

## *Electronic Supplementary Information*

### **Photoinduced Radical Addition of Alkyl-1,4-DHPs to Vinyl Azides**

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## 1. General information and starting materials

### 1.1 General information

Unless otherwise noted, all materials were purchased from commercial suppliers. All photoreactions were set up on the bench top and conducted under air atmosphere while subject to irradiation from blue LEDs (KDE1205PHV3).

The reactions were monitored by thin-layer chromatography on silica gel 60-F254 coated 0.2 mm plates. Visualization was accomplished by UV light (254 nm). Column chromatography was performed on silica gel (normal phase, 200–300 mesh) from Anhui Liangchen Silicon Material Co., Ltd, with petroleum ether (PE, bp. 60 – 90 °C) and ethyl acetate (EtOAc) as eluent.

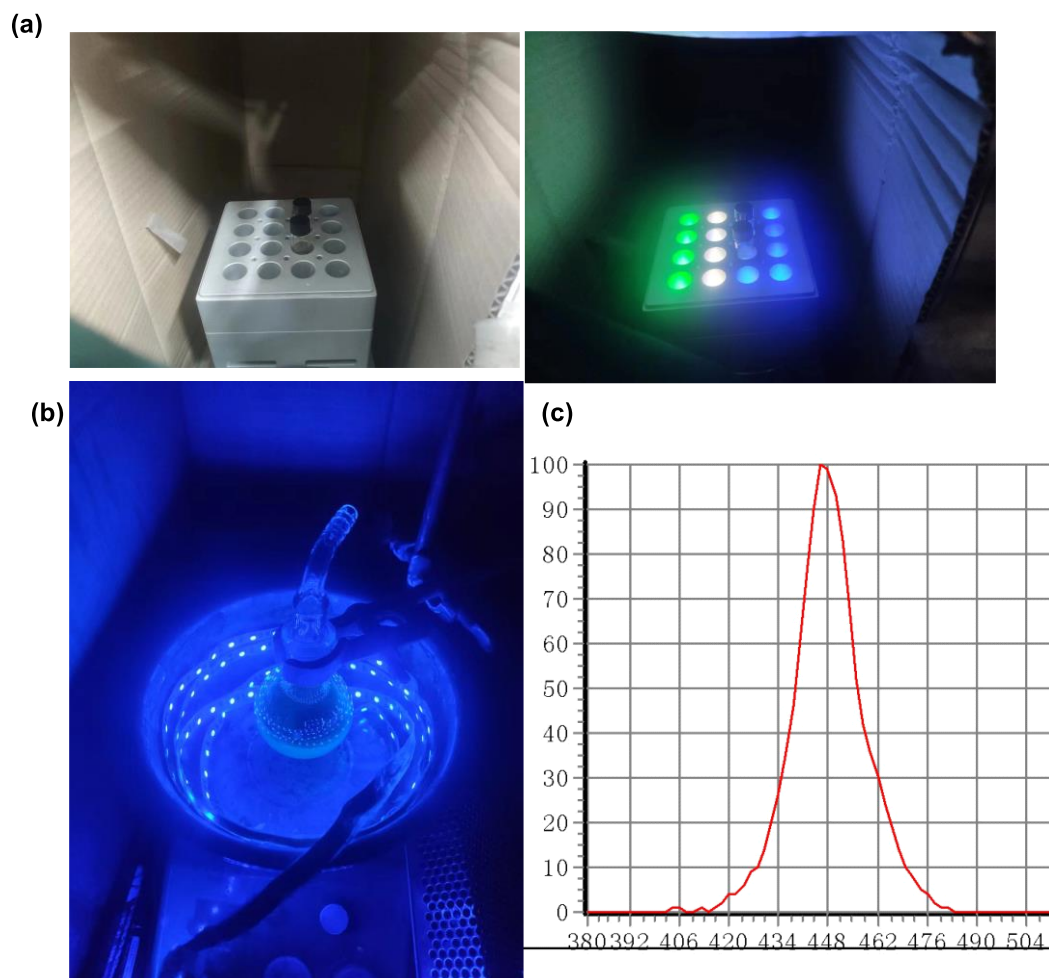
<sup>1</sup>H NMR spectra were recorded on a 400 MHz spectrometer at ambient temperature. Data were reported as follows: (1) chemical shift in parts per million ( $\delta$ , ppm) from TMS (0 ppm); (2) multiplicity (s = singlet, br = broad, d = doublet, t = triplet, q = quartet, and m = multiplet); (3) coupling constants (Hz). <sup>13</sup>C NMR spectra were recorded on a 101 MHz spectrometer at ambient temperature. Chemical shifts were reported in ppm from CDCl<sub>3</sub> (77.0 ppm), DMSO-*d*<sup>6</sup> (39.6 ppm).

Melting points were obtained on a melting point apparatus and the data were uncorrected.

HR-MS analyses were carried out using a time-of-flight (TOF)-MS instrument with an electrospray ionization (ESI) source.

The fluorescence spectra were on F-97 Pro fluorescence spectrophotometer (Shanghai Lengguang, China). UV-vis spectra were obtained by using Shimadzu UV-2500.

## 1.2 Photoreaction set-up and scale-up experimental reaction device

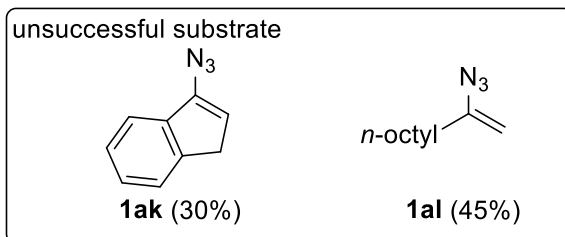
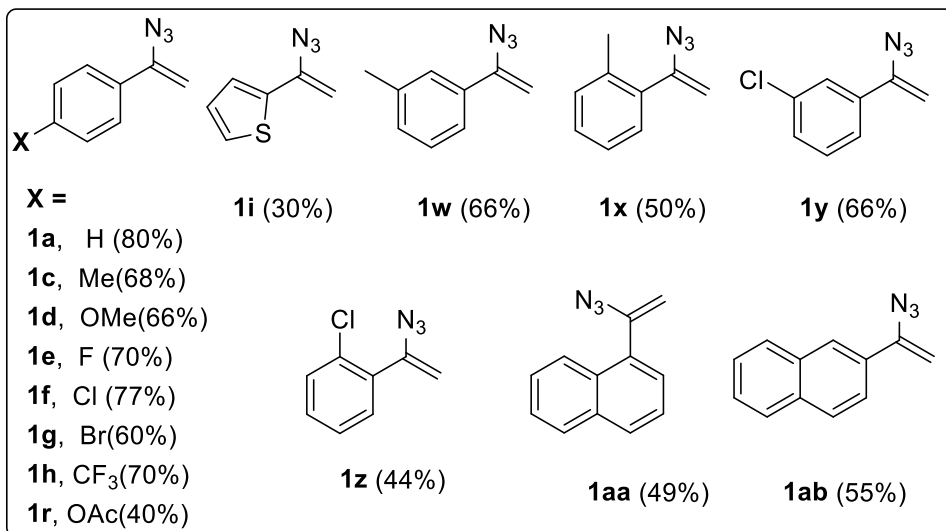


- a) Photoreaction set-up: commercial KDE1205PHV3 with irradiation by blue LEDs (1 W,  $\lambda_{\text{max}} = 447 \text{ nm}$ );
- b) Scale-up experimental reaction device (25 W,  $\lambda_{\text{max}} = 455 \text{ nm}$ );
- c) Emission spectra of the light source on KDE1205PHV3 (maximum emission at  $\lambda = 447 \text{ nm}$ ).

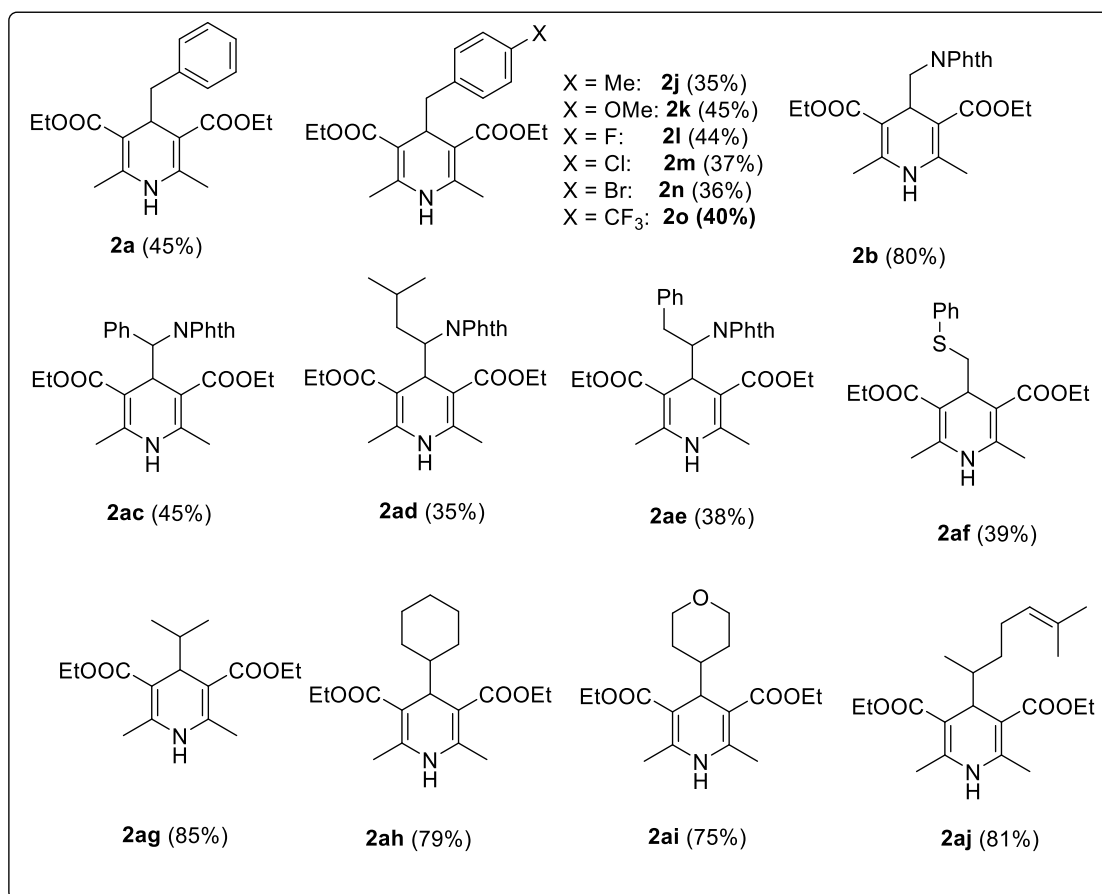
### 1.3 Numbers of All starting materials

The compound numbers of all reactants in manuscript are listed below.

(a) compound numbers of vinyl azides **1**



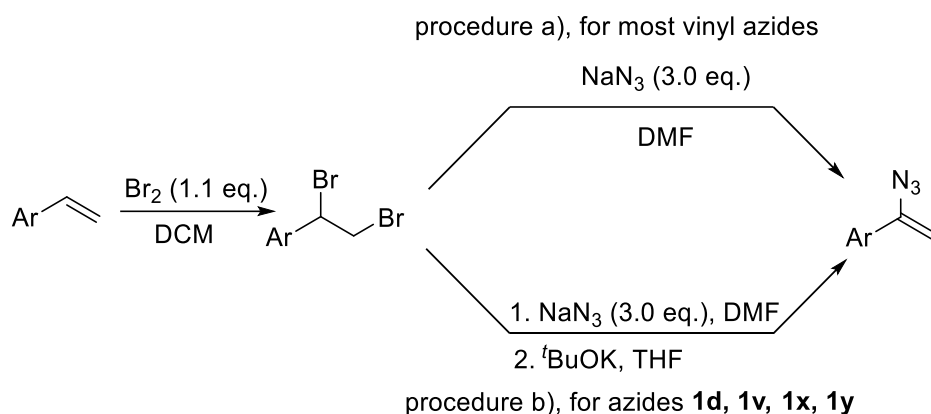
(b) compound numbers of 4-alkyl-1,4-DHPs **2**



## 1.4 Preparation of starting materials

### 1.4.1 Synthesis of vinyl azides **1**.

Vinyl azides **1** were synthesized from the corresponding alkene according to literature<sup>1</sup>.



#### 1) The 1<sup>st</sup> step: dibromization of styrenes:

In a 100 mL round-bottomed flask, styrene (10 mmol, 1.0 equiv) was added and dissolved in 30 mL of CH<sub>2</sub>Cl<sub>2</sub>. Br<sub>2</sub> (0.56 mL, 33 mmol, 1.1 equiv) was added dropwisely, and the above mixture was stirred at room temperature for 4 h. The reaction was monitored by TLC (thin layer chromatography). When the alkene was completely consumed, 50 mL of saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution was added, and the mixture was extracted with EtOAc (30 mL × 3). The organic layer was collected, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo. The dibromoethyl compound were used directly in the next procedure without any further purification.s

#### 2) the 2<sup>nd</sup> step: synthesis of vinyl azides:

Procedure (a): The current method was used for most of vinyl azides.

In a 100 mL round-bottomed flask, dibromoethyl compound (10 mmol, 1.0 equiv) was added and dissolved in 30 mL DMF, followed by the addition of NaN<sub>3</sub> (1.95 g, 30 mmol, 3.0 equiv), and the above mixture was stirred at r. t. When the raw materials

<sup>1</sup> (a) J. Li, X. Jia, J. Qiu, M. Wang, J. Chen, M. Jing, Y. Xu, X. Zheng, H. Dai, *J. Org. Chem.* 2022, **87**, 13945–13954 (b) T. Wang, Y-Y Zong, B. Yang, T. Huang, X-L. Jin, Q. Liu, *Org. Lett.* 2024, **26**, 1683–1687.

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were completely consumed, 50 mL of H<sub>2</sub>O was added to dilute the reaction solution, and the mixture was extracted with EtOAc (30 mL × 3). The organic phases were combined and washed with brine (30 mL × 3). The organic layer was collected, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo. Then the crude product was purified by column chromatography with petroleum ether (PE) as eluent to obtain the vinyl azides.

Procedure (b): the current methods was used for the synthesis of electron-rich and bulky vinyl azides such as **1d**, **1v**, **1x**, **1y**.

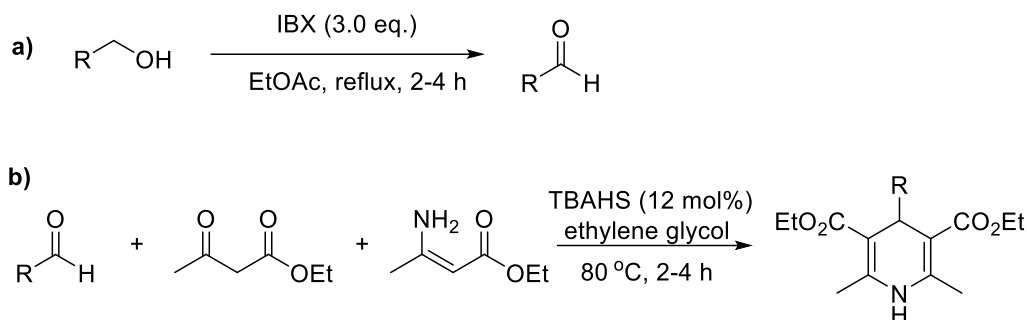
In a 100 mL round-bottomed flask, dibromoethyl compound (10 mmol, 1.0 equiv) was added and dissolved in 30 mL of DMF, followed by NaN<sub>3</sub> (1.95 g, 30 mmol, 3.0 equiv), and the above mixture was stirred at room temperature overnight. When the raw materials were completely consumed, 50 mL of water was added to dilute the reaction solution, and the mixture was extracted with EtOAc (30 mL × 3). The organic phases were combined and washed with brine (30 mL × 3). The organic layer was collected, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo. The crude was dissolved in 20 mL THF, and the reaction system was cooled to 0°C. <sup>t</sup>BuOK (1 M in THF, 1.0 equiv) was added dropwise. The mixture was warmed to room temperature and stirred for 2 h after the addition. When the raw materials were completely consumed, 30 mL of brine was added to dilute the reaction solution, and the mixture was extracted with EtOAc (30 mL × 3). The organic layer was collected, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo. Then the crude was separated and purified by column chromatography with PE as eluent to obtain the vinyl azide products.

#### 1.4.2 Synthesis of 4-alkyl DHPs **2**.

All 4-alkyl-1,4-DHPs were synthesized according to the previous literature.<sup>2</sup>

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<sup>2</sup> L. Liu, P. Jiang, Y. Liu, H. Du and J. Tan, *Org. Chem. Front.*, 2020, **7**, 2278–2283. (b) P. Jiang, L. Liu, J. Tan and H. Du, *Org. Biomol. Chem.*, 2021, **19**, 4487–4491. (c). G. Li, R. Chen, L. Wu, Q. Fu, X. Zhang and Z. Tang, *Angew. Chem. Int. Ed.*, 2013, **52**, 8432–8436.



(a) The current method was used for the synthesis of compound **2i-2m**, **2ac-2ae** due to the aldehydes were not commercially available.<sup>3</sup> A 100 mL round-bottom flask was charged sequentially with 2-iodoxybenzoic acid (IBX, 3.0 equiv.), ethyl acetate (solvent), and the alcohol (1.0 equiv. 0.5 mol/L). The mixture was refluxed for 2–4 hours. After complete consumption of the alcohol with TLC, the reaction was cooled to room temperature and filtered through Celite. The solvent was removed from the filtrate under reduced pressure. The resulting crude product was used directly in the next step (b) without further purification.

(b) A 100 mL round-bottom flask was charged with the corresponding aldehyde (1.0 equiv., 1 M), ethyl acetoacetate (1.0 equiv.), and ethyl 3-aminocrotonate (1.0 equiv.). Then, tetrabutylammonium hydrogen sulfate (TBAHS, 0.12 equiv.) was added, followed by the addition of ethylene glycol (solvent). The reaction mixture was stirred magnetically in an oil bath at 80 °C for 2–4 h. After complete consumption of the aldehyde was confirmed by TLC monitoring, the mixture was removed from the oil bath and allowed to cool to room temperature.

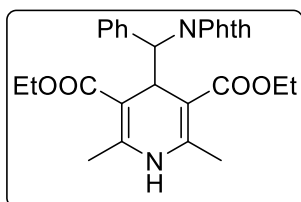
If the solid was formed, it was isolated by filtration and washed with petroleum ether/ethyl acetate (5:1, v/v) to afford the target compound. If the reaction system remained liquid, 40 mL of ethyl acetate and 40 mL of saturated brine were added. The mixture was extracted three times with EtOAc and washed three times with saturated brine. The combined organic phases were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography to give the pure compound.

Analytic characterization of new compounds **2ac-2ae**:

<sup>3</sup> J. Zhou, X. Zhu, M. Huang and Y. Wan, *Eur. J. Org. Chem.*, 2017, **2017**, 2317–2321.



diethyl 4-((1,3-dioxoisindolin-2-yl)(phenyl)methyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**2ac**)



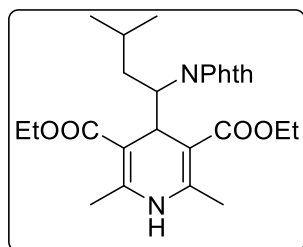
White powder, m.p. 204 – 205°C

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (dd,  $J = 5.4, 3.1$  Hz, 2H, ArH), 7.66 (td,  $J = 6.5, 5.8, 2.5$  Hz, 4H, ArH), 7.23 (td,  $J = 5.7, 2.9$  Hz, 3H, ArH), 6.25 (s, 1H, NH), 5.43 (d,  $J = 10.9$  Hz, 1H, CH in DHP), 4.94 (d,  $J = 10.9$  Hz, 1H, PhCHNPhth), 3.99 (dq,  $J = 10.8, 7.2$  Hz, 1H, CH in  $\text{CH}_2\text{CH}_3$ ), 3.89 (dq,  $J = 10.8, 7.2$  Hz, 2H, 2 CH in  $\text{CH}_2\text{CH}_3$ ), 3.71 (dq,  $J = 10.8, 7.2$  Hz, 1H, CH in  $\text{CH}_2\text{CH}_3$ ), 2.31 (s, 3H,  $\text{CH}_3$ ), 2.28 (s, 3H,  $\text{CH}_3$ ), 1.28 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$  in  $\text{CH}_2\text{CH}_3$ ), 1.13 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$  in  $\text{CH}_2\text{CH}_3$ ).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  168.2(2C), 167.5, 167.1, 145.8, 144.5, 136.3, 133.7, 131.8, 131.0, 127.9, 127.6, 122.9, 101.2, 100.5, 59.8, 59.7, 57.2, 34.8, 19.1(2C), 14.2, 13.9.

HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{28}\text{H}_{29}\text{N}_2\text{O}_6^+$ , 489.2020; found: 489.2033.

diethyl 4-(1-(1,3-dioxoisindolin-2-yl)-3-methylbutyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**2ad**)



White powder, m.p. 202 – 203°C.

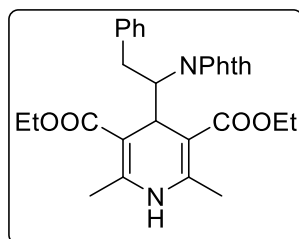
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78 (ddd,  $J = 8.2, 5.6, 2.2$  Hz, 2H, ArH), 7.71 – 7.65 (m, 2H, ArH), 6.16 (s, 1H, NH), 4.65 (d,  $J = 9.4$  Hz, 1H, CH in DHP), 4.32 (dq,  $J = 10.8, 7.1$  Hz, 1H, CH in  $\text{CH}_2\text{CH}_3$ ), 4.17 (dq,  $J = 10.8, 7.1$  Hz, 1H, CH in  $\text{CH}_2\text{CH}_3$ ), 4.02 (ddd,  $J = 12.1, 9.4, 3.9$  Hz, 1H in  $\text{CHNPhth}$ ), 3.77 (dq,  $J = 10.8, 7.1$  Hz, 1H, CH in  $\text{CH}_2\text{CH}_3$ ), 3.60 (dq,  $J = 10.8, 7.1$  Hz, 1H, CH in  $\text{CH}_2\text{CH}_3$ ), 2.50 (ddd,  $J = 13.8, 12.1, 3.4$  Hz, 1H), 2.39 (s, 3H,  $\text{CH}_3$ ), 2.25 (s, 3H,  $\text{CH}_3$ ), 1.40 – 1.30 (m, 4H), 1.20 (ddd,  $J = 13.8, 10.5, 4.0$  Hz, 1H), 1.06 (t,  $J = 7.1$  Hz, 3H,  $\text{CH}_3$  in  $\text{CH}_2\text{CH}_3$ ), 0.84 (d,  $J = 6.6$  Hz,

3H, CH<sub>3</sub> in <sup>i</sup>Pr), 0.74 (d, *J* = 6.5 Hz, 3H, CH<sub>3</sub> in <sup>i</sup>Pr).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.9, 168.5, 167.7, 167.4, 146.3, 145.6, 133.7, 133.5, 132.2, 131.6, 123.1, 122.5, 100.8, 100.4, 59.8, 59.7, 52.9, 35.9, 35.8, 25.2, 23.7, 21.0, 19.4, 19.3, 14.4, 13.9.

HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>26</sub>H<sub>33</sub>N<sub>2</sub>O<sub>6</sub><sup>+</sup>, 469.2333; found: 469.2339

diethyl 4-(1-(1,3-dioxoisindolin-2-yl)-2-phenylethyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**2ae**)



White powder, m.p. 187 – 188°C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.76 (dd, *J* = 5.4, 3.1 Hz, 1H, ArH), 7.67 – 7.55 (m, 3H, ArH), 7.13 – 6.98 (m, 5H, ArH), 6.31 (s, 1H, NH), 4.82 (d, *J* = 9.5 Hz, 1H, CH in DHP), 4.37 – 4.15 (m, 3H), 3.85 – 3.55 (m, 3H), 2.94 (dd, *J* = 14.2, 4.2 Hz, 1H, CHNPhth), 2.43 (s, 3H, CH<sub>3</sub>), 2.27 (s, 3H, CH<sub>3</sub>), 1.39 (t, *J* = 7.1 Hz, 3H, CH<sub>3</sub> in CH<sub>2</sub>CH<sub>3</sub>), 1.07 (t, *J* = 7.1 Hz, 3H, CH<sub>3</sub> in CH<sub>2</sub>CH<sub>3</sub>).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 168.5, 167.5, 167.3, 146.5, 146.1, 138.9, 133.6, 133.4, 132.0, 131.3, 128.6, 128.2, 126.0, 123.0, 122.4, 100.1, 100.4, 60.0, 59.8, 56.0, 35.8, 33.3, 19.5, 19.3, 14.4, 13.9.

HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>29</sub>H<sub>31</sub>N<sub>2</sub>O<sub>6</sub><sup>+</sup>, 503.2177; found: 503.2183

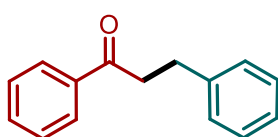
## 2. Analytical Characterization Data of Products

General procedure for products **3** and their characterization data.

(a) In a 3 mL closed screw-top glass vial, 4CzIPN (5 mol%, 10 μmol), 5-NIPA (0.75 equiv, 0.15 mmol), vinyl azides **1** (1.0 equiv, 0.2 mmol), AgOTf (0.3 equiv, 0.06 mmol) and 4-benzyl-1,4-DHPs **2** (2.0 equiv, 0.4 mmol) were dissolved in CH<sub>3</sub>CN (1 mL). The mixture was stirred for 2 h with irradiation of 1 W blue light ( $\lambda$  = 447 nm). After the reaction, the solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel with PE/EtOAc as eluent to afford the desired products **3**.

(b) In a 3 mL closed screw-top glass vial, 4CzIPN (5 mol%, 10  $\mu$ mol), 5-NIPA (0.75 equiv, 0.15 mmol), vinyl azides **1** (1.0 equiv, 0.2 mmol) and 4-benzyl-1,4-DHPs **2** (2.0 equiv, 0.4 mmol) were dissolved in CH<sub>3</sub>CN (1 mL). The mixture was stirred for 2 h with irradiation of 1W blue light ( $\lambda$  = 447 nm). After the reaction, the solvent was evaporated in vacuo, and the residue was purified by column chromatography on silica gel with PE/EtOAc as eluent to afford the desired products **3**.

**1,3-diphenylpropan-1-one (3a)** [cas: 1083-30-3]<sup>4</sup>

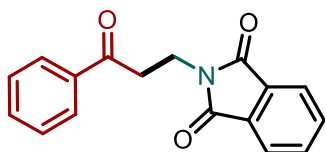


Following the general procedure a, the crude product was purified by silica gel flash chromatography (PE: EtOAc = 50: 1 as the eluent) to give **3a** (27 mg, 65%) as a colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.96 (d,  $J$  = 7.1 Hz, 2H, ArH), 7.55 (t,  $J$  = 7.4 Hz, 1H, ArH), 7.45 (t,  $J$  = 7.7 Hz, 2H, ArH), 7.34 – 7.23 (m, 4H, ArH), 7.20 (t,  $J$  = 7.0 Hz, 1H, ArH), 3.30 (t,  $J$  = 7.7 Hz, 2H, CH<sub>2</sub>), 3.07 (t,  $J$  = 7.7 Hz, 2H, CH<sub>2</sub>).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  199.2, 141.3, 136.8, 133.0, 128.6, 128.5, 128.4, 128.0, 126.1, 40.4, 30.1.

**2-(3-oxo-3-phenylpropyl)isoindoline-1,3-dione (3b)** [cas: 3617-18-3]<sup>5</sup>



Following the general procedure b, the crude product was purified by silica gel flash chromatography (PE: EtOAc: CH<sub>2</sub>Cl<sub>2</sub> = 20: 1: 1 as the eluent) to give **3b** (36 mg, 62%) as a colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.97 – 7.90 (m, 2H, ArH), 7.85 (dd,  $J$  = 5.4, 3.0 Hz, 2H, ArH), 7.72 (dd,  $J$  = 5.4, 3.0 Hz, 2H, ArH), 7.60 – 7.51 (m, 1H, ArH), 7.45 (t,  $J$  =

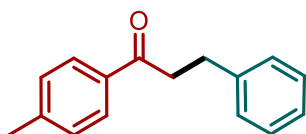
<sup>4</sup> D. Wang, K. Zhao, C. Xu, H. Miao and Y. Ding, *ACS Catal.*, 2014, **4**, 3910–3918.

<sup>5</sup> X. Jie, Y. Shang, X. Zhang and W. Su, *J. Am. Chem. Soc.*, 2016, **138**, 5623–5633.

7.6 Hz, 2H, ArH), 4.15 (t,  $J = 7.2$  Hz, 2H, CH<sub>2</sub>), 3.43 (t,  $J = 7.2$  Hz, 2H, CH<sub>2</sub>).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  197.3, 168.1, 136.4, 134.0, 133.3, 132.1, 128.6, 128.0, 123.2, 36.8, 33.5.

**3-phenyl-1-(p-tolyl)propan-1-one (3c)** [cas: 5012-90-8]<sup>6</sup>

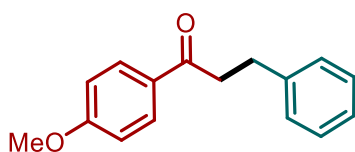


Following the general procedure a, the crude product was purified by silica gel flash chromatography (PE: EtOAc = 50: 1 as the eluent) to give **3c** (29 mg, 65%) as a colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.86 (d,  $J = 8.3$  Hz, 2H, ArH), 7.34 – 7.23 (m, 5H, ArH), 7.26 – 7.16 (m, 2H, ArH), 3.27 (t,  $J = 8.2$  Hz, 2H, CH<sub>2</sub>), 3.06 (t,  $J = 8.2$  Hz, 2H, CH<sub>2</sub>), 2.40 (s, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  198.9, 143.8, 141.4, 134.4, 129.3, 128.5, 128.4, 128.2, 126.1, 40.3, 30.2, 21.6.

**1-(4-methoxyphenyl)-3-phenylpropan-1-one (3d)** [cas: 5739-38-8]<sup>7</sup>



Following the general procedure a, the crude product was purified by silica gel flash chromatography (PE: EtOAc = 20: 1 as the eluent) to give **3d** (17 mg, 35%) as a colorless oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.94 (d,  $J = 9.0$  Hz, 2H, ArH), 7.34 – 7.23 (m, 4H, ArH), 7.23 – 7.17 (m, 1H, ArH), 6.92 (d,  $J = 8.9$  Hz, 2H, ArH), 3.86 (s, 3H, CH<sub>3</sub>), 3.25 (t,  $J = 8.2$  Hz, 2H, CH<sub>2</sub>), 3.05 (t,  $J = 8.2$  Hz, 2H, CH<sub>2</sub>)

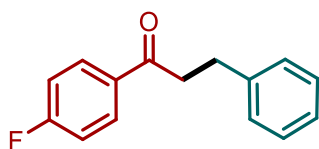
<sup>6</sup> M.-J. Zhang, D.-W. Tan, H.-X. Li, D. J. Young, H.-F. Wang, H.-Y. Li and J.-P. Lang, *J. Org. Chem.*, 2018, **83**, 1204–1215.

<sup>7</sup> A. Sau, D. Mahapatra, T. K. Ghosh, A. Maity, D. Panja, S. Dey and S. Kundu, *ChemSusChem*, 2025, **18**, e202500844.

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$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.8, 163.4, 141.4, 130.3, 129.9, 128.5, 128.4, 126.0, 113.7, 55.4, 40.1, 30.3.

**1-(4-fluorophenyl)-3-phenylpropan-1-one (3e)** [cas: 41938-64-1]<sup>8</sup>



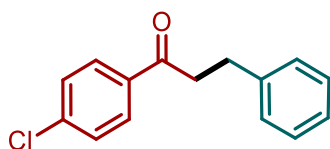
Following the general procedure a, the crude product was purified by silica gel flash chromatography (PE: EtOAc = 50: 1 as the eluent) to give **3e** (29 mg, 64%) as a yellow oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (dd,  $J$  = 8.8, 5.4 Hz, 2H, ArH), 7.36 – 7.26 (m, 2H, ArH), 7.26 – 7.17 (m, 3H, ArH), 7.11 (t,  $J$  = 8.8 Hz, 2H, ArH), 3.27 (t,  $J$  = 7.7 Hz, 2H,  $\text{CH}_2$ ), 3.06 (t,  $J$  = 7.7 Hz, 2H,  $\text{CH}_2$ ).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.6, 165.7 (d,  $J$  = 254.9 Hz), 141.1, 133.3 (d,  $J$  = 2.7 Hz), 130.6 (d,  $J$  = 9.4 Hz), 128.5, 128.4, 126.2, 115.7 (d,  $J$  = 21.8 Hz), 40.3, 30.1.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -105.31.

**1-(4-chlorophenyl)-3-phenylpropan-1-one (3f)** [cas 5739-37-7]<sup>7</sup>



Following the general procedure a, the crude product was purified by silica gel flash chromatography (PE: EtOAc = 50: 1 as the eluent) to give **3f** (40 mg, 82%) as a colorless oil.

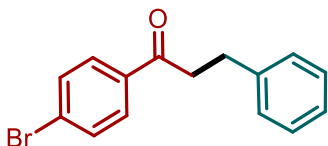
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J$  = 8.6 Hz, 2H, ArH), 7.41 (d,  $J$  = 8.6 Hz, 2H, ArH), 7.29 (t,  $J$  = 7.2 Hz, 2H, ArH), 7.25 – 7.16 (m, 3H, ArH), 3.26 (t,  $J$  = 7.7 Hz, 2H,  $\text{CH}_2$ ), 3.05 (t,  $J$  = 7.7 Hz, 2H,  $\text{CH}_2$ ).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.9, 141.0, 139.4, 135.1, 129.4, 128.9, 128.5, 128.4, 126.2, 40.4, 30.0.

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<sup>8</sup> Y. Wang, X. Shou, Y. Xu and X. Zhou, *Angew. Chem. Int. Ed.*, 2025, **64**, e202502619.

**1-(4-bromophenyl)-3-phenylpropan-1-one (3g)** [cas: 1669-51-8]<sup>8</sup>

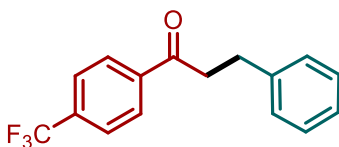


Following the general procedure a, the crude product was purified by silica gel flash chromatography (PE: EtOAc = 50: 1 as the eluent) to give **3g** (32 mg, 56%) as a yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.80 (d, *J* = 8.7 Hz, 2H, ArH), 7.58 (d, *J* = 8.7 Hz, 2H, ArH), 7.34 – 7.25 (m, 2H, ArH), 7.25 – 7.18 (m, 3H, ArH), 3.26 (t, *J* = 7.6 Hz, 2H, CH<sub>2</sub>), 3.05 (t, *J* = 7.6 Hz, 2H, CH<sub>2</sub>).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 198.1, 141.0, 135.5, 131.9, 129.5, 128.5, 128.4, 128.2, 126.2, 40.4, 30.0.

**3-phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-one (3h)** [cas: 67082-00-2]<sup>9</sup>



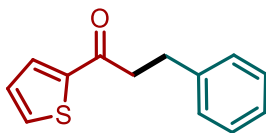
Following the general procedure a, the crude product was purified by silica gel flash chromatography (PE: EtOAc = 50: 1 as the eluent) to give **3h** (47 mg, 85%) as a yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.80 (d, *J* = 8.7 Hz, 2H, ArH), 7.58 (d, *J* = 8.7 Hz, 2H, ArH), 7.34 – 7.25 (m, 2H, ArH), 7.25 – 7.18 (m, 3H, ArH), 3.26 (t, *J* = 7.6 Hz, 2H, CH<sub>2</sub>), 3.05 (t, *J* = 7.6 Hz, 2H, CH<sub>2</sub>).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 198.1, 141.0, 135.5, 131.9, 129.5, 128.5, 128.4, 128.2, 126.2, 40.4, 30.0.

**3-phenyl-1-(thiophen-2-yl)propan-1-one (3i)** [cas: 40027-94-9]<sup>7</sup>

<sup>9</sup> Y. Wang, X. Shou, Y. Xu and X. Zhou, *Angew. Chem. Int. Ed.*, 2025, **64**, e202502619.

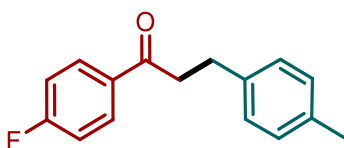


Following the general procedure a, the crude product was purified by silica gel flash chromatography (PE: EtOAc = 50: 1 as the eluent) to give **3i** (25 mg, 58%) as a yellow oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (dd,  $J$  = 3.8, 1.2 Hz, 1H, ArH), 7.62 (dd,  $J$  = 5.0, 1.2 Hz, 1H, ArH), 7.33 – 7.26 (m, 3H, ArH), 7.26 – 7.17 (m, 2H, ArH), 7.11 (dd,  $J$  = 5.0, 3.8 Hz, 1H, ArH), 3.28 – 3.19 (m, 2H,  $\text{CH}_2$ ), 3.07 (t,  $J$  = 7.8 Hz, 2H,  $\text{CH}_2$ ).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  192.2, 144.2, 141.0, 133.5, 131.8, 128.5, 128.4, 128.1, 126.2, 41.1, 30.4.

**1-(4-fluorophenyl)-3-(p-tolyl)propan-1-one (3j)** [cas: 56201-96-8]<sup>10</sup>



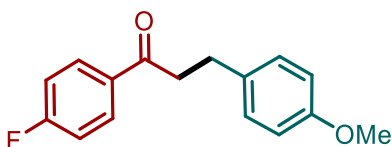
Following the general procedure a, the crude product was purified by silica gel flash chromatography (PE: EtOAc = 50: 1 as the eluent) to give **3j** (24 mg, 50%) as a colorless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 – 7.93 (m, 2H, ArH), 7.18 – 7.05 (m, 6H, ArH), 3.24 (t,  $J$  = 7.7 Hz, 2H,  $\text{CH}_2$ ), 3.02 (t,  $J$  = 7.7 Hz, 2H,  $\text{CH}_2$ ), 2.32 (s, 3H,  $\text{CH}_3$ ).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.7, 165.7 (d,  $J$  = 254.5 Hz), 138.0, 135.7, 133.3 (d,  $J$  = 2.5 Hz), 130.6 (d,  $J$  = 9.4 Hz), 129.2, 128.2, 115.6 (d,  $J$  = 21.8 Hz), 40.5, 29.6, 21.0.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -105.38.

**1-(4-fluorophenyl)-3-(4-methoxyphenyl)propan-1-one (3k)** [cas: 898775-78-5]<sup>11</sup>



<sup>10</sup> D. Gautam, P. S. Gahlaut, S. Pathak and B. Jana, *Org. Biomol. Chem.*, 2023, **21**, 9519–9523.

<sup>11</sup> D. Chen, Y. Wang, X.-M. Cai, X. Cao, P. Jiang, F. Wang and S. Huang, *Org. Lett.*, 2020, **22**, 6847–6851.

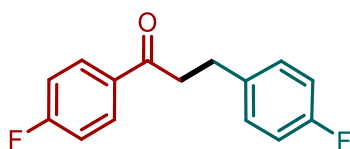
Following the general procedure a, the crude product was purified by silica gel flash chromatography (PE: EtOAc = 20: 1 as the eluent) to give **3k** (20 mg, 39%) as a yellow oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (dd,  $J$  = 9.0, 5.4 Hz, 2H, ArH), 7.21 – 7.07 (m, 4H, ArH), 6.84 (d,  $J$  = 8.7 Hz, 2H, ArH), 3.78 (s, 3H,  $\text{CH}_3$ ), 3.23 (t,  $J$  = 7.6 Hz, 2H,  $\text{CH}_2$ ), 3.00 (t,  $J$  = 7.6 Hz, 2H,  $\text{CH}_2$ ).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.81, 165.72 (d,  $J$  = 254.2 Hz), 158.04, 133.4 (d,  $J$  = 2.9 Hz), 133.16, 130.67 (d,  $J$  = 9.4 Hz), 129.35, 115.69 (d,  $J$  = 21.8 Hz), 113.97, 55.29, 40.64, 29.27.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -105.38.

**1,3-bis(4-fluorophenyl)propan-1-one (3l)** [cas: 104147-29-7]<sup>12</sup>



Following the general procedure a, the crude product was purified by silica gel flash chromatography (PE: EtOAc = 50: 1 as the eluent) to give **3l** (36 mg, 73%) as colorless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (dd,  $J$  = 8.8, 5.4 Hz, 2H, ArH), 7.20 (dd,  $J$  = 8.8, 5.4 Hz, 2H, ArH), 7.12 (t,  $J$  = 8.6 Hz, 2H, ArH), 6.97 (t,  $J$  = 8.6 Hz, 2H, ArH), 3.25 (t,  $J$  = 7.5 Hz, 2H,  $\text{CH}_2$ ), 3.04 (t,  $J$  = 7.5 Hz, 2H,  $\text{CH}_2$ ).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.4, 165.7 (d,  $J$  = 254.9 Hz), 161.4 (d,  $J$  = 243.8 Hz), 136.7 (d,  $J$  = 3.0 Hz), 133.2 (d,  $J$  = 2.8 Hz), 130.6 (d,  $J$  = 9.4 Hz), 129.8 (d,  $J$  = 8.0 Hz), 115.7 (d,  $J$  = 21.8 Hz), 115.3 (d,  $J$  = 21.2 Hz), 40.3, 29.2.

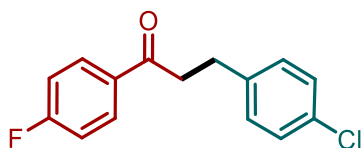
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -105.15, -117.15.

**3-(4-chlorophenyl)-1-(4-fluorophenyl)propan-1-one (3m)** [cas: 56201-99-1]<sup>13</sup>

<sup>12</sup> Z. Luo, X. Zhang, Z.-Q. Liu, C.-M. Hong, Q.-H. Li and T.-L. Liu, *Org. Lett.*, 2022, **24**, 8072–8076.

<sup>13</sup> F. Beltran, E. Bergamaschi, I. Funes-Ardoiz and C. J. Teskey, *Angew. Chem. Int. Ed.*, 2020, **59**, 21176–21182.





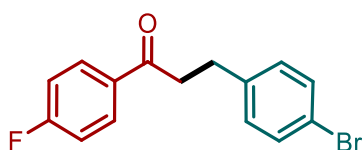
Following the general procedure a, the crude product was purified by silica gel flash chromatography (PE: EtOAc = 50: 1 as the eluent) to give **3m** (27 mg, 52%) as a colorless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (dd,  $J = 8.9, 5.4$  Hz, 2H, ArH), 7.29 – 7.22 (m, 2H, ArH), 7.17 (d,  $J = 8.4$  Hz, 2H, ArH), 7.12 (t,  $J = 8.4$  Hz, 2H, ArH), 3.25 (t,  $J = 7.6$  Hz, 2H,  $\text{CH}_2$ ), 3.03 (t,  $J = 7.6$  Hz, 2H,  $\text{CH}_2$ ).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.2, 165.8 (d,  $J = 254.9$  Hz), 139.6, 133.2 (d,  $J = 2.8$  Hz), 131.9, 130.6 (d,  $J = 9.4$  Hz), 129.8, 128.6, 115.7 (d,  $J = 21.8$  Hz), 40.0, 29.3.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -105.06.

**3-(4-bromophenyl)-1-(4-fluorophenyl)propan-1-one (3n)**



Following the general procedure a, the crude product was purified by silica gel flash chromatography (PE: EtOAc = 50: 1 as the eluent) to give **3n** (42 mg, 68%) as a yellow oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (dd,  $J = 8.9, 5.4$  Hz, 2H, ArH), 7.41 (d,  $J = 8.4$  Hz, 2H, ArH), 7.16 – 7.08 (m, 4H, ArH), 3.25 (t,  $J = 7.5$  Hz, 2H,  $\text{CH}_2$ ), 3.02 (t,  $J = 7.5$  Hz, 2H,  $\text{CH}_2$ ).

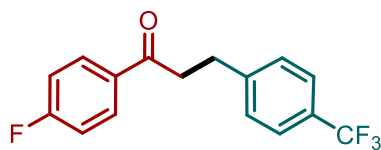
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.2, 165.8 (d,  $J = 255.2$  Hz), 140.1, 133.1 (d,  $J = 2.1$  Hz), 131.6, 130.6 (d,  $J = 9.4$  Hz), 130.2, 119.9, 115.7 (d,  $J = 21.8$  Hz), 40.0, 29.4.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -105.04.

HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{15}\text{H}_{13}\text{BrFO}^+$ , 307.0128; found: 307.0144.

**1-(4-fluorophenyl)-3-(4-(trifluoromethyl)phenyl)propan-1-one (3o)** [cas:

1504562-81-5]<sup>14</sup>



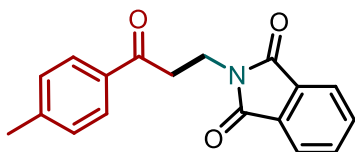
Following the general procedure a, the crude product was purified by silica gel flash chromatography (PE: EtOAc = 50: 1 as the eluent) to give **3o** (43 mg, 73%) as a yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.04 – 7.91 (m, 2H, ArH), 7.55 (d, *J* = 8.2 Hz, 2H, ArH), 7.36 (d, *J* = 8.2 Hz, 2H, ArH), 7.13 (t, *J* = 8.6 Hz, 2H, ArH), 3.30 (t, *J* = 7.4 Hz, 2H, CH<sub>2</sub>), 3.13 (t, *J* = 7.4 Hz, 2H, CH<sub>2</sub>).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 196.9, 165.8 (d, *J* = 254.9 Hz), 145.3, 133.1 (d, *J* = 2.5 Hz), 130.62 (d, *J* = 9.4 Hz), 128.8, 128.6 (q, *J* = 32.1 Hz), 125.4 (q, *J* = 4.2 Hz), 124.4 (q, *J* = 271.7 Hz), 115.8 (d, *J* = 22.2 Hz), 39.7, 29.7.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -62.39, -104.92.

**2-(3-oxo-3-(p-tolyl)propyl)isoindoline-1,3-dione (3p)** [cas: 57500-71-7]<sup>15</sup>



Following the general procedure b, the crude product was purified by silica gel flash chromatography (PE: EtOAc: CH<sub>2</sub>Cl<sub>2</sub> = 20: 1: 1 as the eluent) to give **3p** (38 mg, 65%) as a yellow oil.

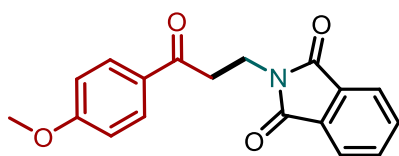
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.90 – 7.81 (m, 4H, ArH), 7.72 (dd, *J* = 5.4, 3.1 Hz, 2H, ArH), 7.24 (t, *J* = 8.0 Hz, 2H, ArH), 4.14 (t, *J* = 7.4 Hz, 2H, CH<sub>2</sub>), 3.40 (t, *J* = 7.4 Hz, 2H, CH<sub>2</sub>), 2.40 (s, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 196.9, 168.2, 144.2, 133.9(2C), 132.1, 129.3, 128.1, 123.2, 36.7, 33.6, 21.6.

**2-(3-(4-methoxyphenyl)-3-oxopropyl)isoindoline-1,3-dione (3q)** [cas: 5739-38-8]

<sup>14</sup> Q. Jiang, T. Guo, Q. Wang, P. Wu and Z. Yu, *Adv. Synth. Catal.*, 2013, **355**, 1874–1880.

<sup>15</sup> B. Ling, S. Yao, S. Ouyang, H. Bai, X. Zhai, C. Zhu, W. Li and J. Xie, *Angew. Chem. Int. Ed.*, 2024, **63**, e202405866.

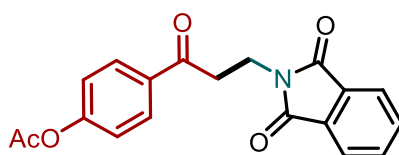


Following the general procedure b, the crude product was purified by silica gel flash chromatography (PE: EtOAc: CH<sub>2</sub>Cl<sub>2</sub> = 10: 1: 1 as the eluent) to give **3q** (30 mg, 48%) as a yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.92 (d, *J* = 8.8 Hz, 2H, ArH), 7.85 (dd, *J* = 5.4, 3.0 Hz, 2H, ArH), 7.71 (dd, *J* = 5.4, 3.0 Hz, 2H, ArH), 6.91 (d, *J* = 8.8 Hz, 2H, ArH), 4.13 (t, *J* = 7.4 Hz, 2H, CH<sub>2</sub>), 3.86 (s, 3H, OCH<sub>3</sub>), 3.37 (t, *J* = 7.4 Hz, 2H, CH<sub>2</sub>).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 195.8, 168.1, 163.6, 133.9, 132.1, 130.3, 129.5, 123.2, 113.8, 55.4, 36.4, 33.7.

