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SUPPLEMENTARY MATERIAL TO

One-pot preparation of carbamoyl benzotriazoles and their applications in the preparation of ureas, hydrazinecarboxamides and carbamic esters

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PHYSICAL, ANALYTICAL AND SPECTRAL DATA FOR THE SYNTHESIZED COMPOUNDS

N-p-*Tolyl-1*H-*benzotriazole-1-carboxamide* (***2a***). Yield: 80 %; white solid; m.p.: 170–171 °C (lit. 169–172 °C[1]); ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 9.11 (1H, *brs*), 8.35 (1H, *d*, *J* = 8.0 Hz), 8.14 (1H, *d*, *J* = 8.0 Hz), 7.65–7.67 (1H, *m*), 7.51–7.57 (3H, *m*), 7.24 (2H, *d*, *J* = 8.0 Hz), 2.38 (3H, *s*); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 146.5, 135.1, 133.5, 131.6, 130.2, 129.9, 125.7, 120.2, 120.1, 114.1, 21.0.

N-*Phenyl-1*H-*benzotriazole-1-carboxamide* (***2b***). Yield: 76 %; white solid; m.p.: 140–142 °C (lit. 141–143 °C[1]); ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 9.18 (1H, *brs*), 8.35 (1H, *d*, *J* = 8.0 Hz), 8.15 (1H, *d*, *J* = 8.0 Hz), 7.66–7.71 (3H, *m*), 7.50–7.54 (1H, *m*), 7.43–7.47 (2H, *m*), 7.24–7.27 (1H, *m*); ^{13}C-NMR (100 Hz, $CDCl_3$, δ / ppm): 146.5, 146.4, 136.2, 131.6, 130.3, 129.4, 125.7, 125.3, 120.2, 120.1, 114.0.

N-o-*Tolyl-1*H-*benzotriazole-1-carboxamide* (***2c***). Yield: 71 %; white solid; m.p.: 118–121 °C; Anal. calcd. for $C_{14}H_{12}N_4O$: C, 66.55, H, 4.79, N, 22.21 %. Found: C, 66.63, H, 4.80, N, 22.20 %; IR (film, cm^{-1}): 3395, 2925, 1745, 1593, 1543, 1460; ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 9.10 (*brs*, 1H), 8.35 (1H, *d*, *J* = 8.4 Hz), 8.16 (1H, *d*, *J* = 8.4 Hz), 8.01 (1H, *d*, *J* = 8.0 Hz), 7.68 (1H, *t*, *J* = 7.8 Hz), 7.52 (1H, *t*, *J* = 7.6Hz), 7.29–7.35 (2H, *m*), 7.19–7.21 (1H, *m*), 2.46 (3H, *s*); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 146.7, 146.6, 134.2, 130.9, 130.3, 129.4, 127.1, 125.9, 125.7, 122.2, 120.3, 114.1, 17.7.

N-m-*Tolyl-1*H-*benzotriazole-1-carboxamide* (***2d***). Yield: 70 %; white solid; m.p.: 122–124 °C; Anal. Calcd. for $C_{14}H_{12}N_4O$: C, 66.65, H, 4.79, N, 22.21 %.

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Found: C, 66.78, H, 4.78, N, 22.23 %; IR (film, cm^{-1}): 3288, 3074, 1731, 1594, 1548, 1446; ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 9.13 (1H, *brs*), 8.34 (1H, *d*, *J* = 8.4 Hz), 8.14 (1H, *d*, *J* = 8.4 Hz), 7.66–7.70 (1H, *m*), 7.46–7.52 (3H, *m*), 7.32 (1H, *t*, *J* = 7.8 Hz), 7.04 (1H, *d*, *J* = 7.6 Hz), 2.41 (3H, *s*); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 146.5, 146.4, 139.5, 136.1, 131.8, 130.3, 129.2, 126.1, 125.7, 120.7, 120.3, 117.2, 114.1, 21.6.

N-*(4-Methoxyphenyl)-1*H-*benzotriazole-1-carboxamide (**2e**)*. Yield: 83 %; white solid; m.p.: 151–152 °C (lit. 152–154 °C[1]); ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 9.06 (1H, *brs*), 8.33 (1H, *d*, *J* = 8.0 Hz), 8.13 (1H, *d*, *J* = 8.0 Hz), 7.64––7.67 (1H, *m*), 7.57–7.59 (2H, *m*), 7.50–7.52 (1H, *m*), 6.95–6.98 (2H, *m*), 3.84 (3H, *s*); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 157.2, 146.7, 146.4, 131.6, 130.2, 129.0, 125.7, 122.1, 120.2, 114.5, 114.1, 55.6.

N-*(4-Iodophenyl)-1*H-*benzotriazole-1-carboxamide (**2f**)*. Yield: 55 %; white solid; m.p.: 201–203 °C (lit. 202–204 °C[1]); ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 9.27 (1H, *brs*), 8.33 (1H, *d*, *J* = 8.2 Hz), 8.15 (1H, *d*, *J* = 8.2 Hz), 7.69––7.76 (3H, *m*), 7.52–7.54 (1H, *m*), 7.48 (2H, *d*, *J* = 8.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 146.6, 138.4, 136.1, 131.4, 130.5, 125.9, 121.76, 127.77, 120.4, 114.1, 88.8.

N-*(2-Chlorophenyl)-1*H-*benzotriazole-1-carboxamide (**2g**)*. Yield: 53 %; white solid; m.p.: 152–154 °C; Anal. Calcd. for $C_{13}H_9ClN_4O$: C, 57.26, H, 3.33, Cl, 13.00, N, 20.55 %. Found: C, 57.18, H, 3.34, Cl, 12.98, N, 20.59 %; IR (film, cm^{-1}): 3346, 1743, 1597, 1538; ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 9.80 (1H, *brs*), 8.42 (1H, *d*, *J* = 8.0 Hz), 8.34 (1H, *d*, *J* = 8.0 Hz), 8.13 (1H, *d*, *J* = 8.0 Hz), 7.67–7.71 (1H, *m*), 7.48–7.54 (2H, *m*), 7.37–7.41 (1H, *m*), 7.15–7.19 (1H, *m*); ^{13}C-NMR (100 Hz, $CDCl_3$, δ / ppm): 146.4, 146.3, 134.1, 132.4, 130.4, 129.5, 127.9, 125.8, 125.6, 123.2, 121.1, 120.4, 113.9.

N-*(4-Chlorophenyl)-1*H-*benzotriazole-1-carboxamide (**2h**)*. Yield: 55 %; white solid; m.p.: 187–188 °C (lit. 188–191 °C[1]); ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 9.20 (1H, *brs*), 8.32 (1H, *d*, *J* = 8.0 Hz), 8.14 (1H, *d*, *J* = 8.0 Hz), 7.64––7.71 (3H, *m*), 7.50–7.54 (1H, *m*), 7.39–7.42 (2H, *m*); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 146.5, 146.4, 134.8, 131.6, 130.5, 129.5, 125.9, 121.3, 120.3, 114.0.

N-*(Naphthalen-1-ylmethyl)-1*H-*benzotriazole-1-carboxamide (**2j**)*. Yield: 49 %; white solid; m.p.: 91–93 °C; Anal. Calcd. for $C_{18}H_{14}N_4O$: C, 71.51, H, 4.67, N, 18.53 %. Found: C, 71.65, H, 4.66, N, 18.51 %; IR (film, cm^{-1}): 3372, 3043, 1730, 1520, 1362; ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 8.35 (1H, *d*, *J* = = 8.4 Hz), 8.08–8.14 (2H, *m*), 7.87–7.93 (2H, *m*), 7.47–7.66 (7H, *m*), 5.21 (2H, *d*, *J* = 5.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 157.5, 137.5, 134.0, 132.1, 131.3, 130.1, 129.2, 129.0, 127.0, 126.9, 126.2, 125.5, 125.4, 123.1, 120.1, 114.0, 42.5.

N-*Pyridin-3-yl-1*H-*benzotriazole-1-carboxamide (**2k**)*. Yield: 45 %; white solid; m.p.: 140–142 °C; Anal. calcd. for $C_{12}H_9N_5O$: C, 60.25, H, 3.79, N, 29.27 %. Found: C, 60.11, H, 3.80, N, 29.25 %; IR (film, cm^{-1}): 3301, 3078, 1714, 1557; ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 9.47 (1H, *brs*), 8.89 (1H, *s*), 8.48––8.49 (1H, *m*), 8.30 (1H, *d*, *J* = 8.4 Hz), 8.22–8.24 (1H, *m*), 8.13 (1H, *d*, *J* = 8.4 Hz), 7.67 (1H, *t*, *J* = 8.0 Hz), 7.51 (1H, *t*, *J* =8.0 Hz), 7.39–7.42 (1H, *m*); ^{13}C--NMR (100 MHz, $CDCl_3$, δ / ppm): 146.7, 146.5, 146.3, 141.7, 133.4, 131.5, 130.5, 127.4, 126.0, 123.9, 120.3, 113.9.

N-*Methyl-1*H-*benzotriazole-1-carboxamide (**2l**)*. Yield: 50 %; white solid; m.p.: 69–70 °C (lit. 69–71 °C[2]); ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 8.29 (1H, *d*, *J* = 8.0 Hz), 8.09 (1H, *d*, *J* = 8.0 Hz), 7.61–7.65 (1H, *m*), 7.44–7.48 (1H, *m*), 7.31 (1H, *s*), 3.16 (3H, *d*, *J* = 4.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 149.9, 146.2, 131.6, 129.9, 125.4, 119.9, 113.9, 27.0.

N-*Propyl-1*H-*benzotriazole-1-carboxamide (**2m**)*: Yield: 57 %; white solid; m.p.: 57–58 °C (lit. 58–59 °C[1]); ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 8.29 (1H, *d*, *J* = 8.0 Hz), 8.10 (1H, *d*, *J* = 8.0 Hz), 7.61–7.64 (1H, *m*), 7.44–7.48 (1H, *m*), 7.28 (1H, *s*), 3.42 (2H, *t*, *J* = 7.4 Hz), 1.91–2.00 (2H, *m*), 1.05 (3H, *t*, *J* = 7.4 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 130.3, 126.1, 120.1, 114.5, 37.3, 18.0, 13.7.

N-*Isopropyl-1*H-*benzotriazole-1-carboxamide (**2n**)*. Yield: 51 %; white solid; m.p.: 73–74 °C; Anal. Calcd. for $C_{10}H_{12}N_4O$: C, 58.81, H, 5.92, N, 27.43 %. Found: C, 58.72, H, 5.93, N, 27.44 %; IR (film, cm^{-1}): 3329, 2975, 2362, 1727, 1523; ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 8.28 (1H, *d*, *J* = 8.0 Hz), 8.09 (1H, *d*, *J* = 8.0 Hz), 7.60–7.64 (1H, *m*), 7.44–7.47 (1H, *m*), 7.19 (1H, *brs*), 4.25–4.31 (1H, *m*), 1.39 (6H, *d*, *J* = 7.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 148.4, 146.3, 131.7, 129.8, 125.3, 119.9, 114.0, 43.1, 22.7.

N-*Hexyl-1*H-*benzotriazole-1-carboxamide (**2o**)*. Yield: 58 %; white solid; m.p.: 42–43 °C (lit. 43–45 °C[3]); ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 8.29 (1H, *d*, *J* = 8.0 Hz), 8.09 (1H, *d*, *J* = 8.0 Hz), 7.60–7.64 (1H, *m*), 7.44–7.48 (1H, *m*), 7.33 (1H, *brs*), 3.53–3.58 (2H, *m*), 1.69–1.73 (2H, *m*), 1.35–1.44 (6H, *m*), 1.05 (3H, *t*); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 149.3, 146.5, 132.1, 129.9, 125.4, 120.0, 114.0, 40.6, 31.4, 29.5, 26.5, 22.6, 14.0.

N-*Cyclohexyl-1*H-*benzotriazole-1-carboxamide (**2p**)*. Yield: 46 %; white solid; m.p.: 76–77 °C (lit. 77–78 °C[3]); ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 8.27 (1H, *d*, *J* = 8.4 Hz), 8.07 (1H, *d*, *J* = 8.4 Hz), 7.59–7.63 (1H, *m*), 7.43–7.46 (1H, *m*), 7.21–7.22 (1H, *m*), 3.93–3.95 (1H, *m*), 2.09–2.12 (2H, *m*), 1.79–1.83 (2H, *m*), 1.66–1.69 (1H, *m*), 1.38–1.50 (4H, *m*), 1.24–1.30 (1H, *m*); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 148.4, 146.3, 131.7, 129.8, 125.3, 119.9, 114.0, 49.8, 33.0, 25.4, 24.8.

N-*Adaman-1-yl-1*H-*benzotriazole-1-carboxamide (**2q**)*. Yield: 42 %; white solid; m.p.: 134–135 °C (lit. 135 °C[3]); ^{1}H-NMR (400 MHz, $CDCl_3$,

δ / ppm): 8.26 (1H, *d*, *J* = 8.4 Hz), 8.08 (1H, *d*, *J* = 8.4 Hz), 7.58–7.62 (1H, *t*, *J* = = 7.8 Hz), 7.42–7.46 (1H, *t*, *J* = 7.8 Hz), 7.16 (1H, *brs*), 2.17–2.21 (9H, *m*), 1.72– –1.76 (6H, *m*); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 147.4, 146.3, 131.6, 129.7, 125.2, 119.9, 114.1, 52.8, 41.6, 36.2, 29.4.

*(*S*)-3-Phenyl-2-(3-phenylureido)propanoic acid (**4a**)*. Yield: 91%; white solid; m.p.: 160–162 °C (lit. 159–163 °C[4]); ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 12.84 (1H, *s*), 8.68 (1H, *s*), 7.20–7.35 (9H, *m*), 6.89 (1H, *t*, *J* = 6.8 Hz), 6.32 (1H, *d*, *J* = 7.6 Hz), 4.43–4.46 (1H, *m*), 3.06–3.10 (1H, *m*), 2.92–2.98 (1H, *m*); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / ppm): 174.1, 155.1, 140.6, 137.7, 129.8, 129.2, 128.8, 127.0, 121.7, 118.0, 54.0, 37.8.

*(*S*)-2-(3-Phenylureido)propanoic acid (**4b**)*. Yield: 94 %; white solid; m.p.: 164–165 °C; Anal. calcd. for $C_{10}H_{12}N_2O_3$: C, 57.68, H, 5.81, N, 13.45 %. Found: C, 57.57, H, 5.82, N, 13.46 %; IR (film, cm^{-1}): 3355, 3268, 2922, 1738, 1628, 1552; ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 12.64 (1H, *s*), 8.60 (1H, *s*), 7.36 (2H, *d*, *J* = 8.0 Hz), 7.21 (2H, *t*, *J* = 7.6 Hz), 6.89 (1H, *t*, *J* = 7.2 Hz), 6.45 (1H, *d*, *J* = 7.2 Hz), 4.15–4.18 (1H, *m*), 1.30 (3H, *d*, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / ppm): 175.4, 155.1, 140.7, 129.2, 121.7, 118.0, 48.4, 18.7.

*(*S*)-4-Methyl-2-(3-phenylureido)pentanoic acid (**4c**)*. Yield: 90 %; white solid; m.p.: 128–129 °C; Anal. Calcd. for $C_{13}H_{18}N_2O_3$: C, 62.38, H, 7.25, N, 11.19 %. Found: C, 62.36, H, 7.23, N, 11.21 %; IR (film, cm^{-1}): 3403, 3309, 2963, 1728, 1654, 1551; ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 12.61(1H, *s*), 8.56 (1H, *s*), 7.36 (2H, *d*, *J* = 8.4 Hz), 7.21 (2H, *t*, *J* = 8.0 Hz), 6.88 (1H, *t*, *J* = = 7.2 Hz), 6.40 (1H, *d*, *J* = 8.4 Hz), 4.15–4.18 (1H, *m*), 1.64–1.69 (1H, *m*), 1.46– –1.53 (2H, *m*), 0.88–0.91 (6H, *m*); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / ppm): 175.4, 155.3, 140.7, 129.2, 121.7, 118.0, 51.1, 41.4, 24.9, 23.3, 22.1.

*(*S*)-2-(3-Phenylureido)-6-((2,2,2-trifluoroacetyl)amino)hexanoic acid (**4d**)*. Yield: 92 %; white solid; m.p.: 157–158 °C; Anal. Calcd. for $C_{15}H_{18}F_3N_3O_4$: C, 49.86, H, 5.02, F, 15.77, N, 11.63 %. Found: C, 49.92, H, 5.01, F, 15.79, N, 11.61 %; IR (film, cm^{-1}): 3389, 3296, 2941, 1719, 1697, 1562; ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 12.62 (1H, *s*), 9.42–9.43 (1H, *m*), 8.60 (1H, *s*), 7.36 (2H, *d*, *J* = 8.0 Hz), 7.21 (2H, *t*, *J* = 8.0 Hz), 6.89 (1H, *t*, *J* = 7.6 Hz), 6.44 (1H, *d*, *J* = 7.6 Hz), 4.12–4.17 (1H, *m*), 3.14–3.19 (2H, *m*), 1.69–1.75 (1H, *m*), 1.55–1.62 (1H, *m*), 1.48–1.49 (,2H *m*), 1.30–1.34 (2H, *m*); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / ppm): 174.8, 156.4, 155.3, 140.7, 137.3, 129.2, 121.7, 118.0, 52.4, 31.9, 28.4, 22.8.

