Supporting Information For

Visible Light Photoredox Catalysis: Regioselective Radical Addition of Aminoalkyl Radicals to 2,3-Allenoates

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General Experimental Methods. All reactions were carried out under dry nitrogen atmosphere. Solvents were dried by the general methods, and degassed before use. 2,3-Allenoates **1a~h**[1,2], and tertiary amines **2b**[3], **2d~h**[4], **2i**[5] were prepared according to literature. The other amines **2a**, **2c** were purchased from Sigma-Aldrich Company and used directly as received. Photoredox catalysts $Ir(ppy)_3$[6,7], $[Ir(ppy)_2bpy]PF_6$[8,9], $[Ir(ppy)_2bpy]BF_4$[8,10], $Ru(bpy)_3(PF_6)_2$[11], $Ru(bpy)_3Cl_2•6H_2O$[12], $Ru(bpy)_3(BF_4)_2$[11] were prepared according to literature. ^1H and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ on 500 MHz or 400 MHz instrument with TMS as internal standard. Low-resolution MS was obtained using EI or ESI ionization. HRMS was obtained using ESI ionization by TOF LC/MS. GC-MS spectra were obtained using a normal analysis method, in which MS spectra were obtained using EI ionization.

General Procedure for Synthesis of all products. In a typical procedure: In a 10 mL two-necked round-bottom flask were placed $K_2HPO_4•3H_2O$ (114 mg, 0.5 mmol), $Ru(bpy)_3(BF_4)_2$ (3.7 mg, 0.005 mmol, 1 mol%) under N_2, and then 2,3-allenolte **1** (0.5 mmol), amine **2** (0.6 mmol) and NMP (2 mL) were added. The reaction mixture was placed at a distance of about 5 cm from a 45 W compact fluorescent lamp (Arrow BHSL 45) and stirred at room temperature. After 24 hrs, purification was done by column chromatography on silica gel (300-400 mesh) with petroleum ether/ethyl acetate (20/1) as the eluent to give the pure product **3** or the mixture of **3** and **4**.

*A Mixture of Ethyl 3-((methyl(phenyl)amino)methyl)but-3-enoate (**3a**) and (E)-Ethyl 3-methyl-4-(methyl(phenyl)amino)but-2-enoate (**4a**):* 78 mg, 67% yield, **3a**/**4a** = 85/15; yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ (**3a**) 7.26 – 7.22 (m, 2H), 6.79 – 6.70 (m, 3H), 5.10 – 5.03 (m, 2H), 4.17 (q, J = 7.1 Hz, 2H), 3.97 (s, 2H), 3.09 (s, 2H), 2.96 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H); δ (**4a**) 7.26 – 7.22 (m, 2H), 6.79 – 6.70 (m, 1H), 6.66 (d, J = 8.0 Hz, 2H), 5.80 – 5.77 (m, 1H), 4.15 (q, J = 7.2 Hz, 2H), 3.91 (s, 2H), 3.00 (s, 3H), 2.18 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (**3a**) 171.2, 149.6, 138.7, 129.0, 116.5, 114.8, 112.3, 60.7, 57.7, 39.4, 38.2, 14.2; δ (**4a**) 166.7, 154.9, 149.2, 129.2, 116.8, 114.7, 112.0, 60.7, 59.6, 38.5, 16.5, 14.3; MS (ESI): ($[M+H]^+$) 234.2; HRMS (ESI) calcd for $C_{14}H_{20}NO_2$ ($[M+H]^+$) 234.1494, found 234.1488; IR (thin film): 3062, 3028, 2982, 2903, 1733, 1600, 1507, 1369, 1328, 1256, 1215, 1158, 1034, 908, 749, 693 cm^{-1}.

*(±)-Ethyl 3-((methyl(phenyl)amino)methyl)-4-phenylbut-3-enoate (**3b**):* 80 mg, 52% yield, E/Z = 1/1; yellow oil; E-isomer: ^1H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 2H), 7.30 – 7.24 (m, 5H), 6.83 (d, J = 8.2 Hz, 2H), 6.75 (t, J = 7.2 Hz, 1H), 6.64 (s, 1H), 4.20 (q, J = 7.1 Hz, 2H), 4.11 (d, J = 1.3 Hz, 2H),

3.26 (s, 2H), 3.02 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 149.2, 136.3, 131.2, 128.6, 128.3, 128.2, 127.8, 126.5, 116.3, 112.1, 61.0, 59.6, 38.5, 35.4, 14.6; MS (ESI): ($[M+H]^+$) 310.2; HRMS (ESI) calcd for $C_{20}H_{24}NO_2$ ($[M+H]^+$) 310.1807, found 310.1810; IR (thin film): 3058, 3026, 2981, 2903, 2817, 1731, 1600, 1506, 1449, 1369, 1320, 1255, 1179, 1020, 1032, 951, 860, 749, 696 cm^{-1}; *Z*-isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (t, J = 7.5 Hz, 2H), 7.31 – 7.25 (m, 3H), 7.20 – 7.15 (m, 2H), 6.70 (t, J = 7.2 Hz, 1H), 6.66 (s, 1H), 6.63 (d, J = 8.1 Hz, 2H), 4.26 (d, J = 1.1 Hz, 2H), 4.12 (q, J = 7.1 Hz, 2H), 3.18 (s, 2H), 2.85 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 149.1, 136.1, 134.2, 131.1, 128.7, 128.5, 127.8, 126.6, 116.5, 112.4, 60.7, 53.1, 40.5, 39.0, 14.7; MS (ESI): ($[M+H]^+$) 310.2; HRMS (ESI) calcd for $C_{20}H_{24}NO_2$ ($[M+H]^+$) 310.1807, found 310.1811; IR (thin film): 3058, 3025, 2981, 2904, 2817, 1731, 1599, 1505, 1447, 1368, 1329, 1255, 1159, 1033, 996, 938, 749, 696 cm^{-1}.

*(±)-Ethyl 4-(4-chlorophenyl)-3-((methyl(phenyl)amino)methyl)but-3-enoate (**3c**):* 57 mg, 33% yield, *E*/*Z* = 1/1; yellow oil; *E*-isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.27 – 7.23 (m, 2H), 7.21 (d, J = 8.4 Hz, 2H), 6.81 (d, J = 8.1 Hz, 2H), 6.75 (t, J = 7.2 Hz, 1H), 6.57 (s, 1H), 4.19 (q, J = 7.1 Hz, 2H), 4.08 (d, J = 1.0 Hz, 2H), 3.21 (s, 2H), 3.01 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.1, 149.8, 135.4, 132.9, 132.6, 130.0, 129.1, 128.5, 127.6, 116.9, 112.6, 61.0, 59.6, 38.3, 35.2, 14.2; MS (ESI): ($[M+H]^+$) 334.1; HRMS (ESI) calcd for $C_{20}H_{23}ClNO_2$ ($[M+H]^+$) 344.1412, found 344.1422; IR (thin film): 3028, 2981, 2903, 1730, 1600, 1506, 1367, 1321, 1255, 1178, 1094, 1032, 947, 864, 749, 692 cm^{-1}; *Z*-isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 2H), 7.23 – 7.15 (m, 4H), 6.72 (t, J = 7.3 Hz, 1H), 6.62 (d, J = 8.3 Hz, 2H), 6.59 (s, 1H), 4.22 (d, J = 1.2 Hz, 2H), 4.12 (q, J = 7.1 Hz, 2H), 3.17 (s, 2H), 2.84 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.6, 149.8, 135.7, 135.1, 133.0, 130.5, 130.3, 129.0, 128.4, 117.2, 112.9, 60.7, 53.0, 40.2, 38.8, 14.2; MS (ESI): ($[M+H]^+$) 334.1; HRMS (ESI) calcd for $C_{20}H_{23}ClNO_2$ ($[M+H]^+$) 344.1412, found 344.1403; IR (thin film): 3028, 2981, 2904, 2819, 1731, 1599, 1505, 1369, 1328, 1157, 1255, 1159, 1093, 1033, 939, 750, 693 cm^{-1}.

*(±)-Ethyl 4-(4-methoxyphenyl)-3-((methyl(phenyl)amino)methyl)but-3-enoate (**3d**):* 68 mg, 40% yield, *E*/*Z* = 1/1; yellow oil; *E*-isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.19 (m, 4H), 6.91 – 6.86 (m, 2H), 6.83 (d, J = 7.8 Hz, 2H), 6.74 (t, J = 6.9 Hz, 1H), 6.56 (s, 1H), 4.19 (q, J = 7.1 Hz, 2H), 4.08 (s, 2H), 3.82 (s, 3H), 3.25 (s, 2H), 3.00 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5, 158.7, 149.9, 130.3, 129.9, 129.4, 129.1, 128.5, 116.8, 113.8, 112.6, 60.8, 59.7, 55.3, 38.2, 35.1,

14.2; MS (ESI): ([M+H]$^+$) 340.2; HRMS (ESI) calcd for $C_{21}H_{26}NO_3$ ([M+H]$^+$) 340.1907, found 340.1914; IR (thin film): 2981, 2905, 2836, 1730, 1603, 1510, 1463, 1369, 1251, 1179, 1033, 943, 832, 751, 694 cm^{-1}; *Z*-isomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.14 (m, 4H), 6.94 – 6.89 (m, 2H), 6.70 (t, *J* = 6.9 Hz, 1H), 6.63 (d, *J* = 7.6 Hz, 2H), 6.59 (s, 1H), 4.26 (s, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 3.16 (s, 2H), 2.86 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.9, 158.7, 149.8, 133.3, 131.2, 130.4, 129.2, 129.0, 116.9, 113.7, 112. 8, 60.6, 55.3, 53.0, 40.3, 38.8, 14.2; MS (ESI): ([M+H]$^+$) 340.2; HRMS (ESI) calcd for $C_{21}H_{26}NO_3$ ([M+H]$^+$) 340.1907, found 340.1907; IR (thin film): 3030, 2980, 2906, 2836, 1731, 1603, 1508, 1462, 1368, 1251, 1176, 1033, 836, 751, 694 cm^{-1}.

*(±)-Ethyl 3-((methyl(phenyl)amino)methyl)pent-3-enoate (**3e**):* 58 mg, 47% yield, *E*/*Z* = 77/23; yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (*E*-isomer) 7.24 (m, 2H), 6.77 (d, *J* = 8.1 Hz, 2H), 6.72 (t, *J* = 7.2 Hz, 1H), 5.58 (q, *J* = 6.8 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.93 (s, 2H), 3.09 (s, 2H), 2.92 (s, 3H), 1.70 (d, *J* = 6.8 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); δ (*Z*-isomer) 5.64 (q, *J* = 7.0 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 1H), 4.05 (s, 2H), 3.00 (s, 2H), 2.86 (s, 3H), 1.81 (d, *J* = 6.9 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), the remaining signals could not be determined; ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.1, 171.3, 150.3, 149.9, 131.8, 129.6, 129.0, 129.0, 126.2, 123.7, 116.9, 116.4, 113.0, 112.4, 60.6, 60.4, 59.0, 51.8, 40.2, 38.0, 37.9, 33.8, 14.2, 14.1, 13.3; MS (ESI): ([M+H]$^+$) 248.2; HRMS (ESI) calcd for $C_{15}H_{22}NO_2$ ([M+H]$^+$) 248.1645, found 248.1648; IR (thin film): 3026, 2980, 2905, 1733, 1600, 1509, 1368, 1318, 1255, 1177, 1033, 940, 749, 693 cm^{-1}.

*Ethyl 3-((methyl(phenyl)amino)methyl)-4,4-diphenylbut-3-enoate (**3f**):* 56 mg, 29% yield; yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 2H), 7.30 (d, *J* = 7.1 Hz, 2H), 7.28 – 7.17 (m, 8H), 6.76 – 6.66 (m, 3H), 4.11 (s, 2H), 3.99 (q, *J* = 7.1 Hz, 2H), 3.18 (s, 2H), 2.85 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.7, 150.0, 143.6, 142.1, 141.4, 130.8, 129.3, 129.1, 1289.0, 128.3, 128.3, 127.2, 127.0, 117.0, 113.1, 60.4, 55.5, 38.8, 36.2, 14.2; MS (ESI): ([M+H]$^+$) 386.2; HRMS (ESI) calcd for $C_{26}H_{28}NO_2$ ([M+H]$^+$) 386.2115, found 386.2117; IR (thin film): 3057, 3024, 2980, 2932, 2815, 1729, 1599, 1504, 1444, 1368, 1254, 1177, 1033, 993, 938, 751, 702 cm^{-1}.

*Ethyl 4-methyl-3-((methyl(phenyl)amino)methyl)pent-3-enoate (**3g**):* 42 mg, 32% yield; yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.9 Hz, 2H), 6.78 (d, *J* = 8.0 Hz, 2H), 6.74 (d, *J* = 7.1 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 2H), 3.09 (s, 2H), 2.82 (s, 3H), 1.86 (s, 3H), 1.80 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 1497, 131.2, 128.3, 123.5, 116.0, 112.3, 60.1, 53.7,

37.4, 34.7, 21.5, 20.3, 14.3; MS (ESI): ([M+H]$^+$) 262.2; HRMS (ESI) calcd for $C_{16}H_{24}NO_2$ ([M+H]$^+$) 262.1807, found 262.1810; IR (thin film): 2981, 2933, 2814, 1731, 1601, 1505, 1450, 1368, 1326, 1254, 1174, 1033, 994, 928, 750, 693 cm^{-1}.

*Methyl 4-methyl-3-((methyl(phenyl)amino)methyl)pent-3-enoate (**3h**):* 20 mg, 25% yield; yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.9 Hz, 2H), 6.86 – 6.63 (m, 3H), 4.00 (s, 2H), 3.61 (s, 3H), 3.11 (s, 2H), 2.82 (s, 3H), 1.86 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.5, 150.6, 132.1, 129.1, 124.2, 116.9, 113.1, 54.0, 51.5, 37.6, 34.5, 21.4, 20.2; MS (ESI): ([M+H]$^+$) 248.2; HRMS (ESI) calcd for $C_{15}H_{22}NO_2$ ([M+H]$^+$) 248.1651, found 248.1646; IR (thin film): 2992, 2949, 2813, 1736, 1600, 1505, 1435, 1368, 1338, 1254, 1169, 1103, 995, 750 693 cm^{-1}.

*A Mixture of Ethyl 3-((diphenylamino)methyl)but-3-enoate (**3i**) and (E)-Ethyl 4-(diphenylamino)-3-methylbut-2-enoate (**4i**):* 34 mg, 23% yield, **3i**/**4i** = 91/9; yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (**3i**) 7.30 – 7.24 (m, 4H), 7.12 – 7.06 (m, 4H), 6.99 – 6.94 (m, 2H), 5.26 (d, *J* = 1.0 Hz, 1H), 5.10 (d, *J* = 1.0 Hz, 1H), 4.44 (s, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.12 (s, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); δ (**4i**) 6.03 (d, *J* = 1.4 Hz, 1H), 4.38 (s, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.20 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), the remaining signals could not be determined; ^{13}C NMR (126 MHz, $CDCl_3$) δ (**3i**) 171.1, 148.0, 138.5, 129.2, 121.4, 120.7, 115.1, 60.8, 57.1, 39.8, 14.2; MS (ESI): ([M+H]$^+$) 296.2; HRMS (ESI) calcd for $C_{19}H_{22}NO_2$ ([M+H]$^+$) 296.1645, found 296.1641; IR (thin film): 3060, 3037, 2982, 2905, 1733, 1590, 1496, 1366, 1230, 1157, 1033, 909, 750, 696 cm^{-1}.

