Supporting Information

Synthesis of Functionalized Cyclopentenes through Allenic Ketone-based Multicomponent Reactions

Qiang Wang,*[a] Tao Zhang,[a] Yunchang Fan[a] and Xuesen Fan*[b]

[a] College of Chemistry and Chemical Engineering, Henan Key Laboratory of Coal Green Conversion, Henan Polytechnic University, Jiaozuo, Henan, 454000, P. R. China. Email: wangqiang@hpu.edu.cn

[b] Henan Key Laboratory of Organic Functional Molecule and Drug Innovation, Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, P. R. China. E-mail: xuesen.fan@htu.cn

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I. General Experimental Information

Reagents and solvents were purchased from commercial suppliers and used without further purification. 1-Aryl or 1-alkyl substituted allenic ketones were prepared through oxidation of the corresponding homopropargyl alcohols,[1] which were prepared through zinc promoted propargylation of aldehydes.[2] 1,4-Disubsituted allenic ketones were prepared from the reaction of 1-(triphenylphosphoranylidene)- 2-propanone or 2-(triphenylphosphoranylidene)acetophenone with phenylacetyl chloride based on a literature procedure.[3] The ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively. Chemical shifts were reported in ppm from the internal standard tetramethylsilane. Multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); m (multiplet); dd (doublet of doublets); td (triplet of doublets); br s (broad singlet), etc. Coupling constants were given in hertz. High-resolution mass spectra (HRMS) were obtained *via* ESI mode by using a MicrOTOF mass spectrometer. The conversion of starting materials was monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm).

II. Experimental Procedures and Spectroscopic Data

1. Typical procedure for the synthesis of 4a and spectroscopic data of 4a−4u, and 5a-5d.

To a flask containing malononitrile (**2a**, 33.0 mg, 0.5 mmol) and K_2CO_3 (82.8 mg, 0.6 mmol) in CH_3CN (5 mL) were added ethyl 4-chloroacetoacetate (**1**, 82.3 mg, 0.5 mmol). The mixture was stirred at room temperature for 20 min. Then 1-phenylbuta-2,3-dien-1-one (**3a**, 72.0 mg, 0.5 mmol) was added. The resulting mixture was stirred at 80 °C for another 1.5 h. Upon completion as determined by TLC analysis, it was allowed to cool to room temperature and quenched with saturated ammonium chloride. The mixture was extracted with ethyl acetate (3×15 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO_2) using EtOAc/petroleum ether (v/v =1/5) as eluent to give **4a** (133.5 mg, 79%). Other cyclopentene derivatives (**4b-4t** and **5a-5d)** were obtained in a similar manner.

Ethyl 2-(2-benzoyl-4,4-dicyano-1-hydroxy-3-methylcyclopent-2-en-1-yl)acetate (4a)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (133.5 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.17 (t, *J* = 7.6 Hz, 3H), 1.87 (s, 3H), 2.82 (d, AB syst., *J* = 16.4 Hz, 1H), 2.98 (d, AB syst., *J* = 16.8 Hz, 1H), 2.99 (s, 2H), 4.12-4.02 (m, 2H), 4.43 (s, 1H), 7.52 (t, *J* = 8.0 Hz, 2H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.6, 14.0, 41.9, 42.2, 48.1, 61.4, 83.8, 113.9, 114.1, 129.2, 129.8, 134.8, 136.3, 136.7, 145.4, 170.9, 194.6. HRMS (ESI): calcd for $C_{19}H_{19}N_2O_4$ $[M+H]^+$: 339.1345; found: 339.1351.

Ethyl 2-(2-(1-naphthoyl)-4,4-dicyano-1-hydroxy-3-methylcyclopent-2-en-1-yl)acetate (4b)

Eluent: ethyl acetate/petroleum ether (1/8). Yellow oil (135.8 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.21 (t, *J* = 7.6 Hz, 3H), 1.76 (s, 3H), 3.14-2.94 (m, 4H), 4.16-4.11 (m, 2H), 4.53 (s, 1H), 7.62-7.55 (m, 2H), 7.68-7.66 (m, 1H), 7.98-7.93 (m, 2H), 8.11 (d, *J* = 8.0 Hz, 1H), 8.79 (d, *J* = 8.4 Hz, 1H). ^{13}CNMR (100 MHz, $CDCl_3$) δ: 13.7, 14.0, 42.1, 42.3, 47.7, 61.3, 83.9, 113.9, 114.0, 124.7, 125.3, 127.1, 128.8, 129.1, 130.1, 132.9, 133.4, 134.0, 135.1, 138.5, 146.7, 170.9, 195.9. HRMS (ESI): calcd for $C_{23}H_{21}N_2O_4$ $[M+H]^+$: 389.1501; found: 389.1504.

Ethyl 2-(2-(3-chlorobenzoyl)-4,4-dicyano-1-hydroxy-3-methylcyclopent-2-en-1-yl)acetate (4c)

Eluent: ethyl acetate/petroleum ether (1/3). Yellow oil (141.4 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ:

1.19 (t, J = 7.6 Hz, 3H), 1.87 (s, 3H), 3.02-2.80 (m, 4H), 4.16-4.02 (m, 2H), 4.42 (s, 1H), 7.47 (t, J = 8.0 Hz, 1H), 7.61 (dd, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H), 7.75 (t, J = 7.6 Hz, 1H), 7.87 (s, 1H). ^{13}CNMR (100 MHz, $CDCl_3$) δ: 13.6, 14.0, 41.9, 42.0, 48.2, 61.5, 83.7, 113.8, 113.9, 128.3, 129.1, 130.5, 134.7, 135.5, 137.1, 137.8, 145.2, 171.0, 193.3. HRMS (ESI): calcd for $C_{19}H_{18}ClN_2O_4$ $[M+H]^+$: 373.0955; found: 373.0961.

Ethyl 2-(4,4-dicyano-2-(2,4-dichlorobenzoyl)-1-hydroxy-3-methylcyclopent-2-en-1-yl)acetate (4d)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (146.2 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.24 (t, J = 6.8 Hz, 3H), 1.79 (s, 3H), 2.78 (d, AB syst., J = 15.2 Hz, 1H), 2.88 (d, AB syst., J = 16.0 Hz, 1H), 2.98 (d, AB syst., J = 14.4 Hz, 1H), 3.09 (d, AB syst., J = 16.4 Hz, 1H), 4.19-4.10 (m, 2H), 4.22 (s, 1H), 7.40 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.50 (d, J = 1.6 Hz, 1H), 7.61 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.5, 14.1, 42.2, 42.3, 47.6, 61.4, 83.7, 113.5, 113.6, 128.0, 131.2, 132.2, 133.3, 135.1, 139.5, 140.9, 145.0, 170.7, 192.1. HRMS (ESI): calcd for $C_{19}H_{17}Cl_2N_2O_4$ $[M+H]^+$: 407.0565; found: 407.0572.

Ethyl 2-(2-(2-bromobenzoyl)-4,4-dicyano-1-hydroxy-3-methylcyclopent-2-en-1-yl)acetate (4e)

Eluent: ethyl acetate/petroleum ether (1/5). White solid (156.0 mg, 75%); Mp: 134-136ºC (ethyl acetate/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.26 (t, J = 7.2 Hz, 3H), 1.74 (s, 3H), 2.91 (d, AB syst., J = 16.4 Hz, 1H), 2.95 (d, AB syst., J = 15.2 Hz, 1H), 3.03 (d, AB syst., J = 14.8 Hz, 1H), 3.12 (d, AB syst., J = 16.0 Hz, 1H), 4.21-4.13 (m, 3H), 7.49-7.39 (m, 2H), 7.58 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.69 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.5, 14.1, 42.4, 42.5, 47.4, 61.4, 83.8, 113.5, 113.6, 120.0, 128.2, 130.9, 133.5, 134.4, 139.0, 141.7, 144.7, 170.5, 193.9. HRMS (ESI): calcd for $C_{19}H_{18}BrN_2O_4$ $[M+H]^+$: 417.0450; found: 417.0457.

Ethyl 2-(2-(3-bromobenzoyl)-4,4-dicyano-1-hydroxy-3-methylcyclopent-2-en-1-yl)acetate (4f)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (143.5 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.19 (t, J = 7.2 Hz, 3H), 1.87 (s, 3H), 3.01-2.80 (m, 4H), 4.14-4.04 (m, 2H), 4.41 (s, 1H), 7.40 (t, J = 8.0 Hz, 1H), 7.78 (t, J = 8.4 Hz 2H), 8.02 (s, 1H). ^{13}CNMR (100 MHz, $CDCl_3$) δ: 13.5, 14.0, 41.9, 42.1, 48.2, 61.5, 83.7, 113.8, 113.9, 123.5, 128.8, 130.7, 132.0, 137.1, 137.5, 138.0, 145.2, 170.9, 193.2. HRMS (ESI): calcd for $C_{19}H_{18}BrN_2O_4$ $[M+H]^+$: 417.0450; found: 417.0458.

Ethyl 2-(4,4-dicyano-2-(4-cyanobenzoyl)-1-hydroxy-3-methylcyclopent-2-en-1-yl)acetate (4g)

Eluent: ethyl acetate/petroleum ether (1/10). Yellow oil (128.8 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.20 (t, *J* = 7.6 Hz, 3H), 1.85 (s, 3H), 3.01-2.81 (m, 4H), 4.14-4.04 (m, 2H), 4.39 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.99 (d, *J* = 7.6 Hz, 2H). ^{13}CNMR (100 MHz, $CDCl_3$) δ: 13.6, 14.0, 41.89, 41.91, 48.3, 61.6, 83.7, 113.7, 113.8, 117.6, 130.1, 132.9, 137.6, 139.2, 145.1, 171.1, 193.3. HRMS (ESI): calcd for $C_{20}H_{18}N_3O_4$ $[M+H]^+$: 364.1297; found: 364.1291.

Ethyl 2-(2-(2-bromo-5-methoxybenzoyl)-4,4-dicyano-1-hydroxy-3-methylcyclopent-2-en-1-yl)acetate (4h)

Eluent: ethyl acetate/petroleum ether (1/5). Colorless oil (182.8 mg, 82%). ^{1}H NMR(400 MHz, $CDCl_3$) δ: 1.24 (t, *J* = 6.8 Hz, 3H), 1.76 (s, 3H), 2.89 (d, AB syst., *J* = 16.4 Hz, 1H), 2.94 (d, AB syst., *J* = 14.4 Hz, 1H), 3.02 (d, AB syst., *J* = 14.0 Hz, 1H), 3.10 (d, AB syst., *J* = 16.0 Hz, 1H), 3.80 (s, 3H), 4.17-4.07 (m, 3H), 6.94 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H), 7.11 (d, *J* = 3.2 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.5, 14.1, 42.4, 42.5, 47.3, 55.8, 61.3, 83.8, 110.0, 113.59, 113.61, 115.7, 119.8, 135.1, 139.6, 141.9, 144.5, 159.4, 170.5, 193.7. HRMS (ESI): calcd for $C_{20}H_{20}BrN_2O_5$ $[M+H]^+$: 447.0506; found: 447.0511.

Ethyl 2-(4,4-dicyano-1-hydroxy-3-methyl-2-(3-methylbenzoyl)cyclopent-2-en-1-yl)acetate (4i)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (112.6 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.17 (t, *J* = 7.2 Hz, 3H), 1.88 (s, 3H), 2.42 (s, 3H), 2.81 (d, AB Syst., *J* = 16.8 Hz, 1H), 2.98 (d, AB Syst., *J* = 15.6 Hz, 1H), 2.99 (s, 2H), 4.13-4.02 (m, 2H), 4.43 (s, 1H), 7.48-7.38 (m, 2H), 7.65 (d, *J* = 7.2 Hz, 1H), 7.70 (s, 1H). ^{13}CNMR (100 MHz, $CDCl_3$) δ: 13.5, 14.0, 21.3, 30.9, 41.9, 42.2, 48.1, 61.3, 83.8, 113.9, 114.1, 127.5, 129.0, 129.7, 135.7, 136.3, 136.5, 139.2, 145.5, 170.8, 194.7. HRMS (ESI): calcd for $C_{20}H_{21}N_2O_4$ $[M+H]^+$: 353.1501; found: 353.1505.

Ethyl 2-(4,4-dicyano-1-hydroxy-3-methyl-2-(4-methylbenzoyl)cyclopent-2-en-1-yl)acetate (4j)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (146.1 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.17 (t, *J* = 6.8 Hz, 3H), 1.87 (s, 3H), 2.43 (s, 3H), 2.80 (d, AB syst., *J* = 16.8 Hz, 1H), 2.96 (d, AB syst., *J* = 17.6 Hz, 1H), 2.99 (s, 2H), 4.12-4.02 (m, 2H), 4.42 (s, 1H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.78 (d, *J* = 8.0Hz, 2H). ^{13}CNMR (100 MHz, $CDCl_3$) δ: 13.5, 14.0, 21.9, 41.9, 42.2, 48.1, 61.3, 83.8, 114.0, 114.2, 129.9, 130.0, 133.8, 136.2, 145.6, 146.2, 170.8, 194.1. HRMS (ESI): calcd for $C_{20}H_{21}N_2O_4$ [M+H]+: 353.1501;

found: 353.1505.

Ethyl 2-(4,4-dicyano-1-hydroxy-2-(4-methoxybenzoyl)-3-methylcyclopent-2-en-1-yl)acetate (4k)

Eluent: ethyl acetate/petroleum ether (1/4). Yellow oil (126.9 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.17 (t, *J* = 6.8 Hz, 3H), 1.89 (s, 3H), 2.98-2.76 (m, 4H), 3.88 (s, 3H), 4.12-4.01 (m, 2H), 4.46 (s, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 7.86 (d, *J* = 9.2 Hz, 2H). ^{13}CNMR (100 MHz, $CDCl_3$) δ: 13.4, 14.0, 41.9, 42.2, 48.1, 55.7, 61.3, 83.8, 114.1, 114.2, 114.4, 129.2, 132.4, 135.6, 145.6, 165.1, 170.8, 192.7. HRMS (ESI): calcd for $C_{20}H_{21}N_2O_5$ $[M+H]^+$: 369.1450; found: 369.1442.

Ethyl 2-(4,4-dicyano-2-(3,4-dimethoxybenzoyl)-1-hydroxy-3-methylcyclopent-2-en-1-yl)acetate (4l)

Eluent: ethyl acetate/petroleum ether (1/10). Colorless oil (121.4 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.17 (t, *J* = 7.2 Hz, 3H), 1.89 (s, 3H), 2.77 (d, AB syst., *J* = 16.4 Hz, 1H), 2.93 (d, AB syst., *J* = 16.8 Hz, 1H), 2.97 (s, 2H), 3.91 (s, 3H), 3.94 (s, 3H), 4.11-4.01 (m, 2H), 4.45 (s, 1H), 6.93 (d, *J* = 8.8 Hz, 1H), 7.46 (s, 1H), 7.47 (d, *J* = 7.2 Hz, 1H). ^{13}CNMR (100 MHz, $CDCl_3$) δ: 13.4, 14.0, 41.8, 42.2, 48.3, 56.0, 56.2, 61.3, 83.7, 110.5, 114.1, 114.2, 126.2, 129.3, 135.5, 145.7, 149.5, 155.0, 170.9, 192.7. HRMS (ESI): calcd for $C_{21}H_{23}N_2O_6$ $[M+H]^+$: 399.1556; found: 399.1550.

Ethyl 3-benzoyl-1-cyano-4-(2-ethoxy-2-oxoethyl)-4-hydroxy-2-methylcyclopent-2-enecarboxylate (4m)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (128.9 mg, 67%). ^{1}H NMR(400 MHz, $CDCl_3$) δ: 1.16 (t, *J* = 6.4 Hz, 3H), 1.36 (t, *J* = 6.8 Hz, 3H),1.69 (s, 3H), 2.82 (d, AB syst., *J* = 14.4 Hz, 1H), 2.85 (d, AB syst., *J* = 14.0 Hz, 1H), 2.96 (d, AB syst., *J* = 15.2 Hz, 1H), 2.97 (d, AB syst., *J* = 15.2 Hz, 1H), 4.10-4.01 (m, 2H), 4.33 (q, *J* = 7.2 Hz, 2H), 4.45 (s, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.91-7.89 (m, 2H). ^{13}CNMR (100 MHz, $CDCl_3$) δ: 13.8, 14.0, 43.1, 47.5, 55.5, 61.0, 63.8, 84.3, 117.6, 128.9, 129.8, 134.4, 136.8, 139.6, 144.3, 167.2, 171.4, 195.7. HRMS (ESI): calcd for $C_{21}H_{24}NO_6$ $[M+H]^+$: 386.1604; found: 386.1599.

Ethyl 3-(1-naphthoyl)-1-cyano-4-(2-ethoxy-2-oxoethyl)-4-hydroxy-2-methylcyclopent-2-enecarboxylate (4n)

Eluent: ethyl acetate/petroleum ether (1/8). White solid (165.3 mg, 76%). Mp: 109-111 ºC (ethyl acetate/petroleum ether). ^{1}H NMR(400 MHz, $CDCl_3$) δ: 1.20 (t, *J* = 6.8 Hz, 3H),1.36 (t, *J* = 7.6 Hz, 3H),

1.57 (s, 3H), 2.85 (d, AB syst., J = 14.4 Hz, 1H), 2.97 (d, AB syst., J = 15.6 Hz, 1H), 3.05 (d, AB syst., J = 14.8 Hz, 1H), 2.12 (d, AB syst., J = 15.6 Hz, 1H), 4.13-4.07 (m, 2H), 4.33 (q, J = 7.2 Hz, 2H), 4.58 (s, 1H), 7.59-7.52 (m, 2H), 7.65 (td, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.98 (td, J_1 = 6.8 Hz, J_2 = 1.2 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H), 8.77 (d, J = 8.4 Hz, 1H). ^{13}CNMR (100 MHz, $CDCl_3$) δ: 13.93, 13.99, 14.0, 43.2, 47.0, 55.7, 61.0, 63.7, 84.3, 117.5, 124.8, 125.4, 126.9, 128.6, 128.7, 130.2, 132.4, 133.9, 134.3, 134.5, 142.0, 145.6, 167.1, 171.2, 197.0. HRMS (ESI): calcd for $C_{25}H_{26}NO_6$ $[M+H]^+$: 436.1760; found: 436.1766.

Ethyl 1-cyano-3-(2,4-dichlorobenzoyl)-4-(2-ethoxy-2-oxoethyl)-4-hydroxy-2-methylcyclopent-2-enecarboxylate (4o)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (183.5 mg, 81%). ^{1}H NMR(400 MHz, $CDCl_3$) δ: 1.22 (t, J = 6.8 Hz, 3H), 1.32 (t, J = 6.4 Hz, 3H), 1.62 (s, 3H), 2.74 (d, AB syst., J = 14.8 Hz, 1H), 2.88 (d, AB syst., J = 15.6 Hz, 1H), 2.98 (d, AB syst., J = 14.8 Hz, 1H), 3.06 (d, AB syst., J = 15.6 Hz, 1H), 4.15-4.09 (m, 2H), 4.32-4.26 (m, 3H), 7.36 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.46 (d, J = 2.0 Hz, 1H), 7.58 (d, J = 8.0Hz, 1H). ^{13}CNMR (100 MHz, $CDCl_3$) δ: 13.7, 14.0, 14.1, 43.2, 46.7, 55.9, 61.1, 63.9, 84.2, 117.2, 127.9, 130.9, 132.1, 133.1, 135.9, 138.8, 144.0, 144.7, 166.6, 171.1, 193.1. HRMS (ESI): calcd for $C_{21}H_{22}Cl_2NO_6$ $[M+H]^+$: 454.0824; found: 454.0829.

