

Supporting Information

Visible-Light-Promoted Syntheses of β -Keto Sulfones from Alkynes and Sulfonylhydrazides

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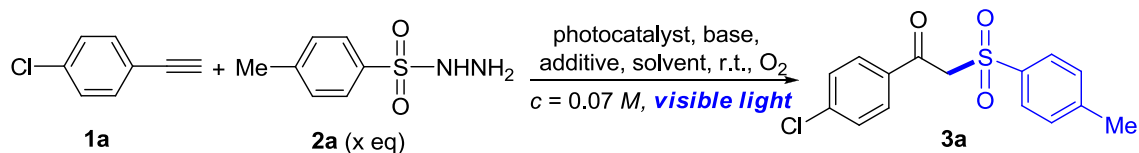
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Materials and methods

All the chemicals were purchased commercially, and used without further purification, unless otherwise noted. Thin-layer chromatography (TLC) was conducted with 0.25 mm Tsingdao silica gel plates (60F-254) and visualized by exposure to UV light (254 nm) or stained with potassium permanganate. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040–0.063 mm). Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. ^1H NMR spectra were recorded on Bruker spectrometers (at 300 or 400 MHz) and were reported relative to deuterated solvent signals. Data for ^1H NMR spectra were reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. ^{13}C NMR spectra were recorded on Bruker Spectrometers (at 75 or 100 MHz). Data for ^{13}C NMR spectra were reported in terms of chemical shift. Mass spectrometric data were obtained using Bruker Apex IV RTMS. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

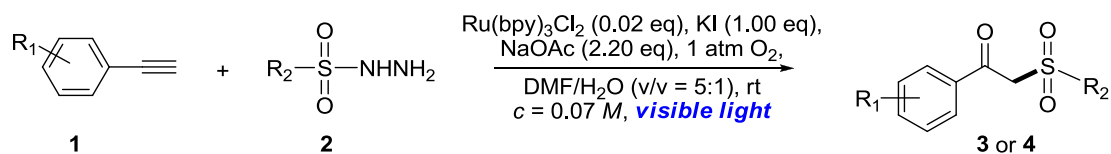
Identification of the optimal reaction conditions



entry	2a (eq)	[Ru] (mol%) ^a	base (eq)	solvent (v/v)	additive (eq)	yield (%) ^c
1	1.5	5	/	MeCN	/	NR
2	1.5	5	Na ₂ CO ₃ (1.5)	MeCN	/	trace
3	1.5	5	Na ₂ CO ₃ (1.5)	MeCN/H ₂ O (3:1)	/	trace
4	1.5	5	Na ₂ CO ₃ (1.5)	MeCN/H ₂ O (3:1)	NaBr (1.5)	decomp
5	1.5	5	Na ₂ CO ₃ (1.5)	MeCN/H ₂ O (3:1)	KI (1.5)	35
6	1.5	5	NaOAc (1.5)	MeCN/H ₂ O (3:1)	KI (1.5)	42
7	1.5	5	NaOAc (1.5)	DMF/H ₂ O (3:1)	KI (1.5)	47
8	1.5	5	Na ₂ HPO ₄ (1.5)	DMF/H ₂ O (3:1)	KI (1.5)	41
9	1.5	5	Na ₃ PO ₄ (1.5)	DMF/H ₂ O (3:1)	KI (1.5)	decomp
10	1.5	5	Cs ₂ CO ₃ (1.5)	DMF/H ₂ O (3:1)	KI (1.5)	decomp
11	1.5	5	pyridine (1.5)	DMF/H ₂ O (3:1)	KI (1.5)	18
12	1.5	5	NEt ₃ (1.5)	DMF/H ₂ O (3:1)	KI (1.5)	NR
13	1.5	5	DBU (1.5)	DMF/H ₂ O (3:1)	KI (1.5)	decomp
14	1.5	5	NaOAc (1.5)	DMF/H ₂ O (3:1)	KI (1.0)	56
15	1.5	5	NaOAc (1.5)	DMF/H ₂ O (3:1)	KI (0.5)	52
16	2.2	5	NaOAc (1.5)	DMF/H ₂ O (3:1)	KI (1.0)	63
17	2.2	5	NaOAc (2.2)	DMF/H ₂ O (3:1)	KI (1.0)	72
18	2.2	5	NaOAc (2.2)	DMF/H ₂ O (5:1)	KI (1.0)	82
19	2.2	5	NaOAc (2.2)	DMF/H ₂ O (8:1)	KI (1.0)	68
20	2.2	2	NaOAc (2.2)	DMF/H ₂ O (5:1)	KI (1.0)	84
21	2.2	2	NaOAc (2.2)	DMSO/H ₂ O (5:1)	KI (1.0)	trace
22	2.2	2	NaOAc (2.2)	DMA/H ₂ O (5:1)	KI (1.0)	58
23	2.2	2	NaOAc (2.2)	MeOH/H ₂ O (5:1)	KI (1.0)	35
24	2.2	2	NaOAc (2.2)	EtOH/H ₂ O (5:1)	KI (1.0)	48
25	2.2	2	NaOAc (2.2)	THF/H ₂ O (5:1)	KI (1.0)	54
26 ^b	2.2	Eosin	NaOAc (2.2)	DMF/H ₂ O (5:1)	KI (1.0)	78

