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Redox-noninnocence of formazanate ligand applied to catalytic formation of α-ketoamides

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Contents

1. General Considerations.

1.1 Materials:

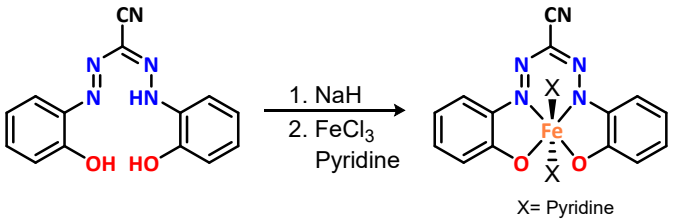
All reactions were carried out using air sensitive manipulations and glove box unless otherwise mentioned. Tetrahydrofuran (THF) was refluxed and freshly distilled over sodium/benzophenone and degassed using three freeze-pump-thaw cycles. All chemicals were purchased from Sigma-Aldrich, Avra, TCI, Alfa Aeaser and GLR innovations. CD_3CN and $CDCl_3$ were purchased from Euroisotope. All chemicals were used as purchased until and unless mentioned. Progress of reactions was monitored by thin-layer chromatography using Merck 60 F_{254} precoated silica gel plate and visualized by short-wave ultraviolet light. Flash chromatography was performed with Silica Flash P60 silica gel (100–200 mesh).

1.2 Physical Measurements.

Absorption spectra were recorded using LAB-INDIA UV/VIS Spectrophotometer UV 3000 in an UV-cuvette of path length 10 mm fitted with cap. The graphs were plotted using Originpro8. ^1H and ^{13}C $\{^1H\}$ NMR spectra were recorded on a Bruker 400 MHz spectrometer at 400 and 101 MHz respectively. The residual solvent signals were taken as the reference ($CDCl_3$, 7.26 ppm for ^1H NMR spectra and $CDCl_3$, 77.16 ppm for ^{13}C NMR spectra). The signals observed are described as: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplets). All coupling constants were reported in hertz. High-resolution mass spectrometry was performed on Waters Synapt-G2S, with analyser configuration Q-ToF, ion mobility and analysed using Masslynx41. Cyclic Voltammetry experiments were performed CHI-610 electrochemical workstation from CH Instruments (USA). For the measurement, the three-electrode setup consisted of a glassy carbon working electrode, a Pt-wire as counter electrode, and an Ag/AgCl (1M KCl) as the reference electrode.

2. Synthesis of Fe(III)-Formazanate complex (1).

The 3-Cyano-1,5-dihydroxyphenylformazan ligand and its iron complex (**1**) were synthesized following prior literature.[1]

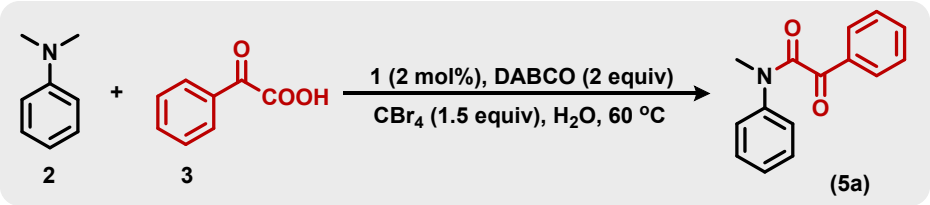


Scheme S1. Synthesis of complex **1**.

3. Optimization of demethylative amidation reaction.

A 20 ml vial was charged with N,N-dimethylaniline (26 µL, 0.2 mmol), α-ketocarboxylic acids (60 mg, 0.4 mmol), DABCO (45 mg, 0.4 mmol) and 2 mL of distilled water was added to it to make a clear solution. A solution of tetrabromomethane (99 mg, 0.3 mmol) in 100 µL of acetonitrile was added to the reaction mixture. The above reaction mixture was loaded with catalyst **1** (2 mol%, 2 mg) and was stirred at 60 °C temperature. After 6 h, the reaction aqueous layer was extracted with ethyl acetate and dried over anhydrous $MgSO_4$. Solvent was removed using rotary evaporator. The yield of the product was determined by GC analysis.

Table S1. Optimization of reaction conditions.



Entry	Acid (3) equiv	Catalyst Loading (mol%)	Oxidant	Base	Yield[a]
1	1	2	CBr_4	DABCO	65
2	1.5	2	CBr_4	DABCO	77
3	**2**	**2**	**CBr_4**	**DABCO**	**89**
4	2	2	CBr_4	DABCO	68[b]
5	2	1	CBr_4	DABCO	62
6	2	0.5	CBr_4	DABCO	24
7	2	-	CBr_4	DABCO	ND
8	2	2	CBr_4	DABCO	25[c]
9	2	2	-	DABCO	ND
10	2	2	CBr_4	-	18
11	2	2	$Na_2S_2O_8$	DABCO	ND
12	2	2	O_2	DABCO	ND
13	2	2	$CBrCl_3$	DABCO	25
15	2	2	TBHP	DABCO	trace
16	2	2	CBr_4	DBU	29
17	2	2	CBr_4	2,6 Lutidine	29
18	2	2	CBr_4	NEt_3	20
19	2	$FeCl_3$	CBr_4	DABCO	trace

Note: a) GC yield b) reaction using H_2O as the only solvent. c) at room temperature.

3.1 General procedure for demethylative amidation catalyzed by 1: Using the optimized condition, the reaction was carried out with N,N-dimethylaniline (65 µL, 0.5 mmol), α-ketocarboxylic acids (150 mg, 1.0 mmol) and DABCO (112 mg, 1.0 mmol). 2 mL of distilled water was added to the vial to make a clear solution. A solution of tetrabromomethane (248 mg, 0.75 mmol) in 100 µL of acetonitrile was added to the reaction mixture. The above reaction mixture was loaded with catalyst **1** (2 mol%, 4.9 mg) and was stirred at a temperature of 60 °C. After 6 h, the reaction aqueous layer was extracted with ethyl acetate and dried over anhydrous $MgSO_4$. Ethyl acetate was removed under reduced pressure and the desired product was separated from crude mixture by flash column chromatography using silica as stationary phase

and hexane:ethylacetate as eluent. All products were characterized by ^{1}H and ^{13}C NMR spectroscopic techniques.

4. Cyclic voltammetry experiment for 1.

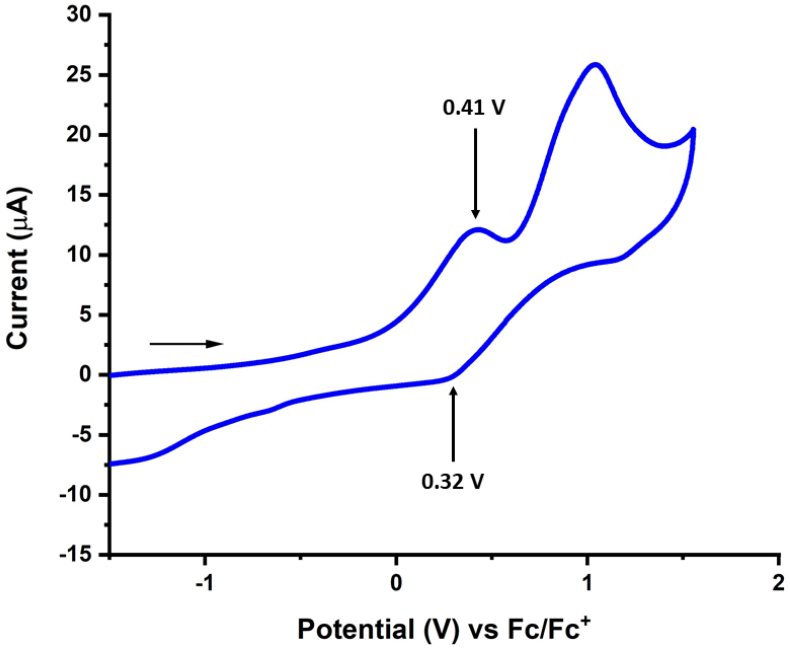


Fig. S1. CV of 1 mM of **1** dissolved in acetonitrile along with 0.1 M solution of tetrabutyl-ammonium hexafluorophosphate salt as an electrolyte. The scan rate was 50 mVs^{-1} for the measurement.

5. Synthesis of $\mathbf{1}^{\cdot+}$

In a Schlenk flask **1** (0.5 mmol) was dissolved in 5 mL of THF and silver triflate (0.5 mmol) was added to the solution. During the addition, the colour of the reaction mixture turned to brown from greenish blue over the course of 1 h. The reaction mixture was further stirred for 12 h at room temperature. At the completion of the reaction, the reaction mixture was filtered and the filtrate was removed under high vacuum. The oxidized product was isolated (205 mg, 83% yield). UV-vis spectroscopic data was collected for both **1** and $\mathbf{1}^{\cdot+}$ under inert condition. (**Fig. S2**). The molecule was paramagnetic and the Evan's magnetic moment was measured to be 2.6 (2) μ_B. Multiple attempts to collect a reliable CHN failed due to the very air-sensitive nature of the sample.

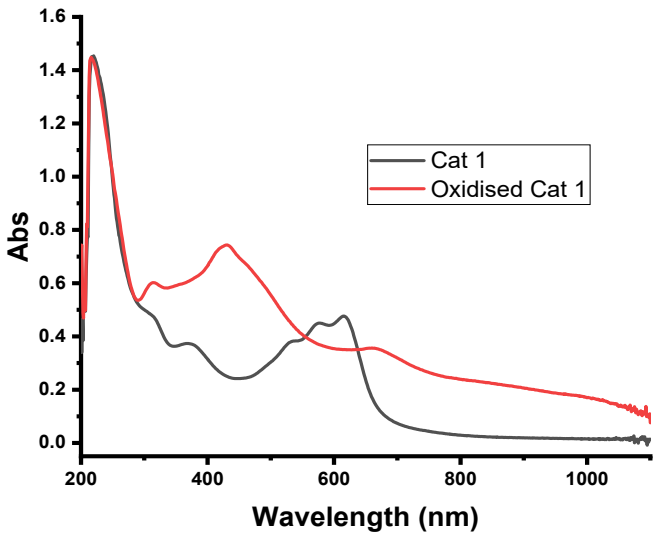


Fig. S2. UV-vis plot for **1** (grey line) and oxidised product **1**$^{\cdot+}$ (red line) recorded in dry and degassed THF at room temperature.

6. Computational details.

All DFT calculations have been carried out using the ORCA 4.2.1 program[2]. Geometry optimizations and single point calculations were carried out by employing the B3LYP[3] functional. All atoms were described by the def2-TZVP[4] basis set. Vibrational calculations were done to ensure that the geometries are true minima.

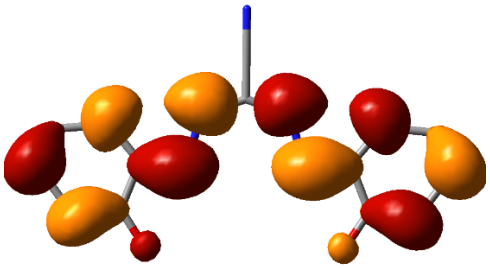


Fig S3: LUMO of the ligand backbone

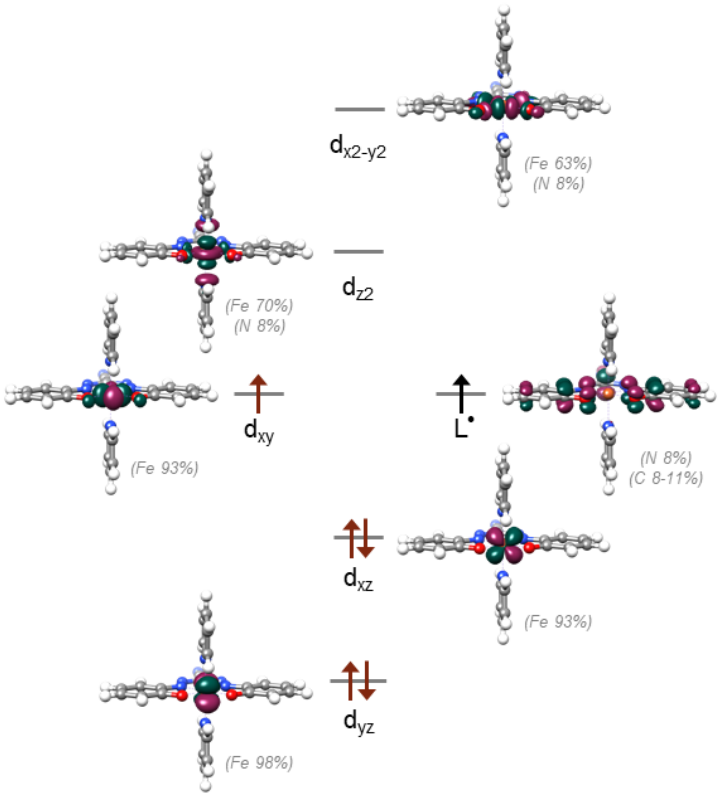


Fig. S4. MO for S = 1 state, $1^{\cdot+}$

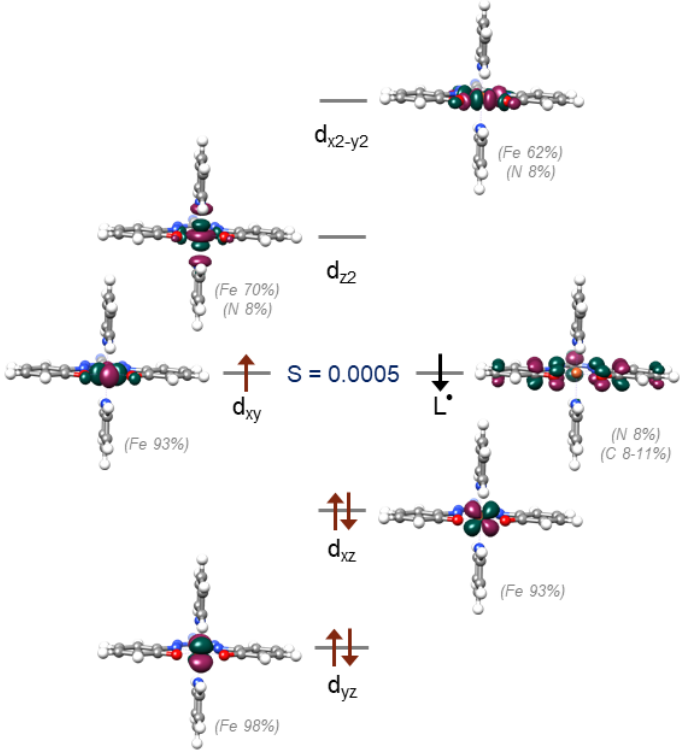


Fig. S5. MO for open-shell singlet structure, $1^{\cdot+}$

7. Intermediate Trapping:

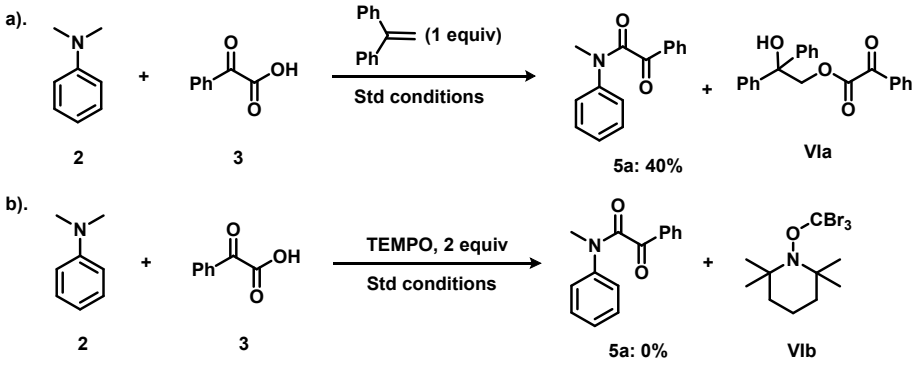
7.1 Carboxyl radical trapping.

Following the standard reaction conditions, A 20 mL vial was charged with N,N-dimethylaniline (26 µL, 0.2 mmol), α-ketocarboxylic acids (60 mg, 0.4 mmol), DABCO (45 mg, 0.4 mmol) and 1,1-Diphenylethylene (36 µL, 0.2 mmol). 2 mL of distilled water was

added to the vial to make a clear solution. A solution of tetrabromomethane (99 mg, 0.3 mmol) in 100 µL of acetonitrile was added to the reaction mixture. The above reaction mixture was loaded with catalyst **1** (2 mol%, 4.9 mg) and was stirred at 60 °C temperature. After 6 h, the product **5a** was obtained in 40% yield and the carboxyl radical adduct (**VIa**) (scheme S2a) was analysed by High-resolution mass spectroscopy. (ESI mode, m/z) calcd. for $C_{22}H_{19}O_4$ $[M+H]^+$: 347.1283; found: 347.1254.

7.2 CBr_3· radical trapping.

Following the standard reaction conditions, A 20 mL vial was charged with N,N-dimethylaniline (26 µL, 0.2 mmol), α-ketocarboxylic acids (60 mg, 0.4 mmol), DABCO (45 mg, 0.4 mmol) and TEMPO (62 mg, 0.4 mmol)). 2 mL of distilled water was added to the vial to make a clear solution. A solution of tetrabromomethane (99 mg, 0.3 mmol) in 100 µL of acetonitrile was added to the reaction mixture. The above reaction mixture was loaded with catalyst **1** (2 mol%, 4.9 mg) and was stirred at a temperature of 60 °C. After 6 h, there was no formation of product as assayed by TLC. The CBr_3 radical adduct (**VIb**) (scheme S2b) was detected by high-resolution mass spectrometry (HRMS). HRMS (ESI, m/z) calcd. for $C_{10}H_{19}Br_3NO$ $[M+H]^+$: 405.9017; found: 405.9030.



Scheme S2. (a) trapping of carboxyl radical adduct (b) trapping of tribromomethane radical.

8. Kinetic experiment:

Following optimised condition 3.1, a 20 mL vial was charged with N,N-Dimethylaniline (130 µL, 1.0 mmol), 2-oxo-2-phenylacetic acid (300 mg, 2.0 mmol) and DABCO (224 mg, 2.0 mmol). 4 mL of distilled water was added to the vial. A solution of tetrabromoethane (496 mg, 1.5 mmol) in 0.3 mL of acetonitrile was added to the reaction mixture. The above reaction mixture was loaded with **1** (2 mol%, 9.8 mg) and was stirred at a temperature of 60 °C. The aliquots (100 µL) were collected from the reaction mixture with some interval of time. The progress of the reaction was analysed by GC. The increasing product concentration (in mmol) was plotted with respect to the time (in min) (Fig. S3 (a)). Following initial rate method, it was concluded that the reaction followed the pseudo-first order kinetics (Fig. S3 (b)).

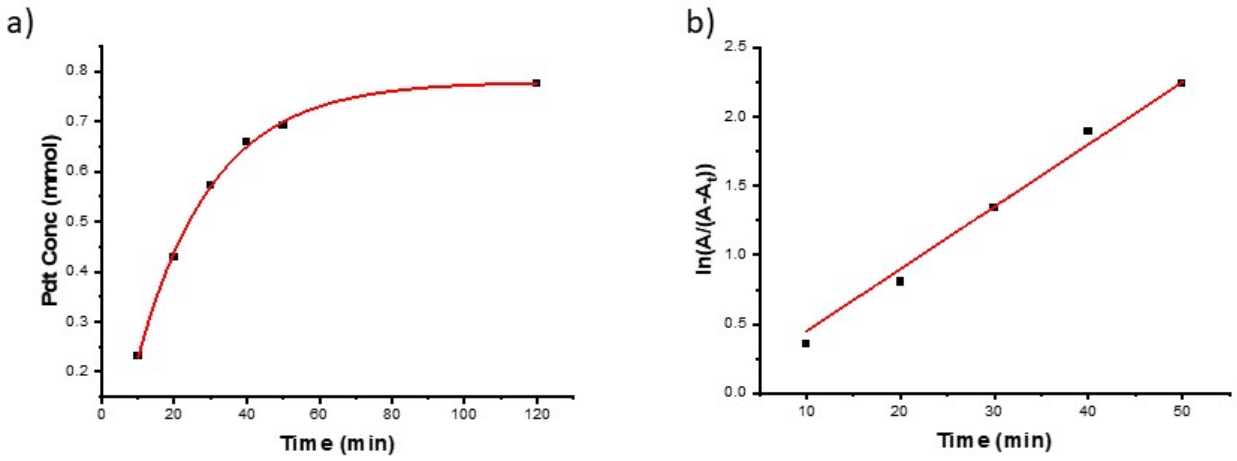
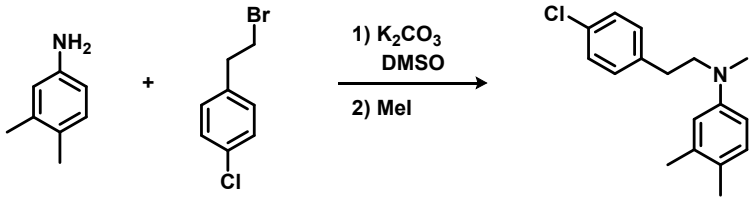


Fig. S6. a) Growth of product vs time (in min) b) Pseudo-first order plot.

9. Gram-scale synthesis of orexin receptor antagonist.[5]

9.1 Synthesis of N-(4-chlorophenethyl)-N,3,4-trimethylaniline

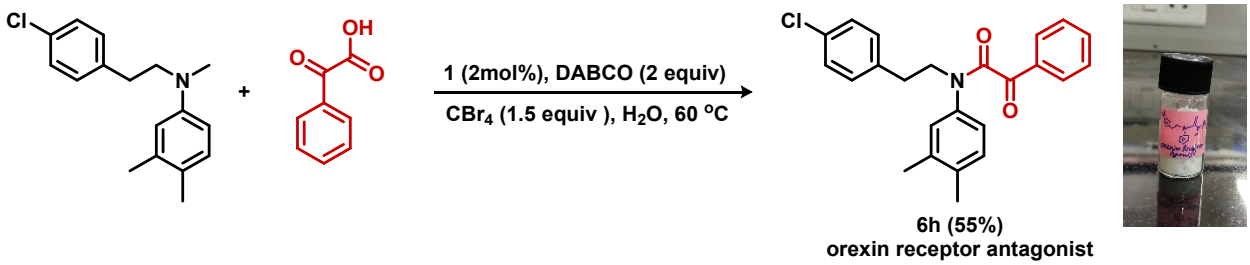


3,4-dimethylaniline (1.22 g, 10 mmol), 1-(2-bromoethyl)-4-chlorobenzene (2.2 g, 10 mmol), K_2CO_3 (6.9 g, 50 mmol) and 10 mL of DMF was taken in 100 mL round bottomed flask. The reaction mixture was stirred for 12 h at room temperature. After that, methyl iodide (0.95 mL, 15 mmol) was added to above reaction mixture and the reaction mixture was stirred for another 12 h at room temperature. Ice-chilled water was added to the reaction mixture and aqueous layer was washed with ethyl acetate. Ethyl acetate was removed under reduced pressure and the desired product was separated from crude mixture by flash column chromatography using silica as the stationary phase and hexane:ethylacetate (9:1) as eluent. The pure product N-(4-chlorophenethyl)-N,3,4-trimethylaniline was obtained in 61% yield (0.99 g) as a yellow liquid.

9.2 Synthesis of orexin receptor antagonist

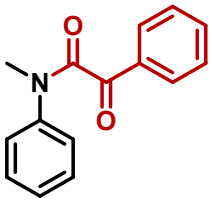
Previously prepared tertiary amine was used for finally forging the orexin receptor antagonist molecule. As per general optimised reaction conditions in section 3.1, a 100 mL round-bottomed flask was charged with N-(4-chlorophenethyl)-N-methylaniline (1.23 g, 5 mmol), 2-oxo-2-phenylacetic acid (1.5 g, 10 mmol), DABCO (1.12 g, 10 mmol) and 40 mL of distilled water was added to make a clear solution. A solution of tetrabromomethane (2.5 g, 7.5 mmol) in 2 mL of acetonitrile was added to the reaction mixture. The above reaction mixture was loaded with catalyst **1** (2 mol%, 49 mg) and was stirred at 60 °C temperature. After 6 h, the reaction aqueous layer was extracted with ethyl acetate and dried over anhydrous $MgSO_4$. Ethyl acetate was removed under reduced pressure and the desired product was separated from crude by flash column chromatography using silica as stationary phase and hexane:ethylacetate (9:1) as eluent. The pure product orexin receptor agonist (**6h**) was obtained in 55% yield (0.99 g) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.60 (m, 2H), 7.57 – 7.52 (m, 1H), 7.39 (t, J = 7.7 Hz, 2H), 7.31 (d, J = 8.3 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 6.93 (d, J = 7.9 Hz, 1H), 6.78 (d, J = 2.4 Hz, 1H), 6.68 (dd, J = 7.9, 2.4 Hz, 1H), 4.21 – 4.15 (m, 2H), 2.92 (t, J = 7.4

Hz, 2H), 2.15 (s, 3H), 2.09 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 190.69, 166.99, 138.20, 137.16, 136.82, 136.73, 134.22, 133.68, 132.47, 130.67, 130.50, 129.44, 128.74, 128.70, 128.66, 125.07, 48.80, 33.03, 19.75, 19.44.

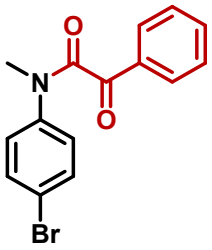


Scheme S3. Gram-scale synthesis of orexin receptor antagonist (**6h**) by **1**.

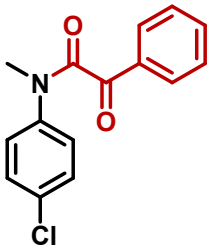
10. Spectroscopic characterization for demethylative amidation products.



N-Methyl-2-oxo-N,2-diphenylacetamide (5a).
The general procedure was followed. Column chromatography (SiO_2, eluting with 85:15 hexane/ethyl acetate) afforded the desired product as a yellow solid (107 mg, yield 89%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.82 (m, 2H), 7.59 – 7.53 (m, 1H), 7.43 (q, J = 7.9 Hz, 2H), 7.35 (d, J = 8.7 Hz, 1H), 7.25 – 7.11 (m, 3H), 7.01 (d, J = 8.7 Hz, 1H), 3.48 and 3.45 (s, 3H, N-CH3, major and minor, conformers).
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.9, 167.2, 141.2, 134.6, 133.6, 129.6, 129.5, 128.9, 128.4, 126.8, 36.3.
HRMS (ESI, m/z) calcd. for $C_{15}H_{14}NO_2$ $[M+H]^+$: 240.1024; found: 290.1026.

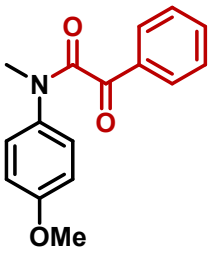


N-(4-bromophenyl)-N-methyl-2-oxo-2-phenylacetamide (5b).
The general procedure was followed. Column chromatography (SiO_2, eluting with 85:15 hexane/ethyl acetate) afforded the desired product as a yellow gummy liquid (100 mg, 63%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, J = 7.3, 1.3 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.20 (d, J = 8.8 Hz, 2H), 7.07 (d, J = 8.8 Hz, 2H), 3.45 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.7, 167.0, 139.8, 134.6, 134.0, 133.4, 129.8, 129.5, 129.0, 128.2, 36.3.
HRMS (ESI, m/z) calcd. for $C_{15}H_{13}BrNO_2$ $[M+H]^+$: 318.0130; found: 318.0147.

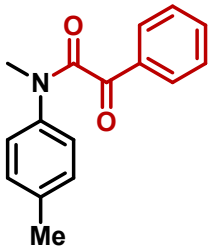


N-(4-chlorophenyl)-N-methyl-2-oxo-2-phenylacetamide (5c).
The general procedure was followed. Column chromatography (SiO_2, eluting with 85:15 hexane/ethyl acetate) afforded the desired product as a yellow gummy liquid (81 mg, 59%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.5 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 7.34 (d, J = 8.7 Hz, 2H), 7.01 (d, J = 8.7 Hz, 2H), 3.44 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 166.9, 140.3, 134.6, 133.3, 132.8, 129.5, 129.0, 128.4, 122.0, 36.3.

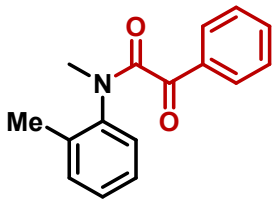
HRMS (ESI, m/z) calcd. for $C_{15}H_{13}ClNO_2$ $[M+H]^+$: 274.0635; found: 274.0639.



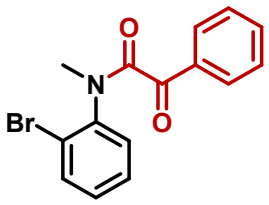
N-(4-methoxyphenyl)-N-methyl-2-oxo-2-phenylacetamide (5d).
The general procedure was followed. Column chromatography (SiO_2, eluting with 80:20 hexane/ethyl acetate) afforded the desired product as a yellow gummy liquid (124 mg, 92%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 6.8 Hz, 2H), 7.05 (d, *J* = 6.5 Hz, 2H), 6.72 (d, *J* = 6.5 Hz, 2H), 3.71 (s, 3H), 3.43 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.3, 167.4, 159.2, 134.4, 133.7, 133.6, 129.5, 128.9, 128.5, 114.7, 55.5, 36.6.
HRMS (ESI, m/z) calcd. for $C_{16}H_{16}NO_3$ $[M+H]^+$: 270.1130; found: 270.1136.



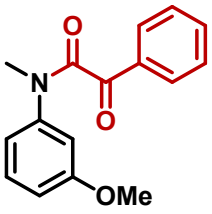
N-methyl-2-oxo-2-phenyl-N-(p-tolyl)acetamide (5e).
The general procedure was followed. Column chromatography (SiO_2, eluting with 85:15 hexane/ethyl acetate) afforded the desired product as a yellow gummy liquid (104 mg, 82%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.82 (m, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.42 (t, J = 7.7 Hz, 2H), 7.01 (s, 4H), 3.45 (s, 3H), 2.23 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.0, 167.2, 138.5, 138.2, 134.3, 133.5, 130.2, 129.5, 128.8, 126.6, 36.3, 21.1.
HRMS (ESI, m/z) calcd. for $C_{16}H_{16}NO_2$ $[M+H]^+$: 254.1181; found: 254.1198.



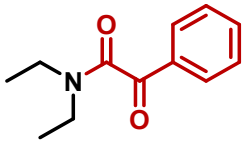
N-methyl-2-oxo-2-phenyl-N-(o-tolyl)acetamide (5f).
The general procedure was followed. Column chromatography (SiO_2, eluting with 90:10 hexane/ethyl acetate) afforded the desired product as a yellow oil (67 mg, 53%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.19 – 7.11 (m, 2H), 6.97 (dd, *J* = 4.7, 1.8 Hz, 2H), 3.36 (s, 3H), 2.30 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.7, 167.1, 139.5, 136.7, 134.3, 133.4, 131.6, 129.4, 129.2, 129.2, 128.8, 128.7, 126.9, 35.4, 17.8.
HRMS (ESI, m/z) calcd. for $C_{16}H_{16}NO_2$ $[M+H]^+$: 254.1181; found: 254.1171.



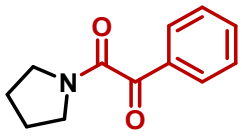
N-(2-bromophenyl)-N-methyl-2-oxo-2-phenylacetamide (5g).
The general procedure was followed. Column chromatography (SiO_2, eluting with 85:15 hexane/ethyl acetate) afforded the desired product as a white solid (75 mg, 47%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.57 – 7.50 (m, 2H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.29 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.13 (td, *J* = 7.6, 1.8 Hz, 1H), 3.42 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.2, 166.8, 139.9, 134.5, 134.0, 133.0, 131.3, 130.4, 129.9, 128.7, 128.6, 123.1, 35.6.
HRMS (ESI, m/z) calcd. for $C_{15}H_{13}BrNO_2$ $[M+H]^+$: 318.0130; found: 318.0144



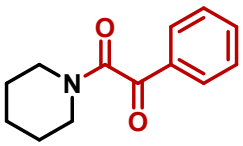
N-(3-methoxyphenyl)-N-methyl-2-oxo-2-phenylacetamide (5h).
The general procedure was followed. Column chromatography (SiO_2, eluting with 80:20 hexane/ethyl acetate) afforded the desired product as a yellow oil (93 mg, 69%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.84 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.13 (t, *J* = 8.1 Hz, 1H), 6.76 – 6.68 (m, 2H), 6.65 (t, *J* = 2.3 Hz, 1H), 3.61 (s, 3H), 3.48 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.8, 167.2, 160.4, 142.4, 134.4, 133.8, 130.4, 129.6, 128.9, 118.8, 114.2, 112.3, 55.4, 36.3.
HRMS (ESI, m/z) calcd. for $C_{16}H_{16}NO_3$ $[M+H]^+$: 270.1130; found: 270.1124.



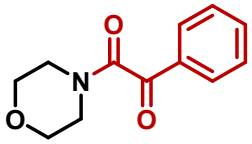
N,N-diethyl-2-oxo-2-phenylacetamide (5i).
The general procedure was followed. Column chromatography (SiO_2, eluting with 85:15 hexane/ethyl acetate) afforded the desired product as a yellow liquid (72 mg, 70%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.67 – 7.59 (m, 1H), 7.50 (dd, *J* = 8.4, 7.1 Hz, 2H), 3.56 (q, *J* = 7.2 Hz, 2H), 3.23 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 166.8, 134.7, 133.3, 129.7, 129.1, 42.2, 38.9, 14.2, 13.0.
HRMS (ESI, m/z) calcd. for $C_{12}H_{16}NO_2$ $[M+H]^+$: 206.1181; found: 206.1194.



