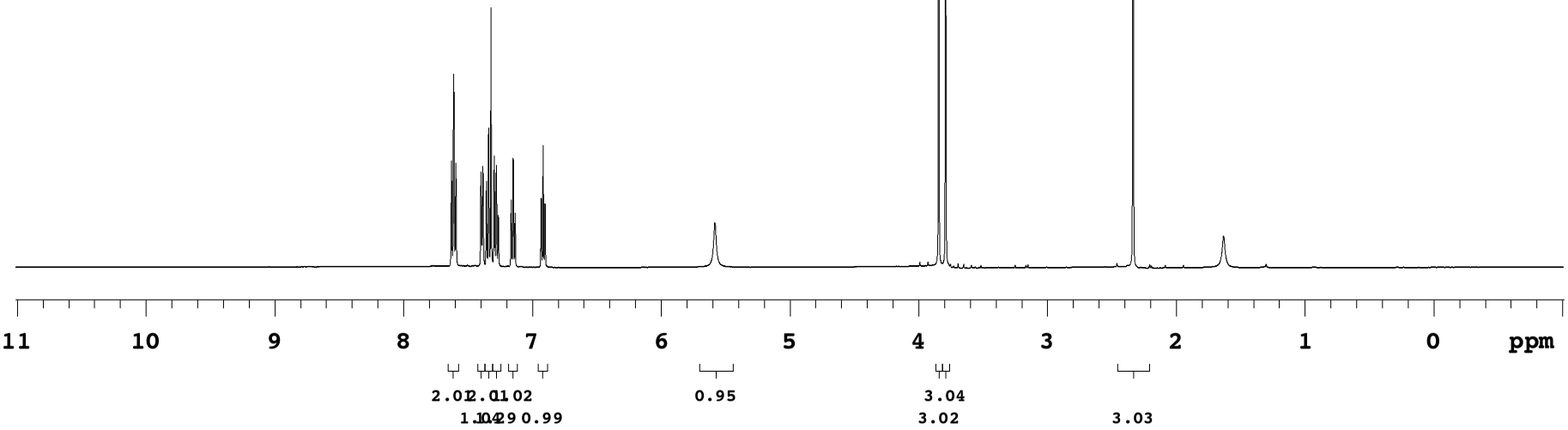
BA Me1

Pulse Sequence: PRESAT

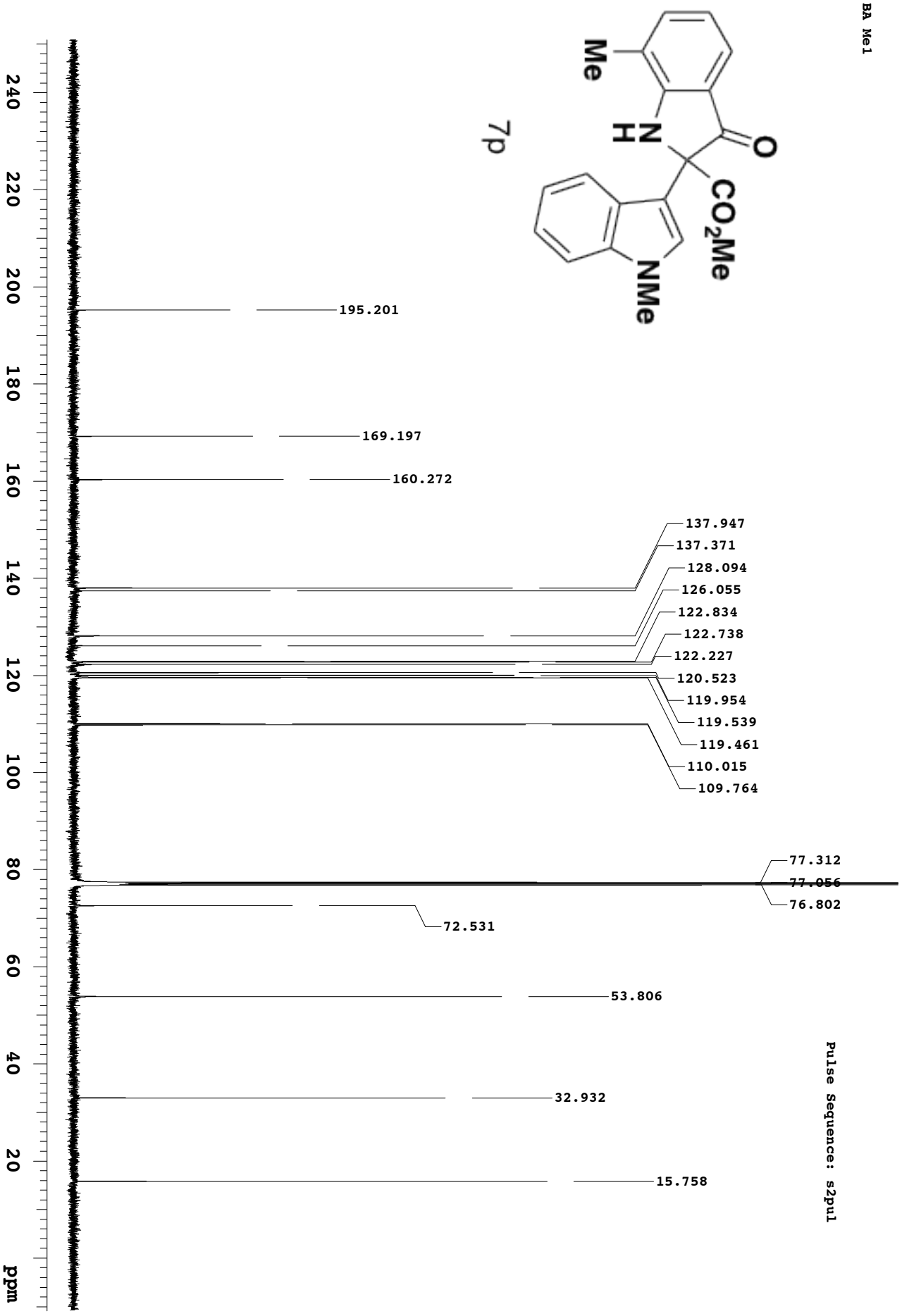


7p

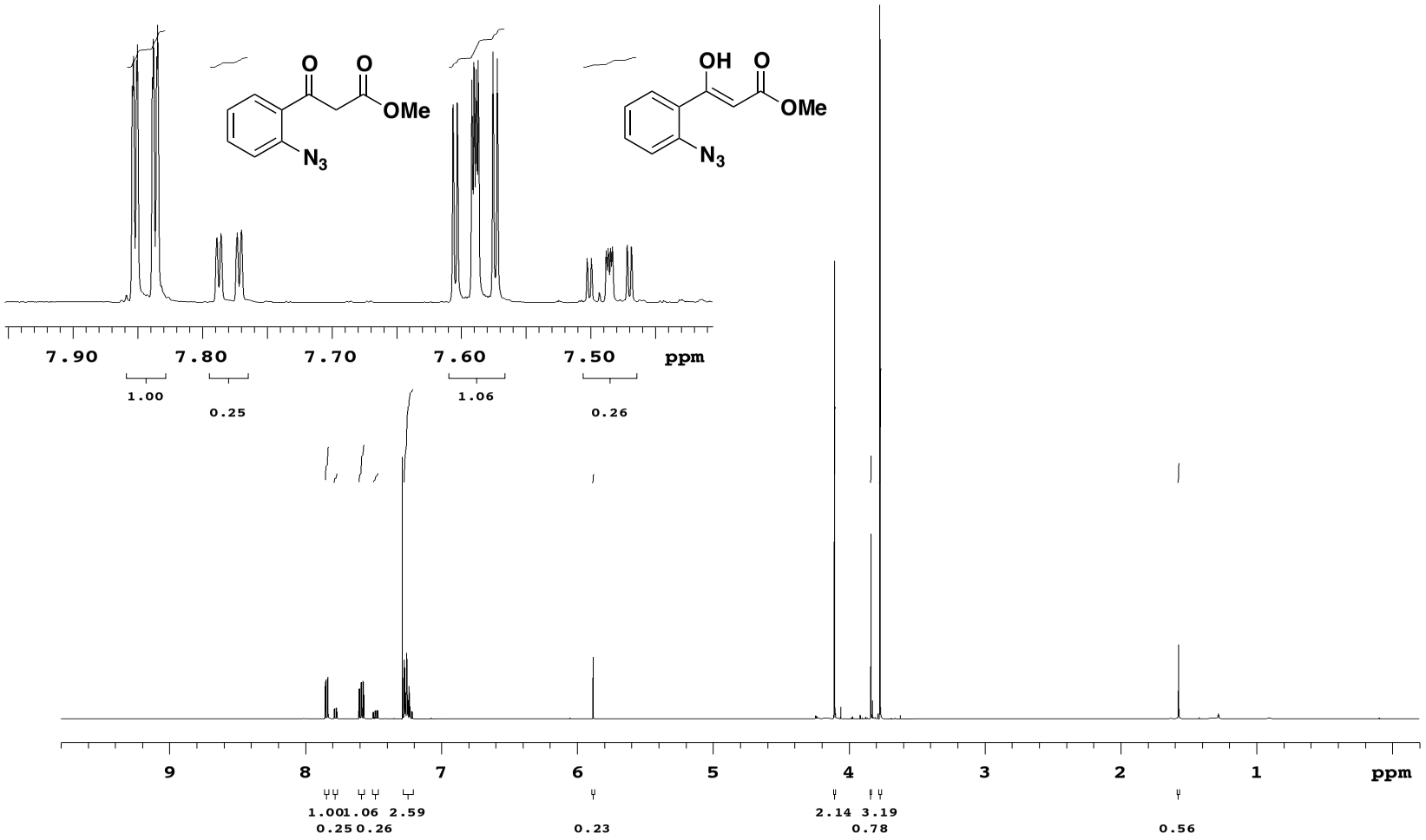




