Supporting Information

Halogenations of 3-aryl-1*H*-pyrazol-5-amines

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CONTENTS

1. General materials and instruments

Unless otherwise noted, all synthetic steps were performed under the air atmosphere using sealed tube. The materials obtained from commercial sources were used without further purification. ^{1}H NMR, ^{13}C NMR spectra were recorded on a Brucker Advance III HD 400 MHz spectrometer in $CDCl_3$ solution. All chemical shifts were reported in ppm (δ) relative to the internal standard TMS (0 ppm). High-resolution mass spectra (HRMS) were acquired in electrospray ionization (APCI) mode using a TOF mass analyzer.

2. Characterization data of the products

4-bromo-3-phenyl-1-tosyl-1H-pyrazol-5-amine (**3a**)

Yield: 99%; Yellow solid; M.p. = 95.5-96.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.82 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.42 – 7.37 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.13 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 146.8, 145.9, 134.1, 130.9, 130.8, 130.0, 129.3, 128.3, 128.0, 127.97, 76.2, 21.8; HRMS(APCI): *m/z* calcd for $C_{16}H_{15}N_3O_2SBr$ $[M+H]^+$ 392.0068, found 392.0070.

4-bromo-3-(p-tolyl)-1-tosyl-1H-pyrazol-5-amine (**3b**)

Yield: 95%; Yellow solid; M.p. = 133.3-134.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 7.7 Hz, 2H), 5.14 (s, 2H), 2.40 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 146.9, 146.0, 139.5, 134.2, 130.1, 129.0, 128.0, 127.9, 76.3, 21.8, 21.5; HRMS(APCI): *m/z* calcd for $C_{17}H_{17}N_3O_2SBr$ $[M+H]^+$ 406.0225, found 406.0230.

4-bromo-3-(m-tolyl)-1-tosyl-1H-pyrazol-5-amine (**3c**)

Yield: 90%; Yellow solid; M.p. = 117.1-123.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 9.1 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 7.4 Hz, 1H), 7.23 – 7.17 (m, 1H), 5.14 (s, 2H), 2.40 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 146.9, 146.0, 138.1, 134.2, 130.8, 130.2, 130.1, 128.7, 128.2, 128.1, 125.2, 76.4,

21.8, 21.5; HRMS(APCI): *m/z* calcd for $C_{17}H_{17}N_3O_2SBr$ $[M+H]^+$ 406.0225, found 406.0224.

4-bromo-3-(o-tolyl)-1-tosyl-1H-pyrazol-5-amine (**3d**)

Yield: 93%; Yellow solid; M.p. = 95.3-97.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 1H), 7.13 (q, *J* = 6.7, 5.4 Hz, 3H), 5.06 (s, 2H), 2.35 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 146.5, 146.0, 137.3, 134.2, 130.4, 130.3, 130.1, 129.3, 128.1, 125.5, 76.8, 21.9, 20.0; HRMS(APCI): *m/z* calcd for $C_{17}H_{17}N_3O_2SBr$ $[M+H]^+$ 406.0225, found 406.0215.

4-bromo-3-(4-chlorophenyl)-1-tosyl-1H-pyrazol-5-amine (**3e**)

Yield: 100%; Yellow solid; M.p. = 143.1-147.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.15 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 147.0, 146.2, 135.5, 134.1, 130.2, 129.43, 129.35, 128.7, 128.1, 76.0, 21.9; HRMS(APCI): *m/z* calcd for $C_{16}H_{14}N_3O_2SClBr$ $[M+H]^+$ 425.9679, found 425.9678.

4-bromo-3-(4-methoxyphenyl)-1-tosyl-1H-pyrazol-5-amine (**3f**)

Yield: 92%; Yellow solid; M.p. = 154.5-159.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 5.13 (s, 2H), 3.82 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 152.5, 146.9, 146.0, 134.2, 130.1, 129.4, 128.1, 123.5, 113.8, 76.2, 55.4, 21.8; HRMS(APCI): *m/z* calcd for $C_{17}H_{17}N_3O_3SBr$ $[M+H]^+$ 422.0169, found 422.0165.

4-bromo-3-phenyl-1-(phenylsulfonyl)-1H-pyrazol-5-amine (**3g**)

Yield: 93%; Yellow solid; M.p. = 123.8-124.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.5, 1.3 Hz, 2H), 7.86 – 7.78 (m, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.43 – 7.36 (m, 3H), 5.18 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 147.1, 137.1, 134.7, 130.8, 129.5, 128.4, 128.03, 127.98, 76.3; HRMS(APCI): *m/z* calcd for $C_{15}H_{13}N_3O_2SBr$ $[M+H]^+$ 377.9912, found 377.9915.

4-bromo-1-(phenylsulfonyl)-3-(p-tolyl)-1H-pyrazol-5-amine (**3h**)

Yield: 92%; Yellow solid; M.p. = 113.2-116.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.2 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.20 (d, *J* = 7.6 Hz, 2H), 5.16 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 147.0, 139.5, 137.1, 134.6, 129.4, 129.1, 128.0, 127.95, 127.92, 76.4, 21.5; HRMS(APCI): *m/z* calcd for $C_{16}H_{15}N_3O_2SBr$ $[M+H]^+$ 392.0068, found 392.0067.

4-bromo-1-(phenylsulfonyl)-3-(m-tolyl)-1H-pyrazol-5-amine (**3i**)

Yield: 95%; Yellow solid; M.p. = 90.9-92.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.7 Hz, 2H), 7.66 – 7.59 (m, 3H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 5.15 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.0, 138.1, 137.2, 134.7, 130.7, 130.3, 129.5, 128.7, 128.2, 128.0, 125.2, 76.6, 21.5; HRMS(APCI): *m/z* calcd for $C_{16}H_{15}N_3O_2SBr$ $[M+H]^+$ 392.0068, found 392.0068.

4-bromo-3-(4-chlorophenyl)-1-(phenylsulfonyl)-1H-pyrazol-5-amine (**3j**)

Yield: 98%; Yellow solid; M.p. = 169.3-170.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.5, 1.2 Hz, 2H), 7.77 (d, *J* = 8.7 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 5.17 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8, 147.1, 137.1, 135.6, 134.9, 129.6, 129.3, 128.7, 128.1, 76.1; HRMS(APCI): *m/z* calcd for $C_{15}H_{12}N_3O_2SClBr$ $[M+H]^+$ 411.9522, found 411.9525.

4-bromo-1-(naphthalen-2-ylsulfonyl)-3-phenyl-1H-pyrazol-5-amine (**3k**)

Yield: 78%; Yellow solid; M.p. = 112.5-113.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.01 – 7.92 (m, 3H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.80 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.62 – 7.58 (m, 1H), 7.43 – 7.34 (m, 3H), 5.22 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 147.0, 135.7, 133.9, 132.0, 130.8, 130.1, 129.93, 129.92, 129.8, 129.5, 128.3, 128.1, 128.0, 122.4, 76.4; HRMS(APCI): *m/z* calcd for $C_{19}H_{15}N_3O_2SBr$ $[M+H]^+$ 428.0068, found 428.0065.

4-bromo-1-((4-(tert-butyl)phenyl)sulfonyl)-3-phenyl-1H-pyrazol-5-amine (**3l**)

Yield: 60%; Yellow solid; M.p. = 217.6-222.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.7 Hz, 2H), 7.88 – 7.80 (m, 2H), 7.54 (d, *J* = 8.7 Hz, 2H), 7.39 (dd, *J* = 5.1, 2.0 Hz, 3H), 5.14 (s, 2H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 152.6, 146.9, 134.2, 131.0, 129.5, 128.4, 128.1, 128.0, 126.6, 76.3, 35.5, 31.1; HRMS(APCI): *m/z* calcd for $C_{19}H_{21}N_3O_2SBr$ $[M+H]^+$ 434.0538, found 434.0541.

4-bromo-3-phenyl-1H-pyrazol-5-amine (**3m)**

Yield: 70%; Yellow solid; M.p. = 107.6-109.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.46 – 7.36 (m, 3H), 3.75 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7, 141.8, 129.2, 129.1, 129.0, 127.2, 80.2. HRMS(APCI): *m/z* calcd for $C_9H_9N_3Br$ $[M+H]^+$ 237.9980, found 237.9985

methyl 5-amino-4-bromo-3-phenyl-1H-pyrazole-1-carboxylate (**3n**)

Yield: 80%; Yellow solid; M.p. = 127.6-129.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.80 (m, 2H), 7.50 – 7.34 (m, 3H), 5.52 (s, 2H), 4.07 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 151.9, 148.2, 131.1, 129.5, 128.5, 128.2, 75.5, 54.9; HRMS(APCI): *m/z* calcd for $C_{11}H_{11}N_3O_2Br$ $[M+H]^+$ 296.0029, found 296.0023.

4-iodo-3-phenyl-1-tosyl-1H-pyrazol-5-amine (**4a**)

Yield: 100%; Red solid; M.p. = 124.1-126.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.82 – 7.67 (m, 2H), 7.42 – 7.35 (m, 3H), 7.31 (d, *J* = 8.2 Hz, 2H), 5.24 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 149.6, 146.0, 134.1, 131.6, 130.1, 129.3, 128.4, 128.2, 128.1, 43.0, 21.8; HRMS(APCI): *m/z* calcd for $C_{16}H_{15}N_3O_2SI$ $[M+H]^+$ 439.9930, found 439.9934.

4-iodo-3-(p-tolyl)-1-tosyl-1H-pyrazol-5-amine (**4b**)

Yield: 98%; Red solid; M.p. = 143.4-144.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 5.22 (s, 2H), 2.40 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 149.6, 149.6, 145.9, 139.4, 134.2, 130.1, 129.0, 128.8, 128.3, 128.1, 43.1, 21.8, 21.5; HRMS(APCI): *m/z*

calcd for $C_{17}H_{17}N_3O_2SI$ $[M+H]^+$ 454.0086, found 454.0092.

4-iodo-3-(m-tolyl)-1-tosyl-1H-pyrazol-5-amine (**4c**)

Yield: 91%; Red solid; M.p. = 139.0-140.8 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 5.13 (s, 2H), 2.31 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 149.6, 146.0, 138.0, 134.2, 131.5, 130.12, 130.09, 129.0, 128.1, 128.0, 125.6, 77.5, 77.2, 76.8, 43.2, 21.8, 21.5; HRMS(APCI): *m/z* calcd for $C_{17}H_{17}N_3O_2SI$ $[M+H]^+$ 454.0086, found 454.0086.

4-iodo-3-(o-tolyl)-1-tosyl-1H-pyrazol-5-amine (**4d**)

Yield: 95%; Red solid; M.p. = 137.6-138.7 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.18 (dd, *J* = 5.5, 2.6 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 3H), 5.13 (s, 2H), 2.34 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 149.4, 146.0, 137.2, 134.3, 131.4, 130.3, 130.09, 130.07, 129.3, 128.1, 125.4, 46.3, 21.9, 20.0; HRMS(APCI): *m/z* calcd for $C_{17}H_{17}N_3O_2SI$ $[M+H]^+$ 454.0086, found 454.0084.

3-(4-chlorophenyl)-4-iodo-1-tosyl-1H-pyrazol-5-amine (**4e**)

Yield: 99%; Red solid; M.p. = 138.7-141.8 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 5.23 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 149.74, 149.72, 146.2, 135.4, 134.1, 130.19, 130.17, 129.7, 128.6, 128.1, 42.7, 21.9; HRMS(APCI): *m/z* calcd for $C_{16}H_{14}N_3O_2SCII$ $[M+H]^+$ 473.9540, found 473.9537.

4-iodo-3-(4-methoxyphenyl)-1-tosyl-1H-pyrazol-5-amine (**4f**)

Yield: 98%; Red solid; M.p. = 139.6-143.6 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.9 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 5.21 (s, 2H), 3.81 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 154.7, 149.6, 145.9, 134.2, 130.1, 129.8, 128.1, 124.2, 113.7, 55.4, 43.0, 21.8; HRMS(APCI): *m/z* calcd for $C_{17}H_{17}N_3O_3SI$ $[M+H]^+$ 470.0035, found 470.0034.

4-iodo-3-phenyl-1-(phenylsulfonyl)-1H-pyrazol-5-amine (**4g**)

Yield: 92%; Red solid; M.p. = 130.5-132.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 7.94 (m, 2H), 7.75 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.44 – 7.35 (m, 3H), 5.25 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 149.7, 137.1, 134.7, 131.6, 129.5, 129.4, 128.4, 128.3, 128.0, 43.2; HRMS(APCI): *m/z* calcd for $C_{17}H_{17}N_3O_3SI$ $[M+H]^+$ 425.9773, found 425.9773.

4-iodo-1-(phenylsulfonyl)-3-(p-tolyl)-1H-pyrazol-5-amine (**4h**)

Yield: 95%; Red solid; M.p. = 129.4-131.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.5, 1.2 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.20(d, *J* = 7.8 Hz, 2H) 5.24 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 149.7, 139.4, 137.1, 134.6, 129.4, 129.0, 128.7, 128.3, 128.0, 43.2, 21.5; HRMS(APCI): *m/z* calcd for $C_{16}H_{15}N_3O_2SI$ $[M+H]^+$ 439.9930, found 439.9931.

4-iodo-1-(phenylsulfonyl)-3-(m-tolyl)-1H-pyrazol-5-amine (**4i**)

Yield: 99%; Red solid; M.p. = 98.7-99.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.7 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.44 (dd, *J* = 14.3, 6.4 Hz, 4H), 7.19 (t, *J* = 8.3 Hz, 1H), 7.11 (d, *J* = 7.5 Hz, 1H), 5.15 (s, 2H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4, 149.7, 138.0, 137.1, 134.7, 131.4, 130.2, 129.5, 129.0, 128.1, 128.0, 125.6, 43.4, 21.5; HRMS(APCI): *m/z* calcd for $C_{16}H_{15}N_3O_2SI$ $[M+H]^+$ 439.9930, found 439.9938.

3-(4-chlorophenyl)-4-iodo-1-(phenylsulfonyl)-1H-pyrazol-5-amine (**4j**)

Yield: 99%; Red solid; M.p. = 160.3-165.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.98 (m, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 5.26 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 149.8, 137.0, 135.5, 134.8, 130.0, 129.7, 129.5, 128.5, 128.0, 42.8; HRMS(APCI): *m/z* calcd for $C_{15}H_{12}N_3O_2SCII$ $[M+H]^+$ 459.9385, found 459.9396.

4-iodo-1-(naphthalen-2-ylsulfonyl)-3-phenyl-1H-pyrazol-5-amine (**4k**)

Yield: 79%; Red solid; M.p. = 60.5-65.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.02 – 7.93 (m, 3H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.76 – 7.70 (m, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 6.8 Hz, 1H), 7.40 – 7.35 (m, 3H), 5.29 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 149.7, 135.7, 134.0, 132.0, 131.6, 130.2, 129.93, 129.91, 129.8, 129.4, 128.5, 128.3, 128.1, 128.0, 122.4, 43.3.; HRMS(APCI): *m/z* calcd for $C_{19}H_{15}N_3O_2SI$ $[M+H]^+$ 475.9930, found 475.9935.

1-((4-(tert-butyl)phenyl)sulfonyl)-4-iodo-3-phenyl-1H-pyrazol-5-amine (**4l**)

Yield: 62%; Red solid; M.p. = 191.7-197.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.8 Hz, 2H), 7.81 – 7.74 (m, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.40 (dd, *J* = 5.1, 1.8 Hz, 3H), 5.23 (s, 2H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 154.9, 149.6, 134.2, 131.7, 129.4, 128.5, 128.3, 128.0, 126.6, 43.1, 35.5, 31.1; HRMS(APCI): *m/z* calcd for $C_{19}H_{21}N_3O_2SI$ $[M+H]^+$ 482.0399, found 482.0405.

4-iodo-3-phenyl-1H-pyrazol-5-amine (**4m**)

Yield: 80%; Brown solid; M.p. = 120.7-123.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.50 – 7.38 (m, 3H), 5.46 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 145.1, 129.9, 129.3, 129.0, 127.7, 47.2; HRMS(APCI): *m/z* calcd for $C_9H_9N_3I$ $[M+H]^+$ 285.9836, found 285.9831.

methyl 5-amino-4-iodo-3-phenyl-1H-pyrazole-1-carboxylate (**4n**)

Yield: 82%; Brown solid; M.p. = 132.5-136.9, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.74 (m, 2H), 7.41 (dd, *J* = 5.0, 2.2 Hz, 3H), 5.62 (s, 2H), 4.05 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 151.7, 151.1, 131.8, 129.3, 128.5, 128.3, 54.9, 42.0; HRMS(APCI): *m/z* calcd for $C_{11}H_{11}N_3O_2I$ $[M+H]^+$ 343.9890, found 343.9885.

4-chloro-3-phenyl-1-tosyl-1H-pyrazol-5-amine (**5a**)

Yield: 69%; Pale yellow solid; M.p. = 121.3-123.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.5 Hz, 2H), 7.88 – 7.81 (m, 2H), 7.39 (dd, *J* = 5.1, 2.0 Hz, 3H), 7.32 (d, *J* = 8.1 Hz, 2H), 5.09 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.7, 146.1, 145.6, 134.2,

130.6, 130.1, 129.5, 128.4, 128.1, 127.8, 91.0, 21.9; HRMS(APCI): *m/z* calcd for $C_{16}H_{15}N_3O_2SCl$ $[M+H]^+$ 348.0574, found 348.0580.

4-chloro-3-(p-tolyl)-1-tosyl-1H-pyrazol-5-amine (**5b**)

Yield: 60%; Pale yellow solid; M.p. = 145.3-151.0 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.06 (s, 2H), 2.41 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8, 146.0, 145.6, 139.5, 134.2, 130.1, 129.1, 128.1, 127.7, 91.1, 21.9, 21.5; HRMS(APCI): *m/z* calcd for $C_{17}H_{17}N_3O_2SCl$ $[M+H]^+$ 362.0730, found 362.0729.

4-chloro-3-(m-tolyl)-1-tosyl-1H-pyrazol-5-amine (**5c**)

Yield: 55%; Pale yellow solid; M.p. = 152.1-155.4 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 12.0 Hz, 2H), 7.27 (d, *J* = 10.3 Hz, 2H), 7.23 (d, *J* = 8.9 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 5.03 (s, 2H), 2.37 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 146.0, 145.6, 138.2, 134.2, 130.4, 130.3, 130.1, 128.4, 128.3, 128.1, 125.0, 91.2, 21.9, 21.5; HRMS(APCI): *m/z* calcd for $C_{17}H_{17}N_3O_2SCl$ $[M+H]^+$ 362.0730, found 362.0731.

4-chloro-3-(4-methoxyphenyl)-1-tosyl-1H-pyrazol-5-amine (**5d**)

Yield: 72%; Pale yellow solid; M.p. = 120.6-123.7 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 8.9 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 5.06 (s, 2H), 3.81 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 151.5, 145.9, 145.6, 134.2, 130.1, 129.2, 128.0, 123.1, 113.8, 90.8, 55.4, 21.8; HRMS(APCI): *m/z* calcd for $C_{17}H_{17}N_3O_3SCl$ $[M+H]^+$ 378.0679, found 378.0681.

4-chloro-3-(4-chlorophenyl)-1-tosyl-1H-pyrazol-5-amine (**5e**)

Yield: 59%; Pale yellow solid; M.p. = 157.2-160.1 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 5.09 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 146.2, 145.7, 135.5, 134.1, 130.2, 129.1, 128.7, 128.1, 90.8, 21.9; HRMS(APCI): *m/z* calcd for $C_{16}H_{14}N_3O_2SCl_2$

$[M+H]^+$ 382.0184, found 382.0182.

4-chloro-3-phenyl-1-(phenylsulfonyl)-1H-pyrazol-5-amine (**5f**)

Yield: 60%; Pale yellow solid; M.p. = 150.6-152.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.4, 1.1 Hz, 2H), 7.89 – 7.77 (m, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.39 (dd, *J* = 5.1, 1.8 Hz, 3H), 5.09 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 145.7, 137.2, 134.7, 130.5, 129.6, 129.5, 128.5, 128.0, 127.8, 91.2; HRMS(APCI): *m/z* calcd for $C_{15}H_{13}N_3O_2SCl$ $[M+H]^+$ 334.0417, found 334.0416.

4-chloro-3-(4-chlorophenyl)-1-(phenylsulfonyl)-1H-pyrazol-5-amine (**5g**)

Yield: 48%; Pale yellow solid; M.p. = 146.4-148.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.3 Hz, 2H), 7.80 (d, *J* = 8.7 Hz, 2H), 7.65 (d, *J* = 8.7 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 5.10 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.7, 145.8, 137.1, 135.6, 134.9, 129.6, 129.1, 129.0, 128.7, 128.1, 91.0; HRMS(APCI): *m/z* calcd for $C_{15}H_{12}N_3O_2SCl_2$ $[M+H]^+$ 368.0027, found 368.0032.

4-chloro-1-(naphthalen-2-ylsulfonyl)-3-phenyl-1H-pyrazol-5-amine (**5h**)

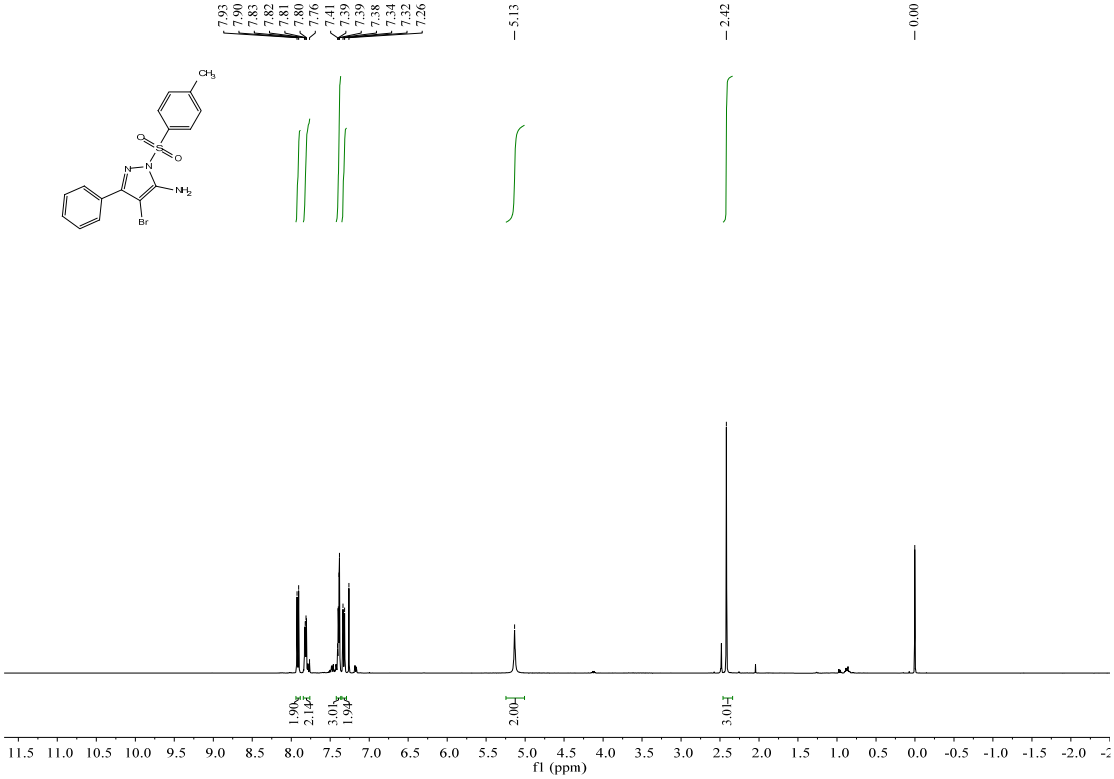
Yield: 32%; Pale yellow solid; M.p. = 102.4-104.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.97 (d, *J* = 1.7 Hz, 2H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.82 (dd, *J* = 6.7, 3.1 Hz, 2H), 7.72 – 7.59 (m, 2H), 7.39 – 7.34 (m, 3H), 5.14 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 145.7, 135.8, 134.0, 132.0, 130.5, 130.2, 130.0, 129.9, 129.8, 129.5, 128.4, 128.1, 128.0, 127.9, 122.4; HRMS(APCI): *m/z* calcd for $C_{19}H_{15}N_3O_2SCl$ $[M+H]^+$ 384.0574, found 384.0574.

