Supporting Information

Deoxygenative Radical Addition of Aryl Carboxylic Acids to Alkenes with Phosphine in a Two−molecule Photoredox System

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Table of Contents

S1. General Information

All reagents and solvents were purchased from commercial suppliers and used as received unless otherwise noted. IR spectra were recorded on an FT-IR spectrometer. NMR spectra were recorded in $CDCl_3$ containing trimethylsilane as internal standard and were acquired on a 400 MHz spectrometer for ^1H and a 100 MHz spectrometer for $^{13}C\{^1H\}$. High−resolution mass spectra were obtained using DART mass spectrometer. Column chromatography was performed on Wakogel C−300 (45–75 µm). Yields and recoveries (phosphine and starting materials) were determined by ^1H NMR using 2,4,6−trimethoxybenzene as an internal standard. Photochemical reactions were irradiated with an 18 W blue LED (λ = 405 nm) unless otherwise specified.

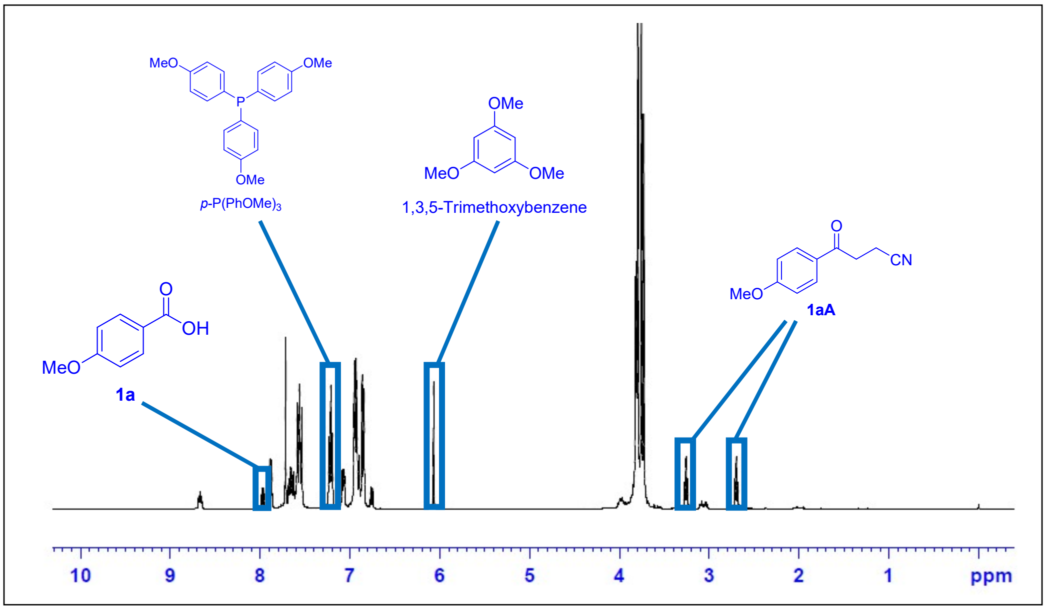


Figure S1. ^1H NMR spectrum of a representative reaction mixture showing the internal standard (2,4,6-trimethoxybenzene) used for product assignment and yield determination.

S2. CV Measurements

Cyclic voltammetry (CV) measurements were performed at 298 K on a ALS 1200B Electrochemical Analyzer in deaerated acetonitrile (CH_3CN) containing 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte ($TBAPF_6$). A conventional three−electrode cell was used with a glass carbon (GC) electrode as the working electrode (surface area of 7 mm^2) and a platinum wire as the counter electrode. The reference electrode was an Ag/AgCl. The cyclic voltammograms were measured with a sweep rate of 0.1 V s^{-1} in a deaerated CH_3CN containing 0.1 M $TBAPF_6$ used as a supporting electrolyte at 298 K. The redox potential values (vs Ag/AgCl) were converted to those vs SCE by referencing ferrocene, subtracting 0.41 V and adding 0.0325 V.

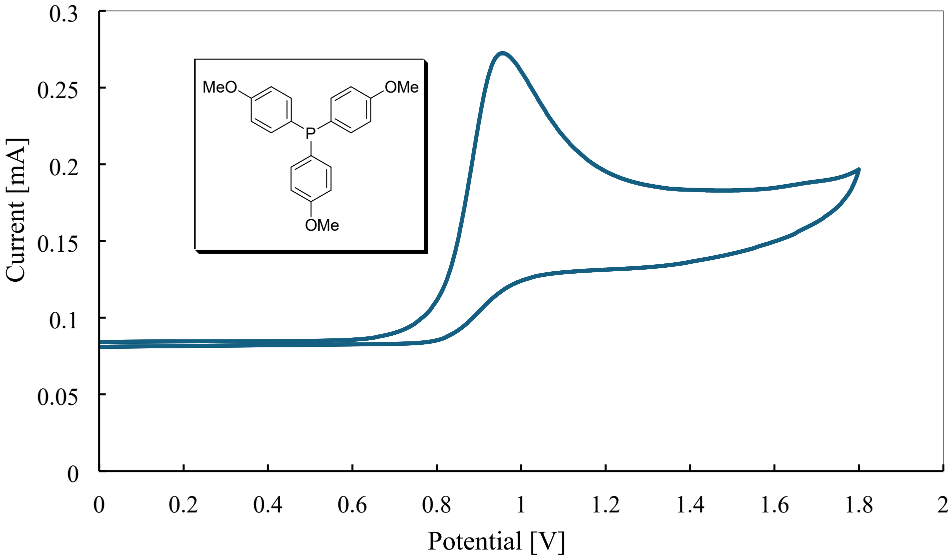


Figure S2a. Cyclic voltammogram of phosphine **I** (*p*-P(PhOMe)$_3$) recorded under the conditions described in Section S2.

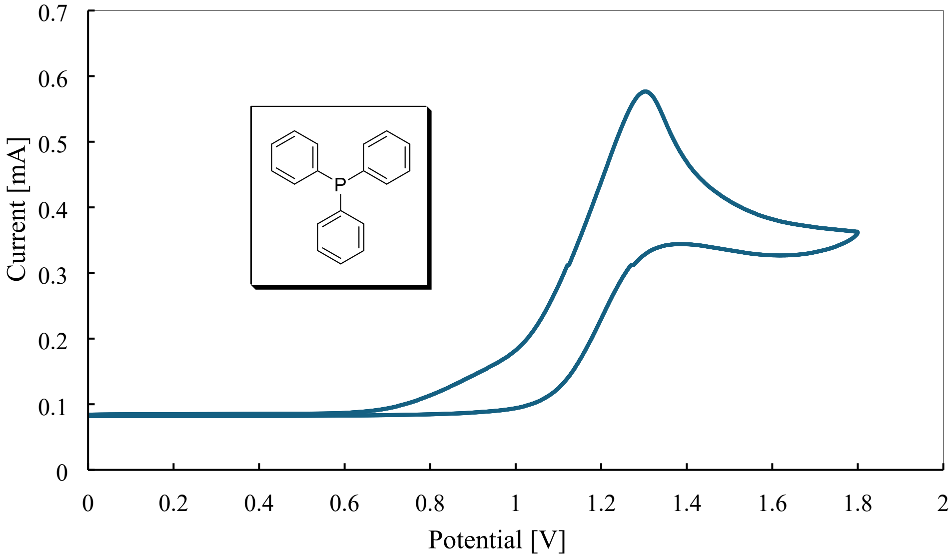


Figure S2b. Cyclic voltammogram of phosphine **II** (PPh_3) recorded under the conditions described in Section S2.

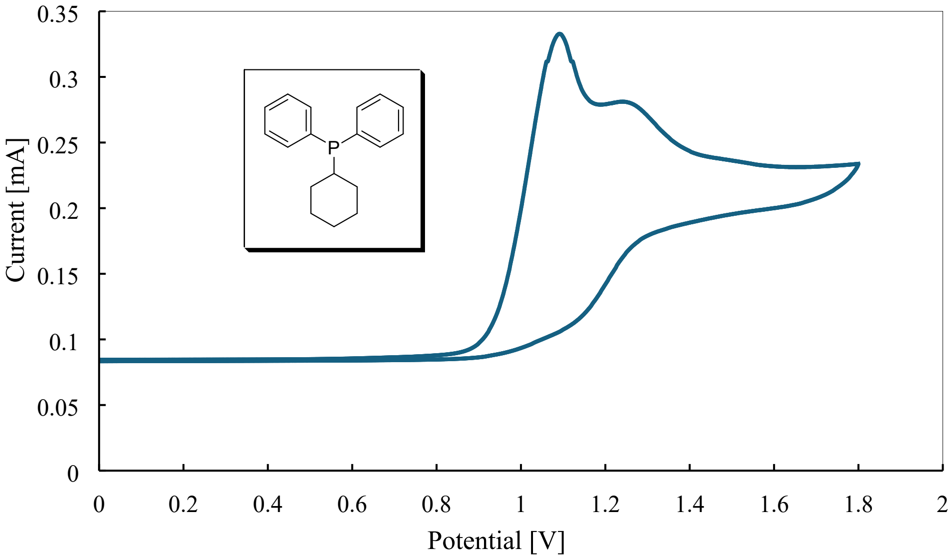


Figure S2c. Cyclic voltammogram of phosphine **III** ($PCyPh_2$) recorded under the conditions described in Section S2.

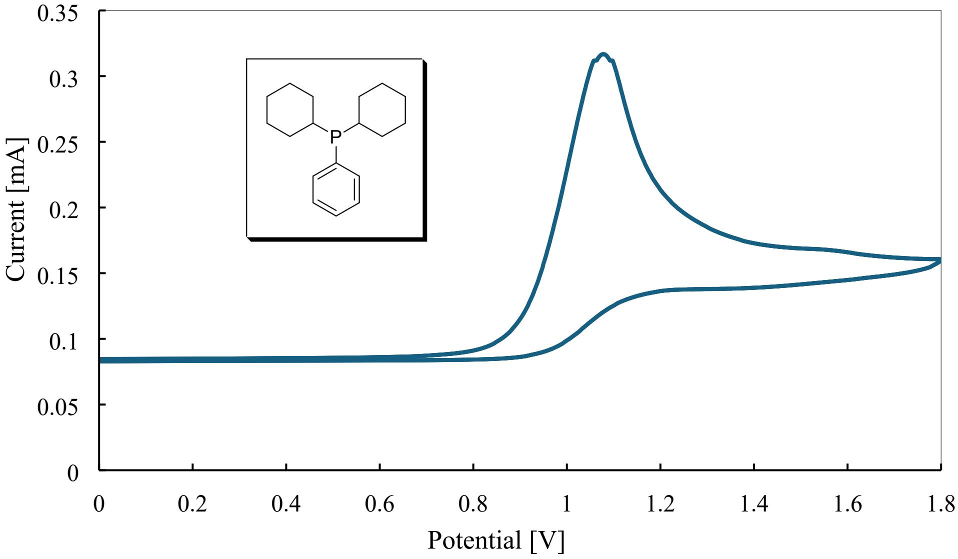


Figure S2d. Cyclic voltammogram of phosphine **IV** (PCy_2Ph) recorded under the conditions described in Section S2.

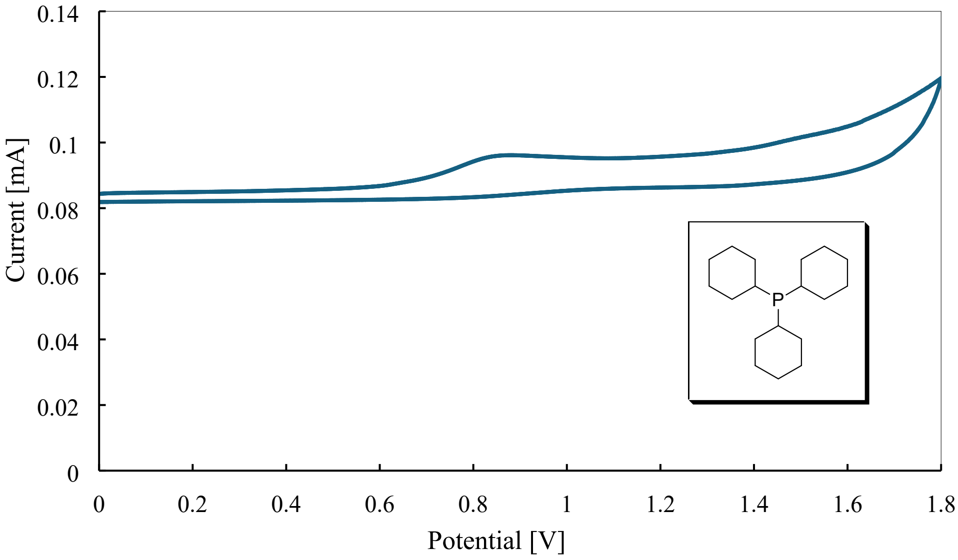


Figure S2e. Cyclic voltammogram of phosphine **V** (PCy_3) recorded under the conditions described in Section S2.

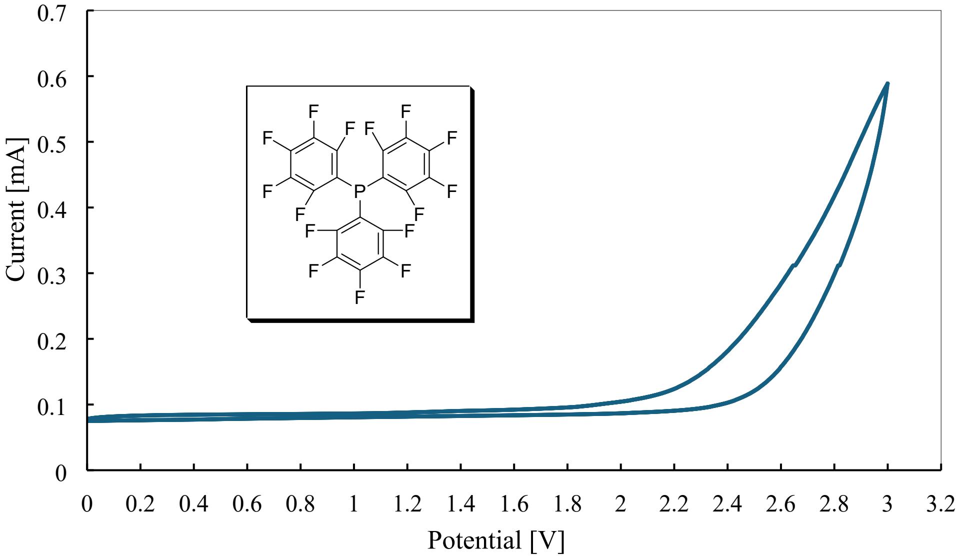


Figure S2f. Cyclic voltammogram of phosphine **VI** ($P(PhF_5)_3$) recorded under the conditions described in Section S2.

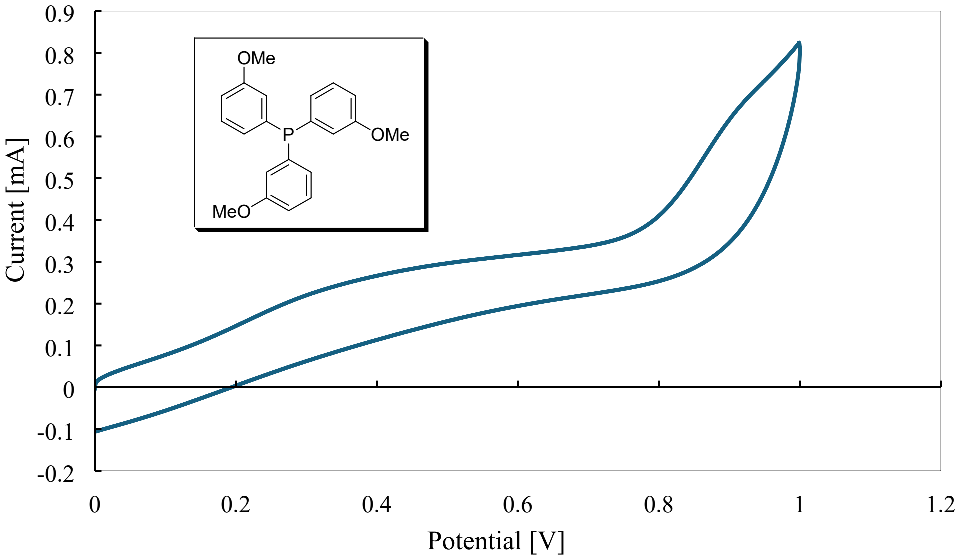


Figure S2g. Cyclic voltammogram of phosphine **VII** *m*−P(PhOMe)$_3$ recorded under the conditions described in Section S2.

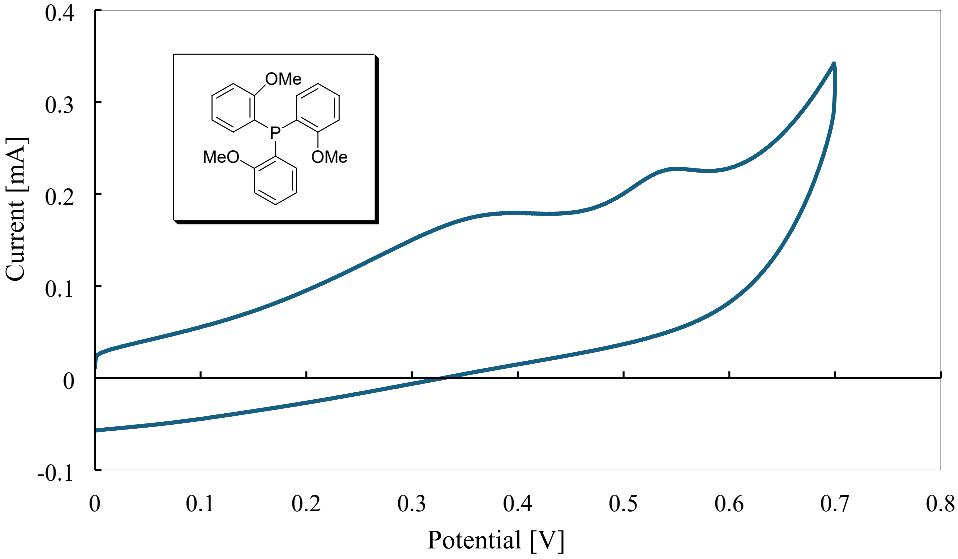
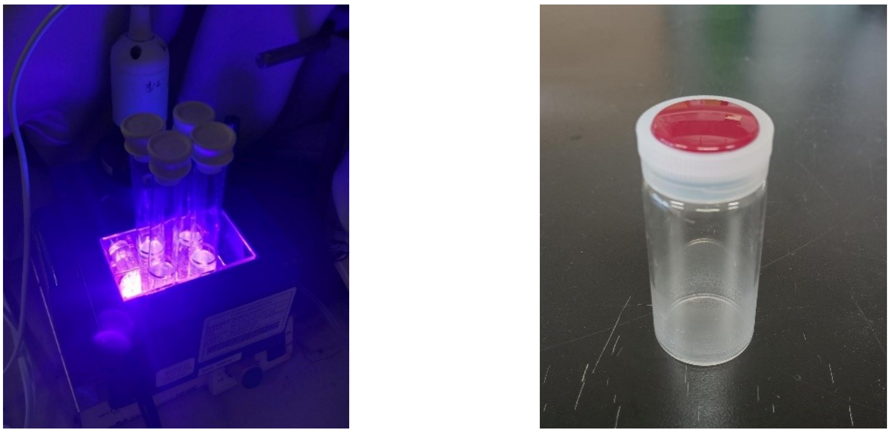


Figure S2h. Cyclic voltammogram of phosphine **VIII** *o*-P(PhOMe)$_3$ recorded under the conditions described in Section S2.

