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Supporting Information

5-(Cyano)dibenzothiophenium Triflate: A Sulfur-Based Reagent for Electrophilic Cyanation and Cyanocyclizations

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Supporting Information

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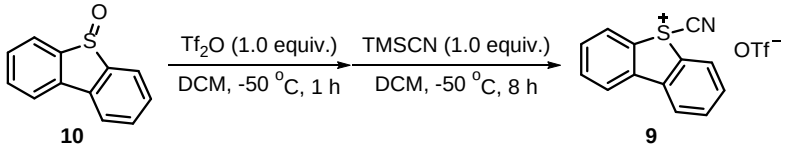
1. General methods

All dry solvents were obtained from a solvent purification system MBSPS7 from M.Braun. All reactions were carried out under nitrogen atmosphere unless stated otherwise. ^{1}H and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$, CD_3CN or DMSO-d_6 on Bruker AV 500, 400 or DPX 300 NMR spectrometer. ^{1}H NMR spectra was recorded with $CDCl_3$ (tetramethylsilane, δ = 0.00 ppm), CD_3CN (δ = 1.94 ppm), Methylene Chloride-d_2 or DMSO-d_6 (δ = 2.50 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (δ = 77.16 ppm), CD_3CN (δ = 1.32 ppm) or DMSO-d_6 (δ = 39.52 ppm) as internal reference. Mass spectra were measured on a Finnigan MAT 8200 (70 eV) (EI), a Finnigan MAT 95 (ESI), or a Bruker APEX III FT-MS (7 T magnet) mass spectrometer. IR spectra were recorded on a JASCO FT/IR-4100 spectrometer at room temperature, the stretching frequencies are reported in wavenumbers (cm^{-1}). Column chromatography was performed either on Merck 60 (40-63 μm) silica gel or Biotage One automated column chromatography system on CHROMABOND® Flash BT 15g (or 25g) SiOH 40-63 μm from Macherey-Nagel. Thin-layer chromatography (TLC) analysis was performed using POLYGRAM® SIL G/UV254 TLC plates from Macherey-Nagel and visualized by UV irradiation and/or phosphomolybdic acid staining. All commercially available compounds (Acros, ABCR, Alfa Aesar, Aldrich, Fluorochem, TCI) were used as received unless stated otherwise.

2. Synthesis of 5-(cyano)dibenzothiophenium triflate 9

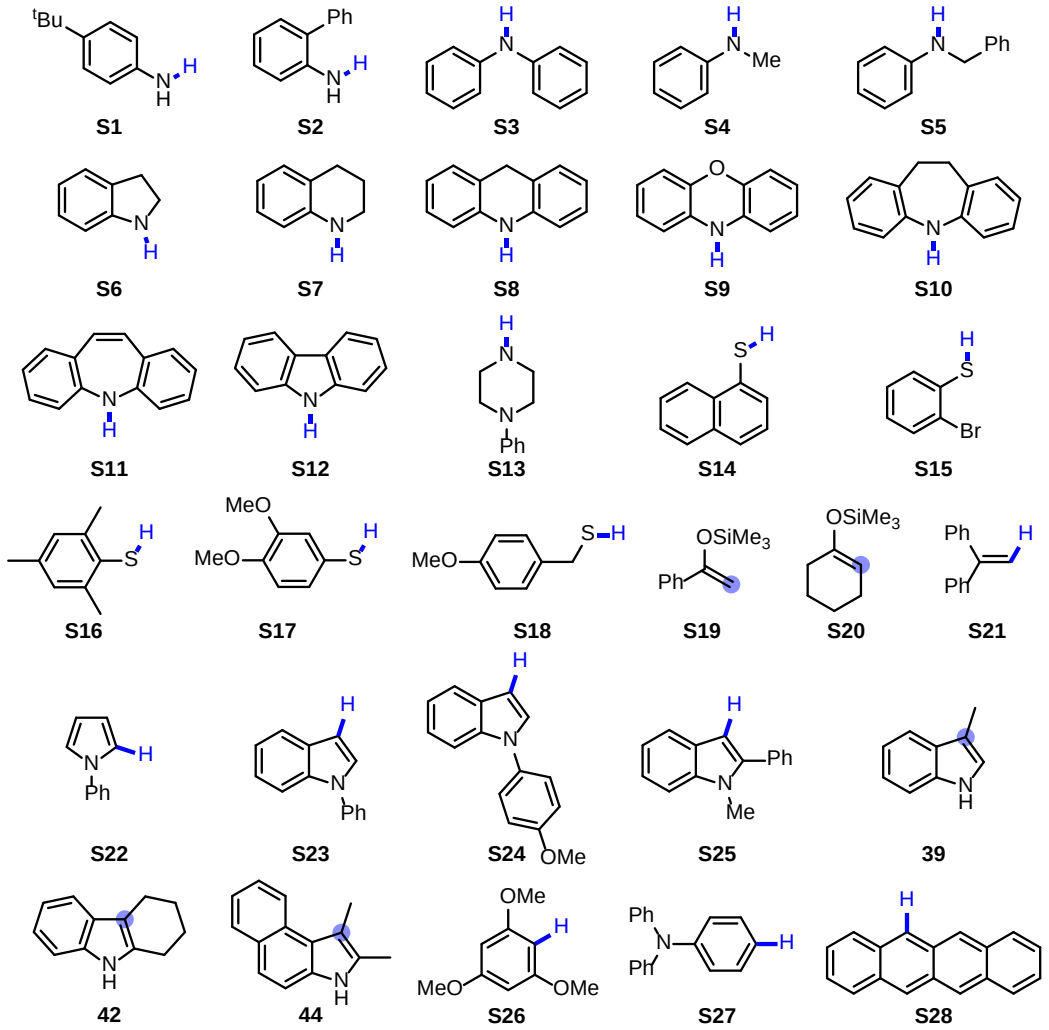


10 **9**

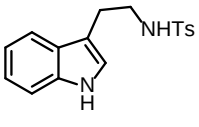
Tf_2O (25 mmol, 1 equiv, 4.205 mL) was added dropwise within 5 minutes to a solution of dibenzo[*b*,*d*]thiophene 5-oxide **10**[1] (1.0 equiv., 25 mmol, 5.007 g) in dry dichloromethane (350 mL) at -50°C under N_2. After stirring the resulting mixture for 1 hour, TMSCN (25 mmol, 1.0 equiv., 3.35 mL) was added dropwise and the mixture was further stirred at -50°C for 8 additional hours. Then, the cooling system was removed, and the formed suspension was allowed reaching room temperature. Filtration of the solvents afforded **9** as a white/beige solid, which was further washed with dichloromethane (2 x 50 mL), and finally dried under vacuum (5.39 g,15.0 mmol, 60%). ^{1}H NMR (300 MHz, Acetonitrile-d_3) δ = 8.56 (d, *J* = 8.4 Hz, 2H), 8.34 (dd, *J* = 7.8, 1.2 Hz, 2H), 8.04 (td, *J* = 7.8, 1.2 Hz, 2H), 7.89-7.83 (m, 2H). ^{13}C NMR (75 MHz, Acetonitrile-d_3) δ 141.7, 137.2, 133.7, 130.0, 127.2, 126.4, 121.9 (q, *J* = 320.4 Hz), 103.9. IR (neat): 3097, 2192, 1578, 1484, 1448, 1423, 1278, 1250, 1221, 1174, 1161, 1152, 1024, 780, 754, 700, 648, 631, 575, 514 cm^{-1}; HRMS calculated m/z for $C_{13}H_8NS^+$ $[M\text{-}OTf]^+$: 210.0372, found (ESI) 210.0365.

3. Preparation of substrates

Anilines **S1**, **S2**, **S3**, **S4**, **S5**, **S6**, **S7**, **S8**, **S9**, **S10**, **S11**, **S27**, carbazole **S12**, amine **S13**, thiols **S14**, **S15**, **S16**, **S17**, **S18**, silyl enol ether **S20**, alkene **S21**, pyrrole **S22**, indoles **S25**, **39**, **42**, 3*H*-benzo[*e*]indole **44**, and arenes **S26**, **S28** are commercially available and used as received. Silyl enol ether **S19** is commercially available and was freshly distilled before use. Indoles **S23**,[2] **S24**[3] were prepared according to the previously reported literature procedures.



Tryptamine derivatives **S29**,[4] **S30**,[5] **S31**,[6] **S32**,[7] **S35**,[8] **S36**,[9] **S38**,[5] tryptophol derivatives **S40,**[10] **S41,**[10] **S42**,[11] and indole derivatives **S44**,[12] **S48**,[13] **S49**[13] were prepared according to the previously reported literature procedures. Tryptophol **S39** is commercially available and used as received. Tryptamine derivatives **S33, S34**, **S37** and indole derivatives **S43**, **S45**, **S46**, **S47**, **S50**, **S51** were prepared according to the following procedure:



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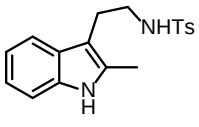

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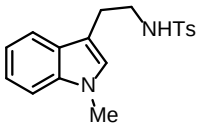

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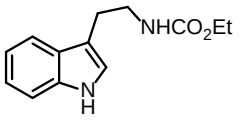

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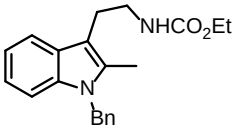

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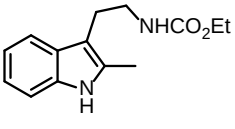

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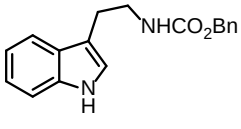

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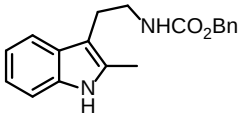

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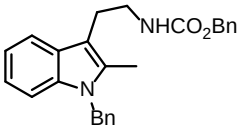

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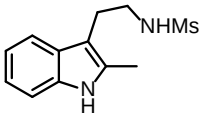

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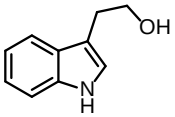

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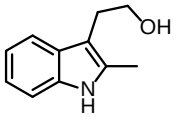

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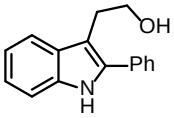

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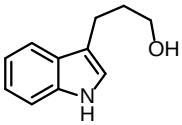

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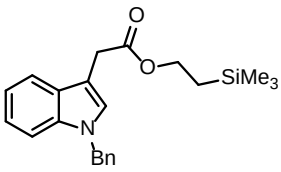

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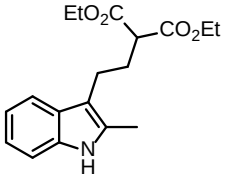

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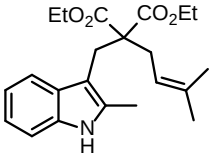

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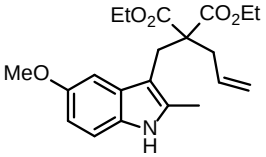

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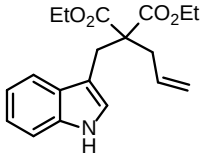

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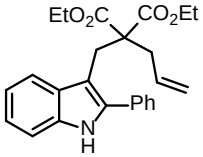

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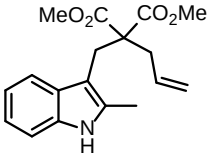

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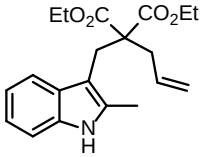
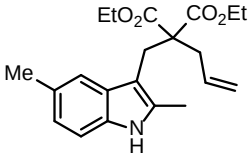
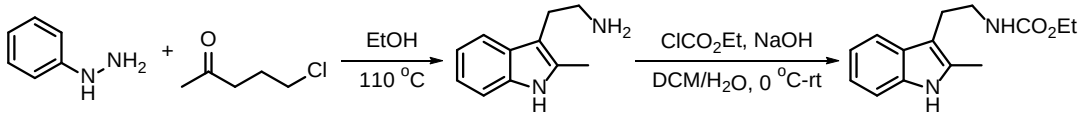


S50



S51

Procedure for the preparation of S34

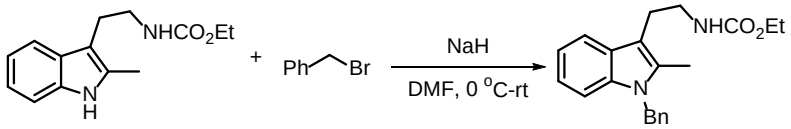


S34

In a sealed tube, 5-chloropentan-2-one (20 mmol, 2.0 equiv, 2.29 mL) was added dropwise to a solution of phenylhydrazine (1.0 equiv., 10 mmol, 985 μL) in ethanol (30 mL) at room temperature. The resulting mixture was stirred at 110 °C for 10 h. After cooling to room temperature, the solvent was removed under vacuum. Then, DCM (20 mL) and NaOH aqueous (800 mg NaOH dissolved in 20 mL H_2O) was added. The resulting mixture was

stirred at 0 °C for 5 minutes. Then, ethyl chloroformiate (952 μL, 10 mmol, 1.0 equiv) was added to the mixture dropwise at 0 °C and the resulting mixture was stirred at room temperature for 5 h. The solution thus obtained was extracted with DCM, washed with brine and dried over anhydrous Na_2SO_4. Solvent evaporation from the organic phase under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 4:1) to afford **S34** (1.53 g, 62% overall yield) as a colorless dense oil. ^{1}H NMR (400 MHz, DMSO-d_6, 100 ^{o}C) δ = 10.34 (bs, 1H), 7.45 – 7.38 (m, 1H), 7.25-7.22 (m, 1H), 7.01 – 6.89 (m, 2H), 6.52 (bs, 1H), 4.02 (q, J = 7.2 Hz, 2H), 3.25 – 3.13 (m, 2H), 2.85 – 2.76 (m, 2H), 2.34 (s, 3H), 1.17 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6, 100 ^{o}C) δ = 155.7, 135.0, 131.5, 128.1, 119.3, 117.5, 116.7, 109.8, 107.2, 58.9, 40.9, 24.1, 14.0, 10.5. IR (neat): 3398, 3318, 2979, 2931, 1623, 1517, 1461, 1436, 1383, 1337, 1300, 1171, 1138, 1107, 1077, 1032, 1010, 955, 873, 778, 671, 584, 565, 507 cm^{-1}; HRMS calculated m/z for $C_{14}H_{19}N_2O_2^+$ $[M+H]^+$: 247.1441, found (ESI) 247.1444.

Procedure for the preparation of S33

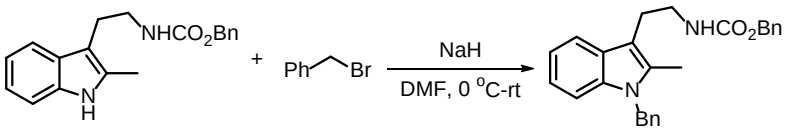


S34 **S33**

To a stirred solution of **S34** (665 mg, 2.70 mmol, 1.0 equiv) in DMF (20 mL), NaH (w/w 60% in mineral oil, 119 mg, 2.97 mmol, 1.1 equiv) was added under nitrogen flow. The resulting mixture was stirred at 0 °C for 0.5 h, Then, benzyl bromide (353 μL, 2.97 mmol, 1.1 equiv) was added to the mixture dropwise. The resulting mixture was stirred at room temperature for 4 h. The reaction was quenched with water, extracted with ethyl acetate and dried over Na_2SO_4. Evaporation of the organic solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 8:1) to afford **S33** (375 mg, 41% yield) as a light yellow sticky oil. ^{1}H NMR (400 MHz, DMSO-d_6, 100 ^{o}C) δ = 7.55 – 7.50 (m, 1H), 7.31 – 7.24 (m, 3H), 7.24 – 7.18 (m, 1H), 7.06 – 6.97 (m, 4H), 6.56 (s, 1H), 5.36 (s, 2H), 4.01 (q, J = 7.2 Hz, 2H), 3.28 – 3.16 (m, 2H), 2.90-2.87 (m, 2H), 2.32 (s, 3H), 1.16 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6, 100

^{o}C) δ = 155.7, 138.0, 135.9, 132.9, 127.9, 127.4, 126.3, 125.6, 119.8, 118.1, 117.0, 108.7, 108.1, 58.9, 45.5, 40.9, 24.4, 14.0, 9.2. IR (neat): 3352, 2978, 2929, 1689, 1612, 1536, 1495, 1468, 1452, 1417, 1336, 1287, 1250, 1204, 1177, 1139, 1090, 1035, 980, 924, 878, 776, 737, 694, 608, 561, 520 cm^{-1}; HRMS calculated m/z for $C_{21}H_{25}N_2O_2^+$ $[M+H]^+$: 337.1911, found (ESI) 337.1917.

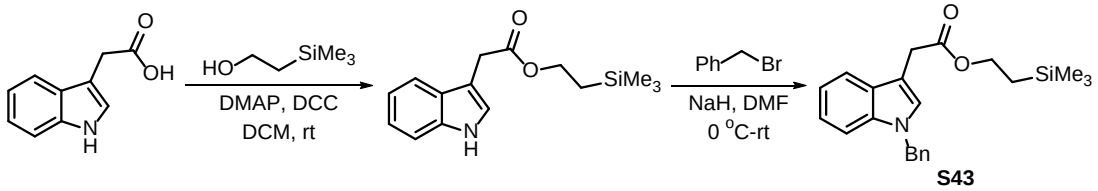
Procedure for the preparation of S37



S36 **S37**

To a stirred solution of **S36**[9] (2.22 g, 7.20 mmol, 1.0 equiv) in DMF (50 mL), NaH (w/w 60% in mineral oil, 317 mg, 7.92 mmol, 1.1 equiv)was added under nitrogen flow. The resulting mixture was stirred at 0 °C for 0.5 h. Then, benzyl bromide (856 μL, 7.20 mmol, 1.0 equiv) was added to the mixture dropwise. The resulting mixture was stirred at room temperature for 10 h. The reaction was quenched with water, extracted with ethyl acetate, dried over Na_2SO_4. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 20:1 to 10:1) to afford **S37** (1.30 g, 45% yield) as a light yellow sticky oil. ^{1}H NMR (400 MHz, DMSO-d_6, 100 ^{o}C) δ = 7.54 – 7.48 (m, 1H), 7.45 – 7.08 (m, 9H), 7.06 – 6.95 (m, 4H), 6.80 (s, 1H), 5.36 (s, 2H), 5.05 (s, 2H), 3.31 – 3.21 (m, 2H), 2.92-2.89 (m, 2H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6, 100 ^{o}C) δ = 155.5, 137.9, 136.9, 135.9, 132.9, 127.9, 127.6, 127.4, 127.0, 126.9, 126.3, 125.6, 119.8, 118.1, 117.0, 108.7, 108.1, 64.7, 45.5, 41.0, 24.4, 9.2. IR (neat): 3380, 2942, 1693, 1532, 1496, 1468, 1453, 1336, 1286, 1242, 1179, 1135, 1002, 737, 697, 608, 555 cm^{-1}; HRMS calculated m/z for $C_{26}H_{27}N_2O_2^+$ $[M+H]^+$: 399.2067, found (ESI) 399.2068.

Procedure for the preparation of S43



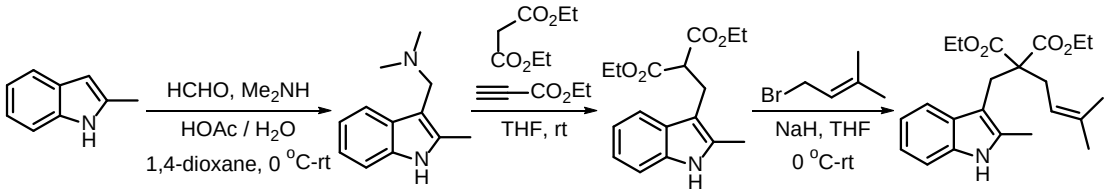
S43

To a stirred solution of indole-3-acetic acid (876 mg, 5.0 mmol, 1.0 equiv) in DCM (25 mL) was added 4-dimethylaminepyridine (30.5 mg, 0.25 mmol, 0.05 equiv), dicyclohexylcarbodiimide (1.135 g, 5.5 mmol, 1.1 equiv) and 2-(trimethylsilyl)ethan-1-ol (1.43 mL, 10 mmol, 2.0 equiv), sequentially. The resulting mixture was stirred at room temperature for 28 h. Then, the reaction mixture was filtered through a pad of celite. The obtained organic phase was washed with water and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 10:1) to afford 2-(trimethylsilyl)ethyl 2-(1*H*-indol-3-yl)acetate.[14]

To a stirred solution of 2-(trimethylsilyl)ethyl 2-(1*H*-indol-3-yl)acetate (1.19 g, 4.33 mmol, 1.0 equiv) in DMF (25 mL), NaH (w/w 60% in mineral oil, 190 mg, 4.76 mmol, 1.1 equiv) was added under nitrogen. The resulting mixture was stirred at 0 °C for 0.5 h. Then, benzyl bromide (540 μL, 4.54 mmol, 1.05 equiv) was added to the mixture dropwise. The resulting reaction mixture was stirred at room temperature for 4 h and subsequently quenched with water and extracted with ethyl acetate. The organic phase wes dried over Na_2SO_4, the solvent evaporated under the reduced pressure and finally the residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 50:1) to afford **S43** (656 mg, 41% yield) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.68 (d, *J* = 8.0 Hz, 1H), 7.36-7.27 (m, 4H), 7.26 – 7.11 (m, 5H), 5.32 (s, 2H), 4.31 – 4.19 (m, 2H), 3.80 (s, 2H), 1.06-1.02 (m, 2H), 0.06 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 172.3, 137.6, 136.7, 128.9, 128.1, 127.7, 127.2, 127.0, 122.0, 119.5, 119.3, 109.8, 107.9, 63.1, 50.1, 31.7, 17.5, -1.4. IR (neat): 2952, 1727, 1614, 1496, 1467, 1454, 1357, 1334, 1248, 1147, 1041, 1014, 963, 857, 834, 735, 695, 608, 551 cm^{-1}; HRMS calculated m/z for $C_{22}H_{28}NO_2Si^+$ $[M+H]^+$: 366.1884, found (ESI) 366.1878.

Procedure for the preparation of S45[15] [16] [17]



To a stirred solution of formaldehyde (37 wt% in water, 1.65 mL, 22 mmol, 1.1 equiv.) in 1,4-dioxane (100 mL) water (1.54 mL) and glacial acetic acid (20 mL) were added sequentially. The resulting solution was stirred at 0 °C for 5 minutes. Then, dimethylamine (40 wt% in water, 2.73 mL, 22 mmol, 1.1 equiv.) and 2-methyl-1*H*-indole (2.624, 20 mmol, 1.0 equiv.) were added to the mixture, sequentially. The mixture was stirred at 0°C for 2 h, and for further 5 hours at room temperature. Then, the reaction was treated with NaOH aqueous (16 g NaOH dissolved in 200 mL H_2O) at 0 °C. The resulting mixture was extracted with ethyl acetate, and the organic phase was washed with brine and dried over anhydrous Na_2SO_4. Evaporation of the solvent under the reduced pressure afforded a residue, which was used directly for the next step without further purification.[15]

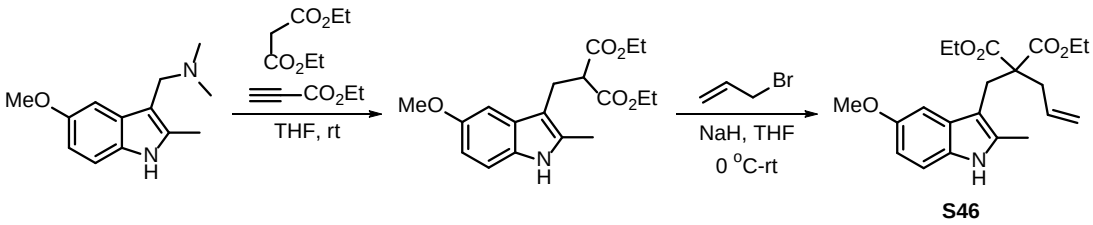
Diethyl malonate (3.04 mL, 20 mmol, 1.0 equiv.) and ethyl propiolate (2.03 mL, 20 mmol, 1.0 equiv.) were added sequentially to a stirred solution of the above residue in THF (100 mL). The resulting solution was stirred at room temperature for 12 h. Then, the reaction was quenched with water, extracted with ethyl acetate and the organic phase dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 8:1) to afford diethyl 2-((2-methyl-1*H*-indol-3-yl)methyl)malonate.[16]

NaH (w/w 60% in mineral oil, 120 mg, 3.0 mmol, 1.0 equiv) was added at 0 °C under nitrogen flow to a stirred solution of diethyl 2-((2-methyl-1*H*-indol-3-yl)methyl)malonate (910 mg, 3.0 mmol, 1.0 equiv) in THF (15 mL).[17] The resulting mixture was stirred at that temperature for 0.5 h. Then, 1-bromo-3-methylbut-2-ene (347 μL, 3.0 mmol, 1.0 equiv) was added to the mixture dropwise and the resulting solution was stirred at room temperature for 2 h. Then, it was quenched with saturated NH_4Cl (aq) and extracted with ethyl acetate. The organic phase was finally dried over anhydrous Na_2SO_4 and the solvent evaporated under reduced pressure. Compound **S45** (931 mg, 84% yield) was obtained as a light yellow sticky

oil after purification by column chromatography on silica gel (eluent: hexane/ethyl acetate = 8:1 to 4:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.84 (bs, 1H), 7.44 (d, *J* = 7.6, 1H), 7.19-7.16 (m, 1H), 7.07-6.98 (m, 2H), 5.27 – 5.19 (m, 1H), 4.17 – 4.00 (m, 4H), 3.40 (s, 2H), 2.59 (d, *J* = 6.8 Hz, 2H), 2.30 (s, 3H), 1.74 (d, *J* = 1.6 Hz, 3H), 1.57 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 172.0, 135.3, 135.2, 133.4, 129.6, 121.0, 119.1, 118.7, 118.7, 110.1, 106.4, 61.2, 59.1, 31.6, 27.9, 26.2, 18.3, 14.0, 12.2. IR (neat): 3350, 2979, 1750, 1713, 1493, 1462, 1444, 1366, 1323, 1297, 1248, 1211, 1175, 1117, 1096, 1071, 1053, 1026, 858, 816, 740, 665, 624, 567, 542, 517 cm^{-1}; HRMS calculated m/z for $C_{22}H_{30}NO_4^+$ $[M+H]^+$: 372.2169, found (ESI) 372.2164.

Procedure for the preparation of S46



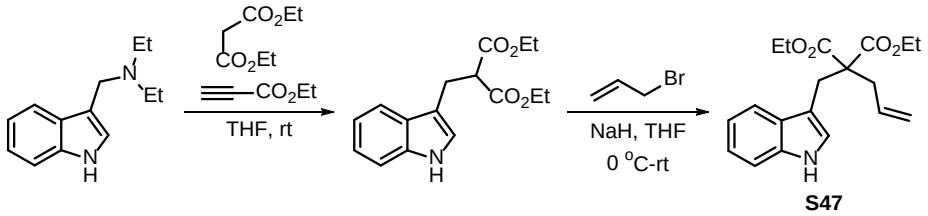
S46

Diethyl malonate (911 μL, 6.0 mmol, 1.0 equiv.) and ethyl propiolate (669 μL, 6.6 mmol, 1.1 equiv.), were added sequentially to a stirred solution of 1-(5-methoxy-2-methyl-1*H*-indol-3-yl)-*N*,*N*-dimethylmethanamine (1.44 g, 6.6 mmol, 1.1 equiv.) in THF (30 mL). The resulting solution was stirred at room temperature for 18 h. Then, the reaction was quenched with water, extracted with ethyl acetate, washed with brine, and the organic phase was dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (hexane/ethyl acetate = 4:1) to afford diethyl 2-((5-methoxy-2-methyl-1*H*-indol-3-yl)methyl)malonate.[16]

NaH (w/w 60% in mineral oil, 198 mg, 4.94 mmol, 1.1 equiv) was added to a stirred solution of diethyl 2-((5-methoxy-2-methyl-1*H*-indol-3-yl)methyl)malonate (1.50 g, 4.49 mmol, 1.0 equiv) in THF (15 mL) at 0 °C under nitrogen. The resulting mixture was stirred at 0 °C for 0.5 h; then, allyl bromide (427 μL, 4.94 mmol, 1.1 equiv) was added to the mixture dropwise and the resulting mixture stirred at room temperature for 3 h. Then, the reaction was quenched with water, extracted with ethyl acetate and the organic phase was dried over anhydrous

Na_2SO_4. Evaporation of the solvent under the reduced pressure let a residue, which was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 5:1) to afford **S46** (1.19 g, 71% yield) as a light yellow sticky oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.77 (bs, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 6.96 (d, *J* = 2.4 Hz, 1H), 6.72 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.98-5.88 (m, 1H), 5.20 – 5.04 (m, 2H), 4.21 – 3.98 (m, 4H), 3.82 (s, 3H), 3.37 (s, 2H), 2.66 (d, *J* = 7.2 Hz, 2H), 2.30 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 171.7, 153.9, 134.3, 133.5, 130.4, 130.0, 118.7, 110.8, 110.8, 106.2, 101.5, 61.3, 59.4, 56.1, 37.9, 28.5, 14.1, 12.5. IR (neat): 3360, 2936, 1747, 1716, 1590, 1487, 1449, 1365, 1303, 1254, 1200, 1093, 1045, 1010, 967, 930, 891, 867, 843, 829, 792, 775, 745, 690, 670, 626, 583, 541 cm^{-1}; HRMS calculated m/z for $C_{21}H_{28}NO_5^+$ $[M+H]^+$: 374.1962, found (ESI) 374.1963.

Procedure for the preparation of S47



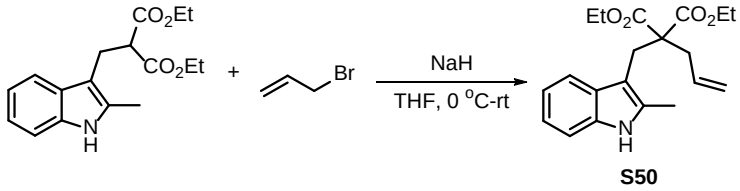
S47

Diethyl malonate (1.52 mL, 10 mmol, 1.0 equiv.) and ethyl propiolate (1.114 mL, 11 mmol, 1.1 equiv.) were subsequently added to a stirred solution of *N*-((1*H*-indol-3-yl)methyl)-*N*-ethylethanamine (2.225 g, 11 mmol, 1.1 equiv.) in THF (30 mL). The resulting solution was stirred at room temperature for 16 h, and then the reaction was quenched with water, extracted with ethyl acetate and the organic phase dried over anhydrous Na_2SO_4. The organic solvent was evaporated under reduced pressure and the residue obtained was used directly for the next step without further purification.

NaH (w/w 60% in mineral oil, 400 mg, 10.0 mmol, 1.0 equiv) was added at 0 °C under nitrogen to a stirred solution of the above residue in THF (50 mL). The resulting mixture was stirred at 0 °C for 0.5 h and then, allyl bromide (865 μL, 10.0 mmol, 1.0 equiv) was added to the mixture dropwise. The solution thus obtained was stirred at room temperature for 1 h and then quenched with water and extracted with ethyl acetate. The organic phase was subsequently dried over anhydrous Na_2SO_4 and the solvent evaporated under the reduced pressure. The residue obtained was purified by column chromatography on silica gel (eluent:

hexane/ethyl acetate = 10:1) to afford **S47** (976 mg, 30% yield) as a light yellow sticky oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.10 (bs, 1H), 7.58-7.55 (m, 1H), 7.32-7.29 (m, 1H), 7.17-7.13 (m, 1H), 7.10-7.06 (m, 1H), 6.98 (d, *J* = 2.8 Hz, 1H), 5.92 – 5.72 (m, 1H), 5.17 – 5.13 (m, 1H), 5.13 – 5.07 (m, 1H), 4.20 – 4.12 (m, 2H), 4.12 – 4.03 (m, 2H), 3.42 (d, *J* = 0.8 Hz, 2H), 2.68 (dt, *J* = 7.6, 1.6 Hz, 2H), 1.19 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 171.4, 135.9, 133.1, 128.3, 123.3, 122.0, 119.4, 119.1, 119.0, 111.2, 110.2, 61.4, 58.9, 37.4, 28.0, 14.1. IR (neat): 3347, 2976, 1752, 1714, 1641, 1459, 1444, 1361, 1290, 1245, 1193, 1151, 1097, 1066, 1039, 1017, 916, 860, 803, 745, 656, 614, 578, 563, 545 cm^{-1}; HRMS calculated m/z for $C_{19}H_{24}NO_4^+$ $[M+H]^+$: 330.1700, found (ESI) 330.1701.

Procedure for the preparation of S50

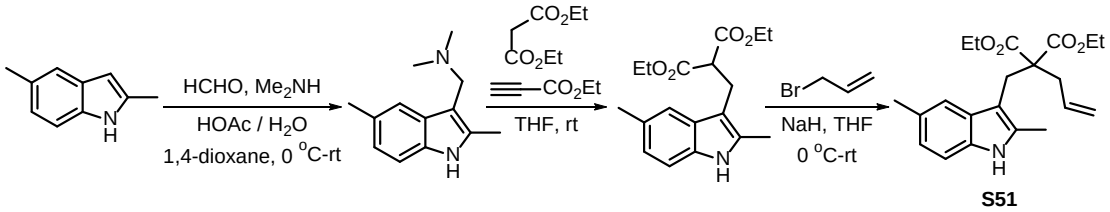


S50

NaH (w/w 60% in mineral oil, 120 mg, 3.0 mmol, 1.0 equiv) was added at 0 °C under nitrogen to a stirred solution of diethyl 2-((2-methyl-1*H*-indol-3-yl)methyl)malonate (910 mg, 3.0 mmol, 1.0 equiv) in THF (15 mL). The resulting mixture was stirred at 0 °C for 0.5 h. and then allyl bromide (260 μL, 3.0 mmol, 1.0 equiv) was added dropwise and stirred at room temperature for two additional hours. Then, the reaction was quenched with saturated NH_4Cl solution, extracted with ethyl acetate and the organic phase was dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 10:1 to 5:1) to afford **S50** (852 mg, 83% yield) as a light yellow sticky oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.82 (bs, 1H), 7.46 (d, *J* = 7.6, 1H), 7.22-7.19 (m, 1H), 7.12 – 6.98 (m, 2H), 5.97-5.87 (m, 1H), 5.20 – 5.01 (m, 2H), 4.25 – 3.93 (m, 4H), 3.40 (s, 2H), 2.66-2.64 (m, 2H), 2.34 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 171.6, 135.3, 133.5, 133.4, 129.6, 121.1, 119.2, 118.7, 118.7, 110.1, 110.1, 106.4, 61.3, 59.4, 38.0, 28.4, 14.1, 12.5. IR (neat): 3372, 2981, 1743, 1713, 1491, 1462, 1440, 1392, 1366, 1297, 1198, 1158, 1120, 1096, 1062,

1046, 1020, 946, 862, 744, 690, 667, 611, 579, 564, 515 cm^{-1}; HRMS calculated m/z for $C_{20}H_{26}NO_4^+$ $[M+H]^+$: 344.1856, found (ESI) 344.1856.

Procedure for the preparation of S51



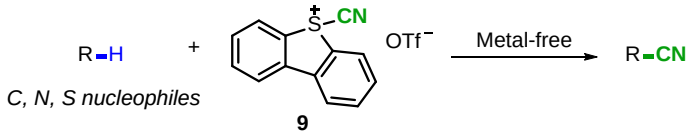
To a stirred solution of formaldehyde (37 wt% in water, 825 μL, 11 mmol, 1.1 equiv.) in 1,4-dioxane (50 mL) water (770 μL) and glacial acetic acid (10 mL) were added sequentially. The resulting solution was stirred at 0 °C for 5 minutes. Then, dimethylamine (40 wt% in water, 1.365 mL, 11 mmol, 1.1 equiv.) and 2,5-dimethyl-1*H*-indole (1.452, 10 mmol, 1.0 equiv.) were added and the mixture stirred 2 h at 0°C and 10 additional hours at room temperature. Then, the reaction was treated with aqueous NaOH solution (8 g NaOH dissolved in 100 mL H_2O) at 0 °C and the resulting mixture extracted with ethyl acetate and washed with brine. The organic solvents were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue thus obtained was used directly for the next step without further purification.[15]

Diethyl malonate (1.52 mL, 10 mmol, 1.0 equiv.) and ethyl propiolate (1.013 mL, 10 mmol, 1.0 equiv.), were sequentially added to a stirred solution of the above prepared residue in THF (30 mL). The resulting solution was stirred at room temperature for 12 h. Then, the reaction was quenched with water, extracted with ethyl acetate and the organic phase dried over anhydrous Na_2SO_4. Evaporation of the solvents under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 8:1 to 4:1) to afford diethyl 2-((2,5-dimethyl-1*H*-indol-3-yl)methyl)malonate.[16]

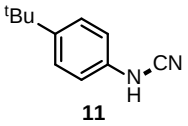
Finally, NaH (w/w 60% in mineral oil, 268 mg, 6.7 mmol, 1.0 equiv) was added at 0 °C to a stirred solution of diethyl 2-((2,5-dimethyl-1*H*-indol-3-yl)methyl)malonate (2.127 g, 6.7 mmol, 1.0 equiv) in THF (30 mL).[17] The resulting mixture was stirred at 0 °C for 0.5 h. and then allyl bromide (580 μL, 6.7 mmol, 1.0 equiv) was added to the mixture dropwise. The resulting mixture was stirred at room temperature for 2 h. and then the reaction was quenched

with saturated NH_4Cl (aq), extracted with ethyl acetate, and the organic phase dried over anhydrous Na_2SO_4. Evaporation of the solvents in vacuo afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 10:1 to 5:1) to afford **S51** (1.378 g, 58% yield) as a light yellow sticky oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.78 (bs, 1H), 7.223-7.217 (m, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.88 (dd, *J* = 8.0, 1.6 Hz, 1H), 5.96-5.86 (m, 1H), 5.19 – 5.05 (m, 2H), 4.20 – 4.01 (m, 4H), 3.37 (s, 2H), 2.65-2.63 (m, 2H), 2.40 (s, 3H), 2.27 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 171.6, 133.6, 133.6, 129.7, 128.1, 122.5, 118.6, 118.4, 109.8, 105.7, 61.2, 59.3, 37.8, 28.4, 21.6, 14.1, 12.5. IR (neat): 3346, 2978, 1746, 1714, 1590, 1440, 1366, 1299, 1200, 1148, 1093, 1060, 1042, 1023, 928, 861, 790, 754, 694, 670, 639, 604, 558, 517 cm^{-1}; HRMS calculated m/z for $C_{21}H_{28}NO_4^+$ $[M+H]^+$: 358.2013, found (ESI) 358.2018.

4. Direct metal-free cyanation of nucleophiles using 9

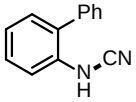


Procedure for the preparation of 11



To a stirred solution of 4-(*tert*-butyl)aniline **S1** (31.9 μL, 0.2 mmol, 1.0 equiv) in DCM (2 mL) was added K_3PO_4 (42.5 mg, 0.2 mmol, 1.0 equiv) and **9** (107.8 mg, 0.3 mmol, 1.5 equiv) at 0 °C under nitrogen flow, sequentially. The resulting mixture was stirred at 0 °C for 2 h. Then, the reaction was quenched with water, extracted with DCM and the organic phase was dried over anhydrous Na_2SO_4. Evaporation of the solvent under the reduced pressure produced a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) to afford **11** (25.2 mg, 72% yield) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.35 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.61 (bs, 1H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 146.8, 134.7, 126.7, 115.3, 111.9, 34.4, 31.5. The spectroscopic data are in agreement with those previously reported.[18]

Procedure for the preparation of 12

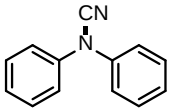


12

To a stirred solution of [1,1'-biphenyl]-2-amine **S2** (33.8 mg, 0.2 mmol, 1.0 equiv) in DCM (2 mL), K_3PO_4 (42.5 mg, 0.2 mmol, 1.0 equiv) and **9** (107.8 mg, 0.3 mmol, 1.5 equiv) were added sequentially at -10 °C. The resulting mixture was stirred at -10 °C for 4 h. and then the reaction was quenched with brine, extracted with DCM, and the organic phase dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 10:1) to afford **12** (37.7 mg, 97% yield) as a white solid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.54 – 7.45 (m, 2H), 7.45 – 7.26 (m, 5H), 7.24-7.21 (m, 1H), 7.18 – 7.09 (m, 1H), 5.96 (bs, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ = 136.7, 134.2, 130.7, 129.6, 129.3, 129.2, 129.1, 128.5, 123.7, 115.2, 110.7. The spectroscopic data are in agreement with those previously reported.[19]

General procedure for the preparation of 13-21

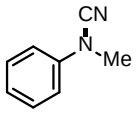
Cs_2CO_3 (65.2 mg, 0.2 mmol, 1.0 equiv) and **9** (107.8 mg, 0.3 mmol, 1.5 equiv) were added sequentially at room temperature to a stirred solution of the desired aniline (0.2 mmol, 1.0 equiv) in DCM (2 mL). The resulting mixture was stirred at room temperature for 1.5-8 hours. Then, the reaction was quenched with brine, extracted with DCM, and the organic phase dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure afforded a residue, which was purified by column chromatography on silica gel.



13

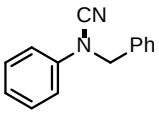
A mixture of diphenylamine **S3** (0.2 mmol, 33.8 mg), Cs_2CO_3 (0.02 mmol, 65.2 mg) and **9** (0.3 mmol, 107.8 mg) in DCM (2 mL) was stirred at room temperature for 6 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 9:1) afforded **13** in 98%

yield (38.0 mg) as a colorless oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.46 – 7.36 (m, 4H), 7.33 – 7.18 (m, 6H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ = 139.2, 130.0, 126.4, 121.4, 112.7. The spectroscopic data are in agreement with those previously reported.[20]



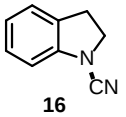
14

A mixture of *N*-methylaniline **S4** (0.2 mmol, 21.7 μL), Cs_2CO_3 (0.02 mmol, 65.2 mg) and **9** (0.3 mmol, 107.8 mg) in DCM (2 mL) was stirred at room temperature for 1.5 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **14** in 90% yield (23.7 mg) as a colorless oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.45 – 7.31 (m, 2H), 7.17 – 7.02 (m, 3H), 3.33 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ = 140.4, 129.7, 123.4, 114.9, 114.2, 36.9. The spectroscopic data are in agreement with those previously reported.[21]



15

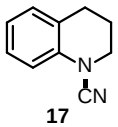
A mixture of *N*-benzylaniline **S5** (0.2 mmol, 36.7 mg), Cs_2CO_3 (0.02 mmol, 65.2 mg) and **9** (0.3 mmol, 107.8 mg) in DCM (2 mL) was stirred at room temperature for 3 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 9:1) afforded **15** in 91% yield (37.7 mg) as a colorless oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.42 – 7.26 (m, 7H), 7.16 – 7.02 (m, 3H), 4.78 (s, 2H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ = 139.8, 134.4, 129.7, 129.1, 128.6, 127.4, 123.8, 116.1, 114.0, 53.8. The spectroscopic data are in agreement with those previously reported.[22]



16

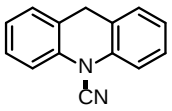
A mixture of indoline **S6** (0.2 mmol, 22.4 μL), Cs_2CO_3 (0.02 mmol, 65.2 mg) and **9** (0.3 mmol, 107.8 mg) in DCM (2 mL) was stirred at room temperature for 2 h. Column

chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **16** in 95% yield (27.3 mg) as a colorless oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.25 – 7.13 (m, 2H), 7.04 – 6.92 (m, 2H), 4.05 (t, *J* = 8.4 Hz, 2H), 3.20 (t, *J* = 8.4Hz, 2H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ = 142.3, 128.2, 127.9, 125.3, 123.3, 112.6, 110.5, 50.8, 28.6. IR (neat): 3052, 2919, 2858, 2209, 1607, 1595, 1486, 1458, 1441, 1379, 1328, 1278, 1197, 1155, 1083, 1029, 935, 866, 825, 751, 602 cm^{-1}; HRMS calculated m/z for $C_9H_9N_2^+$ $[M+H]^+$: 145.0760, found (ESI) 145.0766.



17

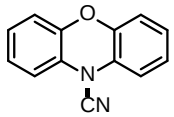
A mixture of 1,2,3,4-tetrahydroquinoline **S7** (0.2 mmol, 26.6 mg), Cs_2CO_3 (0.02 mmol, 65.2 mg) and **9** (0.3 mmol, 107.8 mg) in DCM (2 mL) was stirred at room temperature for 3 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **17** in 92% yield (29.0 mg) as a colorless oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.24 – 7.13 (m, 2H), 7.09-7.05 (m, 1H), 7.01-6.93 (m, 1H), 3.81 – 3.69 (m, 2H), 2.87 – 2.71 (m, 2H), 2.10 – 1.94 (m, 2H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ = 135.6, 129.8, 127.7, 124.0, 122.9, 115.7, 113.6, 48.6, 26.3, 22.0. IR (neat): 2938, 2212, 1605, 1587, 1495, 1455, 1385, 1347, 1290, 1251, 1229, 1198, 1183, 1167, 1113, 1059, 1017, 937, 909, 876, 848, 794, 747, 713, 690, 612, 532, 504 cm^{-1}; HRMS calculated m/z for $C_{10}H_{11}N_2^+$ $[M+H]^+$: 159.0917, found (ESI) 159.0918.



18

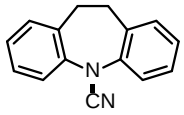
A mixture of 9,10-dihydroacridine **S8** (0.2 mmol, 36.2 mg), Cs_2CO_3 (0.02 mmol, 65.2 mg) and **9** (0.3 mmol, 107.8 mg) in DCM (2 mL) was stirred at room temperature for 3 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 19:1) afforded **18** in 88% yield (36.4 mg) as a colorless oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.41-7.37 (m, 2H), 7.32-7.26 (m, 2H), 7.24 – 7.08 (m, 4H), 4.04 (s, 2H). ^{13}C NMR (75 MHz,

Chloroform-*d*) δ = 134.6, 129.0, 128.9, 125.3, 123.3, 115.8, 109.4, 30.6. IR (neat): 2920, 2218, 1721, 1653, 1604, 1581, 1489, 1455, 1426, 1344, 1316, 1298, 1255, 1196, 1168, 1150, 1097, 1045, 958, 933, 922, 857, 800, 743, 687, 667, 636 cm^{-1}; HRMS calculated m/z for $C_{14}H_{11}N_2^+$ $[M+H]^+$: 207.0917, found (ESI) 207.0917.



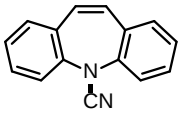
19

A mixture of 10*H*-phenoxazine **S9** (0.2 mmol, 36.6 mg), Cs_2CO_3 (0.02 mmol, 65.2 mg) and **9** (0.3 mmol, 107.8 mg) in DCM (2 mL) was stirred at room temperature for 6 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 19:1) afforded **19** in 71% yield (29.6 mg) as a white solid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.12 – 6.94 (m, 6H), 6.91 – 6.80 (m, 2H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ = 143.5, 126.3, 124.3, 123.9, 117.0, 115.7, 107.2. IR (neat): 2227, 1594, 1488, 1321, 1293, 1273, 1204, 1152, 1137, 1095, 1039, 927, 867, 812, 746, 689, 634 cm^{-1}; HRMS calculated m/z for $C_{13}H_8N_2ONa^+$ $[M+Na]^+$: 231.0529, found (ESI) 231.0532.



20

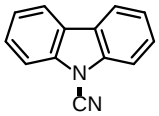
A mixture of 10,11-dihydro-5*H*-dibenzo[*b*,*f*]azepine **S10** (0.2 mmol, 39.1 mg), Cs_2CO_3 (0.02 mmol, 65.2 mg) and **9** (0.3 mmol, 107.8 mg) in DCM (2 mL) was stirred at room temperature for 8 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 9:1) afforded **20** in 94% yield (41.2 mg) as a colorless oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.56-7.53 (m, 2H), 7.30 – 7.10 (m, 6H), 3.16 (s, 4H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ = 139.5, 134.1, 130.7, 127.5, 127.0, 122.4, 114.2, 31.5. IR (neat): 2908, 2202, 1578, 1488, 1448, 1427, 1332, 1286, 1251, 1219, 1177, 1135, 1110, 964, 941, 872, 854, 768,751, 742, 708, 680, 640, 596, 563, 548, 515 cm^{-1}; HRMS calculated m/z for $C_{15}H_{13}N_2^+$ $[M+H]^+$: 221.1073, found (ESI) 221.1075.



21

A mixture of 5*H*-dibenzo[*b*,*f*]azepine **S11** (0.2 mmol, 38.6 mg), Cs_2CO_3 (0.02 mmol, 65.2 mg) and **9** (0.3 mmol, 107.8 mg) in DCM (2 mL) was stirred at room temperature for 6 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 9:1) afforded **21** in 99% yield (43.2 mg) as a white solid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.49-7.46 (m, 2H), 7.41 – 7.32 (m, 2H), 7.28 – 7.14 (m, 4H), 6.74 (s, 2H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ = 140.8, 132.4, 131.1, 130.2, 130.1, 127.6, 122.9, 114.6. IR (neat): 3022, 2219, 1600, 1576, 1489, 1456, 1435, 1288, 1248, 1199, 1161, 1137, 1115, 941, 922, 803, 784, 754, 701, 681, 635, 556, 513 cm^{-1}; HRMS calculated m/z for $C_{15}H_{11}N_2^+$ $[M+H]^+$: 219.0917, found (ESI) 219.0918.

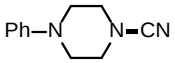
Procedure for the preparation of 22



22

Compound **9** (107.8 mg, 0.3 mmol, 1.5 equiv) was added to a stirred solution of 9*H*-carbazole **S12** (33.4 mg, 0.2 mmol, 1.0 equiv) in DCE (2 mL) at room temperature. The resulting mixture was stirred at 50 °C for 14 h. and then the reaction was quenched with brine, extracted with DCM and the organic phase was dried over anhydrous Na_2SO_4. Evaporation of the solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) to afford **22** (26.0 mg, 68% yield) as a white solid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.98-7.95 (m, 2H), 7.64-7.61 (m, 2H), 7.55-7.50 (m, 2H), 7.44-7.38 (m, 2H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ = 138.1, 127.8, 124.4, 124.3, 121.0, 111.7, 107.0. IR (neat): 33061, 2236, 1904, 1603, 1490, 1476, 1444, 1341, 1304, 1260, 1217, 1152, 1110, 1023, 935, 910, 856, 798, 741, 716, 650, 611, 551, 527 cm^{-1}; HRMS calculated m/z for $C_{13}H_8N_2Na^+$ $[M+Na]^+$: 215.0580, found (ESI) 215.0582.

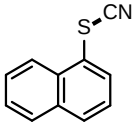
Procedure for the preparation of 23



23

Compound **9** (107.8 mg, 0.3 mmol, 1.5 equiv) was added at -50 °C to a stirred solution of 1-phenylpiperazine **S13** (30.6 μL, 0.2 mmol, 1.0 equiv) in DCM (2 mL). The resulting mixture was stirred at -50 °C for 6 h. Then, the reaction was quenched with brine, extracted with DCM, and the organic phase dried over anhydrous Na_2SO_4. Evaporation of the solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) to afford **23** (15.8 mg, 42% yield) as a colorless oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.36 – 7.22 (m, 2H), 6.99 – 6.86 (m, 3H), 3.44 – 3.34 (m, 4H), 3.29 – 3.18 (m, 4H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ = 150.9, 129.5, 121.3, 117.6, 117.3, 49.2, 49.0. The spectroscopic data are in agreement with those previously reported.[23]

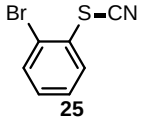
Procedure for the preparation of 24



24

Compound **9** (107.8 mg, 0.3 mmol, 1.5 equiv) was added at -10 °C under nitrogen to a stirred solution of naphthalene-1-thiol **S14** (27.9 μL, 0.2 mmol, 1.0 equiv) in DCM (2 mL). The resulting mixture was stirred at -10 °C for 0.5 h. and then the reaction was quenched with brine, extracted with DCM, and the organic phase dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) to afford **24** (25.2 mg, 68% yield) as a colorless oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 8.22 (d, *J* = 8.7 Hz, 1H), 7.99 – 7.86 (m, 3H), 7.71-7.65 (m, 1H), 7.62-7.57 (m, 1H), 7.51-7.46 (m, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ = 134.5, 132.5, 132.3, 131.7, 129.1, 128.3, 127.3, 126.0, 124.3, 120.9, 110.8. The spectroscopic data are in agreement with those previously reported.[24]

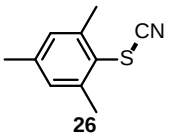
Procedure for the preparation of 25



25

Compound **9** (107.8 mg, 0.3 mmol, 1.5 equiv) was added at -10 °C to a stirred solution of 2-bromobenzenethiol **S15** (23.5 μL, 0.2 mmol, 1.0 equiv) in DCM (2 mL). The resulting mixture was stirred at -10 °C for 2.5 h. Then, the reaction was quenched with brine, extracted with DCM and the organic phase dried over anhydrous Na_2SO_4. Evaporation of the organic solvent under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 50:1) to afford **25** (26.1 mg, 61% yield) as a colorless oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.73-7.70 (m, 1H), 7.63-7.60 (m, 1H), 7.47-7.41 (m, 1H), 7.31 – 7.21 (m, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ = 133.7, 130.2, 129.6, 129.2, 127.3, 121.9, 109.7. The spectroscopic data is in agreement with that previously reported.[25]

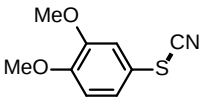
Procedure for the preparation of 26



26

Compound **9** (107.8 mg, 0.3 mmol, 1.5 equiv) was added at -20 °C to a stirred solution of 2,4,6-trimethylbenzenethiol **S16** (29.7 μL, 0.2 mmol, 1.0 equiv) in DCM (2 mL). The resulting mixture was stirred at -20 °C for 1 h. Then, the reaction was quenched with brine, extracted with DCM and the organic phase dried over anhydrous Na_2SO_4. Evaporation of the solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 50:1) to afford **26** (29.8 mg, 84% yield) as a colorless oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.00 (s, 2H), 2.55 (s, 6H), 2.29 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ = 142.8, 141.6, 130.2, 119.2, 111.0, 22.0, 21.2. The spectroscopic data are in agreement with those previously reported.[26]

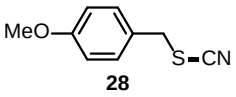
Procedure for the preparation of 27



27

Compound **9** (107.8 mg, 0.3 mmol, 1.5 equiv) was added to a stirred solution of 3,4-dimethoxybenzenethiol **S17** (29.0 μL, 0.2 mmol, 1.0 equiv) in DCM (2 mL) at -20 °C under nitrogen. The resulting mixture was stirred at -20 °C for 0.5 h. Then, the reaction was quenched with brine, extracted with DCM and the organic phase dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) to afford **27** (23.8 mg, 61% yield) as a colorless oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.15 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.05 (d, *J* = 2.1 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 3.91 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ = 151.0, 150.2, 125.4, 114.6, 114.0, 112.3, 111.6, 56.3, 56.2. The spectroscopic data are in agreement with those previously reported.[24]

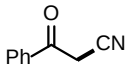
Procedure for the preparation of 28



28

Compound **9** (107.8 mg, 0.3 mmol, 1.5 equiv) was added to a stirred suspension of (4-methoxyphenyl)methanethiol **S18** (27.5 μL, 0.2 mmol, 1.0 equiv) and Cs_2CO_3 (65.2 mg, 0.2 mmol, 1.0 equiv) in DCM (2 mL) at -50 °C. The resulting mixture was stirred at -50 °C for 5 h. Then, the reaction was quenched with brine, extracted with DCM and the organic phase dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 10:1) to afford **28** (25.3 mg, 71% yield) as a colorless oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.28 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 4.14 (s, 2H), 3.81 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ = 160.1, 130.5, 126.3, 114.6, 112.3, 55.4, 38.4. The spectroscopic data are in agreement with those previously reported.[24]

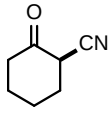
Procedure for the preparation of 29



29

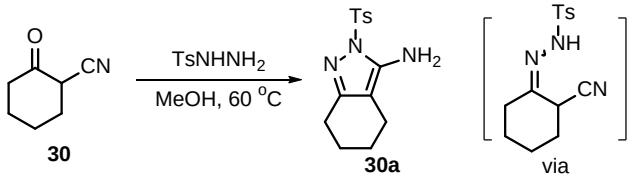
Compound **9** (71.9 mg, 0.2 mmol, 1.0 equiv) was added to a stirred solution of trimethyl((1-phenylvinyl)oxy)silane **S19** (61.5 μL, 0.3 mmol, 1.5 equiv) in DCM (2 mL) at room temperature. The resulting mixture was stirred at room temperature for 15 minutes. Then, the reaction was quenched with brine, extracted with DCM and the organic phase dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 5:1) to afford **29** (27.4 mg, 94% yield) as a light yellow solid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.98 – 7.87 (m, 2H), 7.73 – 7.60 (m, 1H), 7.59 – 7.46 (m, 2H), 4.12 (s, 2H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 187.3, 134.8, 134.3, 129.2, 128.5, 114.0, 29.5. The spectroscopic data are in agreement with those previously reported.[27]

Procedure for the preparation of 30



30

Compound **9** (71.9 mg, 0.2 mmol, 1.0 equiv) was added to a stirred solution of (cyclohex-1-en-1-yloxy)trimethylsilane **20** (58.4 μL, 0.3 mmol, 1.5 equiv) in DCM (2 mL) at room temperature. The resulting mixture was stirred for 10 minutes. Then, the reaction was quenched with brine, extracted with DCM, and the organic phase dried over anhydrous Na_2SO_4. Because **30** is volatile on high vacuum line, the solvent was evaporated under the reduced pressure and then a ^{1}H NMR analysis of the obtained mixture using CH_2Br_2 as internal standard was conducted, which indicated that the desired product **30** had been obtained in 92% NMR yield.

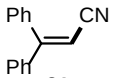


30 **30a** via

To a stirred solution of the above recovered NMR sample in MeOH (3 mL), 4-methylbenzenesulfonohydrazide (55.9 mg, 0.3 mmol, 1.5 equiv.) was added and the

resulting solution stirred at 60 ^{o}C for 18 h. Then, the reaction was quenched with brine, extracted with DCM and the organic phase dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 1:1) to afford a white solid (26.0 mg, 0.0892 mmol, 45% overall yield). ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.95 – 7.76 (m, 2H), 7.34 – 7.27 (m, 2H), 4.66 (bs, 2H), 2.58 – 2.45 (m, 2H), 2.41 (s, 3H), 2.27 – 2.12 (m, 2H), 1.70-1.65 (m, 4H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ = 156.4, 145.1, 144.7, 135.2, 129.9, 127.8, 99.2, 24.1, 22.8, 22.7, 21.8, 19.3. IR (neat): 3457, 3296, 2935, 2857, 1625, 1596, 1476, 1425, 1357, 1309, 1259, 1223, 1188, 1173, 1143, 1130, 1085, 1045, 956, 931, 856, 812, 730, 701, 687, 665, 614, 590, 542 cm^{-1}; HRMS calculated m/z for $C_{14}H_{18}N_3O_2S^+$ $[M+H]^+$: 292.1114, found (ESI) 292.1116.

