Supporting Information:

Highly Stereo-selective Synthesis of Tetra-Substituted (E)-Alkenes through Hydroamination/Acetoxylation of Alkynes

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General method: All the reactions were carried out at 0 ^{o}C in a Schlenk tube equipped with magnetic stir bar. Solvents and all reagents were used as received. ^{1}H NMR spectra were recorded in $CDCl_3$ at 400 MHz and ^{13}C NMR spectra were recorded in $CDCl_3$ at 100 MHz. Respectively, the chemical shifts (d) were referenced to TMS. GC–MS was obtained using electron ionization (EI). IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Brucker Vector 22 spectrometer. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF_{254}), and visualization was effected at 254 nm. All the other chemicals were purchased from Aldrich Chemicals.

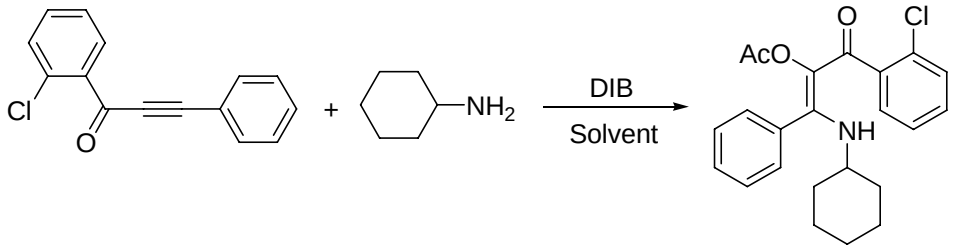
Typical procedure for the synthesis of (*E*)-3-(2-chlorophenyl)-1-(cyclohexylamino)-3-oxo-1-phenylprop-1-en-2-yl acetate (Scheme 2, 3aa): To a 10 mL Schlenk tube was added DIB, (386 mg, 1.2 mmol), dichloromethane (2 mL), 1-(2-chlorophenyl)-3-phenylprop-2-yn-1-one (1a) (240 mg, 1.0 mmol) and cyclohexanamine (**2a**) (99 mg, 1 mmol). The mixture was stirred at 0 °C for overnight. The solution was directly subjected to isolation by PTLC (GF254), eluted with a 10:3 petroleum ether / ethyl acetate mixture, which furnished **3aa** (337.4 mg, 85%) as an orange oil.

Typical procedure for the synthesis of (*E*)-2-methoxy-3-(methylimino)-1-oxo-3-phenyl-1-p-tolylpropan-2-yl acetate (Scheme 3, 4): To a 10 mL Schlenk tube was added DIB, (708 mg, 2.2 mmol), dichloromethane (2 mL), methanol (71 mg, 1.0mmol), 3-phenyl-1-p-tolylprop-2-yn-1-one (220 mg, 1.0 mmol) and methanamine (31 mg, 1.0mmol). The mixture was stirred at 0 °C for overnight. The solution was

directly subjected to isolation by PTLC (GF254), eluted with a 10:3 petroleum ether / ethyl acetate mixture, which furnished **4** (153 mg, 45%) as a yellow viscous oil.

Typical procedure for the synthesis of (*E*)-1-(2-chlorophenyl)-2-methoxy-3-(methylimino)-1-oxo-3-phenylpropan-2-yl acetate (Scheme 3, 5): To a 10 mL Schlenk tube was added DIB, (708 mg, 2.2 mmol), dichloromethane (2 mL), methanol (71 mg, 1.0mmol), 1-(2-chlorophenyl)-3-phenylprop-2-yn-1-one (240 mg, 1.0 mmol) and methanamine (31 mg, 1.0mmol). The mixture was stirred at 0 °C for overnight. The solution was directly subjected to isolation by PTLC (GF254), eluted with a 10:3 petroleum ether / ethyl acetate mixture, which furnished **5** (150.4 mg, 42%) as a yellow viscous oil

Optimization of reaction conditions [a]



1a **2a** **3aa**

Entry	Solvent	Temp (℃)	Reactional time (h)	Yield (%)[b]
1	Toluene	0	overnight	12
2	DCE	0	overnight	75
3	CH_2Cl_2	0	overnight	88
4	Dioxane	0	overnight	63
5	DMSO	0	overnight	28
6	CH_2Cl_2	r. t.	overnight	68
7	CH_2Cl_2	-10	overnight	83
8	CH_2Cl_2	0	6	57
9	CH_2Cl_2	0	24	88

[a] The reaction was carried out using 0.25 mmol of **1a**, 0.25 mmol of **2a**, 1.2 equiv. of DIB, 2.0 ml of solvent; [b] GC yield.

Characterization data for all prepared compounds:

(*E*)-3-(2-chlorophenyl)-1-(cyclohexylamino)-3-oxo-1-phenylprop-1-en-2-yl acetate (Scheme 2, 3aa)

yellow viscous oil, IR vmax (KBr): 3431, 1735, 1688, 1600, 1525, 1380, 1215, 1030, 890, 690; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 10.96 (s, 1H), 7.39-7.16 (m, 10H), 3.06-3.02 (m, 1H), 1.82-1.68 (m, 4H), 1.44-1.37 (m, 2H), 1.31 (s, 3H), 1.22-1.10 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 196.0, 170.5, 159.8, 138.9, 131.0, 130.6, 129.5, 129.2, 128.3, 128.2, 127.8, 127.0, 126.0, 121.4, 53.0, 33.7, 25.0, 24.1, 19.6; GC–MS m/z (% rel inten.): 138.81 (100); Anal. Calcd for $C_{23}H_{24}ClNO_3$: C, 69.43; H, 6.08; Found: C, 69.55; H, 6.22.

(*E*)-3-(2-chlorophenyl)-1-(hexylamino)-3-oxo-1-phenylprop-1-en-2-yl acetate (Scheme 2, 3ab)

orange viscous oil, IR vmax (KBr): 3375, 1727, 1669, 1590, 1555, 1430, 1371, 1233, 1115, 1011, 900, 805, 732; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 10.93 (s, 1H), 7.40-7.19 (m, 9H), 3.06-3.02 (m, 2H), 1.55-1.51 (m, 2H), 1.34 (s, 3H), 1.29-1.17 (m, 6H), 0.84-0.81 (t, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 186.4, 170.7, 161.0, 138.9, 131.0, 130.7, 129.6, 129.4, 129.3, 128.6, 128.4, 128.3, 126.2, 121.7, 44.8, 31.2, 30.4, 26.3, 22.4, 19.7, 13.9; GC–MS m/z (% rel inten.): 138.79 (100); Anal. Calcd for $C_{23}H_{26}ClNO_3$: C, 69.08; H, 6.55; Found: C, 69.14; H, 6.39.