*A Mixture of Ethyl 4-(ethyl(phenyl)amino)-3-methylenepentanoate (**3j**) and (E)-Ethyl 4-(ethyl(phenyl)amino)-3-methylpent-2-enoate (**4j**):* 18 mg, 14% yield, **3j**/**4j** = 88/12; yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (**3j**) 7.23 (t, *J* = 7.8 Hz, 2H), 6.82 (d, *J* = 8.2 Hz, 2H), 6.71 (t, *J* = 7.0 Hz, 1H), 5.17 (s, 2H), 4.59 – 4.52 (d, *J* = 6.7 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.20 – 3.02 (m, 4H), 1.31 (d, *J* = 8.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.12 (t, *J* = 7.0 Hz, 3H); δ (**4j**) 5.81 (s, 1H), 4.31 (d, *J* = 7.3 Hz, 1H), 4.18 (m, 2H), 3.04 (s, 3H), 2.17 (s, 3H), the remaining signals could not be determined; ^{13}C NMR (126 MHz, $CDCl_3$) δ (**3j**) 171.7, 148.4, 144.3, 129.2, 116.8, 115.0, 114.3, 60.7, 57.2, 39.9, 38.8, 15.1, 14.4, 14.2, 13.9; MS (ESI): ([M+H]$^+$) 262.2; HRMS (ESI) calcd for $C_{16}H_{24}NO_2$ ([M+H]$^+$) 262.1802, found 262.1806; IR (thin film): 3092, 3060, 2977, 2934, 2874, 1735, 1597, 1502, 1369, 1269, 1157, 1035, 909, 748, 694 cm^{-1}.

*A Mixture of Ethyl 3-(((4-methoxyphenyl)(methyl)amino)methyl)but-3-enoate (**3k**) and (E)-Ethyl 4-((4-methoxyphenyl)(methyl)amino)-3-methylbut-2-enoate (**4k**):* 50 mg, 38% yield, **3k**/**4k** = 95/5; yellow

oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (**3k**) 6.90 – 6.78 (m, 2H), 6.73 (d, *J* = 9.0 Hz, 2H), 5.07 (dd, *J* = 15.2, 1.2 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 2H), 3.77 (s, 3H), 3.09 (s, 2H), 2.87 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); δ (**4k**) 6.64 – 6.61 (m, 2H), 5.83 (d, *J* = 1.4 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 2H), 2.92 (s, 3H), 2.16 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), the remaining signals could not be determined; ^{13}C NMR (126 MHz, $CDCl_3$) δ (**3k**) 171.3, 151.8, 144.8, 139.4, 114.9, 114.8, 114.3, 60.7, 59.0, 55.9, 39.5, 38.7, 14.2; MS (ESI): ($[M+H]^+$) 264.2; HRMS (ESI) calcd for $C_{15}H_{22}NO_3$ ($[M+H]^+$) 264.1594, found 264.1598; IR (thin film): 2984, 2937, 2905, 2832, 1733, 1515, 1448, 1368, 1245, 1180, 1038, 909, 816 cm^{-1}.

*(±)-Ethyl 3-((methyl(p-tolyl)amino)methyl)-4-phenylbut-3-enoate (**3l**):* 66 mg, 41% yield, *E*/*Z* = 48/52; yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 5H), 7.31 – 7.25 (m, 5H), 7.08 (d, *J* = 8.3 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.76 (d, *J* = 8.3 Hz, 2H), 6.66 (s, 1H), 6.65 (s, 1H), 6.57 (d, *J* = 8.4 Hz, 2H), 4.21 (s, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 4.06 (s, 2H), 3.26 (s, 2H), 3.19 (s, 2H), 2.97 (s, 3H), 2.82 (s, 3H), 2.28 (s, 3H), 2.24 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.9, 171.5, 148.0, 137.0, 136.8, 135.0, 132.1, 131.5, 129.7, 129.6, 129.2, 129.0, 128.7, 128.3, 128.2, 127.0, 127.0, 113.2, 112.9, 60.9, 60.6, 60.1, 53.3, 40.3, 38.9, 38.4, 35.2, 20.3, 20.2, 14.3; MS (ESI): ($[M+H]^+$) 342.2; HRMS (ESI) calcd for $C_{21}H_{26}NO_2$ ($[M+H]^+$) 324.1964, found 324.1966; IR (thin film): 2980, 2920, 2863, 1731, 1618, 1521, 1447, 1367, 1326, 1253, 1180, 1032, 939, 805, 744, 700 cm^{-1}.

*(±)-ethyl 3-(((4-fluorophenyl)(methyl)amino)methyl)-4-phenylbut-3-enoate (**3m**):* 63 mg, 38% yield, *E*/*Z* = 51/49; yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 5H), 7.31 – 7.24 (m, 5H), 6.99 – 6.93 (m, 2H), 6.90 – 6.84 (m, 2H), 6.78 – 6.73 (m, 2H), 6.67 (s, 1H), 6.62 (s, 1H), 6.58 – 6.53 (m, 2H), 4.19 (d, *J* = 1.3 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 4.04 (d, *J* = 1.3 Hz, 2H), 3.25 (s, 2H), 3.18 (s, 2H), 2.97 (s, 3H), 2.80 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.7, 171.4, 156.7, 156.6, 154.8, 154.7, 146.6, 146.6, 136.8, 136.6, 134.5, 131.8, 129.1, 128.6, 128.3, 128.2, 127.1, 127.0, 115.5, 115.4, 115.3, 115.2, 114.2, 114.1, 113.8, 113.7, 60.9, 60.6, 60.4, 53.6, 40.3, 39.3, 38.7, 35.1, 14.2; MS (ESI): ($[M+H]^+$) 328.2; HRMS (ESI) calcd for $C_{20}H_{23}FNO_2$ ($[M+H]^+$) 328.1713, found 328.1710; IR (thin film): 3056, 3025, 2982, 2904, 1731, 1612, 1514, 1448, 1368, 1326, 1229, 1179, 1117, 1032, 939, 816, 743, 700 cm^{-1}.

*(±)-ethyl 3-(((4-chlorophenyl)(methyl)amino)methyl)-4-phenylbut-3-enoate (**3n**):* 58 mg, 34% yield, *E*/*Z* = 40/60; yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (*E*-isomer) 7.42 – 7.26 (m, 5H), 7.21 – 7.17 (m,

2H), 6.76 – 6.71 (m, 2H), 6.58 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 4.08 (d, *J* = 1.3 Hz, 2H), 3.24 (s, 2H), 3.01 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), δ (*Z*-isomer) 7.42 – 7.26 (m, 5H), 7.12 – 7.07 (m, 2H), 6.68 (s, 1H), 6.53 – 6.47 (m, 2H), 4.25 (d, *J* = 1.2 Hz, 2H), 4.15 – 4.09 (m, 2H), 3.15 (s, 2H), 2.85 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{1}H NMR (500 MHz, $CDCl_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.6, 171.3, 148.3, 148.2, 136.7, 136.5, 134.1, 132.0, 129.1, 128.8, 128.7, 128.6, 128.3, 128.2, 127.2, 127.0, 121.7, 121.5, 113.8, 113.6, 60.9, 60.6, 59.5, 52.9, 40.2, 39.0, 38.4, 35.1, 14.2; MS (ESI): ($[M+H]^+$) 344.1; HRMS (ESI) calcd for $C_{20}H_{23}ClNO_2$ ($[M+H]^+$) 344.1417, found 344.1400; IR (thin film): 3056, 3025, 2981, 2903, 1731, 1597, 1503, 1448, 1370, 1320, 1251, 1181, 1121, 1031, 952, 811, 745, 701 cm^{-1}.

*(±)-ethyl 3-(((4-bromophenyl)(methyl)amino)methyl)-4-phenylbut-3-enoate (**3o**):* 73 mg, 38% yield, *E*/*Z* = 46/54; yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (*E*-isomer) 7.43 – 7.20 (m, 7H), 6.71 – 6.67 (m, 2H), 6.57 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 4.08 (d, *J* = 1.3 Hz, 2H), 3.23 (s, 2H), 3.00 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), δ (*Z*-isomer) 7.44 – 7.20 (m, 7H), 6.67 (s, 1H), 6.47 – 6.42 (m, 2H), 4.24 (d, *J* = 1.2 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.14 (s, 2H), 2.85 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.6, 171.3, 148.7, 148.6, 136. 7, 136.5, 134.0, 132.0, 131.7, 131.6, 129.1, 128.6, 128.3, 128.3, 127.2, 127.1, 114.3, 114.0, 108.8, 108.6, 60.9, 60.7, 59.4, 52.8, 40.2, 38.9, 38.4, 35.1, 14.2, 14.2; MS (ESI): ($[M+H]^+$) 388.1; HRMS (ESI) calcd for $C_{20}H_{23}BrNO_2$ ($[M+H]^+$) 388.0912, found 388.0896; IR (thin film): 3057, 3025, 2981, 2903, 2823, 1731, 1593, 1500, 1448, 1370, 1320, 1252, 1181, 1121, 1031, 938, 809, 745, 700 cm^{-1}.

*(E)-ethyl 4-phenyl-3-(1-phenylpyrrolidin-2-yl)but-3-enoate (**3p**):* 20 mg, 12% yield; yellow oil;^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.27 – 7.19 (m, 5H), 6.75 (d, *J* = 8.0 Hz, 2H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.61 (s, 1H), 4.30 (d, *J* = 8.2 Hz, 1H), 4.24 – 4.15 (m, 1H), 4.15 – 4.06 (m, 1H), 3.65 – 3.59 (m, 1H), 3.43 (d, *J* = 15.8 Hz, 1H), 3.35 (td, *J* = 9.2, 6.7 Hz, 1H), 3.18 (d, *J* = 15.8 Hz, 1H), 2.21 – 2.14 (m, 1H), 2.14 – 2.06 (m, 1H), 2.05 – 2.00 (m, 1H), 2.00 – 1.94 (m, 1H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.4, 147.4, 137.3, 134.9, 128.9, 128.6, 128.4, 128.2, 126.8, 116.1, 112.5, 64.6, 60.9, 49.1, 35.5, 31.5, 23.3, 14.2; MS (ESI): ($[M+H]^+$) 336.2; HRMS (ESI) calcd for $C_{22}H_{26}NO_2$ ($[M+H]^+$) 336.1958, found 336.1957; IR (thin film): 3058, 3025, 2974, 2872, 1731, 1598, 1503, 1359, 1173, 1032, 748, 696 cm^{-1}.

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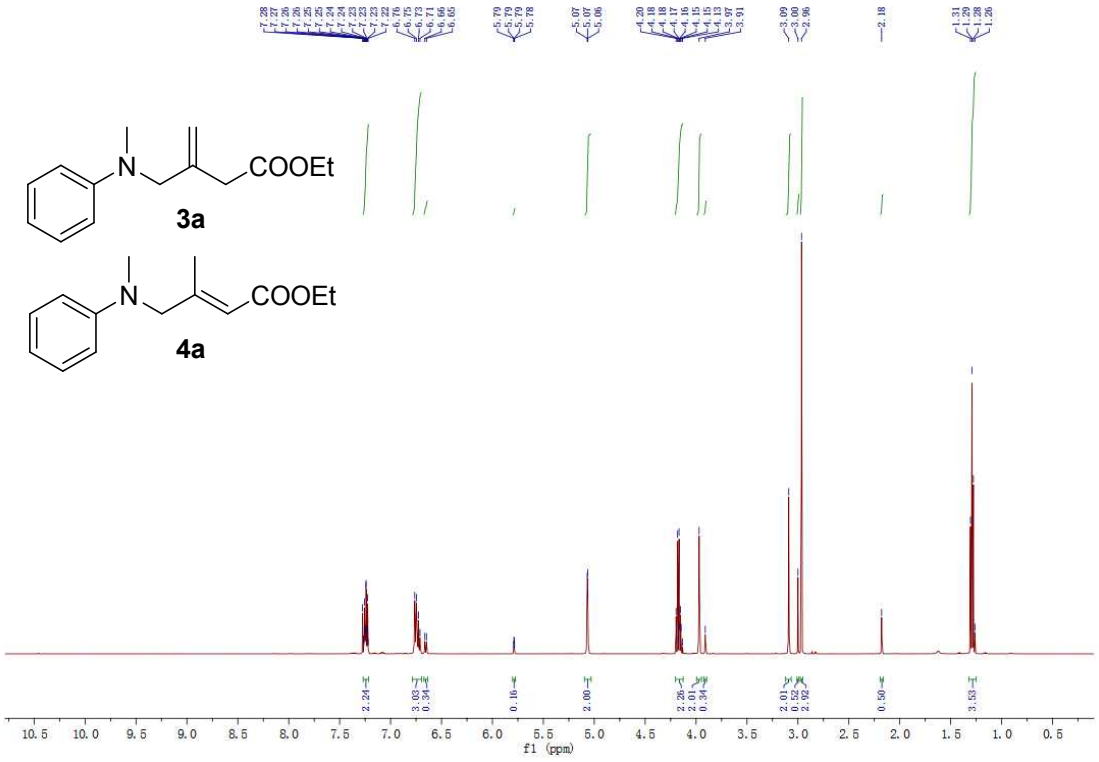
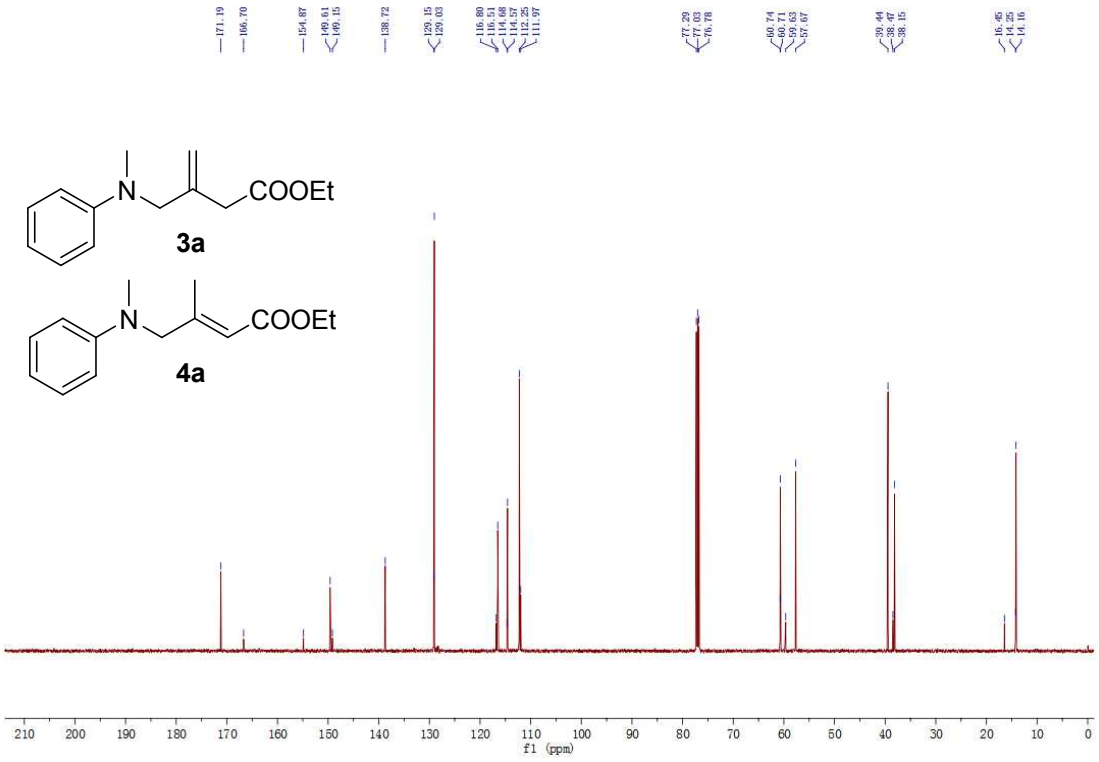
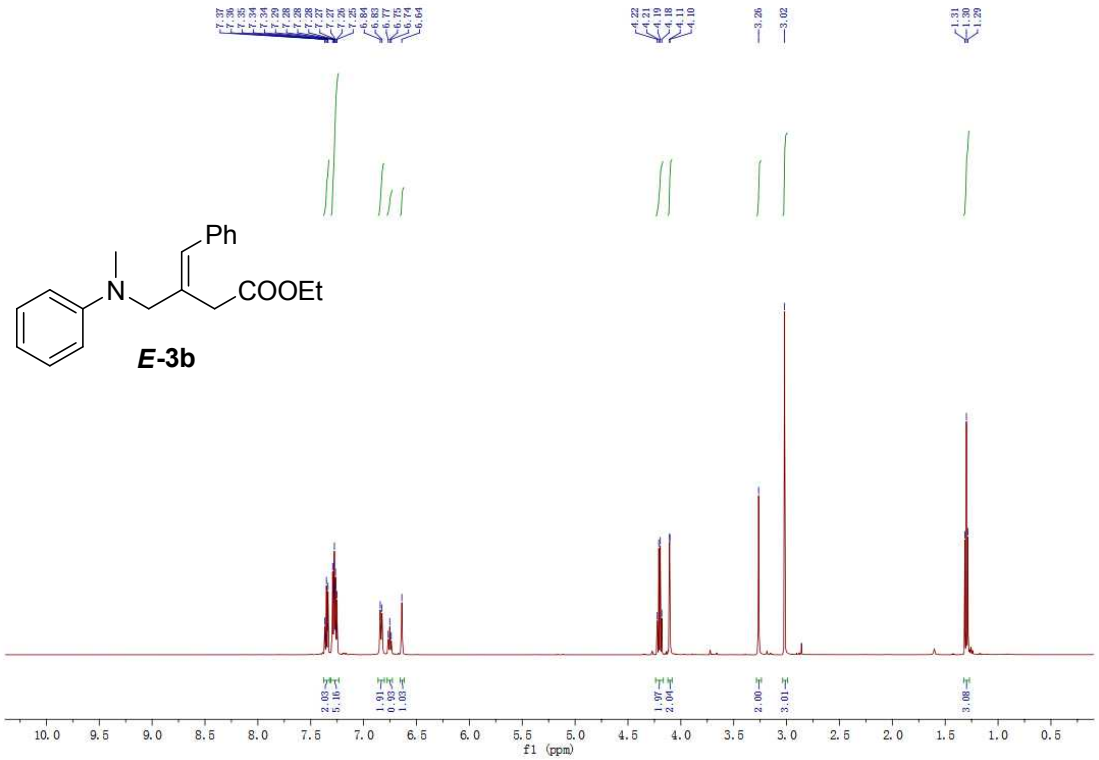
Copies of ^{1}H and ^{13}C NMR spectra