#### 4-(3-(1,3-dioxoisindolin-2-yl)propanoyl)phenyl acetate (**3r**)



Following the general procedure b, the crude product was purified by silica gel flash chromatography (PE: EtOAc: CH<sub>2</sub>Cl<sub>2</sub> = 15: 1: 1 as the eluent) to give **3r** (40 mg, 60%) as a yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.98 (d, *J* = 8.7 Hz, 2H, ArH), 7.85 (dd, *J* = 5.5, 3.0 Hz, 2H, ArH), 7.72 (dd, *J* = 5.5, 3.0 Hz, 2H, ArH), 7.19 (d, *J* = 8.7 Hz, 2H, ArH), 4.14 (t, *J* = 7.4 Hz, 2H, CH<sub>2</sub>), 3.39 (t, *J* = 7.4 Hz, 2H, CH<sub>2</sub>), 2.32 (s, 3H, CH<sub>3</sub>).

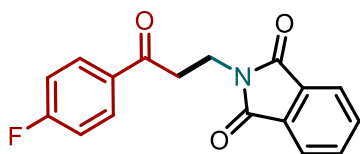
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 196.0, 168.7, 168.1, 154.5, 134.0, 133.9, 132.0, 129.6, 123.3, 121.8, 36.7, 33.4, 21.1.

HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>16</sub>NO<sub>5</sub><sup>+</sup>, 338.1023; found: 338.1023.

#### 2-(3-(4-fluorophenyl)-3-oxopropyl)isoindoline-1,3-dione (**3s**) [cas: 254967-20-9]

<sup>16</sup> V. Marsicano, A. Arcadi, M. Aschi and V. Michelet, *Org. Biomol Chem.*, 2020, **18**, 9438–9447.

<sup>17</sup> Q. Yang, Y. Deng, H. Yang, H. Zhao, P. Yao, J. Chen, Z. Ma and B. Fan, *ACS Catal.*, 2025, **15**, 2666–2676.



Following the general procedure b, the crude product was purified by silica gel flash chromatography (PE: EtOAc: CH<sub>2</sub>Cl<sub>2</sub> = 20: 1: 1 as the eluent) to give **3s** (38 mg, 64%) as yellow solid. M.p. 153–154 °C.

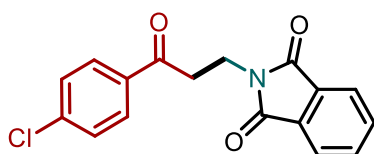
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.97 (dd, *J* = 8.6, 5.3 Hz, 2H, ArH), 7.85 (dd, *J* = 5.5, 3.0 Hz, 2H, ArH), 7.72 (dd, *J* = 5.5, 3.0 Hz, 2H, ArH), 7.12 (dd, *J* = 8.6, 8.6 Hz, 2H, ArH), 4.13 (t, *J* = 7.4 Hz, 2H, CH<sub>2</sub>), 3.40 (t, *J* = 7.4 Hz, 2H, CH<sub>2</sub>).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 195.7, 168.1, 165.8 (d, *J* = 255.2 Hz), 134.0, 132.8 (d, *J* = 2.7 Hz), 132.0, 130.6 (d, *J* = 9.4 Hz), 123.2, 115.7 (d, *J* = 21.8 Hz), 36.7, 33.4.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -104.64.

**2-(3-(4-chlorophenyl)-3-oxopropyl)isoindoline-1,3-dione (3t)** [cas: 112031-92-2]

18



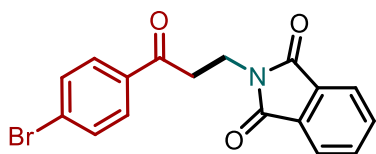
Following the general procedure b, the crude product was purified by silica gel flash chromatography (PE: EtOAc: CH<sub>2</sub>Cl<sub>2</sub> = 20: 1: 1 as the eluent) to give **3t** (39 mg, 63%) as yellow solid. M.p. 147–148°C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.88 (d, *J* = 8.6 Hz, 2H, ArH), 7.85 (dd, *J* = 5.5, 3.0 Hz, 2H, ArH), 7.72 (dd, *J* = 5.5, 3.0 Hz, 2H, ArH), 7.43 (d, *J* = 8.6 Hz, 2H, ArH), 4.14 (t, *J* = 6.8 Hz, 2H, CH<sub>2</sub>), 3.39 (t, *J* = 6.8 Hz, 2H, CH<sub>2</sub>).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 196.1, 168.1, 139.8, 134.7, 134.0, 132.0, 129.4, 129.0, 123.3, 36.8, 33.4.

**2-(3-(4-bromophenyl)-3-oxopropyl)isoindoline-1,3-dione (3u)** [cas: 1835294-83-1<sup>18</sup>]

<sup>18</sup> W. J. Wang Yanzhao, Liu Delong, Zhang Wanbin, *Chin. J. Org. Chem.*, 2014, **34**, 1766–1772.

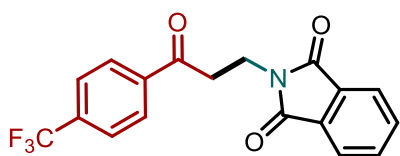


Following the general procedure b, the crude product was purified by silica gel flash chromatography (PE: EtOAc: CH<sub>2</sub>Cl<sub>2</sub> = 20: 1: 1 as the eluent) to give **3u** (41 mg, 57%) as a yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.85 (dd, *J* = 5.4, 3.0 Hz, 2H, ArH), 7.80 (d, *J* = 8.6 Hz, 2H, ArH), 7.72 (dd, *J* = 5.4, 3.0 Hz, 2H, ArH), 7.59 (d, *J* = 8.6 Hz, 2H, ArH), 4.13 (t, *J* = 9.0 Hz, 2H, CH<sub>2</sub>), 3.39 (t, *J* = 9.0 Hz, 2H, CH<sub>2</sub>).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 196.3, 168.1, 135.1, 134.0, 132.04, 131.99, 129.5, 128.6, 123.3, 36.8, 33.4.

**2-(3-oxo-3-(4-(trifluoromethyl)phenyl)propyl)isoindoline-1,3-dione (3v)**



Following the general procedure b, the crude product was purified by silica gel flash chromatography (PE: EtOAc: CH<sub>2</sub>Cl<sub>2</sub> = 20: 1: 1 as the eluent) to give **3v** (41 mg, 59%) as a yellow oil.

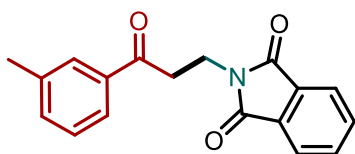
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.05 (d, *J* = 8.2 Hz, 2H, ArH), 7.86 (dd, *J* = 5.5, 3.0 Hz, 2H, ArH), 7.77 – 7.67 (m, 4H, ArH), 4.16 (t, *J* = 7.3 Hz, 2H, CH<sub>2</sub>), 3.45 (t, *J* = 7.3 Hz, 2H, CH<sub>2</sub>).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 196.4, 168.1, 138.9, 134.13 (q, *J* = 34.1 Hz), 134.08, 132.0, 128.4, 126.2 (q, *J* = 282.7 Hz), 125.8 (q, *J* = 3.8 Hz), 123.3, 37.1, 33.3.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -63.18.

HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>13</sub>F<sub>3</sub>NO<sub>3</sub><sup>+</sup>, 348.0842; found: 348.0858.

**2-(3-oxo-3-(*m*-tolyl)propyl)isoindoline-1,3-dione (3w)**



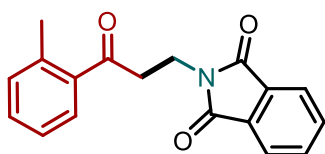
Following the general procedure b, the crude product was purified by silica gel flash chromatography (PE: EtOAc: CH<sub>2</sub>Cl<sub>2</sub> = 20: 1: 1 as the eluent) to give **3w** (32mg, 55%) as a yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.84 (dd, *J* = 5.5, 3.0 Hz, 2H, ArH), 7.77 – 7.69 (m, 4H, ArH), 7.43 – 7.29 (m, 2H, ArH), 4.13 (t, *J* = 7.4 Hz, 2H, CH<sub>2</sub>), 3.41 (t, *J* = 7.4 Hz, 2H, CH<sub>2</sub>), 2.38 (s, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 197.4, 168.1, 138.4, 136.3, 134.0, 133.9, 132.0, 128.4(2C), 125.2, 123.2, 36.8, 33.5, 21.2.

HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>16</sub>NO<sub>3</sub><sup>+</sup>, 294.1125; found: 294.1144.

**2-(3-oxo-3-(*o*-tolyl)propyl)isoindoline-1,3-dione (3x)**



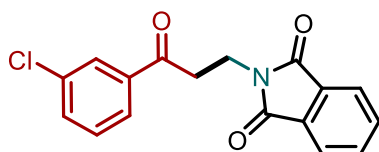
Following the general procedure b, the crude product was purified by silica gel flash chromatography (PE: EtOAc: CH<sub>2</sub>Cl<sub>2</sub> = 20: 1: 1 as the eluent) to give **3x** (29 mg, 50%) as a yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.85 (dd, *J* = 5.5, 3.0 Hz, 2H, ArH), 7.72 (dd, *J* = 5.5, 3.0 Hz, 2H, ArH), 7.66 (d, *J* = 7.9 Hz, 1H, ArH), 7.36 (t, *J* = 7.5 Hz, 1H, ArH), 7.26 – 7.19 (m, 2H, ArH), 4.12 (t, *J* = 7.2 Hz, 2H, CH<sub>2</sub>), 3.36 (t, *J* = 7.2 Hz, 2H, CH<sub>2</sub>), 2.52 (s, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 200.8, 169.1, 140.1, 136.4, 134.0, 132.14, 132.08, 131.7, 128.8, 126.1, 123.2, 39.2, 33.7, 21.5.

HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>16</sub>NO<sub>3</sub><sup>+</sup>, 294.1125; found: 294.1142.

**2-(3-(3-chlorophenyl)-3-oxopropyl)isoindoline-1,3-dione (3y)**



Following the general procedure b, the crude product was purified by silica gel flash chromatography (PE: EtOAc: CH<sub>2</sub>Cl<sub>2</sub> = 20: 1: 1 as the eluent) to give **3y** (36 mg,

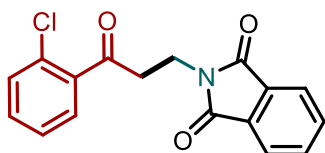
57%) as yellow solid. M.p. 146–147°C

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (t,  $J$  = 2.0 Hz, 1H, ArH), 7.85 (dd,  $J$  = 5.5, 3.0 Hz, 2H, ArH), 7.81 (ddd,  $J$  = 7.7, 2.0, 1.1 Hz, 1H, ArH), 7.72 (dd,  $J$  = 5.5, 3.0 Hz, 2H, ArH), 7.53 (ddd,  $J$  = 7.9, 2.0, 1.1 Hz, 1H, ArH), 7.40 (t,  $J$  = 7.9 Hz, 1H, ArH), 4.14 (t,  $J$  = 7.2 Hz, 2H,  $\text{CH}_2$ ), 3.40 (t,  $J$  = 7.2 Hz, 2H,  $\text{CH}_2$ ).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.0, 168.0, 137.8, 135.0, 134.0, 133.2, 132.0, 130.0, 128.1, 126.0, 123.2, 36.8, 33.3.

HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{17}\text{H}_{13}\text{ClNO}_3^+$ , 314.0578; found: 314.0590.

**2-(3-(2-chlorophenyl)-3-oxopropyl)isoindoline-1,3-dione (3z)**



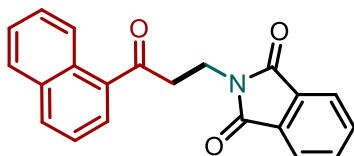
Following the general procedure b, the crude product was purified by silica gel flash chromatography (PE: EtOAc:  $\text{CH}_2\text{Cl}_2$  = 20: 1: 1 as the eluent) to give **3z** (31 mg, 50%) as a yellow oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (dd,  $J$  = 5.4, 3.0 Hz, 2H, ArH), 7.72 (dd,  $J$  = 5.4, 3.0 Hz, 2H, ArH), 7.58 – 7.53 (m, 1H, ArH), 7.42 – 7.36 (m, 2H, ArH), 7.32 (ddd,  $J$  = 7.5, 6.0, 2.8 Hz, 1H, ArH), 4.12 (t,  $J$  = 7.3 Hz, 2H,  $\text{CH}_2$ ), 3.42 (t,  $J$  = 7.3 Hz, 2H,  $\text{CH}_2$ ).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.4, 167.7, 138.3, 134.0, 132.2, 132.0, 131.3, 130.7, 129.5, 127.0, 123.3, 40.9, 33.4.

HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{17}\text{H}_{13}\text{ClNO}_3^+$ , 314.0578; found: 314.0587.

**2-(3-(naphthalen-1-yl)-3-oxopropyl)isoindoline-1,3-dione (3aa)**



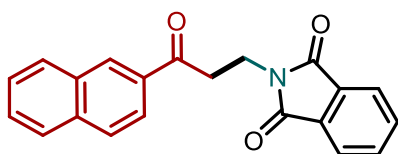
Following the general procedure b, the crude product was purified by silica gel flash chromatography (PE: EtOAc:  $\text{CH}_2\text{Cl}_2$  = 20: 1: 1 as the eluent) to give **3aa** (29 mg, 44%) as a yellow oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.70 (d,  $J = 8.6$  Hz, 1H, ArH), 7.98 (d,  $J = 8.2$  Hz, 1H, ArH), 7.91 (dd,  $J = 7.2, 1.2$  Hz, 1H, ArH), 7.88 – 7.80 (m, 3H, ArH), 7.70 (dd,  $J = 5.5, 3.0$  Hz, 2H, ArH), 7.59 (ddd,  $J = 8.6, 6.8, 1.4$  Hz, 1H, ArH), 7.53 (ddd,  $J = 8.2, 6.8, 1.4$  Hz, 1H, ArH), 7.47 (dd,  $J = 8.2, 7.2$  Hz, 1H, ArH), 4.21 (t,  $J = 7.2$  Hz, 2H,  $\text{CH}_2$ ), 3.52 (t,  $J = 7.2$  Hz, 2H,  $\text{CH}_2$ ).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  201.0, 168.2, 134.7, 134.0, 133.2(2C), 132.0, 130.1, 128.4, 128.3, 128.1, 126.5, 125.8, 124.3, 123.2, 39.7, 33.8.

HRMS (ESI):  $m/z$   $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{16}\text{NO}_3^+$ , 300.1125; found: 300.1137

**2-(3-(naphthalen-2-yl)-3-oxopropyl)isoindoline-1,3-dione (3ab)** [cas: 2521782-69-2]<sup>19</sup>

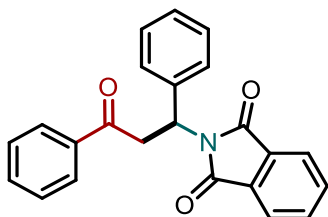


Following the general procedure b, the crude product was purified by silica gel flash chromatography (PE: EtOAc:  $\text{CH}_2\text{Cl}_2 = 20: 1: 1$  as the eluent) to give **3ab** (38 mg, 58%) as a yellow oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.45 (s, 1H), 8.01 (dd,  $J = 8.6, 1.8$  Hz, 1H, ArH), 7.93 (d,  $J = 8.6$  Hz, 1H, ArH), 7.90 – 7.83 (m, 4H, ArH), 7.71 (dd,  $J = 5.5, 3.0$  Hz, 2H, ArH), 7.59 (ddd,  $J = 8.2, 6.9, 1.4$  Hz, 1H, ArH), 7.54 (ddd,  $J = 8.2, 6.9, 1.4$  Hz, 1H, ArH), 4.21 (t,  $J = 7.6$  Hz, 2H,  $\text{CH}_2$ ), 3.57 (t,  $J = 7.6$  Hz, 2H,  $\text{CH}_2$ ).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  198.0, 170.6, 136.0, 134.0, 133.7, 132.4, 132.1, 129.9, 129.6, 128.56, 128.54, 127.8, 126.8, 123.6, 123.3, 36.9, 33.7.

**2-(3-oxo-1,3-diphenylpropyl)isoindoline-1,3-dione (3ac)** [cas: 74726-61-7 <sup>20</sup>]



<sup>19</sup> V. Marsicano, A. Arcadi, M. Aschi and V. Michelet, *Org. Biomol. Chem.*, 2020, **18**, 9438–9447.

<sup>20</sup> X. Jin and L. Zhang, *Org. Biomol. Chem.*, 2022, **20**, 5377–5382.

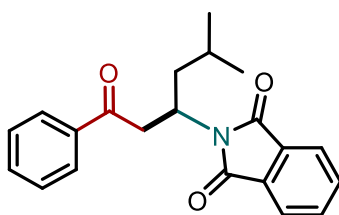


Following the general procedure b, the crude product was purified by silica gel flash chromatography (PE: EtOAc: CH<sub>2</sub>Cl<sub>2</sub> = 20: 1: 1 as the eluent) to give **3ac** (44 mg, 62%) as a yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.98 (dd, *J* = 8.5, 1.3 Hz, 2H, ArH), 7.78 (dd, *J* = 5.5, 3.0 Hz, 2H, ArH), 7.66 (dd, *J* = 5.5, 3.0 Hz, 2H, ArH), 7.60 (d, *J* = 7.3 Hz, 2H, ArH), 7.58 – 7.53 (m, 1H, ArH), 7.44 (t, *J* = 7.7 Hz, 2H, ArH), 7.35 (t, *J* = 7.2 Hz, 2H, ArH), 7.29 (d, *J* = 7.2 Hz, 1H, ArH), 6.08 (dd, *J* = 9.6, 5.2 Hz, 1H, CH), 4.62 (dd, *J* = 18.1, 9.6 Hz, 1H, CH<sub>2</sub>), 3.81 (dd, *J* = 18.1, 5.2 Hz, 1H, CH<sub>2</sub>).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 196.7, 168.3, 139.4, 136.4, 133.9, 133.4, 131.8, 128.8, 128.6, 128.1, 128.0, 127.8, 123.2, 50.4, 40.1.

**2-(4-methyl-1-oxo-1-phenylpentan-3-yl)isoindoline-1,3-dione (3ad)**



Following the general procedure b, the crude product was purified by silica gel flash chromatography (PE: EtOAc: CH<sub>2</sub>Cl<sub>2</sub> = 20: 1: 1 as the eluent) to give **3ad** (50 mg, 75%) as a yellow oil.

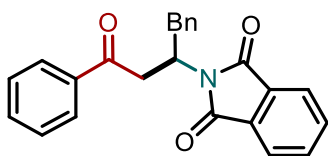
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 7.93 (d, *J* = 8.4 Hz, 2H, ArH), 7.80 (dd, *J* = 5.4, 3.3 Hz, 2H, ArH), 7.68 (dd, *J* = 5.4, 3.3 Hz, 2H, ArH), 7.53 (t, *J* = 7.3 Hz, 1H, ArH), 7.42 (t, *J* = 7.7 Hz, 2H, ArH), 5.08 – 4.97 (m, 1H, CH<sub>2</sub>CHCH<sub>2</sub>), 3.89 (dd, *J* = 17.6, 8.4 Hz, 1H in COCH<sub>2</sub>), 3.43 (dd, *J* = 17.6, 5.6 Hz, 1H in COCH<sub>2</sub>), 2.19 (m, 1H, CH<sub>2</sub>CHCH<sub>2</sub>), 1.60 – 1.44 (m, 2H, CHCH<sub>2</sub>CH(CH<sub>3</sub>)), 1.01 (d, *J* = 6.2 Hz, 3H, CH<sub>3</sub>), 0.91 (d, *J* = 6.2 Hz, 3H, CH<sub>3</sub>).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 197.4, 168.4, 136.6, 133.8, 133.2, 131.8, 128.5, 128.0, 123.1, 45.5, 41.4, 41.1, 25.1, 23.2, 21.7.

HRMS (ESI): *m/z* [M + H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>22</sub>NO<sub>3</sub><sup>+</sup>, 336.1594; found: 336.1605.

**2-(4-oxo-1,4-diphenylbutan-2-yl)isoindoline-1,3-dione (3ae)** [cas: 3061897-08-

0]<sup>21</sup>

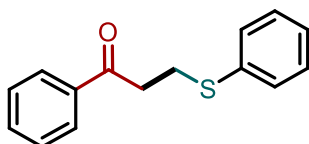


Following the general procedure b, the crude product was purified by silica gel flash chromatography (PE: EtOAc: CH<sub>2</sub>Cl<sub>2</sub> = 20: 1: 1 as the eluent) to give **3ae** (35 mg, 48%) as a yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.91 (dd, *J* = 8.4, 1.4 Hz, 2H, ArH), 7.74 (dd, *J* = 5.4, 3.0 Hz, 2H, ArH), 7.64 (dd, *J* = 5.4, 3.0 Hz, 2H, ArH), 7.57 – 7.49 (m, 1H, ArH), 7.44 – 7.39 (m, 2H, ArH), 7.25 – 7.12 (m, 5H, ArH), 5.26 – 5.14 (m, 1H, CH<sub>2</sub>CHCH<sub>2</sub>), 3.98 (dd, *J* = 17.7, 8.6 Hz, 1H in CHCH<sub>2</sub>Ph), 3.50 (dd, *J* = 17.7, 5.4 Hz, 1H in CHCH<sub>2</sub>Ph), 3.31 (dd, *J* = 13.6, 9.3 Hz, 1H in CHCH<sub>2</sub>CO), 3.22 (dd, *J* = 13.6, 6.7 Hz, 1H in CHCH<sub>2</sub>CO).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 197.2, 168.2, 137.5, 136.5, 133.8, 133.3, 131.6, 129.1, 128.6, 128.5, 128.0, 126.7, 123.1, 48.6, 40.0, 38.6.

**1-phenyl-3-(phenylthio)propan-1-one (3af)** [cas: 22956-36-1]<sup>22</sup>



Following the general procedure b, the crude product was purified by silica gel flash chromatography (PE: EtOAc: CH<sub>2</sub>Cl<sub>2</sub> = 20: 1: 1 as the eluent) to give **3af** (31 mg, 64%) as a yellow oil.

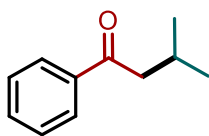
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 – 7.88 (m, 2H, ArH), 7.59 – 7.53 (m, 1H, ArH), 7.47 – 7.42 (m, 2H, ArH), 7.39 – 7.35 (m, 2H, ArH), 7.30 (t, *J* = 7.7 Hz, 2H, ArH), 7.22 – 7.17 (m, 1H, ArH), 3.38 – 3.25 (m, 4H, 2 CH<sub>2</sub>).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 198.1, 136.5, 135.8, 133.3, 129.4, 129.0, 128.6, 128.0, 126.2, 38.4, 27.9.

<sup>21</sup> P. Wang, J. Wang, N. Song, X. Zhou and M. Li, *Chin. Chem. Lett.*, 2025, **36**, 109748.

<sup>22</sup> Y. Saga, Y. Nakayama, T. Watanabe, M. Kondo and S. Masaoka, *Org. Lett.*, 2023, **25**, 1136–1141.

**3-methyl-1-phenylbutan-1-one (3ag)** [cas: 582-62-7]<sup>23</sup>

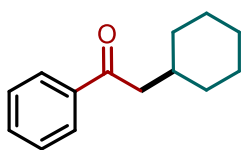


Following the general procedure b, the crude product was purified by silica gel flash chromatography (PE: EtOAc = 50: 1 as the eluent) to give **3ag** (16 mg, 51%) as a yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.98 – 7.92 (m, 2H, ArH), 7.55 (t, *J* = 7.4 Hz, 1H, ArH), 7.45 (t, *J* = 7.4 Hz, 2H, ArH), 2.83 (d, *J* = 6.8 Hz, 2H, ArH), 2.30 (t hept, *J* = 6.8, 6.8 Hz, 1H, CH<sub>3</sub>CHCH<sub>3</sub>), 1.00 (d, *J* = 6.8 Hz, 6H, 2 CH<sub>3</sub>).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 200.2, 137.4, 132.8, 128.5, 128.1, 47.5, 25.1, 22.7.

**2-cyclohexyl-1-phenylethan-1-one (3ah)** [cas: 5653-09-8]<sup>24</sup>



Following the general procedure b, the crude product was purified by silica gel flash chromatography (PE: EtOAc = 50: 1 as the eluent) to give **3ah** (30 mg, 75%) as a yellow oil.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.97 (dd, *J* = 8.4, 1.4 Hz, 2H, ArH), 7.62 – 7.53 (m, 1H, ArH), 7.48 (t, *J* = 7.5 Hz, 2H, ArH), 2.84 (d, *J* = 6.8 Hz, 2H), 2.08 – 1.93 (m, 1H), 1.83 – 1.64 (m, 5H), 1.31 (dtt, *J* = 16.2, 10.0, 3.4 Hz, 2H), 1.20 (qt, *J* = 12.6, 3.4 Hz, 1H), 1.04 (qd, *J* = 12.3, 2.9 Hz, 2H).

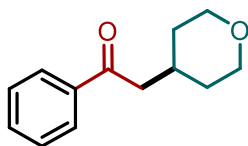
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 200.2, 137.5, 132.8, 128.5, 128.1, 46.2, 34.5, 33.4, 26.2, 26.1.

**1-phenyl-2-(tetrahydro-2H-pyran-4-yl)ethan-1-one (3ai)** [cas: 1247377-66-7]<sup>25</sup>

<sup>23</sup> C. Zhang, H. Tang, X. Zhao, X. Shen and Y. Qiu, *J. Am. Chem. Soc.*, 2025, **147**, 23297–23307.

<sup>24</sup> S. Ji, X. Li, Y. Wang, D. Zhang, J. Lv, Y. Shi and D. Yang, *Org. Lett.*, 2025, **27**, 7892–7897.

<sup>25</sup> S. Zhang, B. Li and S. Li, *J. Am. Chem. Soc.*, 2025, **147**, 11700–11706.

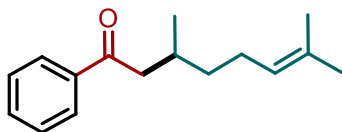


Following the general procedure b, the crude product was purified by silica gel flash chromatography (PE: EtOAc = 50: 1 as the eluent) to give **3ai** (26 mg, 64%) as a yellow oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (dd,  $J = 8.4, 1.4$  Hz, 2H), 7.60 – 7.54 (m, 1H), 7.47 (t,  $J = 7.6$  Hz, 2H), 3.95 (td,  $J = 11.8, 4.0$  Hz, 2H), 3.44 (td,  $J = 11.8, 2.1$  Hz, 2H), 2.90 (d,  $J = 6.8$  Hz, 2H), 2.25 (ttt,  $J = 10.5, 6.8, 3.3$  Hz, 1H), 1.69 (ddd,  $J = 13.2, 4.0, 2.1$  Hz, 2H), 1.39 (dtd,  $J = 13.2, 11.8, 4.5$  Hz, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.2, 137.2, 133.1, 128.6, 128.0, 67.8, 45.3, 33.0, 31.4.

**3,6-dimethyl-1-phenylhept-5-en-1-one (3aj)** [cas: 72237-38-8]<sup>26</sup>



Following the general procedure b, the crude product was purified by silica gel flash chromatography (PE: EtOAc = 50: 1 as the eluent) to give **3aj** (40 mg, 88%) as a yellow oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 – 7.91 (m, 2H), 7.54 (tt,  $J = 7.4, 1.4$  Hz, 1H), 7.45 (t,  $J = 7.4$  Hz, 2H), 5.14 – 5.06 (t hept,  $J = 7.0, 1.2$  Hz, 1H), 2.96 (dd,  $J = 15.8, 5.6$  Hz, 1H), 2.74 (dd,  $J = 15.8, 8.1$  Hz, 1H), 2.26 – 2.12 (m, 1H), 2.11 – 1.94 (m, 1H), 1.68 (d,  $J = 1.2$  Hz, 3H), 1.60 (d,  $J = 1.2$  Hz, 3H), 1.42 (ddt,  $J = 13.6, 9.4, 6.2$  Hz, 1H), 1.29 (dddd,  $J = 13.6, 9.4, 7.7, 6.2$  Hz, 1H), 0.97 (d,  $J = 6.6$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  200.3, 137.4, 132.8, 131.4, 128.5, 128.1, 124.4, 45.9, 37.2, 29.5, 25.7, 25.5, 19.9, 17.6.

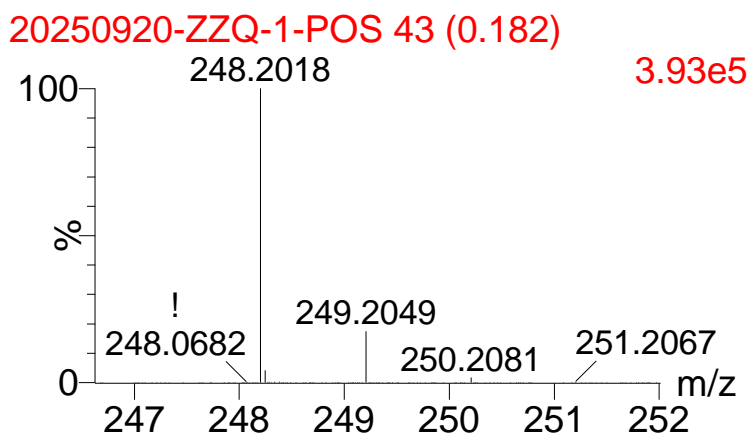
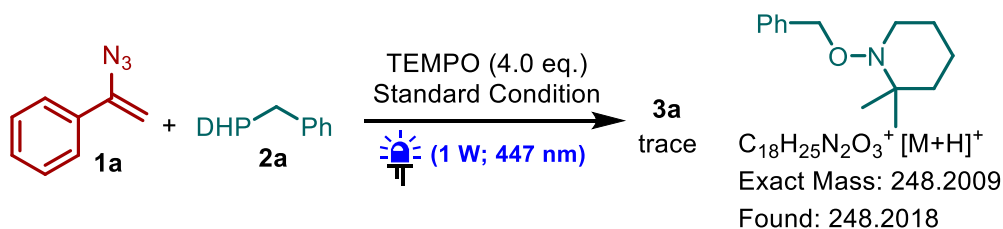
<sup>26</sup> T. Anh To, C. Pei, R. M. Koenigs and T. Vinh Nguyen, *Angew. Chem. Int. Ed.*, 2022, **61**, e202117366.

### 3. Control experiments for Mechanistic studies

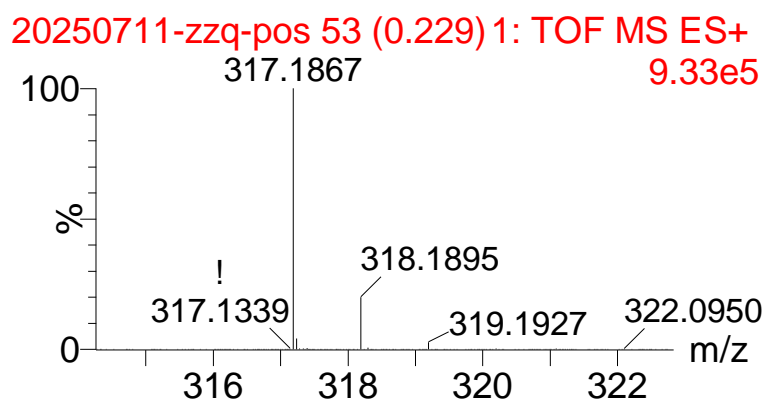
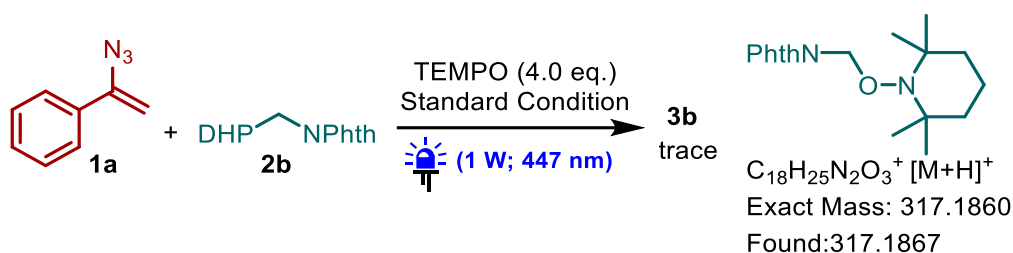
#### 3.1 TEMPO trapping experiment

In a 3 mL closed screw-top glass vial, 4CzIPN (5 mol%, 10  $\mu$ mol), 5-NIPA (0.75 equiv, 0.15 mmol), vinyl azides **1** (1.0 equiv, 0.2 mmol), AgOTf (0.3 equiv, 0.06 mmol) and 4-benzyl-1,4-DHPs **2** (2.0 equiv, 0.4 mmol) were dissolved in CH<sub>3</sub>CN (1 mL). Afterward, (2,6-di*tert*-butyl-4-methyl-phenol) (TEMPO, 4.0 equiv) was added in the mixture. Then the mixture was stirred for 5 h with irradiation of 1 W blue light ( $\lambda$  = 447 nm).

High-resolution mass spectrometry (HRMS) was used to analyze the reaction solution.



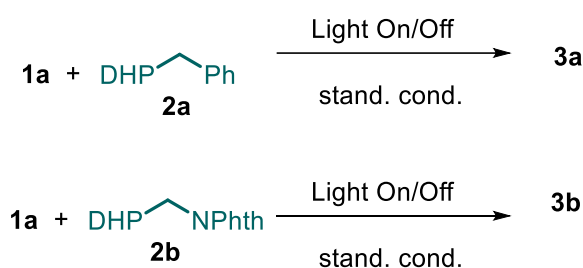
Scheme S1 TEMPO radical trapping experiment of **2a**



Scheme S2 TEMPO radical trapping experiment of **2b**

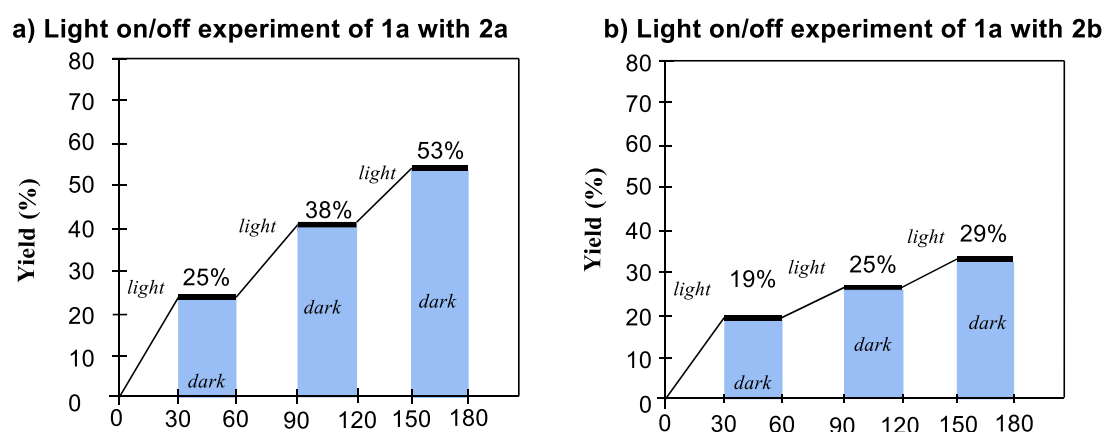
### 3.2 Light on/off experiment

On/Off experiment



(a) In a 3 mL closed screw-top glass vial, AgOTf (30 mol%, 0.06 mmol), 4CzIPN (5 mol%, 10  $\mu$ mol), 5-NIPA (0.75 equiv., 0.15 mmol), vinyl azides **1a** (1.0 equiv, 0.2 mmol) and 4-alkyl-1,4-DHPs **2a** (2.0 equiv, 0.4 mmol) were dissolved in CH<sub>3</sub>CN (1 mL). 1,3,5-Trimethoxybenzene (22.4 mg, 0.133 mmol) was then added to the system as the internal standard. The mixture was irradiated under blue-LEDs Light (447 nm, 1W) for 30 min. 10  $\mu$ L of the solution was abstracted and dissolved in 0.5 mL CDCl<sub>3</sub> and the yield of **3a** was determined by <sup>1</sup>H NMR. The vial was then stirred in a dark box for 30 min and <sup>1</sup>H NMR yield was determined. The steps above were repeated in 60 min and 90 min.

(b) In a 3 mL closed screw-top glass vial, AgOTf (30 mol%, 0.06 mmol), 4CzIPN (5 mol%, 10  $\mu$ mol), 5-NIPA (0.75 equiv., 0.15 mmol), vinyl azides **1a** (1.0 equiv, 0.2 mmol) and 4-alkyl-1,4-DHPs **2b** (2.0 equiv, 0.4 mmol) were dissolved in CH<sub>3</sub>CN (1 mL). 1,3,5-Trimethoxybenzene (22.4 mg, 0.133 mmol) was then added to the system as the internal standard. The mixture was irradiated under blue-LEDs Light (447 nm, 1W) for 30 min. 10  $\mu$ L of the solution was abstracted and dissolved in 0.5 mL CDCl<sub>3</sub> and the yield of **3b** was determined by <sup>1</sup>H NMR. The vial was then stirred in a dark box for 30 min and <sup>1</sup>H NMR yield was determined. The steps above were repeated in 60 min and 90 min.

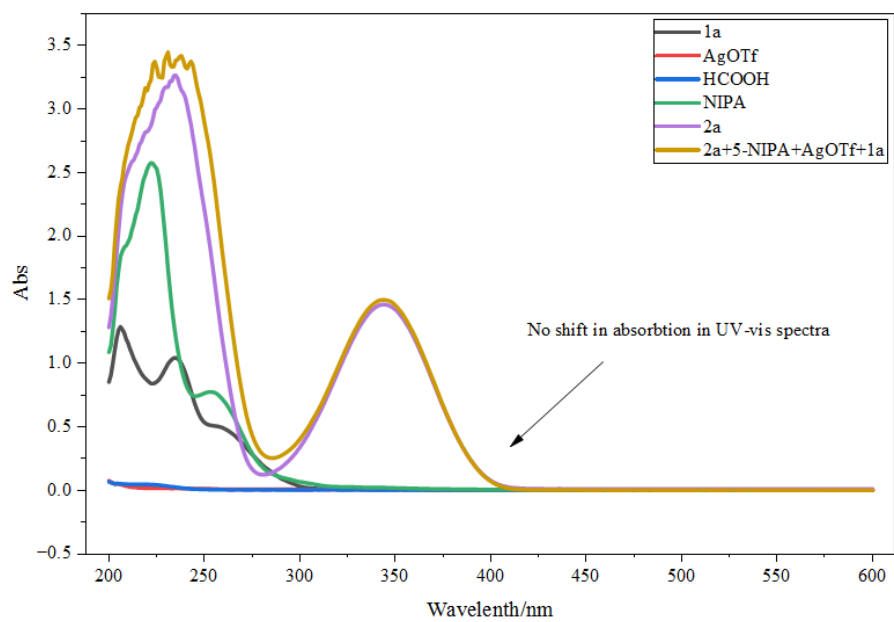


**Figure S3** Light ON/OFF experiment.

#### 4. UV-vis absorption spectra of **1a**, **2a**, AgOTf and 5-NIPA.

UV-vis spectra experiments were performed with a freshly prepared solution of  $1 \times 10^{-5}$  M solution of **1a**, **2a**, AgOTf and 5-NIPA in CH<sub>3</sub>CN (Figure S4).

No obvious wavelength peak shift was observed, indicating that no electron-donor-acceptor (EDA) complex were generated in current condition.



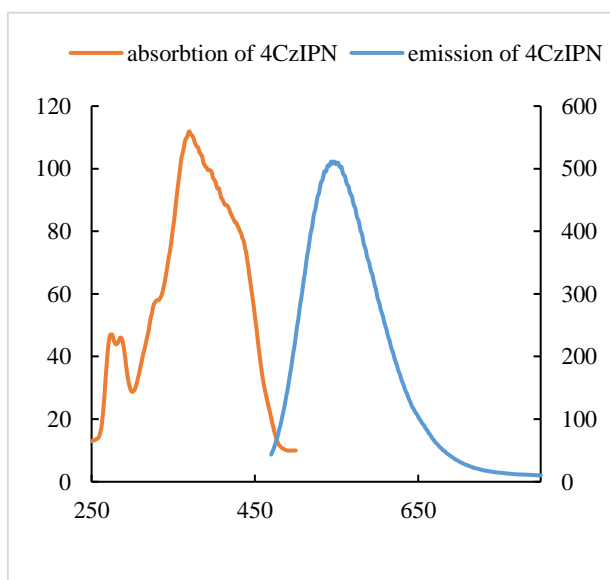
**Figure S4.** Absorption spectra of **1a**, **2a**, AgOTf and 5-NIPA and mixture of **1a**, **2a**, AgOTf and 5-NIPA.



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## 5. Fluorescence studies

Stern-Volmer fluorescence quenching experiments were run with a freshly prepared solution of  $1 \times 10^{-5}$  M solution of 4CzIPN in  $\text{CH}_3\text{CN}$  added the appropriate amount of a quencher in a screw-top quartz cuvette at room temperature (Figure S7). The fluorescence spectra were examined on F-97 Pro fluorescence spectrophotometer (Shanghai Lengguang, China). The fluorescence emission spectrum was measured from 200 nm to 800 nm. After degassing the sample with a stream of  $\text{N}_2$  for 5 minutes, the emission intensity at 545 nm was collected with excited wavelength of 370 nm in  $\text{CH}_3\text{CN}$ .

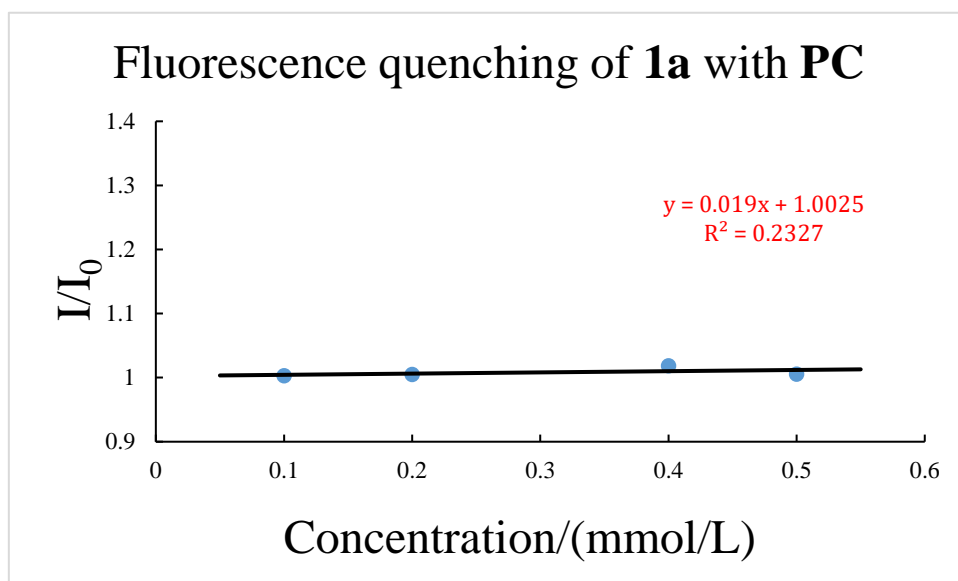


**Figure S5.** Emission spectra of PC (4CzIPN)

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Concentration[mmol/L]	0.1	0.2	0.4	0.5
$I_0/I$	1.003	1.005	1.019	1.006

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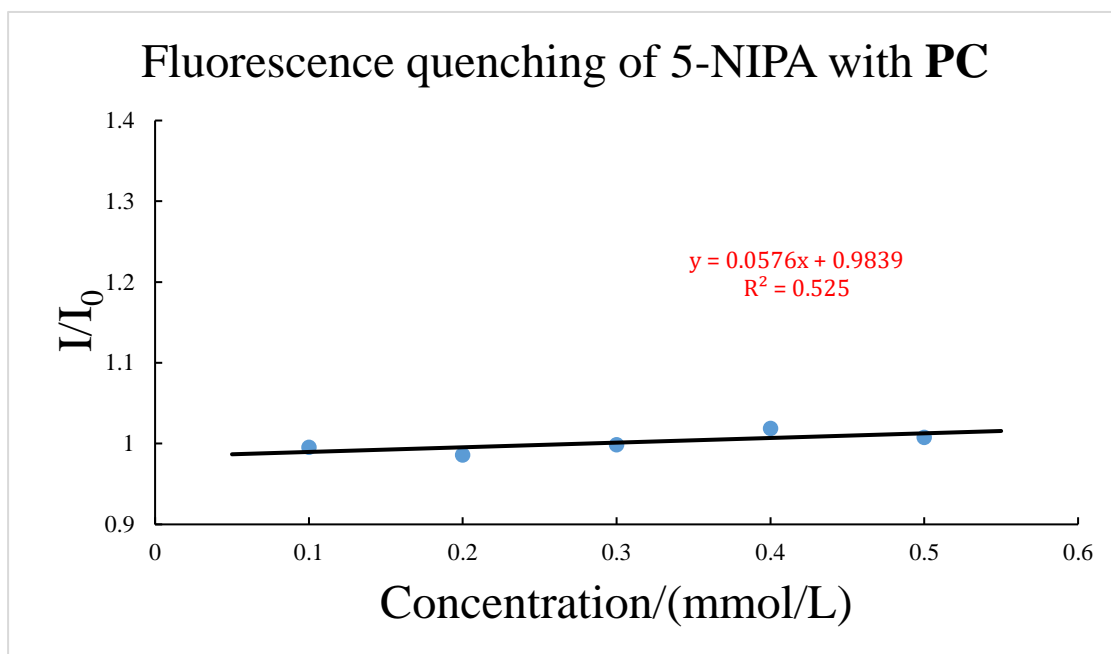


**Figure S6.** Fluorescence quenching of PC with **1a**.

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Concentration[mmol/L]	0.1	0.2	0.3	0.4	0.5
$I_0/I$	0.9953	0.9857	0.9986	1.019	1.008

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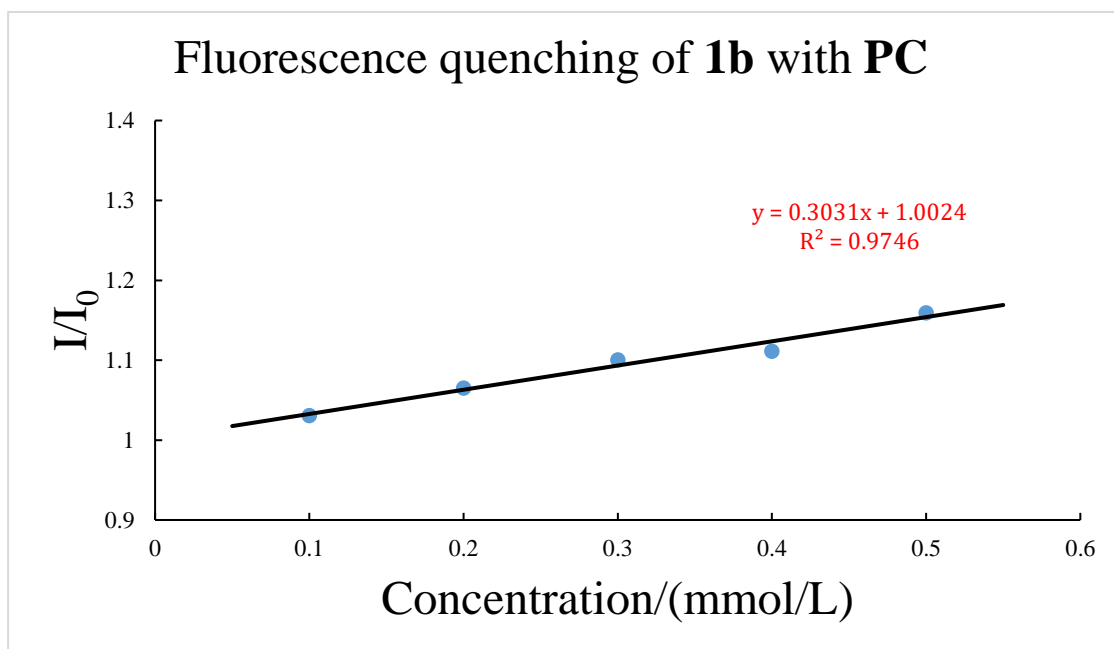


**Figure S7.** Fluorescence quenching of PC with 5-NIPA.

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Concentration[mmol/L]	0.1	0.2	0.3	0.4	0.5
$I_0/I$	1.031	1.065	1.100	1.111	1.159

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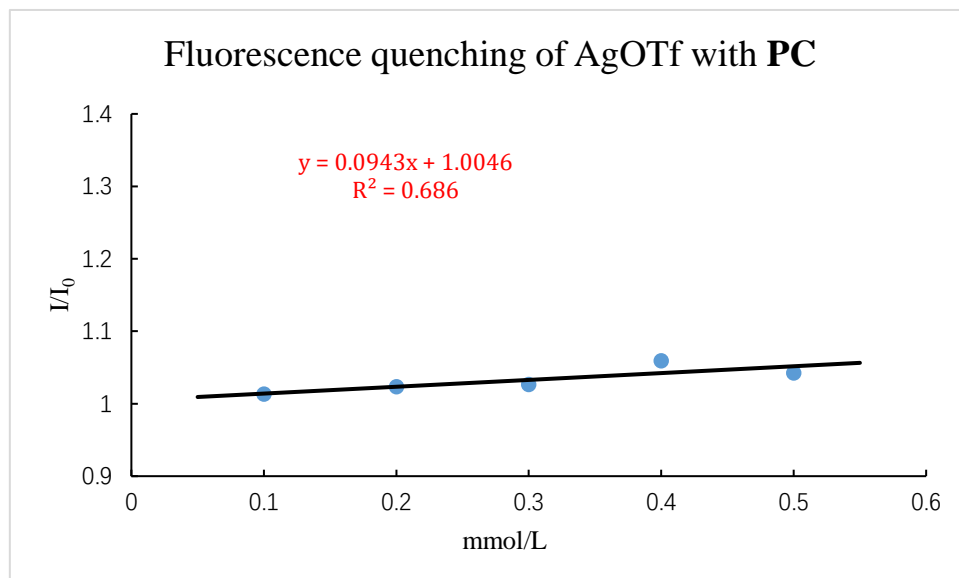


**Figure S8.** Fluorescence quenching of PC with **1b**.

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Concentration[mmol/L]	0.1	0.2	0.3	0.4	0.5
$I_0/I$	1.0131	1.0234	1.0264	1.0590	1.0424

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**Figure S9.** Fluorescence quenching of PC with AgOTf.

