



## Supporting Information

for

### **Molecular diversity of the base-promoted reaction of phenacylmalononitriles with dialkyl but-2-ynedioates**

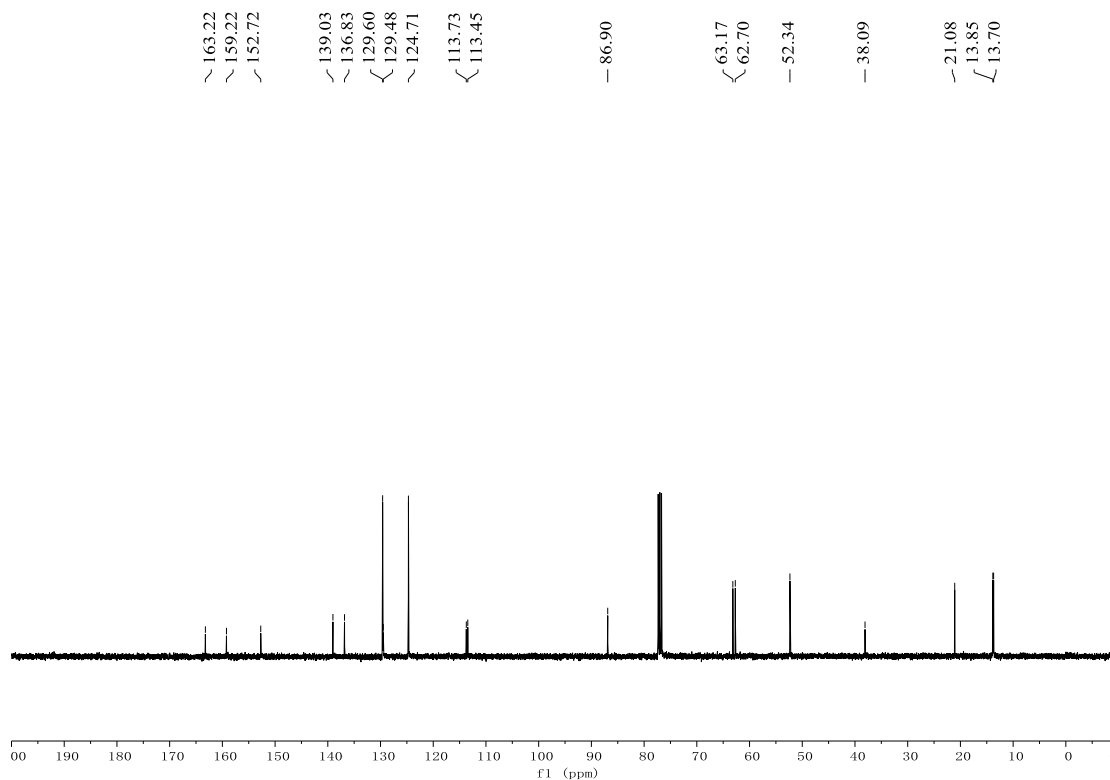
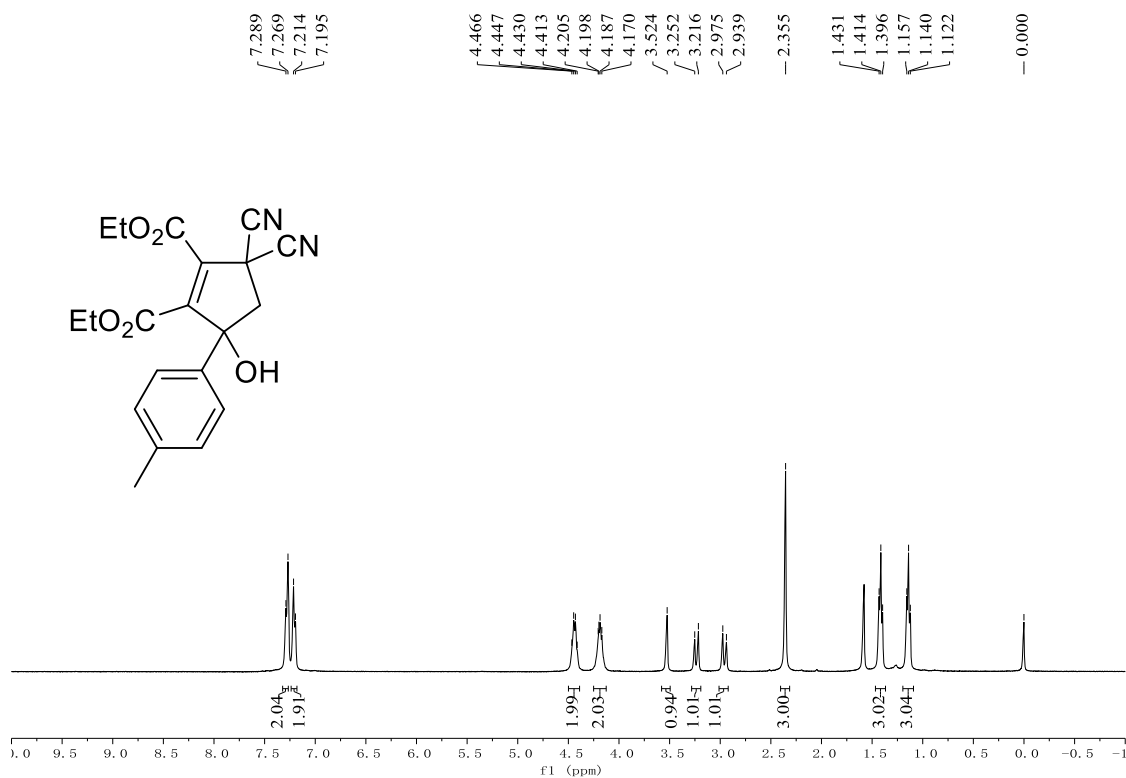
Hui Zheng, Ying Han, Jing Sun and Chao-Guo Yan

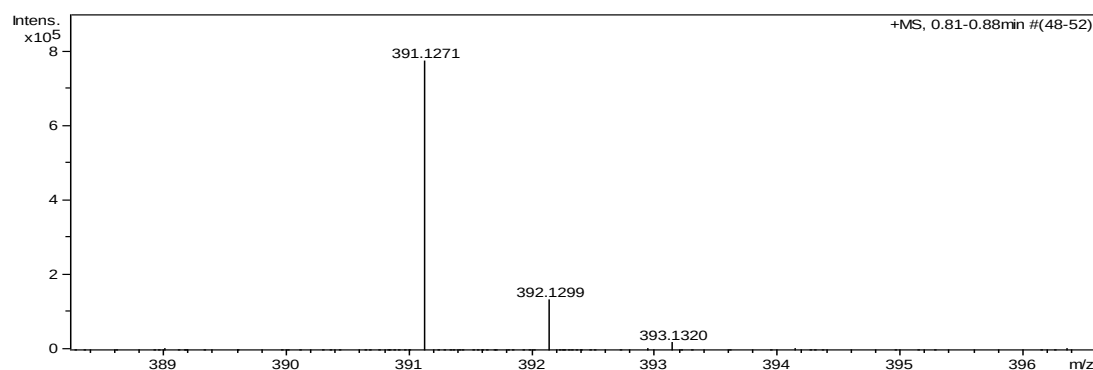
*Beilstein J. Org. Chem.* **2022**, *18*, 991–998. doi:10.3762/bjoc.18.99

### **Characterization data and $^1\text{H}$ NMR, $^{13}\text{C}$ NMR, and HRMS spectra of the compounds**

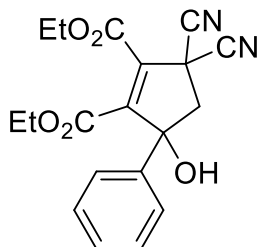
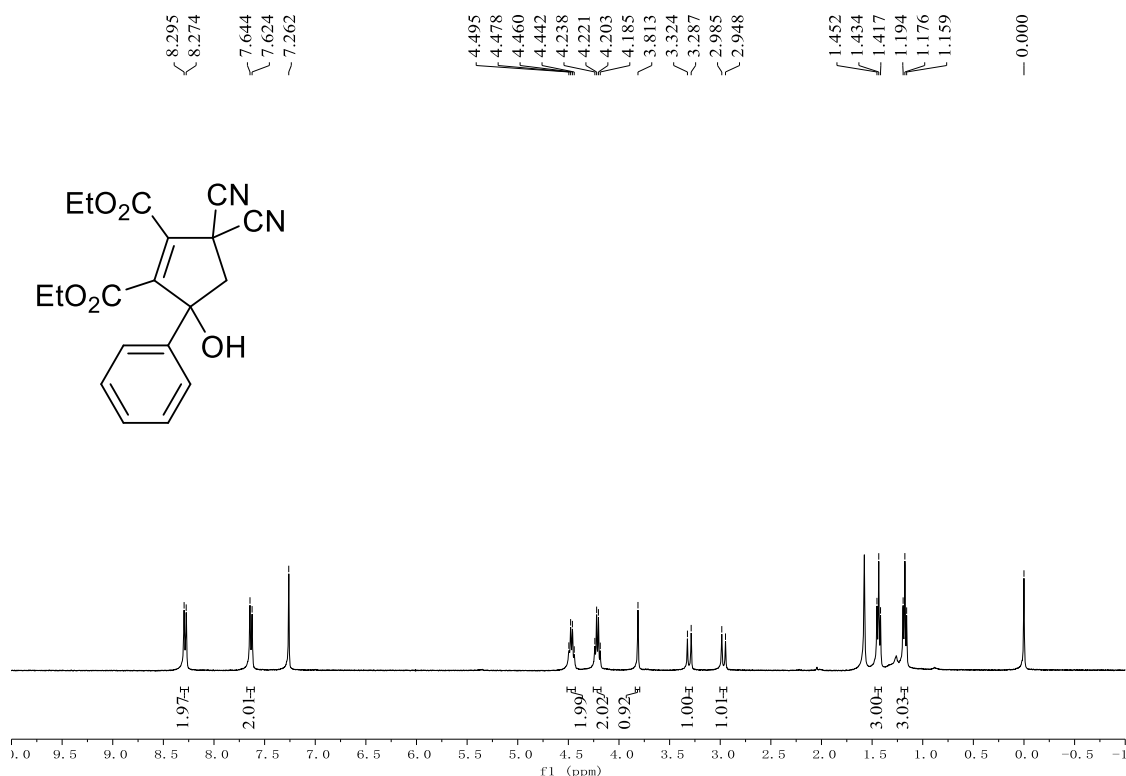
**Diethyl 3,3-dicyano-5-hydroxy-5-(*p*-tolyl)cyclopent-1-ene-1,2-dicarboxylate (3a):**

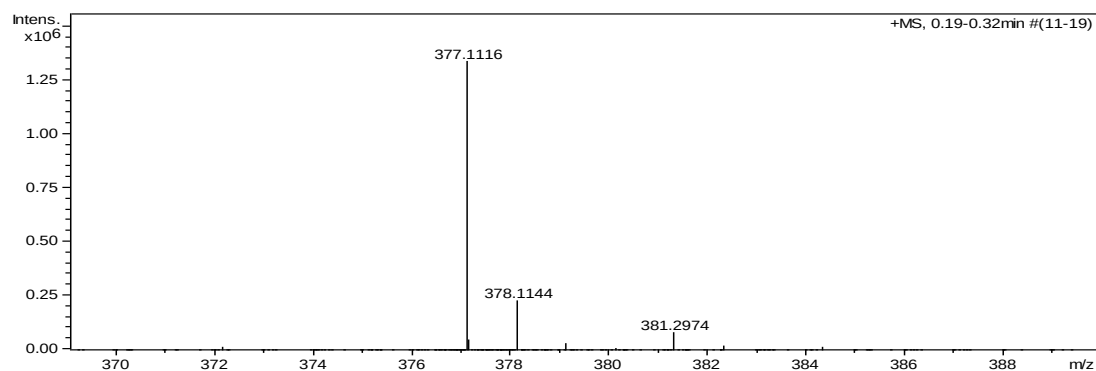
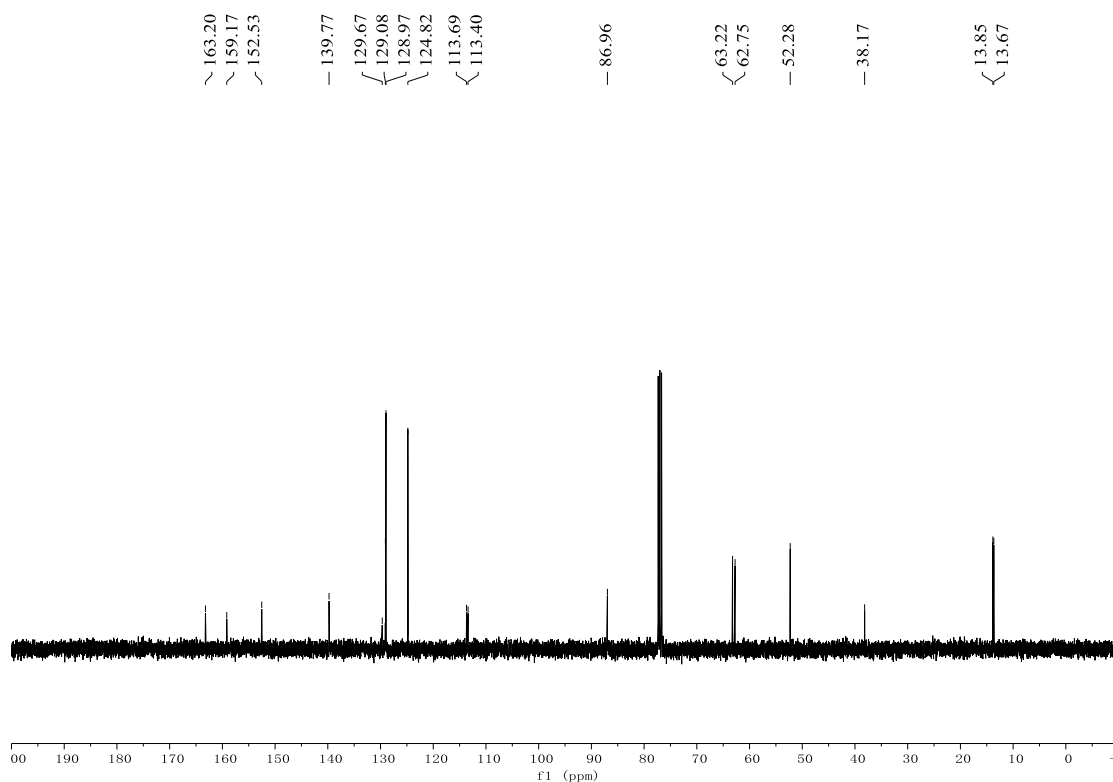
For characterization data set, see main text.



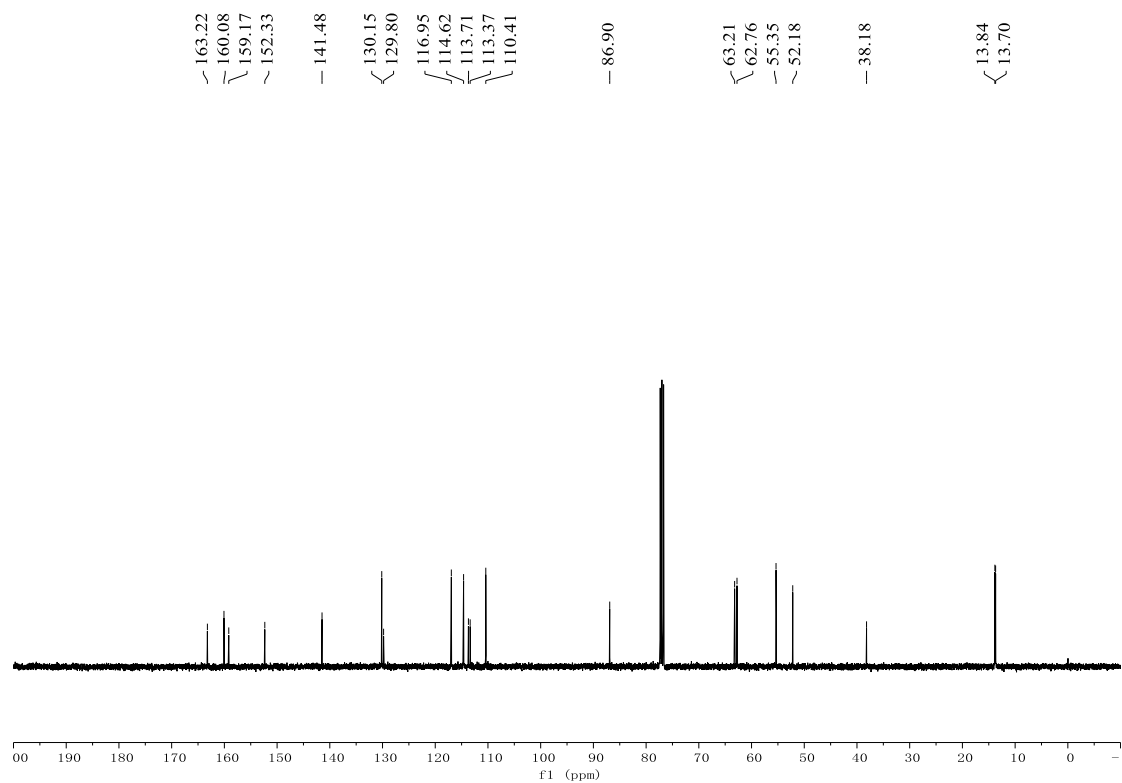
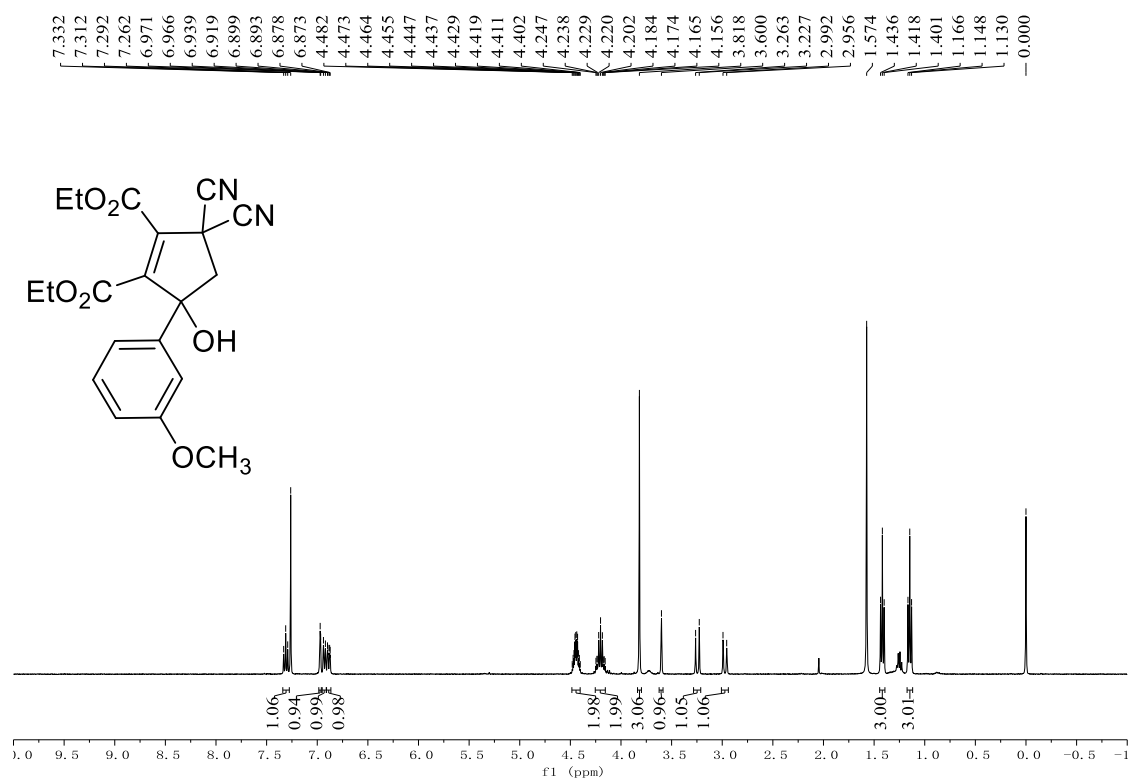


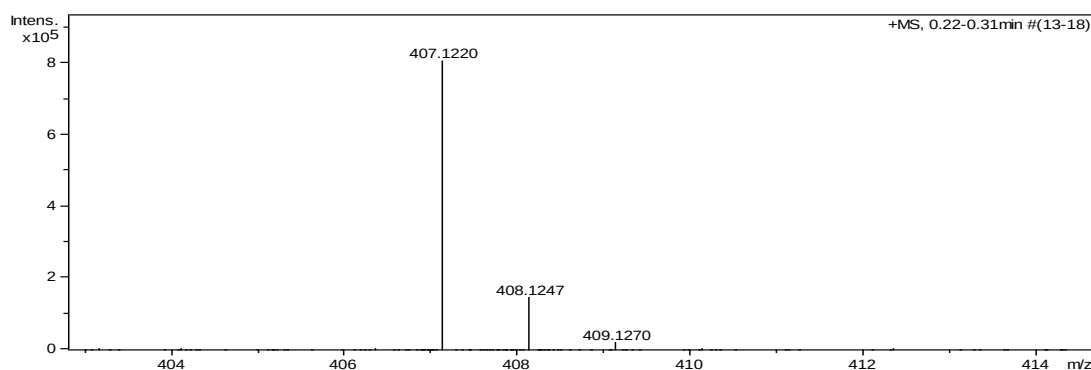
**Diethyl 3,3-dicyano-5-hydroxy-5-phenylcyclopent-1-ene-1,2-dicarboxylate (3b):** white solid, 75%, m.p. 97-99 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.41-7.40 (m, 4H, ArH), 7.38-7.35 (m, 1H, ArH), 4.47-4.42 (m, 2H, OCH<sub>2</sub>), 4.21-4.13 (m, 2H, OCH<sub>2</sub>), 3.63 (s, 1H, OH), 3.26 (d, *J* = 14.4 Hz, 1H, CH<sub>2</sub>), 2.99 (d, *J* = 14.4 Hz, 1H, CH<sub>2</sub>), 1.41 (t, *J* = 7.2 Hz, 3H, CH<sub>3</sub>), 1.11 (t, *J* = 7.2 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.2, 159.2, 152.5, 139.8, 129.7, 129.1, 129.0, 124.8, 113.7, 113.4, 89.0, 63.2, 62.8, 52.3, 38.2, 13.9, 13.7. MS (*m/z*): HRMS (ESI) Calcd. for C<sub>19</sub>H<sub>18</sub>NaN<sub>2</sub>O<sub>5</sub> ([M+Na]<sup>+</sup>): 377.1113, found: 377.1116.





**Diethyl 3,3-dicyano-5-hydroxy-5-(3-methoxyphenyl)cyclopent-1-ene-1,2-dicarboxylate (3c):** white solid, 73%, m.p. 127-128 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (m, 1H, ArH), 6.97-6.96 (m, 1H, ArH), 6.93 (t,  $J$  = 8.0 Hz, 1H, ArH), 6.90-6.87 (m, 1H, ArH), 4.48-4.40 (m, 2H,  $\text{OCH}_2$ ), 4.25-4.16 (m, 2H,  $\text{OCH}_2$ ), 3.82(s, 3H,  $\text{OCH}_3$ ), 3.60 (s, 1H, OH), 3.24 (d,  $J$  = 14.4 Hz, 1H,  $\text{CH}_2$ ), 2.97 (d,  $J$  = 14.4 Hz, 1H,  $\text{CH}_2$ ), 1.42 (t,  $J$  = 7.2 Hz, 3H,  $\text{CH}_3$ ), 1.15 (t,  $J$  = 7.2 Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.2, 160.1, 159.2, 152.3, 141.5, 130.2, 129.8, 117.0, 114.6, 113.7, 113.4, 110.4, 86.9, 63.2, 62.8, 55.4, 52.2, 38.2, 13.8, 13.7. MS ( $m/z$ ): HRMS (ESI) Calcd. for  $\text{C}_{20}\text{H}_{20}\text{NaN}_2\text{O}_6$  ( $[\text{M}+\text{Na}]^+$ ): 407.1219, found: 407.1220.

