Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information for

Facile Synthesis of 1,3,4-Benzotriazepines and 1-Arylamide-1*H*-indazoles via Palladium Catalyzed Cyclization of Aryl Isocyanates and Aryl Hydrazones under Microwave Irradiation

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1) General information

Unless otherwise noted, reagents and materials were obtained from commercial suppliers and were used without further purification. All solvents were purified according to reported procedures. Reactions were monitored by thin layer chromatography (TLC) and column chromatography purifications were performed using 230-400 mesh silica gel.

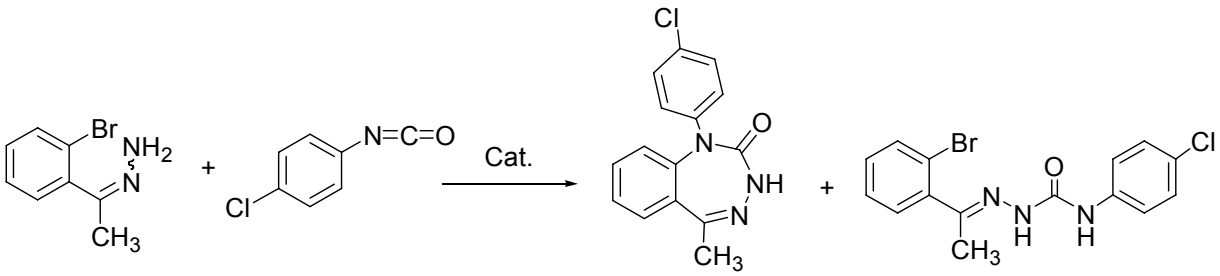
Melting points were uncorrected and measured on an SGW X-4 apparatus. IR spectra were recorded from KBr pellets at a range of 400-4000 cm^{-1} on a Thermo Nicolet Nexus 470 FTIR spectrometer. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker DPX400 apparatus in $CDCl_3$ with TMS as internal standard. Single-crystal X-ray-diffraction measurements were carried out on a Bruker Smart-APEX-CCD diffractometer. All microwave irradiation experiments were carried out using the microwave oven XH-100B from Xianghu Company, China. The reactions were performed in microwave vials sealed with a septum. The irradiation power was set at 500W. The temperature in the MW experiments was measured by an eternal IR sensor.

2) Optimized conditions for the reaction of 1a with 3d catalyzed by palladium complexes (*Table S1*).

Under a stream of argon, to a solution of catalyst (2-5 mol%) and ligand (10-40 mol%) in dried solvent (3 mL) was added hydrazone **1a** (0.36 mmol) followed by the isocyanate **3d** (0.432 mmol) and base (0.54 mmol). The resulting mixture was stirred at room temperature for 0.5 h and then the mixture was transferred into the microwave vial. The

vial was sealed; the irradiation power was set at 500W and irradiated in the microwave reactor at 80℃ for 20min. When the vial was removed from the apparatus, the solvent was evaporated under vacuum. The residue was added 5 mL of water and extracted with ethyl acetate (3 × 20 mL). Then the organic layer was washed with brine and dried with anhydrous sodium sulfate. Evaporation of ethyl acetate gave a pale yellow residue, which was purified by column chromatography to afford the pure product.

Table S1 Optimized Conditions for the Reaction of **1a** with **3d** Catalyzed by Palladium Complex [a]



1a **3d** **4d** **6d**

Entry	Catalyst [b] (mol%)	Solvent	T (℃)	Overall yield	**4d/6d**
1	**A** (5/20)	Toluene	110	75%	1/2.0
2	**A** (5/20)	THF	80	65%	1/2.2
3	**A (5/20)**	**CH_3CN**	**80**	**51%**	**1/1.3**
4	**A** (5/20)	DMF	120	0	---
5	**A** (5/40)	CH_3CN	80	60%	1/1.6
6	**B** (5/10)	CH_3CN	80	98%	1/2.7
7	**B** (5/20)	CH_3CN	80	40%	1/1.4
8	**B** (5/10)	Toluene	110	47%	1/2.1
9[c]	**C** (5/20)	CH_3CN	80	41%	1/8.0
10[c, d]	**C** (5/20)	CH_3CN	80	trace	trace
11[c]	**C** (5/20)	Toluene	110	43%	1/1.9
12[c]	**C** (5/20)	DMF	120	0	---
13	**D** (2.5/5)	Toluene	110	63%	1/2
14[d]	**E** (5/10)	Toluene	110	0	---

15[e]	**A** (5/20)	Toluene	110	90%	1/1.9
16[e]	**A** (5/20)	THF	80	88%	1/2.0
17[e]	**A (5/20)**	**CH_3CN**	**80**	**93%**	**1/1.1**

[a] Unless otherwise specified, the reaction was carried out with 0.36 mmol of **1a** and 0.432 mmol of **3d**, 0.54 mmol of K_2CO_3 in 3 mL solvent at indicated temperature for 18 h. [b] Catalyst: **A** ($Pd(OAc)_2/PPh_3$); **B** ($Pd_2(dba)_3/PPh_3$); **C** ($Pd(OAc)_2$/norbornene); **D** ($[Rh(COD\text{-})Cl]_2$/norbornene); **E** (CuI/dppf). [c] BTEAC was added as PTC. [d] Cs_2CO_3 was used as base. [e] Microwave irradiation power: 500 W, the reaction mixture was held at 80℃ for 20 min. The temperature in the MW experiments was measured by an eternal IR sensor.

3) General procedure for the cyclization of aryl hydrazones with aryl isocyanates under microwave irradiation

Under a stream of argon, to a solution of $Pd(OAc)_2$ (11.1 mg, 0.05 mmol, 5 mol%) and PPh_3 (52.5 mg, 0.2 mmol, 20 mol%) in dried acetonitrile (5 mL) was added hydrazone **1** (1 mmol) followed by the isocyanate **3** (1.2 mmol) and K_2CO_3 (1.5 mmol). The resulting mixture was stirred at room temperature for 0.5 h and then the mixture was transferred into the microwave vial. The vial was sealed; the irradiation power was set at 500W and irradiated in the microwave reactor at 80℃ for 20 min. When the vial was removed from the apparatus, the solvent was evaporated under vacuum. The residue was added 5 mL of water and extracted with ethyl acetate (3 × 20 mL). Then the organic layer was washed with brine and dried with anhydrous sodium sulfate. Evaporation of ethyl acetate gave a pale yellow residue, which was purified by column chromatography to afford the pure product, and the side product, if any of which was observed.

4) Characterization data for 4 and 5

4a: The product was purified with silica gel chromatography (Petroleum ether/Ethyl ether/CH_2Cl_2 = 1:1:1), white solid, m. p. 194-196℃; IR (KBr, cm^{-1}): ν 3243, 2962, 1675,

1528, 1498; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.23 (s, 3H), 6.99 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 1.4 Hz, 1H), 7.27-7.16 (m, 3H), 7.36 (dt, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 1H), 8.12 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 22.84, 118.51, 119.31, 122.33, 127.35, 127.60, 127.95, 128.14, 129.91, 130.18, 132.72, 134.50, 136.93, 146.14, 151.47; MS (m/z): 252. $[M + H]^+$.

4b: The product was purified with silica gel chromatography (Petroleum ether/Ethyl ether/CH_2Cl_2 = 1:1:1), light yellow solid, m. p. 183-185℃; IR (KBr, cm^{-1}): ν 3264, 1655, 1557, 1508, 1316; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.29 (s, 3H), 2.30 (s, 3H), 7.11-7.44 (m, 7H), 7.66 (d, J = 8.0 Hz, 1H), 8.12 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 20.80, 23.85, 119.75, 120.36, 128.40, 128.61, 129.47, 129.60, 131.17, 132.93, 133.73, 135.33, 135.59, 146.9574, 152.62; MS (m/z): 265 $[M]^+$.

4c: The product was purified with silica gel chromatography (Petroleum ether/Ethyl ether/CH_2Cl_2 = 2:1:1), white solid, m. p. 179-182℃; IR (KBr, cm^{-1}): ν 3264, 1669, 1557, 1488, 827; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.23 (s, 3H), 7.04 (d, *J* = 1.2 Hz, 1H), 7.18-7.39 (m, 7H), 8.13 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 23.88, 115.77, 120.27, 120.97, 128.31, 128.65, 131.27, 131.87, 133.77, 135.39, 137.15, 147.62, 152.25; MS (m/z): 330 $[M]^+$.

