Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2020

Substrate-controlled, PBu_3-catalyzed annulation of phenacylmalononitriles with allenoates enables tunable access to cyclopentenes

SUPPORTING INFORMATION

Content:

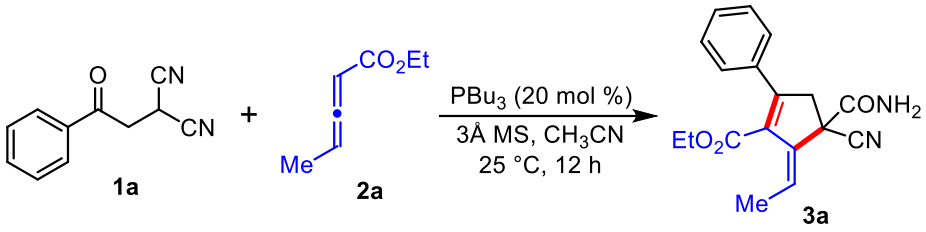
General experimental information

Unless otherwise specified, all reactions were performed in oven-dried glasswares under nitrogenous atmosphere using dry deoxygenated solvent. The reactions were monitored by TLC visualized by UV (254 nm) and/or with iodine. Column chromatography was performed on 100-200 mesh silica gel using the gradient system ethyl acetate-hexane. NMR data were recorded at Bruker AV 400 MHz in DMSO-d_6/$CDCl_3$ using as internal standards the residual DMSO signal for ^1H NMR (δ = 2.50 ppm), $CHCl_3$ (δ = 7.26 ppm). The corresponding deuterated solvent signal for ^{13}C were assigned as DMSO (δ = 39.51 ppm), $CHCl_3$ (δ = 77.16 ppm). Coupling constants are given in Hertz (Hz) and the classical abbreviations are used to describe the signal multiplicities. Melting points were measured with a Büchi B-540 apparatus and are uncorrected. High resolution mass spectra were obtained using Q-TOF mass spectrometer. All commercially available reagents were used as received. All allenic esters [1] and phenacylmalononitriles [2] were synthesized following literature procedure.

---

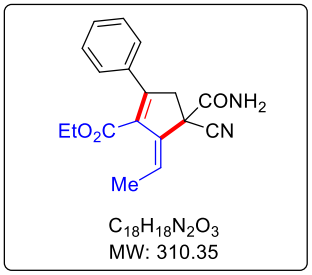
1. L. Rout and A. M. Harned, *Chem. - Eur. J.* 2009, **15**, 12926−12928.
2. (a) M. A. Saleh, S. M. Moustafa, M. Herbert, K. Heinz and H. E. Mohamed, *Molecules* 2009, **14**, 798-806; (b) F. M. Abdelrazek, H. M. Hassaneen, E. M. Nassar and A. Jager, *J. Heterocycl. Chem.* 2014, **51**, 475-479.

General procedure for the synthesis of substituted cyclopentenes 3a-3t



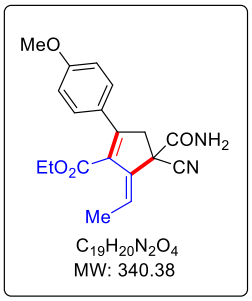
An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-(2-oxo-2-phenylethyl)malononitrile **1a** (37 mg, 0.20 mmol) and 3Å MS (100 mg). Subsequently, it was sealed, evacuated, and backfilled with nitrogen. Freshly distilled CH_3CN (2.0 mL) and ethyl penta-2,3-dienoate **2a** (50 mg, 0.40 mmol) were added via syringe followed by the addition of PBu_3 (8 mg, 0.04 mmol). The reaction mixture was stirred at 25 ˚C for 12 h. After the completion of the reaction, as indicated by TLC, the solvent was evaporated under reduced pressure. The residue was purified using column chromatography (100-200 mesh silica gel) using ethyl acetate/hexane as the eluent.

Compound 3a: ethyl 4-carbamoyl-4-cyano-5-ethylidene-2-phenylcyclopent-1-ene-1-carboxylate



Following the general procedure, treatment of 2-(2-oxo-2-phenylethyl)malononitrile **1a** (37 mg, 0.20 mmol) with ethyl penta-2,3-dienoate **2a** (50 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 ˚C for 12 h followed by column chromatography afforded the product **3a** as white solid (47 mg, 75%). **R_f** (EtOAc/Hexane : 4/6) = 0.30. **Mp** 150-152 ˚C. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 169.1 (C), 167.3 (C), 146.1 (C), 140.2 (C), 133.5 (C), 129.7 (CH), 129.5 (C), 128.7 (CH), 128.7 (CH), 127.1 (CH), 127.1 (CH), 122.7 (CH), 120.0 (C), 61.9 (CH_2), 51.4 (C), 44.7 (CH_2), 14.0 (CH_3), 13.9 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 7.35 (s, 5H), 6.40 (s, 1H), 6.36 (s, 1H), 5.94 (q, *J* = 7.4 Hz, 1H), 4.29-4.21 (m, 2H), 3.59 (d, *J* = 17.2 Hz, 1H), 3.52 (d, *J* = 17.2 Hz, 1H), 1.79 (d, *J* = 7.6 Hz, 3H), 1.23 (t, *J* = 7.2 Hz, 3H). **HRMS** for $C_{18}H_{19}N_2O_3^+$: calcd. $[M+H]^+$: 311.1390, found: 311.1387.

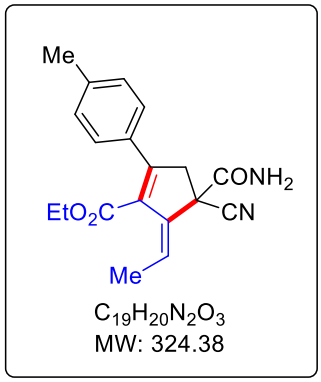
Compound 3b: ethyl 4-carbamoyl-4-cyano-5-ethylidene-2-(4-methoxyphenyl)cyclopent-1-ene-1-carboxylate



Following the general procedure, treatment of 2-(2-(4-methoxyphenyl)-2-oxoethyl)malononitrile **1b** (43 mg, 0.20 mmol) with ethyl penta-2,3-dienoate **2a** (50 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 ˚C for 12 h followed by column chromatography afforded the product **3b** as white solid (42 mg, 62%). **R_f** (EtOAc/Hexane : 4/6) = 0.25. **Mp** 137-139 ˚C. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 168.9 (C), 167.7 (C), 160.8 (C), 145.5 (C), 140.4 (C), 128.8

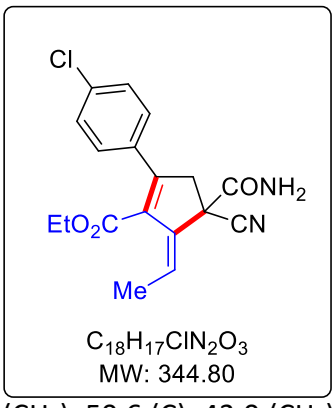
(CH), 128.8 (CH), 127.8 (C), 125.9 (C), 121.8 (CH), 120.0 (C), 114.2 (CH), 114.2 (CH), 61.9 (CH_2), 55.5 (CH_3), 51.6 (C), 44.6 (CH_2), 14.0 (CH_3), 14.0 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 7.31 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.28 (s, 1H), 5.90 (q, *J* = 7.4 Hz, 2H), 4.33-4.24 (m, 2H), 3.82 (s, 3H), 3.58 (d, *J* = 17.2 Hz, 1H), 3.51 (d, *J* = 16.8 Hz, 1H), 1.79 (d, *J* = 7.6 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H). **HRMS** for $C_{19}H_{21}N_2O_4^+$: calcd. $[M+H]^+$: 341.1496, found: 341.1496.

Compound 3c: ethyl 4-carbamoyl-4-cyano-5-ethylidene-2-(*p*-tolyl)cyclopent-1-ene-1-carboxylate



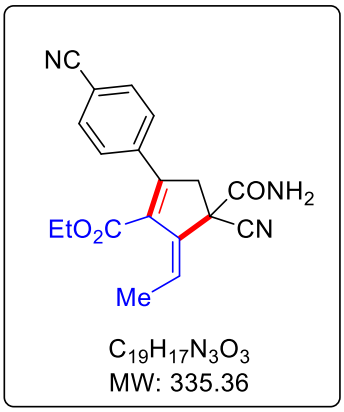
Following the general procedure, treatment of 2-(2-oxo-2-(p-tolyl)ethyl)malononitrile **1c** (40 mg, 0.20 mmol) with ethyl penta-2,3-dienoate **2a** (50 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 °C for 12 h followed by column chromatography afforded the product **3c** as brown solid (40 mg, 62%). **R_f**(EtOAc/Hexane : 4/6) = 0.30. **Mp** 168-170 °C. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 168.9 (C), 167.5 (C), 146.0 (C), 140.3 (C), 140.0 (C), 130.6 (C), 129.5 (CH), 129.5 (CH), 128.8 (C), 127.1 (CH), 127.1 (CH), 122.2 (CH), 120.0 (C), 61.9 (CH_2), 51.6 (C), 44.7 (CH_2), 21.5 (CH_3), 14.0 (CH_3), 14.0 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 7.25 (d, *J* = 6.4 Hz, 2H), 7.18-7.16 (m, 2H), 6.28 (s, 1H), 5.99 (s, 1H), 5.92 (q, *J* = 7.6 Hz, 1H), 4.32-4.21 (m, 2H), 3.59 (d, *J* = 18.0 Hz, 1H), 3.52 (d, *J* = 16.8 Hz, 1H), 2.36 (s, 3H), 1.80 (d, *J* = 7.2 Hz, 3H), 1.27 (t, *J* = 7.0 Hz, 3H). **HRMS** for $C_{19}H_{21}N_2O_3^+$: calcd. $[M+H]^+$: 325.1547, found: 325.1544.

Compound 3d: ethyl 4-carbamoyl-2-(4-chlorophenyl)-4-cyano-5-ethylidenecyclopent-1-ene-1-carboxylate



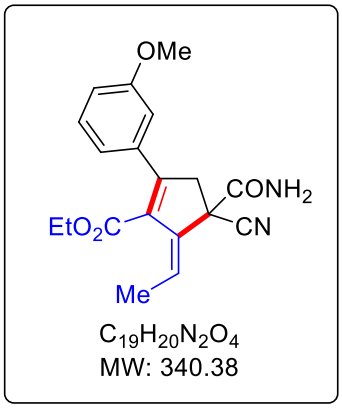
Following the general procedure, treatment of 2-(2-(4-chlorophenyl)-2-oxoethyl)malononitrile **1d** (44 mg, 0.20 mmol) with ethyl penta-2,3-dienoate **2a** (50 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 °C for 12 h followed by column chromatography afforded the product **3d** as white solid (45 mg, 65%). **R_f**(EtOAc/Hexane : 4/6) = 0.30. **Mp** 140-142 °C. **^{13}C NMR** (100 MHz, δ ppm/DMSO-d_6): 167.4 (C), 166.9 (C), 144.0 (C), 140.4 (C), 133.9 (C), 132.2 (C), 129.0 (C), 128.7 (CH), 128.7 (CH), 128.7 (CH), 128.7 (CH), 121.3 (CH), 120.5 (C), 61.6 (CH_2), 50.6 (C), 43.0 (CH_2), 13.6 (CH_3), 13.3 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/DMSO-d_6): 7.70 (s, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 5.94 (q, *J* = 7.6 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 3.59-3.49 (m, 2H), 1.70 (d, *J* = 7.2 Hz, 3H), 1.20 (t, *J* = 7.2 Hz, 3H). **HRMS** for $C_{18}H_{18}ClN_2O_3^+$: calcd. $[M+H]^+$: 345.1000, found: 345.0996.

Compound 3e: ethyl 4-carbamoyl-4-cyano-2-(4-cyanophenyl)-5-ethylidenecyclopent-1-ene-1-carboxylate



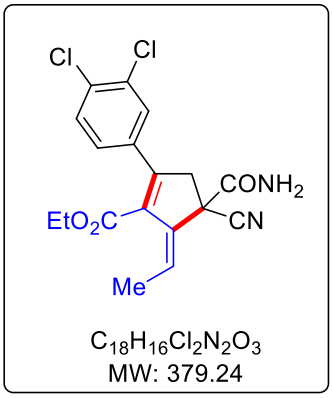
Following the general procedure, treatment of 2-(2-(4-cyanophenyl)-2-oxoethyl)malononitrile **1e** (42 mg, 0.20 mmol) with ethyl penta-2,3-dienoate **2a** (50 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 °C for 12 h followed by column chromatography afforded the product **3e** as white solid (42 mg, 62%). **R_f** (EtOAc/Hexane : 4/6) = 0.30. **Mp** 145-147 °C. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 168.5 (C), 167.1 (C), 144.8 (C), 140.2 (C), 135.7 (C), 132.0 (C), 130.0 (C), 129.0 (CH), 129.0 (CH), 128.5 (CH), 128.5 (CH), 123.2 (CH), 123.2 (C), 119.9 (C), 62.1 (CH_2), 51.3 (C), 44.5 (CH_2), 14.1 (CH_3), 14.0 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 7.35-7.32 (m, 2H), 7.30-7.28 (m, 2H), 6.32 (s, 1H), 6.03 (s, 1H), 5.97 (q, *J* = 7.6 Hz, 1H), 4.30-4.22 (m, 2H), 3.59 (d, *J* = 17.2 Hz, 1H), 3.47 (d, *J* = 17.2 Hz, 1H), 1.80 (d, *J* = 7.6 Hz, 3H), 1.25 (t, *J* = 7.2 Hz, 3H). **HRMS** for $C_{19}H_{18}N_3O_3^+$: calcd. $[M+H]^+$: 336.1343, found: 336.1321.

Compound 3f: ethyl 4-carbamoyl-4-cyano-5-ethylidene-2-(3-methoxyphenyl)cyclopent-1-ene-1-carboxylate



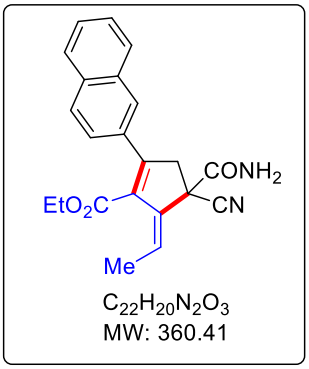
Following the general procedure, treatment of 2-(2-(3-methoxyphenyl)-2-oxoethyl)malononitrile **1f** (43 mg, 0.20 mmol) with ethyl penta-2,3-dienoate **2a** (50 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 °C for 12 h followed by column chromatography afforded the product **3f** as white solid (45 mg, 66%). **R_f** (EtOAc/Hexane : 4/6) = 0.25. **Mp** 152-154 °C. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 168.9 (C), 167.3 (C), 159.8 (C), 145.9 (C), 140.2 (C), 134.8 (C), 129.8 (CH), 129.8 (C), 122.8 (CH), 120.0 (C), 119.6 (CH), 115.3 (CH), 112.7 (CH), 62.0 (CH_2), 55.4 (CH_3), 51.4 (C), 44.8 (CH_2), 14.0 (CH_3), 13.9 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 7.26-7.22 (m, 1H), 6.91-6.86 (m, 3H), 6.29 (s, 1H), 6.20 (s, 1H), 5.92 (q, *J* = 7.6 Hz, 1H), 4.27-4.19 (m, 2H), 3.77 (s, 3H), 3.56 (d, *J* = 17.6 Hz, 1H), 3.48 (d, *J* = 17.6 Hz, 1H), 1.77 (d, *J* = 7.6 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H). **HRMS** for $C_{19}H_{21}N_2O_4^+$: calcd. $[M+H]^+$: 341.1496, found: 341.1498.

Compound 3g: ethyl 4-carbamoyl-4-cyano-2-(3,4-dichlorophenyl)-5-ethylidenecyclopent-1-ene-1-carboxylate



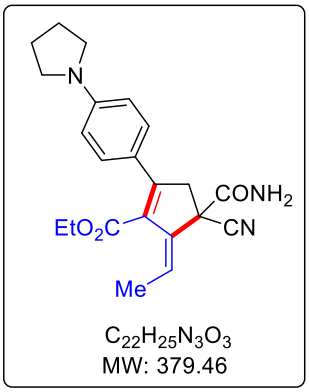
Following the general procedure, treatment of 2-(2-(3,4-dichlorophenyl)-2-oxoethyl)malononitrile **1g** (51 mg, 0.20 mmol) with ethyl penta-2,3-dienoate **2a** (50 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 °C for 12 h followed by column chromatography afforded the product **3g** as white solid (56 mg, 74%). R_f (EtOAc/Hexane : 4/6) = 0.30. **Mp** 166-168 °C. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 168.3 (C), 166.7 (C), 143.4 (C), 140.0 (C), 133.8 (C), 133.5 (C), 133.1 (C), 130.9 (C), 130.8 (CH), 129.1 (CH), 126.4 (CH), 123.9 (CH), 119.8 (C), 62.3 (CH_2), 51.1 (C), 44.3 (CH_2), 14.1 (CH_3), 14.0 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 7.46-7.43 (m, 2H), 7.20-7.17 (m, 1H), 6.33 (s, 1H), 6.03 (s, 1H), 6.00 (q, *J* = 7.6 Hz, 1H), 4.32-4.25 (m, 2H), 3.58 (d, *J* = 17.2 Hz, 1H), 3.44 (d, *J* = 17.2 Hz, 1H), 1.80 (d, *J* = 7.6 Hz, 3H), 1.28 (t, *J* = 7.0 Hz, 3H). **HRMS** for $C_{18}H_{17}Cl_2N_2O_3^+$: calcd. $[M+H]^+$: 379.0611, found: 379.0606.

Compound 3h: ethyl 4-carbamoyl-4-cyano-5-ethylidene-2-(naphthalen-2-yl)cyclopent-1-ene-1-carboxylate



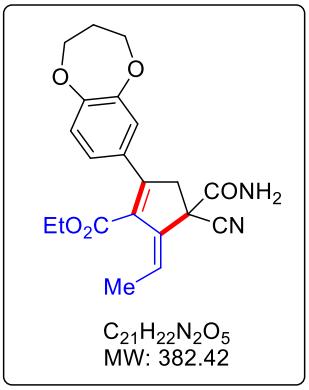
Following the general procedure, treatment of 2-(2-(naphthalen-2-yl)-2-oxoethyl)malononitrile **1h** (47 mg, 0.20 mmol) with ethyl penta-2,3-dienoate **2a** (50 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 °C for 12 h followed by column chromatography afforded the product **3h** as brown solid (50 mg, 70%). R_f (EtOAc/Hexane : 4/6) = 0.55. **Mp** 156-158 °C. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 168.7 (C), 167.4 (C), 146.0 (C), 140.4 (C), 133.7 (C), 133.1 (C), 131.0 (C), 129.8 (C), 128.6 (CH), 128.4 (CH), 127.8 (CH), 127.3 (CH), 127.1 (CH), 126.9 (CH), 124.3 (CH), 122.8 (CH), 120.0 (C), 62.0 (CH_2), 51.5 (C), 44.8 (CH_2), 14.1 (CH_3), 14.0 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 7.83-7.77 (m, 4H), 7.54-7.50 (m, 2H), 7.44 (d, *J* = 8.8 Hz, 1H), 6.34 (s, 1H), 5.99 (q, *J* = 7.4 Hz, 1H), 5.90 (s, 1H), 4.32-4.23 (m, 2H), 3.73 (d, *J* = 16.8 Hz, 1H), 3.65 (d, *J* = 16.8 Hz, 1H), 1.83 (d, *J* = 7.2 Hz, 3H), 1.24 (t, *J* = 7.4 Hz, 3H). **HRMS** for $C_{22}H_{21}N_2O_3^+$: calcd. $[M+H]^+$: 361.1547, found: 361.1544.

Compound 3i: ethyl 4-carbamoyl-4-cyano-5-ethylidene-2-(4-(pyrrolidin-1-yl)phenyl)cyclopent-1-ene-1-carboxylate



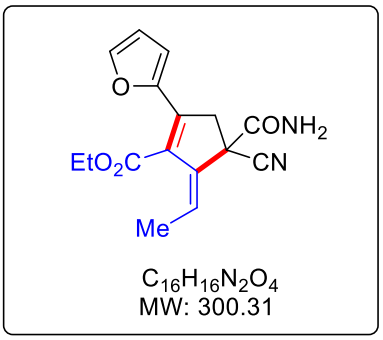
Following the general procedure, treatment of 2-(2-oxo-2-(4-(pyrrolidin-1-yl)phenyl)ethyl)malononitrile **1i** (51 mg, 0.20 mmol) with ethyl penta-2,3-dienoate **2a** (50 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 °C for 12 h followed by column chromatography afforded the product **3i** as white solid (49 mg, 64%). $\mathbf{R_f}$ (EtOAc/Hexane : 4/6) = 0.25. **Mp** 132-134 °C. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 169.3 (C), 168.5 (C), 148.8 (C), 145.8 (C), 140.7 (C), 128.7 (CH), 128.7 (CH), 124.8 (C), 120.1 (C), 119.9 (CH), 119.8 (C), 111.5 (CH), 111.5 (CH), 61.8 (CH_2), 51.9 (C), 47.6 (CH_2), 47.6 (CH_2), 44.5 (CH_2), 25.6 (CH_2), 25.6 (CH_2), 14.1 (CH_3), 13.9 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 7.32 (d, *J* = 8.4 Hz, 2H), 6.56 (d, *J* = 8.8 Hz, 2H), 6.31 (s, 1H), 5.88 (q, *J* = 7.2 Hz, 1H), 5.81 (s, 1H), 4.43-4.34 (m, 2H), 3.62 (s, 2H), 3.38 (t, *J* = 7.0 Hz, 4H) 2.10-2.04 (m, 4H), 1.85 (d, *J* = 7.2 Hz, 3H), 1.39 (t, *J* = 7.2 Hz, 3H). **HRMS** for $C_{22}H_{26}N_3O_3^+$: calcd. $[M+H]^+$: 380.1969, found: 380.1970.

Compound 3j: ethyl 4-carbamoyl-4-cyano-2-(3,4-dihydro-2H-benzo[1,4]dioxepin-7-yl)-5-ethylidenecyclopent-1-ene-1-carboxylate



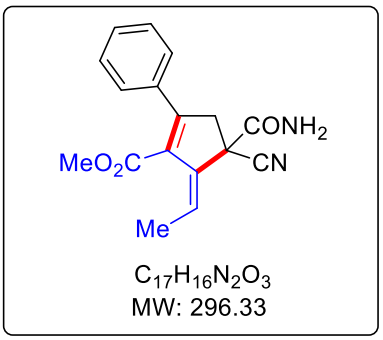
Following the general procedure, treatment of 2-(2-(3,4-dihydro-2H-benzo[1,4]dioxepin-7-yl)-2-oxoethyl)malononitrile **1j** (51 mg, 0.20 mmol) with ethyl penta-2,3-dienoate **2a** (50 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 °C for 12 h followed by column chromatography afforded the product **3j** as brown solid (43 mg, 56%). $\mathbf{R_f}$ (EtOAc/Hexane : 4/6) = 0.25. **Mp** 136-138 °C. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 169.0 (C), 167.5 (C), 152.3 (C), 150.9 (C), 144.7 (C), 140.3 (C), 128.6 (C), 128.4 (C), 122.4 (CH), 122.2 (CH), 121.8 (CH), 120.6 (CH), 119.9 (C), 70.6 (CH_2), 70.5 (CH_2), 62.0 (CH_2), 51.4 (C), 44.5 (CH_2), 31.5 (CH_2), 14.0 (CH_3), 14.0 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 6.98 (s, 1H), 6.92 (s, 2H), 6.30 (s, 1H), 6.16 (s, 1H), 5.90 (q, *J* = 6.0 Hz, 1H), 4.31-4.27 (m, 2H), 4.25-4.20 (m, 4H), 3.54 (d, *J* = 18.0 Hz, 1H), 3.46 (d, *J* = 13.6 Hz, 1H), 2.22-2.16 (m, 2H), 1.78 (d, *J* = 5.6 Hz, 3H), 1.29 (t, *J* = 5.6 Hz, 3H). **HRMS** for $C_{21}H_{23}N_2O_5^+$: calcd. $[M+H]^+$: 383.1601, found: 383.1600.

Compound 3k: ethyl 4-carbamoyl-4-cyano-5-ethylidene-2-(furan-2-yl)cyclopent-1-ene-1-carboxylate



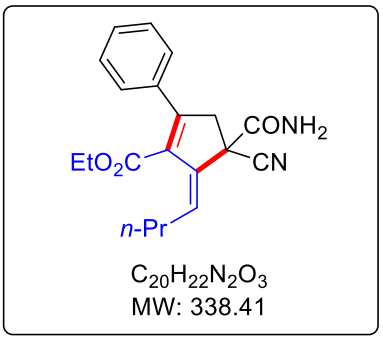
Following the general procedure, treatment of 2-(2-(furan-2-yl)-2-oxoethyl)malononitrile **1k** (35 mg, 0.20 mmol) with ethyl penta-2,3-dienoate **2a** (50 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 °C for 12 h followed by column chromatography afforded the product **3k** as brown solid (44 mg, 73%). $\mathbf{R_f}$ (EtOAc/Hexane : 4/6) = 0.30. **Mp** 138-140 °C. **^{13}C NMR** (100 MHz, δ ppm/DMSO-d_6): 167.4 (C), 166.7 (C), 147.9 (C), 145.5 (CH), 140.2 (C), 132.4 (C), 125.3 (C), 120.5 (C), 120.5 (CH), 113.0 (CH), 112.4 (CH), 61.3 (CH_2), 50.4 (C), 40.5 (CH_2), 13.8 (CH_3), 13.2 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/DMSO-d_6): 7.82 (d, *J* = 1.6 Hz, 1H), 7.71-7.70 (m, 2H), 6.79 (d, *J* = 3.6 Hz, 1H), 6.64-6.62 (m, 1H), 5.87 (q, *J* = 7.0 Hz, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 3.55 (d, *J* = 17.2 Hz, 1H), 3.34 (d, *J* = 16.4 Hz, 1H), 1.70 (d, *J* = 7.6 Hz, 3H), 1.30 (t, *J* = 7.2 Hz, 3H). **HRMS** for $C_{16}H_{17}N_2O_4^+$: calcd. $[M+H]^+$: 301.1183, found: 301.1180.

Compound 3l: methyl 4-carbamoyl-4-cyano-5-ethylidene-2-phenylcyclopent-1-ene-1-carboxylate



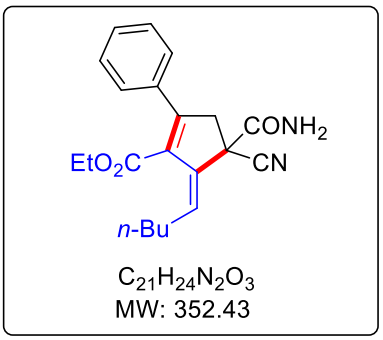
Following the general procedure, treatment of 2-(2-oxo-2-phenylethyl)malononitrile **1a** (37 mg, 0.20 mmol) with methyl penta-2,3-dienoate **2b** (45 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 °C for 12 h followed by column chromatography afforded the product **3l** as white solid (40 mg, 67%). $\mathbf{R_f}$ (EtOAc/Hexane : 4/6) = 0.35. **Mp** 152-154 °C. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 166.8 (C), 167.7 (C), 146.3 (C), 140.2 (C), 133.5 (C), 129.8 (CH), 129.0 (C), 128.8 (CH), 128.8 (CH), 127.1 (CH), 127.1 (CH), 122.7 (CH), 119.9 (C), 52.6 (CH_3), 51.4 (C), 44.6 (CH_2), 13.9 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 7.37-7.34 (m, 5H), 6.32 (s, 1H), 6.15 (s, 1H), 5.95 (q, *J* = 7.2 Hz, 1H), 3.79 (s, 3H), 3.61 (d, *J* = 17.2 Hz, 1H), 3.52 (d, *J* = 17.2 Hz, 1H), 1.78 (d, *J* = 7.6 Hz, 3H). **HRMS** for $C_{17}H_{17}N_2O_3^+$: calcd. $[M+H]^+$: 297.1234, found: 297.1227.

Compound 3m: ethyl 5-butylidene-4-carbamoyl-4-cyano-2-phenylcyclopent-1-ene-1-carboxylate



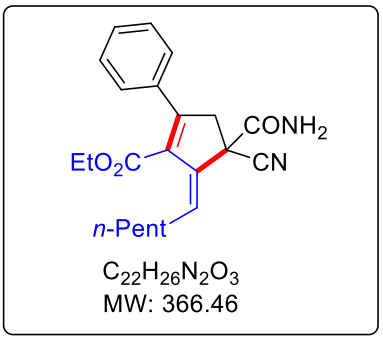
Following the general procedure, treatment of 2-(2-oxo-2-phenylethyl)malononitrile **1a** (37 mg, 0.20 mmol) with ethyl hepta-2,3-dienoate **2c** (62 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 °C for 12 h followed by column chromatography afforded the product **3m** as white solid (45 mg, 66%). $\mathbf{R_f}$ (EtOAc/Hexane : 4/6) = 0.35. **Mp** 123-125 °C. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 168.7 (C), 167.3 (C), 146.0 (C), 139.4 (C), 133.6 (C), 129.7 (C), 129.7 (CH), 128.8 (CH), 128.8 (CH), 128.7 (CH), 127.1 (CH), 127.1 (CH), 119.9 (C), 62.0 (CH_2), 51.6 (C), 44.7 (CH_2), 30.4 (CH_2), 22.8 (CH_2), 13.9 (CH_3), 13.9 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 7.36 (s, 5H), 6.28 (s, 1H), 5.86 (t, *J* = 7.8 Hz, 2H), 4.31-4.21 (m, 2H), 3.61 (d, *J* = 17.2 Hz, 1H), 3.54 (d, *J* = 16.8 Hz, 1H), 2.16-2.10 (m, 2H), 1.54-1.44 (m, 2H), 1.24 (t, *J* = 7.0 Hz, 3H), 0.93 (t, *J* = 7.2 Hz, 3H). **HRMS** for $C_{20}H_{23}N_2O_3^+$: calcd. $[M+H]^+$: 339.1703, found: 339.1704.

Compound 3n: ethyl 4-carbamoyl-4-cyano-5-pentylidene-2-phenylcyclopent-1-ene-1-carboxylate



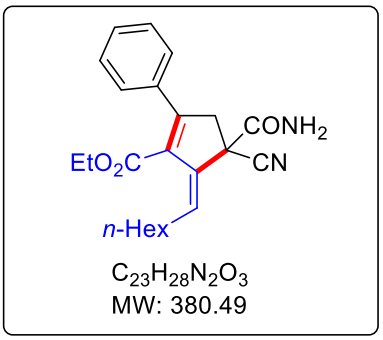
Following the general procedure, treatment of 2-(2-oxo-2-phenylethyl)malononitrile **1a** (37 mg, 0.20 mmol) with ethyl octa-2,3-dienoate **2d** (67 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 °C for 12 h followed by column chromatography afforded the product **3n** as white solid (45 mg, 64%). $\mathbf{R_f}$ (EtOAc/Hexane : 4/6) = 0.35. **Mp** 145-147 °C. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 169.0 (C), 167.4 (C), 145.9 (C), 139.1 (C), 133.6 (C), 129.7 (C), 129.7 (CH), 128.9 (CH), 128.7 (CH), 128.7 (CH), 127.1 (CH), 127.1 (CH), 119.9 (C), 62.0 (CH_2), 51.6 (C), 44.6 (CH_2), 31.6 (CH_2), 28.2 (CH_2), 22.5 (CH_2), 14.0 (CH_3), 13.9 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 7.37-7.32 (m, 5H), 6.30 (s, 1H), 6.14 (s, 1H), 5.85 (t, *J* = 7.6 Hz, 1H), 4.29-4.20 (m, 2H), 3.59 (d, *J* = 17.2 Hz, 1H), 3.53 (d, *J* = 16.8 Hz, 1H), 2.18-2.10 (m, 2H), 1.48-1.40 (m, 2H), 1.36-1.30 (m, 2H), 1.23 (t, *J* = 7.0 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H). **HRMS** for $C_{21}H_{24}N_2NaO_3^+$: calcd. $[M+Na]^+$: 375.1679, found: 375.1680.

Compound 3o: ethyl 4-carbamoyl-4-cyano-5-hexylidene-2-phenylcyclopent-1-ene-1-carboxylate



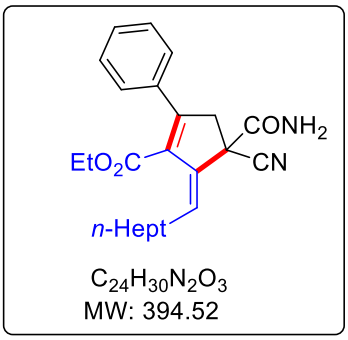
Following the general procedure, treatment of 2-(2-oxo-2-phenylethyl)malononitrile **1a** (37 mg, 0.20 mmol) with ethyl nona-2,3-dienoate **2e** (73 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 °C for 12 h followed by column chromatography afforded the product **3o** as white solid (47 mg, 64%). $\mathbf{R_f}$ (EtOAc/Hexane : 2/8) = 0.35. **Mp** 115-117 °C. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 169.0 (C), 167.4 (C), 145.9 (C), 139.1 (C), 133.6 (C), 129.7 (C), 129.7 (CH), 129.0 (CH), 128.7 (CH), 128.7 (CH), 127.1 (CH), 127.1 (CH), 119.9 (C), 61.9 (CH_2), 51.6 (C), 44.6 (CH_2), 31.6 (CH_2), 29.2 (CH_2), 28.5 (CH_2), 22.5 (CH_2), 14.1 (CH_3), 13.9 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 7.37-7.32 (m, 5H), 6.30 (s, 1H), 6.19 (s, 1H), 5.85 (t, *J* = 7.6 Hz, 1H), 4.29-4.20 (m, 2H), 3.59 (d, *J* = 17.2 Hz, 1H), 3.53 (d, *J* = 17.2 Hz, 1H), 2.19-2.09 (m, 2H), 1.49-1.42 (m, 2H), 1.32-1.27 (m, 4H), 1.23 (t, *J* = 7.2 Hz, 3H), 0.89 (t, *J* = 6.8 Hz, 3H). **HRMS** for $C_{22}H_{26}N_2NaO_3^+$: calcd. $[M+Na]^+$: 389.1836, found: 389.1838.

Compound 3p: ethyl 4-carbamoyl-4-cyano-5-heptylidene-2-phenylcyclopent-1-ene-1-carboxylate



Following the general procedure, treatment of 2-(2-oxo-2-phenylethyl)malononitrile **1a** (37 mg, 0.20 mmol) with ethyl deca-2,3-dienoate **2f** (79 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 °C for 12 h followed by column chromatography afforded the product **3p** as white solid (57 mg, 75%). $\mathbf{R_f}$ (EtOAc/Hexane : 4/6) : 2/8) = 0.35. **Mp** 140-142 °C. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 168.8 (C), 167.4 (C), 145.9 (C), 139.1 (C), 133.6 (C), 129.7 (C), 129.7 (CH), 129.0 (CH), 128.8 (CH), 128.8 (CH), 127.1 (CH), 127.1 (CH), 119.9 (C), 61.9 (CH_2), 51.6 (C), 44.7 (CH_2), 31.7 (CH_2), 29.5 (CH_2), 29.1 (CH_2), 28.5 (CH_2), 22.7 (CH_2), 14.2 (CH_3), 13.9 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 7.37-7.33 (m, 5H), 6.28 (s, 1H), 5.96 (s, 1H), 5.86 (t, *J* = 7.6 Hz, 1H), 4.29-4.20 (m, 2H), 3.60 (d, *J* = 17.2 Hz, 1H), 3.54 (d, *J* = 17.2 Hz, 1H), 2.17-2.12 (m, 2H), 1.49-1.41 (m, 2H), 1.33-1.25 (m, 6H), 1.24 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 6.8 Hz, 3H). **HRMS** for $C_{23}H_{28}N_2NaO_3^+$: calcd. $[M+Na]^+$: 403.1992, found: 403.1993.

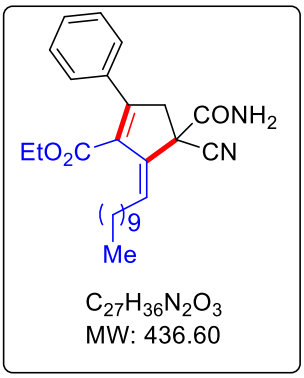
Compound 3q: ethyl 4-carbamoyl-4-cyano-5-octylidene-2-phenylcyclopent-1-ene-1-carboxylate



$C_{24}H_{30}N_2O_3$
MW: 394.52

Following the general procedure, treatment of 2-(2-oxo-2-phenylethyl)malononitrile **1a** (37 mg, 0.20 mmol) with ethyl undeca-2,3-dienoate **2g** (84 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 °C for 12 h followed by column chromatography afforded the product **3q** as brown solid (59 mg, 75%). $\mathbf{R_f}$ (EtOAc/Hexane : 4/6) = 0.40. **Mp** 155-157 °C. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 168.8 (C), 167.4 (C), 145.9 (C), 139.1 (C), 133.6 (C), 129.7 (C), 129.7 (CH), 129.0 (CH), 128.8 (CH), 128.8 (CH), 127.1 (CH), 127.1 (CH), 119.9 (C), 62.0 (CH_2), 51.6 (C), 44.6 (CH_2), 31.9 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 28.6 (CH_2), 22.8 (CH_2), 14.2 (CH_3), 13.9 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 7.38-7.32 (m, 5H), 6.29 (s, 1H), 5.88 (s, 1H), 5.86 (t, *J* = 7.8 Hz, 1H), 4.29-4.20 (m, 2H), 3.60 (d, *J* = 17.2 Hz, 1H), 3.54 (d, *J* = 17.2 Hz, 1H), 2.17-2.10 (m, 2H), 1.47-1.41 (m, 2H), 1.32-1.26 (m, 8H), 1.24 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 6.8 Hz, 3H). **HRMS** for $C_{24}H_{31}N_2O_3^+$: calcd. $[M+H]^+$: 395.2329, found: 395.2321.

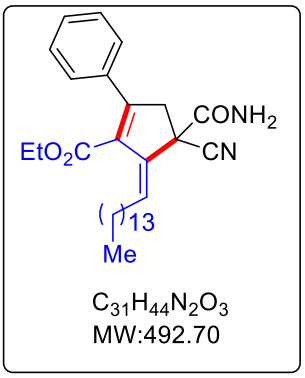
Compound 3r: ethyl 4-carbamoyl-4-cyano-2-phenyl-5-undecylidenecyclopent-1-ene-1-carboxylate



$C_{27}H_{36}N_2O_3$
MW: 436.60

Following the general procedure, treatment of 2-(2-oxo-2-phenylethyl)malononitrile **1a** (37 mg, 0.20 mmol) with ethyl tetradeca-2,3-dienoate **2h** (101 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 °C for 12 h followed by column chromatography afforded the product **3r** as brown solid (59 mg, 68%). $\mathbf{R_f}$ (EtOAc/Hexane : 4/6) = 0.45. **Mp** 70-72 °C. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 169.0 (C), 167.4 (C), 145.9 (C), 139.1 (C), 133.6 (C), 129.7 (C), 129.7 (CH), 129.6 (CH), 128.7 (CH), 128.7 (CH), 127.1 (CH), 127.1 (CH), 119.9 (C), 62.0 (CH_2), 51.6 (C), 44.6 (CH_2), 32.0 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 28.6 (CH_2), 22.8 (CH_2), 14.2 (CH_3), 13.9 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 7.38-7.34 (m, 5H), 6.30 (s, 1H), 6.11 (s, 1H), 5.85 (t, *J* = 7.8 Hz, 1H), 4.29-4.20 (m, 2H), 3.59 (d, *J* = 17.2 Hz, 1H), 3.53 (d, *J* = 17.2 Hz, 1H), 2.16-2.11 (m, 2H), 1.48-1.41 (m, 2H), 1.31-1.25 (m, 14H), 1.23 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H). **HRMS** for $C_{27}H_{37}N_2O_3^+$: calcd. $[M+H]^+$: 437.2799, found: 437.2791.

