Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

A direct strategy to hybrid benzothiazole-carbamate moieties via O-acylation of phenols under metal-organic framework catalysis

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Supporting Information

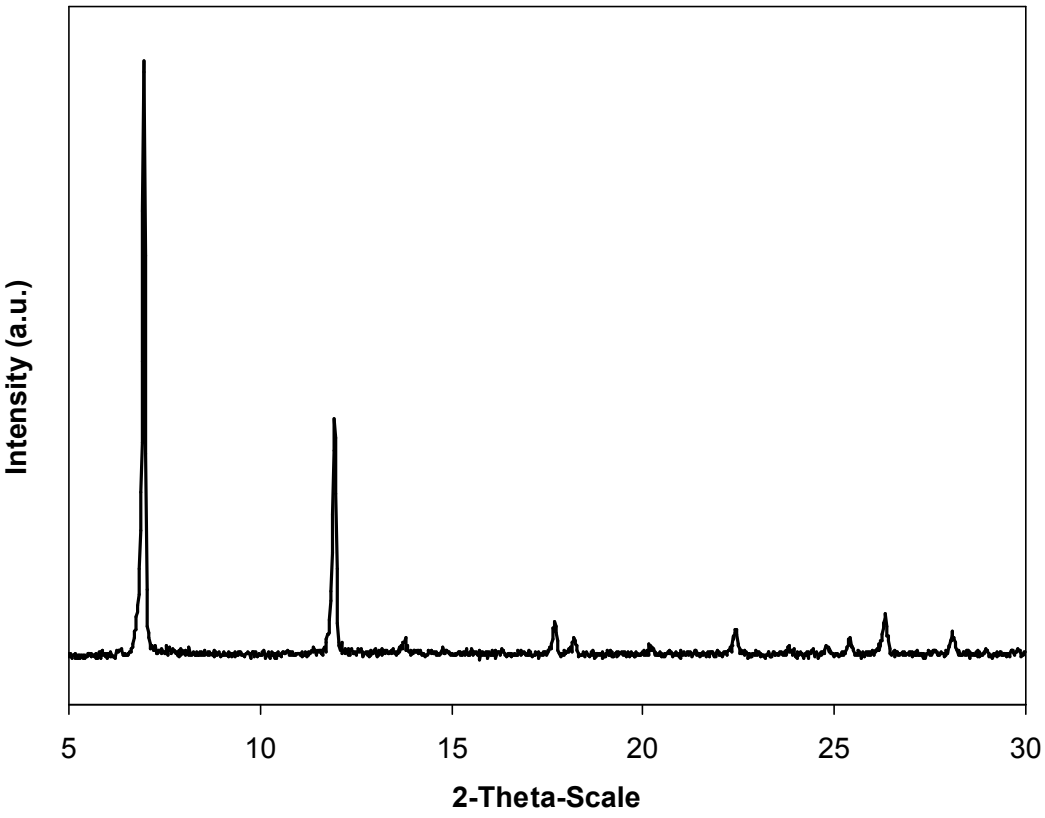

Fig. S1. X-ray powder diffractograms of the Cu-CPO-27.

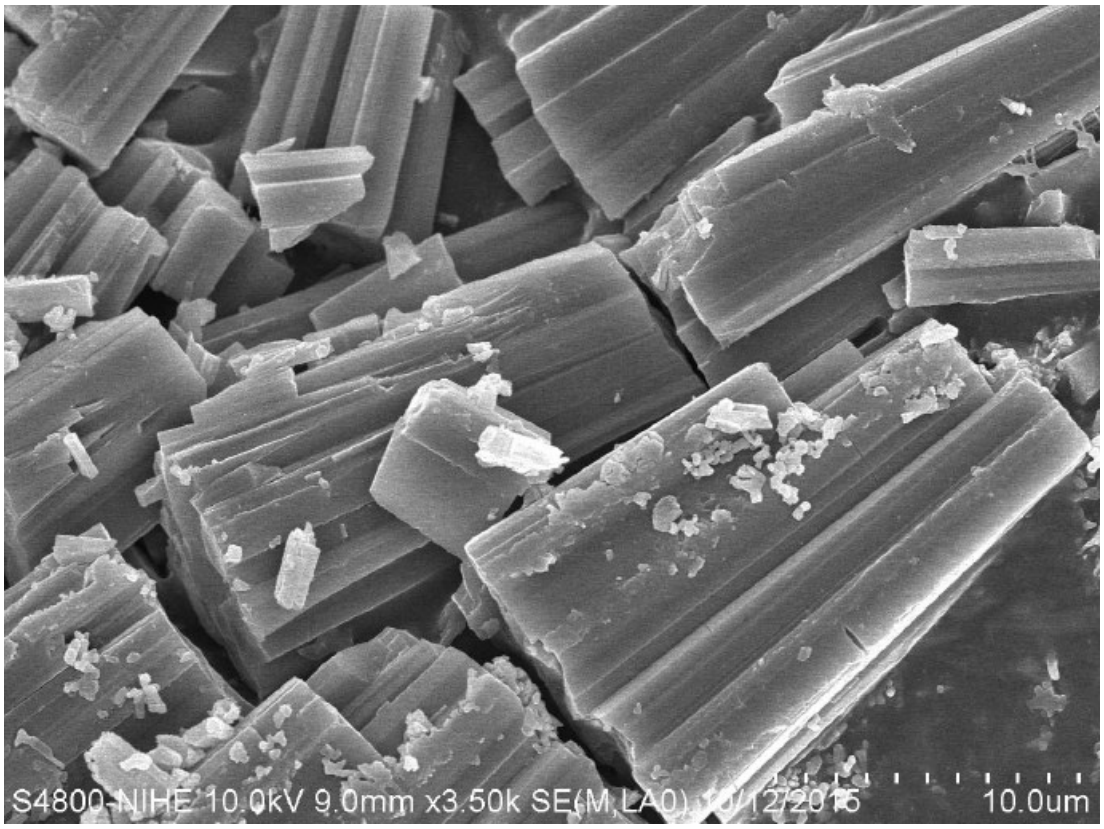

Fig. S2. SEM micrograph of the Cu-CPO-27.

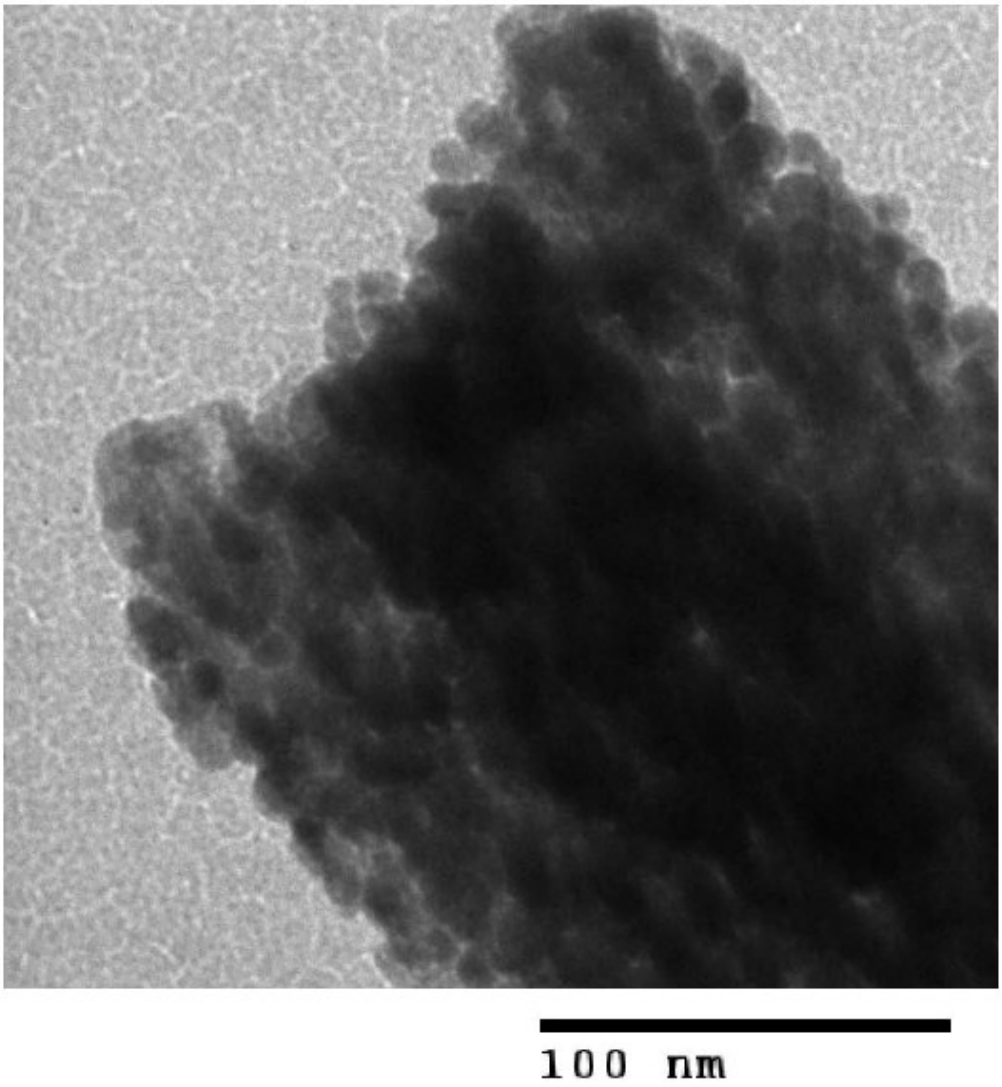

Fig. S3. TEM micrograph of the Cu-CPO-27.

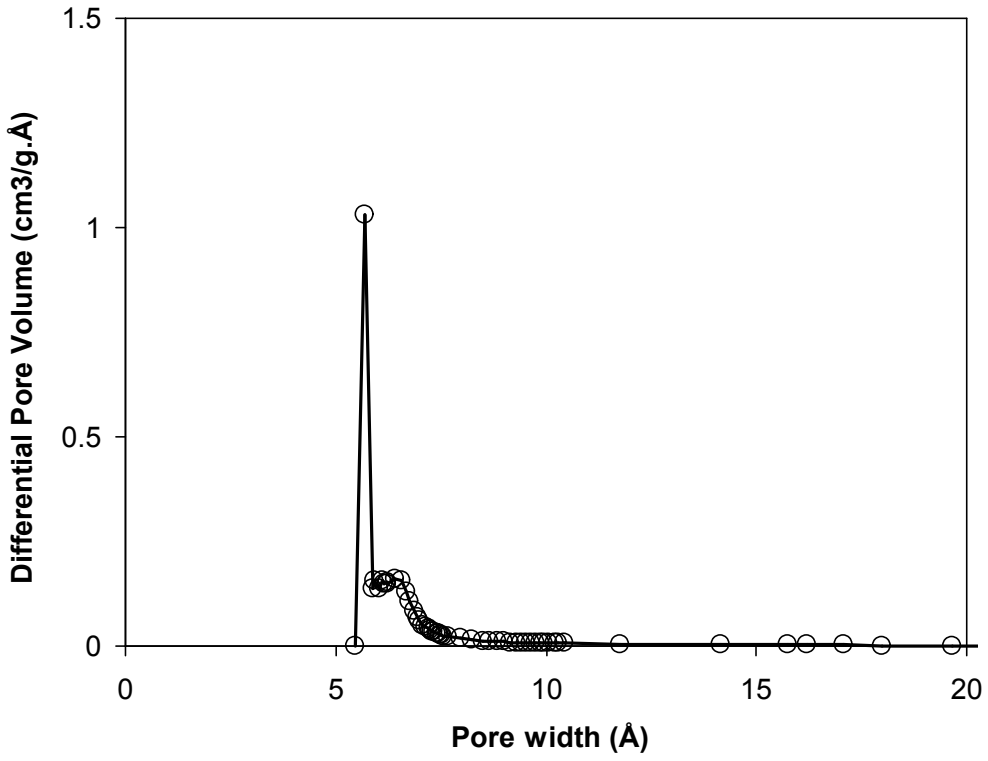

Fig. S4. Pore size distribution of the Cu-CPO-27.