4d: The product was purified with silica gel chromatography (Petroleum ether/Ethyl ether/CH_2Cl_2 = 1:1:1), light yellow solid, m. p. 187-189℃; IR (KBr, cm^{-1}): ν 3267, 1670, 1554, 1492, 827; ^{1}H-NMR(400 MHz, $CDCl_3$): δ = 2.30 (s, 3H), 7.12 (d, *J* = 1.6 Hz, 1H), 7.26-7.35 (m, 3H), 7.42-7.67 (m, 3H), 7.69 (d, 1H), 8.20 (s, 1H); ^{13}C-NMR (100 MHz,

$CDCl_3$): δ = 22.84, 119.22, 119.61, 127.14, 127.28, 127.59, 127.87, 130.21, 132.70, 134.36, 135.62, 146.55, 151.28; MS: (m/z) 285.5 $[M]^+$.

4f: The product was purified with silica gel chromatography (Petroleum ether/Ethyl ether/CH_2Cl_2 = 2:1:1), white solid, m. p. 140-143℃; IR (KBr, cm^{-1}): ν 3194, 2954, 1686, 1525, 1403; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.83 (t, *J* = 6.9 Hz, 3H), 1.28-1.33 (m, 4H), 1.51-1.57 (m, 2H), 2.50 (t, *J* = 5.2 Hz, 2H), 6.97-7.03 (m, 2H), 7.17-7.27 (m, 3H), 7.35 (d, *J* = 6.7 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 1H), 8.13 (s, 1H); ^{13}C-NMR(100 MHz, $CDCl_3$): δ = 14.04, 22.51, 25.64, 31.44, 37.23, 119.51, 119.81, 120.77, 123.34, 128.38, 128.91, 128.98, 131.10, 133.75, 134.95, 137.99, 150.57, 152.61; MS (m/z): 308.1 $[M+H]^+$.

4g: The product was purified with silica gel chromatography (Petroleum ether/Ethyl ether/CH_2Cl_2 = 2:1:1), light yellow solid, m. p. 146-149℃; IR (KBr, cm^{-1}): ν 3269, 2917, 1660, 1555; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.84 (t, *J* = 6.9 Hz, 3H), 1.28-1.33 (m, 4H), 1.50-1.55 (m, 2H), 2.24 (s, 3H), 2.52 (dt, *J* = 5.3 Hz, 2H), 7.01-7.04 (m, 3H), 7.06-7.59 (m, 4H), 7.60 (d, *J* = 7.4 Hz, 1H), 8.04 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 13.01, 19.78, 21.48, 24.63, 28.68, 30.43, 36.19, 118.70, 119.78, 127.34, 127.92, 128.46, 130.04, 131.88, 132.72, 133.99, 134.33, 149.32, 151.70; MS (m/z): 321 $[M]^+$.

4h: The product was purified with silica gel chromatography (Petroleum ether/Ethyl ether/CH_2Cl_2 = 3:1:1), white solid, m. p. 144-146℃; IR (KBr, cm^{-1}): ν 3368, 2924, 1690, 1524, 1129, 825; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.83 (t, *J* = 7.0 Hz, 3H), 1.24-1.36 (m,

4H), 1.40-1.46 (m, 2H), 2.79 (t, *J* = 7.4 Hz, 2H), 7.26-7.46 (m, 7H), 7.65 (d, *J* = 7.9 Hz, 1H), 8.38 (s, 1H); MS (m/z): 386 $[M]^+$.

4i: The product was purified with silica gel chromatography (Petroleum ether/Ethyl ether/CH_2Cl_2 = 2:1:1), light yellow solid, m. p. 154-157℃; IR (KBr, cm^{-1}): ν 3270, 2955, 1661, 1557, 1402; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.84 (t, *J* = 7.0 Hz, 3H), 1.30-1.33 (m, 4H), 1.49-1.56 (m, 2H), 2.52 (t, *J* = 1.3 Hz, 2H), 7.00 (d, *J* = 1.3 Hz, 1H), 7.17-7.27 (m, 4H), 7.35-7.41 (m, 2H), 7.60 (d, *J* = 7.9 Hz, 1H), 8.13 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 14.04, 22.49, 25.65, 31.44, 37.26, 120.63, 120.71, 128.19, 128.40, 128.88, 128.93, 131.17, 133.76, 134.82, 136.66, 151.03, 152.45; MS (m/z): 341.5 $[M]^+$.

4j: The product was purified with silica gel chromatography (Petroleum ether/Ethyl ether/CH_2Cl_2 = 2:1:1), white solid, m. p. 186-189℃; IR (KBr, cm^{-1}): ν 3261, 2956, 1681, 1594, 1427, 775; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 6.9 Hz, 3H), 1.23-1.35 (m, 4H), 1.58-1.66 (m, 2H), 2.61 (t, *J* = 6.8 Hz, 2H), 7.04 (d, *J* = 1.0 Hz, 1H), 7.06 (d, *J* = 1.0 Hz, 1H), 7.10-7.47 (m, 5H), 7.69 (d, *J* = 8.0 Hz, 1H), 8.25 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 13.86, 22.38, 29.72, 31.71, 37.32 119.51, 119.81, 120.77, 123.34, 128.38, 128.91, 128.98, 131.10, 133.75, 134.95, 137.99, 150.57, 152.61; MS (m/z): 342 $[M+H]^+$.

4k: The product was purified with silica gel chromatography (Petroleum ether/Ethyl ether/CH_2Cl_2 = 4:1:1), white solid, m. p. 200-202℃; IR (KBr, cm^{-1}): ν 3262, 3083, 1659, 1618, 1560, 1498; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.03-7.05 (m, 1H), 7.15-7.18 (m, 2H), 7.26-7.50 (m, 10H), 7.70 (d, *J* = 8.0 Hz, 1H), 8.24 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ

= 119.70, 122.33, 123.64, 126.73, 128.65, 128.71, 129.06, 129.82, 130.29, 130.93, 131.68, 133.05, 134.00, 135.39, 137.73, 147.02, 152.34; MS (m/z): 313 $[M]^+$.

4l: The product was purified with silica gel chromatography (Petroleum ether/Ethyl ether/CH_2Cl_2 = 6:1:1), white solid, m. p. 151-154℃; IR (KBr, cm^{-1}): ν 3263, 2922, 1658, 1557, 1464, 1126; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 3H), 7.06 (d, J = 8.2 Hz, 2H), 7.13-7.18 (m, 1H), 7.29-7.45 (m, 9H), 7.68 (d, J = 8.0 Hz, 1H), 8.16(s, 1H); ^{13}C-NMR(100 MHz, $CDCl_3$): δ = 20.86, 119.98, 122.36, 126.74, 128.64, 128.68, 129.57, 129.77, 130.31, 131.64, 133.14, 133.28, 133.97, 135.07, 135.48, 146.97, 152.66; MS (m/z): 327 $[M]^+$.

4m: The product was purified with silica gel chromatography (Petroleum ether/Ethyl ether/CH_2Cl_2 = 4:1:1), light yellow, m. p. 122-124℃; IR (KBr, cm^{-1}): 3340, 1700, 1521, 1488, 824; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.12(dd, J = 5.8 Hz, 1.6Hz, 1H), 7.29-7.45(m, 11H), 7.69(d, J = 7.2 Hz, 1H), 8.27(s, 1H); MS (m/z): 392 $[M]^+$.

4n: The product was purified with silica gel chromatography (Petroleum ether/Ethyl ether/CH_2Cl_2 = 6:1:1), white solid, m. p. 161-163℃; IR (KBr, cm^{-1}): ν 3266, 1693, 1524, 1491, 829; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.13-7.24 (m, 3H), 7.43-7.45 (m, 5H), 7.31-7.36 (m, 4H), 7.69 (d, J = 8.0 Hz, 1H), 8.24 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 120.85, 122.27, 126.79, 128.53, 128.68, 128.73, 129.93, 130.25, 131.74, 132.98, 134.02, 135.30, 136.43, 147.44, 152.20; MS (m/z): 348.5 $[M+H]^+$.

5a: The product was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 3:1), white solid, m. p. 69-71℃; IR (KBr, cm^{-1}): ν 3446, 1683, 1593, 1526, 1456; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.53 (s, 3H), 7.06 (t, J = 8.0 Hz, 1H), 7.22 (t, J = 8.0 Hz,

2H), 7.24 (t, J = 8.0 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 8.32 (d, *J* = 8.0 Hz, 1H), 8.96 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 12.1, 110.0, 114.8, 119.6, 123.1, 124.7, 129.1, 129.2, 137.3, 139.7, 146.9, 148.9; MS (m/z): 252 $[M + H]^+$.

5b: The product was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 4:1), white solid, m. p. 114-116℃; IR (KBr, cm^{-1}): ν 3446, 1716, 1558, 1076; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.28 (s, 3H), 2.53 (s,3H), 7.11 (d, *J* = 8.0 Hz, 1H), 8.90 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 11.1, 19.8, 113.8, 118.6, 122.0, 124.8, 128.1, 132.6, 133.7, 138.3, 145.7, 147.9; MS (m/z): 265.5 $[M]^+$, 267.5 $[M+2H]^+$.