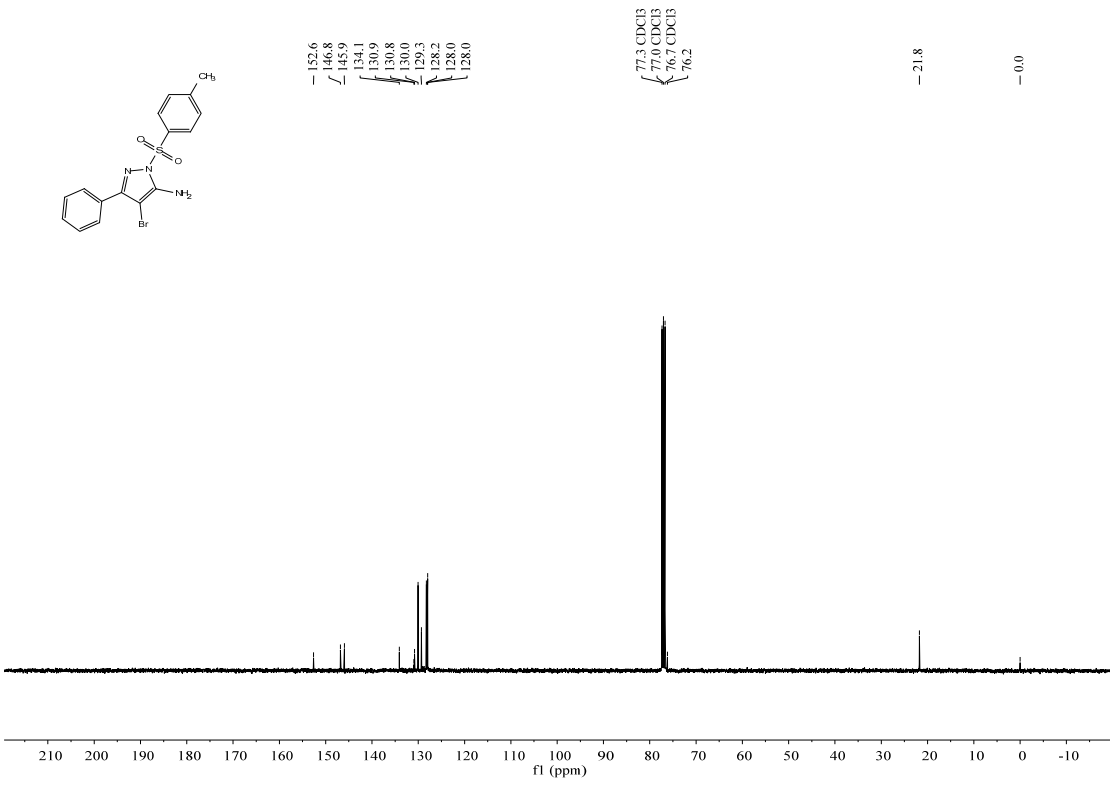
1-phenyl-3H-pyrazolo[3,4-e]pyrrolo[1,2-a]pyrazine (**4aa**)

Yield: 36%; White solid; M.p. = 102.4-104.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.85 (s, 1H), 8.73 (s, 1H), 7.78 (d, *J* = 6.8 Hz, 2H), 7.72 (d, *J* = 2.6 Hz, 1H), 7.57 (t, *J* = 7.3 Hz, 2H), 7.51 (d, *J* = 7.3 Hz, 1H), 7.03 (dd, *J* = 4.2, 1.2 Hz, 1H), 6.78 (dd, *J* = 4.2, 2.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 132.5, 129.12, 129.05, 128.9, 127.2, 116.7, 113.7, 110.8, 108.4; HRMS(APCI): *m/z* calcd for $C_{14}H_{14}N_4[M+H]^+$ 235.0978, found 235.0976.

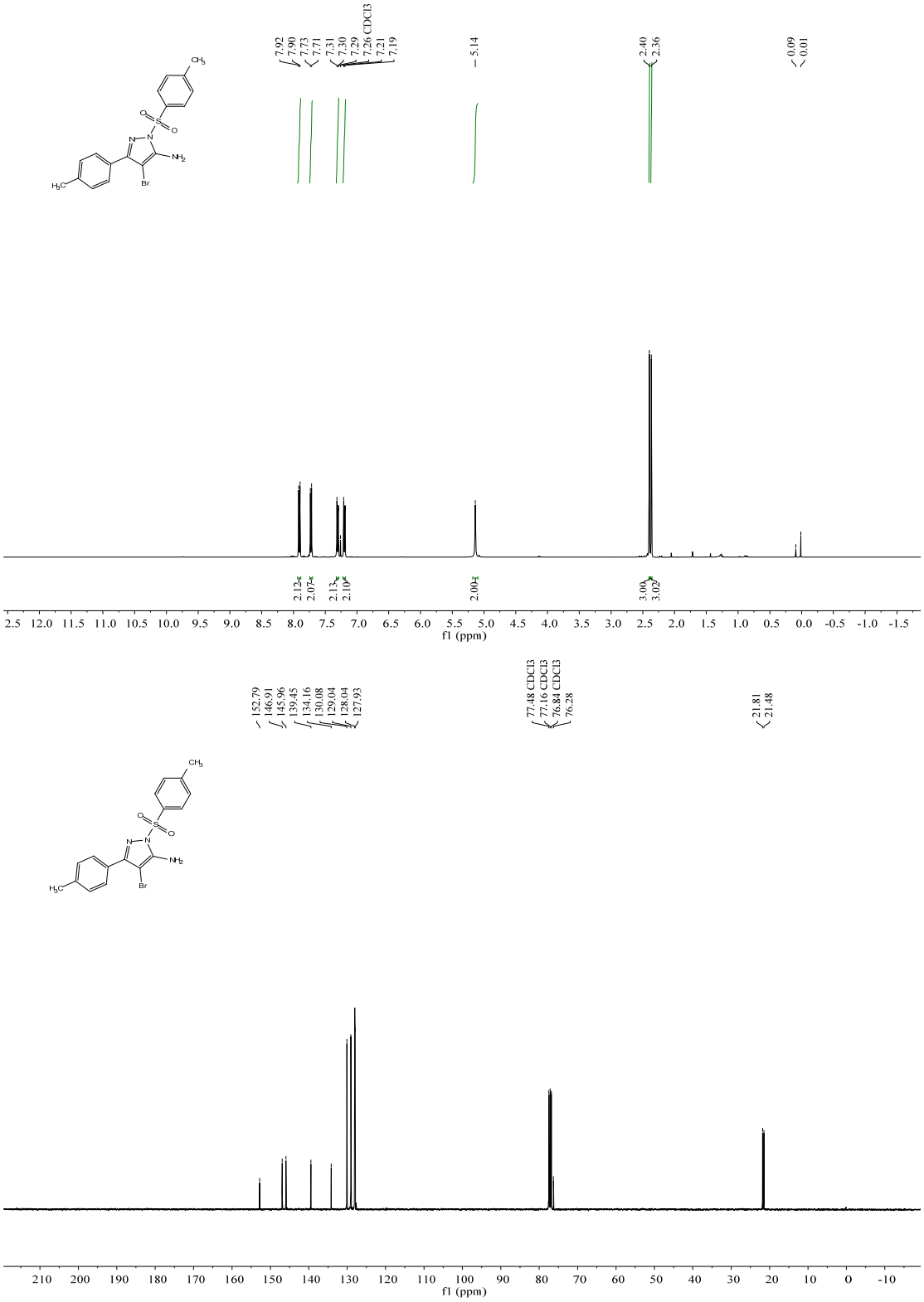
3. ^{1}H NMR、^{13}C NMR spectra of the products

4-bromo-3-phenyl-1-tosyl-1H-pyrazol-5-amine (**3a**)

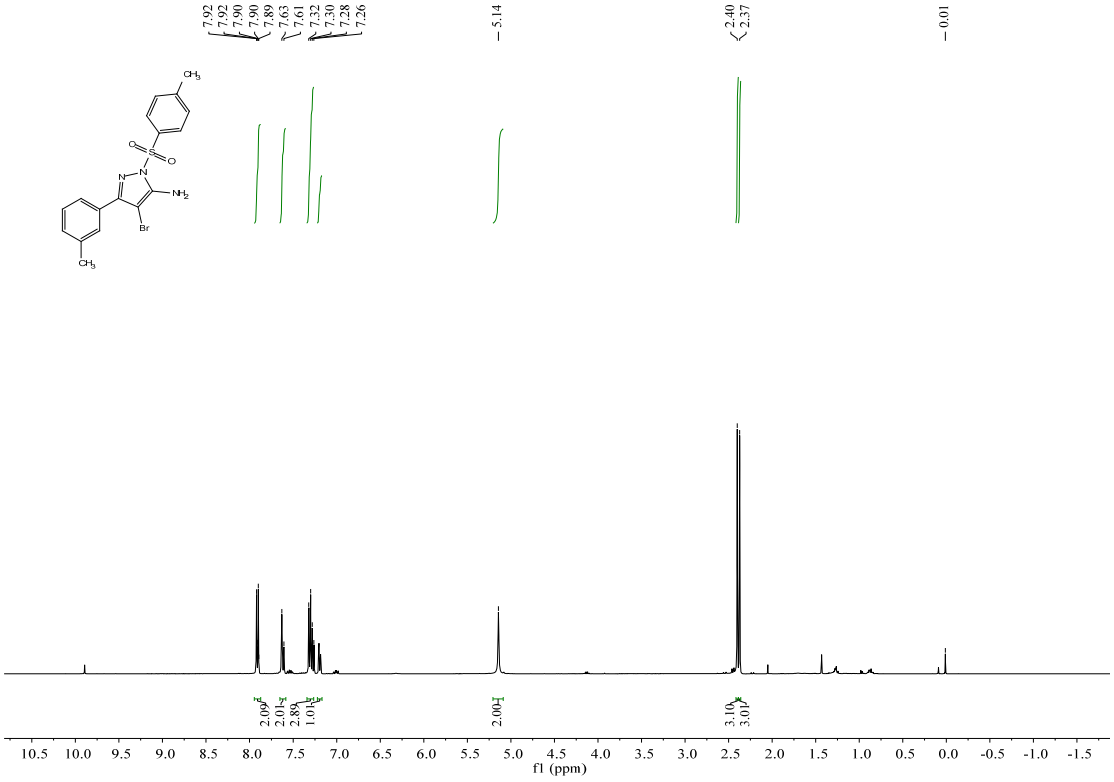


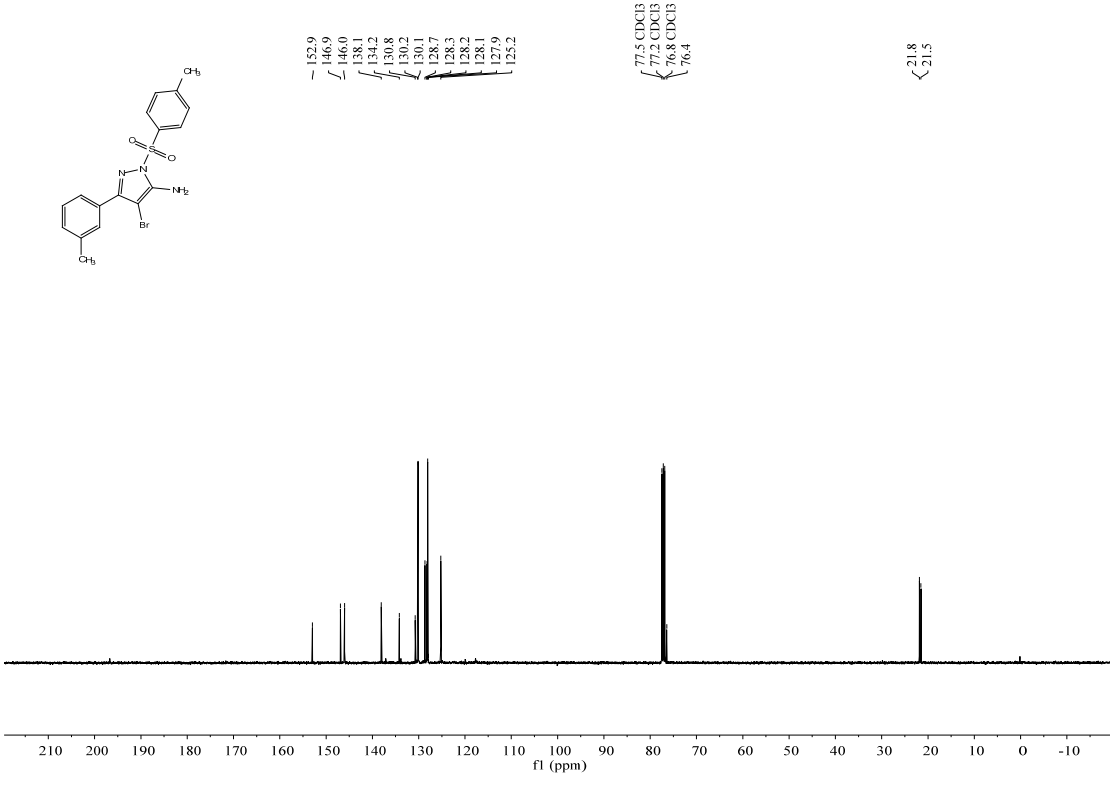


4-bromo-3-(p-tolyl)-1-tosyl-1H-pyrazol-5-amine (**3b**)

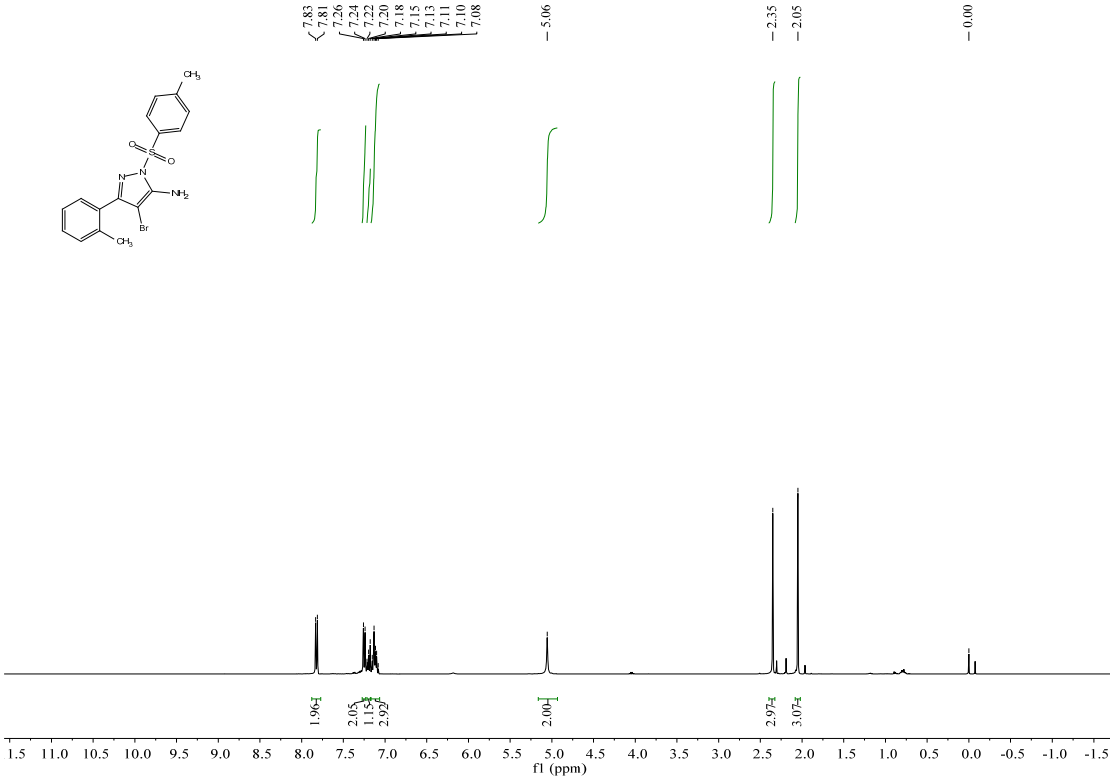


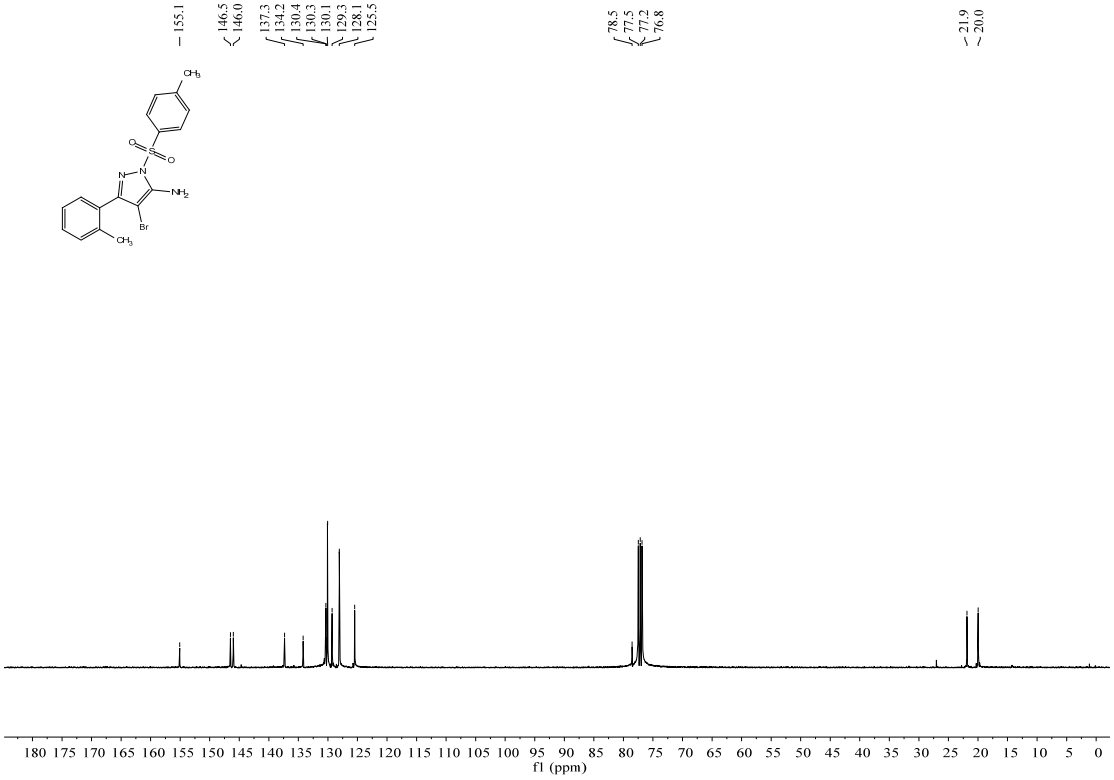
4-bromo-3-(m-tolyl)-1-tosyl-1H-pyrazol-5-amine (**3c**)



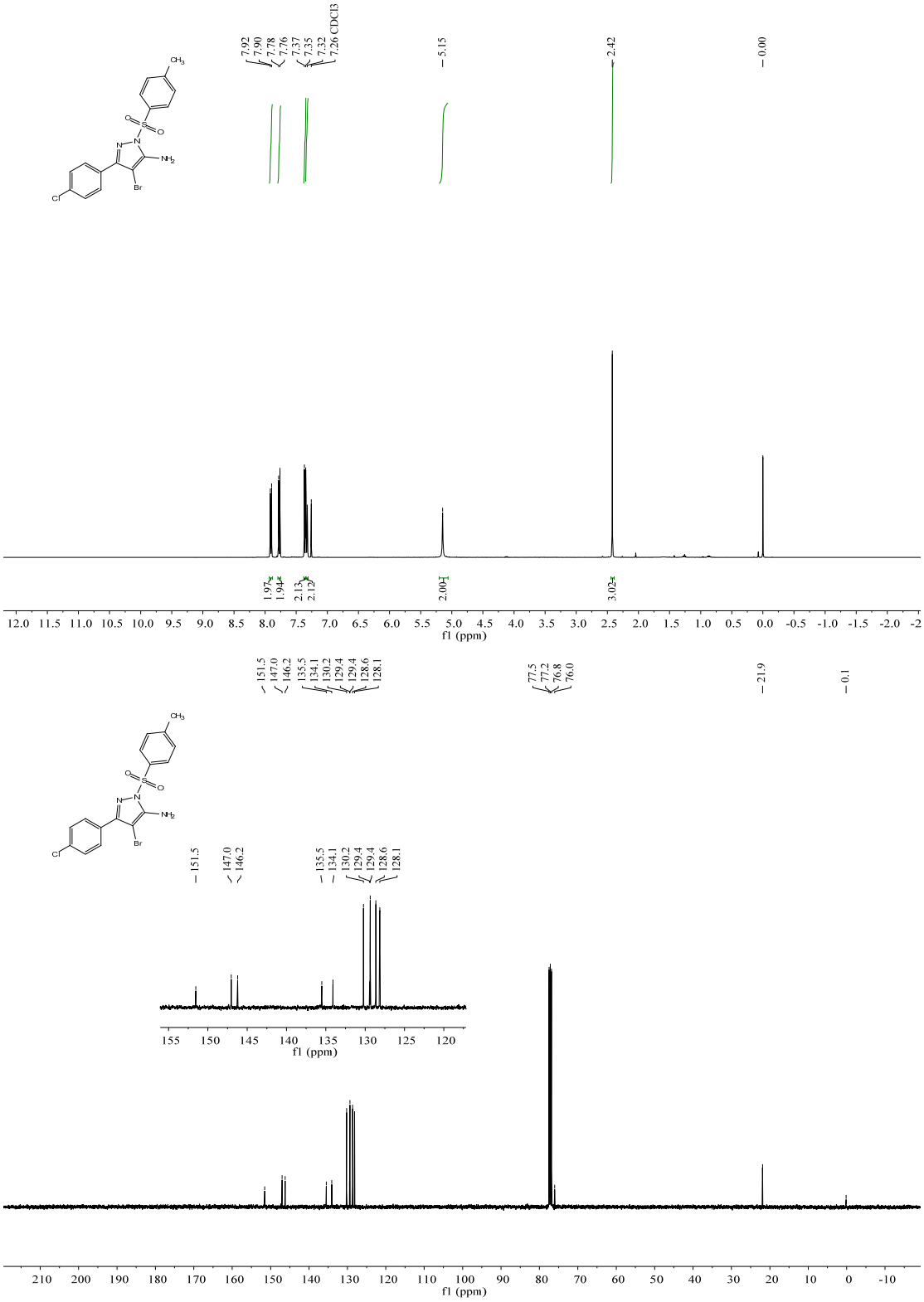


4-bromo-3-(o-tolyl)-1-tosyl-1H-pyrazol-5-amine (**3d**)

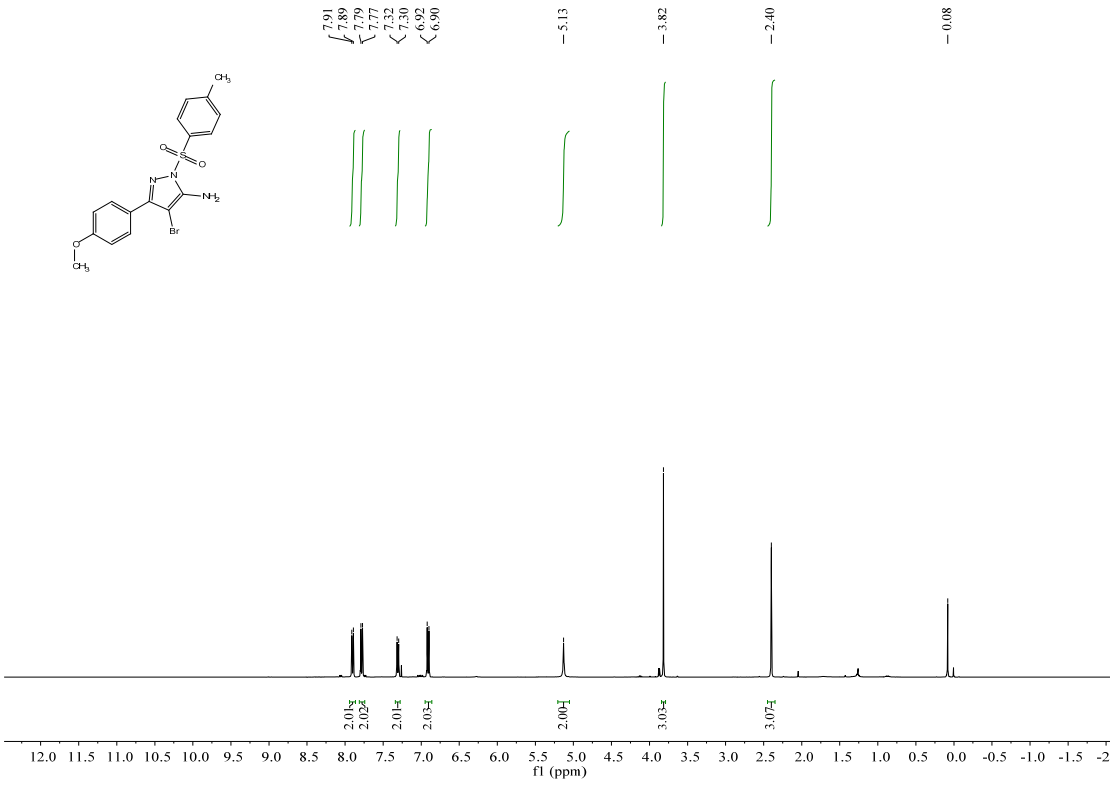


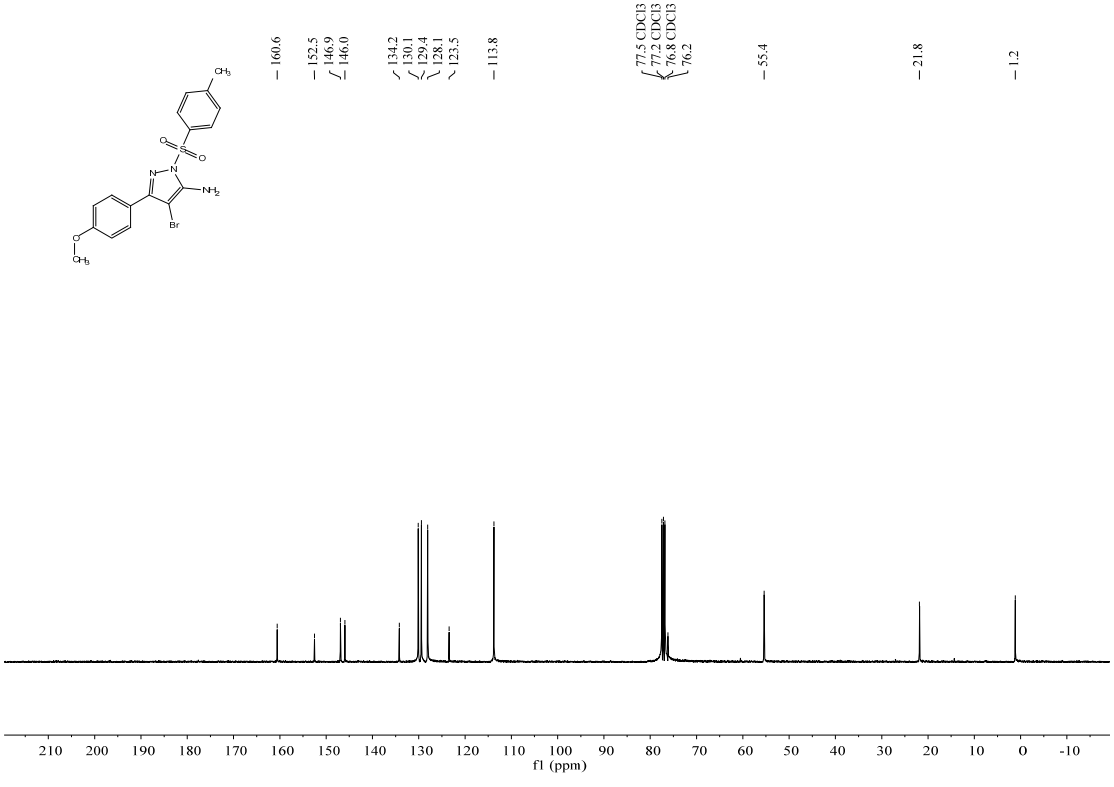


4-bromo-3-(4-chlorophenyl)-1-tosyl-1H-pyrazol-5-amine (**3e**)