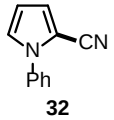
Procedure for the preparation of 31



31

Compound **9** (107.8 mg, 0.3 mmol, 1.5 equiv) dissolved in CH_3CN (0.7 mL)was added to a stirred solution of ethene-1,1-diphenylethylene **S21** (36.1 mg, 0.2 mmol, 1.0 equiv) in DCE (1.4 mL) at room temperature. The resulting mixture was stirred at room temperature for 21 h. Then, the reaction was quenched with brine, extracted with DCM and the organic phase dried over anhydrous Na_2SO_4. Evaporation of the solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) to afford **31** (30.5 mg, 74% yield) as a colorless oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.48 – 7.33 (m, 8H), 7.32 – 7.26 (m, 2H), 5.73 (s, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ = 163.2, 139.0, 137.2, 130.5, 130.1, 129.7, 128.8, 128.6, 128.6, 118.0, 95.0. The spectroscopic data is in agreement with that previously reported.[28]

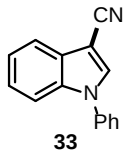
Procedure for the preparation of 32



32

Compound **9** (107.8 mg, 0.3 mmol, 1.5 equiv) was added to a stirred suspension of 1-phenyl-1*H*-pyrrole **S22** (28.6 mg, 0.2 mmol, 1.0 equiv) and Cs_2CO_3 (65.2 mg, 0.2 mmol, 1.0 equiv) in DCM (2 mL) at 0 °C. The resulting mixture was stirred at that temperature for 12 h. Then, the reaction was quenched with brine, extracted with DCM and the organic phase dried over anhydrous Na_2SO_4. Evaporation of the solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 10:1) to afford **32** (33.5 mg, 99% yield) as a colorless liquid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.49 – 7.27 (m, 5H), 7.00 (dd, *J* = 2.8, 1.6 Hz, 1H), 6.91 (dd, *J* = 4.0, 1.6 Hz, 1H), 6.27 (dd, *J* = 4.0, 2.8 Hz, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ = 138.3, 129.8, 128.4, 127.1, 124.3, 122.3, 113.9, 110.7, 104.1. The spectroscopic data are in agreement with those previously reported.[29]

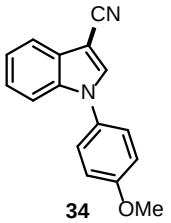
Procedure for the preparation of 33



33

Compound **9** (143.7 mg, 0.4 mmol, 2.0 equiv) was added to a stirred suspension of 1-phenyl-1*H*-indole **S23** (38.7 mg, 0.2 mmol, 1.0 equiv) and K_3PO_4 (63.7 mg, 0.3 mmol, 1.5 equiv) in DCM (2 mL) at 15 °C under nitrogen and the resulting mixture was stirred at that temperature for 20 h. Then, the reaction was quenched with brine, extracted with DCM and the organic phase dried over anhydrous Na_2SO_4. Evaporation of the solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 10:1) to afford **33** (30.4 mg, 70% yield) as a light yellow solid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.86 – 7.80 (m, 1H), 7.78 (s, 1H), 7.62 – 7.53 (m, 2H), 7.53 – 7.42 (m, 4H), 7.37 – 7.29 (m, 2H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ = 137.9, 135.7, 134.7, 130.1, 128.5, 128.0, 125.0, 124.6, 122.9, 120.1, 115.6, 111.6, 88.2. The spectroscopic data are in agreement with those previously reported.[30]

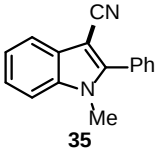
Procedure for the preparation of 34



34

Compound **9** (143.7 mg, 0.4 mmol, 2.0 equiv) was added to a stirred suspension of 1-(4-methoxyphenyl)-1*H*-indole **S24** (44.7 mg, 0.2 mmol, 1.0 equiv) and K_3PO_4 (42.5 mg, 0.2 mmol, 1.0 equiv) in DCM (2 mL) at 10 °C under nitrogen. The resulting mixture was stirred at that temperature for 5 h. Then, the reaction was quenched with brine, extracted with DCM, and the organic phase dried over anhydrous Na_2SO_4. Evaporation of the solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 10:1) to afford **34** (39.3 mg, 79% yield) as a white solid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.85 – 7.76 (m, 1H), 7.72 (s, 1H), 7.47 – 7.26 (m, 5H), 7.11 – 6.99 (m, 2H), 3.89 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ = 159.2, 136.1, 135.1, 130.7, 127.8, 126.5, 124.5, 122.7, 120.0, 115.8, 115.2, 111.6, 87.5, 55.8. The spectroscopic data are in agreement with those previously reported.[31]

Procedure for the preparation of 35

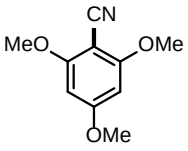


35

Compound **9** (71.9 mg, 0.2 mmol, 1.0 equiv) was added to a stirred solution of 1-methyl-2-phenyl-1*H*-indole **S25** (62.2 mg, 0.3 mmol, 1.5 equiv) in DCM (2 mL) at room temperature and the resulting mixture was stirred at that temperature for 5 minutes. Then, the reaction was quenched with brine, extracted with DCM and the organic phase dried over anhydrous Na_2SO_4. Evaporation of the solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 10:1) to afford **35** (24.6 mg, 53% yield) as a colorless oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.82 – 7.73 (m, 1H), 7.62 – 7.47 (m, 5H), 7.45 – 7.27 (m, 3H), 3.74 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ = 148.2, 137.0, 130.0, 129.9, 129.1, 128.8, 127.7, 124.0,

122.5, 119.6, 116.7, 110.6, 85.6, 31.8. The spectroscopic data are in agreement with those previously reported.[23]

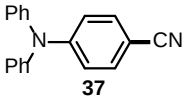
Procedure for the preparation of 36



36

Compound **9** (107.8 mg, 0.3 mmol, 1.5 equiv) was added to a stirred suspension of 1,3,5-trimethoxybenzene **S26** (33.6 mg, 0.2 mmol, 1.0 equiv) and Cs_2CO_3 (65.2 mg, 0.2 mmol, 1.0 equiv) in DCM (2 mL) at room temperature. The resulting mixture was stirred at room temperature for 4 h and then, quenched with brine, extracted with DCM, and the organic phase dried over anhydrous Na_2SO_4. Evaporation of the solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) to afford **36** (30.8 mg, 80% yield) as a white solid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 6.04 (s, 2H), 3.85 (s, 6H), 3.84 (s, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ = 165.4, 163.8, 114.7, 90.4, 84.0, 56.2, 55.8. The spectroscopic data is in agreement with that previously reported.[32]

Procedure for the preparation of 37

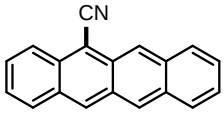


37

Salt **9** (143.7 mg, 0.4 mmol, 2.0 equiv) was added to a stirred solution of triphenylamine **S27** (49.1 mg, 0.2 mmol, 1.0 equiv) in DCE (2 mL) at room temperature under nitrogen and the resulting mixture stirred at 50 °C for 14 h. Then, the reaction was quenched with brine, extracted with DCM and the organic phase dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the residue obtained purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 20:1) to afford **37** (17.8 mg, 33% yield) as a light yellow solid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.45 – 7.38 (m, 2H), 7.37 – 7.28 (m, 4H), 7.21 – 7.08 (m, 6H), 7.00 – 6.90 (m, 2H). ^{13}C NMR (75 MHz,

Chloroform-*d*) δ = 151.7, 146.1, 133.3, 129.9, 126.3, 125.3, 119.8, 102.6. The spectroscopic data are in agreement with those previously reported.[33]

Procedure for the preparation of 38



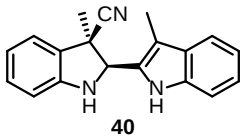
38

Salt **9** (71.9 mg, 0.2 mmol, 1.0 equiv) was added to a stirred solution of tetracene **S28** (45.7 mg, 0.2 mmol, 1.0 equiv) in DCE (2 mL) at room temperature. The resulting mixture was stirred at 50 °C for 7 h. After this another portion of **9** (71.9 mg, 0.2 mmol, 1.0 equiv) was added and the stirring continued for additional 11 h at the same temperature. Subsequently, the reaction was quenched with water, extracted with DCM and the organic phase dried over anhydrous Na_2SO_4. Evaporation of the solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 40:1) to afford **38** (13.8 mg, 27% yield) as a red solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.95 (s, 1H), 8.83 (s, 1H), 8.66 (s, 1H), 8.35 (d, *J* = 8.8 Hz, 1H), 8.08 – 7.96 (m, 3H), 7.67 – 7.59 (m, 1H), 7.53 – 7.45 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 134.5, 133.5, 133.4, 132.0, 130.3, 130.3, 129.3, 128.9, 128.5, 128.3, 128.0, 127.2, 126.4, 126.0, 125.4, 123.9, 117.9, 104.9. IR (neat): 2918, 2849, 2220, 1674, 1483, 1457, 1259, 1098, 1019, 890, 801, 747, 697, 644, 626, 609, 577, 532 cm^{-1}; HRMS calculated m/z for $C_{19}H_{11}N^+$ $[M]^+$: 253.0886, found (ESI) 253.0885.

Procedure for the preparation of 40 and 41

Salt **9** (107.8 mg, 0.3 mmol, 1.5 equiv) was added to a stirred suspension of 3-methyl-1*H*-indole **39** (26.2 mg, 0.2 mmol, 1.0 equiv) and Cs_2CO_3 (65.2 mg, 0.2 mmol, 1.0 equiv) in DCM (2 mL) at 0 °C under nitrogen. The resulting mixture was stirred at that temperature for 2 h. Then, the reaction was quenched with brine, extracted with DCM and the organic phase dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 3:1) to afford **40** (14.4 mg, 50% yield) and **41** (9.3

mg, 30% yield), both as a white solids.



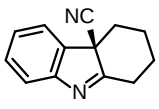
40

^{1}H NMR (300 MHz, Dichoromethane-d_2) δ = 8.69 (bs, 1H), 7.63-7.60 (m, 1H), 7.40 – 7.32 (m, 1H), 7.32 – 7.09 (m, 4H), 7.00 – 6.91 (m, 1H), 6.89 – 6.79 (m, 1H), 5.06 – 4.92 (m, 1H), 4.31 (bs, 1H), 2.40 (s, 3H), 1.84 (s, 3H). ^{13}C NMR (75 MHz, Dichloromethane-d_2) δ = 150.0, 135.9, 130.6, 129.7, 129.4, 128.6, 124.1, 123.1, 121.5, 121.2, 119.8, 119.2, 111.5, 111.4, 111.0, 67.3, 47.5, 22.8, 9.3. IR (neat): 3441, 3334, 2922, 2226, 1607, 1479, 1463, 1385, 1336, 1314, 1304, 1252, 1214, 1154, 1131, 1036, 1012, 945, 876, 854, 819, 782, 758, 707, 694, 635, 607, 578, 566, 555, 528 cm^{-1}; HRMS calculated m/z for $C_{19}H_{18}N_3^+$ $[M+H]^+$: 288.1495, found (ESI) 288.1496.

41

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.33 (bs, 1H), 7.65 – 7.58 (m, 1H), 7.50-7.46 (m, 1H), 7.43 – 7.33 (m, 2H), 7.31 – 7.22 (m, 2H), 7.21 – 7.12 (m, 2H), 5.35 (s, 1H), 2.43 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 141.3, 136.7, 131.4, 128.3, 127.3, 125.5, 124.3, 124.2, 122.7, 120.1, 119.5, 119.4, 115.4, 112.0, 111.8, 110.2, 69.6, 46.0, 23.4, 9.1. IR (neat): 3304, 2919, 2222, 1597, 1481, 1464, 1336, 1316, 1241, 1172, 1099, 987, 934, 795, 745, 651, 597, 566 cm^{-1}; HRMS calculated m/z for $C_{20}H_{17}N_4^+$ $[M+H]^+$: 313.1448, found (ESI) 313.1447.

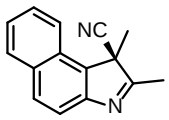
Procedure for the preparation of 43



43

Salt **9** (107.8 mg, 0.3 mmol, 1.5 equiv) was added to a stirred solution of 2,3,4,9-tetrahydro-1*H*-carbazole **42** (34.2 mg, 0.2 mmol, 1.0 equiv) in CH_3CN (2 mL) at room temperature and the resulting mixture stirred for 10 minutes. Then, the reaction was quenched with water, extracted with DCM, and the organic phase dried over anhydrous Na_2SO_4. Evaporation of the solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) to afford **43** (30.0 mg, 76% yield) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.65-7.63 (m, 1H), 7.57-7.54 (m, 1H), 7.47-7.43 (m, 1H), 7.33-7.29 (m, 1H), 3.08 – 2.96 (m, 1H), 2.93 – 2.75 (m, 2H), 2.36 – 2.23 (m, 1H), 2.12 – 1.97 (m, 1H), 1.98 – 1.86 (m, 1H), 1.60 – 1.43 (m, 1H), 1.32 – 1.17 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 178.6, 155.1, 137.2, 130.0, 126.6, 122.7, 121.3, 117.6, 51.9, 39.2, 30.2, 28.4, 22.4. IR (neat): 2941, 2854, 2236, 1731, 1618, 1592, 1440, 1347, 1273, 1231, 1187, 1139, 1093, 1043, 1012, 956, 934, 906, 867, 854, 772, 757, 689, 672, 635, 608, 563, 525 cm^{-1}; HRMS calculated m/z for $C_{13}H_{13}N_2^+$ $[M+H]^+$: 197.1073, found (ESI) 197.1074.

Procedure for the preparation of 45



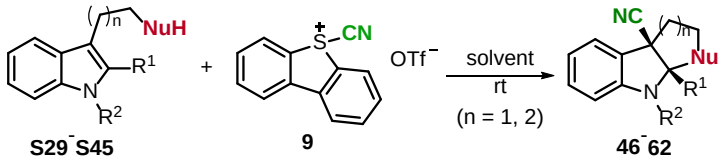
45

Salt **9** (107.8 mg, 0.3 mmol, 1.5 equiv) was added to a stirred solution of 1,2-dimethyl-3*H*-benzo[*e*]indole **44** (39.1 mg, 0.2 mmol, 1.0 equiv) in CH_3CN (2 mL) at room temperature and the resulting mixture stirred for 10 minutes. Then, the reaction was quenched with water, extracted with DCM and the organic phase dried over anhydrous Na_2SO_4. Evaporation of the solvent under the reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) to afford **45** (38.1 mg, 86% yield) as a light yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.06-8.04 (m, 1H), 7.99 – 7.90 (m, 2H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.66-7.62 (m, 1H), 7.54-7.50 (m, 1H), 2.60 (s, 3H), 1.85 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 178.3, 152.1, 132.7, 131.3, 131.3, 129.7, 128.0, 127.9, 125.8, 122.3, 119.9, 117.9, 50.2, 22.5, 16.1. IR (neat): 3054, 2236, 1626, 1602, 1574, 1520, 1443, 1380, 1261, 1228, 1215, 1201, 1103, 1078, 1022, 968,

908, 866, 771, 755, 691, 662, 598, 589, 569, 553, 525 cm^{-1}; HRMS calculated m/z for $C_{15}H_{13}N_2^+$ $[M+H]^+$: 221.1073, found (ESI) 221.1072.

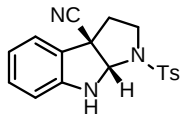
5. Metal-free cyano-cyclization of indole derivatives

General procedure of the cyano-cyclisation of indole derivatives: preparation of 46-62.



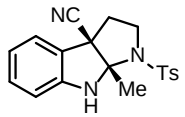
S29-S45 **9** **46-62**

Compound **9** was added to a stirred solution of indole derivatives **S29-S45** (0.2 mmol, 1.0 equiv) in the appropriate solvent (2 mL) at room temperature under nitrogen flow and the resulting mixture was stirred at room temperature for the specified time (vide infra). Then, the reaction was quenched with water, extracted with DCM and the organic phase dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure afforded a residue, which was was purified by column chromatography on silica gel to afford the desired products.



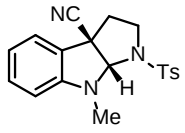
46

A mixture of **S29** (0.2 mmol, 62.9 mg, 1.0 equiv) and **9** (0.3 mmol, 107.8 mg, 1.5 equiv) in CH_3CN (2 mL) was stirred at room temperature for 10 minutes. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **46** in 69% yield (46.5 mg) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.83 – 7.70 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.20-7.16 (m, 2H), 6.83 (t, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 7.6 Hz, 1H), 5.73 (s, 1H), 5.02 (bs, 1H), 3.58 – 3.44 (m, 1H), 3.30 – 3.13 (m, 1H), 2.54 – 2.24 (m, 5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 148.5, 144.6, 135.1, 130.9, 130.3, 127.3, 123.79, 123.5, 120.4, 119.5, 110.5, 82.6, 49.7, 46.8, 37.4, 21.7. IR (neat): 3370, 2917, 2238, 1608, 1486, 1337, 1311, 1266, 1201, 1164, 1091, 1060, 1009, 931, 895, 848, 820, 707, 661, 592, 570, 543 cm^{-1}; HRMS calculated m/z for $C_{18}H_{18}N_3O_2S^+$ $[M+H]^+$: 340.1114, found (ESI) 340.1117.



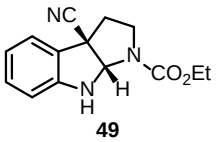
47

A mixture of **S30** (0.2 mmol, 65.7 mg, 1.0 equiv) and **9** (0.3 mmol, 107.8 mg, 1.5 equiv) in CH_3CN (2 mL) was stirred at room temperature for 15 minutes. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **47** in 85% yield (59.9 mg) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.63 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.20 – 7.08 (m, 2H), 6.79 (t, *J* = 7.6 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 5.36 (bs, 1H), 3.55 – 3.41 (m, 1H), 3.14 – 2.98 (m, 1H), 2.59 – 2.49 (m, 2H), 2.38 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 148.1, 143.8, 136.5, 130.7, 129.8, 127.2, 123.7, 123.7, 120.3, 118.6, 110.3, 90.6, 55.2, 47.0, 34.0, 25.1, 21.6. IR (neat): 3361, 2889, 2236, 1610, 1485, 1470, 1403, 1378, 1328, 1311, 1247, 1210, 1165, 1023, 1011, 959, 893, 816, 764, 706, 695, 617, 518 cm^{-1}; HRMS calculated m/z for $C_{19}H_{20}N_3O_2S^+$ $[M+H]^+$: 354.1271, found (ESI) 354.1274.



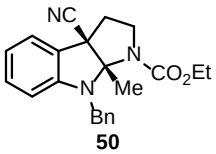
48

A mixture of **S31** (0.2 mmol, 65.7 mg, 1.0 equiv) and **9** (0.3 mmol, 107.8 mg, 1.5 equiv) in CH_3CN (2 mL) was stirred at room temperature for 15 minutes. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **48** in 61% yield (42.9 mg) as a white solid. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.87 – 7.74 (m, 2H), 7.44 – 7.35 (m, 2H), 7.23-7.18 (m, 1H), 7.16 – 7.06 (m, 1H), 6.75-6.69 (m, 1H), 6.45 (d, *J* = 7.8 Hz, 1H), 5.85 (s, 1H), 3.72-3.64 (m, 1H), 3.16-3.06 (m, 1H), 3.01 (s, 3H), 2.47 (s, 3H), 2.22-2.15 (m, 1H), 1.90-1.79 (m, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ = 149.9, 144.8, 135.50, 131.0, 130.5, 127.4, 123.7, 123.5, 119.8, 118.7, 106.9, 88.7, 48.7, 47.4, 39.1, 31.1, 21.7. IR (neat): 2890, 2233, 1603, 1497, 1445, 1430, 1349, 1318, 1306, 1254, 1211, 1159, 1105, 1089, 1021, 969, 919, 876, 841, 815, 802, 751, 724, 660, 603, 574, 532 cm^{-1}; HRMS calculated m/z for $C_{19}H_{20}N_3O_2S^+$ $[M+H]^+$: 354.1271, found (ESI) 354.1278.



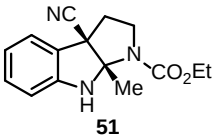
49

A mixture of **S32** (0.2 mmol, 46.5 mg, 1.0 equiv) and **9** (0.3 mmol, 107.8 mg, 1.5 equiv) in CH_3CN (2 mL) was stirred at room temperature for 2 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **49** in 68% yield (35.0 mg) as a colorless oil. ^{1}H NMR (400 MHz, DMSO-d_6, 100 ^{o}C) δ = 7.34-7.31 (m, 1H), 7.17-7.13 (m, 1H), 6.78-6.74 (m, 1H), 6.70-6.68 (m, 1H), 6.54 (bs, 1H), 5.764-5.758 (m, 1H), 4.17-4.10 (m, 2H), 3.78-3.73 (m, 1H), 3.06-3.30 (m, 1H), 2.94 (s, 2H), 2.70-2.62 (m, 1H), 2.56 – 2.51 (m, 1H), 1.26 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6, 100 ^{o}C) δ = 153.1, 149.1, 129.6, 123.7, 123.1, 119.8, 118.3, 109.3, 79.5, 60.4, 48.3, 44.1, 35.4, 13.8. IR (neat): 3276, 2981, 2240, 1692, 1607, 1471, 1416, 1380, 1346, 1319, 1258, 1237, 1201, 1172, 1111, 1026, 1008, 894, 820, 747, 609, 527 cm^{-1}; HRMS calculated m/z for $C_{14}H_{16}N_3O_2^+$ $[M+H]^+$: 258.1237, found (ESI) 258.1237.



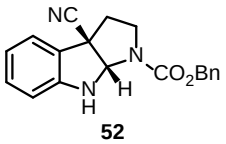
50

A mixture of **S33** (0.2 mmol, 67.3 mg, 1.0 equiv) and **9** (0.3 mmol, 107.8 mg, 1.5 equiv) in CH_3CN (2 mL) was stirred at room temperature for 10 minutes. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **50** in 89% yield (64.5 mg) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6, 100 ^{o}C) δ = 7.38-7.36 (m, 1H), 7.34 – 7.25 (m, 2H), 7.27 – 7.17 (m, 3H), 7.11-7.06 (m, 1H), 6.77-6.73 (m, 1H), 6.26 (d, J = 8.0 Hz, 1H), 4.97 – 4.61 (m, 2H), 4.08-3.96 (m, 2H), 3.79-3.74 (m, 1H), 3.27 – 3.09 (m, 1H), 2.69 – 2.58 (m, 2H), 2.00 (s, 3H), 1.17 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6, 100 ^{o}C) δ = 153.1, 147.8, 138.5, 129.7, 127.8, 126.0, 125.6, 123.4, 122.8, 118.6, 117.8, 107.2, 89.7, 60.2, 54.8, 46.5, 45.8, 32.2, 19.3, 13.7. IR (neat): 3417, 2982, 2241, 1702, 1681, 1605, 1488, 1465, 1449, 1401, 1376, 1347, 1313, 1232, 1212, 1186, 1157, 1118, 1103, 1073, 1055, 1027, 1007, 919, 880, 838, 771, 751, 739, 726, 694, 653, 637, 608, 555, 545, 530 cm^{-1}; HRMS calculated m/z for $C_{22}H_{24}N_3O_2^+$ $[M+H]^+$: 362.1863, found (ESI) 362.1867.



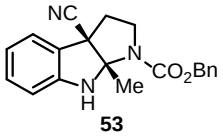
51

A mixture of **S34** (0.2 mmol, 49.3 mg, 1.0 equiv) and **9** (0.3 mmol, 107.8 mg, 1.5 equiv) in CH_3CN (2 mL) was stirred at room temperature for 10 minutes. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **51** in 71% yield (38.5 mg) as a colorless oil. ^{1}H NMR (400 MHz, DMSO-d_6, 100 ^{o}C) δ = 7.36-7.33 (m, 1H), 7.17-7.12 (m, 1H), 6.79-6.75 (m, 1H), 6.73-6.71 (m, 1H), 6.50 (bs, 1H), 4.10 (q, J = 7.2 Hz, 2H), 3.64-.3.59 (m, 1H), 3.08-3.01 (m, 1H), 2.70 – 2.55 (m, 2H), 1.86 (s, 3H), 1.22 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6, 100 ^{o}C) δ = 152.6, 148.5, 129.6, 123.8, 123.2, 118.6, 118.4, 109.5, 86.5, 60.1, 53.7, 45.0, 31.7, 21.7, 13.8. IR (neat): 3369, 2981, 2239, 1687, 1609, 1485, 1470, 1407, 1377, 1333, 1233, 1205, 1160, 1103, 1075, 1055, 1028, 956, 881, 838, 820, 773, 750, 662, 608, 541 cm^{-1}; HRMS calculated m/z for $C_{15}H_{18}N_3O_2^+$ $[M+H]^+$: 272.1394, found (ESI) 272.1394.



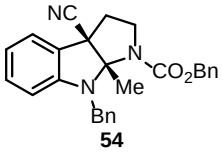
52

A mixture of **S35** (0.2 mmol, 58.9 mg, 1.0 equiv) and **9** (0.3 mmol, 107.8 mg, 1.5 equiv) in CH_3CN (2 mL) was stirred at room temperature for 2 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **52** in 56% yield (35.9 mg) as a colorless oil. ^{1}H NMR (400 MHz, DMSO-d_6, 100 ^{o}C) δ = 7.50 – 7.26 (m, 6H), 7.17-7.13 (m, 1H), 6.79-6.75 (m, 1H), 6.71-6.68 (m, 1H), 6.58 (bs, 1H), 5.823-5.817 (m, 1H), 5.26 – 5.09 (m, 2H), 3.86 – 3.73 (m, 1H), 3.11-3.04 (m, 1H), 2.72-2.64 (m, 1H), 2.58 – 2.51 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6, 100 ^{o}C) δ = 152.9, 149.0, 136.2, 129.7, 127.8, 127.2, 127.0, 123.7, 123.1, 119.8, 118.4, 109.4, 79.6, 66.0, 48.4, 44.3, 35.4. IR (neat): 3254, 2953, 2240, 1698, 1606, 1485, 1471, 1411, 1353, 1318, 1258, 1236, 1200, 1108, 1027, 1008, 943, 888, 820, 747, 697, 585, 522 cm^{-1}; HRMS calculated m/z for $C_{19}H_{18}N_3O_2^+$ $[M+H]^+$: 320.1394, found (ESI) 320.1396.



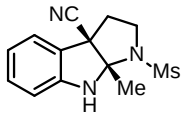
53

A mixture of **S36** (0.2 mmol, 61.7 mg, 1.0 equiv) and **9** (0.3 mmol, 107.8 mg, 1.5 equiv) in CH_3CN (2 mL) was stirred at room temperature for 10 minutes. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **53** in 81% yield (53.9 mg) as a colorless oil. ^{1}H NMR (400 MHz, DMSO-d_6, 100 ^{o}C) δ = 7.44 – 7.26 (m, 6H), 7.17-7.13 (m, 1H), 6.80-6.76 (m, 1H), 6.73-6.71 (m, 1H), 6.54 (bs, 1H), 5.14 (s, 2H), 3.70-3.64 (m, 1H), 3.19 – 3.03 (m, 1H), 2.74 – 2.55 (m, 2H), 1.88 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6, 100 ^{o}C) δ = 152.5, 148.4, 136.2, 129.7, 127.8, 127.20 126.9, 123.8, 123.2, 118.6, 118.5, 109.5, 86.7, 65.6, 53.7, 45.1, 31.7, 21.6. IR (neat): 3371, 2982, 2239, 1692, 1609, 1486, 1470, 1401, 1350, 1267, 1233, 1204, 1161, 1103, 1072, 1053, 1027, 955, 894, 820, 749, 697, 661, 608, 587, 542, 523 cm^{-1}; HRMS calculated m/z for $C_{20}H_{20}N_3O_2^+$ $[M+H]^+$: 334.1550, found (ESI) 334.1552.



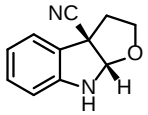
54

A mixture of **S37** (0.2 mmol, 79.7 mg, 1.0 equiv) and **9** (0.3 mmol, 107.8 mg, 1.5 equiv) in CH_3CN (2 mL) was stirred at room temperature for 10 minutes. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **54** in 93% yield (78.8 mg) as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6, 100 ^{o}C) δ = 7.46 – 7.25 (m, 8H), 7.24 – 7.16 (m, 3H), 7.11-7.07 (m, 1H), 6.83 – 6.69 (m, 1H), 6.26 (d, J = 7.6 Hz, 1H), 5.07 (s, 2H), 4.87 (d, J = 17.2 Hz, 1H), 4.63 (d, J = 17.2 Hz, 1H), 3.85-3.80 (m, 1H), 3.36 – 3.14 (m, 1H), 2.73 – 2.58 (m, 2H), 2.02 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6, 100 ^{o}C) δ = 153.0, 147. 8, 138.4, 135.9, 129.7, 127.8, 127.3, 127.1, 126.0, 125.6, 123.4, 122.8, 118.5, 117.8, 107.2, 89.9, 65.9, 54.8, 46.5, 45.9, 32.1, 19.2. IR (neat): 3031, 2239, 1699, 1606, 1488, 1452, 1397, 1349, 1266, 1211, 1185, 1148, 1101, 1071, 1053, 1026, 917, 887, 858, 819, 787, 769, 696, 636, 590, 554, 523 cm^{-1}; HRMS calculated m/z for $C_{27}H_{26}N_3O_2^+$ $[M+H]^+$: 424.2020, found (ESI) 424.2019.



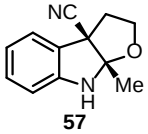
55

A mixture of **S38** (0.2 mmol, 50.5 mg, 1.0 equiv) and **9** (0.3 mmol, 107.8 mg, 1.5 equiv) in CH_3CN (2 mL) was stirred at room temperature for 30 minutes. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 2:1) afforded **55** in 68% yield (37.8 mg) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.30 – 7.25 (m, 1H), 7.25-7.20 (m, 1H), 6.92-6.88 (m, 1H), 6.71-6.69 (m, 1H), 5.17 (bs, 1H), 3.66-3.61 (m, 1H), 3.17-3.11 (m, 1H), 2.80 (s, 3H), 2.70 – 2.55 (m, 2H), 2.02 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 148.0, 131.2, 124.2, 124.1, 121.0, 118.5, 110.6, 90.0, 55.5, 47.2, 38.9, 33.8, 25.6. IR (neat): 3366, 2876, 2234, 1609, 1484, 1472, 1400, 1386, 1346, 1329, 1244, 1205, 1165, 1110, 1035, 889, 863, 813, 732, 693, 652, 608, 555, 529 cm^{-1}; HRMS calculated m/z for $C_{13}H_{16}N_3O_2S^+$ $[M+H]^+$: 278.0958, found (ESI) 278.0956.



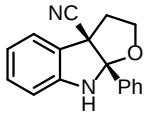
56

A mixture of **S39** (0.2 mmol, 32.2 mg, 1.0 equiv) and **9** (0.3 mmol, 107.8 mg, 1.5 equiv) in CH_3CN (2 mL) was stirred at room temperature for 15 minutes. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 5:1) afforded **56** in 55% yield (20.4 mg) as a colorless oil. ^{1}H NMR (300 MHz, Chloroform-*d*) δ = 7.28 (d, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 6.84 (t, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 7.8 Hz, 1H), 6.01 (d, *J* = 2.4 Hz, 1H), 4.75 (bs, 1H), 4.14-4.08 (m, 1H), 3.67-3.59 (m, 1H), 2.99 – 2.60 (m, 1H), 2.48-2.41 (m, 1H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ = 149.0, 130.5, 124.7, 124.5, 120.8, 120.2, 109.4, 97.6, 66.5, 49.8, 40.9. IR (neat): 3383, 2952, 2870, 2244, 1420, 1356, 1333, 1316, 1258, 1229, 1208, 1170, 1118, 1053, 945, 849, 778, 611, 585, 561, 544 cm^{-1}; HRMS calculated m/z for $C_{11}H_{11}N_2O^+$ $[M+H]^+$: 187.0866, found (ESI) 187.0868.



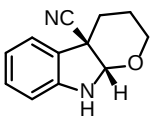
57

A mixture of **S40** (0.2 mmol, 35.0 mg, 1.0 equiv) and **9** (0.24 mmol, 86.2 mg, 1.2 equiv) in CH_3CN (2 mL) was stirred at room temperature for 10 minutes. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **57** in 66% yield (26.3 mg) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.28-7.25 (m, 1H), 7.17-7.13 (m, 1H), 6.84-6.80 (m, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 4.44 (bs, 1H), 4.07-4.02 (m, 1H), 3.65-3.59 (m, 1H), 2.78 – 2.54 (m, 1H), 2.46-2.42 (m, 1H), 1.81 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 148.5, 130.5, 125.2, 124.7, 120.2, 120.0, 109.1, 103.7, 65.9, 53.5, 41.7, 24.8. IR (neat): 3348, 2991, 2874, 2243, 1609, 1487, 1471, 1416, 1383, 1343, 1318, 1282, 1198, 1181, 1133, 1110, 1092, 991, 943, 911, 896, 861, 678, 608, 567, 542 cm^{-1}; HRMS calculated m/z for $C_{12}H_{13}N_2O^+$ $[M+H]^+$: 201.1022, found (ESI) 201.1022.



58

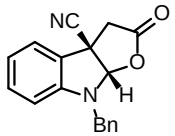
A mixture of **S41** (0.2 mmol, 47.5 mg, 1.0 equiv) and **9** (0.24 mmol, 86.2 mg, 1.2 equiv) in CH_3CN (2 mL) was stirred at room temperature for 10 minutes. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **58** in 89% yield (46.5 mg) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.67 – 7.55 (m, 2H), 7.47 – 7.34 (m, 3H), 7.29 – 7.15 (m, 2H), 6.87-6.83 (m, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 4.79 (bs, 1H), 4.42 – 4.20 (m, 1H), 3.83-3.76 (m, 1H), 2.89 – 2.66 (m, 1H), 2.53-2.49 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 149.2, 139.2, 130.6, 129.5, 128.6, 126.6, 124.8, 124.2, 120.1, 119.6, 108.7, 106.4, 67.0, 56.8, 41.1. IR (neat): 3390, 2895, 2232, 1610, 1486, 1470, 1445, 1392, 1354, 1324, 1281, 1232, 1133, 1094, 1070, 1035, 1022, 958, 942, 916, 889, 852, 762, 699, 662, 583, 536 cm^{-1}; HRMS calculated m/z for $C_{17}H_{15}N_2O^+$ $[M+H]^+$: 263.1179, found (ESI) 263.1183.



59

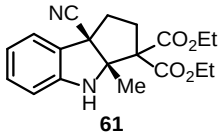
A mixture of **S42** (0.2 mmol, 35.0 mg, 1.0 equiv) and **9** (0.24 mmol, 86.2 mg, 1.2 equiv) in CH_3CN (2 mL) was stirred at room temperature for 10 minutes. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **59** in 64% yield (25.8 mg)

as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.25 (d, *J* = 7.2 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 6.88 (t, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 5.35 (s, 1H), 4.45 (bs, 1H), 3.91 – 3.79 (m, 1H), 3.69 – 3.52 (m, 1H), 2.34-2.31 (m, 2H), 1.79 – 1.64 (m, 1H), 1.61 – 1.46 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 148.1, 130.1, 125.7, 123.4, 121.2, 120.5, 110.9, 91.3, 61.7, 42.0, 29.1, 19.9. IR (neat): 3300, 2975, 2936, 2873, 2231, 1607, 1486, 1470, 1420, 1362, 1348, 1323, 1271, 1238, 1211, 1159, 1090, 1066, 1051, 1004, 970, 943, 909, 891, 868, 762, 747, 706, 665, 596, 558, 529, 506 cm^{-1}; HRMS calculated m/z for $C_{12}H_{13}N_2O^+$ $[M+H]^+$: 201.1022, found (ESI) 201.1022.



60

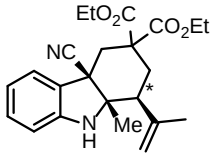
A mixture of **S43** (0.2 mmol, 73.1 mg, 1.0 equiv) and **9** (0.24 mmol, 86.2 mg, 1.2 equiv) in DCM (2 mL) was stirred at room temperature for 12 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **60** in 19% yield (11.0 mg) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.44 – 7.22 (m, 7H), 6.99 – 6.89 (m, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 5.97 (s, 1H), 4.73 – 4.35 (m, 2H), 3.48 – 3.17 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 170.7, 147.9, 135.3, 131.8, 129.2, 128.3, 128.1, 124.6, 124.4, 121.3, 117.6, 109.3, 98.8, 49.2, 44.1, 40.1. IR (neat): 2918, 2849, 2248, 1783, 1706, 1600, 1485, 1454, 1417, 1384, 1338, 1303, 1284, 1249, 1205, 1188, 1144, 1100, 1066, 1043, 1026, 1006, 973, 920, 905, 852, 825, 805, 740, 696, 655, 599, 561, 547 cm^{-1}; HRMS calculated m/z for $C_{18}H_{15}N_2O_2^+$ $[M+H]^+$: 291.1128, found (ESI) 291.1128.



61

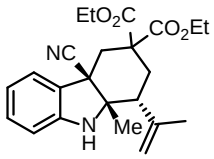
A mixture of **S44** (0.2 mmol, 63.5 mg, 1.0 equiv) and **9** (0.3 mmol, 107.8 mg, 1.5 equiv) in CH_3CN (2 mL) was stirred at room temperature for 5 minutes. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) afforded **61** in 86% yield (59.1 mg) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.29 (d, *J* = 7.6 Hz, 1H), 7.13-7.09 (m,

1H), 6.83-6.79 (m, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 4.39 – 4.20 (m, 4H), 4.07 (bs, 1H), 3.01-2.93 (m, 1H), 2.45-2.36 (m, 1H), 2.33 – 2.24 (m, 1H), 2.22 – 2.07 (m, 1H), 1.79 (s, 3H), 1.41 – 1.22 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 170.2, 169.4, 147.6, 129.74, 128.7, 124.3, 121.1, 120.0, 110.0, 79.4, 69.1, 62.1, 61.5, 55.4, 39.8, 32.8, 21.7, 14.1, 14.0. IR (neat): 3350, 2980, 2239, 1721, 1605, 1487, 1469, 1445, 1366, 1316, 1262, 1223, 1174, 1147, 1107, 1061, 1037, 1016, 941, 912, 858, 745, 649, 569, 532 cm^{-1}; HRMS calculated m/z for $C_{19}H_{23}N_2O_4^+$ $[M+H]^+$: 343.1652, found (ESI) 343.1656.



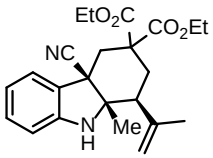
62, (*d.r.= 4.7:1)

A mixture of **S45** (0.2 mmol, 74.3 mg, 1.0 equiv) and **9** (0.24 mmol, 86.2 mg, 1.2 equiv) in DCM (2 mL) was stirred at room temperature for 11 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 10:1) afforded **62-minor** in 17% yield (13.4 mg) and **62-major** in 79% yield (62.6 mg) both as a colorless oils.



62-minor

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.33 – 7.26 (m, 1H), 7.16-7.12 (m, 1H), 6.85-6.81 (m, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 5.14 – 4.94 (m, 2H), 4.48 – 4.35 (m, 1H), 4.33 – 4.19 (m, 1H), 4.23 – 4.03 (m, 2H), 3.59 (bs, 1H), 2.87-2.83 (m, 1H), 2.71-2.67 (m, 1H), 2.34 – 2.23 (m, 1H), 2.10 – 1.95 (m, 2H), 1.96 – 1.87 (m, 3H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.31 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 170.8, 169.7, 146.9, 145.9, 130.3, 129.5, 123.3, 120.0, 119.6, 114.4, 111.5, 67.8, 62.0, 62.0, 52.7, 47.7, 44.4, 38.4, 32.4, 25.1, 24.5, 14.1, 14.0. IR (neat): 3357, 2977, 2240, 1641, 1608, 1482, 1466, 1444, 1376, 1318, 1239, 1218, 1175, 1147, 1127, 1077, 1056, 1020, 907, 859, 807, 749, 732, 635, 601, 561, 516 cm^{-1}; HRMS calculated m/z for $C_{23}H_{29}N_2O_4^+$ $[M+H]^+$: 397.2122, found (ESI) 397.2127.

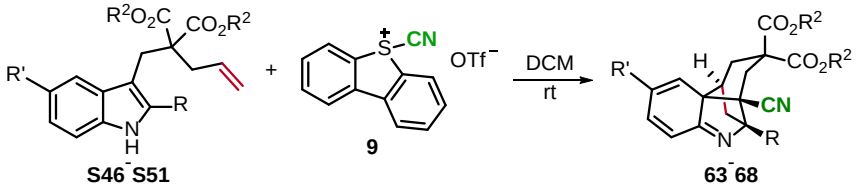


62-major

^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.21 (d, *J* = 7.6 Hz, 1H), 7.14-7.10 (m, 1H), 6.79-6.75 (m, 1H), 6.63 (d, *J* = 7.6 Hz, 1H), 5.03 (t, *J* = 1.6 Hz, 1H), 4.80 – 4.62 (m, 1H), 4.42 (bs, 1H), 4.34 – 4.15 (m, 2H), 4.16 – 4.03 (m, 1H), 4.02 – 3.87 (m, 1H), 3.11-3.07 (m, 1H), 2.76 (d, *J* = 15.2 Hz, 1H), 2.72-2.68 (m, 1H), 2.30-2.25 (m, 1H), 1.85 (t, *J* = 13.6 Hz, 1H), 1.80 (s, 3H), 1.47 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 170.8, 170.0, 148.6, 143.9, 130.3, 125.5, 124.7, 120.6, 119.4, 116.0, 110.9, 68.0, 62.3, 61.9, 52.6, 50.0, 44.3, 32.1, 30.6, 21.8, 18.5, 14.1, 13.8. IR (neat): 3362, 2980, 2231, 1727, 1607, 1482, 1467, 1385, 1368, 1328, 1299, 1248, 1197, 1156, 1093, 1050, 1020, 964, 908, 858, 797, 730, 647, 621, 591, 551 cm^{-1}; HRMS calculated m/z for $C_{23}H_{29}N_2O_4^+$ $[M+H]^+$: 397.2122, found (ESI) 397.2126.

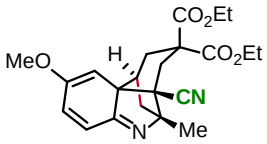
6. Metal-free cyanation/Povarov cycloaddition of indole derivatives

General procedure of the cyanation/Povarov cycloaddition of indole derivatives: preparation of 63-68.



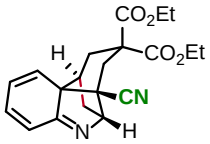
S46-S51 **9** **63-68**

Compound **9** was added to a stirred solution of indole derivatives **S46-S51** (0.2 mmol, 1.0 equiv) in DCM (2 mL) at room temperature and the resulting mixture was stirred for the specified time (vide infra). Then, the reaction was quenched with water, extracted with DCM, and the organic phase dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure afforded a residue, which was purified by column chromatography on silica gel to afford the desired products.



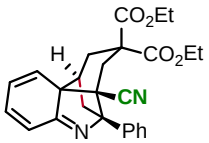
63

A mixture of **S46** (0.2 mmol, 74.7 mg, 1.0 equiv) and **9** (0.3 mmol, 107.8 mg, 1.5 equiv) in DCM (2 mL) was stirred at room temperature for 4 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 2:1) afforded **63** in 80% yield (63.9 mg) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 6.63 – 6.40 (m, 2H), 5.36 (s, 1H), 4.42 – 4.11 (m, 4H), 3.72 (s, 3H), 3.03 (d, *J* = 16.4 Hz, 1H), 2.81-2.76 (m, 1H), 2.63-2.58 (m, 1H), 2.42 (d, *J* = 16.4 Hz, 1H), 1.72 (s, 3H), 1.70 – 1.60 (m, 1H), 1.37 – 1.21 (m, 7H), 1.08-1.03 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 175.2, 172.3, 172.1, 156.0, 135.5, 122.9, 120.2, 94.6, 78.5, 67.1, 62.7, 62.6, 59.5, 55.0, 50.2, 35.0, 31.7, 30.5, 29.8, 16.8, 14.0, 14.0. IR (neat): 2963, 2254, 1724, 1642, 1568, 1463, 1414, 1386, 1367, 1239, 1212, 1189, 1141, 1086, 1029, 977, 913, 886, 860, 813, 784, 731, 649, 612, 541, 510 cm^{-1}; HRMS calculated m/z for $C_{22}H_{27}N_2O_5^+$ $[M+H]^+$: 399.1914, found (ESI) 399.1918.



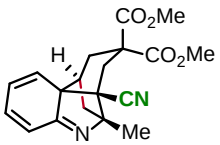
64

A mixture of **S47** (0.2 mmol, 65.9 mg, 1.0 equiv) and **9** (0.2 mmol, 71.9 mg, 1.0 equiv) in DCM (2 mL) was stirred at room temperature for 3 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 1:1) followed by preparative HPLC afforded **64** in 67% yield (47.6 mg) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 6.79 – 6.67 (m, 1H), 6.65 – 6.46 (m, 3H), 4.60 (d, *J* = 3.6 Hz, 1H), 4.37 – 4.15 (m, 4H), 2.99 (d, *J* = 16.4 Hz, 1H), 2.83-2.79 (m, 1H), 2.61 – 2.46 (m, 2H), 1.75 – 1.65 (m, 1H), 1.65 – 1.55 (m, 1H), 1.36 – 1.21 (m, 6H), 0.97-0.92 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 176.9, 172.4, 171.6, 134.6, 130.1, 128.7, 122.3, 120.4, 72.8, 64.5, 62.7, 62.7, 59.4, 50.2, 32.9, 30.9, 25.9, 14.1. IR (neat): 2981, 2237, 1633, 1560, 1444, 1367, 1253, 1190, 1145, 1092, 1051, 1019, 934, 909, 858, 809, 746, 696, 648, 627, 589, 565 cm^{-1}; HRMS calculated m/z for $C_{20}H_{23}N_2O_4^+$ $[M+H]^+$: 355.1652, found (ESI) 355.1654.



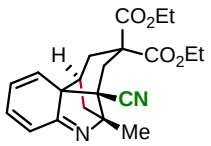
65

A mixture of **S48** (0.2 mmol, 81.1 mg, 1.0 equiv) and **9** (0.3 mmol, 107.8 mg, 1.5 equiv) in DCM (2 mL) was stirred at room temperature for 36 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 2:1) afforded **65** in 78% yield (66.8 mg) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.65 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.41 – 7.32 (m, 1H), 6.81-6.77 (m, 1H), 6.72 – 6.53 (m, 3H), 4.42 – 4.09 (m, 4H), 3.05 (dd, *J* = 14.8, 3.6 Hz, 1H), 2.86 (d, *J* = 17.2 Hz, 1H), 2.67 (d, *J* = 17.2 Hz, 1H), 2.44 – 2.27 (m, 2H), 1.90-1.87 (m, 1H), 1.39 – 1.15 (m, 7H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 176.0, 172.6, 172.1, 136.2, 134.9, 130.8, 128.4, 128.4, 128.2, 128.0, 122.1, 119.7, 83.1, 69.6, 62.8, 62.7, 61.3, 49.3, 34.9, 31.4, 29.5, 28.9, 14.0. IR (neat): 2977, 2235, 1748, 1720, 1634, 1566, 1499, 1445, 1365, 1316, 1298, 1252, 1234, 1193, 1147, 1093, 1073, 1031, 1007, 902, 864, 813, 763, 747, 720, 695, 645, 632, 607, 584, 552 cm^{-1}; HRMS calculated m/z for $C_{26}H_{27}N_2O_4^+$ $[M+H]^+$: 431.1965, found (ESI) 431.1966.



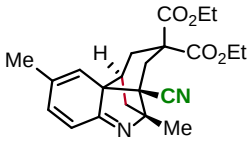
66

A mixture of **S49** (0.2 mmol, 63.1 mg, 1.0 equiv) and **9** (0.2 mmol, 71.9 mg, 1.0 equiv) in DCM (2 mL) was stirred at room temperature for 4 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 1:1) afforded **66** in 76% yield (51.4 mg) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 6.77 – 6.69 (m, 1H), 6.64 – 6.55 (m, 2H), 6.52-6.49 (m, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 3.03 (d, *J* = 16.4 Hz, 1H), 2.85-2.80 (m, 1H), 2.58-2.54 (m, 1H), 2.49 (d, *J* = 16.4 Hz, 1H), 1.81 – 1.74 (m, 1H), 1.73 (s, 3H), 1.32-1.28 (m, 1H), 1.05-0.99 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 175.5, 172.7, 172.2, 134.7, 130.4, 128.5, 122.0, 119.9, 78.2, 67.5, 60.1, 53.8, 53.7, 50.3, 34.8, 31.3, 30.7, 29.8, 16.7. IR (neat): 2956, 2239, 1719, 1635, 1560, 1457, 1431, 1383, 1340, 1269, 1234, 1201, 1179, 1148, 1106, 1086, 1004, 969, 911, 872, 861, 838, 797, 749, 731, 649, 632, 611, 572 cm^{-1}; HRMS calculated m/z for $C_{19}H_{21}N_2O_4^+$ $[M+H]^+$: 341.1496, found (ESI) 341.1500.



67

A mixture of **S50** (0.2 mmol, 68.7 mg, 1.0 equiv) and **9** (0.2 mmol, 71.9 mg, 1.0 equiv) in DCM (2 mL) was stirred at room temperature for 3 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 1:1) afforded **67** in 85% yield (62.7 mg) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 6.75 – 6.71 (m, 1H), 6.62-6.56 (m, 2H), 6.50 (d, *J* = 9.6 Hz, 1H), 4.40 – 4.16 (m, 4H), 3.02 (d, *J* = 16.4 Hz, 1H), 2.83-2.78 (m, 1H), 2.60 – 2.51 (m, 1H), 2.51 – 2.40 (m, 1H), 1.74 (m, 4H), 1.30 (m, 7H), 1.04-0.99 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 175.5, 172.3, 171.7, 134.6, 130.6, 128.4, 121.9, 120.0, 78.2, 67.4, 62.7, 62.7, 60.2, 50.3, 34.9, 31.2, 30.6, 29.7, 16.7, 14.1, 14.0. IR (neat): 2976, 2235, 1721, 1632, 1561, 1467, 1444, 1380, 1366, 1298, 1245, 1190, 1147, 1079, 1040, 1016, 909, 861, 819, 782, 749, 629, 608, 572, 511 cm^{-1}; HRMS calculated m/z for $C_{21}H_{25}N_2O_4^+$ $[M+H]^+$: 369.1809, found (ESI) 369.1812.



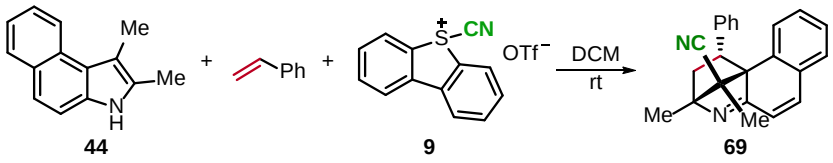
68

A mixture of **S51** (0.2 mmol, 71.5 mg, 1.0 equiv) and **9** (0.2 mmol, 71.9 mg, 1.0 equiv) in DCM (2 mL) was stirred at room temperature for 3 h. Column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 1:1) afforded **68** in 81% yield (61.6 mg) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 6.59-6.56 (m, 1H), 6.47-6.45 (m, 1H), 6.26-6.24 (m, 1H), 4.43 – 3.99 (m, 4H), 3.01 (d, *J* = 16.4 Hz, 1H), 2.80-2.75 (m, 1H), 2.58-2.54 (m, 1H), 2.44 (d, *J* = 16.4 Hz, 1H), 2.05 (d, *J* = 1.6 Hz, 3H), 1.73-1.69 (m, 4H), 1.34-1.26 (m, 7H), 1.04-0.98 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 175.5, 172.3, 171.7, 139.1, 136.5, 124.5, 121.5, 120.2, 78.3, 67.3, 62.7, 62.6, 60.0, 50.3, 34.7, 31.5, 30.4, 29.7, 22.4, 16.7, 14.0, 14.0. IR (neat): 2980, 1727, 1563, 1441, 1383, 1234, 1196, 1176, 1142, 1083, 1065,

1022, 905, 857, 799, 723, 644, 607, 549, 512 cm^{-1}; HRMS calculated m/z for $C_{22}H_{27}N_2O_4^+$ $[M+H]^+$: 383.1965, found (ESI) 383.1968.

7. Intermolecular cyanation-[4+2] cycloaddition

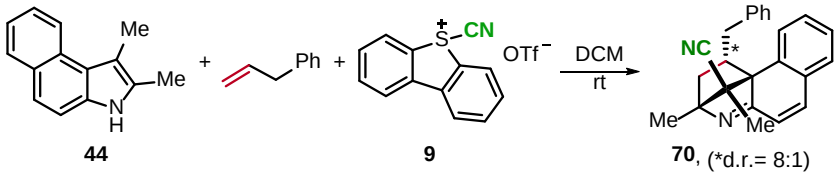
Procedure for the preparation of 69



44 **9** **69**

Salt **9** (86.2 mg, 0.24 mmol, 1.2 equiv) was added to a stirred solution of 1,2-dimethyl-3*H*-benzo[*e*]indole **44** (39.1 mg, 0.2 mmol, 1.0 equiv) in DCM (2 mL) at room temperature and the resulting mixture was stirred for 10 minutes. Then, styrene (34.5 μL, 0.3 mmol, 1.5 equiv) was added and the resulting mixture stirred at room temperature for additional 11 h. Subsequently, the reaction was quenched with water, extracted with DCM and the organic phase dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) to afford **69** (57.7 mg, 89% yield) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.99 (d, *J* = 7.6 Hz, 1H), 7.49 – 7.40 (m, 1H), 7.34 – 7.24 (m, 1H), 7.11 – 7.00 (m, 2H), 6.95 (t, *J* = 7.6 Hz, 2H), 6.72 – 6.61 (m, 2H), 6.55 (d, *J* = 9.6 Hz, 1H), 6.22 (d, *J* = 9.6 Hz, 1H), 4.08-4.04 (m, 1H), 2.75-2.69 (m, 1H), 1.85 – 1.73 (m, 4H), 0.97 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 173.0, 139.1, 137.1, 135.3, 133.5, 129.4, 129.1, 128.2, 128.0, 127.5, 127.1, 125.8, 122.3, 121.8, 77.9, 67.5, 63.1, 51.0, 34.8, 16.8, 13.6. IR (neat): 2976, 2225, 1614, 1571, 1498, 1451, 1373, 1294, 1173, 1160, 1093, 1035, 909, 870, 847, 805, 754, 729, 706, 601, 581, 555, 535, 510 cm^{-1}; HRMS calculated m/z for $C_{23}H_{21}N_2^+$ $[M+H]^+$: 325.1699, found (ESI) 325.1703.

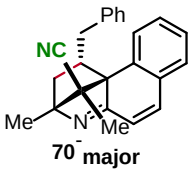
Procedure for the preparation of 70



44 **9** **70**, (*d.r.= 8:1)

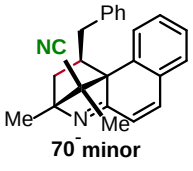
Salt **9** (86.2 mg, 0.24 mmol, 1.2 equiv) and allylbenzene (39.8 μL, 0.3 mmol, 1.5 equiv) were successively added to a stirred solution of 1,2-dimethyl-3*H*-benzo[*e*]indole **44** (39.1 mg, 0.2 mmol, 1.0 equiv) in DCM (2 mL) at room temperature, and the resulting mixture was

stirred at room temperature for 37 h. Then, the reaction was quenched with water, extracted with DCM and the organic phase dried over anhydrous Na_2SO_4. Evaporation of the solvents under reduced pressure afforded a residue, which was purified by column chromatography on silica gel (eluent: hexane to hexane/ethyl acetate = 4:1) to afford **70** (58.7 mg, 87% yield, d.r.= 8:1 based on ^{1}H NMR analysis). Separation of the isomers was only possible by preparative HPLC.



70$^-$ major

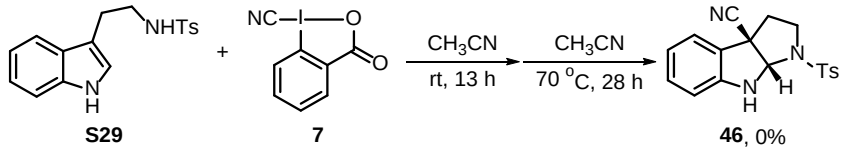
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.89 (d, *J* = 7.6 Hz, 1H), 7.49 – 7.33 (m, 3H), 7.23 – 7.06 (m, 4H), 6.98 – 6.83 (m, 2H), 6.65 – 6.48 (m, 1H), 3.21 – 3.02 (m, 1H), 2.42-2.38 (m, 1H), 2.34 – 2.22 (m, 1H), 2.01 – 1.89 (m, 1H), 1.63 (s, 3H), 1.07-1.02 (m, 1H), 0.94 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 173.4, 140.1, 139.5, 135.8, 133.7, 129.8, 129.5, 128.6, 128.4, 128.4, 126.3, 125.7, 122.2, 121.9, 65.5, 63.0, 48.2, 36.3, 34.0, 16.9, 13.5. IR (neat): 2974, 2933, 2227, 1612, 1571, 1497, 1450, 1388, 1376, 1296, 1212, 1166, 1119, 982, 943, 906, 867, 808, 753, 735, 705, 660, 623, 585, 544, 509 cm^{-1}; HRMS calculated m/z for $C_{24}H_{23}N_2^+$ $[M+H]^+$: 339.1856, found (ESI) 339.1857.



70$^-$ minor

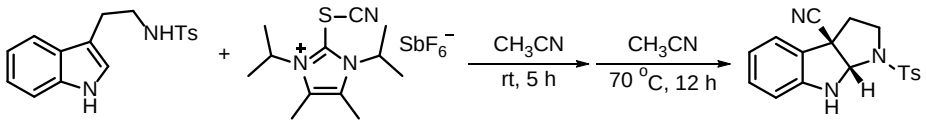
^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.87 – 7.78 (m, 1H), 7.47 – 7.35 (m, 3H), 7.24 – 7.17 (m, 2H), 7.18 – 7.11 (m, 2H), 7.11 – 7.03 (m, 2H), 6.43 (d, *J* = 9.6 Hz, 1H), 3.36 (t, *J* = 13.2 Hz, 1H), 2.62-2.57 (m, 1H), 2.11-2.06 (m, 1H), 2.01 – 1.87 (m, 1H), 1.68 (s, 3H), 1.39-1.33 (m, 1H), 1.00 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ = 176.0, 140.0, 139.9, 134.8, 133.0, 130.0, 128.8, 128.7, 128.6, 128.4, 128.3, 126.3, 123.5, 119.4, 65.1, 58.0, 43.0, 37.0, 36.9, 16.6, 14.9. IR (neat): 3026, 2968, 2934, 2226, 1614, 1573, 1496, 1450, 1404, 1384, 1293, 1210, 1163, 1119, 1030, 988, 951, 909, 864, 813, 757, 730, 700, 660, 642, 611, 584, 548, 531, 515 cm^{-1}; HRMS calculated m/z for $C_{24}H_{23}N_2^+$ $[M+H]^+$: 339.1856, found (ESI) 339.1859.

8. Control experiments



S29 **7** **46**, 0%

Compound **7**[25] (81.9 mg, 0.3 mmol, 1.5 equiv) was added at room temperature under nitrogen flow to a stirred solution of **S29** (62.9 mg, 0.2 mmol, 1.0 equiv) in CH_3CN (2 mL). The resulting mixture was stirred at room temperature for 13 h. No trace of desired product **46** was observed. Then, the reaction was stirred at 70 °C for additional 28 h. without observing any change.