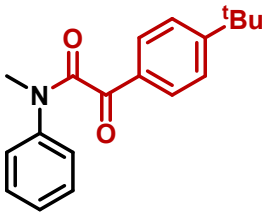
1-phenyl-2-(pyrrolidin-1-yl)ethane-1,2-dione (5j).
The general procedure was followed. Column chromatography (SiO_2, eluting with 85:15 hexane/ethyl acetate) afforded the desired product as a yellow liquid (68 mg, 67%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 3.64 (t, *J* = 6.6 Hz, 2H), 3.41 (t, *J* = 6.4 Hz, 2H), 1.98 – 1.89 (m, 4H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 165.0, 134.7, 133.0, 130.0, 129.0, 46.8, 45.3, 26.0, 24.1.
HRMS (ESI, m/z) calcd. for $C_{12}H_{14}NO_2$ $[M+H]^+$: 204.1024; found: 204.1035.



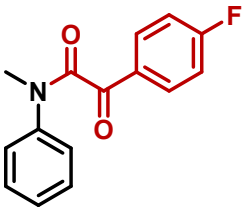
1-phenyl-2-(piperidin-1-yl)ethane-1,2-dione (5k).
The general procedure was followed. Column chromatography (SiO_2, eluting with 85:15 hexane/ethyl acetate) afforded the desired product as a yellow liquid (67 mg, 62%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.90 (m, 2H), 7.66 – 7.59 (m, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 3.73 – 3.66 (m, 2H), 3.33 – 3.24 (m, 2H), 1.68 (p, *J* = 2.9 Hz, 4H), 1.58 – 1.49 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 165.5, 134.8, 133.3, 129.7, 129.1, 47.1, 42.2, 26.3, 25.5, 24.5.
HRMS (ESI, m/z) calcd. for $C_{13}H_{16}NO_2$ $[M+H]^+$: 218.1181; found: 218.1172.



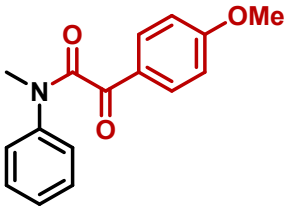
1-Morpholino-2-phenylethane-1,2-dione (5l).
The general procedure was followed. Column chromatography (SiO_2, eluting with 75:25 hexane/ethyl acetate) afforded the desired product as a yellow liquid (60 mg, 55%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.89 (m, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 3.76 (s, 4H), 3.61 (t, *J* = 4.8 Hz, 2H), 3.37 – 3.32 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2, 165.5, 135.0, 133.0, 129.6, 129.1, 66.7, 66.6, 46.2, 41.6.
HRMS (ESI, m/z) calcd. for $C_{12}H_{14}NO_3$ $[M+H]^+$: 220.0974; found: 220.0994.



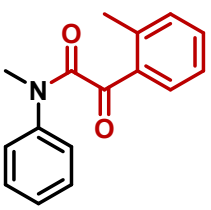
2-(4-(Tert-butyl)phenyl)-N-methyl-2-oxo-N-phenylacetamide (6a).
The general procedure was followed. Column chromatography (SiO_2, eluting with 90:10 hexane/ethyl acetate) afforded the desired product as a yellow solid (94 mg, 69%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.8 Hz, 2H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.27 – 7.19 (m, 3H), 7.17 – 7.13 (m, 2H), 3.48 (s, 3H), 1.31 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 167.4, 158.3, 141.5, 131.1, 129.6, 129.5, 128.1, 126.8, 125.9, 36.3, 35.4, 31.1.



2-(4-Fluorophenyl)-N-methyl-2-oxo-N-phenylacetamide (6b).
The general procedure was followed. Column chromatography (SiO_2, eluting with 85:15 hexane/ethyl acetate) afforded the desired product as a yellow gummy liquid (80 mg, 62%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.9, 5.3 Hz, 2H), 7.26 – 7.18 (m, 3H), 7.15 – 7.05 (m, 4H), 3.47 and 3.32 (s, 3H, N-CH3, Major and Minor conformers).
^{13}C NMR (101 MHz, $CDCl_3$) δ 189.2, 167.7, 166.9, 165.1, 141.2, 132.3, 132.2, 129.7, 128.3, 126.8, 116.3, 116.1, 36.3.

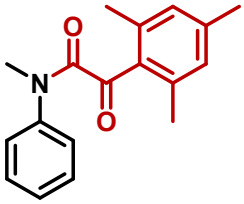


2-(4-Methoxyphenyl)-N-methyl-2-oxo-N-phenylacetamide (6c).
The general procedure was followed. Column chromatography (SiO_2, eluting with 80:20 hexane/ethyl acetate) afforded the desired product as a yellow gummy liquid (110 mg, 79%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 9.0 Hz, 2H), 7.22 (dd, *J* = 10.6, 7.1 Hz, 3H), 7.13 (dd, *J* = 8.1, 1.6 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 3.85 (s, 3H), 3.47 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 189.6, 167.5, 164.5, 141.5, 132.0, 129.6, 128.1, 126.8, 114.2, 55.7, 36.3.
HRMS (ESI, m/z) calcd. for $C_{16}H_{16}NO_3$ $[M+H]^+$: 270.1130; found: 270.1124.

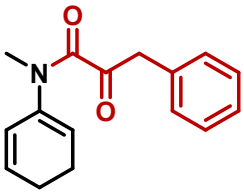


N-Methyl-2-oxo-N-phenyl-2-(o-tolyl)acetamide (6d)
The general procedure was followed. Column chromatography (SiO_2, eluting with 80:15 hexane/ethyl acetate) afforded the desired product as a yellow solid (67 mg, 85%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, J = 7.8, 1.6 Hz, 1H), 7.36 (td, J = 7.5, 1.5 Hz, 1H), 7.25 (t, J = 7.2 Hz, 1H), 7.23 – 7.16 (m, 3H), 7.13 –

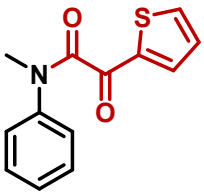
7.06 (m, 3H), 3.43 (s, 3H), 2.26 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 193.3, 167.6, 141.1, 140.7, 133.1, 132.3, 132.2, 131.8, 129.5, 128.1, 127.1, 125.8, 36.2, 21.2.



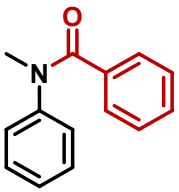
2-mesityl-N-methyl-2-oxo-N-phenylacetamide (6e).
The general procedure was followed. Column chromatography (SiO_2, eluting with 80:20 hexane/ethyl acetate) afforded the desired product as a pale-yellow solid (67 mg, 75%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (dd, J = 5.3, 1.9 Hz, 3H), 7.08 – 7.02 (m, 2H), 6.69 (s, 2H), 3.37 (s, 3H), 2.21 (s, 3H), 2.18 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 167.0, 141.5, 141.4, 137.7, 133.0, 129.7, 129.4, 128.1, 127.0, 37.8, 21.2, 20.8.
HRMS (ESI, m/z) calcd. for $C_{18}H_{20}NO_2$ $[M+H]^+$: 282.1494; found: 282.1465. C18H19NO2



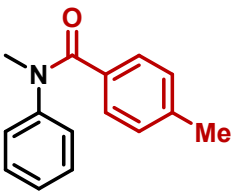
N-methyl-N,2-diphenylacetamide (6f).
The general procedure was followed. Column chromatography (SiO_2, eluting with 80:20 hexane/ethyl acetate) afforded the desired product as a yellow gummy liquid (99 mg, 78%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.21 (m, 7H), 7.06 – 7.01 (m, 2H), 6.82 (dd, J = 7.6, 2.1 Hz, 2H), 3.89 (s, 2H), 3.29 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0, 166.9, 141.3, 131.7, 130.1, 129.5, 128.8, 128.2, 127.5, 126.7, 47.0, 36.8.



N-Methyl-2-oxo-N-phenyl-2-(thiophen-2-yl)acetamide (6g).
The general procedure was followed. Column chromatography (SiO_2, eluting with 80:20 hexane/ethyl acetate) afforded the desired product as a yellow solid (75 mg, 61%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 3.9 Hz, 1H), 7.72 (d, J = 6.1 Hz, 1H), 7.30 (d, J = 7.3 Hz, 3H), 7.20 – 7.14 (m, 3H), 3.48 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 182.7, 166.1, 141.7, 140.8, 136.0, 135.6, 132.9, 129.7, 128.6, 128.2, 126.6, 36.8, 29.8.

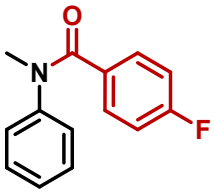


N-methyl-N-phenylbenzamide (7a).
The general procedure was followed. Column chromatography (SiO_2, eluting with 80:20 hexane/ethyl acetate) afforded the desired product as a yellow solid (69 mg, 65%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 6.8 Hz, 2H), 7.24 – 7.18 (m, 3H), 7.17 – 7.09 (m, 3H), 7.02 (d, J = 7.2 Hz, 2H), 3.49 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 144.9, 135.9, 129.6, 129.2, 128.8, 127.8, 127.0, 126.5, 38.5.

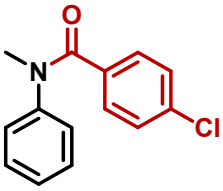


N,4-dimethyl-N-phenylbenzamide (7b).
The general procedure was followed. Column chromatography (SiO_2, eluting with 80:20 hexane/ethyl acetate) afforded the desired product as a yellow solid (77 mg, 68%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.11 (m, 5H), 7.03 (d, J = 7.1 Hz, 2H), 6.95 (d, J = 8.1 Hz, 2H), 3.48 (s, 3H), 2.24 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 145.3, 139.9, 133.0, 129.2, 129.0, 128.5, 127.0, 126.4, 38.6, 21.4.

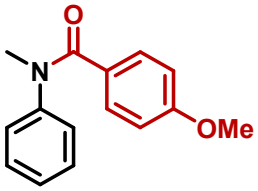
HRMS (ESI, m/z) calcd. for $C_{15}H_{16}NO$ $[M+H]^+$: 226.1232; found: 226.1222.



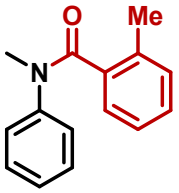
4-fluoro-N-methyl-N-phenylbenzamide (7c).
The general procedure was followed. Column chromatography (SiO_2, eluting with 80:15 hexane/ethyl acetate) afforded the desired product as a yellow solid (81 mg, 71%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 15.2, 8.4 Hz, 4H), 7.15 (t, *J* = 6.8 Hz, 1H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 3.74 (s, 3H), 3.50 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 160.7, 145.5, 131.0, 129.3, 128.0, 126.9, 126.4, 113.1, 55.3, 38.7.



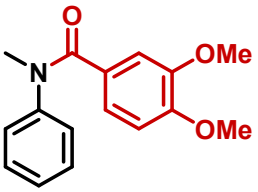
4-chloro-N-methyl-N-phenylbenzamide (7d).
The general procedure was followed. Column chromatography (SiO_2, eluting with 85:15 hexane/ethyl acetate) afforded the desired product as a yellow solid (85 mg, 69%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 8.3, 3.5 Hz, 4H), 7.19 – 7.11 (m, 3H), 7.02 (d, *J* = 7.8 Hz, 2H), 3.49 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 144.6, 135.7, 134.3, 130.3, 129.4, 128.0, 126.9, 126.8, 38.5.



4-methoxy-N-methyl-N-phenylbenzamide (7e).
The general procedure was followed. Column chromatography (SiO_2, eluting with 75:25 hexane/ethyl acetate) afforded the desired product as a yellow solid (90 mg, 75%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 15.2, 8.4 Hz, 4H), 7.15 (t, *J* = 6.8 Hz, 1H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 3.74 (s, 3H), 3.50 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 160.7, 145.5, 131.0, 129.3, 128.0, 126.9, 126.4, 113.1, 55.3, 38.7.

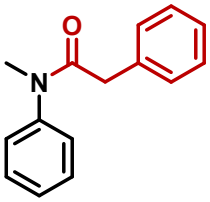


N,2-dimethyl-N-phenylbenzamide (7f).
The general procedure was followed. Column chromatography (SiO_2, eluting with 80:20 hexane/ethyl acetate) afforded the desired product as a yellow solid (42 mg, 37%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 2.0 Hz, 1H), 7.27 (d, *J* = 4.6 Hz, 4H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.12 – 7.05 (m, 3H), 6.31 (d, *J* = 8.5 Hz, 1H), 3.47 (s, 3H), 2.83 (d, *J* = 3.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 147.1, 145.7, 134.0, 130.4, 129.40, 126.9, 126.4, 124.2, 108.8, 38.9, 30.4.

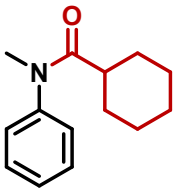


3,4-dimethoxy-N-methyl-N-phenylbenzamide (7g).
The general procedure was followed. Column chromatography (SiO_2, eluting with 80:20 hexane/ethyl acetate) afforded the desired product as a yellow gummy liquid (149 mg, 55%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 2H), 7.16 – 7.10 (m, 1H), 7.03 (d, *J* = 8.1 Hz, 2H), 6.91 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.82 (d, *J* = 2.1 Hz, 1H), 6.61 (d, *J* = 8.4 Hz, 1H), 3.78 (s, 3H), 3.61 (s, 3H), 3.47 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.19, 150.26, 147.94, 145.67, 129.35,

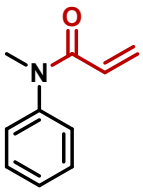
127.89, 126.91, 126.47, 122.91, 112.49, 109.96, 55.90, 55.77, 38.77.



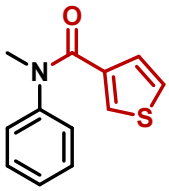
N-methyl-N,2-diphenylacetamide (7h).
The general procedure was followed. Column chromatography (SiO_2, eluting with 85:15 hexane/ethyl acetate) afforded the desired product as a yellow oil. (46 mg, 41%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 3H), 7.21 (dd, *J* = 10.5, 7.0 Hz, 3H), 7.12 (d, *J* = 7.7 Hz, 2H), 7.05 (d, *J* = 6.6 Hz, 2H), 3.46 (s, 2H), 3.28 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 144.1, 135.6, 129.8, 129.2, 128.4, 128.1, 127.8, 126.7, 41.0, 37.8.
HRMS (ESI, m/z) calcd. for $C_{15}H_{16}NO$ $[M+H]^+$: 226.1232; found: 226.1254.



N-methyl-N-phenylcyclohexanecarboxamide (7i).
The general procedure was followed. Column chromatography (SiO_2, eluting with 80:15 hexane/ethyl acetate) afforded the desired product as a yellow liquid (89 mg, 82%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 7.7 Hz, 2H), 3.21 (s, 3H), 2.16 (s, 1H), 1.62 (d, *J* = 13.0 Hz, 4H), 1.50 (q, *J* = 12.7, 11.2 Hz, 3H), 1.15 (q, *J* = 13.0 Hz, 1H), 0.94 (t, *J* = 12.9 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 144.3, 129.8, 127.7, 127.3, 41.4, 37.5, 29.5, 25.7, 25.6.
HRMS (ESI, m/z) calcd. for $C_{14}H_{20}NO$ $[M+H]^+$: 218.1545; found: 218.1540.



N-methyl-N-phenylacrylamide (7j).
The general procedure was followed. Column chromatography (SiO_2, eluting with 80:20 hexane/ethyl acetate) afforded the desired product as a white solid (36 mg, 45%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (t, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.22 – 7.14 (m, 2H), 6.37 (dd, *J* = 16.8, 2.1 Hz, 1H), 6.07 (dd, *J* = 16.8, 10.3 Hz, 1H), 5.51 (dd, *J* = 10.3, 2.1 Hz, 1H), 3.36 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 143.6, 129.7, 128.6, 127.8, 127.6, 127.4, 37.6.



N-methyl-N-phenylthiophene-3-carboxamide (7k).
The general procedure was followed. Column chromatography (SiO_2, eluting with 80:20 hexane/ethyl acetate) afforded the desired product as a yellow solid (62 mg, 57%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.3 Hz, 2H), 7.30 – 7.25 (m, 1H), 7.20 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.17 – 7.12 (m, 2H), 7.03 (dd, *J* = 5.1, 3.0 Hz, 1H), 6.88 (dd, *J* = 5.1, 1.3 Hz, 1H), 3.48 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 144.9, 136.8, 129.9, 129.5, 128.6, 127.3, 127.2, 124.4, 38.6.

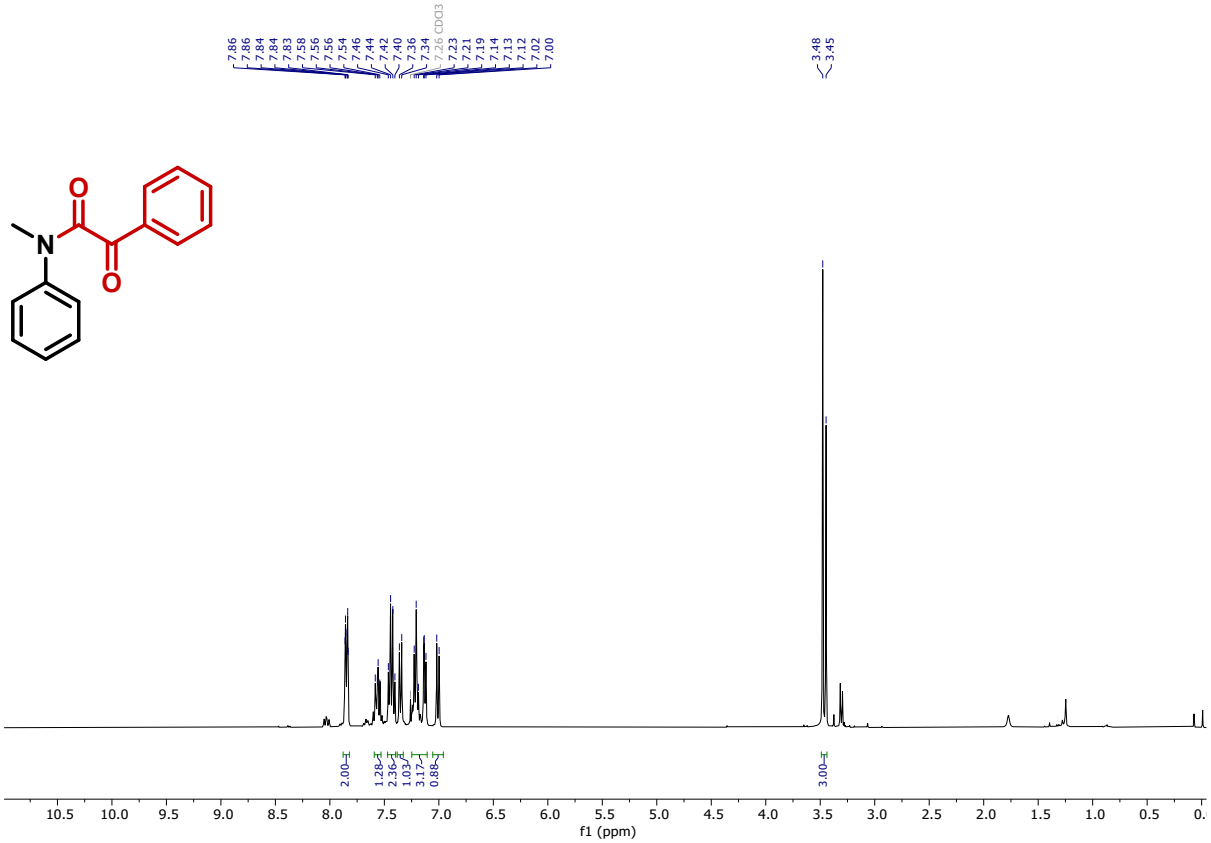


Fig S7. ^{1}H NMR spectrum (400 MHz) of **5a** in $CDCl_3$ (7.26 ppm).

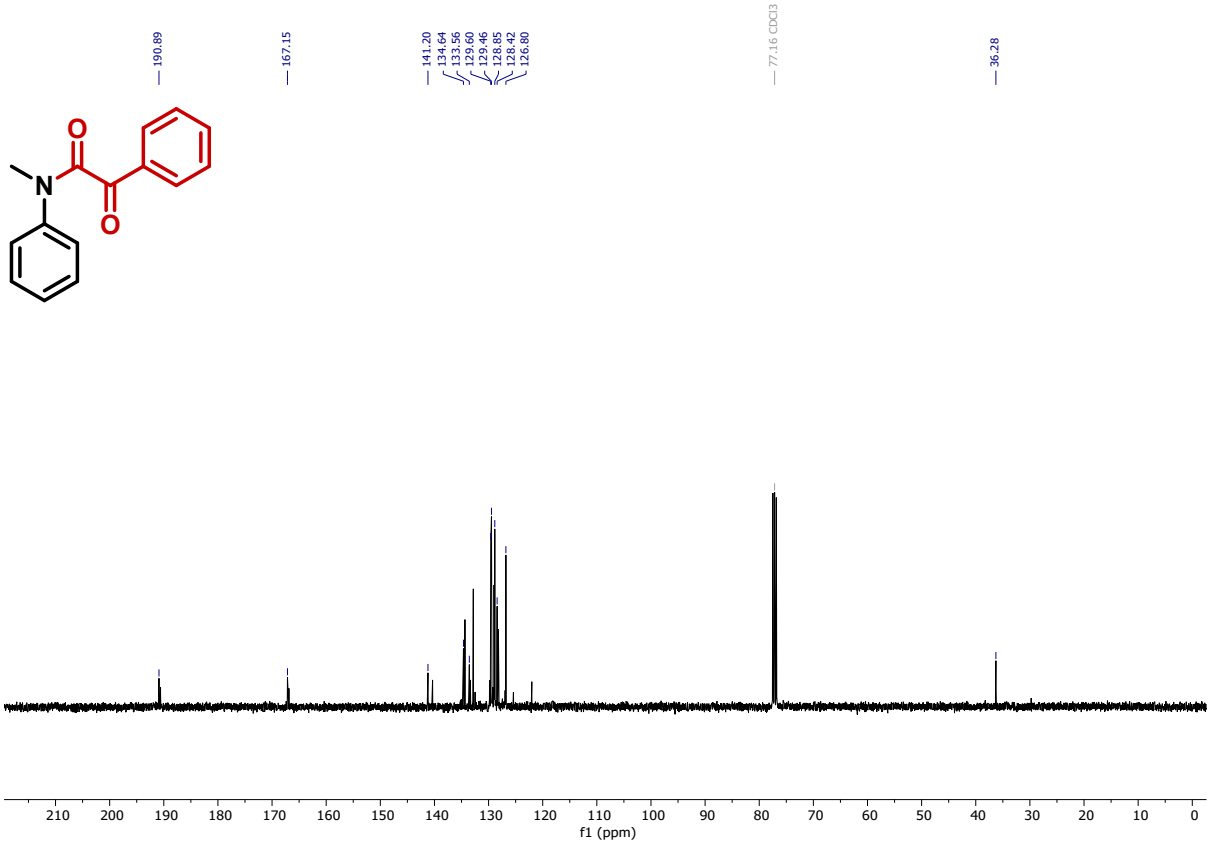


Fig S8. ^{13}C NMR spectrum (101 MHz) of **5a** in $CDCl_3$ (77.16 ppm).

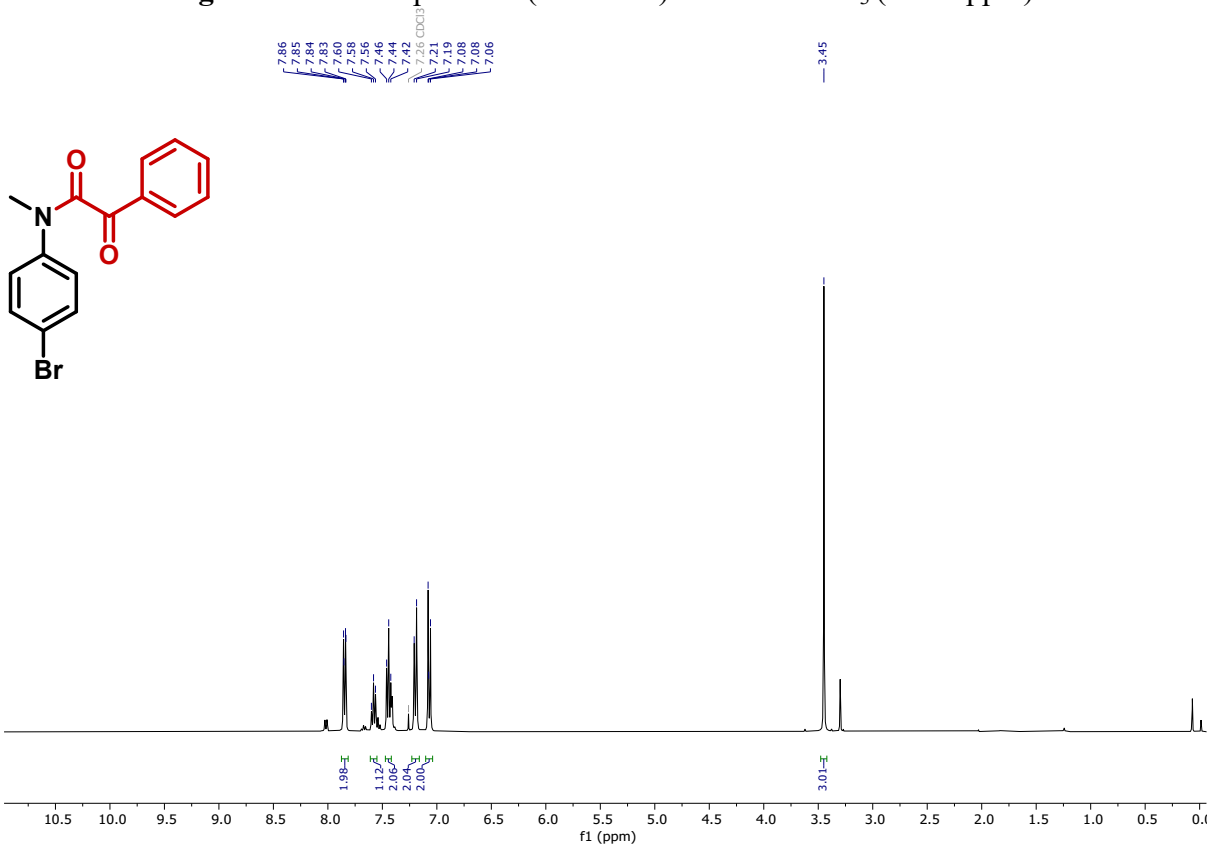


Fig S9. ^{1}H NMR spectrum (400 MHz) of **5b** in $CDCl_3$ (7.26 ppm).

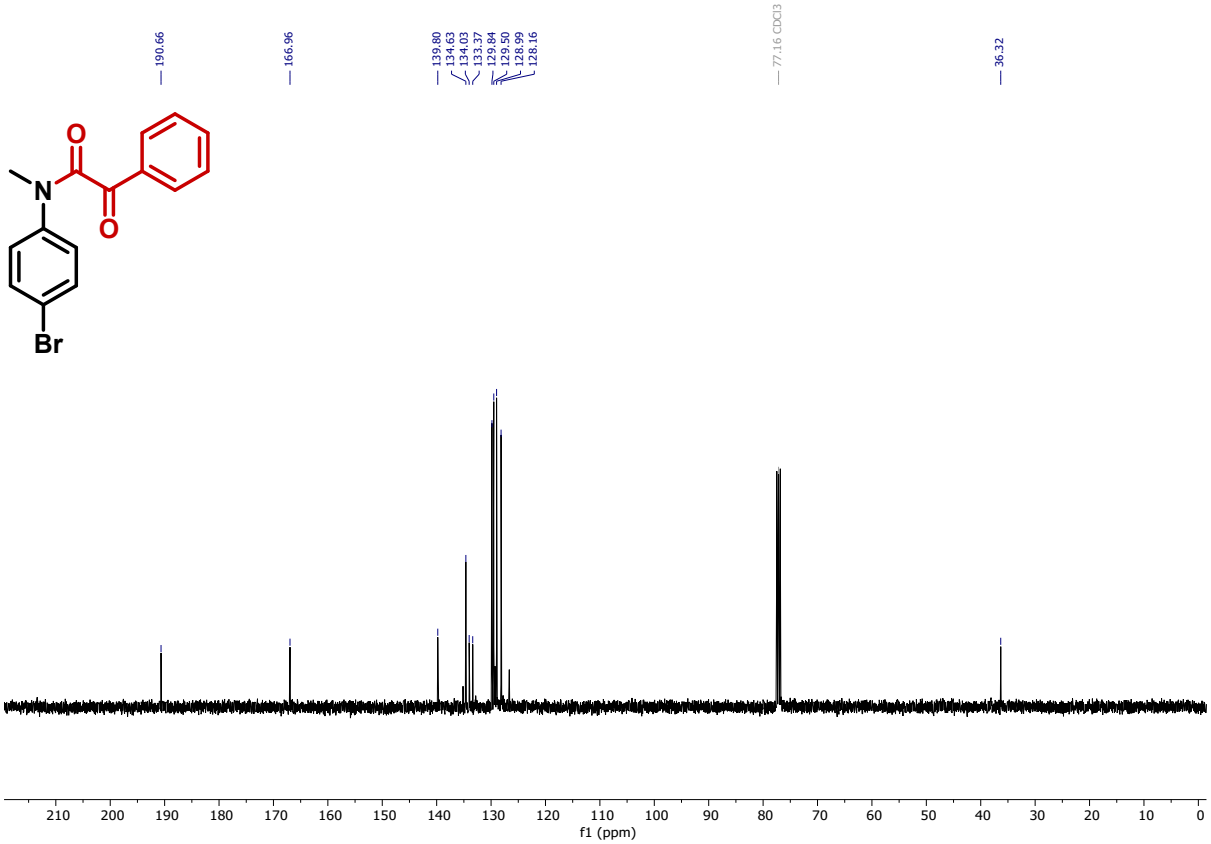


Fig S10. ^{13}C NMR spectrum (101 MHz) of **5b** in $CDCl_3$ (77.16 ppm).

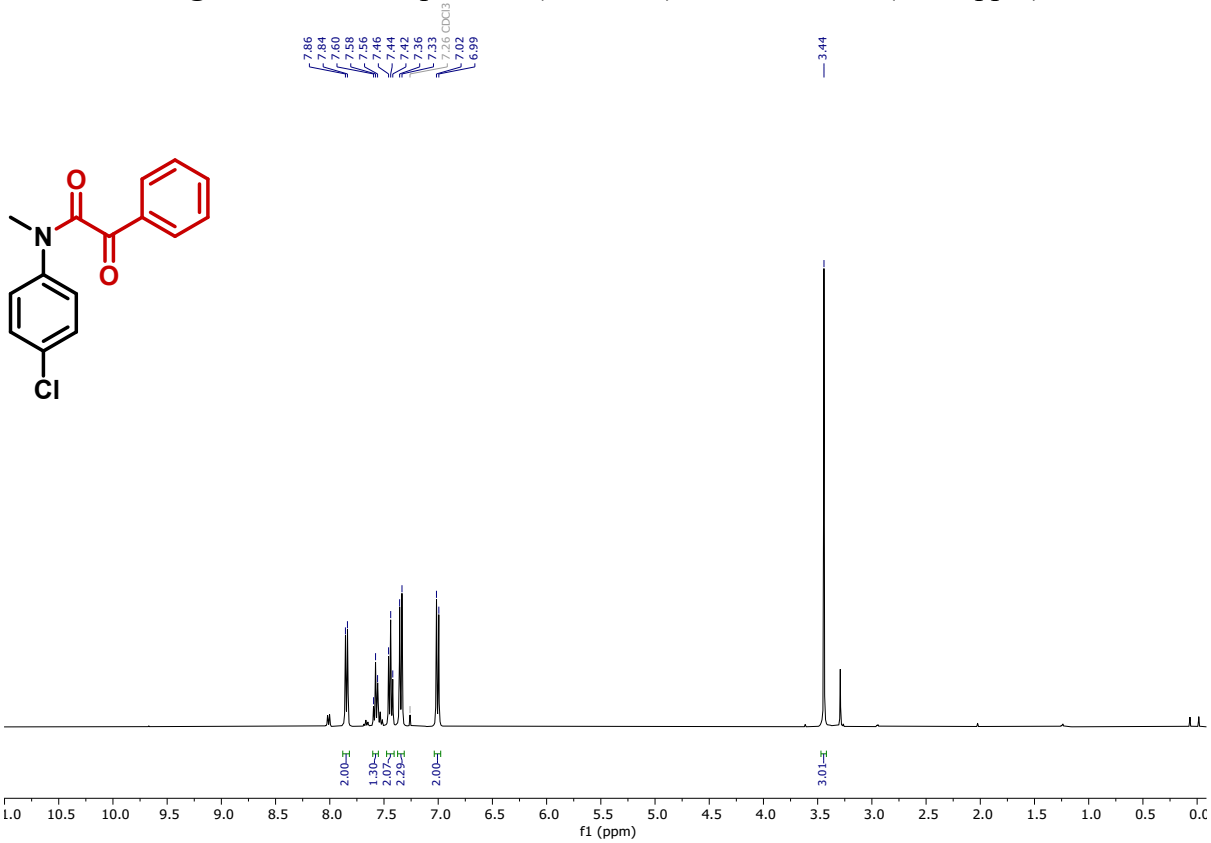


Fig S11. ^{1}H NMR spectrum (400 MHz) of **5c** in $CDCl_3$ (7.26 ppm).