5c: The product was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 3:1), light yellow, m. p. 129-130℃; IR (KBr, cm^{-1}): ν 3445, 1691, 1593, 1532, 1403; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.53 (s, 3H), 7.19-7.61 (m, 7H), 8.32(d, *J* = 8.0 Hz, 1H), 8.98 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 12.1, 114.8, 116.6, 120.3, 121.0, 126.0, 129.3, 132.1, 136.5, 139.5, 147.2, 148.7; MS (m/z): 330 $[M]^+$.

5d: The product was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 3:1), light yellow, m. p. 123-126℃; IR (KBr, cm^{-1}): ν 3443, 1640, 1535, 1407; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.61 (s, 3H), 7.26 (m, 3H), 7.34 (t, 1H), 7.56 (dd, J = 8.0, 12 Hz, 3H), 8.37 (d, J = 12.0 Hz, 1H), 9.06 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 12.1, 114.3, 120.3, 120.6, 123.2, 125.9, 129.0, 129.1, 136.0, 139.6, 147.1, 148.7; MS: (m/z) 285.5 $[M]^+$.

5e: The product was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 5:1), white powder, m. p. 102-105℃; IR (KBr, cm^{-1}): ν 3445, 1720, 1596, 1540, 1426; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.60 (s, 3H), 7.11 (d, *J* = 4.0 Hz, 1H), 7.28 (m, 2H), 7.50-7.81 (m, 4H), 8.38 (d, *J* = 8.0 Hz, 1H), 9.08(s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 12.1, 114.8, 117.4, 119.5, 123.3, 124.0, 129.4, 130.1, 134.8, 138.5, 139.3, 147.3, 148.3; MS (m/z): 285.5 $[M]^+$.

5f: The product was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 4:1), yellow oil, IR (KBr, cm^{-1}): ν 3445, 1720, 1596, 1540, 1426; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.8 (t, *J* = 4.0 Hz, 3H), 1.30 (br, 4H), 1.93 (br, 2H), 2.87 (t, *J* = 8.0 Hz, 2H), 7.03 (t, *J* = 4.0 Hz, 1H), 7.06-7.19 (m, 3H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.31 (m, 3H), 8.32 (d, *J* = 8.0 Hz, 1H), 8.97 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 12.9, 21.4, 23.0, 25.9, 30.5, 113.8, 118.5, 119.3, 121.9, 123.0, 126.9, 127.4, 128.0, 136.3, 138.8, 147.9, 149.9; MS (m/z): 308 $[M+H]^+$.

5g: The product was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 4:1), white solid, m. p. 51-53℃, IR (KBr, cm^{-1}): ν 3447, 2923, 1722, 1649, 1532, 1401; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.84 (t, *J* = 8.0 Hz, 3H), 1.36 (br, 4H), 1.84 (t, *J* = 8.0 Hz, 2H), 2.85 (t, *J* = 8.0 Hz, 2H), 7.09 (dt, *J* = 8.0 Hz, 2H), 7.18 (m, 1H), 7.42 (m, 3H), 7.56 (d, *J* = 8.0 Hz, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 8.80 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 14.0, 20.8, 22.4, 27.5, 31.7, 114.9, 119.3, 120.3, 122.9, 125.4, 127.5, 128.0, 129.1, 133.3, 134.7, 139.9, 149.1, 150.9; MS (m/z): 321 $[M]^+$.

5h: The product was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 6:1), white solid, m. p. 74-75℃; IR (KBr, cm^{-1}): ν 3445, 2956,1708, 1648, 1523, 1425; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.81 (br, 3H), 1.30 (br, 4H), 1.75 (br, 2H), 2.90 (t, *J* = 4 Hz, 2H), 7.22 (m, 1H), 7.36-7.48 (m, 5H), 7.49 (d, *J* = 4 Hz, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 8.99 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 12.9, 21.4, 25.7, 26.0, 30.6, 113.8, 115.5, 119.4, 120.0, 124.5, 128.2, 131.0, 135.5, 138.8, 147.8, 150.2 ; MS (m/z): 386 $[M]^+$.

5i: The product was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 7:1), yellow solid, m. p. 86-88℃; IR (KBr, cm^{-1}): ν 3375, 2920, 1683, 1592, 1533, 1404; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 8 Hz, 3H), 1.38 (br, 4H), 1.86 (t, *J* = 8 Hz, 2H), 2.97(t, *J* = 8 Hz, 2H), 7.26-7.32 (m, 3H), 7.34 (t, *J* = 8 Hz, 1H), 7.54(d, *J* = 12 Hz, 2H), 7.57(d, 1H), 8.41 (d, *J* = 8.0 Hz, 1H), 9.03(s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 14.0, 22.4, 27.0, 31.7, 114.8, 120.4, 120.8, 123.1, 125.5, 129.0, 129.1, 136.0, 139.8, 148.9, 151.3; MS (m/z): 341.5 $[M]^+$.

5j: The product was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 8:1), white, m. p. 57-60℃; IR (KBr, cm^{-1}): ν 3371, 1720, 1599, 1530, 1445; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 8 Hz, 3H), 1.34 (br, 4H), 1.78 (br, 2H), 2.88 (t, *J* = 8 Hz, 2H), 7.02 (d, *J* = 8 Hz, 1H), 7.18(m, 2H), 7.21 (m, 2H), 7.45 (d, *J* = 12 Hz, 1H), 7.70 (s, 1H), 8.30 (d, *J* = 12 Hz, 1H), 9.00(s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 12.9, 21.4, 24.9, 25.9, 30.6, 113.8, 116.4, 117.9, 119.4, 122.1, 123.9, 125.0, 128.2, 133.3, 137.5, 138.7, 147.3, 150.3; MS (m/z): 341.5 $[M]^+$.

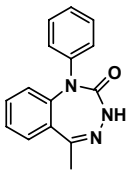
5k: The product was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1), white, m. p. 104-107℃; IR (KBr, cm^{-1}): ν 3445, 2921, 1652, 1557, 1401; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.00-7.26 (m, 6H), 7.40-7.46 (m, 5H), 7.52 (m, 1H), 7.62 (m, 1H), 8.56 (d, *J* = 8.0 Hz, 1H), 9.22 (s, 1H); MS (m/z): 313 $[M]^+$.

5l: The product was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1), light yellow, m. p. 113-114℃, IR (KBr, cm^{-1}): ν 3445, 2959, 1633, 1536, 1411; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.44-7.65 (m, 6H), 8.02 (d, *J* = 8.0 Hz, 3H), 8.56 (d, *J* = 8.0 Hz, 1H), 9.17 (s, 1H) ; MS (m/z): 327 $[M]^+$.

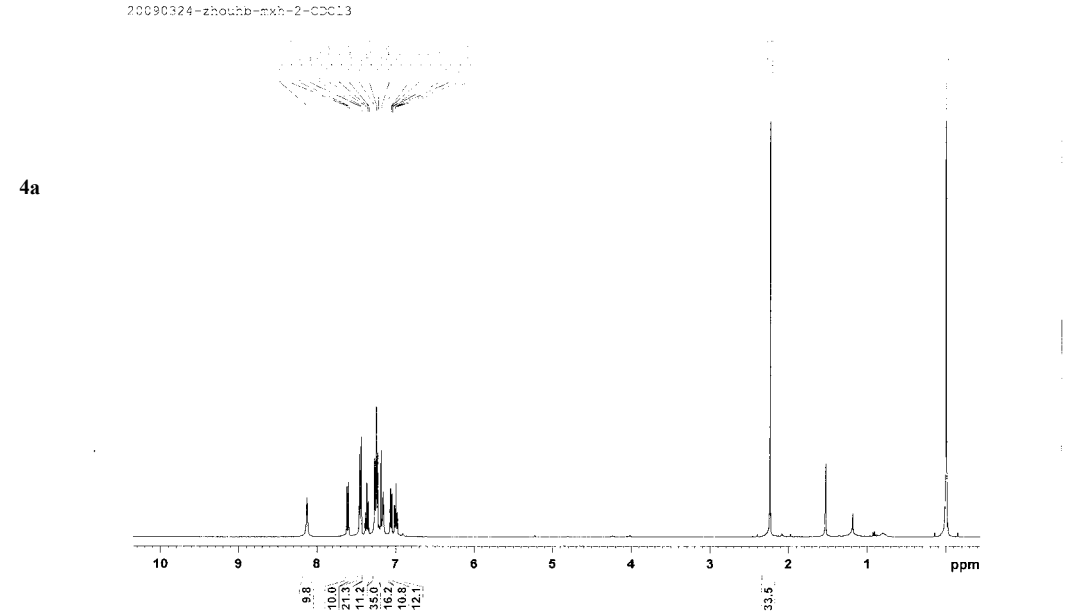
5m: The product was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1), light yellow, m. p. 122-124℃; IR (KBr, cm^{-1}): ν 3379, 2923, 1683, 1527, 1489; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.34 (t, *J* = 8.0 Hz, 1H), 7.44-7.55 (m, 8H), 7.92 (t, *J* = 8.0 Hz, 3H), 8.44 (d, *J* = 8.0 Hz, 1H), 9.15 (s, 1H); MS (m/z): 392 $[M]^+$.