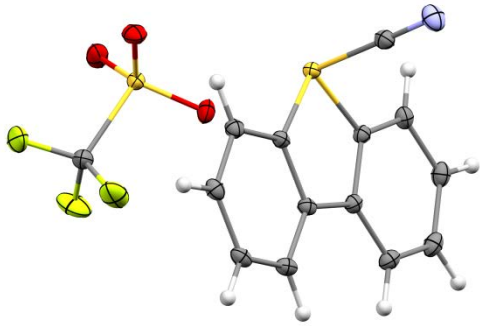


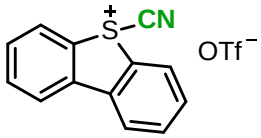
S29 **8** **46**, 0%

To a stirred solution of **S29** (62.9 mg, 0.2 mmol, 1.0 equiv) in CH_3CN (2 mL) **8**[23] (142.2 mg, 0.3 mmol, 1.5 equiv) was added at room temperature under nitrogen flow. The resulting mixture was stirred at room temperature for 5 h. No desired product **46** was observed. Stirring the reaction at 70 °C for additional 12 h. did not change the result.

9. X-ray crystal structure

X-ray crystal structure of 9

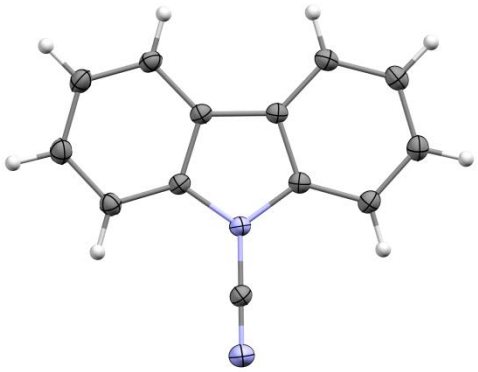


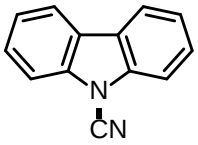


9

Empirical formula	$C_{14}H_8F_3NO_3S_2$
Formula weight	359.33
Temperature/K	101.44
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	6.7928(3)
b/Å	14.0411(6)
c/Å	15.2306(7)
α/°	90
β/°	90.599(2)
γ/°	90
Volume/Å^3	1452.59(11)
Z	4
ρ_{calc}g/cm^3	1.643
μ/mm^{-1}	0.413
F(000)	728.0
Crystal size/mm^3	0.416 × 0.27 × 0.263
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.35 to 63.02
Index ranges	$-9 \le h \le 9$, $-20 \le k \le 20$, $-22 \le l \le 22$
Reflections collected	66179
Independent reflections	4789 [R_{int} = 0.0186, R_{sigma} = 0.0104]
Data/restraints/parameters	4789/0/208
Goodness-of-fit on F^2	1.079
Final R indexes [I>=2σ (I)]	R_1 = 0.0251, wR_2 = 0.0680
Final R indexes [all data]	R_1 = 0.0252, wR_2 = 0.0682
Largest diff. peak/hole / e Å^{-3}	0.50/-0.34

X-ray crystal structure of 22

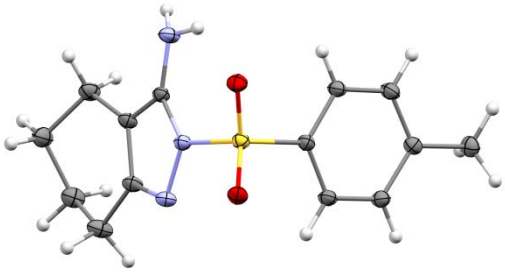


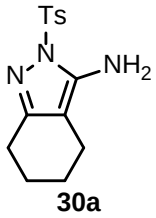


22

Empirical formula	$C_{13}H_8N_2$
Formula weight	192.21
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	8.0477(7)
b/Å	8.1521(7)
c/Å	14.5994(14)
α/°	94.263(3)
β/°	93.278(3)
γ/°	93.638(3)
Volume/Å^3	951.38(15)
Z	4
ρ_{calc}g/cm^3	1.342
μ/mm^{-1}	0.081
F(000)	400.0
Crystal size/mm^3	0.421 × 0.22 × 0.219
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.082 to 63.192
Index ranges	$-11 \leq h \leq 11$, $-11 \leq k \leq 12$, $-21 \leq l \leq 21$
Reflections collected	34993
Independent reflections	6331 [R_{int} = 0.0279, R_{sigma} = 0.0205]
Data/restraints/parameters	6331/0/271
Goodness-of-fit on F^2	1.153
Final R indexes [I>=2σ (I)]	R_1 = 0.0476, wR_2 = 0.1259
Final R indexes [all data]	R_1 = 0.0503, wR_2 = 0.1277
Largest diff. peak/hole / e Å^{-3}	0.49/-0.21

X-ray crystal structure of 30a

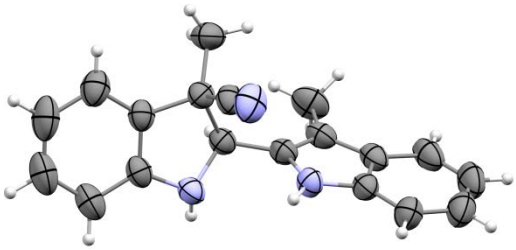


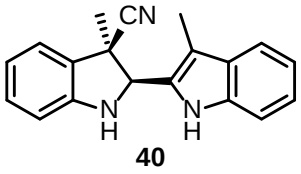


30a

Empirical formula	$C_{14}H_{17}N_3O_2S$
Formula weight	291.36
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.7293(12)
b/Å	8.4475(6)
c/Å	12.0428(9)
α/°	90
β/°	100.898(4)
γ/°	90
Volume/Å^3	1371.51(19)
Z	4
ρ_{calc}g/cm^3	1.411
μ/mm^{-1}	0.241
F(000)	616.0
Crystal size/mm^3	0.45 × 0.316 × 0.214
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.692 to 63.138
Index ranges	$-16 \leq h \leq 20$, $-12 \leq k \leq 12$, $-17 \leq l \leq 17$
Reflections collected	18342
Independent reflections	4579 [R_{int} = 0.0280, R_{sigma} = 0.0257]
Data/restraints/parameters	4579/0/209
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0363, wR_2 = 0.1021
Final R indexes [all data]	R_1 = 0.0398, wR_2 = 0.1052
Largest diff. peak/hole / e Å^{-3}	0.83/-0.62

X-ray crystal structure of 40

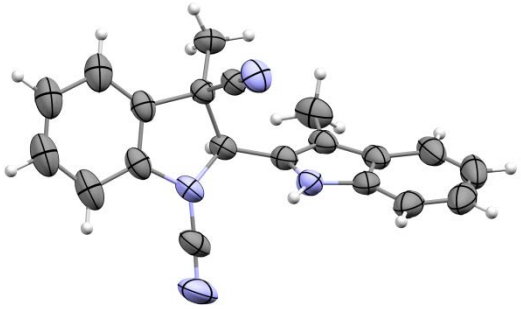


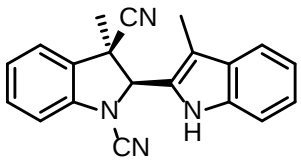


40

Empirical formula	$C_{19}H_{17}N_3$
Formula weight	287.35
Temperature/K	298
Crystal system	monoclinic
Space group	Cc
a/Å	10.0946(8)
b/Å	15.6754(11)
c/Å	10.9099(11)
α/°	90
β/°	113.486(3)
γ/°	90
Volume/Å^3	1583.3(2)
Z	4
ρ_{calc}g/cm^3	1.205
μ/mm^{-1}	0.073
F(000)	608.0
Crystal size/mm^3	0.363 × 0.286 × 0.166
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.33 to 58.25
Index ranges	$-13 \leq h \leq 13$, $-21 \leq k \leq 21$, $-14 \leq l \leq 14$
Reflections collected	19130
Independent reflections	4229 [R_{int} = 0.0210, R_{sigma} = 0.0216]
Data/restraints/parameters	4229/2/207
Goodness-of-fit on F^2	1.071
Final R indexes [I>=2σ (I)]	R_1 = 0.0386, wR_2 = 0.1132
Final R indexes [all data]	R_1 = 0.0398, wR_2 = 0.1147
Largest diff. peak/hole / e Å^{-3}	0.18/-0.15
Flack parameter	-0.1(4)

X-ray crystal structure of 41

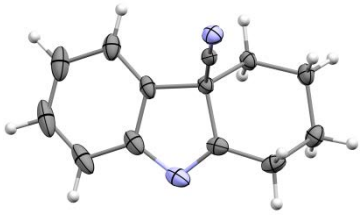


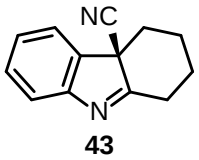


41

Empirical formula	$C_{20}H_{16}N_4$
Formula weight	312.37
Temperature/K	298
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	6.7642(4)
b/Å	25.5858(14)
c/Å	9.4556(5)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	1636.46(16)
Z	4
$\rho_{calc}g/cm^3$	1.268
μ/mm^{-1}	0.078
F(000)	656.0
Crystal size/mm^3	0.363 × 0.354 × 0.136
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.592 to 57.446
Index ranges	$-9 \leq h \leq 9$, $-34 \leq k \leq 34$, $-12 \leq l \leq 12$
Reflections collected	44432
Independent reflections	4209 [R_{int} = 0.0252, R_{sigma} = 0.0174]
Data/restraints/parameters	4209/38/222
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0377, wR_2 = 0.1114
Final R indexes [all data]	R_1 = 0.0389, wR_2 = 0.1127
Largest diff. peak/hole / e $Å^{-3}$	0.21/-0.20
Flack parameter	0.0(3)

X-ray crystal structure of 43

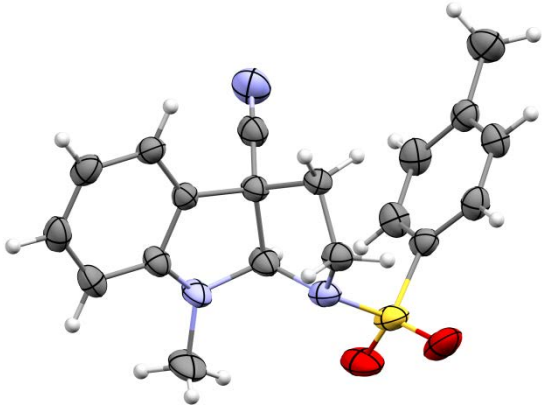


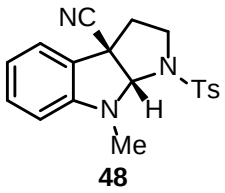


43

Empirical formula	$C_{13}H_{12}N_2$
Formula weight	196.25
Temperature/K	100.01
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	6.7185(13)
b/Å	6.7629(15)
c/Å	23.087(4)
α/°	90
β/°	90.519(7)
γ/°	90
Volume/Å^3	1048.9(4)
Z	4
ρ_{calc}g/cm^3	1.243
μ/mm^{-1}	0.075
F(000)	416.0
Crystal size/mm^3	0.5 × 0.406 × 0.088
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.064 to 54.348
Index ranges	$-8 \le h \le 8$, $-8 \le k \le 8$, $-28 \le l \le 29$
Reflections collected	24225
Independent reflections	2344 [R_{int} = 0.0331, R_{sigma} = 0.0174]
Data/restraints/parameters	2344/0/136
Goodness-of-fit on F^2	1.093
Final R indexes [I>=2σ (I)]	R_1 = 0.0439, wR_2 = 0.1107
Final R indexes [all data]	R_1 = 0.0471, wR_2 = 0.1126
Largest diff. peak/hole / e Å^{-3}	0.24/-0.19

X-ray crystal structure of 48

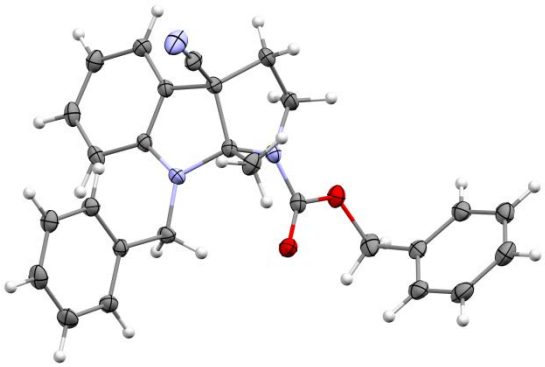


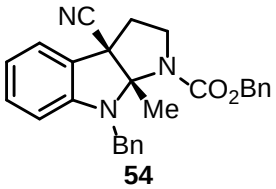


48

Empirical formula	$C_{19}H_{19}N_3O_2S$
Formula weight	353.43
Temperature/K	199.98
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.1603(18)
b/Å	10.1311(13)
c/Å	15.642(3)
α/°	90
β/°	96.422(8)
γ/°	90
Volume/Å^3	1757.5(5)
Z	4
ρ_{calc}g/cm^3	1.336
μ/mm^{-1}	0.202
F(000)	744.0
Crystal size/mm^3	0.601 × 0.144 × 0.096
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.446 to 57.424
Index ranges	$-15 \le h \le 15$, $-13 \le k \le 13$, $-21 \le l \le 21$
Reflections collected	40943
Independent reflections	4531 [R_{int} = 0.0201, R_{sigma} = 0.0126]
Data/restraints/parameters	4531/0/232
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0377, wR_2 = 0.1064
Final R indexes [all data]	R_1 = 0.0404, wR_2 = 0.1091
Largest diff. peak/hole / e Å^{-3}	0.30/-0.42

X-ray crystal structure of 54

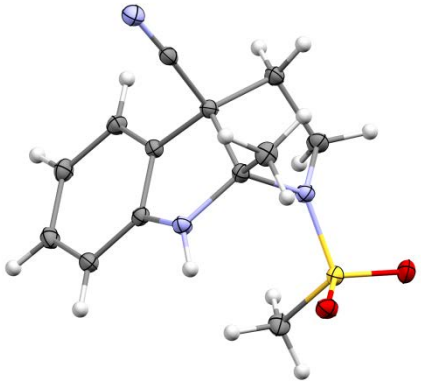


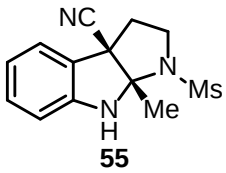


54

Empirical formula	$C_{27}H_{25}N_3O_2$
Formula weight	423.50
Temperature/K	99.96
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	18.5268(18)
b/Å	7.8990(7)
c/Å	15.0062(15)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2196.1(4)
Z	4
ρ_{calc}g/cm^3	1.281
μ/mm^{-1}	0.082
F(000)	896.0
Crystal size/mm^3	0.67 × 0.634 × 0.586
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.158 to 59.232
Index ranges	$-25 \leq h \leq 25$, $-10 \leq k \leq 10$, $-20 \leq l \leq 18$
Reflections collected	33215
Independent reflections	6071 [R_{int} = 0.0301, R_{sigma} = 0.0244]
Data/restraints/parameters	6071/0/291
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0399, wR_2 = 0.1039
Final R indexes [all data]	R_1 = 0.0417, wR_2 = 0.1065
Largest diff. peak/hole / e Å^{-3}	0.30/-0.22

X-ray crystal structure of 55

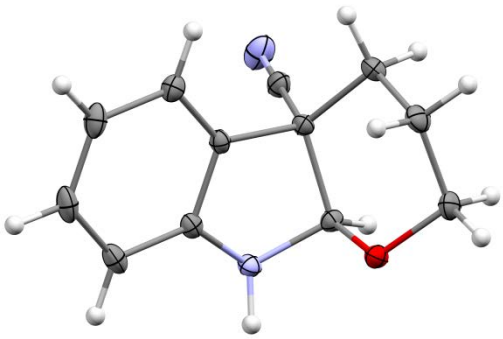


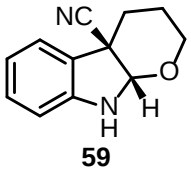


55

Empirical formula	$C_{13}H_{15}N_3O_2S$
Formula weight	277.34
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.2046(16)
b/Å	9.1200(10)
c/Å	11.4034(15)
α/°	90
β/°	110.802(4)
γ/°	90
Volume/Å^3	1283.7(3)
Z	4
ρ_{calc}g/cm^3	1.435
μ/mm^{-1}	0.254
F(000)	584.0
Crystal size/mm^3	0.936 × 0.364 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.554 to 57.434
Index ranges	$-17 \leq h \leq 17$, $-11 \leq k \leq 12$, $-15 \leq l \leq 15$
Reflections collected	13200
Independent reflections	3291 [R_{int} = 0.0244, R_{sigma} = 0.0217]
Data/restraints/parameters	3291/0/177
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0301, wR_2 = 0.0765
Final R indexes [all data]	R_1 = 0.0323, wR_2 = 0.0785
Largest diff. peak/hole / e Å^{-3}	0.41/-0.44

X-ray crystal structure of 59

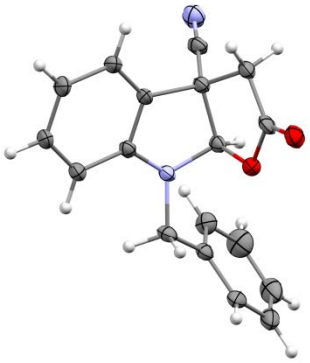


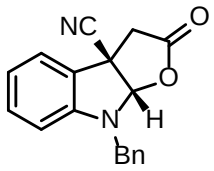


59

Empirical formula	$C_{12}H_{12}N_2O$
Formula weight	200.24
Temperature/K	99.98
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.9515(8)
b/Å	7.1269(6)
c/Å	14.6312(11)
α/°	90
β/°	97.573(3)
γ/°	90
Volume/Å^3	1028.64(14)
Z	4
ρ_{calc}g/cm^3	1.293
μ/mm^{-1}	0.084
F(000)	424.0
Crystal size/mm^3	0.596 × 0.575 × 0.55
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.128 to 61.154
Index ranges	$-14 \le h \le 14$, $-10 \le k \le 10$, $-20 \le l \le 20$
Reflections collected	31056
Independent reflections	3122 [R_{int} = 0.0254, R_{sigma} = 0.0119]
Data/restraints/parameters	3122/0/140
Goodness-of-fit on F^2	1.087
Final R indexes [I>=2σ (I)]	R_1 = 0.0362, wR_2 = 0.1008
Final R indexes [all data]	R_1 = 0.0375, wR_2 = 0.1032
Largest diff. peak/hole / e Å^{-3}	0.39/-0.24

X-ray crystal structure of 60

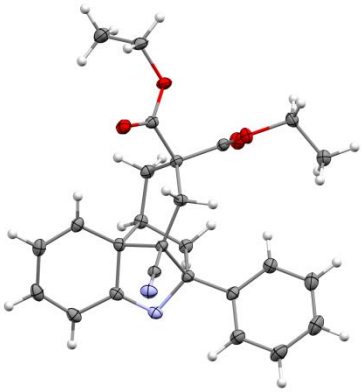


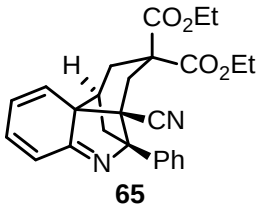


60

Empirical formula	$C_{18}H_{14}N_2O_2$
Formula weight	290.31
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	8.3733(5)
b/Å	8.8124(6)
c/Å	9.8006(7)
α/°	92.376(3)
β/°	94.925(2)
γ/°	91.733(2)
Volume/Å^3	719.47(8)
Z	2
ρ_{calc}g/cm^3	1.340
μ/mm^{-1}	0.089
F(000)	304.0
Crystal size/mm^3	0.308 × 0.225 × 0.22
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.096 to 59.182
Index ranges	$-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-13 \leq l \leq 13$
Reflections collected	18340
Independent reflections	4034 [R_{int} = 0.0232, R_{sigma} = 0.0213]
Data/restraints/parameters	4034/403/374
Goodness-of-fit on F^2	1.191
Final R indexes [I>=2σ (I)]	R_1 = 0.0555, wR_2 = 0.1200
Final R indexes [all data]	R_1 = 0.0572, wR_2 = 0.1207
Largest diff. peak/hole / e Å^{-3}	0.30/-0.26

X-ray crystal structure of 65

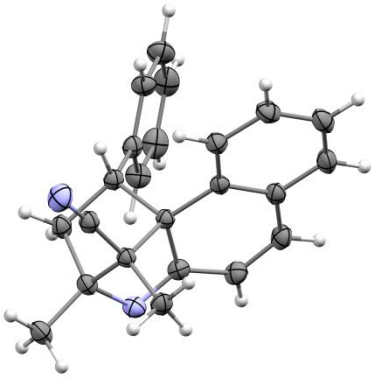


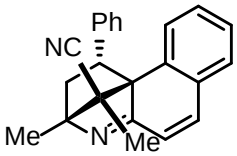


65

Empirical formula	$C_{26}H_{26}N_2O_4$
Formula weight	430.49
Temperature/K	100.01
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.4697(7)
b/Å	20.5978(15)
c/Å	11.0885(7)
α/°	90
β/°	116.053(2)
γ/°	90
Volume/Å^3	2148.3(3)
Z	4
ρ_{calc}g/cm^3	1.331
μ/mm^{-1}	0.090
F(000)	912.0
Crystal size/mm^3	0.496 × 0.446 × 0.198
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.76 to 59.232
Index ranges	$-14 \leq h \leq 14$, $-28 \leq k \leq 28$, $-15 \leq l \leq 15$
Reflections collected	41436
Independent reflections	5990 [R_{int} = 0.0270, R_{sigma} = 0.0174]
Data/restraints/parameters	5990/0/291
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0360, wR_2 = 0.0933
Final R indexes [all data]	R_1 = 0.0400, wR_2 = 0.0978
Largest diff. peak/hole / e Å^{-3}	0.40/-0.23

X-ray crystal structure of 69

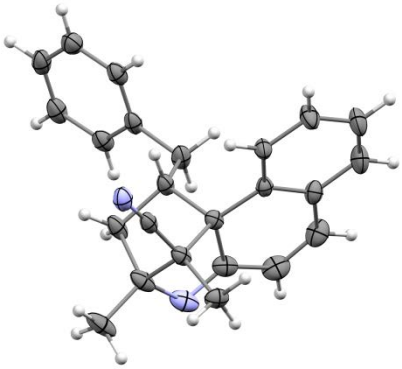


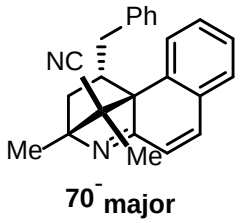


69

Empirical formula	$C_{23}H_{20}N_2$
Formula weight	324.41
Temperature/K	175
Crystal system	triclinic
Space group	P-1
a/Å	6.9386(7)
b/Å	10.8785(10)
c/Å	12.1498(10)
α/°	92.955(3)
β/°	99.134(3)
γ/°	107.607(3)
Volume/Å^3	858.20(14)
Z	2
ρ_{calc}g/cm^3	1.255
μ/mm^{-1}	0.074
F(000)	344.0
Crystal size/mm^3	0.517 × 0.459 × 0.152
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.266 to 57.404
Index ranges	$-9 \leq h \leq 9$, $-14 \leq k \leq 14$, $-16 \leq l \leq 16$
Reflections collected	21504
Independent reflections	4423 [R_{int} = 0.0220, R_{sigma} = 0.0206]
Data/restraints/parameters	4423/0/229
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0393, wR_2 = 0.1033
Final R indexes [all data]	R_1 = 0.0415, wR_2 = 0.1054
Largest diff. peak/hole / e Å^{-3}	0.34/-0.19

X-ray crystal structure of 70-major





70⁻ major

Empirical formula	$C_{24}H_{22}N_2$
Formula weight	338.43
Temperature/K	99.97
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	15.504(2)
b/Å	16.8542(18)
c/Å	7.0717(9)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1847.9(4)
Z	4
ρ_{calc}g/cm^3	1.217
μ/mm^{-1}	0.071
F(000)	720.0
Crystal size/mm^3	0.27 × 0.236 × 0.182
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.254 to 57.502
Index ranges	$-20 \le h \le 20$, $-22 \le k \le 22$, $-9 \le l \le 9$
Reflections collected	41884
Independent reflections	4791 [R_{int} = 0.0313, R_{sigma} = 0.0184]
Data/restraints/parameters	4791/1/237
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0343, wR_2 = 0.0922
Final R indexes [all data]	R_1 = 0.0352, wR_2 = 0.0932
Largest diff. peak/hole / e Å^{-3}	0.33/-0.20
Flack parameter	-0.2(5)

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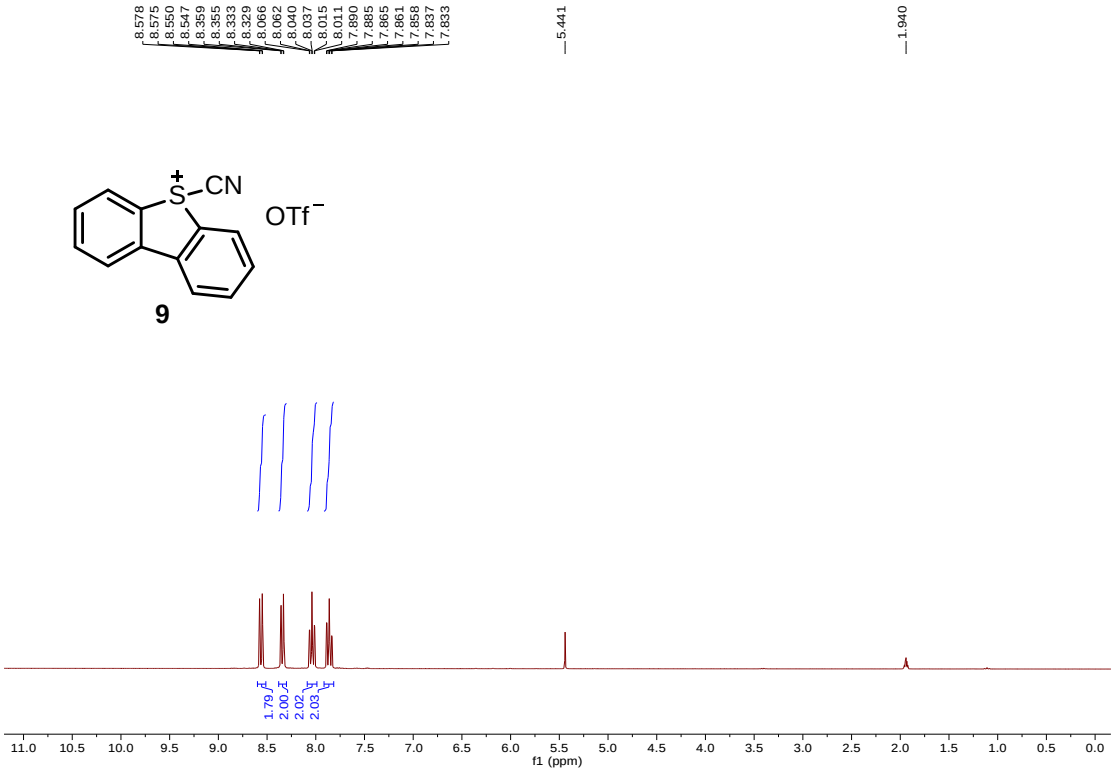
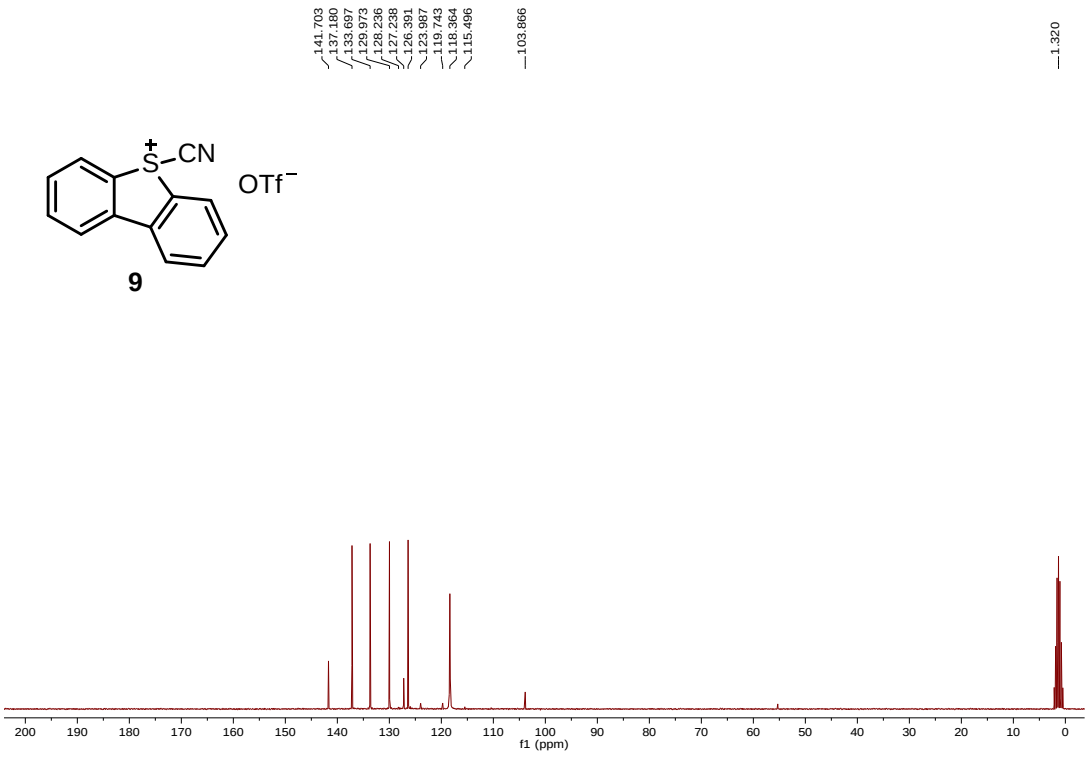
11. NMR spectra

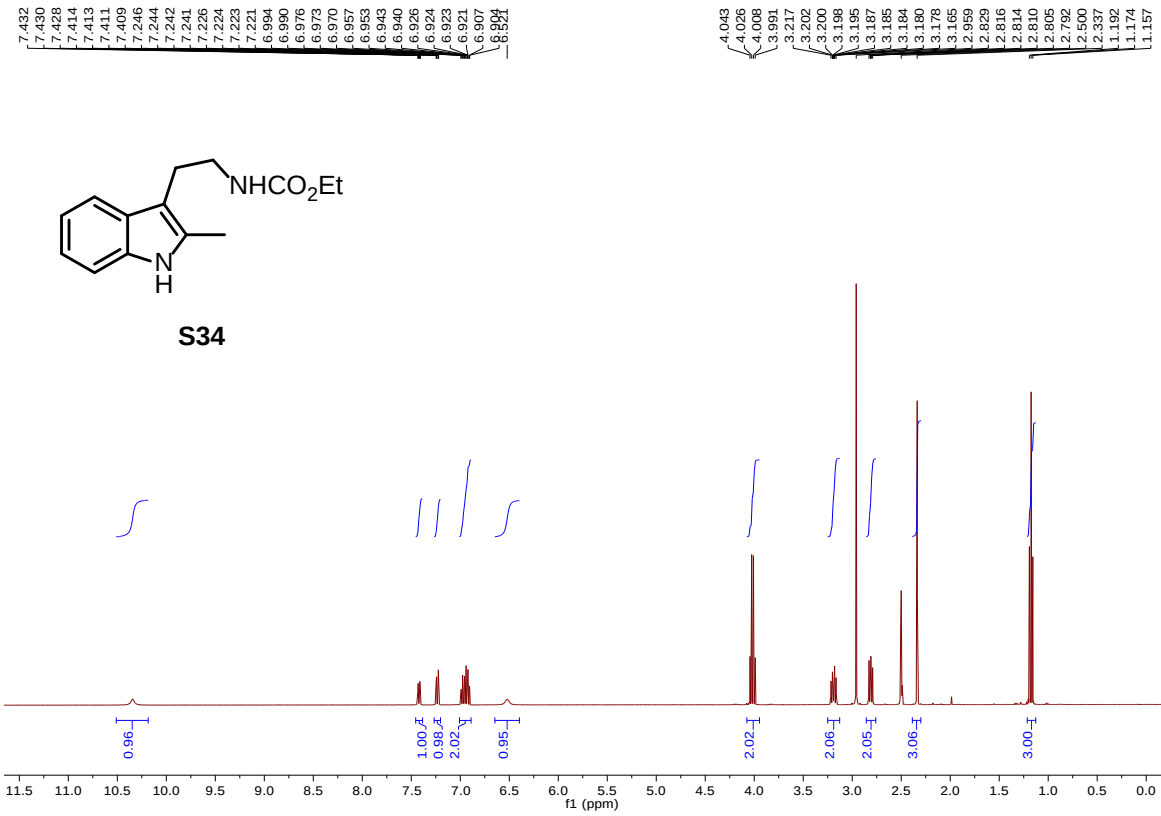
^{1}H NMR (300 MHz, CD_3CN)



^{13}C NMR (75 MHz, CD_3CN)



^{1}H NMR (400 MHz, DMSO-d_6, 100 ^{o}C)



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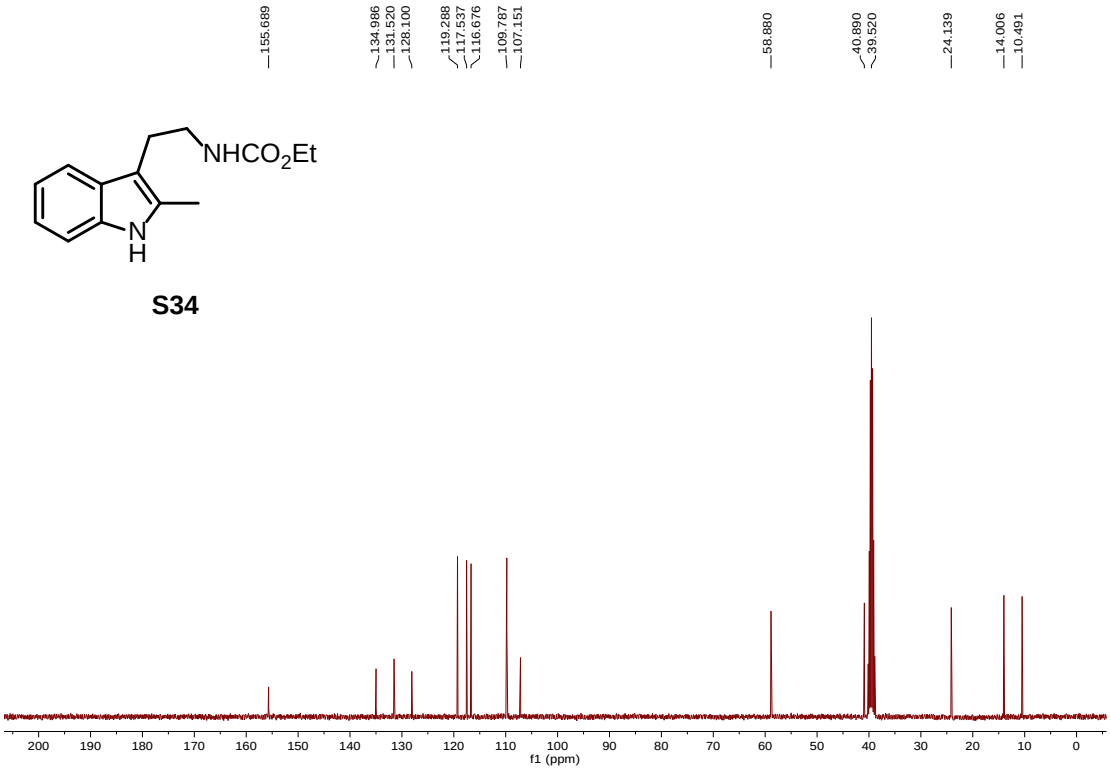

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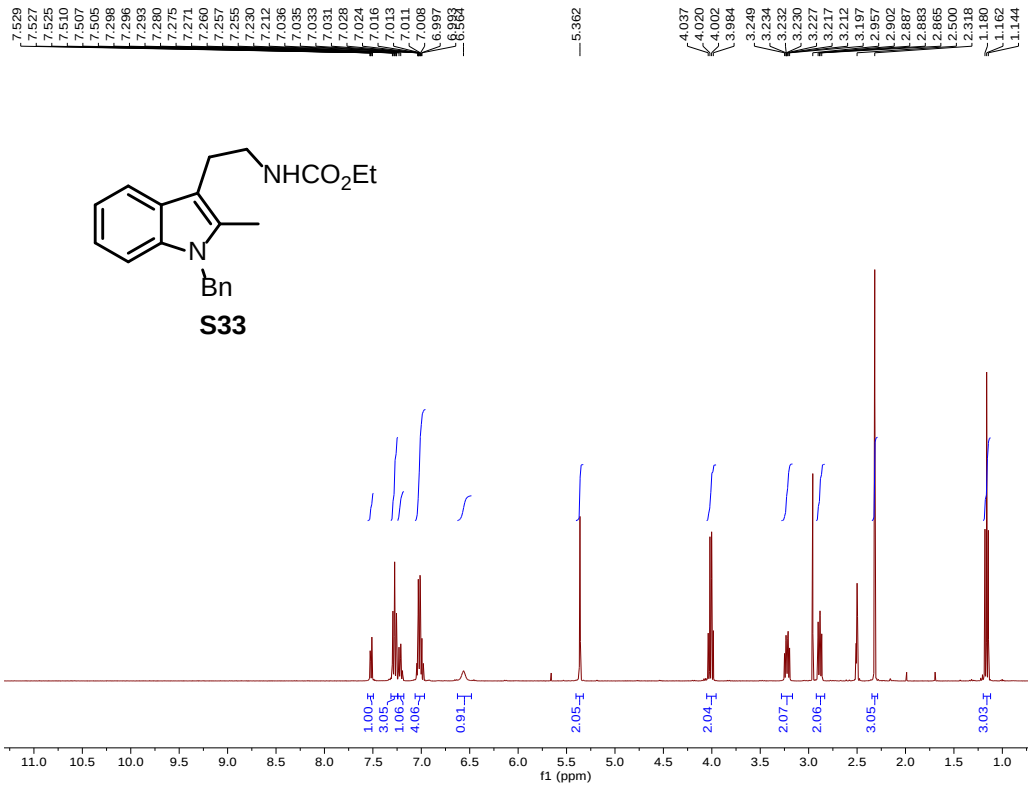

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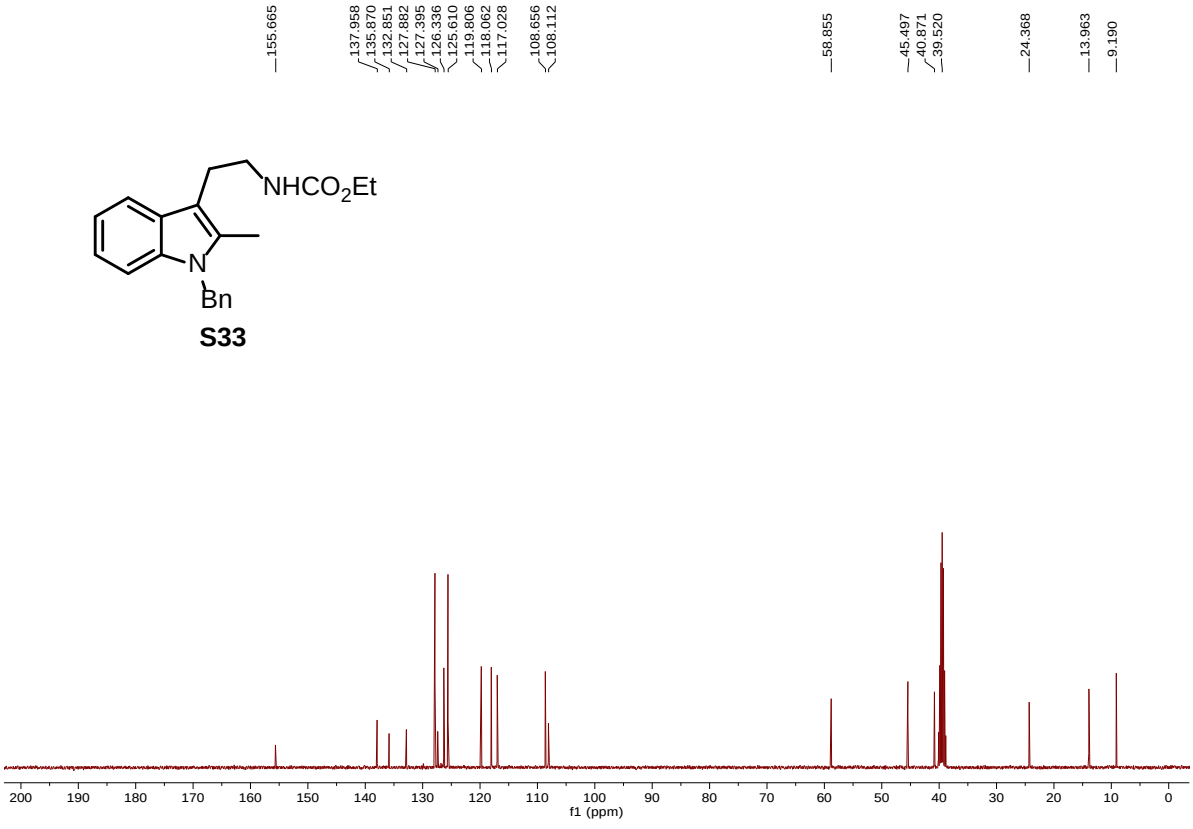
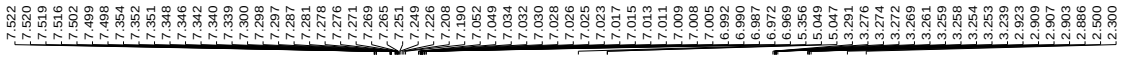
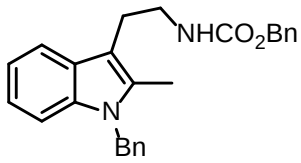
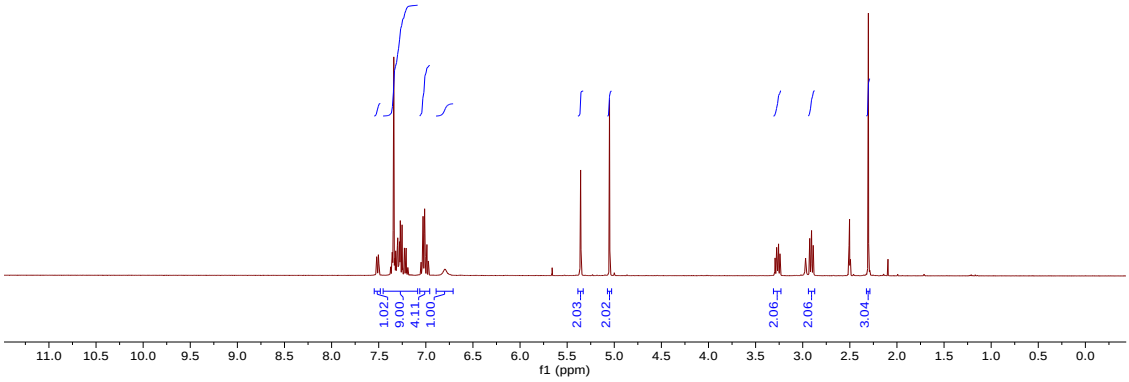


^{1}H NMR (400 MHz, DMSO-d_6, 100 ^{o}C)

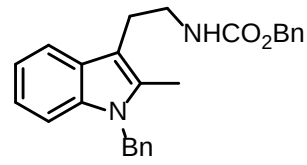




S37



^{13}C NMR (101 MHz, DMSO-d_6, 100 ^{o}C)



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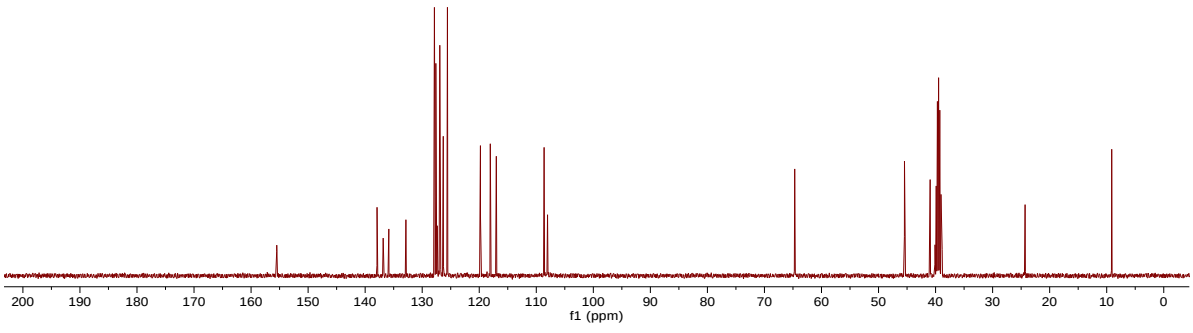
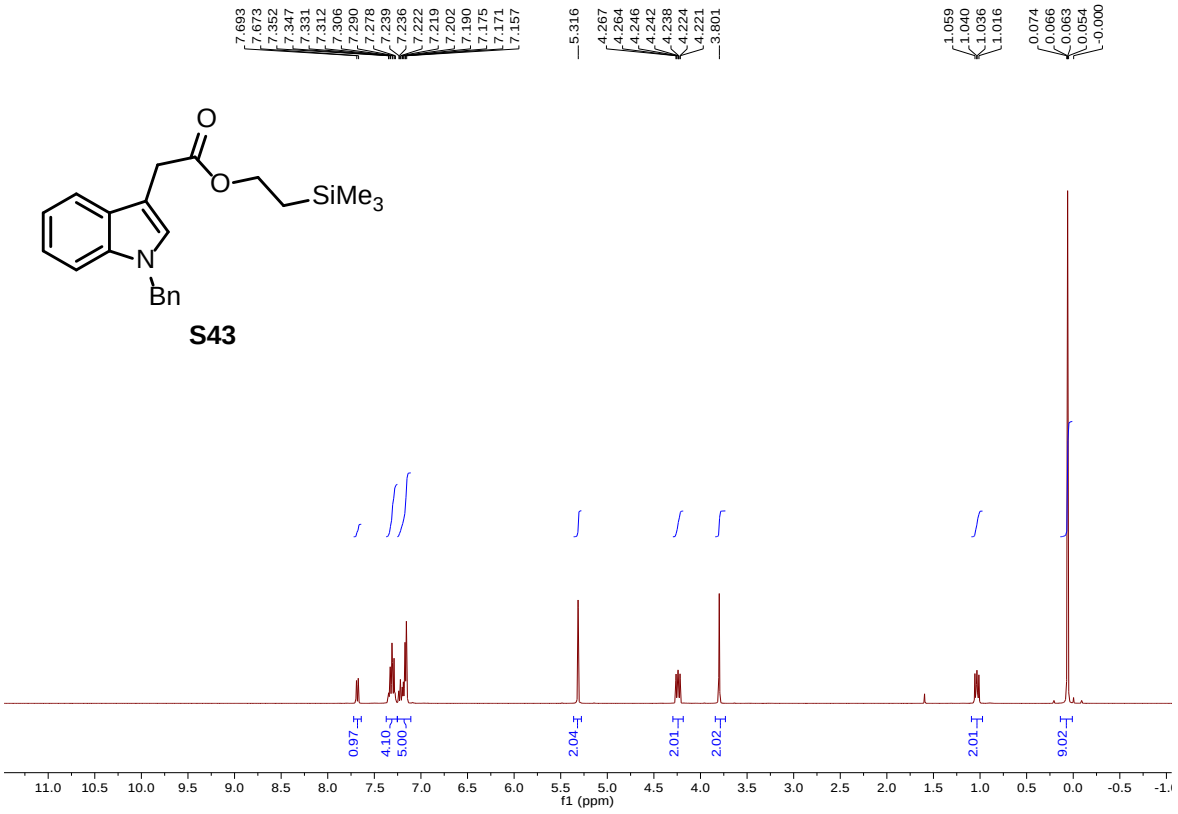


^{1}H NMR (400 MHz, Chloroform-*d*)



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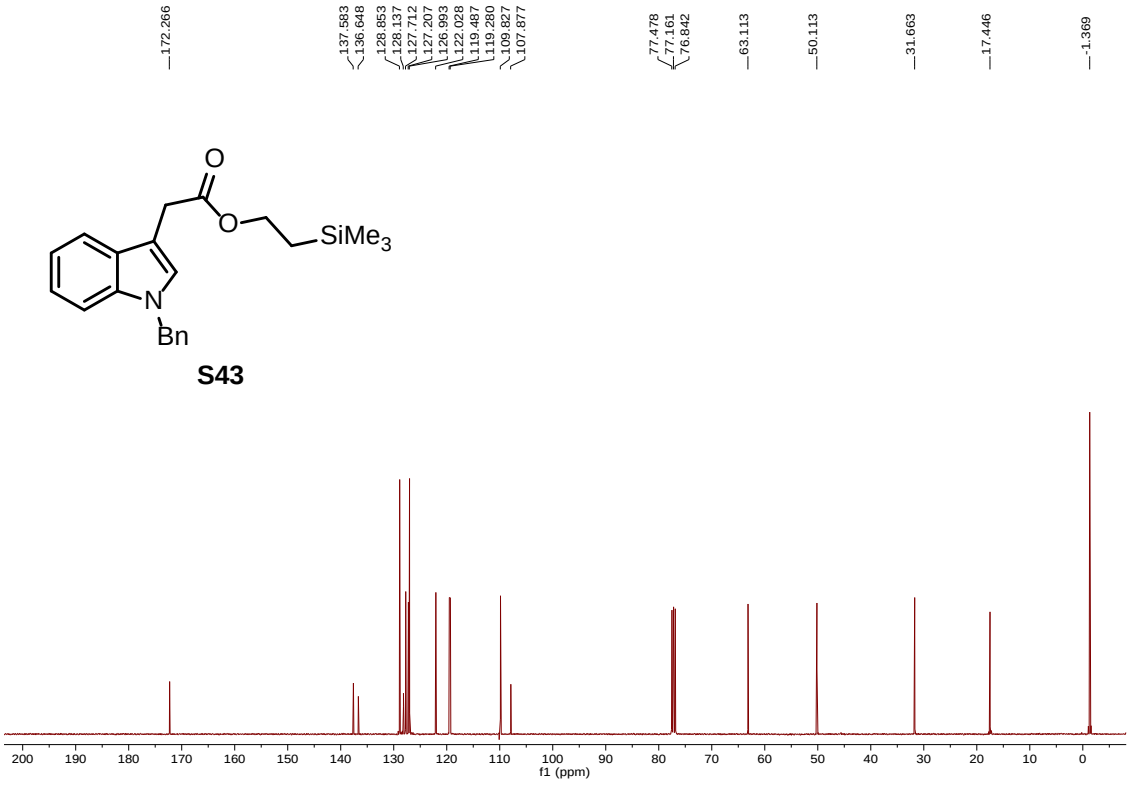

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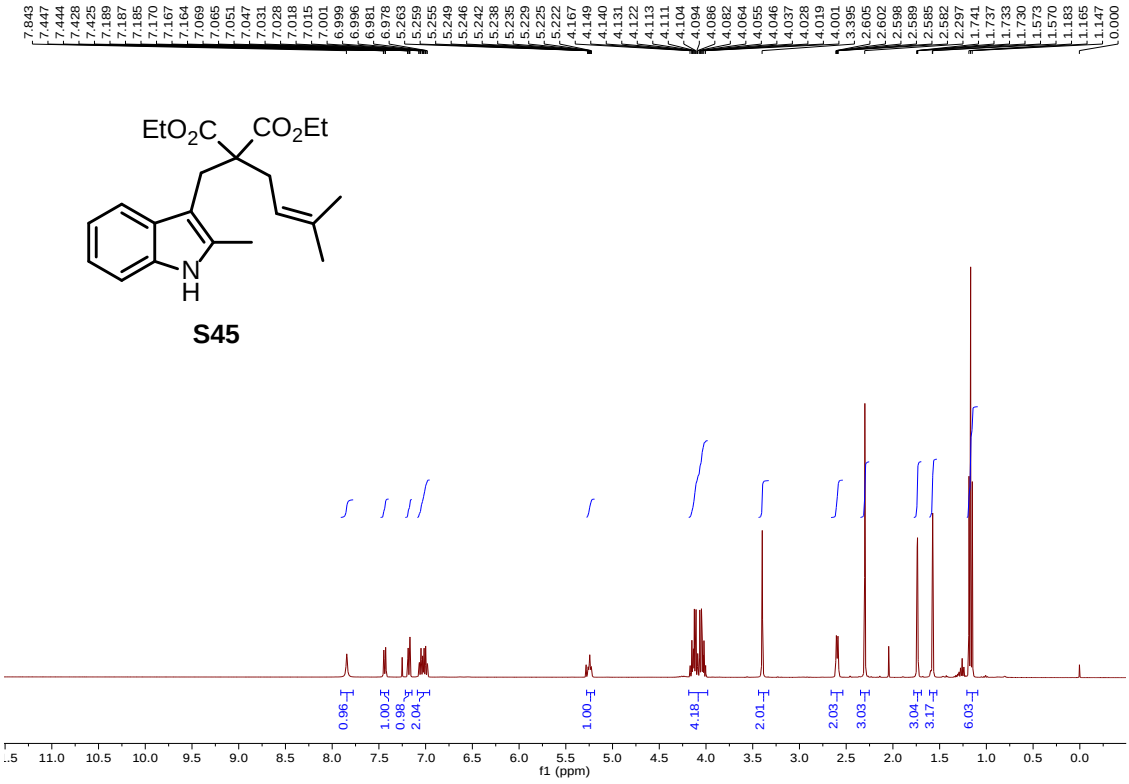

S45

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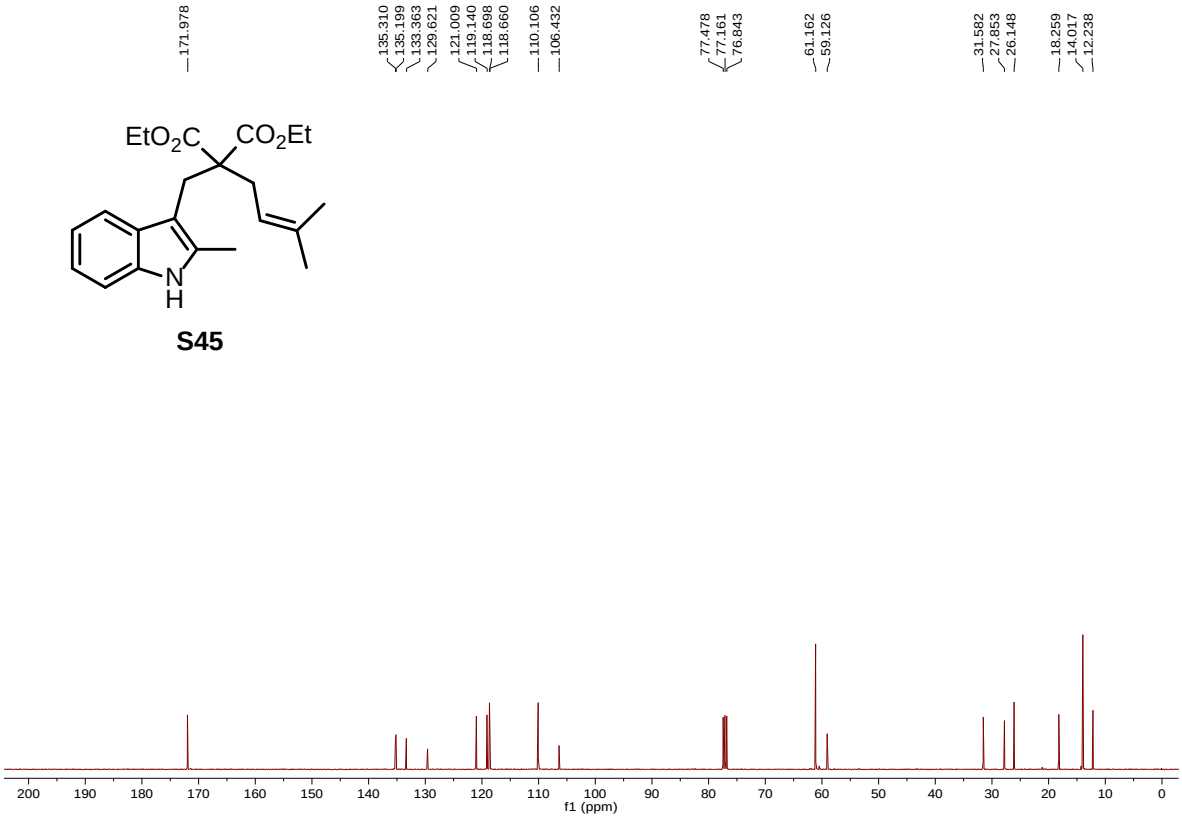