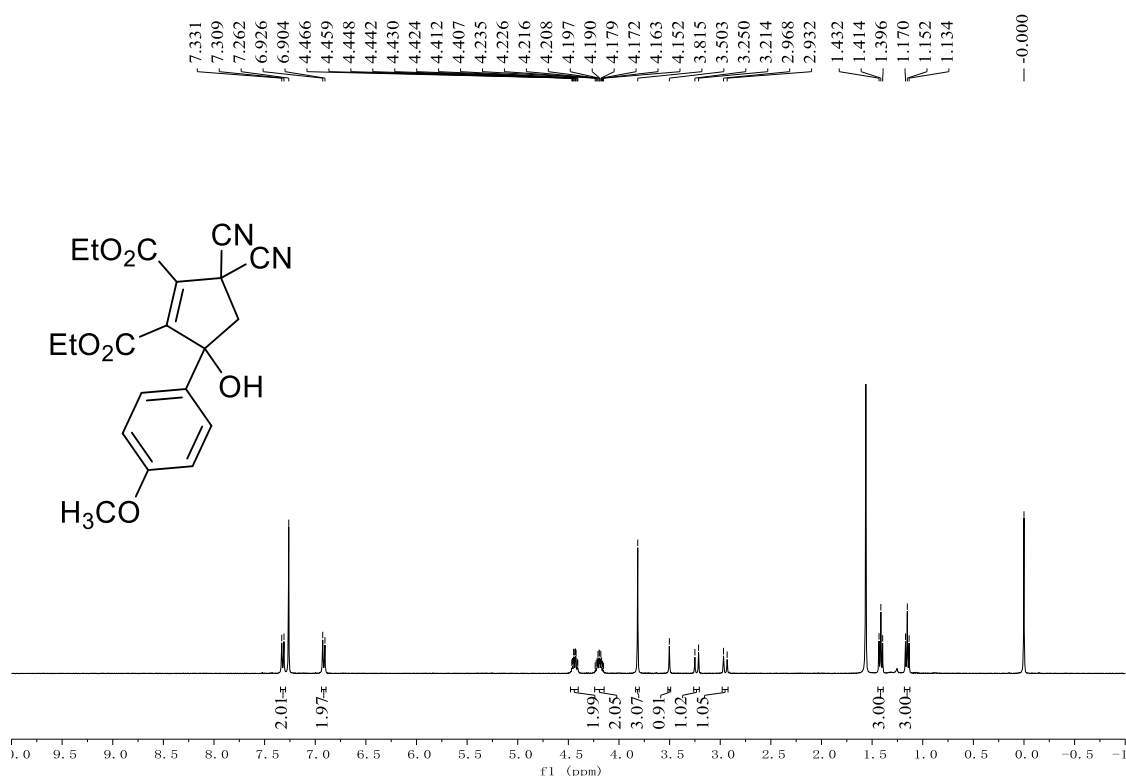


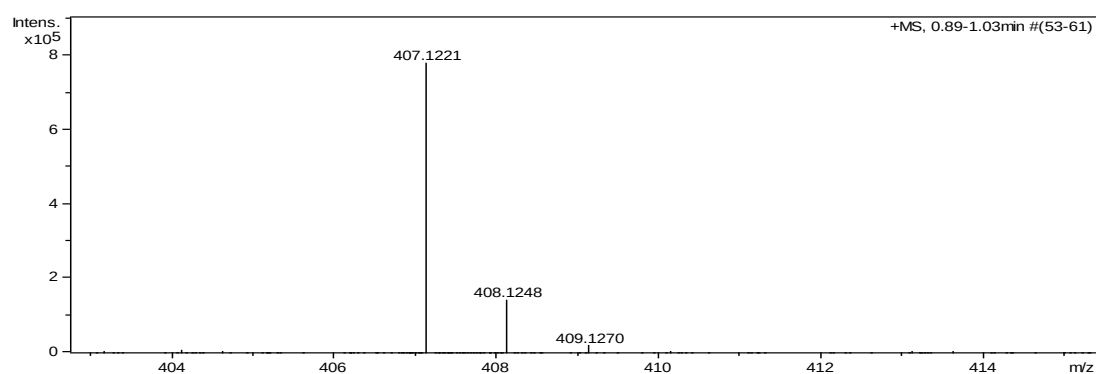
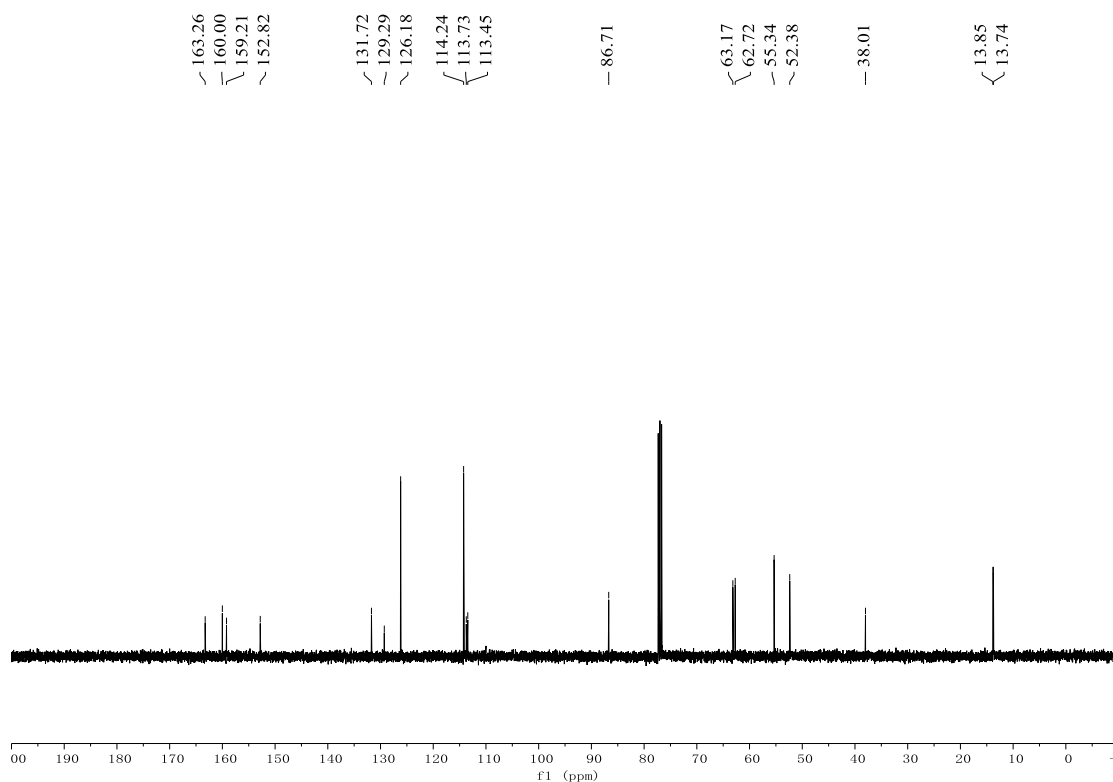


**Diethyl 3,3-dicyano-5-hydroxy-5-(4-methoxyphenyl)cyclopent-1-ene-1,2-dicarboxylate (3d):**

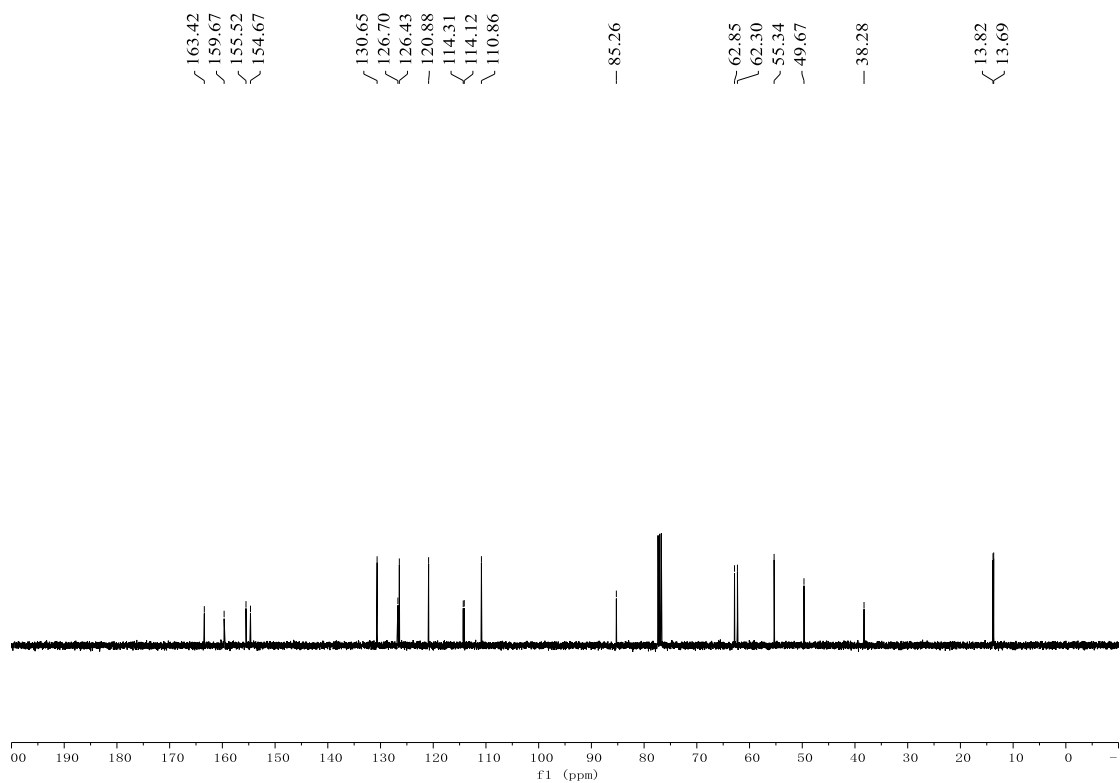
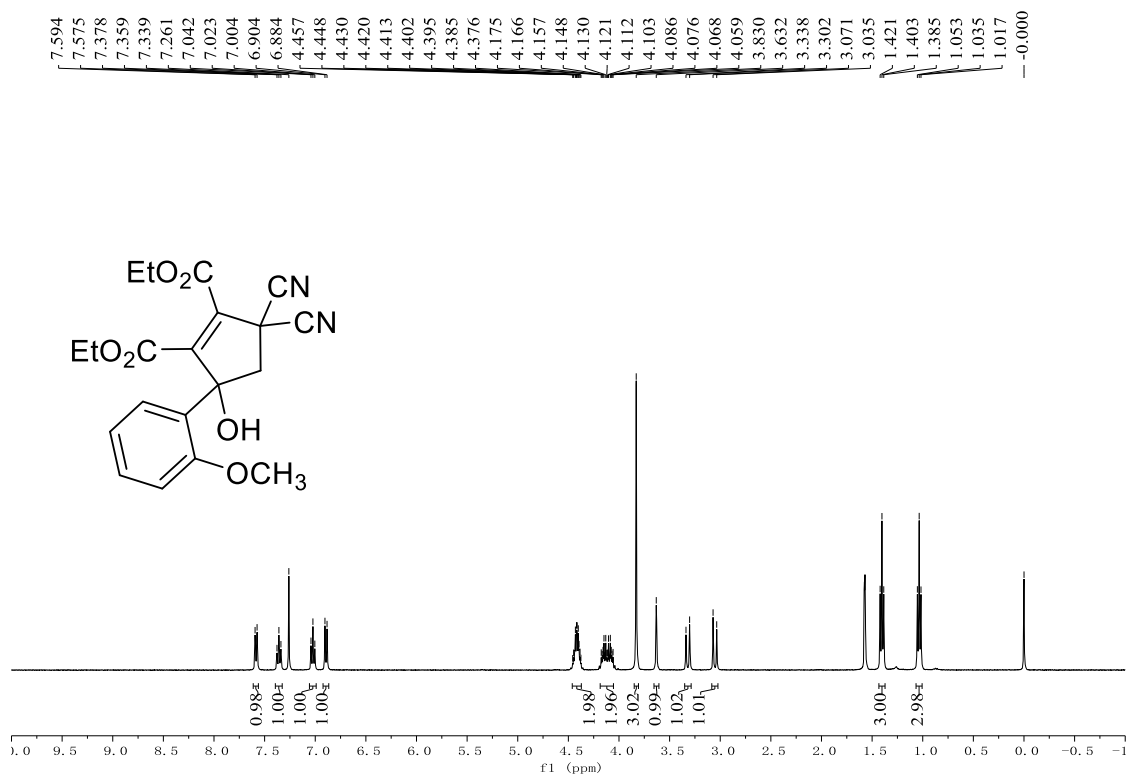
white solid, 88%, m.p. 151-152 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.32 (d, *J* = 8.8 Hz, 2H, ArH), 6.92 (d, *J* = 8.8 Hz, 2H, ArH), 4.47-4.41 (m, 2H, OCH<sub>2</sub>), 4.24-4.15 (m, 2H, OCH<sub>2</sub>), 3.82 (s, 3H, OCH<sub>3</sub>), 3.50 (s, 1H, OH), 3.23 (d, *J* = 14.4 Hz, 1H, CH<sub>2</sub>), 2.95 (d, *J* = 14.4 Hz, 1H, CH<sub>2</sub>), 1.41 (t, *J* = 7.2 Hz, 3H, CH<sub>3</sub>), 1.15 (t, *J* = 7.2 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.3, 160.0, 159.2, 152.8, 131.7, 129.3, 126.2, 114.2, 113.7, 113.5, 86.7, 63.2, 62.7, 55.3, 52.4, 38.0, 13.9, 13.7.

MS (*m/z*): HRMS (ESI) Calcd. for C<sub>20</sub>H<sub>20</sub>NaN<sub>2</sub>O<sub>6</sub> ([M+Na]<sup>+</sup>): 407.1219, found: 407.1221.

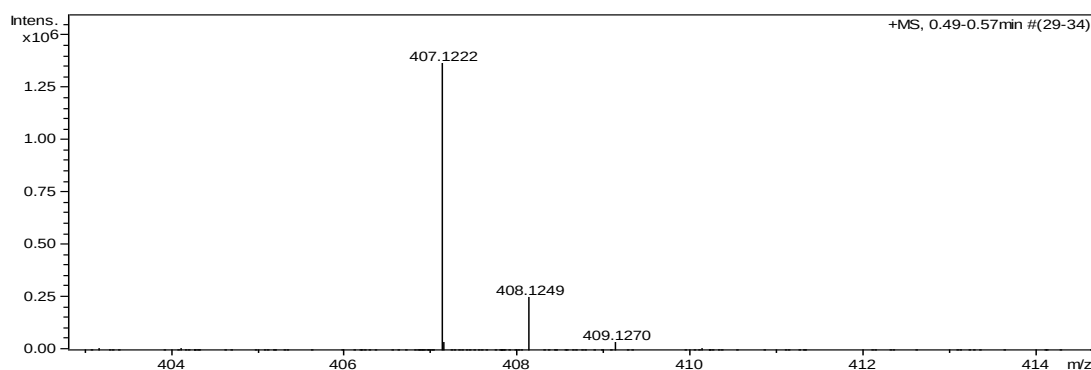




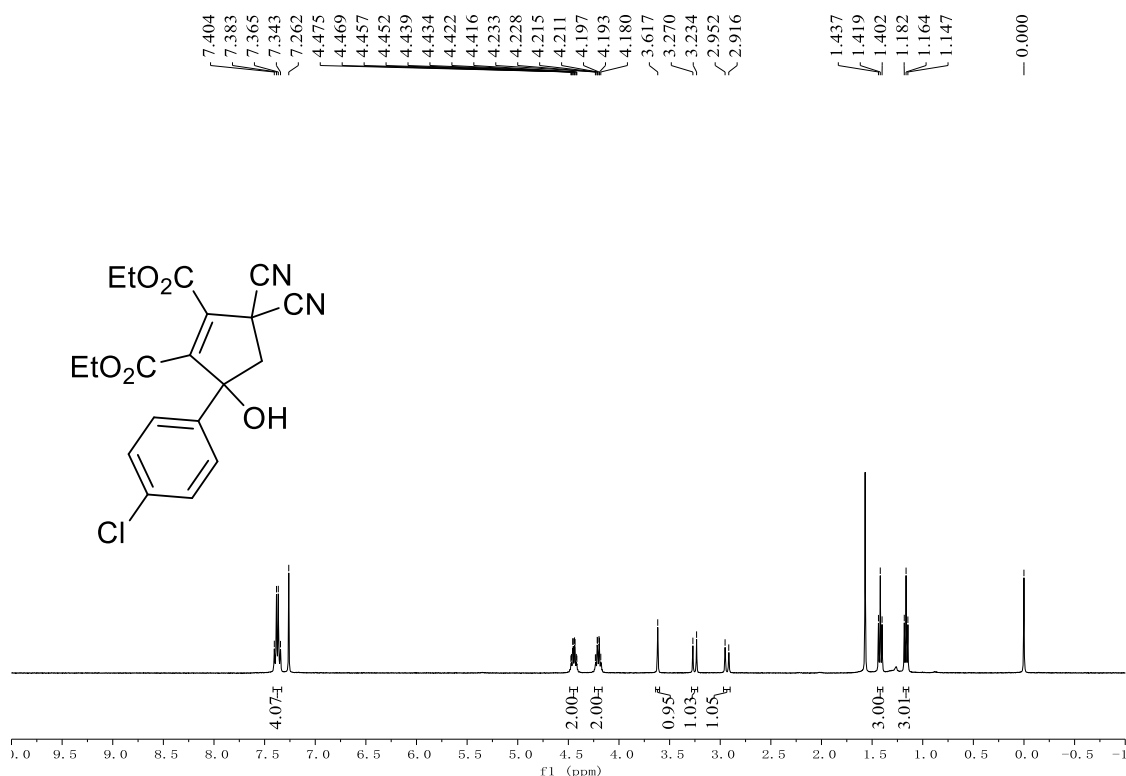
**Diethyl 3,3-dicyano-5-hydroxy-5-(2-methoxyphenyl)cyclopent-1-ene-1,2-dicarboxylate (3e):** white solid, 62%, m.p. 154-156 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (d,  $J = 7.6$  Hz, 1H, ArH), 7.36 (d,  $J = 8.0$  Hz, 1H, ArH), 7.02 (t,  $J = 7.6$  Hz, 1H, ArH), 6.89 (d,  $J = 8.0$  Hz, 1H, ArH), 4.45-4.38 (m, 2H,  $\text{OCH}_2$ ), 4.18-4.06 (m, 2H,  $\text{OCH}_2$ ), 3.83 (s, 3H,  $\text{OCH}_3$ ), 3.63 (s, 1H, OH), 3.32 (d,  $J = 14.4$  Hz, 1H,  $\text{CH}_2$ ), 3.05 (d,  $J = 14.4$  Hz, 1H,  $\text{CH}_2$ ), 1.40 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ), 1.04 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.4, 159.7, 155.5, 154.7, 130.7, 126.7, 126.4, 120.9, 114.3, 114.1, 110.9, 85.3, 62.9, 62.3, 55.3, 49.7, 38.3, 13.8, 13.7. MS ( $m/z$ ): HRMS (ESI) Calcd. for  $\text{C}_{20}\text{H}_{20}\text{NaN}_2\text{O}_6$  ( $[\text{M}+\text{Na}]^+$ ): 407.1219, found: 407.1222.

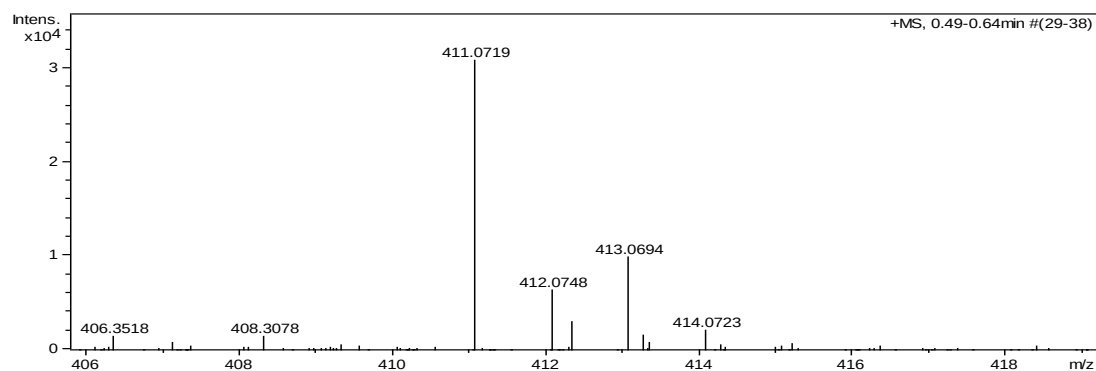
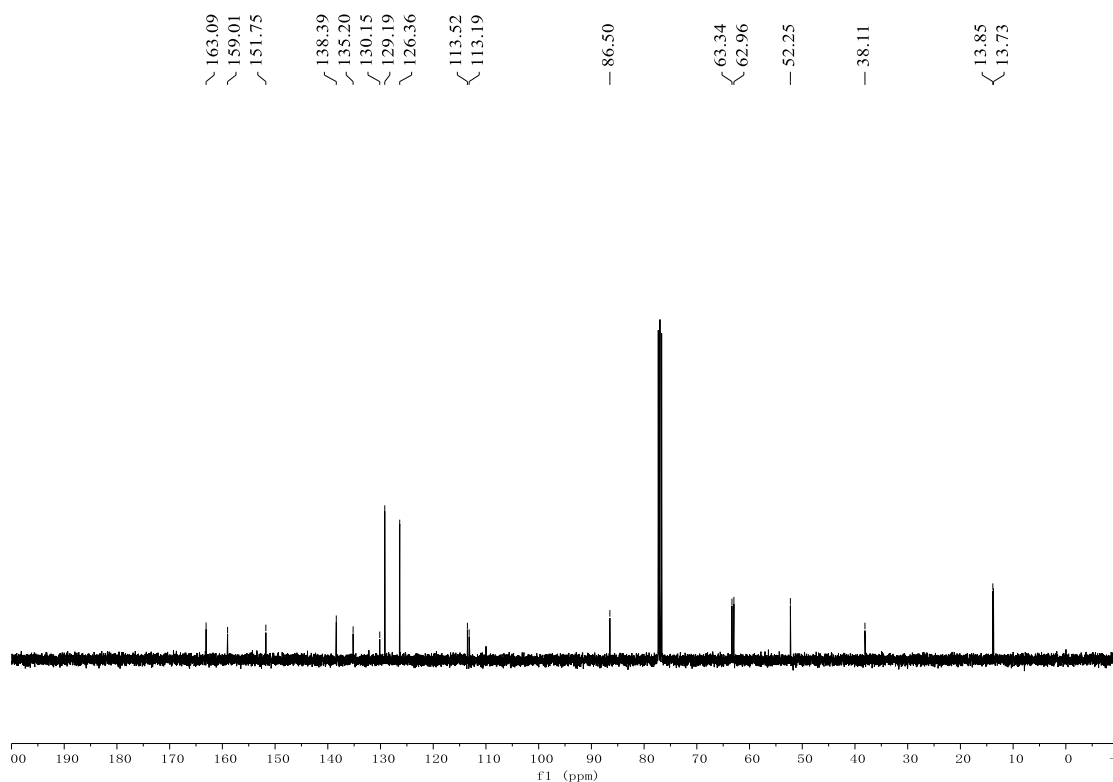




