Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

An effective and general method for highly regioselective synthesis of 1-phenylpyrazoles from β-enaminoketoesters, tandem Blaise-acylation adducts

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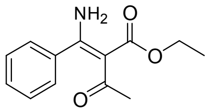
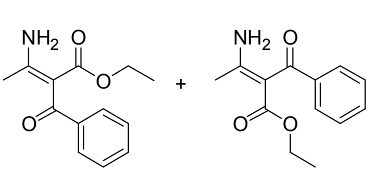
General. All reactions and manipulations were performed in a nitrogen atmosphere using standard Schelenk techniques. The reaction solvents were distilled prior to use (THF: distilled from sodium benzophenone ketyl). All purchased reagents were used without further purification. Anhydrous solvents were transferred by oven-dried syringe. Flasks were flames dried under a stream of nitrogen. The NMR spectra were recorded at 250 MHz (^{1}H)/62.5 MHz (^{13}C). The chemical shifts were relative to TMS (as an internal reference) for ^{1}H NMR.

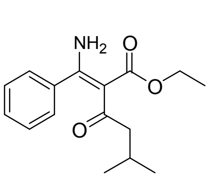
General Procedures for the Synthesis of β-Enaminoketoesters 1. To a stirred suspension of commercial zinc dust (Aldrich, 10 µm, 0.65 g, 10 mmol) in THF (2.5 mL) was added 5 mol% of methansulfonic acid and the mixture was heated at reflux for 10 min. To the mixture was added benzonitrile (0.52 mL, 5 mmol) in one portion followed by addition of ethyl bromoacetate (0.83 mL, 7.5 mmol) over 1h by using syringe pump while maintaining the reflux temperature. After 1h stirring, the reaction mixture was cooled to 0 ℃ and added 1.0 equivalent of *n*-BuLi (2M in cyclohexane, 2.5 mL, 5 mmol) and acetic anhydride (0.62 mL, 6.5 mmol) in sequence. The reaction temperature was allowed to room temperature and stirred for 3 h. The reaction was quenched by addition of sat'd NH_4Cl (aq.) and extracted with ethyl acetate. The organic layer was washed with water, brine, and dried over anhydrous $MgSO_4$. After evaporation of solvent, the residue was purified by column chromatography on silica gel (eluent: n-henxane: EtOAc = 1: 1) to afford the product **1a** (0.96 g, 4 mmol, 82 %).



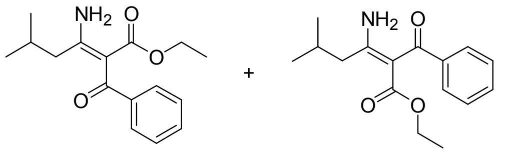
1a: Yield : 82 %, ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.71 (t, *J* = 7.2 Hz, 3H), 2.38 (s, 3H), 3.76 (q, *J* = 7.2 Hz, 2H), 5.49 (bs, 1H), 7.36 ~ 7.45 (m, 5H), 11.00 (bs, 1H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 13.3, 29.4, 60.0, 104.1, 126.6, 128.6, 130.0, 138.4, 166.9, 169.8, 197.1 ppm; HRMS (ESI) Cal. for (M^++H):$C_{13}H_{16}NO_3$:234.1130. Found: 234.1121.



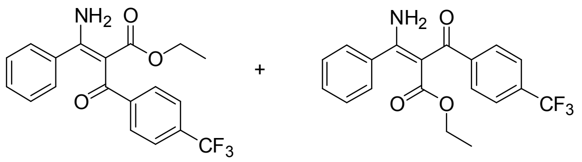
1b: Yield : 81 % (E/Z = 1:1), ^{1}H NMR (250 MHz, $CDCl_3$) δ [0.68 (t, *J* = 7.2 Hz) + 0.77 (t, *J* = 7.1 Hz)] (3H), [2.13 (s) + 2.33 (s)] (3H), [3.77 (q, *J* = 7.1 Hz) + 3.89 (q, *J* = 7.1 Hz)] (2H), [5.80 (bs) + 6.35 (bs)] (1H), 7.29 ~ 7.74 (m, 10H), [9.05 (bs) + 10.71 (bs)] (1H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 13.2, 13.6, 21.6, 22.5, 59.1, 60.0, 99.0, 102.0, 126.4, 127.9, 128.0, 128.3, 129.8, 131.5, 141.7, 143.4, 165.1, 168.1, 169.3, 170.0, 195.0, 196.3 ppm; HRMS (ESI) Cal. for (M^++H):$C_{13}H_{16}NO_3$:234.1130. Found: 234.1144.



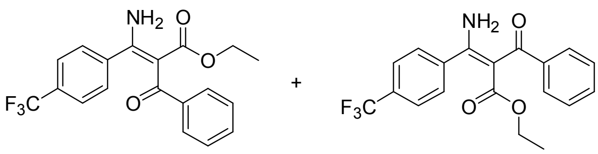
1c: Yield : 94 %, ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.70 (t, *J* = 7.2 Hz, 3H), 0.95 (d, *J* = 6.6 Hz, 6H), 2.11 ~ 2.22 (m, 1H), 2.58 (d, *J* = 7.0 Hz, 2H), 3.73 (q, *J* = 7.2 Hz, 2H), 5.58 (bs, 1H), 7.35 ~ 7.47 (m, 5H), 11.39 (bs, 1H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 13.3, 22.8, 25.5, 49.4, 60.1, 104.6, 126.6, 128.6, 130.0, 138.4, 166.4, 169.9, 199.1 ppm; HRMS (ESI) Cal. for (M^++H):$C_{16}H_{22}NO_3$:276.1600. Found: 276.1586.



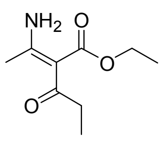
1d: Yield : 90 % (E/Z = 1:1), ^{1}H NMR (250 MHz, $CDCl_3$) δ [0.68 (t, *J* = 7.1 Hz) + 0.75 (t, *J* = 7.1 Hz)] (3H), [0.91 (d, *J* = 6.6 Hz) + 0.99 (d, *J* = 6.6 Hz)] (6H), [1.80 ~ 1.96 (m) + 1.98 ~ 2.11 (m)] (1H), [2.36 (d, *J* = 7.5 Hz) + 2.56 (d, *J* = 7.3 Hz)] (2H), [3.75 (q, *J* = 7.1 Hz) + 3.89 (q, *J* = 7.1 Hz)] (2H), [5.64 (bs) + 6.14 (bs,)] (1H), 7.34 ~ 7.76 (m, 5H), [9.14 (bs) + 10.81 (bs)] (1H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 13.2, 13.6, 22.3, 22.4, 28.1, 28.5, 42.8, 43.6, 59.1, 60.0, 99.0, 102.2, 126.4, 127.9, 128.0, 128.3, 128.4, 129.8, 130.0, 131.5, 141.9, 143.4, 167.7, 169.5, 170.0, 170.6, 195.2, 196.3 ppm; HRMS (ESI) Cal. for (M^++H):$C_{16}H_{22}NO_3$:276.1600. Found: 276.1618.



1e: Yield : 84 % (E/Z = 1.23/1), ^{1}H NMR (250 MHz, $CDCl_3$) δ [0.62 (t, *J* = 7.1 Hz) + 0.92 (t, *J* = 7.1 Hz)] (3H), [3.60 (q, *J* = 7.1Hz) + 4.03 (q, *J* = 7.1 Hz)] (2H), [5.45 (bs) + 5.94 (bs)] (1H), 7.26-7.86 (m, 9H), [9.15 (bs) + 10.78 (bs)] (1H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 13.1, 13.8, 59.7, 60.3, 99.7, 103.6, 124.89, 124.92, 124.95, 124.98, 126.7, 126.8, 127.3, 128.6, 128.7, 128.9, 130.2, 130.3, 136.8, 137.1, 144.0, 145.8, 166.0, 168.2, 168.5, 169.0, 193.1, 194.2 ppm; HRMS (ESI) Cal. for (M^++H):$C_{19}H_{17}F_3NO_3$:364.1161. Found: 364.1157.

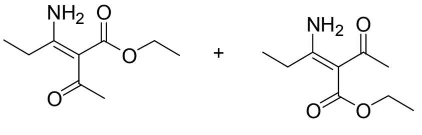


1f: Yield : 89 % (E/Z = 2/1), ^{1}H NMR (250 MHz, $CDCl_3$) δ [0.61 (t, *J* = 7.1 Hz) + 0.92 (t, *J* = 7.1 Hz)] (3H), [3.60 (q, *J* = 7.1 Hz) + 4.03 (q, *J* = 7.1 Hz)] (2H), [5.38 (bs) + 5.81 (bs)] (1H), 7.19-7.73 (m, 9H), [9.02 (bs) + 10.6 (bs)] (1H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 13.1, 13.8, 59.7, 60.3, 100,9, 103.7, 125.5, 126.0, 126.5, 127.5, 128.0, 128.1, 128.7, 130.4, 131.4, 132.0, 132.1, 140.4, 140.6, 140.7, 142.2, 163.1, 165.5, 168.6, 168.9, 194.9, 195.0 ppm; HRMS (ESI) Cal. for (M^++H):$C_{19}H_{17}F_3NO_3$:364.1161. Found: 364.1164.

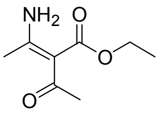


1g: Yield : 82 %, ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.09 (t, *J* = 7.4 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H), 2.20 (s, 3H), 2.60 (q, *J* = 7.4 Hz, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 6.34 (bs, 1H), 11.1 (bs, 1H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 9.6, 14.1, 23.0, 34.3, 60.2, 102.9, 166.6, 169.9, 200.0 ppm;

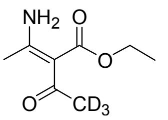
HRMS (ESI) Cal. for (M^++H):$C_9H_{16}NO_3$:186.1130. Found: 186.1139.



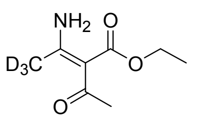
1h: Yield : 86 % (E/Z = 1:1), ^{1}H NMR (250 MHz, $CDCl_3$) δ [1.21 (t, J = 7.5 Hz) + 1.22 (t, J = 7.5 Hz)] (3H), [1.32 (t, J = 7.1 Hz) + 1.33 (t, J = 7.1 Hz)] (3H), [2.27 (s) + 2.28 (s)] (3H), 2.53 (q, J = 7.5 Hz, 2H), [4.23 (q, J = 7.1 Hz) + 4.24 (q, J = 7.1 Hz)] (2H), [5.65 (bs) + 5.67 (bs)] (1H), 11.2 (bs, 1H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 12.4, 14.2, 28.9, 29.9, 60.2, 104.3, 169.7, 171.3, 196.9 ppm; HRMS (ESI) Cal. for (M^++H):$C_9H_{16}NO_3$:186.1130. Found: 186.1129.



1i: Yield : 83 %, ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.33 (t, J = 7.1 Hz, 3H), 2.24 (s, 3H), 2.30 (s, 3H), 4.23 (q, J = 7.1 Hz, 2H), 6.20 (bs, 1H), 11.18 (bs, 1H) ppm, ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 14.3, 23.4, 30.1, 60.1, 103.2, 167.3, 169.7, 197.0 ppm; HRMS (ESI) Cal. for (M^++H):$C_8H_{14}NO_3$: 172.0974. Found: 172.0979.

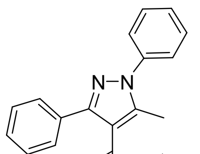


1j: Yield : 68 %, ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.33 (t, J = 7.1 Hz, 3H), 2.23 (s, 3H), 4.23 (q, J = 7.1 Hz, 2H), 5.99 (bs, 1H), 11.20 (bs, 1H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 14.2, 23.5, 60.1, 103.3, 167.2, 169.6, 197.2 ppm; HRMS (ESI) Cal. for (M^++H):$C_8H_{11}D_3NO_3$: 175.1159. Found: 175.1172.

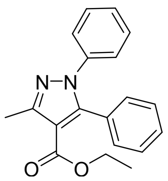


1k: Yield : 70 %, ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.33 (t, J = 7.1 Hz, 3H), 2.29 (s, 3H), 4.23 (q, J = 7.1 Hz, 2H), 6.82 (bs, 1H), 11.15 (bs, 1H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 14.1, 30.0, 60.0, 102.9, 167.7, 169.7, 196.8 ppm; HRMS (ESI) Cal. for (M^++H):$C_8H_{11}D_3NO_3$: 175.1159. Found: 175.1156.

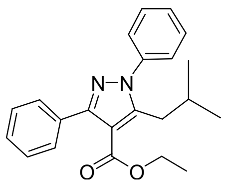
General Procedures for the Synthesis of Pyrazoles 2. To a solution of **1a** (165 mg, 0.5 mmol) in absolute ethanol (1 mL) was added phenyl hydrazine (0.3 mL, 2.5 mmol) and *p*-toluenesulfonic acid (5 mg, 5 mol%) and stirred at room temperature for 1 h. The reaction mixture was refluxed for 1 h, and cooled to room temperature. After evaporation of solvent, the residue was dissolved in ethyl acetate, and organic layer was washed subsequently with sat'd $NaHCO_3$(aq), 1N HCl(aq), and brine, and then dried with anhydrous $MgSO_4$. After comcentration under reduced pressure, the residue was purified by column chromatography on silica gel to afford the product **2a** (139 mg, 0.45 mmol, 91 %).



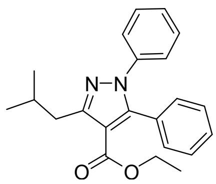
2a: Yield : 91 %, ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.22 (t, J = 7.1 Hz, 3H), 2.59 (s, 3H), 4.24 (q, J = 7.1 Hz, 2H), 7.38 ~ 7.51 (m, 8H), 7.65 ~ 7.69 (m, 2H) ppm**;** ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 12.8, 14.1, 60.0, 110.6, 125.8, 127.6, 128.2, 128.7, 129.2, 129.5, 133.1, 138.8, 144.8, 153.6, 164.2 ppm**;** HRMS (ESI) Cal. for (M^++H):$C_{19}H_{19}N_2O_2$: 307.1447. Found: 307.1457.



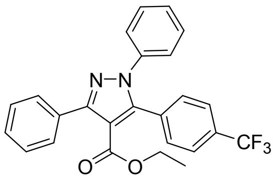
2b: Yield : 88 %, ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.13 (t, *J* = 7.1 Hz, 3H), 2.60 (s, 3H), 4.15 (q, *J* = 7.1 Hz, 2H), 7.15 ~ 7.34 (m, 10H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 14.0, 14.3, 59.8, 111.9, 125.3, 127.6, 127.9, 128.7, 128.8, 129.9, 130.4, 139.2, 146.3, 151.8, 163.8 ppm; HRMS (ESI) Cal. for (M^++H):$C_{19}H_{19}N_2O_2$:307.1447. Found: 307.1457.



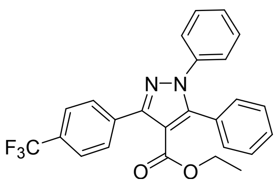
2c: Yield : 87 %, ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.78 (d, *J* = 6.7 Hz, 6H), 1.21 (t, *J* = 7.0 Hz, 3H), 1.89 ~ 1.83 (m, 1H), 2.92 (d, *J* = 7.3 Hz, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 7.36 ~ 7.49 (m, 8H), 7.65 ~ 7.69 (m, 2H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 13.9, 22.2, 28.9, 33.8, 59.9, 110.2, 126.7, 127.6, 128.1, 128.8, 129.2, 129.4, 133.1, 139.1, 148.5, 153.5, 164.2 ppm; HRMS (ESI) Cal. for (M^++H):$C_{22}H_{25}N_2O_2$:349.1916. Found: 349.1909.



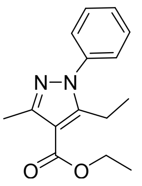
2d: Yield : 85 %, ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.03 (d, *J* = 6.6 Hz, 6H), 1.12 (t, *J* = 7.1 Hz, 3H), 2.10 ~ 2.20 (m, 1H), 2.89 (d, *J* = 7.1 Hz, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 7.17 ~ 7.33 (m, 10H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 13.9, 22.6, 28.5, 36.9, 59.8, 111.7, 125.3, 127.5, 127.8, 128.7, 130.1, 130.4, 139.2, 146.3, 154.8, 163.9 ppm; HRMS (ESI) Cal. for (M^++H):$C_{22}H_{25}N_2O_2$:349.1916. Found: 349.1923.



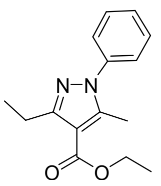
2e: Yield : 83 %; ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.97 (t, *J* = 7.1 Hz, 3H), 4.08 (q, *J* = 7.1 Hz, 2H), 7.22 ~ 7.48 (m, 10H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.75 ~ 7.79 (m, 2H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 13.6, 60.4, 112.5, 124.9, 125.1, 125.5, 127.9, 128.3, 128.6, 129.1, 129.3, 131.0, 132.4, 133.3, 138.7, 144.8, 153.6, 163.4 ppm; HRMS (ESI) Cal. for (M^++H):$C_{25}H_{20}F_3N_2O_2$:437.1477. Found: 437.1455.



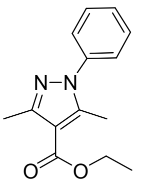
2f: Yield : 88 %, ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.96 (t, *J* = 7.1 Hz, 3H), 4.08 (q, *J* = 7.1 Hz, 2H), 7.25 ~ 7.39 (m, 10H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.93 (d, *J* = 8.0 Hz, 2H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 13.6, 60.4, 112.2, 124.7, 124.8, 124.9, 125.4, 128.1, 129.0, 129.2, 129.4, 129.6, 130.4, 136.4, 139.0, 146.7, 152.0, 162.9 ppm; HRMS (ESI) Cal. for (M^++H):$C_{25}H_{20}F_3N_2O_2$:437.1477. Found: 437.1498.



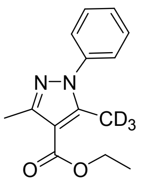
2g: Yield : 91 %, ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.17 (t, *J* = 7.4 Hz, 3H), 1.39 (t, *J* = 7.1 Hz, 3H), 2.50 (s, 3H), 2.90 (q, *J* = 7.4 Hz, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 7.36 ~ 7.50 (m, 5H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 13.7, 14.3, 19.1, 59.7, 109.7, 126.1, 128.7, 129.2, 138.9, 150.4, 151.5, 164.3 ppm; HRMS (ESI) Cal. for $(M^{+}+H)$:$C_{15}H_{19}N_2O_2$: 259.1447. Found: 259.1435.



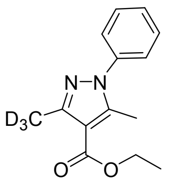
2h: Yield : 90 %, ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.29 (t, *J* = 7.6 Hz, 3H), 1.39 (t, *J* = 7.1 Hz, 3H), 2.52 (s, 3H), 2.94 (q, *J* = 7.1 Hz, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 7.27 ~ 7.50 (m, 5H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 12.6, 13.5, 14.3, 21.7, 59.6, 110.0, 125.6, 128.3, 129.1, 138.8, 144.4, 156.6, 164.3 ppm; HRMS (ESI) Cal. for $(M^{+}+H)$:$C_{15}H_{19}N_2O_2$:259.1447. Found: 259.1438.



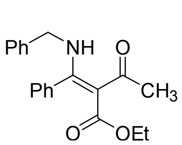
2i: Yield : 97 %, ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.38 (t, *J* = 7.1 Hz, 3H), 2.50 (s, 3H), 2.52 (s, 3H), 4.33 (q, J = 7.1 Hz, 2H), 7.37 ~ 7.49 (m, 5H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 12.6, 14.3, 14.4, 59.7, 110.8, 125.6, 128.4, 129.2, 138.8, 144.5, 151.3, 164.6 ppm; HRMS (ESI) Cal. for $(M^{+}+H)$:$C_{14}H_{17}N_2O_2$: 245.1290. Found: 245.1311.



2j: Yield : 79 %, ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.38 (t, *J* = 7.1 Hz, 3H), 2.50 (s, 3H), 4.33 (q, *J* = 7.1 Hz, 2H), 7.27 ~ 7.49 (m, 5H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 14.36, 14.43, 59.7, 110.9, 125.6, 128.4, 129.2, 138.8, 144.4, 151.5, 164.6 ppm; HRMS (ESI) Cal. for $(M^{+}+H)$:$C_{14}H_{14}D_3N_2O_2$: 248.1475. Found: 248.1493.



