Electronic Supplementary Information (ESI)

Visible-light-driven Net-1,2-Hydrogen Atom Transfer of Amidyl Radicals to Access β-Amido Ketone Derivatives

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Supplementary methods:

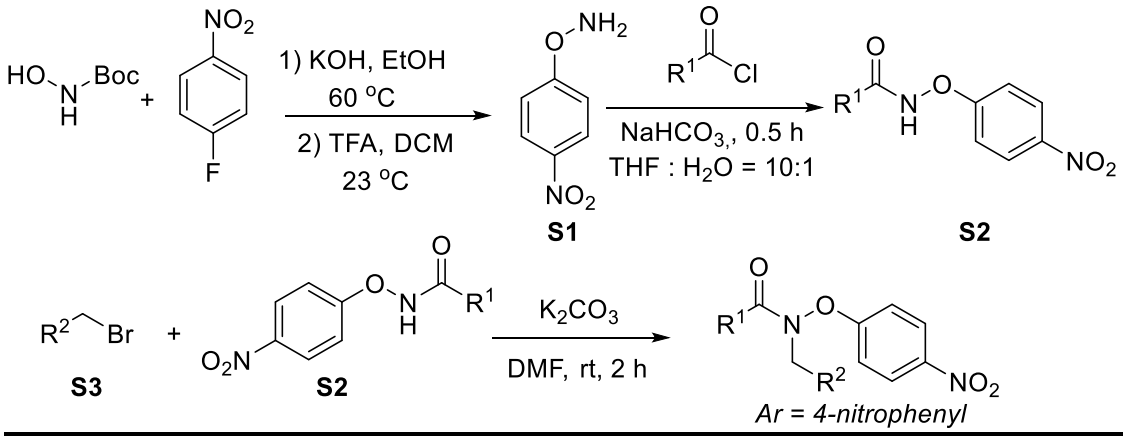
General methods

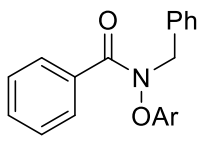
All air- and moisture-sensitive solutions and chemicals were handled under a nitrogen atmosphere of a glovebox and solutions were transferred via a “Titan” brand pipettor. Anhydrous solvents, including DMSO (dimethyl sulfoxide), DCM (dichloromethane), DME (dimethoxyethane), CPME (cyclopentyl methyl ether), THF (tetrahydrofuran), toluene, and acetonitrile were purchased from Sigma-Aldrich and used without further purification. Unless otherwise stated, all the reagents were commercially available and used as received without further purification. Chemicals were obtained from Sigma-Aldrich, Acros, TCI and Alfa-Aesar. Thin layer chromatography (TLC) was performed with Merck TLC Silica gel60 F254 plates with detection under UV light at 254 nm. Silica gel (200−300 mesh, Qingdao) was used for flash chromatography. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on Bruker DRX 400 and Bruker DRX 600 spectrometers at 400 and 600 MHz. Carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra were recorded on Bruker DRX 400 and Bruker DRX 600 spectrometers at 100, and 150 MHz. Chemical shifts are reported as δ values in parts per million (ppm) relative to tetramethylsilane (TMS) for all recorded NMR spectra. High resolution mass spectra were taken on an AB QSTAR Pulsar mass spectrometer. Melting points were obtained on a XT-4 melting point apparatus and were uncorrected. Cyclic voltammetry studies were carried out on a CHI 760E electrochemical workstation (Shanghai CH Instruments Co., China). EPR spectra were recorded by a ADANlSPlNSCAN X spectrometer. Fluorescence measurements were made with a Leng guang F98 fluorescence spectrophotometer (Shanghai Lengguang, China).

Preparation of amides

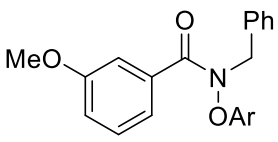
Amides (1a-1u) were prepared according to the literature procedure.[1]

General procedure for the synthesis of amides (1a-1u) from *O*-aryl-hydroxylamines (S1) – GP1





1a



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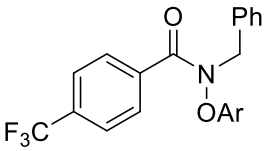

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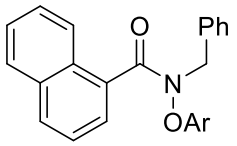

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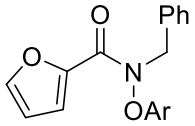

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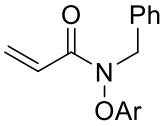

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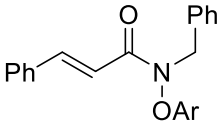

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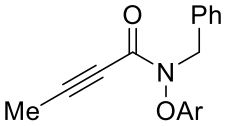

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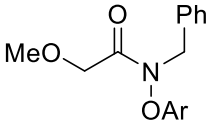

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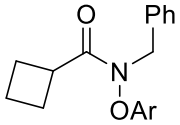

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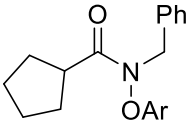
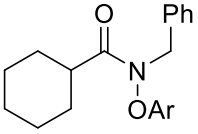
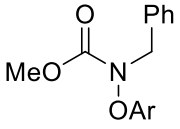


1k



1l



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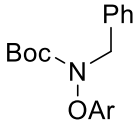

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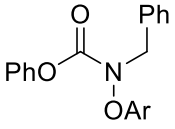

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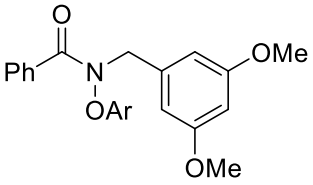

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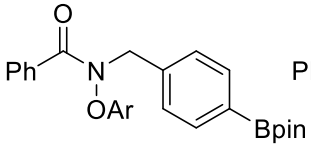

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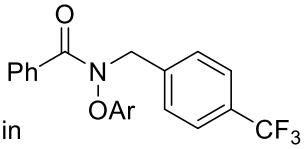

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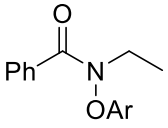
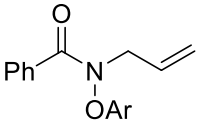


1t



1u

The literature[2] procedure was followed for the synthesis of *O*-(4-nitrophenyl)hydroxylamine **S1**.

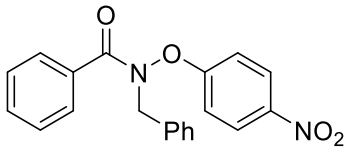
To a solution of KOH (1.1 equiv.) in 50 mL ethanol was added *tert*-butyl-*N*-hydroxy carbamate (1.2 equiv.) at room temperature. 1-Fluoro-4-nitrobenzene (1.0 equiv.) was added to the resulting mixture and the solution was warmed to 60 ℃. After stirring for 72 h, the reaction mixture was allowed to cool and concentrated in vacuo. The resulting red oil was redissolved in EtOAc (80 mL) and washed with a saturated NH_4Cl solution (3 X 10 mL). The combined organic phase was washed with a saturated brine solution (5 mL), dried over Na_2SO_4, filtered and concentrated in vacuo to give the crude product. The product was dissolved in 50 mL CH_2Cl_2 and treated with 5.5 mL trifluoroacetic acid at room temperature. After consumption of the substrate by TLC, the reaction mixture was concentrated in vacuo and dissolved in 80 mL CH_2Cl_2. The solution was washed with saturated $NaHCO_3$ solution (3 X 10 mL) and saturated brine solution (5 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. Purification by column chromatography (hexanes: ethyl acetate = 4:1) afforded the product **S1** as a light yellow solid.

In air, to a stirring suspension of *O*-(4-nitrophenyl)hydroxylamine **S1** (1.1 equiv.) and $NaHCO_3$ (2.0 equiv.) in THF/H_2O (10:1, 0.5 M) was added benzoyl chloride (1.0 equiv.) dropwise over 20 min at the room temperature. The reaction mixture was allowed to stir for 30 min and was then diluted with 10 mL of H_2O. The mixture was extracted with ethyl acetate (3 X 20 mL). The organic layers were combined, washed with saturated brine solution (100 mL), dried over Na_2SO_4, and filtered. The filtrate was concentrated in vacuo. The resultant solid was submitted to the next step without further purification.

In a dry Schlenk tube equipped with a stirring bar the Alkyl bromide **S3** (1.0 equiv.) and *N*-(4-nitrophenoxy)benzamide **S2** (1.0 equiv.) in DMF (1.0 M) was added K_2CO_3 (1.5 equiv.). The reaction mixture was allowed to stir for 2 h, and was then diluted with 5 mL H_2O. The mixture was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with saturated brine solution (20 mL), dried (Na_2SO_4),

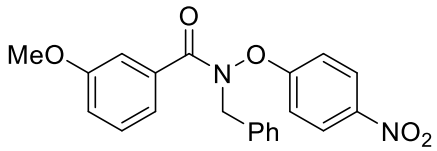
filtered and evaporated. Purification by column chromatography on silica gel eluting with (petroleum ether: ethyl acetate = 8:1) to give **1a** - **1u**.

***N*-benzyl-*N*-(4-nitrophenoxy)benzamide (1a)**



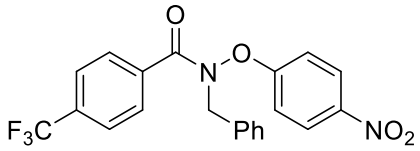
The ^{1}H and ^{13}C data for this compound match the literature data.[1]

***N*-benzyl-3-methoxy-*N*-(4-nitrophenoxy)benzamide (1b)**



The reaction was performed following **GP1**, compound **1b** was obtained as yellow solid (38%, over three steps); m.p. = 85 – 87 °C; R_f = 0.40 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 – 8.08 (m, 2H), 7.27 – 7.24 (m, 5H), 7.20 – 7.16 (m, 1H), 7.09 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.05 (dd, *J* = 2.4, 1.6 Hz, 1H), 7.00 – 6.96 (m, 2H), 6.92 –6.89 (m, 1H), 4.94 (s, 2H), 3.65 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.8, 161.7, 158.4, 142.3, 133.5, 133.0, 128.5, 127.9, 127.8, 127.3, 125.0, 119.1, 116.6, 112.8, 112.2, 54.3, 52.6 ppm; HRMS calc'd for $C_{21}H_{19}N_2O_5^+$: 379.1288, found : 379.1291 $[M+H]^+$.

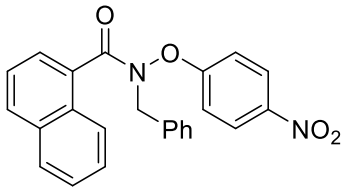
***N*-benzyl-*N*-(4-nitrophenoxy)-4-(trifluoromethyl)benzamide (1c)**



The reaction was performed following **GP1**, compound **1c** was obtained as yellow solid (33%, over three steps); m.p. = 105 – 107 °C; R_f = 0.57 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 – 8.17 (m, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.34 (s, 5H), 7.06 – 7.02 (m, 2H), 5.04 (s, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.6, 162.2, 143.7, 136.4, 134.2, 133.2 (q, J_{C-F} = 32.6 Hz),

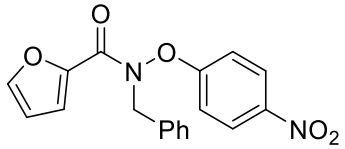
129.0, 128.9, 128.6, 128.3, 126.2, 125.4 (q, $J_{C\text{-}F}$ = 3.8 Hz), 123.4 (q, $J_{C\text{-}F}$ = 271.3 Hz), 113.8, 52.8 ppm. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.1 ppm; HRMS calc'd for $C_{21}H_{16}F_3N_2O_4^+$: 417.1057, found: 417.1062 $[M+H]^+$.

_N_-benzyl-_N_-(4-nitrophenoxy)-1-naphthamide (1d)



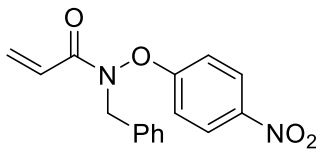
The reaction was performed following **GP1**, compound **1d** was obtained as yellow solid (31%, over three steps); m.p. = 130 – 132 °C; R_f = 0.47 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 9.2 Hz, 2H), 7.86 – 7.82 (m, 3H), 7.53 – 7.49 (m, 2H), 7.44 (d, *J* = 7.6 Hz,1H), 7.37 – 7.33 (m, 6H), 6.93 (d, *J* = 8.8 Hz, 2H), 5.04 (s, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.8, 143.3, 134.5, 133.4, 131.2, 130.7, 129.8, 129.2, 128.8, 128.6, 128.5, 127.3, 126.6, 125.8, 124.7, 124.6, 124.5, 113.7, 53.5 ppm. (one resonance was not observed due to overlapping peaks); HRMS calc'd for $C_{24}H_{19}N_2O_4^+$: 399.1339, found: 399.1335 $[M+H]^+$.

_N_-benzyl-_N_-(4-nitrophenoxy)furan-2-carboxamide (1e)



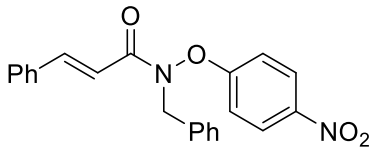
The reaction was performed following **GP1**, compound **1e** was obtained as yellow solid (54%, over three steps); m.p. = 123 – 125 °C; R_f = 0.40 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 8.8 Hz, 2H), 7.43 (s, 1H), 7.27 – 7.20 (m, 5H), 7.07 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 2.8 Hz,1H), 6.34 (s, 1H), 4.95 (s, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.7, 160.6, 146.3, 144.9, 143.7, 134.4, 129.3, 128.7, 128.4, 126.2, 119.3, 114.0, 112.0, 52.5 ppm; HRMS calc'd for $C_{18}H_{15}N_2O_5^+$: 339.0975, found: 339.0968 $[M+H]^+$.

_N_-benzyl-_N_-(4-nitrophenoxy)acrylamide (1f)



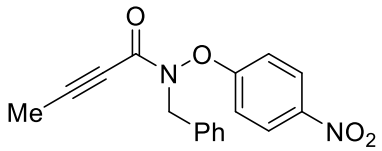
The reaction was performed following **GP1**, compound **1f** was obtained as yellow solid (38%, over three steps); m.p. = 93 – 95 °C; R_f = 0.53 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 – 8.18 (m, 2H), 7.32 – 7.28 (m, 5H), 7.10 – 7.06 (m, 2H), 6.57 (dd, *J* = 16.8, 2.0 Hz, 1H), 6.43 (dd, *J* = 16.8, 10.0 Hz, 1H), 5.81 (dd, *J* = 10.0, 2.0 Hz, 1H), 4.96 (s, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.0, 162.9, 143.7, 134.6, 131.8, 129.2, 128.7, 128.3, 126.1, 125.3, 113.9, 51.7 ppm; HRMS calc'd for $C_{16}H_{15}N_2O_4^+$: 299.1026 found: 299.1021 $[M+H]^+$.

(*E*)-*N*-benzyl-*N*-(4-nitrophenoxy)cinnamamide (1g)



The reaction was performed following **GP1**, compound **1g** was obtained as white solid (30%, over three steps); m.p. = 125 – 127 °C; R_f = 0.6 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 – 8.11 (m, 2H), 7.78 (d, *J* = 15.6 Hz, 1H), 7.35 (dd, *J* = 7.6, 2.0 Hz, 2H), 7.26 – 7.20 (m, 8H), 7.08 – 7.04 (m, 2H), 6.63 (d, *J* = 15.6 Hz, 1H), 4.92 (s, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.7, 163.1, 146.2, 143.7, 134.8, 134.4, 130.6, 129.2, 128.9, 128.7, 128.29, 128.26, 126.2, 114.7, 114.1, 51.8 ppm; HRMS calc'd for $C_{22}H_{19}N_2O_4^+$: 375.1339 found: 375.1336 $[M+H]^+$.

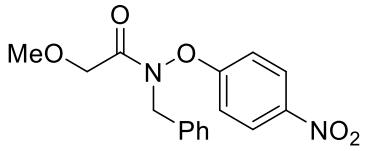
***N*-benzyl-*N*-(4-nitrophenoxy)but-2-ynamide (1h)**



The reaction was performed following **GP1**, compound **1h** was obtained as white solid (42%, over three steps); m.p. = 107 – 109 °C; R_f = 0.43 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 – 8.15 (m, 2H), 7.33 – 7.30 (m, 5H), 7.06 – 7.02 (m, 2H), 4.97 (s, 2H), 1.93 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ

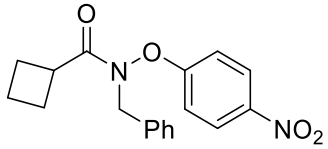
163.0, 143.5, 134.0, 129.0, 128.8, 128.5, 125.9, 113.8, 92.6, 72.1, 4.2 ppm (two resonances were not observed due to overlapping peaks); HRMS calc'd for $C_{17}H_{15}N_2O_4^+$: 311.1026 found: 311.1024 $[M+H]^+$.

_N_-benzyl-2-methoxy-_N_-(4-nitrophenoxy)acetamide (1i)



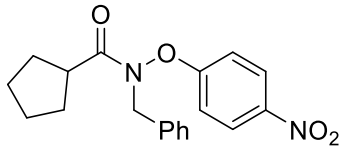
The reaction was performed following **GP1**, compound **1i** was obtained as yellow solid (36%, over three steps); m.p. = 89 – 91 °C; R_f = 0.30 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 – 8.07 (m, 2H), 7.21 – 7.18 (m, 5H), 7.02 – 6.98 (m, 2H), 4.81 (s, 2H), 4.05 (s, 2H), 3.31 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.6, 162.4, 143.7, 134.3, 129.3, 128.7, 128.4, 126.2, 113.6, 70.1, 59.5, 51.9 ppm; HRMS calc'd for $C_{16}H_{17}N_2O_5^+$: 317.1132 found: 317.1133 $[M+H]^+$.

_N_-benzyl-_N_-(4-nitrophenoxy)cyclobutanecarboxamide (1j)



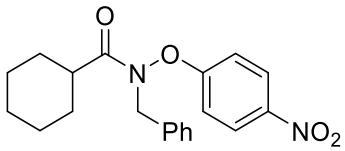
The reaction was performed following **GP1**, compound **1j** was obtained as yellow solid (30%, over three steps); m.p. = 96 – 98 °C; R_f = 0.67 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 – 8.09 (m, 2H), 7.23 – 7.20 (m, 5H), 6.98 – 6.94 (m, 2H), 4.80 (s, 2H), 3.21 – 3.13 (m, 1H), 2.28 – 2.18 (m, 2H), 1.96 – 1.87 (m, 2H), 1.85 – 1.73 (m, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 177.7, 163.0, 143.4, 134.9, 129.1, 128.7, 128.2, 126.1, 113.5, 51.9, 37.0, 24.6, 18.1 ppm; HRMS calc'd for $C_{18}H_{19}N_2O_4^+$: 327.1339 found: 327.1338 $[M+H]^+$.

_N_-benzyl-_N_-(4-nitrophenoxy)cyclopentanecarboxamide (1k)



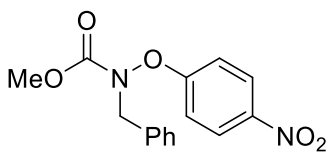
The reaction was performed following **GP1**, compound **1k** was obtained as yellow solid (32%, over three steps); m.p. = 122 – 124 °C; R_f = 0.70 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 9.2 Hz, 2H), 7.31 – 7.28 (m, 5H), 7.09 (d, *J* = 9.2 Hz, 2H), 4.89 (s, 2H), 2.87 – 2.79 (m, 1H), 1.84 – 1.65 (m, 6H), 1.55 – 1.46 (m, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.4, 163.0, 143.4, 135.0, 129.1, 128.7, 128.2, 126.1, 113.7, 51.7, 41.2, 29.7, 26.1 ppm; HRMS calc'd for $C_{19}H_{21}N_2O_4^+$: 341.1496 found : 341.1491 $[M+H]^+$.

_N_-benzyl-_N_-(4-nitrophenoxy)cyclohexanecarboxamide (1l)



The reaction was performed following **GP1**, compound **1l** was obtained as yellow solid (28%, over three steps); m.p. = 148 – 150 °C; R_f = 0.77 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 – 8.20 (m, 2H), 7.31 – 7.25 (m, 5H), 7.10 – 7.07 (m, 2H), 4.87 (s, 2H), 2.43 (tt, *J* = 11.6, 3.2 Hz, 1H), 1.76 – 1.71 (m, 4H), 1.66 – 1.59 (m, 1H), 1.53 – 1.44 (m, 2H), 1.28 – 1.22 (m, 1H), 1.21 – 1.10 (m, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 179.0, 163.0, 143.5, 135.0, 129.0, 128.7, 128.2, 126.2, 113.7, 51.4, 40.9, 28.6, 25.6, 25.5 ppm; HRMS calc'd for $C_{20}H_{23}N_2O_4^+$: 355.1652 found : 355.1647 $[M+H]^+$.

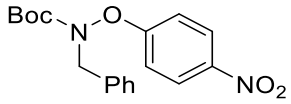
methyl benzyl(4-nitrophenoxy)carbamate (1m)



The reaction was performed following **GP1**, compound **1m** was obtained as yellow solid (32%, over three steps); m.p. = 67 – 69 °C; R_f = 0.65 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 8.00 (m, 2H), 7.25 – 7.16 (m, 5H),

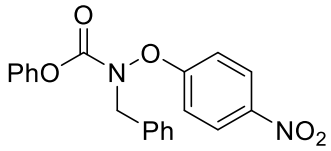
6.96 – 6.92 (m, 2H), 4.72 (s, 2H), 3.71 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.8, 157.8, 143.1, 134.6, 129.2, 128.7, 128.3, 125.7, 113.6, 55.0, 54.1 ppm; HRMS calc'd for $C_{15}H_{15}N_2O_5^+$: 303.0975 found: 303.0976 $[M+H]^+$.

***tert*-butyl benzyl(4-nitrophenoxy)carbamate (1n)**



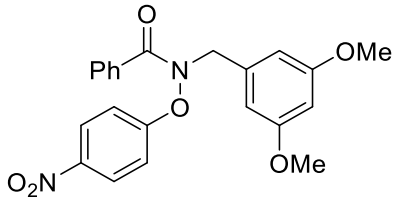
The reaction was performed following **GP1**, compound **1n** was obtained as white solid (46%, over three steps); m.p. = 104 – 106 °C; R_f = 0.80 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 – 8.12 (m, 2H), 7.36 – 7.28 (m, 5H), 7.06 – 7.02 (m, 2H), 4.77 (s, 2H), 1.44 (s, 9H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.2, 156.1, 142.8, 135.2, 129.0, 128.6, 128.1, 125.7, 113.5, 83.5, 55.0, 28.1 ppm; HRMS calc'd for $C_{18}H_{21}N_2O_5^+$: 345.1445 found : 345.1442 $[M+H]^+$.

phenyl benzyl(4-nitrophenoxy)carbamate (1o)



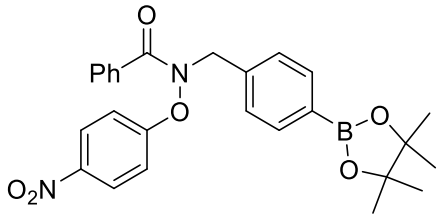
The reaction was performed following **GP1**, compound **1o** was obtained as yellow solid (32%, over three steps); m.p. = 87 – 89 °C; R_f = 0.72 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 – 8.16 (m, 2H), 7.42 – 7.40 (m, 2H), 7.39 – 7.32 (m, 5H), 7.26 – 7.22 (m, 1H), 7.16 – 7.12 (m, 2H), 7.10 – 7.07 (m, 2H), 4.94 (s, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.6, 155.4, 150.5, 143.3, 134.3, 129.6, 129.2, 128.8, 128.5, 126.3, 125.9, 121.3, 113.6, 55.1 ppm; HRMS calc'd for $C_{20}H_{17}N_2O_5^+$: 365.1132 found : 365.1135 $[M+H]^+$.

***N*-(3,5-dimethoxybenzyl)-*N*-(4-nitrophenoxy)benzamide (1p)**



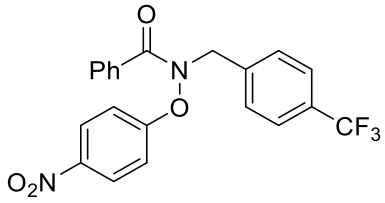
The reaction was performed following **GP1**, compound **1p** was obtained as colorless oil (21%, over three steps); R_f = 0.45 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 – 8.15 (m, 2H), 7.62 – 7.60 (m, 2H), 7.47 – 7.43 (m, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.09 – 7.05 (m, 2H), 6.47 (d, *J* = 2.4 Hz, 2H), 6.40 (t, *J* = 2.4 Hz, 1H), 4.95 (s, 2H), 3.74 (s, 6H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.9, 162.7, 161.1, 143.4, 136.9, 132.9, 131.7, 128.4, 128.0, 126.1, 113.8, 106.7, 100.0, 55.4, 53.5 ppm; HRMS calc'd for $C_{22}H_{21}N_2O_6^+$: 409.1394 found : 409.1392 $[M+H]^+$.

_N_-(4-nitrophenoxy)-_N_-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)benzamide (**1q**)



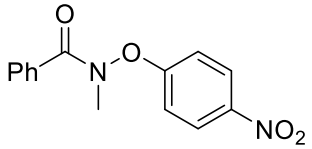
The reaction was performed following **GP1**, compound **1q** was obtained as white solid (17%, over three steps); m.p. = 125 – 127 °C; R_f = 0.62 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 – 8.15 (m, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.59 – 7.57 (m, 2H), 7.47 – 7.42 (m, 1H), 7.36 – 7.32 (m, 4H), 7.06 – 7.02 (m, 2H), 5.03 (s, 2H), 1.34 (s, 12H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.0, 162.6, 143.4, 137.6, 135.2, 132.9, 131.7, 128.4, 128.1, 128.0, 126.1, 113.8, 84.0, 53.4, 24.9 ppm (one resonance was not observed due to overlapping peaks); HRMS calc'd for $C_{26}H_{28}BN_2O_6^+$: 475.2035 found : 475.2036 $[M+H]^+$.

_N_-(4-nitrophenoxy)-_N_-(4-(trifluoromethyl)benzyl)benzamide (1r)



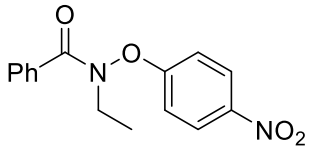
The reaction was performed following **GP1**, compound **1r** was obtained as yellow oil (24%, over three steps); R_f = 0.62 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 – 8.20 (m, 2H), 7.63 – 7.57 (m, 4H), 7.49 – 7.44 (m, 3H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.12 – 7.08 (m, 2H), 5.08 (s, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.1, 162.3, 143.6, 138.6, 132.4, 131.9, 130.4 (q, $J_{C\text{-}F}$ = 32.4 Hz), 129.1, 128.5, 128.0, 126.3, 125.8 (q, $J_{C\text{-}F}$ = 3.8 Hz), 123.9 (q, $J_{C\text{-}F}$ = 270.7 Hz), 113.8, 52.5 ppm; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.6 ppm; HRMS calc'd for $C_{21}H_{16}F_3N_2O_4^+$: 417.1057 found: 417.1058 $[M+H]^+$.

_N_-methyl-_N_-(4-nitrophenoxy)benzamide (1s)



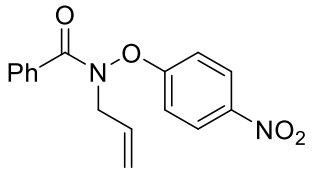
The ^{1}H and ^{13}C data for this compound match the literature data[1].

_N_-ethyl-_N_-(4-nitrophenoxy)benzamide (1t)



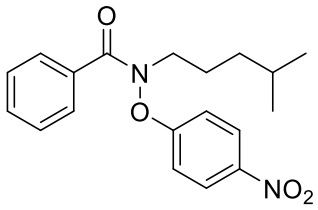
The reaction was performed following **GP1**, compound **1t** was obtained as colorless solid (32%, over three steps); m.p. = 107 – 109 °C; R_f = 0.62 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 (d, *J* = 9.2 Hz, 2H), 7.60 – 7.57 (m, 2H), 7.49 – 7.44 (m, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 9.2 Hz, 2H), 3.91 – 3.89 (m, 2H), 1.33 (t, *J* = 6.8 Hz, 3H) ppm. ^{13}C NMR (100 MHz, Chloroform-d) δ 172.2, 163.1, 143.3, 133.2, 131.6, 128.4, 127.8, 126.2, 113.7, 45.4, 12.0 ppm. HRMS calc'd for $C_{15}H_{15}N_2O_4^+$: 287.1026 found: 287.1031 $[M+H]^+$.

***N*-allyl-*N*-(4-nitrophenoxy)benzamide (1u)**



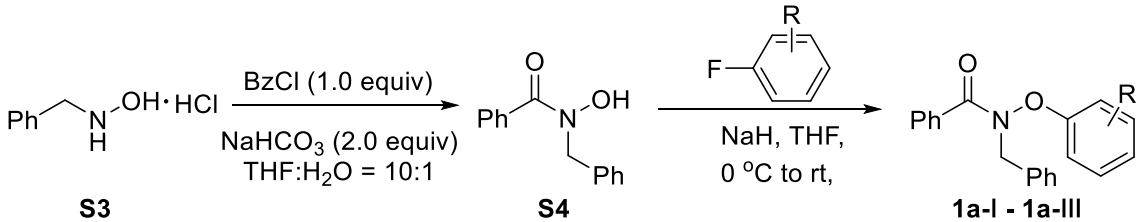
The reaction was performed following **GP1**, compound **1u** was obtained as colorless solid (42%, over three steps); m.p. = 90 – 92 °C; R_f = 0.42 (hexanes: ethyl acetate = 4:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 – 8.08 (m, 2H), 7.52 – 7.49 (m, 2H), 7.37 – 7.33 (m, 1H), 7.27 – 7.23 (m, 2H), 7.07 – 7.03 (m, 2H), 5.86 (ddt, *J* = 16.4, 10.4, 6.0 Hz, 1H), 5.20 – 5.14 (m, 2H), 4.32 (d, *J* = 6.0 Hz, 2H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.2, 162.9, 143.3, 132.9, 131.7, 130.6, 128.4, 127.9, 126.1, 120.1, 113.8, 53.0 ppm. HRMS calc'd for $C_{16}H_{15}N_2O_4^+$: 299.1026 found: 299.1031 $[M+H]^+$.

***N*-(4-methylpentyl)-*N*-(4-nitrophenoxy)benzamide (1v)**



Amide **1v** was prepared according to the literature procedure.[1]

General procedure for the synthesis of different *N*-aryloxyamides– GP2

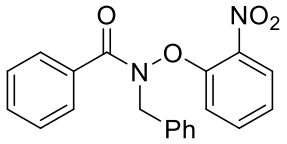


Following the literature procedure[1] with slight modifications, to a stirring suspension of *N*-Benzylhydroxylamine hydrochloride **S3** (1.1 equiv) and $NaHCO_3$ (2.0 equiv) in THF/H_2O (10:1, 0.5 M) was added Benzoyl chloride (1.0 equiv) dropwise over 20 min. The reaction mixture was allowed to stir for 1 h, and was then diluted with H_2O. The

mixture was extracted with ethyl acetate (3 X 20 mL). The organic layers were combined, washed with saturated brine solution (100 mL), dried over Na_2SO_4, and filtered. The filtrate was concentrated in *vacuo*. The resultant solid was submitted to the next step without further purification.

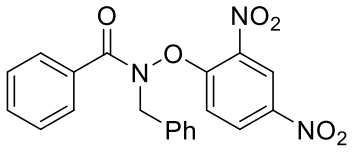
In a dry Schlenk tube equipped with a stirring bar the *N*-benzyl-*N*-hydroxybenzamide **S4** (1.0 equiv) was added, dissolved in anhydrous THF (0.2 M), cooled to 0 °C and stirred for 15 minutes. NaH (1.1 equiv, 60%) was added and the reaction mixture was stirred for 1 hour. Fluorobenzene derivatives (1.1 equiv) was added portion wise and the reaction mixture was allowed to warm up to room temperature overnight. The mixture was diluted with H_2O and ethyl acetate, the layers were separated and the aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with saturated brine solution, dried (Na_2SO_4), filtered and evaporated. The product was purified by column chromatography on silica gel eluting with (petrol: ethyl acetate = 8:1) to give **1a-I - 1a-III**.

_N_-benzyl-_N_-(2-nitrophenoxy)benzamide (1a-I)



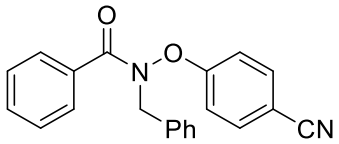
The reaction was performed following **GP2**, compound **1a-I** was obtained as colorless solid (78%, over two steps); m.p. = 84 – 86 °C; R_f = 0.40 (hexanes:ethyl acetate = 5:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.57 – 7.55 (m, 2H), 7.33 – 7.26 (m, 4H), 7.23 – 7.12 (m, 6H), 6.94 – 6.89 (m, 1H), 4.91 (s, 2H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.8, 151.7, 137.6, 134.61, 134.58, 132.8, 131.6, 129.0, 128.7, 128.4, 128.3, 128.2, 126.0, 122.9, 115.0, 54.0 ppm. HRMS calc'd for $C_{20}H_{17}N_2O_4^+$: 349.1183, found: 349.1189 $[M+H]^+$.

_N_-benzyl-_N_-(2,4-dinitrophenoxy)benzamide (1a-II)



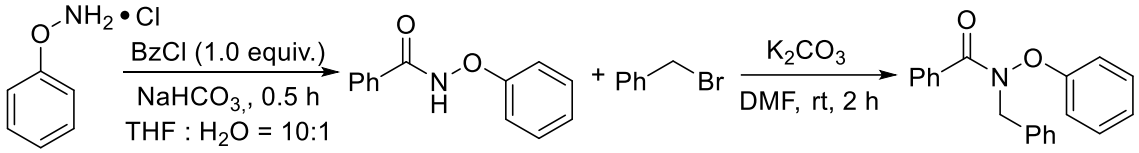
The reaction was performed following **GP2**, compound **1a-II** was obtained as colorless solid (82%, over two steps); m.p. = 104 – 106 °C; R_f = 0.40 (hexanes:ethyl acetate = 5:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.58 (d, *J* = 2.8 Hz, 1H), 8.12 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.57 – 7.55 (m, 2H), 7.41 – 7.37 (m, 1H), 7.32 – 7.28 (m, 3H), 7.25 – 7.22 (m, 2H), 7.20 – 7.15 (m, 3H), 4.92 (s, 2H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.2, 156.6, 141.7, 136.4, 133.8, 132.3, 129.14, 129.09, 128.9, 128.8, 128.7, 128.1, 122.1, 116.0, 56.1 ppm (one resonance was not observed due to overlapping peaks). HRMS calc'd for $C_{20}H_{16}N_3O_6^+$: 394.1034, found: 394.1043 $[M+H]^+$.

_N_-benzyl-_N_-(4-cyanophenoxy)benzamide (1a-III)



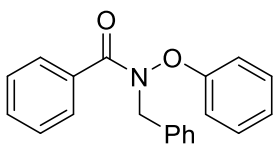
The reaction was performed following **GP2**, compound **1a-III** was obtained as colorless oil (42%, over two steps); R_f = 0.40 (hexanes:ethyl acetate = 5:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.48 (m, 4H), 7.38 – 7.34 (m, 1H), 7.28 – 7.24 (m, 7H), 6.98 – 6.94 (m, 2H), 4.92 (s, 2H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.9, 161.1, 134.7, 134.3, 133.0, 131.6, 128.9, 128.8, 128.33, 128.30, 128.0, 118.5, 114.4, 106.8, 53.1 ppm. HRMS calc'd for $C_{21}H_{17}N_2O_2^+$: 329.1285, found: 329.1286 $[M+H]^+$.

Synthesis of 1a-I from _O_-Phenylhydroxylamine Hydrochloride according to GP1.



S5 **1a-IV**

_N_-benzyl-_N_-phenoxybenzamide (1a-IV)



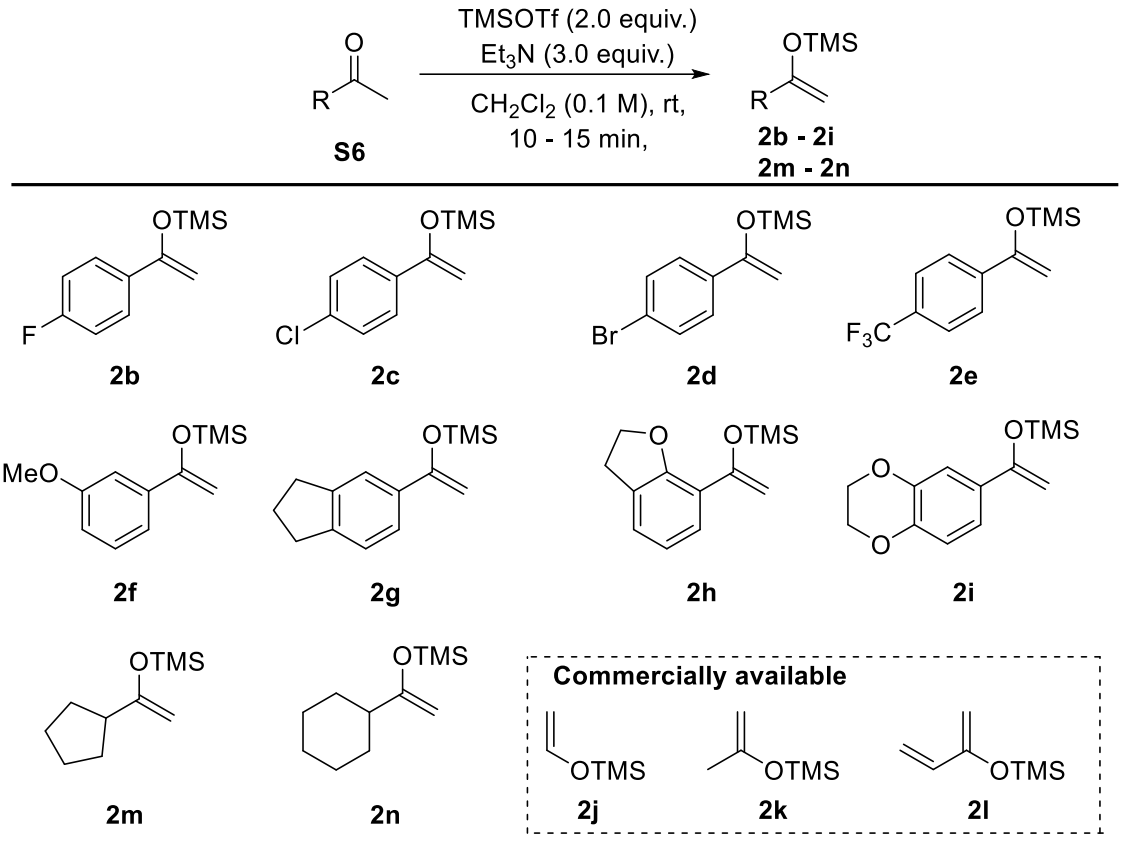
The reaction was performed following **GP1**, compound **1a-IV** was obtained as

colorless solid (42%, over three steps); m.p. = 92 – 94 °C; R_f = 0.32 (hexanes:ethyl acetate = 8:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.53 (m, 2H), 7.28 – 7.22 (m, 4H), 7.21 – 7.15 (m, 6H), 6.93 (t, *J* = 7.2 Hz, 1H), 6.89 – 6.85 (m, 2H), 4.90 (s, 2H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.4, 157.4, 135.6, 133.4, 131.2, 129.9, 128.9, 128.6, 128.3, 128.1, 128.0, 123.4, 113.8, 51.3 ppm. HRMS calc'd for $C_{20}H_{18}NO_2^+$: 304.1332, found: 304.1341 $[M+H]^+$.

General procedure for preparation of silyl enol ethers

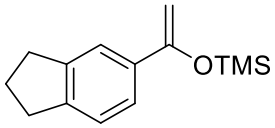
General procedure for the synthesis of (hetero)aryl silyl enol ethers (2b-2k) from ketones (S6)– GP3

An oven-dried flask was charged with ketone precursor (1 mmol) dissolved in anhydrous CH_2Cl_2 (25 mL) and the resulting mixture was stirred for 5 minutes under nitrogen atmosphere. Anhydrous triethylamine (3 mmol) and trimethylsilyl trifluoromethanesulfonate (2 mmol) were sequentially added to the mixture dropwise for 5 min, and the reaction was stirred for 10-15 min at room temperature. The reaction was quenched by addition of sat. aq. of NH_4Cl (50 mL) and the crude mixture was extracted with pentane (50 mL x 3). The combined organic layers were washed with H_2O (50 mL) and sat. aq. NH_4Cl (50 mL), dried over Na_2SO_4 and filtered. Evaporation of the solvents under reduced pressure delivered the desired silyl enol ether product. Unless otherwise stated, these materials were used in the photochemical protocol without any further purification.



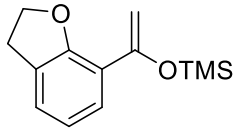
Note: Silyl enol ethers (**2b**)[3], (**2c**)[3], (**2d**)[3], (**2e**)[3], (**2f**)[3], (**2n**)[4] were prepared following reported procedures. Compounds **2j**-**2l** were purchased from Bidepharm and directly used.

((1-(2,3-dihydro-1*H*-inden-5-yl)vinyl)oxy)trimethylsilane (2g)



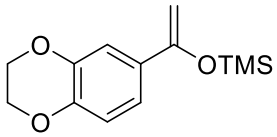
The reaction was performed following **GP3**, compound **2g** was obtained (95%, colorless oil); R_f = 0.72 (hexanes: ethyl acetate = 20:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 (s, 1H), 7.23 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 4.72 (d, *J* = 1.6 Hz, 1H), 4.22 (d, *J* = 1.6 Hz, 1H), 2.77 – 2.72 (m, 4H), 1.93 (h, *J* = 7.6 Hz, 2H), 0.12 (s, 9H) ppm. ^{13}C NMR (100 MHz, Chloroform-d) δ 156.0, 144.4, 144.0, 135.6, 123.7, 123.3, 121.0, 90.2, 32.7, 32.5, 25.4, 0.01 ppm. HRMS calc'd for $C_{14}H_{21}OSi^+$: 233.1356 found: 233.1352 $[M+H]^+$.

((1-(2,3-dihydrobenzofuran-7-yl)vinyl)oxy)trimethylsilane (2h)



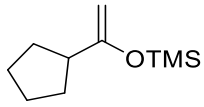
The reaction was performed following **GP3**, compound **2h** was obtained (97%, colorless oil); R_f = 0.68 (hexanes: ethyl acetate = 20:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.31 (m, 1H), 7.05 (dd, *J* = 7.2, 1.2 Hz, 1H), 6.77 (t, *J* = 7.2, 1H), 5.31 (d, *J* = 0.9 Hz, 1H), 4.59 – 4.54 (m, 3H), 3.17 – 3.12 (m, 2H), 0.20 (s, 9H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 157.0, 151.4, 127.2, 125.5, 124.2, 120.2, 95.6, 71.0, 29.3, 0.0.07 ppm (one resonance was not observed due to overlapping peaks). HRMS calc'd for $C_{13}H_{19}O_2Si^+$: 235.1149 found: 235.1142 $[M+H]^+$.

((1-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)vinyl)oxy)trimethylsilane (2i)



The reaction was performed following **GP3**, compound **2i** was obtained (96%, colorless oil); R_f = 0.66 (hexanes: ethyl acetate = 20:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.04 – 7.01 (m, 2H), 6.73 (d, *J* = 8.4 Hz, 1H), 4.71 (d, *J* = 1.6 Hz, 1H), 4.26 (d, *J* = 1.6 Hz, 1H), 4.18 (s, 4H), 0.19 (s, 9H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.0, 143.6, 142.9, 131.2, 118.5, 116.7, 114.2, 89.7, 64.4, 64.2, 0.006 ppm. HRMS calc'd for $C_{13}H_{19}O_3Si^+$: 251.1098 found: 251.1098 $[M+H]^+$.

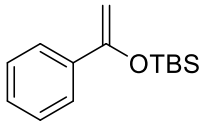
((1-cyclopentylvinyl)oxy)trimethylsilane (2m)



The reaction was performed following **GP3**, compound **2m** was obtained (96%, colorless oil); R_f = 0.76 (hexanes: ethyl acetate = 20:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.87 (s, 1H), 3.77 (s, 1H), 2.22 (p, *J* = 8.0 Hz, 1H), 2.00 – 1.92 (m, 1H), 1.47 – 1.39 (m, 3H), 1.36 – 1.26 (m, 4H), -0.001 (s, 9H) ppm. ^{13}C NMR (100 MHz,

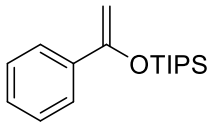
Chloroform-*d*) δ 162.3, 87.7, 45.85, 30.5, 25.3, 0.01 ppm. HRMS calc'd for $C_{10}H_{21}OSi^+$: 185.1356 found: 185.1358 $[M+H]^+$.

tert-butyldimethyl((1-phenylvinyl)oxy)silane (2a-I)



Silyl enol ether **2a-I** was prepared according to the literature procedure.[5]

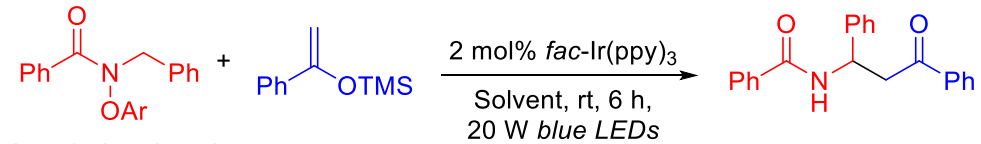
triisopropyl((1-phenylvinyl)oxy)silane (2a-II)



Silyl enol ether **2a-II** was prepared according to the literature procedure.[6]

Detailed reaction optimizations

Table S1. Screening of solvent



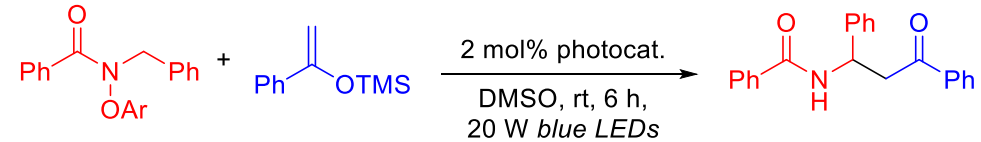
entry[a]	Solvent	yield[b] (%)
1	DMF	40
2	DMSO	68
3	CH_3CN	27
4	DCM	0
5	DCE	12
6	THF	18
7	PhCl	20
8	$PhCF_3$	trace

9	EtOH	0

[a]Unless otherwise noted, reactions were carried out with **1a** (52.2 mg, 0.15 mmol), **2a** (19.2 mg, 0.1 mmol), *fac*-Ir(ppy)$_3$ (2% mol, 1.3 mg) and in solvent (1.0 mL) at rt under 20 W blue LEDs for 6 h. [b]Assay yields determined by ^{1}H NMR spectroscopy of the crude reaction mixtures using CH_2Br_2 as an internal standard.

As shown in Table *S1*, among the solvent tested, DMSO gave the best results (68% yield), and was thus selected for further studies.

Table S2. Screening of photocatalysts



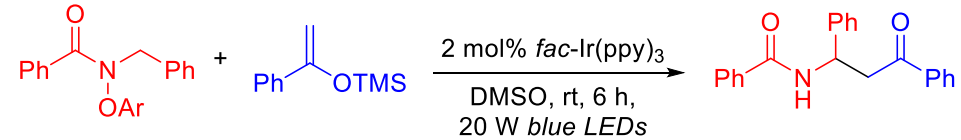
Ar = 4-nitrophenyl
1a (0.15 mmol) **2a** (0.1 mmol) **3aa**

entry[a]	Photocat.	yield[b] (%)
1	*fac*-Ir(ppy)$_3$	68
2	4CzIPN	13
3	[Ir(dtbbpy)(ppy)$_2$][PF$_6$]	31
4	[Ir(ppy)$_2$(bpy)]PF$_6$	26
5	Eosin Y	18

[a]Unless otherwise noted, reactions were carried out with **1a** (52.2 mg, 0.15 mmol), **2a** (19.2 mg, 0.1 mmol), photocatalysts (2% mol, 1.3 mg) and in DMSO (1.0 mL) at rt under 20 W blue LEDs for 6 h. [b]Assay yields determined by ^{1}H NMR spectroscopy of the crude reaction mixtures using CH_2Br_2 as an internal standard.

As shown in Table *S2*, among the photocatalysts tested, *fac*-Ir(ppy)$_3$ gave the best results (68% yield) and was thus selected for further studies.

Table S3. Screening of ratio of 1a/2a



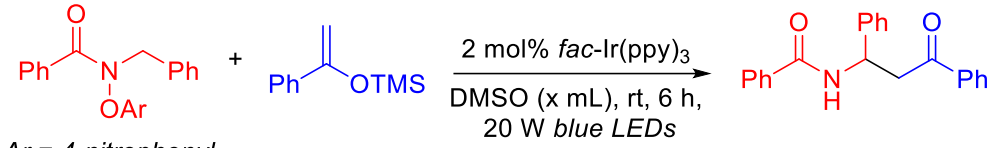
Ar = 4-nitrophenyl
1a (x. equiv.) **2a** (y. equiv.) **3aa**

entry[a]	**1a** (x equiv.)	**2a** (y equiv.)	yield[b] (%)
1	1.0	1.5	68
2	1.5	1.0	94 (90) [c]

[a]Unless otherwise noted, reactions were carried out with **1a** (x. equiv.), **2a** (y. equiv.), *fac*-Ir(ppy)$_3$ (2% mol, 1.3 mg) and in DMSO (1.0 mL) at rt under 20 W blue LEDs for 6 h. [b]Assay yields determined by ^{1}H NMR spectroscopy of the crude reaction mixtures using CH_2Br_2 as an internal standard. [c]Isolated yield after chromatographic purification.

As shown in Table *S3*, among the ratio of **1a**/**2a** tested, the ratio of **1a** and **2a** from 1:1.5 to 1.5:1 gave the best results (94% yield) and was thus selected for further studies.

Table S4. Screening of concentration



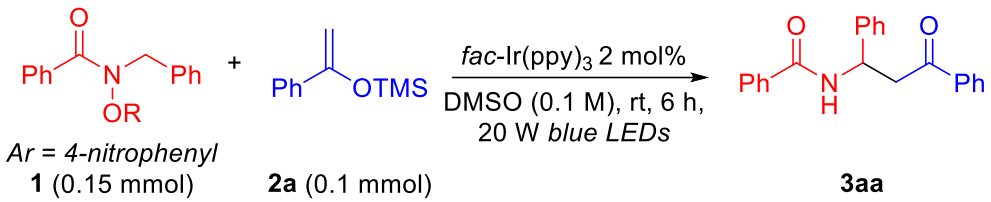
Ar = 4-nitrophenyl
1a (0.15 mmol) **2a** (0.1 mmol) **3aa**

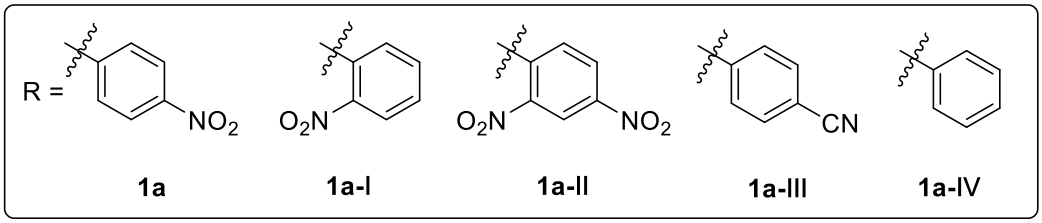
entry[a]	Solvent volume (x mL)	yield[b] (%)
1	1	94
2	0.5	86
3	2	77

[a]Unless otherwise noted, reactions were carried out with **1a** (52.2 mg, 0.15 mmol), **2a** (19.2 mg, 0.10 mmol), *fac*-Ir(ppy)$_3$ (2% mol, 1.3 mg) and in DMSO (x mL) at rt under 20 W blue LEDs for 6 h. [b]Assay yields determined by ^{1}H NMR spectroscopy of the crude reaction mixtures using CH_2Br_2 as an internal standard.

As shown in Table *S4*, among the concentration tested, DMSO (1 mL, 0.1 M) gave the best results (94% yield) and was thus selected for further studies.

Table S5. Screen of the leaving groups of the Amide

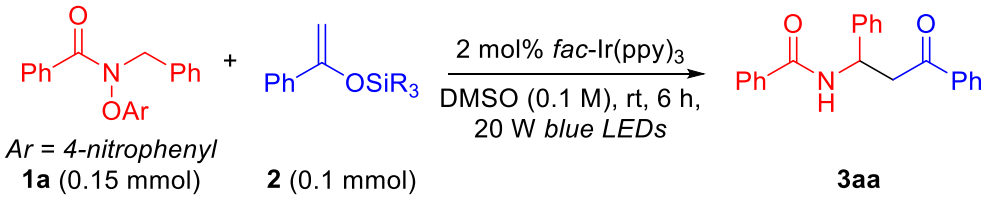


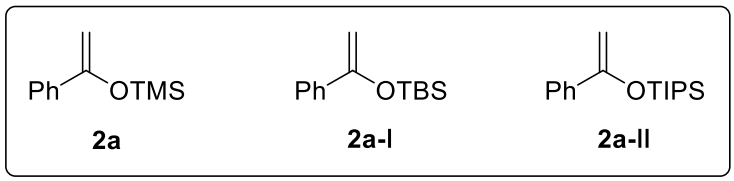


entry[a]	amides	yield[b] (%)
1	**1a**	**94**
2	**1a-I**	no
3	**1a-II**	51
4	**1a-III**	trace
5	**1a-IV**	trace

[a]Unless otherwise noted, reactions were carried out with **1** (0.15 mmol), **2a** (19.2 mg, 0.10 mmol), *fac*-Ir(ppy)$_3$ (2 mol%, 1.3 mg) and in DMSO (1 mL) at rt under 20 W blue LEDs for 6 h. [b]Assay yields determined by ^{1}H NMR spectroscopy of the crude reaction mixtures using CH_2Br_2 as an internal standard.

Table S6. Different types of silyl enol ethers



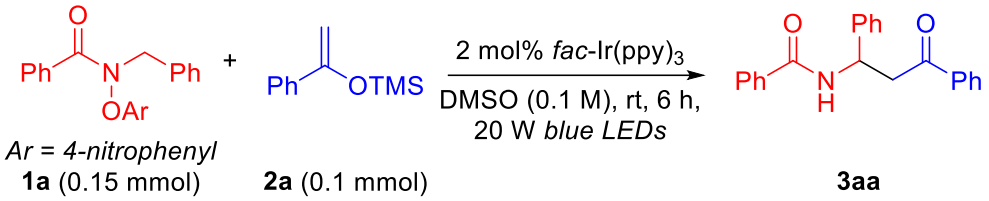


entry[a]	silyl enol ethers	yield[b] (%)
1	**2a**	**94**
2	**2a-I**	30

3	**2a-II**	trace

[a]Unless otherwise noted, reactions were carried out with **1a** (52.2 mg, 0.15 mmol), **2** (0.10 mmol), *fac*-Ir(ppy)$_3$ (2 mol%, 1.3 mg) and in DMSO (1 mL) at rt under 20 W blue LEDs for 6 h. [b]Assay yields determined by ^{1}H NMR spectroscopy of the crude reaction mixtures using CH_2Br_2 as an internal standard.

Table S7. Controlled experiment



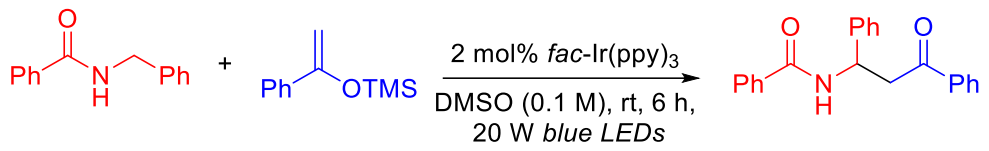
Ar = 4-nitrophenyl
1a (0.15 mmol) **2a** (0.1 mmol) **3aa**

entry[a]	Controlled experiment	yield[b] (%)
1	without light	0
2	without *fac*-Ir(ppy)$_3$	0

[a]Unless otherwise noted, reactions were carried out with **1a** (52.2 mg, 0.15 mmol), **2a** (19.2 mg, 0.10 mmol), *fac*-Ir(ppy)$_3$ (2% mol, 1.3 mg) and in DMSO (1 mL) at rt under 20 W blue LEDs for 6 h. [b]Assay yields determined by ^{1}H NMR spectroscopy of the crude reaction mixtures using CH_2Br_2 as an internal standard.

As shown in Table *S7*, control experiments showed that the photocatalyst and light irradiation are necessary for the success of this transformation.

Table S8. Using *N*-benzylbenzamide **1a'** and silyl enol ether **2a** under the standard reaction conditions.

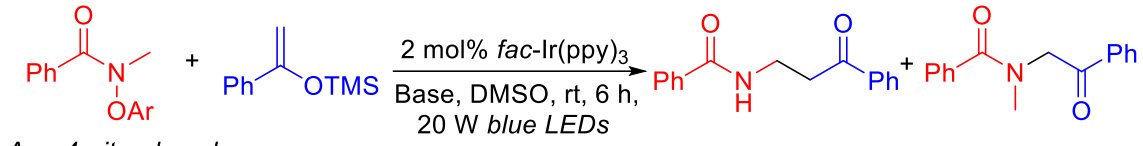


1a' (0.15 mmol) **2a** (0.1 mmol) **3aa**, not detected

Not: The reaction was carried out with **1a'** (31.7 mg, 0.15 mmol), **2a** (19.2 mg, 0.10 mmol), *fac*-Ir(ppy)$_3$ (2% mol, 1.3 mg) and in DMSO (1 mL) at rt under 20 W blue LEDs for 6 h.

As shown in Table *S8*, we did not observe the formation of the coupling product **3aa**.

Table S9. Screening of base using *N*-methylamide 1s



Ar = 4-nitrophenyl

1s (0.15 mmol) **2a** (0.1 mmol) **3sa** **3sa'**

entry[a]	Base (x. equiv.)	**3sa**/**3sa'** [b] (%)
1	DIPEA (3.0)	0/42
2	Et_3N (3.0)	13/28
3	DBU (3.0)	0/0
4	2,6-lutidine (3.0)	0/80
5	NaO^tBu (3.0)	0/0
6	LiO^tBu (3.0)	0/0
7	Na_2CO_3 (3.0)	0/0
8	$NaHCO_3$ (3.0)	50/13
9	Na_2HPO_4 (3.0)	24/18
10	NaH_2PO_4 (3.0)	Trace/20
11	K_2CO_3 (3.0)	0/0
12	$KHCO_3$ (3.0)	18/7
13	K_2HPO_4 (3.0)	23/10
14	Cs_2CO_3 (3.0)	0/32
15	$NaHCO_3$ (1.5)	44/12
16	$NaHCO_3$ (4.5)	65/25
17	$NaHCO_3$ (6.0)	44/12

[a]Unless otherwise noted, reactions were carried out with **1s** (40.81 mg, 0.15 mmol), **2a** (19.21 mg, 0.1 mmol), photocatalysts (2% mol, 1.3 mg) and in DMSO (1.0 mL) at rt under 20 W blue LEDs for 6 h. [b]Assay yields determined by ^1H NMR spectroscopy of the crude reaction mixtures using CH_2Br_2 as an internal standard.

As shown in Table *S9*, among the base tested, $NaHCO_3$ (4.5 equiv.) gave the best results (65% yield).

General procedure for the synthesis of *β*-aminoketone derivatives–GP4

An oven-dried 10 mL reaction vial equipped with a stir bar was charged with amide **1** (1.5 equiv., 0.3 mmol) and *fac*-Ir(ppy)$_3$ (0.004 mmol, 2.6 mg) under a nitrogen atmosphere in a glove box. A solution of silyl enol ether **2** (1.0 equiv., 0.2 mmol) in 2.0 mL dry DMSO was added by a "Eppendorf" brand 1000 µL pipettor to the reaction vial. The vial was capped, removed from the glove box, and stirred for 6 h in front of 20 W blue LEDs irradiation. After the reaction period, the lights were turned off, the reaction mixture was opened to air and quenched with three drops of H_2O. The aqueous layer was extracted with ethyl acetate (3 X 15 mL) and the combined organic layers were washed with saturated brine solution, dried (Na_2SO_4), filtered and evaporated. The product was purified by column chromatography on silica gel to afford the corresponding product.

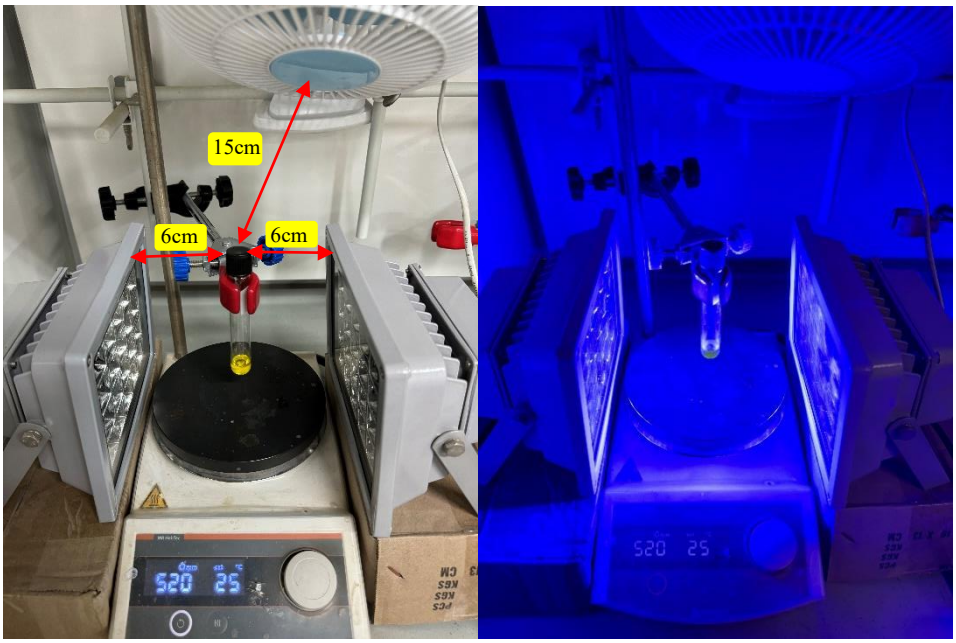
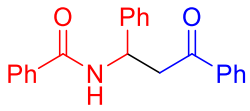


Figure S1. Reaction setup

The reaction was set up as shown in Fig. S1. The reaction was carried out on a magnetic stirrer with a distance of 6 cm between the reaction vials and the LED lamps. To counteract the heat generated between the two LED lamps, the fan was placed at a distance of 15 cm from the reaction vials. Irradiation was performed at 25 ^oC.

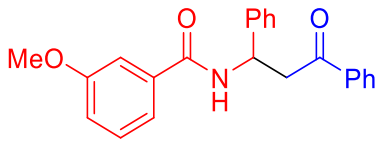
***N*-(3-oxo-1,3-diphenylpropyl)benzamide (3aa)**



The reaction was performed following the **GP4** with *N*-benzyl-*N*-(4-nitrophenoxy)benzamide **1a** (104.5 mg, 0.3 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (38.5 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3aa** (59.3 mg, 90%) as yellow solid.

m.p. = 147 – 149 °C; R_f = 0.33 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.84 (m, 2H), 7.78 – 7.76 (m, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.40 – 7.35 (m, 4H), 7.33 (d, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 2H), 7.18 – 7.14 (m, 1H), 5.70 (dt, *J* = 8.0, 5.6 Hz, 1H), 3.82 (dd, *J* = 16.8, 4.8 Hz, 1H), 3.46 (dd, *J* = 16.8, 5.6 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ 198.2, 165.7, 139.9, 135.6, 133.2, 132.6, 130.6, 127.7, 127.7, 127.6, 127.2, 126.5, 126.0, 125.5, 49.3, 41.9 ppm; HRMS calc'd for $C_{22}H_{20}NO_2^+$: 330.1489 found: 330.1491 $[M+H]^+$.

3-methoxy-*N*-(3-oxo-1,3-diphenylpropyl)benzamide (3ba)

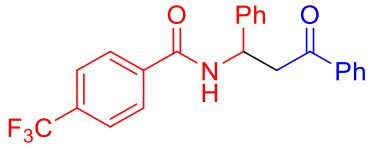


The reaction was performed following the **GP4** with *N*-benzyl-3-methoxy-*N*-(4-nitrophenoxy)benzamide **1b** (113.5 mg, 0.3 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (38.5 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3ba** (56.1 mg, 78%) as white solid.

m.p. = 138 – 140 °C; R_f = 0.34 (hexanes: ethyl acetate = 2:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.91 (m, 2H), 7.61 – 7.55 (m, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.43 – 7.39 (m, 3H), 7.36 – 7.30 (m, 4H), 7.26 – 7.21 (m, 1H), 7.06 – 7.03 (m, 1H),

5.76 (dt, *J* = 8.0, 5.6 Hz, 1H), 3.88 (dd, *J* = 16.8, 5.2 Hz, 1H), 3.84 (s, 3H), 3.53 (dd, *J* = 16.8, 6.0 Hz, 1H) ppm (amide proton was not observed); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.1, 166.6, 159.9, 140.9, 136.7, 135.8, 133.6, 129.6, 128.8, 128.7, 128.2, 127.5, 126.5, 118.8, 117.9, 112.4, 55.5, 50.4, 43.0 ppm; HRMS calc'd for $C_{23}H_{22}NO_3^+$: 360.1594 found: 360.1599 $[M+H]^+$.

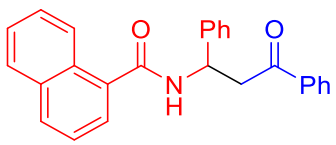
_N_-(3-oxo-1,3-diphenylpropyl)-4-(trifluoromethyl)benzamide (3ca)



The reaction was performed following the **GP4** with *N*-benzyl-*N*-(4-nitrophenoxy)-4-(trifluoromethyl)benzamide **1c** (124.9 mg, 0.3 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (38.5 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3ca** (44.5 mg, 56%) as colorless oil.

R_f = 0.47 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.83 (m, 4H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.53 – 7.49 (m, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.32 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.27 – 7.23 (m, 2H), 7.20 – 7.15 (m, 1H), 5.69 (dt, *J* = 8.0, 5.2 Hz, 1H), 3.81 (dd, *J* = 17.2, 5.2 Hz, 1H), 3.46 (dd, *J* = 17.2, 5.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 198.3, 164.4, 139.6, 136.5, 135.5, 132.8, 132.2 (q, J_{C-F} = 32.2 Hz), 127.8, 127.2, 126.6, 126.5, 125.4, 124.6 (q, J_{C-F} = 3.6 Hz), 122.7 (q, J_{C-F} = 270.7 Hz), 49.5, 41.6 ppm; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.9 ppm; HRMS calc'd for $C_{23}H_{19}F_3NO_2^+$: 398.1362 found : 398.1359 $[M+H]^+$.

_N_-(3-oxo-1,3-diphenylpropyl)-1-naphthamide (3da)

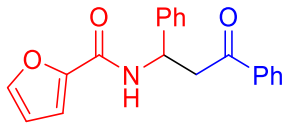


The reaction was performed following the **GP4** with *N*-benzyl-*N*-(4-nitrophenoxy)-1-

naphthamide **1d** (119.5 mg, 0.3 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (38.5 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3da** (69.8 mg, 92%) as yellow solid.

m.p. = 160 – 162 °C; R_f = 0.37 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.25 – 8.22 (m, 1H), 7.88 (d, *J* = 7.2 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.80 – 7.78 (m, 1H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.41 – 7.38 (m, 5H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 5.83 (dt, *J* = 8.4, 6.0 Hz, 1H), 3.82 (dd, *J* = 16.8, 5.4 Hz, 1H), 3.56 (dd, *J* = 16.8, 6.0 Hz, 1H) ppm; ^{13}C NMR (150 MHz, Chloroform-*d*) δ 197.5, 167.9, 140.1, 135.6, 133.2, 132.7, 132.6, 129.8, 129.2, 127.79, 127.76, 127.3, 127.2, 126.6, 126.1, 125.5, 125.4, 124.5, 124.0, 123.7, 49.4, 42.4 ppm; HRMS calc'd for $C_{26}H_{22}NO_2^+$: 380.1645 found : 380.1645 $[M+H]^+$.