(*E*)-3-(2-chlorophenyl)-3-oxo-1-(pentylamino)-1-phenylprop-1-en-2-yl acetate (Scheme 2, 3ac)

orange viscous oil, IR vmax (KBr): 3402, 1718, 1690, 1512, 1395, 1270, 1033, 770; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 10.94 (s, 1H), 7.42-7.19 (m, 9H), 3.06-3.02 (m, 2H), 1.55-1.51 (m, 2H), 1.34 (s, 3H), 1.25-1.16 (m, 4H), 0.84-0.81 (t, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 186.3, 170.6, 161.0, 138.8, 130.8, 130.6, 129.6, 129.3, 128.7, 128.3, 128.2, 127.8, 126.1, 121.6, 44.7, 31.1, 30.3, 26.2, 22.3, 13.8; GC–MS m/z (% rel inten.): 138.57 (100); Anal. Calcd for $C_{22}H_{24}ClNO_3$: C, 68.45; H, 6.27; Found: C, 68.33; H, 6.37.

(*E*)-1-(butylamino)-3-(2-chlorophenyl)-3-oxo-1-phenylprop-1-en-2-yl acetate (Scheme 2, 3ad)

orange viscous oil, IR vmax (KBr): 3281, 1715, 1675, 1600, 1496, 1380, 1220, 1011, 980, 750; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 10.94 (s, 1H), 7.39-7.20 (m, 9H), 3.06-3.02 (t, 2H), 1.55-1.50 (m, 2H), 1.34-1.21 (m, 5H), 0.90-0.82 (t, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 186.4, 170.7, 161.0, 139.0, 131.0, 129.6, 129.4, 128.4, 128.3, 127.9, 127.5, 126.2, 121.7, 44.5, 32.4, 19.8, 19.7, 13.6; GC–MS m/z (% rel inten.): 138.84 (100); Anal. Calcd for $C_{21}H_{22}ClNO_3$: C, 67.83; H, 5.96; Found: C, 67.95; H, 6.05.

(*E*)-3-(2-chlorophenyl)-3-oxo-1-phenyl-1-(propylamino)prop-1-en-2-yl acetate (Scheme 2, 3ae)

orange viscous oil, IR vmax (KBr): 3335, 1733, 1700, 1589, 1460, 1370, 1225, 1131, 1050, 900, 801, 732; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 10.95 (s, 1H), 7.40-7.19 (m, 9H), 3.06-3.00 (t,

2H), 1.59-1.53 (m, 2H), 1.34 (s, 3H), 0.91-0.88 (t, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 186.4, 170.7, 161.2, 138.9, 130.8, 129.7, 129.3, 128.5, 128.3, 127.9, 126.5, 126.2, 121.7, 46.5, 26.3, 19.7, 11.2; GC–MS m/z (% rel inten.): 263.83 (100); Anal. Calcd for $C_{20}H_{20}ClNO_3$: C, 67.13; H, 5.63; Found: C, 67.01; H, 5.49.

(*E*)-3-(2-chlorophenyl)-1-(ethylamino)-3-oxo-1-phenylprop-1-en-2-yl acetate (Scheme 2, 3af)

orange viscous oil, IR vmax (KBr): 3300, 1742, 1677, 1601, 1509, 1425, 1372, 1230, 1031, 910, 833, 690; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 10.84 (s, 1H), 7.38-7.17 (m, 9H), 3.08-3.07 (d, 2H), 1.32 (s, 3H),1.17-1.13 (t, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 186.4, 170.6, 160.7, 138.8, 130.8, 130.6, 129.6, 129.3, 128.5, 128.4, 128.3, 127.7, 126.1, 121.5, 39.5, 19.6, 15.7; GC–MS m/z (% rel inten.): 249.97 (100); Anal. Calcd for $C_{19}H_{18}ClNO_3$: C, 66.38; H, 5.28; Found: C, 66.30; H, 5.42.

(*E*)-1-(benzylamino)-3-(2-chlorophenyl)-3-oxo-1-phenylprop-1-en-2-yl acetate (Scheme 2, 3ag)

orange viscous oil, IR vmax (KBr): 3392, 1733, 1682, 1511, 1472, 1378, 1212, 1075, 888, 765; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 11.13 (s, 1H), 7.37-7.16 (m, 14H), 4.25-4.24 (d, 2H), 1.34 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 187.0, 170.3, 160.3, 138.5, 130.5, 130.4, 129.5, 129.3, 129.1, 128.5, 128.2, 127.3, 126.8, 126.0, 125.7, 122.0, 48.2, 19.5; GC–MS m/z (% rel inten.): 311.97 (100); Anal. Calcd for $C_{24}H_{20}ClNO_3$: C, 71.02; H, 4.97; Found: C, 71.19; H, 5.05.

(*E*)-1-(cyclohexylamino)-3-oxo-1-phenyl-3-p-tolylprop-1-en-2-yl acetate (Scheme 2, 3ba)

orange viscous oil, IR vmax (KBr): 3366, 1748, 1703, 1588, 1452, 1380, 1115, 1052, 822, 739; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 11.20-11.18 (d, 1H), 7.58-7.56 (d, 2H), 7.39-7.23 (m, 5H), 7.12-7.10 (d, 2H), 3.99-2.96 (m, 1H), 2.31 (s, 3H), 1.74-1.66 (m, 4H), 1.50 (s, 3H), 1.44-134 (m, 2H), 1.23-1.17 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 187.0, 170.8, 159.6, 140.2, 136.8, 131.8, 131.2, 129.5, 128.9, 128.3, 127.7, 121.7, 52.9, 34.1, 25.2, 24.2, 21.4, 20.3; GC–MS m/z (% rel inten.): 118.85 (100); Anal. Calcd for $C_{24}H_{27}NO_3$: C, 76.36; H, 7.21; Found: C, 76.44; H, 7.03.