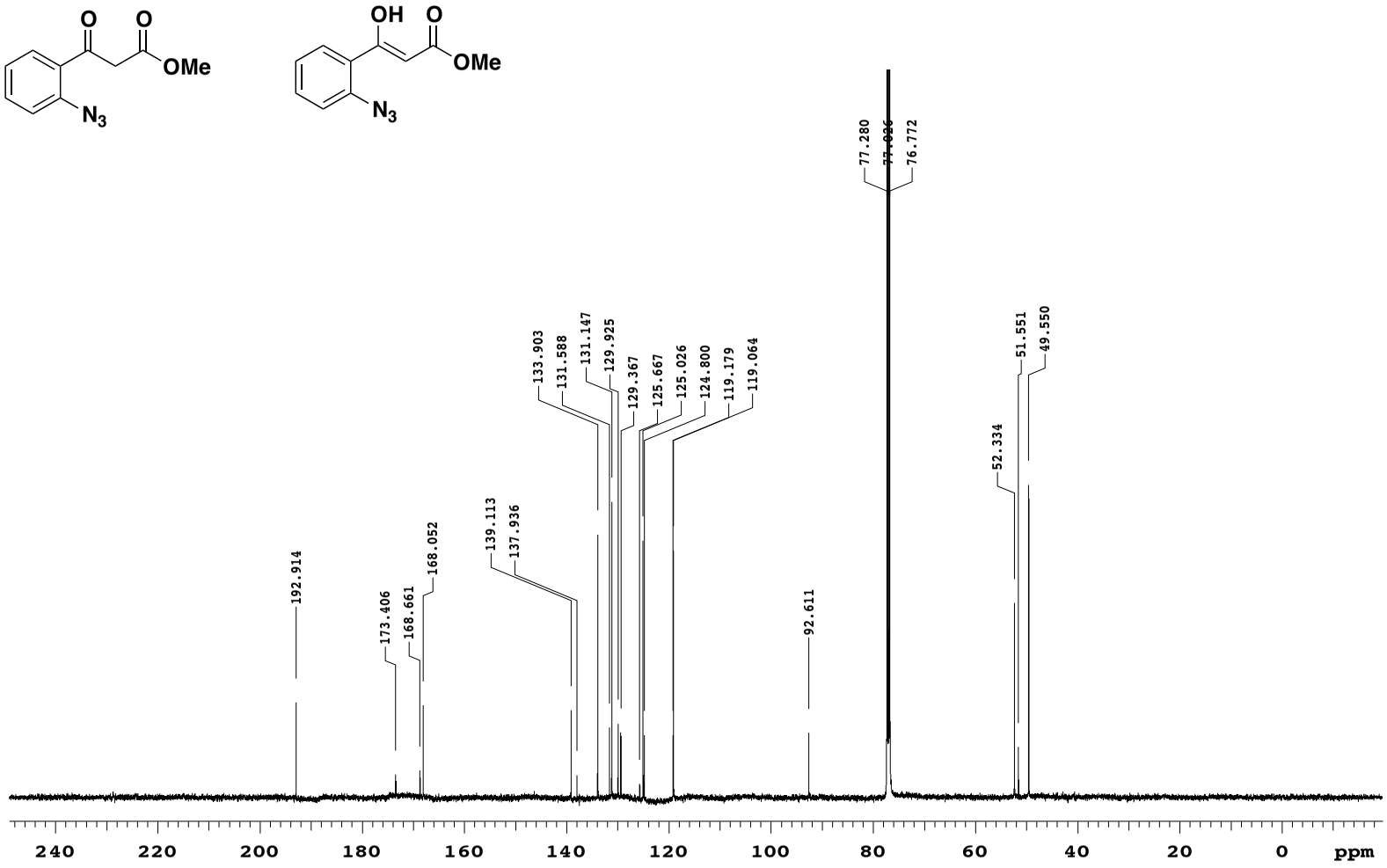
S-62

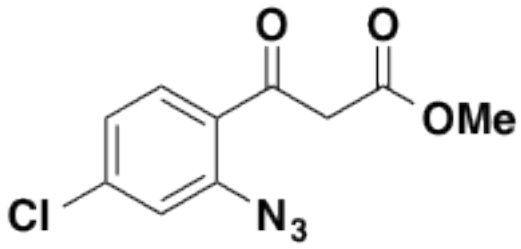

BA Me1
Me
N
H
O
CO2Me
NMe
7p
195.201
169.197
160.272
137.947
137.371
128.094
126.055
122.834
122.738
122.227
120.523
119.954
119.539
119.461
110.015
109.764
77.312
77.056
76.802
72.531
53.806
32.932
15.758
240
220
200
180
160
140
120
100
80
60
40
20
ppm
Pulse Sequence: s2pul

Mixture of compounds 9 and 9'



Mixture of Compounds 9 and 9'

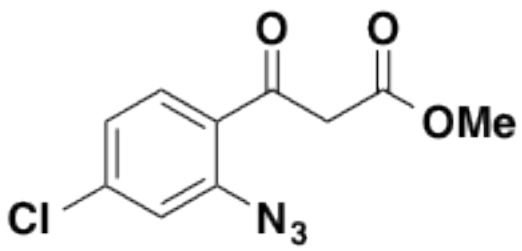



O
O
OMe
Cl
N3

10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
0.38
2.74
0.38
2.20
1.38
3.00