***N*-(3-oxo-1,3-diphenylpropyl)furan-2-carboxamide (3ea)**

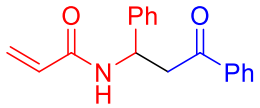


The reaction was performed following the **GP4** with *N*-benzyl-*N*-(4-nitrophenoxy)furan-2-carboxamide **1e** (101.5 mg, 0.3 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (38.5 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3ea** (40.2 mg, 63%) as white solid.

m.p. = 150 – 152 °C; R_f = 0.77 (hexanes: ethyl acetate = 1:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.84 (m, 2H), 7.51 – 7.47 (m, 2H), 7.39 – 7.37 (m, 2H), 7.36 – 7.32 (m, 2H), 7.27 – 7.23 (m, 2H), 7.19 – 7.14 (m, 1H), 7.04 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.41 (dd, *J* = 3.6, 1.6 Hz, 1H), 5.67 (dt, *J* = 8.4, 5.6 Hz, 1H), 3.80 (dd, *J* = 17.2, 5.2 Hz, 1H), 3.46 (dd, *J* = 17.2, 6.0 Hz, 1H) ppm (amide proton was not observed); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 198.4, 157.8, 147.9, 144.1, 140.7, 136.6, 133.6, 128.7, 128.2, 127.6, 126.6, 114.5, 112.2, 49.6, 43.2 ppm (one resonance was not observed due

to overlapping peaks); HRMS calc'd for $C_{20}H_{18}NO_3^+$: 320.1281 found: 320.1278 $[M+H]^+$.

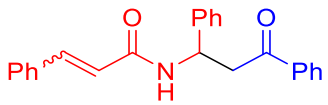
_N_-(3-oxo-1,3-diphenylpropyl)acrylamide (3fa)



The reaction was performed following the **GP4** with *N*-benzyl-*N*-(4-nitrophenoxy)acrylamide **1f** (89.5 mg, 0.3 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (38.5 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3fa** (54.2 mg, 97%) as white solid.

m.p. = 142 – 144 °C; R_f = 0.65 (hexanes: ethyl acetate = 1:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.82 (m, 2H), 7.51 – 7.46 (m, 1H), 7.39 – 7.35 (m, 2H), 7.28 – 7.21 (m, 4H), 7.17 – 7.13 (m, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.23 (dd, *J* = 17.2, 1.6 Hz, 1H), 6.07 (dd, *J* = 17.2, 10.0 Hz, 1H), 5.59 – 5.55 (m, 2H), 3.74 (dd, *J* = 17.2, 5.2 Hz, 1H), 3.39 (dd, *J* = 16.8, 6.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 198.7, 164.9, 140.7, 136.6, 133.6, 130.8, 128.8, 128.7, 128.2, 127.5, 126.9, 126.5, 50.0, 43.0 ppm; HRMS calc'd for $C_{18}H_{18}NO_2^+$: 280.1332 found: 280.1334 $[M+H]^+$.

_N_-(3-oxo-1,3-diphenylpropyl)cinnamamide (3ga)

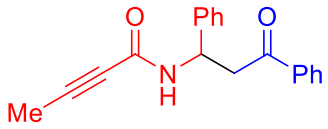


The reaction was performed following the **GP4** with (*E*)-*N*-benzyl-*N*-(4-nitrophenoxy)cinnamamide **1g** (112.3 mg, 0.3 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (38.5 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3ga** (67.5 mg, 95%) as yellow solid.

m.p. = 144 – 146 °C; R_f = 0.80 (hexanes: ethyl acetate = 1:1); *E*/*Z* = 94:6. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.85 – 7.83 (m, 1.88H), 7.77 – 7.74 (m, 0.12H), 7.56 (d, J = 15.6 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.41 – 7.34 (m, 3.76H), 7.31 – 7.25 (m, 5H), 7.22

(t, J = 7.6 Hz, 2H), 7.16 – 7.12 (m, 1H), 7.11 – 7.06 (m, 0.24H), 6.96 (d, J = 8.0 Hz, 0.94H), 6.72 (d, J = 12.4 Hz, 0.06H), 6.40 (d, J = 15.6 Hz, 0.94H), 5.95 (d, J = 12.4 Hz, 0.06H), 5.66 – 5.61 (m, 0.94H), 5.55 – 5.50 (m, 0.06H), 3.76 (dd, J = 16.8, 5.2 Hz, 0.94H), 3.58 (dd, J = 17.2, 5.2 Hz, 0.06H), 3.41 (dd, J = 17.2, 6.0 Hz, 0.94H), 3.76 (dd, J = 16.8, 5.2 Hz, 0.06H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 198.7, 165.3, 141.4, 140.9, 136.6, 134.8, 133.6, 129.7, 128.8, 128.74, 128.71, 128.2, 127.9, 127.5, 126.6, 120.7, 50.1, 43.1 ppm; HRMS calc'd for $C_{24}H_{22}NO_2^+$: 356.1645 found: 356.1642 $[M+H]^+$.

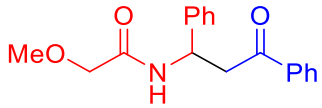
_N_-(3-oxo-1,3-diphenylpropyl)but-2-ynamide (3ha)



The reaction was performed following the **GP4** with *N*-benzyl-*N*-(4-nitrophenoxy)but-2-ynamide **1h** (93.1 mg, 0.3 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (38.5 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3ha** (52.4 mg, 90%) as yellow oil.

R_f = 0.63 (hexanes: ethyl acetate = 1:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.81 (m, 2H), 7.52 – 7.47 (m, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.22 (m, 4H), 7.18 – 7.14 (m, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 5.55 – 5.50 (m, 1H), 3.71 (dd, *J* = 17.2, 4.8 Hz, 1H), 3.39 (dd, *J* = 17.2, 6.0 Hz, 1H), 1.87 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 198.3, 152.9, 140.2, 136.5, 133.6, 128.8, 128.7, 128.1, 127.6, 126.5, 83.9, 50.0, 42.9, 3.7 ppm (one resonance was not observed due to overlapping peaks); HRMS calc'd for $C_{19}H_{18}NO_2^+$: 292.1332 found : 292.1332 $[M+H]^+$.

2-methoxy-_N_-(3-oxo-1,3-diphenylpropyl)acetamide (3ia)

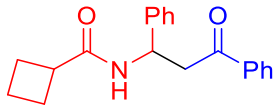


The reaction was performed following the **GP4** with *N*-benzyl-2-methoxy-*N*-(4-

nitrophenoxy)acetamide **1i** (94.9 mg, 0.3 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (38.5 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3ia** (56.5 mg, 95%) as colorless oil.

R_f = 0.49 (hexanes:ethyl acetate = 1:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.83 (m, 2H), 7.50 – 7.46 (m, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.30 – 7.22 (m, 4H), 7.19 – 7.14 (m, 1H), 5.58 – 5.53 (m, 1H), 3.84 (s, 2H), 3.68 (dd, *J* = 16.8, 5.6 Hz, 1H), 3.40 (dd, *J* = 16.8, 6.4 Hz, 1H), 3.34 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.8, 169.0, 140.8, 136.7, 133.5, 128.73, 128.71, 128.1, 127.6, 126.6, 72.0, 59.3, 49.3, 43.6 ppm; HRMS calc'd for $C_{18}H_{20}NO_3^+$: 298.1438 found: 298.1434 $[M+H]^+$.

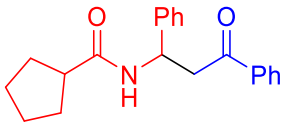
***N*-(3-oxo-1,3-diphenylpropyl)cyclobutanecarboxamide (3ja)**



The reaction was performed following the **GP4** with *N*-benzyl-*N*-(4-nitrophenoxy)cyclobutanecarboxamide **1j** (97.9 mg, 0.3 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (38.5 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3ja** (36.9 mg, 60%) as white solid.

m.p. = 155 – 157 °C; R_f = 0.80 (hexanes: ethyl acetate = 1:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.89 (m, 2H), 7.58 – 7.53 (m, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.33 – 7.27 (m, 4H), 7.24 – 7.20 (m, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 5.55 (dt, *J* = 8.0, 5.6 Hz, 1H), 3.75 (dd, *J* = 16.8, 5.2 Hz, 1H), 3.41 (dd, *J* = 16.8, 6.0 Hz, 1H), 3.08 – 3.00 (m, 1H), 2.32 – 2.22 (m, 2H), 2.19 – 2.10 (m, 2H), 2.00 – 1.91 (m, 1H), 1.89 – 1.83 (m, 1H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 198.7, 174.4, 141.1, 136.7, 133.5, 128.7, 128.7, 128.2, 127.4, 126.5, 49.8, 43.3, 40.0, 25.3, 18.2 ppm; HRMS calc'd for $C_{20}H_{22}NO_2^+$: 308.1645 found: 308.1643 $[M+H]^+$.

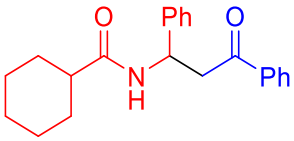
***N*-(3-oxo-1,3-diphenylpropyl)cyclopentanecarboxamide (3ka)**



The reaction was performed following the **GP4** with *N*-benzyl-*N*-(4-nitrophenoxy)cyclopentanecarboxamide **1k** (102.1 mg, 0.3 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (38.5 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3ka** (42.4 mg, 66%) as colorless oil.

R_f = 0.33 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.26 – 7.20 (m, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 5.56 (dt, *J* = 8.0, 5.6 Hz, 1H), 3.75 (dd, *J* = 16.8, 5.2 Hz, 1H), 3.42 (dd, *J* = 16.8, 6.0 Hz, 1H), 2.58 (p, *J* = 8.0 Hz, 1H), 1.91 – 1.68 (m, 6H), 1.62 – 1.51 (m, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 198.8, 175.7, 141.2, 136.7, 133.5, 128.74, 128.68, 128.2, 127.4, 126.5, 49.8, 45.9, 43.3, 30.3, 25.9 ppm; HRMS calc'd for $C_{21}H_{24}NO_2^+$: 322.1802 found: 322.1801 $[M+H]^+$.

***N*-(3-oxo-1,3-diphenylpropyl)cyclohexanecarboxamide (3la)**

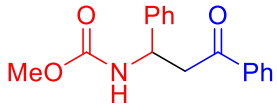


The reaction was performed following the **GP4** with *N*-benzyl-*N*-(4-nitrophenoxy)cyclohexanecarboxamide **1l** (106.3 mg, 0.3 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (38.5 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3la** (45.6 mg, 68%) as colorless oil.

R_f = 0.42 (hexanes: ethyl acetate = 2:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 6.8 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.20 (m, 4H), 7.17 – 7.13 (m, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 5.48 (dt, *J* = 8.0, 5.6 Hz, 1H), 3.69 (dd, *J* = 16.8, 5.2 Hz, 1H), 3.34 (dd, *J* = 16.8, 6.0 Hz, 1H), 2.06 (tt, *J* = 11.6, 3.6 Hz, 1H), 1.84 – 1.79 (m, 2H), 1.74 – 1.70 (m, 2H), 1.61 – 1.58 (m, 2H), 1.42 – 1.32 (m, 2H), 1.25 –

1.11 (m, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.9, 174.5, 140.1, 135.6, 132.5, 127.7, 127.6, 127.1, 126.3, 125.4, 48.5, 44.5, 42.1, 28.63, 28.57, 24.7 ppm; HRMS calc'd for $C_{22}H_{26}NO_2^+$: 336.1958 found: 336.1955 $[M+H]^+$.

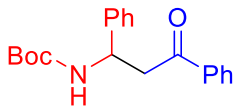
Methyl (3-oxo-1,3-diphenylpropyl)carbamate (3ma)



The reaction was performed following the **GP4** with methyl benzyl(4-nitrophenoxy)carbamate **1m** (90.7 mg, 0.3 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (38.5 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3ma** (53.3 mg, 94%) as white solid.

m.p. = 118 – 120 °C; R_f = 0.42 (hexanes: ethyl acetate = 2:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.88 (m, 2H), 7.57 – 7.53 (m, 1H), 7.45 – 7.41 (m, 2H), 7.36 – 7.28 (m, 4H), 7.25 – 7.21 (m, 1H), 5.84 (s, 1H), 5.31 (dt, *J* = 8.0, 6.0 Hz, 1H), 3.70 – 3.63 (m, 4H), 3.44 (dd, *J* = 16.8, 6.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 198.0, 156.4, 141.4, 136.6, 133.5, 128.7, 128.7, 128.1, 127.5, 126.4, 52.2, 51.8, 44.0 ppm; HRMS calc'd for $C_{17}H_{18}NO_3^+$: 284.1281 found: 284.1286 $[M+H]^+$.

***tert*-butyl (3-oxo-1,3-diphenylpropyl)carbamate (3na)**

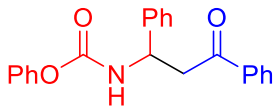


The reaction was performed following the **GP4** with *tert*-butyl benzyl(4-nitrophenoxy)carbamate **1n** (103.3 mg, 0.3 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (38.5 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3na** (56.0 mg, 86%) as white solid.

m.p. = 140 – 142 °C; R_f = 0.68 (hexanes: ethyl acetate = 2:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.6 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.20 (m, 4H), 7.13 (t, *J* = 7.2 Hz, 1H), 5.55 (s, 1H), 5.20 – 5.15 (m, 1H),

3.59 – 3.55 (m, 1H), 3.34 (dd, *J* = 16.8, 6.0 Hz, 1H), 1.33 (s, 9H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 198.1, 155.3, 141.8, 136.7, 133.4, 128.7, 128.6, 128.1, 127.3, 126.4, 79.7, 51.4, 44.3, 28.4 ppm; HRMS calc'd for $C_{20}H_{24}NO_3^+$: 326.1751 found: 326.1749 $[M+H]^+$.

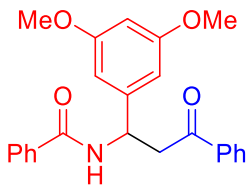
Phenyl (3-oxo-1,3-diphenylpropyl)carbamate (3oa)



The reaction was performed following the **GP4** with phenyl benzyl(4-nitrophenoxy)carbamate **1o** (109.3 mg, 0.3 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (38.5 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3oa** (60.8 mg, 88%) as colorless oil.

R_f = 0.57 (hexanes: ethyl acetate = 2:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.82 (m, 2H), 7.50 – 7.46 (m, 1H), 7.38 – 7.31 (m, 4H), 7.27 – 7.22 (m, 4H), 7.20 – 7.15 (m, 1H), 7.11 – 7.07 (m, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.17 (d, *J* = 7.6 Hz, 1H), 5.30 (d, *J* = 7.2 Hz, 1H), 3.70 (dd, *J* = 17.2, 5.2 Hz, 1H), 3.43 (dd, *J* = 16.8, 6.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 198.1, 154.1, 151.0, 140.9, 136.6, 133.6, 129.3, 128.79, 128.76, 128.2, 127.7, 126.5, 125.4, 121.6, 52.0, 43.7 ppm; HRMS calc'd for $C_{22}H_{20}NO_3^+$: 346.1438 found: 346.1435 $[M+H]^+$.

***N*-(1-(3,5-dimethoxyphenyl)-3-oxo-3-phenylpropyl)benzamide (3pa)**

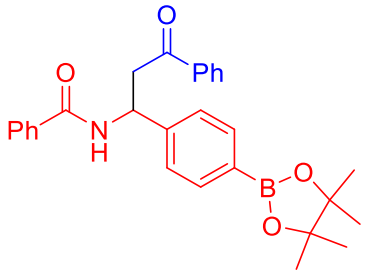


The reaction was performed following the **GP4** with *N*-(3,5-dimethoxybenzyl)-*N*-(4-nitrophenoxy)benzamide **1p** (122.5 mg, 0.3 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (38.5 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product

3pa (52.2 mg, 67%) as colorless oil.

R_f = 0.68 (hexanes: ethyl acetate = 1:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.75 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.52 – 7.47 (m, 2H), 7.44 – 7.34 (m, 5H), 6.47 (d, *J* = 2.0 Hz, 2H), 6.25 (t, *J* = 2.4 Hz, 1H), 5.61 (dt, *J* = 8.0, 5.4 Hz, 1H), 3.77 (d, *J* = 5.4 Hz, 1H), 3.66 (s, 6H), 3.41 (dd, *J* = 16.8, 6.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 198.0, 165.7, 160.0, 142.5, 135.7, 133.2, 132.6, 130.6, 127.7, 127.6, 127.2, 126.0, 103.8, 98.0, 54.3, 49.5, 41.9 ppm; HRMS calc'd for $C_{24}H_{24}NO_4^+$: 390.1700 found: 390.1697 $[M+H]^+$.

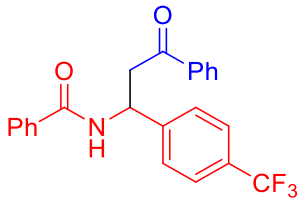
***N*-(3-oxo-3-phenyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl)benzamide (3qa)**



The reaction was performed following the **GP4** with *N*-(4-nitrophenoxy)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)benzamide **1q** (142.3 mg, 0.3 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (38.5 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3qa** (79.2 mg, 87%) as white solid.

m.p. = 166 – 168 °C; R_f = 0.34 (hexanes: ethyl acetate = 2:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.90 (m, 2H), 7.85 – 7.82 (m, 2H), 7.78 – 7.76 (m, 2H), 7.62 – 7.58 (m, 1H), 7.57 – 7.55 (m, 1H), 7.53 – 7.49 (m, 1H), 7.47 – 7.45 (m, 3H), 7.44 – 7.43 (m, 1H); 7.41 (d, *J* = 8.0 Hz, 2H), 5.78 (dt, *J* = 8.0, 5.2 Hz, 1H), 3.89 (dd, *J* = 17.2, 4.8 Hz, 1H), 3.54 (dd, *J* = 17.2, 5.6 Hz, 1H), 1.31 (s, 12H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.1, 166.7, 144.0, 136.7, 135.2, 134.3, 133.7, 131.6, 128.8, 128.6, 128.2, 127.1, 125.8, 83.8, 50.4, 42.8, 24.8 ppm (one resonance was not observed due to broadening by boron); HRMS calc'd for $C_{28}H_{31}BNO_4^+$: 456.2341 found: 456.2335 $[M+H]^+$.

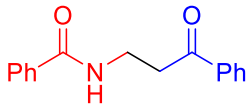
***N*-(3-oxo-3-phenyl-1-(4-(trifluoromethyl)phenyl)propyl)benzamide (3ra)**



The reaction was performed following the **GP4** with *N*-(4-nitrophenoxy)-*N*-(4-(trifluoromethyl)benzyl)benzamide **1r** (124.9 mg, 0.3 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (38.5 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3ra** (56.4 mg, 71%) as white solid.

m.p. = 159 – 161 °C; R_f = 0.40 (hexanes: ethyl acetate = 2:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.90 (m, 2H), 7.86 – 7.84 (m, 2H), 7.61 – 7.51 (m, 6H), 7.48 – 7.44 (m, 4H), 5.81 (dt, *J* = 8.4, 5.2 Hz, 1H), 3.89 (dd, *J* = 17.2, 4.8 Hz, 1H), 3.56 (dd, *J* = 17.2, 5.6 Hz, 1H) ppm (amide proton was not observed); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.0, 166.8, 145.2, 136.4, 134.0, 133.9, 131.9, 128.9, 128.7, 128.2, 127.1, 126.9, 126.3 (q, $J_{C\text{-}F}$ = 270.1 Hz), 125.7 (q, $J_{C\text{-}F}$ = 3.8 Hz), 49.9, 42.5 ppm; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.6 ppm; HRMS calc'd for $C_{23}H_{19}F_3NO_2^+$: 398.1362 found: 398.1359 $[M+H]^+$.

***N*-(3-oxo-3-phenylpropyl)benzamide (3sa)**

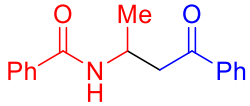


The reaction was performed following the **GP4** with *N*-methyl-*N*-(4-nitrophenoxy)benzamide **1s** (81.7 mg, 0.3 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (38.5 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3sa** (32.4 mg, 64%) as yellow solid.

m.p. = 158 – 160 °C; R_f = 0.41 (hexanes: ethyl acetate = 2:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.52 – 7.48 (m, 1H),

7.41 – 7.37 (m, 3H), 7.32 (t, *J* = 7.6 Hz, 2H), 6.96 (t, *J* = 6.0 Hz, 1H), 3.81 (q, *J* = 5.6 Hz, 2H), 3.27 (t, *J* = 5.6 Hz, 2H) ppm. ^{13}C NMR (100 MHz, Chloroform-d) δ 198.8, 166.4, 135.3, 132.6, 130.4, 127.7, 127.5, 127.0, 125.9, 37.1, 33.8 (one resonance was not observed due to overlapping peaks); HRMS calc'd for $C_{16}H_{16}NO_2^+$: 254.1176 found: 254.1178 $[M+H]^+$.

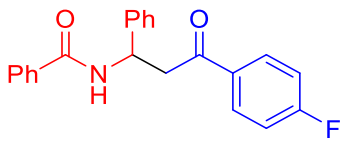
_N_-(4-oxo-4-phenylbutan-2-yl)benzamide (3ta)



The reaction was performed following the **GP4** with *N*-ethyl-*N*-(4-nitrophenoxy)benzamide **1t** (85.9 mg, 0.3 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (38.5 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3ta** (17.1 mg, 32%) as colorless oil.

R_f = 0.41 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 7.2 Hz, 2H), 7.71 (d, *J* = 7.2 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.44 – 7.40 (m, 3H), 7.36 (t, *J* = 7.8 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 1H), 4.63 (hept, *J* = 6.6 Hz, 1H), 3.41 (dd, *J* = 16.8, 4.2 Hz, 1H), 3.14 (dd, *J* = 16.8, 6.0 Hz, 1H), 1.35 (d, *J* = 6.6 Hz, 3H) ppm. ^{13}C NMR (150 MHz, Chloroform-*d*) δ 198.7, 165.7, 135.9, 133.6, 132.5, 130.4, 127.8, 127.5, 127.1, 125.9, 42.2, 41.9, 19.1 ppm. HRMS calc'd for $C_{17}H_{18}NO_2^+$: 268.1332 found: 268.1336 $[M+H]^+$.

_N_-(3-(4-fluorophenyl)-3-oxo-1-phenylpropyl)benzamide (3ab)

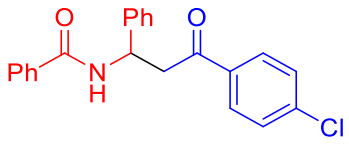


The reaction was performed following the **GP4** with *N*-benzyl-*N*-(4-nitrophenoxy)benzamide **1a** (104.5 mg, 0.3 mmol) and ((1-(4-fluorophenyl)vinyl)oxy)trimethylsilane **2b** (42.1 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to

give the product **3ab** (45.2 mg, 65%) as colorless oil.

R_f = 0.50 (hexanes: ethyl acetate = 2:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.83 (m, 2H), 7.76 – 7.73 (m, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.44 – 7.39 (m, 1H), 7.36 – 7.29 (m, 4H), 7.25 – 7.21 (m, 2H), 7.18 – 7.13 (m, 1H), 7.04 – 7.00 (m, 2H), 5.67 (dt, *J* = 8.0, 5.6 Hz, 1H), 3.76 (dd, *J* = 16.8, 5.2 Hz, 1H), 3.39 (dd, *J* = 16.8, 6.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.4, 166.8, 166.0 (d, $^1J_{C\text{-}F}$ = 254.2 Hz), 140.8, 134.2, 133.1 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 131.7, 130.9 (d, $^3J_{C\text{-}F}$ = 9.2 Hz), 128.8, 128.6, 127.6, 127.1, 126.5, 115.9 (d, $^2J_{C\text{-}F}$ = 21.9 Hz), 50.4, 43.0 ppm; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -104.1 ppm; HRMS calc'd for $C_{22}H_{19}FNO_2^+$: 348.1394 found: 348.1393 $[M+H]^+$.

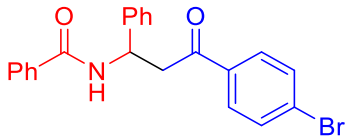
_N_-(3-(4-chlorophenyl)-3-oxo-1-phenylpropyl)benzamide (3ac)



The reaction was performed following the **GP4** with *N*-benzyl-*N*-(4-nitrophenoxy)benzamide **1a** (104.5 mg, 0.3 mmol) and ((1-(4-chlorophenyl)vinyl)oxy)trimethylsilane **2c** (45.4 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3ac** (56.0 mg, 77%) as colorless oil.

R_f = 0.58 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.74 (m, 4H), 7.44 – 7.41 (m, 1H), 7.38 – 7.30 (m, 6H), 7.24 (t, *J* = 7.6 Hz, 2H), 7.18 (t, *J* = 6.4 Hz, 1H), 5.67 (dt, *J* = 8.0, 5.6 Hz, 1H), 3.78 (dd, *J* = 16.8, 5.2 Hz, 1H), 3.41 (dd, *J* = 16.8, 6.0 Hz, 1H) ppm (amide proton was not observed); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.8, 166.8, 140.7, 140.1, 135.0, 134.2, 131.7, 129.6, 129.1, 128.8, 128.7, 127.7, 127.1, 126.5, 50.4, 43.0 ppm; HRMS calc'd for $C_{22}H_{19}ClNO_2^+$: 364.1099 found: 364.1092 $[M+H]^+$.

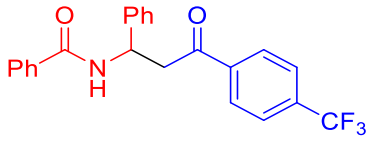
_N_-(3-(4-bromophenyl)-3-oxo-1-phenylpropyl)benzamide (3ad)



The reaction was performed following the **GP4** with *N*-benzyl-*N*-(4-nitrophenoxy)benzamide **1a** (104.5 mg, 0.3 mmol) and ((1-(4-bromophenyl)vinyl)oxy)trimethylsilane **2d** (54.3 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3ad** (67.0 mg, 82%) as white solid.

m.p. = 147 – 149 °C; R_f = 0.58 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 7.6 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.53 – 7.49 (m, 2H), 7.44 (d, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 6.4 Hz, 1H), 5.74 (dt, *J* = 7.6, 5.6 Hz, 1H), 3.85 (dd, *J* = 16.8, 4.8 Hz, 1H), 3.47 (dd, *J* = 16.8, 6.0 Hz, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 198.0, 166.8, 140.7, 135.3, 134.2, 132.1, 131.7, 129.7, 128.9, 128.8, 128.7, 127.7, 127.1, 126.5, 50.4, 43.0 ppm; HRMS calc'd for $C_{22}H_{19}BrNO_2^+$: 408.0594 found: 408.0591 $[M+H]^+$.

_N_-(3-oxo-1-phenyl-3-(4-(trifluoromethyl)phenyl)propyl)benzamide (3ae)

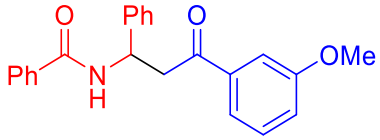


The reaction was performed following the **GP4** with *N*-benzyl-*N*-(4-nitrophenoxy)benzamide **1a** (104.5 mg, 0.3 mmol) and trimethyl((1-(4-(trifluoromethyl)phenyl)vinyl)oxy)silane **2e** (52.1 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3ae** (43.7 mg, 55%) as yellow solid.

m.p. = 121 – 123 °C; R_f = 0.60 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.76 – 7.74 (m, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.47 – 7.43 (m, 1H), 7.40 – 7.36 (m, 2H), 7.34 – 7.25 (m, 5H), 7.22 – 7.18 (m, 1H), 5.70 (ddd, *J* = 8.0, 6.0, 4.8 Hz, 1H), 3.87 (dd, *J* = 16.8, 4.8 Hz, 1H), 3.49 (dd, *J* = 16.8,

6.4 Hz, 1H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 198.0, 166.8, 140.5, 139.2, 134.8 (q, J_{C-F} = 32.8 Hz), 134.1, 131.8, 128.9, 128.7, 128.6, 127.8, 127.0, 126.5, 125.8 (q, J_{C-F} = 3.8 Hz), 123.5 (q, J_{C-F} = 271.3 Hz), 50.4, 43.5 ppm; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.2 ppm; HRMS calc'd for $C_{23}H_{19}F_3NO_2^+$: 398.1362 found: 398.1364 $[M+H]^+$.

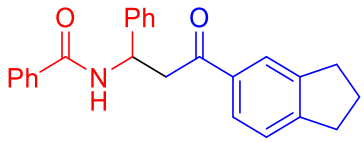
_N_-(3-(3-methoxyphenyl)-3-oxo-1-phenylpropyl)benzamide (3af)



The reaction was performed following the **GP4** with *N*-benzyl-*N*-(4-nitrophenoxy)benzamide **1a** (104.5 mg, 0.3 mmol) and ((1-(3-methoxyphenyl)vinyl)oxy)trimethylsilane **2f** (44.5 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3af** (57.5 mg, 80%) as white solid.

m.p. = 122 – 124 °C; R_f = 0.43 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.73 (m, 2H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.38 (m, 2H), 7.34 – 7.30 (m, 5H), 7.27 – 7.20 (m, 3H), 7.16 – 7.12 (m, 1H), 7.01 (ddd, *J* = 8.4, 2.8, 1.2 Hz, 1H), 5.68 (dt, *J* = 8.0, 5.2 Hz, 1H), 3.79 – 3.73 (m, 1H), 3.72 (s, 3H), 3.45 – 3.38 (m, 1H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 198.9, 166.8, 159.9, 141.0, 138.0, 134.3, 131.6, 129.8, 128.7, 128.6, 127.5, 127.1, 126.5, 120.9, 120.2, 112.3, 55.5, 50.4, 43.2 ppm; HRMS calc'd for $C_{23}H_{22}NO_3^+$: 360.1594 found: 360.1589 $[M+H]^+$.

_N_-(3-(2,3-dihydro-1*H*-inden-5-yl)-3-oxo-1-phenylpropyl)benzamide (3ag)

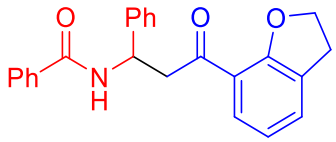


The reaction was performed following the **GP4** with *N*-benzyl-*N*-(4-nitrophenoxy)benzamide **1a** (104.5 mg, 0.3 mmol) and ((1-(2,3-dihydro-1*H*-inden-5-yl)vinyl)oxy)trimethylsilane **2g** (46.5 mg, 0.2 mmol). The crude material was separated

by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3ag** (54.7 mg, 74%) as yellow solid.

m.p. = 119 – 121 °C; R_f = 0.57 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.83 (m, 2H), 7.80 – 7.76 (m, 2H), 7.71 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.44 – 7.38 (m, 4H), 7.32 – 7.25 (m, 3H), 7.24 – 7.19 (m, 1H), 5.75 (dt, *J* = 8.0, 5.2 Hz, 1H), 3.83 (dd, *J* = 16.8, 5.2 Hz, 1H), 3.49 (dd, *J* = 16.8, 5.6 Hz, 1H), 2.94 – 2.89 (m, 4H), 2.09 (p, *J* = 7.6 Hz, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.3, 166.7, 151.0, 145.0, 141.2, 135.2, 134.3, 131.6, 128.7, 128.6, 127.4, 127.1, 126.8, 126.5, 124.5, 124.1, 50.4, 42.9, 33.1, 32.5, 25.4 ppm; HRMS calc'd for $C_{25}H_{24}NO_2^+$: 370.1802 found: 370.1800 $[M+H]^+$.

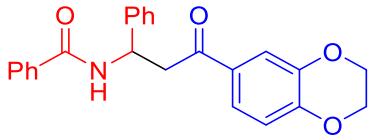
_N_-(3-(2,3-dihydrobenzofuran-7-yl)-3-oxo-1-phenylpropyl)benzamide (3ah)



The reaction was performed following the **GP4** with *N*-benzyl-*N*-(4-nitrophenoxy)benzamide **1a** (104.5 mg, 0.3 mmol) and ((1-(2,3-dihydrobenzofuran-7-yl)vinyl)oxy)trimethylsilane **2h** (46.9 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3ah** (55.0 mg, 74%) as yellow solid.

m.p. = 135 – 137 °C; R_f = 0.50 (hexanes: ethyl acetate = 2:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.81 (m, 2H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.64 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.44 – 7.41 (m, 4H), 7.37 – 7.29 (m, 3H), 7.24 – 7.20 (m, 1H), 6.87 (t, *J* = 7.6 Hz, 1H), 5.74 (dt, *J* = 8.4, 5.6 Hz, 1H), 4.72 (td, *J* = 8.8, 4.4 Hz, 2H), 3.77 (dd, *J* = 16.8, 6.0 Hz, 1H), 3.60 (dd, *J* = 16.8, 5.2 Hz, 1H), 3.25 (t, *J* = 8.4 Hz, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.9, 166.6, 160.3, 141.7, 134.5, 131.5, 130.2, 129.4, 128.6, 128.1, 127.2, 127.1, 126.4, 120.7, 120.2, 72.2, 50.2, 47.4, 28.9 ppm (one resonance was not observed due to overlapping peaks); HRMS calc'd for $C_{24}H_{22}NO_3^+$: 372.1594 found: 372.1594 $[M+H]^+$.

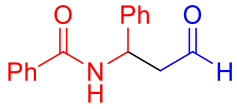
***N*-(3-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-3-oxo-1-phenylpropyl)benzamide (3ai)**



The reaction was performed following the **GP4** with *N*-benzyl-*N*-(4-nitrophenoxy)benzamide **1a** (104.5 mg, 0.3 mmol) and ((1-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)vinyl)oxy)trimethylsilane **2i** (50.1 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3ai** (48.0 mg, 62%) as white solid.

m.p. = 194 – 196 °C; R_f = 0.44 (hexanes: ethyl acetate = 2:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.76 (m, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.46 – 7.35 (m, 5H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.17 – 7.13 (m, 1H), 6.83 – 6.80 (m, 1H), 5.66 (dt, *J* = 8.4, 5.6 Hz, 1H), 4.23 (dd, *J* = 6.0, 2.8 Hz, 2H), 4.19 (dd, *J* = 6.0, 2.8 Hz, 2H), 3.70 (dd, *J* = 16.8, 5.2 Hz, 1H), 3.36 (dd, *J* = 16.8, 5.6 Hz, 1H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 197.7, 166.7, 148.6, 143.4, 141.1, 134.3, 131.6, 130.5, 128.7, 128.6, 127.4, 127.1, 126.4, 122.5, 117.8, 117.4, 64.7, 64.1, 50.4, 42.5 ppm; HRMS calc'd for $C_{24}H_{22}NO_4^+$: 388.1543 found: 388.1539 $[M+H]^+$.

***N*-(3-oxo-1-phenylpropyl)benzamide (3aj)**

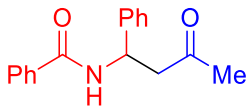


The reaction was performed following the **GP4** with *N*-benzyl-*N*-(4-nitrophenoxy)benzamide **1a** (104.5 mg, 0.3 mmol) and trimethyl(vinyloxy)silane **2j** (23.3 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3aj** (20.3 mg, 40%) as colorless oil.

R_f = 0.35 (hexanes: ethyl acetate = 2:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.81 (d, *J* = 1.2 Hz, 1H), 7.79 – 7.76 (m, 2H), 7.52 – 7.48 (m, 1H), 7.44 – 7.39 (m, 2H), 7.37 – 7.34 (m, 4H), 7.32 – 7.27 (m, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 5.71 (dt, *J* = 8.0, 6.4 Hz,

1H), 3.21 (ddd, *J* = 17.2, 6.4, 2.4 Hz, 1H), 3.06 (ddd, *J* = 17.2, 6.0, 1.2 Hz, 1H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 200.6, 166.9, 140.4, 134.0, 131.8, 129.0, 128.7, 128.0, 127.0, 126.6, 49.2, 48.8 ppm; HRMS calc'd for $C_{16}H_{16}NO_2^+$: 254.1176 found : 254.1171 $[M+H]^+$.

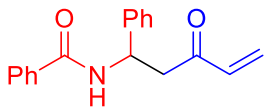
_N_-(3-oxo-1-phenylbutyl)benzamide (3ak)



The reaction was performed following the **GP4** with *N*-benzyl-*N*-(4-nitrophenoxy)benzamide **1a** (104.5 mg, 0.3 mmol) and trimethyl(prop-1-en-2-yloxy)silane **2k** (26.1 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3ak** (32.1 mg, 60%) as yellow solid.

m.p. = 119 – 121 °C; R_f = 0.40 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.73 (m, 3H), 7.49 – 7.43 (m, 1H), 7.42 – 7.35 (m, 4H), 7.28 – 7.26 (m, 2H), 7.21 – 7.18 (m, 1H), 5.54 (dt, *J* = 8.4, 5.6 Hz, 1H), 3.18 (dd, *J* = 16.8, 5.2 Hz, 1H), 2.97 (dd, *J* = 16.8, 5.6 Hz, 1H), 2.07 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 208.3, 166.6, 140.8, 134.2, 132.1, 131.7, 128.8, 128.6, 127.6, 127.4, 127.1, 126.4, 50.0, 47.9, 31.0 ppm; HRMS calc'd for $C_{17}H_{18}NO_2^+$: 268.1332 found: 268.1335 $[M+H]^+$.

_N_-(3-oxo-1-phenylpent-4-en-1-yl)benzamide (3al)

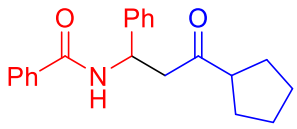


The reaction was performed following the **GP4** with *N*-benzyl-*N*-(4-nitrophenoxy)benzamide **1a** (104.5 mg, 0.3 mmol) and (buta-1,3-dien-2-yloxy)trimethylsilane **2l** (28.5 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3al** (38.0 mg, 68%) as colorless oil.

R_f = 0.40 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.76 (d,

J = 7.8 Hz, 2H), 7.47 – 7.43 (m, 2H), 7.40 – 7.36 (m, 2H), 7.30 – 7.25 (m, 4H), 6.26 (dd, *J* = 18.0, 10.2 Hz, 1H), 6.17 (d, *J* = 17.4 Hz, 1H), 5.81 (d, *J* = 10.2 Hz, 1H), 5.59 (q, *J* = 6.0 Hz, 1H), 3.39 (dd, *J* = 16.2, 4.8 Hz, 1H), 3.10 (dd, *J* = 16.8, 6.0 Hz, 1H) ppm (amide proton was not observed). ^{13}C NMR (150 MHz, Chloroform-d) δ 198.7, 165.6, 139.8, 135.5, 130.6, 128.6, 127.7, 127.6, 126.5, 126.2, 126.0, 125.4, 49.1, 42.8; HRMS calc'd for $C_{18}H_{18}NO_2^+$: 280.1332 found: 280.1335 $[M+H]^+$.

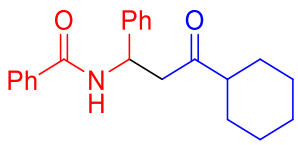
_N_-(3-cyclopentyl-3-oxo-1-phenylpropyl)benzamide (3am)



The reaction was performed following the **GP4** with *N*-benzyl-*N*-(4-nitrophenoxy)benzamide **1a** (104.5 mg, 0.3 mmol) and ((1-cyclopentylvinyl)oxy)trimethylsilane **2m** (36.9 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3am** (39.9 mg, 62%) as yellow solid.

m.p. = 130 – 132 °C; R_f = 0.60 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.83 (m, 3H), 7.53 – 7.49 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.35 – 7.30 (m, 4H), 7.26 – 7.22 (m, 1H), 5.60 (dt, *J* = 8.0, 5.2 Hz, 1H), 3.27 (dd, *J* = 16.8, 4.8 Hz, 1H), 3.02 (dd, *J* = 16.8, 5.6 Hz, 1H), 2.79 (p, *J* = 7.6 Hz, 1H), 1.77 – 1.62 (m, 4H), 1.58 – 1.47 (m, 4H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 213.2, 166.5, 141.2, 134.3, 131.6, 128.7, 128.6, 127.4, 127.1, 126.3, 52.4, 50.2, 46.1, 28.3, 25.9 ppm; HRMS calc'd for $C_{21}H_{24}NO_2^+$: 322.1802 found: 322.1801 $[M+H]^+$.

_N_-(3-cyclohexyl-3-oxo-1-phenylpropyl)benzamide (3an)

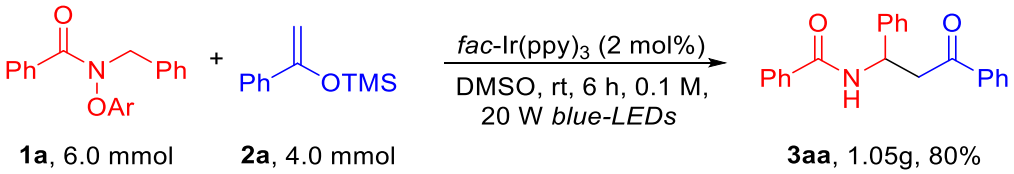


The reaction was performed following the **GP4** with *N*-benzyl-*N*-(4-nitrophenoxy)benzamide **1a** (104.5 mg, 0.3 mmol) and ((1-

cyclohexylvinyl)oxy)trimethylsilane **2n** (39.7 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3an** (42.9 mg, 64%) as yellow solid.

m.p. = 136 – 138 °C; R_f = 0.63 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.81 (m, 3H), 7.53 – 7.49 (m, 1H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.34 – 7.30 (m, 4H), 7.26 – 7.22 (m, 1H), 5.59 (dt, *J* = 8.4, 5.2 Hz, 1H), 3.28 (dd, *J* = 16.8, 4.8 Hz, 1H), 2.99 (dd, *J* = 16.8, 5.6 Hz, 1H), 2.27 – 2.22 (m, 1H), 1.75 – 1.61 (m, 5H), 1.30 – 1.21 (m, 2H), 1.18 – 1.07 (m, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 214.2, 166.5, 141.1, 134.3, 131.6, 128.7, 128.6, 127.4, 127.1, 126.3, 51.6, 50.1, 44.9, 27.8, 25.7, 25.5 ppm; HRMS calc'd for $C_{22}H_{26}NO_2^+$: 336.1958 found: 336.1961 $[M+H]^+$.

Gram-scale synthesis of 3aa



1a, 6.0 mmol **2a**, 4.0 mmol **3aa**, 1.05g, 80%

An oven-dried 100 mL reaction vial equipped with a stir bar was charged with amide **1a** (2.09 g, 6.0 mmol) and *fac*-Ir(ppy)$_3$ (52.38 mg, 0.08 mmol) under a nitrogen atmosphere in a glove box. A solution of silyl enol ethers (0.77 g, 4.0 mmol) in 40.0 mL dry DMSO was added by a "Eppendorf" brand 1000 μ L pipettor to the reaction vial. The vial was capped, removed from the glove box, and stirred for 6 h in front of 20 W blue LEDs irradiation. After the reaction period, the lights were turned off, the reaction mixture was opened to air and quenched with 3mL of H_2O. The aqueous layer was extracted with ethyl acetate (3 X 50 mL) and the combined organic layers were washed with saturated brine solution, dried (Na_2SO_4), filtered and evaporated. The product was purified by column chromatography on silica gel (ethyl acetate: hexanes = 1:10) to afford the product **3aa** (1.05 g, 80%).

Cyclic voltammetry experiments

Tetrabutylammonium hexafluorophosphate (1.0 mmol, 387.4 mg) and *N*-benzyl-*N*-(4-nitrophenoxy)benzamide **1a** (0.10 mmol, 34.8 mg) were dissolved in dry DMSO (10 mL) and the solution was vigorously bubbled with N_2 for 5 minutes prior to the measurement. The oxidation potential was measured using a glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) at 0.1 V/s scan rate.

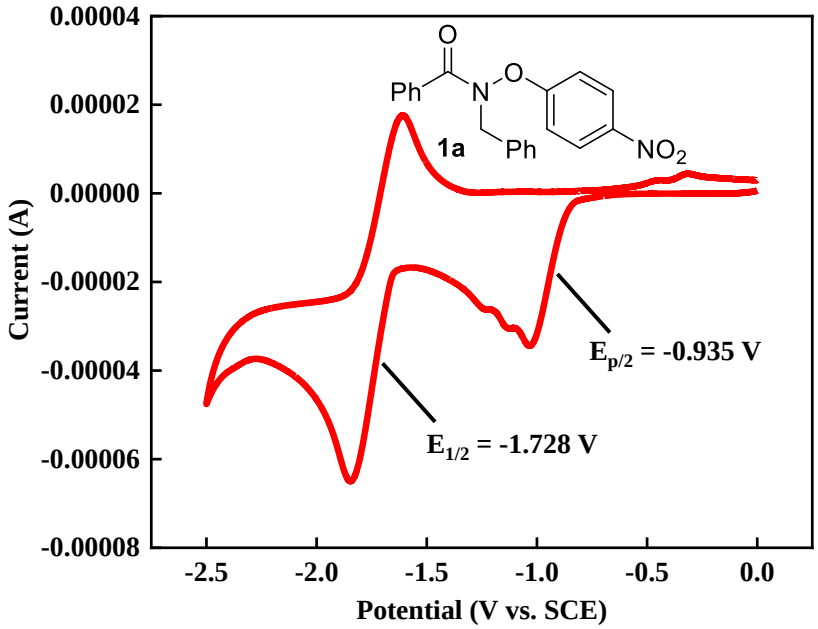


Figure S2. Cyclic voltammogram of *N*-benzyl-*N*-(4-nitrophenoxy)benzamide **1a** in DMSO

Tetrabutylammonium hexafluorophosphate (1.0 mmol, 387.4 mg) and *N*-benzyl-*N*-(4-nitrophenoxy)cyclobutanecarboxamide **1j** (0.10 mmol, 32.6 mg) were dissolved in dry DMSO (10 mL) and the solution was vigorously bubbled with N_2 for 5 minutes prior to the measurement. The oxidation potential was measured using a glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) at 0.1 V/s scan rate.

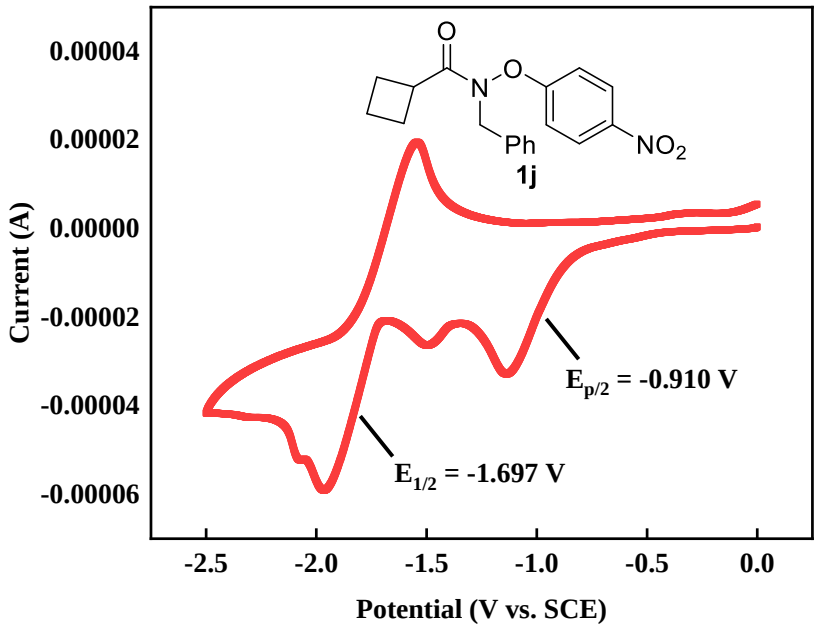


Figure S3. Cyclic voltammogram of *N*-benzyl-*N*-(4-nitrophenoxy)cyclobutanecarboxamide **1j** in DMSO

Tetrabutylammonium hexafluorophosphate (1.0 mmol, 387.4 mg) and *N*-benzyl-*N*-(4-nitrophenoxy)cyclohexanecarboxamide **1l** (0.10 mmol, 35.4 mg) were dissolved in dry DMSO (10 mL) and the solution was vigorously bubbled with N_2 for 5 minutes prior to the measurement. The oxidation potential was measured using a glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) at 0.1 V/s scan rate.

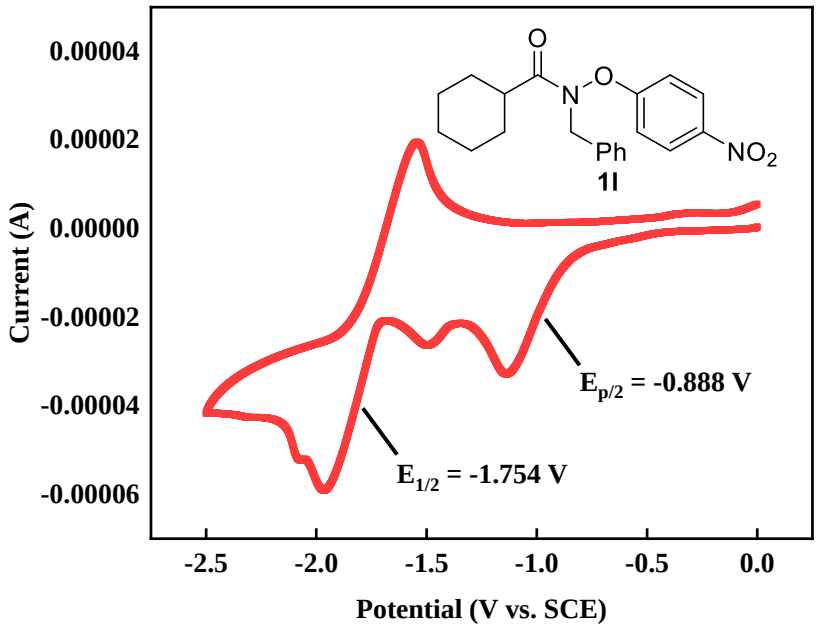


Figure S4. Cyclic voltammogram of *N*-benzyl-*N*-(4-nitrophenoxy)cyclohexanecarboxamide **1l** in DMSO

Tetrabutylammonium hexafluorophosphate (1.0 mmol, 387.4 mg) and phenyl benzyl(4-nitrophenoxy)carbamate **1o** (0.10 mmol, 36.4 mg) were dissolved in dry DMSO (10 mL) and the solution was vigorously bubbled with N_2 for 5 minutes prior to the measurement. The oxidation potential was measured using a glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) at 0.1 V/s scan rate.

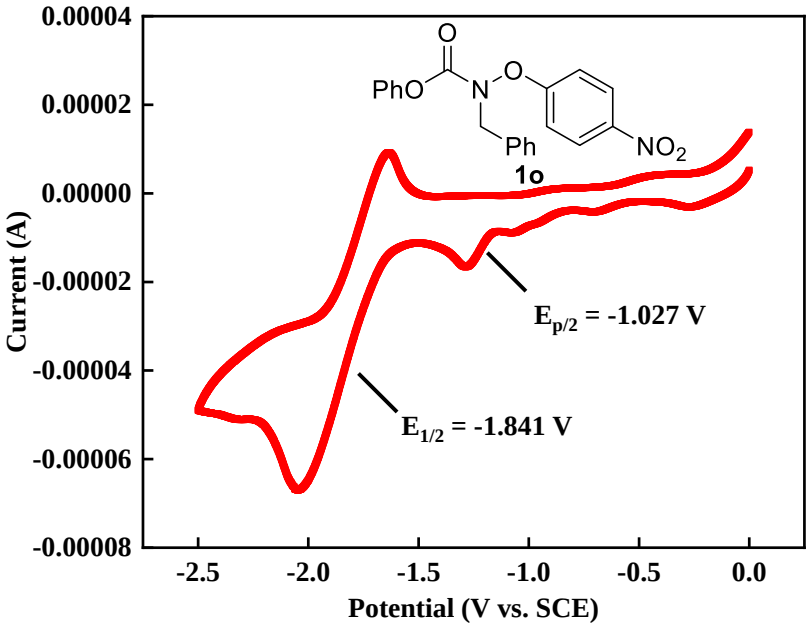


Figure S5. Cyclic voltammogram of phenyl benzyl(4-nitrophenoxy)carbamate **1o** in DMSO

Tetrabutylammonium hexafluorophosphate (1.0 mmol, 387.4 mg) and *N*-methyl-*N*-(4-nitrophenoxy)benzamide **1s** (0.10 mmol, 27.2 mg) were dissolved in dry DMSO (10 mL) and the solution was vigorously bubbled with N_2 for 5 minutes prior to the measurement. The oxidation potential was measured using a glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) at 0.1 V/s scan rate.

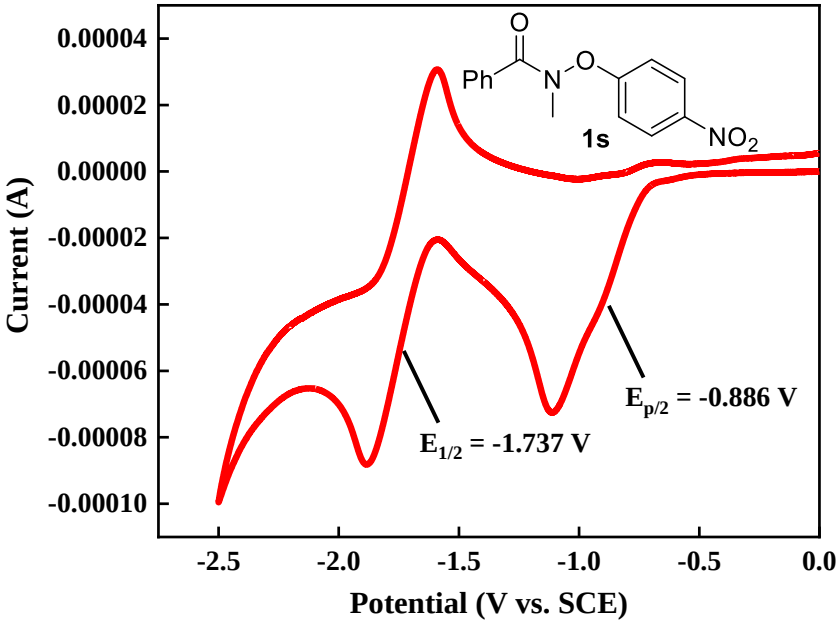


Figure S6. Cyclic voltammogram of *N*-methyl-*N*-(4-nitrophenoxy)benzamide **1s** in DMSO

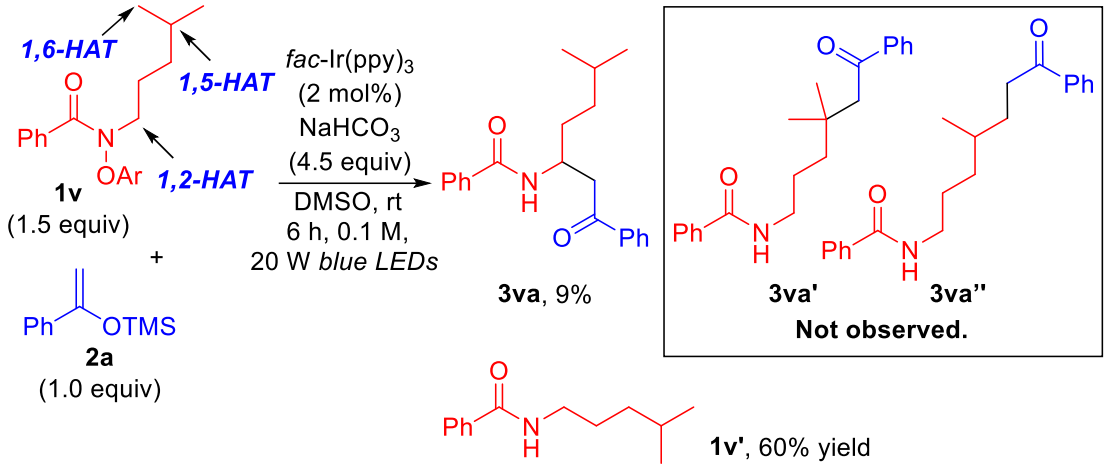
Table S10. Reduction potential and reduction profile of 0.01 M aryloxy-amide species at 0.1 V/s scan rate.

Compound No	$E_{p/2}$ (V vs SCE)
1a	-0.935
1j	-0.910
1l	-0.888
1o	-1.027
1s	-0.886

Table S11. Reduction potential and reduction profile of second-electron transfer of nitro groups of aryloxy-amide compound at 0.1 V/s scan rate.[5]

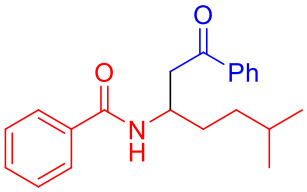
Compound No	$E_{1/2}$ (V vs SCE)
1a	-1.728
1j	-1.697
1l	-1.754
1o	-1.841
1s	-1.737

Site-selectivity studies



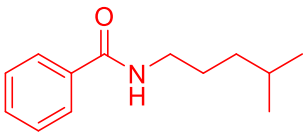
The reaction was performed following the **GP3** with *N*-(4-methylpentyl)-*N*-(4-nitrophenoxy)benzamide **1v** (102.7 mg, 0.3 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (38.5 mg, 0.2 mmol). The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3va** (5.8 mg, 9%) as colorless oil.

***N*-(6-methyl-1-oxo-1-phenylheptan-3-yl)benzamide (3va)**



R_f = 0.40 (hexanes:ethyl acetate = 5:1); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 7.2 Hz, 2H), 7.71 (d, *J* = 7.2 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.44 – 7.40 (m, 3H), 7.36 (t, *J* = 7.2 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 1H), 4.47 – 4.45 (m, 1H), 3.40 (dd, *J* = 17.4, 4.2 Hz, 1H), 3.18 (dd, *J* = 16.8, 5.4 Hz, 1H), 1.78 – 1.72 (m, 1H), 1.66 – 1.60 (m, 1H), 1.50 – 1.46 (m, 1H), 1.28 – 1.20 (m, 2H), 0.80 (dd, *J* = 6.6, 4.2 Hz, 6H) ppm. ^{13}C NMR (150 MHz, Chloroform-*d*) δ 199.9, 166.9, 137.0, 135.0, 133.5, 131.4, 128.8, 128.6, 128.1, 126.9, 47.3, 41.7, 35.7, 31.9, 27.9, 22.6, 22.5 ppm. HRMS calc'd for $C_{21}H_{26}NO_2^+$: 324.1958, found: 324.1964 $[M+H]^+$.

***N*-(4-methylpentyl)benzamide (1v')**



R_f = 0.23 (hexanes:ethyl acetate = 5:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.68 (m, 2H), 7.45 – 7.40 (m, 1H), 7.38 – 7.34 (m, 2H), 6.09 (s, 1H), 3.39 – 3.34 (m, 2H), 1.58 – 1.47 (m, 3H), 1.22 – 1.16 (m, 2H), 0.83 (d, *J* = 6.4 Hz, 6H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.5, 134.9, 131.3, 128.6, 126.8, 40.4, 36.1, 27.8, 27.6, 22.6 ppm. HRMS calc'd for $C_{13}H_{20}NO^+$: 206.1539, found: 206.1540 $[M+H]^+$.

Emission quenching experiments – stern-volmer studies

Experimental procedures: All the *fac*-Ir(ppy)$_3$ solutions were excited at 399 nm and the emission intensity was collected at 522 nm at room temperature. A screw-top quartz cuvette was charged with a 0.1 mM solution of *fac*-Ir(ppy)$_3$ in DMSO (2.0 mL) and the initial emission was collected. Another two series of samples, 0.1 mM *fac*-Ir(ppy)$_3$ in DMSO with N-benzyl aryl amide **1a** or phenylenolsilyl ether **2a** as quencher in gradient concentrations (5 mM, 10 mM, 15 mM and 20 mM), were tested and the emissions were collected.

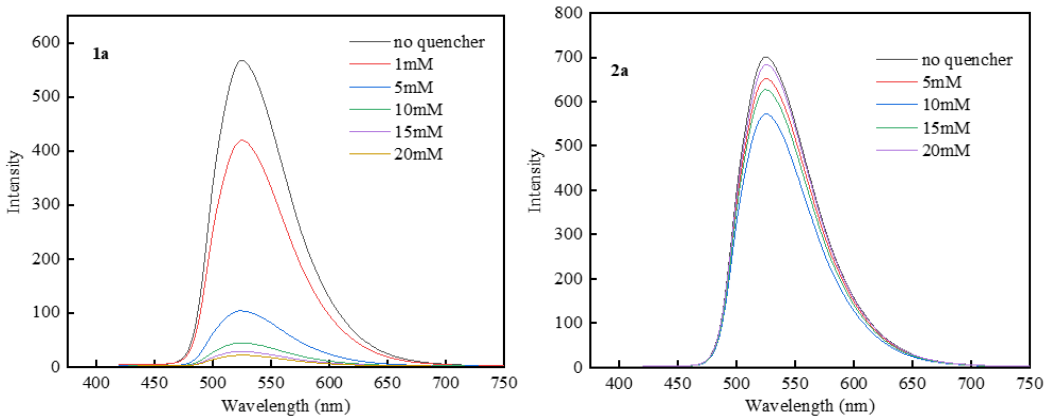


Figure S7. Luminescence Quenching Experiments

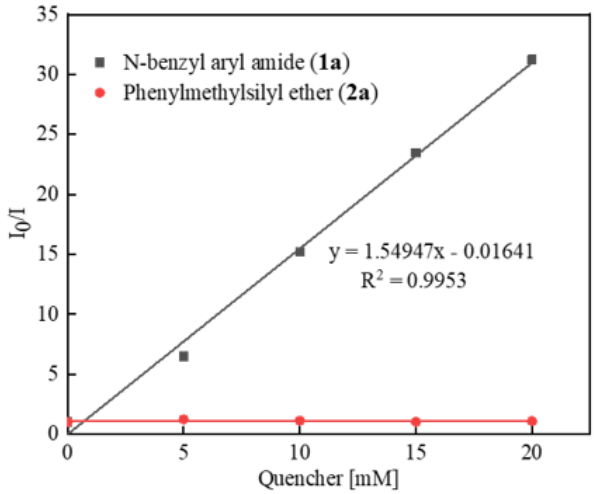
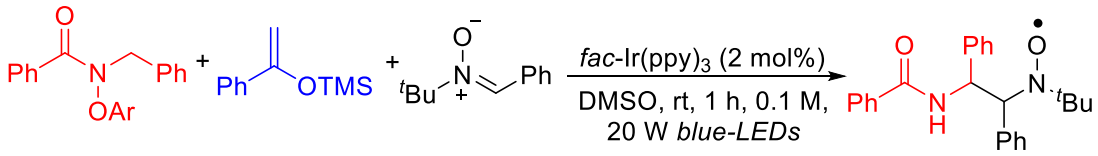


Figure S8. Stern-Volmer plots for N-benzyl aryl amide **1a** and phenylenolsilyl ether **2a** as quenchers

Mechanistic studies

EPR experiments

X-band EPR spectrum of a carbon radical (probably the α-amide benzyl radical intermediate) trapped with PBN:



1a, (1.5 equiv) **2a**, (1.0 equiv) (2.5 equiv) **4**, HRMS detected

(1) Settings: microwave frequency: 9.434834 GHz; power: 0.2 mW; center field: 336.00 mT; sweep width: 15.00 mT; modulation frequency: 43750 Hz; modulation amplitude: 100 μT.

(2) The reaction was performed following the **GP3** with trimethyl((1-phenylvinyl)oxy)silane **2a** (19.2 mg, 0.1 mmol), *N*-benzyl-*N*-(4-nitrophenoxy)benzamide **1a** (40.8 mg, 0.15 mmol), PBN (44.3 mg, 0.25 mmol) and 1 mL dry DMSO and stirred for 1 h in front of 20 W blue LEDs irradiation at room temperature.

(3) The resulting EPR signal:

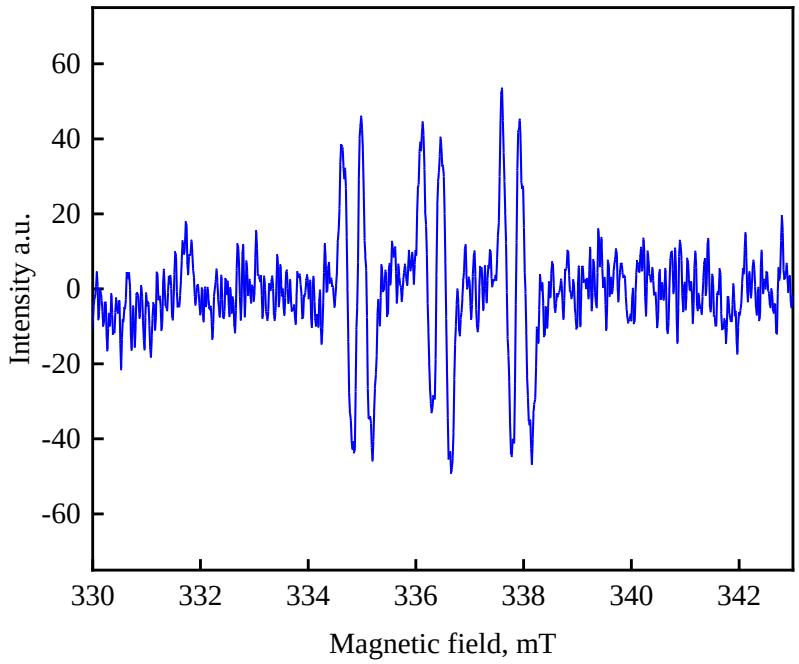


Figure S9: EPR spectrum of the PBN-trapped carbon-centered radical.

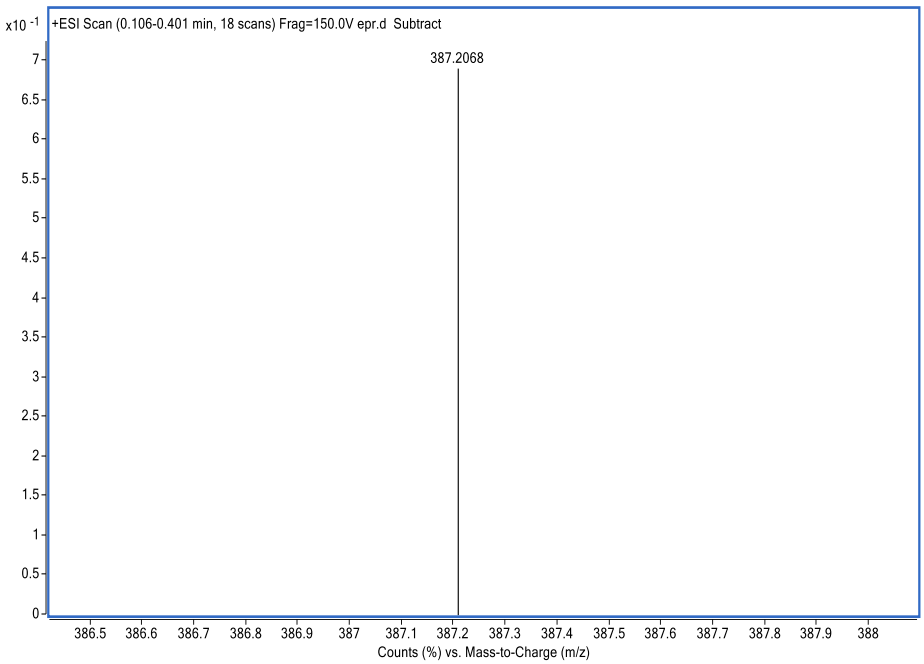
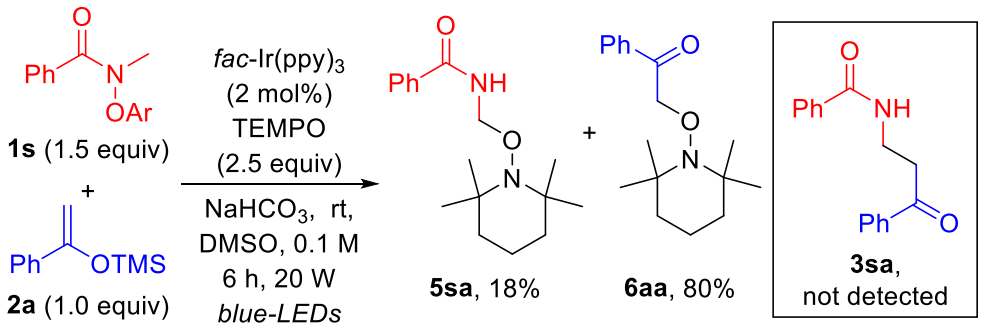


Figure S10: HRMS of radical intermediate **4**. HRMS calc'd for $C_{25}H_{27}N_2O_2^{\bullet+}$ 387.2067, found 387.2068 $[M]^{\bullet+}$.