S3. General Procedure for the Photoreaction

An aqueous CH_3CN solution (CH_3CN 9.8 mL, H_2O 0.2 mL) of benzoic acids **1** (30 mM, 0.3 mmol), K_2HPO_4 (30 mM, 0.3 mmol, 0.0523 g), DBC (2 mM, 0.02 mmol, 0.0066 g), and 1.4−DCB (10 mM, 0.1 mmol, 0.0128 g), phosphine (40 mM, 0.4 mmol) in Pyrex vessels (10 mm x 120 mm) was purged with argon for 20 min, and acrylonitrile **2A** (90 mM, 0.9 mmol, 0.006 mL) was added under argon atmosphere. The mixture was irradiated with a 18 W blue LEDs for 3 h at room temperature, and then the solvent was removed under reduced pressure. The crude product was purified by silica−gel column chromatography using hexane/EtOAc as the eluents to yield adducts **3**.



Photoreaction□□□□□□□□□□□□□□Products

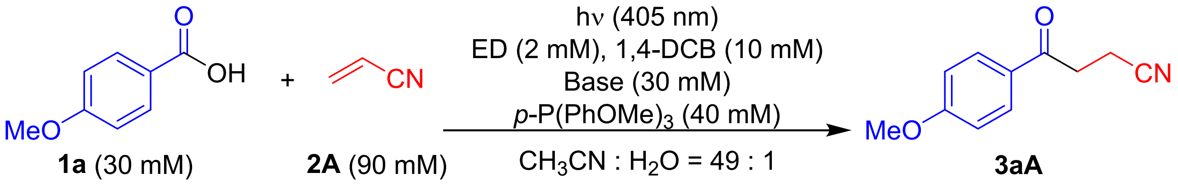
Figure S3. Reaction set−up

S4. Optimization of the Photoreaction Conditions

Optimization studies were carried out by varying key parameters including phosphine concentration, phosphine identity, electron donors (EDs), irradiation time and solvent; representative data tables and plots are provided below.

S4. 1. Effect of Base

Table S1 shows that K_2HPO_4 was proven to be suitable base in the photoreaction.



Entry	Base	Yield of **3aA** (%)	Recovery of **1a** (%)	Recovery of *p*−P(PhOMe)$_3$ (%)
1	Na_2HPO_4	78	0	17
2	KH_2PO_4	85	10	12
3	K_2CO_3	41	11	41
4	KOH	15	0	66
5[a]	2,6-lutidine	69	0	25

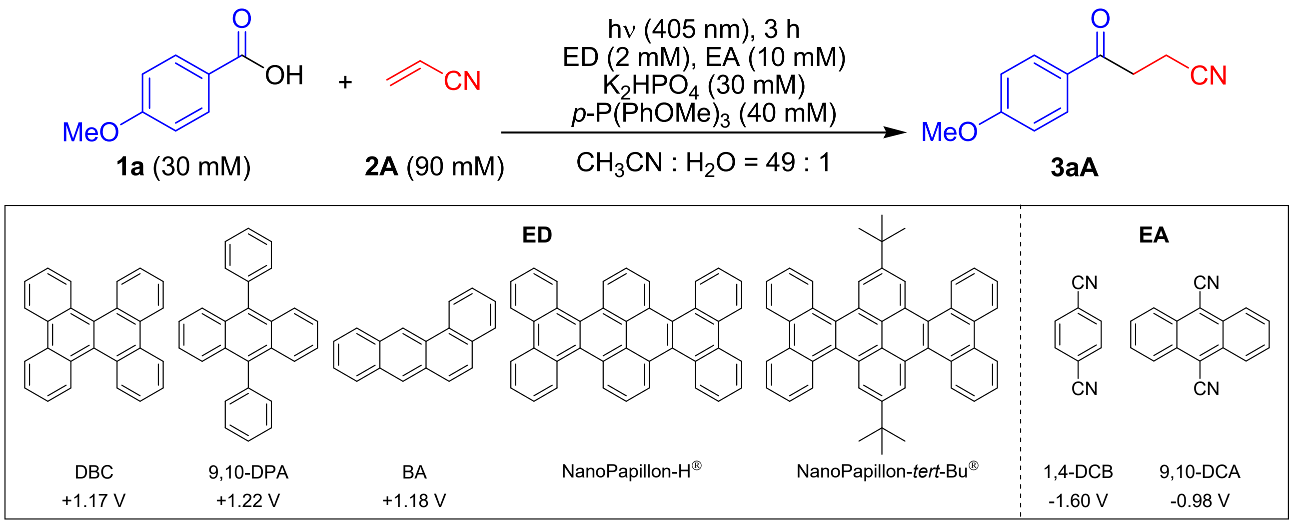
[a] The photoreaction was carried out in dry CH_3CN

Reaction conditions: **1a** (0.3 mmol), **2A** (0.9 mmol), phosphine **I** (*p*-P(PhOMe)$_3$) (0.4 mmol), DBC (0.02 mmol), 1,4-DCB (0.1 mmol), Base (0.3 mmol), CH_3CN solution (CH_3CN 9.8 mL, H_2O 0.2 mL), blue LEDs (405 nm), 25 °C, 3 h; The yield of the adduct **3aA**, the recovery of phosphine and the recovery of **1a** were determined by ^1H NMR.

S4.2. Effects of EDs

Effect of electron donors (EDs) under optimized conditions was evaluated, and DBC was proven to be suitable ED in the photoreaction.

Table S2. Effect of EDs.



Entry	ED (mM)	EA (mM)	Yield of **3aA** (%)	Recovery of **1a** (%)
1	none	1,4−DCB	4	80
2	9,10−DPA	1,4−DCB	83	0
3	BA	1,4−DCB	64	25
4	NanoPapillon−H®	1,4−DCB	93	0
5	NanoPapillon−*tert*−Bu®	1,4−DCB	86	trace
6	none	none	0	quant.
7*	DBC	1,4−DCB	0	quant.

*No irradiation.

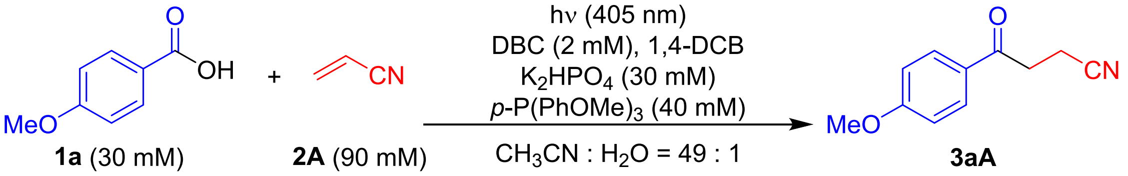
Reaction conditions: **1a** (0.3 mmol), **2A** (0.9 mmol), phosphine **I** (p-P(PhOMe)$_3$) (0.4 mmol), ED (0.02 mmol), EA (0.1 mmol), K_2HPO_4 (0.3 mmol), CH_3CN solution (CH_3CN 9.8 mL, H_2O 0.2 mL), blue LEDs (405 nm), 25 °C, 3 h; The yield of the adduct **3aA** and the recovery of **1a** were determined by ^{1}H NMR.

The authors gratefully acknowledge Taoka Chemical Co., Ltd. for kindly providing NanoPapillon® and NanoPapillon−*tert*−Bu®.

S4.3. Effects of 1,4-DCB concentrations.

The effect of the concentration of 1,4-DCB was examined, and a concentration of 10 mM was found to be optimal for this photoreaction.

Table S3. Effects of 1,4-DCB concentrations.



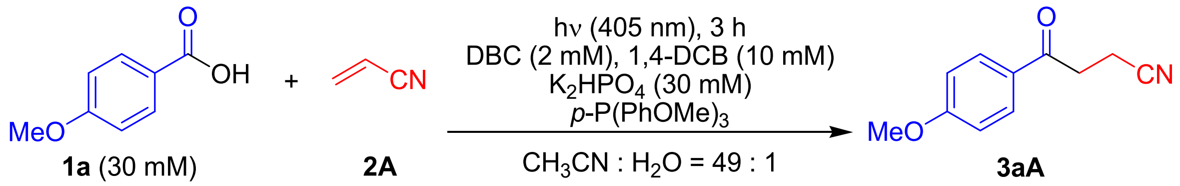
Entry	1,4-DCB (mM)	Yield of **3aA** (%)	Recovery of **1a** (%)
1	2	66	16
2	4	85	5
3	8	89	0
4	20	95	0

Reaction conditions: **1a** (0.3 mmol), **2A** (0.9 mmol), phosphine **I** (*p*-P(PhOMe)$_3$) (0.4 mmol), DBC (0.02 mmol), 1,4-DCB, K_2HPO_4 (0.3 mmol), CH_3CN solution (CH_3CN 9.8 mL, H_2O 0.2 mL), blue LEDs (405 nm), 25 °C, 3 h; The yield of the adduct **3aA** and the recovery of **1a** were determined by ^{1}H NMR.

S4.4. Effect of phosphine concentration

Table S4 shows that the suitable concentrations of phosphine **I** (*p*-P(PhOMe)$_3$) (entry 3, 40 mM) and acrylonitrile **2A** (entry 7, 60 mM) led to the high yield of **3aA** in the photoreaction.

Table S4. Optimization of phosphine **I** and acrylonitrile **2A** concentration.



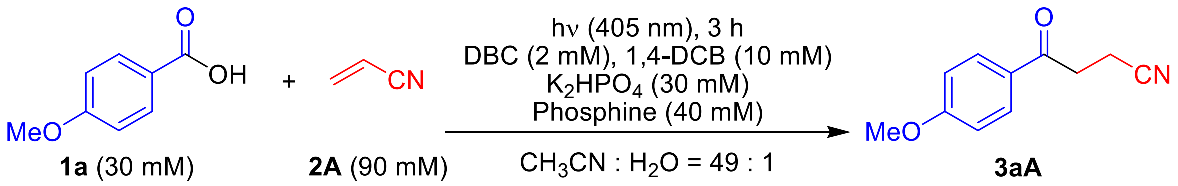
Entry	Phosphine **I** (*p*-P(PhOMe)$_3$) (mM)	**2A** (mM)	Yield of **3aA** (%)	Recovery of **1a** (%)
1	none	90	0	97
2	30	90	86	0
3	40	90	96	0
4	50	90	52	55
5	60	90	38	60
6	40	30	61	0
7	40	60	90	0
8	40	120	30	0

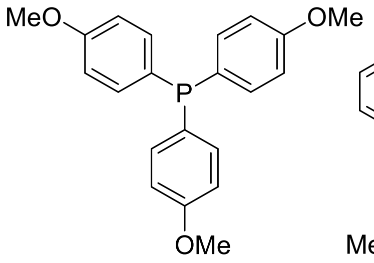
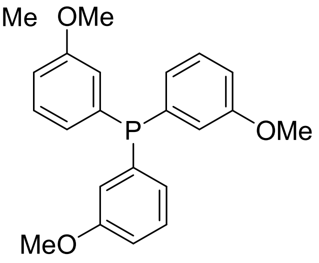
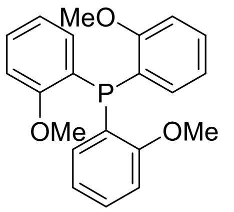
Reaction conditions: **1a** (0.3 mmol), **2A** (0.9 mmol), phosphine **I** (*p*-P(PhOMe)$_3$), DBC (0.02 mmol), 1,4-DCB (0.1 mmol), K_2HPO_4 (0.3 mmol), CH_3CN solution (CH_3CN 9.8 mL, H_2O 0.2 mL), blue LEDs (405 nm), 25 °C, 3 h; The yield of the adduct **3aA** and the recovery of **1a** were determined by ^{1}H NMR.

S4.5. Scope of Phosphines

Table S5 shows that the suitable phosphine is phosphine **I** (*p*–P(PhOMe)$_3$) in the photoreaction.

Table S5. Scope of phosphines.



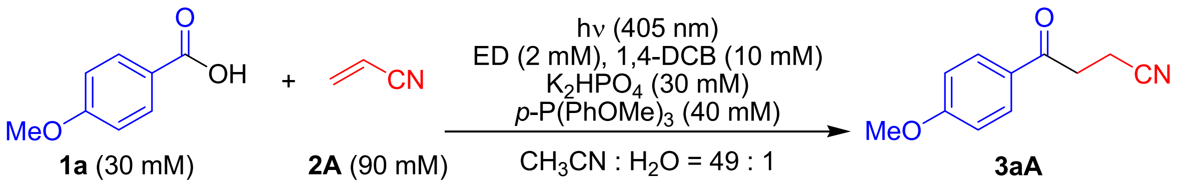
		
p-P(PhOMe)$_3$ **I**	*m*-P(PhOMe)$_3$ **VII**	*o*-P(PhOMe)$_3$ **VIII**
96 %	72 %	37 %

Reaction conditions: **1a** (0.3 mmol), **2A** (0.9 mmol), Phosphine (0.4 mmol), DBC (0.02 mmol), 1,4-DCB (0.1 mmol), K_2HPO_4 (0.3 mmol), CH_3CN solution (CH_3CN 9.8 mL, H_2O 0.2 mL), blue LED (405 nm), 25 °C, 3 h; The yield of the adduct **3aA** was determined by ^{1}H NMR.

S4.6. Effect of Irradiation Time

Table S6 shows that irradiation time is enough for 3 h.

Table S6. Irradiation time.



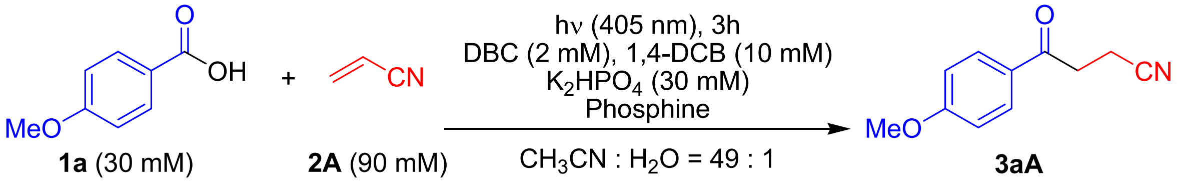
Entry	Irradiation time (h)	Yield of **3aA** (%)		
		DBC	NanoPapillon−H	NanoPapillon−*tert*−Bu
1	1	49	38	74
2	2	81	68	83
3	3	96	93	86

Reaction conditions: **1a** (0.3 mmol), **2A** (0.9 mmol), phosphine **I** (*p*-P(PhOMe)$_3$) (0.4 mmol), ED (0.02 mmol), 1,4-DCB (0.1 mmol), K_2HPO_4 (0.3 mmol), CH_3CN solution (CH_3CN 9.8 mL, H_2O 0.2 mL), blue LEDs (405 nm), 25 °C, 3 h; The yield of the adduct **3aA** and the recovery of **1a** were determined by ^{1}H NMR.

S4.7. Comparison of Phosphine **II** (PPh_3) and Phosphine **I** (p−$P(PhOMe)_3$) concentrations

Direct comparison experiments with phosphine **II** and **I** are summarized in Table S5, and phosphine I was preferred in the photoreaction.

Table S7. Comparison of phosphione **II** (PPh_3) and phosphione **I**(p−$P(PhOMe)_3$) concentrations.



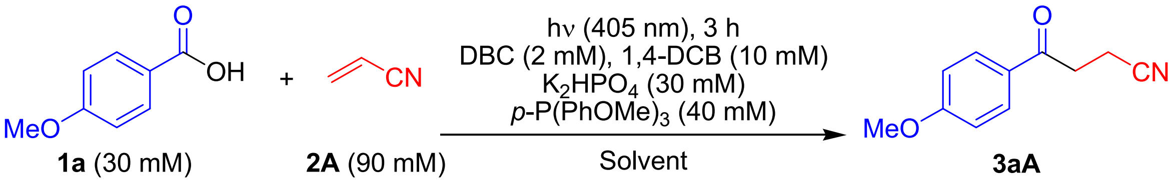
Entry	Concentration of Phosphine (mM)	PPh_3		p−$P(PhOMe)_3$	
		Yield of **3aA** (%)	Recovery of **1a** (%)	Yield of **3aA** (%)	Recovery of **1a** (%)
1	30	57	0	88	0
2	40	78	0	97	0
3	50	22	0	52	55
4	60	15	0	39	60

Reaction conditions: **1a** (0.3 mmol), **2A** (0.9 mmol), Phosphine, DBC (0.02 mmol), 1,4-DCB (0.1 mmol), K_2HPO_4 (0.3 mmol), CH_3CN solution (CH_3CN 9.8 mL, H_2O 0.2 mL), blue LEDs (405 nm), 25 °C, 3 h; The yield of the adduct **3aA** and the recovery of **1a** were determined by ^1H NMR.

S4.8. Effect of Solvent

Table S8 shows that the best solvent in the photoreaction is aqueous acetonitrile ($CH_3CN:H_2O$ = 49:1, v/v) (entry 1).

Table S8. Effects of solvent.



Entry	Solvent (mL)	Yield of **3aA** (%)	Recovery of **1a** (%)	Recovery of *p*–P(PhOMe)$_3$ (%)
1	CH_3CN : H_2O = 49 : 1	96	0	21
2	EtOH : H_2O = 49 : 1	0	30	0
3	*tert*–BuOH : H_2O = 49 : 1	14	80	33
4	DMF : H_2O = 49 : 1	0	0	0
5	DMSO : H_2O = 49 : 1	23	3	11
6	DCM	34	0	19
7	Ethyl acetate	0	19	quant.
8	Toluene	0	4	quant.

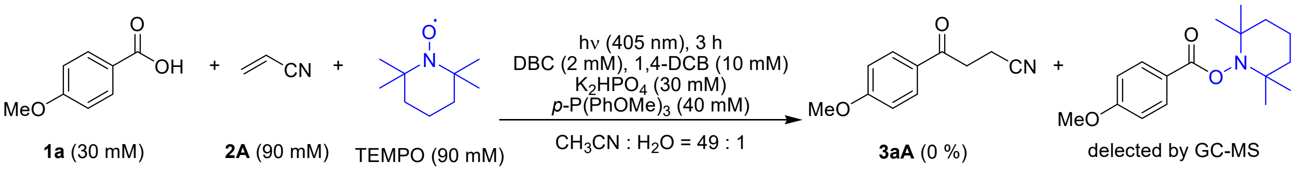
Reaction conditions: **1a** (0.3 mmol), **2A** (0.9 mmol), phosphine **I** (*p*-P(PhOMe)$_3$) (40 mM), DBC (0.02 mmol), 1,4-DCB (0.1 mmol), K_2HPO_4 (0.3 mmol), Solvent (10 mL), blue LEDs (405 nm), 25 °C, 3 h; The yield of the adduct **3aA**, the recovery of phosphine and the recovery of **1a** were determined by ^1H NMR.

S5. Mechanistic Investigations

Mechanistic experiments were conducted to probe radical pathways using TEMPO.

