

**DBU-promoted Ring-opening Reactions of Multi-substituted Donor-Acceptor
Cyclopropane: Access to Functionalized Chalcones With a Quaternary Carbon
Group**

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Experimental

General. All melting points were determined in a Yanaco melting point apparatus and are uncorrected. IR spectra were recorded in a Nicolet FT-IR 5DX spectrometer. The ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in a Bruker AV-400 spectrometer with TMS as internal reference in CDCl_3 solution. The J values are given in hertz. Only discrete or characteristic signals for the ^1H NMR are reported. High-resolution ESI mass spectra were obtained on a UHR-TOF maXis (ESI) mass spectrometer. X-ray crystallographic analysis was performed with a SMART APEX-II diffractometer using monochromatic Mo KR radiation (λ) 0.71073 Å) and integrated with the SAINT-Plus program. All calculations were performed with programs from the SHELXTL crystallographic software package. Flash chromatography was performed on silica gel (230-400 mesh) eluting with ethyl acetate-hexanes mixture. All reactions were monitored by thin layer chromatography (TLC). Substituted cyanocyclopropanecarboxylates were prepared according to reported methods, other reagents and solvents were purchased from commercial suppliers and purified by standard techniques.

All starting cyanocyclopropanecarboxylates derivatives were prepared according to the following reported methods.

Reference: (a) Raveendran, A. E.; Paul, R. R.; Suresh, E.; Nair, V. *Org. Biomole. Chem.* **2010**, *8*, 901. (b) Rama, V.; Kanagaraj, K.; Subramanian, T.; Suresh, P.; Pitchumani, K. *Catal. Commun.* **2012**, *26*, 39. (c) Wang, Q.; Song, X.; Chen, J.; Yan, C. *J. Combi. Chem.* **2009**, *11*, 1007.

General procedure for the synthesis of compounds 3a-z.

To a mixture of substituted cyanocyclopropanecarboxylates (1.0 mmol) and haloalkanes (5 mmol) was added DBU (152 mg, 1.0 mmol). The mixture was stirred at 80°C for 7-24 h. After completion of the reaction (monitored by TLC, EtOAc/hexanes, 1/15, silica gel), then recovery of excess haloalkanes via reduced pressure distillation, the cooled reaction mixture was added water (10 mL) and

extracted with ethyl acetate (10 mL X 2). The organic phase was washed with water (10 mL) and brine (10 mL), and dried over anhydrous sodium sulfate. After removal of ethyl acetate, the crude product was purified by flash chromatography (EtOAc/hexanes, 1/30, silica gel) to give the desirable products **3a-z**.

Ethyl (Z)-2-cyano-2-(3-oxo-3-phenyl-1-(m-tolyl)prop-1-en-2-yl)pentanoate (**3a**)

Colorless liquid, yield: 92%; IR (KBr, cm^{-1}): 2969, 1746, 1657, 1599, 1494, 1455, 1233, 1089, 1025, 916, 837, 755, 697. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.65 (d, $J = 7.7$ Hz, 2H), 7.38 (s, 1H), 7.29 (t, $J = 7.4$ Hz, 1H), 7.16 (dd, $J = 15.6, 7.9$ Hz, 2H), 6.94-6.74 (m, 4H), 4.14-3.92 (m, 2H), 2.25-2.07 (m, 2H), 2.06 (s, 3H), 1.70-1.55 (m, 1H), 1.53-1.41 (m, 1H), 1.07 (t, $J = 7.1$ Hz, 3H), 0.94 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 196.3, 166.4, 137.8, 136.0, 135.9, 133.8, 133.3, 132.2, 130.0, 129.5, 129.2, 128.2, 128.1, 126.2, 117.5, 63.2, 55.0, 37.8, 21.0, 18.9, 13.7, 13.6. HRMS (ESI) calcd. for $\text{C}_{24}\text{H}_{25}\text{NNaO}_3$ [(M+Na) $^+$]: 398.1732. Found: 398.1740.

Ethyl (Z)-4-(4-bromophenyl)-3-(4-chlorobenzoyl)-2-cyano-2-isopropylbut-3-enoate (**3b**)

White solid, yield 92%; m.p. 122-123°C (EA/PE); IR (KBr, cm^{-1}): 3123, 2977, 1742, 1667, 1580, 1240, 1019, 939, 805. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.57 (d, $J = 8.2$ Hz, 2H), 7.32 (s, 1H), 7.20 (t, $J = 7.2$ Hz, 4H), 6.97 (d, $J = 8.3$ Hz, 2H), 3.98-3.88 (m, 1H), 3.81-3.71 (m, 1H), 2.88-2.76 (m, 1H), 1.18 (d, $J = 6.7$ Hz, 2H), 1.07 (d, $J = 6.6$ Hz, 2H), 1.00 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 193.2, 164.9, 139.3, 133.0, 132.6, 131.5, 130.7, 130.5, 129.3, 129.1, 128.0, 122.3, 114.2, 62.40, 62.25, 33.09, 17.97, 17.00, 12.61. HR-MS (ESI) calcd. for $\text{C}_{23}\text{H}_{21}\text{BrClINaO}_3$ [(M+Na) $^+$]: 496.0291. Found: 496.0287.

Ethyl (Z)-3-(4-chlorobenzoyl)-2-cyano-2-isopropyl-4-(4-phenoxyphenyl)but-3-enoate (**3c**)

White solid, yield: 91%; m.p. 100-101°C (EA/PE); IR (KBr, cm^{-1}): 3085, 2975, 1741, 1667, 1581, 1480, 1241, 1086, 1018, 941, 895, 764. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.53 (d, $J = 8.3$ Hz, 2H), 7.37 (s, 1H), 7.22 (t, $J = 7.8$ Hz, 2H), 7.17 (d, $J = 8.5$ Hz, 2H), 7.03 (t, $J = 7.5$ Hz, 2H), 6.84 (d, $J = 7.6$ Hz, 1H), 6.72 (d, $J = 8.8$ Hz, 2H), 6.64 (d, $J = 8.0$ Hz, 2H), 3.98-3.88 (m, 1H), 3.82-3.72 (m, 1H), 2.89-2.77 (m, 1H), 1.17 (d, $J = 6.7$ Hz, 3H), 1.06 (d, $J = 6.6$ Hz, 3H), 0.99 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 193.9, 166.11, 157.0, 156.7, 139.9, 135.5, 134.5, 134.2, 131.5, 130.2, 129.9, 129.7, 128.8, 124.1, 123.4, 119.8, 119.0, 118.5, 115.3, 62.2, 62.1,

32.9, 17.9, 17.0, 12.5. HR-MS (ESI) calcd. for C₂₉H₂₆ClNNaO₄ [(M+Na)⁺]: 510.1448. Found: 510.1443.

Ethyl (Z)-3-(4-chlorobenzoyl)-4-(3-chlorophenyl)-2-cyano-2-isopropylbut-3-enoate
(3d)

White solid, yield 92%; m.p. 118-119°C (EA/PE); IR (KBr, cm⁻¹): 3076, 2979, 2934, 1737, 1667, 1579, 1472, 1403, 1369, 1258, 1085, 891, 823. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.56 (d, *J* = 8.2 Hz, 2H), 7.34 (s, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.10 (s, 1H), 7.04 (t, *J* = 8.6 Hz, 2H), 6.98 (t, *J* = 7.0 Hz, 2H), 4.01-3.89 (m, 1H), 3.85-3.73(m, 1H), 2.96-2.74 (m, 1H), 1.19 (d, *J* = 6.7 Hz, 1H), 1.08 (d, *J* = 6.6 Hz, 1H), 1.01 (t, *J* = 7.1 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 192.9, 165.0, 139.2, 134.4, 133.4, 133.1, 132.5, 131.3, 129.1, 128.7, 128.0, 127.9, 127.8, 125.8, 114.1, 62.3, 33.1, 17.9, 17.0, 12.6. HR-MS (ESI) calcd. for C₂₃H₂₁Cl₂NNaO₃ [(M+Na)⁺]: 452.0796. Found: 452.0791.

Ethyl (Z)-3-(4-chlorobenzoyl)-2-cyano-4-(2,4-dichlorophenyl)-2-isopropylbut-3-enoate **(3e)**

White solid, yield: 92%; m.p. 85.4-85.9°C(EA/PE); IR (KBr, cm⁻¹): 3067, 2985, 1731, 1667, 1571, 1480, 1231, 1081, 1019, 941, 885, 766. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.54 (d, *J* = 8.6 Hz, 2H), 7.45 (s, 1H), 7.21 – 7.14 (m, 3H), 6.89 (M, 1H), 4.09-3.98 (m, 1H), 3.96 – 3.85 (m, 1H), 2.91-2.80 (m, 1H), 1.23 (d, *J* = 6.7 Hz, 3H), 1.10 (d, *J* = 6.7 Hz, 3H), 1.08 – 1.02 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 192.5, 165.0, 139.3, 134.5, 133.2, 133.0, 132.8, 130.7, 130.3, 130.2, 128.9, 128.2, 127.9, 126.0, 114.0, 62.3, 61.4, 33.2, 17.9, 17.1, 12.6. HR-MS (ESI) calcd. for C₂₃H₂₀Cl₃NNaO₃ [(M+Na)⁺]: 486.0406. Found: 486.0415.

Ethyl (Z)-3-(4-chlorobenzoyl)-2-cyano-2-isopropyl-4-(pyridin-3-yl)but-3-enoate **(3f)**

White solid, yield 88%; m.p. 137.8-138.3°C (EA/PE); IR (KBr, cm⁻¹): 3039, 2989, 1752, 1688, 1562, 1493, 1220, 1072, 1010, 941, 885, 741. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.39 (s, 1H), 8.31 (d, *J* = 4.7 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 9.4 Hz, 2H), 7.18 (s, 1H), 7.00 (dd, *J* = 7.8, 5.1 Hz, 1H), 4.03 – 3.91 (m, 1H), 3.86 – 3.76 (m, 1H), 2.86 (dt, *J* = 13.4, 6.7 Hz, 1H), 1.20 (d, *J* = 6.7 Hz, 3H), 1.09 (d, *J* = 6.6 Hz, 3H), 1.02 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm):

192.72, 164.93, 148.89, 148.75, 139.53, 134.56, 132.92, 132.49, 130.33, 129.23, 128.71, 128.11, 122.11, 114.12, 62.37, 33.25, 17.99, 17.04, 12.63. HR-MS (ESI) calcd. for $C_{22}H_{21}ClN_2NaO_3 [(M+Na)^+]$: 419.1149. Found: 419.1138.

Ethyl (Z)-4-(4-bromophenyl)-2-cyano-2-isopropyl-3-(4-methoxybenzoyl)but-3-enoate (**3g**)

White solid, yield 93%; m.p. 130-131°C(EA/PE); IR (KBr, cm^{-1}): 3061, 1737, 1653, 1599, 1567, 1421, 1246, 1171, 1105, 1024, 890, 830, 808. 1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.62 (d, $J = 8.0$ Hz, 2H), 7.25 (s, 1H), 7.19 (d, $J = 8.0$ Hz, 2H), 7.01 (d, $J = 8.3$ Hz, 2H), 6.68 (d, $J = 8.6$ Hz, 2H), 3.94-3.83 (m, 1H), 3.72 (s, 3H), 3.70-3.63 (m, 1H), 2.90-2.77 (m, , 1H), 1.18 (d, $J = 6.7$ Hz, 3H), 1.06 (d, $J = 6.6$ Hz, 3H), 0.96 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 192.7, 164.9, 131.9, 131.6, 130.5, 130.3, 129.4, 127.7, 121.9, 114.4, 112.8, 62.5, 54.5, 32.7, 18.0, 16.9, 12.5. HR-MS (ESI) calcd. for $C_{24}H_{24}BrNNaO_4 [(M+Na)^+]$:492.0786. Found: 492.0779.

Ethyl (Z)-2-cyano-2-isopropyl-3-(4-methoxybenzoyl)-4-(m-tolyl)but-3-enoate (**3h**)

White solid, yield: 89%; m.p. 103-104°C(EA/PE); IR (KBr, cm^{-1}): 2974, 1737, 1648, 1599, 1502, 1458, 1254, 1169, 1026, 987, 845, 786. 1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.63 (d, $J = 8.2$ Hz, 2H), 7.30 (s, 1H), 6.98-6.89 (m, 3H), 6.86 (d, $J = 4.4$ Hz, 1H), 6.66 (d, $J = 8.1$ Hz, 2H), 4.00-3.79 (m, 1H), 3.77-3.63 (m, 4H), 2.93-2.78 (m, 1H), 2.11 (s, 2H), 1.18 (d, $J = 6.7$ Hz, 3H), 1.06 (d, $J = 6.6$ Hz, 3H), 0.97 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 194.18, 166.22, 137.89, 134.33, 133.92, 131.32, 130.89, 129.87, 129.44, 129.18, 128.19, 126.02, 115.66, 113.67, 63.47, 62.95, 55.3 , 33.68, 21.15, 19.07, 17.99, 13.57. HR-MS (ESI) calcd. for $C_{25}H_{27}NNaO_4 [(M+Na)^+]$:428.1838. Found: 428.1842.