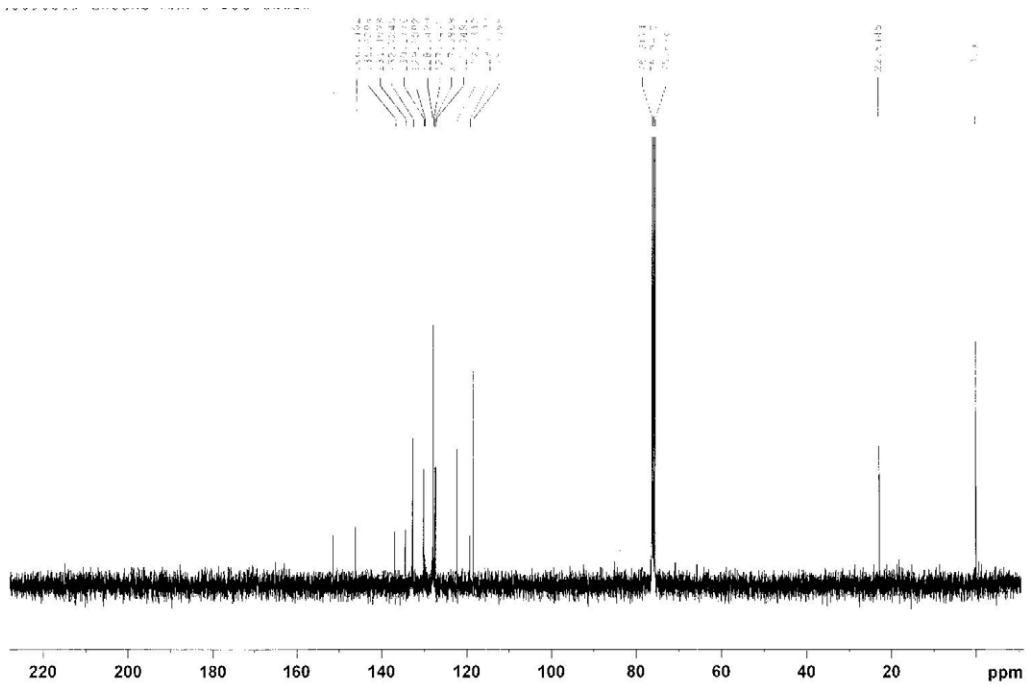
5n: The product was purified with silica gel chromatography (Petroleum ether/Ethyl acetate = 10:1), white, m. p. 161-164℃; IR (KBr, cm^{-1}): ν 3446, 2924, 1694, 1589, 1527, 1404; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.32 (t, *J* = 8.0 Hz, 3H), 7.45-7.58 (m, 6H), 7.92 (dd, *J* = 8.0 Hz, 3H), 8.44 (d, *J* = 8.0 Hz, 1H), 9.15 (s, 1H); MS (m/z): 348.5 $[M+H]^+$.

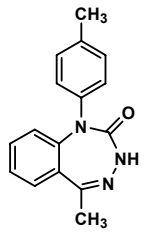
5) Copies of ^{1}H NMR、^{13}C NMR spectra