2k: Yield : 78 %, ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.38 (t, *J* = 7.1 Hz, 3H), 2.52 (s, 3H), 4.33 (q, *J* = 7.1 Hz, 2H), 7.38 ~ 7.51 (m, 5H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 12.6, 14.4, 59.7, 110.8, 125.6, 128.4, 129.2, 138.7, 144.4, 151.3, 164.5 ppm; HRMS (ESI) Cal. for $(M^{+}+H)$:$C_{14}H_{14}D_3N_2O_2$: 248.1475. Found: 248.1485.



3: Yield : 64 %, ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.70 (t, *J* = 7.2 Hz, 3H), 2.35 (s, 3H), 3.67 (q, *J* = 7.2 Hz, 2H), 4.23 (d, *J* = 6.2 Hz), 7.10 ~ 7.13 (m, 2H), 7.20 ~ 7.40 (m, 8H), 12.57 (bs, 1H) ppm; ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 13.38, 29.30, 48.44, 59.93, 104.75, 126.91, 127.30, 127.58, 128.40, 128.75, 129.31, 134.10, 137.37, 167.97, 169.71, 196.36 ppm.

Table S1-1. Crystal data for 2a (CCDS 708928)

Empirical formula	C19 H18 N2 O2	
Formula weight	306.35	
Temperature	170(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 8.2775(12) Å	α= 90.00°
	b = 15.616(2) Å	β= 98.896(3)°
	c = 12.3892(18) Å	γ = 90.00°
Volume	1582.2(4) $Å^3$	
Z	4	
Density (calculated)	1.286 Mg/m^3	
Absorption coefficient	0.084 mm^{-1}	
F(000)	648	
Crystal size	0.13 x 0.08 x 0.08 mm^3	
Theta range for data collection	2.11 to 26.00 .	
Index ranges	$-9 \leq h \leq 10, -19 \leq k \leq 19, -12 \leq l \leq 15$	
Reflections collected	8739	
Independent reflections	3094 [R(int) = 0.0571]	
Completeness to theta = 26.00	99.5 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3094 / 0 / 211	
Goodness-of-fit on F^2	0.885	
Final R indices [I>2sigma(I)]	R1 = 0.0421, wR2 = 0.0862	
R indices (all data)	R1 = 0.0793, wR2 = 0.0943	
Extinction coefficient	0.0065(10)	
Largest diff. peak and hole	0.176 and -0.157 e.$Å^{-3}$	

Table S2. Crystal data for 2b (CCDS 708929).

Empirical formula	C19 H18 N2 O2	
Formula weight	306.35	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 10.468(8) Å	α= 90.00°
	b = 15.676(12) Å	β= 103.79°
	c = 10.468(8) Å	γ = 90.00°
Volume	1668(2) $Å^3$	
Z	4	
Density (calculated)	1.220 Mg/m^3	
Absorption coefficient	0.080 mm^{-1}	
F(000)	648	
Crystal size	0.15 x 0.10 x 0.08 mm^3	
Theta range for data collection	2.39 to 25.99 .	
Index ranges	$-12 \leq h \leq 12$, $-17 \leq k \leq 19$, $-9 \leq l \leq 12$	
Reflections collected	9153	
Independent reflections	3264 [R(int) = 0.1063]	
Completeness to theta = 25.99	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3264 / 0 / 211	
Goodness-of-fit on F^2	0.681	
Final R indices [I>2sigma(I)]	R1 = 0.0587, wR2 = 0.1324	
R indices (all data)	R1 = 0.1489, wR2 = 0.1464	
Extinction coefficient	0.017(2)	
Largest diff. peak and hole	0.233 and -0.188 e.$Å^{-3}$	

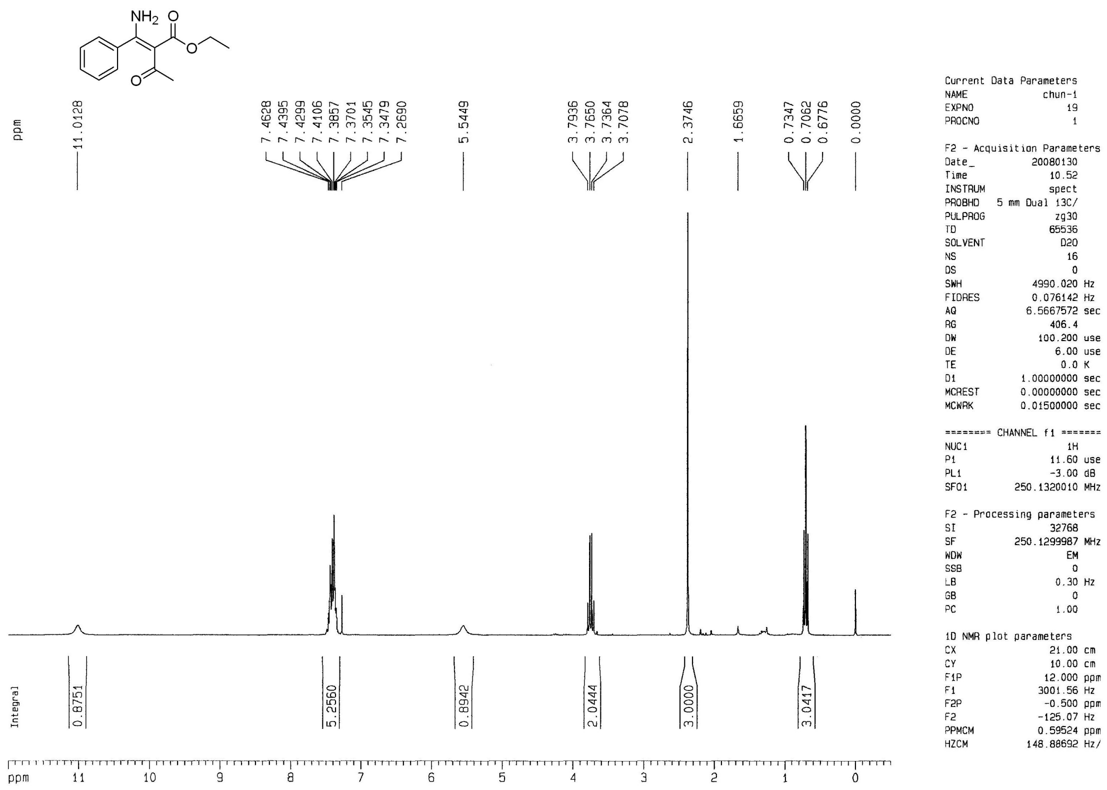
Table S3. Crystal data for 2e(CCDS 708930).

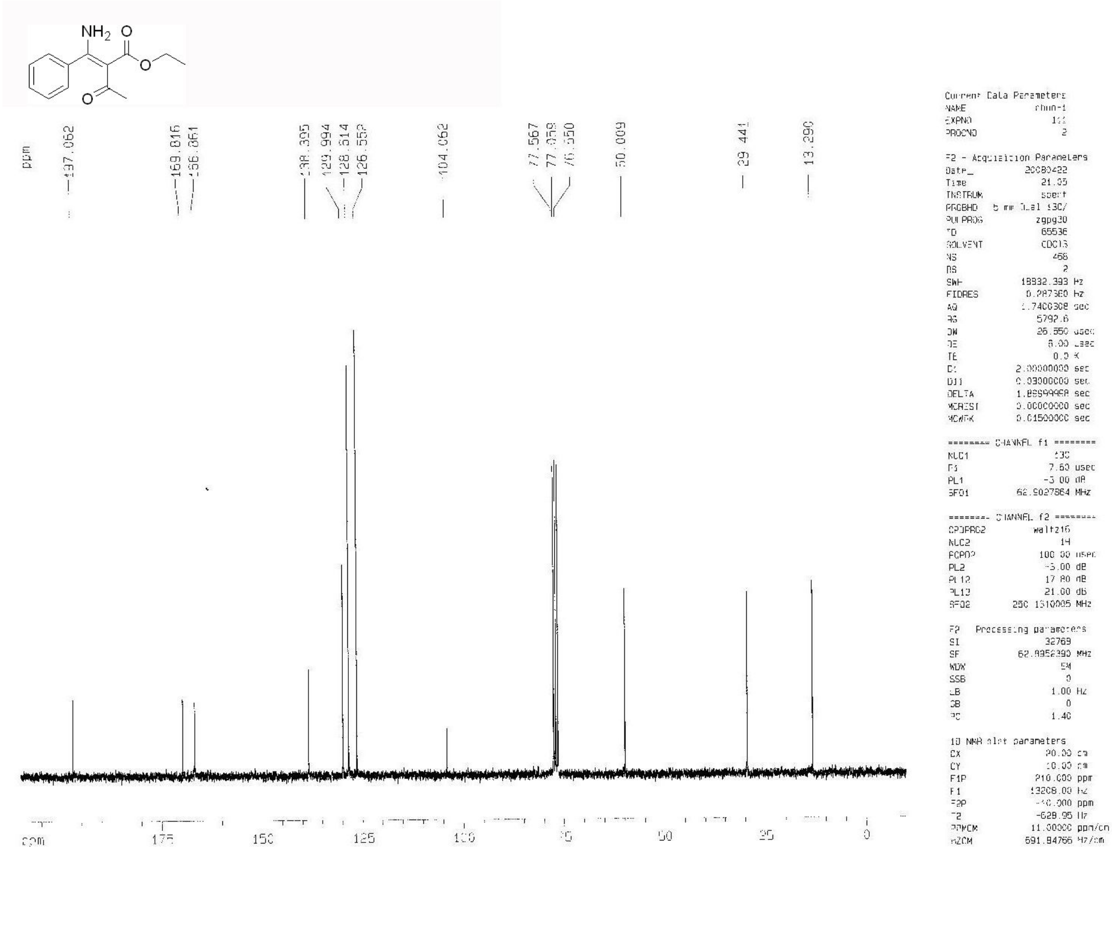
Empirical formula	C25 H19 F3 N2 O2	
Formula weight	436.42	
Temperature	170(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 12.182(2) Å	α= 90.00°
	b = 19.321(4) Å	β= 98.535(4)°
	c = 9.0766(17) Å	γ = 90.00°
Volume	2112.7(7) $Å^3$	
Z	4	
Density (calculated)	1.372 Mg/m^3	
Absorption coefficient	0.106 mm^{-1}	
F(000)	904	
Crystal size	0.15 x 0.08 x 0.08 mm^3	
Theta range for data collection	1.69 to 26.00 .	
Index ranges	$-15 \leq h \leq 15$, $-23 \leq k \leq 21$, $-11 \leq l \leq 10$	
Reflections collected	11696	
Independent reflections	4139 [R(int) = 0.0557]	
Completeness to theta = 26.00	99.7 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4139 / 0 / 290	
Goodness-of-fit on F^2	0.676	
Final R indices [I>2sigma(I)]	R1 = 0.0341, wR2 = 0.0551	
R indices (all data)	R1 = 0.0749, wR2 = 0.0586	
Largest diff. peak and hole	0.159 and -0.167 e.$Å^{-3}$	

Table S4. Crystal data for 2f (CCDS 708931).

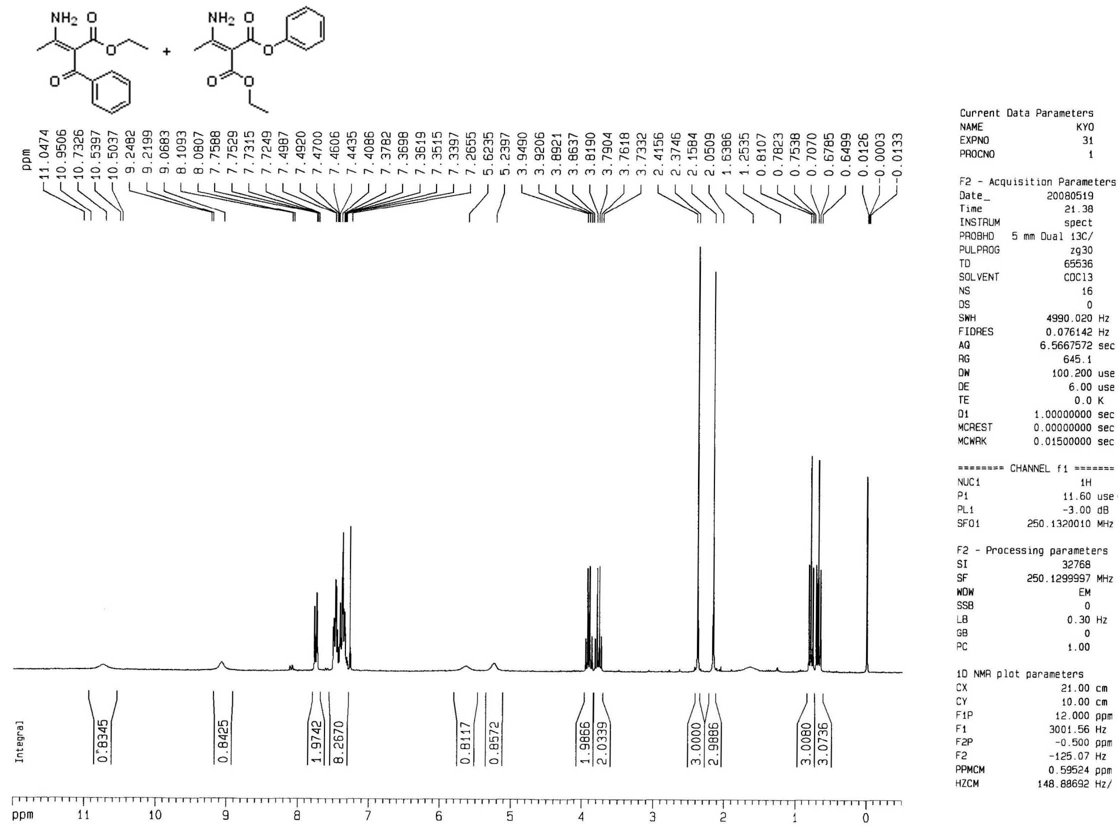
Empirical formula	C25 H19 F3 N2 O2	
Formula weight	436.42	
Temperature	170(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.801(2) Å	α= 78.875(5)°
	b = 9.982(2) Å	β= 88.801(5)°
	c = 12.377(3) Å	γ = 64.005(4)°
Volume	1065.2(4) $Å^3$	
Z	2	
Density (calculated)	1.361 Mg/m^3	
Absorption coefficient	0.105 mm^{-1}	
F(000)	452	
Crystal size	0.10 x 0.08 x 0.05 mm^3	
Theta range for data collection	1.68 to 26.00 .	
Index ranges	$-12 \le h \le 12$, $-12 \le k \le 11$, $-10 \le l \le 15$	
Reflections collected	5963	
Independent reflections	4052 [R(int) = 0.2207]	
Completeness to theta = 26.00	96.8 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4052 / 0 / 291	
Goodness-of-fit on F^2	0.714	
Final R indices [I>2sigma(I)]	R1 = 0.0684, wR2 = 0.1151	
R indices (all data)	R1 = 0.2089, wR2 = 0.1613	
Extinction coefficient	0.0067(14)	
Largest diff. peak and hole	0.345 and -0.398 $e.Å^{-3}$	