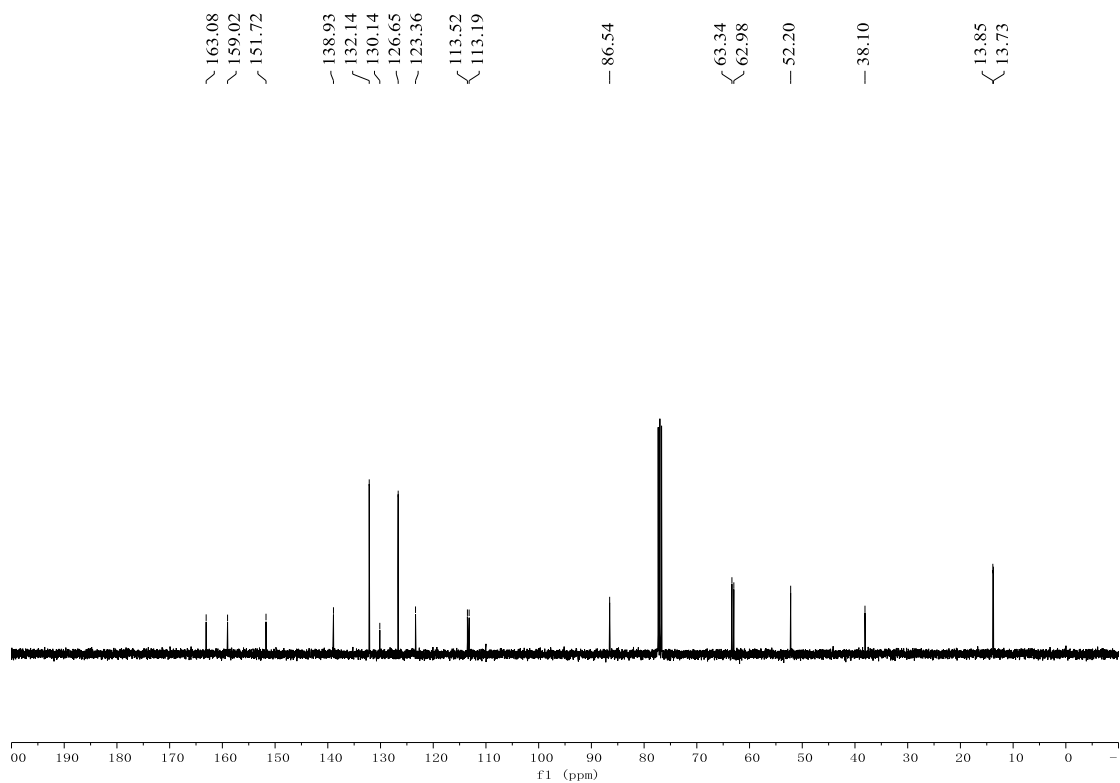
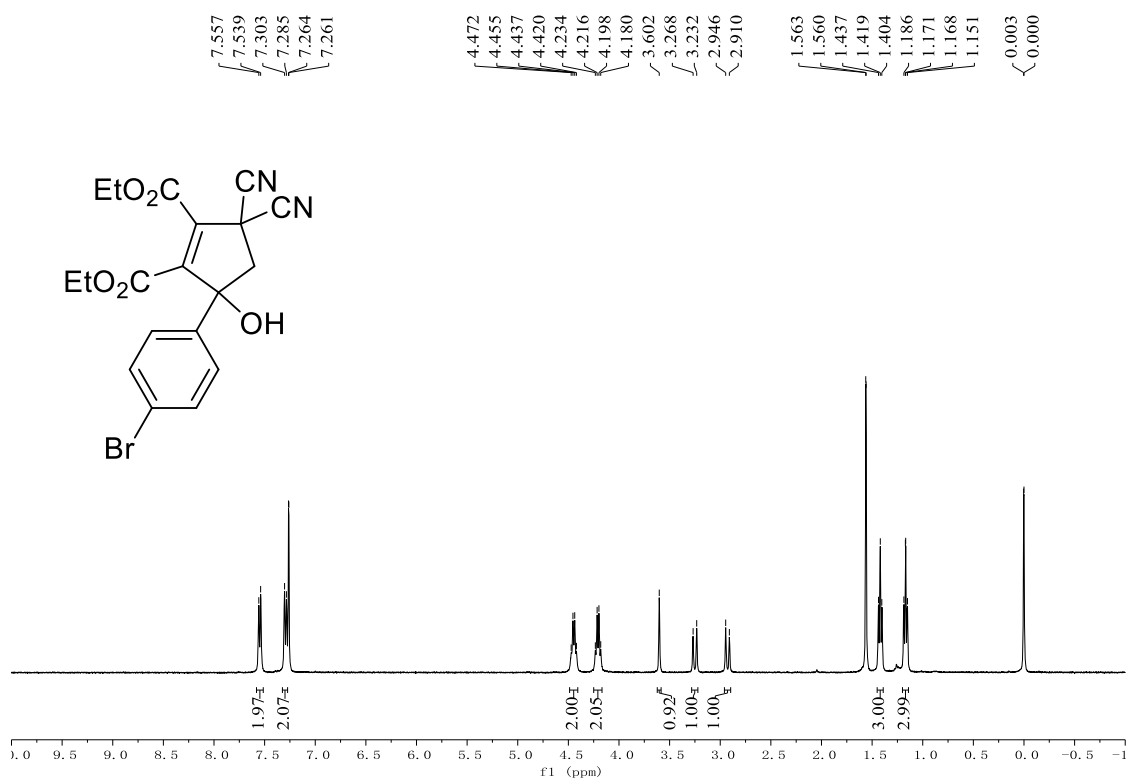


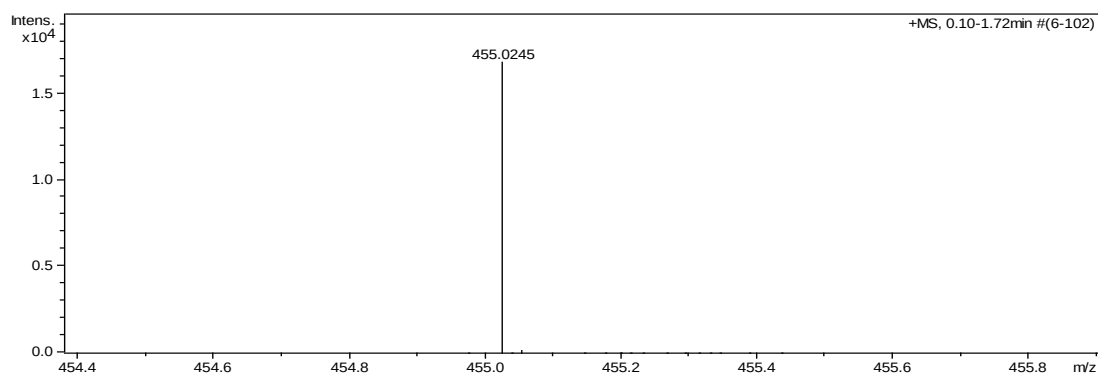
**Diethyl 3-(4-chlorophenyl)-5,5-dicyano-3-hydroxycyclopent-1-ene-1,2-dicarboxylate (3f):** white solid, 60%, m.p. 129-130 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40-7.34 (m, 4H, ArH), 4.48-4.42 (m, 2H,  $\text{OCH}_2$ ), 4.23-4.18 (m, 2H,  $\text{OCH}_2$ ), 3.62 (s, 1H, OH), 3.25 (d,  $J = 14.4$  Hz, 1H,  $\text{CH}_2$ ), 2.94 (d,  $J = 14.4$  Hz, 1H,  $\text{CH}_2$ ), 1.42 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ), 1.16 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.1, 159.0, 151.8, 138.4, 135.2, 130.2, 129.2, 126.4, 113.5, 113.2, 86.5, 63.3, 63.0, 52.3, 38.1, 13.9, 13.7. MS ( $m/z$ ): HRMS (ESI) Calcd. for  $\text{C}_{19}\text{H}_{17}\text{ClNaN}_2\text{O}_5$  ( $[\text{M}+\text{Na}]^+$ ): 411.0724, found: 411.0719.





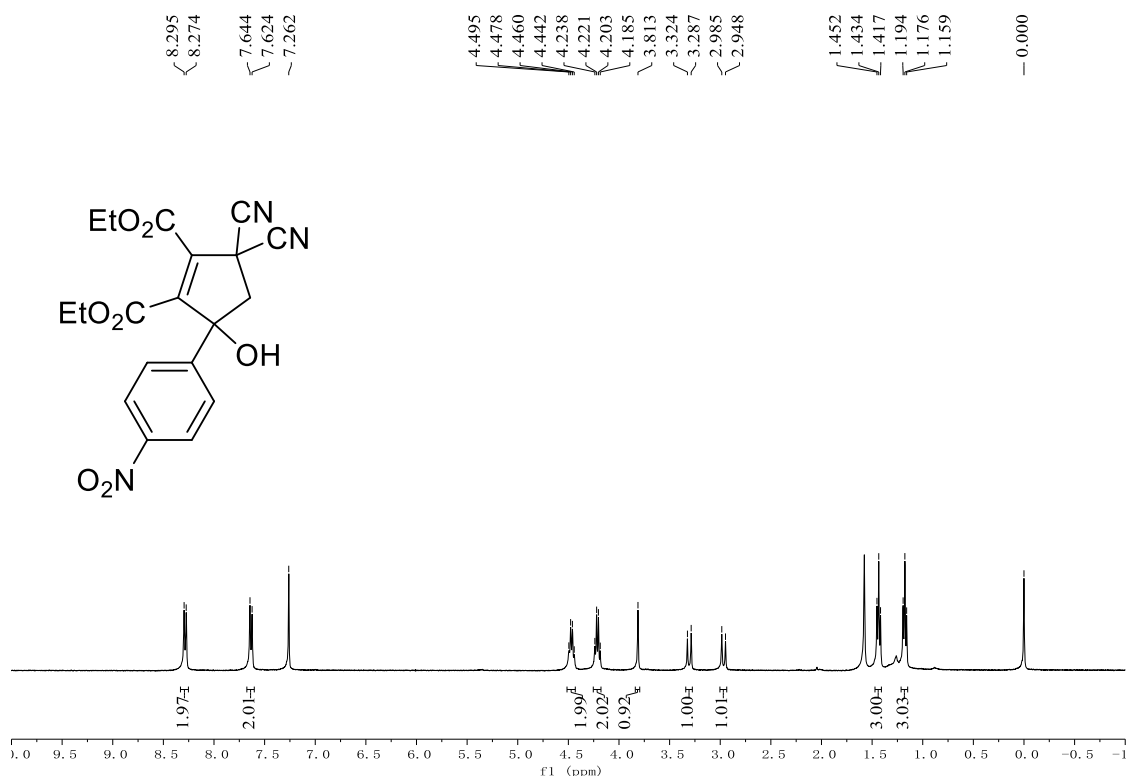
**Diethyl 3-(4-bromophenyl)-5,5-dicyano-3-hydroxycyclopent-1-ene-1,2-dicarboxylate (3g):** white solid, 62%, m.p. 149-150 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (d,  $J = 7.2$  Hz, 2H, ArH), 7.29 (d,  $J = 7.2$  Hz, 2H, ArH), 4.47-4.42 (m, 2H,  $\text{OCH}_2$ ), 4.23-4.18 (m, 2H,  $\text{OCH}_2$ ), 3.60 (s, 1H, OH), 3.25 (d,  $J = 14.4$  Hz, 1H,  $\text{CH}_2$ ), 2.93 (d,  $J = 14.4$  Hz, 1H,  $\text{CH}_2$ ), 1.42 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ), 1.17 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.1, 159.0, 151.7, 138.9, 132.1, 130.1, 126.7, 123.4, 113.5, 113.2, 86.5, 63.3, 63.0, 52.2, 38.1, 13.9, 13.7. MS ( $m/z$ ): HRMS (ESI) Calcd. for  $\text{C}_{19}\text{H}_{17}\text{BrNaN}_2\text{O}_5$  ( $[\text{M}+\text{Na}]^+$ ): 455.0219, found: 455.0245.

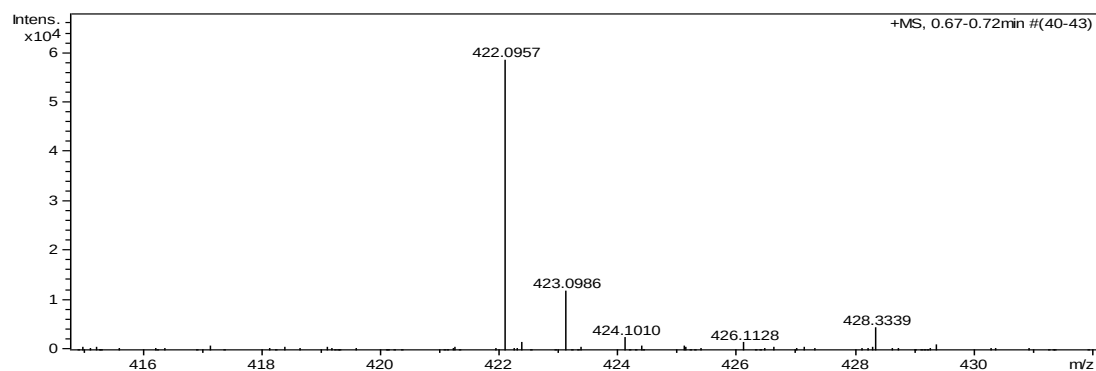
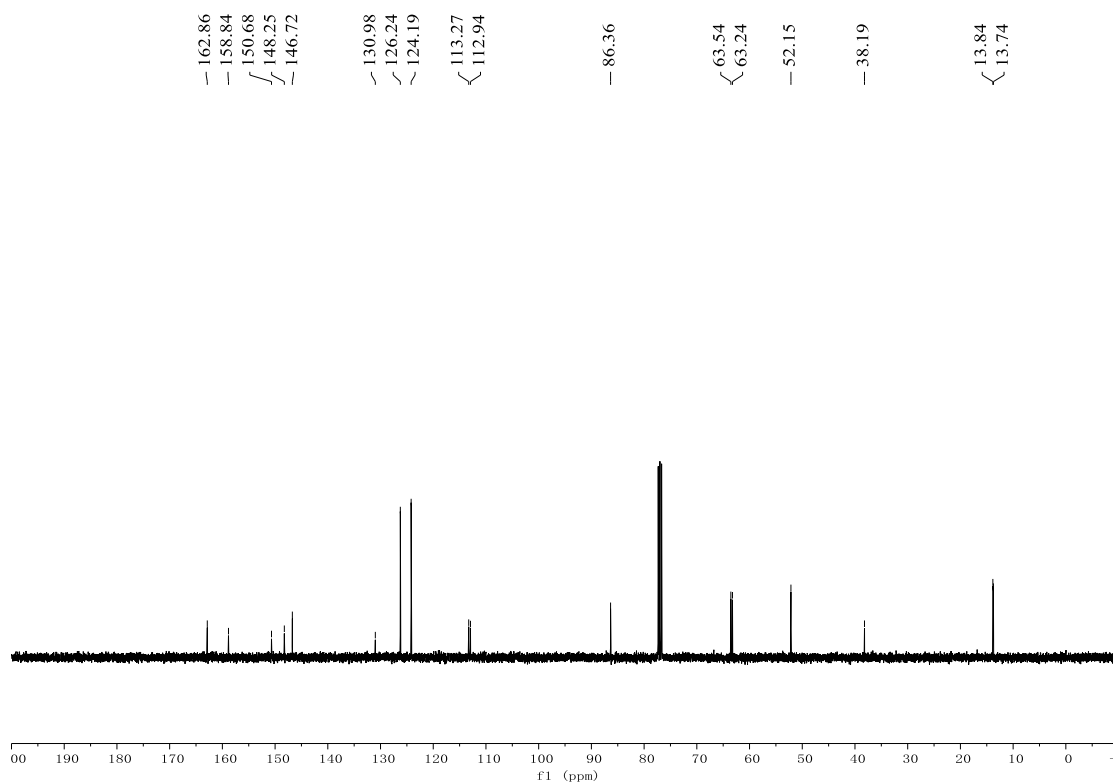




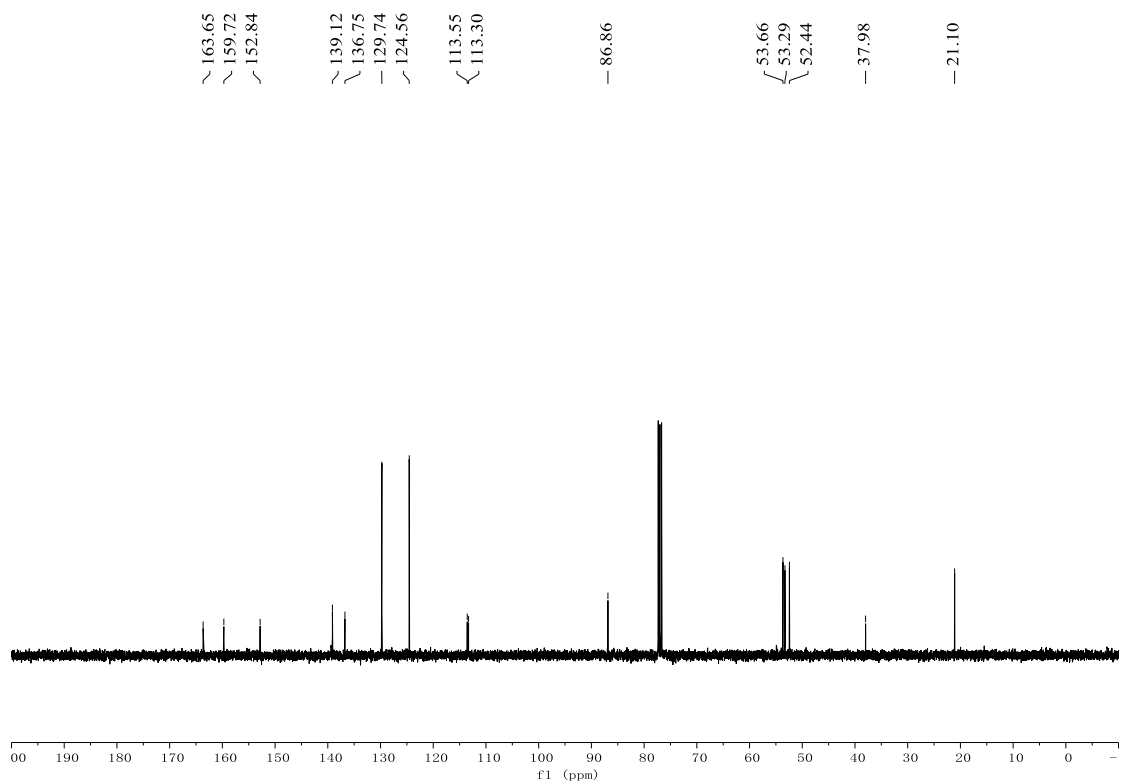
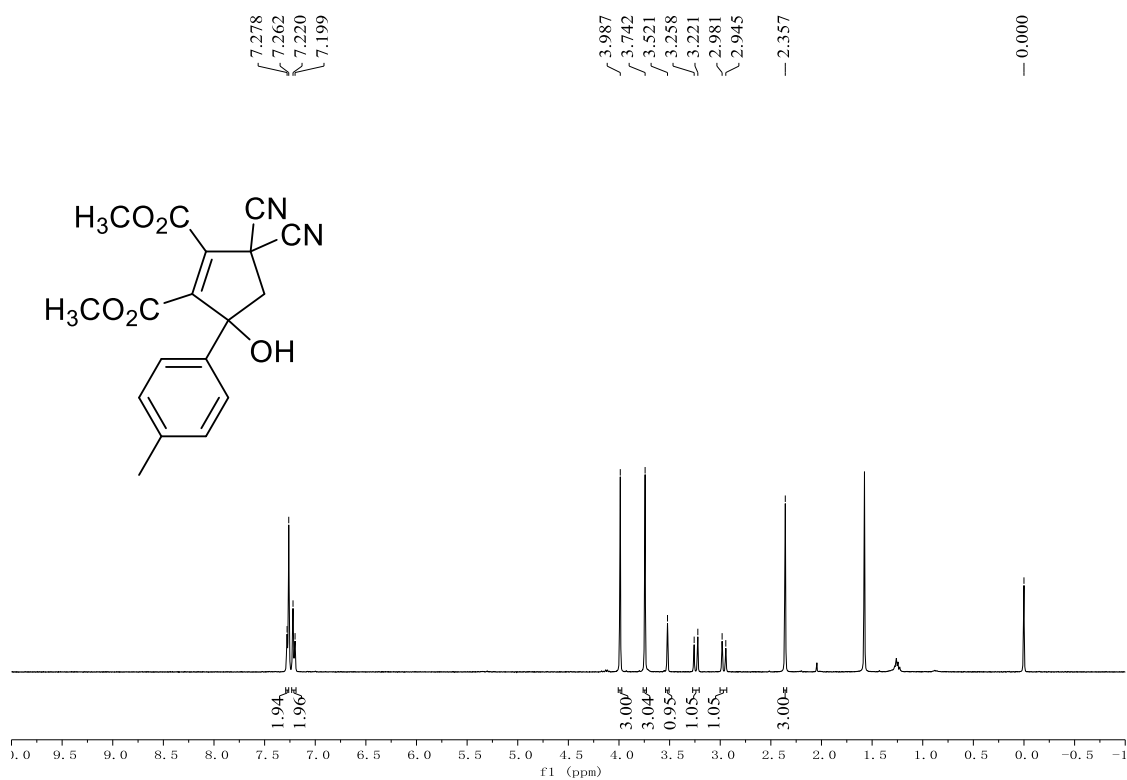
**Diethyl 3,3-dicyano-5-hydroxy-5-(4-nitrophenyl)cyclopent-1-ene-1,2-dicarboxylate (3h):**

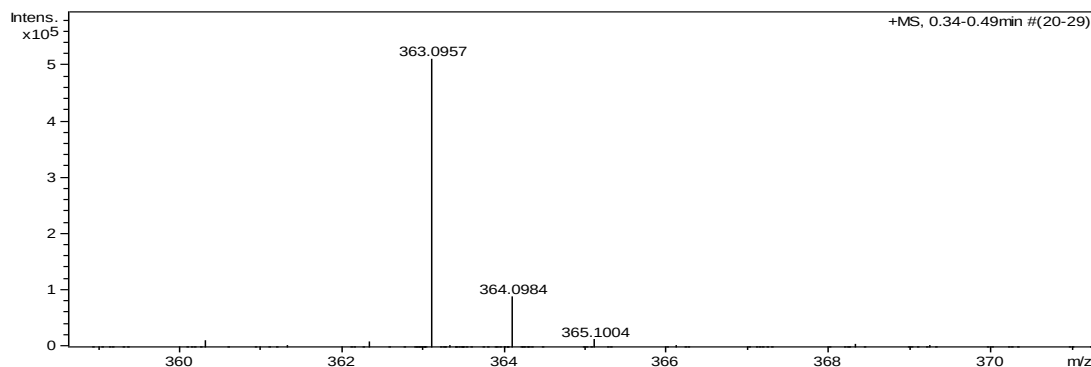
white solid, 56%, m.p. 139-140 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.28 (d,  $J = 8.4$  Hz, 2H, ArH), 7.63 (d,  $J = 8.0$  Hz, 2H, ArH), 4.50-4.44 (m, 2H,  $\text{OCH}_2$ ), 4.24-4.19 (m, 2H,  $\text{OCH}_2$ ), 3.81 (s, 1H, OH), 3.30 (d,  $J = 14.8$  Hz, 1H,  $\text{CH}_2$ ), 2.96 (d,  $J = 14.8$  Hz, 1H,  $\text{CH}_2$ ), 1.43 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ), 1.18 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.9, 158.8, 150.7, 148.3, 146.7, 131.0, 126.2, 124.2, 113.3, 112.9, 86.4, 63.5, 63.2, 52.2, 38.2, 13.8, 13.7. MS ( $m/z$ ): HRMS (ESI) Calcd. for  $\text{C}_{19}\text{H}_{17}\text{NaN}_3\text{O}_7$  ( $[\text{M}+\text{Na}]^+$ ): 422.0964, found: 422.0957.