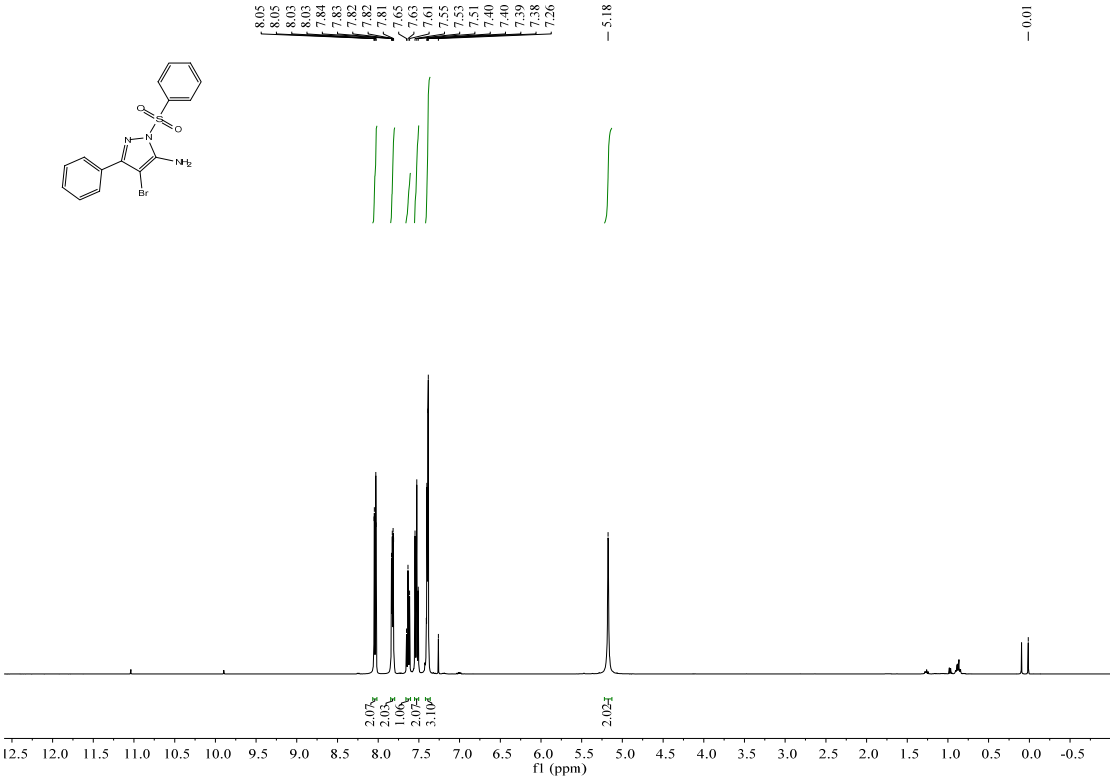


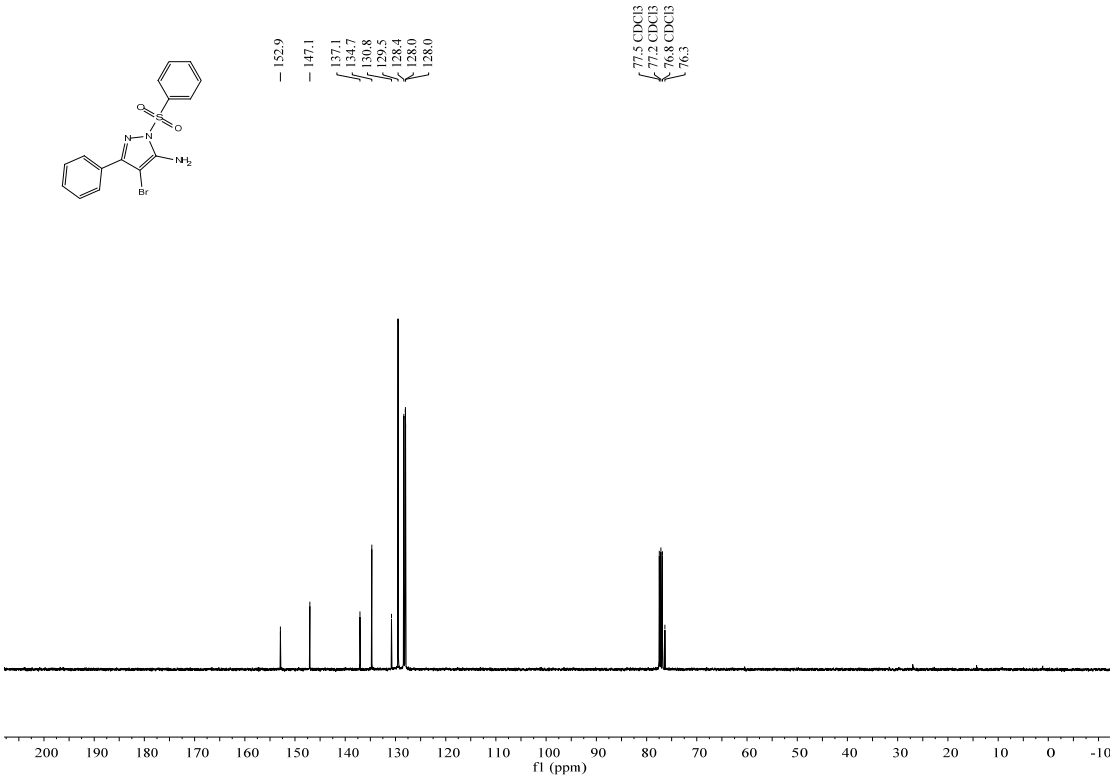
4-bromo-3-(4-methoxyphenyl)-1-tosyl-1H-pyrazol-5-amine (**3f**)



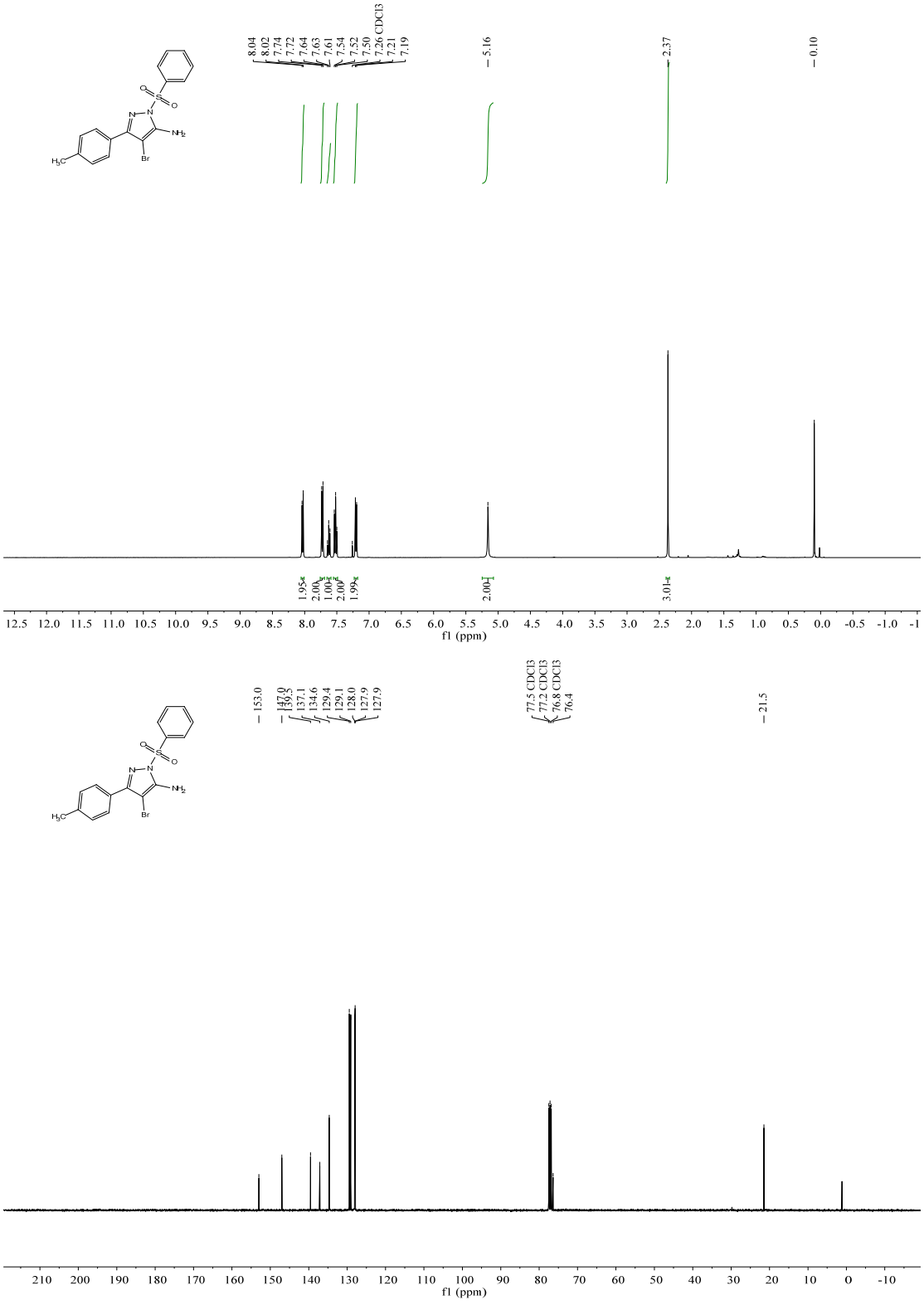


4-bromo-3-phenyl-1-(phenylsulfonyl)-1H-pyrazol-5-amine (**3g**)

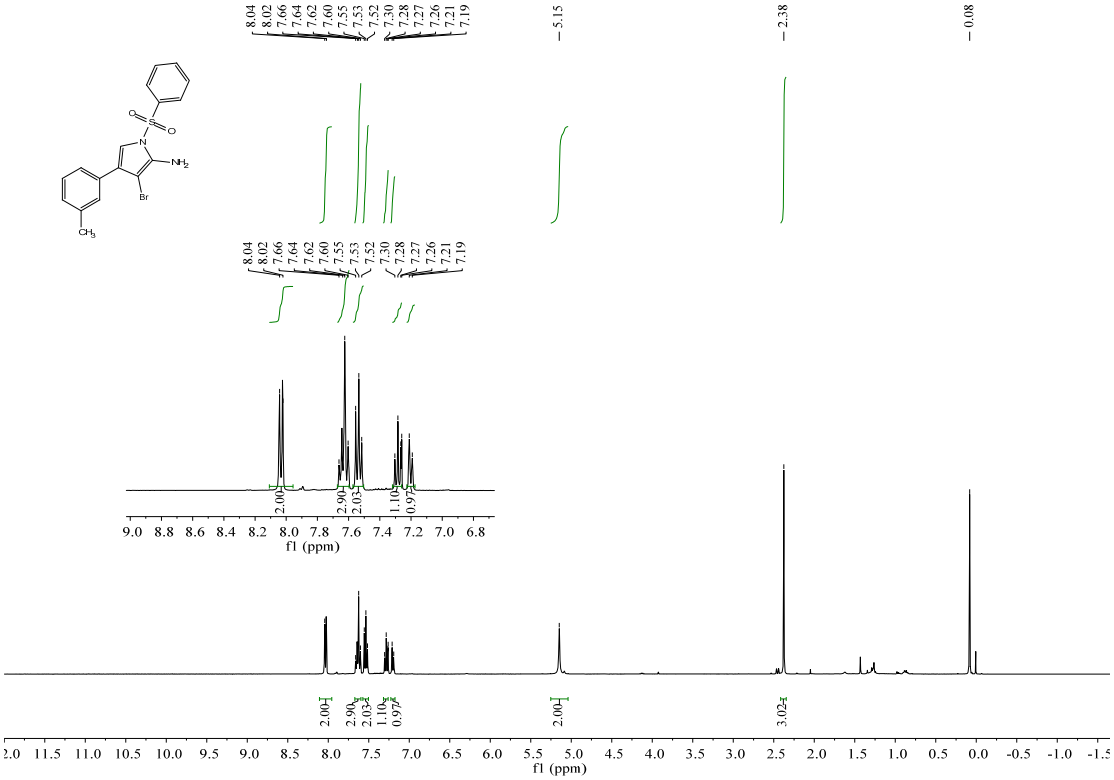


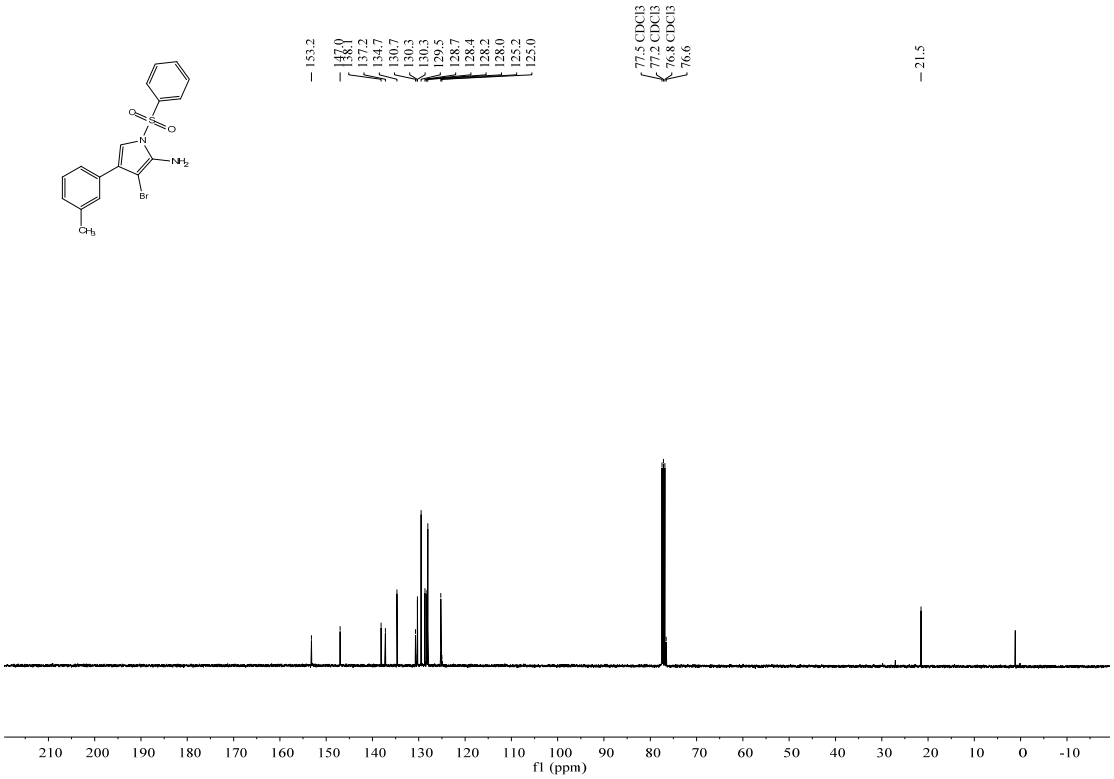


4-bromo-1-(phenylsulfonyl)-3-(p-tolyl)-1H-pyrazol-5-amine (**3h**)

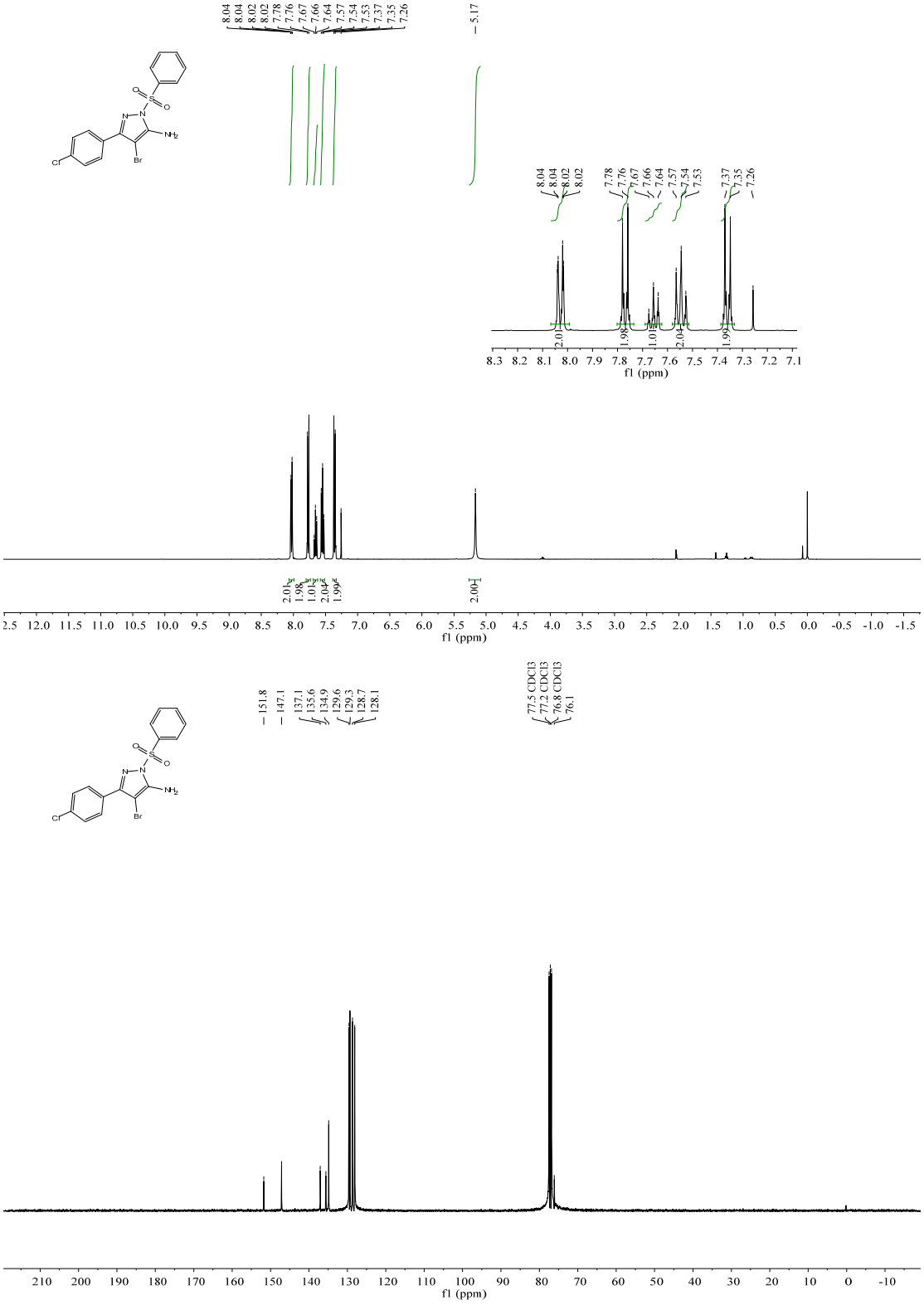


4-bromo-1-(phenylsulfonyl)-3-(m-tolyl)-1H-pyrazol-5-amine (**3i**)

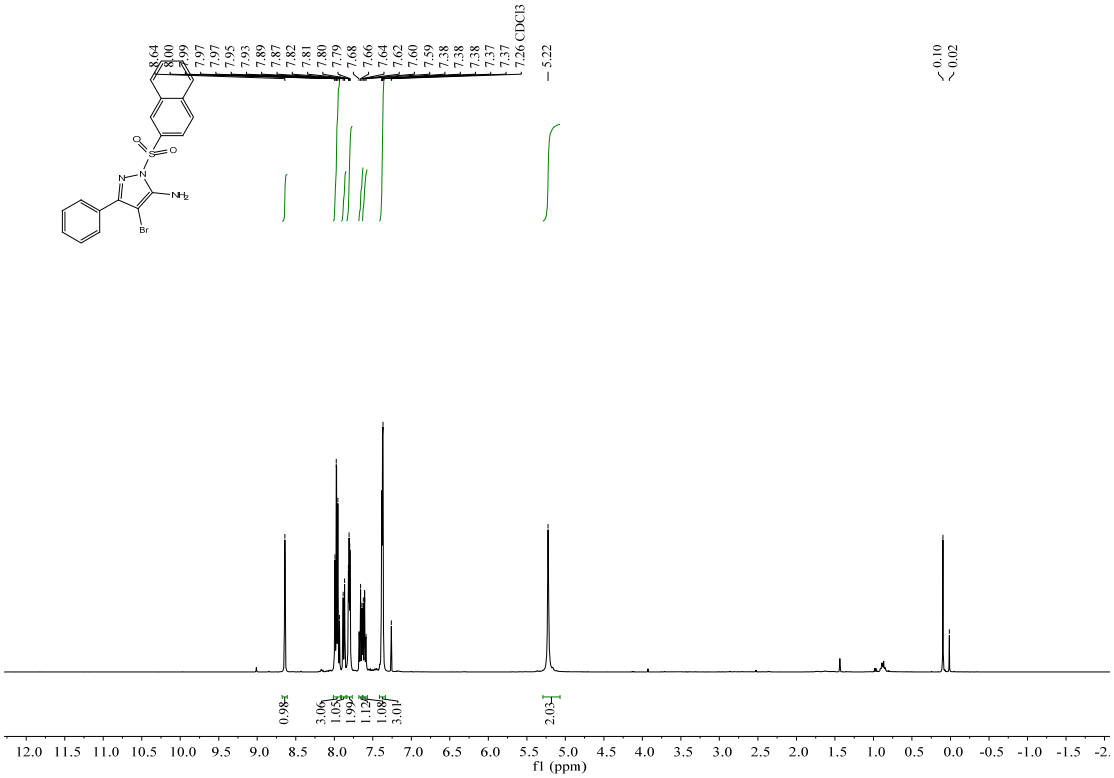


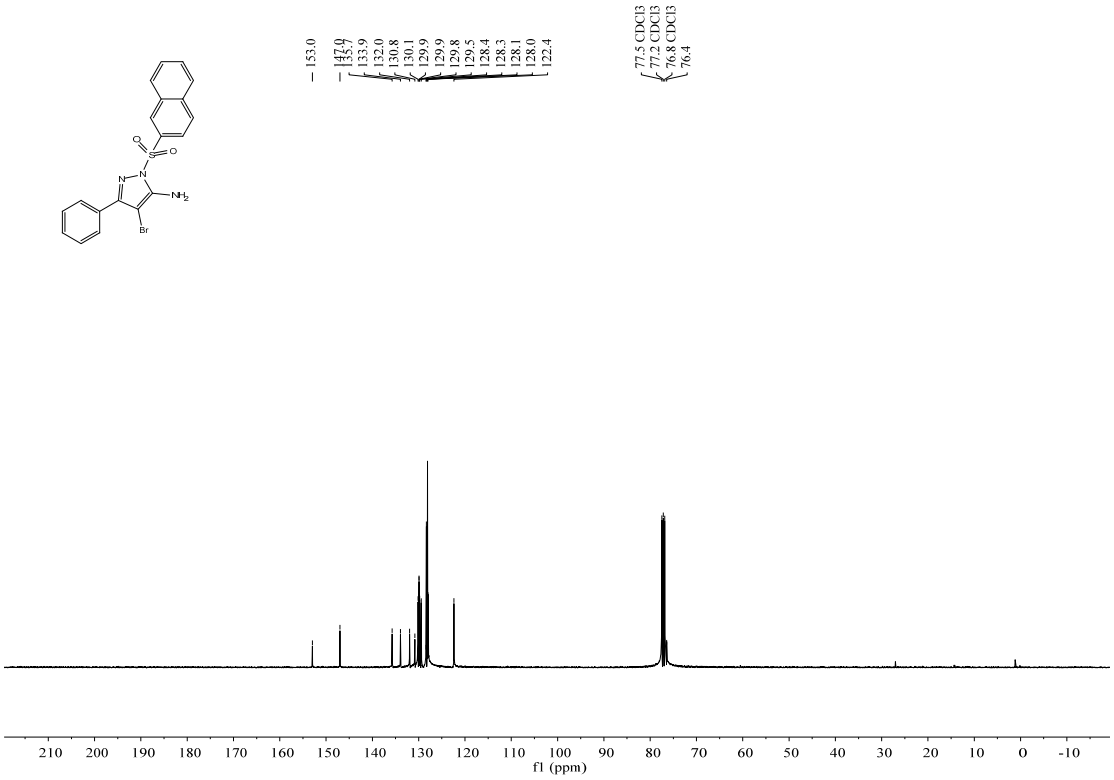


4-bromo-3-(4-chlorophenyl)-1-(phenylsulfonyl)-1H-pyrazol-5-amine (**3j**)