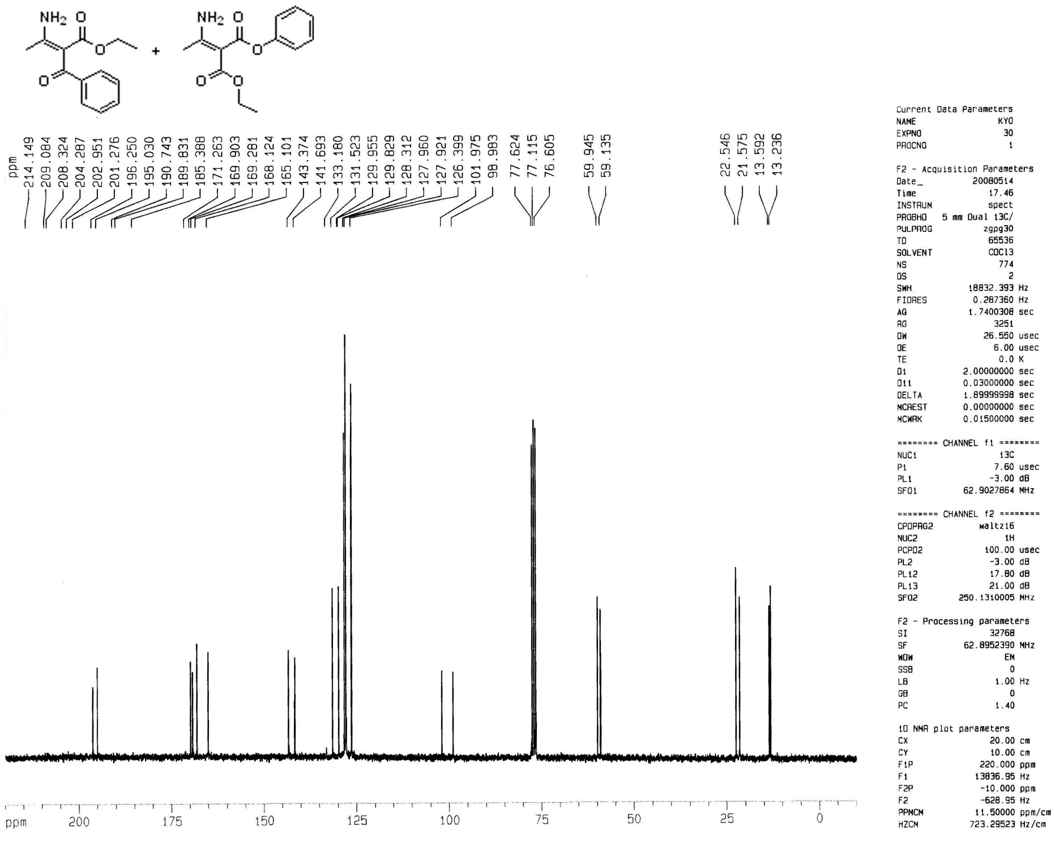
^{1}H and ^{13}C NMR spectra of **1a**



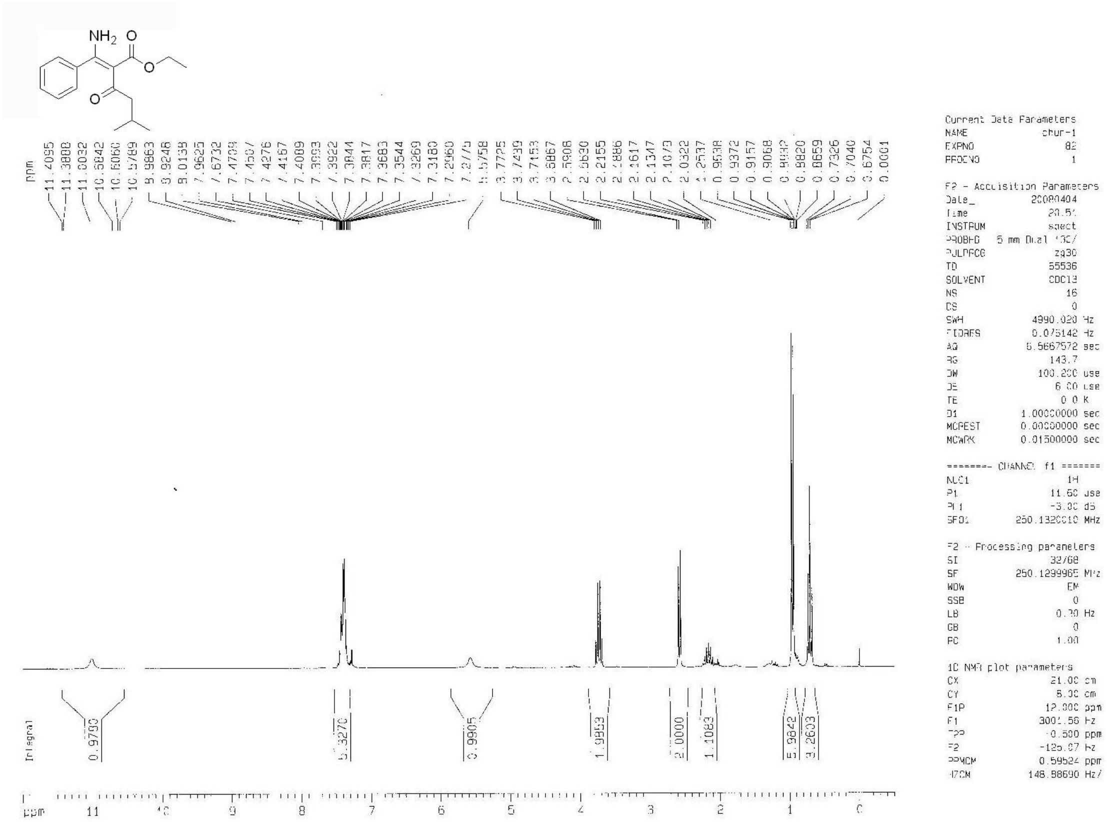


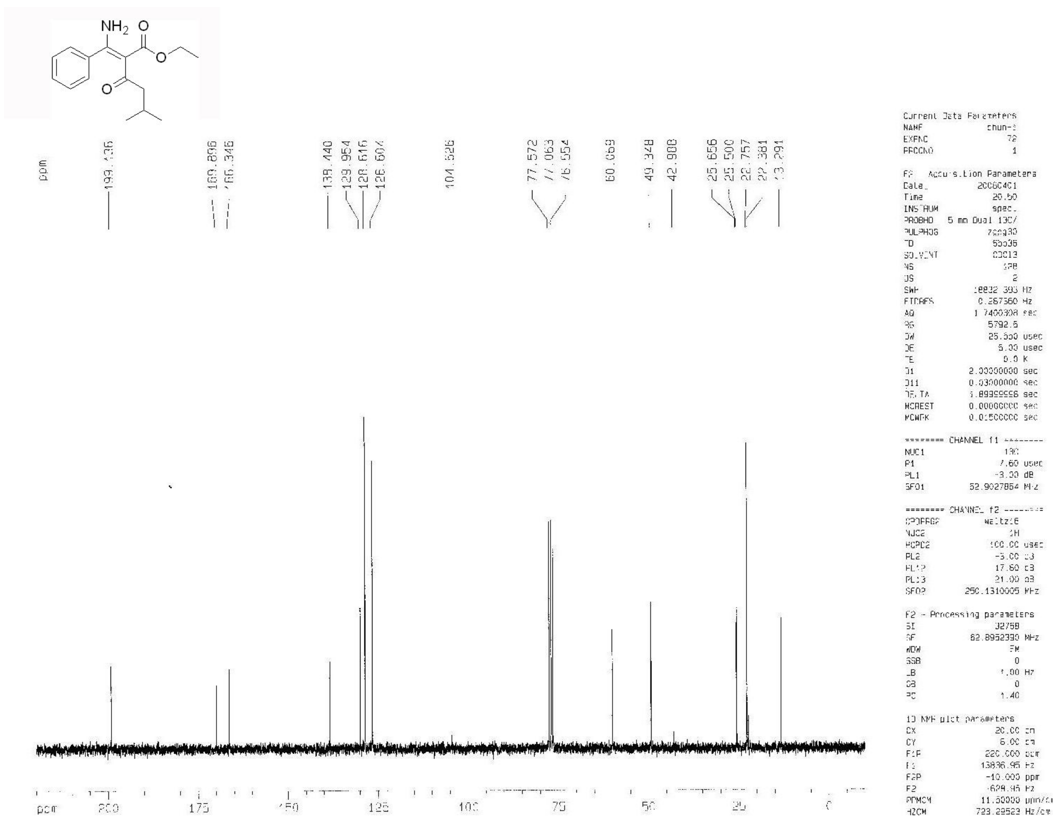
^{1}H and ^{13}C NMR spectra of **1b**



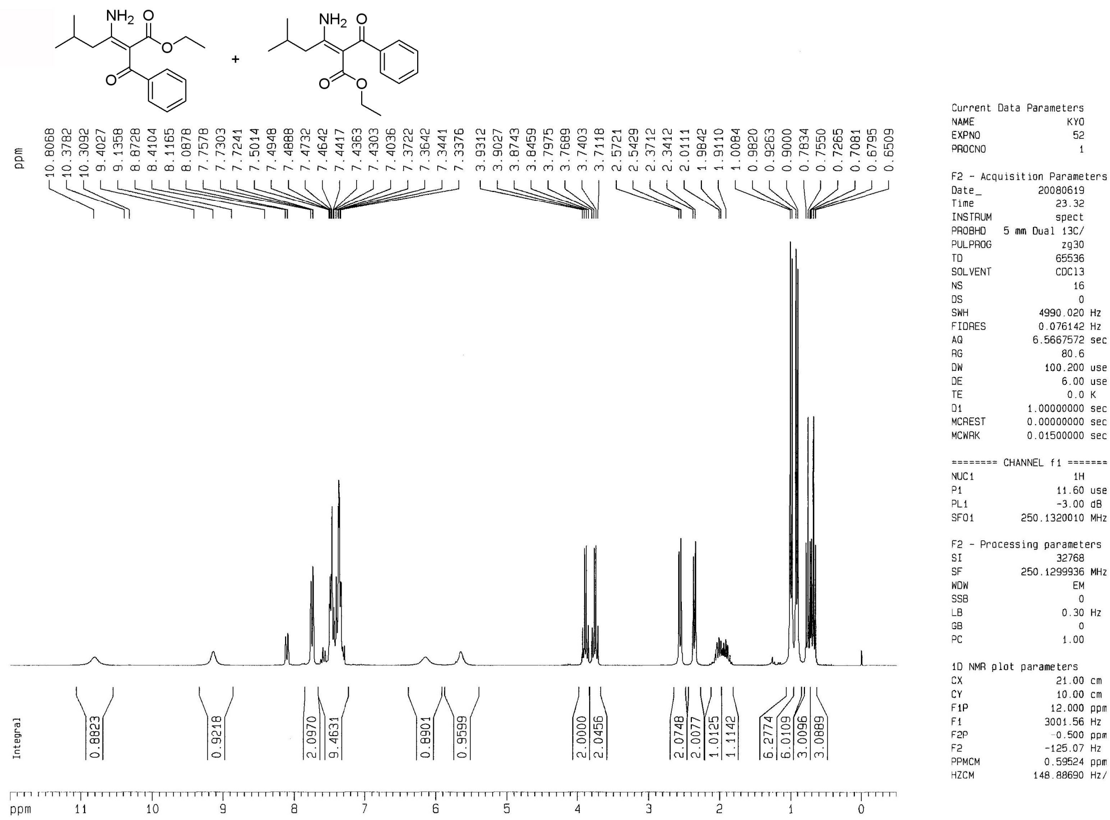


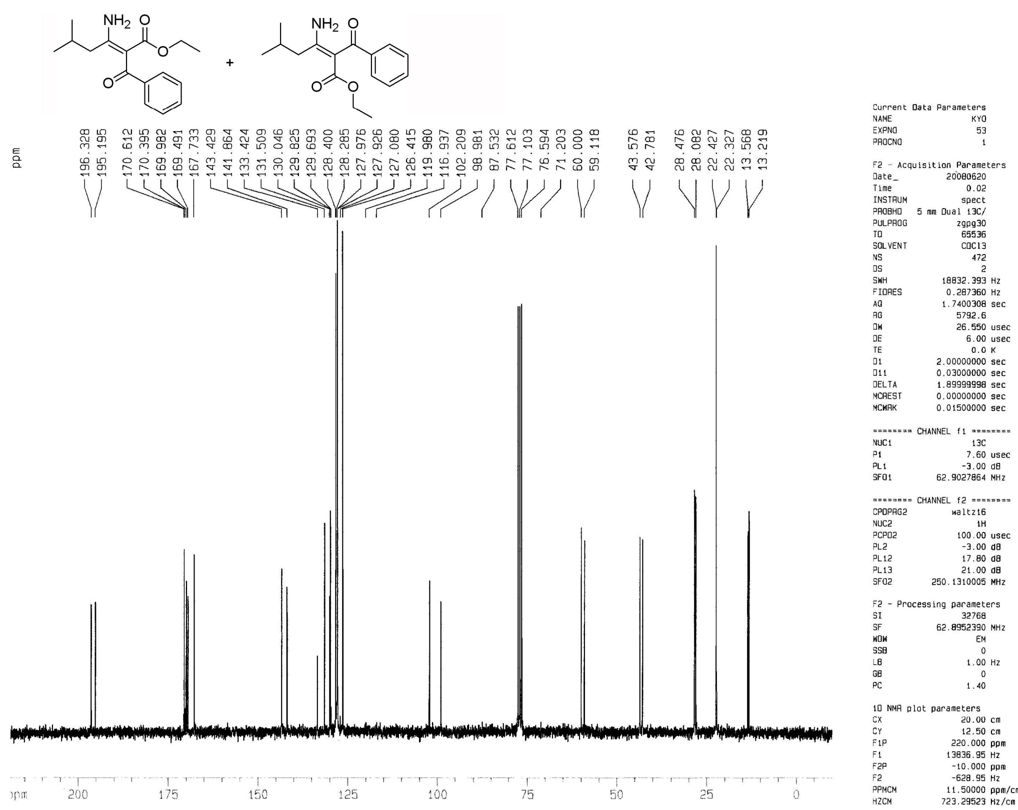
^{1}H and ^{13}C NMR spectra of **1c**



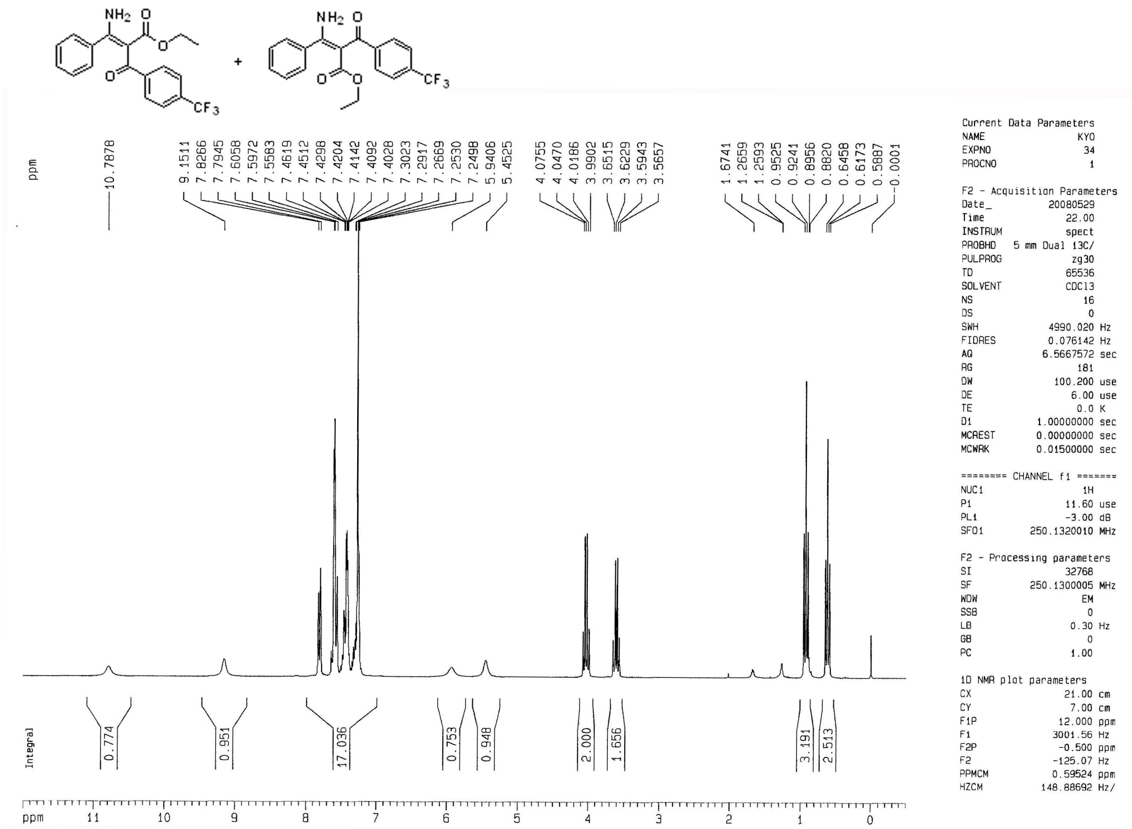


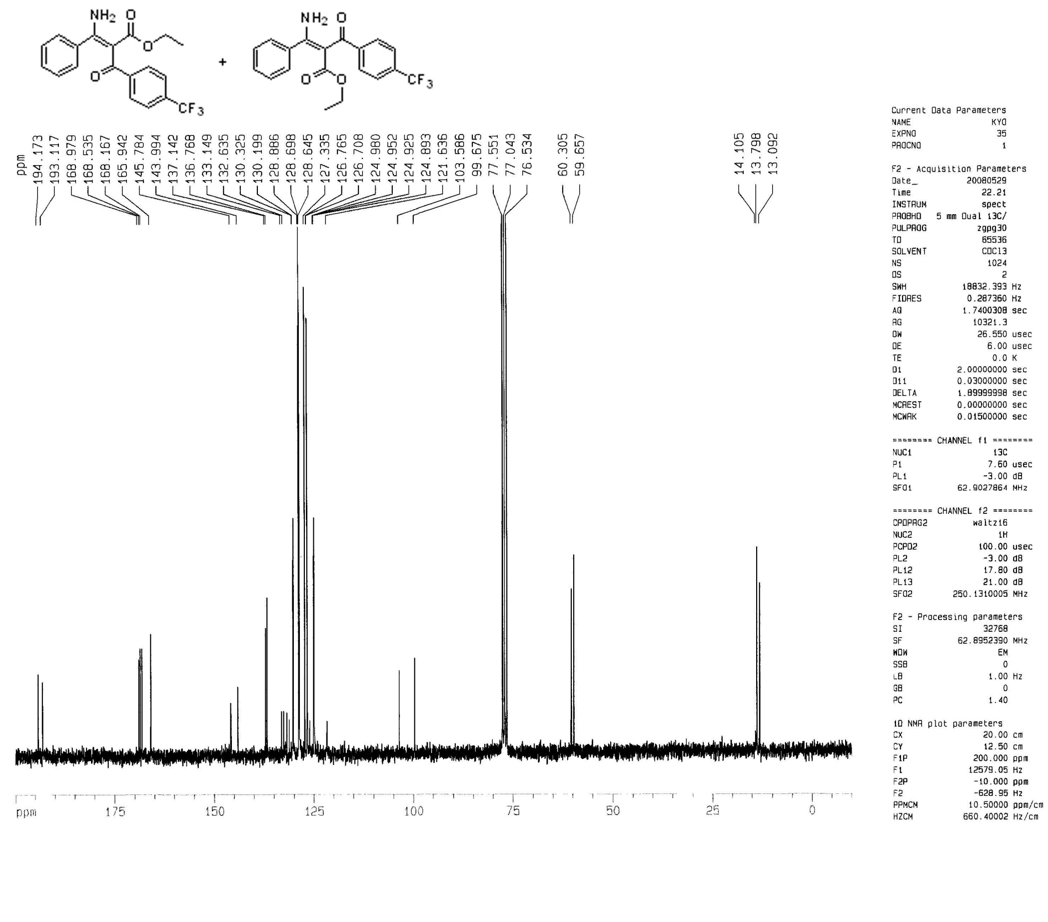
^{1}H and ^{13}C NMR spectra of **1d**