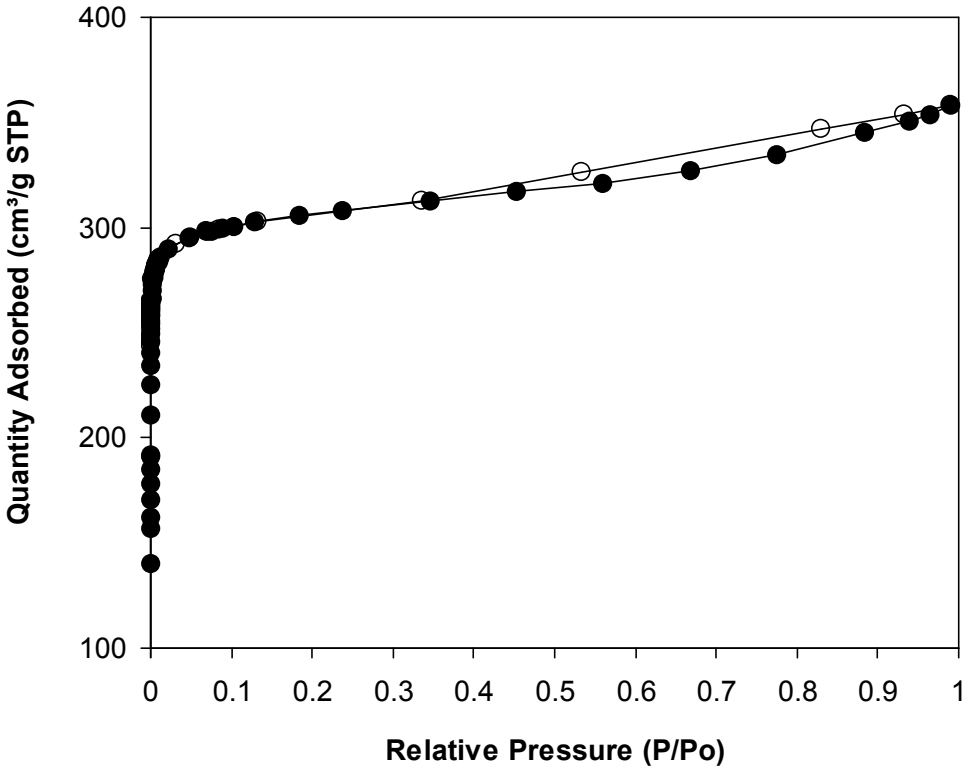

Fig. S5. Nitrogen adsorption/desorption isotherm of the Cu-CPO-27. Adsorption data are shown as closed circles and desorption data as open circles.

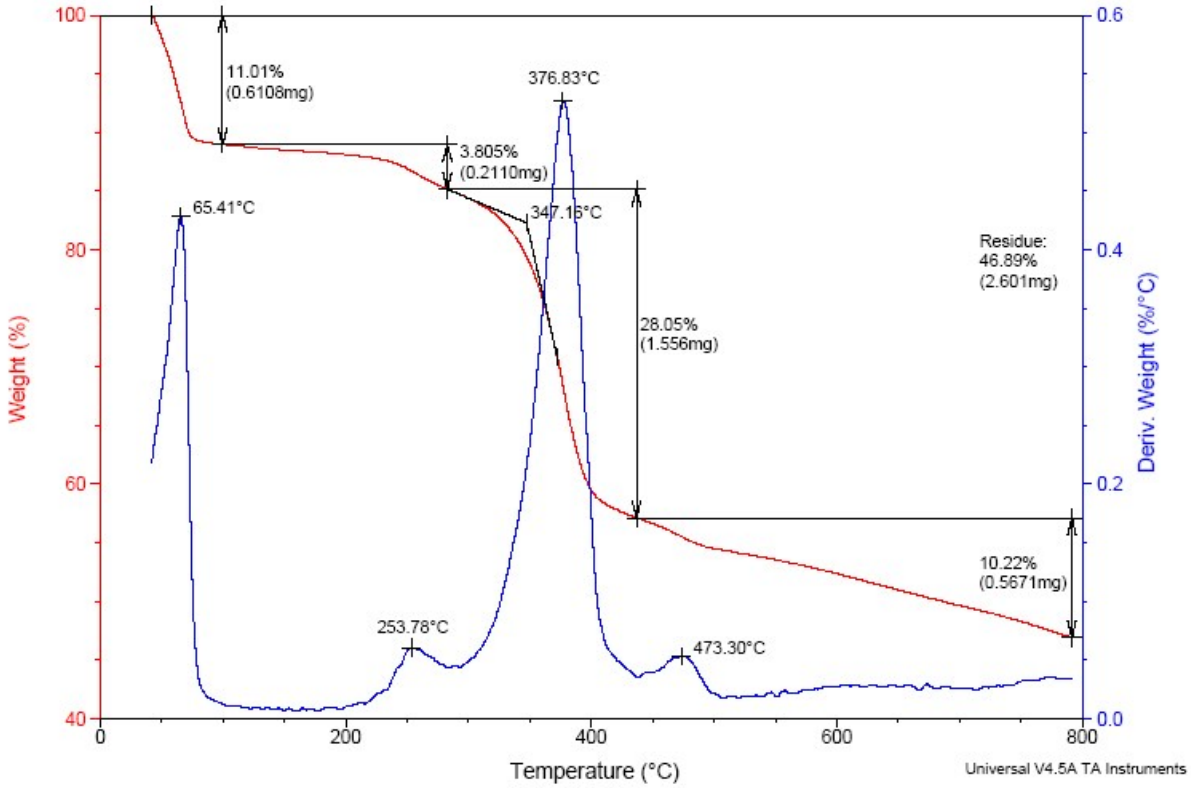

Fig. S6. TGA analysis of the Cu-CPO-27.

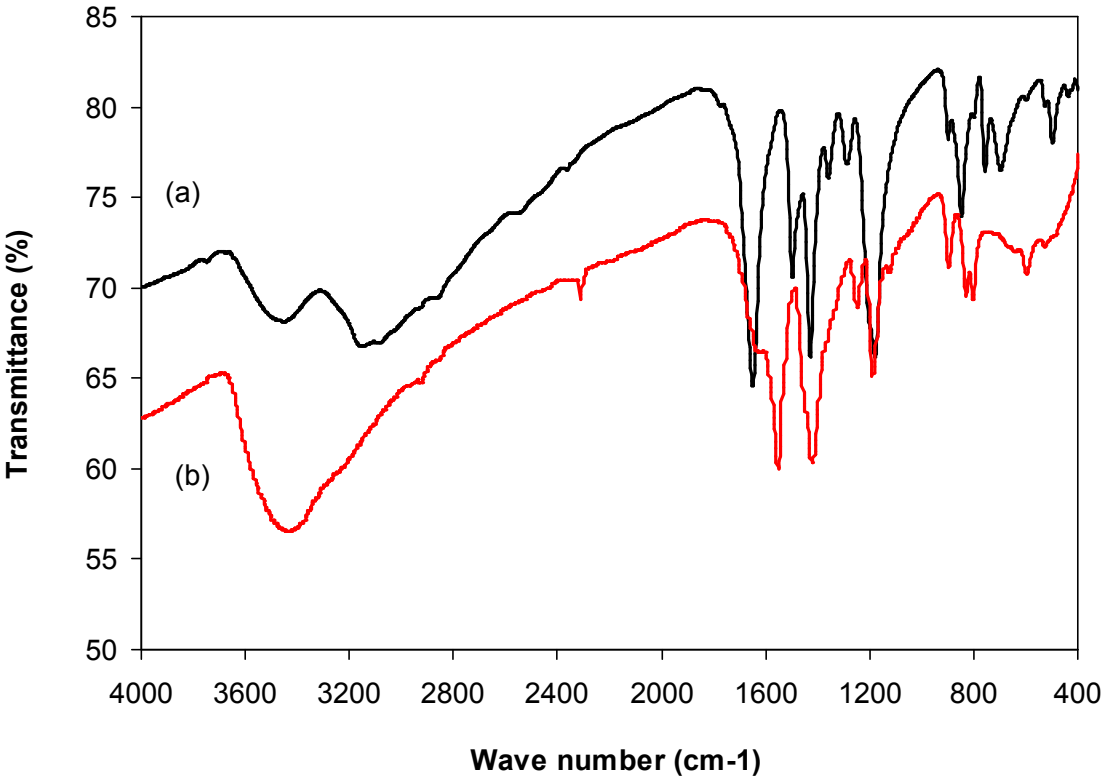

Fig. S7. FT-IR spectra of dihydroxyterephthalic acid (a), and the Cu-CPO-27 (b).