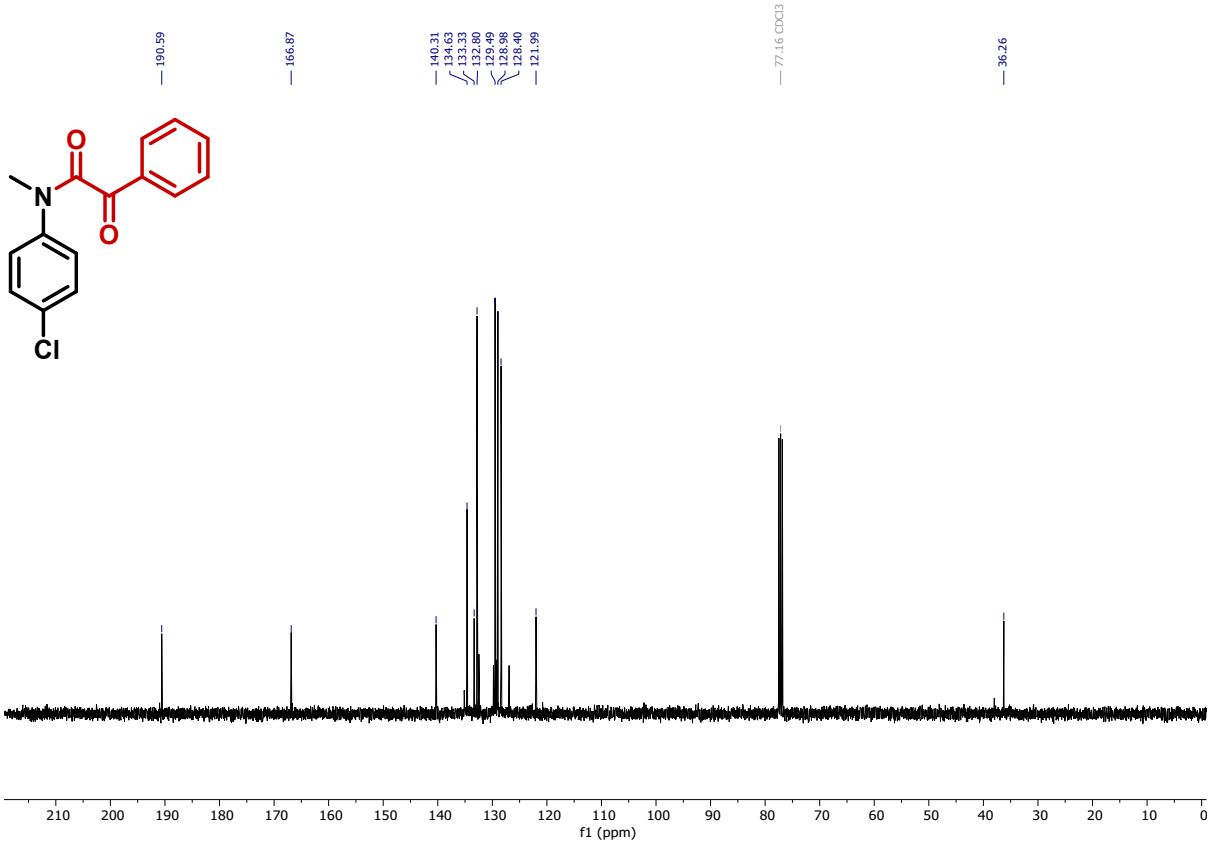


Fig S12. ^{13}C NMR spectrum (101 MHz) of **5c** in $CDCl_3$ (77.16 ppm).

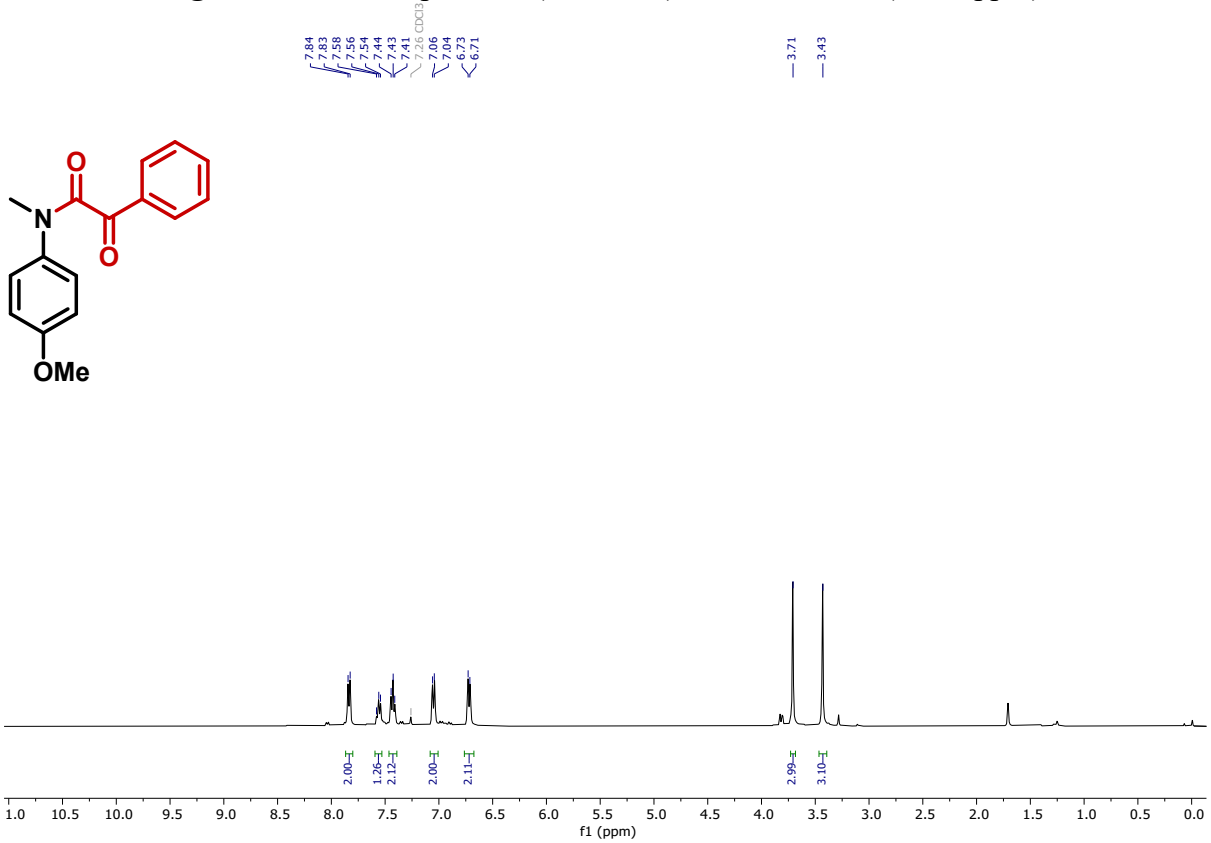


Fig S13. ^{1}H NMR spectrum (400 MHz) of **5d** in $CDCl_3$ (7.26 ppm).

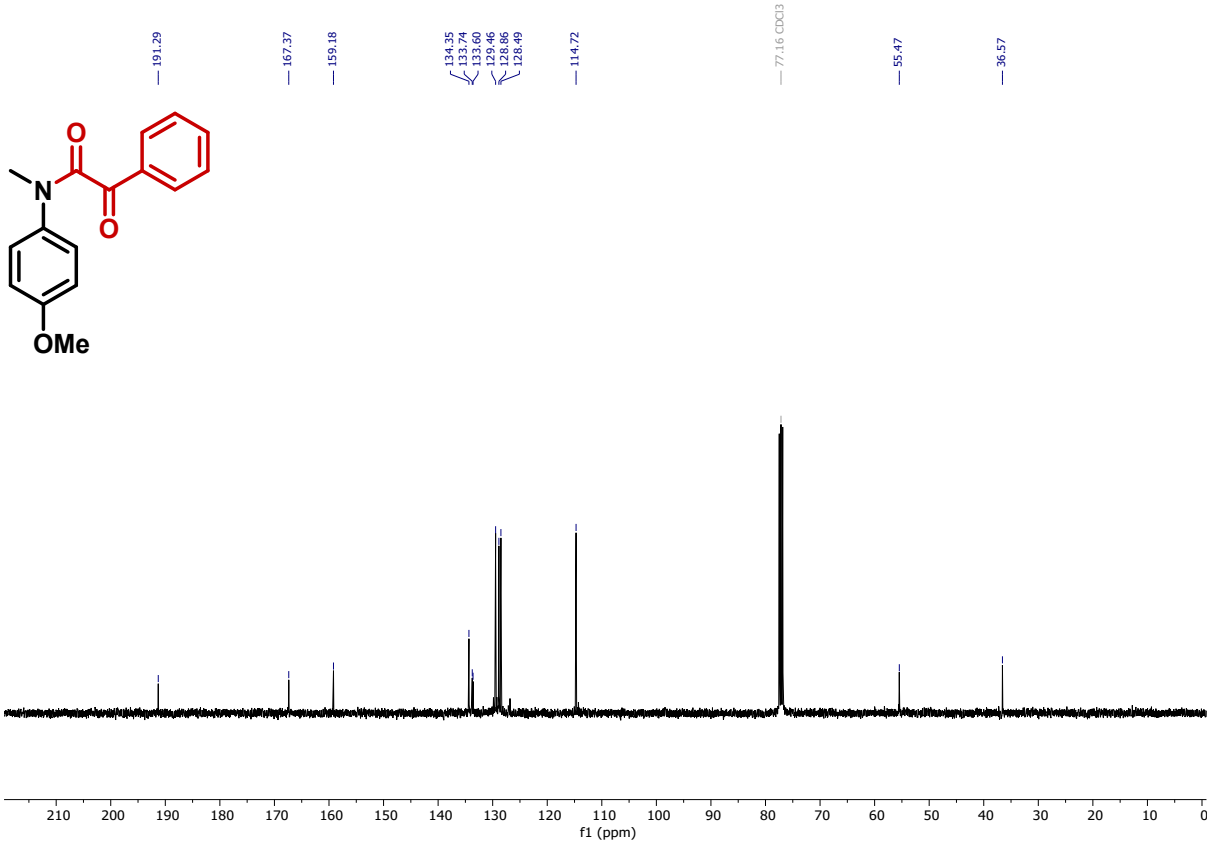


Fig S14. ^{13}C NMR spectrum (101 MHz) of **5d** in $CDCl_3$ (77.16 ppm).

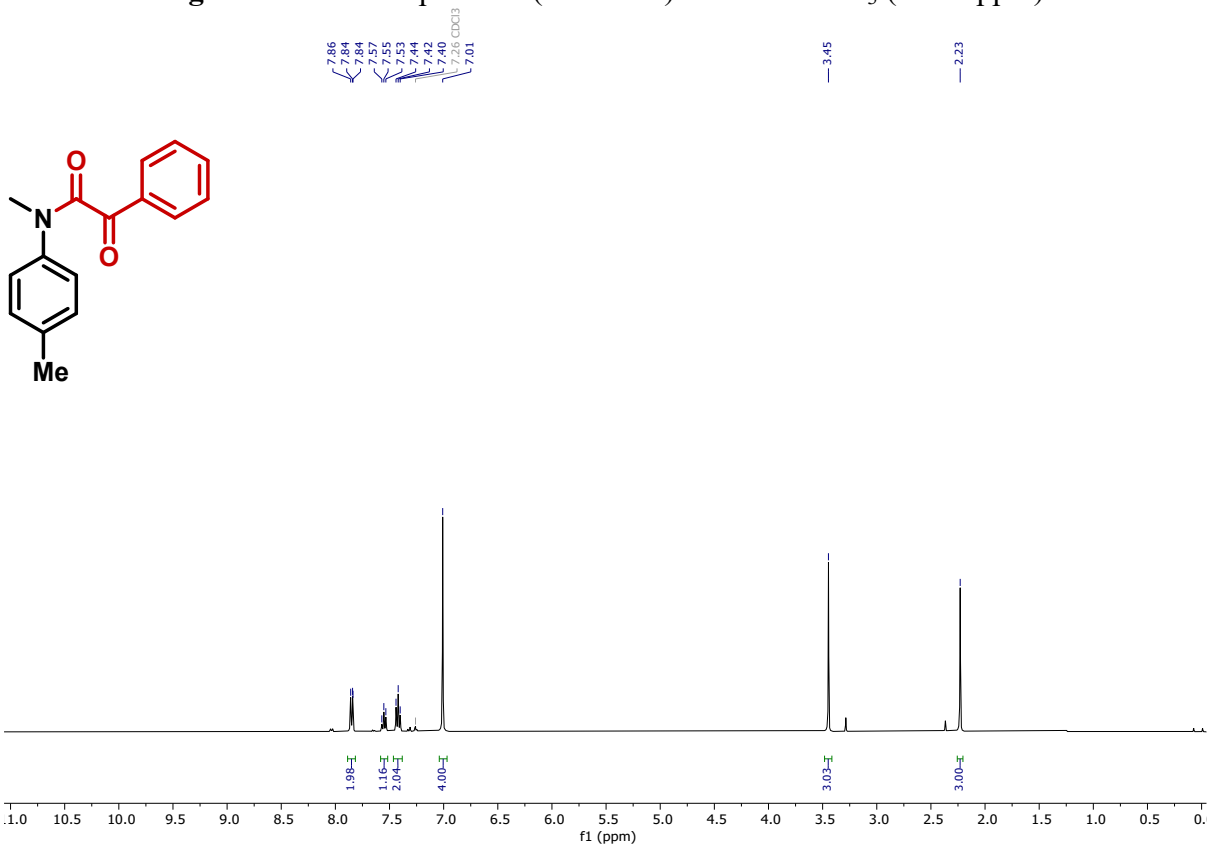


Fig S15. ^{1}H NMR spectrum (400 MHz) of **5e** in $CDCl_3$ (7.26 ppm).

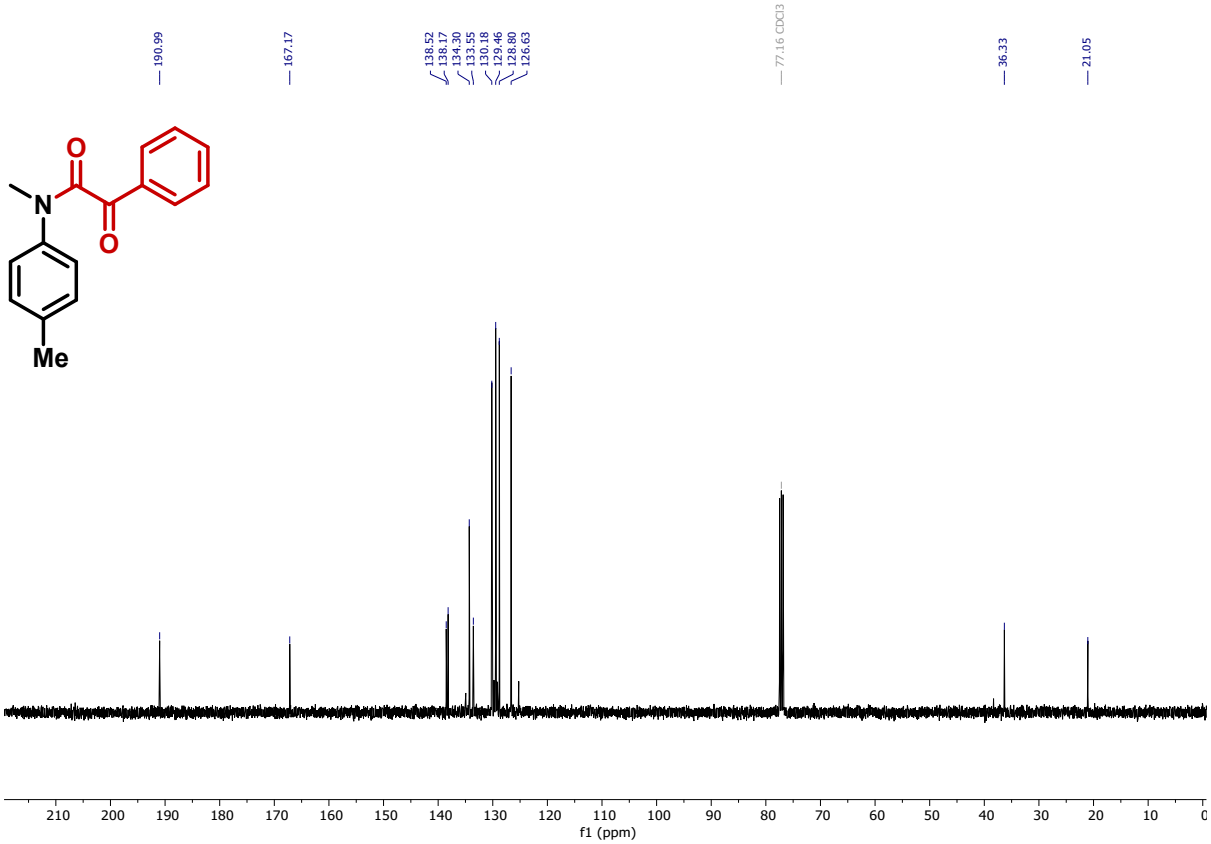


Fig S16. ^{13}C NMR spectrum (101 MHz) of **5e** in $CDCl_3$ (77.16 ppm).

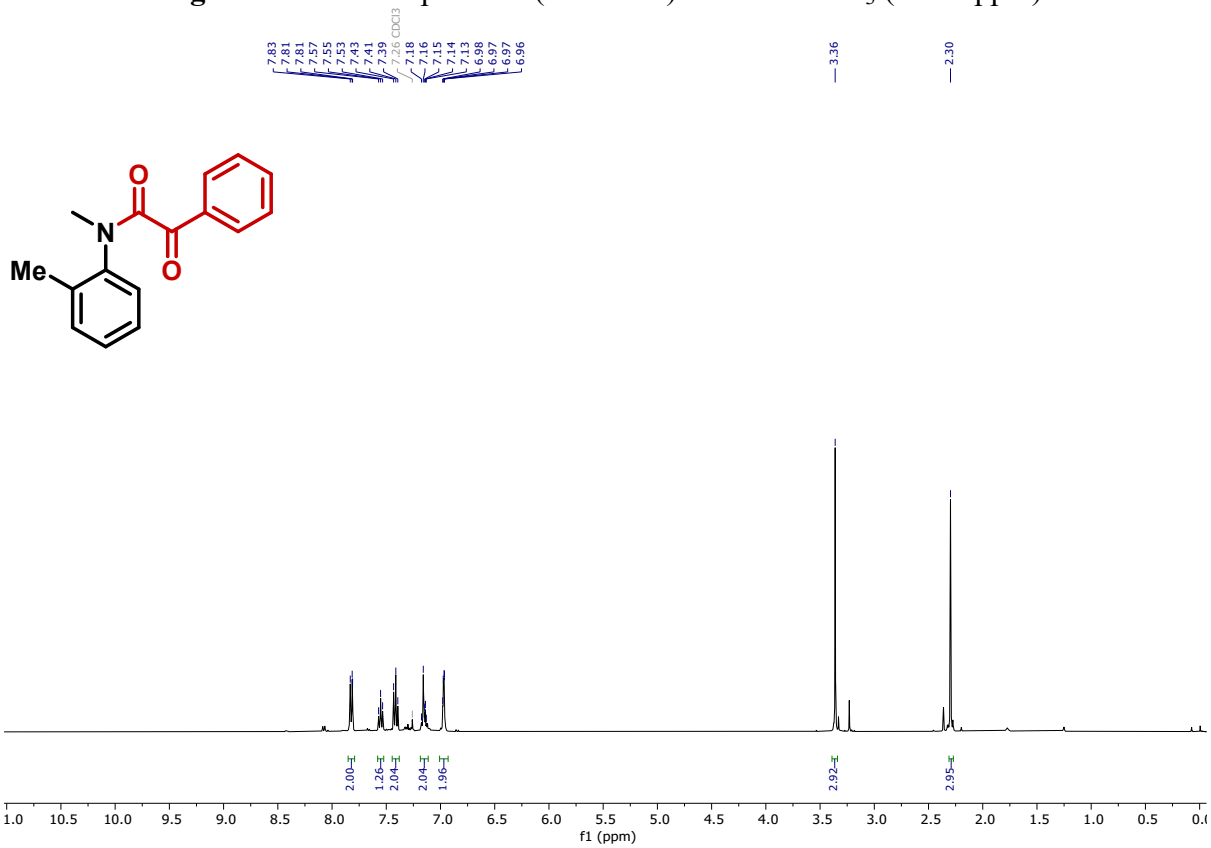


Fig S17. ^{1}H NMR spectrum (400 MHz) of **5f** in $CDCl_3$ (7.26 ppm).

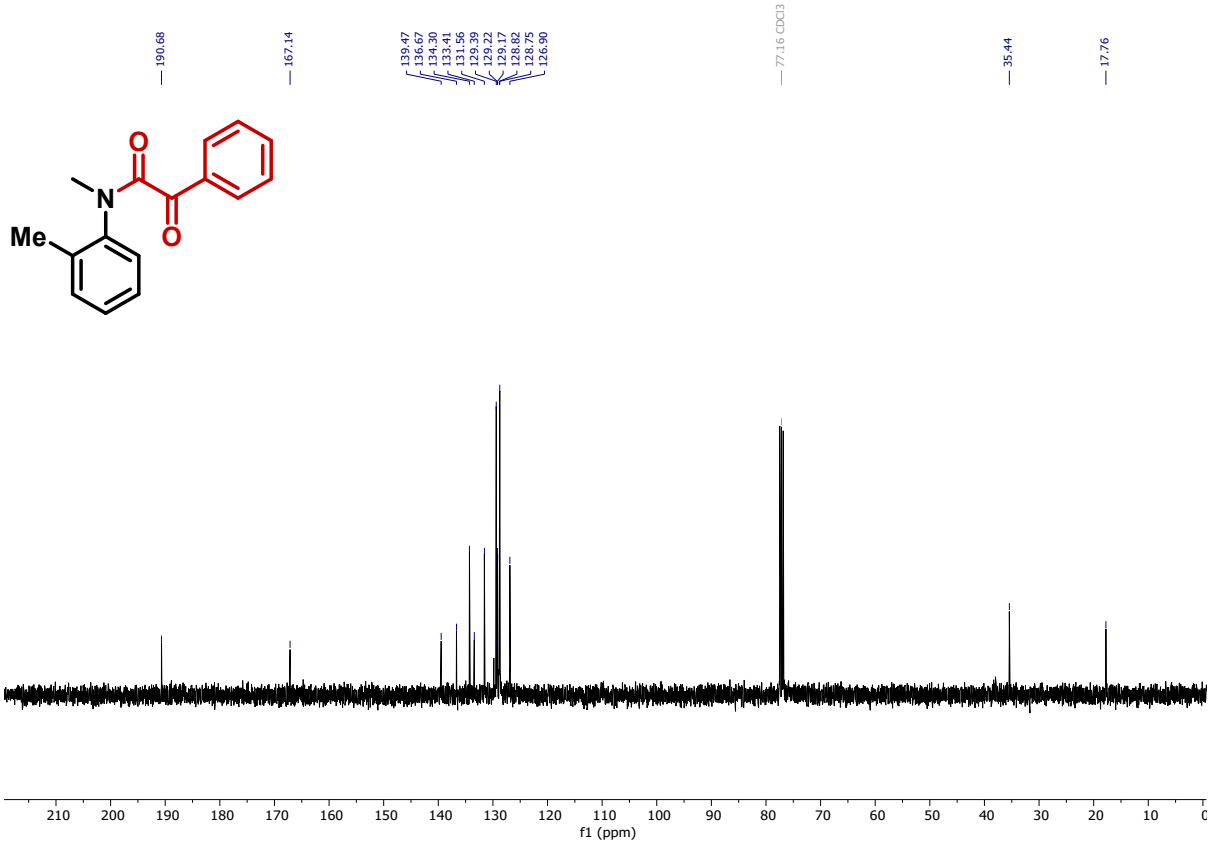


Fig S18. ^{13}C NMR spectrum (101 MHz) of **5f** in $CDCl_3$ (77.16 ppm).

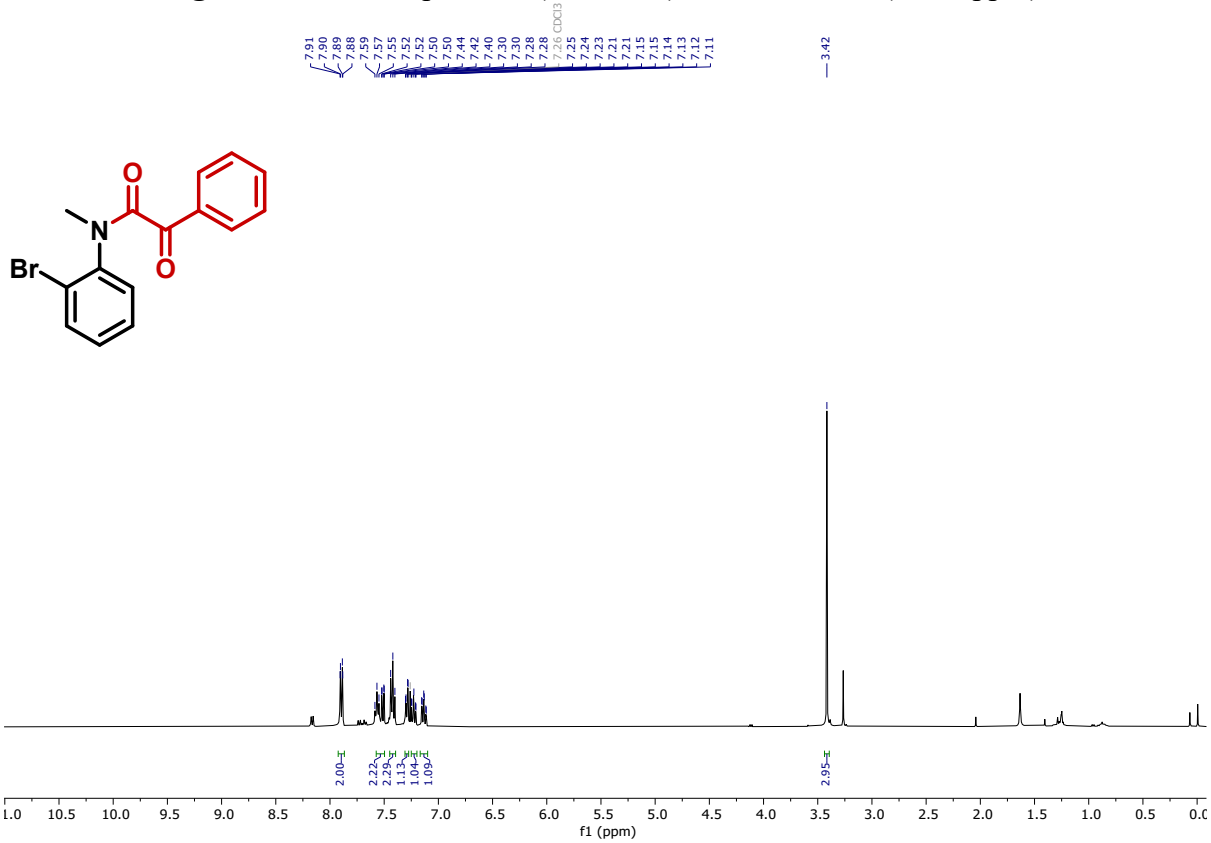


Fig S19. ^{1}H NMR spectrum (400 MHz) of **5g** in $CDCl_3$ (7.26 ppm).

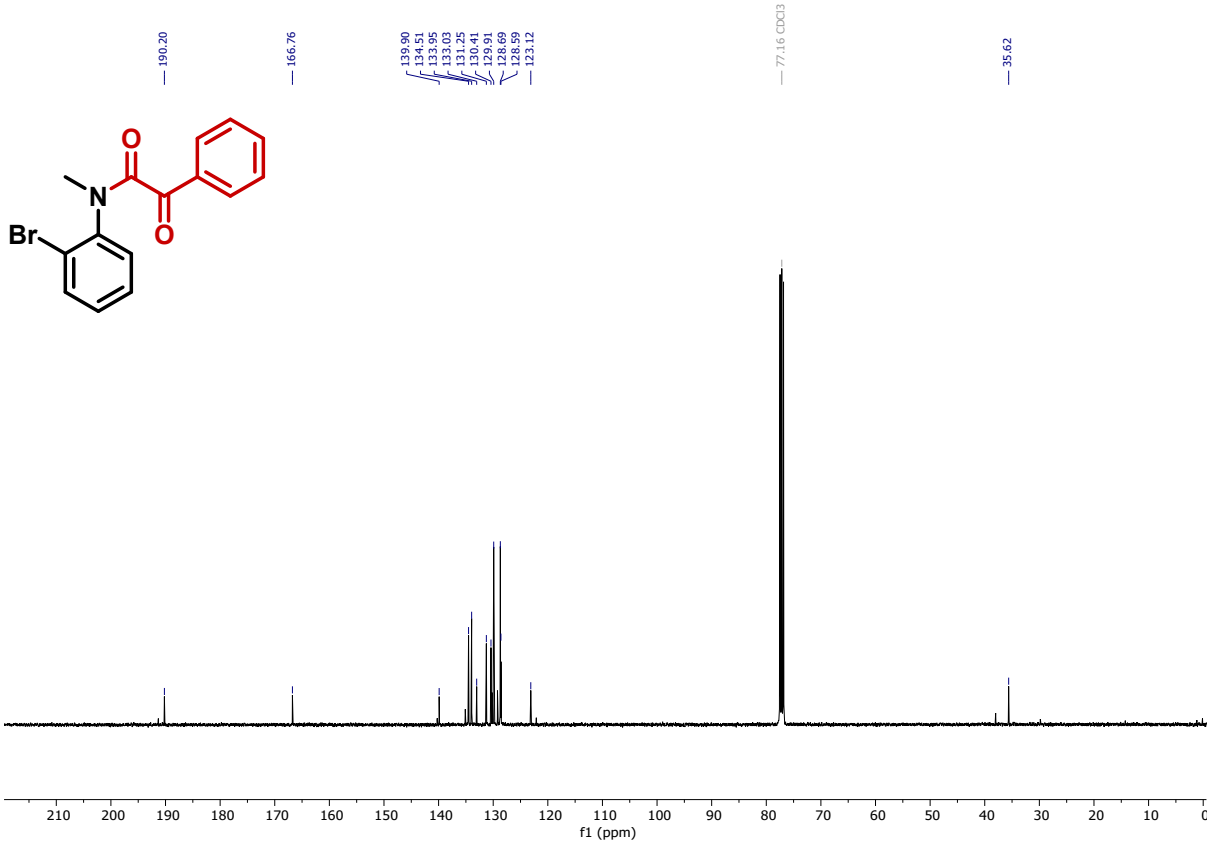


Fig S20. ^{13}C NMR spectrum (101 MHz) of **5g** in $CDCl_3$ (77.16 ppm).

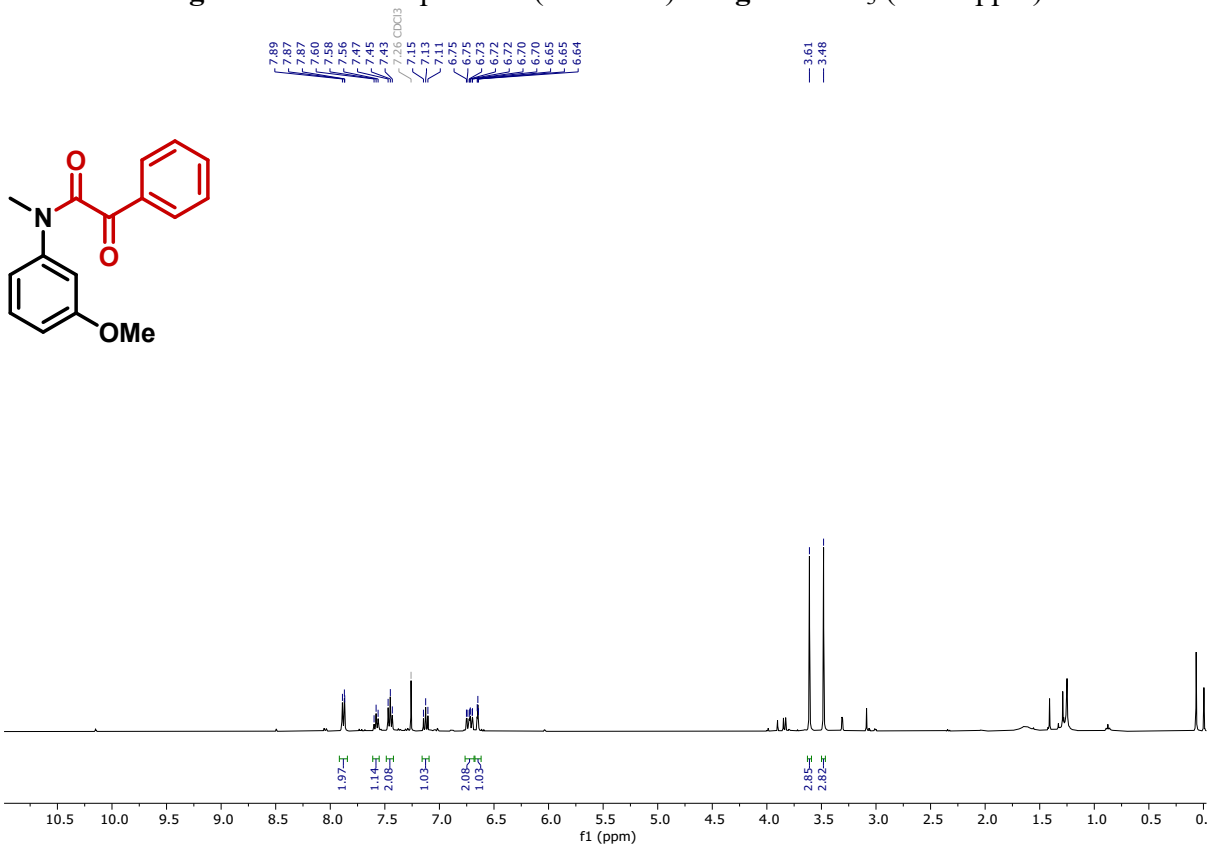


Fig S21. ^{1}H NMR spectrum (400 MHz) of **5h** in $CDCl_3$ (7.26 ppm).