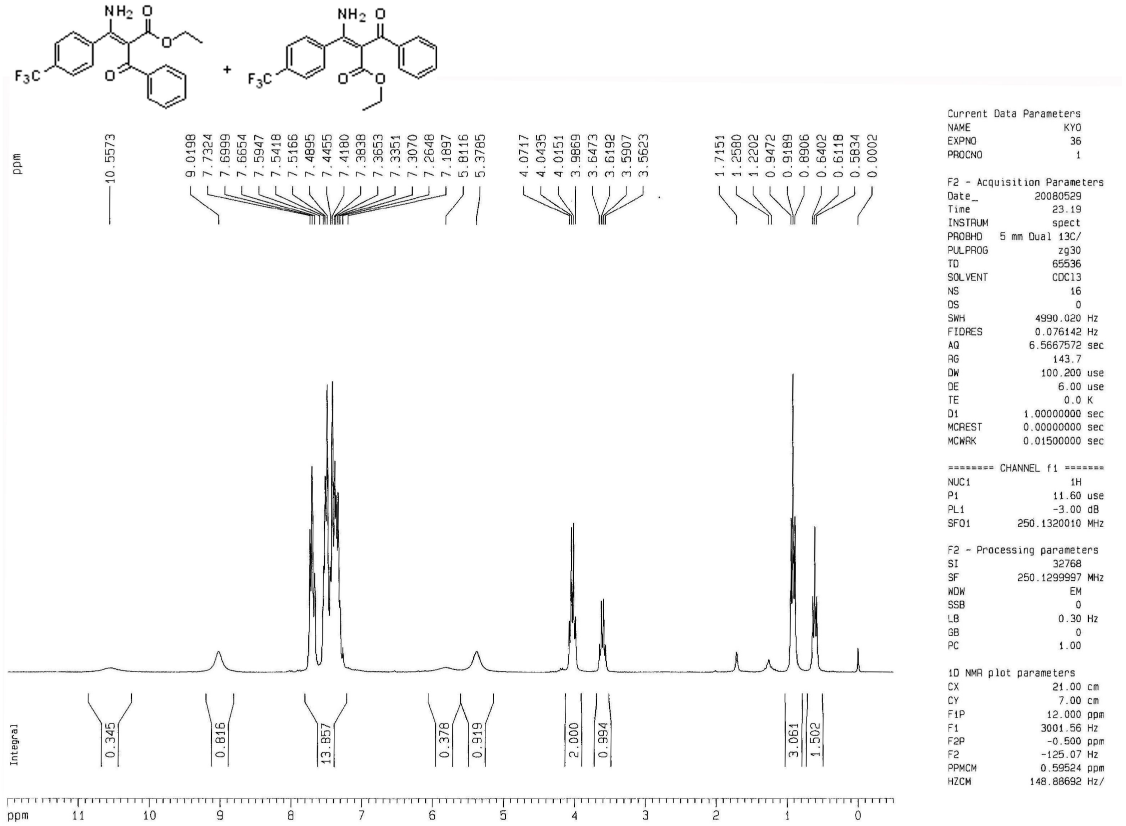


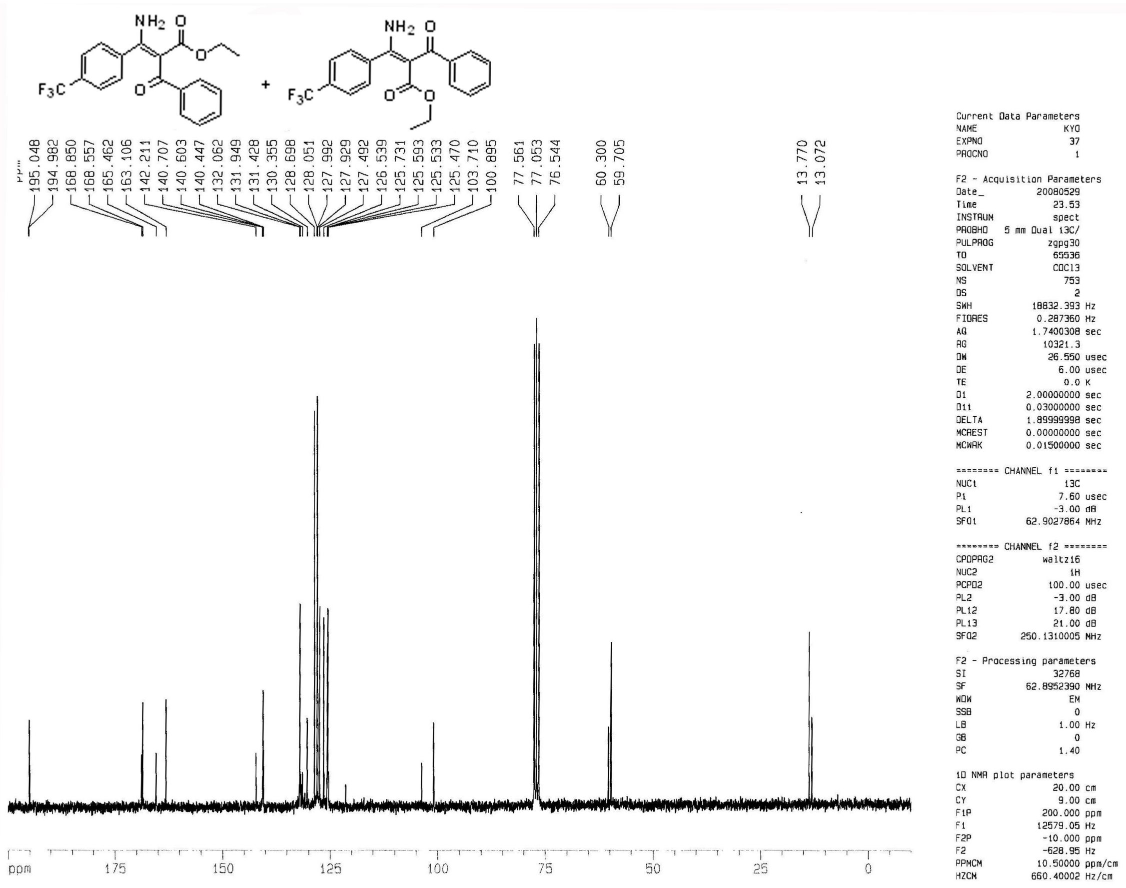
^{1}H and ^{13}C NMR spectra of **1e**



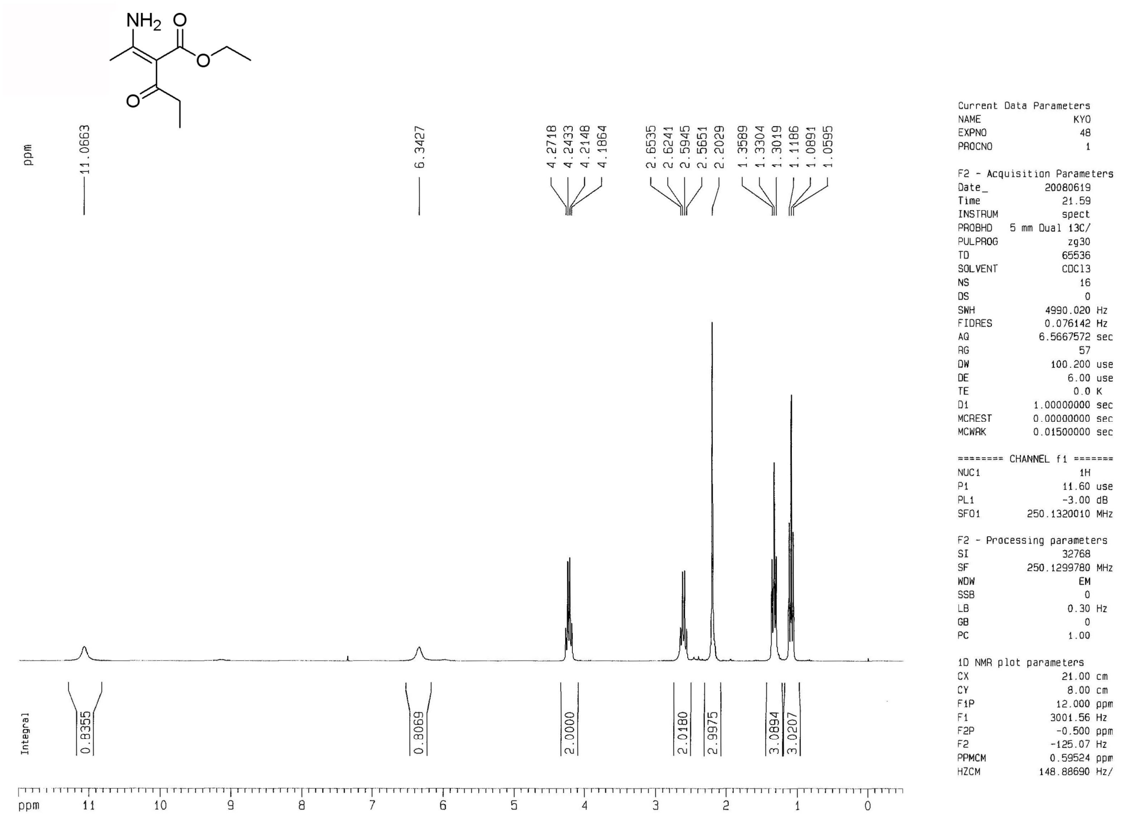


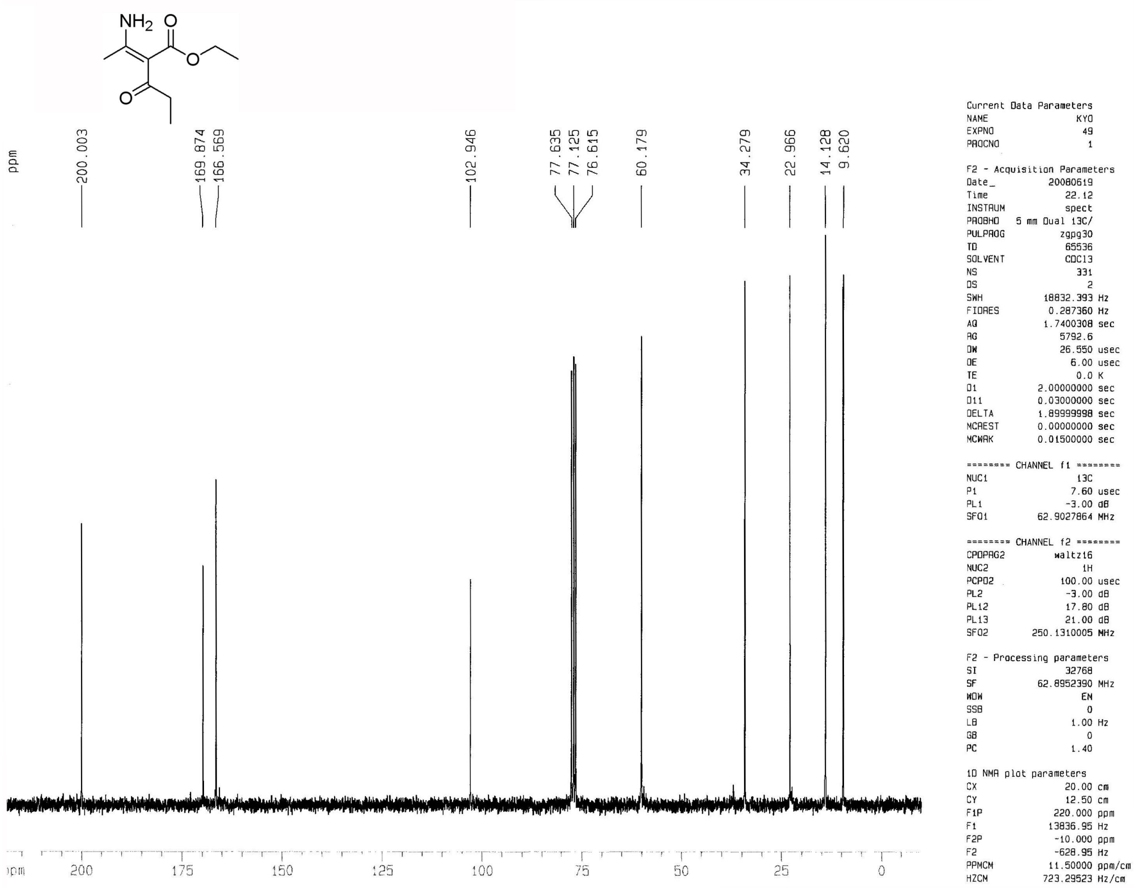
^{1}H and ^{13}C NMR spectra of **1f**



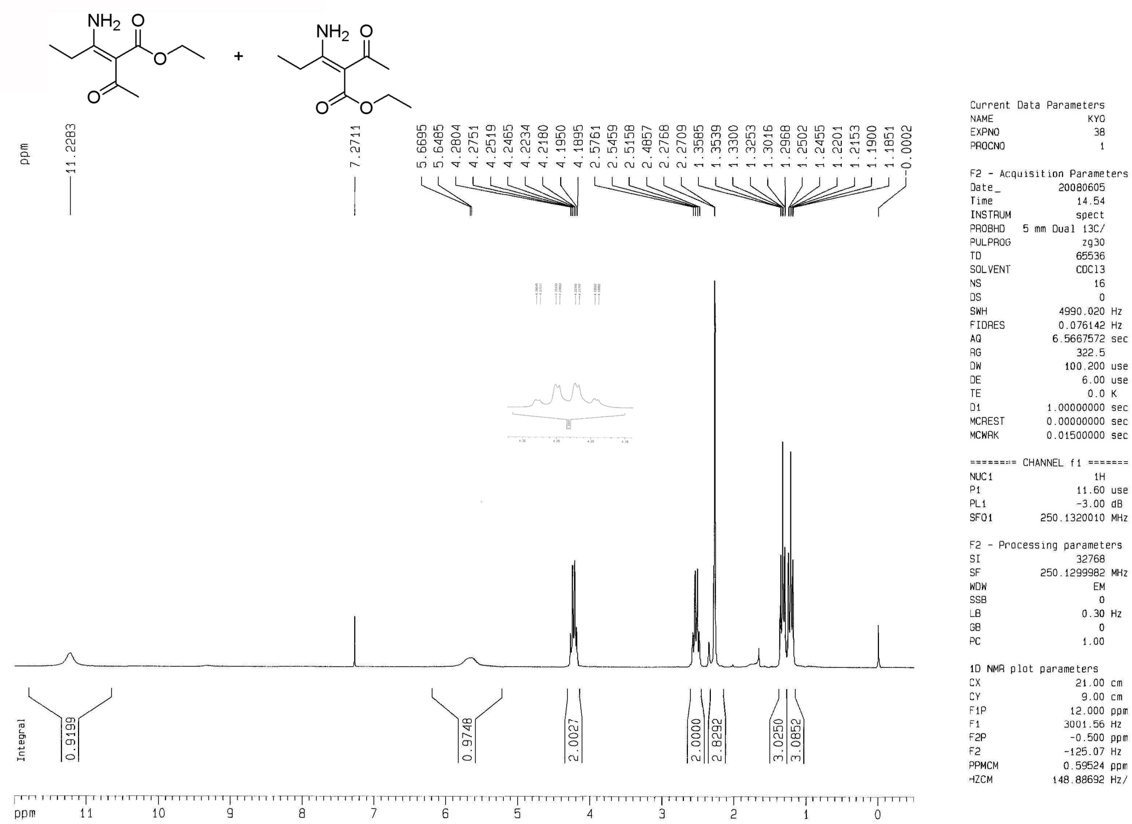


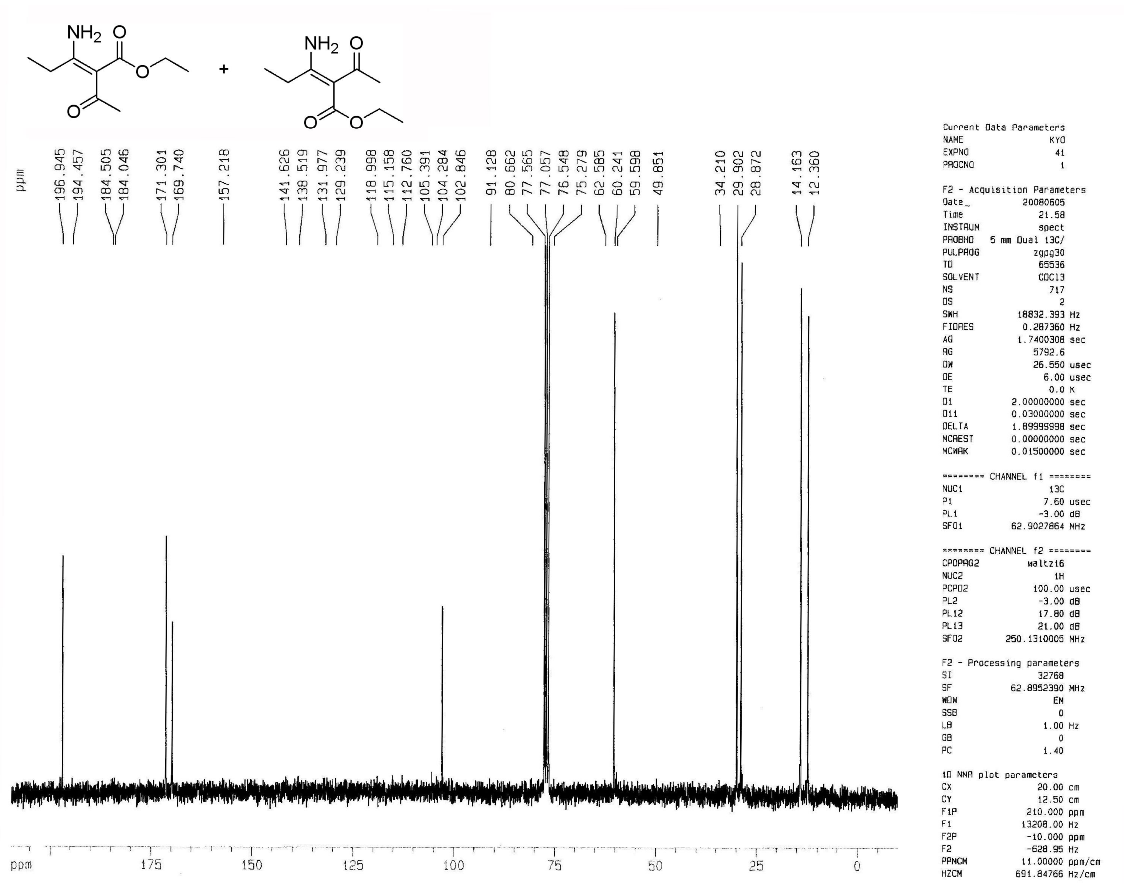
^{1}H and ^{13}C NMR spectra of **1g**



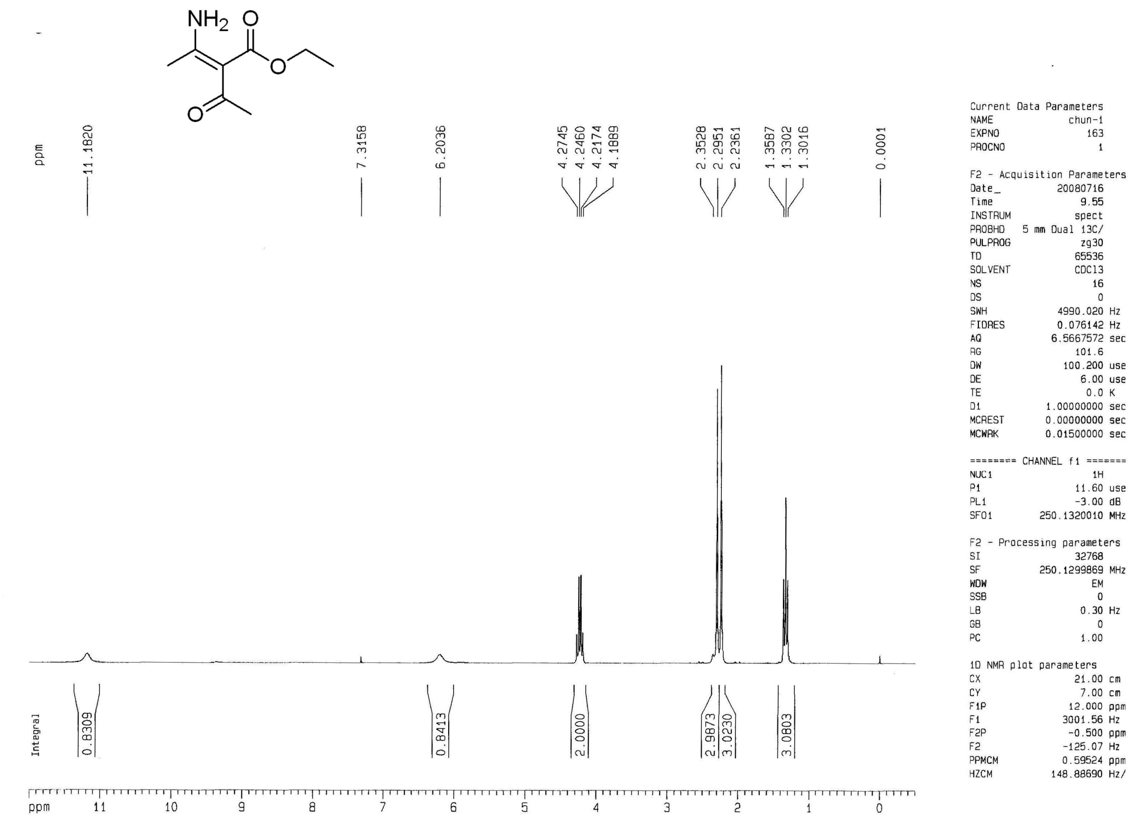