*(*S*)-3-(1*H*-Indol-3-yl)-2-(3-phenylureido)propanoic acid (**4e**)*. Yield: 80 %; white solid; m.p.: 170–171 °C; Anal. Calcd. for $C_{18}H_{17}N_3O_3$: C, 66.86, H, 5.30, N, 13.00 %. Found: C, 66.81, H, 5.31, N, 12.99 %; IR (film, cm^{-1}): 3416, 3290, 2914, 1714, 1560; ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 12.75 (1H, s), 10.92 (1H, *s*), 8.70 (1H, *s*), 7.52 (1H, *d*, *J* = 8.0 Hz), 7.32–7.35 (3H, *m*), 7.20 (2H, *t*, *J* = = 8.0 Hz), 7.12–7.13 (1H, *m*), 7.06 (1H, *t*, *J* = 7.2 Hz), 6.96 (1H, *t*, *J* = 7.2 Hz),

6.88 (1H, *t*, *J* = 7.6 Hz), 6.30 (1H, *d*, *J* = 7.6 Hz), 4.47–4.52 (1H, *m*), 3.09–3.22 (2H, *m*); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / ppm): 174.5, 155.2, 140.7, 136.6, 129.2, 127.9, 124.2, 121.6, 121.4, 118.88, 118.86, 118.0, 111.8, 109.8, 53.5, 28.1.

*(*S*)-3-Methyl-2-(3-phenylureido)butanoic acid (**4f**)*. Yield: 94 %; white solid; m.p.: 126–128 °C; Anal. Calcd. for $C_{12}H_{16}N_2O_3$: C, 61.00, H, 6.83, N, 11.86 %. Found: C, 61.11, H, 6.82, N, 11.85 %; IR (film, cm^{-1}): 3396, 2967, 2626, 1709, 1673, 1567; ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 12.68 (1H, *s*), 8.61 (1H, *s*), 7.36 (2H, *d*, *J* = 8.0 Hz), 7.21 (2H, *t*, *J* = 8.0 Hz), 6.89 (1H, *t*, *J* = 7.2 Hz), 6.39 (1H, *d*, *J* = 8.8 Hz), 4.09–4.13 (1H, *m*), 2.04–2.10 (1H, *m*), 0.91 (3H, *d*, *J* = 6.8 Hz), 0.86 (3H, *d*, *J* = 6.8 Hz); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / ppm): 174.3, 155.5, 140.7, 129.2, 121.7, 117.9, 57.6, 30.7, 19.7, 18.0.

*(*S*)-3-Hydroxy-2-(3-phenylureido)propanoic acid (**4g**)*. Yield: 72 %; white solid; m.p.: 156–157 °C; Anal. Calcd. for $C_{10}H_{12}N_2O_4$: C, 53.57, H, 5.39, N, 12.49 %. Found: C, 53.55, H, 5.38, N, 12.51 %; IR (film, cm^{-1}): 3368, 3323, 2941, 1740, 1642, 1573; ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 12.62 (1H, *s*), 8.85 (1H, *s*), 7.36 (2H, *d*, *J* = 8.0 Hz), 7.21 (2H, *t*, *J* = 8.0 Hz), 6.89 (1H, *t*, *J* = = 7.2 Hz), 6.44 (1H, *d*, *J* = 8.4 Hz), 4.18–4.22 (1H, *m*), 3.80 (1H, *dd*, *J* = 3.6 Hz, & 10.4 Hz), 3.63 (1H, *dd*, *J* = 3.6 and 10.4 Hz); ^{13}C-NMR (100 MHz, DMSO--d_6, δ / ppm): 173.4, 155.3, 140.8, 129.2, 121.7, 117.9, 62.3, 55.0.

*(*S*)-1-(Phenylcarbamoyl)pyrrolidine-2-carboxylic acid (**4h**)*. Yield: 85 %; white solid; m.p.: 158–159 °C; Anal. Calcd. for $C_{12}H_{14}N_2O_3$: C, 61.53, H, 6.02, N, 11.96 %. Found: C, 61.48, H, 6.03, N, 11.93 %; IR (film, cm^{-1}): 3371, 2984, 2876, 1717, 1634, 1540; ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 12.43 (1H, *s*), 8.25 (1H, *s*), 7.48 (2H, *d*, *J* = 8.0 Hz), 7.21 (2H, *t*, *J* = 8.4 Hz), 6.92 (1H, *t*, *J* = = 7.2 Hz), 4.29–4.31 (1H, *m*), 3.52–3.56 (1H, *m*), 3.43–3.49 (1H, *m*), 2.13–2.18 (1H, *m*), 1.85–1.95 (3H, *m*); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / ppm): 174.8, 154.2, 140.8, 128.7, 122.2, 119.9, 59.2, 46.5, 29.7, 24.7.

*(*S*)-3-Phenyl-2-(3-*p*-tolylureido)propanoic acid (**4i**)*. Yield: 90 %; white solid; m.p.: 146–148 °C; Anal. Calcd. for $C_{17}H_{18}N_2O_3$: C, 68.44, H, 6.0, N, 9.39 %. Found: C, 68.52, H, 6.07, N, 9.41 %; IR (film, cm^{-1}): 3343, 3031, 2921, 2650, 1712, 1635, 1561; ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 12.82 (1H, *s*), 8.57 (1H, *s*), 7.28–7.31 (2H, *m*), 7.19–7.24 (5H, *m*), 7.01 (2H, *d*, *J* = 8.4 Hz), 6.27 (1H, *d*, *J* = 7.6 Hz), 4.42–4.46 (1H, *m*), 3.04–3.09 (1H, *m*), 2.91–2.97 (1H, *m*), 2.19 (3H, *s*); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / ppm): 174.1, 155.2, 138.1, 137.7, 130.4, 129.8, 129.6, 128.7, 127.0, 118.0, 54.0, 37.8, 20.8.

*(*S*)-4-Methyl-2-(3-*p*-tolylureido)pentanoic acid (**4j**)*. Yield: 95 %; white solid; m.p.: 57–58 °C; Anal. Calcd. for $C_{14}H_{20}N_2O_3$: C, 63.62, H, 7.63, N, 10.60 %. Found: C, 63.52, H, 7.61, N, 10.65 %; IR (film, cm^{-1}): 3360, 2960, 1720, 1650, 1555; ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 12.57 (1H, *s*), 8.43 (1H, *s*), 7.24 (2H, *d*, *J* = 8.4 Hz), 7.01 (2H, *d*, *J* = 7.6 Hz), 6.32 (1H, *d*, *J* = 8.0 Hz), 4.14–4.19

(1H, *m*), 2.20 (3H, *s*), 1.64–1.70 (1H, *m*), 1.45–1.54 (2H, *m*), 0.90 (3H, *d*, *J* = 6.8 Hz), 0.88 (3H, *d*, *J* = 6.8 Hz); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / ppm): 175.5, 155.4, 138.1, 130.4, 129.6, 118.1, 51.1, 41.4, 24.8, 23.3, 22.0, 20.8.

*(*S*)-2-[3-(4-Chlorophenyl)ureido]-3-phenylpropanoic acid (**4k**)*. Yield: 91 %; white solid; m.p.: 156–158 °C; Anal. Calcd. for $C_{16}H_{15}ClN_2O_3$: C, 60.29, H, 4.74, Cl, 11.12, N, 8.79 %. Found: C, 60.18; H, 4.73; Cl, 11.11; N, 8.80 %; IR (film, cm^{-1}): 3340, 3029, 1701, 1646, 1552; ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 8.82 (1H, *s*), 7.38 (2H, *d*, *J* = 8.4 Hz), 7.20–7.31 (7H, *m*), 6.37 (1H, *d*, *J* = 7.6 Hz), 4.45–4.48 (1H, *m*), 3.08 (1H, *m*), 2.96 (1H, *m*); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / ppm): 173.9, 155.1, 139.5, 137.6, 129.7, 129.5, 128.8, 127.0, 125.2, 118.0, 54.0, 37.8.

*(*S*)-3-Phenyl-2-(3-propylureido)propanoic acid (**4l**)*. Yield: 96 %; white solid; m.p.: 64–65 °C (lit. 63–65 °C[5]); ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 12.45 (1H, *s*), 7.27 (2H, *d*, *J* = 7.2 Hz), 7.21 (1H, *t*, *J* = 6.4 Hz), 7.16 (2H, *d*, *J* = = 7.2 Hz), 6.06–6.08 (1H, *m*), 5.98 (1H, *d*, *J* = 8.2 Hz), 4.30–4.35 (1H, *m*), 2.81– –3.00 (4H, *m*), 1.29–1.34 (2H, *m*), 0.79 (3H, *t*, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / ppm): 174.5, 157.9, 138.0, 129.7, 128.6, 126.9, 54.3, 41.4, 38.1, 23.6, 11.8.

1-Methyl-N-*phenylhydrazinecarboxamide (**6a**)*. Yield: 90 %; white solid; m.p.: 90–92 °C (lit. 90.0–92.5 °C[6]); ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 8.60 (1H, *s*, NH), 7.46 (2H, *d*, *J* = 8.0 Hz), 7.27–7.30 (2H, *m*), 6.99 (1H, *t*, *J* = 7.4 Hz), 3.77 (2H, *s*, NH_2), 3.22 (3H, *s*); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 156.5, 139.1, 128.9, 122.5, 118.7, 38.3.

N-*(4-Chlorophenyl)-1-methylhydrazinecarboxamide (**6b**)*. Yield: 89 %; white solid; m.p.: 159–162 °C; Anal. Calcd. for $C_8H_{10}ClN_3O$: C, 48.13, H, 5.05; Cl, 17.76, N, 21.05 %. Found: C, 48.20, H, 5.04, Cl, 17.73, N, 21.08 %; IR (film, cm^{-1}): 3438, 3318, 3217, 1741, 1660; ^{1}H-NMR (600 MHz, $CDCl_3$, δ / ppm): 8.60 (1H, *s*, NH), 7.41 (2H, *d*, *J* = 8.8 Hz), 7.22 (2H, *d*, *J* = 8.8 Hz), 3.78 (2H, *s*, NH_2), 3.20 (3H, *s*); ^{13}C-NMR (150 MHz, $CDCl_3$, δ / ppm): 156.2, 137.8, 128.8, 127.2, 119.8, 38.3.

*1,4-Diphenylsemicarbazide (**6c**)*. Yield: 45 %; white solid; m.p.: 202–204 °C (lit. 204–205 °C[7]); ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 9.21 (1H, *s*, NH), 8.34 (1H, *d*, *J* = 8.4 Hz, NH), 8.13 (1H, *d*, *J* = 8.4 Hz, NH), 7.65–7.71 (3H, *m*), 7.42– –7.53 (4H, *m*), 7.22–7.30 (2H, *m*), 6.91–7.07 (1H, *m*); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 156.6, 146.5, 136.2, 131.6, 130.3, 129.4, 125.7, 125.3, 120.2, 120.1, 114.1.

*4-Ethyl-1-phenylsemicarbazide (**6d**)*. Yield: 53 %; white solid; m.p.: 149– –151 °C; Anal. Calcd. for $C_9H_{13}N_3O$: C, 60.32; H, 7.31; N, 23.45 %. Found: C, 60.57; H, 7.36; N, 23.53 %; ^{1}H-NMR (600 MHz, $CDCl_3$, δ / ppm): 7.94 (2H, *d*, *J* = 7.5 Hz), 7.59–7.51 (3H, *m*), 6.55 (1H, *s*), 3.57–3.52 (2H, *m*), 1.31 (*t*, 3H, *J* =

= 7.2 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$, δ/ppm): 160.5, 151.1, 133.5, 129.3, 123.9, 35.7, 14.7.

N-*Phenylcarbamic acid ethyl ester (**8a**)*. Yield: 83 %; white solid; m.p.: 49––51°C (lit. 51–52 °C[8]); Anal. Calcd. for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48 %. Found: C, 65.67; H, 6.75; N, 8.51 %; IR (film, cm^{-1}): 3453, 2972, 2870, 1649; ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 7.38 (2H, *d*, *J* = 8.0 Hz), 7.28–7.32 (2H, *m*), 7.06 (1H, *t*, *J* = 7.2 Hz), 7.62 (1H, *brs*), 4.23 (2H, *q*, *J* = 8.0 Hz), 1.31 (3H, *t*, *J* = 7.2 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$, δ / ppm): 153.8, 138.1, 129.0, 123.3, 118.8, 61.2, 14.6.

N-*Phenylcarbamic acid butyl ester (**8b**)*. Yield: 80 %; white solid; m.p.: 60–62 °C (lit. 62.0–63.5 °C[9]); Anal. Calcd. for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25 %. Found: C, 68.48; H, 7.74; N, 7.33 %; IR (film, cm^{-1}): 3463, 2977, 2869, 1717; ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 7.37–7.39 (2H, *m*), 7.30 (2H, *t*, *J* = = 8.0 Hz), 7.04–7.07 (1H, *m*), 6.58 (1H, *brs*), 4.17 (2H, *t*, *J* = 6.8 Hz), 1.63–1.68 (2H, *m*), 1.40–1.45 (2H, *m*), 0.96 (3H, *t*, *J* = 8.0 Hz). ^{13}C-NMR (150 MHz, $CDCl_3$, δ / ppm): 154.0, 138.1, 129.0, 123.3, 118.7, 65.1, 31.0, 19.1, 13.8.

N-p-*Tolylcarbamic acid ethyl ester (**8c**)*. Yield: 77 %; white solid; m.p.: 50––51 °C (lit. 49–51 °C[10]); Anal. Calcd. for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.22; N, 7.82 %. Found: C, 66.81; H, 7.32; N, 7.90 %; IR (film, cm^{-1}): 3470, 2976, 2871, 2281, 1713; ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 7.25 (2H, *d*, *J* = 8.0 Hz), 7.10 (2H, *d*, *J* = 8.0 Hz), 6.4 (1H, *brs*), 4.21 (2H, *q*, *J* = 8.0 Hz), 2.30 (3H, *s*), 1.30 (3H, *t*, *J* = 7.2 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$, δ / ppm): 153.7, 135.4, 133.0, 129.5, 118.8, 61.1, 20.8, 14.6.

N-p-*Tolylcarbamic acid butyl ester (**8d**)*. Yield: 78 %; white solid; m.p.: 62––63 °C (lit. 64–65 °C[11]); Anal. Calcd. for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76 %. Found: C, 69.68; H, 8.19; N, 6.81 %; IR (film, cm^{-1}): 3442, 2973, 2862, 1722; ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 7.25 (2H, *d*, *J* = 8.0 Hz), 7.10 (2H, *d*, *J* = 8.0 Hz), 6.51 (1H, *brs*), 4.16 (2H, *t*, *J* = 6.8 Hz), 2.30 (3H, *s*), 1.59–1.67 (2H, *m*), 1.39–1.44 (2H, *m*), 0.95 (3H, *t*, *J* = 7.2 Hz). ^{13}C-NMR (150 MHz, $CDCl_3$, δ / ppm): 154.0, 135.5, 132.8, 129.5, 118.8, 65.0, 31.0, 20.8, 19.1, 13.8.

N-*(4-Chlorophenyl)carbamic acid ethyl ester (**8e**)*. Yield: 85 %; white solid; m.p.: 66–67 °C (lit. 68–69 °C[12]); IR (film, cm^{-1}): 3299, 3114, 2938, 1686; ^{1}H--NMR (400 MHz, $CDCl_3$, δ / ppm): 7.33, (2H *d*, *J* = 8.0 Hz), 7.26 (2H, *d*, *J* = 8.0 Hz), 6.58 (1H, *brs*), 4.22 (2H, *q*, *J* = 7.2 Hz), 1.30 (3H, *t*, *J* = 7.2 Hz).

N-*(4-Chlorophenyl)carbamic acid butyl ester (**8f**)*. Yield: 85 %; white solid; m.p.: 50–52 °C (lit. 53–54 °C[13]); Anal. Calcd. for $C_{11}H_{14}ClNO_2$: C, 58.03; H, 6.20; N, 6.15 %. Found: C, 57.91; H, 6.14; N, 6.23 %; IR (film, cm^{-1}): 3287, 3131, 2931, 1689; ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 7.33 (2H, *d*, *J* = 8.0 Hz), 7.25 (2H, *d*, *J* = 8.0 Hz), 6.63 (1H, *brs*), 4.16 (2H, *t*, *J* = 6.8 Hz), 1.62–1.69 (2H, *m*), 1.38–1.44 (2H, *m*), 0.95 (3H, *t*, *J* = 7.2 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$, δ / ppm): 153.7, 136.6, 129.0, 128.3, 119.9, 65.3, 30.9, 19.1, 13.7.