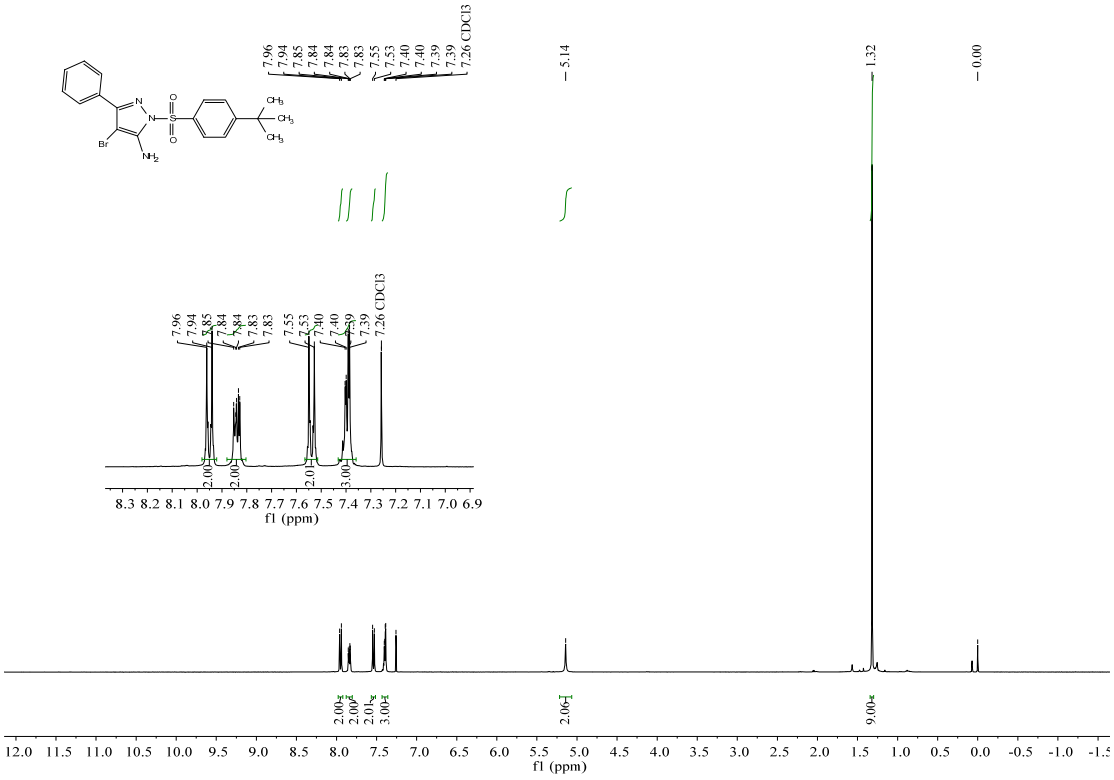


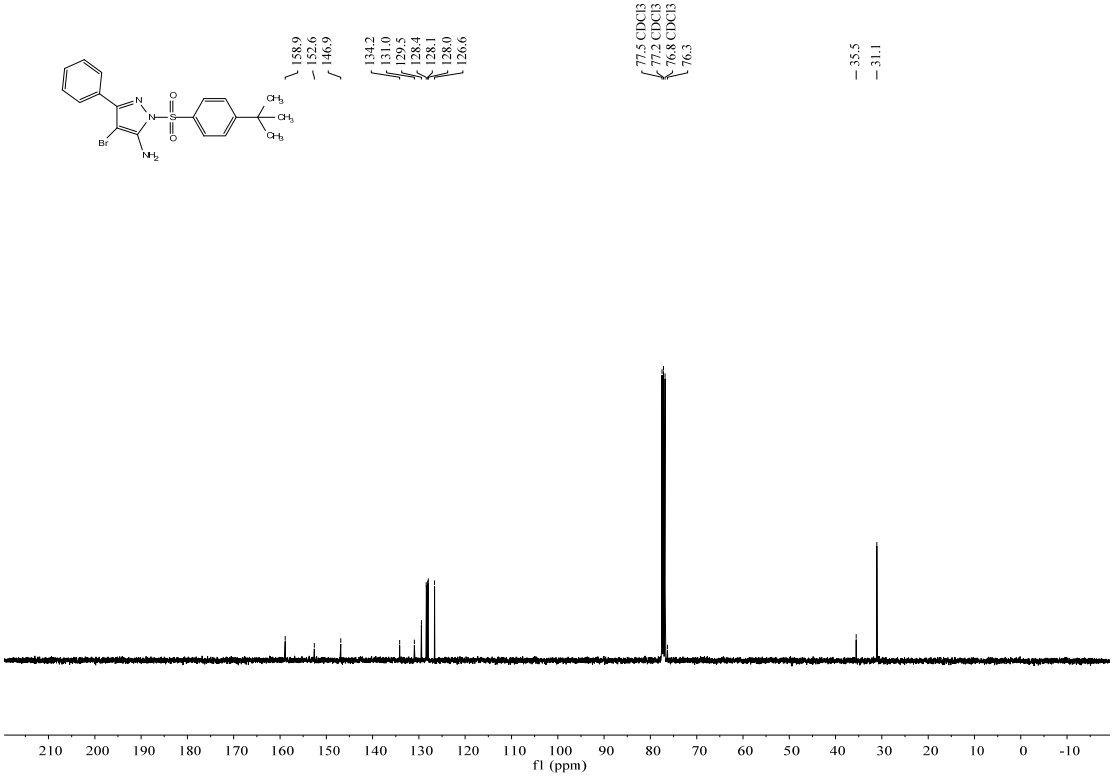
4-bromo-1-(naphthalen-2-ylsulfonyl)-3-phenyl-1H-pyrazol-5-amine (**3k**)



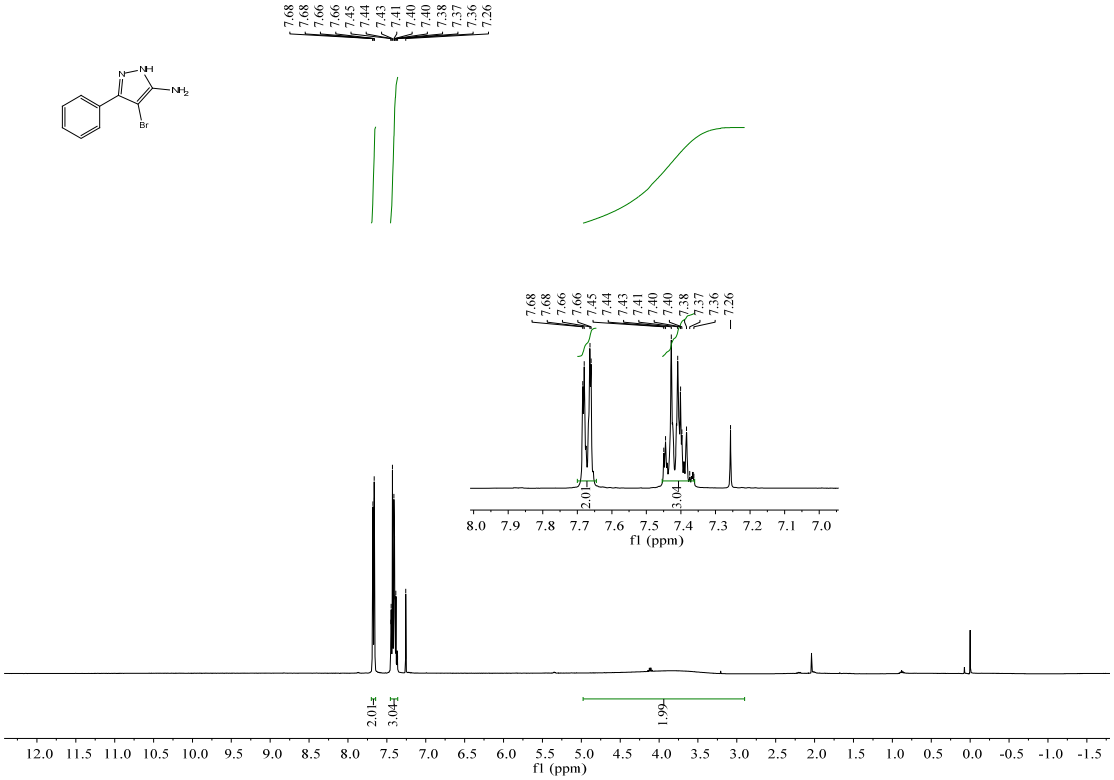


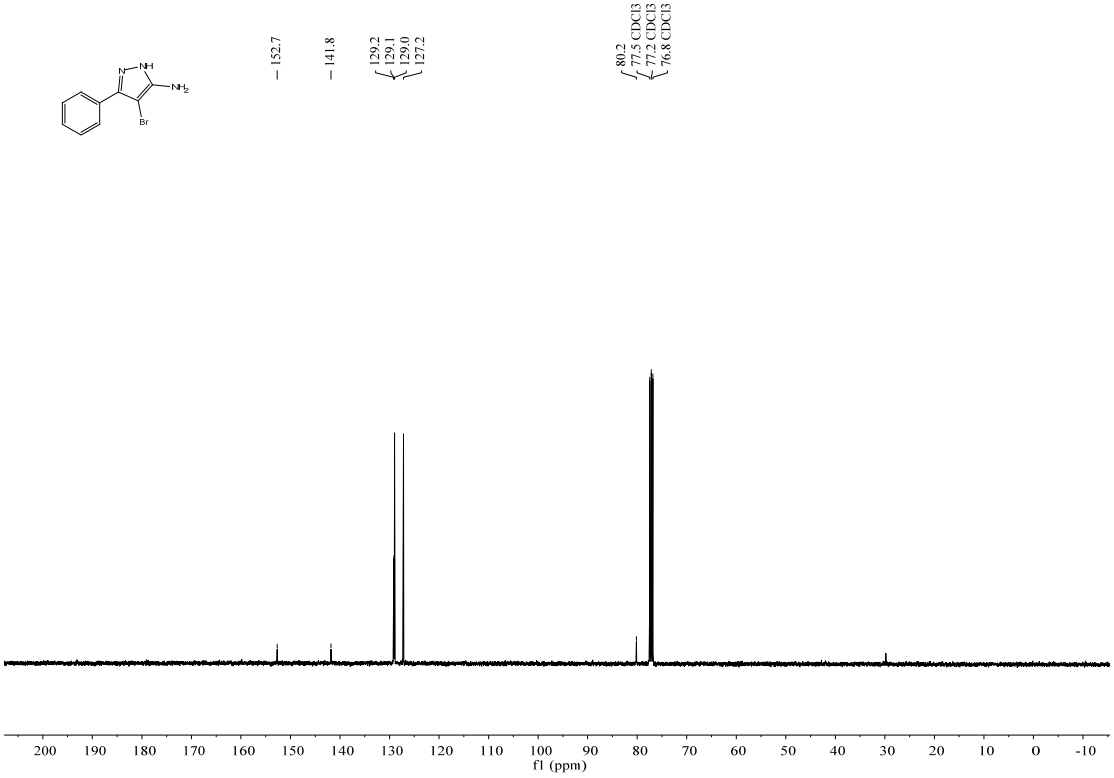
4-bromo-1-((4-(tert-butyl)phenyl)sulfonyl)-3-phenyl-1H-pyrazol-5-amine (**3l**)



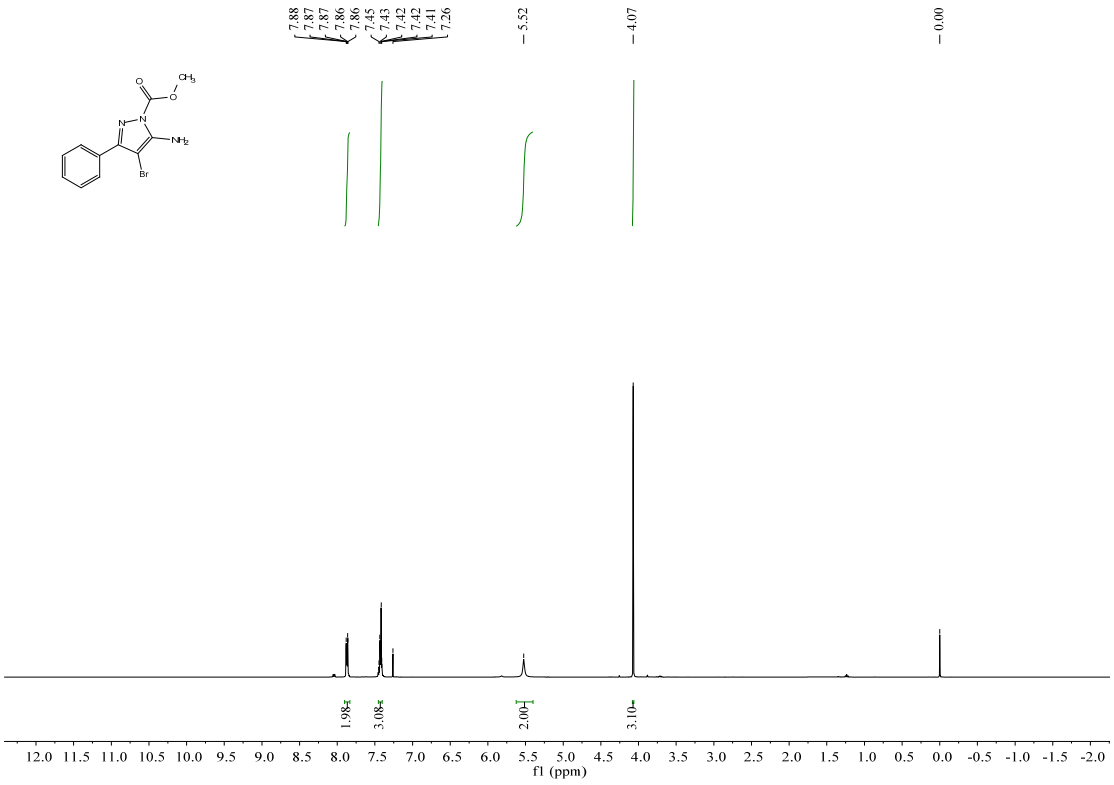


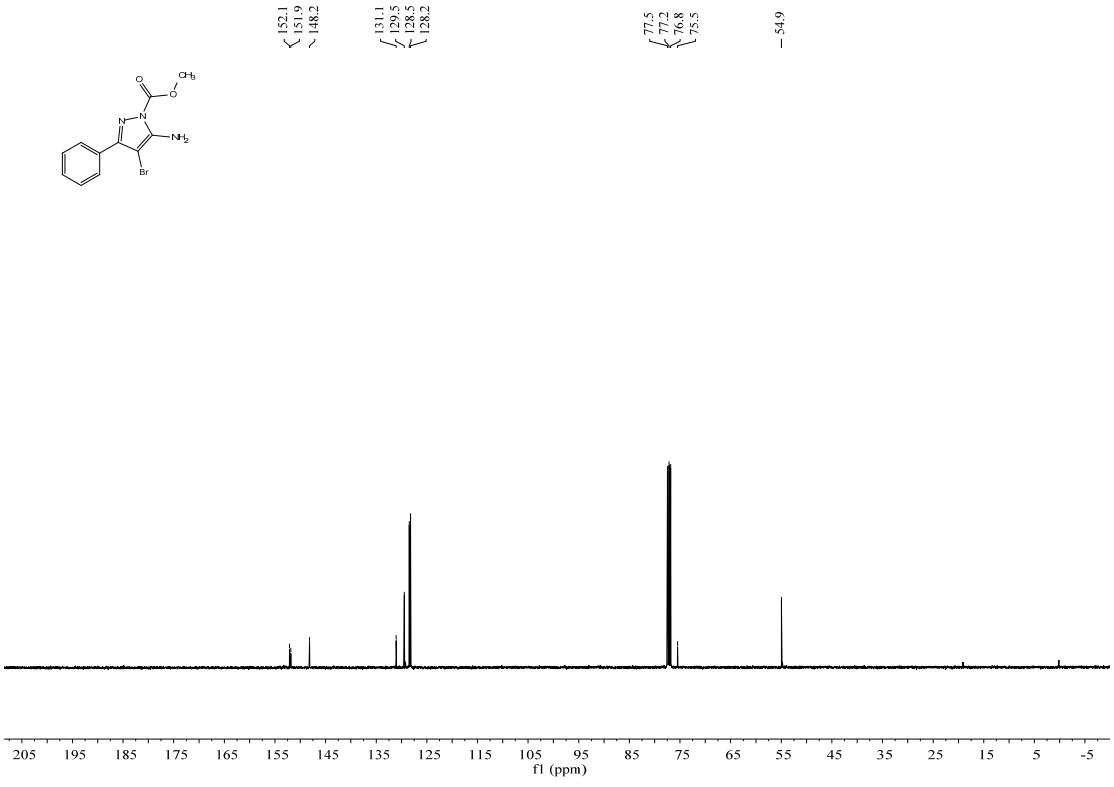
4-bromo-3-phenyl-1H-pyrazol-5-amine (**3m**)



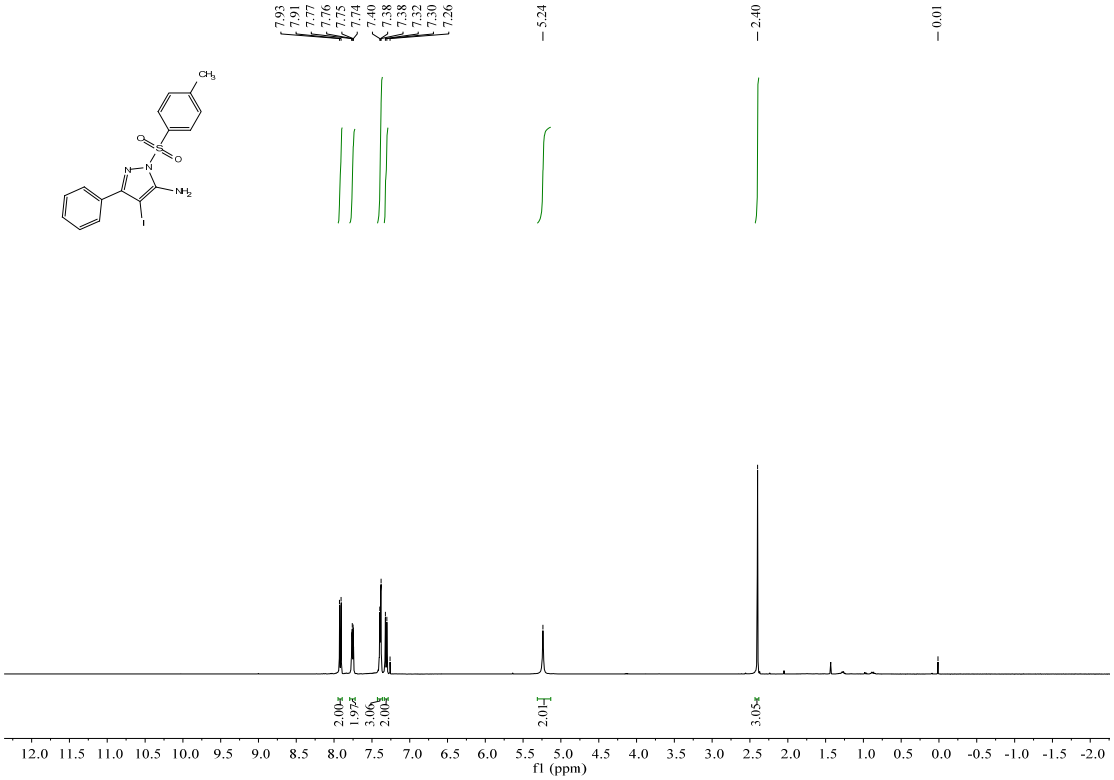


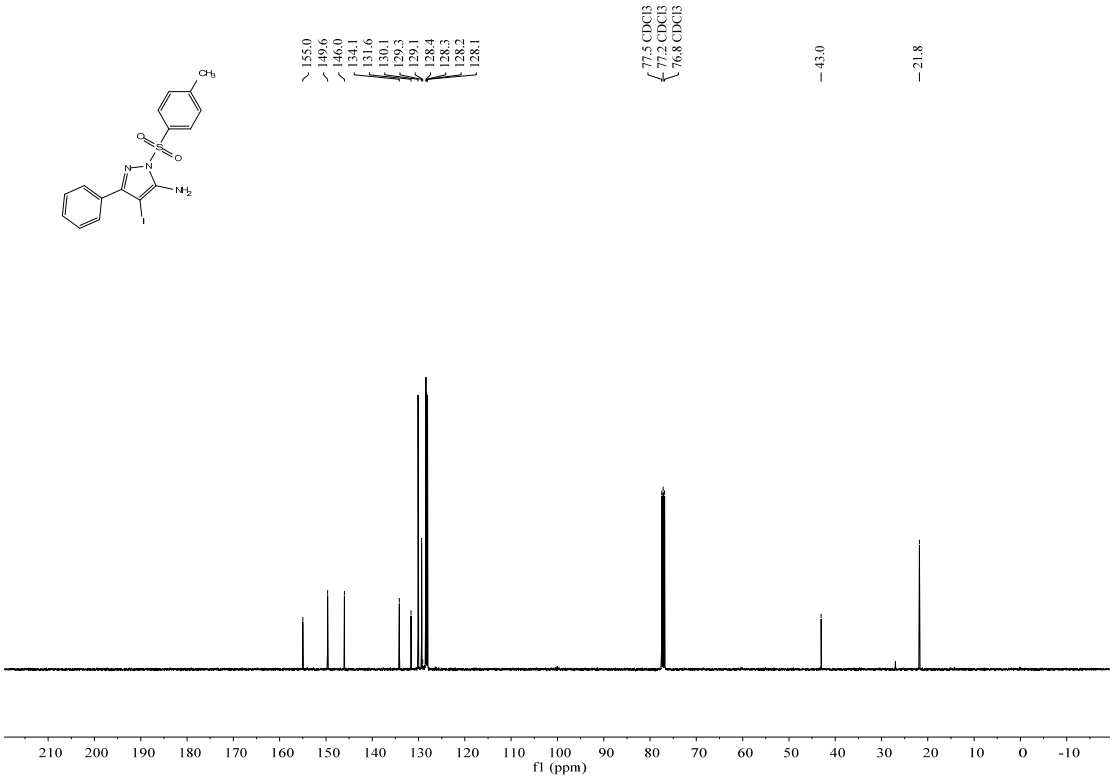
methyl 5-amino-4-bromo-3-phenyl-1H-pyrazole-1-carboxylate (**3n**)



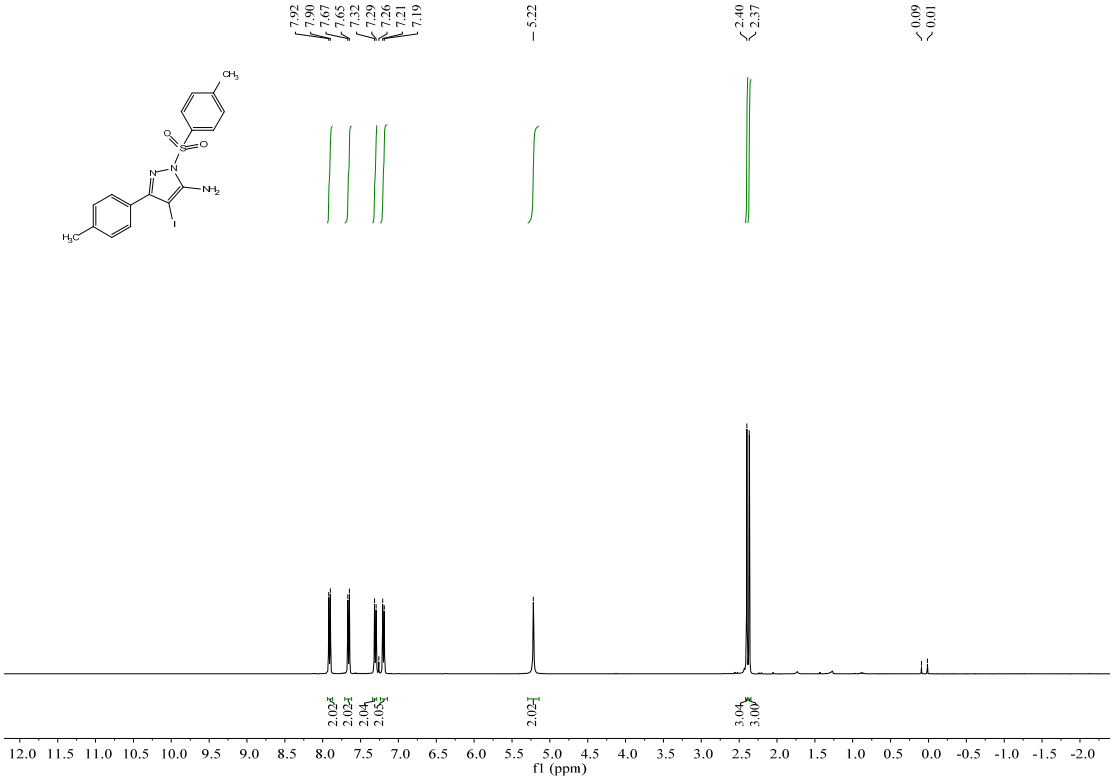


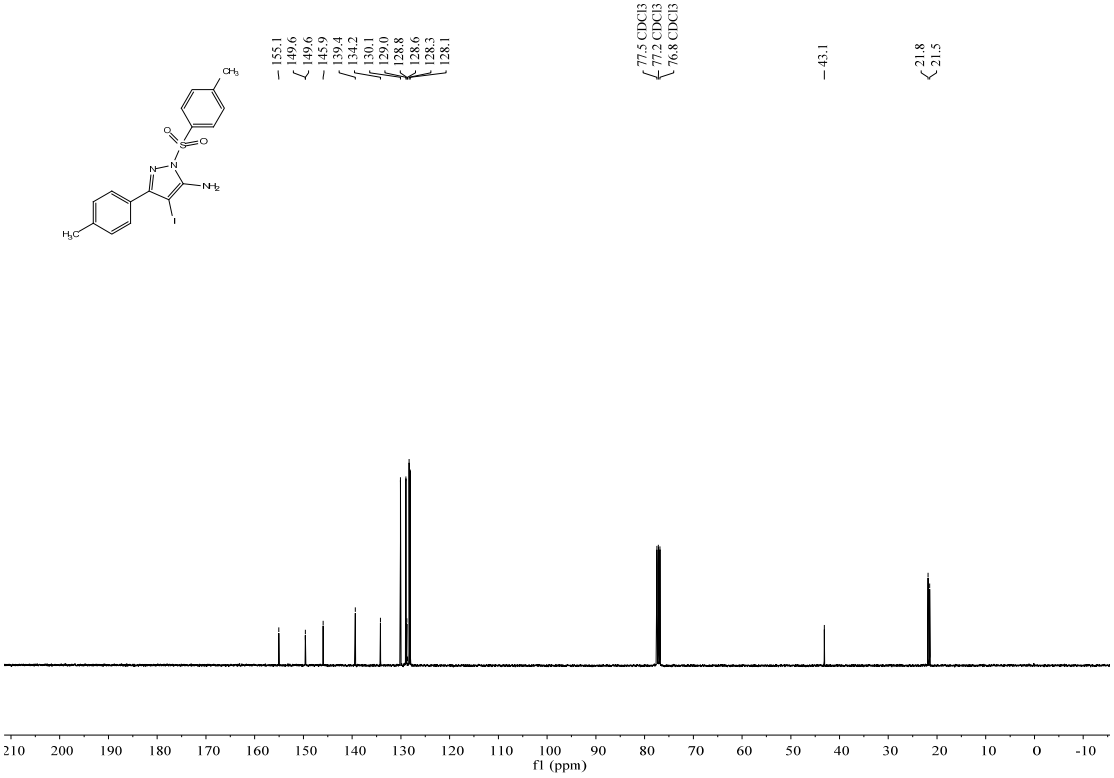
4-iodo-3-phenyl-1-tosyl-1H-pyrazol-5-amine (**4a**)