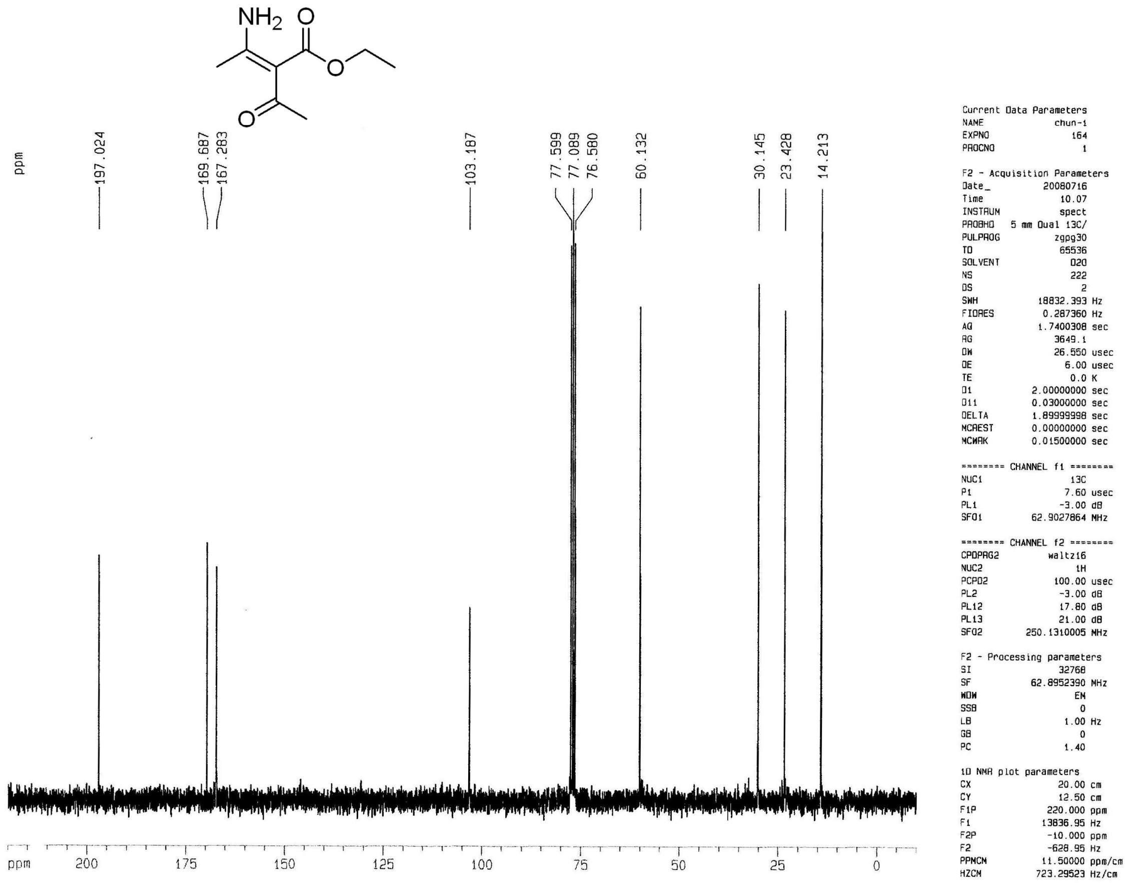
^{1}H and ^{13}C NMR spectra of **1h**



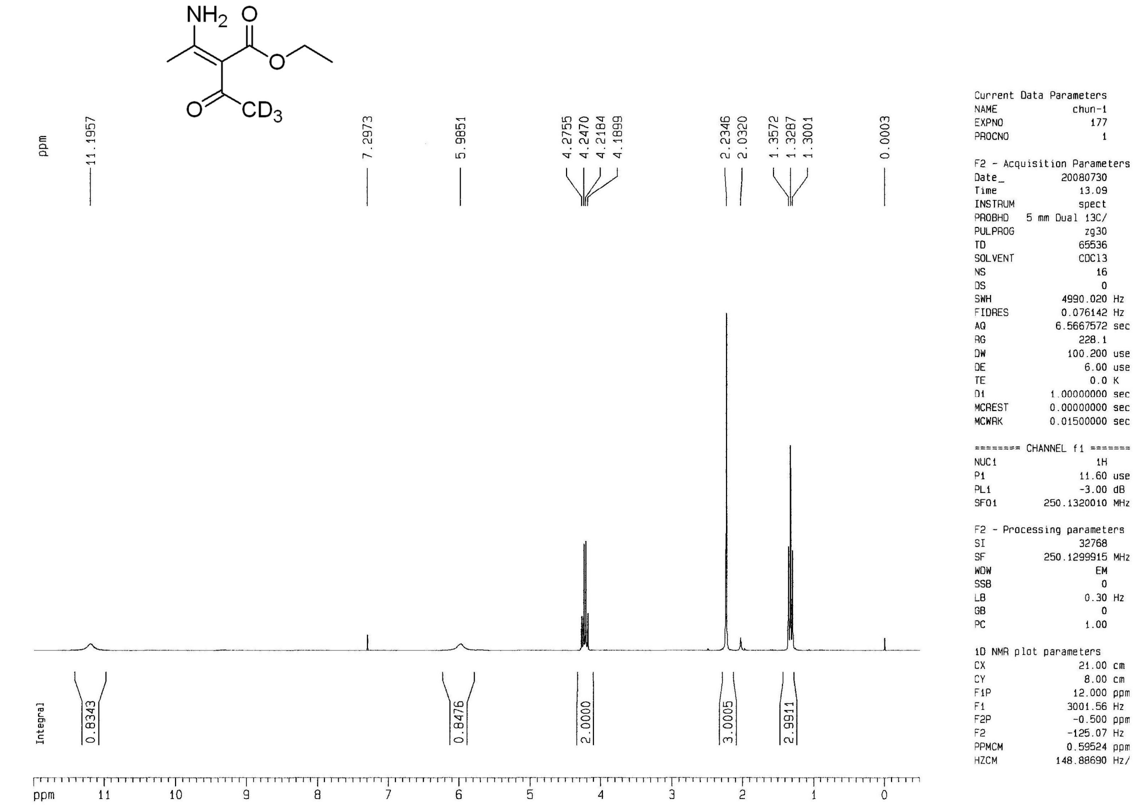


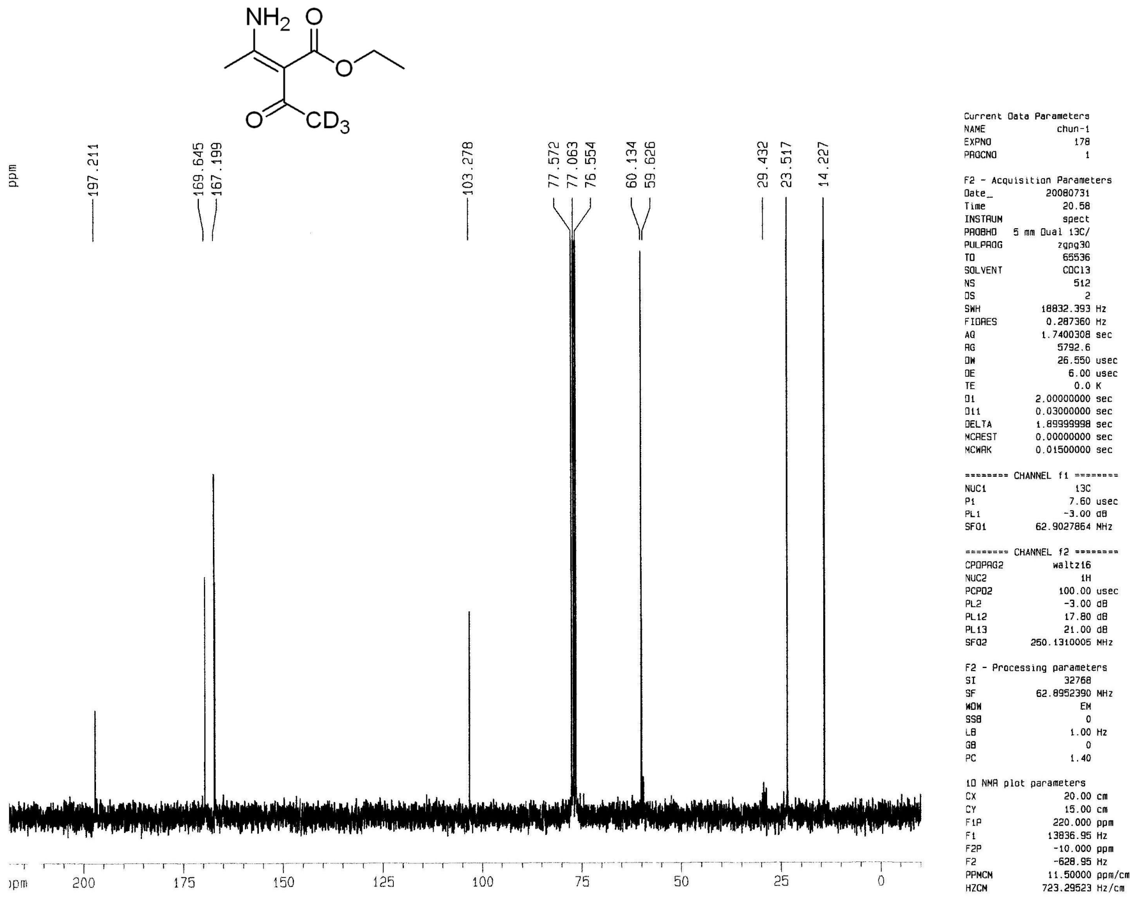
^{1}H and ^{13}C NMR spectra of **1i**



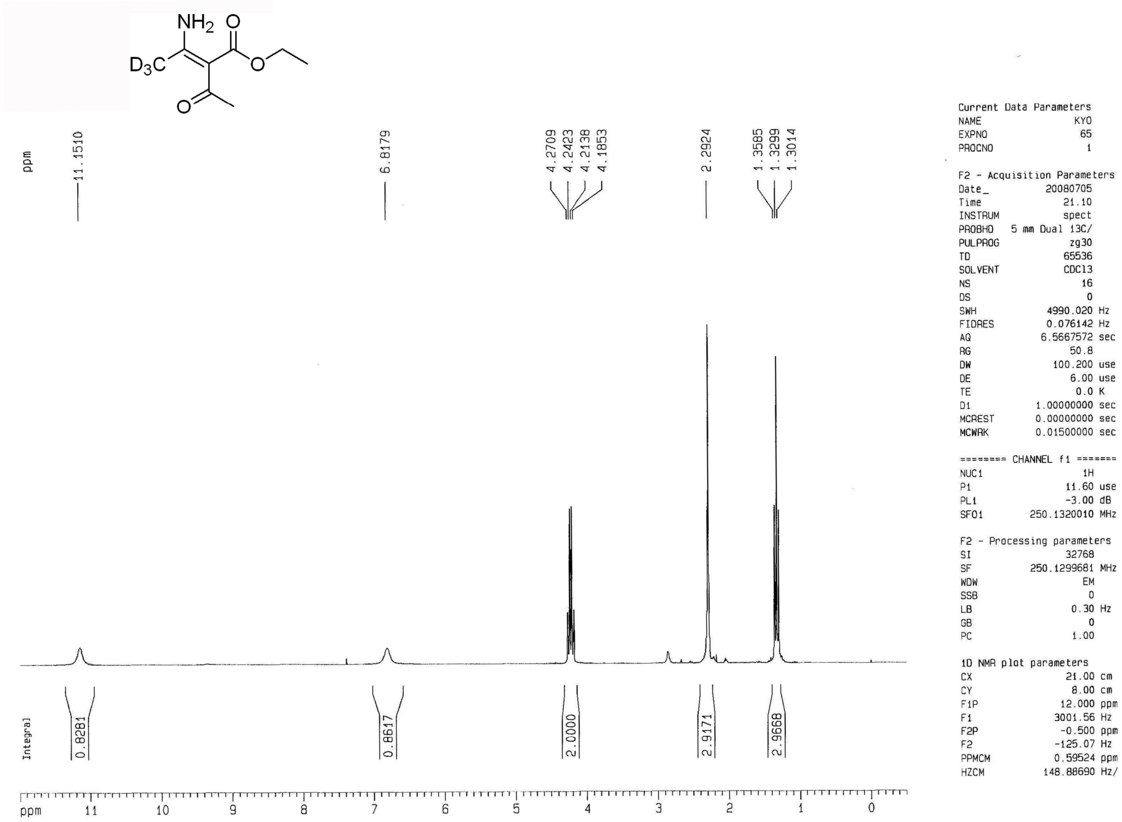


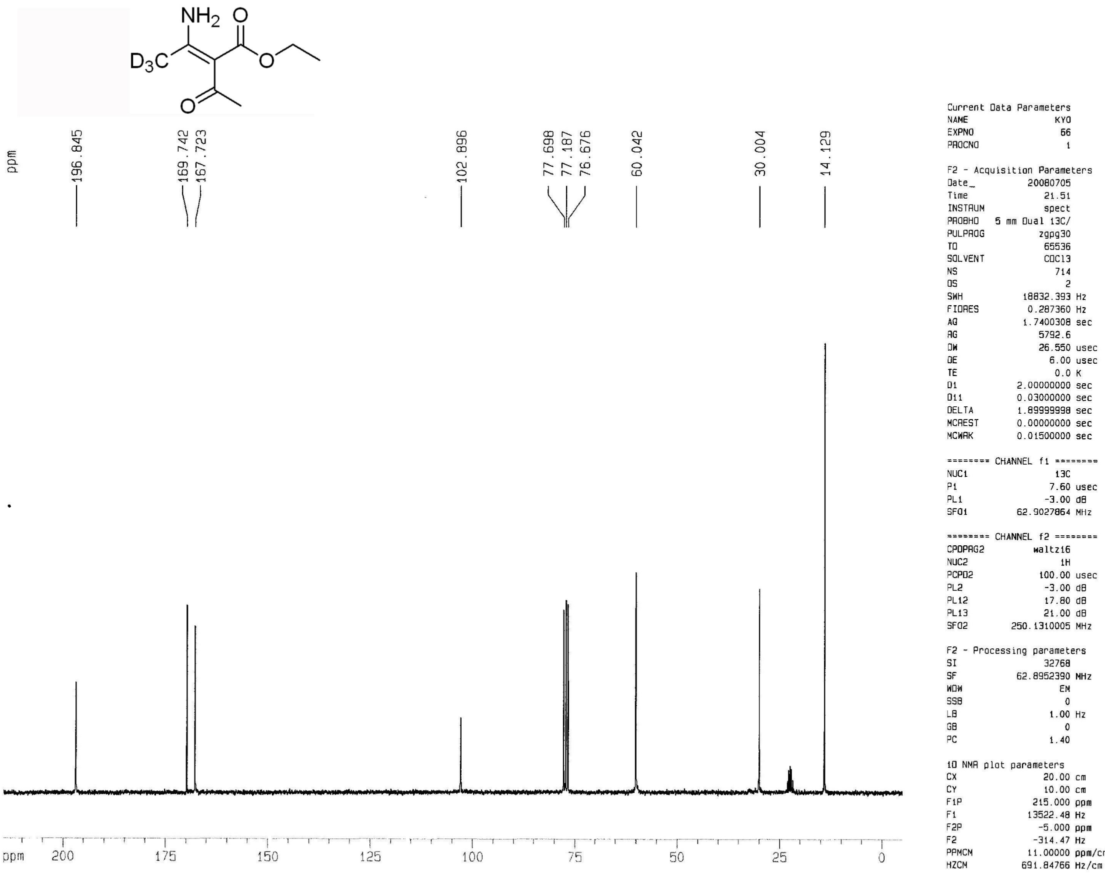
^{1}H and ^{13}C NMR spectra of **1j**



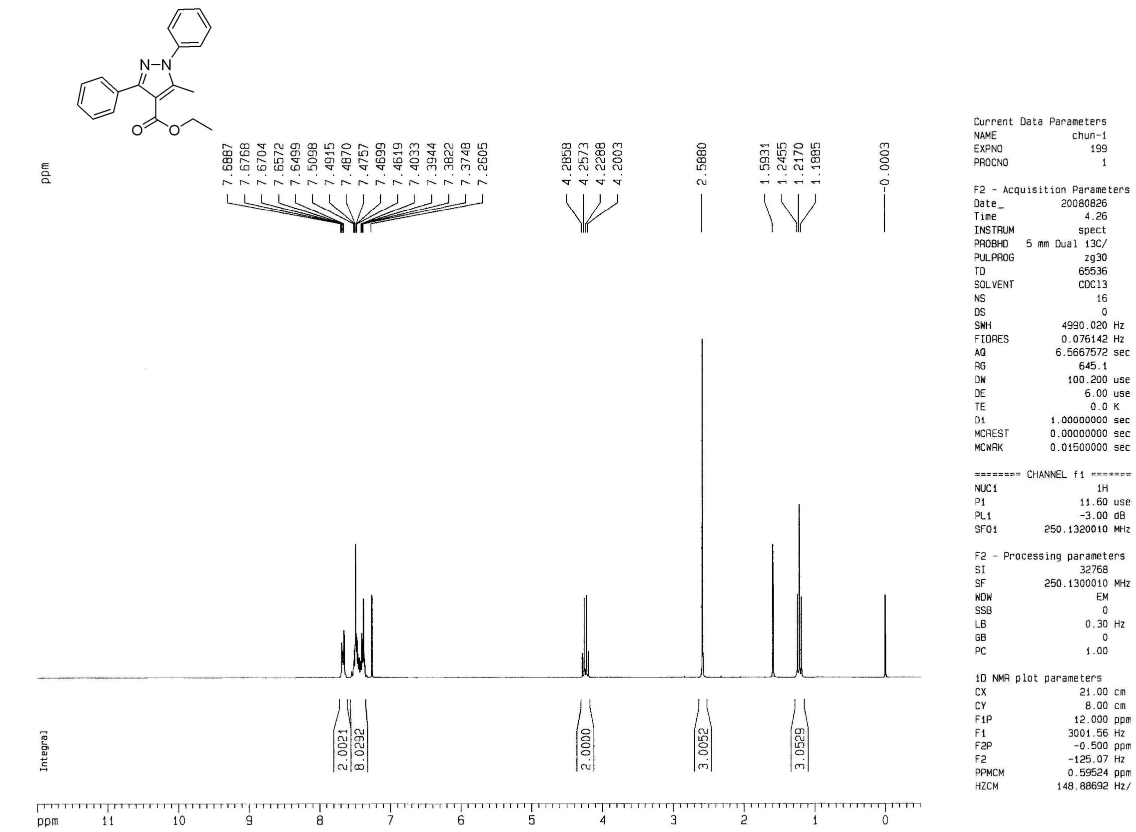


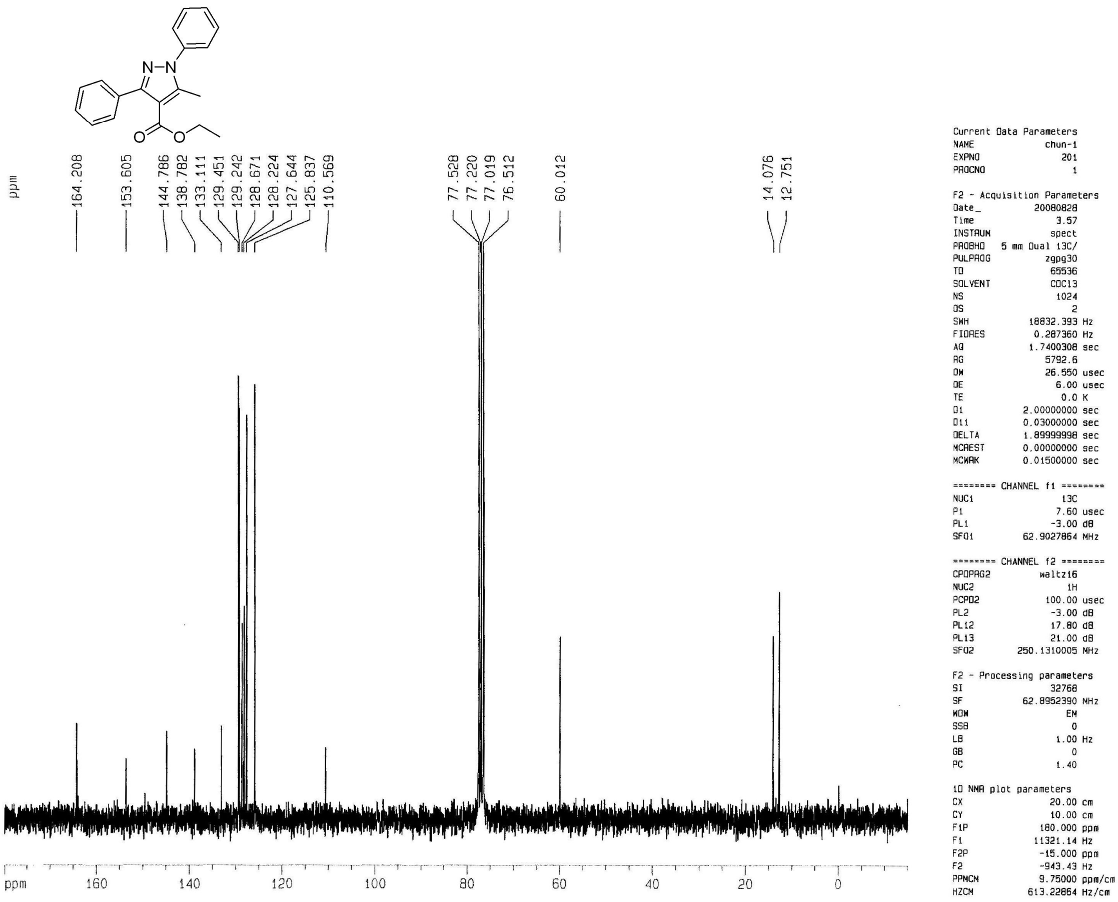
^{1}H and ^{13}C NMR spectra of **1k**