(*E*)-3-(cyclohexylamino)-1-oxo-1-phenylnon-2-en-2-yl acetate (Scheme 2, 3ca)

orange viscous oil, IR vmax (KBr): 3398, 1732, 1655, 1603, 1578, 1512, 1460, 1372, 1262, 1066, 901, 725; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 11.40 (s, 1H), 7.97-7.95 (d, 1H), 7.61-7.51 (m, 2H), 7.32-7.24 (d, 2H), 3.41 (s, 1H), 1.59-1.17 (m, 23H), 0.90-0.88 (t, 3H); ^{13}C-NMR (100

MHz, $CDCl_3$): δ = 1191.0, 169.3, 134.1, 133.6, 130.1, 129.4, 128.7, 128.4, 39.2, 31.4, 28.5, 22.8, 22.3, 20.5, 13.9; GC–MS m/z (% rel inten.): 103.81 (100); Anal. Calcd for $C_{19}H_{25}NO_4$: C, 68.86; H, 7.60; Found: C, 69.03; H, 7.65.

(*E*)-ethyl 2-acetoxy-3-(cyclohexylamino)-3-phenylacrylate (Scheme 2, 3da)

orange viscous oil, IR vmax (KBr): 3346, 1700, 1678, 1625, 1600, 1512, 1460, 1270, 1225, 1113, 1035, 988, 915, 755, 678; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.18 (s, 1H), 7.36-7.34 (m, 3H), 7.22-7.20 (m, 2H), 4.19-4.13 (q, 2H), 2.79-2.77 (m, 1H), 1.72-1.70 (m, 5H), 1.61-1.59 (m, 2H), 1.41-1.39 (m, 1H), 1.25-1.05 (m, 8H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 170.7, 165.9, 156.1, 132.4, 128.9, 128.7, 128.2, 111.1, 59.6, 52.4, 34.4, 25.2, 24.4, 20.0, 14.4; GC–MS m/z (% rel inten.): 103.81 (100); Anal. Calcd for $C_{19}H_{25}NO_4$: C, 68.86; H, 7.60; Found: C, 69.03; H, 7.65.

diethyl 2-acetoxy-3-(cyclohexylamino)fumarate (Scheme 2, 3ea)

orange viscous oil, IR vmax (KBr): 3376, 1705, 1695, 1470, 1391, 1369, 1215, 1013, 905, 833, 706; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.63 (s, 1H), 4.39-4.11 (m, 5H), 1.97-1.56 (m, 6H), 1.40-1.17 (m, 13H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 167.4, 163.9, 103.2, 77.3, 77.0, 76.6, 62.1, 60.2, 34.3, 25.2, 24.4, 14.2, 14.0; GC–MS m/z (% rel inten.): 149.36 (100); Anal. Calcd for $C_{16}H_{25}NO_6$: C, 58.70; H, 7.70; Found: C, 58.92; H, 7.81.

(*E*)-ethyl 2-acetoxy-3-phenyl-3-(phenylamino)acrylate (Scheme 2, 3dh)

orange viscous oil, IR vmax (KBr): 3452, 1695, 1671, 1613, 1495, 1451, 1380, 1225, 1046, 982, 775, 699; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 10.03 (s, 1H), 7.30-7.27 (m,5H), 7.03-6.99 (m, 2H), 6.87-6.85 (m, 1H), 6.59-6.57 (d, 2H), 4.27-4.22 (q, 2H), 1.88 (s, 3H), 1.31-1.28 (t, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 170.5, 165.9, 151.1, 139.8, 134.2, 131.7, 129.3, 128.8, 128.3, 123.0, 122.0, 115.0, 60.4, 20.2, 14.3; GC–MS m/z (% rel inten.): 149.36 (100); Anal. Calcd for $C_{19}H_{19}NO_4$: C, 70.14; H, 5.89; Found: C, 70.19; H, 5.75.

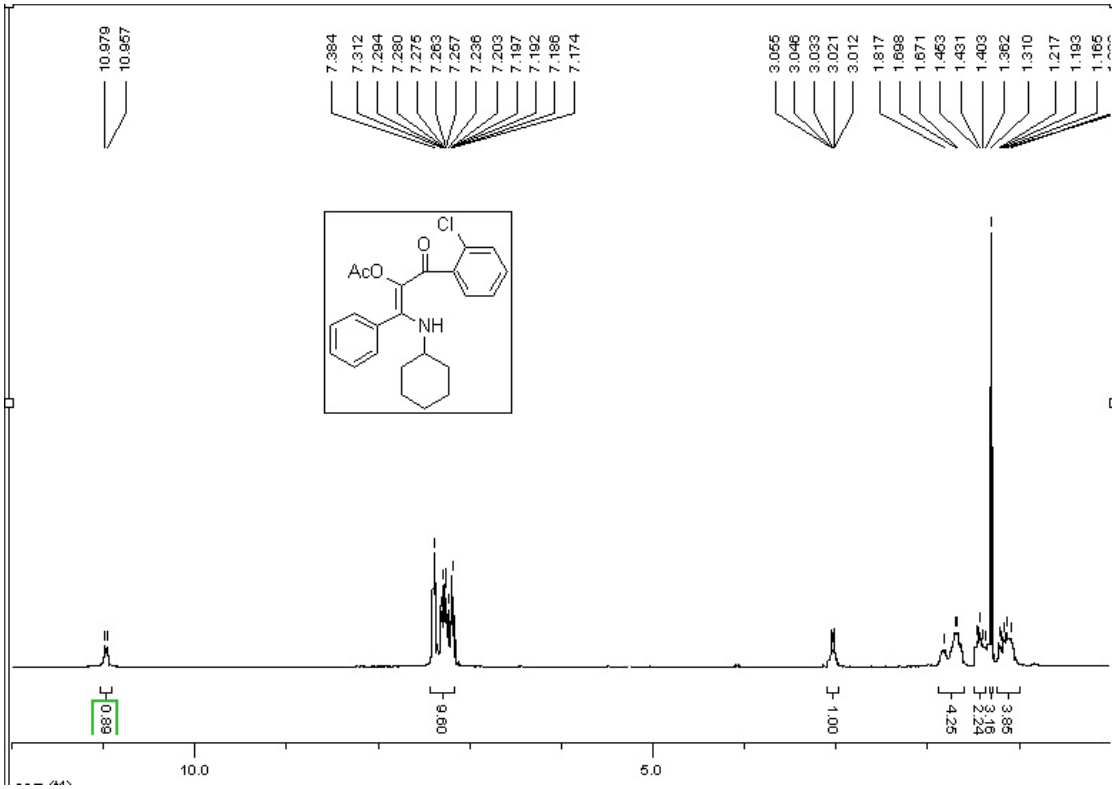
(*E*)-2-methoxy-3-(methylimino)-1-oxo-3-phenyl-1-p-tolylpropan-2-yl acetate (Scheme 3, 4)