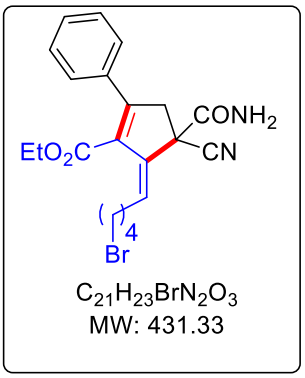
Compound 3s: ethyl 4-carbamoyl-4-cyano-5-pentadecylidene-2-phenylcyclopent-1-ene-1-carboxylate



$C_{31}H_{44}N_2O_3$
MW:492.70

Following the general procedure, treatment of 2-(2-oxo-2-phenylethyl)malononitrile **1a** (37 mg, 0.20 mmol) with ethyl octadeca-2,3-dienoate **2i** (123 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 ˚C for 12 h followed by column chromatography afforded the product **3s** as brown solid (59 mg, 60%). $\mathbf{R_f}$ (EtOAc/Hexane : 4/6) = 0.50. **Mp** 115-117 ˚C. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 168.9 (C), 167.4 (C), 145.9 (C), 139.1 (C), 133.6 (C), 129.7 (C), 129.7 (CH), 129.0 (CH), 128.8 (CH), 128.8 (CH), 127.1 (CH), 127.1 (CH), 119.9 (C), 62.0 (CH_2), 51.6 (C), 44.6 (CH_2), 32.1 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 28.6 (CH_2), 22.9 (CH_2), 14.2 (CH_3), 13.9 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 7.38-7.32 (m, 5H), 6.29 (s, 1H), 6.01 (s, 1H), 5.85 (t, *J* = 7.8 Hz, 1H), 4.29-4.20 (m, 2H), 3.60 (d, *J* = 17.6 Hz, 1H), 3.54 (d, *J* = 17.6 Hz, 1H), 2.17-2.11 (m, 2H), 1.48-1.38 (m, 2H), 1.32-1.26 (m, 22H), 1.23 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 6.8 Hz, 3H). **HRMS** for $C_{31}H_{45}N_2O_3^+$: calcd. $[M+H]^+$: 493.3425, found: 493.3416.

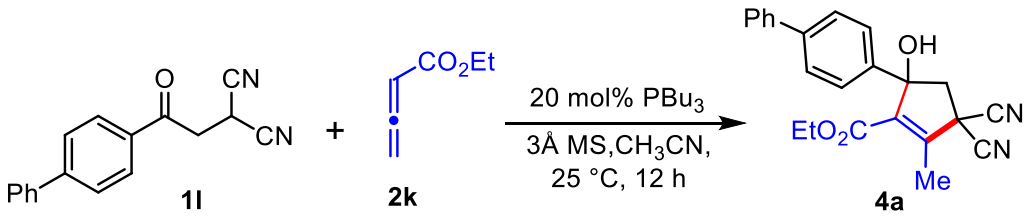
Compound 3t: ethyl 5-(5-bromopentylidene)-4-carbamoyl-4-cyano-2-phenylcyclopent-1-ene-1-carboxylate



$C_{21}H_{23}BrN_2O_3$
MW: 431.33

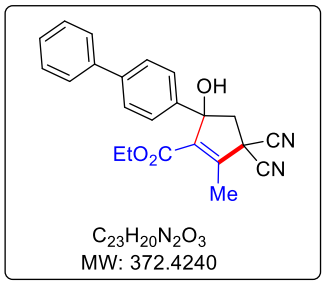
Following the general procedure, treatment of 2-(2-oxo-2-phenylethyl)malononitrile **1a** (37 mg, 0.20 mmol) with ethyl 8-bromoocta-2,3-dienoate **2j** (99 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 ˚C for 12 h followed by column chromatography afforded the product **3n** as white solid (45 mg, 52%). $\mathbf{R_f}$ (EtOAc/Hexane : 4/6) = 0.35. **Mp** 153-155 ˚C. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 168.9 (C), 167.3 (C), 145.6 (C), 139.8 (C), 133.5 (C), 129.7 (CH), 129.5 (C), 128.7 (CH), 128.7 (CH), 127.5 (CH), 127.1 (CH), 127.1 (CH), 119.9 (C), 62.0 (CH_2), 51.4 (C), 44.6 (CH_2), 33.4 (CH_2), 32.2 (CH_2), 27.9 (CH_2), 27.4 (CH_2), 13.9 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 7.37-7.31 (m, 5H), 6.36 (s, 2H), 5.81 (t, *J* = 7.6 Hz, 1H), 4.28-4.20 (m, 2H), 3.59 (d, *J* = 17.6 Hz, 1H), 3.52 (d, *J* = 17.6 Hz, 1H), 3.40 (t, *J* = 7.0 Hz, 2H), 2.21-2.15 (m, 2H), 1.90-1.83 (m, 2H), 1.65-1.59 (m, 2H), 1.22 (t, *J* = 7.2 Hz, 3H). **HRMS** for $C_{21}H_{24}BrN_2O_3^+$: calcd. $[M+H]^+$: 431.0965, found: 431.0965.

General procedure for the synthesis of cyclopentenols 4a-4k.



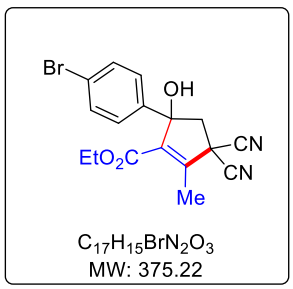
An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-(2-([1,1'-biphenyl]-4-yl)-2-oxoethyl)malononitrile **1l** (37 mg, 0.20 mmol) and 3Å MS (100 mg). Subsequently it was sealed, evacuated, and backfilled with nitrogen. Then, freshly distilled CH_3CN (2.0 mL), ethyl buta-2,3-dienoate **2k** (45 mg, 0.40 mmol) were added via syringe followed by addition of PBu_3 (8 mg, 0.04 mmol). This reaction mixture was stirred at 25 °C for 12 h. After the completion of reaction, as indicated by TLC, solvent was evaporated under reduced pressure. The residue was purified using column chromatography (100-200 mesh silica gel) using ethyl acetate/hexane as the eluent.

Compound 4a: ethyl 5-([1,1'-biphenyl]-4-yl)-3,3-dicyano-5-hydroxy-2-methylcyclopent-1-ene-1-carboxylate



Following the general procedure, treatment of 2-(2-([1,1'-biphenyl]-4-yl)-2-oxoethyl)malononitrile **1l** (52 mg, 0.20 mmol) with ethyl buta-2,3-dienoate **2k** (45 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 °C for 12 h followed by column chromatography afforded the product **4a** as yellow viscous liquid (66 mg, 88%). $\mathbf{R_f}$(EtOAc/Hexane : 2/8) = 0.15. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 163.7 (C), 144.8 (C), 142.5 (C), 141.4 (C), 140.4 (C), 139.4 (C), 129.0 (CH), 129.0 (CH), 127.7 (CH), 127.7 (CH), 127.7 (CH), 127.2 (CH), 127.2 (CH), 124.8 (CH), 124.8 (CH), 113.9 (C), 113.9 (C), 86.2 (C), 62.0 (CH_2), 51.0 (C), 42.8 (CH_2), 14.0 (CH_3), 13.8 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 7.61-7.57 (m, 4H), 7.46-7.40 (m, 4H), 7.38-7.35 (m, 1H), 4.28-4.12 (m, 2H), 3.66 (s, 1H), 3.15 (d, *J* = 11.6 Hz, 1H), 2.85 (d, *J* = 11.6 Hz, 1H), 2.49 (s, 3H), 1.16 (t, *J* = 5.6 Hz, 3H). **HRMS** for $C_{23}H_{20}N_2NaO_3^+$: calcd. $[M+Na]^+$: 395.1366, found: 395.1353.

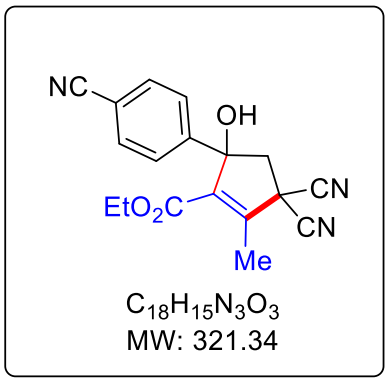
Compound 4b: ethyl 5-(4-bromophenyl)-3,3-dicyano-5-hydroxy-2-methylcyclopent-1-ene-1-carboxylate



Following the general procedure, treatment of 2-(2-(4-bromophenyl)-2-oxoethyl)malononitrile **1m** (53 mg, 0.20 mmol) with ethyl buta-2,3-dienoate **2k** (45 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 °C for 12 h followed by column chromatography afforded the product **4b** as white solid (47 mg, 62%). $\mathbf{R_f}$(EtOAc/Hexane : 2/8) = 0.15. **Mp** 146-148 °C. **^{13}C NMR**

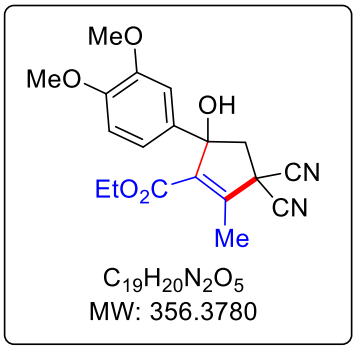
(100 MHz, δ ppm/$CDCl_3$): 163.5 (C), 145.3 (C), 142.7 (C), 138.9 (C), 132.2 (CH), 132.2 (CH), 126.2 (CH), 126.2 (CH), 122.6 (C), 113.7 (C), 113.6 (C), 85.9 (C), 62.1 (CH_2), 50.8 (C), 42.7 (CH_2), 14.0 (CH_3), 13.9 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 7.52-7.48 (m, 2H), 7.24-7.20 (m, 2H), 4.25-4.16 (m, 2H), 3.64 (s, 1H), 3.10 (d, *J* = 14.4 Hz, 1H), 2.75 (d, *J* = 13.2 Hz, 1H), 2.46 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H). **HRMS** for $C_{17}H_{16}BrN_2O_3^+$: calcd. $[M+H]^+$: 375.0339, found: 375.0333.

Compound 4c: ethyl 3,3-dicyano-5-(4-cyanophenyl)-5-hydroxy-2-methylcyclopent-1-ene-1-carboxylate



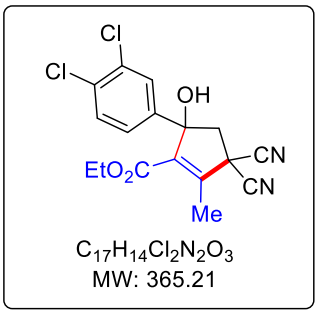
Following the general procedure, treatment of 2-(2-(4-cyanophenyl)-2-oxoethyl)malononitrile **1e** (42 mg, 0.20 mmol) with ethyl buta-2,3-dienoate **2k** (45 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 °C for 12 h followed by column chromatography afforded the product **4c** as white solid (42 mg, 65%). **R_f** (EtOAc/Hexane : 2/8) = 0.20. **Mp** 112-114 °C. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 163.5 (C), 145.3 (C), 142.1 (C), 139.0 (C), 134.5 (CH), 129.3 (CH), 129.3 (CH), 125.9 (CH), 125.9 (C), 113.7 (C), 113.7 (C), 113.7 (C), 85.9 (C), 62.1 (CH_2), 50.9 (C), 42.7 (CH_2), 14.1 (CH_3), 13.9 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 7.37-7.33 (m, 2H), 7.30-7.27 (m, 2H), 4.25-4.12 (m, 2H), 3.63 (s, 1H), 3.10 (d, *J* = 14.4 Hz, 1H), 2.75 (d, *J* = 14.4 Hz, 1H), 2.47 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H). **HRMS** for $C_{18}H_{14}N_3O_3^-$: calcd. $[M-H]^-$: 320.1041, found: 320.1035

Compound 4d: ethyl 3,3-dicyano-5-(3,4-dimethoxyphenyl)-5-hydroxy-2-methylcyclopent-1-ene-1-carboxylate



Following the general procedure, treatment of 2-(2-(3,4-dimethoxyphenyl)-2-oxoethyl)malononitrile **1n** (49 mg, 0.20 mmol) with ethyl buta-2,3-dienoate **2k** (45 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 °C for 12 h followed by column chromatography afforded the product **4d** as brown solid (50 mg, 70%). **R_f** (EtOAc/Hexane : 2/8) = 0.10. **Mp** 144-146 °C. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 163.8 (C), 149.5 (C), 149.1 (C), 144.3 (C), 139.4 (C), 136.1 (C), 116.5 (CH), 113.9 (C), 113.8 (C), 111.3 (CH), 107.7 (CH), 86.1 (C), 61.9 (CH_2), 56.1 (CH_3), 56.0 (CH_3), 51.1 (C), 42.6 (CH_2), 14.1 (CH_3), 13.9 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 6.92 (d, *J* = 2.0 Hz, 1H), 6.83-6.76 (m, 2H), 4.26-4.12 (m, 2H), 3.87 (s, 3H), 3.86 (s, 3H), 3.65 (s, 1H), 3.08 (d, *J* = 14.4 Hz, 1H), 2.79 (d, *J* = 14.0 Hz, 1H), 2.46 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H). **HRMS** for $C_{19}H_{21}N_2O_5^+$: calcd. $[M+H]^+$: 357.1445, found: 357.1442.

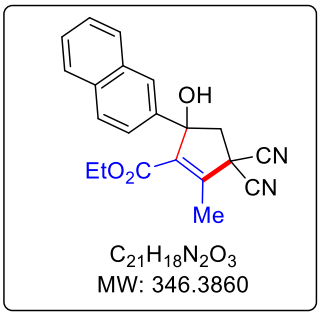
Compound 4e: ethyl 3,3-dicyano-5-(3,4-dichlorophenyl)-5-hydroxy-2-methylcyclopent-1-ene-1-carboxylate



$C_{17}H_{14}Cl_2N_2O_3$
MW: 365.21

Following the general procedure, treatment of 2-(2-(3,4-dichlorophenyl)-2-oxoethyl)malononitrile **1g** (51 mg, 0.20 mmol) with ethyl buta-2,3-dienoate **2k** (45 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 °C for 12 h followed by column chromatography afforded the product **4e** as white solid (51 mg, 70%). R_f (EtOAc/Hexane : 2/8) = 0.15. **Mp** 125-127 °C. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 163.5(C), 145.8 (C), 143.9 (C), 138.4 (C), 133.6 (C), 132.8 (C), 131.1 (CH), 126.9 (CH), 123.8 (CH), 113.6 (C), 113.5 (C), 85.5 (C), 62.3 (CH_2), 50.7 (C), 42.7 (CH_2), 14.1 (CH_3), 14.0 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 7.51 (d, *J* = 2.4 Hz, 1H), 7.45-7.43 (m, 1H), 7.14-7.11 (m, 1H), 4.28-4.15 (m, 2H), 3.68 (s, 1H), 3.10 (d, *J* = 14.8 Hz, 1H), 2.74 (d, *J* = 14.4 Hz, 1H), 2.48 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H). **HRMS** for $C_{17}H_{15}Cl_2N_2O_3^+$: calcd. $[M+H]^+$: 365.0454, found: 365.0450.

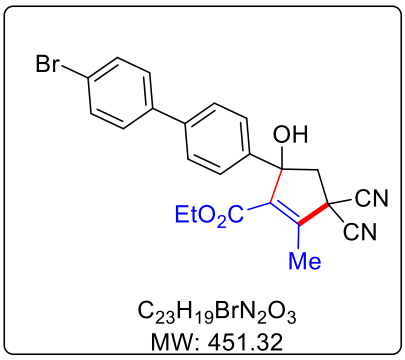
Compound 4f: ethyl 3,3-dicyano-5-hydroxy-2-methyl-5-(naphthalen-2-yl)cyclopent-1-ene-1-carboxylate



$C_{21}H_{18}N_2O_3$
MW: 346.3860

Following the general procedure, treatment of 2-(2-(naphthalen-2-yl)-2-oxoethyl)malononitrile **1h** (47 mg, 0.20 mmol) with ethyl buta-2,3-dienoate **2k** (45 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 °C for 12 h followed by column chromatography afforded the product **4f** as white solid (51 mg, 73%). R_f (EtOAc/Hexane : 2/8) = 0.15. **Mp** 134-136 °C. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 163.7(C), 144.9 (C), 140.8 (C), 139.5 (C), 133.3 (C), 133.1 (C), 129.3 (CH), 128.4 (CH), 127.8 (CH), 126.9 (CH), 126.7 (CH), 123.5 (CH), 122.2 (CH), 113.9 (C), 113.9 (C), 86.5 (C), 62.0 (CH_2), 51.0 (C), 42.9 (CH_2), 14.0 (CH_3), 13.9 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 7.87-7.83 (m, 4H), 7.54-7.49 (m, 2H), 7.40-7.38 (m, 1H), 4.20-4.09 (m, 2H), 3.75 (s, 1H), 3.17 (d, *J* = 11.6 Hz, 1H), 2.88 (d, *J* = 11.6 Hz, 1H), 2.52 (s, 3H), 1.09 (t, *J* = 5.8 Hz, 3H). **HRMS** for $C_{21}H_{18}N_2NaO_3^+$: calcd. $[M+Na]^+$: 369.1210, found: 369.1212.

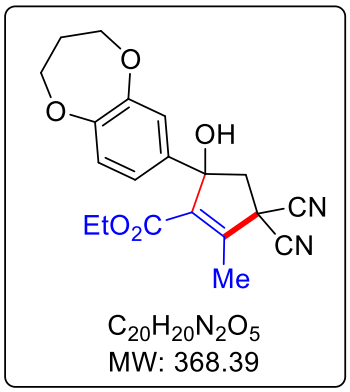
Compound 4g: ethyl 5-(4'-bromo-[1,1'-biphenyl]-4-yl)-3,3-dicyano-5-hydroxy-2-methylcyclopent-1-ene-1-carboxylate



$C_{23}H_{19}BrN_2O_3$
MW: 451.32

Following the general procedure, treatment of 2-(2-(4'-bromo-[1,1'-biphenyl]-4-yl)-2-oxoethyl)malononitrile **1o** (68 mg, 0.20 mmol) with ethyl buta-2,3-dienoate **2k** (45 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 °C for 12 h followed by column chromatography afforded the product **4g** as brown solid (77 mg, 85%). **R_f** (EtOAc/Hexane : 2/8) = 0.15. **Mp** 156-158 °C. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 163.7 (C), 145.0 (C), 143.0 (C), 140.2 (C), 139.3 (C), 139.3 (C), 132.1 (CH), 132.1 (CH), 128.8 (CH), 128.8 (CH), 127.6 (CH), 127.6 (CH), 125.0 (CH), 125.0 (CH), 122.1 (C), 113.8 (C), 113.8 (C), 86.2 (C), 62.0 (CH_2), 51.0 (C), 42.8 (CH_2), 14.1 (CH_3), 13.9 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 7.57-7.54 (m, 4H), 7.45-7.40 (m, 4H), 4.29-4.11 (m, 2H), 3.68 (s, 1H), 3.14 (d, *J* = 14.0 Hz, 1H), 2.83 (d, *J* = 14.4 Hz, 1H), 2.49 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H). **HRMS** for $C_{23}H_{19}BrN_2NaO_3^+$: calcd. $[M+Na]^+$: 473.0471, found: 473.0472.

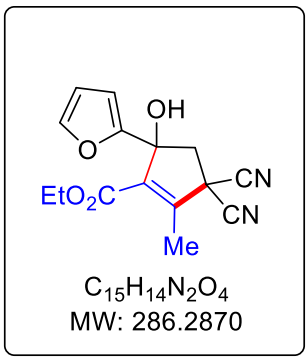
Compound 4h: ethyl 3,3-dicyano-5-(3,4-dihydro-2H-benzo [1,4]dioxepin-7-yl)-5-hydroxy-2-methylcyclopent-1-ene-1-carboxylate



$C_{20}H_{20}N_2O_5$
MW: 368.39

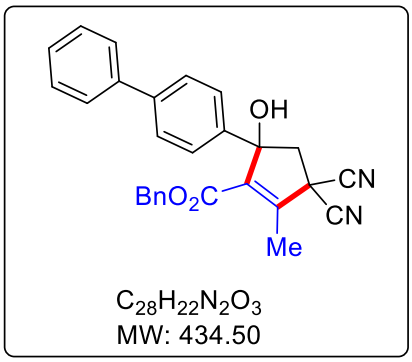
Following the general procedure, treatment of 2-(2-(3,4-dihydro-2H-benzo[1,4]dioxepin-7-yl)-2-oxoethyl)malononitrile **1j** (51 mg, 0.20 mmol) with ethyl buta-2,3-dienoate **2k** (45 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 °C for 12 h followed by column chromatography afforded the product **4h** as brown solid (52 mg, 71%). **R_f** (EtOAc/Hexane : 2/8) = 0.10. **Mp** 146-148 °C. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 163.7 (C), 151.4 (C), 151.0 (C), 144.6 (C), 139.3 (C), 138.8 (C), 122.1 (CH), 119.2 (CH), 117.9 (CH), 113.9 (C), 113.8 (C), 85.8 (C), 70.6 (CH_2), 70.6 (CH_2), 61.9 (CH_2), 50.9 (C), 42.6 (CH_2), 31.7 (CH_2), 14.1 (CH_3), 13.8 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 6.95-6.93 (m, 2H), 6.85-6.83 (m, 1H), 4.27-4.11 (m, 6H), 3.56 (s, 1H), 3.06 (d, *J* = 14.4 Hz, 1H), 2.76 (d, *J* = 14.0 Hz, 1H), 2.44 (s, 3H), 2.22-2.16 (m, 2H), 1.16 (t, *J* = 7.4 Hz, 3H). **HRMS** for $C_{20}H_{20}N_2NaO_5^+$: calcd. $[M+Na]^+$: 391.1264, found: 391.1264.

Compound 4i: ethyl 3,3-dicyano-5-(furan-2-yl)-5-hydroxy-2-methylcyclopent-1-ene-1-carboxylate



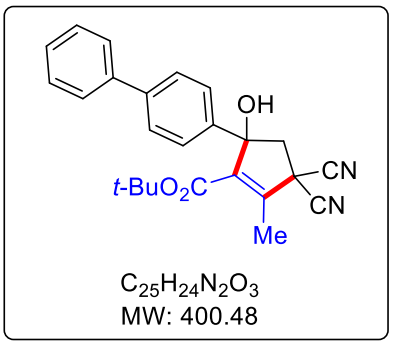
Following the general procedure, treatment of 2-(2-(furan-2-yl)-2-oxoethyl)malononitrile **1k** (35 mg, 0.20 mmol) with ethyl buta-2,3-dienoate **2k** (45 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 ˚C for 12 h followed by column chromatography afforded the product **4i** as white solid (44 mg, 77%). $\mathbf{R_f}$ (EtOAc/Hexane : 2/8) = 0.15. **Mp** 135-137 ˚C. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 163.5(C), 154.2 (C), 145.0 (C), 142.9 (CH), 137.3 (C), 113.8 (C), 113.4 (C), 110.9 (CH), 106.9 (CH), 82.1 (C), 62.1 (CH_2), 47.9 (C), 42.3 (CH_2), 14.1 (CH_3), 14.1 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 7.36-7.34 (m, 1H), 6.37-6.34 (m, 2H), 4.34-4.20 (m, 2H), 3.96 (s, 1H), 3.10 (d, *J* = 14.0 Hz, 1H), 2.98 (d, *J* = 14.4 Hz, 1H), 2.44 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H). **HRMS** for $C_{15}H_{15}N_2O_4^+$: calcd. $[M+H]^+$: 287.1026, found: 287.1024.

Compound 4j: benzyl 5-([1,1'-biphenyl]-4-yl)-3,3-dicyano-5-hydroxy-2-methylcyclopent-1-ene-1-carboxylate



Following the general procedure, treatment of 2-(2-([1,1'-biphenyl]-4-yl)-2-oxoethyl)malononitrile **1l** (52 mg, 0.20 mmol) with benzyl buta-2,3-dienoate **2l** (70 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 ˚C for 12 h followed by column chromatography afforded the product **4j** as white solid (81 mg, 93%). $\mathbf{R_f}$ (EtOAc/Hexane : 2/8) = 0.15. **Mp** 155-157 ˚C. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 163.4 (C), 145.7 (C), 142.4 (C), 141.4 (C), 140.3 (C), 139.2 (C), 134.4 (C), 129.0 (CH), 129.0 (CH), 128.8 (CH), 128.8 (CH), 128.8 (CH), 128.4 (CH), 128.4 (CH), 127.8 (CH), 127.8 (CH), 127.8 (CH), 127.2 (CH), 127.2 (CH), 124.8 (CH), 124.8 (CH), 113.8 (C), 113.8 (C), 86.1 (C), 67.6 (CH_2), 51.0 (C), 42.8 (CH_2), 13.9 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 7.59-7.56 (m, 4H), 7.48-7.43 (m, 2H), 7.39-7.34 (m, 3H), 7.26-7.20 (m, 3H), 7.02-7.00 (m, 2H), 5.22 (d, *J* = 12.0 Hz, 1H), 5.02 (d, *J* = 12.0 Hz, 1H), 3.56 (s, 1H), 3.12 (d, *J* = 14.4 Hz, 1H), 2.81 (d, *J* = 14.4 Hz, 1H), 2.47 (s, 3H). **HRMS** for $C_{28}H_{23}N_2O_3^+$: calcd. $[M+H]^+$: 435.1703, found: 435.1680

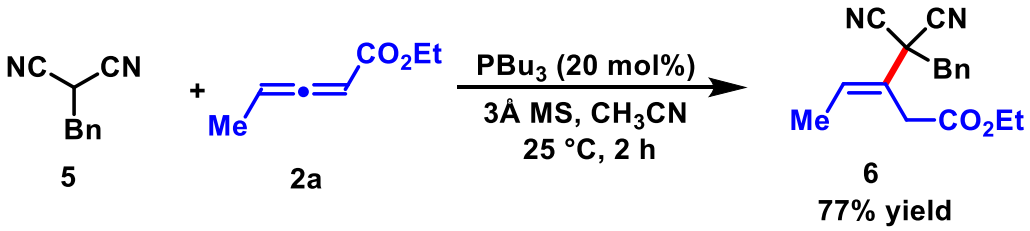
Compound 4k: *tert*-butyl 5-([1,1'-biphenyl]-4-yl)-3,3-dicyano-5-hydroxy-2-methylcyclopent-1-ene-1-carboxylate



Following the general procedure, treatment of 2-(2-([1,1'-biphenyl]-4-yl)-2-oxoethyl)malononitrile **1l** (52 mg, 0.20 mmol) with *tert*-butyl buta-2,3-dienoate **2m** (56 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 °C for 12 h followed by column chromatography afforded the product **4k** as white solid (63 mg, 79%). $\mathbf{R_f}$ (EtOAc/Hexane : 2/8) = 0.15. **Mp** 156-158 °C. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 162.7 (C), 144.0 (C), 142.8 (C), 141.3 (C), 140.8 (C), 140.4 (C), 129.0 (CH), 129.0 (CH), 127.8 (CH), 127.6 (CH), 127.6 (CH), 127.2 (CH), 127.2 (CH), 124.9 (CH), 124.9 (CH), 114.0 (C), 114.0 (C), 86.1 (C), 84.2 (C), 50.9 (C), 42.7 (CH_2), 28.0 (CH_3), 28.0 (CH_3), 28.0 (CH_3), 13.5 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 7.63-7.58 (m, 4H), 7.47-7.35 (m, 5H), 3.56 (s, 1H), 3.15 (d, *J* = 14.4 Hz, 1H), 2.80 (d, *J* = 14.4 Hz, 1H), 2.46 (s, 3H), 1.31 (s, 9H). **HRMS** for $C_{25}H_{24}N_2NaO_3^+$: calcd. $[M+Na]^+$: 423.1679, found: 423.1672.

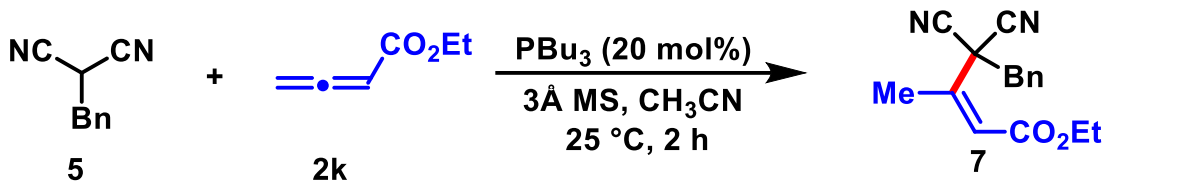
Mechanistic Experiments

Reaction of 2-benzylmalononitrile with γ-substituted allenic ester



An oven-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with 2-benzylmalononitrile **5** (31 mg, 0.20 mmol) and 3Å MS (100 mg). Subsequently, it was sealed, evacuated, and backfilled with nitrogen. Freshly distilled CH_3CN (2.0 mL) and ethyl penta-2,3-dienoate **2a** (50 mg, 0.40 mmol) were added via syringe followed by the addition of PBu_3 (8 mg, 0.04 mmol). The reaction mixture was stirred at 25 °C for 12 h. After the completion of the reaction, as indicated by TLC, the solvent was evaporated under reduced pressure. The residue was purified using column chromatography to afford the product **6** as colorless oil (43 mg, 77%). $\mathbf{R_f}$ (EtOAc/Hexane : 1/9) = 0.40. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 169.3 (C), 132.6 (CH), 132.0 (C), 130.5 (CH), 130.5 (CH), 128.9 (CH), 128.9 (CH), 128.9 (CH), 124.1 (C), 114.2 (C), 114.2 (C), 61.7 (CH_2), 46.2 (C), 44.3 (CH_2), 33.8 (CH_2), 14.4 (CH_3), 14.2 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 7.38-7.36 (m, 5H), 6.24 (q, *J* = 9.6 Hz, 1H), 4.21 (q, *J* = 9.6 Hz, 2H), 3.33 (s, 2H), 3.32 (s, 2H), 1.76 (d, *J* = 9.2 Hz, 3H), 1.29 (t, *J* = 9.4 Hz, 3H). **HRMS** for $C_{17}H_{19}N_2O_2^+$: calcd. $[M+H]^+$: 283.1441, found: 283.1444.

Reaction of 2-benzylmalononitrile with unsubstituted allenic ester



75% yield
(isomerization takes place)

Following the above mention procedure, treatment of 2-benzylmalononitrile **5** (31 mg, 0.20 mmol) with ethyl buta-2,3-dienoate **2k** (45 mg, 0.40 mmol) in the presence of PBu_3 (8 mg, 0.04 mmol) in CH_3CN (2 mL) at 25 °C for 2 h followed by column chromatography afforded the product **7** as colorless oil (40 mg, 75%). $\mathbf{R_f}$(EtOAc/Hexane : 1/9) = 0.45. **^{13}C NMR** (100 MHz, δ ppm/$CDCl_3$): 164.6 (C), 144.6 (C), 131.2 (C), 134.4 (CH), 134.4 (CH), 129.2 (CH), 129.1 (CH), 129.1 (CH), 122.3 (CH), 113.3 (C), 113.3 (C), 61.0 (CH_2), 47.0 (C), 43.8 (CH_2), 15.7 (CH_3), 14.2 (CH_3). **^{1}H NMR** (400 MHz, δ ppm/$CDCl_3$): 7.41-7.39 (m, 3H), 7.35-7.32 (m, 2H), 6.20 (q, *J* = 1.4 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.33 (s, 2H), 2.41 (d, *J* = 1.2 Hz, 3H), 1.29 (t, *J* = 7.6 Hz, 3H). **HRMS** for $C_{16}H_{17}N_2O_2^+$: calcd. $[M+H]^+$: 269.1285, found: 269.1284.

X-Ray Data Collection and Structure Refinement Details for compound 3a:

A good quality single crystal of size 0.33 x 0.21 x 0.15 mm, was selected under a polarizing microscope and was mounted on a glass fiber for data collection. Single crystal X-ray data for compound **3a** were collected on the Bruker APEX-II CCD area-detector at 100(2) K. Data collection was performed using ω-scans of at 100(2) K by Bruker APEX2[1]. Cell determination, and data reduction was performed using the Bruker SAINT software. Structure solution and refinement were performed by using SHELX-97[2]. Refinement of coordinates and anisotropic thermal parameters of non-hydrogen atoms were carried out by the full-matrix least-squares method. The hydrogen atoms attached to carbon atoms were generated with idealized geometries and isotropically refined using a riding model.

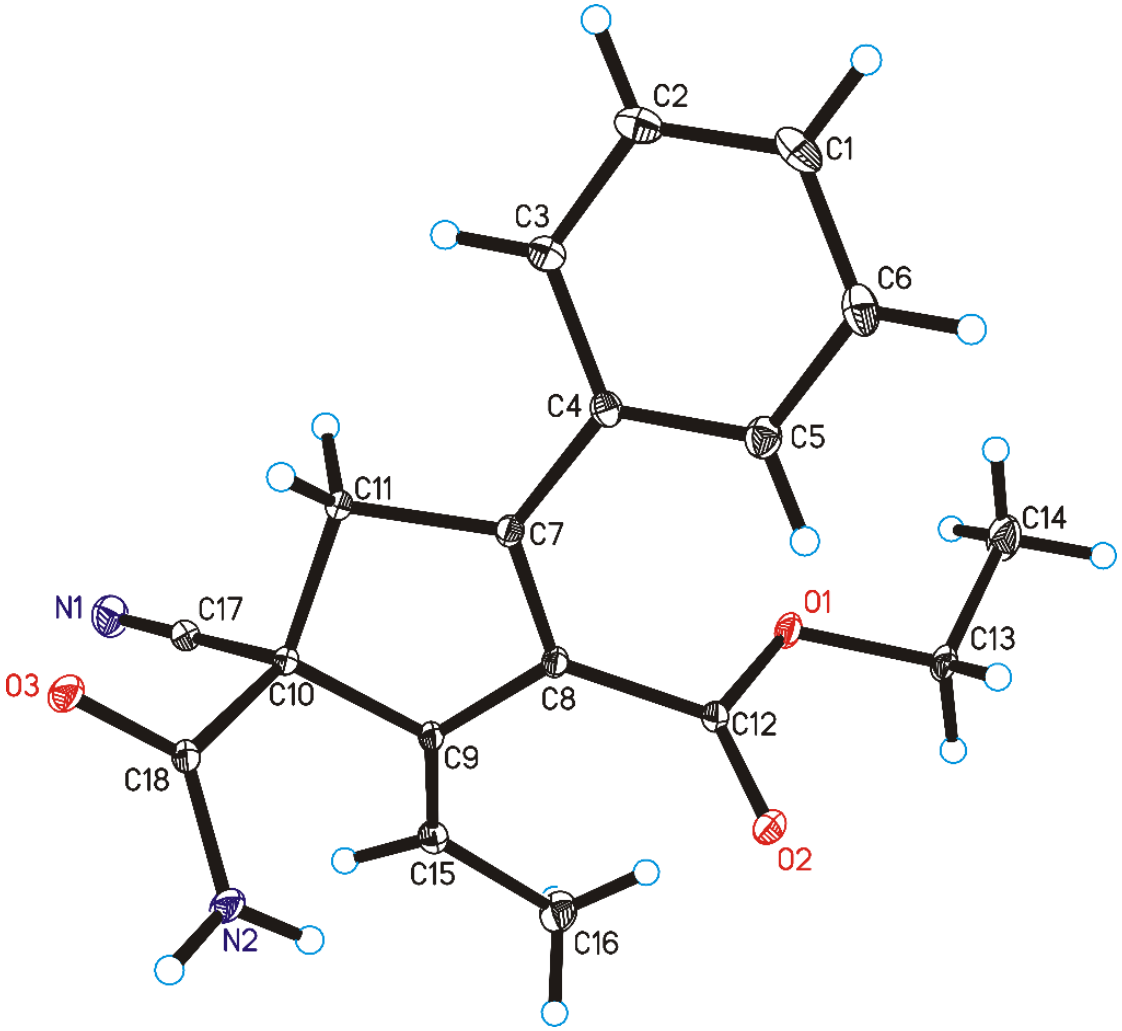


Figure S1. ORTEP diagram drawn with 30% ellipsoid probability for non-H atoms of the crystal structure of compound **3a** determined at 293 K.

Table S1 Crystal data and structure refinement details for **3a**.

Compound	**3a**
Empirical formula	$C_{18}H_{18}N_2O_3$
Formula weight	310.34
Crystal System	Triclinic
Space group	*P*-1
a (Å)	7.6107(6)
b (Å)	9.6669(8)
c (Å)	11.6421(10)
α (°)	74.194(2)
β (°)	82.375(2)
γ (°)	75.798(2)
V (Å^3)	796.96(11)
Z	2
D_c (g/cm^3)	1.293
F_{000}	328
μ (mm^{-1})	0.089
θ_{max} (°)	28.34
Total reflections	12550
Unique reflections	3943
Reflections [$I > 2\sigma(I)$]	3520
Parameters	210
R_{int}	0.0294
Goodness-of-fit	1.132
R [$F^2 > 2\sigma(F^2)$]	0.0420
wR (F^2, all data)	0.1272
CCDC No.	2006551

X-Ray Data Collection and Structure Refinement Details for compound 4b:

A good quality single crystal of size 0.29 x 0.17 x 0.12 mm, was selected under a polarizing microscope and was mounted on a glass fiber for data collection. Single crystal X-ray data for compound **4b** were collected on the Bruker APEX-II CCD area-detector at 100(2) K. Data collection was performed using ω-scans of at 100(2) K by Bruker APEX2[1]. Cell determination, and data reduction was performed using the Bruker SAINT software. Structure solution and refinement were performed by using SHELX-97[2]. Refinement of coordinates and anisotropic thermal parameters of non-hydrogen atoms were carried out by the full-matrix least-squares method. The hydrogen atoms attached to carbon atoms were generated with idealized geometries and isotropically refined using a riding model.