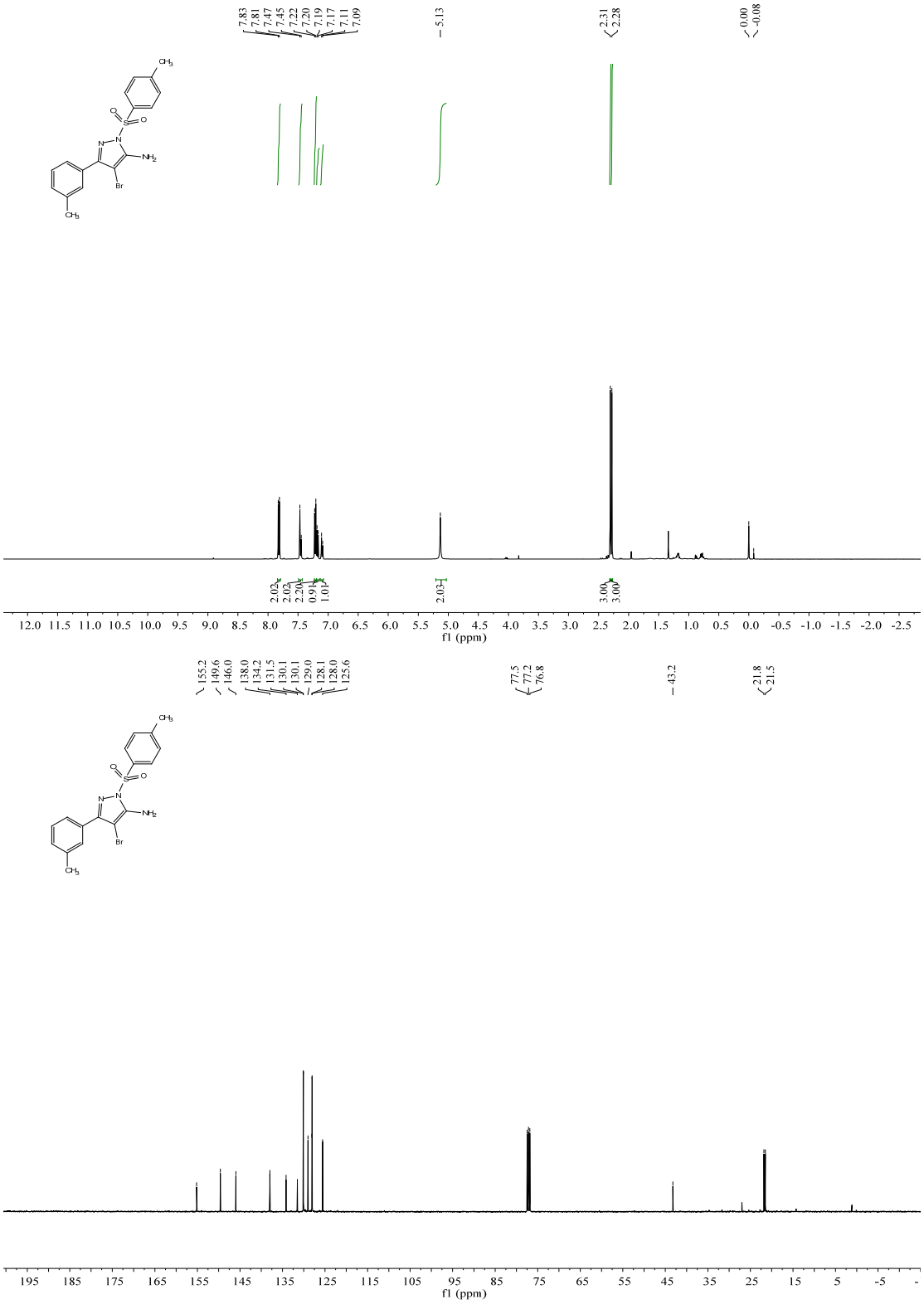


4-iodo-3-(p-tolyl)-1-tosyl-1H-pyrazol-5-amine (**4b**)

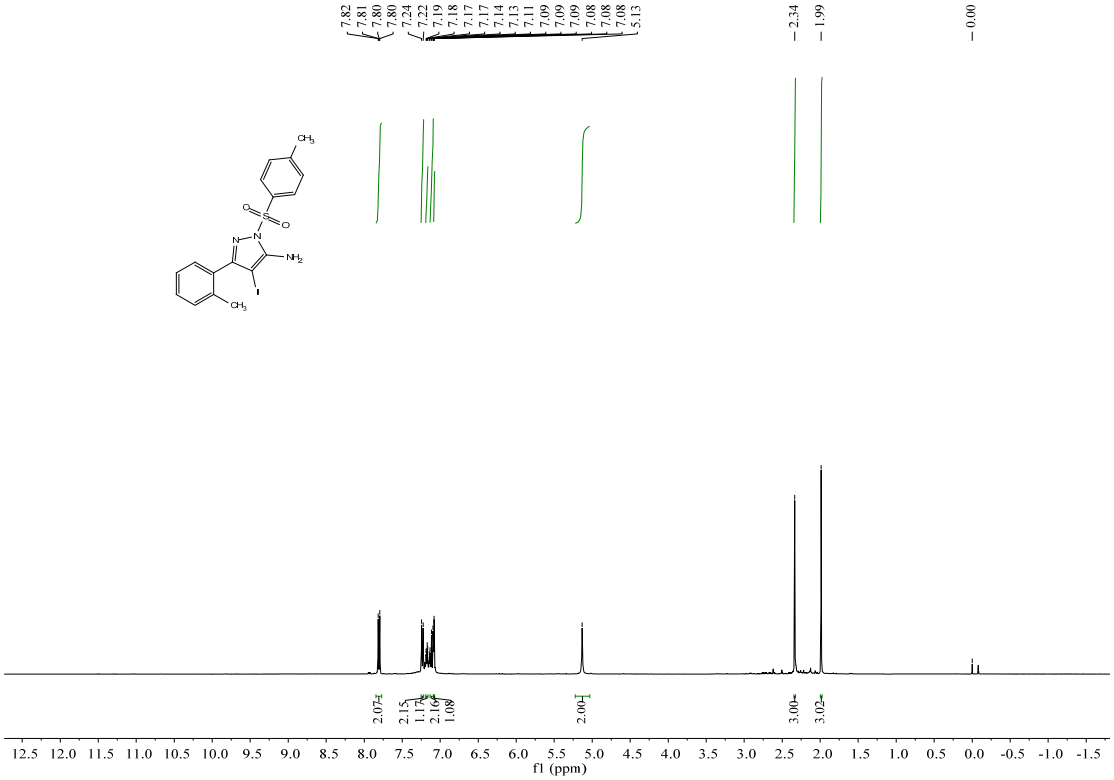


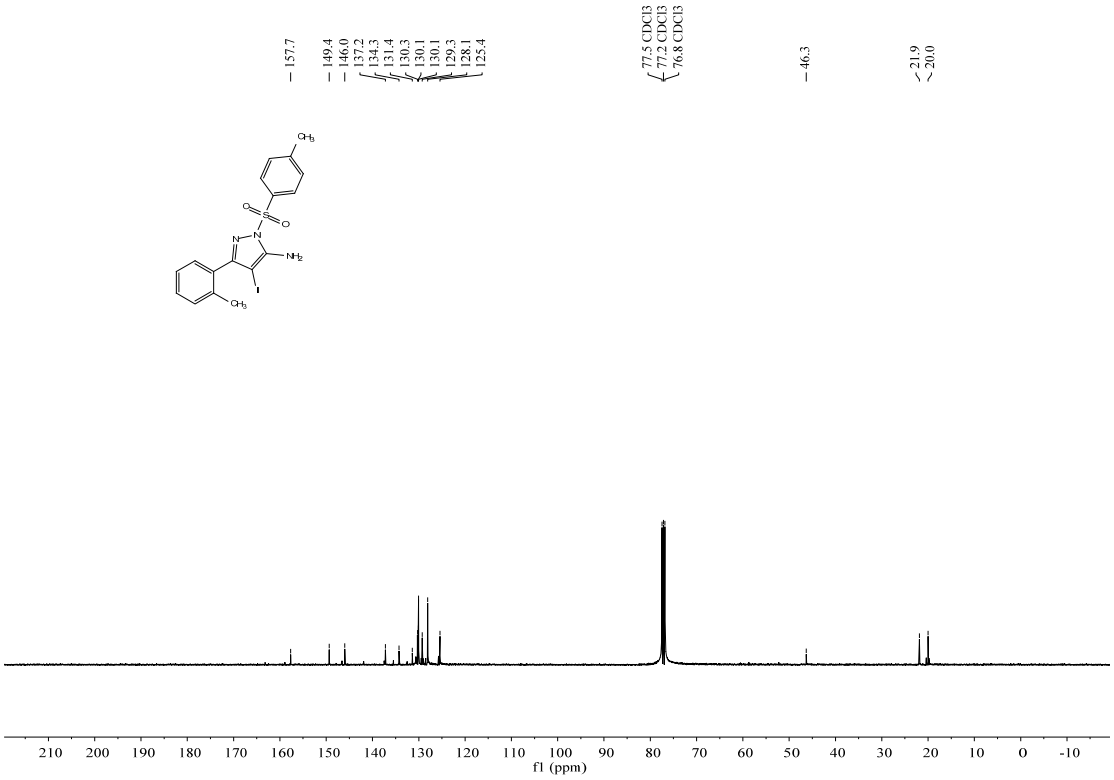


4-iodo-3-(m-tolyl)-1-tosyl-1H-pyrazol-5-amine (**4c**)

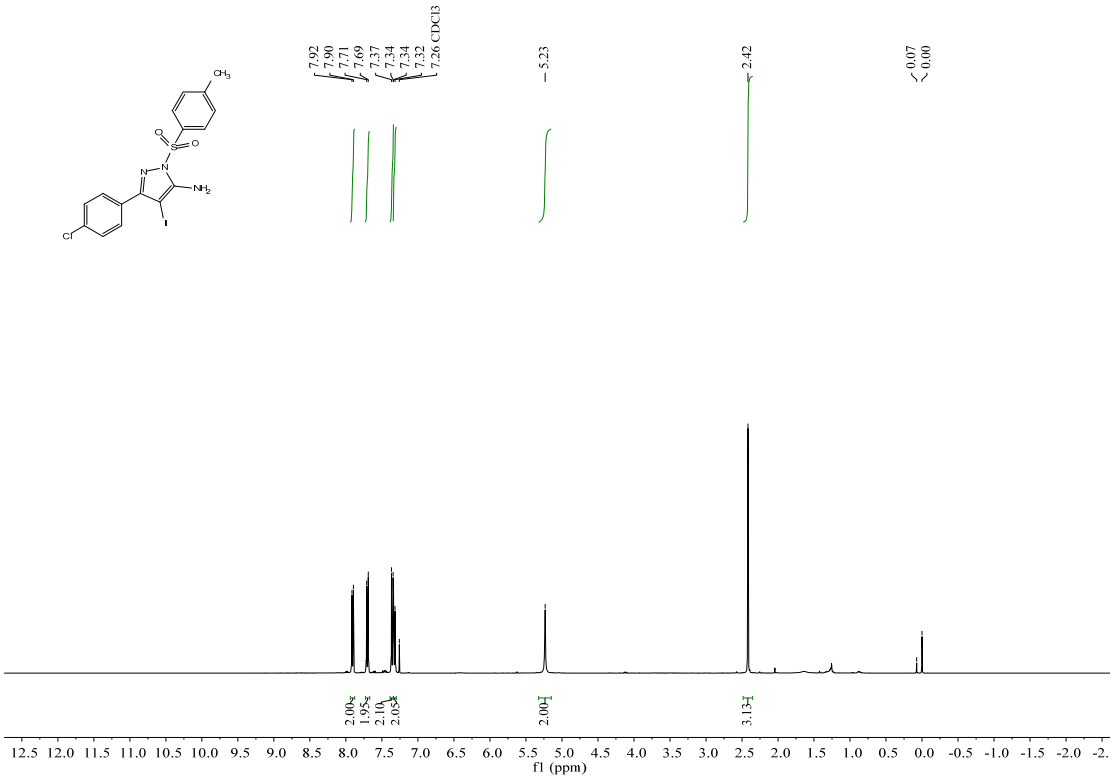


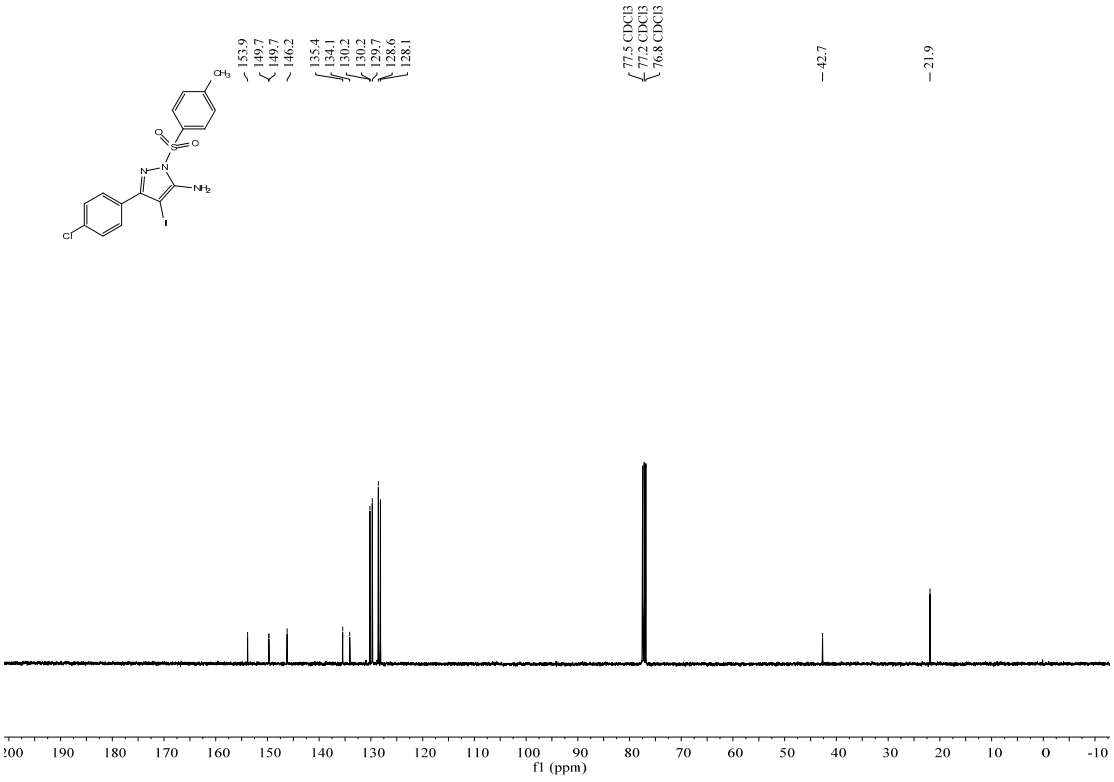
4-iodo-3-(o-tolyl)-1-tosyl-1H-pyrazol-5-amine (**4d**)



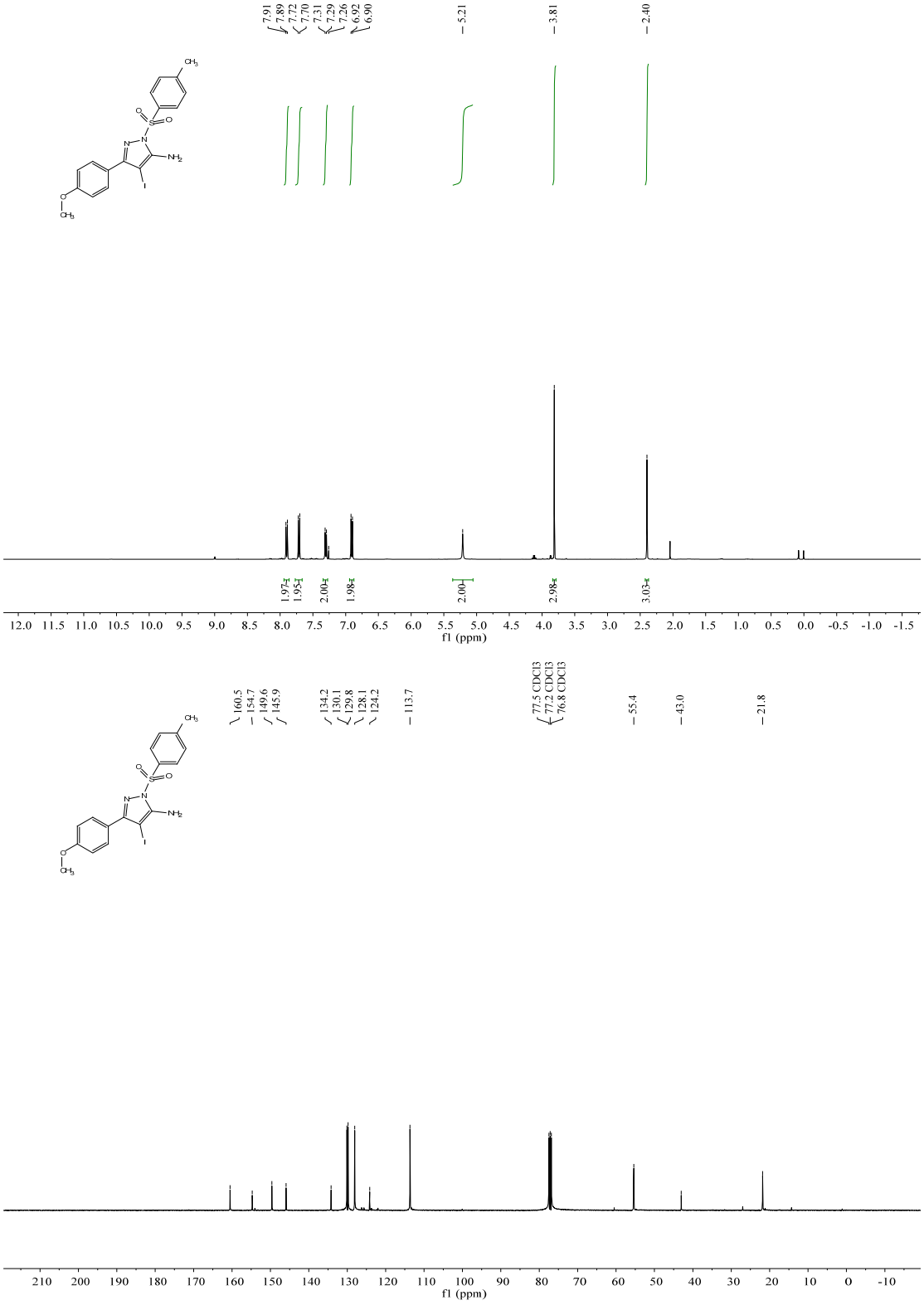


3-(4-chlorophenyl)-4-iodo-1-tosyl-1H-pyrazol-5-amine (**4e**)

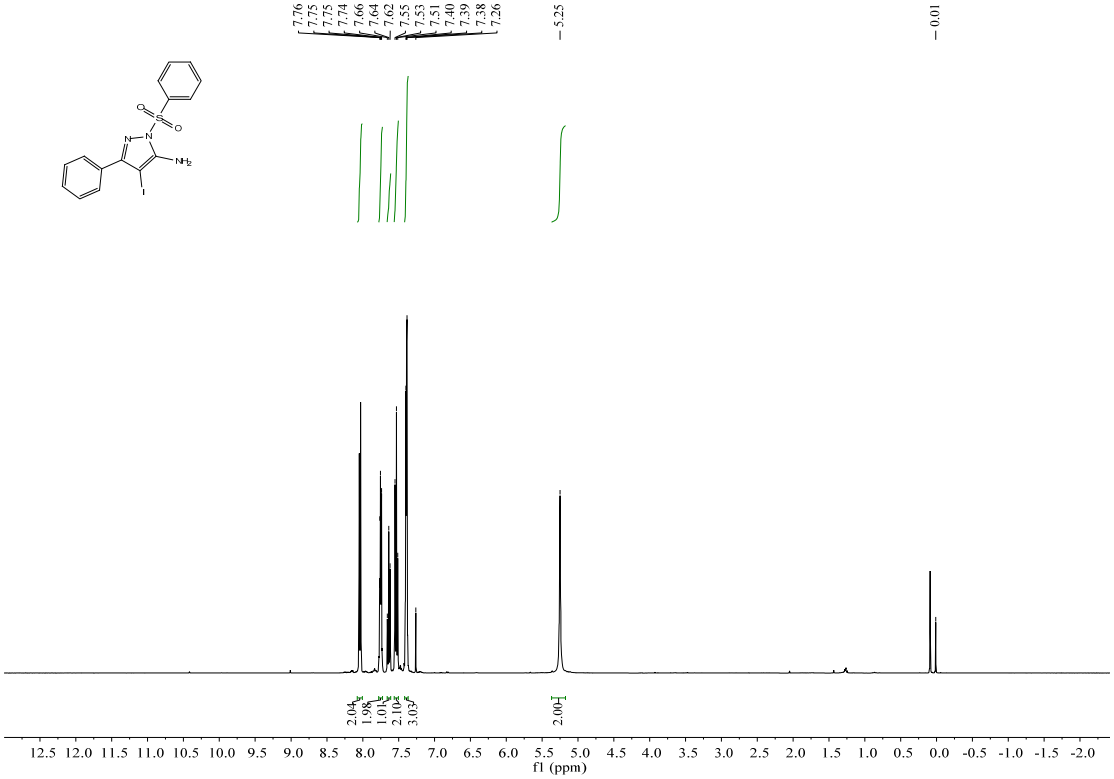


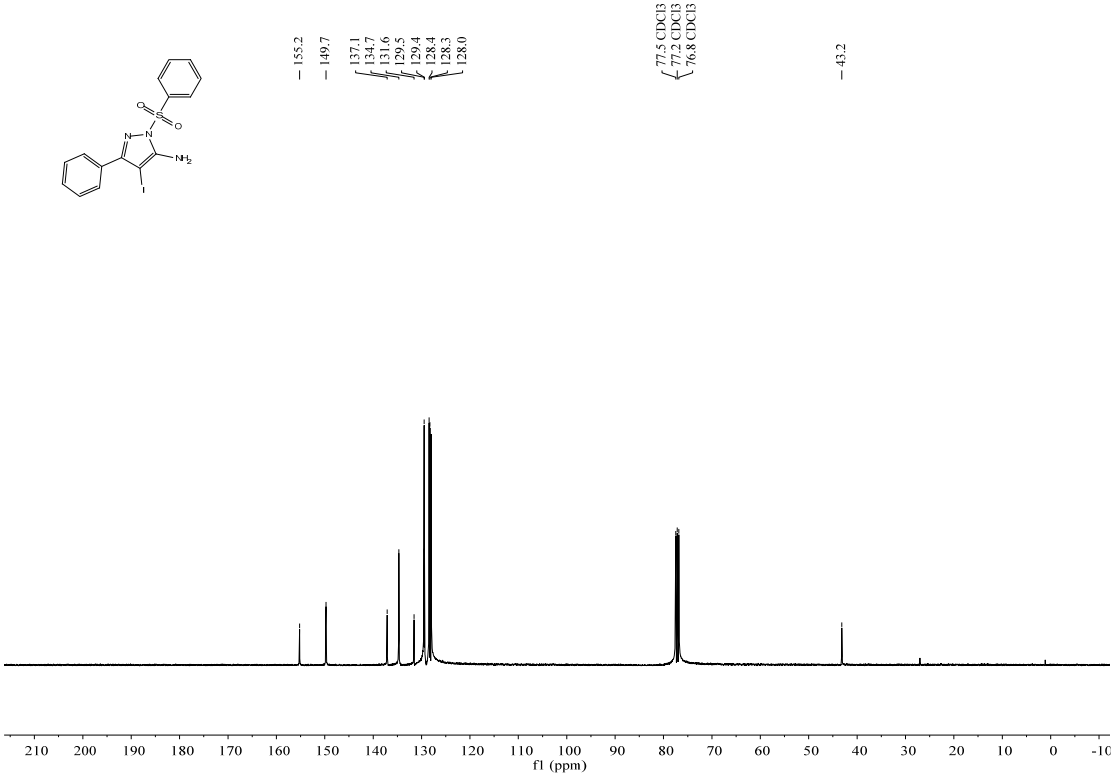


4-iodo-3-(4-methoxyphenyl)-1-tosyl-1H-pyrazol-5-amine (**4f**)