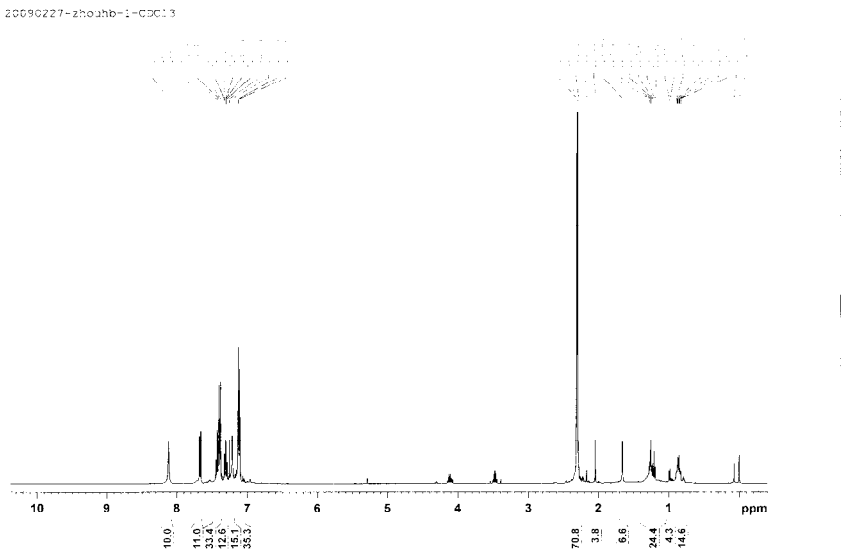
4a

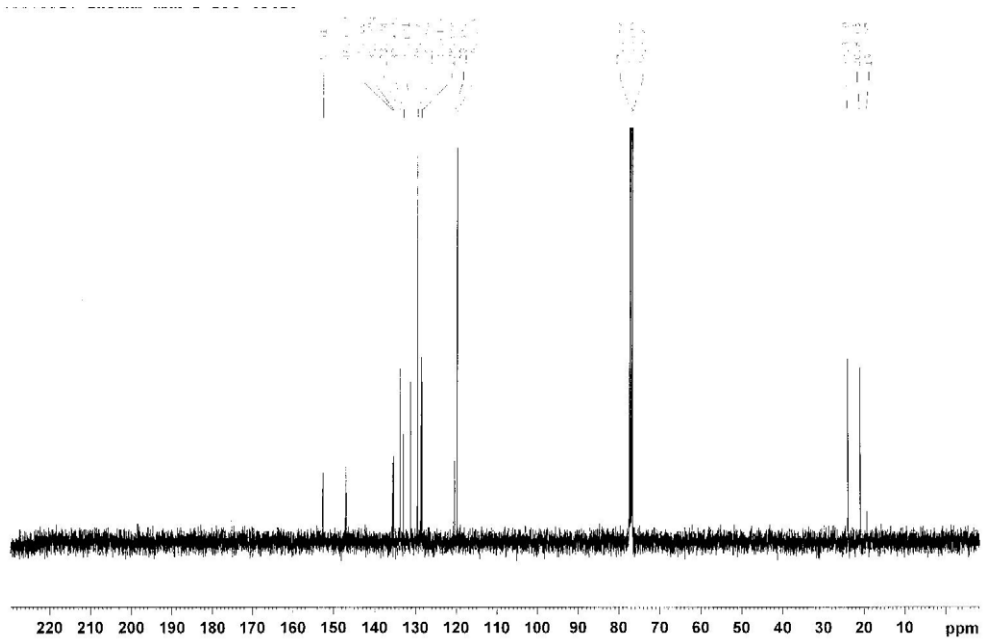


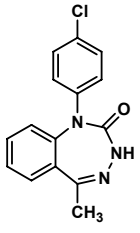




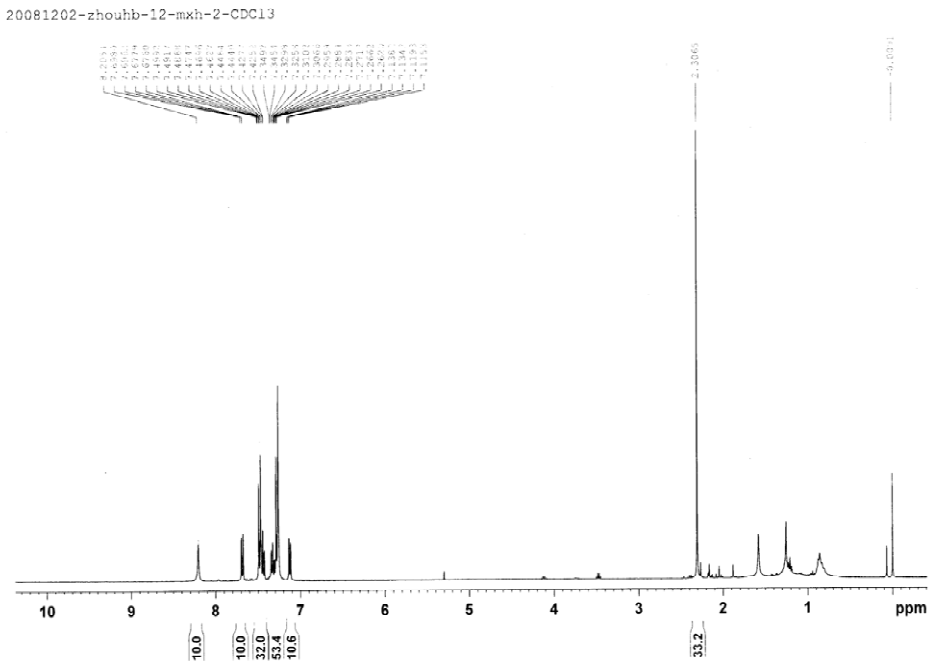
4b

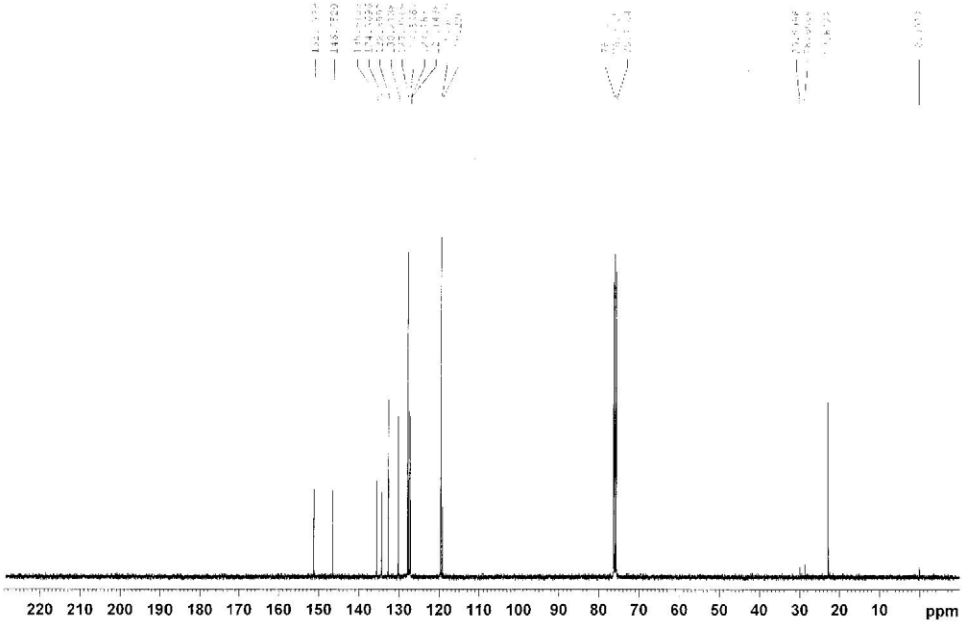

20090227-zhouhb-1-CDCl3
10
9
8
7
6
5
4
3
2
1
ppm
10.0
11.0
33.4
12.6
15.1
35.3
70.8
3.8
6.6
24.4
4.3
14.6

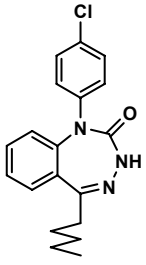

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Cl
O
N
NH
N
CH3

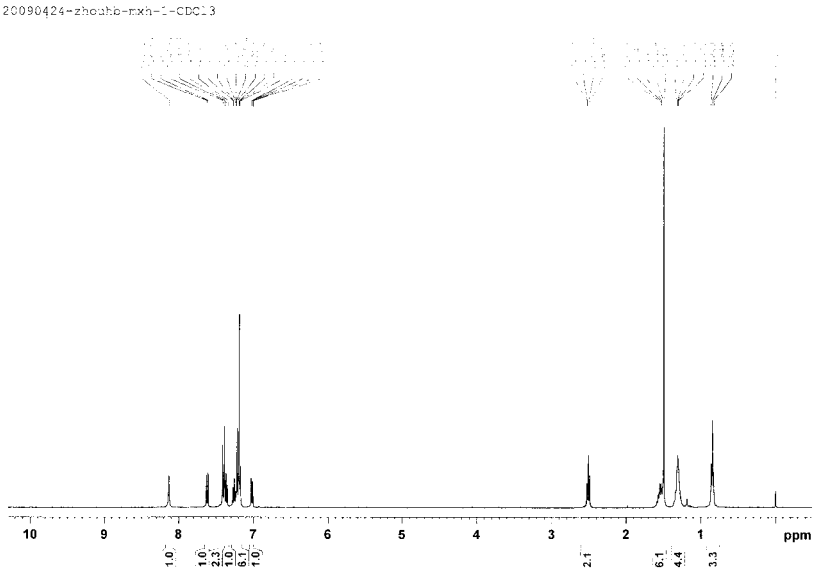
4d

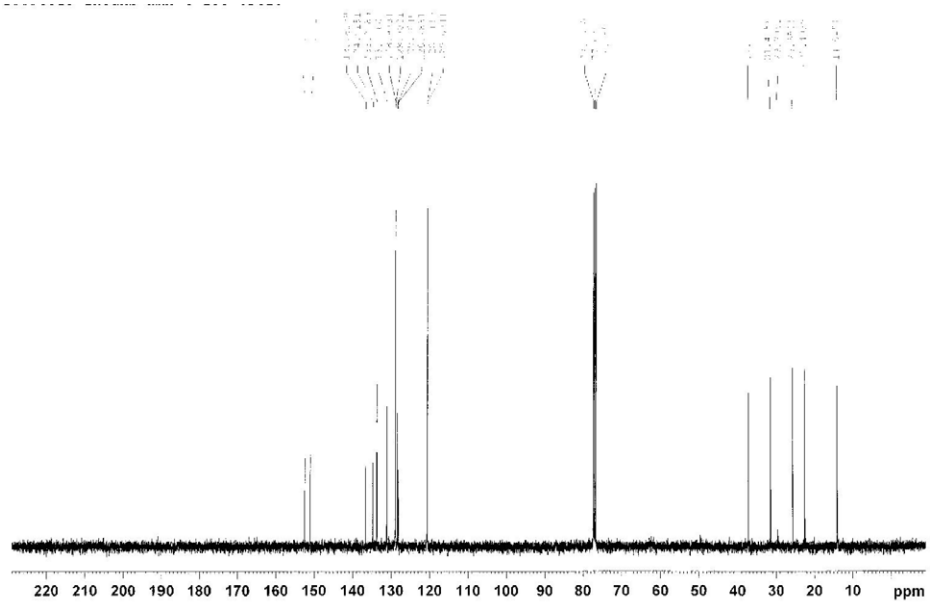

20081202-zhouhb-12-mxh-2-CDCl3
10
9
8
7
6
5
4
3
2
1
ppm
10.0
10.0
32.0
53.4
10.6
33.2