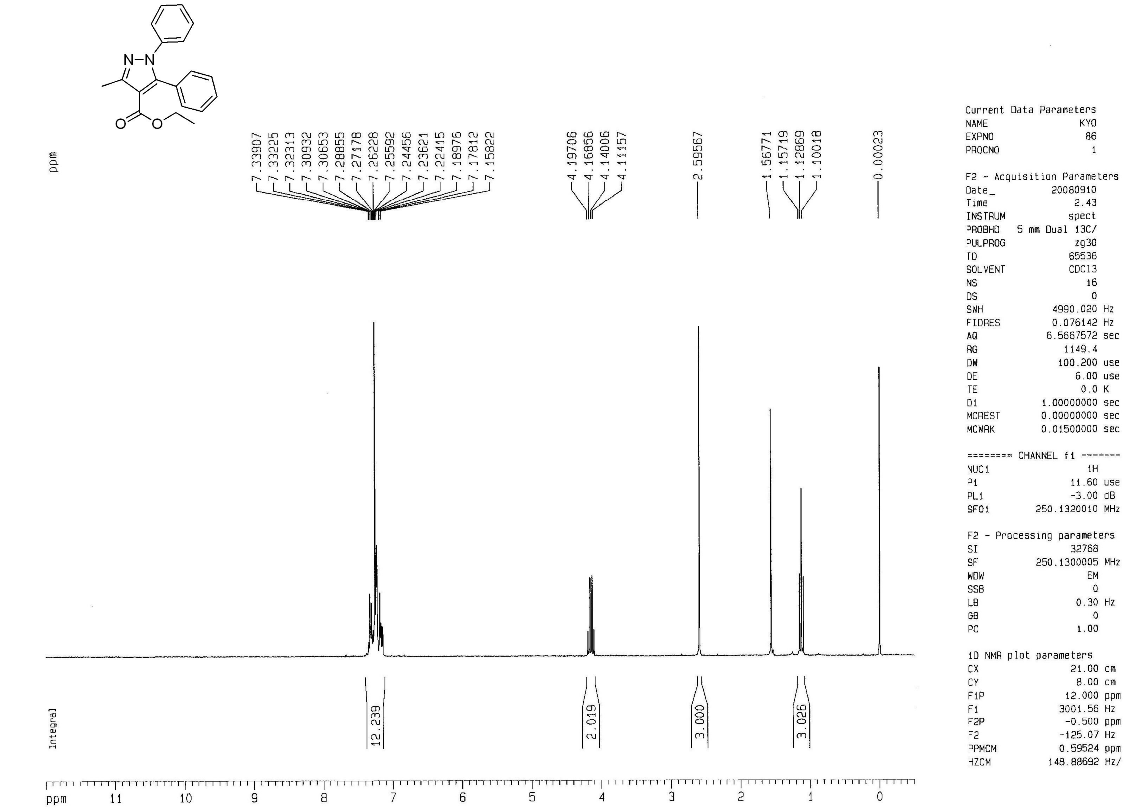


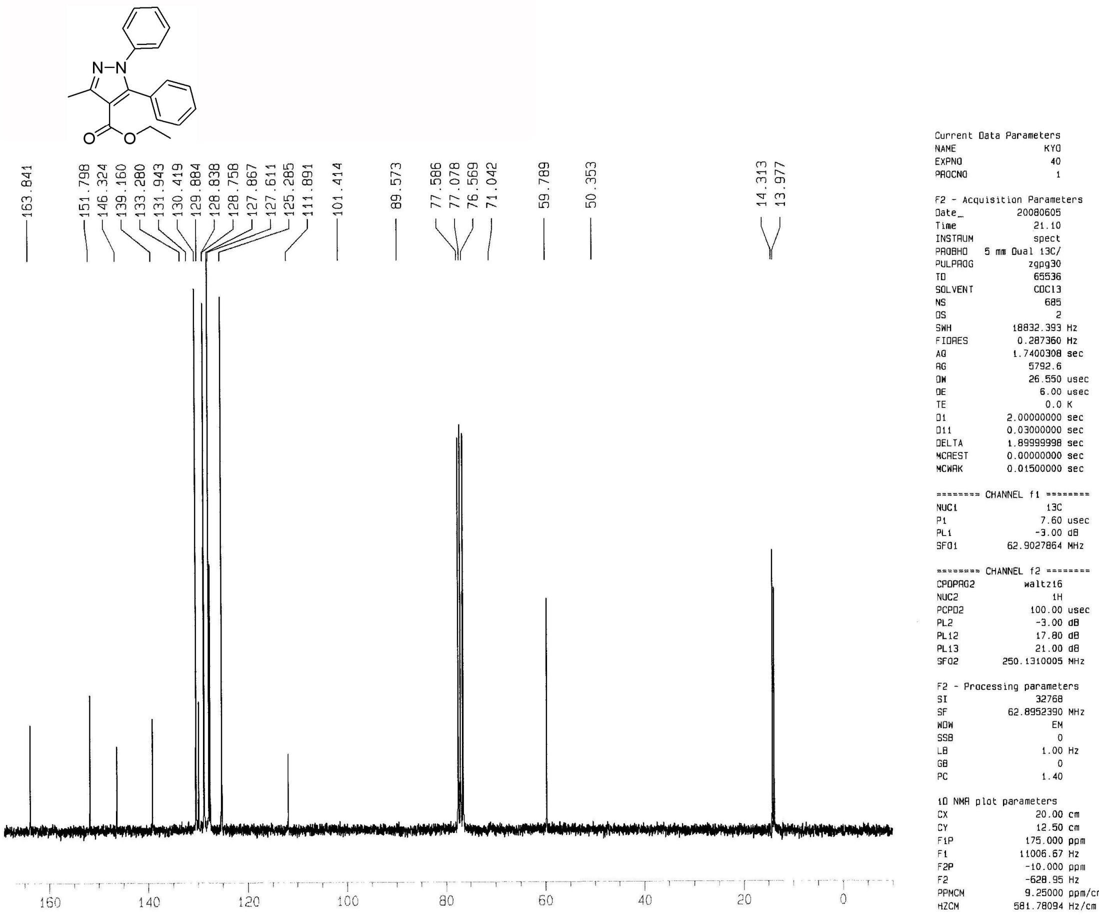
^{1}H and ^{13}C NMR spectra of **2a**



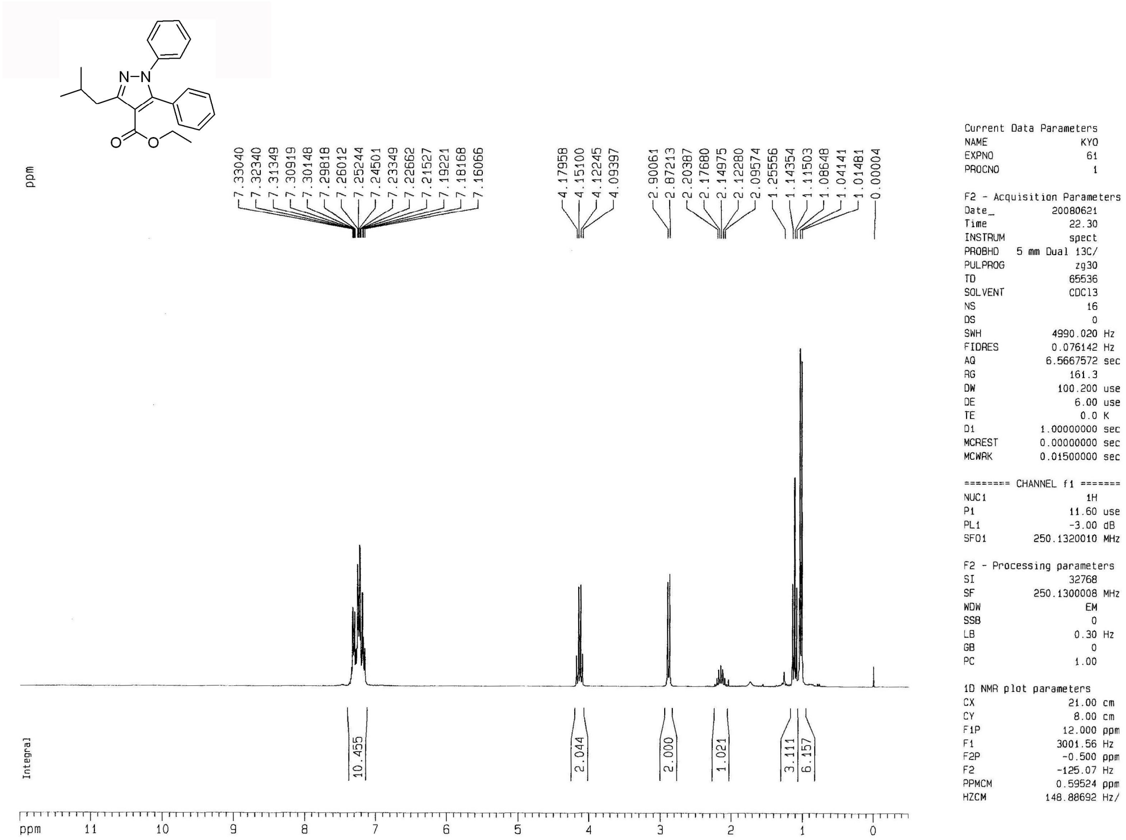


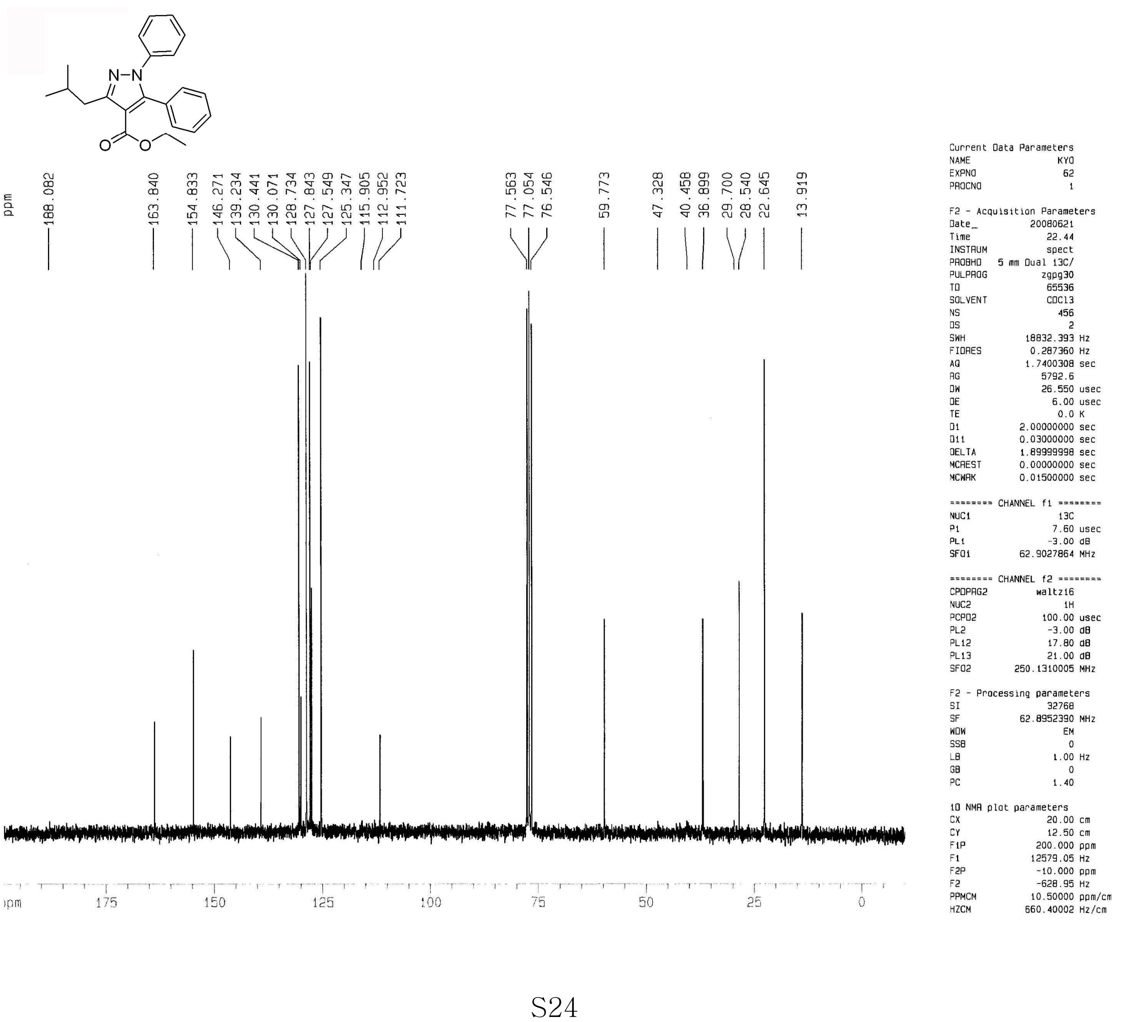
[1]H and [13]C NMR spectra of **2b**



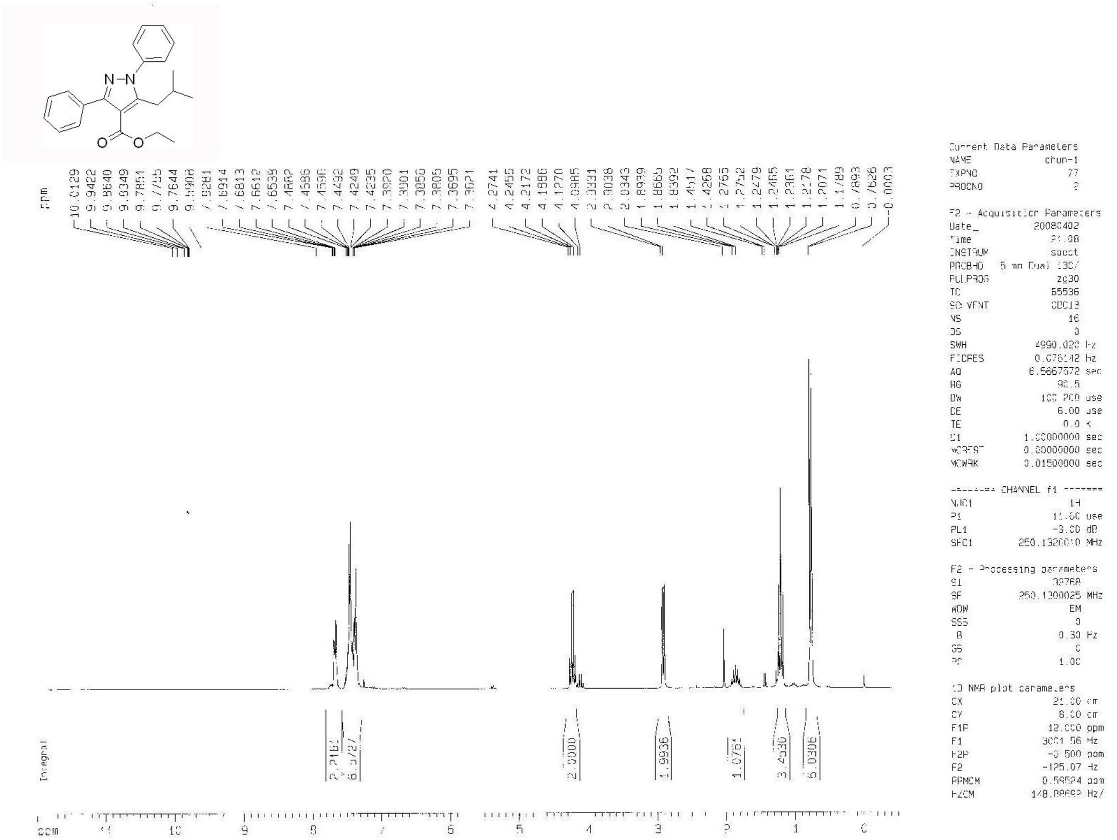


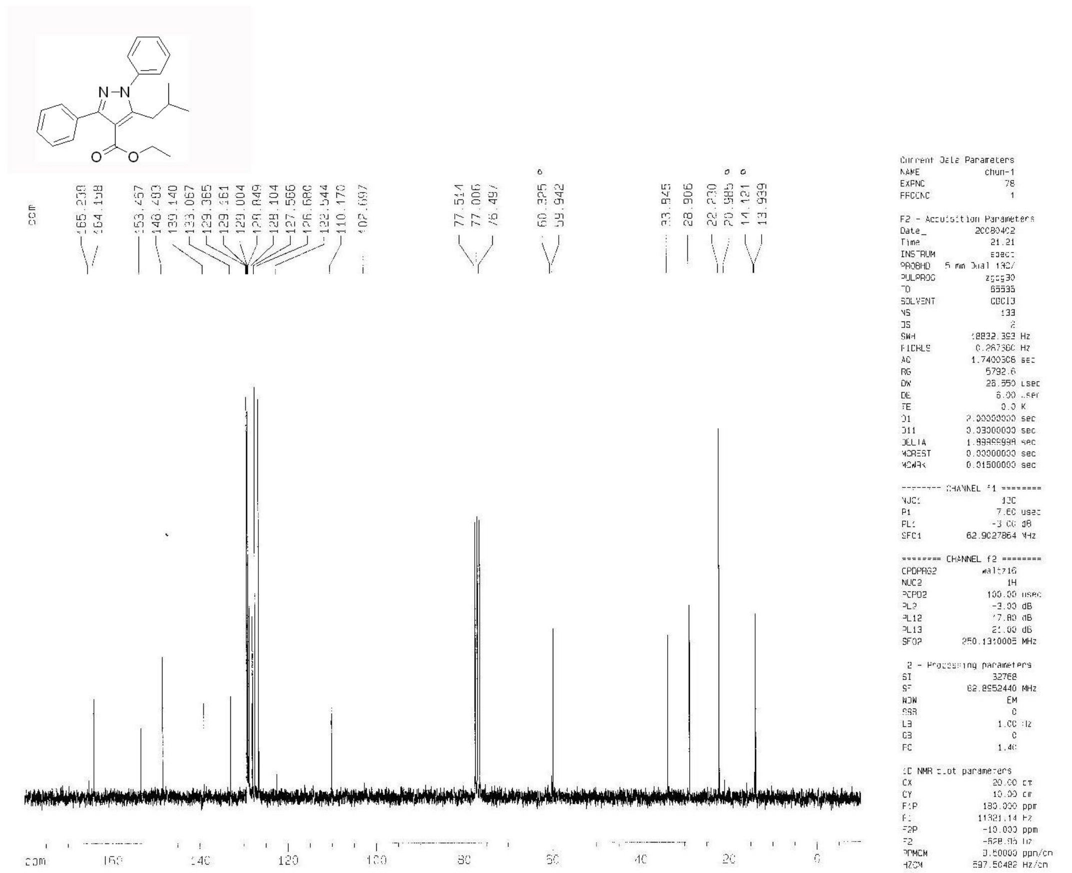
^{1}H and ^{13}C NMR spectra of 2c



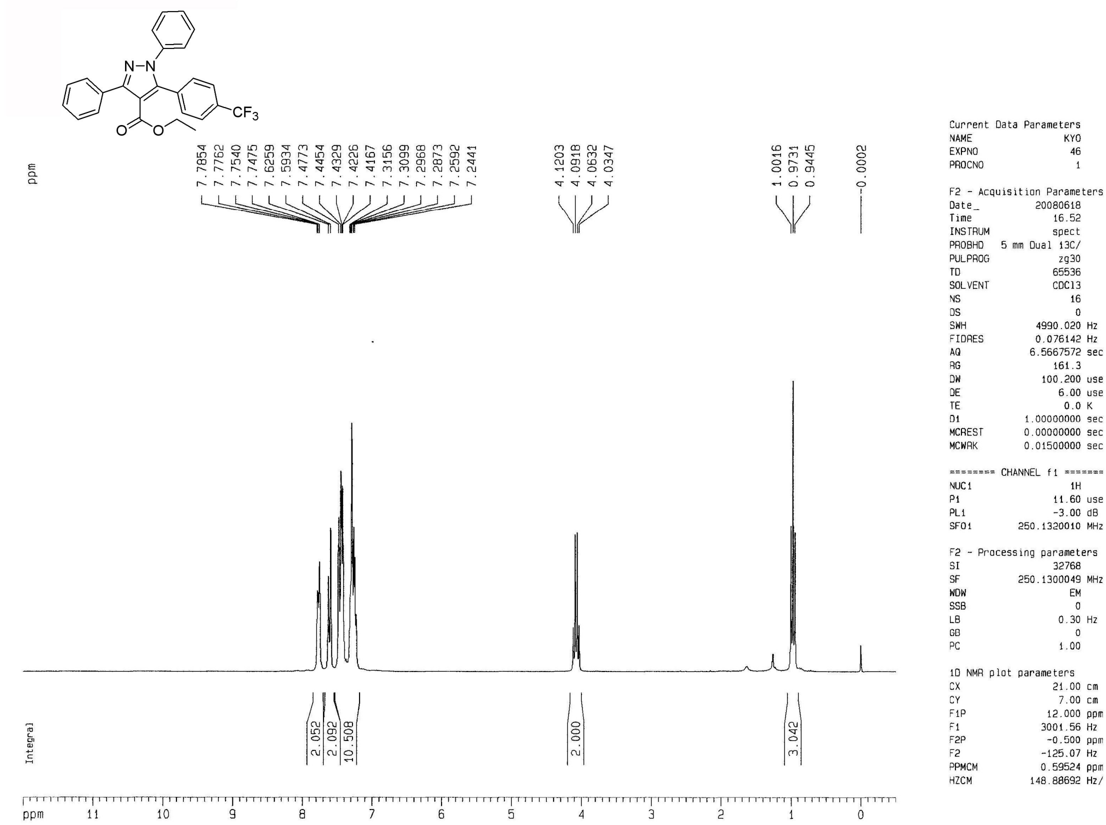


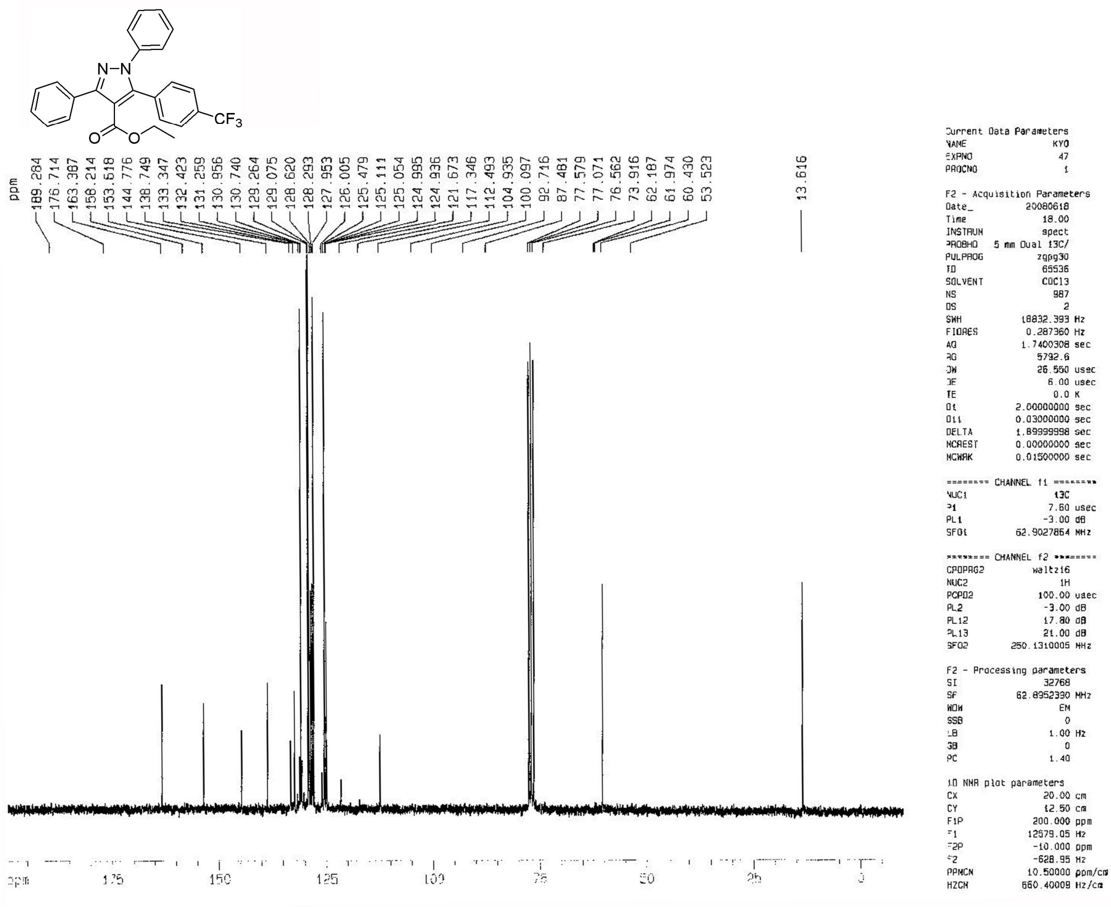