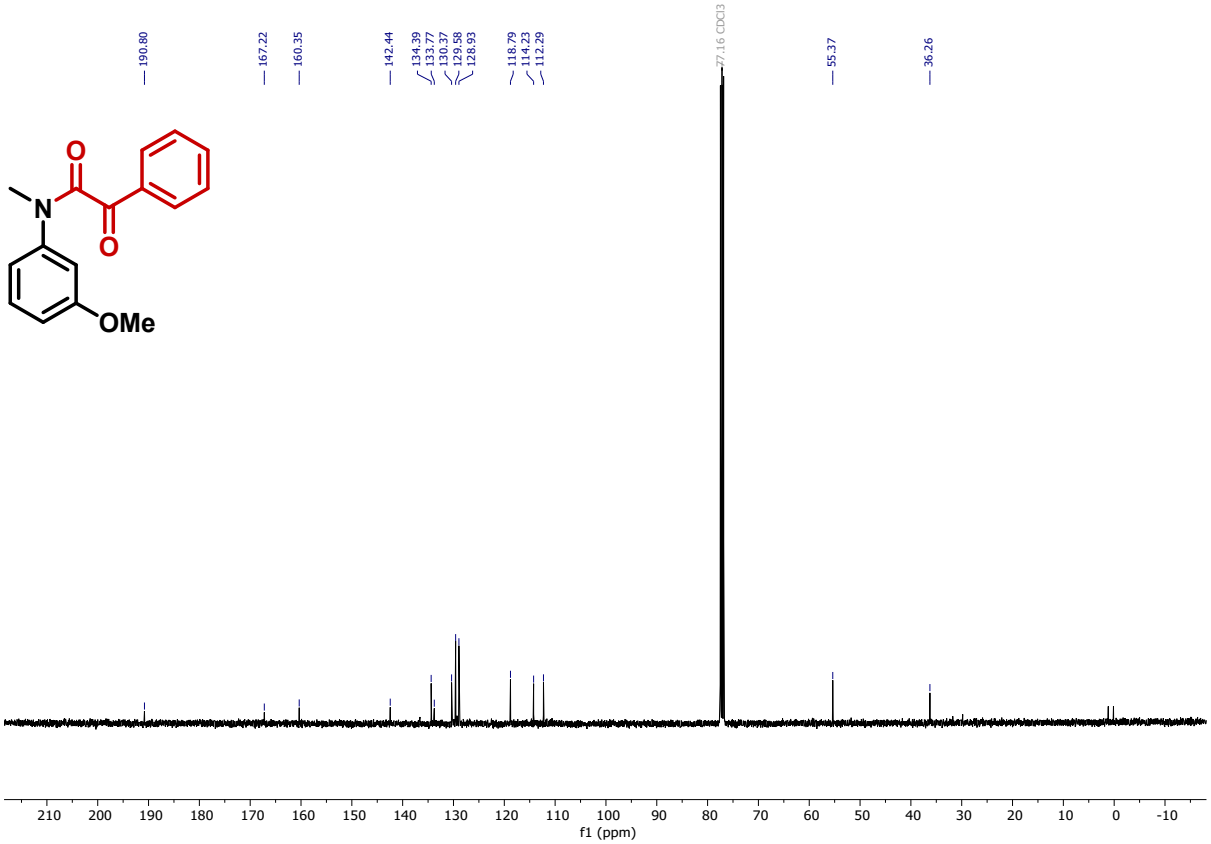


Fig S22. ^{13}C NMR spectrum (101 MHz) of **5h** in $CDCl_3$ (77.16 ppm).

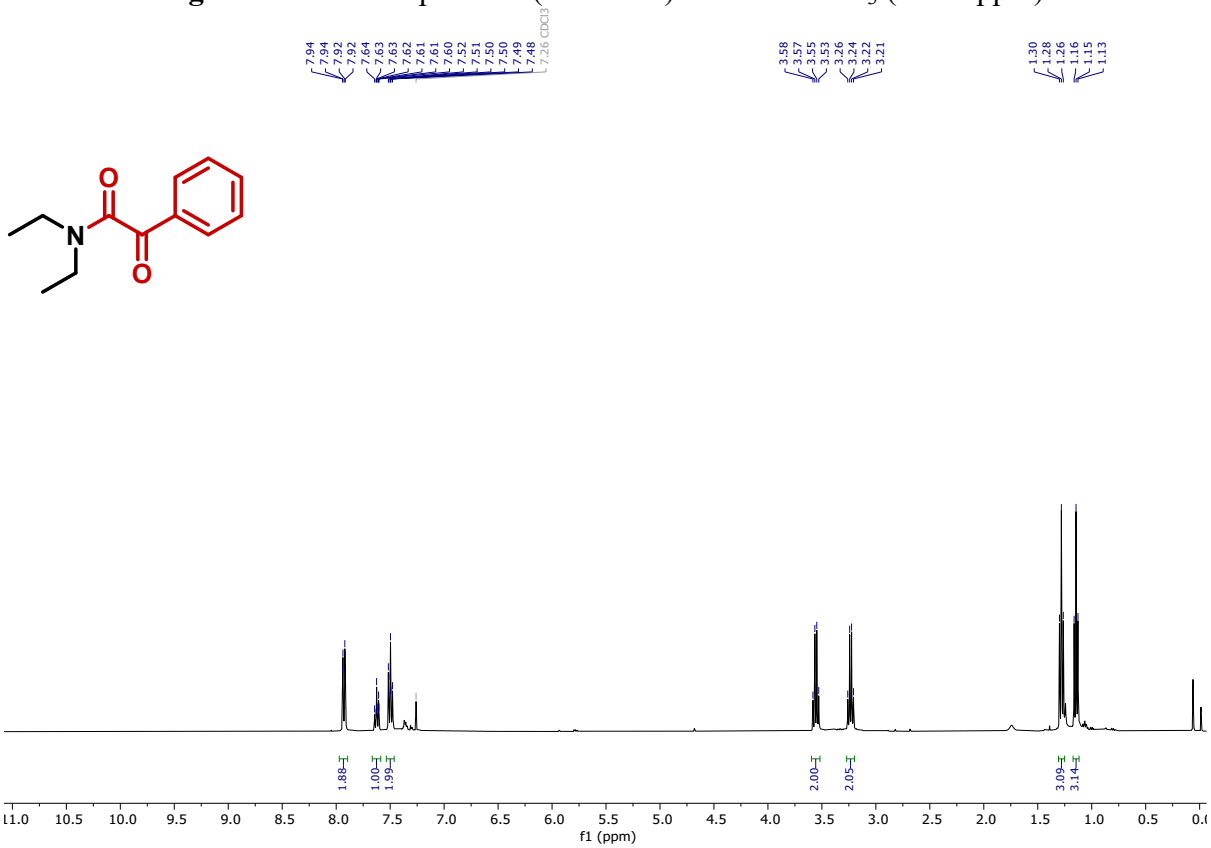


Fig S23. ^{1}H NMR spectrum (400 MHz) of **5i** in $CDCl_3$ (7.26 ppm).

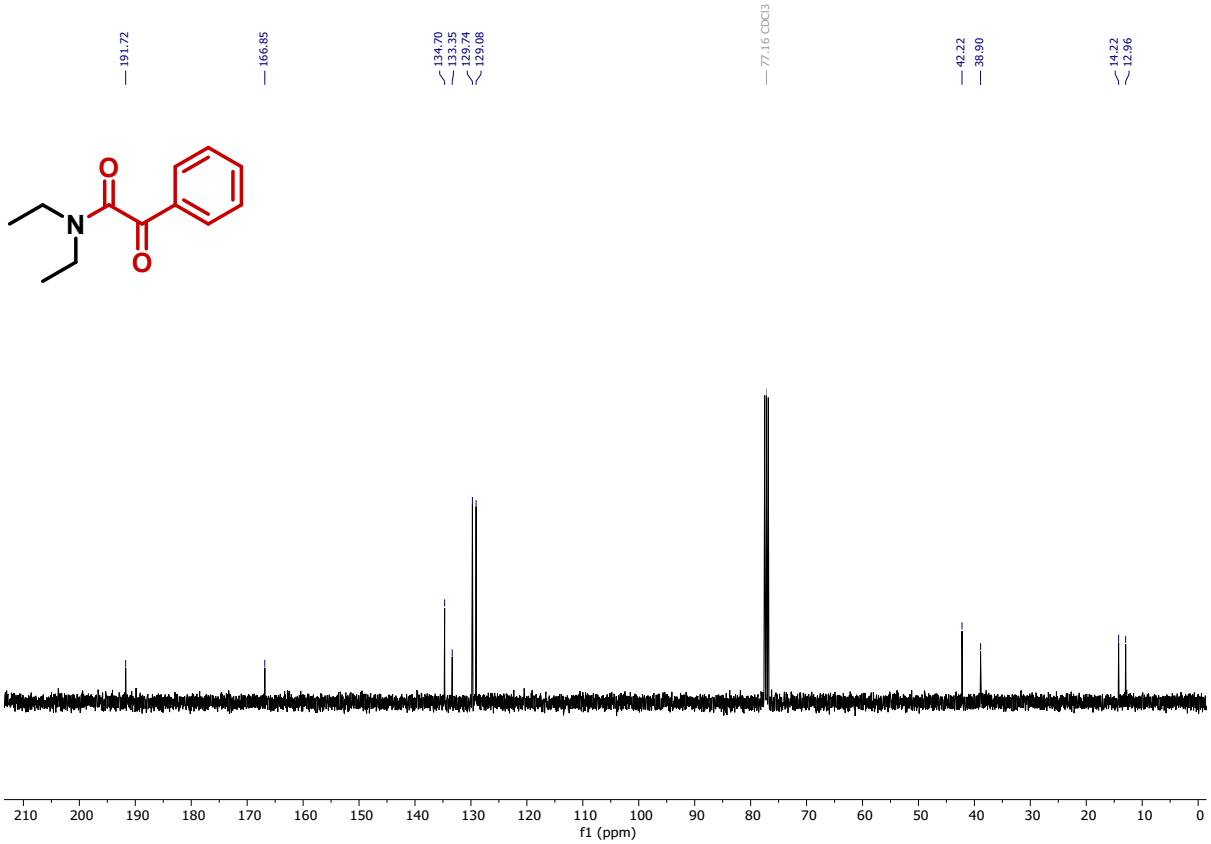


Fig S24. ^{13}C NMR spectrum (101 MHz) of **5i** in $CDCl_3$ (77.16 ppm).

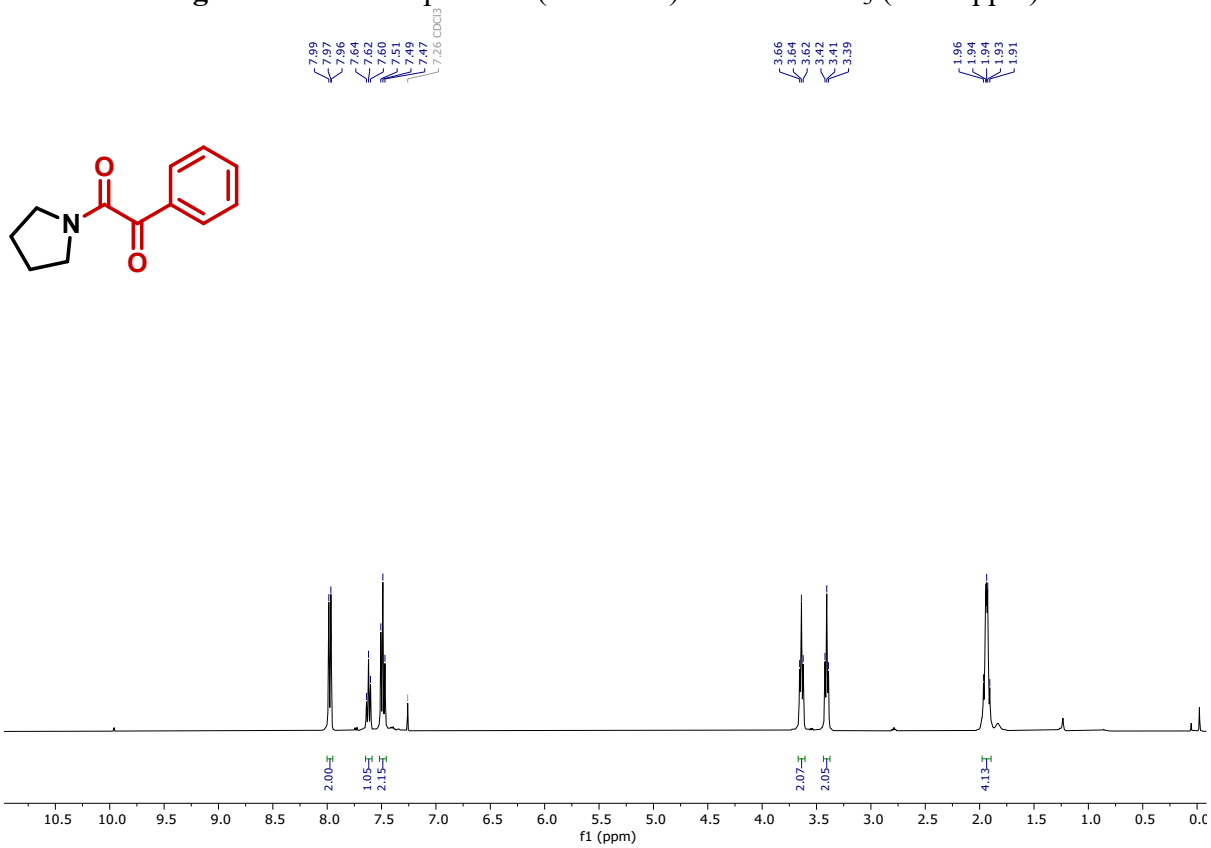


Fig S25. ^{1}H NMR spectrum (400 MHz) of **5j** in $CDCl_3$ (7.26 ppm).

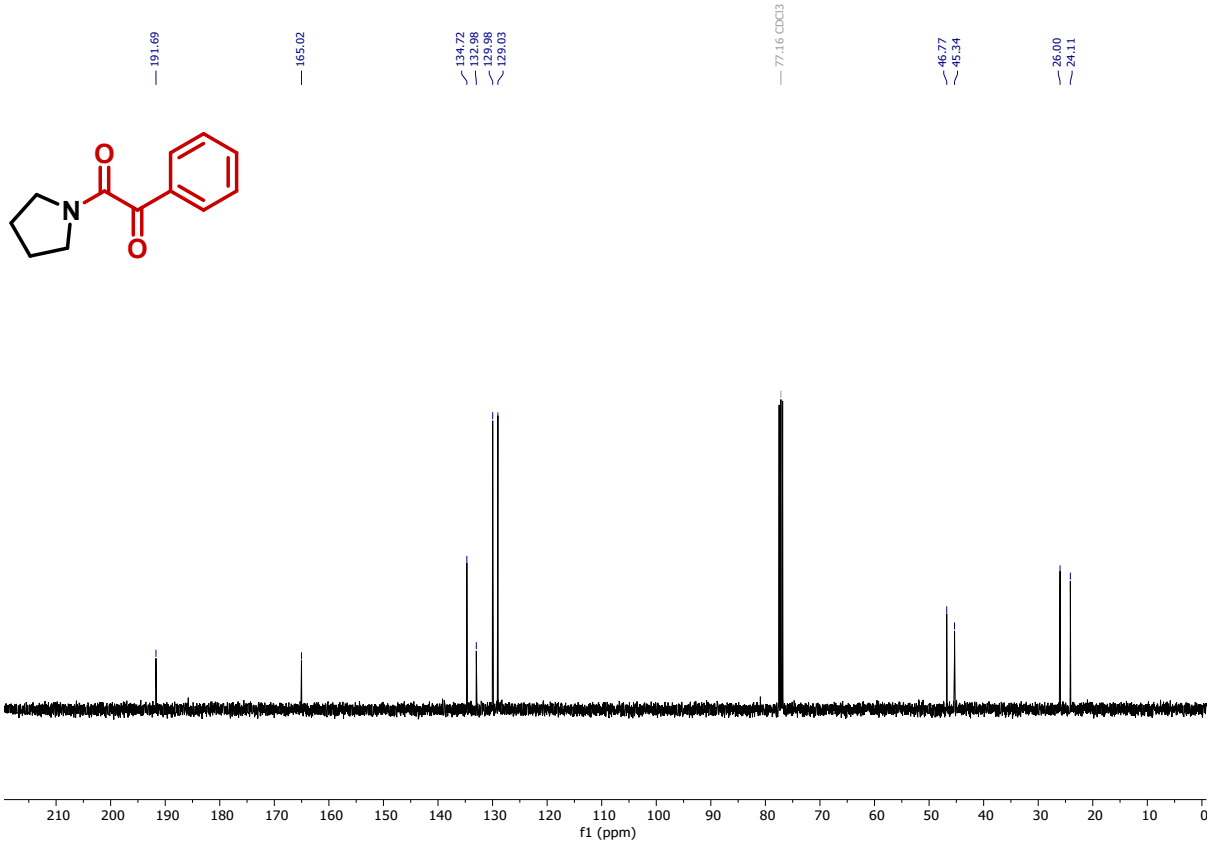


Fig S26. ^{13}C NMR spectrum (101 MHz) of **5j** in $CDCl_3$ (77.16 ppm).

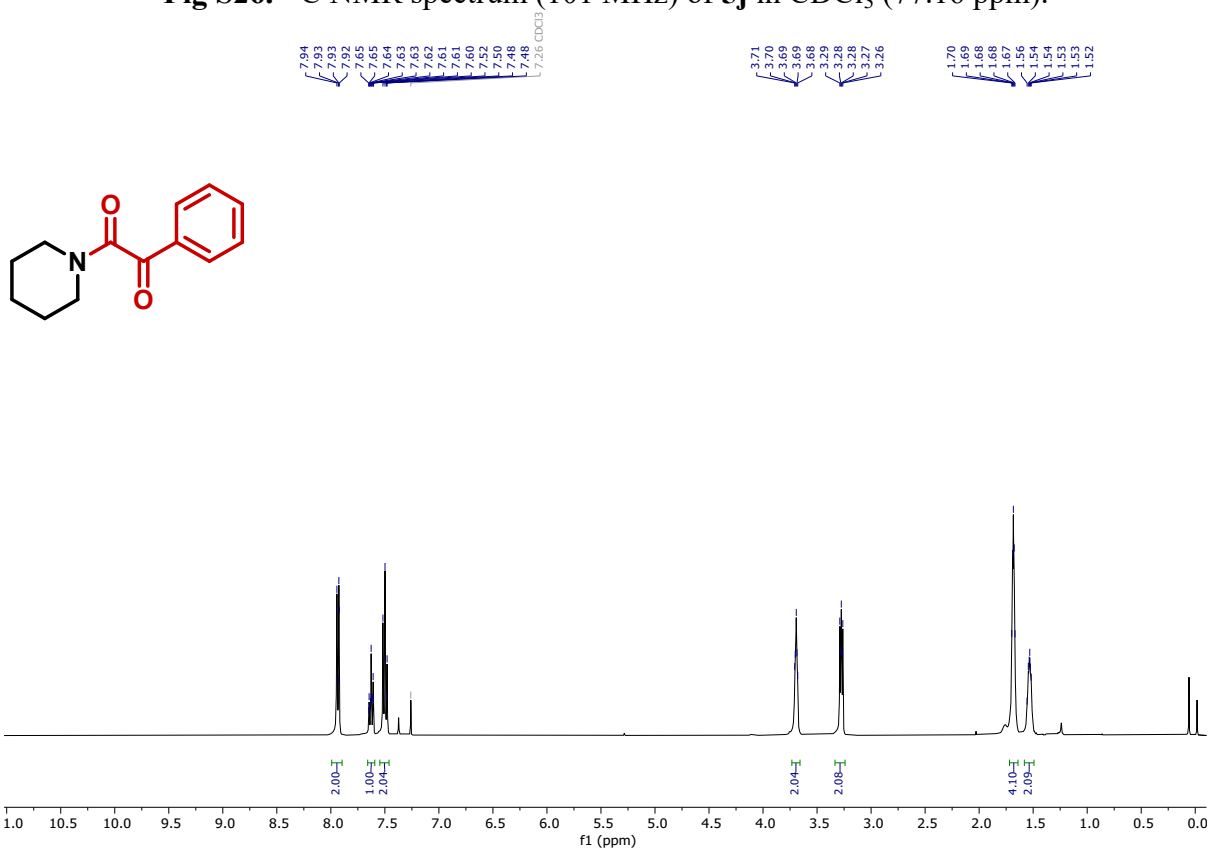


Fig S27. ^{1}H NMR spectrum (400 MHz) of **5k** in $CDCl_3$ (7.26 ppm).

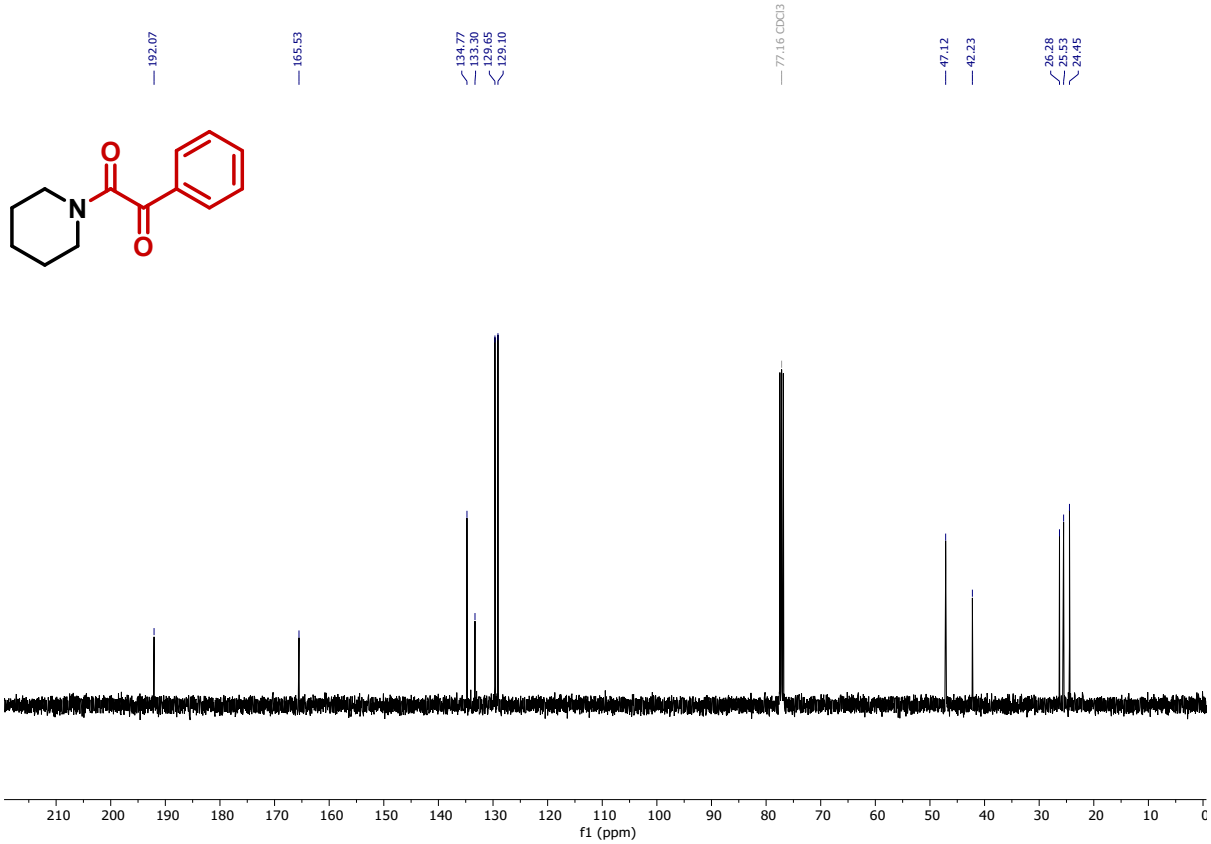


Fig S28. ^{13}C NMR spectrum (101 MHz) of **5k** in $CDCl_3$ (77.16 ppm).

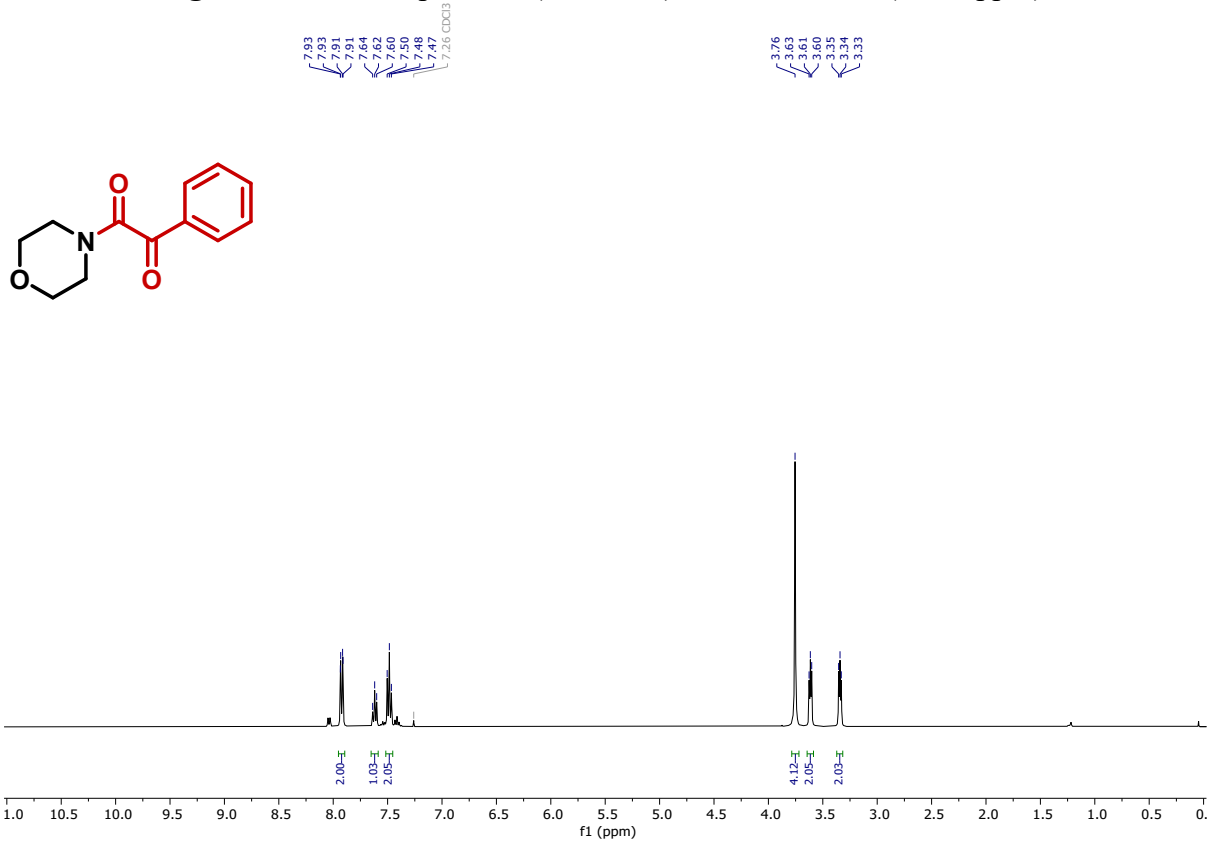


Fig S29. ^{1}H NMR spectrum (400 MHz) of **5l** in $CDCl_3$ (7.26 ppm).

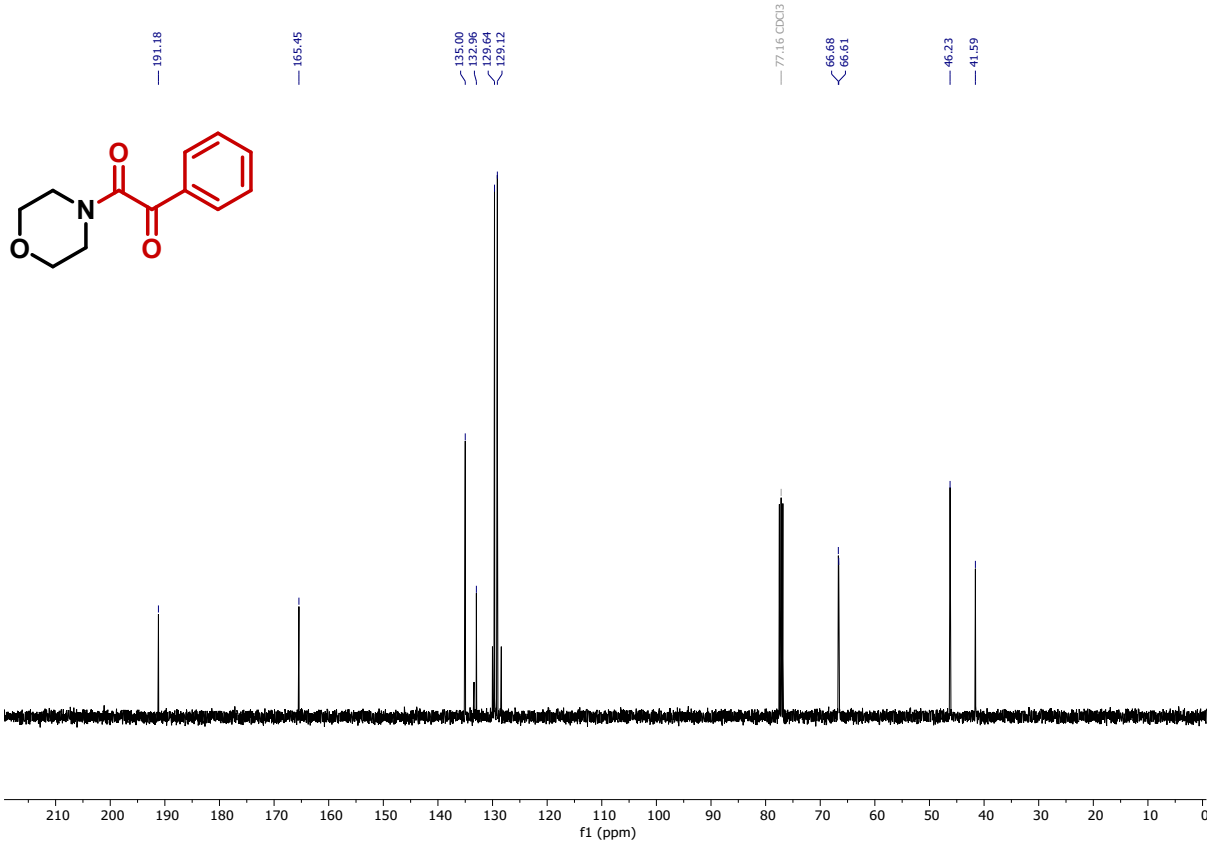


Fig S30. ^{13}C NMR spectrum (101 MHz) of **5l** in $CDCl_3$ (77.16 ppm).

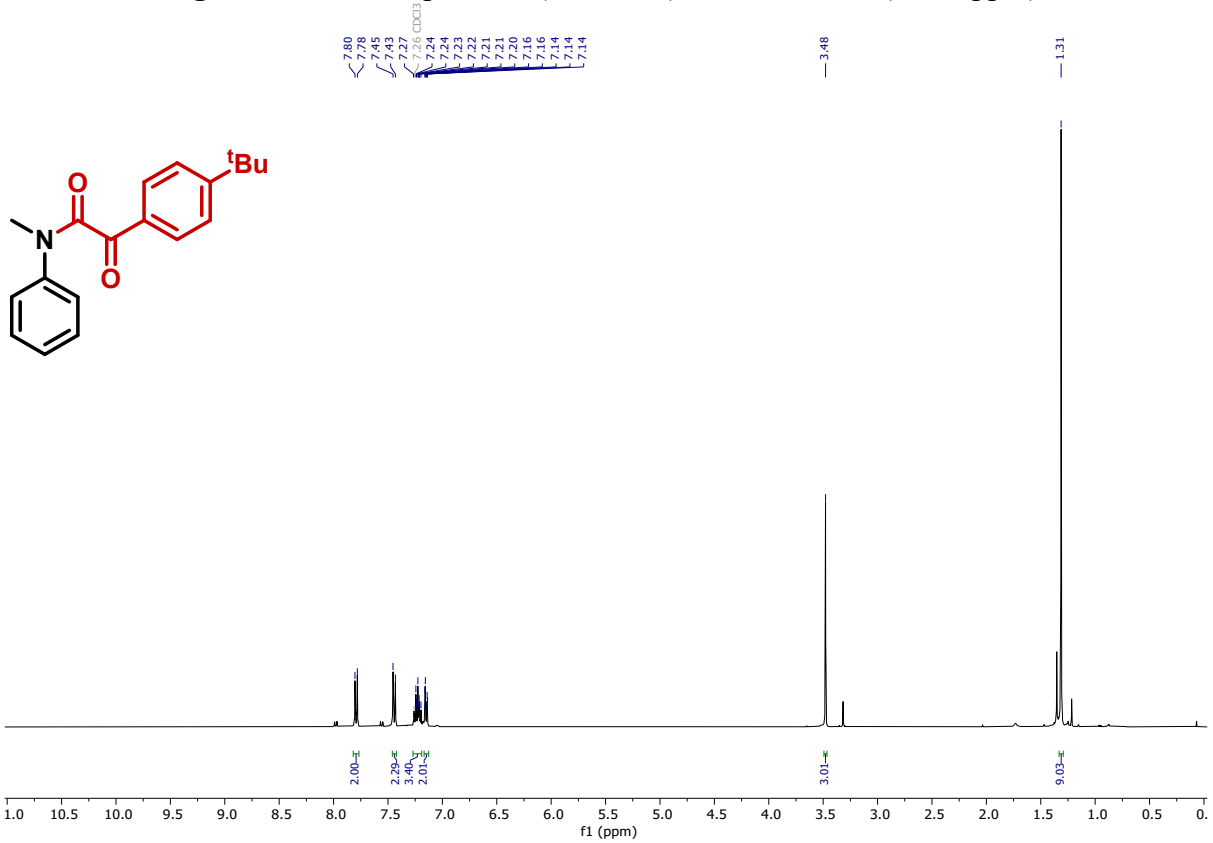


Fig S31. ^{1}H NMR spectrum (400 MHz) of **6a** in $CDCl_3$ (7.26 ppm).