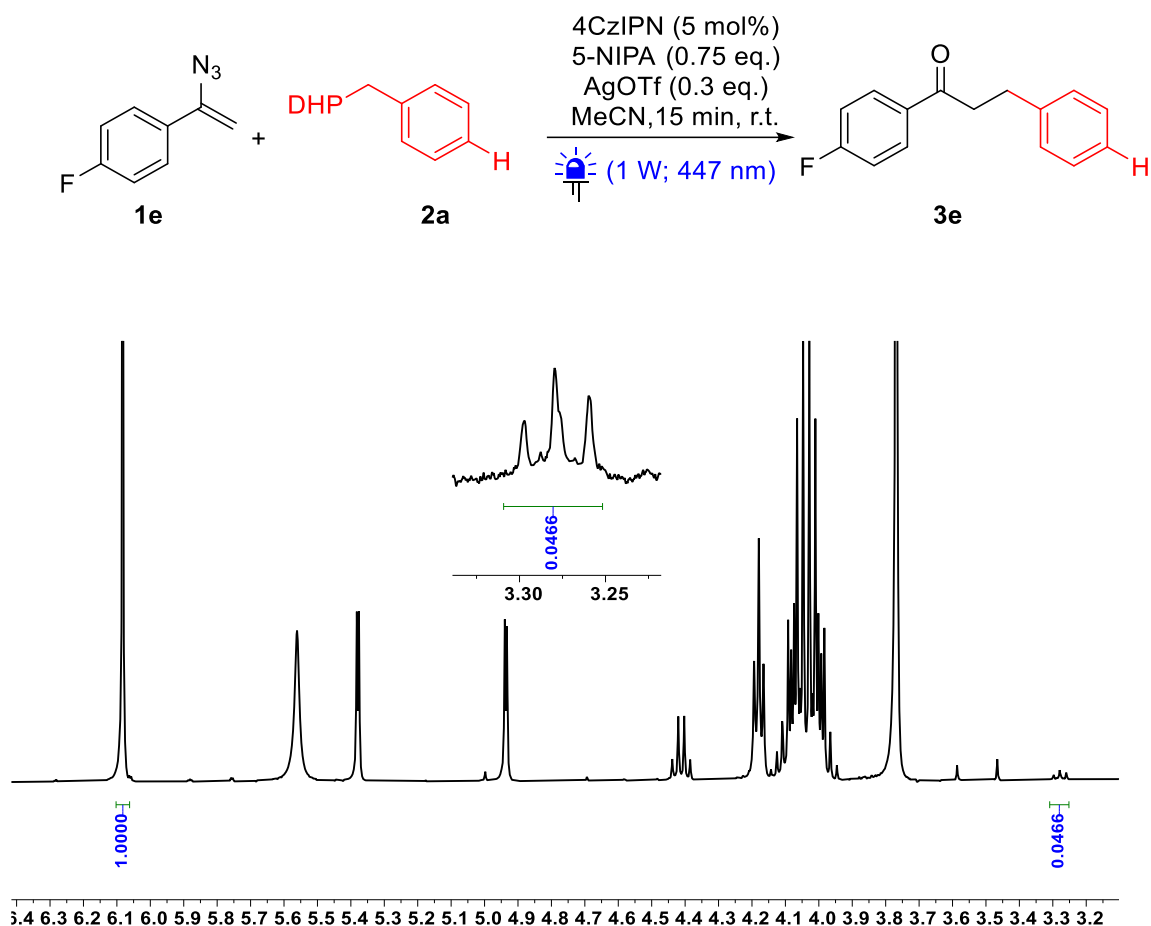
## 6. Hammett analysis for the competition reactions

### 5.1. Hammett analysis for the competition reactions of 1,4-alkyl-DHPs with **1e**.

Add 79 mg of 4CzIPN (0.1 mmol), 316.7 mg of 5-NIPA (1.5 mmol), 154 mg of AgOTf (0.6 mmol) and 1-(1-azidovinyl)-4-fluorobenzene **1e** (33 mg, 2 mmol) to a 10 mL volumetric flask and add CH<sub>3</sub>CN to make up to 10 mL to prepare a standard solution for subsequent experiments.

#### 5.1.1. The reaction of **3e** and integration ratio of 1,3,5-trimethoxybenzene to **3e** in <sup>1</sup>H NMR.

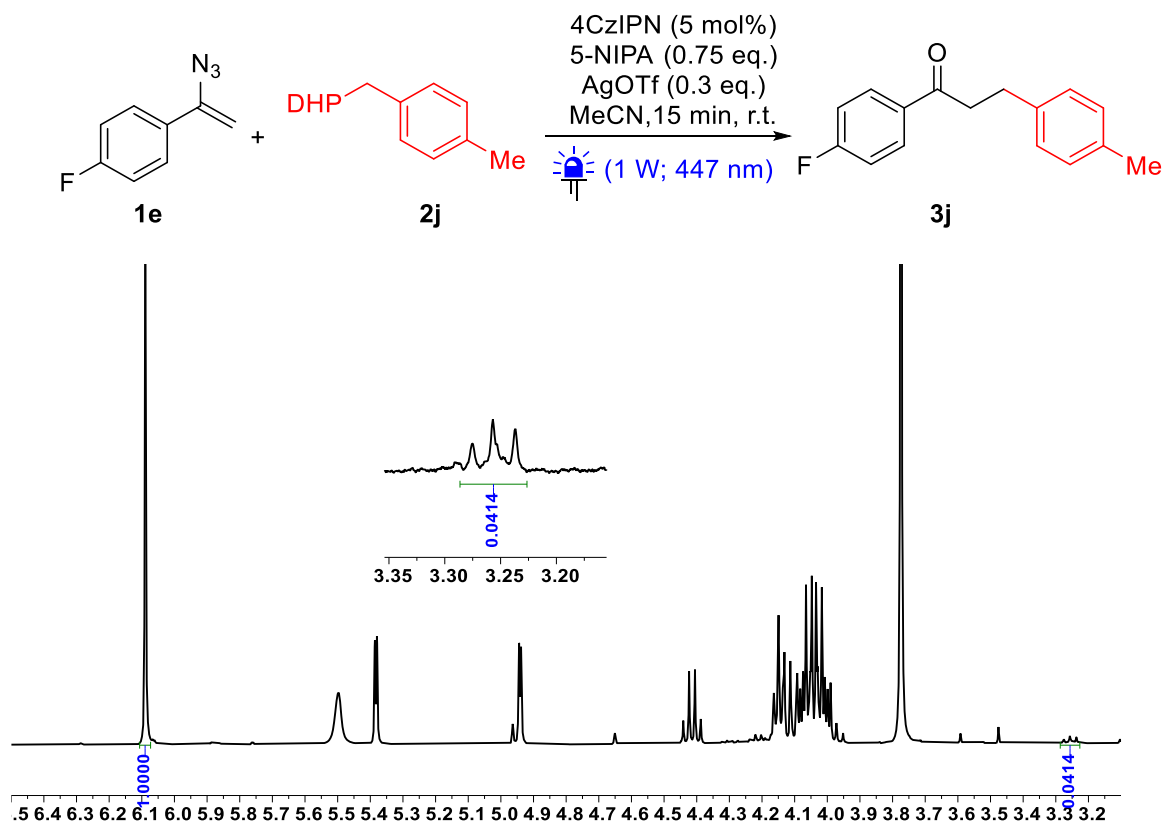
In a 3 mL closed screw-top glass vial, 0.4 mmol of 4-benzyl-1,4-DHPs **2** was added, then 1 mL standard solution was then added to the reaction system. The vial was stirred for 15 min with irradiation of 1W blue light ( $\lambda = 447$  nm). The product ratio was detected directly by <sup>1</sup>H NMR of reaction system.



Exact integration of 1,3,5-trimethoxybenzene: **3e** is 1.000: 0.0466.

5.1.2. The reaction of **3j** and integration ratio of 1,3,5-trimethoxybenzene to **3j** in  $^1\text{H}$  NMR.

In a 3 mL closed screw-top glass vial, 0.4 mmol of 4-(*p*-methylbenzyl)-1,4-DHPs **2** was added, then 1 mL standard solution was then added to the reaction system. The vial was stirred for 15 min with irradiation of 1 W blue light ( $\lambda = 447$  nm). The product ratio was detected directly by  $^1\text{H}$  NMR of reaction system.

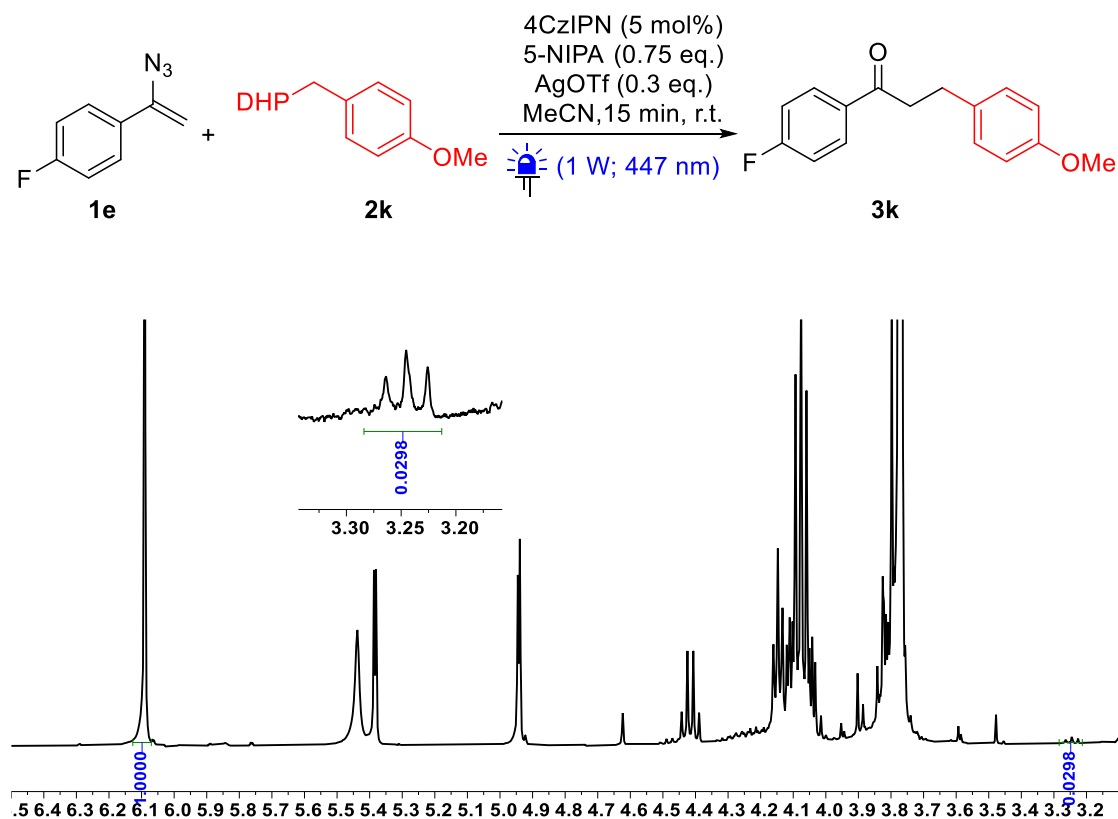


Exact integration of 1,3,5-trimethoxybenzene: **3j** is 1.000: 0.0414. The ratio of **3j/3e** = 0.888.

$$\ln(\mathbf{3j/3e}) = -0.118.$$

### 5.1.3. The reaction of **3k** and integration ratio of 1,3,5-trimethoxybenzene to **3k** in $^1\text{H}$ NMR.

In a 3 mL closed screw-top glass vial, 0.4 mmol of 4-(*p*-methoxybenzyl)-1,4-DHPs **2** was added, then 1 mL standard solution was then added to the reaction system. The vial was stirred for 15 min with irradiation of 1 W blue light ( $\lambda = 447$  nm). The product ratio was detected directly by  $^1\text{H}$  NMR of reaction system.



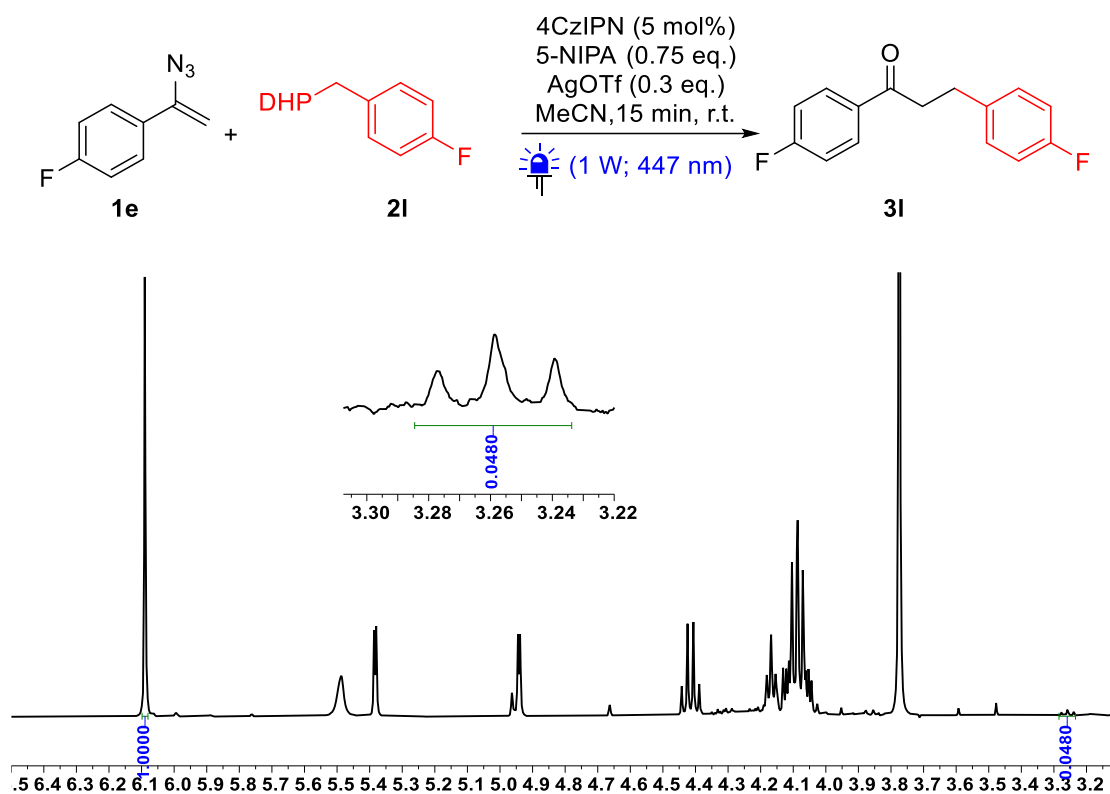
Exact integration of 1,3,5-trimethoxybenzene: **3k** is 1.000: 0.0298. The ratio of **3k/3e** = 0.639.

$$\ln(\mathbf{3k/3e}) = -0.447.$$



5.1.4. The reaction of **3I** and integration ratio of 1,3,5-trimethoxybenzene to **3I** in  $^1\text{H}$  NMR.

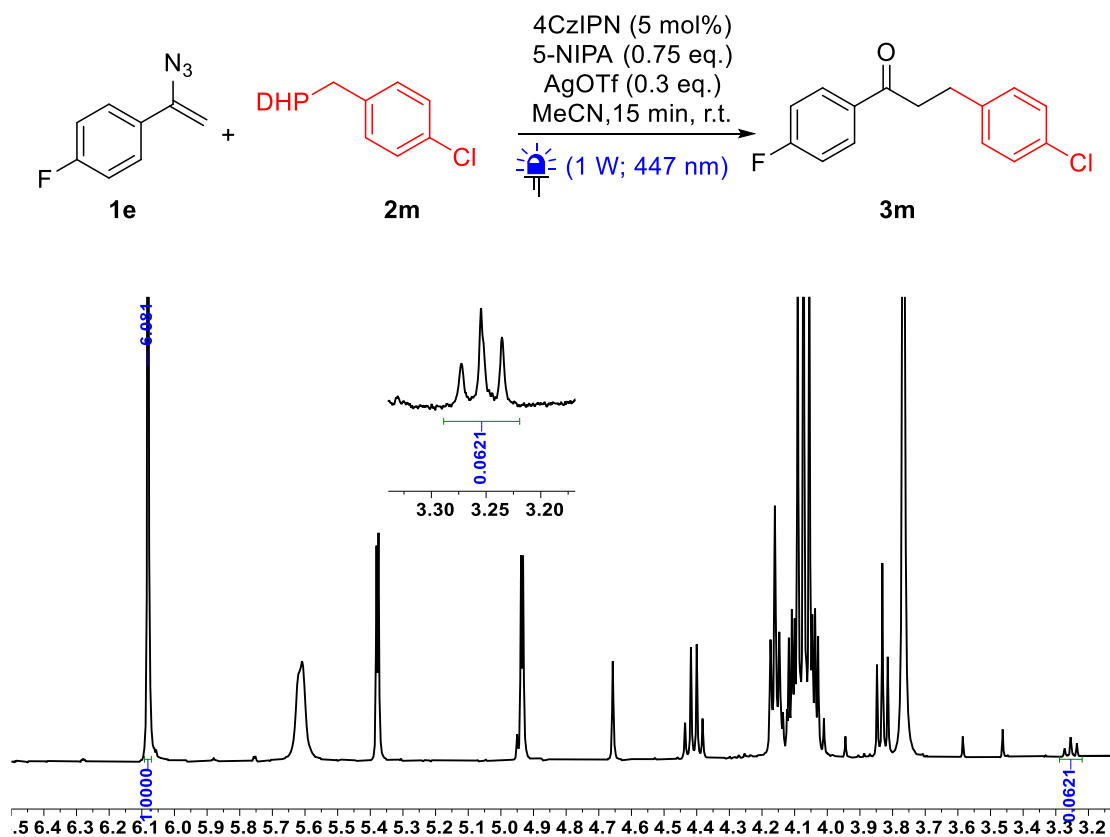
In a 3 mL closed screw-top glass vial, 0.4 mmol of 4-(*p*-chlorobenzyl)-1,4-DHPs **2** was added, then 1 mL standard solution was then added to the reaction system. The vial was stirred for 15 min with irradiation of 1W blue light ( $\lambda = 447$  nm). The product ratio was detected directly by  $^1\text{H}$  NMR of reaction system.



Exact integration of 1,3,5-trimethoxybenzene: **3I** is 1.000: 0.0480. The ratio of **3I/3e** = 1.030.  
 $\ln(\mathbf{3I/3e}) = 0.030$ .

5.1.4. The reaction of **3m** and integration ratio of 1,3,5-trimethoxybenzene to **3m** in  $^1\text{H}$  NMR.

In a 3 mL closed screw-top glass vial, 0.4 mmol of 4-(*p*-fluorobenzyl)-1,4-DHPs **2** was added, then 1 mL standard solution was then added to the reaction system. The vial was stirred for 15 min with irradiation of 1 W blue light ( $\lambda = 447$  nm). The product ratio was detected directly by  $^1\text{H}$  NMR of reaction system.

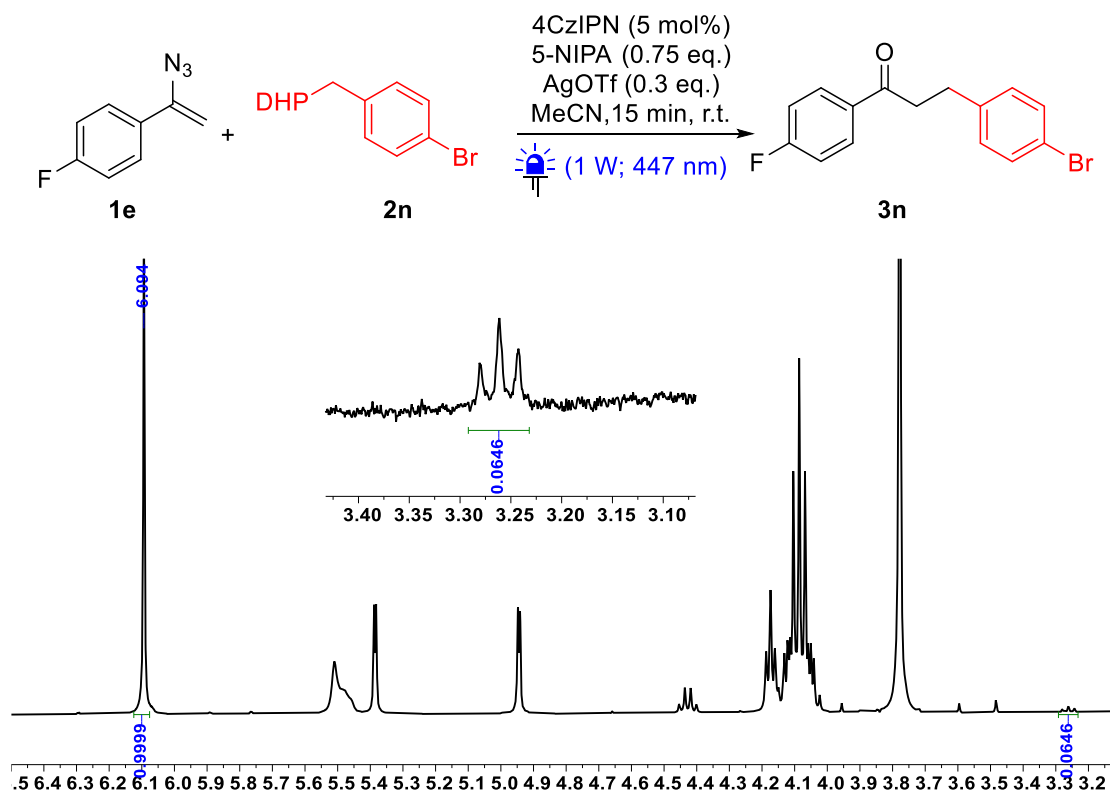


Exact integration of 1,3,5-trimethoxybenzene: **3m** is 1.000: 0.0621. The ratio of **3m/3e** = 1.332.

$$\ln(\mathbf{3m/3e}) = 0.287.$$

5.1.4. The reaction of **3n** and integration ratio of 1,3,5-trimethoxybenzene to **3n** in  $^1\text{H}$  NMR.

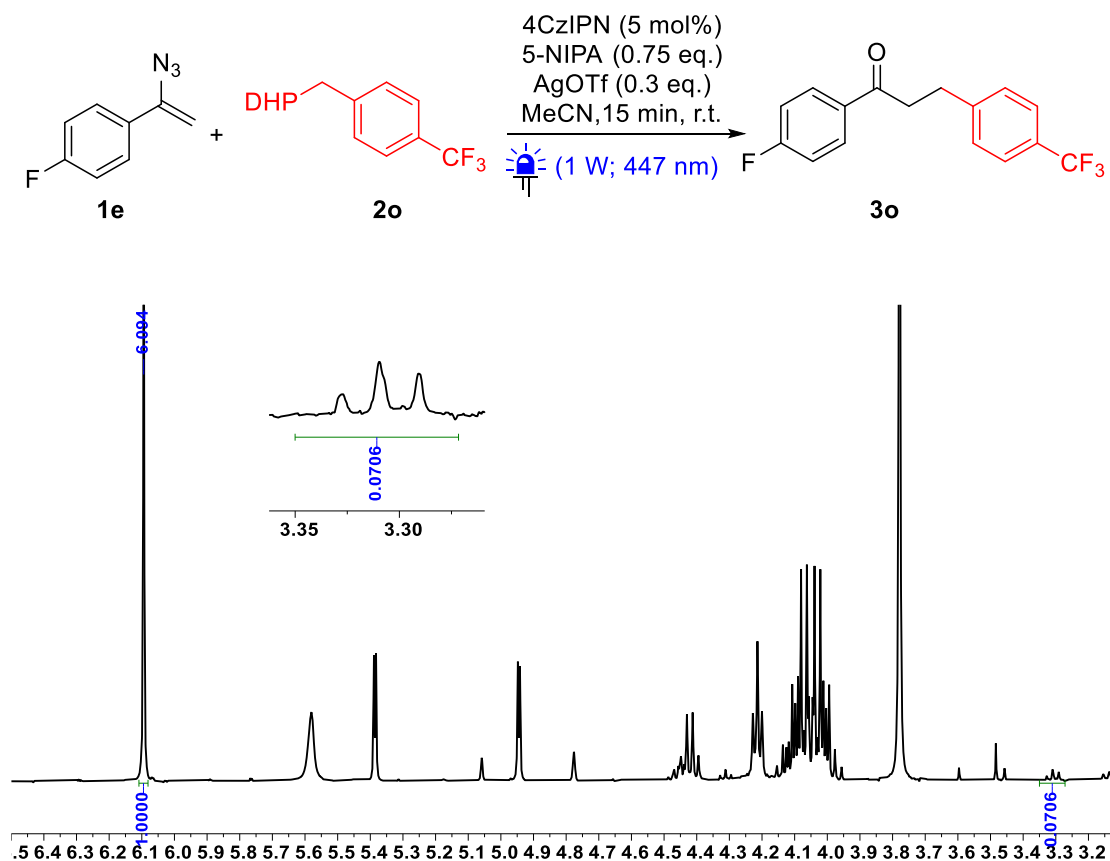
In a 3 mL closed screw-top glass vial, 0.4 mmol of 4-(*p*-bromobenzyl)-1,4-DHPs **2** was added, then 1 mL standard solution was then added to the reaction system. The vial was stirred for 15 min with irradiation of 1W blue light ( $\lambda = 447$  nm). The product ratio was detected directly by  $^1\text{H}$  NMR of reaction system.



Exact integration of 1,3,5-trimethoxybenzene: **3n** is 1.000: 0.0646. The ratio of **3n/3e** = 1.386.  
 $\ln(\mathbf{3n/3e}) = 0.327$ .

5.1.4. The reaction of **3o** and integration ratio of 1,3,5-trimethoxybenzene to **3o** in <sup>1</sup>H NMR.

In a 3 mL closed screw-top glass vial, 0.4 mmol of 4-(*p*-bromobenzyl)-1,4-DHPs **2** was added, then 1 mL standard solution was then added to the reaction system. The vial was stirred for 15 min with irradiation of 1 W blue light ( $\lambda = 447$  nm). The product ratio was detected directly by <sup>1</sup>H NMR of reaction system.



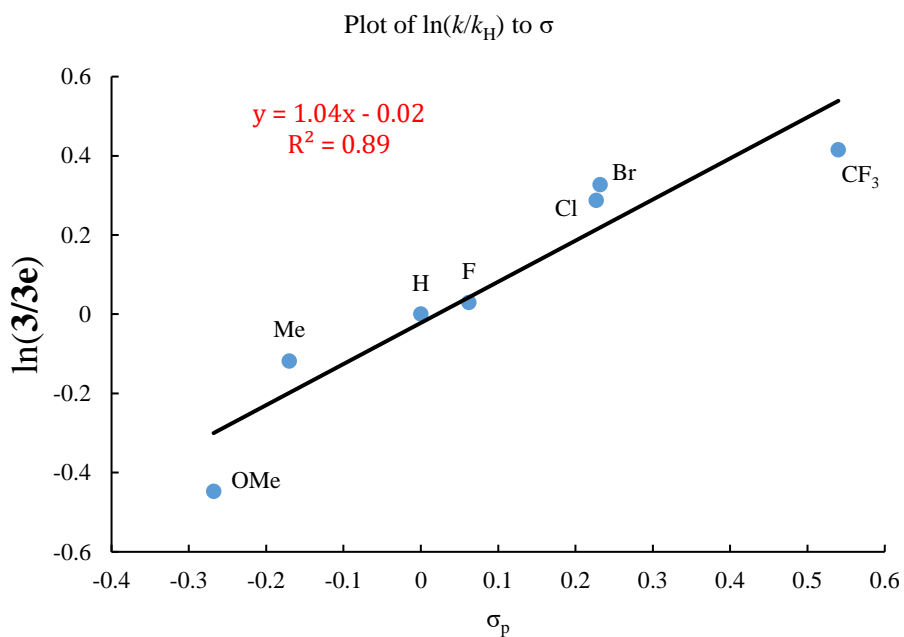
Exact integration of 1,3,5-trimethoxybenzene: **3o** is 1.000: 0.0706. The ratio of **3o/3e** = 1.515.

$\ln(\mathbf{3o/3e}) = 0.415$ .

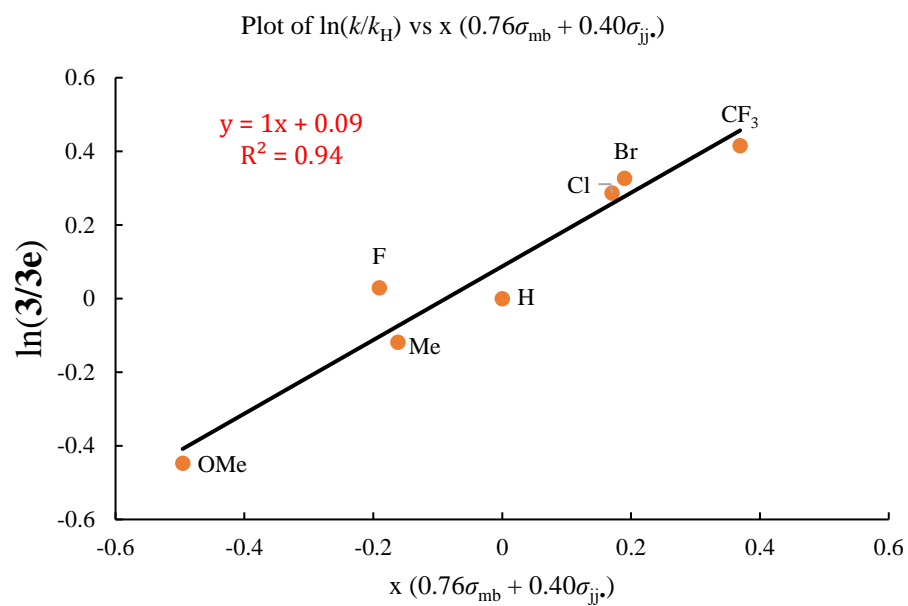
**Table S1.** Dual-parameter correlation with polar substituent constants ( $\sigma_{mb}$ ) and spin effect parameters ( $\sigma_{ij}$ ) of vinyl azides **1e** with **2**

Entry	<b>2</b>	$\ln(k/k_H)^a$	$\sigma^b$	$\sigma_{mb}^c$	$\sigma_{ij}^c$	$0.76\sigma_{mb} + 0.40\sigma_{ij}^d$
1	<b>2a</b> ( <i>p</i> -H)	0	0	0	0	0
2	<b>2j</b> ( <i>p</i> -Me)	-0.118	-0.17	-0.29	0.15	-0.162
3	<b>2k</b> ( <i>p</i> -OMe)	-0.447	-0.268	-0.77	0.23	-0.496
4	<b>2l</b> ( <i>p</i> -F)	0.030	0.062	-0.24	-0.02	-0.191
5	<b>2m</b> ( <i>p</i> -Cl)	0.287	0.227	0.11	0.22	0.171
6	<b>2n</b> ( <i>p</i> -Br)	0.327	0.232	0.13	0.23	0.190
7	<b>2o</b> ( <i>p</i> -CF <sub>3</sub> )	0.415	0.54	0.49	-0.01	0.369

<sup>a</sup> Relative rate is calculated by the ratio of **3/3e**. <sup>b</sup> Hammett constants. <sup>c</sup> polar substituent constants  $\sigma_{mb}$  and spin effect parameters ( $\sigma_{ij}$ ) were obtained from ref 45. <sup>d</sup> quadratic linear regression analysis was obtained from excel analysis.



**Figure S10** Hammett plot analysis of **1e** and 4-benzyl-1,4-DHPs **2**.



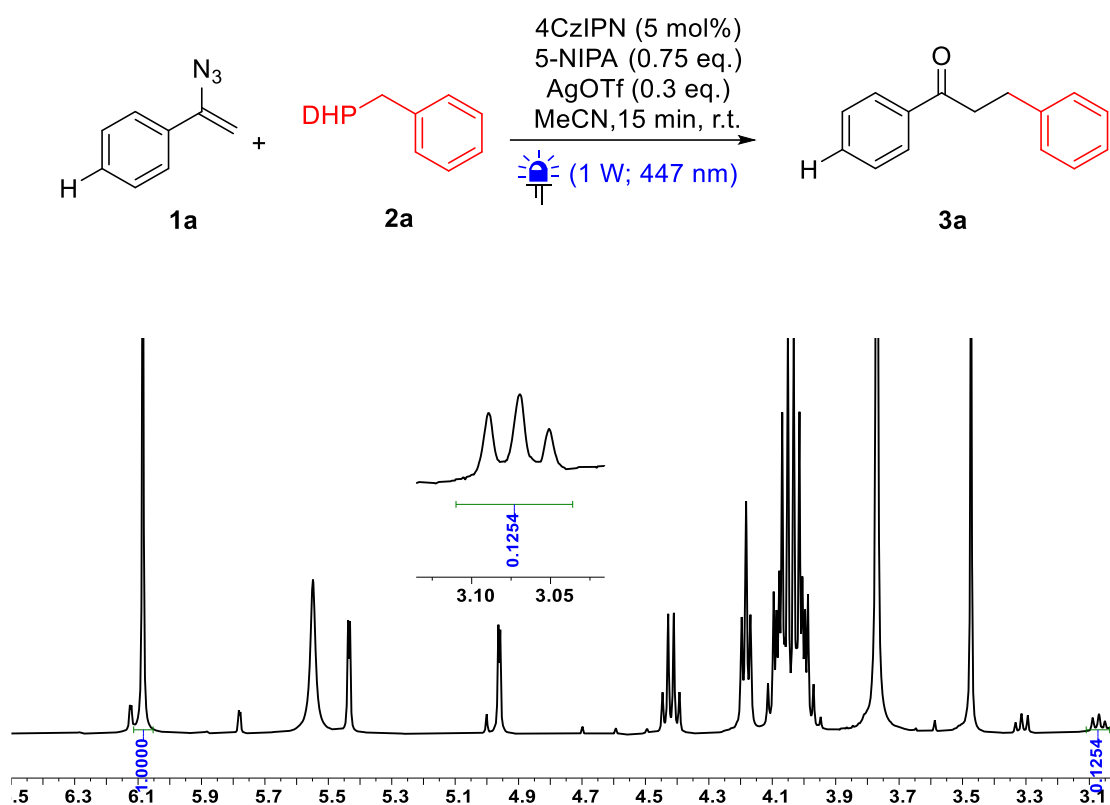
**Figure S11** Hammett plot analysis of **1e** and 4-benzyl-1,4-DHPs **2** with  $\sigma_{mb}$  and  $\sigma_{jj}$ .

## 5.2. Hammett analysis for the competition reactions of vinyl azides with **2a**.

Add 79 mg of 4CzIPN (0.1 mmol), 316.7 mg of 5-NIPA (1.5 mmol), 154 mg of AgOTf (0.6 mmol) and 4-benzyl-1,4-DHPs **2a** (4 mmol) to a 10 mL volumetric flask and add CH<sub>3</sub>CN to make up to 10 mL to prepare a standard solution for subsequent experiments.

### 5.2.1. The reaction of **3a** and integration ratio of 1,3,5-trimethoxybenzene to **3a** in <sup>1</sup>H NMR.

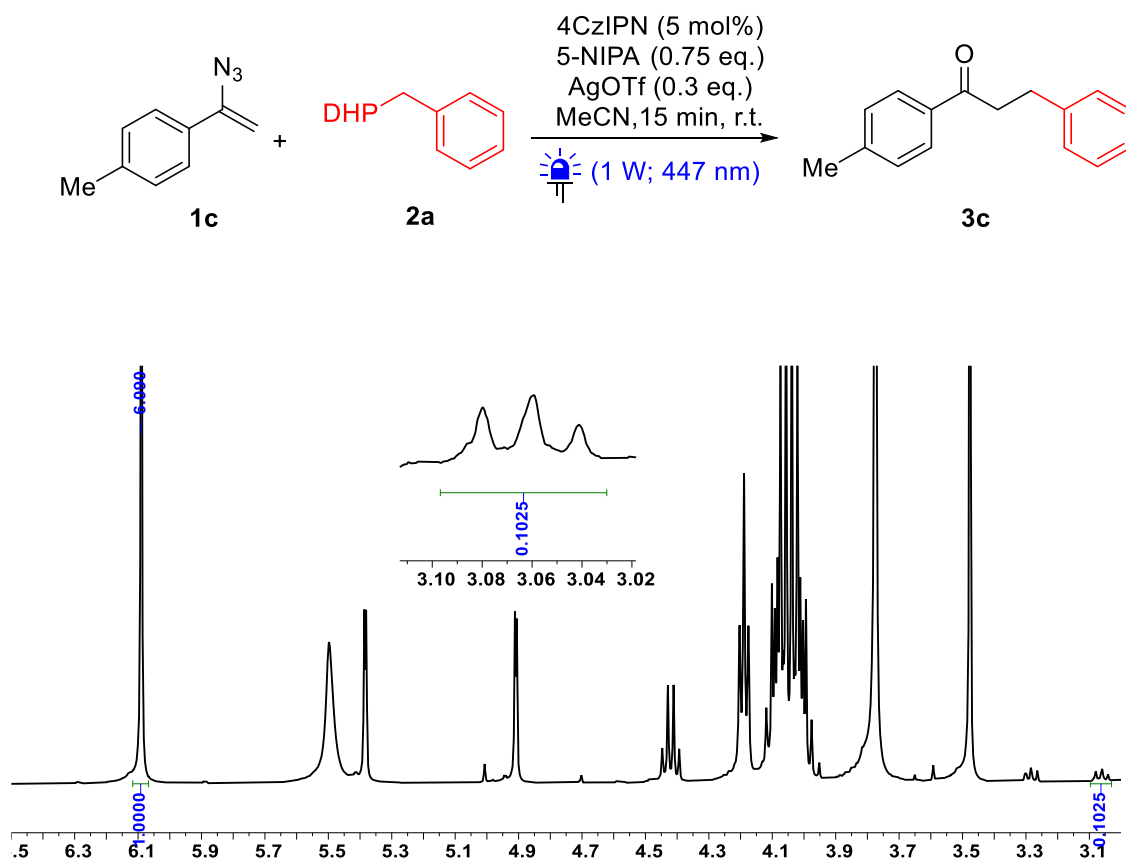
In a 3 mL closed screw-top glass vial, 1 mL standard solution was then added to the reaction system, then 29 mg of vinyl azide **1a** was injected to the solution. The vial was stirred for 15 min with irradiation of 1W blue light ( $\lambda = 447$  nm). The product ratio was detected directly by <sup>1</sup>H NMR of reaction system.



Exact integration of 1,3,5-trimethoxybenzene: **3a** is 1.000: 0.1254.

5.2.2. The reaction of **3c** and integration ratio of 1,3,5-trimethoxybenzene to **3c** in  $^1\text{H}$  NMR.

In a 3 mL closed screw-top glass vial, 1 mL standard solution was then added to the reaction system, then 32 mg of vinyl azide **1c** was injected to the solution. The vial was stirred for 15 min with irradiation of 1W blue light ( $\lambda = 447$  nm). The product ratio was detected directly by  $^1\text{H}$  NMR of reaction system.



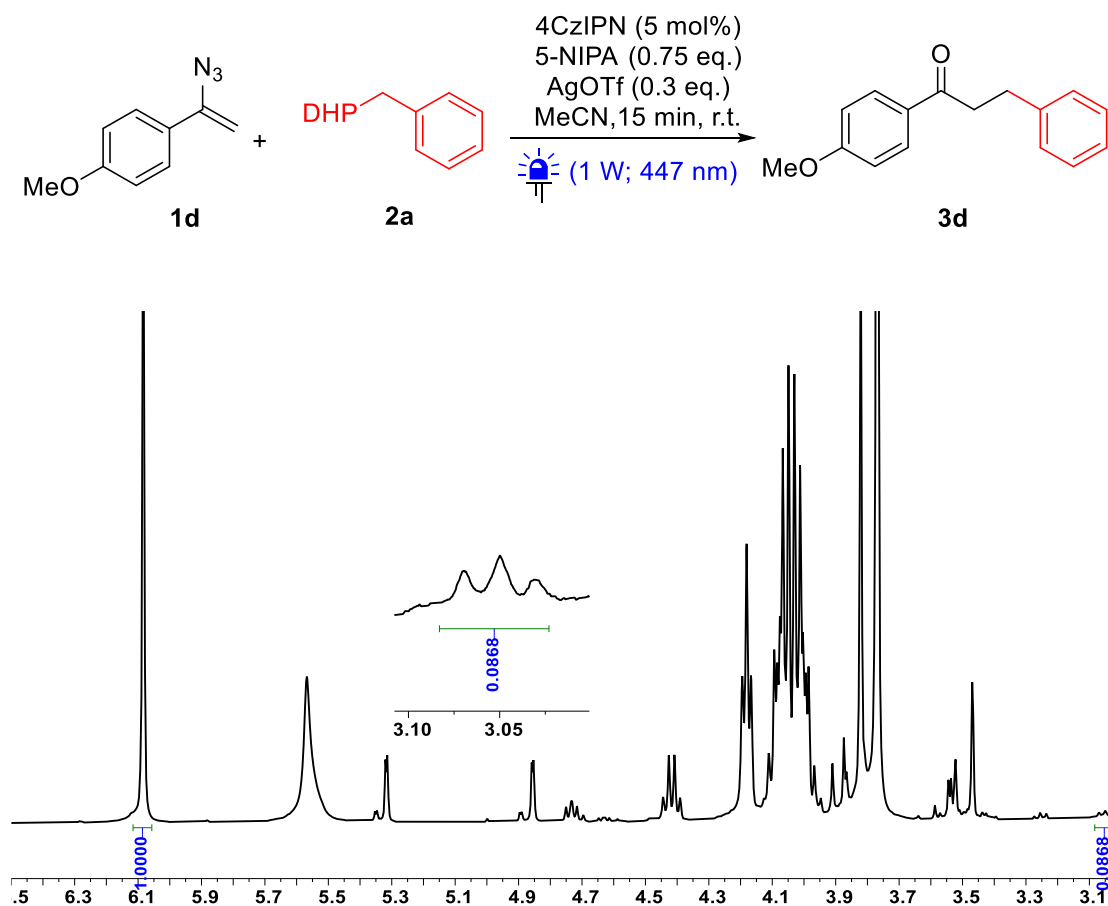
Exact integration of 1,3,5-trimethoxybenzene: **3c** is 1.000: 0.1025. The ratio of **3c/3a** = 0.817.

$$\ln(\mathbf{3c/3a}) = -0.202.$$



### 5.2.3. The reaction of **3d** and integration ratio of 1,3,5-trimethoxybenzene to **3d** in $^1\text{H}$ NMR.

In a 3 mL closed screw-top glass vial, 1 mL standard solution was then added to the reaction system, then 35 mg of vinyl azide **1d** was injected to the solution. The vial was stirred for 15 min with irradiation of 1W blue light ( $\lambda = 447$  nm). The product ratio was detected directly by  $^1\text{H}$  NMR of reaction system.

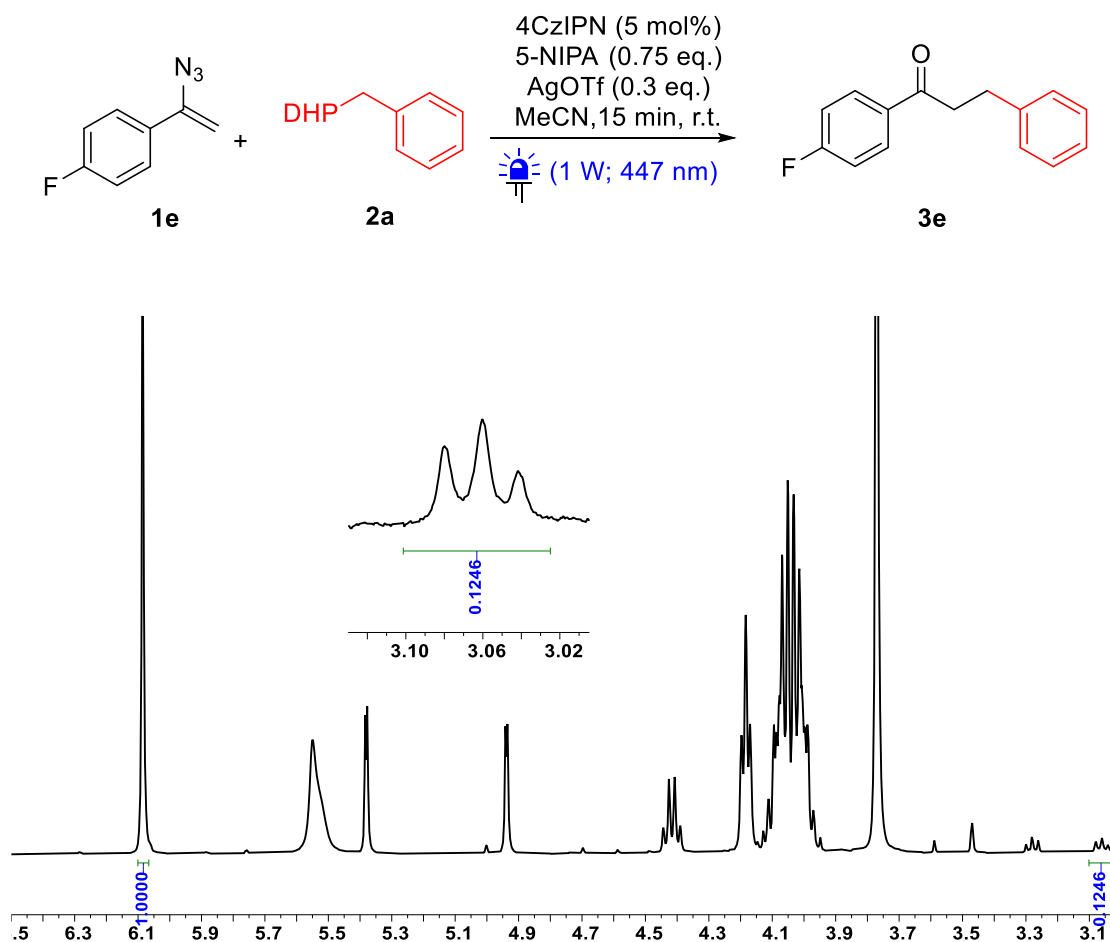


Exact integration of 1,3,5-trimethoxybenzene: **3d** is 1.000: 0.0868. The ratio of **3d/3a** = 0.692.