S5.1. Radical Trapping Experiments with TEMPO

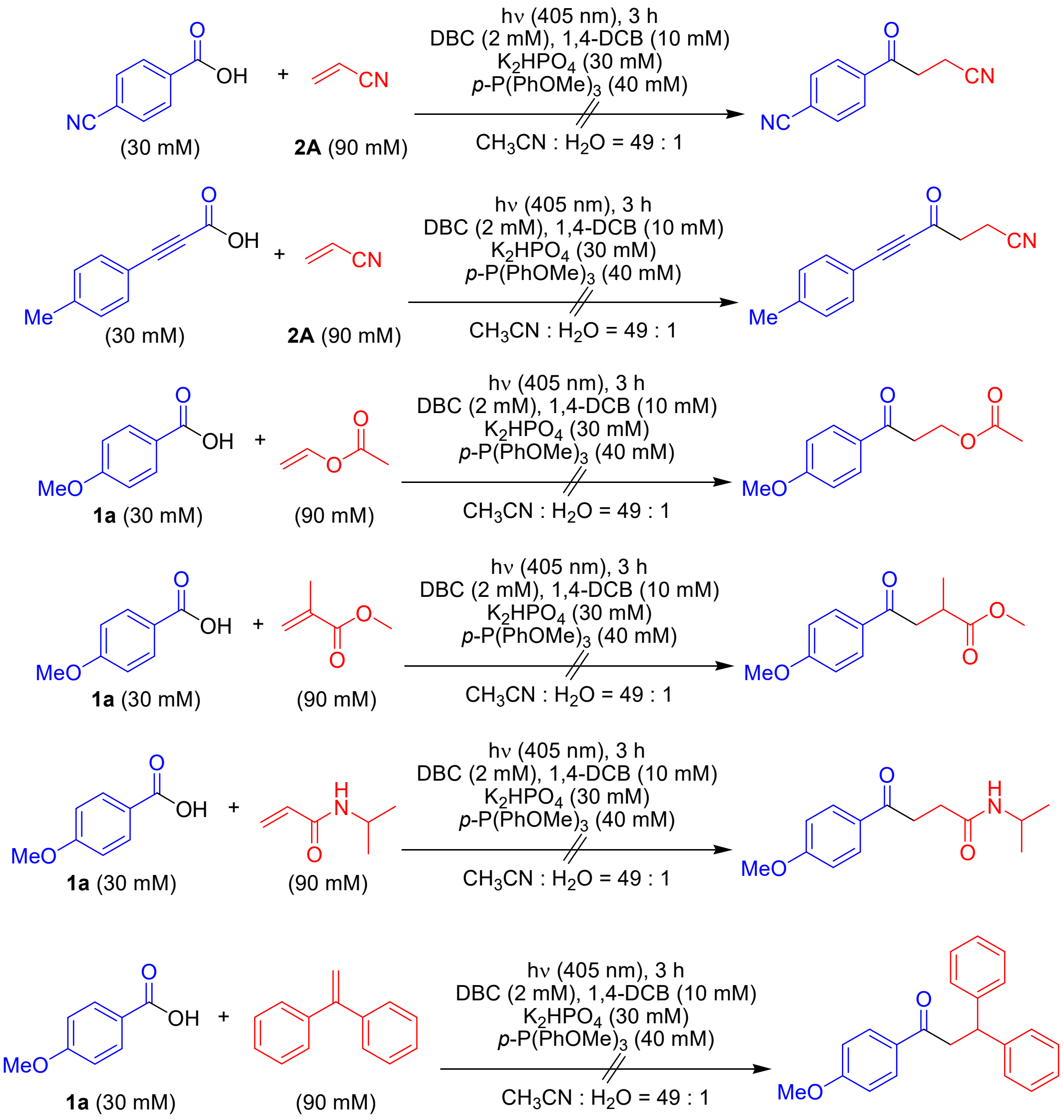
The photoreaction performed in the presence of TEMPO suppressed product formation and afforded TEMPO–adducts detectable by GC–MS, supporting a radical mechanism (Scheme S1).



Scheme S1. Radical trapping experiments with TEMPO

S6. Unsuccessful substrates and alkens

Under the optimized conditions, the photoreaction using the below−mentioned carboxylic acids and alkenes did not proceed to lead no formation of adducts.



Scheme S3. Unsuccessful substrates and alkenes.

S7. Characterization of Photoproducts

Adducts (**3aA**, **3bA**, **3cA**, **3hA**, **3iA**)[1S], (**3dA**, **3eA**, **3hA**, **3kA**, **3mA**)[2S], (**3lA**, **3aC**)[3S], **3aD**[4S], **3aE**[5S], **3aF**[6S], **3aH**[7S] and **4nA**[8S] have been previously reported. References in SI.

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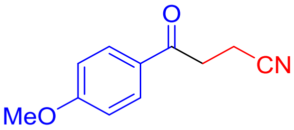
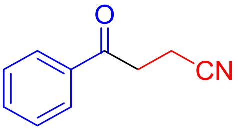
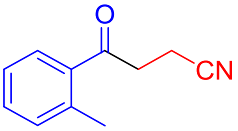


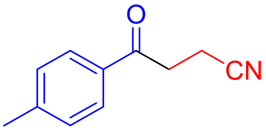
3aA: using hexane/EtOAc = 20:1 to 15:1 as the eluent, 0.0352 g, 96%, colorless oil, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.94 (d, J = 8.8 Hz, 2H), 7.01 (d, J = 8.7 Hz, 2H), 3.89 (s, 3H), 3.34 (t, J = 7.3 Hz, 2H), 2.77 (t, J = 7.3 Hz, 2H); ^{13}C{^{1}H} NMR (100 Hz, CDCl$_3$) δ 193.8, 164.1, 130.4, 129.7, 119.4, 114.0, 55.6, 33.9, 11.9.



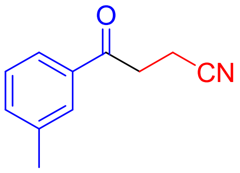
3bA: using hexane/EtOAc = 20:1 to 15:1 as the eluent, 0.0185 g, 66%, white solid, ^{1}H NMR (400 MHz, CDCl$_3$)δ 7.96 (d, J = 7.6 Hz, 2H), 7.64−7.61 (m,1H), 7.52−7.49 (m, 2H), 3.40 (t, J = 7.2 Hz, 2H), 2.79 (t, J = 7.2 Hz, 2H); ^{13}C{^{1}H} NMR (100 Hz, CDCl$_3$) δ 195.3, 135.6, 133.9, 128.9, 128.4, 119.2, 34.3, 11.8.



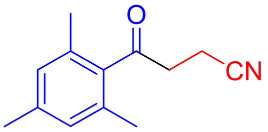
3cA: using hexane/EtOAc = 20:1 to 15:1 as the eluent, 0.0311 g, 92%, colorless oil, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.68 (d, J = 7.7 Hz, 1H), 7.45−7.41 (m, 1H), 7.32−7.27 (m, 2H), 3.31 (t, J = 7.0 Hz, 2H), 2.76 (t, J = 3.6 Hz, 2H), 2.53 (s, 3H); ^{13}C{^{1}H} NMR (100 Hz, CDCl$_3$) δ 198.4, 139.3, 135.7, 132.5, 132.4, 128.9, 126.0, 119.3, 36.5, 21.8, 12.0.



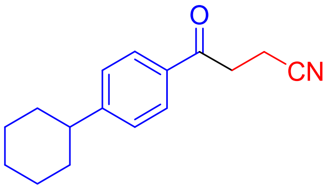
3dA: using hexane/EtOAc = 20:1 to 15:1 as the eluent, 0.0281 g, 83%, white solid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.85 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 3.36 (t, J = 7.2 Hz, 2H), 2.77 (t, J = 7.3 Hz, 2H), 2.43 (s, 3H) ; ^{13}C{^{1}H} NMR (100 Hz, CDCl$_3$) δ 195.0, 144.9, 133.2, 129.6, 128.2, 119.4, 34.1, 21.8, 11.8.



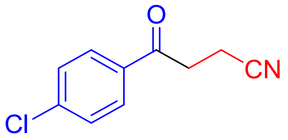
3eA: using hexane/EtOAc = 20:1 to 15:1 as the eluent, 0.0247 g, 73%, white solid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.76−7.73 (m, 2H), 7.44−7.36 (m, 2H), 3.37 (t, J = 7.2 Hz, 2H), 2.76 (t, J = 7.1 Hz, 2H), 2.42 (s, 3H) ; ^{13}C{^{1}H} NMR (100 Hz, CDCl$_3$) δ 195.6, 138.8, 135.7, 134.7, 128.8, 128.6, 125.3, 119.3, 34.3, 21.4, 11.8.



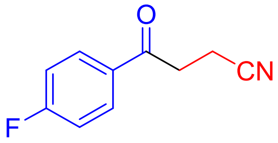
3fA: using hexane/EtOAc = 15:1 to 9:1 as the eluent, 0.0374 g, 93%, colorless oil, IR (neat, cm^{-1}) ; 2922, 2251, 1698, ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.86 (s, 2H), 3.04 (t, J = 7.0 Hz, 2H), 2.76 (t, J = 7.0 Hz, 2H), 2.29 (s, 3H), 2.19 (s, 6H) ; ^{13}C{^{1}H} NMR (100 Hz, CDCl$_3$) δ 205.9. 139.2, 137.8, 132.7, 128.7, 118.9, 39.8, 29.7, 19.1, 11.5. HRMS (DART) calced for (M + H)$^+$ $C_{13}H_{16}NO$, 202.1226; found, 202.1228.



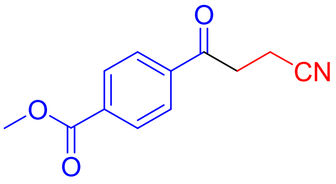
3gA: using hexane/EtOAc = 25:1 to 10:1 as the eluent, 0.0466 g, 88%, white solid, mp; 78−79°C; IR (KBr, cm^{-1}) ; 2924, 2252, 1692, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.88 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 3.36 (t, J = 7.3 Hz, 2H), 2.77 (t, J = 7.3 Hz, 2H), 2.60−2.55 (m, 1H), 1.88−1.86 (m, 4H), 1.79−1.76 (m, 1H), 1.45−1.13 (m, 4H), 1.31−1.25 (m, 1H) ; ^{13}C{^{1}H} NMR (100 Hz, CDCl$_3$) δ 195.0, 154.8, 133.5, 128.3, 127.4, 119.4, 44.8, 34.2, 34.1, 26.7, 26.0, 11.9. HRMS (FAB) calced for (M + H)$^+$ $C_{16}H_{20}NO$, 242.1539; found, 242.1538.



3hA: using hexane/EtOAc = 15:1 to 6:1 as the eluent, 0.0160 g, 42%, white solid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.90 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 3.36 (t, J = 7.2 Hz, 2H), 2.78 (t, J = 7.2 Hz, 2H) ; ^{13}C{^{1}H} NMR (100 Hz, CDCl$_3$) δ 194.2, 140.5, 133.9, 129.4, 129.3, 119.0, 34.3, 11.8.

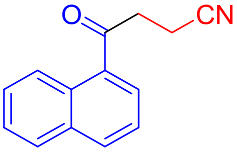


3iA: using hexane/EtOAc = 15:1 to 5:1 as the eluent, 0.0161 g, 64%, colorless oil, ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.00 (d, J = 8.1 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 3.37 (t, J = 7.1 Hz, 2H), 2.78 (t, J = 7.1 Hz, 2H) ; ^{13}C{^{1}H} NMR (100 Hz, CDCl$_3$) δ 193.8, 166.2 , (d, J = 254.6 Hz) 164.0, 132.1 (d, J = 2.9 Hz), 132.01, 130.8 (d, J = 9.4 Hz) , 119.2, 116.1 (d, J = 21.9 Hz) , 34.2, 11.8.

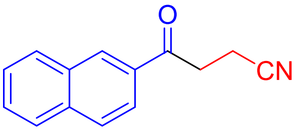


3jA: using hexane/EtOAc = as the eluent, 0.0161 g, 36%, white solid, mp; 95−96°C;

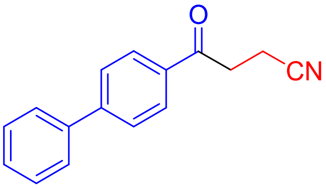
IR (KBr, cm^{-1}) ; 2923, 2248, 1721, 1695, ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.16 (d, *J* = 8.2 Hz, 2H), 8.02 (d, *J* = 8.3 Hz, 2H), 3.97 (s, 3H), 3.42 (t, *J* = 7.1 Hz, 2H), 2.80 (t, *J* = 7.1 Hz, 2H) ; ^{13}C{^{1}H} NMR (100 Hz, CDCl$_3$) δ 194.9, 166.0, 138.7, 134.7, 130.8, 130.1, 128.7, 128.0, 119.0, 52.6, 34.7, 11.8. HRMS (DART) calced for (M + H)$^+$ $C_{12}H_{12}NO_3$, 218.0811; found, 218.0801.



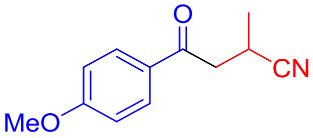
3kA: using hexane/EtOAc = 20:1 to 1:1 as the eluent, 0.0281 g, 68%, white solid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.73 (d, *J* = 8.5 Hz, 1H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.92−7.88 (m, 2H), 7.64−7.49 (m, 3H), 3.46 (t, *J* = 7.2 Hz, 2H), 2.83 (t, *J* = 7.1 Hz, 2H); ^{13}C{^{1}H} NMR (100 Hz, CDCl$_3$) δ 198.8, 134.0, 133.9, 133.6, 128.6, 128.6, 128.5, 126.8, 125.7, 124.3, 119.3.



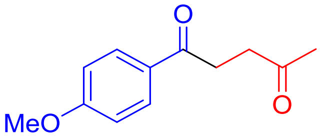
3lA: using hexane/EtOAc = 20:1 to 1:1 as the eluent, 0.0238 g, 56%, white solid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.47 (s, 1H), 8.03−7.89 (m, 4H), 7.66−7.57 (m, 2H), 3.54 (t, *J* = 7.3 Hz, 2H), 2.84 (t, *J* = 7.2 Hz, 2H); ^{13}C{^{1}H} NMR (100 Hz, CDCl$_3$) δ 195.3, 135.9, 133.0, 132.4, 130.0, 129.7, 129.0, 128.9, 127.9, 127.2, 123.5, 119.3, 34.4, 12.0.



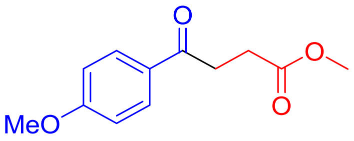
3mA: using hexane/EtOAc = 15:1 to 5:1 as the eluent, 0.0266 g, 53%, white solid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.04 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 7.9 Hz, 2H), 7.51−7.41 (m, 3H), 3.43 (t, *J* = 7.2 Hz, 2H), 2.81 (t, *J* = 7.3 Hz, 2H); ^{13}C{^{1}H} NMR (100 Hz, CDCl$_3$) δ 194.0, 146.7, 139.6, 134.3, 129.1, 128.7, 128.5, 127.5, 127.3, 119.3, 34.3, 11.9.



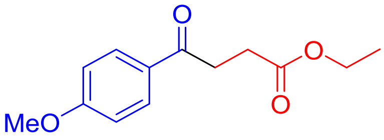
3aB: using hexane/EtOAc = 20:1 to 2:1 as the eluent, 0.0212 g, 62%, colorless oil, IR (neat, cm^{-1}); 2938, 2242, 1673, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.93 (d, *J* = 8.6 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 2H), 3.88 (s, 3H), 3.39−3.29 (m, 2H), 3.20−3.13 (m, 1H), 1.42 (d, *J* = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (100 Hz, CDCl$_3$) δ 193.7, 164.1, 130.4, 129.0, 122.8, 114.0, 55.6, 41.9, 20.6, 18.0. HRMS (DART) calced for (M + H)$^+$ $C_{12}H_{14}NO_2$, 204.1019; found, 204.1017.



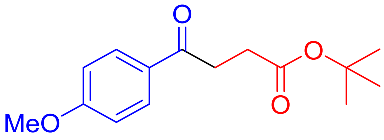
3aC: using hexane/EtOAc = 20:1 to 1:1 as the eluent, 0.0235 g, 70%, white solid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.96 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H), 3.23 (t, *J* = 6.3 Hz, 2H), 2.86 (t, *J* = 6.3 Hz, 2H), 2.25 (s, 3H); ^{13}C{^{1}H} NMR (100 Hz, $CDCl_3$) δ 207.6, 197.0, 163.5, 130.3, 129.7, 113.7, 55.5, 37.1, 32.0, 30.1.



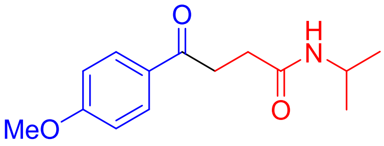
3aD: using hexane/EtOAc = 20:1 to 2:1 as the eluent, 0.0160 g, 64%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 3.87 (s, 3H), 3.71 (s, 3H), 3.28 (t, *J* = 6.6 Hz, 2H), 2.76 (t, *J* = 6.6 Hz, 2H) ; ^{13}C{^{1}H} NMR (100 Hz, $CDCl_3$) δ 196.6, 173.6, 163.6, 130.3, 129.7, 113.8, 55.5, 51.8, 33.0, 28.1.



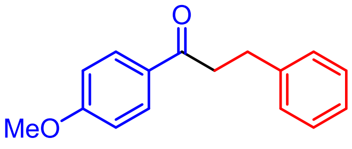
3aE: using hexane/EtOAc = 20:1 to 3:1 as the eluent, 0.0159 g, 54%, colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.97 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 4.19−4.13 (m, 2H), 3.87 (s, 3H), 3.27 (t, *J* = 6.7 Hz, 2H), 2.74 (t, *J* = 6.7 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H) ; ^{13}C{^{1}H} NMR (100 Hz, $CDCl_3$) δ 196.7, 173.1, 163.6, 130.3, 129.8, 113.8, 60.6, 55.5, 33.0, 28.4, 14.2.



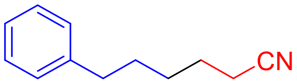
3aF: using hexane/EtOAc = 20:1 to 3:1 as the eluent, 0.0121 g, 46%, white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 3.87 (s, 3H), 3.21 (t, *J* = 6.7 Hz, 2H), 2.67 (t, *J* = 6.7 Hz, 2H), 1.45 (s, 9H) ; ^{13}C{^{1}H} NMR (100 Hz, $CDCl_3$) δ 196.9, 172.3, 163.5, 132.8, 130.3, 129.9, 117.0, 116.7, 113.7, 80.5, 55.5, 33.1, 29.6, 28.1.



3aG: using hexane/EtOAc = 20:1 to 2:1 as the eluent, 0.0134 g, 48%, white solid, mp; 111−112°C; IR (KBr, cm^{-1}) ; 3300, 2933, 1673, 1664, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.3 Hz, 2H), 5.64 (s, 1H), 4.10−3.83 (m, 1H), 3.87 (s, 3H), 3.31 (t, *J* = 6.5 Hz, 2H), 2.56 (t, *J* = 6.6 Hz, 2H), 1.16−1.14 (m, 6H) ; ^{13}C{^{1}H} NMR (100 Hz, $CDCl_3$) δ 197.7, 171.4, 130.4, 129.7, 113.8, 55.5, 41.4, 33.8, 30.7, 22.8. HRMS (DART) calced for $(M + H)^+$ $C_{14}H_{20}NO_3$, 250.1438; found, 250.1440.

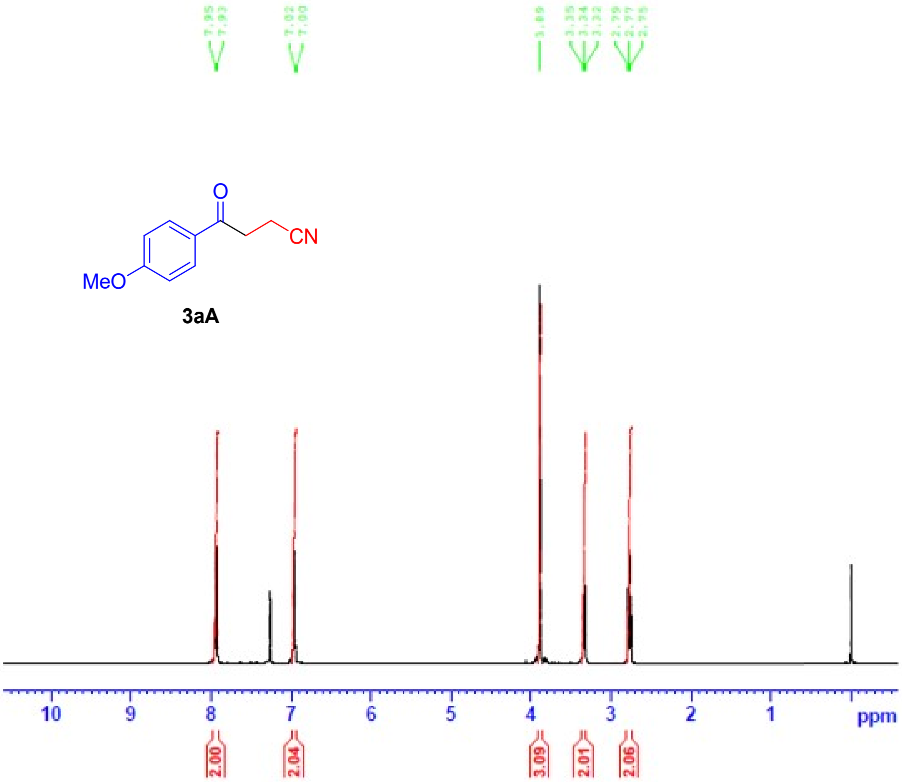


3aH: using hexane/EtOAc = 30:1 to 25:1 as the eluent, 0.0202 g, 28%, white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.6 Hz, 2H), 7.32−7.21 (m, 5H), 6.93 (d, *J* = 8.6 Hz, 2H), 3.87 (s, 3H), 3.26 (t, *J* = 7.7 Hz, 2H), 3.06 (t, *J* = 7.7 Hz, 2H); ^{13}C{^{1}H} NMR (100 Hz, $CDCl_3$) δ 197.9, 163.5, 141.5, 130.3, 130.0, 128.6, 128.5, 126.1, 113.8, 55.5, 40.2, 30.4.