Ethyl (Z)-2-cyano-2-isopropyl-3-(4-methoxybenzoyl)-4-(4-nitrophenyl)but-3-enoate (**3i**)

Yellow liquid, yield: 87%; IR (KBr, cm^{-1}): 2973, 1747, 1652, 1579, 1241, 1015, 936, 803. 1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.92 (d, $J = 7.9$ Hz, 2H), 7.60 (d, $J = 7.2$ Hz, 2H), 7.37 (s, 1H), 7.32 (d, $J = 7.8$ Hz, 2H), 6.68 (d, $J = 8.4$ Hz, 2H), 3.97-3.86 (m, 1H), 3.77-3.66 (m, 4H), 2.98-2.76 (m, 1H), 1.20 (d, $J = 6.5$ Hz, 3H), 1.08 (d, $J = 6.4$ Hz, 3H), 0.98 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 192.01,

164.73, 146.33, 139.52, 134.49, 130.47, 130.32, 128.61, 127.48, 122.58, 114.22, 113.03, 62.72, 62.31, 55.5, 33.03, 18.08, 17.02, 12.54. HR-MS (ESI) calcd. for $C_{24}H_{24}N_2NaO_6$ [(M+Na)⁺]: 459.1532. Found: 459.1524.

Methyl (Z)-3-(4-chlorobenzoyl)-2-cyano-2-isopropyl-4-(o-tolyl)but-3-enoate (**3j**)

White solid, yield 93%; m.p. 128.3-128.9°C (EA/PE); IR (KBr, cm^{-1}): 3031, 2923, 1756, 1659, 1587, 1479, 1231, 1081, 1018, 944, 881, 749. ¹H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.54 (s, 1H), 7.45 (d, $J = 8.4$ Hz, 2H), 7.11 (d, $J = 8.5$ Hz, 2H), 6.97 – 6.92 (m, 2H), 6.89 (d, $J = 7.6$ Hz, 1H), 6.83 – 6.74 (m, 1H), 3.54 – 3.47 (m, 3H), 2.96-2.86 (m, 1H), 2.29 (s, 3H), 1.23 (d, $J = 6.7$ Hz, 3H), 1.10 (d, $J = 6.7$ Hz, 3H). ¹³C NMR (100 MHz, $CDCl_3$) δ (ppm): 193.32, 165.93, 138.64, 135.03, 134.24, 133.78, 132.14, 131.7, 128.99, 128.77, 128.24, 128.21, 127.58, 124.75, 114.42, 61.60, 52.43, 32.95, 18.94, 18.13, 17.16. HR-MS (ESI) calcd. for $C_{23}H_{22}ClNNaO_3$ [(M+Na)⁺]: 418.1174. Found: 418.1186.

Methyl (Z)-4-(3-bromophenyl)-2-cyano-2-isopropyl-3-(4-methoxybenzoyl)but-3-enoate (**3k**)

White solid, yield 94%; m.p. 116.5-116.9°C (EA/PE); IR (KBr, cm^{-1}): 3079, 2968, 1743, 1678, 1553, 1493, 1271, 1026, 1019, 995, 879, 779. ¹H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.60 (d, $J = 8.3$ Hz, 2H), 7.30 (s, 1H), 7.25 (s, 1H), 7.20-7.15 (m, 1H), 7.06 (d, $J = 7.8$ Hz, 1H), 6.91 (t, $J = 7.9$ Hz, 1H), 6.69 (d, $J = 9.0$ Hz, 2H), 3.71 (s, 3H), 3.39 (s, 3H), 2.88-2.78 (m, 1H), 1.18 (d, $J = 6.7$ Hz, 3H), 1.06 (d, $J = 6.6$ Hz, 3H). ¹³C NMR (100 MHz, $CDCl_3$) δ (ppm): 192.7, 164.9, 131.9, 131.6, 131.0, 130.5, 130.3, 129.4, 127.7, 121.9, 114.4, 112.8, 62.5, 62.0, 54.4, 32.7, 18.0, 16.9, 12.5; HR-MS (ESI) calcd. for $C_{23}H_{22}BrNNaO_3$ [(M+Na)⁺]: 478.0630. Found: 478.0641.

Ethyl (Z)-3-(4-bromobenzoyl)-2-cyano-2-isopropyl-4-(m-tolyl)but-3-enoate (**3l**)

White solid, yield: 90%; m.p. 114-115°C (EA/PE); IR (KBr, cm^{-1}): 2974, 1742, 1661, 1578, 1467, 1383, 1230, 1171, 1025, 928, 831. ¹H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.49 (d, $J = 8.3$ Hz, 2H), 7.39 (s, 1H), 7.32 (d, $J = 8.4$ Hz, 2H), 6.98-6.84 (m, 4H), 4.04-3.87 (m, 1H), 8.85-3.69 (m, 1H), 2.89-2.76 (m, 1H), 2.11 (s, 3H), 1.19 (d, $J = 6.7$ Hz, 3H), 1.08 (d, $J = 6.6$ Hz, 3H), 1.00 (t, $J = 7.1$ Hz, 3H). ¹³C NMR (100 MHz,

CDCl₃) δ (ppm): 193.7, 165.2, 137.0, 134.7, 134.4, 133.8, 132.6, 130.7, 129.2, 128.8, 127.7, 127.3, 124.9, 114.4, 62.2, 62.1, 32.9, 20.0, 17.9, 17.0, 12.6. HR-MS (ESI) calcd. for C₂₄H₂₄BrNNaO₃ [(M+Na)⁺]: 476.0837. Found: 476.0829.

Methyl (Z)-3-(4-bromobenzoyl)-4-(2-chlorophenyl)-2-cyano-2-isopropylbut-3-enoate
(3m)

White solid, yield: 94%; m.p. 132-133°C(EA/PE); IR (KBr, cm⁻¹): 3096, 2969, 1746, 1663, 1576, 1466, 1434, 1241, 1172, 1063, 1018, 889, 811, 758. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.54 (s, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.23-7.13 (m, 1H), 7.04-6.91 (m, 2H), 6.88 (t, *J* = 7.5 Hz, 1H), 3.56 (s, 3H), 2.97-2.76 (m, 1H), 1.25 (d, *J* = 6.7 Hz, 3H), 1.10 (d, *J* = 6.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 193.0, 165.7, 133.7, 132.3, 132.3, 132.2, 132.1, 131.7, 130.7, 129.6, 129.3, 129.0, 128.2, 127.9, 125.6, 114.1, 61.0, 52.6, 33.0, 18.0, 17.15. HR-MS (ESI) calcd. for C₂₂H₁₉BrClNNaO₃ [(M+Na)⁺]: 482.0135. Found: 482.0125.

Ethyl (Z)-2-(1-(4-bromophenyl)-3-(4-chlorophenyl)-3-oxoprop-1-en-2-yl)-2-cyano
pentanoate **(3n)**

Colorless liquid, yield: 94%; IR (KBr, cm⁻¹): 3055, 2964, 1743, 1663, 1581, 1479, 1228, 1081, 1017, 804, 723. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.59 (d, *J* = 8.4 Hz, 2H), 7.31 (s, 1H), 7.18 (t, *J* = 7.6 Hz, 4H), 6.93 (d, *J* = 8.1 Hz, 2H), 4.15-3.87 (m, 2H), 2.27-1.93 (m, 2H), 1.66-1.54 (m, 1H), 1.53-1.40 (m, 1H), 1.10 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 193.6, 165.1, 139.3, 133.0, 131.9, 131.6, 131.2, 130.6, 129.6, 129.5, 127.9, 122.4, 116.1, 62.4, 54.1, 36.9, 17.9, 12.7, 12.6. HR-MS (ESI) calcd. for C₂₃H₂₁BrClNNaO₃ [(M+Na)⁺]: 496.0291. Found: 496.0288.

Ethyl (Z)-2-(1-(2-bromophenyl)-3-(4-bromophenyl)-3-oxoprop-1-en-2-yl)-2-cyano
pentanoate **(3o)**

Colorless liquid, yield: 94%; IR (KBr, cm⁻¹): 2966, 1747, 1650, 1594, 1454, 1252, 1181, 1093, 1015, 790, 732. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.47 (d, *J* = 6.8 Hz, 3H), 7.38-7.30 (m, 1H), 7.28 (d, *J* = 7.7 Hz, 2H), 6.90 (s, 3H), 4.24-4.06 (m, 2H), 2.23 (t, *J* = 8.3 Hz, 2H), 1.73-1.45 (m, 2H), 1.17 (t, *J* = 7.0 Hz, 3H), 0.98 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 194.6, 166.4, 136.1, 135.1, 134.7,

134.1, 132.4, 131.5, 131.1, 130.5, 130.4, 128.6, 127.1, 123.3, 117.1, 63.4, 54.1, 37.7, 18.8, 13.8, 13.7. HR-MS (ESI) calcd. for $C_{23}H_{21}Br_2NNaO_3$ [(M+Na)⁺]: 541.9765. Found: 541.9758.

Ethyl (Z)-3-(4-bromobenzoyl)-4-(2-bromophenyl)-2-(2-chloroethyl)-2-cyanobut-3-enoate (**3p**)

White solid, yield: 94%; m.p. 120-121°C (EA/PE); IR (KBr, cm^{-1}): 3121, 1748, 1548, 1469, 1307, 1141, 937, 804, 724. ¹H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.56 (s, 1H), 7.46 (d, $J = 8.7$ Hz, 2H), 7.37 (dd, $J = 7.5, 1.6$ Hz, 1H), 7.29 (d, $J = 8.7$ Hz, 2H), 7.19 (s, 1H), 6.98-6.90 (m, 1H), 6.90-6.86 (m, 1H), 4.22-4.08 (m, 2H), 3.82-3.64 (m, 2H), 2.78 (t, $J = 7.8$ Hz, 2H), 1.15 (t, $J = 7.2$ Hz, 3H). ¹³C NMR (100 MHz, $CDCl_3$) δ (ppm): 193.2, 164.2, 135.9, 134.28, 133.2, 131.8, 131.4, 130.5, 129.9, 129.7, 129.3, 127.8, 126.1, 122.3, 115.0, 62.9, 51.6, 38.2, 37.2, 12.6; HR-MS (ESI) calcd. for $C_{22}H_{18}Br_2ClNNaO_3$ [(M+Na)⁺]: 561.9219. Found: 561.9218.

Ethyl (Z)-4-(4-bromophenyl)-3-(4-chlorobenzoyl)-2-(2-chloroethyl)-2-cyanobut-3-enoate (**3q**)

Colorless liquid, yield 94%; IR (KBr, cm^{-1}): 3109, 1758, 1546, 1459, 1308, 1228, 1071, 1015, 803, 721. ¹H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.59 (d, $J = 8.5$ Hz, 2H), 7.40 (s, 1H), 7.19 (dd, $J = 10.4, 8.5$ Hz, 4H), 6.93 (d, $J = 8.4$ Hz, 2H), 4.10-3.99 (m, 2H), 3.80-3.56 (m, 2H), 2.73 (t, $J = 7.7$ Hz, 2H), 1.08 (t, $J = 7.1$ Hz, 3H); ¹³C NMR (101 MHz, $CDCl_3$) δ (ppm): 194.4, 165.1, 136.5, 134.3, 133.7, 132.2, 131.9, 130.9, 130.4, 130.1, 129.8, 128.2, 126.2, 122.7, 115.5, 64.0, 53.5, 39.4, 38.3, 13.6; HR-MS (ESI) calcd. for $C_{22}H_{18}BrCl_2NNaO_3$ [(M+Na)⁺]: 515.9745. Found: 515.9741.

Ethyl (Z)-3-(4-bromobenzoyl)-2-(2-chloroethyl)-4-(3-chlorophenyl)-2-cyanobut-3-enoate (**3r**)

Colorless liquid, yield: 93%; IR (KBr, cm^{-1}): 2974, 1746, 1654, 1493, 1265, 1087, 912, 826, 754. ¹H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.49 (d, $J = 8.0$ Hz, 2H), 7.44 (s, 1H), 7.33 (d, $J = 8.1$ Hz, 2H), 7.06 (d, $J = 8.7$ Hz, 2H), 6.99 (t, $J = 7.7$ Hz, 1H), 6.92 (d, $J = 7.6$ Hz, 1H), 4.07 (dd, $J = 12.9, 5.9$ Hz, 1H), 3.79-3.62 (m, 1H), 2.75 (t, $J = 7.7$ Hz, 1H). ¹³C NMR (100 MHz, $CDCl_3$) δ (ppm): 193.7, 164.3, 134.5, 134.2, 133.6, 133.6, 131.5, 131.0, 129.8, 128.9, 128.6, 128.4, 128.3, 126.2, 115.4, 63.2, 52.7, 38.6,

37.6, 12.8. HR-MS (ESI) calcd. for $C_{22}H_{18}BrCl_2NNaO_3 [(M+Na)^+]$:515.9745. Found: 515.9741.

Ethyl (Z)-3-(4-chlorobenzoyl)-2-(2-chloroethyl)-4-(3-chlorophenyl)-2-cyanobut-3-enoate (**3s**)

Colorless liquid, yield: 93%; IR (KBr, cm^{-1}): 2993, 1747, 1658, 1580, 1302, 1181, 1093, 1015, 790, 732. 1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.57 (d, $J = 8.6$ Hz, 2H), 7.44 (s, 1H), 7.16 (d, $J = 8.5$ Hz, 2H), 7.06 (d, $J = 7.6$ Hz, 2H), 6.99 (t, $J = 7.9$ Hz, 1H), 6.93 (d, $J = 7.7$ Hz, 1H), 4.11-4.01 (m, 1H), 3.77-3.63 (m, 1H), 2.75 (t, $J = 7.7$ Hz, 1H), 1.09 (t, $J = 7.1$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 193.3, 164.1, 139.3, 134.3, 134.0, 133.4, 132.9, 131.4, 129.6, 128.7, 128.4, 128.1, 127.8, 126.0, 115.2, 63.0, 52.4, 38.4, 37.3, 12.6. HR-MS (ESI) calcd. for $C_{22}H_{19}Cl_3NO_3 [(M+H)^+]$:450.0431. Found: 450.0434.