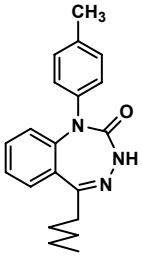

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm


Cl
N
O
NH
N

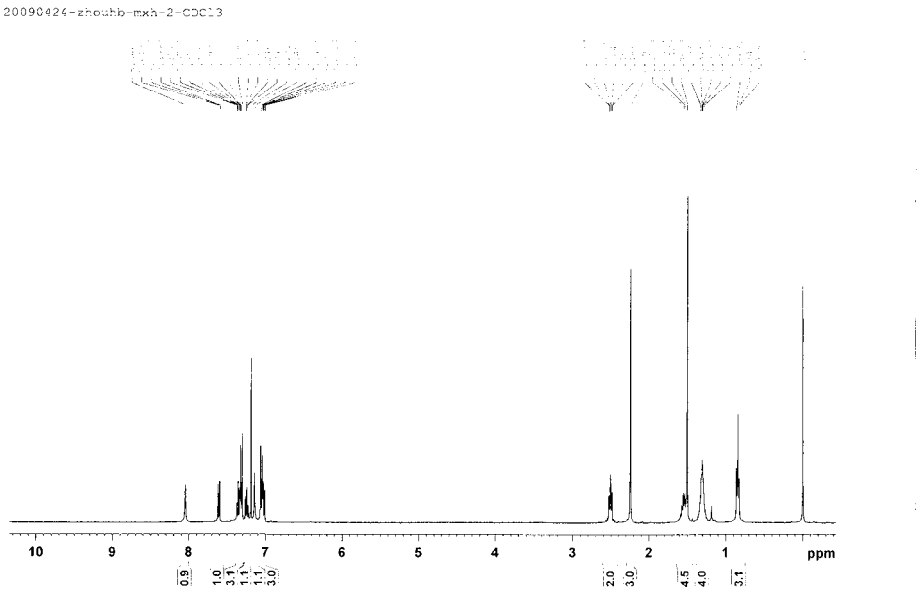
4i

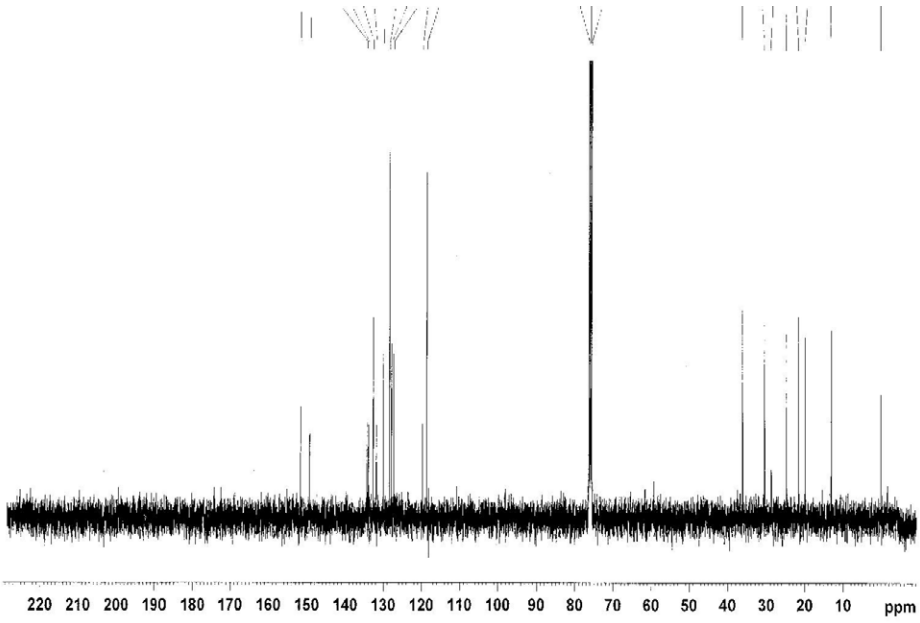

20090424-zhoubb-mxh-1-CDCl3
10
9
8
7
6
5
4
3
2
1
ppm
1.0
1.6
2.3
1.0
6.1
1.0
2.1
6.1
4.4
3.3

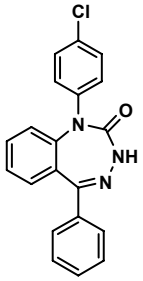

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm


CH3
O
N
NH
N

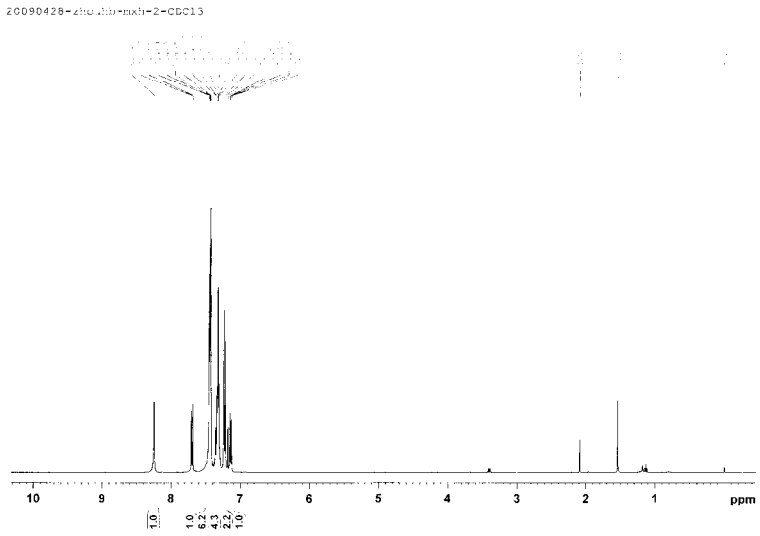
4g

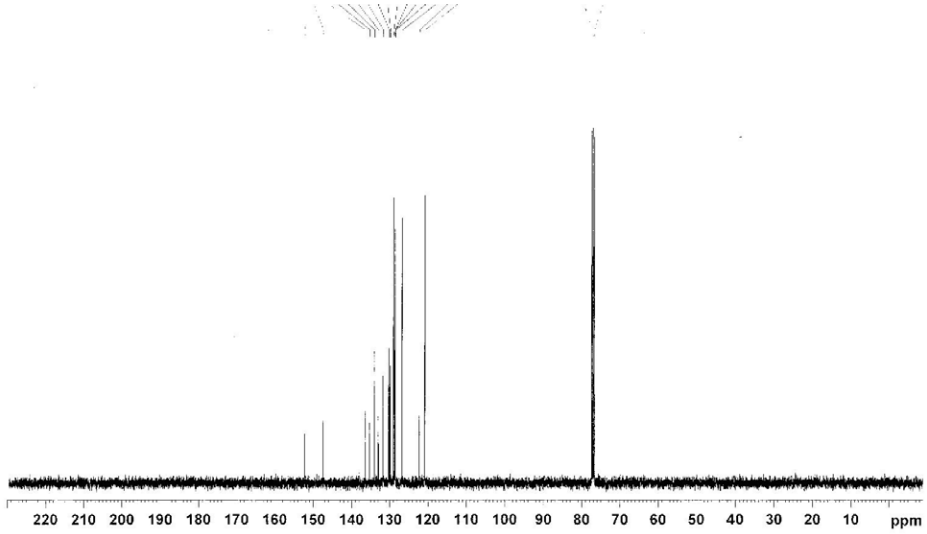

20090424-zhoubb-mxh-2-CDCl3
10
9
8
7
6
5
4
3
2
1
ppm
0.9
1.0
3.1
1.1
1.1
3.0
2.0
3.0
4.5
4.0
3.1