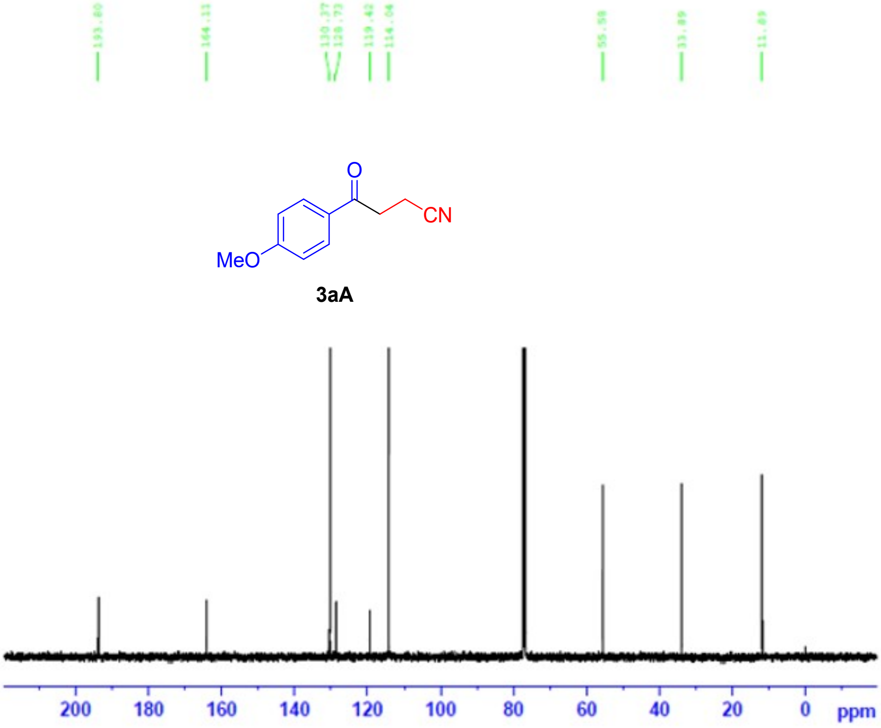

4nA: using hexane/EtOAc = 20:1 to 2:1 as the eluent, 0.0252 g, 54%, white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.25 (m, 2H), 7.18 (m, 3H), 2.63 (t, *J* = 7.6 Hz, 2H), 2.33 (t, *J* = 7.1 Hz, 2H), 1.70−1.57 (m, 4H), 1.53−1.47 (m, 2H) ; $^{13}C\{^1H\}$ NMR (100 Hz, $CDCl_3$) δ 142.0, 128.4, 128.3, 125.9, 119.8, 35.6, 30.6, 28.3, 17.1.

S8. ^{1}H and ^{13}C{^{1}H} NMR Spectra

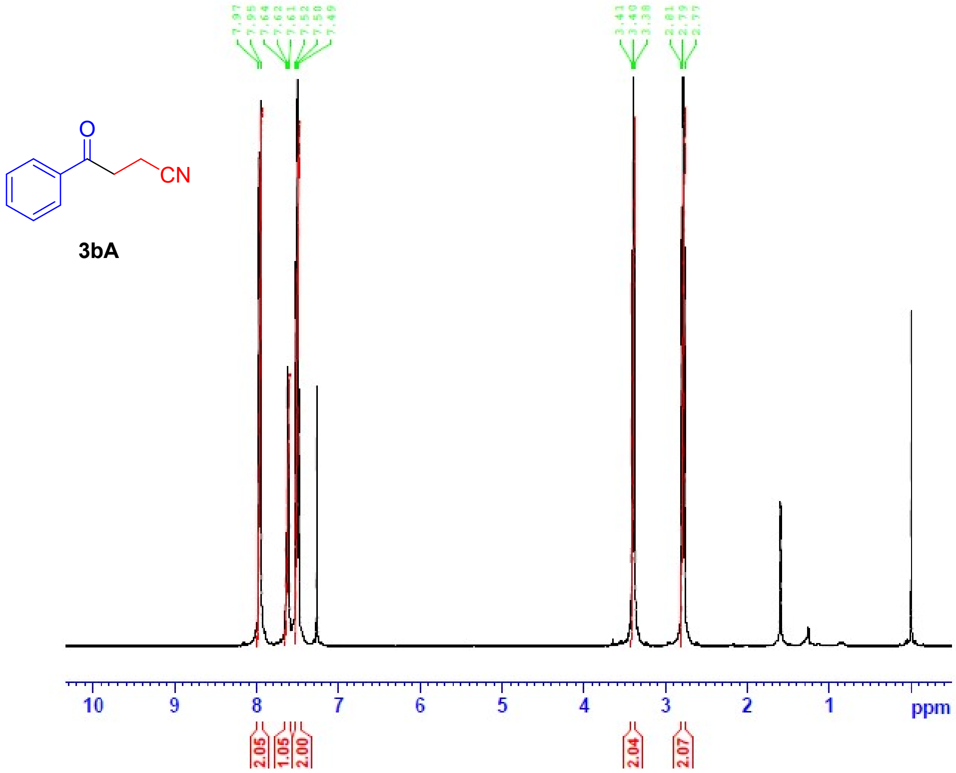
^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3aA**



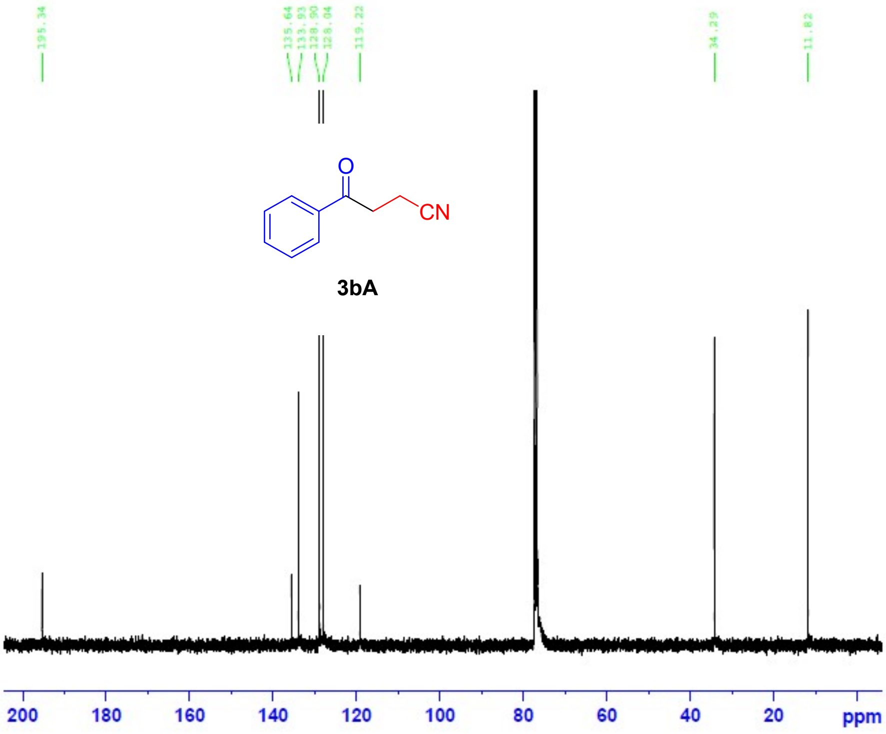
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectra for compound **3aA**



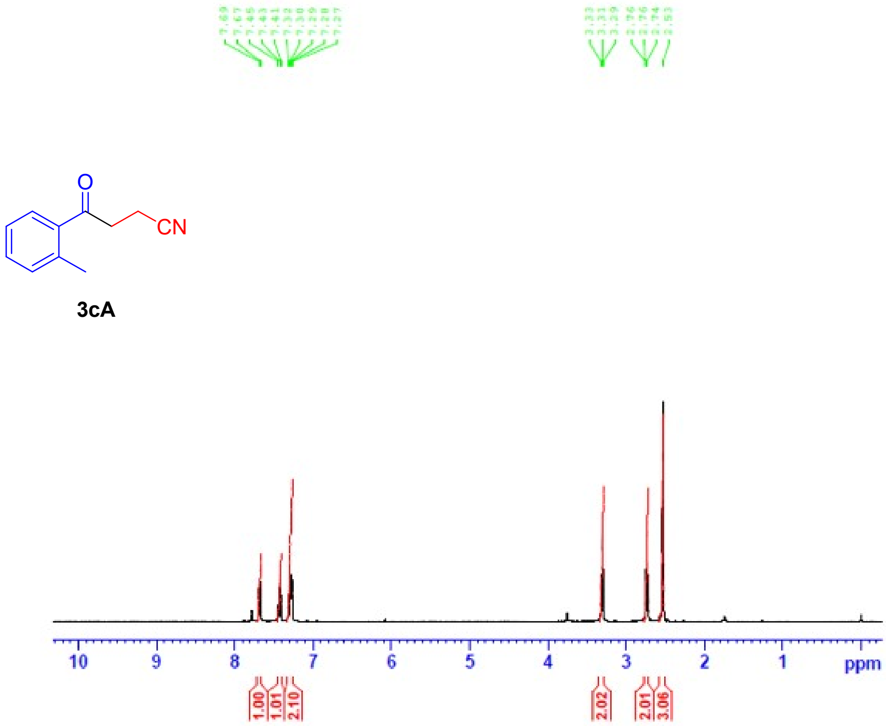
^1H NMR (400 MHz, $CDCl_3$) spectra for compound **3bA**



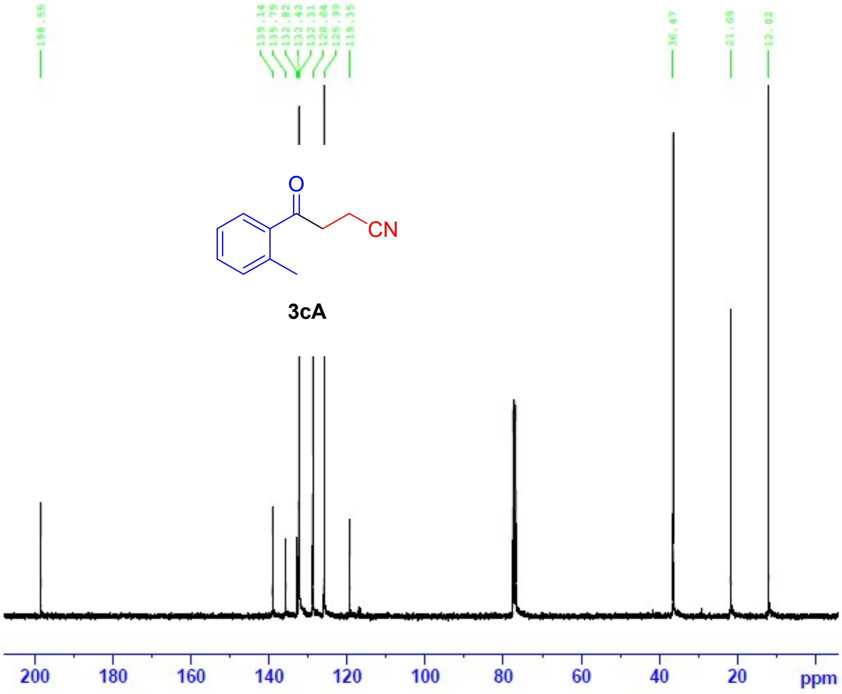
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectra for compound **3bA**



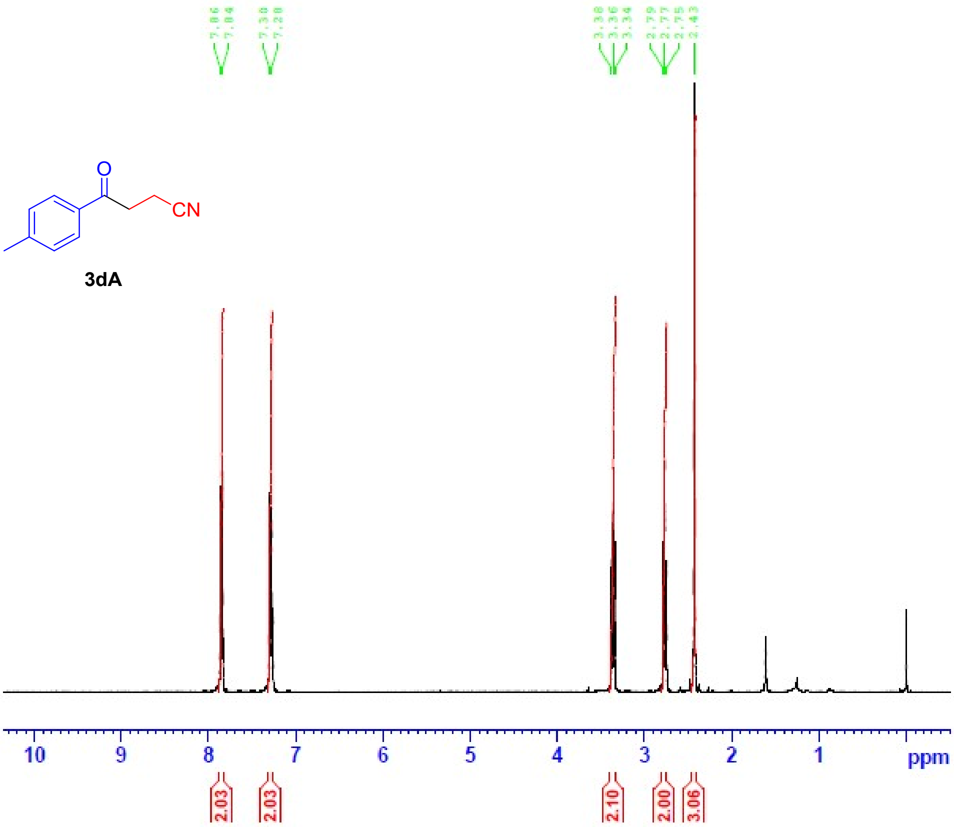
^{1}H NMR (400 MHz, CDCl$_3$) spectra for compound **3cA**



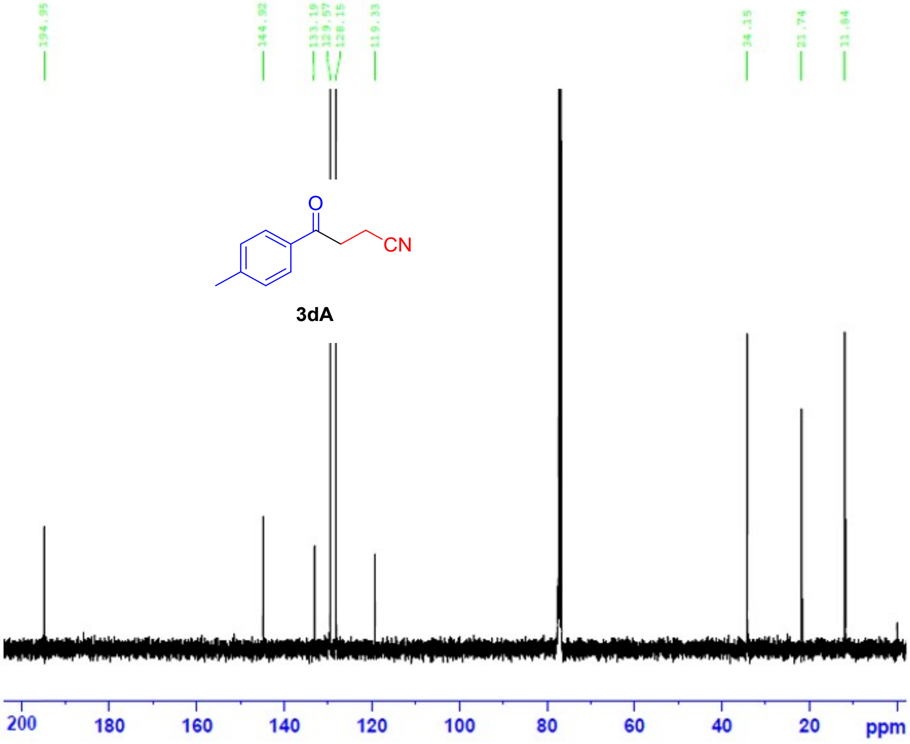
^{13}C{^{1}H } NMR (100 MHz, CDCl$_3$) spectra for compound **3cA**



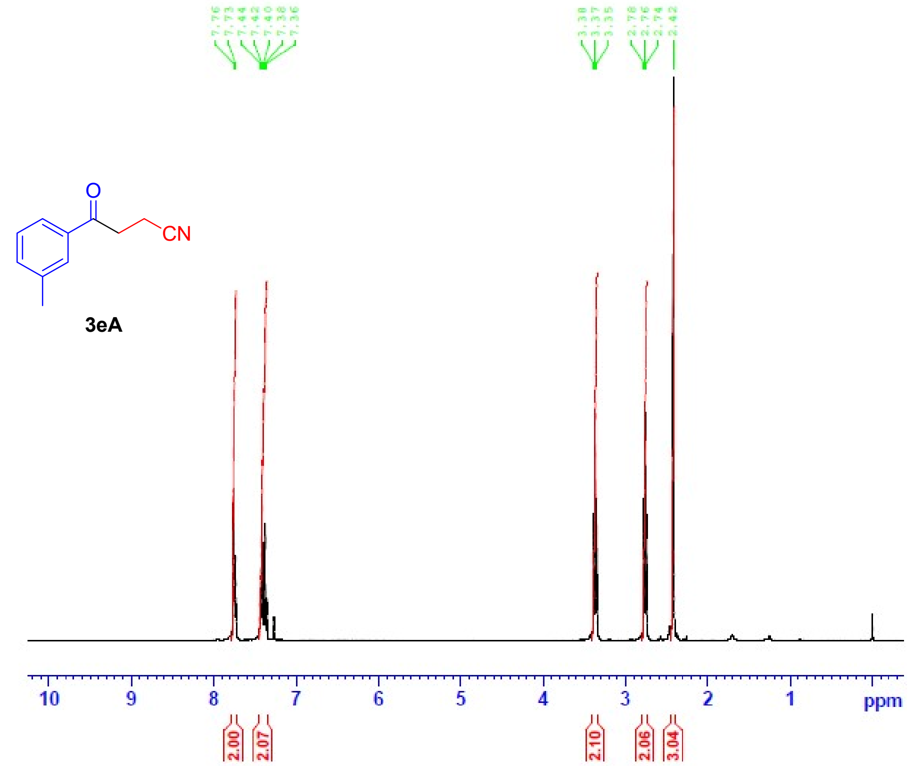
^{1}H NMR (400 MHz, CDCl$_3$) spectra for compound **3dA**