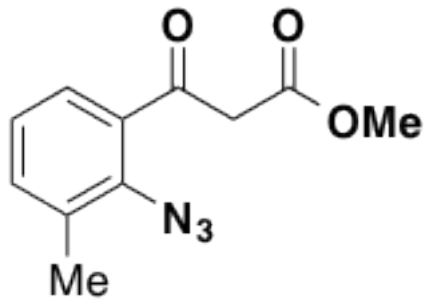
BA CHLORO AZIDO KETOENOL 13C

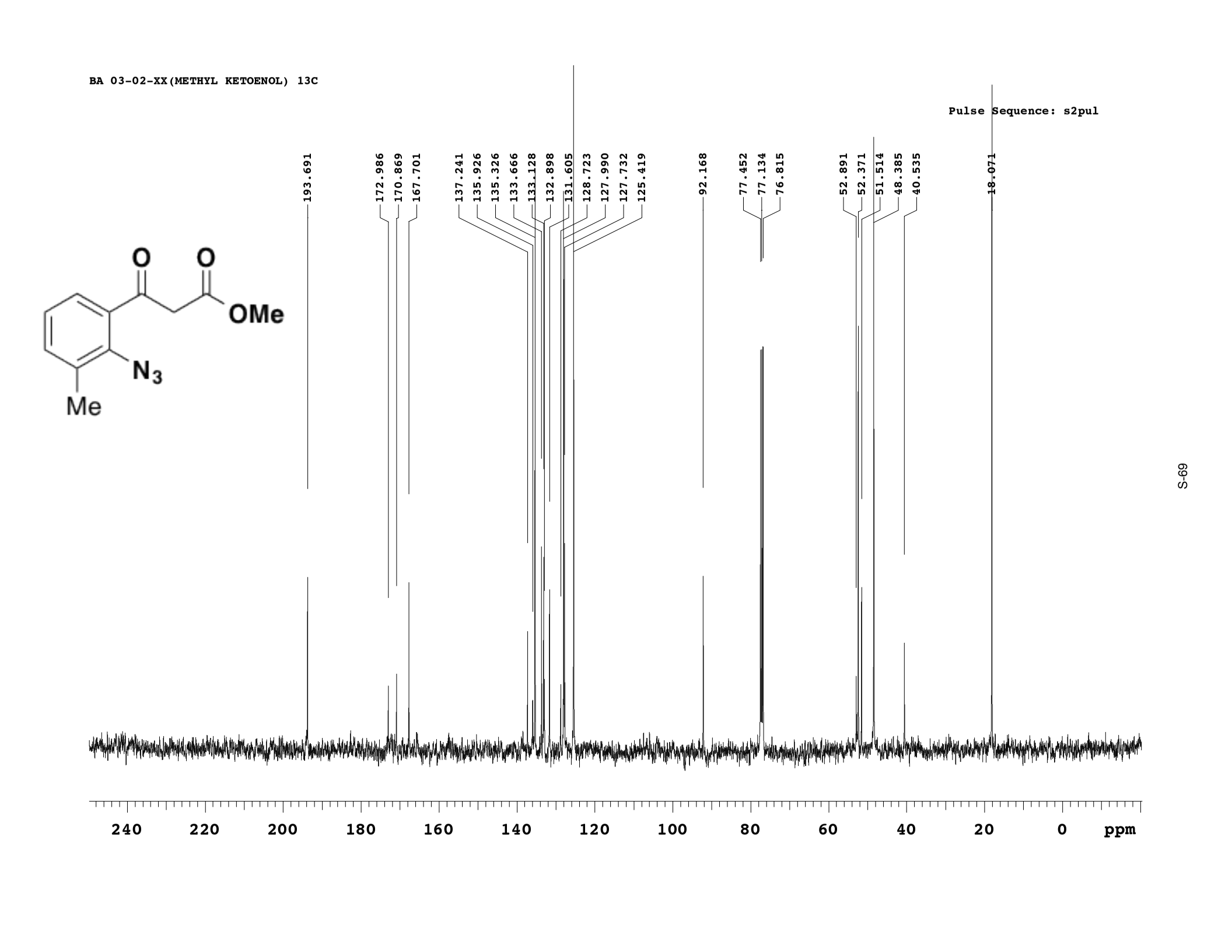
Pulse Sequence: s2pul



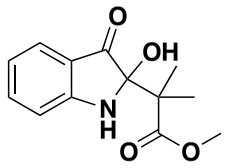
BA 03-02-XX(METHYL KETOENOL) CDCl3 1H-CLEAN