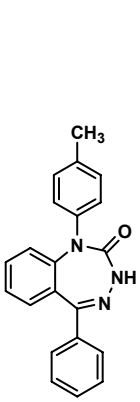

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm


Cl
N
O
NH
N

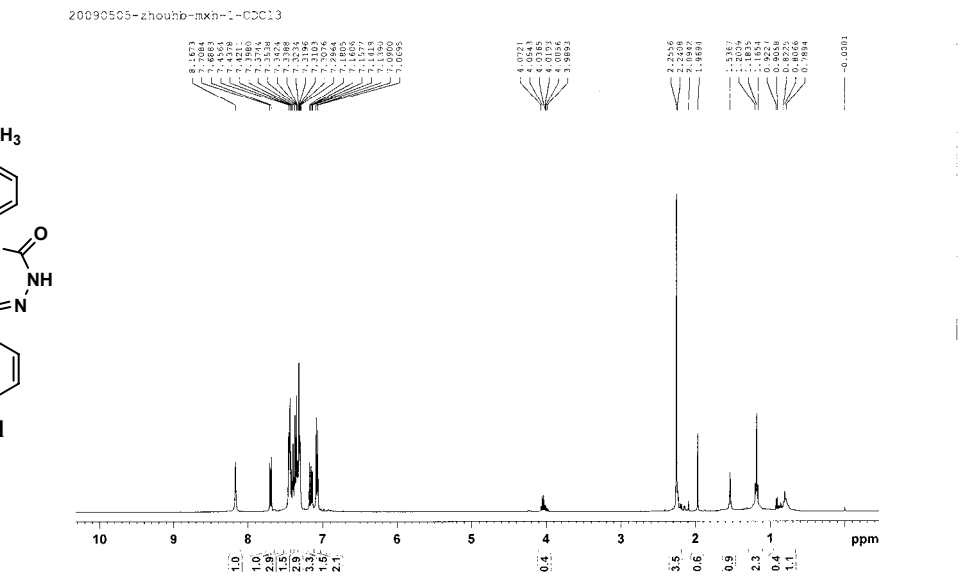
4n

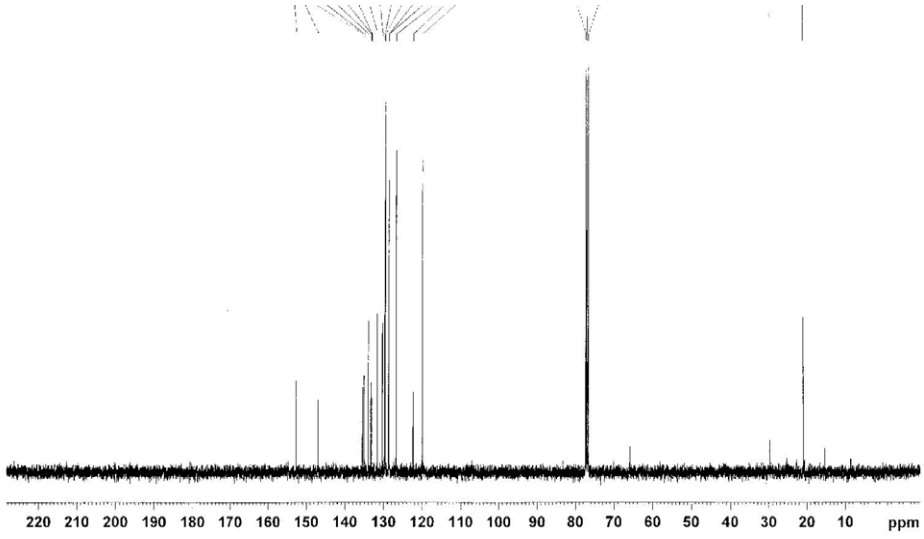

ZC090428-zhc.1h-mxh-2-CDCl3
10
9
8
7
6
5
4
3
2
1
ppm
1.0
1.0
6.2
4.3
2.2
1.0

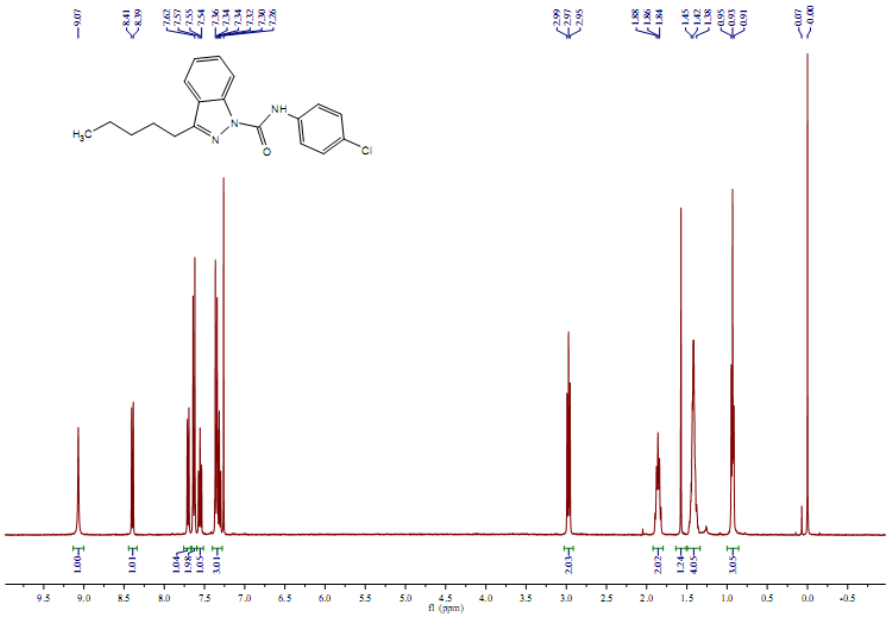

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

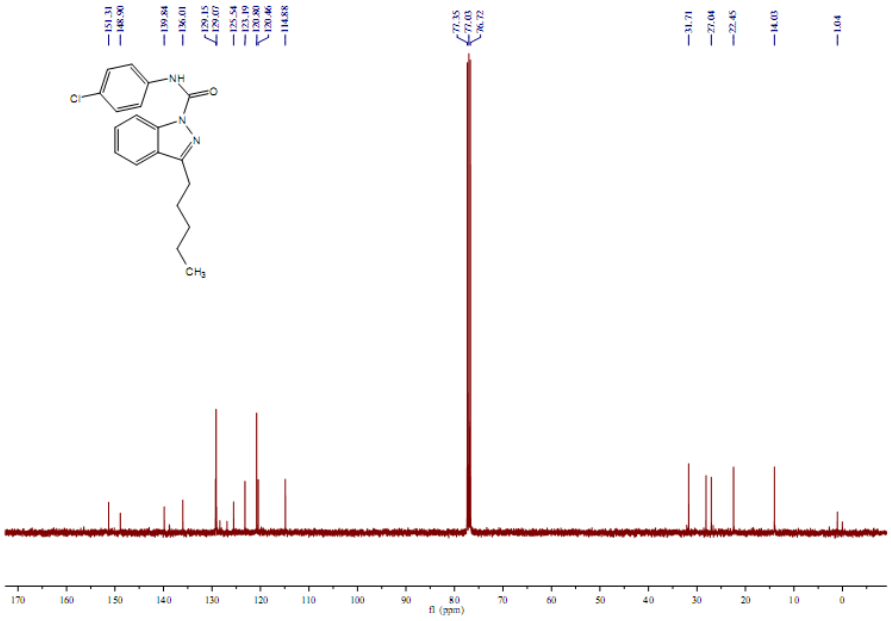

CH3
O
N
NH
N

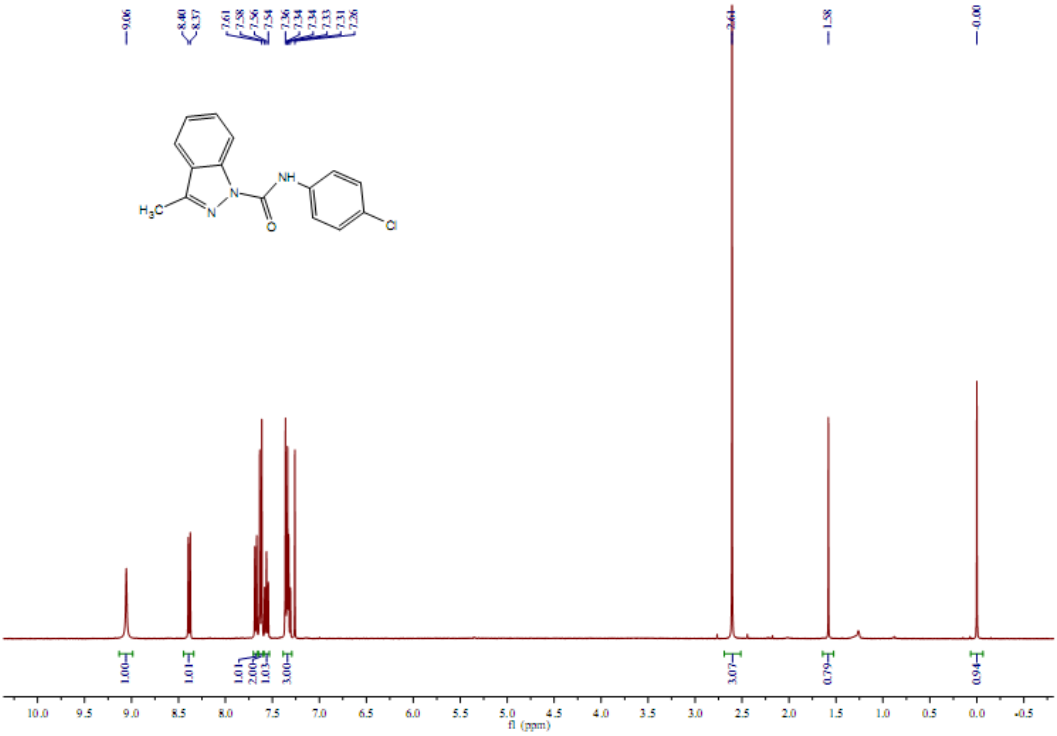
4l

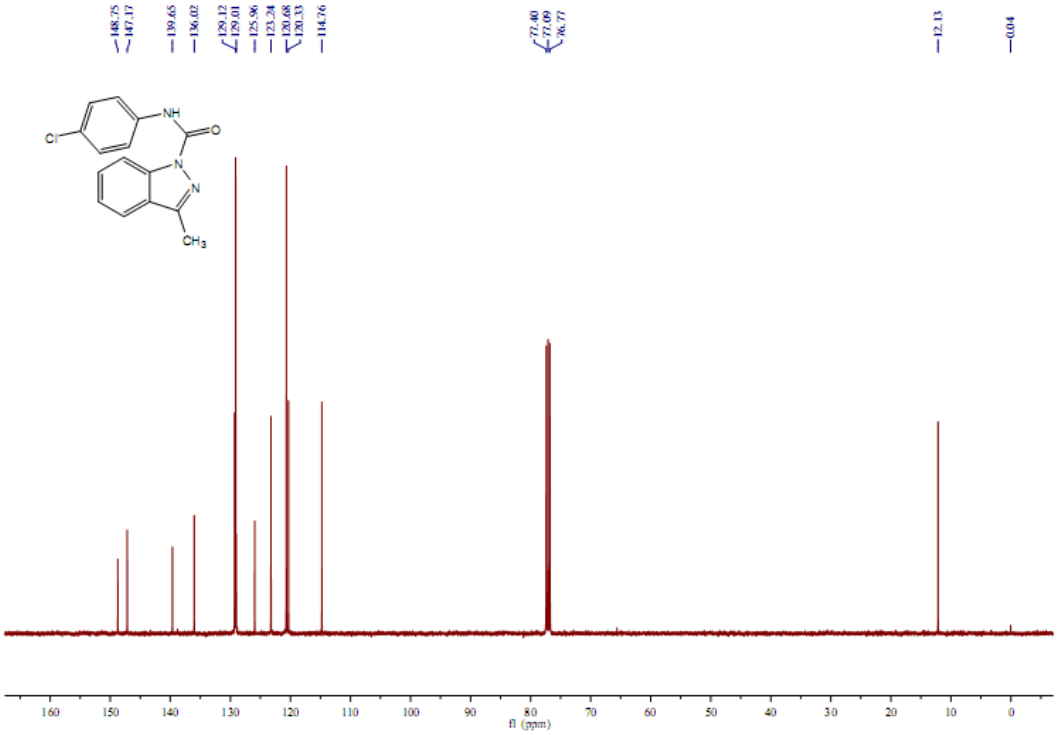

20090503-zhoubb-mxh-1-CDCl3
10
9
8
7
6
5
4
3
2
1
ppm

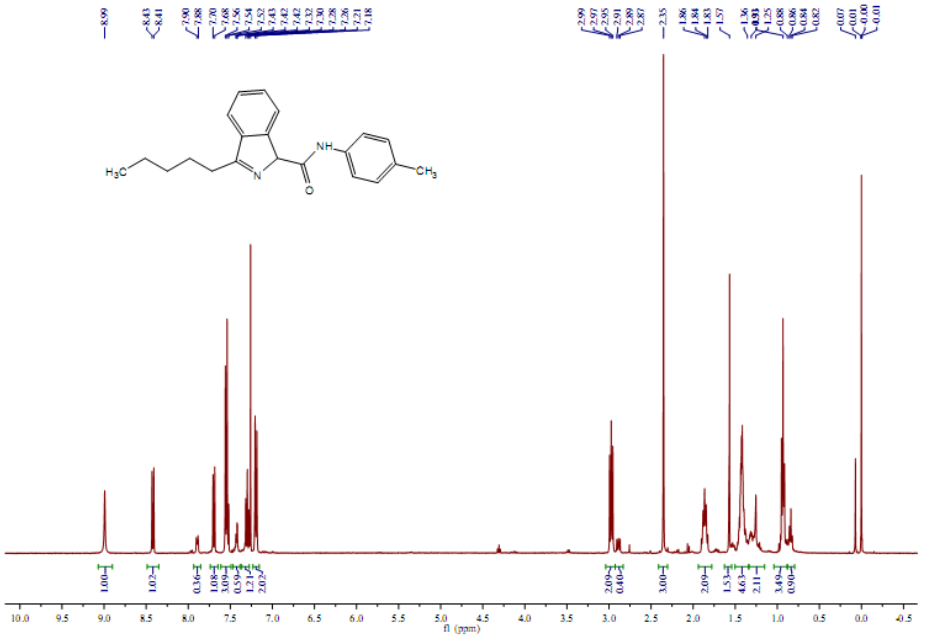

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

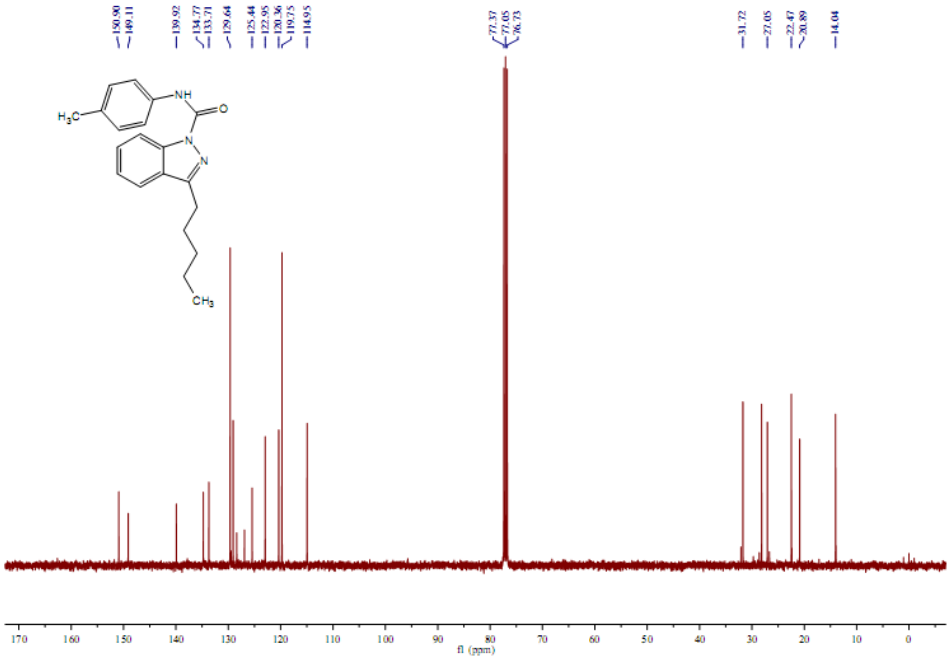

9.07
8.41
8.39
7.62
7.57
7.55
7.54
7.36
7.34
7.34
7.32
7.30
7.26
2.99
2.97
2.95
1.88
1.86
1.84
1.45
1.42
1.38
0.95
0.93
0.91
0.07
0.00
NH
N
N
O
Cl
H3C
1.00
1.01
1.04
1.98
1.03
3.01
2.03
2.02
1.24
4.05
3.05
fl (ppm)


151.31
148.90
139.84
136.01
129.15
129.07
125.54
123.19
120.80
120.46
114.88
77.35
77.03
76.72
31.71
27.04
22.45
14.03
1.04
NH
O
N
N
Cl
CH3
fl (ppm)

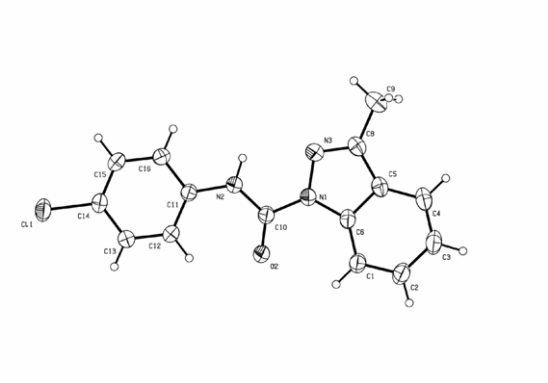

9.06
8.40
8.37
7.61
7.58
7.56
7.54
7.36
7.34
7.34
7.33
7.31
7.26
2.64
1.58
0.00
NH
N
N
O
H3C
Cl
1.00
1.01
1.01
2.00
1.03
3.00
3.07
0.79
0.94
f1 (ppm)


148.75