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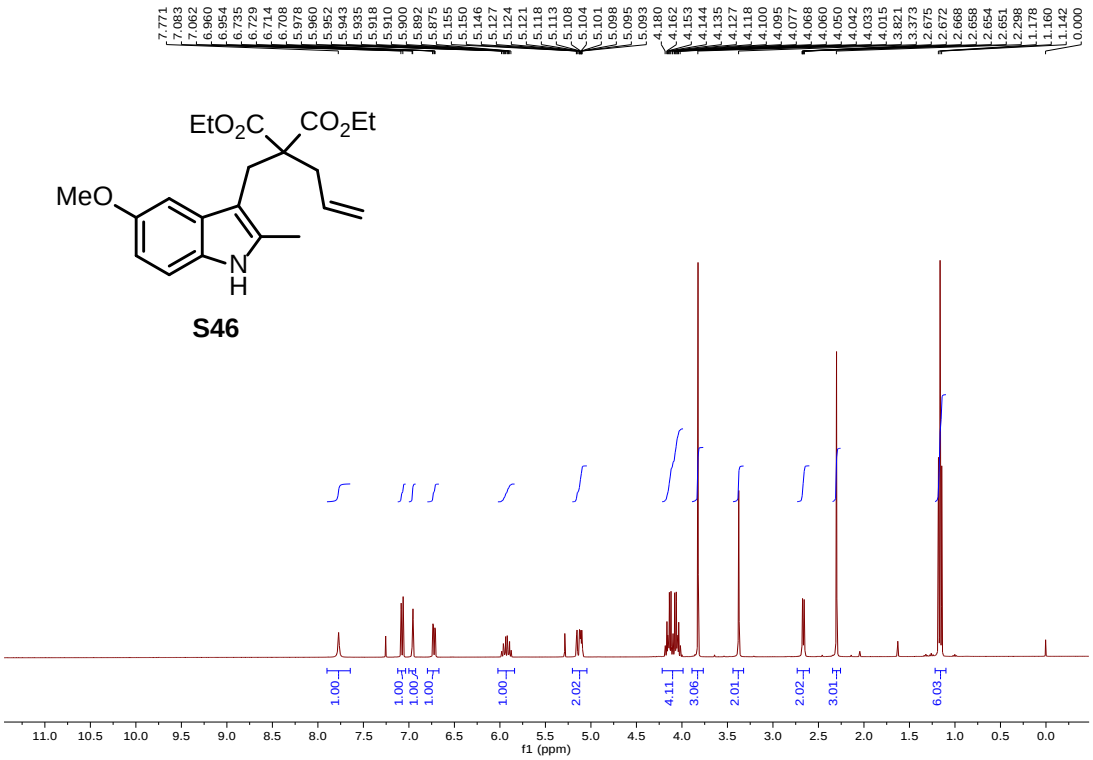
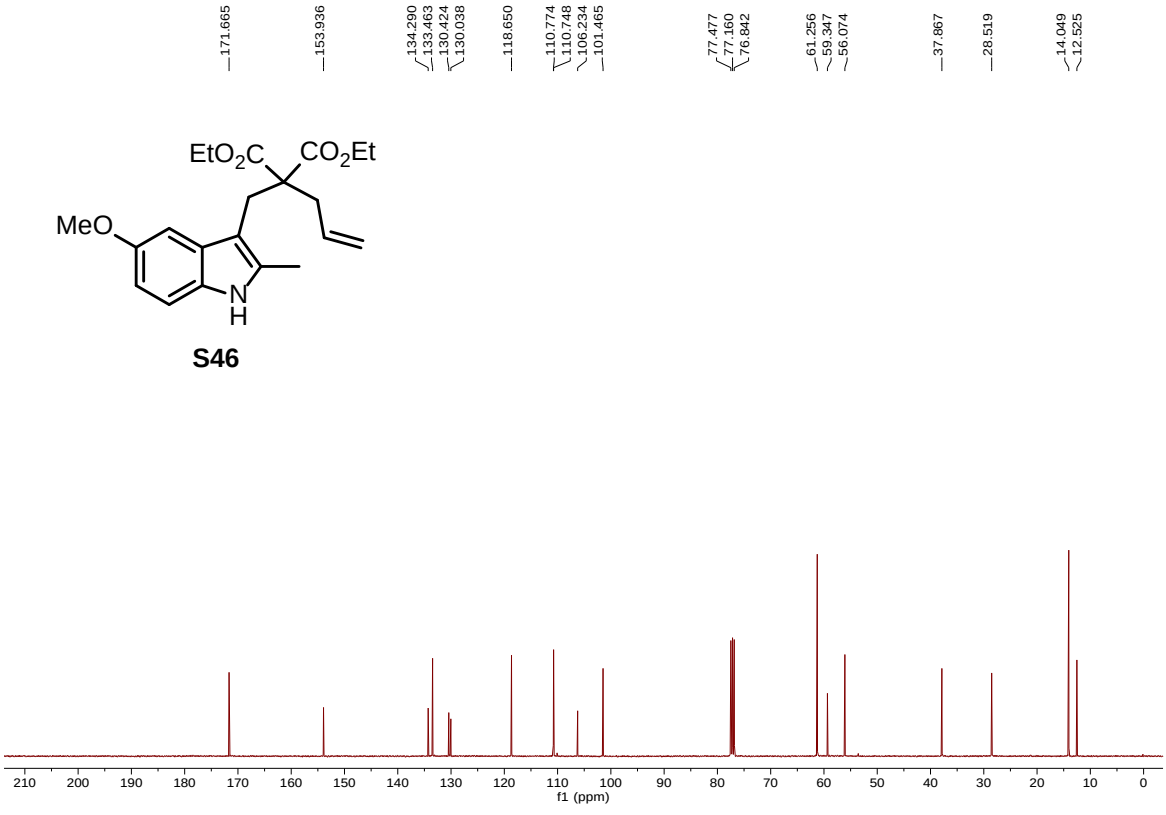


S46

^{13}C NMR (101 MHz, Chloroform-*d*)



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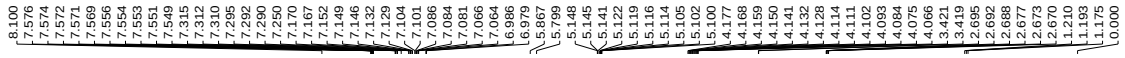
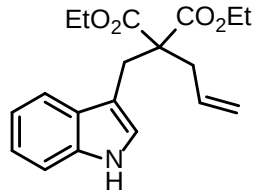
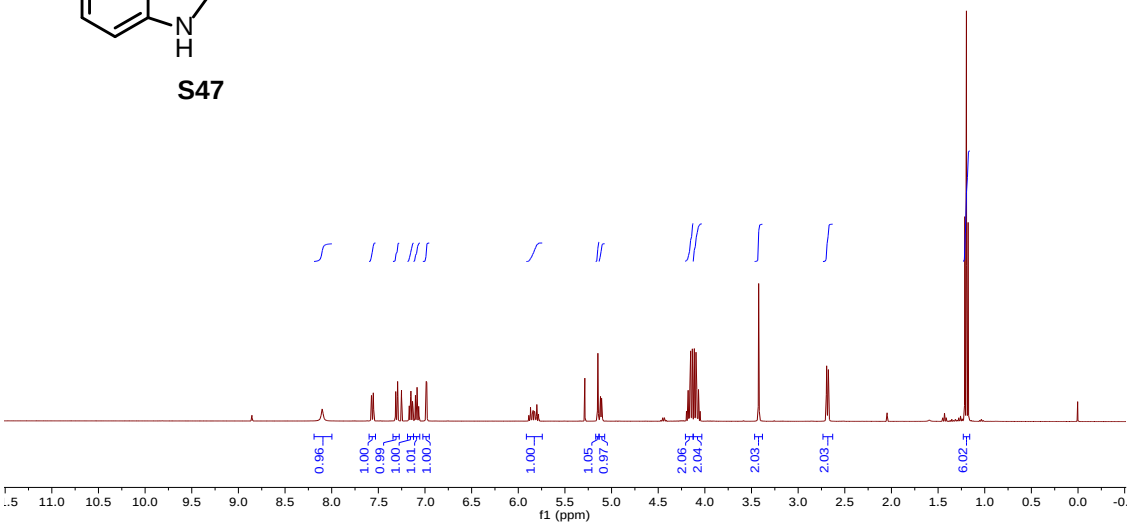




S47



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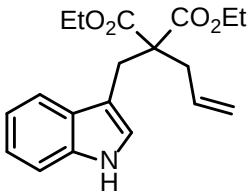
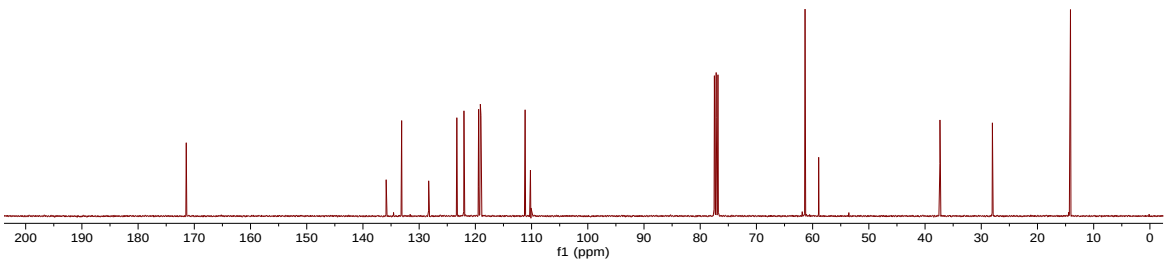
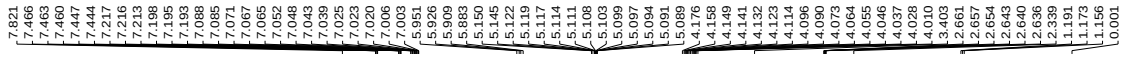
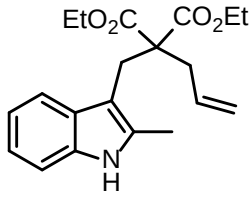


S47



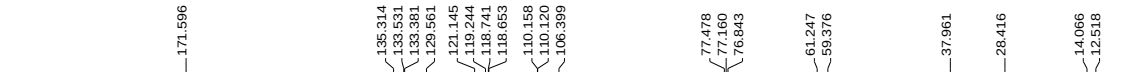
^{1}H NMR (400 MHz, Chloroform-*d*)

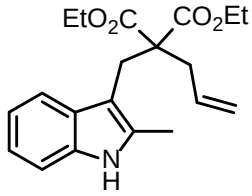




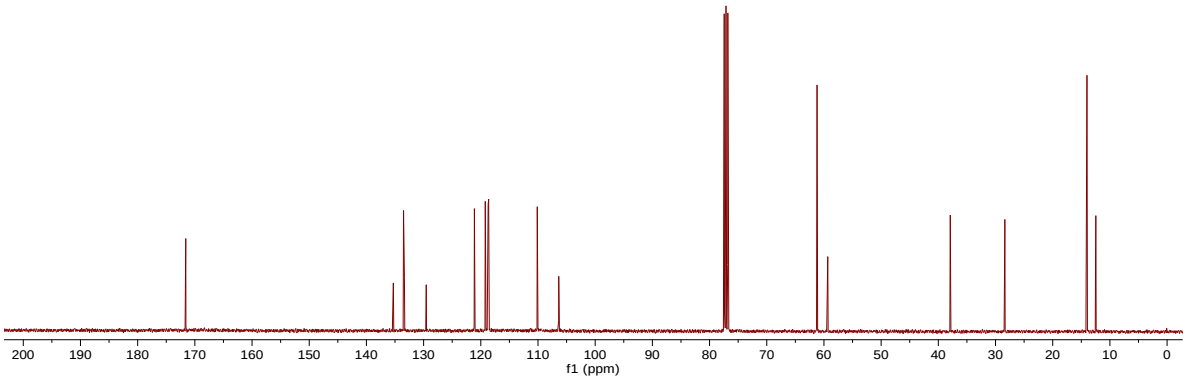
S50

^{13}C NMR (101 MHz, Chloroform-*d*)





S50



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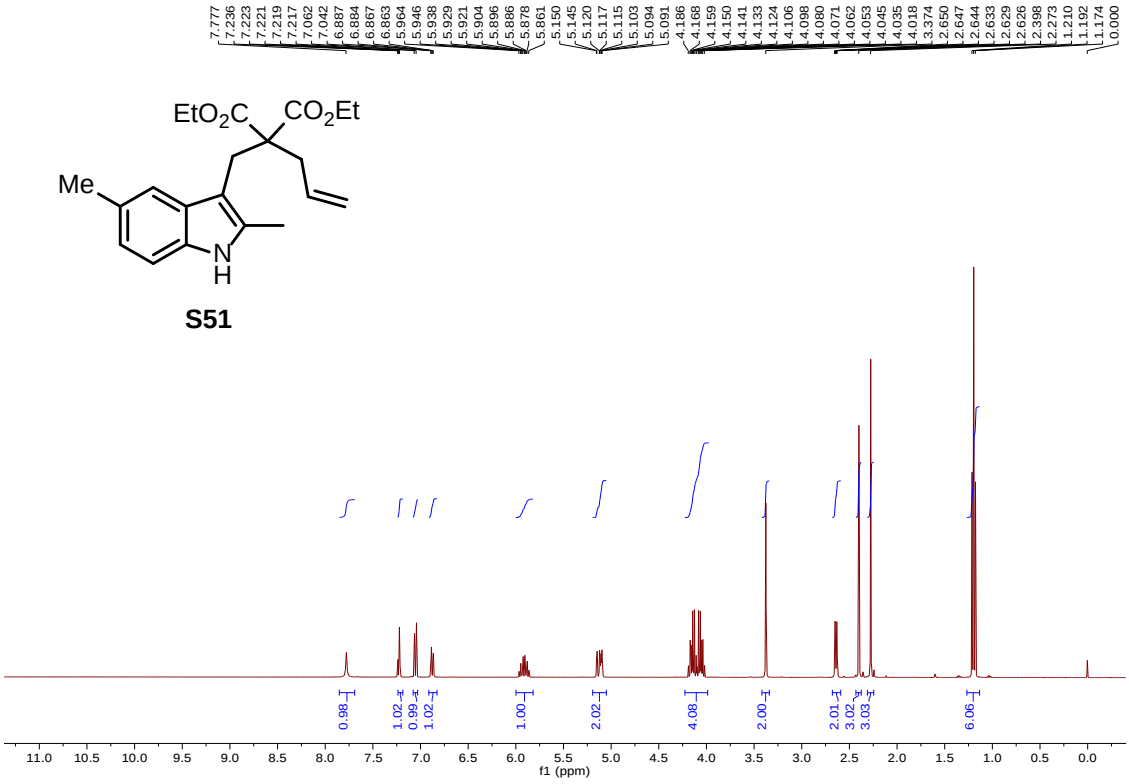

S51

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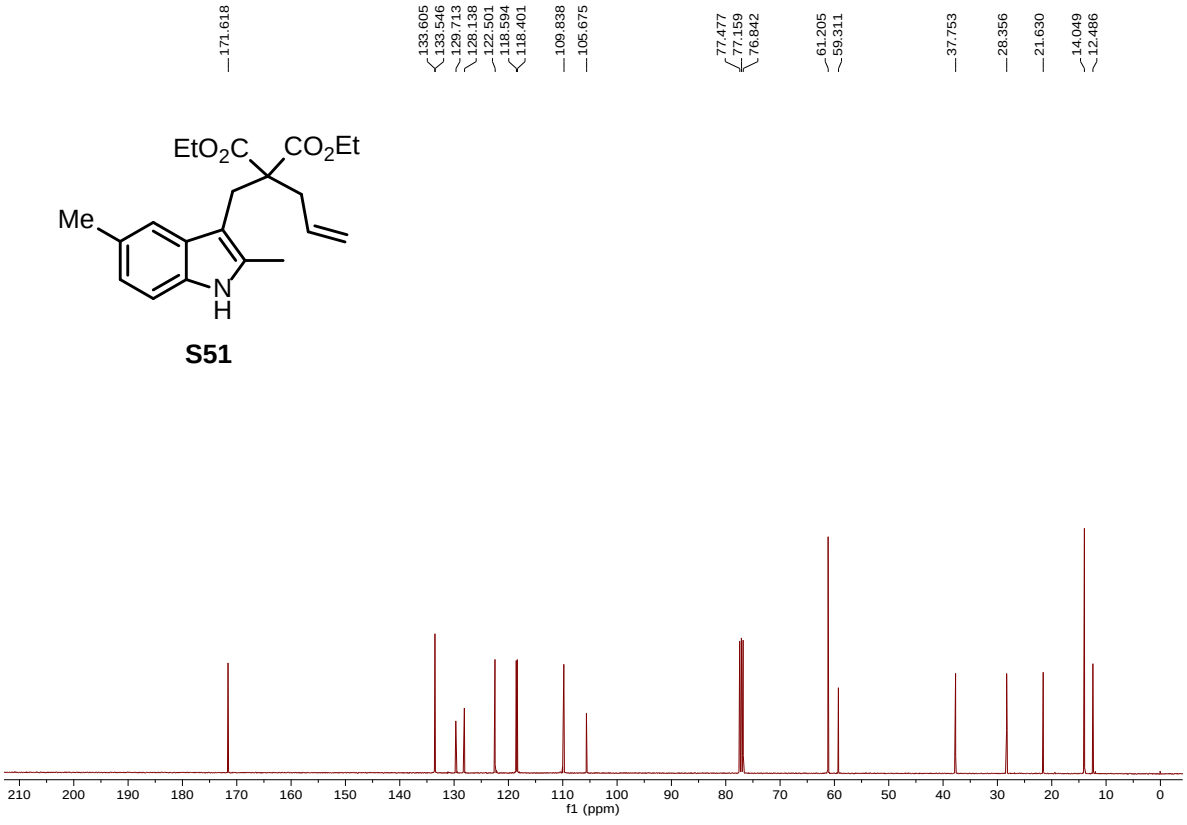
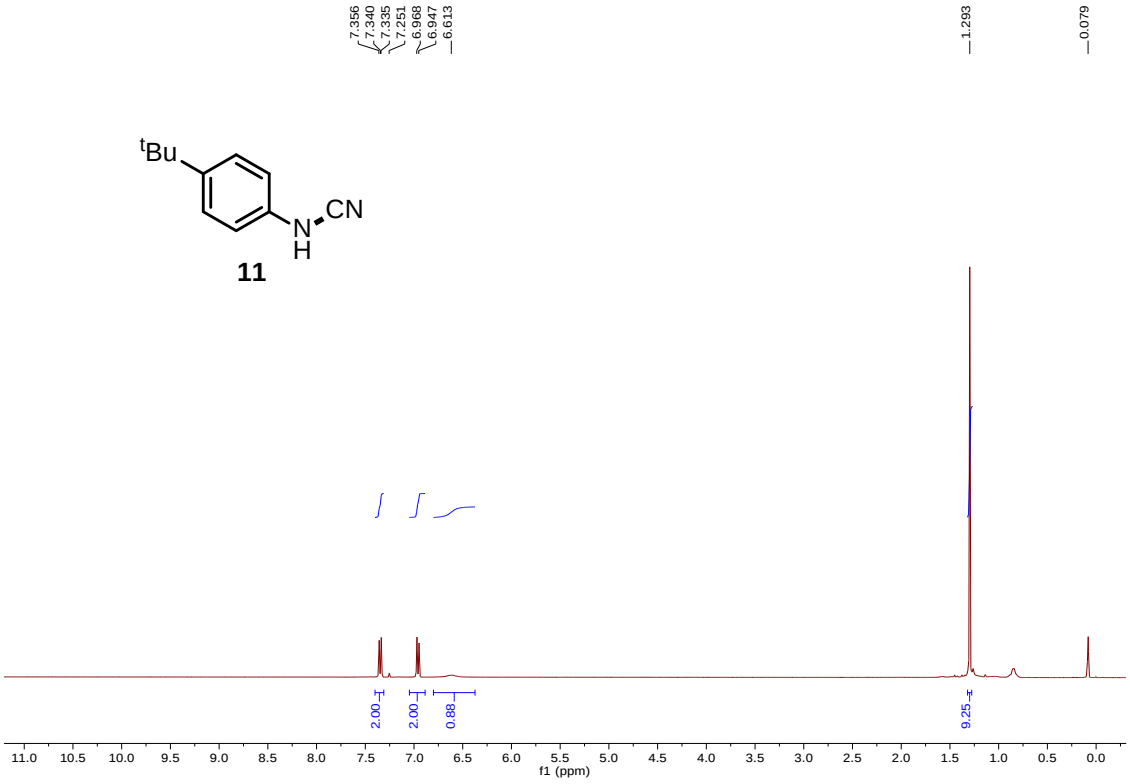
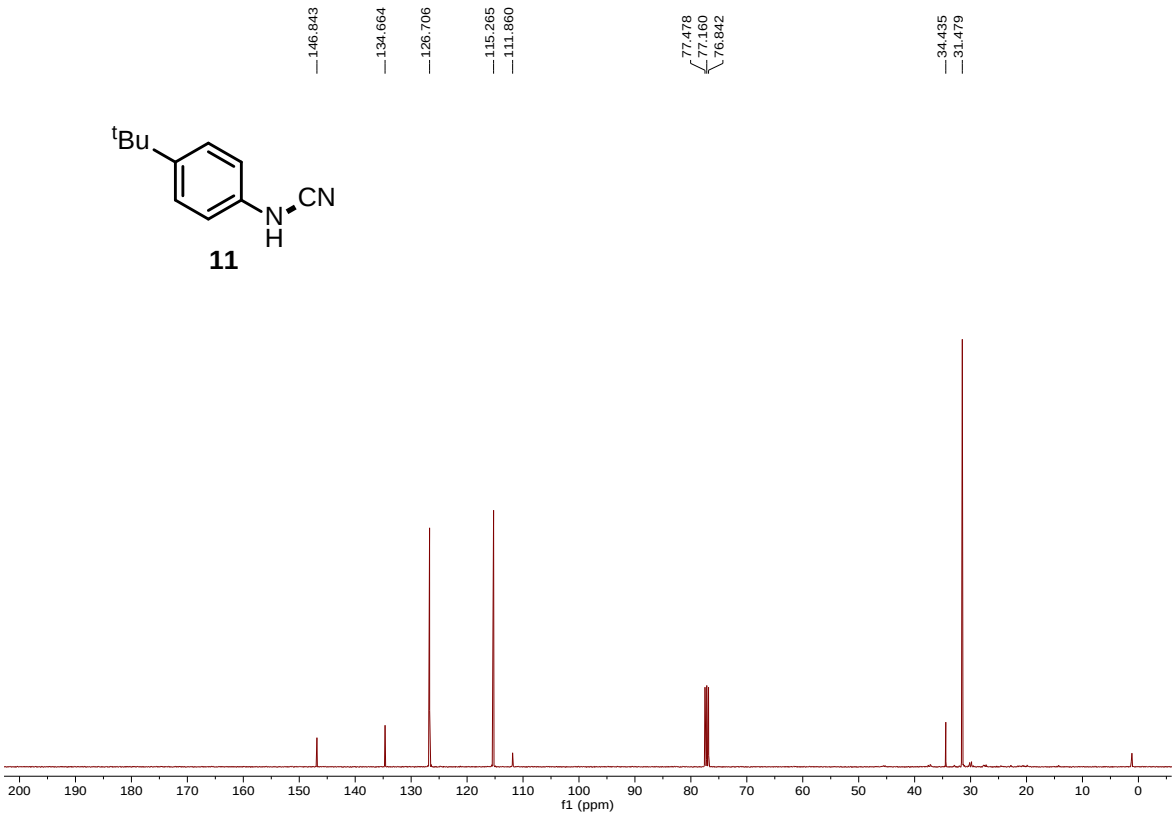


S51

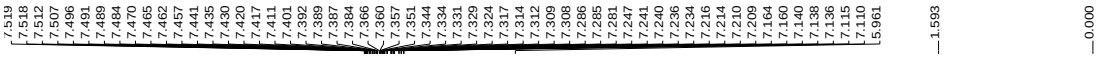
^{1}H NMR (400 MHz, Chloroform-*d*)

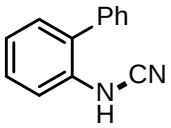


^{13}C NMR (101 MHz, Chloroform-*d*)



^{1}H NMR (300 MHz, Chloroform-*d*)





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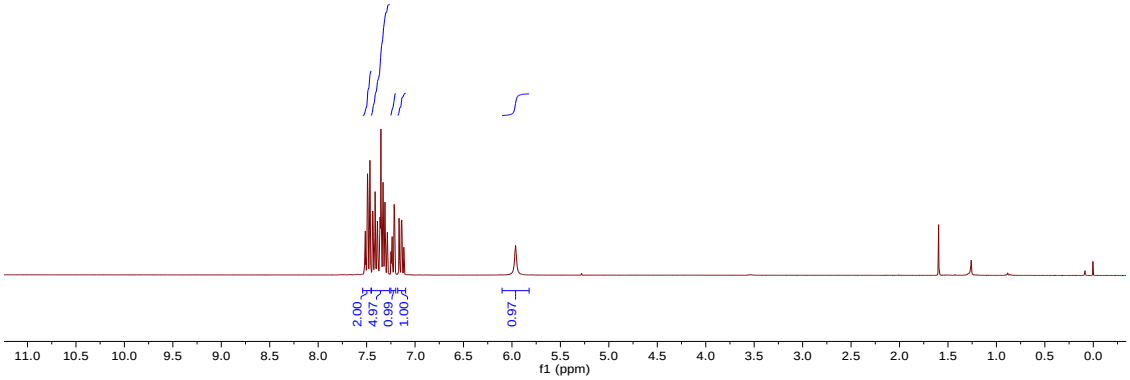
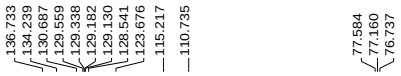
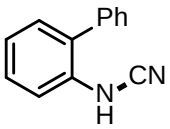


^{13}C NMR (75 MHz, Chloroform-*d*)





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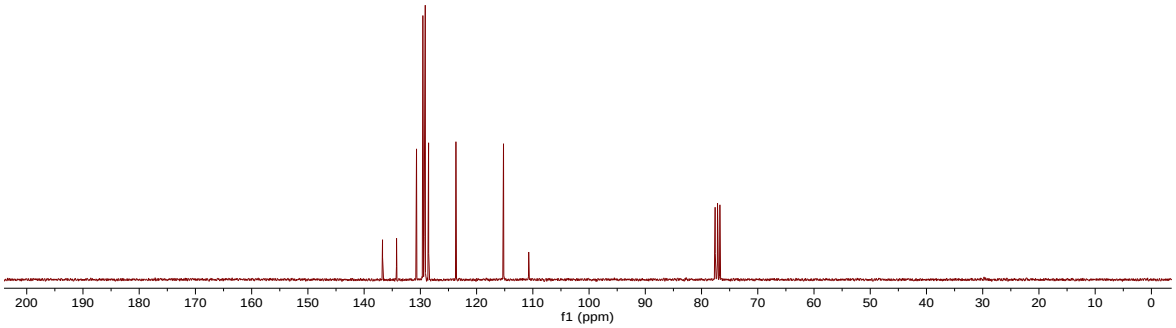
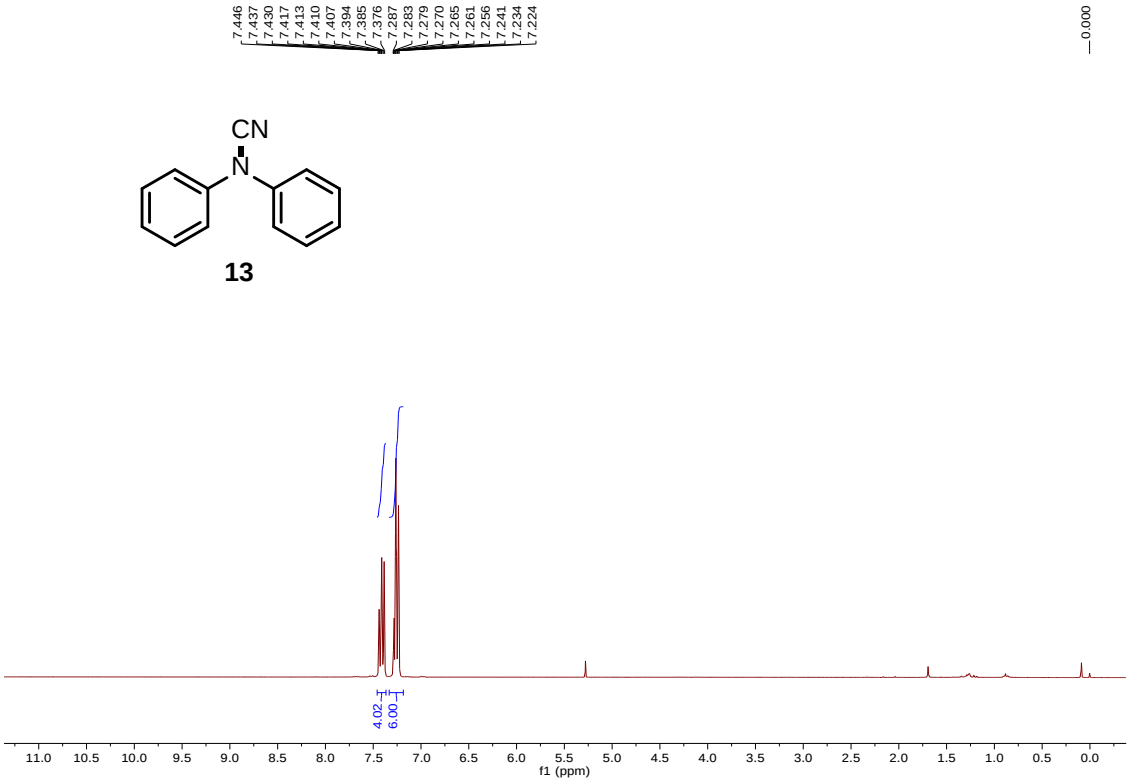
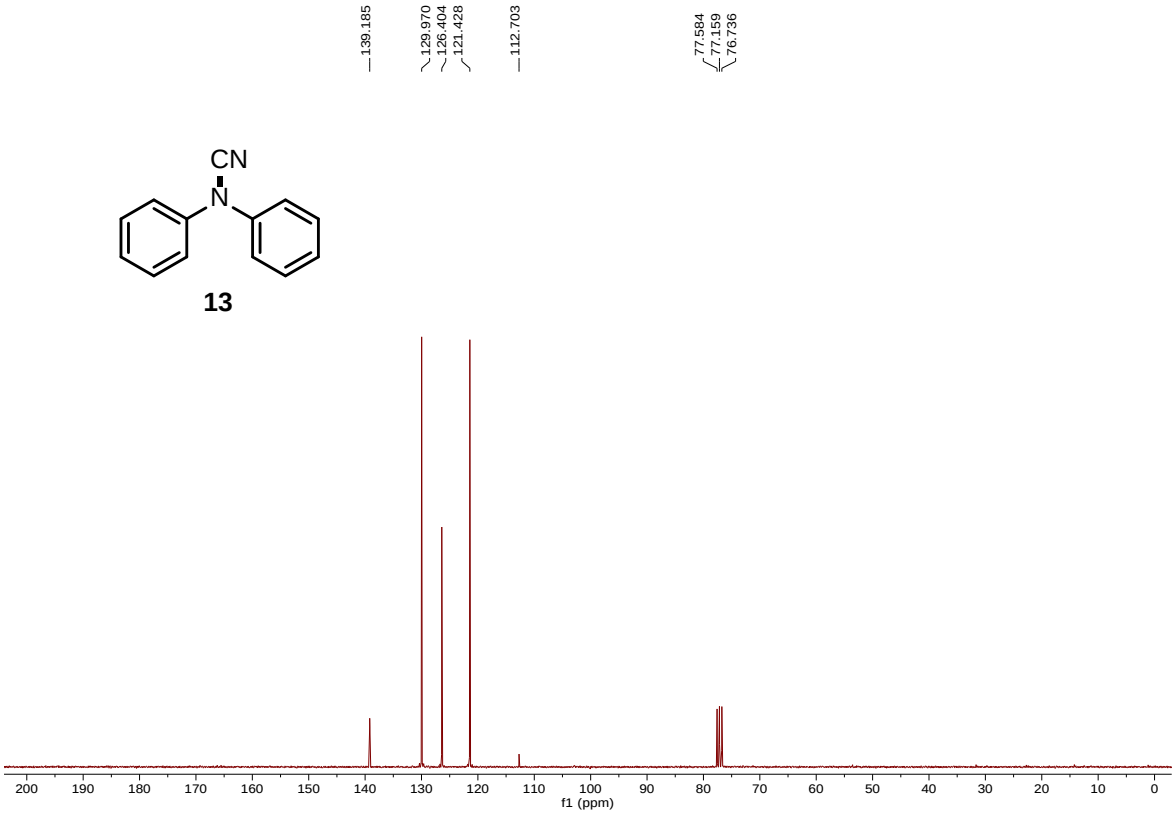


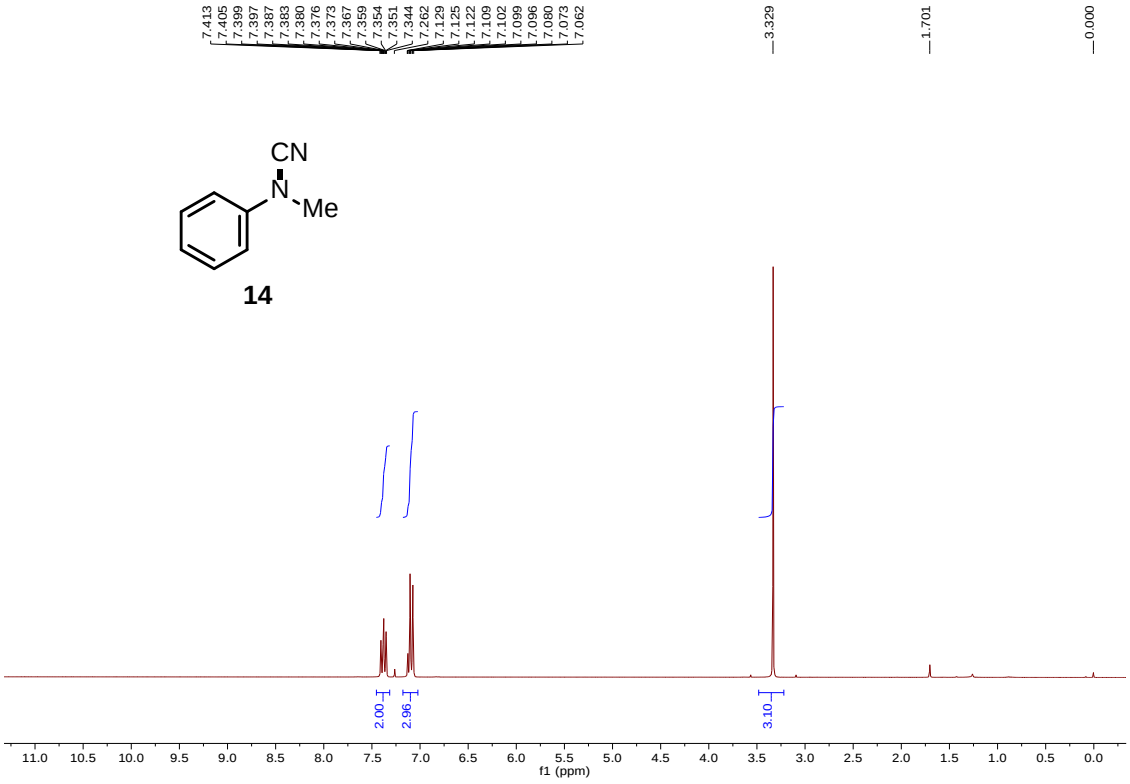
^{1}H NMR (300 MHz, Chloroform-*d*)



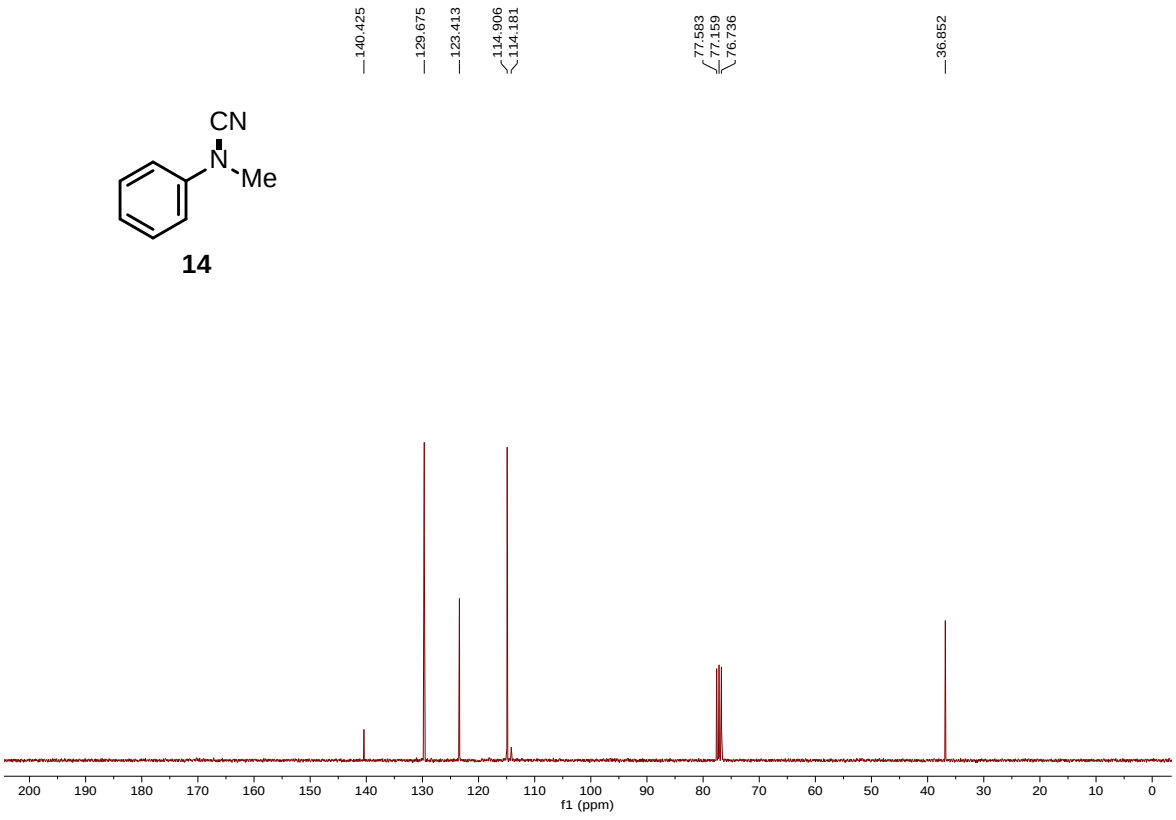
^{13}C NMR (75 MHz, Chloroform-*d*)



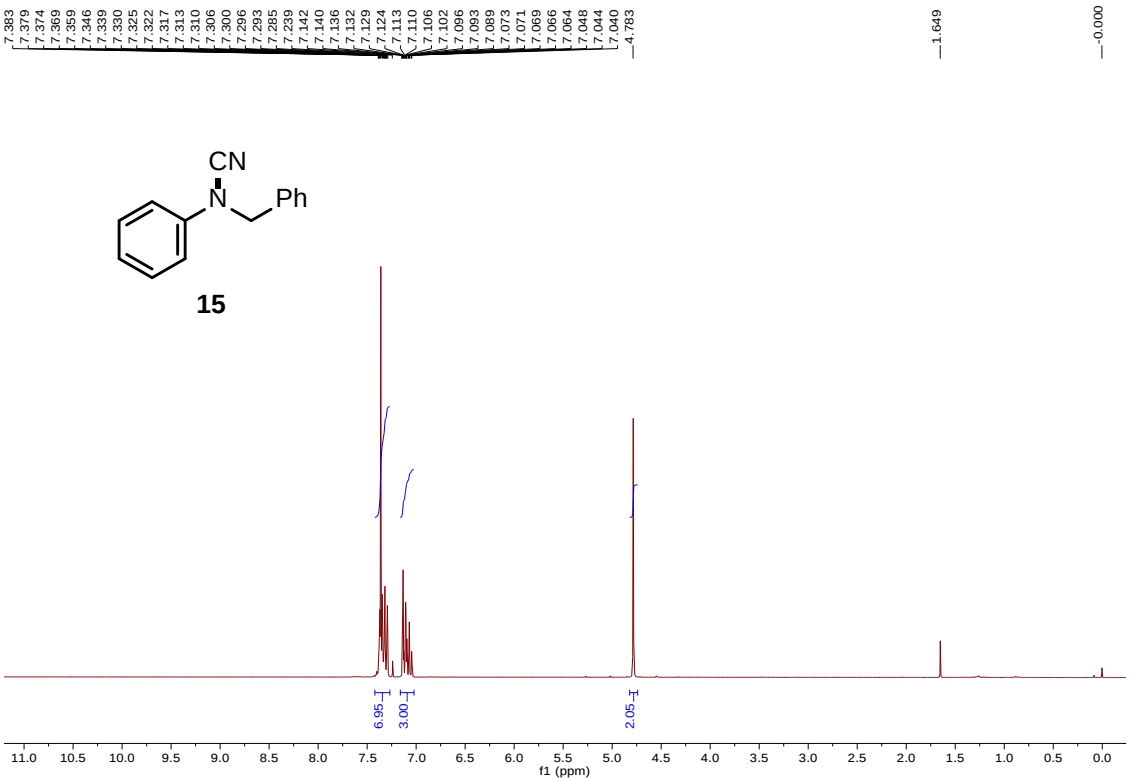
^{1}H NMR (300 MHz, Chloroform-d)



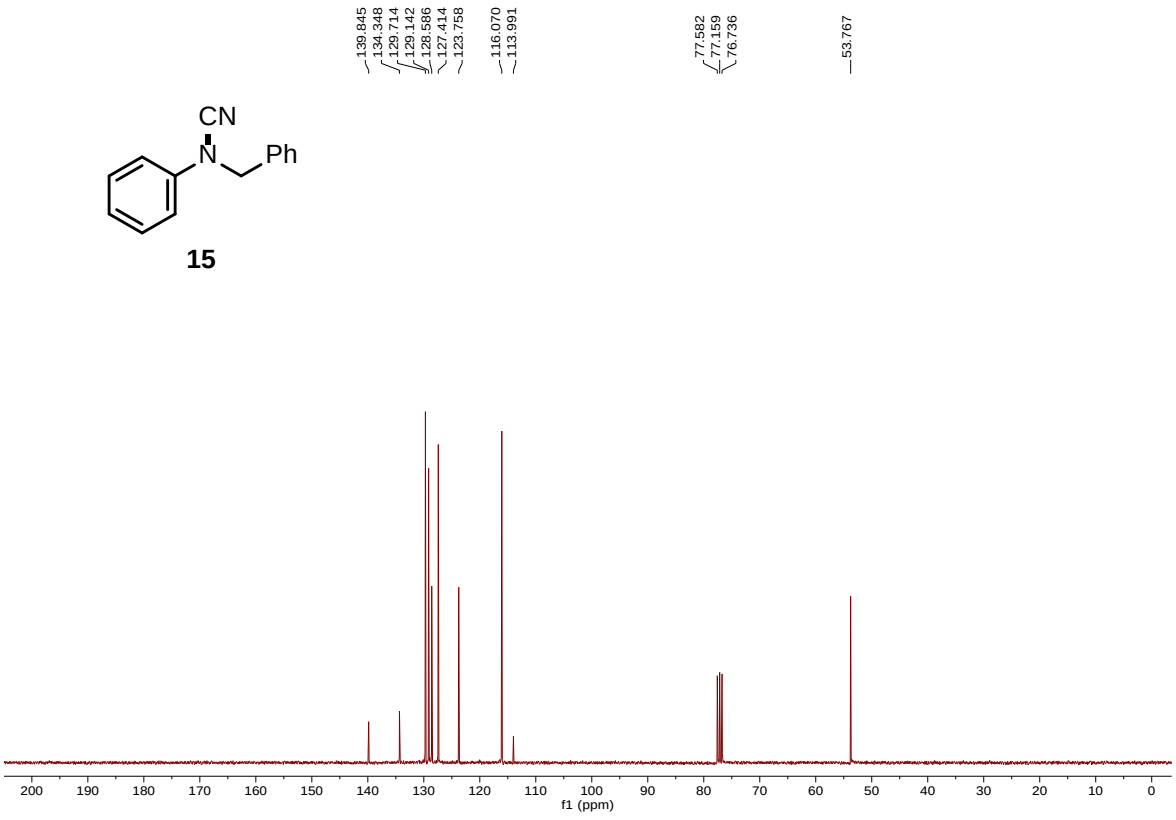
^{13}C NMR (75 MHz, Chloroform-d)



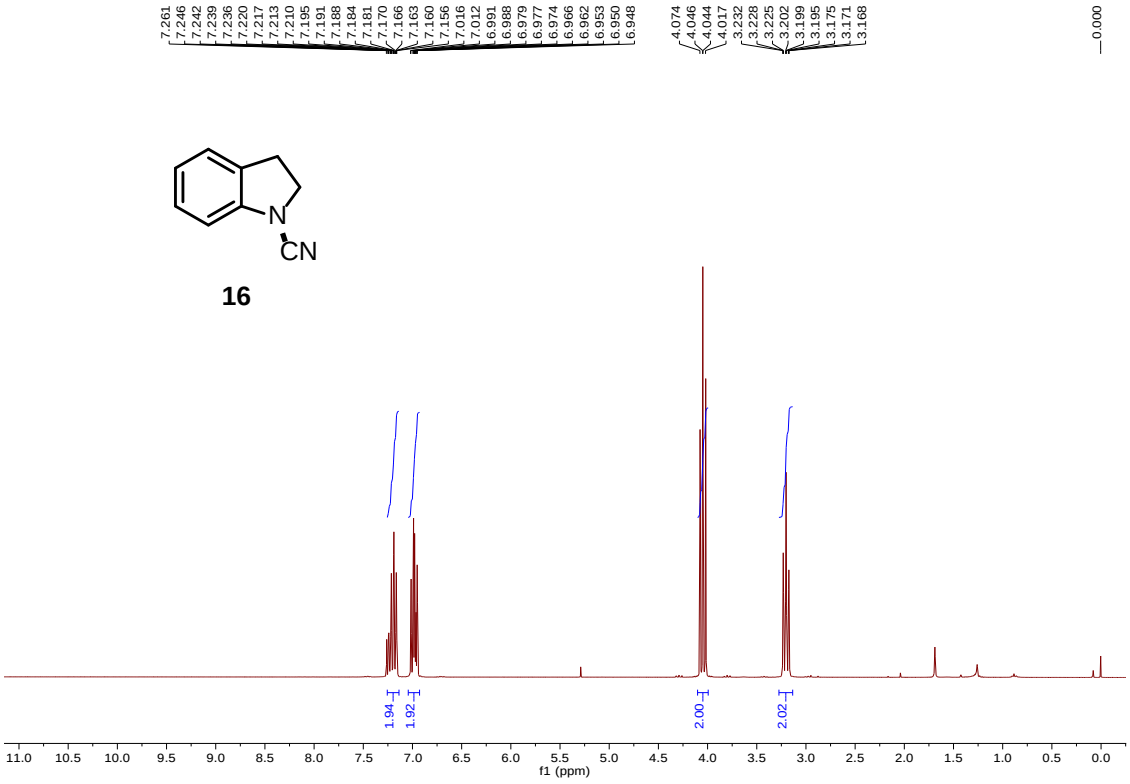
^{1}H NMR (300 MHz, Chloroform-*d*)



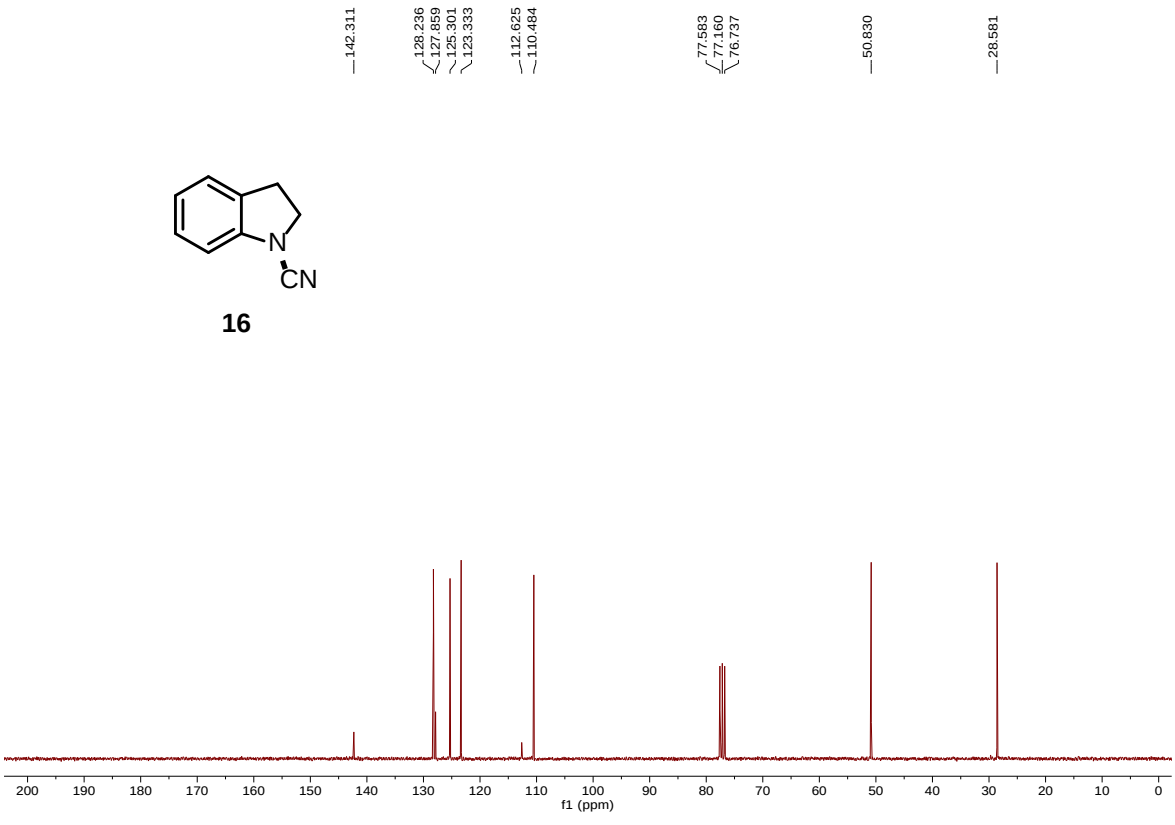
^{13}C NMR (75 MHz, Chloroform-*d*)



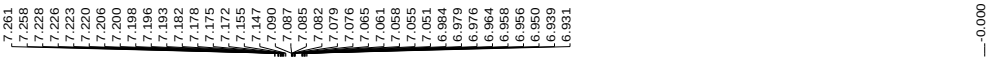
^{1}H NMR (300 MHz, Chloroform-*d*)

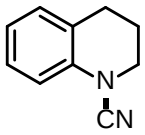


^{13}C NMR (75 MHz, Chloroform-*d*)



^{1}H NMR (300 MHz, Chloroform-*d*)





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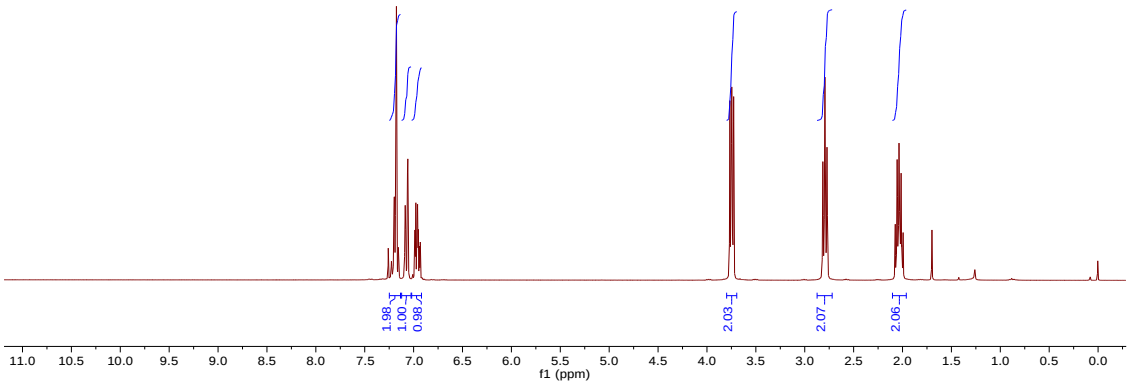
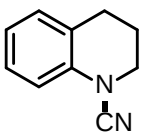


^{13}C NMR (75 MHz, Chloroform-*d*)



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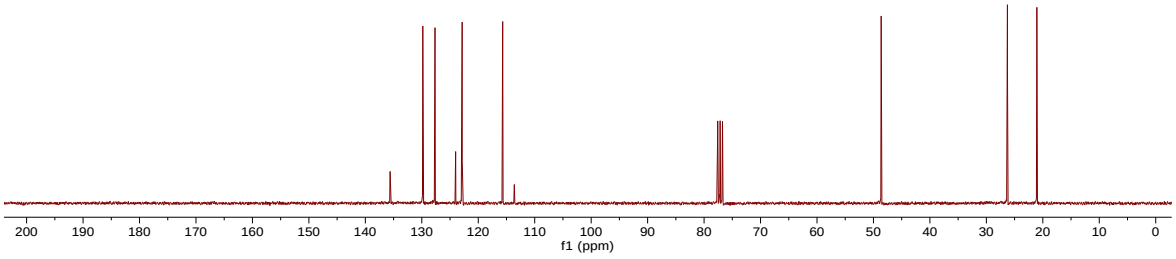
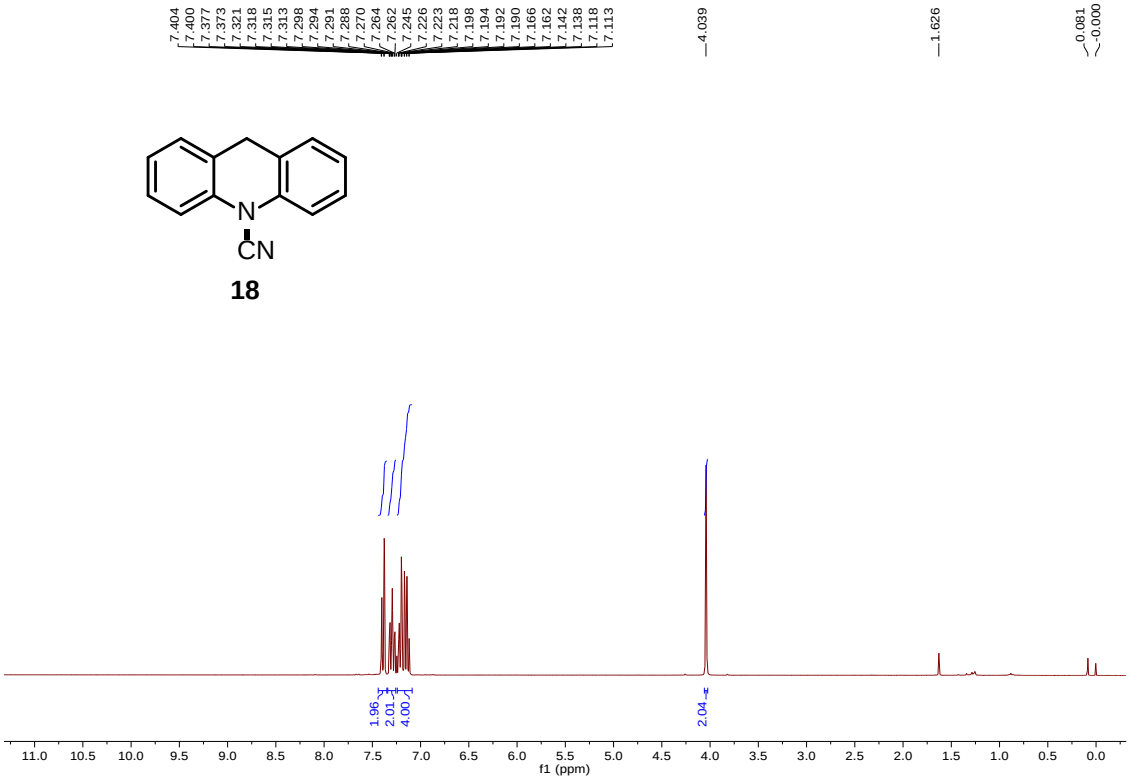
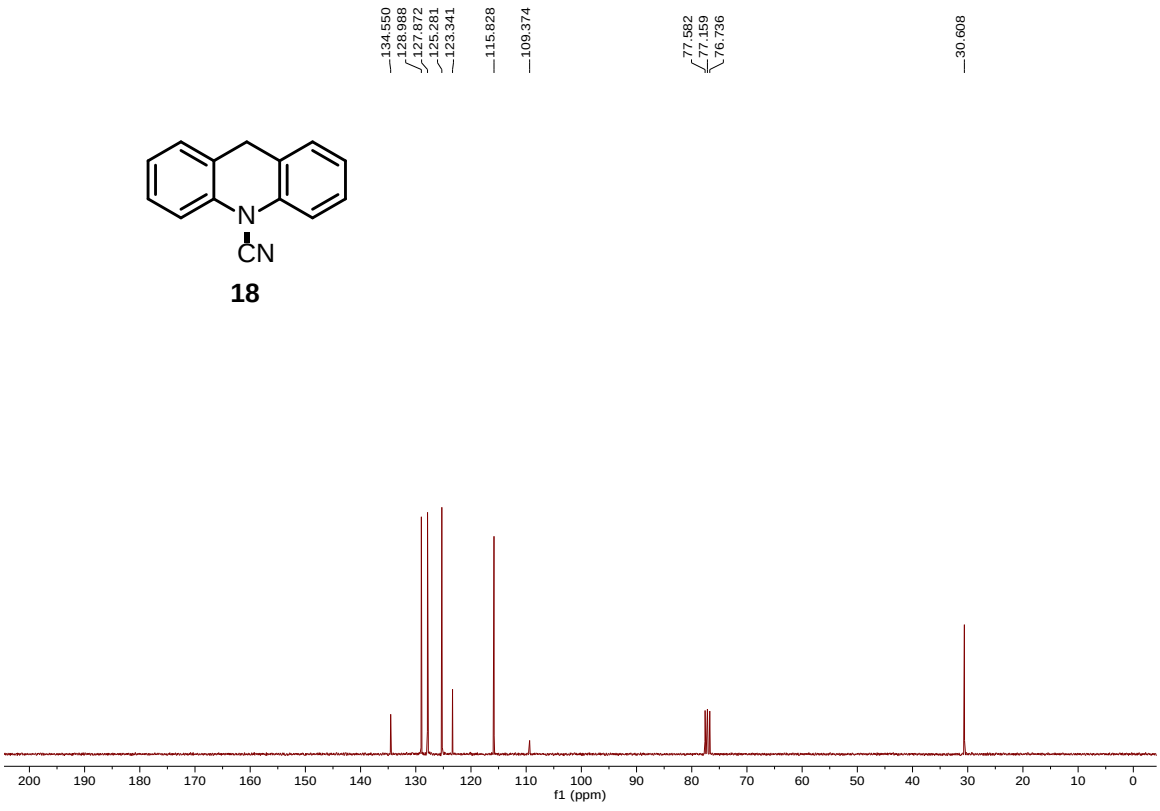


^{1}H NMR (300 MHz, Chloroform-*d*)



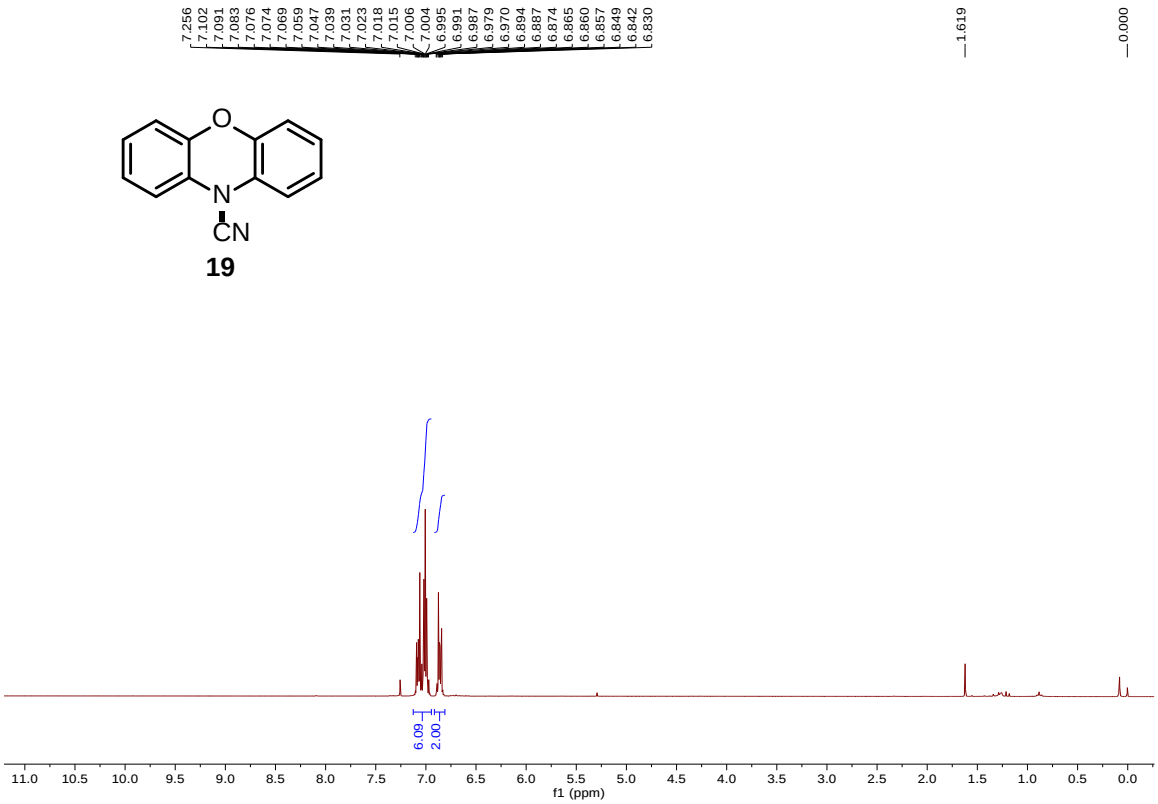
18

^{13}C NMR (75 MHz, Chloroform-*d*)