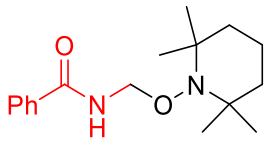
Control experiments

a) Trapping with TEMPO



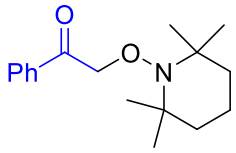
The reaction was performed following the **GP3** with *N*-methyl-*N*-(4-nitrophenoxy)benzamide **1s** (204.2 mg, 0.75 mmol), trimethyl((1-phenylvinyl)oxy)silane **2a** (96.2 mg, 0.5 mmol), 2,2,6,6- tetramethylpiperidine-1-oxyl (195.3 mg, 1.25 mmol), $NaHCO_3$ (189.0 mg, 2.25 mmol), *fac*-Ir(ppy)$_3$ (6.5 mg, 0.01 mmol) and 5 mL dry DMSO and stirred for 6 h in front of 20 W blue LEDs irradiation at room temperature. The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **5sa** (26.1 mg, 18%) and **6aa** (110.2 mg, 80%).

N-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)benzamide (5sa)



The ^1H and $^{13}C\{^1H\}$ data for this compound match the literature data.[1]

1-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethan-1-one (6aa)



The ^1H and $^{13}C\{^1H\}$ data for this compound match the literature data.[6]

According to the reference[6], the mechanism of formation of compounds **5sa** and **6aa** as follows:

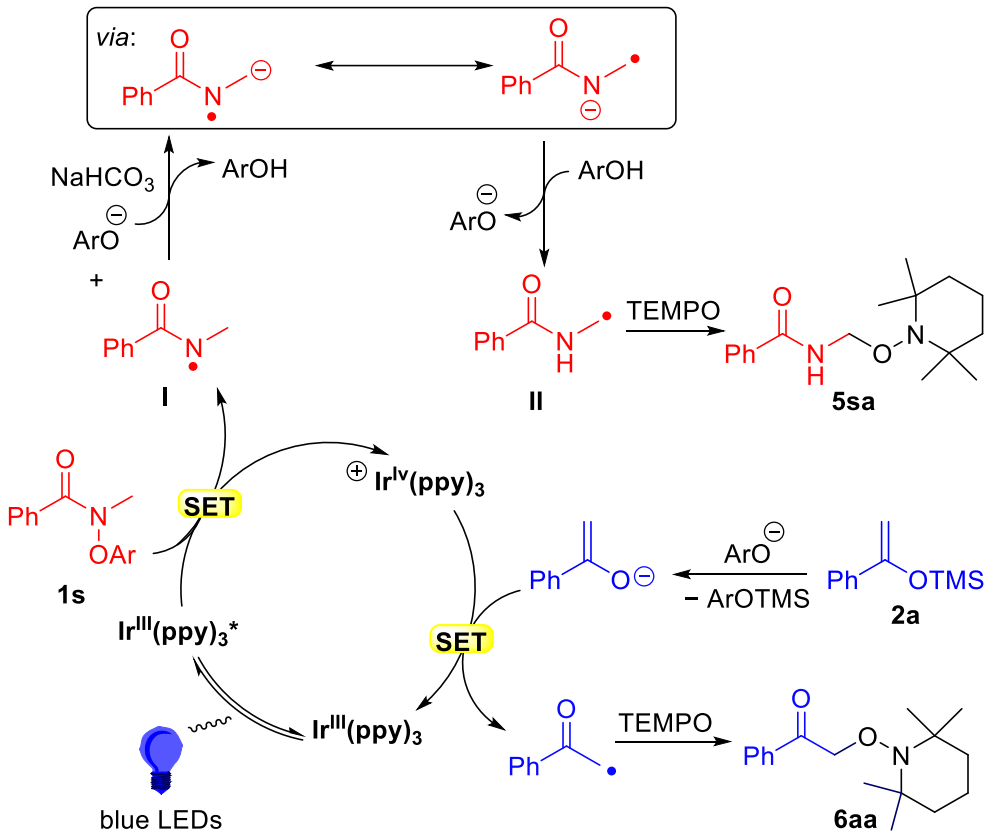
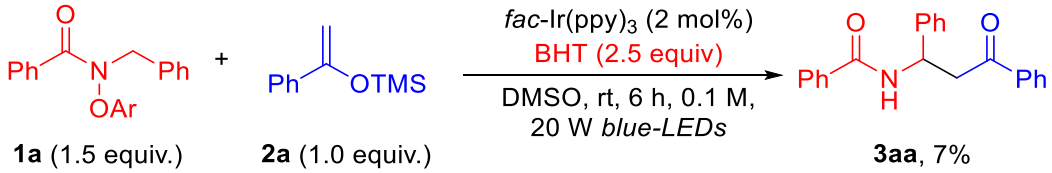


Figure S11. Proposed mechanism for the generation of compound **5sa** and **6aa**

b) Butylated hydroxytoluene（BHT）is added to standard conditions

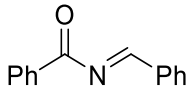


The reaction was performed following the **GP3** with *N*-benzyl-*N*-(4-nitrophenoxy)benzamide **1a** (52.2 mg, 0.15 mmol), trimethyl((1-phenylvinyl)oxy)silane **2a** (19.2 mg, 0.1 mmol), butylated hydroxytoluene (55.1 mg, 0.25 mmol) and 1 mL dry DMSO and stirred for 6 h in front of 20 W blue LEDs irradiation at room temperature. The coupling product **3aa** was obtained in 7% yield. (determined by ^{1}H NMR integration of the product against an internal standard).

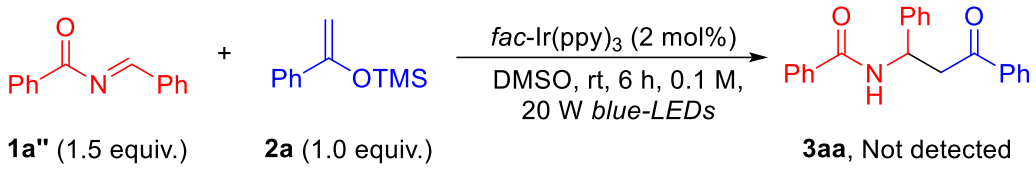
c) Using (*E*)-*N*-benzylidenebenzamide **1a''** and silyl enol ethers **2a** reaction under the standard conditions.

(*E*)-*N*-benzylidenebenzamide 1a'' was prepared according to the literature

procedure.[7]



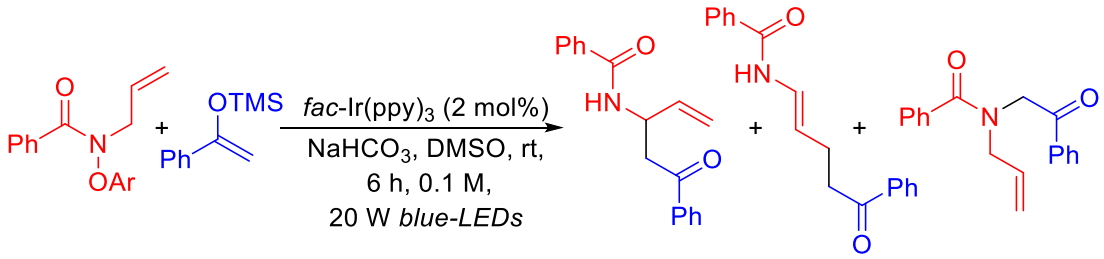
The ^{1}H and ^{13}C data for this compound matched the literature data.[7]



1a'' (1.5 equiv.) **2a** (1.0 equiv.) **3aa**, Not detected

The reaction was performed following the **GP3** with (*E*)-*N*-benzylidenebenzamide **1a''** (31.4 mg, 0.15 mmol), trimethyl((1-phenylvinyl)oxy)silane **2a** (19.2 mg, 0.1 mmol), and 1 mL dry DMSO and stirred for 6 h in front of 20 W blue LEDs irradiation at room temperature. We did not observe the formation of the coupling product **3aa**.

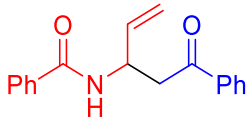
Radical trapping experiment



1u **2a** **3ua,** 10% **3ua'**, 55% **3ua''**, 28%

The reaction was performed following the **GP3** with *N*-allyl-*N*-(4-nitrophenoxy)benzamide **1u** (223.7 mg, 0.75 mmol), trimethyl((1-phenylvinyl)oxy)silane **2a** (96.2 mg, 0.5 mmol) and 5 mL dry DMSO and stirred for 6 h in front of 20 W blue LEDs irradiation at room temperature. The crude material was separated by flash chromatography on silica gel (ethyl acetate: hexanes = 1:10) to give the product **3ua** (14.0 mg, 10%), **3ua'** (76.8 mg, 55%) and **3ua''** (39.1 mg , 28%).

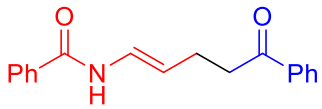
***N*-(5-oxo-5-phenylpent-1-en-3-yl)benzamide (3ua)**



R_f = 0.42 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.90 (d,

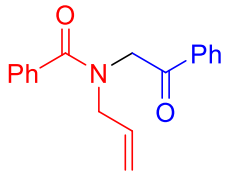
J = 7.8 Hz, 2H), 7.74 (d, *J* = 6.6 Hz, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.45 – 7.40 (m, 3H), 7.37 (t, *J* = 7.2 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 1H), 6.02 – 5.96 (m, 1H), 5.22 (d, *J* = 17.4 Hz, 1H), 5.12 (d, *J* = 10.2 Hz, 2H), 3.53 (dd, *J* = 16.8, 3.6 Hz, 1H), 3.29 (dd, *J* = 17.4, 5.4 Hz, 1H) ppm. ^{13}C NMR (150 MHz, Chloroform-*d*) δ 198.3, 165.6, 136.0, 135.7, 133.3, 132.7, 130.6, 127.8, 127.6, 127.1, 126.0, 115.0, 47.7, 40.8 ppm. HRMS calc'd for $C_{18}H_{18}NO_2^+$: 280.1332 found: 280.1337 $[M+H]^+$.

(*E*)-*N*-(5-oxo-5-phenylpent-1-en-1-yl)benzamide (3ua')



R_f = 0.42 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.96 (m, 2H), 7.79 (d, *J* = 7.6 Hz, 2H), 7.72 (d, *J* = 10.4 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.54 – 7.49 (m, 2H), 7.47 – 7.43 (m, 3H), 7.08 – 7.01 (m, 1H), 5.47 – 5.40 (m, 1H), 3.11 (t, *J* = 7.2 Hz, 2H), 2.54 (q, *J* = 7.2 Hz, 2H) ppm. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.5, 164.4, 136.8, 133.7, 133.2, 131.9, 128.8, 128.7, 128.1, 127.0, 123.7, 112.5, 38.8, 24.5 ppm. HRMS calc'd for $C_{18}H_{18}NO_2^+$: 280.1332 found: 280.1335 $[M+H]^+$.

***N*-allyl-*N*-(2-oxo-2-phenylethyl)benzamide (3ua'')**

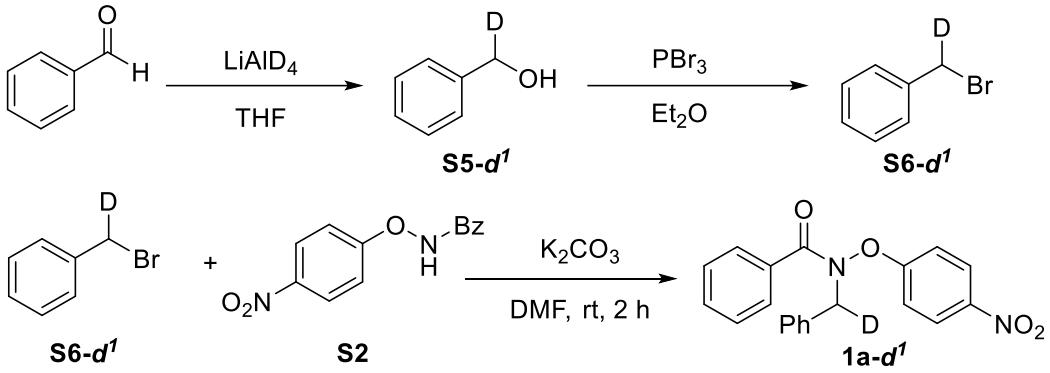


R_f = 0.42 (hexanes: ethyl acetate = 3:1); ^{1}H NMR (600 MHz, Chloroform-*d*): (mixture of rotamers) ^{1}H NMR (600 MHz, Chloroform-d) δ 7.94 (major rotamer, d, J = 7.8 Hz, 1.53H), 7.71 (minor rotamer, d, J = 7.2 Hz, 0.47H), 7.55 – 7.50 (m, 1H), 7.48 – 7.42 (m, 3H), 7.38 – 7.31 (major rotamer, m, 3.26H), 7.27 – 7.24 (minor rotamer, m, 0.74H), 5.85 – 5.83 (minor rotamer, m, 0.24H), 5.75 – 5.69 (major rotamer, m, 0.76H), 5.19 – 5.11 (m, 2H), 4.86 (major rotamer, s, 1.55H), 4.58 (minor rotamer, s, 0.45H), 4.18 (minor rotamer, d, J = 6.0 Hz, 0.43H), 3.93 (major rotamer, d, J = 5.4 Hz, 1.57H) ppm. ^{13}C NMR (150 MHz, Chloroform-*d*) δ 192.8, 171.4, 134.5, 134.3, 132.6, 132.2, 128.9,

127.8, 127.4, 127.0, 125.9, 117.0, 51.9, 49.8 ppm. HRMS calc'd for $C_{18}H_{18}NO_2^+$: 280.1332 found: 280.1329 $[M+H]^+$.

Deuterium experiment

Synthesis of isotope material 1a-*d*[1]



The literature[8] procedure was followed for the synthesis of (bromomethyl-*d*)benzene **S6-*d*[1]**.

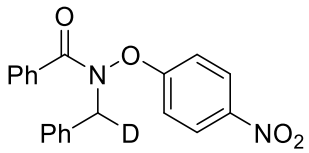
In a nitrogen-filled glove box, $LiAlD_4$ (105 mg, 2.5 mmol) was added to a 50 mL glass vial equipped with a stir bar. The vial was sealed with a teflon-lined septum cap and transferred out of the glove box. A nitrogen balloon was connected to the vial via a needle in the septum to maintain a constant pressure. Anhydrous THF (5 mL) was added to the vial, followed by the addition of a solution benzaldehyde (0.52 mL, 5.1 mmol) in anhydrous THF (5 mL) at 0 °C. The mixture was stirred for 30 minutes at 0 °C. Then, the reaction mixture was carefully quenched by sequential addition of H_2O-15 wt% NaOH solution (Caution: gas evolution). The resulting white slurry was filtered through celite and washed thoroughly with diethyl ether. The combined solution was transferred to a separatory funnel, washed with saturated brine solution (10 mL X 2) and dried over magnesium sulfate. The solvent was removed under reduced pressure. Purification using silica gel column chromatography (0→20% Et_2O/petroleum ether) afforded **S5-*d*[1]** (0.43 g, 78% yield) as colorless oil.

In air, a 40 mL glass vial equipped with a stir bar was sealed with a teflon-lined septum cap, connected to a vacuum manifold via a needle through the septum, and evacuated and back-filled with nitrogen for three cycles. A nitrogen balloon was connected to the

vial via a needle in the septum to maintain a constant pressure. A solution of phosphorus tribromide (1.1 g, 3.9 mmol) in anhydrous Et_2O (10 mL) was then added to the vial via a syringe under nitrogen. The mixture was then stirred at 0 °C for 10 minutes before a solution of **S5-*d*^{1}** (430 mg, 3.9 mmol) in anhydrous Et_2O (10 mL) was added dropwise via a syringe at 0 °C. The reaction mixture was stirred for 20 minutes at 0 °C, quenched with saturated aqueous $NaHCO_3$ (15 mL) at 0 °C, and transferred to a separatory funnel with the aid of Et_2O (10 mL X 3). The combined organic layers were washed with saturated brine solution (50 mL X 3), dried over magnesium sulfate and filtered. The filtrate was collected and the solvent was removed under reduced pressure (Caution: volatile and irritating liquid, avoid using high vacuum). The crude product **S6-*d*^{1}** was used in the next step without further purification.

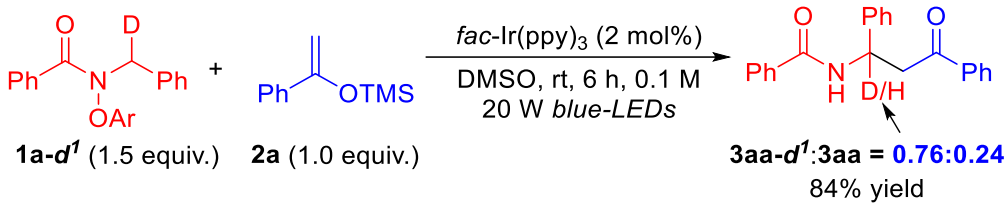
In a dry Schlenk tube equipped with a stirring bar, the (bromomethyl-*d*)benzene **S6-*d*^{1}** (650 mg, 3.8 mmol) and *N*-(4-nitrophenoxy)benzamide **S2** (976 mg, 3.8 mmol) in DMF (4 mL, 1.0 M) was added K_2CO_3 (522 mg, 3.8 mmol) at room temperature. The reaction mixture was allowed to stir for 2 h and was then diluted with 5 mL H_2O. The mixture was extracted with ethyl acetate (3 X 10 mL). The combined organic layers were washed with saturated brine solution (20 mL), dried (Na_2SO_4), filtered and evaporated. Purification by column chromatography on silica gel eluting with (petroleum ether: ethyl acetate = 8:1) to give white solid **1a-*d*^{1}** (660 mg, 50%).

***N*-(4-nitrophenoxy)-*N*-(phenylmethyl-*d*)benzamide (1a-*d*^{1})**



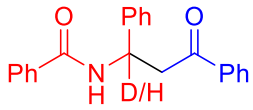
m.p. = 134 – 135 °C, R_f = 0.40 (ethyl acetate:methanol= 5:1), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 9.2 Hz, 2H), 7.54 – 7.51 (m, 2H), 7.39 – 7.35 (m, 1H), 7.27 – 7.25 (m, 7H), 6.98 (d, *J* = 9.2 Hz, 2H), 4.93 (s, 1H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.0, 162.7, 143.3, 134.5, 132.9, 131.7, 128.9, 128.8, 128.42, 128.39, 128.0, 126.1, 113.8, 53.1 (t, *J* = 21.3 Hz) ppm. HRMS calc'd for $C_{20}H_{16}DN_2O_4^+$, 350.1246, found: 350.1244 $[M+H]^+$.

Mechanistic experiments with isotope material 1a-*d*^{1}



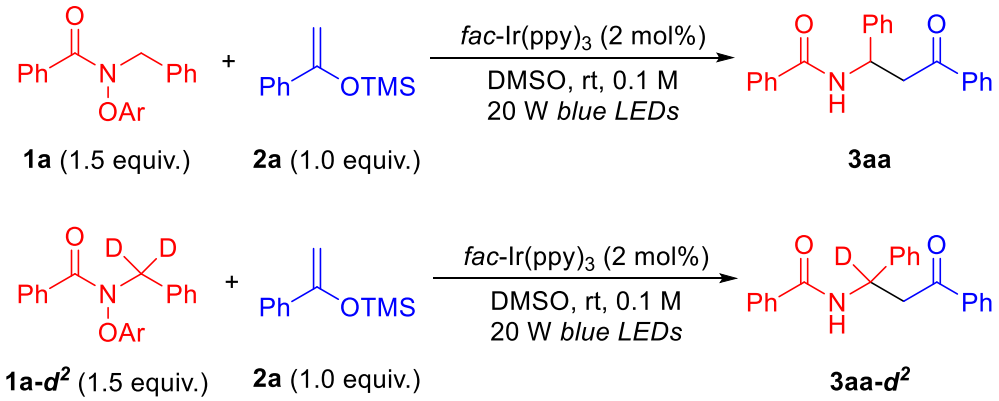
The reaction was performed following the **GP3** with *N*-(4-nitrophenoxy)-*N*-(phenylmethyl-*d*)benzamide **1a-*d*^{1}** (104.8 mg, 0.3 mmol), trimethyl((1-phenylvinyl)oxy)silane **2a** (38.5 mg, 0.2 mmol) and 2 mL dry DMSO and stirred for 6 h in front of 20 W blue LEDs irradiation at room temperature. The crude material was separated by flash chromatography on silica gel (ethyl acetate:hexanes = 1:10) to give the product **3aa-*d*^{1}** (55.7 mg, 84%).

Deuterated coupling product (3aa-*d*^{1})

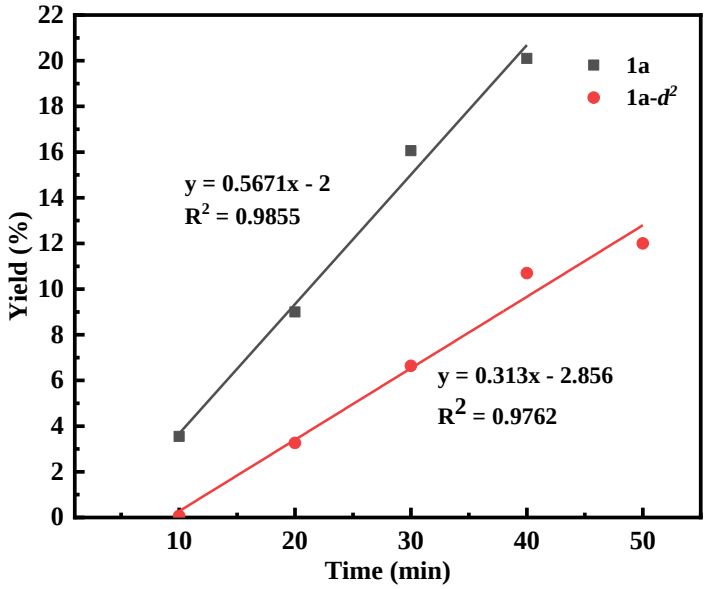


R_f = 0.42 (hexanes:ethyl acetate = 3:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.90 (m, 2H), 7.85 – 7.82 (m, 2H), 7.65 (s, 1H), 7.56 (td, *J* = 7.2, 1.2 Hz, 1H), 7.52 – 7.48 (m, 1H), 7.46 – 7.39 (m, 6H), 7.33 – 7.29 (m, 2H), 7.25 – 7.21 (m, 1H), 5.80 – 5.75 (m, 0.24 H), 3.87 (dd, *J* = 16.8, 5.2 Hz, 1H), 3.52 (dd, *J* = 16.8, 5.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, Chloroform-d) δ 199.2, 166.7, 140.9, 136.7, 134.3, 133.6, 131.6, 128.8, 128.7, 128.6, 128.2, 127.5, 127.1, 126.5, 50.1 (t, *J* = 29.2 Hz), 42.9 ppm.

Intermolecular Parallel Reaction



An oven-dried 10 mL reaction vial equipped with a stir bar was charged with amide **1a** or **1a-*d*²** (0.15 mmol) and *fac*-Ir(ppy)$_3$ (2 mol%, 1.3 mg) under a nitrogen atmosphere in a glove box. A solution of silyl enol ether **2a** (0.1 mmol, 19.2 mg) in 1.0 mL dry DMSO was added by a "Eppendorf" brand 1000 µL pipettor to the reaction vial. The vial was capped, removed from the glove box, and the mixture was stirred at room temperature for 10 minutes. Then the reaction was placed in the photoreactor and the light was turned on. The reaction mixture was stirred for different times at this temperature. After the reaction period, the lights were turned off, the reaction mixture was opened to air and quenched with three drops of H_2O. The aqueous layer was extracted with ethyl acetate (3 X 15 mL) and the combined organic layers were washed with saturated brine solution, dried (Na_2SO_4), filtered and evaporated. The crude mixture was analyzed by ^{1}H-NMR with CH_2Br_2 as an internal standard.



$$KIE = k_H/k_D = 1.8$$

Figure S12. Reaction time-course data for amide **1a** and **1a-*d*₂**

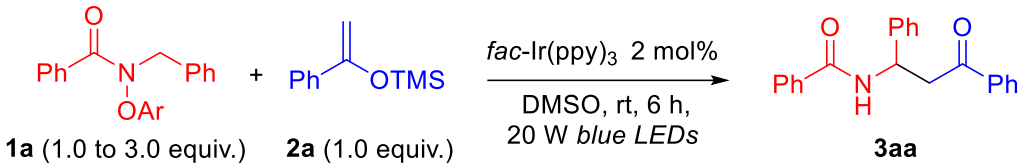
Kinetic Experiments

General procedure for kinetic experiments

An oven-dried 10 mL reaction vial equipped with a stir bar was charged with amide **1a**

(0.15 mmol) and *fac*-Ir(ppy)$_3$ (2 mol%) under a nitrogen atmosphere in a glove box. A solution of silyl enol ether **2a** (0.1 mmol) in 1.0 mL dry DMSO was added by a "Eppendorf" brand 1000 μL pipettor to the reaction vial. The vial was capped, removed from the glove box, and the mixture was stirred at room temperature for 10 minutes. Then the reaction was placed in the photoreactor and the light was turned on. The reaction mixture was stirred for different times at this temperature. The initial reaction rate was determined by plotting product formation over time (up to approximately 20% conversion). This reaction progress plot used to determine d[P]/dt for this is provided below.

(a) Rate order determination of amide 1a



1a (1.0 to 3.0 equiv.) **2a** (1.0 equiv.) **3aa**

Table S12. Rates determined by varying [Amide]

1a (M)	Average Rate (M/min)
0.10	2.33 x 10^{-4}
0.15	3.20 x 10^{-4}
0.20	3.79 x 10^{-4}
0.25	4.31 x 10^{-4}
0.30	4.80 x 10^{-4}

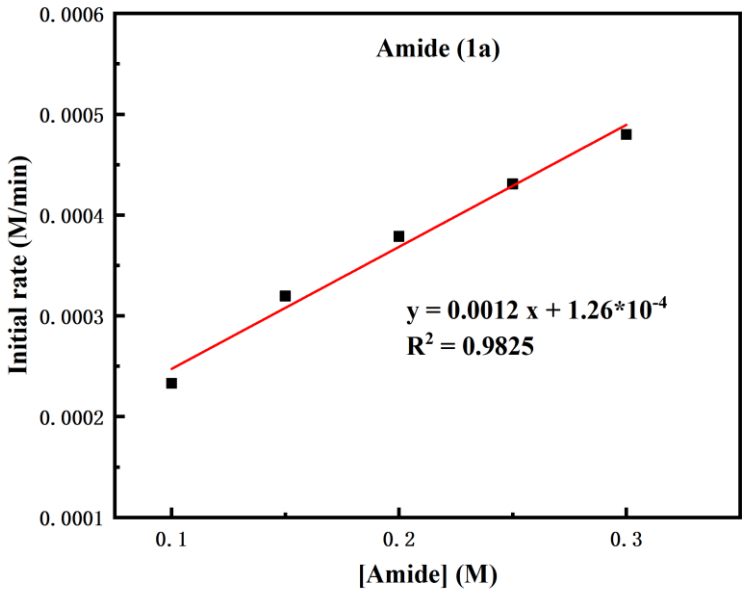
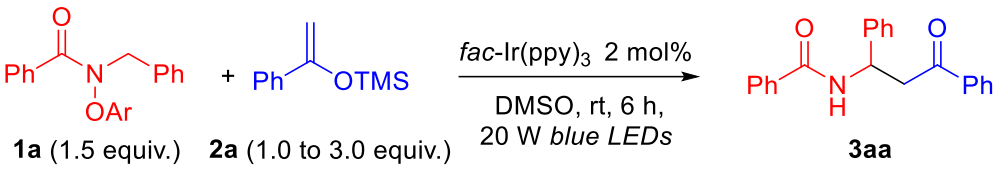


Figure S13. Initial rate / [Amide] method: first-order in Amide **1a**.

(b) Rate order determination of silyl enol ether 2a



1a (1.5 equiv.) **2a** (1.0 to 3.0 equiv.) **3aa**

Table S13. Rates determined by varying [silyl enol ether]

2a (M)	Average Rate (M/min)
0.10	5.21×10^{-4}
0.15	5.23×10^{-4}
0.20	5.26×10^{-4}
0.25	5.28×10^{-4}
0.30	5.21×10^{-4}

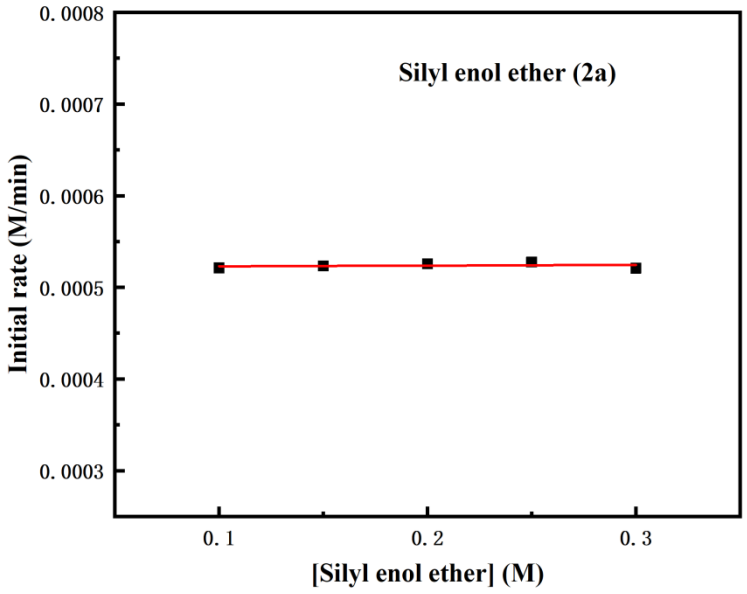
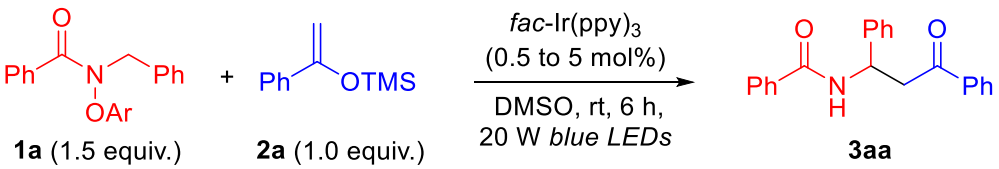


Figure S14. Initial rate / [silyl enol ether] method: zero-order in silyl enol ether **2a**.

(c) Rate order determination of *fac*-Ir(ppy)$_3$



1a (1.5 equiv.) **2a** (1.0 equiv.) **3aa**

Table S14. Rates determined by varying [*fac*-Ir(ppy)$_3$]

fac-Ir(ppy)$_3$ (M)	Average Rate (M/min)
0.005	1.99 x 10^{-4}
0.010	3.22 x 10^{-4}
0.020	4.94 x 10^{-4}
0.030	4.93 x 10^{-4}
0.040	4.93 x 10^{-4}
0.050	4.92 x 10^{-4}

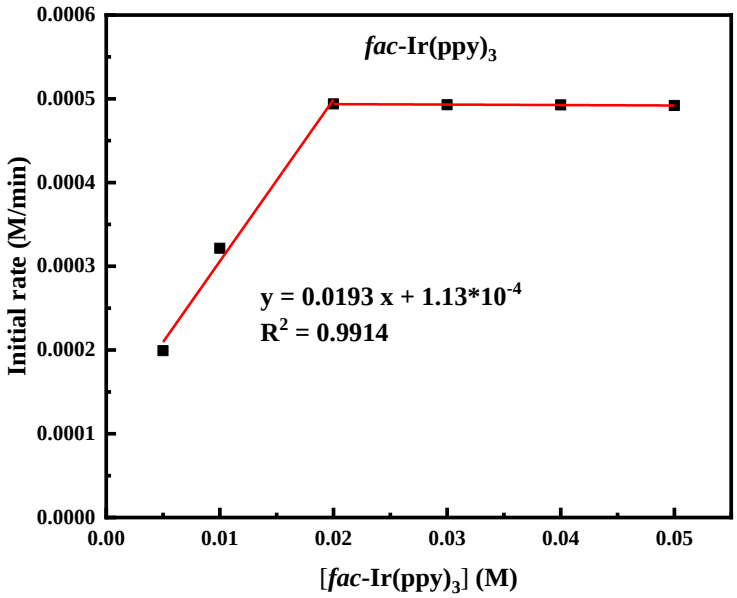


Figure S15. Initial rate / [*fac*-Ir(ppy)$_3$] method: first-order at 0 < [*fac*-Ir(ppy)$_3$] < 2 mol% and zero-order at [*fac*-Ir(ppy)$_3$] > 2 mol%).

Supplementary references

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NMR spectra

Figure S16. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-benzyl-*N*-(4-nitrophenoxy)benzamide (1a)

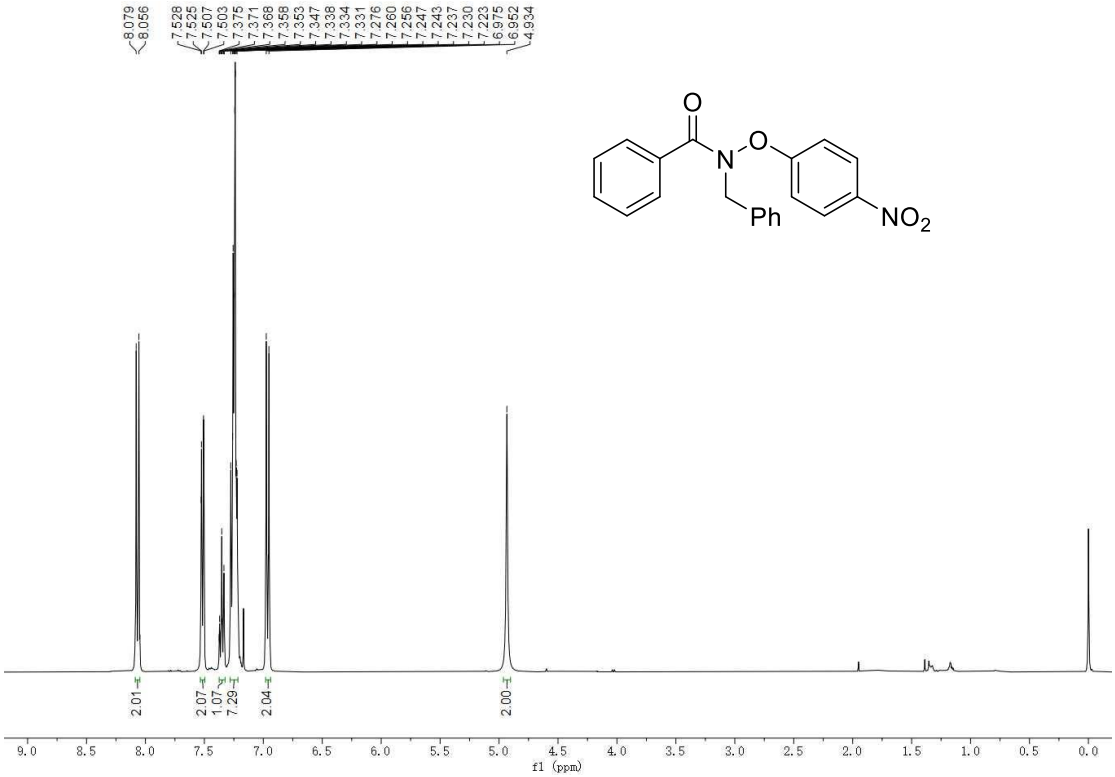

Figure S17. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-benzyl-*N*-(4-nitrophenoxy)benzamide (1a)

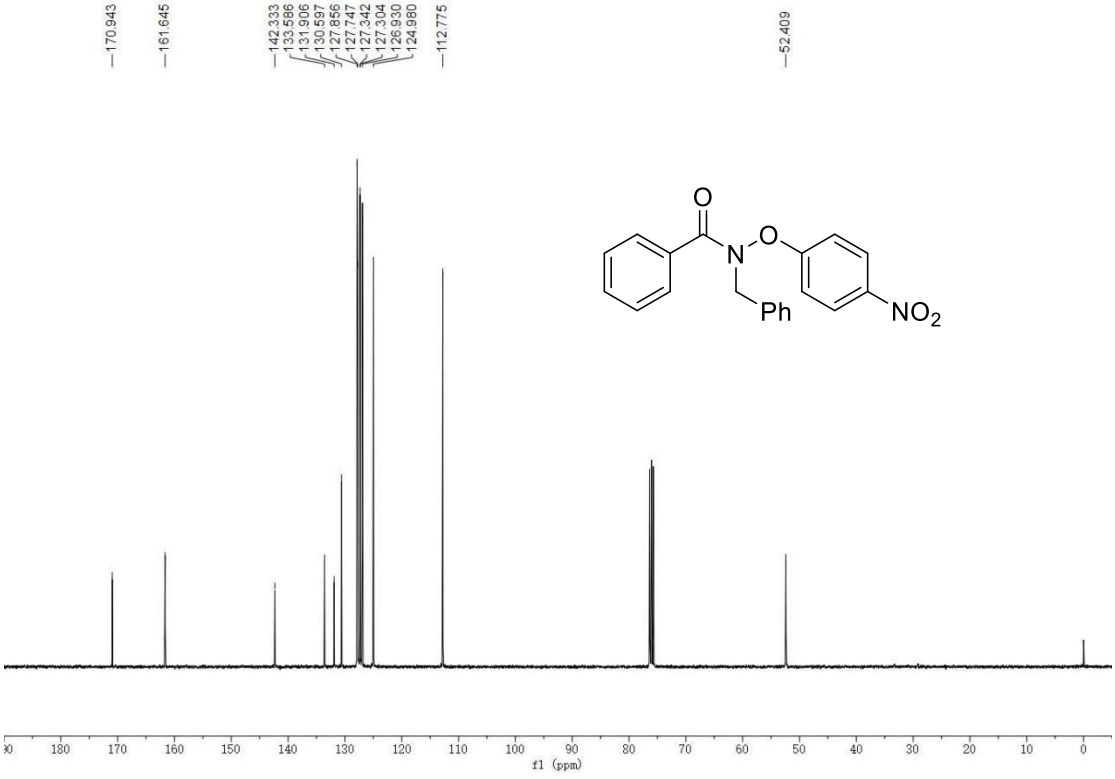

Figure S18. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-benzyl-*N*-(2-nitrophenoxy)benzamide (1a-I)

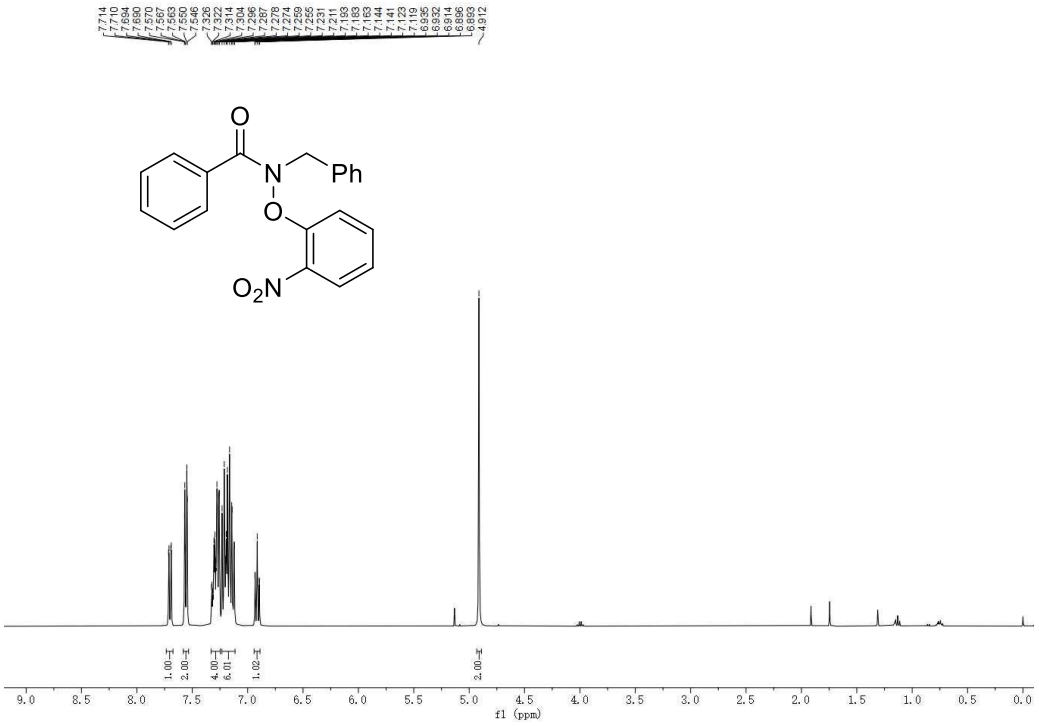

Figure S19. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-benzyl-*N*-(2-nitrophenoxy)benzamide (1a-I)

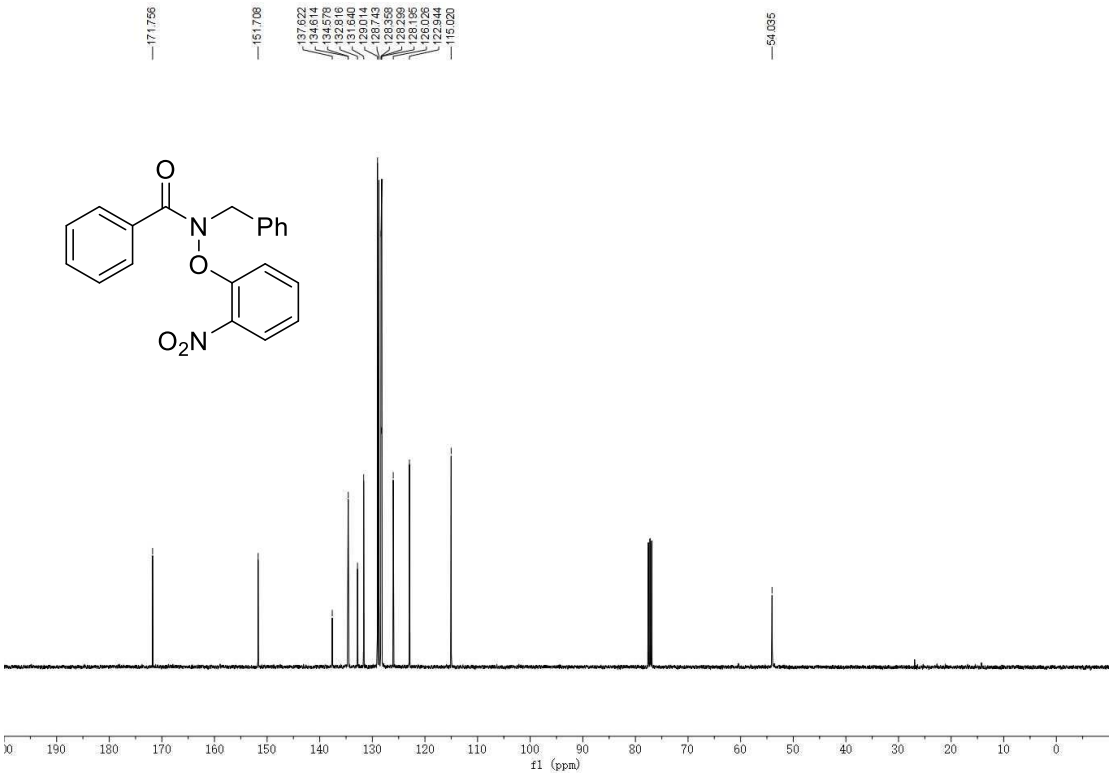

Figure S20. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-benzyl-*N*-(2,4-dinitrophenoxy)benzamide (1a-II)

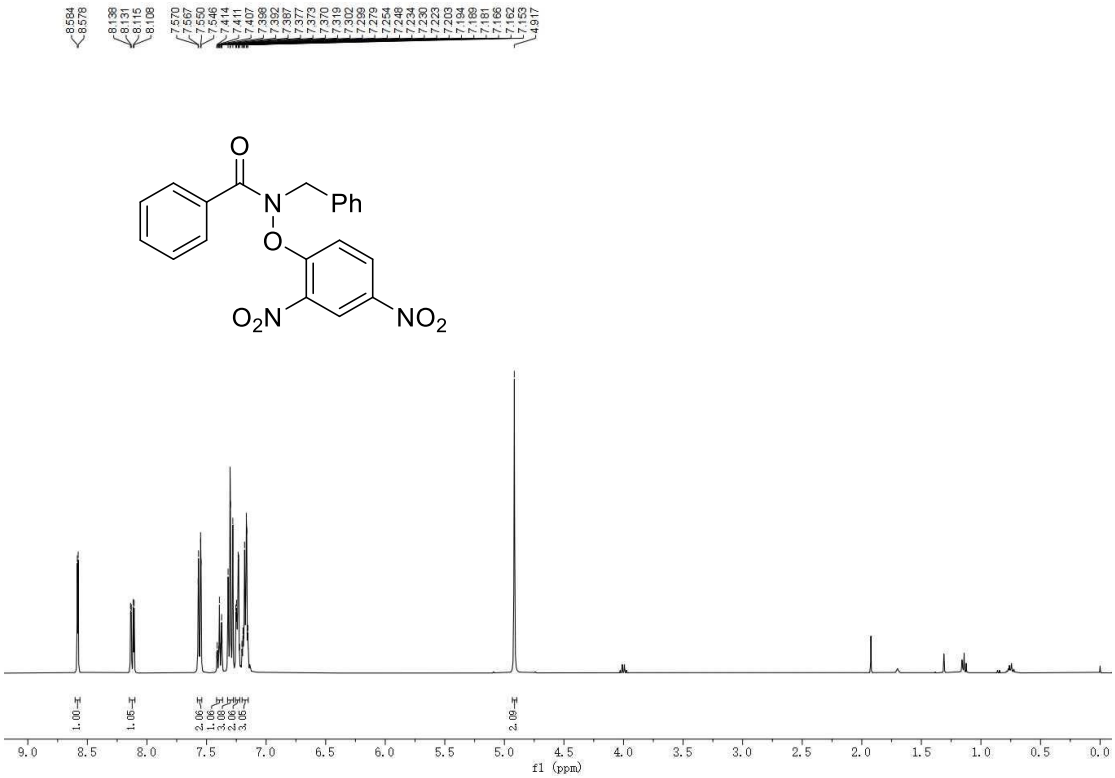

Figure S21. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-benzyl-*N*-(2,4-dinitrophenoxy)benzamide (1a-II)

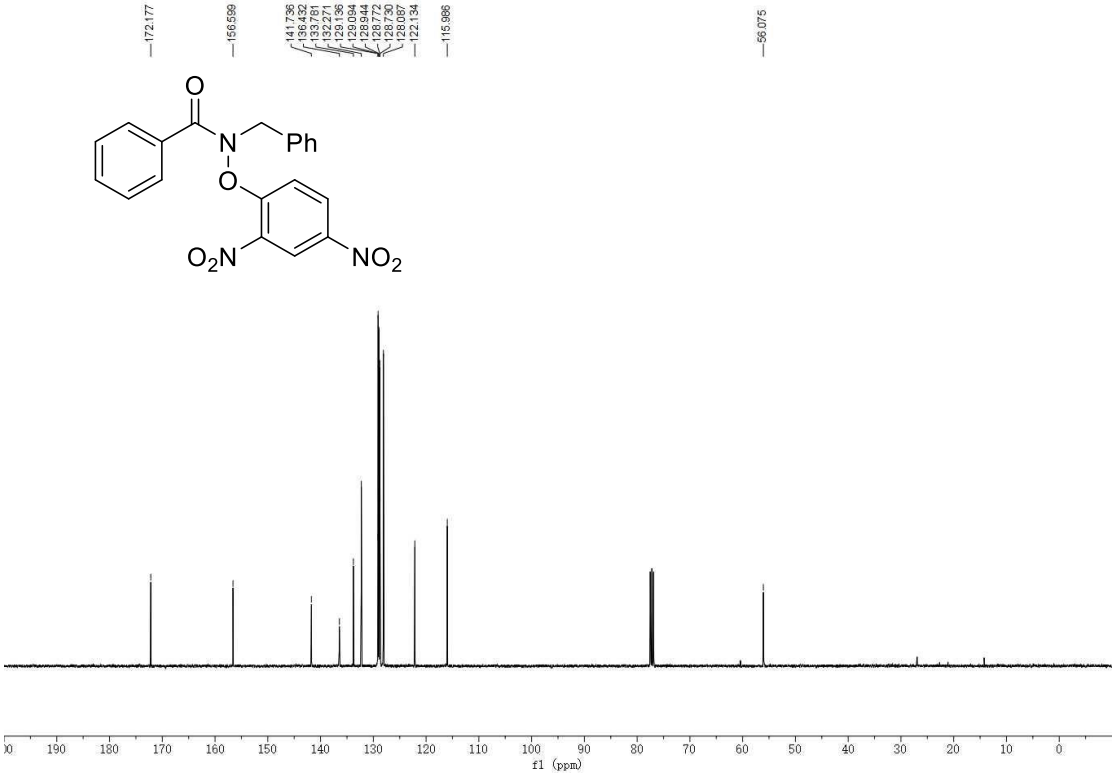

Figure S22. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-benzyl-*N*-(4-cyanophenoxy)benzamide (1a-III)

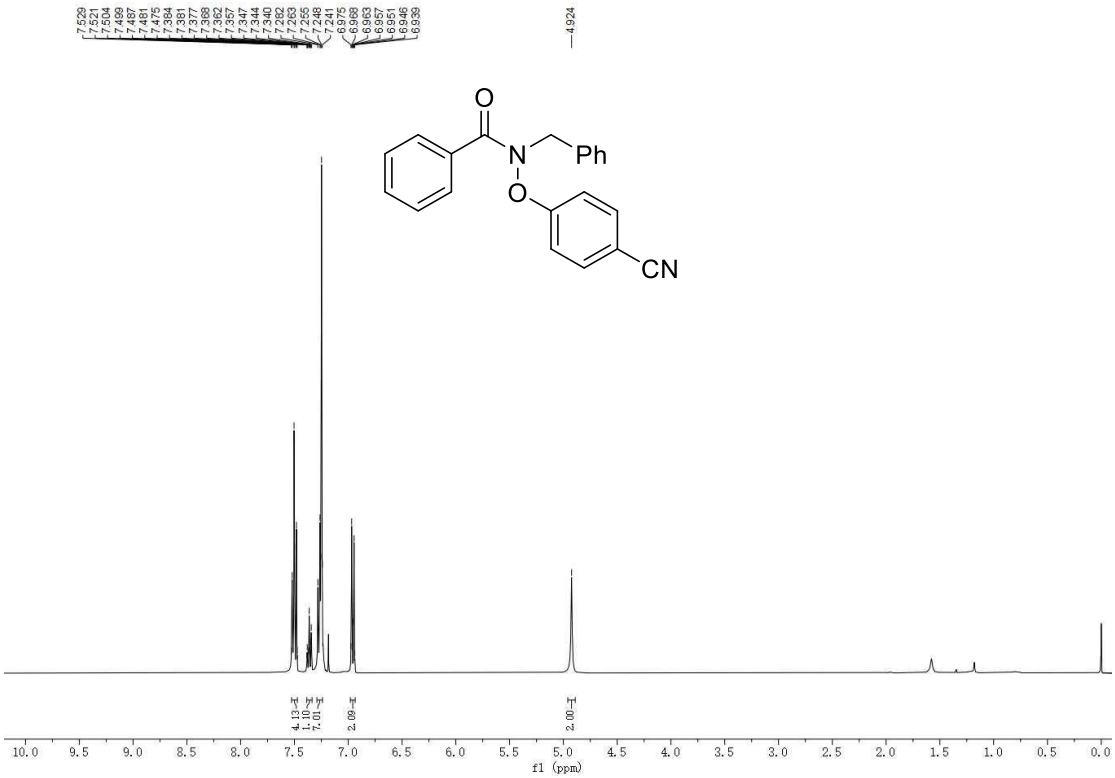

Figure S23. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-benzyl-*N*-(4-cyanophenoxy)benzamide (1a-III)

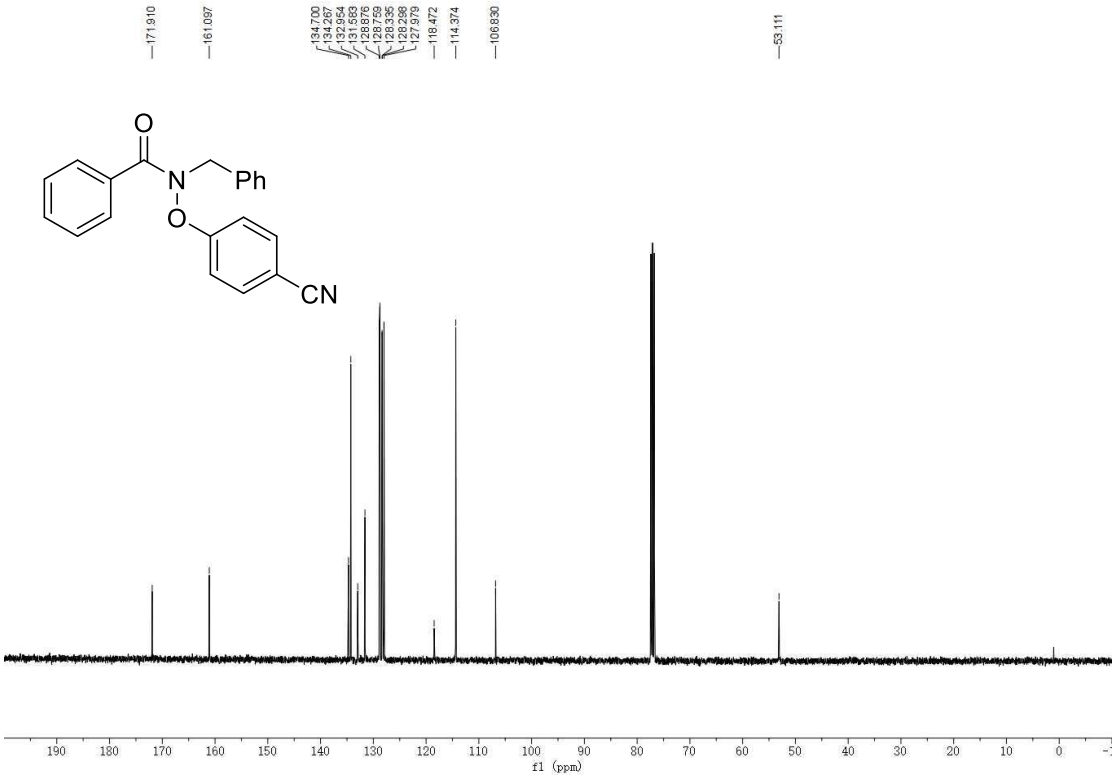

Figure S24. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-benzyl-*N*-phenoxybenzamide (1a-IV)

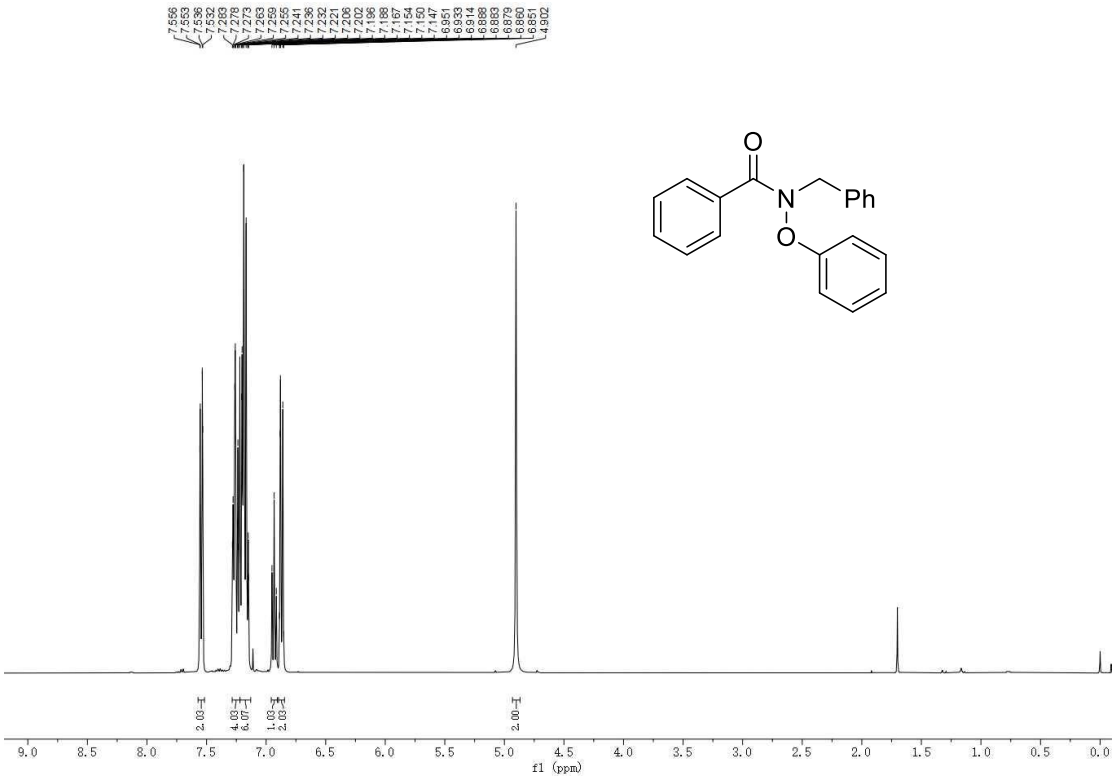

Figure S25. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-benzyl-*N*-phenoxybenzamide (1a-IV)

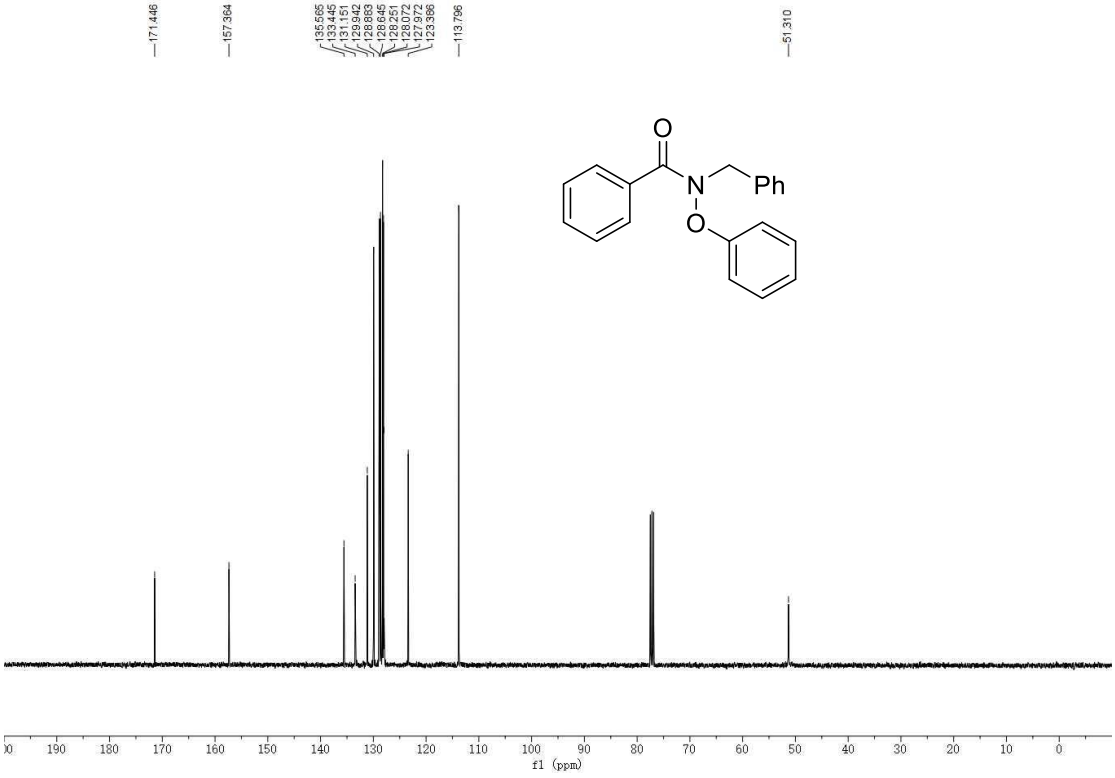

Figure S26. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-benzyl-3-methoxy-*N*-(4-nitrophenoxy)benzamide (1b)

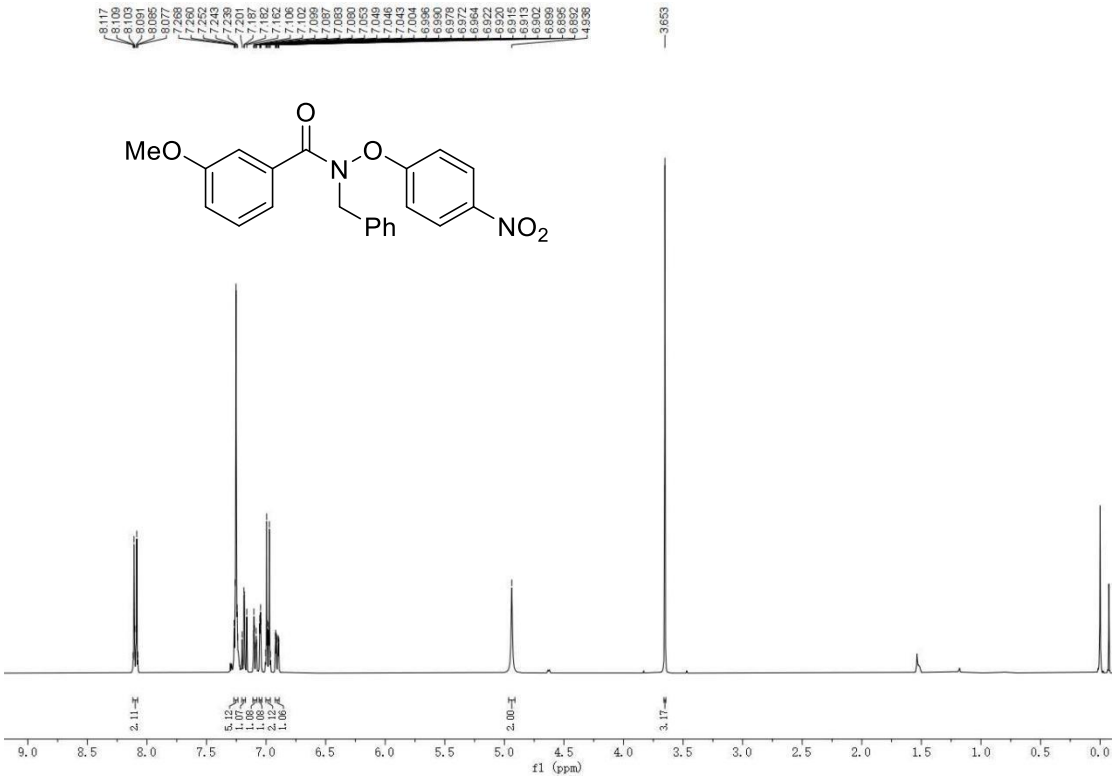

Figure S27. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-benzyl-3-methoxy-*N*-(4-nitrophenoxy)benzamide (1b)

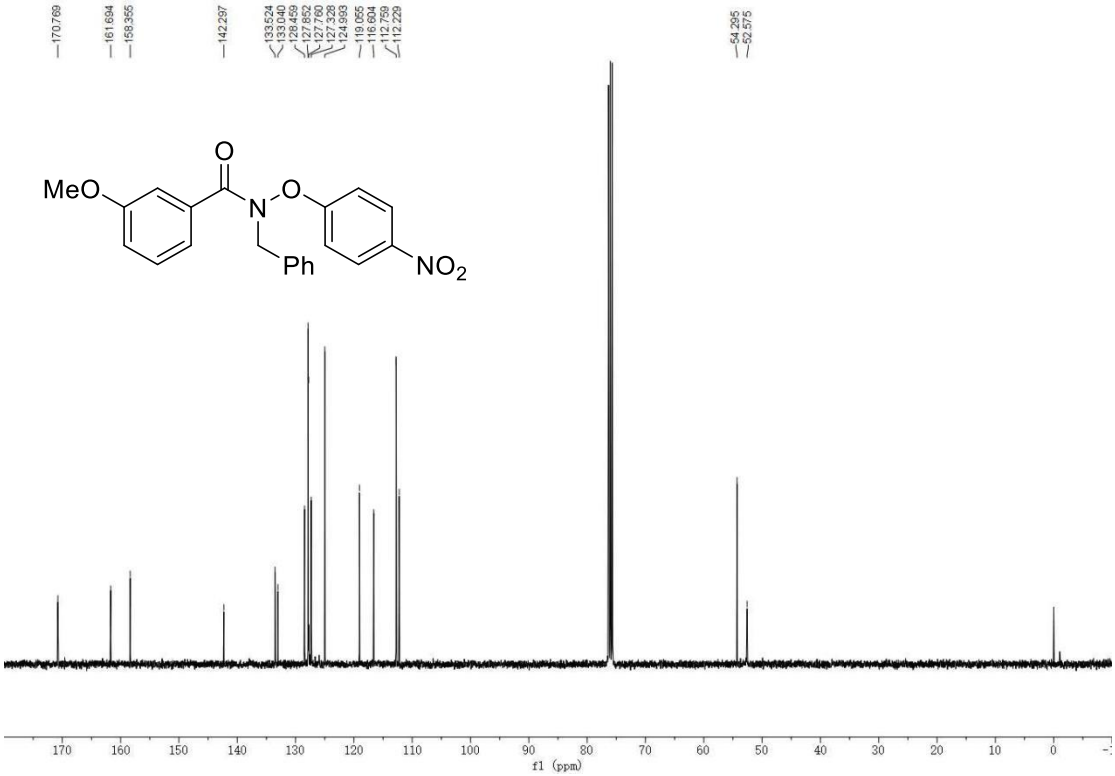

Figure S28. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-benzyl-*N*-(4-nitrophenoxy)-4-(trifluoromethyl)benzamide (1c)

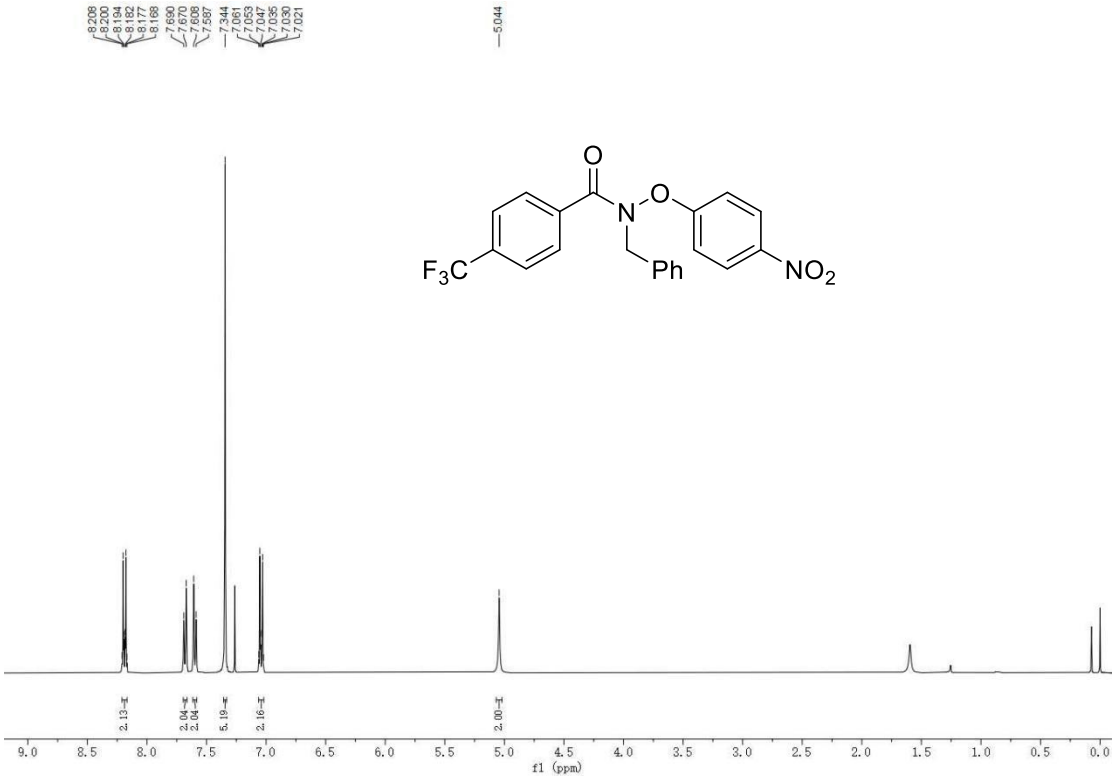

Figure S29. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-benzyl-*N*-(4-nitrophenoxy)-4-(trifluoromethyl)benzamide (1c)