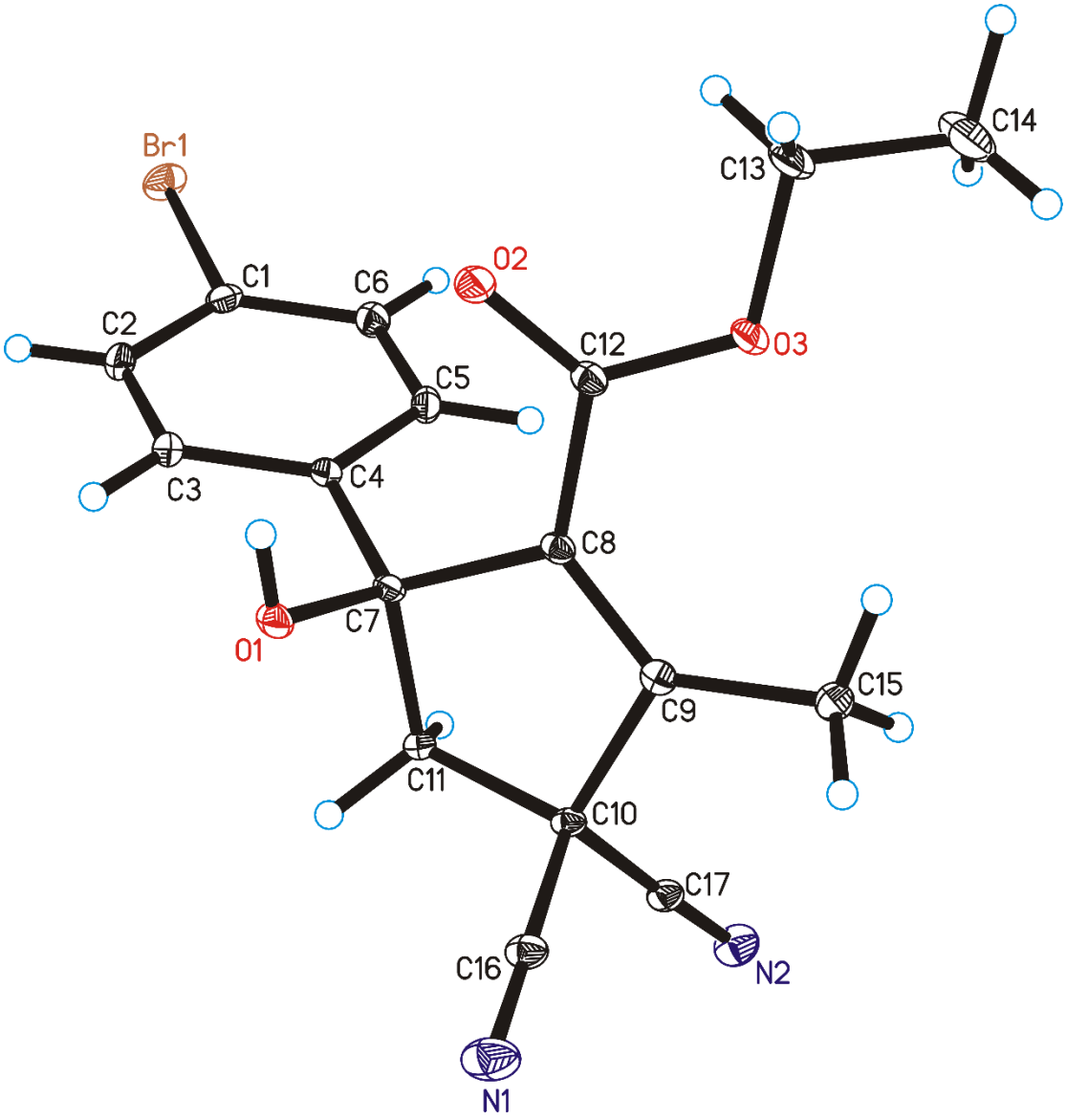
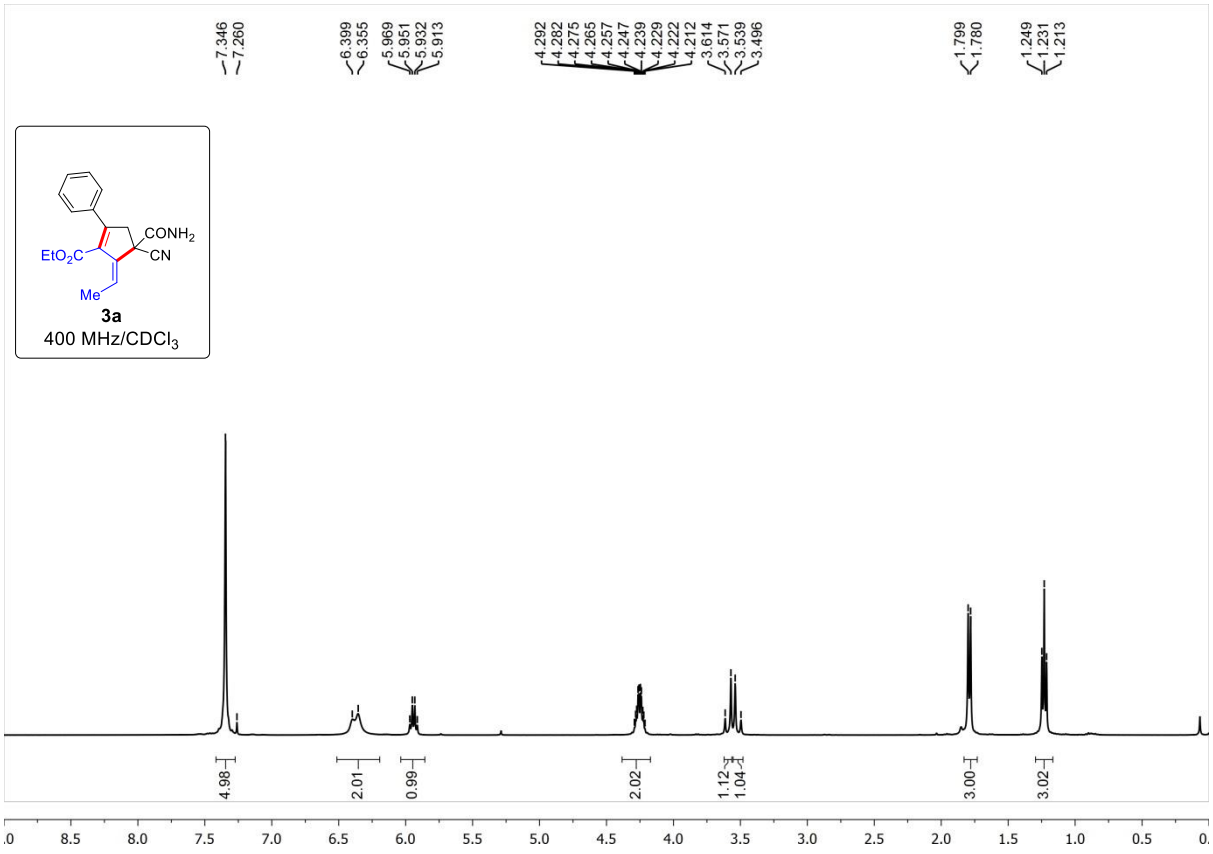


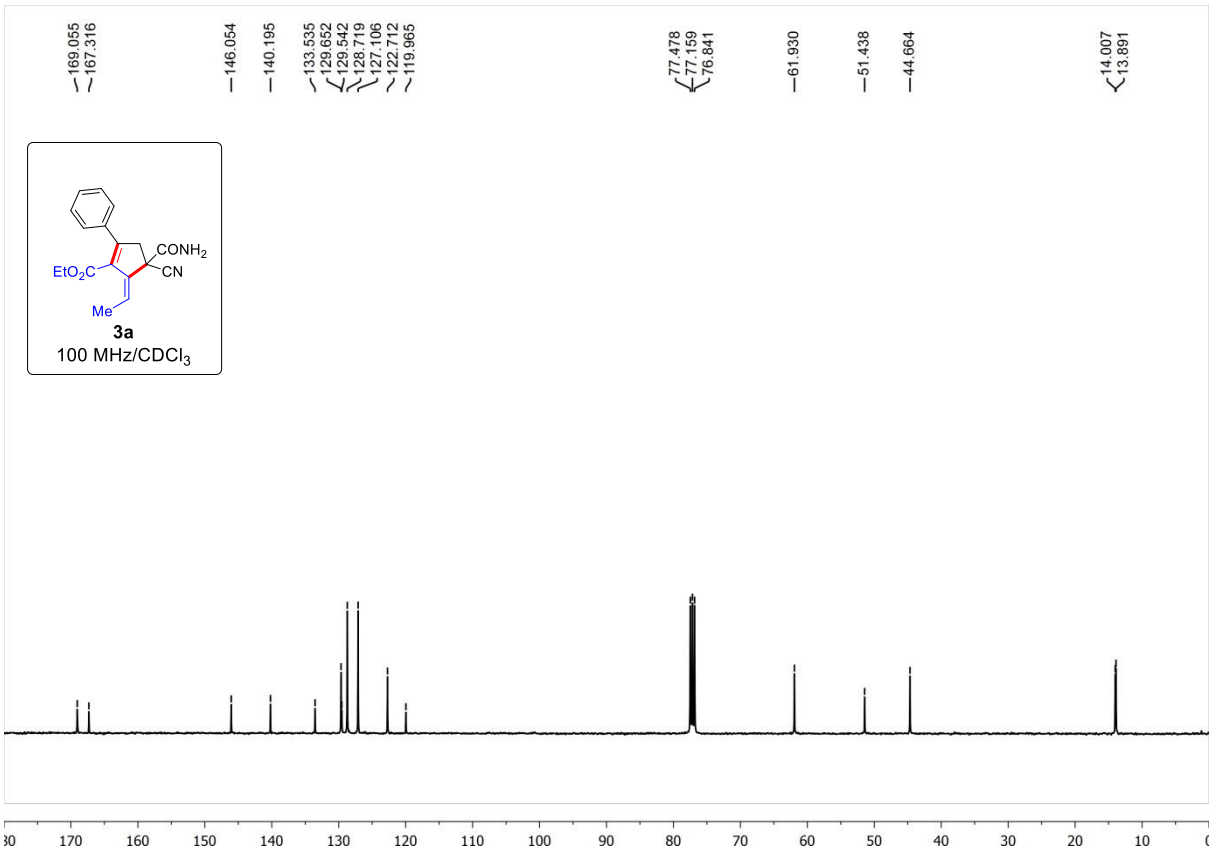
Figure S2. ORTEP diagram drawn with 30% ellipsoid probability for non-H atoms of the crystal structure of compound **4b** determined at 293 K.

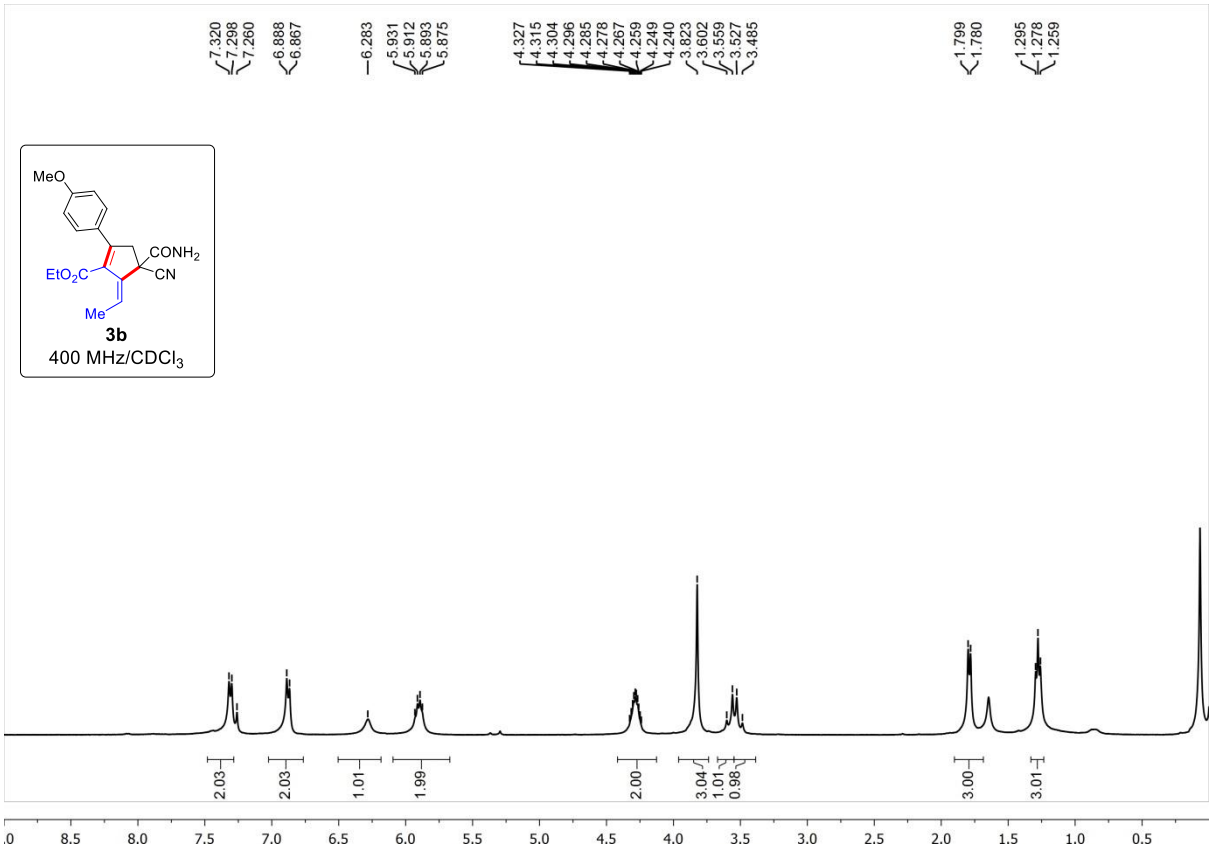
Table S2 Crystal data and structure refinement details for **4b**.

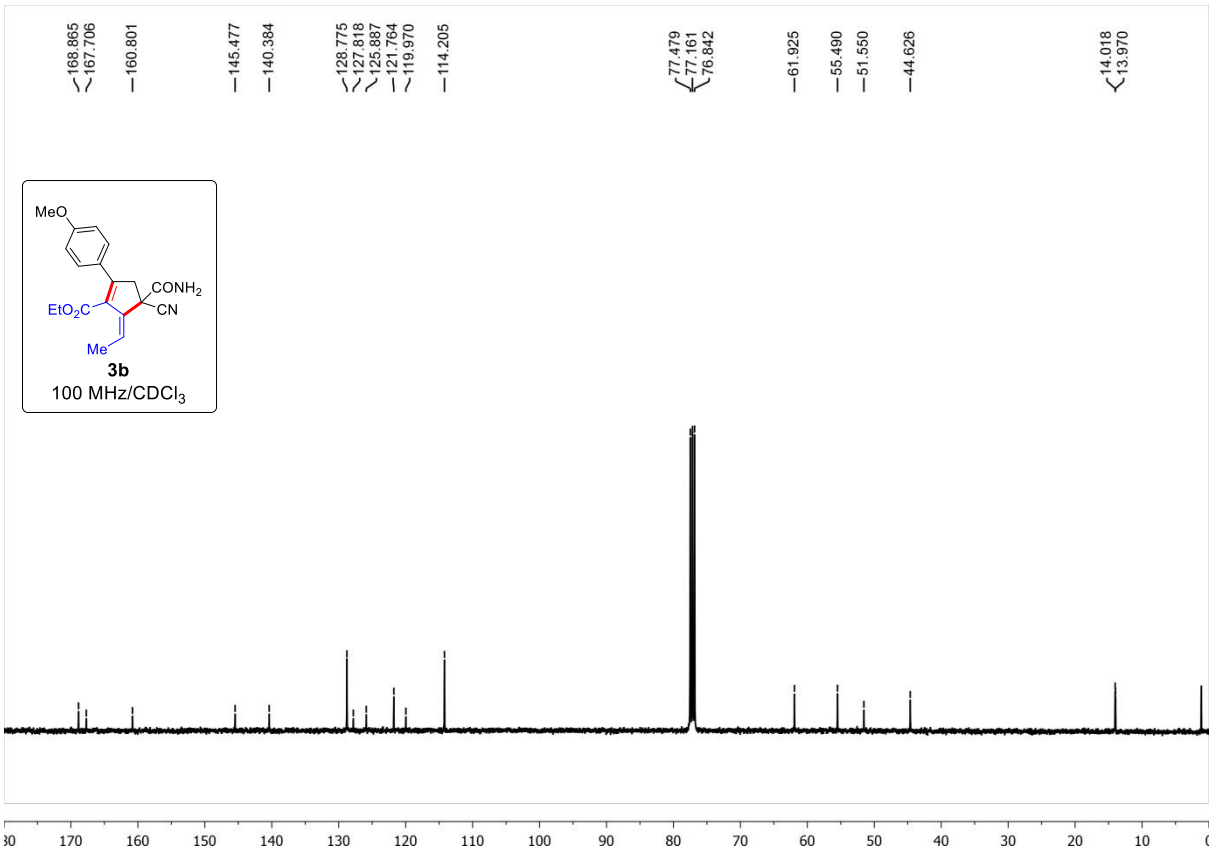
Compound	**4b**
Empirical formula	C_{17} H_{15} Br N_2 O_3
Formula weight	375.22
Crystal System	Monoclinic
Space group	*C* 2/c
a (Å)	24.827(6)
b (Å)	6.5559(16)
c (Å)	21.173(5)
α (°)	90.00
β (°)	107.267(6)
γ (°)	90.00
V (Å^3)	3291.0(13)
Z	8
D_c (g/cm^3)	1.515
F_{000}	1520
μ (mm^{-1})	2.514
θ_{max} (°)	28.43
Total reflections	22762
Unique reflections	4131
Reflections [$I > 2\sigma(I)$]	3626
Parameters	211
R_{int}	0.0578
Goodness-of-fit	1.066
R [$F^2 > 2\sigma(F^2)$]	0.0316
wR (F^2, all data)	0.0775
CCDC No.	2006837

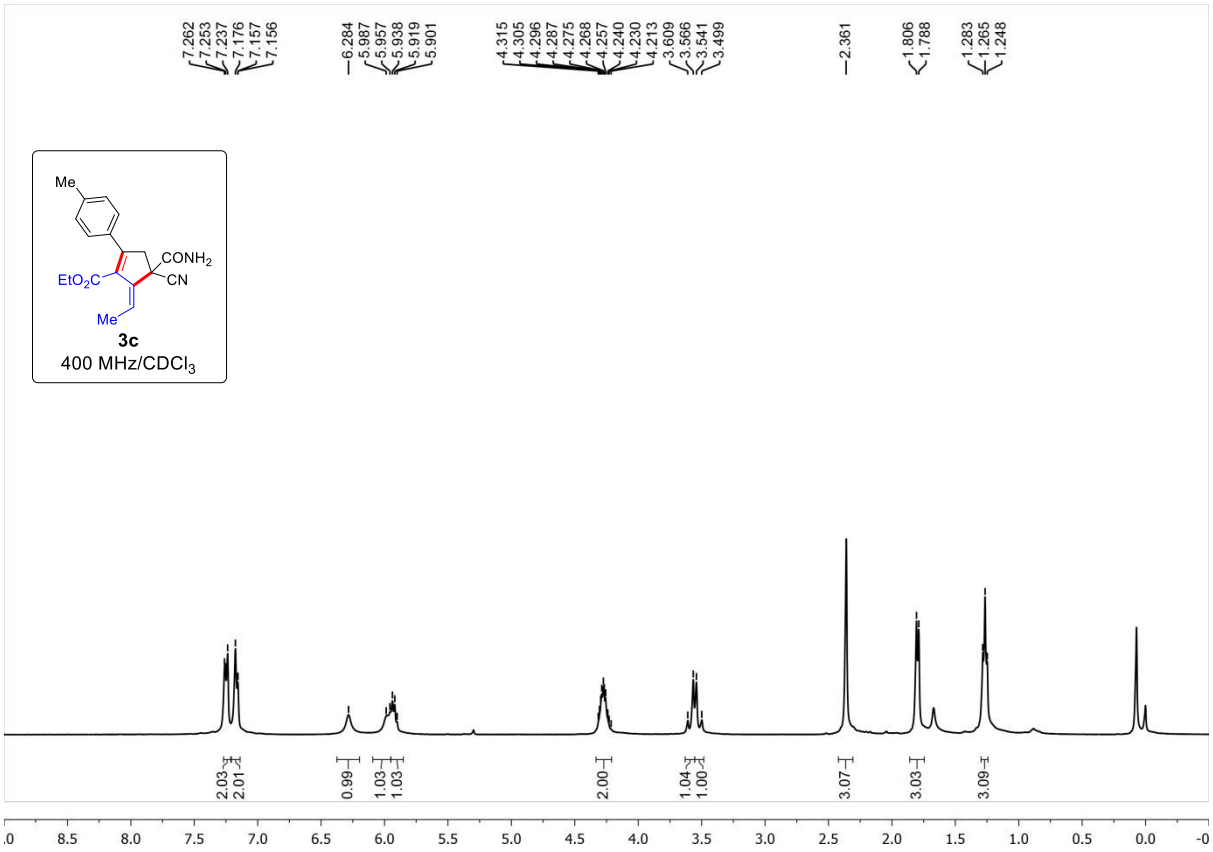
1. CrystalClear 2.1, Rigaku Corporation, Tokyo, Japan
2. Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.

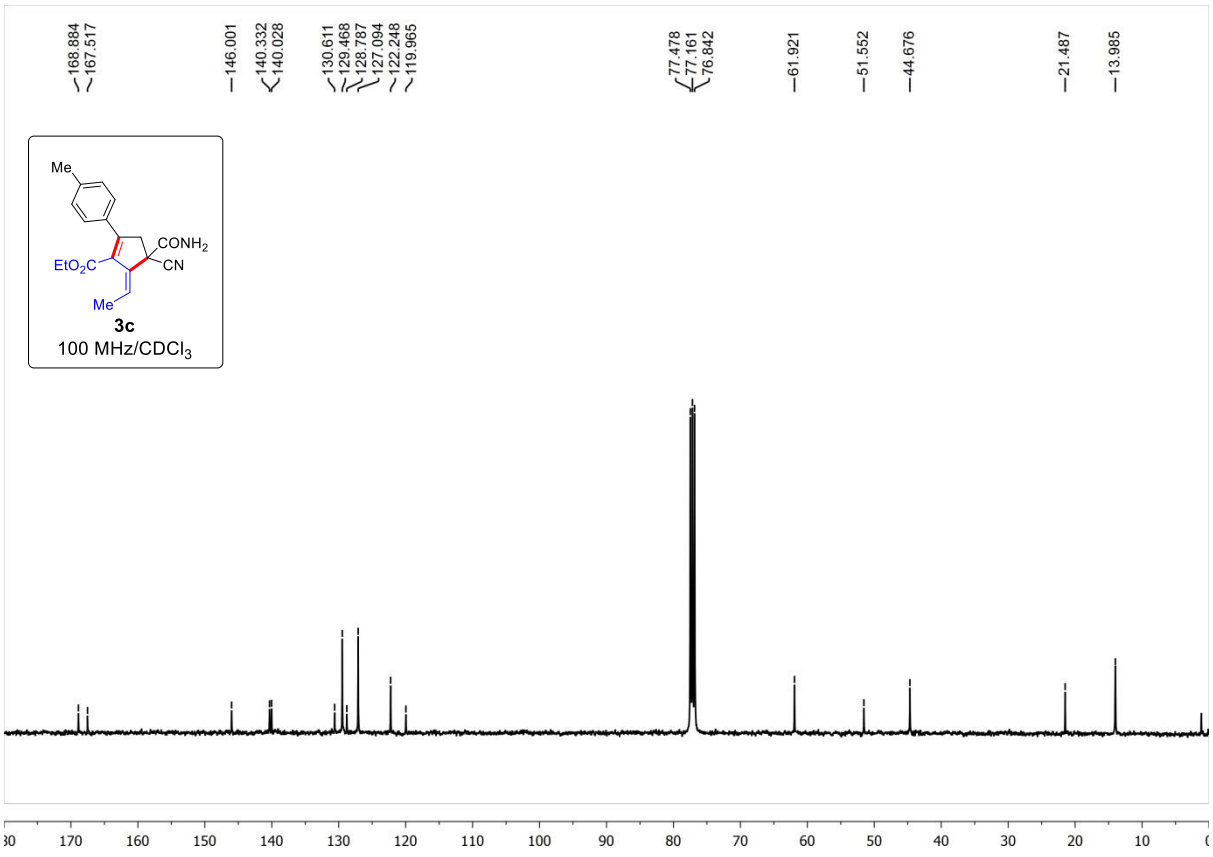

7.346
7.260
6.399
6.355
5.969
5.951
5.932
5.913
4.292
4.282
4.275
4.265
4.257
4.247
4.239
4.229
4.222
4.212
3.614
3.571
3.539
3.496
1.799
1.780
1.249
1.231
1.213
CONH2
EtO2C
CN
Me
3a
400 MHz/CDCl3
4.98
2.01
0.99
2.02
1.12
1.04
3.00
3.02

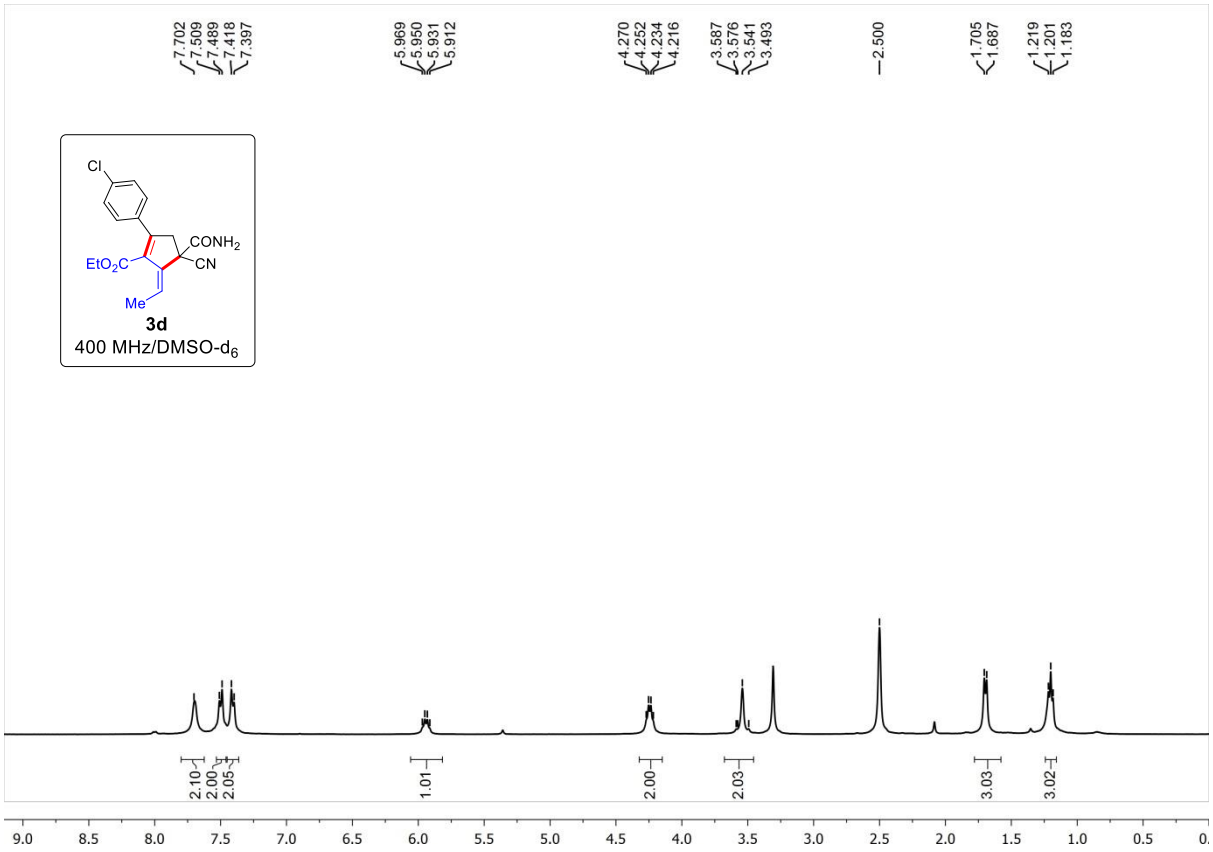

169.055
167.316
146.054
140.195
133.535
129.652
129.542
128.719
127.106
122.712
119.965
77.478
77.159
76.841
61.930
51.438
44.664
14.007
13.891
CONH2
EtO2C
CN
Me
3a
100 MHz/CDCl3

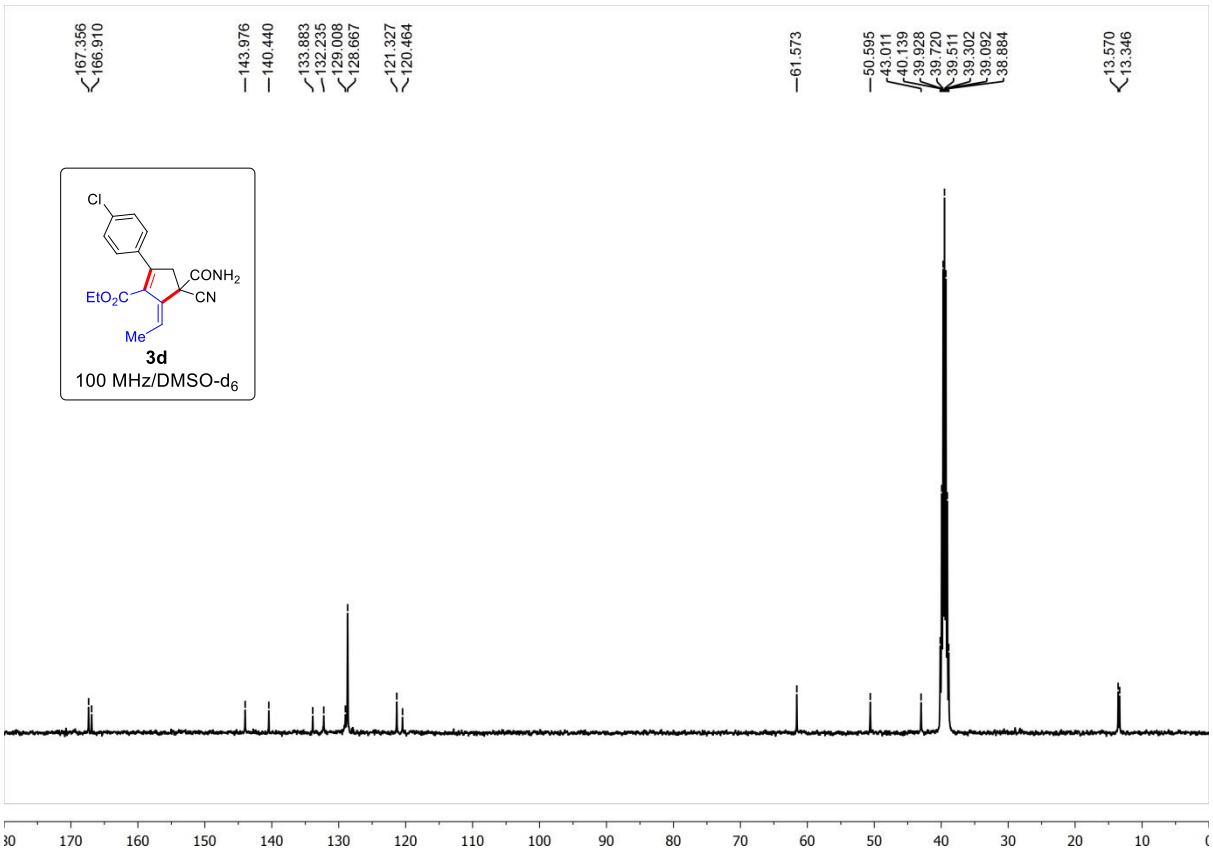

7.320
7.298
7.260
6.888
6.867
6.283
5.931
5.912
5.893
5.875
4.327
4.315
4.304
4.296
4.285
4.278
4.267
4.259
4.249
4.240
3.823
3.602
3.559
3.527
3.485
1.799
1.780
1.295
1.278
1.259
MeO
CONH2
EtO2C
CN
Me
3b
400 MHz/CDCl3
2.03
2.03
1.01
1.99
2.00
3.04
1.01
0.98
3.00
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

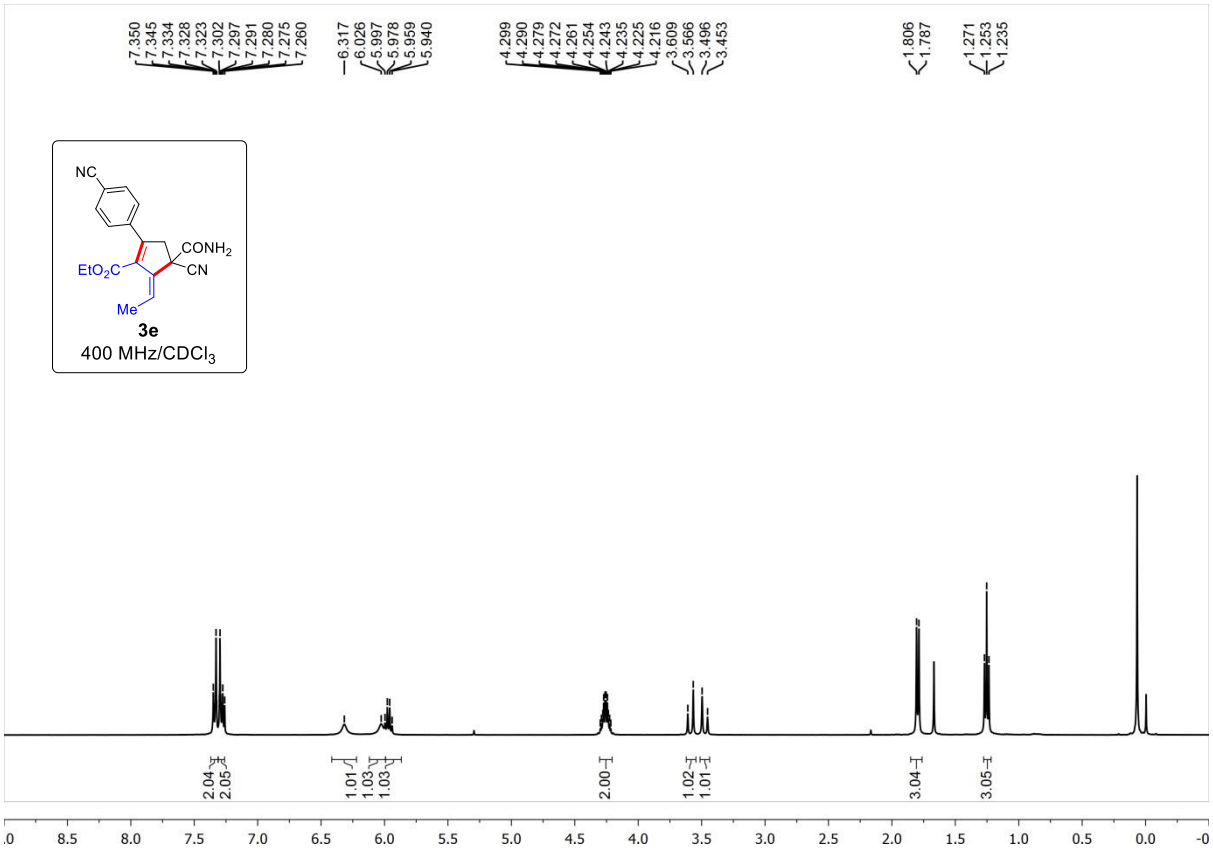

168.865
167.706
160.801
145.477
140.384
128.775
127.818
125.887
121.764
119.970
114.205
77.479
77.161
76.842
61.925
55.490
51.550
44.626
14.018
13.970
MeO
CONH2
EtO2C
CN
Me
3b
100 MHz/CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

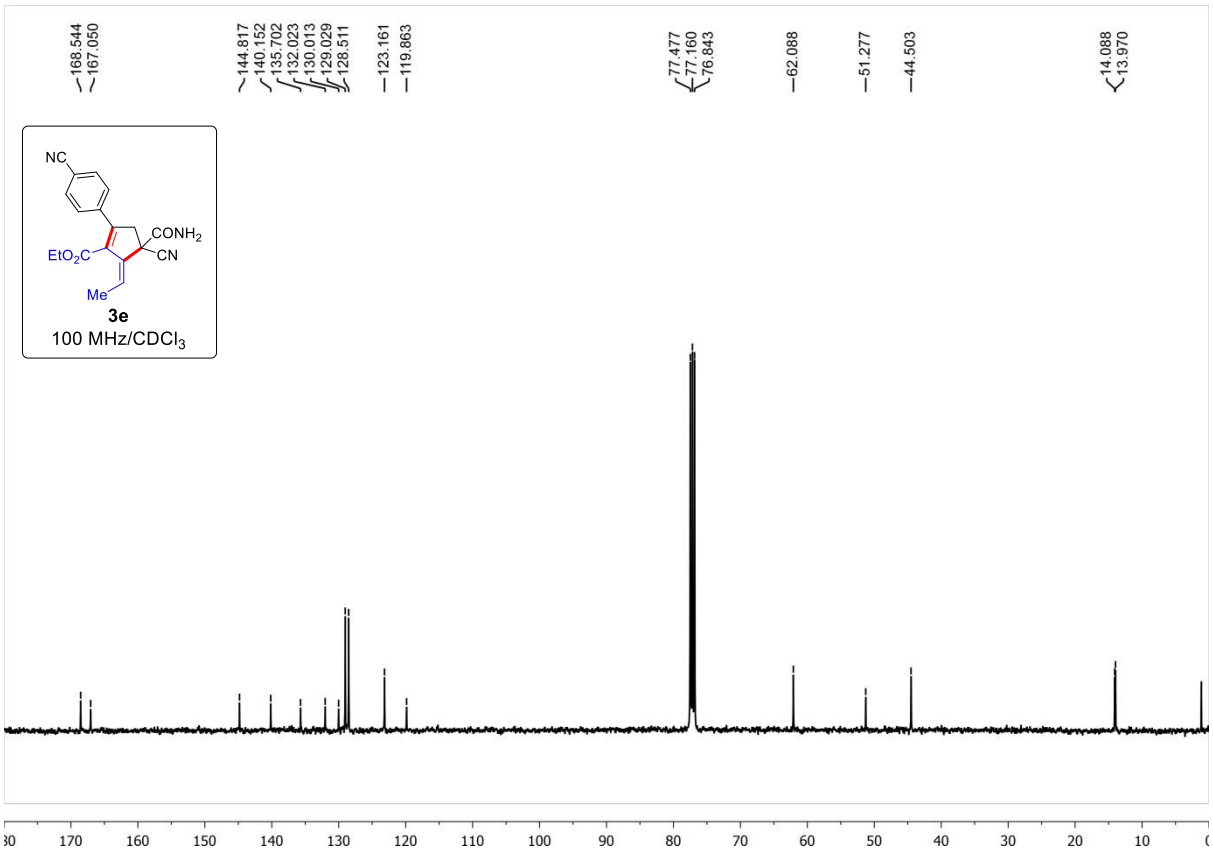

7.262
7.253
7.237
7.176
7.157
7.156
6.284
5.987
5.957
5.938
5.919
5.901
4.315
4.305
4.296
4.287
4.275
4.268
4.257
4.240
4.230
4.213
3.609
3.566
3.541
3.499
2.361
1.806
1.788
1.283
1.265
1.248
Me
CONH2
EtO2C
CN
Me
3c
400 MHz/CDCl3
2.03
2.01
0.99
1.03
1.03
2.00
1.04
1.00
3.07
3.03
3.09

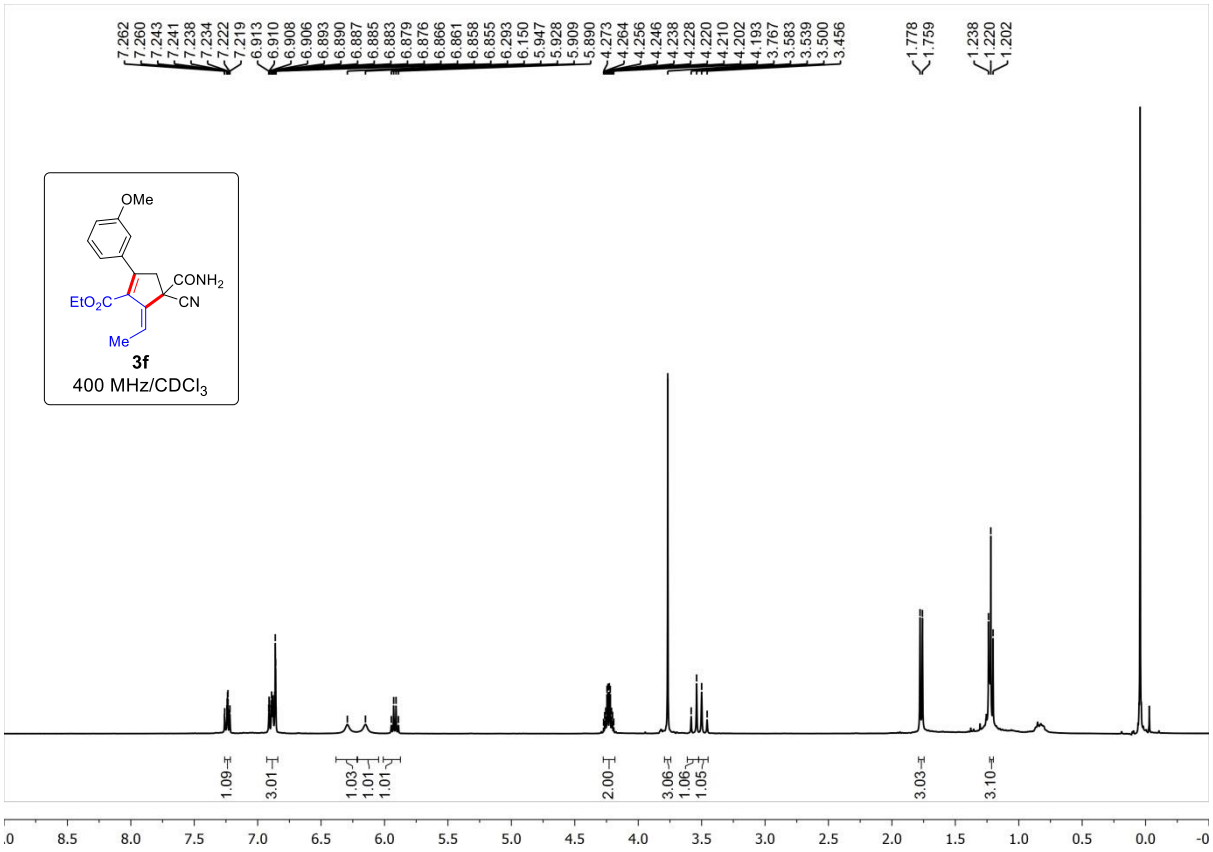

168.884
167.517
146.001
140.332
140.028
130.611
129.468
128.787
127.094
122.248
119.965
77.478
77.161
76.842
61.921
51.552
44.676
21.487
13.985
Me
CONH2
EtO2C
CN
Me
3c
100 MHz/CDCl3