^{1}H- AND ^{13}C-NMR SPECTRA FOR THE NEWLY SYNTHESIZED COMPOUNDS **2**

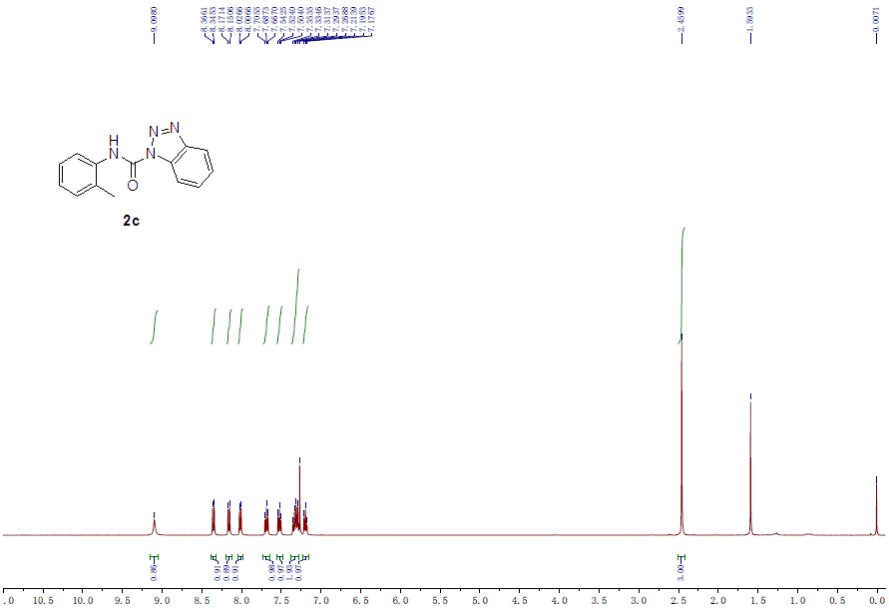

Fig. S-1. ^{1}H-NMR spectrum of compound **2c**.

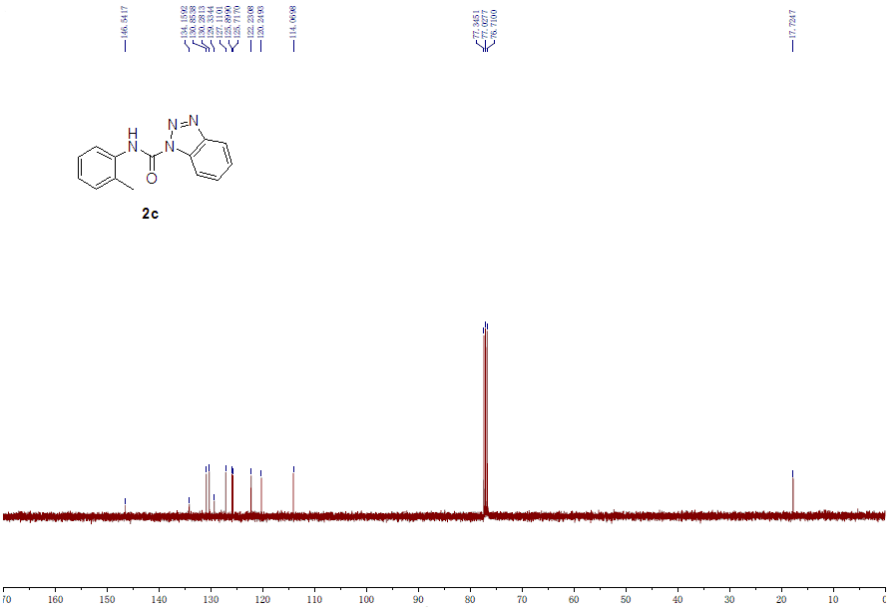

Fig. S-2. ^{13}C-NMR spectrum of compound **2c**.

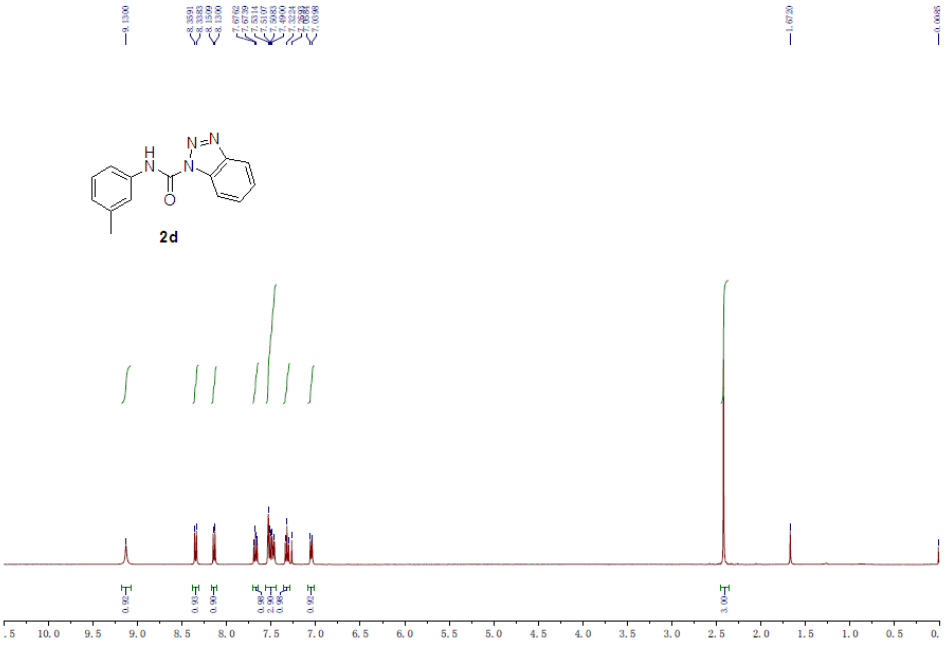

Fig. S-3. ^{1}H-NMR spectrum of compound **2d**.

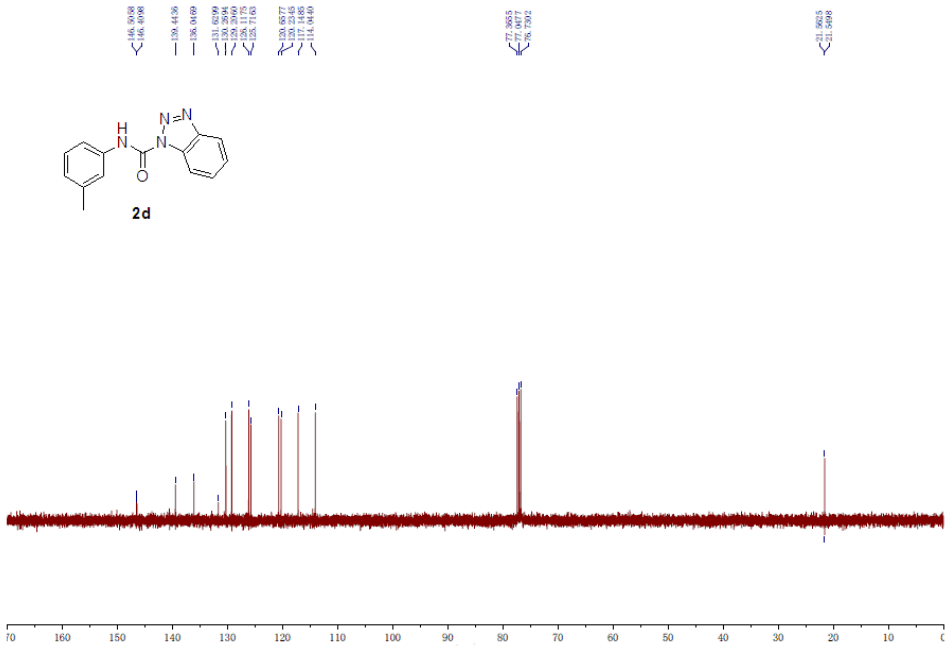

Fig. S-4. ^{13}C-NMR spectrum of compound **2d**.

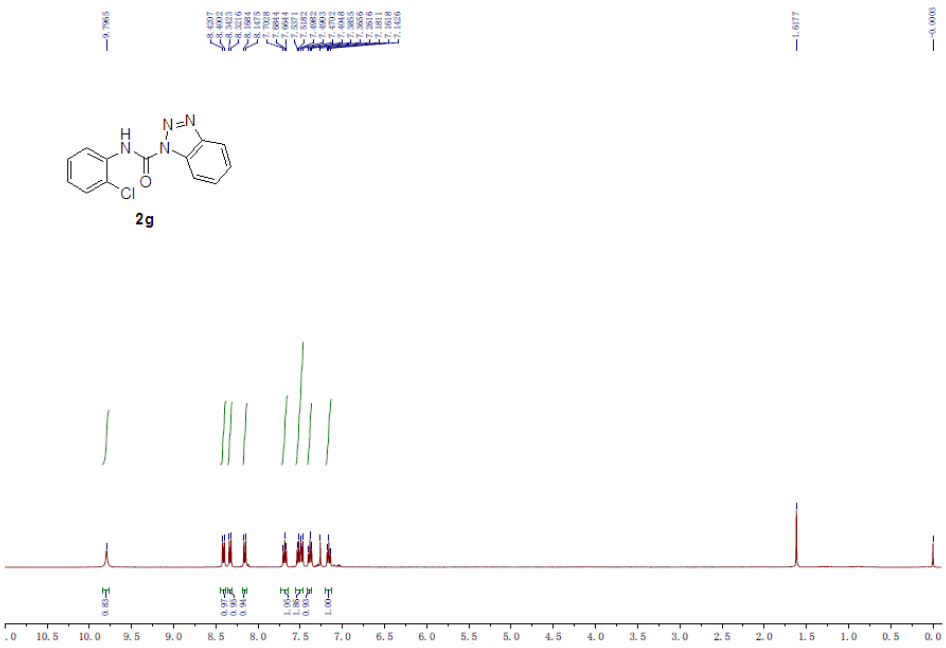

Fig. S-5. ^{1}H-NMR spectrum of compound **2g**.

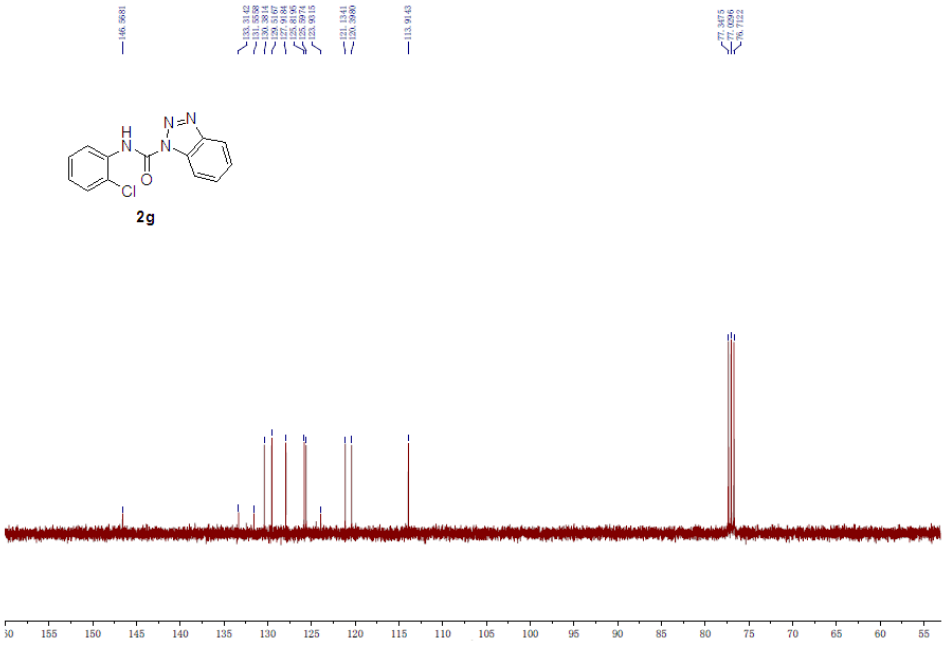

Fig. S-6. ^{13}C-NMR spectrum of compound **2g**.

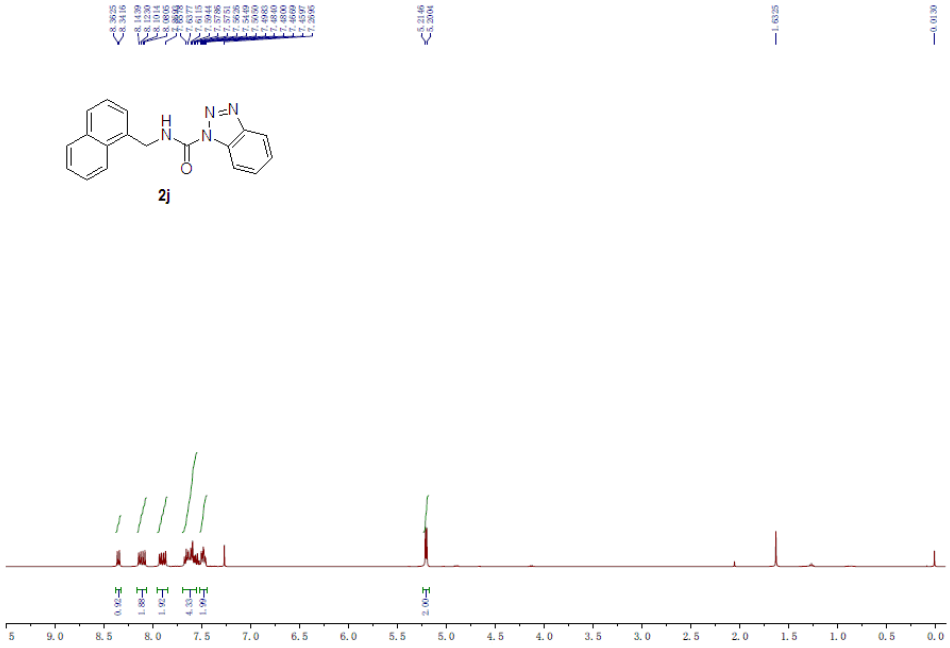

Fig. S-7. ^{1}H-NMR spectrum of compound **2j**.

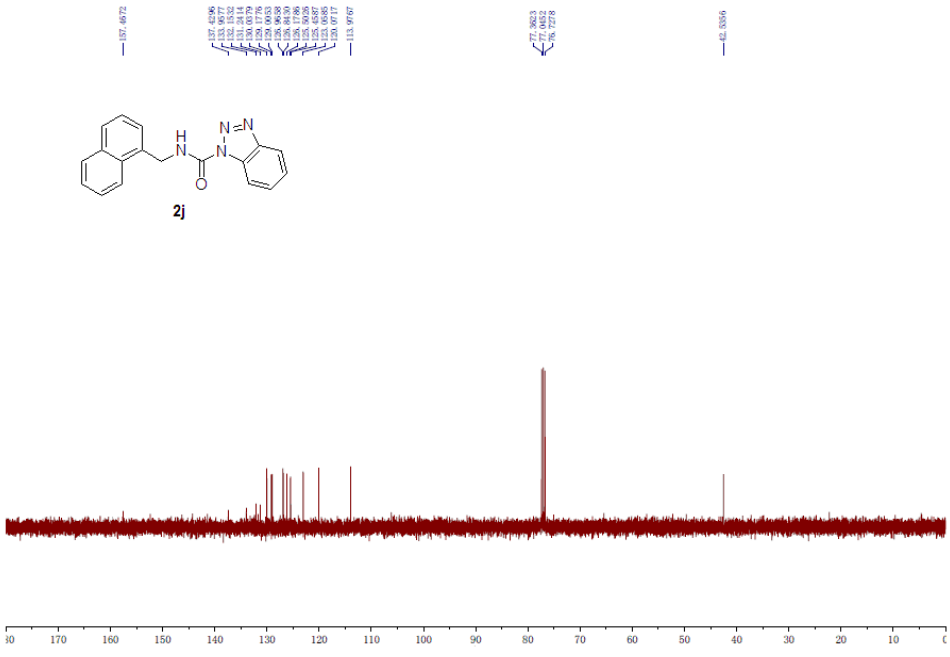

Fig. S-8. ^{13}C-NMR spectrum of compound **2j**.

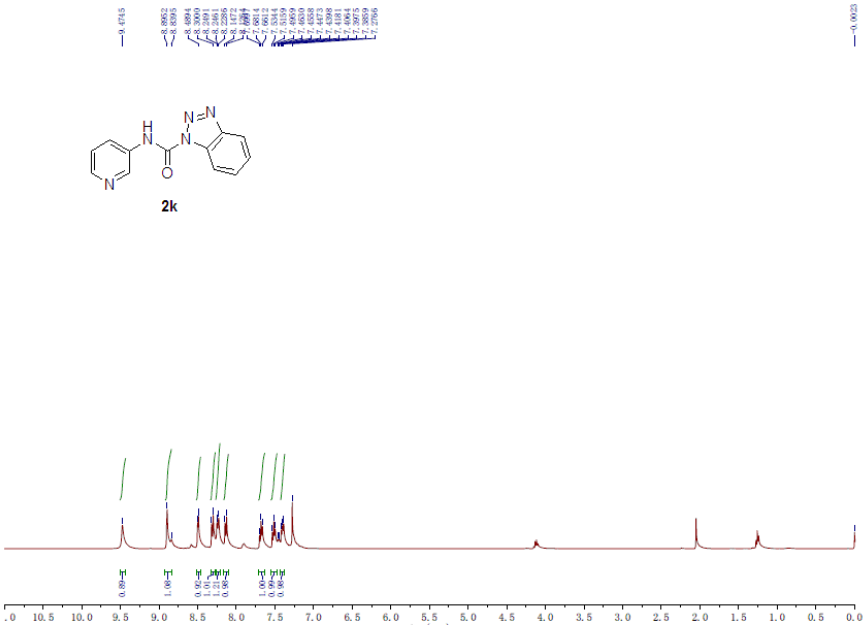

Fig. S-9. ^{1}H-NMR spectrum of compound **2k**.