Ethyl (Z)-4-(4-bromophenyl)-2-(2-chloroethyl)-2-cyano-3-(4-methoxybenzoyl)but-3-enoate (**3t**)

Colorless liquid, yield: 94%; IR (KBr, cm^{-1}): 2966, 1747, 1650, 1594, 1454, 1252, 1170, 1020, 847, 805, 750. 1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.64 (d, $J = 8.5$ Hz, 2H), 7.30 (s, 1H), 7.20 (d, $J = 8.3$ Hz, 2H), 6.98 (d, $J = 8.3$ Hz, 2H), 6.68 (d, $J = 8.6$ Hz, 2H), 4.09-3.95 (m, 2H), 3.77-3.60 (m, 5H), 2.72-2.63 (m, 2H), 1.07 (t, $J = 7.1$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 192.6, 163.2, 132.6, 132.7, 131.5, 131.0, 130.8, 130.6, 129.6, 127.2, 122.4, 115.4, 112.9, 62.8, 54.5, 52.5, 38.5, 37.1, 12.5; HR-MS (ESI) calcd. for $C_{23}H_{21}BrClNNaO_4 [(M+Na)^+]$: 512.0240. Found: 512.0242.

Ethyl (Z)-2-(1-(3-chlorophenyl)-3-oxo-3-phenylprop-1-en-2-yl)-2-cyanohexanoate (**3u**)

Colorless liquid, yield: 82%; IR (KBr, cm^{-1}): 2996, 2871, 1746, 1661, 1566, 1464, 1371, 1229, 1025, 889, 755, 690. 1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.64 (d, $J = 7.4$ Hz, 2H), 7.37-7.27 (m, 2H), 7.18 (t, $J = 7.7$ Hz, 2H), 7.06 (s, 1H), 7.01-6.85 (m, 3H), 4.12-3.90 (m, 2H), 2.27-2.11 (m, 2H), 1.67-1.51 (m, 1H), 1.48-1.39 (m, 1H), 1.41-1.28 (m, 2H), 1.08 (t, $J = 7.1$ Hz, 3H), 0.86 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 195.6, 166.1, 135.7, 134.1, 133.8, 133.6, 129.5, 129.2, 129.1, 128.8, 128.4, 127.0, 117.3, 63.3, 55.1, 35.6, 27.5, 22.3, 13.7, 13.6; HR-MS (ESI)

calcd. for C₂₄H₂₄ClNNaO₃ [(M+Na)⁺] :432.1342. Found: 432.1344.

Ethyl (Z)-2-(1-(4-bromophenyl)-3-(4-chlorophenyl)-3-oxoprop-1-en-2-yl)-2-cyanoheptanoate (**3v**)

Colorless liquid, yield: 75%; IR (KBr, cm⁻¹): 2931, 2864, 1746, 1662, 1583, 1479, 1235, 1086, 1013, 956, 845, 815. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.59 (d, *J* = 8.4 Hz, 2H), 7.31 (s, 1H), 7.18 (t, *J* = 8.0 Hz, 4H), 6.93 (d, *J* = 8.3 Hz, 2H), 4.13-3.98 (m, 2H), 2.24-2.08 (m, 2H), 1.55 (m, 1H), 1.61-1.49 (m, 1H), 1.33-1.18 (m, 4H), 1.10 (t, *J* = 7.2 Hz, 3H), 0.82 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 194.6, 166.1, 139.52, 133.36, 133.22, 132.11, 131.88, 130.88, 129.83, 129.74, 128.12, 122.68, 116.38, 63.4, 55.2, 35.9, 31.2, 25.0, 22.2, 13.9, 13.7. HR-MS (ESI) calcd. for C₂₅H₂₅BrClNNaO₃ [(M+Na)⁺] :524.0604. Found: 524.0597.

Ethyl (Z)-8-bromo-2-(1-(4-bromophenyl)-3-(4-chlorophenyl)-3-oxoprop-1-en-2-yl)-2-cyano-octanoate (**3w**)

Colorless liquid, yield: 72%; IR(KBr, cm⁻¹): 2930, 2860, 1744, 1659, 1593, 1490, 1247, 1086, 1016, 823, 756, 698; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.59 (d, *J* = 8.5 Hz, 2H), 7.31 (s, 1H), 7.17 (dd, *J* = 8.4, 6.7 Hz, 4H), 6.93 (d, *J* = 8.4 Hz, 2H), 4.13-3.91 (m, 2H), 3.31 (t, *J* = 6.7 Hz, 2H), 2.32-2.03 (m, 2H), 1.88-1.62 (m, 2H), 1.45-1.27 (m, 6H), 1.09 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 194.6, 166.0, 139.35, 133.24, 132.99, 131.74, 131.62, 130.69, 129.64, 129.55, 127.93, 122.52, 116.07, 63.5, 55.1, 35.8, 33.6, 32.4, 28.2, 27.7, 25.2, 13.7; HR-MS (ESI) calcd. for C₂₆H₂₆Br₂ClNNaO₃ [(M+Na)⁺] :617.9845. Found: 617.9825.

Ethyl (Z)-2-(1-(4-bromophenyl)-3-(4-chlorophenyl)-3-oxoprop-1-en-2-yl)-2-cyanopent-4-enoate (**3x**)

Colorless liquid, yield: 96%; IR (KBr, cm⁻¹): 3100, 2926, 2860, 2241, 1746, 1660, 1582, 1477, 1401, 1229, 1080, 1002, 850, 723. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.59 (d, *J* = 8.4 Hz, 2H), 7.31 (s, 1H), 7.17 (t, *J* = 8.7 Hz, 4H), 6.91 (d, *J* = 8.4 Hz, 2H), 5.87-5.73 (m, 1H), 5.22 (dd, *J* = 13.5, 7.6 Hz, 2H), 4.19-3.92 (m, 2H), 2.97 (dd, *J* = 7.1, 2.6 Hz, 2H), 1.09 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 193.7, 164.5, 140.3, 135.1, 134.0, 132.6, 131.6, 130.7, 130.5, 128.8, 123.5, 121.9, 116.7, 62.5, 53.8, 39.1, 28.6, 12.7. HR-MS (ESI) calcd. for C₂₃H₁₉BrClNNaO₃

[(M+Na)⁺]:494.0135. Found: 494.0122.

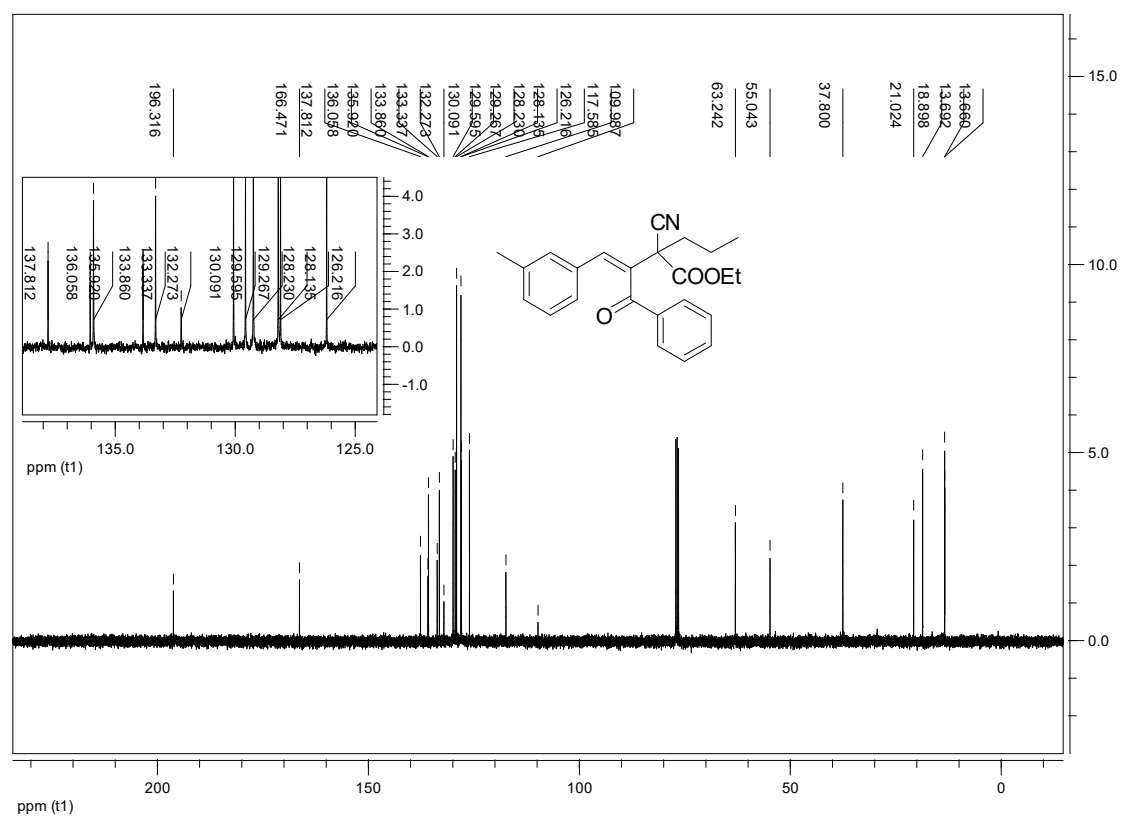
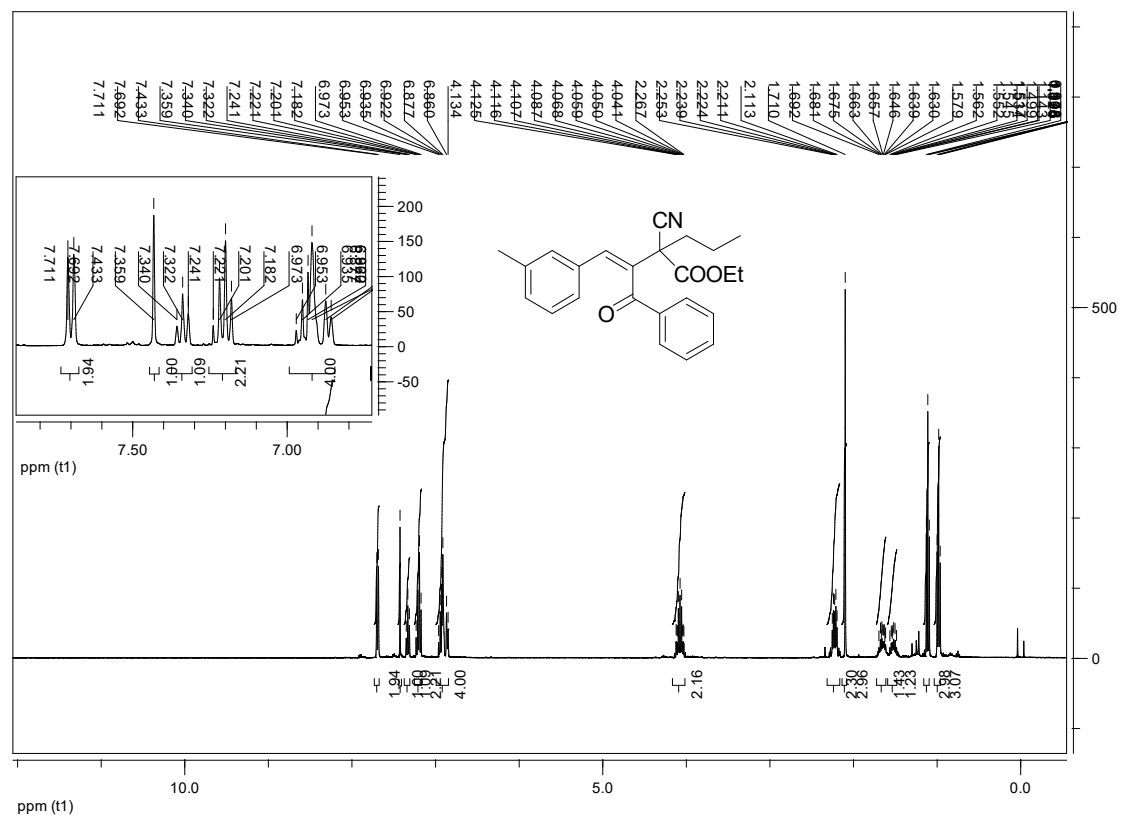
Ethyl (Z)-2-cyano-2-(3-oxo-3-phenyl-1-(m-tolyl)prop-1-en-2-yl)pent-4-enoate (**3y**)

Colorless liquid, yield: 95%; IR (KBr, cm⁻¹): 2924, 2858, 1747, 1656, 587, 1449, 1372, 1229, 998, 930, 787, 730, 696. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.64 (d, *J* = 7.7 Hz, 2H), 7.39 (s, 1H), 7.27 (t, *J* = 7.4 Hz, 1H), 7.13 (t, *J* = 7.7 Hz, 2H), 6.92-6.73 (m, 4H), 5.93-5.68 (m, 1H), 5.22 (t, *J* = 12.4 Hz, 2H), 4.10-3.96 (m, 2H), 2.99 (d, *J* = 7.2 Hz, 2H), 2.05 (s, 3H), 1.06 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 195.3, 164.9, 136.7, 135.8, 135.0, 132.7, 132.3, 130.5, 129.6, 129.1, 128.6, 128.3, 127.1, 127.1, 125.2, 120.5, 116.1, 62.3, 53.7, 39.0, 28.6, 20.0, 12.6; HR-MS (ESI) calcd. for C₂₃H₂₁BrClNNaO₄ [(M+Na)⁺]: 396.1576. Found: 396.1571.