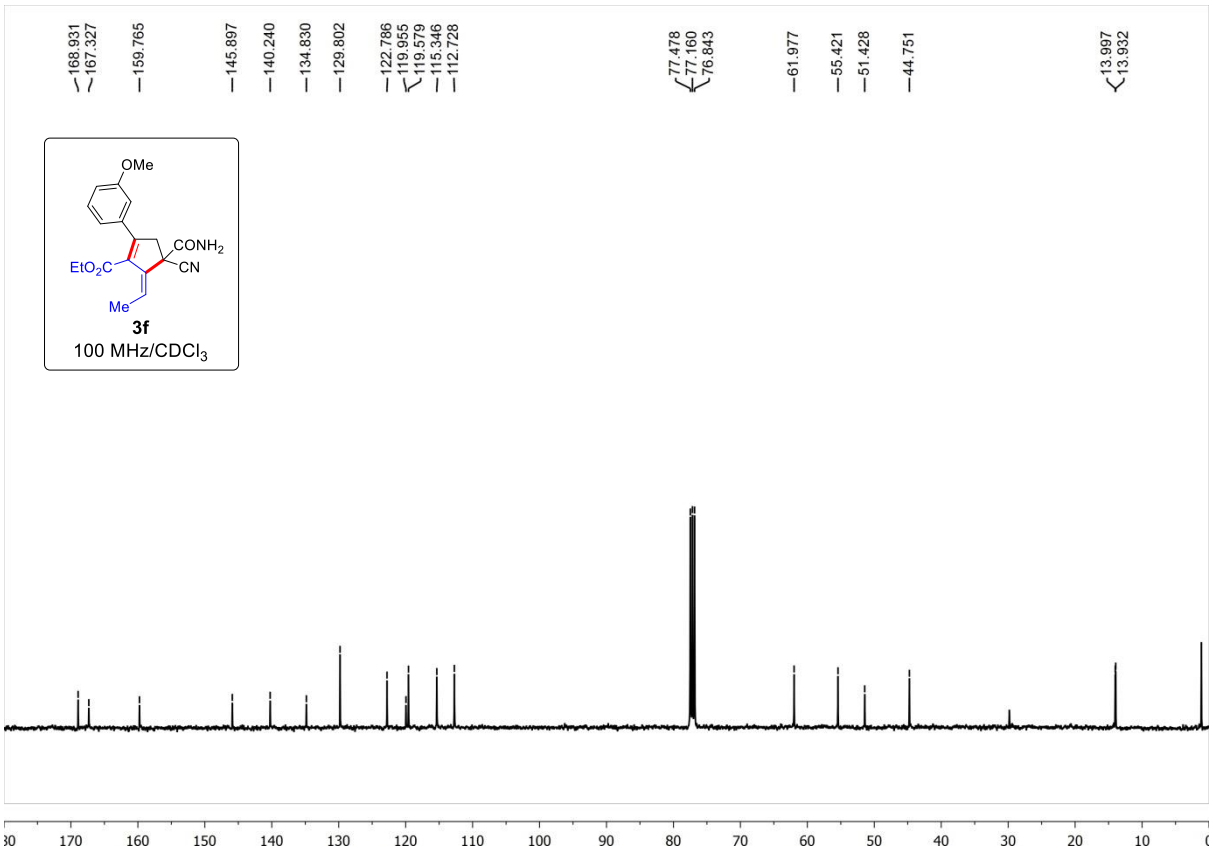

7.702
7.509
7.489
7.418
7.397
5.969
5.950
5.931
5.912
4.270
4.252
4.234
4.216
3.587
3.576
3.541
3.493
2.500
1.705
1.687
1.219
1.201
1.183
Cl
CONH2
EtO2C
CN
Me
3d
400 MHz/DMSO-d6
2.10
2.00
2.05
1.01
2.00
2.03
3.03
3.02

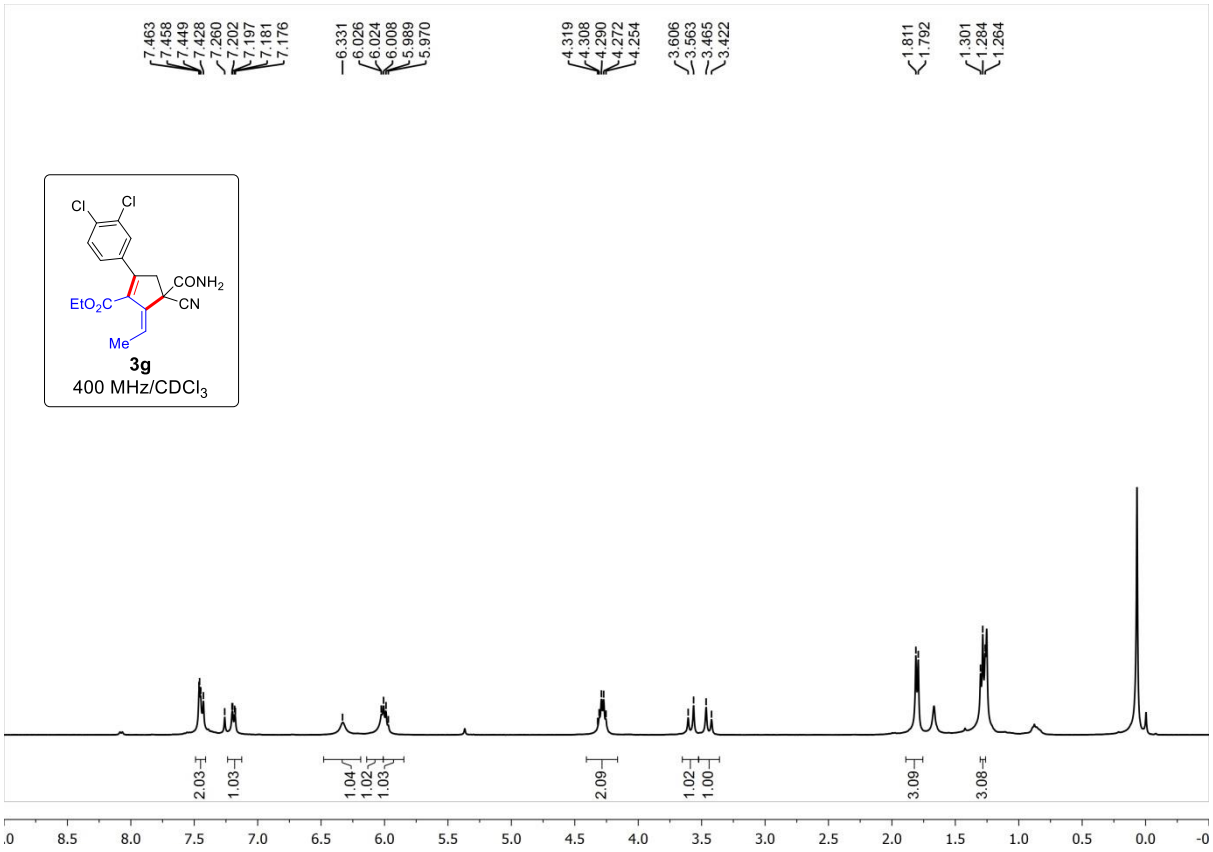

167.356
166.910
143.976
140.440
133.883
132.235
129.008
128.667
121.327
120.464
61.573
50.595
43.011
40.139
39.928
39.720
39.511
39.302
39.092
38.884
13.570
13.346
Cl
CONH2
EtO2C
CN
Me
3d
100 MHz/DMSO-d6

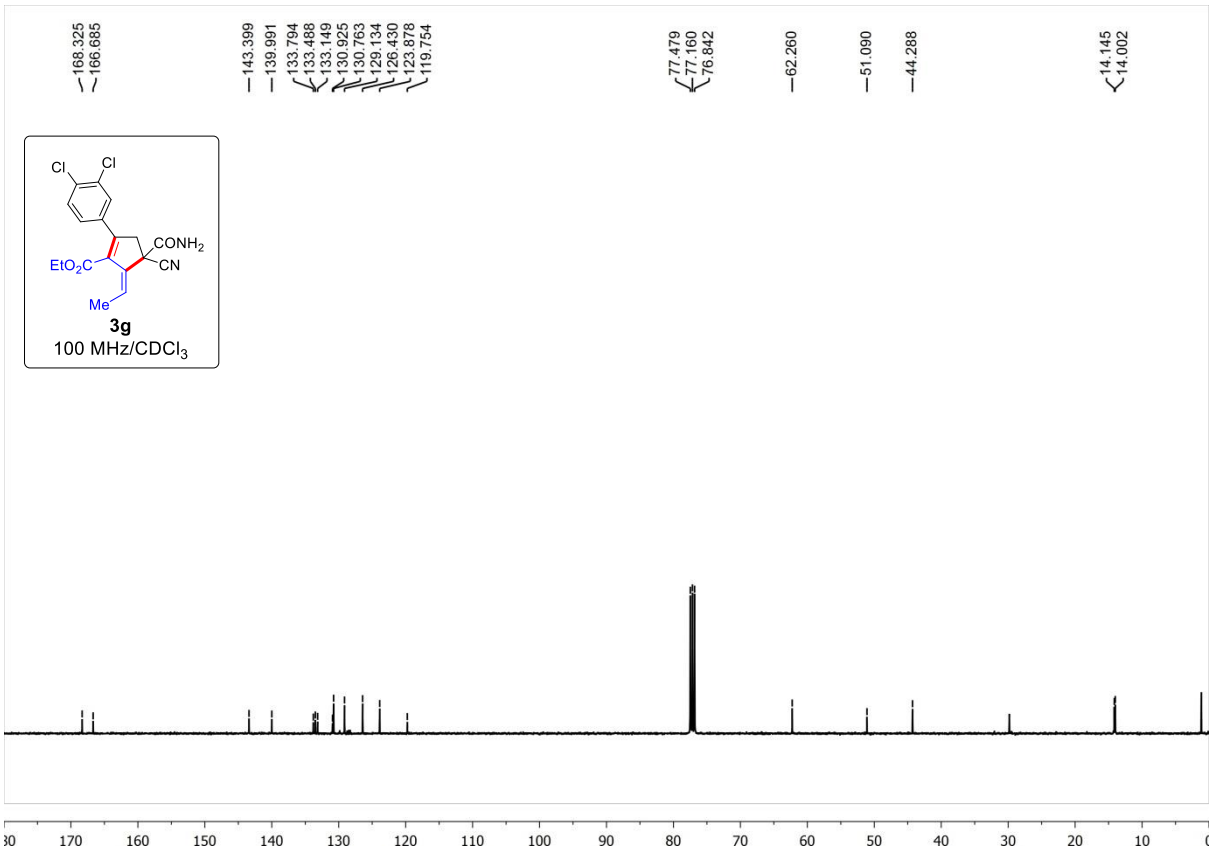

7.350
7.345
7.334
7.328
7.323
7.302
7.297
7.291
7.280
7.275
7.260
6.317
6.026
5.997
5.978
5.959
5.940
4.299
4.290
4.279
4.272
4.261
4.254
4.243
4.235
4.225
4.216
3.609
3.566
3.496
3.453
1.806
1.787
1.271
1.253
1.235
NC
CONH2
EtO2C
CN
Me
3e
400 MHz/CDCl3
2.04
2.05
1.01
1.03
1.03
2.00
1.02
1.01
3.04
3.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

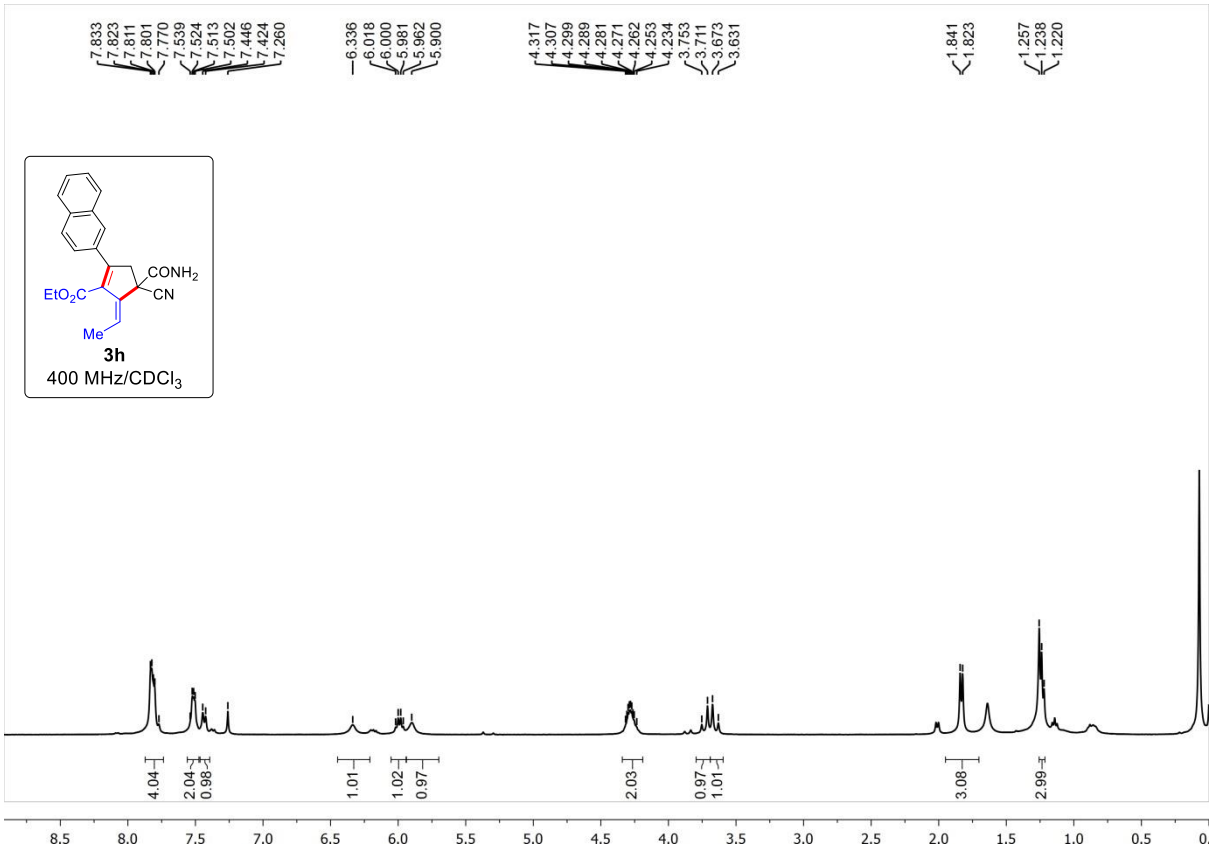

168.544
167.050
144.817
140.152
135.702
132.023
130.013
129.029
128.511
123.161
119.863
77.477
77.160
76.843
62.088
51.277
44.503
14.088
13.970
NC
CONH2
EtO2C
CN
Me
3e
100 MHz/CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

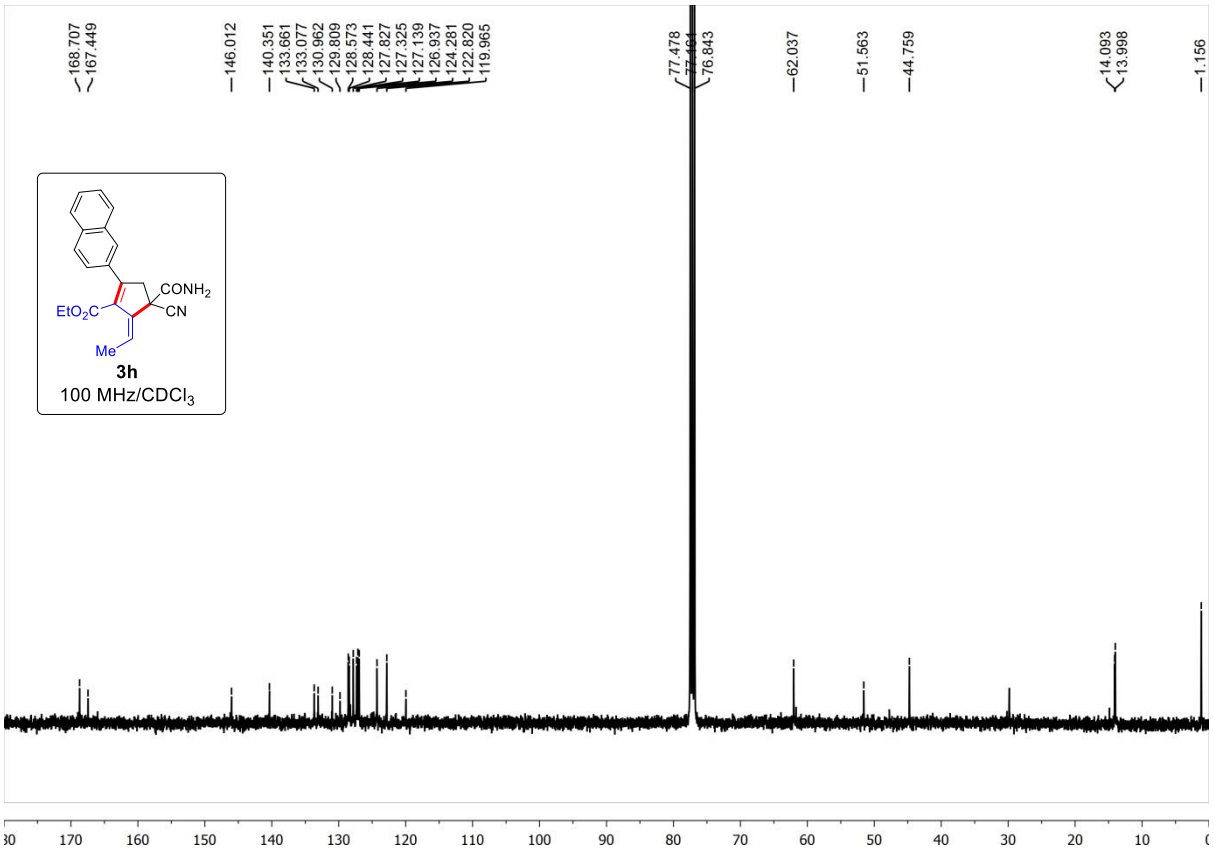

7.262
7.260
7.243
7.241
7.238
7.234
7.222
7.219
6.913
6.910
6.908
6.906
6.893
6.890
6.887
6.885
6.883
6.879
6.876
6.866
6.861
6.858
6.855
6.293
6.150
5.947
5.928
5.909
5.890
4.273
4.264
4.256
4.246
4.238
4.228
4.220
4.210
4.202
4.193
3.767
3.583
3.539
3.500
3.456
1.778
1.759
1.238
1.220
1.202
OMe
CONH2
EtO2C
CN
Me
3f
400 MHz/CDCl3
1.09
3.01
1.03
1.01
1.01
2.00
3.06
1.06
1.05
3.03
3.10
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0

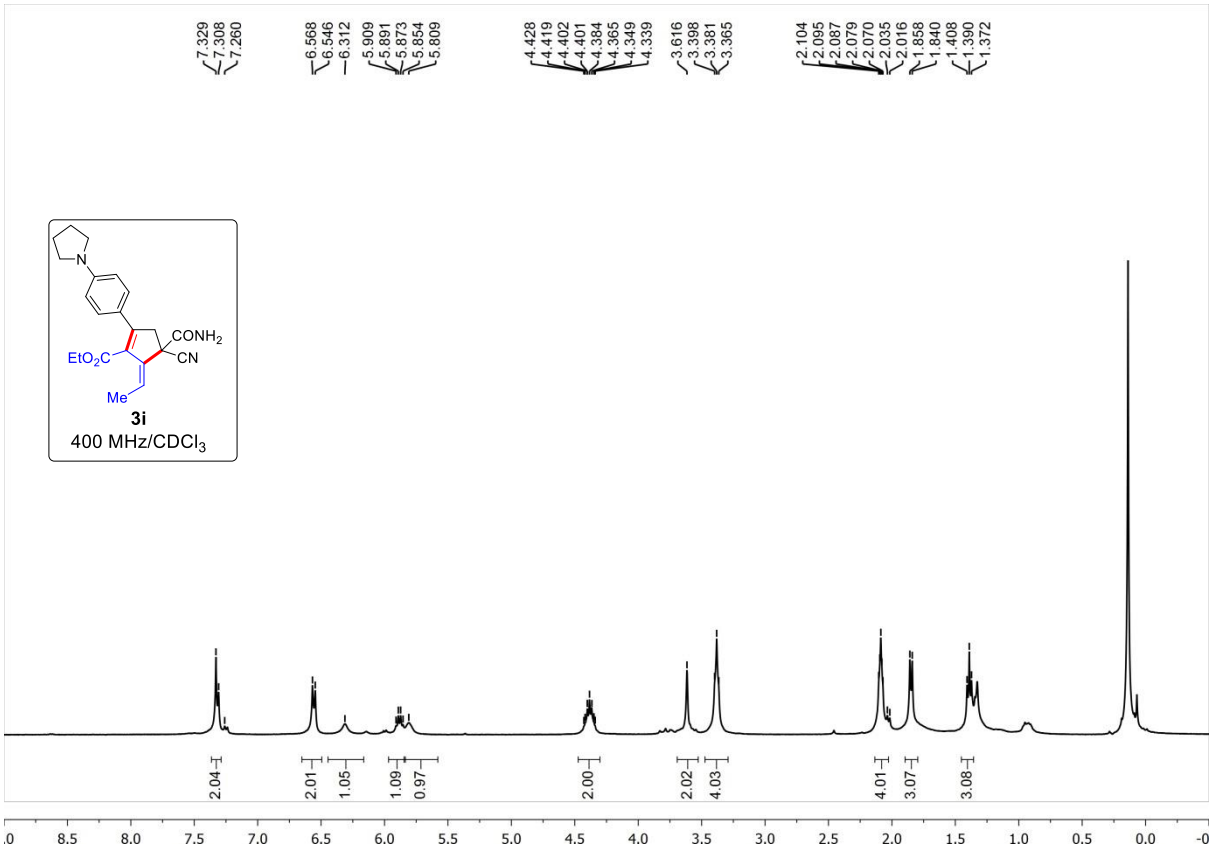

168.931
167.327
159.765
145.897
140.240
134.830
129.802
122.786
119.955
119.579
115.346
112.728
77.478
77.160
76.843
61.977
55.421
51.428
44.751
13.997
13.932
OMe
CONH2
EtO2C
CN
Me
3f
100 MHz/CDCl3
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

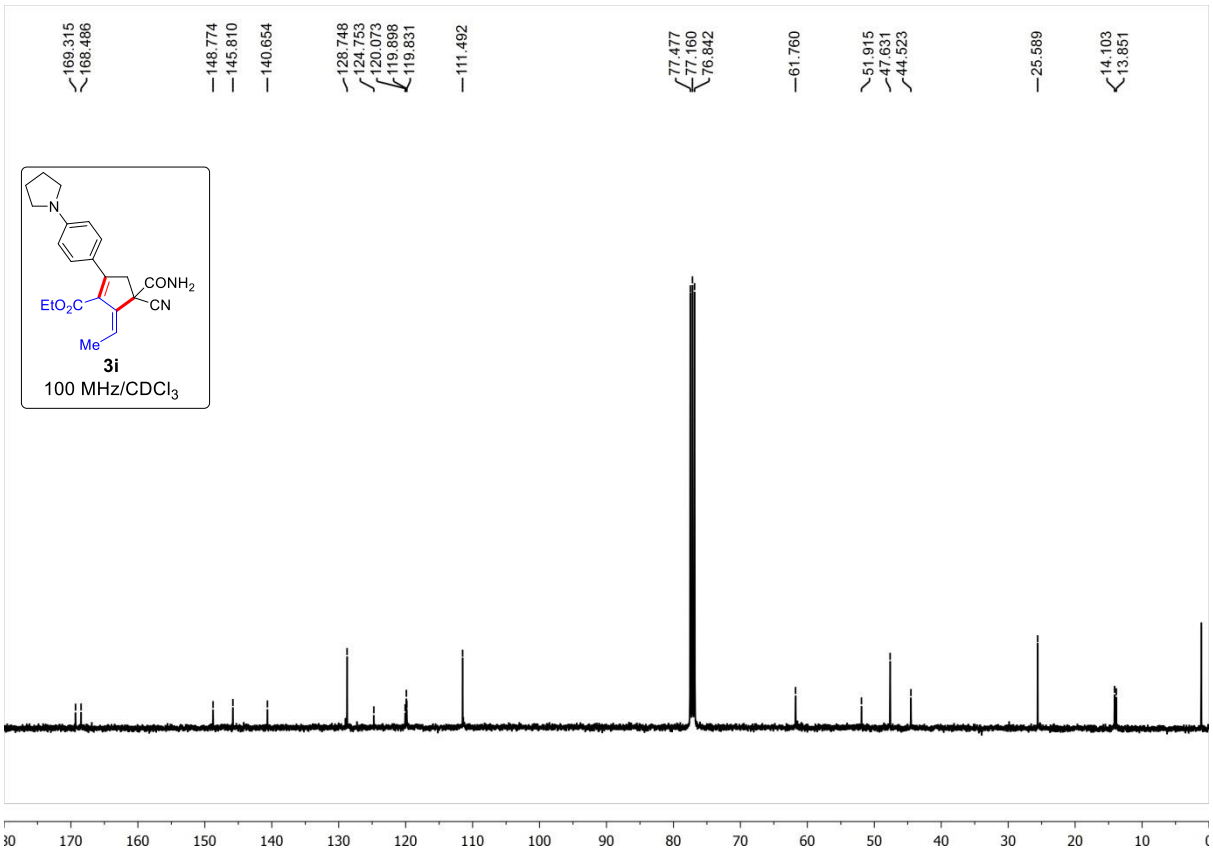

7.463
7.458
7.449
7.428
7.260
7.202
7.197
7.181
7.176
6.331
6.026
6.024
6.008
5.989
5.970
4.319
4.308
4.290
4.272
4.254
3.606
3.563
3.465
3.422
1.811
1.792
1.301
1.284
1.264
Cl
Cl
CONH2
EtO2C
CN
Me
3g
400 MHz/CDCl3
2.03
1.03
1.04
1.02
1.03
2.09
1.02
1.00
3.09
3.08

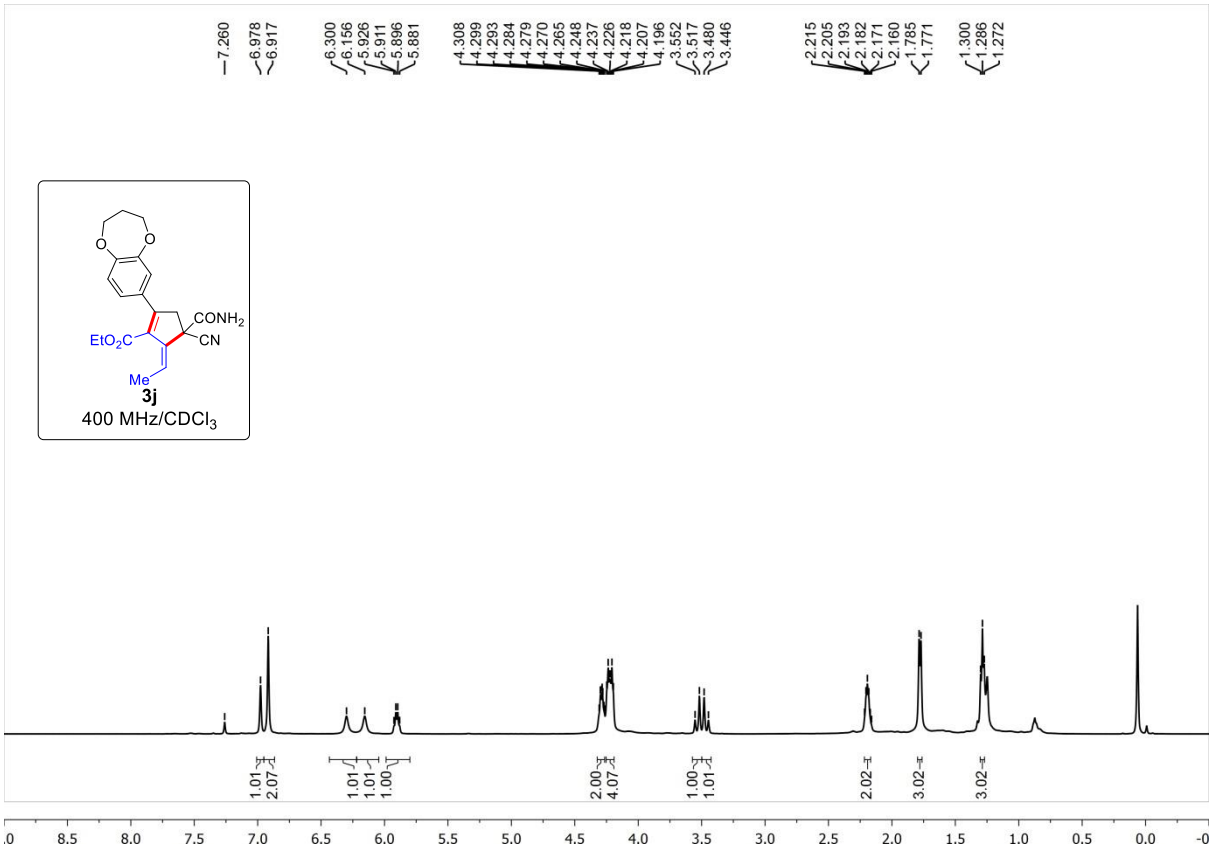

168.325
166.685
143.399
139.991
133.794
133.488
133.149
130.925
130.763
129.134
126.430
123.878
119.754
77.479
77.160
76.842
62.260
51.090
44.288
14.145
14.002
Cl
Cl
CONH2
EtO2C
CN
Me
3g
100 MHz/CDCl3

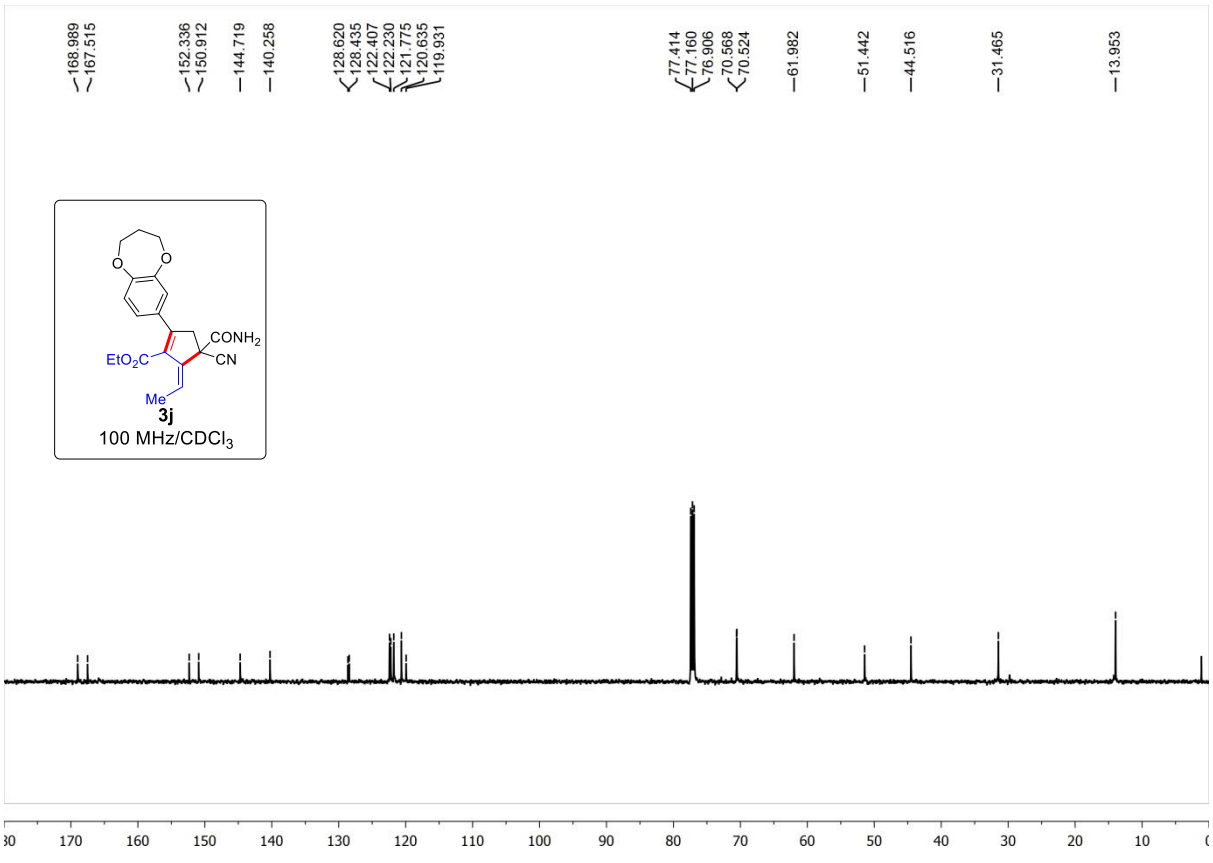

7.833
7.823
7.811
7.801
7.770
7.539
7.524
7.513
7.502
7.446
7.424
7.260
6.336
6.018
6.000
5.981
5.962
5.900
4.317
4.307
4.299
4.289
4.281
4.271
4.262
4.253
4.234
3.753
3.711
3.673
3.631
1.841
1.823
1.257
1.238
1.220
CONH2
CN
EtO2C
Me
3h
400 MHz/CDCl3
4.04
2.04
0.98
1.01
1.02
0.97
2.03
0.97
1.01
3.08
2.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

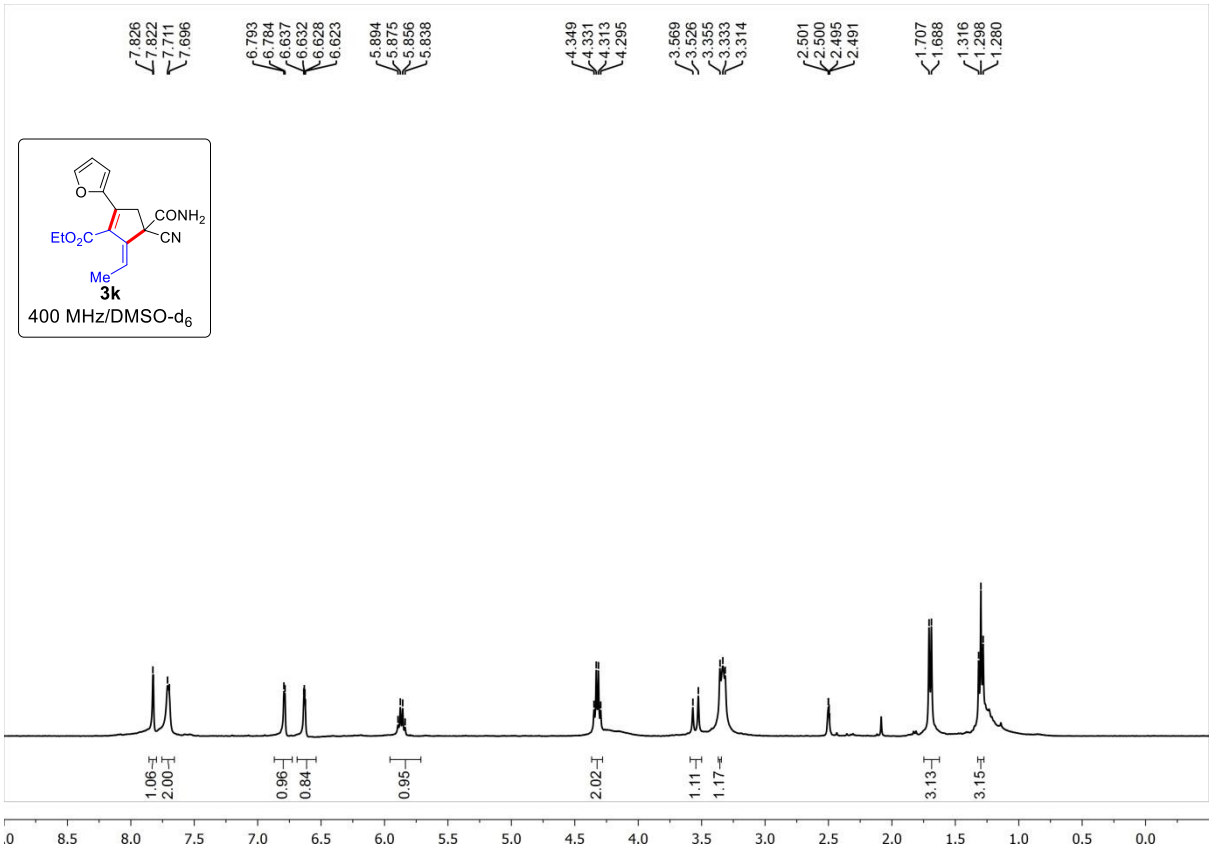

168.707
167.449
146.012
140.351
133.661
133.077
130.962
129.809
128.573
128.441
127.827
127.325
127.139
126.937
124.281
122.820
119.965
77.478
77.161
76.843
62.037
51.563
44.759
14.093
13.998
1.156
CONH2
CN
EtO2C
Me
3h
100 MHz/CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