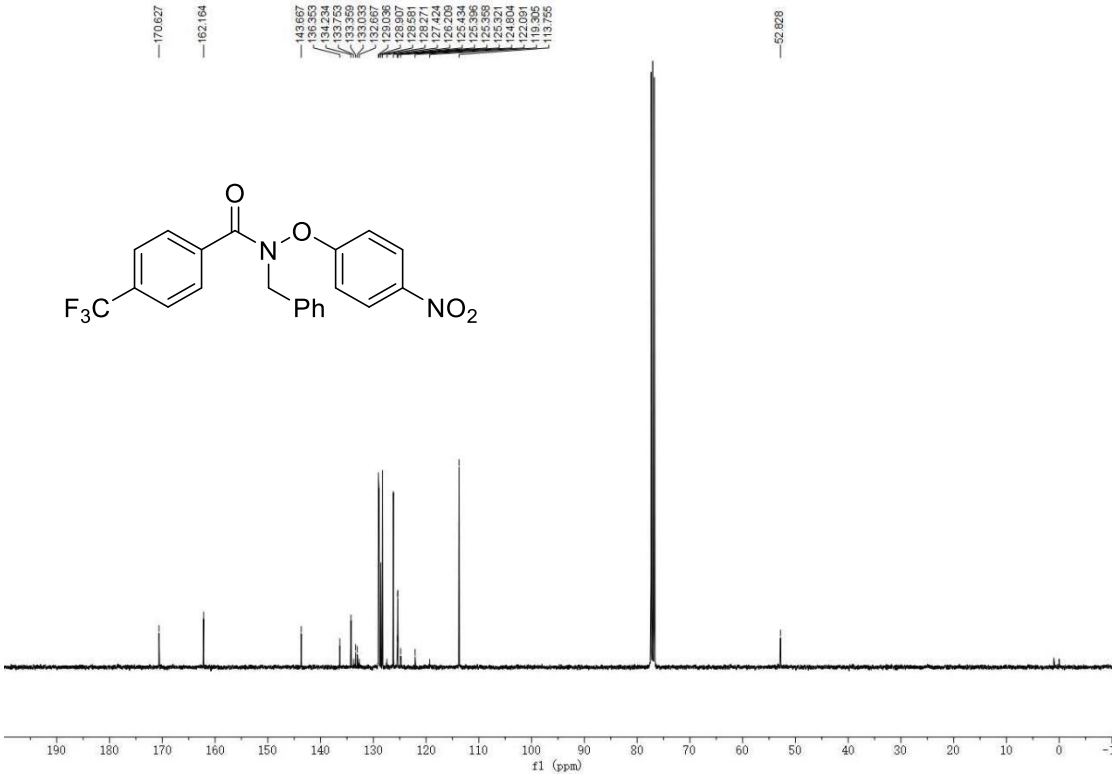

Figure S30. ^{19}F NMR spectra (376 MHz, Chloroform-*d*) of *N*-benzyl-*N*-(4-nitrophenoxy)-1-naphthamide (1c)

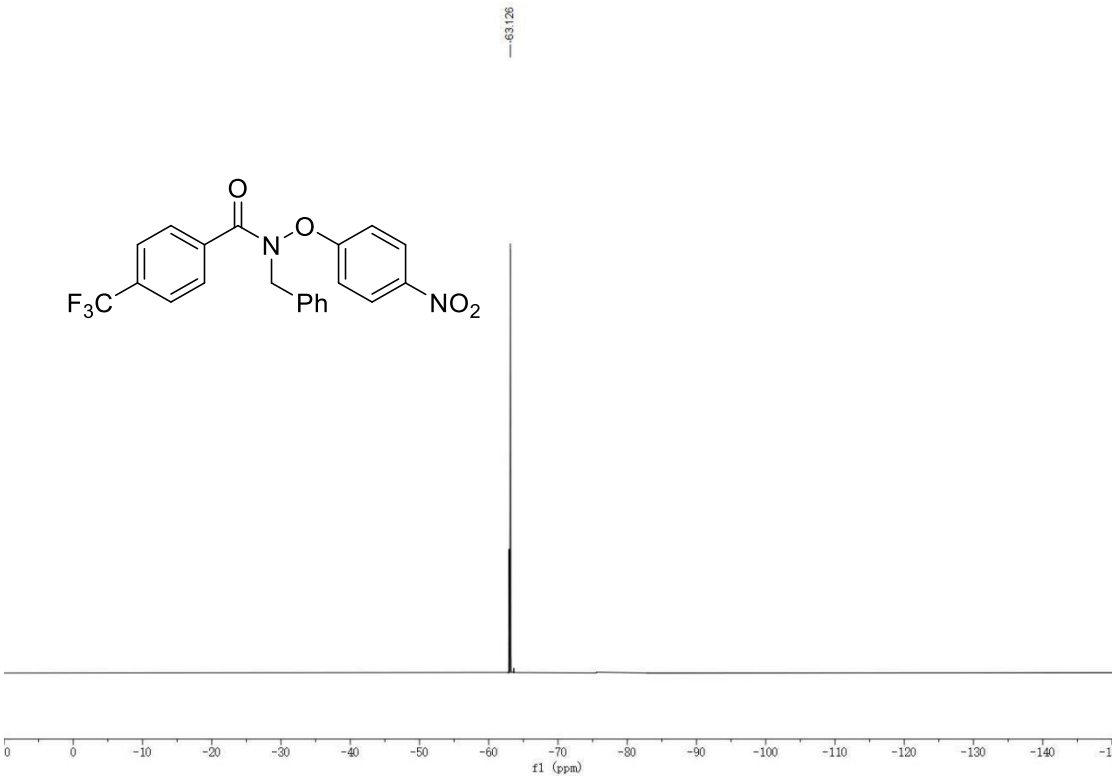

Figure S31. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-benzyl-*N*-(4-nitrophenoxy)-1-naphthamide (1d)

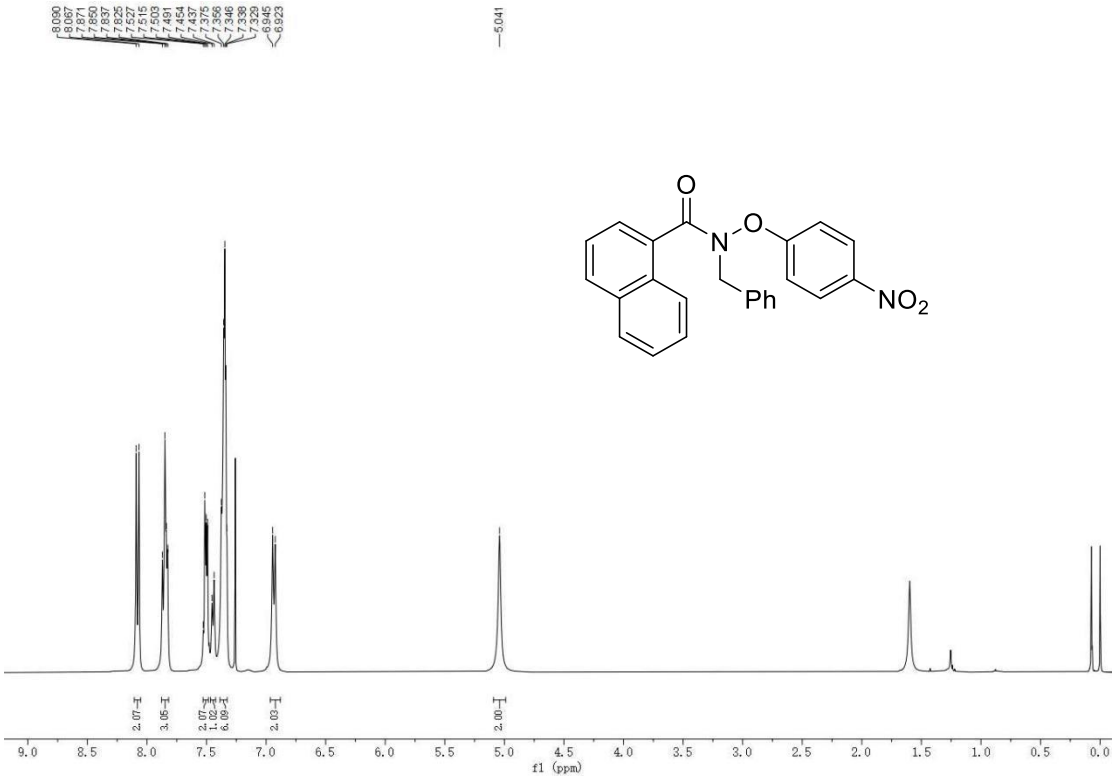

Figure S32. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-benzyl-*N*-(4-nitrophenoxy)-1-naphthamide (1d)

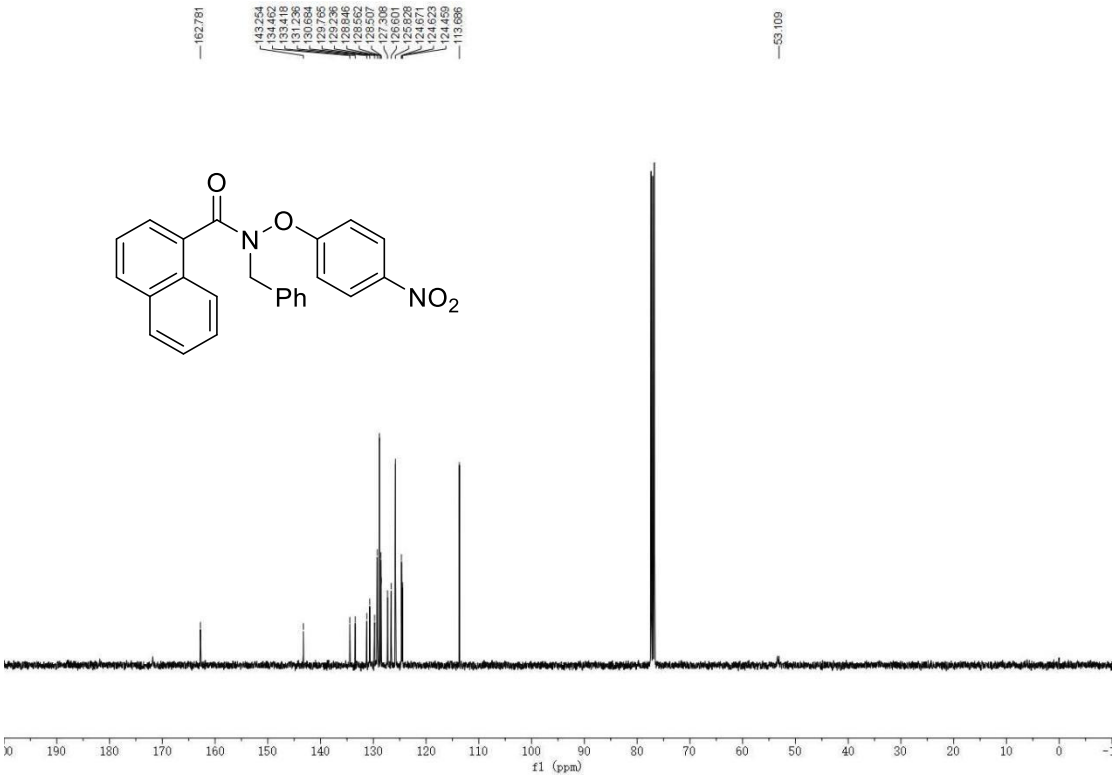

Figure S33. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-benzyl-*N*-(4-nitrophenoxy)furan-2-carboxamide (1e)

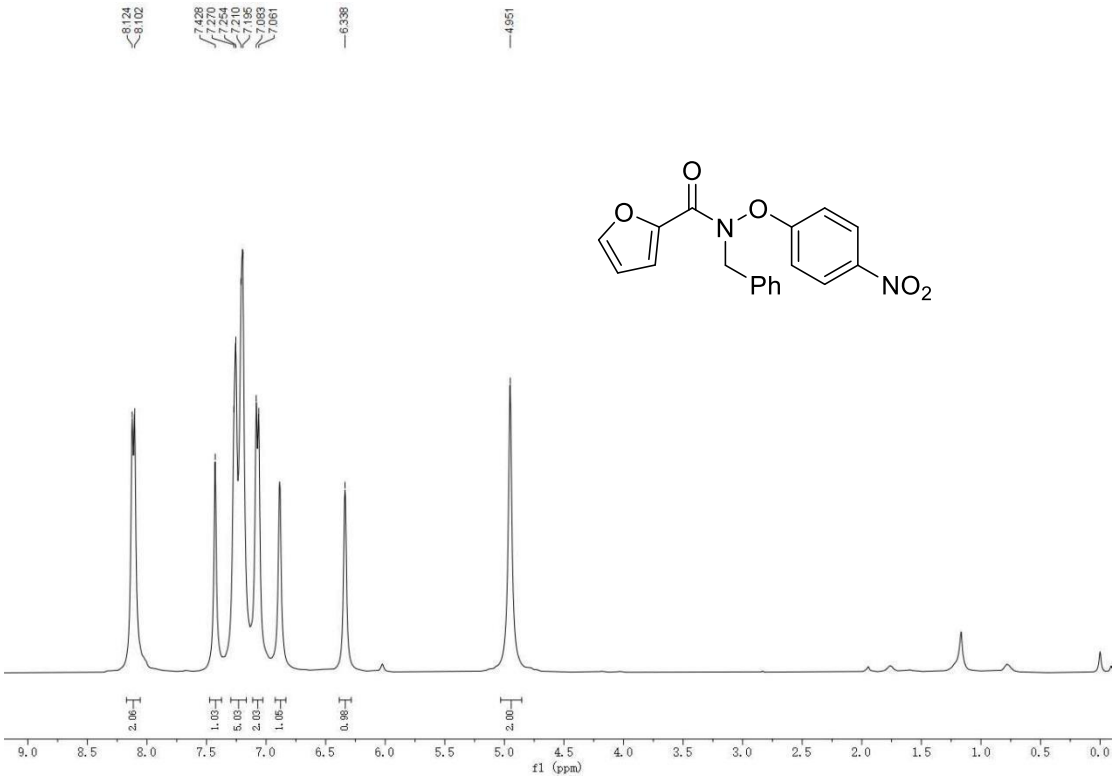

Figure S34. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-benzyl-*N*-(4-nitrophenoxy)furan-2-carboxamide (1e)

Figure S35. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-benzyl-*N*-(4-nitrophenoxy)acrylamide (1f)

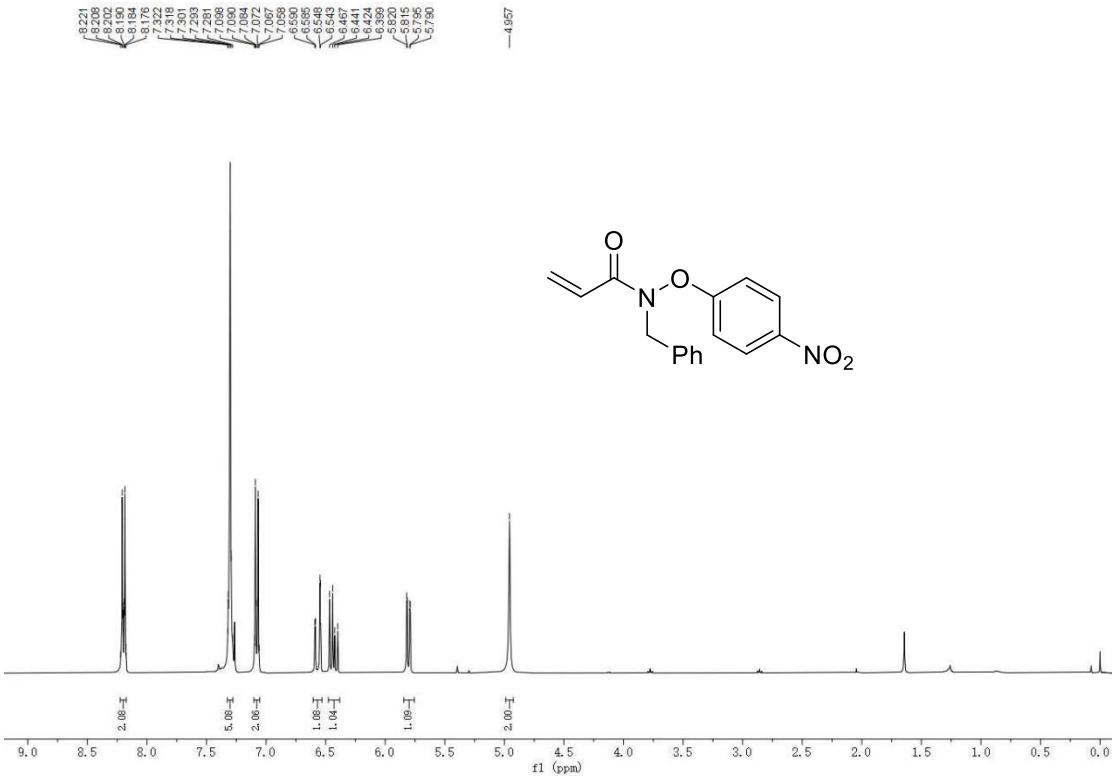

Figure S36. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-benzyl-*N*-(4-nitrophenoxy)acrylamide (1f)

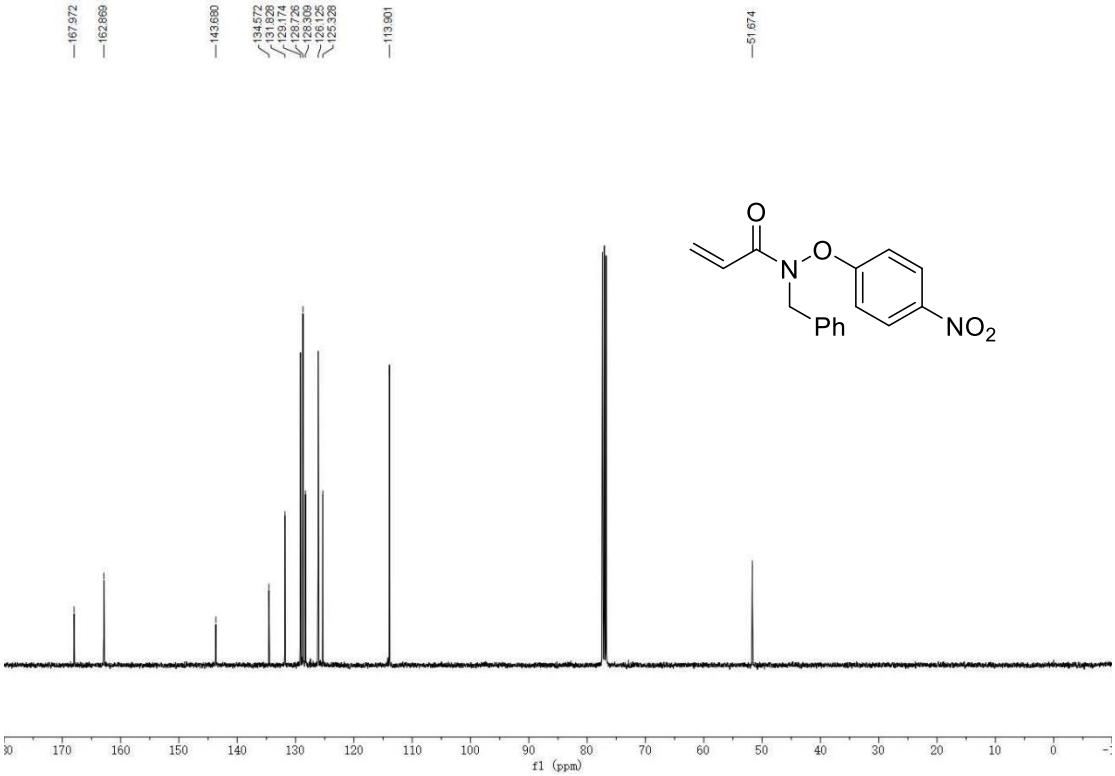

Figure S37. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of (*E*)-*N*-benzyl-*N*-(4-nitrophenoxy)cinnamamide (1g)

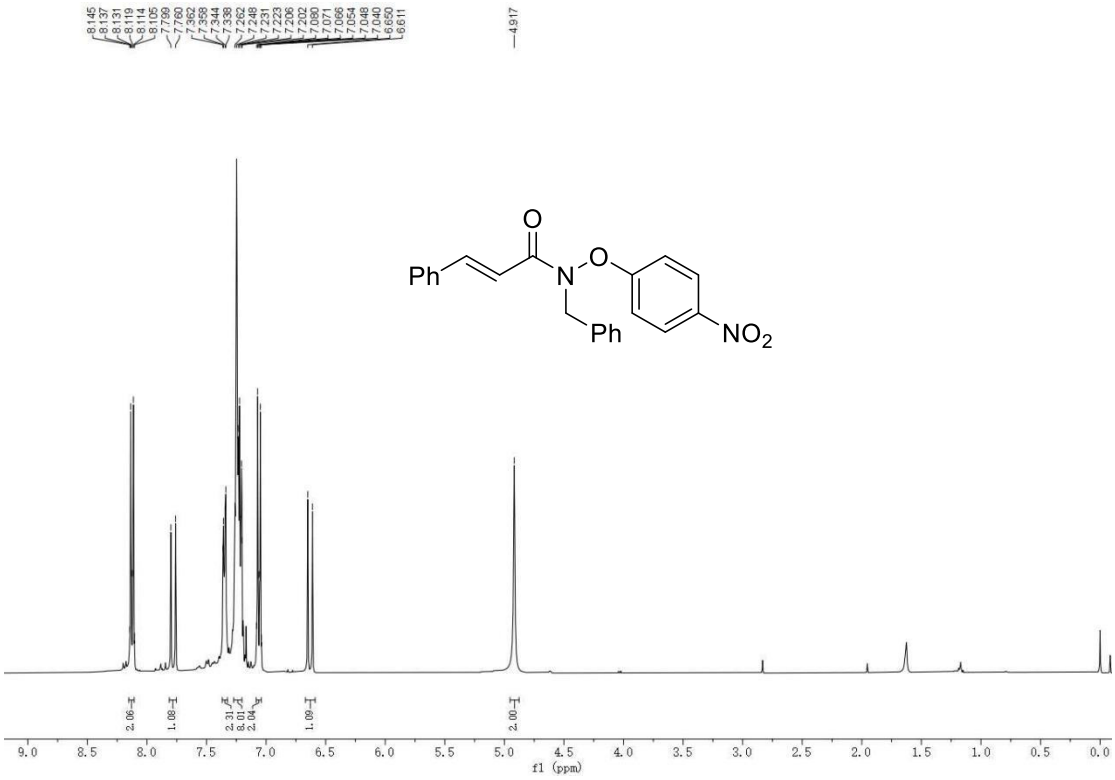

Figure S38. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of (*E*)-*N*-benzyl-*N*-(4-nitrophenoxy)cinnamamide (1g)

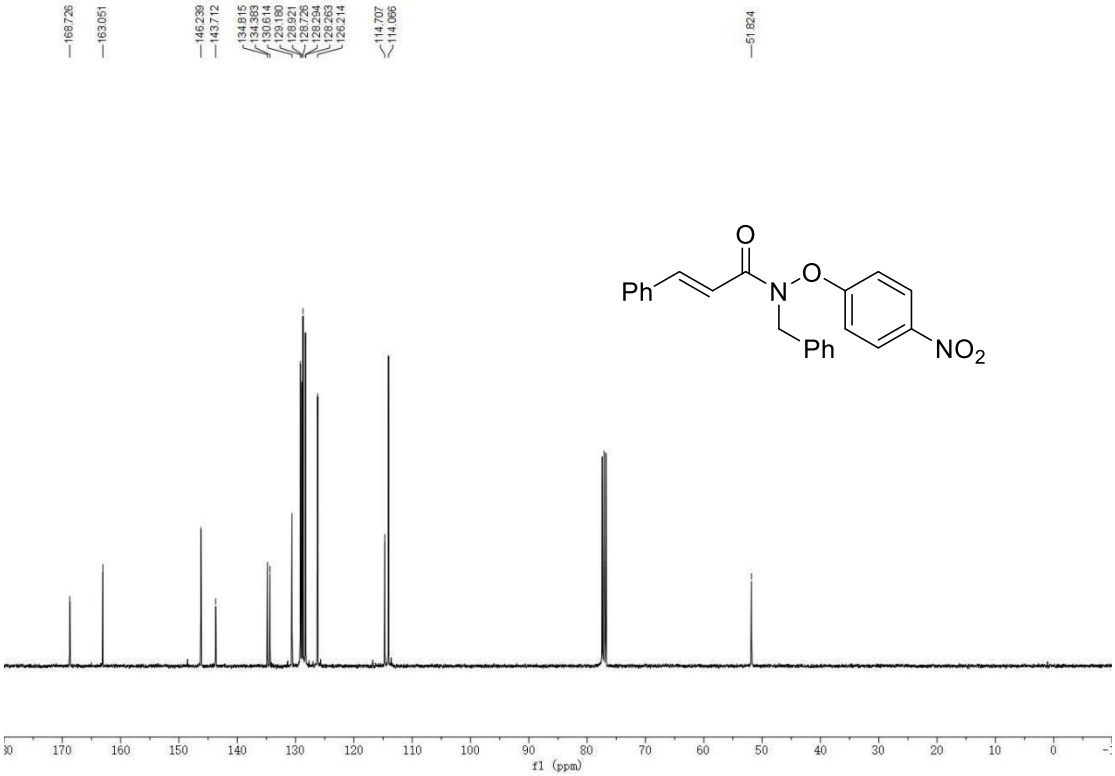

Figure S39. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-benzyl-*N*-(4-nitrophenoxy)but-2-ynamide (1h)

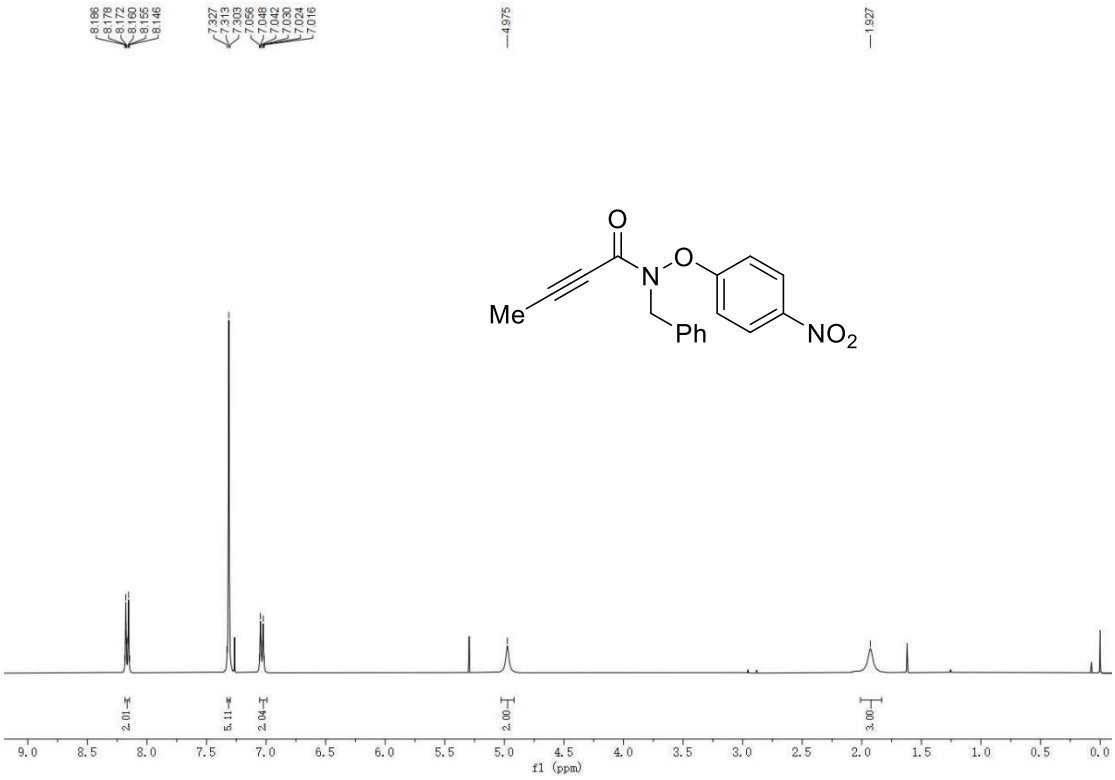

Figure S40. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-benzyl-*N*-(4-nitrophenoxy)but-2-ynamide (1h)

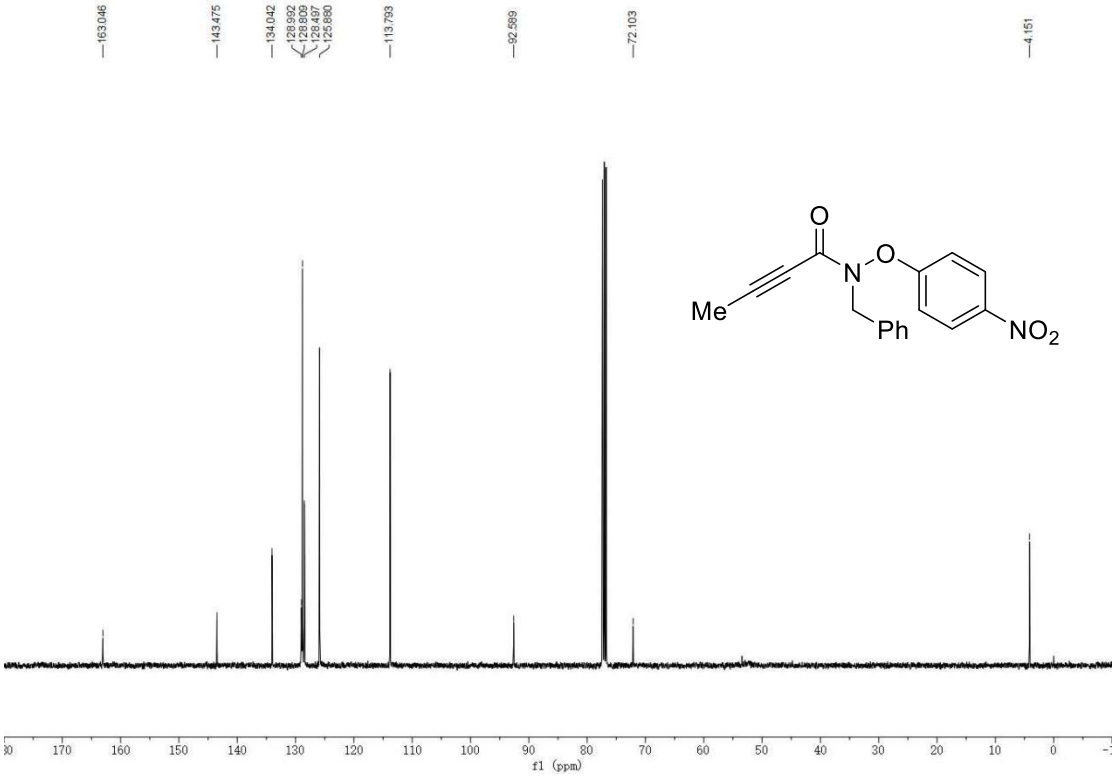

Figure S41. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-benzyl-2-methoxy-*N*-(4-nitrophenoxy)acetamide (1i)

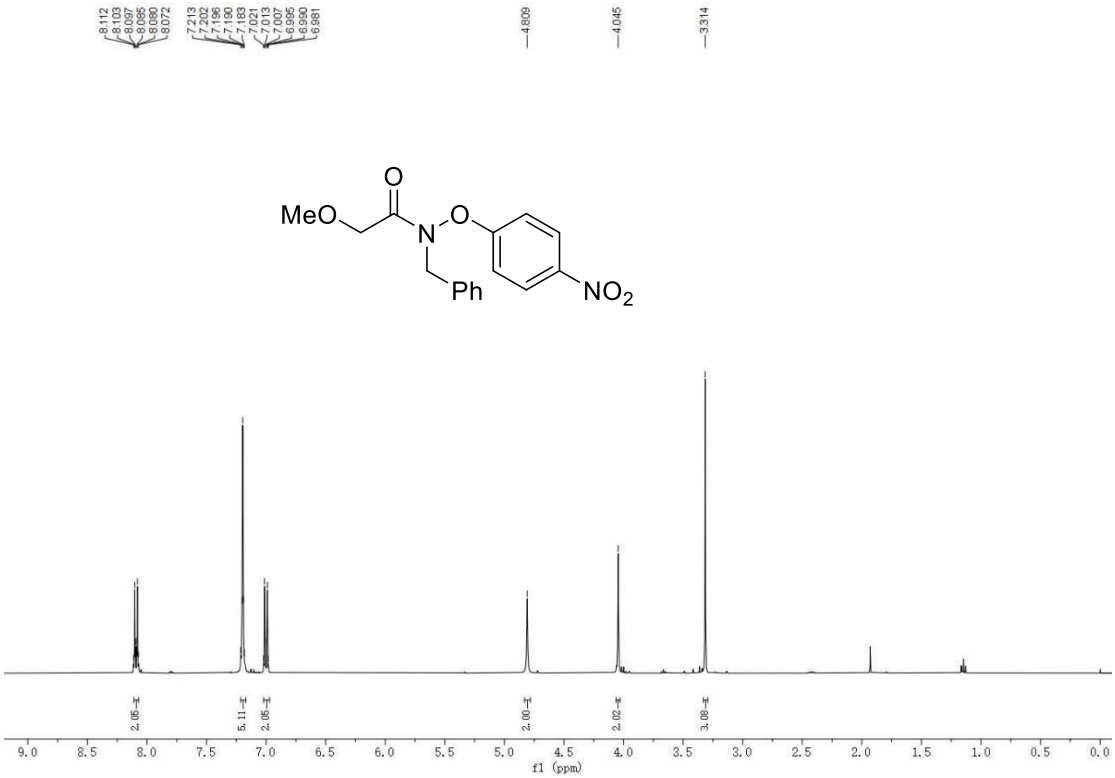

Figure S42. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-benzyl-2-methoxy-*N*-(4-nitrophenoxy)acetamide (1i)

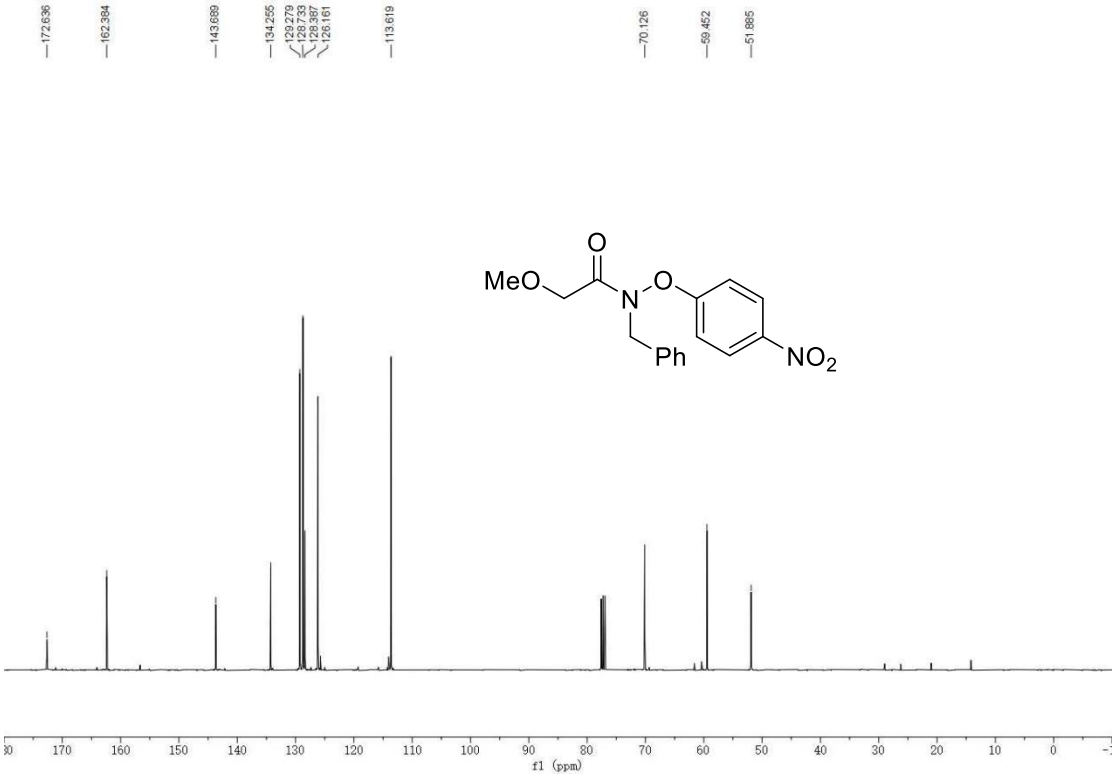

Figure S43. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-benzyl-*N*-(4-nitrophenoxy)cyclobutanecarboxamide (1j)

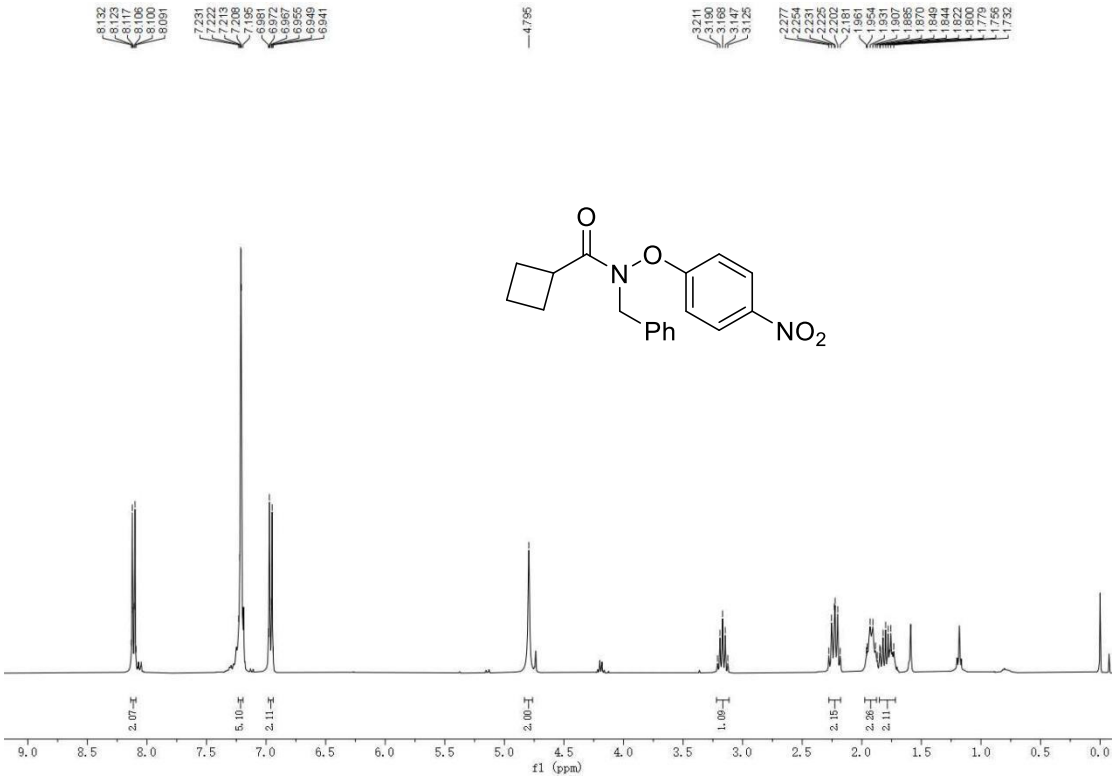

Figure S44. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-benzyl-*N*-(4-nitrophenoxy)cyclobutanecarboxamide (1j)

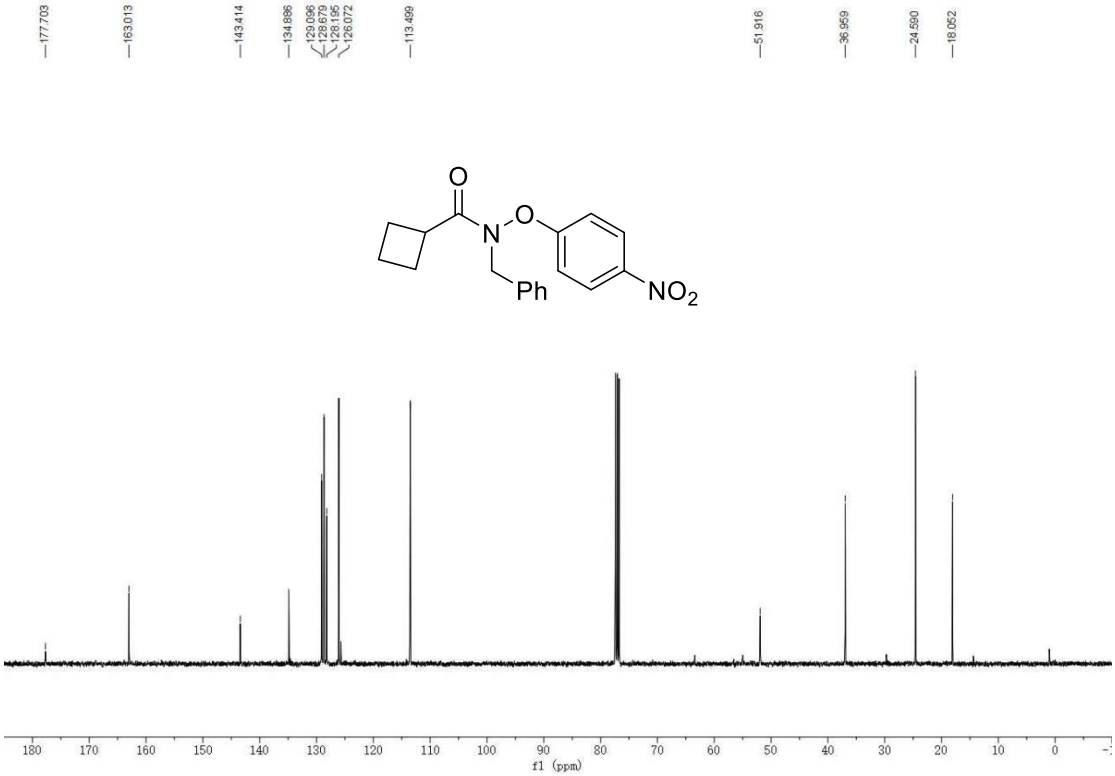

Figure S45. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-benzyl-*N*-(4-nitrophenoxy)cyclopentanecarboxamide (1k)

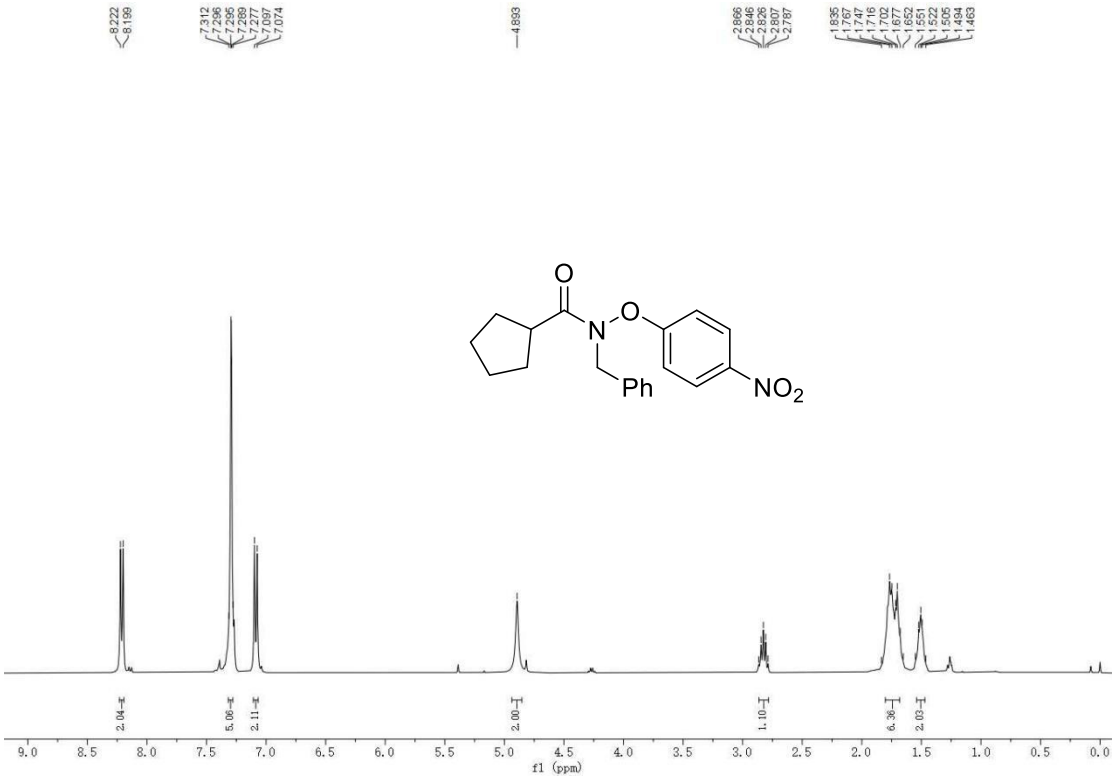

Figure S46. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-benzyl-*N*-(4-nitrophenoxy)cyclopentanecarboxamide (1k)

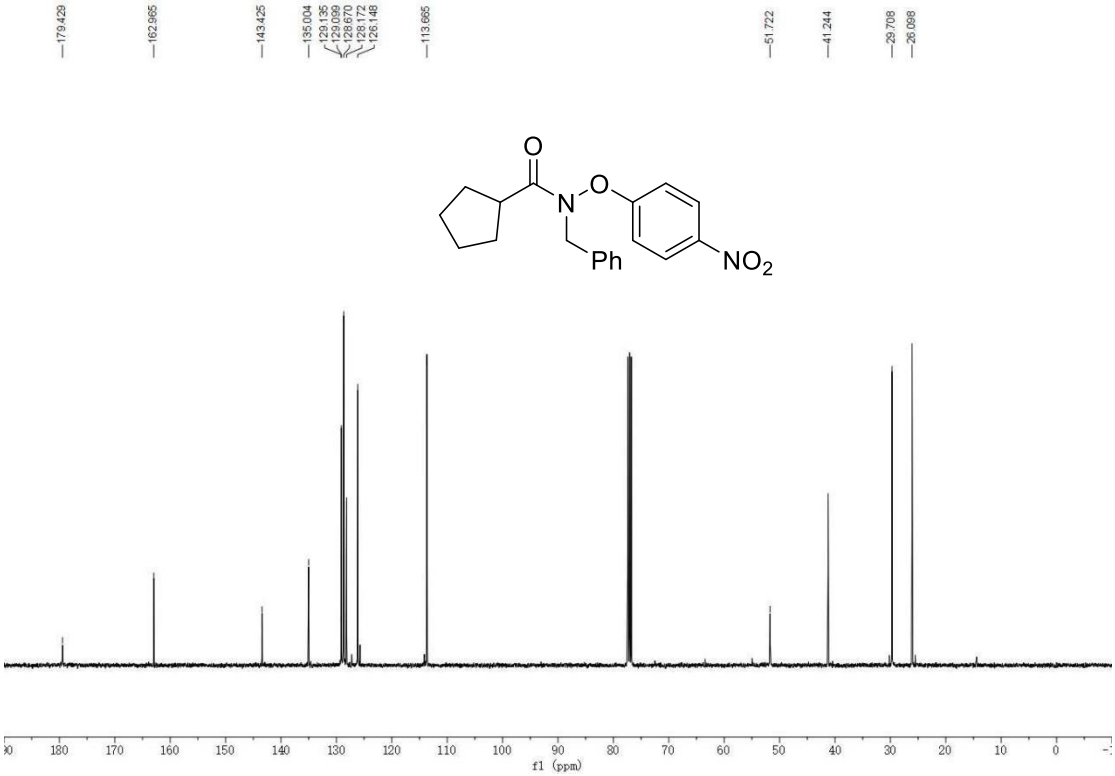

Figure S47. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-benzyl-*N*-(4-nitrophenoxy)cyclohexanecarboxamide (1l)

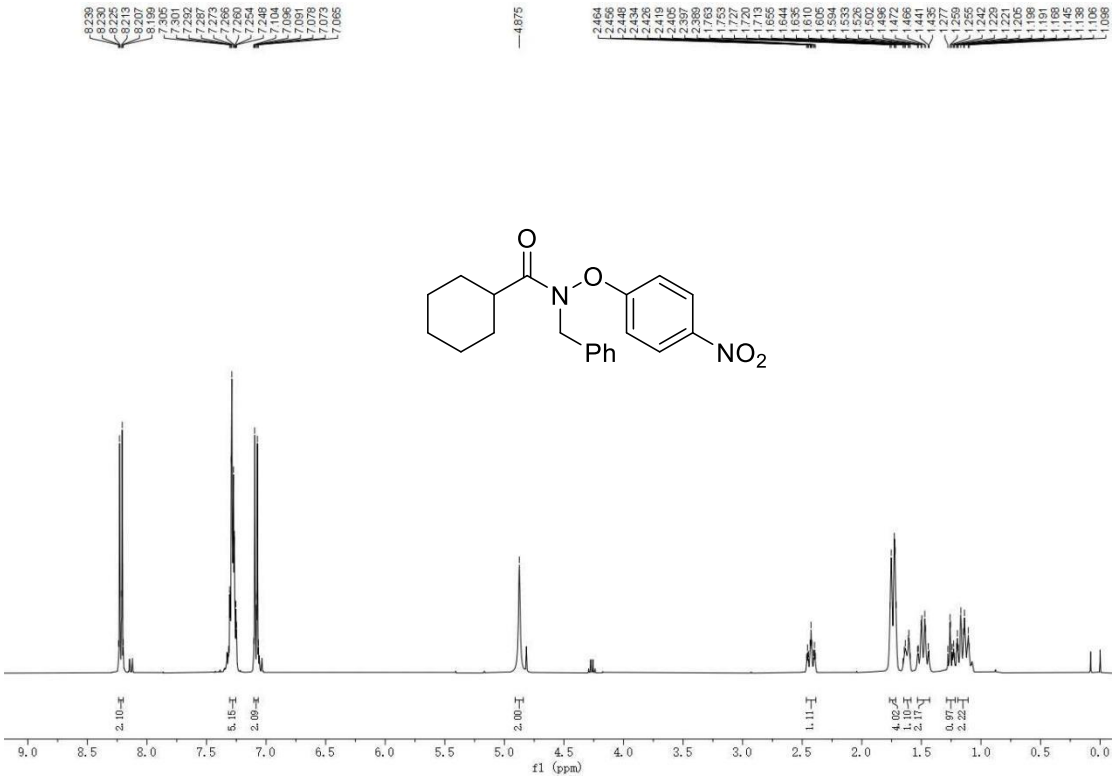

Figure S48. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-benzyl-*N*-(4-nitrophenoxy)cyclohexanecarboxamide (1l)

Figure S49. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of methyl benzyl(4-nitrophenoxy)carbamate (1m)

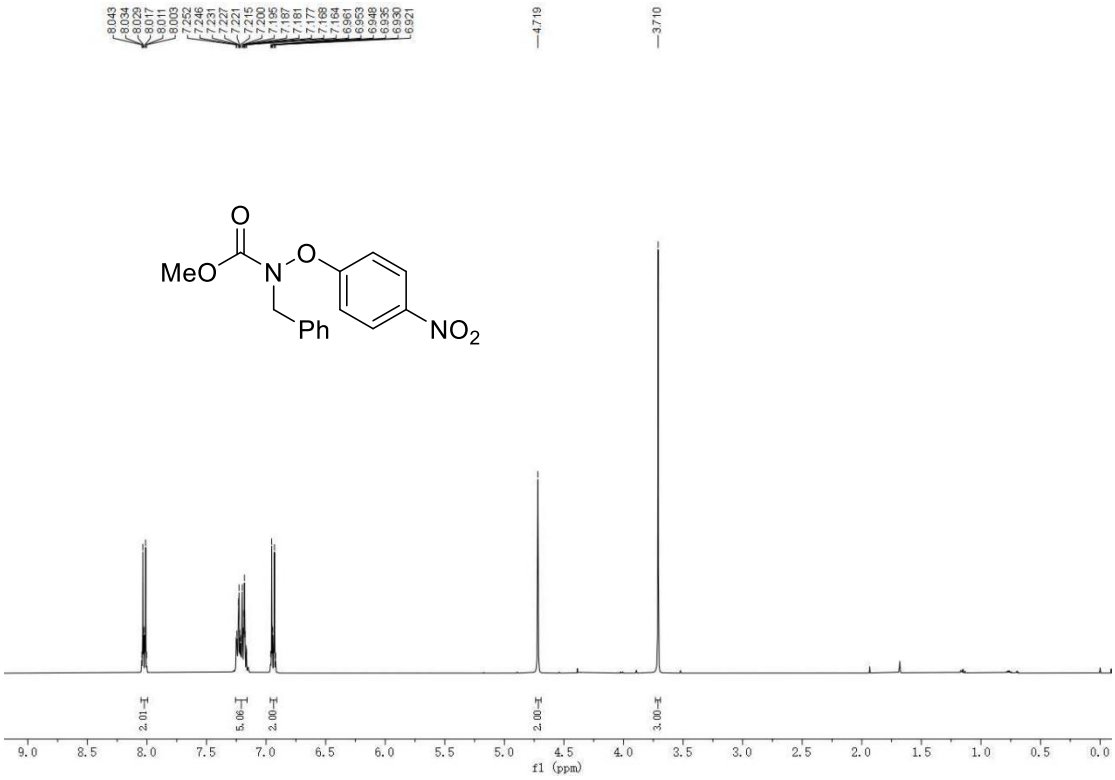

Figure S50. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of methyl benzyl(4-nitrophenoxy)carbamate (1m)

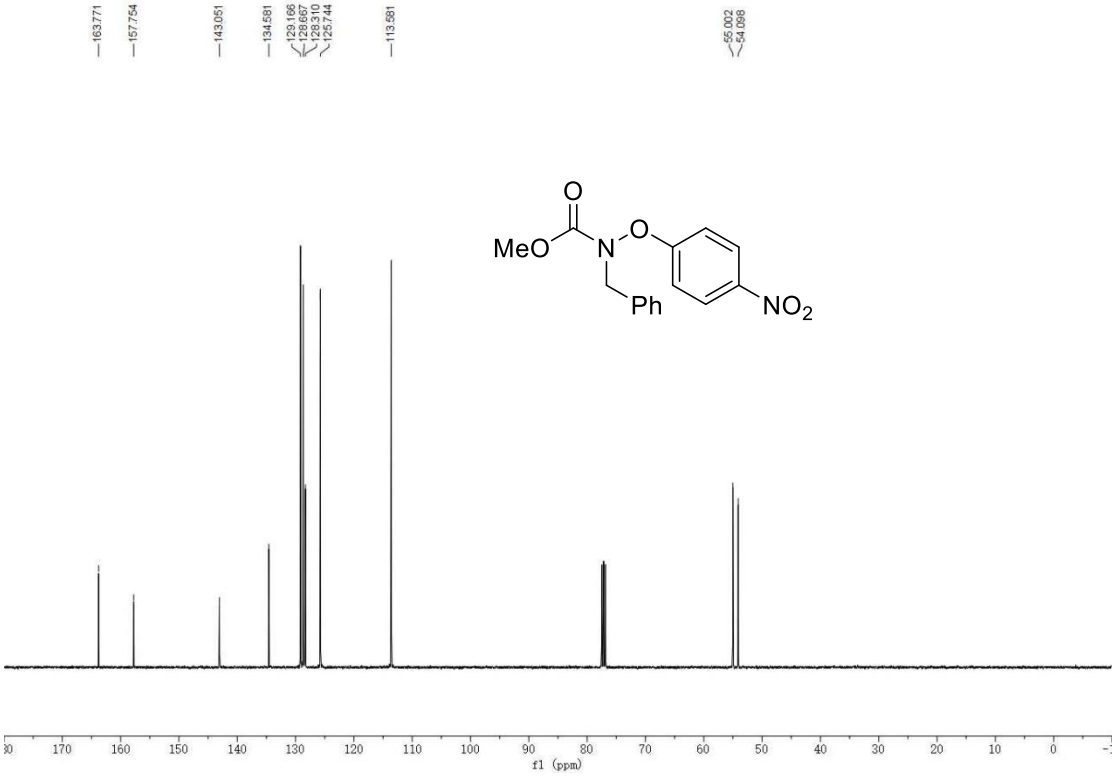

Figure S51. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *tert*-butyl benzyl(4-nitrophenoxy)carbamate (1n)

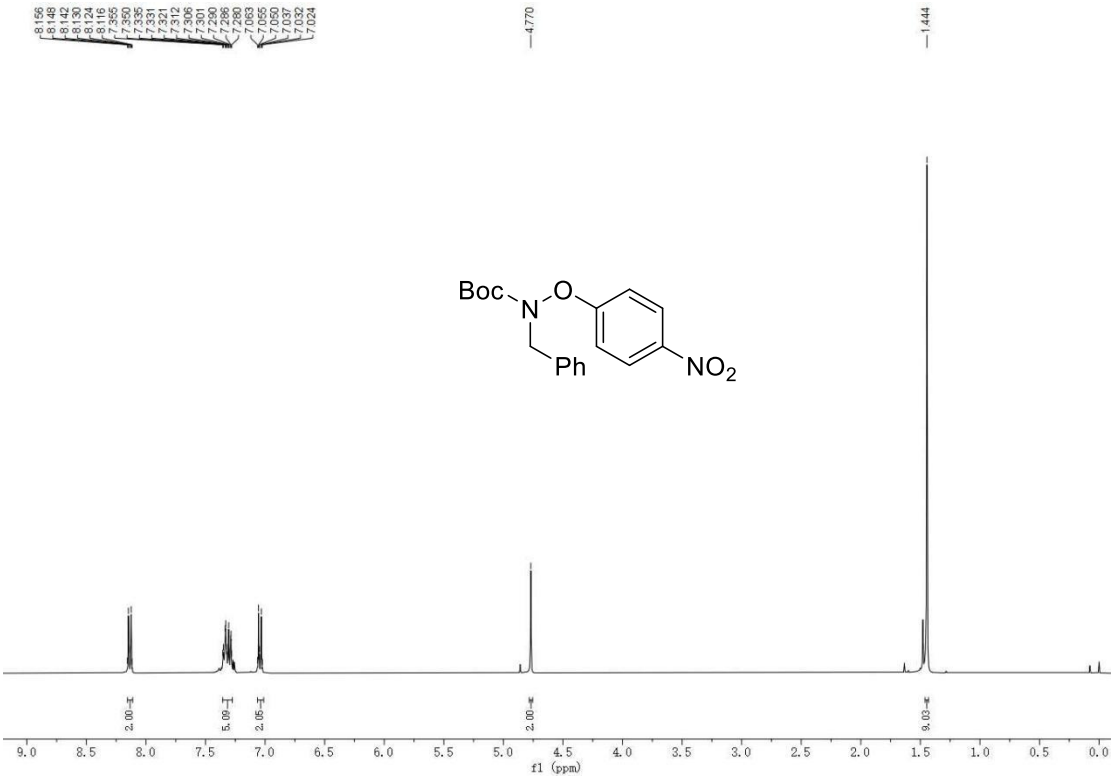

Figure S52. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *tert*-butyl benzyl(4-nitrophenoxy)carbamate (1n)

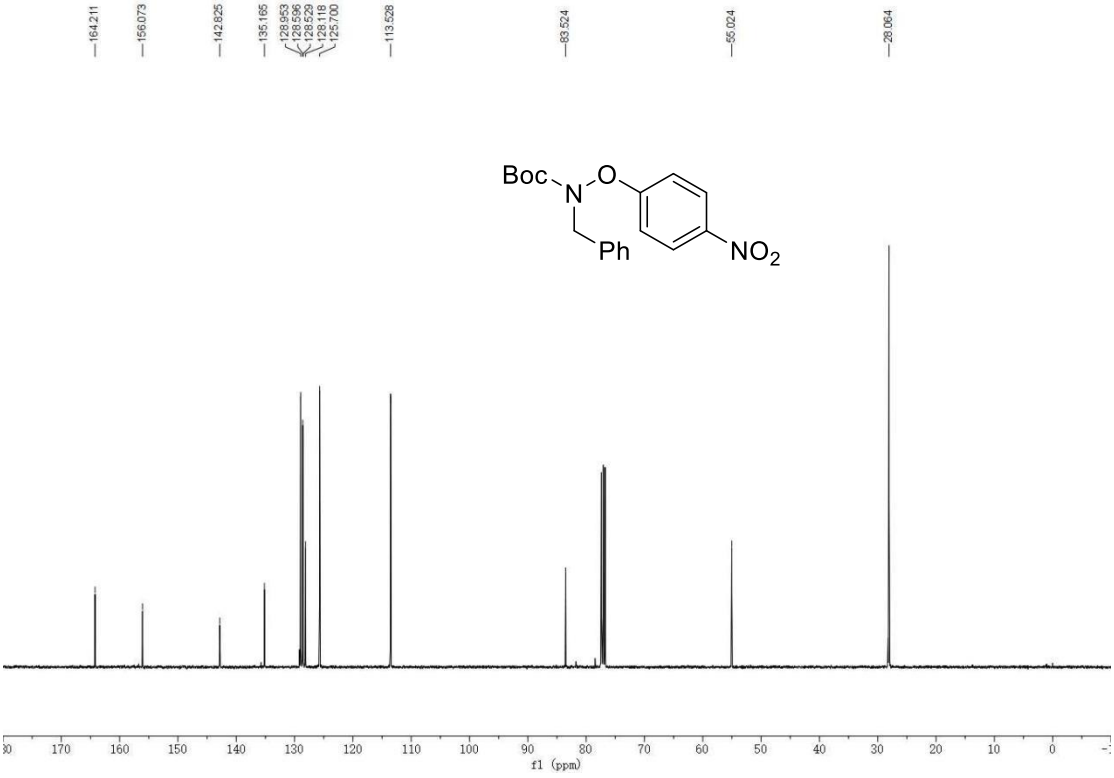

Figure S53. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of phenyl benzyl(4-nitrophenoxy)carbamate (1o)

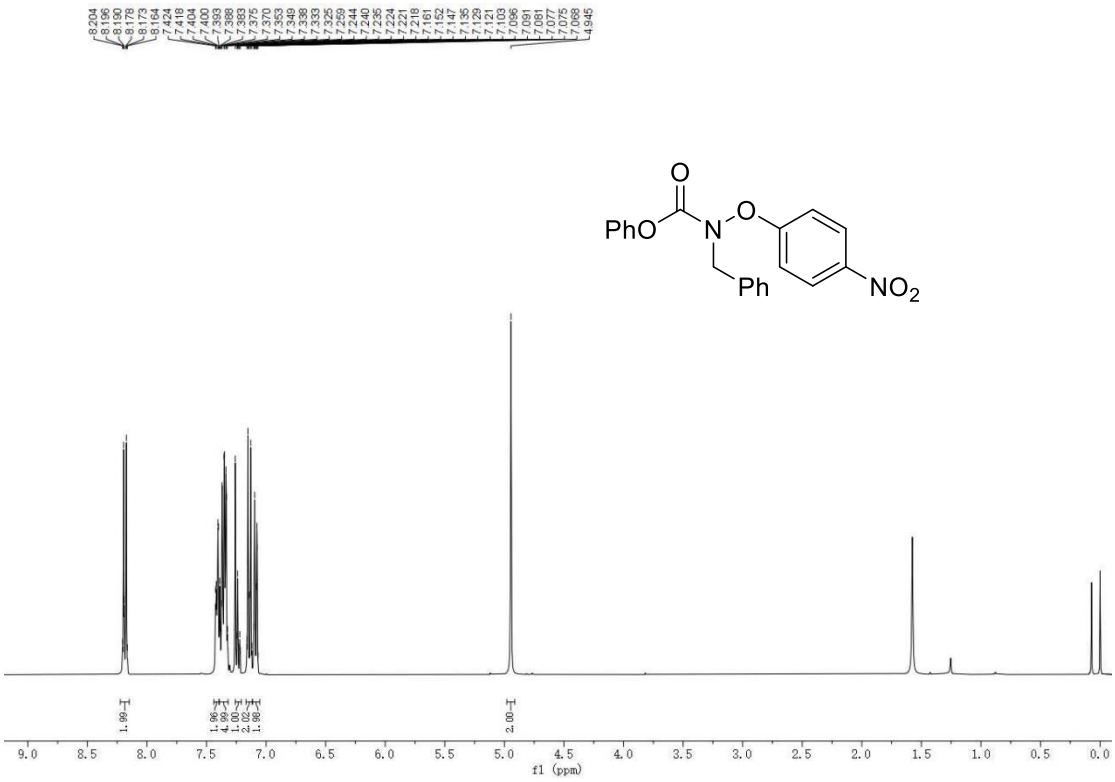

Figure S54. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of phenyl benzyl(4-nitrophenoxy)carbamate (1o)

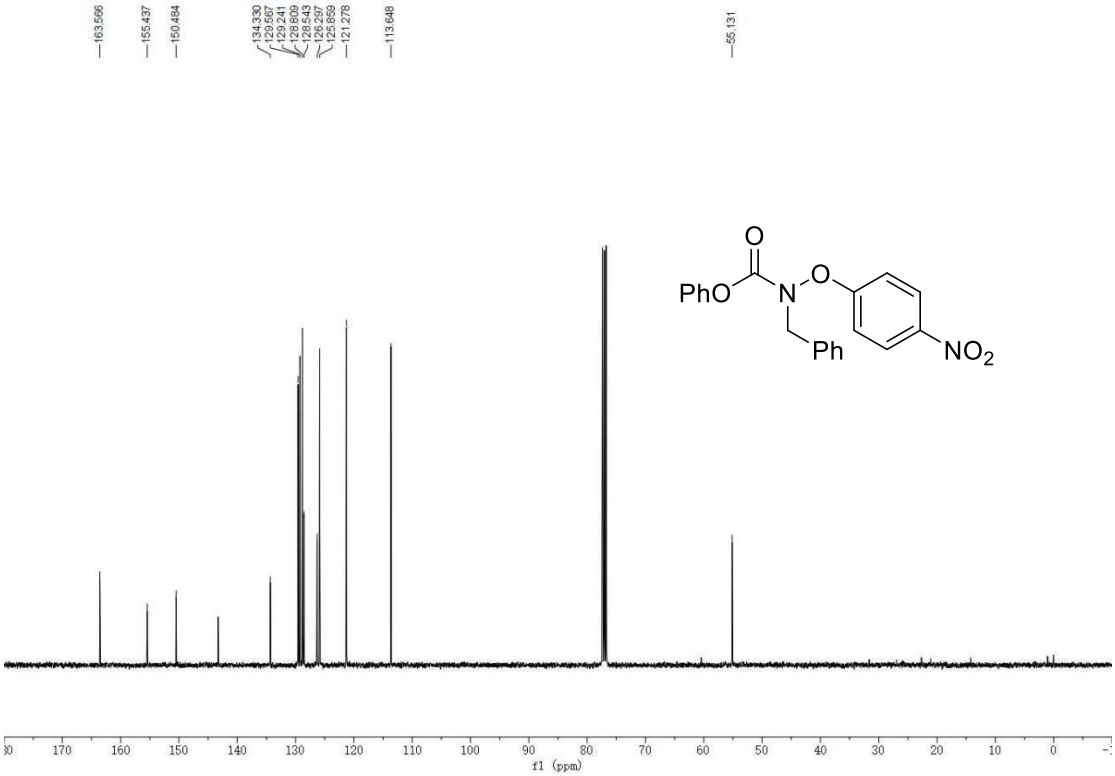

Figure S55. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(3,5-dimethoxybenzyl)-*N*-(4-nitrophenoxy)benzamide (1p)