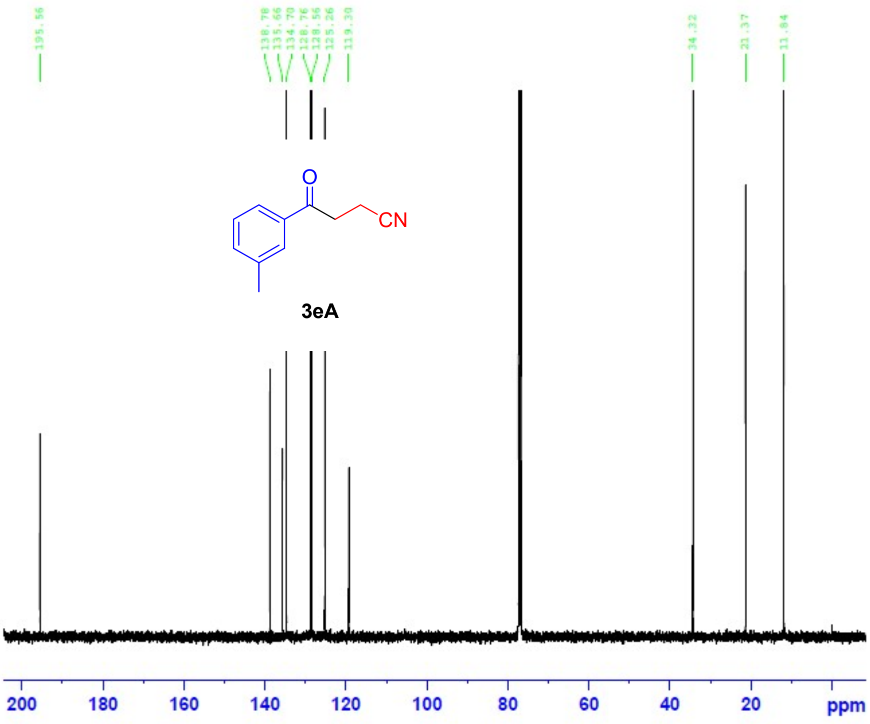
^{13}C{^{1}H } NMR (100 MHz, CDCl$_3$) spectra for compound **3dA**



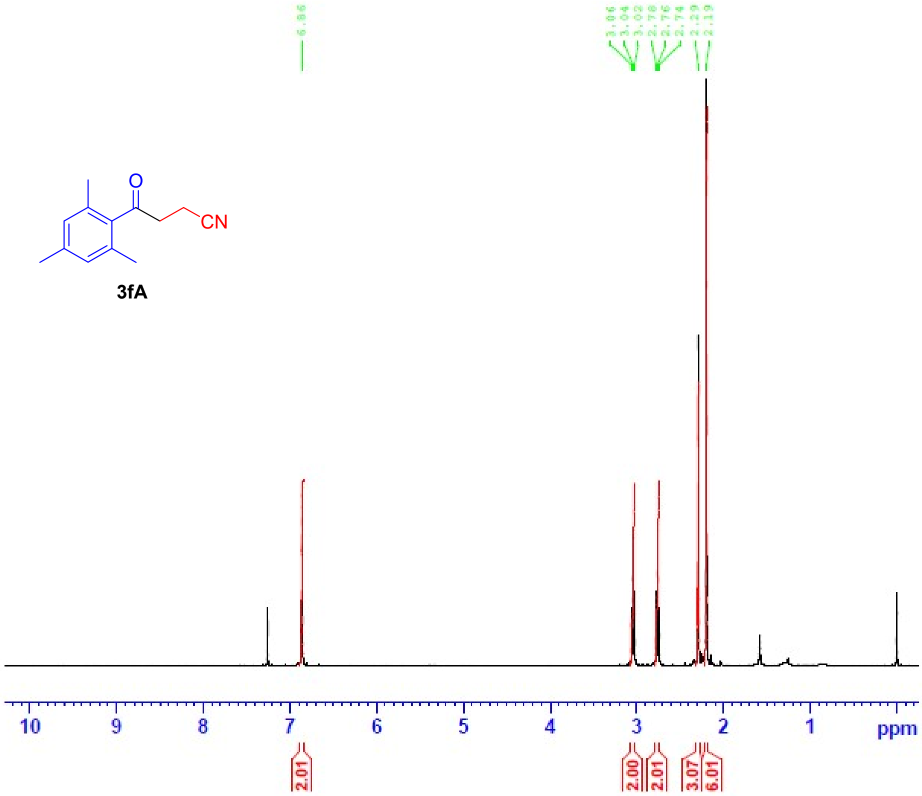
^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3eA**



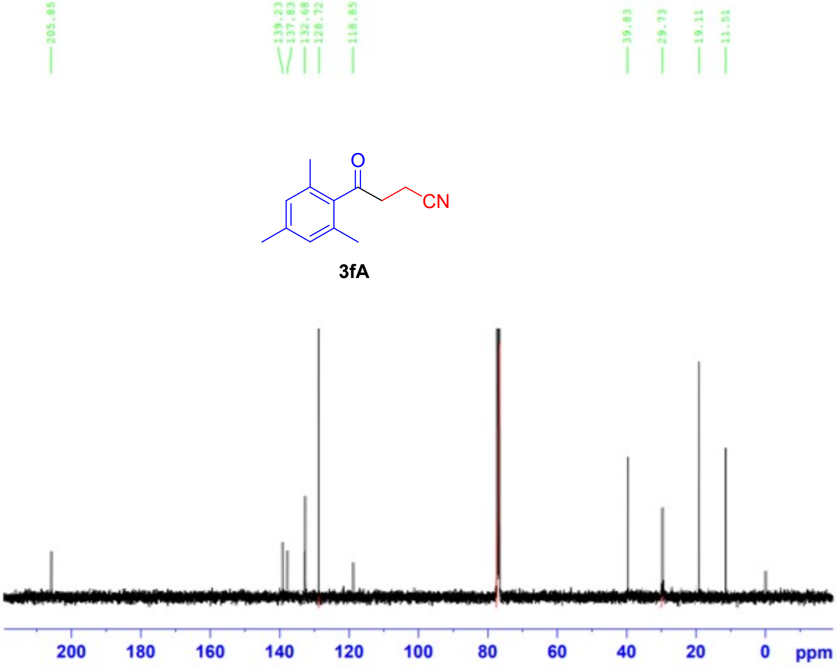
^{13}C{^{1}H } NMR (100 MHz, $CDCl_3$) spectra for compound **3eA**



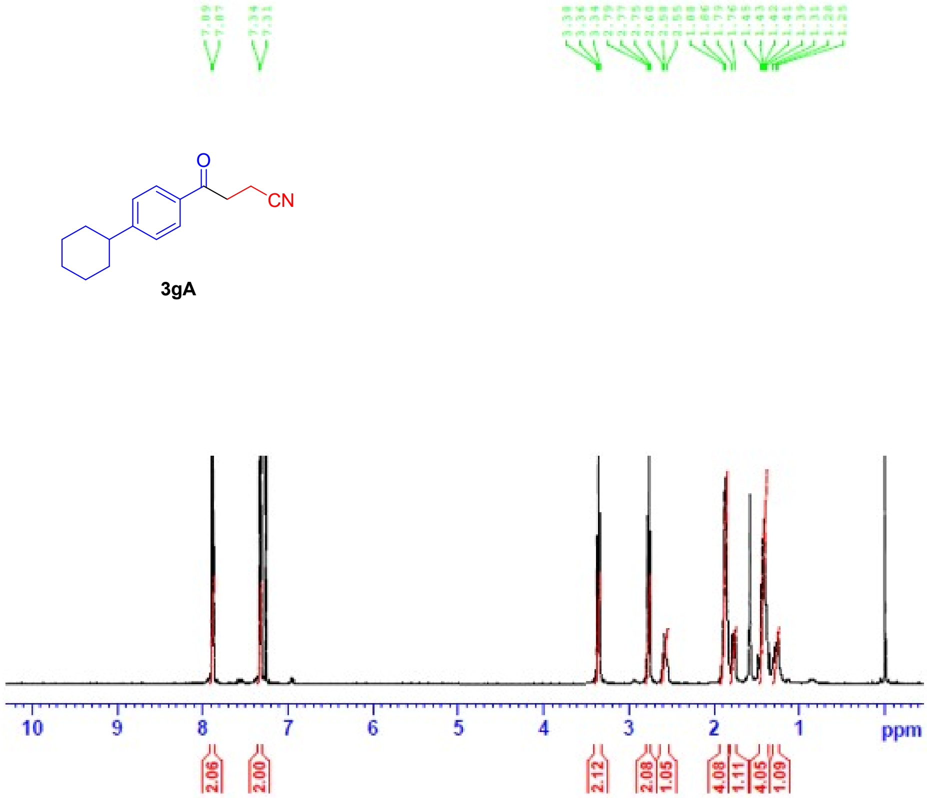
^{1}H NMR (400 MHz, CDCl$_3$) spectra for compound **3fA**



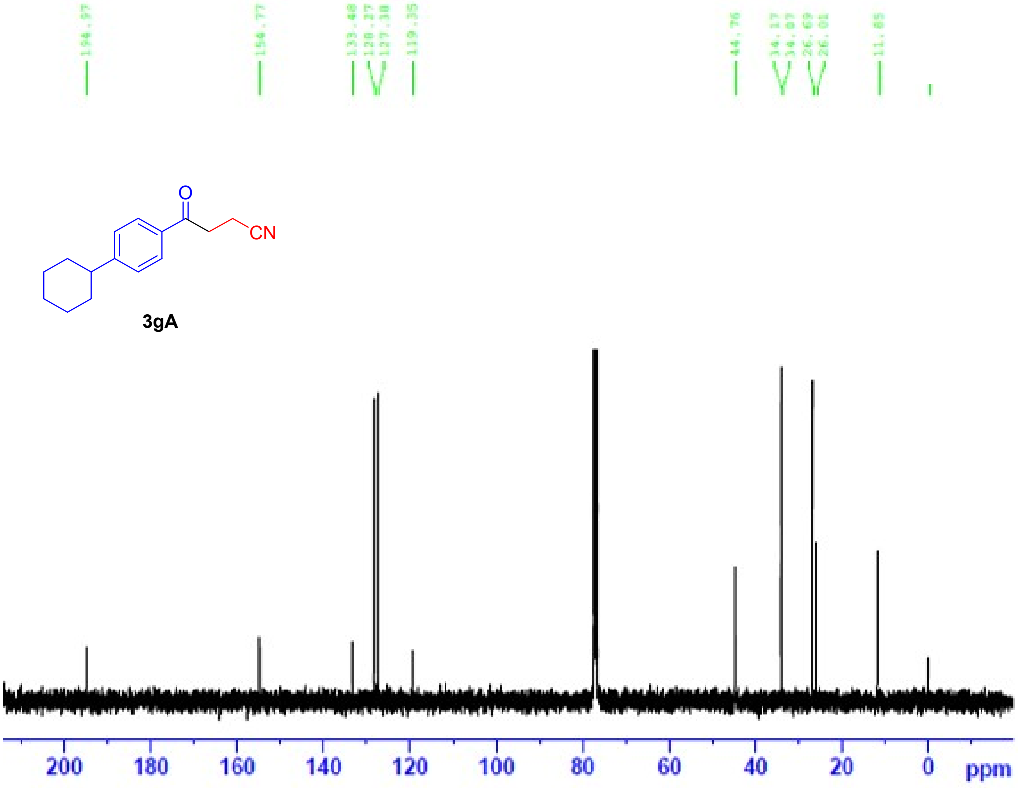
^{13}C{^{1}H } NMR (100 MHz, CDCl$_3$) spectra for compound **3fA**



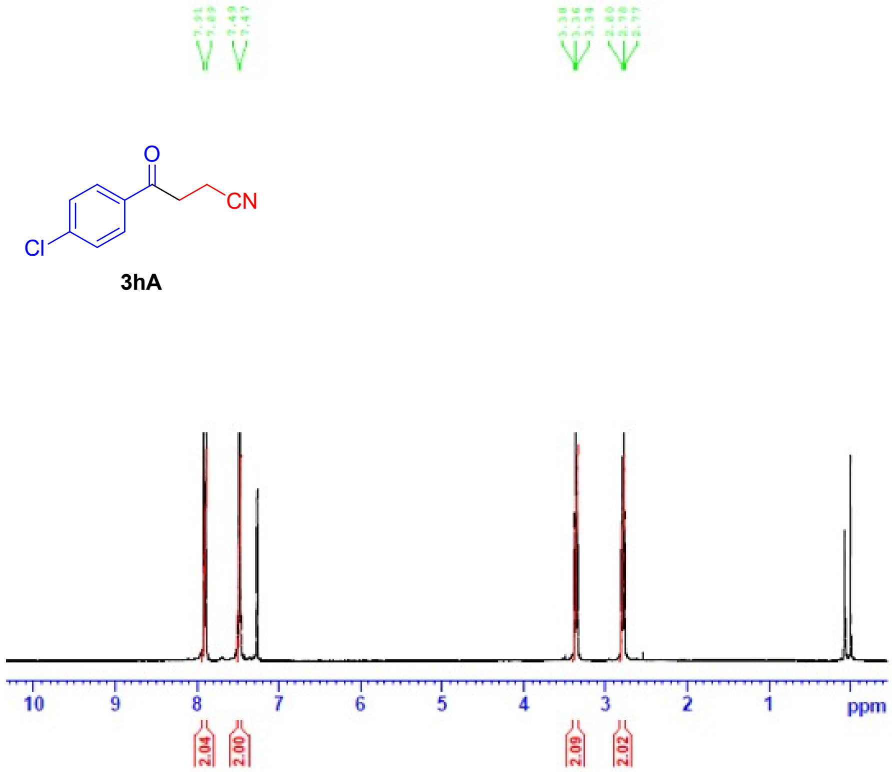
^{1}H NMR (400 MHz, CDCl$_3$) spectra for compound **3gA**