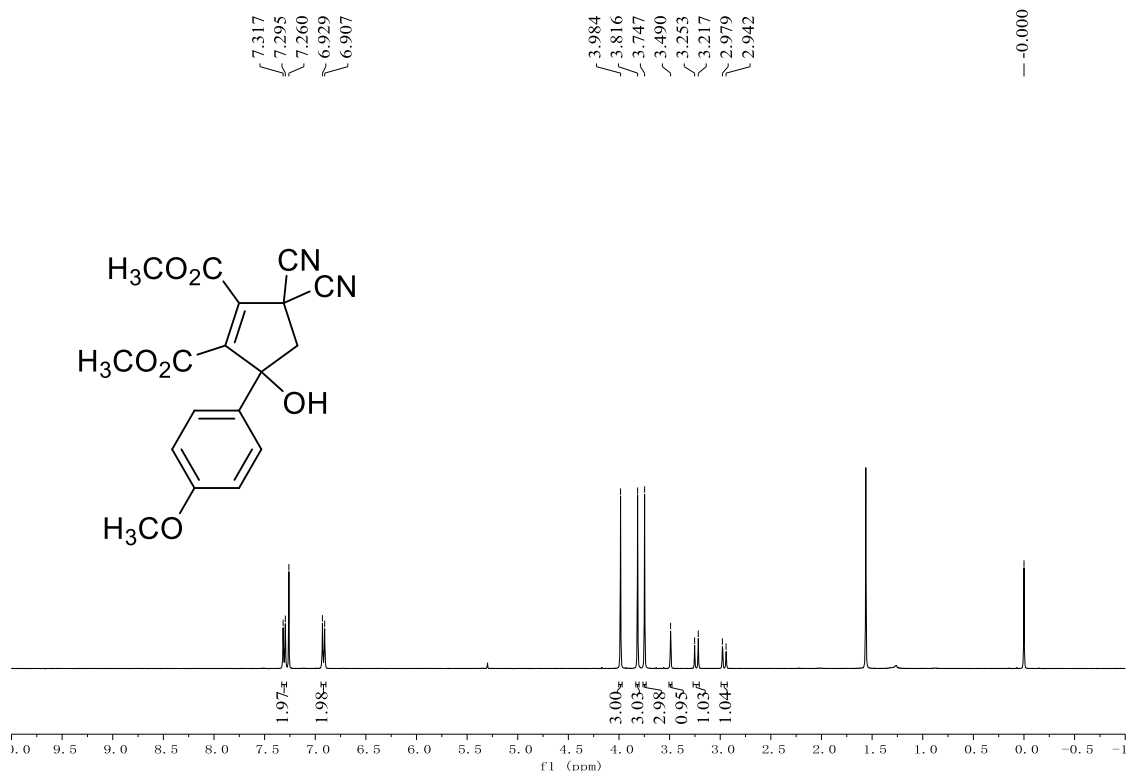


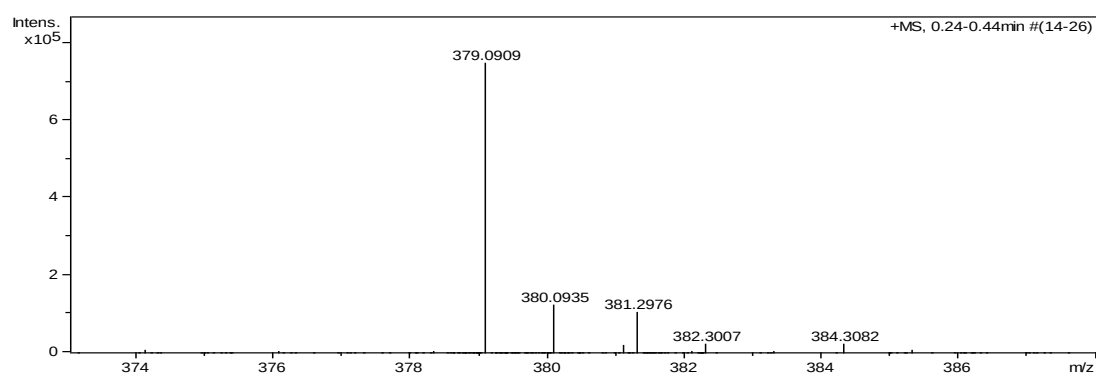
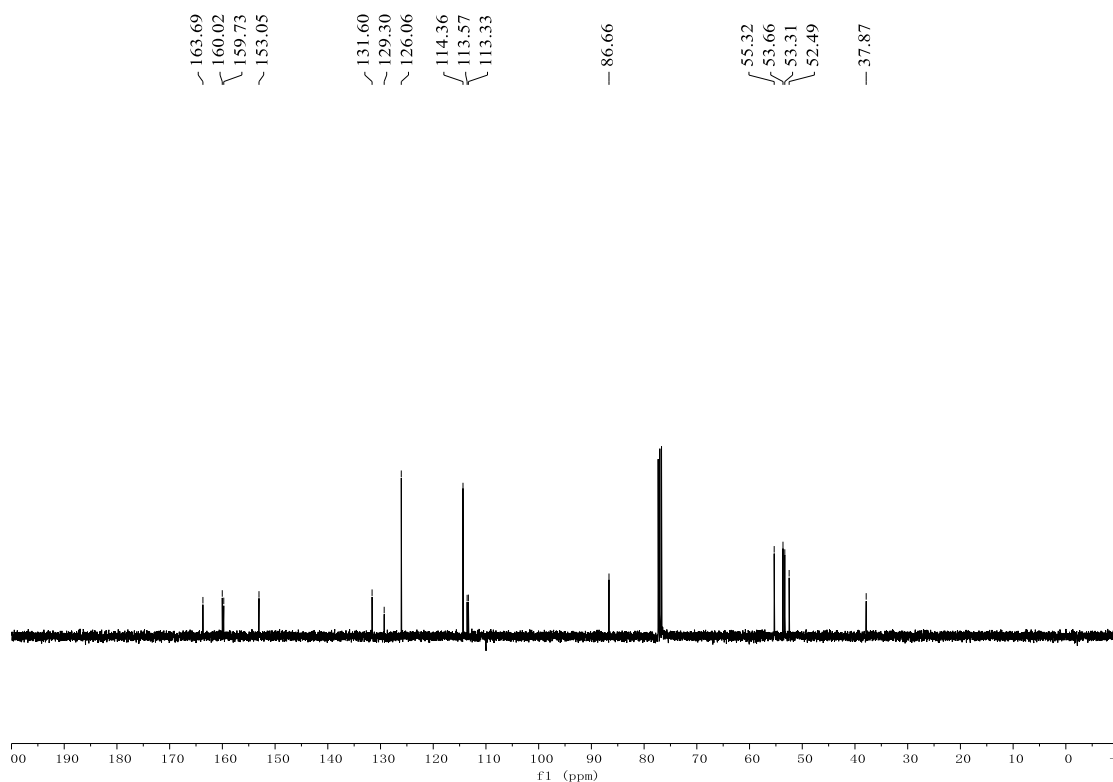
**Dimethyl 3,3-dicyano-5-hydroxy-5-(*p*-tolyl)cyclopent-1-ene-1,2-dicarboxylate (3i):** white solid, 78%, m.p. 141-142 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28-7.27 (m, 2H, ArH), 7.21 (d,  $J = 8.4$  Hz, 2H, ArH), 3.99 (s, 3H,  $\text{OCH}_3$ ), 3.74 (s, 3H,  $\text{OCH}_3$ ), 3.52 (s, 1H, OH), 3.24 (d,  $J = 14.8$  Hz, 1H,  $\text{CH}_2$ ), 2.96 (d,  $J = 14.8$  Hz, 1H,  $\text{CH}_2$ ), 2.36 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.7, 159.7, 152.8, 139.1, 136.8, 129.7, 124.6, 113.6, 113.3, 86.9, 53.7, 53.3, 52.4, 38.0, 21.1. MS ( $m/z$ ): HRMS (ESI) Calcd. for  $\text{C}_{18}\text{H}_{16}\text{NaN}_2\text{O}_5$  ( $[\text{M}+\text{Na}]^+$ ): 363.0957, found: 363.0957.





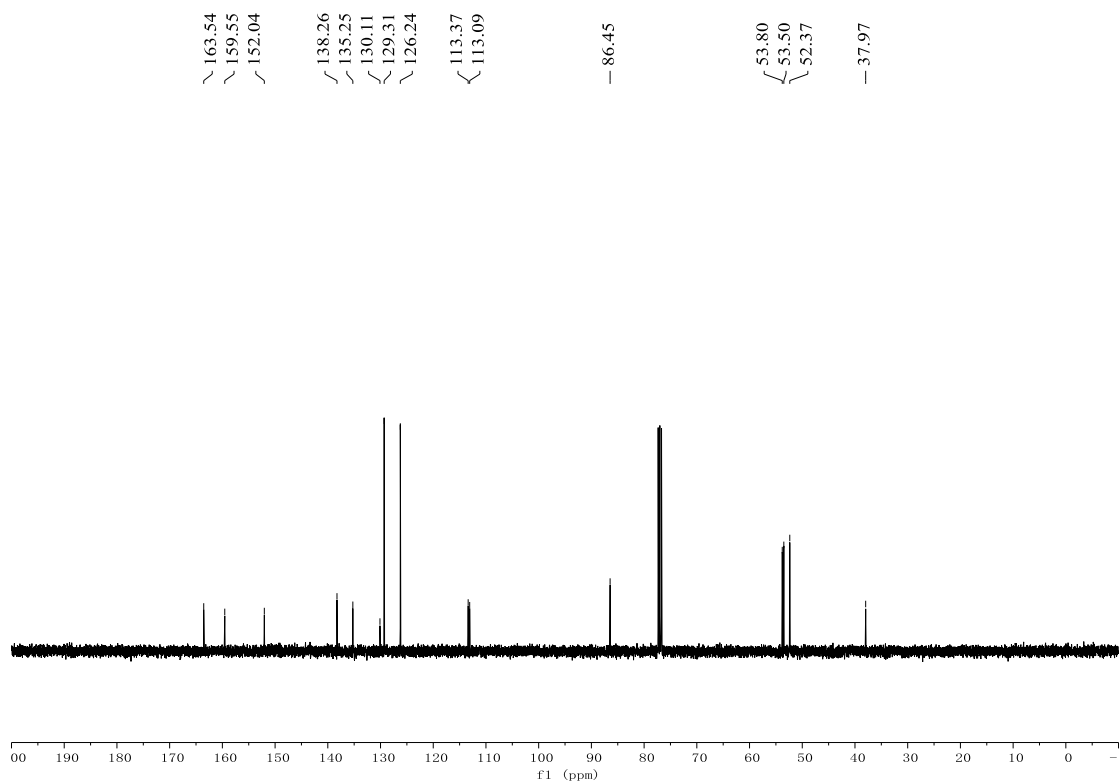
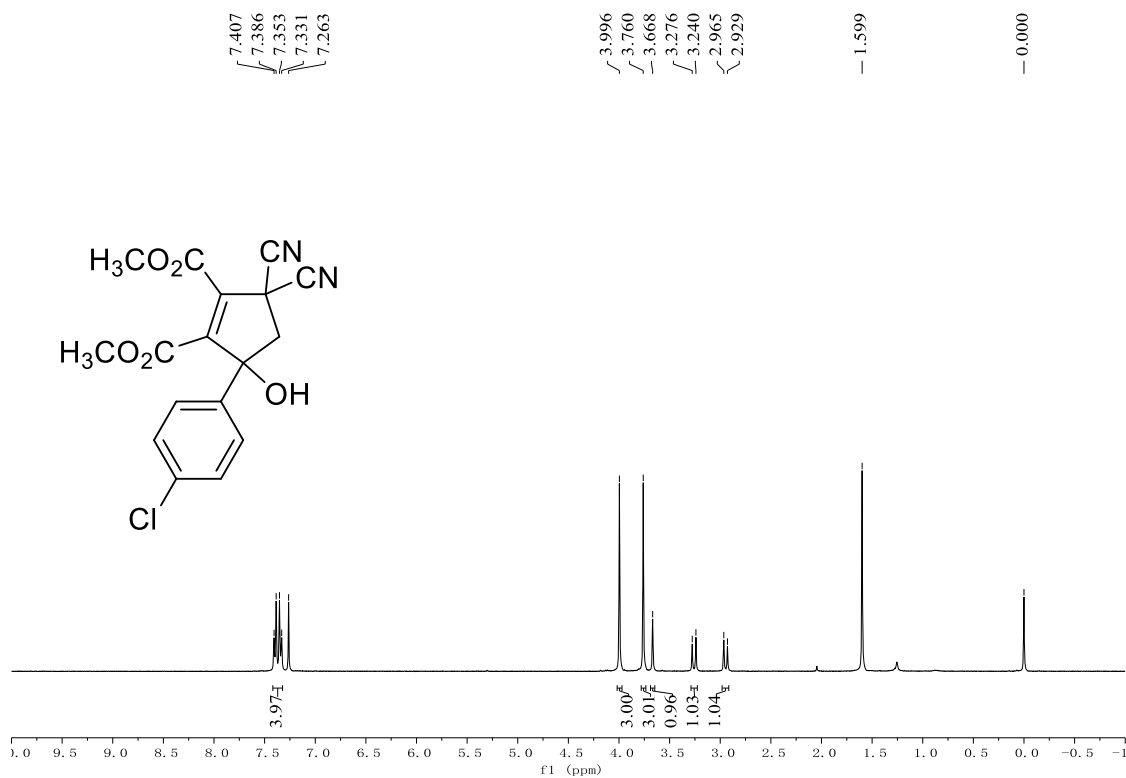
**Dimethyl 3,3-dicyano-5-hydroxy-5-(4-methoxyphenyl)cyclopent-1-ene-1,2-dicarboxylate (3j):** white solid, 80%, m.p. 150-152 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.31 (d, *J* = 8.8 Hz, 2H, ArH), 6.92 (d, *J* = 8.8 Hz, 2H, ArH), 3.98 (s, 3H, OCH<sub>3</sub>), 3.82 (s, 3H, OCH<sub>3</sub>), 3.75 (s, 3H, OCH<sub>3</sub>), 3.49 (s, 1H, OH), 3.23 (d, *J* = 14.4 Hz, 1H, CH<sub>2</sub>), 2.96 (d, *J* = 14.8 Hz, 1H, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.7, 160.0, 159.7, 153.1, 131.6, 129.3, 126.1, 114.4, 113.6, 113.3, 86.7, 55.3, 53.7, 53.3, 52.5, 37.9. MS (*m/z*): HRMS (ESI) Calcd. for C<sub>18</sub>H<sub>16</sub>NaN<sub>2</sub>O<sub>6</sub> ([M+Na]<sup>+</sup>): 379.0906, found: 379.0909.

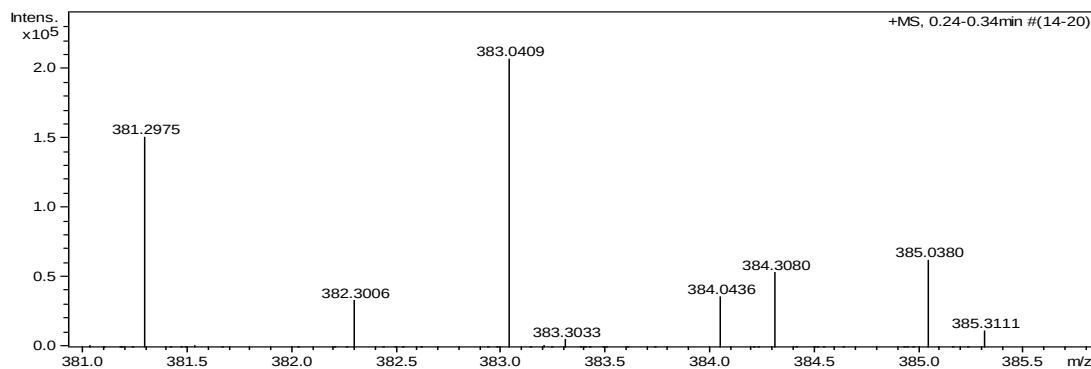




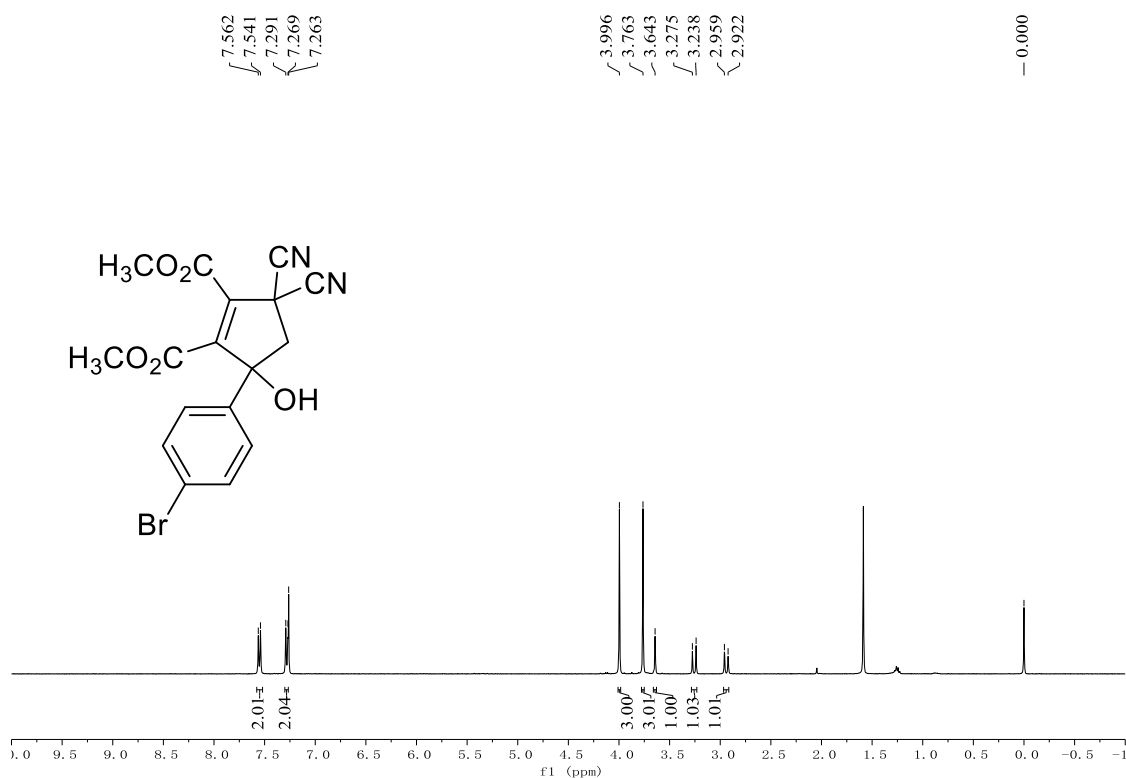
**Dimethyl 3-(4-chlorophenyl)-5,5-dicyano-3-hydroxycyclopent-1-ene-1,2-dicarboxylate (3k):** white solid, 52%, m.p. 176-178 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41-7.33 (m, 4H, ArH), 4.00 (s, 3H,  $\text{OCH}_3$ ), 3.76 (s, 3H,  $\text{OCH}_3$ ), 3.67 (s, 1H, OH), 3.26 (d,  $J = 14.4$  Hz, 1H,  $\text{CH}_2$ ), 2.94 (d,  $J = 14.4$  Hz, 1H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.5, 159.6, 152.0, 138.3, 135.3, 130.1, 129.3, 126.2, 113.4, 113.1, 86.5, 53.8, 53.5, 52.4, 38.0. MS ( $m/z$ ): HRMS (ESI) Calcd. for  $\text{C}_{17}\text{H}_{13}\text{ClNaN}_2\text{O}_5$  ( $[\text{M}+\text{Na}]^+$ ): 383.0411, found: 383.0409.

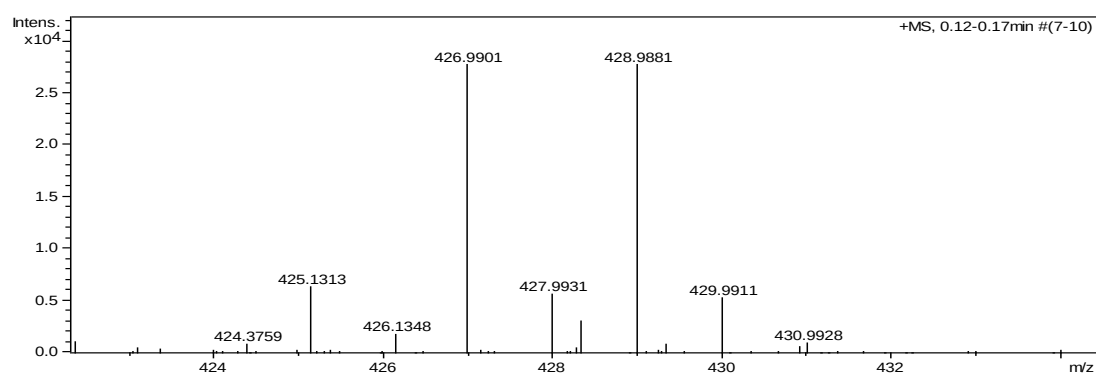
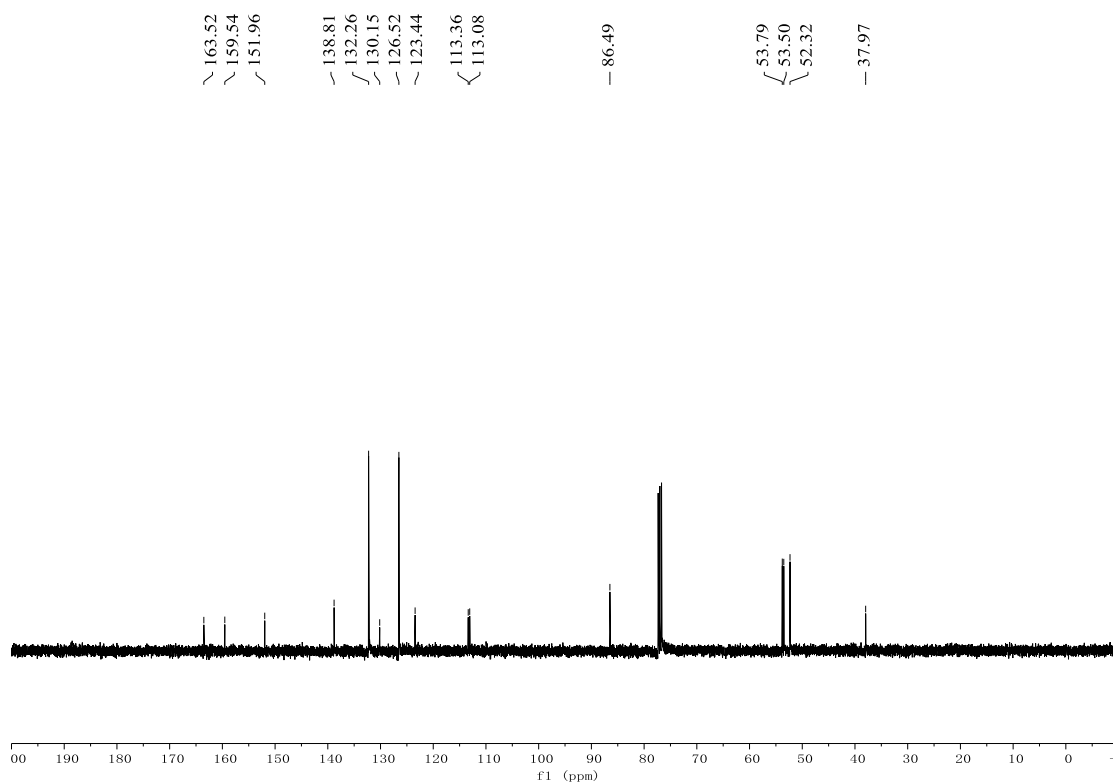