$\ln(\mathbf{3d/3a}) = -0.368$

5.2.4. The reaction of **3e** and integration ratio of 1,3,5-trimethoxybenzene to **3e** in  $^1\text{H}$  NMR.

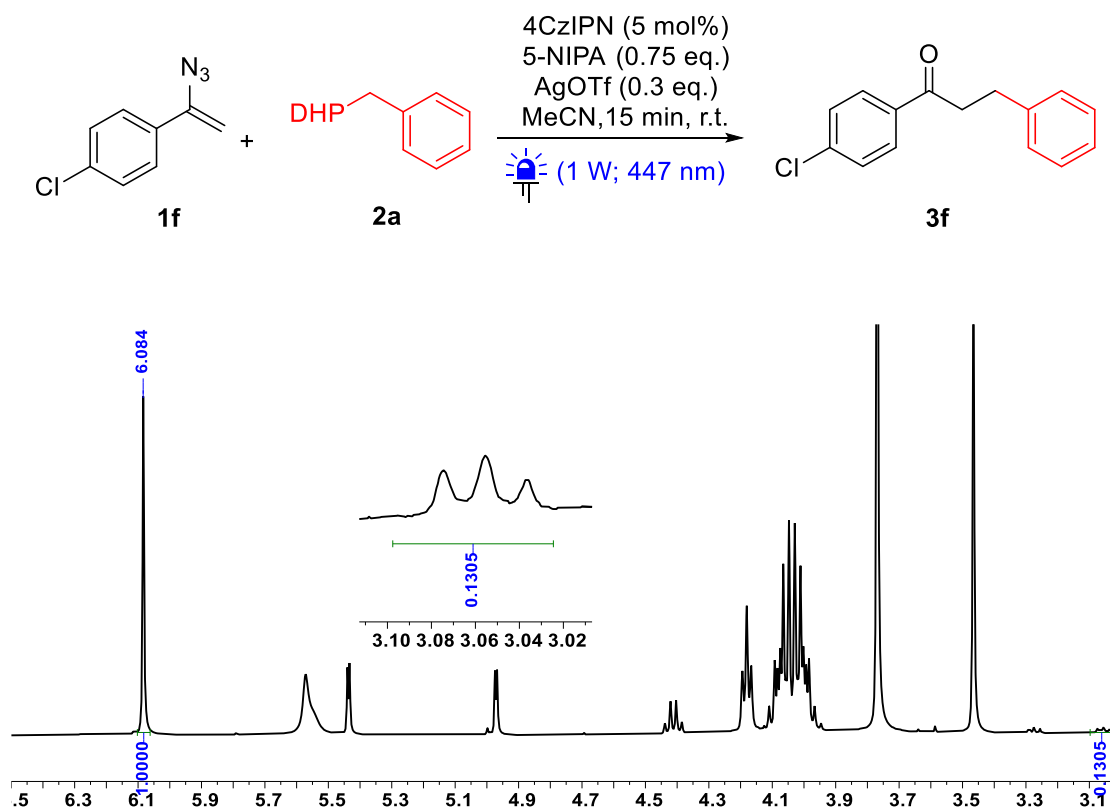
In a 3 mL closed screw-top glass vial, 1 mL standard solution was then added to the reaction system, then 33 mg of vinyl azide **1e** was injected to the solution. The vial was stirred for 15 min with irradiation of 1W blue light ( $\lambda = 447$  nm). The product ratio was detected directly by  $^1\text{H}$  NMR of reaction system.



Exact integration of 1,3,5-trimethoxybenzene: **3e** is 1.000: 0.1246. The ratio of **3e/3a** = 0.994.  $\ln(\mathbf{3e/3a}) = -0.006$

5.2.5. The reaction of **3f** and integration ratio of 1,3,5-trimethoxybenzene to **3f** in  $^1\text{H}$  NMR.

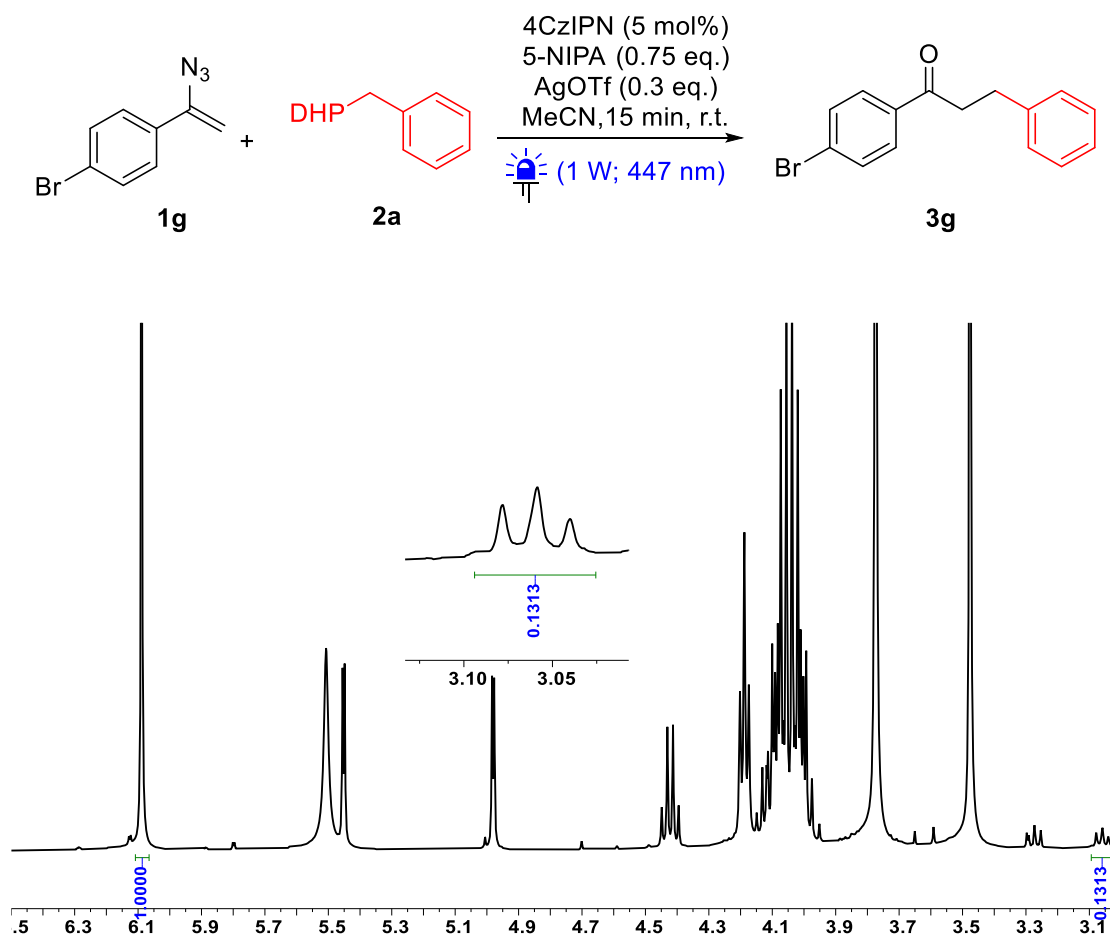
In a 3 mL closed screw-top glass vial, 1 mL standard solution was then added to the reaction system, then 36 mg of vinyl azide **1f** was injected to the solution. The vial was stirred for 15 min with irradiation of 1W blue light ( $\lambda = 447$  nm). The product ratio was detected directly by  $^1\text{H}$  NMR of reaction system.



Exact integration of 1,3,5-trimethoxybenzene: **3f** is 1.000: 0.1305. The ratio of **3f/3a** = 1.04.  $\ln(\mathbf{3f/3a}) = 0.040$

5.2.6. The reaction of **3g** and integration ratio of 1,3,5-trimethoxybenzene to **3g** in  $^1\text{H}$  NMR.

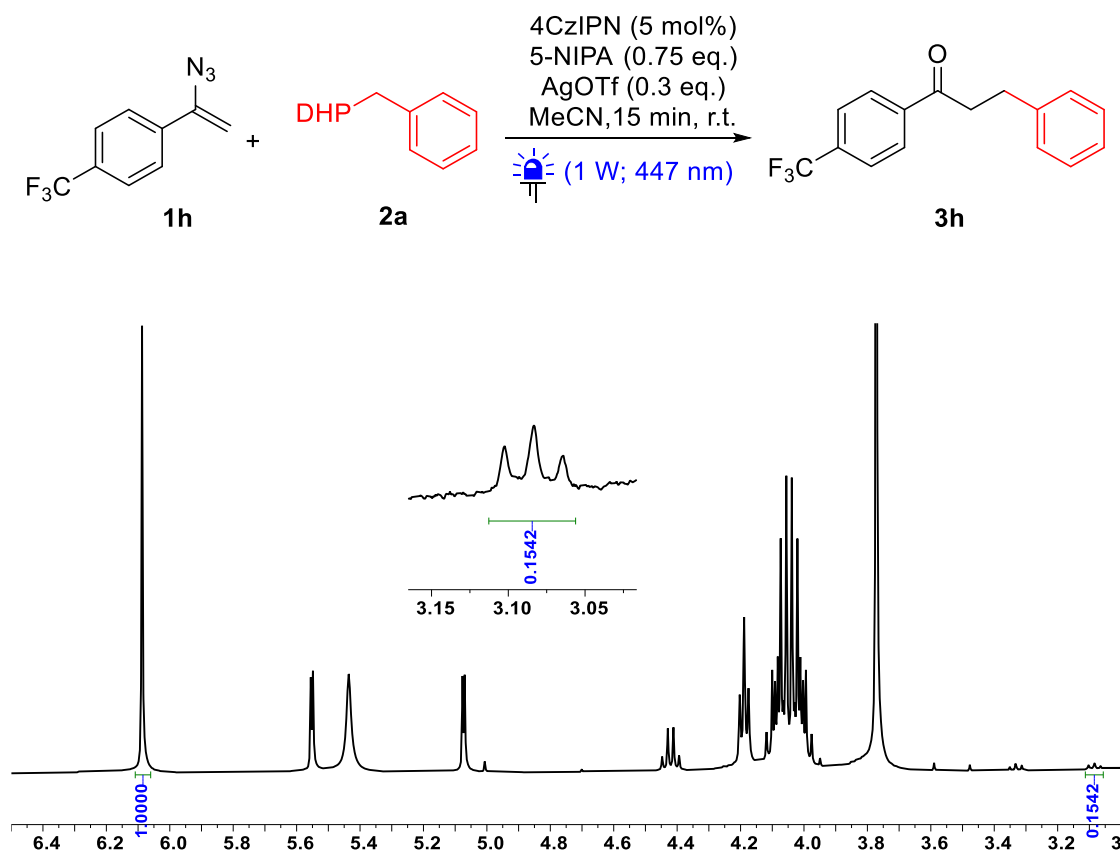
In a 3 mL closed screw-top glass vial, 1 mL standard solution was then added to the reaction system, then 45 mg of vinyl azide **1g** was injected to the solution. The vial was stirred for 15 min with irradiation of 1W blue light ( $\lambda = 447$  nm). The product ratio was detected directly by  $^1\text{H}$  NMR of reaction system.



Exact integration of 1,3,5-trimethoxybenzene: **3g** is 1.000: 0.1313. The ratio of **3g/3a** = 1.05.  $\ln(\mathbf{3g/3a})$  = 0.046

5.2.7. The reaction of **3h** and integration ratio of 1,3,5-trimethoxybenzene to **3h** in <sup>1</sup>H NMR.

In a 3 mL closed screw-top glass vial, 1 mL standard solution was then added to the reaction system, then 43 mg of vinyl azide **1h** was injected to the solution. The vial was stirred for 15 min with irradiation of 1W blue light ( $\lambda = 447$  nm). The product ratio was detected directly by <sup>1</sup>H NMR of reaction system.



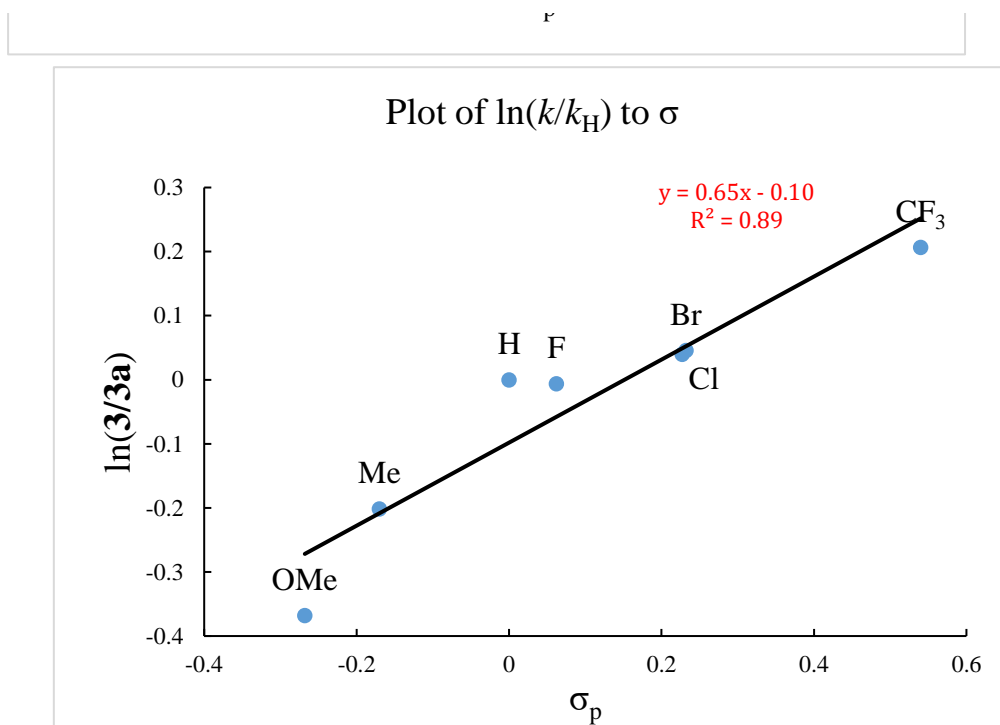
Exact integration of 1,3,5-trimethoxybenzene: **3h** is 1.000: 0.1542. The ratio of **3h/3a** = 1.23.  $\ln(3h/3a) = 0.207$ .

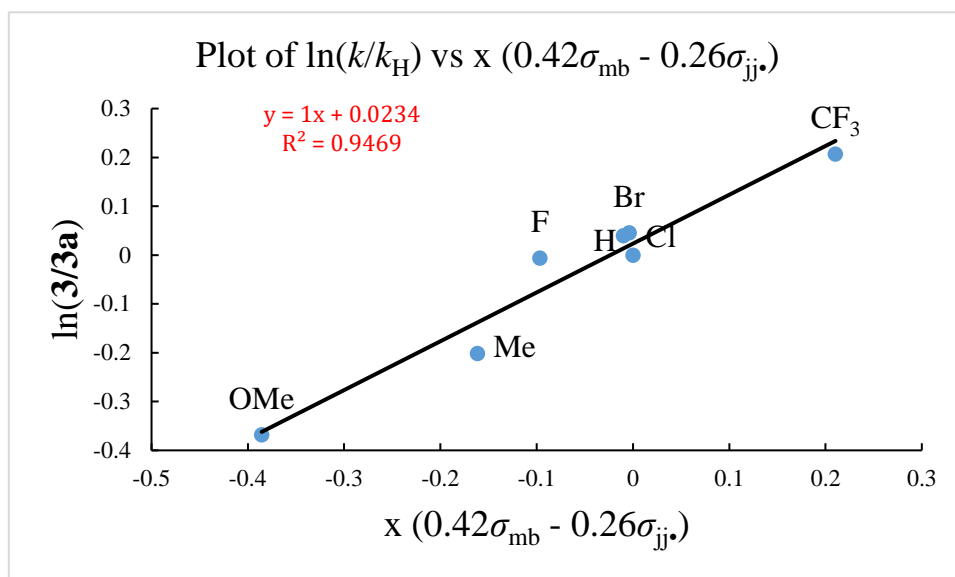
**Table S2.** Dual-parameter correlation with polar substituent constants ( $\sigma_{mb}$ ) and spin effect parameters ( $\sigma_{ij}$ ) of vinyl azides **1** with **2a**.

4CzIPN (5 mol%)  
5-NIPA (0.75 eq.)  
AgOTf (0.3 eq.)  
MeCN, 15 min, r.t.  
(1 W; 447 nm)

Entry	2	$\ln(k/k_H)^a$	$\sigma^b$	$\sigma_{mb}^c$	$\sigma_{ij}^c$	$0.42\sigma_{mb} - 0.26\sigma_{ij}^d$
1	<b>1a</b> ( <i>p</i> -H)	0	0	0	0	0
2	<b>1c</b> ( <i>p</i> -Me)	-0.202	-0.17	-0.29	0.15	-0.162
3	<b>1d</b> ( <i>p</i> -OMe)	-0.368	-0.268	-0.77	0.23	-0.386
4	<b>1e</b> ( <i>p</i> -F)	-0.006	0.062	-0.24	-0.02	-0.096
5	<b>1f</b> ( <i>p</i> -Cl)	0.040	0.227	0.11	0.22	-0.010
6	<b>1g</b> ( <i>p</i> -Br)	0.046	0.232	0.13	0.23	-0.004
7	<b>1h</b> ( <i>p</i> -CF <sub>3</sub> )	0.207	0.54	0.49	-0.01	0.210

<sup>a</sup> Relative rate is calculated by the ratio of **3/3e**. <sup>b</sup> Hammett constants. <sup>c</sup> polar substituent constants  $\sigma_{mb}$  and spin effect parameters ( $\sigma_{ij}$ ) were obtained from ref 45. <sup>d</sup> quadratic linear regression analysis was obtained from excel analysis.

**Figure S12** Hammett plot analysis of vinyl azides **1** and 4-benzyl-1,4-DHPs **2a**



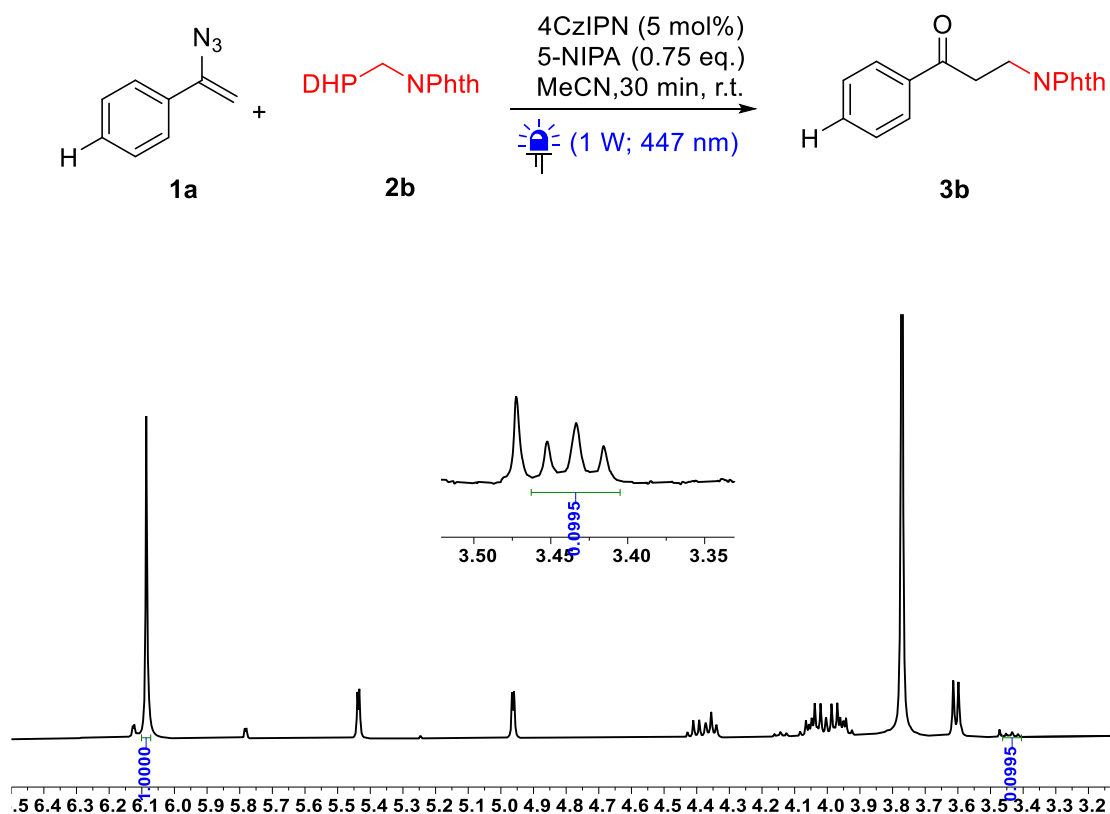
**Figure S13** Hammett plot analysis of vinyl azides **1** and **2a** with  $\sigma_{mb}$  and  $\sigma_{jj}$ .

### 5.3. Hammett analysis for the competition reactions of vinyl azides with **2b**.

Add 79 mg of 4CzIPN (0.1 mmol), 316.7 mg of 5-NIPA (1.5 mmol), and 154 mg of AgOTf (0.6 mmol) to a 10 mL volumetric flask and add CH<sub>3</sub>CN to make up to 10 mL to prepare a standard solution for subsequent experiments.

#### 5.3.1. The reaction of **3b** and integration ratio of 1,3,5-trimethoxybenzene to **3b** in <sup>1</sup>H NMR.

In a 3 mL closed screw-top glass vial, 160 mg of **2b** was added. Then 1 mL standard solution was added to the reaction system, and 29 mg of vinyl azide **1a** was injected to the solution. The vial was stirred for 30 min with irradiation of 1W blue light ( $\lambda = 447$  nm). The product ratio was detected directly by <sup>1</sup>H NMR of reaction system.

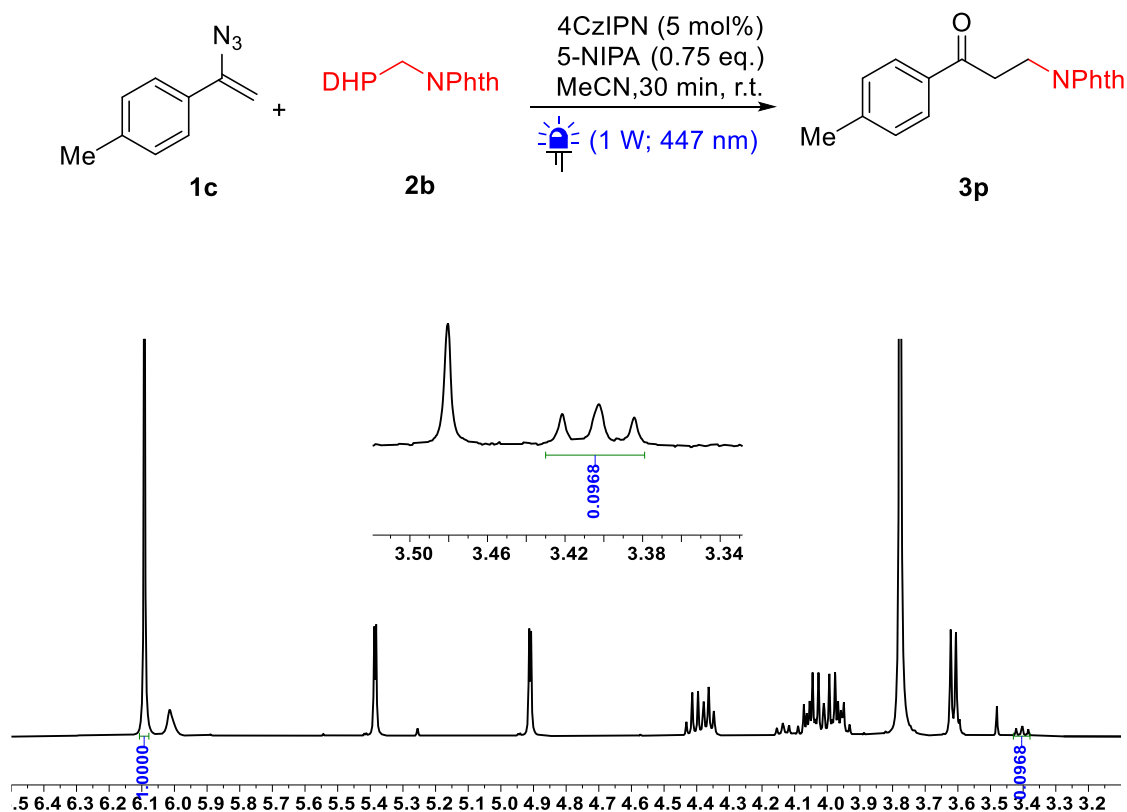


Exact integration of 1,3,5-trimethoxybenzene: **3b** is 1.000: 0.0995.



### 5.3.2. The reaction of **3p** and integration ratio of 1,3,5-trimethoxybenzene to **3p** in <sup>1</sup>H NMR.

In a 3 mL closed screw-top glass vial, 160 mg of **2b** was added. 1 mL standard solution was then added to the reaction system, then 32 mg of vinyl azide **1c** was injected to the solution. The vial was stirred for 30 min with irradiation of 1 W blue light ( $\lambda = 447$  nm). The product ratio was detected directly by <sup>1</sup>H NMR of reaction system.

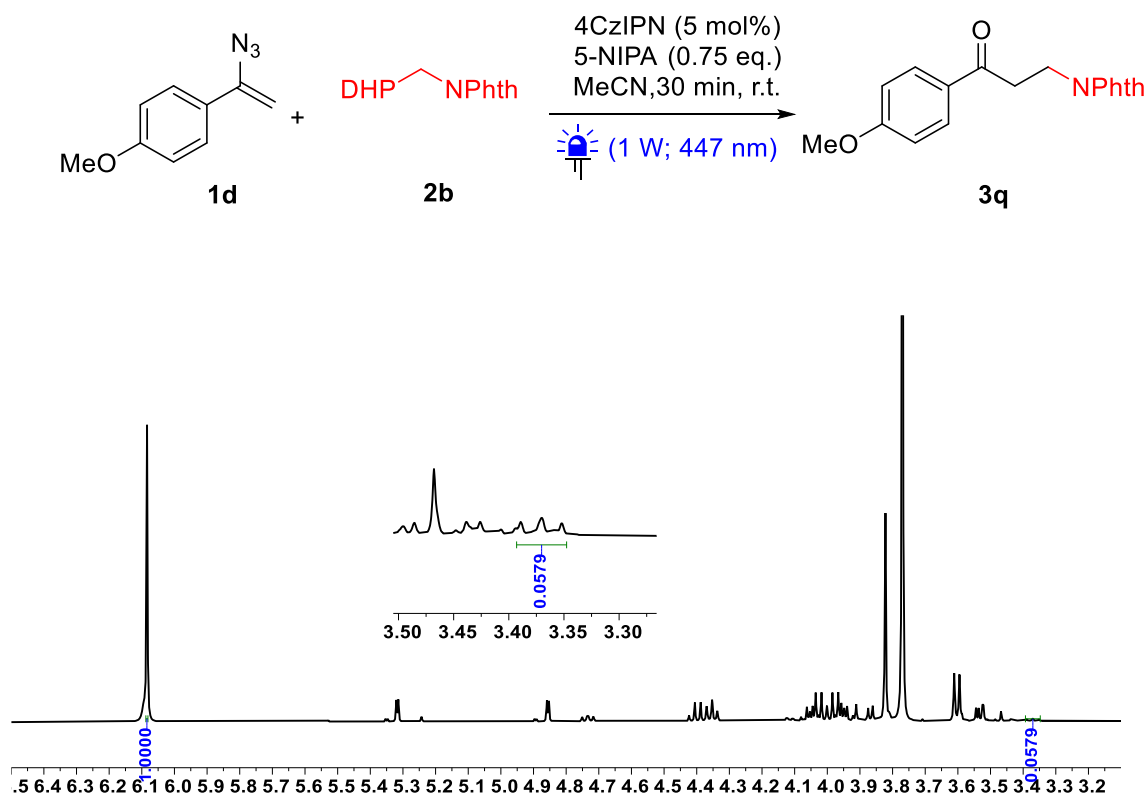


Exact integration of 1,3,5-trimethoxybenzene: **3p** is 1.000: 0.0968. The ratio of **3p/3b** = 0.973.

$\ln(\mathbf{3p/3b}) = -0.028$ .

### 5.3.3. The reaction of **3q** and integration ratio of 1,3,5-trimethoxybenzene to **3q** in $^1\text{H}$ NMR.

In a 3 mL closed screw-top glass vial, 160 mg of **2b** was added. 1 mL standard solution was then added to the reaction system, then 35 mg of vinyl azide **1d** was injected to the solution. The vial was stirred for 30 min with irradiation of 1 W blue light ( $\lambda = 447$  nm). The product ratio was detected directly by  $^1\text{H}$  NMR of reaction system.

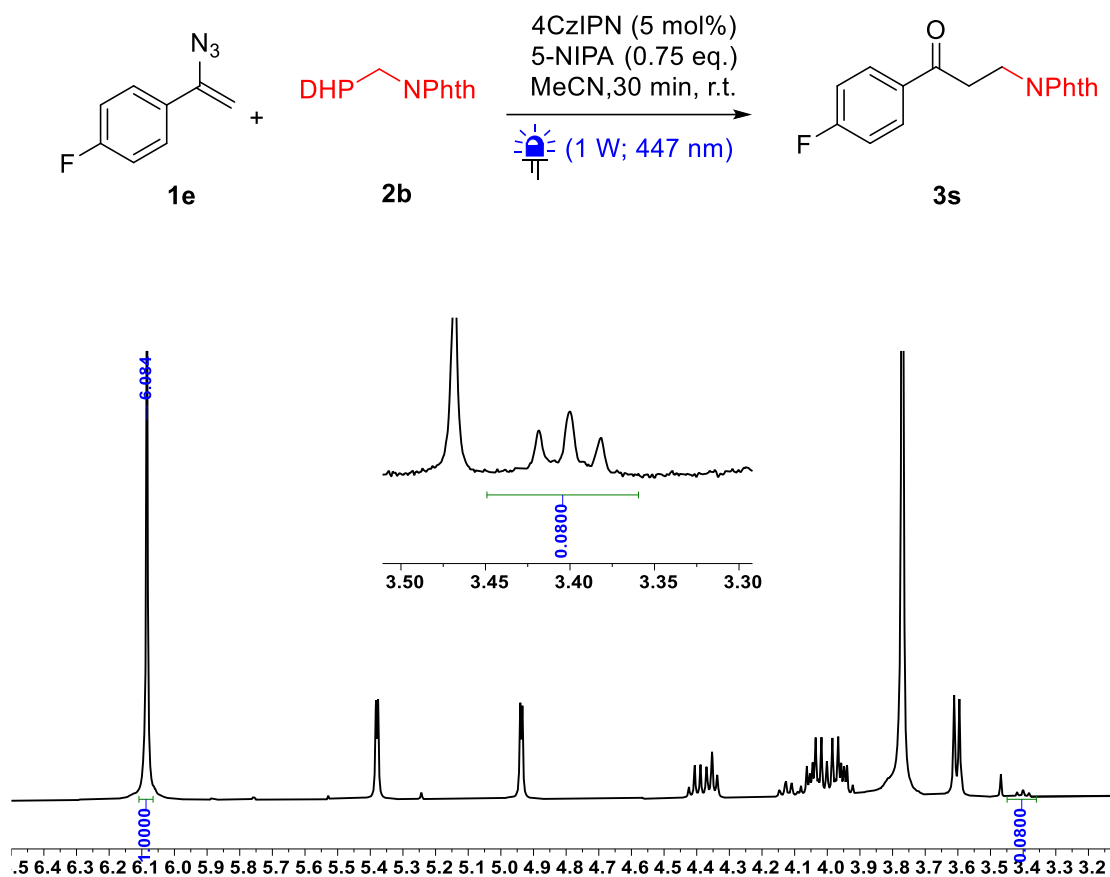


Exact integration of 1,3,5-trimethoxybenzene: **3q** is 1.000: 0.0579. The ratio of **3q/3b** = 0.582.

$\ln(\mathbf{3q/3b}) = -0.541$ .

### 5.3.4. The reaction of **3s** and integration ratio of 1,3,5-trimethoxybenzene to **3s** in $^1\text{H}$ NMR.

In a 3 mL closed screw-top glass vial, 160 mg of **2b** was added. 1 mL standard solution was then added to the reaction system, then 33 mg of vinyl azide **1e** was injected to the solution. The vial was stirred for 30 min with irradiation of 1W blue light ( $\lambda = 447$  nm). The product ratio was detected directly by  $^1\text{H}$  NMR of reaction system.

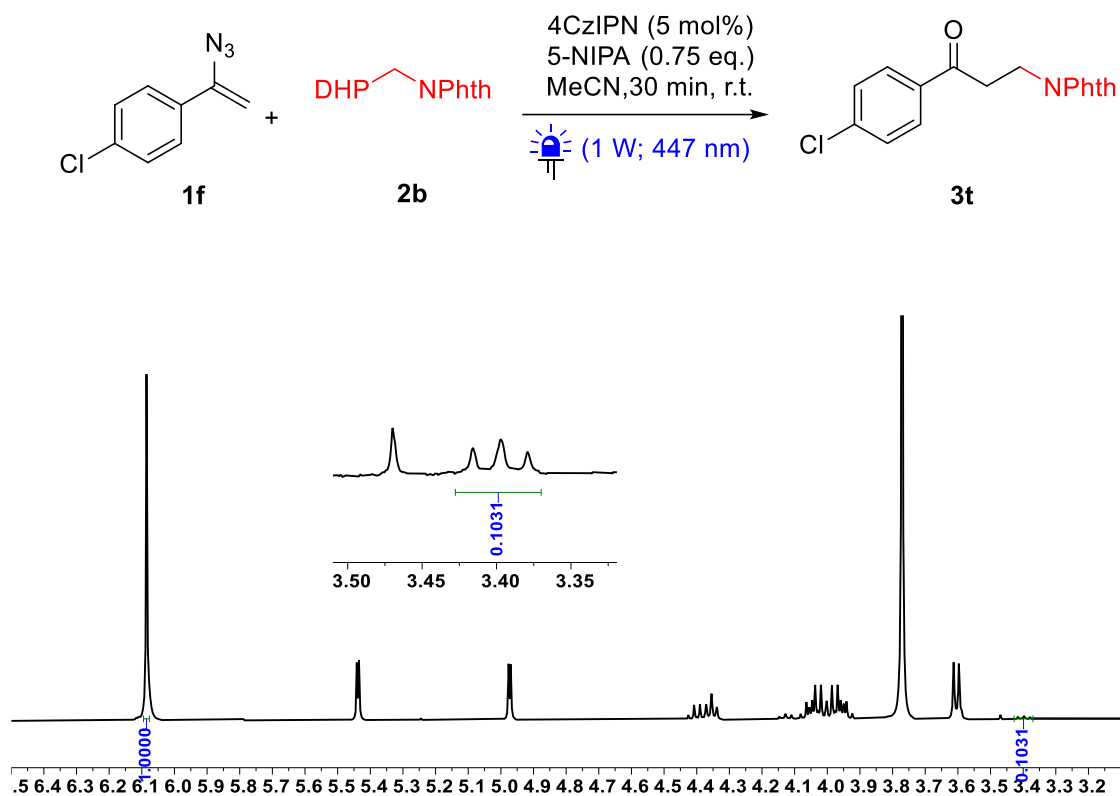


Exact integration of 1,3,5-trimethoxybenzene: **3s** is 1.000: 0.0800. The ratio of **3s/3b** = 0.804.

$$\ln(\mathbf{3s/3b}) = -0.218$$

5.3.5. The reaction of **3t** and integration ratio of 1,3,5-trimethoxybenzene to **3t** in  $^1\text{H}$  NMR.

In a 3 mL closed screw-top glass vial, 160 mg of **2b** was added. 1 mL standard solution was then added to the reaction system, then 33 mg of vinyl azide **1f** was injected to the solution. The vial was stirred for 30 min with irradiation of 1W blue light ( $\lambda = 447$  nm). The product ratio was detected directly by  $^1\text{H}$  NMR of reaction system.

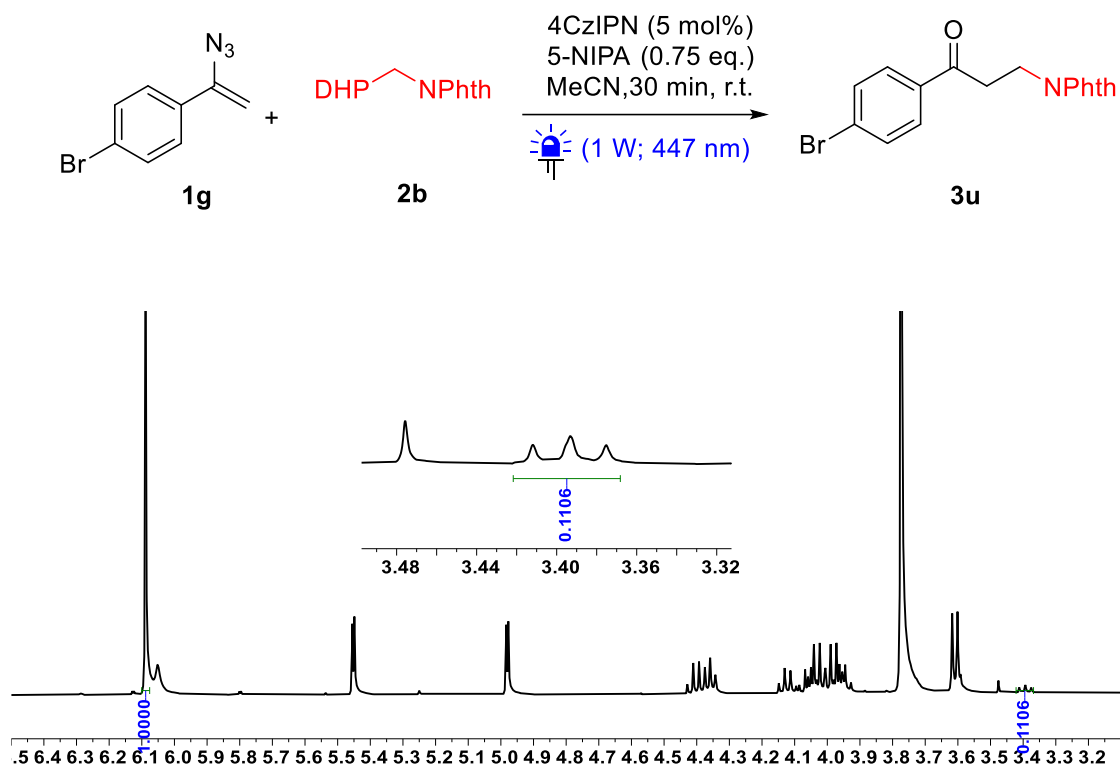


Exact integration of 1,3,5-trimethoxybenzene: **3t** is 1.000: 0.1031. The ratio of **3t/3b** = 1.036.

$$\ln(\mathbf{3t/3b}) = 0.036$$

5.3.6. The reaction of **3u** and integration ratio of 1,3,5-trimethoxybenzene to **3u** in  $^1\text{H}$  NMR.

In a 3 mL closed screw-top glass vial, 160 mg of **2b** was added. 1 mL standard solution was then added to the reaction system, then 33 mg of vinyl azide **1g** was injected to the solution. The vial was stirred for 30 min with irradiation of 1W blue light ( $\lambda = 447$  nm). The product ratio was detected directly by  $^1\text{H}$  NMR of reaction system.

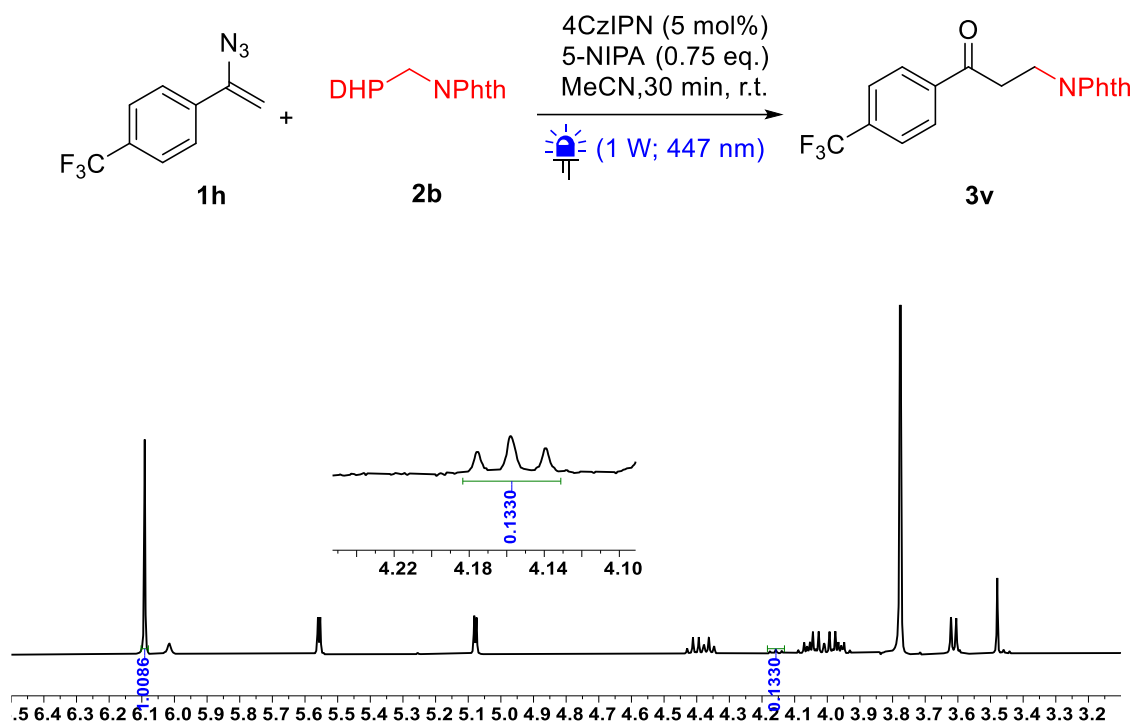


Exact integration of 1,3,5-trimethoxybenzene: **3u** is 1.000: 0.1106. The ratio of **3u/3b** = 1.112.

$\ln(\mathbf{3u/3b}) = 0.106$ .

5.3.7. The reaction of **3v** and integration ratio of 1,3,5-trimethoxybenzene to **3v** in <sup>1</sup>H NMR.

In a 3 mL closed screw-top glass vial, 160 mg of **2b** was added. 1 mL standard solution was then added to the reaction system, then 33 mg of vinyl azide **1h** was injected to the solution. The vial was stirred for 30 min with irradiation of 1W blue light ( $\lambda = 447$  nm). The product ratio was detected directly by <sup>1</sup>H NMR of reaction system.



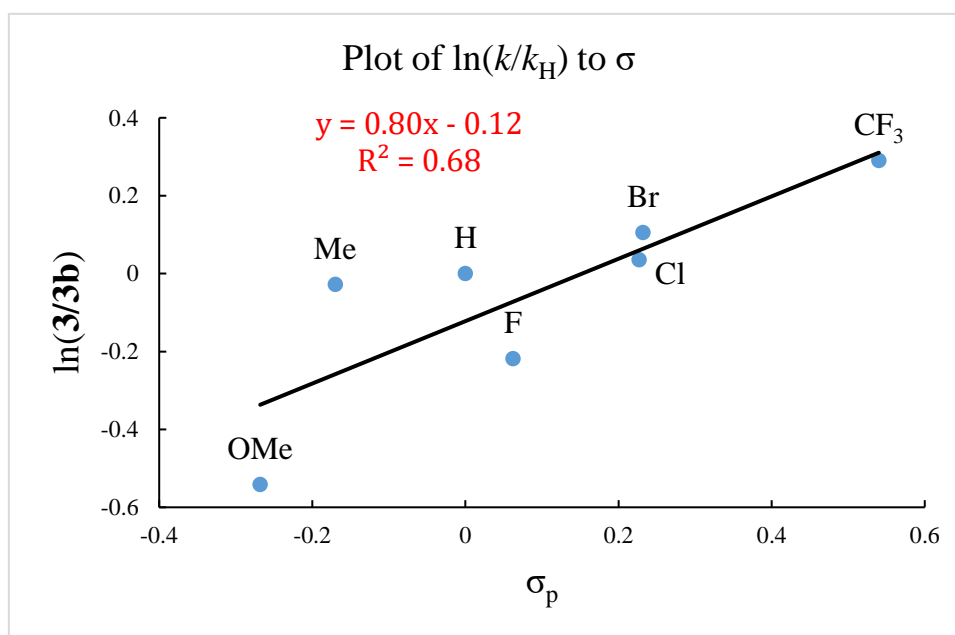
Exact integration of 1,3,5-trimethoxybenzene: **3v** is 1.000: 0.1330. The ratio of **3v/3b** = 1.337.  
 $\ln(\mathbf{3v/3b}) = 0.290$ .

**Table S3.** Dual-parameter correlation with polar substituent constants ( $\sigma_{\text{mb}}$ ) and spin effect parameters ( $\sigma_{\text{ij}}$ ) of vinyl azides **1** with **2b**

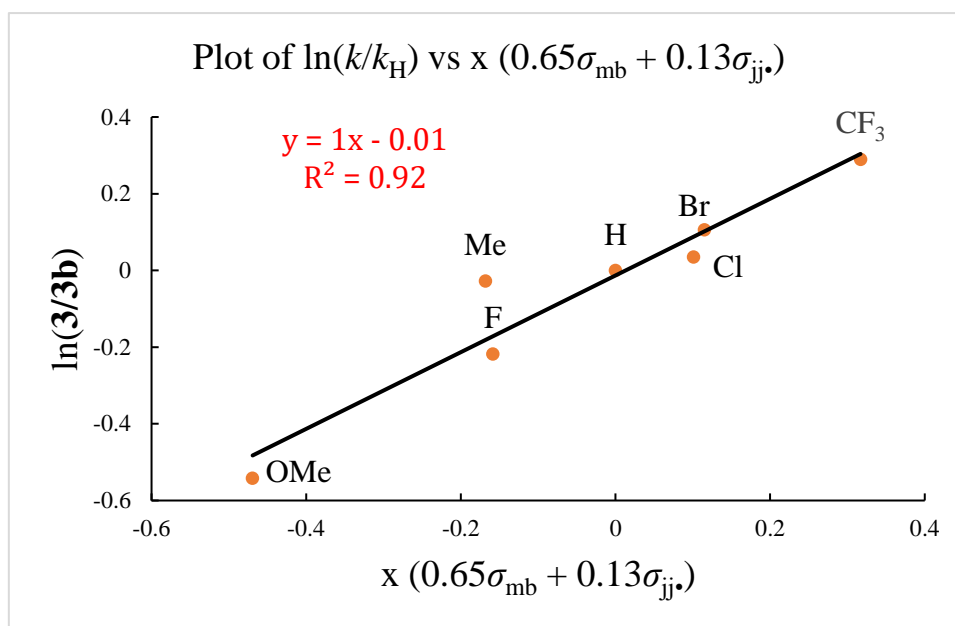
**1** + **2b**  $\xrightarrow[\text{4CzIPN (5 mol\%), 5-NIPA (0.75 eq.), MeCN, 30 min, r.t., (1 W; 447 nm)}]{}$  **3**

Entry	<b>1</b>	$\ln(k/k_{\text{H}})^{\text{a}}$	$\sigma^{\text{b}}$	$\sigma_{\text{mb}}^{\text{c}}$	$\sigma_{\text{ij}}^{\text{c}}$	$0.65\sigma_{\text{mb}} + 0.13\sigma_{\text{ij}}^{\text{d}}$
1	<b>1a</b> ( <i>p</i> -H)	0.000	0	0	0	0.000
2	<b>1c</b> ( <i>p</i> -Me)	-0.028	-0.17	-0.29	0.15	-0.168
3	<b>1d</b> ( <i>p</i> -OMe)	-0.541	-0.268	-0.77	0.23	-0.469
4	<b>1e</b> ( <i>p</i> -F)	-0.218	0.062	-0.24	-0.02	-0.158
5	<b>1f</b> ( <i>p</i> -Cl)	0.036	0.227	0.11	0.22	0.101
6	<b>1g</b> ( <i>p</i> -Br)	0.106	0.232	0.13	0.23	0.115
7	<b>1h</b> ( <i>p</i> -CF <sub>3</sub> )	0.290	0.54	0.49	-0.01	0.316

<sup>a</sup> Relative rate is calculated by the ratio of **3/3e**. <sup>b</sup> Hammett constants. <sup>c</sup> polar substituent constants  $\sigma_{\text{mb}}$  and spin effect parameters ( $\sigma_{\text{ij}}$ ) were obtained from ref 45. <sup>d</sup> quadratic linear regression analysis was obtained from excel analysis.