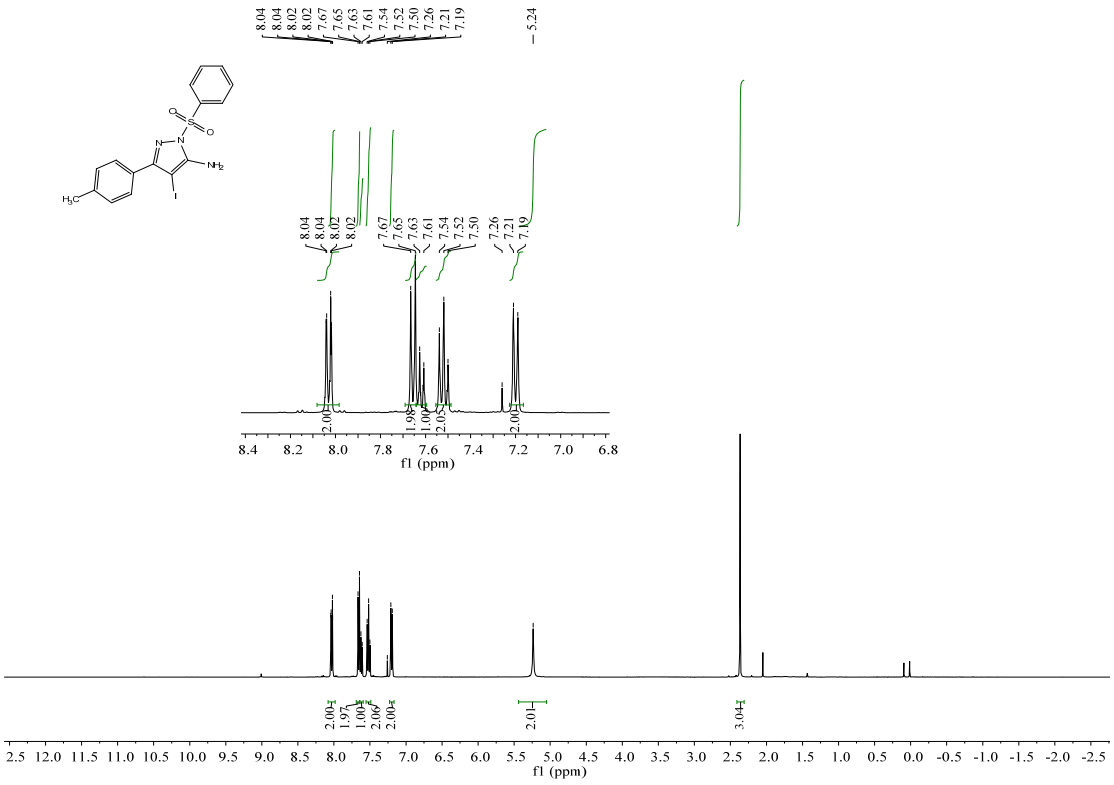


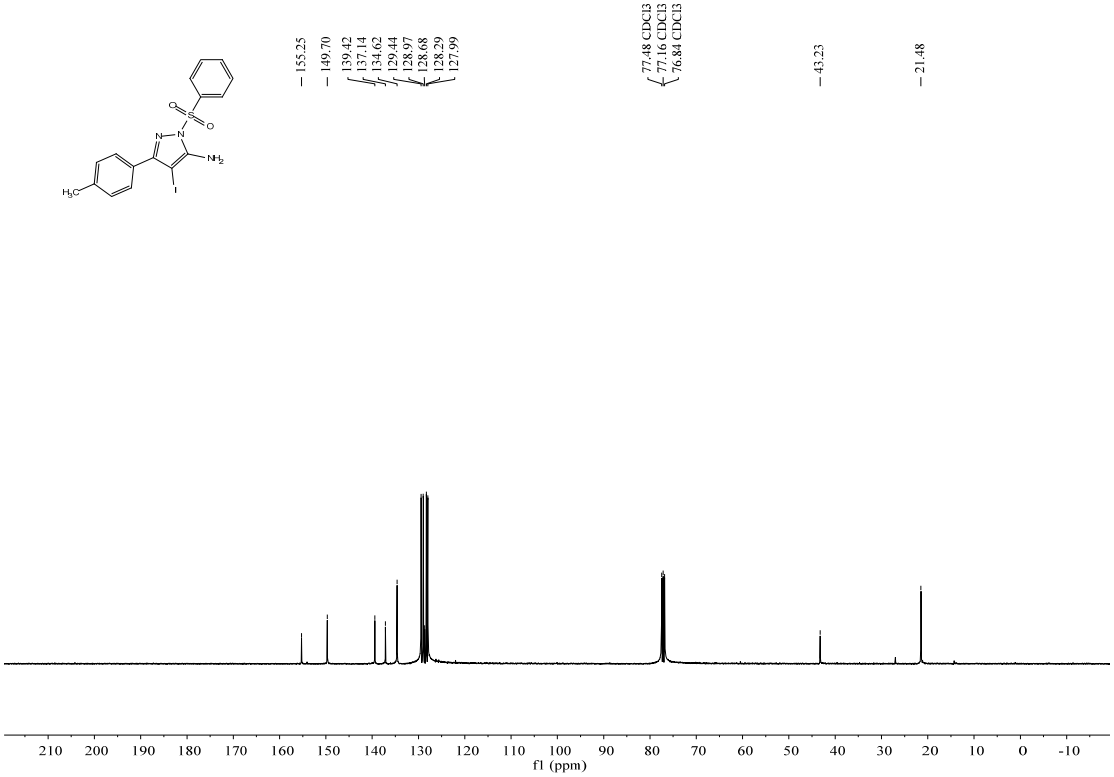
4-iodo-3-phenyl-1-(phenylsulfonyl)-1H-pyrazol-5-amine (**4g**)



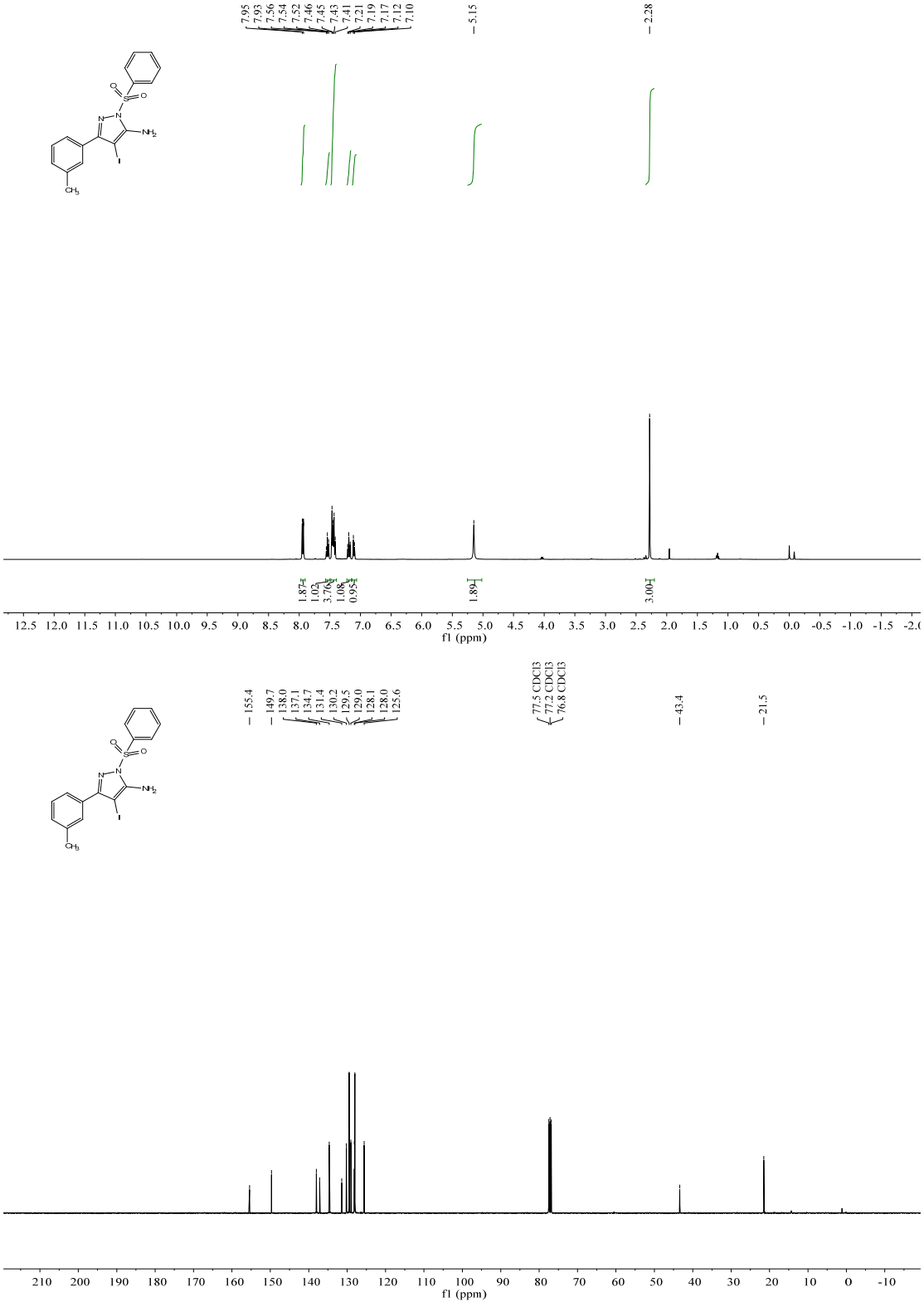


4-iodo-1-(phenylsulfonyl)-3-(p-tolyl)-1H-pyrazol-5-amine (**4h**)

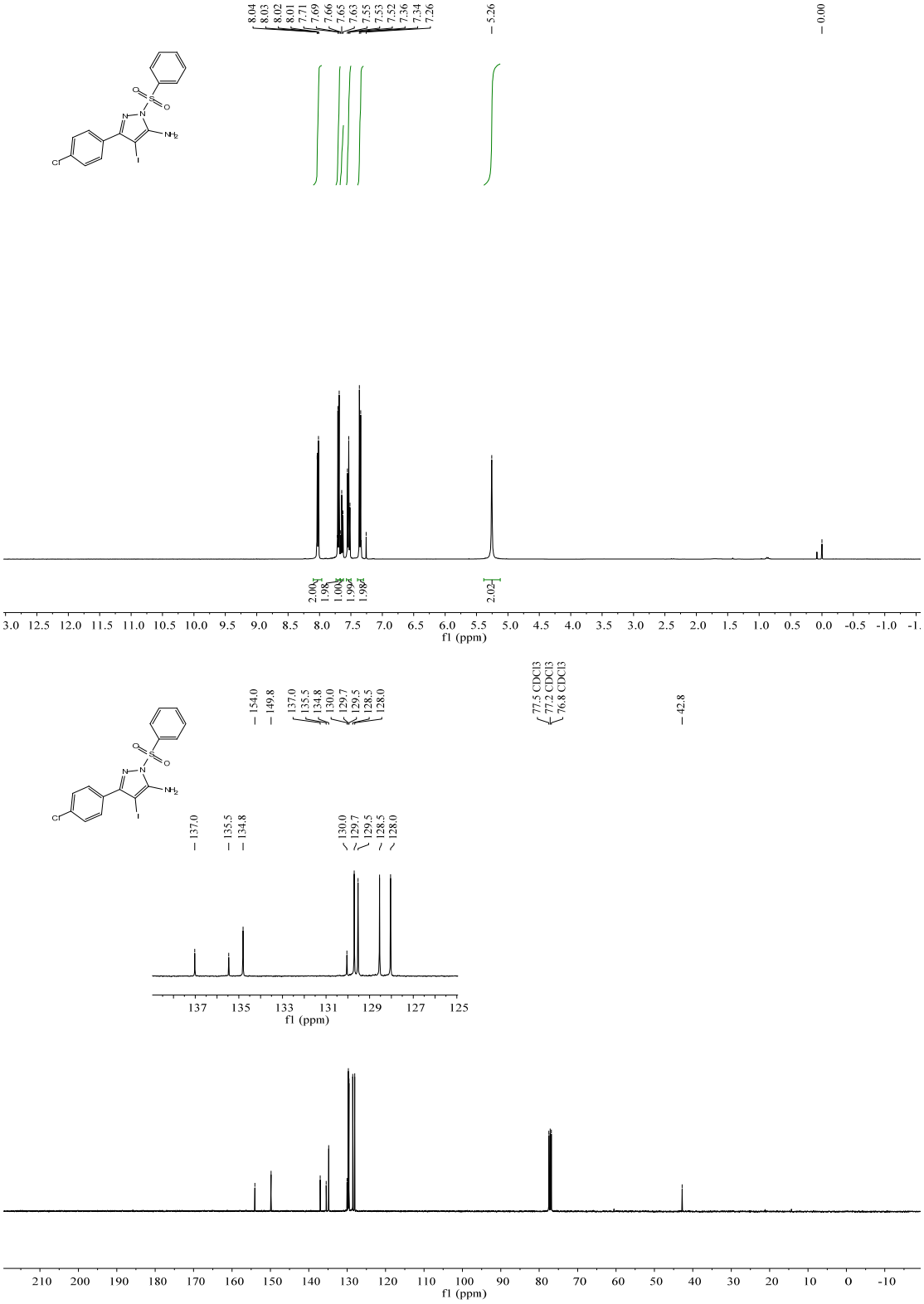




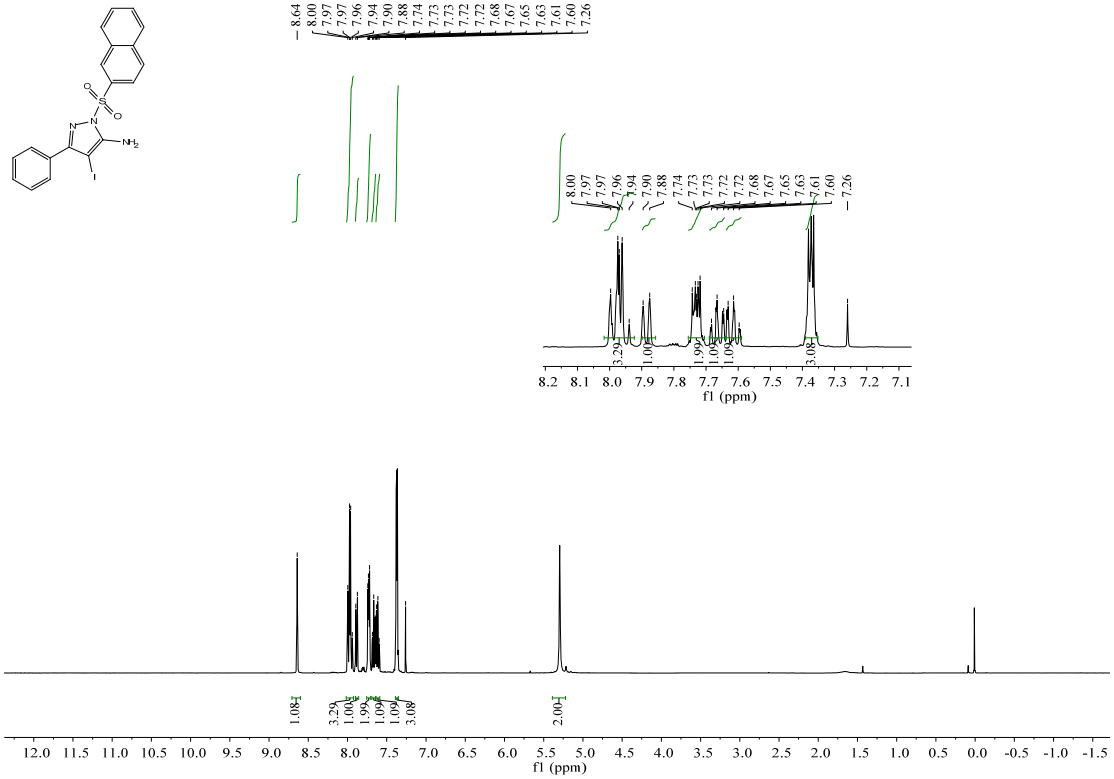
4-iodo-1-(phenylsulfonyl)-3-(m-tolyl)-1H-pyrazol-5-amine (**4i**)

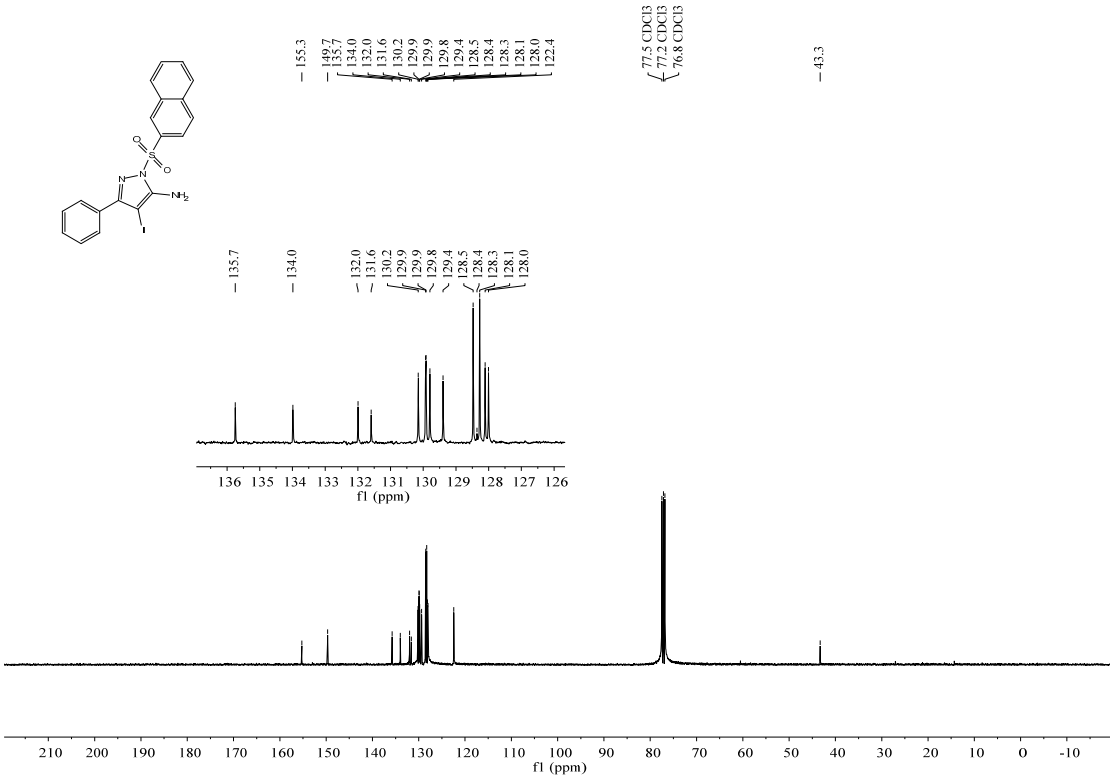


3-(4-chlorophenyl)-4-iodo-1-(phenylsulfonyl)-1H-pyrazol-5-amine (**4j**)

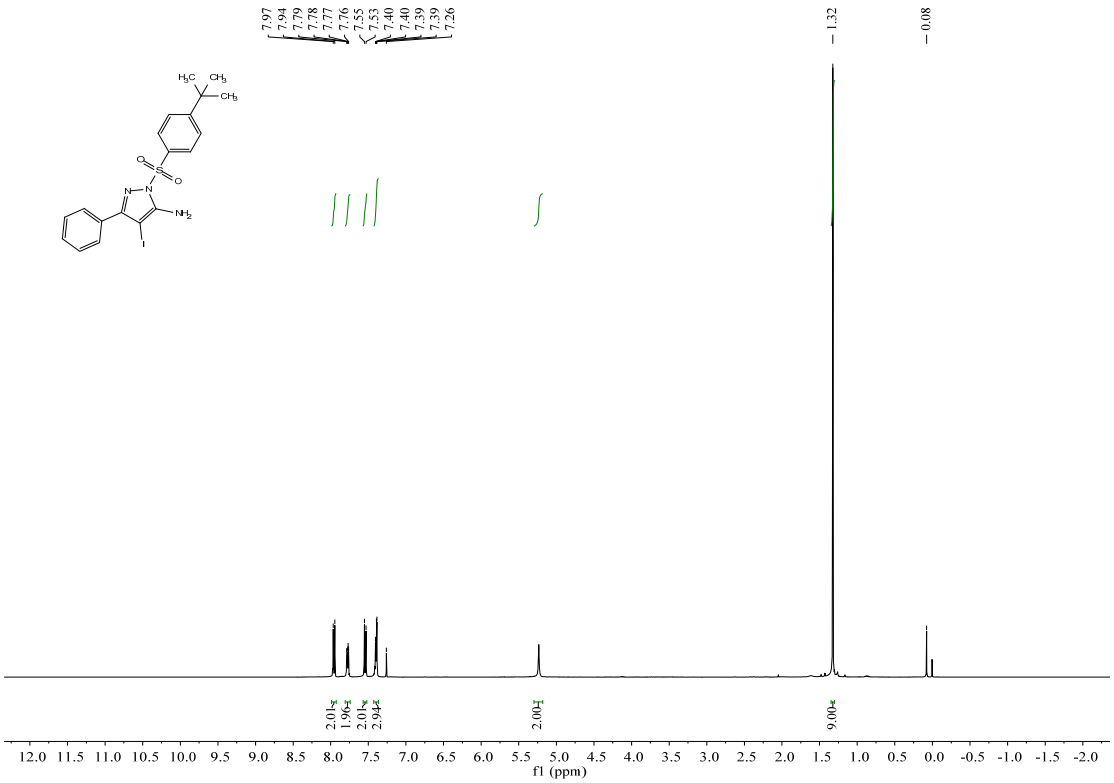


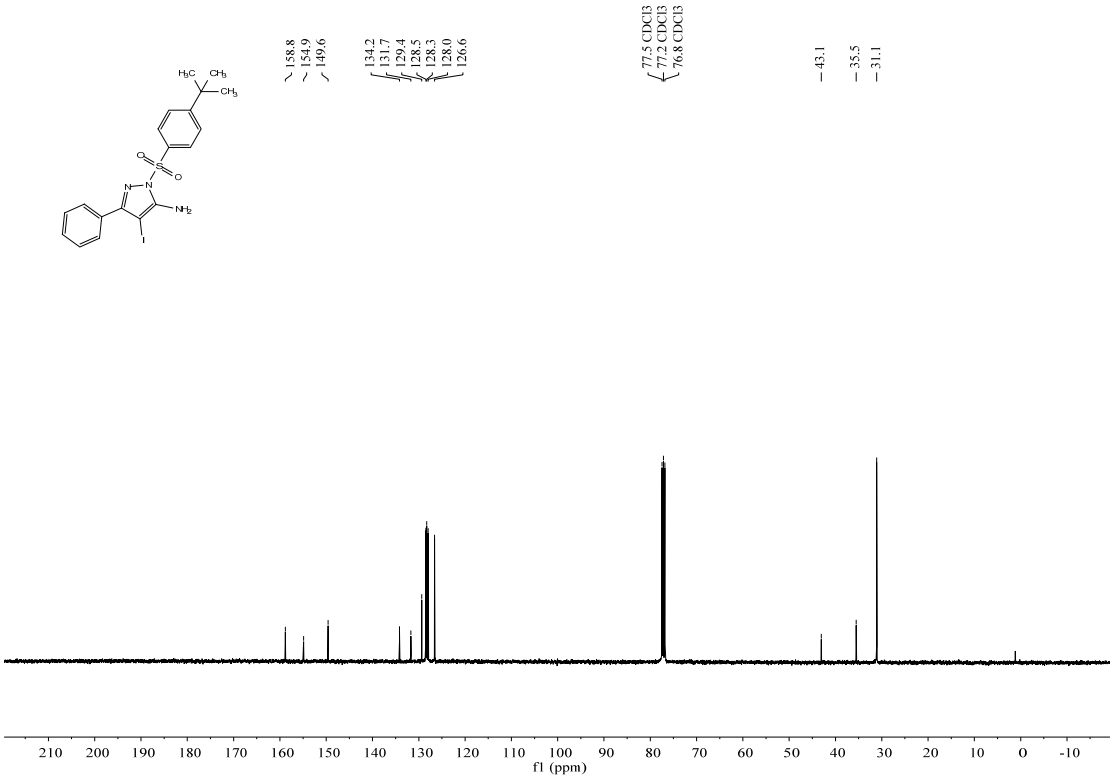
4-iodo-1-(naphthalen-2-ylsulfonyl)-3-phenyl-1H-pyrazol-5-amine (**4k**)