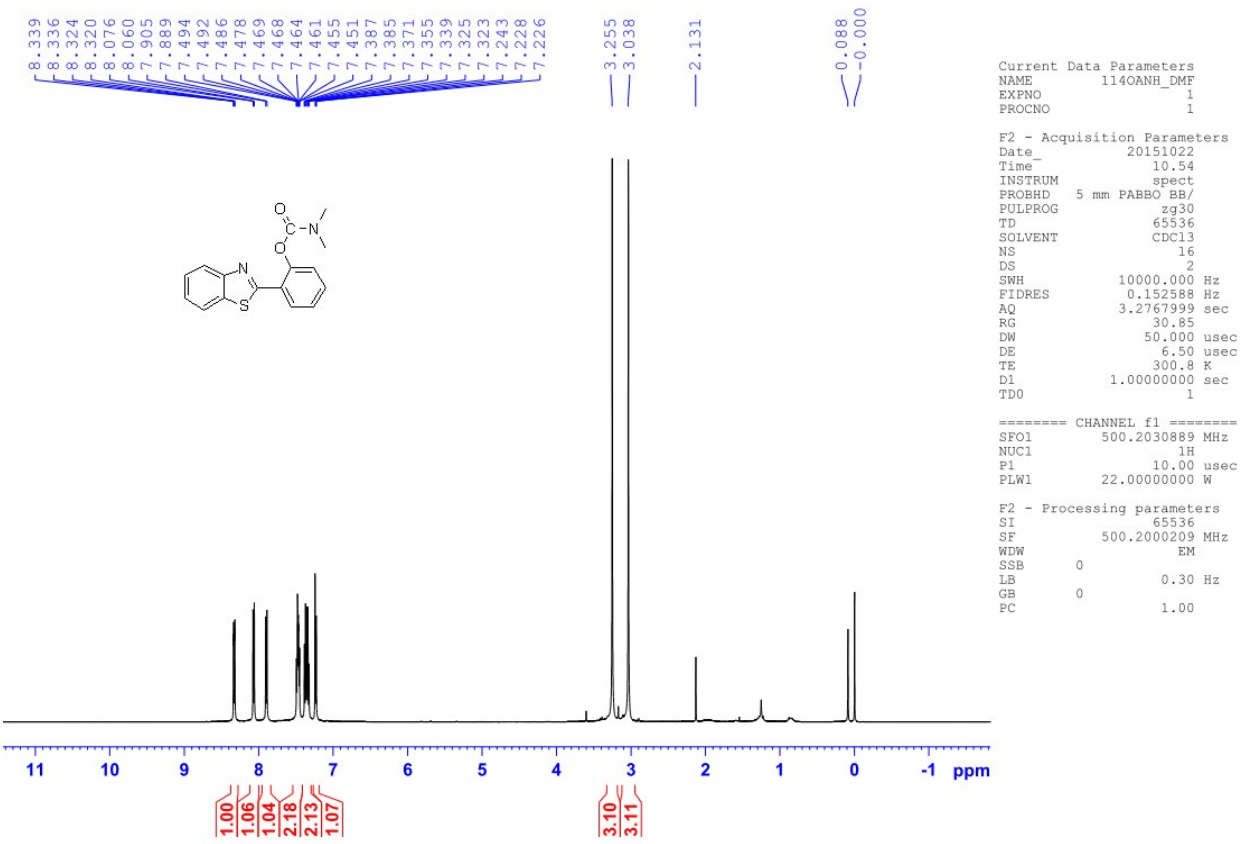

Fig. S8. ^{1}H-NMR spectra of 2-(benzo[*d*]thiazol-2-yl)phenyl dimethylcarbamate.

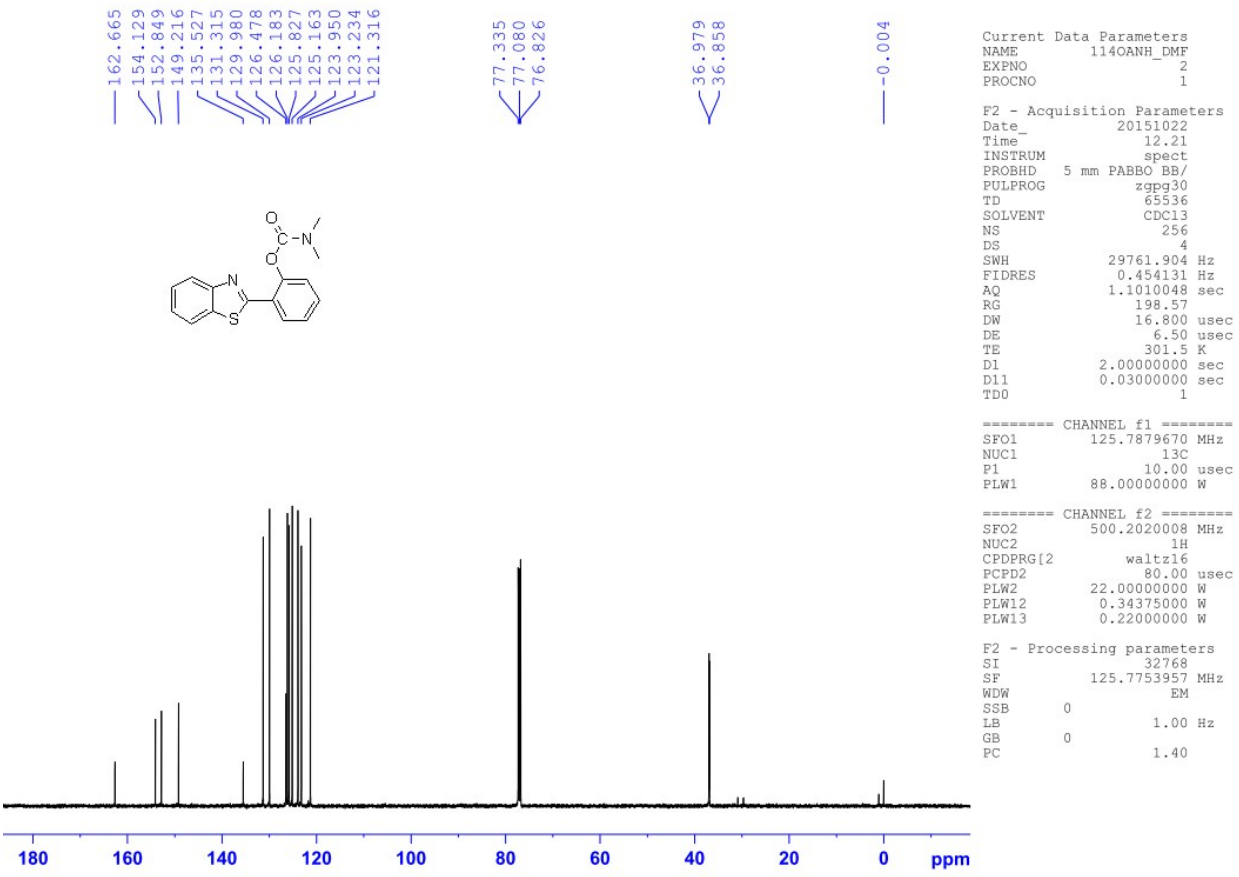

Fig. S9. ^{13}C-NMR spectra of 2-(benzo[*d*]thiazol-2-yl)phenyl dimethylcarbamate.

Characterization Data for 2-(benzo[*d*]thiazol-2-yl)phenyl dimethylcarbamate

Prepared as shown in the general experimental procedure and purified on silica gel (hexane/ethyl acetate = 6:1): light yellow gummy, 77% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.34 – 8.32 (m, 1H, ArH), 8.07 (d, *J*=8.0 Hz, 1H, ArH), 7.90 (d, *J*=8.0 Hz, 1H, ArH), 7.49 – 7.45 (m, 2H, ArH), 7.39 – 7.32 (m, 2H, ArH), 7.24 – 7.23 (m, 1H, ArH), 3.26 (s, 3H, NCH_3), 3.04 (s, 3H, NCH_3); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 162.7, 154.1, 152.8, 149.2, 135.5, 131.3, 130.0, 126.5, 126.2, 125.8, 125.2, 124.0, 123.2, 121.3, 37.0, 36.9; GC/MS (EI), m/z, 298+1, $[M+H]^+$.

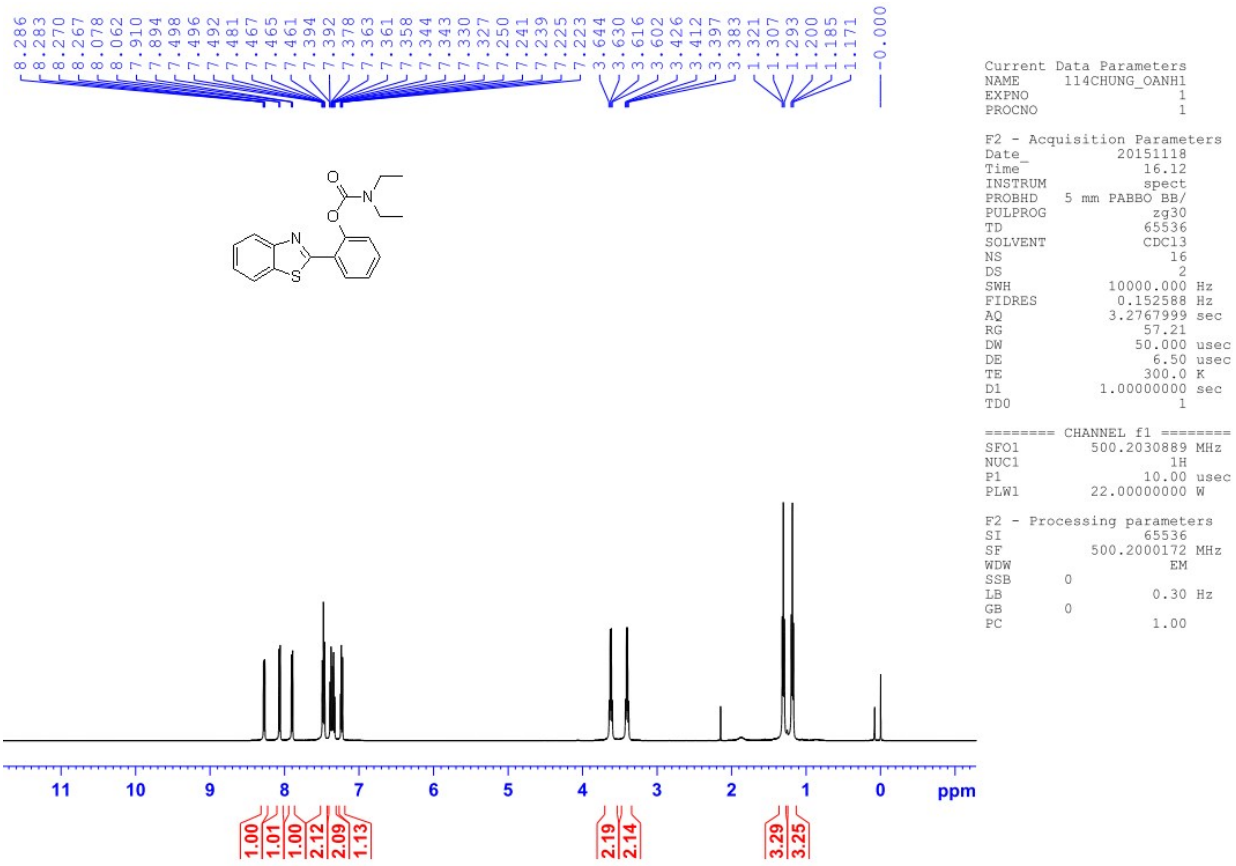

Fig. S10. ^{1}H-NMR spectra of 2-(benzo[*d*]thiazol-2-yl)phenyl diethylcarbamate.