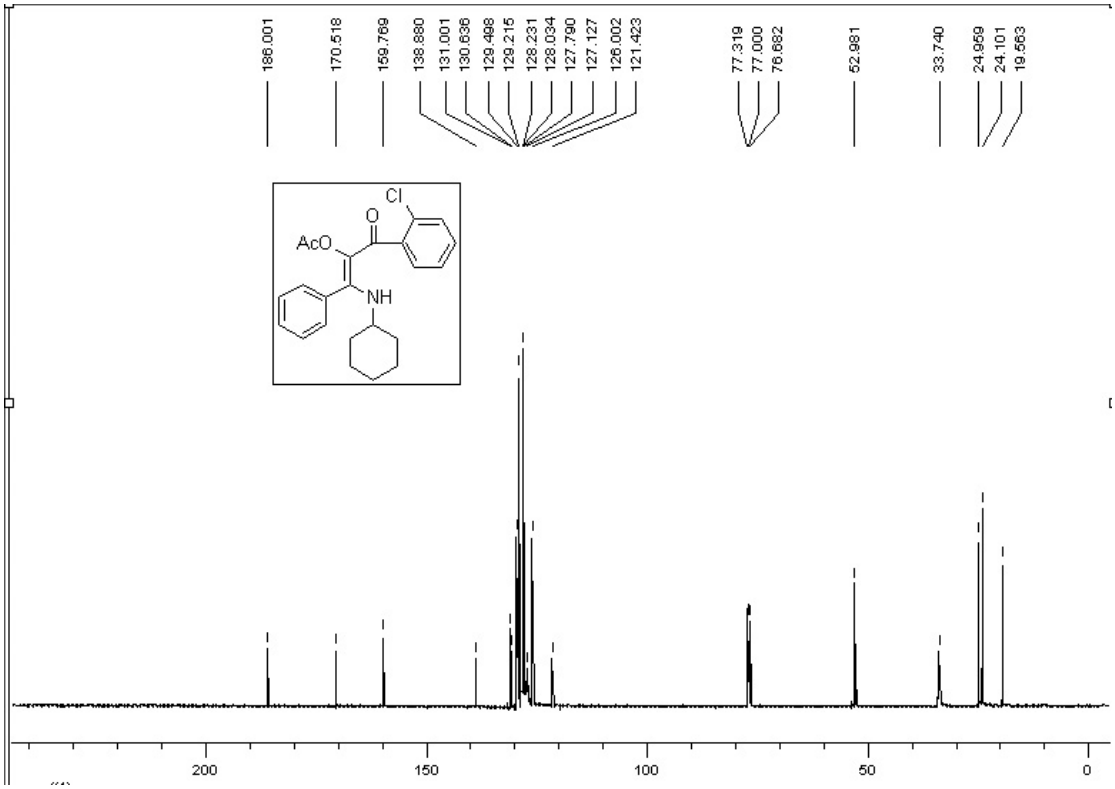
yellow viscous oil, IR vmax (KBr): 3088, 1744, 1688, 1576, 1385, 1211, 1033, 800, 745, 692; 1H-NMR (400 MHz, CDCl3): δ = 7.91-7.68 (m, 5H), 7.36-7.16 (m, 4H), 3.44 (s, 3H), 2.99 (s, 3H), 2.34 (s, 3H), 2.21 (s, 3H); 13C-NMR (100 MHz, CDCl3): δ = 186.0, 174.6, 143.7, 135.4, 132.3, 131.4, 130.6, 129.0, 128.8, 128.6, 127.9, 94.4, 52.6, 33.9, 21.9, 21.7; GC–MS m/z (% rel inten.): 296.12 (100); Anal. Calcd for $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24; Found: C, 70.65; H, 6.05.

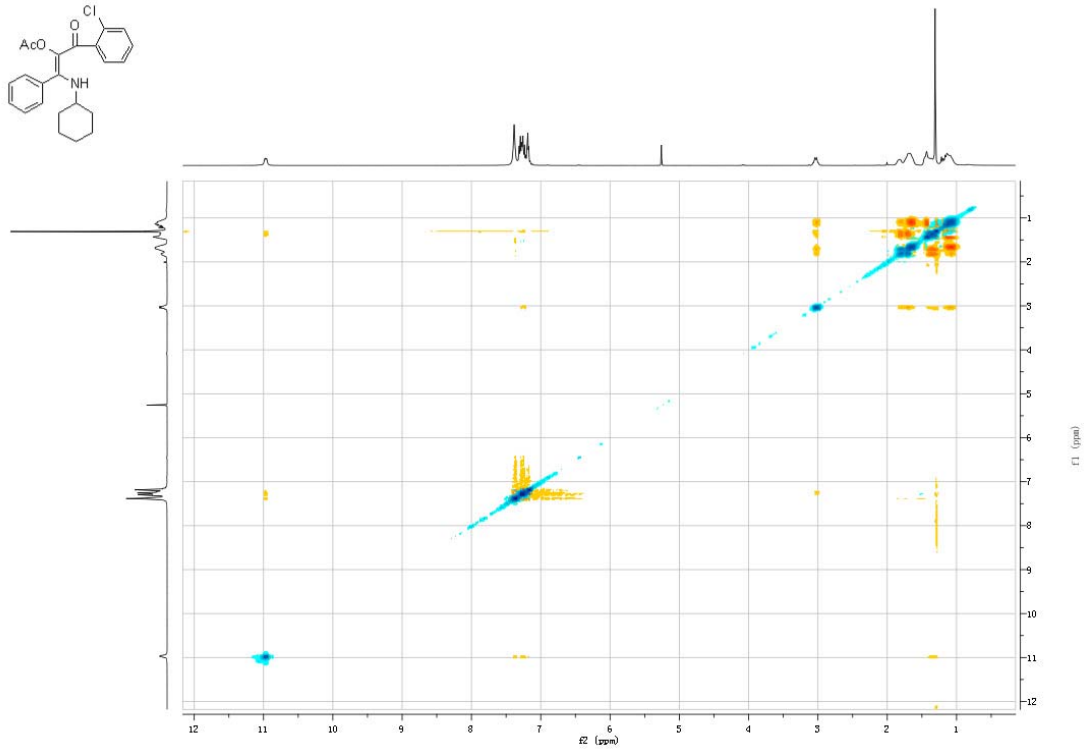
(*E*)-1-(2-chlorophenyl)-2-methoxy-3-(methylimino)-1-oxo-3-phenylpropan-2-yl acetate (Scheme 3, 5)