Ethyl (Z)-2-(1-(4-bromophenyl)-3-(4-methoxyphenyl)-3-oxoprop-1-en-2-yl)-2-cyanopent-4-enoate (**3z**)

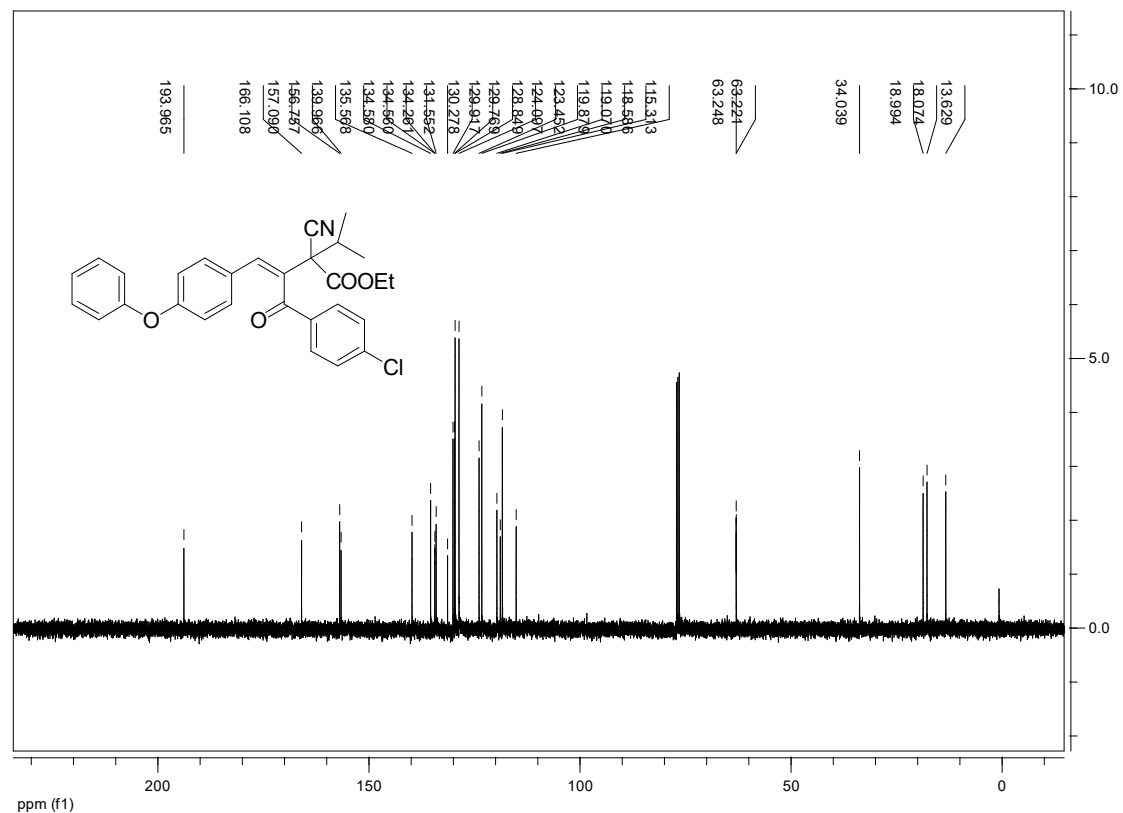
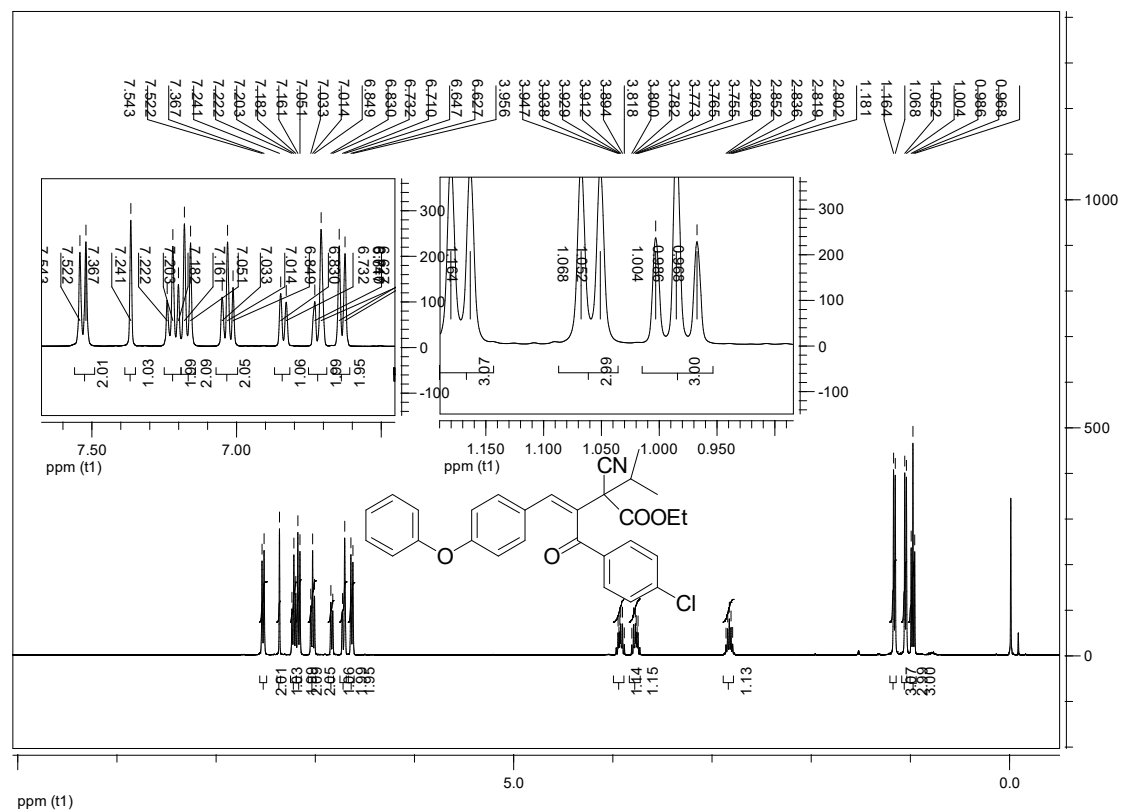
Colorless liquid, yield: 96%; IR (KBr, cm⁻¹): 3083, 2930, 1746, 1650, 1594, 1371, 1251, 1168, 1019, 935, 895, 847. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.65 (d, *J* = 8.6 Hz, 2H), 7.23 (s, 1H), 7.18 (d, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 8.3 Hz, 2H), 6.67 (d, *J* = 8.6 Hz, 2H), 5.89-.67 (m, 1H), 5.31-5.11 (m, 2H), 4.12-3.93 (m, 2H), 3.72 (s, 3H), 3.02-2.82(m, 2H), 1.08 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 193.0, 164.5, 132.6, 131.9, 131.7, 130.9, 129.6, 129.5, 127.5, 122.1, 120.7, 115.9, 112.7, 62.4, 55.5, 54.4, 53.9, 38.9, 28.6, 12.6. HR-MS (ESI) calcd. for C₂₃H₂₁BrClNNaO₄ [(M+Na)⁺]:490.0630. Found: 490.0626.

Ethyl (Z)-2-cyano-2-(3-oxo-3-phenyl-1-(m-tolyl)prop-1-en-2-yl)pentanoate (**3a**)

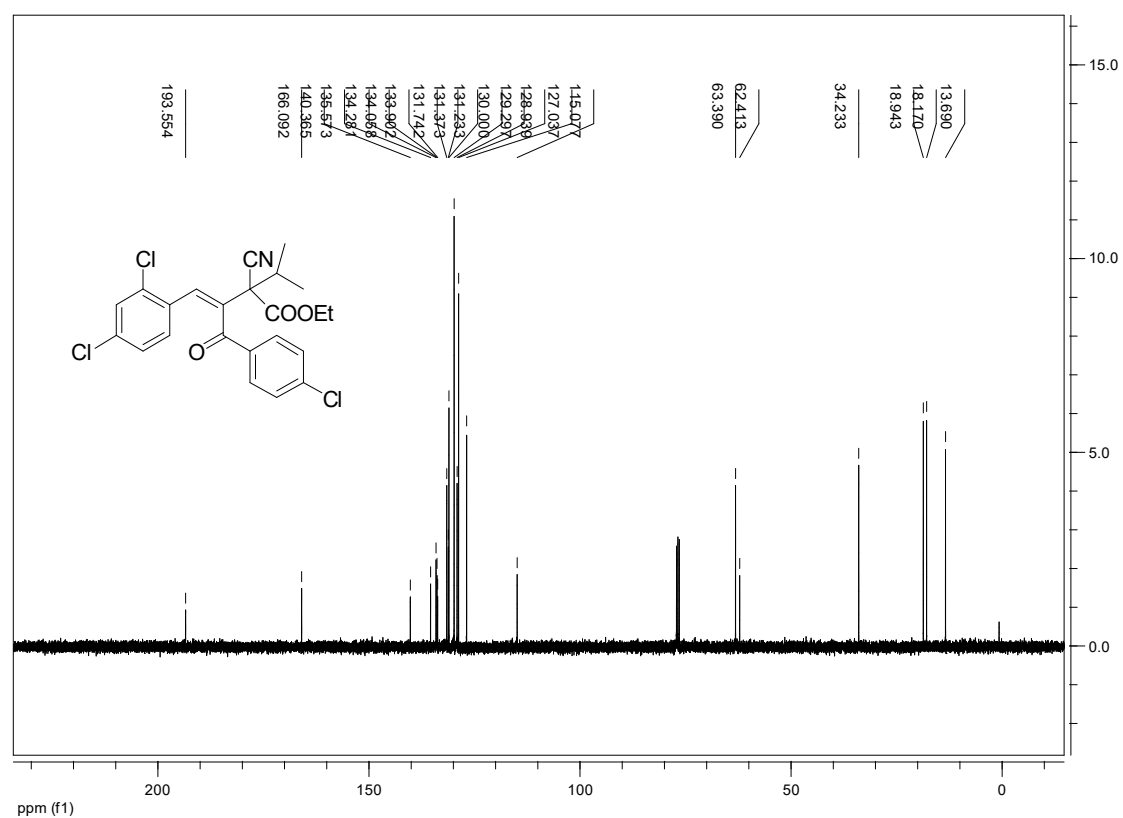
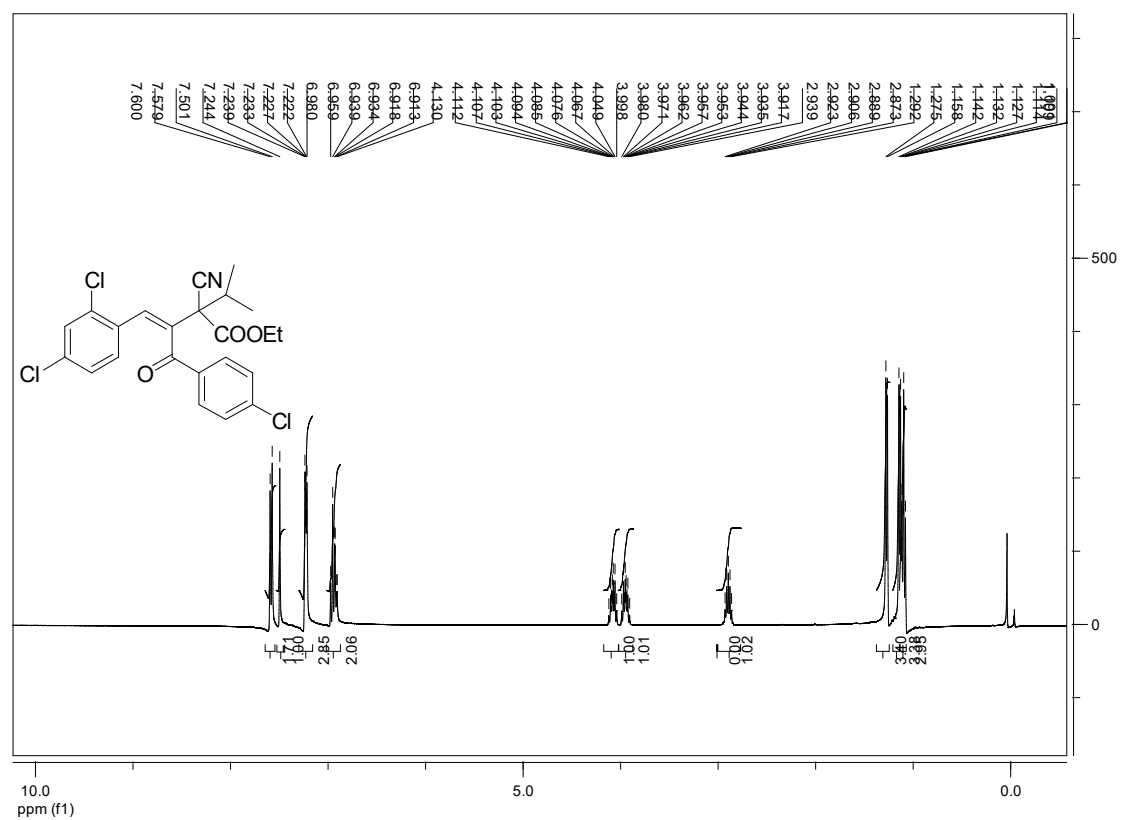