^{13}C{^{1}H } NMR (100 MHz, CDCl$_3$) spectra for compound **3gA**

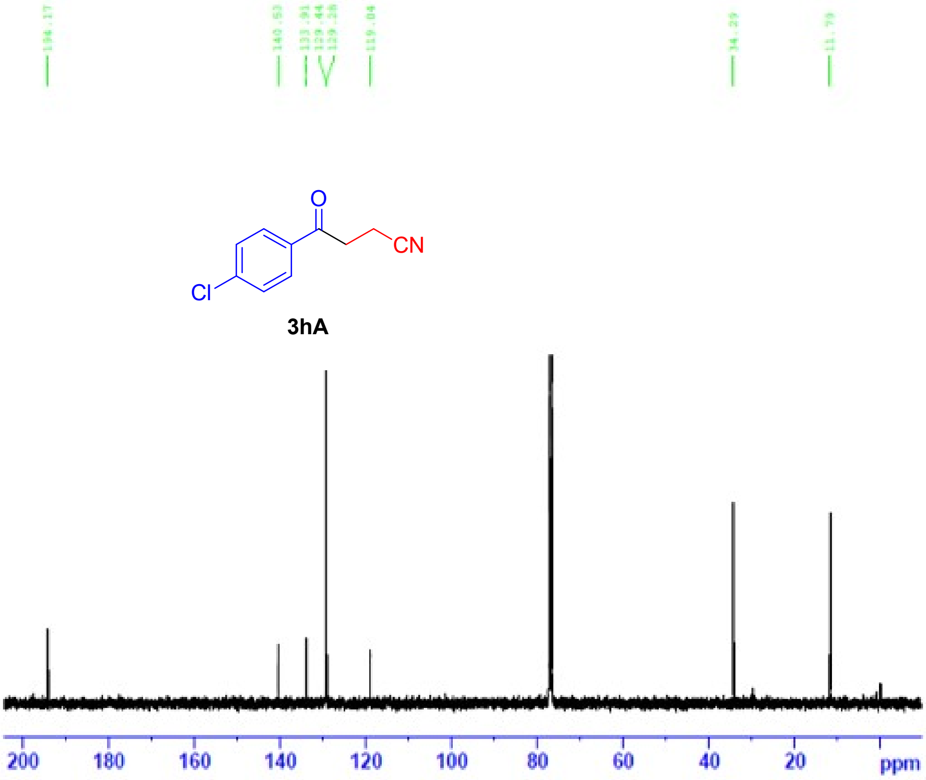


^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3hA**



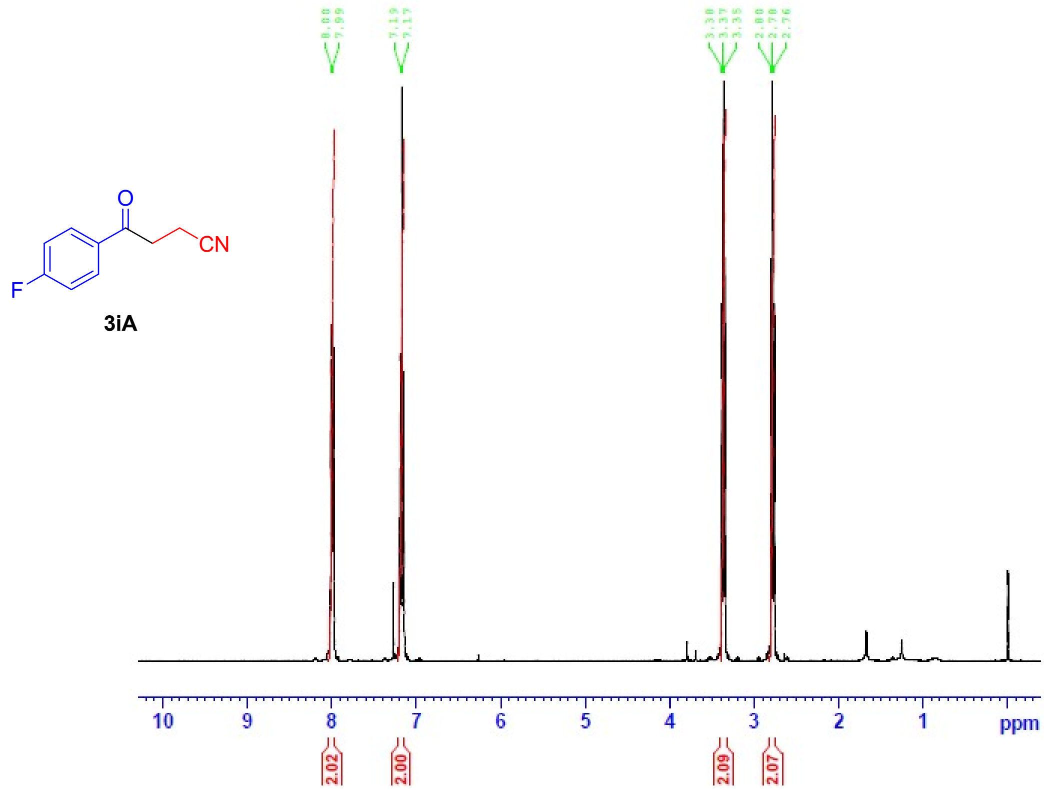
3hA

^{13}C{^{1}H } NMR (100 MHz, $CDCl_3$) spectra for compound **3hA**

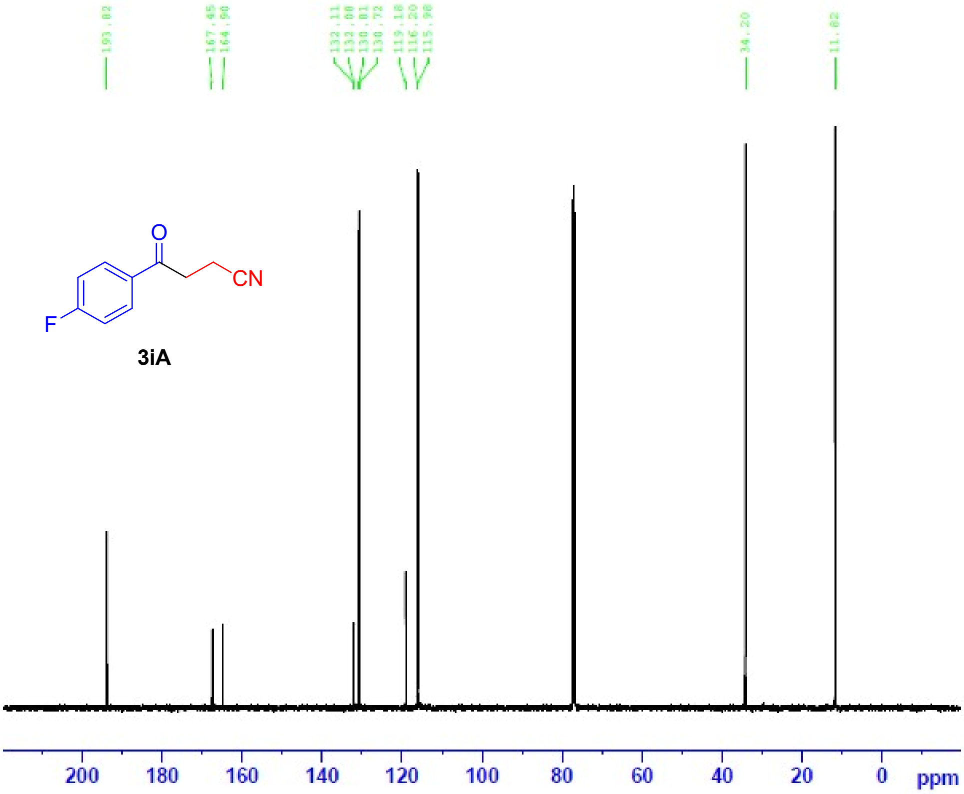


3hA

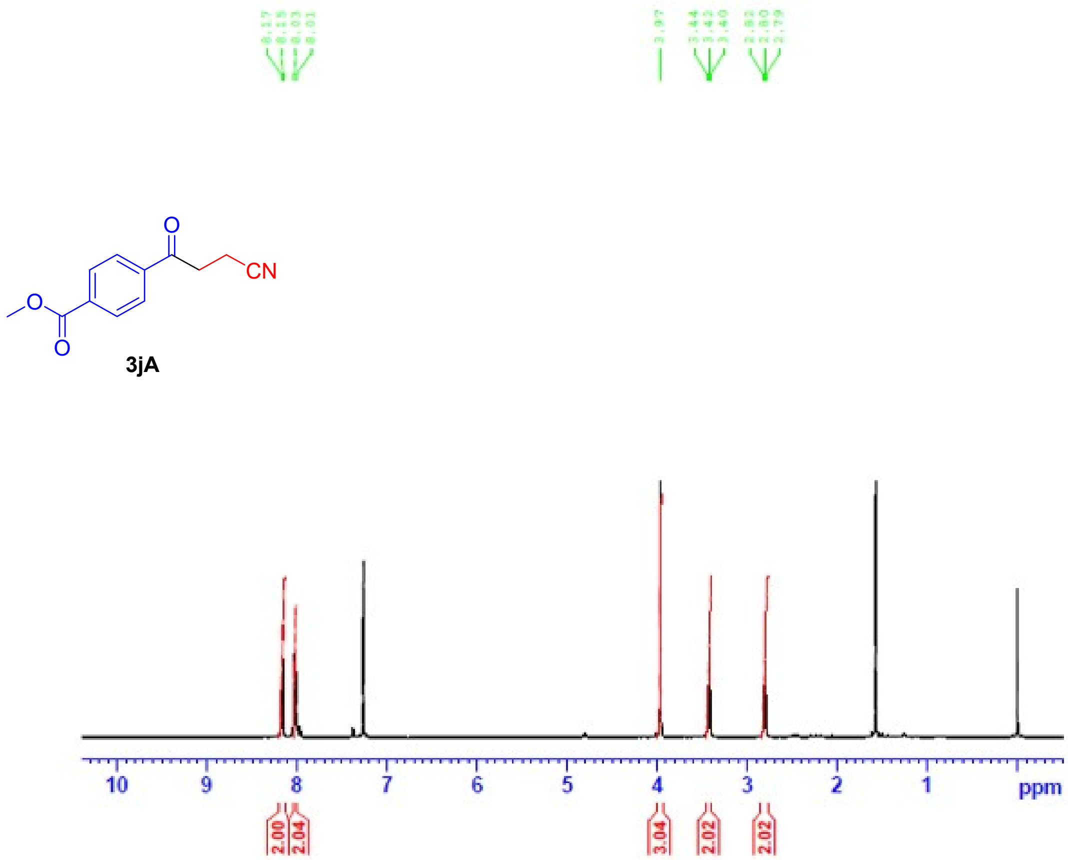
^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3iA**



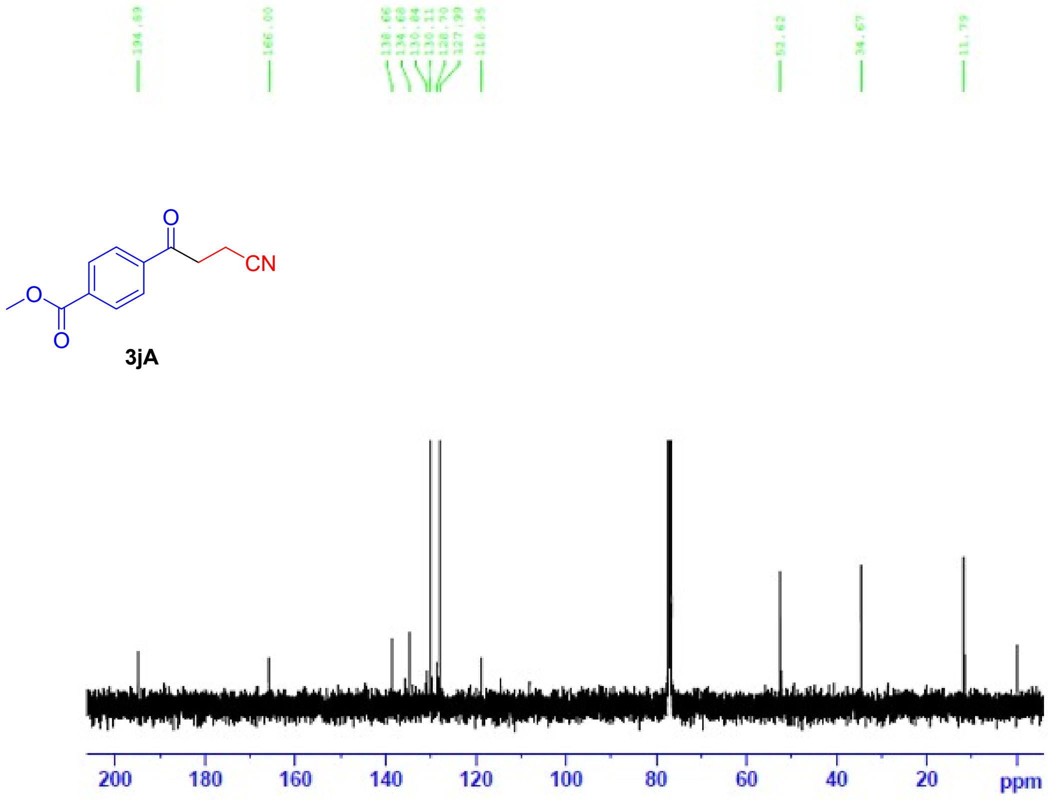
^{13}C{^{1}H } NMR (100 MHz, $CDCl_3$) spectra for compound **3iA**



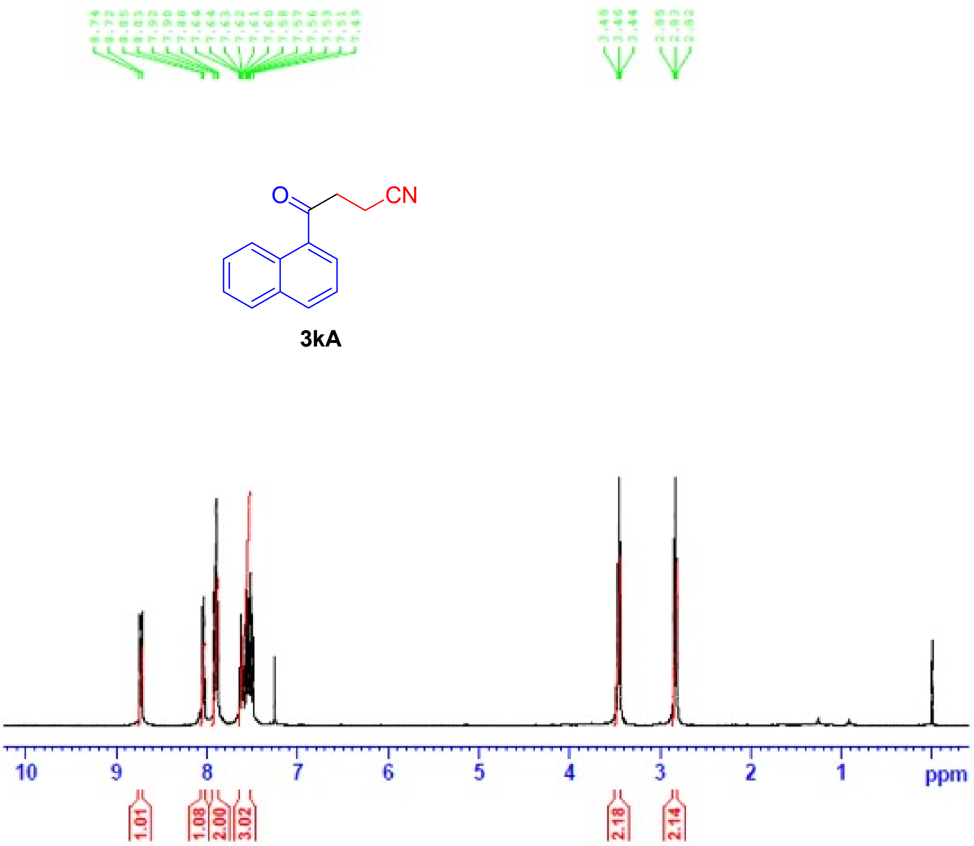
^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3jA**



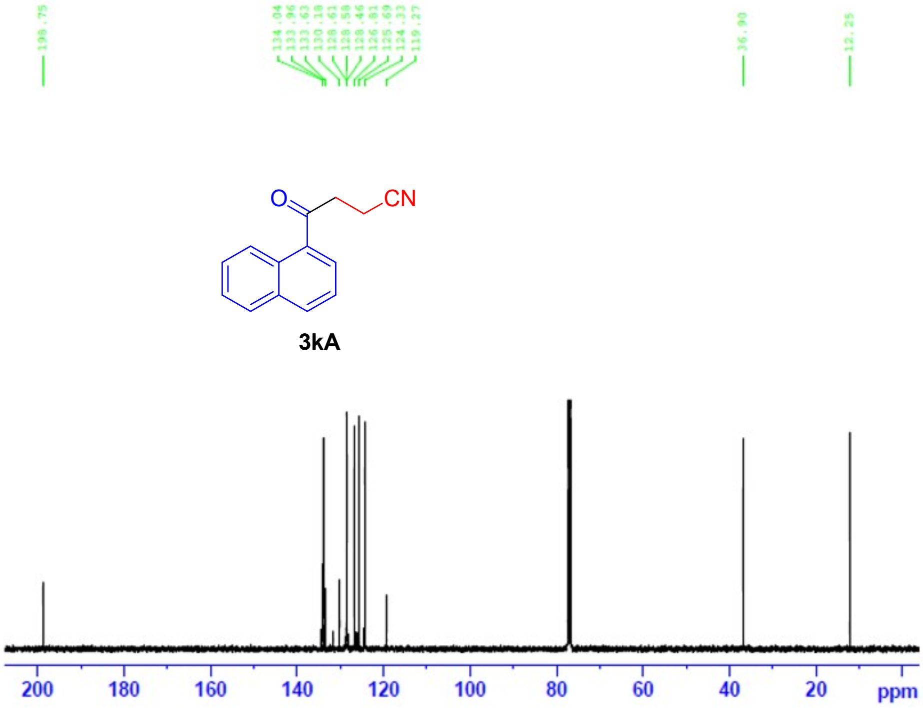
^{13}C{^{1}H } NMR (100 MHz, $CDCl_3$) spectra for compound **3jA**



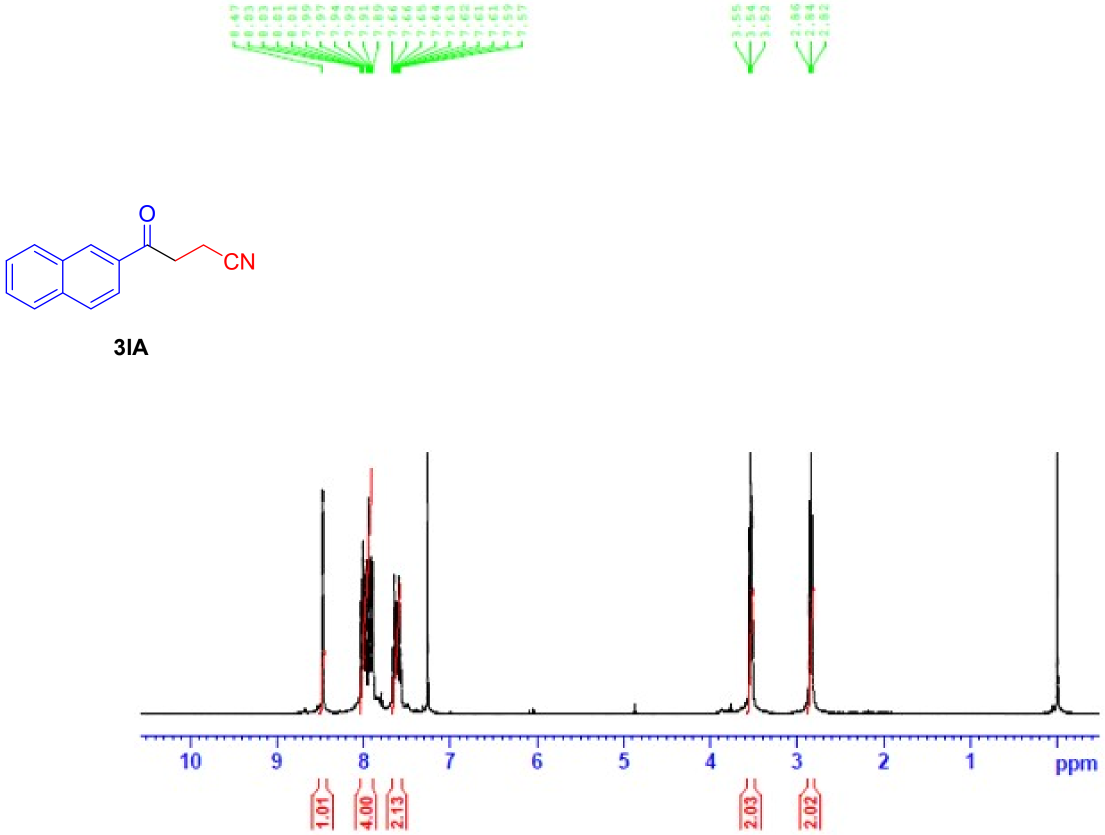
^{1}H NMR (400 MHz, CDCl$_3$) spectra for compound **3kA**



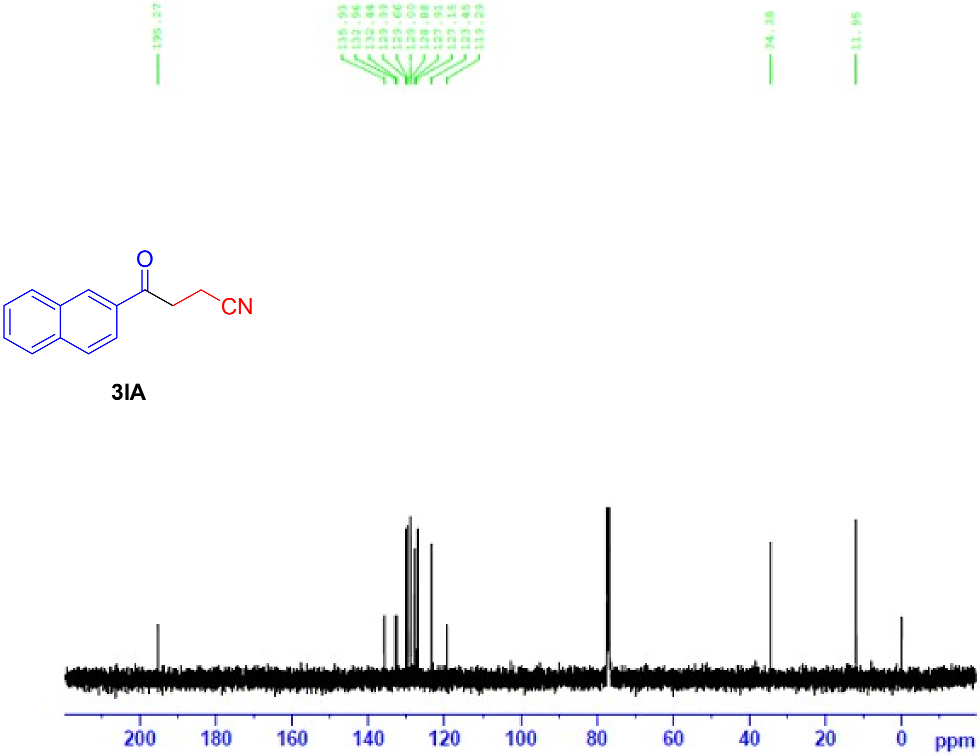
^{13}C{^{1}H } NMR (100 MHz, CDCl$_3$) spectra for compound **3kA**



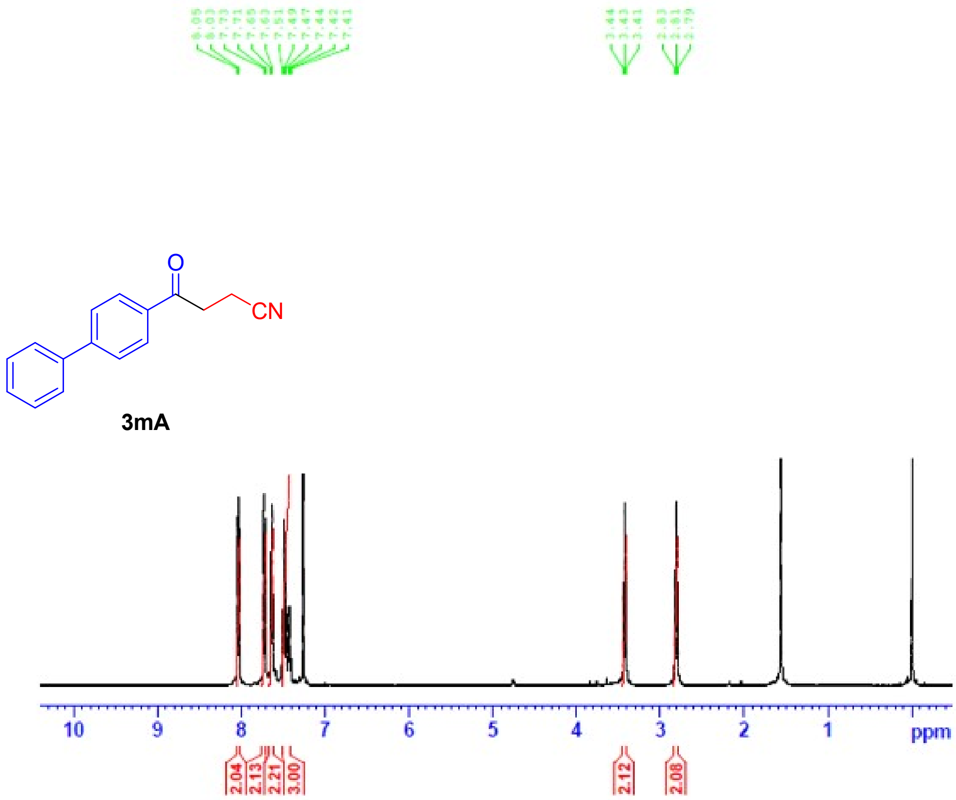
^{1}H NMR (400 MHz, CDCl$_3$) spectra for compound **3IA**