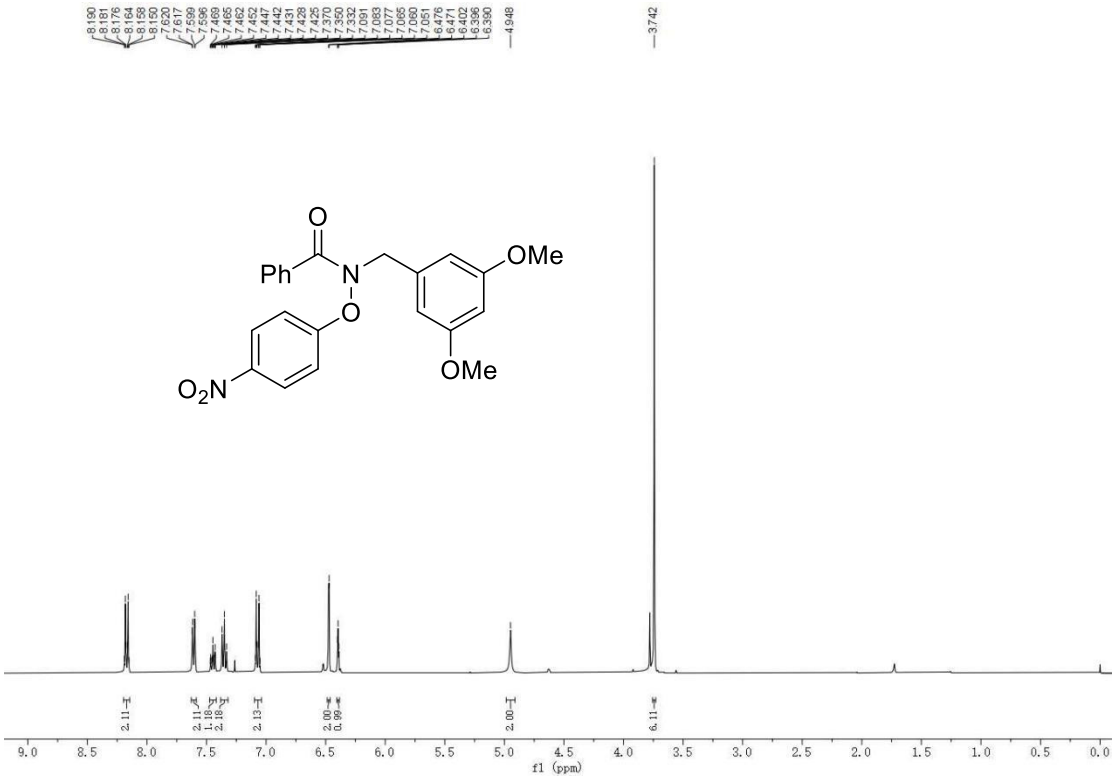

Figure S56. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-(3,5-dimethoxybenzyl)-*N*-(4-nitrophenoxy)benzamide (1p)

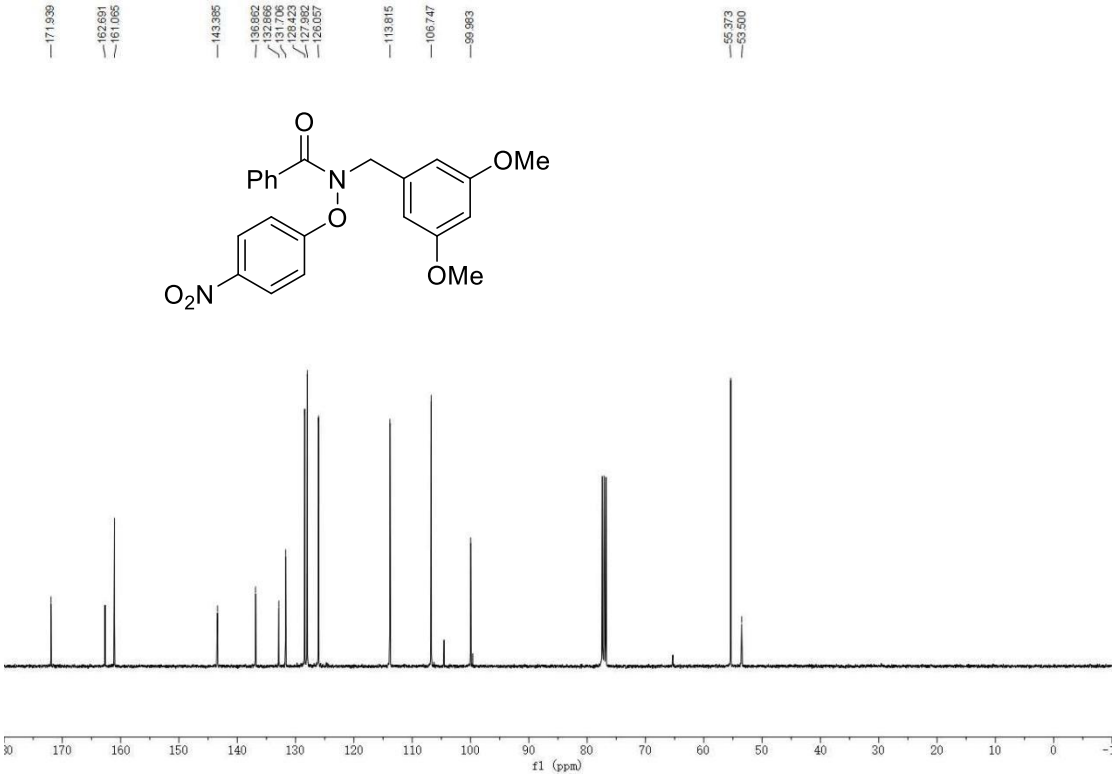

Figure S57. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(4-nitrophenoxy)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)benzamide (1q)

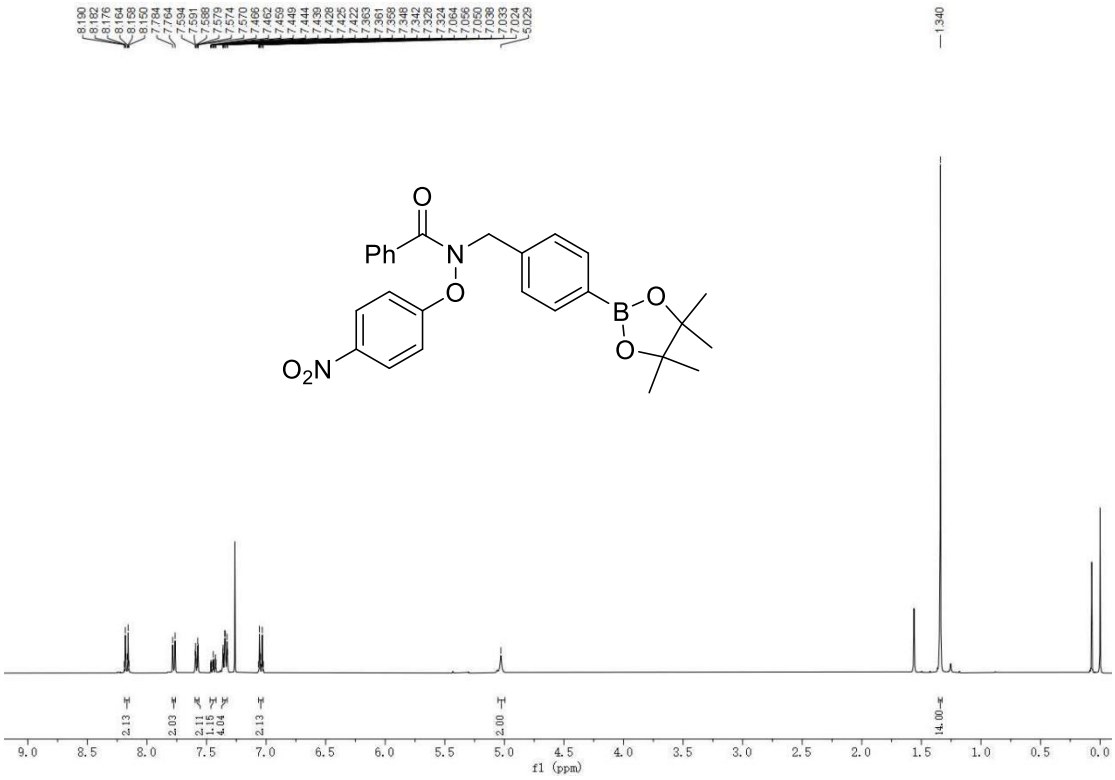

Figure S58. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-(4-nitrophenoxy)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)benzamide (1q)

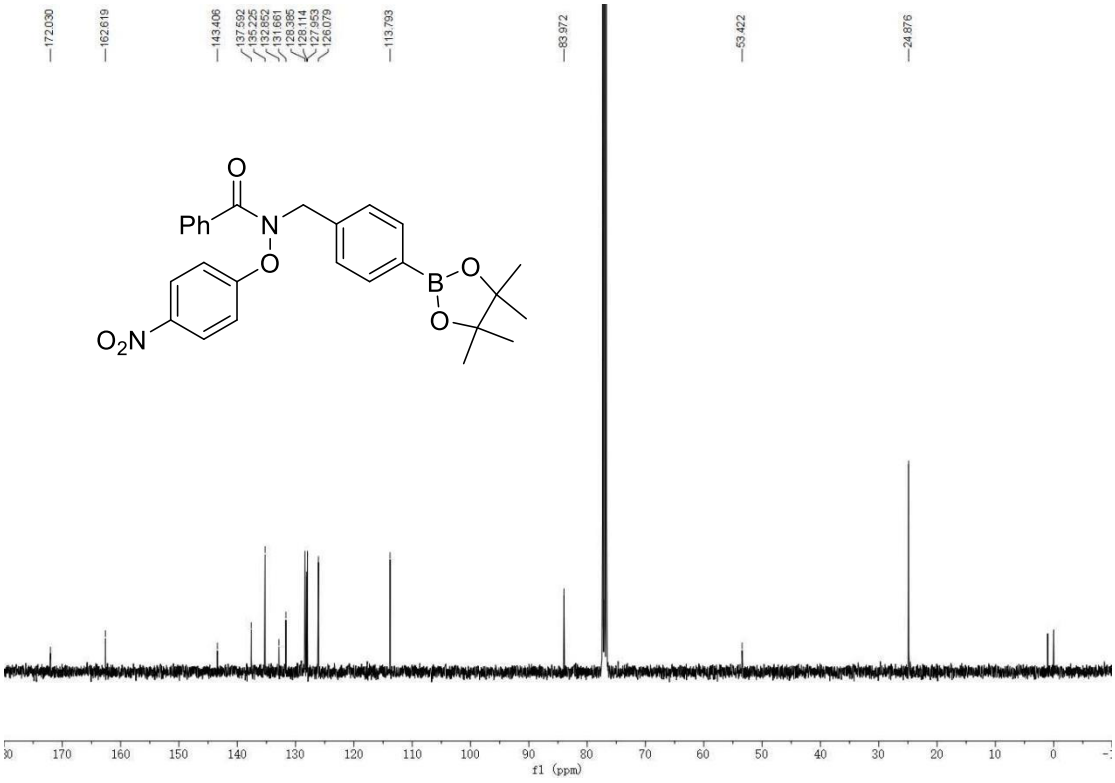

Figure S59. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(4-nitrophenoxy)-*N*-(4-(trifluoromethyl)benzyl)benzamide (1r)

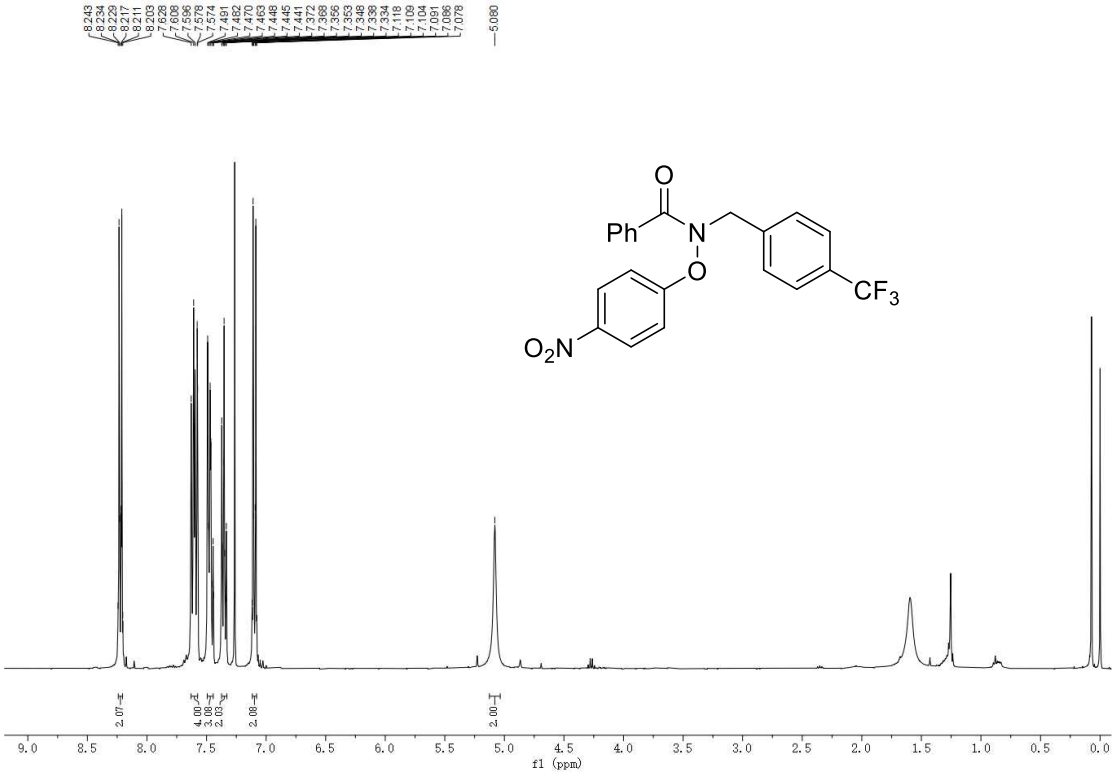

Figure S60. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-(4-nitrophenoxy)-*N*-(4-(trifluoromethyl)benzyl)benzamide (1r)

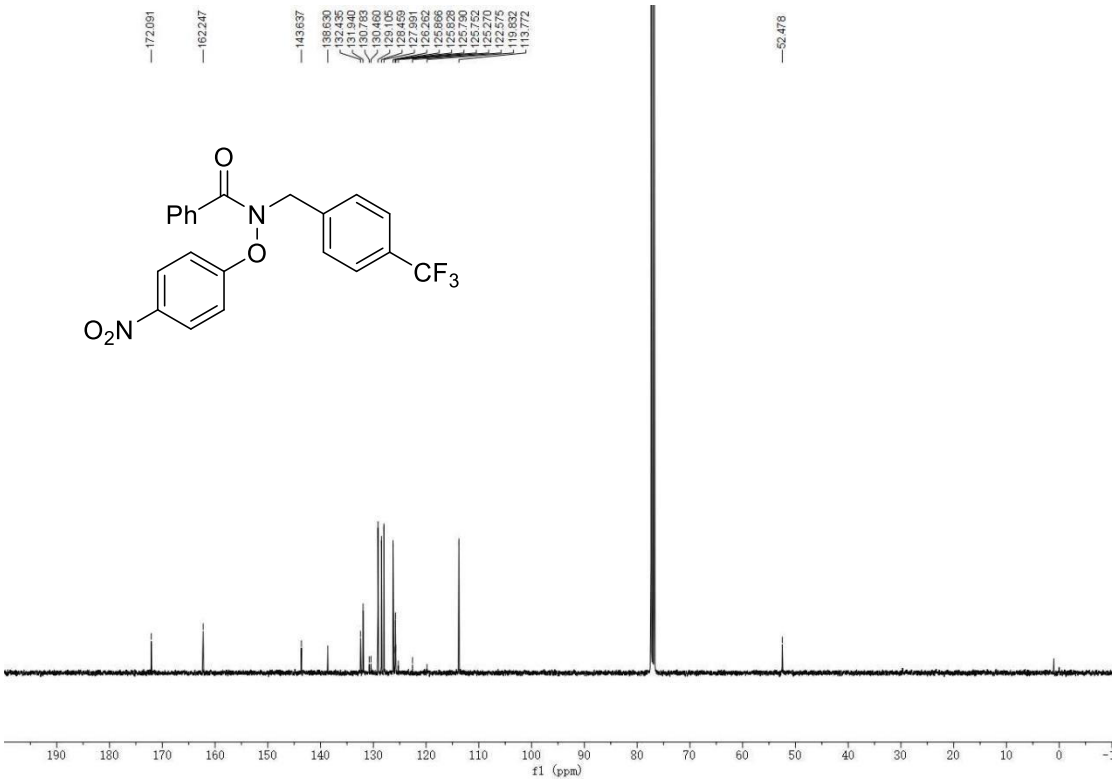

Figure S61. ^{19}F NMR spectra (376 MHz, Chloroform-*d*) of *N*-(4-nitrophenoxy)-*N*-(4-(trifluoromethyl)benzyl)benzamide (1r)

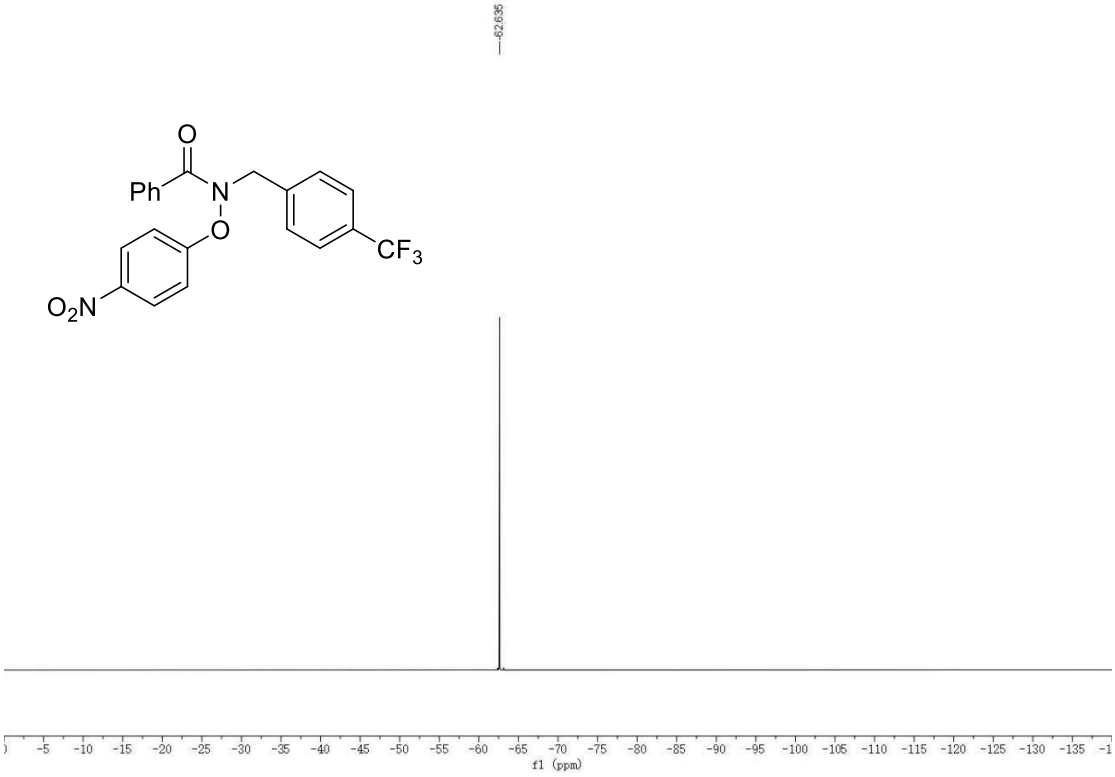

Figure S62. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-methyl-*N*-(4-nitrophenoxy)benzamide (1s)

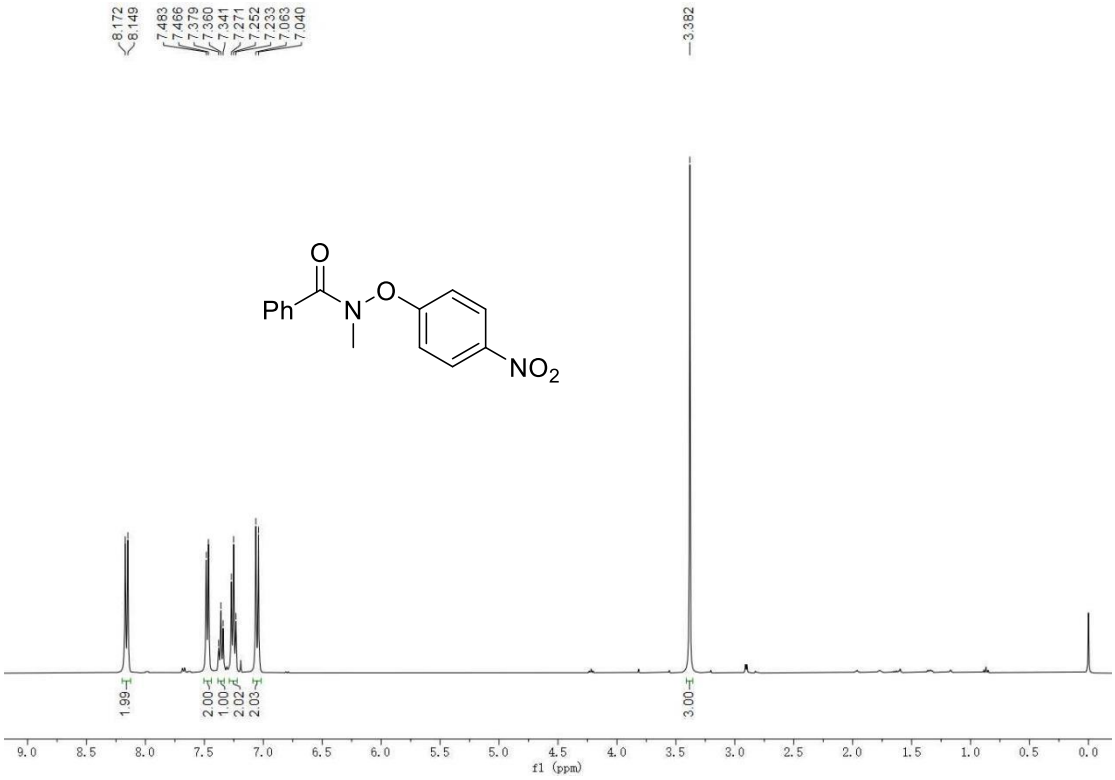

Figure S63. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-methyl-*N*-(4-nitrophenoxy)benzamide (1s)

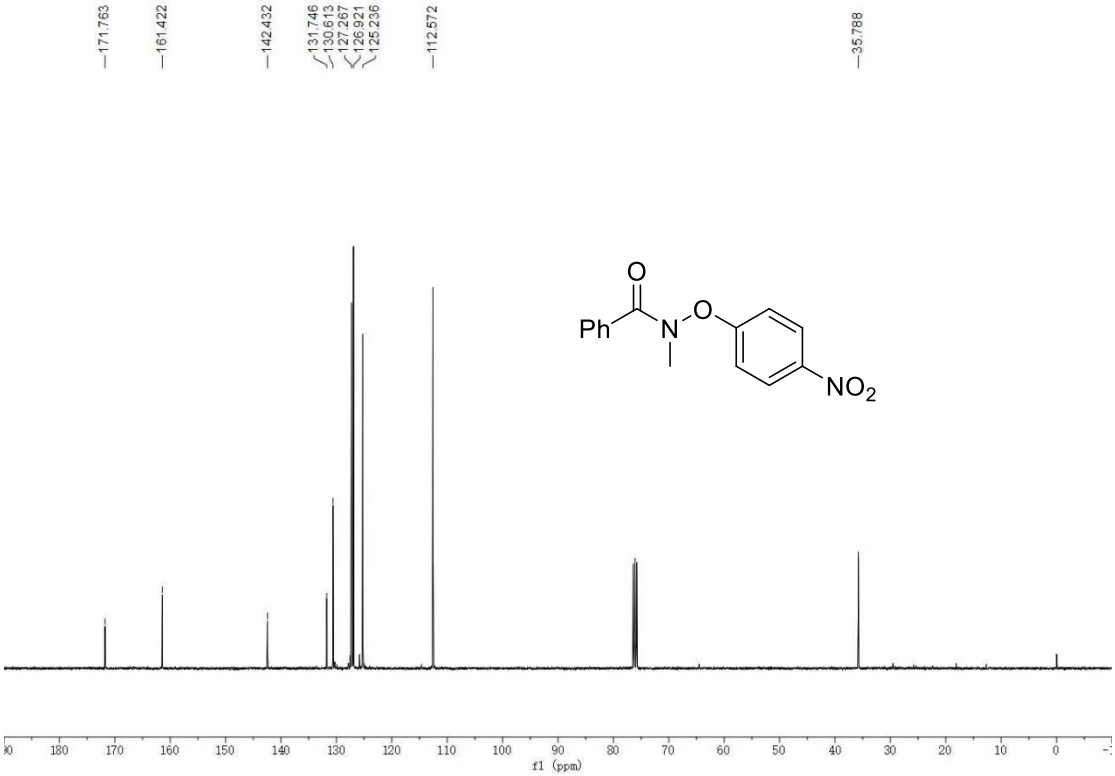

Figure S64. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-ethyl-*N*-(4-nitrophenoxy)benzamide (1t)

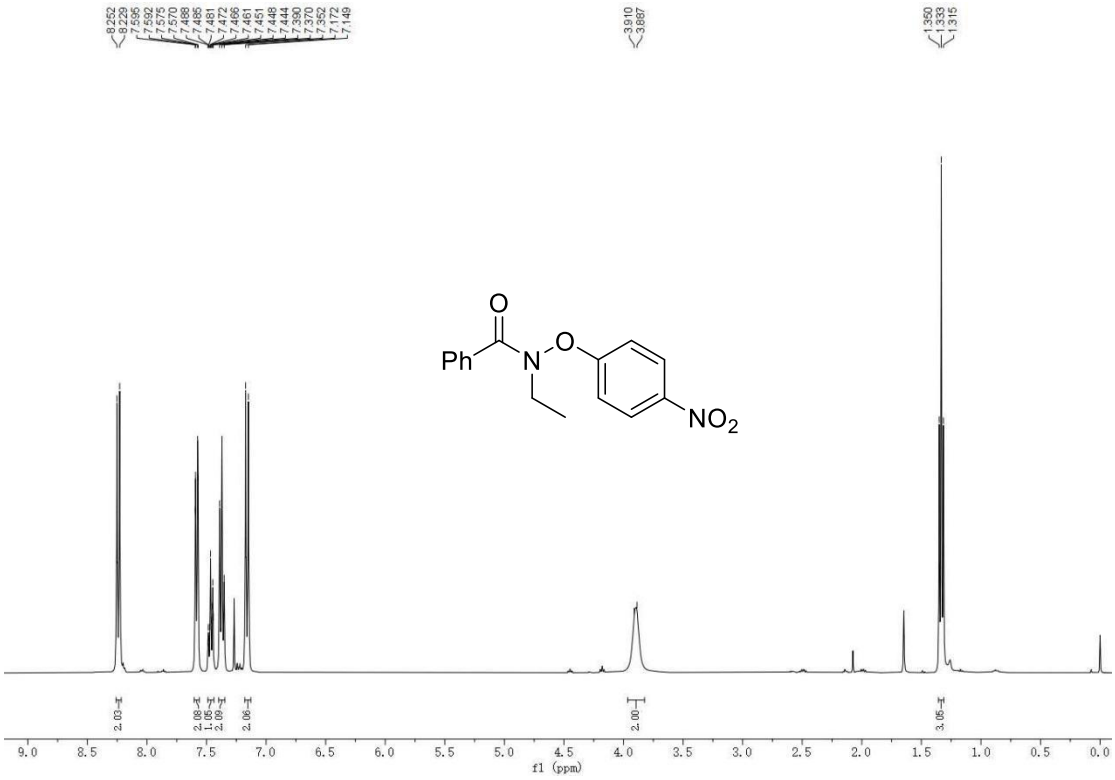

Figure S65. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-ethyl-*N*-(4-nitrophenoxy)benzamide (1t)

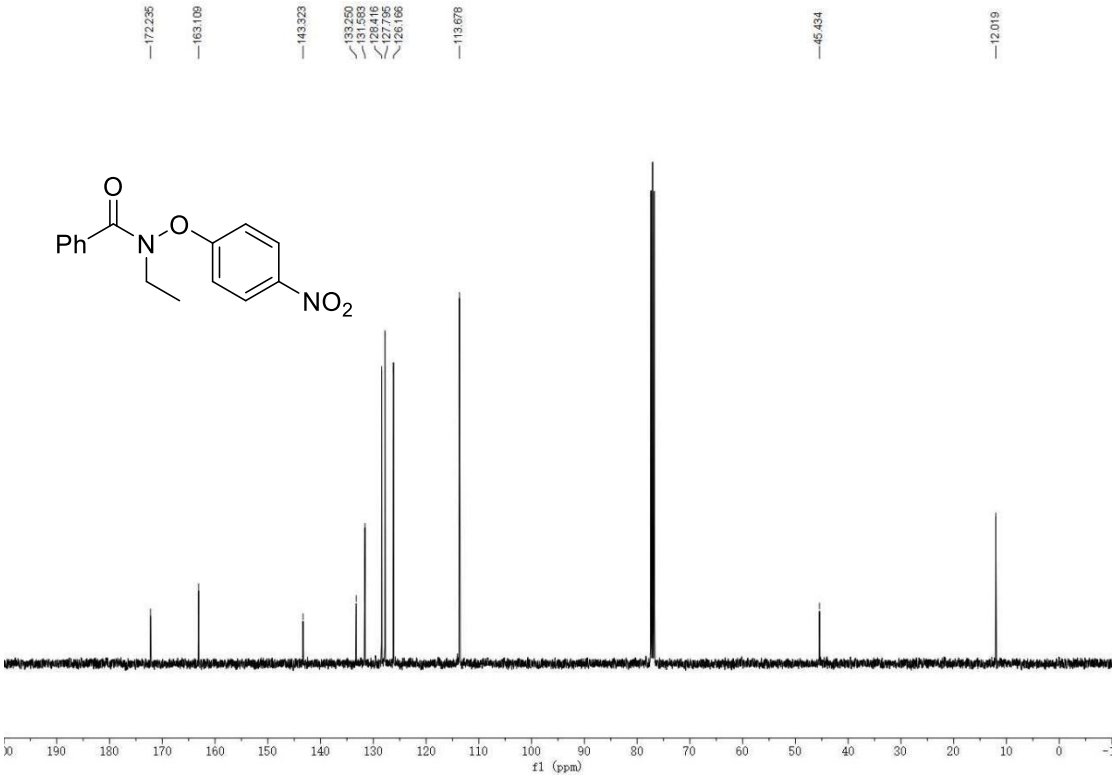

Figure S66. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-allyl-*N*-(4-nitrophenoxy)benzamide (1u)

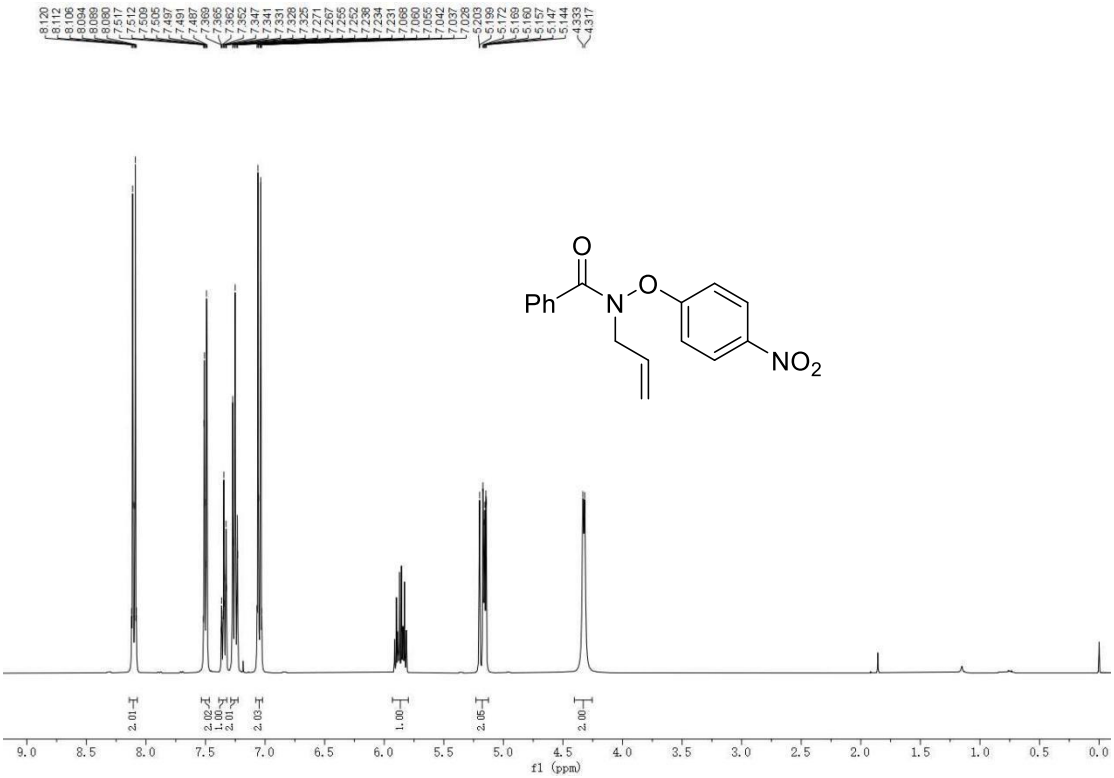

Figure S67. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-allyl-*N*-(4-nitrophenoxy)benzamide (1u)

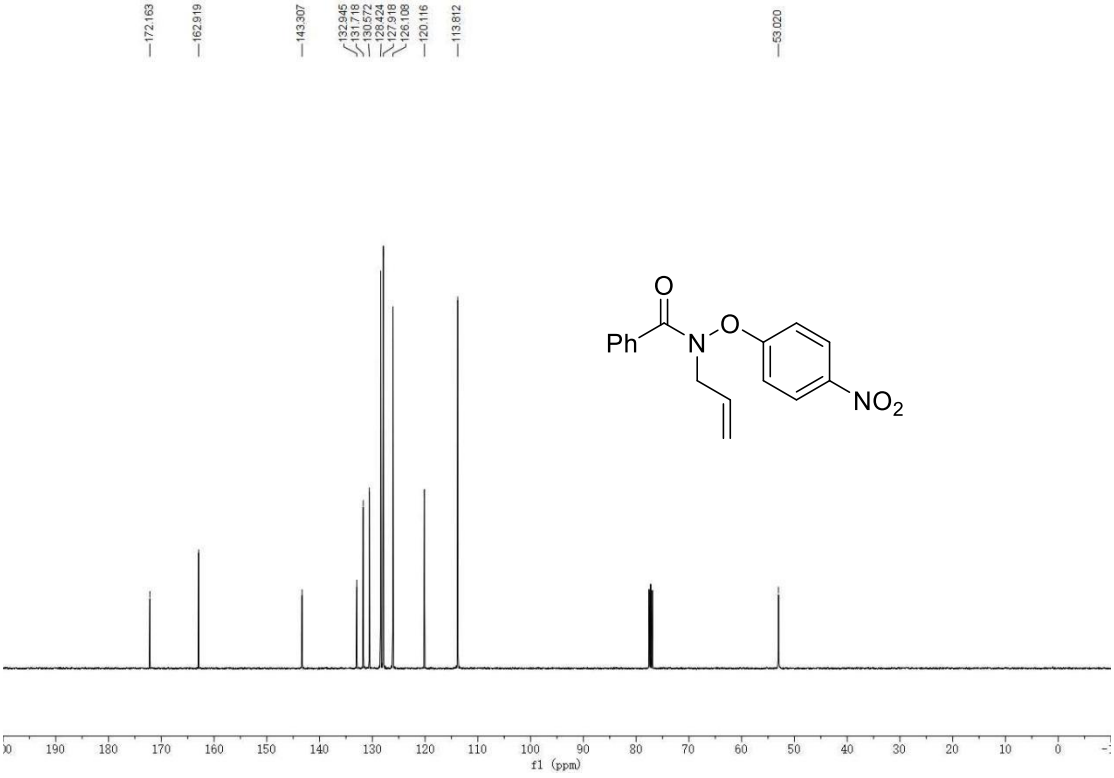

Figure S68. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(4-nitrophenoxy)-*N*-(phenylmethyl-*d*)benzamide (1a-d^1)

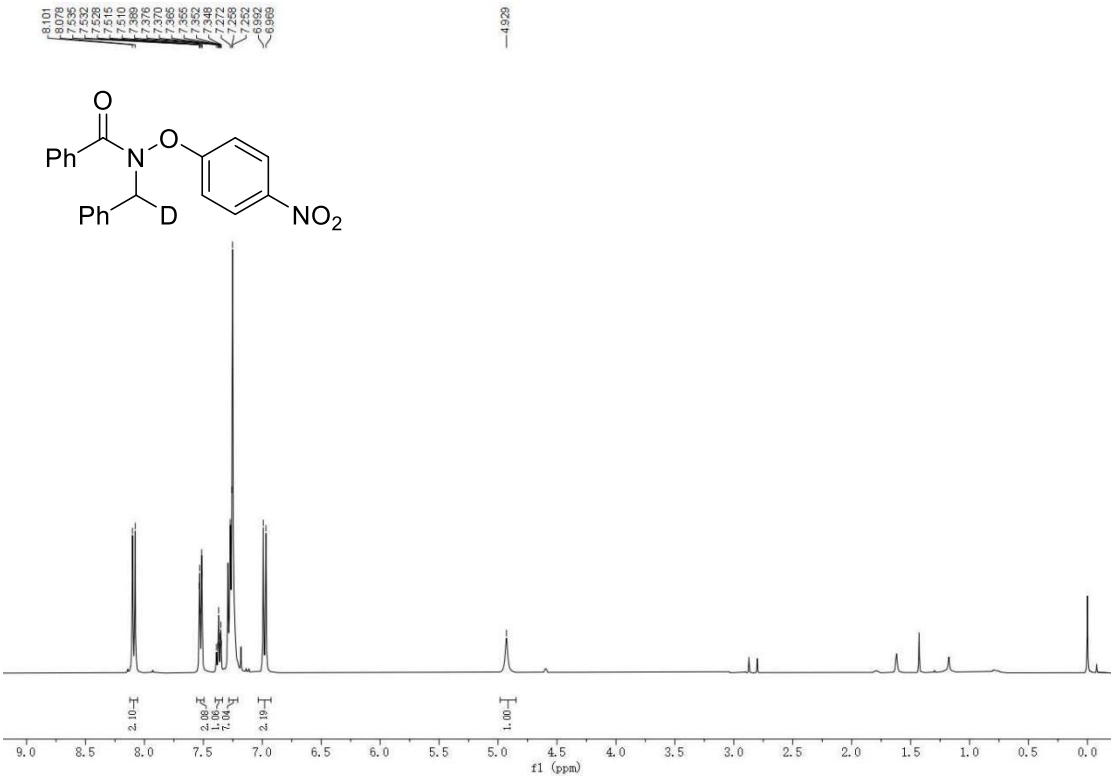

Figure S69. ^{13}C NMR spectra (100 MHz, Chloroform-d) of *N*-(4-nitrophenoxy)-*N*-(phenylmethyl-*d*)benzamide (1a-d^1)

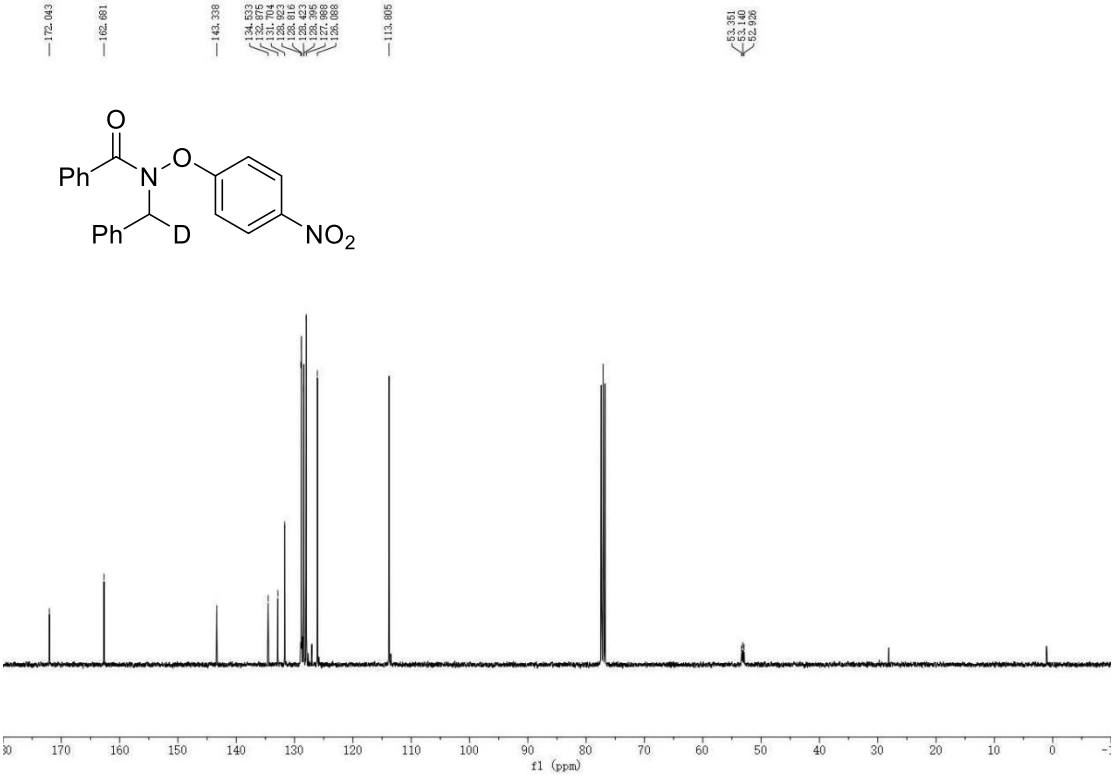

Figure S70. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(3-oxo-1,3-diphenylpropyl)benzamide (3aa)

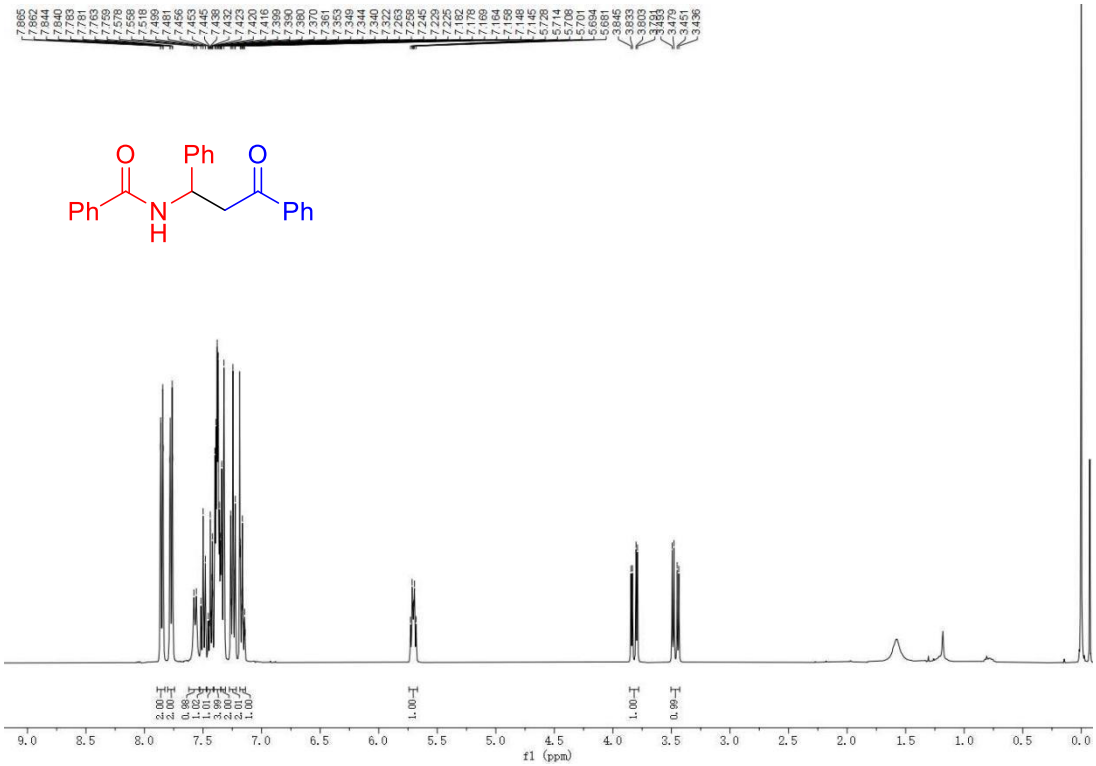

Figure S71. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-(3-oxo-1,3-diphenylpropyl)benzamide (3aa)

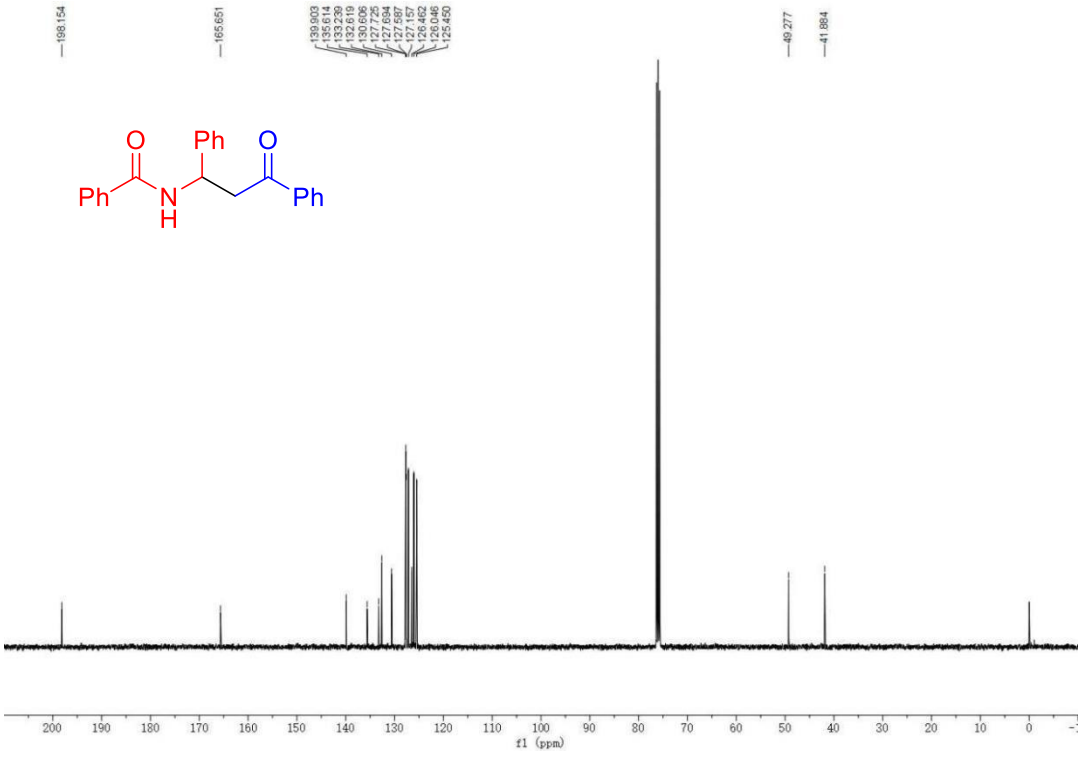

Figure S72. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of 3-methoxy-*N*-(3-oxo-1,3-diphenylpropyl)benzamide (3ba)

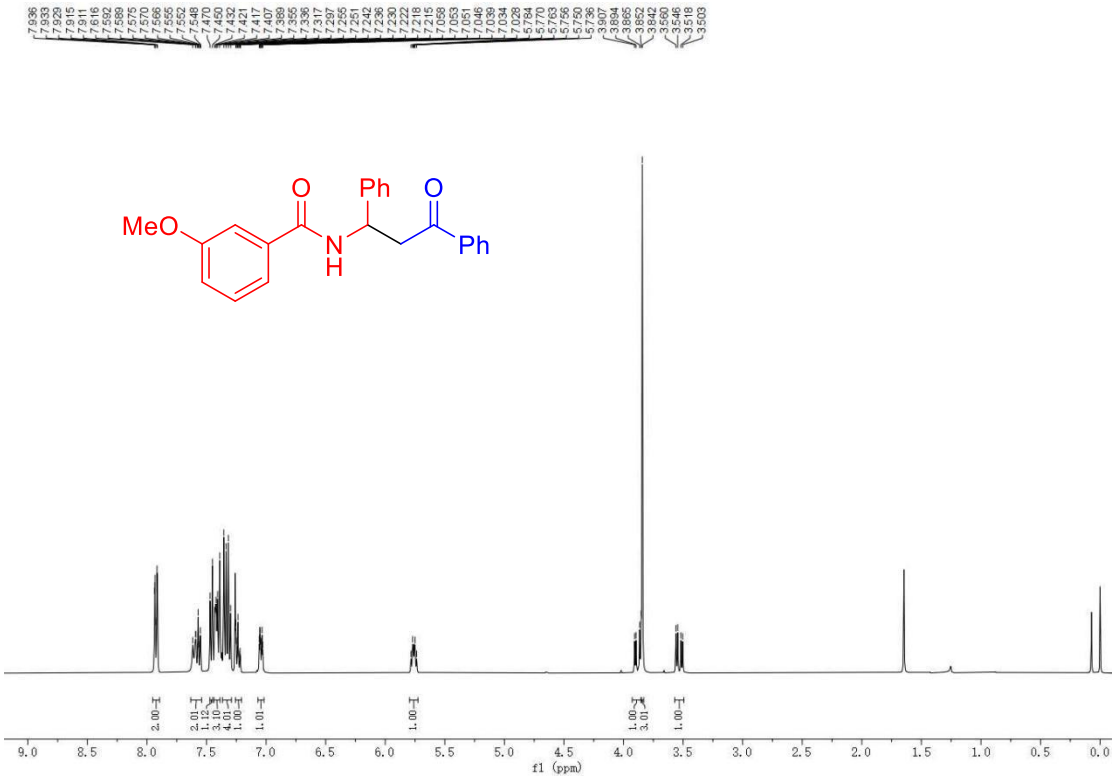

Figure S73. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of 3-methoxy-*N*-(3-oxo-1,3-diphenylpropyl)benzamide (3ba)

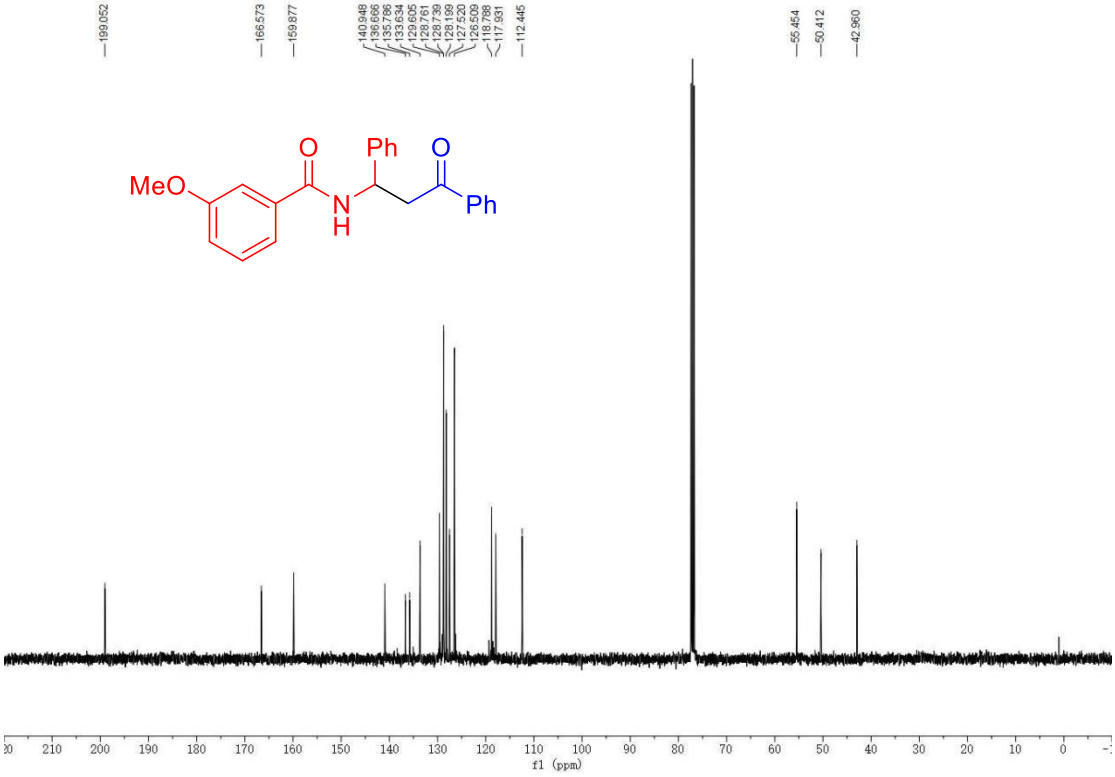

Figure S74. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(3-oxo-1,3-diphenylpropyl)-4-(trifluoromethyl)benzamide (3ca)

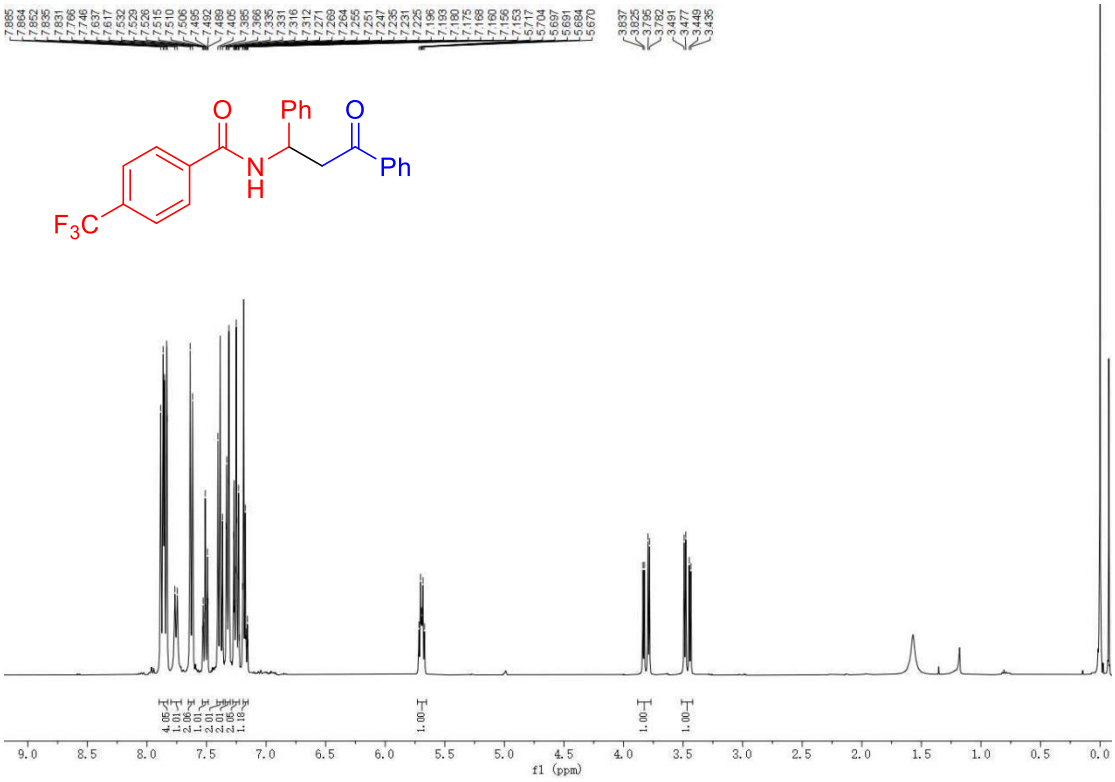

Figure S75. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-(3-oxo-1,3-diphenylpropyl)-4-(trifluoromethyl)benzamide (3ca)

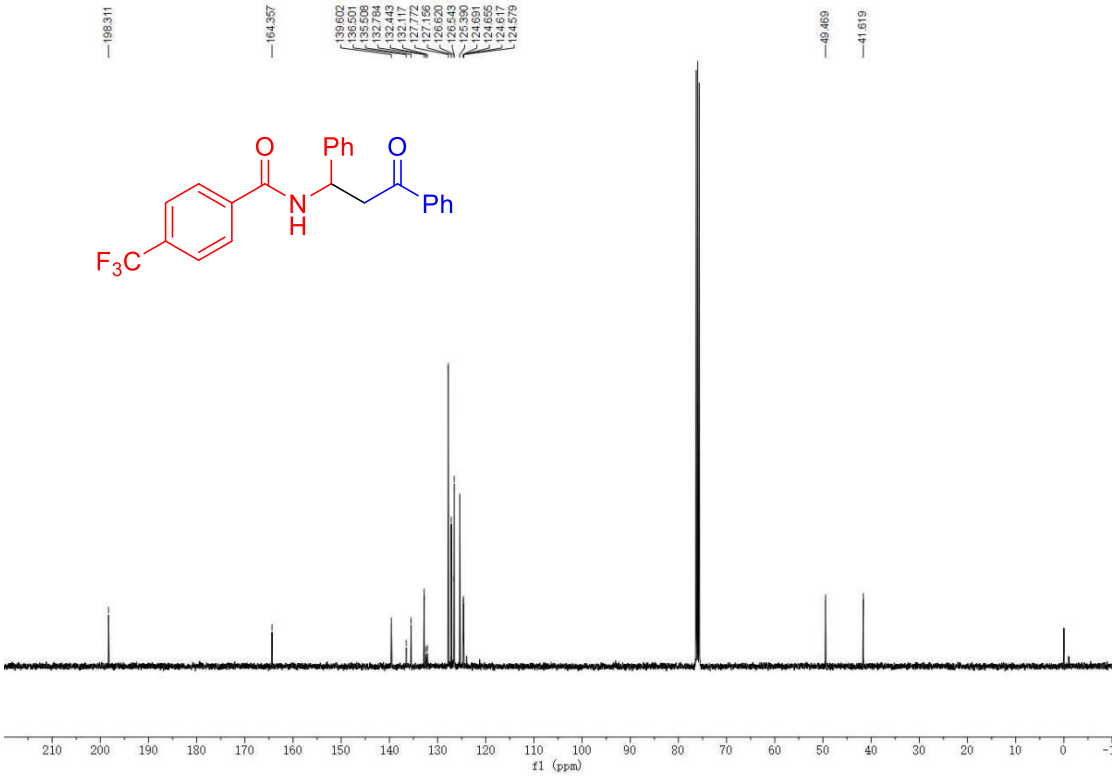

Figure S76. ^{19}F NMR spectra (376 MHz, Chloroform-*d*) of *N*-(3-oxo-1,3-diphenylpropyl)-4-(trifluoromethyl)benzamide (3ca)

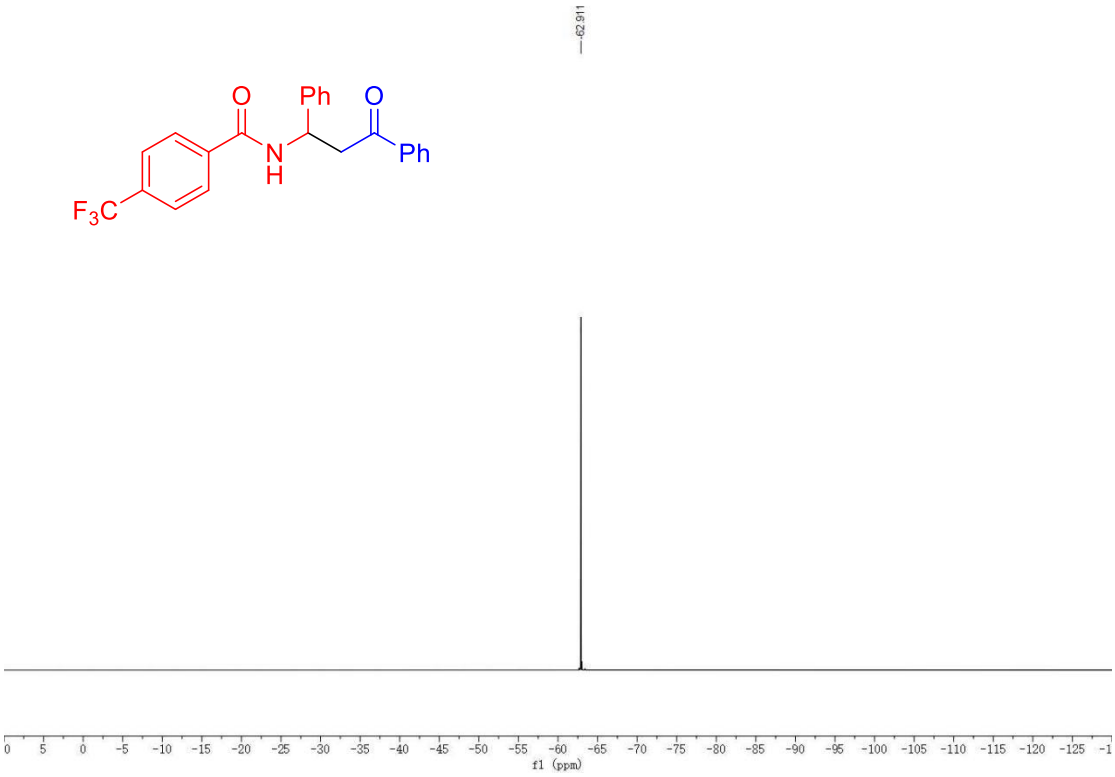

Figure S77. ^{1}H NMR spectra (600 MHz, Chloroform-*d*) of *N*-(3-oxo-1,3-diphenylpropyl)-1-naphthamide (3da)

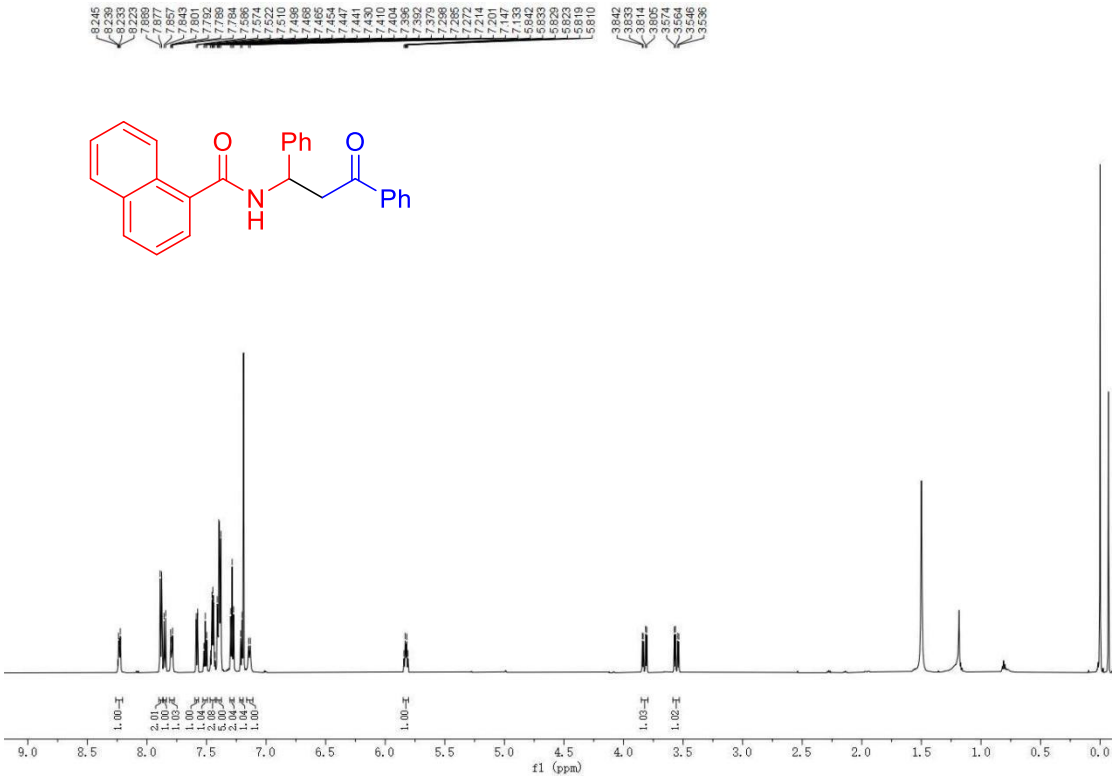

Figure S78. ^{13}C NMR spectra (150 MHz, Chloroform-*d*) of *N*-(3-oxo-1,3-diphenylpropyl)-1-naphthamide (3da)

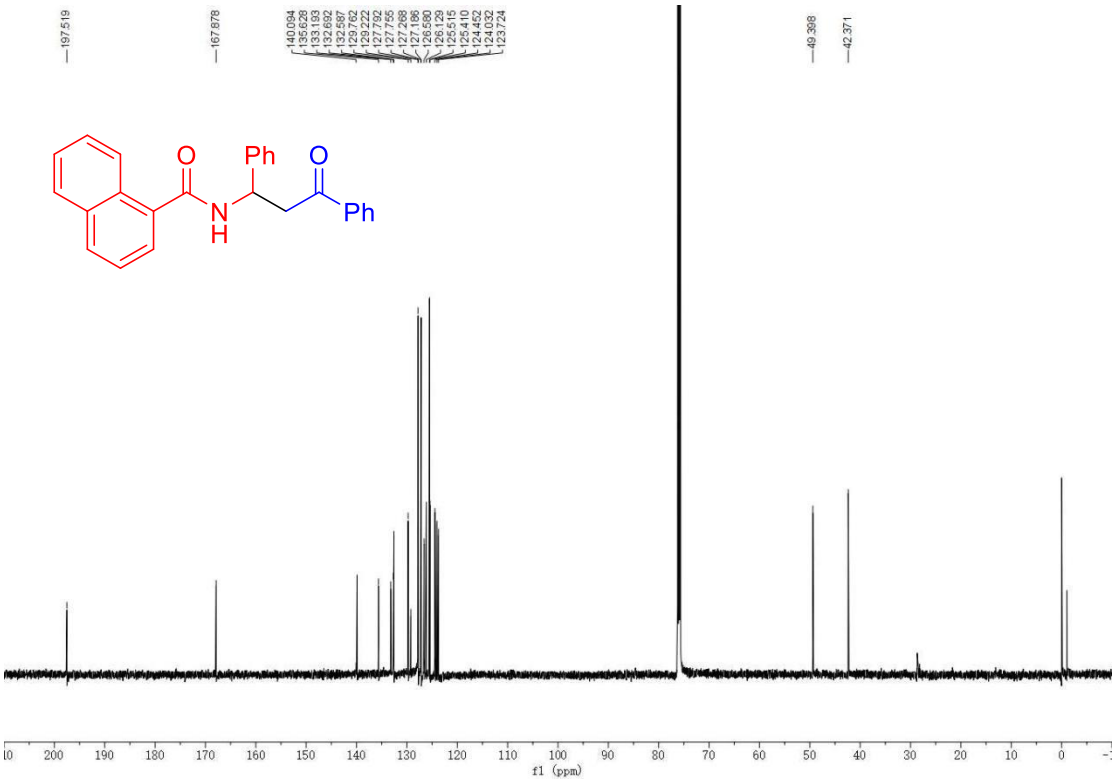

Figure S79. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(3-oxo-1,3-diphenylpropyl)furan-2-carboxamide (3ea)