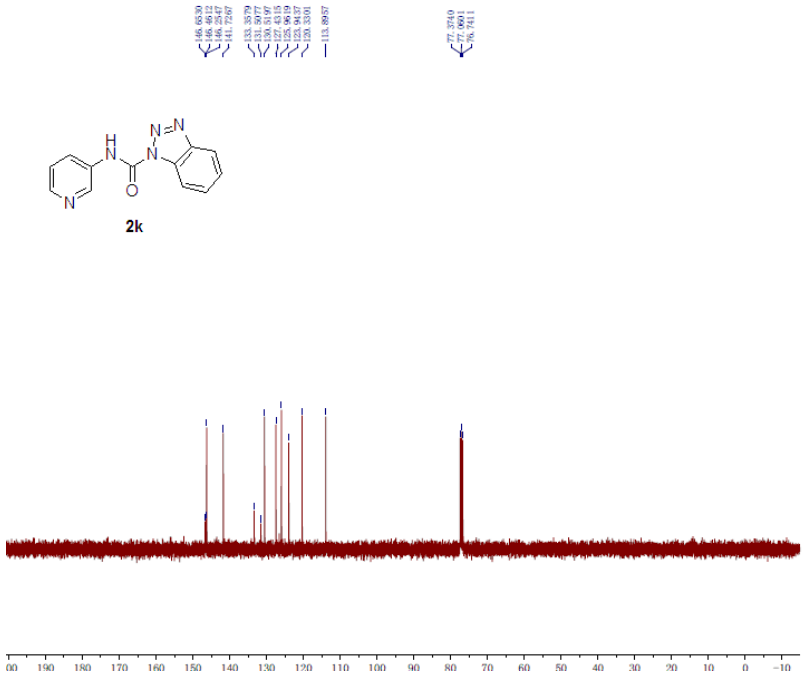

Fig. S-10. ^{13}C-NMR spectrum of compound **2k**.

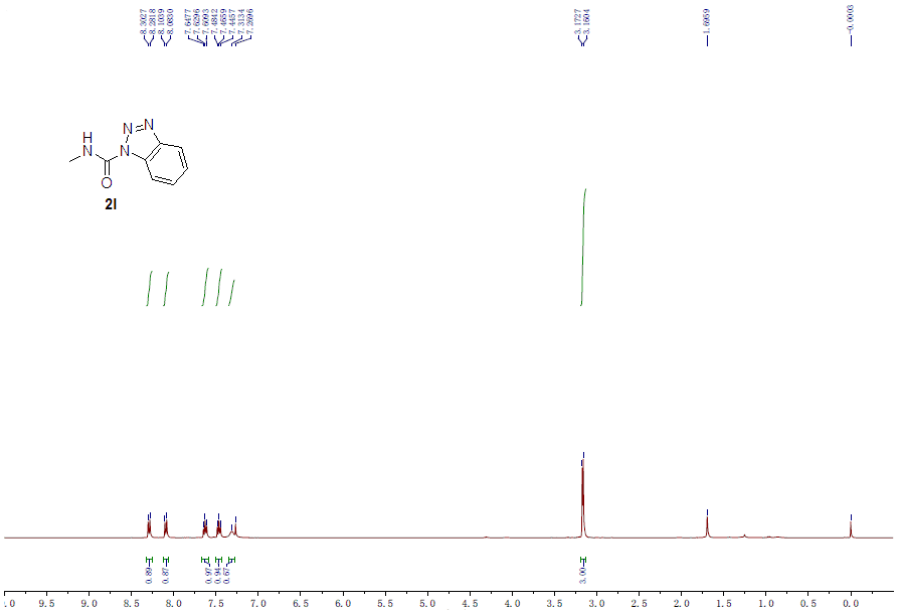

Fig. S-11. ^{1}H-NMR spectrum of compound **2l**.

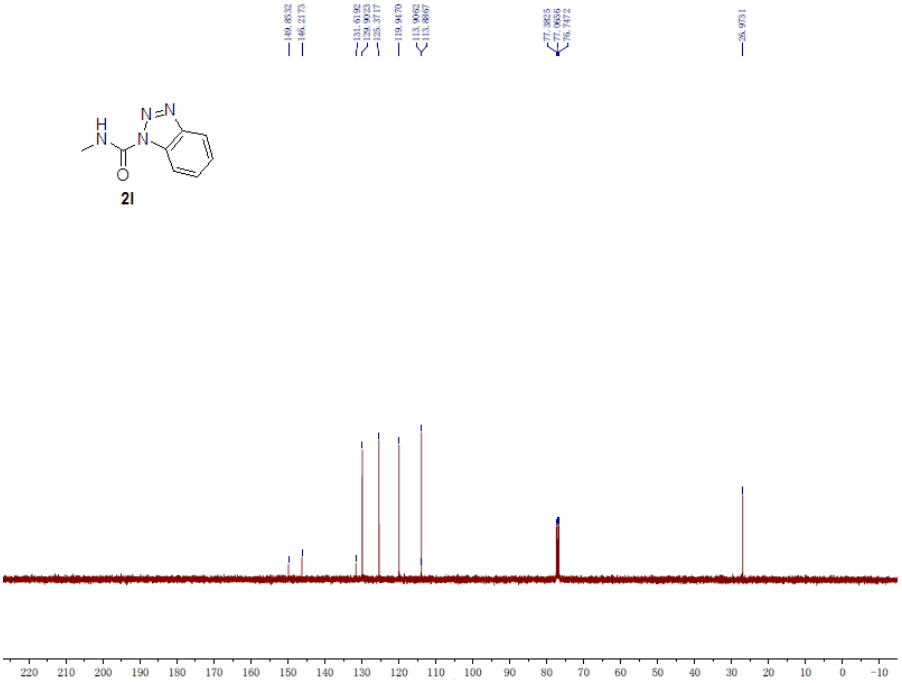

Fig. S-12. ^{13}C-NMR spectrum of compound **2l**.

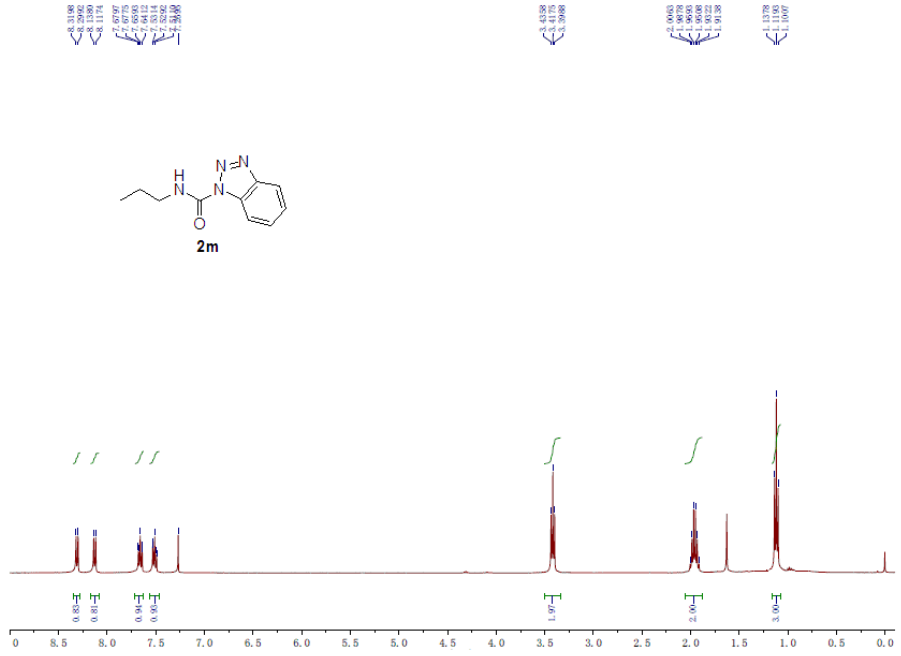

Fig. S-13. ^{1}H-NMR spectrum of compound **2m**.

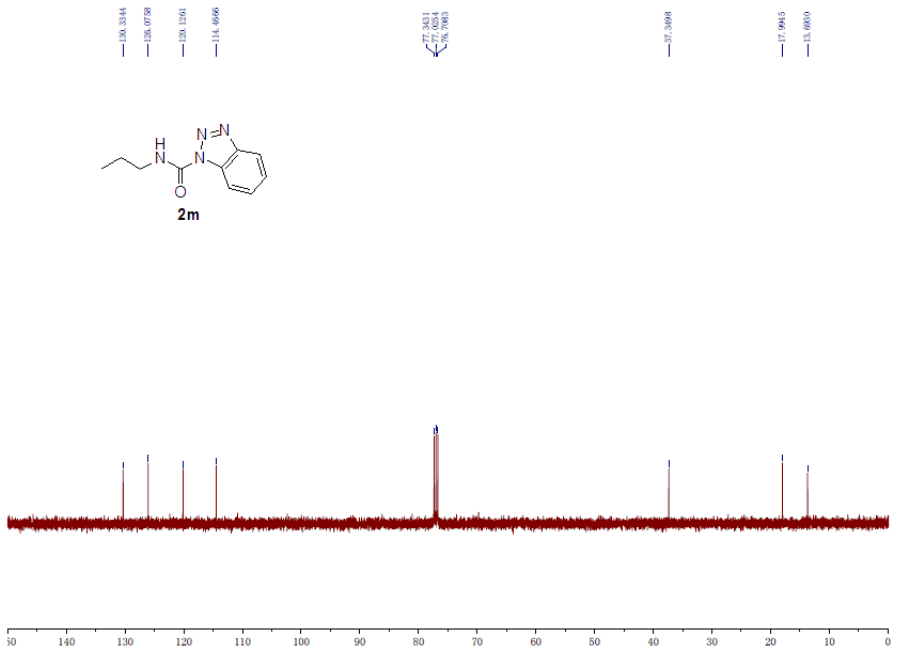

Fig. S-14. ^{13}C-NMR spectrum of compound **2m**.

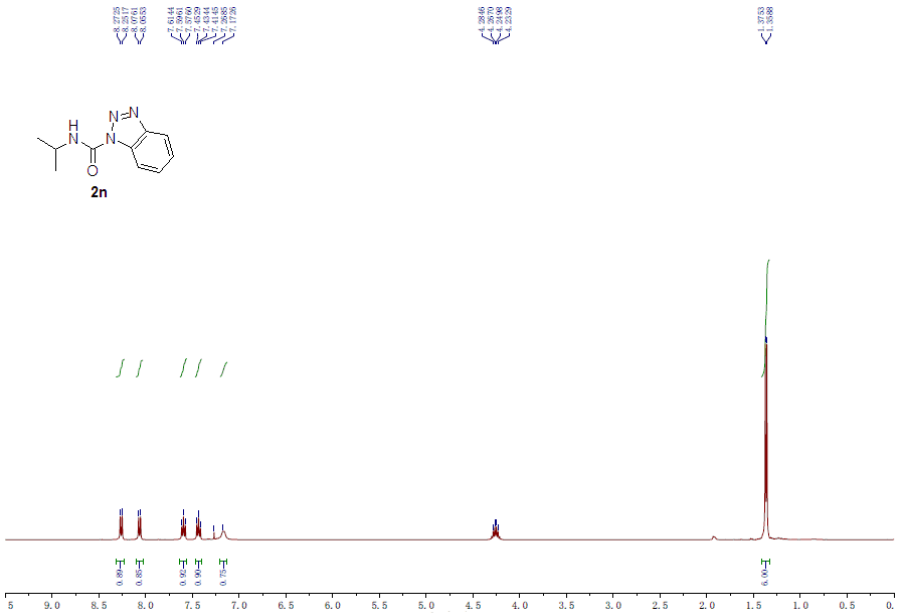

Fig. S-15. ^{1}H-NMR spectrum of compound **2n**.

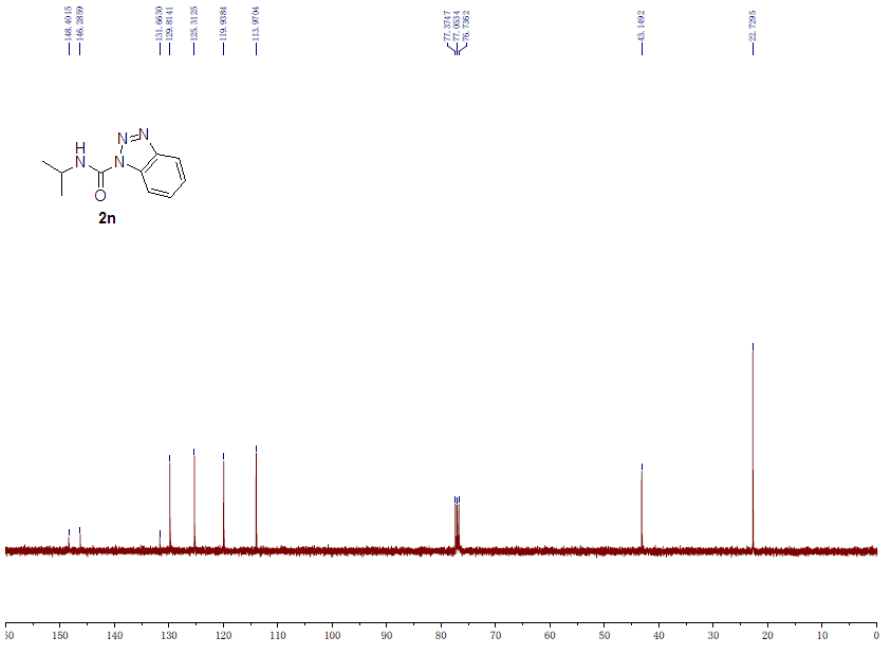

Fig. S-16. ^{13}C-NMR spectrum of compound **2n**.

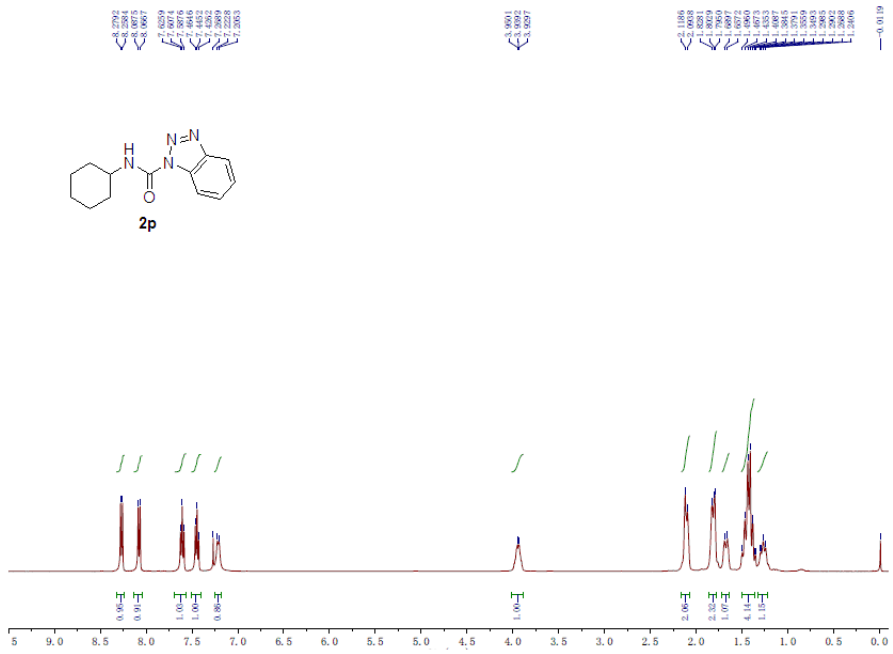

Fig. S-17. ^{1}H-NMR spectrum of compound **2p**.