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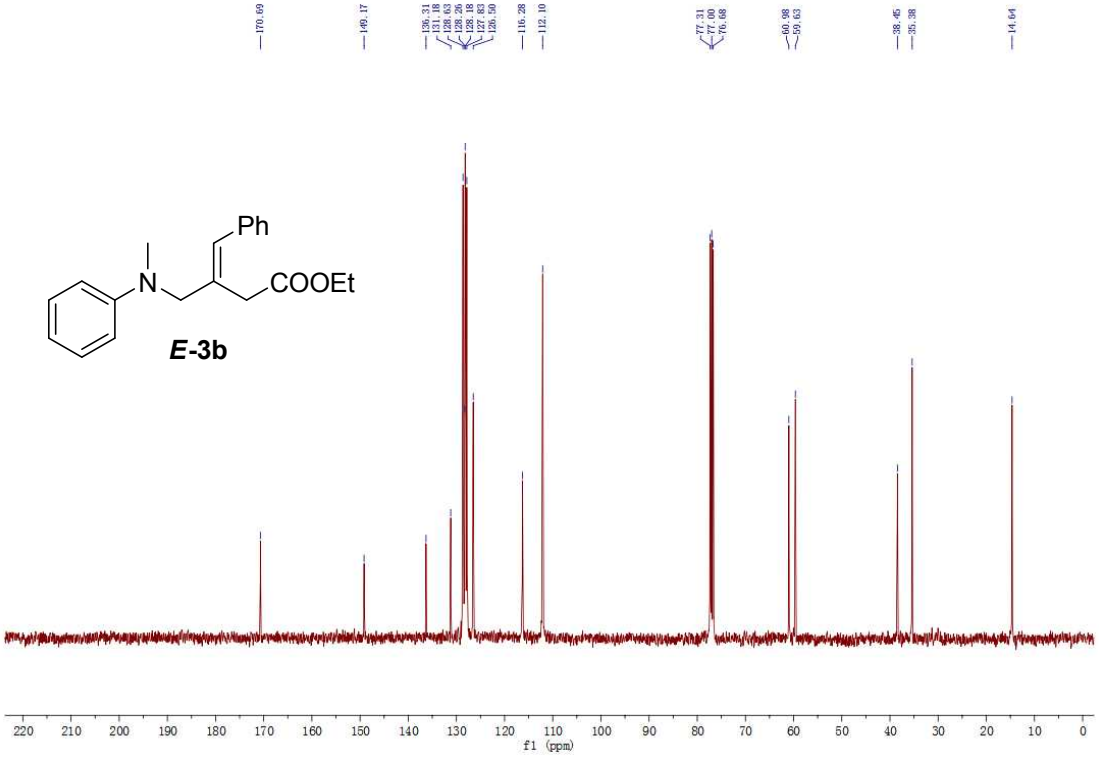
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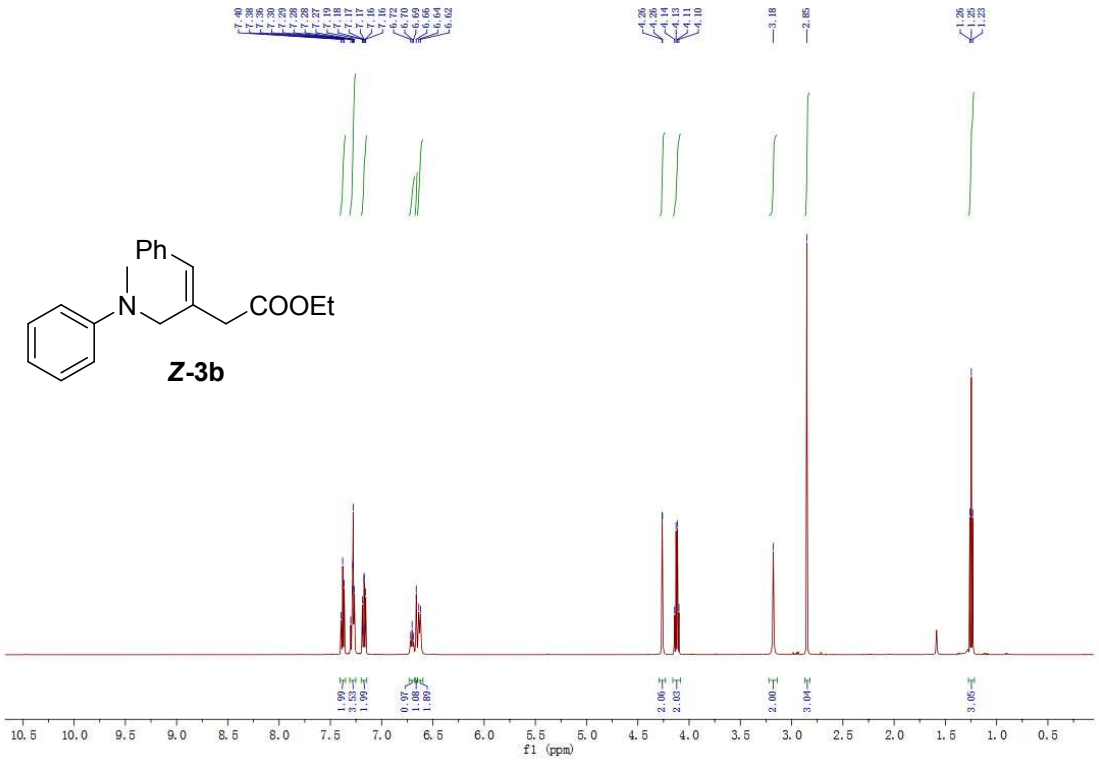
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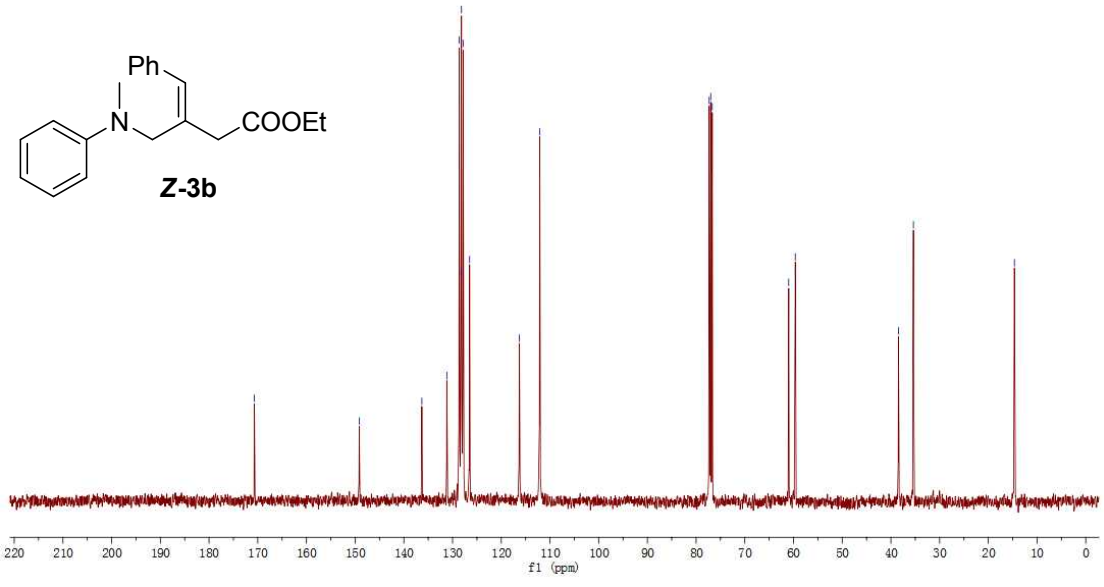
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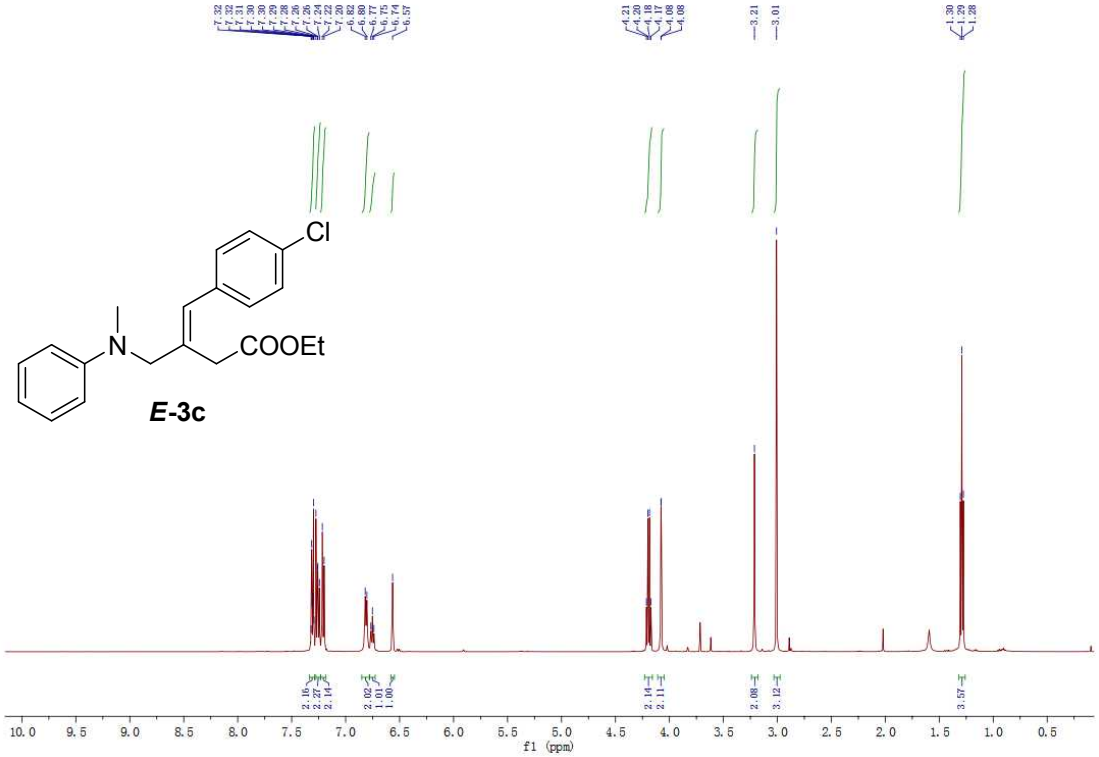
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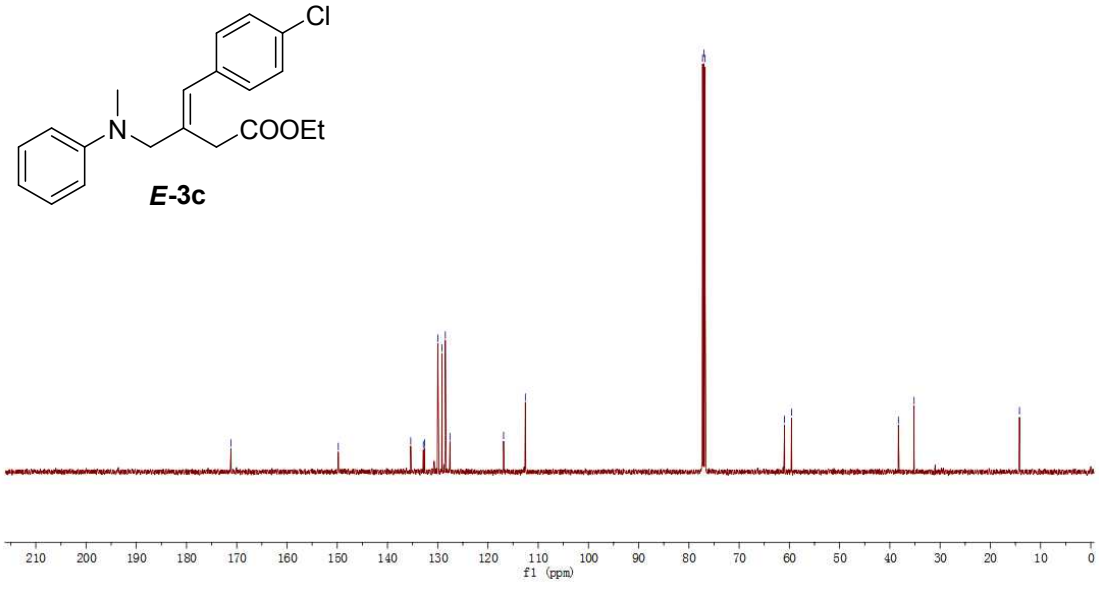
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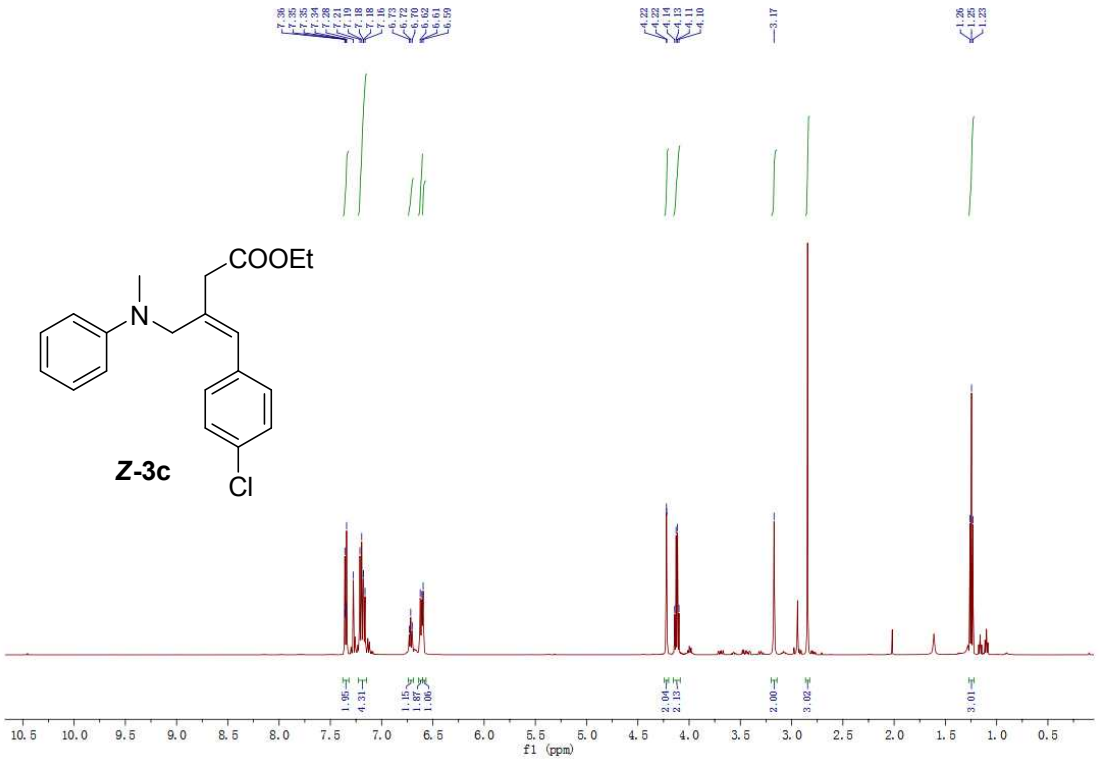
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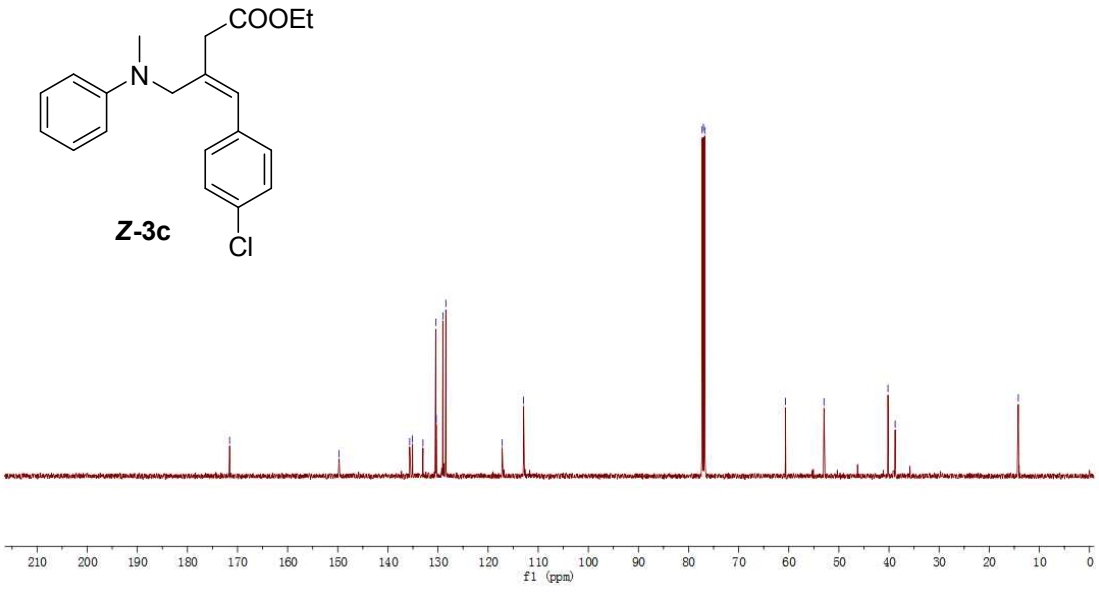