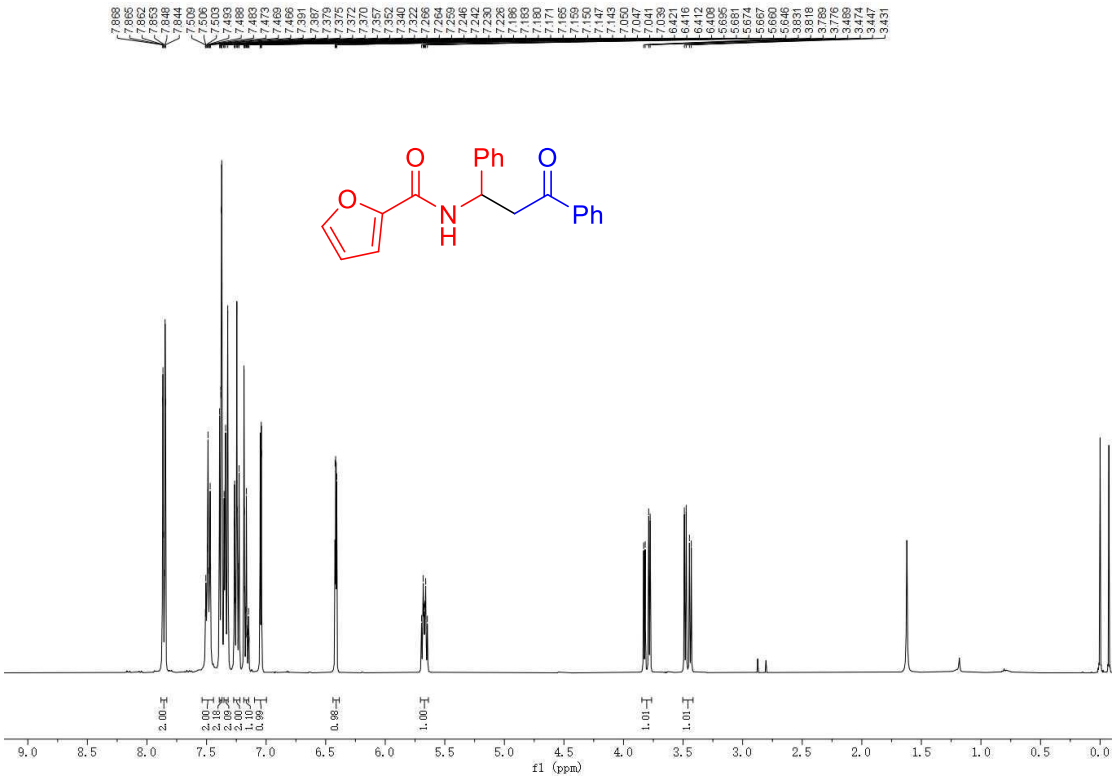

Figure S80. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-(3-oxo-1,3-diphenylpropyl)furan-2-carboxamide (3ea)

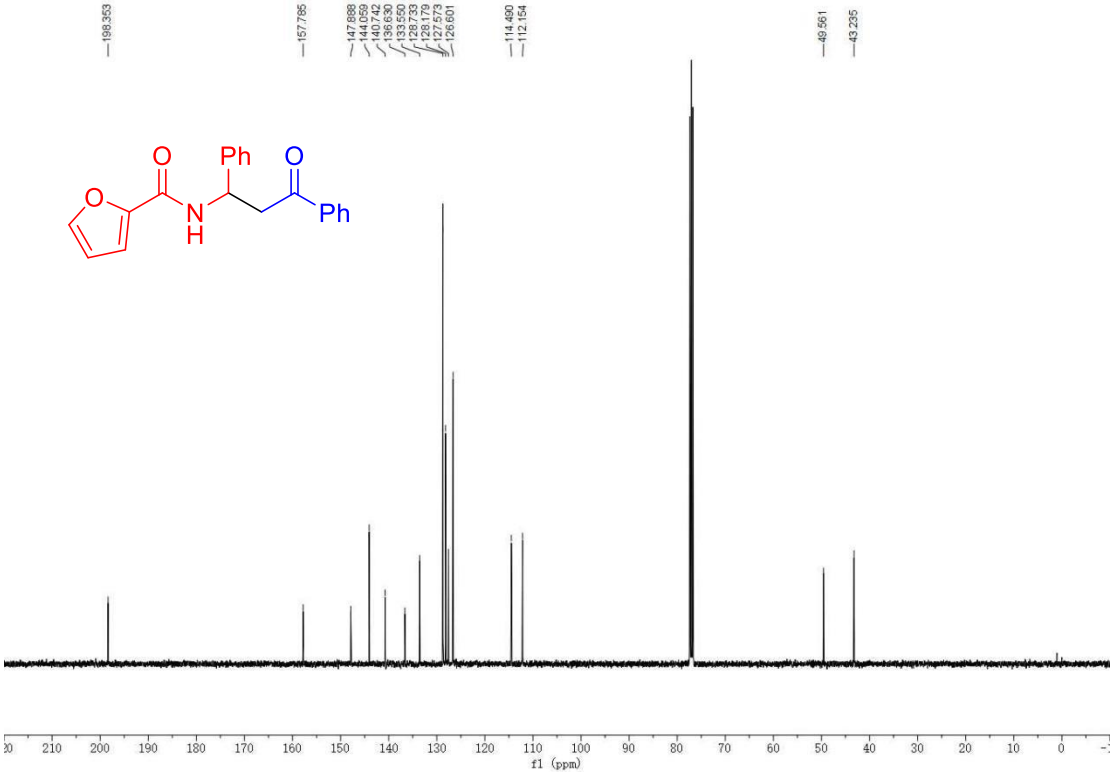

Figure S81. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(3-oxo-1,3-diphenylpropyl)acrylamide (3fa)

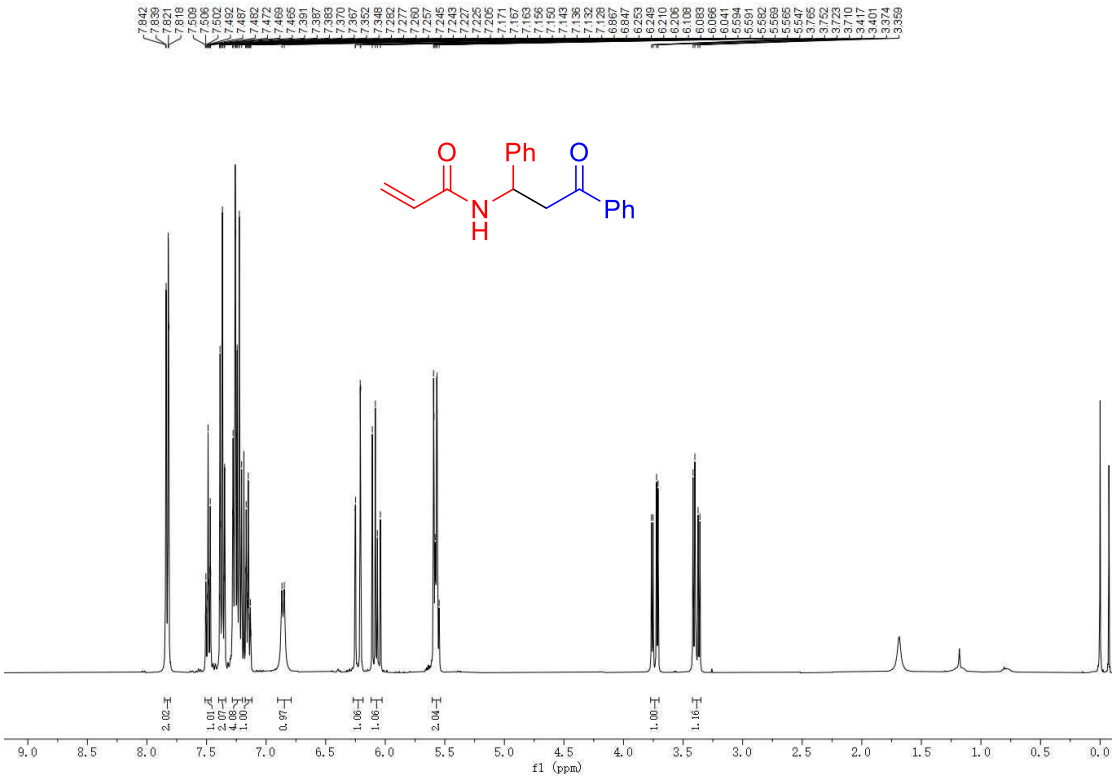

Figure S82. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-(3-oxo-1,3-diphenylpropyl)acrylamide (3fa)

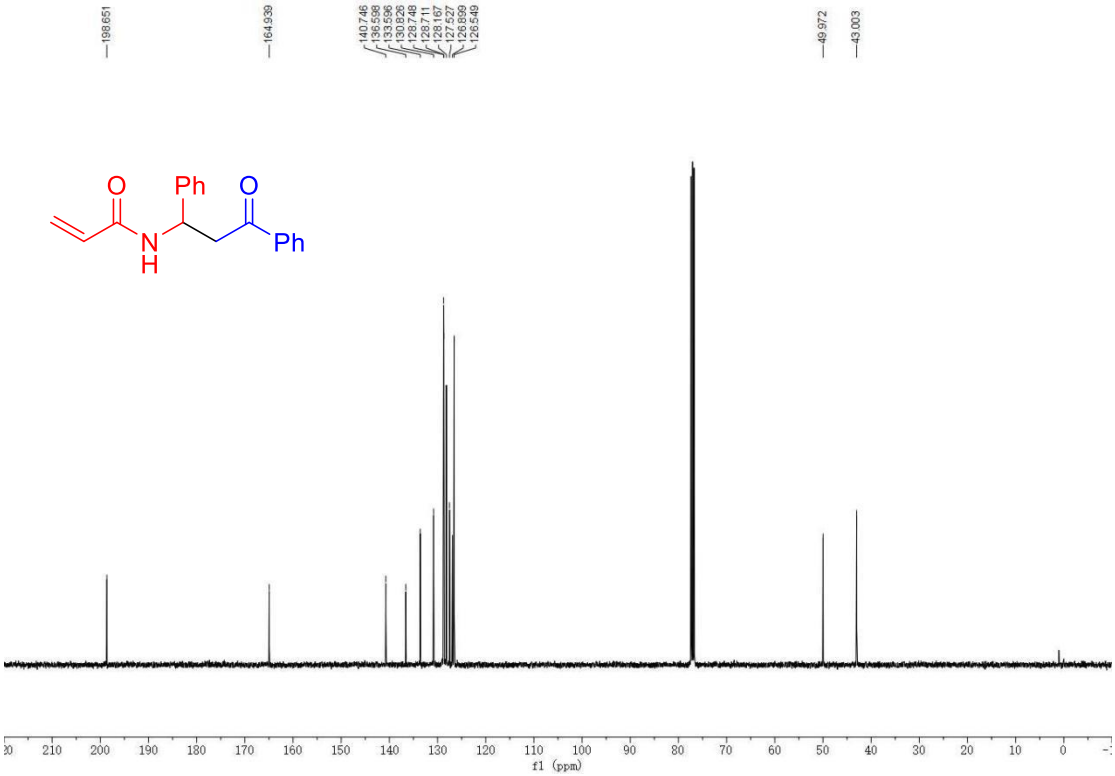

Figure S83. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(3-oxo-1,3-diphenylpropyl)cinnamamide (3ga)

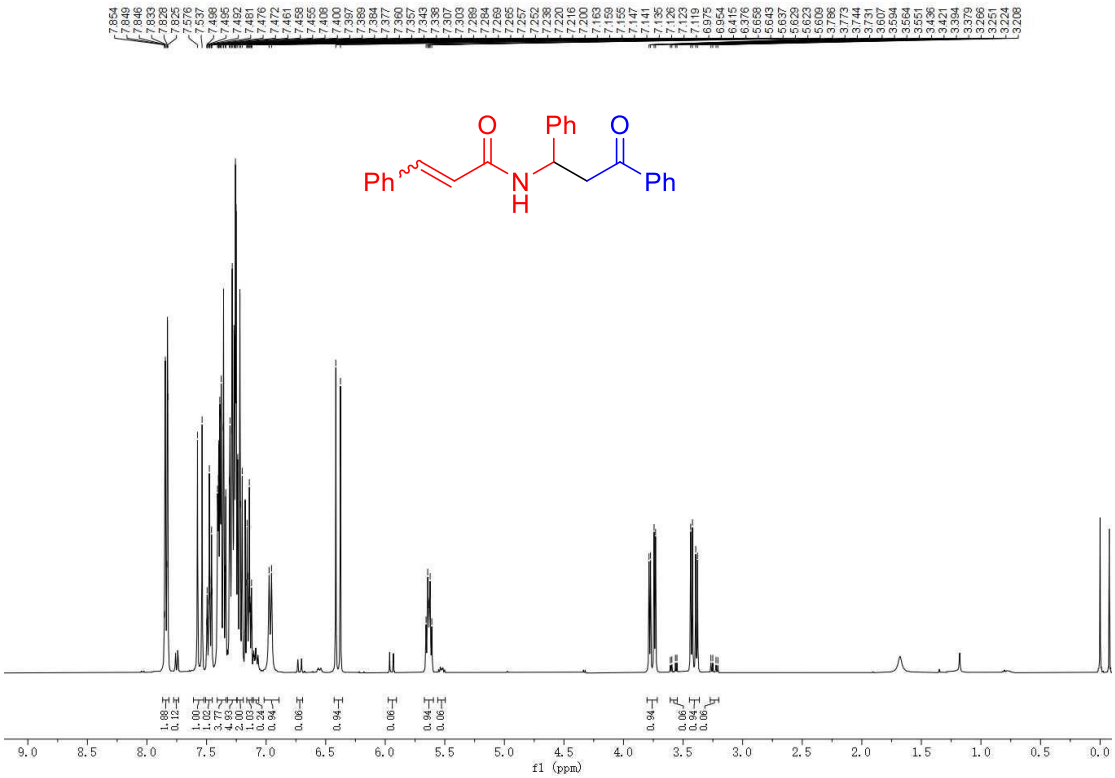

Figure S84. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-(3-oxo-1,3-diphenylpropyl)cinnamamide (3ga)

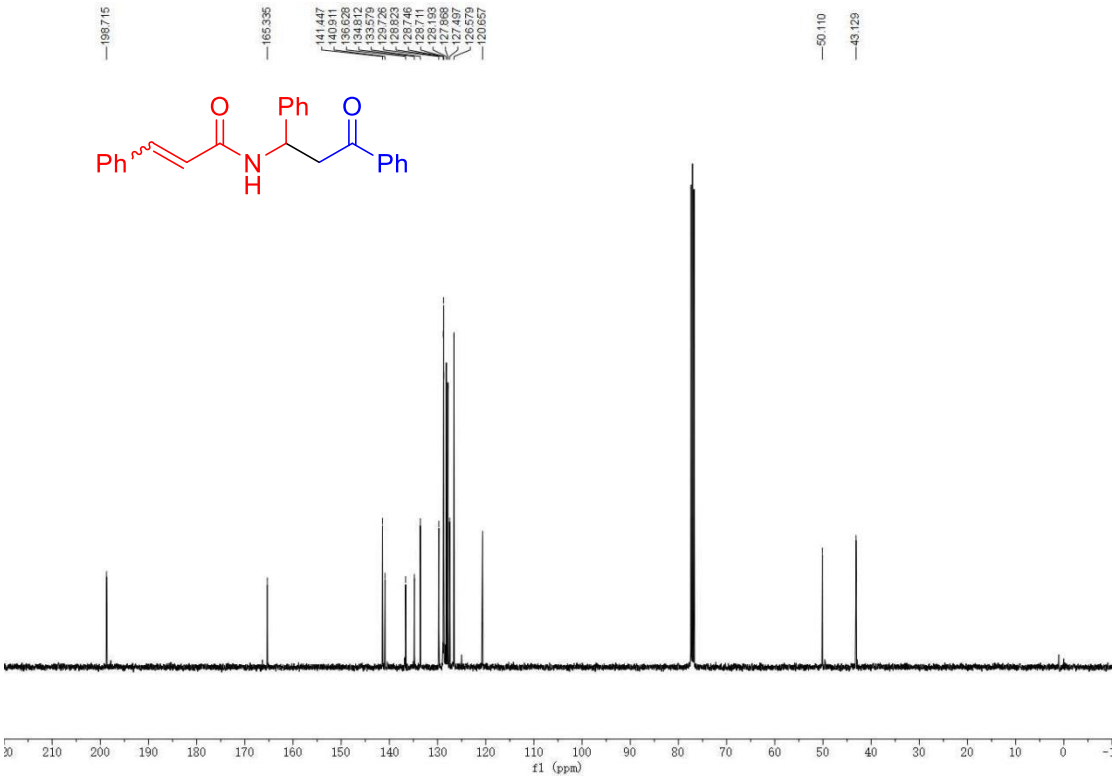

Figure S85. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(3-oxo-1,3-diphenylpropyl)but-2-ynamide (3ha)

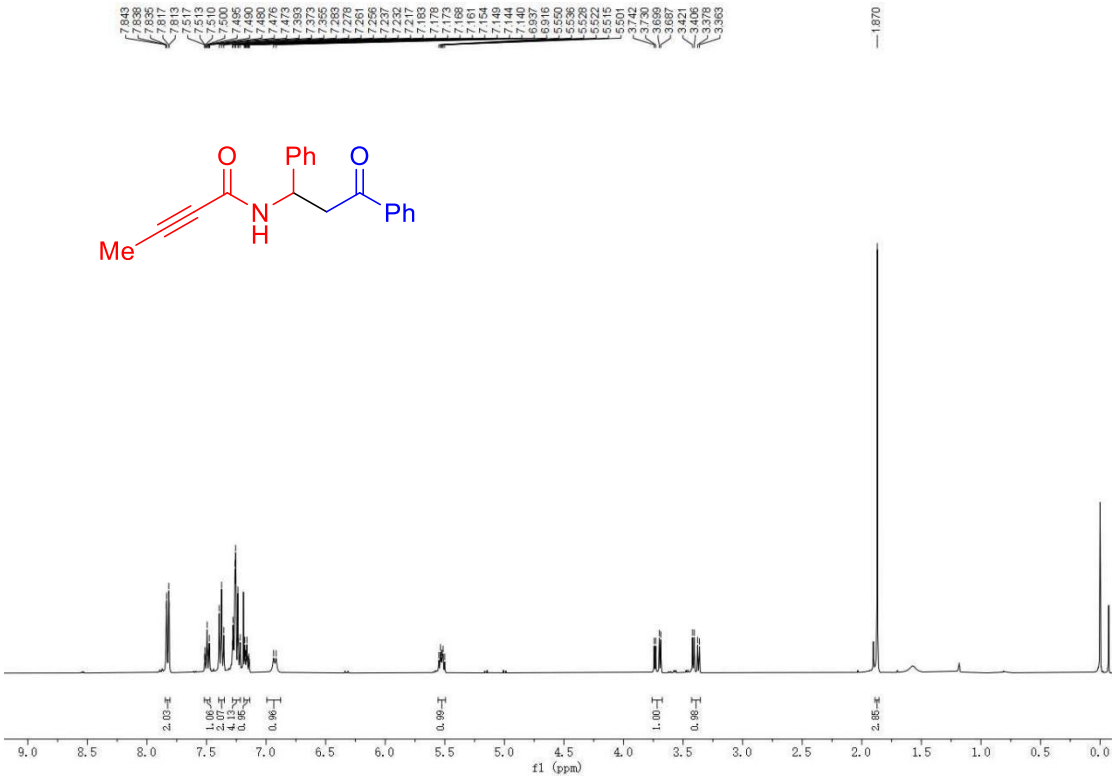

Figure S86. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-(3-oxo-1,3-diphenylpropyl)but-2-ynamide (3ha)

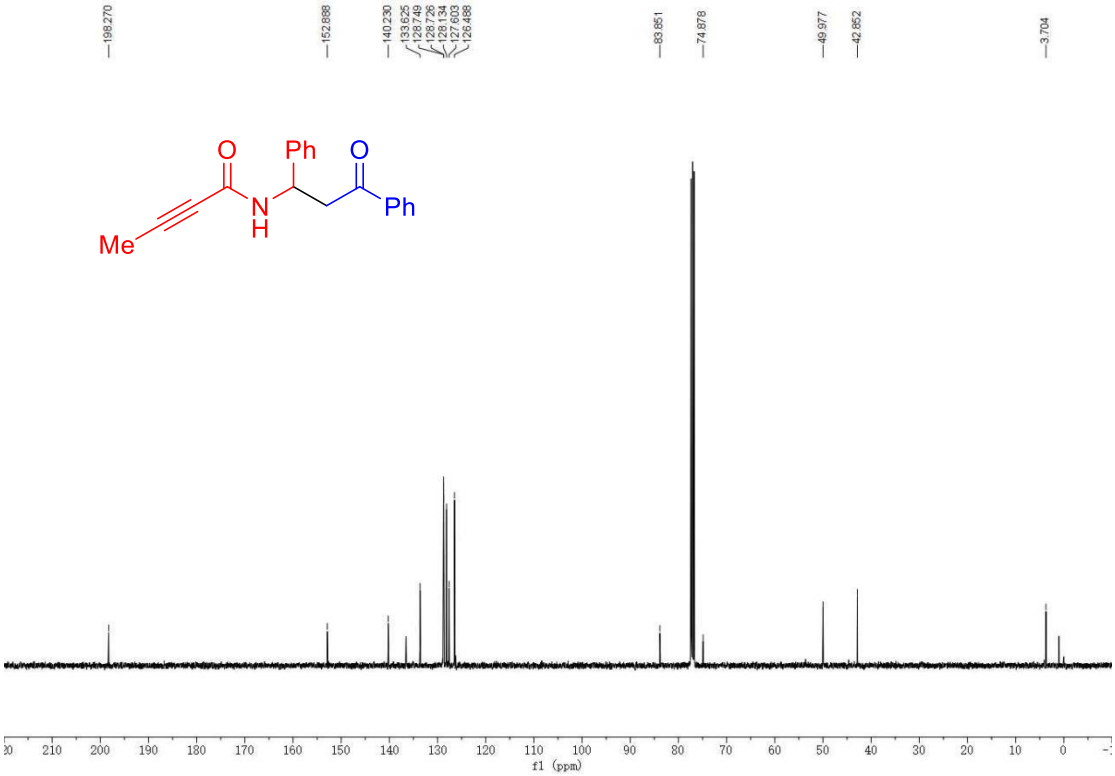

Figure S87. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of 2-methoxy-*N*-(3-oxo-1,3-diphenylpropyl)acetamide (3ia)

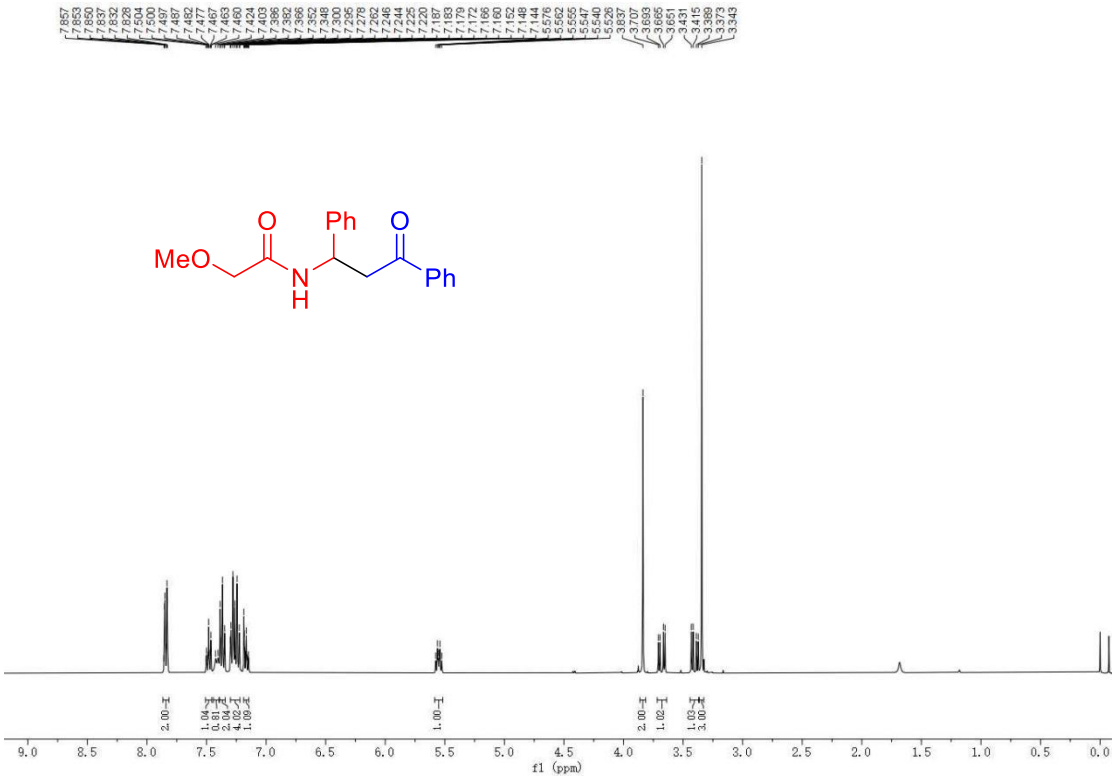

Figure S88. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of 2-methoxy-*N*-(3-oxo-1,3-diphenylpropyl)acetamide (3ia)

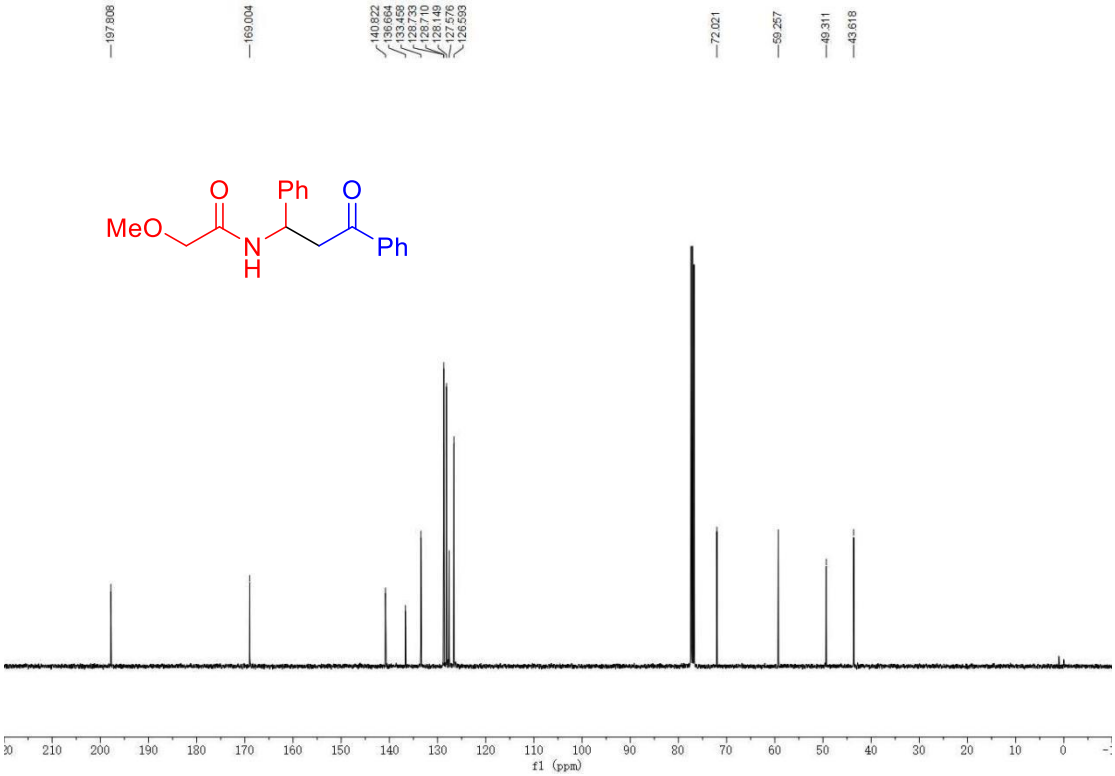

Figure S89. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(3-oxo-1,3-diphenylpropyl)cyclobutanecarboxamide (3ja)

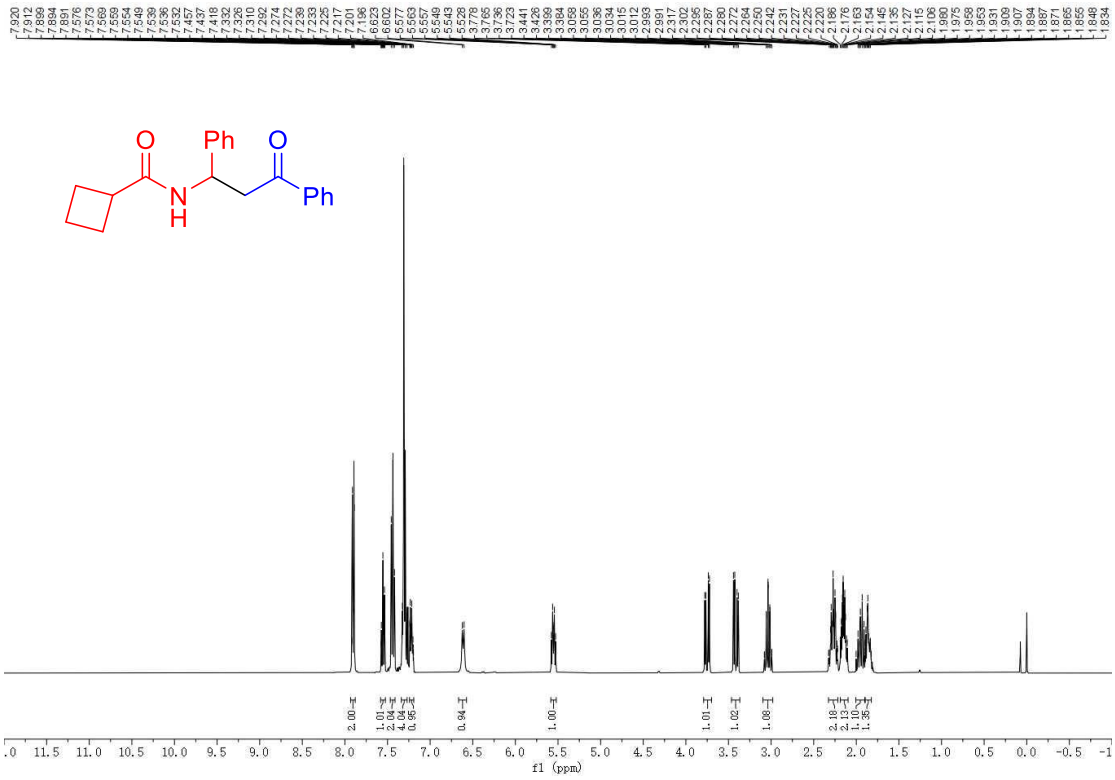

Figure S90. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-(3-oxo-1,3-diphenylpropyl)cyclobutanecarboxamide (3ja)

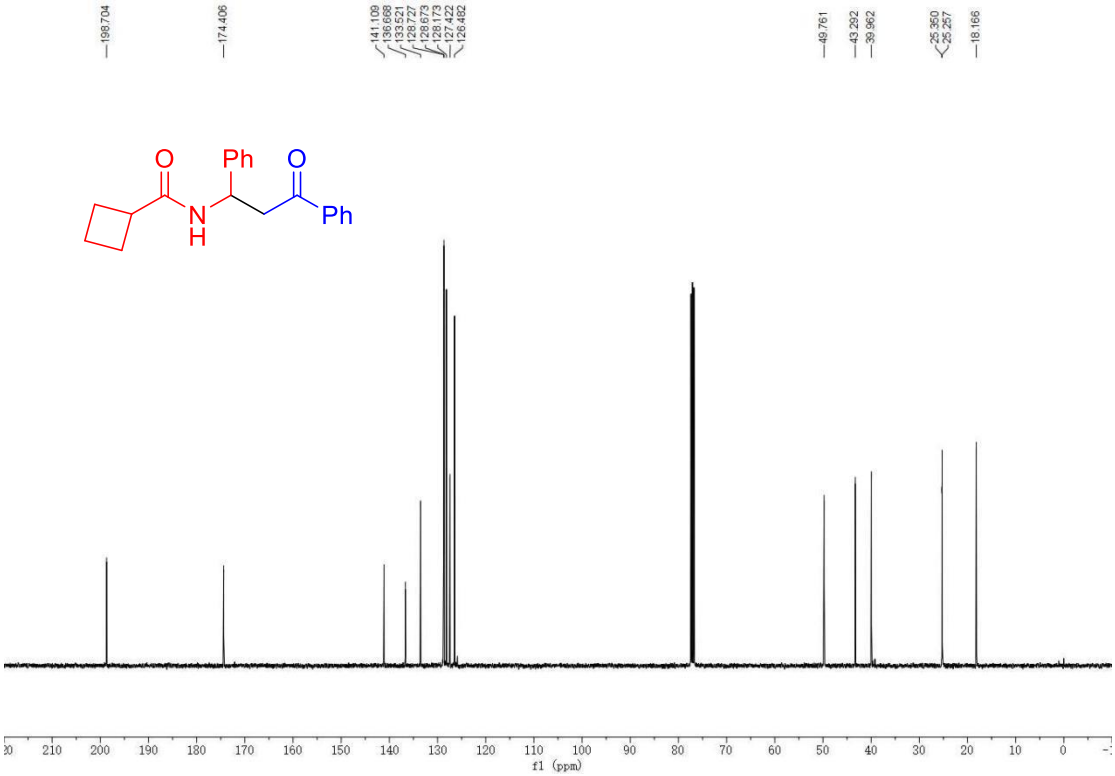

Figure S91. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(3-oxo-1,3-diphenylpropyl)cyclopentanecarboxamide (3ka)

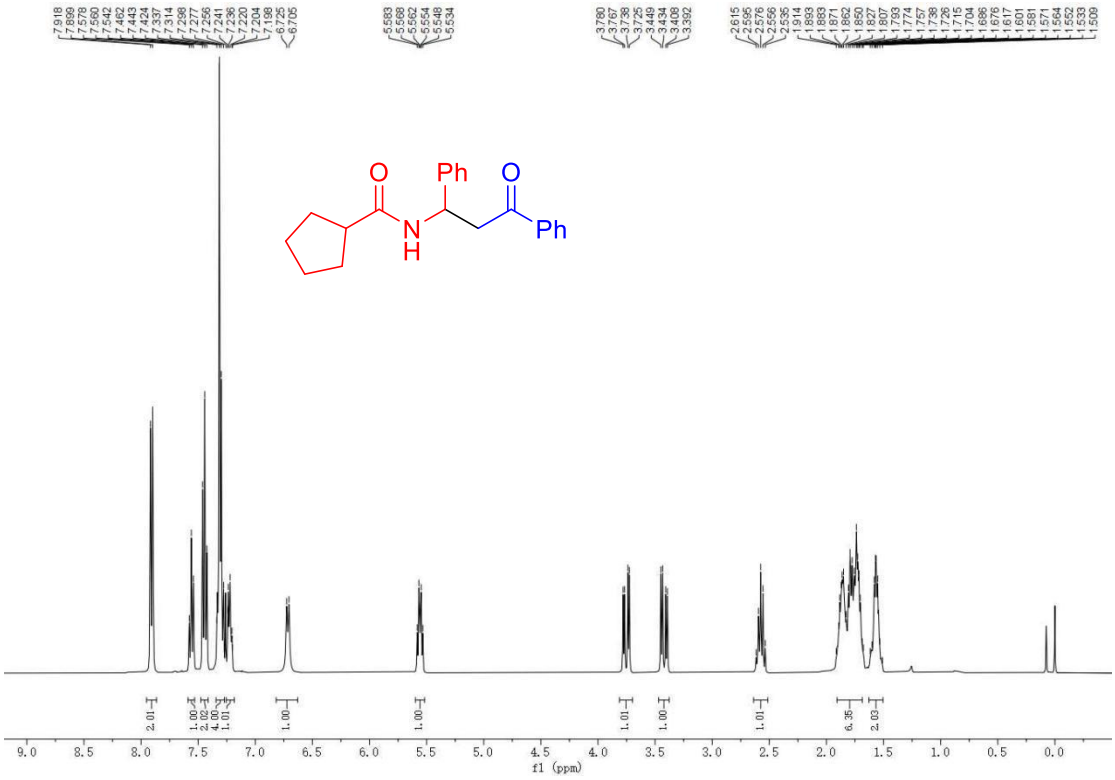

Figure S92. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-(3-oxo-1,3-diphenylpropyl)cyclopentanecarboxamide (3ka)

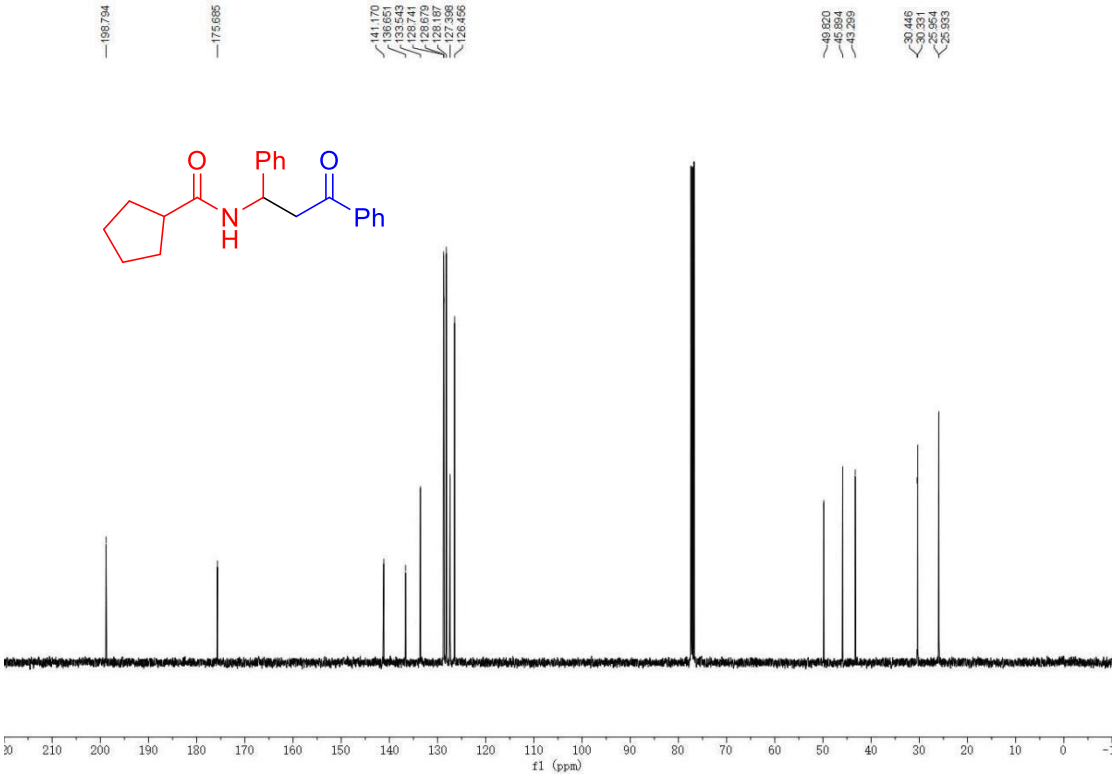

Figure S93. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(3-oxo-1,3-diphenylpropyl)cyclohexanecarboxamide (3la)

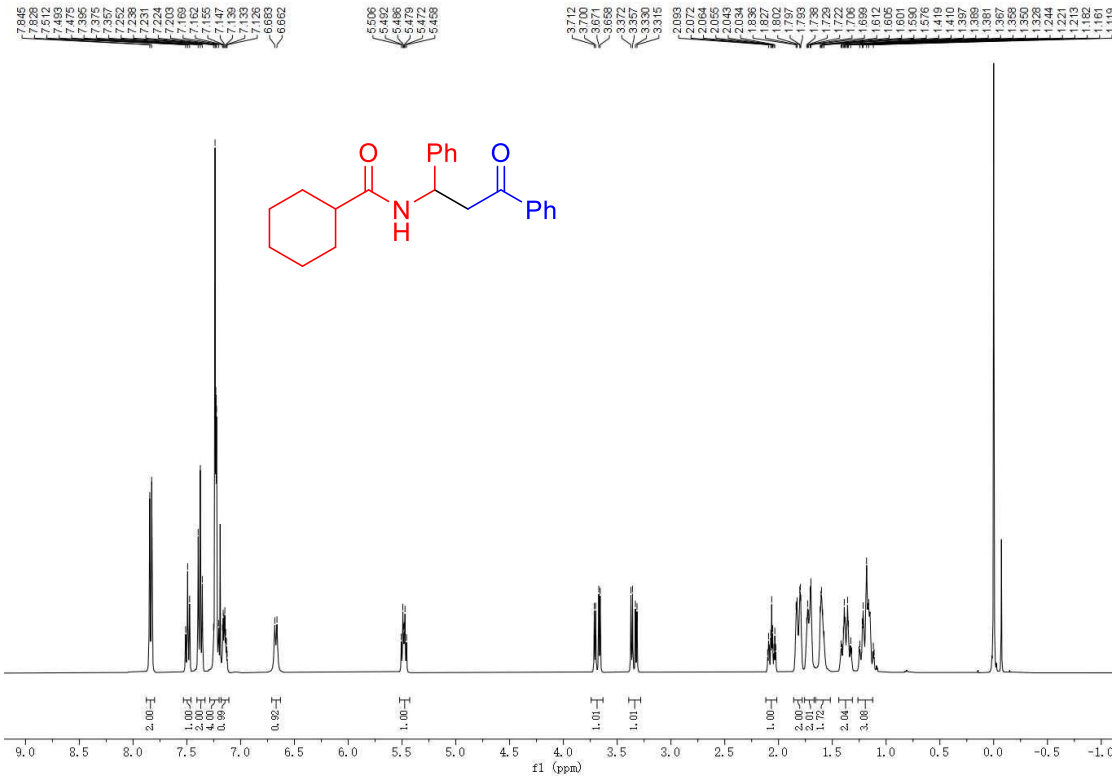

Figure S94. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-(3-oxo-1,3-diphenylpropyl)cyclohexanecarboxamide (3la)

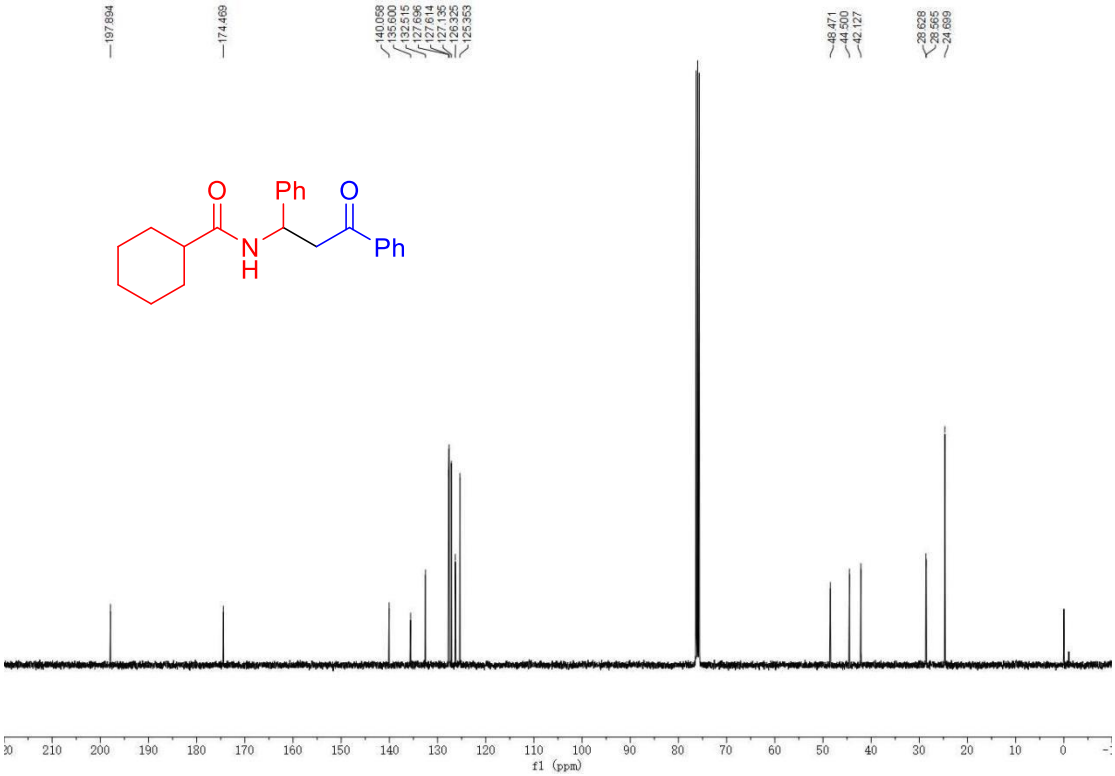

Figure S95. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of Methyl (3-oxo-1,3-diphenylpropyl)carbamate (3ma)

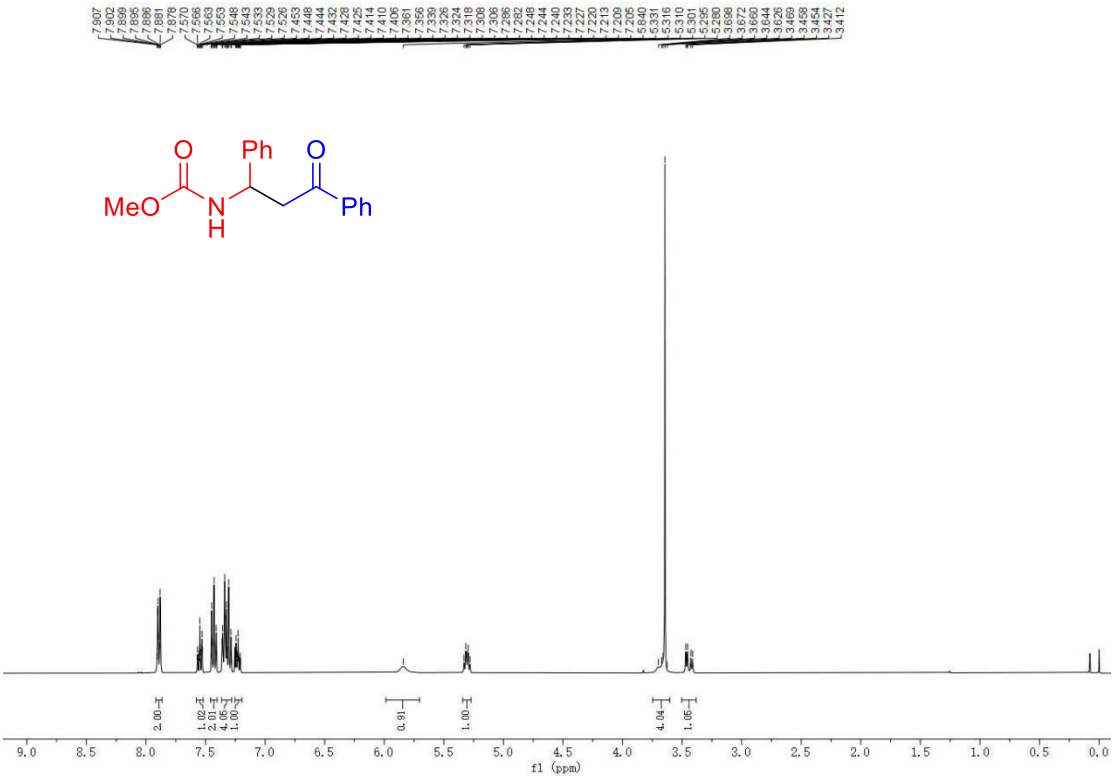

Figure S96. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of Methyl (3-oxo-1,3-diphenylpropyl)carbamate (3ma)

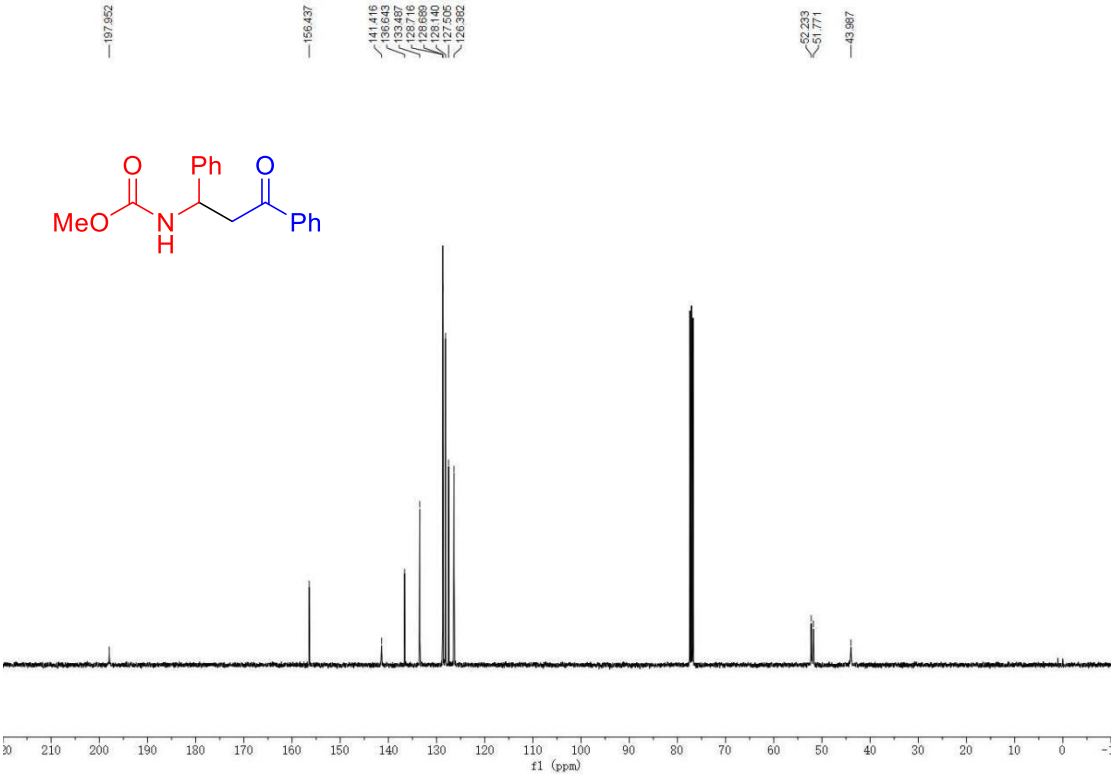

Figure S97. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *tert*-butyl (3-oxo-1,3-diphenylpropyl)carbamate (3na)

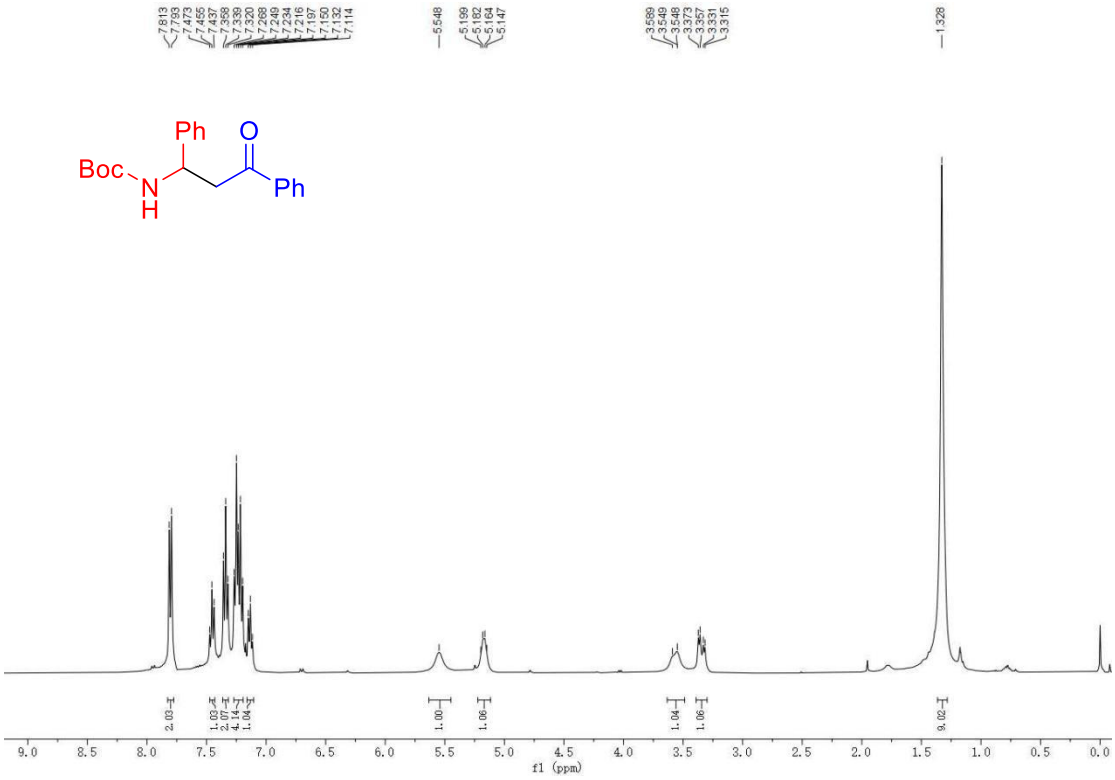

Figure S98. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *tert*-butyl (3-oxo-1,3-diphenylpropyl)carbamate (3na)

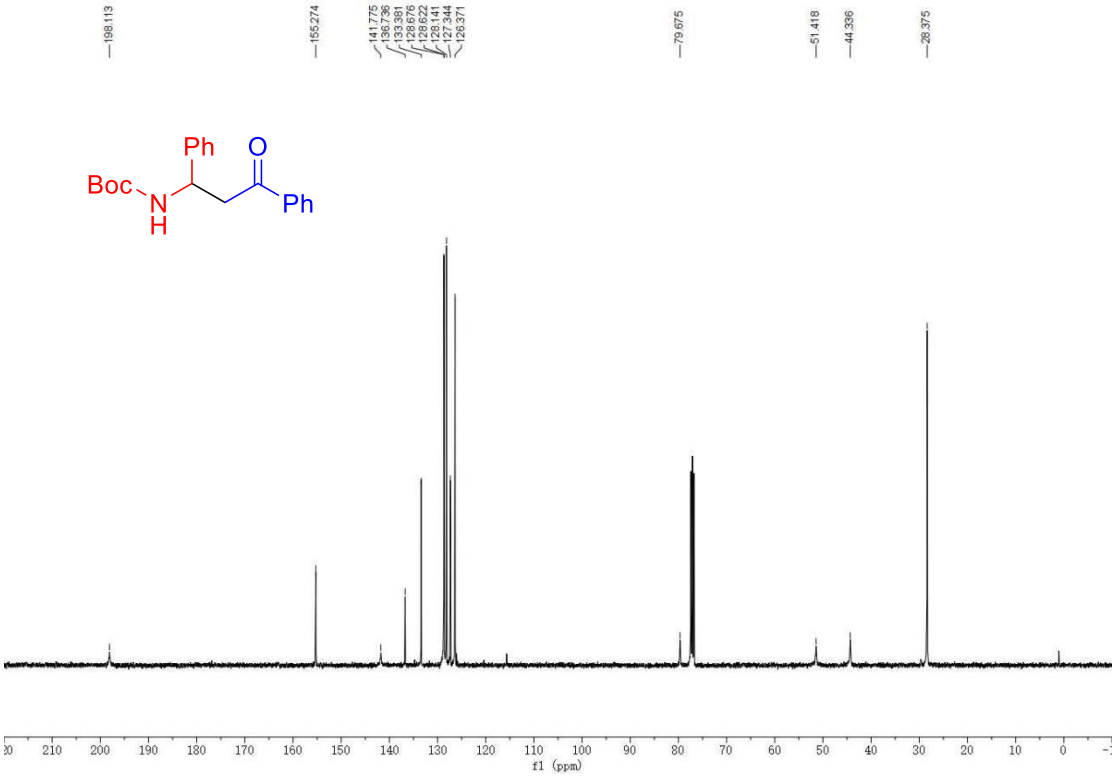

Figure S99. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of Phenyl (3-oxo-1,3-diphenylpropyl)carbamate (3oa)

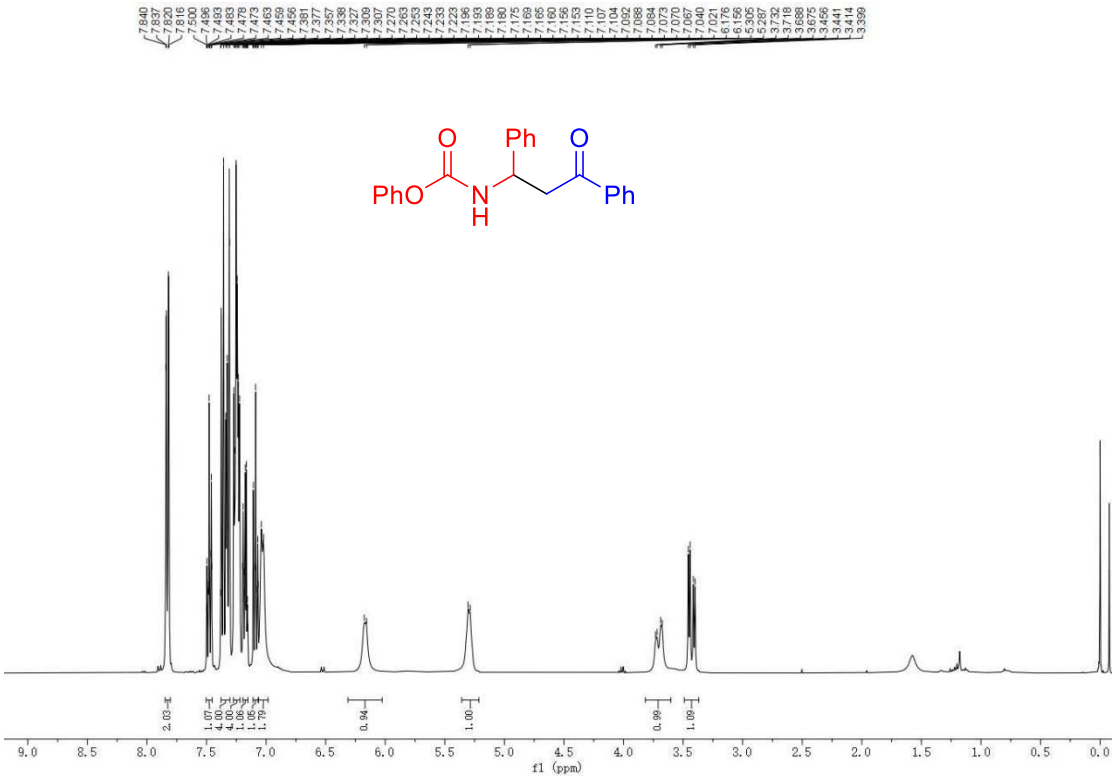

Figure S100. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of Phenyl (3-oxo-1,3-diphenylpropyl)carbamate (3oa)

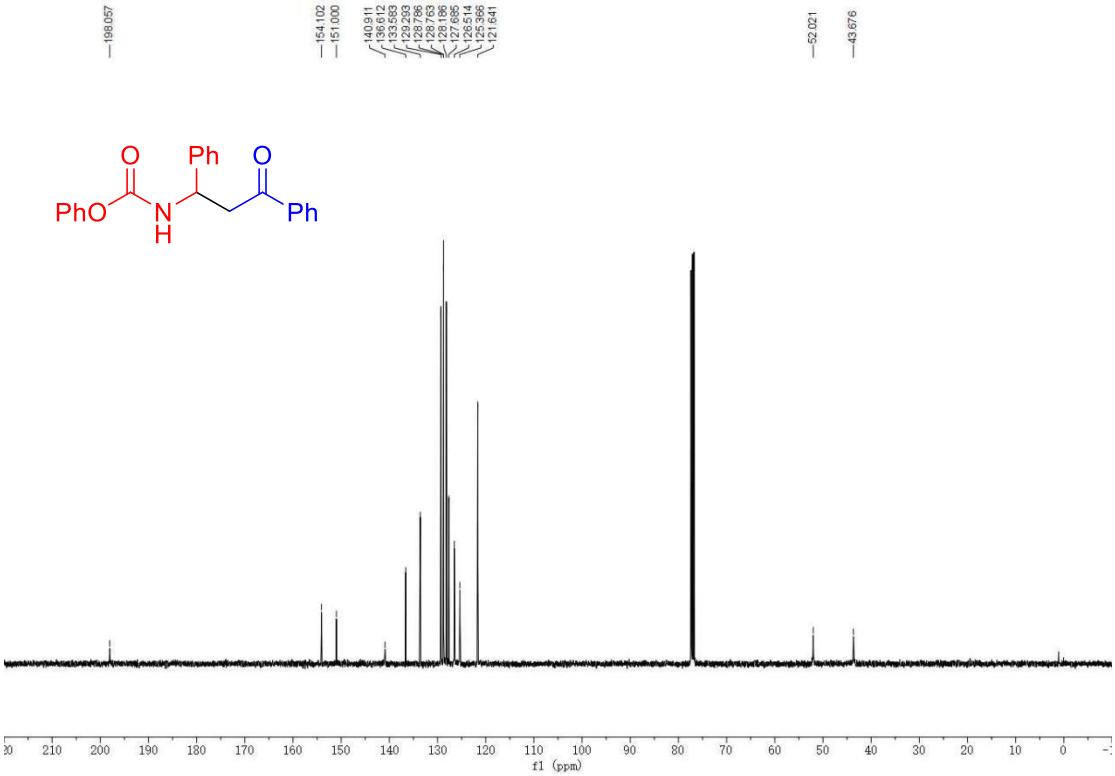

Figure S101. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(1-(3,5-dimethoxyphenyl)-3-oxo-3-phenylpropyl)benzamide (3pa)

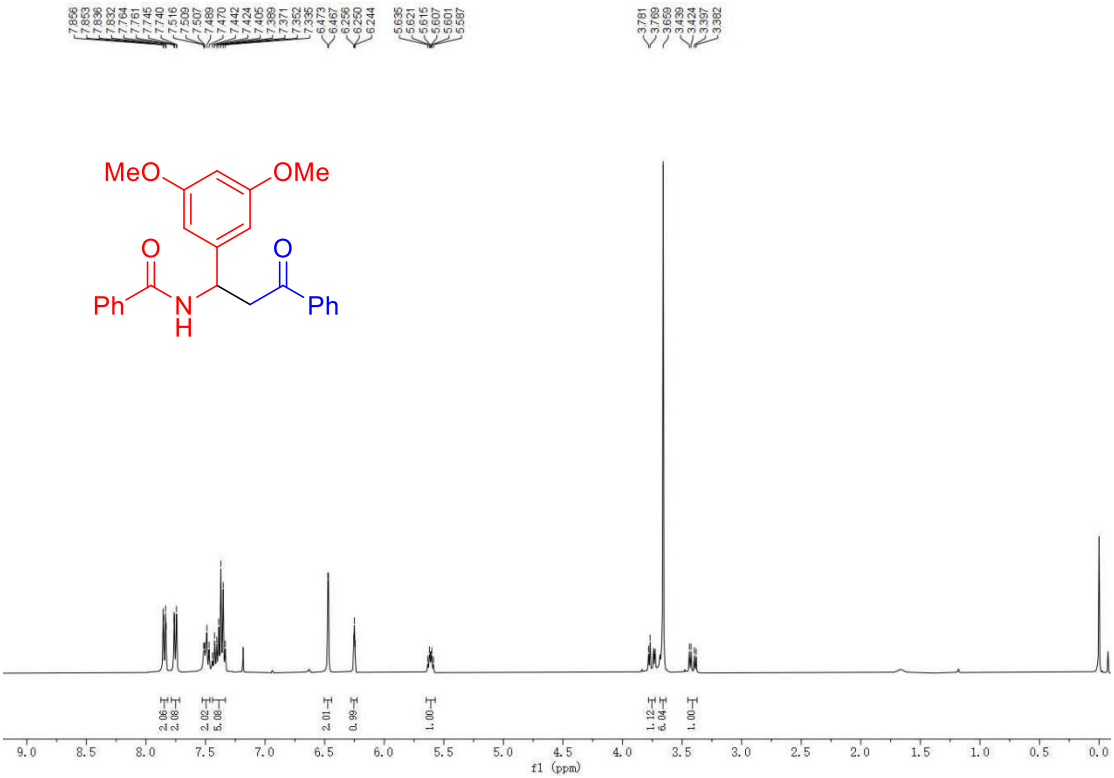

Figure S102. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-(1-(3,5-dimethoxyphenyl)-3-oxo-3-phenylpropyl)benzamide (3pa)

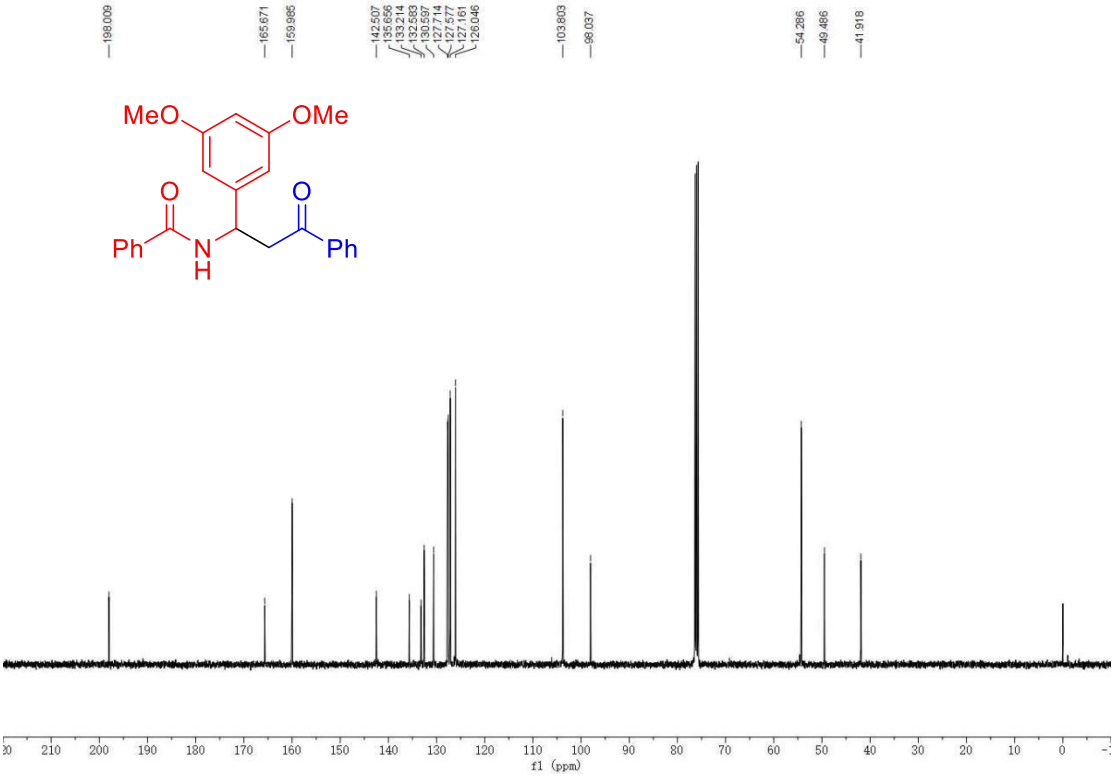

Figure S103. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(3-oxo-3-phenyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl)benzamide (3qa)

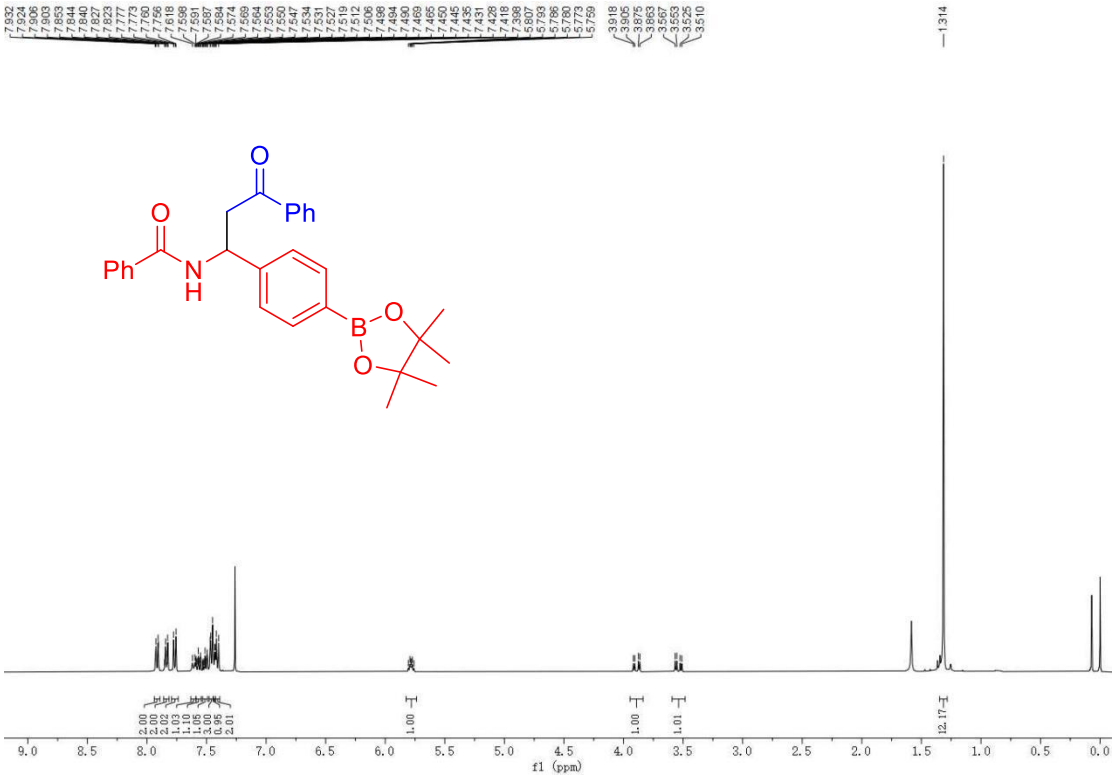

Figure S104. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-(3-oxo-3-phenyl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl)benzamide (3qa)