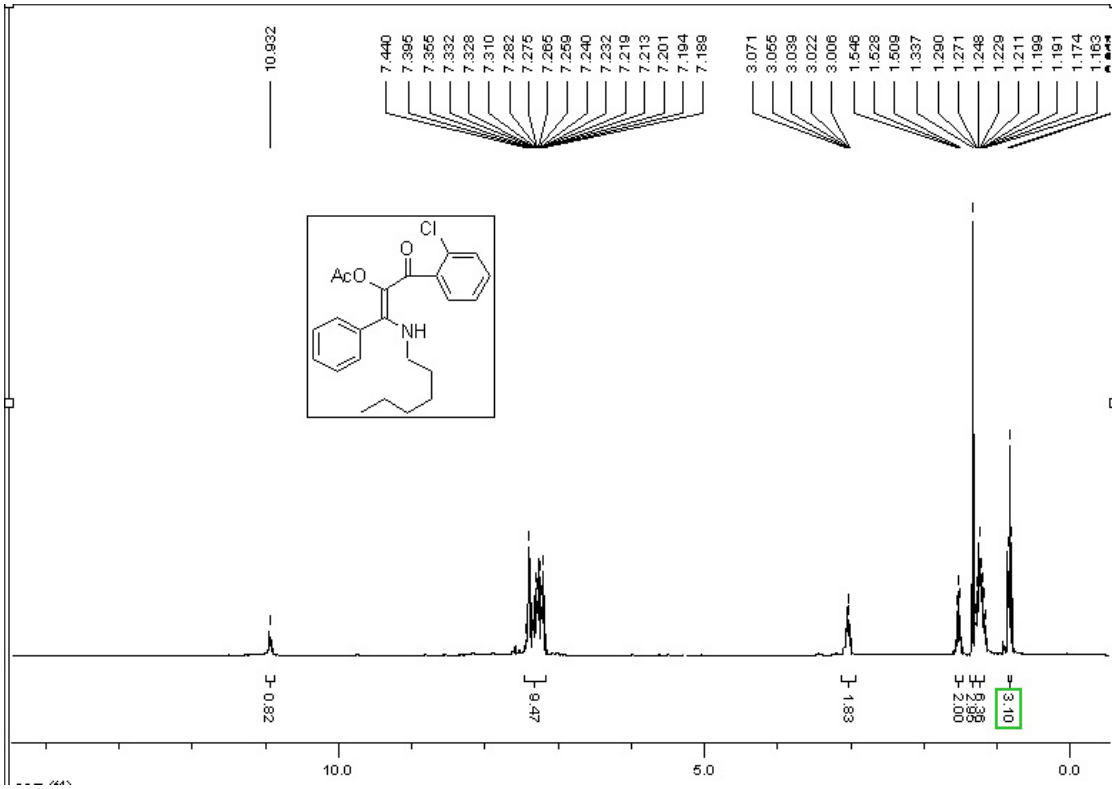
yellow viscous oil, IR vmax (KBr): 3100, 3035, 1785, 1710, 1634, 1385, 1234, 1075, 1027, 747, 699; 1H-NMR (400 MHz, CDCl3): δ = 7.76-7.74 (m, 2H), 7.60-7.58 (m, 1H), 7.36-7.26 (m, 6H), 3.43 (s, 3H), 3.00 (s, 3H), 2.26 (s, 3H); 13C-NMR (100 MHz, CDCl3): δ = 187.1, 181.6, 174.7, 134.9, 134.2, 132.4, 131.5, 130.9, 130.0, 129.2, 129.0, 128.1, 125.9, 93.9, 52.5, 33.6, 21.7, 14.1; GC–MS m/z (% rel inten.): 316.71 (100); Anal. Calcd for $C_{19}H_{18}ClNO_4$: C, 63.42; H, 5.04; Found: C, 63.55; H, 5.19.