**Figure S14** Hammett plot analysis of vinyl azides **1** and **2b**

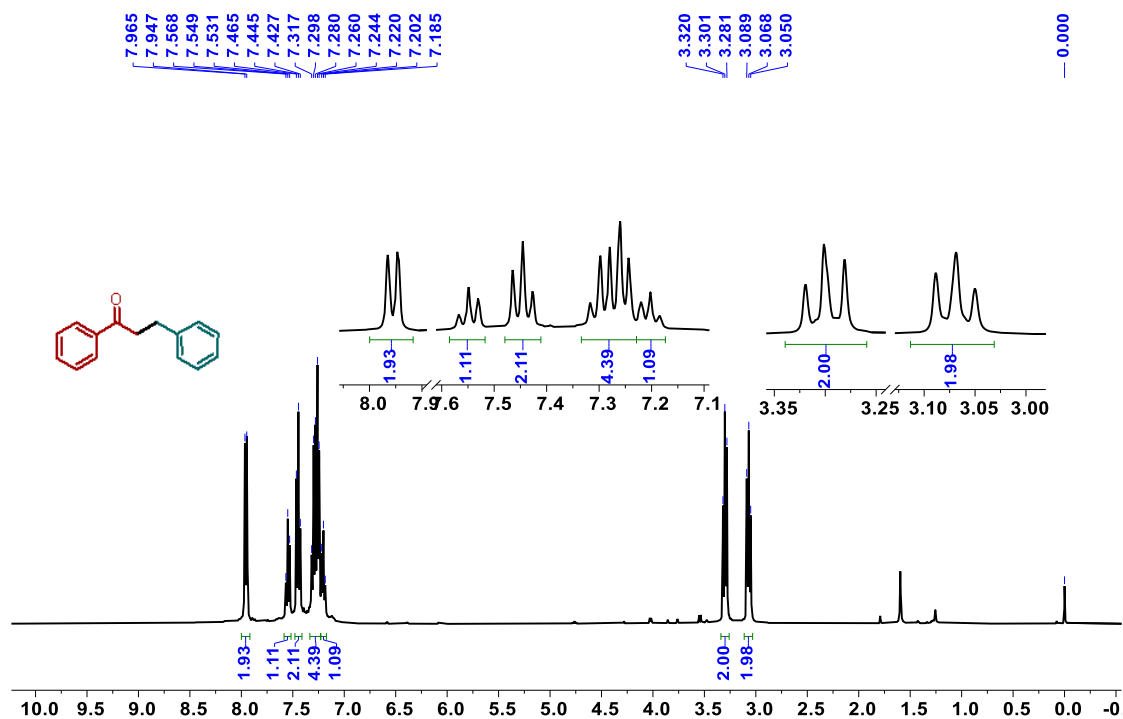


**Figure S15** Hammett plot analysis of vinyl azides **1** and **2b** with  $\sigma_{mb}$  and  $\sigma_{jj}$ .

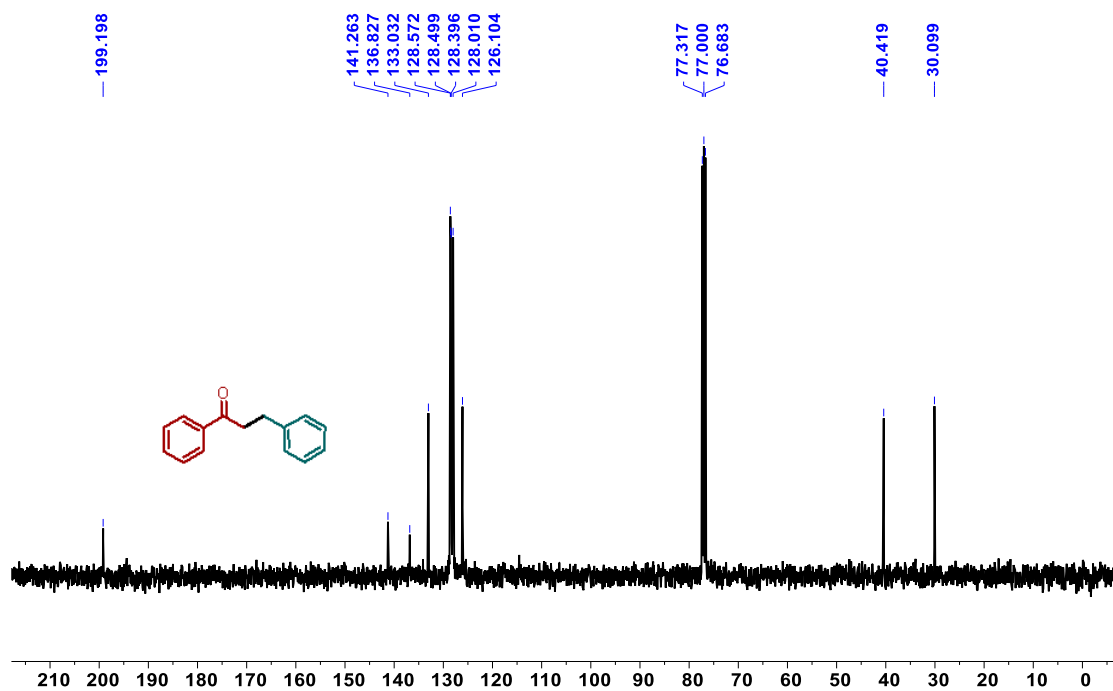


## 7. All NMR Spectra of 3

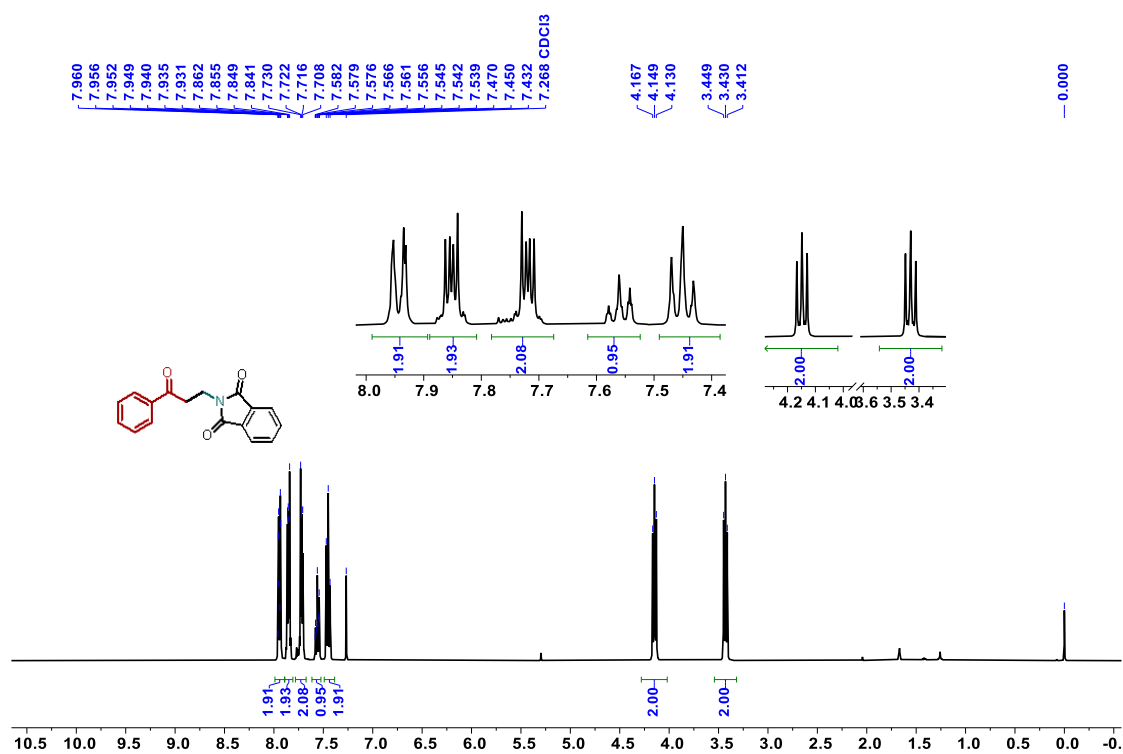
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3a**



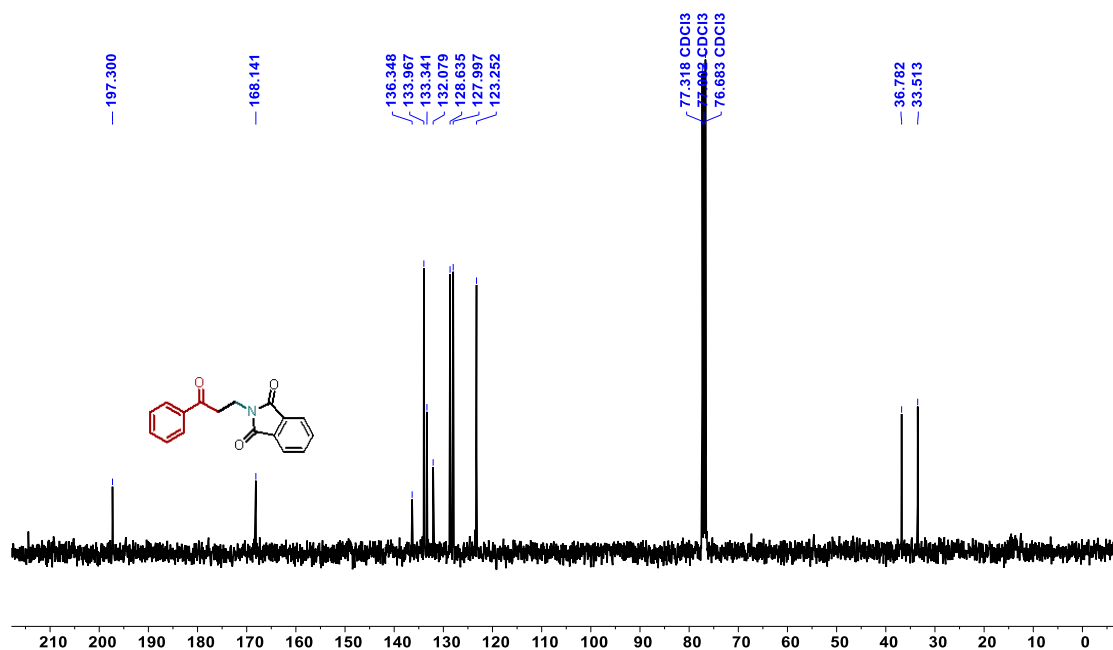
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3a**



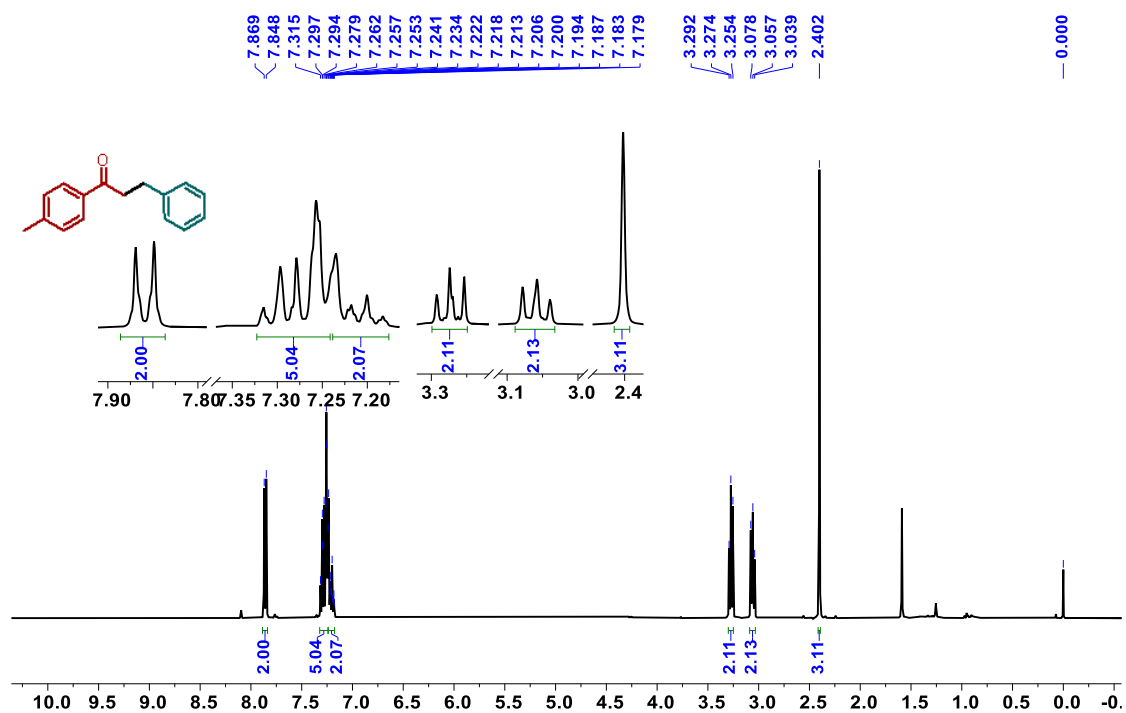
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3b**



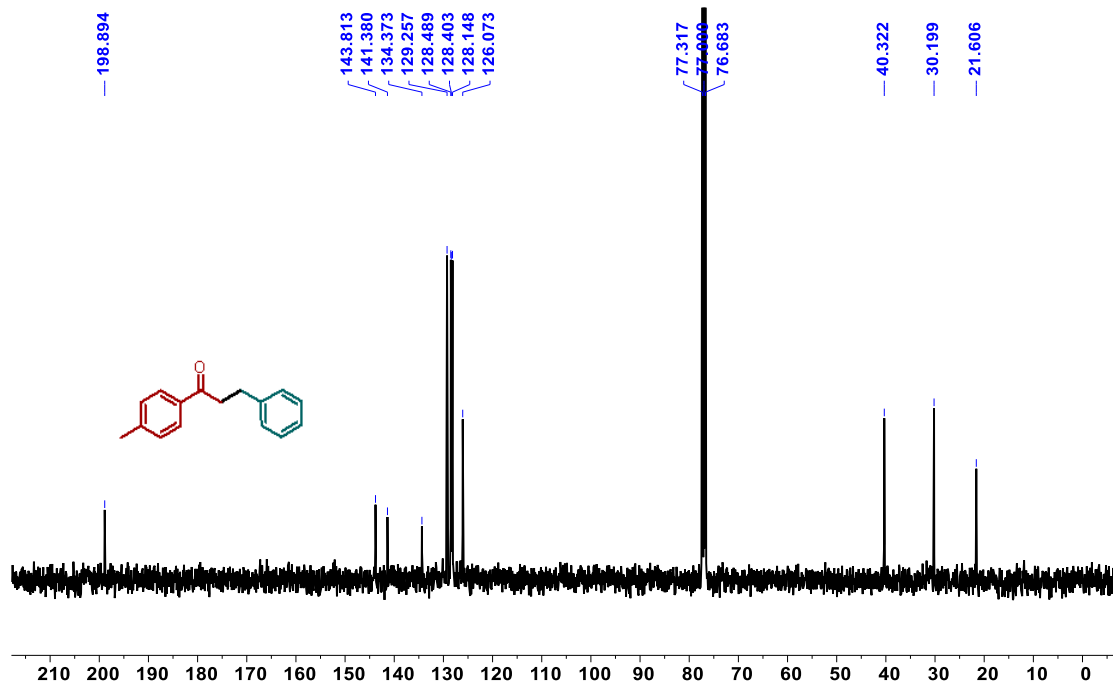
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3b**



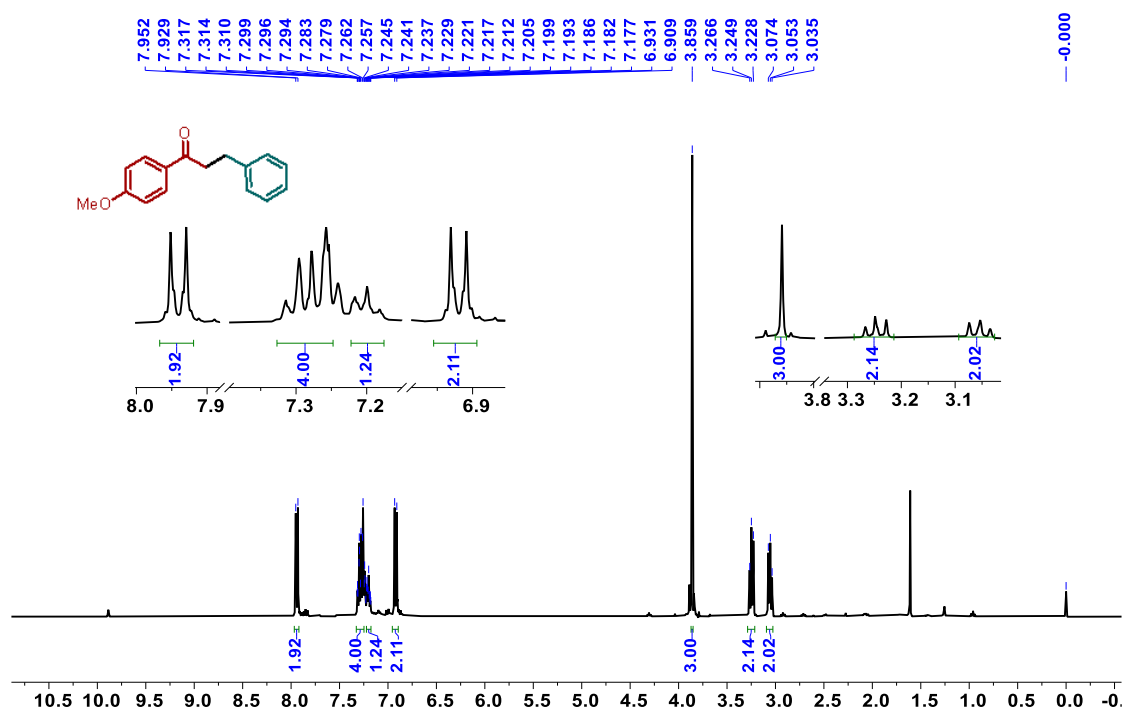
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3c**



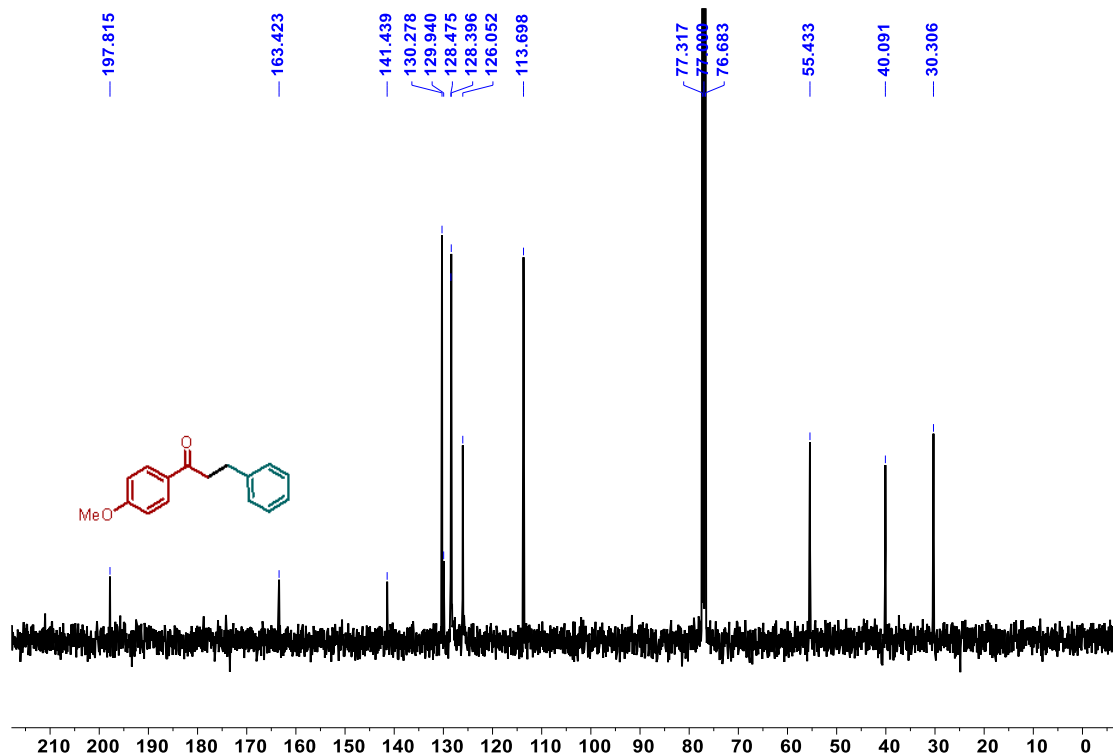
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3c**



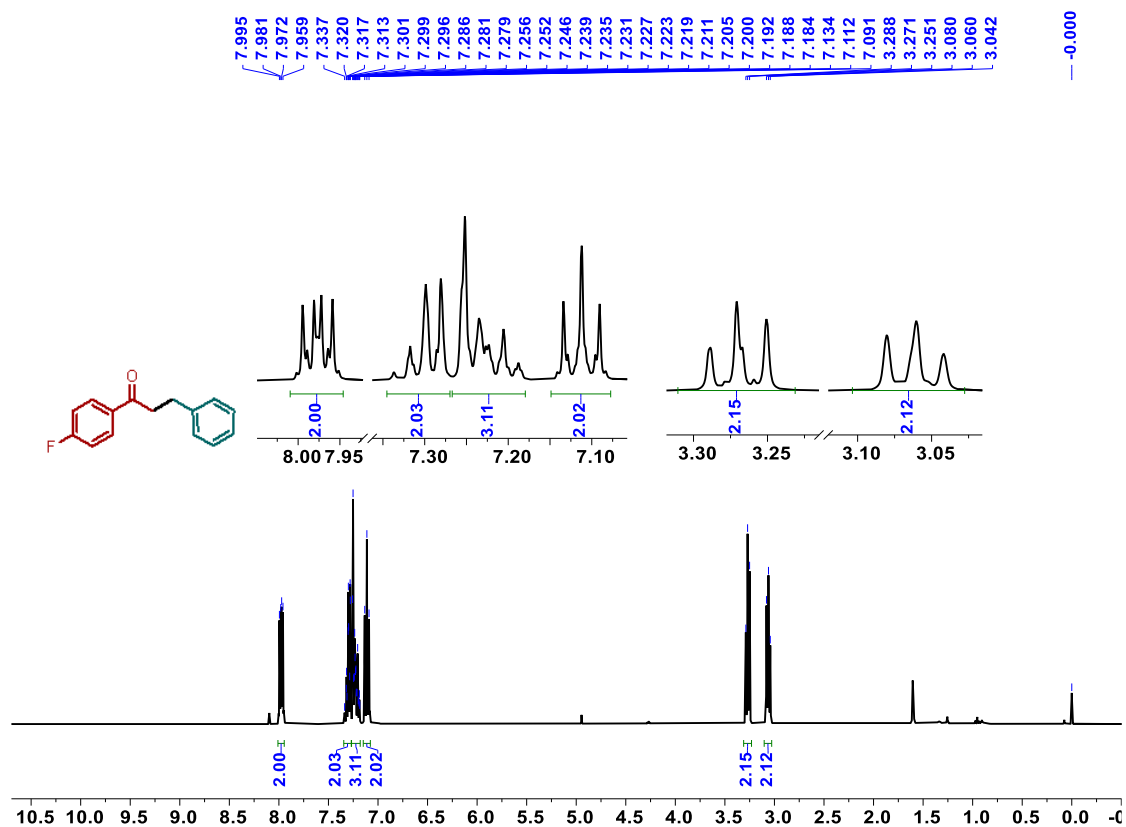
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3d**



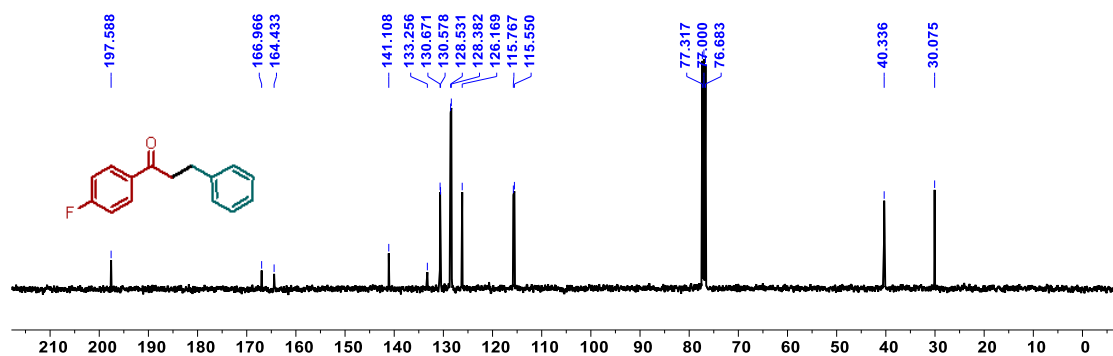
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3d**



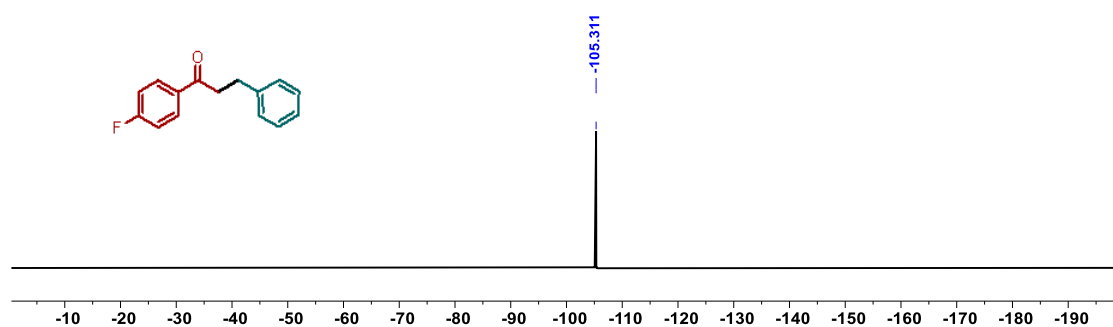
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3e**



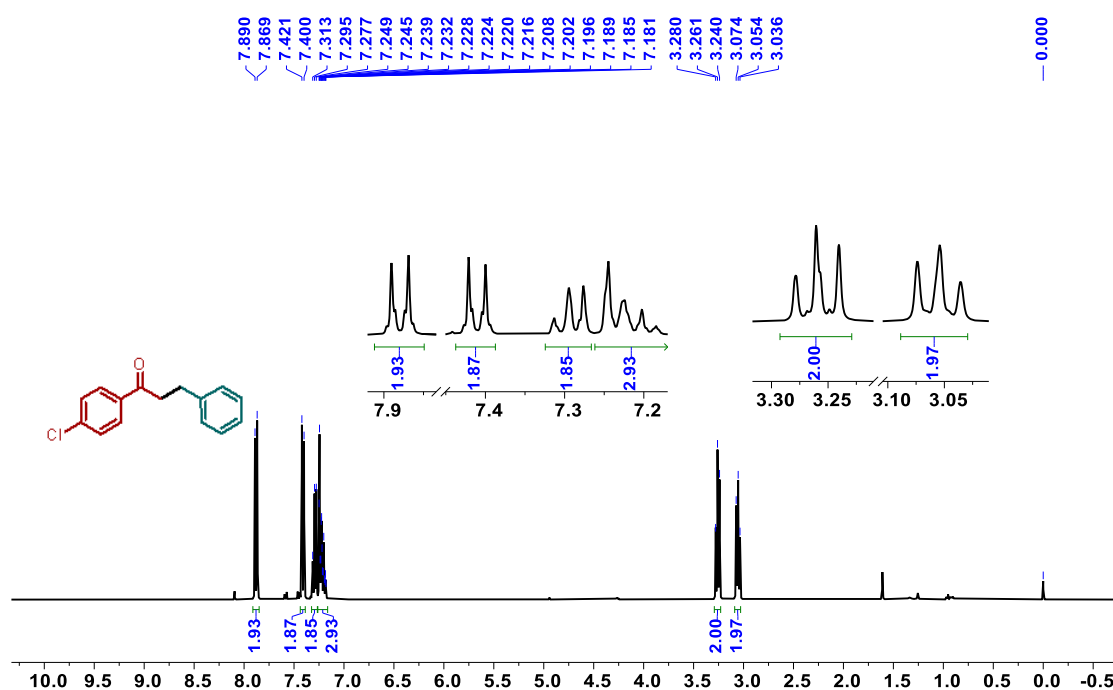
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3e**



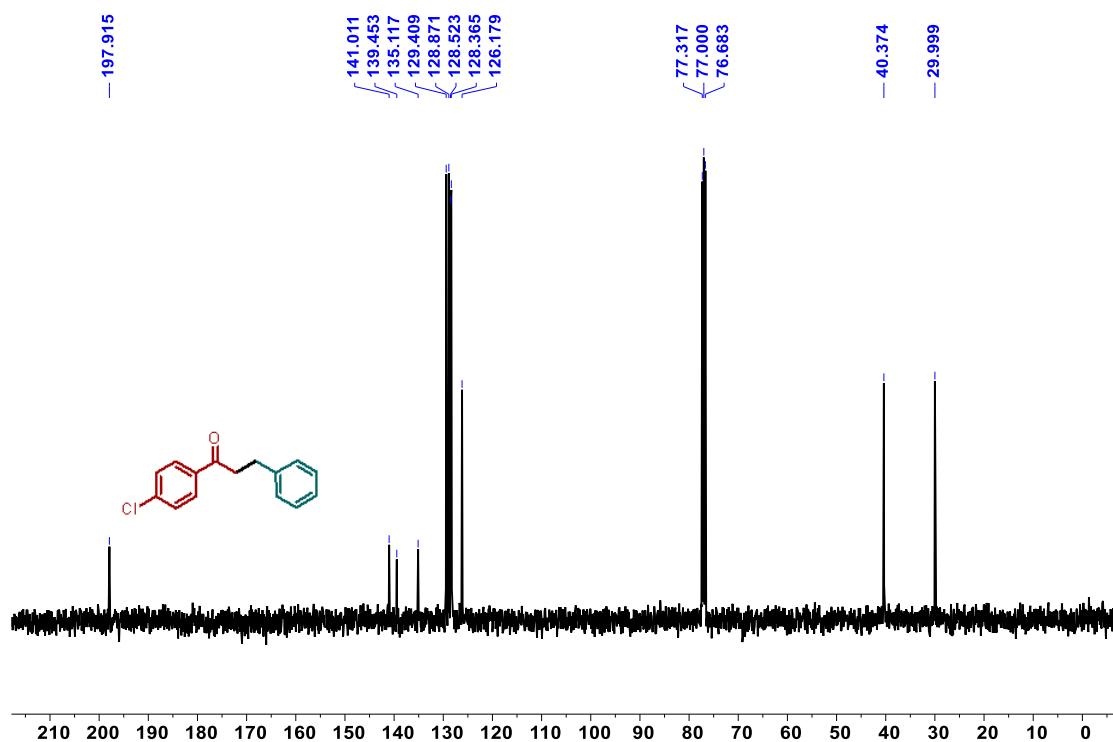
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **3e**



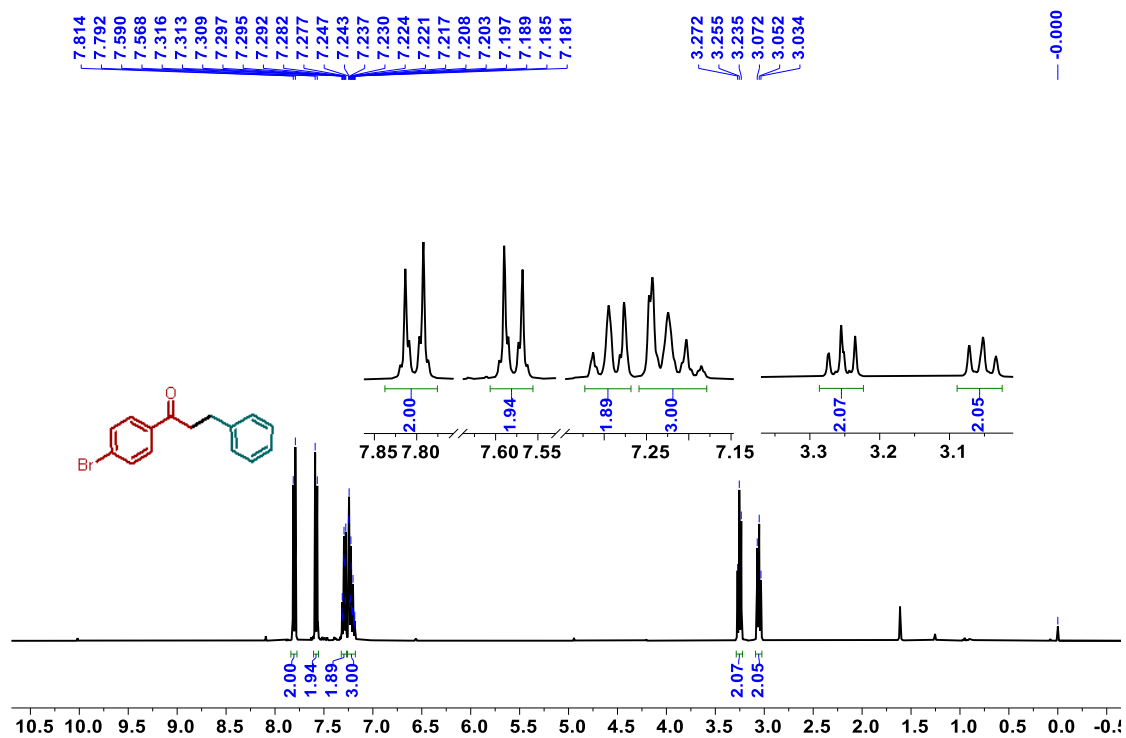
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3f**



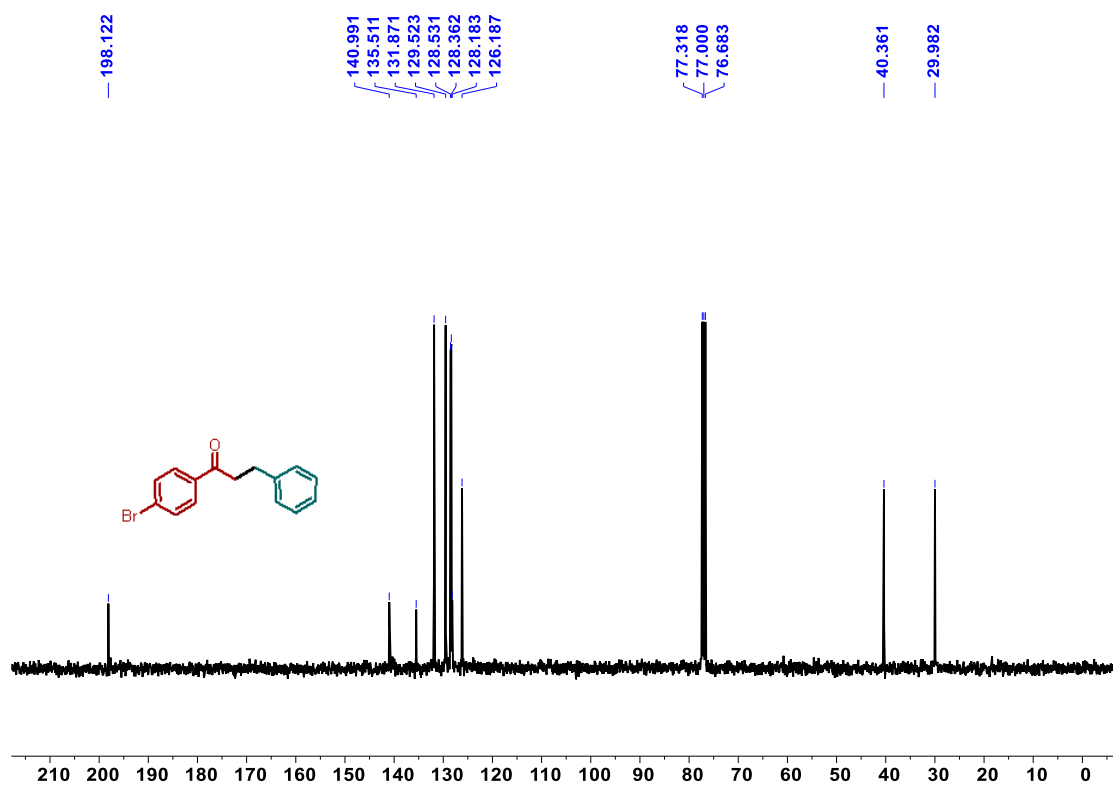
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3f**



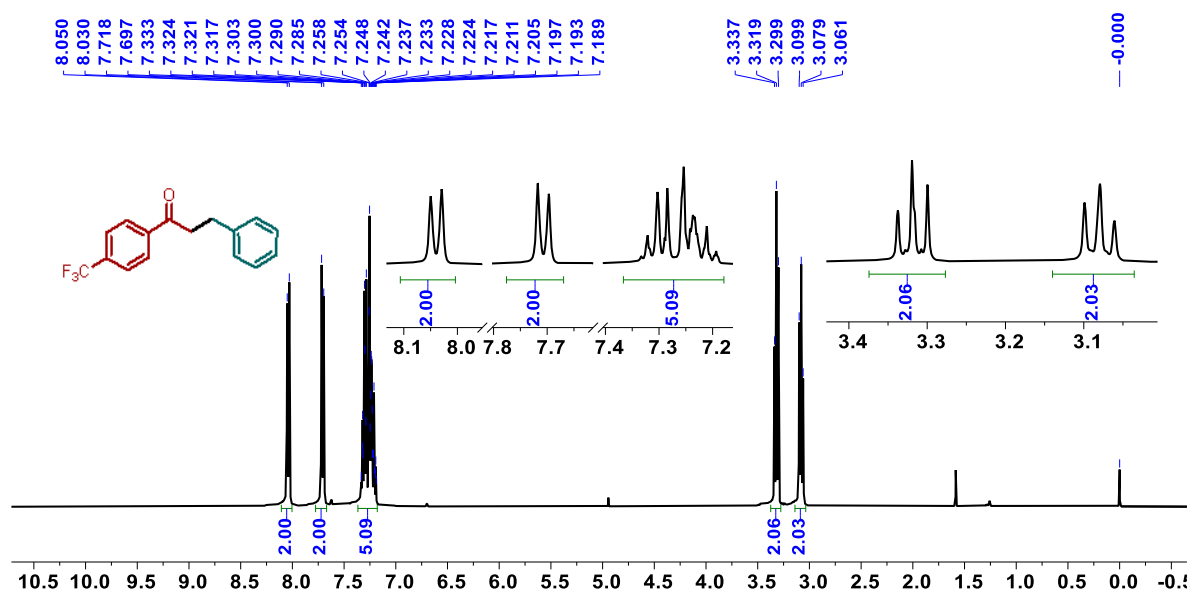
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3g**



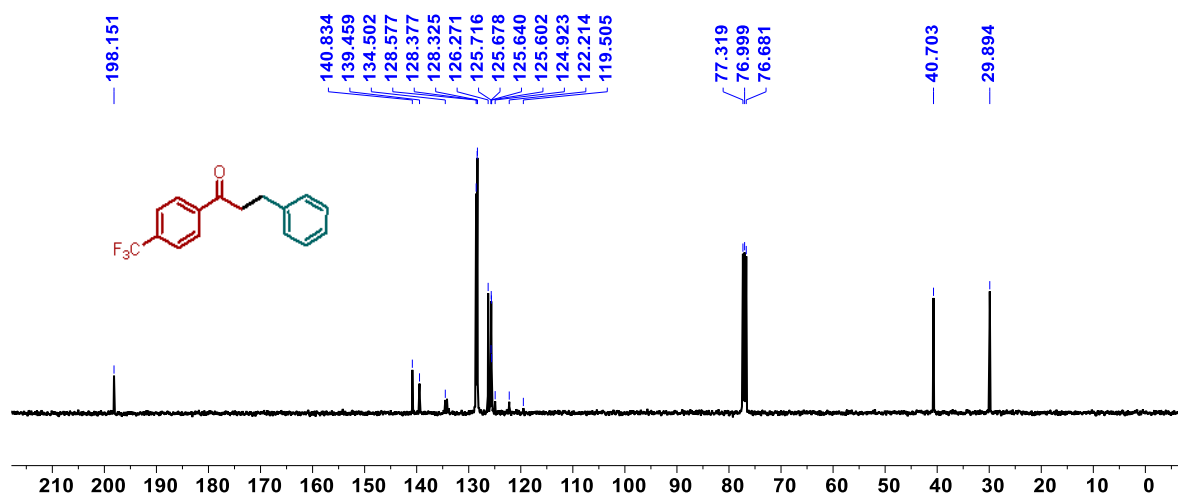
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3g**



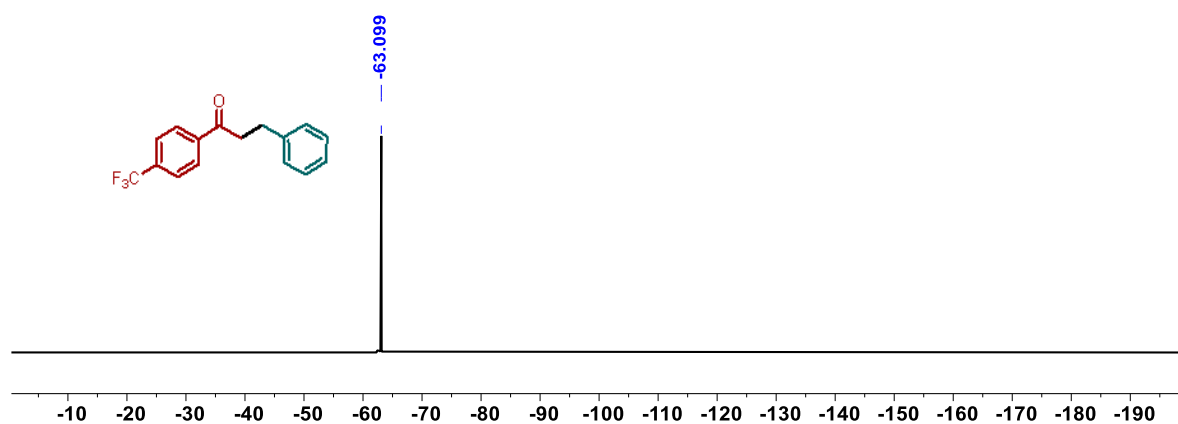
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3h**



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3h**

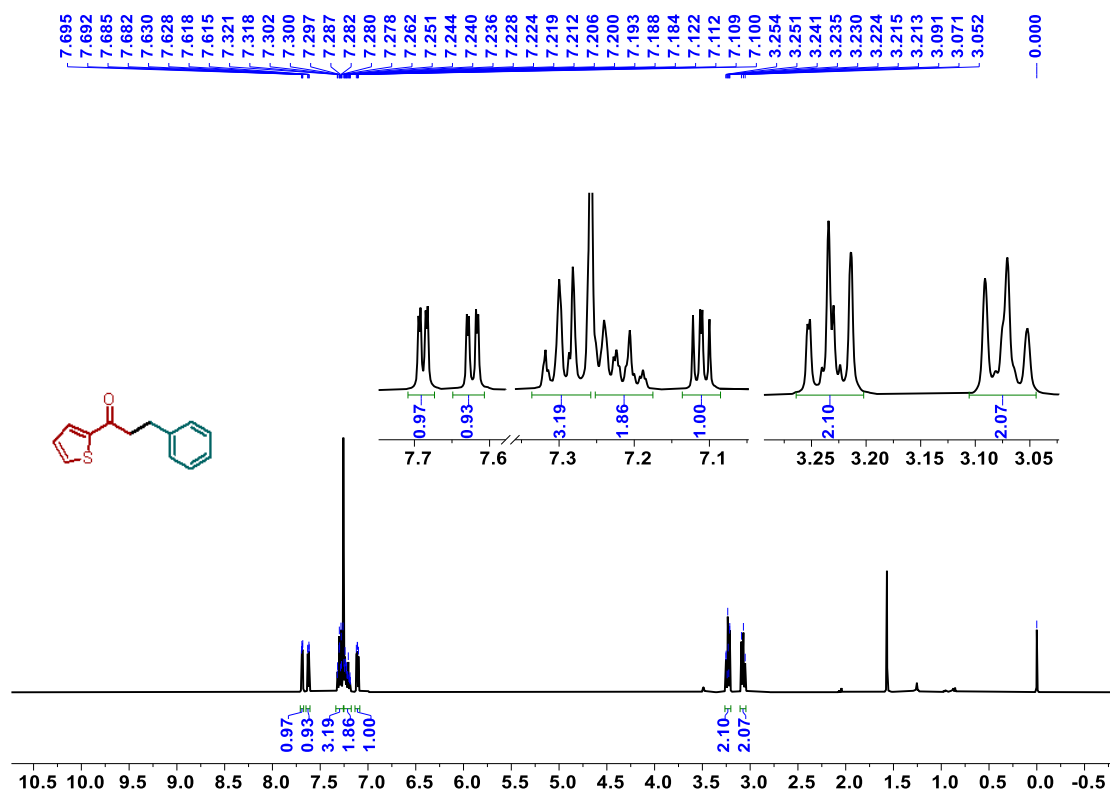


$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **3h**

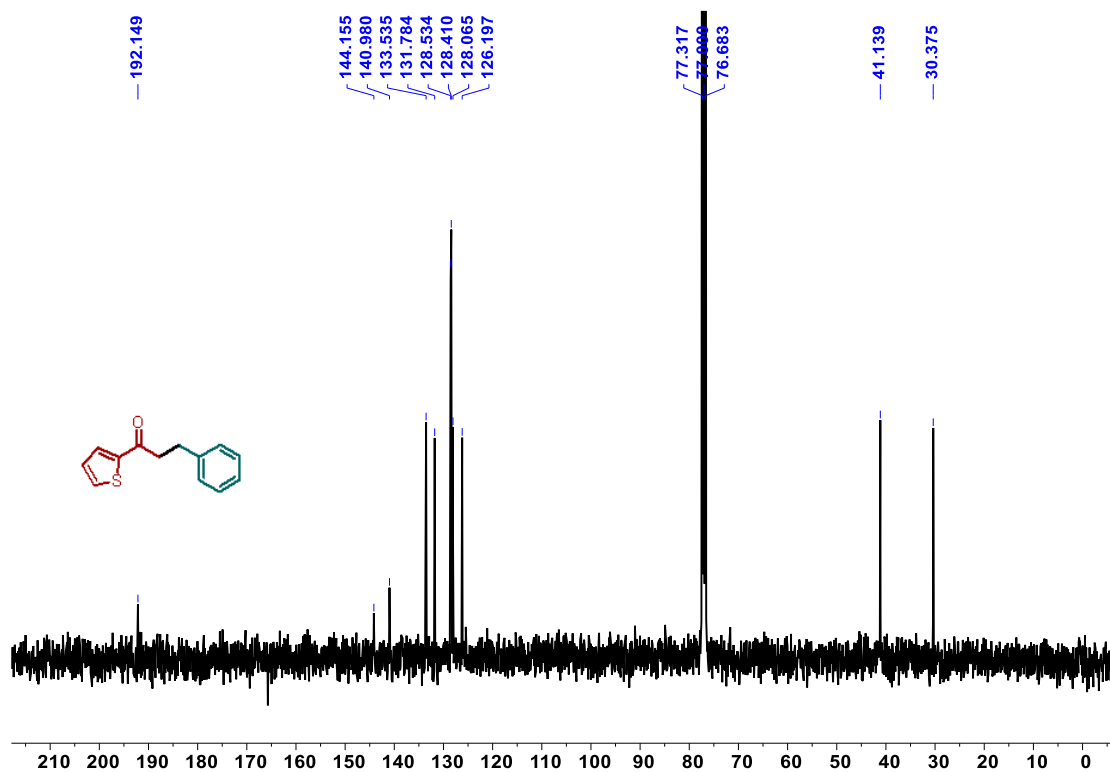




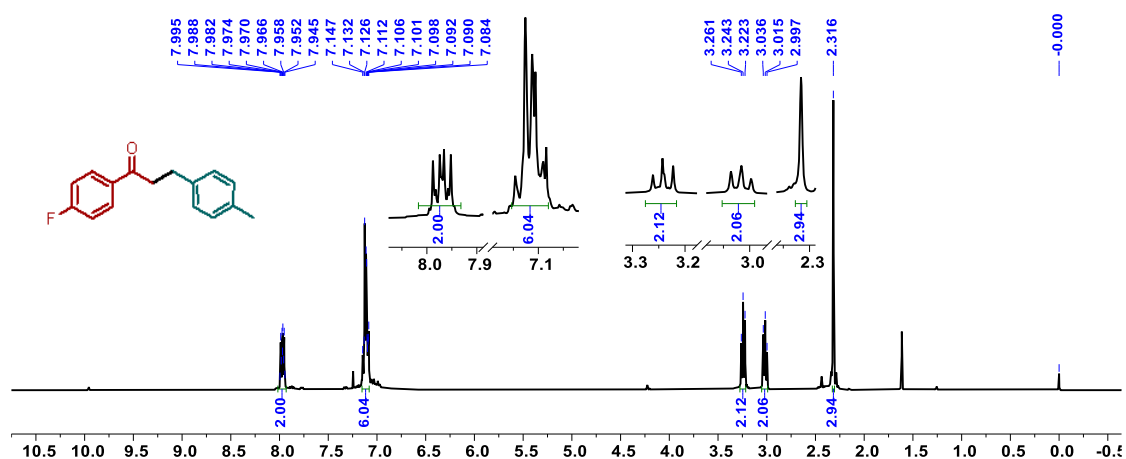
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3i**