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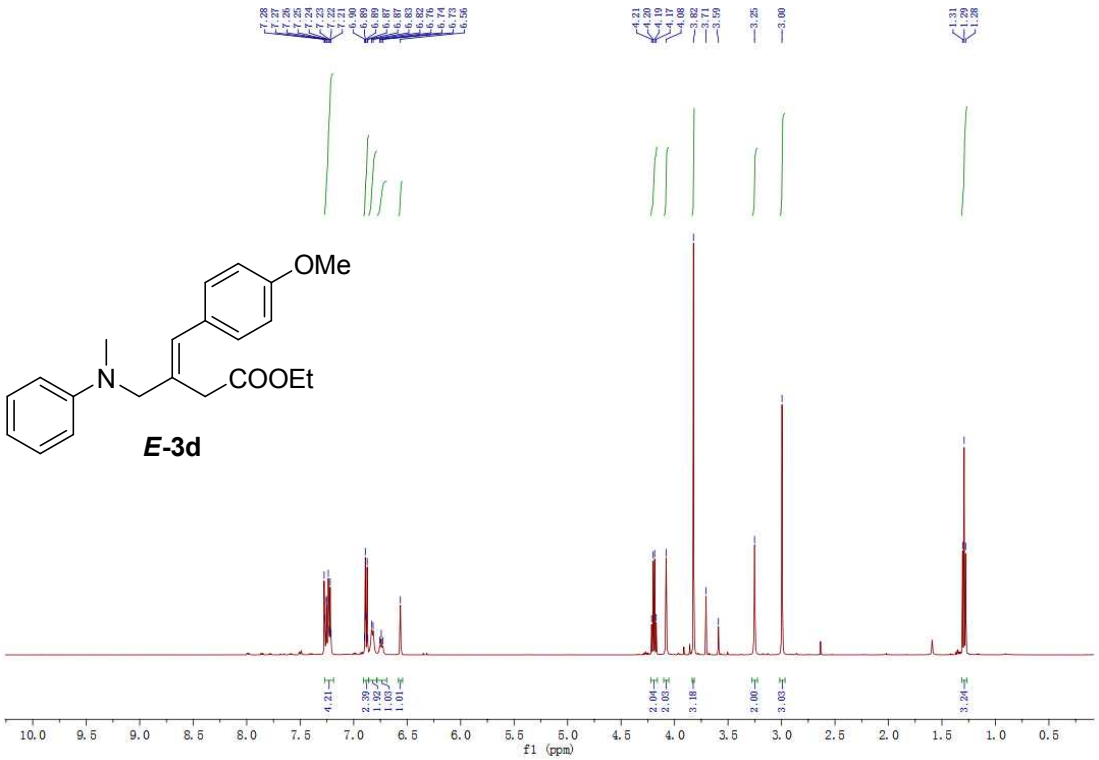
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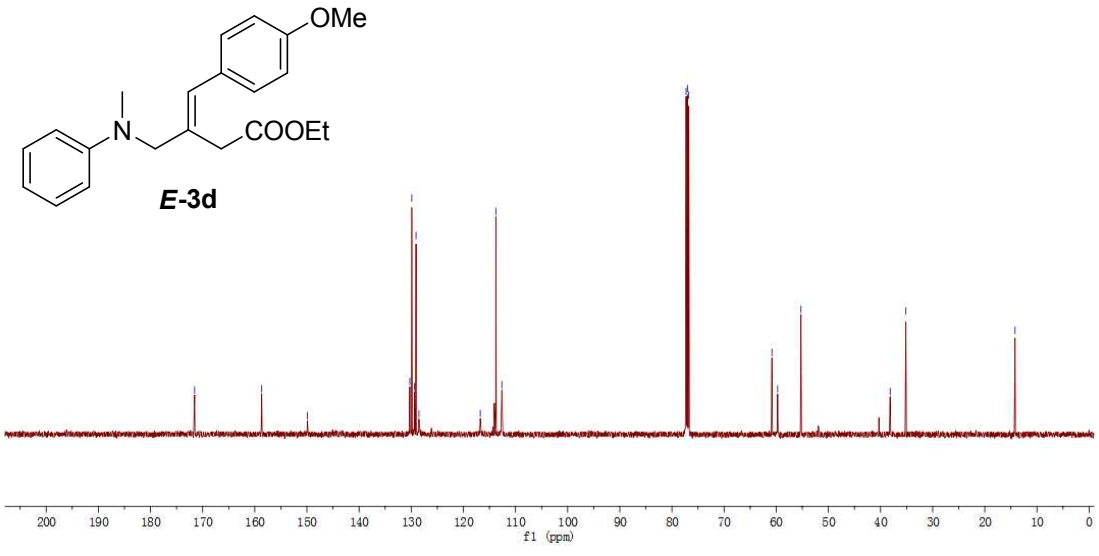
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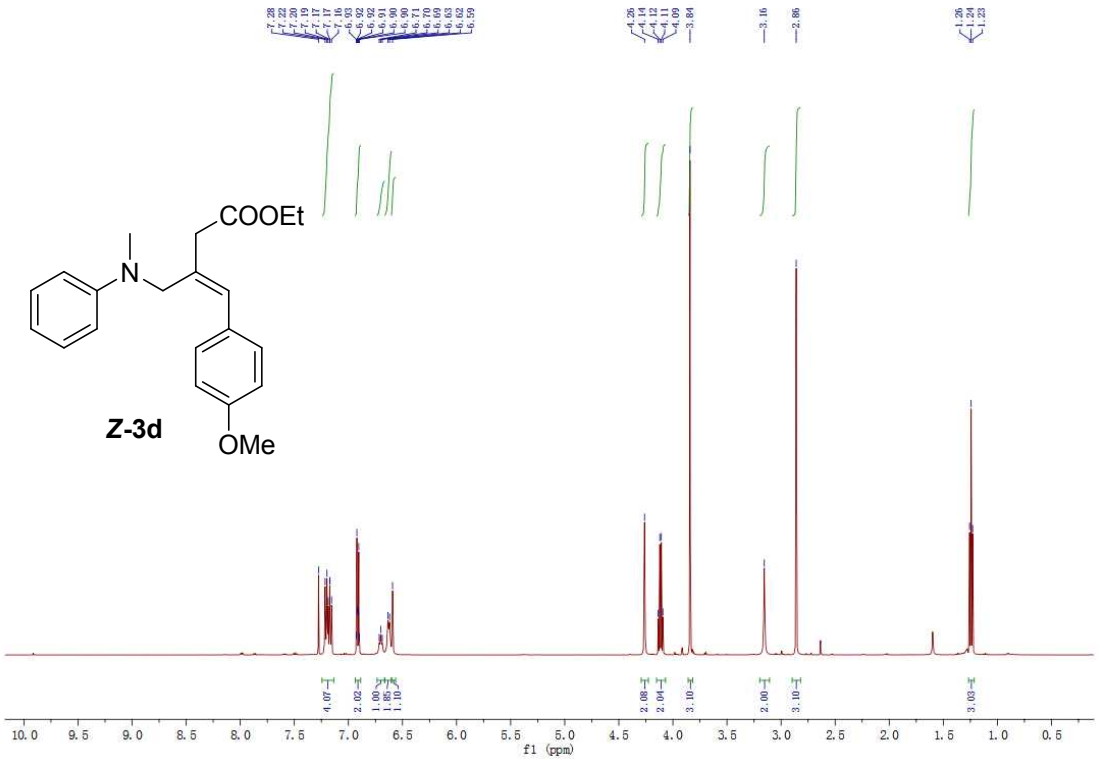
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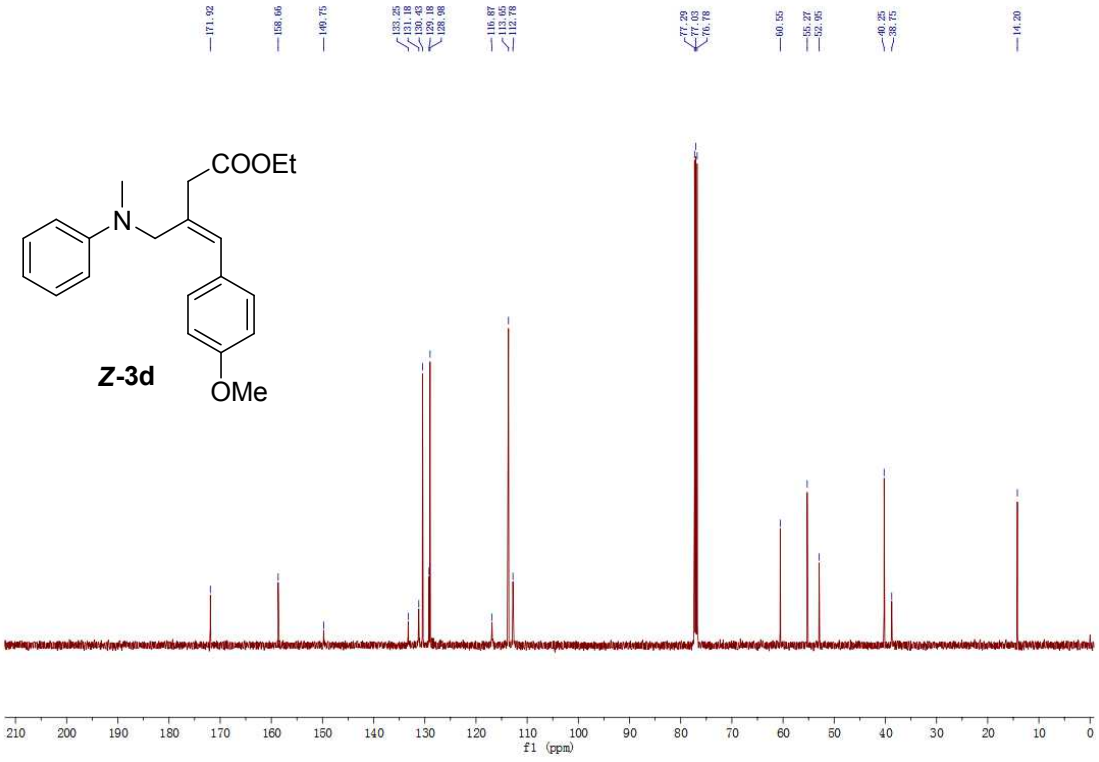
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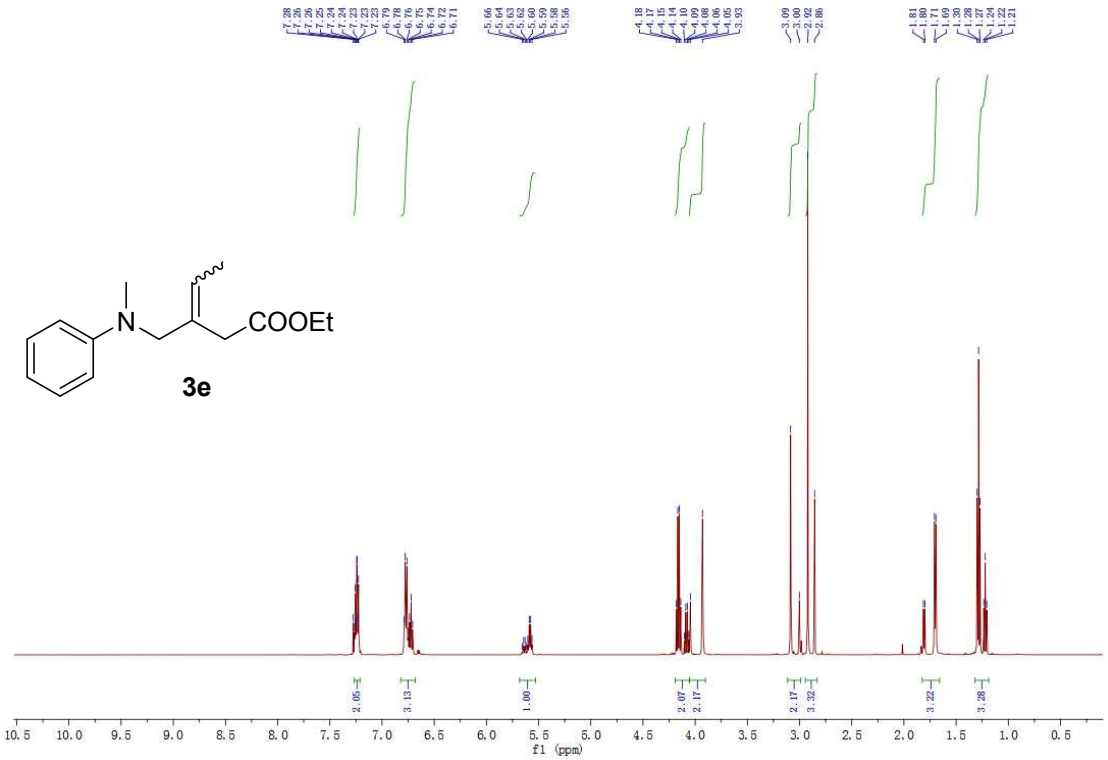
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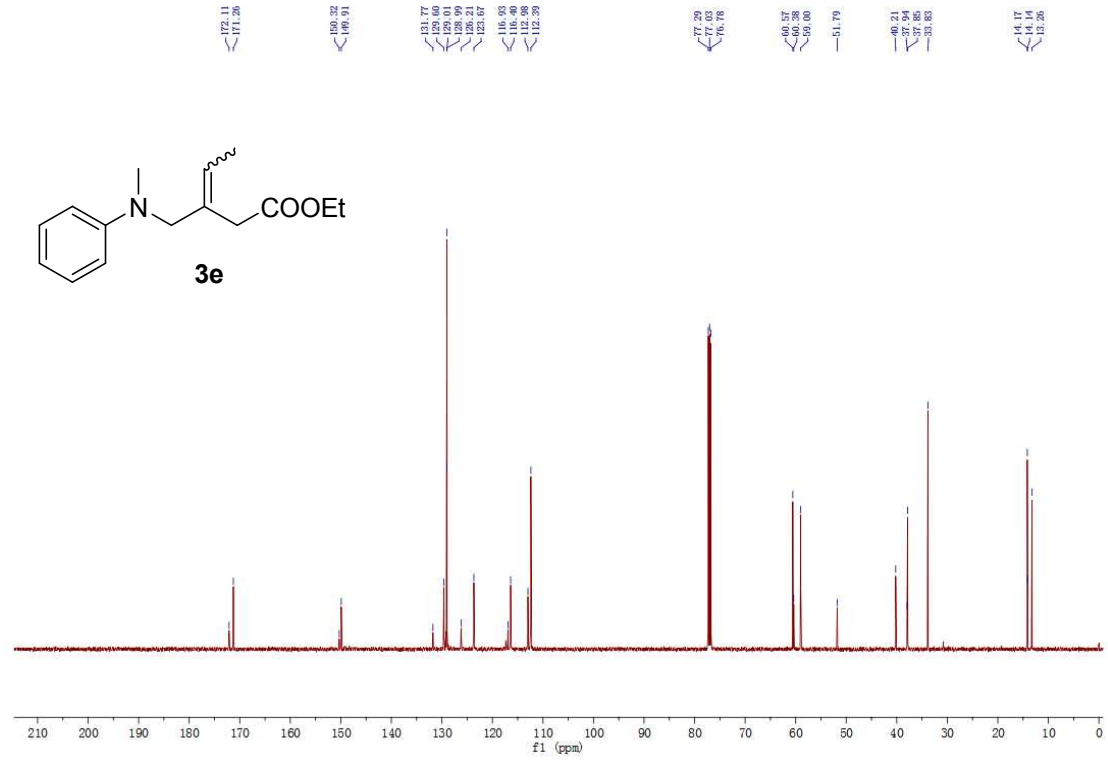
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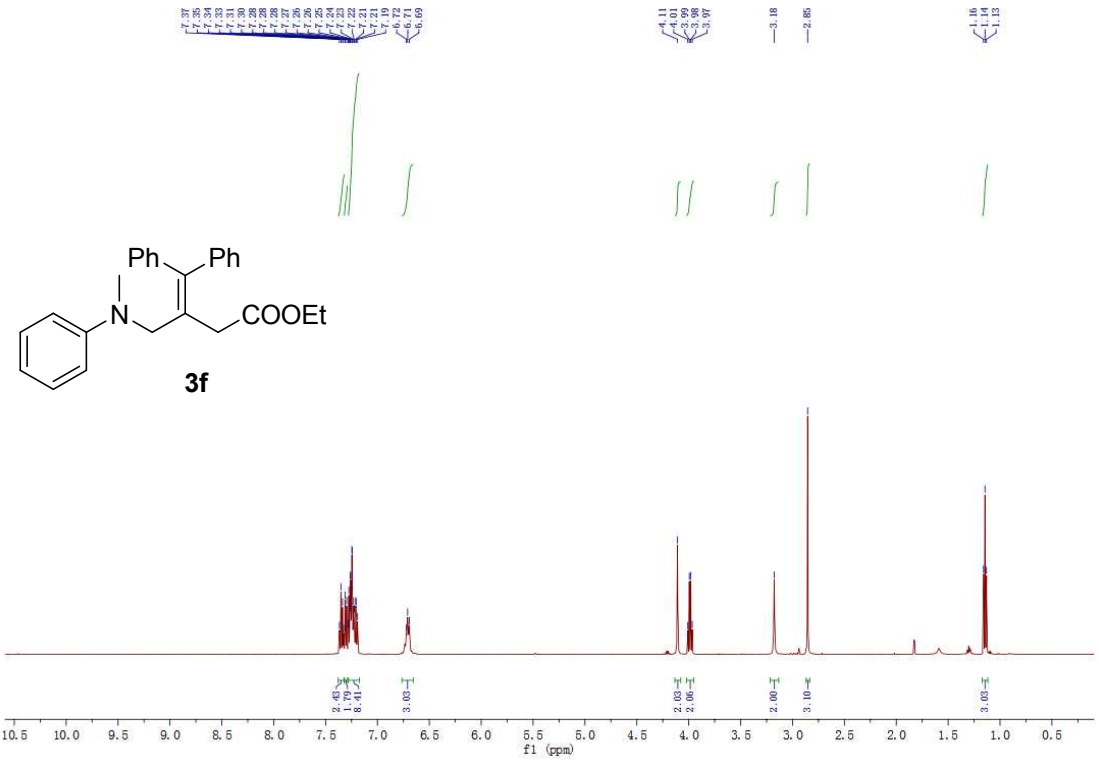
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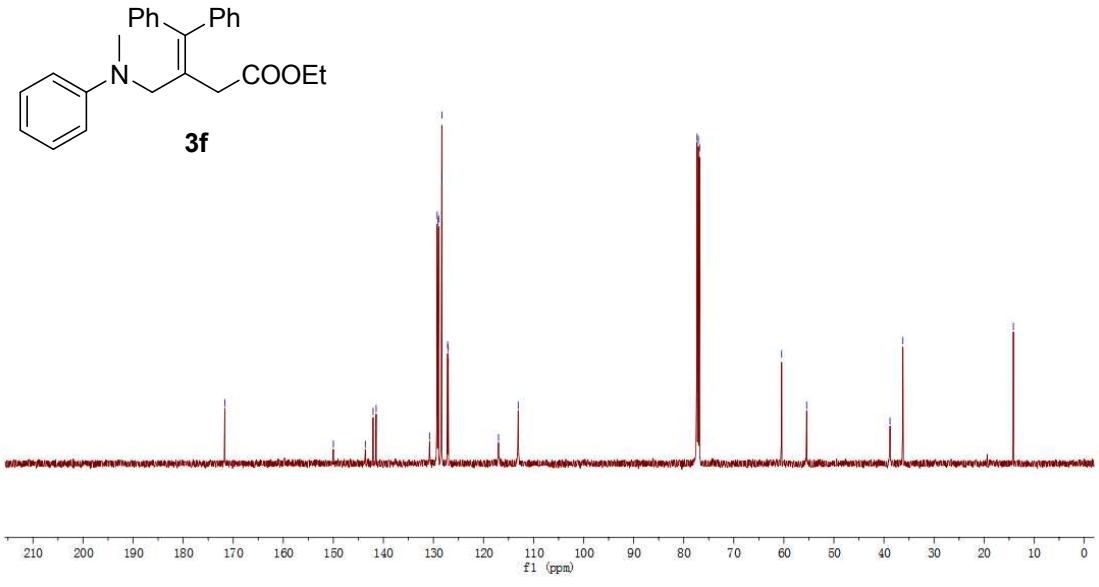