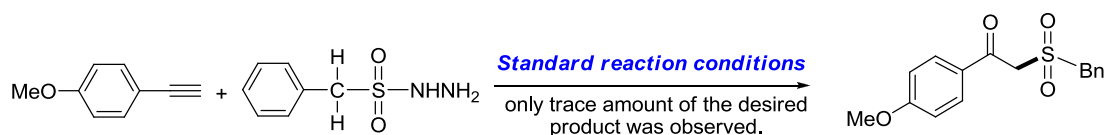
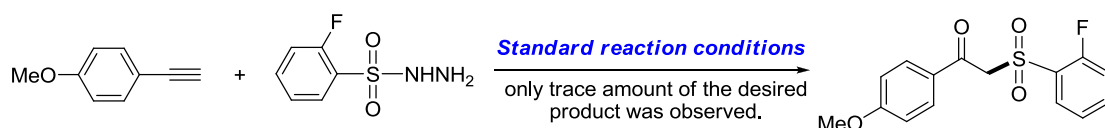
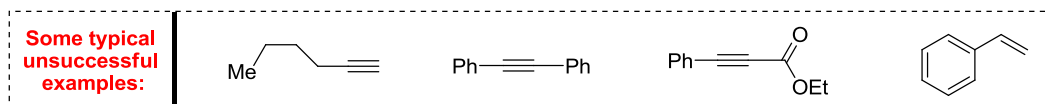
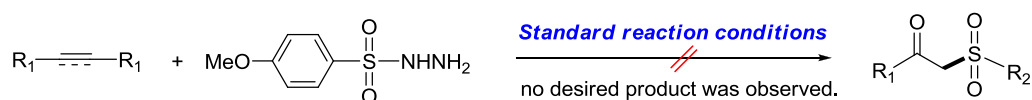
^a[Ru] = Ru(bpy)₃Cl₂•6H₂O. ^b2 mol% of Eosin Y was used. ^cYield of isolated product.

General procedure for β -keto sulfones synthesis



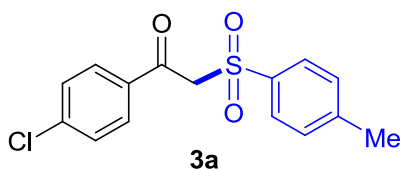
A flame-dried round bottom flask (5 mL) was equipped with magnetic stir bar and charged with alkynes **1** (0.073 mmol, 1.0 equiv), sulfonylhydrazides **2** (0.161 mmol, 2.2 equiv), $\text{Ru(bpy)}_3\text{Cl}_2$ (0.0014 mmol, 0.02 equiv), NaOAc (0.161 mmol, 2.2 equiv), KI (0.073 mmol, 1.0 equiv) and DMF/ H_2O (v/v = 5:1, 1.0 mL). The mixture was then irradiated by household bulbs (45 W) under a balloon oxygen atmosphere at room temperature until the starting material disappeared from the TLC. After that the reaction mixture was treated with water and extracted with EtOAc, and the combined organic layer was washed with brine and dried over Na_2SO_4 . Then the organic layer was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography using hexane/EtOAc (4/1) to afford the desired pure product **3** or **4** in 31-93% yield.

Examinations of other alkynes and sulfonylhydrazides under standard reaction conditions



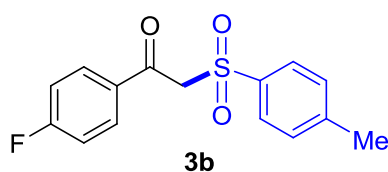
Other alkynes and sulfonylhydrazides had also been examined. However, we did not obtain the desired products under standard reaction conditions.