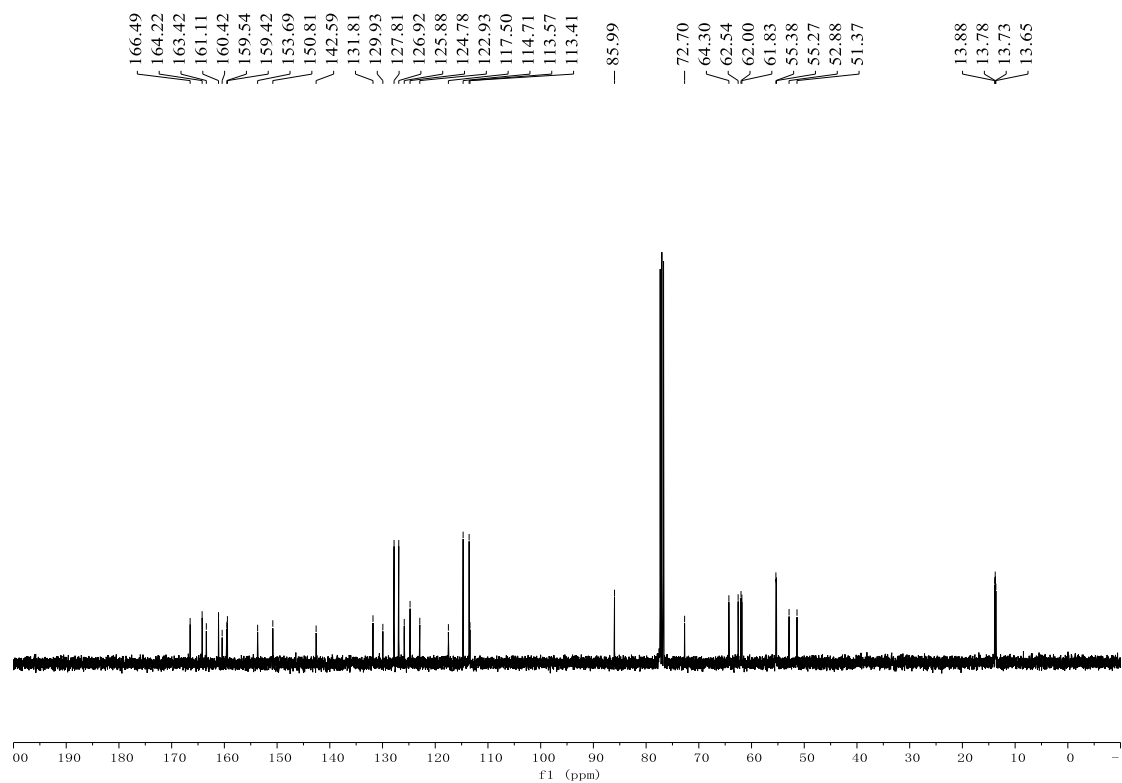
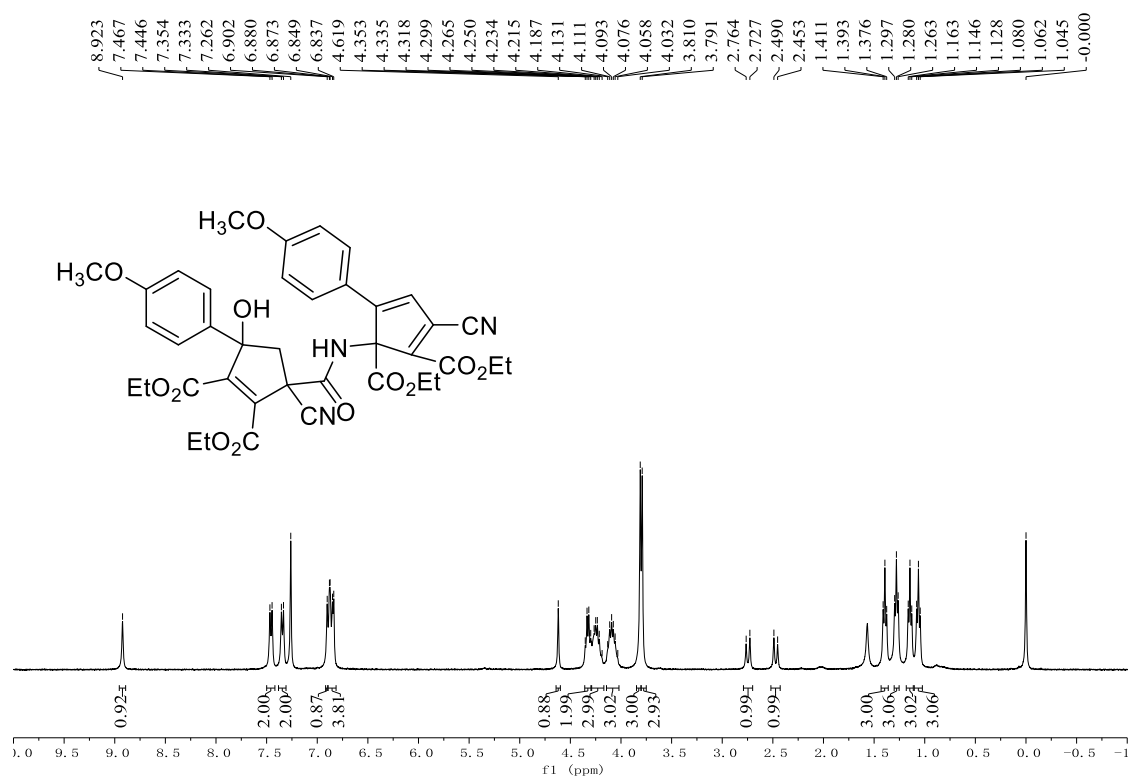
**Dimethyl 3-(4-bromophenyl)-5,5-dicyano-3-hydroxycyclopent-1-ene-1,2-dicarboxylate (3l):** white solid, 55%, m.p. 189-191 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (d,  $J$  = 8.4 Hz, 2H, ArH), 7.28 (d,  $J$  = 8.8 Hz, 2H, ArH), 4.00 (s, 3H,  $\text{OCH}_3$ ), 3.76 (s, 3H,  $\text{OCH}_3$ ), 3.64 (s, 1H, OH), 3.26 (d,  $J$  = 14.8 Hz, 1H,  $\text{CH}_2$ ), 2.94 (d,  $J$  = 14.8 Hz, 1H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.5, 159.5, 152.0, 138.8, 132.3, 130.2, 126.5, 123.4, 113.4, 113.1, 86.5, 53.8, 53.5, 52.3, 38.0. MS ( $m/z$ ): HRMS (ESI) Calcd. for  $\text{C}_{17}\text{H}_{13}\text{BrNaN}_2\text{O}_5$  ( $[\text{M}+\text{Na}]^+$ ): 426.9906, found: 426.9901.

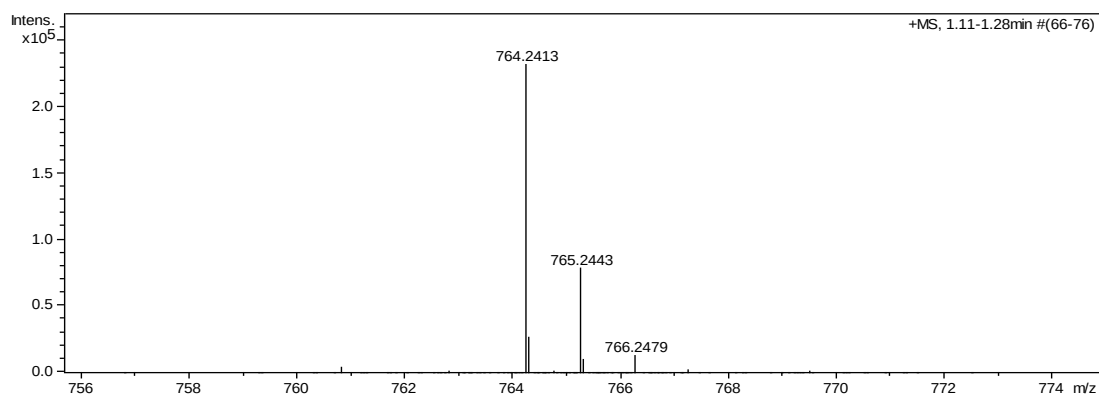




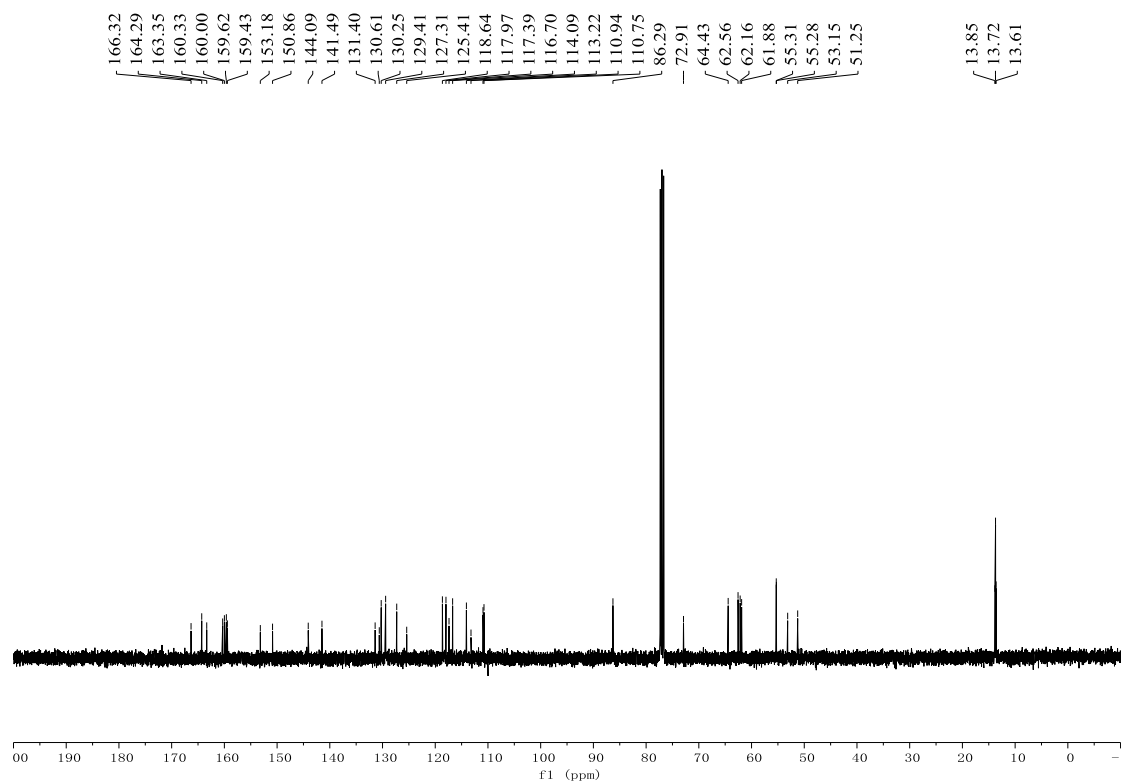
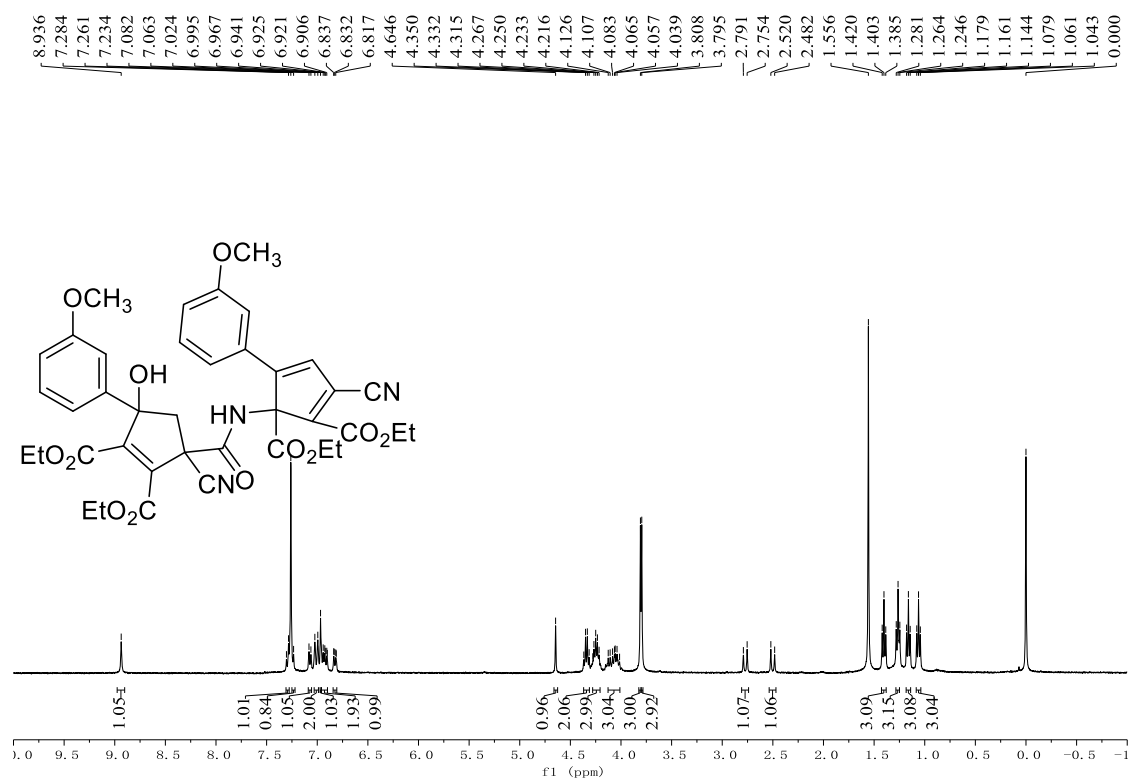
**Diethyl 3-cyano-1-(1-cyano-2,3-bis(ethoxycarbonyl)-4-hydroxy-4-(4-methoxyphenyl)cyclopent-2-ene-1-carboxamido)-5-(4-methoxyphenyl)cyclopenta-2,4-diene-1,2-dicarboxylate (4a):**

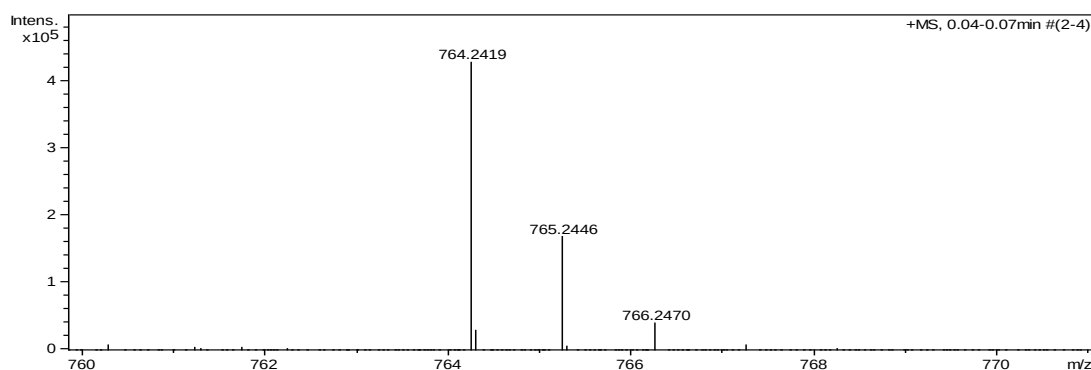
For characterization data set, see main text.



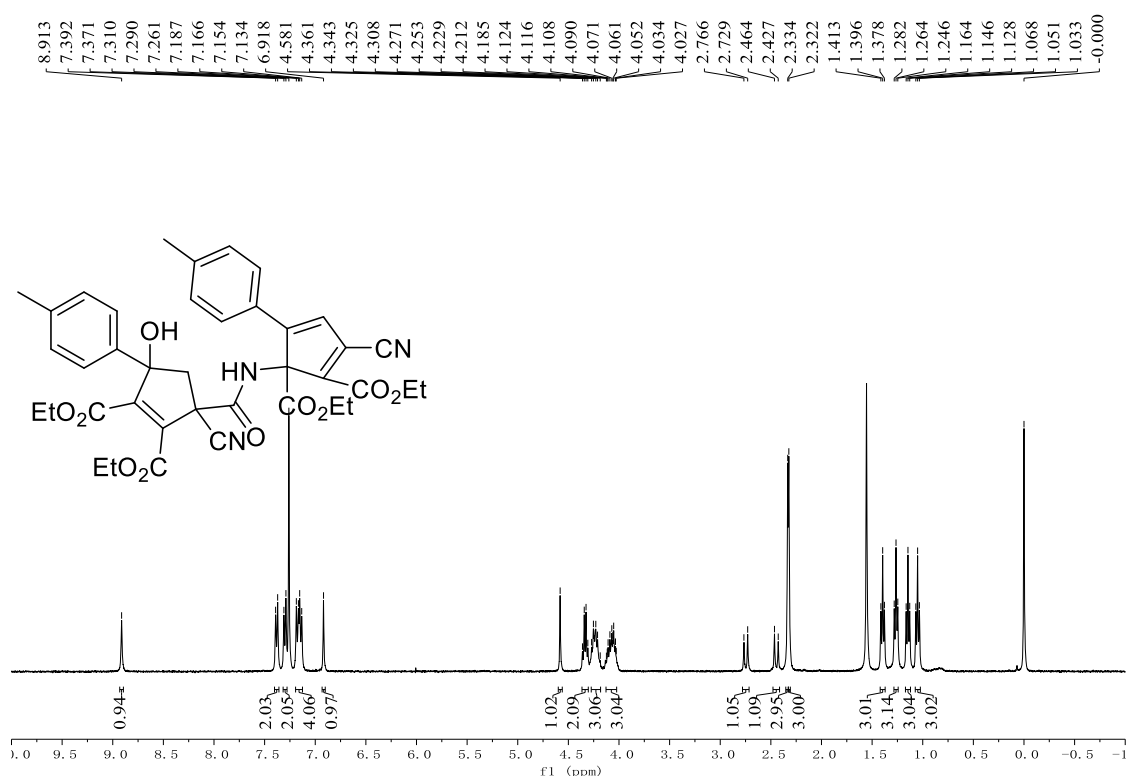


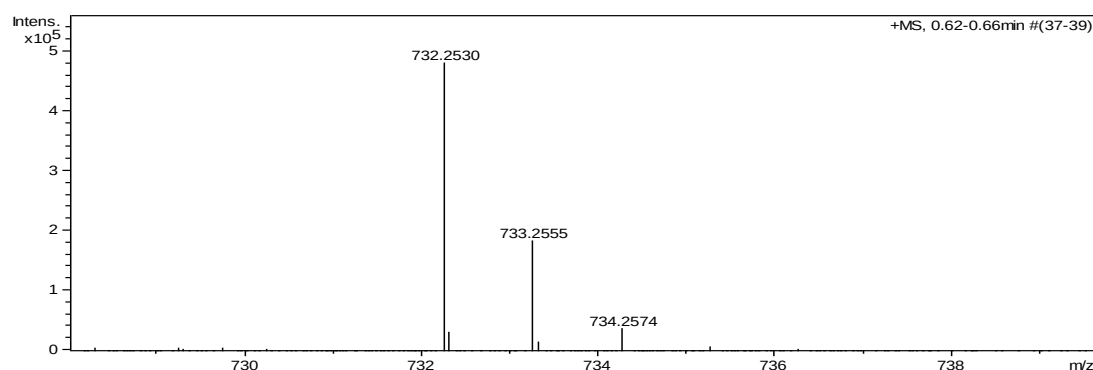
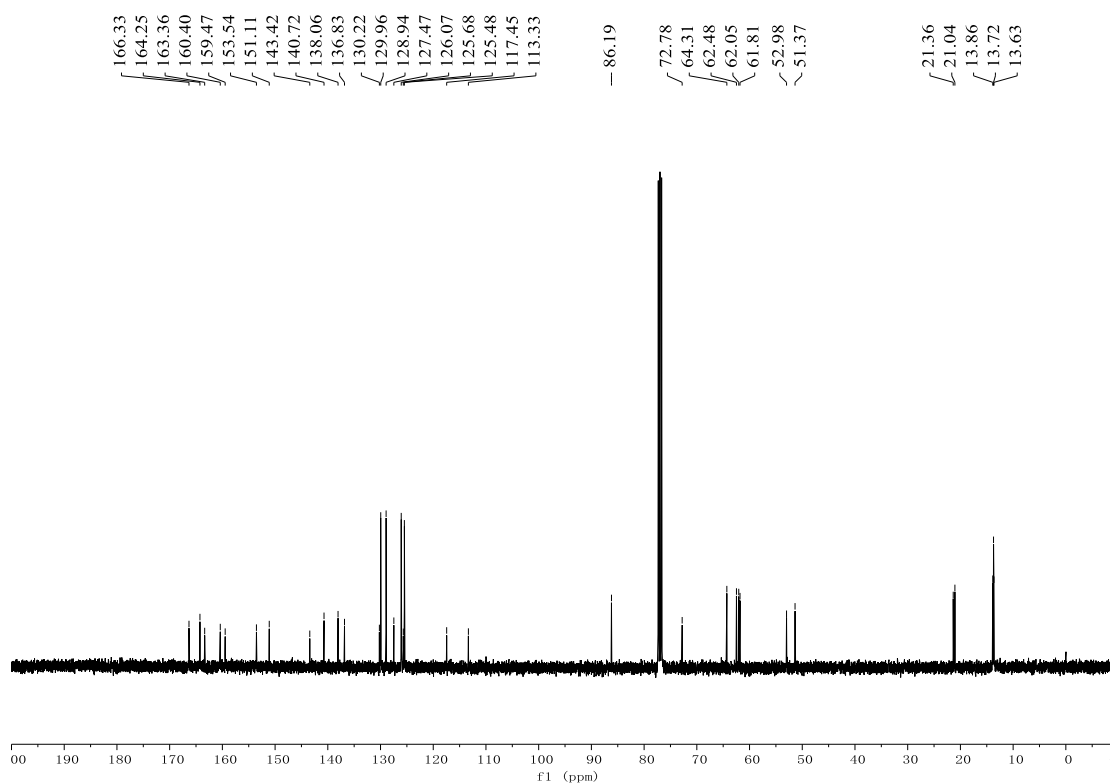
**Diethyl 3-cyano-1-(1-cyano-2,3-bis(ethoxycarbonyl)-4-hydroxy-4-(3-methoxyphenyl)cyclopent-2-ene-1-carboxamido)-5-(3-methoxyphenyl)cyclopenta-2,4-diene-1,2-dicarboxylate (4b):** fluorescent green solid, 40%, m.p. 108-110 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.94 (s, 1H, NH), 7.30-7.28 (m, 1H, ArH), 7.26-7.23 (m, 1H, ArH), 7.07 (d,  $J = 7.6$  Hz, 1H, ArH), 7.01 (d,  $J = 7.6$  Hz, 2H, ArH), 6.97 (s, 1H, CH), 6.94-6.90 (m, 2H, ArH), 6.84-6.81 (m, 1H, ArH), 4.65 (s, 1H, OH), 4.37-4.32 (m, 2H,  $\text{OCH}_2$ ), 4.28-4.22 (m, 3H,  $\text{OCH}_2$ ), 4.13-4.01 (m, 3H,  $\text{OCH}_2$ ), 3.81 (s, 3H,  $\text{OCH}_3$ ), 3.80 (s, 3H,  $\text{OCH}_3$ ), 2.77 (d,  $J = 14.8$  Hz, 1H,  $\text{CH}_2$ ), 2.50 (d,  $J = 15.2$  Hz, 1H,  $\text{CH}_2$ ), 1.40 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ), 1.26 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ), 1.16 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ), 1.06 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.3, 164.3, 163.4, 160.3, 160.0, 159.6, 159.4, 153.2, 150.9, 144.1, 141.5, 131.4, 130.6, 130.3, 129.4, 127.3, 125.4, 118.6, 118.0, 117.4, 116.7, 114.1, 113.2, 110.9, 110.8, 86.3, 72.9, 64.4, 62.6, 62.2, 61.9, 55.3, 55.2, 53.2, 51.3, 13.9, 13.7, 13.6. MS ( $m/z$ ): HRMS (ESI) Calcd. for  $\text{C}_{39}\text{H}_{39}\text{NaN}_3\text{O}_{12}$  ( $[\text{M}+\text{Na}]^+$ ): 764.2431, found: 764.2419.