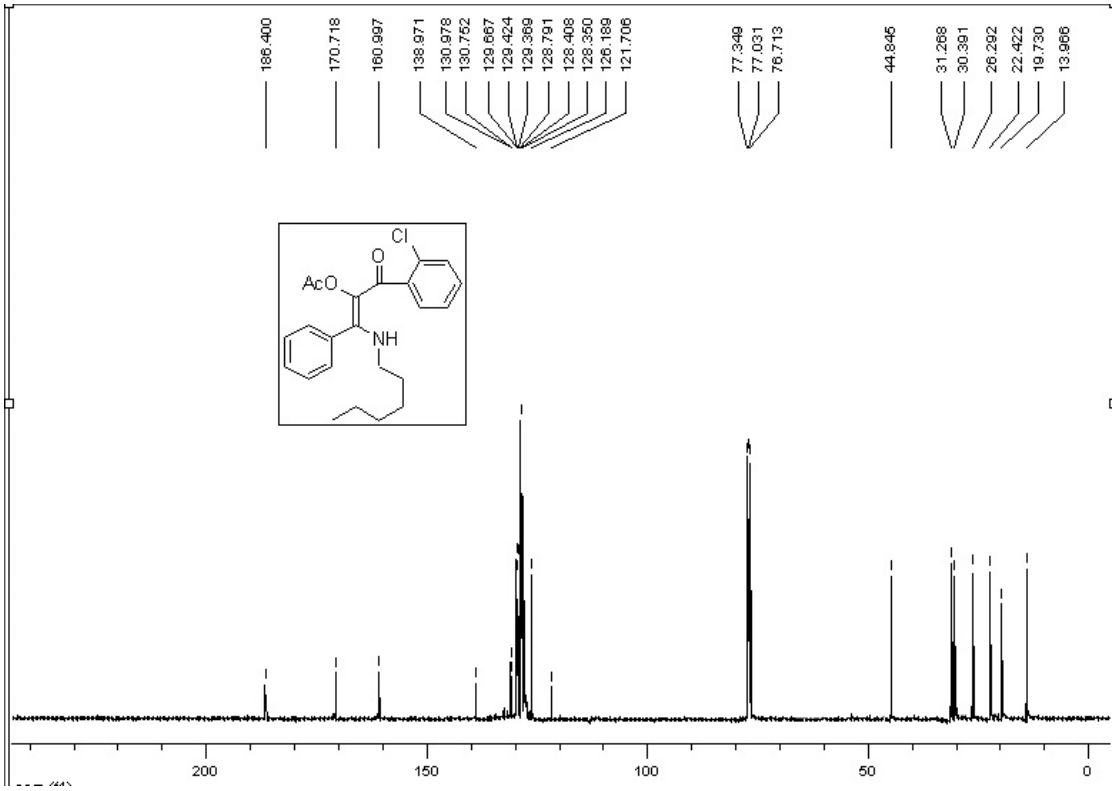
NMR Spectra

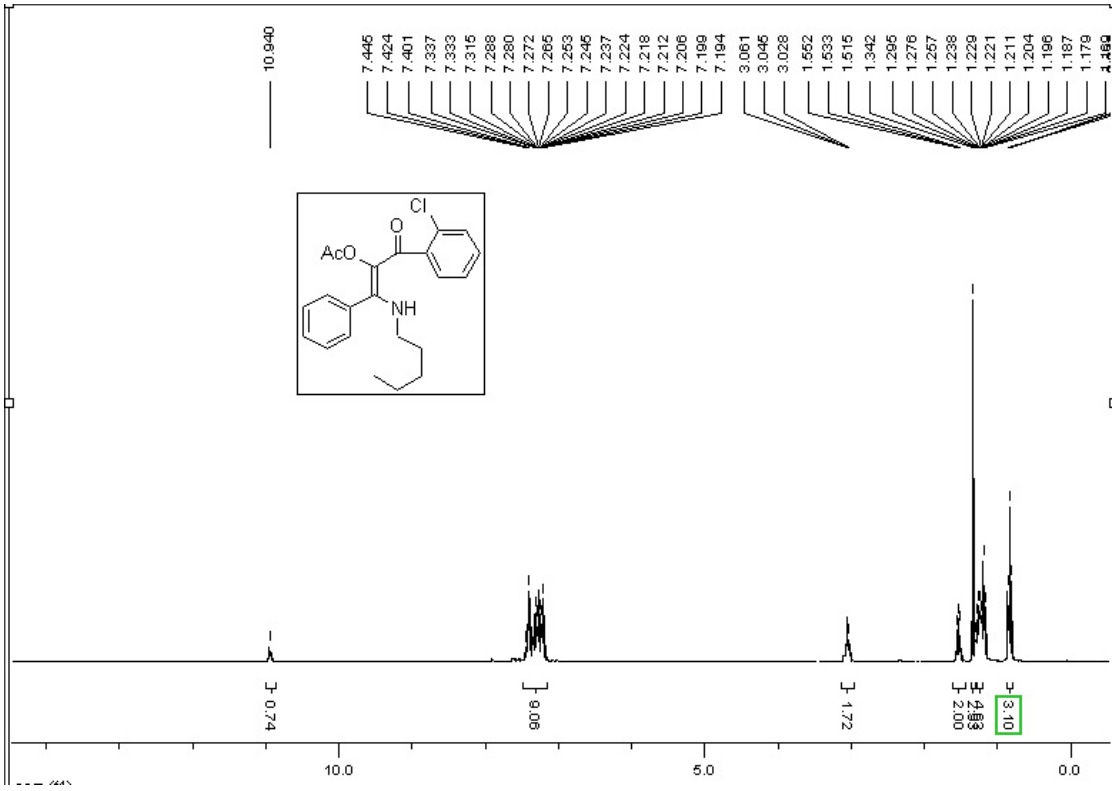


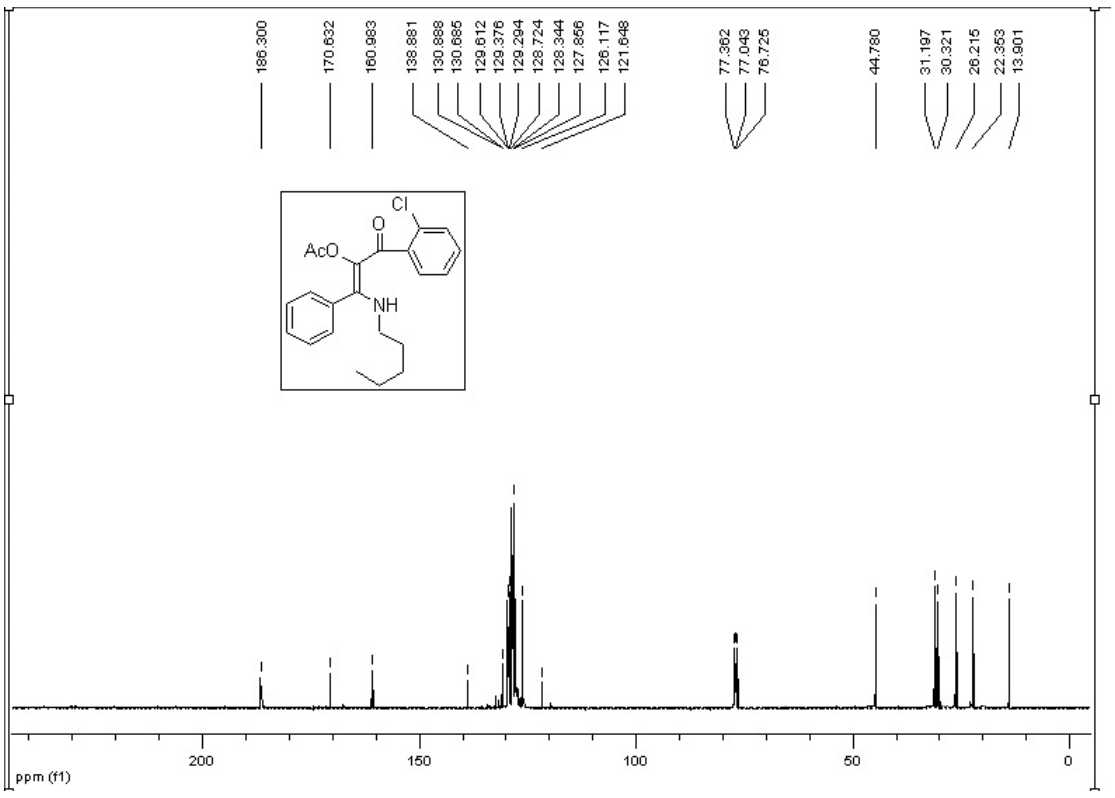


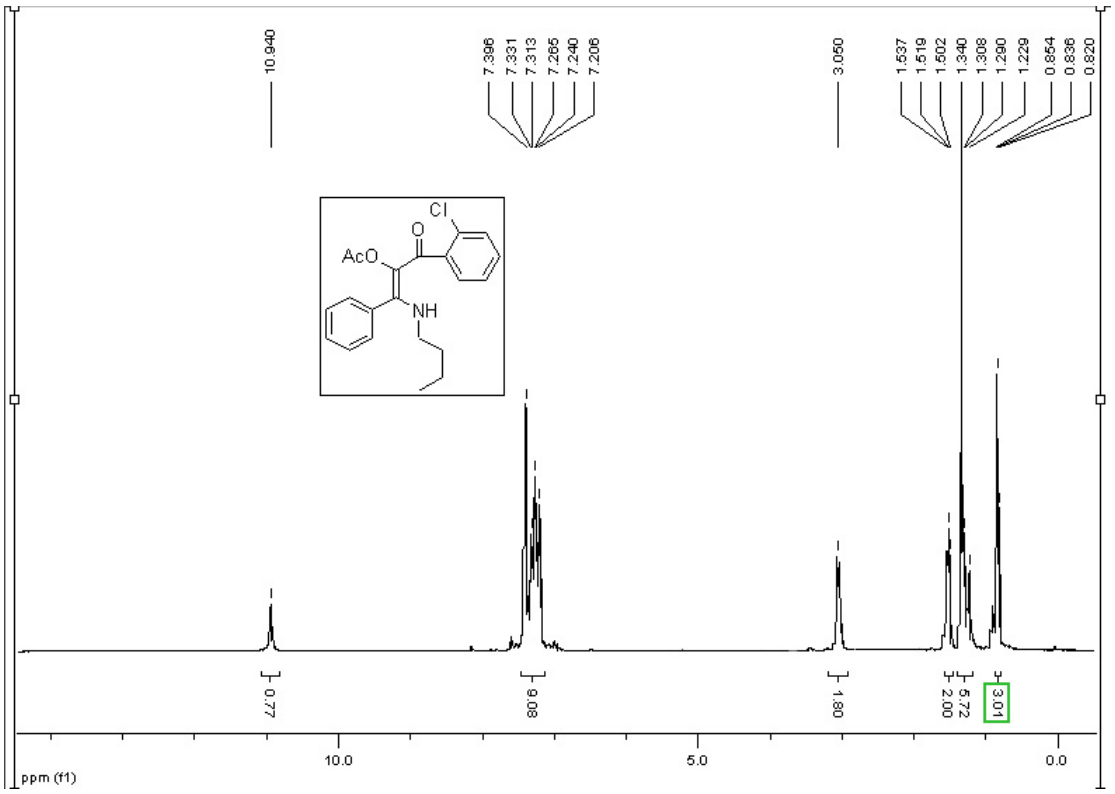