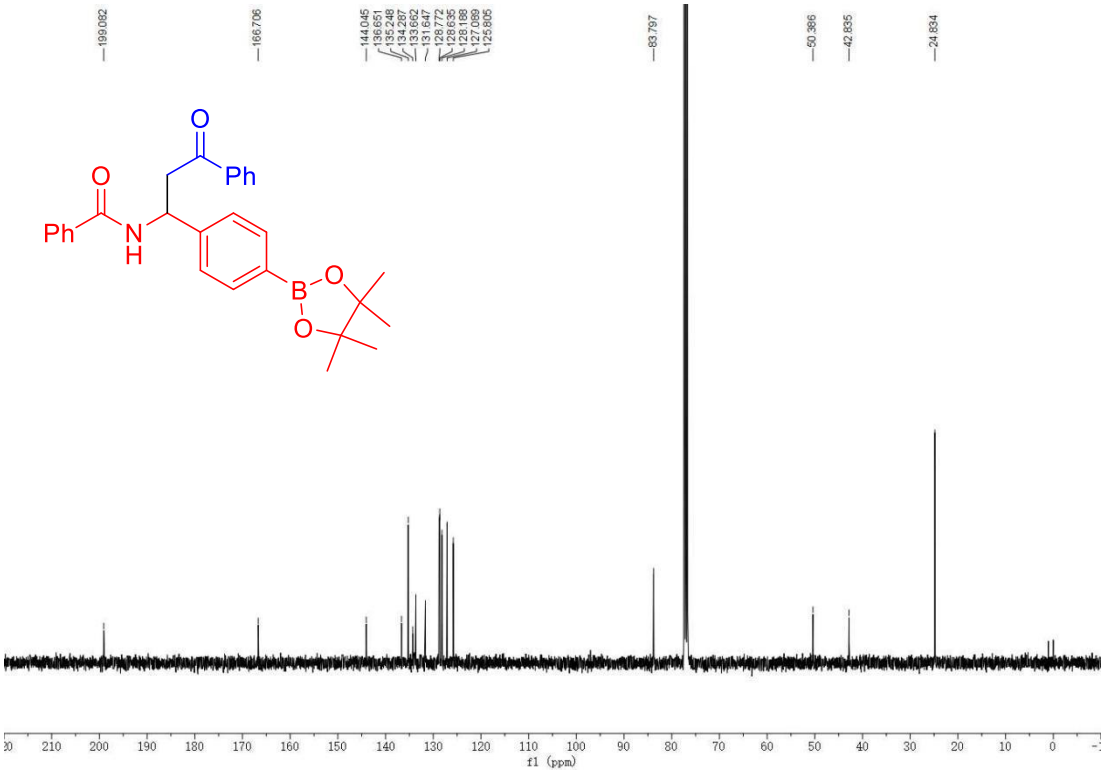

Figure S105. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(3-oxo-3-phenyl-1-(4-(trifluoromethyl)phenyl)propyl)benzamide (3ra)

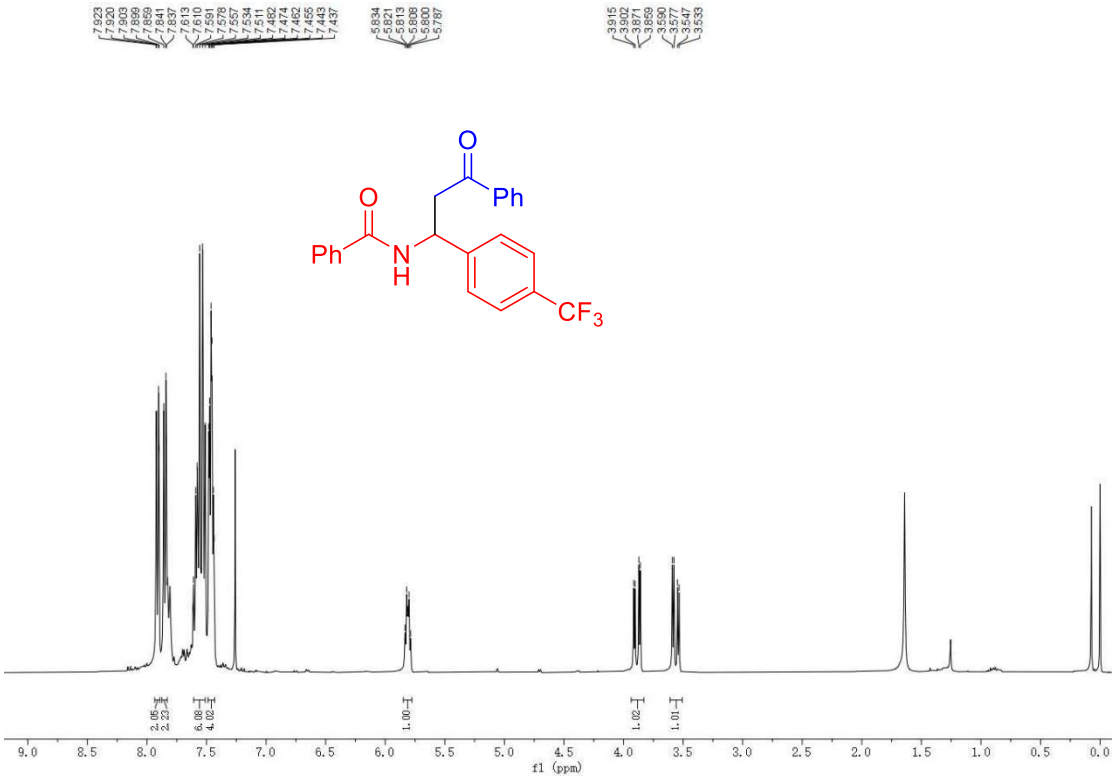

Figure S106. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-(3-oxo-3-phenyl-1-(4-(trifluoromethyl)phenyl)propyl)benzamide (3ra)

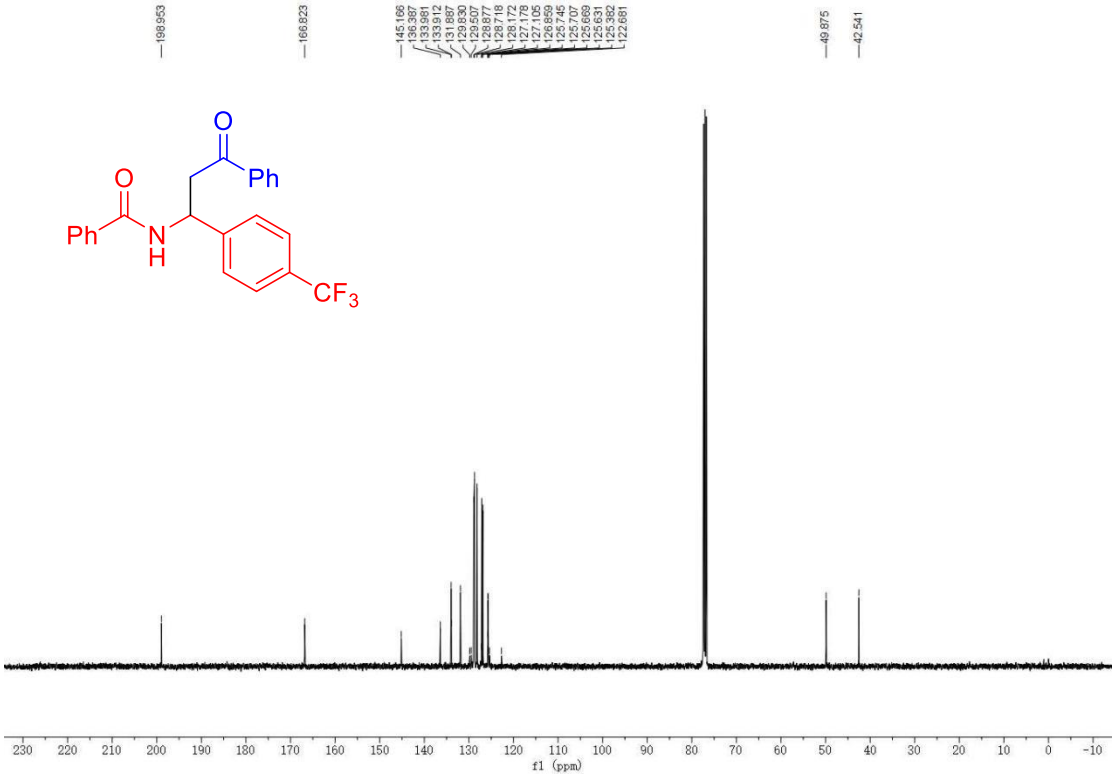

Figure S107. ^{19}F NMR spectra (376 MHz, Chloroform-*d*) of *N*-(3-oxo-3-phenyl-1-(4-(trifluoromethyl)phenyl)propyl)benzamide (3ra)

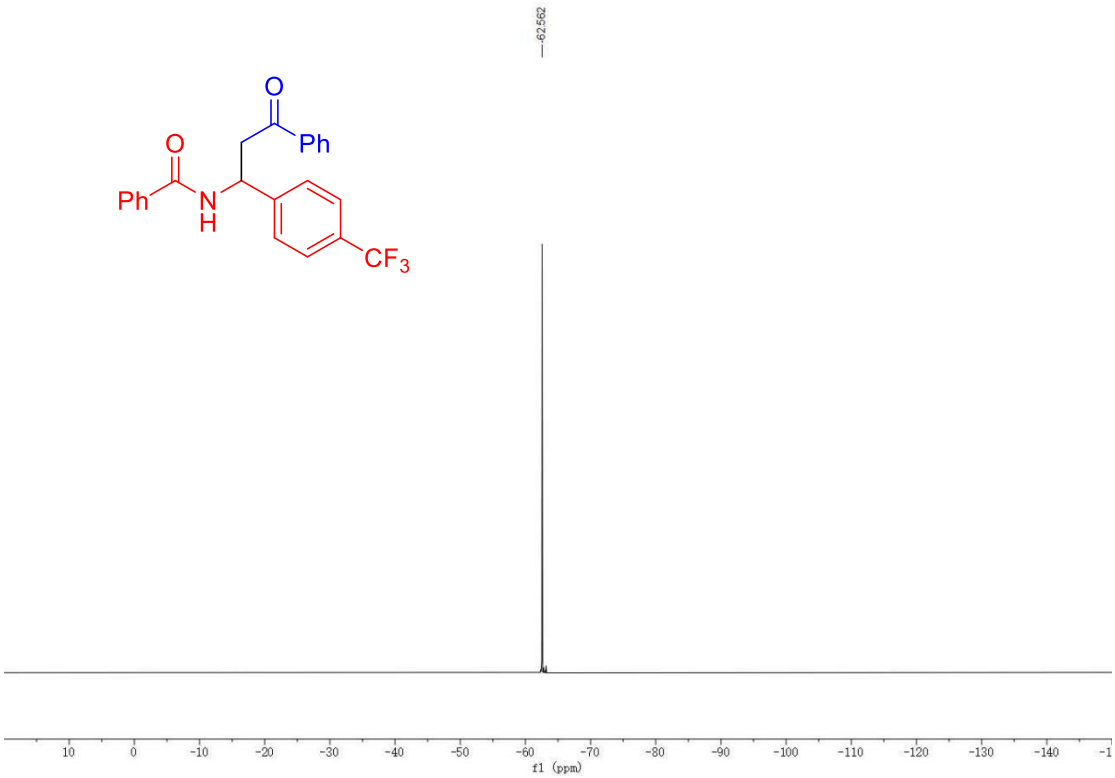

Figure S108. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(3-oxo-3-phenylpropyl)benzamide (3sa)

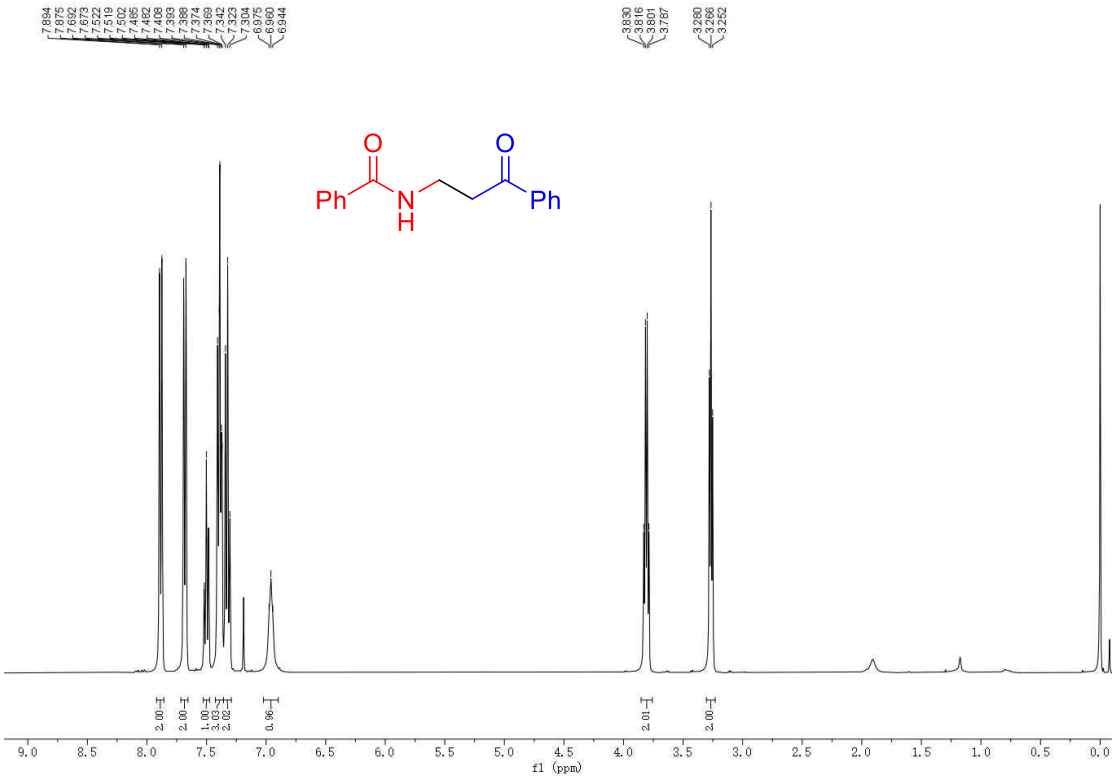

Figure S109. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-(3-oxo-3-phenylpropyl)benzamide (3sa)

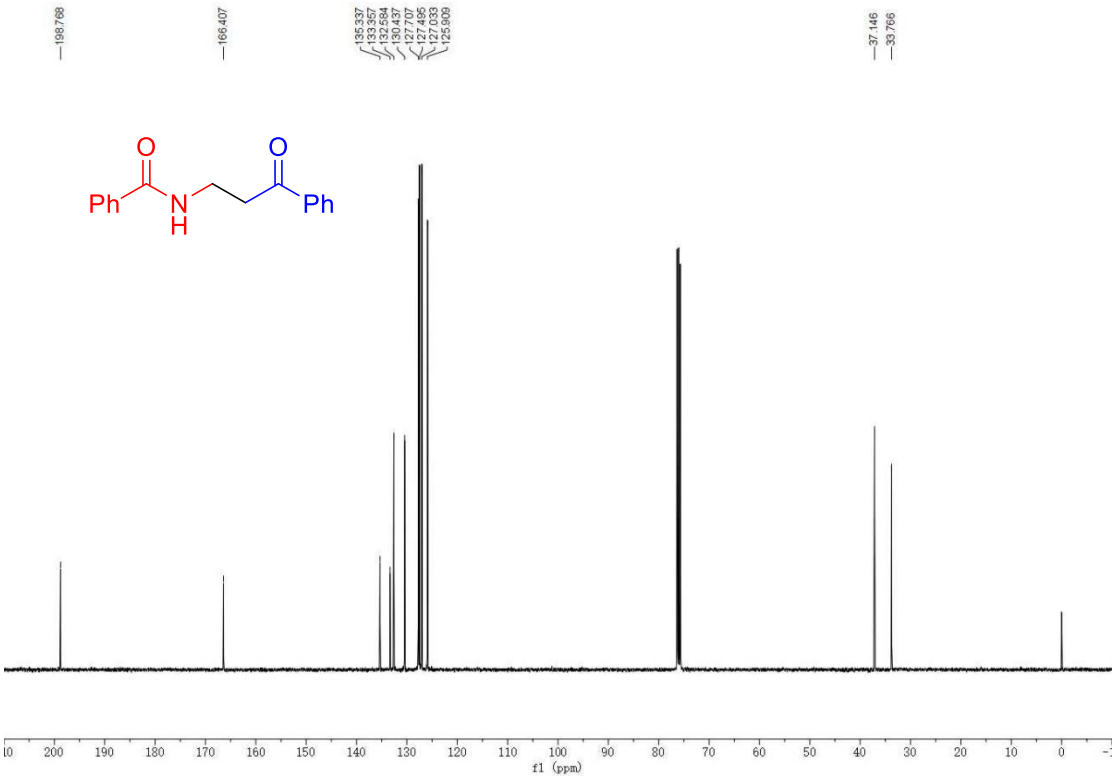

Figure S110. ^{1}H NMR spectra (600 MHz, Chloroform-*d*) of *N*-(4-oxo-4-phenylbutan-2-yl)benzamide (3ta)

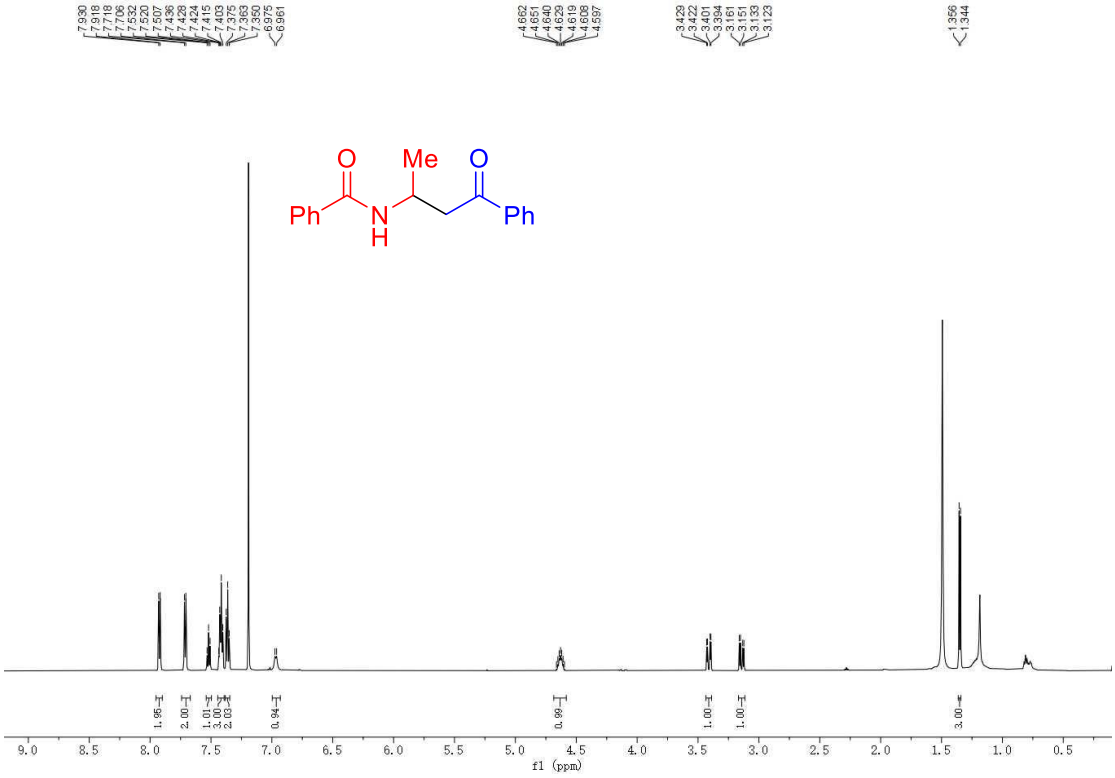

Figure S111. ^{13}C NMR spectra (150 MHz, Chloroform-*d*) of *N*-(4-oxo-4-phenylbutan-2-yl)benzamide (3ta)

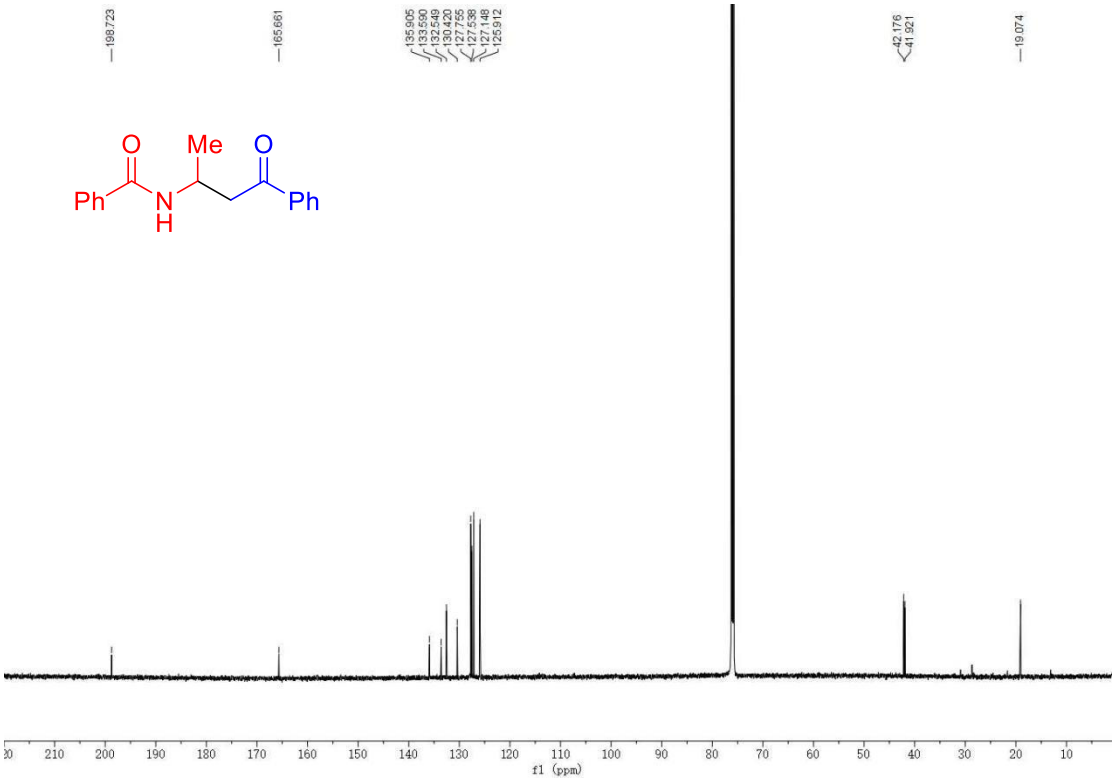

Figure S112. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(3-(4-fluorophenyl)-3-oxo-1-phenylpropyl)benzamide (3ab)

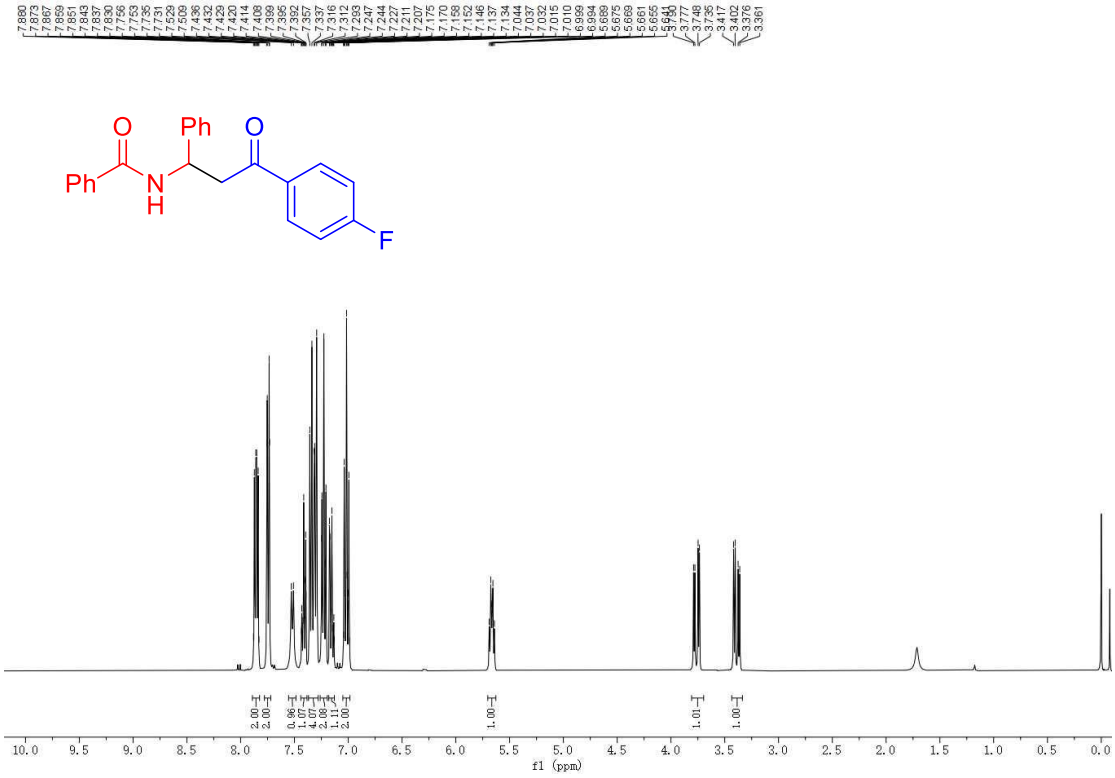

Figure S113. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-(3-(4-fluorophenyl)-3-oxo-1-phenylpropyl)benzamide (3ab)

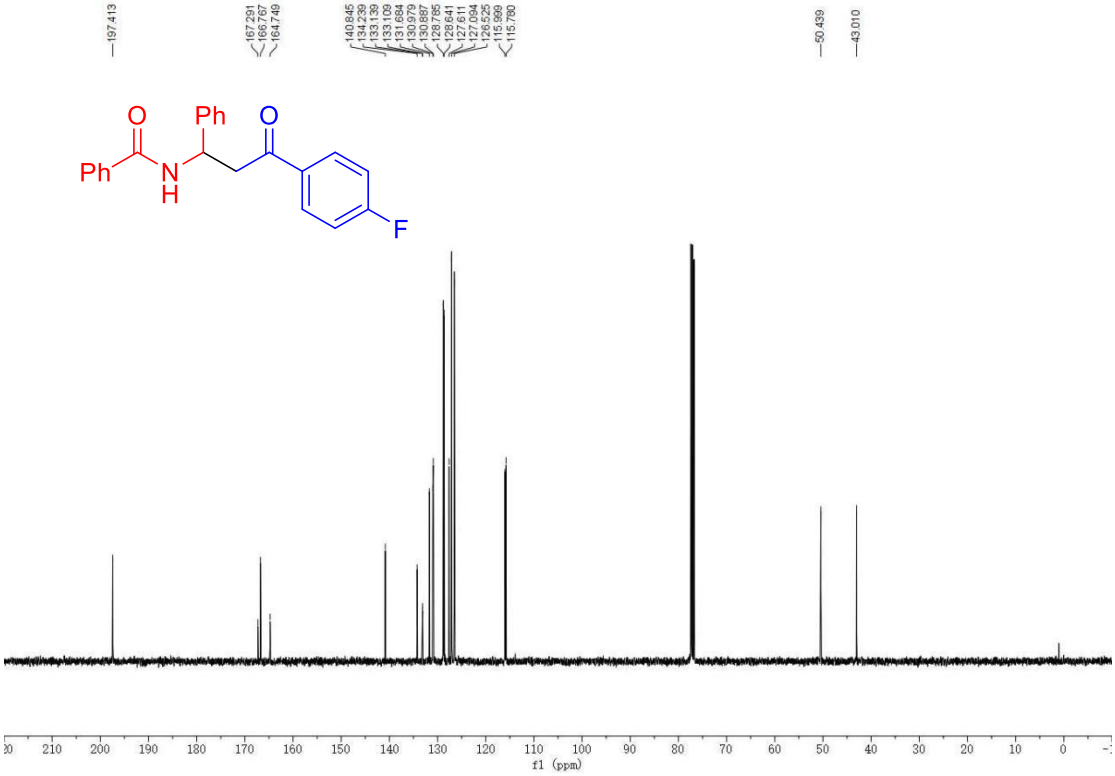

Figure S114. ^{19}F NMR spectra (376 MHz, Chloroform-*d*) of *N*-(3-(4-fluorophenyl)-3-oxo-1-phenylpropyl)benzamide (3ab)

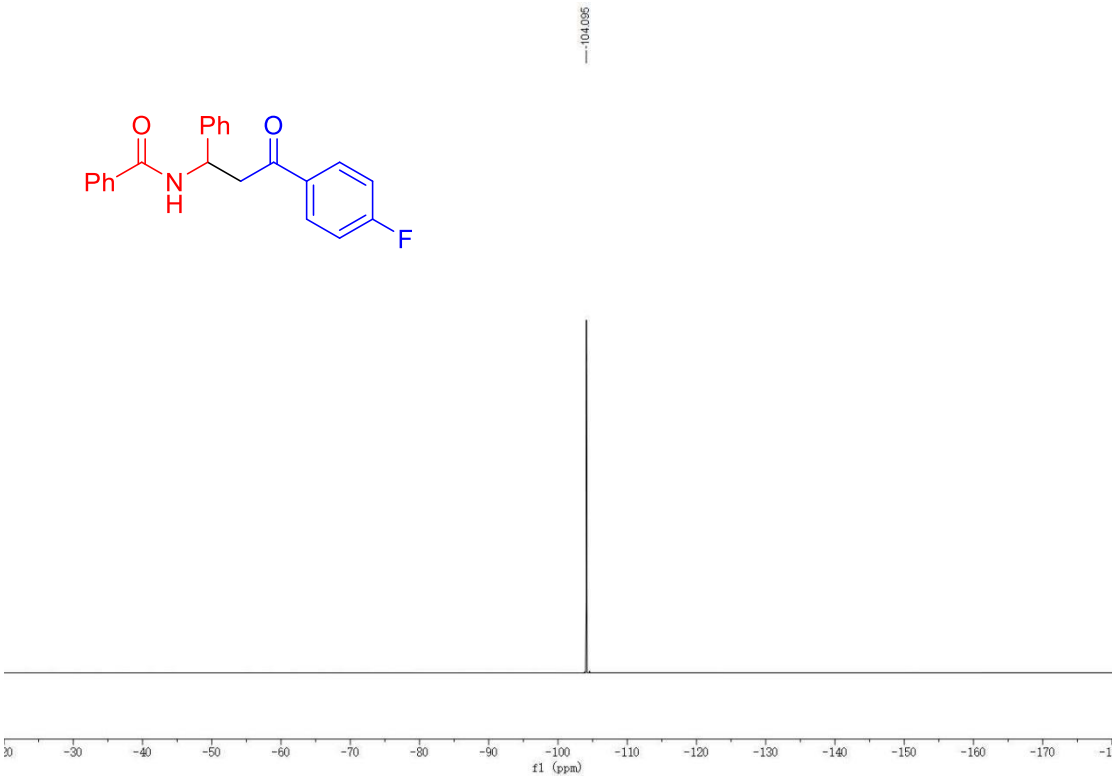

Figure S115. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(3-(4-chlorophenyl)-3-oxo-1-phenylpropyl)benzamide (3ac)

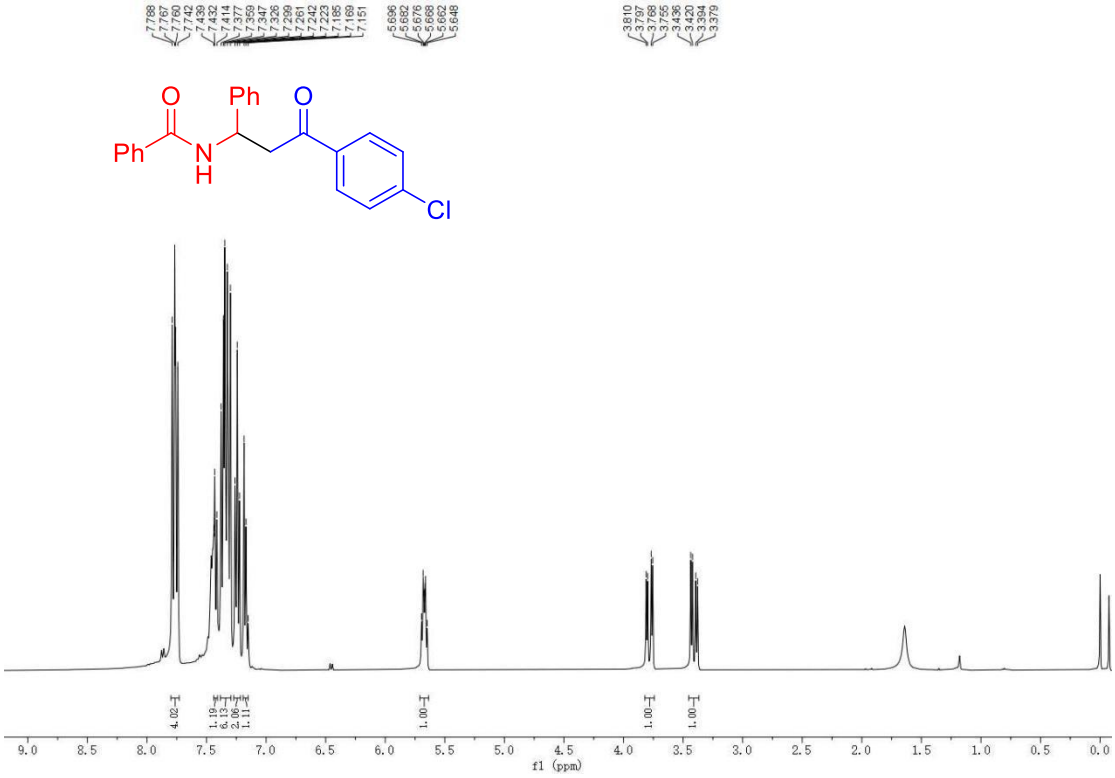

Figure S116. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-(3-(4-chlorophenyl)-3-oxo-1-phenylpropyl)benzamide (3ac)

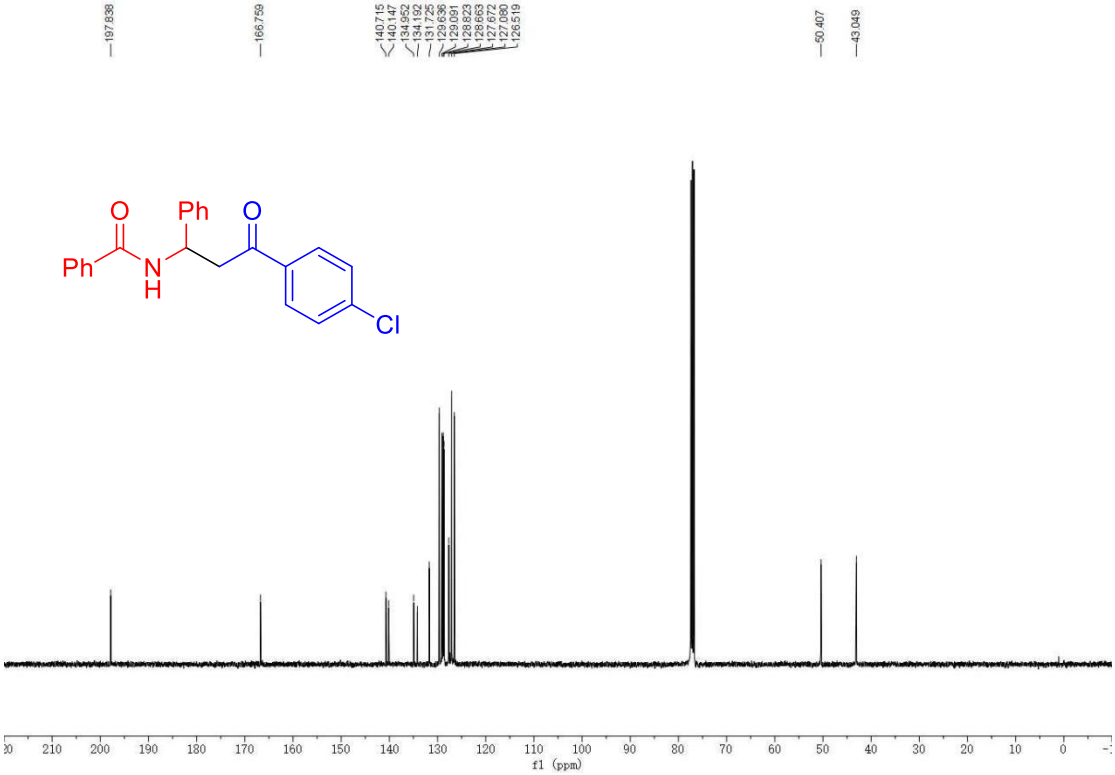

Figure S117. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(3-(4-bromophenyl)-3-oxo-1-phenylpropyl)benzamide (3ad)

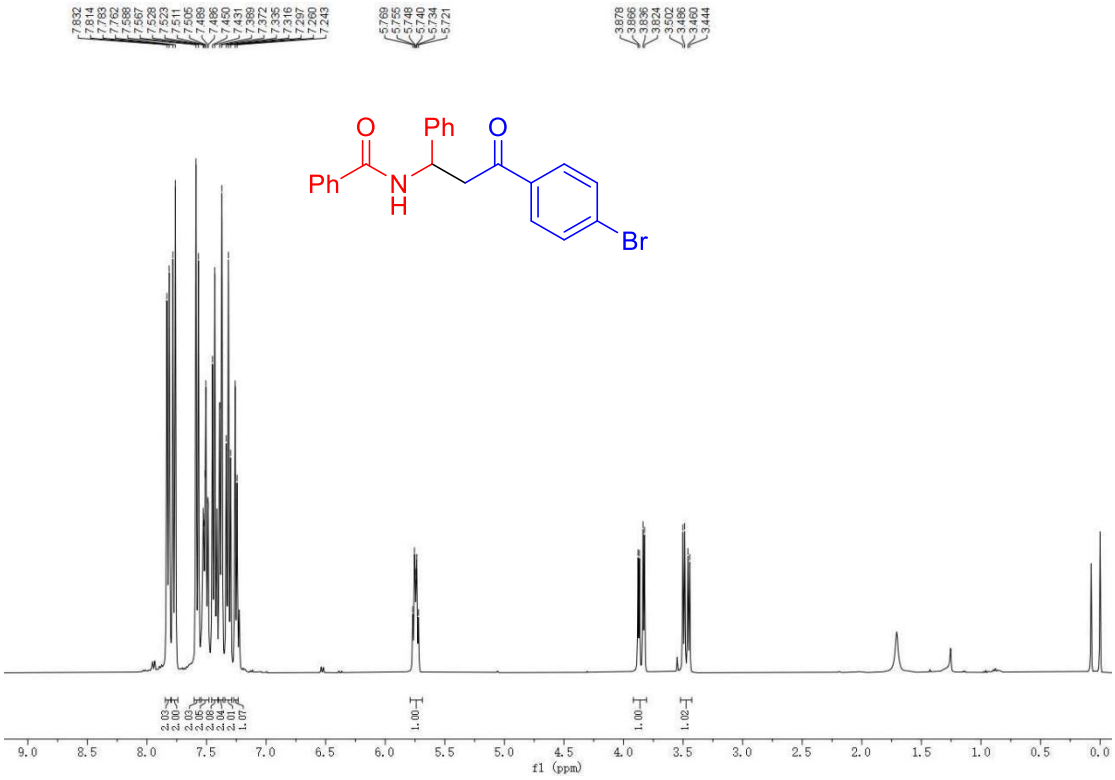

Figure S118. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-(3-(4-bromophenyl)-3-oxo-1-phenylpropyl)benzamide (3ad)

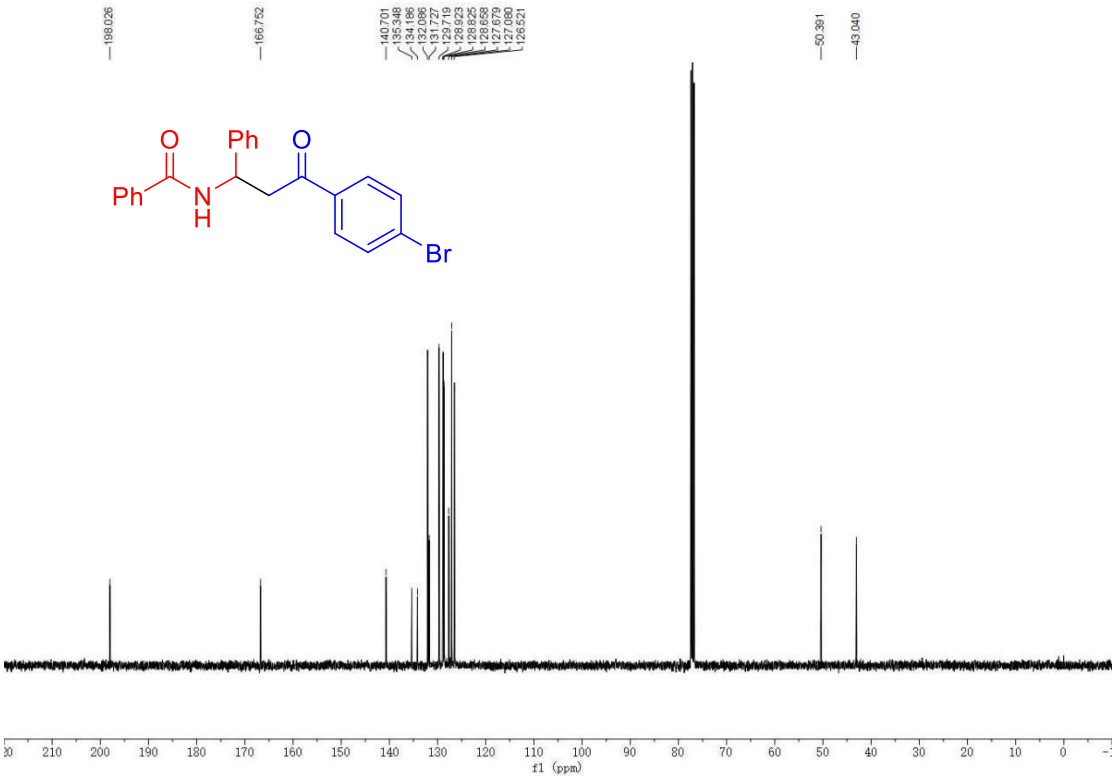

Figure S119. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(3-oxo-1-phenyl-3-(4-(trifluoromethyl)phenyl)propyl)benzamide (3ae)

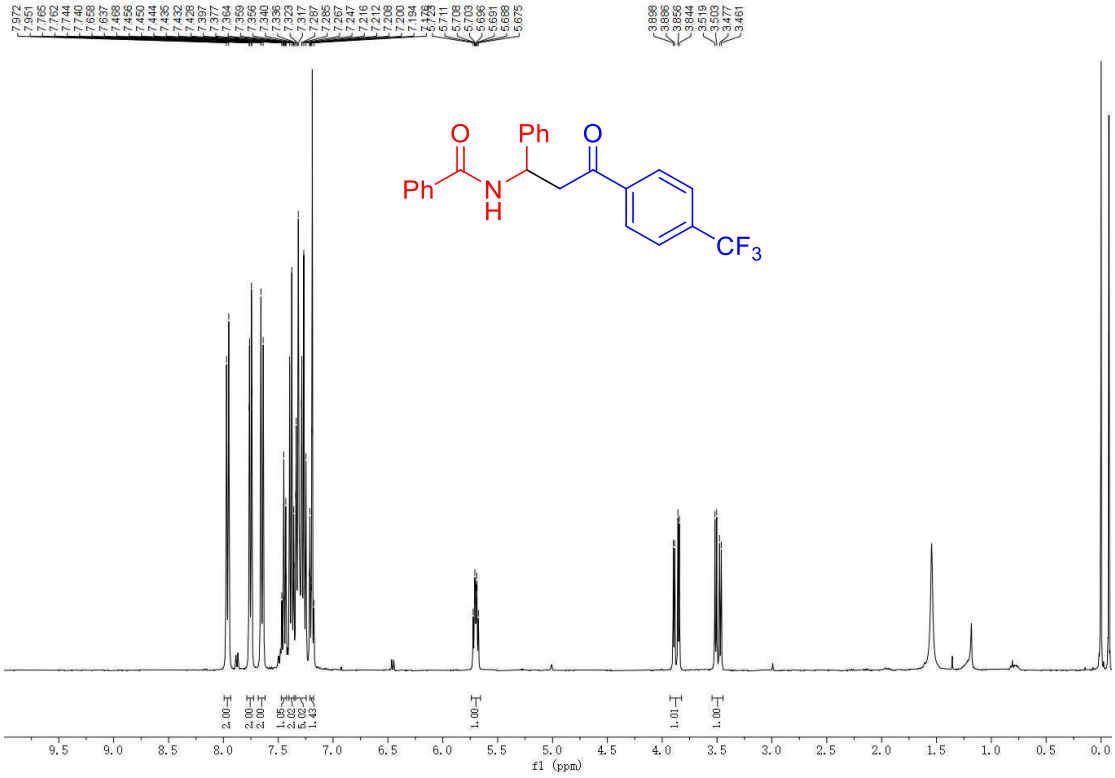

Figure S120. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-(3-oxo-1-phenyl-3-(4-(trifluoromethyl)phenyl)propyl)benzamide (3ae)

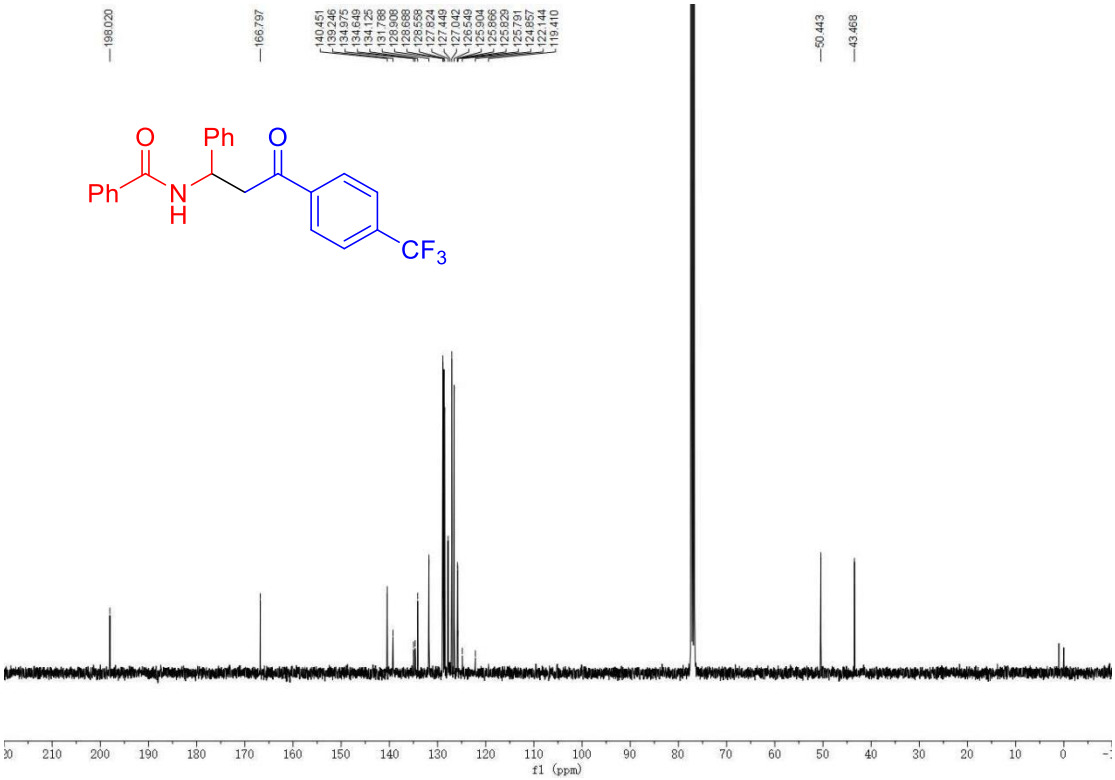

Figure S121. ^{19}F NMR spectra (376 MHz, Chloroform-*d*) of *N*-(3-oxo-1-phenyl-3-(4-(trifluoromethyl)phenyl)propyl)benzamide (3ae)

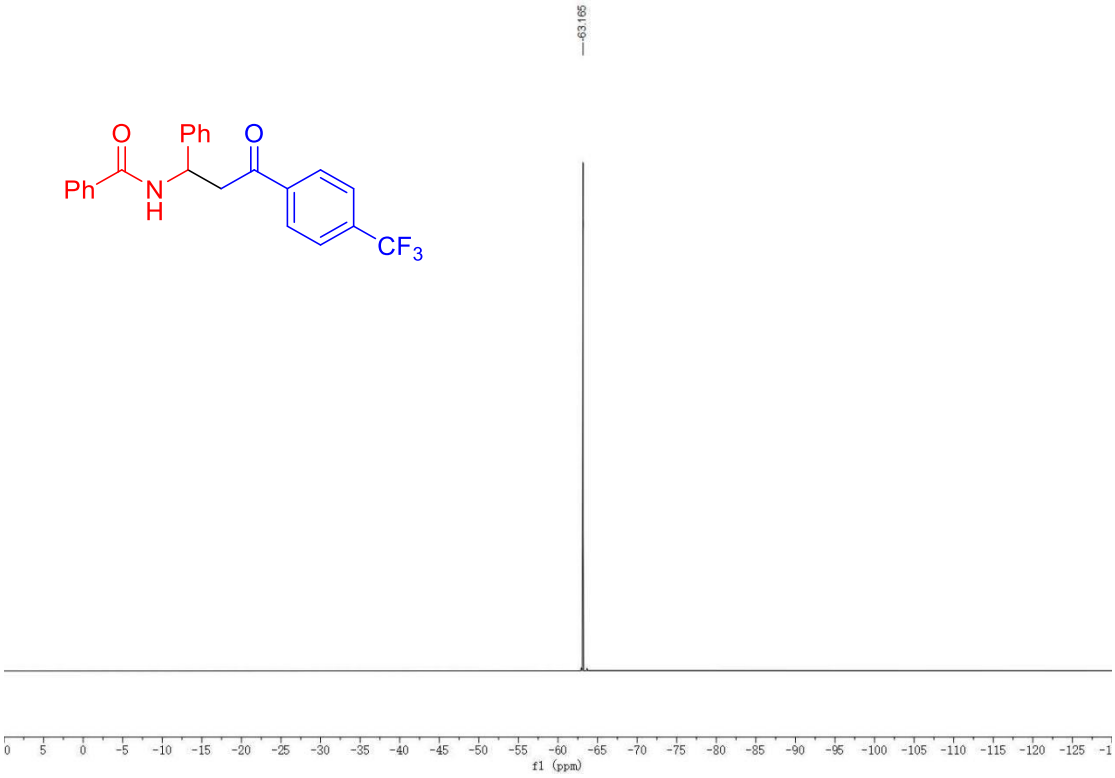

Figure S122. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(3-(3-methoxyphenyl)-3-oxo-1-phenylpropyl)benzamide (3af)

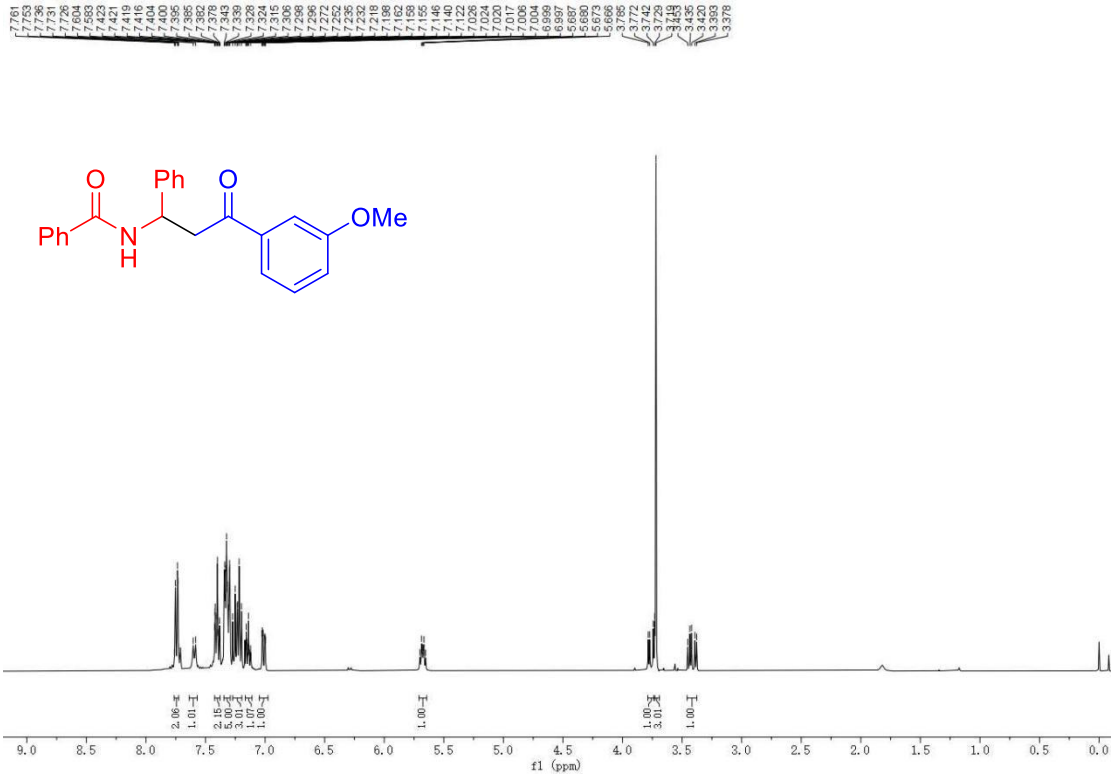

Figure S123. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-(3-(3-methoxyphenyl)-3-oxo-1-phenylpropyl)benzamide (3af)

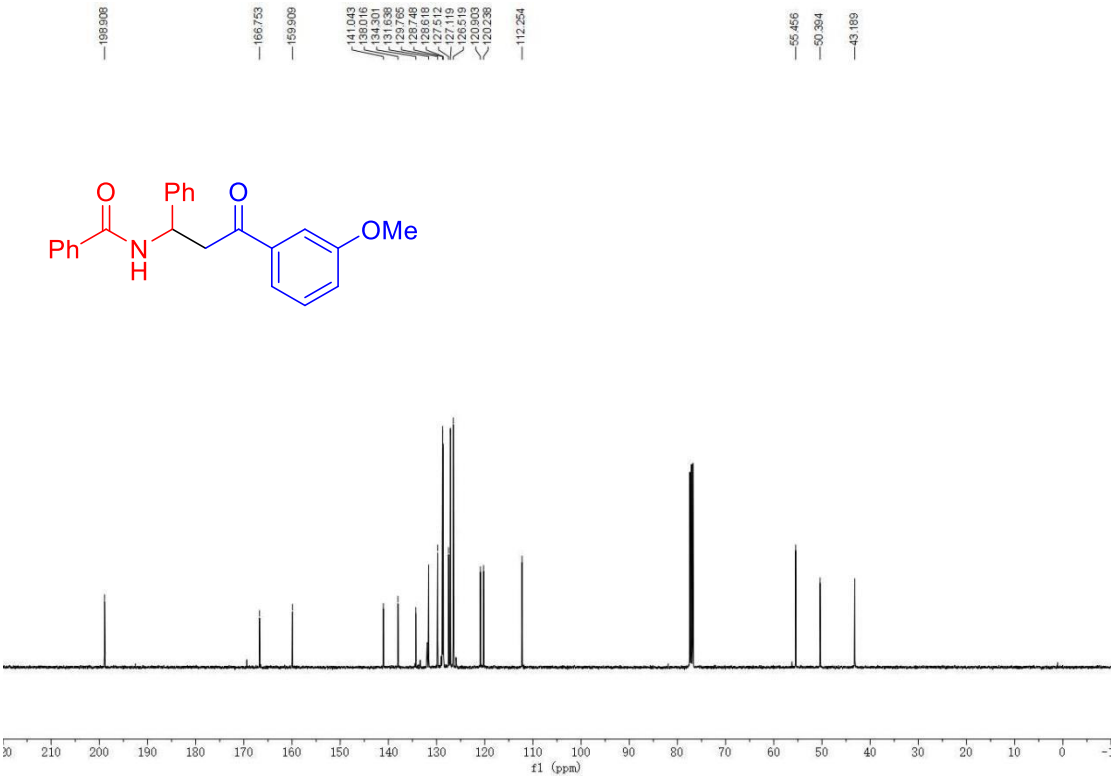

Figure S124. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(3-(2,3-dihydro-1*H*-inden-5-yl)-3-oxo-1-phenylpropyl)benzamide (3ag)

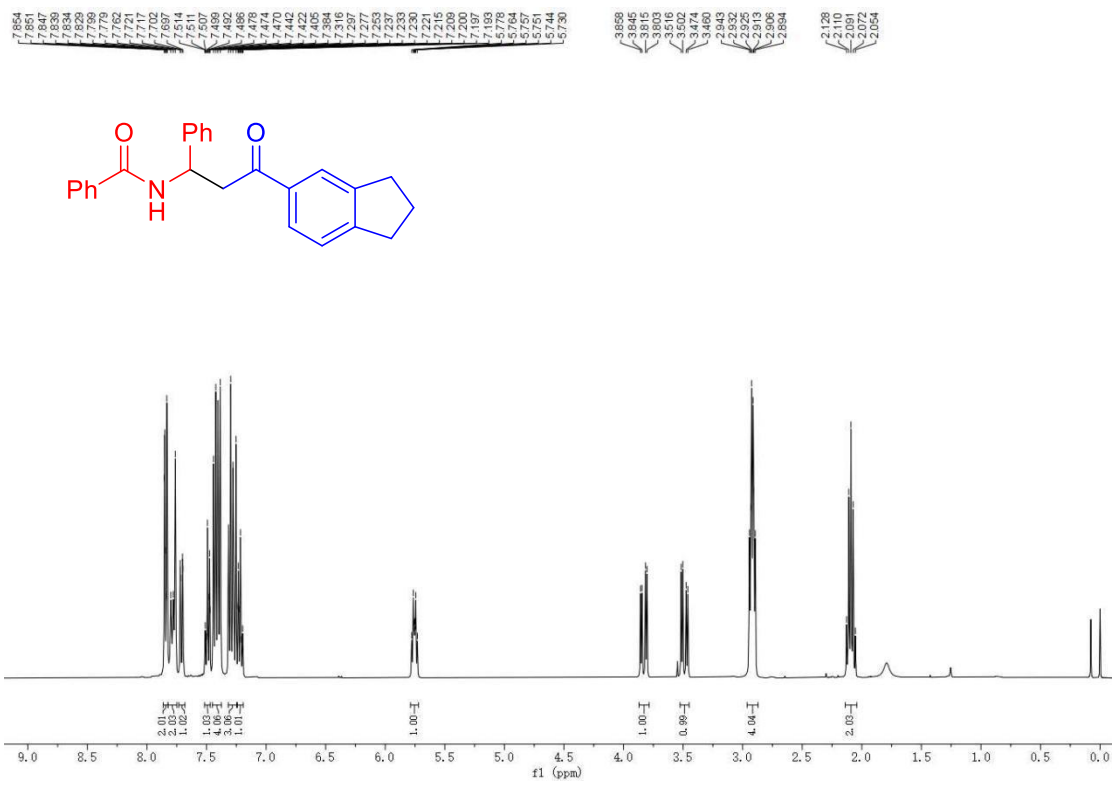

Figure S125. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-(3-(2,3-dihydro-1*H*-inden-5-yl)-3-oxo-1-phenylpropyl)benzamide (3ag)

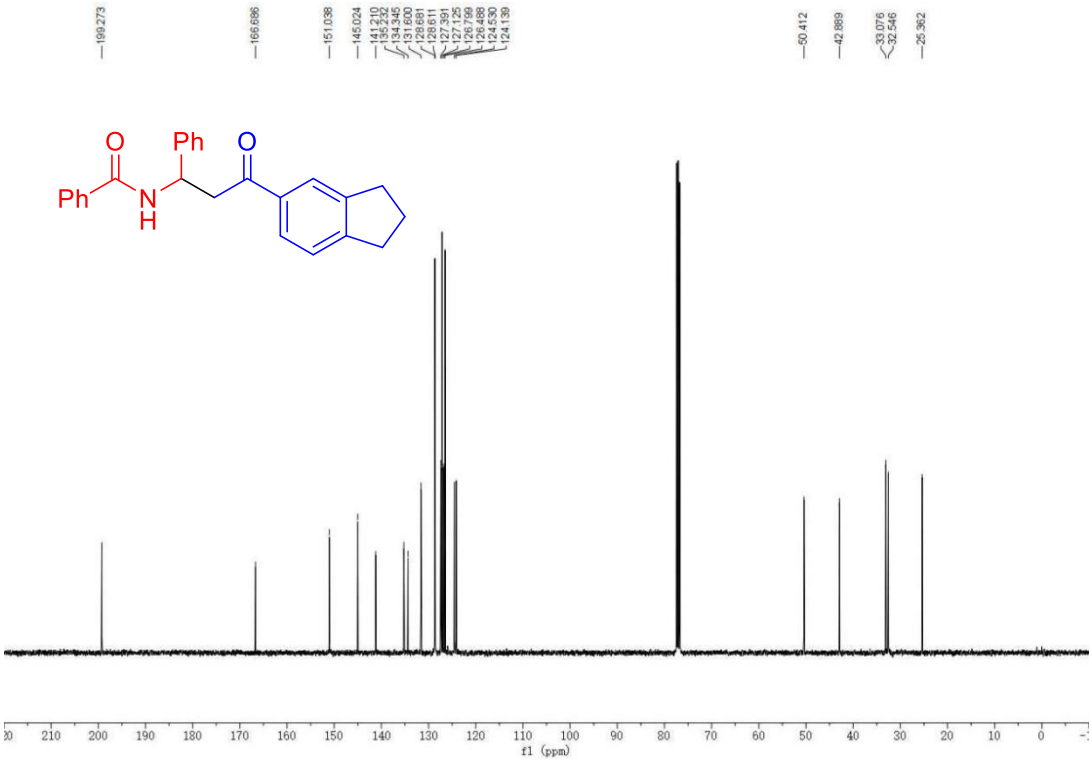

Figure S126. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(3-(2,3-dihydrobenzofuran-7-yl)-3-oxo-1-phenylpropyl)benzamide (3ah)

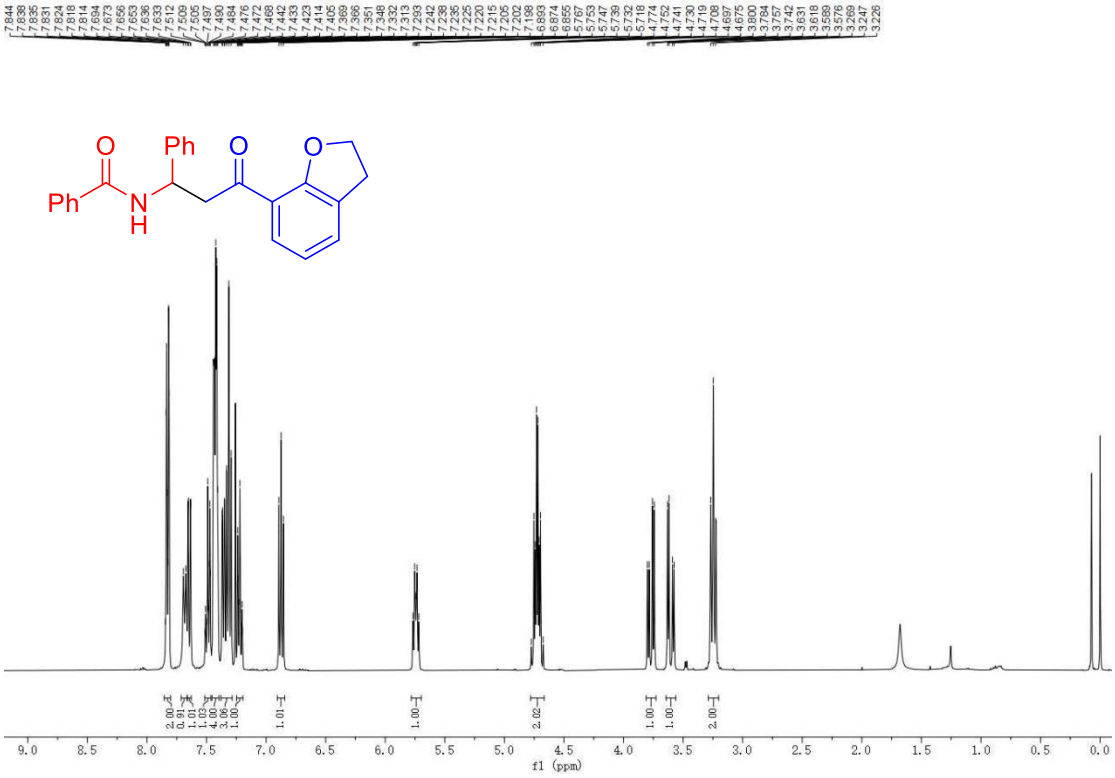

Figure S127. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-(3-(2,3-dihydrobenzofuran-7-yl)-3-oxo-1-phenylpropyl)benzamide (3ah)

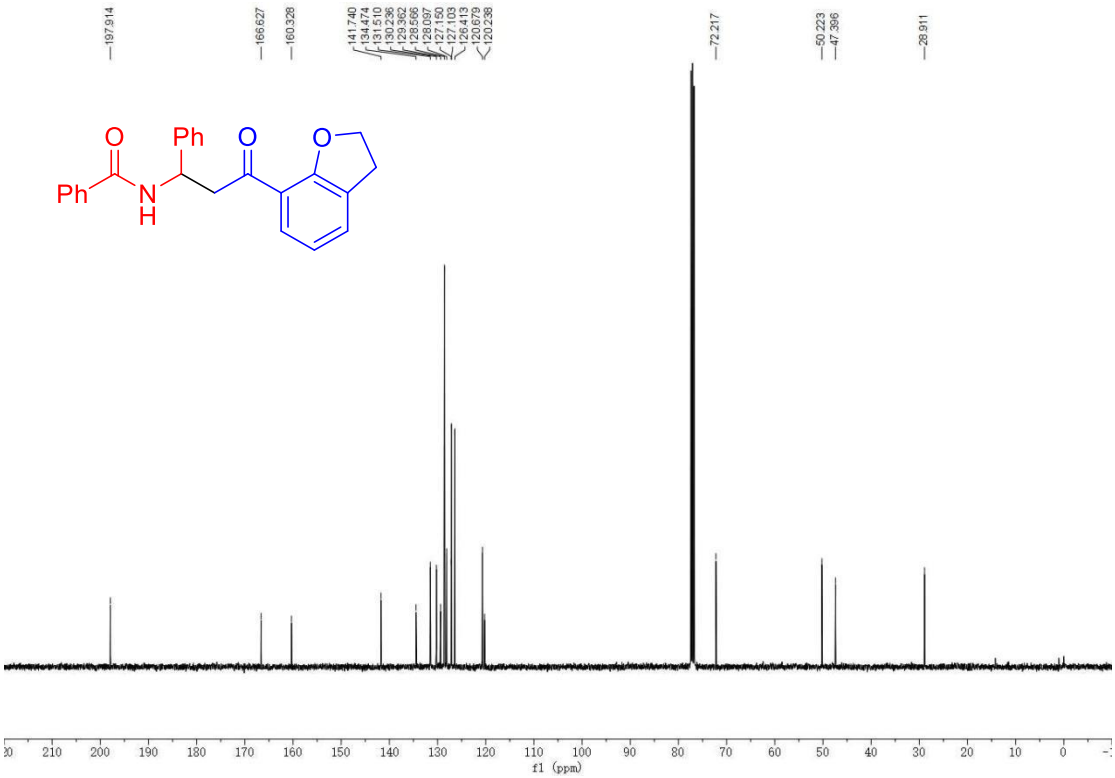

Figure S128. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(3-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-3-oxo-1-phenylpropyl)benzamide (3ai)