¹H NMR and ¹³C NMR spectra data of compounds 3a-3o, 4a-4o

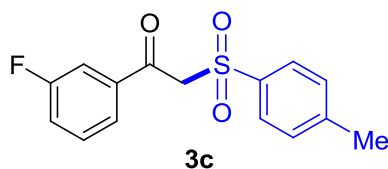


1-(4-chlorophenyl)-2-tosylethanone (3a): ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 8.4 Hz,

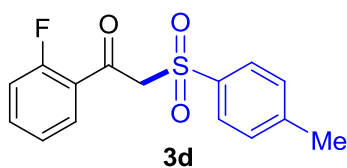
2H), 4.69 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 187.1, 145.6, 141.0, 135.6, 134.1, 130.8, 129.9, 129.2, 128.5, 63.6, 21.7; HRMS calculated for $\text{C}_{15}\text{H}_{13}\text{ClNaO}_3\text{S}$ ($\text{M} + \text{Na}^+$): 331.0172, found: 331.0163. (White solid, 19.0 mg, 84% isolated yield).



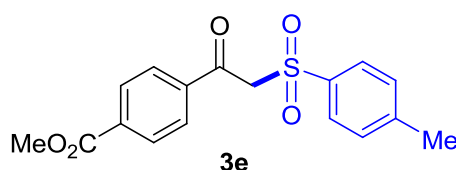
1-(4-fluorophenyl)-2-tosylethanone (3b): ^1H NMR (400 MHz, CDCl_3) δ 8.01-7.98 (m, 2H), 7.75 (d, $J = 8.4$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.17-7.12 (m, 2H), 4.69 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 186.5, 167.7, 165.2, 145.5, 135.6, 132.3, 132.2, 129.9, 128.5, 123.8, 116.2, 115.9, 63.7, 21.7; HRMS calculated for $\text{C}_{15}\text{H}_{13}\text{FNaO}_3\text{S}$ ($\text{M} + \text{Na}^+$): 315.0467, found: 315.0453. (White solid, 17.1 mg, 80% isolated yield).



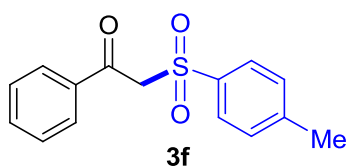
1-(3-fluorophenyl)-2-tosylethanone (3c): ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 6.8$ Hz, 3H), 7.62-7.59 (m, 1H), 7.50-7.45 (m, 1H), 7.35-7.30 (m, 3H), 4.69 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 187.1, 164.0, 161.6, 145.6, 137.8, 135.6, 130.6, 130.5, 129.9, 128.6, 125.4, 125.3, 121.6, 121.3, 115.9, 115.7, 63.7, 21.7; HRMS calculated for $\text{C}_{15}\text{H}_{13}\text{FNaO}_3\text{S}$ ($\text{M} + \text{Na}^+$): 315.0467, found: 315.0457. (White solid, 12.6 mg, 59% isolated yield).



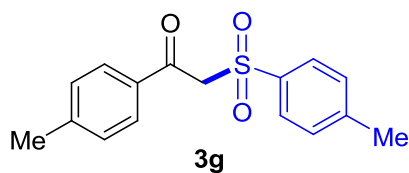
1-(2-fluorophenyl)-2-tosylethanone (3d): ^1H NMR (300 MHz, CDCl_3) δ 7.83-7.76 (m, 3H), 7.58-7.53 (m, 1H), 7.33 (d, J = 8.1 Hz, 2H), 7.26-7.14 (m, 1H), 7.11-7.07 (m, 1H), 7.78 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 186.2, 186.1, 163.6, 160.2, 145.3, 136.2, 136.1, 136.0, 131.2, 131.1, 129.8, 128.6, 124.9, 124.8, 124.6, 117.0, 116.7, 67.2, 67.1, 21.7; HRMS calculated for $\text{C}_{15}\text{H}_{14}\text{FO}_3\text{S}$ ($\text{M} + \text{H}^+$): 293.0648, found: 293.0653. (Pale yellow oil, 15.6 mg, 73% isolated yield).