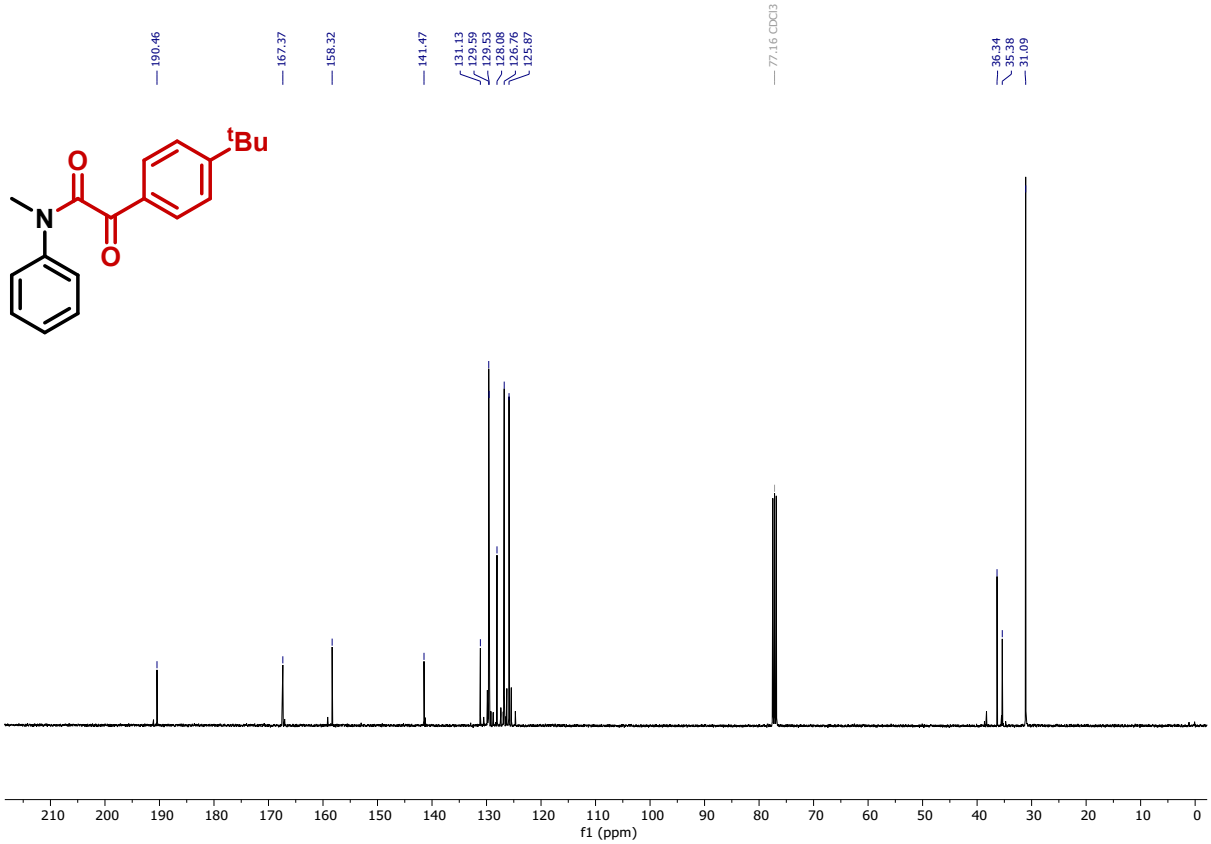


Fig S32. ^{13}C NMR spectrum (101 MHz) of **6a** in $CDCl_3$ (77.16 ppm).

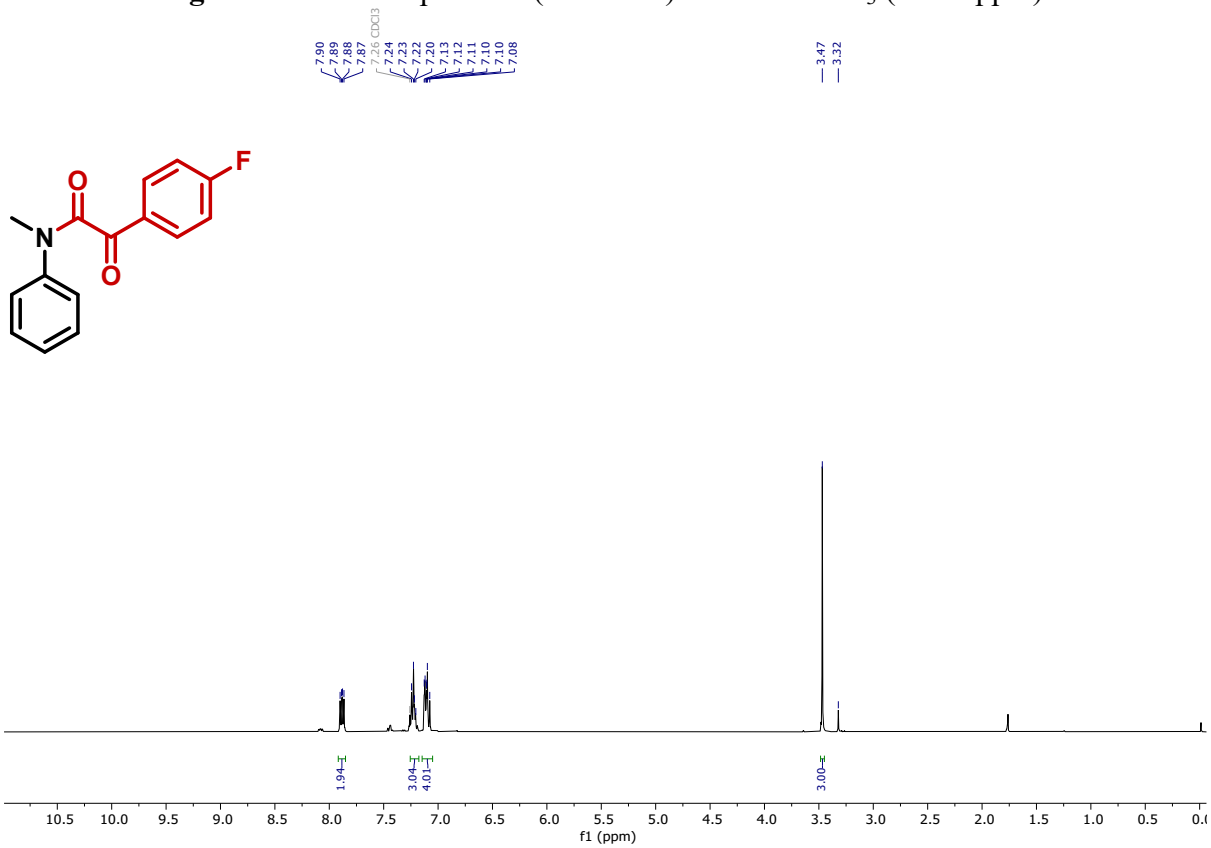


Fig S33. ^{1}H NMR spectrum (400 MHz) of **6b** in $CDCl_3$ (7.26 ppm).

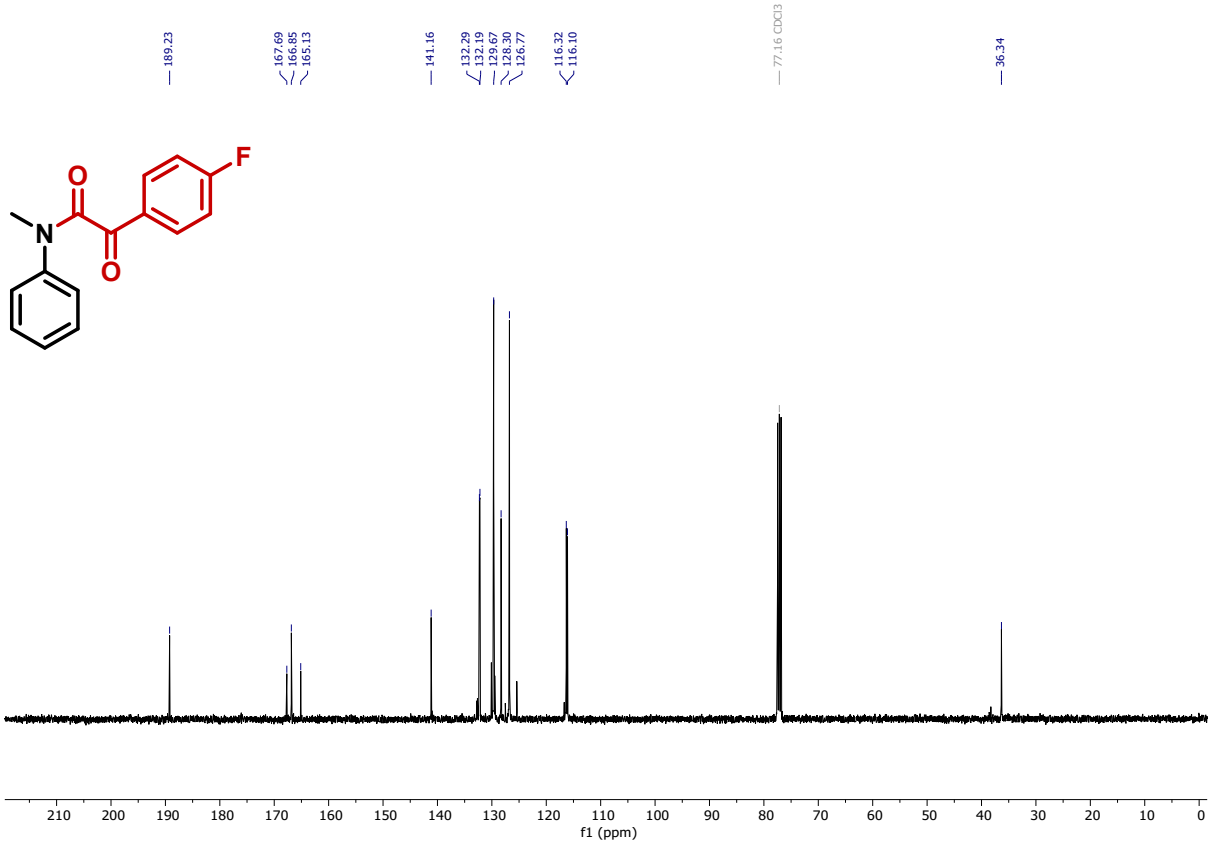


Fig S34. ^{13}C NMR spectrum (101 MHz) of **6b** in $CDCl_3$ (77.16 ppm).

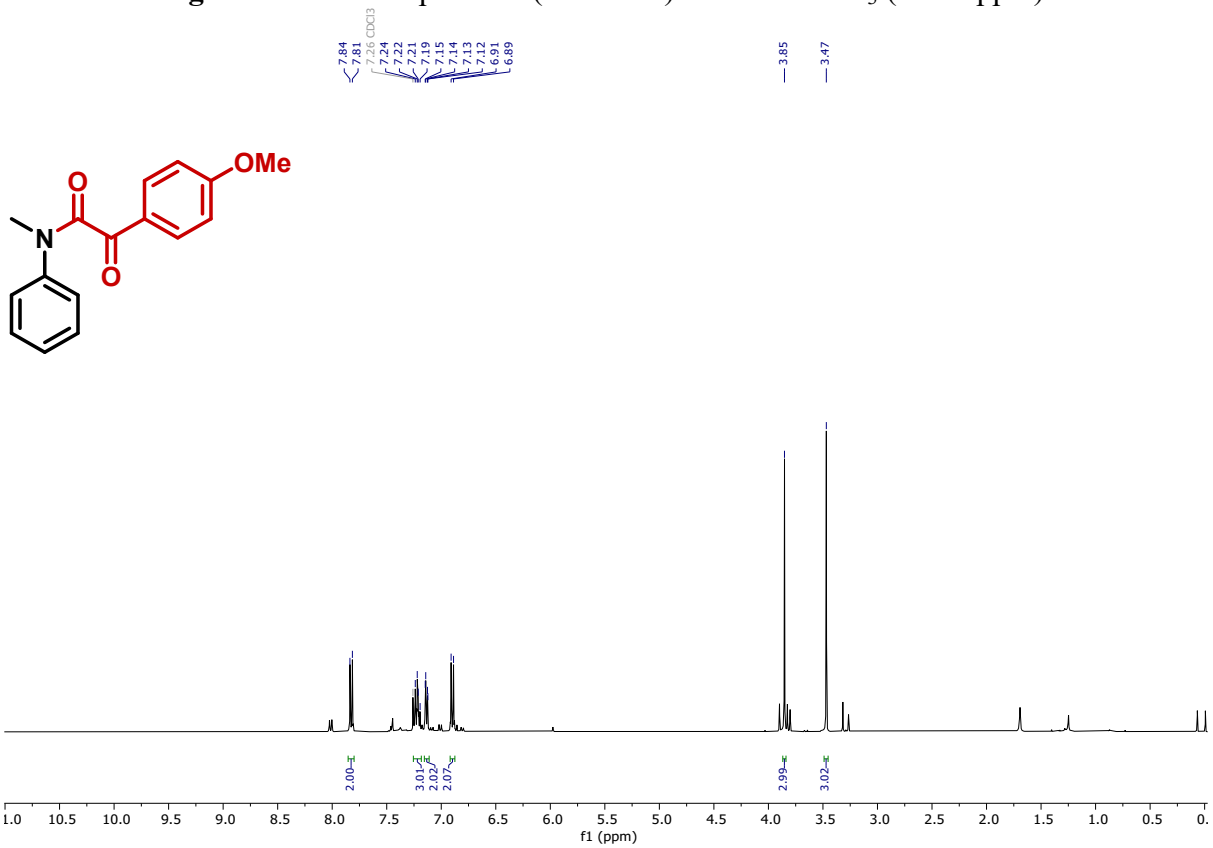


Fig S35. ^{1}H NMR spectrum (400 MHz) of **6c** in $CDCl_3$ (7.26 ppm).

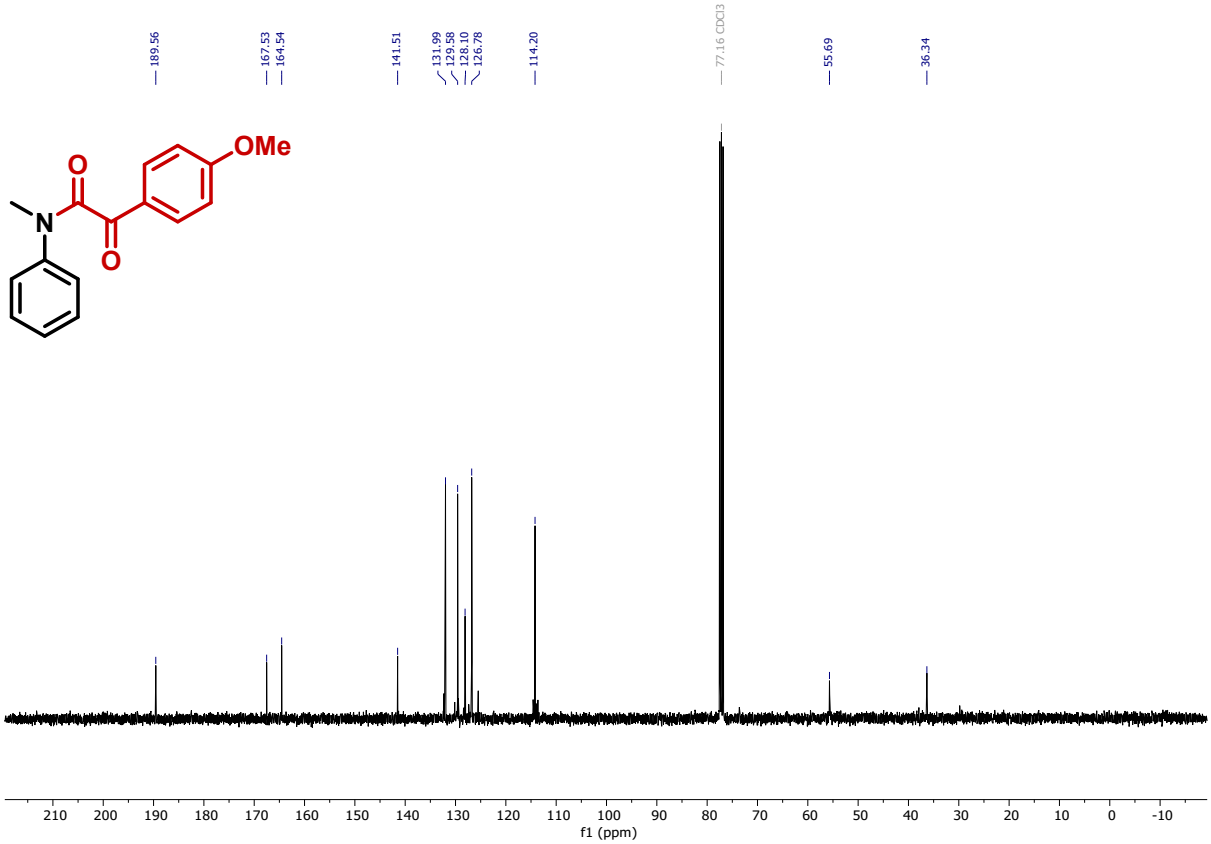


Fig S36. ^{13}C NMR spectrum (101 MHz) of **6c** in $CDCl_3$ (77.16 ppm).

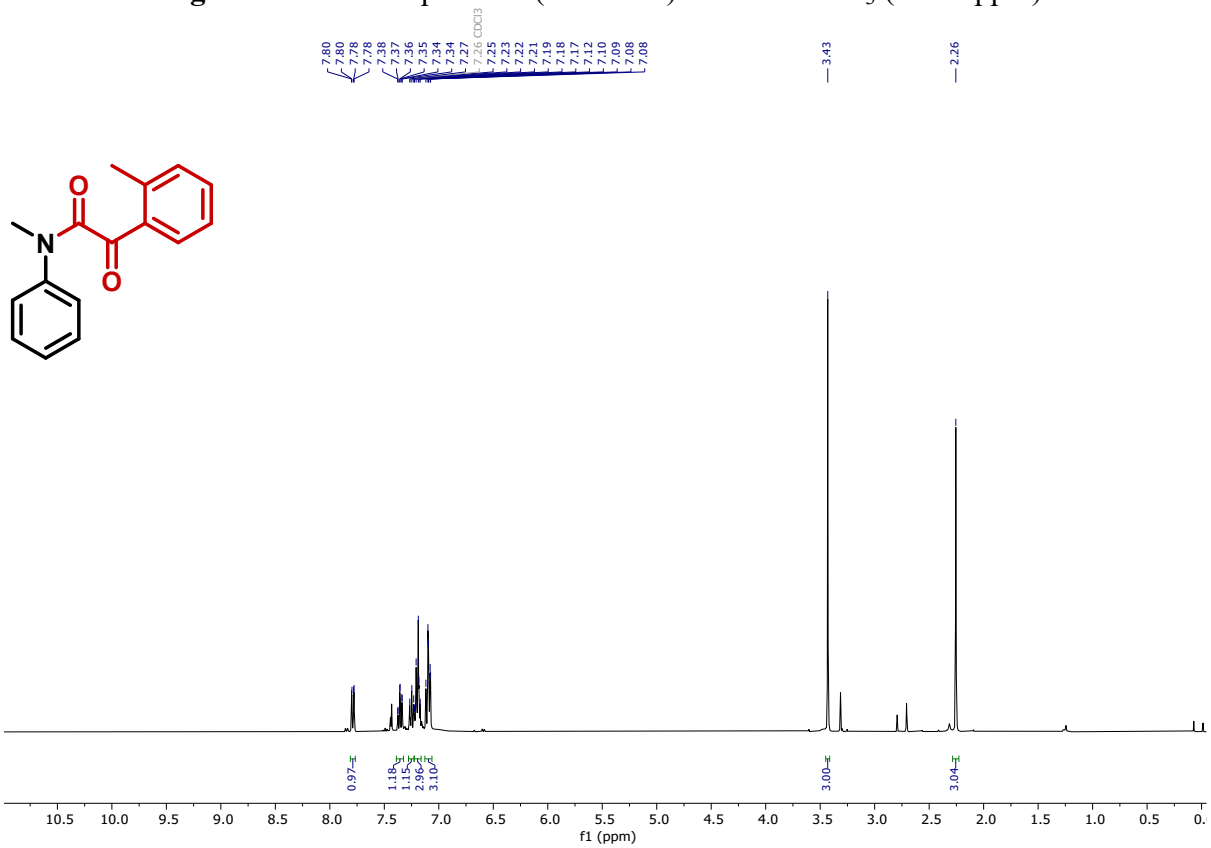


Fig S37. ^{1}H NMR spectrum (400 MHz) of **6d** in $CDCl_3$ (7.26 ppm).

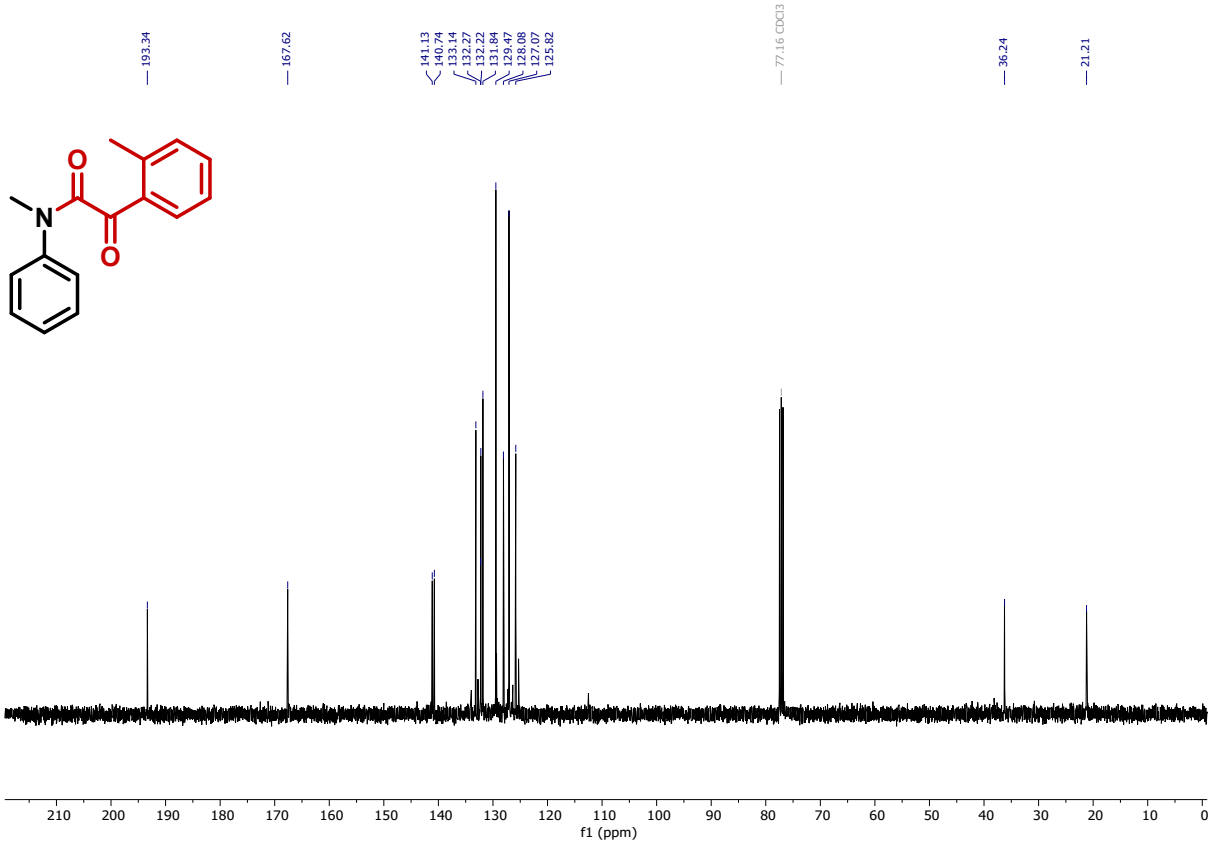


Fig S38. ^{13}C NMR spectrum (101 MHz) of **6d** in $CDCl_3$ (77.16 ppm).

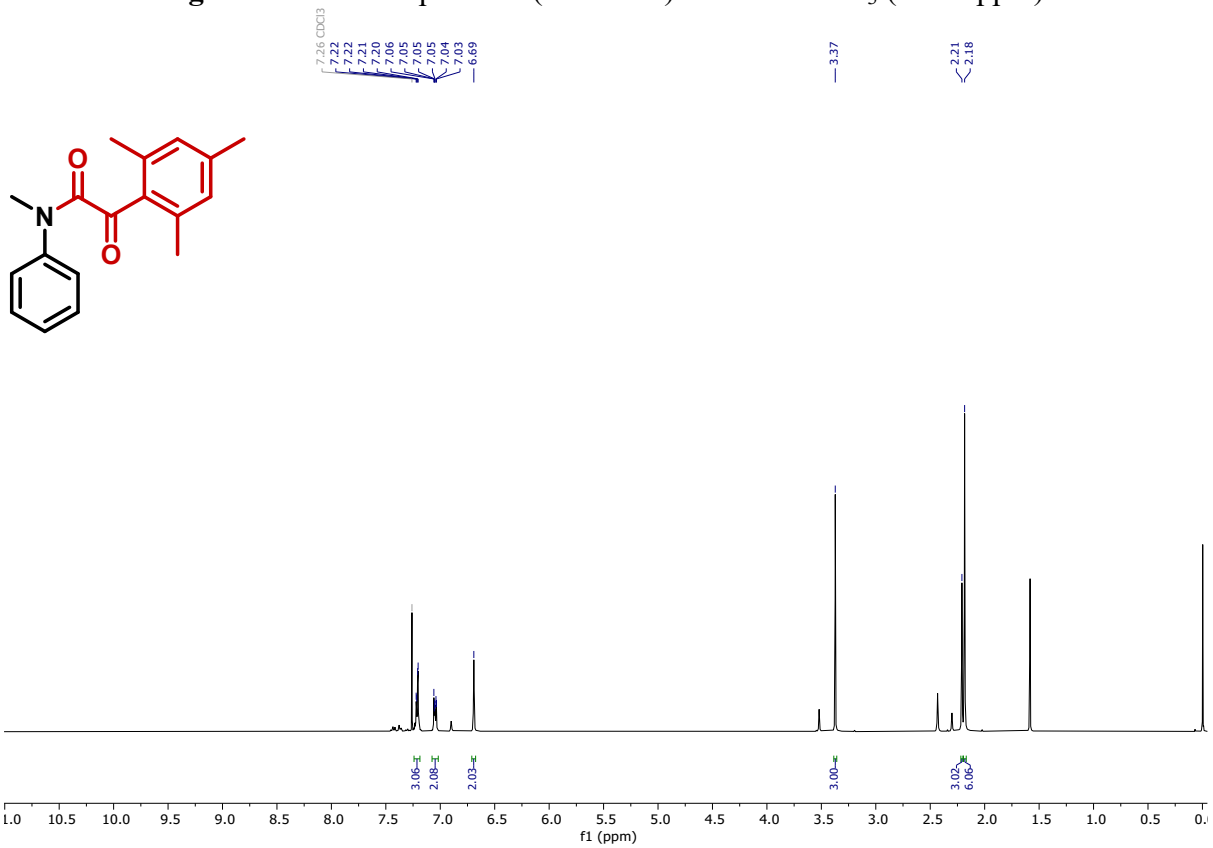


Fig S39. ^{1}H NMR spectrum (400 MHz) of **6e** in $CDCl_3$ (7.26 ppm).

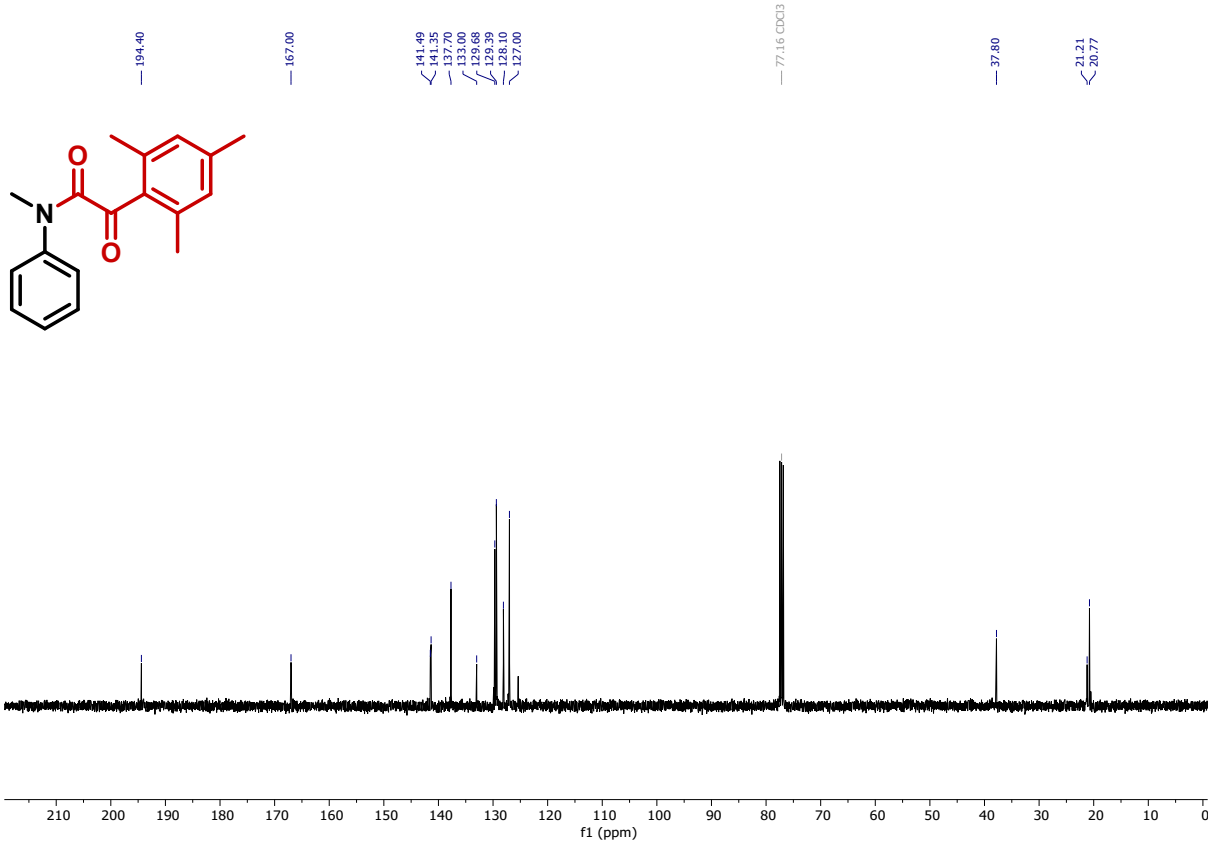


Fig S40. ^{13}C NMR spectrum (101 MHz) of **6e** in $CDCl_3$ (77.16 ppm).

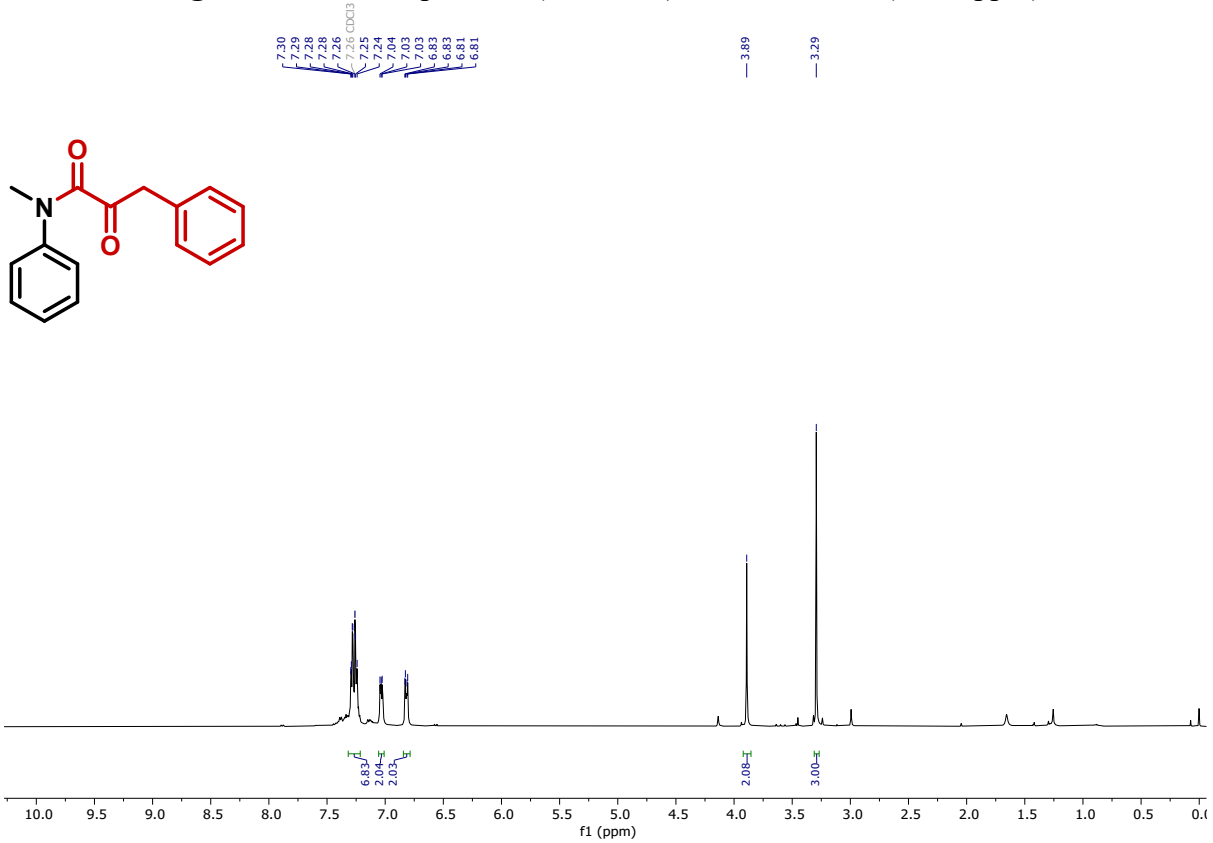


Fig S41. ^{1}H NMR spectrum (400 MHz) of **6f** in $CDCl_3$ (7.26 ppm).