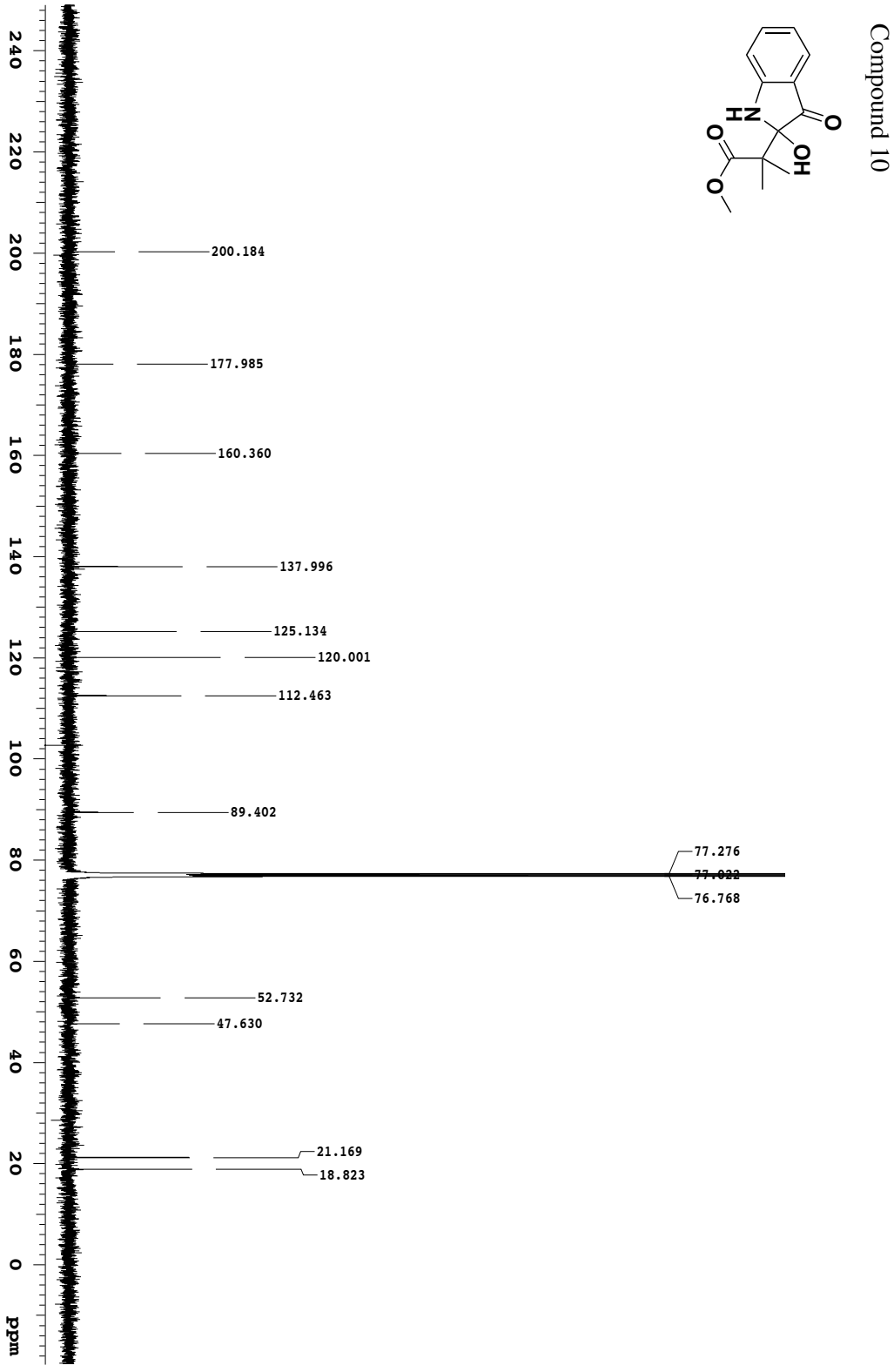
Pulse Sequence: s2pul



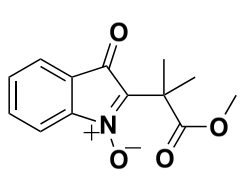

BA 03-02-XX(METHYL KETOENOL) 13C
Pulse Sequence: s2pul
193.691
172.986
170.869
167.701
137.241
135.926
135.326
133.666
133.128
132.898
131.605
128.723
127.990
127.732
125.419
92.168
77.452
77.134
76.815
52.891
52.371
51.514
48.385
40.535
18.071
O
O
OMe
N3
Me
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm

Compound 10

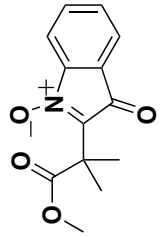



Compound 10
200.184
177.985
160.360
137.996
125.134
120.001
112.463
89.402
77.276
77.022
76.768
52.732
47.630
21.169
18.823
ppm