Ethyl 3-(2-bromobenzoyl)-1-cyano-4-(2-ethoxy-2-oxoethyl)-4-hydroxy-2-methylcyclopent-2-enecarboxylate (4p)

Eluent: ethyl acetate/petroleum ether (1/3). Yellow solid (180.5 mg, 78%). Mp: 110-111 ºC (ethyl acetate/petroleum ether). ^{1}H NMR(400 MHz, $CDCl_3$) δ: 1.23 (t, J = 7.2 Hz, 3H), 1.31 (t, J = 7.2 Hz, 3H), 1.55 (s, 3H), 2.73 (d, AB syst., J = 14.0 Hz, 1H), 2.91 (d, AB syst., J = 16.0 Hz, 1H), 3.06 (d, AB syst., J = 14.0 Hz, 1H), 3.13 (d, AB syst., J = 15.6 Hz, 1H), 4.16-4.11 (m, 2H), 4.31-4.24 (m, 3H), 7.35 (td, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.53 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H). ^{13}CNMR (100 MHz, $CDCl_3$) δ: 13.8, 14.0, 14.1, 43.2, 46.4, 56.2, 61.0, 63.8, 84.3, 117.2, 119.8, 128.0, 130.7, 133.0, 134.1, 139.7, 143.6, 145.7, 166.6, 171.0, 194.9. HRMS (ESI): calcd for $C_{21}H_{23}BrNO_6$ $[M+H]^+$: 464.0709; found: 464.0703.

Ethyl 3-(3-bromobenzoyl)-1-cyano-4-(2-ethoxy-2-oxoethyl)-4-hydroxy-2-methylcyclopent-2-

enecarboxylate (4q)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (164.3 mg, 71%). ^{1}H NMR(400 MHz, $CDCl_3$) δ: 1.19 (t, *J* = 7.6 Hz, 3H), 1.37 (t, *J* = 6.8 Hz, 3H), 1.71 (s, 3H), 2.99-2.80 (m, 4H), 4.12-4.04 (m, 2H), 4.34 (q, *J* = 7.2 Hz, 2H), 4.42 (s, 1H), 7.39 (t, *J* = 8.4 Hz, 1H), 7.75-7.73 (m, 1H), 7.83 (d, *J* = 7.2 Hz, 1H), 8.04 (s, 1H). ^{13}CNMR (100 MHz, $CDCl_3$) δ: 13.8, 14.0, 43.0, 47.6, 55.5, 61.1, 63.8, 84.3, 117.4, 123.3, 128.7, 130.6, 132.1, 137.1, 138.6, 140.2, 144.0, 167.0, 171.4, 194.2. HRMS (ESI): calcd for $C_{21}H_{23}BrNO_6$ $[M+H]^+$: 464.0709; found: 464.0713.

Ethyl 1-cyano-3-(4-cyanobenzoyl)-4-(2-ethoxy-2-oxoethyl)-4-hydroxy-2-methylcyclopent-2-enecarboxylate (4r)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (123.3 mg, 60%). ^{1}H NMR(400 MHz, $CDCl_3$) δ: 1.19 (t, *J* = 7.2 Hz, 3H), 1.35 (t, *J* = 6.8 Hz, 3H), 1.67 (s, 3H), 2.80 (d, AB syst., *J* = 14.0 Hz, 1H), 2.86 (d, AB syst., *J* = 15.6 Hz, 1H), 2.90 (d, AB syst., *J* = 13.6 Hz, 1H), 2.97 (d, AB syst., *J* = 16.0 Hz, 1H), 4.14-4.03 (m, 2H), 4.35-4.30 (m, 2H), 4.42 (s, 1H), 7.80 (d, *J* = 8.8 Hz, 2H), 8.01 (d, *J* = 8.8 Hz, 2H). ^{13}CNMR (100 MHz, $CDCl_3$) δ: 13.8, 14.0, 42.8, 47.6, 55.4, 61.2, 63.9, 84.3, 117.3, 117.7, 130.1, 132.8, 139.8, 140.5, 143.9, 166.9, 171.6, 194.3. HRMS (ESI): calcd for $C_{22}H_{23}N_2O_6$ $[M+H]^+$: 411.1556; found: 411.1562.

Ethyl 3-(2-bromo-5-methoxybenzoyl)-1-cyano-4-(2-ethoxy-2-oxoethyl)-4-hydroxy-2-methylcyclopent-2-enecarboxylate (4s)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (189.8 mg, 77%). ^{1}H NMR(400 MHz, $CDCl_3$) δ: 1.23 (t, *J* = 7.2 Hz, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.60 (s, 3H), 2.73 (d, AB syst., *J* = 14.0 Hz, 1H), 2.91 (d, AB syst., *J* = 15.6 Hz, 1H), 3.04 (d, AB syst., *J* = 14.8 Hz, 1H), 3.09 (d, AB syst., *J* = 15.2 Hz, 1H), 3.79 (s, 3H), 4.14 (q, *J* = 7.2 Hz, 2H), 4.21 (s, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 6.90 (dd, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H), 7.09 (d, *J* = 3.2 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 1H). ^{13}CNMR (100 MHz, $CDCl_3$) δ: 13.8, 14.0, 14.1, 43.2, 46.4, 55.7, 56.2, 60.9, 63.8, 84.3, 109.8, 115.5, 117.2, 119.4, 134.9, 140.4, 143.4, 145.9, 159.3, 166.6, 171.0, 194.7. HRMS (ESI): calcd for $C_{22}H_{25}BrNO_7$ $[M+H]^+$: 494.0814; found: 494.0820.

Ethyl 2-(4,4-dicyano-1-hydroxy-3-methyl-2-(3-phenylpropanoyl)cyclopent-2-en-1-yl)acetate(4t)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (161.0 mg, 78%). ^{1}H NMR(400 MHz, $CDCl_3$) δ: 1.25 (t, *J* = 6.8 Hz, 3H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.95 (s, 3H), 2.90-2.63 (m, 4H), 2.98-2.96 (m, 2H), 3.07-

3.03 (m, 2H), 4.13 (q, J = 7.2 Hz, 2H), 4.34-4.23 (m, 3H), 7.21-7.19 (m, 3H), 7.29-7.26 (m, 2H). ^{13}CNMR (100 MHz, $CDCl_3$) δ: 13.7, 14.0, 14.1, 29.4, 43.2, 45.6, 46.8, 55.7, 61.1, 61.12, 63.8, 83.9, 117.5, 126.2, 126.3, 128.4, 128.5, 128.6, 140.6. HRMS (ESI): calcd for $C_{23}H_{28}NO_6$ $[M+H]^+$: 414.1917; found: 414.1910.

Ethyl 1-cyano-4-(2-ethoxy-2-oxoethyl)-4-hydroxy-3-(3-methylbenzoyl)-2- methylenecy clopentanecarboxylate (5a)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (137.3 mg, 69%). ^{1}H NMR(400 MHz, $CDCl_3$) δ: 1.11 (t, J = 7.6 Hz, 3H), 1.34 (t, J = 6.8 Hz, 3H), 2.40 (s, 3H), 2.83-2.64 (m, 4H), 4.05-4.01 (m, 2H), 4.32 (q, J = 7.2 Hz, 2H), 4.63 (t, J = 2.8 Hz, 1H), 4.95 (t, J = 2.0 Hz, 1H), 5.39 (s, 1H), 5.62 (t, J = 2.4 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.45 (d, J = 7.2 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.75 (s, 1H). ^{13}CNMR (100 MHz, $CDCl_3$) δ: 13.9, 14.0, 21.3, 43.2, 47.0, 50.0, 54.9, 60.9, 63.7, 80.2, 116.3, 119.0, 126.3, 129.1, 129.12, 136.7, 136.9, 139.1, 147.1, 167.9, 169.9, 201.3. HRMS (ESI): calcd for $C_{22}H_{26}NO_6$ $[M+H]^+$: 400.1760; found: 400.1768.

Ethyl 1-cyano-4-(2-ethoxy-2-oxoethyl)-4-hydroxy-3-(4-methylbenzoyl)-2-methylene cyclopentanecarboxylate (5b)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (141.6 mg, 71%). ^{1}H NMR(400 MHz, $CDCl_3$) δ: 1.10 (t, J = 7.2 Hz, 3H), 1.32 (t, J = 6.8 Hz, 3H), 2.40 (s, 3H), 2.82-2.62 (m, 4H), 4.07-3.95 (m, 2H), 4.33 - 4.28 (m, 2H), 4.61 (s, 1H), 4.93 (s, 1H), 5.43 (s, 1H), 5.59 (s, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 7.6 Hz, 2H). ^{13}CNMR (100 MHz, $CDCl_3$) δ: 13.9, 14.0, 21.8, 43.2, 47.0, 50.0, 54.7, 60.8, 63.6, 80.2, 116.1, 119.0, 129.0, 129.9, 134.4, 146.2, 147.2, 167.9, 169.9, 200.6. HRMS (ESI): calcd for $C_{22}H_{26}NO_6$ $[M+H]^+$: 400.1760; found: 400.1764.

Ethyl 1-cyano-4-(2-ethoxy-2-oxoethyl)-4-hydroxy-3-(4-methoxybenzoyl)-2-methylene cyclopentanecarboxylate (5c)

Eluent: ethyl acetate/petroleum ether (1/3). Yellow oil (151.4 mg, 73%). ^{1}H NMR(400 MHz, $CDCl_3$) δ: 1.11 (t, J = 7.2 Hz, 3H), 1.32 (t, J = 7.6 Hz, 3H), 2.81-2.61 (m, 4H), 3.85 (s, 3H), 4.07-3.98 (m, 2H), 4.33 - 4.27 (m, 2H), 4.57 (t, J = 1.6 Hz, 1H), 4.94 (s, 1H), 5.55 (s, 1H), 5.59 (t, J = 2.0 Hz, 1H), 6.94 (d, J = 8.4 Hz, 2H), 7.90 (d, J = 9.2 Hz, 2H). ^{13}CNMR (100 MHz, $CDCl_3$) δ: 13.9, 14.0, 43.1, 47.0, 50.0, 54.4, 55.7, 60.8, 63.6, 80.2, 114.4, 116.0, 119.1, 129.8, 131.4, 147.2, 165.0, 168.0, 169.9, 199.2. HRMS (ESI): calcd

for $C_{22}H_{26}NO_7$ $[M+H]^+$: 416.1709; found: 416.1702.

Ethyl 1-cyano-3-(3,4-dimethoxybenzoyl)-4-(2-ethoxy-2-oxoethyl)-4-hydroxy-2-methylene cyclopentanecarboxylate (5d)

Eluent: ethyl acetate/petroleum ether (1/3). White solid (151.3 mg, 68%). Mp: 112-113 ºC (ethyl acetate/petroleum ether). ^{1}H NMR(400 MHz, $CDCl_3$) δ: 1.08 (t, *J* = 6.8 Hz, 3H), 1.25 (t, *J* = 6.4 Hz, 3H), 2.81-2.58 (m, 4H), 3.81 (s, 3H), 3.86 (s, 3H), 4.03-3.93 (m, 2H), 4.29 -4.24 (m, 2H), 4.81 (s, 1H), 5.43 (s, 1H), 5.49 (s, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.49 (s, 1H), 7.62 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H). ^{13}CNMR (100 MHz, $CDCl_3$) δ: 14.2, 14.4, 43.4, 46.9, 50.1, 56.0, 56.4, 56.6, 60.5, 63.6, 80.2, 111.0, 111.5, 116.2, 119.9, 124.6, 130.7, 147.4, 149.2, 154.5, 167.8, 170.3, 198.2. HRMS (ESI): calcd for $C_{23}H_{28}NO_8$ $[M+H]^+$: 446.1815; found: 446.1810.

2. Preparation of 3-benzoyl-4-hydroxy-2-methyl-4-phenylcyclopent-2-ene-1,1-dicarbonitrile (7) from the reaction 2a with 3a and 2-bromo-1-phenylethanone (6)

To a flask containing malononitrile (**2a**, 33.0 mg, 0.5 mmol) and K_2CO_3 (82.8 mg, 0.6 mmol) in CH_3CN (5 mL) were added 2-bromo-1-phenylethanone (**6**, 99.5 mg, 0.5 mmol). The mixture was stirred at room temperature for 20 min. Then 1-phenylbuta-2,3-dien-1-one (**3a**, 72 mg, 0.5 mmol) was added. The resulting mixture was stirred at 80 °C for another 1.5 h. Upon completion as determined by TLC analysis, it was allowed to cool to room temperature and quenched with saturated ammonium chloride. The mixture was extracted with ethyl acetate (3×15 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO_2) using EtOAc/petroleum ether (v/v =1/5) as eluent to give 3-benzoyl-4-hydroxy-2-methyl-4-phenylcyclopent- 2-ene-1,1-dicarbonitrile (**7**, 91.8 mg, 56%).

3-Benzoyl-4-hydroxy-2-methyl-4-phenylcyclopent-2-ene-1,1-dicarbonitrile (**7**)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow solid (91.8 mg, 88%). Mp: 116-117ºC (ethyl acetate/petroleum ether). ^{1}H NMR(400 MHz, $CDCl_3$) δ: 2.03 (s, 3H), 2.91 (d, AB syst., *J* = 14.0 Hz, 1H), 3.12 (d, AB syst., *J* = 14.0 Hz, 1H), 4.33 (s, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.30 (t, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 7.2 Hz, 2H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 2H). ^{13}CNMR (100 MHz, $CDCl_3$) δ: 14.3, 43.2, 51.5, 88.4, 114.0, 114.3, 124.7, 128.3, 128.9, 129.3, 129.6, 134.9, 135.9, 139.3,

142.3, 145.9, 194.7. HRMS (ESI): calcd for $C_{14}H_{16}N_3O_3$ $[M+H]^+$: 274.1186; found: 274.1189. HRMS (ESI): calcd for $C_{21}H_{17}N_2O_2$ $[M+H]^+$: 329.1290; found: 329.1282.

3. Preparation of ethyl 3,3-dicyano-4-methyl-6-oxo-6-phenylhex-4-enoate (9) from the reaction 2a, 3a and ethyl 2-chloroacetate (8)

To a flask containing malononitrile (**2a**, 33.0 mg, 0.5 mmol) and K_2CO_3 (82.8 mg, 0.6 mmol) in CH_3CN (5 mL) were added ethyl 2-chloroacetate (**8**, 61.3 mg, 0.5 mmol). The mixture was stirred at room temperature for 20 min. Then 1-phenylbuta-2,3-dien-1-one (**3a**, 72.0 mg, 0.5 mmol) was added. The resulting mixture was stirred at 80 °C for another 1.5 h. As completion as determined by TLC analysis, it was allowed to cool to room temperature and quenched with saturated ammonium chloride. The mixture was extracted with ethyl acetate (3×15 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO_2) using EtOAc/petroleum ether (v/v =1/5) as eluent to give ethyl 3,3-dicyano-4-methyl-6-oxo-6-phenylhex-4-enoate (**9**, 91.8 mg, 62%).

Ethyl 3,3-dicyano-4-methyl-6-oxo-6-phenylhex-4-enoate (9)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (91.8 mg, 62%). ^{1}H NMR(400 MHz, $CDCl_3$) δ: 1.32 (t, J = 7.2 Hz, 3H), 2.28 (d, J = 0.8 Hz, 3H), 3.19 (s, 2H), 4.29 (q, J = 6.8 Hz, 2H), 7.40 (d, J = 0.8 Hz, 1H), 7.53-7.49 (m, 2H), 7.64-7.60 (m, 1H), 7.95-7.93 (m, 2H). ^{13}CNMR (100 MHz, $CDCl_3$) δ: 14.0, 15.5, 40.7, 41.2, 62.6, 113.0, 127.3, 128.7, 129.0, 134.0, 137.1, 140.7, 165.8, 190.3. HRMS (ESI): calcd for $C_{17}H_{17}N_2O_3$ $[M+H]^+$: 297.1239; found: 297.1235.

III. Control experiments

1. Reaction of 1 with 2a leading to the formation of intermediate A

To a flask containing malononitrile (**2a**, 33.0 mg, 0.5 mmol) and K_2CO_3 (69.0 mg, 0.5 mmol) in CH_3CN (5 mL) were added ethyl 4-chloroacetoacetate (**1**, 82.3 mg, 0.5 mmol). The mixture was stirred at room temperature for 30 min. Upon completion as determined by TLC analysis, it was allowed to cool to room temperature and quenched by saturated ammonium chloride. The mixture was extracted with ethyl acetate (3×15 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO_2) using EtOAc/petroleum ether

(v/v =1/3) as eluent to give ethyl 5,5-dicyano-3-oxopentanoate (**A**,79.5mg, 82%).

Ethyl 5,5-dicyano-3-oxopentanoate (A)

Eluent: ethyl acetate/petroleum ether (1/3). Yellow oil (79.5mg, 82%). ^{1}H NMR(400 MHz, DMSO-d_6) δ: 1.19 (t, *J* = 7.2 Hz, 3H), 3.49 (d, *J* = 6.8 Hz, 2H), 3.69 (s, 2H), 4.10 (q, *J* = 6.8 Hz, 2H), 4.91 (t, *J* = 5.6 Hz, 1H). ^{13}CNMR (100 MHz, DMSO-d_6) δ: 14.3, 17.8, 41.6, 48.2, 61.3, 114.4, 167.0, 199.0. HRMS (ESI): calcd for $C_9H_{11}N_2O_3$ $[M+H]^+$:195.0770; found:195.0777.

2. Reaction of A with 3a leading to the formation of 4a

To a flask containing ethyl 5,5-dicyano-3-oxopentanoate (**A**, 97.0mg, 0.5 mmol) and 1-phenylbuta-2,3-dien-1-one (**3a**, 72.0 mg, 0.5 mmol) in CH_3CN (5 mL) were added K_2CO_3 (69.0 mg, 0.5 mmol). The mixture was stirred at 80 °C for 1.5 h. Upon completion as determined by TLC analysis, it was allowed to cool to room temperature and quenched by saturated ammonium chloride. The mixture was extracted with ethyl acetate (3×15 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated uner reduced pressure. The resulting residue was purified by flash chromatography (SiO_2) using EtOAc/petroleum ether (v/v =1/5) as eluent to give **4a** (148.7mg, 88%).

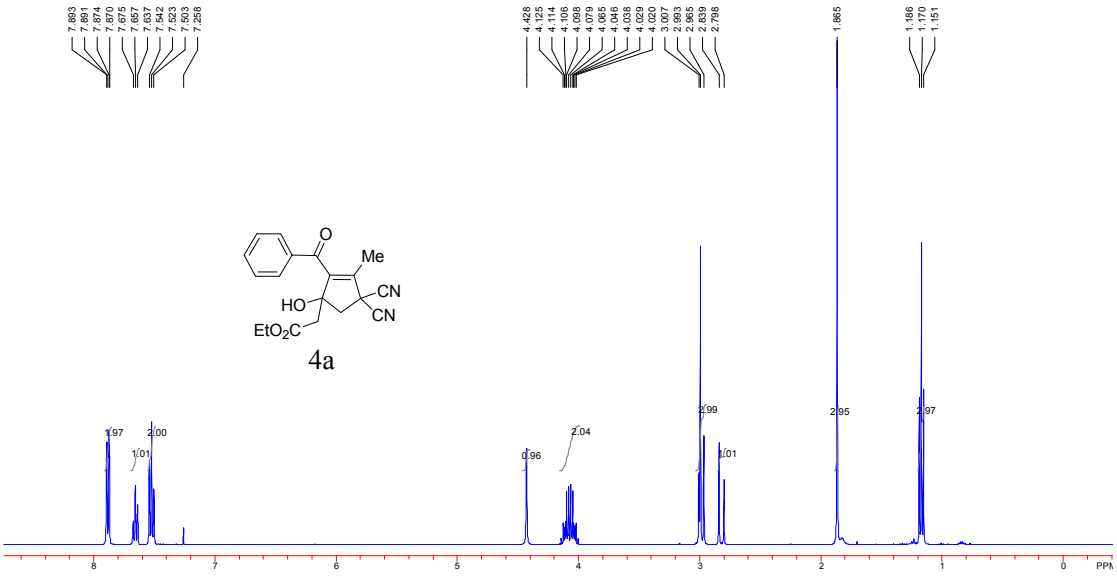
3. Isomerization reaction of 5a toward 4u

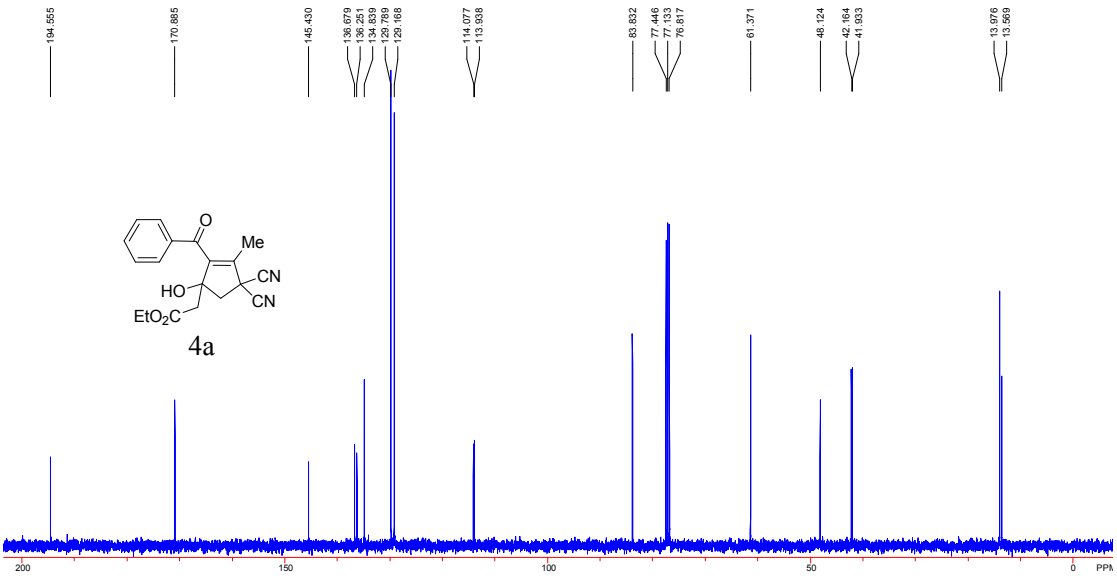
To a flask containing ethyl 1-cyano-4-(2-ethoxy-2-oxoethyl)-4-hydroxy-3-(3-methylbenzoyl)-2-methylene cyclopentanecarboxylate (**5a**, 200.1 mg, 0.5 mmol) in DMSO (5 mL) were added NaOH (24.0 mg, 0.6 mmol). The mixture was stirred at 100 °C for 1.0 h. Upon completion as determined by TLC analysis, it was allowed to cool to room temperature and quenched by saturated ammonium chloride. The mixture was extracted with ethyl acetate (3×15 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated uner reduced pressure. The resulting residue was purified by flash chromatography (SiO_2) using EtOAc/petroleum ether (v/v =1/7) as eluent to give **4u** (30.0 mg, 15%).