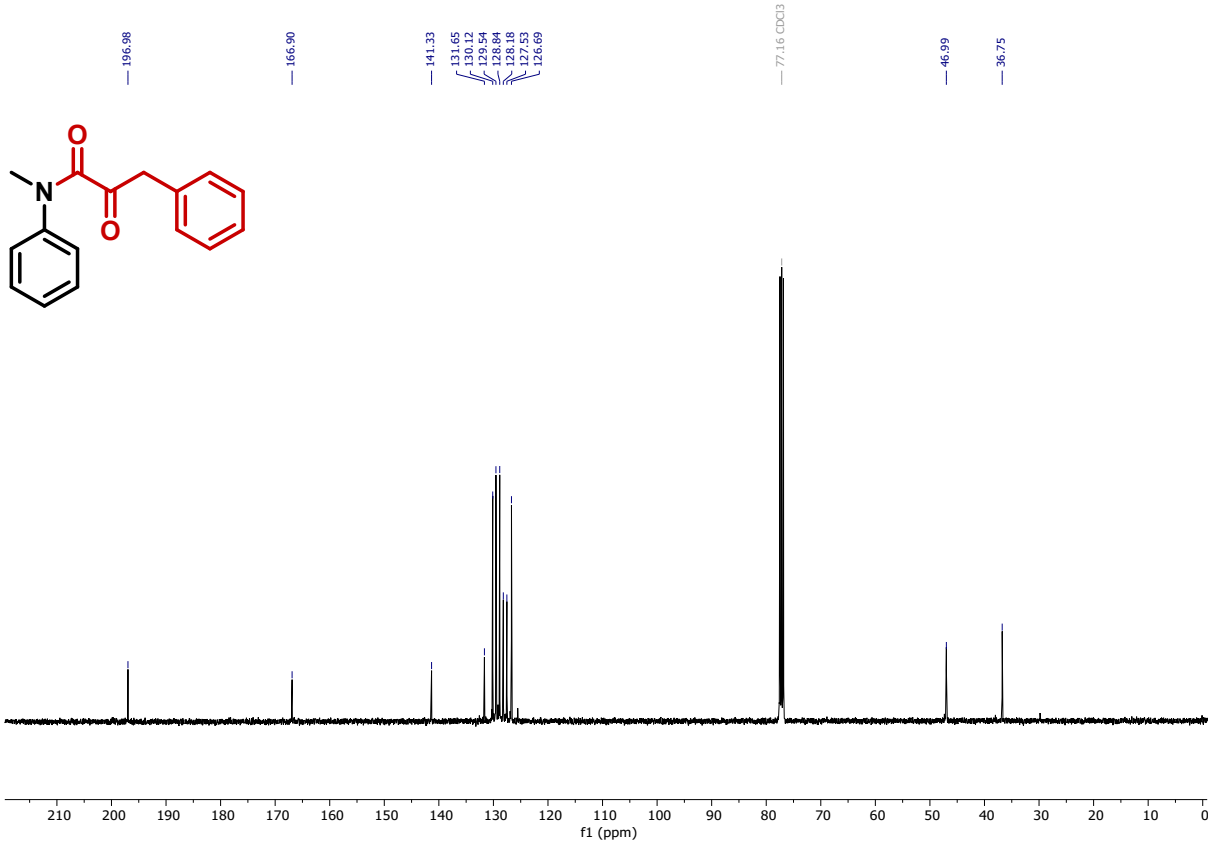


Fig S42. ^{13}C NMR spectrum (101 MHz) of **6f** in $CDCl_3$ (77.16 ppm).

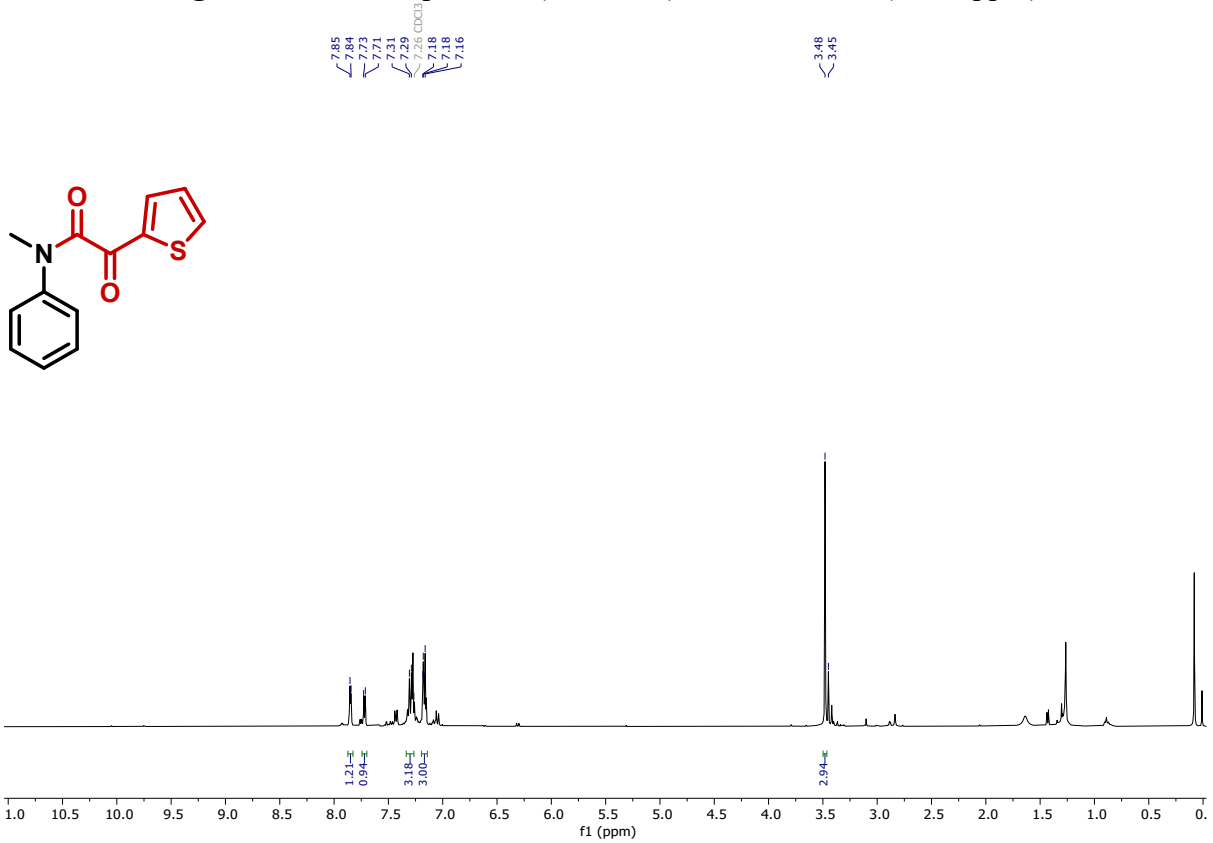


Fig S43. ^{1}H NMR spectrum (400 MHz) of **6g** in $CDCl_3$ (7.26 ppm).

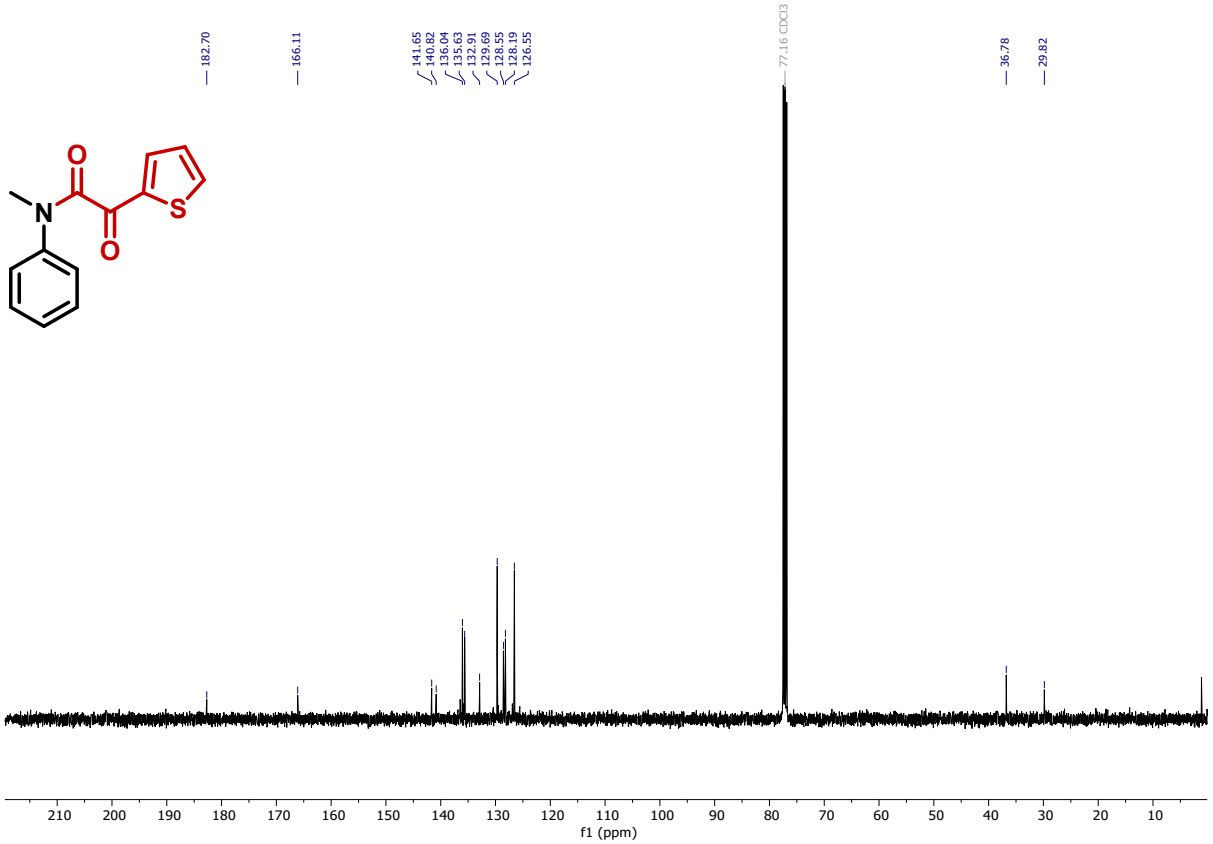


Fig S44. ^{13}C NMR spectrum (101 MHz) of **6g** in $CDCl_3$ (77.16 ppm).

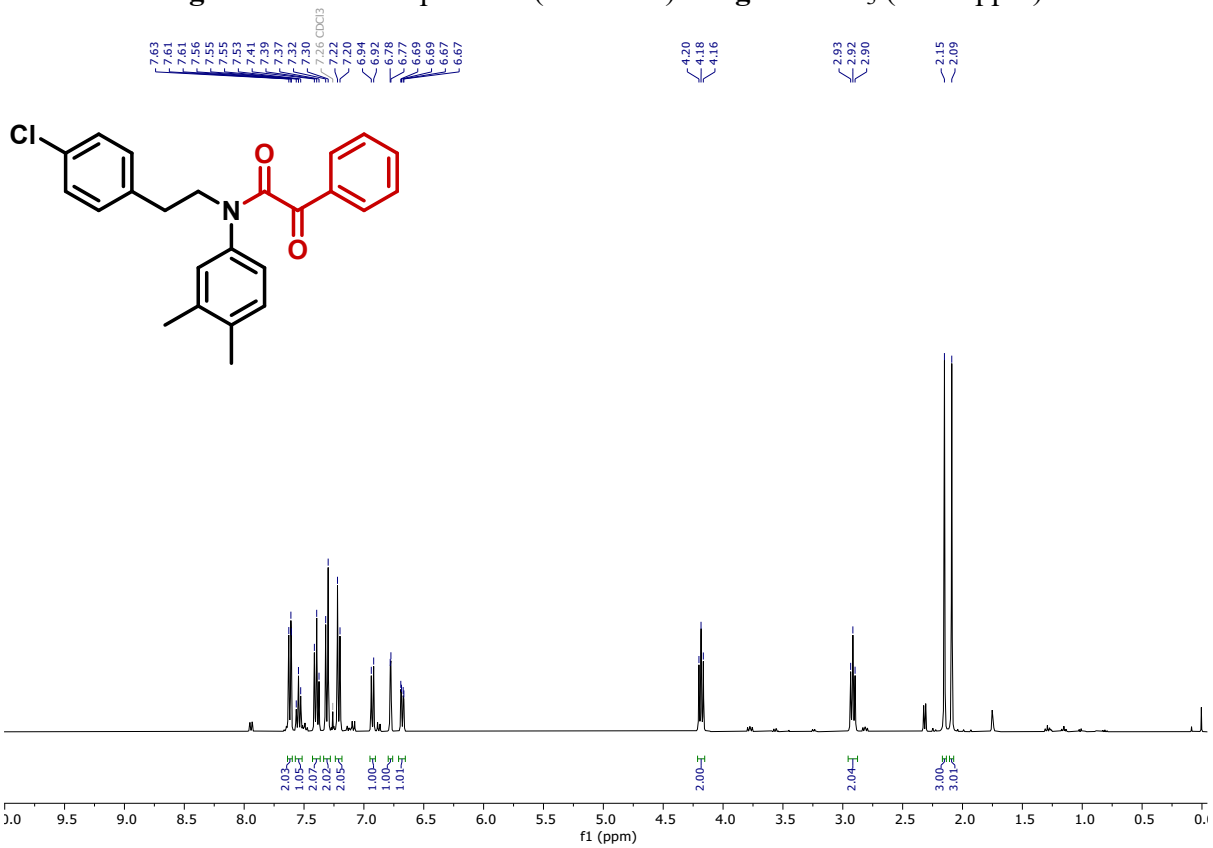


Fig S45. ^{1}H NMR spectrum (400 MHz) of **6h** in $CDCl_3$ (7.26 ppm).

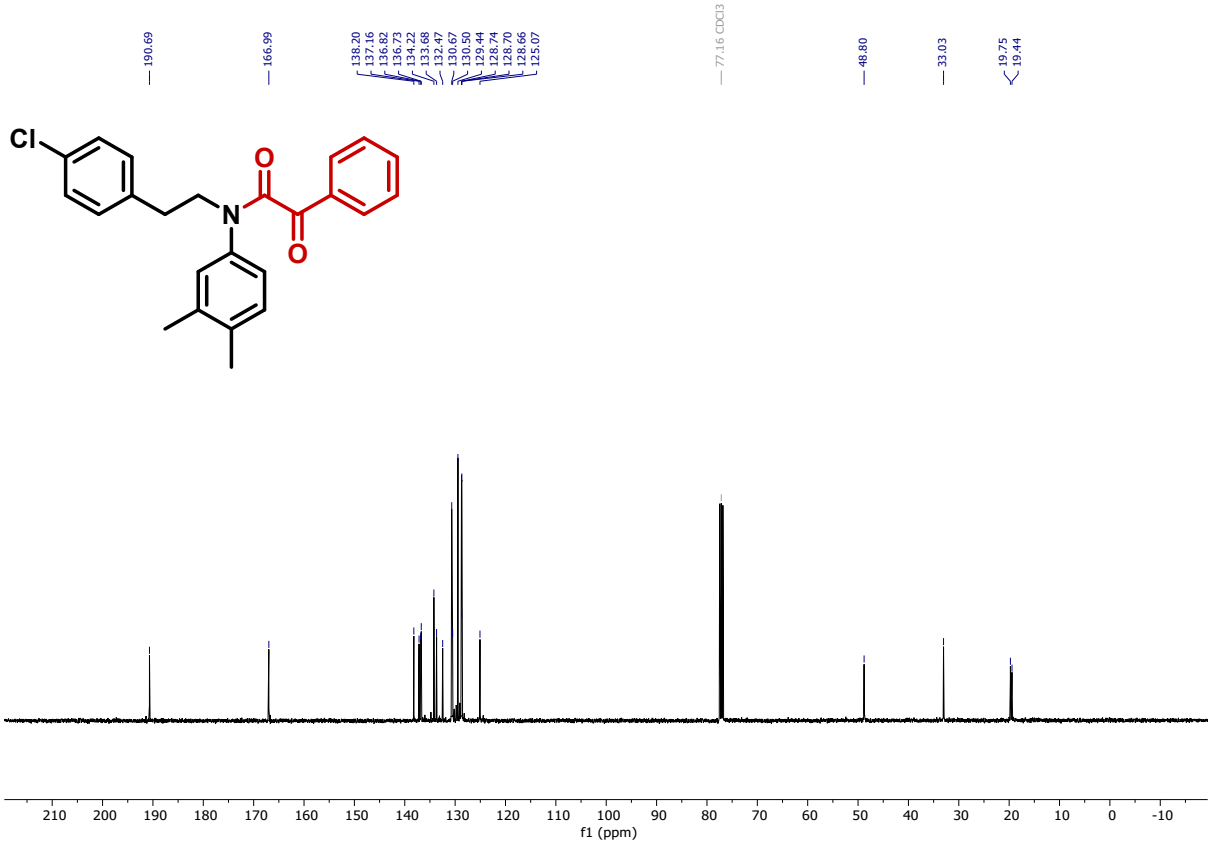


Fig S46. ^{13}C NMR spectrum (101 MHz) of **6h** in $CDCl_3$ (77.16 ppm).

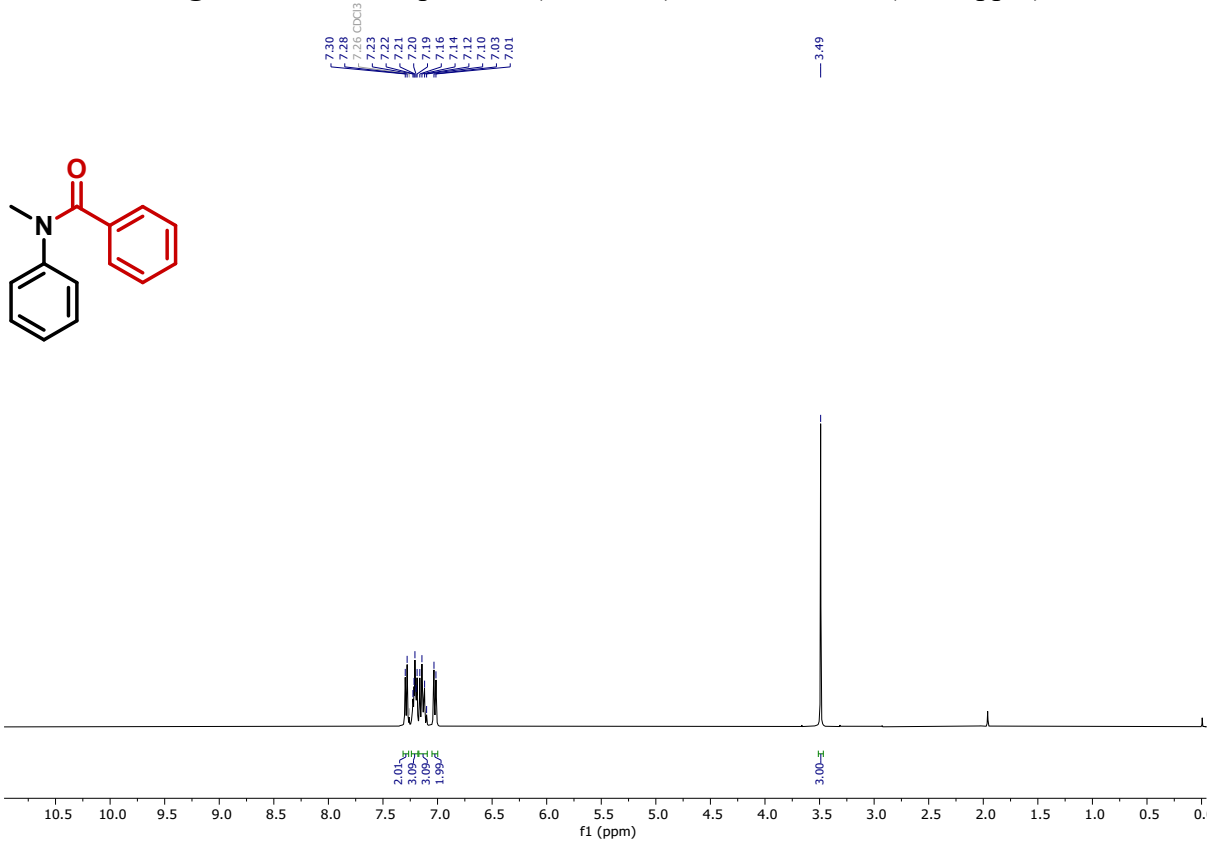


Fig S47. ^{1}H NMR spectrum (400 MHz) of **7a** in $CDCl_3$ (7.26 ppm).

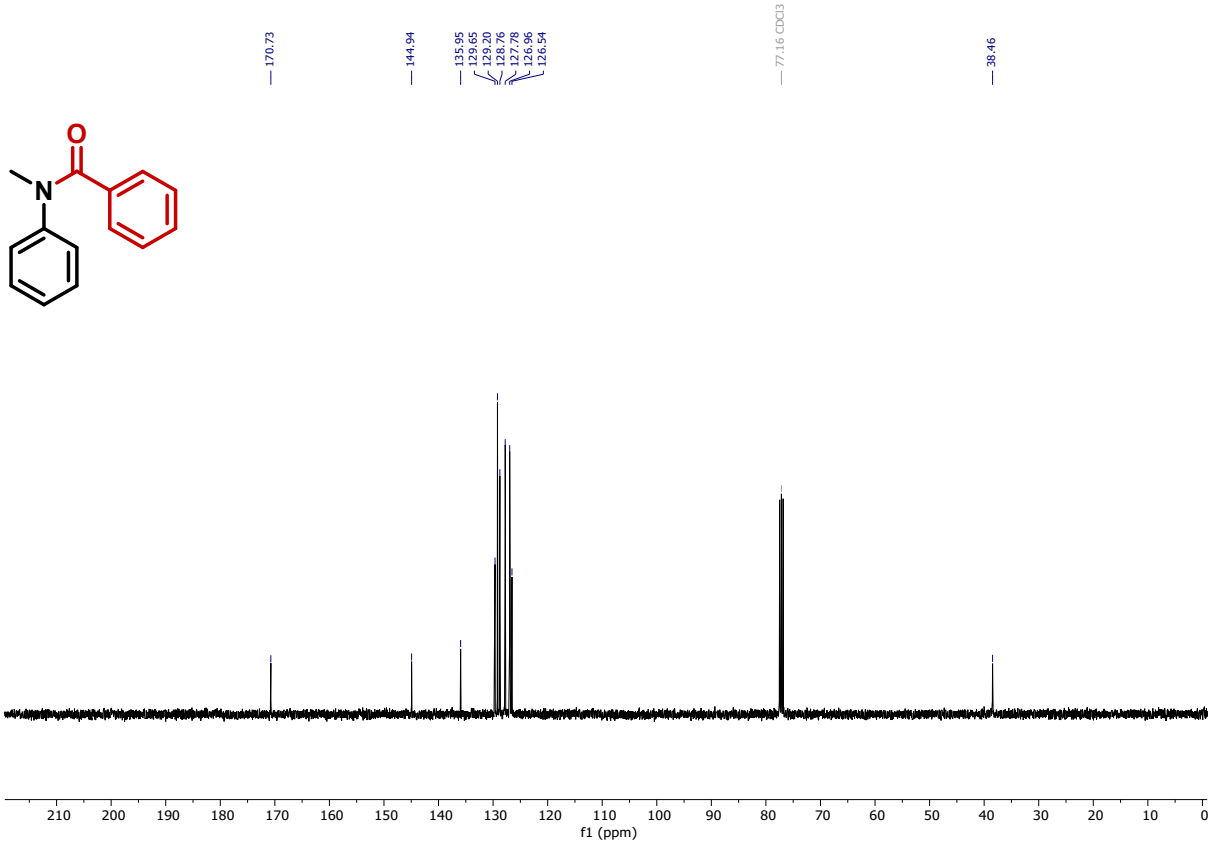


Fig S48. ^{13}C NMR spectrum (101 MHz) of **7a** in $CDCl_3$ (77.16 ppm).

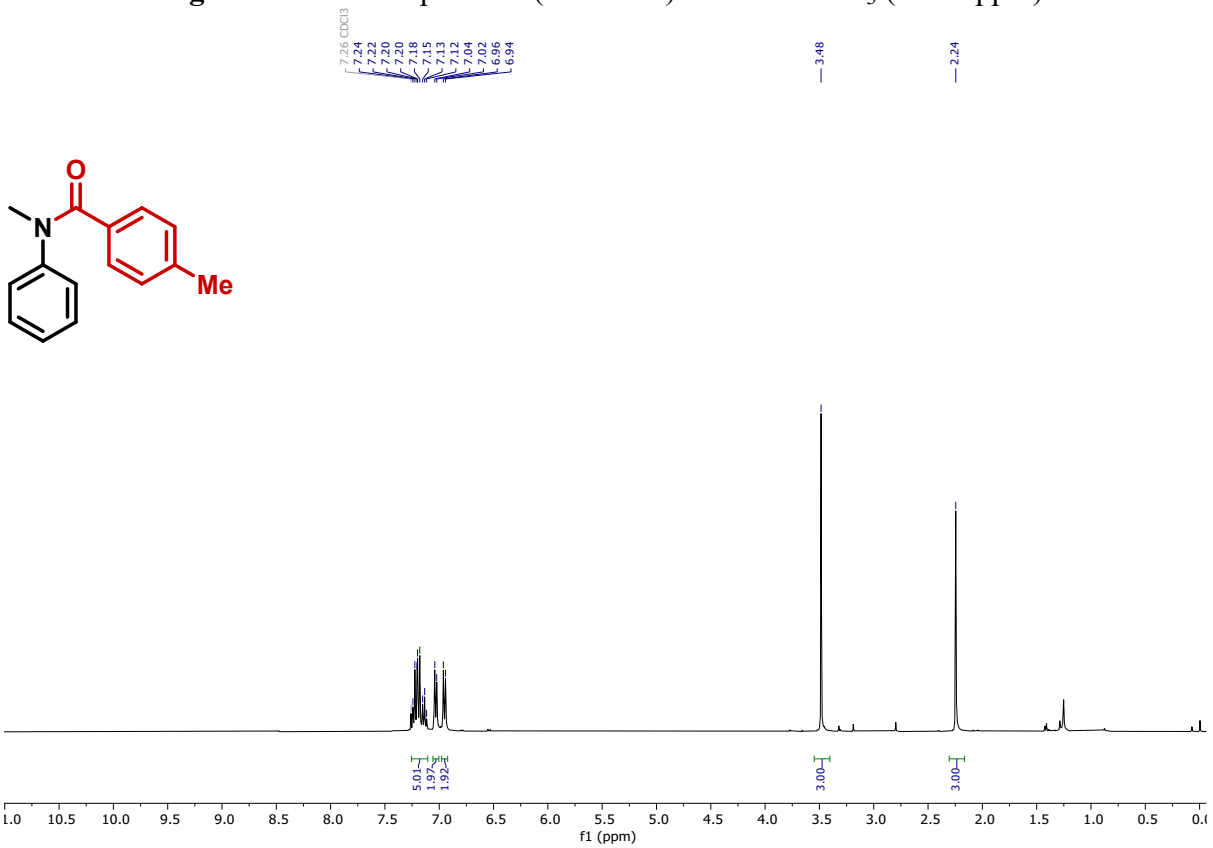


Fig S49. ^{1}H NMR spectrum (400 MHz) of **7b** in $CDCl_3$ (7.26 ppm).

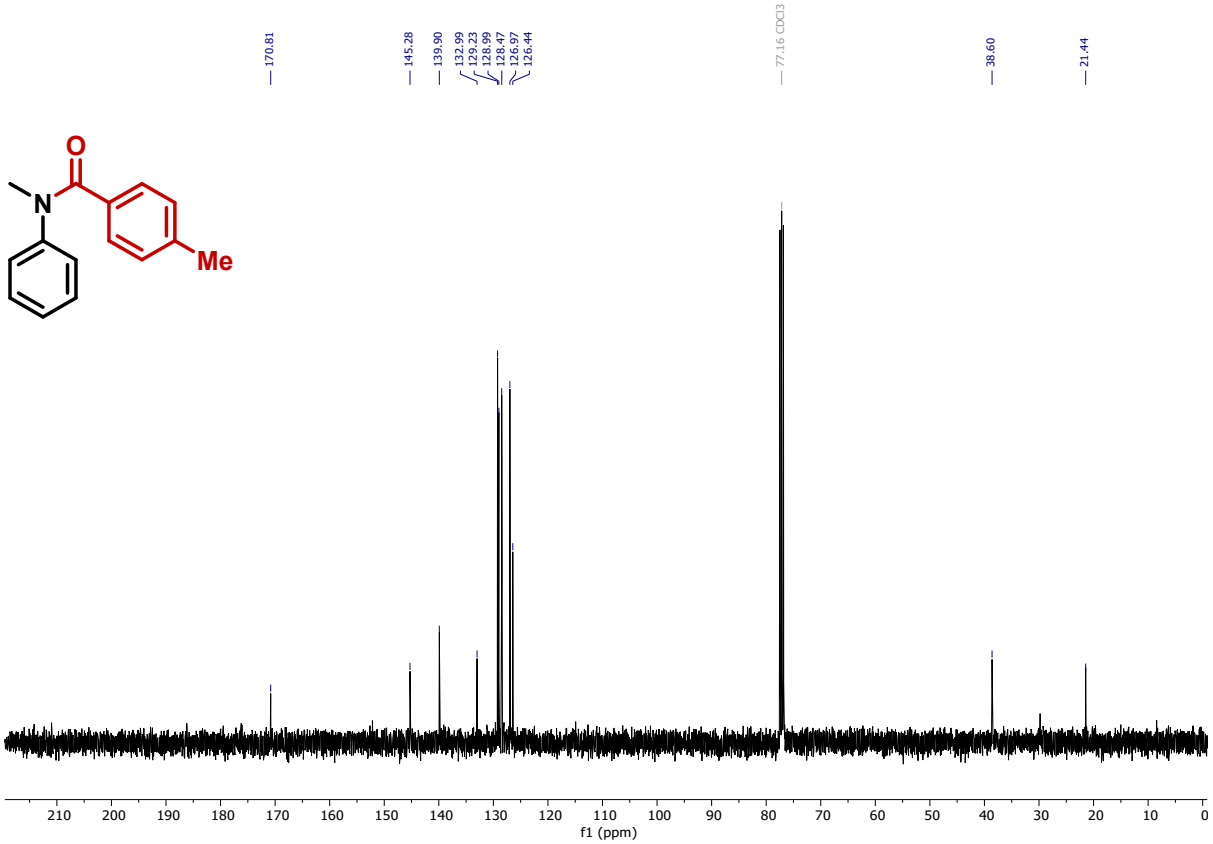


Fig S50. ^{13}C NMR spectrum (101 MHz) of **7b** in $CDCl_3$ (77.16 ppm).

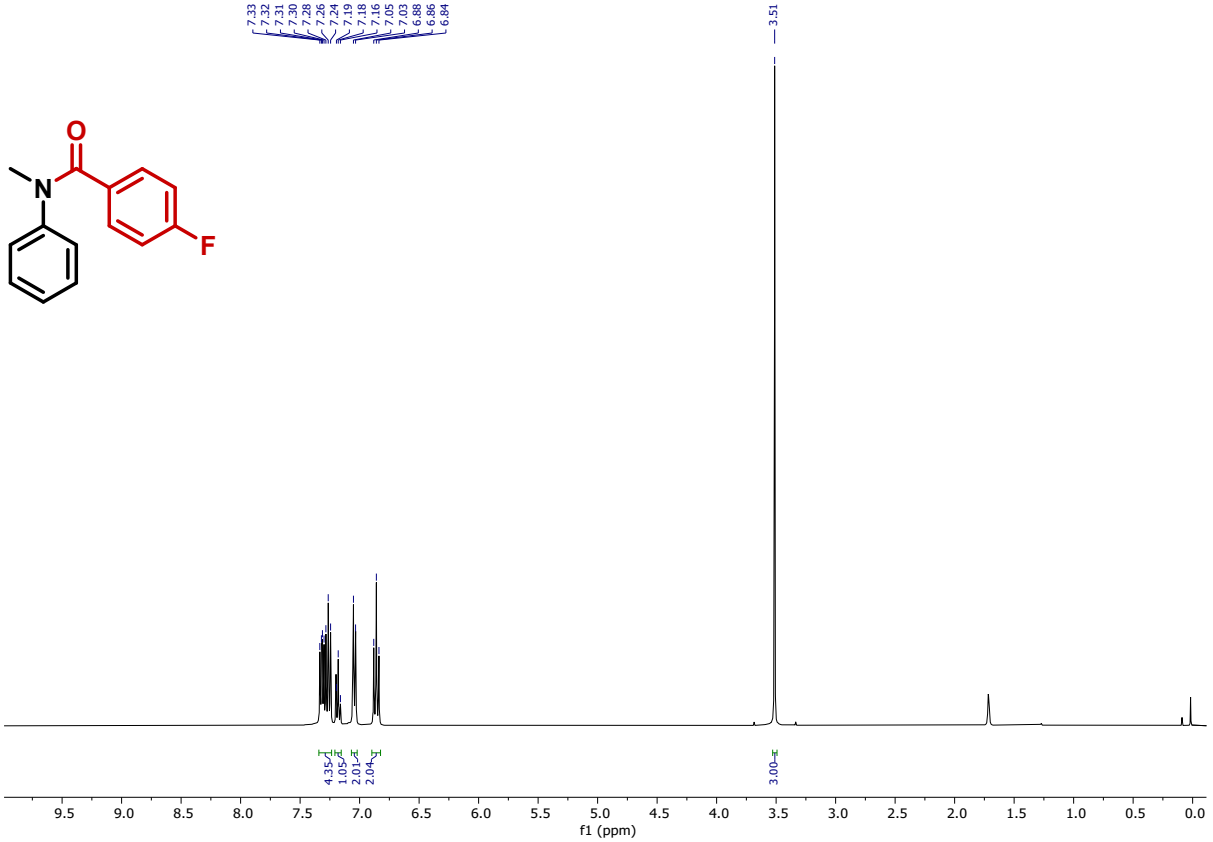


Fig S51. ^{1}H NMR spectrum (400 MHz) of **7c** in $CDCl_3$ (7.26 ppm).