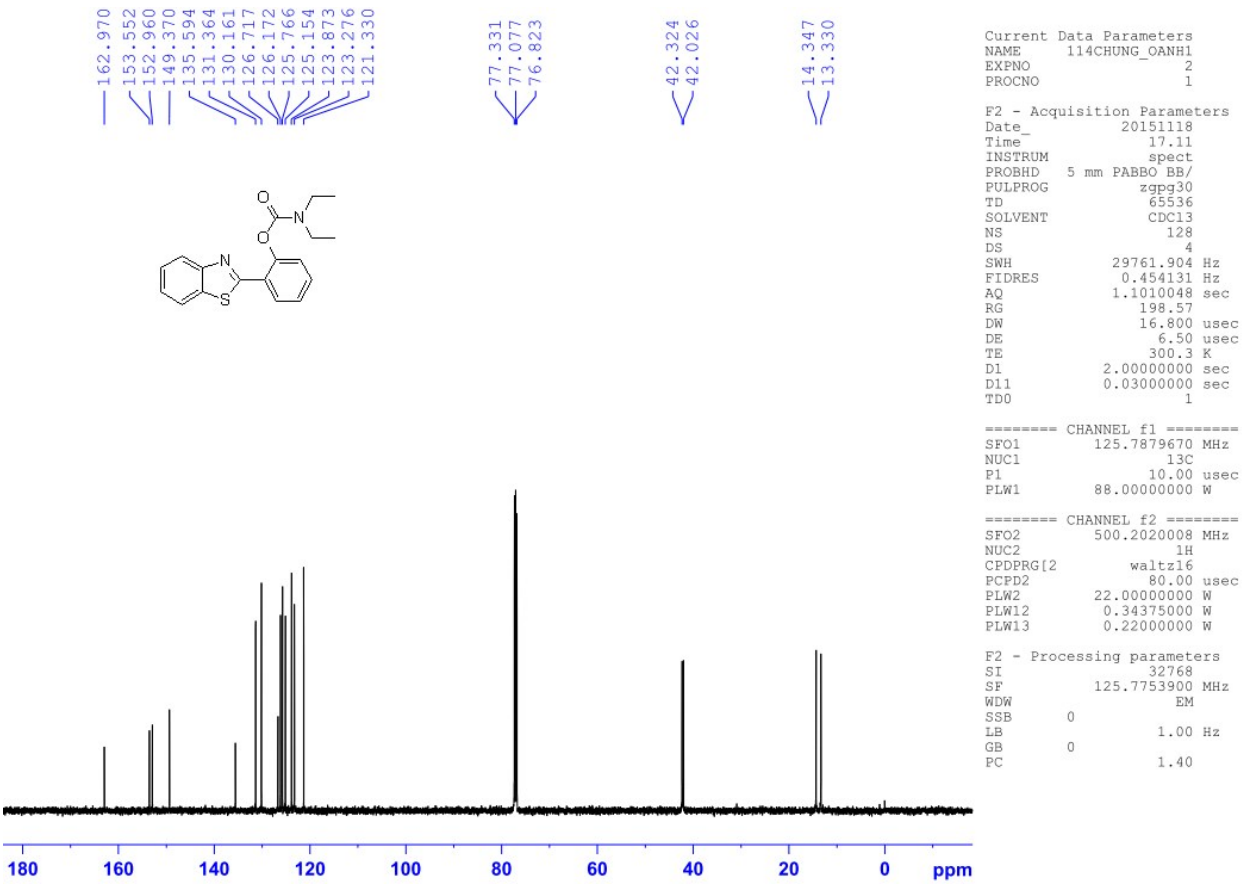

Fig. S11. ^{13}C-NMR spectra of 2-(benzo[*d*]thiazol-2-yl)phenyl diethylcarbamate.

Characterization Data for 2-(benzo[*d*]thiazol-2-yl)phenyl diethylcarbamate

Prepared as shown in the general experimental procedure and purified on silica gel (hexane/ethyl acetate = 6:1): light yellow gummy, 72% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.28 (dd, *J*=1.5 Hz, *J*=8.0 Hz, 1H, ArH), 8.07 (d, *J*=8.0 Hz, 1H, ArH), 7.90 (d, *J*=8.0 Hz, 1H, ArH), 7.50 – 7.46 (m, 2H, ArH), 7.39 – 7.33 (m, 2H, ArH), 7.25 – 7.22 (m, 1H, ArH), 3.62 (q, *J*=7.0 Hz, 2H, CH_2CH_3), 3.40 (q, *J*=7.0 Hz, 2H, CH_2CH_3), 1.31 (t, *J*=7.0 Hz, 3H, CH_2CH_3), 1.19 (t, *J*=7.0 Hz, 3H, CH_2CH_3); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 163.0, 153.6, 153.0, 149.4, 135.6, 131.4, 130.2,

126.7, 126.2, 125.8, 125.2, 123.9, 123.3, 121.3, 42.3, 42.0, 14.3, 13.3; GC/MS (EI), m/z, 326+1, $[M+H]^+$.

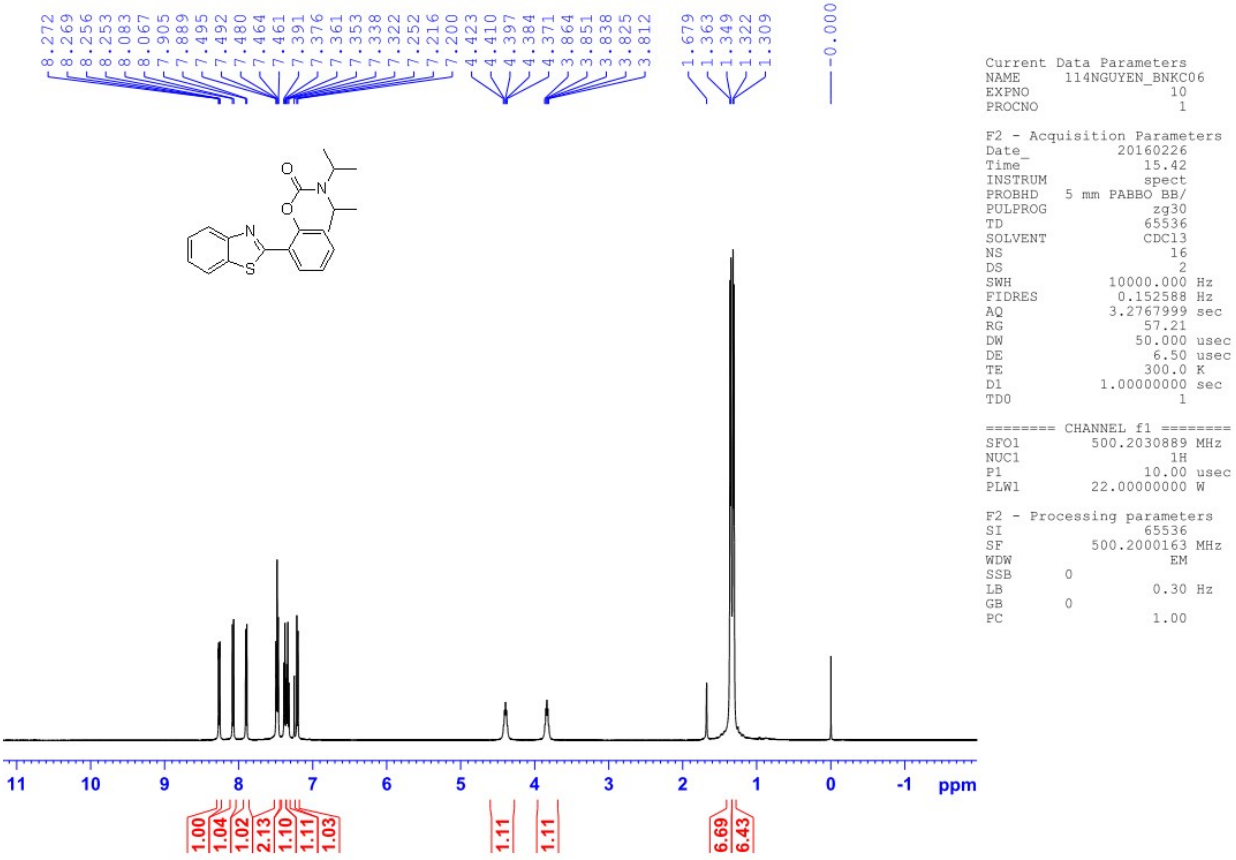

Fig. S12. ^{1}H-NMR spectra of 2-(benzo[*d*]thiazol-2-yl)phenyl diisopropylcarbamate.

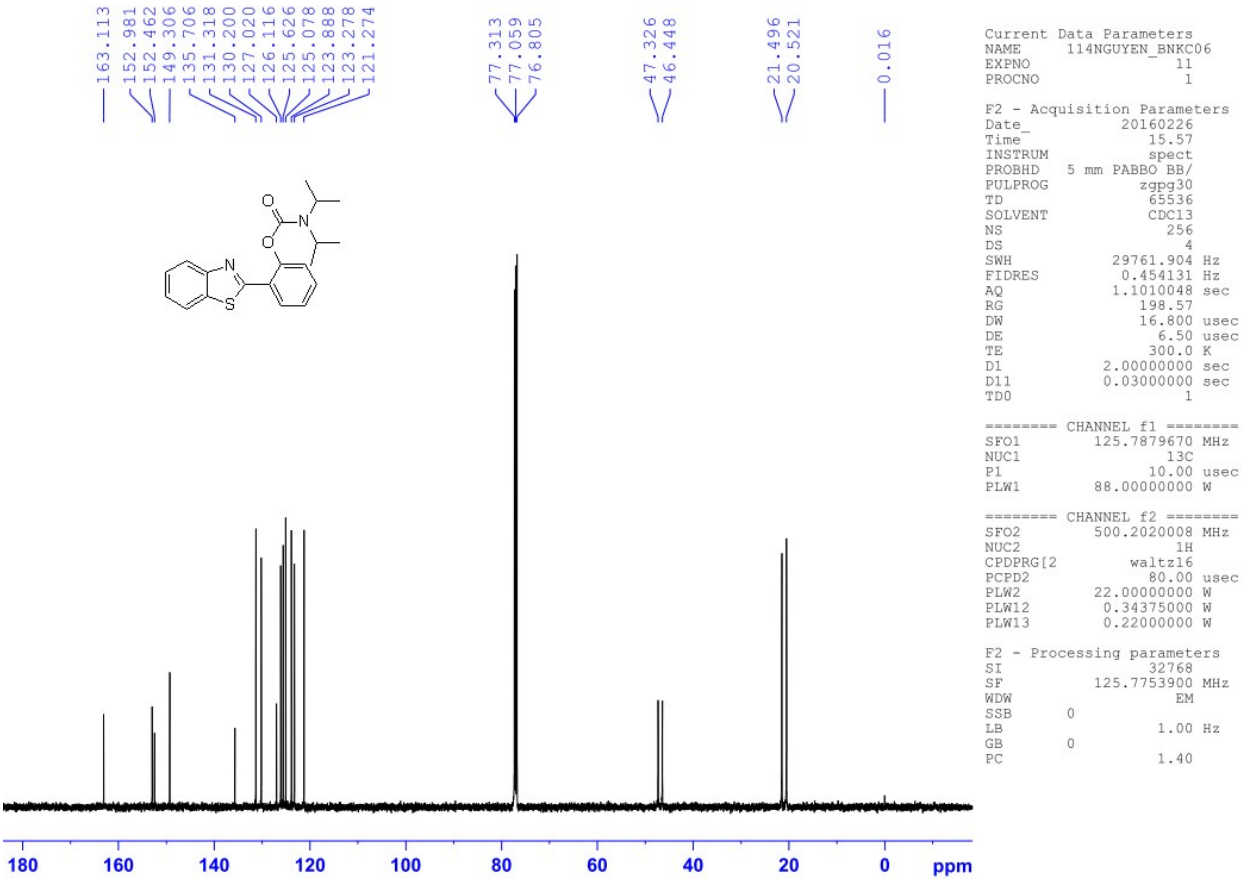

Fig. S13. ^{13}C-NMR spectra of 2-(benzo[*d*]thiazol-2-yl)phenyl diisopropylcarbamate.