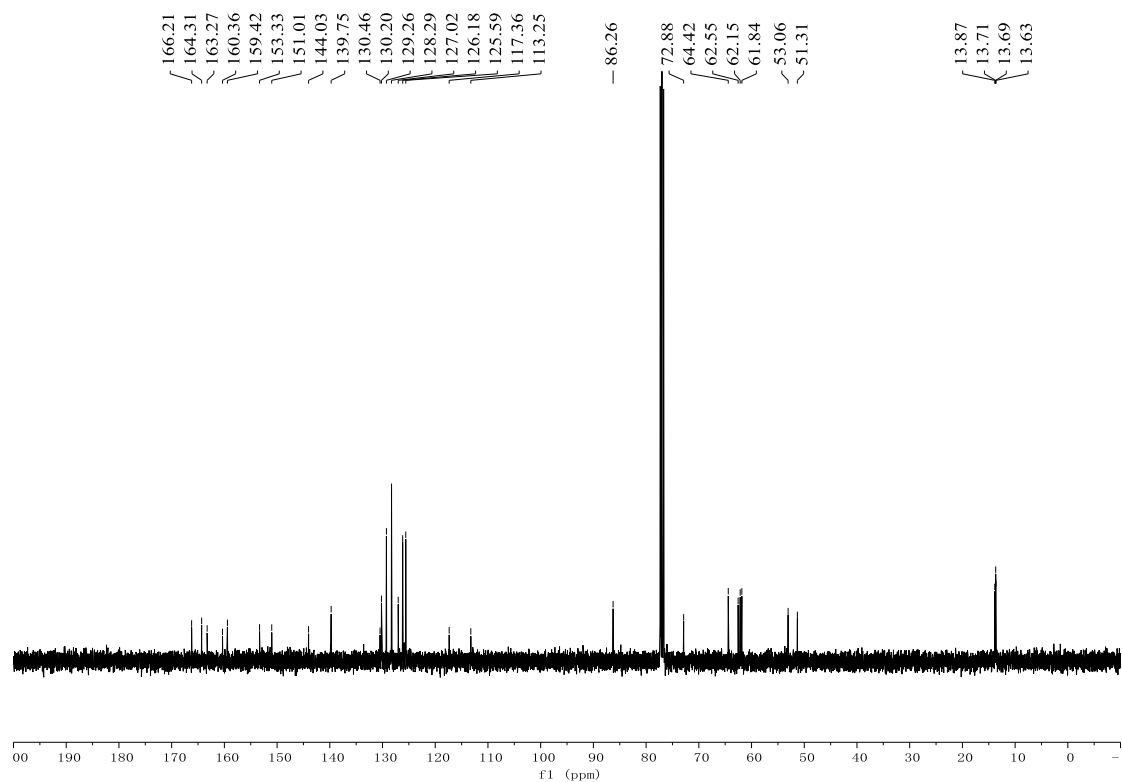
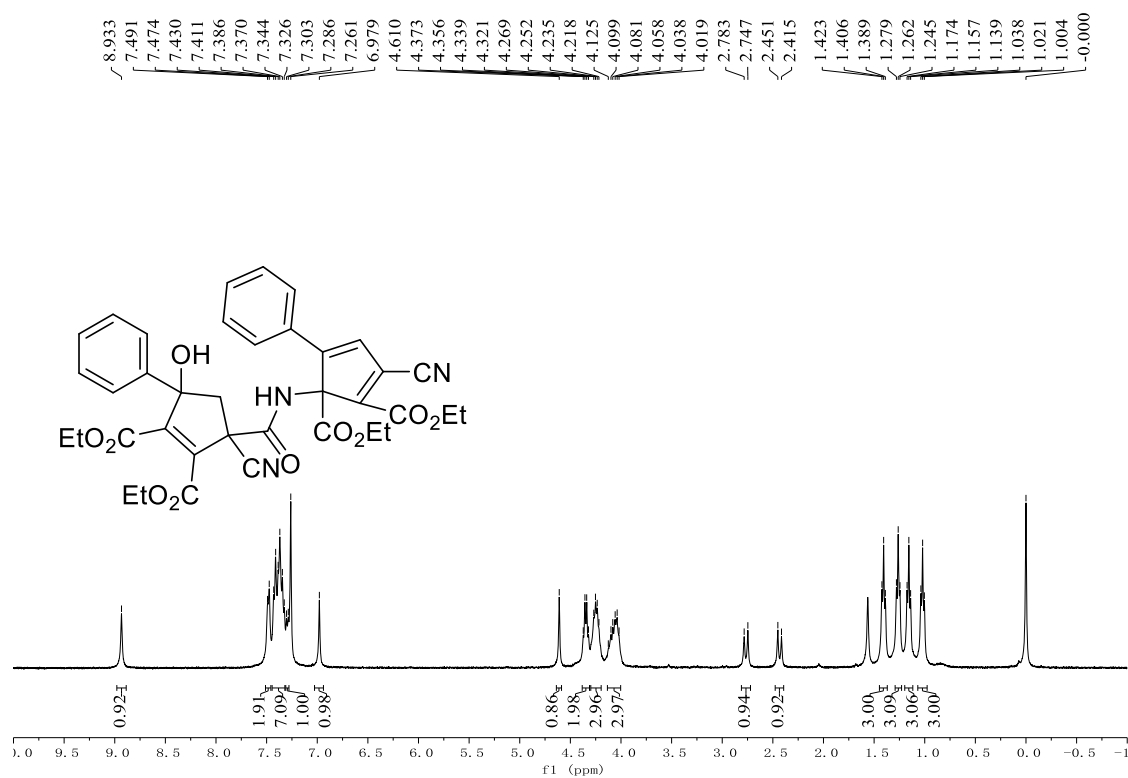
**Diethyl 3-cyano-1-(1-cyano-2,3-bis(ethoxycarbonyl)-4-hydroxy-4-(*p*-tolyl)cyclopent-2-ene-1-carboxamido)-5-(*p*-tolyl)cyclopenta-2,4-diene-1,2-dicarboxylate (4c):** fluorescent green solid, 60%, m.p. 178-180 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.91 (s, 1H, NH), 7.38 (d,  $J = 8.4$  Hz, 2H, ArH), 7.30 (d,  $J = 8.0$  Hz, 2H, ArH), 7.19-7.13 (m, 4H, ArH), 6.92 (s, 1H, CH), 4.58 (s, 1H, OH), 4.36-4.31 (m, 2H,  $\text{OCH}_2$ ), 4.27-4.19 (m, 3H,  $\text{OCH}_2$ ), 4.12-4.03 (m, 3H,  $\text{OCH}_2$ ), 2.75 (d,  $J = 14.8$  Hz, 1H,  $\text{CH}_2$ ), 2.44 (d,  $J = 14.8$  Hz, 1H,  $\text{CH}_2$ ), 2.33 (s, 3H,  $\text{CH}_3$ ), 2.32 (s, 3H,  $\text{CH}_3$ ), 1.40 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ), 1.26 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ), 1.15 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ), 1.05 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.3, 164.3, 163.4, 160.4, 159.5, 153.5, 151.1, 143.4, 140.7, 138.1, 136.8, 130.2, 130.0, 128.9, 127.5, 126.1, 125.7, 125.5, 117.5, 113.3, 86.2, 72.8, 64.3, 62.5, 62.1, 61.8, 53.0, 51.4, 21.4, 21.0, 13.9, 13.7, 13.6. MS ( $m/z$ ): HRMS (ESI) Calcd. for  $\text{C}_{39}\text{H}_{39}\text{NaN}_3\text{O}_{10}$  ( $[\text{M}+\text{Na}]^+$ ): 732.2533, found: 732.2530.

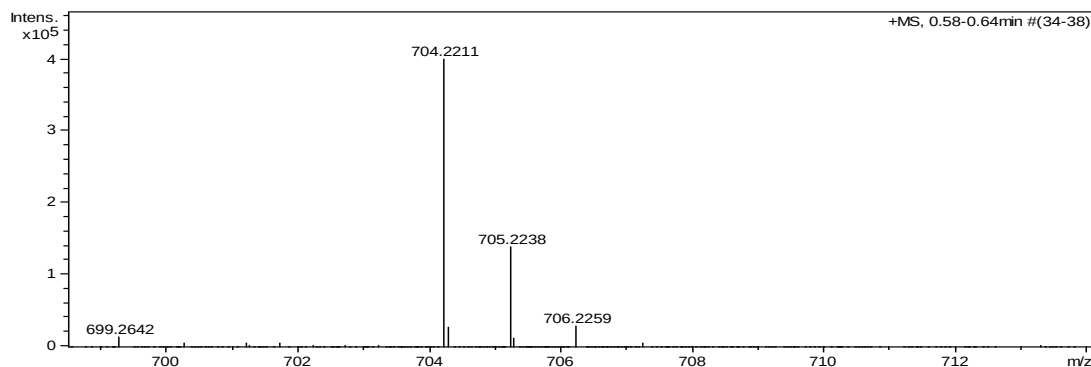




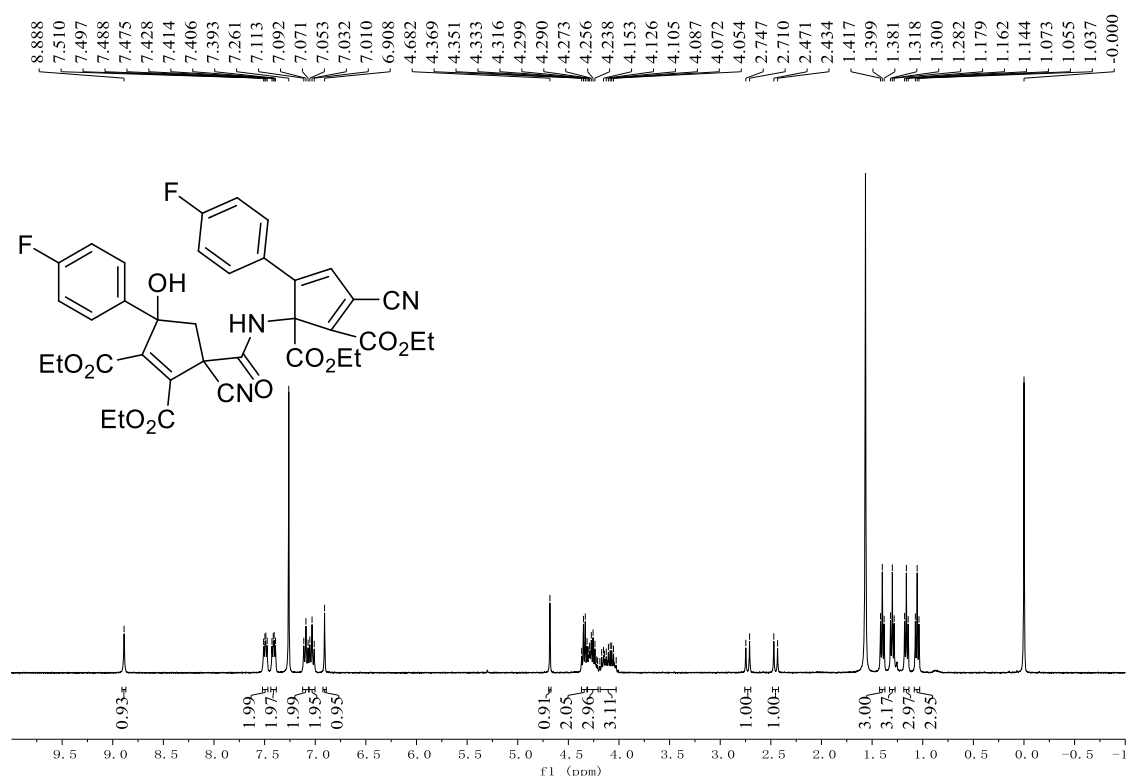
**Diethyl 3-cyano-1-(1-cyano-2,3-bis(ethoxycarbonyl)-4-hydroxy-4-phenylcyclopent-2-ene-1-carboxamido)-5-phenylcyclopenta-2,4-diene-1,2-dicarboxylate (4d):** fluorescent green solid, 56%, m.p. 169-171 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.93 (s, 1H, NH), 7.49-7.47 (m, 2H, ArH), 7.43-7.33 (m, 7H, ArH), 7.29 (d,  $J$  = 6.8 Hz, 1H, ArH), 6.98 (s, 1H, CH), 4.61 (s, 1H, OH), 4.37-4.32 (m, 2H,  $\text{OCH}_2$ ), 4.27-4.22 (m, 3H,  $\text{OCH}_2$ ), 4.13-4.02 (m, 3H,  $\text{OCH}_2$ ), 2.76 (d,  $J$  = 14.4 Hz, 1H,  $\text{CH}_2$ ), 2.43 (d,  $J$  = 14.4 Hz, 1H,  $\text{CH}_2$ ), 1.41 (t,  $J$  = 7.2 Hz, 3H,  $\text{CH}_3$ ), 1.26 (t,  $J$  = 7.2 Hz, 3H,  $\text{CH}_3$ ), 1.16 (t,  $J$  = 7.2 Hz, 3H,  $\text{CH}_3$ ), 1.02 (t,  $J$  = 7.2 Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.2, 164.3, 163.3, 160.4, 159.4, 153.3, 151.0, 144.0, 139.8, 130.5, 130.2, 129.3, 128.3, 127.0, 126.2, 125.6, 117.4, 113.3, 86.3, 72.9, 64.4, 62.6, 62.2, 61.8, 53.1, 51.3, 13.9, 13.8, 13.7, 13.6. MS ( $m/z$ ): HRMS (ESI) Calcd. for  $\text{C}_{39}\text{H}_{39}\text{N}_3\text{O}_{12}$  ( $[\text{M}+\text{Na}]^+$ ): 704.2220, found: 704.2211.

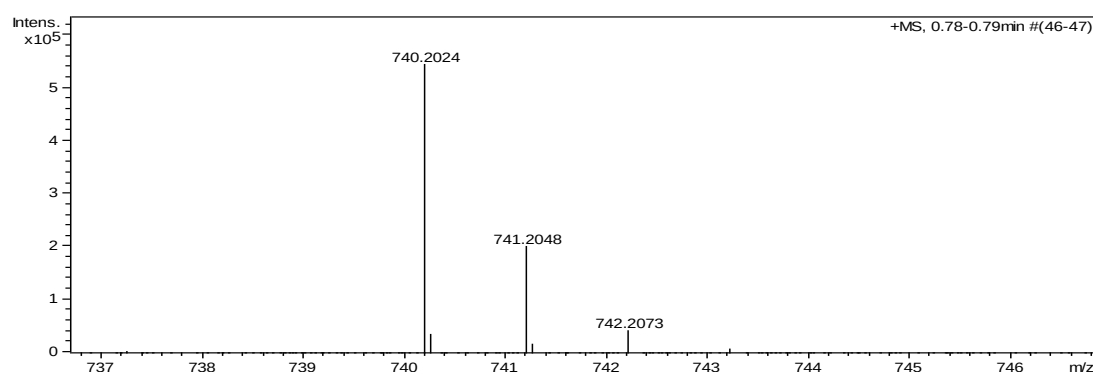
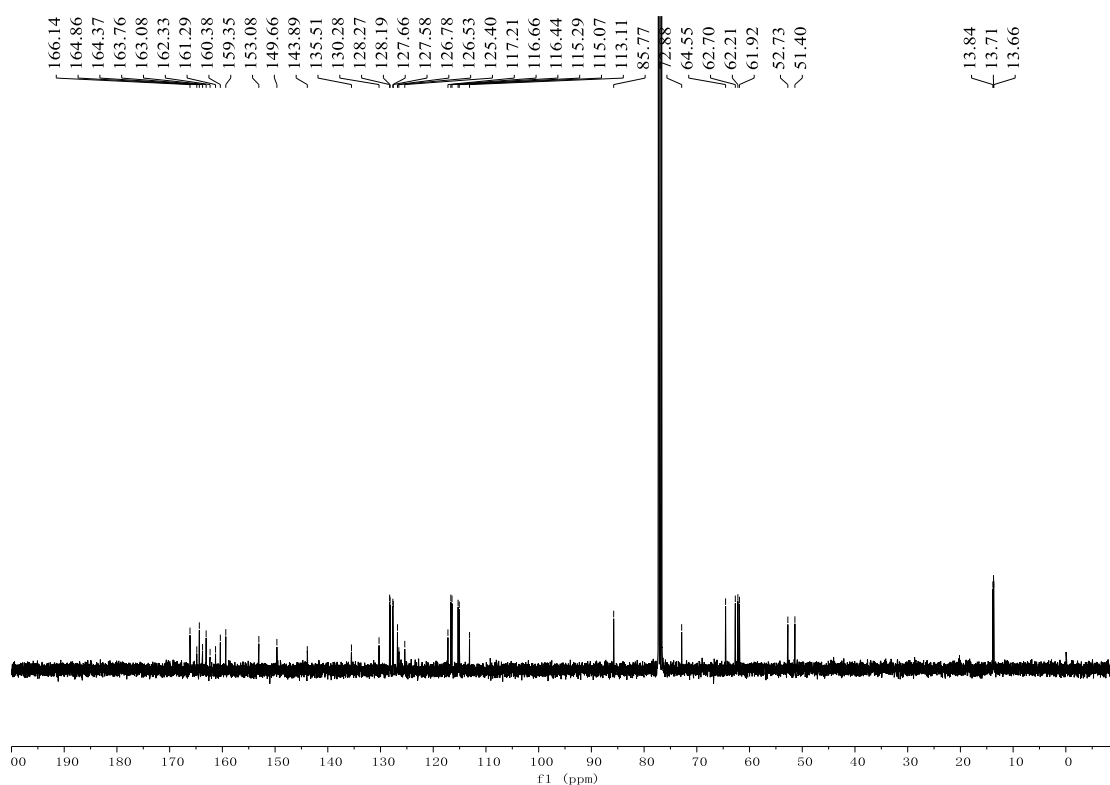




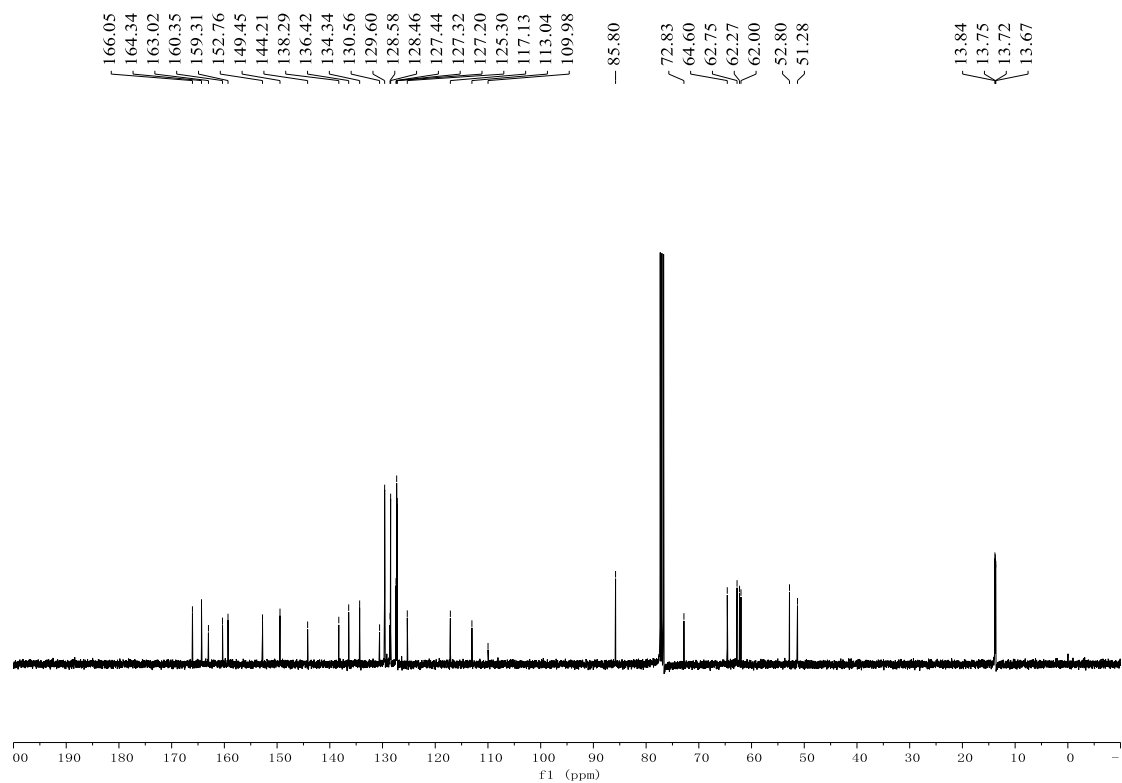
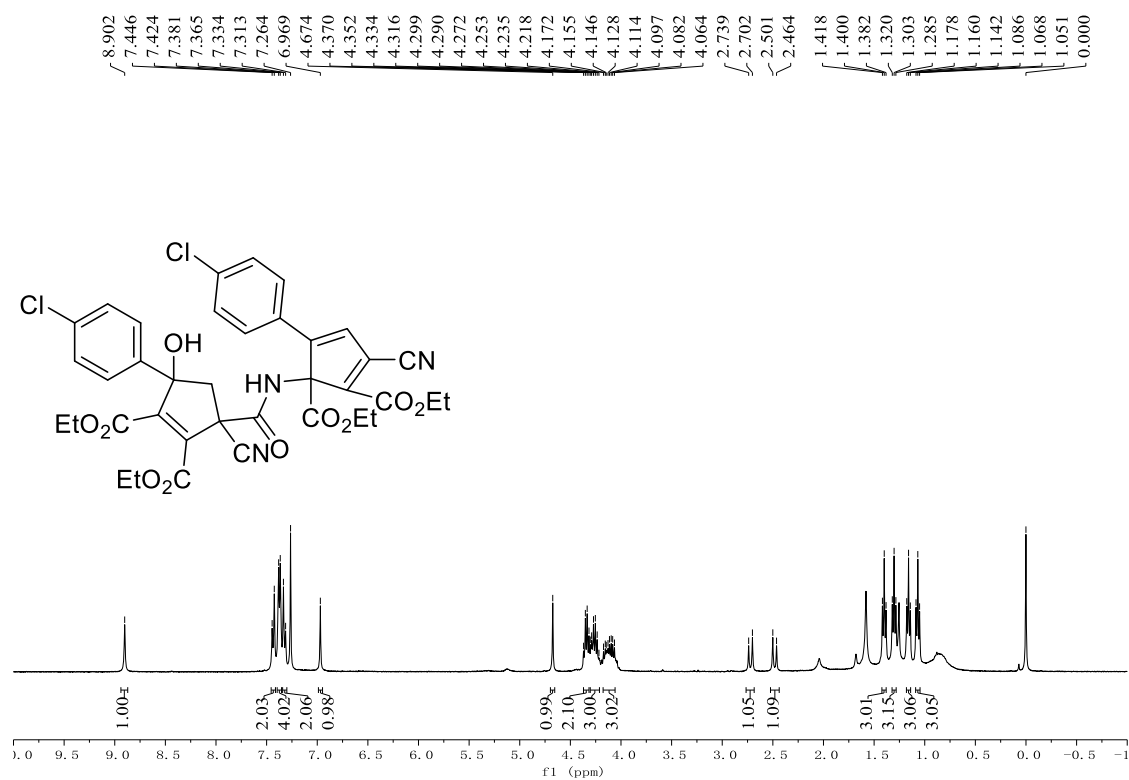


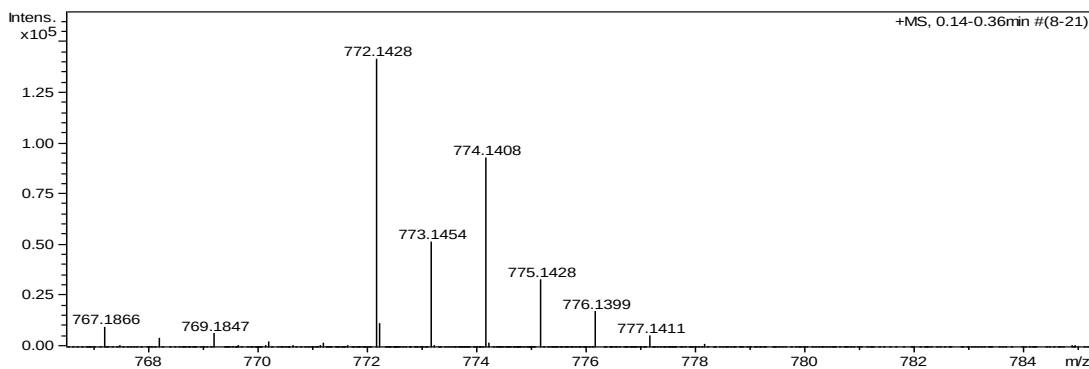
**Diethyl 3-cyano-1-(1-cyano-2,3-bis(ethoxycarbonyl)-4-(4-fluorophenyl)-4-hydroxycyclopent-2-ene-1-carboxamido)-5-(4-fluorophenyl)cyclopenta-2,4-diene-1,2-dicarboxylate (4e):** pale green solid, 35%, m.p. 198-200 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.89 (s, 1H, NH), 7.51-7.48 (m, 2H, ArH), 7.43-7.39 (m, 2H, ArH), 7.09 (t,  $J = 8.4$  Hz, 2H, ArH), 7.03 (t,  $J = 8.4$  Hz, 2H, ArH), 6.91 (s, 1H, CH), 4.68 (s, 1H, OH), 4.37-4.32 (m, 2H,  $\text{OCH}_2$ ), 4.29-4.21 (m, 3H,  $\text{OCH}_2$ ), 4.19-4.03 (m, 3H,  $\text{OCH}_2$ ), 2.73 (d,  $J = 14.8$  Hz, 1H,  $\text{CH}_2$ ), 2.45 (d,  $J = 14.8$  Hz, 1H,  $\text{CH}_2$ ), 1.40 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ), 1.30 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ), 1.16 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ), 1.06 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.1, 164.9, 164.4, 163.8, 163.1, 162.3, 161.3, 160.4, 159.4, 153.1, 149.7, 143.9, 135.5, 130.3, 128.3, 128.2, 127.8, 127.6, 126.8, 126.5, 125.4, 117.2, 116.7, 116.4, 115.3, 115.1, 113.1, 85.8, 72.9, 64.6, 62.7, 62.2, 61.9, 52.7, 51.4, 13.8, 13.7, 13.6. MS ( $m/z$ ): HRMS (ESI) Calcd. for  $\text{C}_{37}\text{H}_{33}\text{F}_2\text{N}_3\text{O}_{10}$  ( $[\text{M}+\text{Na}]^+$ ): 740.2032, found: 740.2024.