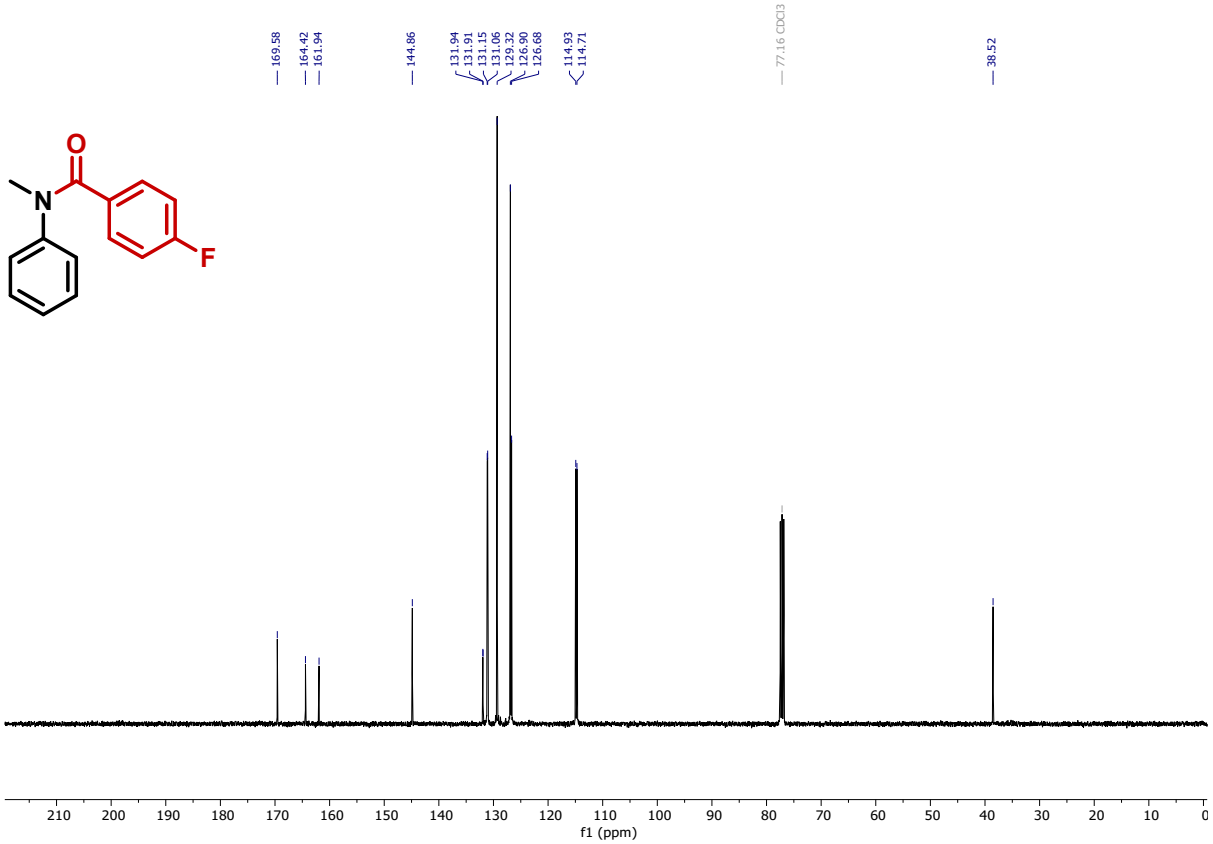


Fig S52. ^{13}C NMR spectrum (101 MHz) of **7c** in $CDCl_3$ (77.16 ppm).

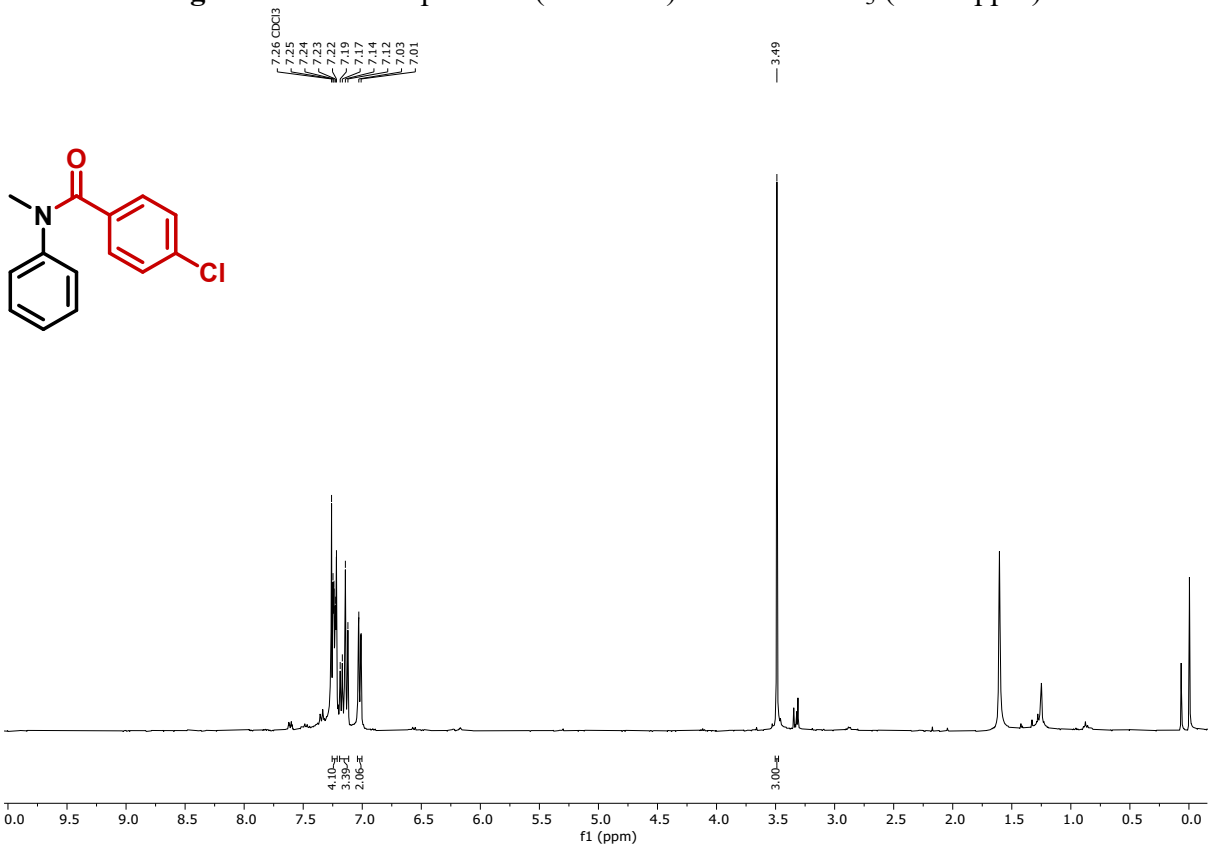


Fig S53. ^{1}H NMR spectrum (400 MHz) of **7d** in $CDCl_3$ (7.26 ppm).

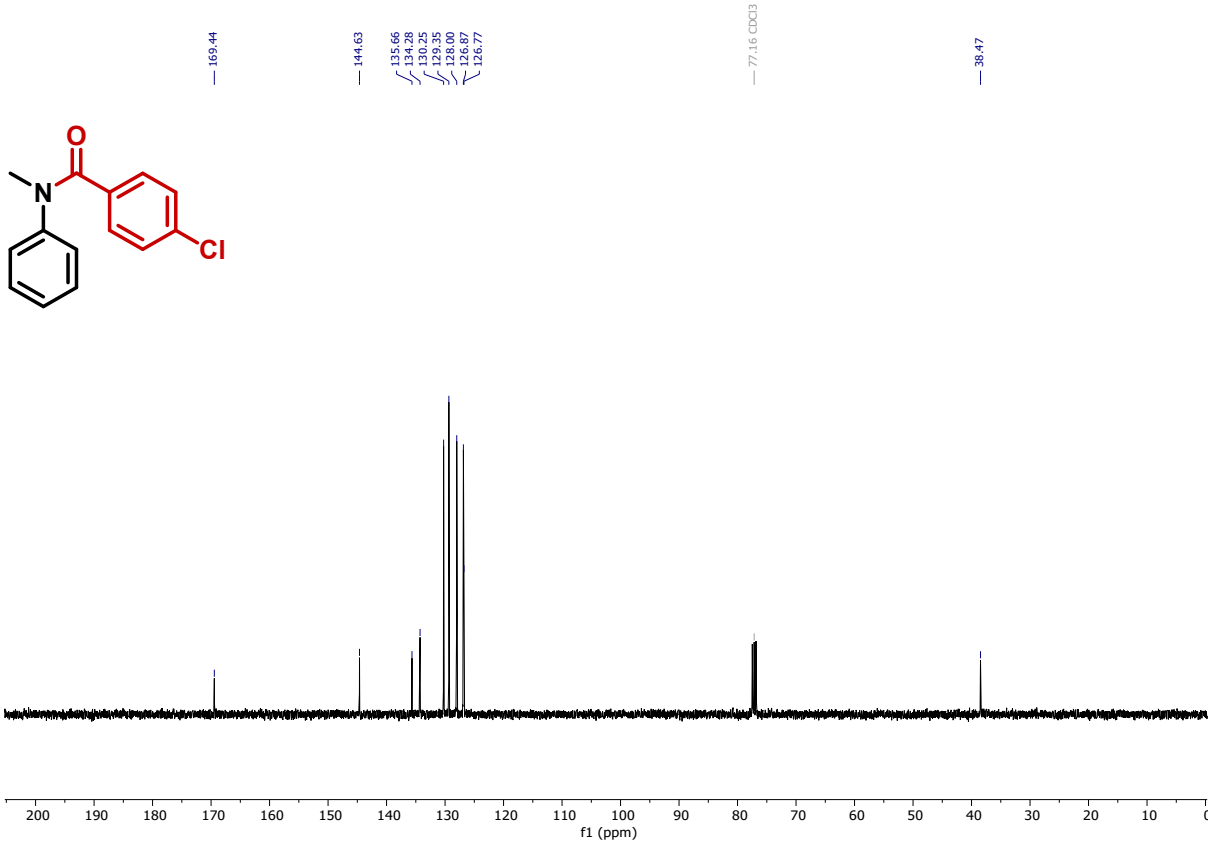


Fig S54. ^{13}C NMR spectrum (101 MHz) of **7d** in $CDCl_3$ (77.16 ppm).

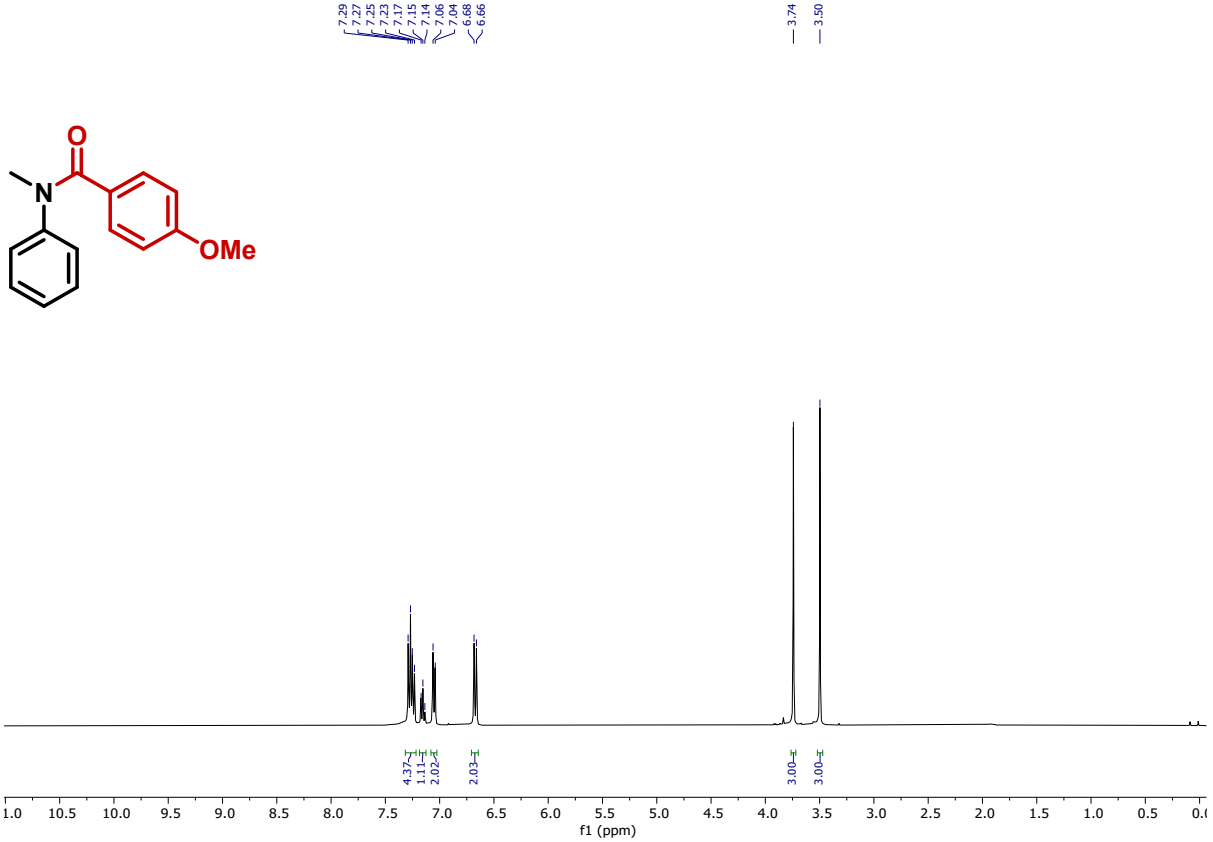


Fig S55. ^{1}H NMR spectrum (400 MHz) of **7e** in $CDCl_3$ (7.26 ppm).

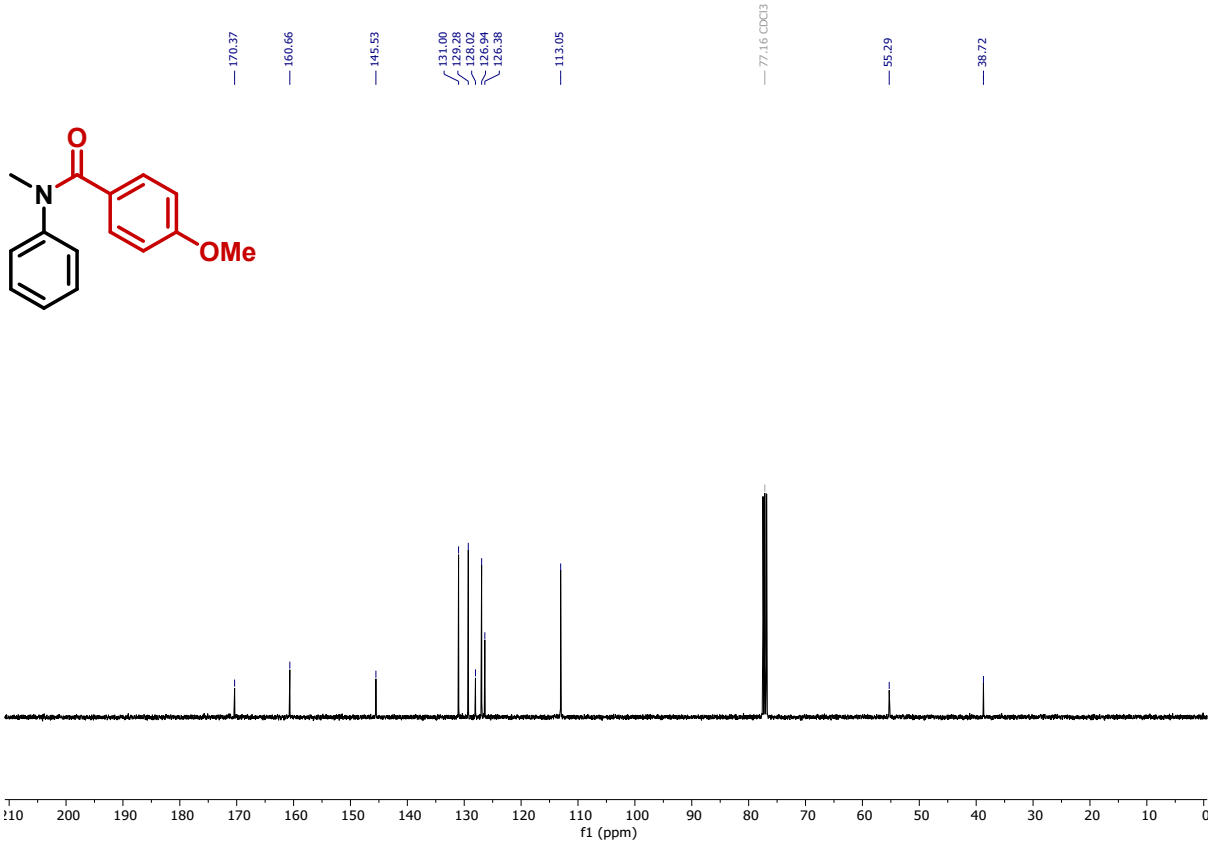


Fig S56. ^{13}C NMR spectrum (101 MHz) of **7e** in $CDCl_3$ (77.16 ppm).

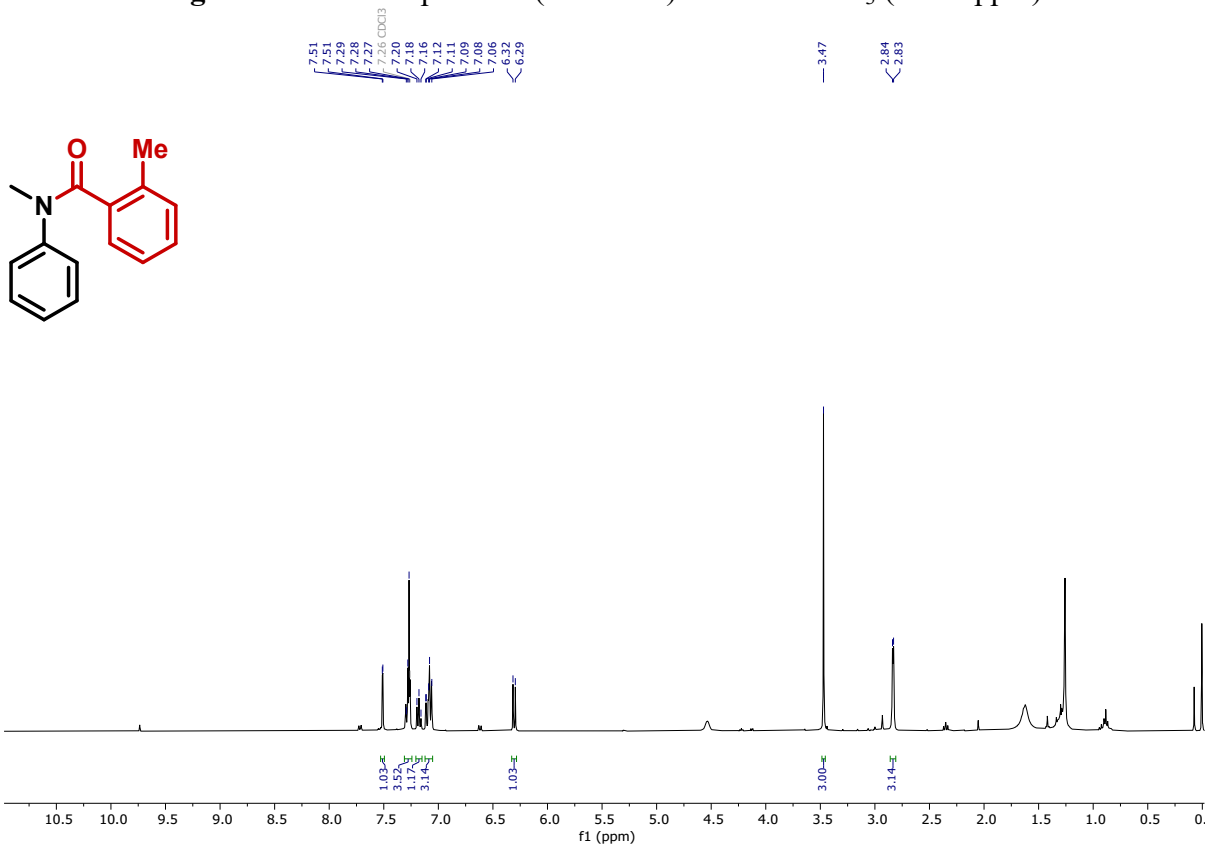


Fig S57. ^{1}H NMR spectrum (400 MHz) of **7f** in $CDCl_3$ (7.26 ppm).

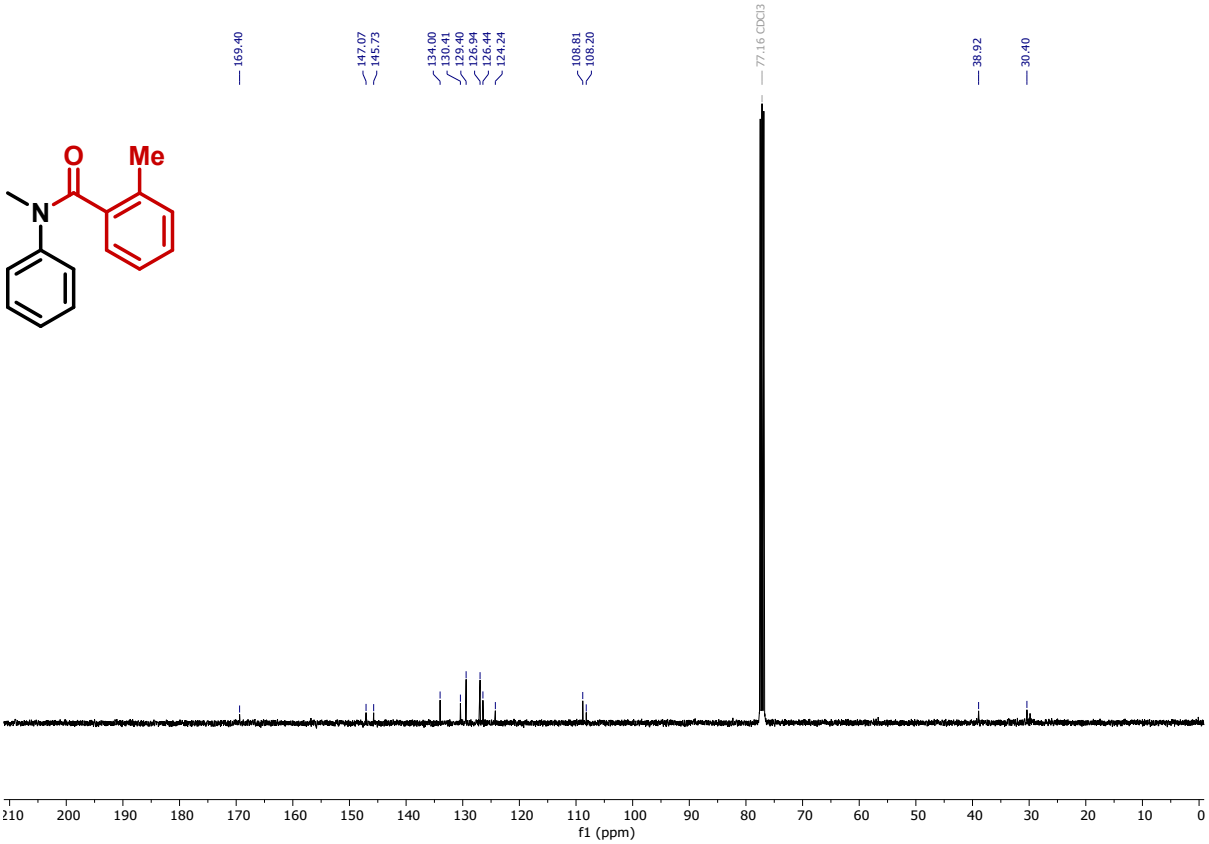


Fig S58. ^{13}C NMR spectrum (101 MHz) of **7f** in $CDCl_3$ (77.16 ppm).

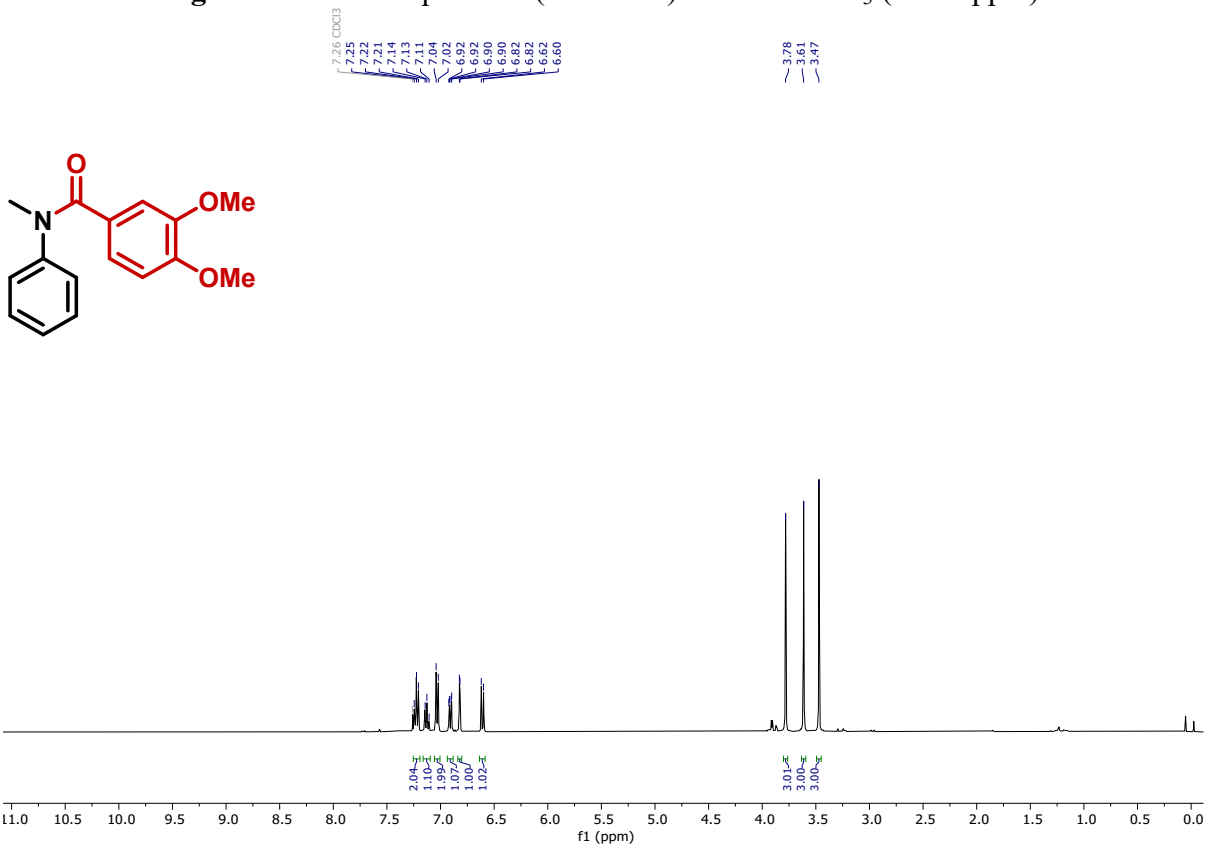


Fig S59. ^{1}H NMR spectrum (400 MHz) of **7g** in $CDCl_3$ (7.26 ppm).

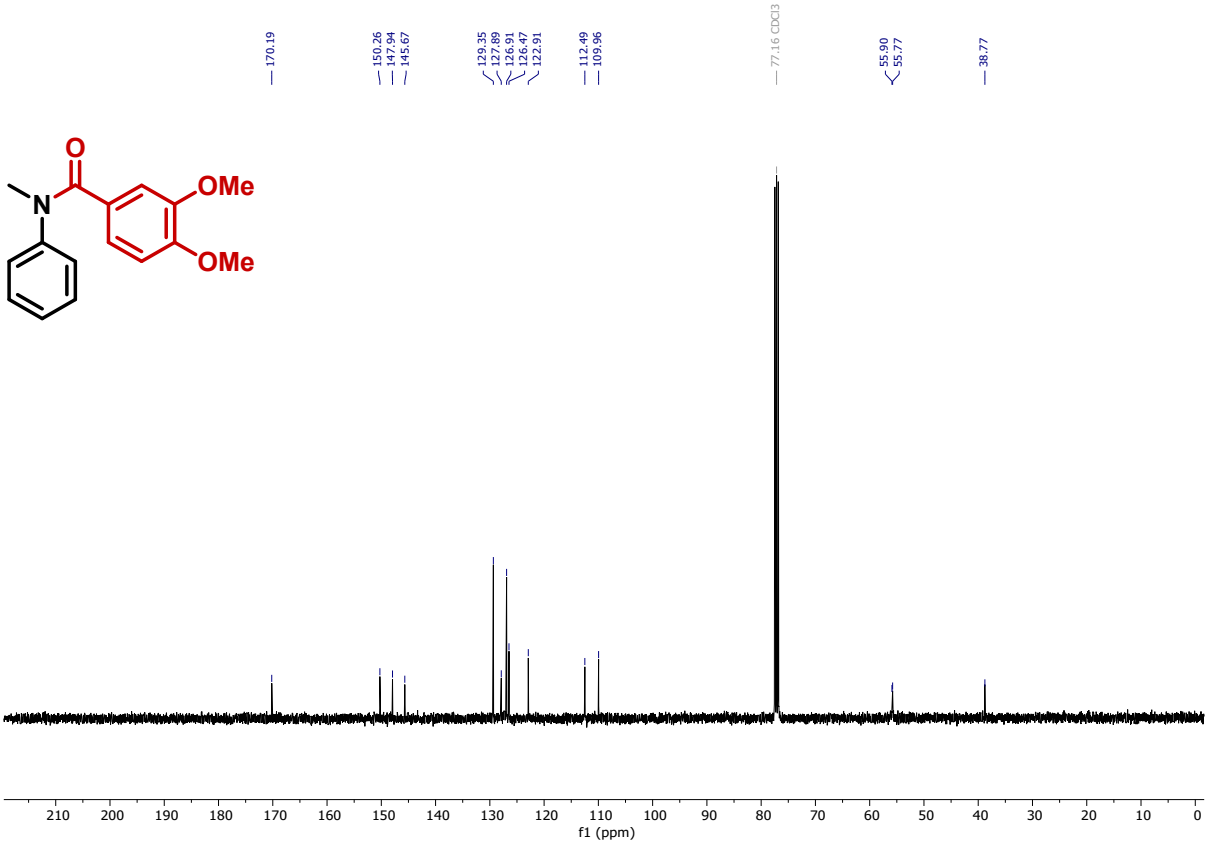


Fig S60. ^{13}C NMR spectrum (101 MHz) of **7g** in $CDCl_3$ (77.16 ppm).

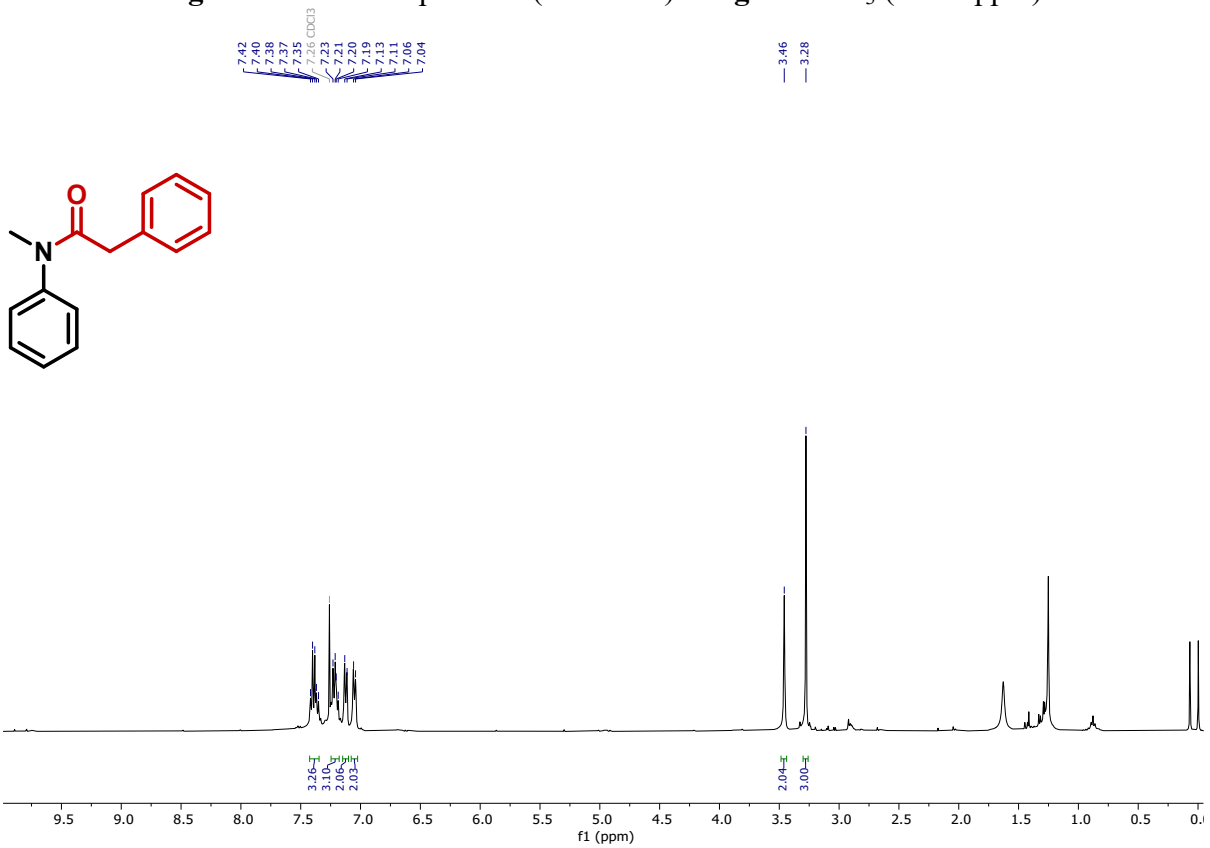


Fig S61. ^{1}H NMR spectrum (400 MHz) of **7h** in $CDCl_3$ (7.26 ppm).