Ethyl (Z)-3-(4-chlorobenzoyl)-2-cyano-2-isopropyl-4-(4-phenoxyphenyl)but-3-enoate

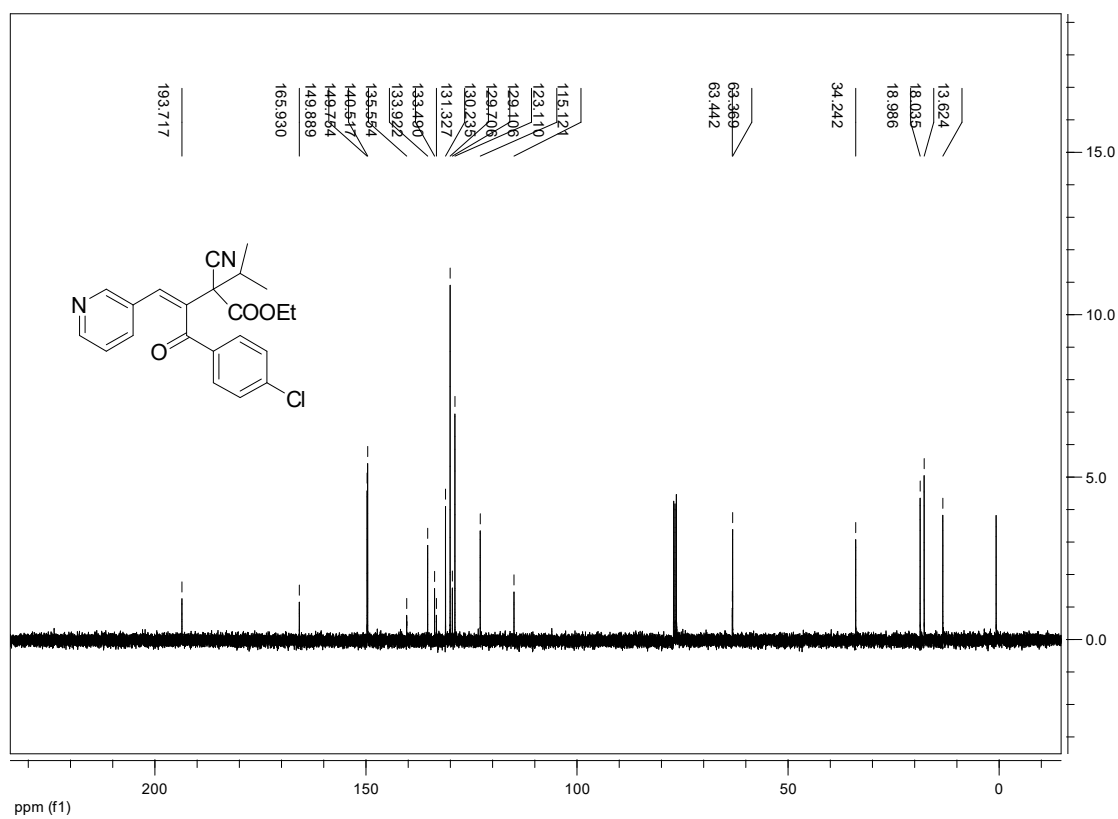
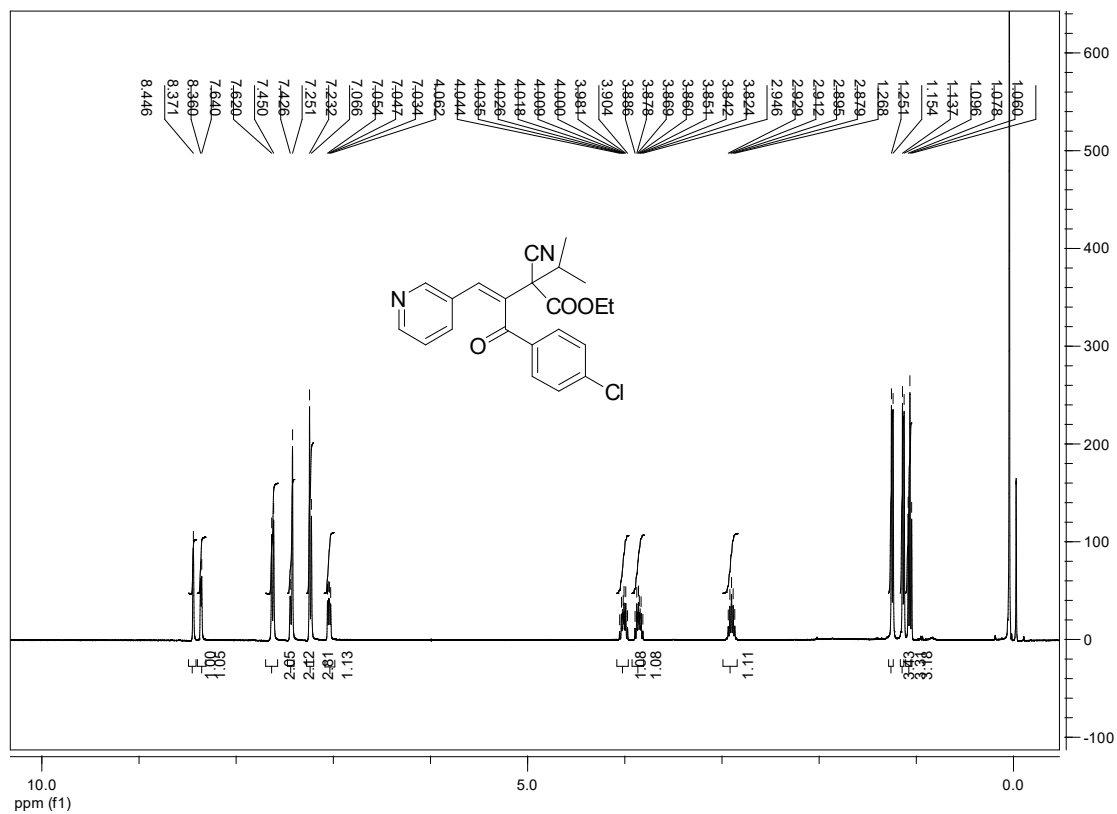
(3c)



Ethyl (Z)-3-(4-chlorobenzoyl)-2-cyano-4-(2,4-dichlorophenyl)-2-isopropylbut-3-enoate (**3e**)

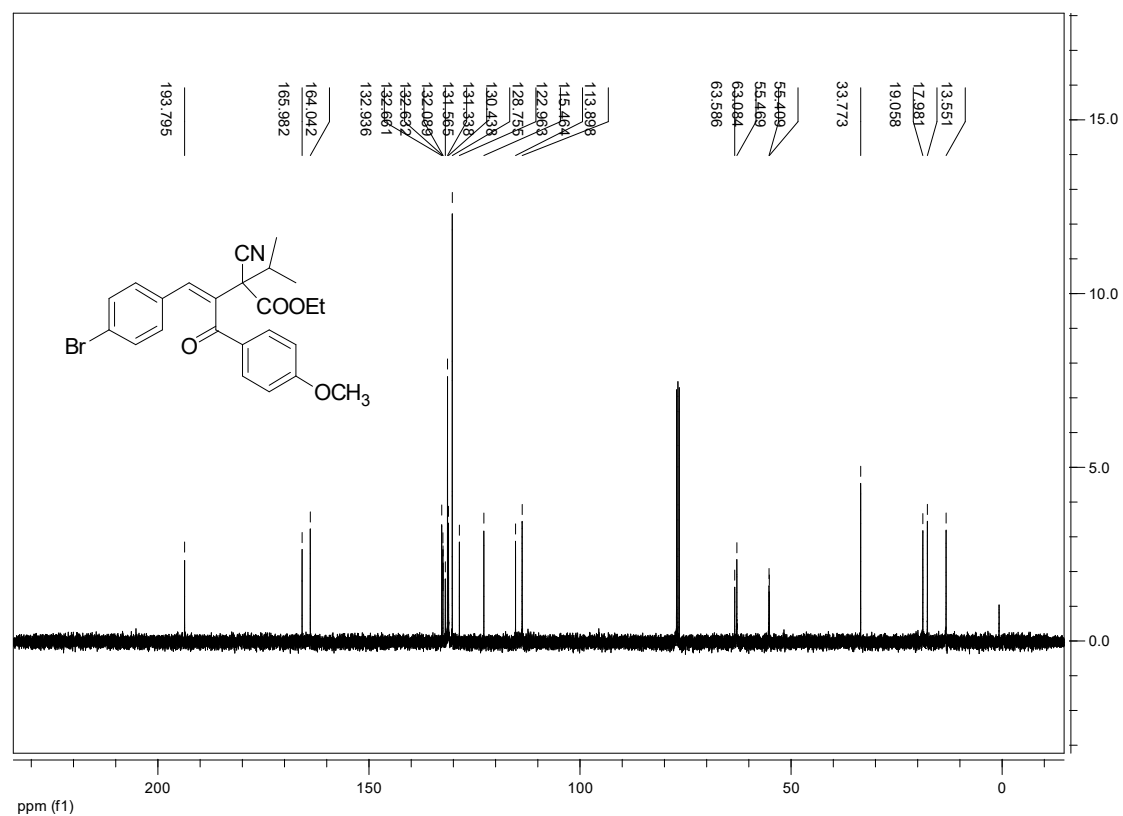
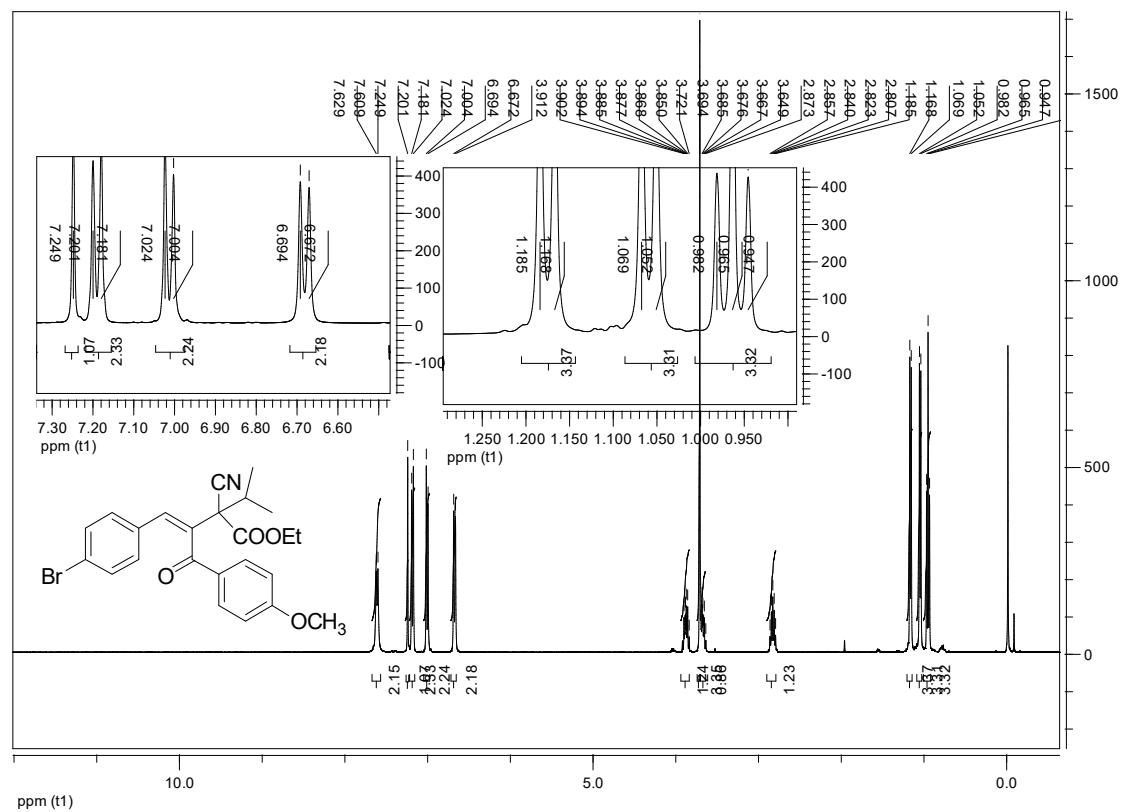


Ethyl (Z)-3-(4-chlorobenzoyl)-2-cyano-2-isopropyl-4-(pyridin-3-yl)but-3-enoate (**3f**)