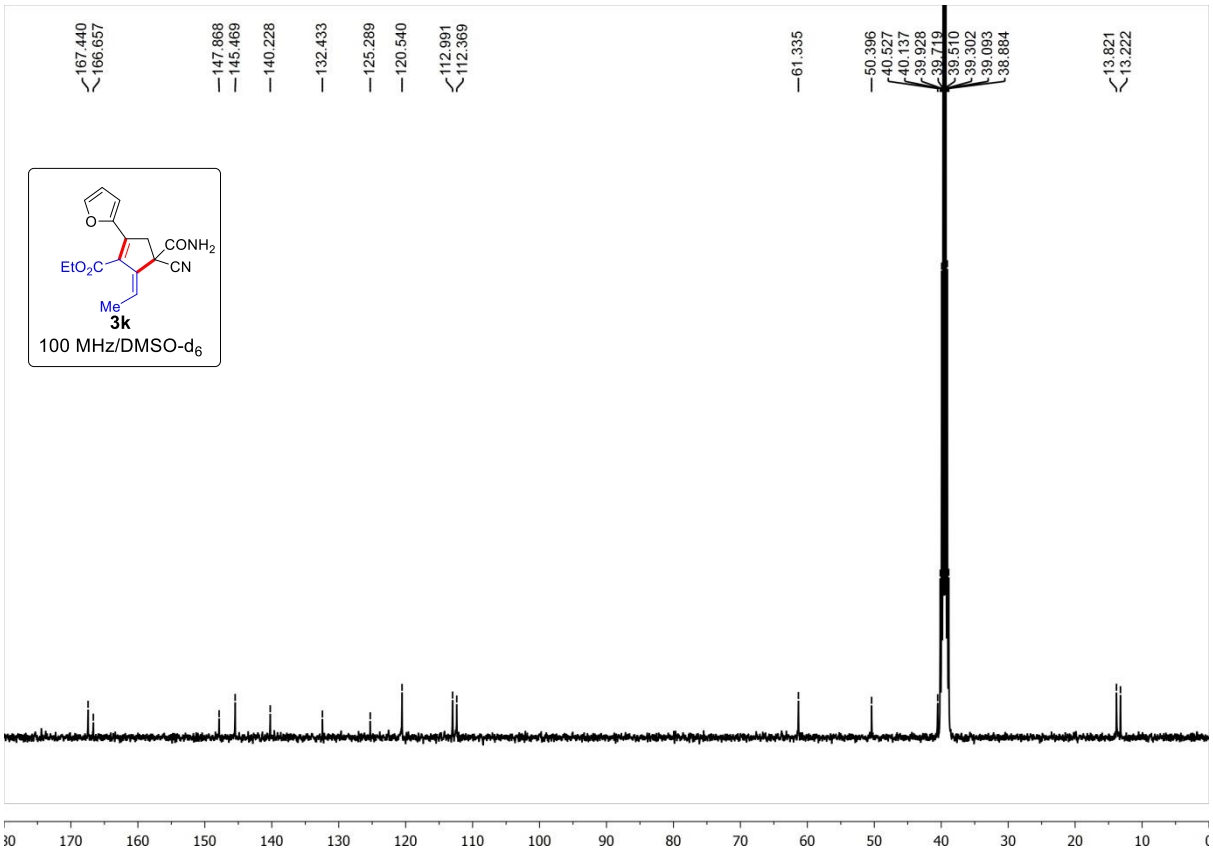

7.329
7.308
7.260
6.568
6.546
6.312
5.909
5.891
5.873
5.854
5.809
4.428
4.419
4.402
4.401
4.384
4.365
4.349
4.339
3.616
3.398
3.381
3.365
2.104
2.095
2.087
2.079
2.070
2.035
2.016
1.858
1.840
1.408
1.390
1.372
CONH2
CN
EtO2C
Me
3i
400 MHz/CDCl3
2.04
2.01
1.05
1.09
0.97
2.00
2.02
4.03
4.01
3.07
3.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

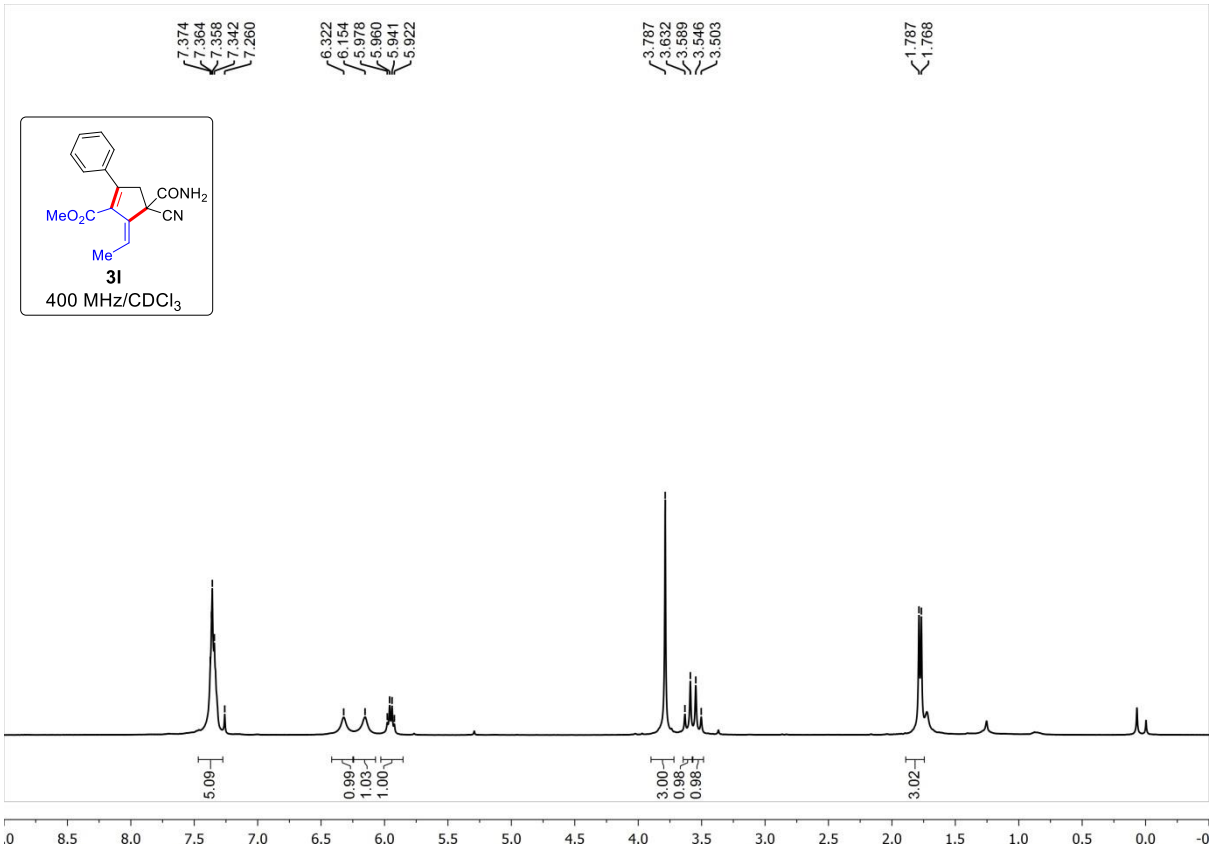

169.315
168.486
148.774
145.810
140.654
128.748
124.753
120.073
119.898
119.831
111.492
77.477
77.160
76.842
61.760
51.915
47.631
44.523
25.589
14.103
13.851
CONH2
CN
EtO2C
Me
3i
100 MHz/CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

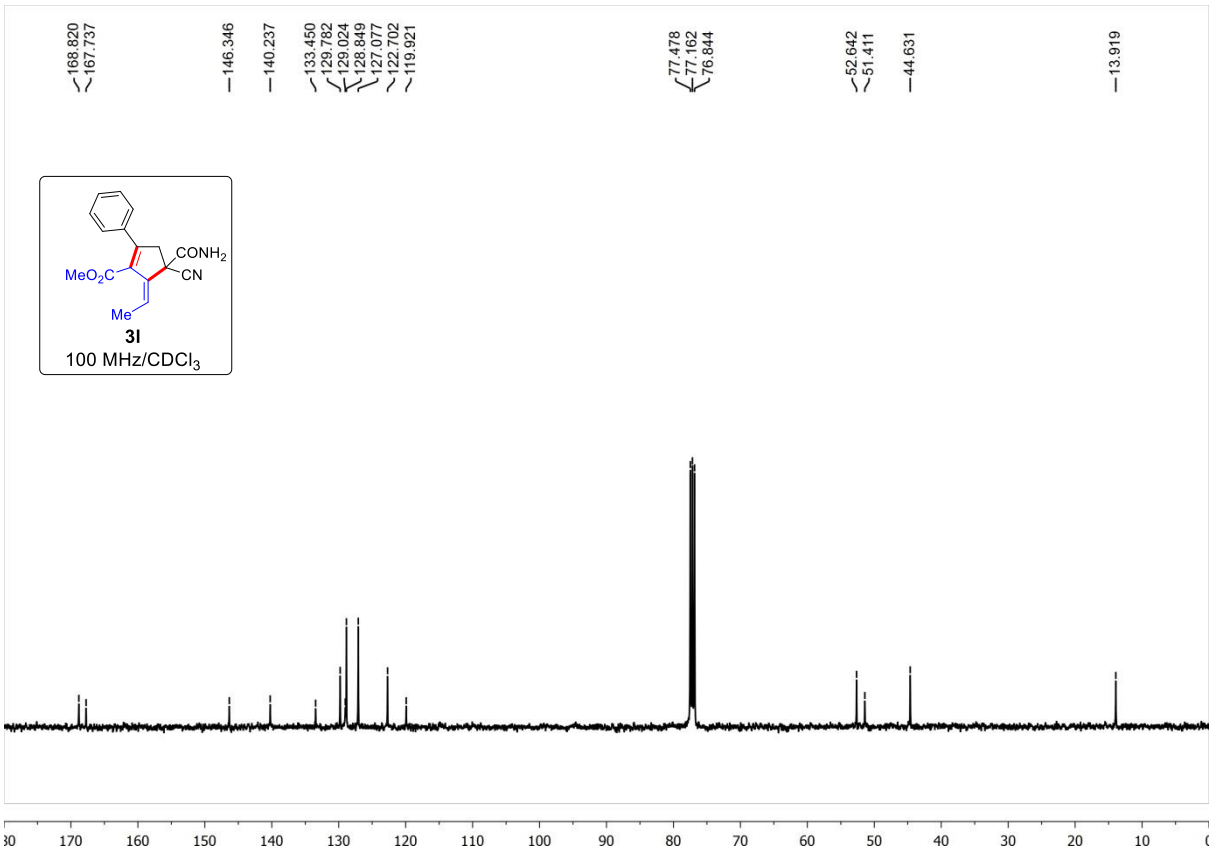

7.260
6.978
6.917
6.300
6.156
5.926
5.911
5.896
5.881
4.308
4.299
4.293
4.284
4.279
4.270
4.265
4.248
4.237
4.226
4.218
4.207
4.196
3.552
3.517
3.480
3.446
2.215
2.205
2.193
2.182
2.171
2.160
1.785
1.771
1.300
1.286
1.272
CONH2
EtO2C
CN
Me
3j
400 MHz/CDCl3
1.01
2.07
1.01
1.01
1.00
2.00
4.07
1.00
1.01
2.02
3.02
3.02

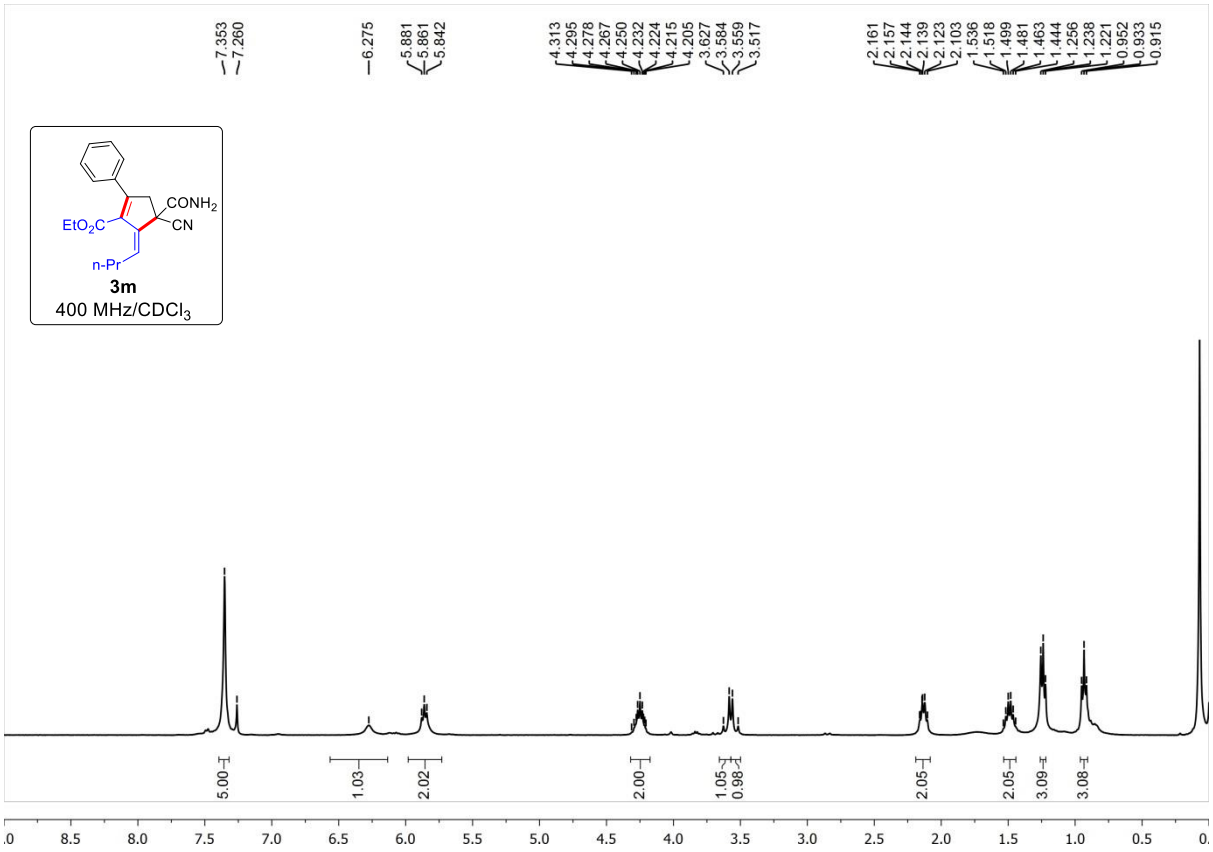

168.989
167.515
152.336
150.912
144.719
140.258
128.620
128.435
122.407
122.230
121.775
120.635
119.931
77.414
77.160
76.906
70.568
70.524
61.982
51.442
44.516
31.465
13.953
CONH2
EtO2C
CN
Me
3j
100 MHz/CDCl3

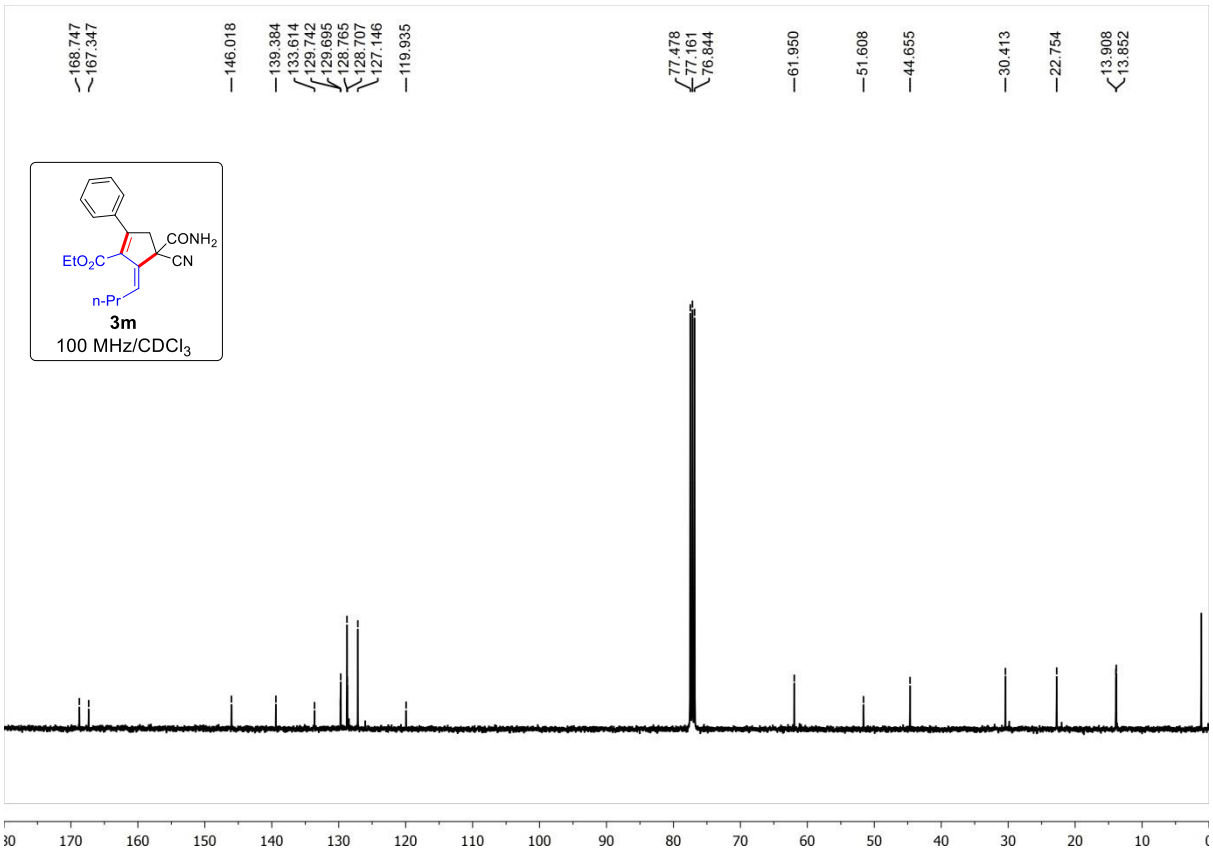

7.826
7.822
7.711
7.696
6.793
6.784
6.637
6.632
6.628
6.623
5.894
5.875
5.856
5.838
4.349
4.331
4.313
4.295
3.569
3.526
3.355
3.333
3.314
2.501
2.500
2.495
2.491
1.707
1.688
1.316
1.298
1.280
CONH2
EtO2C
CN
Me
3k
400 MHz/DMSO-d6
1.06
2.00
0.96
0.84
0.95
2.02
1.11
1.17
3.13
3.15

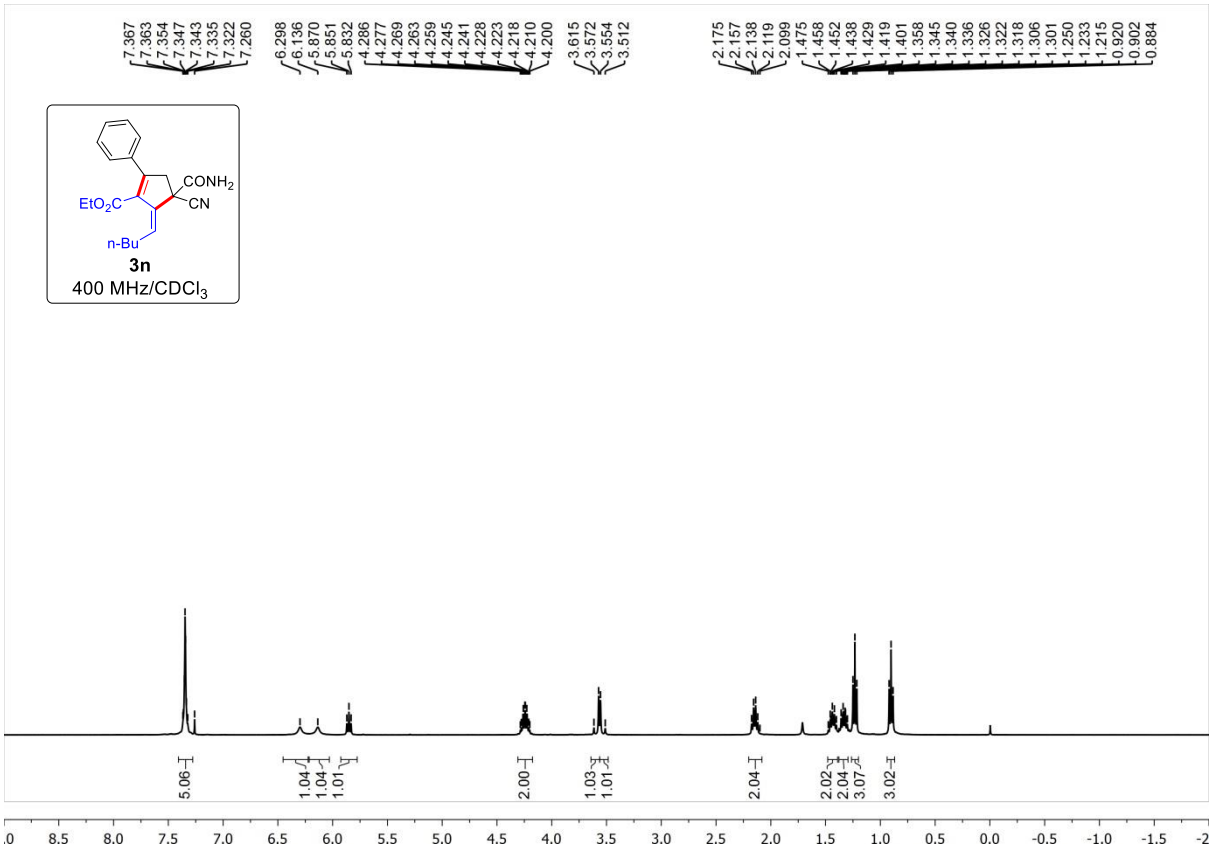

167.440
166.657
147.868
145.469
140.228
132.433
125.289
120.540
112.991
112.369
61.335
50.396
40.527
40.137
39.928
39.719
39.510
39.302
39.093
38.884
13.821
13.222
CONH2
EtO2C
CN
Me
3k
100 MHz/DMSO-d6

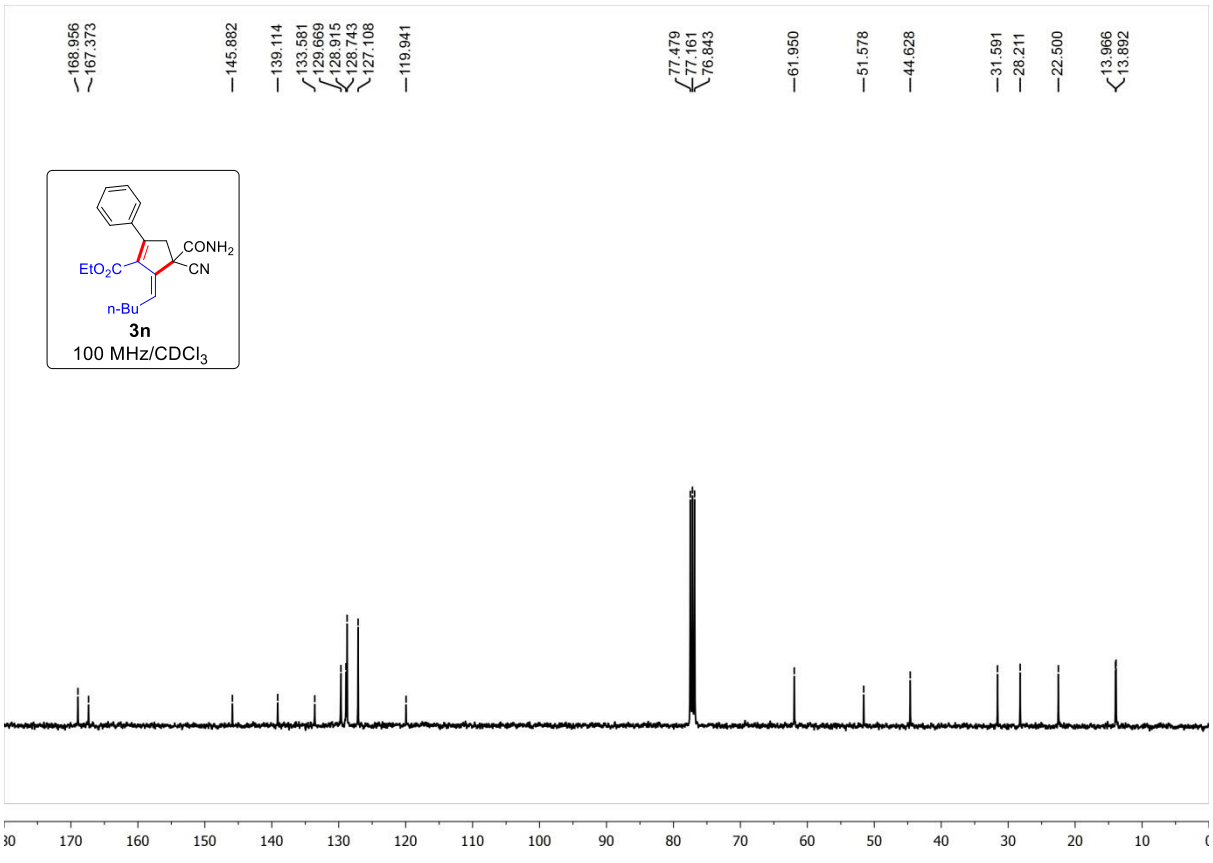

7.374
7.364
7.358
7.342
7.260
6.322
6.154
5.978
5.960
5.941
5.922
3.787
3.632
3.589
3.546
3.503
1.787
1.768
CONH2
MeO2C
CN
Me
3l
400 MHz/CDCl3
5.09
0.99
1.03
1.00
3.00
0.98
0.98
3.02

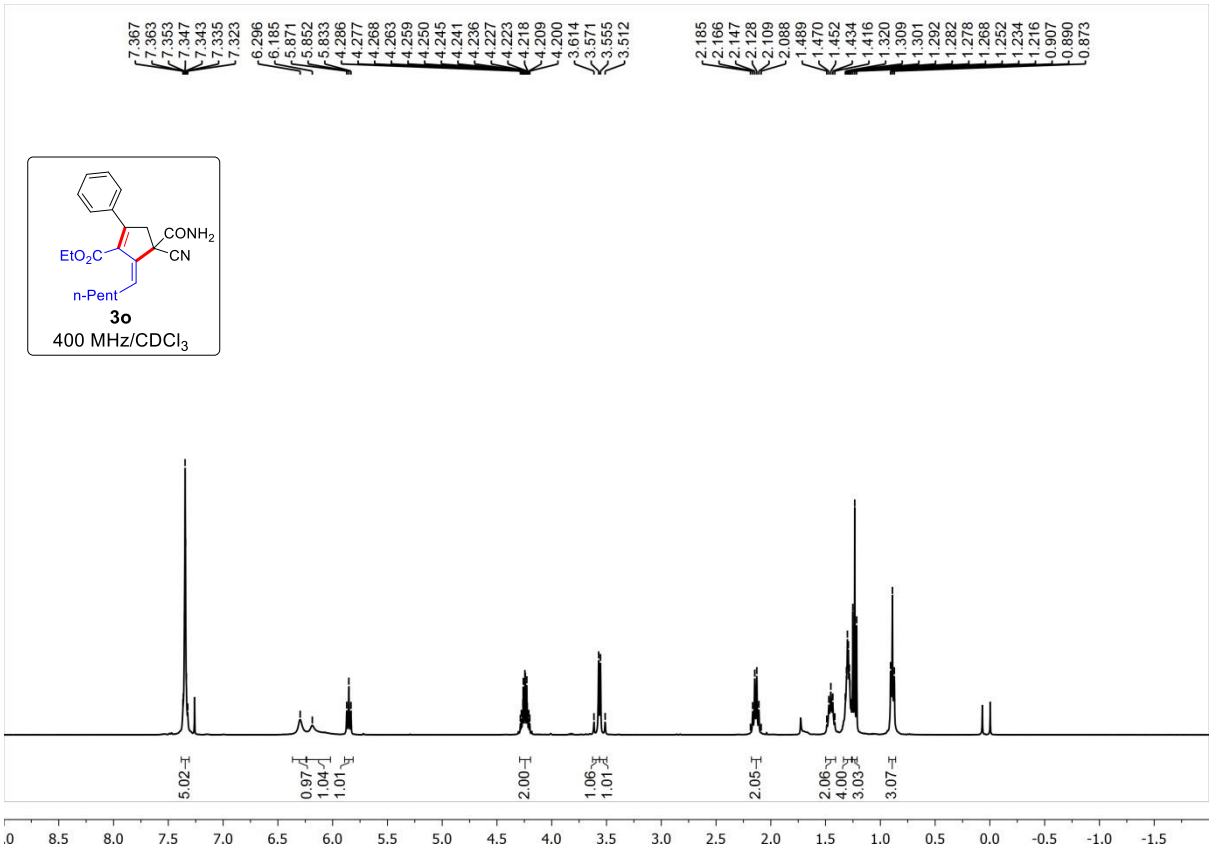

168.820
167.737
146.346
140.237
133.450
129.782
129.024
128.849
127.077
122.702
119.921
77.478
77.162
76.844
52.642
51.411
44.631
13.919
CONH2
MeO2C
CN
Me
3l
100 MHz/CDCl3

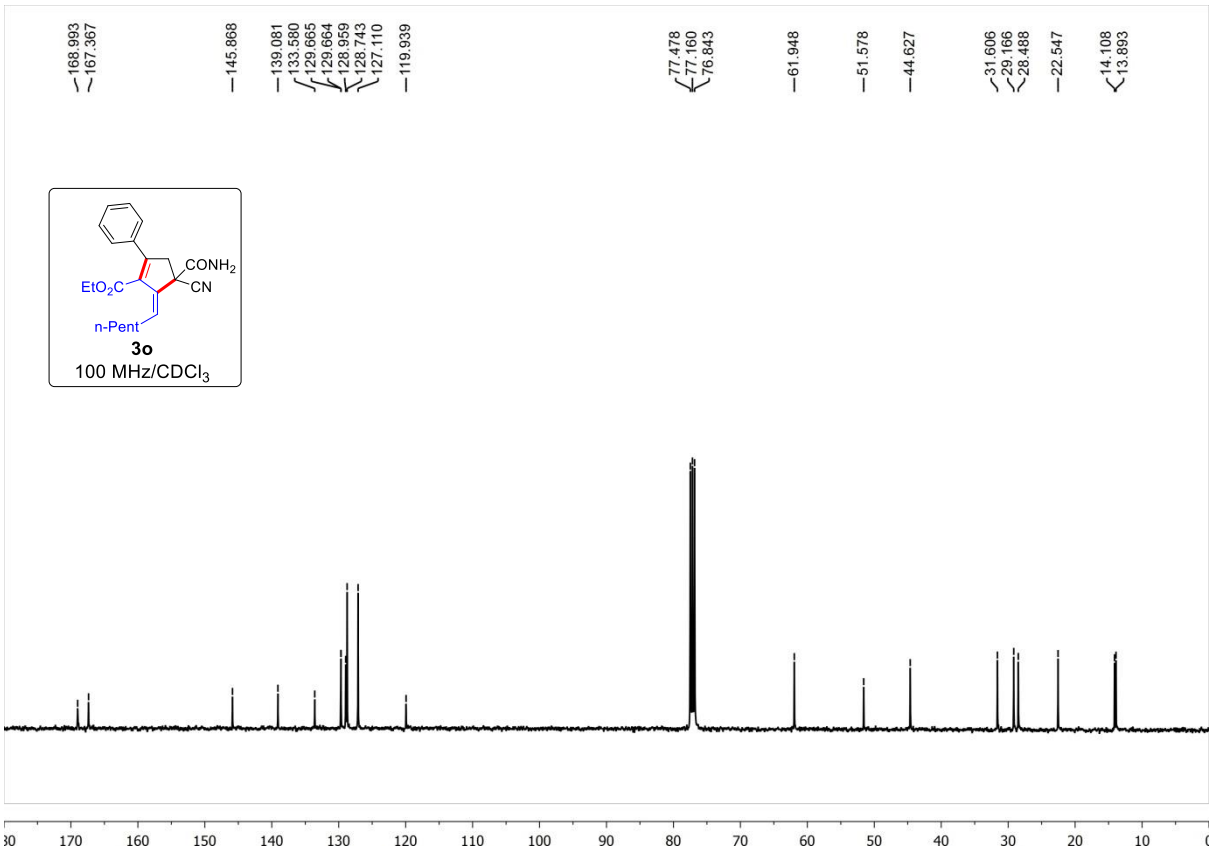

7.353
7.260
6.275
5.881
5.861
5.842
4.313
4.295
4.278
4.267
4.250
4.232
4.224
4.215
4.205
3.627
3.584
3.559
3.517
2.161
2.157
2.144
2.139
2.123
2.103
1.536
1.518
1.499
1.481
1.463
1.444
1.256
1.238
1.221
0.952
0.933
0.915
CONH2
CN
EtO2C
n-Pr
3m
400 MHz/CDCl3
5.00
1.03
2.02
2.00
1.05
0.98
2.05
2.05
3.09
3.08

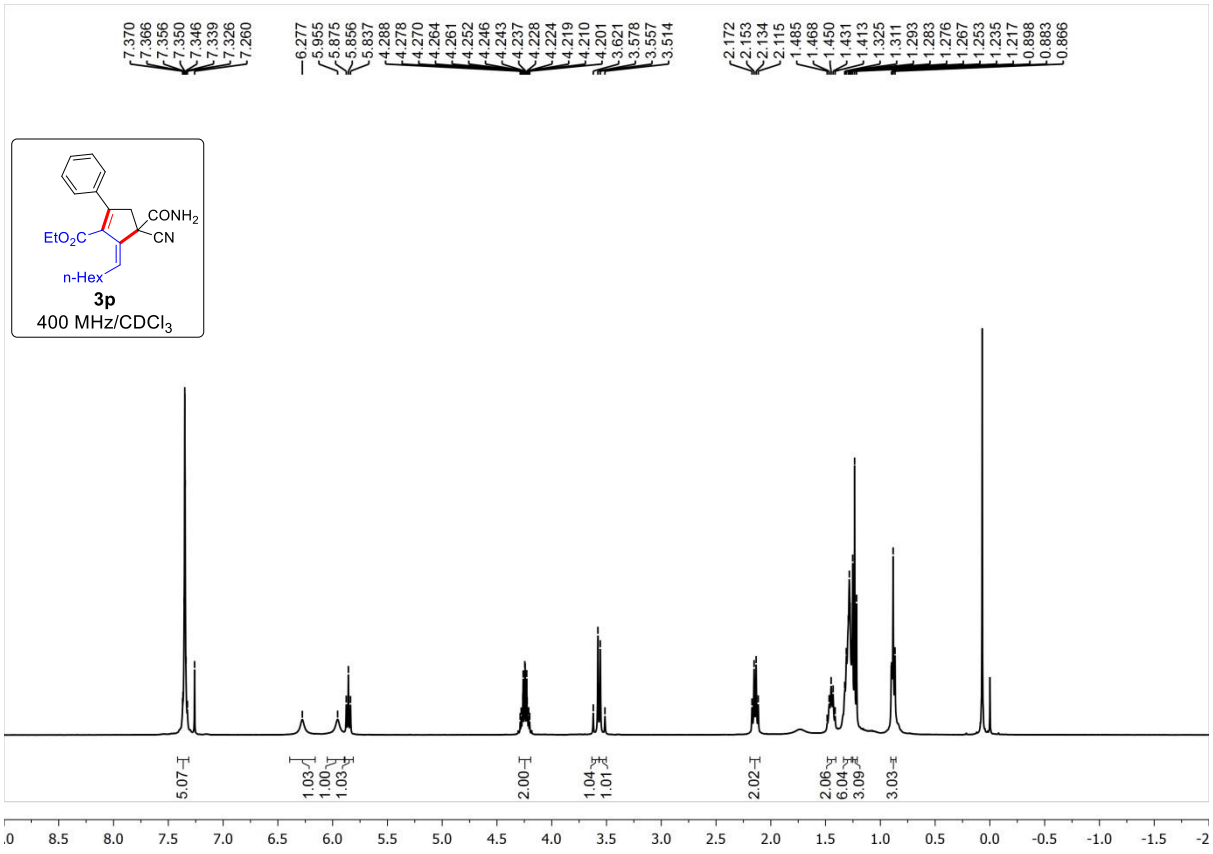

168.747
167.347
146.018
139.384
133.614
129.742
129.695
128.765
128.707
127.146
119.935
77.478
77.161
76.844
61.950
51.608
44.655
30.413
22.754
13.908
13.852
CONH2
CN
EtO2C
n-Pr
3m
100 MHz/CDCl3

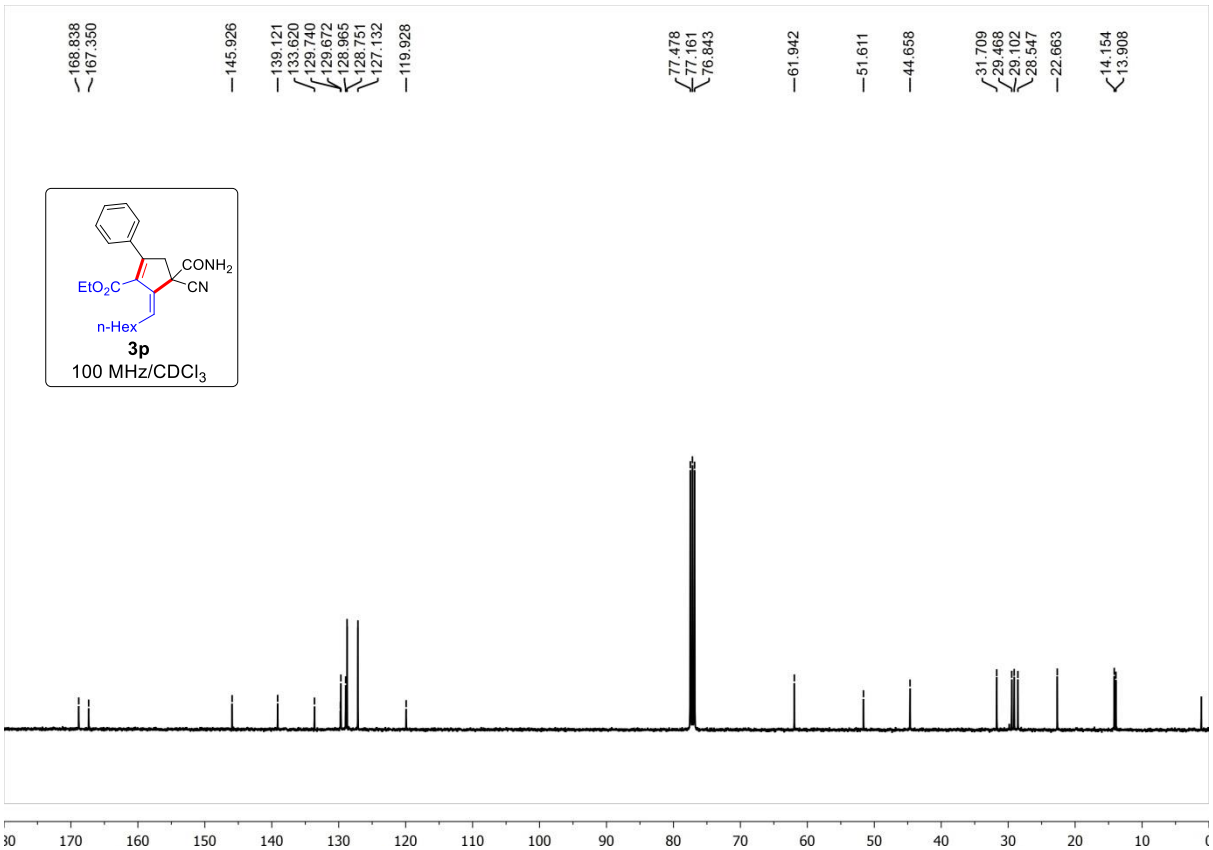

7.367
7.363
7.354
7.347
7.343
7.335
7.322
7.260
6.298
6.136
5.870
5.851
5.832
4.286
4.277
4.269
4.263
4.259
4.245
4.241
4.228
4.223
4.218
4.210
4.200
3.615
3.572
3.554
3.512
2.175
2.157
2.138
2.119
2.099
1.475
1.458
1.452
1.438
1.429
1.419
1.401
1.358
1.345
1.340
1.336
1.326
1.322
1.318
1.306
1.301
1.250
1.233
1.215
0.920
0.902
0.884
CONH2
CN
EtO2C
n-Bu
3n
400 MHz/CDCl3
5.06
1.04
1.04
1.01
2.00
1.03
1.01
2.04
2.02
2.04
3.07
3.02