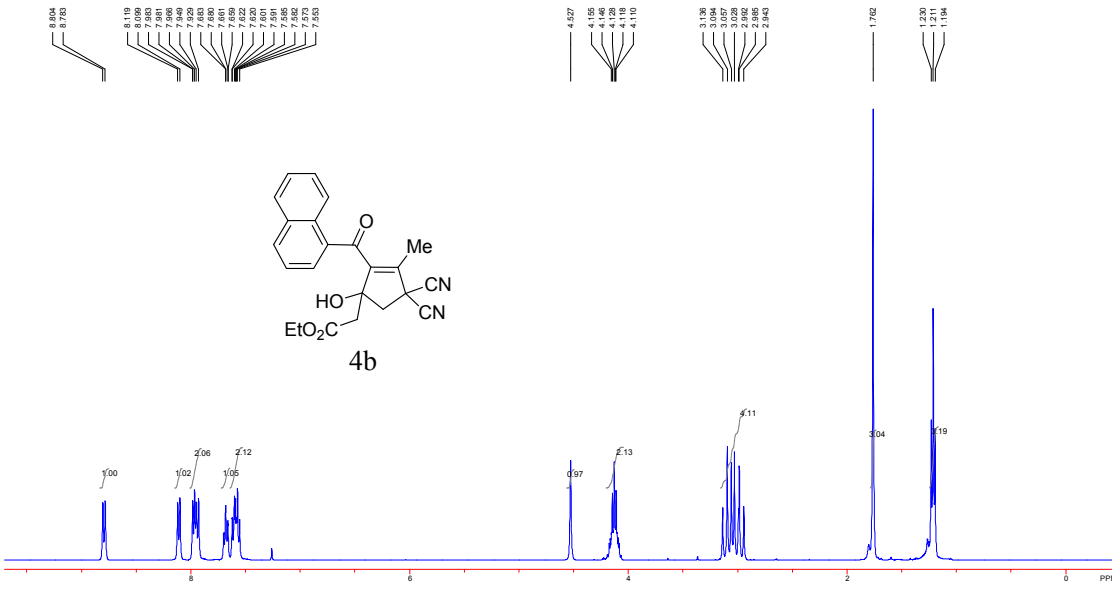
ethyl 1-cyano-4-(2-ethoxy-2-oxoethyl)-4-hydroxy-2-methyl-3-(3-methylbenzoyl)cyclopent-2-ene carboxylate (4u), Eluent: ethyl acetate/petroleum ether (1/7). Yellow oil (30.0 mg, 15%). ^{1}H NMR(400 MHz, $CDCl_3$) δ: 1.17 (t, *J* = 6.4 Hz, 3H), 1.37 (t, *J* = 7.6 Hz, 3H), 2.42 (s, 3H), 2.99-2.72 (m, 4H), 4.11-4.04 (m, 2H), 4.37-4.30 (m, 2H), 4.46 (s, 1H), 7.44-7.36 (m, 2H), 7.79-7.68 (m, 2H). ^{13}CNMR (100 MHz, $CDCl_3$) δ: 13.8, 14.0, 21.3, 30.9, 43.1, 47.5, 55.5, 61.0, 63.7, 84.3, 117.6, 127.4, 128.8, 129.7, 135.2, 136.9,

138.9, 139.5, 143.4, 167.2, 171.4, 195.8. HRMS (ESI): calcd for $C_{22}H_{26}NO_6$ $[M+H]^+$: 400.1760; found: 400.1755.

IV. (1) Copies of ^{1}H and ^{13}C NMR spectra of 4a-4t



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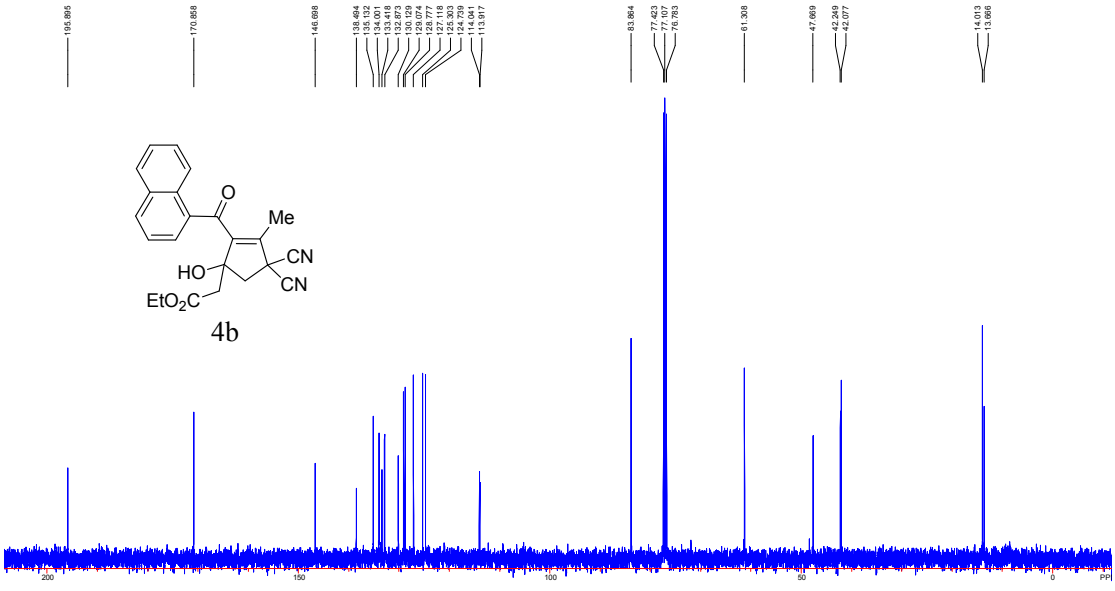
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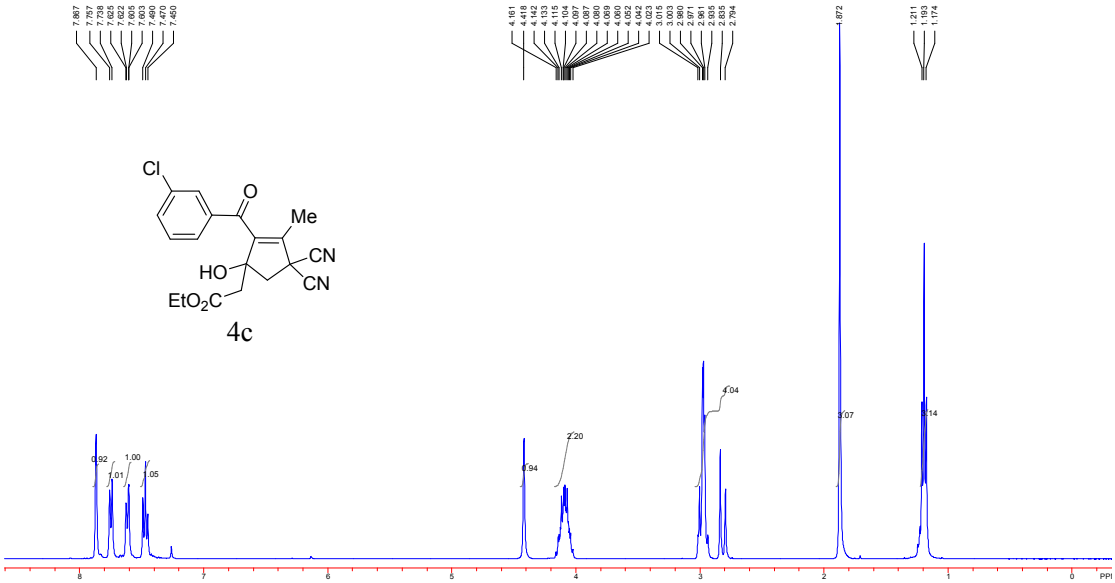
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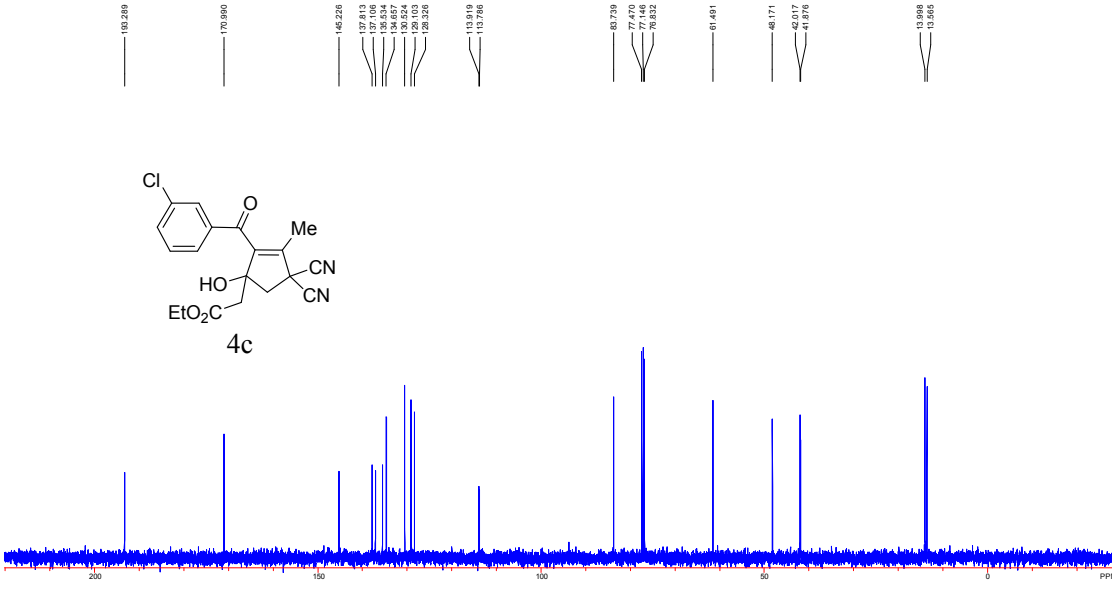
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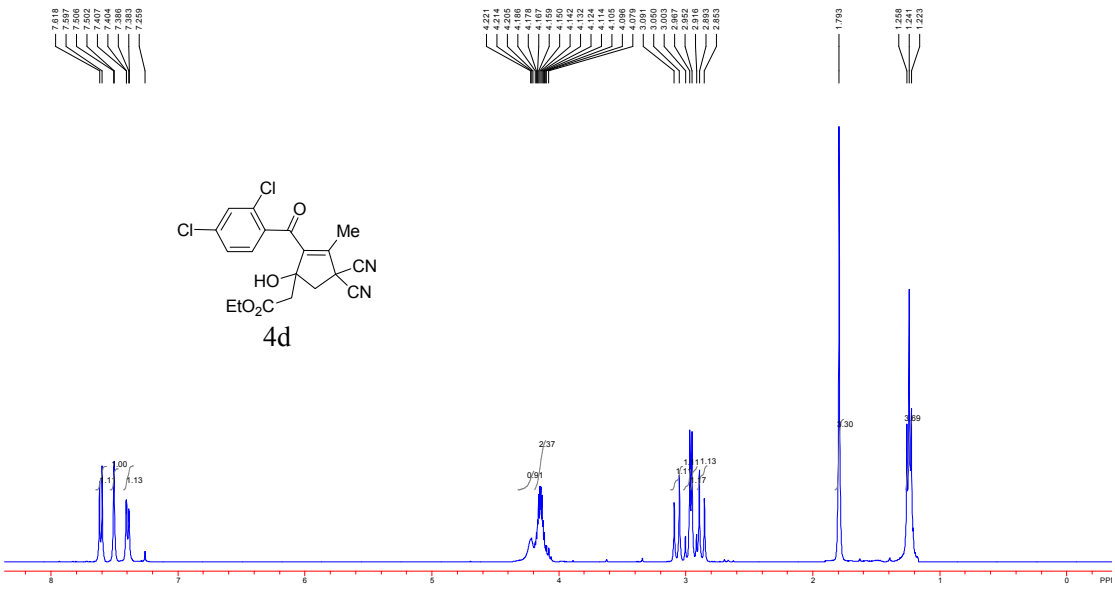
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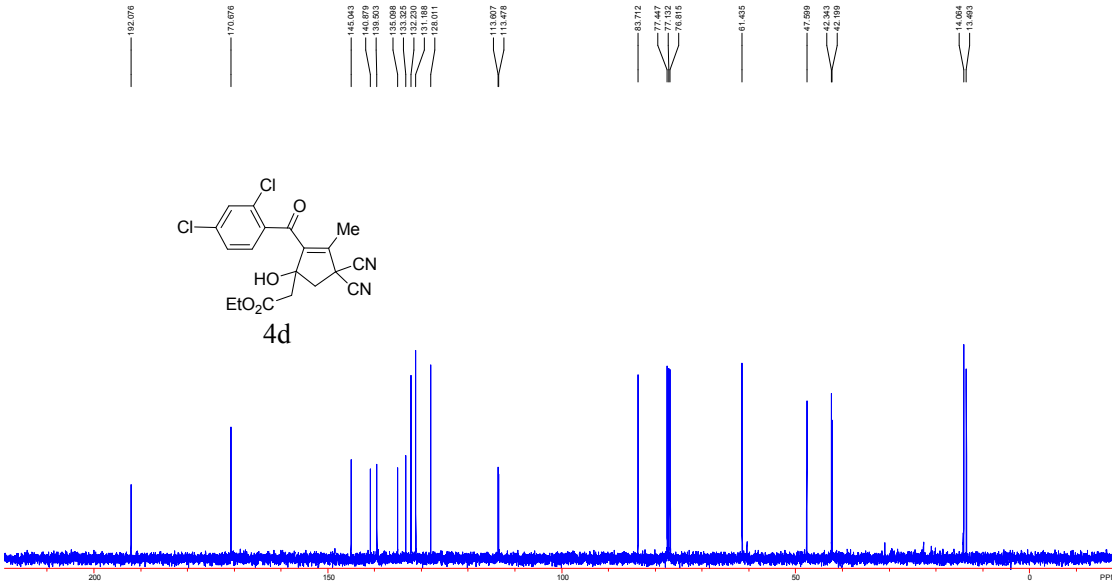
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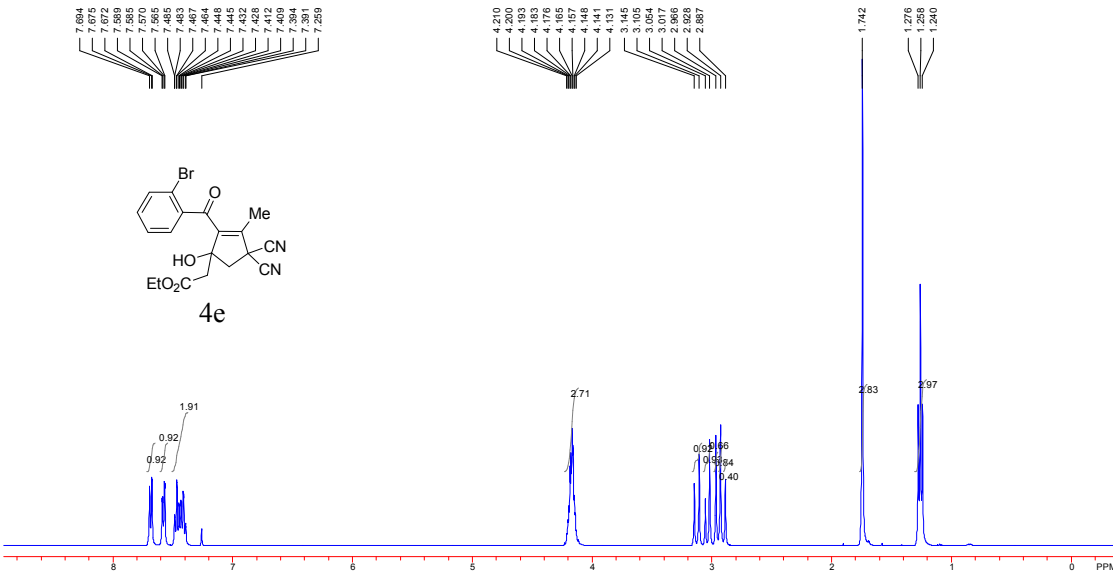
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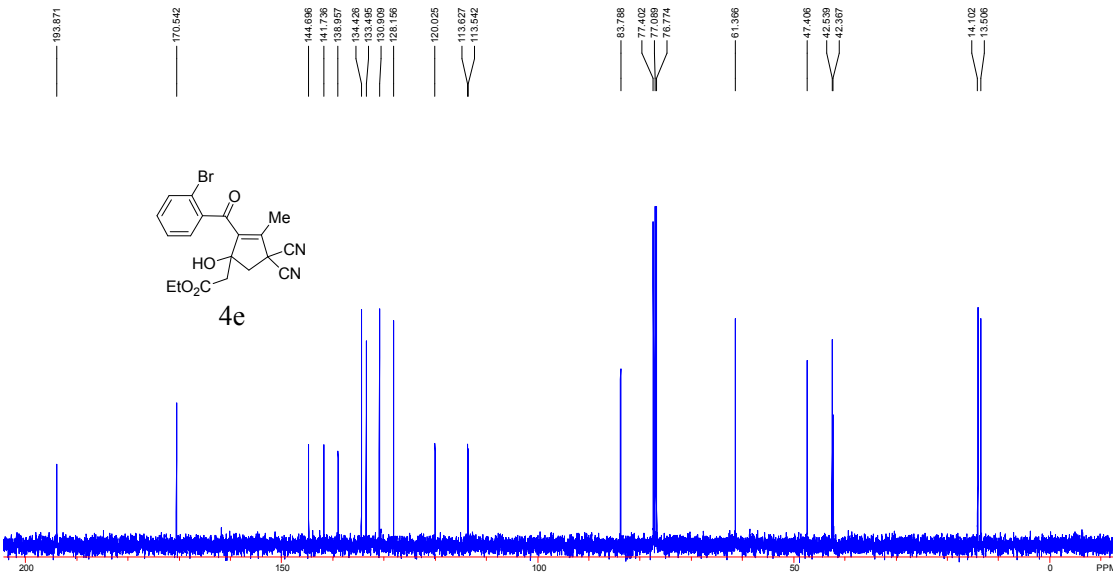
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CN
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EtO2C
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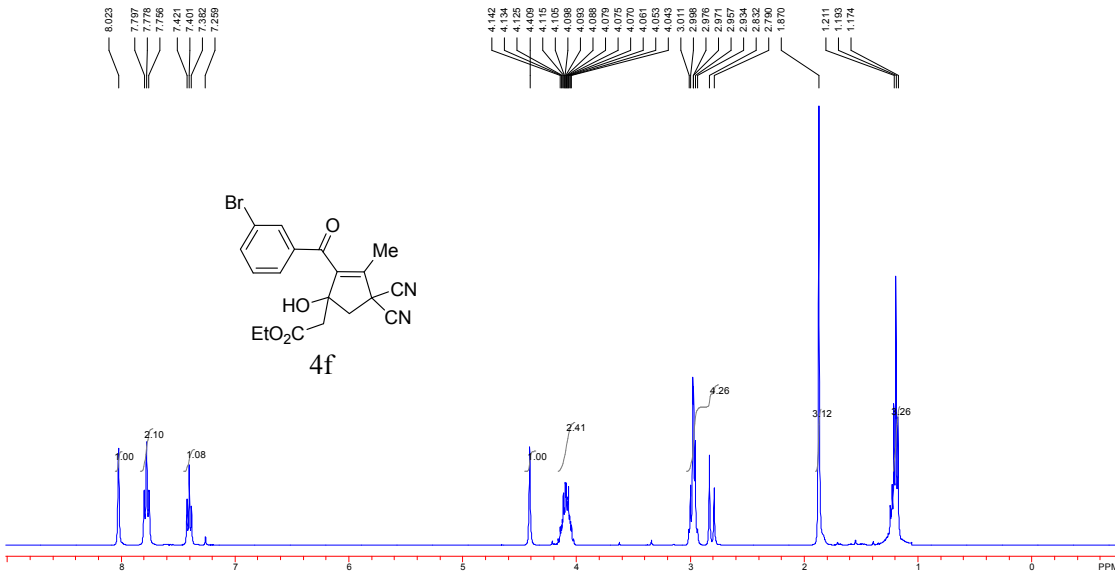
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4.088
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4.075
4.070
4.061
4.053
4.043
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2.976
2.971
2.957
2.934
2.892
2.756
1.870
1.211
1.193
1.174
Br
O
Me
CN
CN
HO
EtO2C
4f
1.00
2.10
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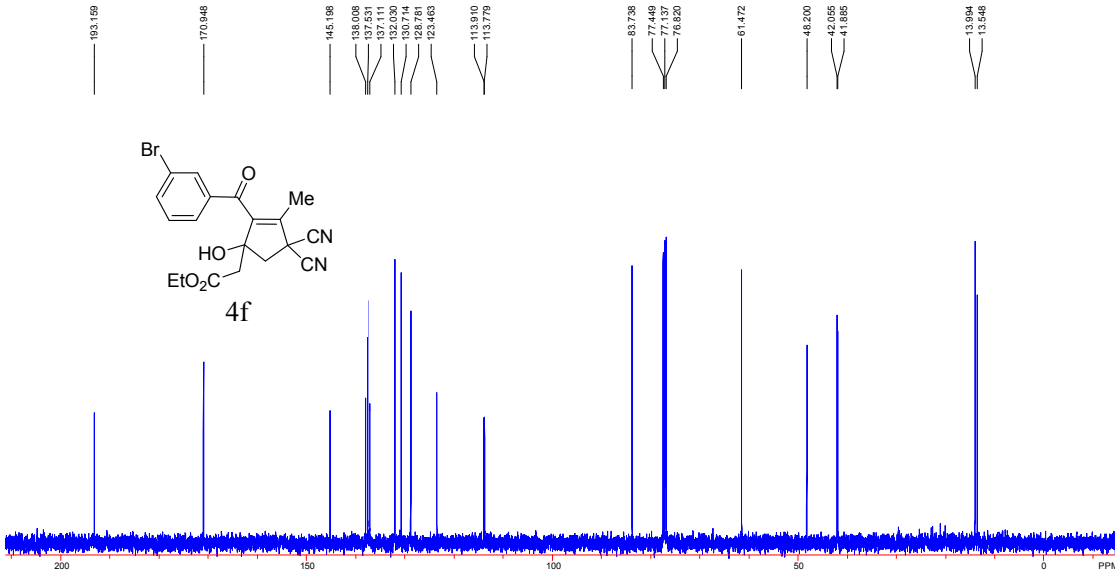
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77.137
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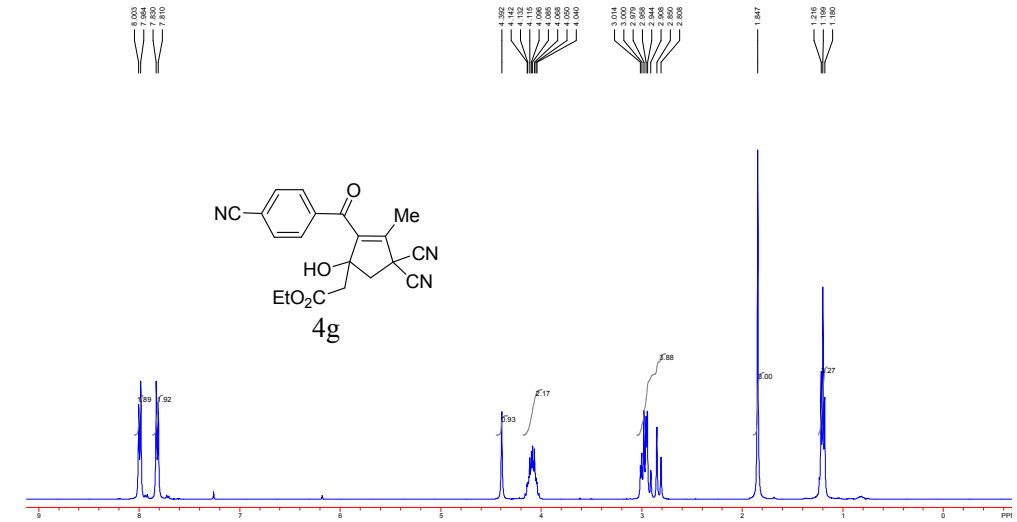