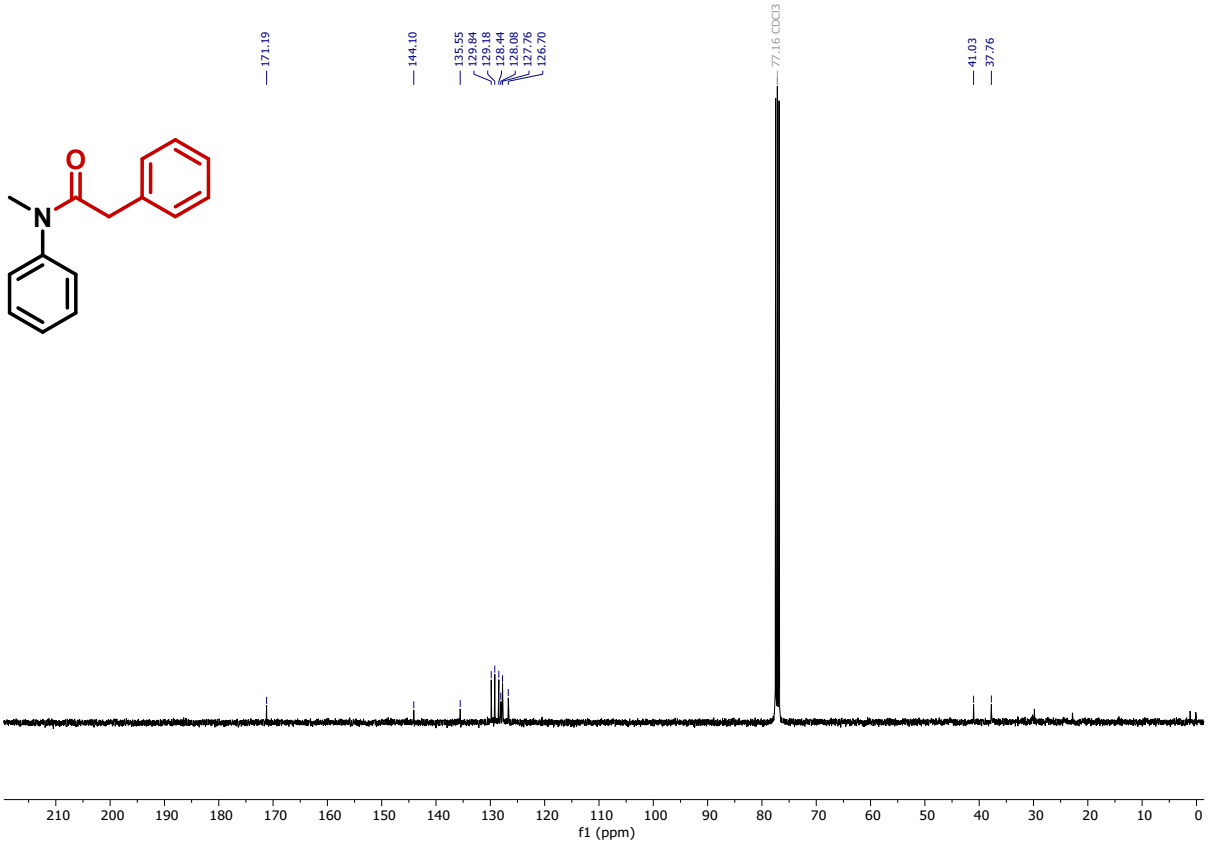


Fig S62. ^{13}C NMR spectrum (101 MHz) of **7h** in $CDCl_3$ (77.16 ppm).

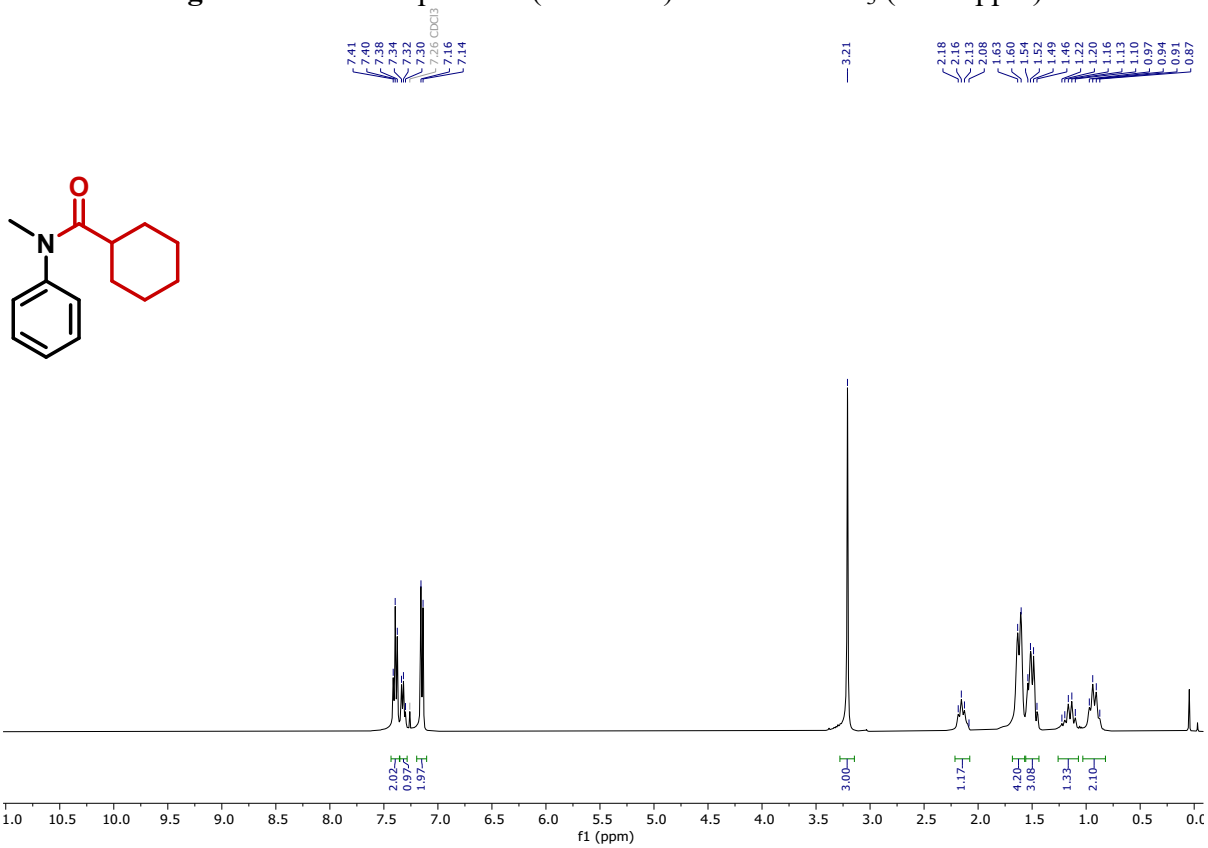


Fig S63. ^{1}H NMR spectrum (400 MHz) of **7i** in $CDCl_3$ (7.26 ppm).

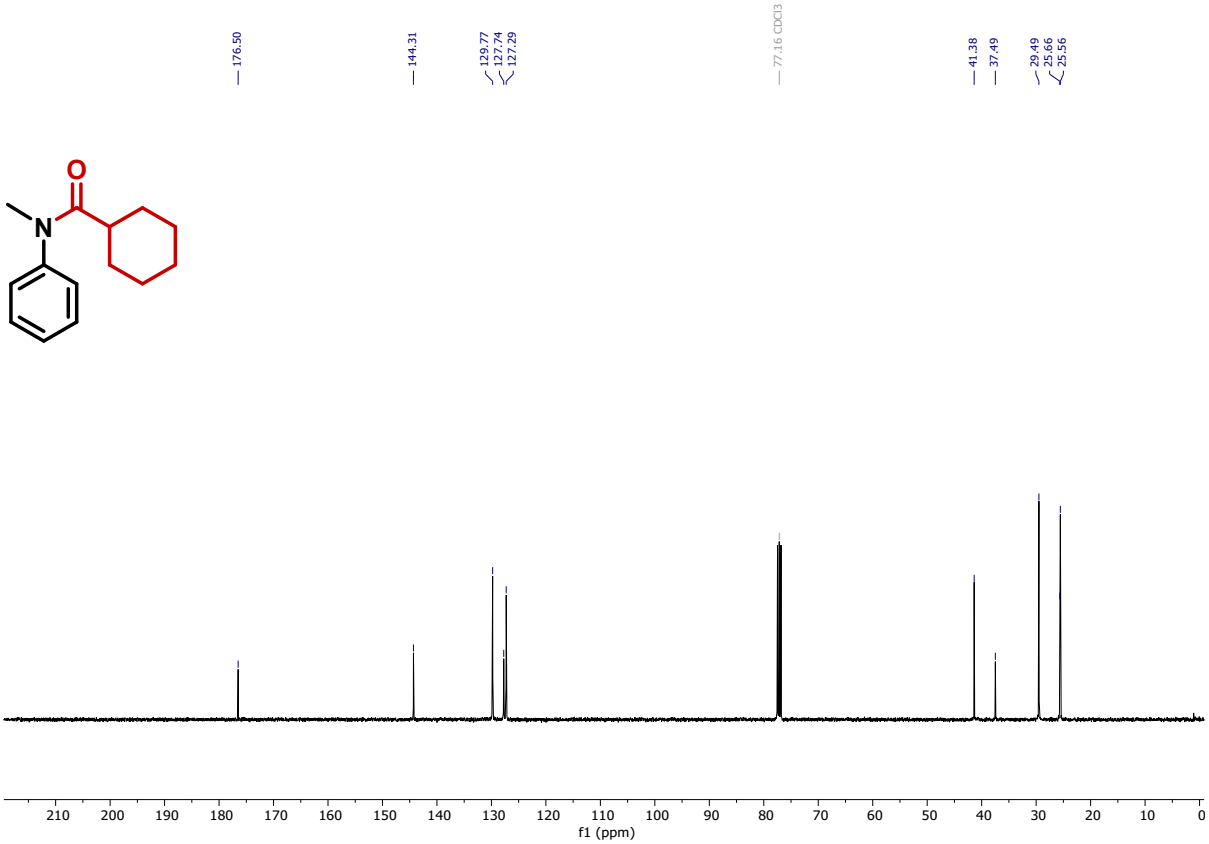


Fig S64. ^{13}C NMR spectrum (101 MHz) of **7i** in $CDCl_3$ (77.16 ppm).

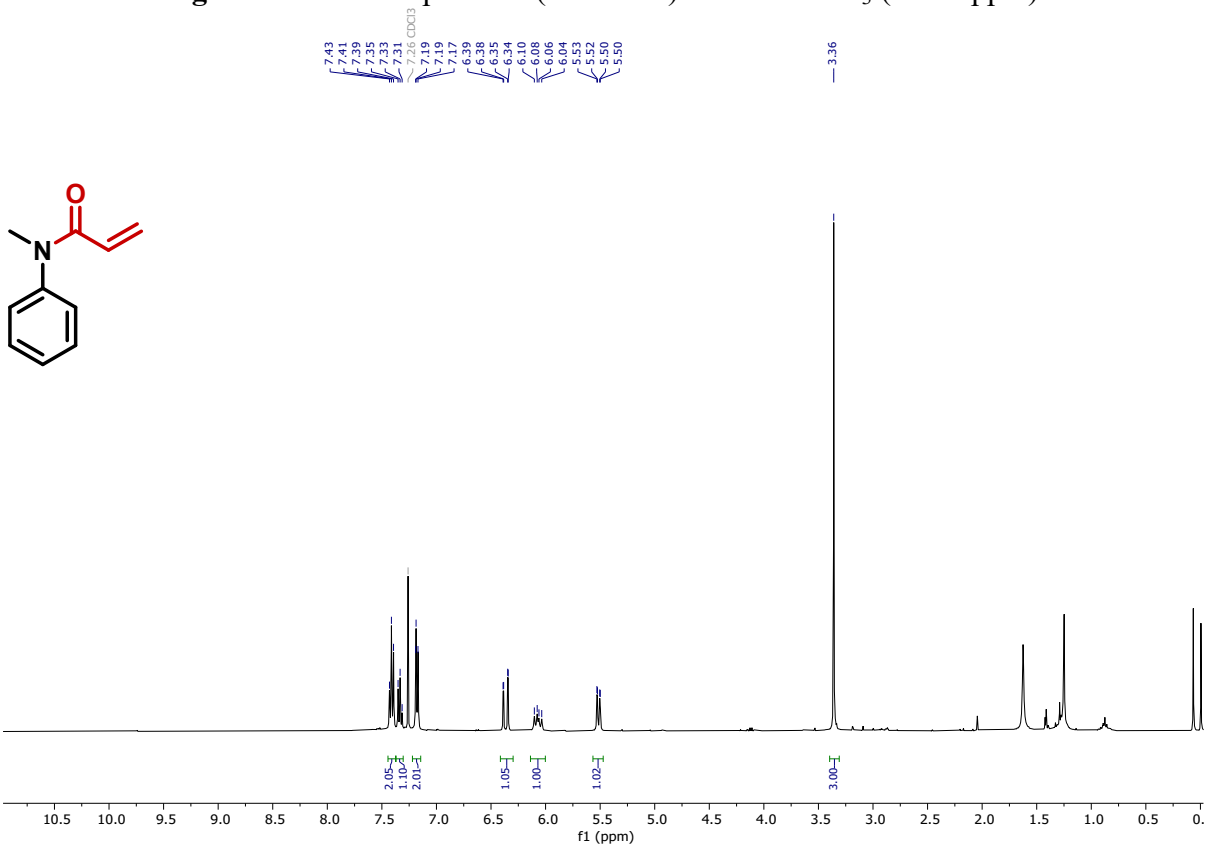


Fig S65. ^{1}H NMR spectrum (400 MHz) of **7j** in $CDCl_3$ (7.26 ppm).

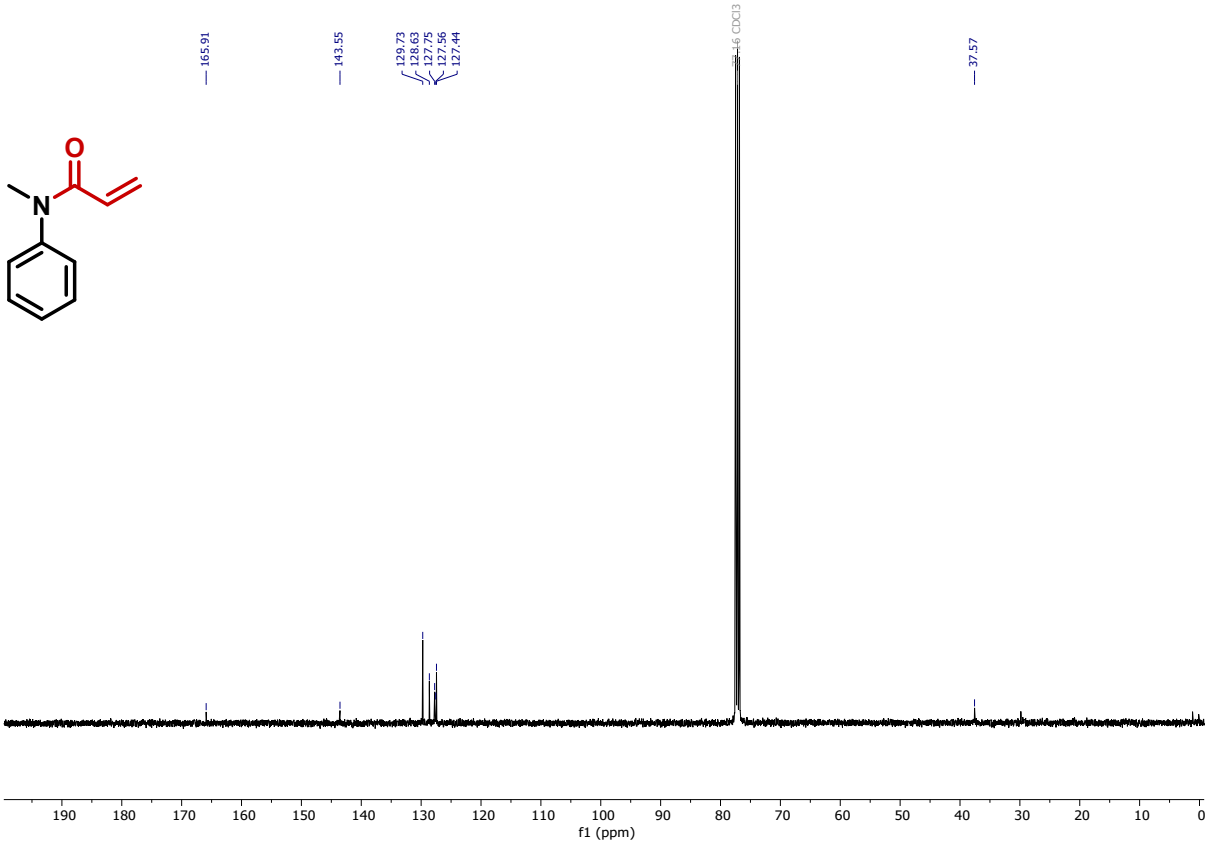


Fig S66. ^{13}C NMR spectrum (101 MHz) of **7j** in $CDCl_3$ (77.16 ppm).

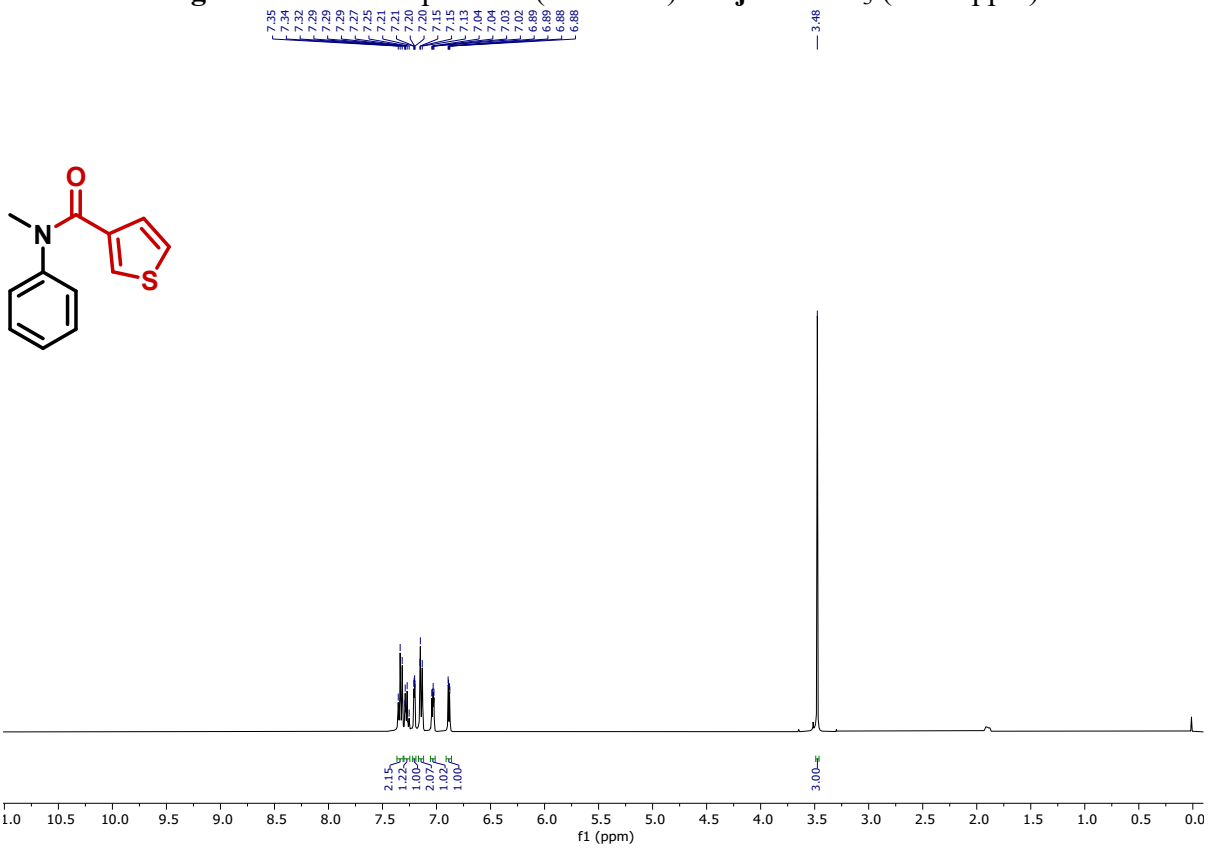


Fig S67. ^{1}H NMR spectrum (400 MHz) of **7k** in $CDCl_3$ (7.26 ppm).

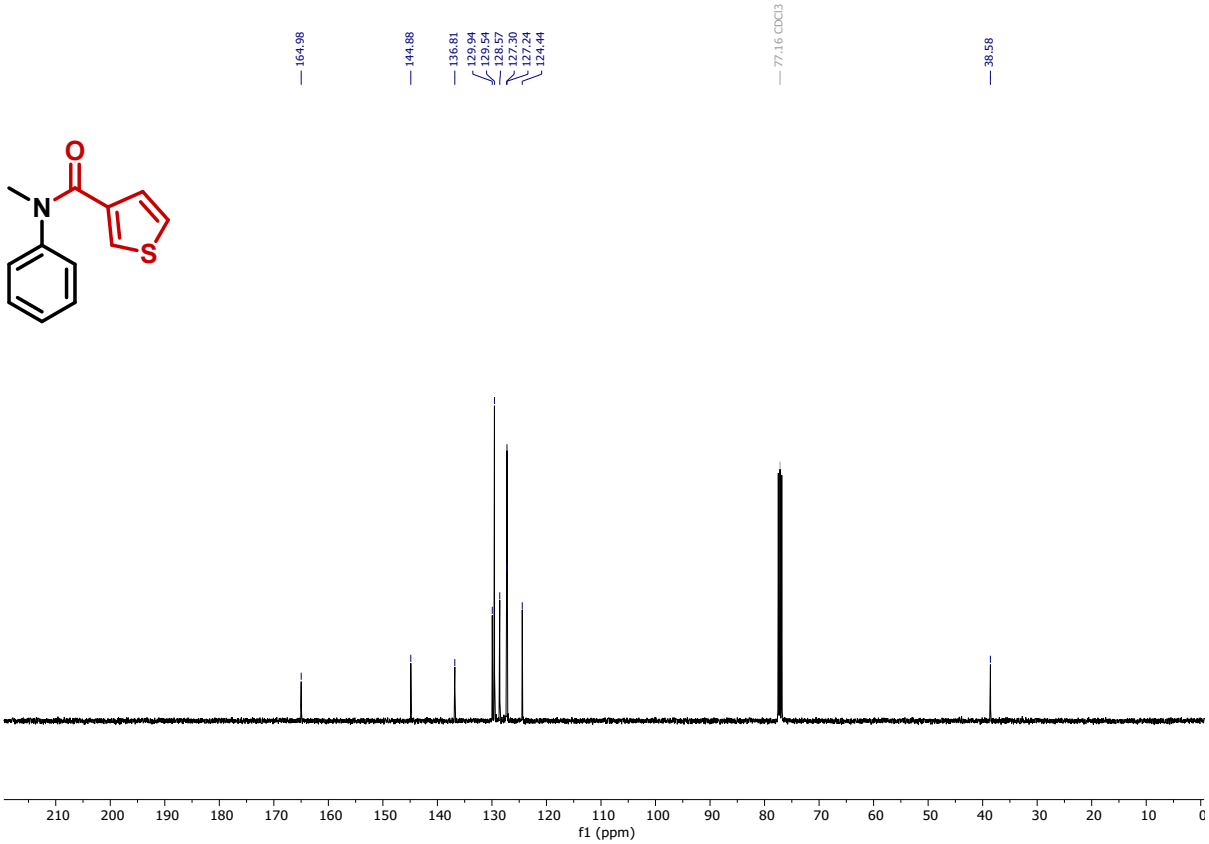


Fig S68. ^{13}C NMR spectrum (101 MHz) of **7k** in $CDCl_3$ (77.16 ppm).

11. Coordinates of optimized geometries

1

0 2

Fe	-0.00002500	0.00004600	-0.38681600
O	-1.43384200	0.00024300	-1.67473100
O	1.43375100	0.00024400	-1.67477500
N	-1.23681300	-0.00034400	2.21021900
N	-1.36201200	-0.00012700	0.92188600
N	1.23683900	-0.00035100	2.21018200
N	1.36200000	-0.00013200	0.92184400
N	0.00061100	-0.00149300	5.36874700
N	-0.00002600	-2.03859600	-0.51508300
N	-0.00002100	2.03872600	-0.51453600
C	0.00002100	-0.00044400	2.76577100
C	0.00003600	-0.00061300	4.20447300
C	-2.64698300	0.00000500	0.35706800
C	-2.60864400	0.00019500	-1.06632300
C	-3.83595800	0.00032800	-1.76300600
H	-3.81739700	0.00047200	-2.84924400
C	-5.03561900	0.00027200	-1.05644900
H	-5.97525700	0.00037700	-1.60401300
C	-5.05497700	0.00008500	0.35231700
H	-6.00224600	0.00004600	0.88394400
C	-3.85897000	-0.00005000	1.06342400

H	-3.84239700	-0.00019600	2.14855600
C	2.64695500	-0.00000600	0.35698700
C	2.60857100	0.00018900	-1.06640400
C	3.83586300	0.00031800	-1.76312500
H	3.81726900	0.00046600	-2.84936200
C	5.03554600	0.00025500	-1.05660500
H	5.97516700	0.00035600	-1.60419800
C	5.05494900	0.00006300	0.35216000
H	6.00223400	0.00001800	0.88375700
C	3.85896400	-0.00006800	1.06330500
H	3.84242500	-0.00021800	2.14843700
C	0.00002000	-2.86250900	0.54812400
H	0.00005500	-2.39840900	1.52710900
C	0.00002400	-4.24822800	0.41293800
H	0.00006200	-4.87197800	1.30093000
C	-0.00002100	-4.79978300	-0.86889400
H	-0.00001900	-5.87748800	-1.00720100
C	-0.00006800	-3.94084800	-1.96839400
H	-0.00010300	-4.32229600	-2.98449900
C	-0.00006900	-2.56459900	-1.75391000
H	-0.00010500	-1.85107400	-2.56791700
C	0.00006600	2.86233600	0.54890600
H	0.00012500	2.39795700	1.52776000
C	0.00008000	4.24809400	0.41411400
H	0.00015100	4.87159100	1.30228300
C	0.00000300	4.80001200	-0.86756100
H	0.00001200	5.87775600	-1.00556200
C	-0.00008600	3.94139000	-1.96730500
H	-0.00014700	4.32312600	-2.98330100
C	-0.00009500	2.56508000	-1.75321200
H	-0.00016400	1.85178400	-2.56742000

Open-shell singlet of $\mathbf{1^{\cdot+}}$:

Fe	-0.000028	0.000049	-0.455429
O	-1.476202	0.000225	-1.668476
O	1.476082	0.000254	-1.668554
N	-1.228177	-0.000264	2.192353
N	-1.372778	-0.000122	0.911180
N	1.228264	-0.000285	2.192287
N	1.372796	-0.000136	0.911108
N	0.000133	-0.001705	5.347500
N	-0.000009	-2.000247	-0.541724
N	-0.000034	2.000362	-0.541223
C	0.000057	-0.000243	2.747006
C	0.000096	-0.001020	4.187472
C	-2.634536	-0.000011	0.374288
C	-2.622932	0.000198	-1.070133
C	-3.867596	0.000337	-1.754469
H	-3.865424	0.000492	-2.845633

C	-5.036997	0.000277	-1.022129
H	-5.996053	0.000386	-1.545593
C	-5.033070	0.000078	0.406028
H	-5.983719	0.000042	0.942502
C	-3.846513	-0.000066	1.106168
H	-3.809775	-0.000217	2.195758
C	2.634527	-0.000034	0.374148
C	2.622846	0.000197	-1.070272
C	3.867471	0.000331	-1.754676
H	3.865240	0.000502	-2.845840
C	5.036913	0.000250	-1.022398
H	5.995941	0.000358	-1.545914
C	5.033063	0.000032	0.405758
H	5.983741	-0.000019	0.942180
C	3.846544	-0.000109	1.105962
H	3.809866	-0.000273	2.195554
C	0.000004	-2.808016	0.533500
H	-0.000005	-2.335830	1.515766
C	0.000028	-4.194927	0.417940
H	0.000041	-4.809790	1.319363
C	0.000037	-4.765587	-0.856722
H	0.000056	-5.851139	-0.979998
C	0.000018	-3.922248	-1.969430
H	0.000022	-4.320835	-2.985268
C	-0.000004	-2.544266	-1.773401
H	-0.000015	-1.845344	-2.609955
C	-0.000014	2.807834	0.534225
H	-0.000019	2.335368	1.516358
C	0.000009	4.194776	0.419049
H	0.000028	4.809393	1.320639
C	0.000010	4.765785	-0.855458
H	0.000029	5.851371	-0.978437
C	-0.000016	3.922752	-1.968398
H	-0.000020	4.321619	-2.984126
C	-0.000037	2.544716	-1.772751
H	-0.000054	1.846026	-2.609497

Triplet of $\mathbf{1}^{\cdot+}$

Fe	-0.000022	0.000029	-0.456511
O	-1.477906	0.000250	-1.666698
O	1.477800	0.000265	-1.666775
N	-1.227700	-0.000430	2.193250
N	-1.371246	-0.000195	0.911908
N	1.227793	-0.000442	2.193186
N	1.371273	-0.000204	0.911839
N	0.000131	-0.000210	5.349154
N	-0.000010	-2.000240	-0.544428
N	-0.000024	2.000321	-0.543832
C	0.000060	-0.000637	2.748588

C	0.000097	-0.000369	4.189154
C	-2.633911	-0.000063	0.376332
C	-2.624371	0.000181	-1.067684
C	-3.869250	0.000324	-1.751419
H	-3.867981	0.000509	-2.842625
C	-5.038064	0.000230	-1.018053
H	-5.997740	0.000340	-1.540494
C	-5.032503	-0.000009	0.409911
H	-5.982691	-0.000076	0.947341
C	-3.845197	-0.000155	1.109200
H	-3.808316	-0.000340	2.198813
C	2.633910	-0.000075	0.376196
C	2.624296	0.000180	-1.067820
C	3.869140	0.000318	-1.751620
H	3.867815	0.000511	-2.842825
C	5.037992	0.000213	-1.018313
H	5.997641	0.000321	-1.540803
C	5.032505	-0.000034	0.409650
H	5.982721	-0.000110	0.947031
C	3.845235	-0.000177	1.109001
H	3.808412	-0.000369	2.198616
C	0.000010	-2.808760	0.530264
H	0.000015	-2.336856	1.512737
C	0.000024	-4.195525	0.413822
H	0.000041	-4.810951	1.314938
C	0.000014	-4.765480	-0.861197
H	0.000024	-5.851012	-0.985132
C	-0.000010	-3.921420	-1.973375
H	-0.000020	-4.319297	-2.989552
C	-0.000022	-2.543587	-1.776336
H	-0.000039	-1.844003	-2.612465
C	-0.000004	2.808498	0.531118
H	-0.000001	2.336275	1.513436
C	0.000011	4.195299	0.415120
H	0.000029	4.810439	1.316431
C	0.000003	4.765660	-0.859717
H	0.000014	5.851232	-0.983308
C	-0.000022	3.921954	-1.972165
H	-0.000032	4.320157	-2.988214
C	-0.000035	2.544059	-1.775567
H	-0.000052	1.844742	-2.611919

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1) (i) J. B. Gilroy, P. O. Otieno, M. J. Ferguson, R. McDonald, and R. G. Hicks, *Inorg. Chem.* **2008**, *47*, 1279-1286. (ii) J. B. Gilroy, B. O. Patrick, R. McDonald, and R. G. Hicks, *Inorg. Chem*. **2008***, 47,* 1287-1294
2) F. Neese, *Wiley Interdisciplinary Reviews: Computational Molecular Science*, **2018**, *8*, e1327.)
3) (i) A. D. Becke, *J. Chem. Phys*.**1993**, *98*, 5648−5652. (ii) C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B: Condens. Matter Mater. Phys*.**1988**, *37*, 785−789.
4) (i) F. Weigend, and R. Ahlrichs, *Phys. Chem. Chem. Phys.***2005**, *7*, 3297-3305. (ii) A. Schaafer, H. Horn, and R. Ahlrichs, *J. Chem. Phys*.**1992**, *97*, 2571-2577.
5) M. K. Reddy, I. Ramakrishna, and M. Baidya; *Org. Lett*. **2018**, *20*, 4610−4613