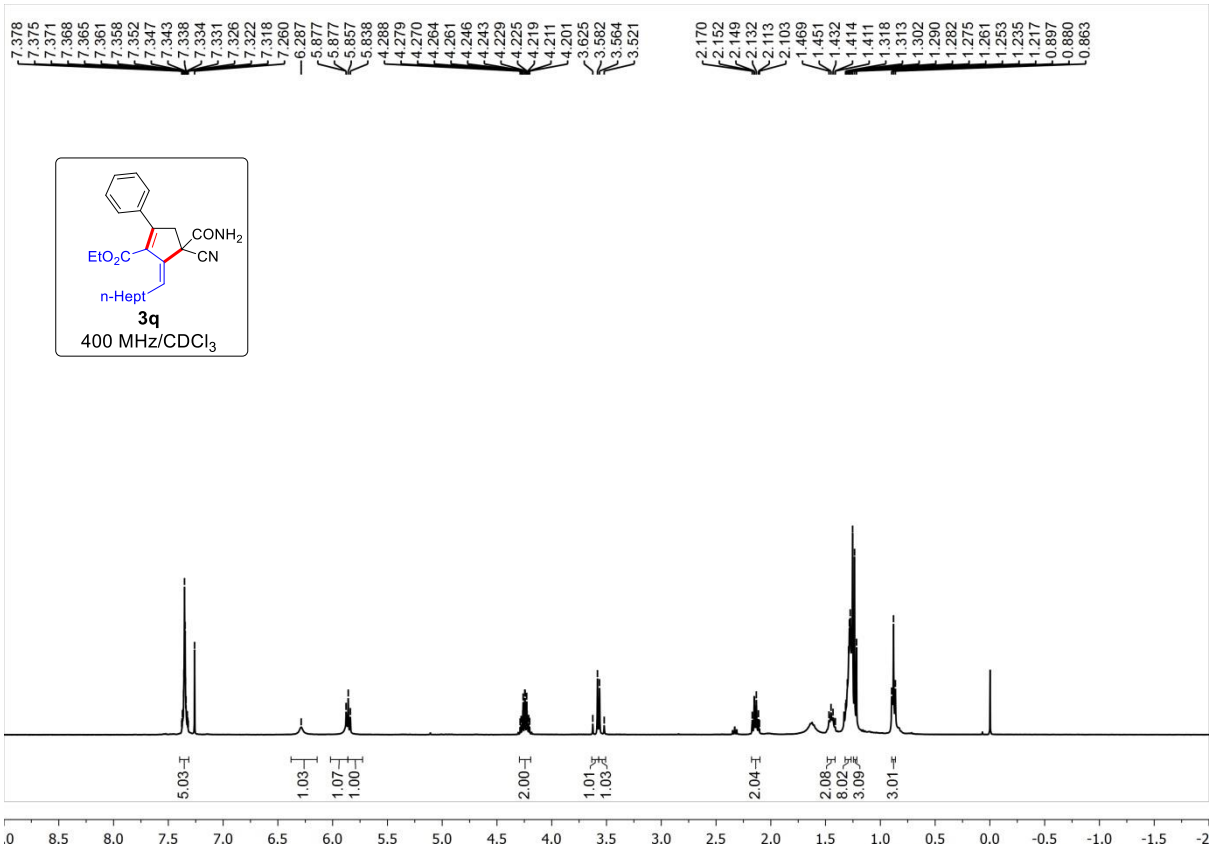

168.956
167.373
145.882
139.114
133.581
129.669
128.915
128.743
127.108
119.941
77.479
77.161
76.843
61.950
51.578
44.628
31.591
28.211
22.500
13.966
13.892
CONH2
CN
EtO2C
n-Bu
3n
100 MHz/CDCl3

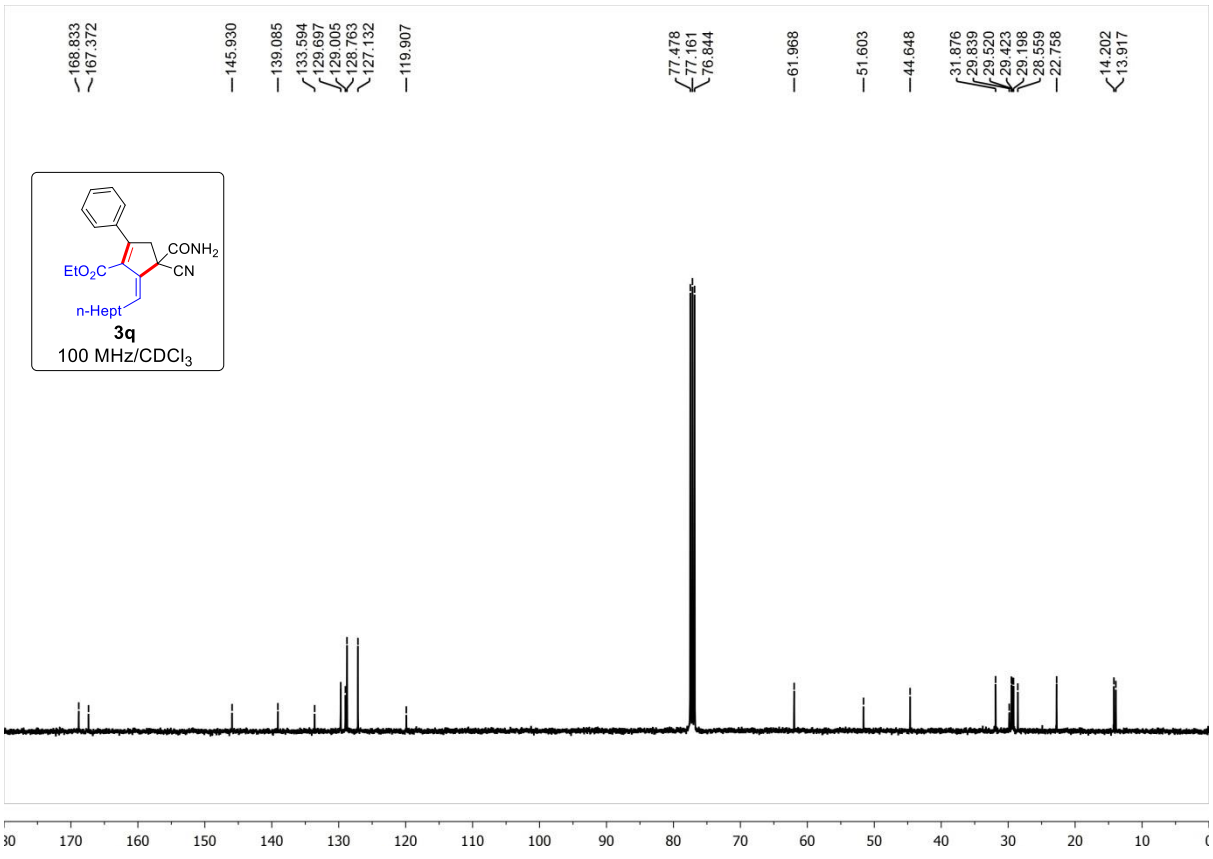

7.367
7.363
7.353
7.347
7.343
7.335
7.323
6.296
6.185
5.871
5.852
5.833
4.286
4.277
4.268
4.263
4.259
4.250
4.245
4.241
4.236
4.227
4.223
4.218
4.209
4.200
3.614
3.571
3.555
3.512
2.185
2.166
2.147
2.128
2.109
2.088
1.489
1.470
1.452
1.434
1.416
1.320
1.309
1.301
1.292
1.282
1.278
1.268
1.252
1.234
1.216
0.907
0.890
0.873
CONH2
CN
EtO2C
n-Pent
3o
400 MHz/CDCl3
5.02
0.97
1.04
1.01
2.00
1.06
1.01
2.05
2.06
4.00
3.03
3.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5

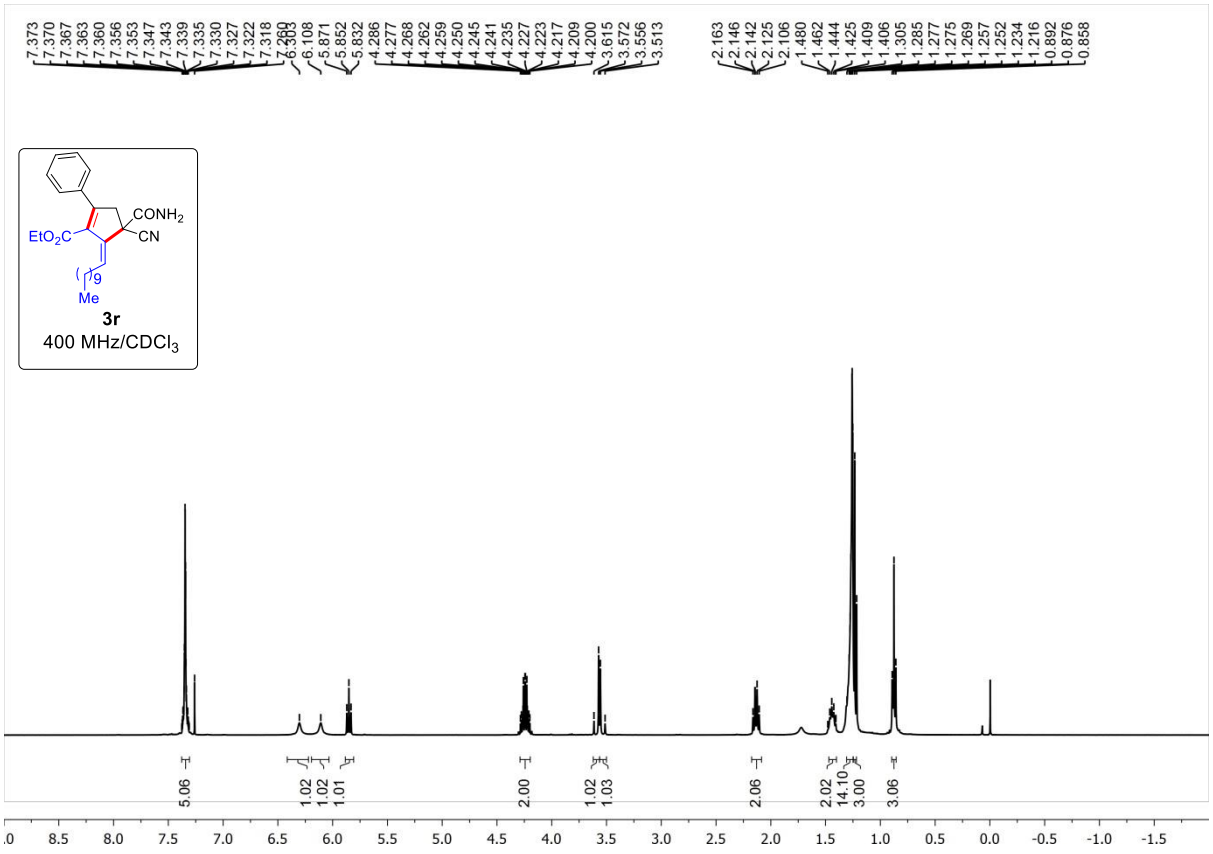

168.993
167.367
145.868
139.081
133.580
129.665
129.664
128.959
128.743
127.110
119.939
77.478
77.160
76.843
61.948
51.578
44.627
31.606
29.166
28.488
22.547
14.108
13.893
CONH2
CN
EtO2C
n-Pent
3o
100 MHz/CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

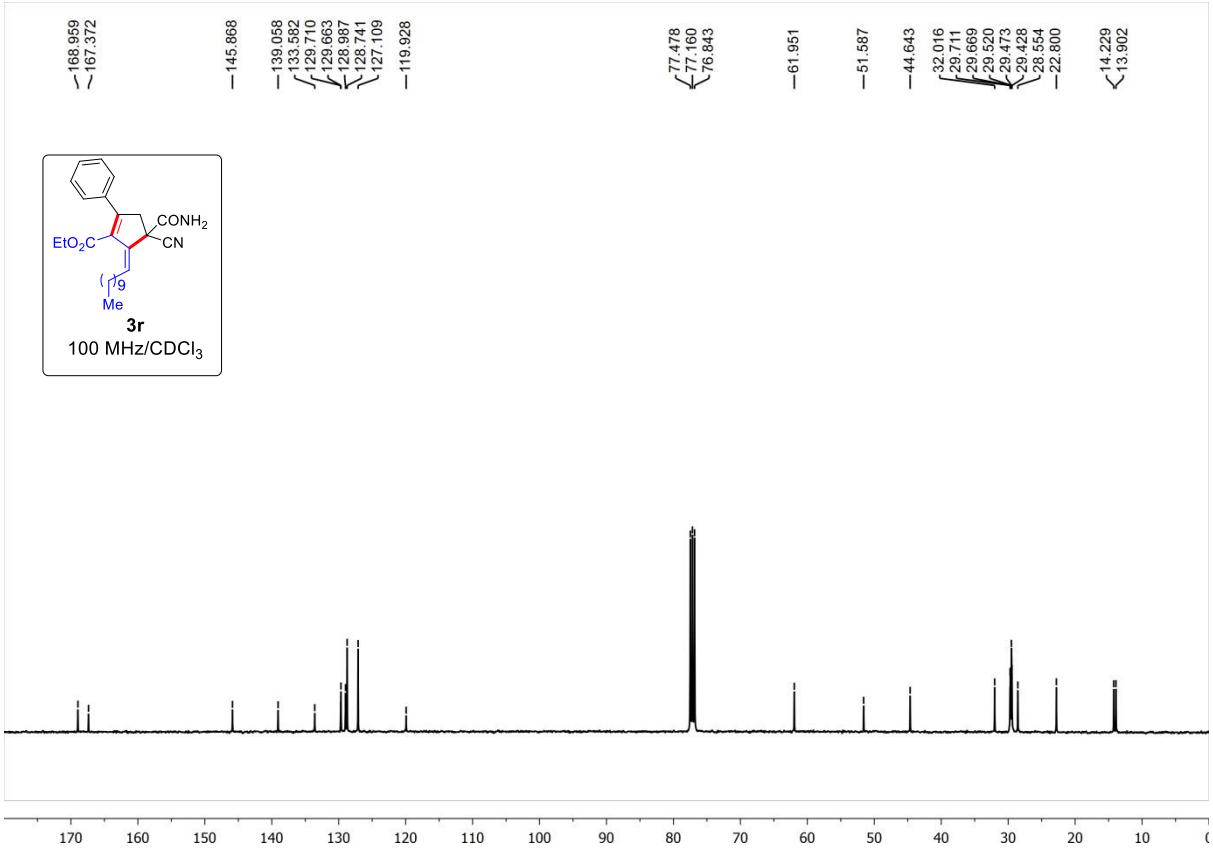

7.370
7.366
7.356
7.350
7.346
7.339
7.326
7.260
6.277
5.955
5.875
5.856
5.837
4.288
4.278
4.270
4.264
4.261
4.252
4.246
4.243
4.237
4.228
4.224
4.219
4.210
4.201
3.621
3.578
3.557
3.514
2.172
2.153
2.134
2.115
1.485
1.468
1.450
1.431
1.413
1.325
1.311
1.293
1.283
1.276
1.267
1.253
1.235
1.217
0.898
0.883
0.866
CONH2
CN
EtO2C
n-Hex
3p
400 MHz/CDCl3
5.07
1.03
1.00
1.03
2.00
1.04
1.01
2.02
2.06
6.04
3.09
3.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5

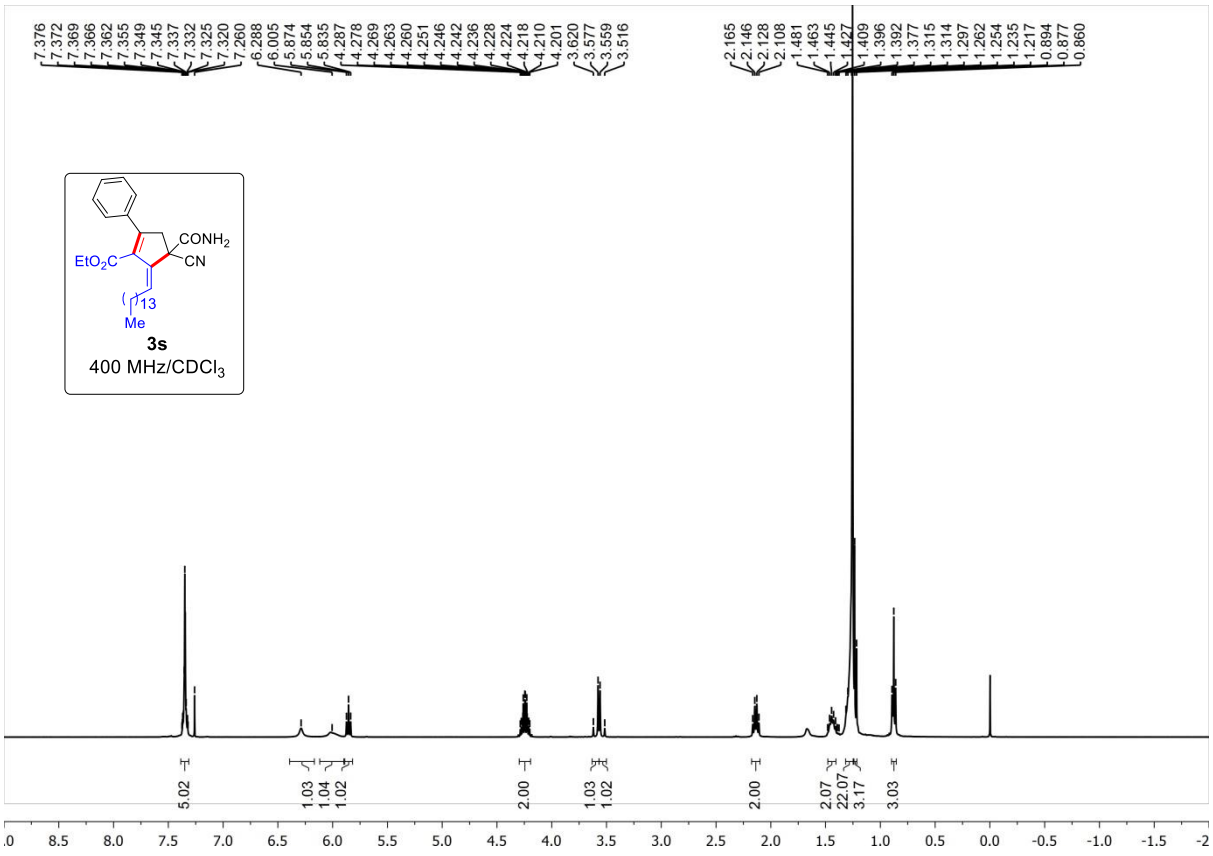

168.838
167.350
145.926
139.121
133.620
129.740
129.672
128.965
128.751
127.132
119.928
77.478
77.161
76.843
61.942
51.611
44.658
31.709
29.468
29.102
28.547
22.663
14.154
13.908
CONH2
CN
EtO2C
n-Hex
3p
100 MHz/CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

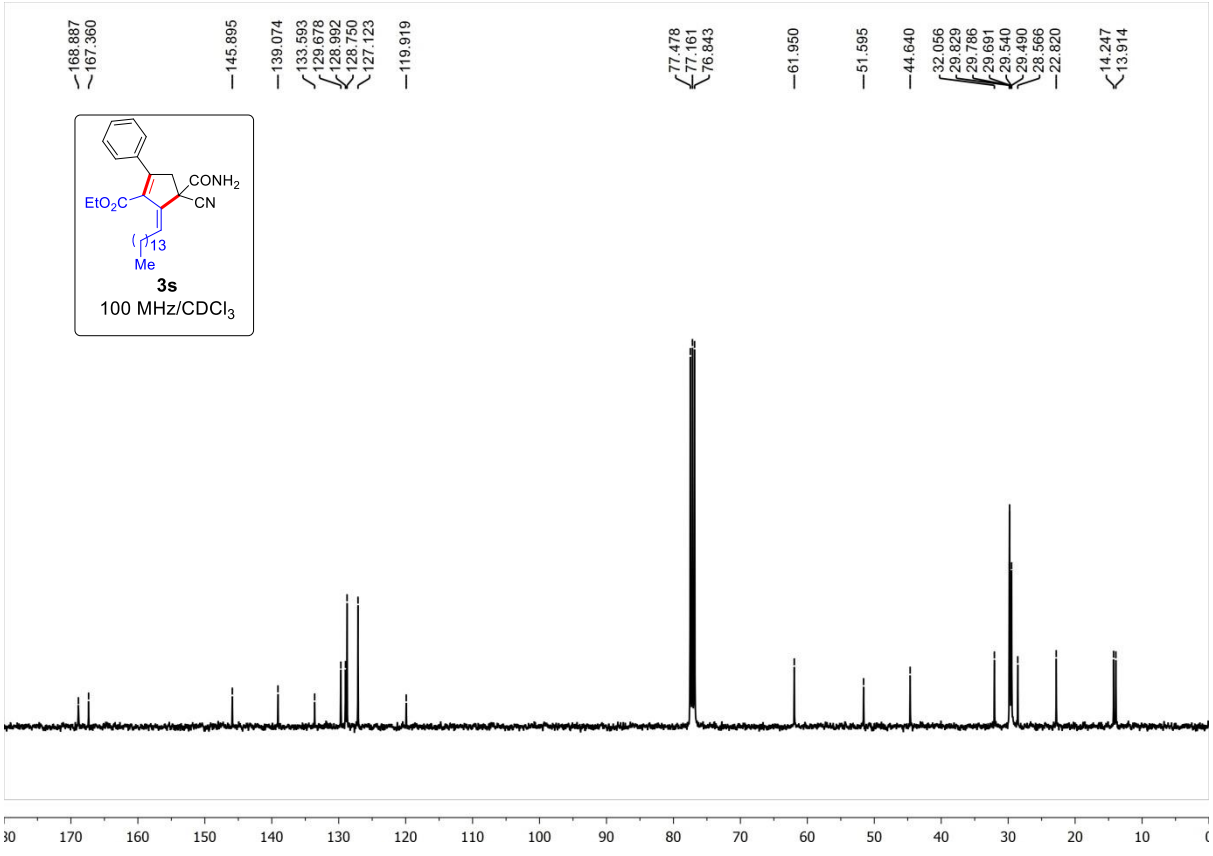

7.378
7.375
7.371
7.368
7.365
7.361
7.358
7.352
7.347
7.343
7.338
7.334
7.331
7.326
7.322
7.318
7.260
6.287
5.877
5.877
5.857
5.838
4.288
4.279
4.270
4.264
4.261
4.246
4.243
4.229
4.225
4.219
4.211
4.201
3.625
3.582
3.564
3.521
2.170
2.152
2.149
2.132
2.113
2.103
1.469
1.451
1.432
1.414
1.411
1.318
1.313
1.302
1.290
1.282
1.275
1.261
1.253
1.235
1.217
0.897
0.880
0.863
CONH2
CN
EtO2C
n-Hept
3q
400 MHz/CDCl3
5.03
1.03
1.07
1.00
2.00
1.01
1.03
2.04
2.08
8.02
3.09
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5

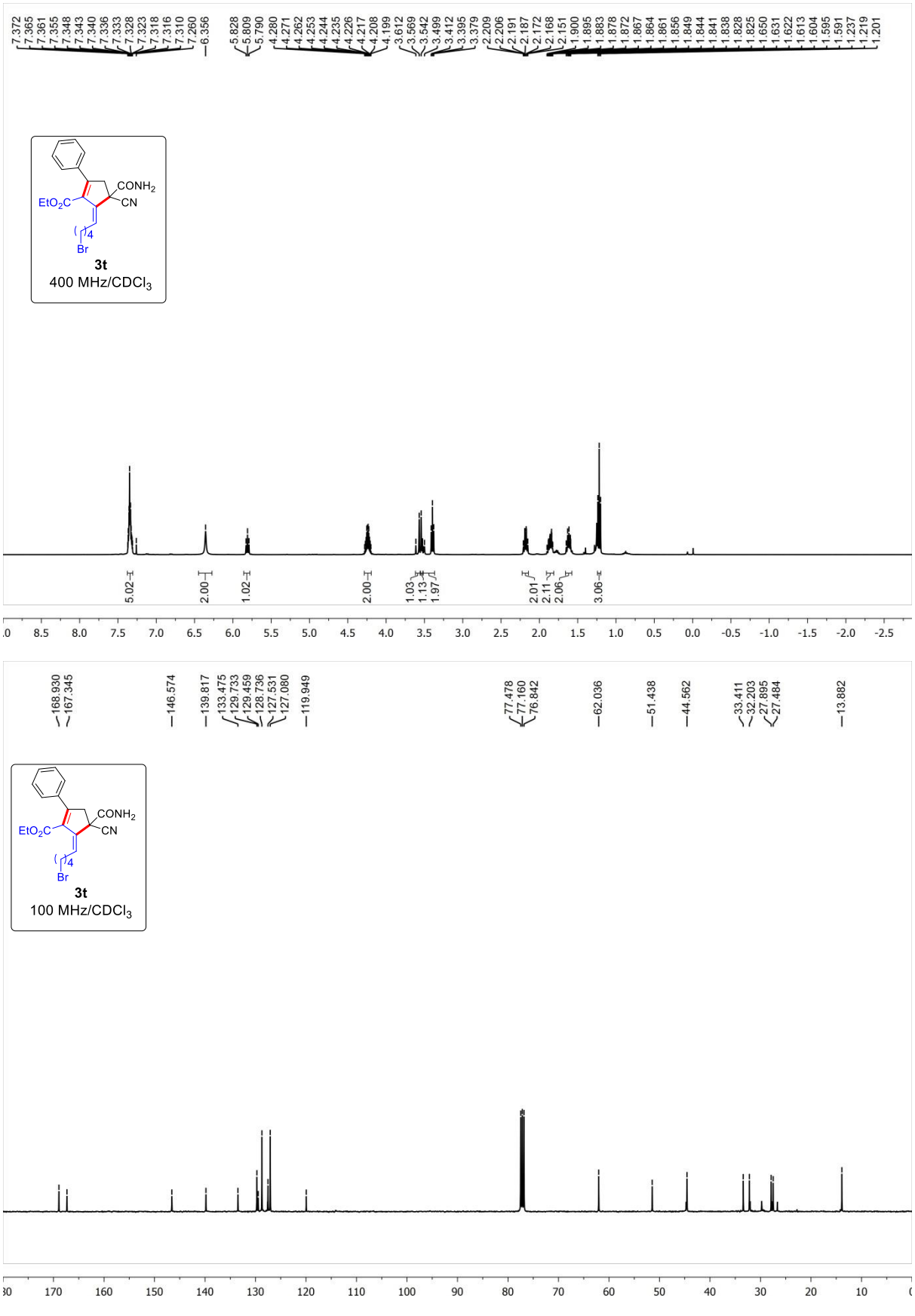

168.833
167.372
145.930
139.085
133.594
129.697
129.005
128.763
127.132
119.907
77.478
77.161
76.844
61.968
51.603
44.648
31.876
29.839
29.520
29.423
29.198
28.559
22.758
14.202
13.917
CONH2
CN
EtO2C
n-Hept
3q
100 MHz/CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

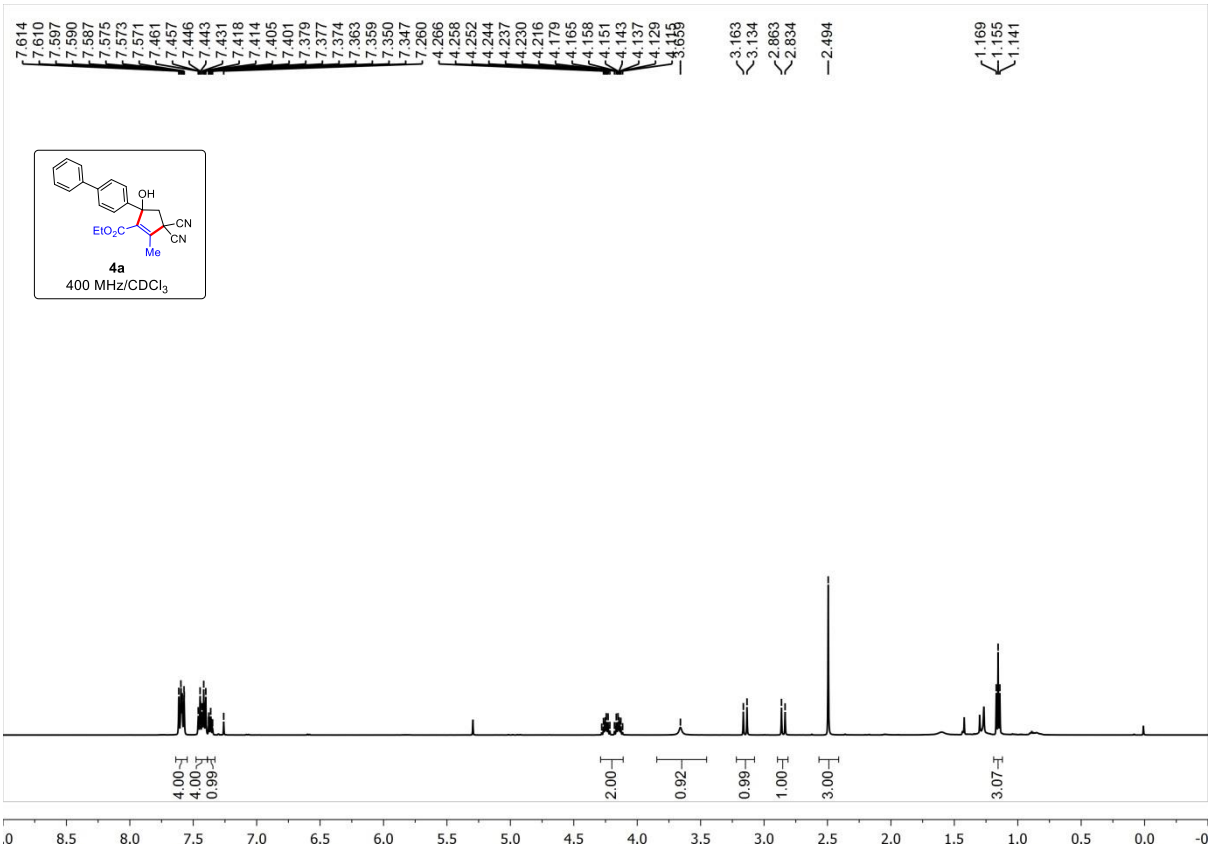

7.373
7.370
7.367
7.363
7.360
7.356
7.353
7.347
7.343
7.339
7.335
7.330
7.327
7.322
7.318
6.303
6.108
5.871
5.852
5.832
4.286
4.277
4.268
4.262
4.259
4.250
4.245
4.241
4.235
4.227
4.223
4.217
4.209
4.200
3.615
3.572
3.556
3.513
2.163
2.146
2.142
2.125
2.106
1.480
1.462
1.444
1.425
1.409
1.406
1.305
1.285
1.277
1.275
1.269
1.257
1.252
1.234
1.216
0.892
0.876
0.858
CONH2
CN
EtO2C
9
Me
3r
400 MHz/CDCl3
5.06
1.02
1.02
1.01
2.00
1.02
1.03
2.06
2.02
14.10
3.00
3.06

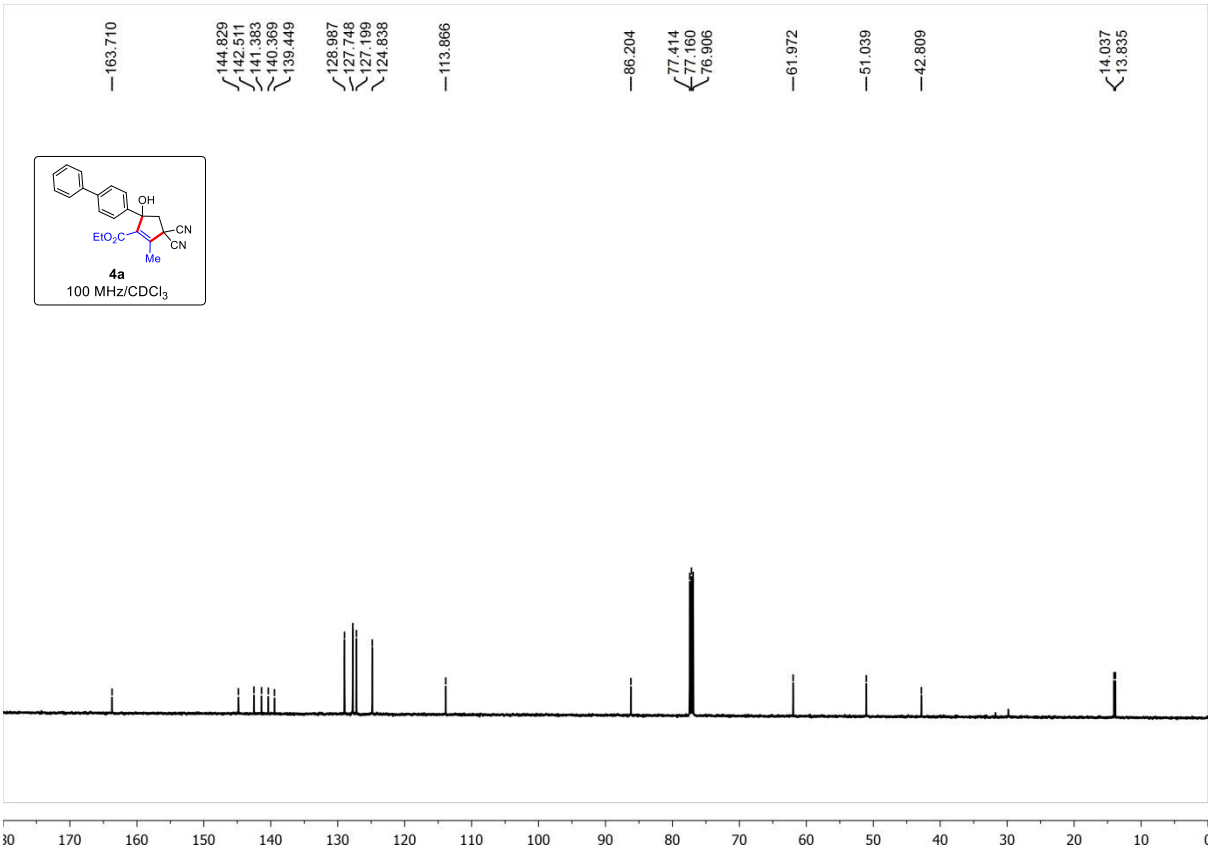

168.959
167.372
145.868
139.058
133.582
129.710
129.663
128.987
128.741
127.109
119.928
77.478
77.160
76.843
61.951
51.587
44.643
32.016
29.711
29.669
29.520
29.473
29.428
28.554
22.800
14.229
13.902
CONH2
CN
EtO2C
9
Me
3r
100 MHz/CDCl3

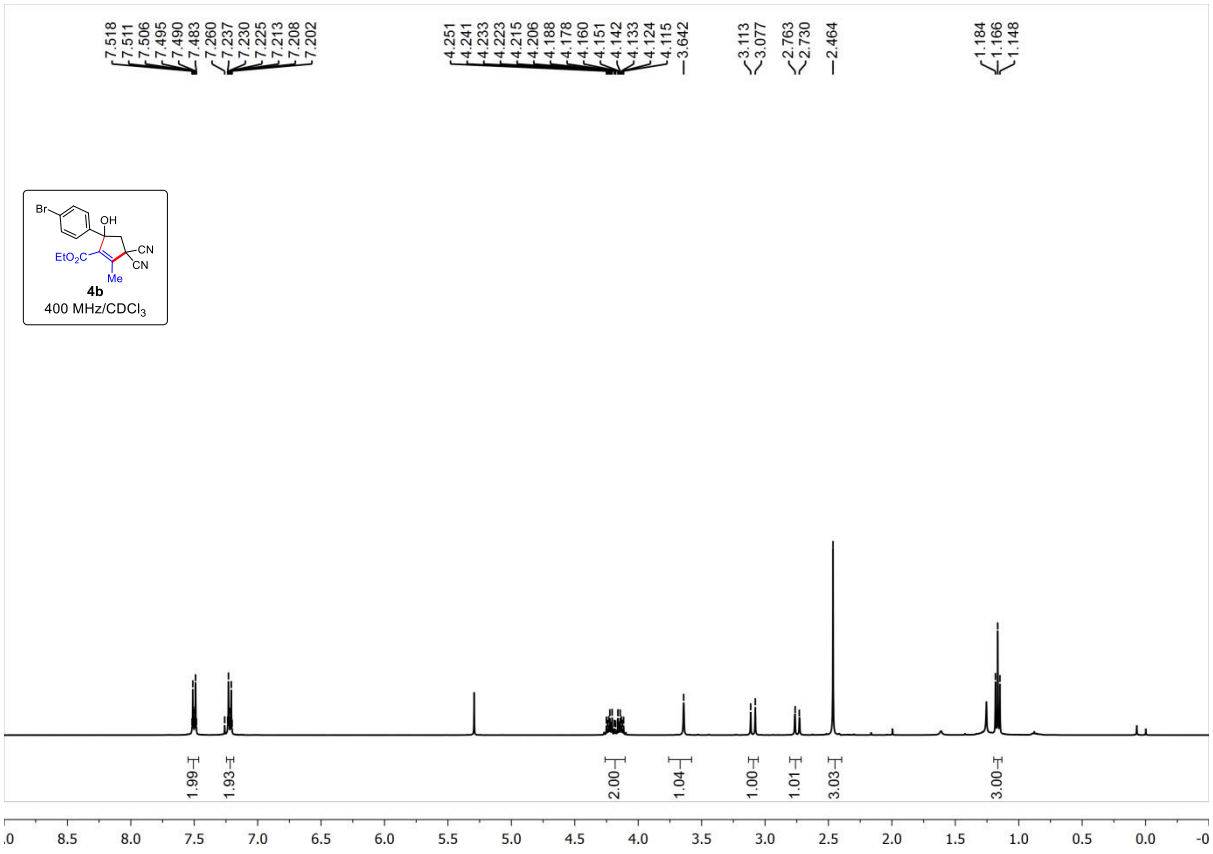

7.376
7.372
7.369
7.366
7.362
7.355
7.349
7.345
7.337
7.332
7.325
7.320
7.260
6.288
6.005
5.874
5.854
5.835
4.287
4.278
4.269
4.263
4.260
4.251
4.246
4.242
4.236
4.228
4.224
4.218
4.210
4.201
3.620
3.577
3.559
3.516
2.165
2.146
2.128
2.108
1.481
1.463
1.445
1.427
1.409
1.396
1.392
1.377
1.315
1.314
1.297
1.262
1.254
1.235
1.217
0.894
0.877
0.860
CONH2
EtO2C
CN
13
Me
3s
400 MHz/CDCl3
5.02
1.03
1.04
1.02
2.00
1.03
1.02
2.00
2.07
22.07
3.17
3.03