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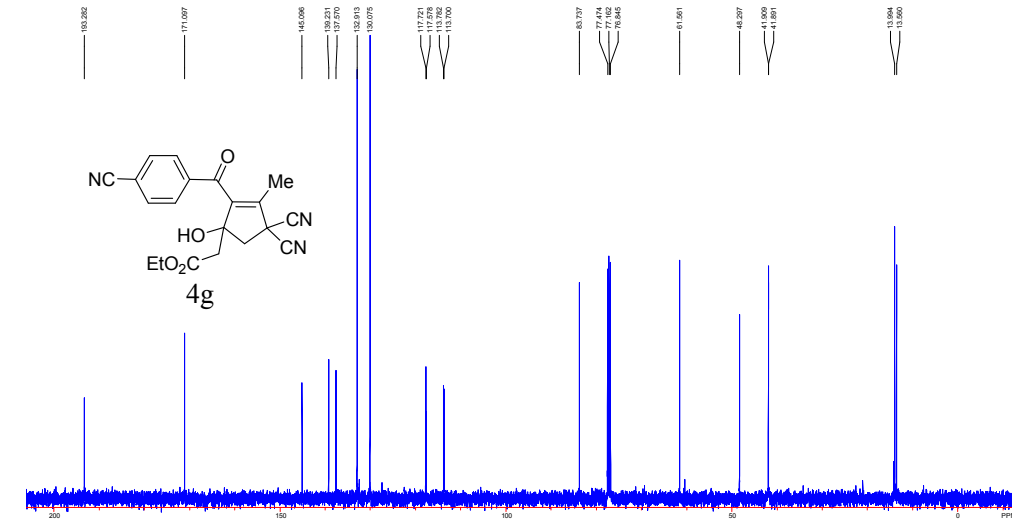

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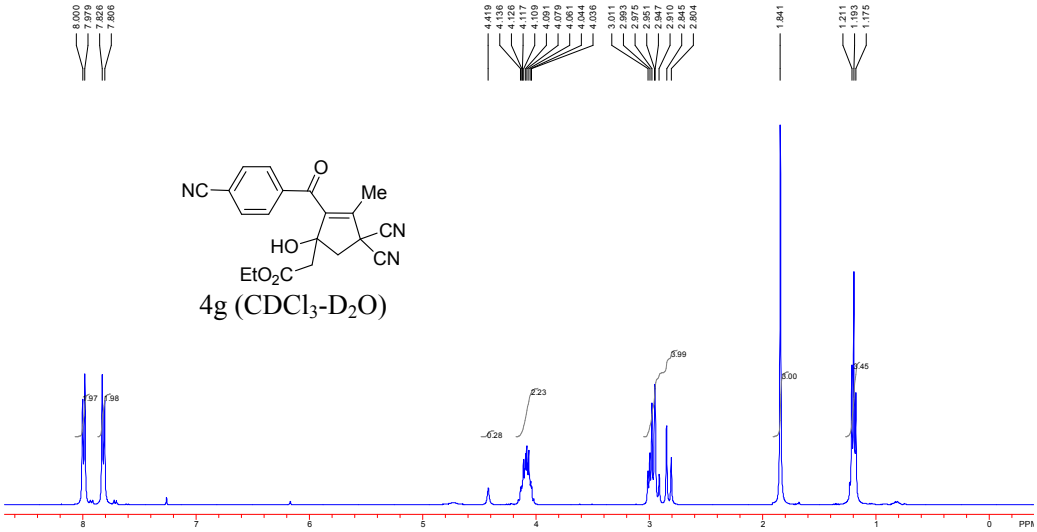
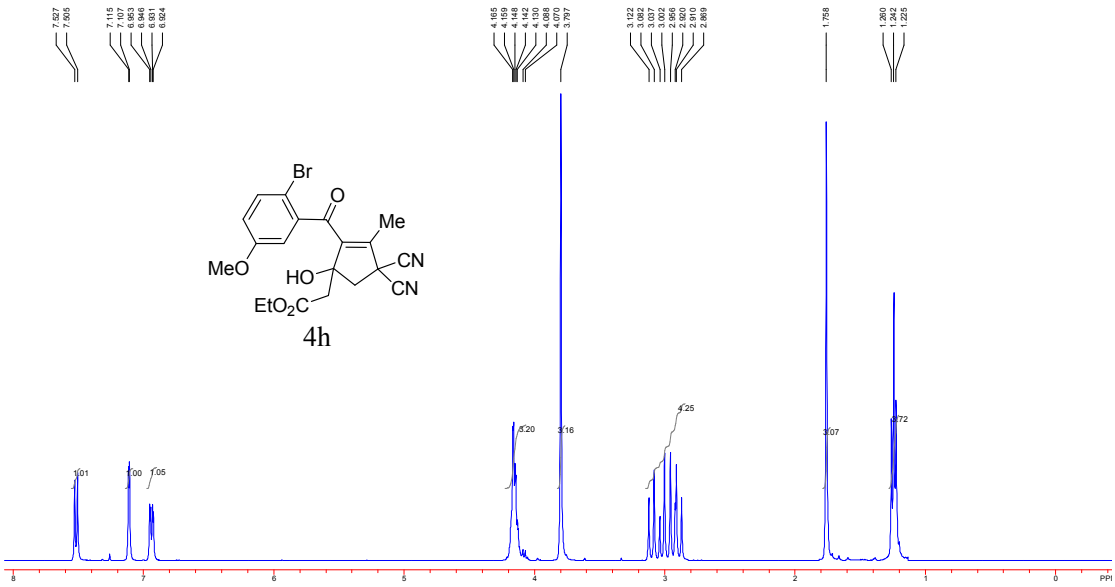