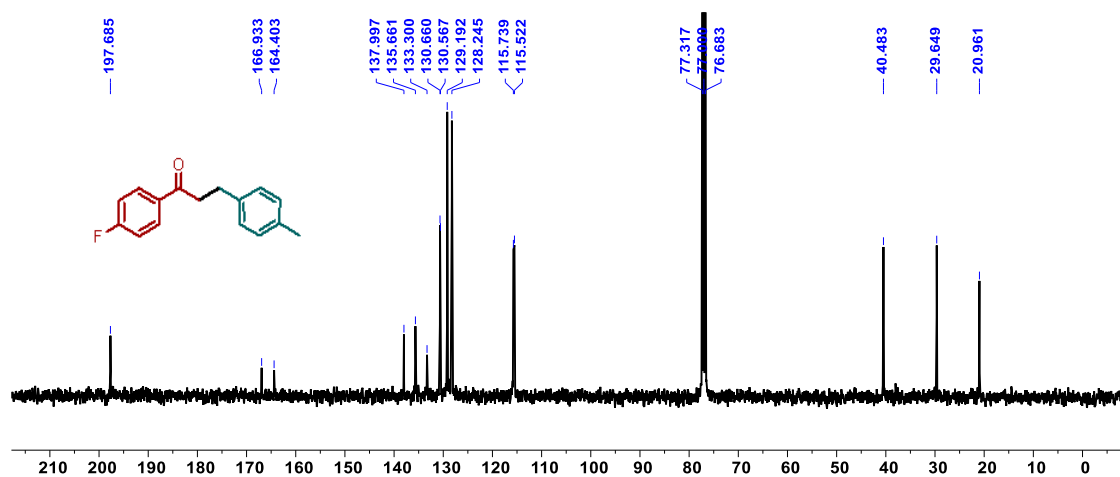
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of **3i**



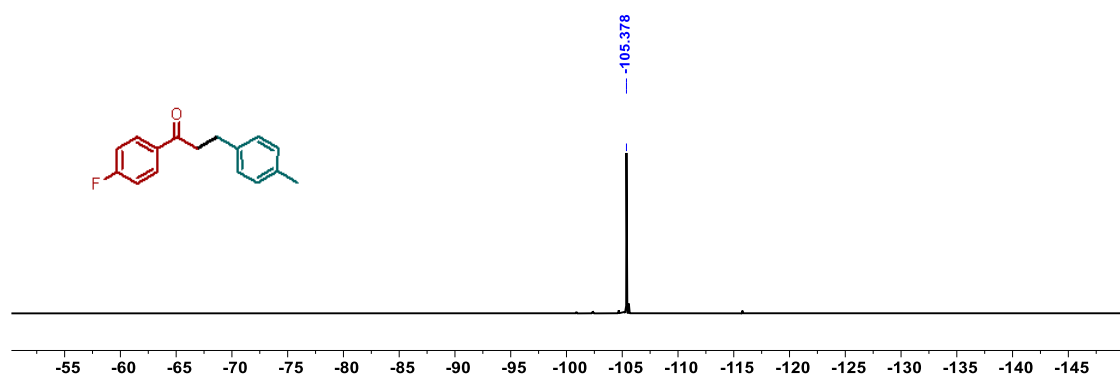
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3j**



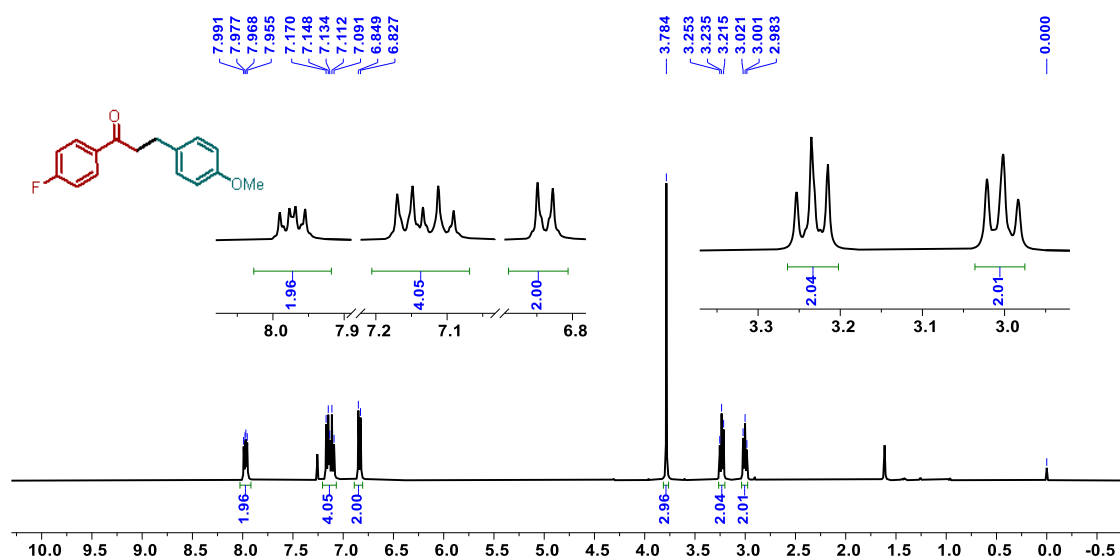
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3j**



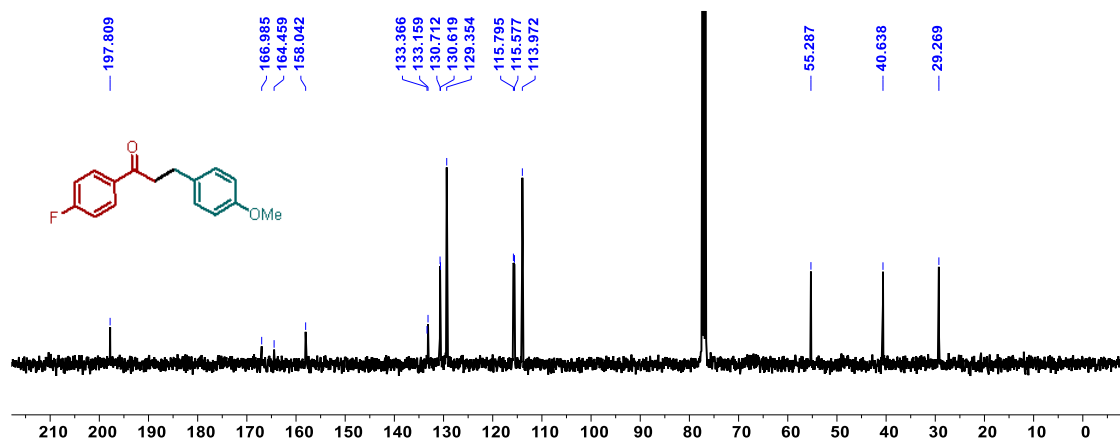
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **3j**



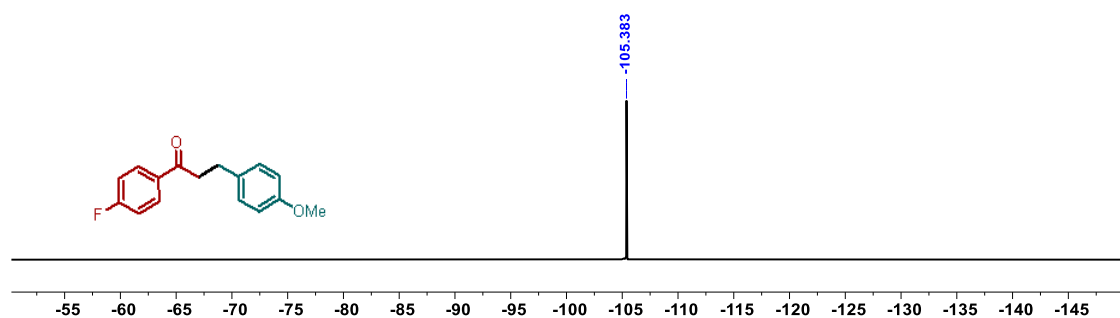
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3k**

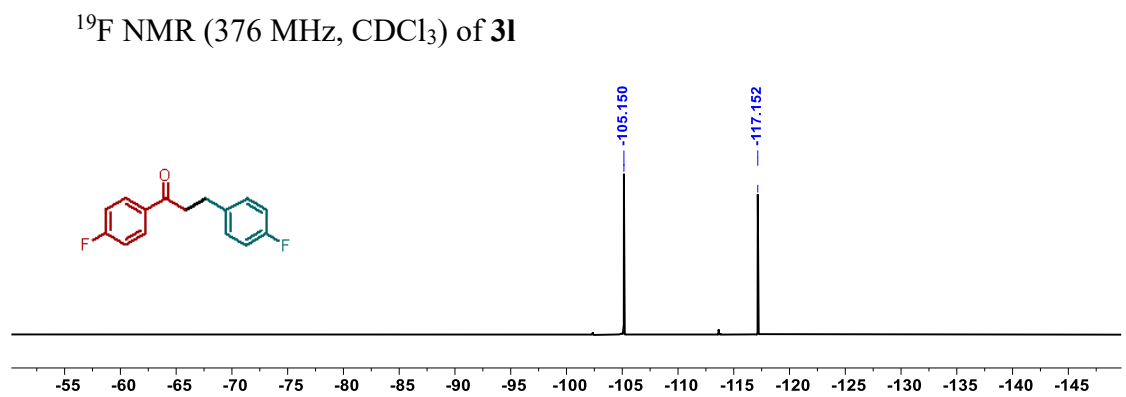
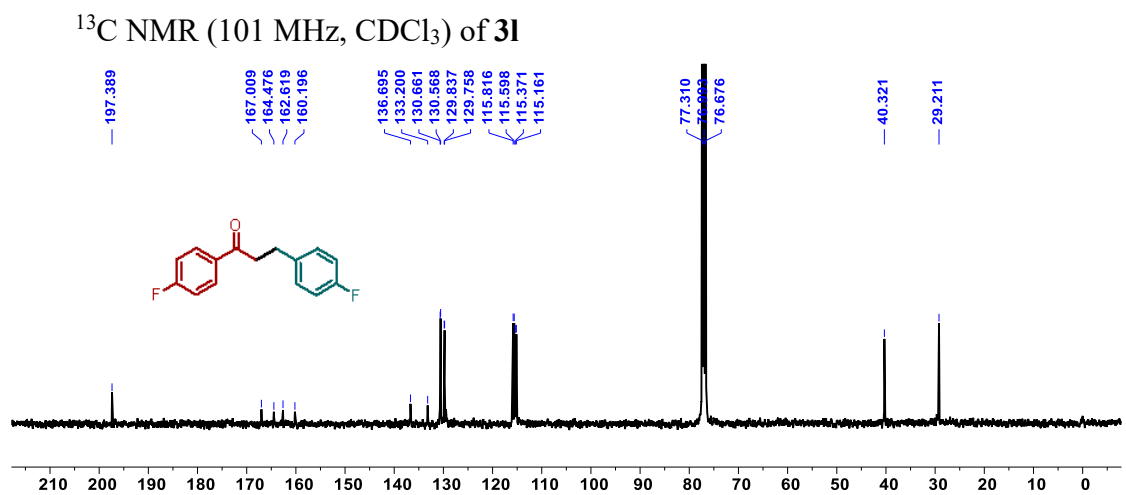
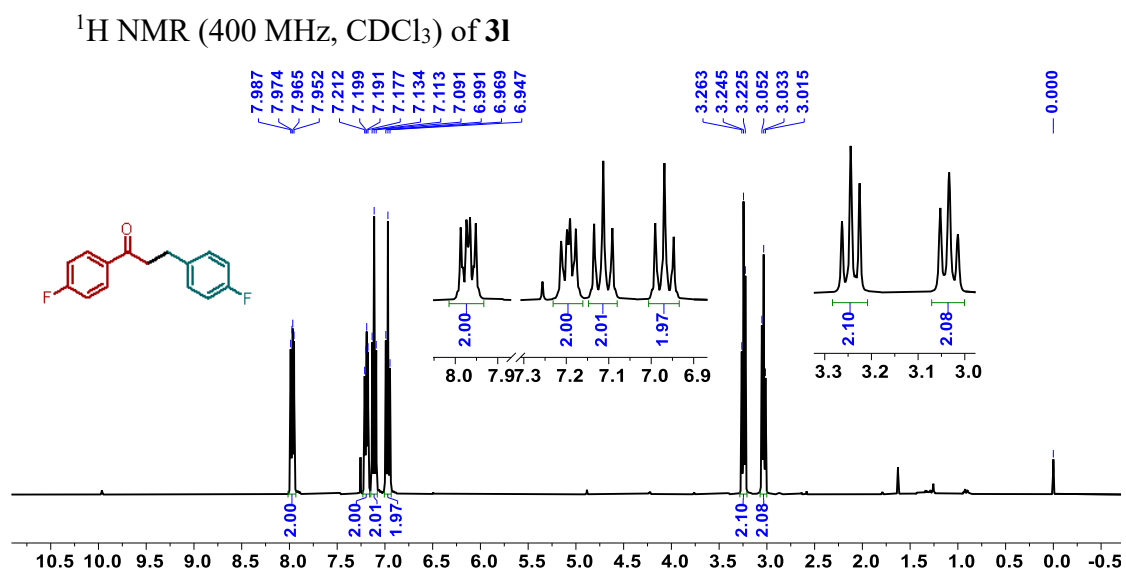


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3k**

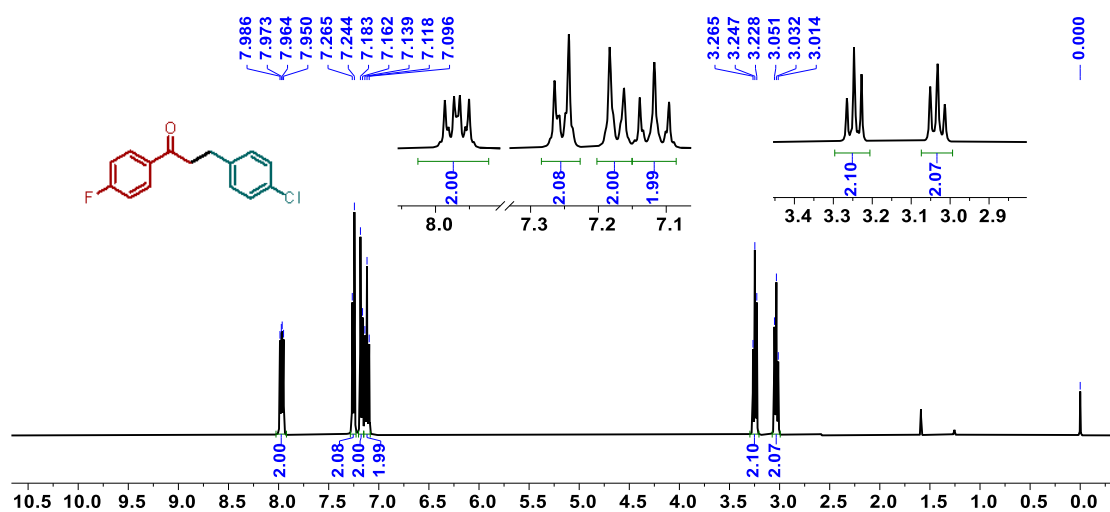


$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **3k**

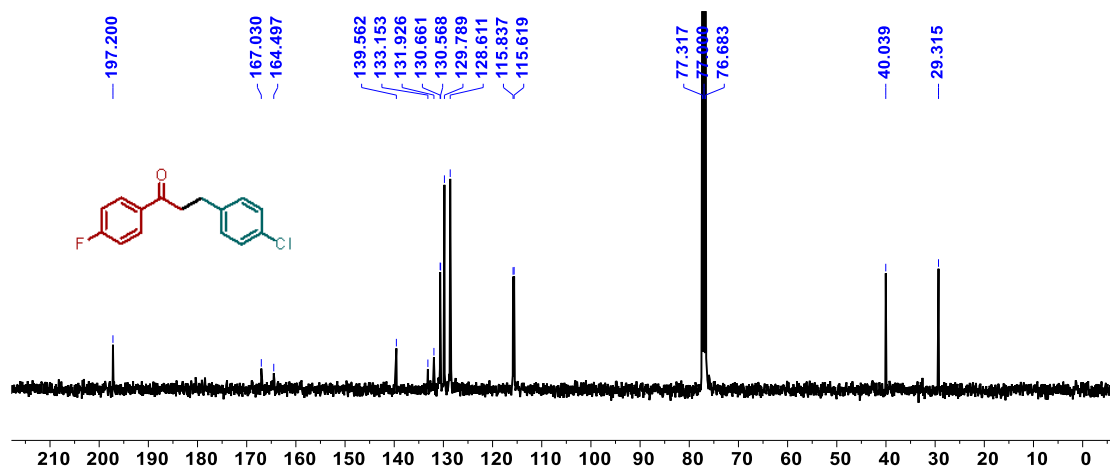




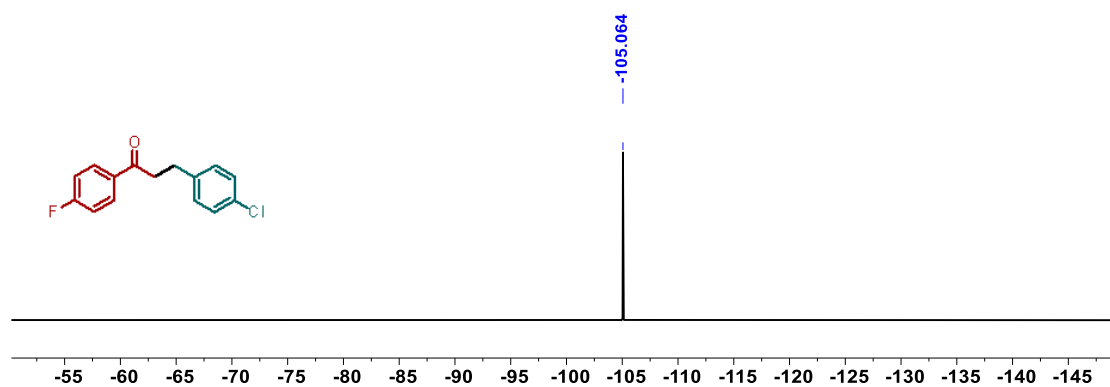
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3m**



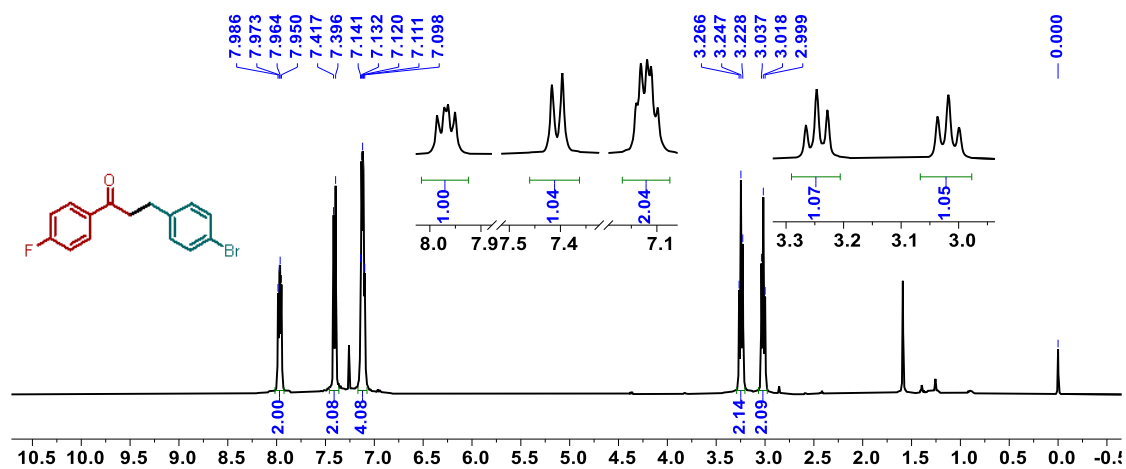
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3m**



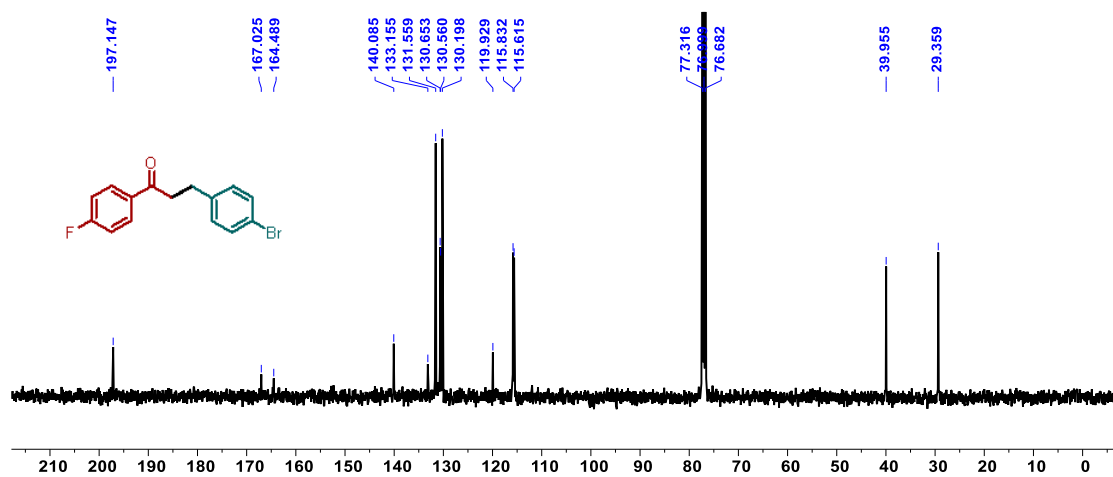
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **3m**



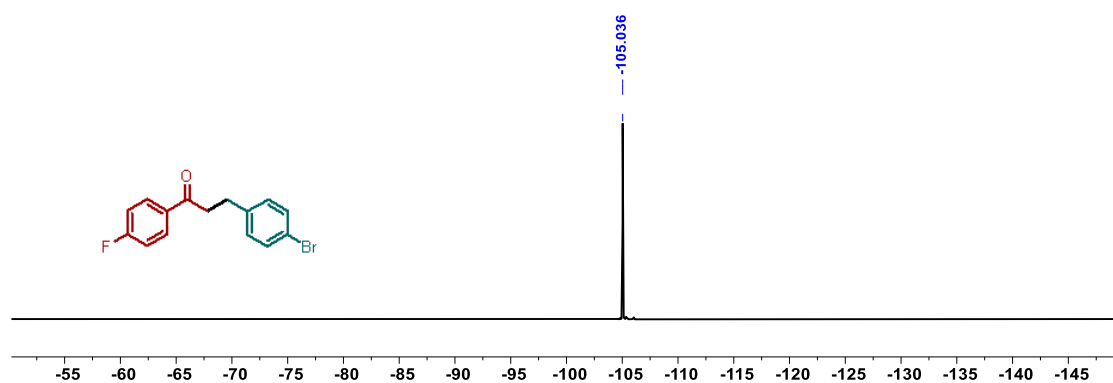
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3n**



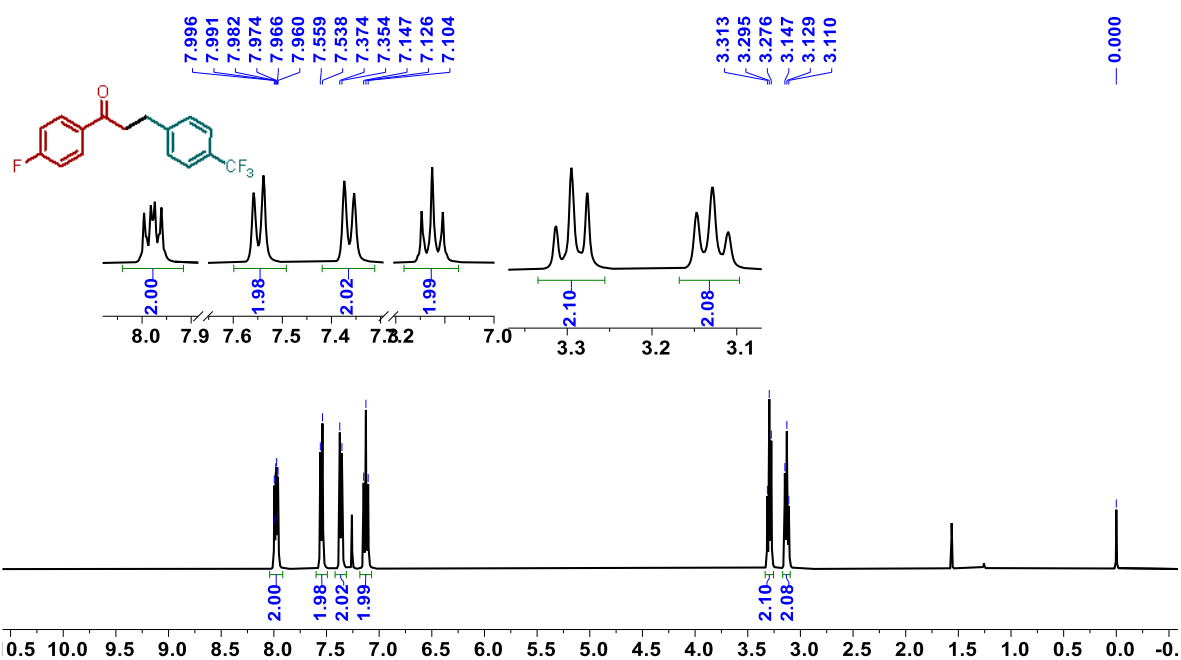
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3n**



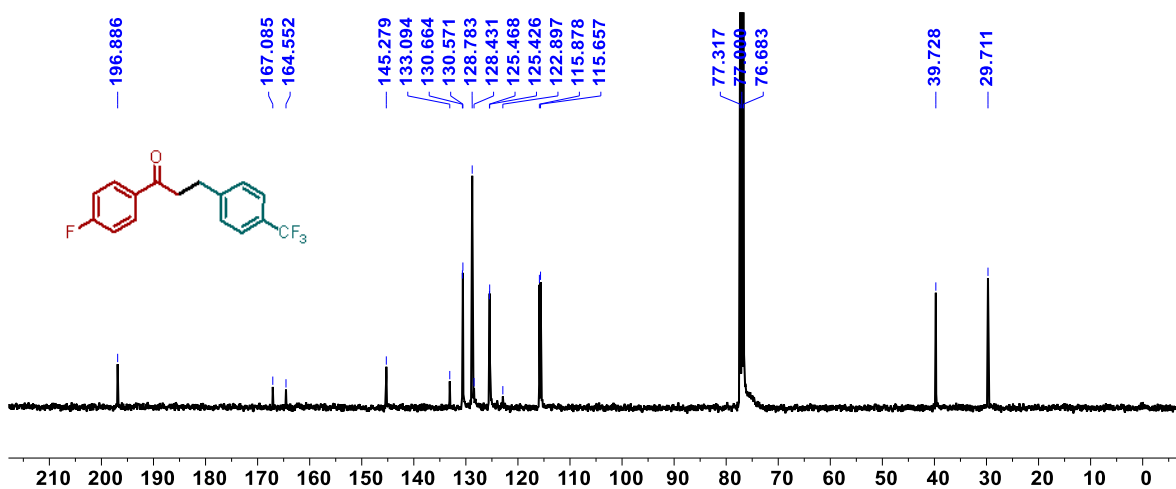
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **3n**



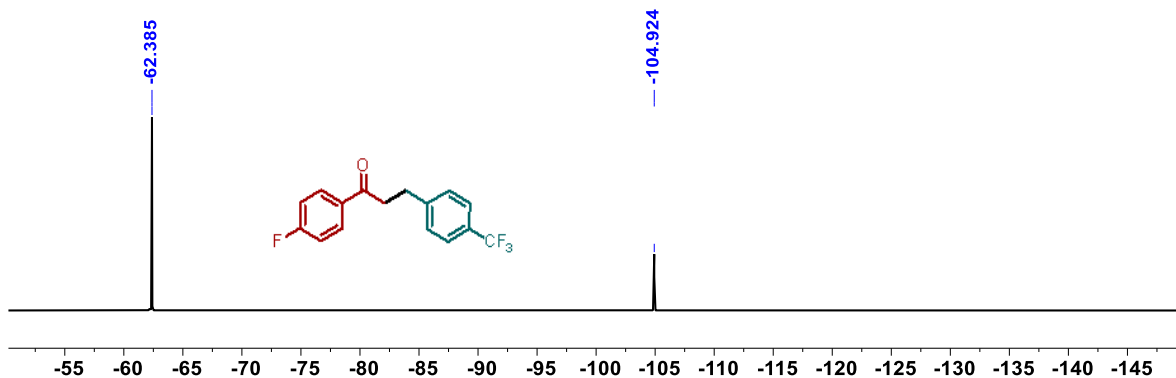
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3o**



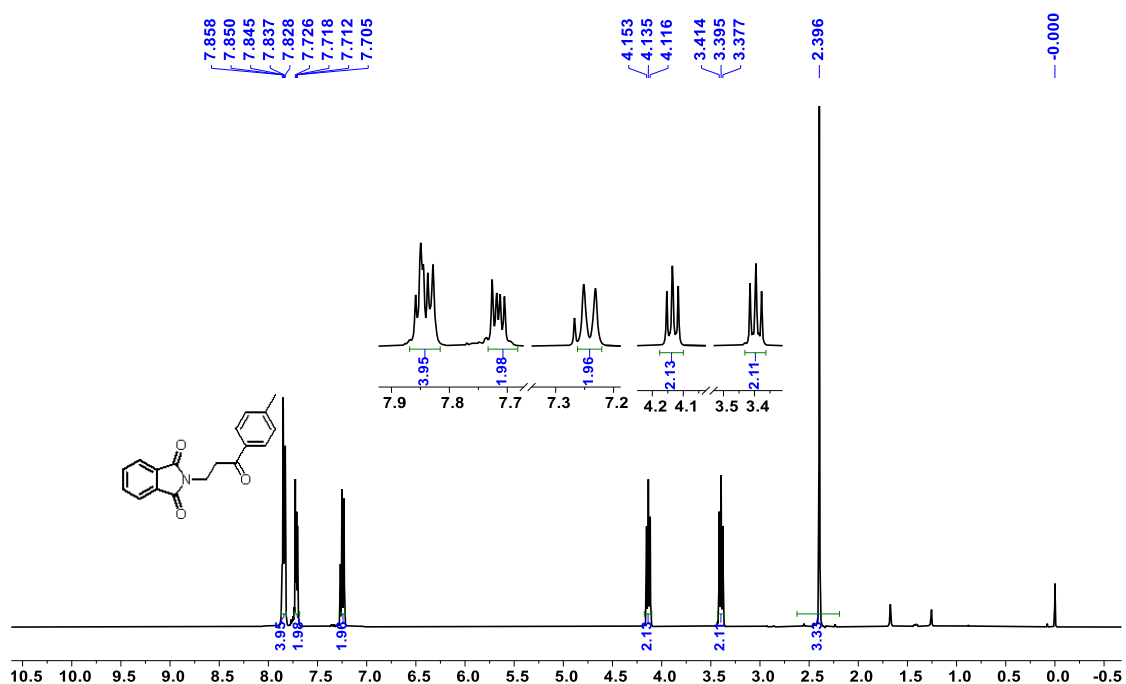
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3o**



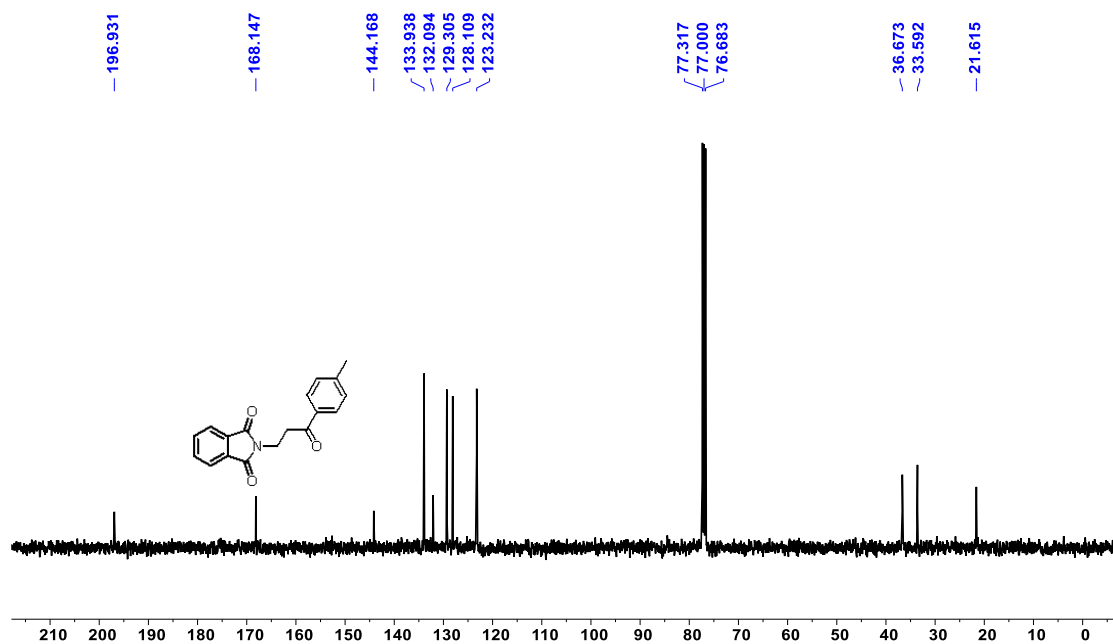
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **3o**



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3p**

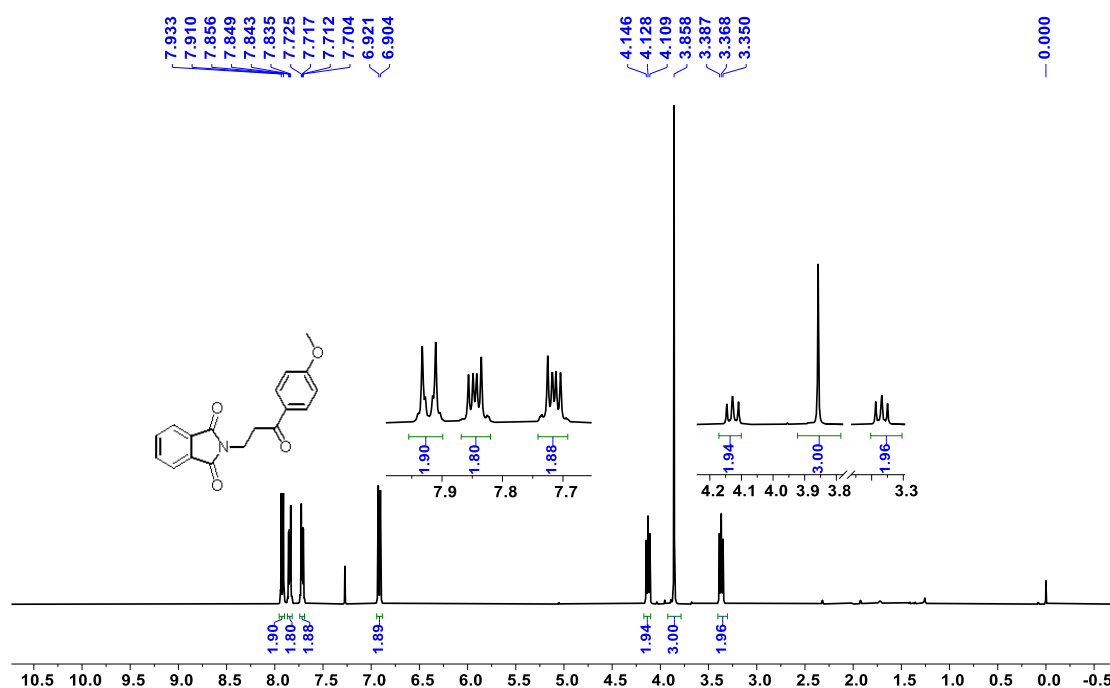


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3p**

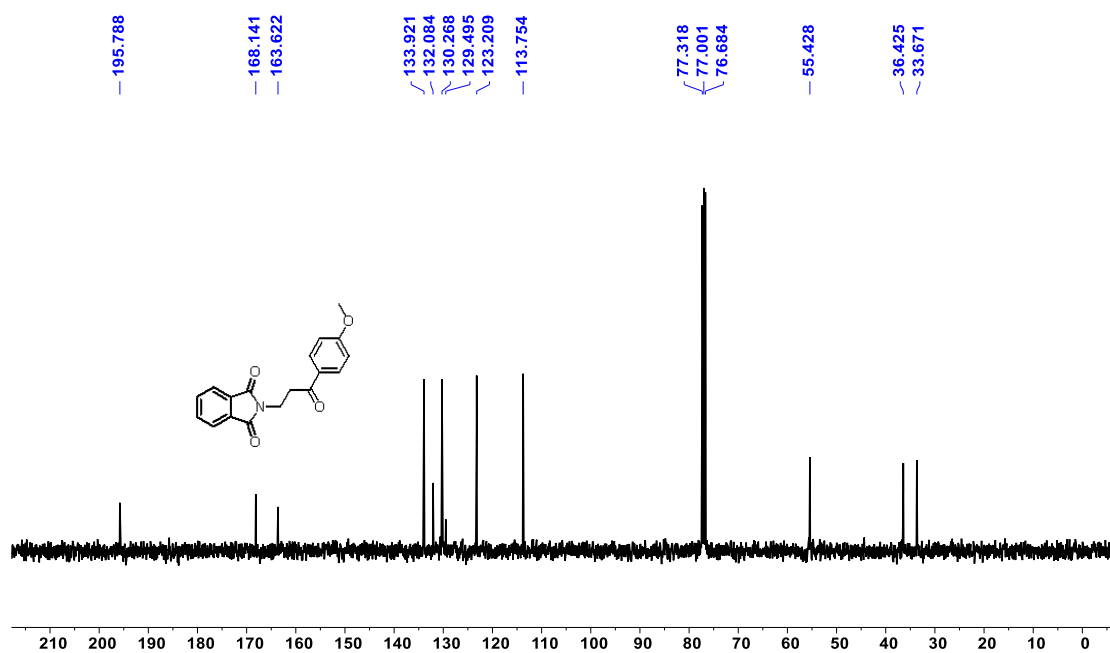




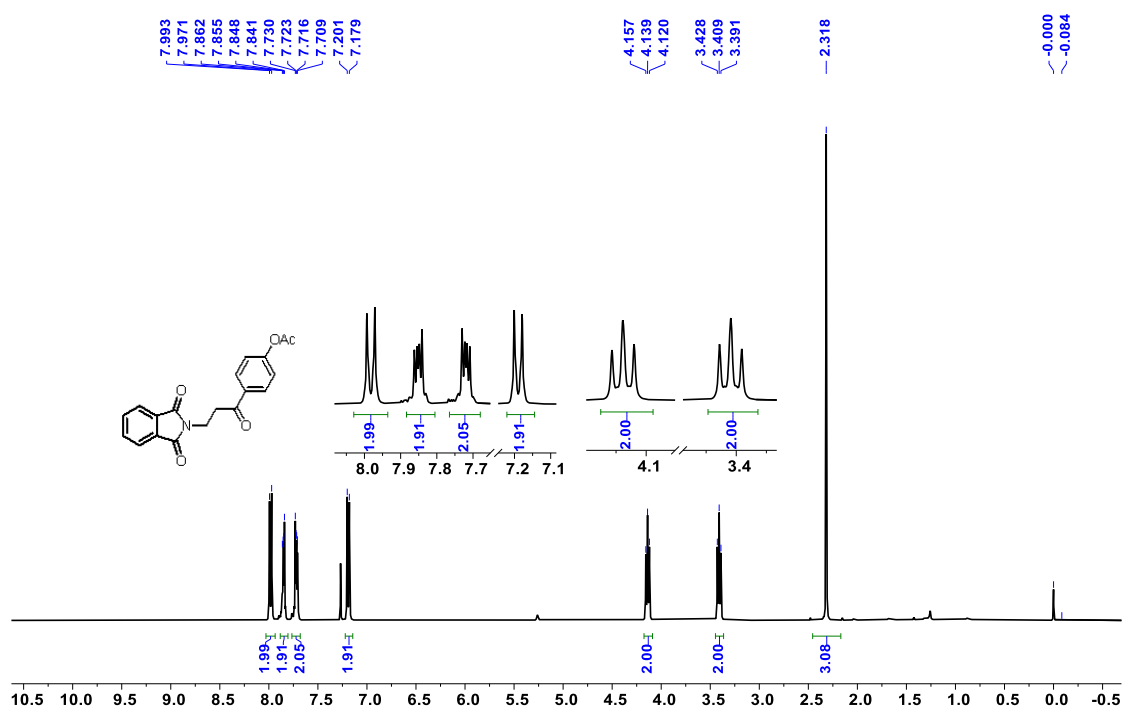
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3q**



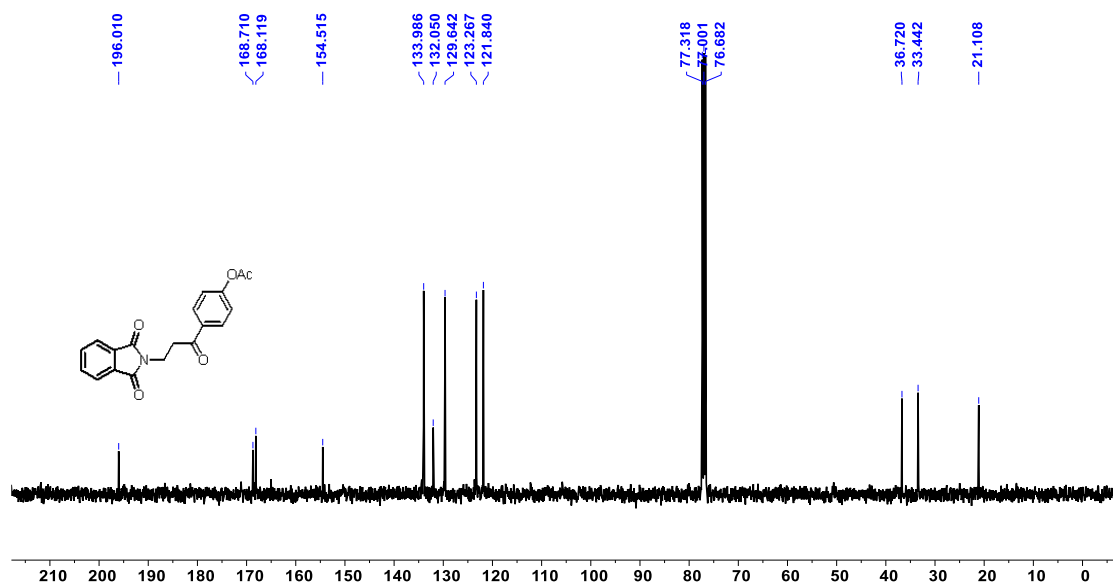
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3q**



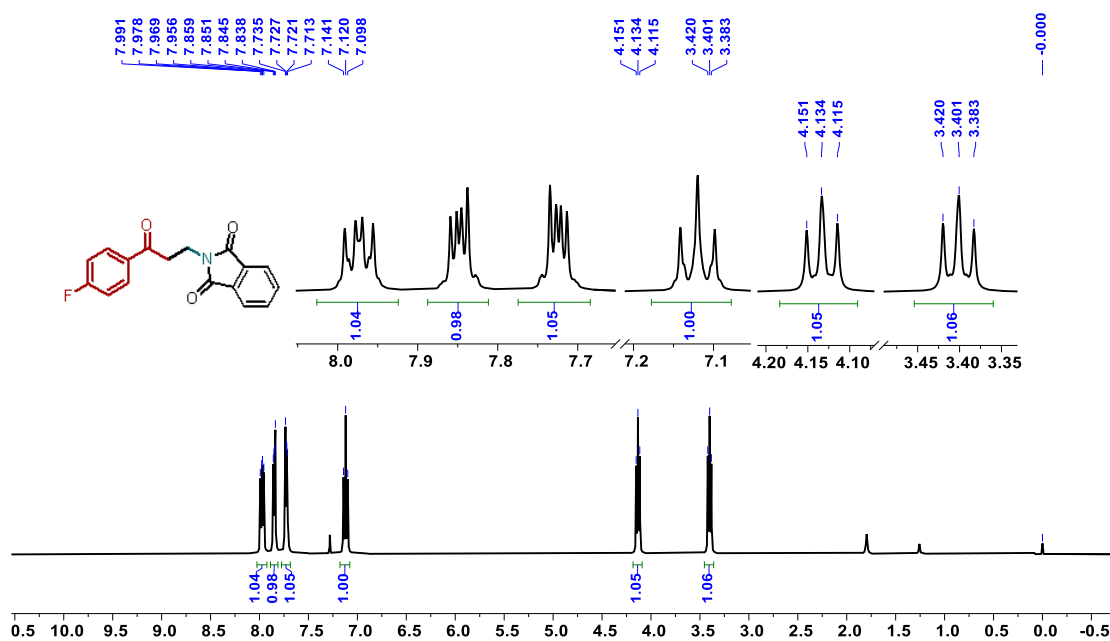
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3r**



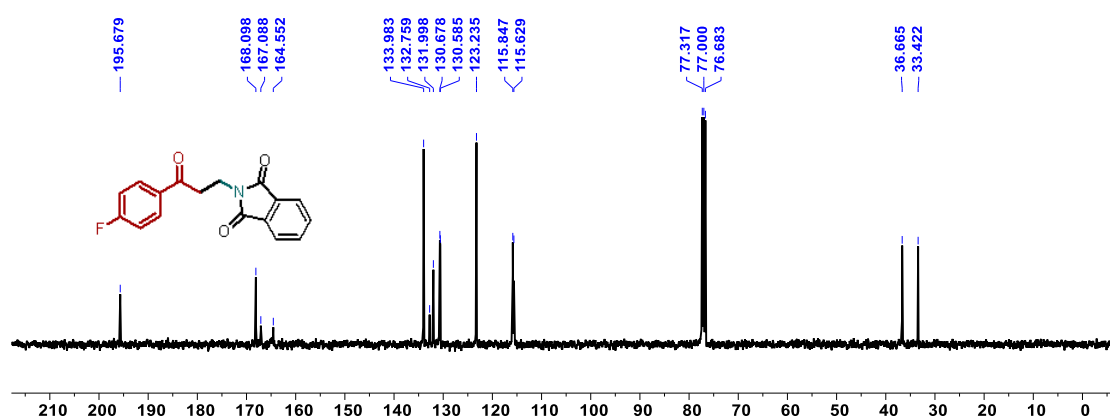
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3r**