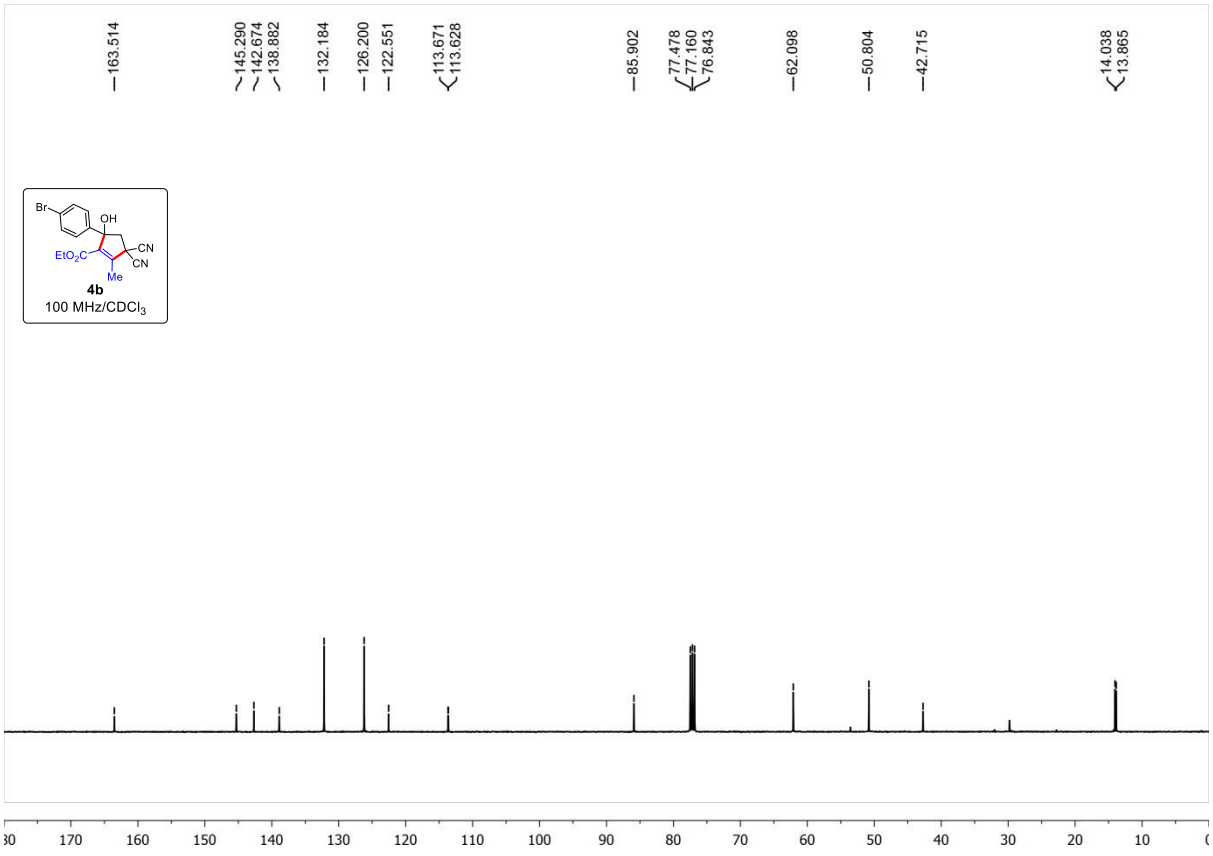

168.887
167.360
145.895
139.074
133.593
129.678
128.992
128.750
127.123
119.919
77.478
77.161
76.843
61.950
51.595
44.640
32.056
29.829
29.786
29.691
29.540
29.490
28.566
22.820
14.247
13.914
CONH2
EtO2C
CN
13
Me
3s
100 MHz/CDCl3

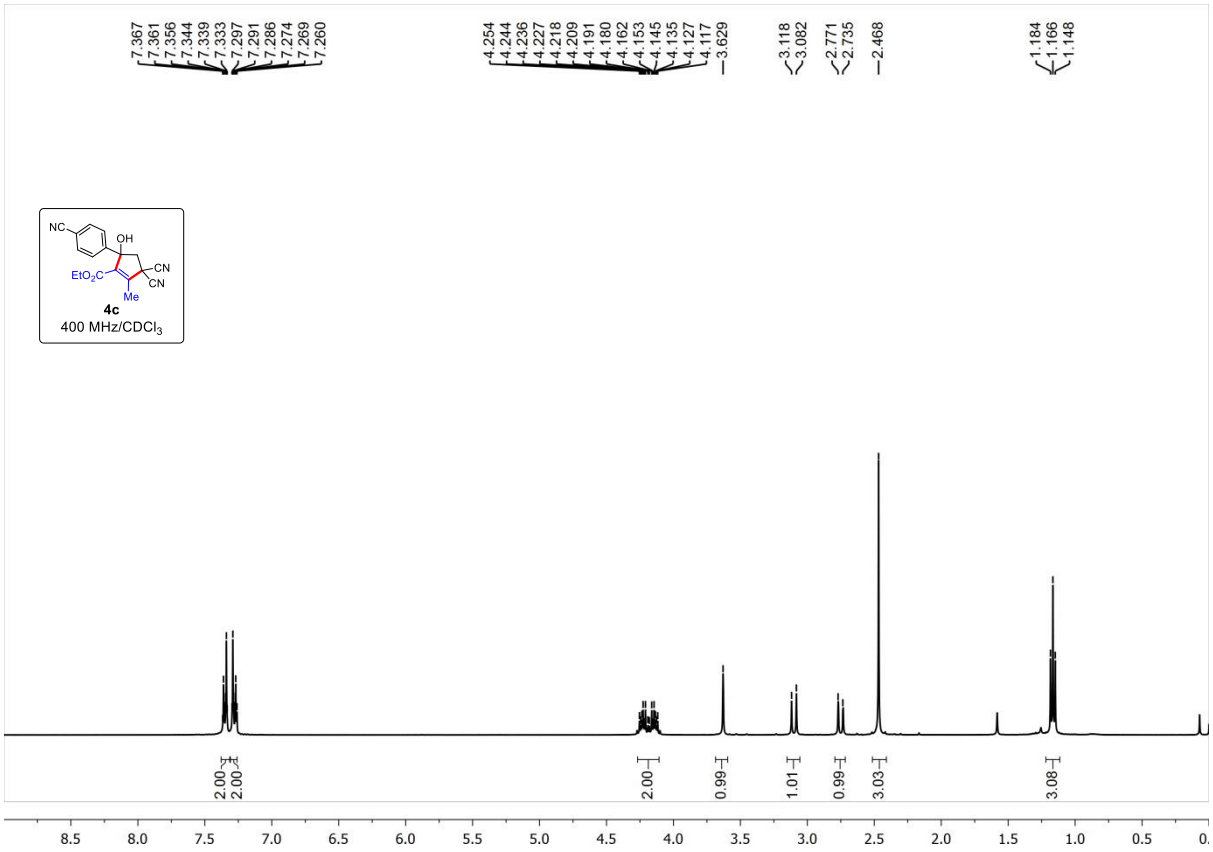

7.372
7.365
7.361
7.355
7.348
7.343
7.340
7.336
7.333
7.328
7.323
7.318
7.316
7.310
7.260
6.356
5.828
5.809
5.790
4.280
4.271
4.262
4.253
4.244
4.235
4.226
4.217
4.208
4.199
3.612
3.569
3.542
3.499
3.412
3.395
3.379
2.209
2.206
2.191
2.187
2.172
2.168
2.151
1.900
1.895
1.883
1.878
1.872
1.867
1.864
1.861
1.856
1.849
1.844
1.841
1.838
1.828
1.825
1.650
1.631
1.622
1.613
1.604
1.595
1.591
1.237
1.219
1.201
CONH2
CN
EtO2C
4
Br
3t
400 MHz/CDCl3
5.02
2.00
1.02
2.00
1.03
1.13
1.97
2.01
2.11
2.06
3.06
168.930
167.345
146.574
139.817
133.475
129.733
129.459
128.736
127.531
127.080
119.949
77.478
77.160
76.842
62.036
51.438
44.562
33.411
32.203
27.895
27.484
13.882
CONH2
CN
EtO2C
4
Br
3t
100 MHz/CDCl3

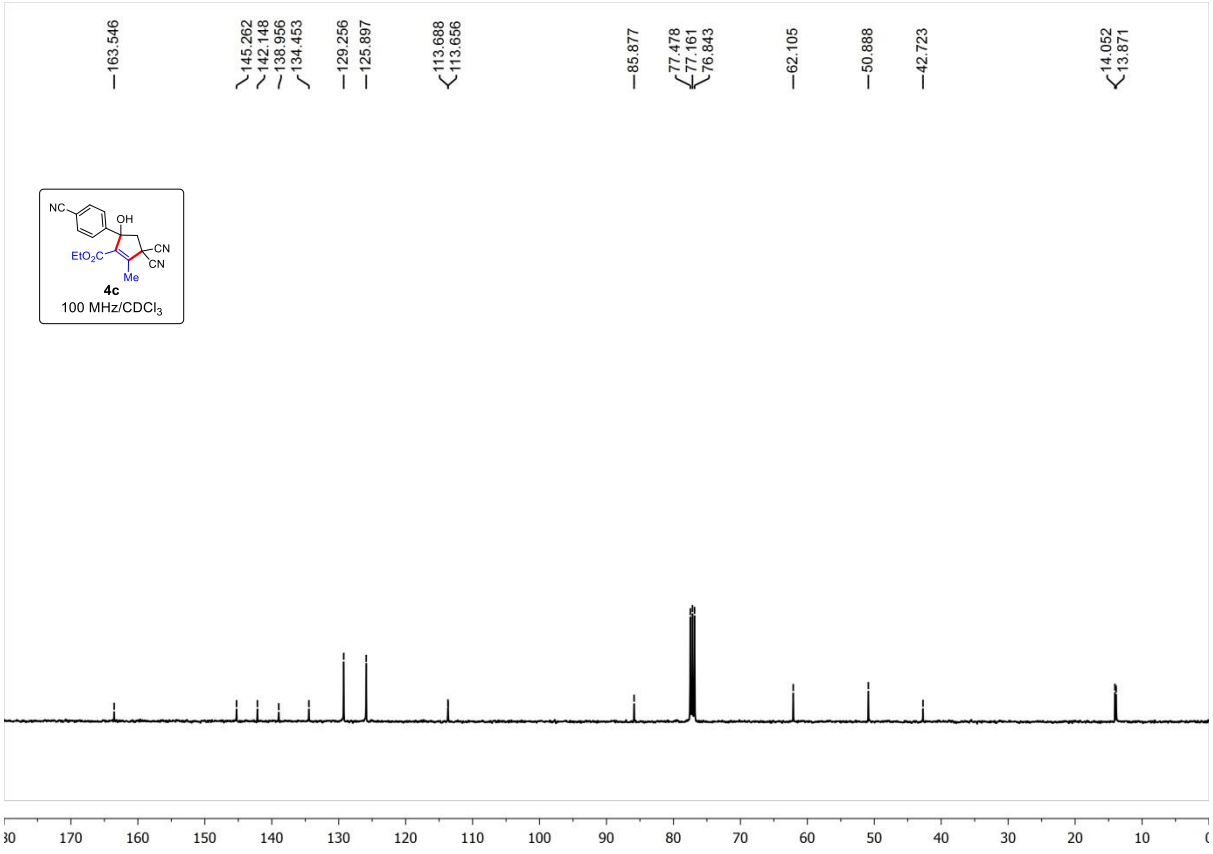

7.614
7.610
7.597
7.590
7.587
7.575
7.573
7.571
7.461
7.457
7.446
7.443
7.431
7.418
7.414
7.405
7.401
7.379
7.377
7.374
7.363
7.359
7.350
7.347
7.260
4.266
4.258
4.252
4.244
4.237
4.230
4.216
4.179
4.165
4.158
4.151
4.143
4.137
4.129
3.659
3.163
3.134
2.863
2.834
2.494
1.169
1.155
1.141
OH
CN
CN
EtO2C
Me
4a
400 MHz/CDCl3
4.00
4.00
0.99
2.00
0.92
0.99
1.00
3.00
3.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

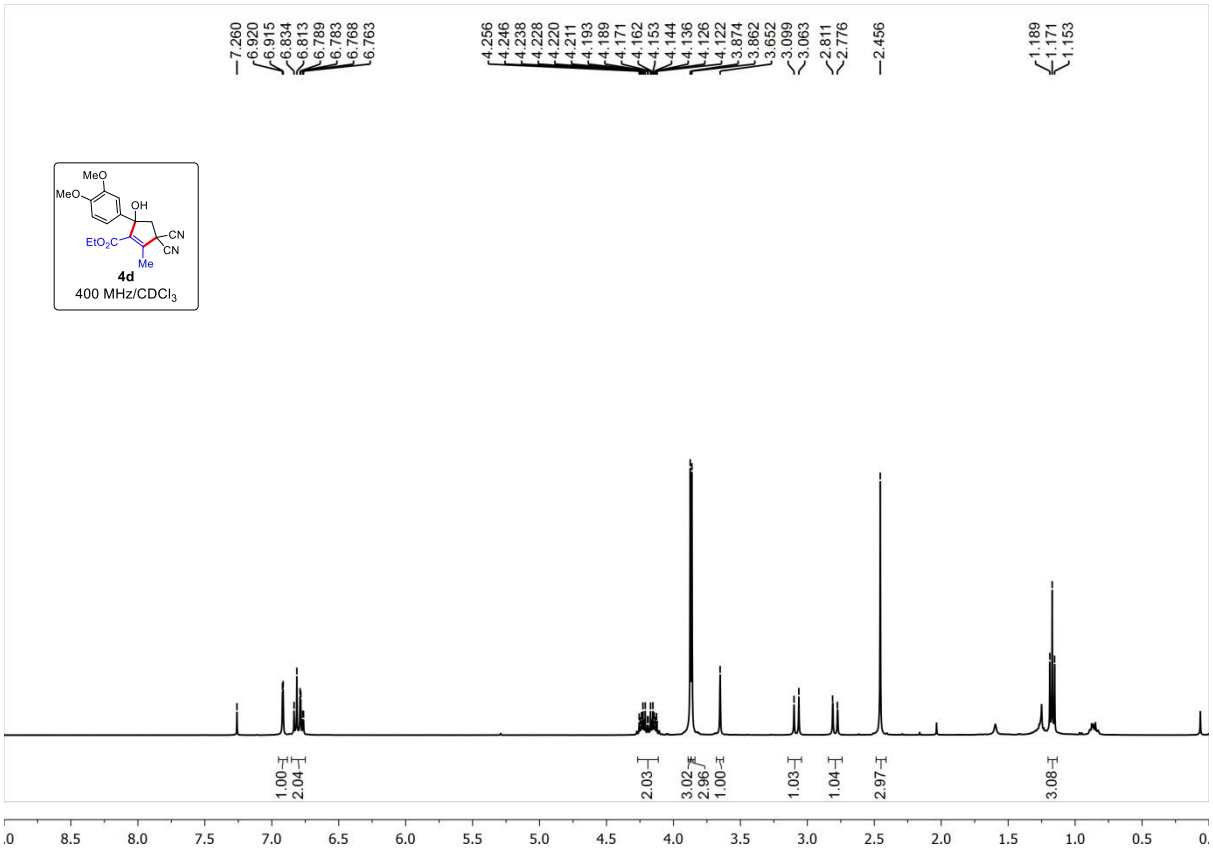

163.710
144.829
142.511
141.383
140.369
139.449
128.987
127.748
127.199
124.838
113.866
86.204
77.414
77.160
76.906
61.972
51.039
42.809
14.037
13.835
OH
CN
CN
EtO2C
Me
4a
100 MHz/CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

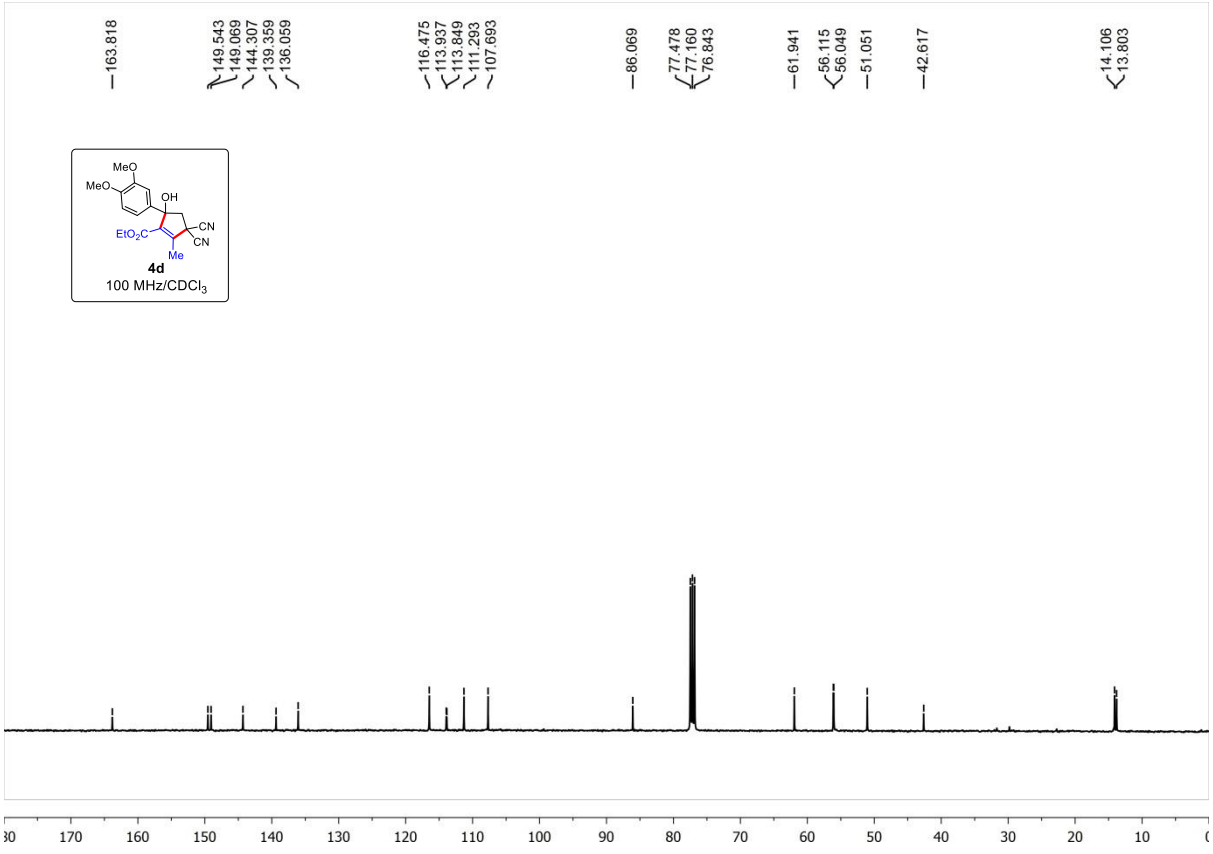

7.518
7.511
7.506
7.495
7.490
7.483
7.260
7.237
7.230
7.225
7.213
7.208
7.202
4.251
4.241
4.233
4.223
4.215
4.206
4.188
4.178
4.160
4.151
4.142
4.133
4.124
4.115
3.642
3.113
3.077
2.763
2.730
2.464
1.184
1.166
1.148
Br
OH
EtO2C
CN
CN
Me
4b
400 MHz/CDCl3
1.99
1.93
2.00
1.04
1.00
1.01
3.03
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

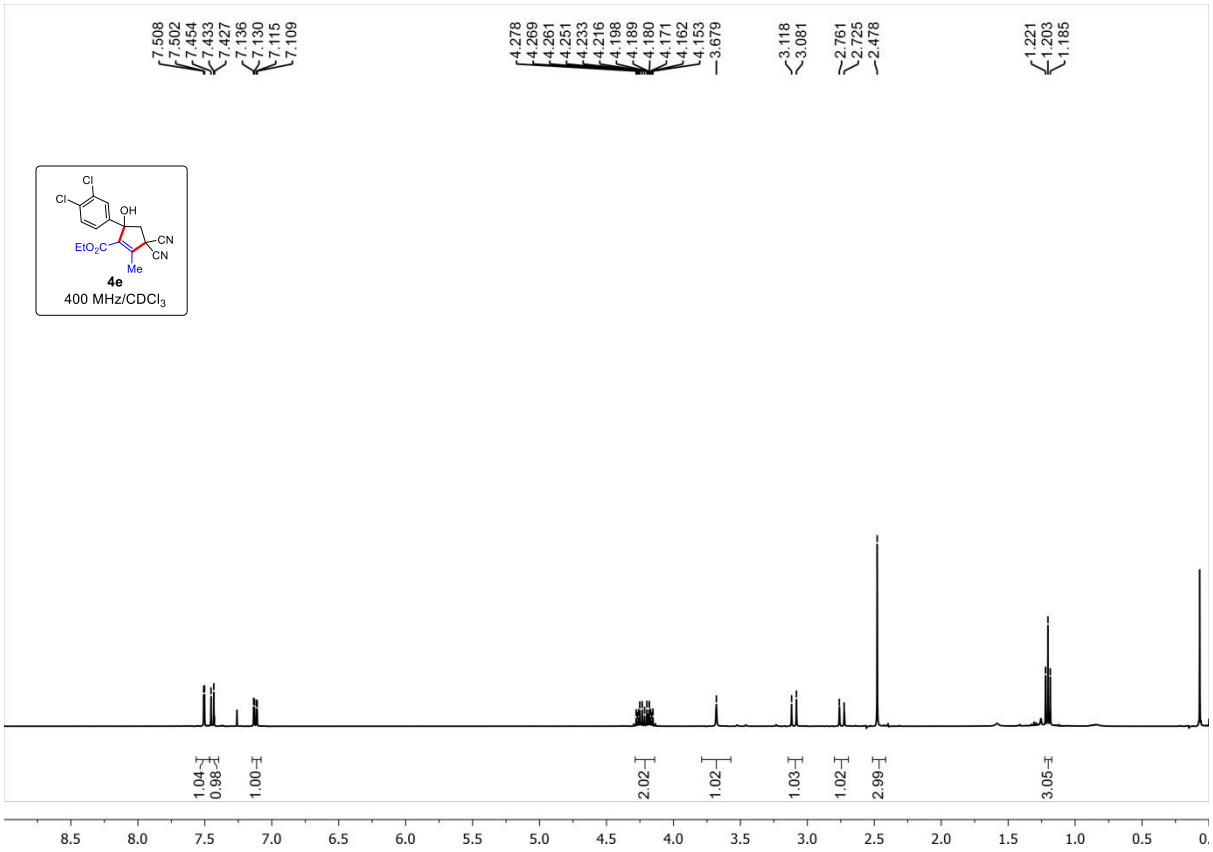

163.514
145.290
142.674
138.882
132.184
126.200
122.551
113.671
113.628
85.902
77.478
77.160
76.843
62.098
50.804
42.715
14.038
13.865
Br
OH
EtO2C
CN
CN
Me
4b
100 MHz/CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

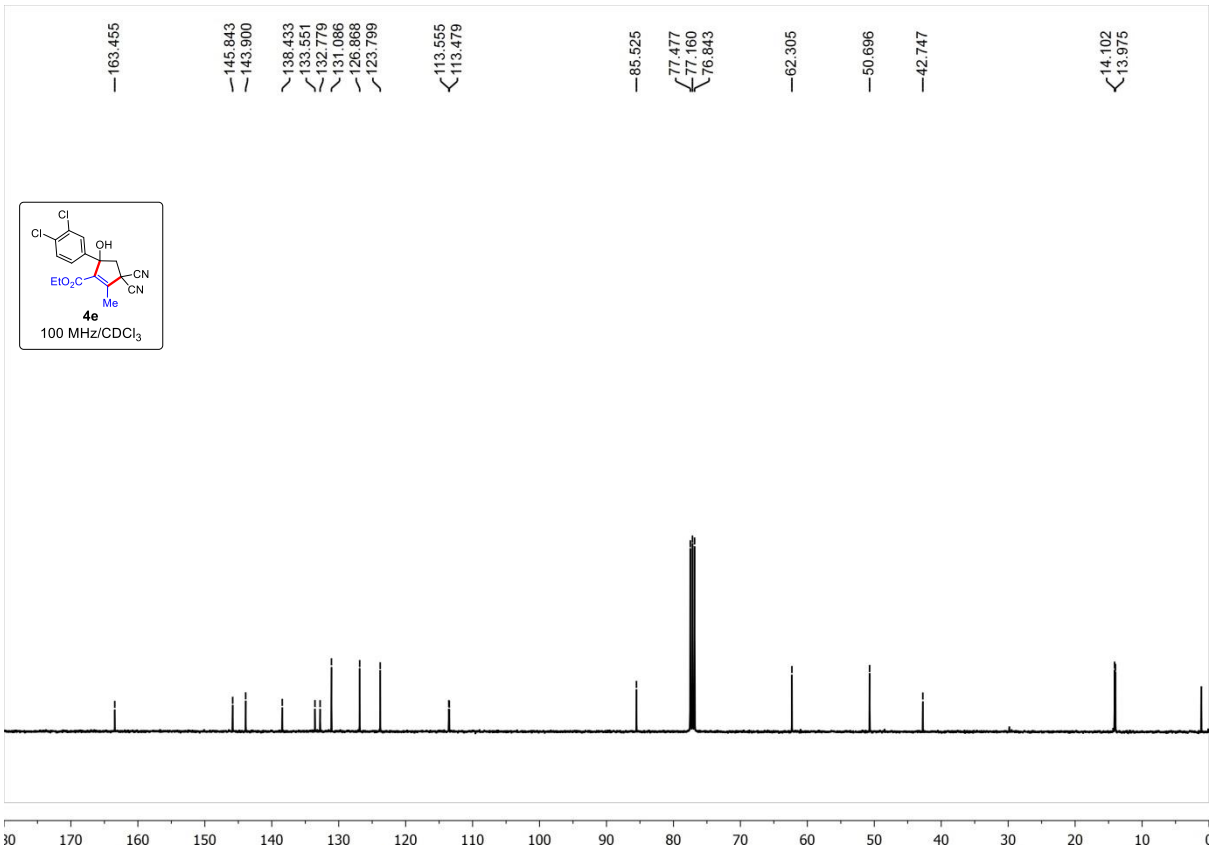

7.367
7.361
7.356
7.344
7.339
7.333
7.297
7.291
7.286
7.274
7.269
7.260
4.254
4.244
4.236
4.227
4.218
4.209
4.191
4.180
4.162
4.153
4.145
4.135
4.127
4.117
3.629
3.118
3.082
2.771
2.735
2.468
1.184
1.166
1.148
NC
OH
CN
CN
EtO2C
Me
4c
400 MHz/CDCl3
2.00
2.00
2.00
0.99
1.01
0.99
3.03
3.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

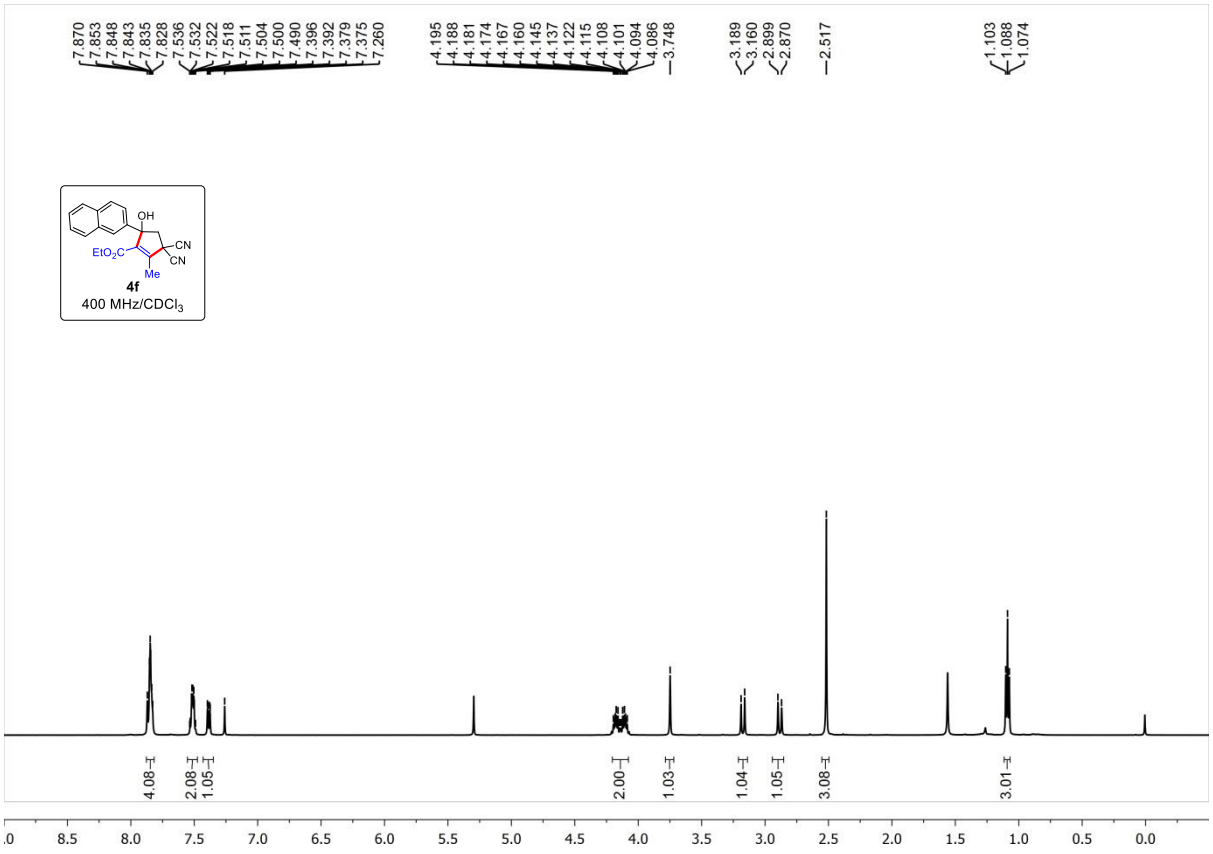

163.546
145.262
142.148
138.956
134.453
129.256
125.897
113.688
113.656
85.877
77.478
77.161
76.843
62.105
50.888
42.723
14.052
13.871
NC
OH
CN
CN
EtO2C
Me
4c
100 MHz/CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

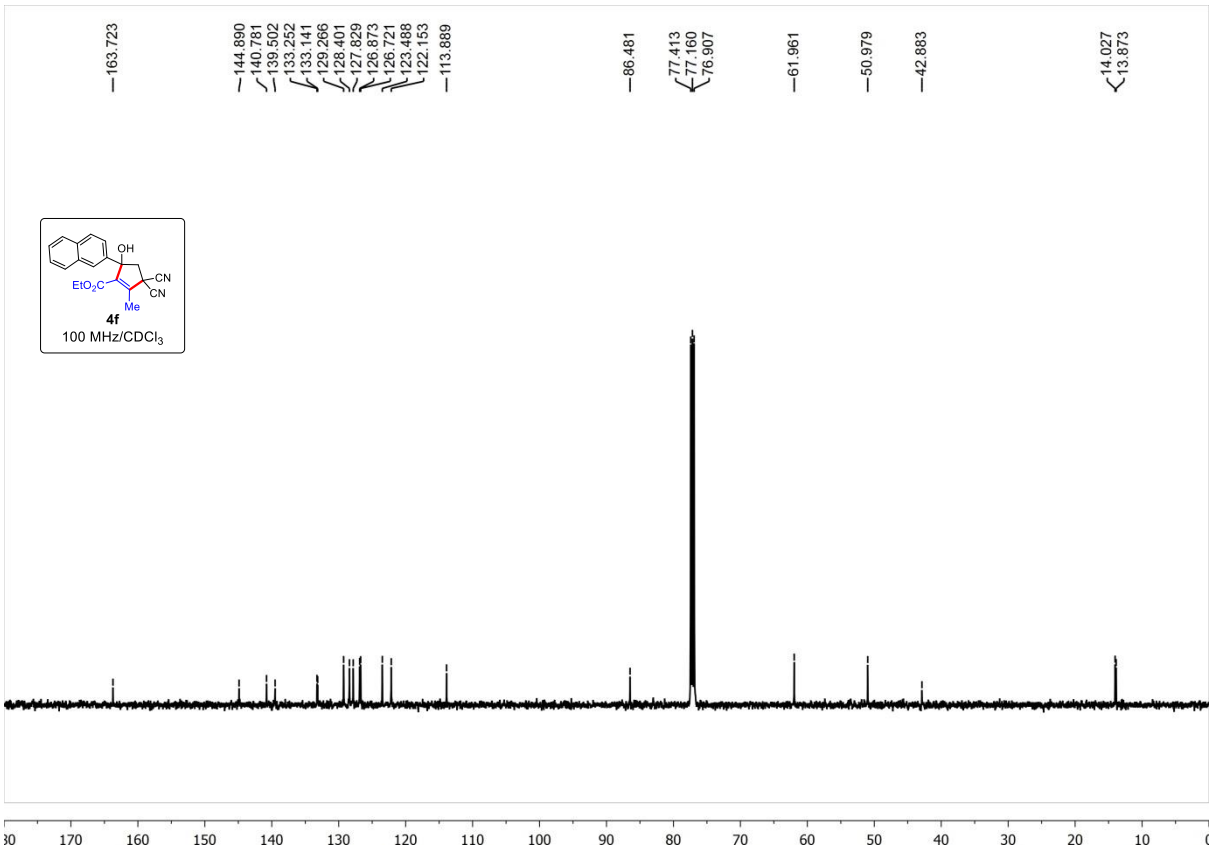

7.260
6.920
6.915
6.834
6.813
6.789
6.783
6.768
6.763
4.256
4.246
4.238
4.228
4.220
4.211
4.193
4.189
4.171
4.162
4.153
4.144
4.136
4.126
4.122
3.874
3.862
3.652
3.099
3.063
2.811
2.776
2.456
1.189
1.171
1.153
MeO
MeO
OH
CN
CN
EtO2C
Me
4d
400 MHz/CDCl3
1.00
2.04
2.03
3.02
2.96
1.00
1.03
1.04
2.97
3.08

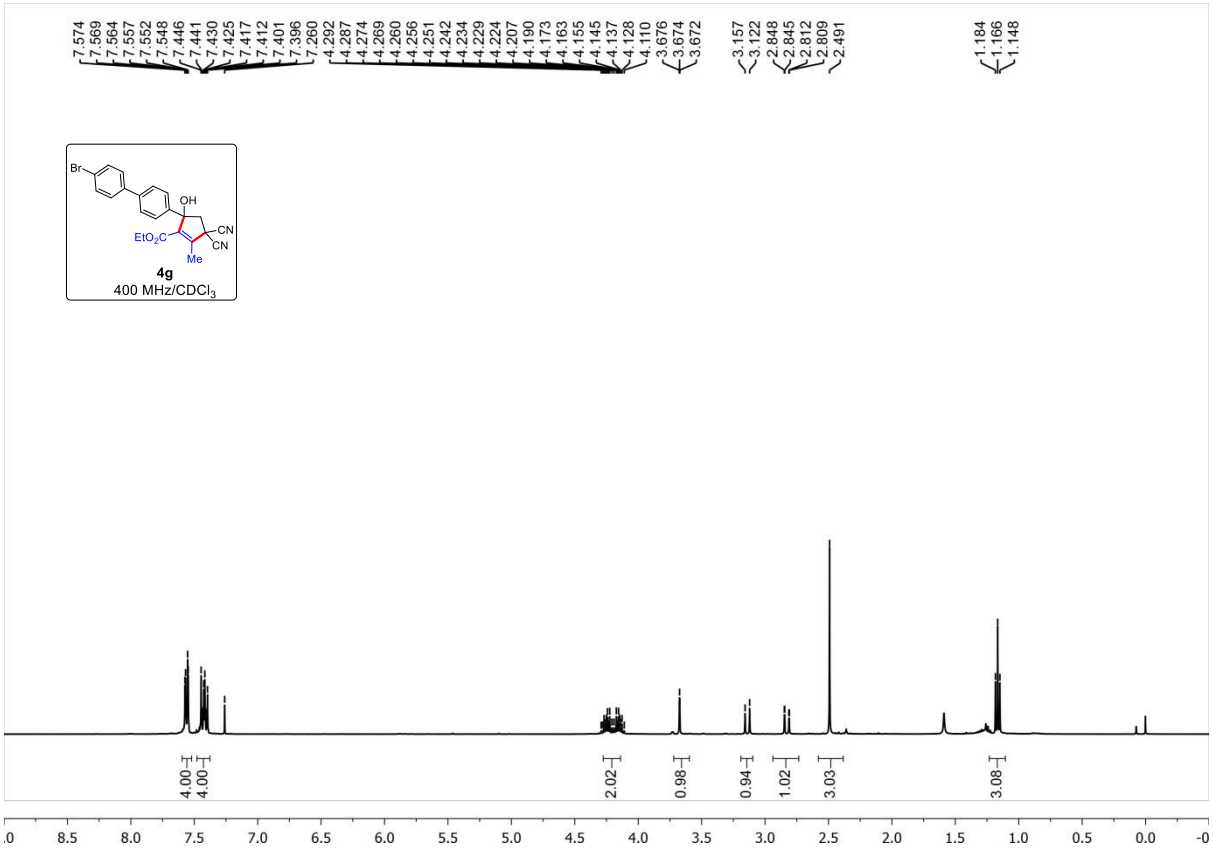

163.818
149.543
149.069
144.307
139.359
136.059
116.475
113.937
113.849
111.293
107.693
86.069
77.478
77.160
76.843
61.941
56.115
56.049
51.051
42.617
14.106
13.803
MeO
MeO
OH
CN
CN
EtO2C
Me
4d
100 MHz/CDCl3

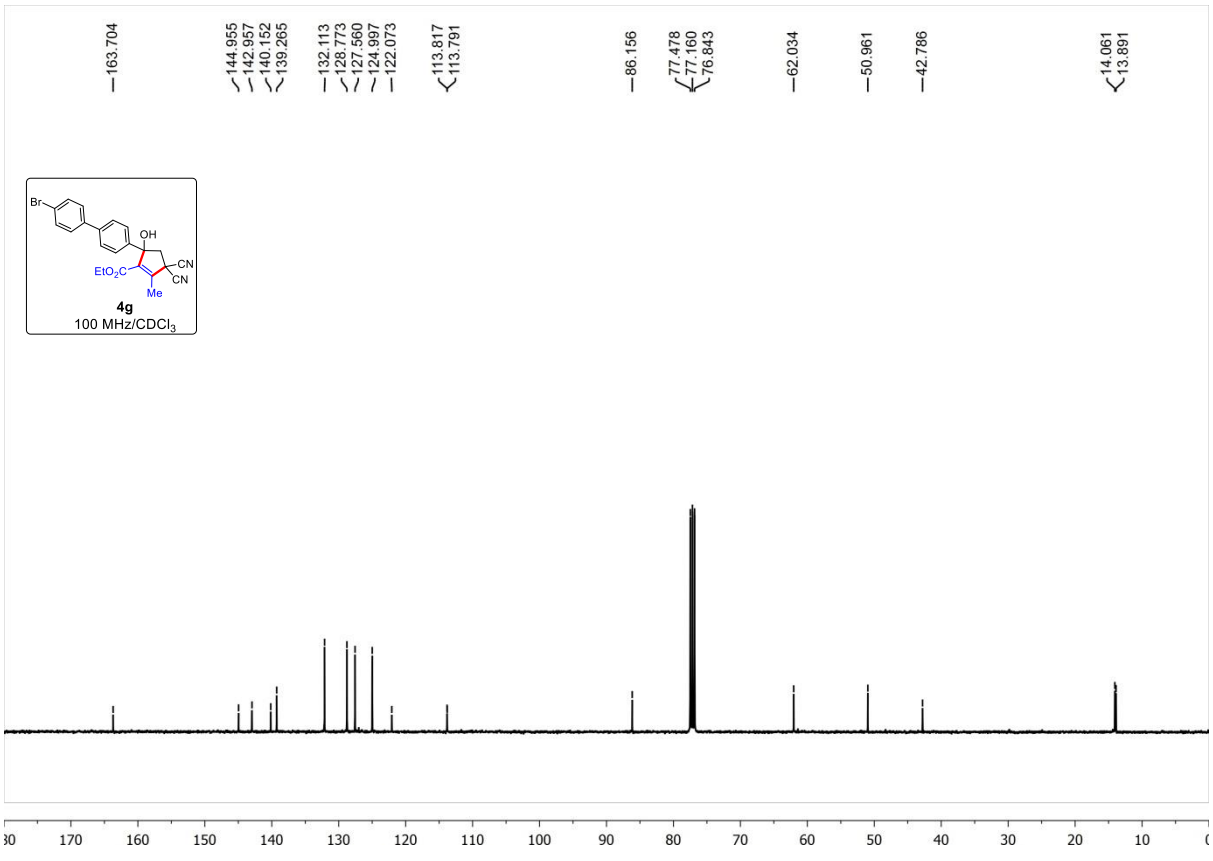

7.508
7.502
7.454
7.433
7.427
7.136
7.130
7.115
7.109
4.278
4.269
4.261
4.251
4.233
4.216
4.198
4.189
4.180
4.171
4.162
4.153
3.679
3.118
3.081
2.761
2.725
2.478
1.221
1.203
1.185
Cl
Cl
OH
EtO2C
CN
CN
Me
4e
400 MHz/CDCl3
1.04
0.98
1.00
2.02
1.02
1.03
1.02
2.99
3.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