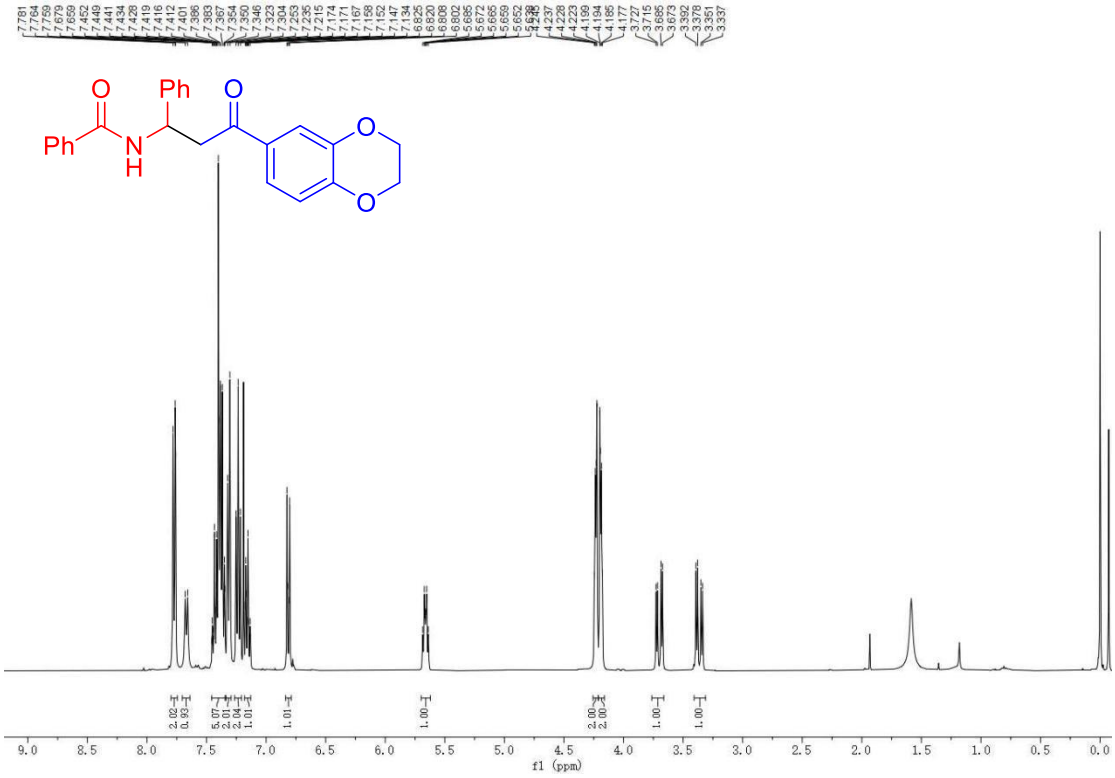

Figure S129. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-(3-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-3-oxo-1-phenylpropyl)benzamide (3ai)

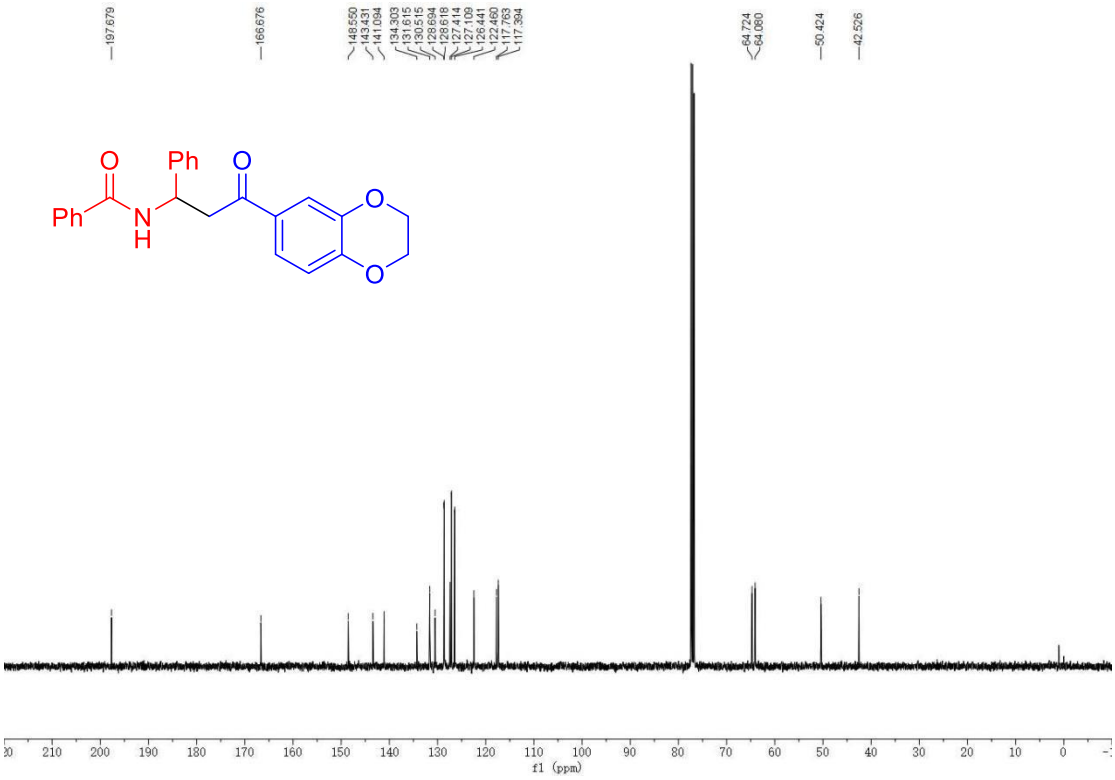

Figure S130. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(3-oxo-1-phenylpropyl)benzamide (3aj)

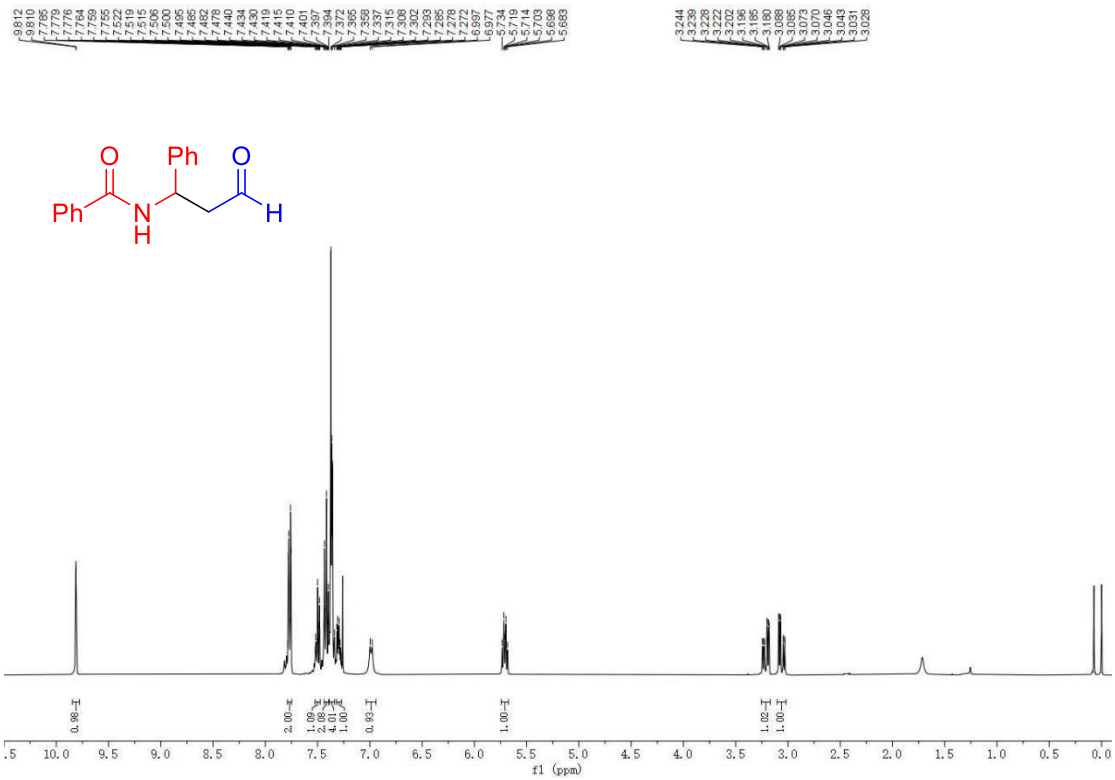

Figure S131. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-(3-oxo-1-phenylpropyl)benzamide (3aj)

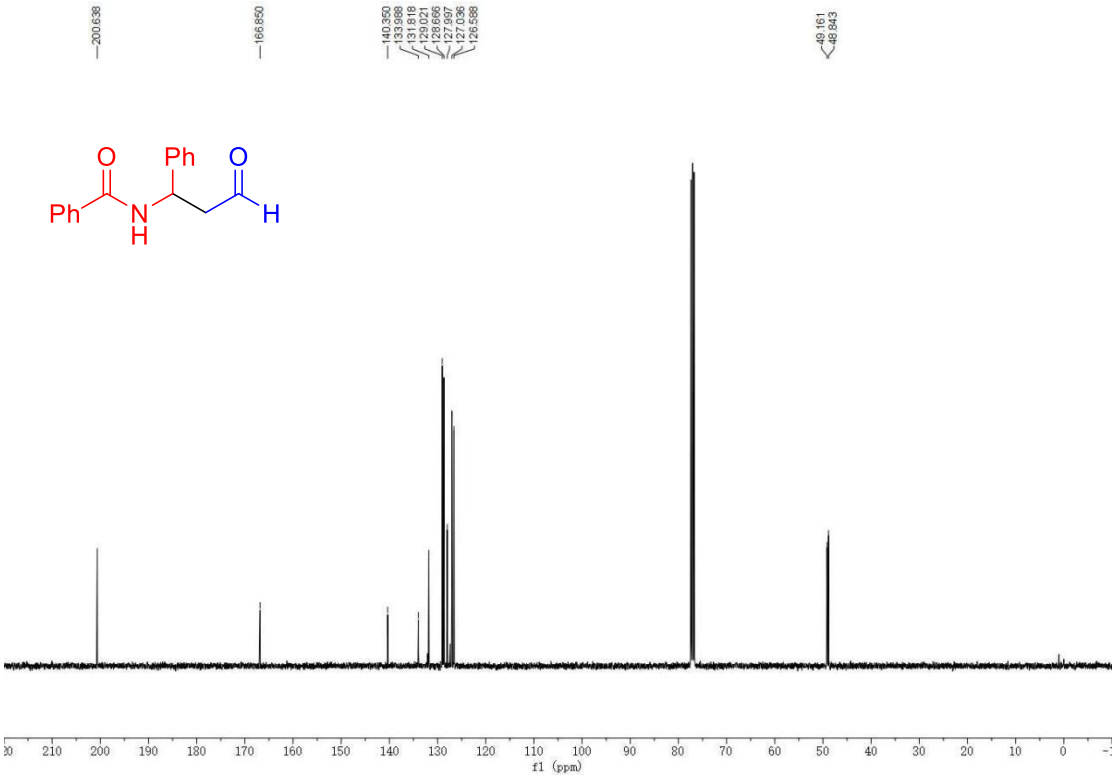

Figure S132. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(3-oxo-1-phenylbutyl)benzamide (3ak)

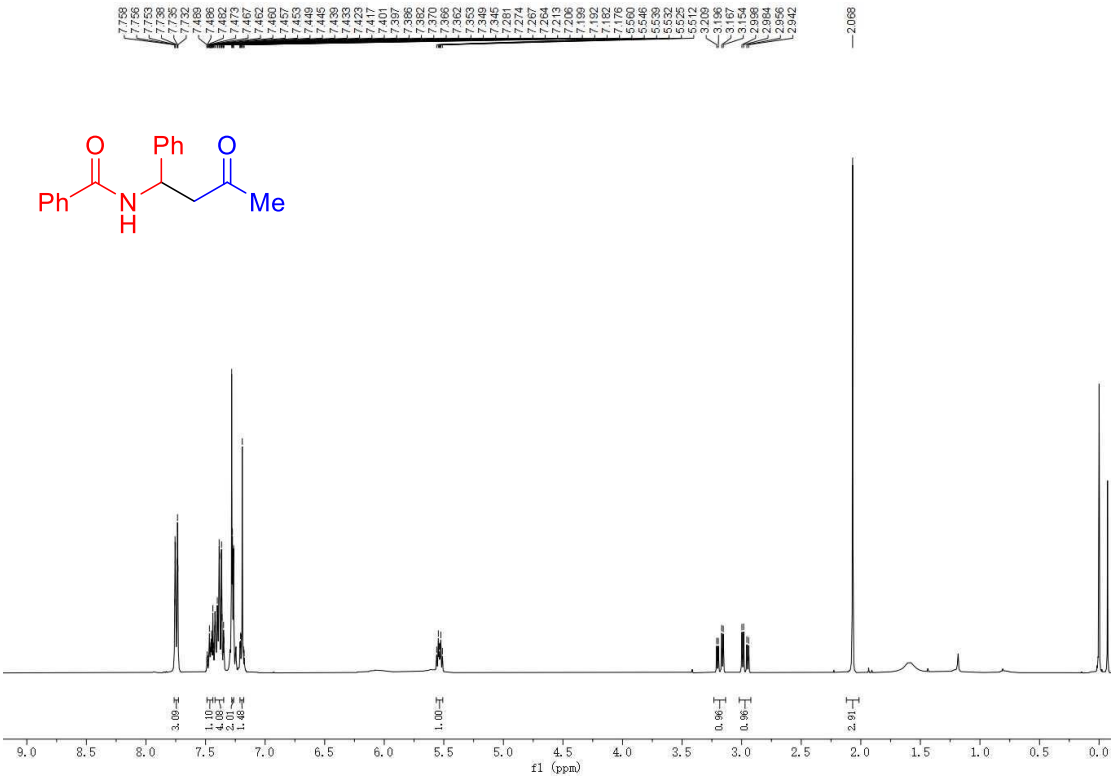

Figure S133. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-(3-oxo-1-phenylbutyl)benzamide (3ak)

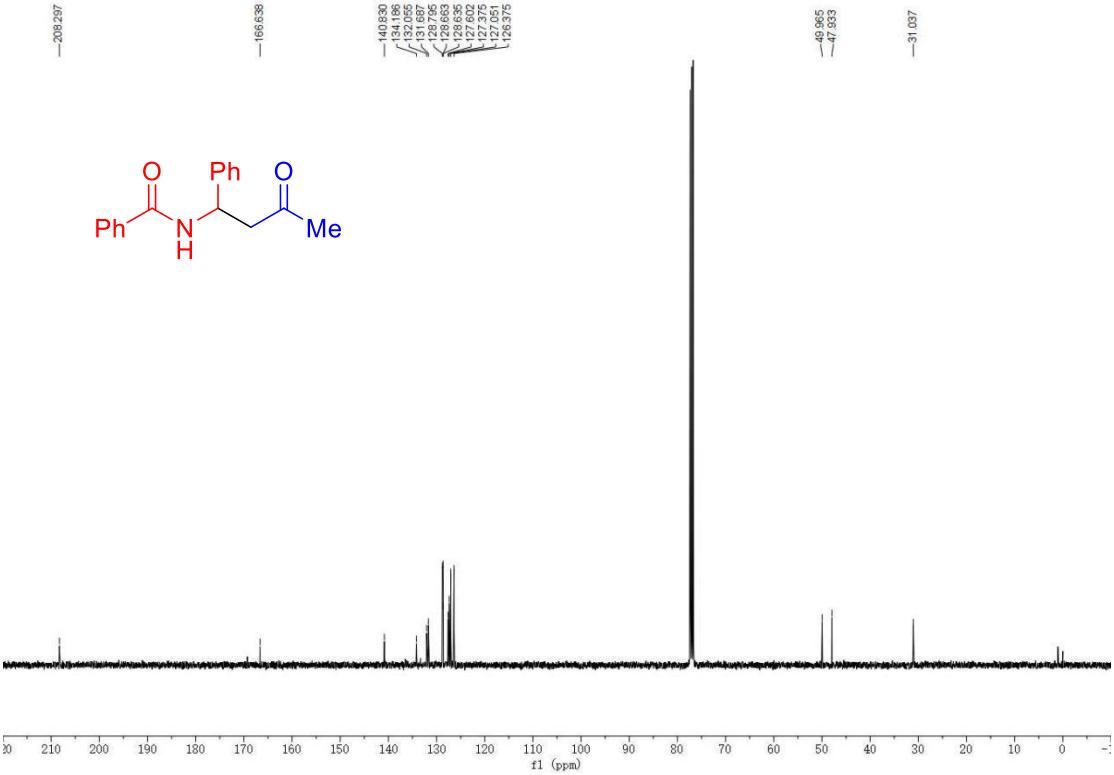

Figure S134. ^{1}H NMR spectra (600 MHz, Chloroform-*d*) of *N*-(3-oxo-1-phenylpent-4-en-1-yl)benzamide (3al)

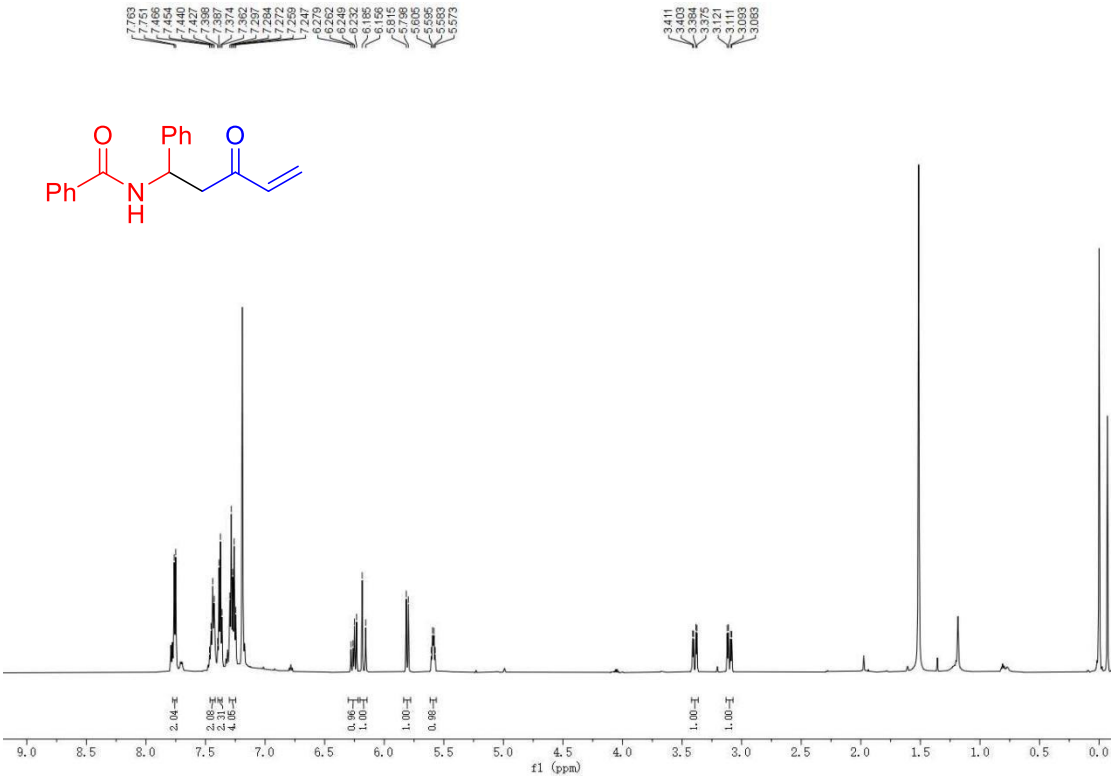

Figure S135. ^{13}C NMR spectra (150 MHz, Chloroform-d) of *N*-(3-oxo-1-phenylpent-4-en-1-yl)benzamide (3al)

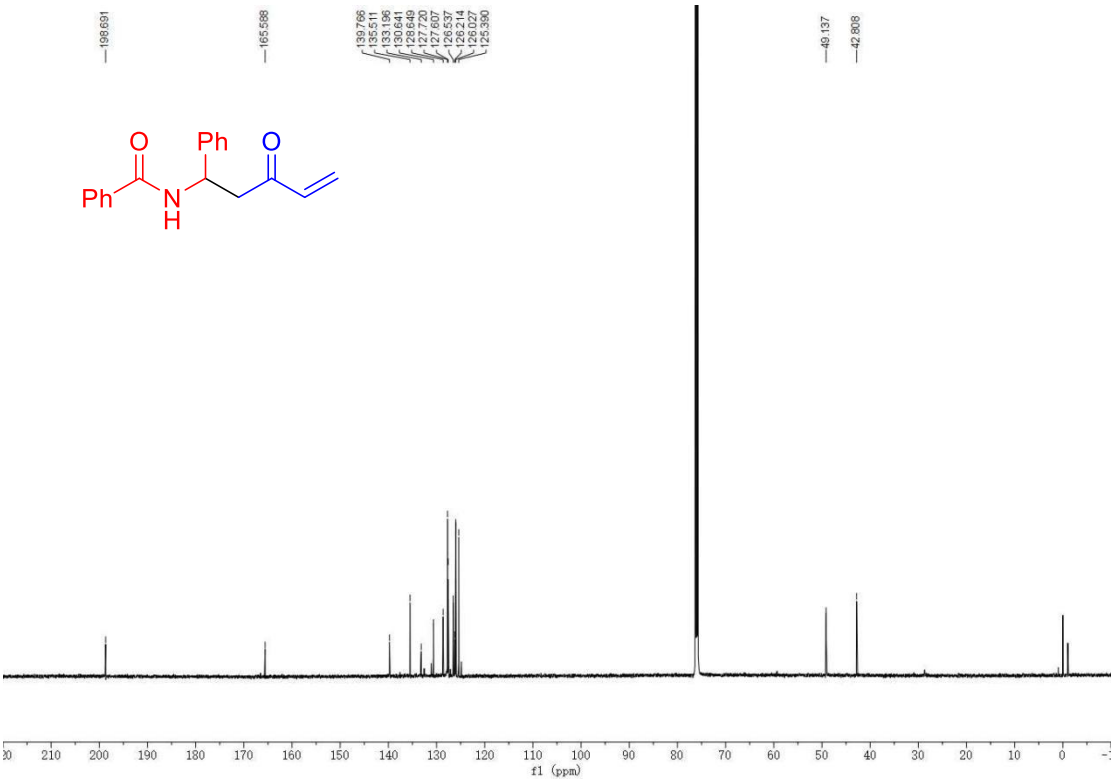

Figure S136. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(3-cyclopentyl-3-oxo-1-phenylpropyl)benzamide (3am)

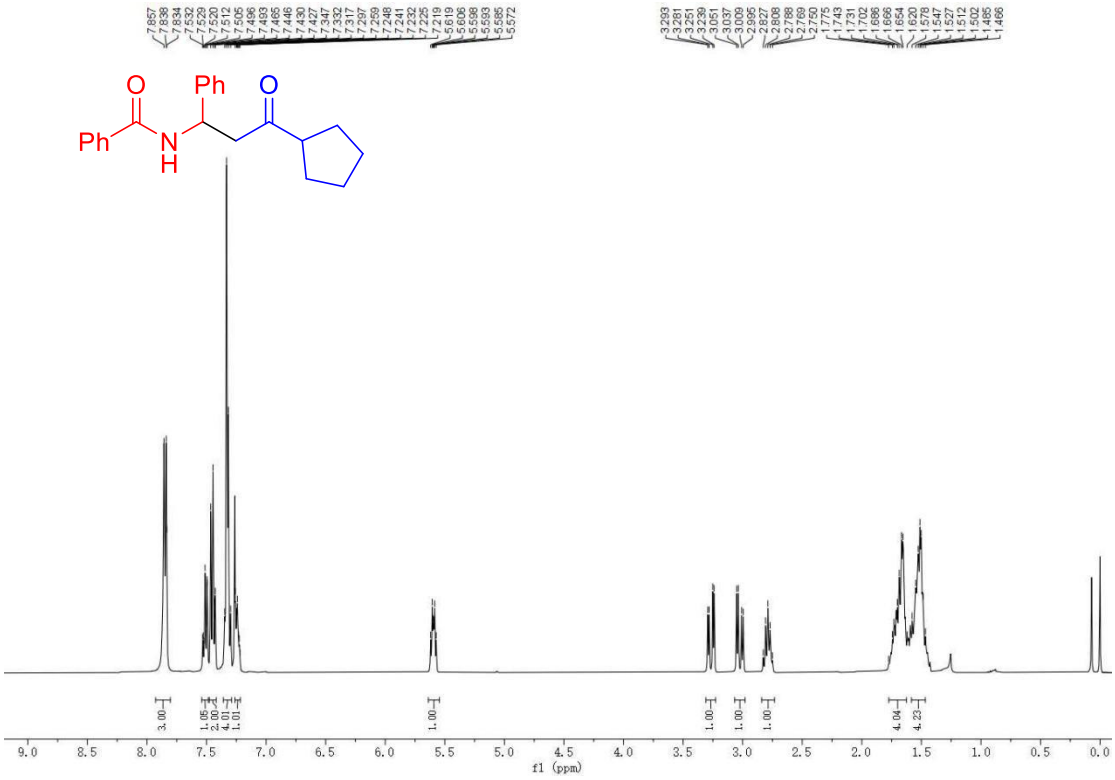

Figure S137. ^{13}C NMR spectra (100 MHz, Chloroform-d) of *N*-(3-cyclopentyl-3-oxo-1-phenylpropyl)benzamide (3am)

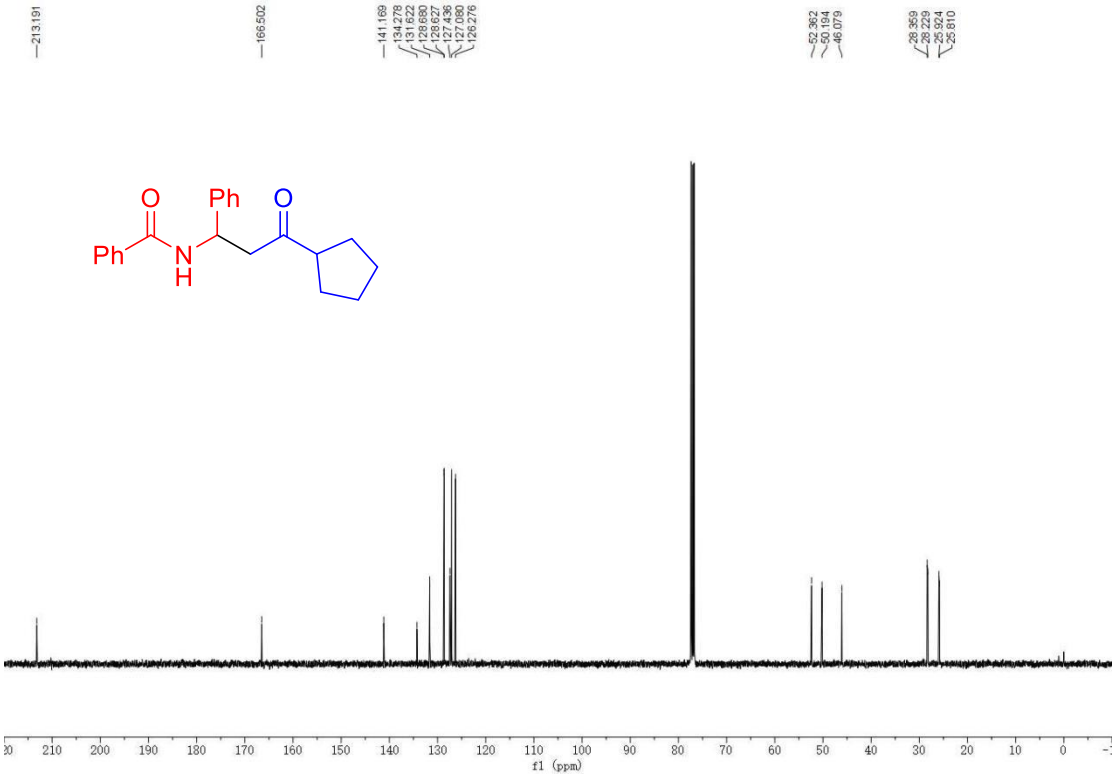

Figure S138. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(3-cyclohexyl-3-oxo-1-phenylpropyl)benzamide (3an)

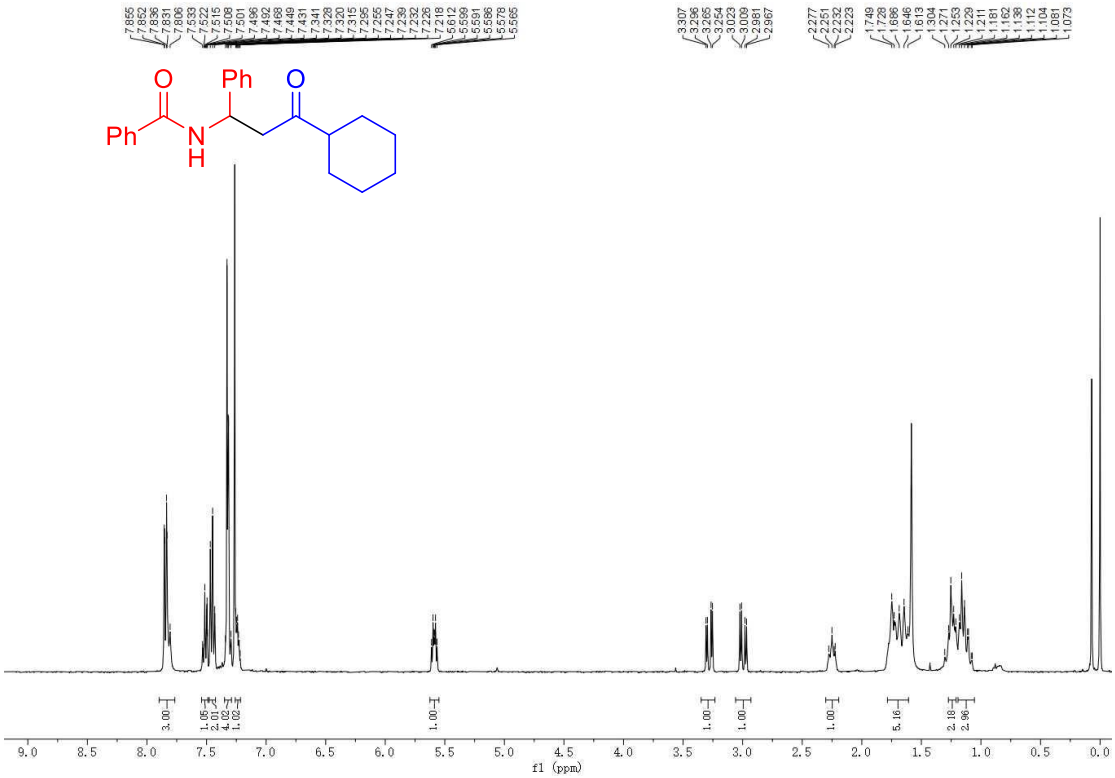

Figure S139. ^{13}C NMR spectra (100 MHz, Chloroform-d) of *N*-(3-cyclohexyl-3-oxo-1-phenylpropyl)benzamide (3an)

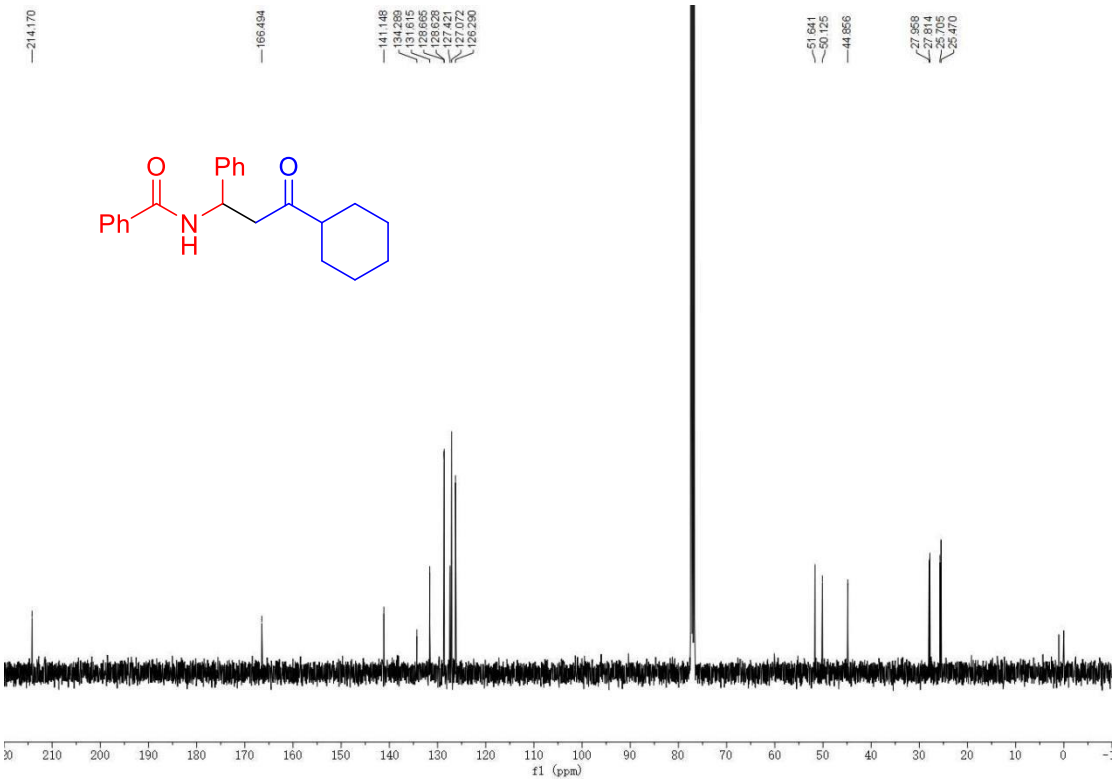

Figure S140. ^{1}H NMR spectra (600 MHz, Chloroform-*d*) of *N*-(5-oxo-5-phenylpent-1-en-3-yl)benzamide (3ua)

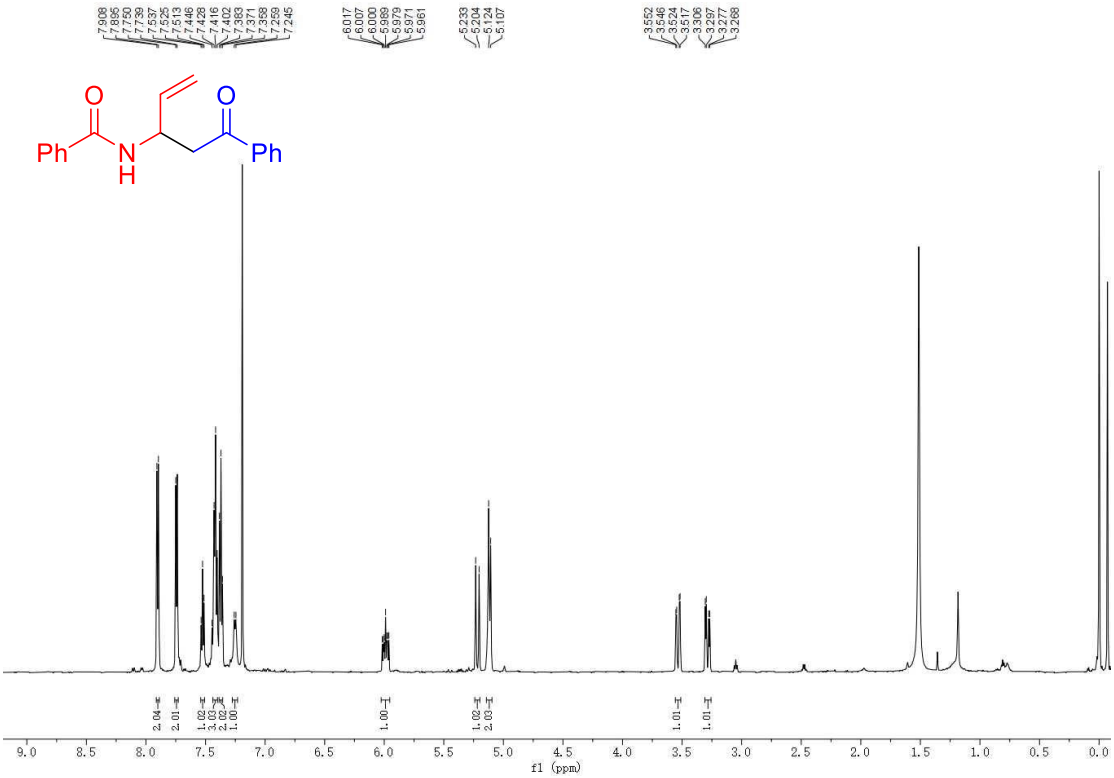

Figure S141. ^{13}C NMR spectra (150 MHz, Chloroform-d) of *N*-(5-oxo-5-phenylpent-1-en-3-yl)benzamide (3ua)

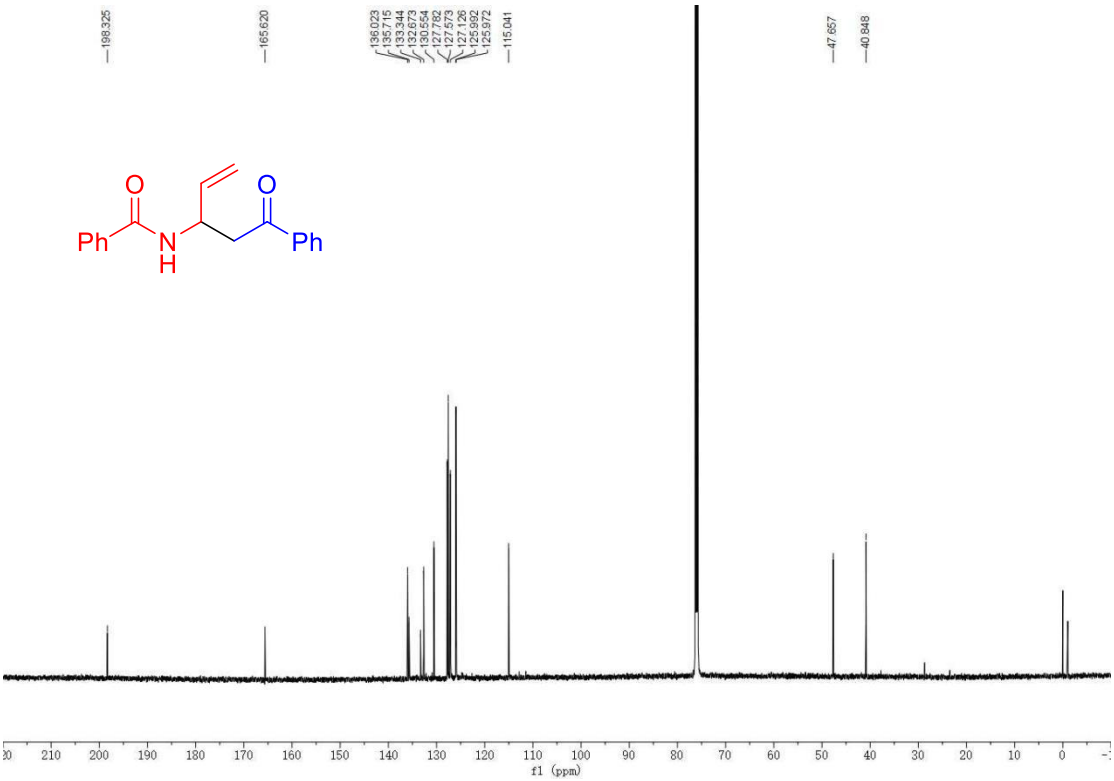

Figure S142. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of (*E*)-*N*-(5-oxo-5-phenylpent-1-en-1-yl)benzamide (3ua')

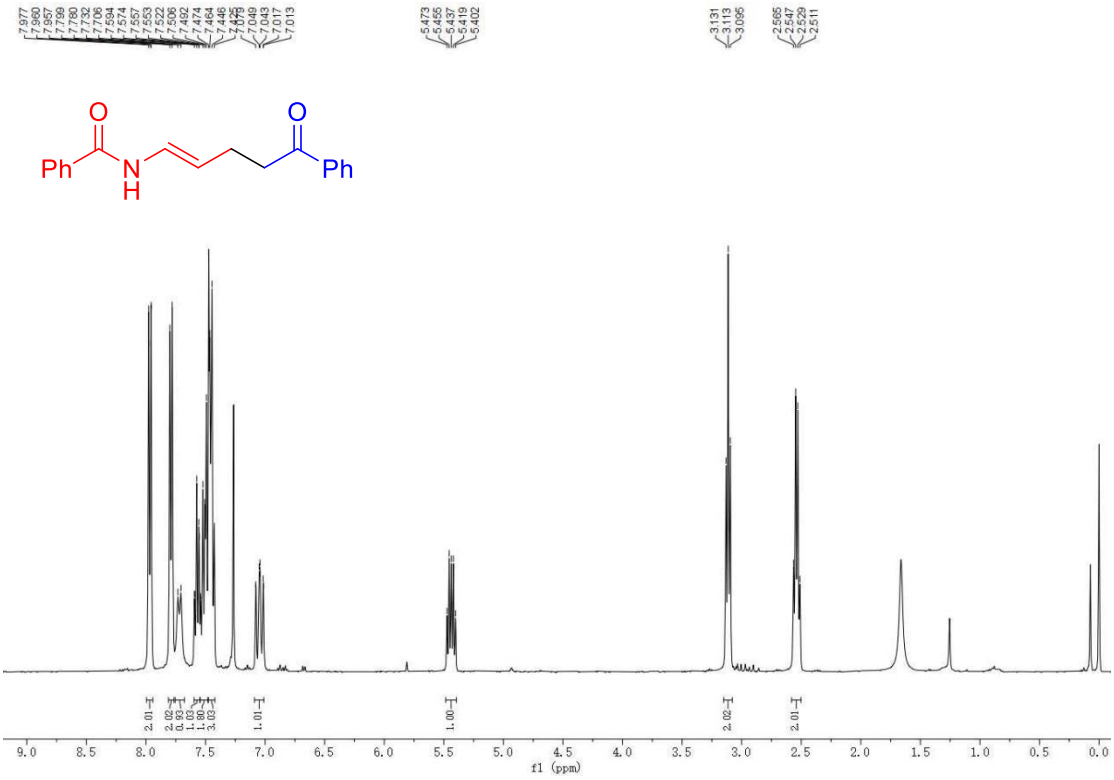

Figure S143. ^{13}C NMR spectra (100 MHz, Chloroform-d) of (*E*)-*N*-(5-oxo-5-phenylpent-1-en-1-yl)benzamide (3ua')

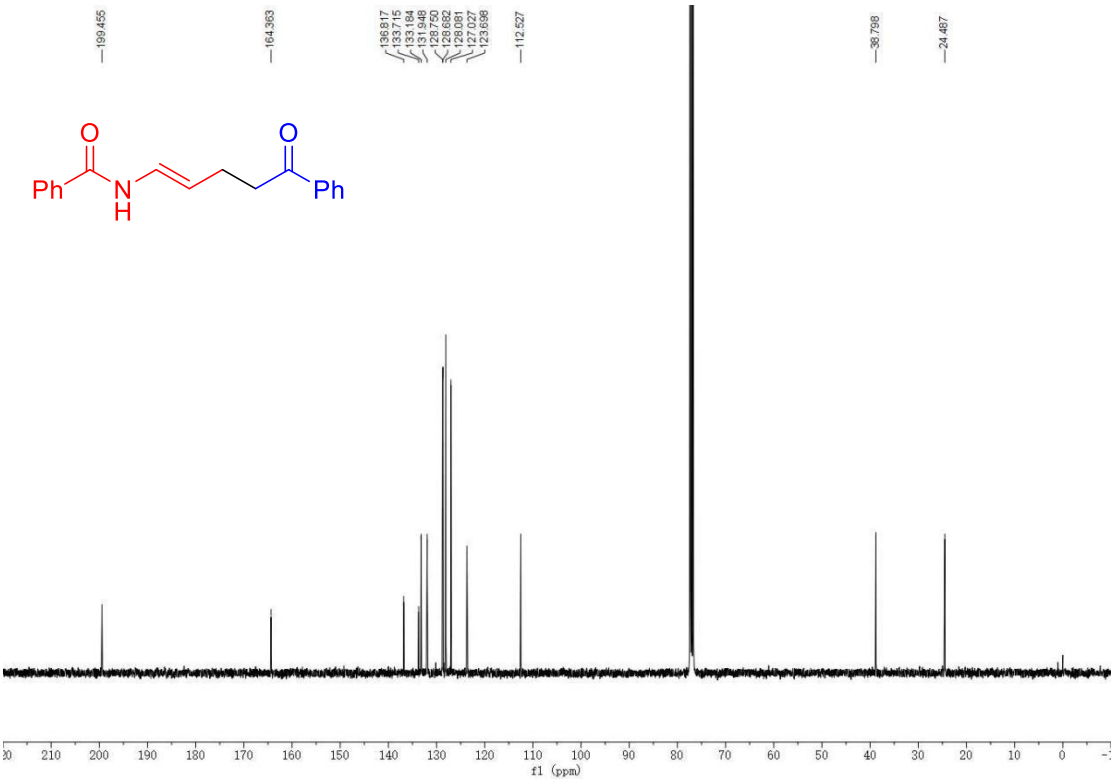

Figure S144. ^{1}H NMR spectra (600 MHz, Chloroform-*d*) of *N*-allyl-*N*-(2-oxo-2-phenylethyl)benzamide (3ua")

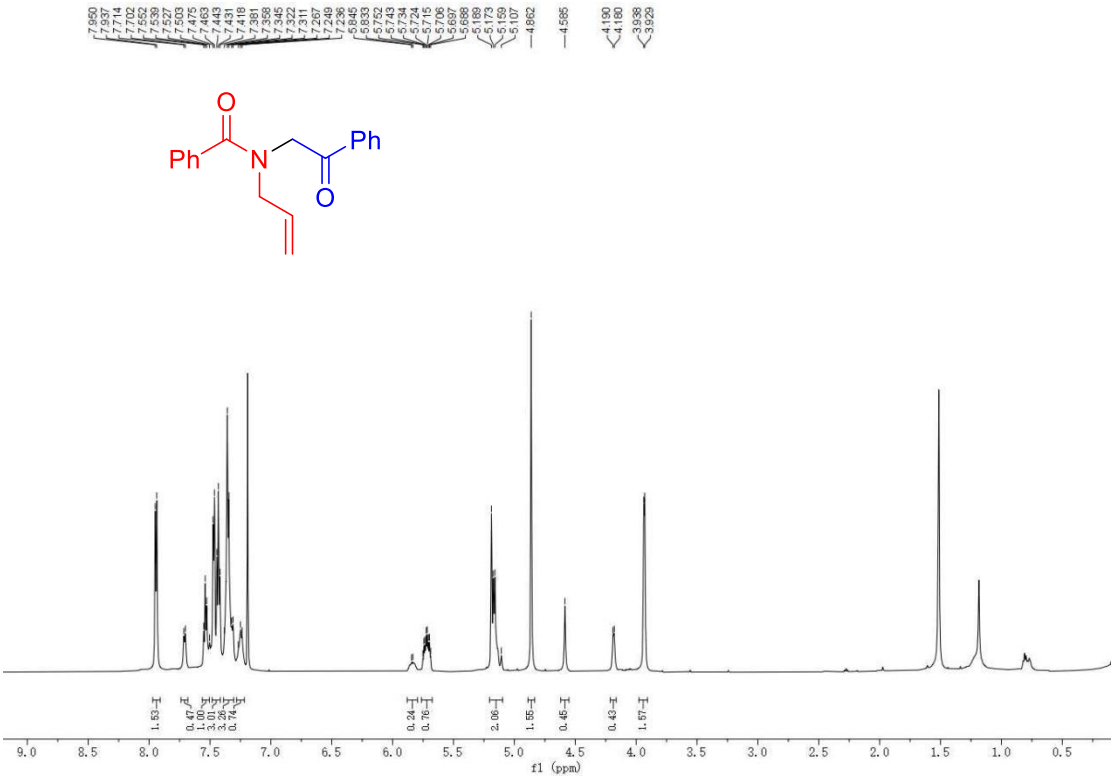

Figure S145. ^{13}C NMR spectra (150 MHz, Chloroform-d) of *N*-allyl-*N*-(2-oxo-2-phenylethyl)benzamide (3ua")

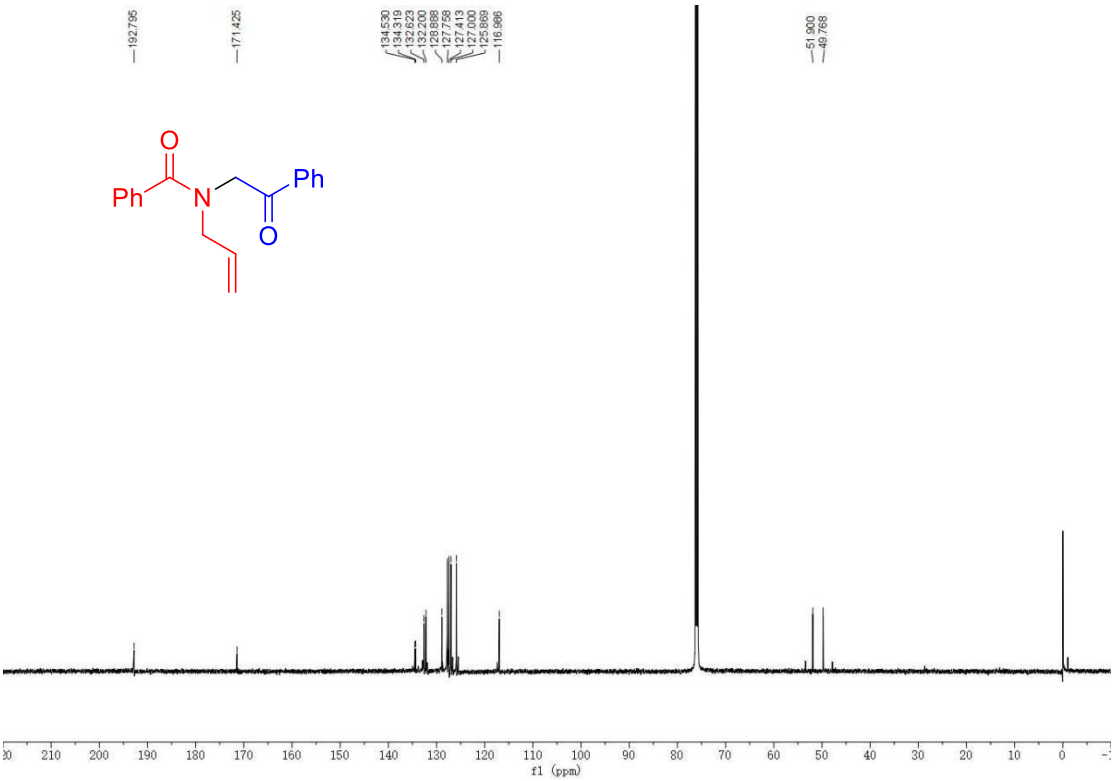

Figure S146. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of Deuterated coupling product (3aa-*d*^{1})

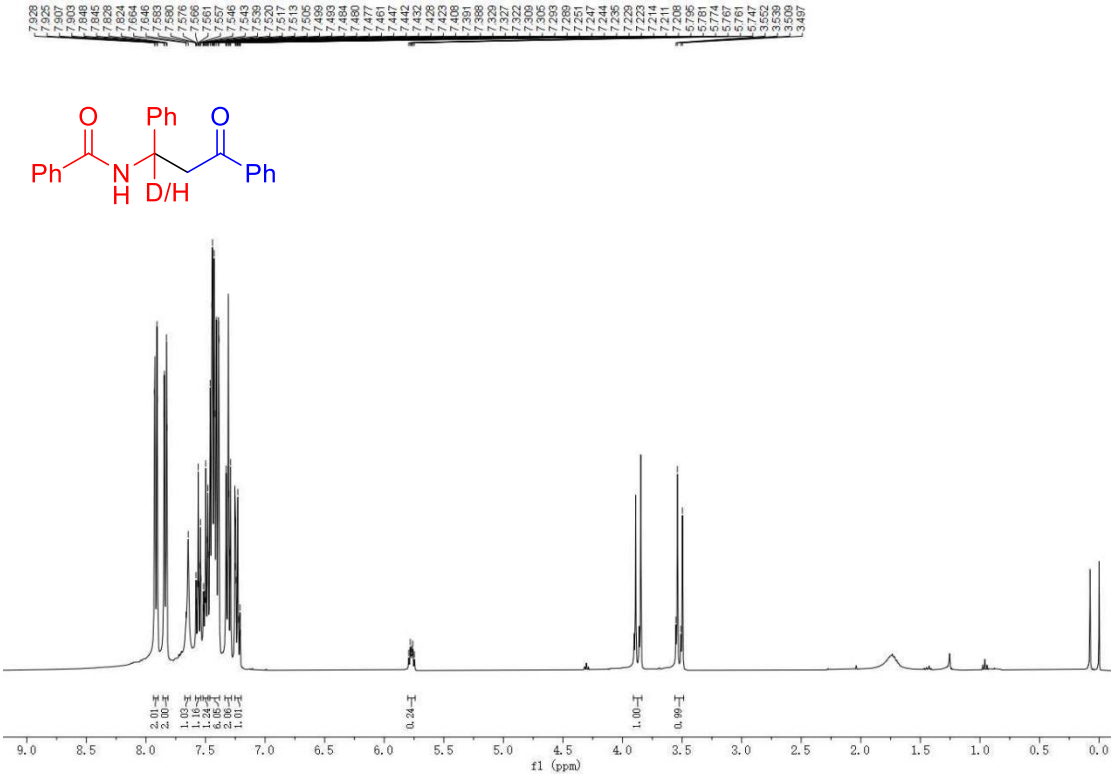

Figure S147. ^{13}C NMR spectra (100 MHz, Chloroform-d) of Deuterated coupling product (3aa-*d*^{1})

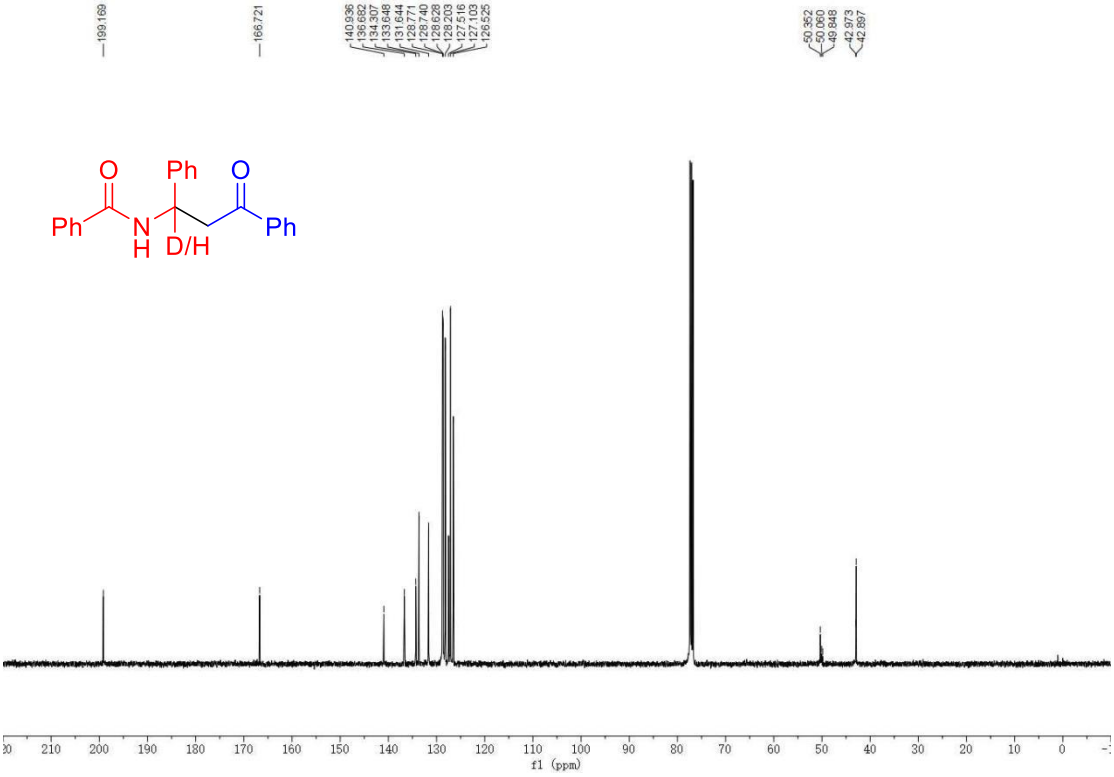

Figure S148. ^{1}H NMR spectra (600 MHz, Chloroform-*d*) of *N*-(6-methyl-1-oxo-1-phenylheptan-3-yl)benzamide (3va)

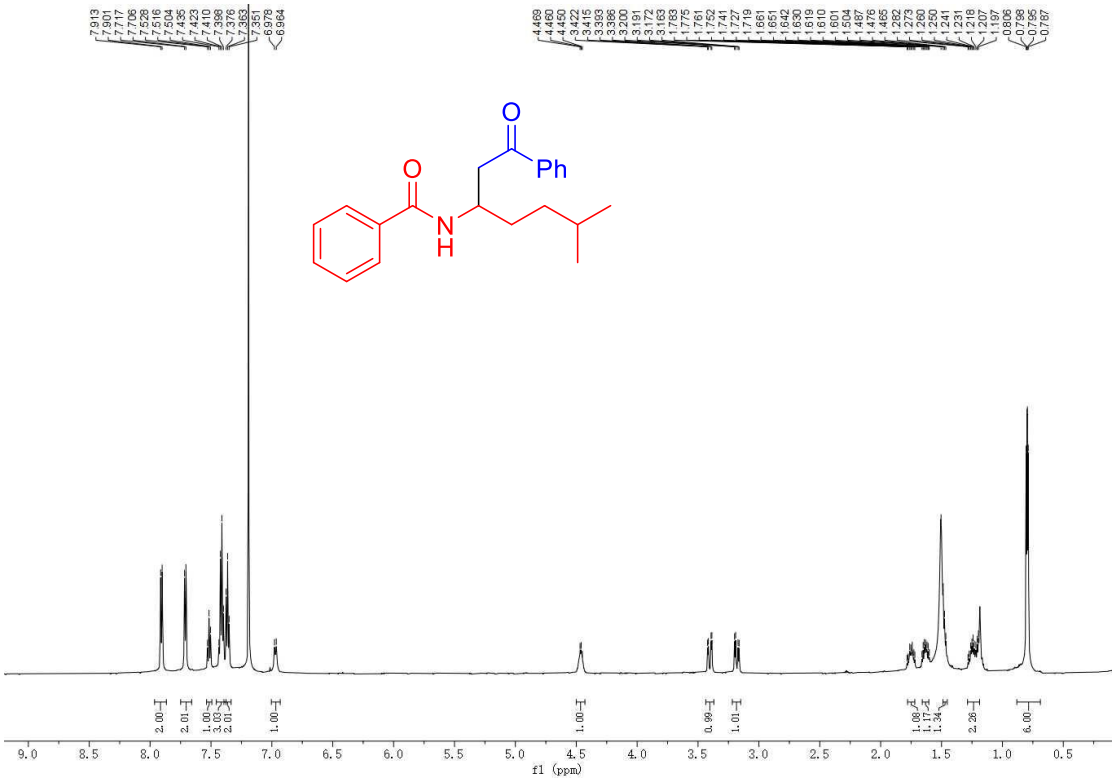

Figure S149. ^{13}C NMR spectra (150 MHz, Chloroform-*d*) of *N*-(6-methyl-1-oxo-1-phenylheptan-3-yl)benzamide (3va)

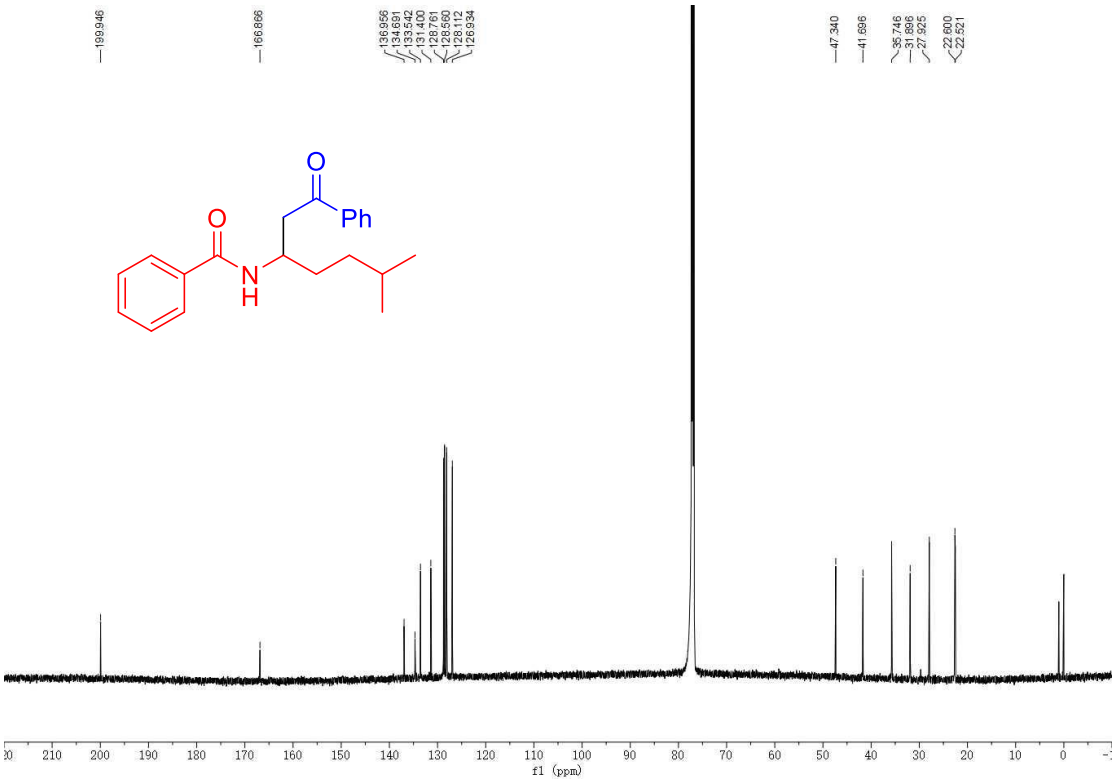

Figure S150. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of *N*-(4-methylpentyl)benzamide (1v')

Figure S151. ^{13}C NMR spectra (100 MHz, Chloroform-*d*) of *N*-(4-methylpentyl)benzamide (1v')

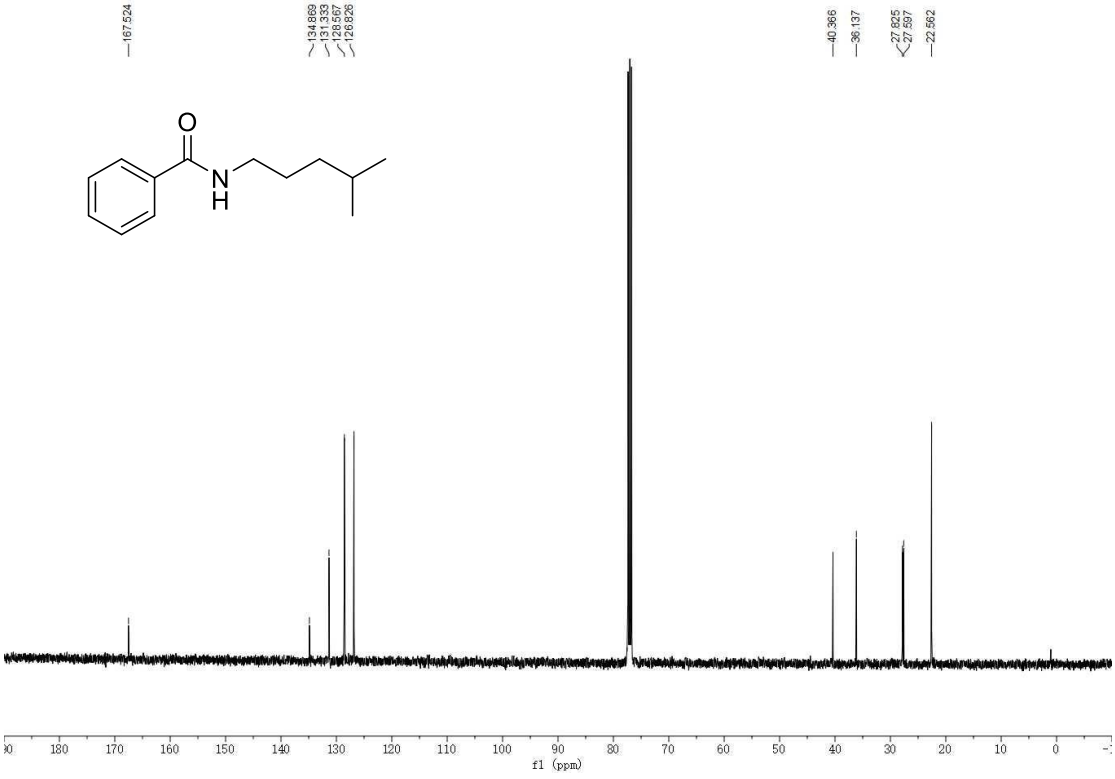

Figure S152. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of 1-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethan-1-one (6aa)

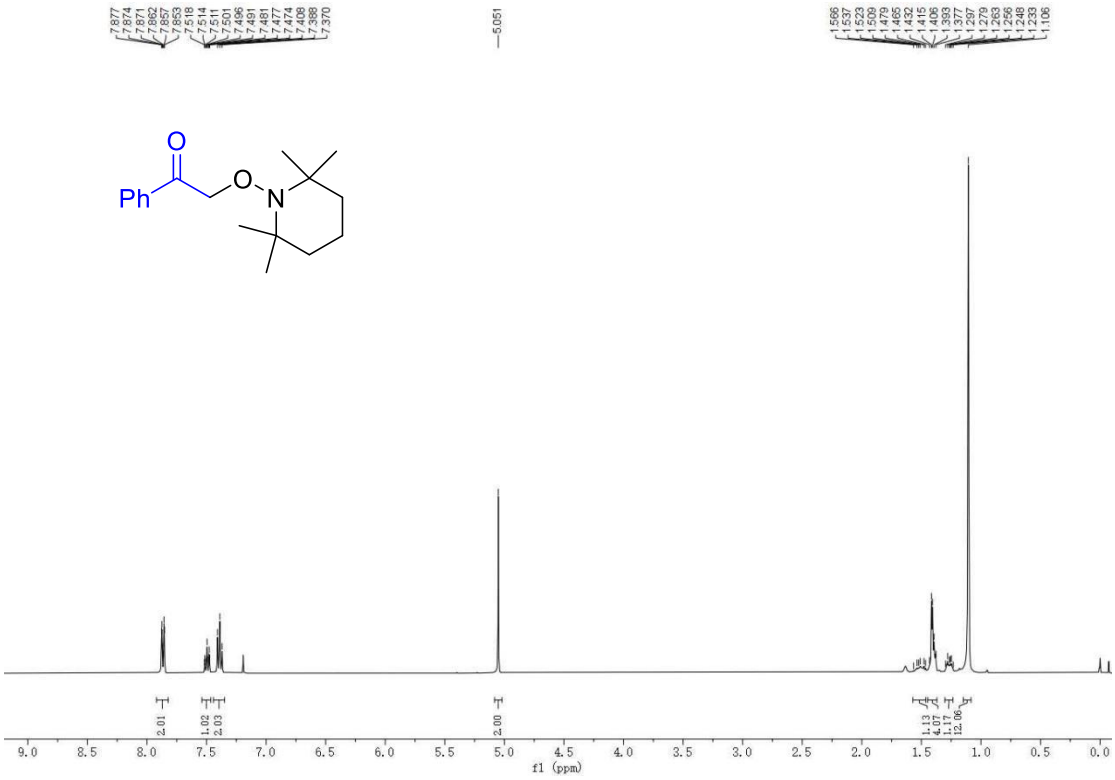

Figure S153. ^{13}C NMR spectra (100 MHz, Chloroform-d) of 1-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethan-1-one (6aa)