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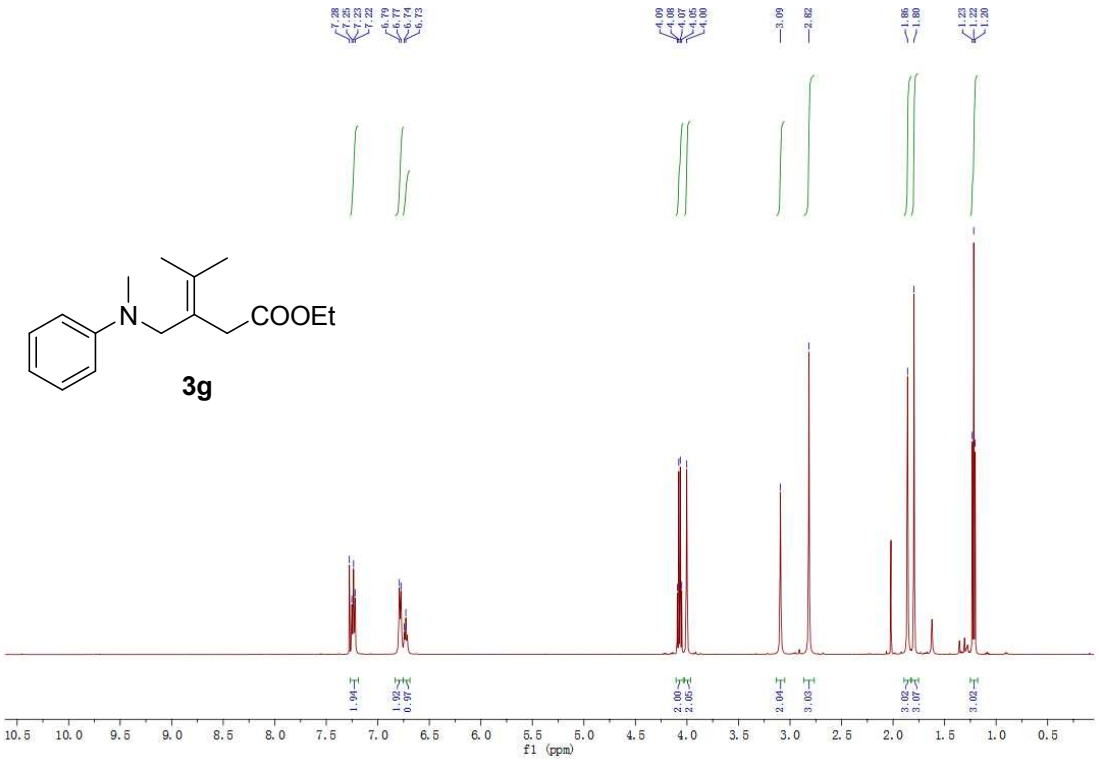
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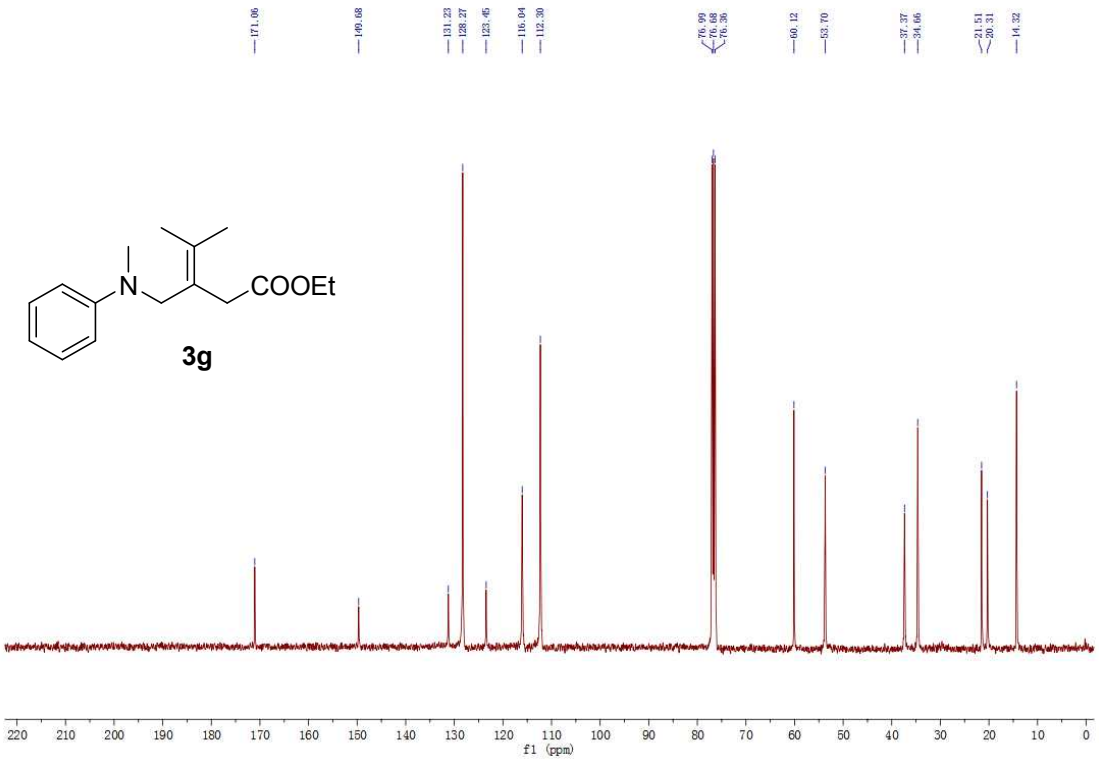
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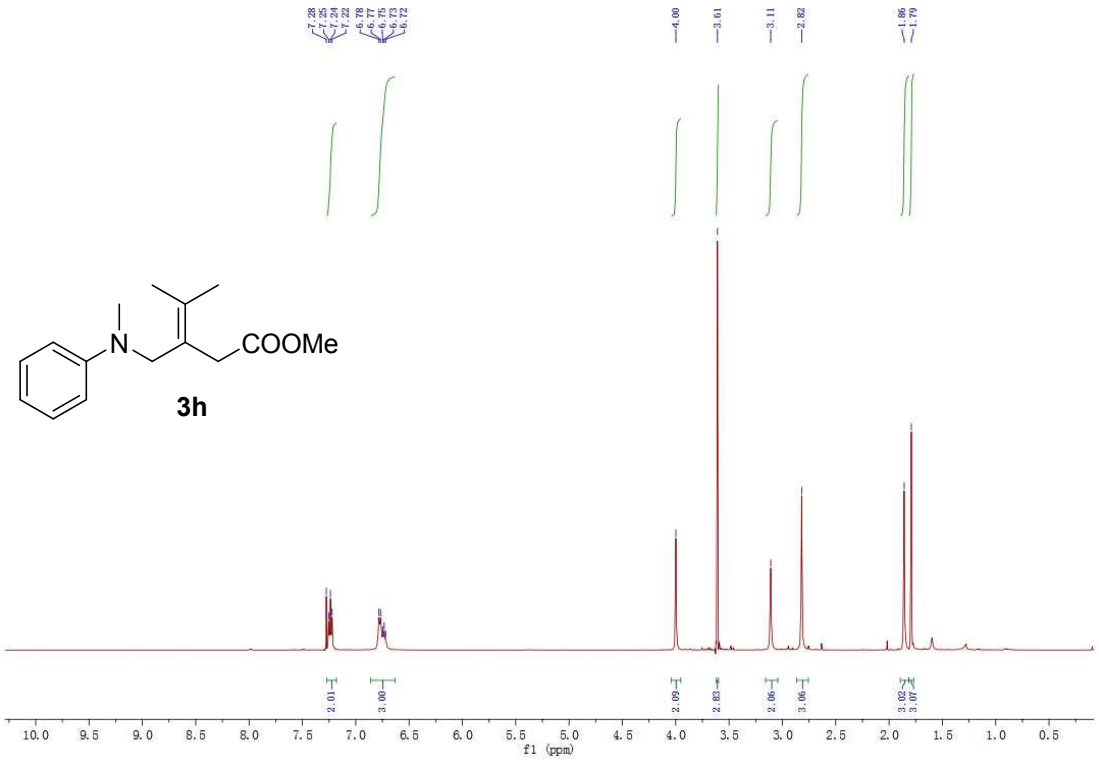
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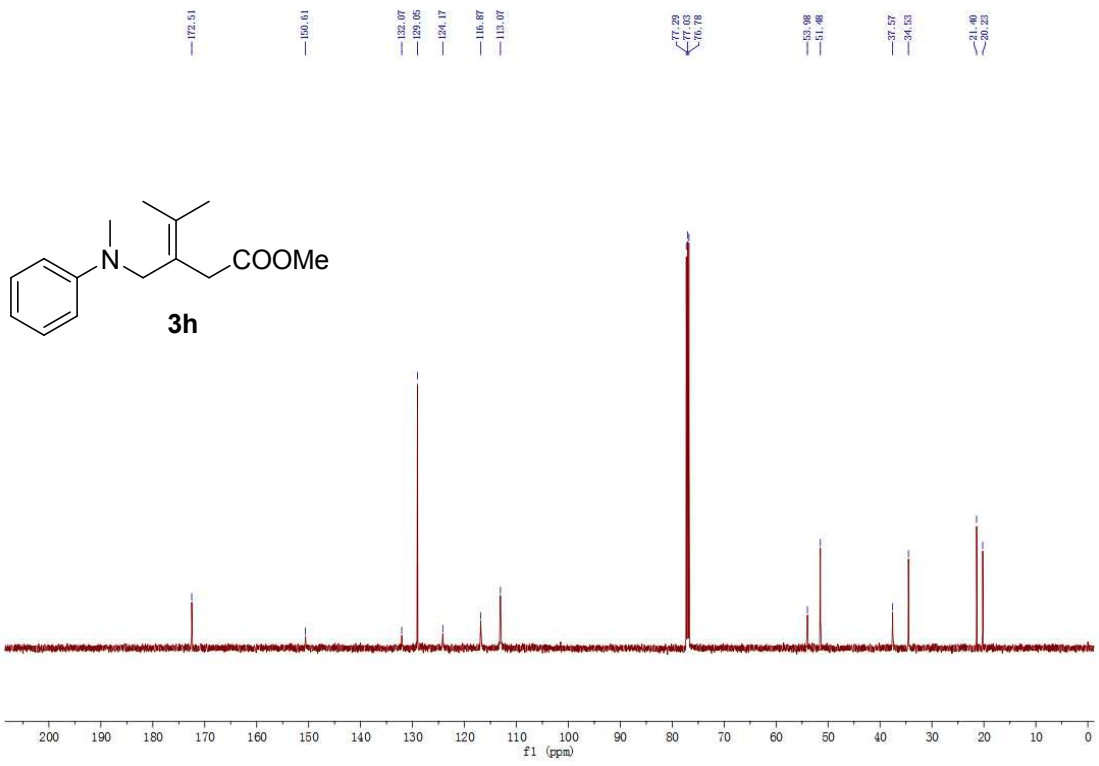
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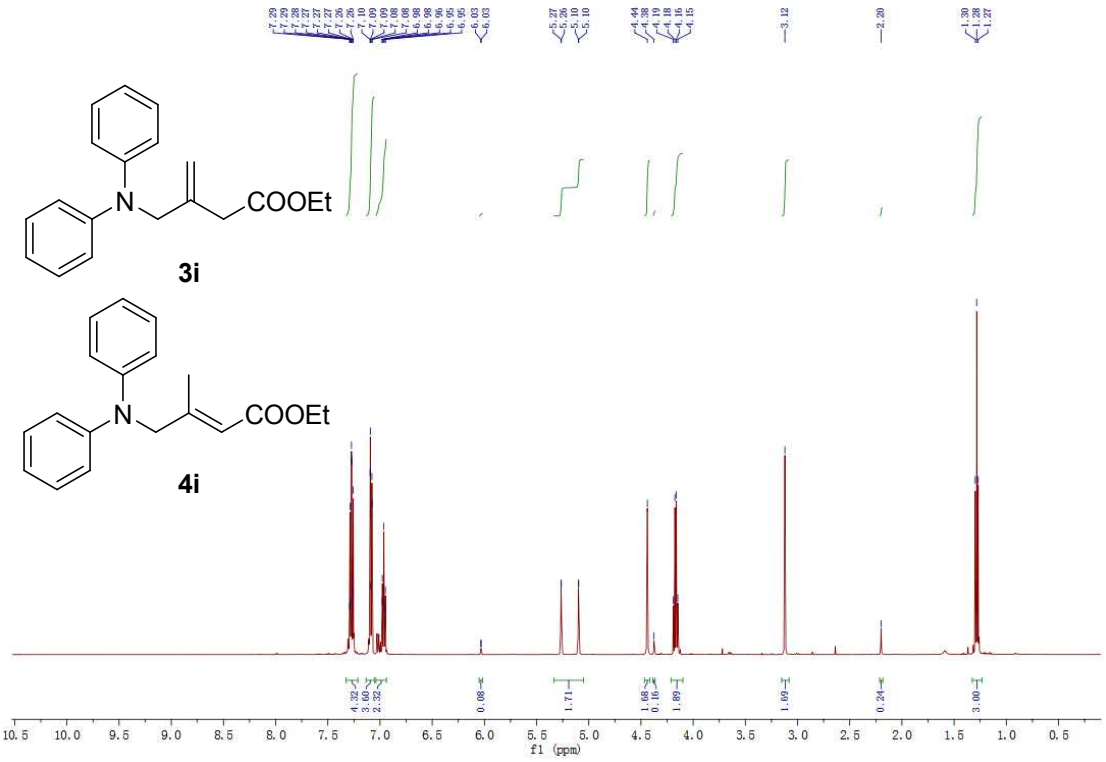
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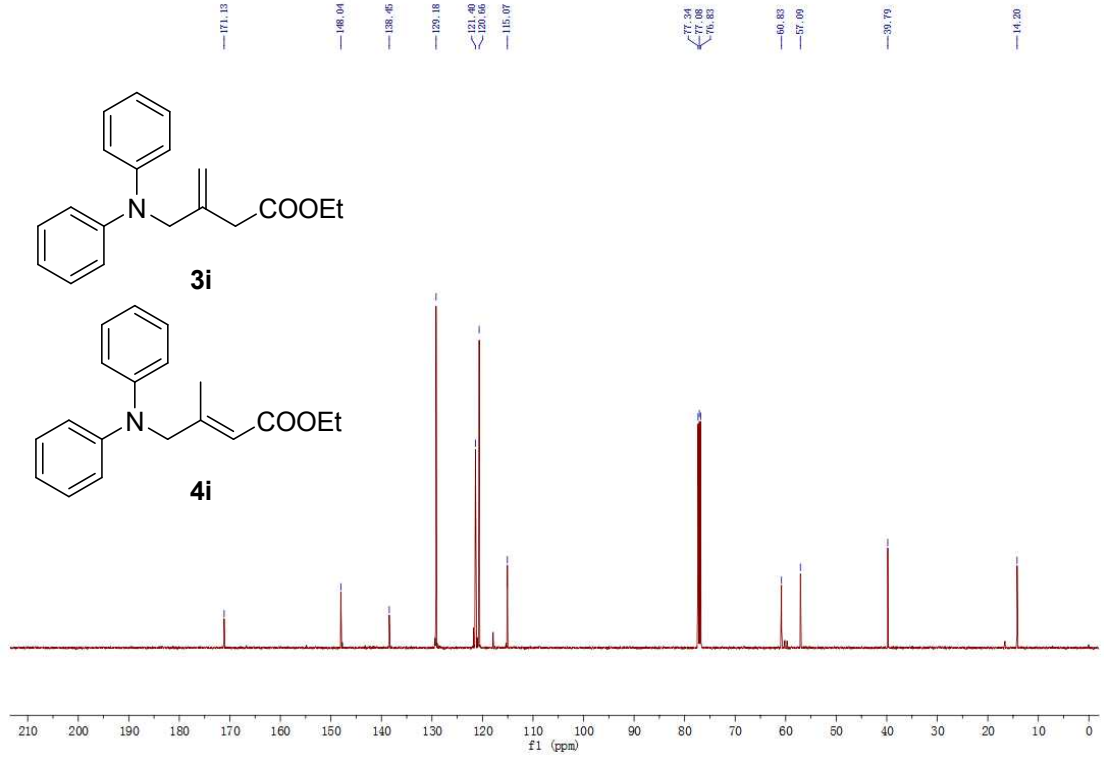
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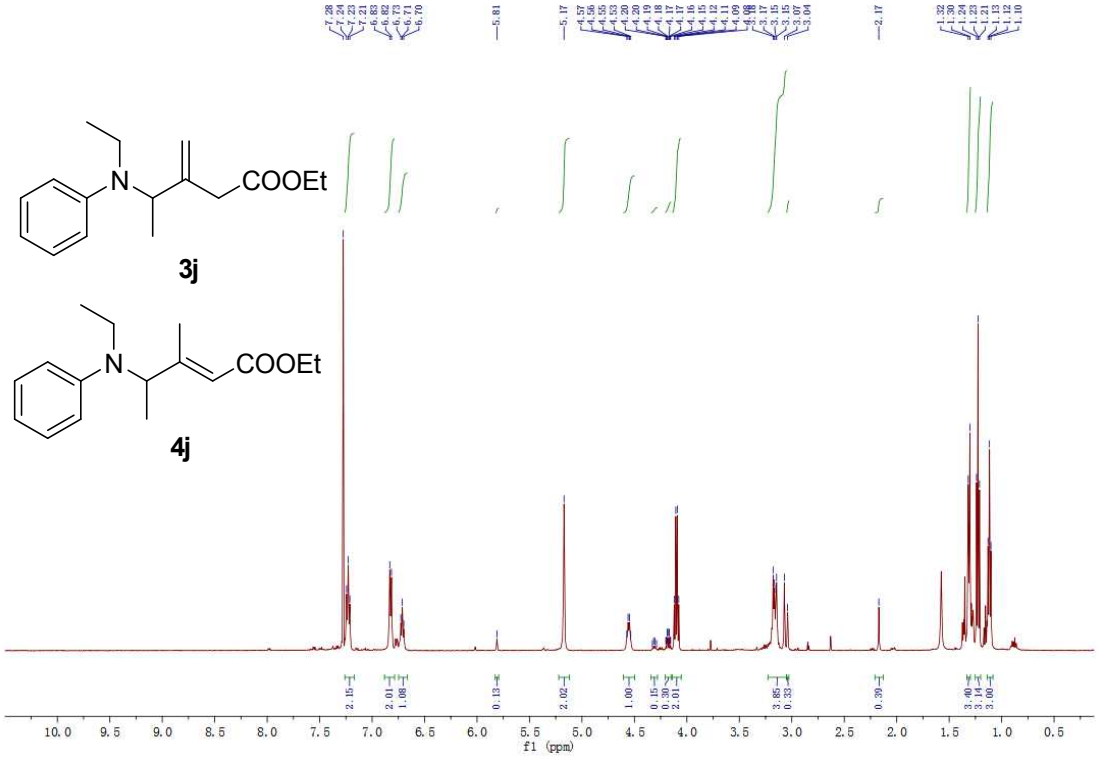