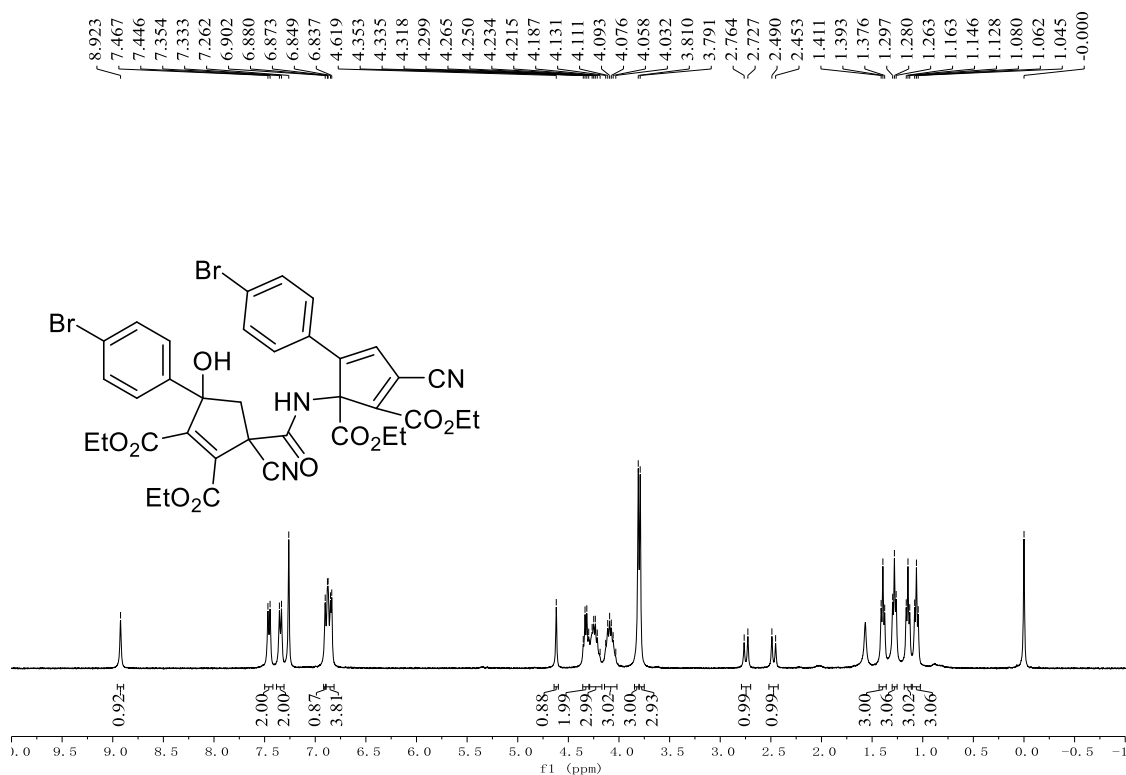


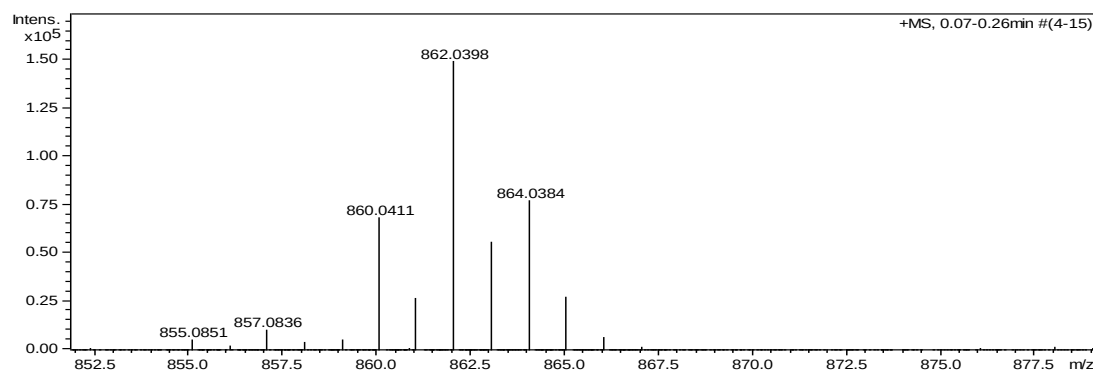
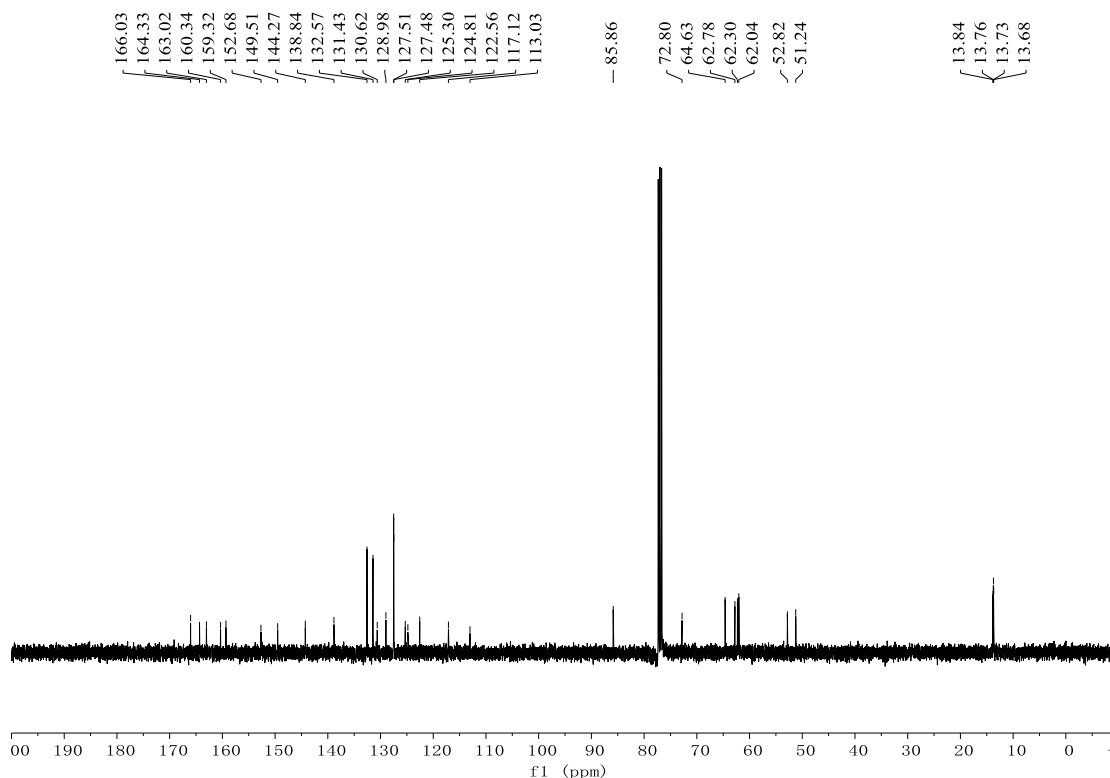
**Diethyl 5-(4-chlorophenyl)-1-(4-(4-chlorophenyl)-1-cyano-2,3-bis(ethoxycarbonyl)-4-hydroxycyclopent-2-ene-1-carboxamido)-3-cyanocyclopenta-2,4-diene-1,2-dicarboxylate (4f):** pale green solid, 42%, m.p. 197-199 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.90 (s, 1H, NH), 7.45-7.42 (m, 2H, ArH), 7.37 (d,  $J$  = 6.4 Hz, 4H, ArH), 7.33-7.31 (m, 2H, ArH), 6.97 (s, 1H, CH), 4.67 (s, 1H, OH), 4.37-4.32 (m, 2H,  $\text{OCH}_2$ ), 4.30-4.22 (m, 3H,  $\text{OCH}_2$ ), 4.17-4.06 (m, 3H,  $\text{OCH}_2$ ), 2.72 (d,  $J$  = 14.8 Hz, 1H,  $\text{CH}_2$ ), 2.48 (d,  $J$  = 14.8 Hz, 1H,  $\text{CH}_2$ ), 1.40 (t,  $J$  = 7.2 Hz, 3H,  $\text{CH}_3$ ), 1.30 (t,  $J$  = 7.2 Hz, 3H,  $\text{CH}_3$ ), 1.16 (t,  $J$  = 7.2 Hz, 3H,  $\text{CH}_3$ ), 1.07 (t,  $J$  = 7.2 Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.1, 164.3, 163.0, 160.4, 159.3, 152.8, 149.5, 144.2, 138.3, 136.4, 134.3, 130.6, 129.6, 128.6, 128.5, 127.4, 127.3, 127.2, 125.3, 117.1, 113.0, 110.0, 85.8, 72.8, 64.6, 62.8, 62.3, 62.0, 52.8, 51.3, 13.9, 13.8, 13.7, 13.6. MS ( $m/z$ ): HRMS (ESI) Calcd. for  $\text{C}_{37}\text{H}_{33}\text{N}_3\text{O}_{10}$  ( $[\text{M}+\text{Na}]^+$ ): 772.1441, found: 772.1428.



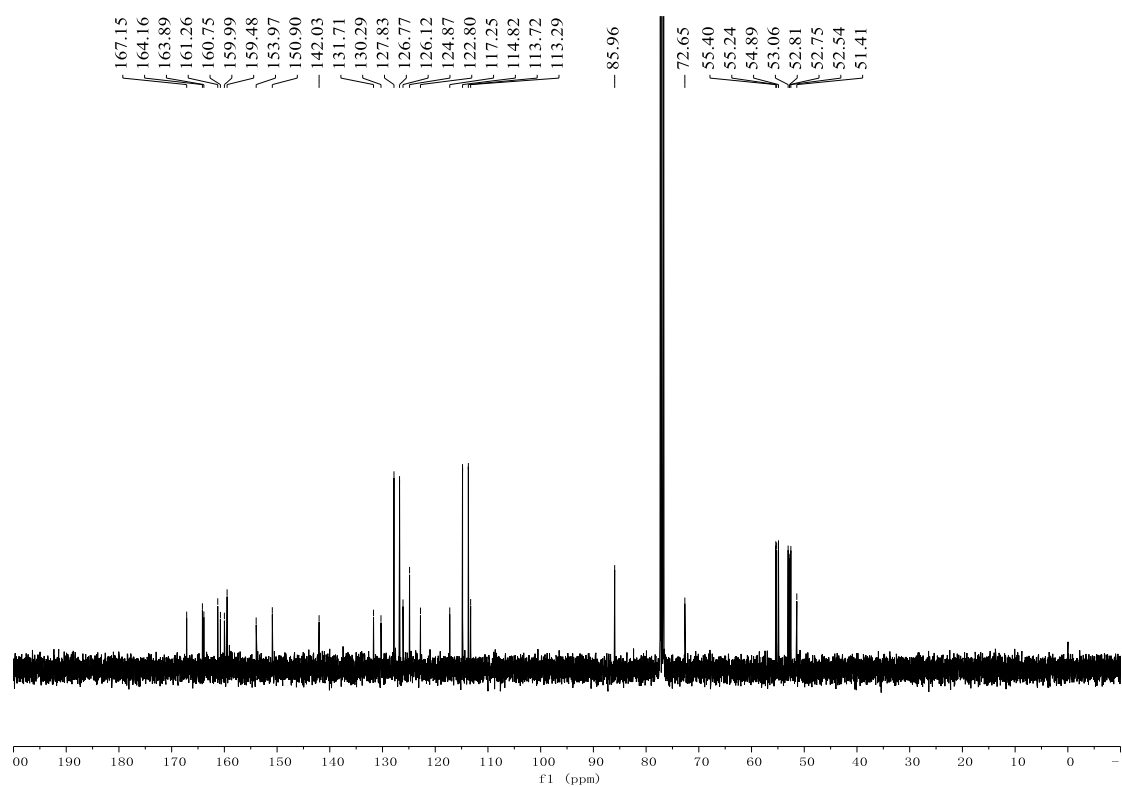
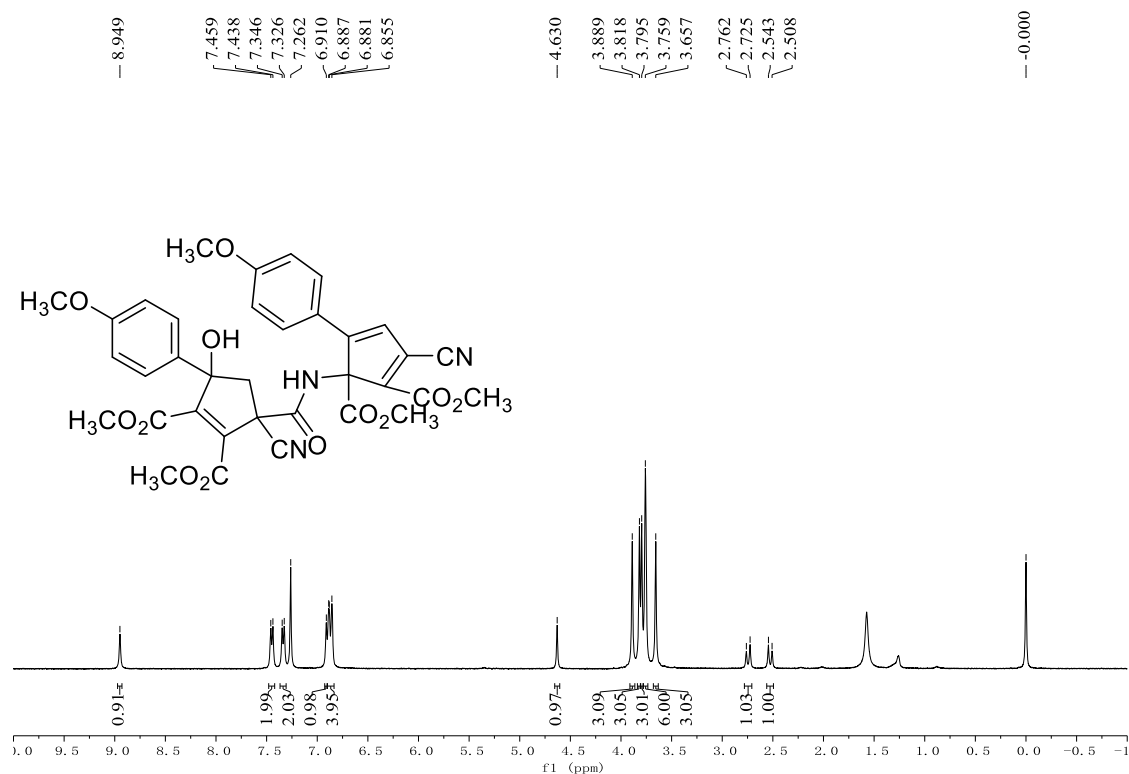


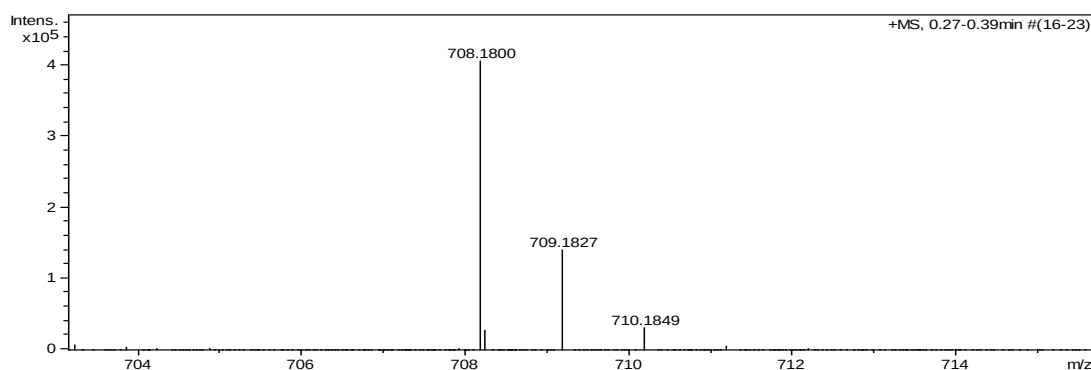
**Diethyl 5-(4-bromophenyl)-1-(4-(4-bromophenyl)-1-cyano-2,3-bis(ethoxycarbonyl)-4-hydroxycyclopent-2-ene-1-carboxamido)-3-cyanocyclopenta-2,4-diene-1,2-dicarboxylate (4g):** pale green solid, 46%, m.p. 199-201 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.89 (s, 1H, NH), 7.54-7.47 (m, 4H, ArH), 7.37-7.30 (m, 4H, ArH), 6.98 (s, 1H, CH), 4.66 (s, 1H, OH), 4.37-4.23 (m, 5H, OCH<sub>2</sub>), 4.17-4.07 (m, 3H, OCH<sub>2</sub>), 2.72 (d, *J* = 14.8 Hz, 1H, CH<sub>2</sub>), 2.49 (d, *J* = 15.2 Hz, 1H, CH<sub>2</sub>), 1.40 (t, *J* = 7.2 Hz, 3H, CH<sub>3</sub>), 1.30 (t, *J* = 7.2 Hz, 3H, CH<sub>3</sub>), 1.16 (t, *J* = 7.2 Hz, 3H, CH<sub>3</sub>), 1.07 (t, *J* = 7.2 Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 166.0, 164.3, 163.0, 160.3, 159.3, 152.7, 149.5, 144.3, 138.8, 132.6, 131.4, 130.6, 129.0, 127.5, 127.4, 125.3, 124.8, 122.6, 117.1, 113.0, 85.9, 72.8, 64.6, 62.8, 62.3, 62.0, 52.8, 51.2, 13.9, 13.8, 13.7, 13.6. MS (*m/z*): HRMS (ESI) Calcd. for C<sub>37</sub>H<sub>33</sub>Br<sub>2</sub>NaN<sub>3</sub>O<sub>10</sub> ([M+Na]<sup>+</sup>): 860.0430, found: 860.0411.



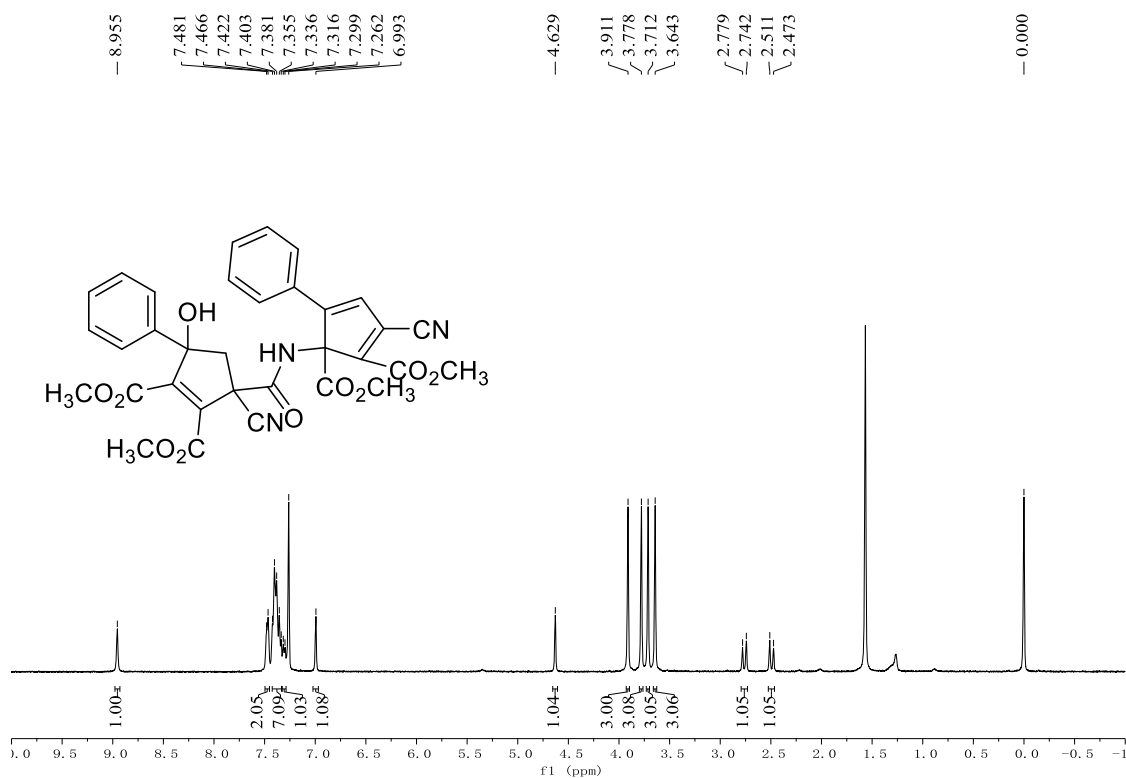


**Dimethyl 3-cyano-1-(1-cyano-4-hydroxy-2,3-bis(methoxycarbonyl)-4-(4-methoxyphenyl)cyclopent-2-ene-1-carboxamido)-5-(4-methoxyphenyl)cyclopenta-2,4-diene-1,2-dicarboxylate (4h):** yellow solid, 54%, m.p. 172-174 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.95 (s, 1H, NH), 7.45 (d,  $J$  = 8.4 Hz, 2H, ArH), 7.34 (d,  $J$  = 8.0 Hz, 2H, ArH), 6.91 (s, 1H, CH), 6.89-6.86 (m, 4H, ArH), 4.63 (s, 1H, OH), 3.89 (s, 3H,  $\text{OCH}_3$ ), 3.82 (s, 3H,  $\text{OCH}_3$ ), 3.80 (s, 3H,  $\text{OCH}_3$ ), 3.76 (s, 6H,  $\text{OCH}_3$ ), 3.66 (s, 3H,  $\text{OCH}_3$ ), 2.74 (d,  $J$  = 14.8 Hz, 1H,  $\text{CH}_2$ ), 2.53 (d,  $J$  = 14.0 Hz, 1H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.2, 164.2, 163.9, 161.3, 160.8, 160.0, 159.5, 154.0, 150.9, 142.0, 131.7, 130.3, 127.8, 126.8, 126.1, 124.9, 122.8, 117.3, 114.8, 113.7, 113.3, 86.0, 72.7, 55.4, 55.2, 54.9, 53.1, 52.8, 52.7, 52.5, 51.4. MS ( $m/z$ ): HRMS (ESI) Calcd. for  $\text{C}_{35}\text{H}_{31}\text{N}_3\text{O}_{12}$  ( $[\text{M}+\text{Na}]^+$ ): 708.1805, found: 708.1800.