Characterization Data for 2-(benzo[*d*]thiazol-2-yl)phenyl diisopropylcarbamate

Prepared as shown in the general experimental procedure and purified on silica gel (hexane/ethyl acetate = 3:1): brown gummy, 67% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.26 (dd, *J*=1.5 Hz, *J*=8.0 Hz, 1H, ArH), 8.08 (d, *J*=8.0 Hz, 1H, ArH), 7.90 (d, *J*=8.0 Hz, 1H, ArH), 7.50 – 7.46 (m, 2H, ArH), 7.38 (t, *J*=7.5 Hz, 1H, ArH), 7.34 (t, *J*=7.5 Hz, 1H, ArH), 7.21 (d, *J*=8.0 Hz, 1H, ArH), 4.42 – 4.37 (m, 1H, NC*H*$(CH_3)_2$), 3.86 – 3.81 (m, 1H, NC*H*$(CH_3)_2$), 1.36 (d, *J*=7.0 Hz, 6H, NCH(C*H*$_3)_2$), 1.32 (d, *J*=7.0 Hz, 6H, NCH(C*H*$_3)_2$); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 163.1,

153.0, 152.5, 149.3, 135.7, 131.3, 130.2, 127.0, 126.1, 125.6, 125.1, 123.9, 123.3, 121.3, 47.3, 46.4, 21.5, 20.5; GC/MS (EI), m/z, 354+1, $[M+H]^+$.

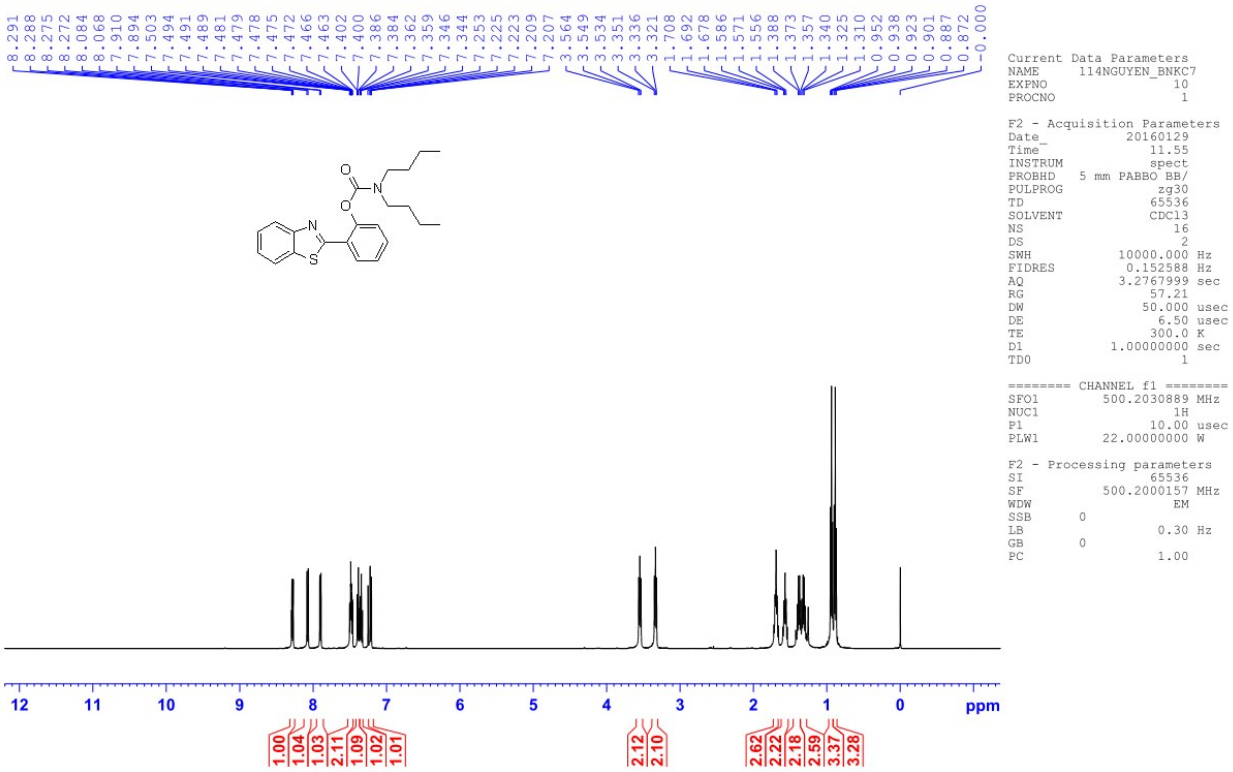

Fig. S14. ^{1}H-NMR spectra of 2-(benzo[*d*]thiazol-2-yl)phenyl dibutylcarbamate.

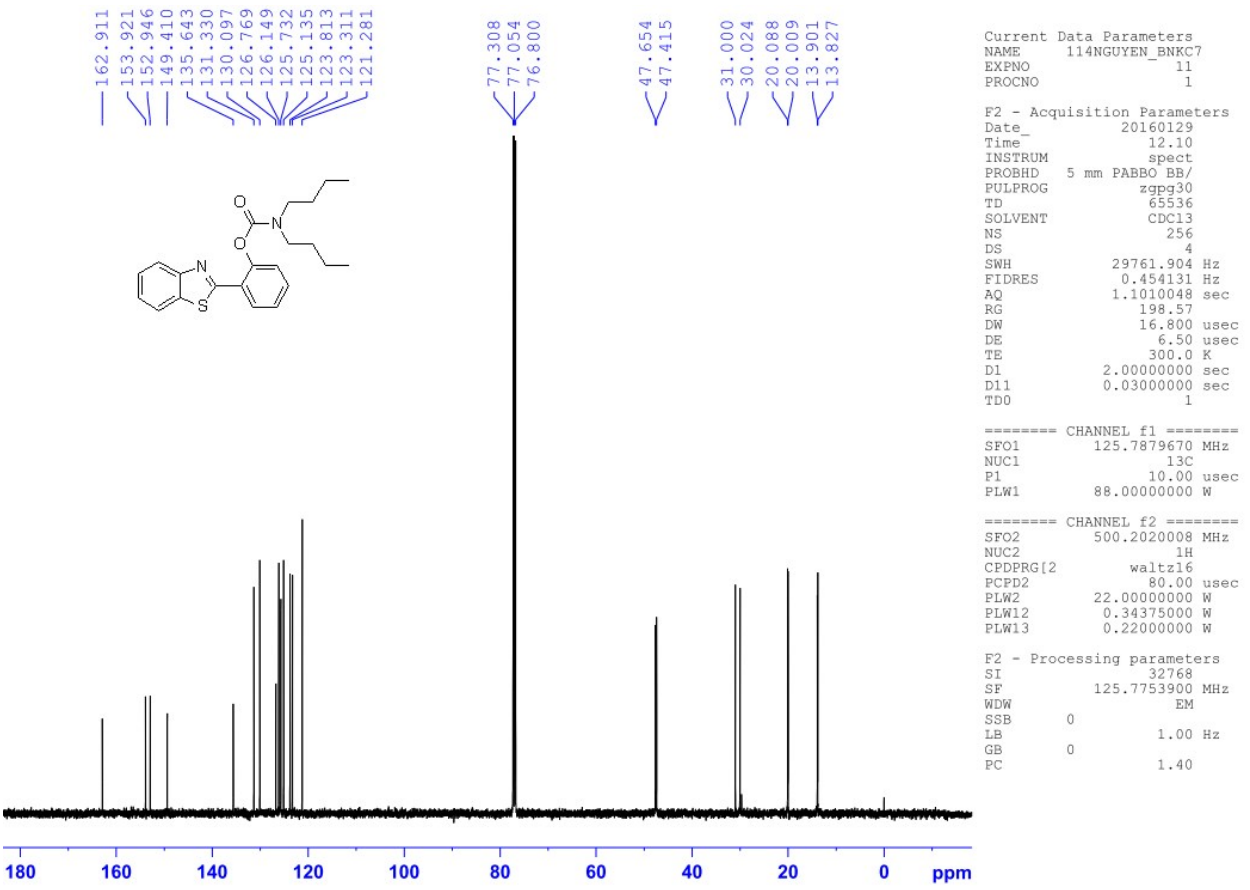

Fig. S15. ^{13}C-NMR spectra of 2-(benzo[*d*]thiazol-2-yl)phenyl dibutylcarbamate.

Characterization Data for 2-(benzo[*d*]thiazol-2-yl)phenyl dibutylcarbamate

Prepared as shown in the general experimental procedure and purified on silica gel (hexane/ethyl acetate = 5:1): brown gummy, 61% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.28 (dd, *J*=1.5 Hz, *J*=8.0 Hz, 1H, ArH), 8.08 (d, *J*=8.0 Hz, 1H, ArH), 7.90 (d, *J*=8.0 Hz, 1H, ArH), 7.51 – 7.46 (m, 2H, ArH), 7.39 (td, *J*=1.0 Hz, *J*=8.0 Hz, 1H, ArH), 7.35 (td, *J*=1.0 Hz, *J*=7.5 Hz, 1H, ArH), 7.22 (dd, *J*=1.0 Hz, *J*=8.0 Hz, 1H, ArH), 3.55 (t, *J*=7.5 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 3.34 (t, *J*=7.5 Hz, 2H, $NCH_2CH_2CH_2CH_3$), 1.72 – 1.66 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.60 – 1.54 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.43 – 1.36 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.34 – 1.26 (m, 2H,

$NCH_2CH_2C\mathit{H}_2CH_3$), 0.94 (t, *J*=7.5 Hz, 3H, $NCH_2CH_2CH_2C\mathit{H}_3$), 0.89 (t, *J*=7.5 Hz, 3H, $NCH_2CH_2CH_2C\mathit{H}_3$); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 162.9, 153.9, 152.9, 149.4, 135.6, 131.3, 130.1, 126.8, 126.1, 125.7, 125.1, 123.8, 123.3, 121.3, 47.7, 47.4, 31.0, 30.0, 20.1, 20.0, 13.9, 13.8; GC/MS (EI), m/z, 382+1, $[M+H]^+$.