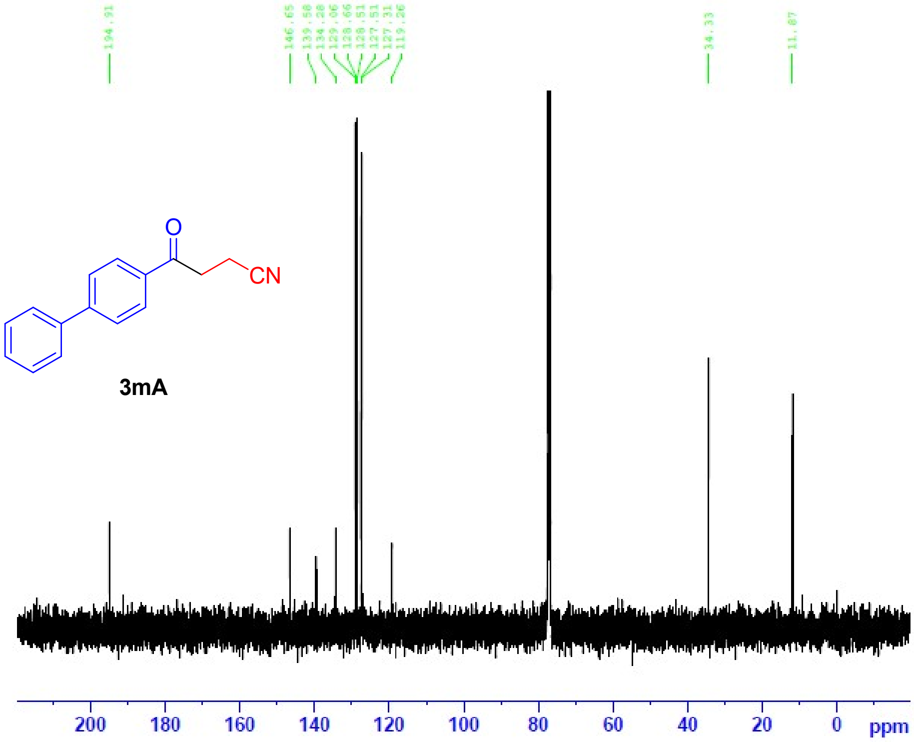
^{13}C{^{1}H } NMR (100 MHz, CDCl$_3$) spectra for compound **3IA**



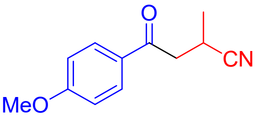
^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3mA**



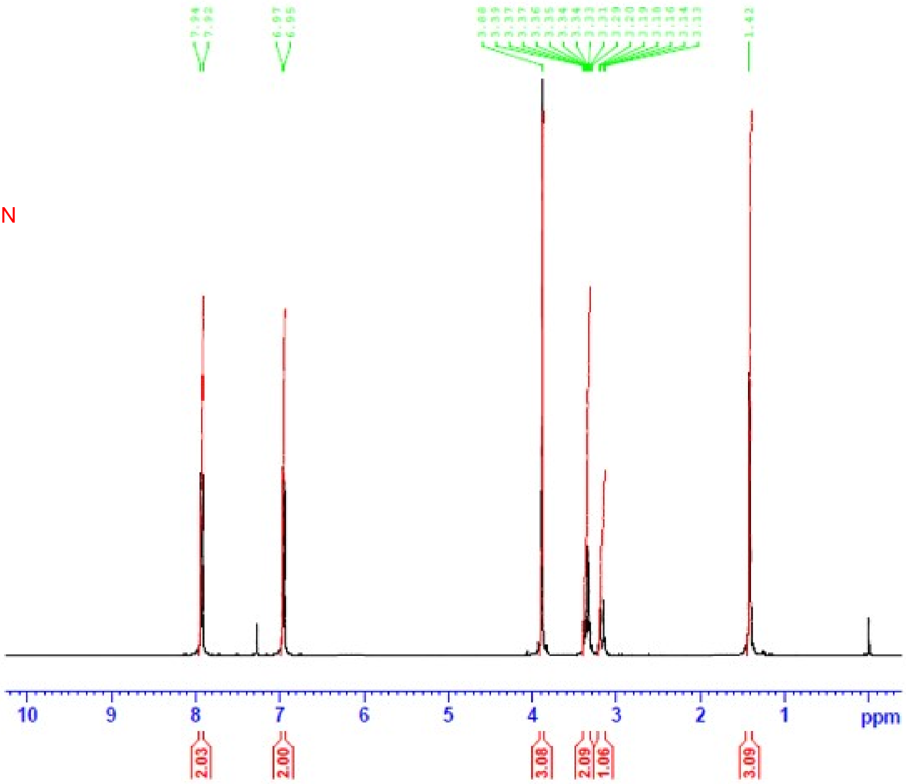
^{13}C{^{1}H } NMR (100 MHz, $CDCl_3$) spectra for compound **3mA**



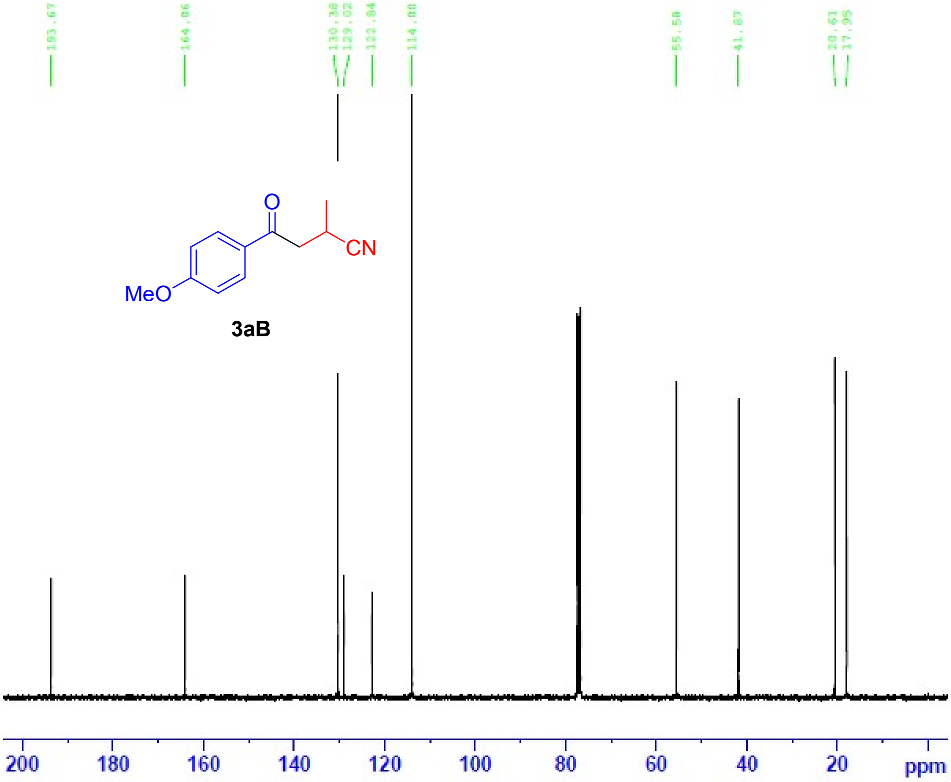
^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3aB**



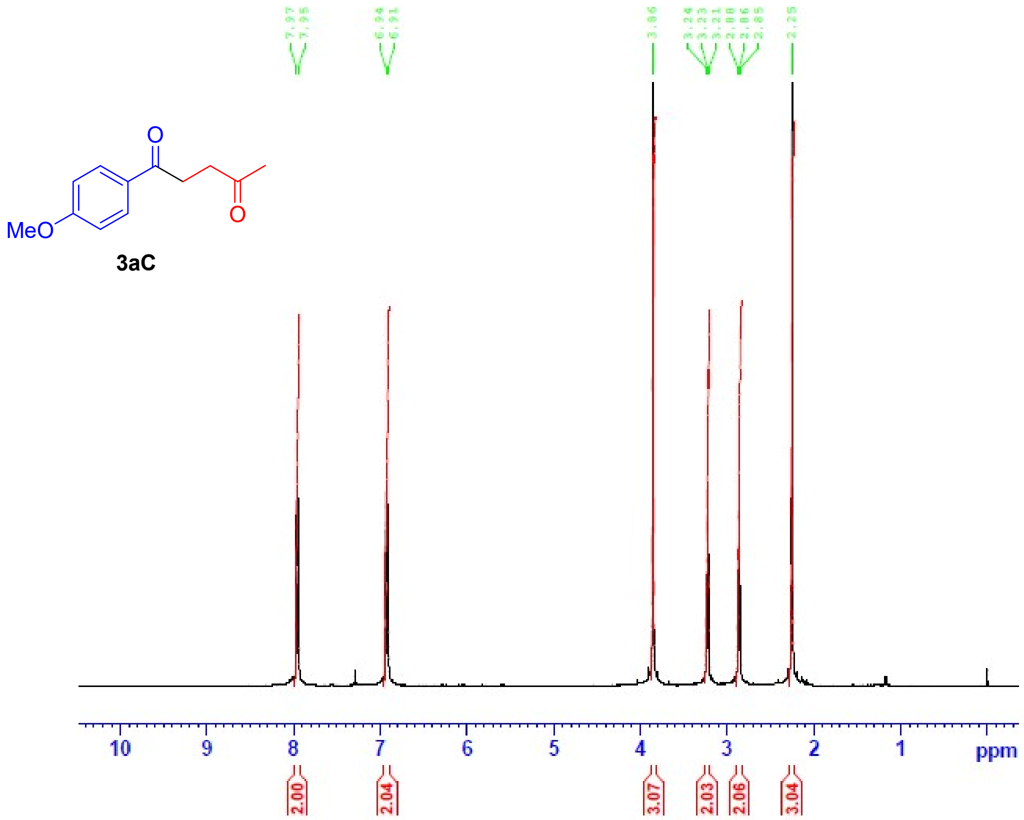
3aB



^{13}C{^{1}H } NMR (100 MHz, $CDCl_3$) spectra for compound **3aB**

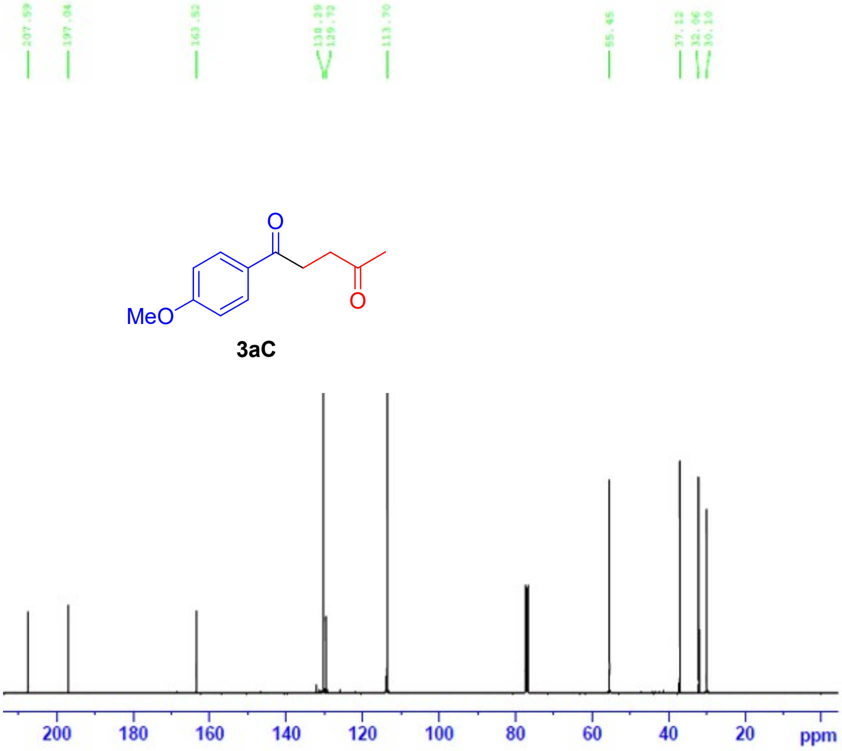


^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3aC**



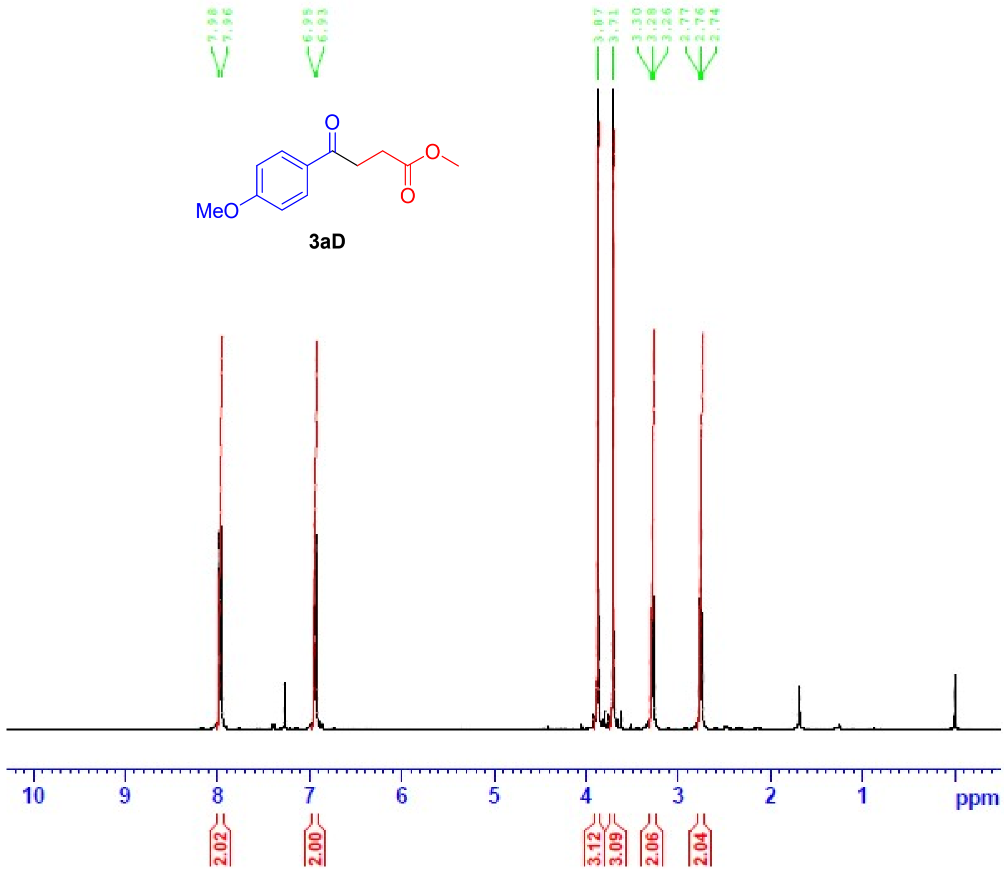
3aC

^{13}C{^{1}H } NMR (100 MHz, $CDCl_3$) spectra for compound **3aC**

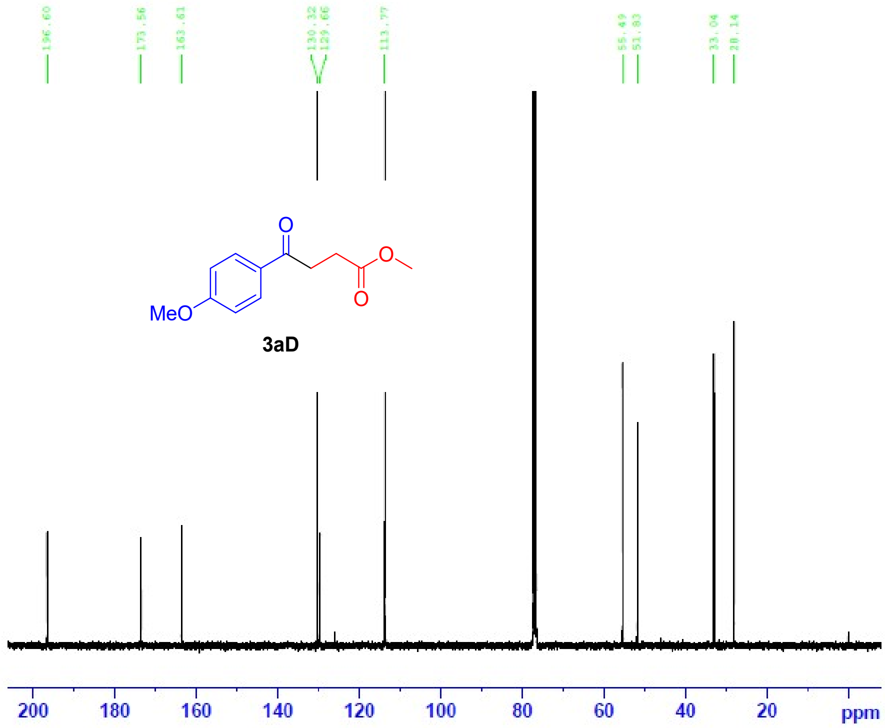


3aC

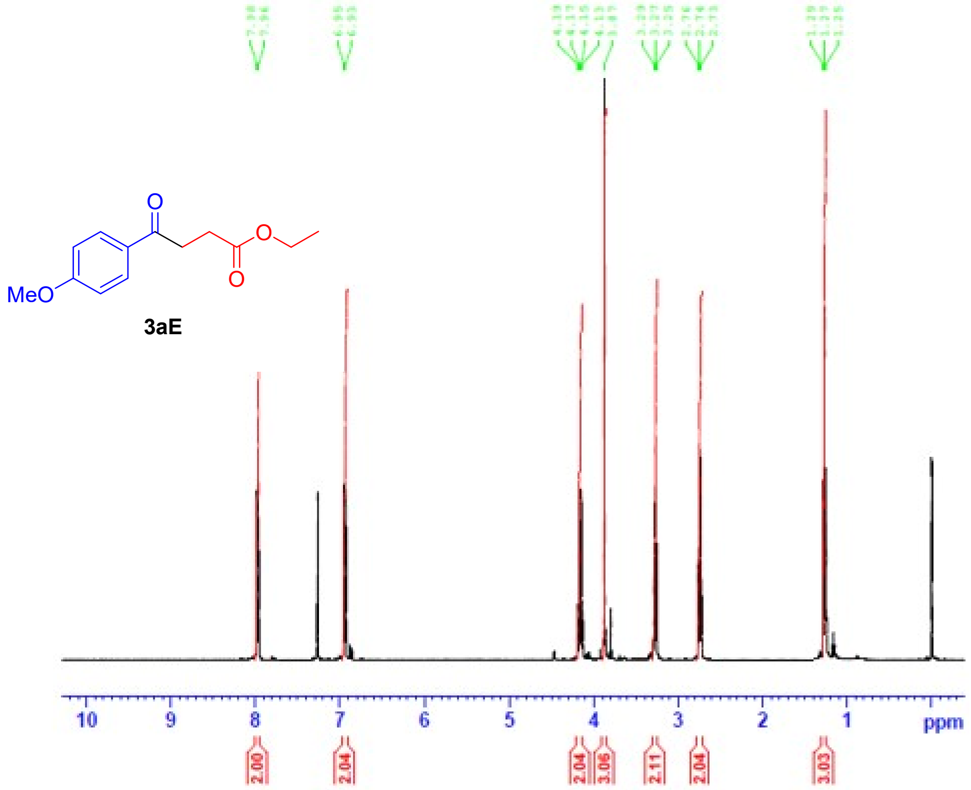
^{1}H NMR (400 MHz, CDCl$_3$) spectra for compound **3aD**