147.17
139.65
136.02
129.12
129.01
125.96
123.24
120.68
120.33
114.76
77.40
77.09
76.77
12.13
0.04
NH
O
N
N
Cl
CH3
f1 (ppm)


8.99
8.43
8.41
7.90
7.88
7.70
7.68
7.56
7.54
7.52
7.43
7.42
7.32
7.30
7.28
7.26
7.23
7.18
2.99
2.97
2.95
2.91
2.89
2.87
2.35
1.86
1.84
1.83
1.57
1.36
1.25
0.88
0.86
0.84
0.82
0.07
0.01
0.00
-0.01
NH
N
O
CH3
1.00
1.02
0.36
1.08
3.09
0.59
1.21
2.02
2.09
0.40
3.00
2.09
1.53
4.63
2.11
3.49
0.90
f1 (ppm)


150.90
149.11
139.92
134.77
133.71
129.64
125.44
122.95
120.36
119.75
114.95
77.37
77.05
76.73
31.72
27.05
22.47
20.89
14.04
NH
O
N
N
H3C
CH3
f1 (ppm)

6) Crystallographic data for 5d



Bond precision: C-C = 0.0021 A Wavelength=0.71073

Cell: a=23.441(6) b=6.2204(15) c=18.816(5)
alpha=90 beta=98.452(4) gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	2713.8(12)	2713.7(11)
Space group	C 2/c	C2/c
Hall group	-C 2yc	?
Moiety formula	C15 H12 Cl N3 O	?
Sum formula	C15 H12 Cl N3 O	C15 H12 Cl N3 O
Mr	285.73	285.73
Dx,g cm-3	1.399	1.399
Z	8	8
Mu (mm-1)	0.280	0.280
F000	1184.0	1184.0
F000'	1185.58	
h,k,lmax	28,7,23	28,7,23
Nref	2667	2666
Tmin,Tmax	0.914,0.925	0.916,0.926
Tmin'	0.914	

Correction method= MULTI-SCAN

Data completeness= 1.000 Theta(max)= 26.000

R(reflections)= 0.0329(2268) wR2(reflections)= 0.0923(2666)

S = 1.020 Npar= 183