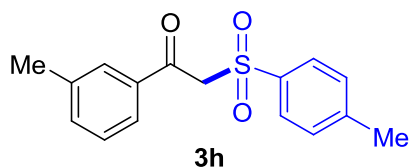
methyl 4-(2-tosylacetyl)benzoate (3e): ^1H NMR (400 MHz, CDCl_3) δ 8.13 (d, J = 6.8 Hz, 2H), 8.01 (d, J = 6.8 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 4.74 (s, 2H), 3.95 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 187.9, 165.9, 145.6, 138.8, 134.8, 130.0, 129.9, 129.2, 128.6, 64.8, 52.6, 21.7; HRMS calculated for $\text{C}_{17}\text{H}_{16}\text{NaO}_5\text{S}$ ($\text{M} + \text{Na}^+$): 355.0616, found: 355.0610. (Pale yellow solid, 17.5 mg, 72% isolated yield).



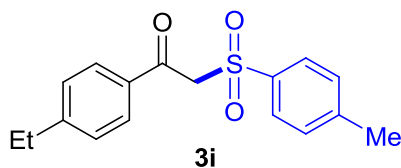
1-phenyl-2-tosylethanone (3f): ^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 6.8 Hz, 2H), 7.63-7.59 (m, 1H), 7.49-7.45 (m, 2H), 7.33 (d, J = 8.0 Hz, 2H), 4.72 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 188.2, 145.4, 135.8, 134.3, 129.8, 129.3, 128.8, 128.6, 63.5, 21.7; HRMS calculated for $\text{C}_{15}\text{H}_{14}\text{NaO}_3\text{S}$ ($\text{M} + \text{Na}^+$): 297.0561, found: 297.0551. (White solid, 18.2 mg, 91% isolated yield).



1-p-tolyl-2-tosylethanone (3g): ^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.40 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 4.69 (s, 2H), 2.43 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 187.7, 145.6, 145.3, 135.8, 133.4, 129.8, 129.6, 129.5, 128.6, 63.5, 21.8, 21.7; HRMS calculated for $\text{C}_{16}\text{H}_{17}\text{O}_3\text{S}$ ($\text{M} + \text{H}^+$): 289.0898, found: 289.0895. (White solid, 17.7 mg, 84% isolated yield).

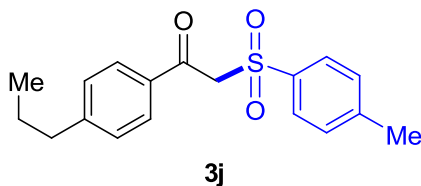


1-m-tolyl-2-tosylethanone (3h): ^1H NMR (400 MHz, CDCl_3) δ 7.77-7.71 (m, 4H), 7.41 (m, 1H), 7.36-7.32 (m, 1H), 7.26 (s, 2H), 4.70 (s, 2H), 2.44 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 188.3, 145.3, 138.7, 135.8, 135.1, 129.8, 129.7, 128.7, 128.6, 126.6, 63.6, 21.7, 21.3; HRMS calculated for $\text{C}_{16}\text{H}_{17}\text{O}_3\text{S}$ ($\text{M} + \text{H}^+$): 289.0898, found: 289.0894. (Pale yellow solid, 18.7 mg, 89% isolated yield).

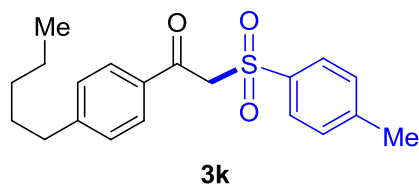


1-(4-ethylphenyl)-2-tosylethanone (3i): ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.33-7.26 (m, 4H), 4.69 (s, 2H), 2.73-2.68 (q, J = 7.6 Hz, 2H), 2.43 (s, 3H), 1.27-1.23 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 187.6, 151.6, 145.3, 135.8, 133.6, 129.8, 129.6, 128.6, 128.4, 63.5, 29.0, 21.7, 15.0; HRMS calculated for $\text{C}_{17}\text{H}_{19}\text{O}_3\text{S}$ ($\text{M} + \text{H}^+$): 303.1055, found: 303.1059.

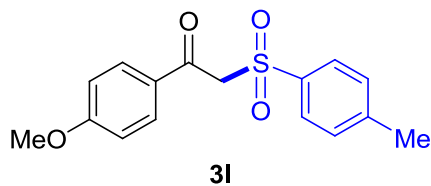
(White solid, 20.3 mg, 92% isolated yield).