4g ($CDCl_3$-D_2O)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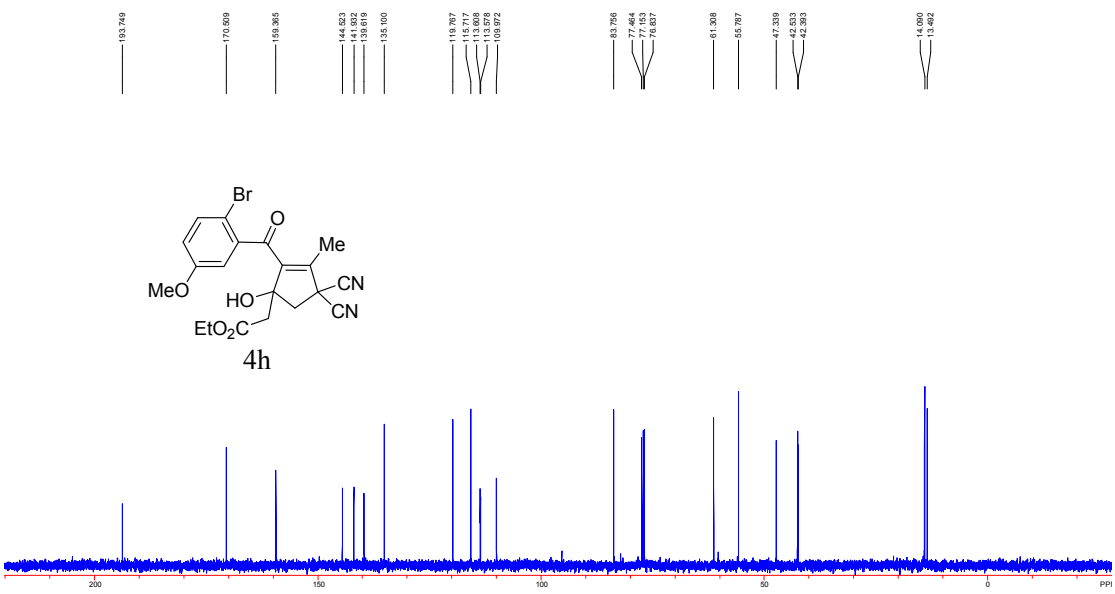
Me
MeO
HO
CN
CN
EtO2C
4h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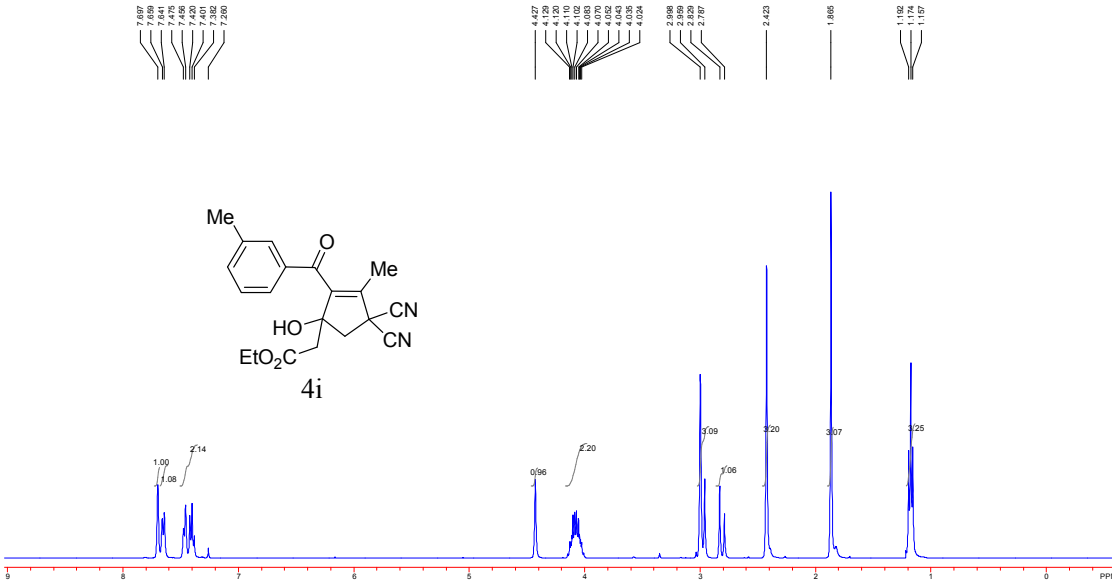
4h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4.043
4.035
4.024
2.998
2.959
2.829
2.787
2.423
1.865
1.192
1.174
1.157
Me
O
Me
CN
HO
CN
EtO2C
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2.20
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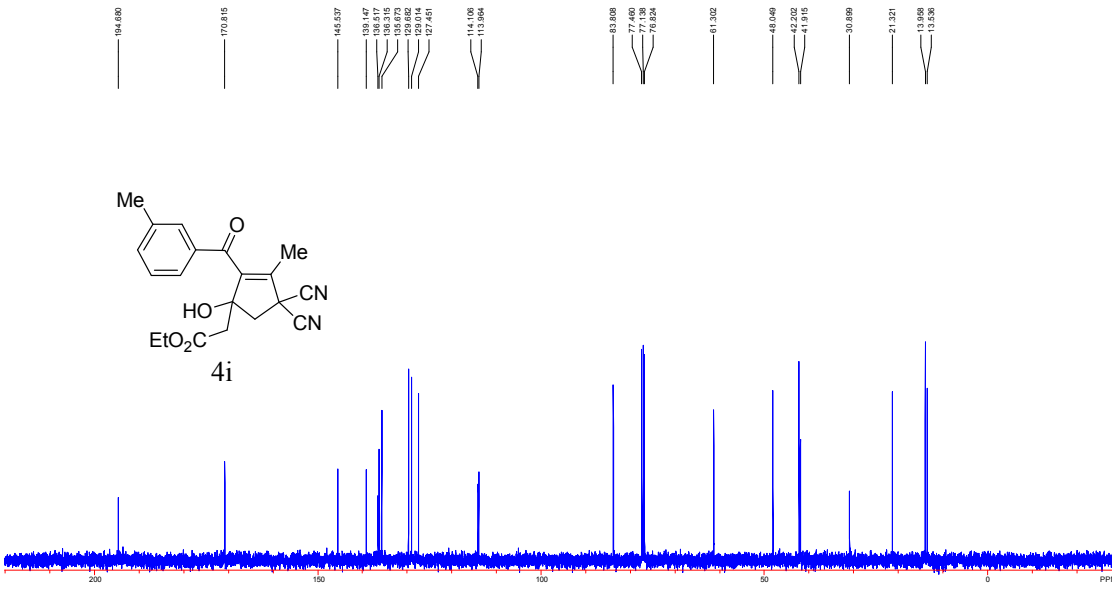
PPI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77.236
76.834
61.302
48.049
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CN
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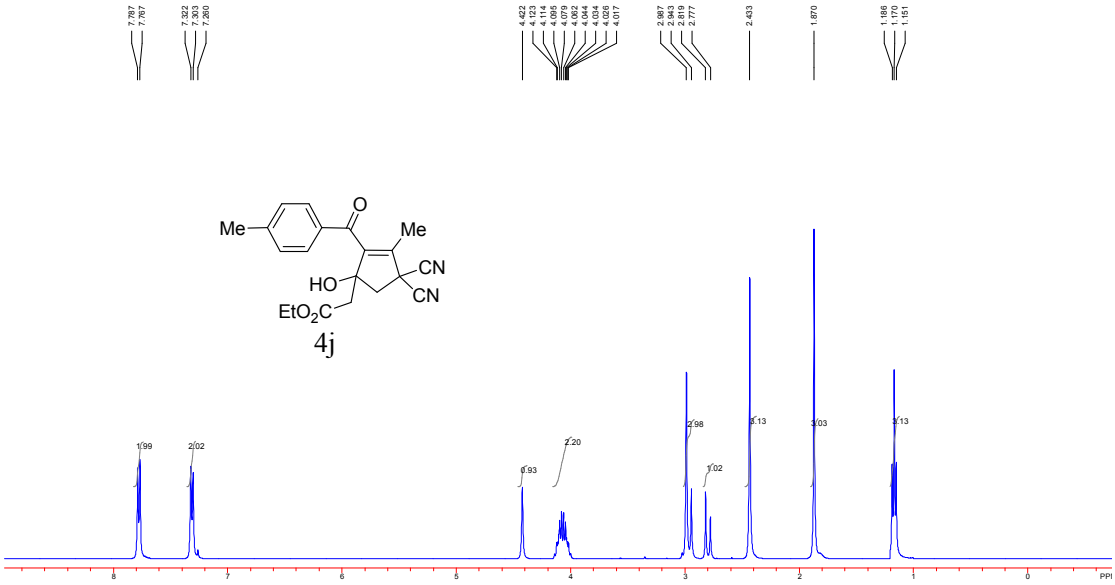
CN
EtO2C
4i
PPI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4.026
4.017
2.987
2.843
2.819
2.777
2.433
1.870
1.166
1.070
1.151
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O
Me
CN
HO
CN
EtO2C
4j
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0.93
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3.13
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3.13
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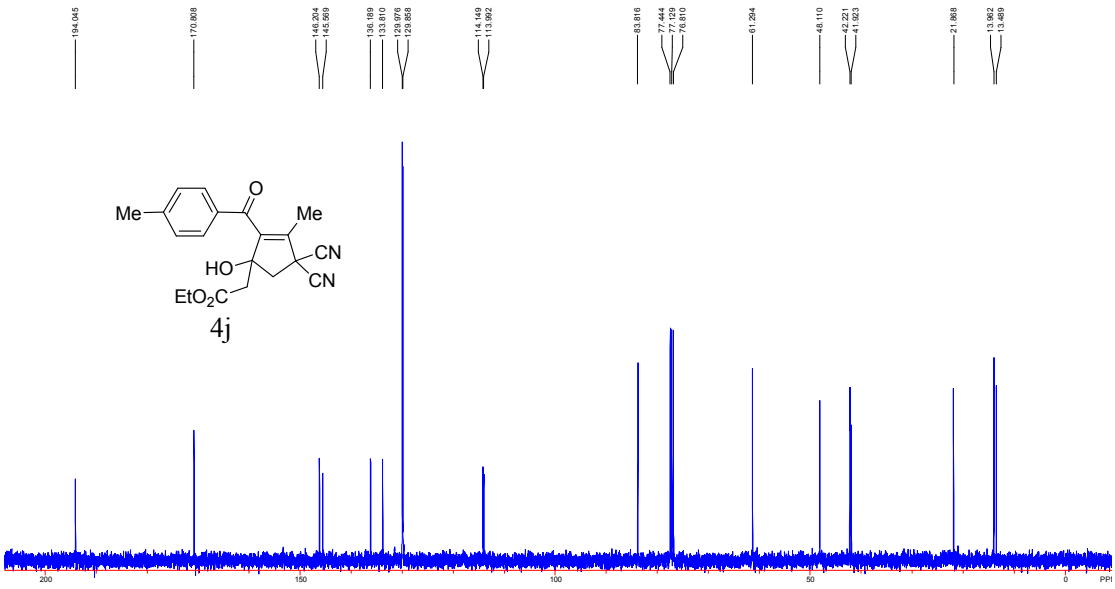
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76.810
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48.110
42.221
41.923
21.868
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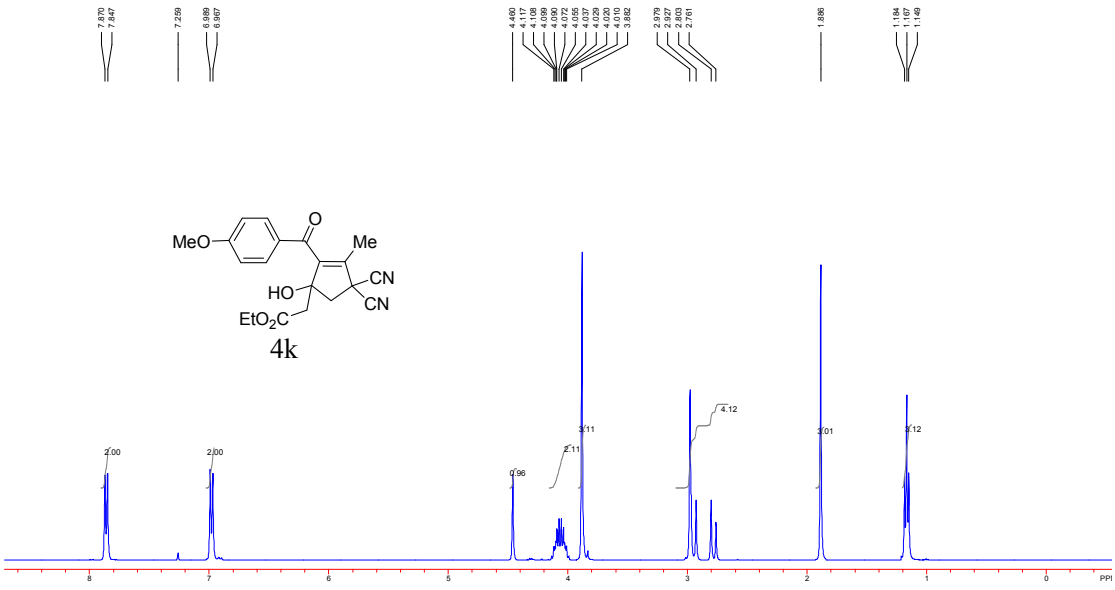
CN
HO
CN
EtO2C
4j
200
150
100
50
0
PPI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CN
CN
HO
EtO2C
4k
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2.00
0.96
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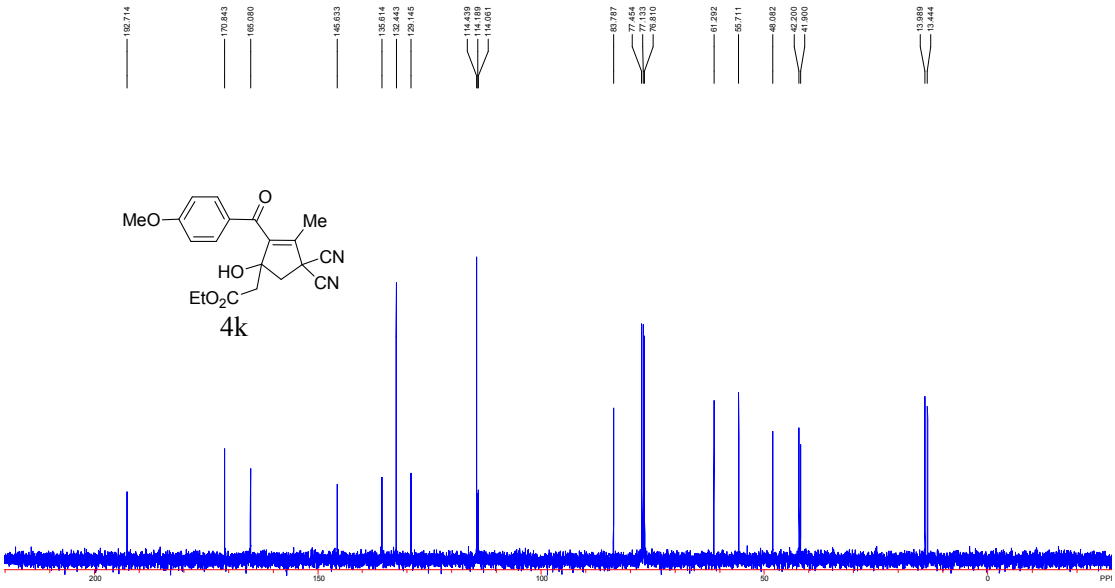
3.11
4.12
3.01
3.12
PPI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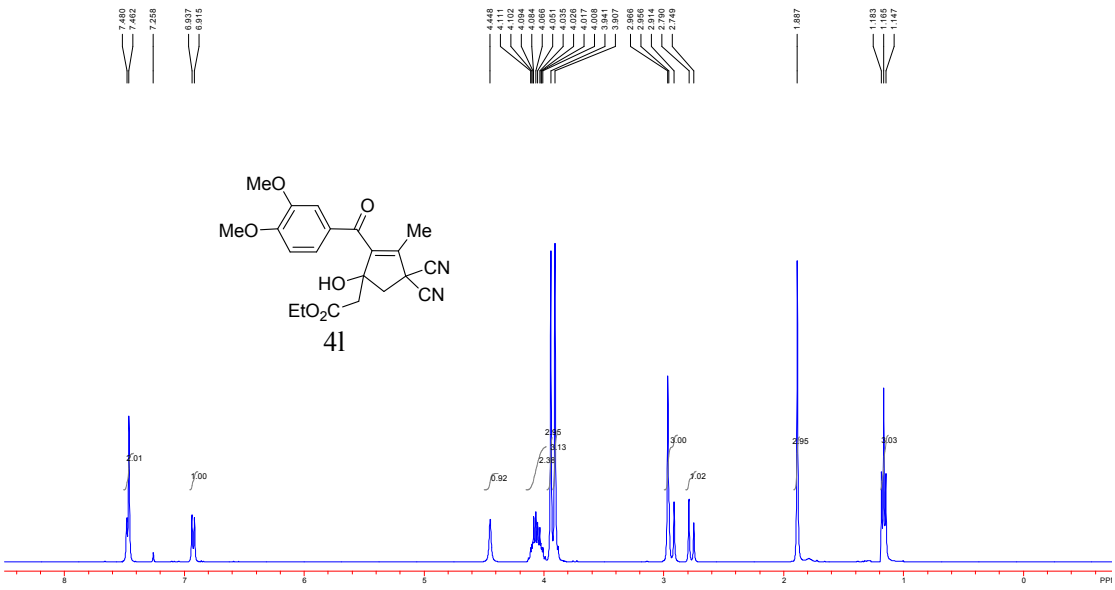
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4.102
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4.035
4.026
4.017
4.008
3.941
3.907
2.966
2.946
2.914
2.790
2.749
1.887
1.183
1.165
1.147
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MeO
O
Me
CN
CN
HO
EtO2C
41
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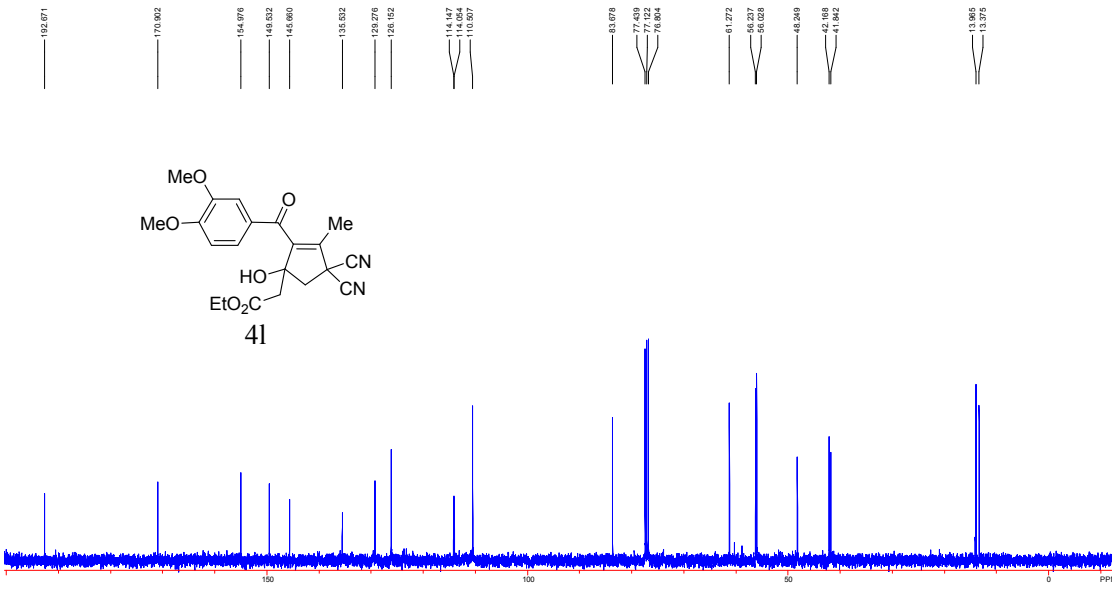
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77.439
77.122
76.804
61.272
56.237
56.028
48.249
42.168
41.842
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MeO
MeO
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Me
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CN
HO
EtO2C
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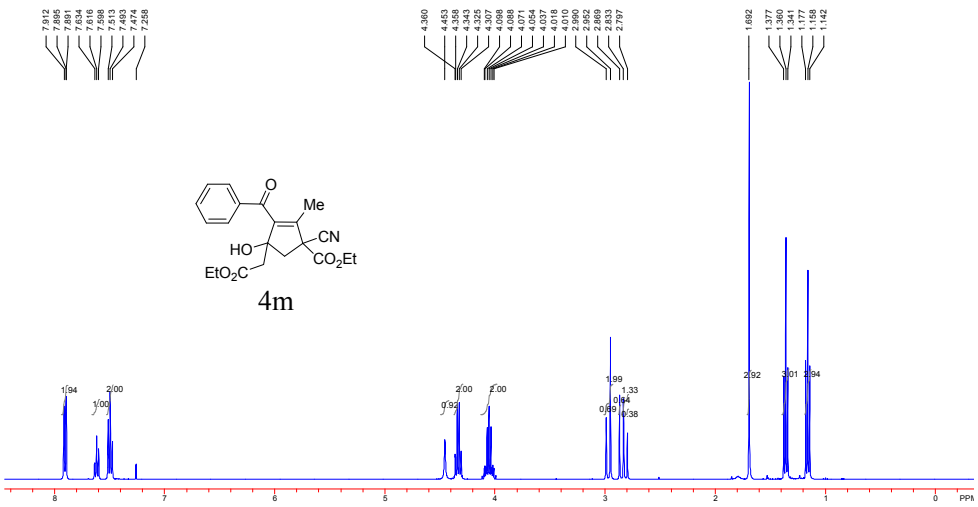
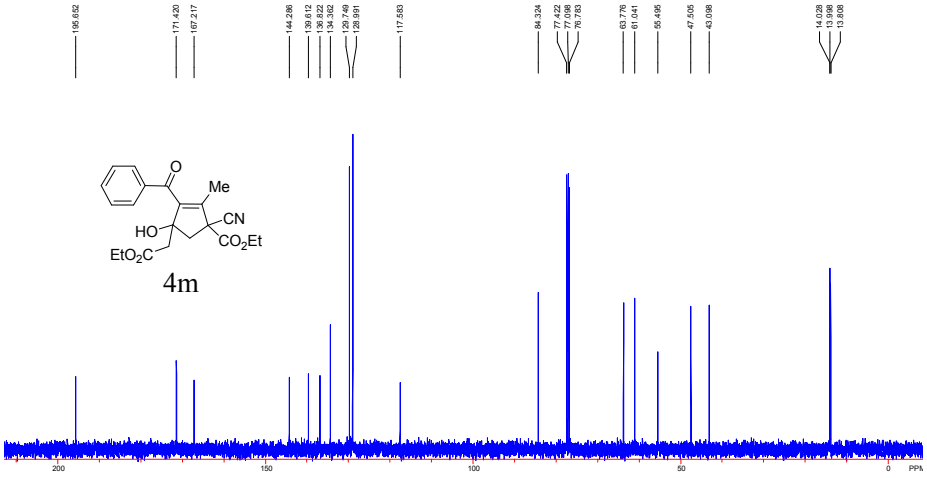
150
100
50
0
PPI



4m



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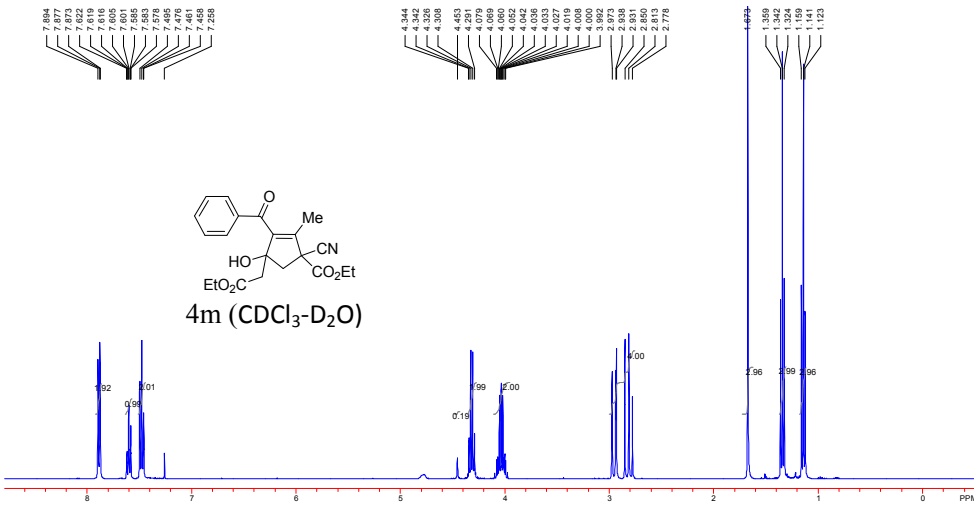
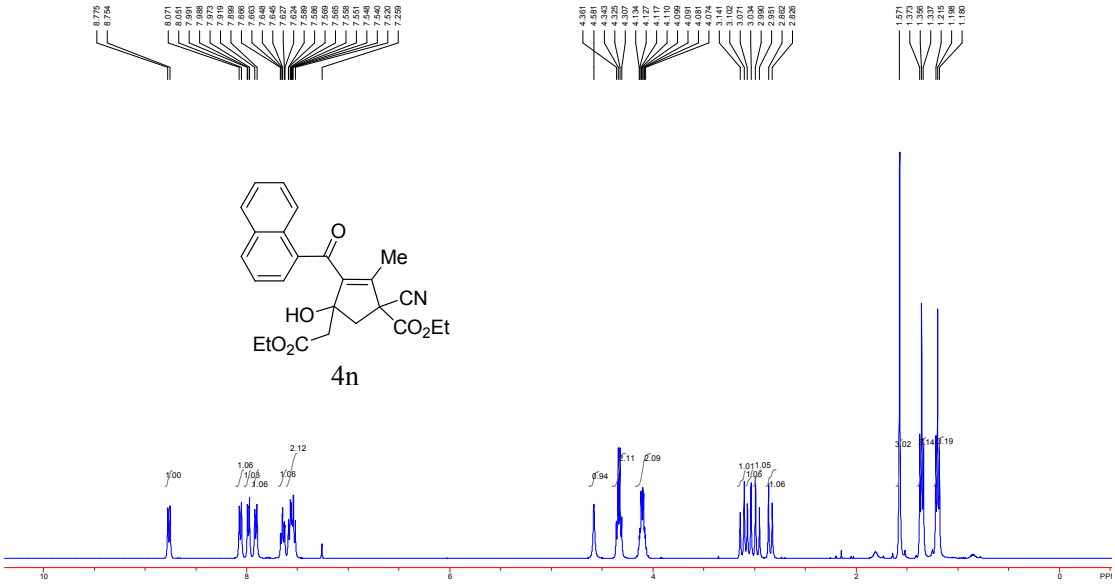
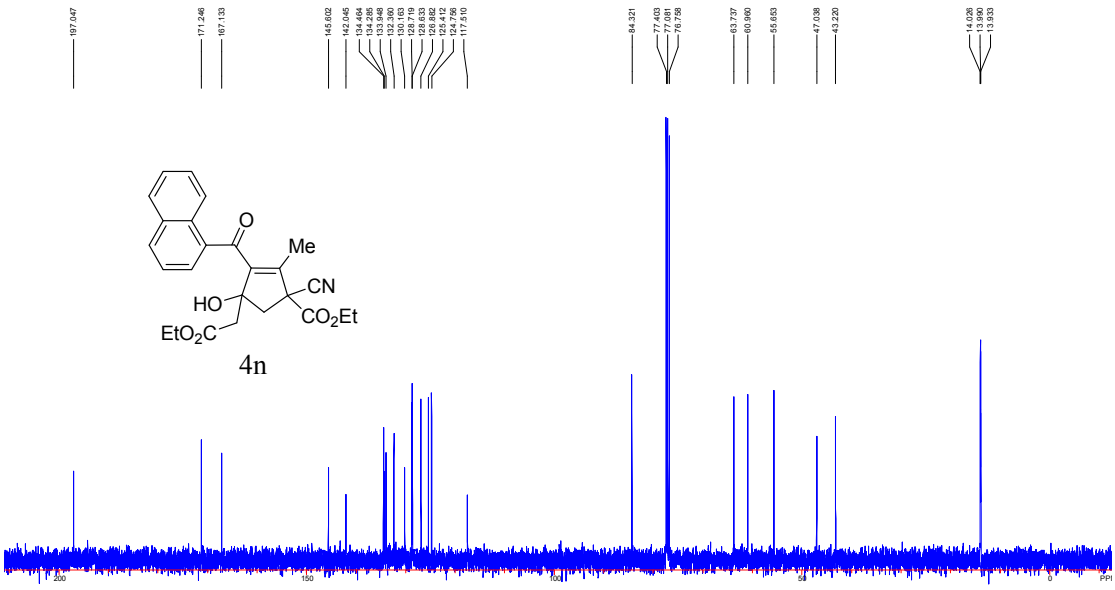