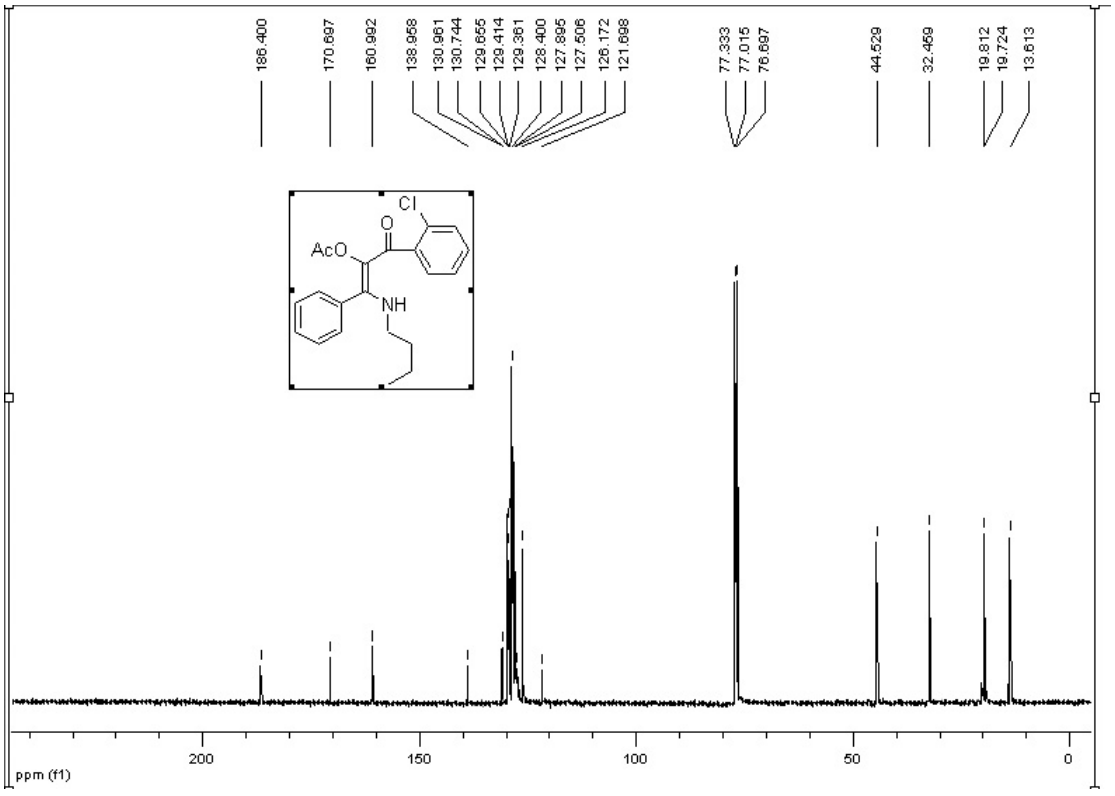


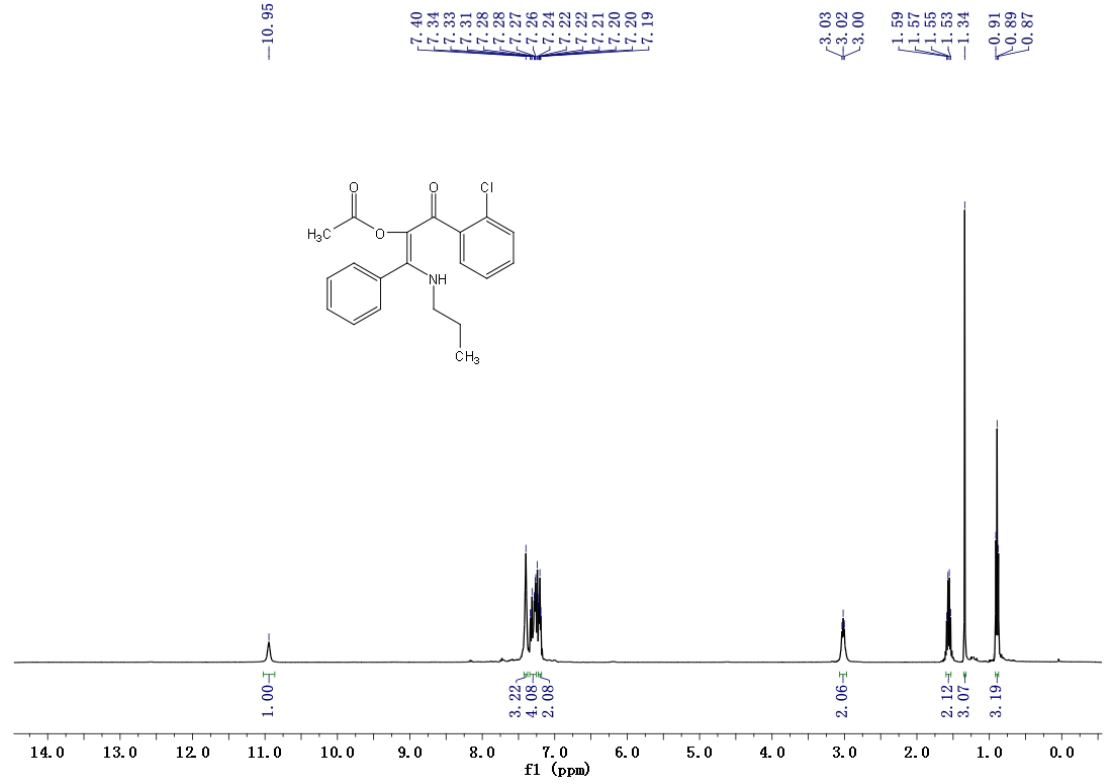








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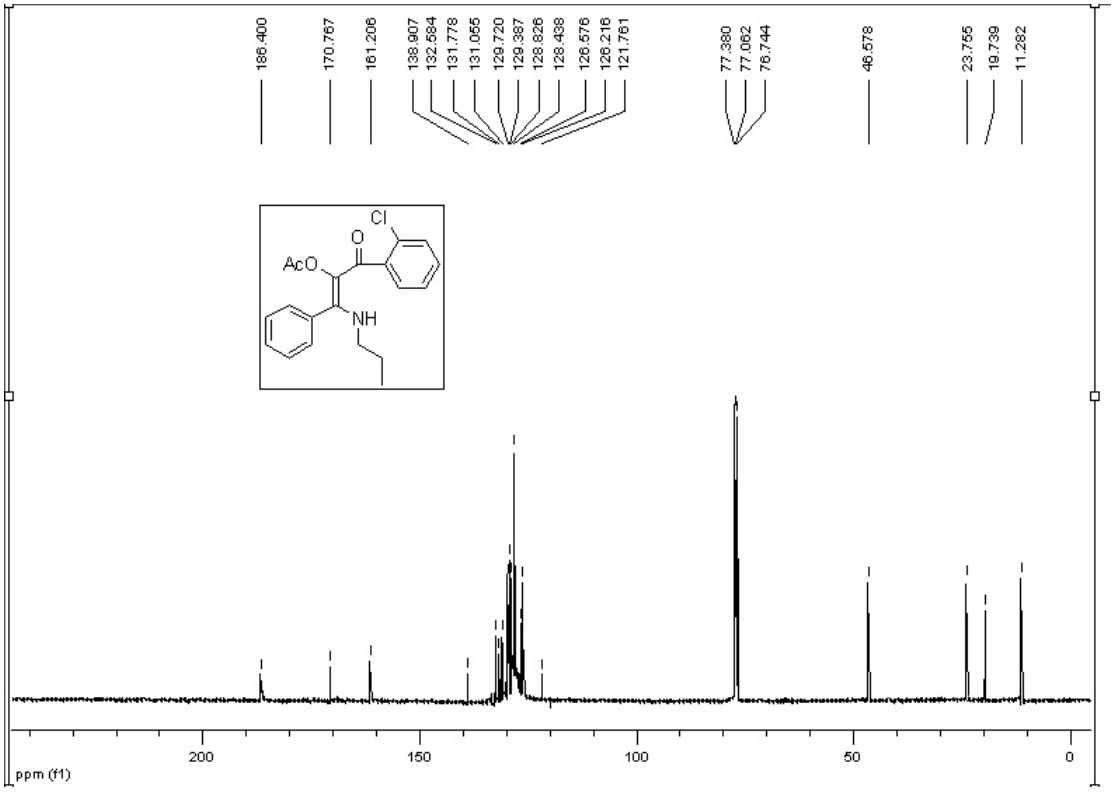
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Cl
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AcO
NH
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150
100
50
0
ppm (f1)