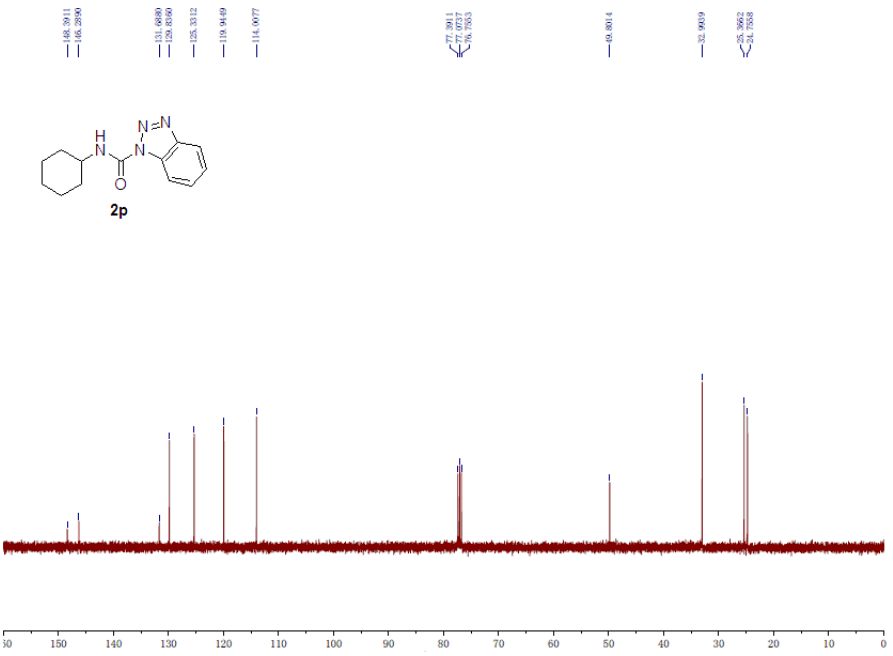

Fig. S-18. ^{13}C-NMR spectrum of compound **2p**.

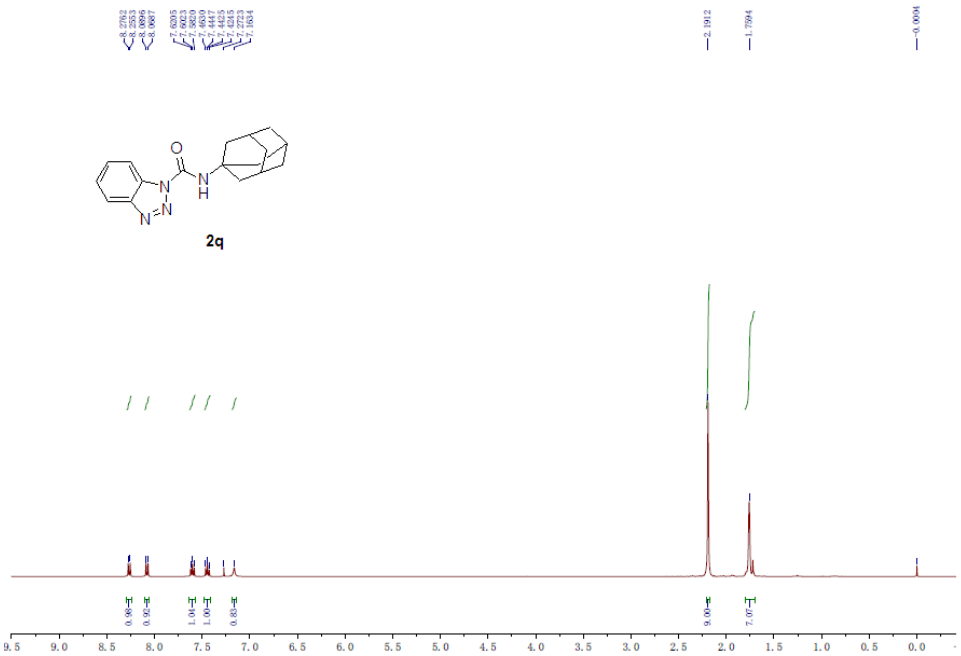

Fig. S-19. ^{1}H-NMR spectrum of compound **2q**.

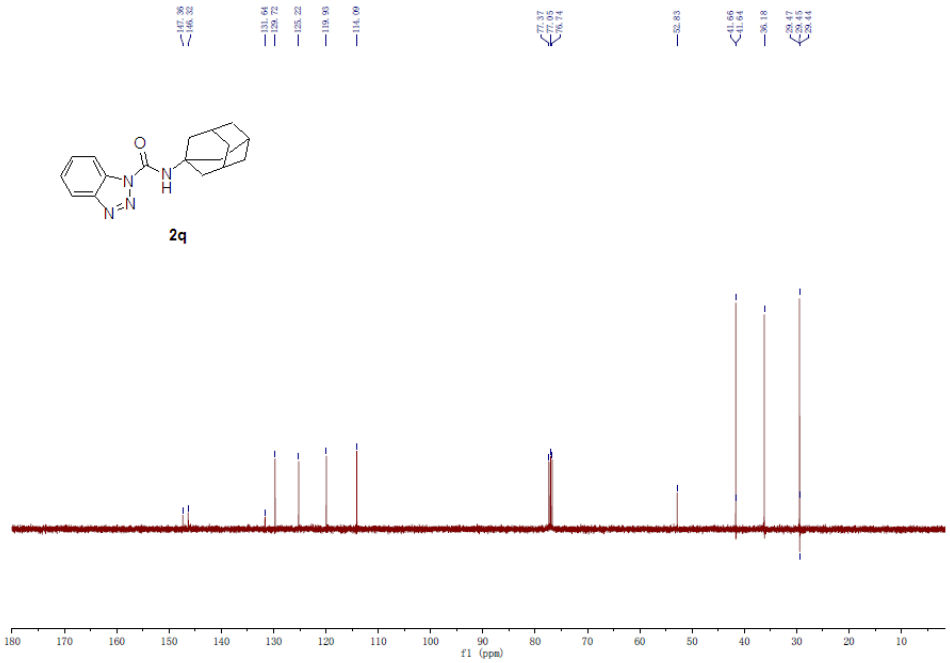

Fig. S-20. ^{13}C-NMR spectrum of compound **2q**.

^{1}H- AND ^{13}C-NMR SPECTRA FOR THE NEWLY SYNTHESIZED COMPOUNDS **4**

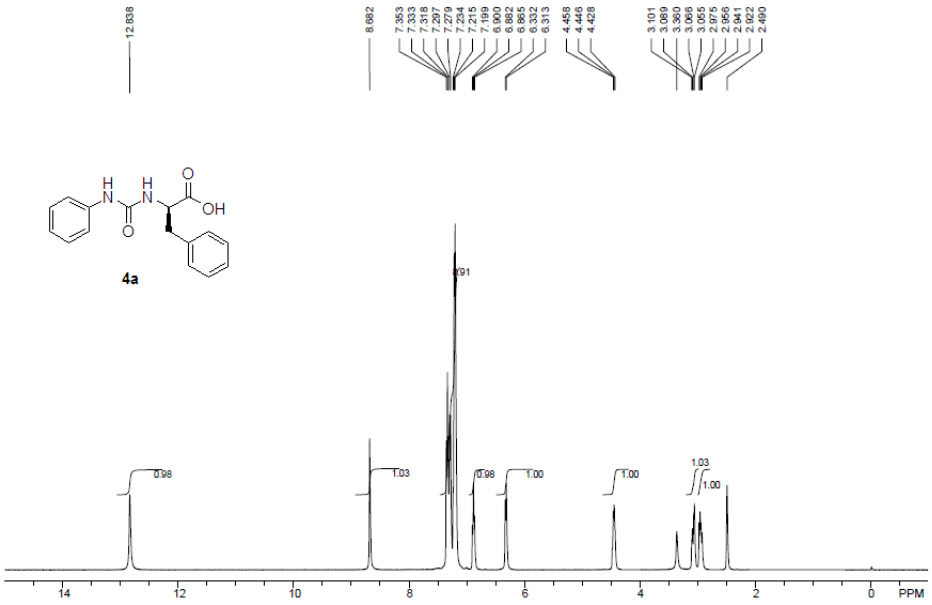

Fig. S-21. ^{1}H-NMR spectrum of compound **4a**.

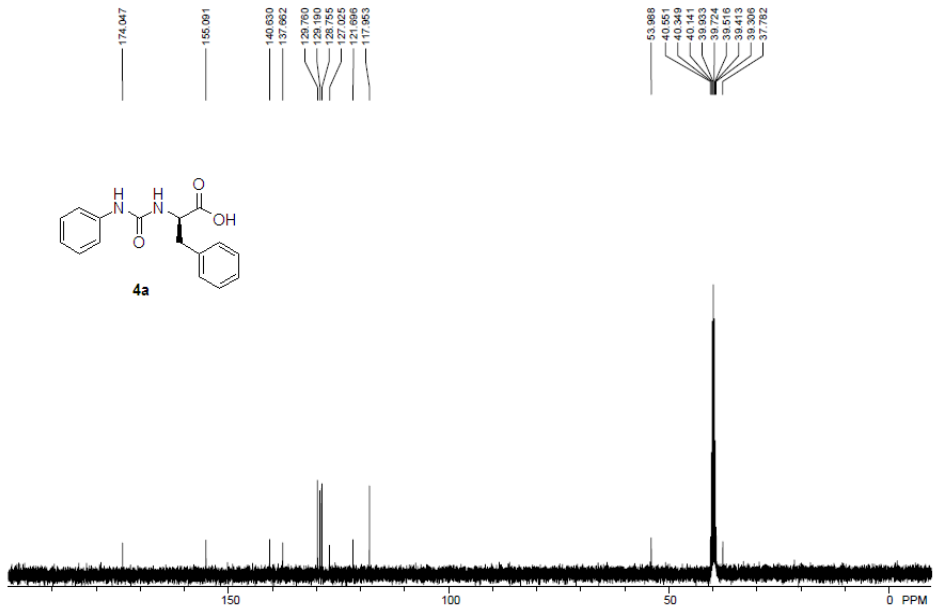

Fig. S-22. ^{13}C-NMR spectrum of compound **4a**.

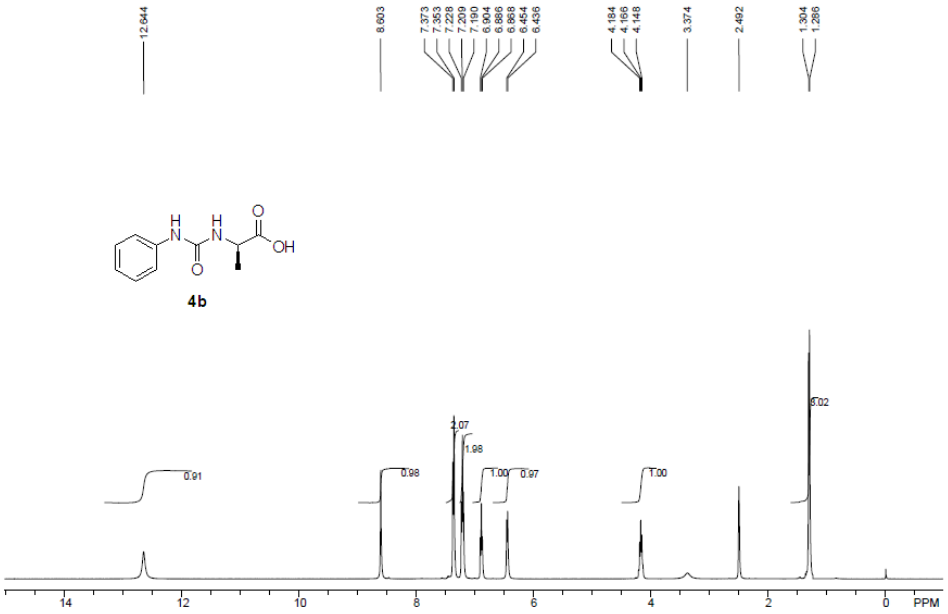

Fig. S-23. ^{1}H-NMR spectrum of compound **4b**.

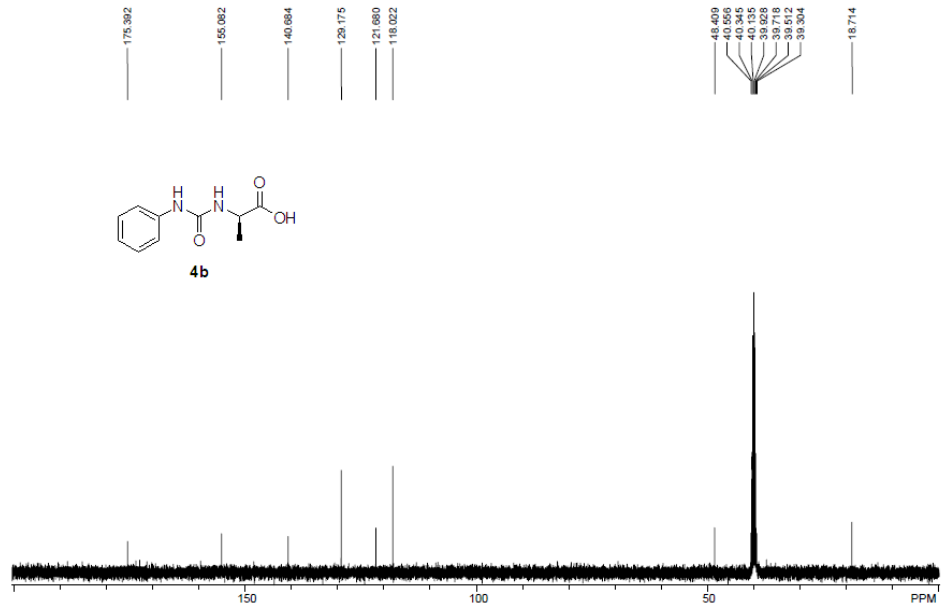

Fig. S-24. ^{13}C-NMR spectrum of compound **4b**.

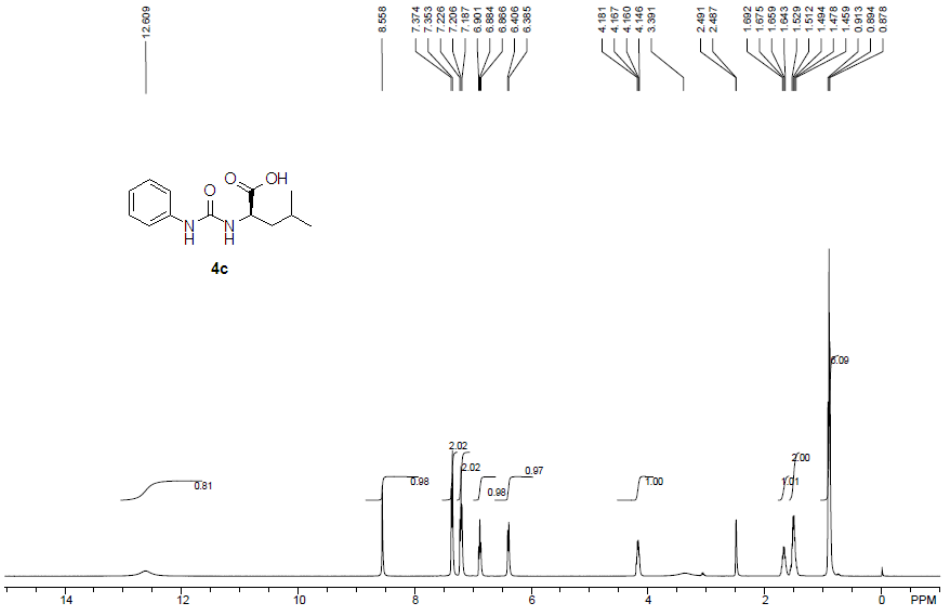

Fig. S-25. ^{1}H-NMR spectrum of compound **4c**.

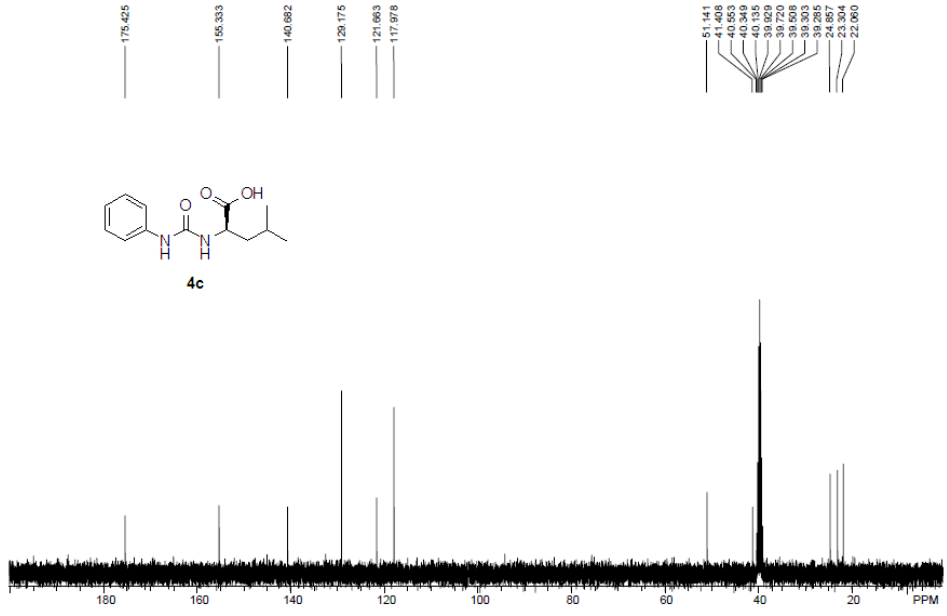

Fig. S-26. ^{13}C-NMR spectrum of compound **4c**.