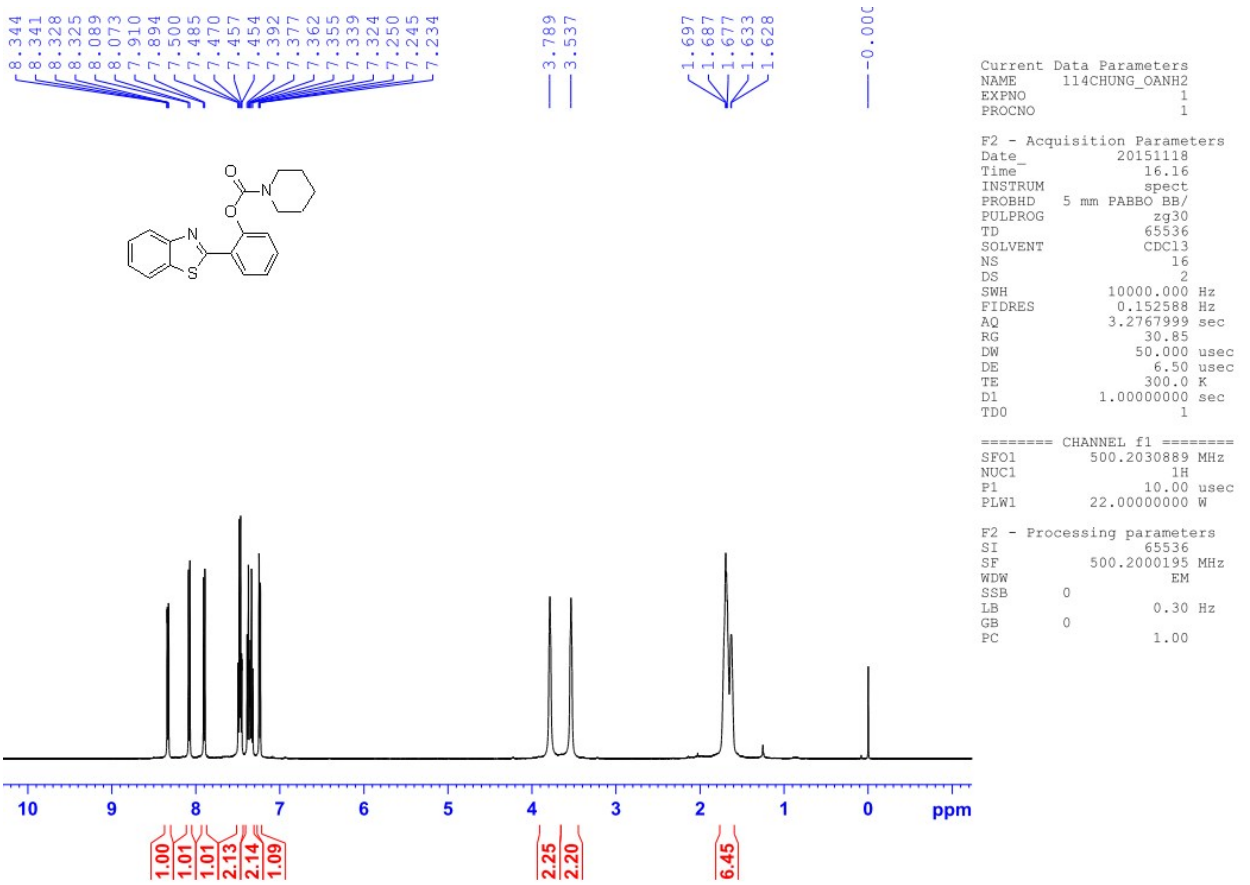

Fig. S16. ^{1}H-NMR spectra of 2-(benzo[*d*]thiazol-2-yl)phenyl piperidine-1-carboxylate.

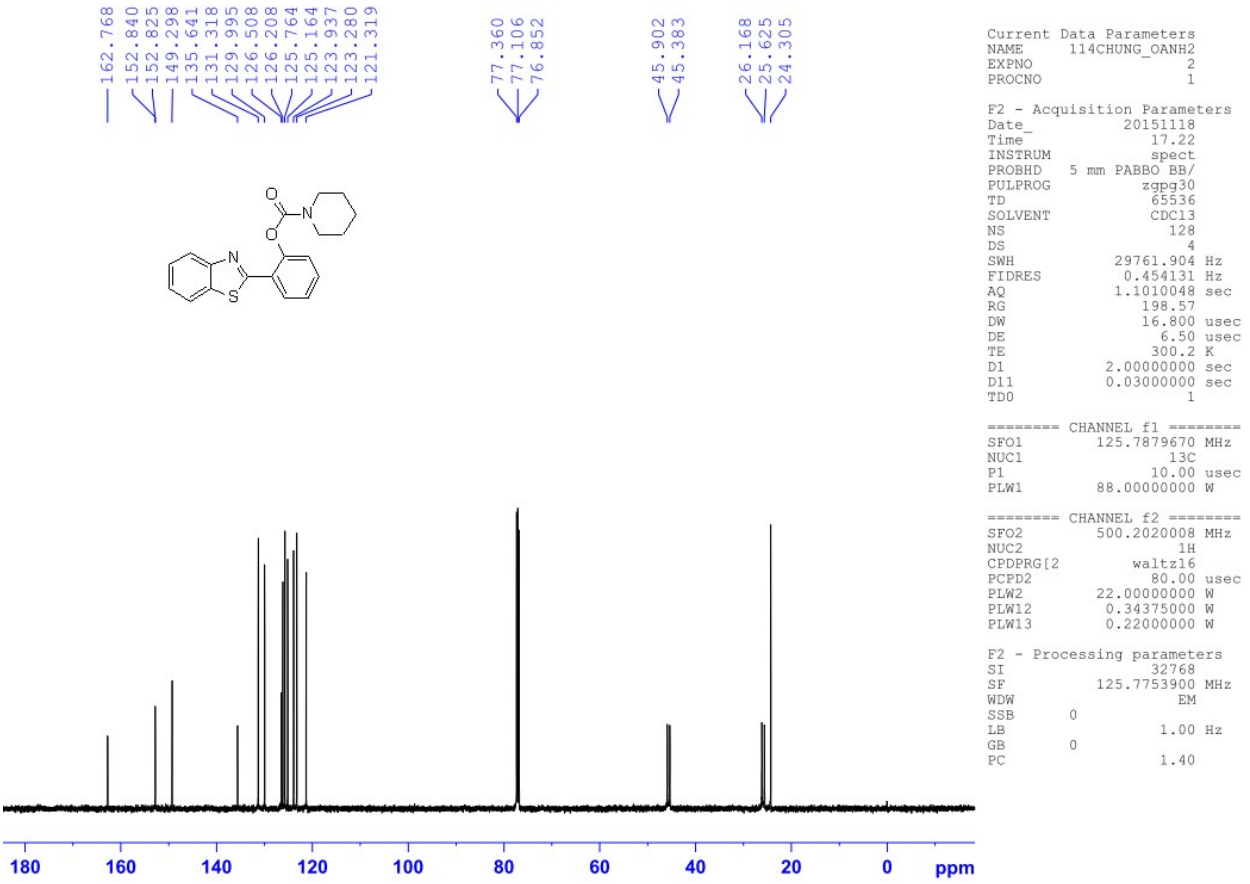

Fig. S17. ^{13}C-NMR spectra of 2-(benzo[*d*]thiazol-2-yl)phenyl piperidine-1-carboxylate.

Characterization Data for 2-(benzo[*d*]thiazol-2-yl)phenyl piperidine-1-carboxylate

Prepared as shown in the general experimental procedure and purified on silica gel (hexane/ethyl acetate = 5:1): yellow solid, 66% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.33 (dd, *J*=1.5 Hz, *J*=8.0 Hz, 1H, ArH), 8.08 (d, *J*=8.0 Hz, 1H, ArH), 7.90 (d, *J*=8.0 Hz, 1H, ArH), 7.50 – 7.45 (m, 2H, ArH), 7.39 – 7.32 (m, 2H, ArH), 7.25 – 7.23 (m, 1H, ArH), 3.79 (s, 2H, NCH_2), 3.54 (s, 2H, NCH_2), 1.70 – 1.63 (m, 6H, $NCH_2CH_2CH_2$); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 162.8, 152.8, 152.8, 149.3, 135.6, 131.3, 130.0, 126.5, 126.2, 125.8, 125.2, 123.9, 123.3, 121.3, 45.9, 45.4, 26.2, 25.6, 24.3; GC/MS (EI), m/z, 338+1, $[M+H]^+$.

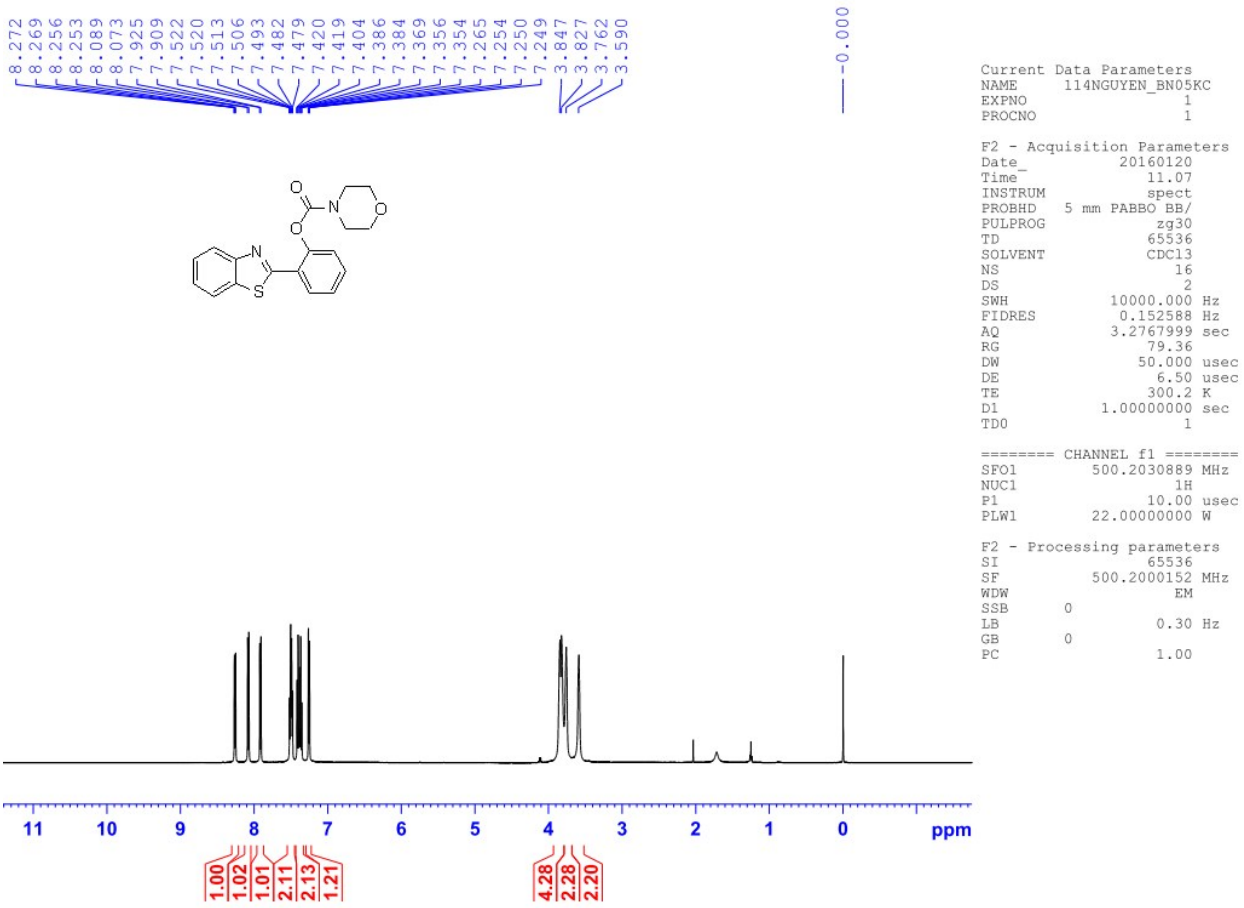

Fig. S18. ^{1}H-NMR spectra of 2-(benzo[*d*]thiazol-2-yl)phenyl morpholine-4-carboxylate.