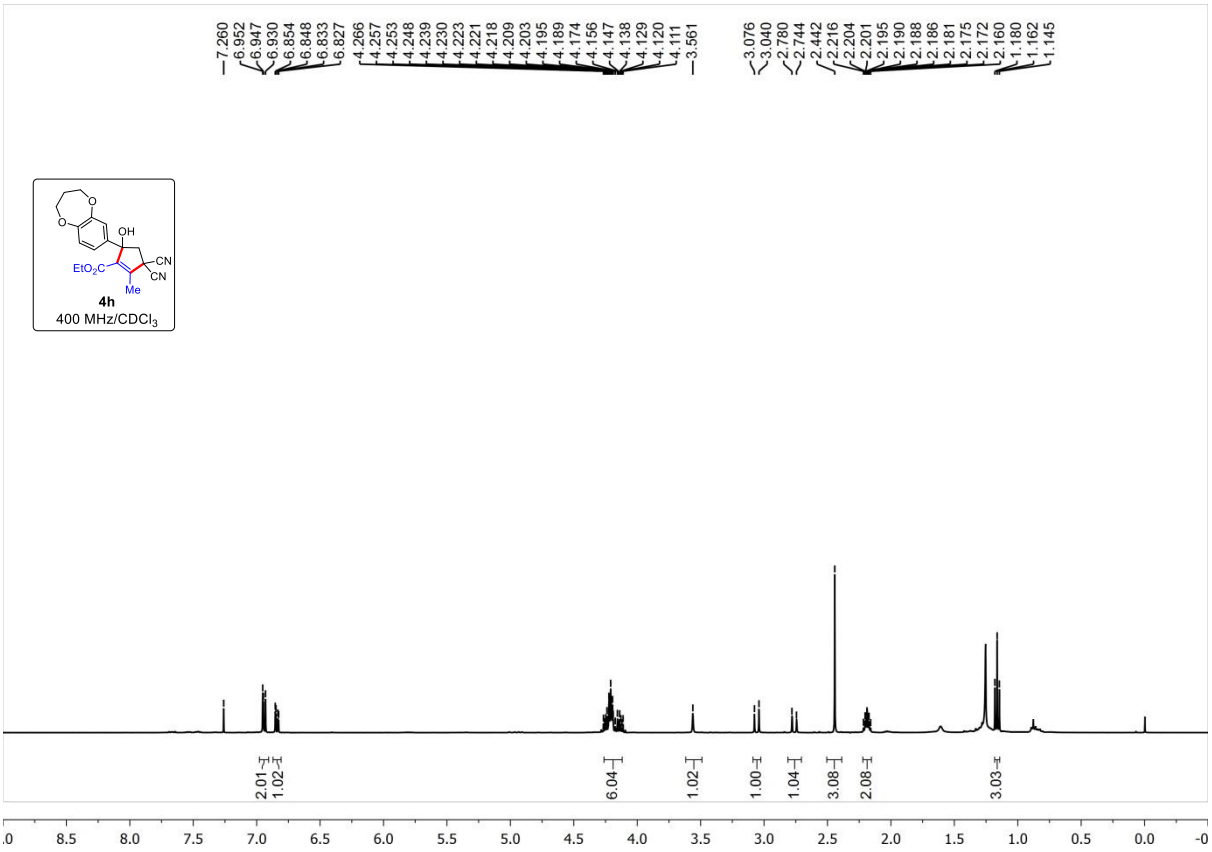

163.455
145.843
143.900
138.433
133.551
132.779
131.086
126.868
123.799
113.555
113.479
85.525
77.477
77.160
76.843
62.305
50.696
42.747
14.102
13.975
Cl
Cl
OH
EtO2C
CN
CN
Me
4e
100 MHz/CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

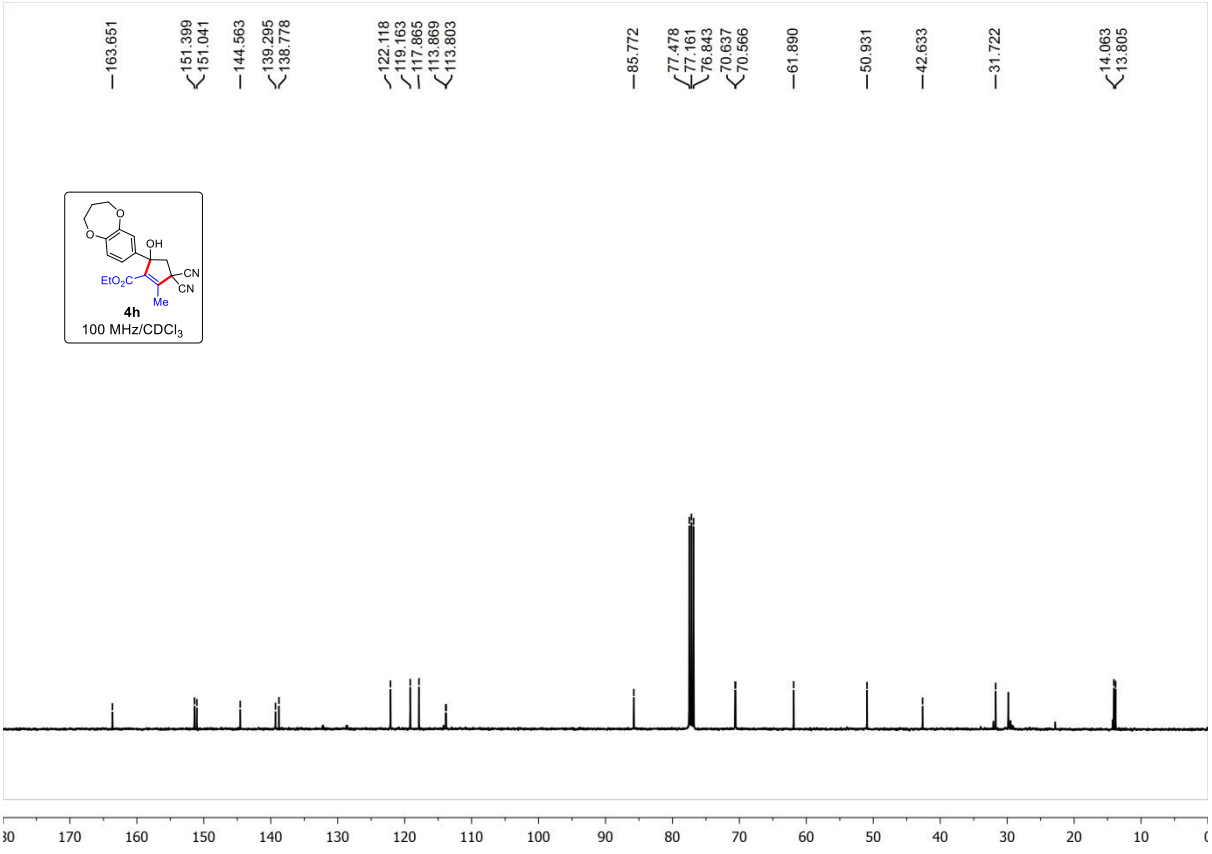

7.870
7.853
7.848
7.843
7.835
7.828
7.536
7.532
7.522
7.518
7.511
7.504
7.500
7.490
7.396
7.392
7.379
7.375
7.260
4.195
4.188
4.181
4.174
4.167
4.160
4.145
4.137
4.122
4.115
4.108
4.101
4.094
4.086
3.748
3.189
3.160
2.899
2.870
2.517
1.103
1.088
1.074
OH
EtO2C
CN
CN
Me
4f
400 MHz/CDCl3
4.08
2.08
1.05
2.00
1.03
1.04
1.05
3.08
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

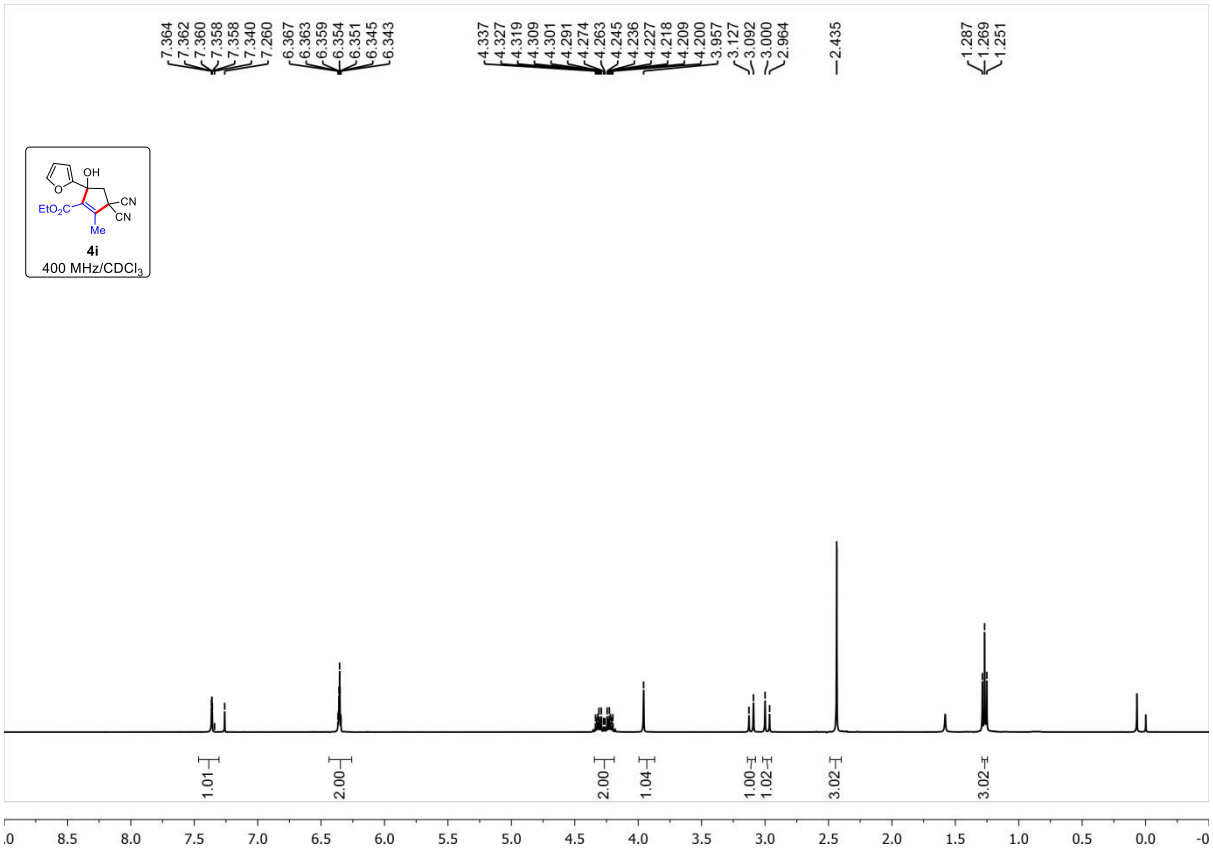

163.723
144.890
140.781
139.502
133.252
133.141
129.266
128.401
127.829
126.873
126.721
123.488
122.153
113.889
86.481
77.413
77.160
76.907
61.961
50.979
42.883
14.027
13.873
OH
EtO2C
CN
CN
Me
4f
100 MHz/CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

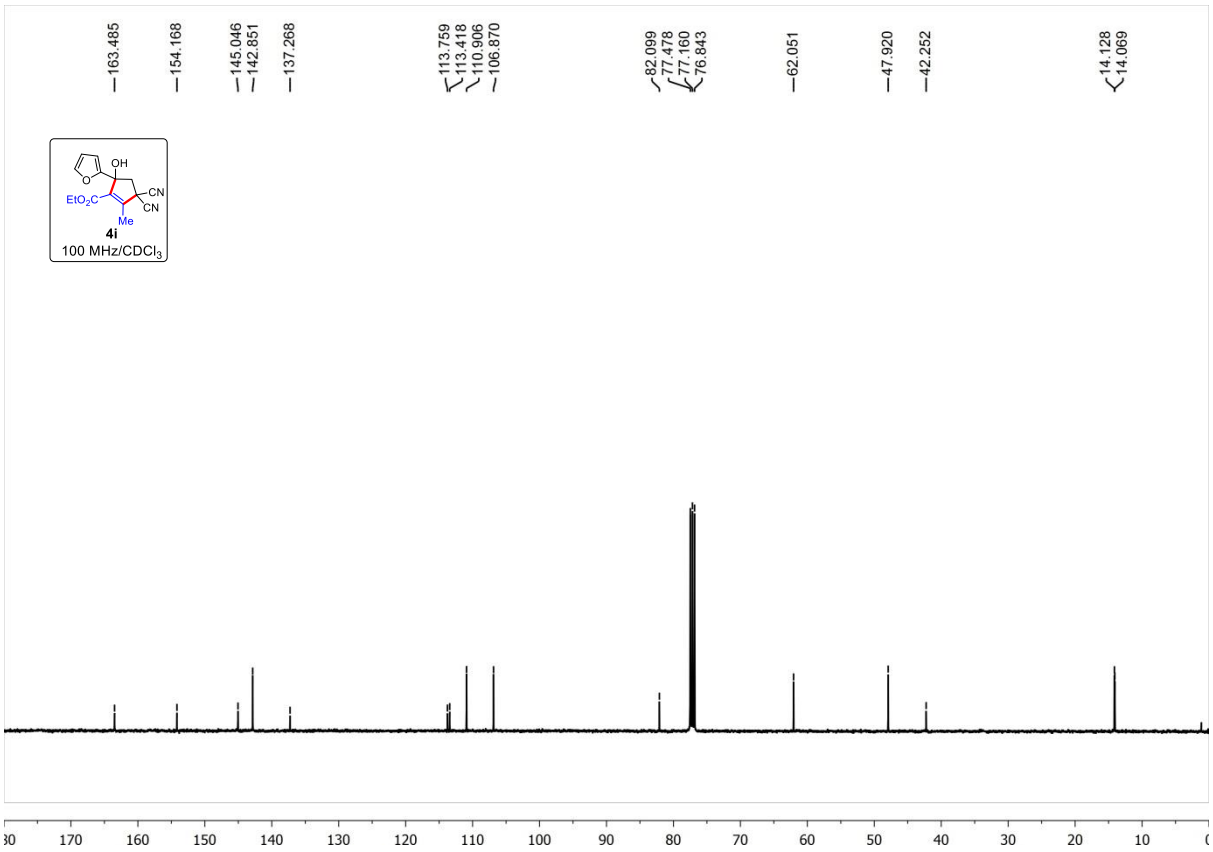

7.574
7.569
7.564
7.557
7.552
7.548
7.446
7.441
7.430
7.425
7.417
7.412
7.401
7.396
7.260
4.292
4.287
4.274
4.269
4.260
4.256
4.251
4.242
4.234
4.229
4.224
4.207
4.190
4.173
4.163
4.155
4.145
4.137
4.128
4.110
3.676
3.674
3.672
3.157
3.122
2.848
2.845
2.812
2.809
2.491
1.184
1.166
1.148
Br
OH
EtO2C
CN
CN
Me
4g
400 MHz/CDCl3
4.00
4.00
2.02
0.98
0.94
1.02
3.03
3.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

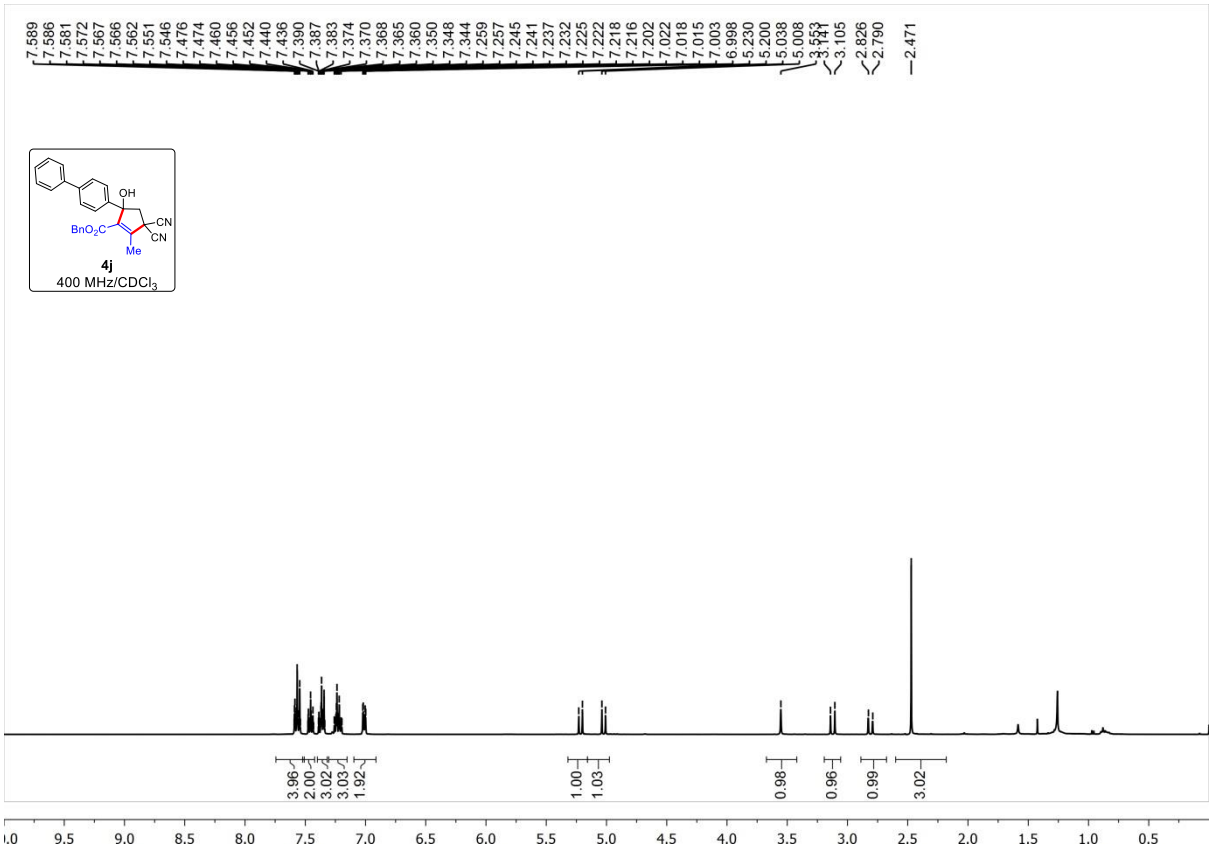

163.704
144.955
142.957
140.152
139.265
132.113
128.773
127.560
124.997
122.073
113.817
113.791
86.156
77.478
77.160
76.843
62.034
50.961
42.786
14.061
13.891
Br
OH
EtO2C
CN
CN
Me
4g
100 MHz/CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

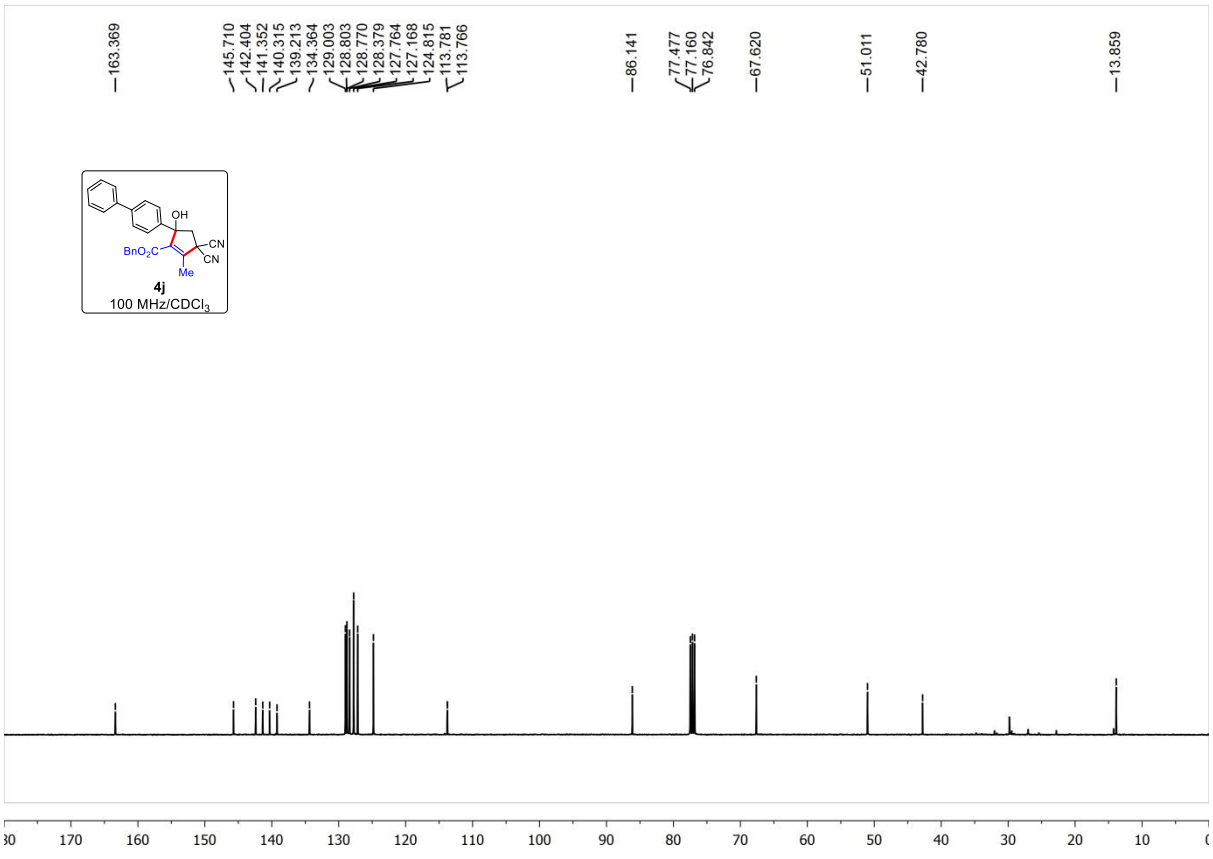

7.260
6.952
6.947
6.930
6.854
6.848
6.833
6.827
4.266
4.257
4.253
4.248
4.239
4.230
4.223
4.221
4.218
4.209
4.203
4.195
4.189
4.174
4.156
4.147
4.138
4.129
4.120
4.111
3.561
3.076
3.040
2.780
2.744
2.442
2.216
2.204
2.201
2.195
2.190
2.188
2.186
2.181
2.175
2.172
2.160
1.180
1.162
1.145
OH
CN
CN
EtO2C
Me
4h
400 MHz/CDCl3
2.01
1.02
6.04
1.02
1.00
1.04
3.08
2.08
3.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

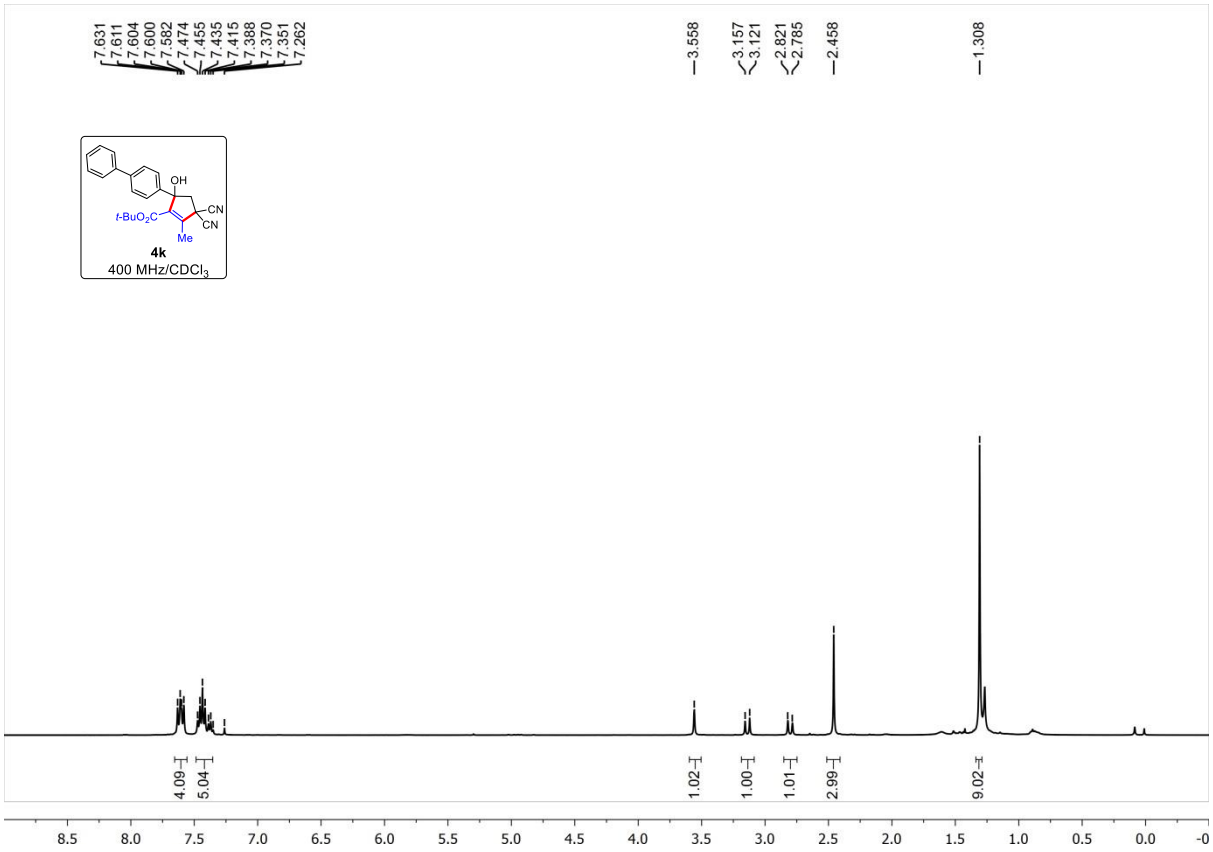

163.651
151.399
151.041
144.563
139.295
138.778
122.118
119.163
117.865
113.869
113.803
85.772
77.478
77.161
76.843
70.637
70.566
61.890
50.931
42.633
31.722
14.063
13.805
OH
CN
CN
EtO2C
Me
4h
100 MHz/CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

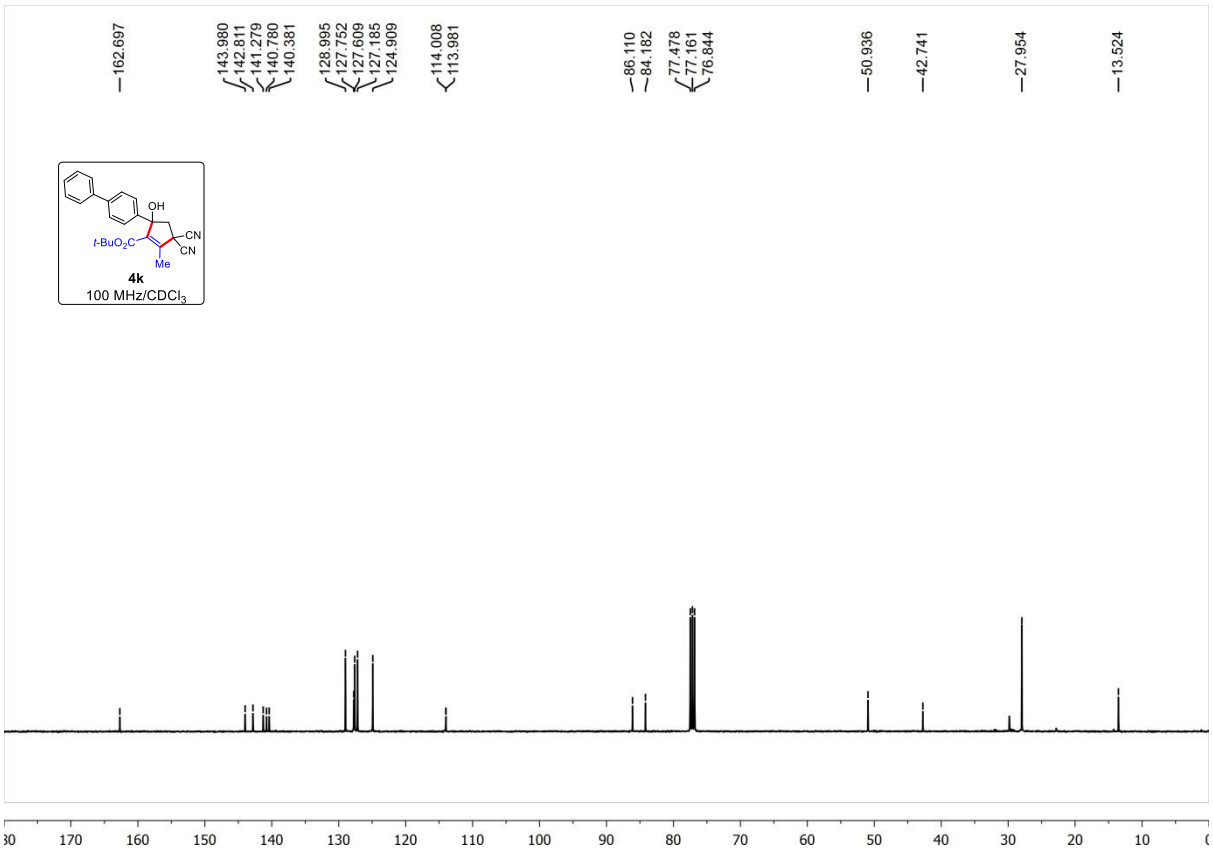

7.364
7.362
7.360
7.358
7.356
7.340
7.260
6.367
6.363
6.359
6.354
6.351
6.345
6.343
4.337
4.327
4.319
4.309
4.301
4.291
4.274
4.263
4.245
4.236
4.227
4.218
4.209
4.200
3.957
3.127
3.092
3.000
2.964
2.435
1.287
1.269
1.251
OH
CN
CN
EtO2C
Me
4i
400 MHz/CDCl3
1.01
2.00
2.00
1.04
1.00
1.02
3.02
3.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

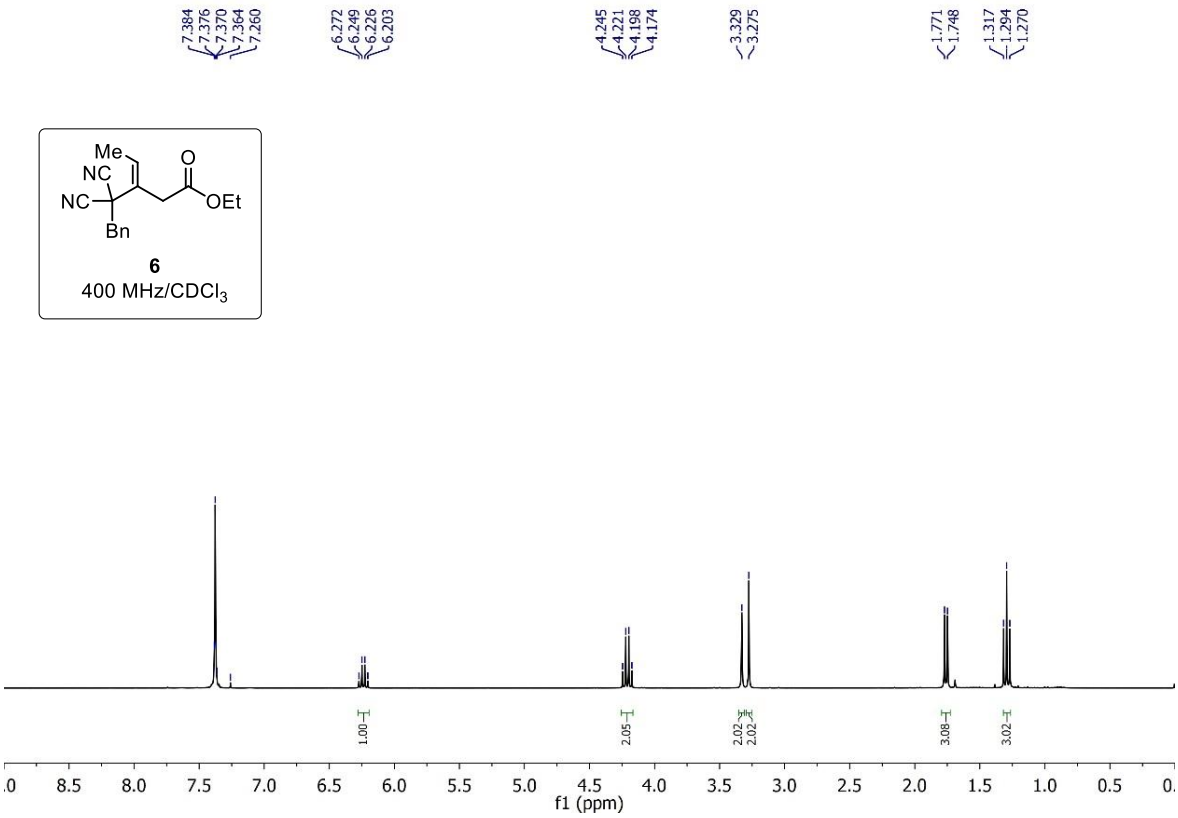

163.485
154.168
145.046
142.851
137.268
113.759
113.418
110.906
106.870
82.099
77.478
77.160
76.843
62.051
47.920
42.252
14.128
14.069
OH
CN
CN
EtO2C
Me
4i
100 MHz/CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

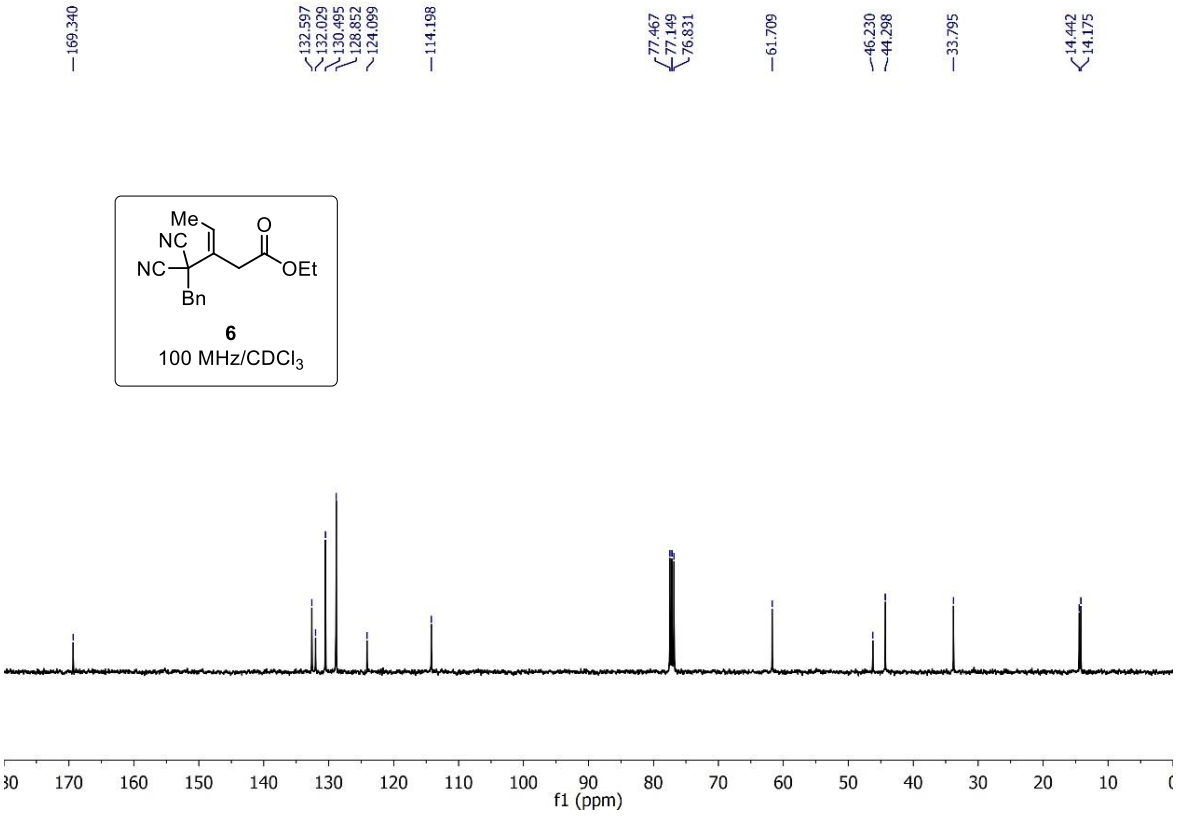

7.589
7.586
7.581
7.572
7.567
7.566
7.562
7.551
7.546
7.476
7.474
7.460
7.456
7.452
7.440
7.436
7.390
7.387
7.383
7.374
7.370
7.368
7.365
7.360
7.350
7.348
7.344
7.259
7.257
7.245
7.241
7.237
7.232
7.225
7.222
7.218
7.216
7.202
7.022
7.018
7.015
7.003
6.998
5.230
5.200
5.038
5.008
3.553
3.141
3.105
2.826
2.790
2.471
OH
BnO2C
CN
CN
Me
4j
400 MHz/CDCl3
3.96
2.00
3.02
3.03
1.92
1.00
1.03
0.98
0.96
0.99
3.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

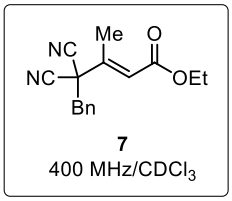

163.369
145.710
142.404
141.352
140.315
139.213
134.364
129.003
128.803
128.770
128.379
127.764
127.168
124.815
113.781
113.766
86.141
77.477
77.160
76.842
67.620
51.011
42.780
13.859
OH
BnO2C
CN
CN
Me
4j
100 MHz/CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


7.631
7.611
7.604
7.600
7.582
7.474
7.455
7.435
7.415
7.388
7.370
7.351
7.262
3.558
3.157
3.121
2.821
2.785
2.458
1.308
OH
t-BuO2C
CN
CN
Me
4k
400 MHz/CDCl3
4.09
5.04
1.02
1.00
1.01
2.99
9.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

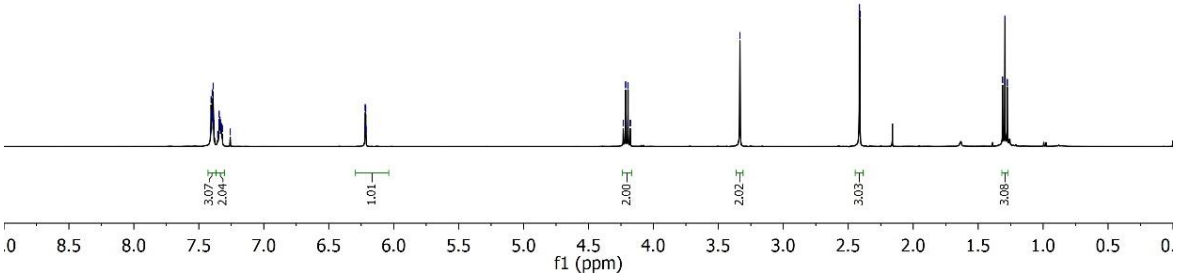

162.697
143.980
142.811
141.279
140.780
140.381
128.995
127.752
127.609
127.185
124.909
114.008
113.981
86.110
84.182
77.478
77.161
76.844
50.936
42.741
27.954
13.524
OH
t-BuO2C
CN
CN
Me
4k
100 MHz/CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

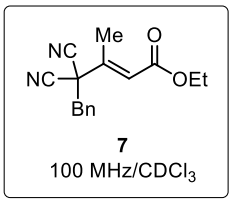

7.384
7.376
7.370
7.364
7.260
6.272
6.249
6.226
6.203
4.245
4.221
4.198
4.174
3.329
3.275
1.771
1.748
1.317
1.294
1.270
Me
NC
NC
Bn
O
OEt
6
400 MHz/CDCl3
1.00
2.05
2.02
2.02
3.08
3.02
f1 (ppm)


169.340
132.597
132.029
130.495
128.852
124.099
114.198
77.467
77.149
76.831
61.709
46.230
44.298
33.795
14.442
14.175
Me
NC
NC
Bn
O
OEt
6
100 MHz/CDCl3
f1 (ppm)



7
400 MHz/$CDCl_3$





7
100 MHz/$CDCl_3$