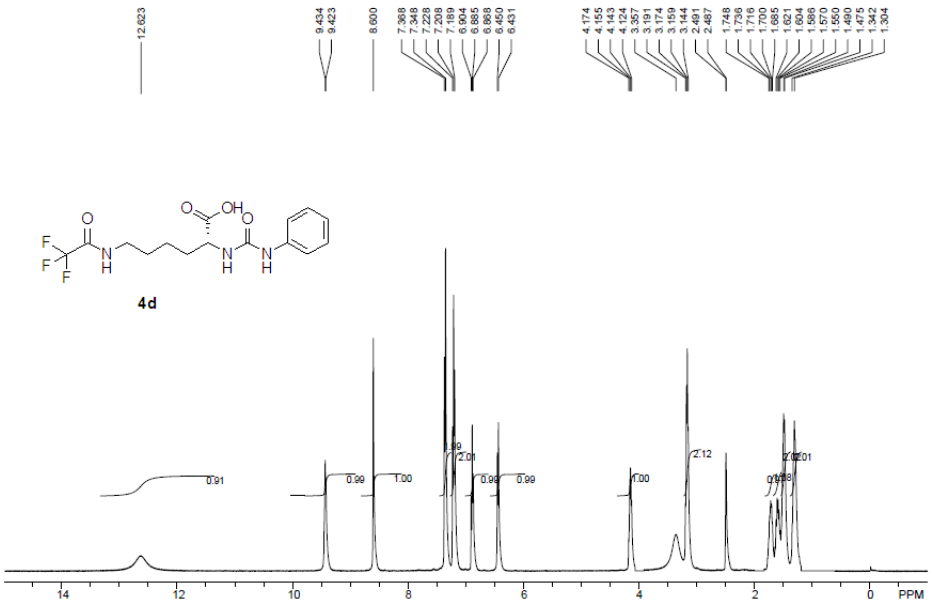

Fig. S-27. ^{1}H-NMR spectrum of compound **4d**.

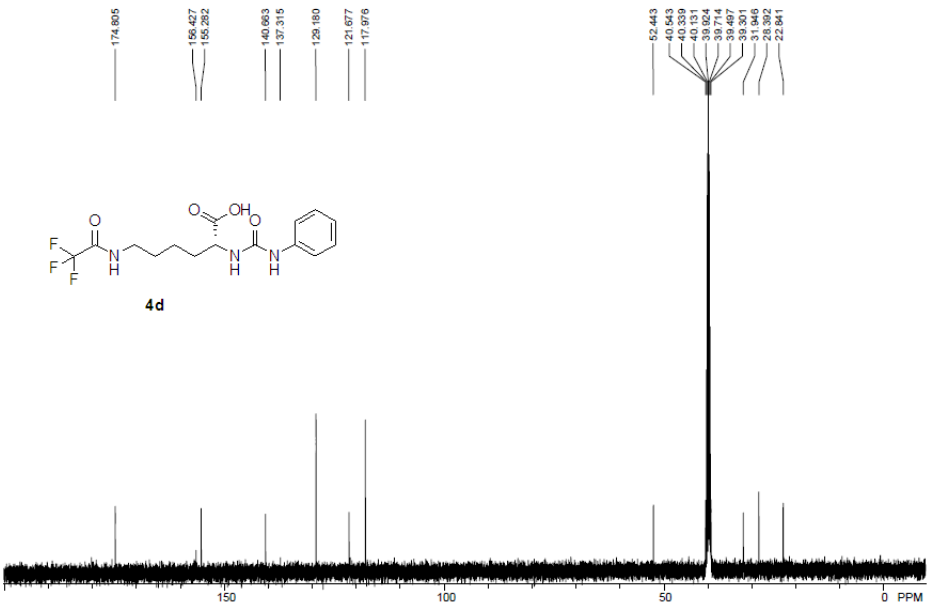

Fig. S-28. ^{13}C-NMR spectrum of compound **4d**.

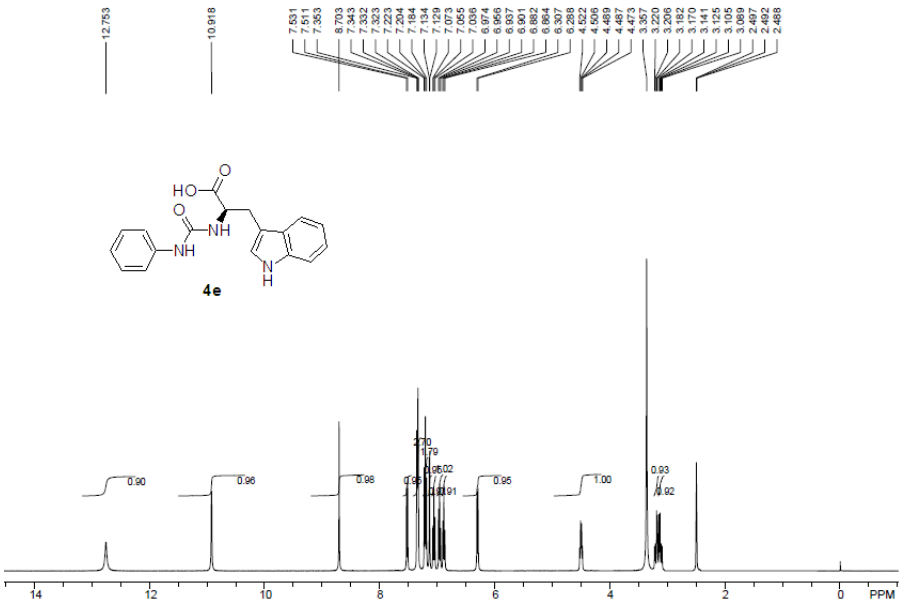

Fig. S-29. ^{1}H-NMR spectrum of compound **4e**.

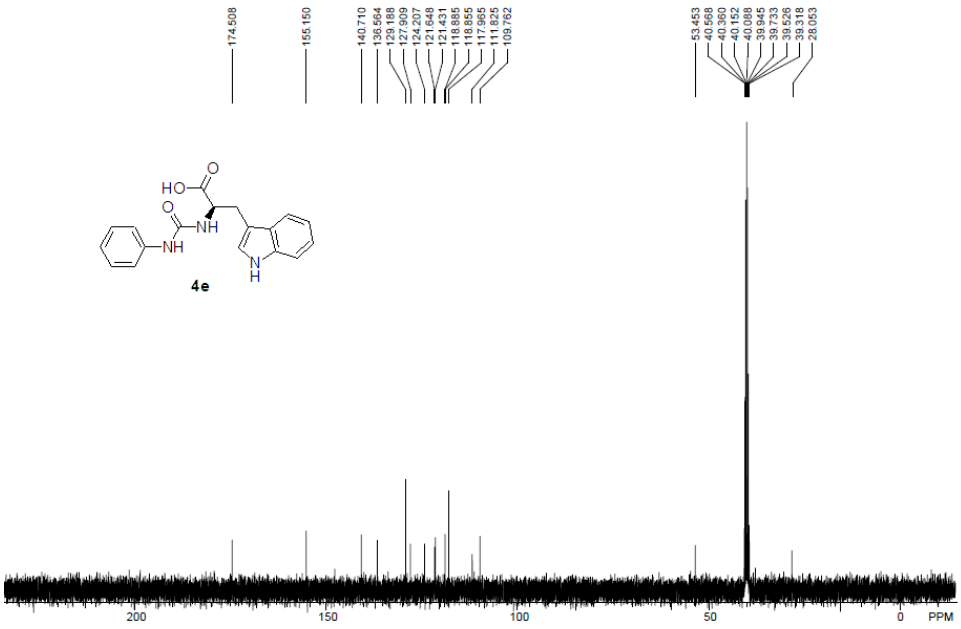

Fig. S-30. ^{13}C-NMR spectrum of compound **4e**.

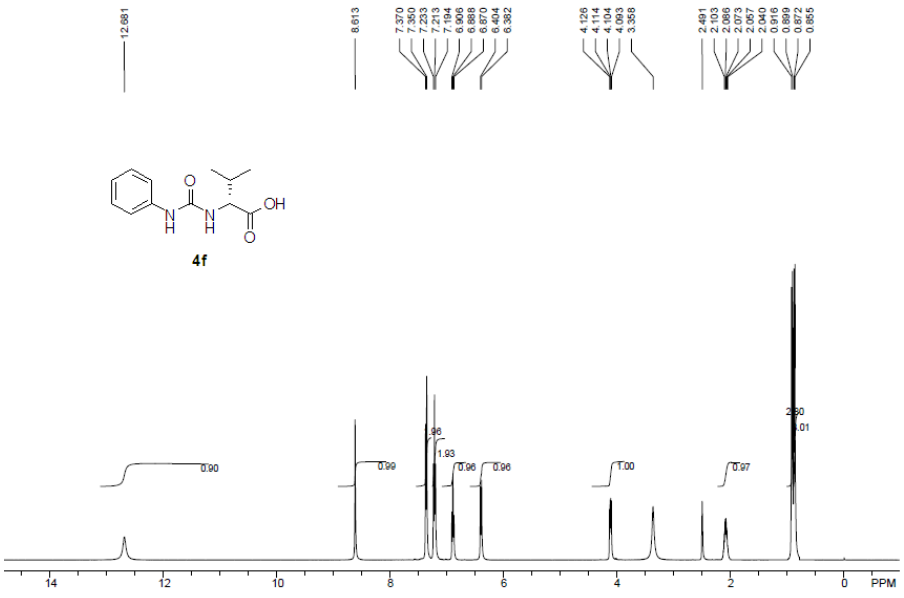

Fig. S-31. ^{1}H-NMR spectrum of compound **4f**.

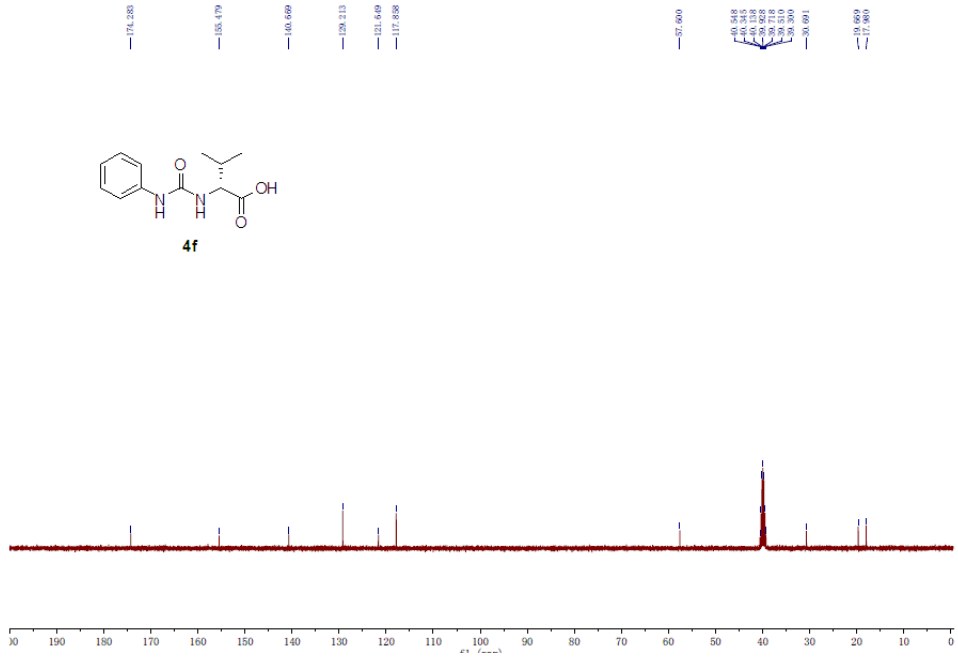

Fig. S-32. ^{13}C-NMR spectrum of compound **4f**.

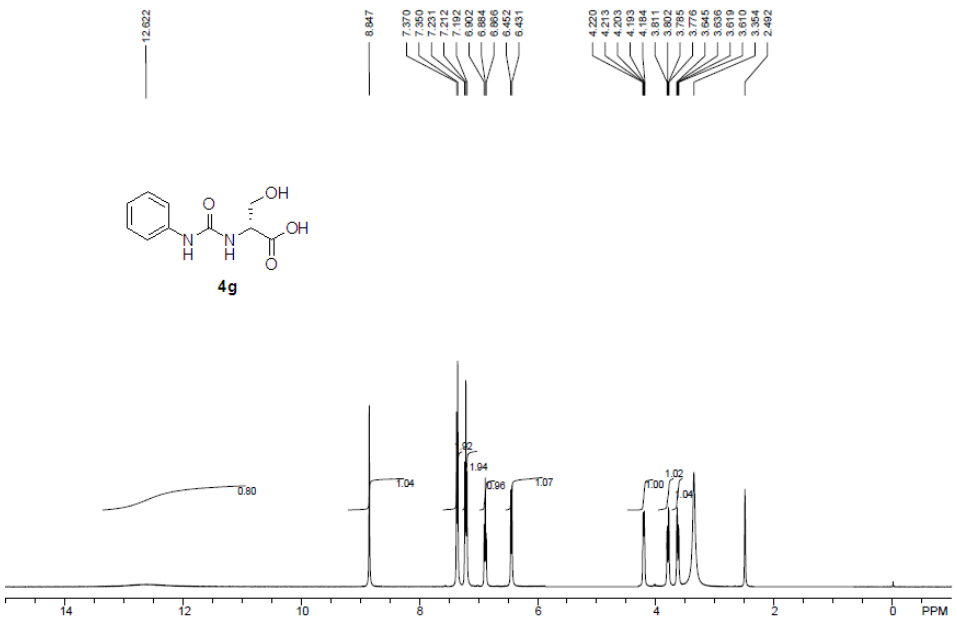

Fig. S-33. ^{1}H-NMR spectrum of compound **4g**.

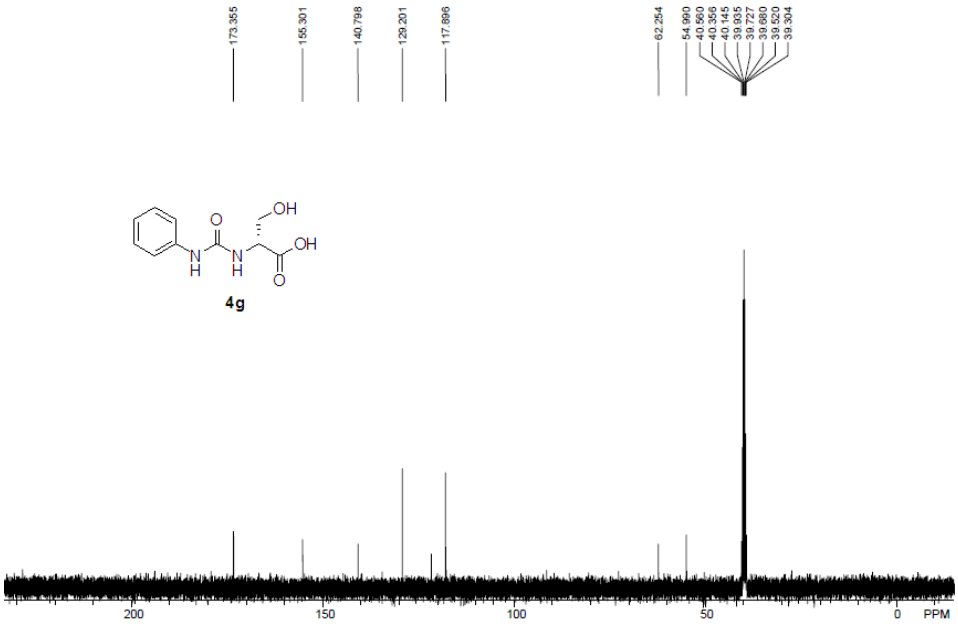

Fig. S-34. ^{13}C-NMR spectrum of compound **4g**.

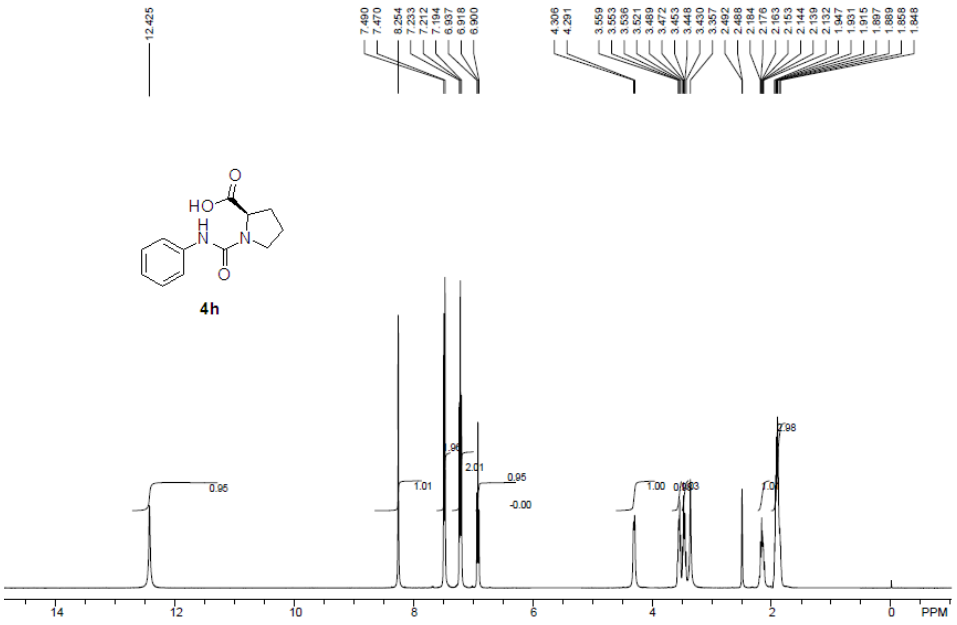

Fig. S-35. ^{1}H-NMR spectrum of compound **4h**.