Compound 11



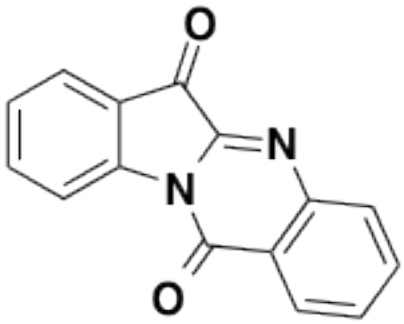
Compound 11



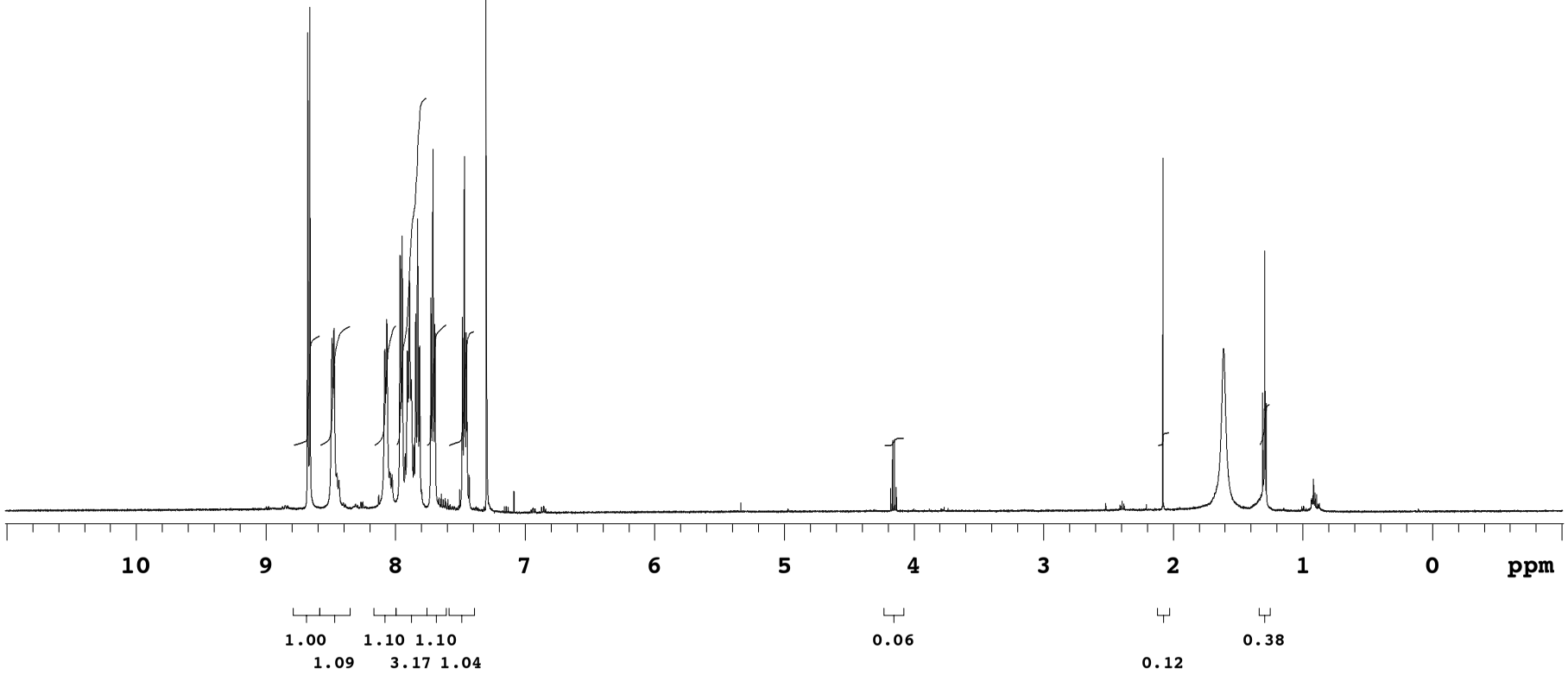
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm
173.369
162.765
159.328
146.097
136.429
128.569
128.452
127.154
116.972
77.261
77.006
76.753
52.807
49.253
23.541

Bren+Jordan, TRYPTANTHRIN

Pulse Sequence: PRESAT



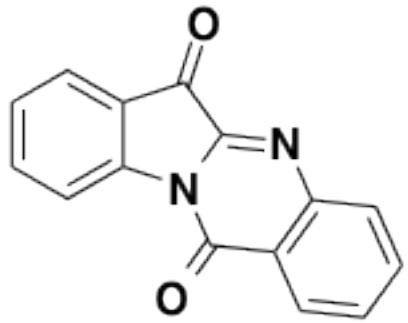
13



Tryptanthrin 13C CDCl3

Pulse Sequence: s2pul

182.593
158.127
146.665
146.373
144.368
138.302
135.153
130.759
130.270
127.580
127.227
125.430
123.776
121.969
117.999
77.290
77.037
76.781



13

180 160 140 120 100 80 60 40 ppm