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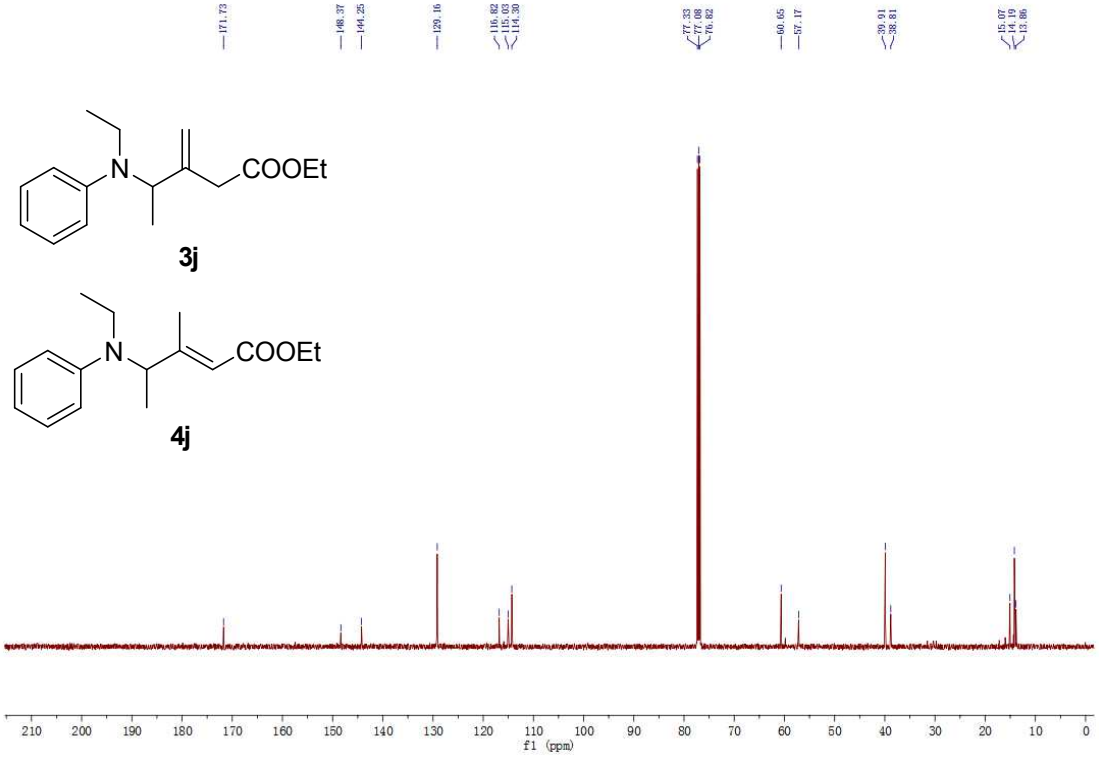
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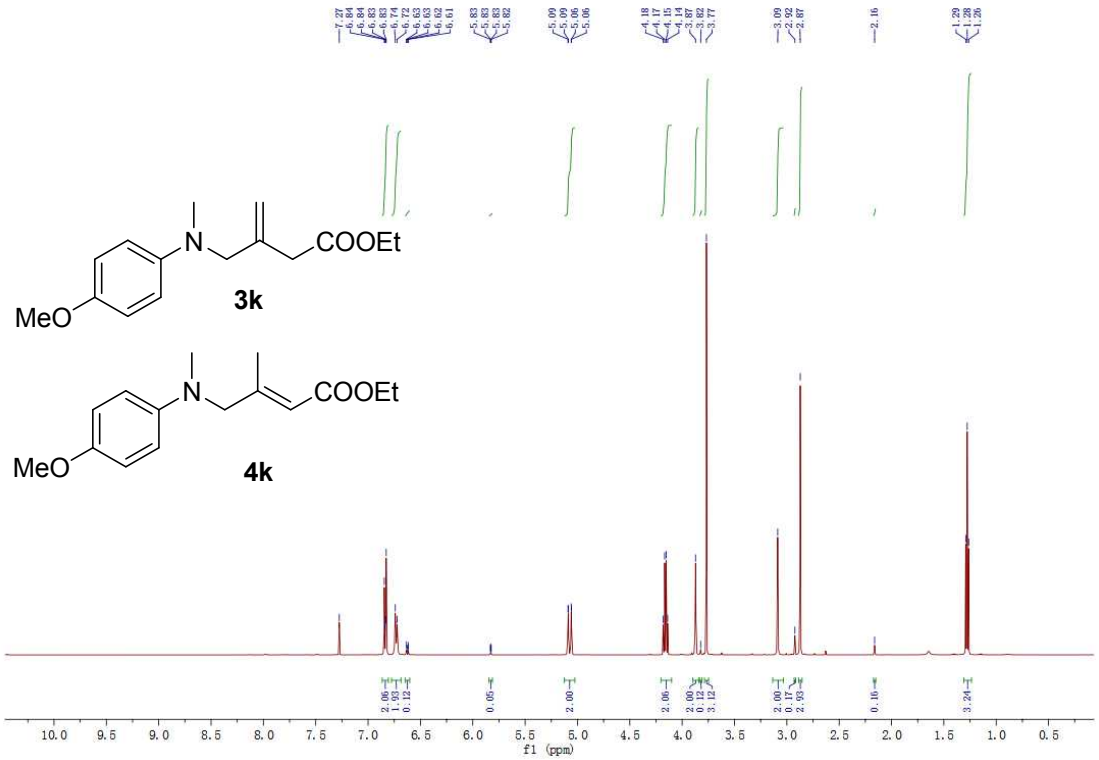
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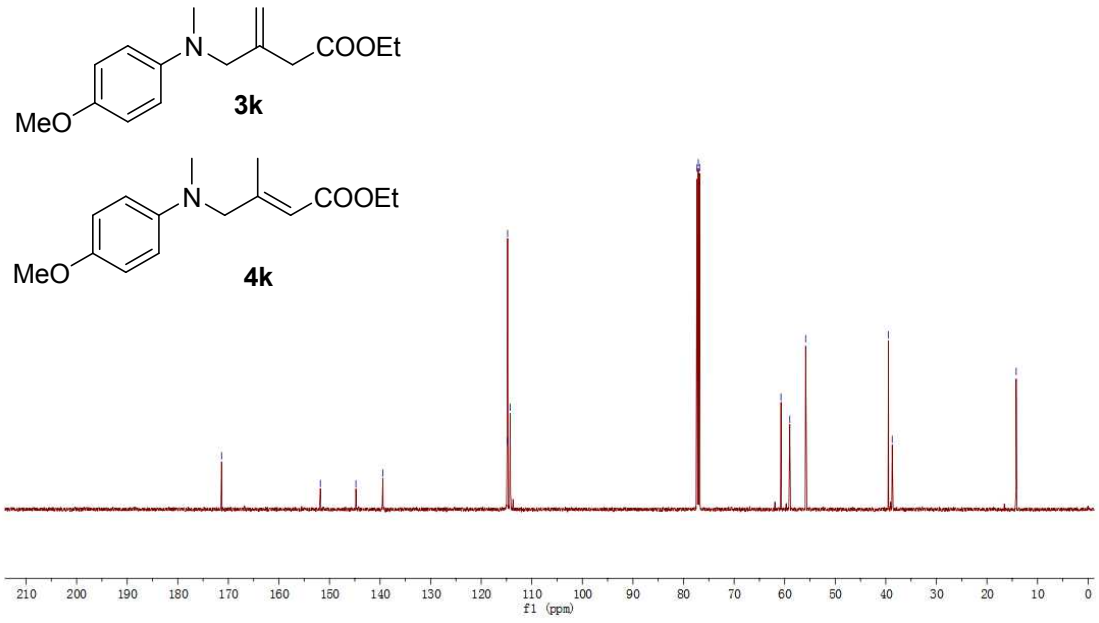
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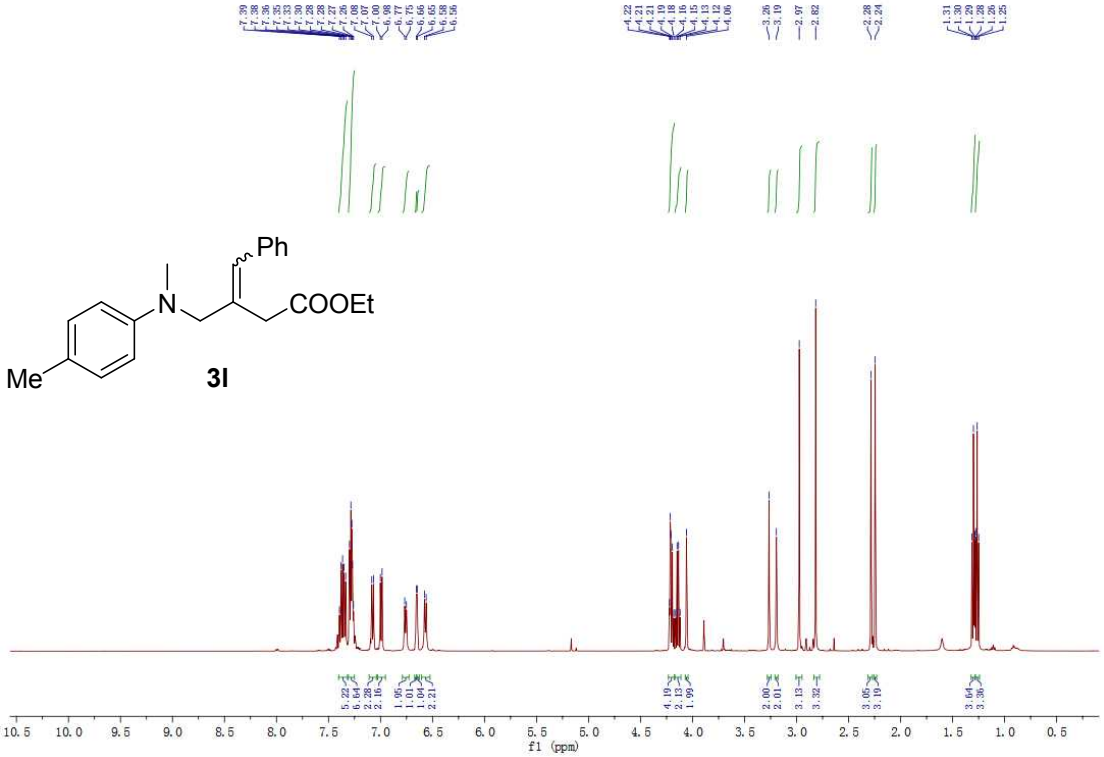
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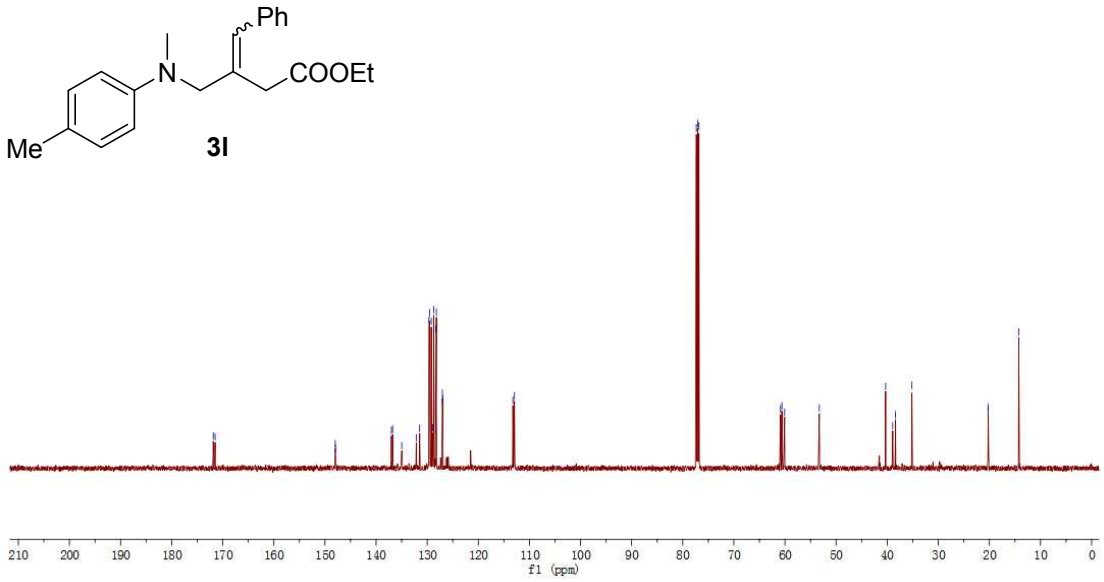
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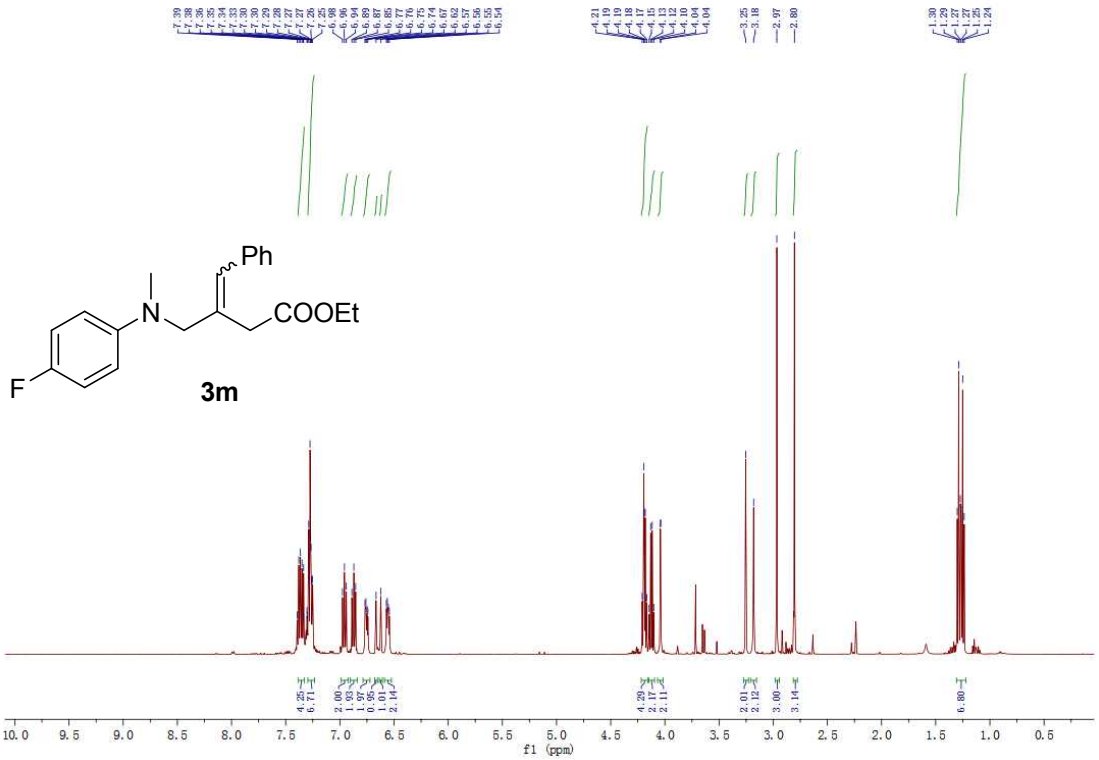
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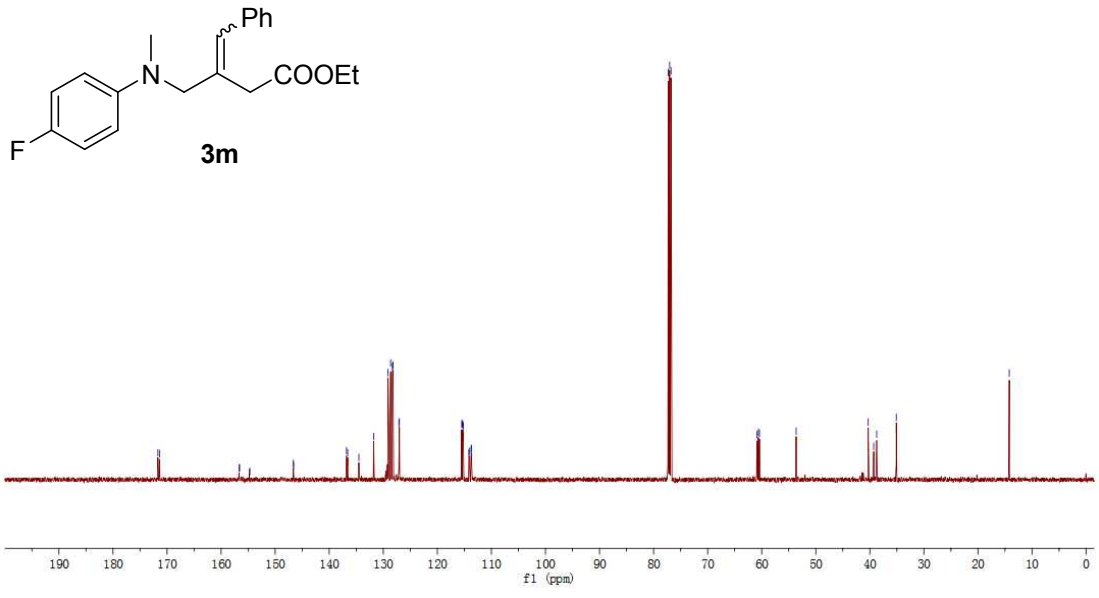
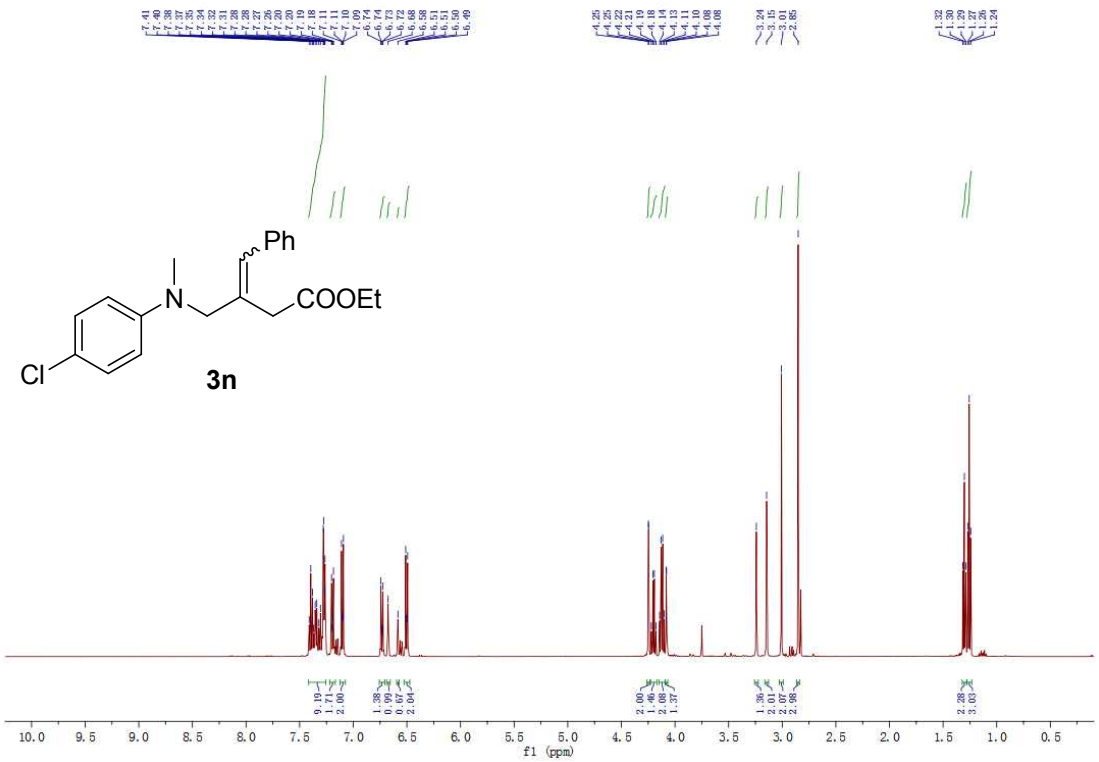