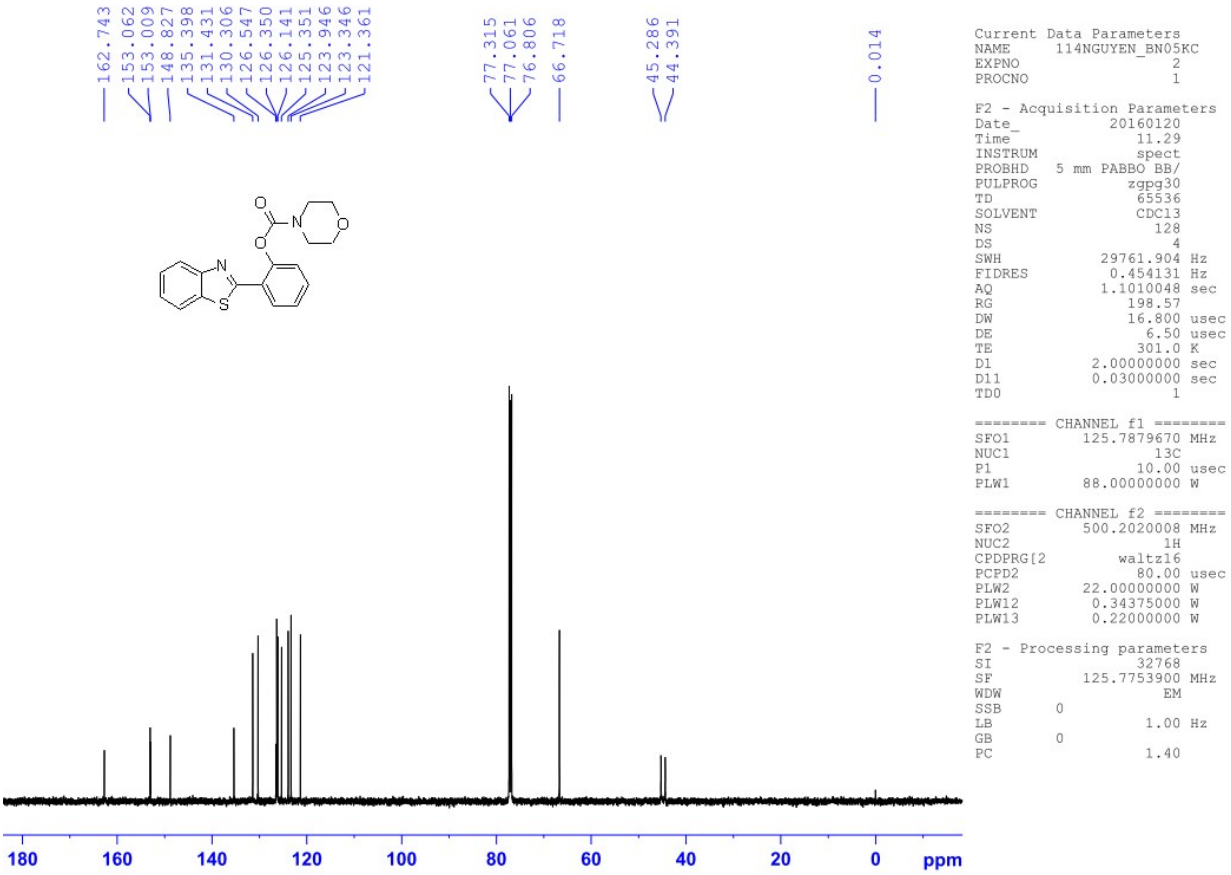

Fig. S19. ^{13}C-NMR spectra of 2-(benzo[*d*]thiazol-2-yl)phenyl morpholine-4-carboxylate.

Characterization Data for 2-(benzo[*d*]thiazol-2-yl)phenyl morpholine-4-carboxylate

Prepared as shown in the general experimental procedure and purified on silica gel (hexane/ethyl acetate = 3:1): light yellow solid, 64% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.26 (dd, *J*=1.5 Hz, *J*=8.0 Hz, 1H, ArH), 8.08 (d, *J*=8.0 Hz, 1H, ArH), 7.92 (d, *J*=8.0 Hz, 1H, ArH), 7.52 – 7.48 (m, 2H, ArH), 7.42 – 7.35 (m, 2H, ArH), 7.27 – 7.25 (m, 1H, ArH), 3.84 (d, *J*=10 Hz, 4H, NCH_2), 3.76 (s, 2H, OCH_2), 3.59 (s, 2H, OCH_2); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 162.7, 153.1, 153.0, 148.8, 135.4, 131.4, 130.3, 126.5, 126.4, 126.1, 125.4, 123.9, 123.3, 121.4, 66.7, 45.3, 44.4; GC/MS (EI), m/z, 340+1, $[M+H]^+$.

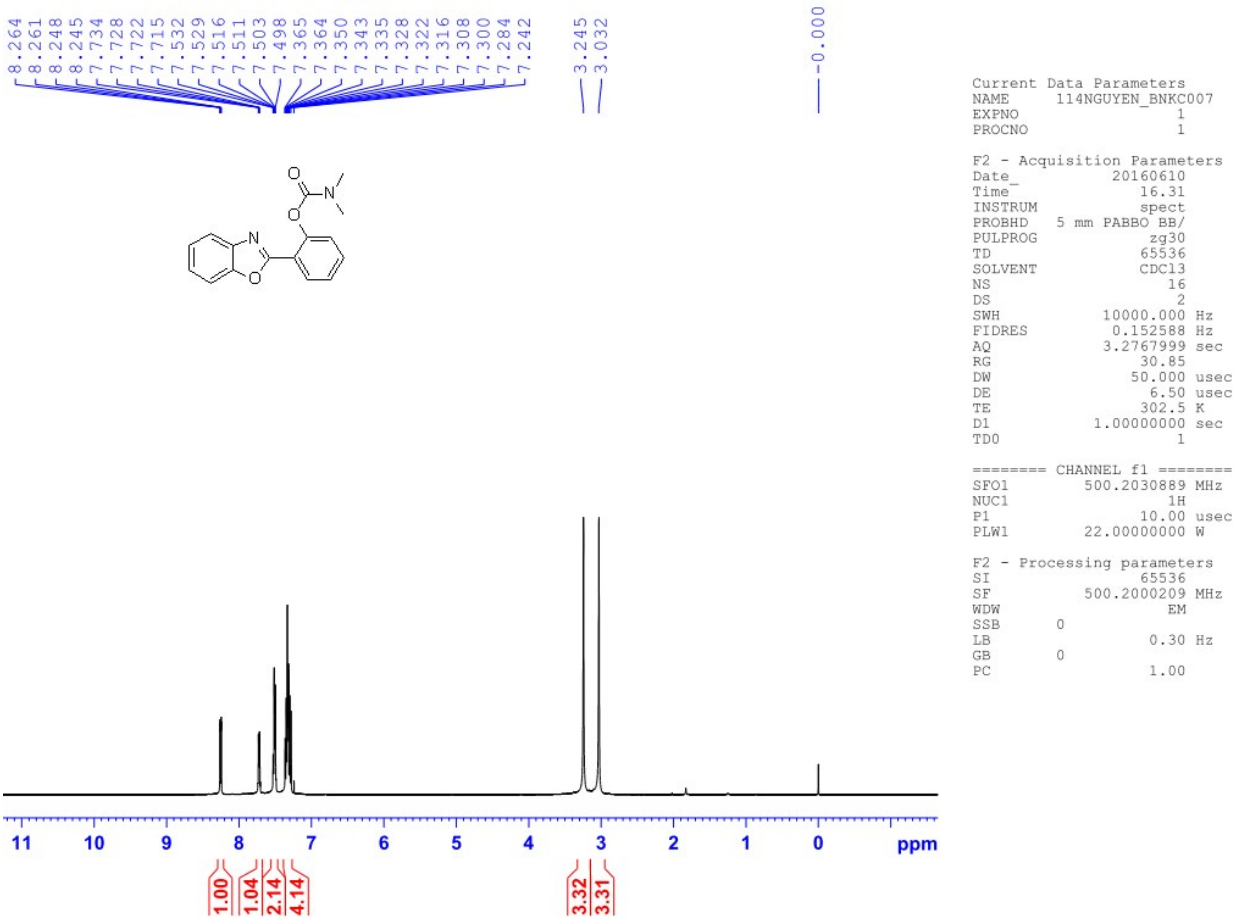

Fig. S20. ^{1}H-NMR spectra of 2-(benzo[*d*]oxazol-2-yl)phenyl dimethylcarbamate.