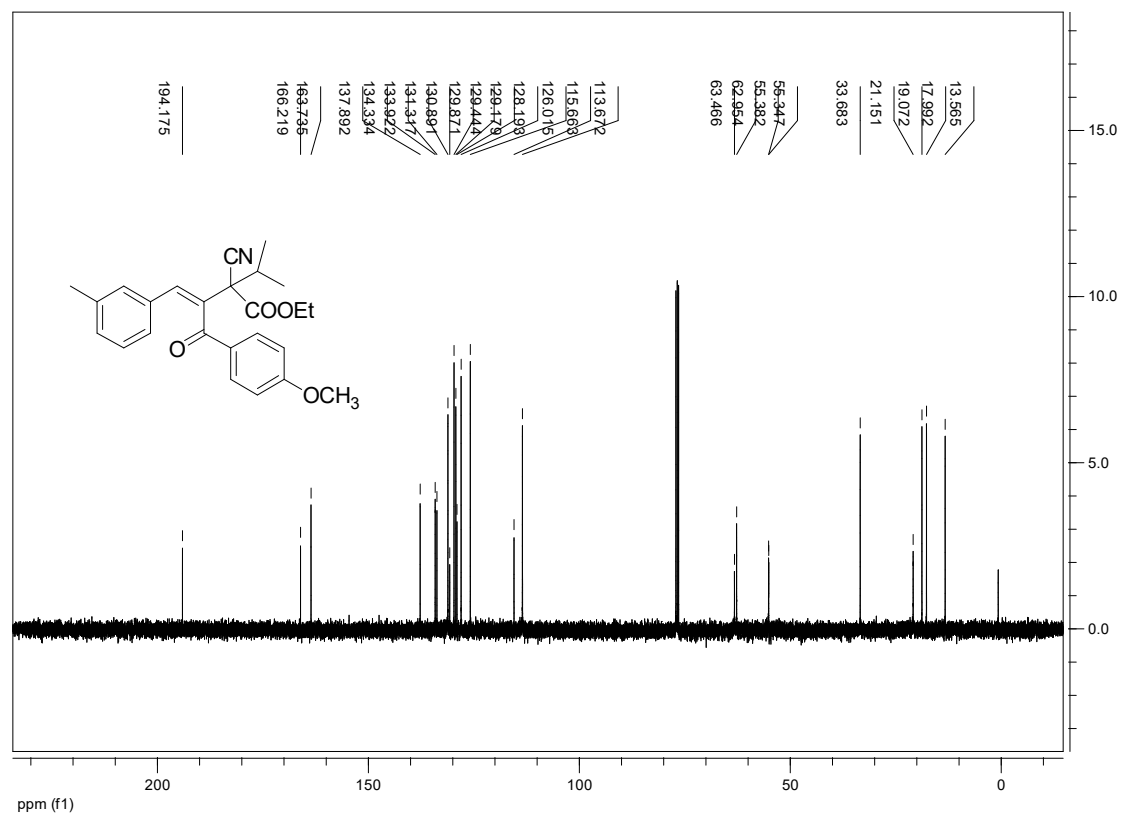
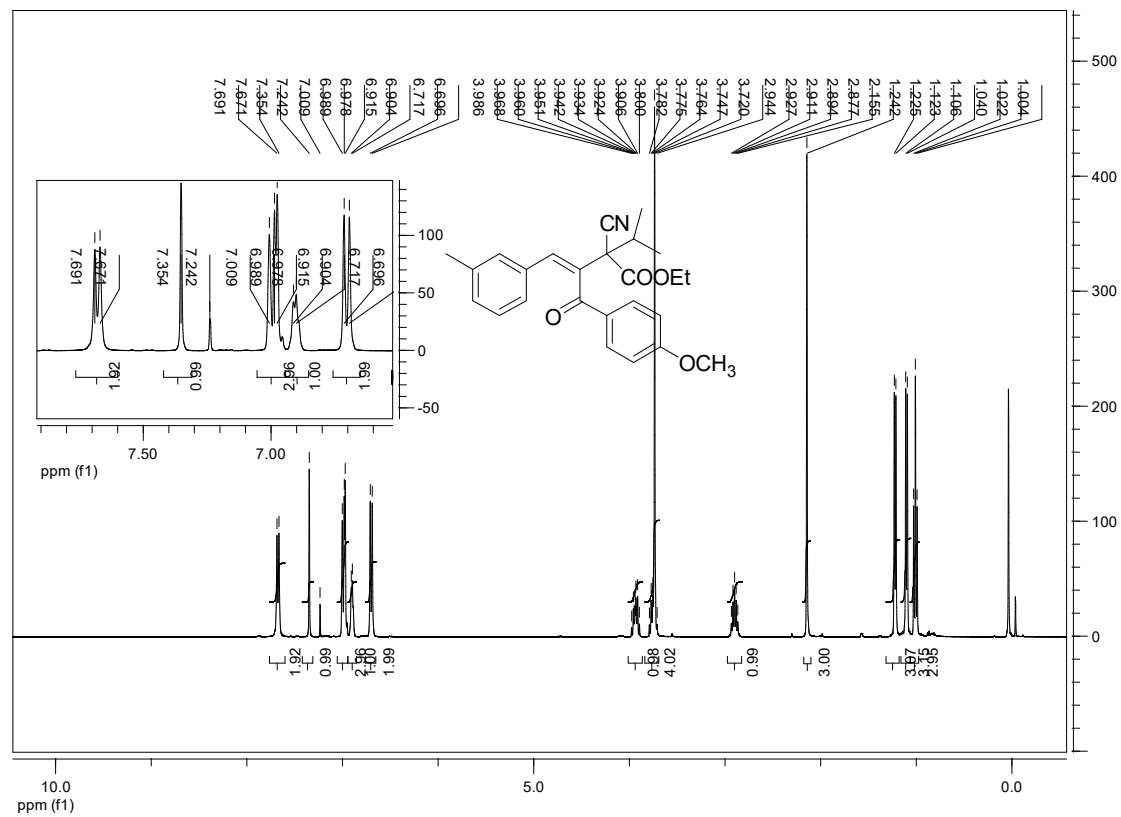


Ethyl (Z)-4-(4-bromophenyl)-2-cyano-2-isopropyl-3-(4-methoxybenzoyl)but-3-enoate

(3g)

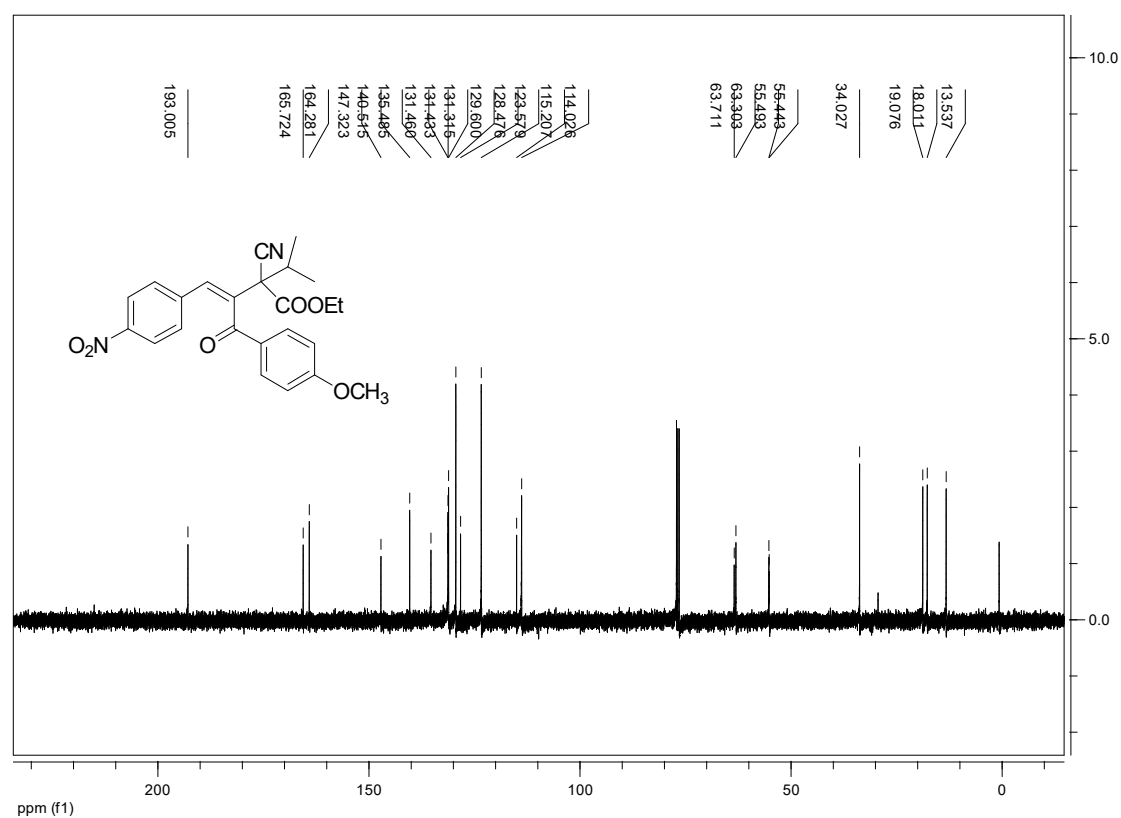
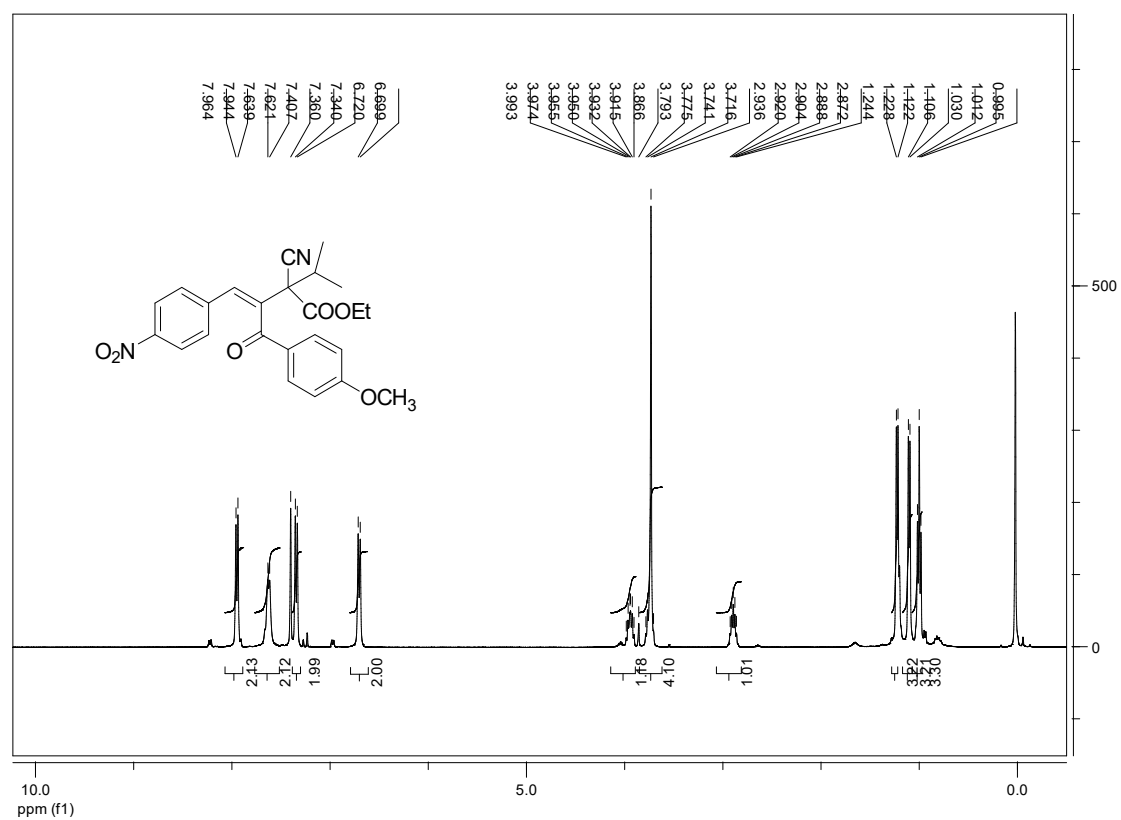


Ethyl (Z)-2-cyano-2-isopropyl-3-(4-methoxybenzoyl)-4-(m-tolyl)but-3-enoate (**3h**)