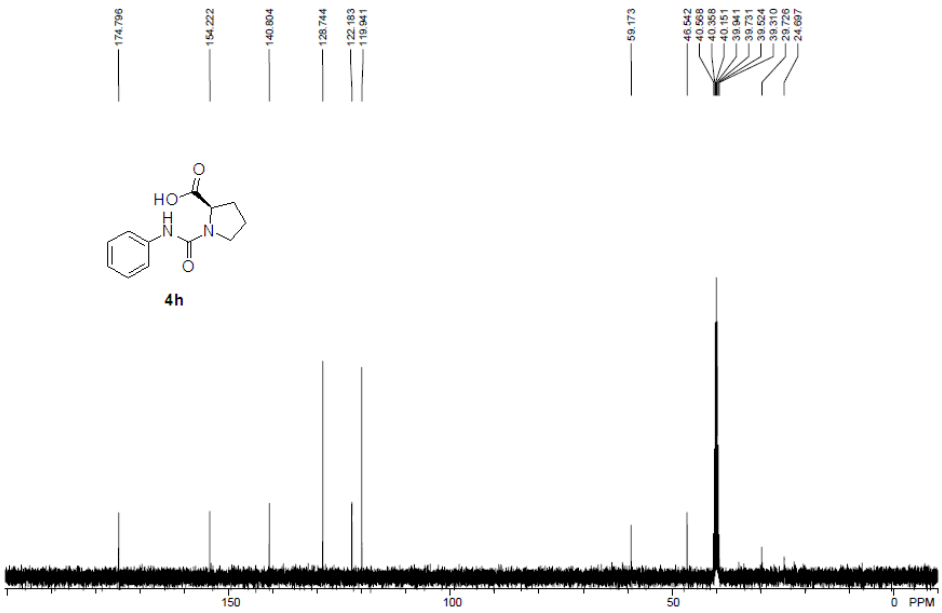

Fig. S-36. ^{13}C-NMR spectrum of compound **4h**.

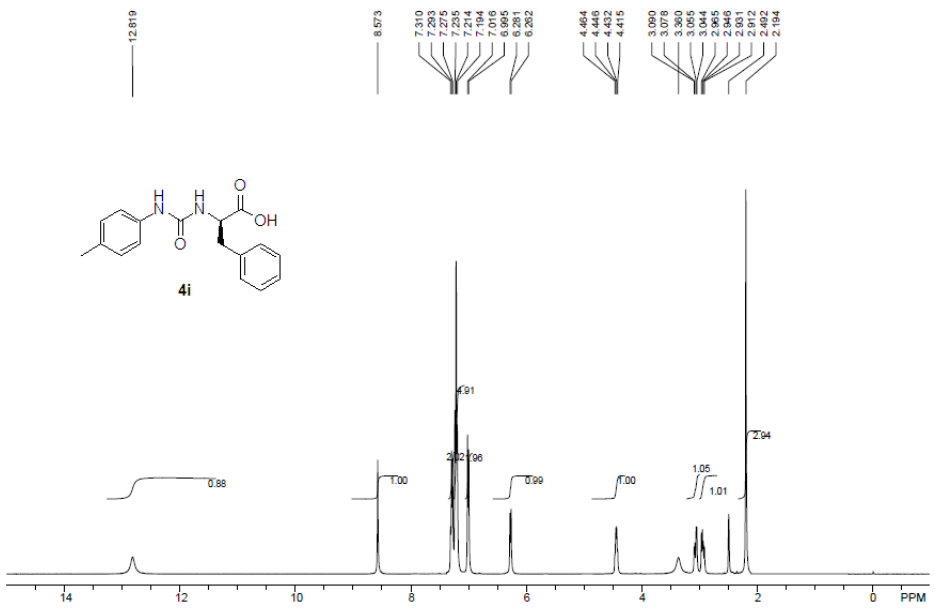

Fig. S-37. ^{1}H-NMR spectrum of compound **4i**.

Fig. S-38. ^{13}C-NMR spectrum of compound **4i**.

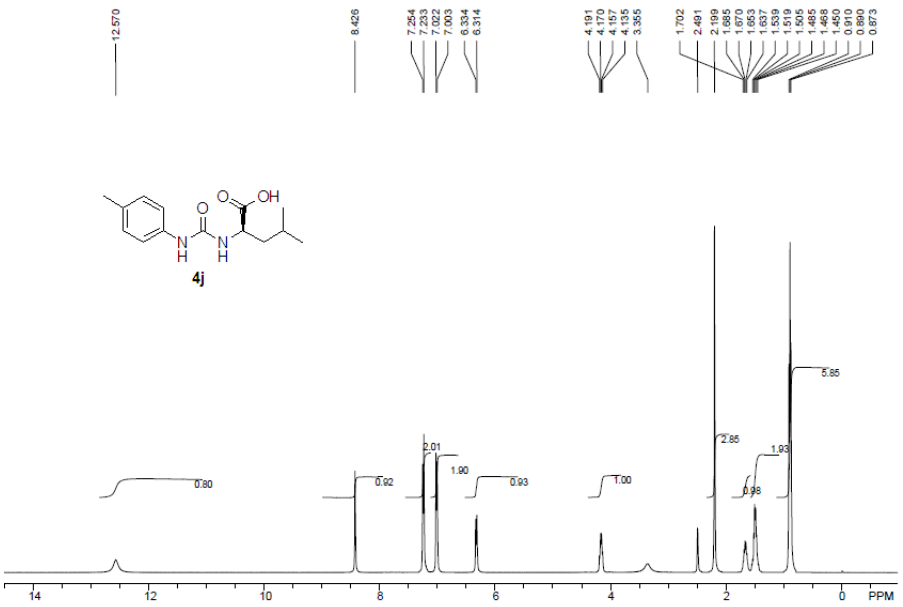

Fig. S-39. ^{1}H-NMR spectrum of compound **4j**.

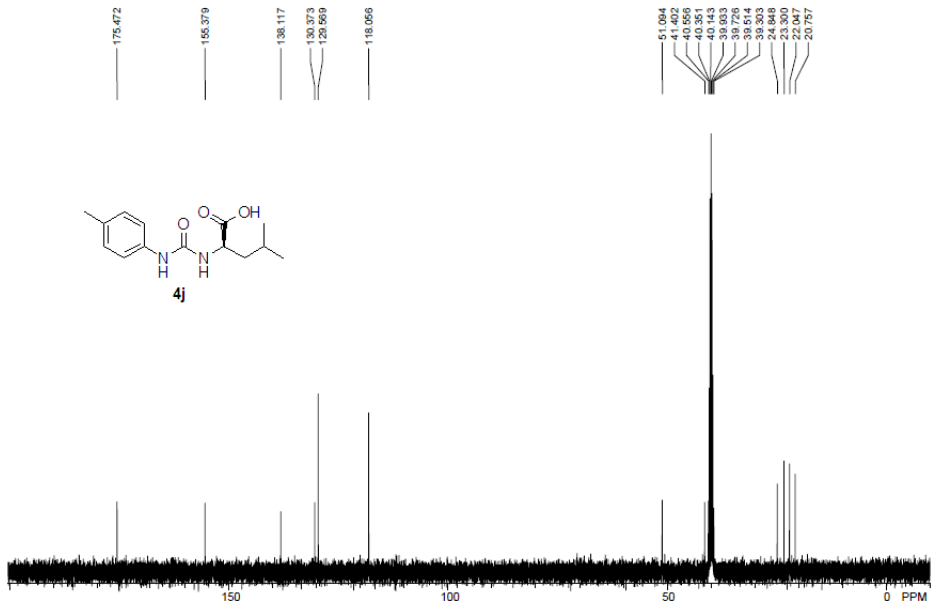

Fig. S-40. ^{13}C-NMR spectrum of compound **4j**.

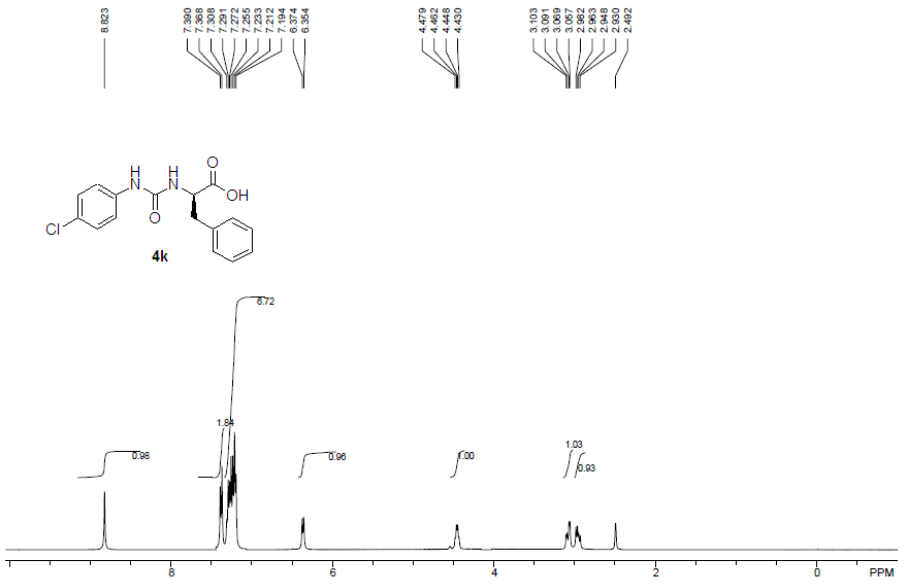

Fig. S-41. ^{1}H-NMR spectrum of compound **4k**.

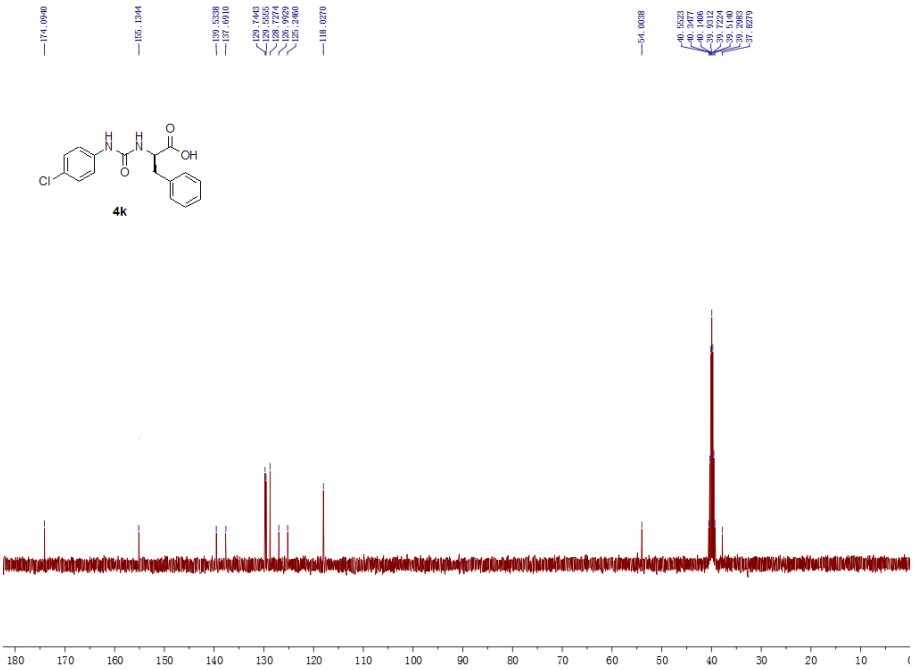

Fig. S-42. ^{13}C-NMR spectrum of compound **4k**.

^{1}H- AND ^{13}C-NMR SPECTRA FOR THE NEWLY SYNTHESIZED COMPOUNDS **6**

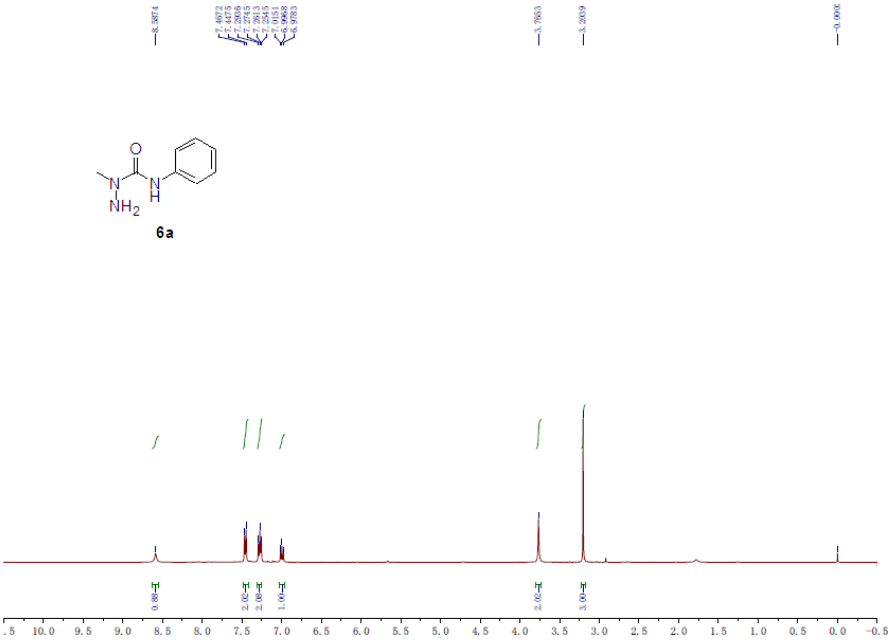

Fig. S-43. ^{1}H-NMR spectrum of compound **6a**.

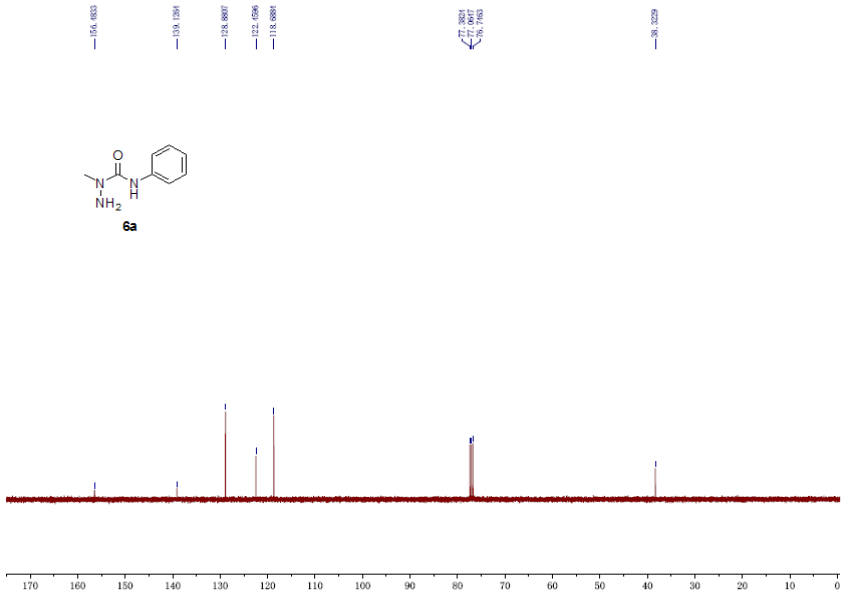

Fig. S-44. ^{13}C-NMR spectrum of compound **6a**.