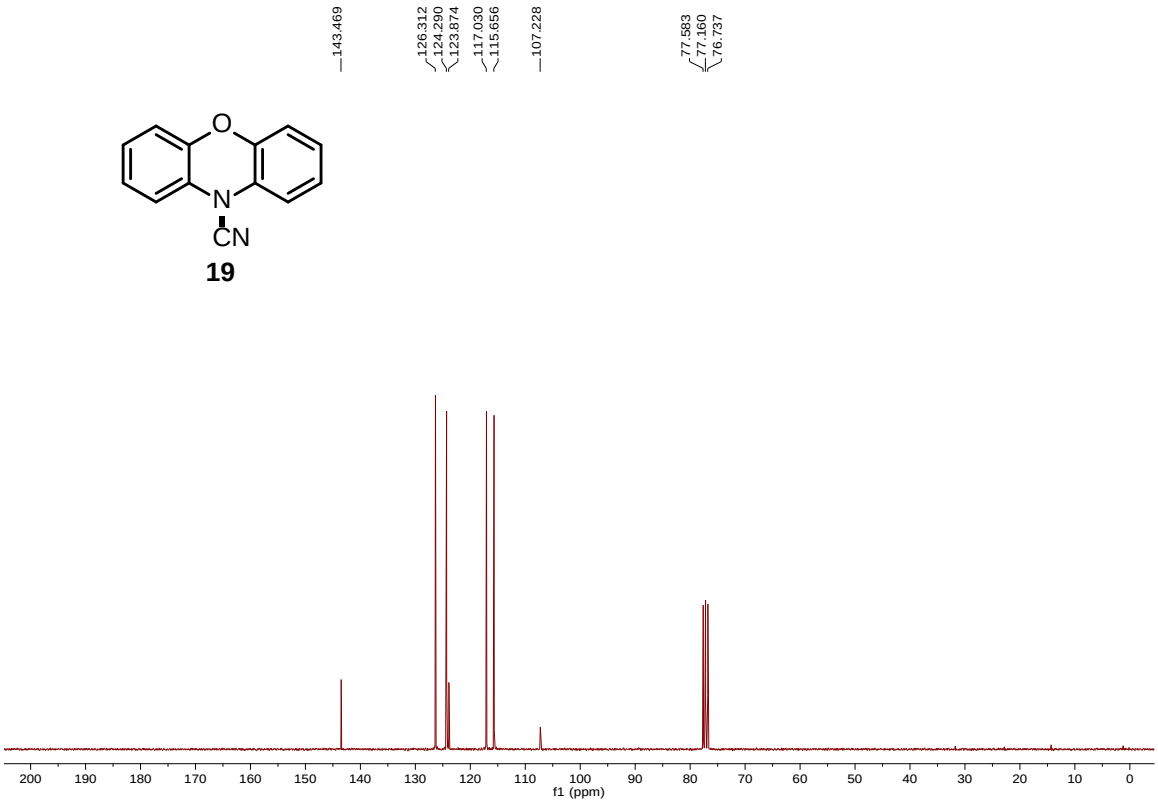


18

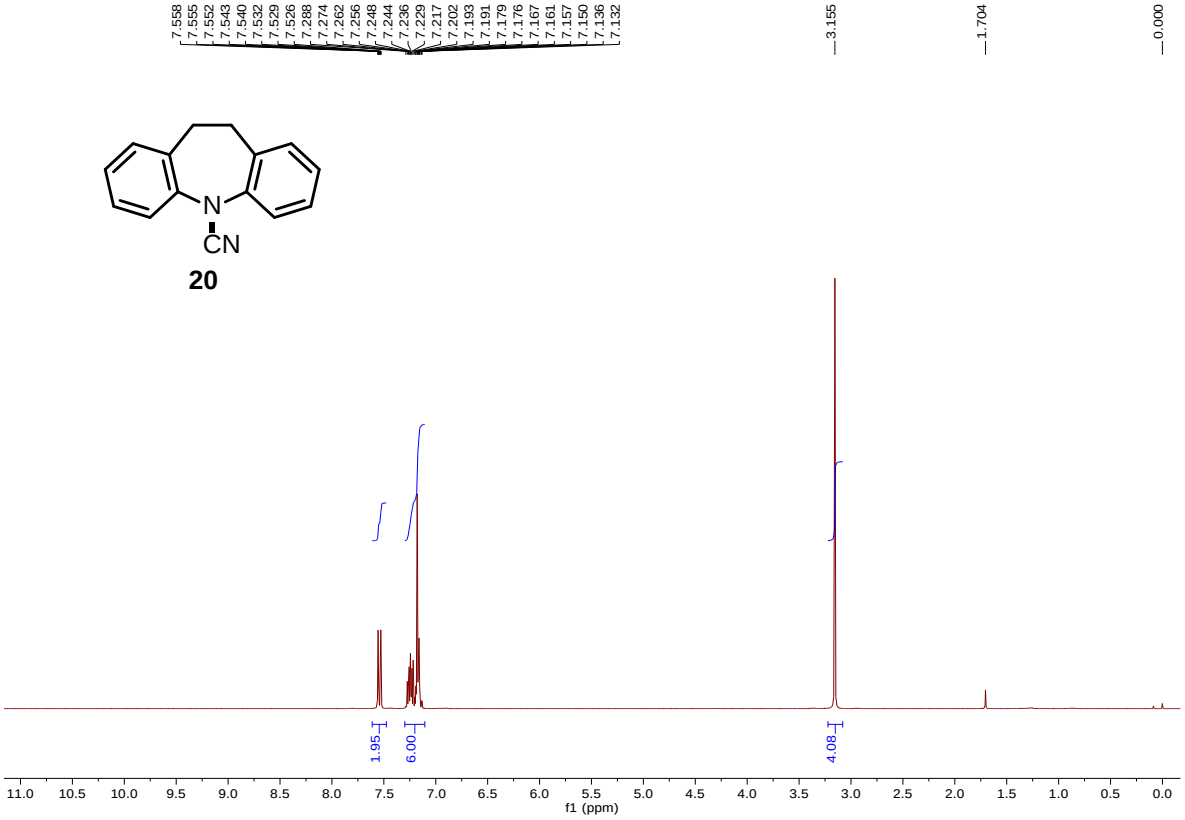
^{1}H NMR (300 MHz, Chloroform-*d*)



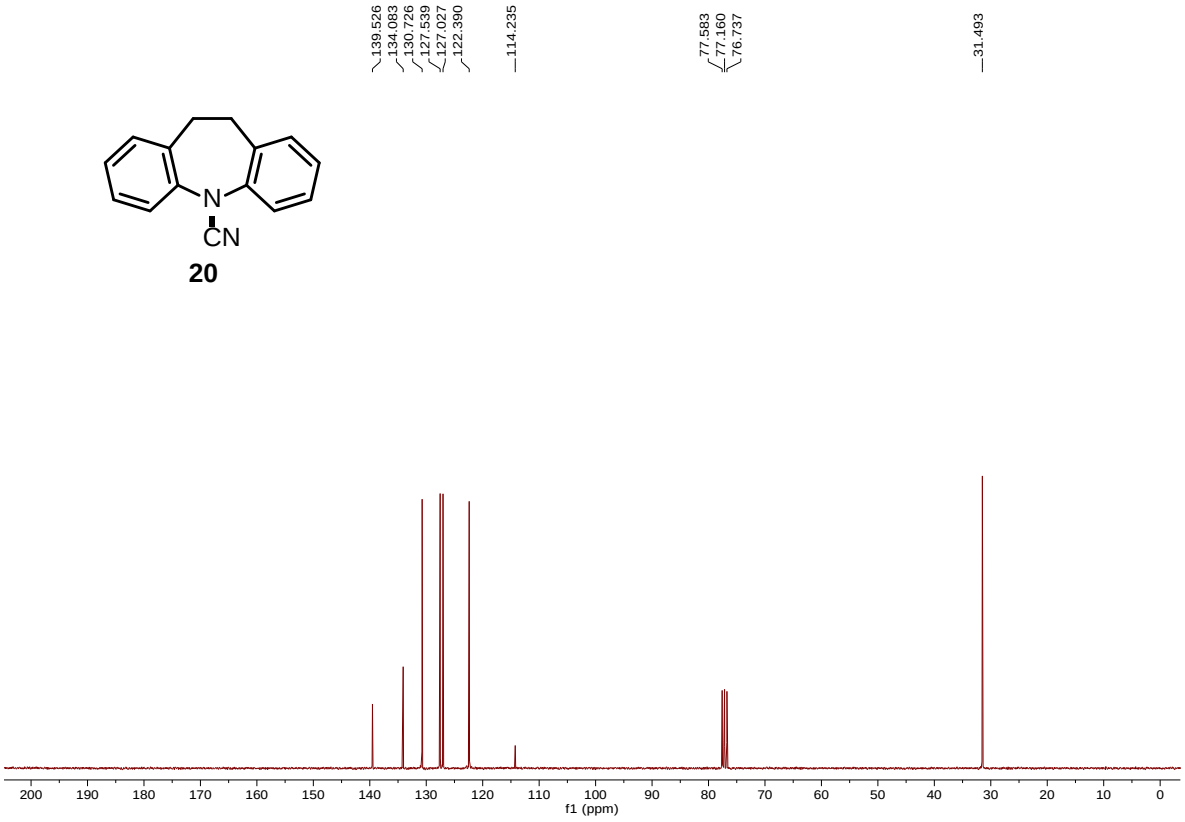
^{13}C NMR (75 MHz, Chloroform-*d*)



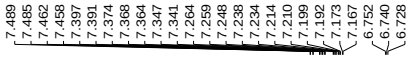
^{1}H NMR (300 MHz, Chloroform-*d*)

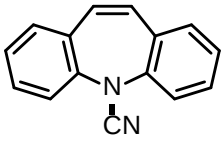


^{13}C NMR (75 MHz, Chloroform-*d*)



^{1}H NMR (300 MHz, Chloroform-*d*)





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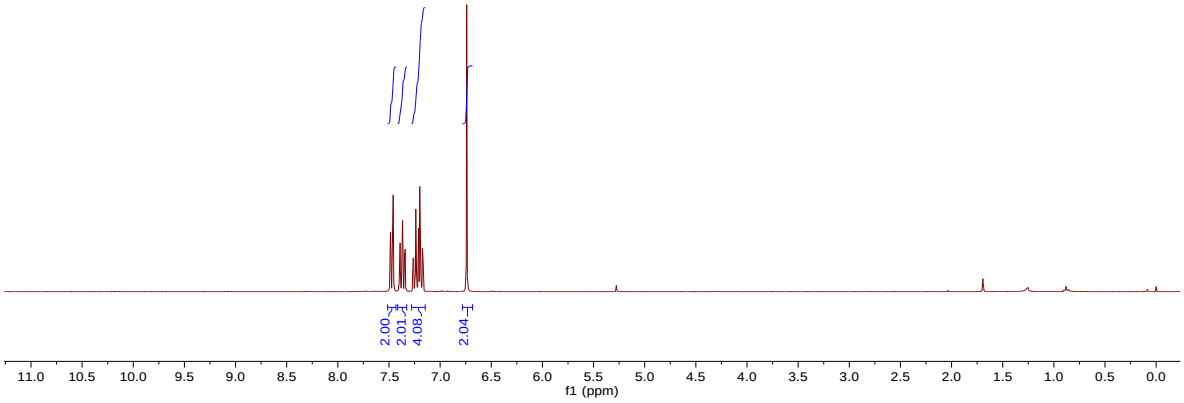
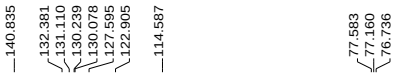
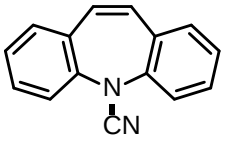


^{13}C NMR (75 MHz, Chloroform-*d*)





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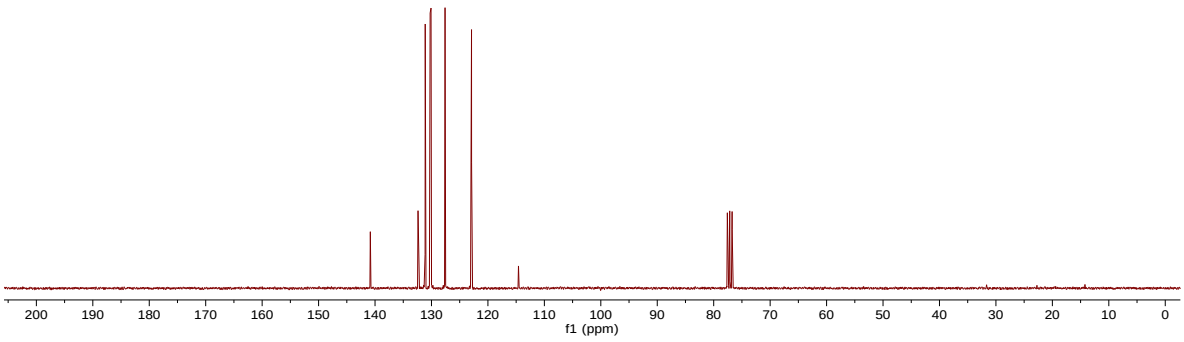
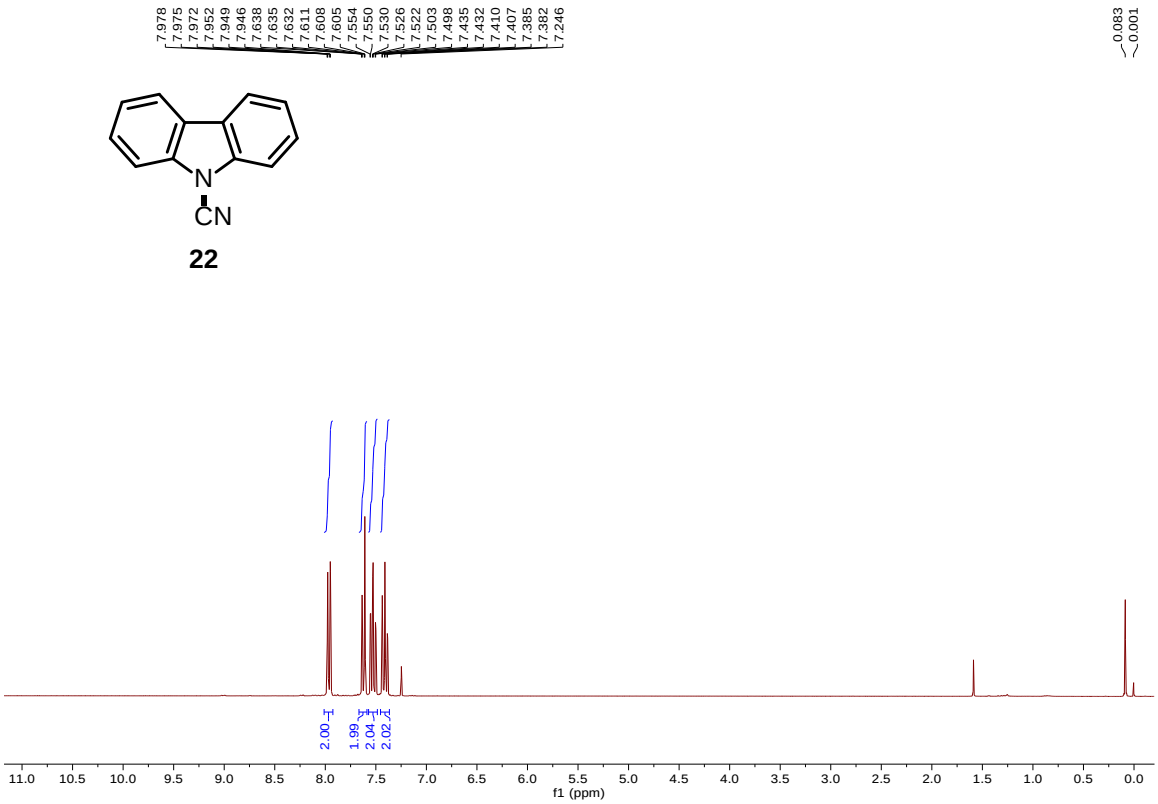
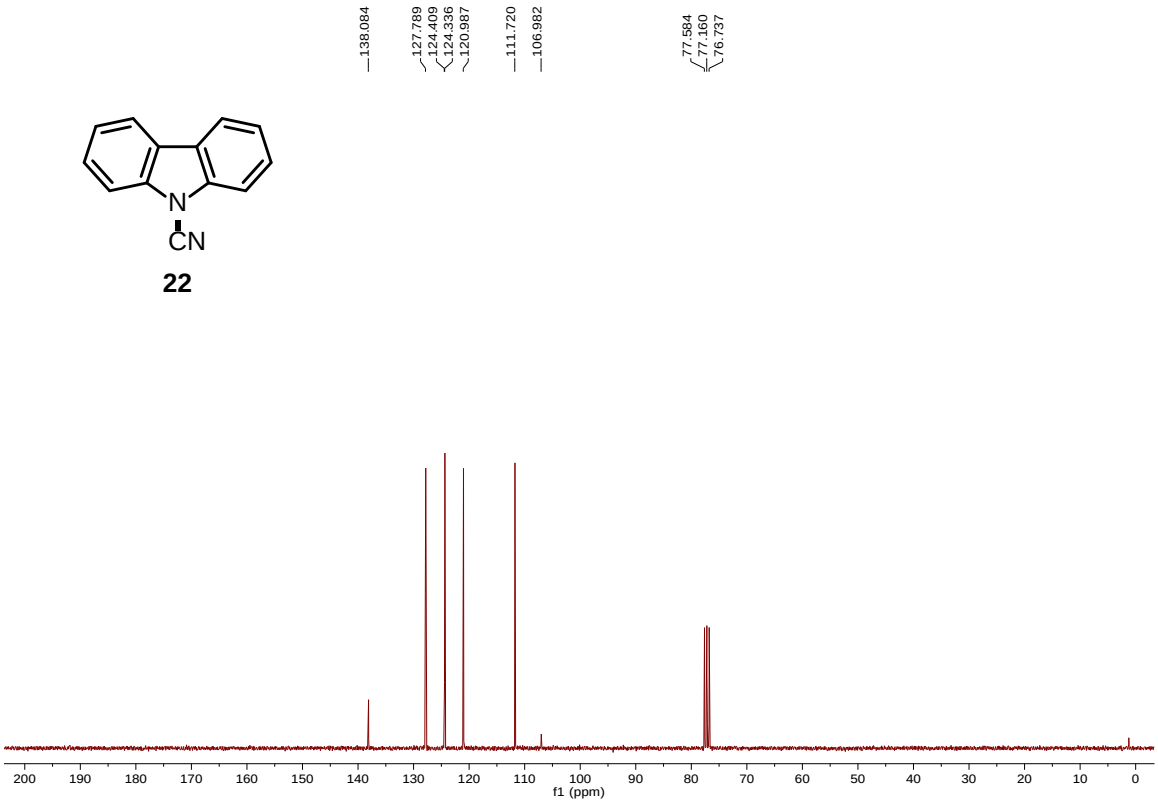


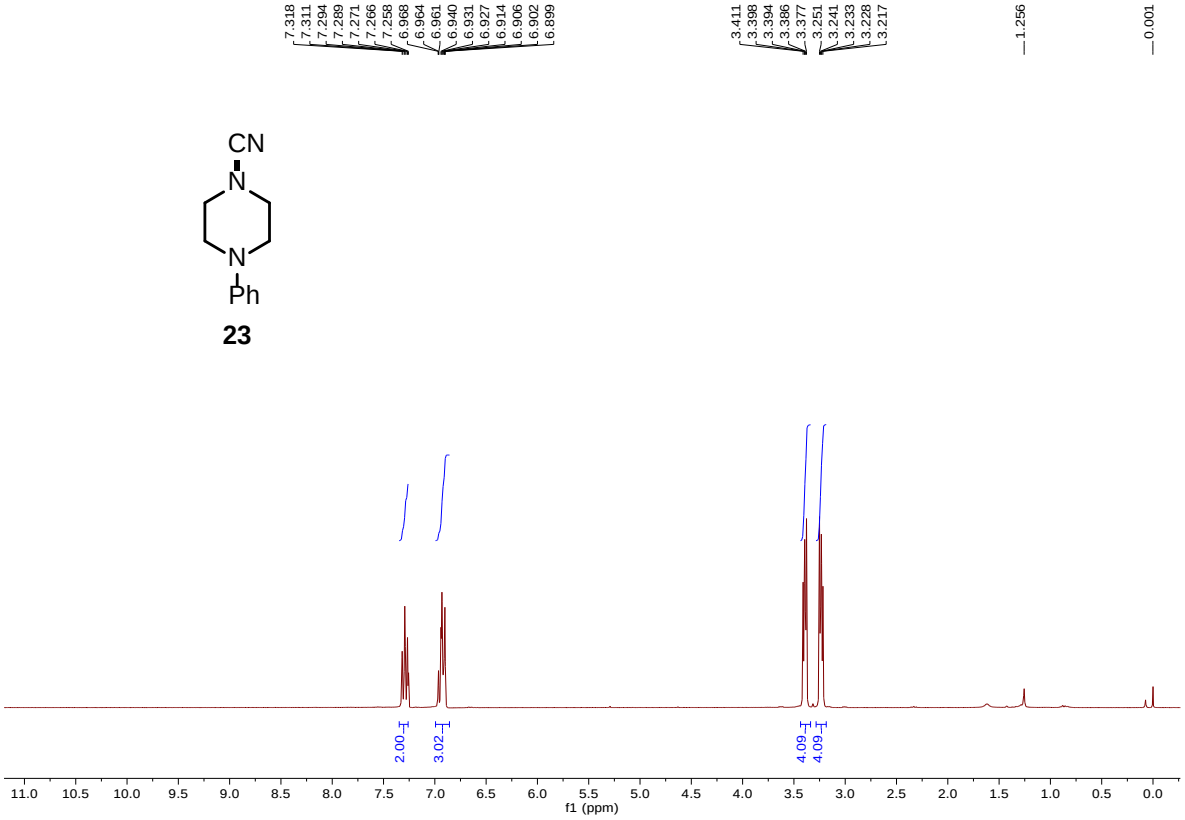
^{1}H NMR (300 MHz, Chloroform-*d*)



^{13}C NMR (75 MHz, Chloroform-*d*)

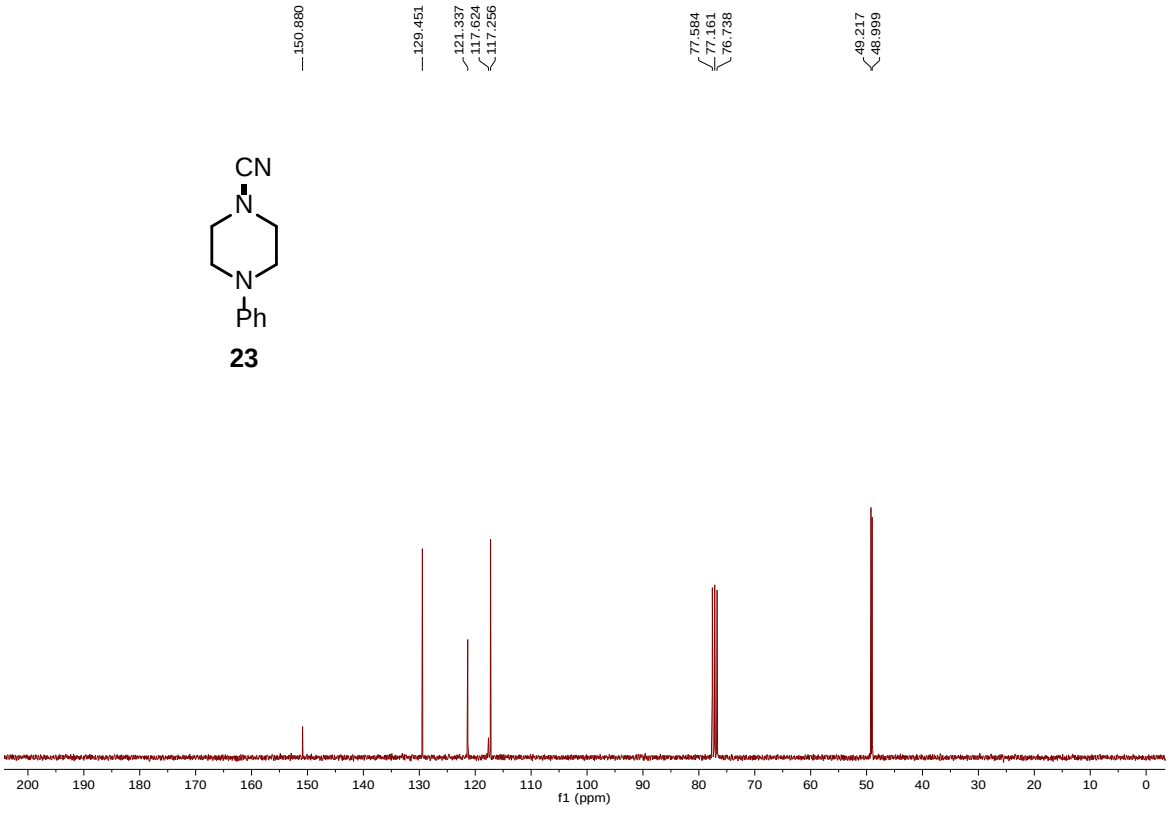


^{1}H NMR (300 MHz, Chloroform-*d*)



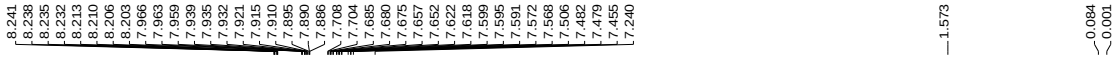
23

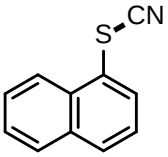
^{13}C NMR (75 MHz, Chloroform-*d*)



23

^{1}H NMR (300 MHz, Chloroform-*d*)





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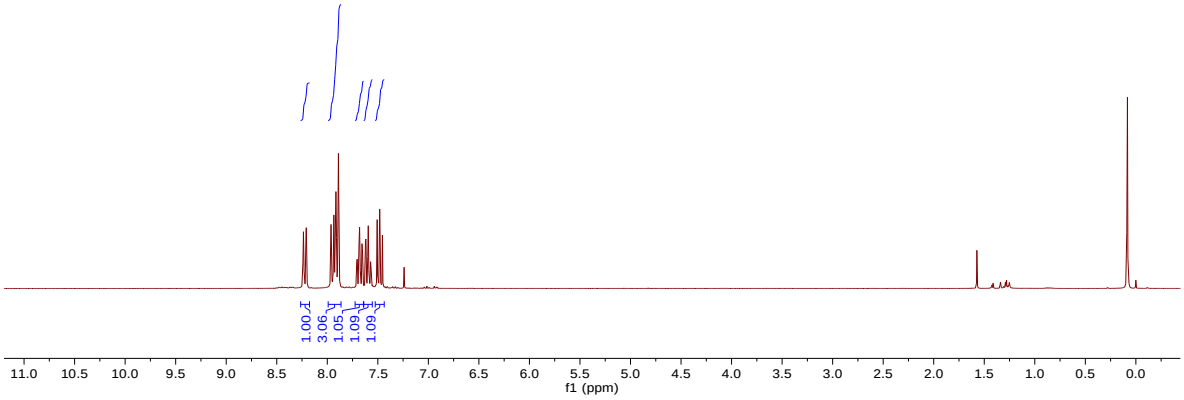
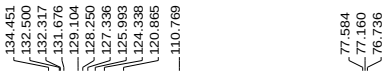
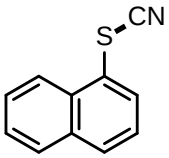


^{13}C NMR (75 MHz, Chloroform-*d*)





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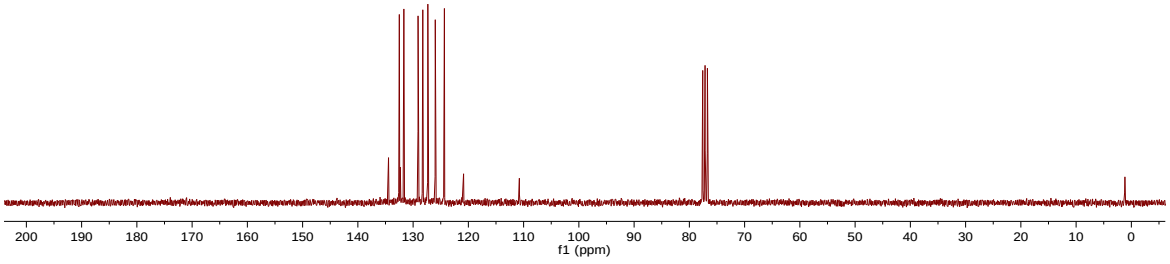
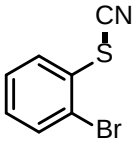


^{1}H NMR (300 MHz, Chloroform-*d*)



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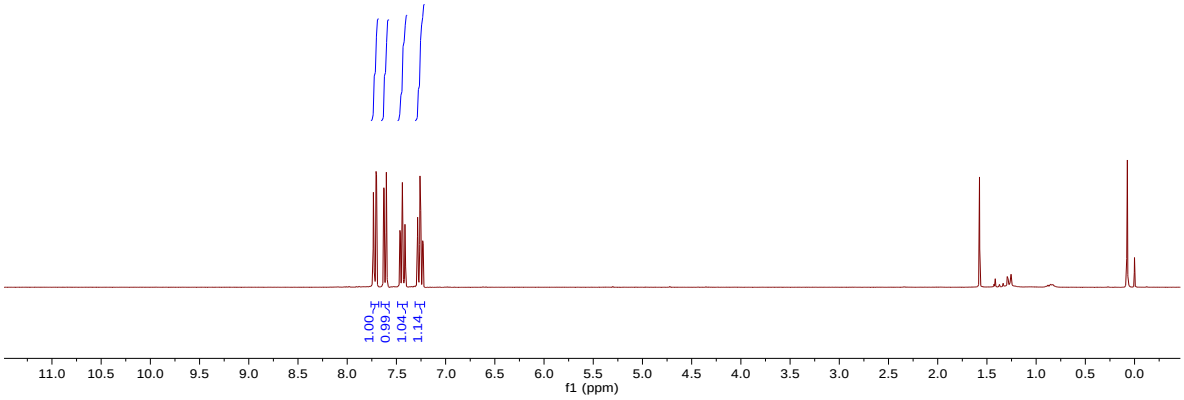
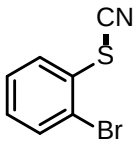


^{13}C NMR (75 MHz, Chloroform-*d*)



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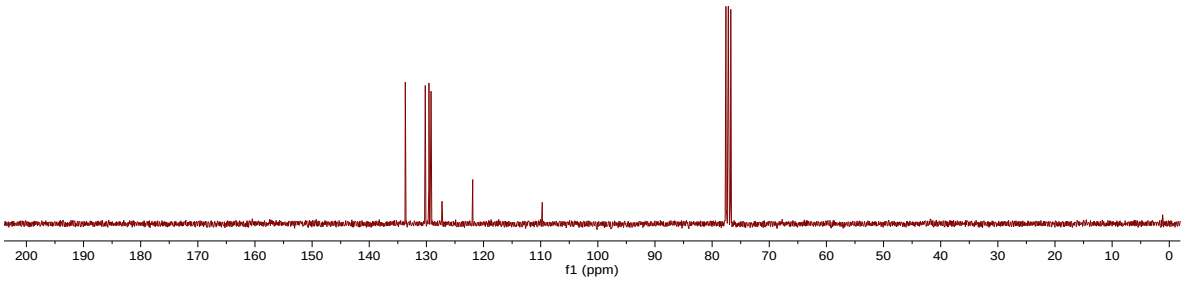
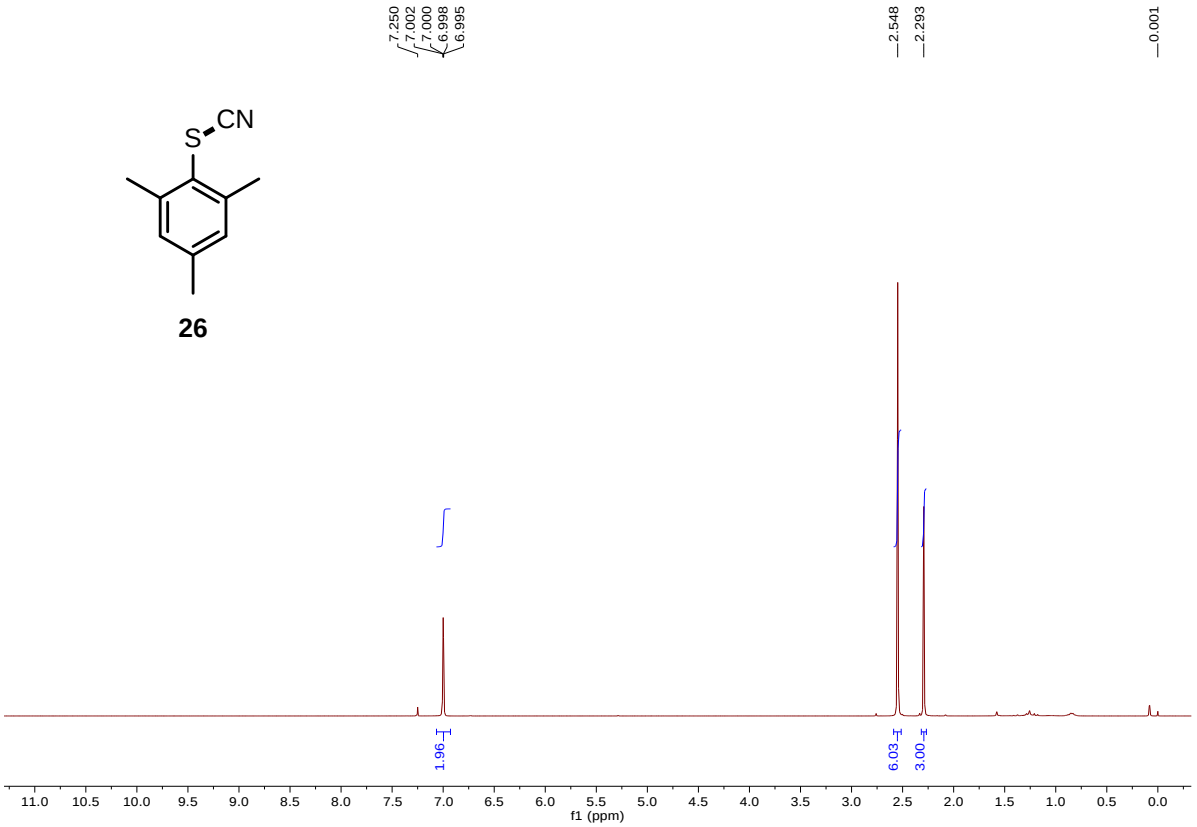
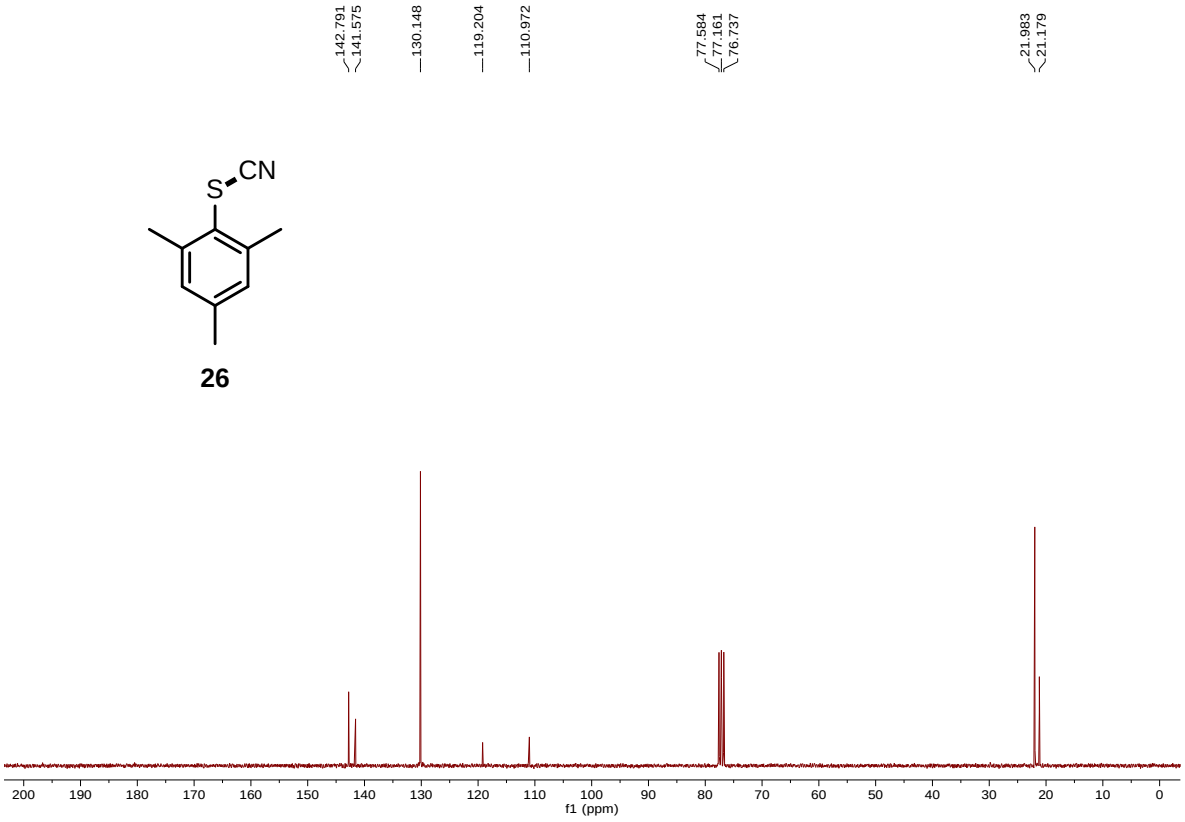


^{1}H NMR (300 MHz, Chloroform-*d*)



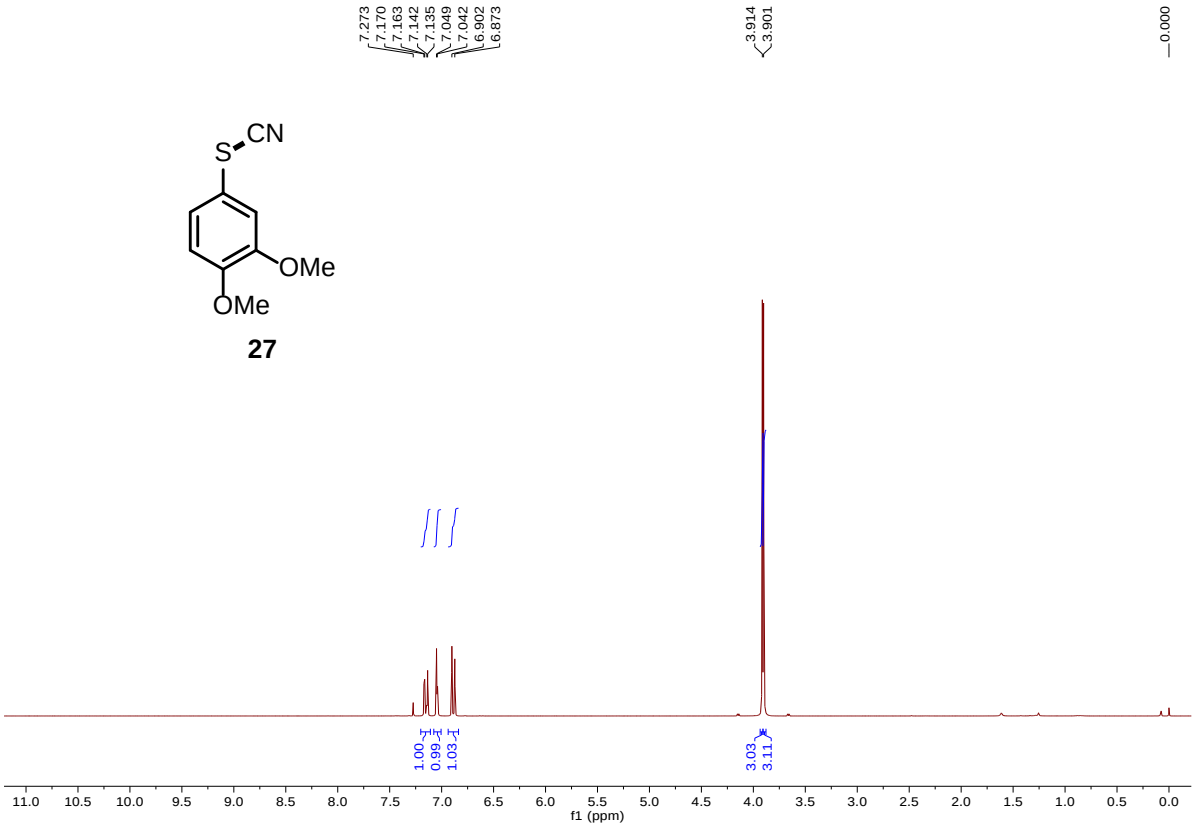
26

^{13}C NMR (75 MHz, Chloroform-*d*)



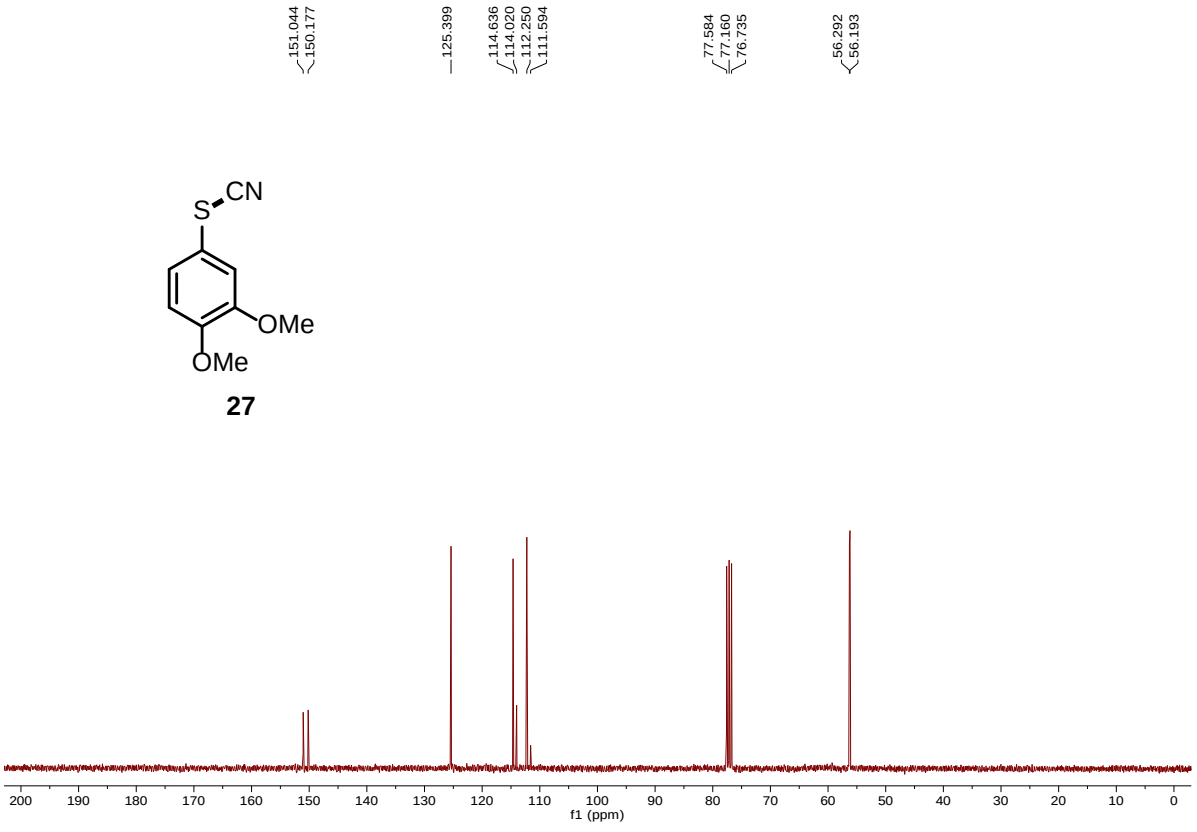
26

^{1}H NMR (300 MHz, Chloroform-*d*)



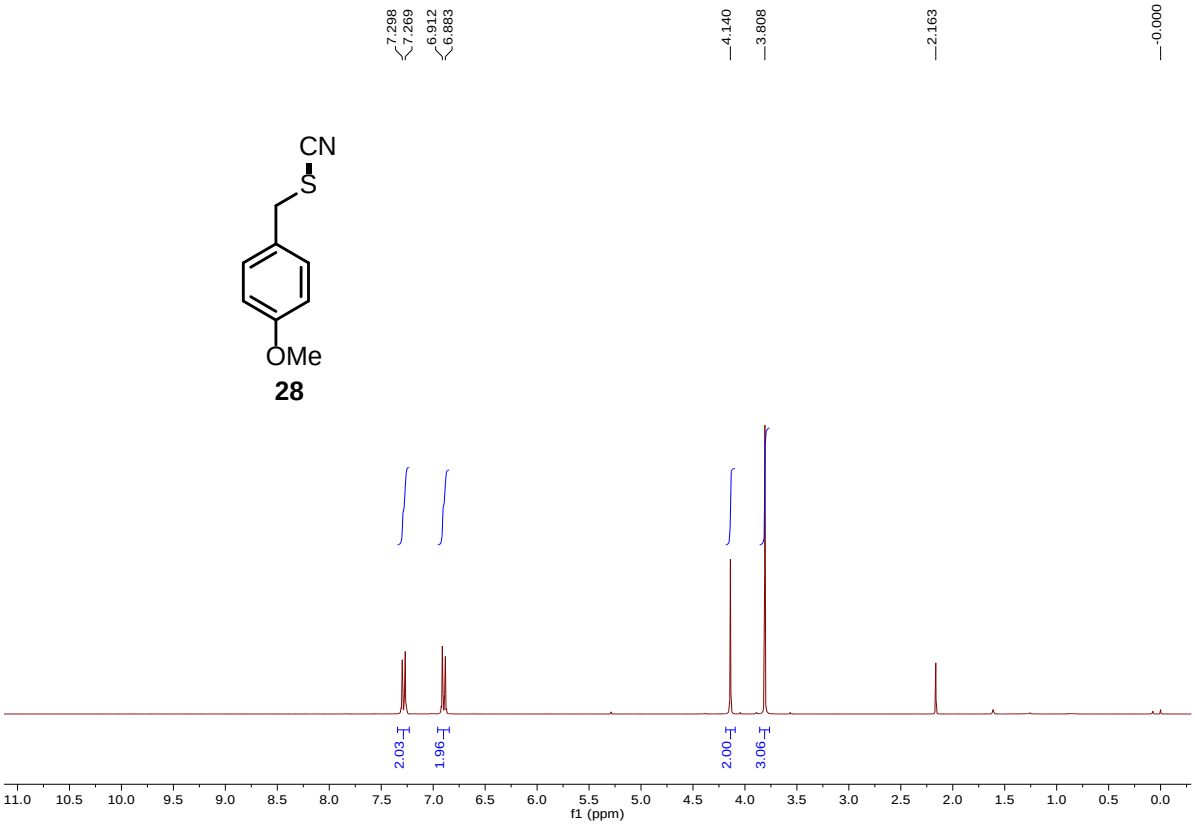
27

^{13}C NMR (75 MHz, Chloroform-*d*)

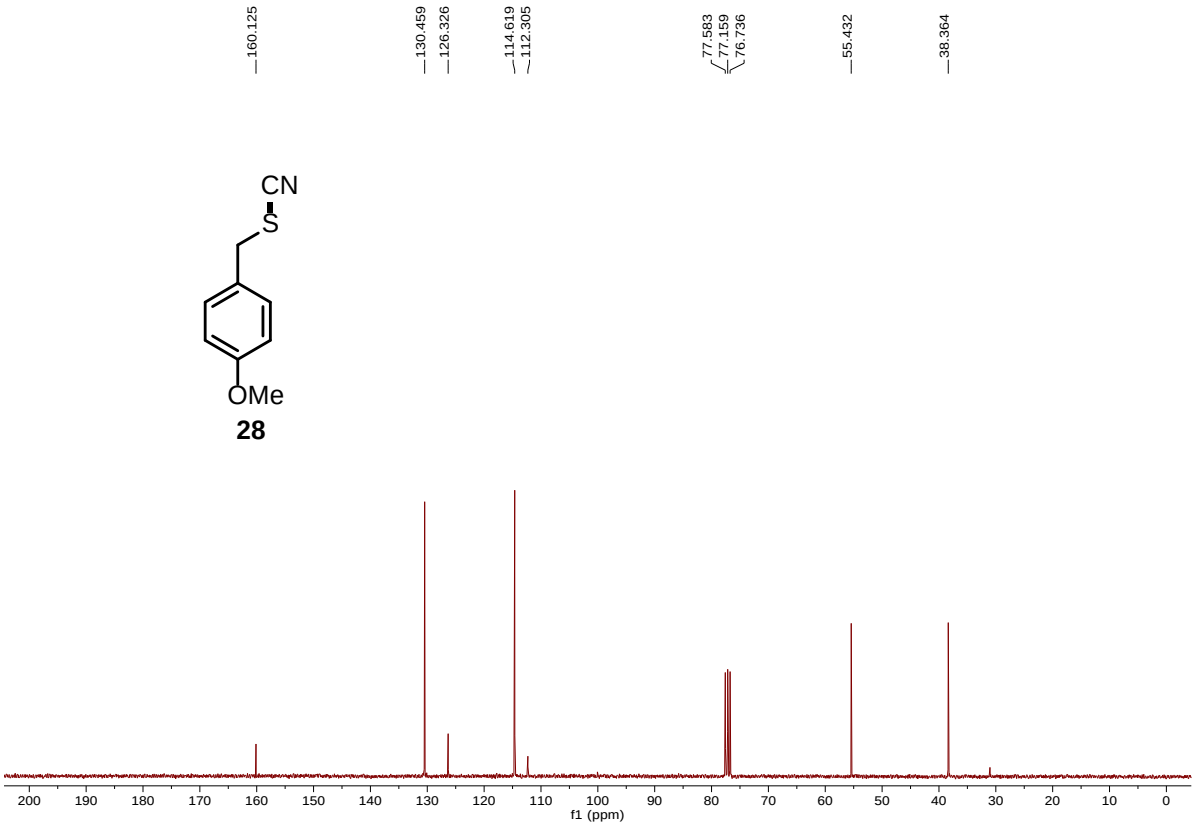


27

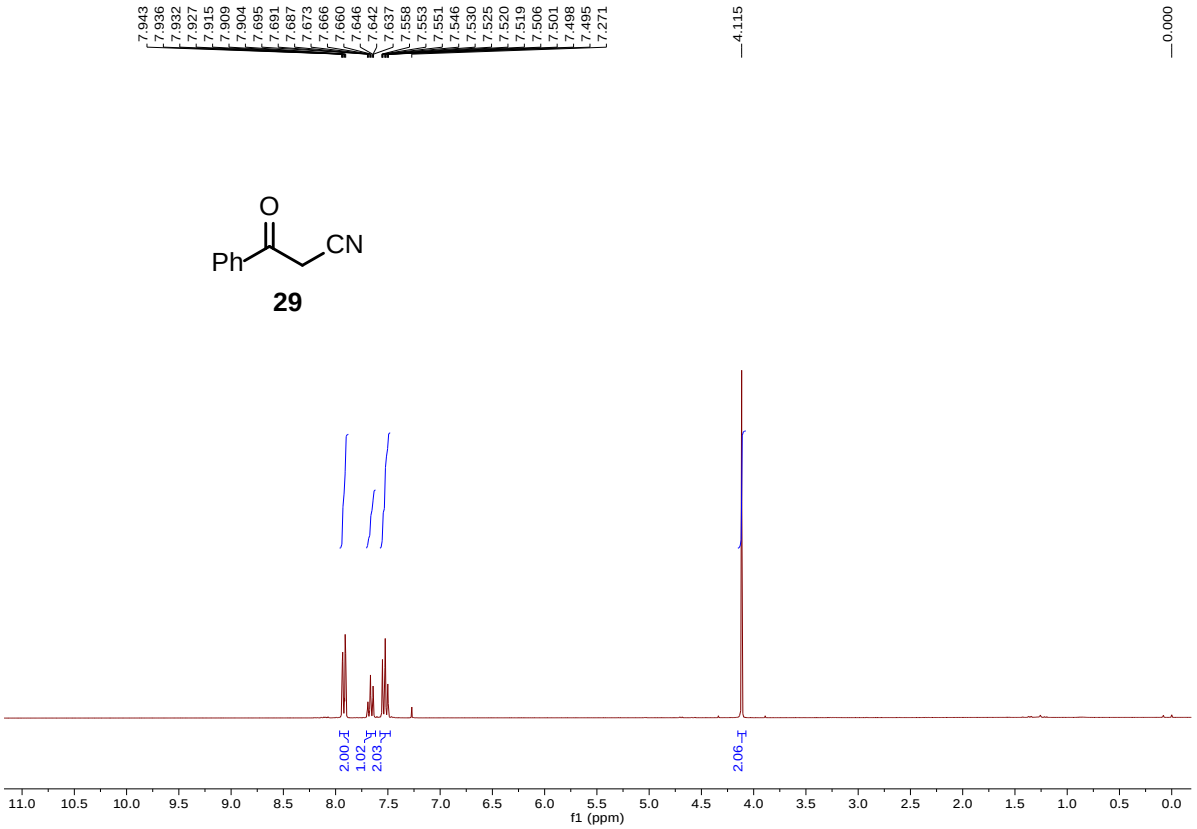
^{1}H NMR (300 MHz, Chloroform-*d*)



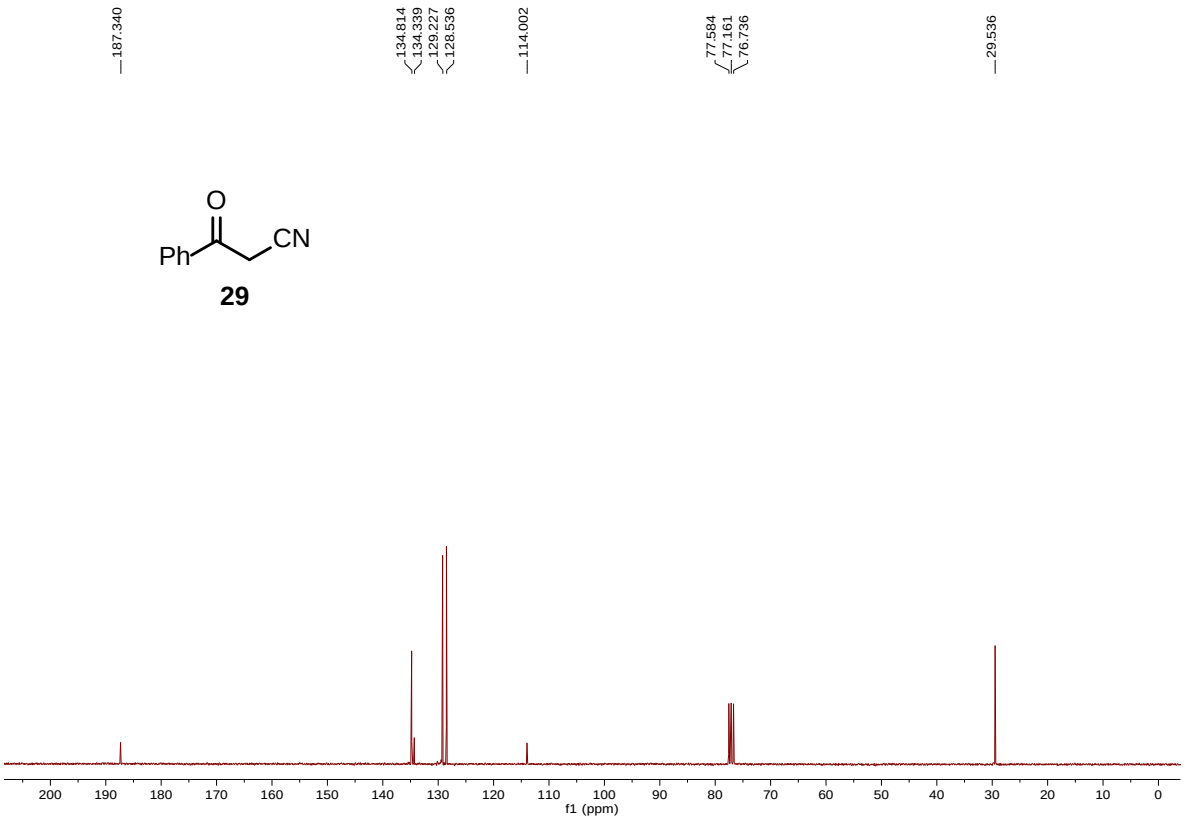
^{13}C NMR (75 MHz, Chloroform-*d*)



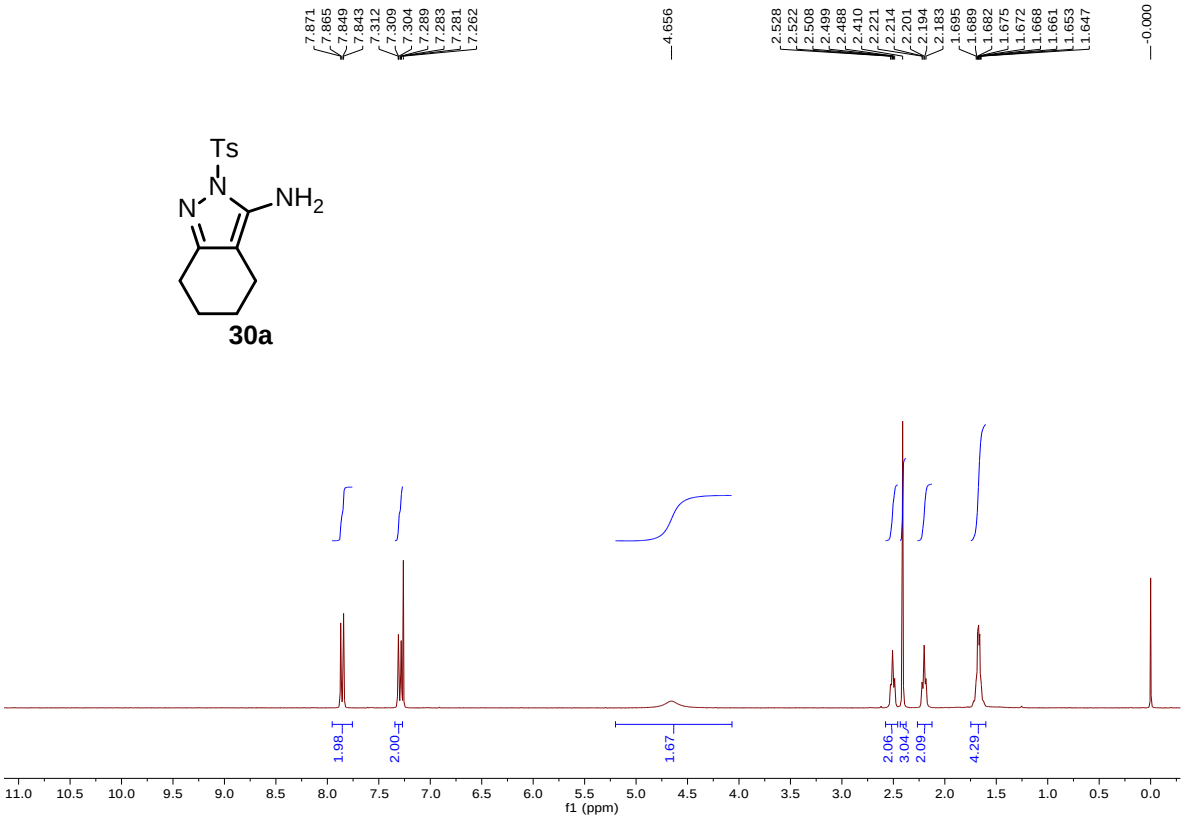
^{1}H NMR (300 MHz, Chloroform-*d*)