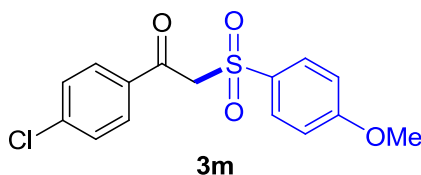
1-(4-propylphenyl)-2-tosylethanone (3j): ^1H NMR (300 MHz, CDCl_3) δ 7.87 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 4.69 (s, 2H), 2.67-2.62 (t, J = 7.2 Hz, 2H), 2.43 (s, 3H), 1.69-1.62 (m, 2H), 0.97-0.92 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 187.7, 150.2, 145.3, 135.8, 133.6, 129.8, 129.5, 129.0, 128.6, 63.5, 33.1, 24.1, 21.7, 13.8; HRMS calculated for $\text{C}_{18}\text{H}_{20}\text{NaO}_3\text{S}$ ($\text{M} + \text{Na}^+$): 339.1031, found: 339.1025. (Pale yellow solid, 21.2 mg, 92% isolated yield).



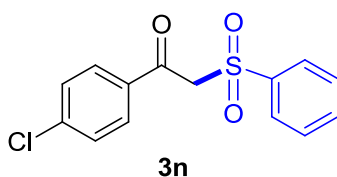
1-(4-pentylphenyl)-2-tosylethanone (3k): ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 4.69 (s, 2H), 2.68-2.64 (t, J = 7.6 Hz, 2H), 2.44 (s, 3H), 1.67-1.59 (m, 2H), 1.34-1.31 (m, 4H), 0.91-0.88 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 187.7, 150.5, 145.3, 135.8, 133.5, 129.8, 129.5, 128.9, 128.6, 63.5, 36.0, 31.4, 30.6, 22.5, 21.7, 14.0; HRMS calculated for $\text{C}_{20}\text{H}_{25}\text{O}_3\text{S}$ ($\text{M} + \text{H}^+$): 345.1524, found: 345.1506. (White solid, 23.4 mg, 93% isolated yield).



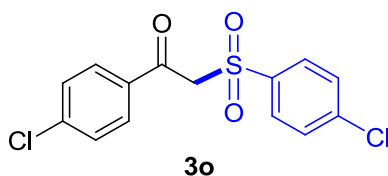
1-(4-methoxyphenyl)-2-tosylethanone (3l): ^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, J = 10.0 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.33-7.26 (m, 2H), 6.96 (d, J = 9.6 Hz, 2H), 4.66 (s, 2H), 3.88 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 186.4, 164.6, 145.3, 135.8, 131.9, 129.8, 128.9, 128.6, 114.1, 63.6, 55.6, 21.7; HRMS calculated for $\text{C}_{16}\text{H}_{17}\text{O}_4\text{S}$ ($\text{M} + \text{H}^+$): 305.0848, found: 305.0834. (White solid, 20.2 mg, 91% isolated yield).



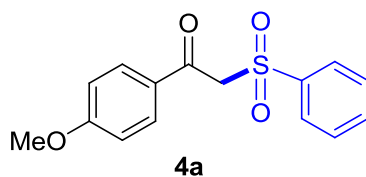
1-(4-chlorophenyl)-2-(4-methoxyphenylsulfonyl)ethanone (3m): ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, J = 9.2 Hz, 2H), 7.79 (d, J = 7.2 Hz, 2H), 7.48 (d, J = 9.2 Hz, 2H), 7.00 (d, J = 6.8 Hz, 2H), 4.68 (s, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 187.2, 164.3, 141.1, 134.1, 130.3, 130.0, 129.2, 124.4, 63.9, 55.7, 29.7; HRMS calculated for $\text{C}_{15}\text{H}_{13}\text{ClNaO}_4\text{S}$ ($\text{M} + \text{Na}^+$): 347.0121, found: 347.0124. (White solid, 21.3 mg, 90% isolated yield).



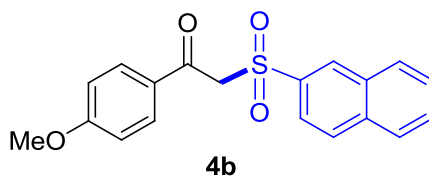
1-(4-chlorophenyl)-2-(phenylsulfonyl)ethanone (3n): ^1H NMR (400 MHz, CDCl_3) δ 7.90-7.87 (m, 4H), 7.70-7.66 (m, 1H), 7.58-7.54 (m, 2H), 7.47 (d, J = 6.8 Hz, 2H), 4.71 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 186.9, 141.2, 138.5, 134.4, 134.0, 130.8, 129.3, 129.2, 128.5, 63.6; These data are consistent with literature values, see: A. K. Singh, R. Chawla, T. Keshari, V. K. Yadav, L. D. S. Yadav, *Org. Biomol. Chem.* **2014**, 12, 8550. (Pale yellow solid, 17.4 mg, 81% isolated yield).