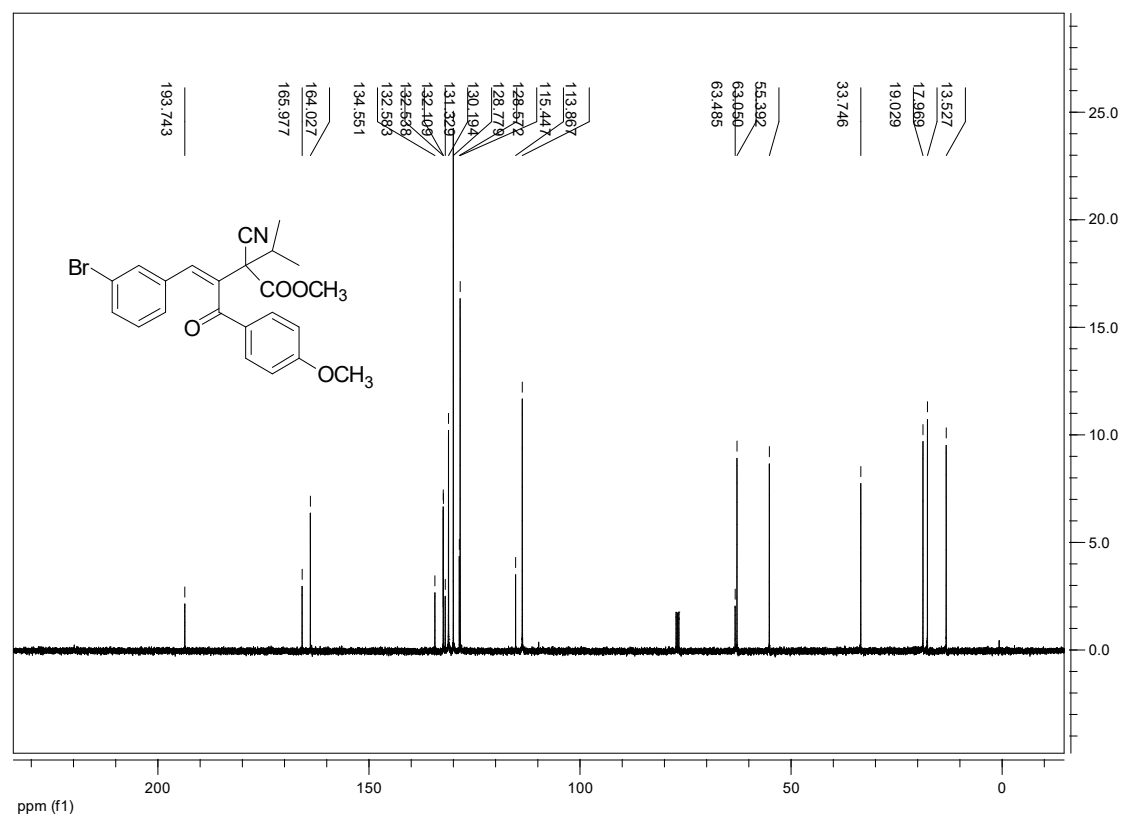
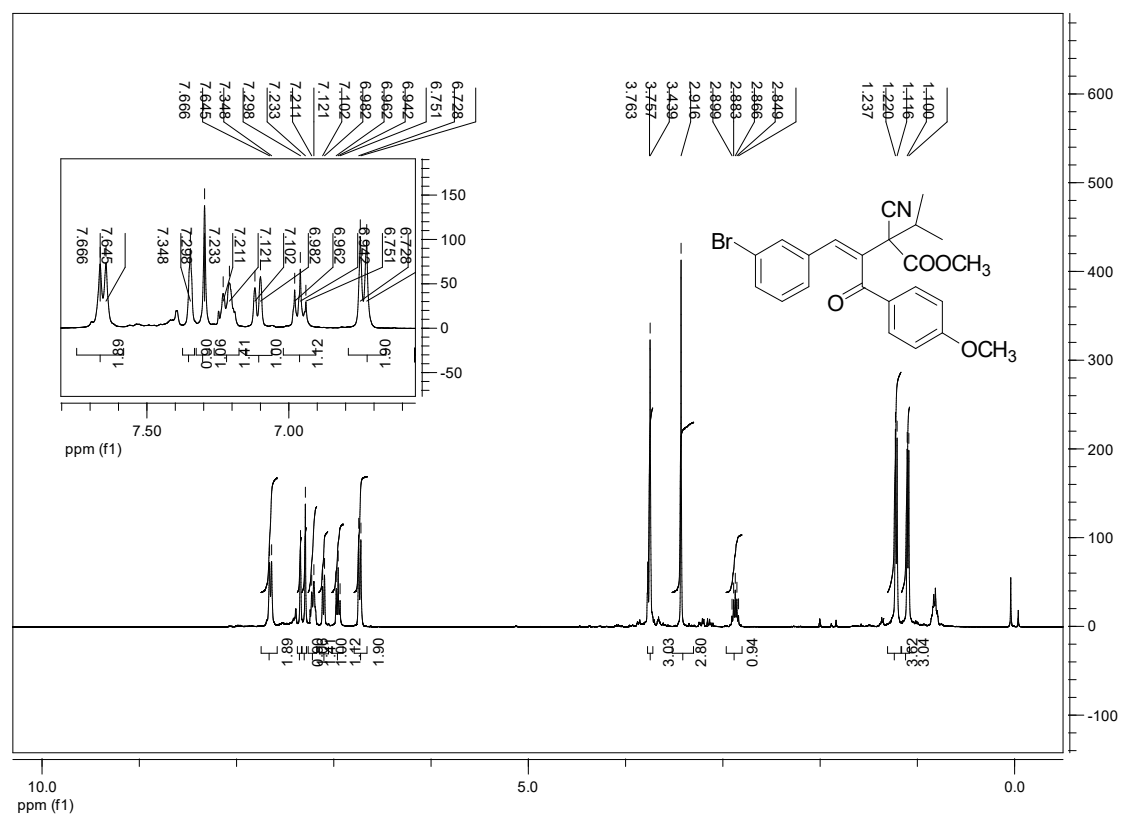


Ethyl (Z)-2-cyano-2-isopropyl-3-(4-methoxybenzoyl)-4-(4-nitrophenyl)but-3-enoate

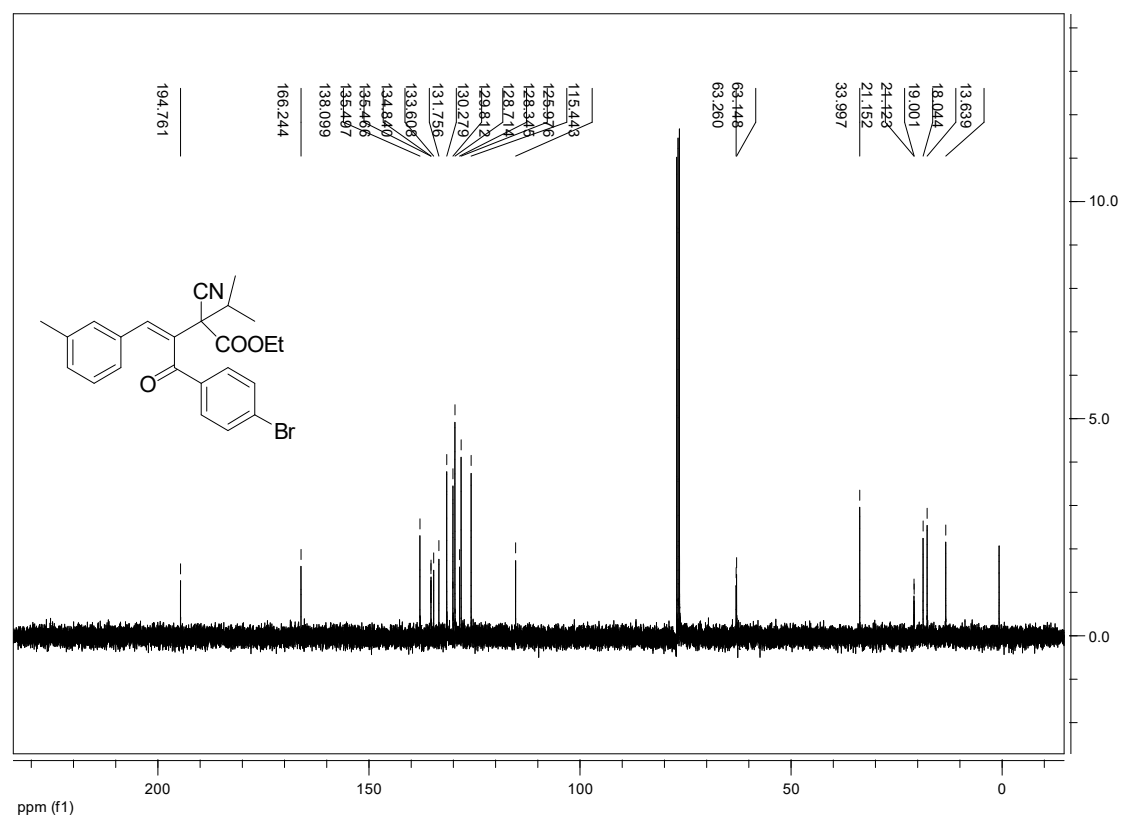
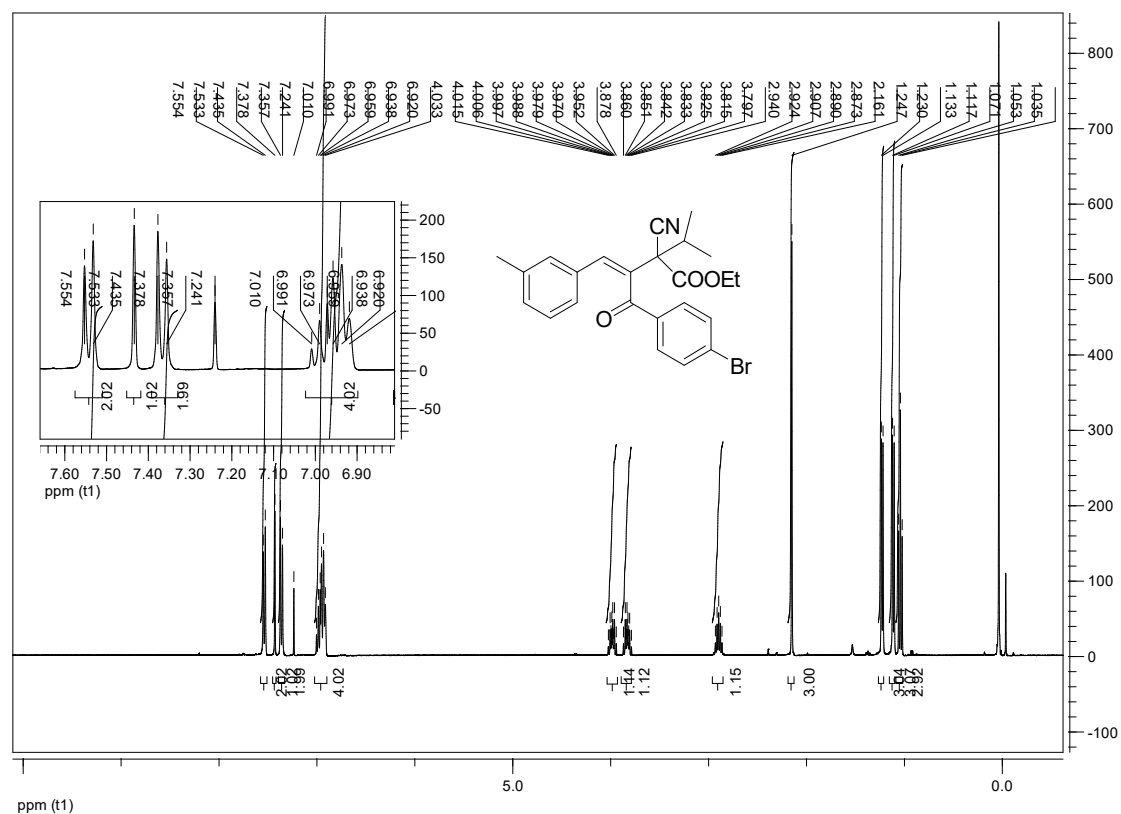
(3i)



Methyl (Z)-4-(3-bromophenyl)-2-cyano-2-isopropyl-3-(4-methoxybenzoyl)but-3-enoate (**3k**)

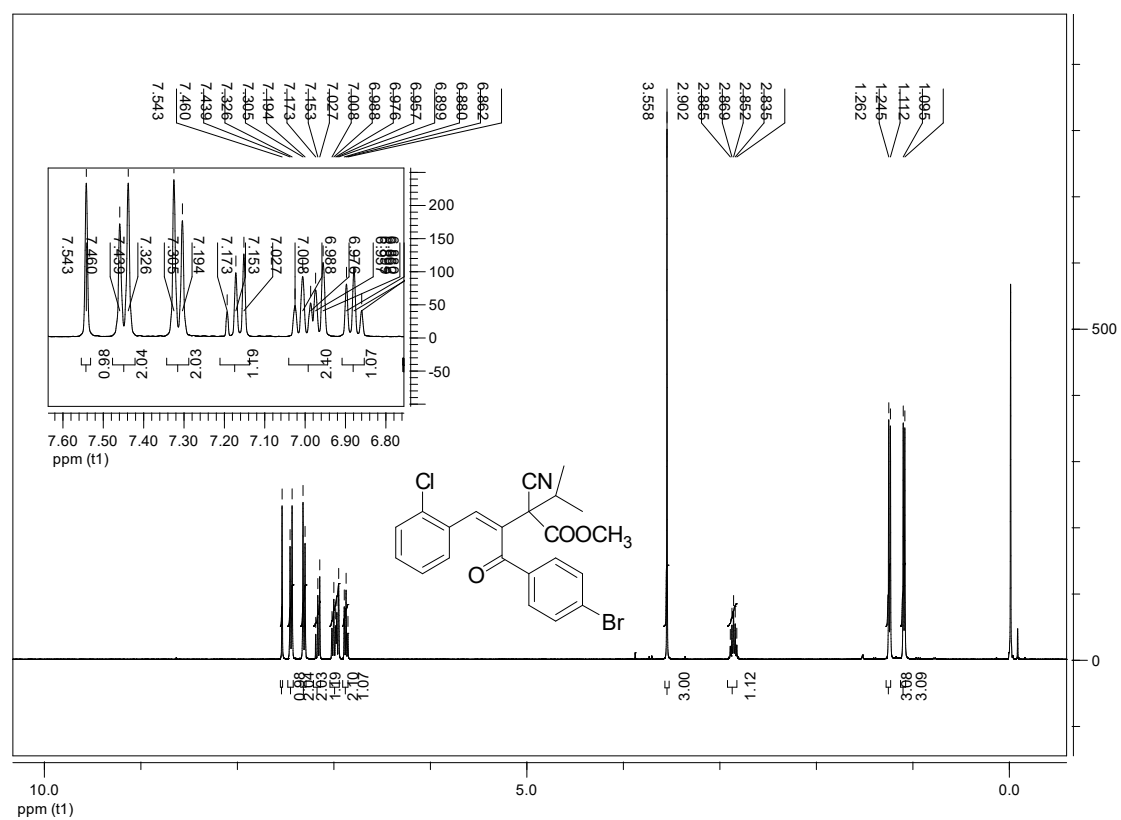


Ethyl (Z)-3-(4-bromobenzoyl)-2-cyano-2-isopropyl-4-(m-tolyl)but-3-enoate (**31**)