Ph
N
COOEt
F
3m
f1 (ppm)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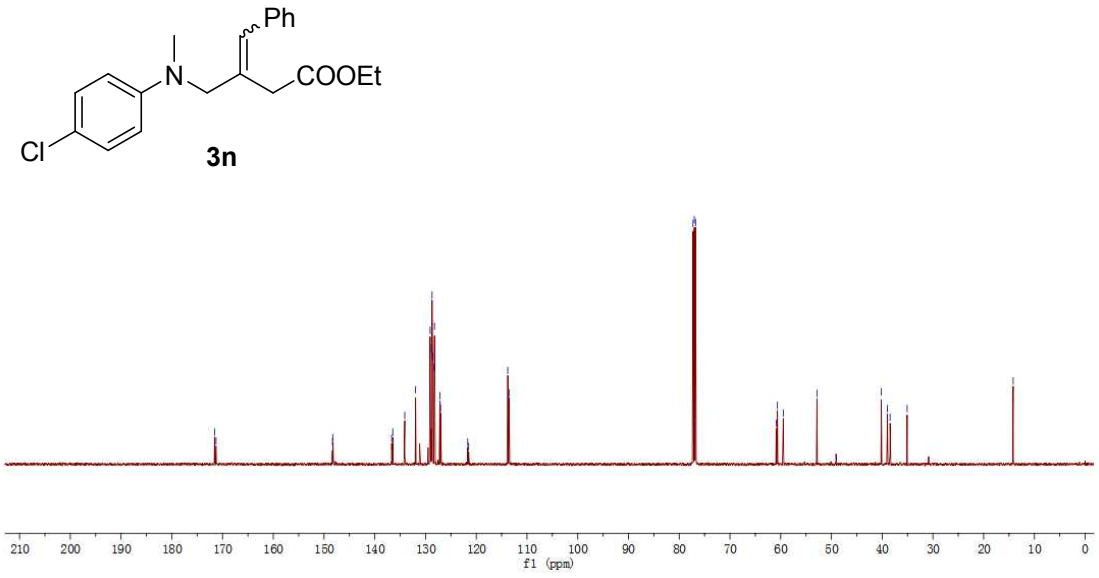
N
COOEt
Cl
3n
f1 (ppm)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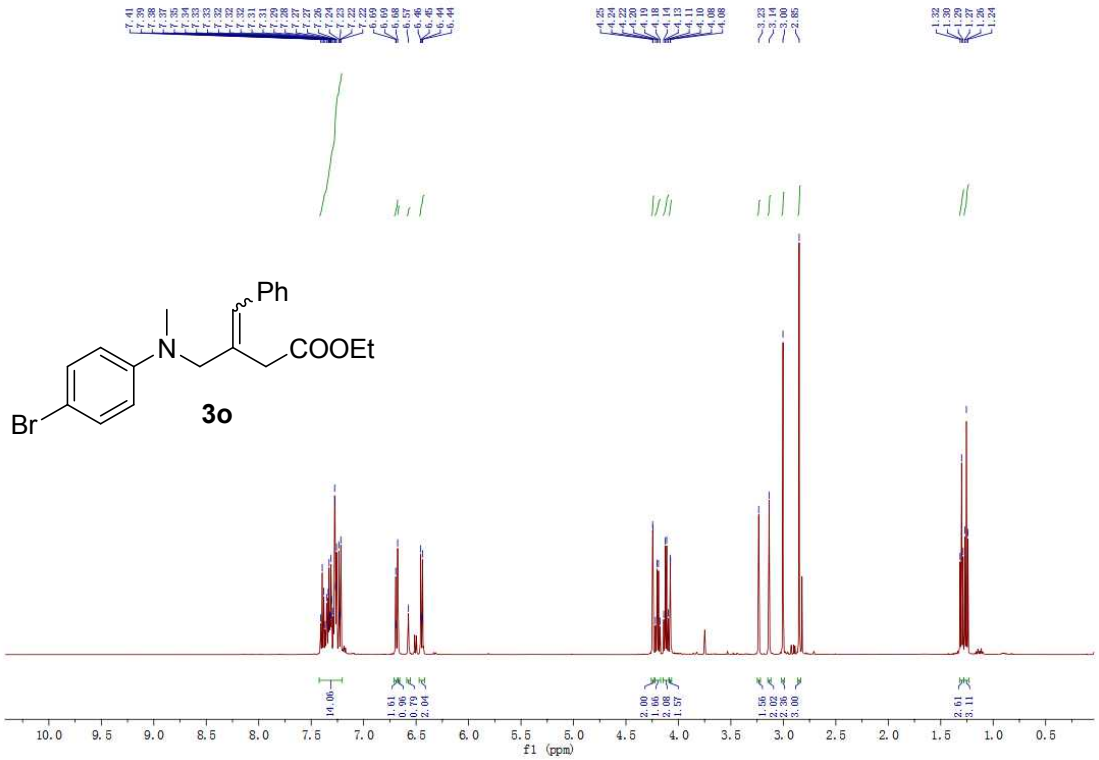
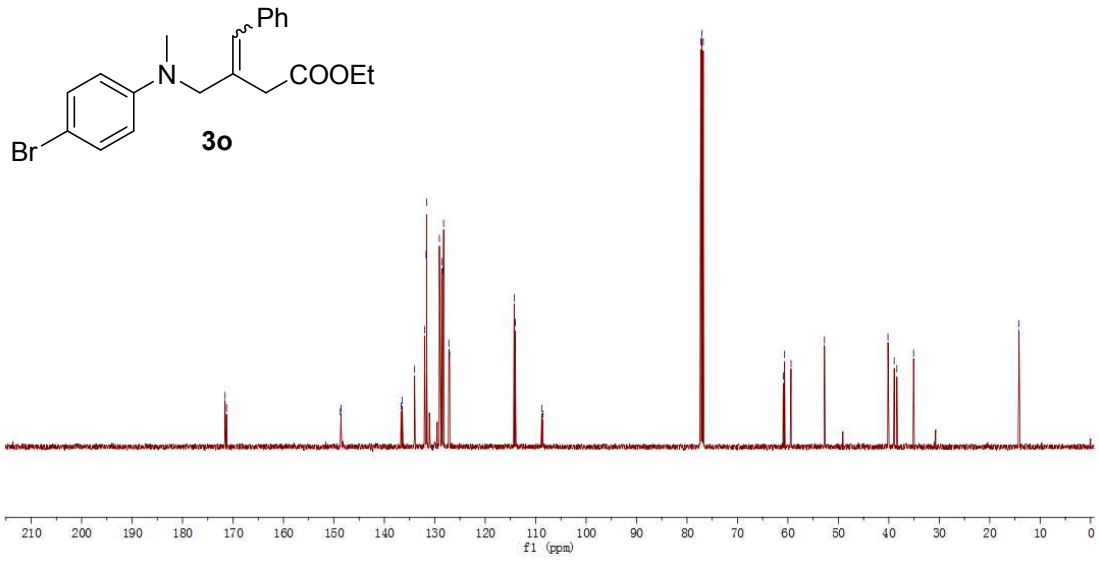
COOEt
Cl
3n
f1 (ppm)