4m ($CDCl_3$-D_2O)


Me
CN
HO
CO2Et
EtO2C
4n


Me
CN
HO
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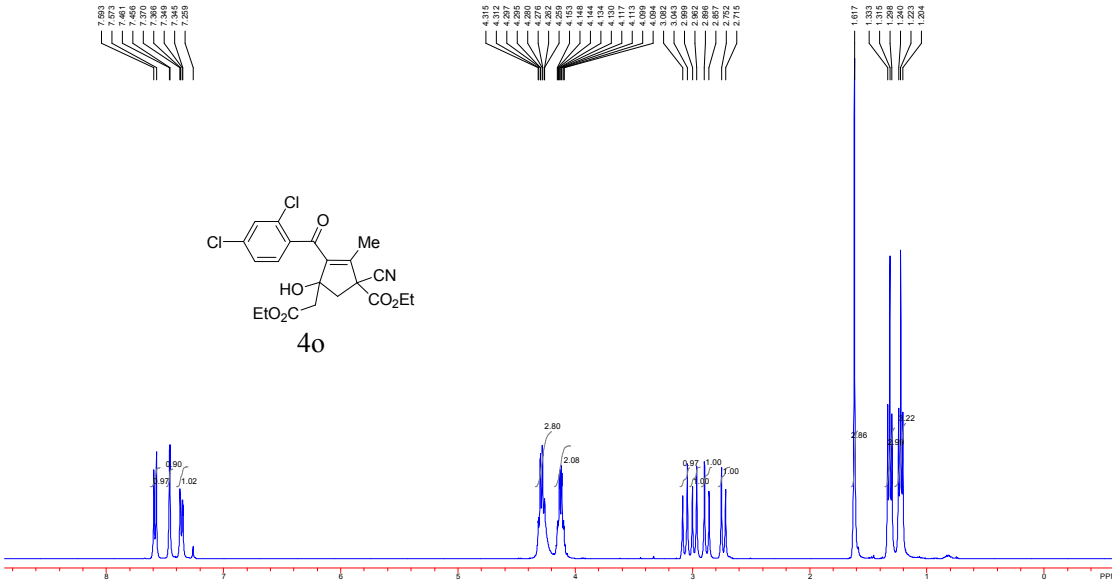
4n



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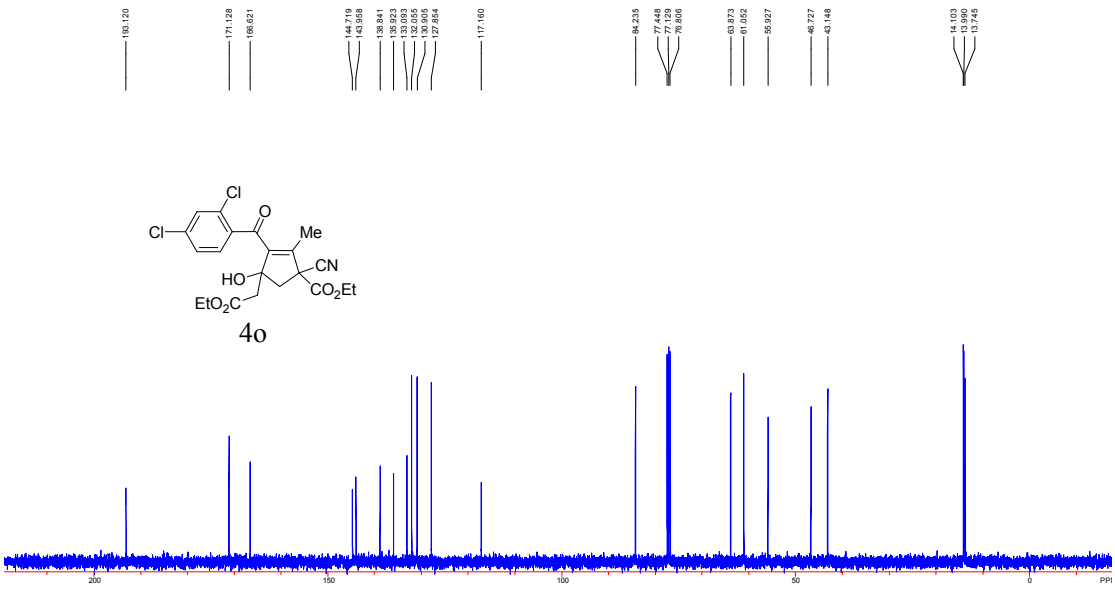

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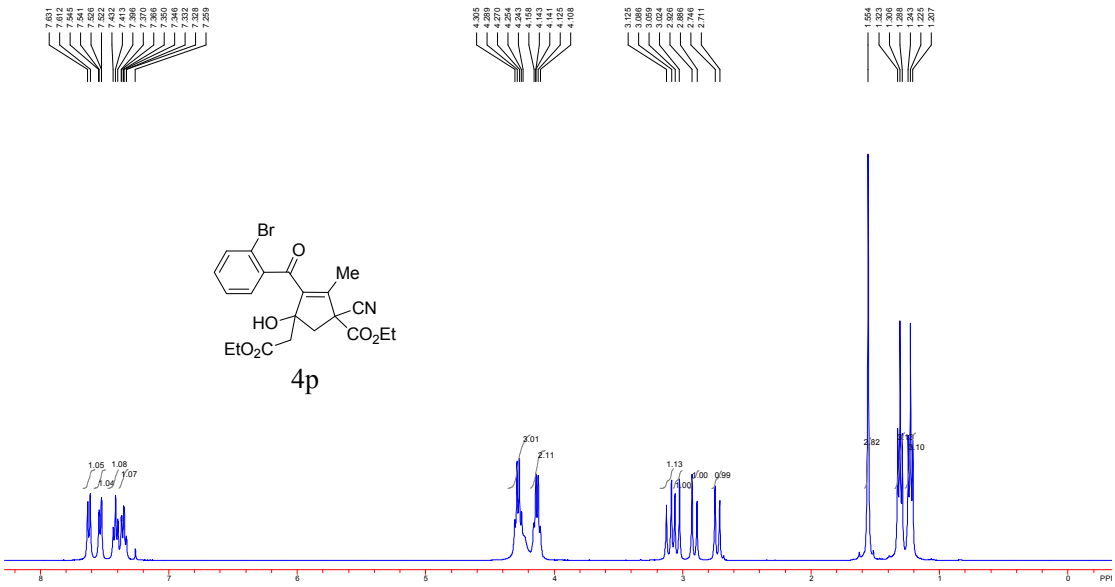
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Br
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Me
CN
HO
CO2Et
EtO2C
4p
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1.08
1.07
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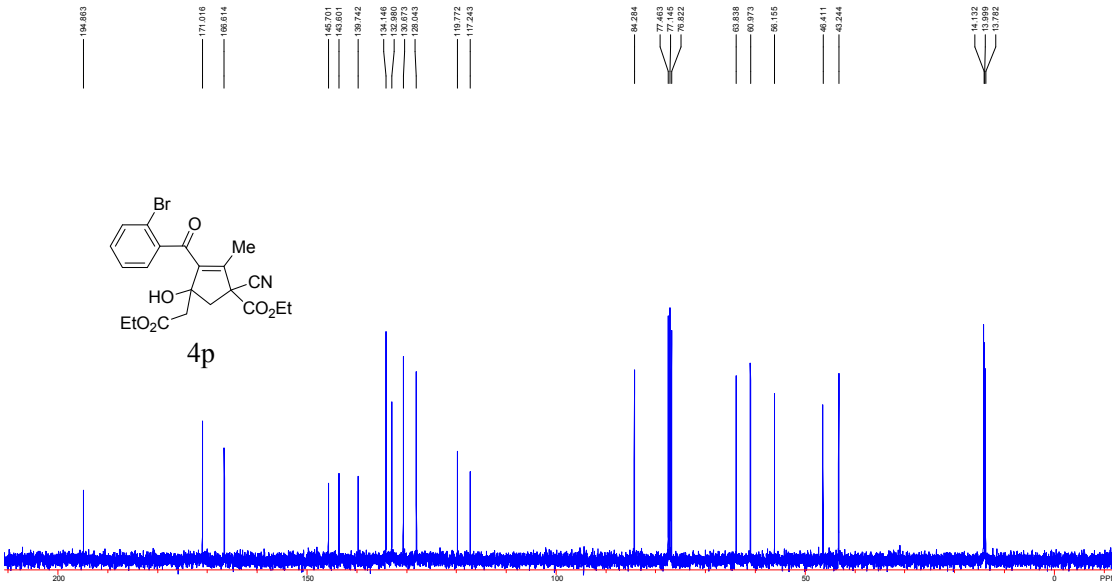
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77.463
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63.838
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56.155
46.411
43.244
14.132
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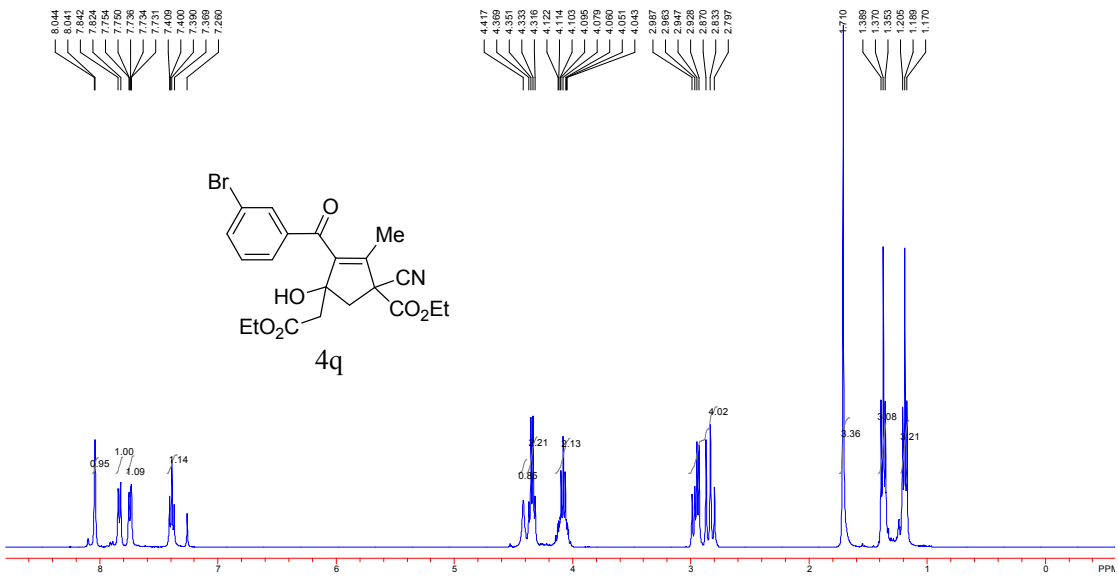
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4.114
4.103
4.095
4.079
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2.928
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CO2Et
EtO2C
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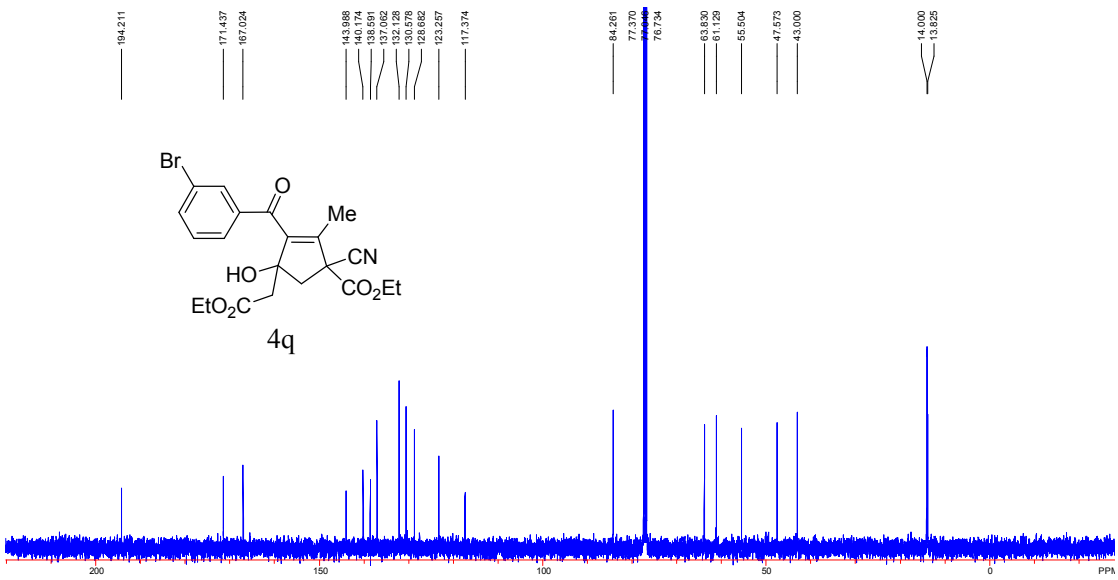
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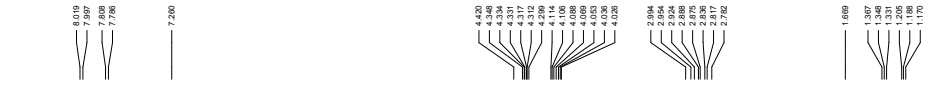

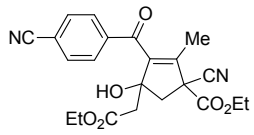

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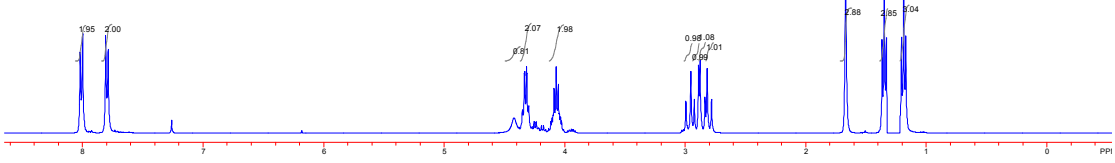

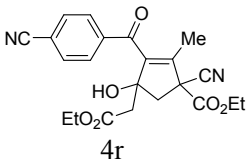

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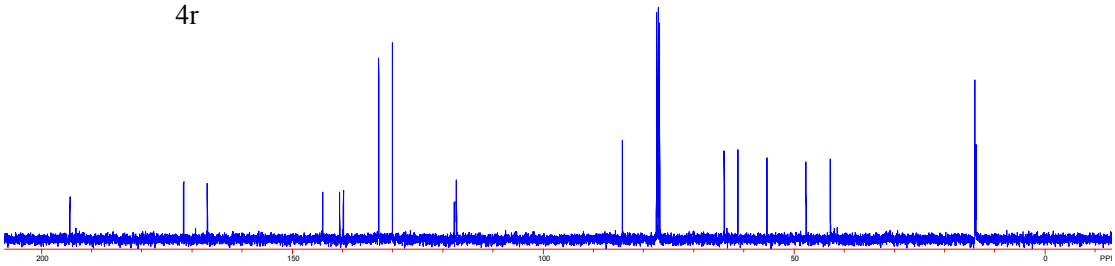

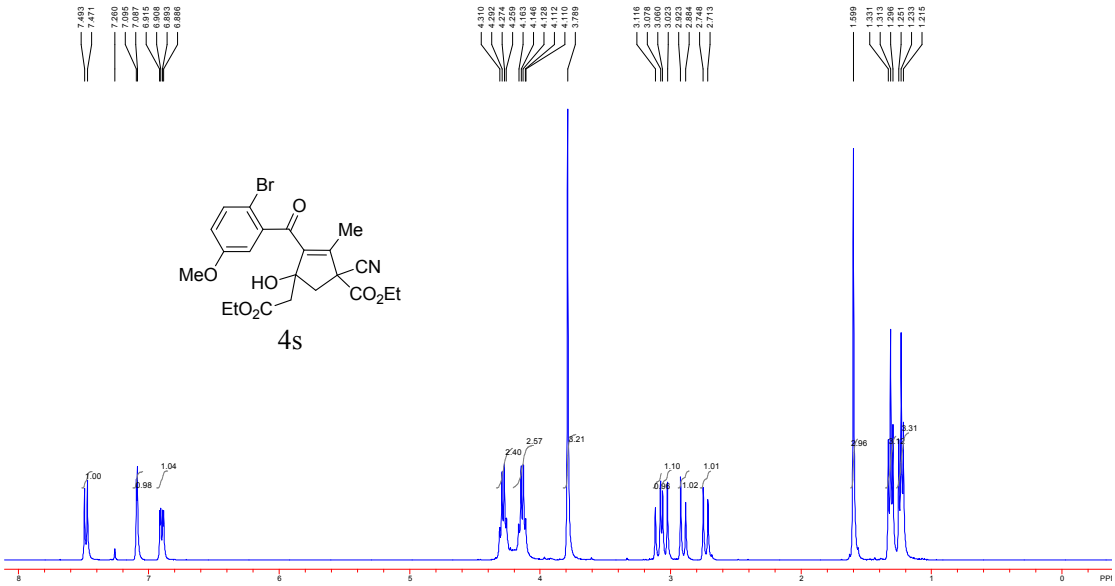

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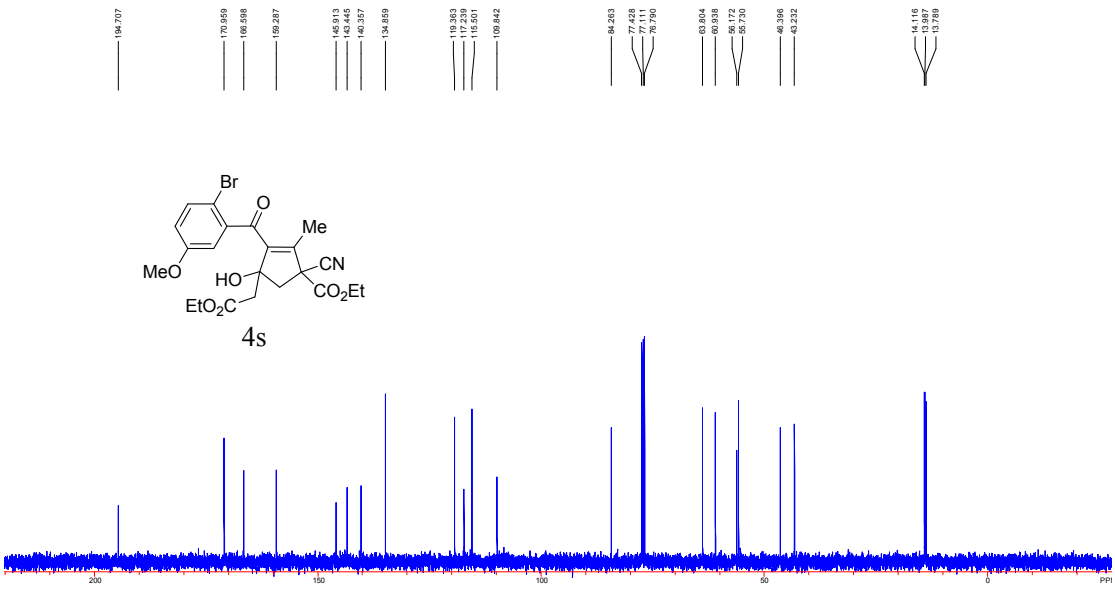
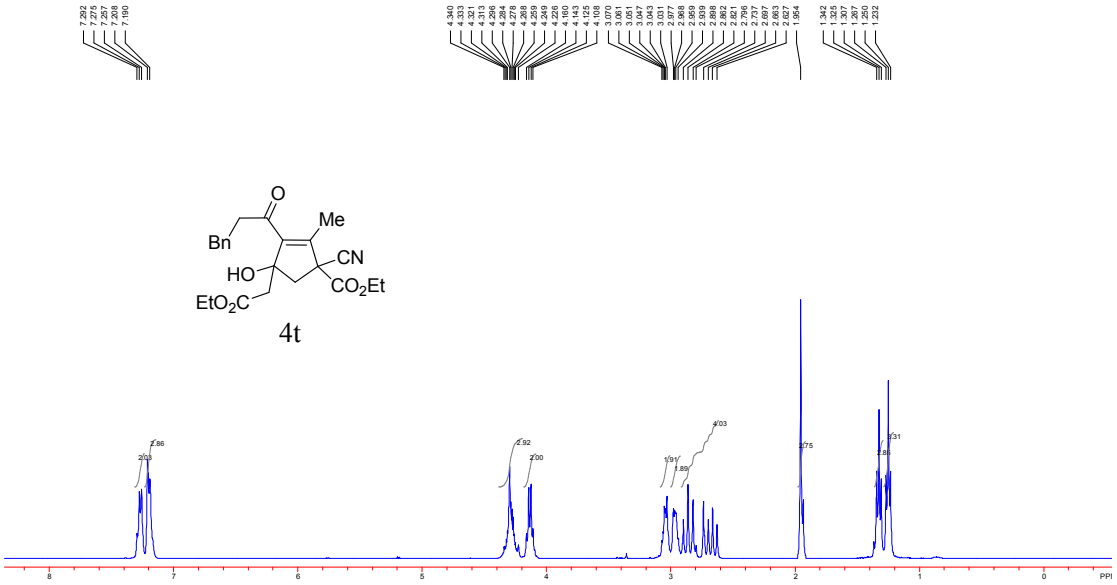
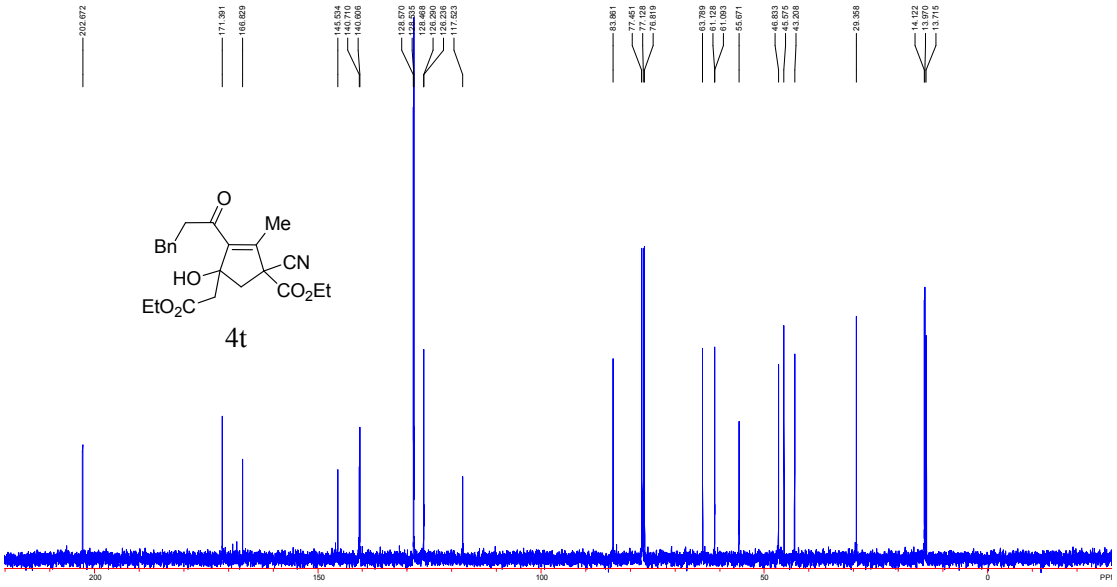