^{1}H and ^{13}C NMR spectra of **2d**



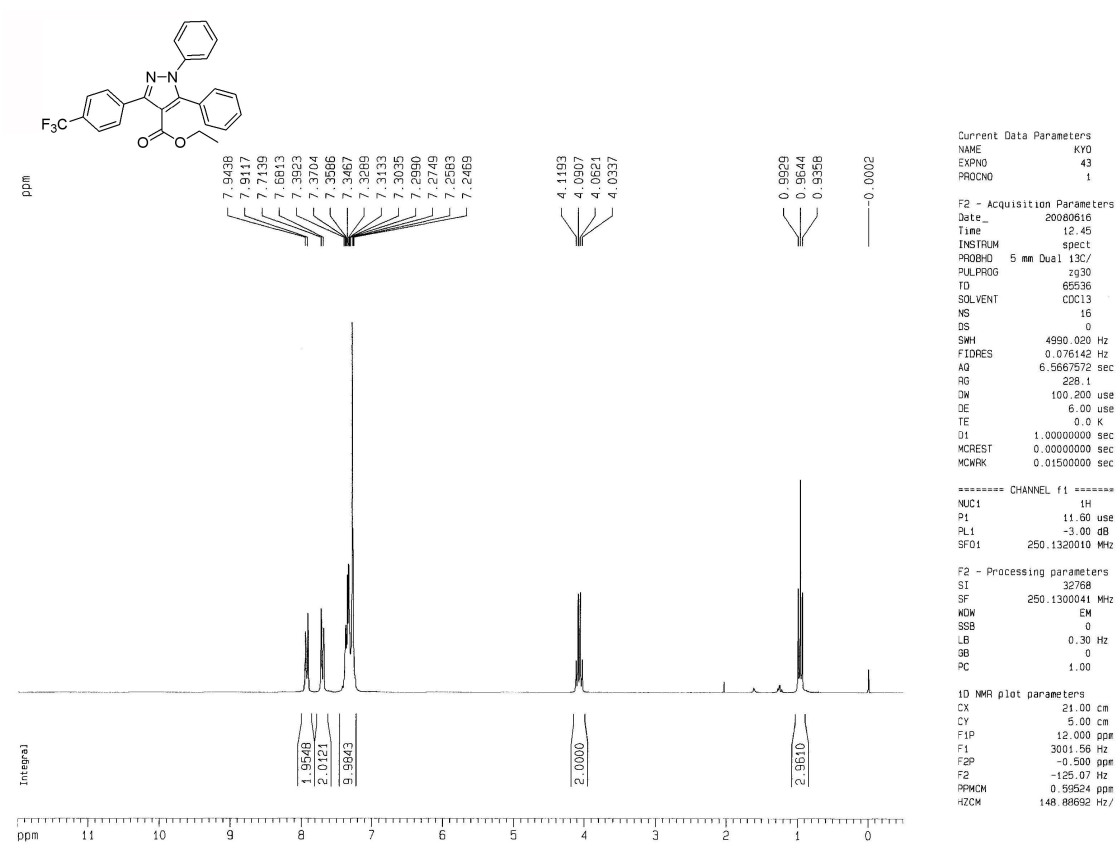


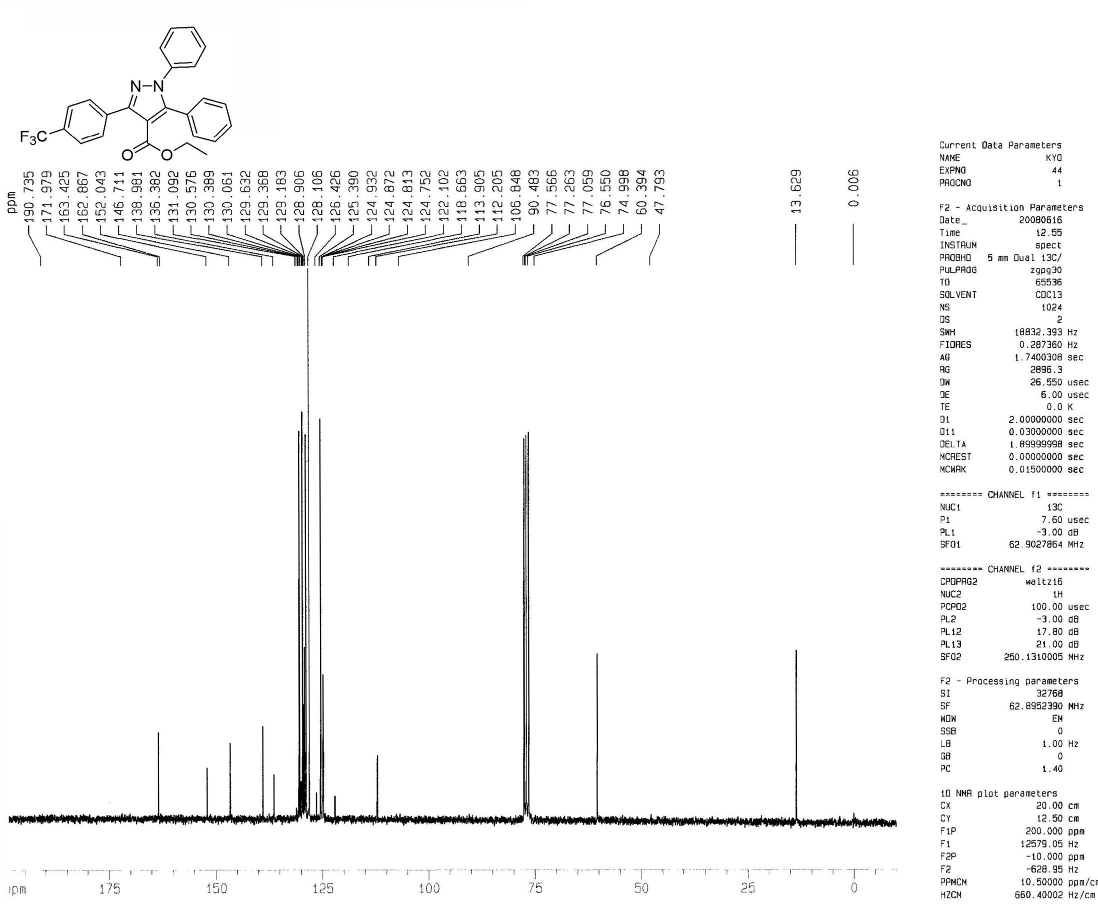
^{1}H and ^{13}C NMR spectra of **2e**



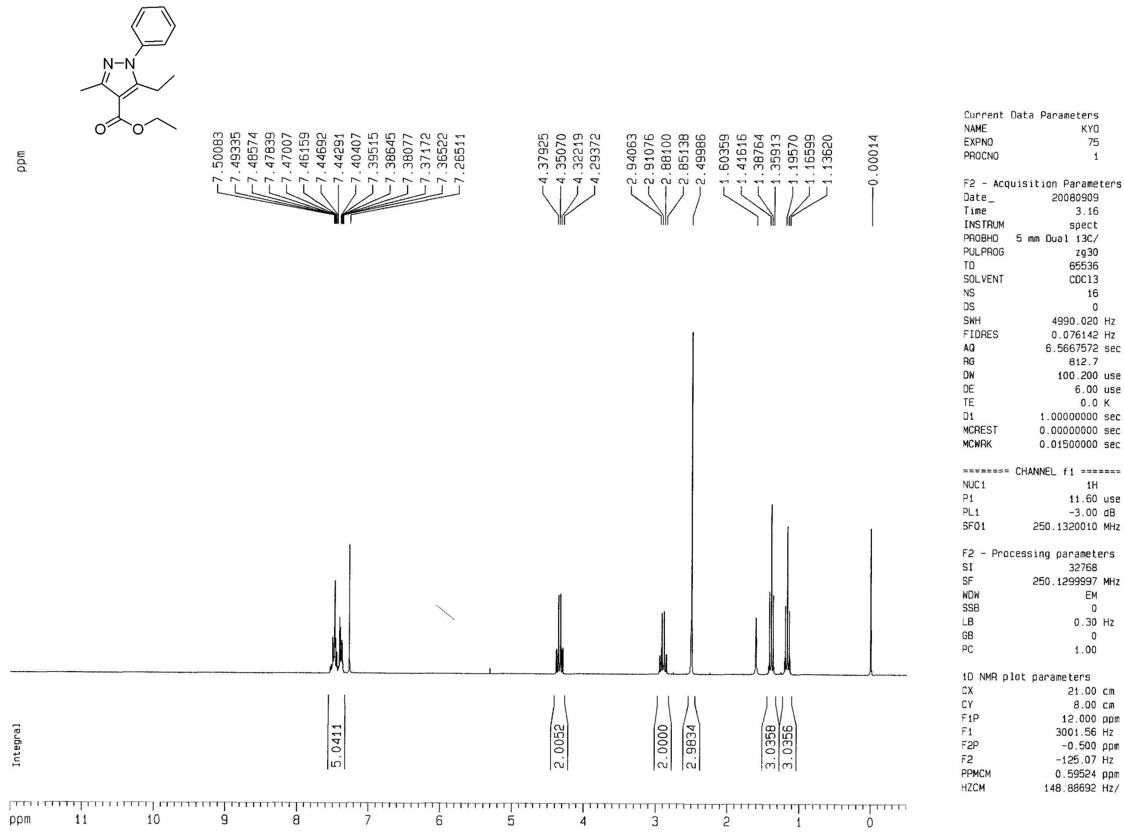


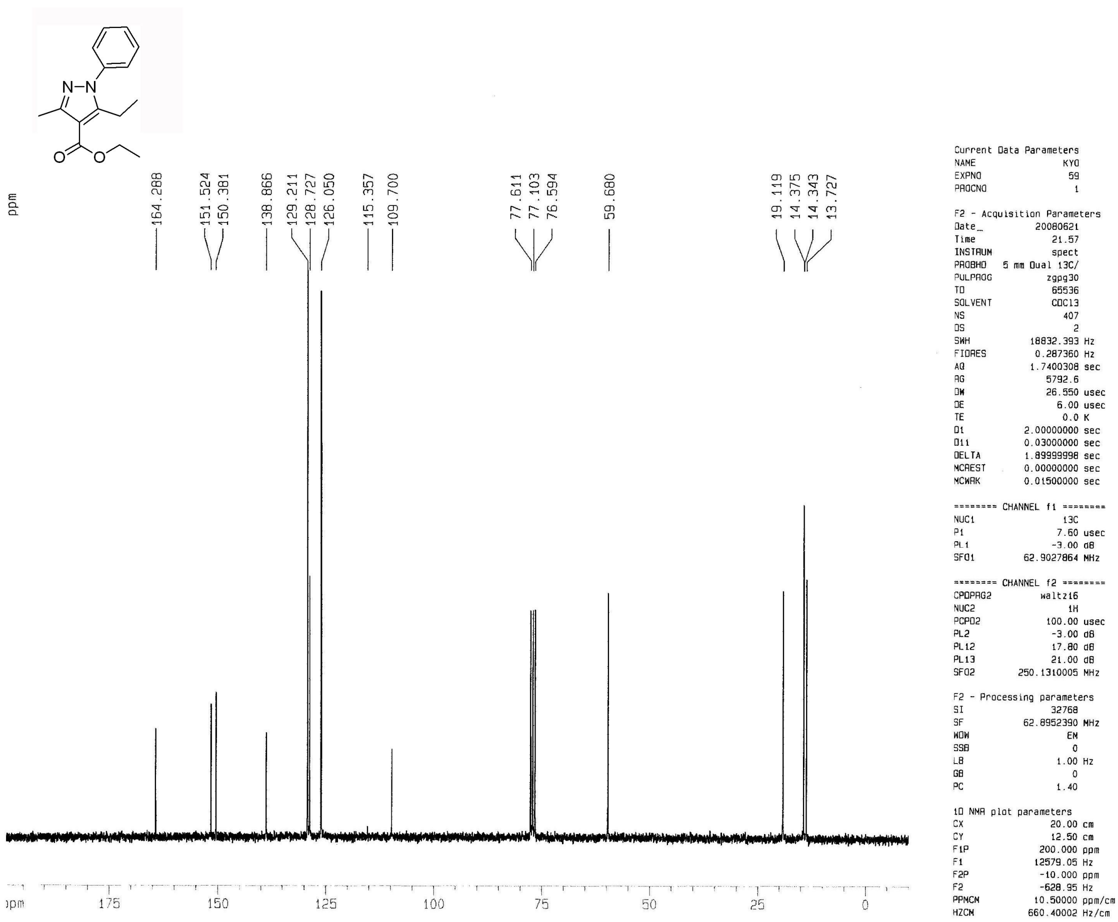
^{1}H and ^{13}C NMR spectra of **2f**



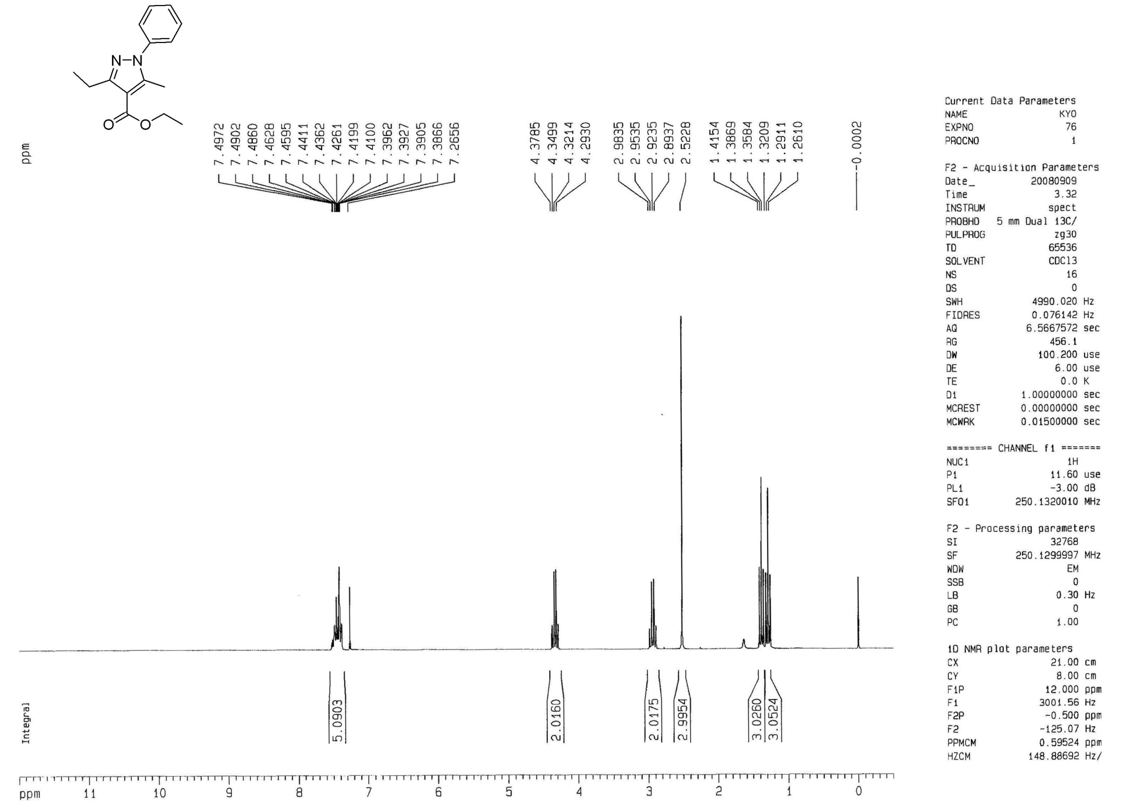


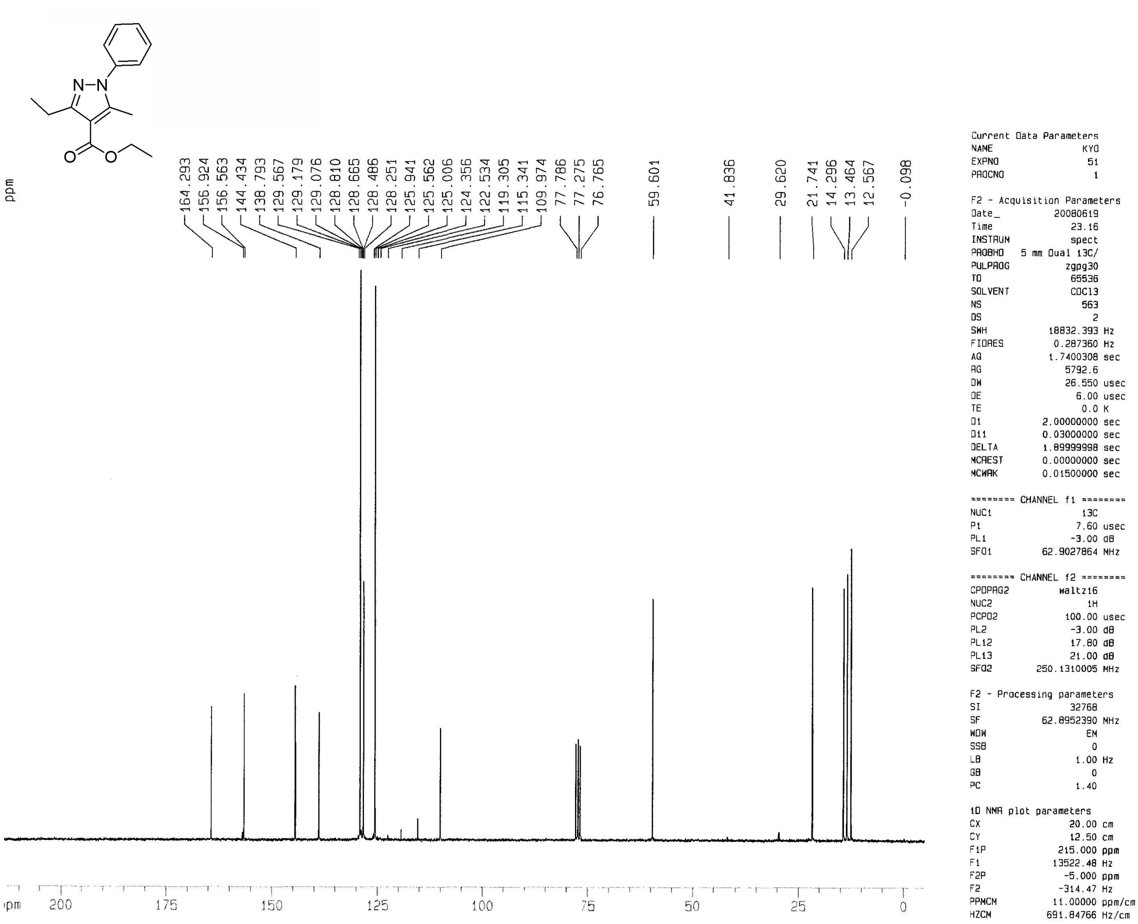
^{1}H and ^{13}C NMR spectra of **2g**