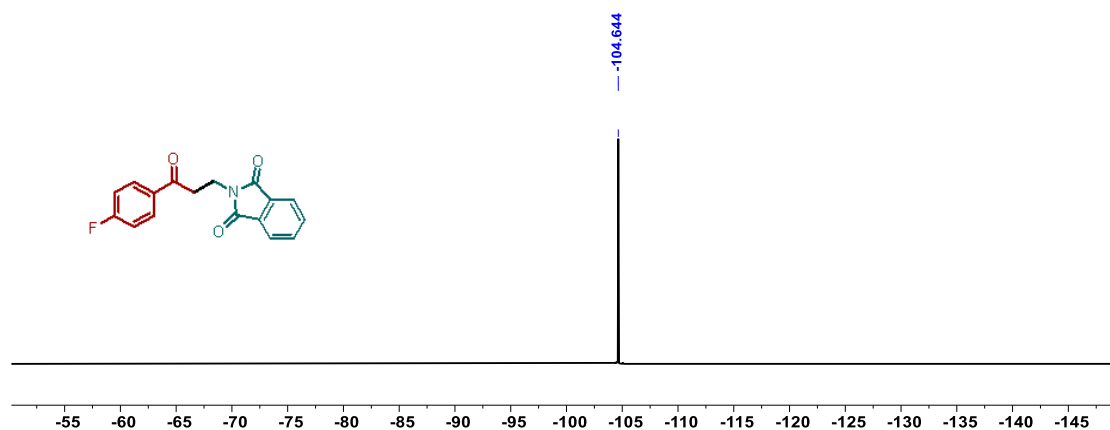
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3s**



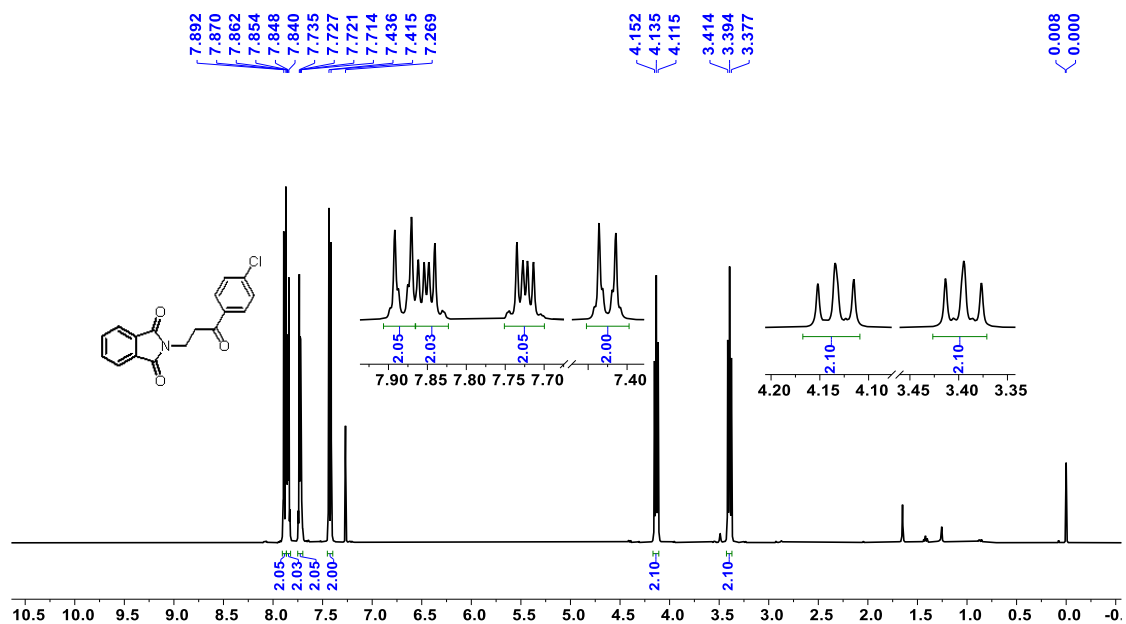
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3s**



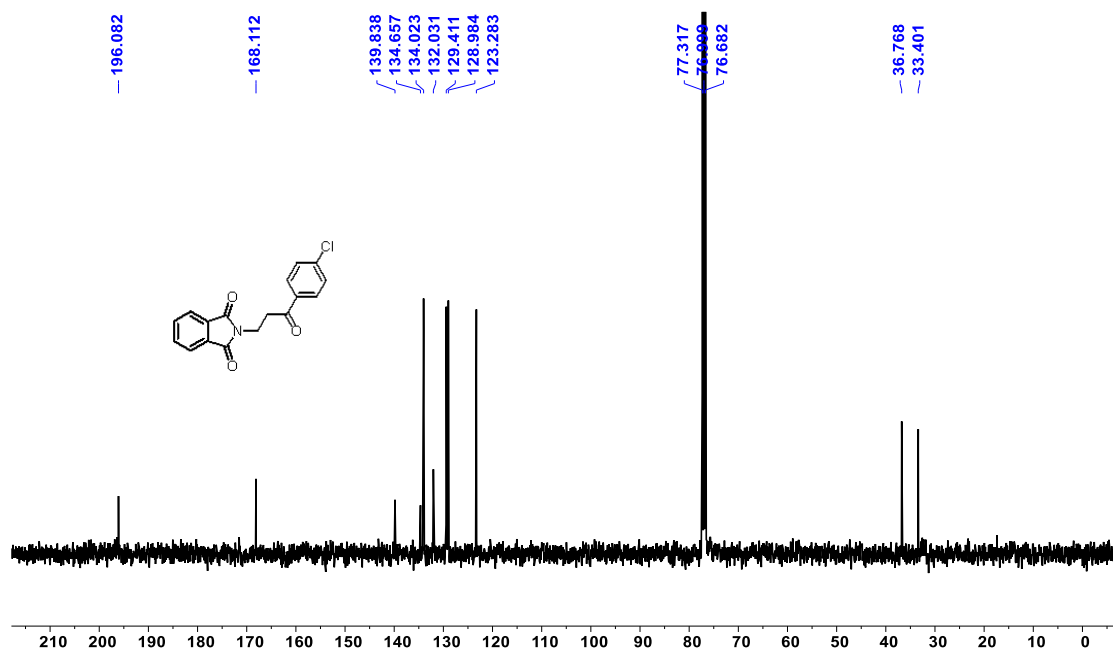
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **3s**



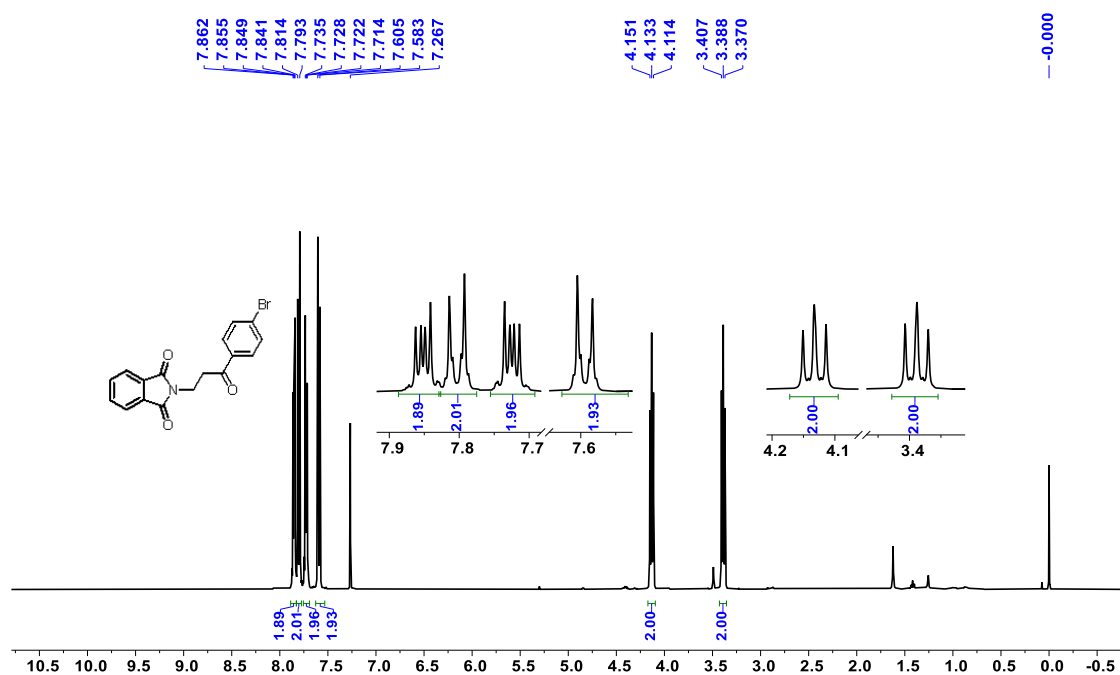
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3t**



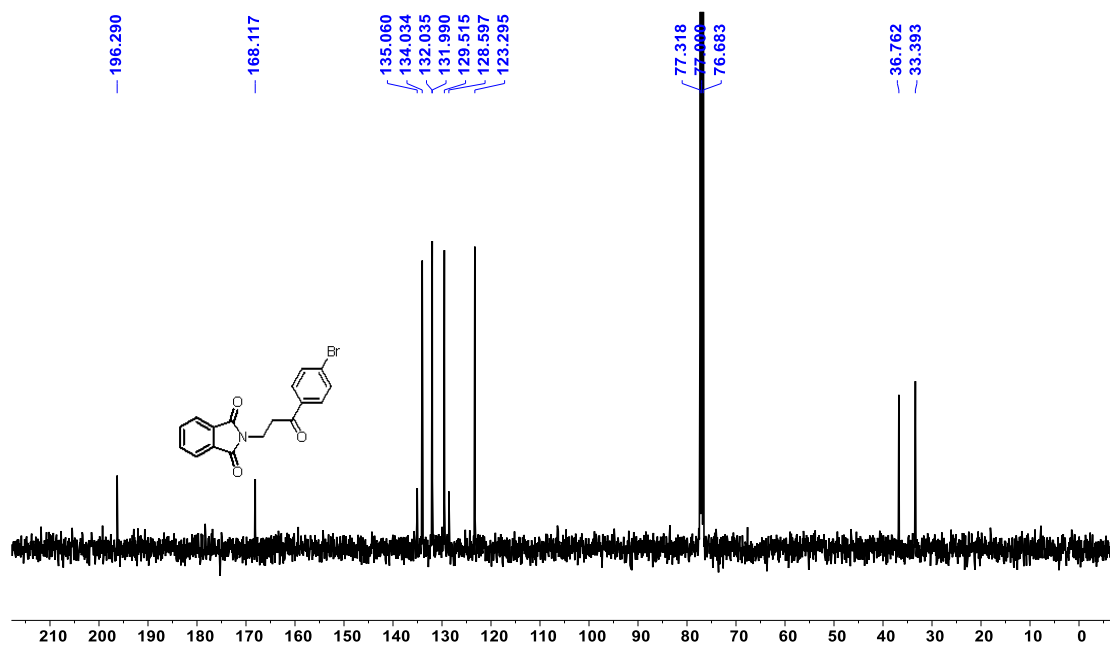
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3t**



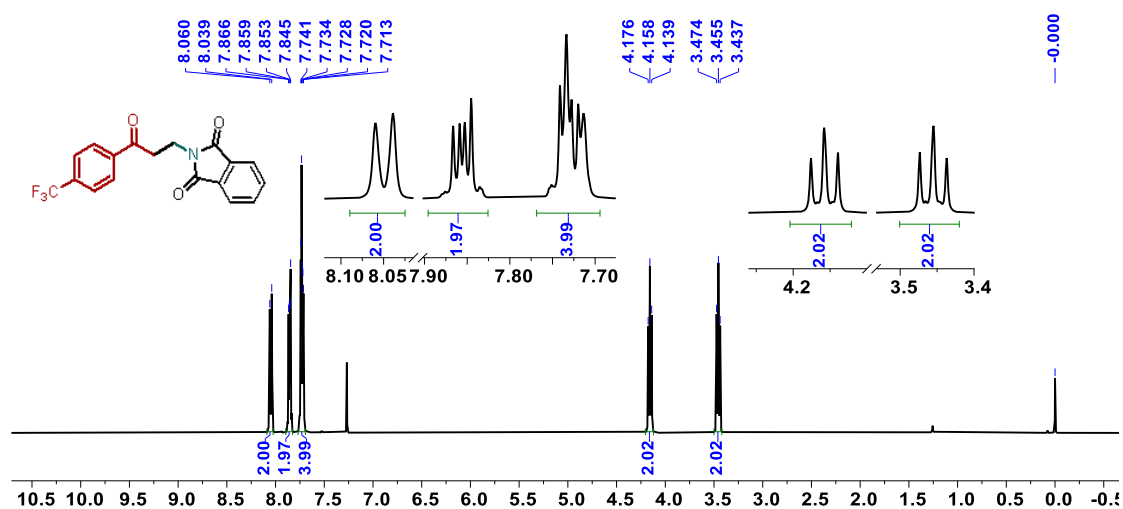
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3u**



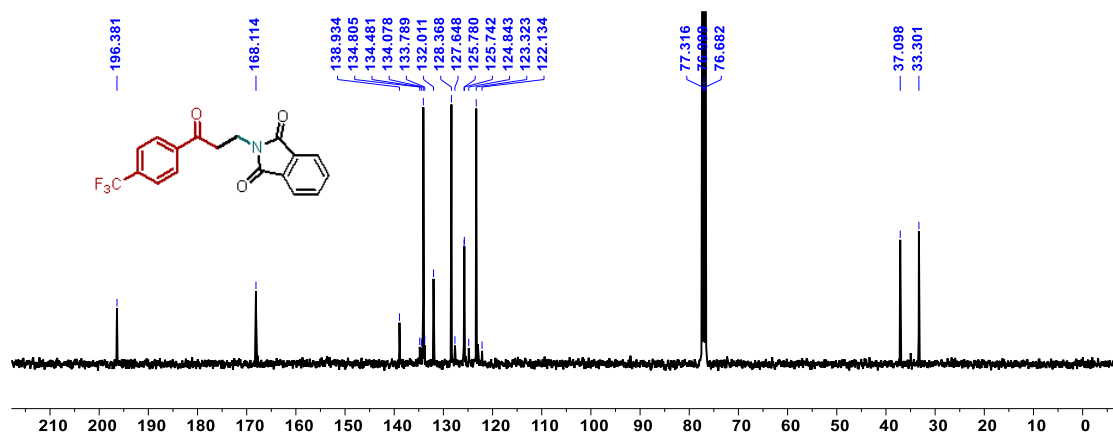
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3u**



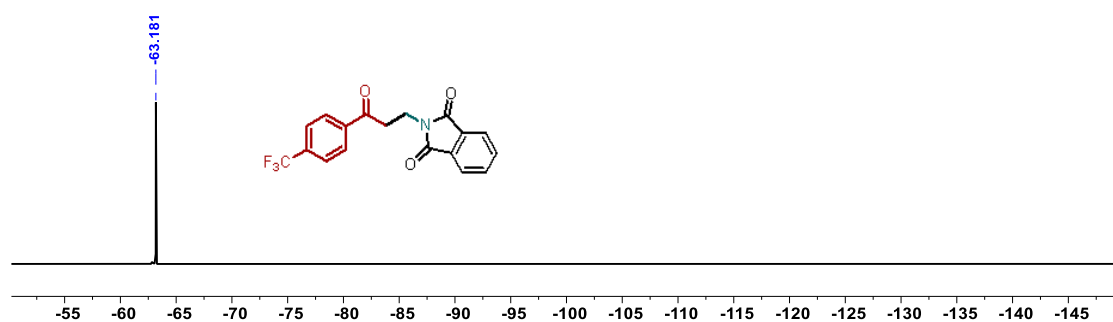
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3v**



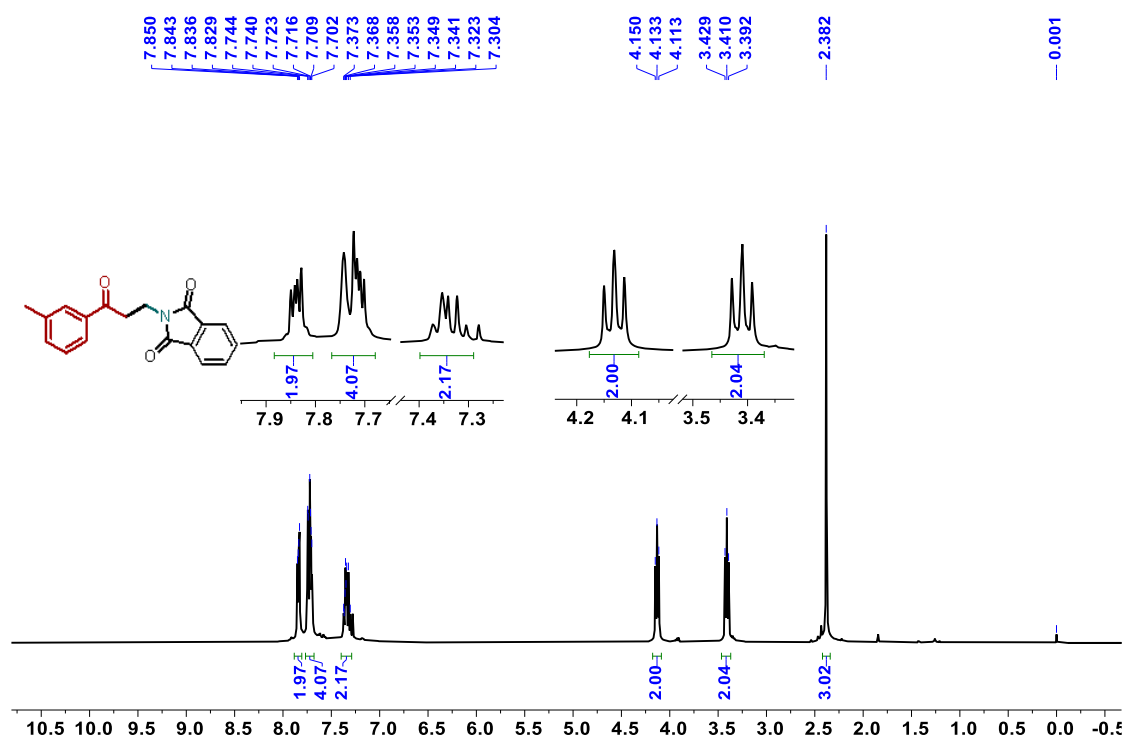
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3v**



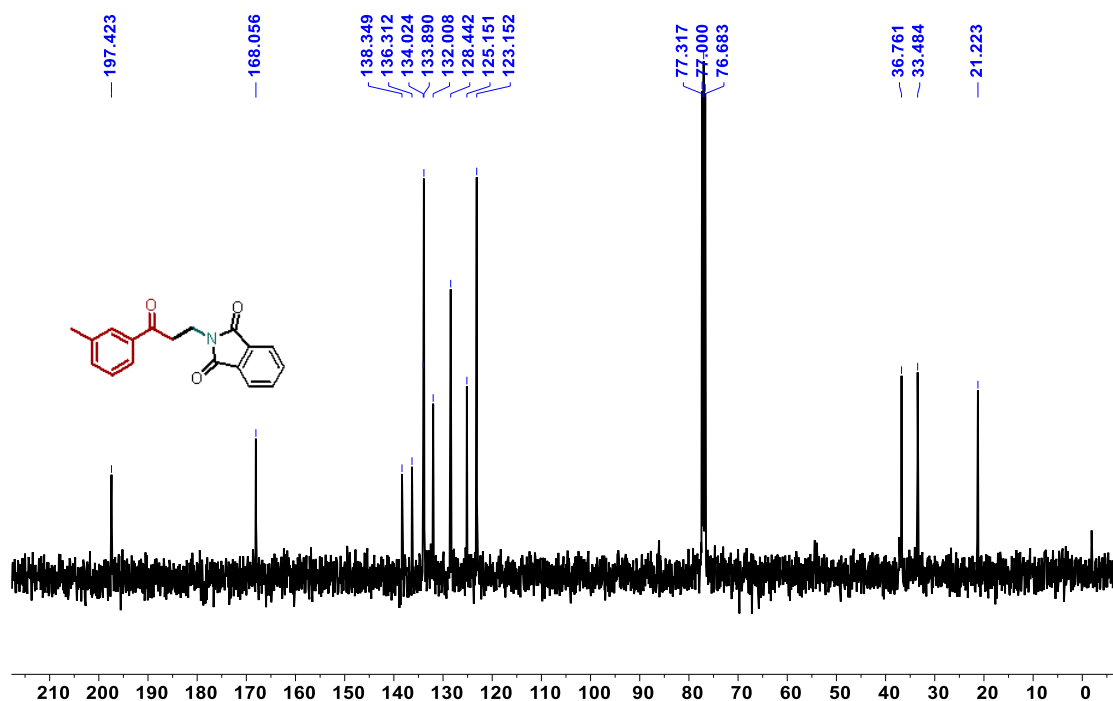
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **3v**



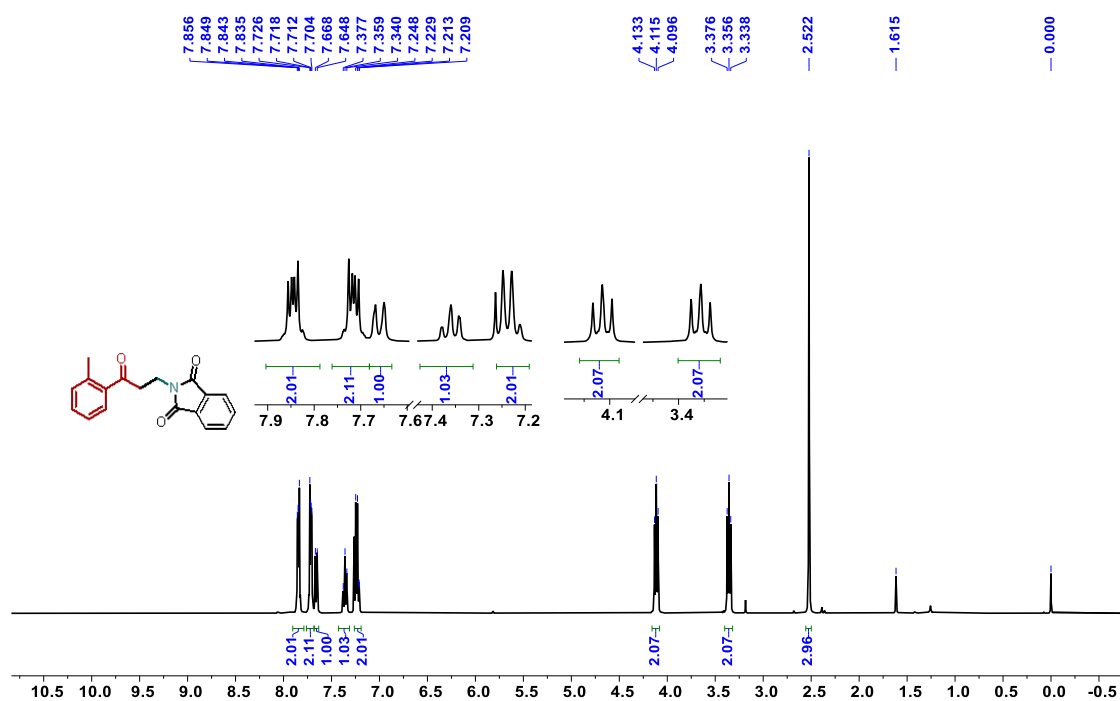
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3w**



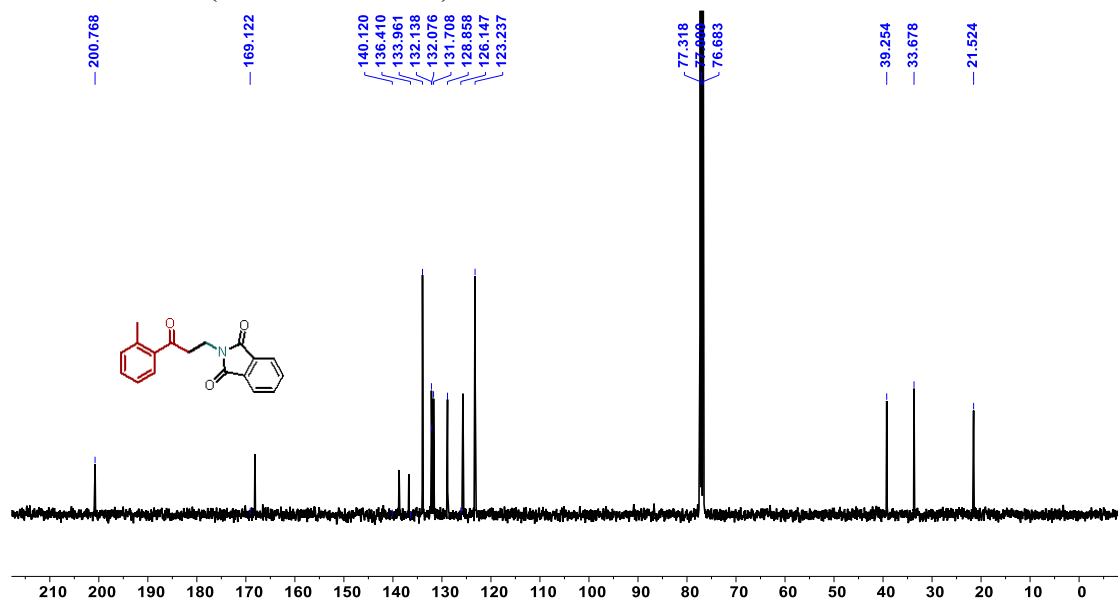
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3w**



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3x**

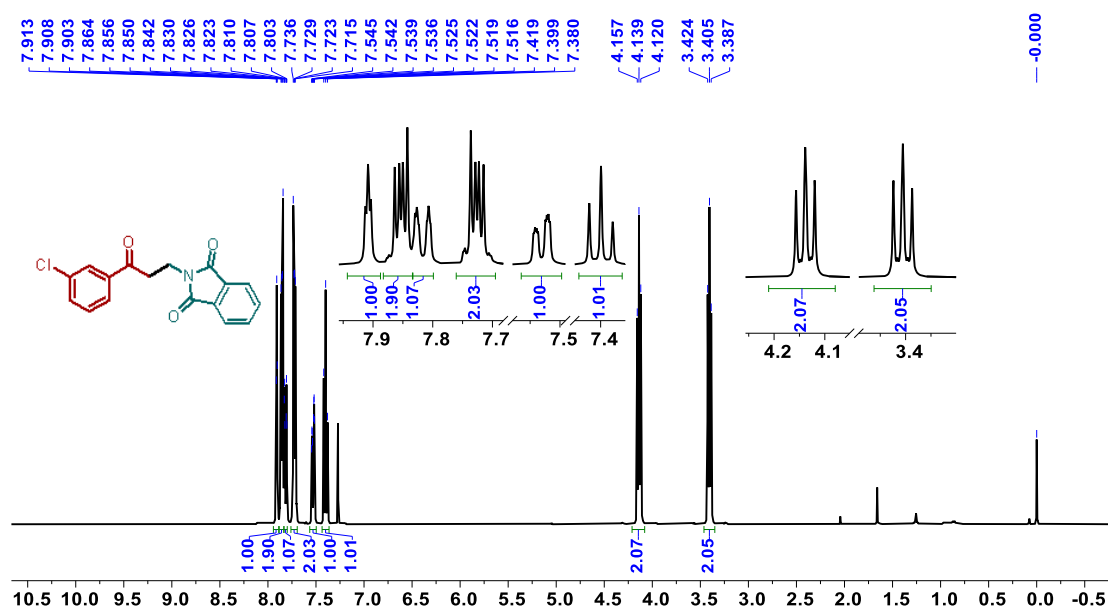


$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3x**

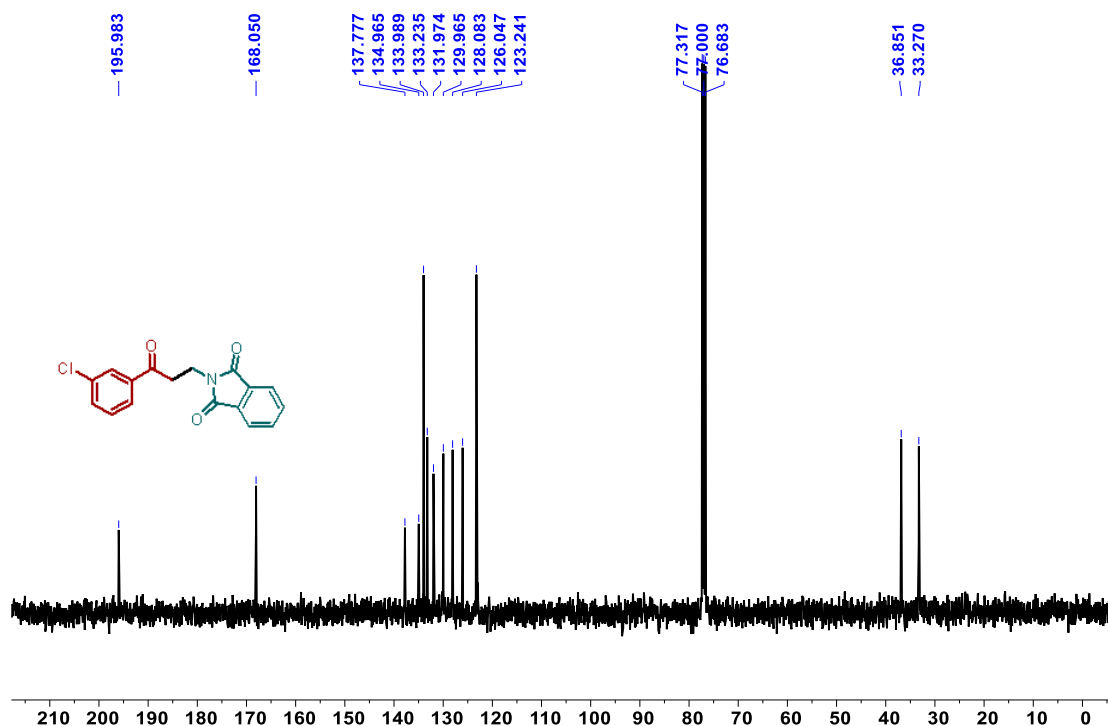




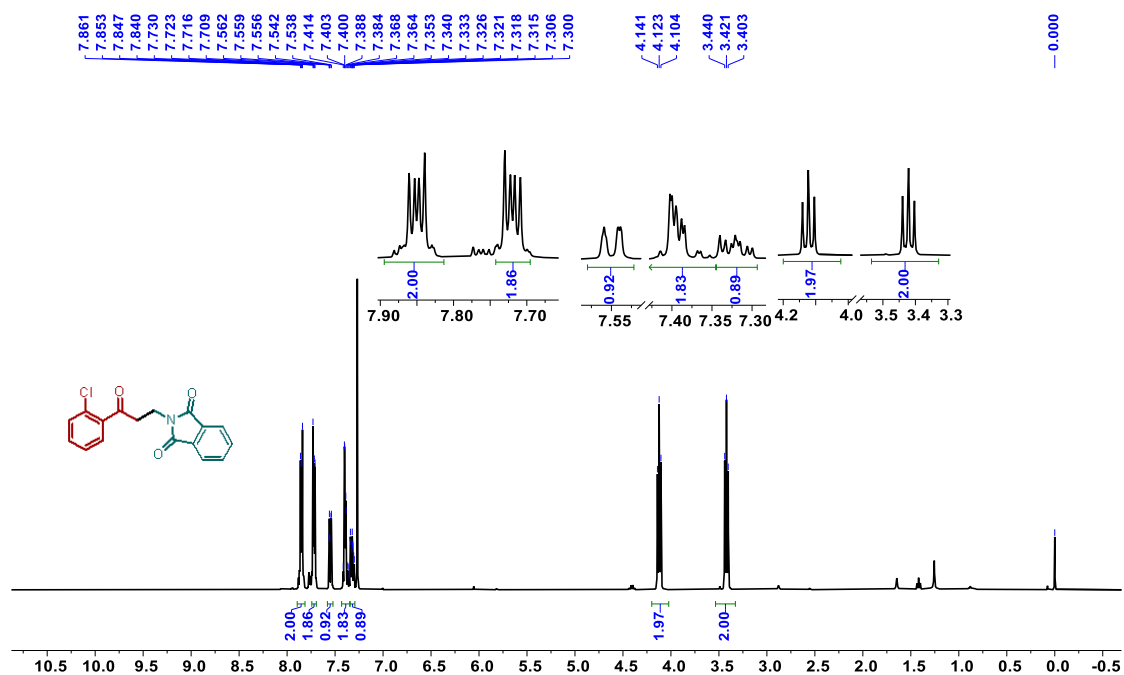
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3y**



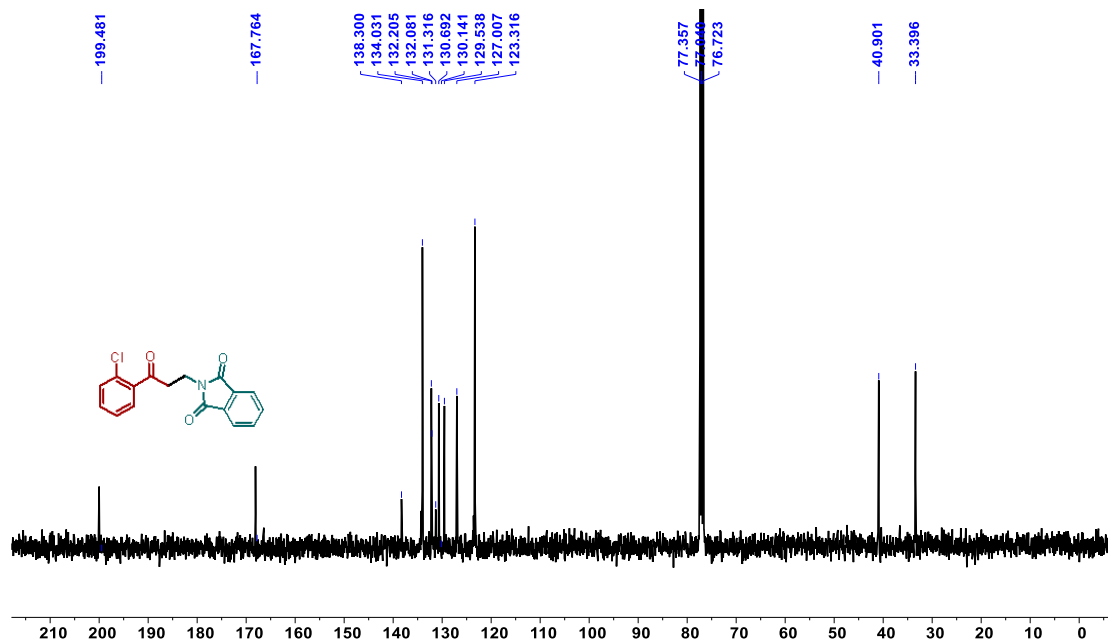
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of **3y**



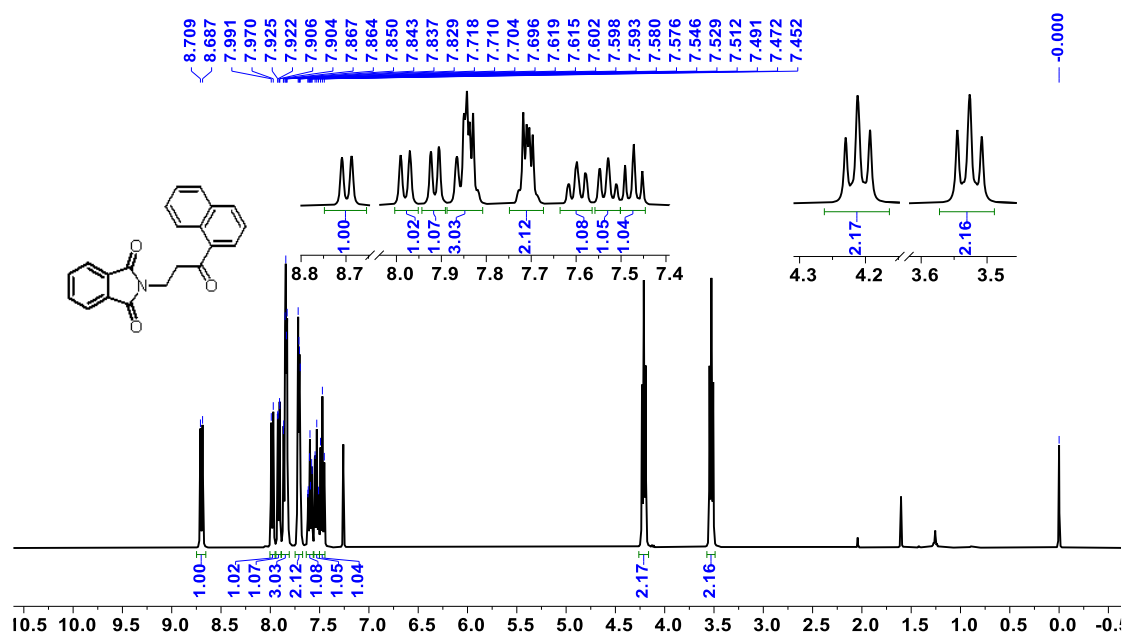
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3z**



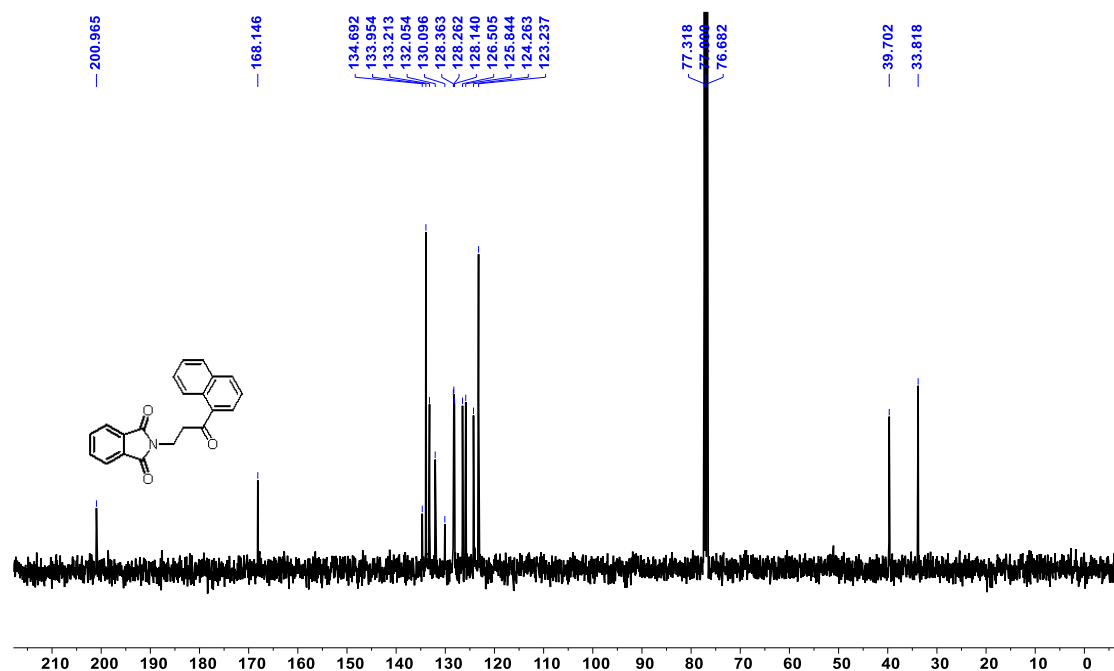
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of **3z**



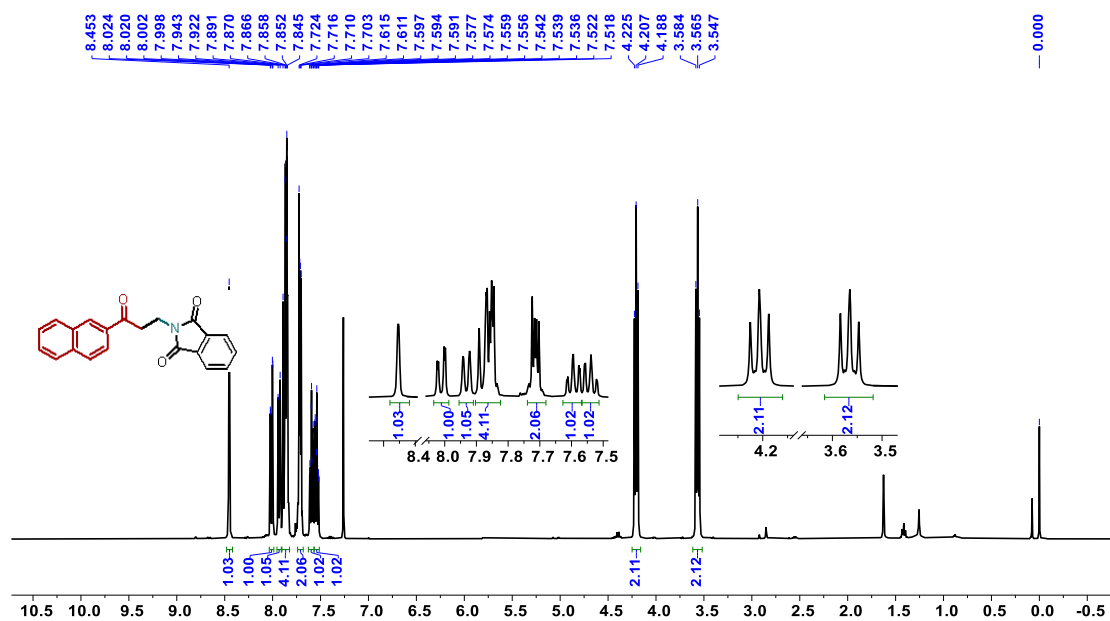
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3aa**



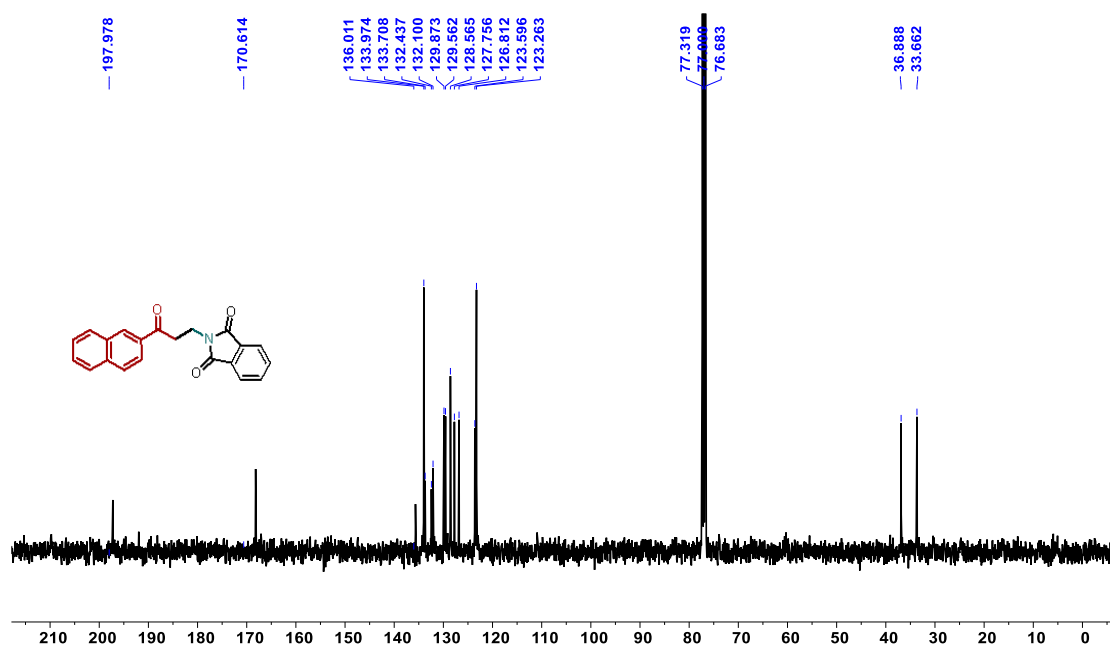
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of **3aa**



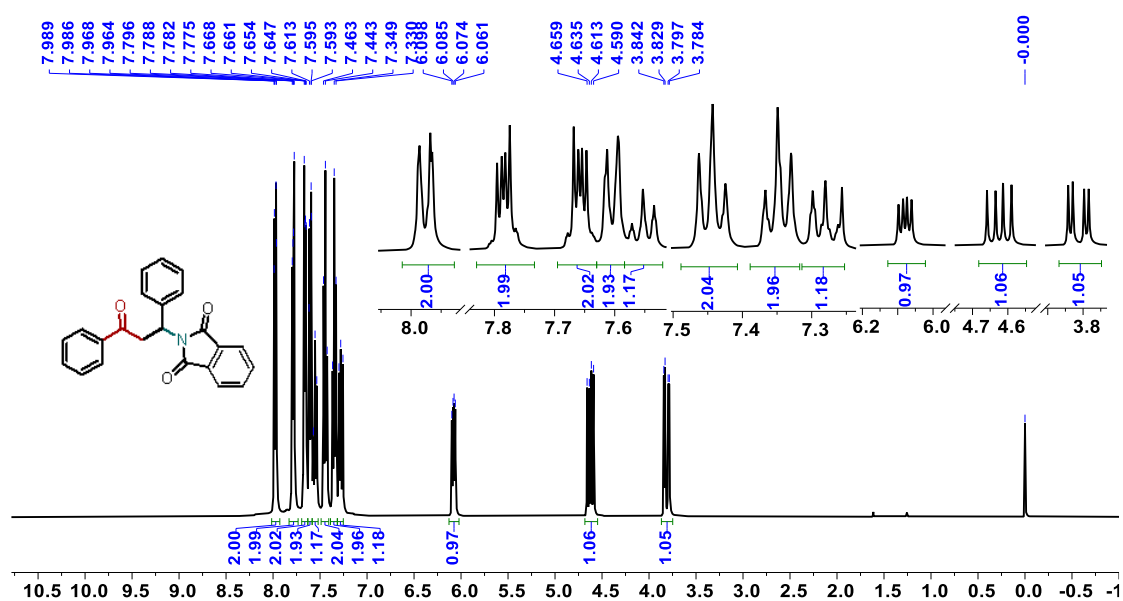
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3ab**



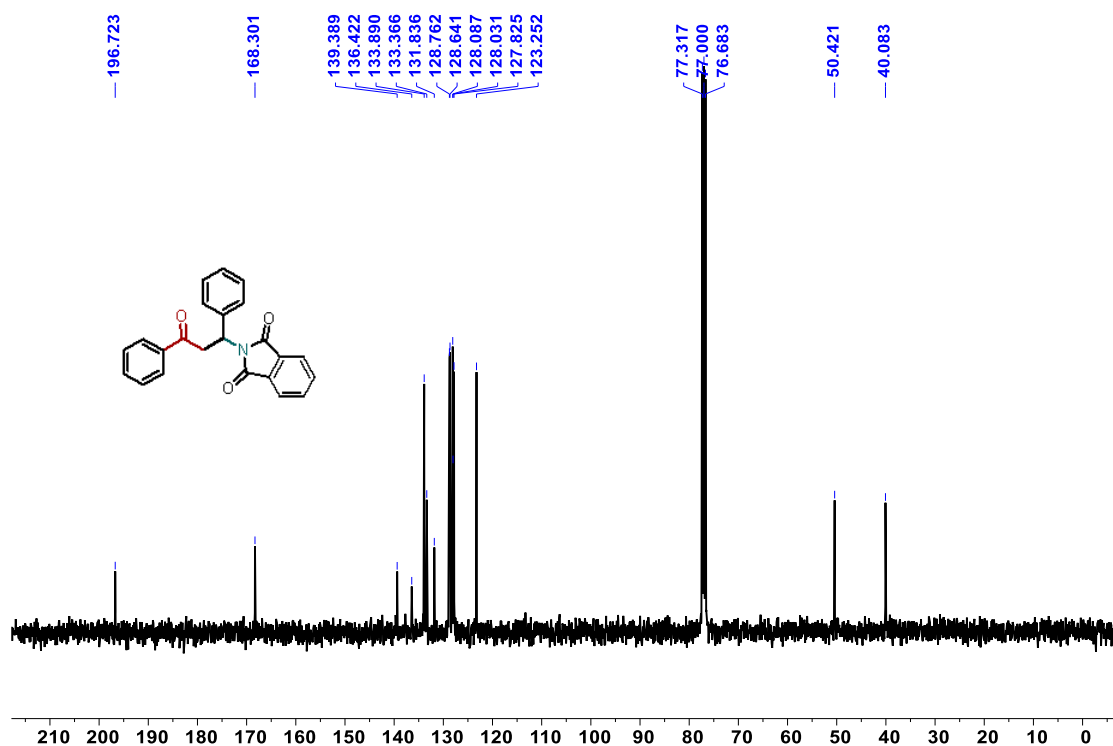
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of **3ab**