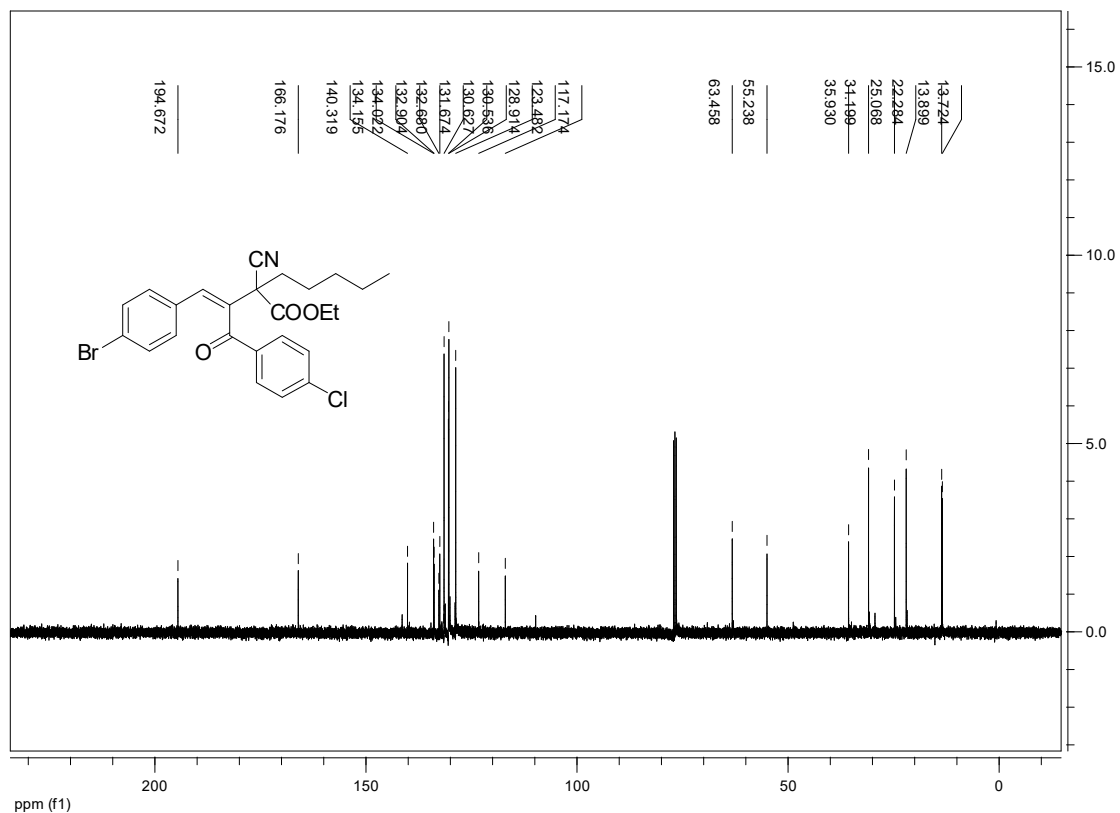
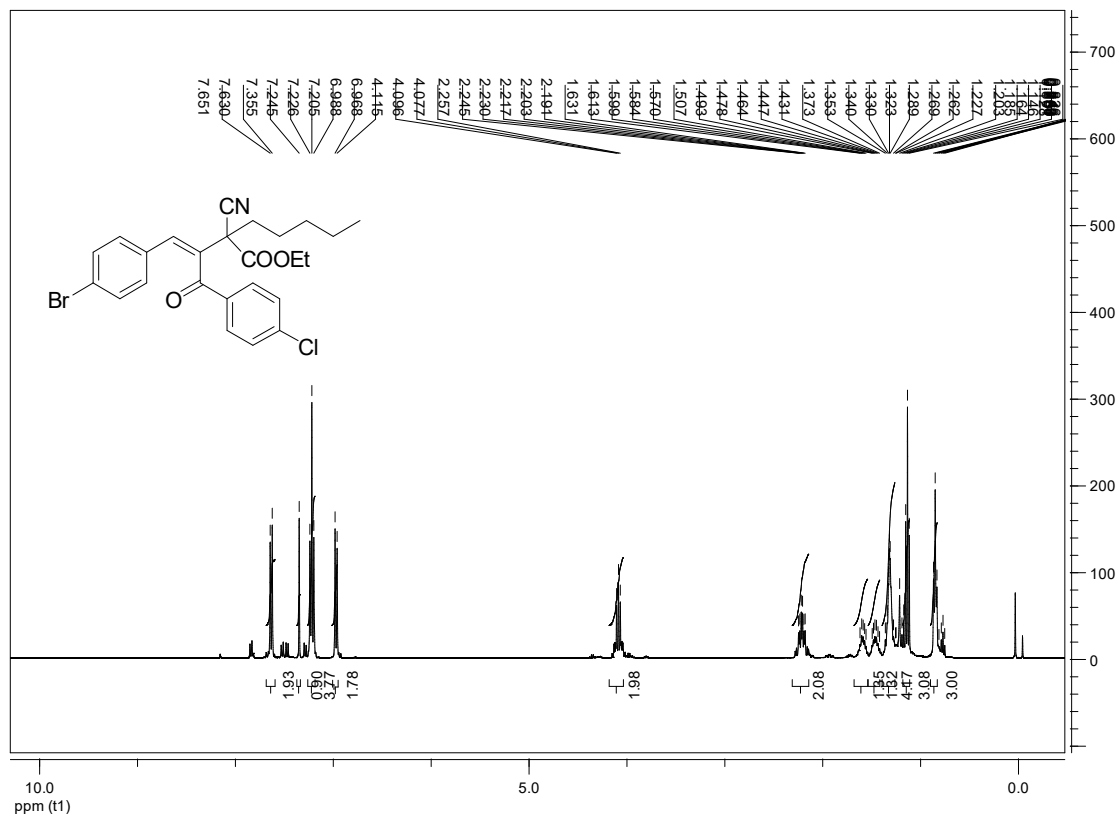


Methyl (Z)-3-(4-bromobenzoyl)-4-(2-chlorophenyl)-2-cyano-2-isopropylbut-3-enoate

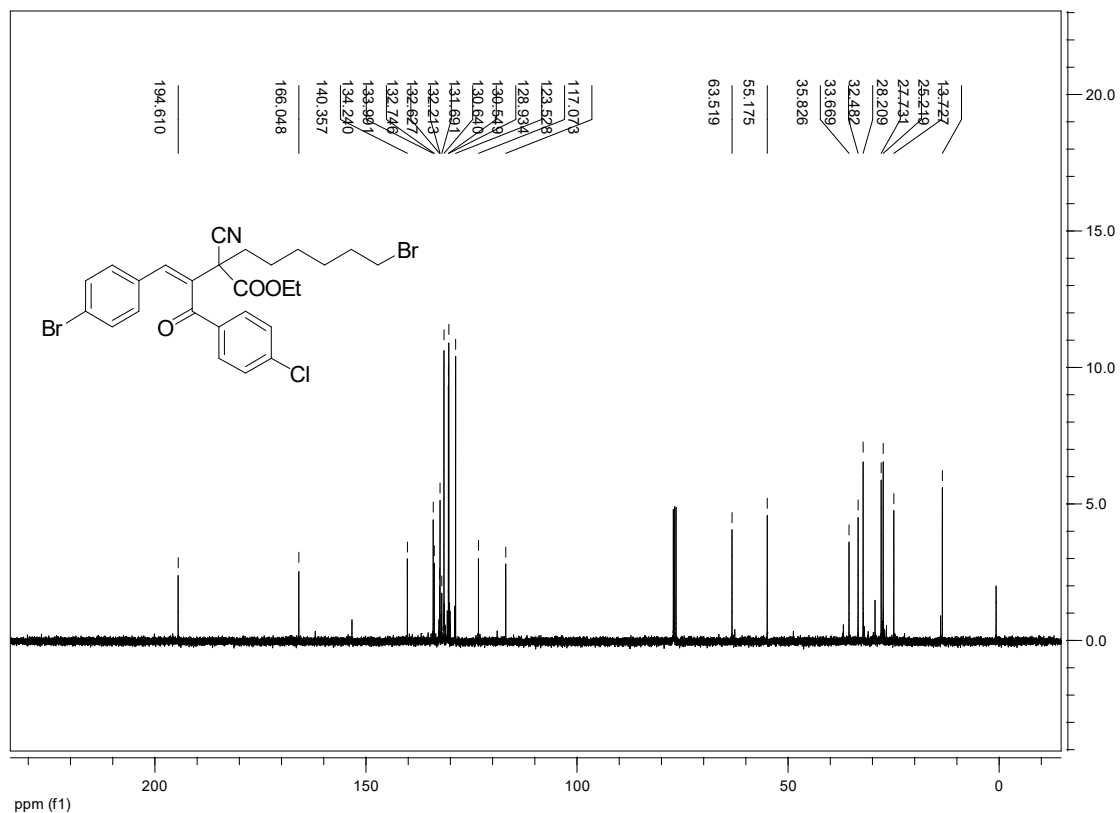
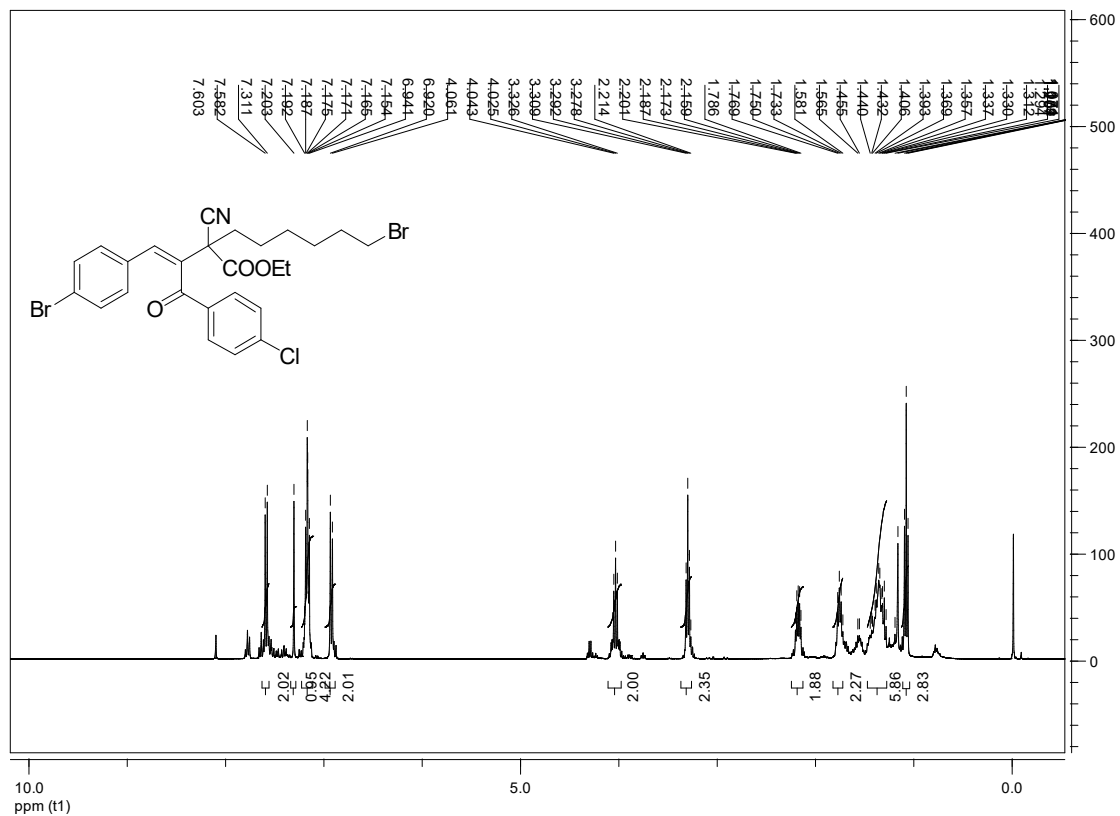
(3m)



Ethyl (Z)-2-(1-(4-bromophenyl)-3-(4-chlorophenyl)-3-oxoprop-1-en-2-yl)-2-cyanoheptanoate (**3v**)



Ethyl (Z)-8-bromo-2-(1-(4-bromophenyl)-3-(4-chlorophenyl)-3-oxoprop-1-en-2-yl)-2-cyanoctanoate (**3w**)



Ethyl (Z)-2-(1-(4-bromophenyl)-3-(4-methoxyphenyl)-3-oxoprop-1-en-2-yl)-2-cyanopent-4-enoate (**3z**)