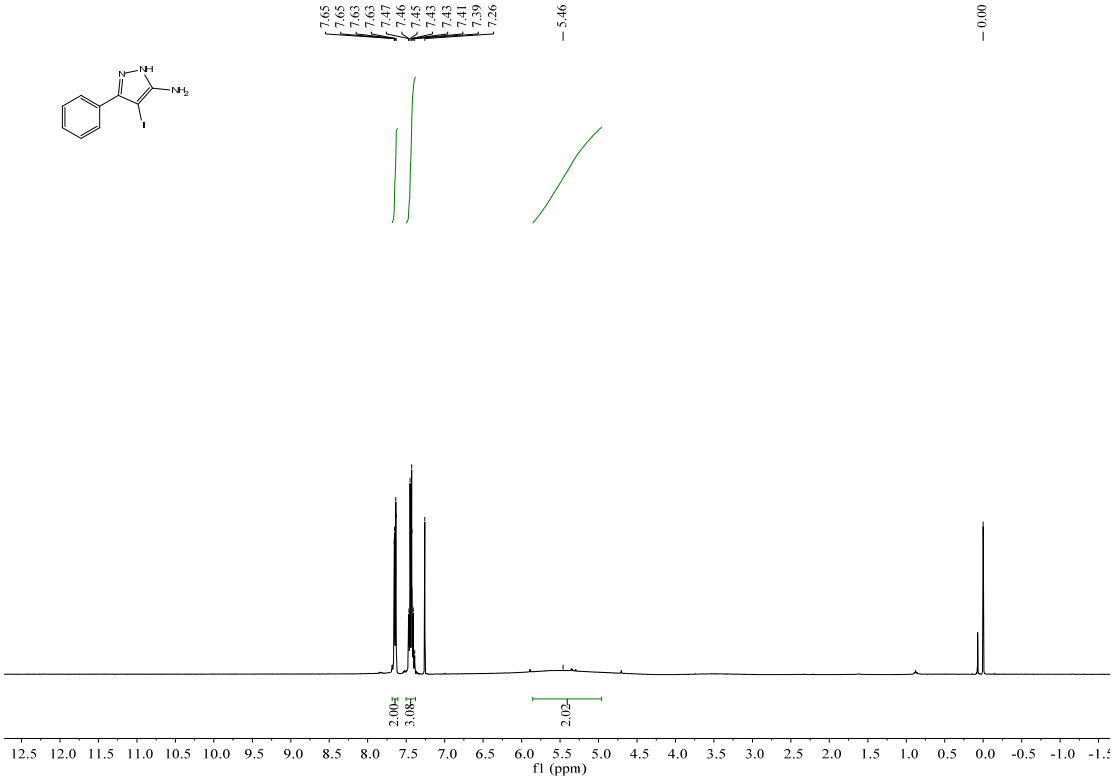


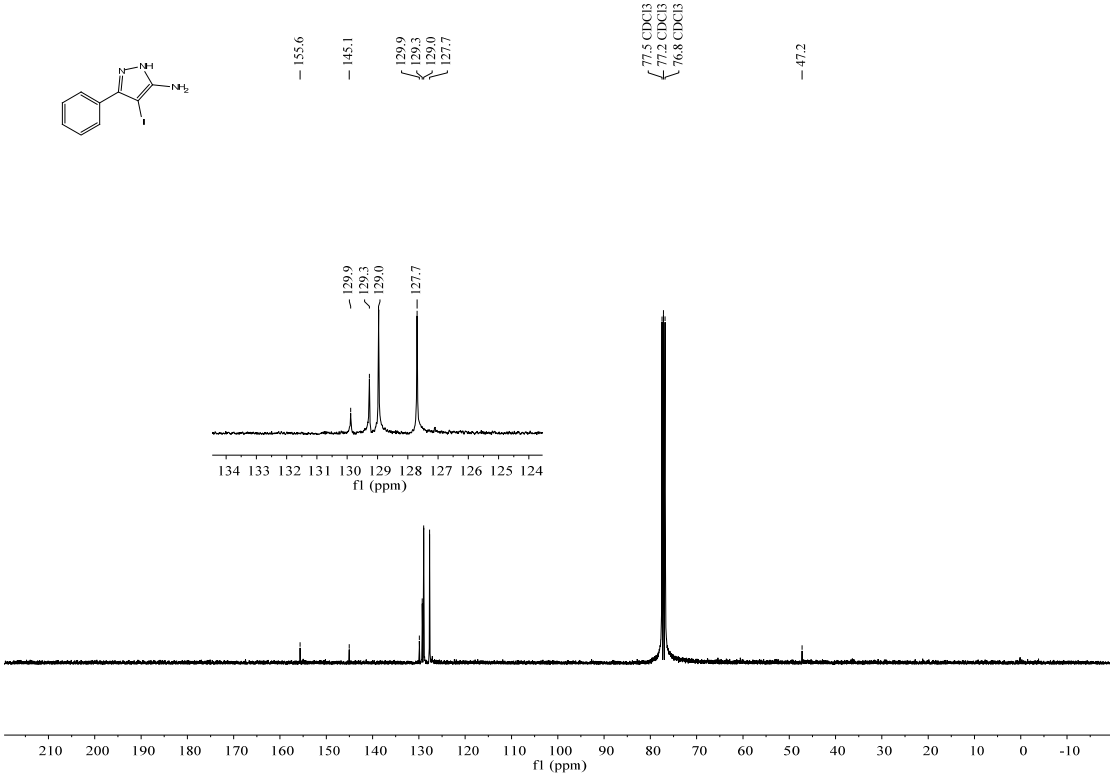
1-((4-(tert-butyl)phenyl)sulfonyl)-4-iodo-3-phenyl-1H-pyrazol-5-amine (**4l**)



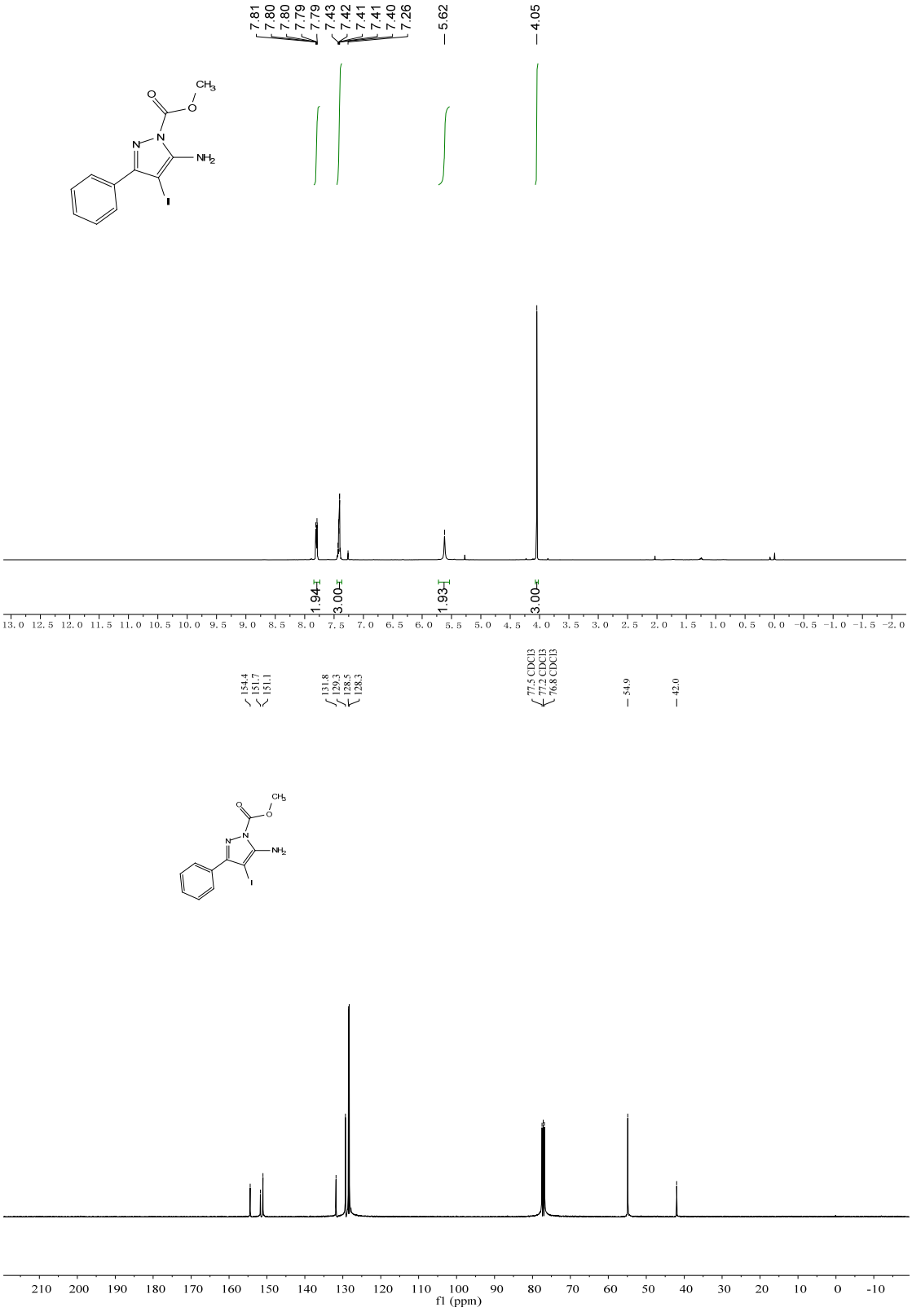


4-bromo-3-phenyl-1H-pyrazol-5-amine（**4m**）

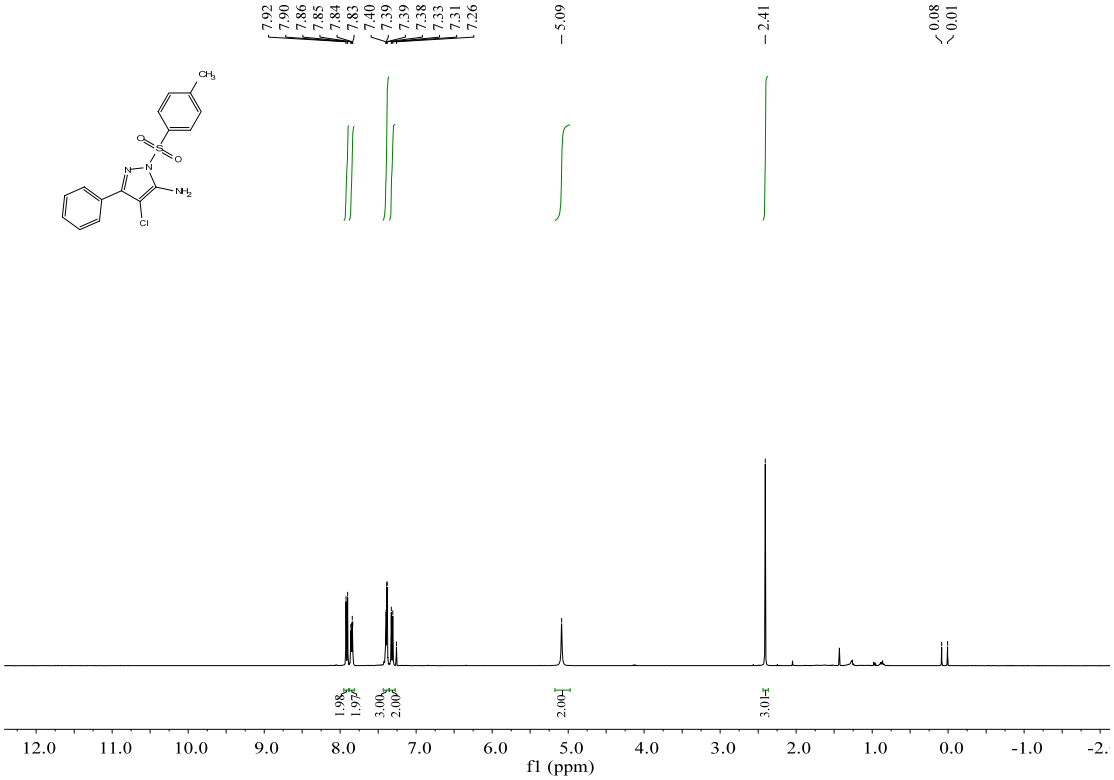


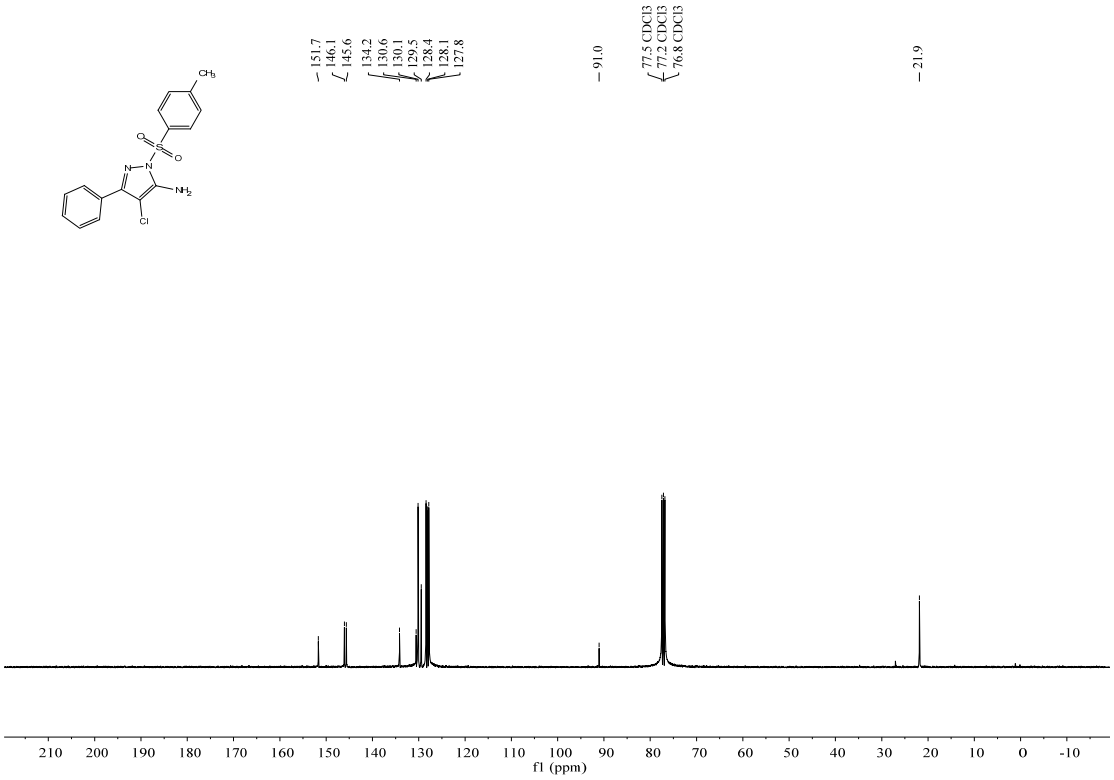


methyl 5-amino-4-iodo-3-phenyl-1H-pyrazole-1-carboxylate (**4n**)

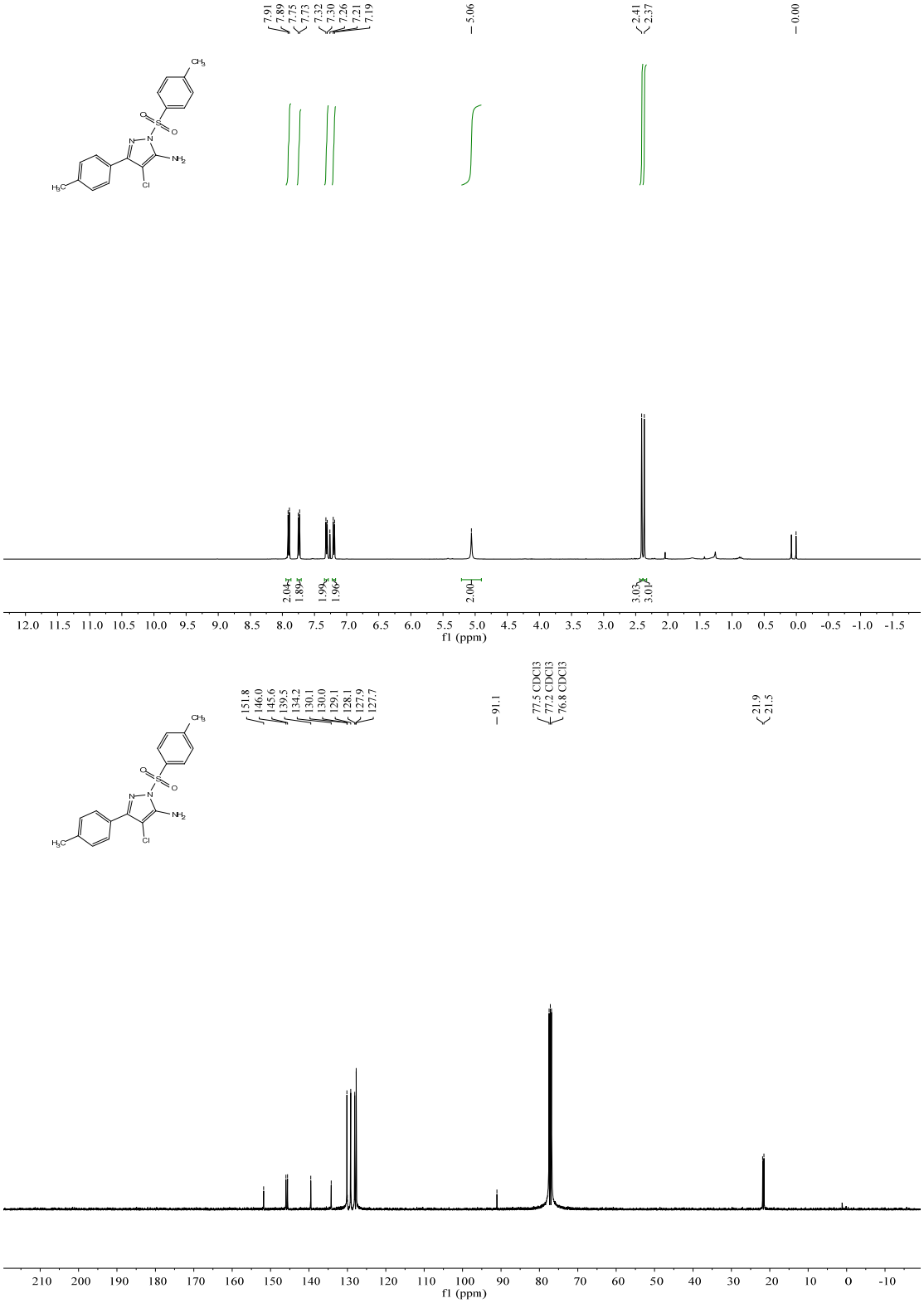


4-chloro-3-phenyl-1-tosyl-1H-pyrazol-5-amine (**5a**)

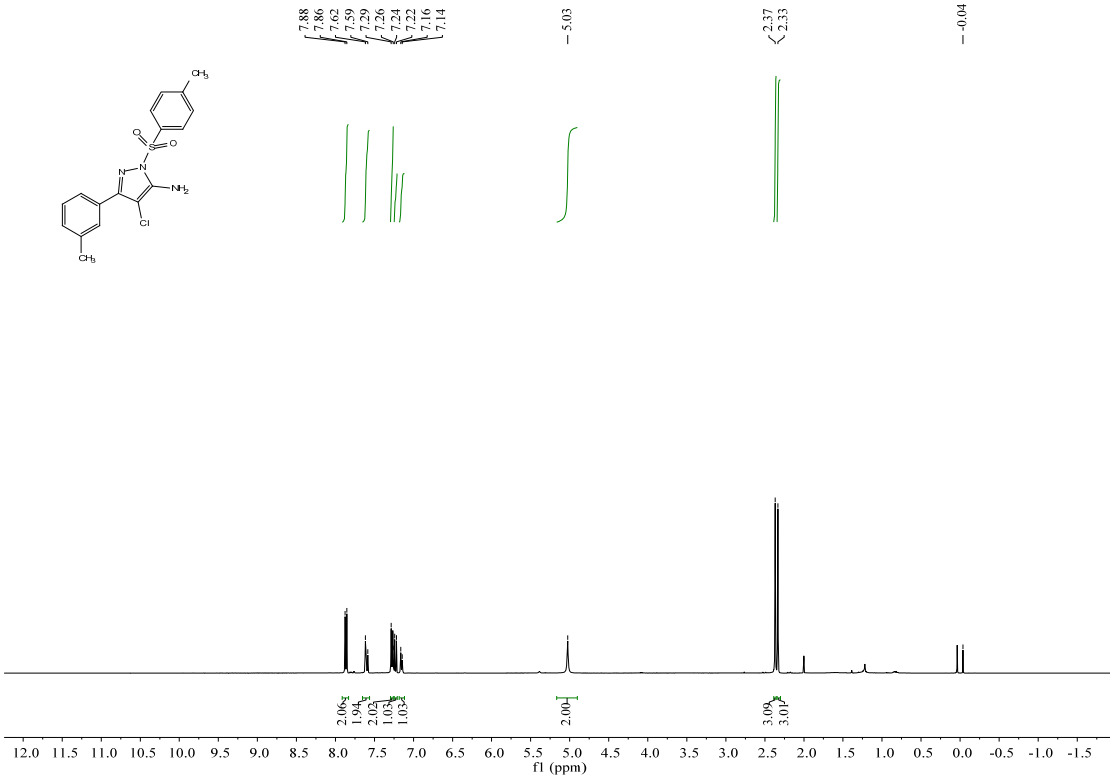


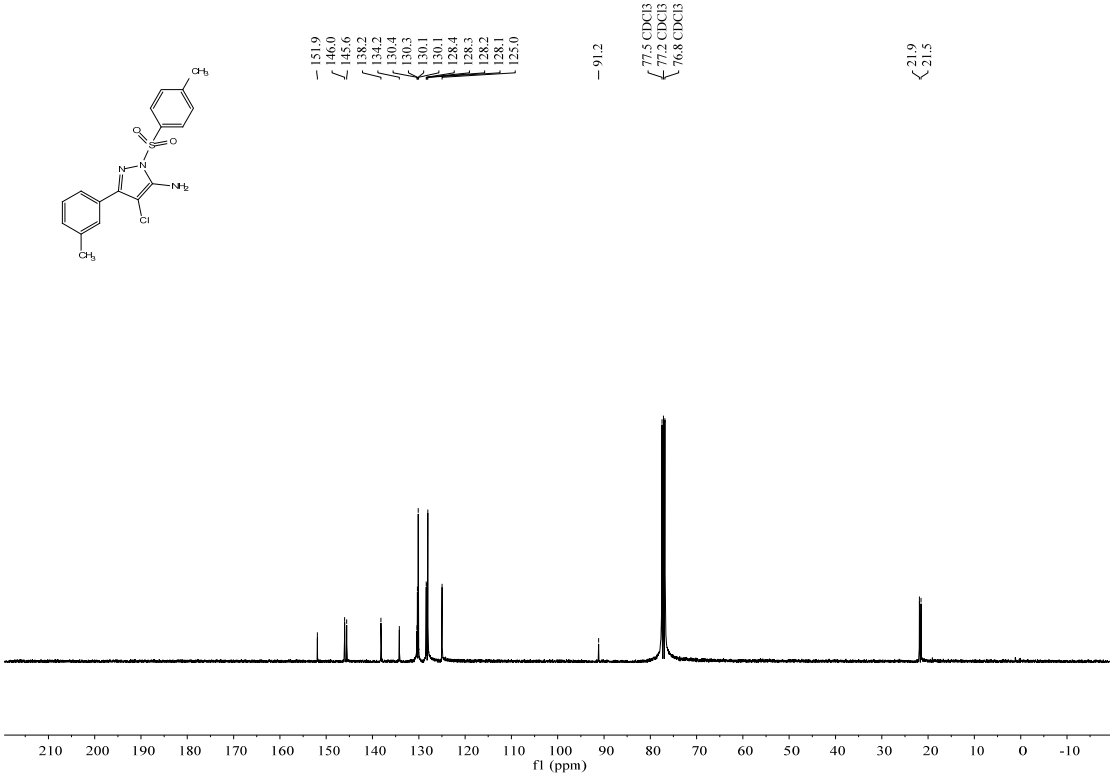


4-chloro-3-(p-tolyl)-1-tosyl-1H-pyrazol-5-amine (**5b**)