4s

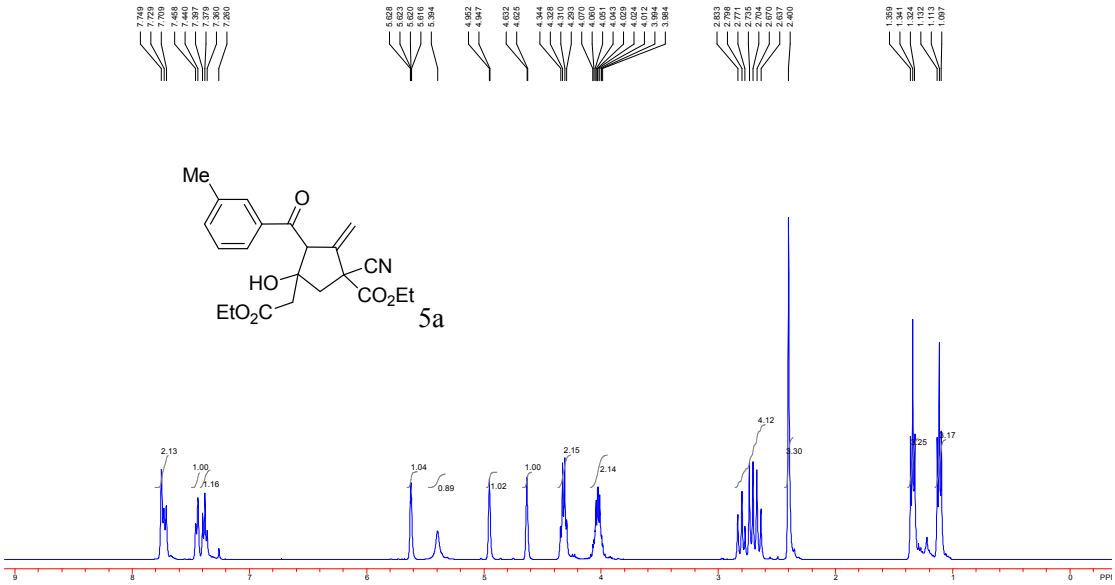


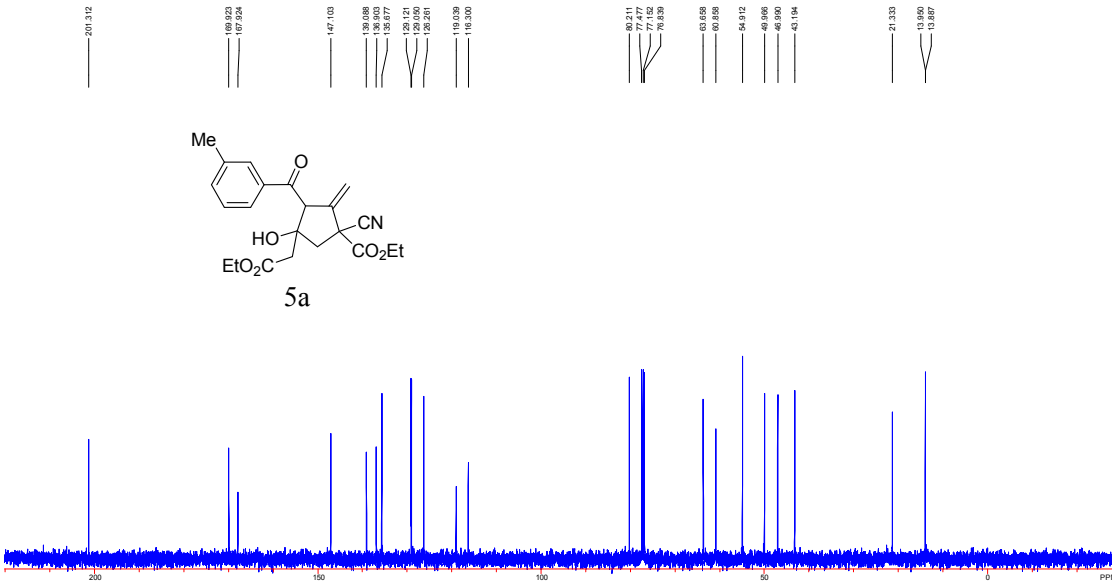
4t

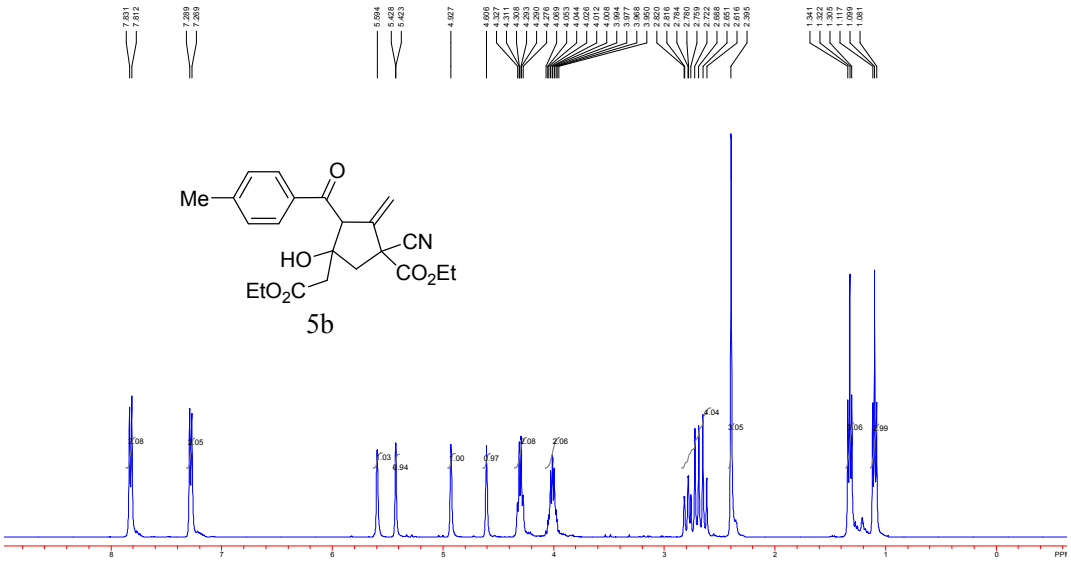


4t

(2) Copies of ^{1}H and ^{13}C NMR spectra of 5a-5e







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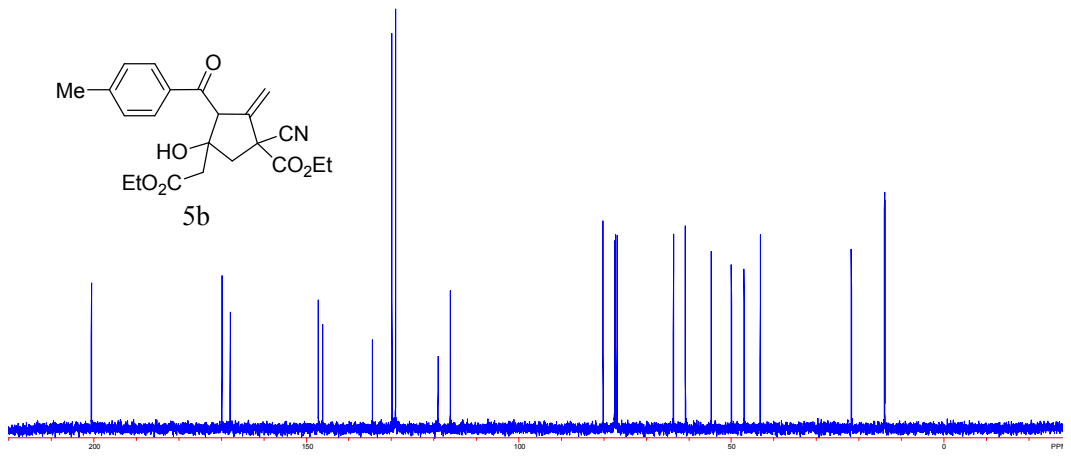

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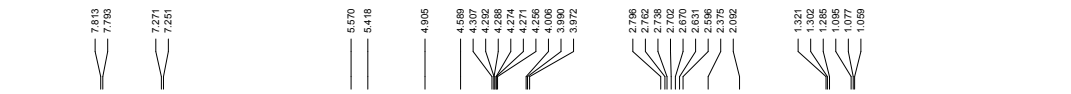
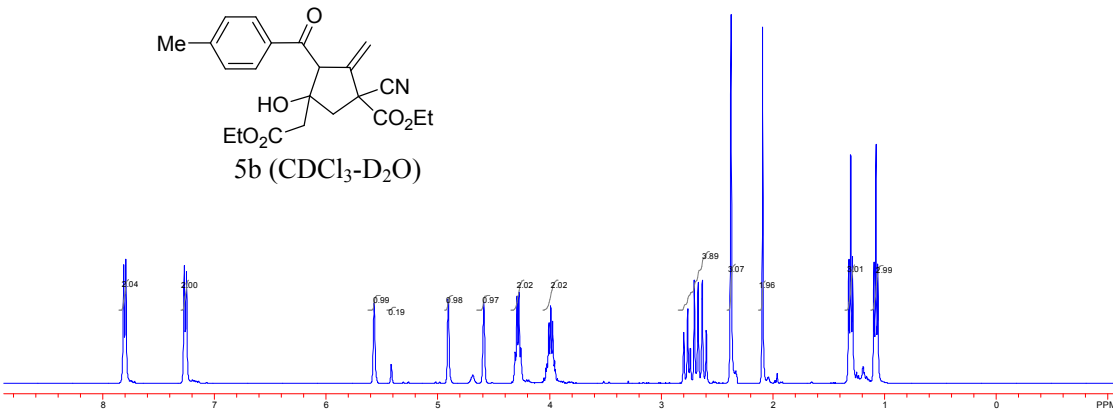
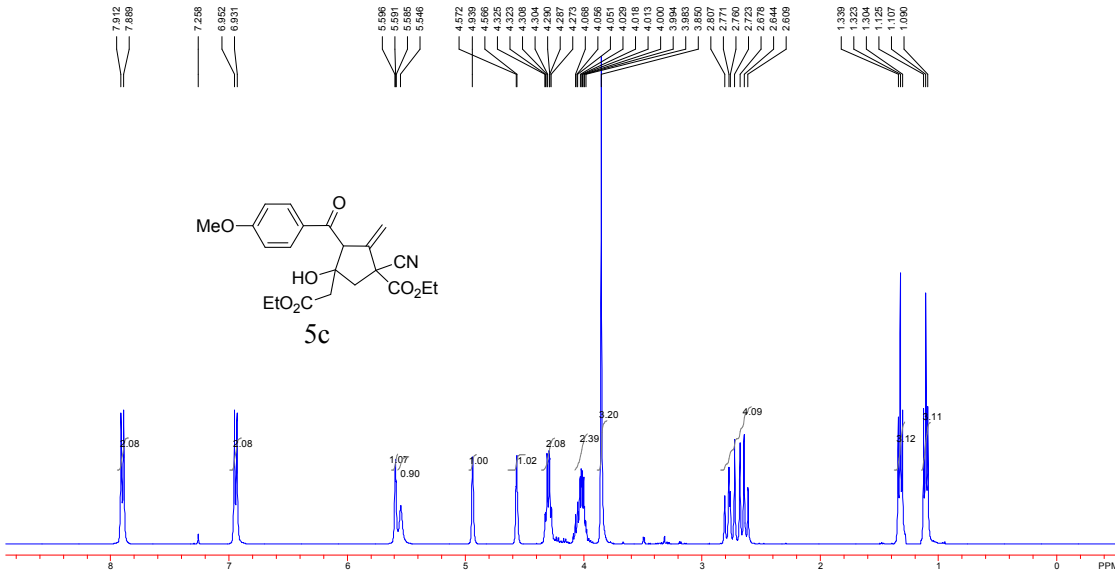