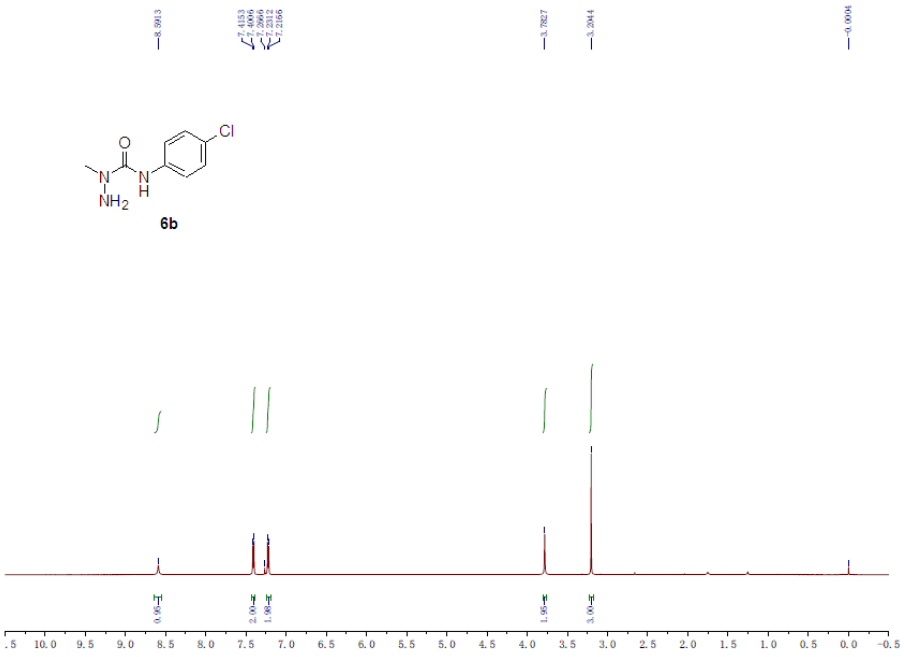

Fig. S-45. ^{1}H-NMR spectrum of compound **6b**.

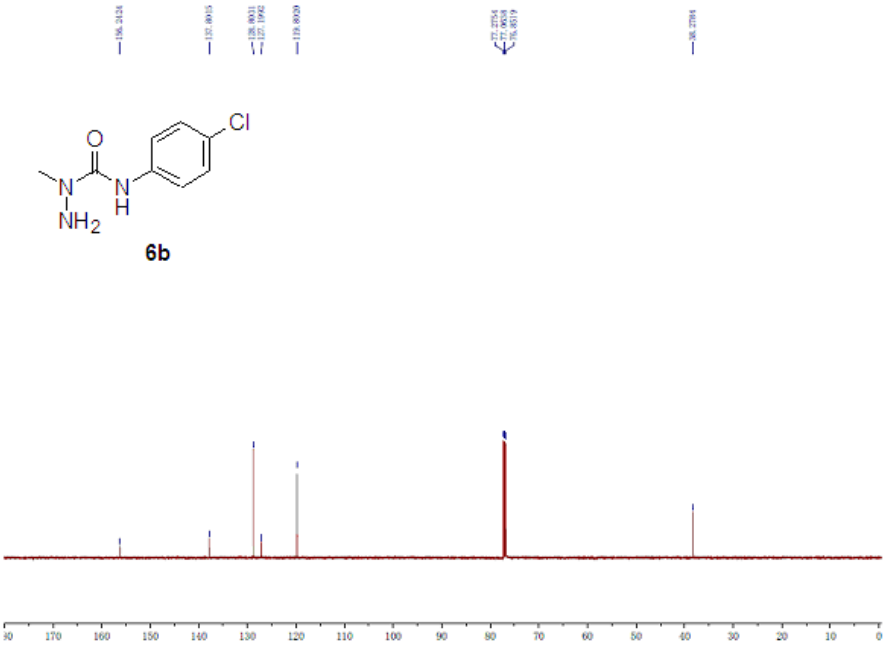

Fig. S-46. ^{13}C-NMR spectrum of compound **6b**.

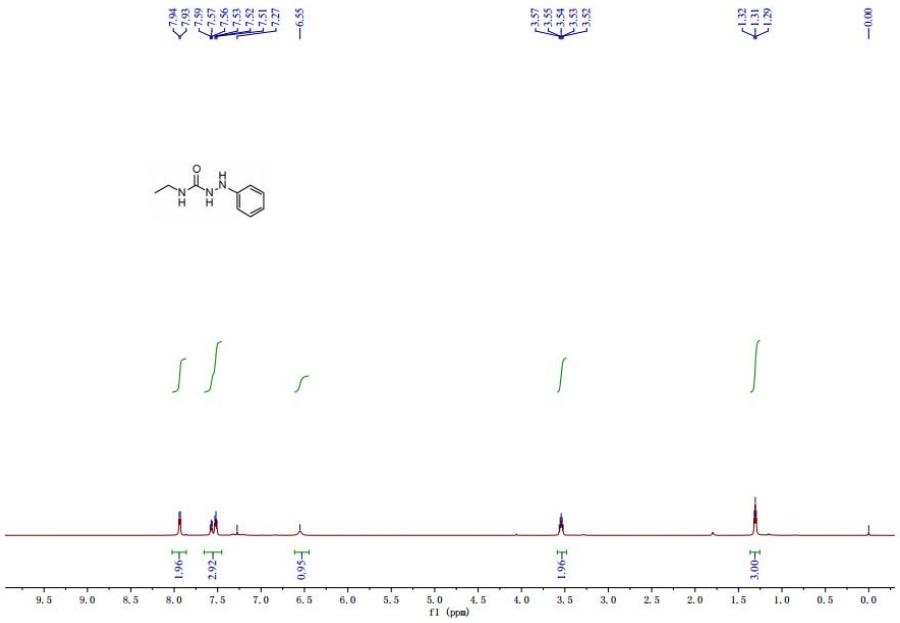

Fig. S-47. ^{1}H-NMR spectrum of compound **6d**.

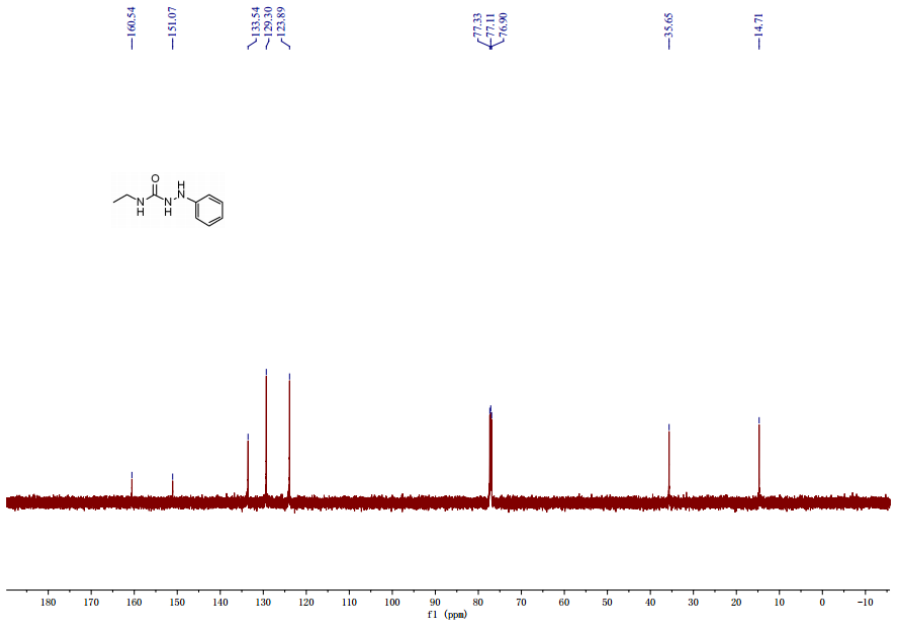

Fig. S-48. ^{13}C-NMR spectrum of compound **6d**.

^{1}H- AND ^{13}C-NMR SPECTRA FOR THE NEWLY SYNTHESIZED COMPOUNDS **8**

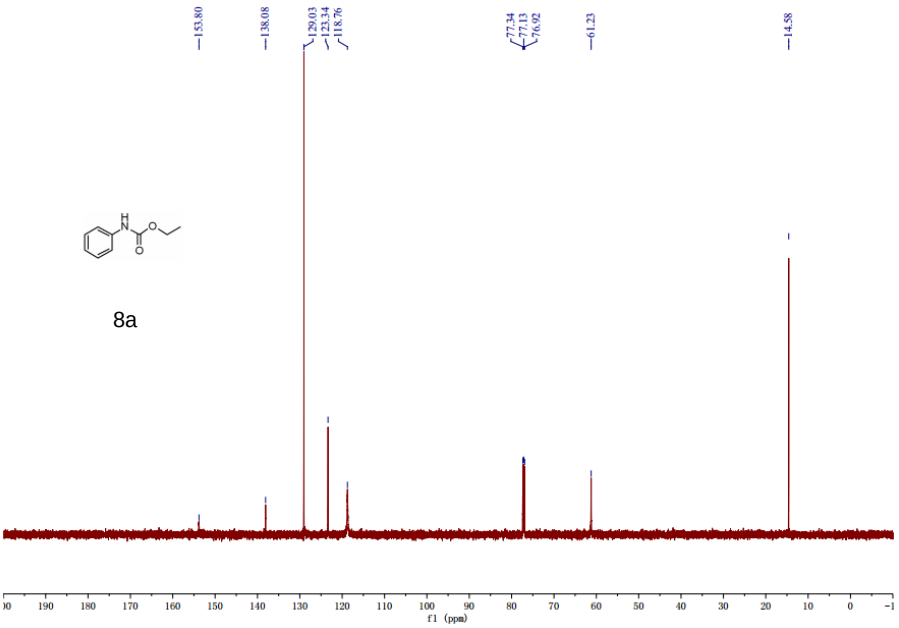

Fig. S-49. ^{1}H-NMR spectrum of compound **8a**.

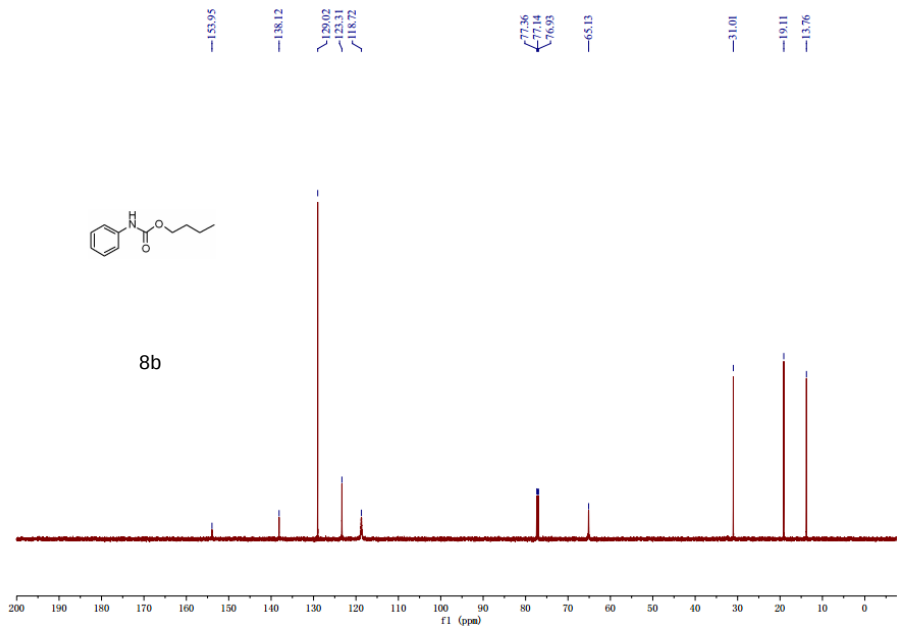

Fig. S-50. ^{13}C-NMR spectrum of compound **8a**.

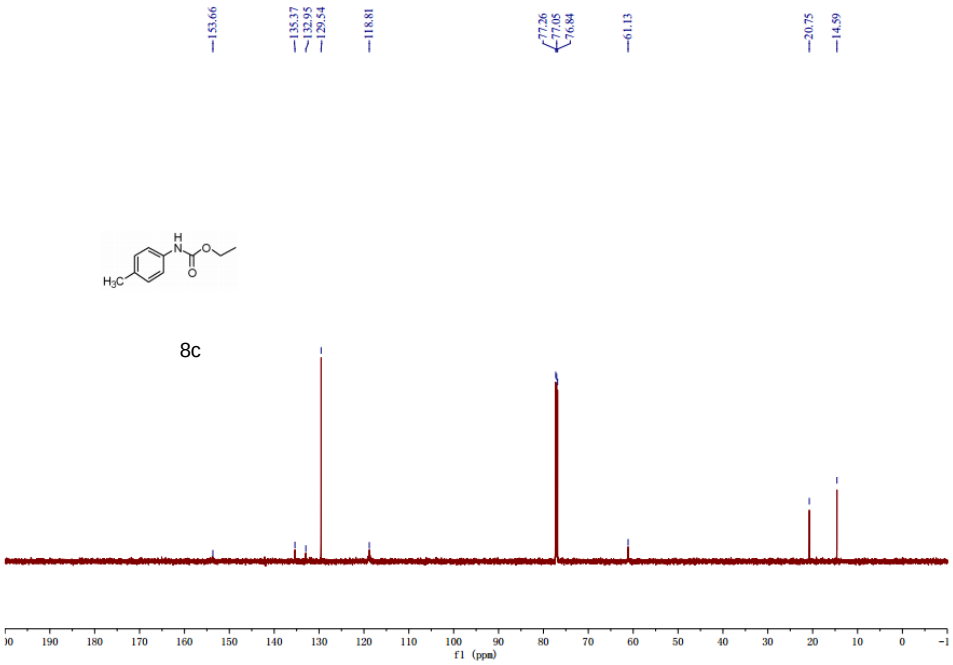

Fig. S-51. ^{13}C-NMR spectrum of compound **8c**.

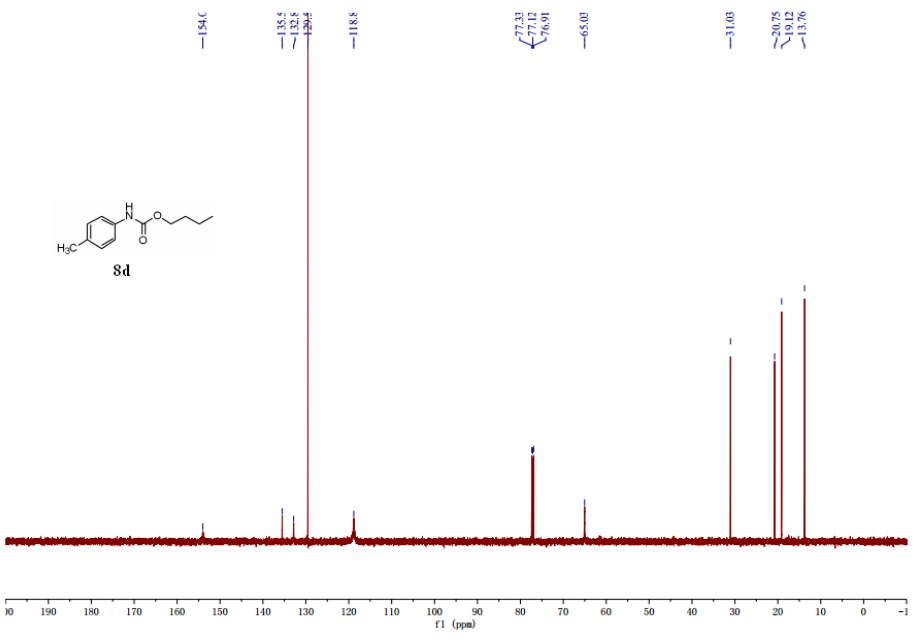

Fig. S-52. ^{13}C-NMR spectrum of compound **8d**.

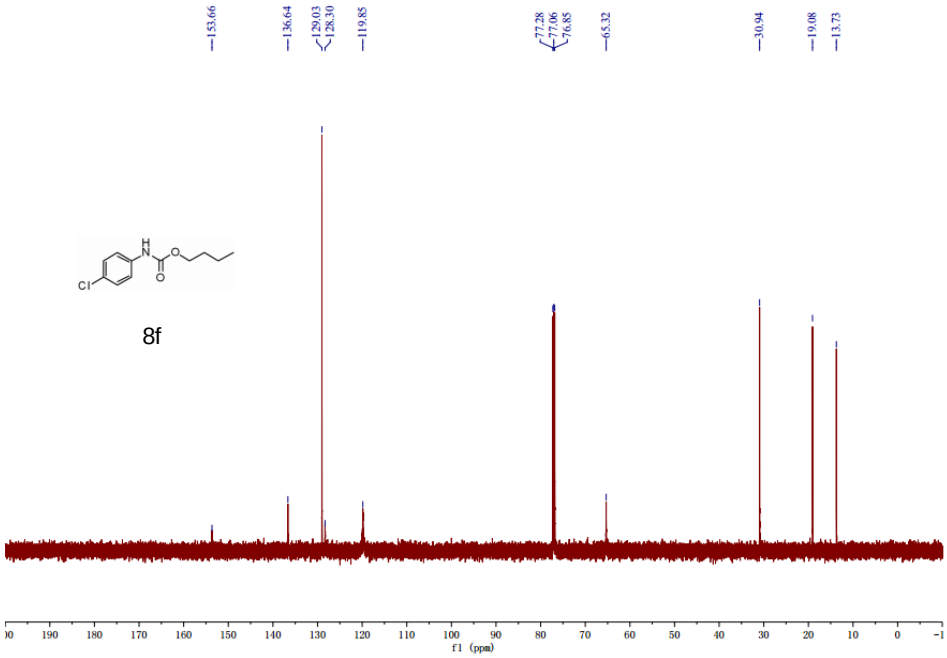

Fig. S-53. ^{13}C-NMR spectrum of compound **8f**.

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