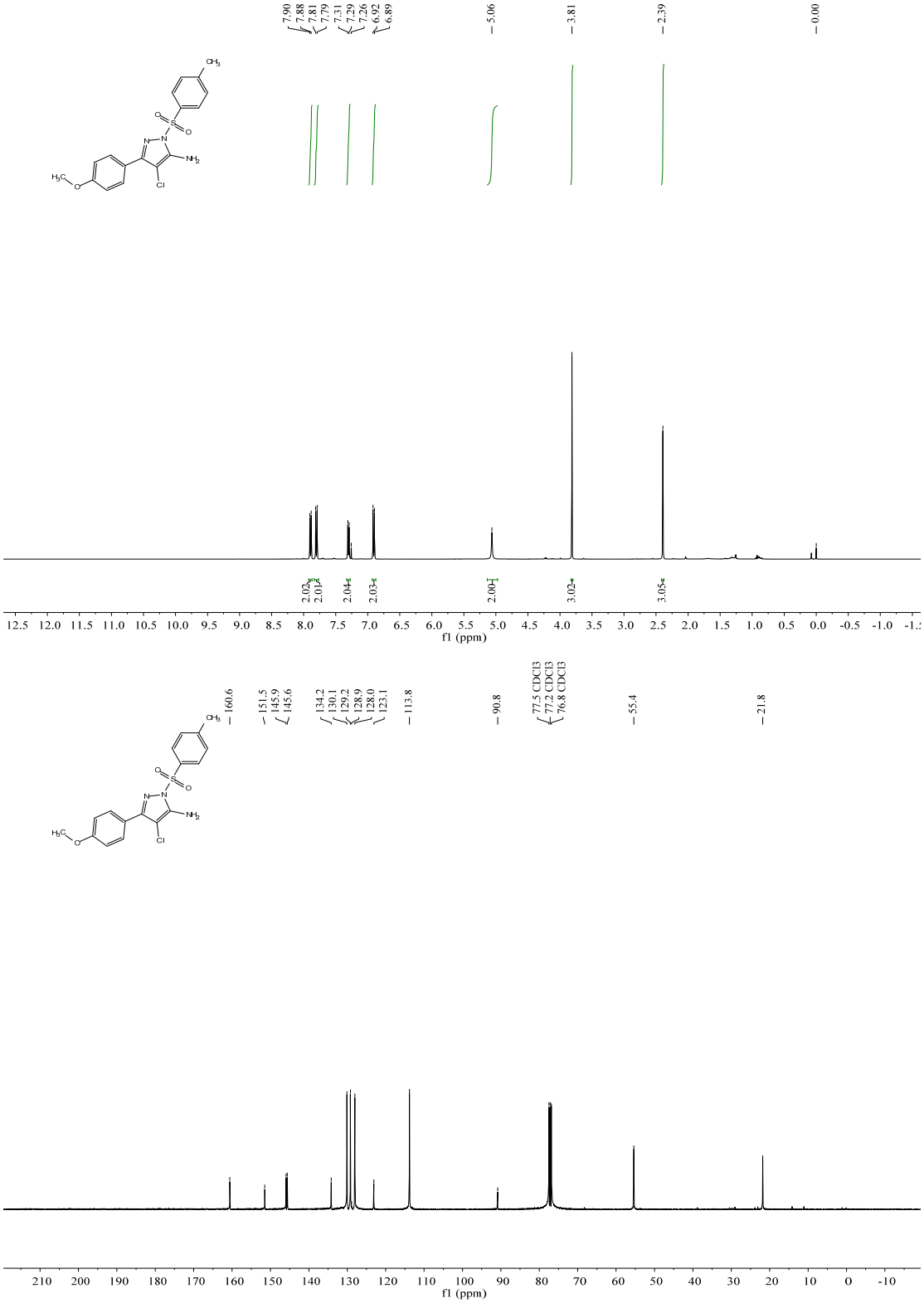


4-chloro-3-(m-tolyl)-1-tosyl-1H-pyrazol-5-amine (**5c**)

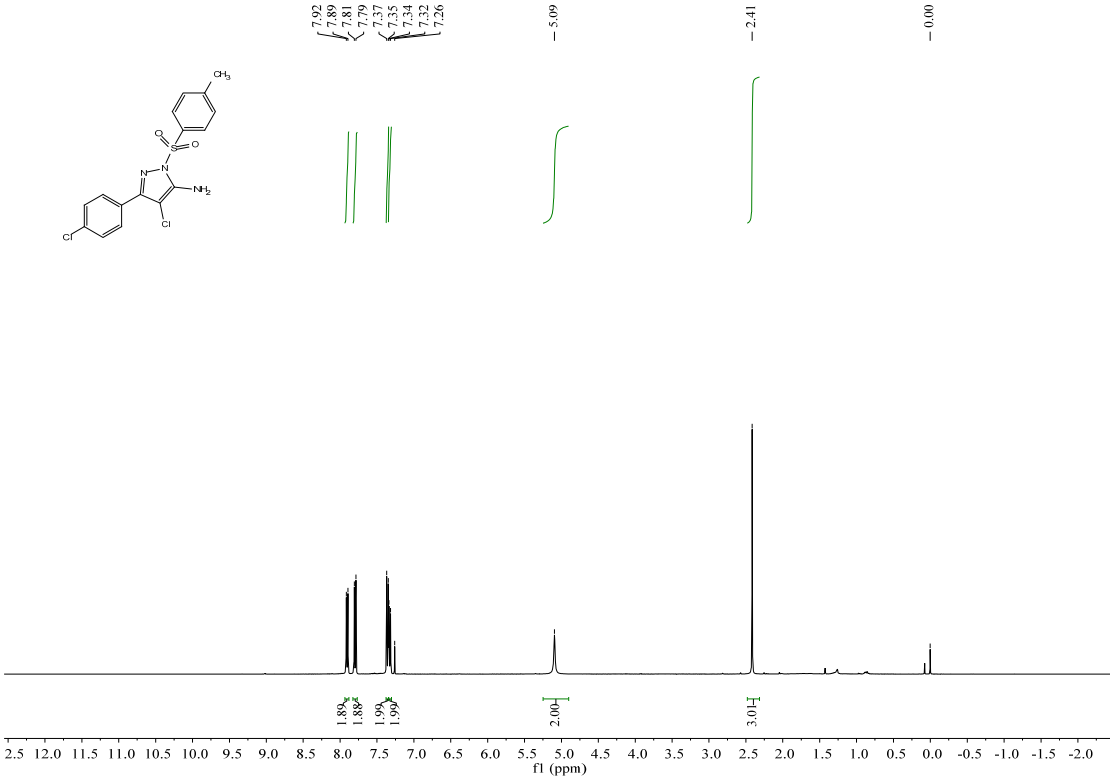


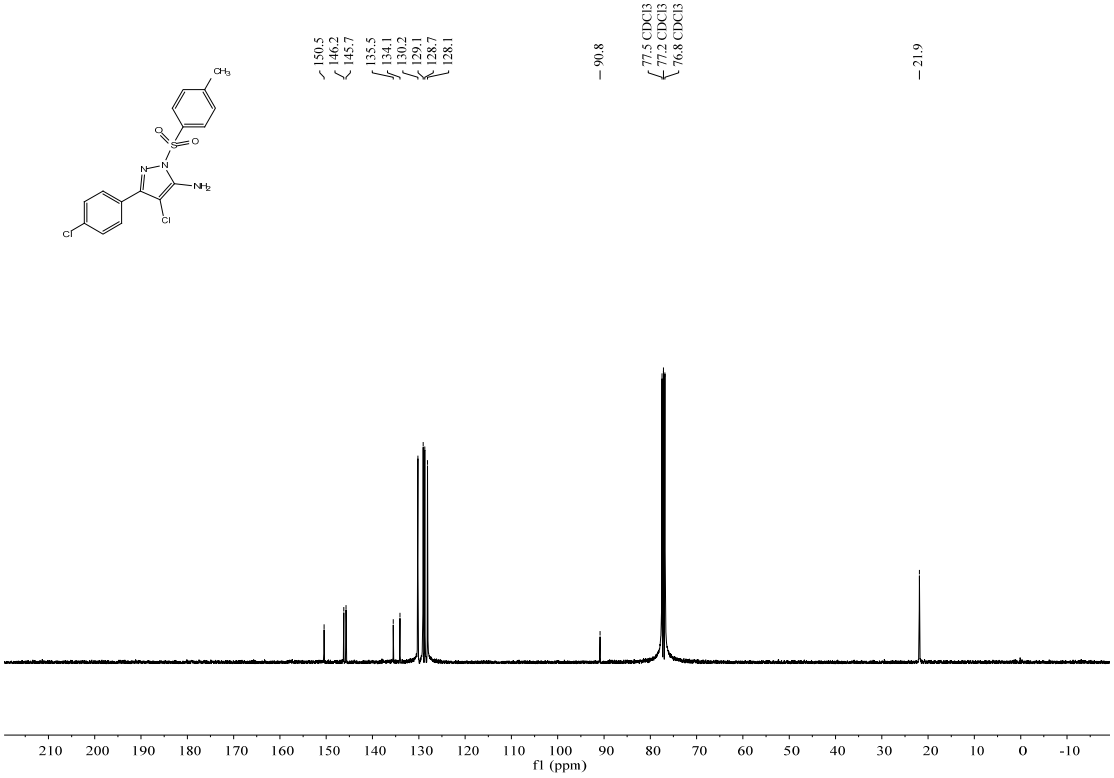


4-chloro-3-(4-methoxyphenyl)-1-tosyl-1H-pyrazol-5-amine (**5d**)

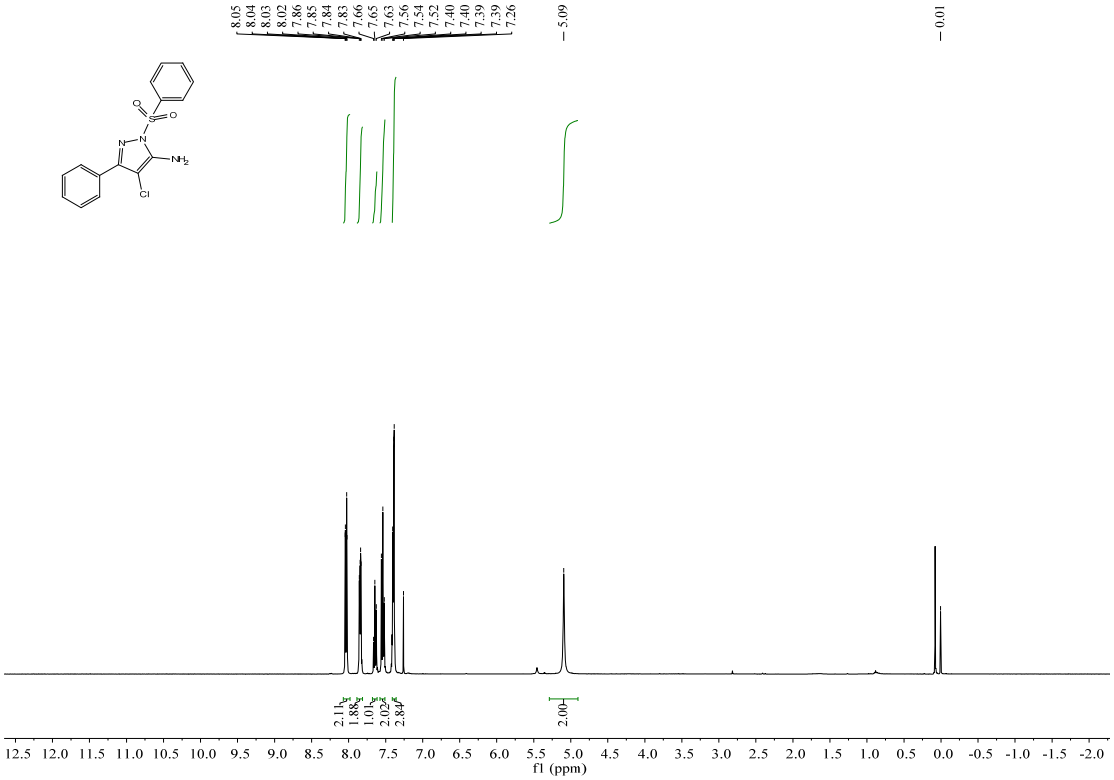


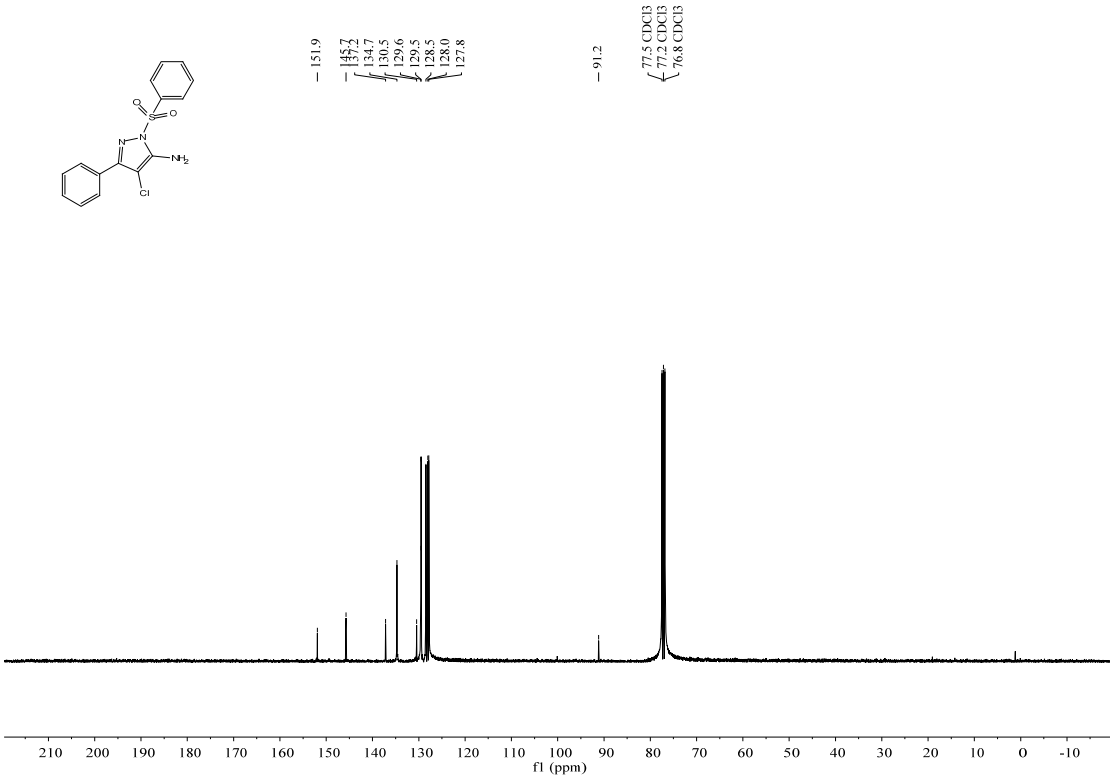
4-chloro-3-(4-chlorophenyl)-1-tosyl-1H-pyrazol-5-amine (**5e**)



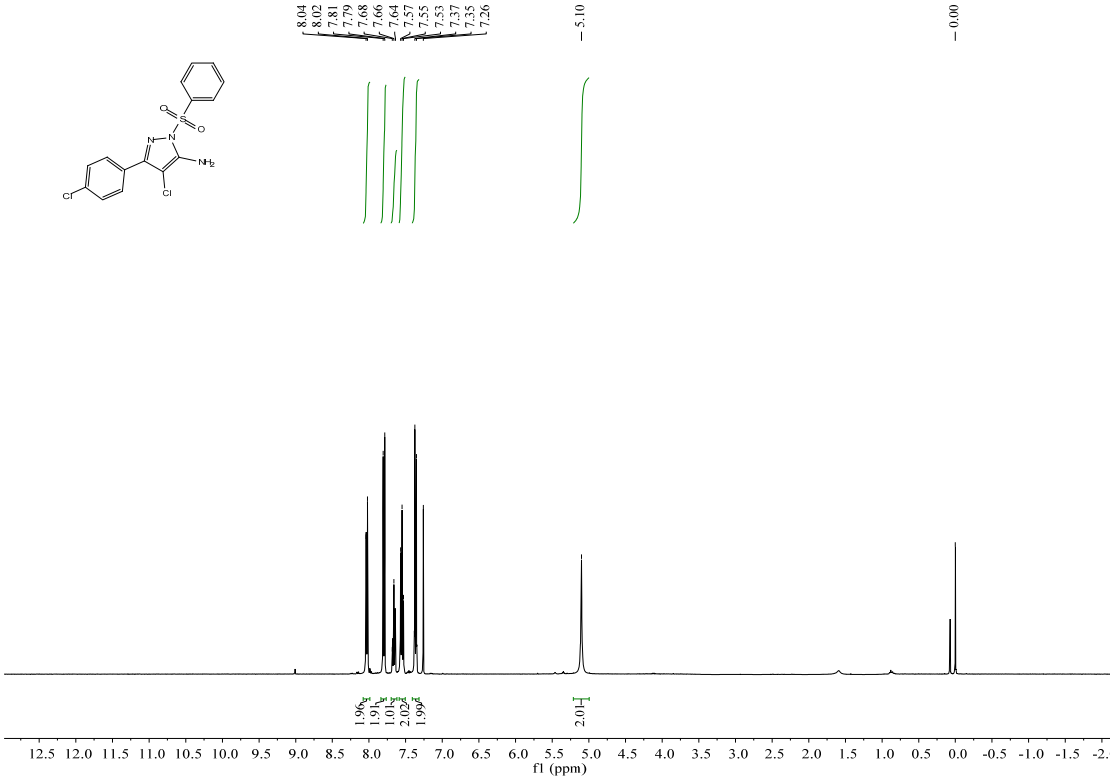


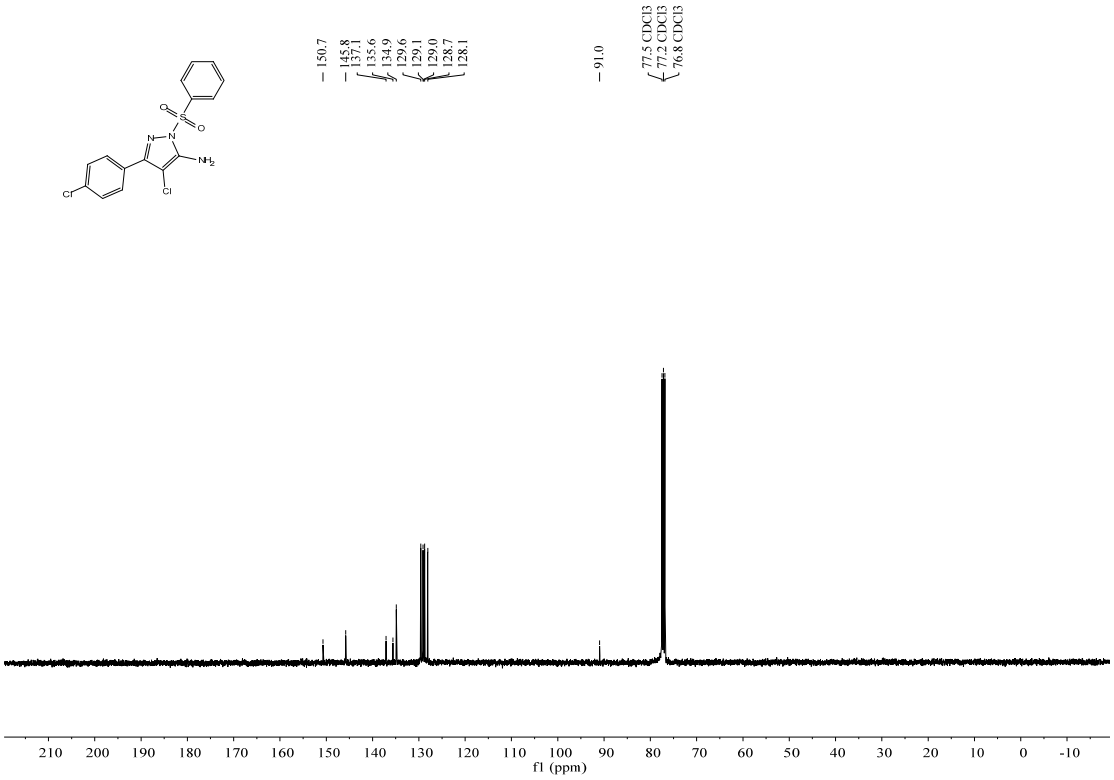
4-chloro-3-phenyl-1-(phenylsulfonyl)-1H-pyrazol-5-amine (**5f**)



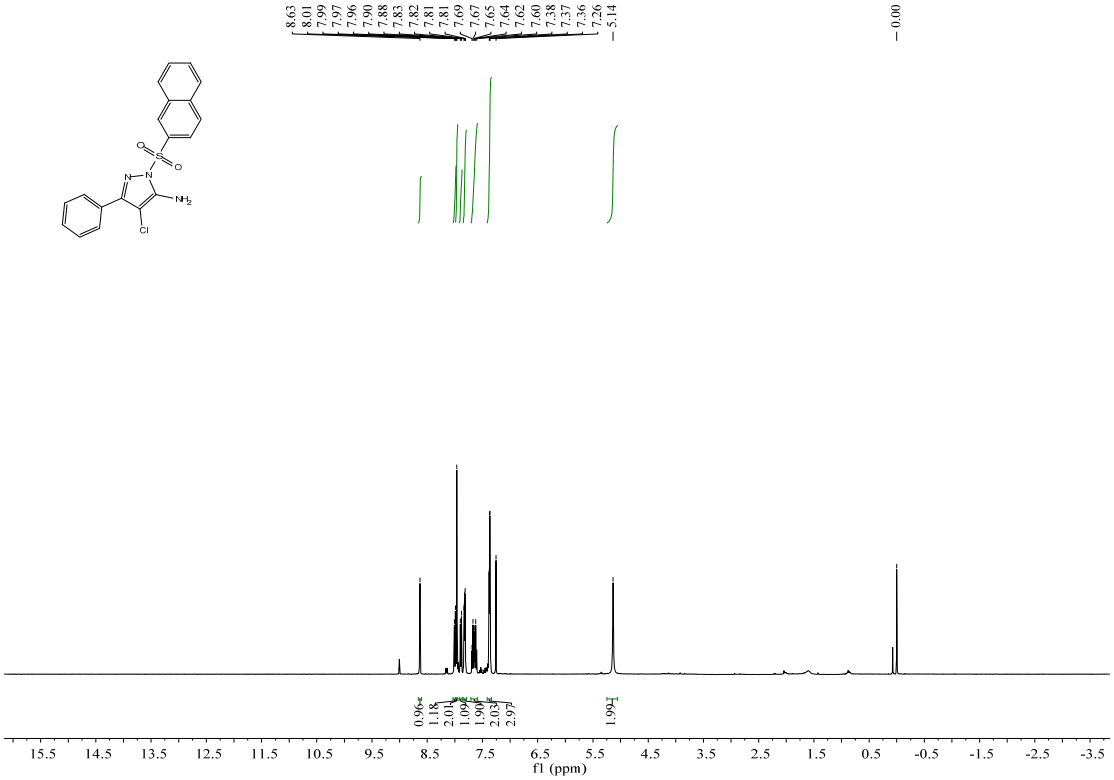


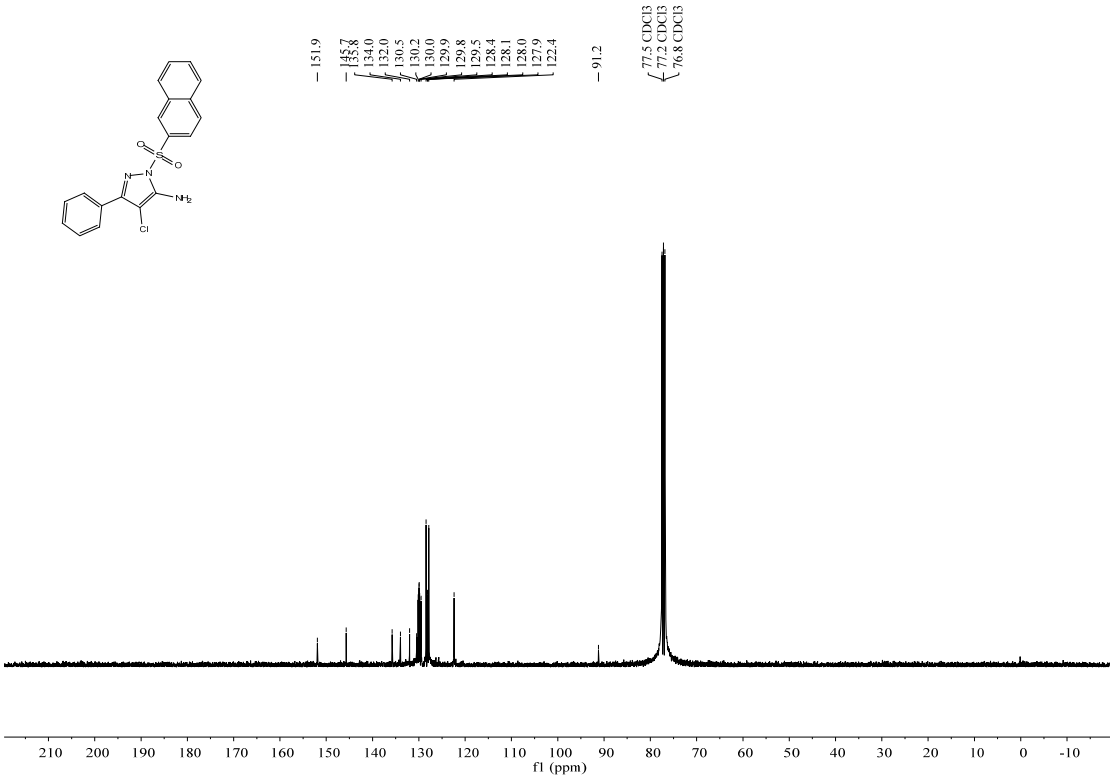
4-chloro-3-(4-chlorophenyl)-1-(phenylsulfonyl)-1H-pyrazol-5-amine (**5g**)





4-chloro-1-(naphthalen-2-ylsulfonyl)-3-phenyl-1H-pyrazol-5-amine (**5h**)





1-phenyl-3H-pyrazolo[3,4-e]pyrrolo[1,2-a]pyrazine（**4aa**）