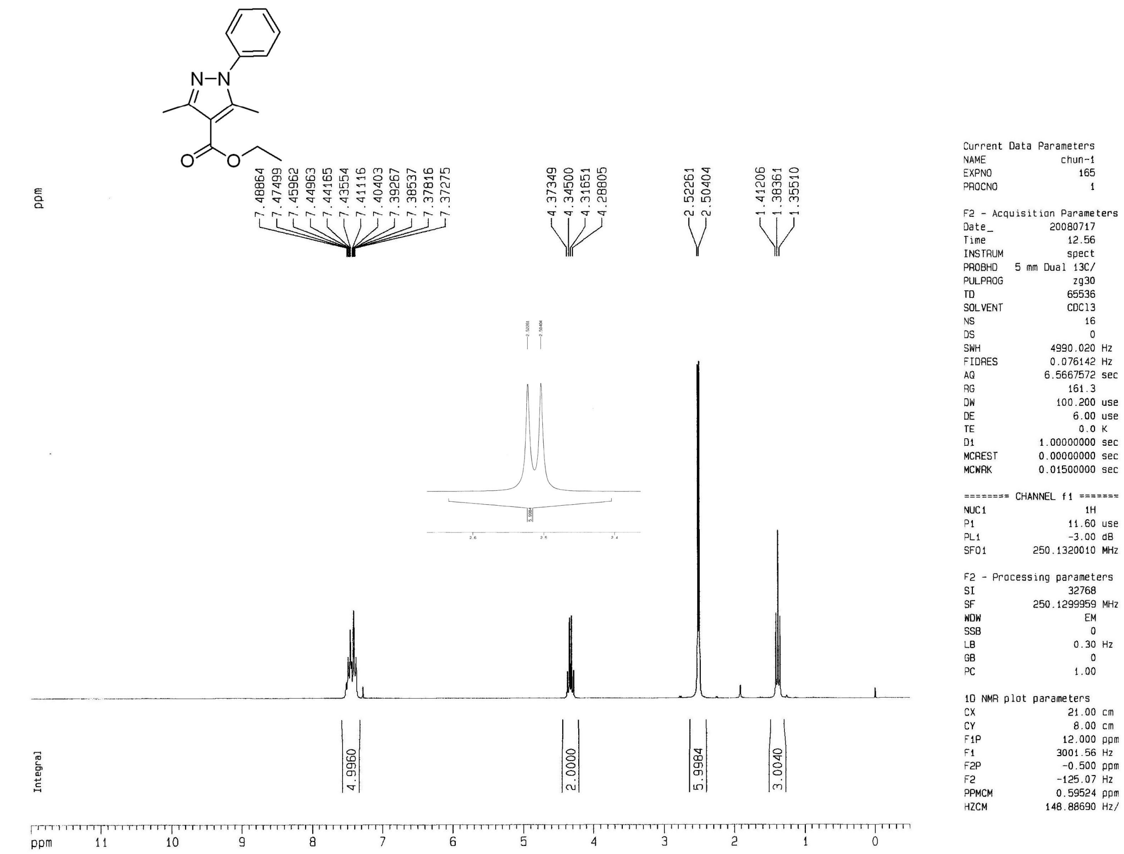


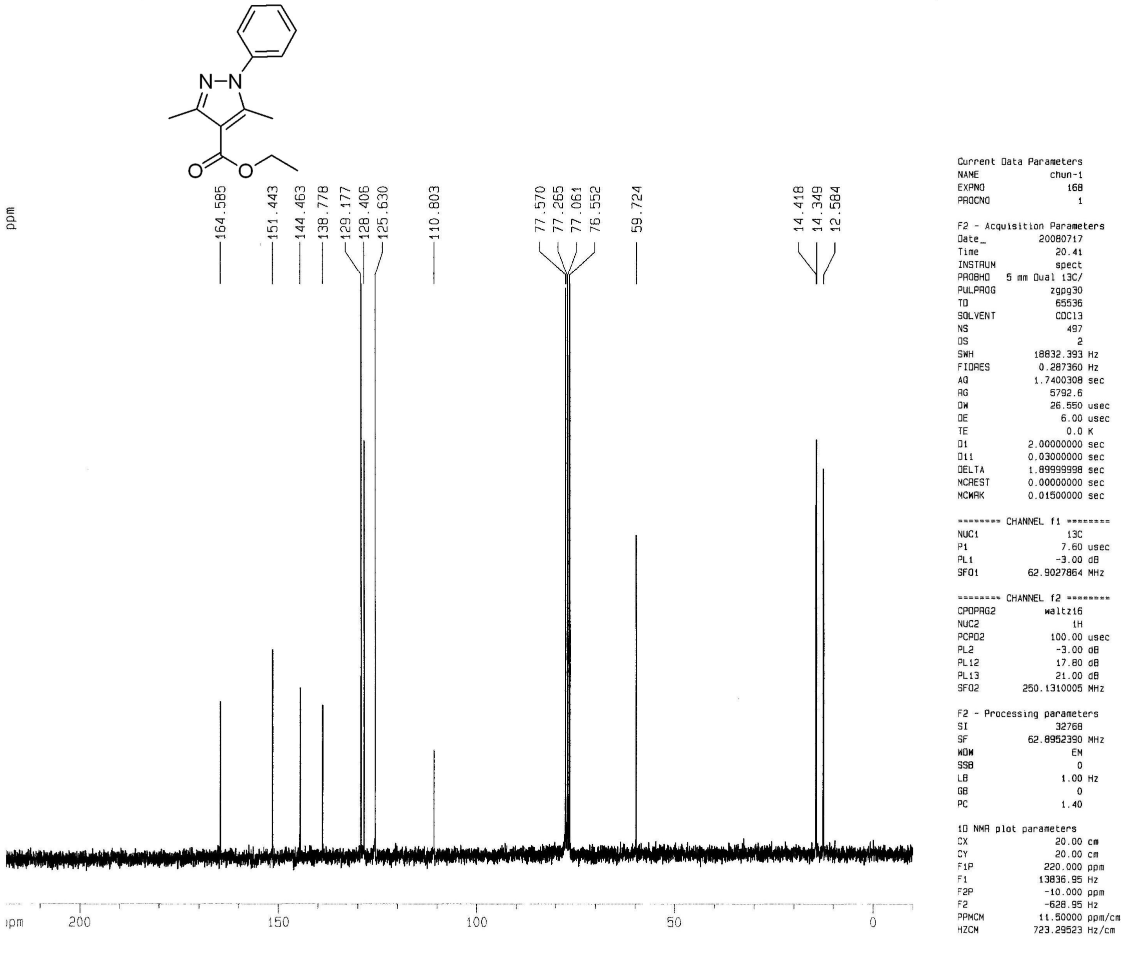
^{1}H and ^{13}C NMR spectra of **2h**



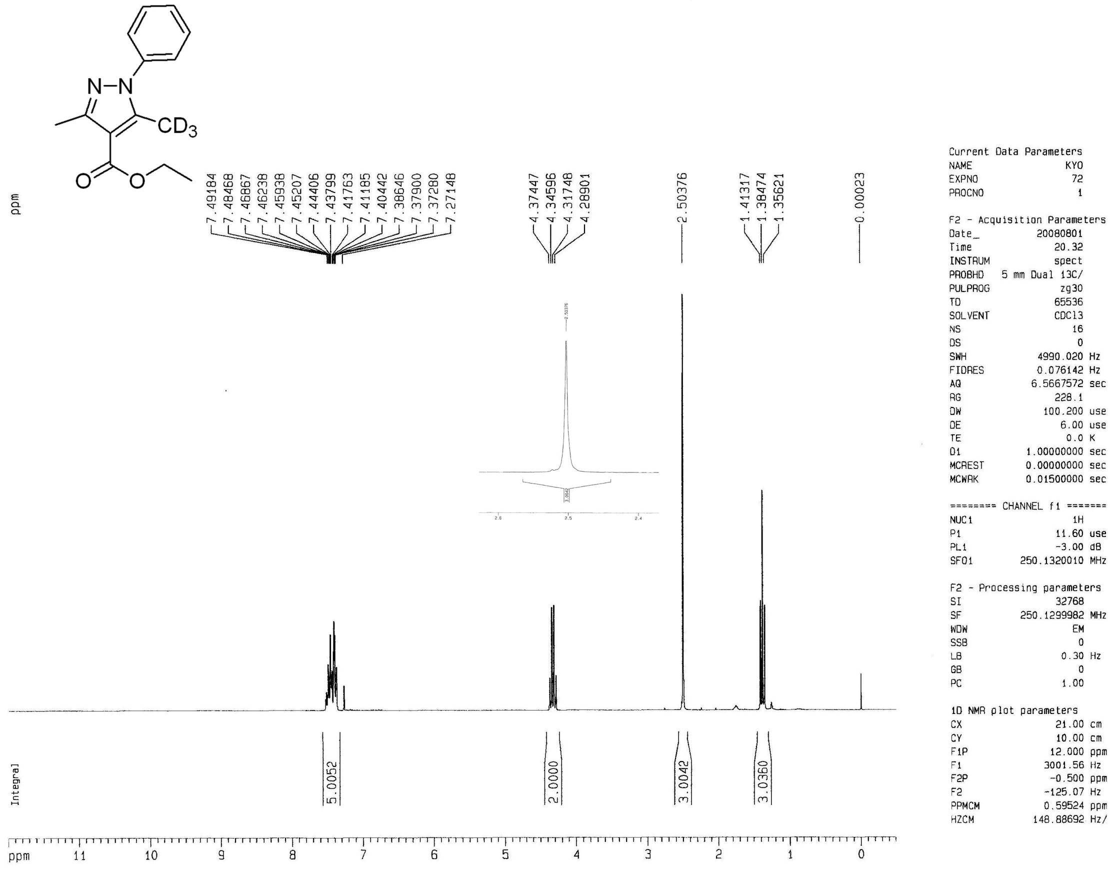


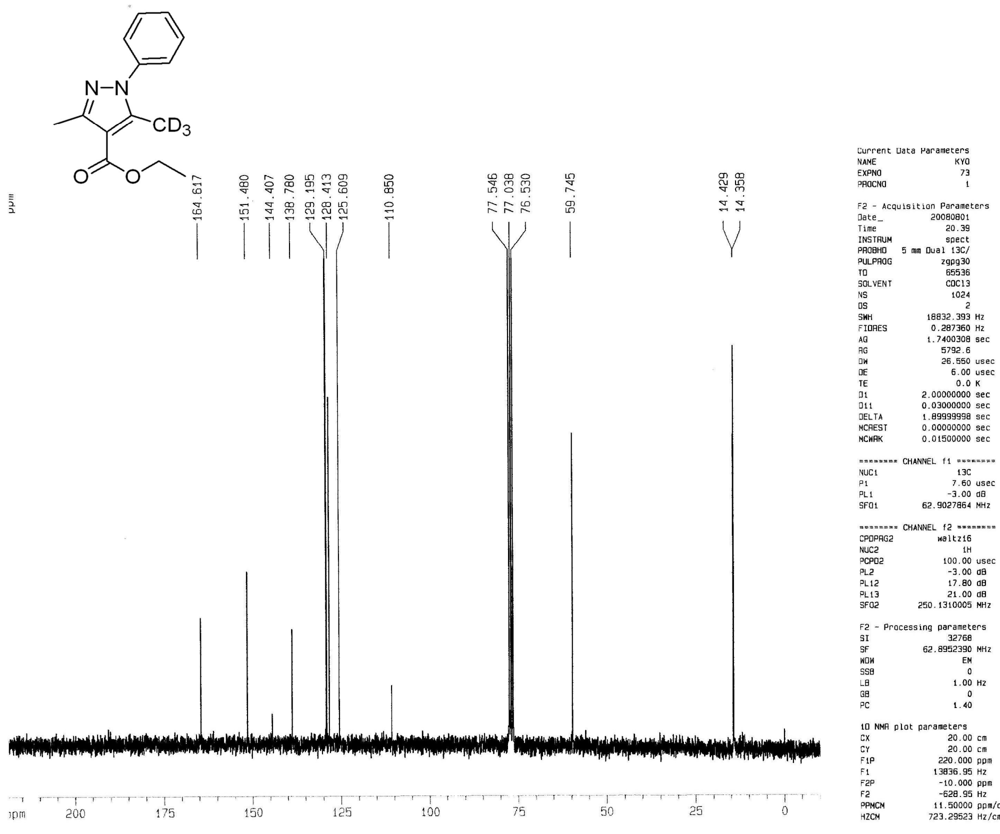
[1]H and [13]C NMR spectra of **2i**



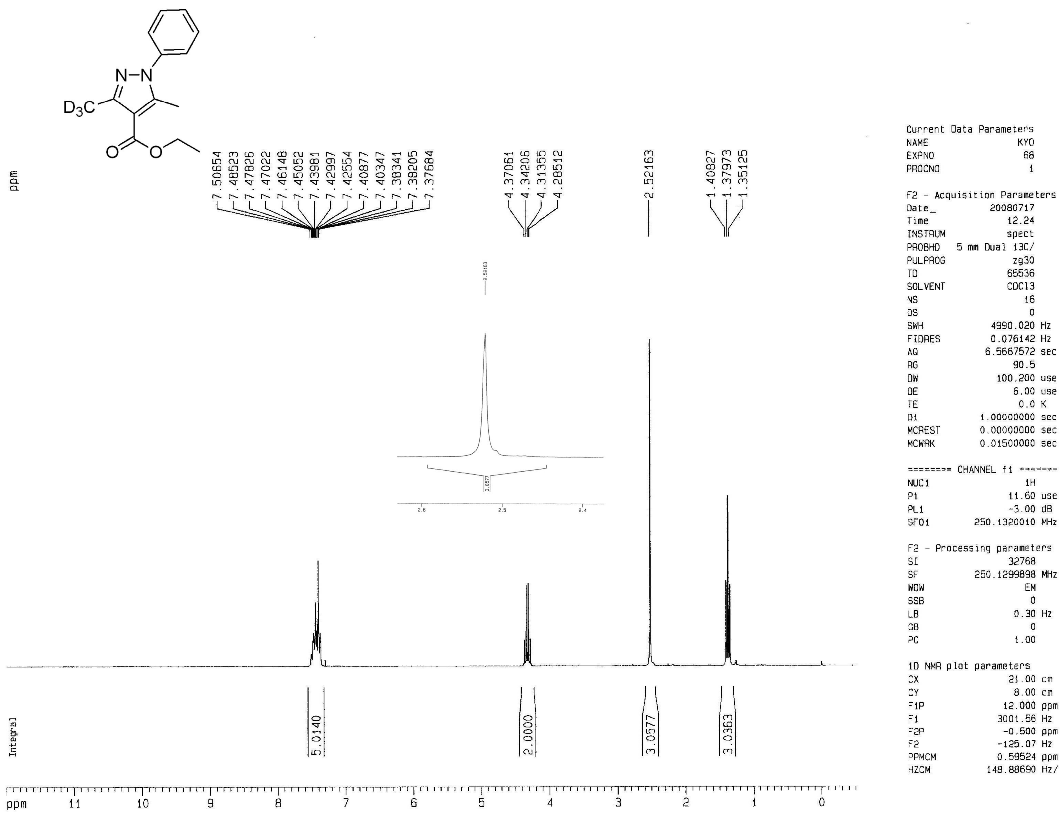


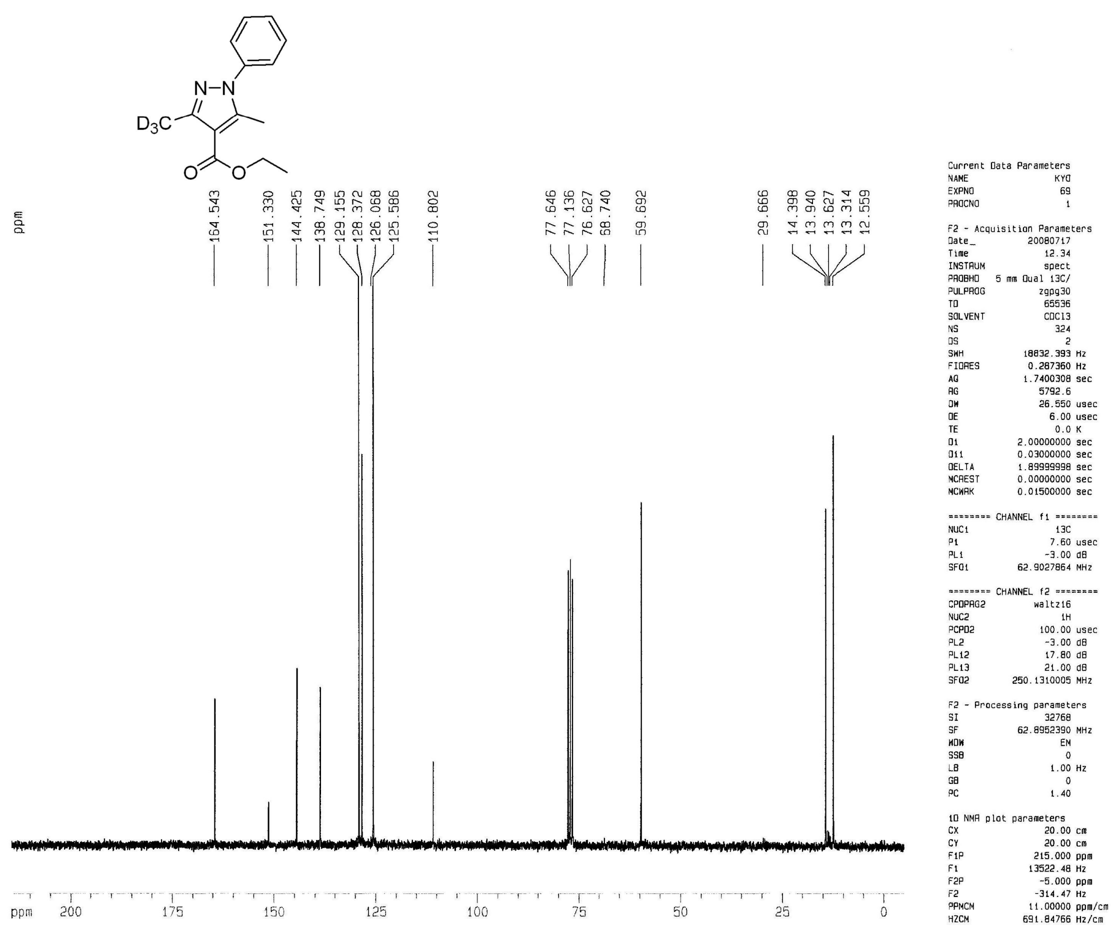
^{1}H and ^{13}C NMR spectra of 2j





^{1}H and ^{13}C NMR spectra of **2k**





^{1}H and ^{13}C NMR spectra of 3