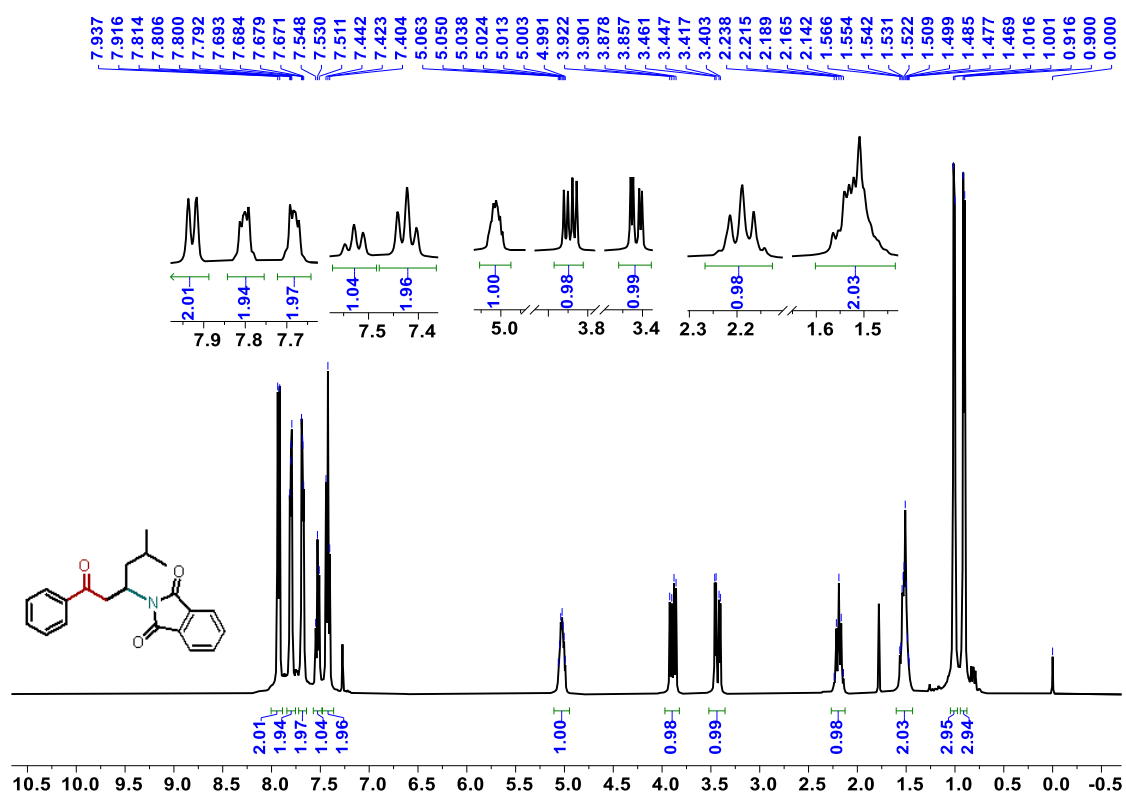
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3ac**



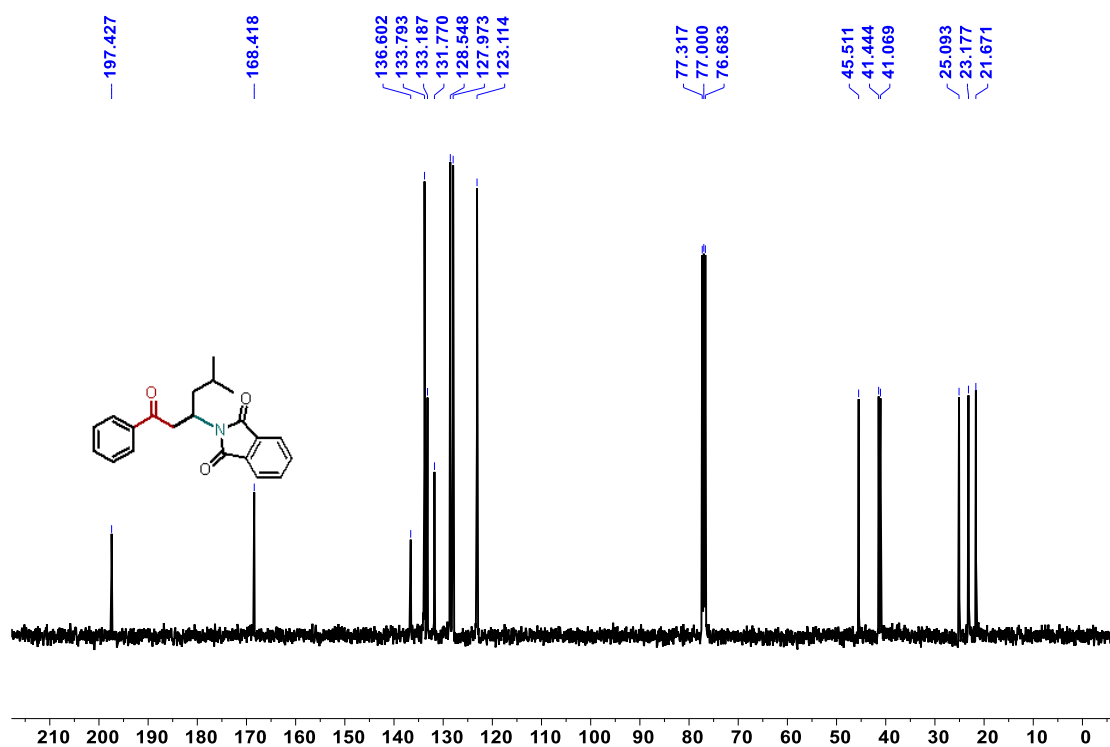
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of **3ac**



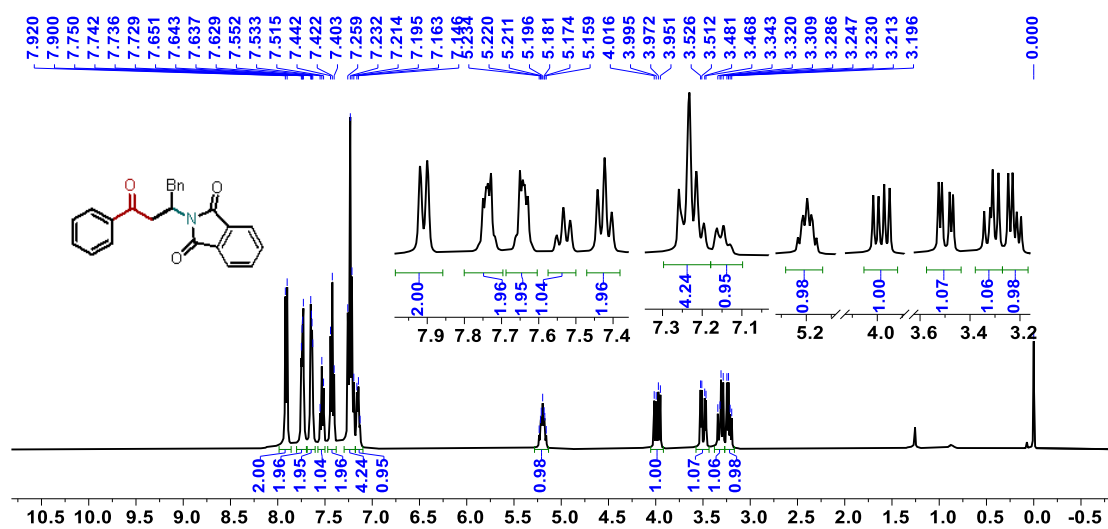
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3ad**



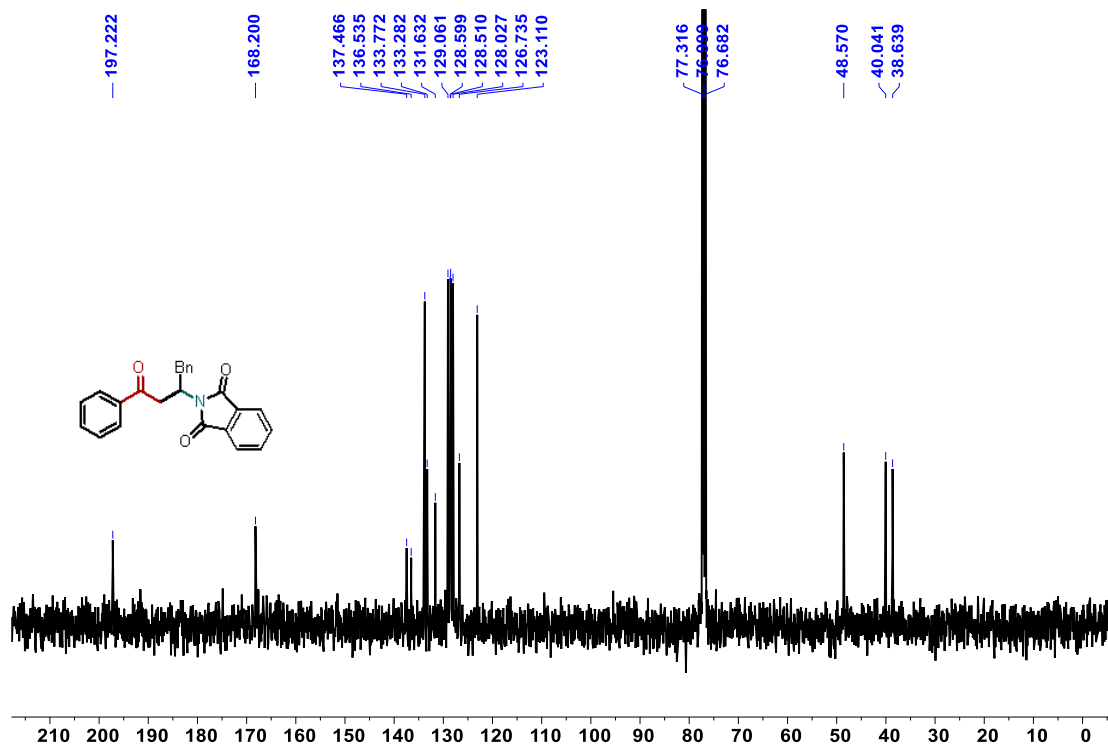
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3ad**



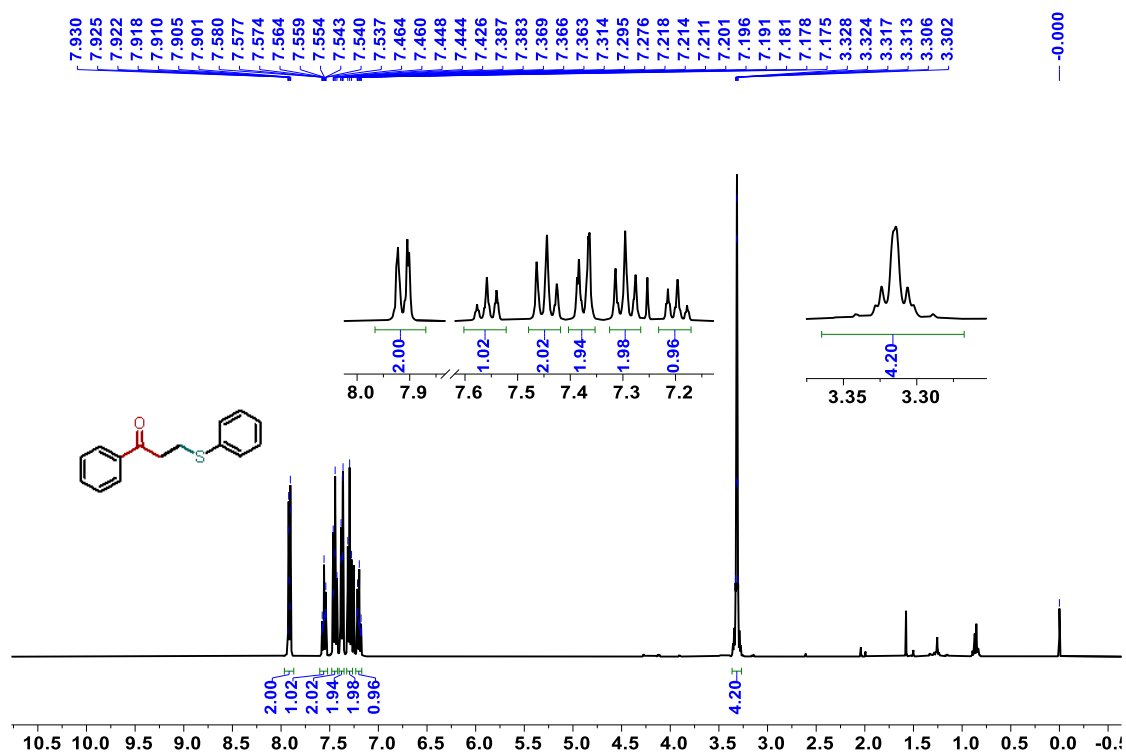
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3ae**



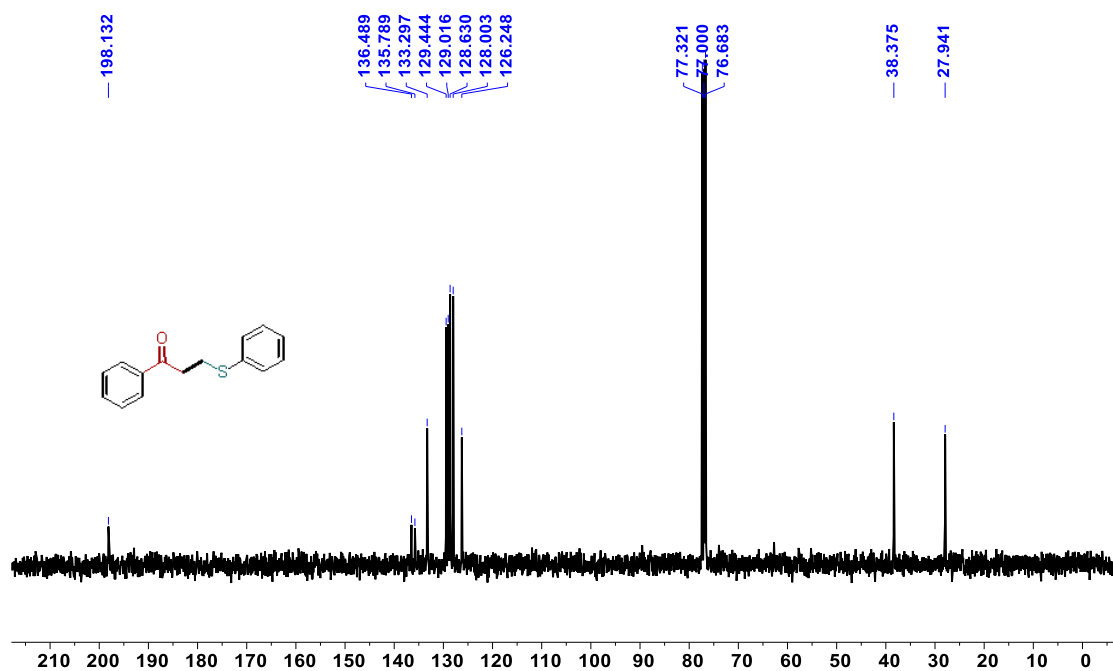
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3ae**



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3af**

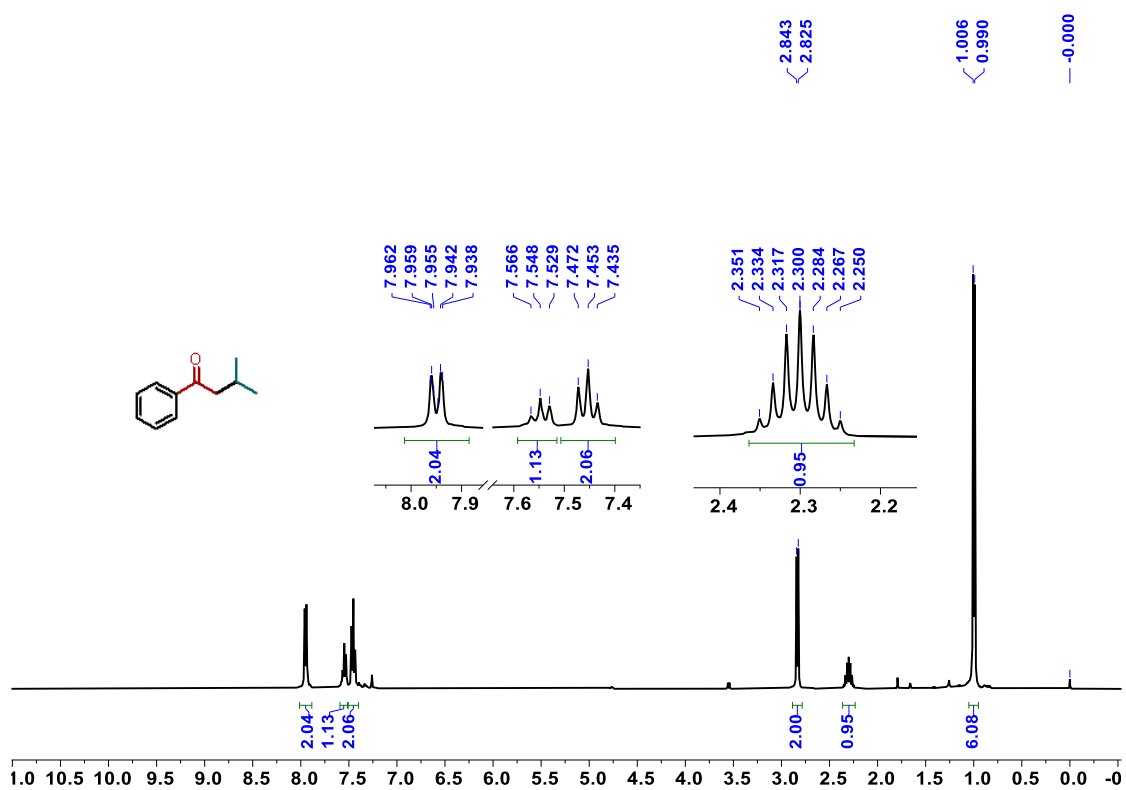


<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of **3af**

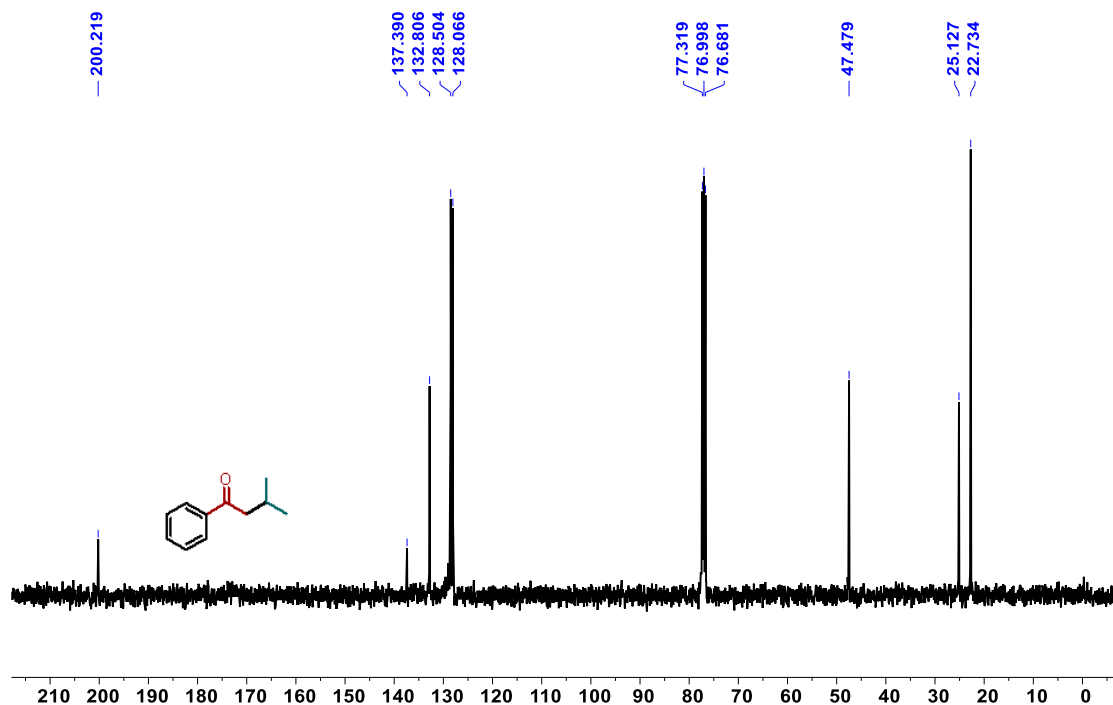




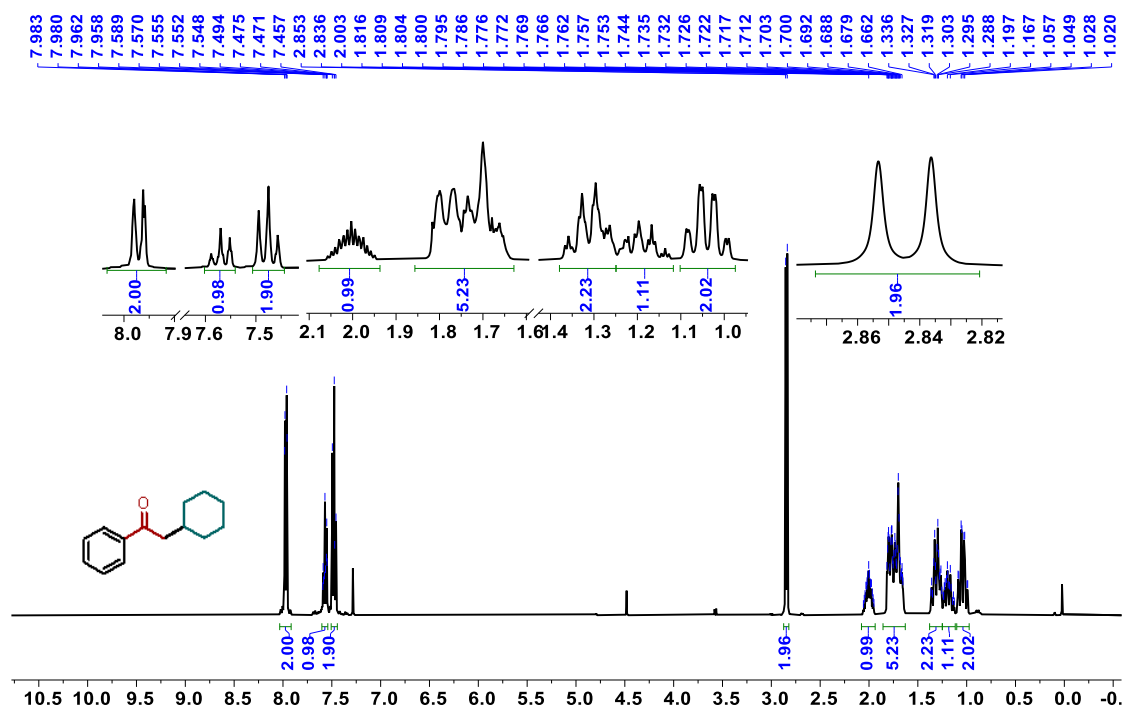
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3ag**



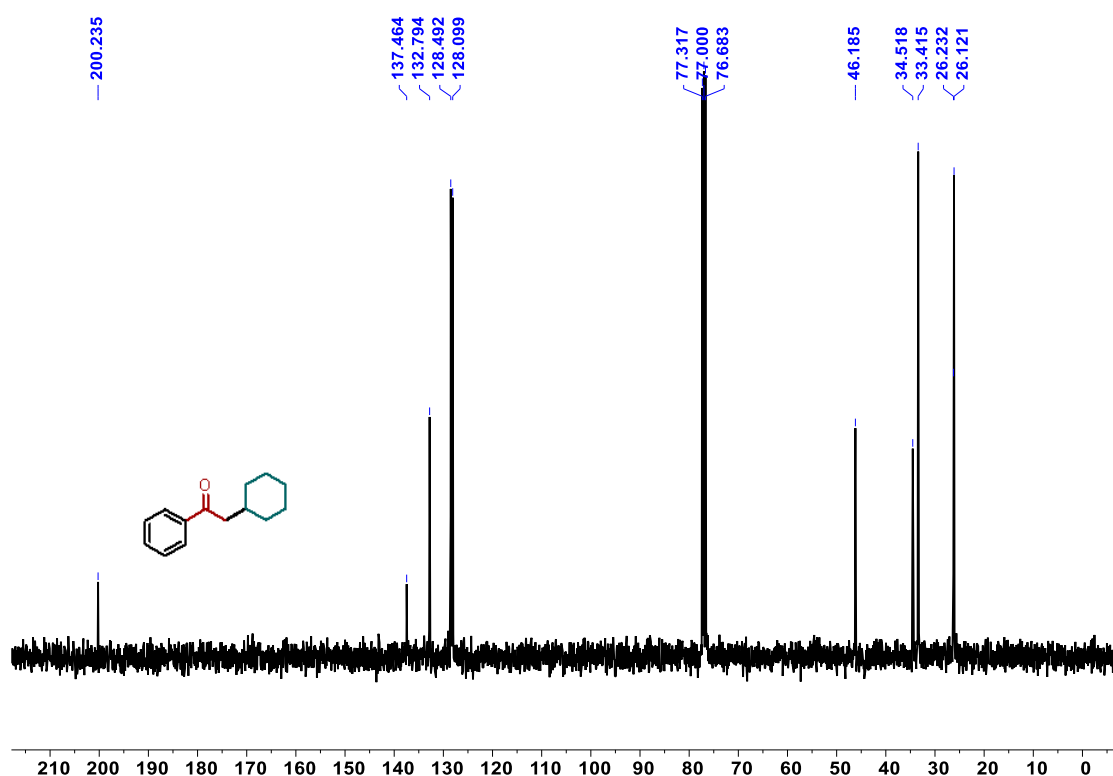
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3ag**



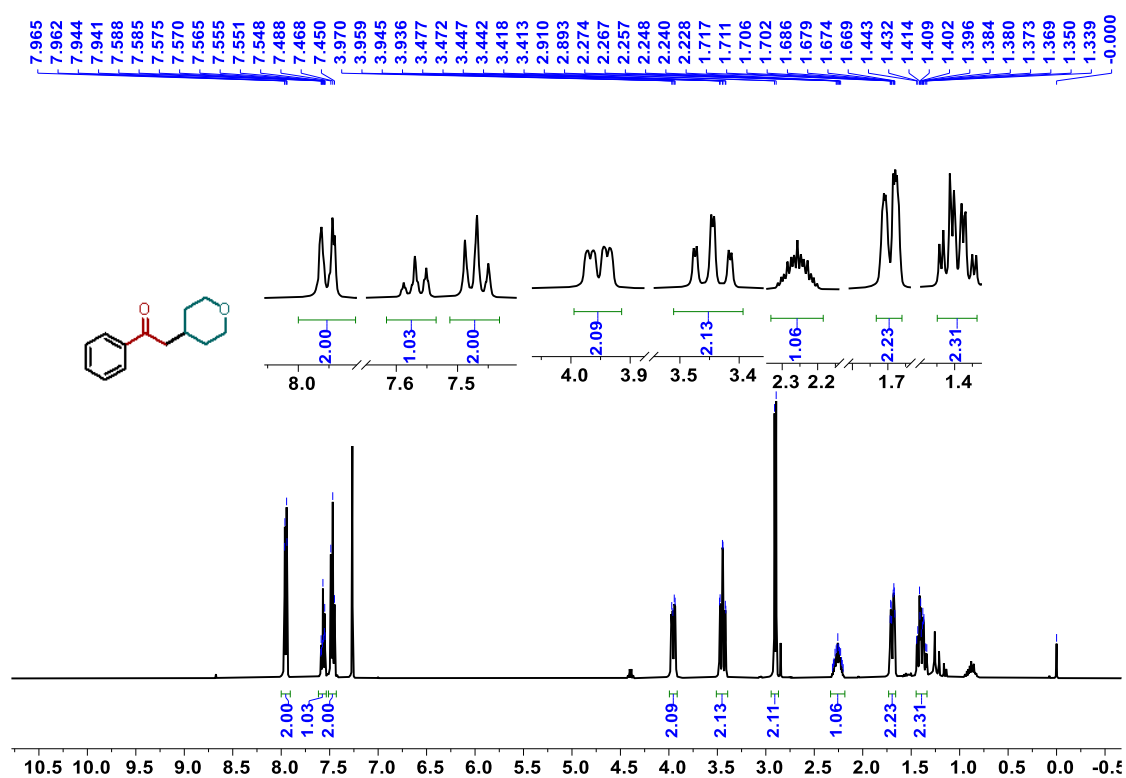
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3ah**



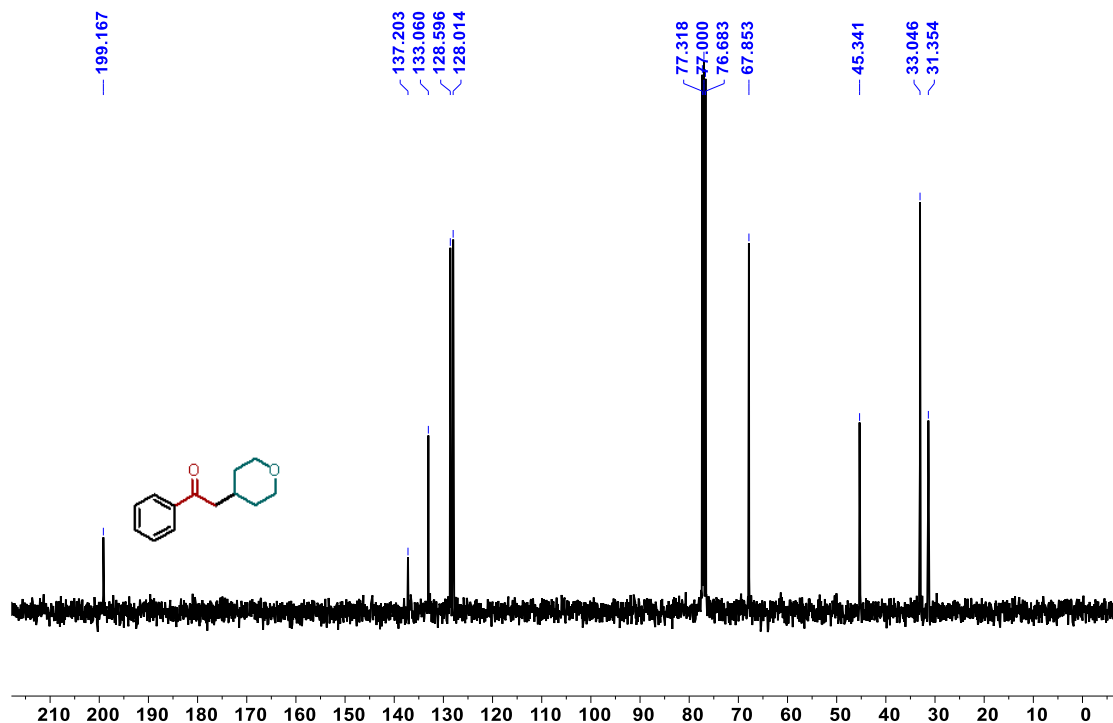
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of **3ah**



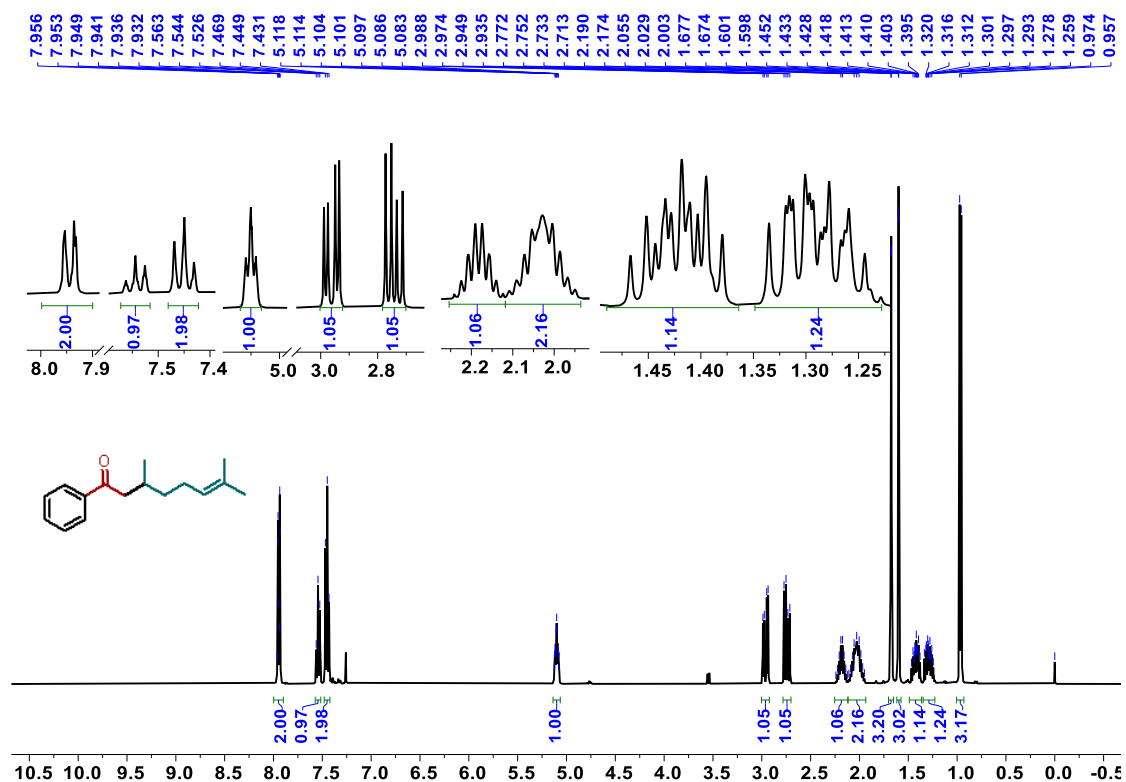
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3ai**



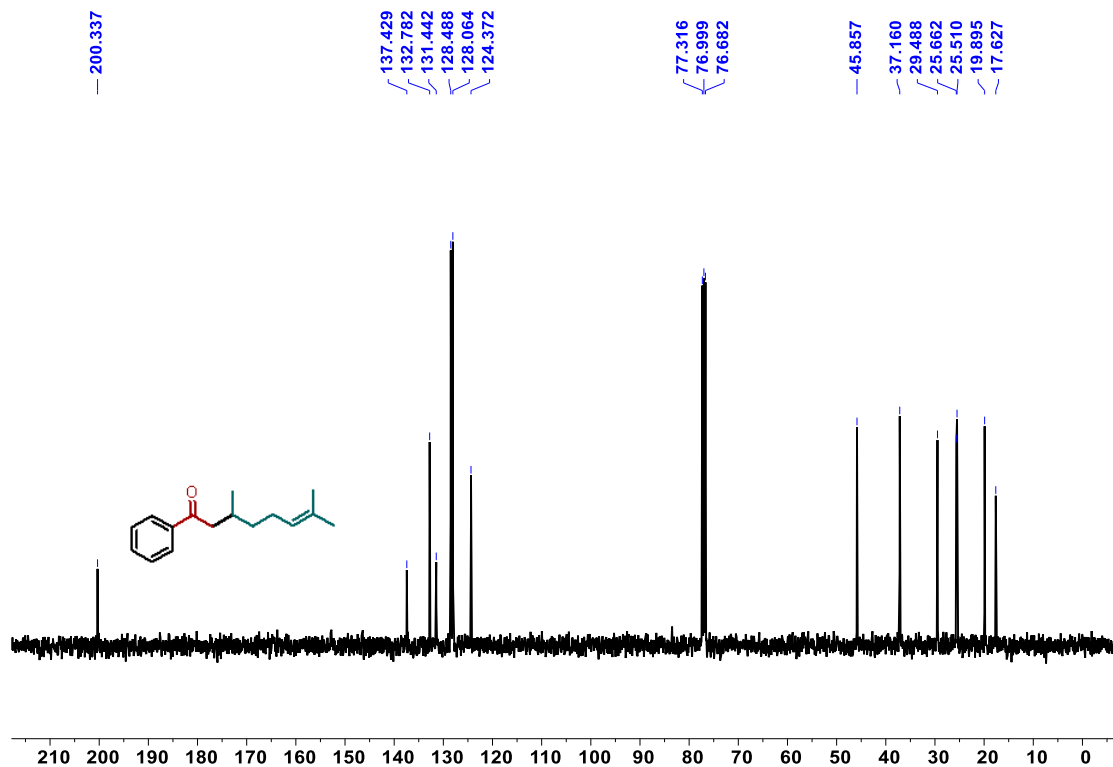
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3ai**



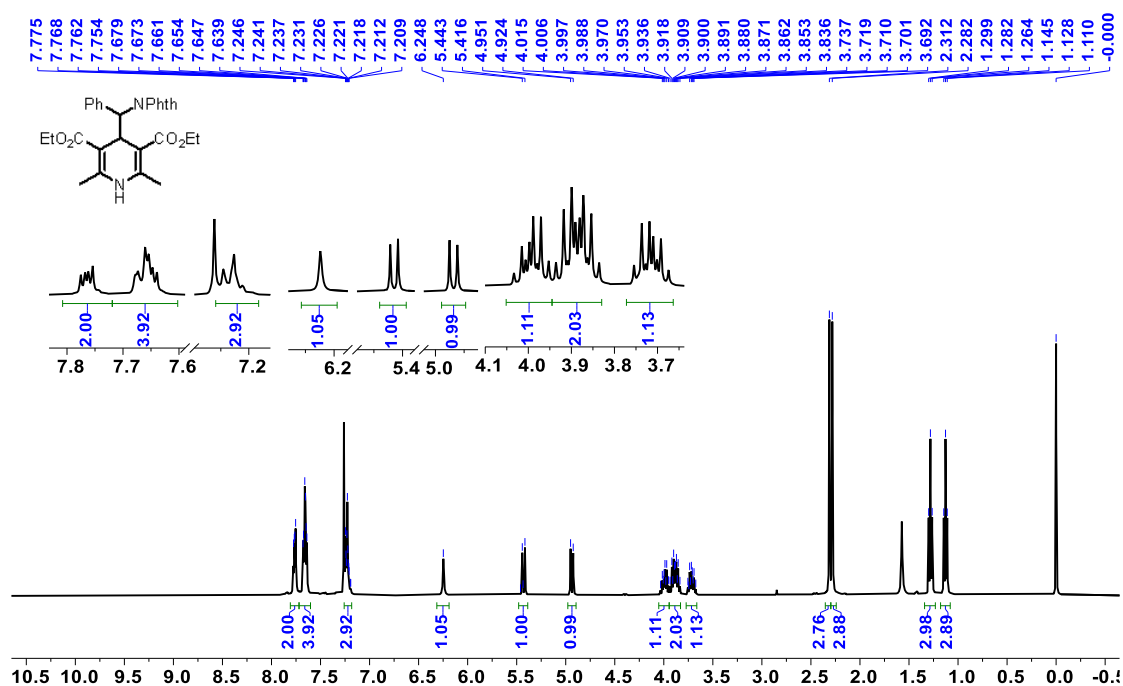
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **3aj**



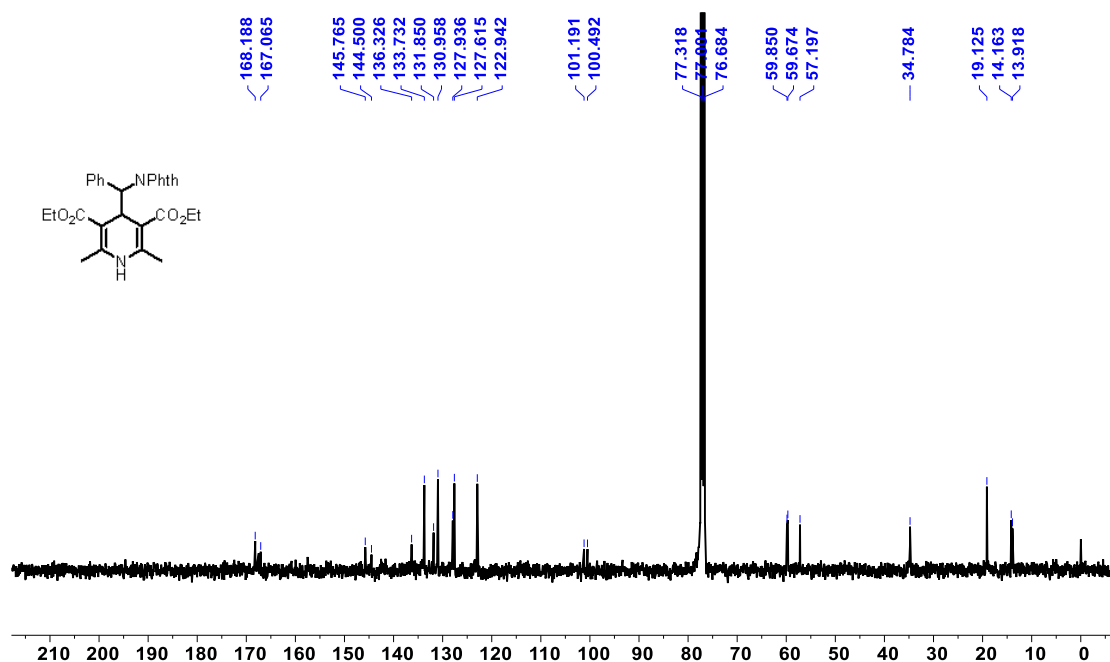
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of **3aj**



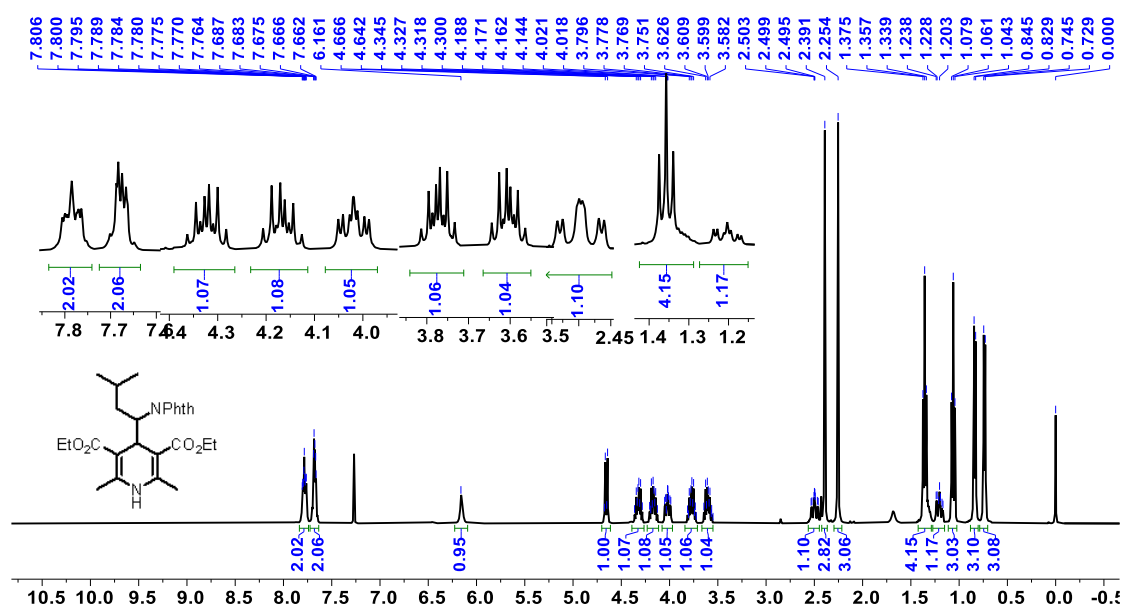
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **2ac**



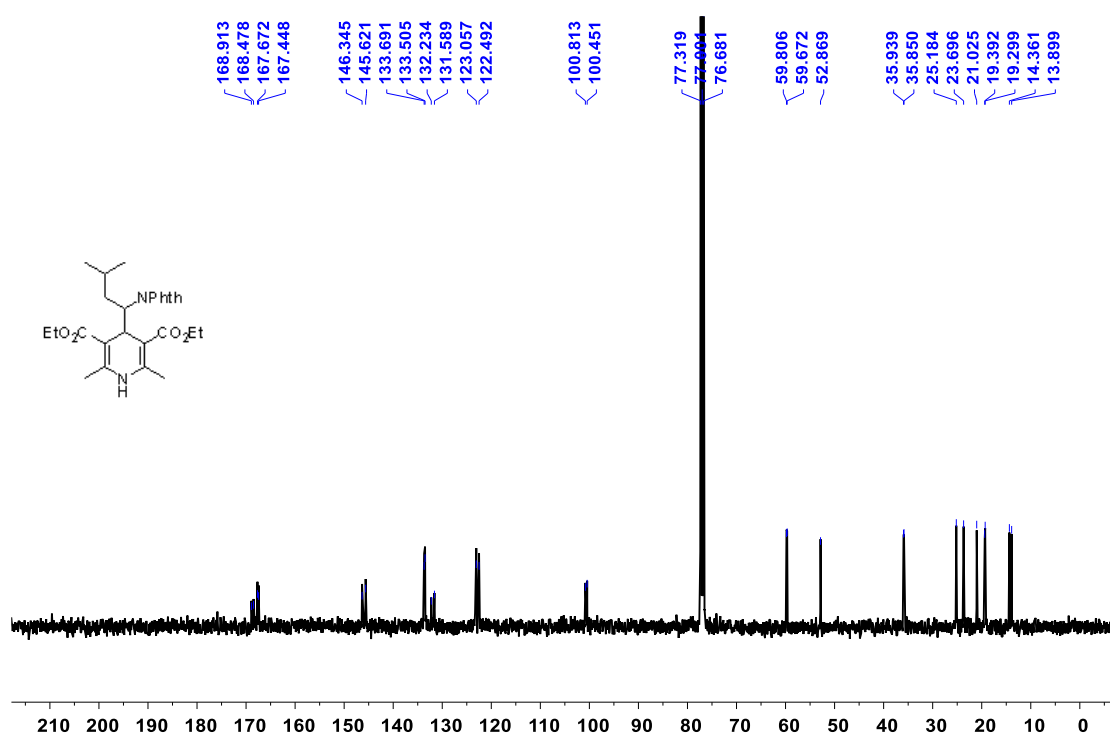
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of **2ac**



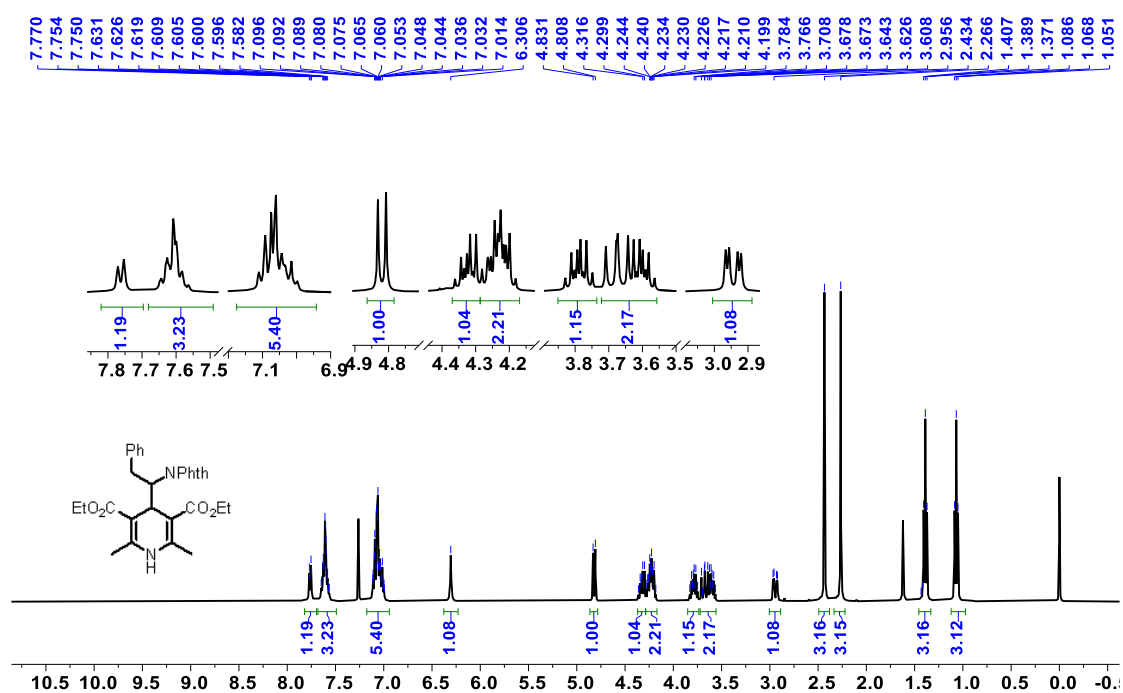
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **2ad**



<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of **2ad**



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **2ae**



<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of **2ae**