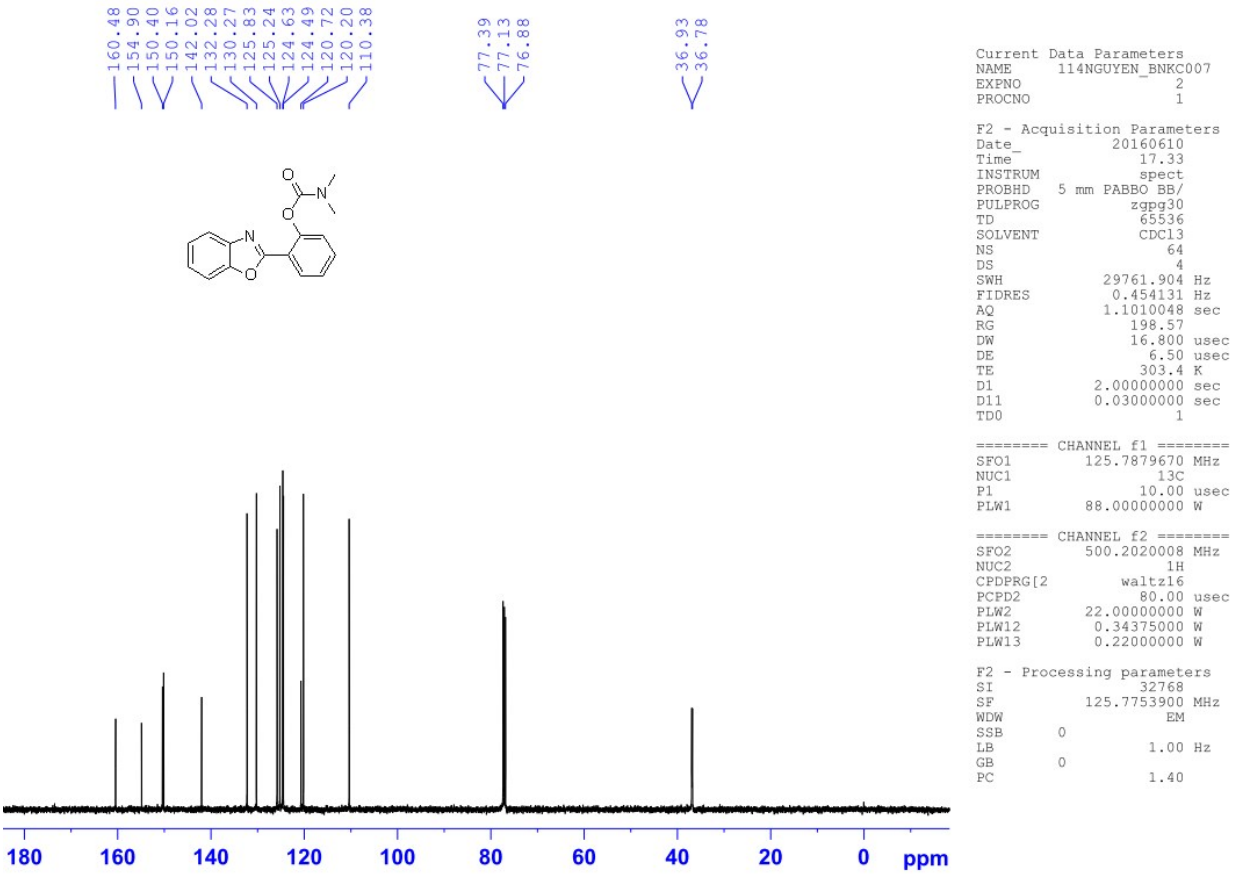

Fig. S21. ^{13}C-NMR spectra of 2-(benzo[*d*]oxazol-2-yl)phenyl dimethylcarbamate.

Characterization Data for 2-(benzo[d]oxazol-2-yl)phenyl dimethylcarbamate

Prepared as shown in the general experimental procedure and purified on silica gel (hexane/ethyl acetate = 1:3): white solid, 66% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.25 (dd, *J*=1.5 Hz, *J*=8.0, 1H, ArH), 7.73 – 7.72 (m, 1H, ArH), 7.53 – 7.50 (m, 2H, ArH), 7.37 – 7.28 (m, 4H, ArH), 3.25 (s, 3H, NCH_3), 3.03 (s, 3H, NCH_3); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 160.5, 154.9, 150.4, 150.2, 142.0, 132.3, 130.3, 125.8, 125.2, 124.6, 124.5, 120.7, 120.2, 110.4, 36.9, 36.8; GC/MS (EI), m/z, 282+1, $[M+H]^+$.

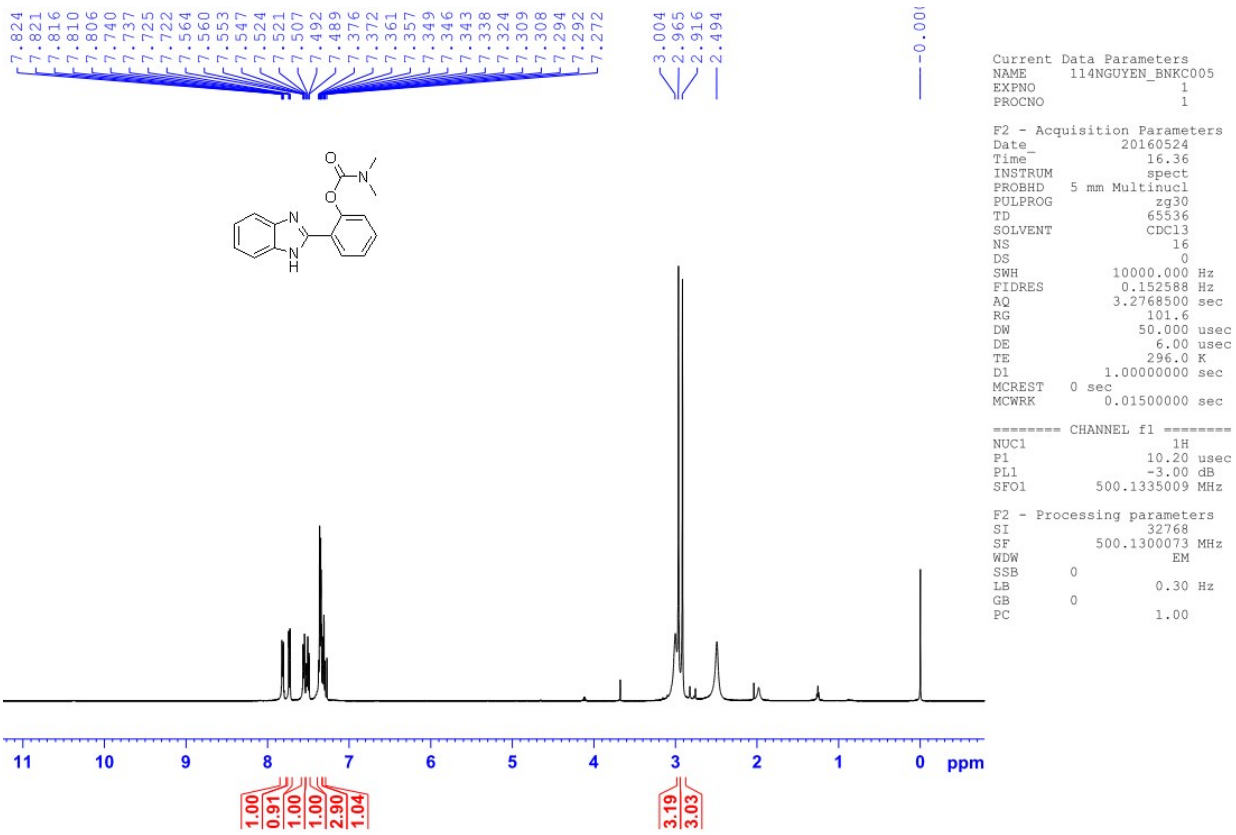

Fig. S22. ^{1}H-NMR spectra of 2-(1*H*-benzo[*d*]imidazol-2-yl)phenyl dimethylcarbamate.

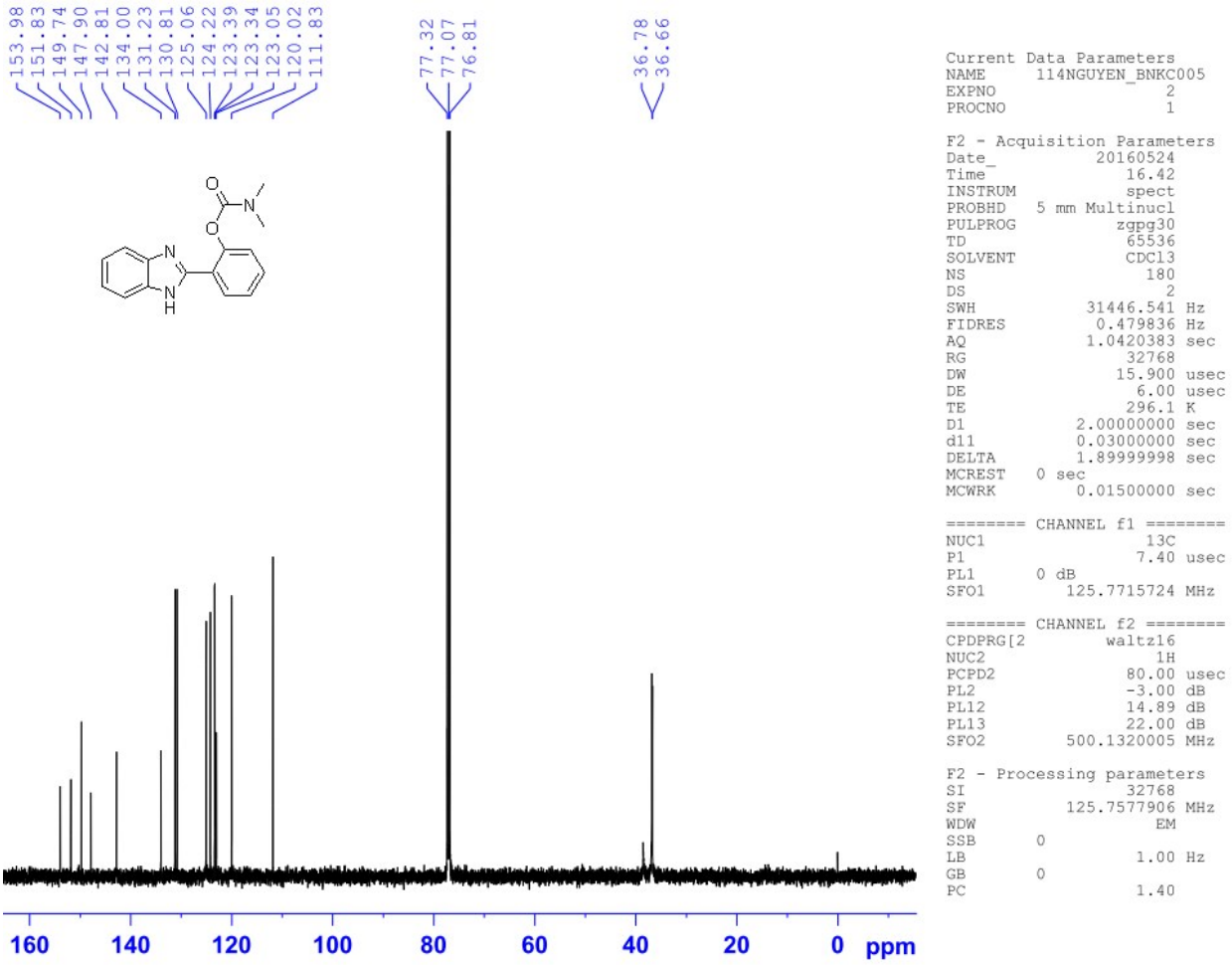

Fig. S23. ^{13}C-NMR spectra of 2-(1*H*-benzo[*d*]imidazol-2-yl)phenyl dimethylcarbamate.

Characterization Data for 2-(1*H*-benzo[*d*]imidazol-2-yl)phenyl dimethylcarbamate

Prepared as shown in the general experimental procedure and purified on silica gel (hexane/ethyl acetate = 1:3): white solid, 70% yield. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.81 (m, 1H, ArH), 7.73 (dd, *J*=1.5 Hz, *J*=7.5, 1H, ArH), 7.56 – 7.55 (m, 1H, ArH), 7.52 – 7.49 (m, 1H, ArH), 7.38 – 7.34 (m, 3H, ArH), 7.32 – 7.29 (m, 1H, ArH), 2.97 (s, 3H, NCH_3), 2.92 (s, 3H, NCH_3); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 154.0, 151.8, 149.7, 147.9, 142.8, 134.0, 131.2, 130.8, 125.1, 124.2, 123.4, 123.3, 123.1, 120.0, 111.8, 36.7; GC/MS (EI), m/z, 281+1, $[M+H]^+$.