Ph
N
COOEt
Br
3o
f1 (ppm)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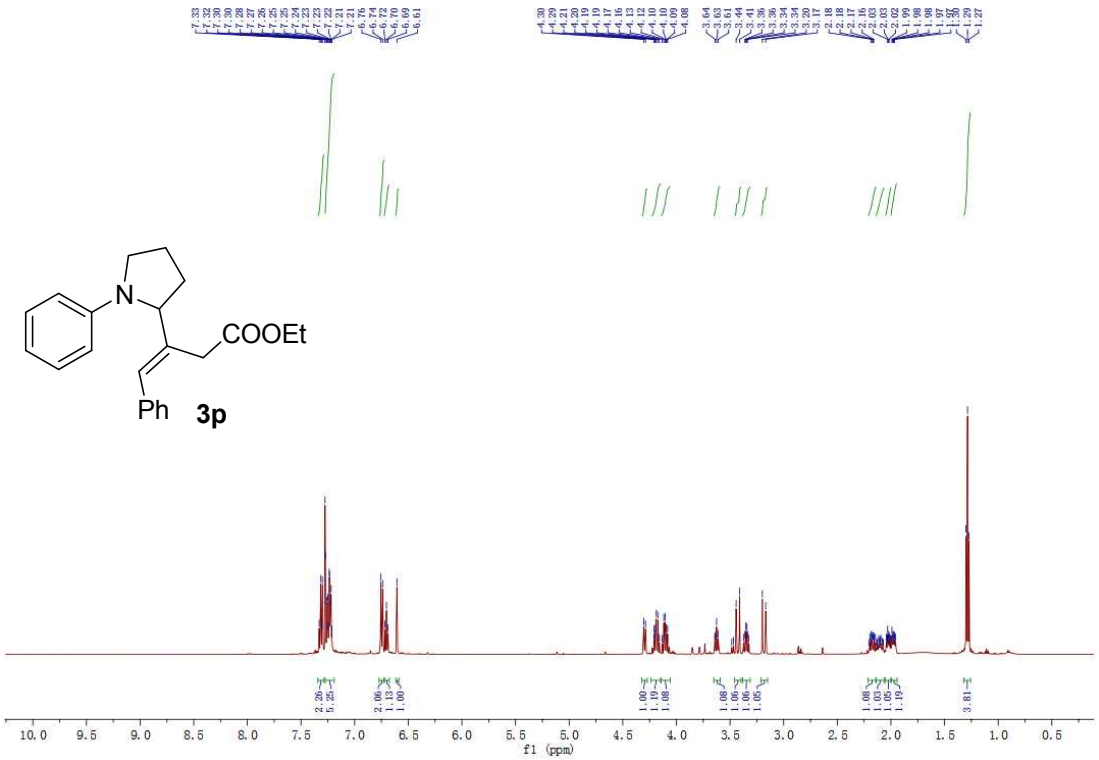
COOEt
Br
3o
f1 (ppm)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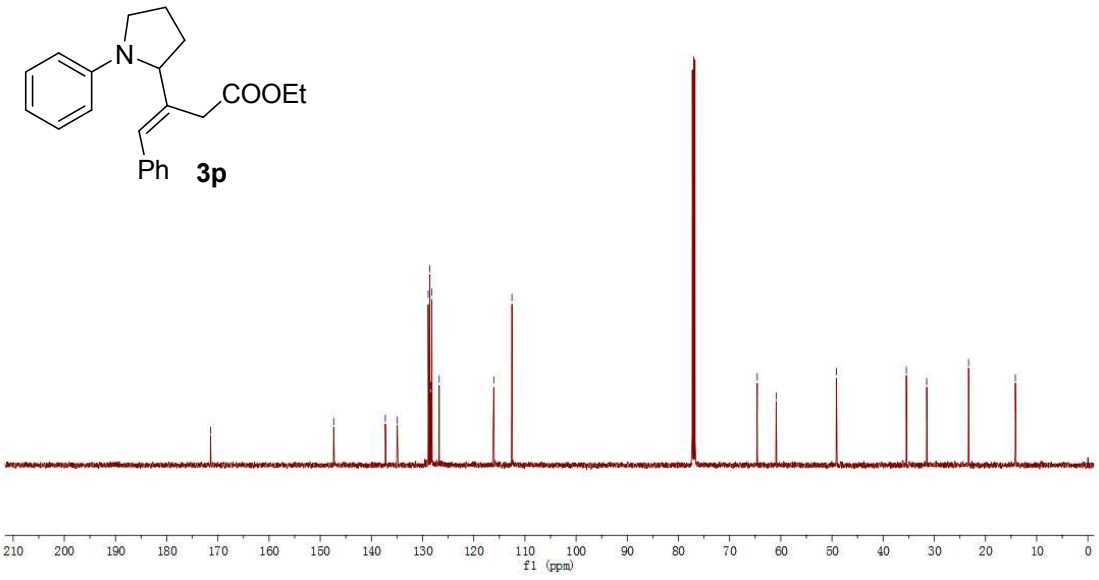
Ph
3p
f1 (ppm)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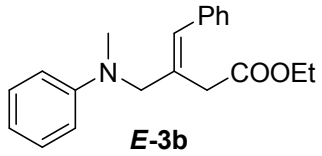
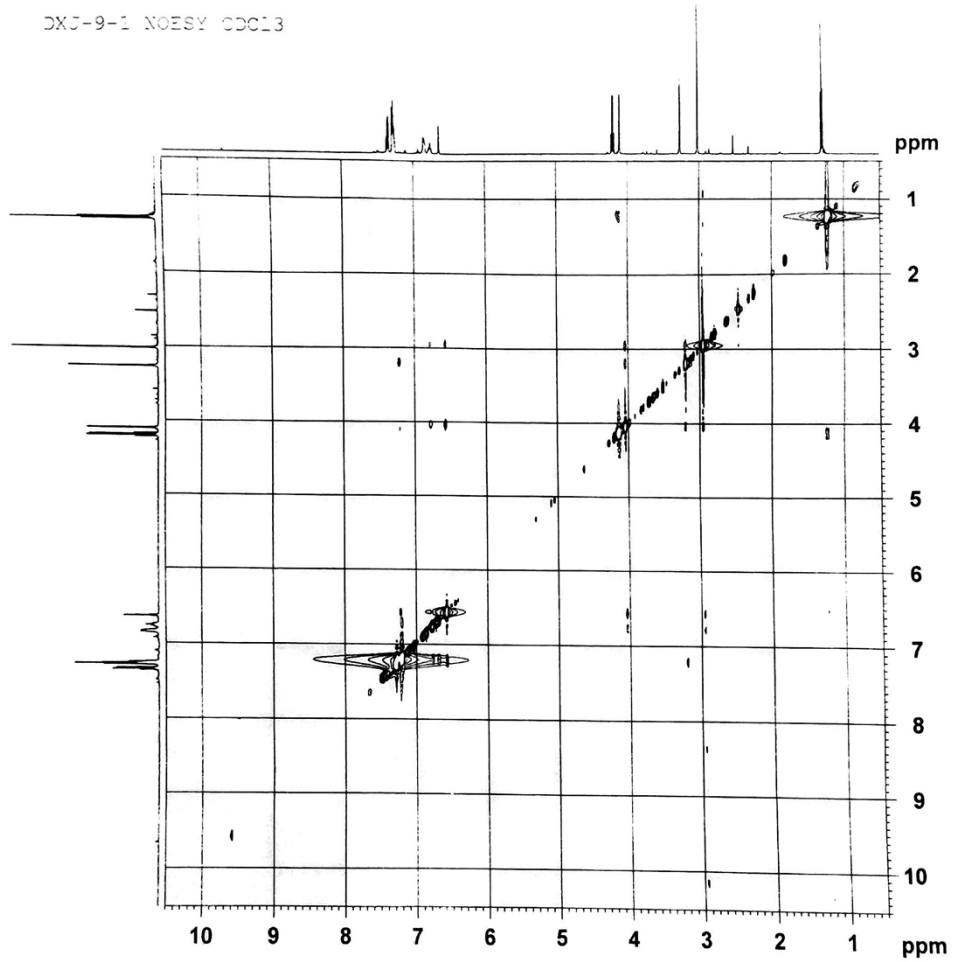
COOEt
Ph
3p
f1 (ppm)


Ph
N
COOEt

***E*-3b**


DXC-9-1 NOESY CDCl3
ppm
1
2
3
4
5
6
7
8
9
10
10
9
8
7
6
5
4
3
2
1
ppm