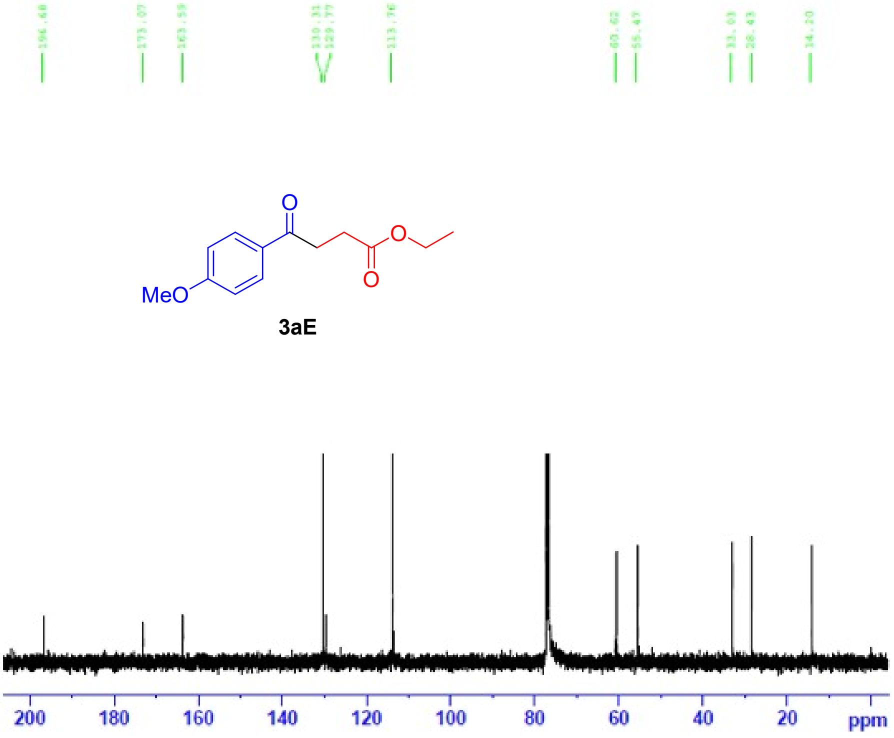
^{13}C{^{1}H } NMR (100 MHz, CDCl$_3$) spectra for compound **3aD**



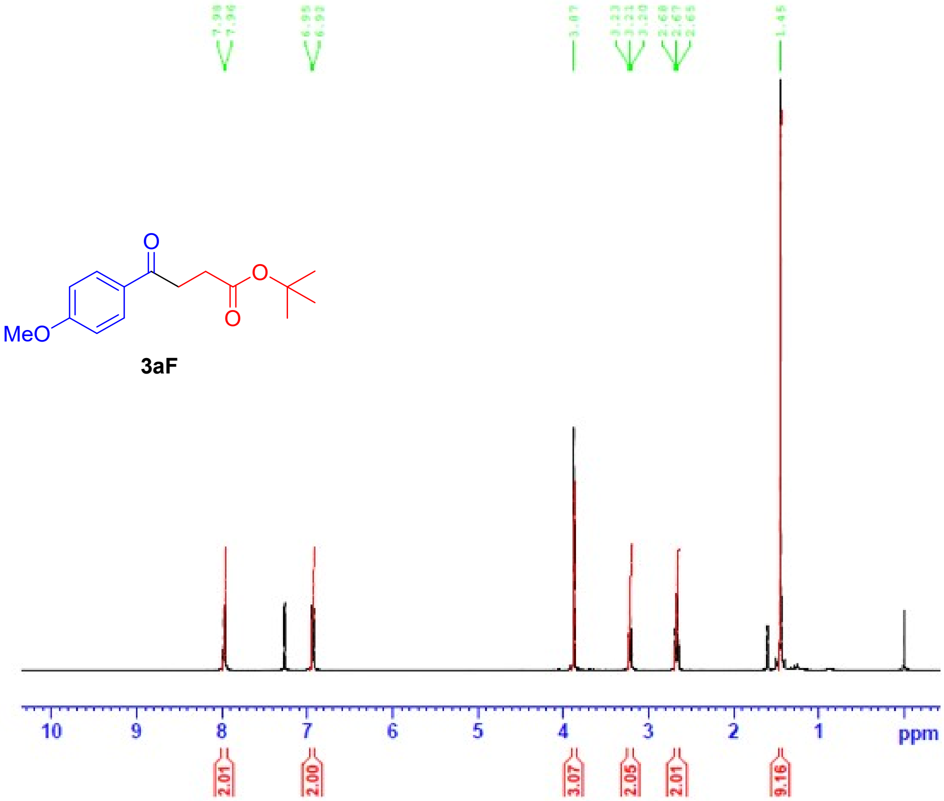
^{1}H NMR (400 MHz, CDCl$_3$) spectra for compound **3aE**



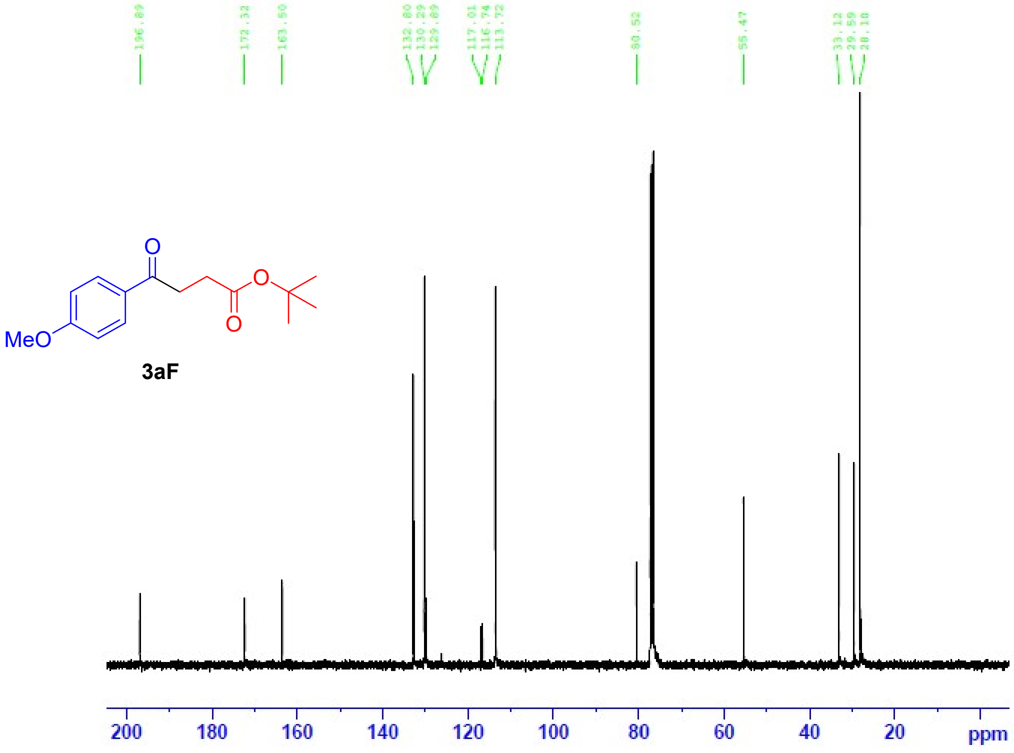
^{13}C{^{1}H } NMR (100 MHz, CDCl$_3$) spectra for compound **3aE**



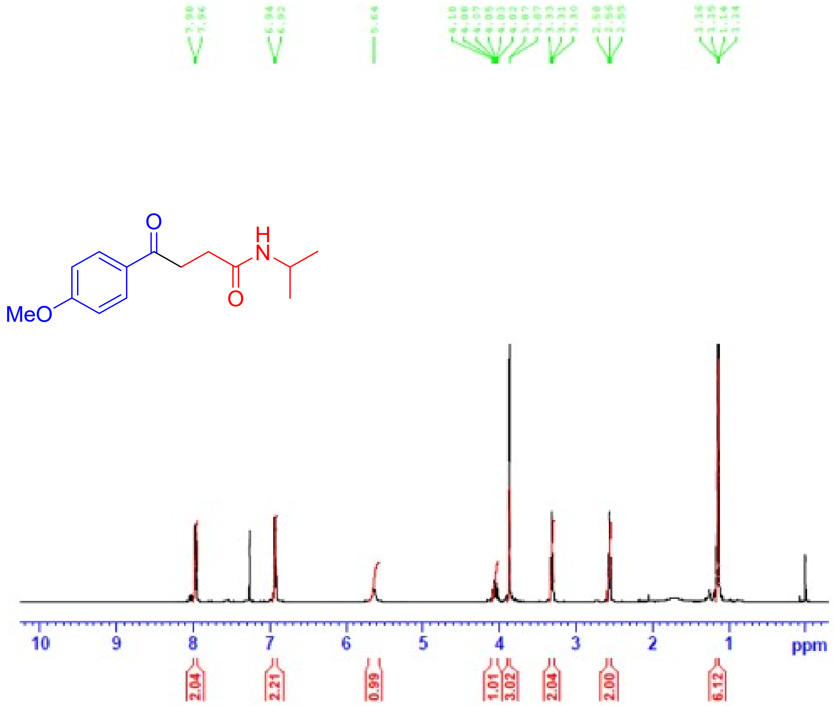
^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3aF**



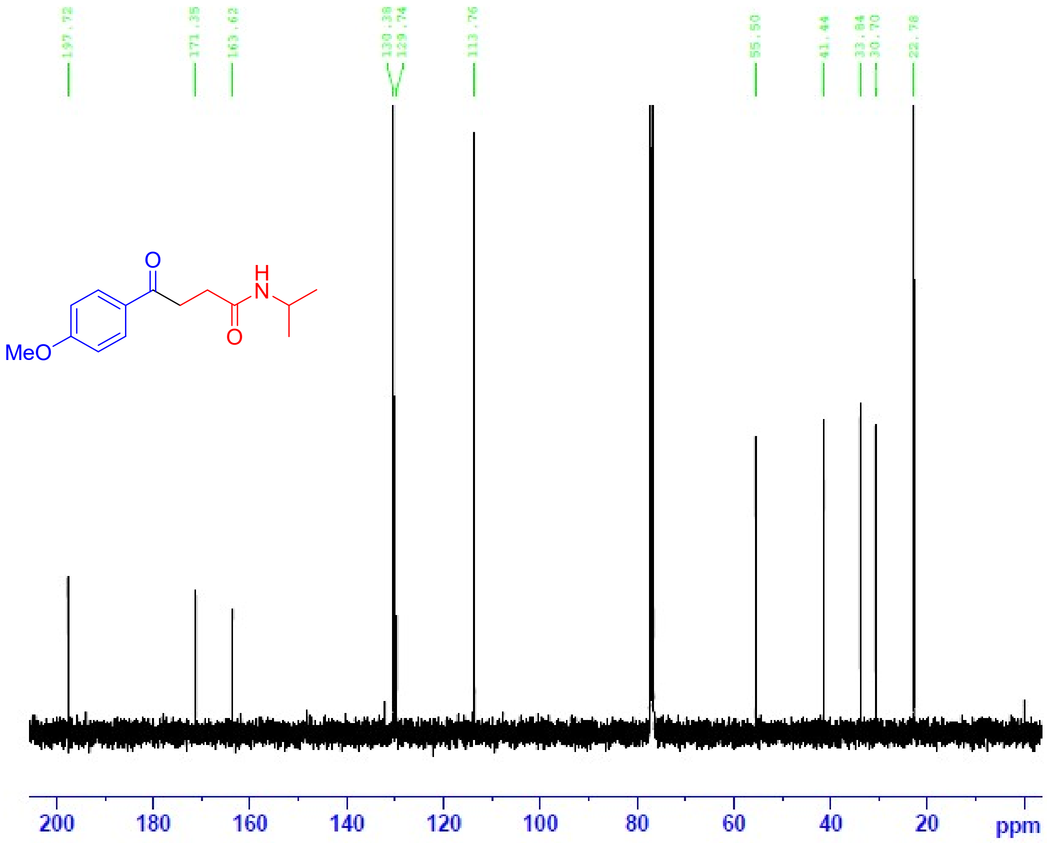
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) spectra for compound **3aF**



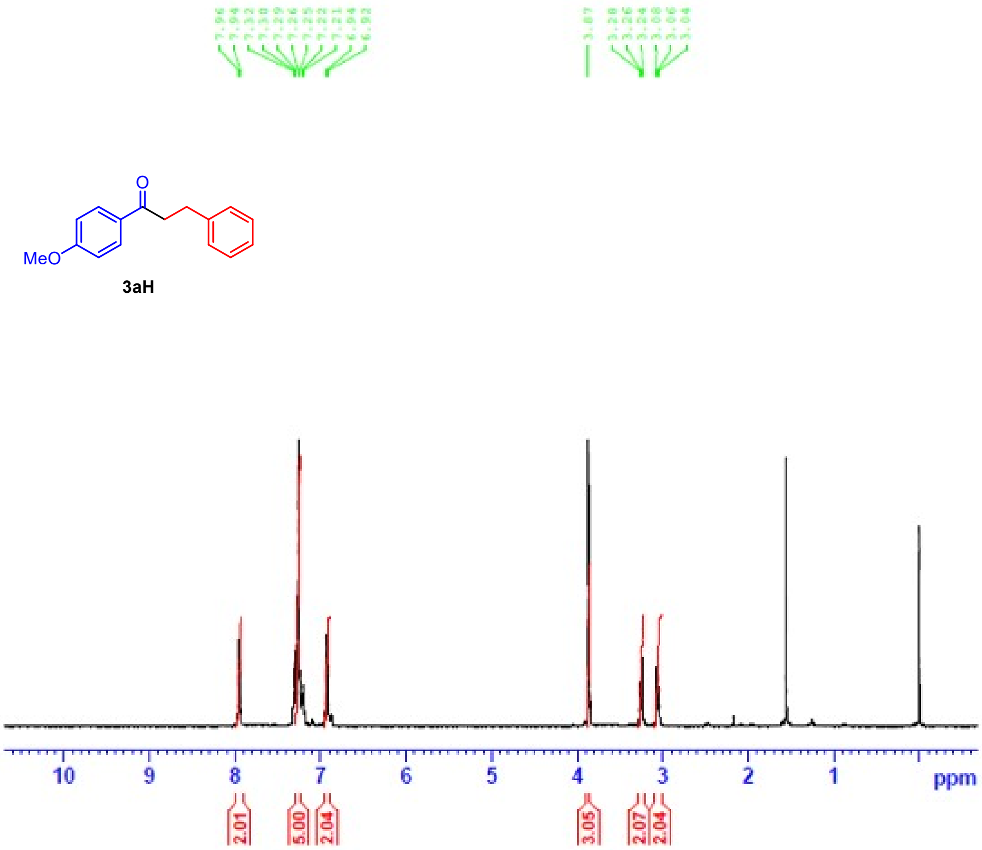
^{1}H NMR (400 MHz, CDCl$_3$) spectra for compound **3aG**



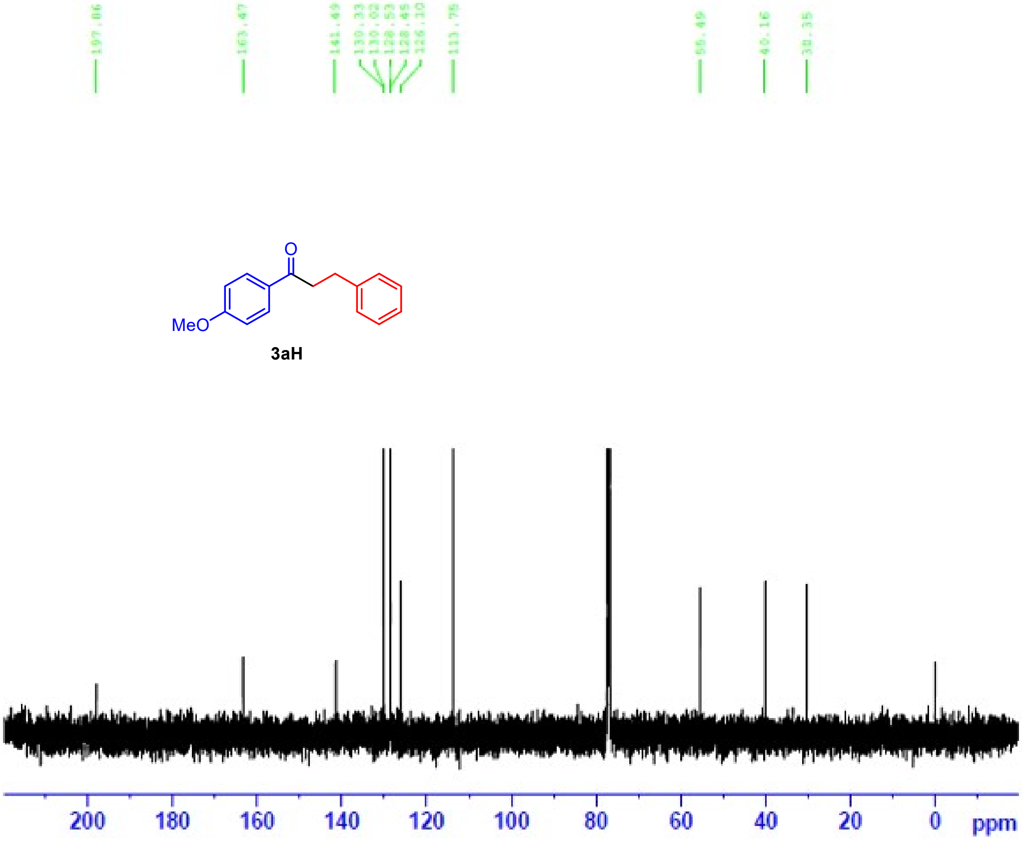
^{13}C{^{1}H } NMR (100 MHz, CDCl$_3$) spectra for compound **3aG**



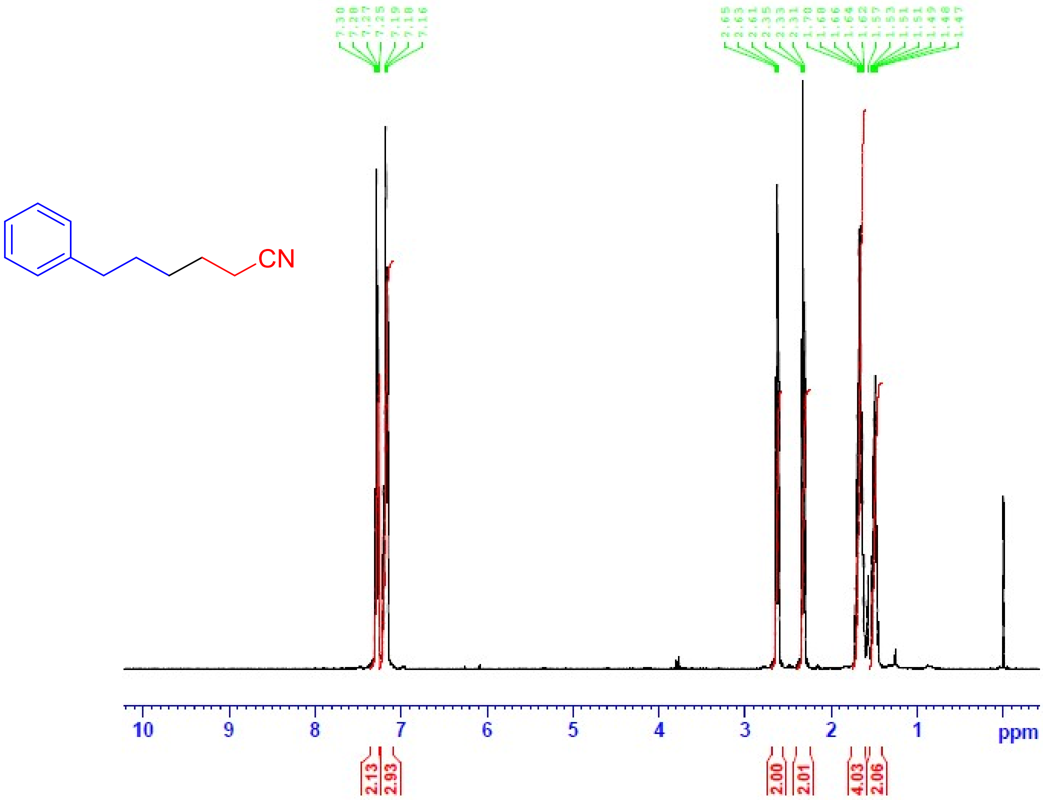
^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3aH**



^{13}C{^{1}H } NMR (100 MHz, $CDCl_3$) spectra for compound **3aH**



^{1}H NMR (400 MHz, CDCl$_3$) spectra for compound **4nA**



^{13}C{^{1}H } NMR (100 MHz, CDCl$_3$) spectra for compound **4nA**