5b ($CDCl_3$-D_2O)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4.051
4.029
4.018
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4.000
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2.644
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HO
CN
CO2Et
EtO2C
5c
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2.08
1.07
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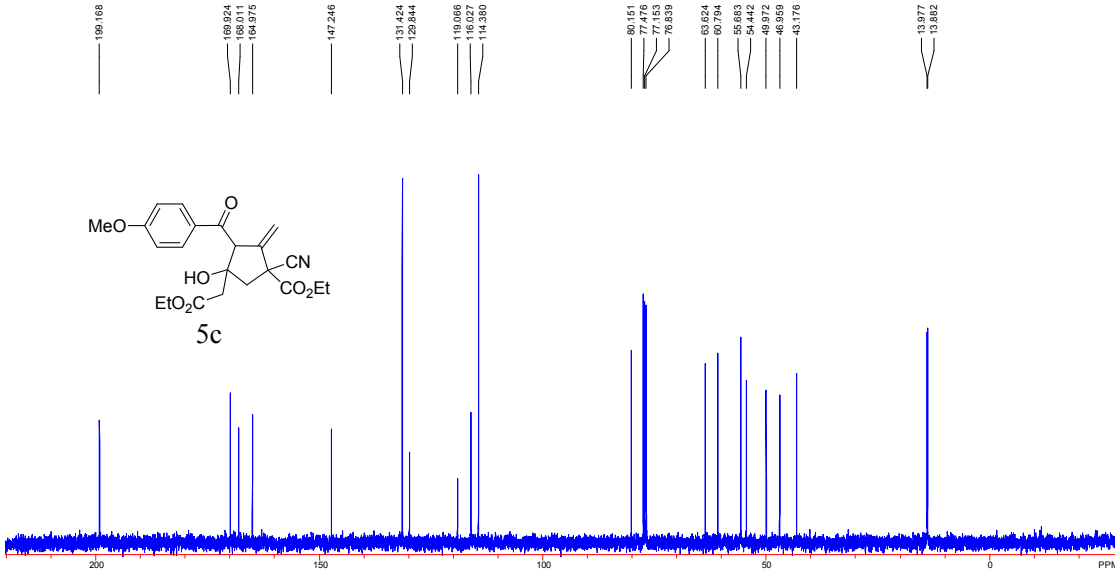
PPM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76.839
63.624
60.794
55.683
54.442
49.972
46.959
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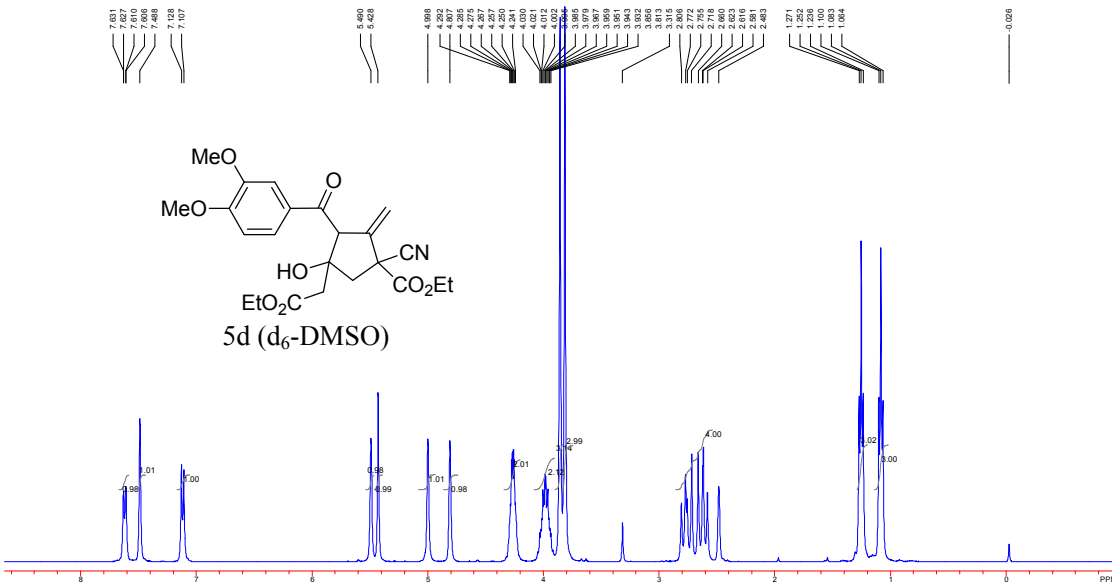
O
HO
CN
CO2Et
EtO2C
5c
200
150
100
50
0
PPM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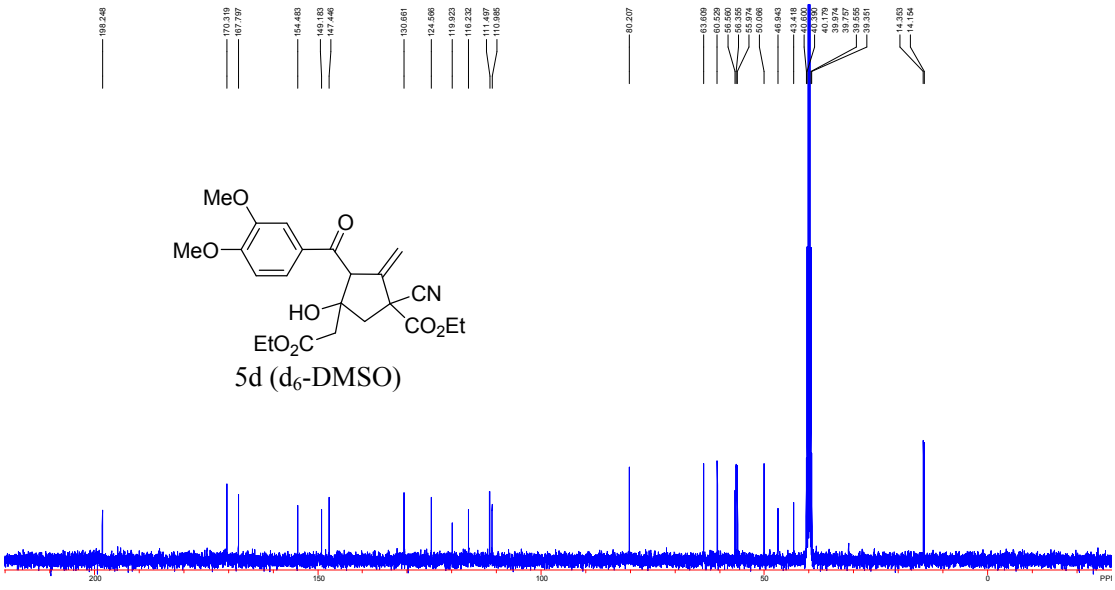
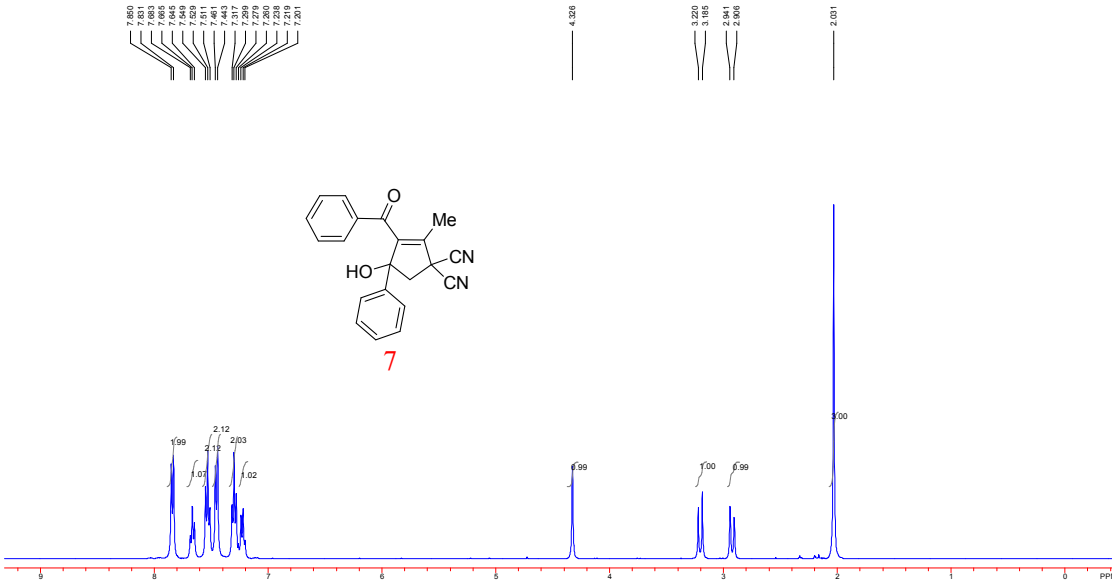
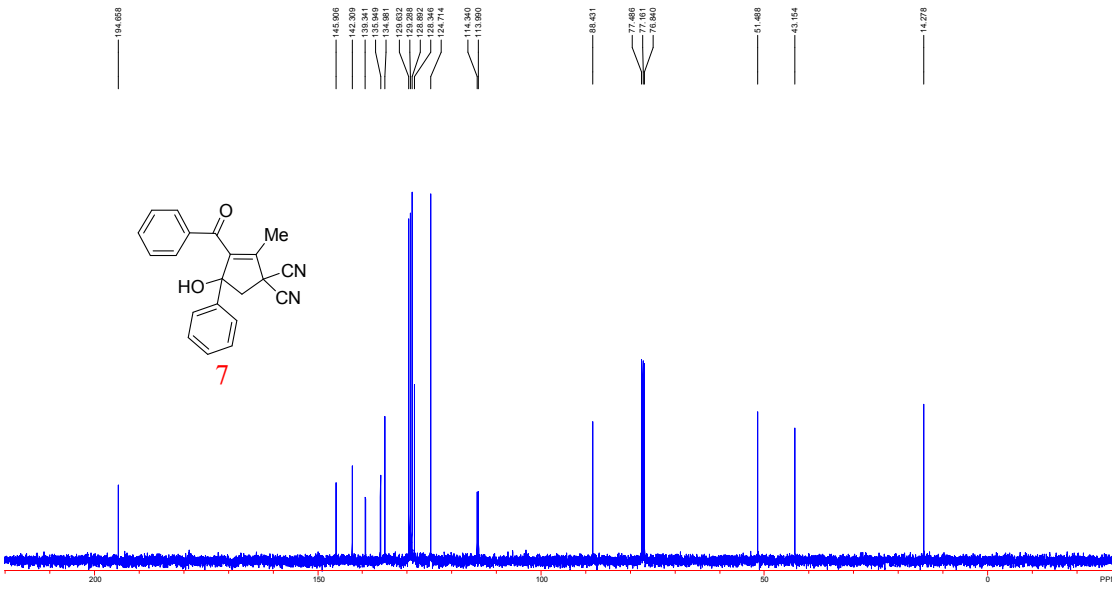
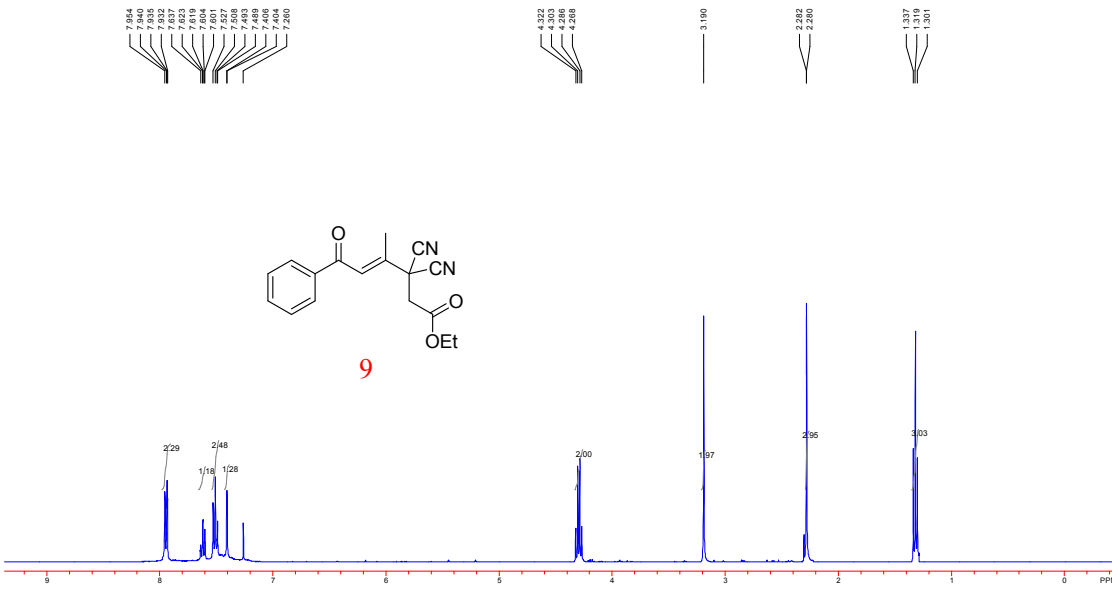
MeO
O
CN
HO
CO2Et
EtO2C
5d (d6-DMSO)


MeO
MeO
O
CN
HO
CO2Et
EtO2C
5d (d6-DMSO)

(3) Copies of ^{1}H and ^{13}C NMR spectra of 7, 9, A and 4u



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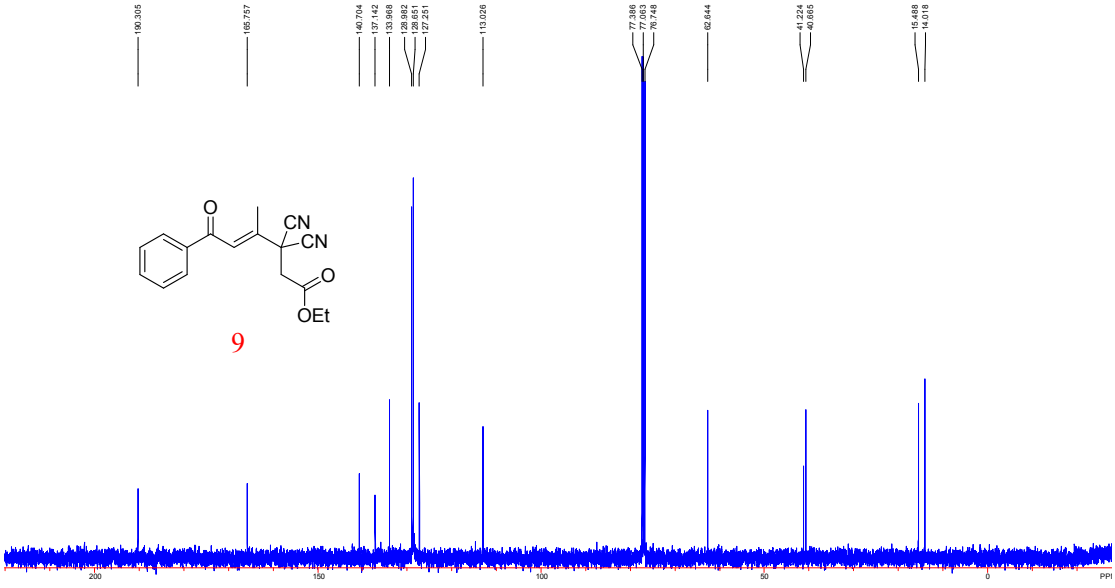
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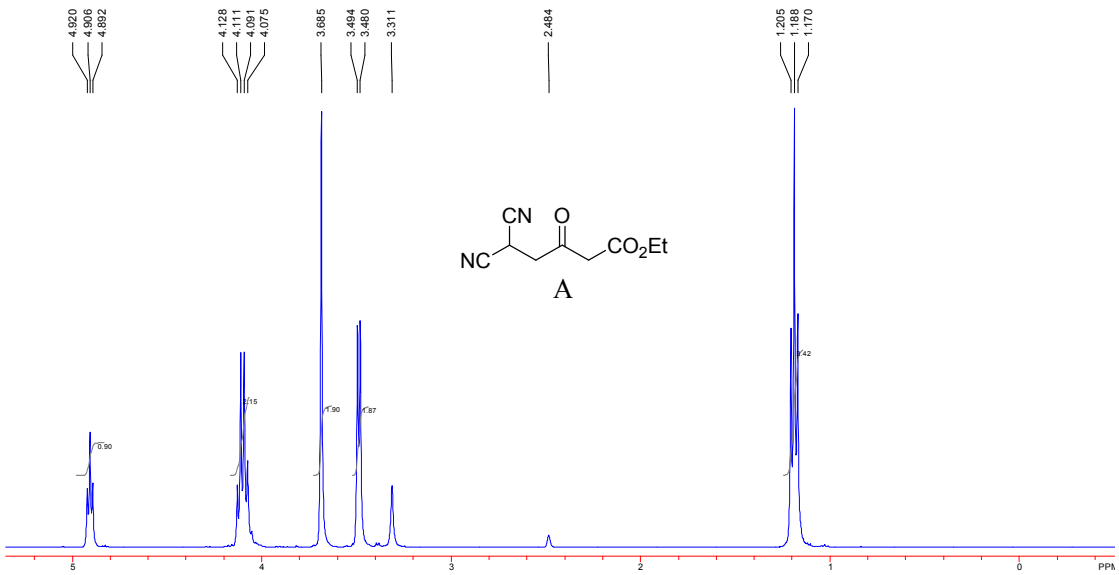
O
OEt
9
PPI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1.170
CN
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0
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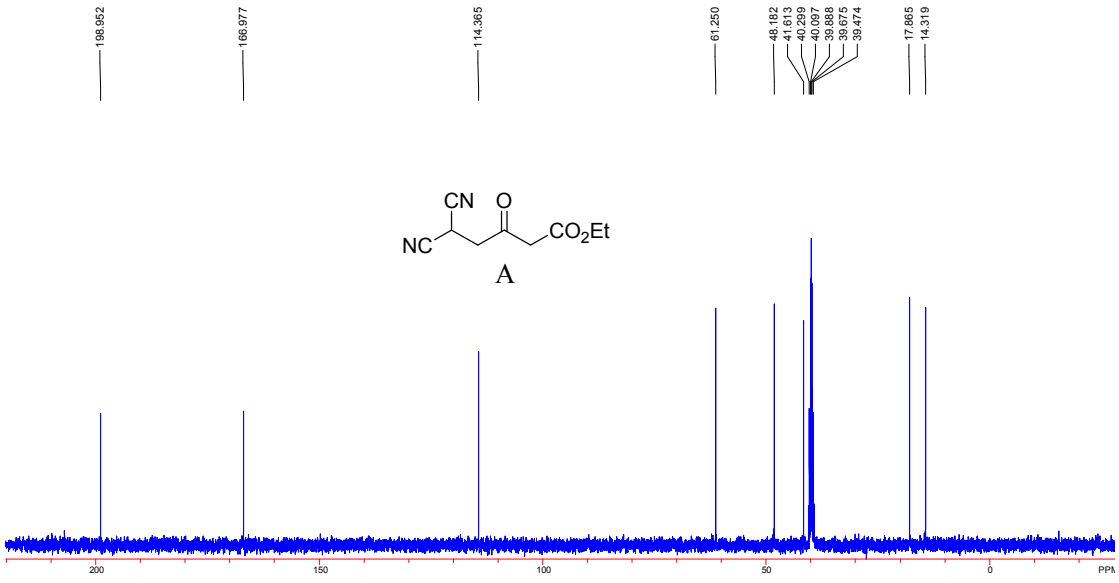
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17.865
14.319
CN
O
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CO2Et
A
200
150
100
50
0
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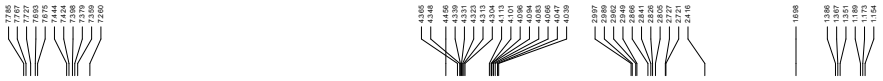
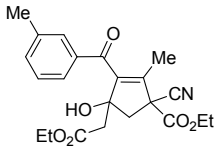
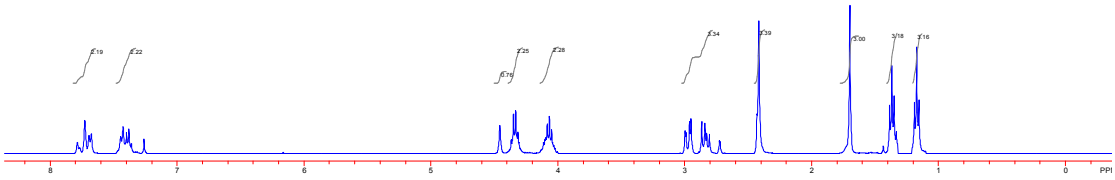
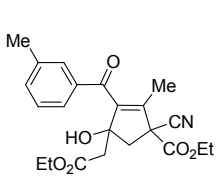


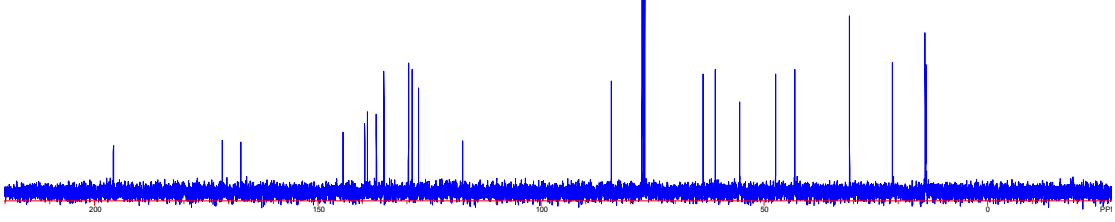


4u

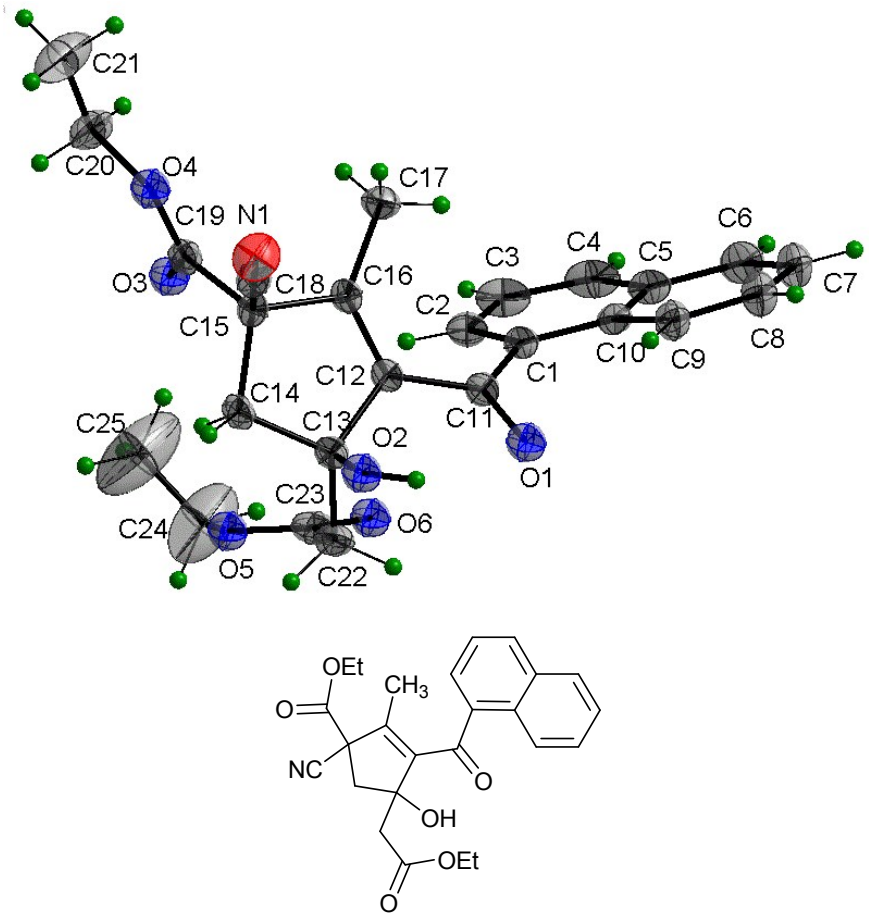




4u



V. X-ray crystal structure and data of 4n



Fiure 1 The X-ray crystal structure of of 4n

X-ray structure determination. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a EtOAc/petroleum ether (v/v =1/8) solution of **4n**. Crystal data collection and refinement parameters of **4n** are summarized in Table 1. Intensity data were collected at 290 K on a SuperNova Dual diffractometer using mirror-monochromated Mo Kα radiation, λ = 0.71073 Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. The structure was solved by a combination of direct methods in SHELXTL and the difference Fourier technique, and refined by full-matrix least-squares procedures. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model. The crystallographic data (excluding structure factors) for **4n** has been deposited at the Cambridge Crystallographic Data Centre. CCDC 1875026 contains the supplementary

crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1 Crystallographic data and structure refinement results of **4n**

Empirical formula	$C_{25}H_{25}NO_6$
Formula weight	435.46
Temp, K	296 (2)
Crystal system	Orthorhombic
Space group	*Pbca*
a, Å	10.932(3)
b, Å	15.037 (4)
c, Å	28.078 (7)
α (°)	90
β (°)	90
γ (°)	90
Volume, Å^3	4616
Z	8
d_{calc}, g cm^{-3}	1.253
λ, Å	0.71073
μ, mm^{-1}	0.09
No. of data collected	22067
No. of unique data	4050
R_{int}	0.050
Goodness-of-fit on F^2	1.068
R_1, wR_2 ($I > 2\sigma(I)$)	0.0556, 0.1794
R_1, wR_2 (all data)	0.0906, 0.1550

VI. References

1 A. Sniady, M. S. Morreale and R. Dembinski, *Org. Synth*., 2007, **84**, 199.

2 W.-L. Wu, Z.-J. Yao, Y.-L. Li, J.-C. Li, Y. Xia and Y.-L. Wu, *J. Org. Chem*., 1995, **60**, 3257.

3 N. A. Petasis and K. A. Teets, *J. Am. Chem. Soc*., 1992, **114***,* 10328.