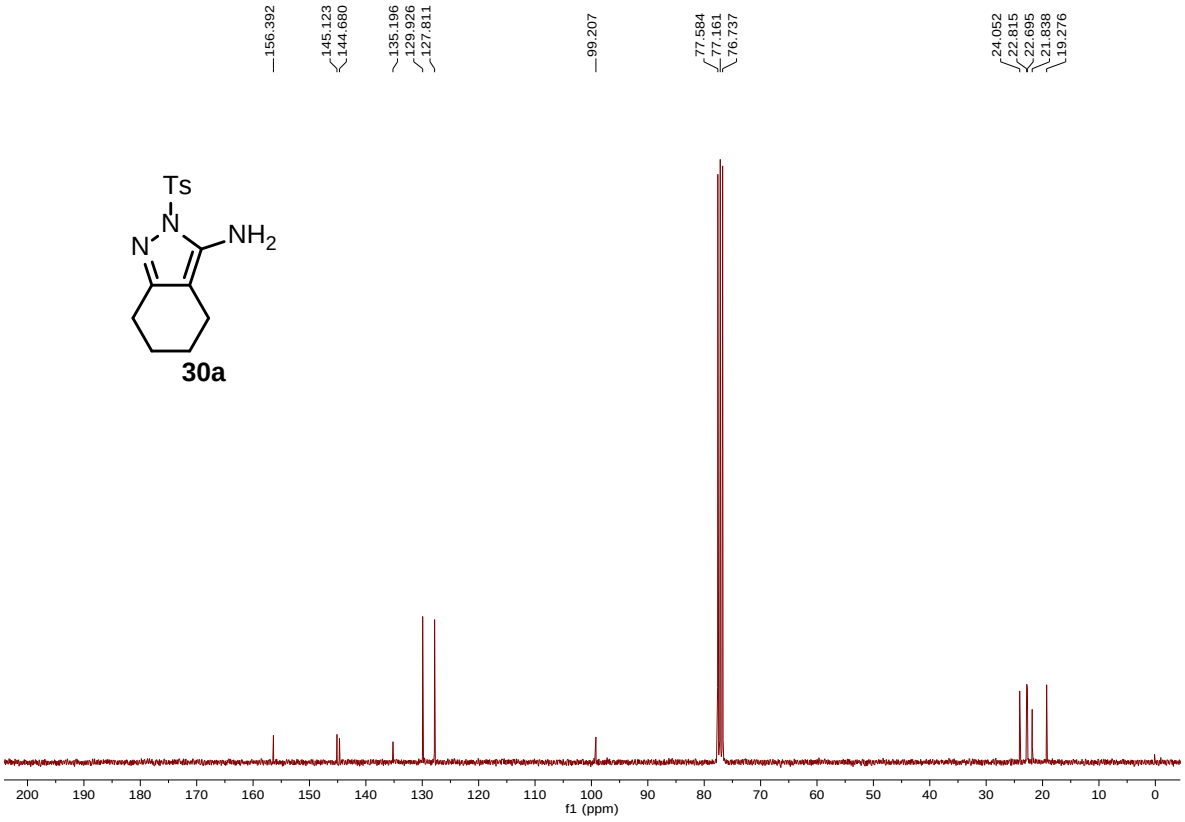
^{13}C NMR (75 MHz, Chloroform-*d*)



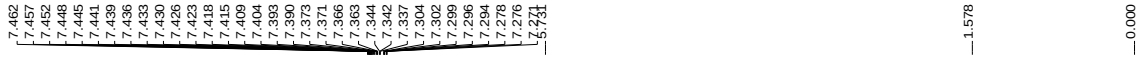
^{1}H NMR (300 MHz, Chloroform-*d*)

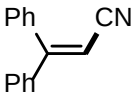


^{13}C NMR (75 MHz, Chloroform-*d*)



^{1}H NMR (300 MHz, Chloroform-*d*)





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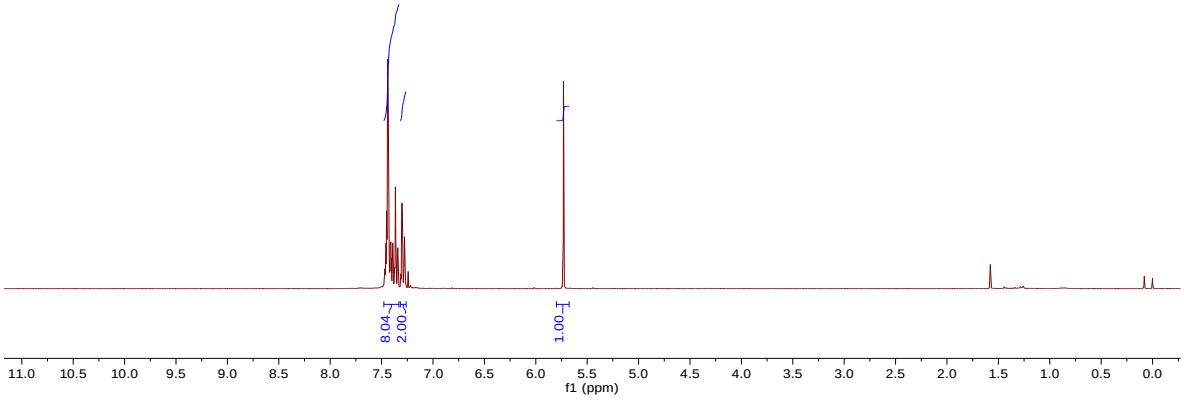
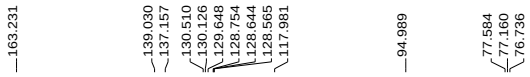
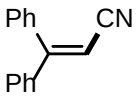


^{13}C NMR (75 MHz, Chloroform-*d*)





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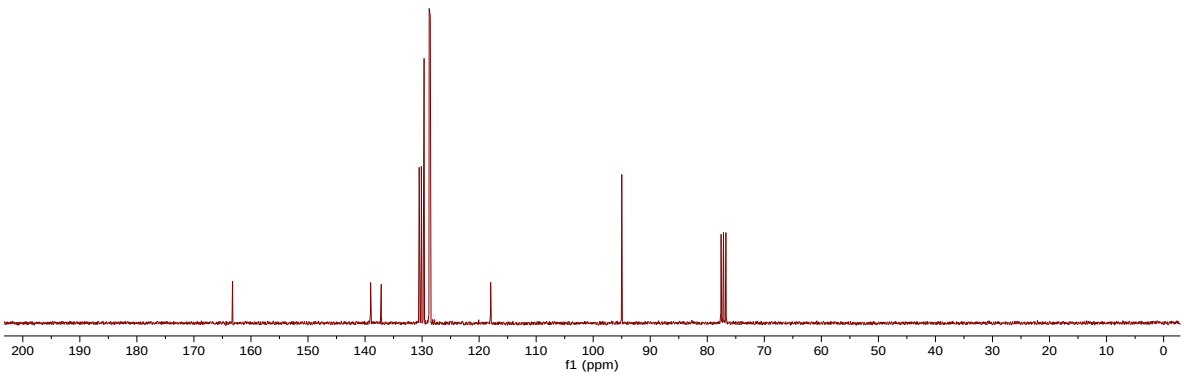
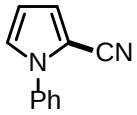


^{1}H NMR (300 MHz, Chloroform-*d*)



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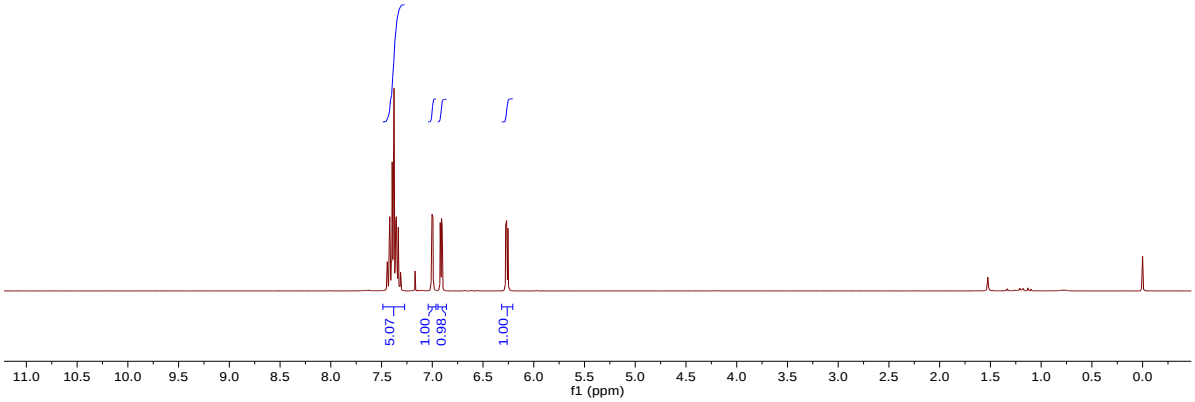
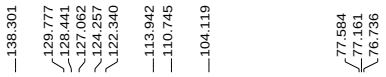
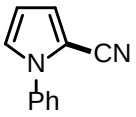


^{13}C NMR (75 MHz, Chloroform-*d*)





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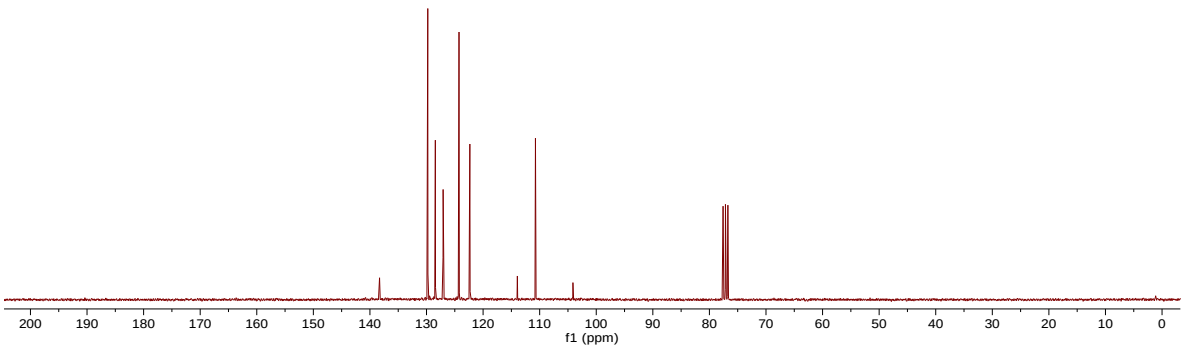
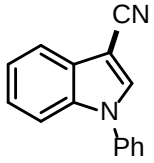


^{1}H NMR (300 MHz, Chloroform-*d*)



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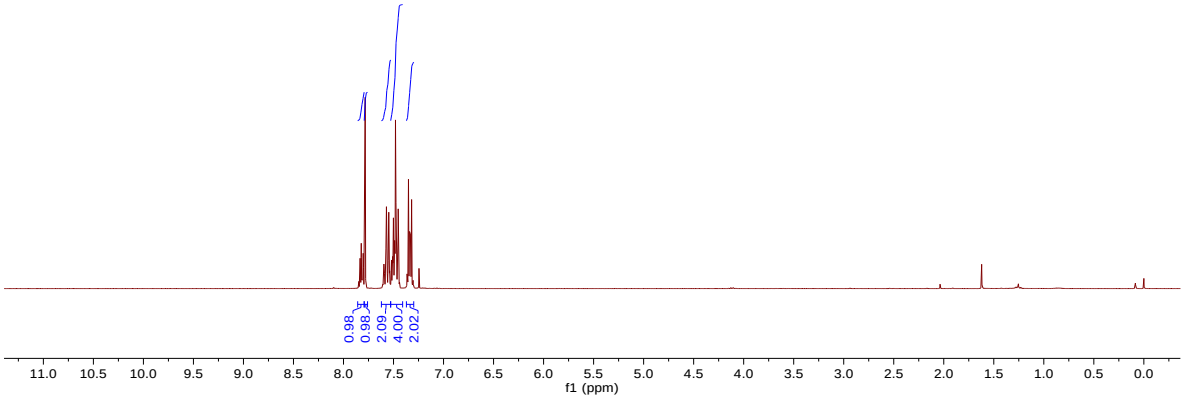
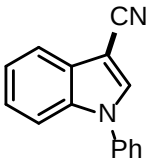


^{13}C NMR (75 MHz, Chloroform-*d*)



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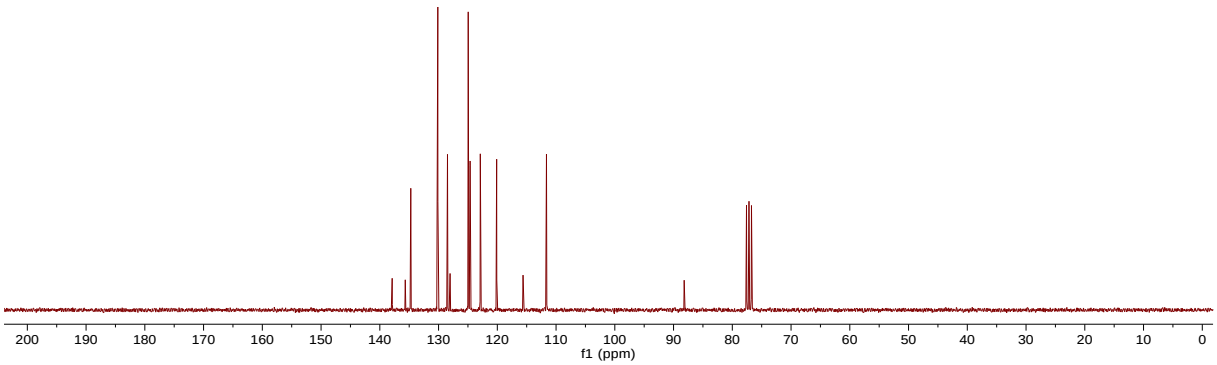
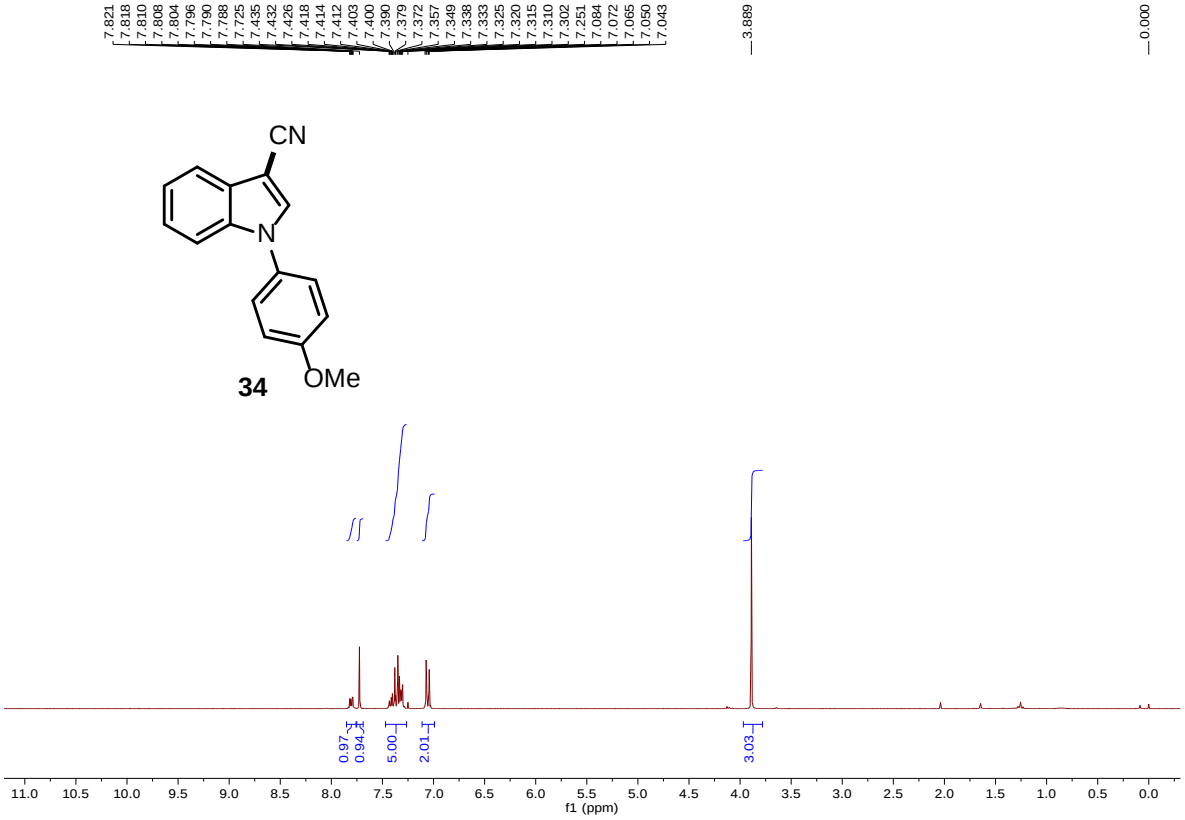
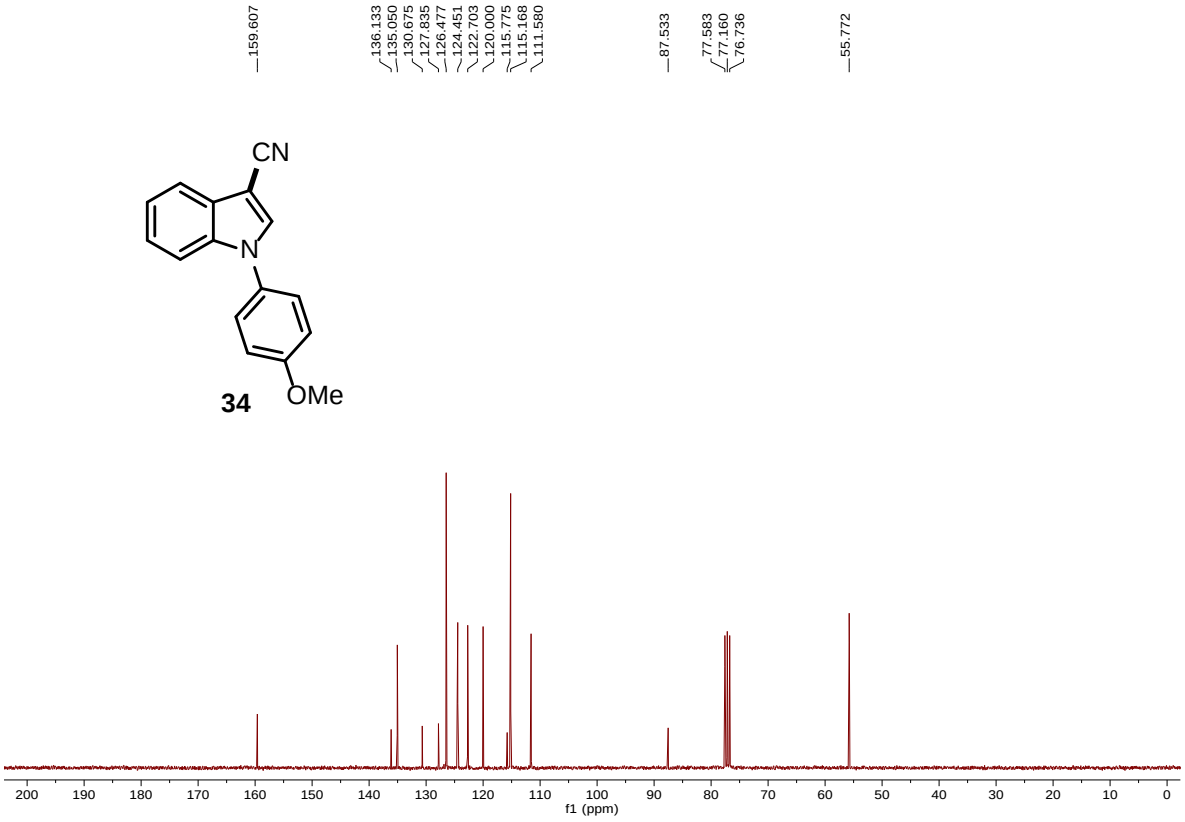


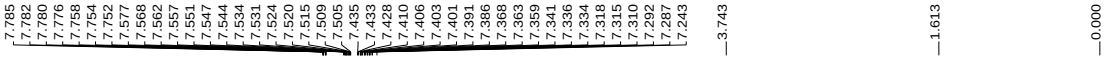
^{1}H NMR (300 MHz, Chloroform-*d*)

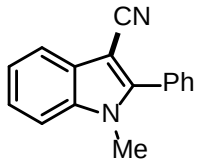


^{13}C NMR (75 MHz, Chloroform-*d*)



^{1}H NMR (300 MHz, Chloroform-*d*)





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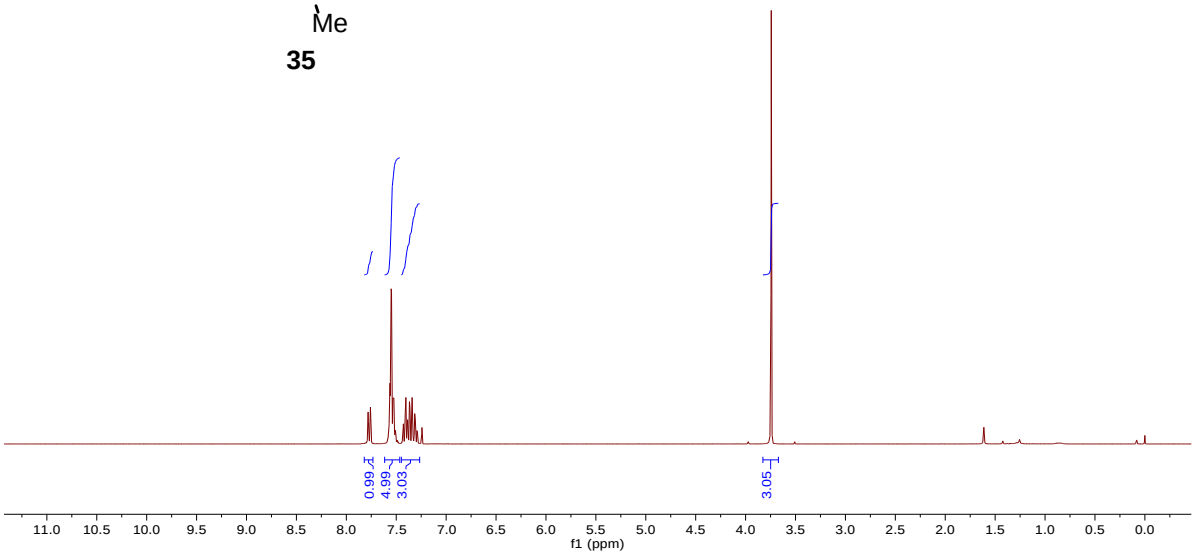
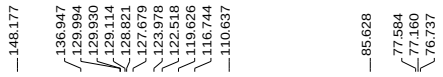
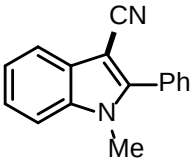


^{13}C NMR (75 MHz, Chloroform-*d*)





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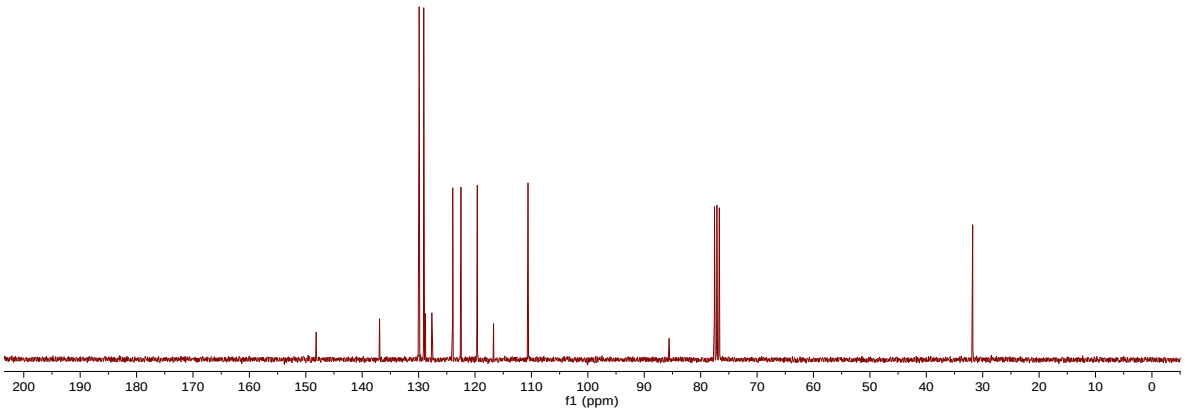
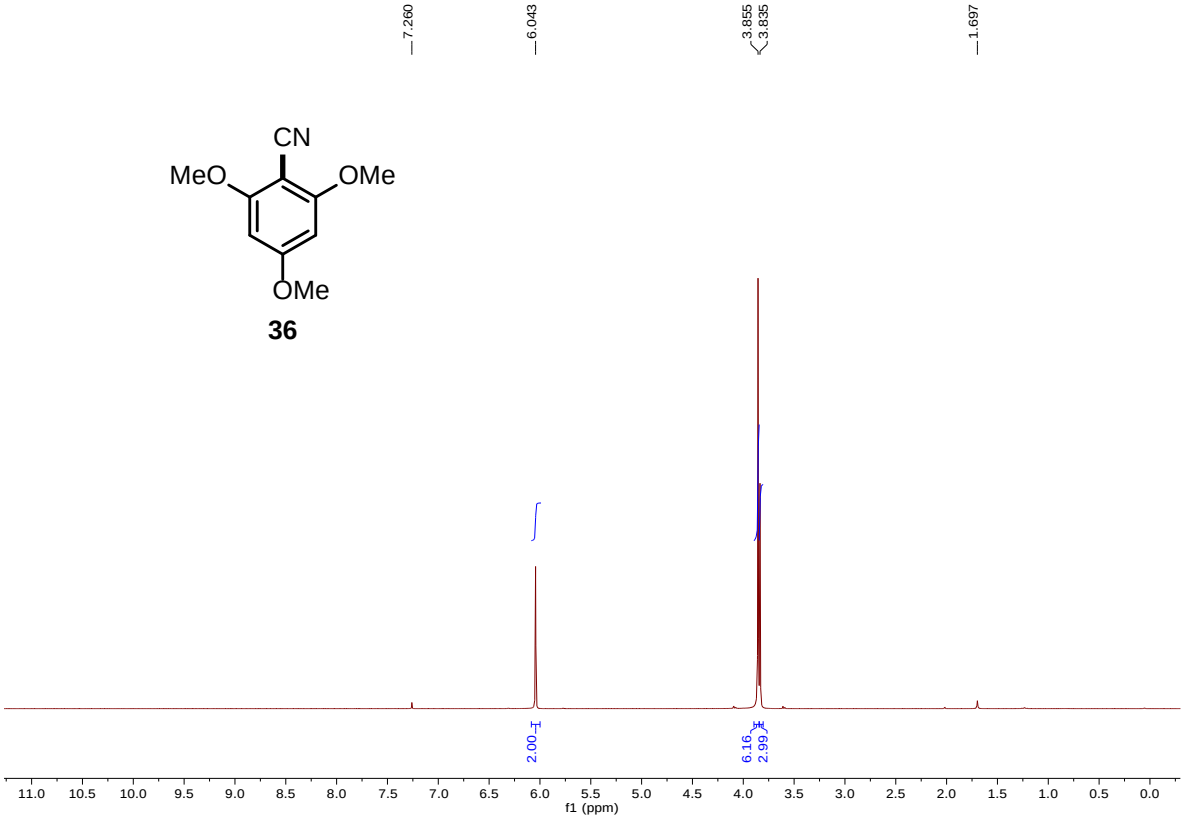
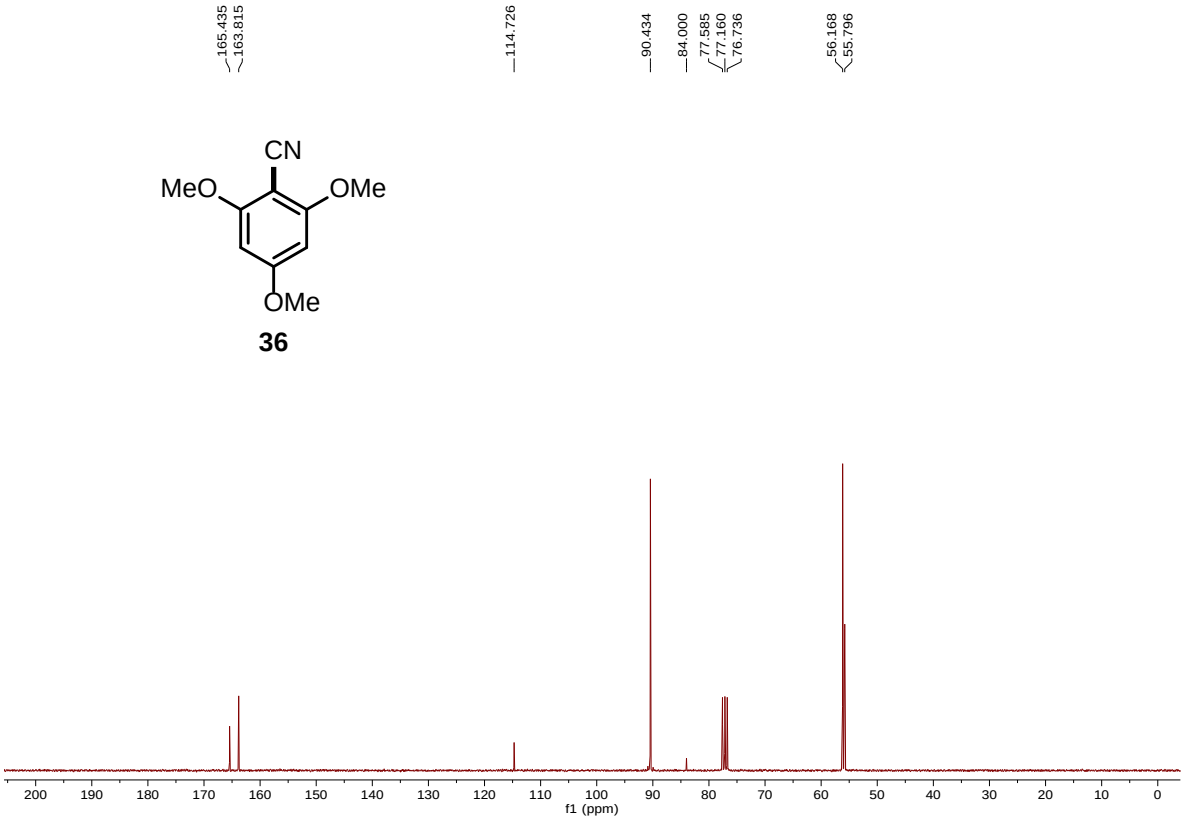


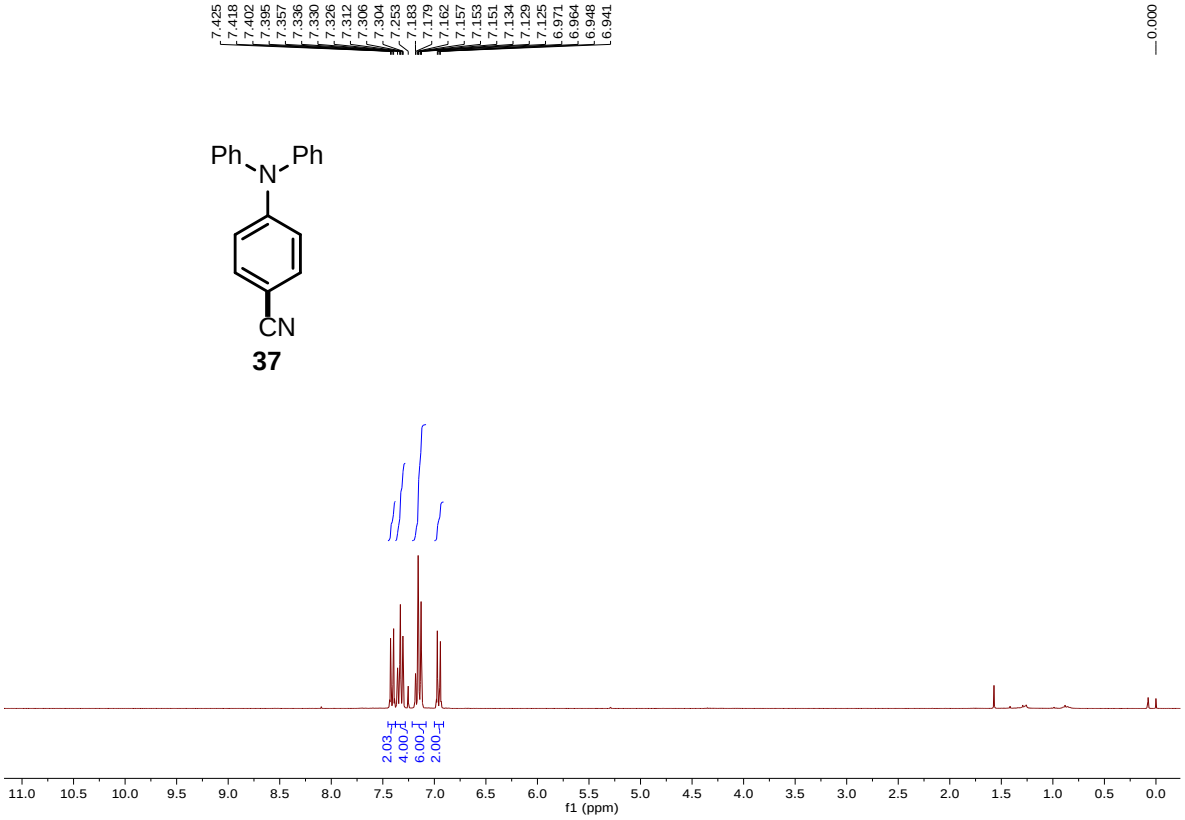
^{1}H NMR (300 MHz, Chloroform-*d*)



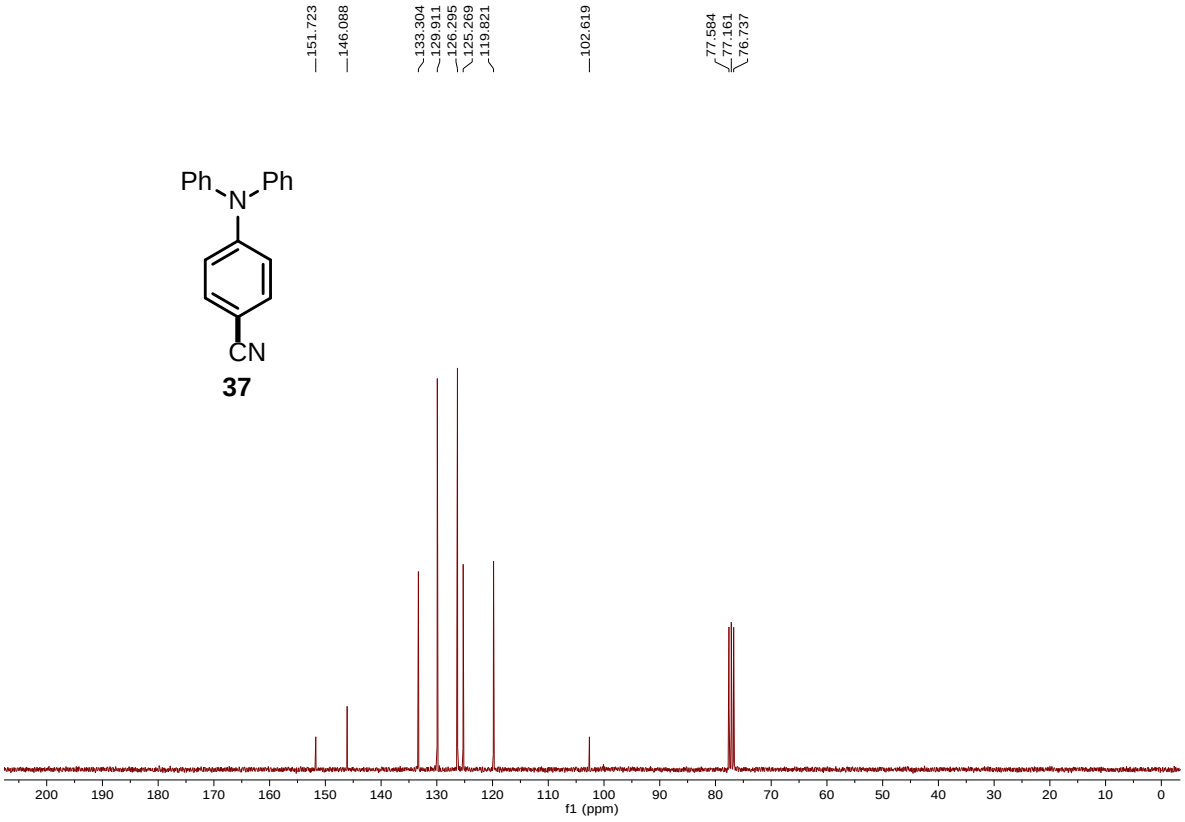
^{13}C NMR (75 MHz, Chloroform-*d*)



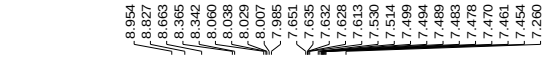
^{1}H NMR (300 MHz, Chloroform-*d*)

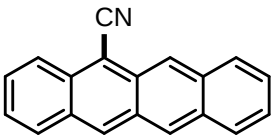


^{13}C NMR (75 MHz, Chloroform-*d*)



^{1}H NMR (400 MHz, Chloroform-*d*)





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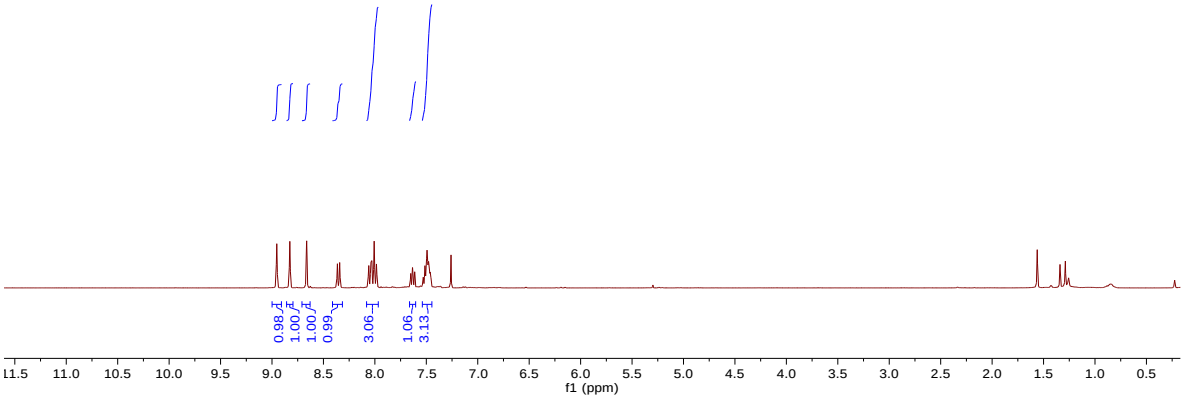
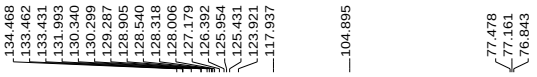
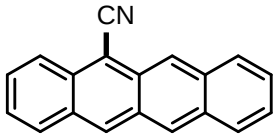


^{13}C NMR (101 MHz, Chloroform-*d*)





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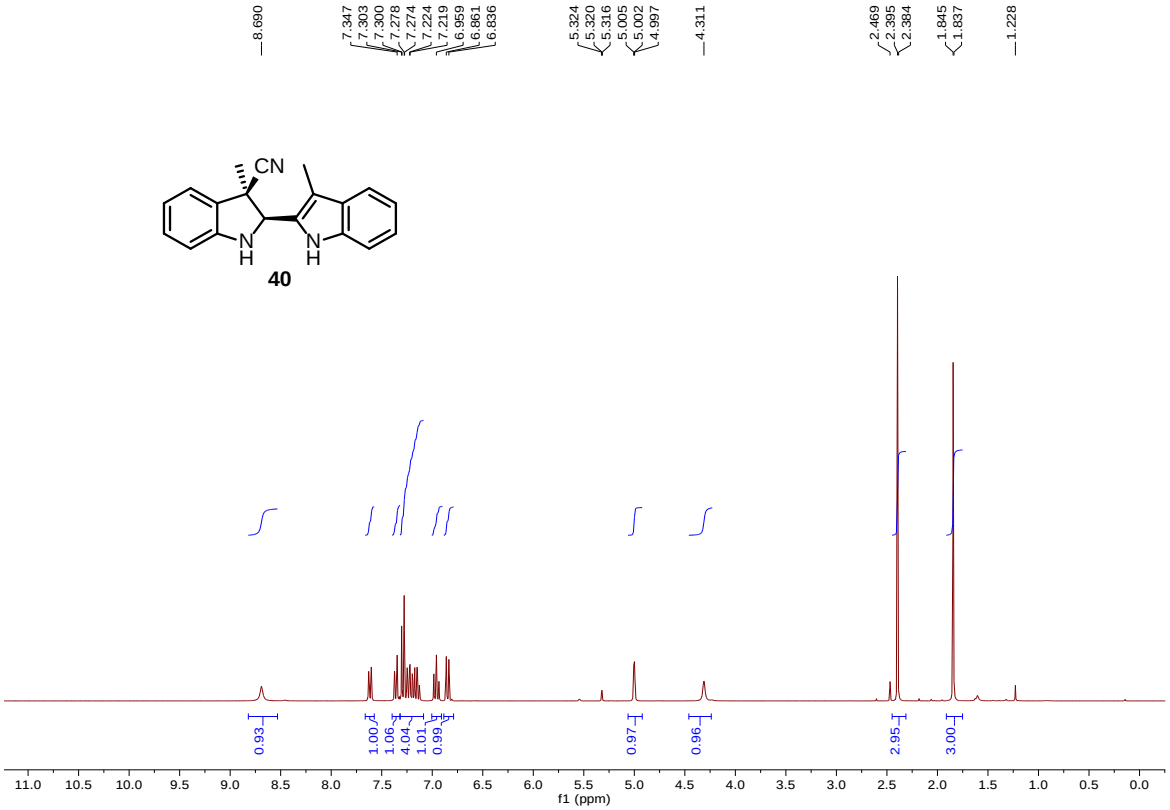
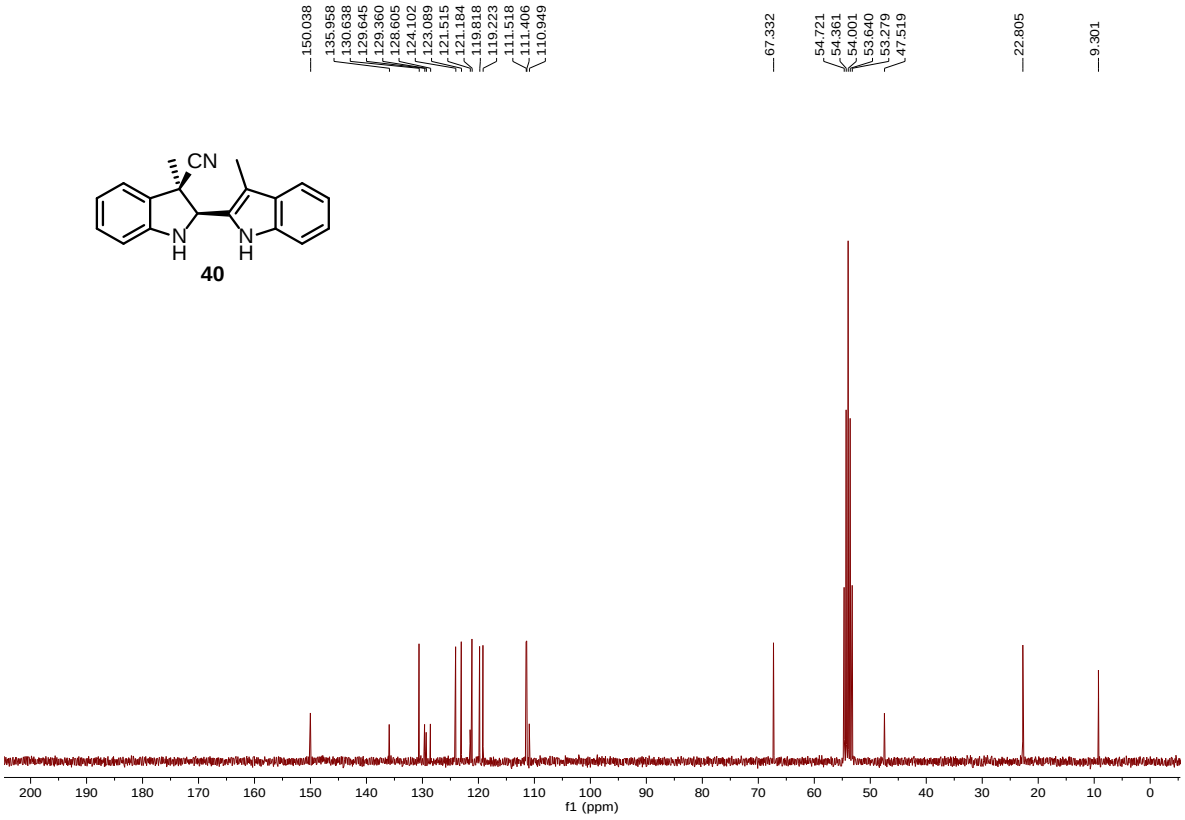
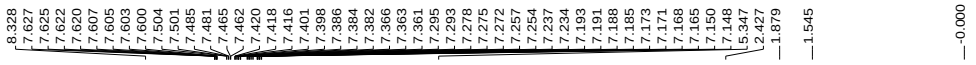
^{1}H NMR (300 MHz, Methylene Chloride-d_2)

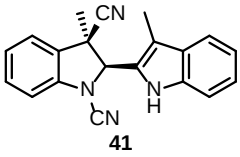


^{13}C NMR (75 MHz, Methylene Chloride-d_2)



^{1}H NMR (400 MHz, Chloroform-*d*)





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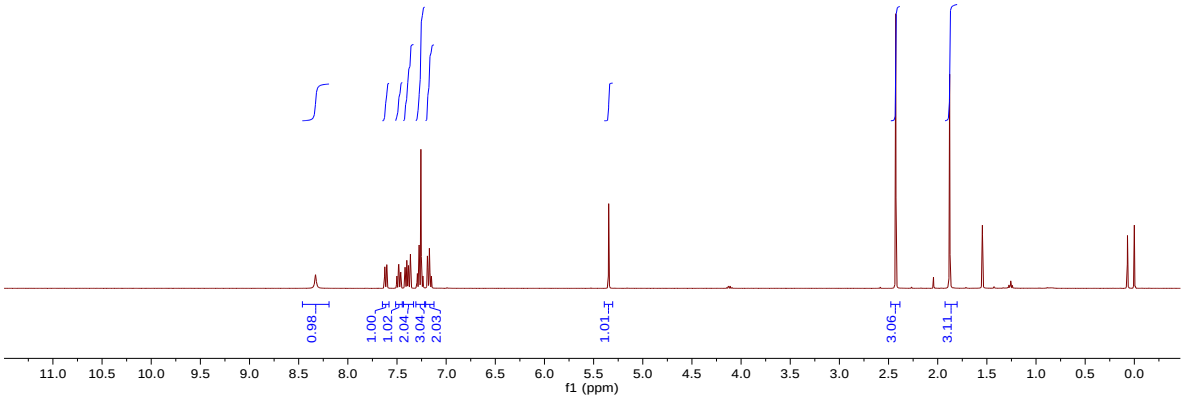
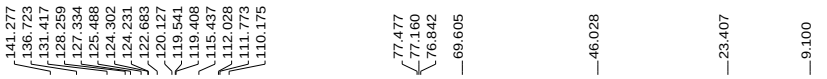
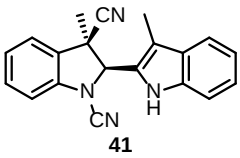


^{13}C NMR (101 MHz, Chloroform-*d*)





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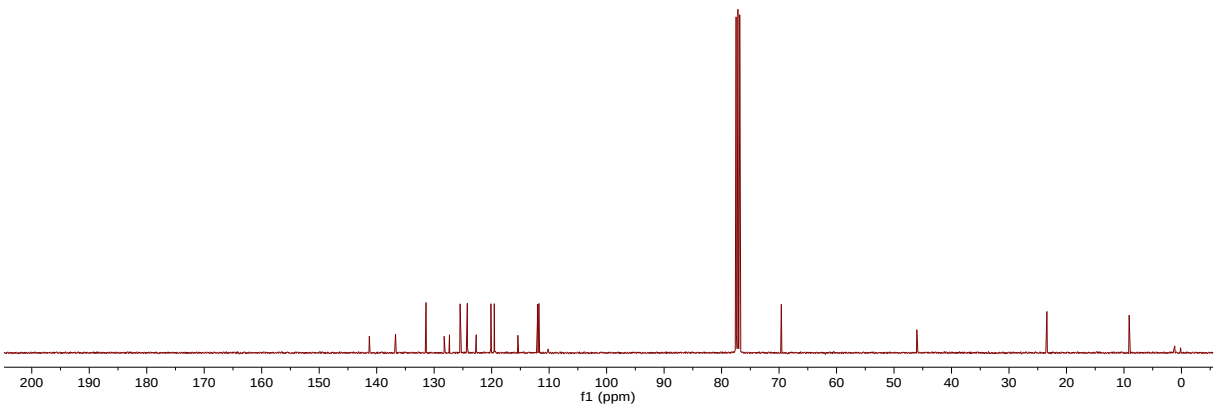
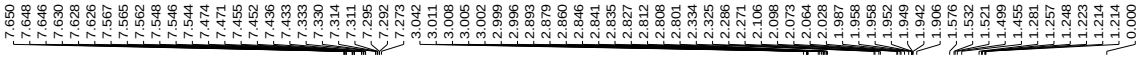
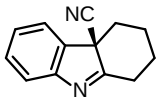


^{1}H NMR (400 MHz, Chloroform-*d*)





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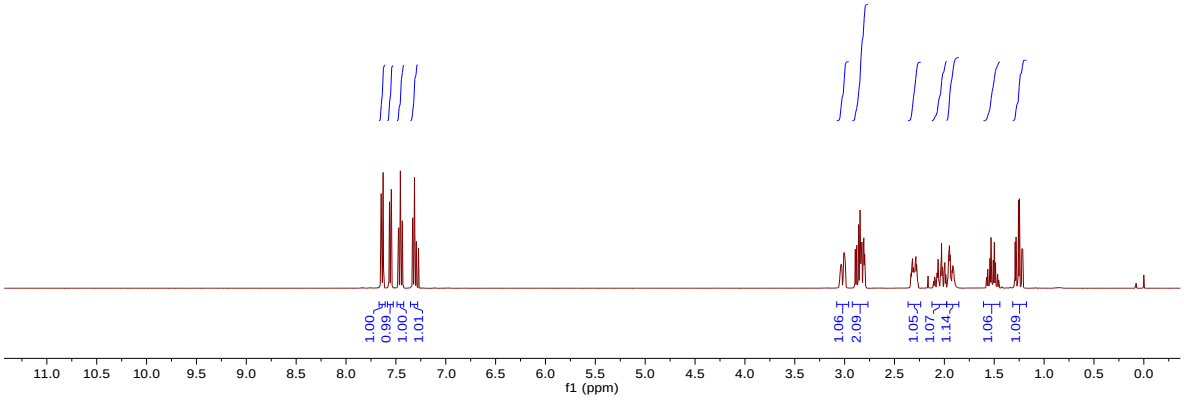
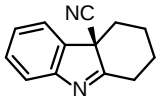


^{13}C NMR (101 MHz, Chloroform-*d*)



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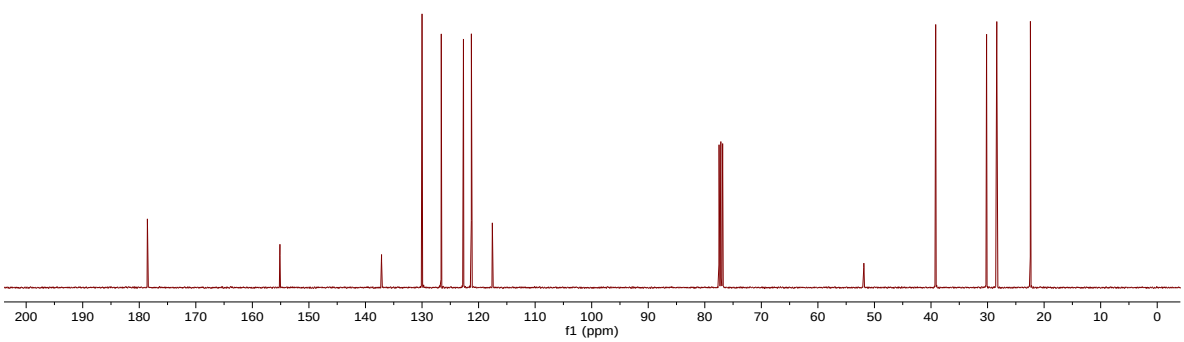
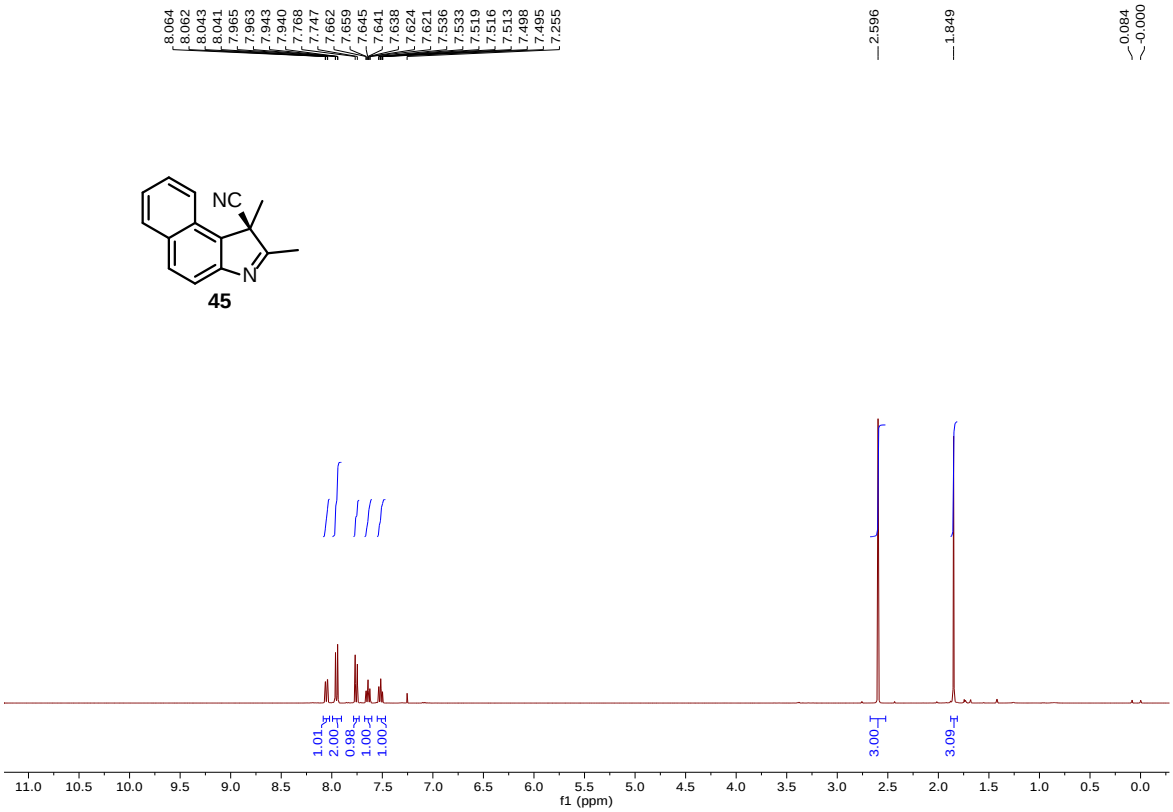
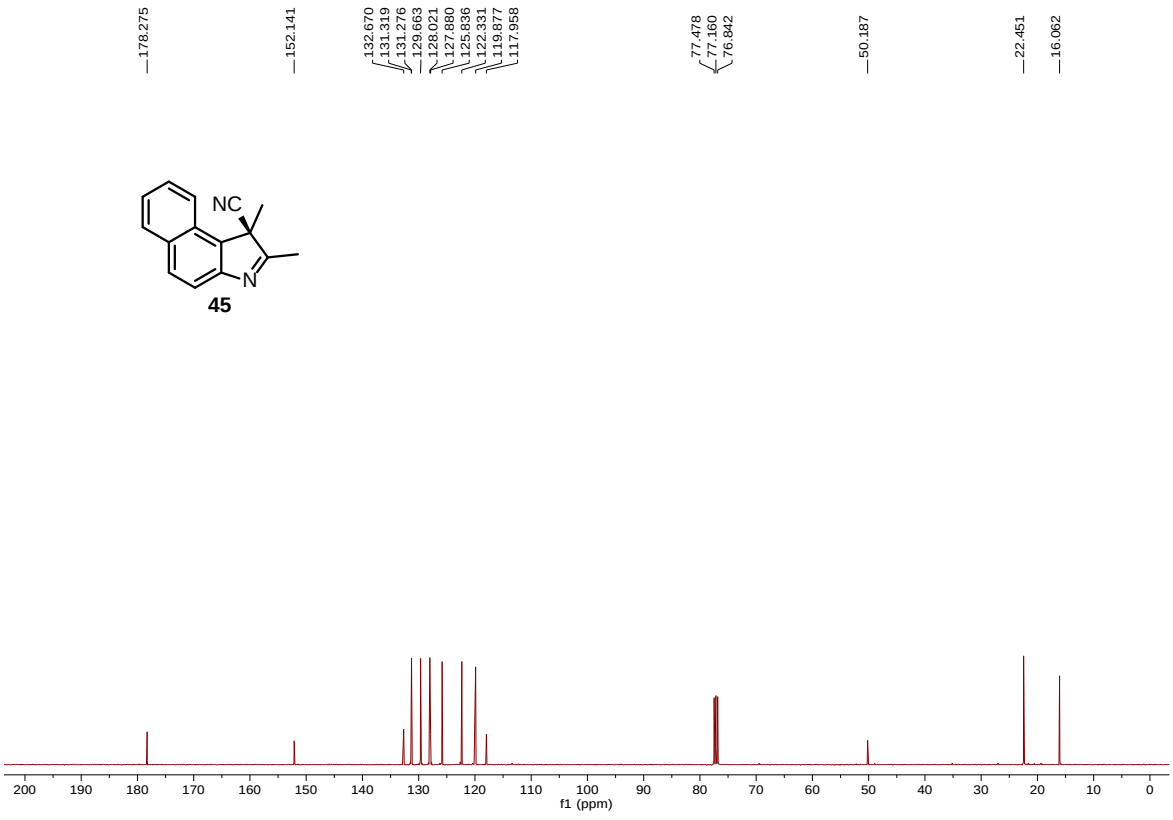