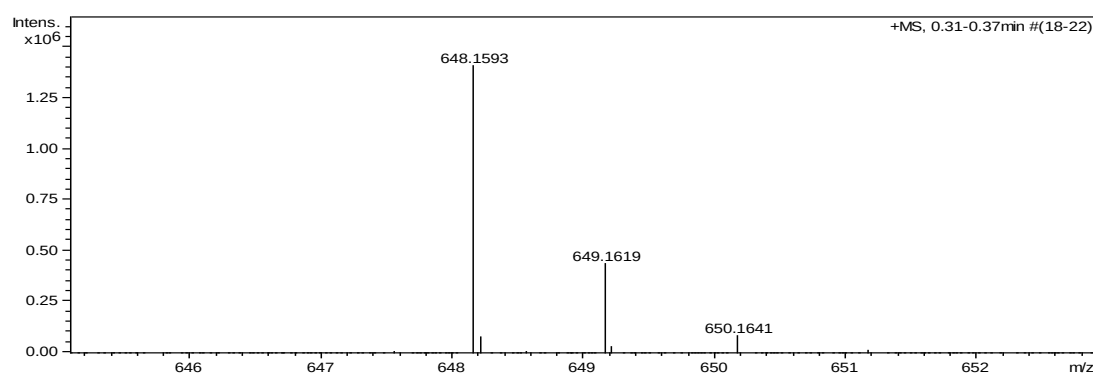
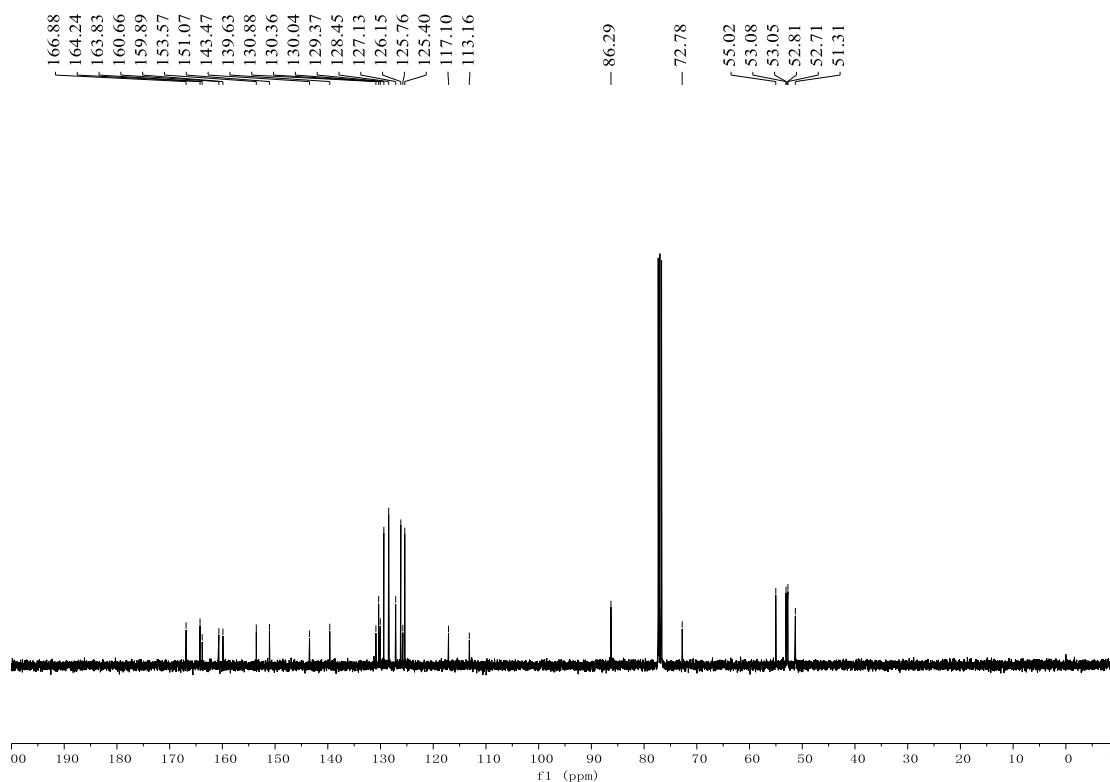




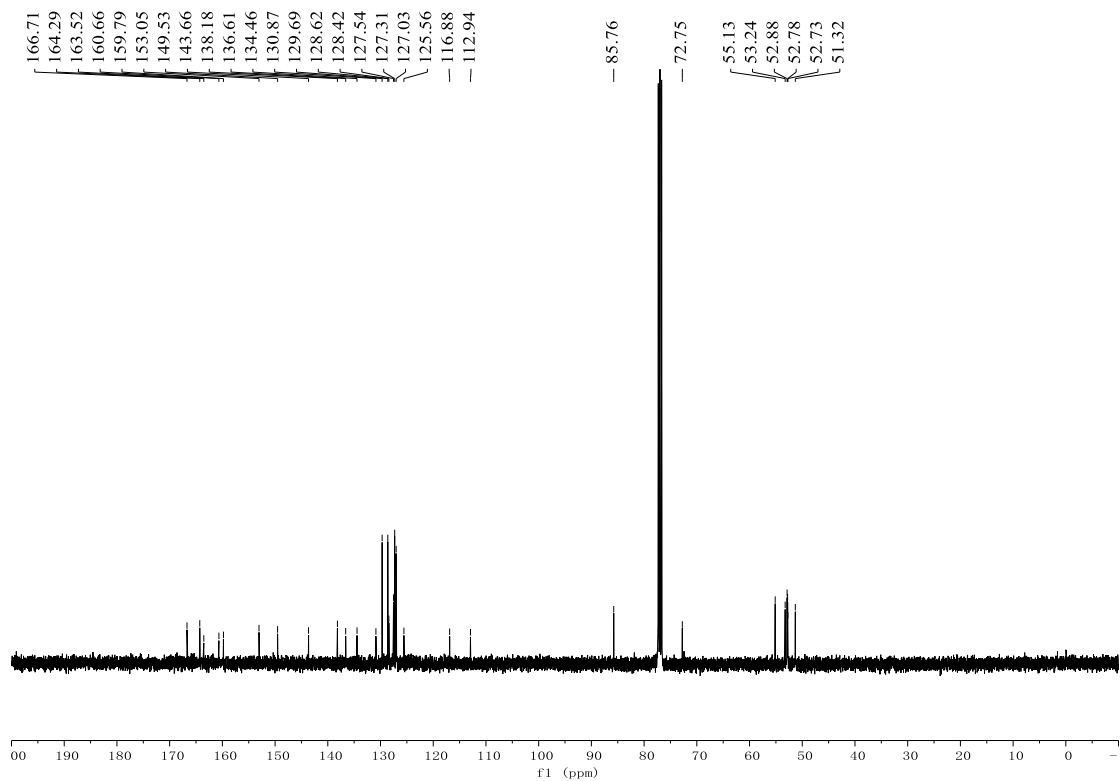
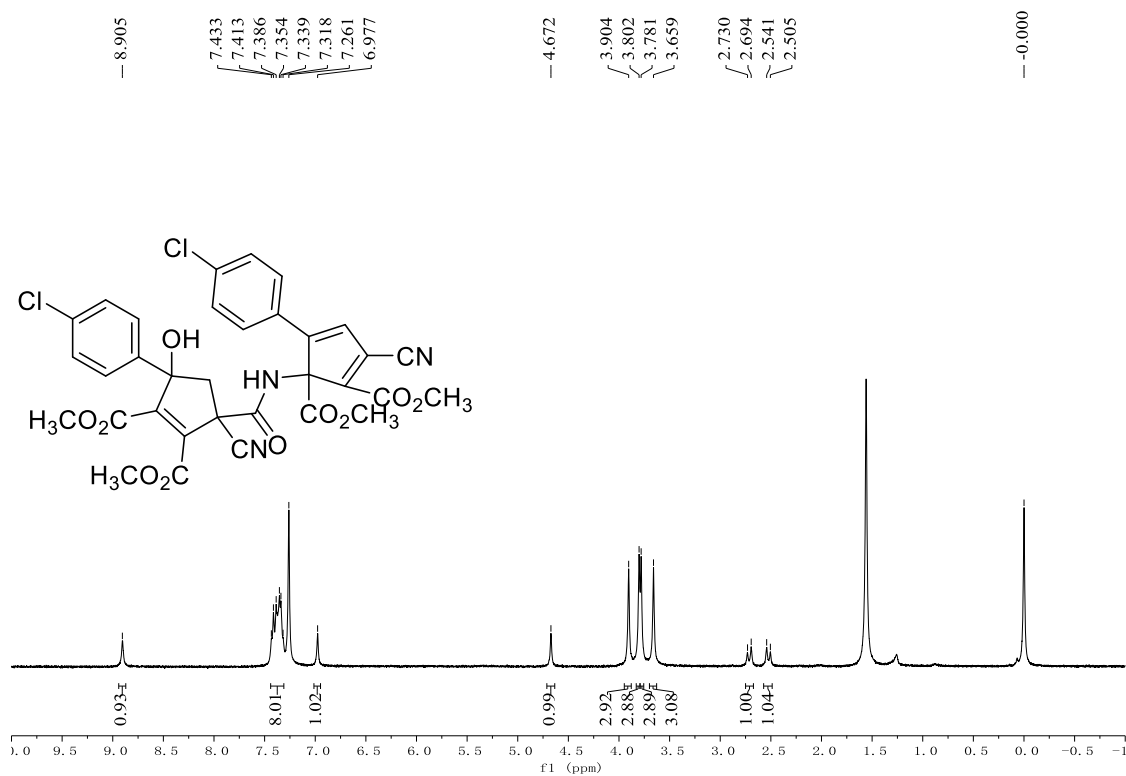
**Dimethyl 3-cyano-1-(1-cyano-4-hydroxy-2,3-bis(methoxycarbonyl)-4-phenylcyclopent-2-ene-1-carboxamido)-5-phenylcyclopenta-2,4-diene-1,2-dicarboxylate (4i):** fluorescent green solid, 53%, m.p. 181-183 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.96 (s, 1H, NH), 7.48-7.47 (m, 2H, ArH), 7.42-7.36 (m, 7H, ArH), 7.31 (d,  $J = 6.8$  Hz, 1H, ArH), 6.99 (s, 1H, CH), 4.63 (s, 1H, OH), 3.91 (s, 3H,  $\text{OCH}_3$ ), 3.78 (s, 3H,  $\text{OCH}_3$ ), 3.71 (s, 3H,  $\text{OCH}_3$ ), 3.64 (s, 3H,  $\text{OCH}_3$ ), 2.76 (d,  $J = 14.8$  Hz, 1H,  $\text{CH}_2$ ), 2.49 (d,  $J = 15.2$  Hz, 1H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.9, 164.2, 163.8, 160.7, 159.9, 153.6, 151.1, 143.5, 139.6, 130.9, 130.4, 130.0, 129.4, 128.5, 127.1, 126.2, 125.8, 125.4, 117.1, 113.2, 86.3, 72.8, 55.0, 53.1, 53.0, 52.8, 52.7, 51.3. MS ( $m/z$ ): HRMS (ESI) Calcd. for  $\text{C}_{33}\text{H}_{27}\text{NaN}_3\text{O}_{10}$  ( $[\text{M}+\text{Na}]^+$ ): 648.1594, found: 648.1593.

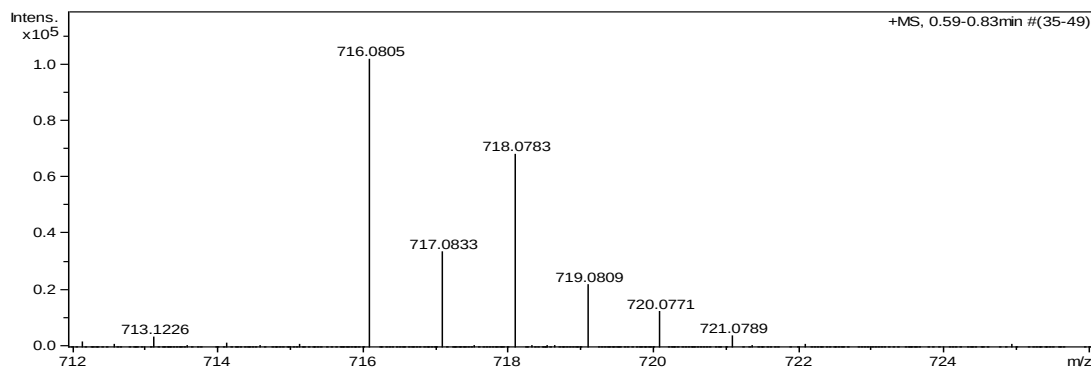




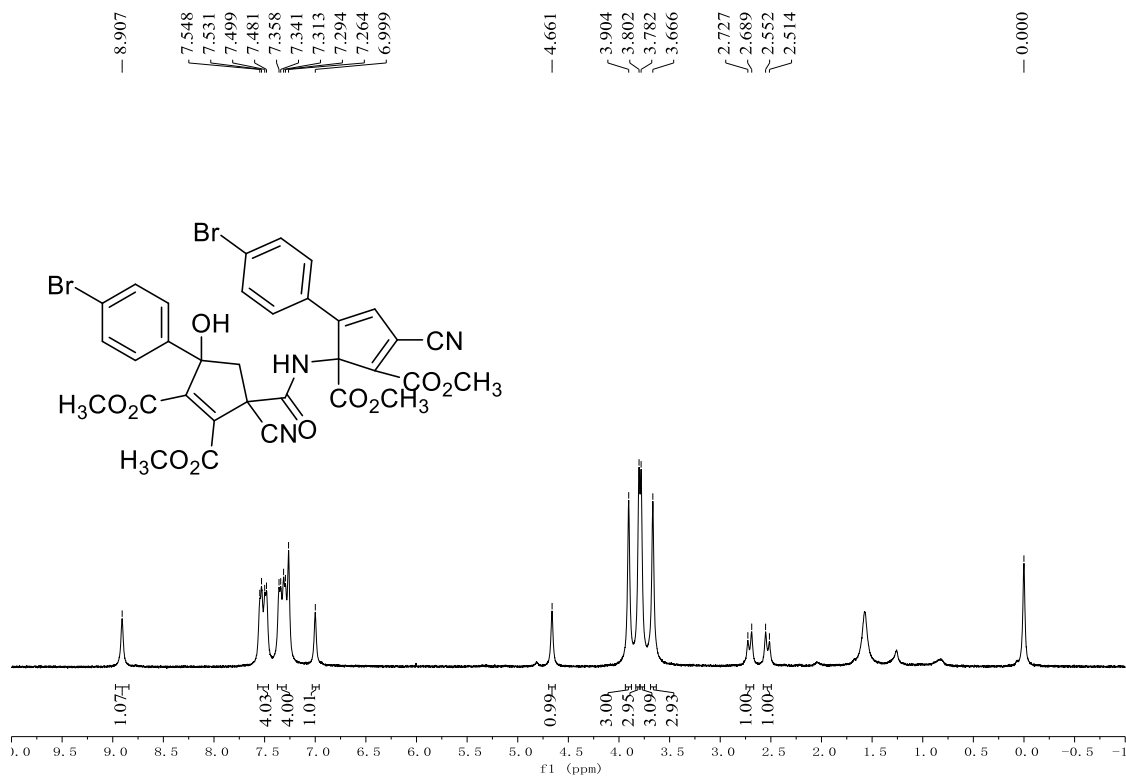


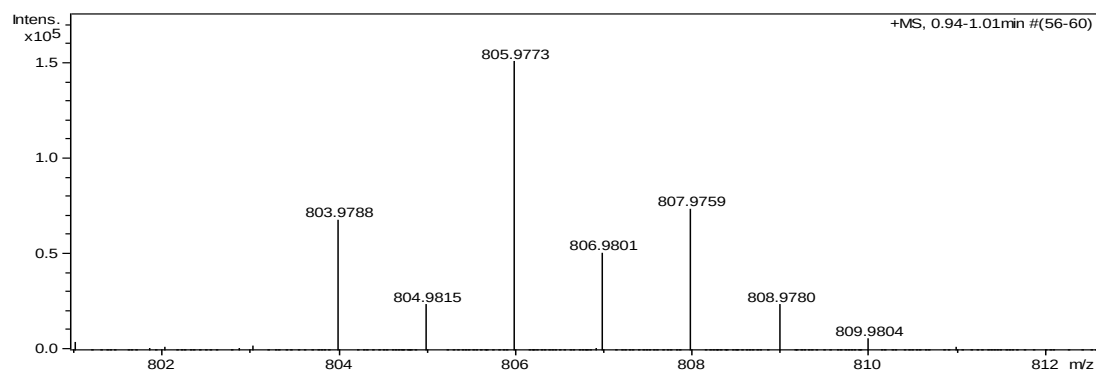
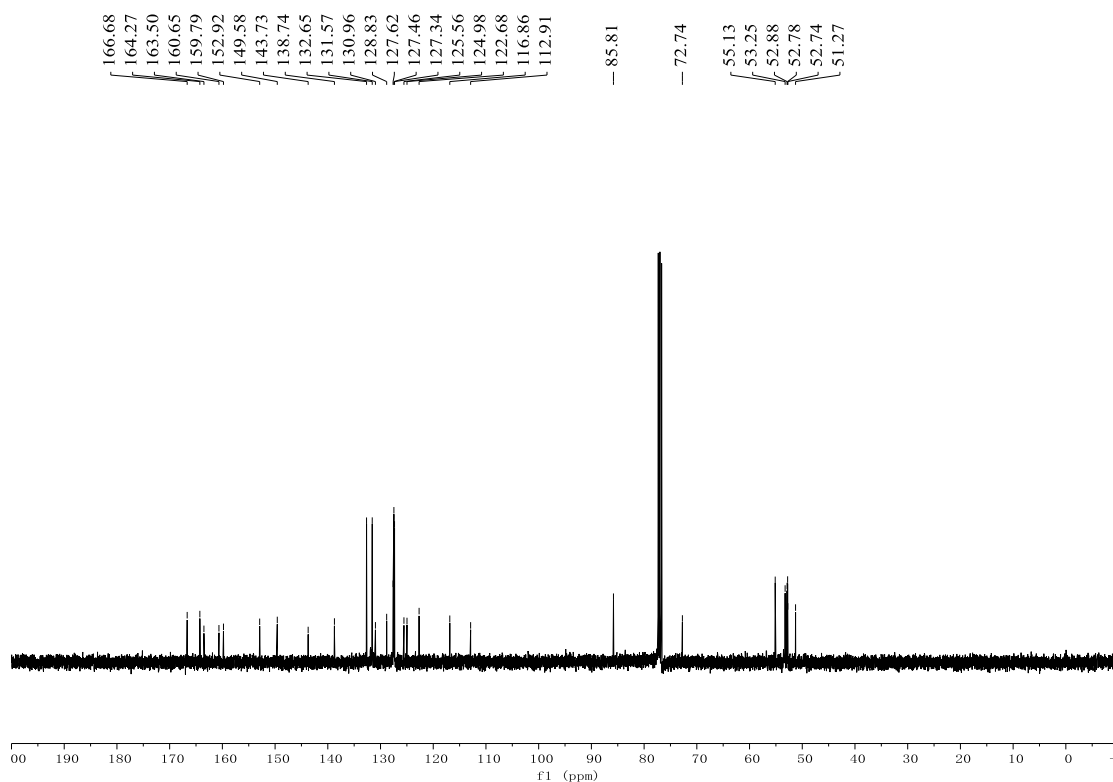
**Dimethyl 5-(4-chlorophenyl)-1-(4-(4-chlorophenyl)-1-cyano-4-hydroxy-2,3-bis(methoxycarbonyl)cyclopent-2-ene-1-carboxamido)-3-cyanocyclopenta-2,4-diene-1,2-dicarboxylate (4j):** pale green solid, 38%, m.p. 192-194 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.91 (s, 1H, NH), 7.43-7.32 (m, 8H, ArH), 6.98 (s, 1H, CH), 4.67 (s, 1H, OH), 3.90 (s, 3H,  $\text{OCH}_3$ ), 3.80 (s, 3H,  $\text{OCH}_3$ ), 3.78 (s, 3H,  $\text{OCH}_3$ ), 3.66 (s, 3H,  $\text{OCH}_3$ ), 2.71 (d,  $J = 14.4$  Hz, 1H,  $\text{CH}_2$ ), 2.52 (d,  $J = 14.4$  Hz, 1H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.7, 164.3, 163.5, 160.7, 159.8, 153.1, 149.5, 143.7, 138.2, 136.6, 134.5, 130.9, 129.7, 128.6, 128.4, 127.5, 127.3, 127.0, 125.6, 116.9, 112.9, 85.8, 72.8, 55.1, 53.2, 52.9, 52.8, 52.7, 51.3. MS ( $m/z$ ): HRMS (ESI) Calcd. for  $\text{C}_{33}\text{H}_{25}\text{Cl}_2\text{NaN}_3\text{O}_{10}$  ( $[\text{M}+\text{Na}]^+$ ): 716.0815, found: 716.0805.





**Dimethyl 5-(4-bromophenyl)-1-(4-(4-bromophenyl)-1-cyano-4-hydroxy-2,3-bis(methoxycarbonyl)cyclopent-2-ene-1-carboxamido)-3-cyanocyclopenta-2,4-diene-1,2-dicarboxylate (4k):** pale green solid, 42%, m.p. 188-190 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.91 (s, 1H, NH), 7.55-7.48 (m, 4H, ArH), 7.36-7.29 (m, 4H, ArH), 7.00 (s, 1H, CH), 4.66 (s, 1H, OH), 3.90 (s, 3H,  $\text{OCH}_3$ ), 3.80 (s, 3H,  $\text{OCH}_3$ ), 3.78 (s, 3H,  $\text{OCH}_3$ ), 3.67 (s, 3H,  $\text{OCH}_3$ ), 2.71 (d,  $J = 15.2$  Hz, 1H,  $\text{CH}_2$ ), 2.53 (d,  $J = 15.2$  Hz, 1H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.7, 164.3, 163.5, 160.7, 159.8, 152.9, 149.6, 143.7, 138.7, 132.7, 131.6, 131.0, 128.8, 127.6, 127.5, 127.3, 125.6, 125.0, 122.7, 116.9, 112.9, 85.8, 72.7, 55.1, 53.3, 52.9, 52.8, 52.7, 51.3. MS ( $m/z$ ): HRMS (ESI) Calcd. for  $\text{C}_{33}\text{H}_{25}\text{Br}_2\text{NaN}_3\text{O}_{10}$  ( $[\text{M}+\text{Na}]^+$ ): 803.9804, found: 803.9788.





**Diethyl 2-(1,1-dicyano-3-(4-methoxyphenyl)-3-oxopropyl)maleate (5):** white solid, 12%. m.p. 58-60 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.91 (d, *J* = 6.8 Hz, 2H, ArH), 6.97 (d, *J* = 6.8 Hz, 2H, ArH), 6.84 (s, 1H, CH), 4.36-4.27 (m, 4H, OCH<sub>2</sub>), 4.03 (s, 2H, CH<sub>2</sub>), 3.89 (s, 3H, OCH<sub>3</sub>), 1.33 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 189.4, 164.7, 163.2, 135.3, 130.6, 129.3, 127.4, 114.2, 112.3, 63.3, 62.1, 55.6, 45.4, 36.6, 14.0, 13.7. MS (*m/z*): HRMS (ESI) Calcd. for C<sub>20</sub>H<sub>20</sub>NaN<sub>2</sub>O<sub>6</sub> ([M+Na]<sup>+</sup>): 407.1219, found: 407.1216.