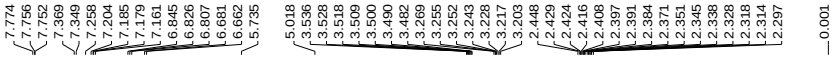
^{1}H NMR (400 MHz, Chloroform-*d*)

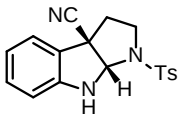


^{13}C NMR (101 MHz, Chloroform-*d*)



^{1}H NMR (400 MHz, Chloroform-*d*)





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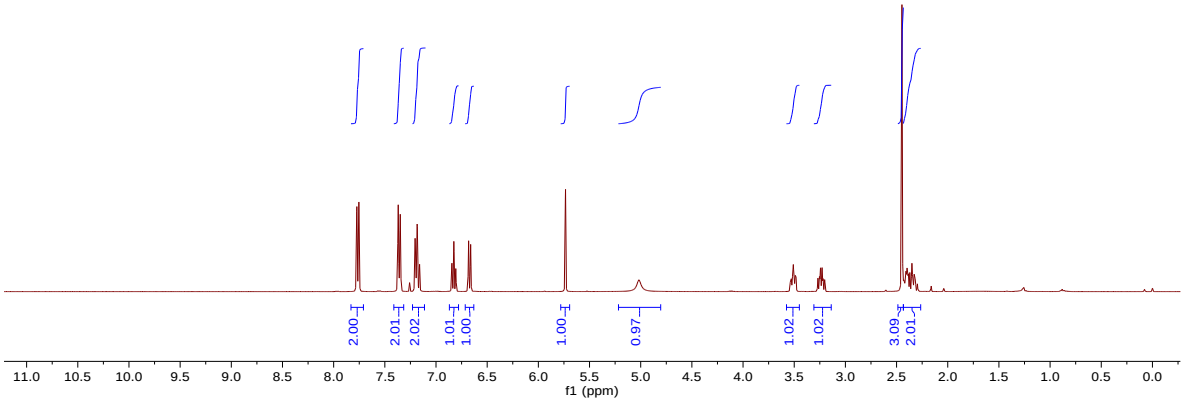
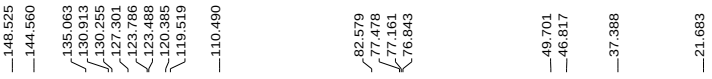
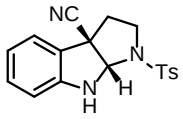


^{13}C NMR (101 MHz, Chloroform-*d*)





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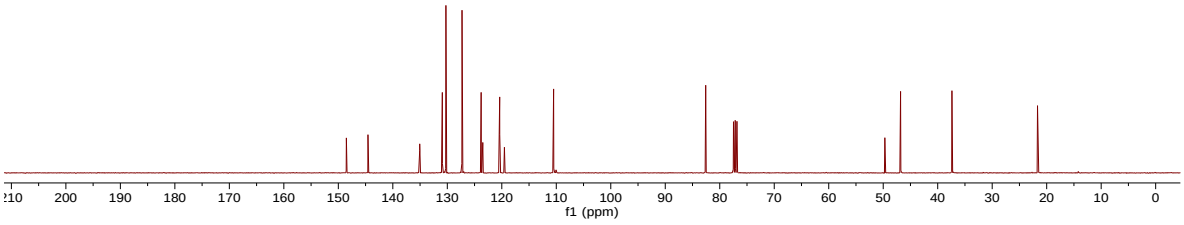
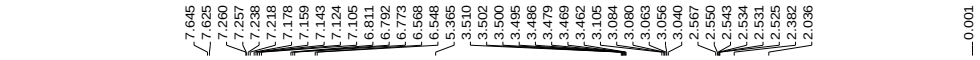
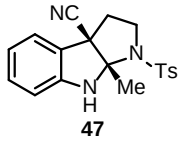


^{1}H NMR (400 MHz, Chloroform-*d*)





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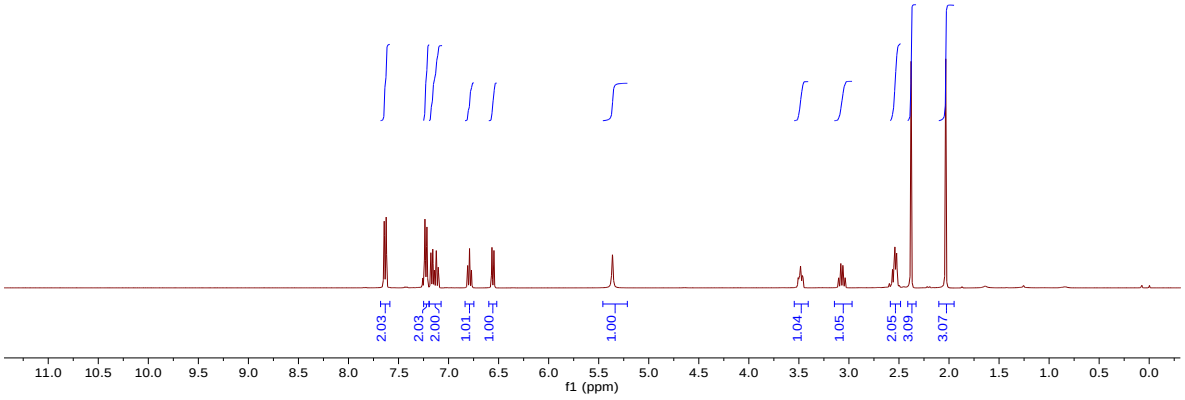
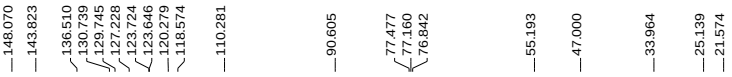
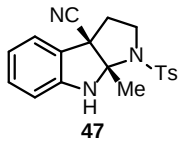


^{13}C NMR (101 MHz, Chloroform-*d*)





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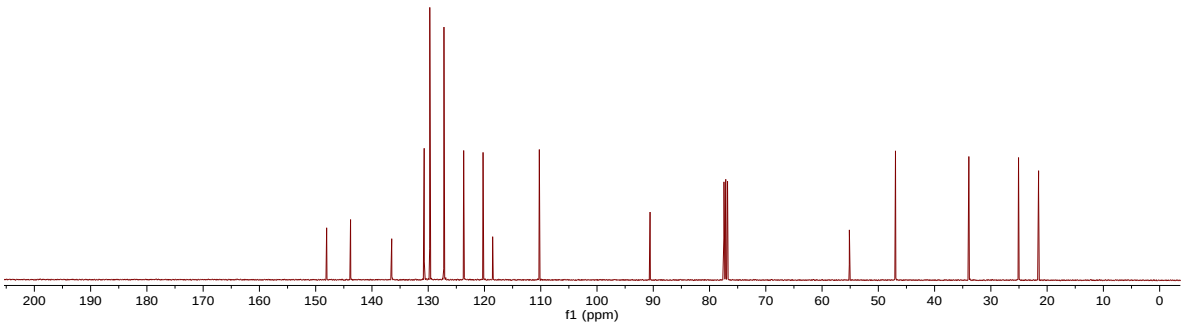
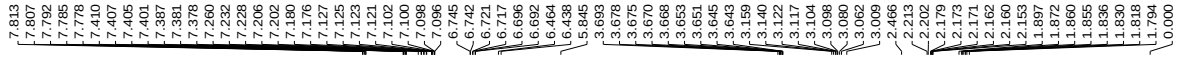
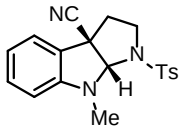


^{1}H NMR (300 MHz, Chloroform-*d*)





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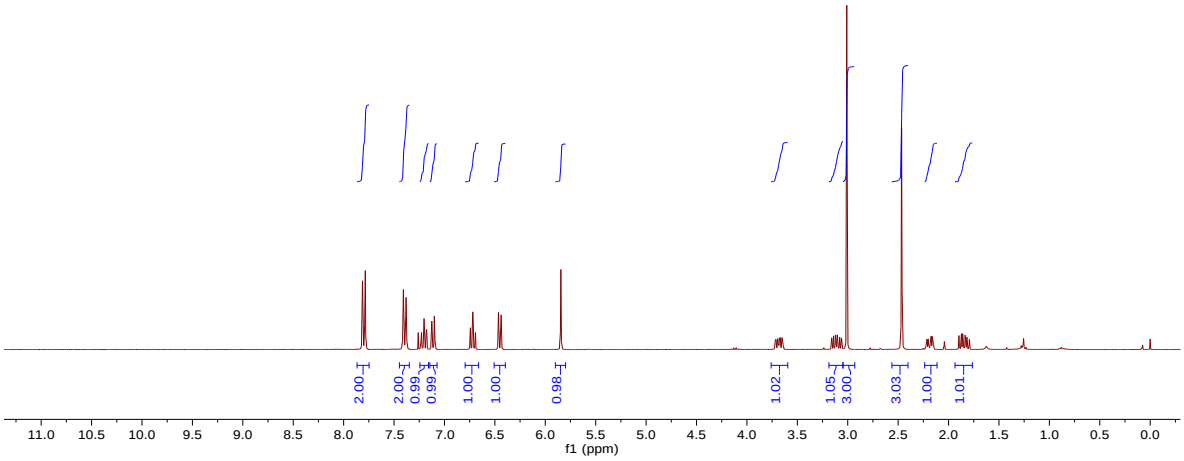
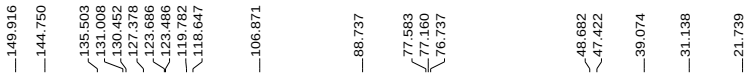
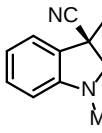


^{13}C NMR (75 MHz, Chloroform-*d*)





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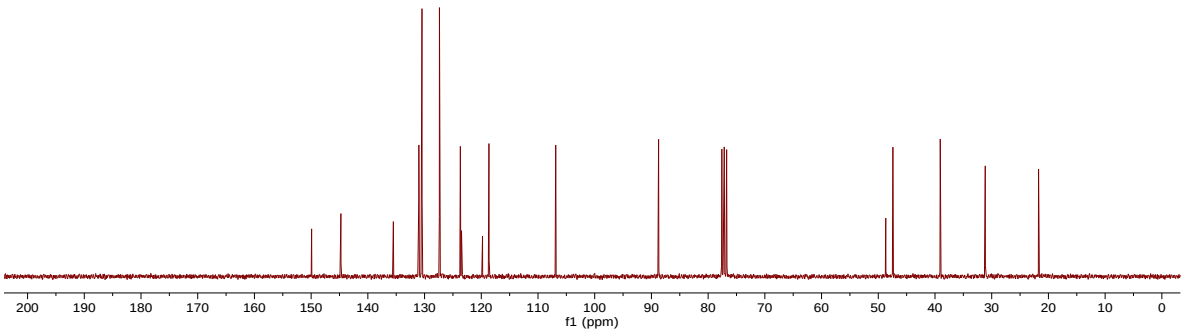
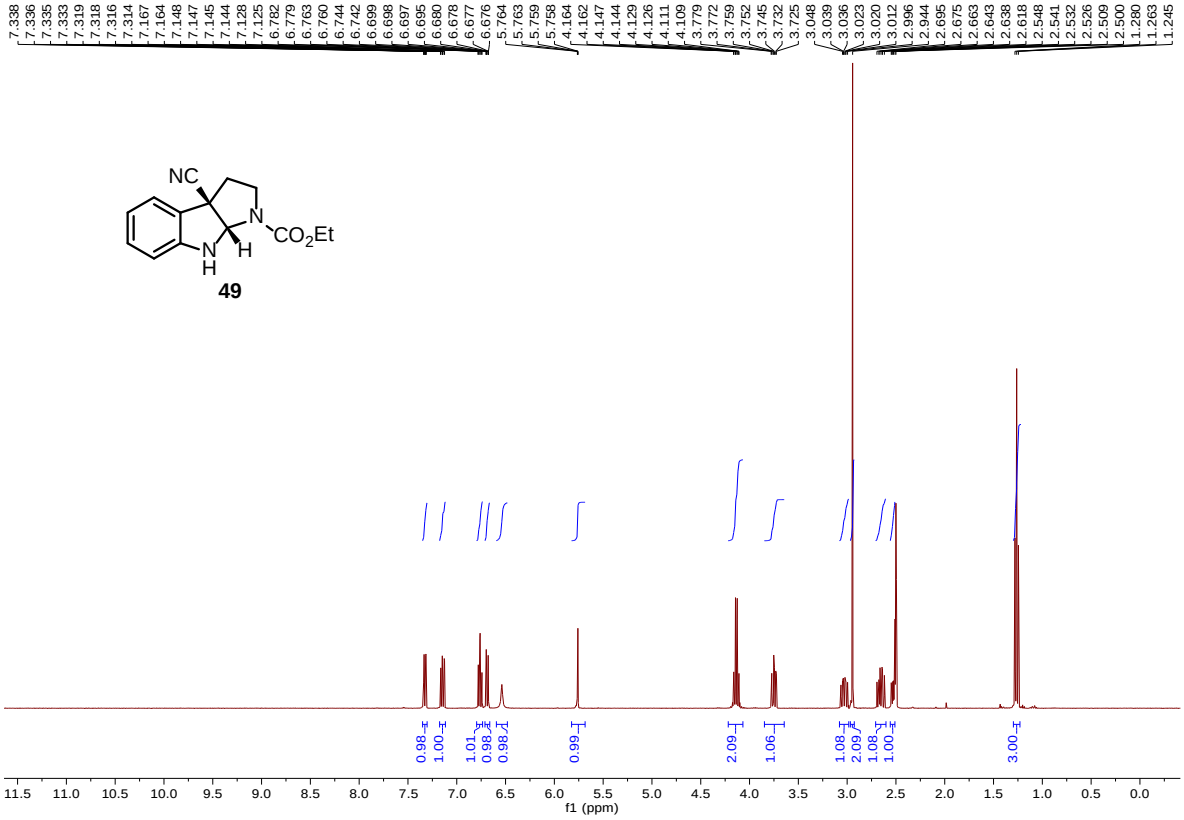


^{1}H NMR (400 MHz, DMSO-d_6, 100 ^{o}C)



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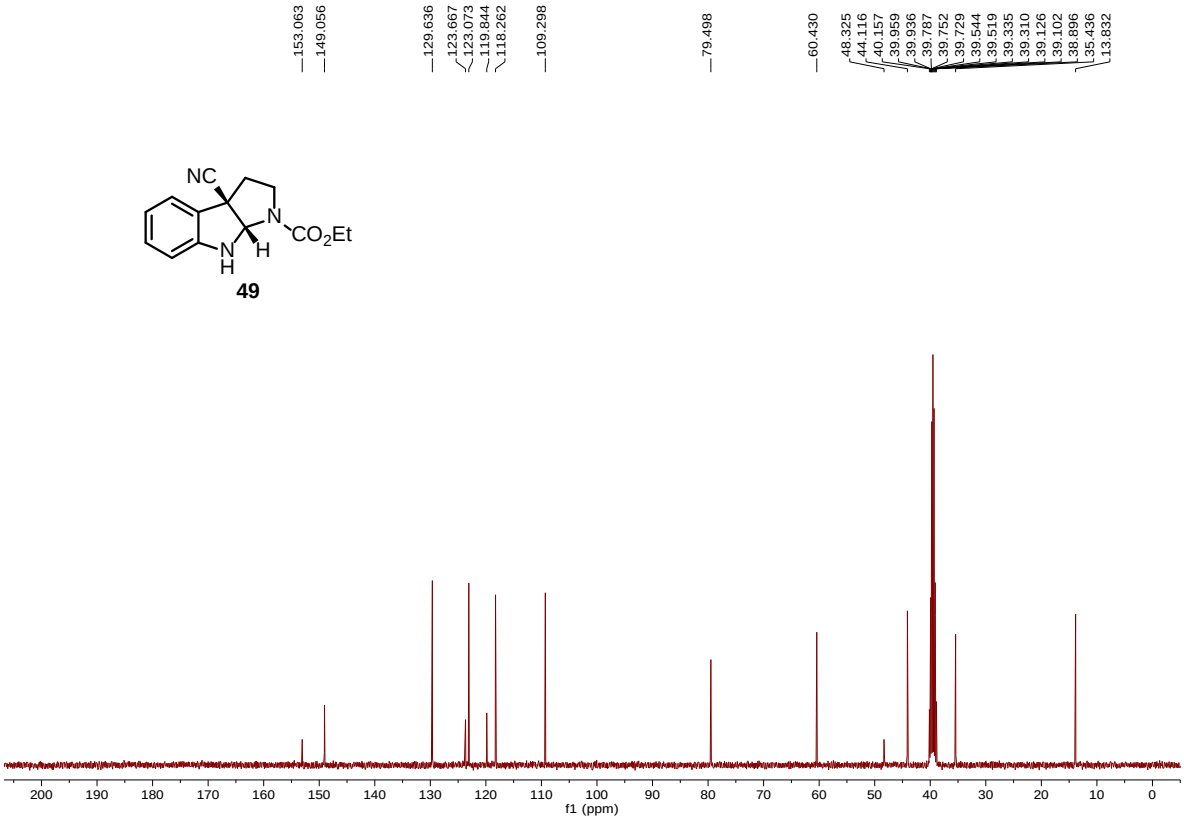
^{13}C NMR (101 MHz, DMSO-d_6, 100 ^{o}C)



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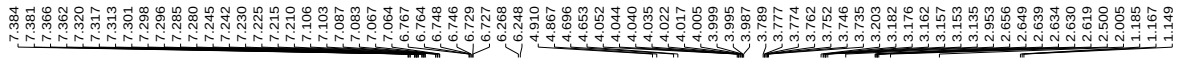
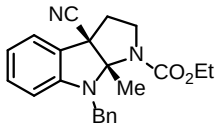
^{1}H NMR (400 MHz, DMSO-d_6, 100 ^{o}C)





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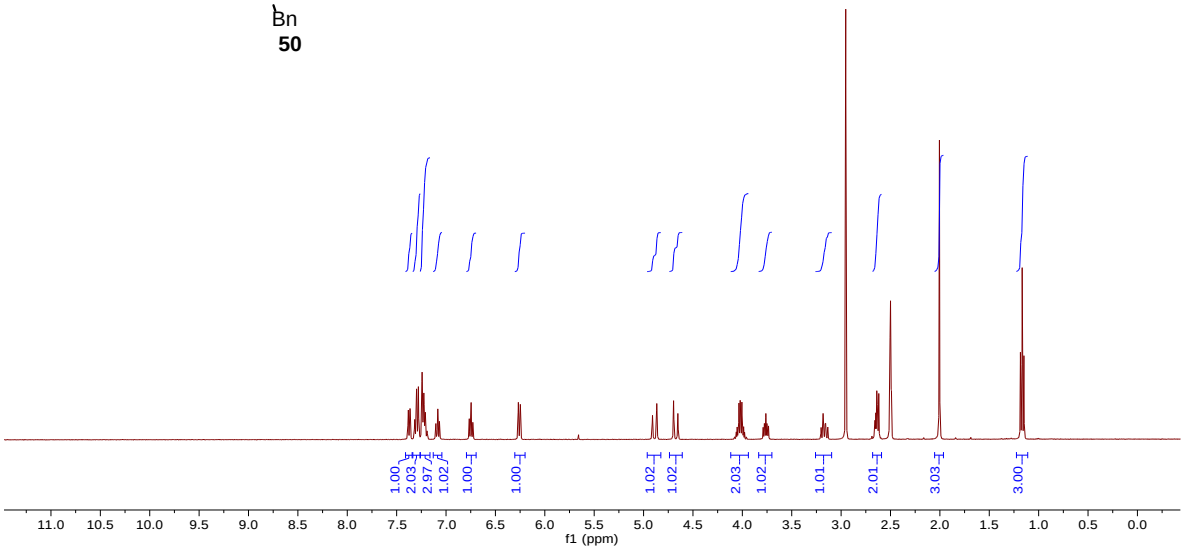
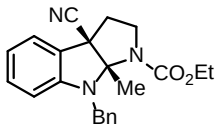


^{13}C NMR (101 MHz, DMSO-d_6, 100 ^{o}C)



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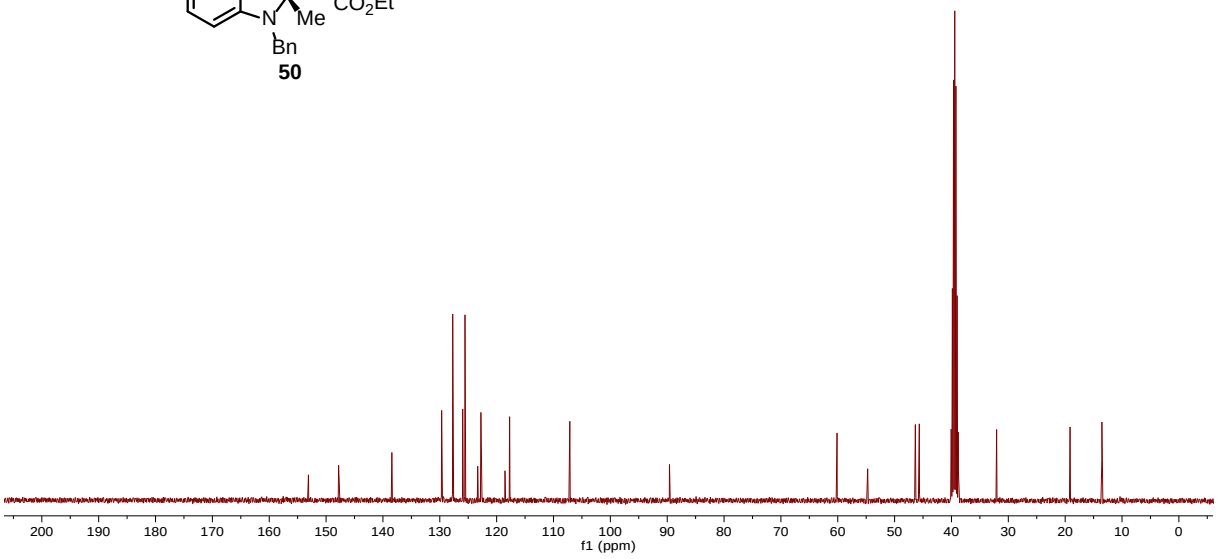
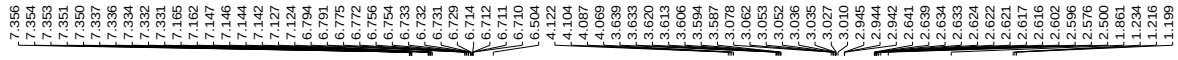
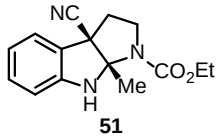


^{1}H NMR (400 MHz, DMSO-d_6, 100 ^{o}C)





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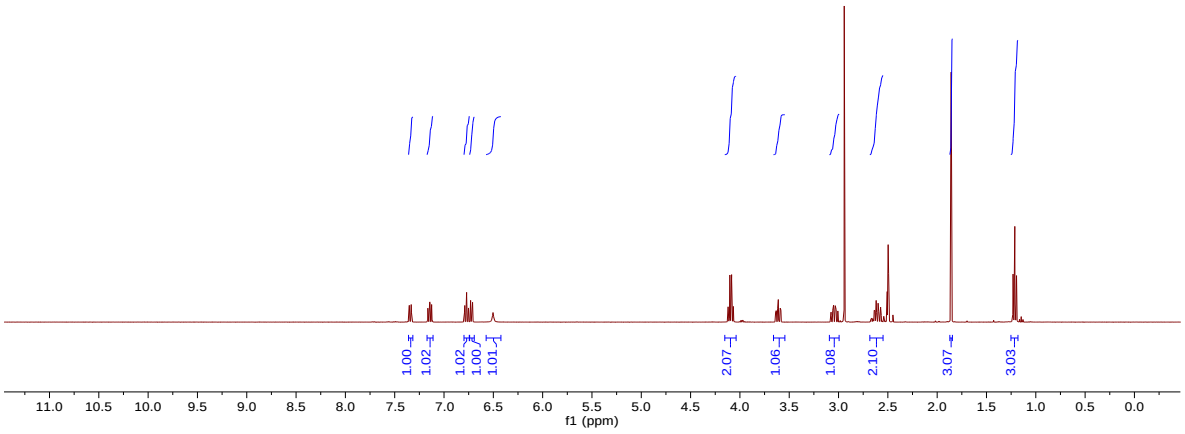
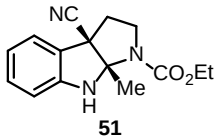


^{13}C NMR (101 MHz, DMSO-d_6, 100 ^{o}C)



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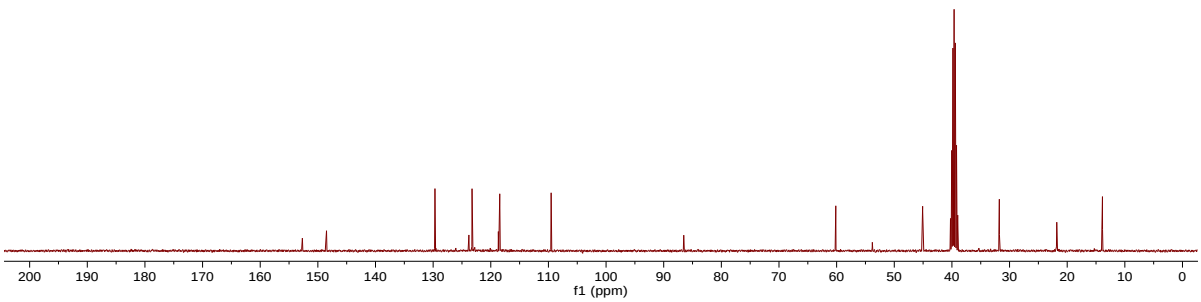
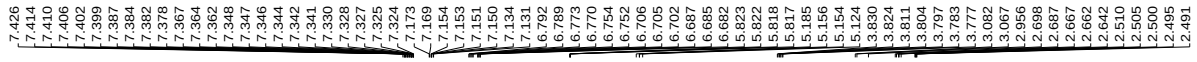
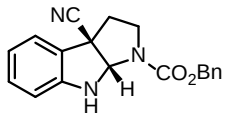


^{1}H NMR (400 MHz, DMSO-d_6, 100 ^{o}C)





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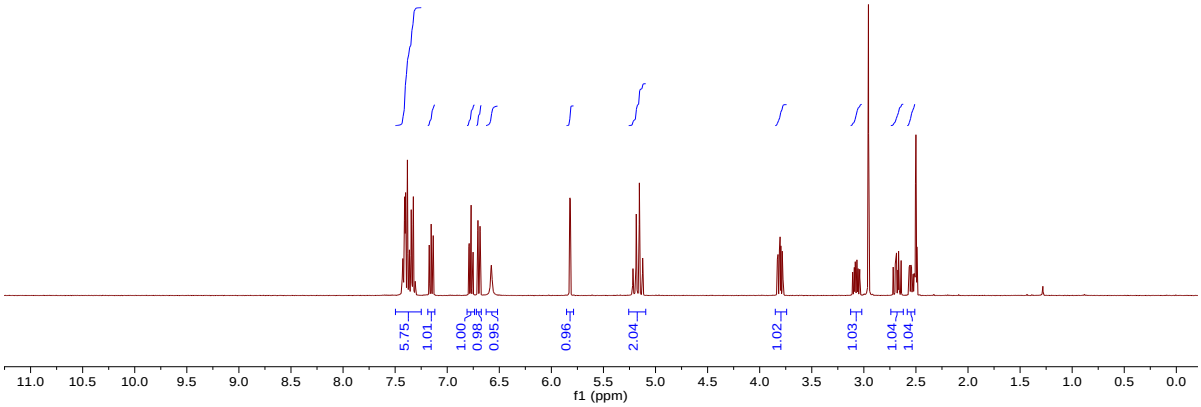
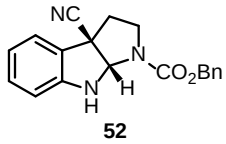


^{13}C NMR (101 MHz, DMSO-d_6, 100 ^{o}C)



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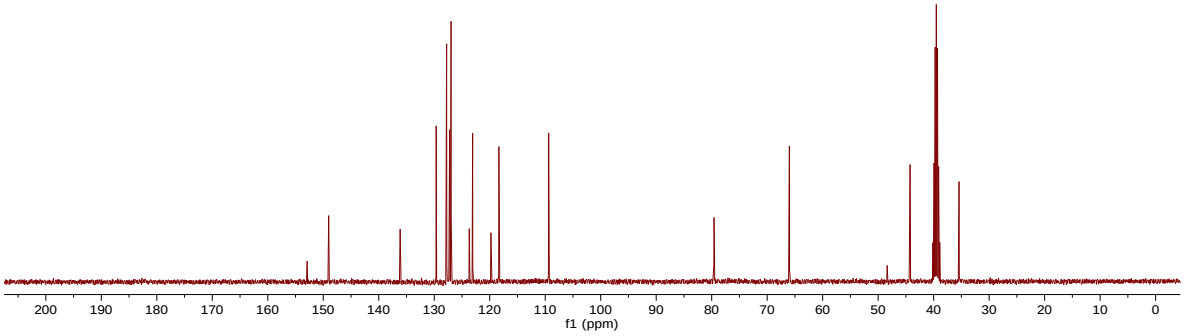
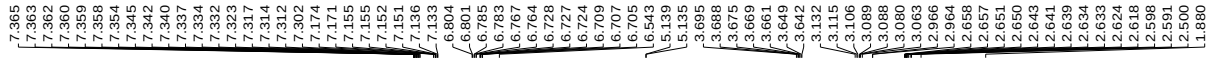
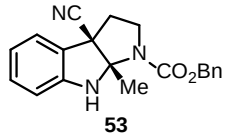


^{1}H NMR (400 MHz, DMSO-d_6, 100 ^{o}C)





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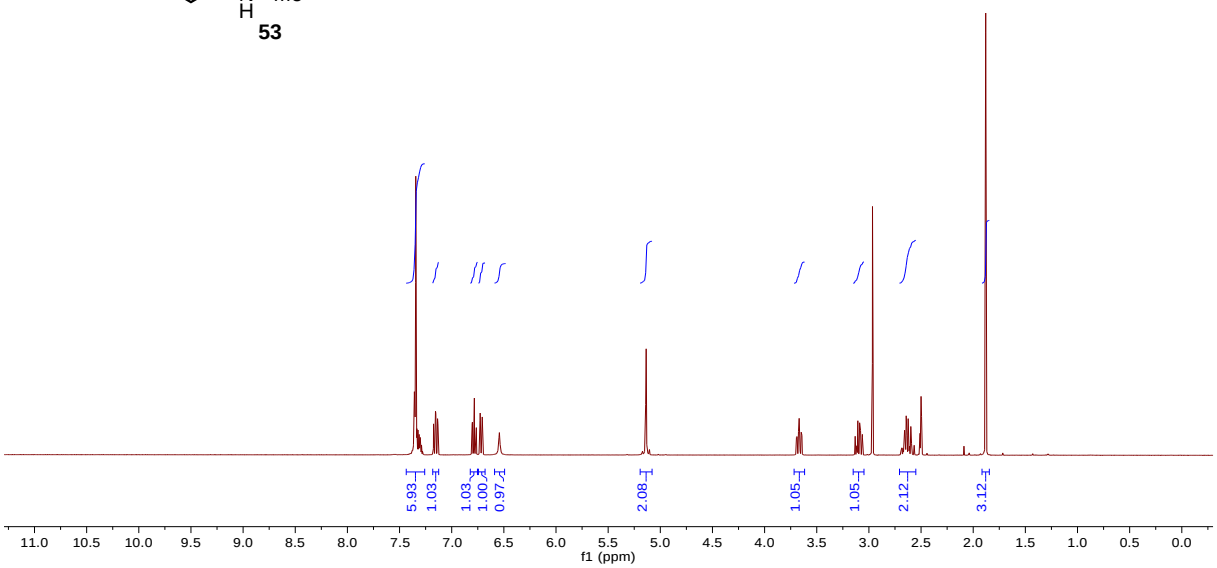
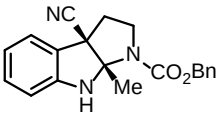


^{13}C NMR (101 MHz, DMSO-d_6, 100 ^{o}C)



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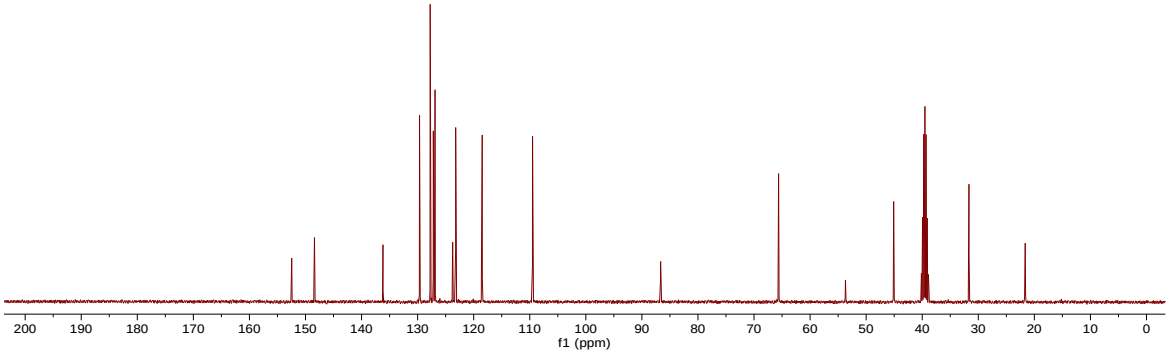
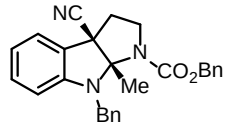


^{1}H NMR (400 MHz, DMSO-d_6, 100 ^{o}C)



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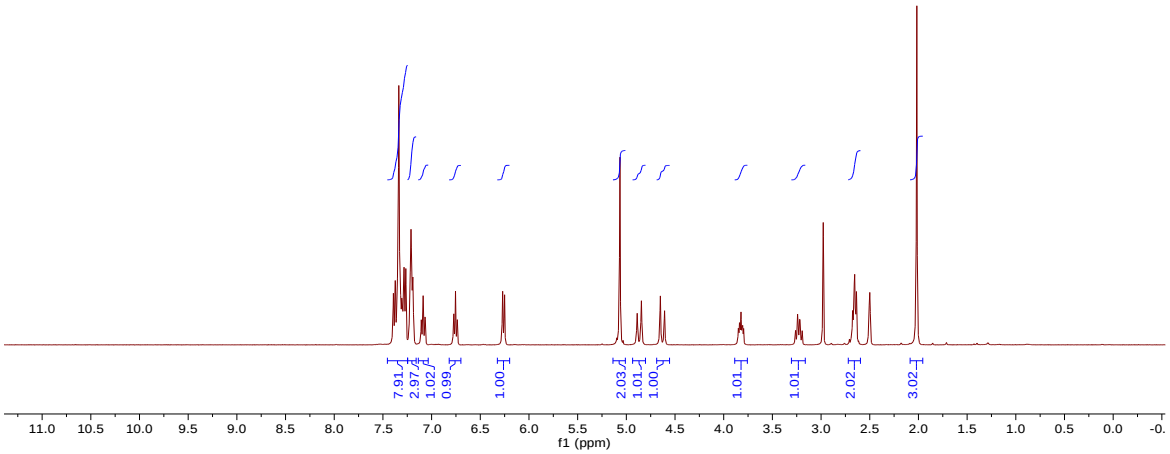
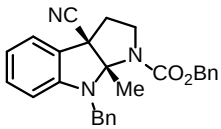


^{13}C NMR (101 MHz, DMSO-d_6, 100 ^{o}C)



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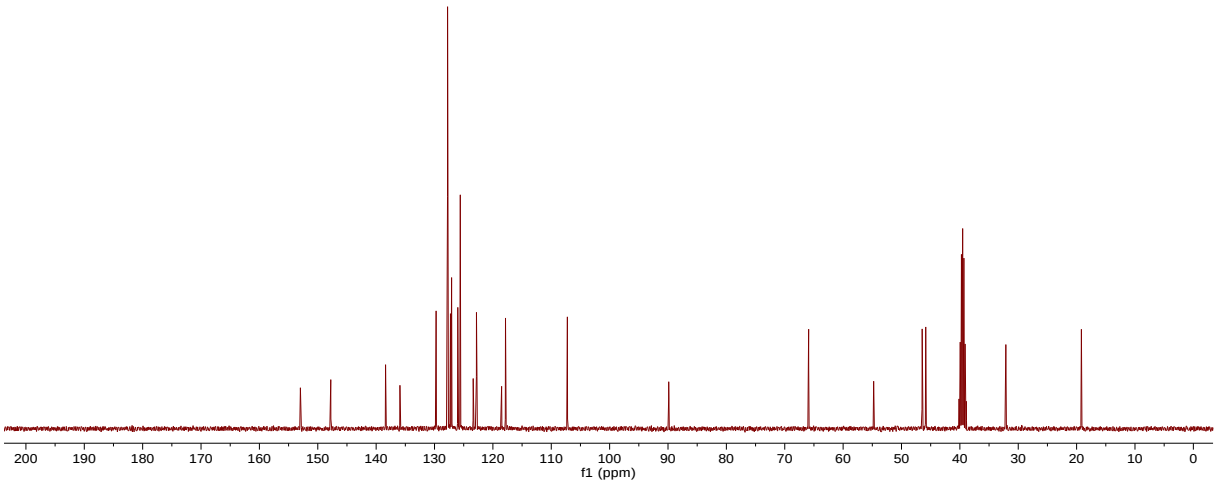
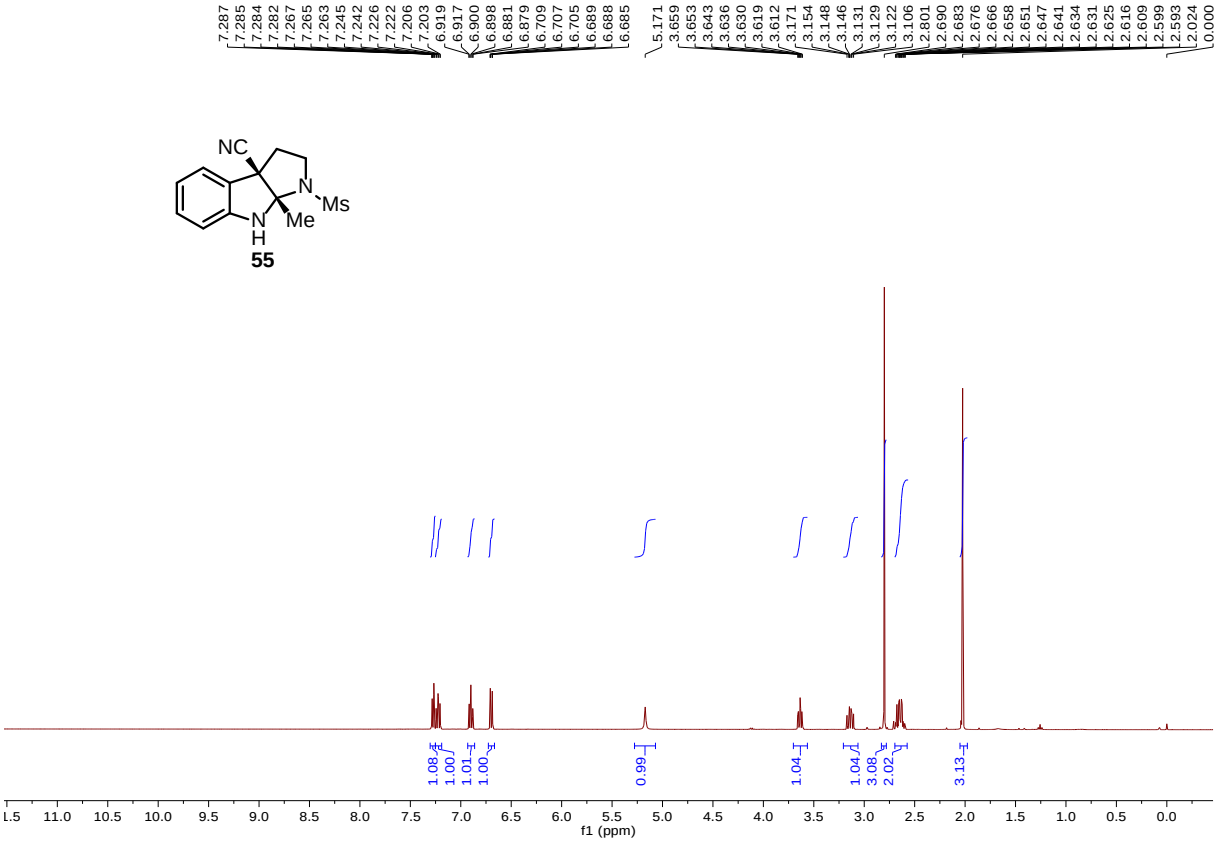
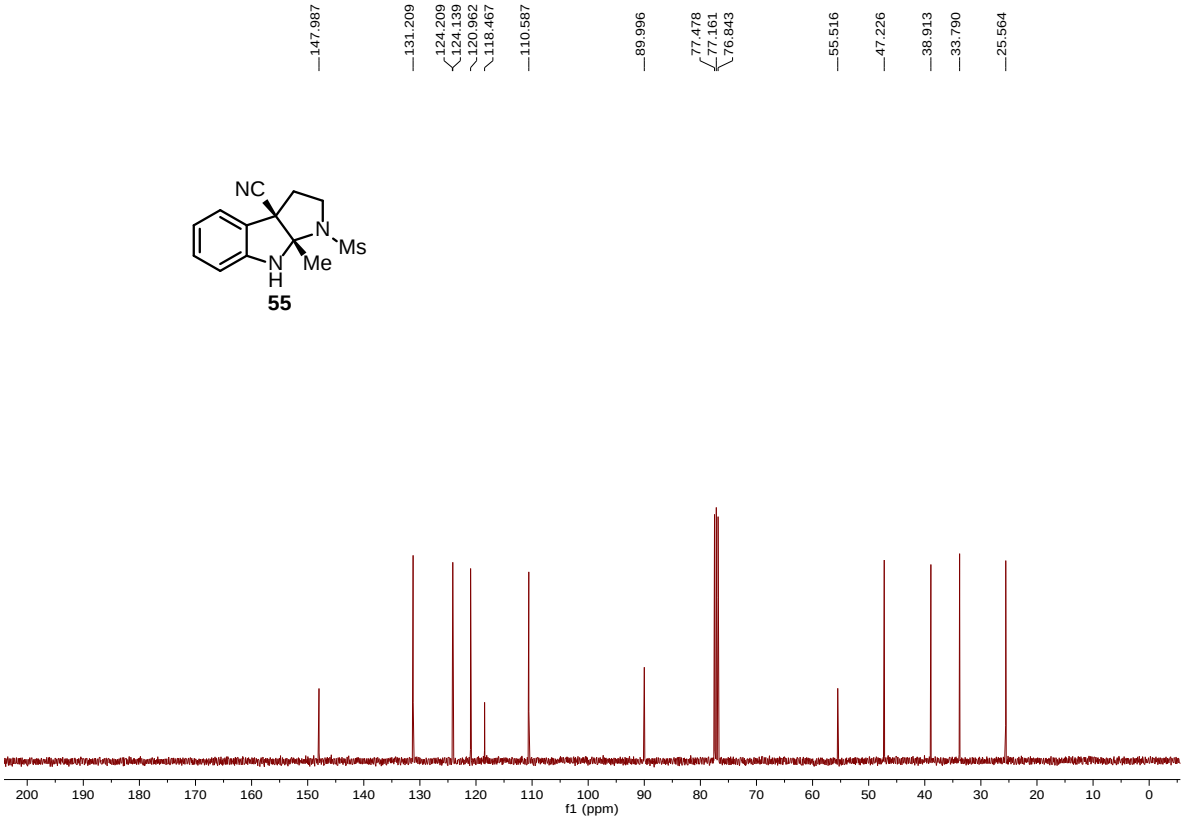


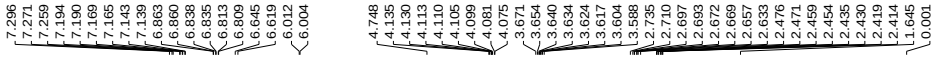
^{1}H NMR (400 MHz, Chloroform-*d*)



^{13}C NMR (101 MHz, Chloroform-*d*)



^{1}H NMR (300 MHz, Chloroform-*d*)



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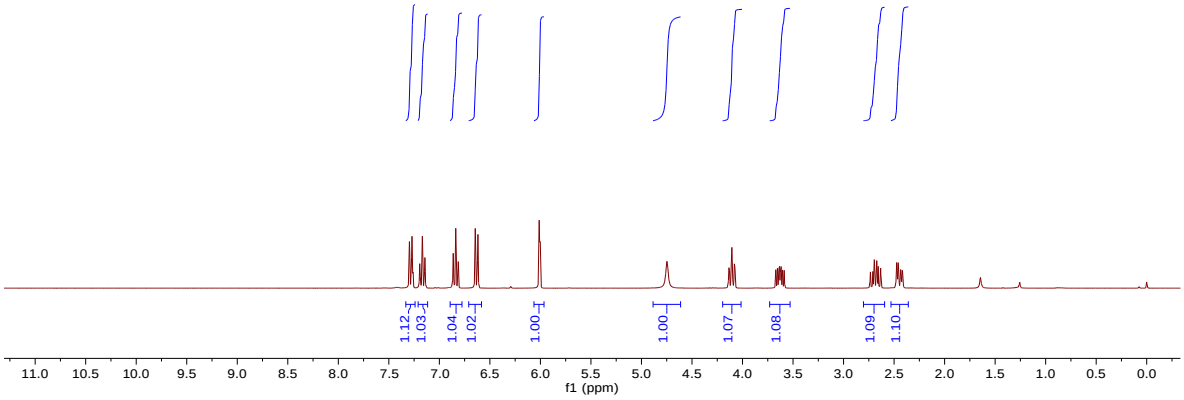
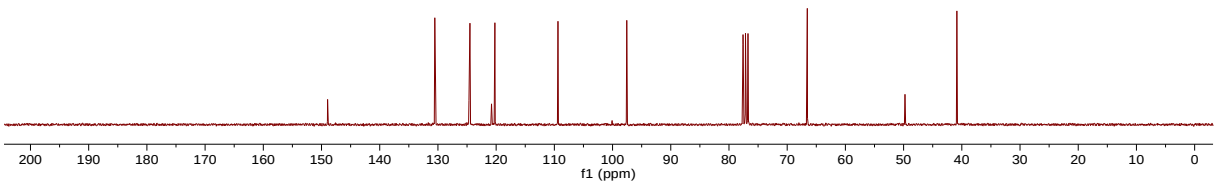
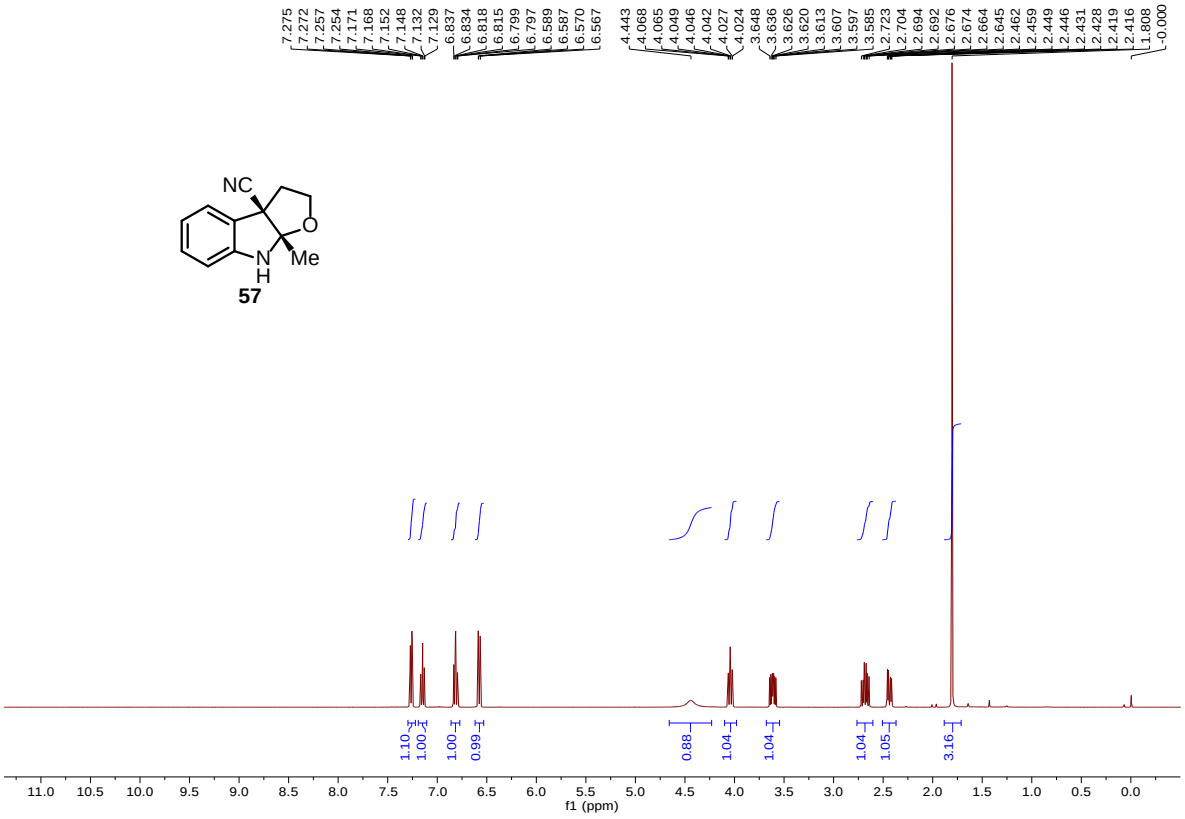


^{13}C NMR (75 MHz, Chloroform-*d*)

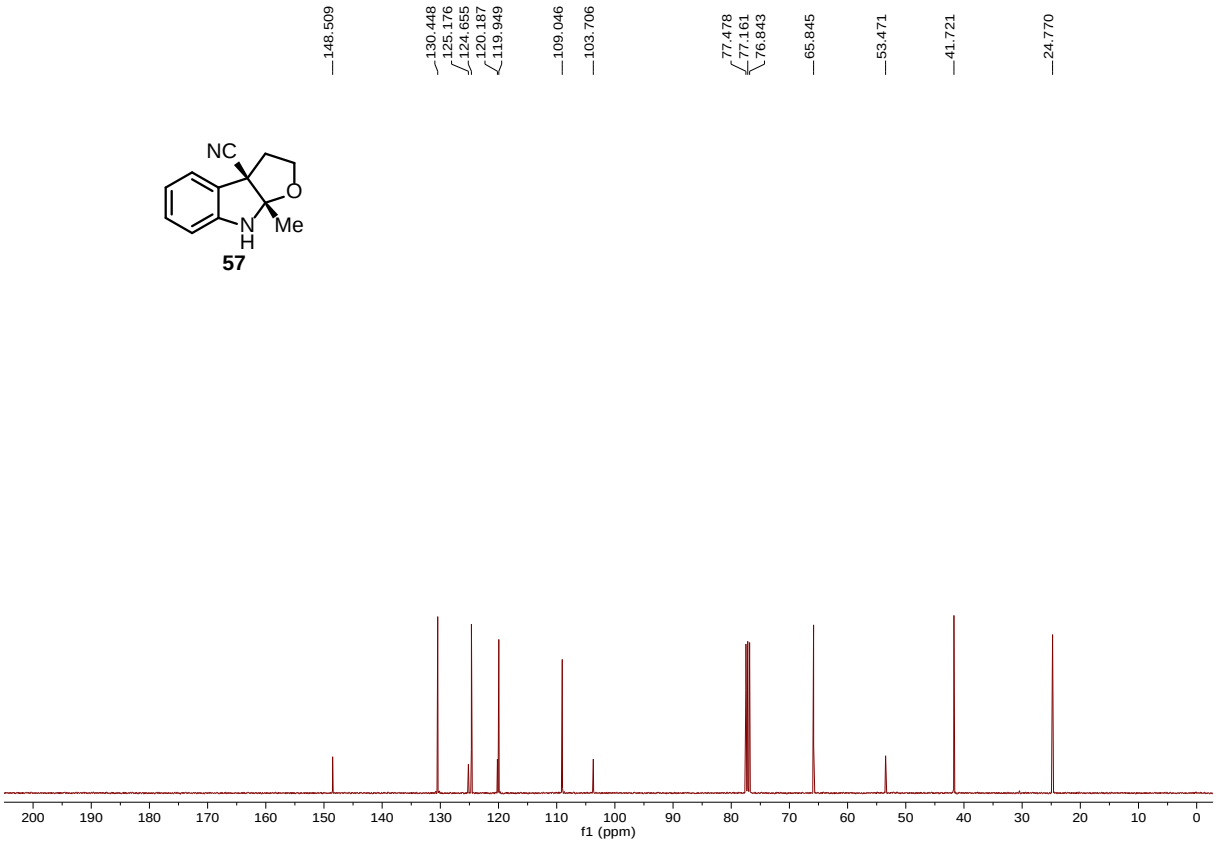
56



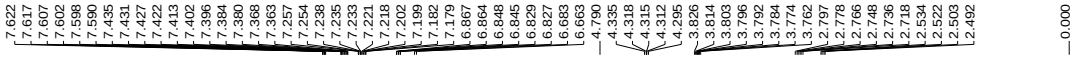
^{1}H NMR (400 MHz, Chloroform-*d*)

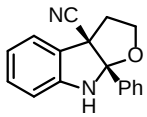


^{13}C NMR (101 MHz, Chloroform-*d*)



^{1}H NMR (400 MHz, Chloroform-*d*)





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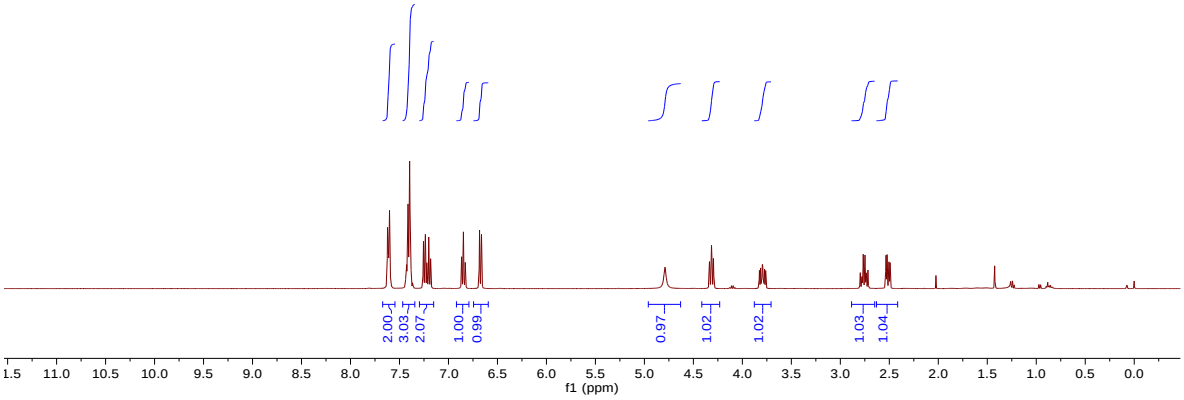
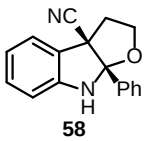


^{13}C NMR (101 MHz, Chloroform-*d*)



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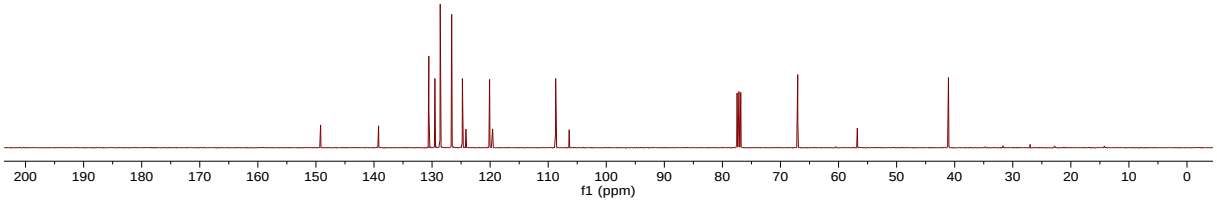
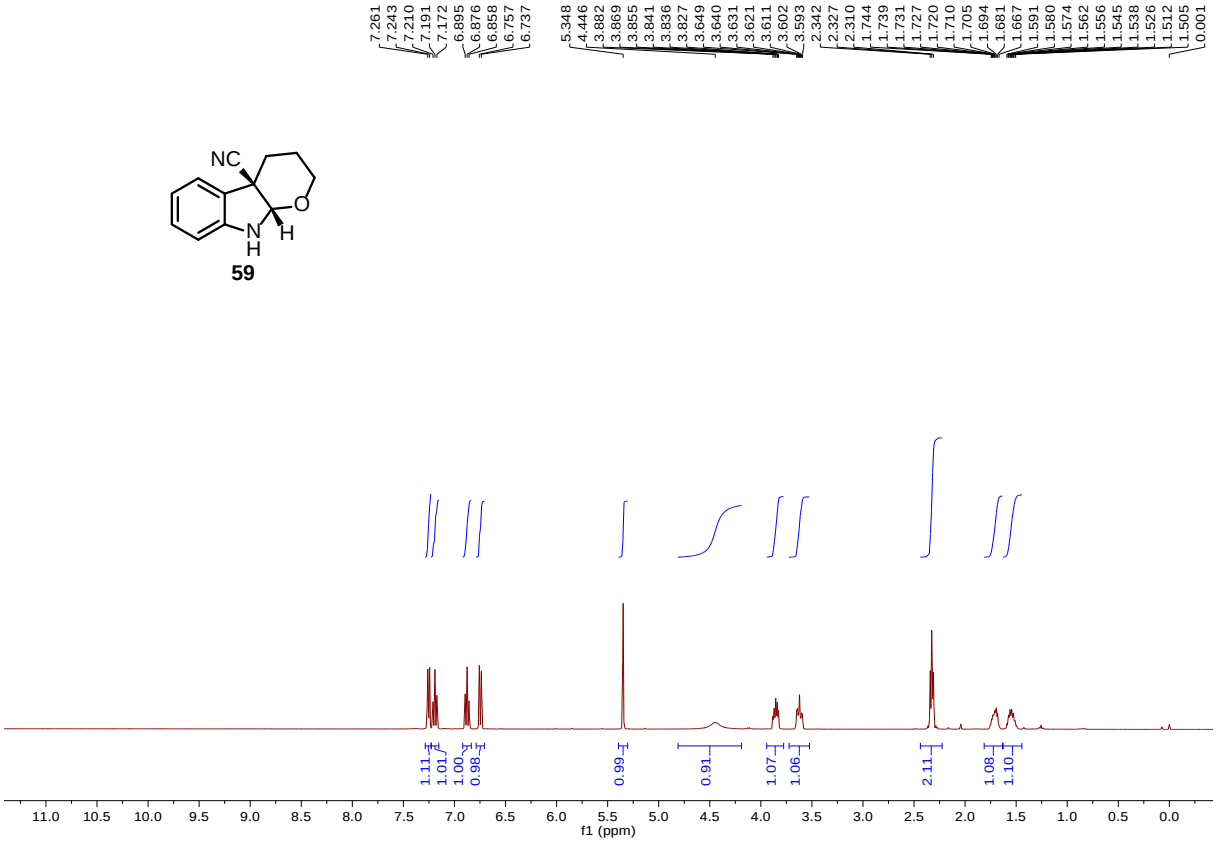
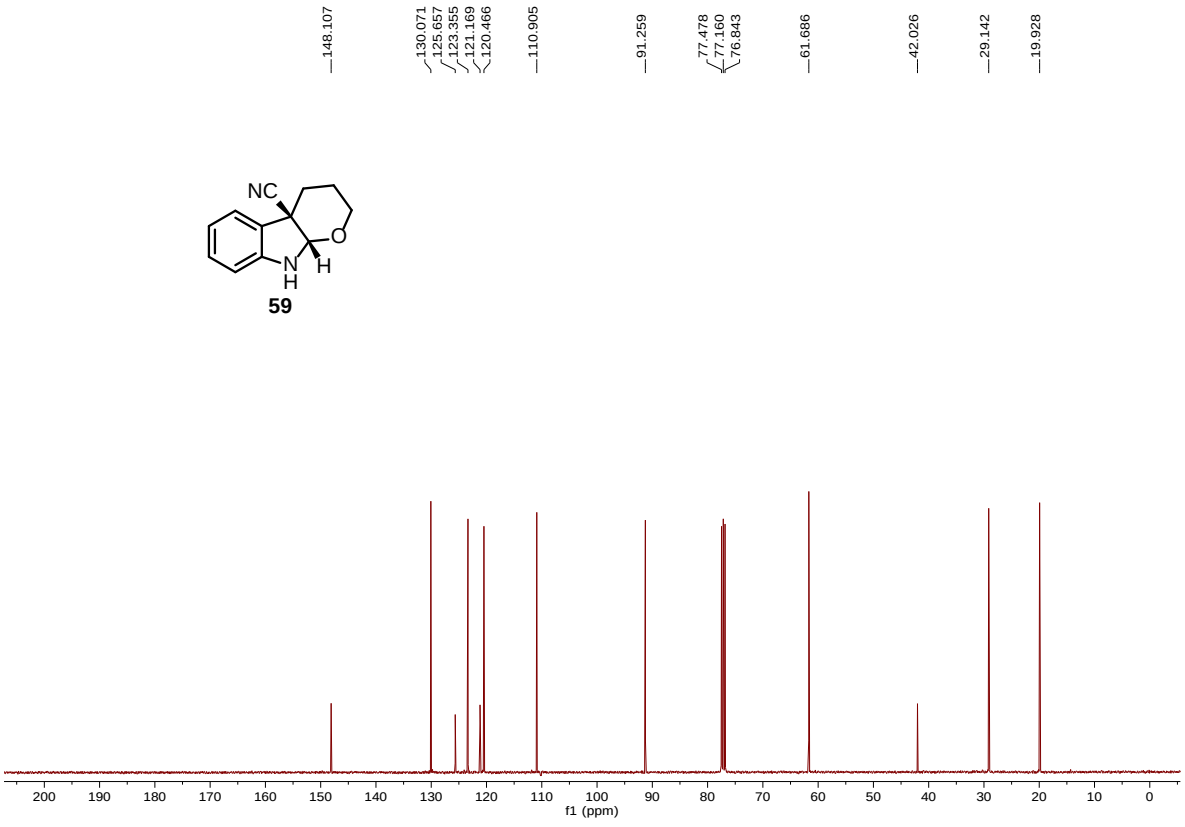


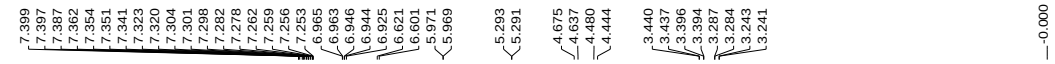
^{1}H NMR (400 MHz, Chloroform-*d*)

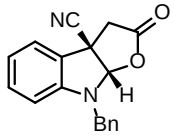


^{13}C NMR (101 MHz, Chloroform-*d*)



^{1}H NMR (400 MHz, Chloroform-*d*)





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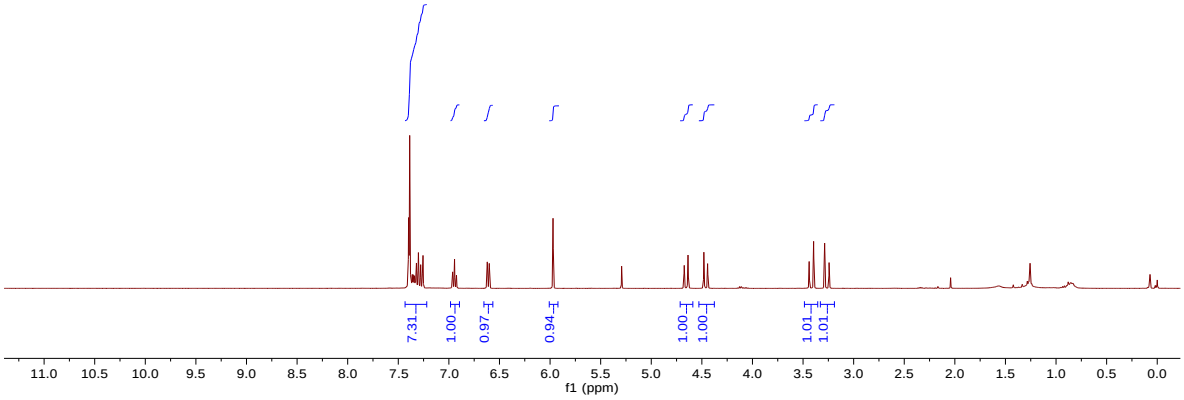
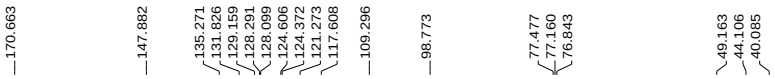
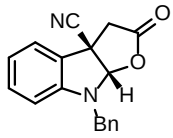


^{13}C NMR (101 MHz, Chloroform-*d*)





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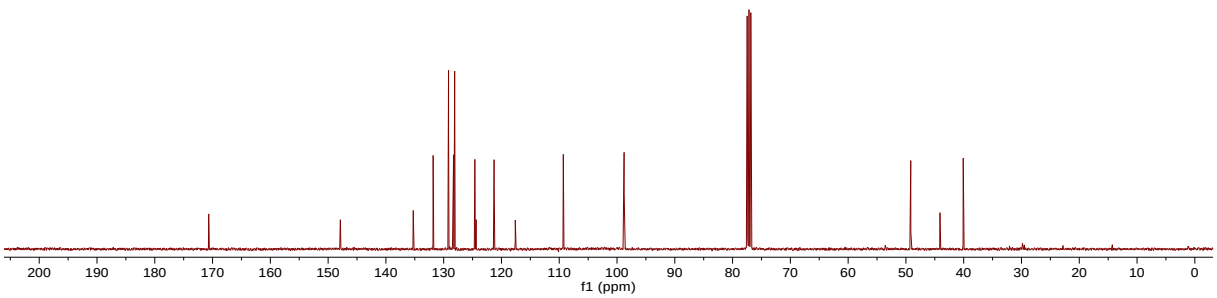
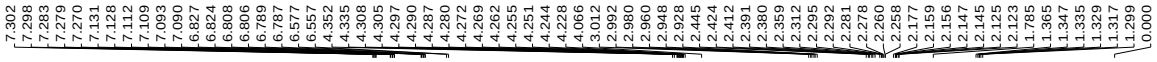
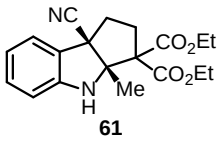


^{1}H NMR (400 MHz, Chloroform-*d*)





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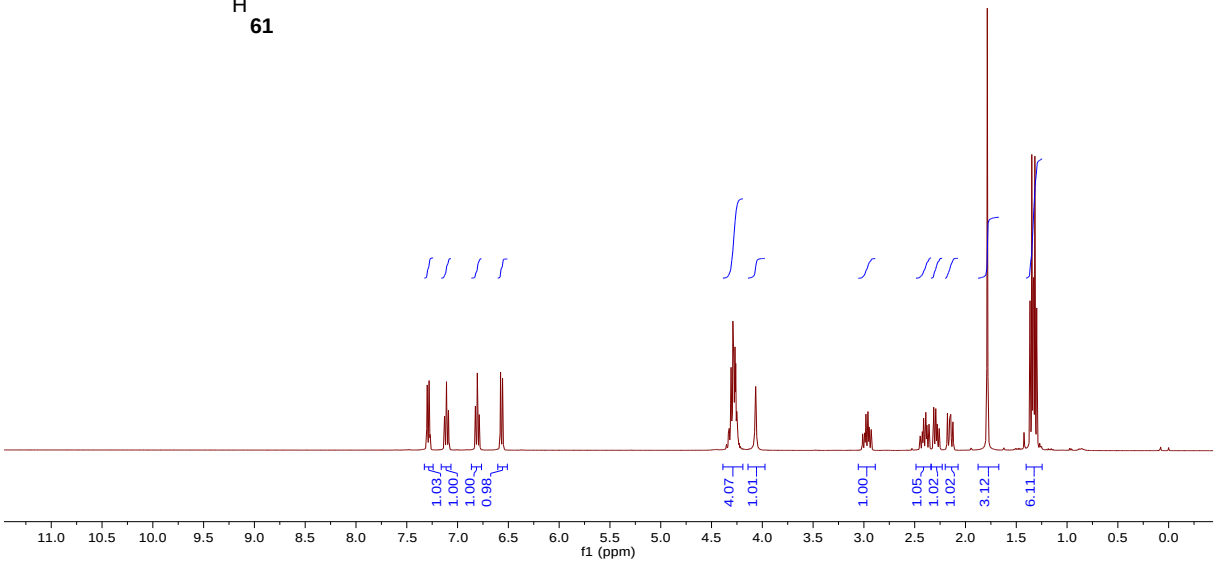
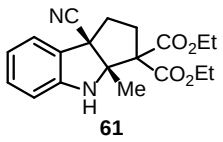


^{13}C NMR (101 MHz, Chloroform-*d*)



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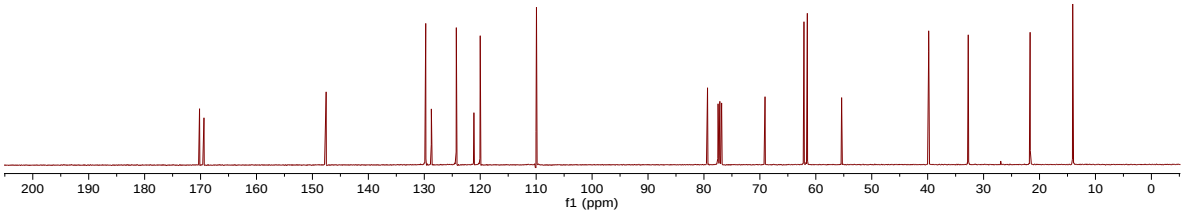
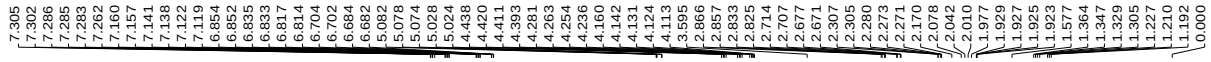
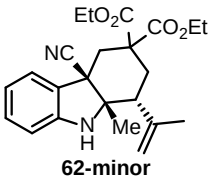
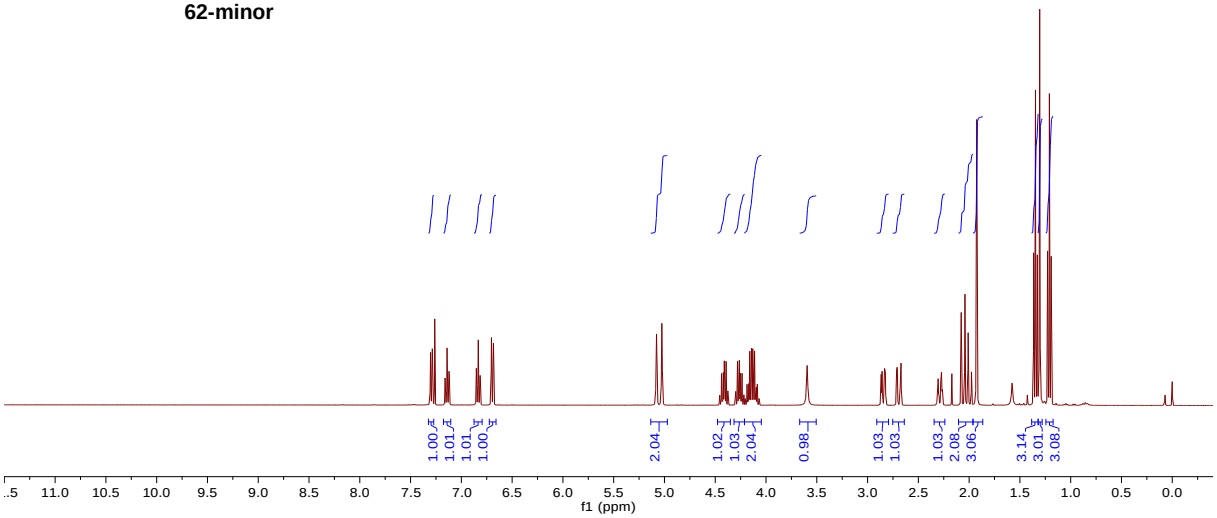


^{1}H NMR (400 MHz, Chloroform-*d*)

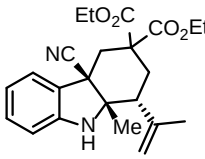




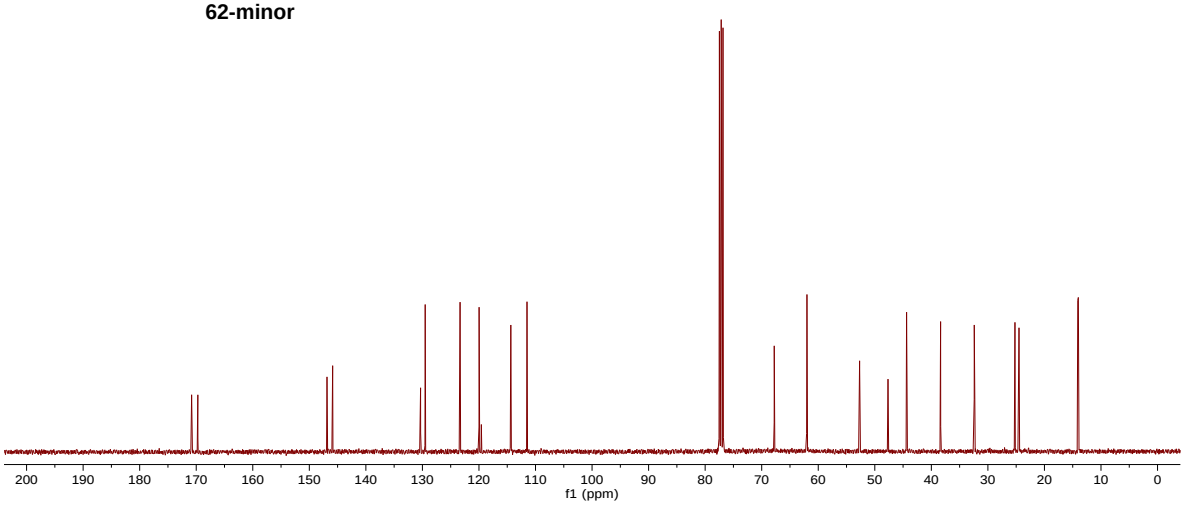
62-minor



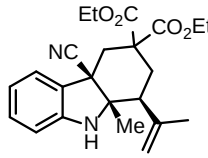
^{13}C NMR (101 MHz, Chloroform-*d*)



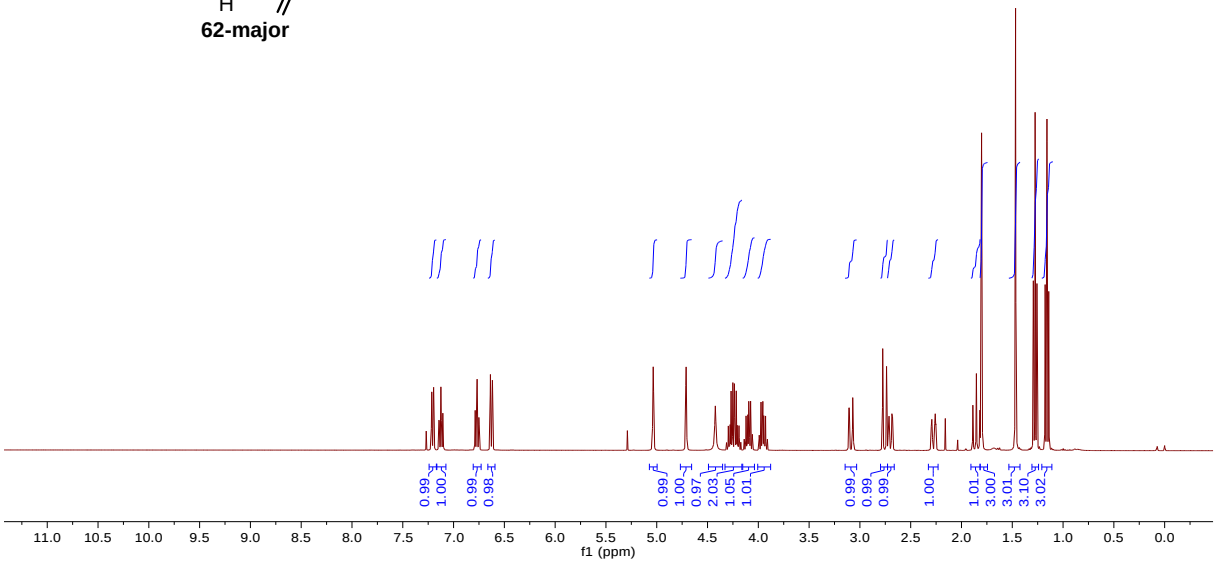
62-minor



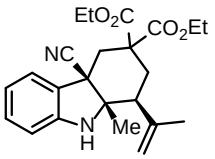
^{1}H NMR (400 MHz, Chloroform-*d*)



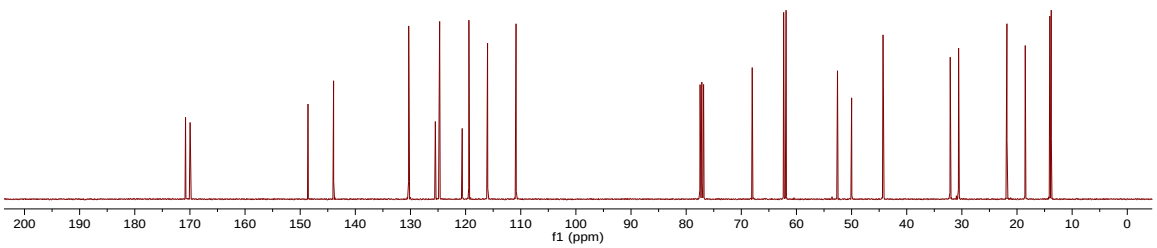
62-major



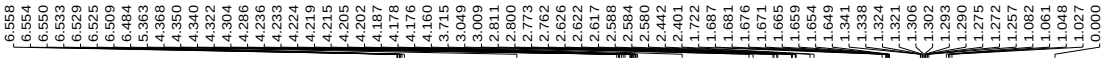
^{13}C NMR (101 MHz, Chloroform-*d*)

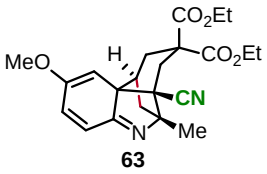


62-major



^{1}H NMR (400 MHz, Chloroform-*d*)





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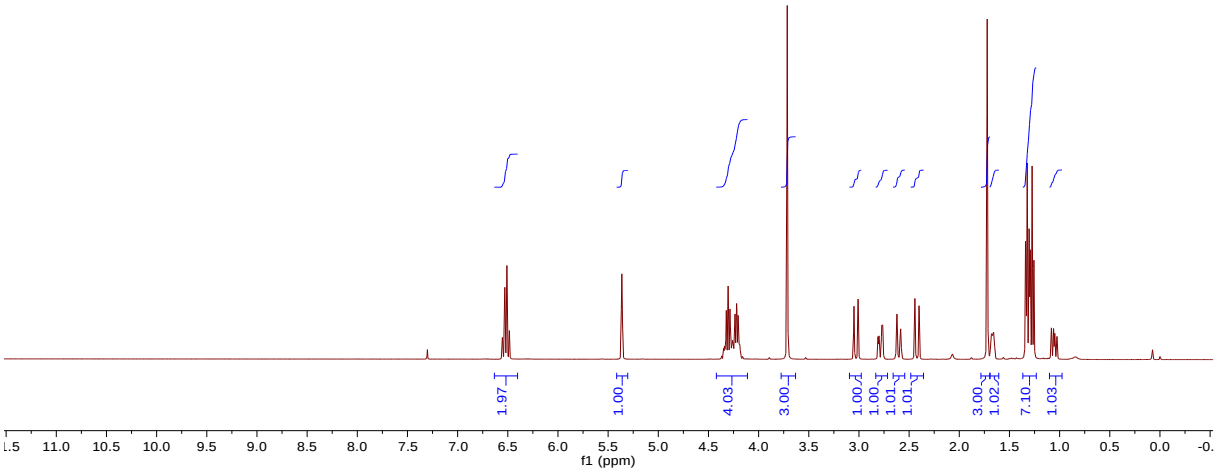
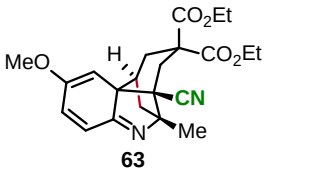


^{13}C NMR (101 MHz, Chloroform-*d*)



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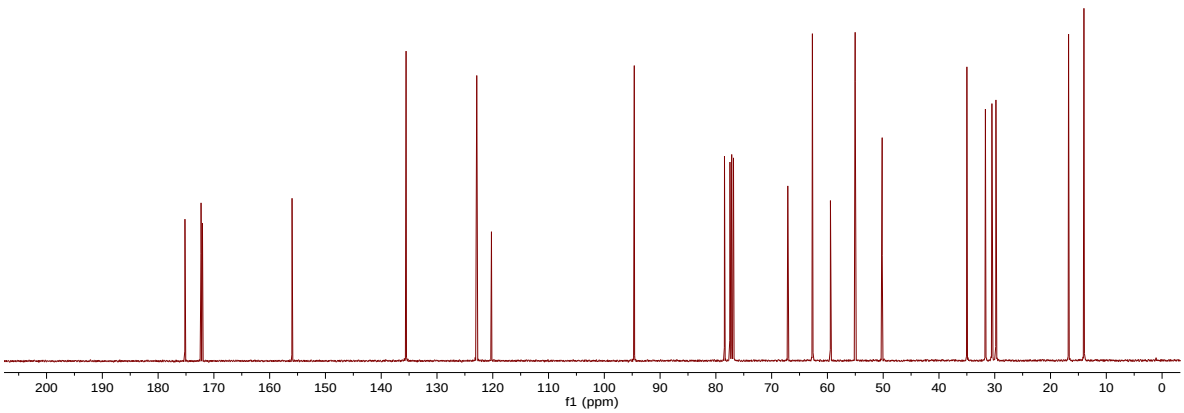
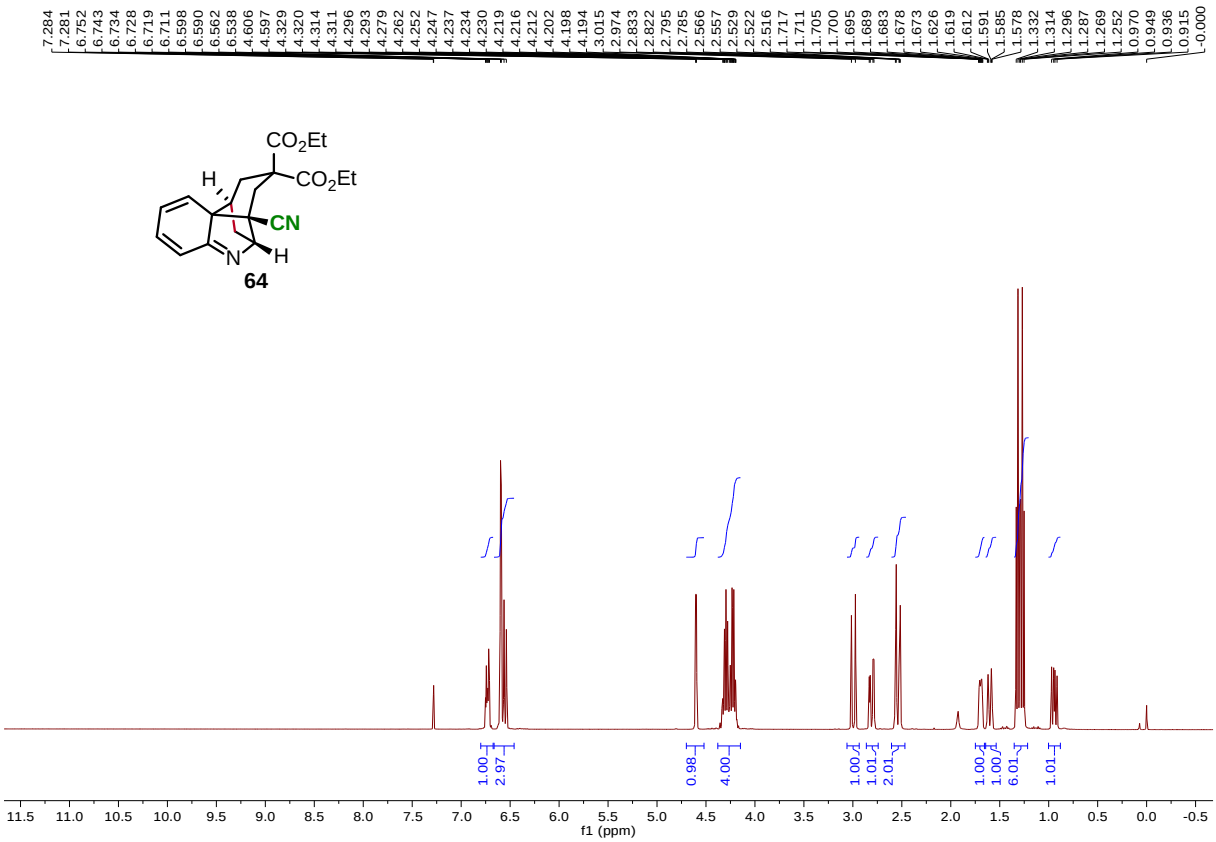
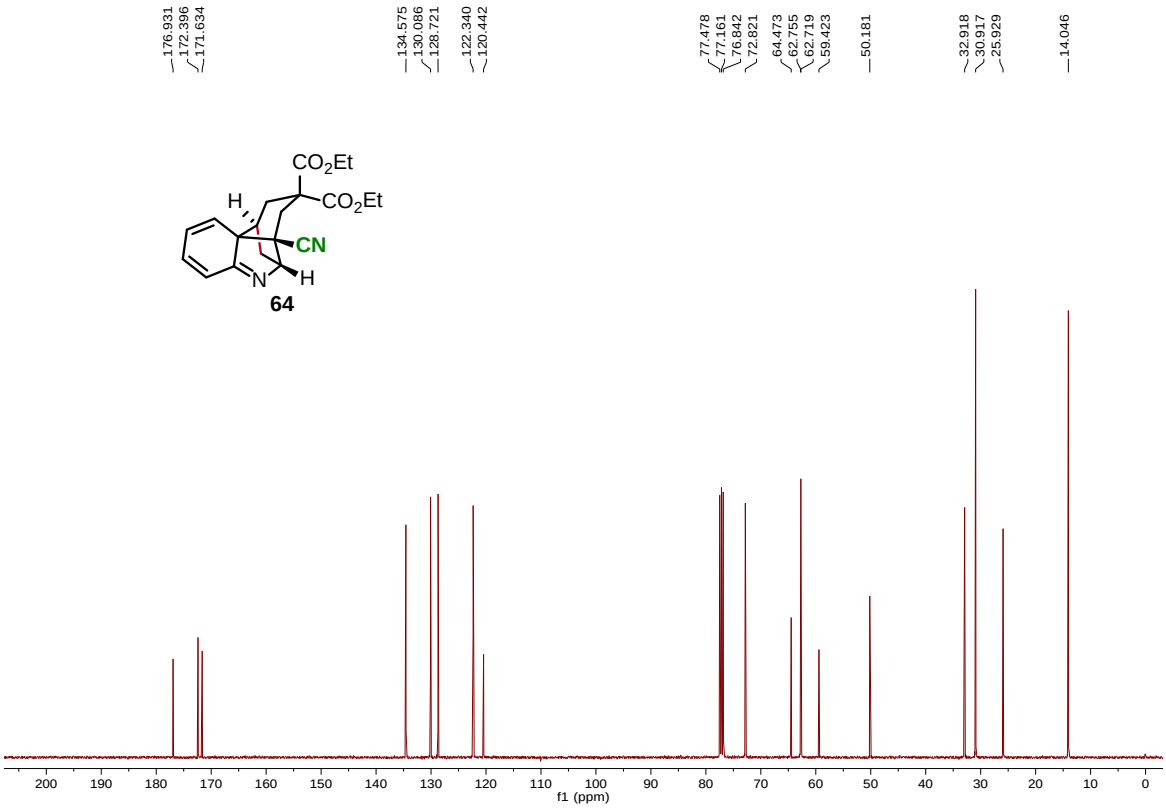


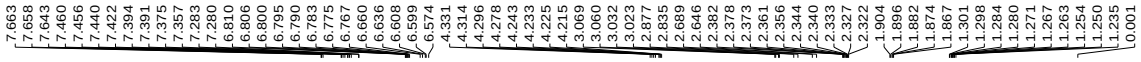
^{1}H NMR (400 MHz, Chloroform-*d*)

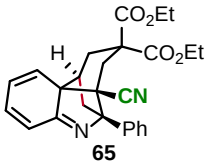


^{13}C NMR (101 MHz, Chloroform-*d*)



^{1}H NMR (400 MHz, Chloroform-*d*)





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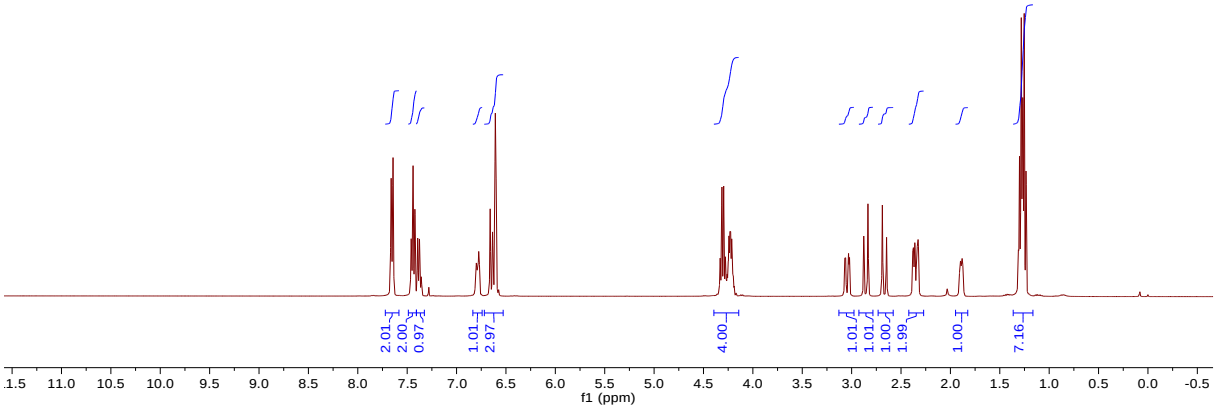

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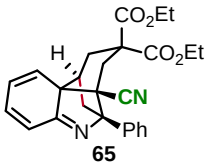

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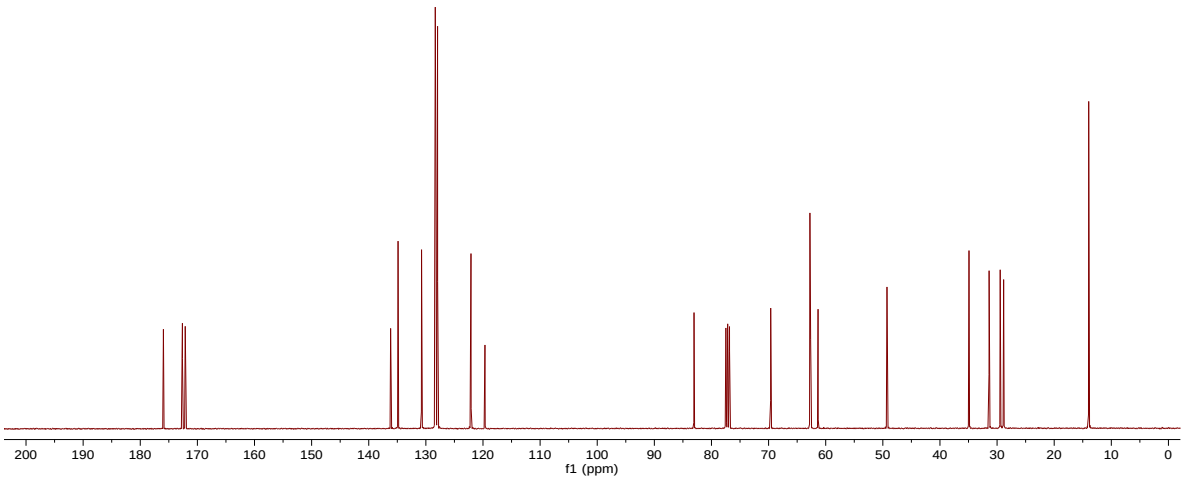
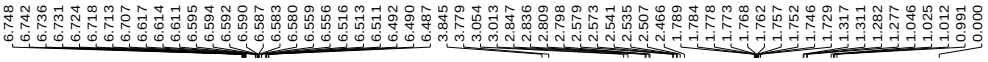
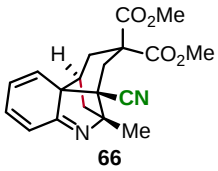


^{1}H NMR (400 MHz, Chloroform-*d*)





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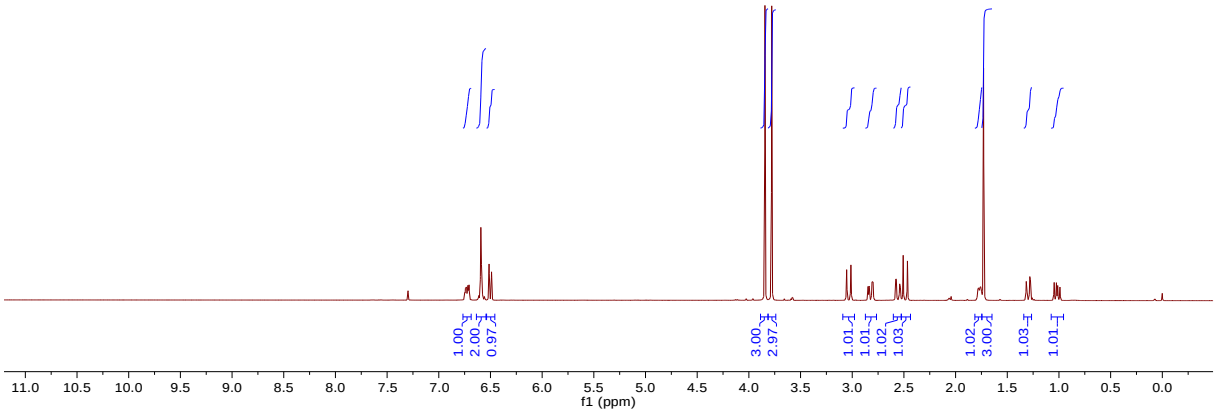

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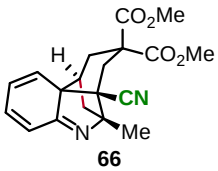

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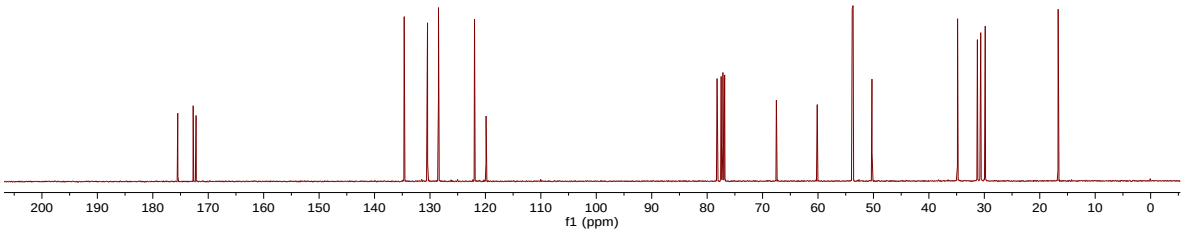

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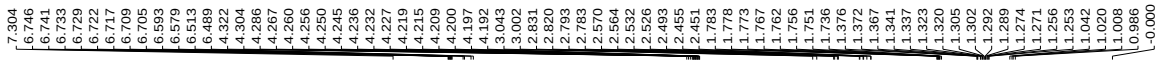

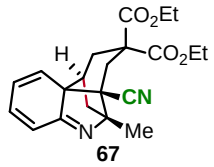

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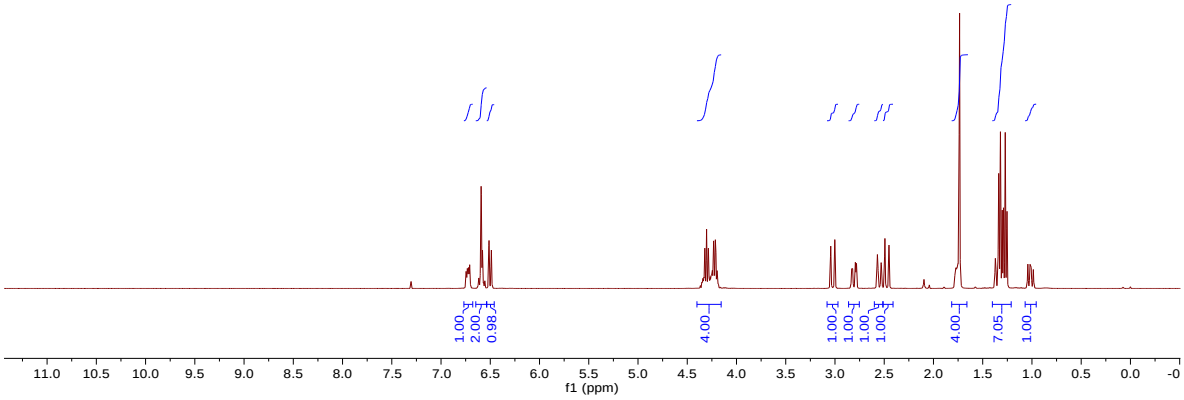
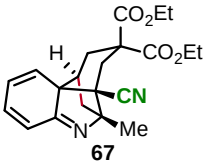


^{13}C NMR (101 MHz, Chloroform-*d*)



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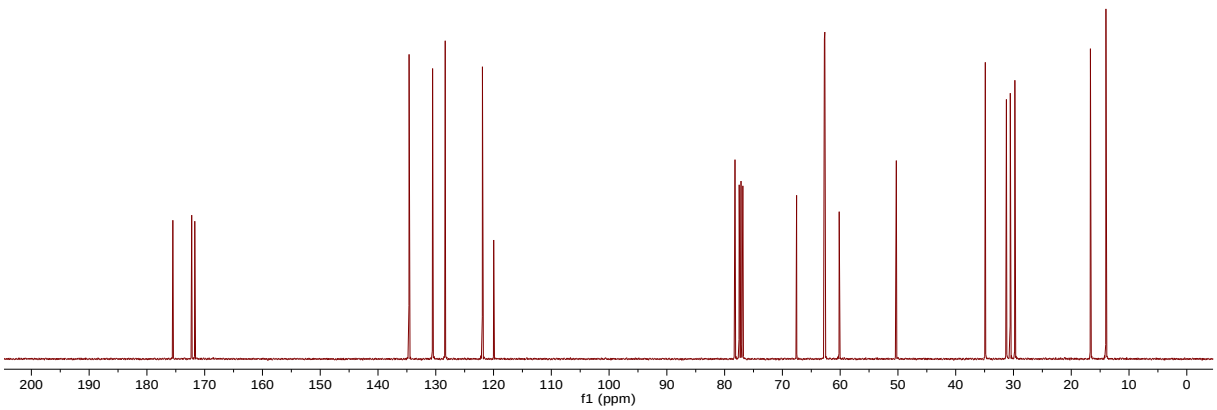
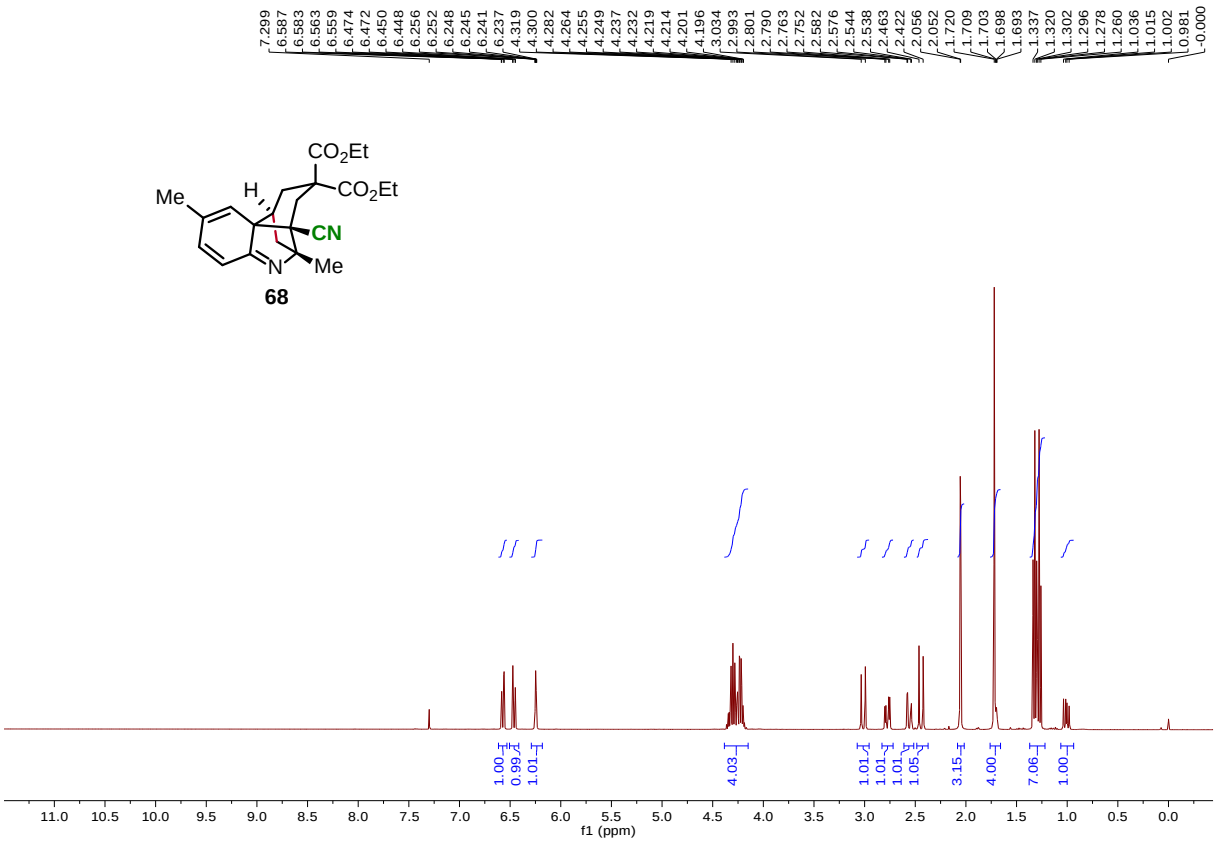


^{1}H NMR (400 MHz, Chloroform-*d*)



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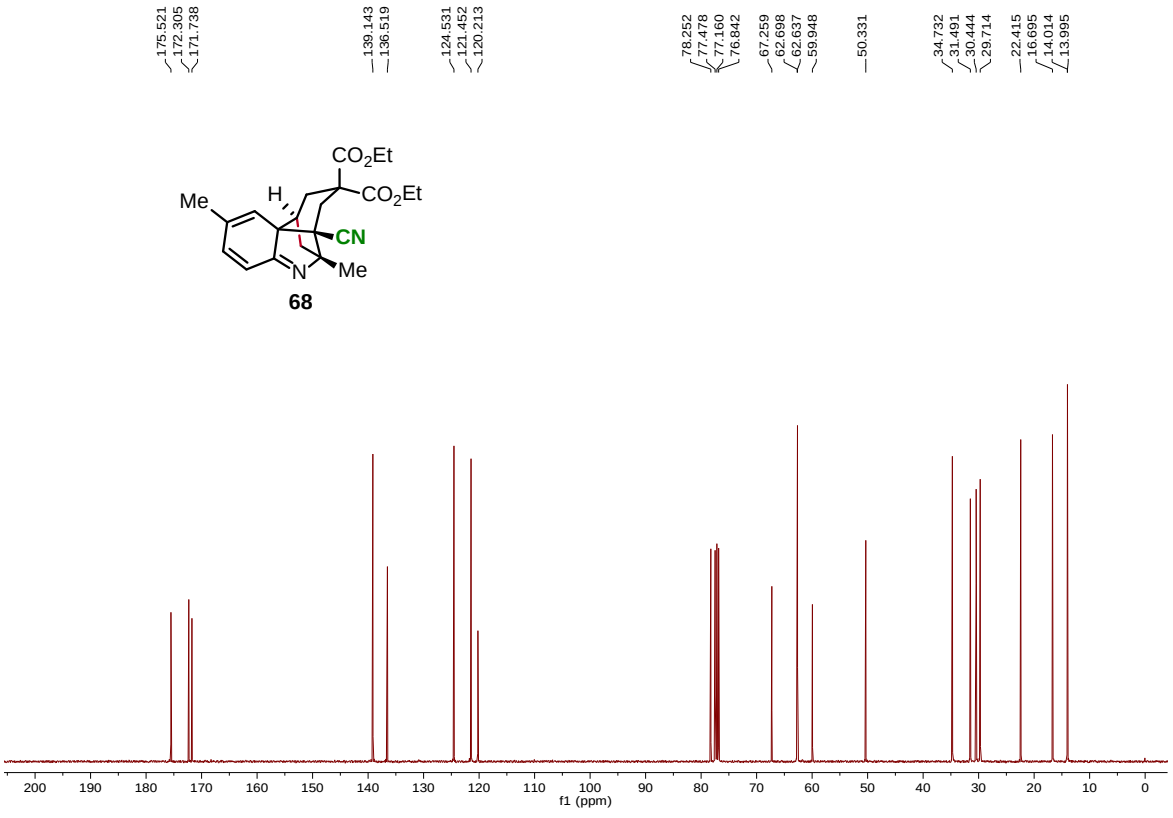
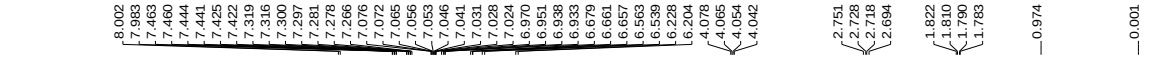
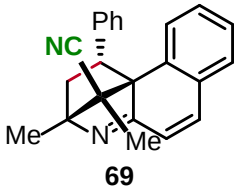


^{1}H NMR (400 MHz, Chloroform-*d*)





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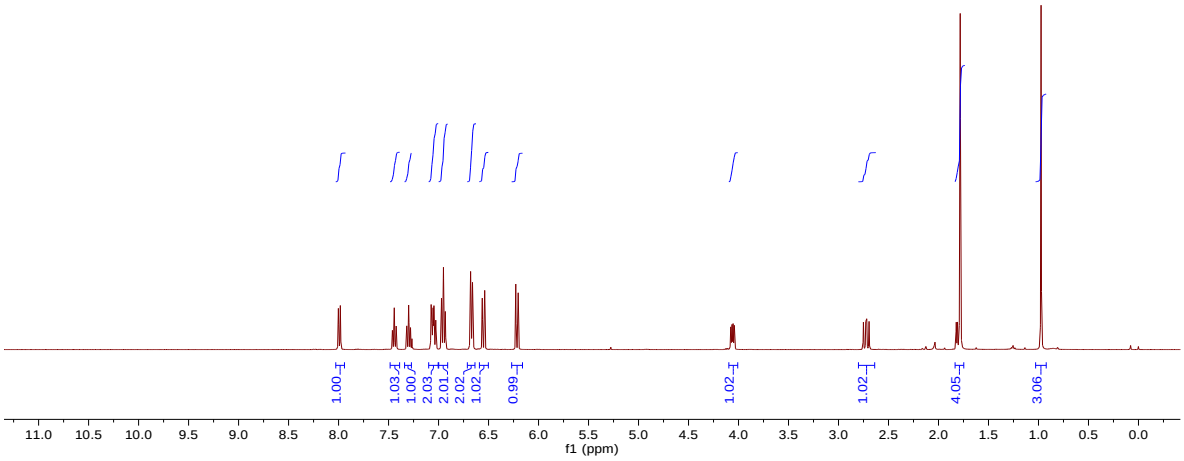

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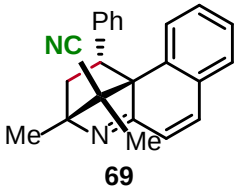

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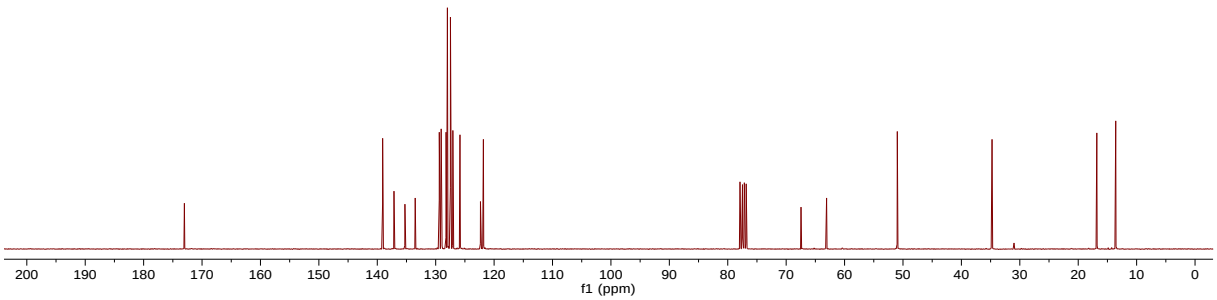

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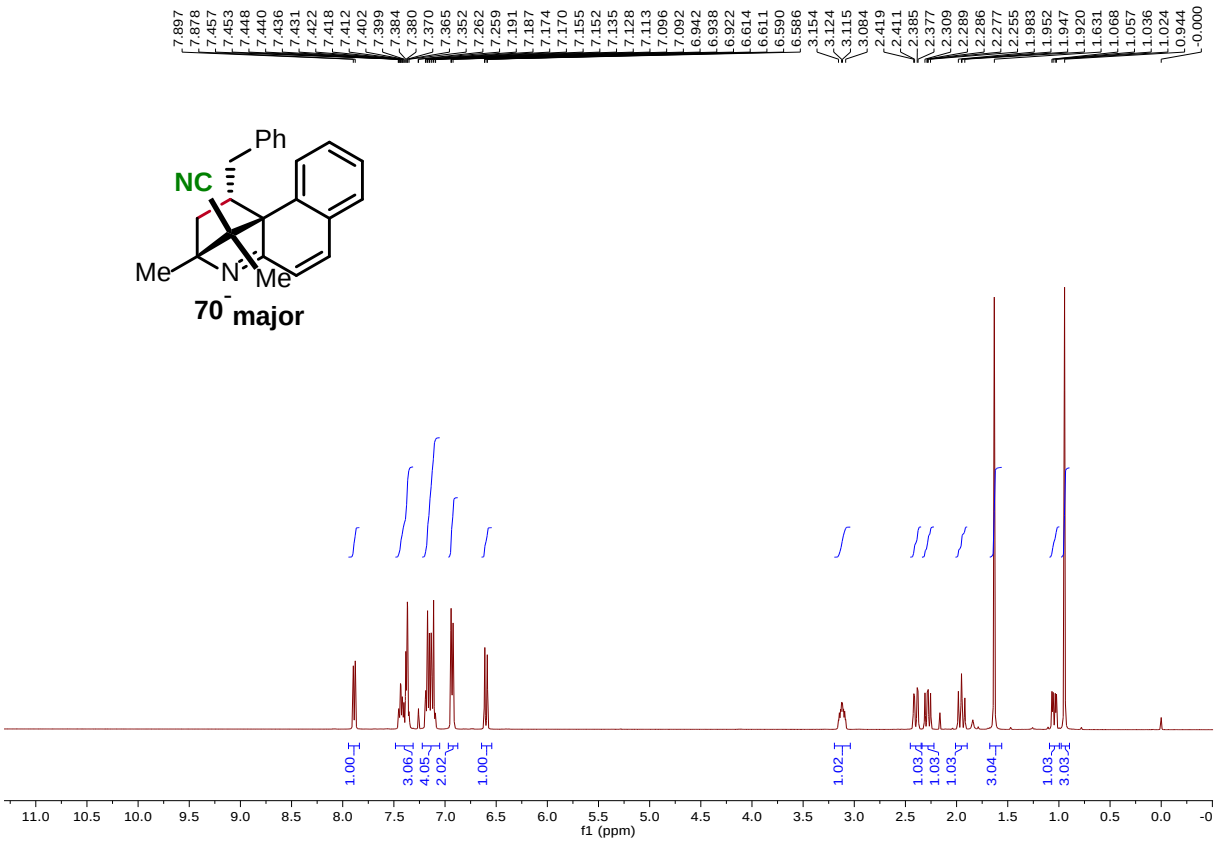
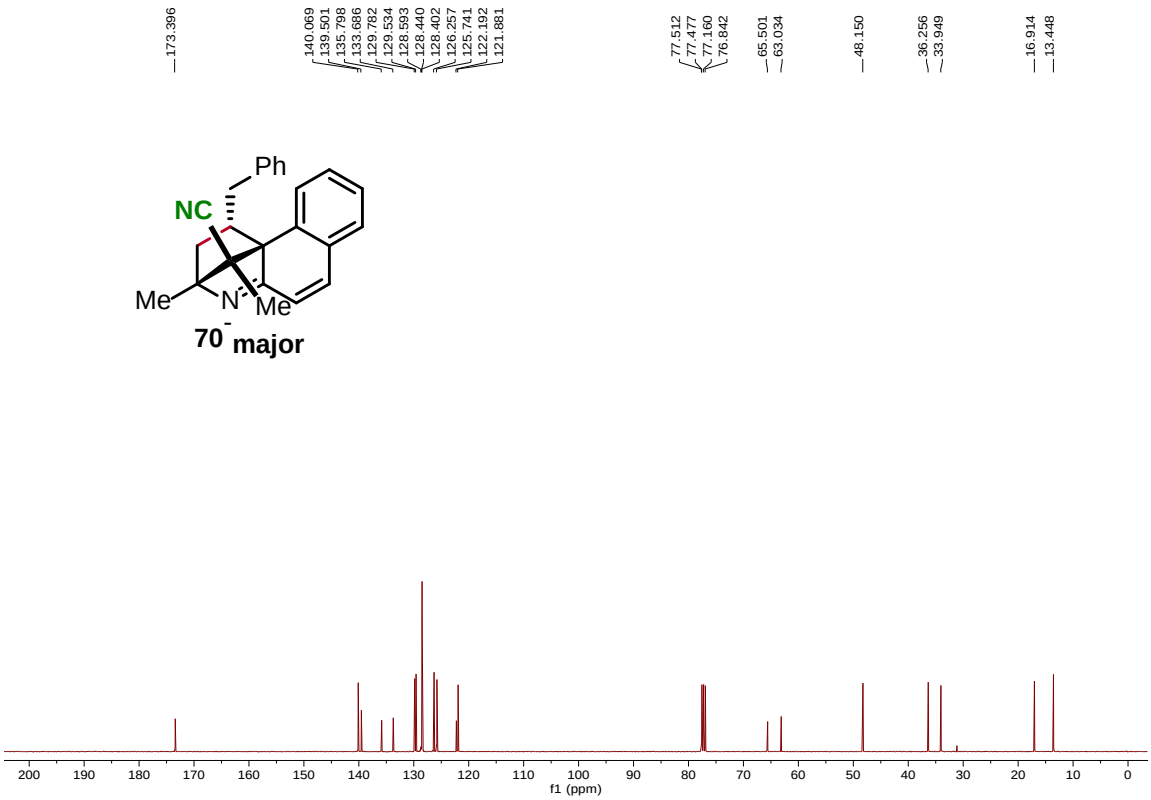


^{13}C NMR (101 MHz, Chloroform-*d*)



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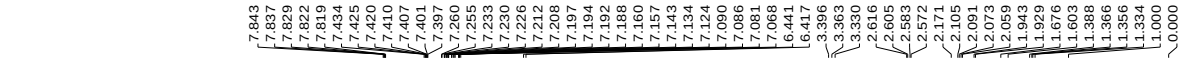
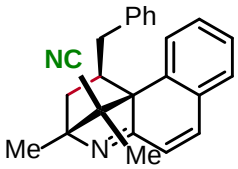
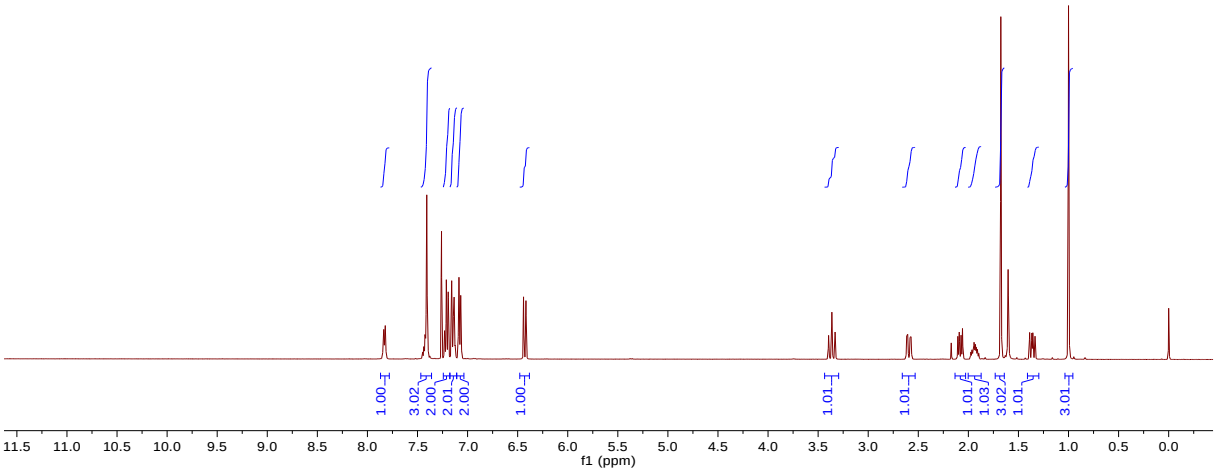




70˙minor



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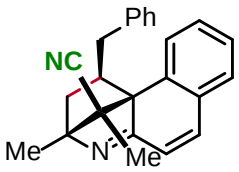

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