1-(4-chlorophenyl)-2-(4-chlorophenylsulfonyl)ethanone (3o): ^1H NMR (400 MHz, CDCl_3) δ 7.91 (d, J = 6.8 Hz, 1H), 7.83 (d, J = 6.8 Hz, 1H), 7.54 (d, J = 6.8 Hz, 1H), 7.49 (d, J = 6.8 Hz, 1H), 4.71 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 186.8, 141.4, 141.3, 136.8, 133.9, 130.7, 130.1, 129.6, 129.3, 63.4; HRMS calculated for $\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{NaO}_3\text{S}$ ($\text{M} + \text{Na}^+$): 350.9625, found: 350.9620. (White solid, 18.3 mg, 76% isolated yield).

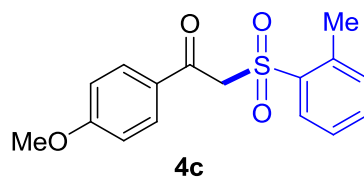


1-(4-methoxyphenyl)-2-(phenylsulfonyl)ethanone (4a): ^1H NMR (400 MHz, CDCl_3) δ 7.93-7.87 (m, 4H), 7.66-7.62 (m, 1H), 7.55-7.51 (m, 2H), 6.94-6.91 (dd, J = 7.2, 2.0 Hz, 2H), 4.69 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 186.2, 164.6, 138.8, 134.2, 131.9, 129.2, 128.8, 128.5, 114.1, 63.4, 55.6; HRMS calculated for $\text{C}_{15}\text{H}_{15}\text{O}_4\text{S}$ ($\text{M} + \text{H}^+$): 291.0691, found: 291.0684. (White solid, 19.7 mg, 93% isolated yield).

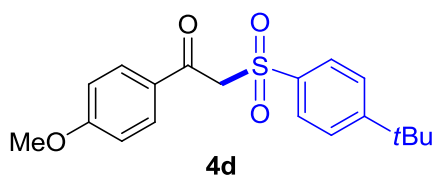


1-(4-methoxyphenyl)-2-(naphthalen-2-ylsulfonyl)ethanone (4b): ^1H NMR (400 MHz, CDCl_3) δ 8.44 (s, 1H), 7.99 (s, 1H), 7.97-7.94 (m, 4H), 7.93-7.91 (m, 2H), 7.87

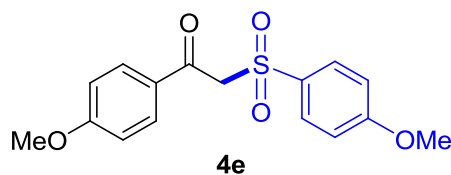
(d, $J = 8.4$ Hz, 1H), 7.69-7.65 (m, 1H), 7.63-7.59 (m, 1H), 6.92 (d, $J = 10.0$ Hz, 2H), 4.76 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 186.2, 164.6, 135.7, 135.5, 132.0, 131.9, 130.6, 129.6, 129.5, 129.4, 128.9, 128.0, 127.7, 123.0, 114.1, 63.5, 55.6; HRMS calculated for $\text{C}_{19}\text{H}_{16}\text{NaO}_4\text{S}$ ($\text{M} + \text{Na}^+$): 363.0667, found: 363.0654. (White solid, 22.6 mg, 91% isolated yield).



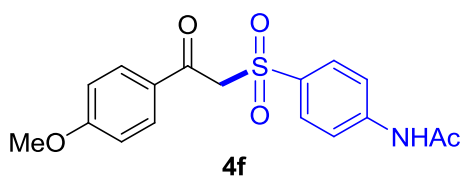
1-(4-methoxyphenyl)-2-(o-tolylsulfonyl)ethanone (4c): ^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 8.6$ Hz, 2H), 7.89 (d, $J = 7.6$ Hz, 1H), 7.53-7.49 (m, 1H), 7.35-7.30 (m, 2H), 6.96 (d, $J = 8.6$ Hz, 2H), 4.70 (s, 2H), 3.88 (s, 3H), 2.72 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 186.1, 164.6, 138.4, 137.0, 134.2, 132.8, 132.0, 130.5, 129.0, 126.6, 114.1, 62.9, 55.6, 20.6; HRMS calculated for $\text{C}_{16}\text{H}_{17}\text{O}_4\text{S}$ ($\text{M} + \text{H}^+$): 305.0848, found: 305.0856. (White solid, 20.0 mg, 90% isolated yield).



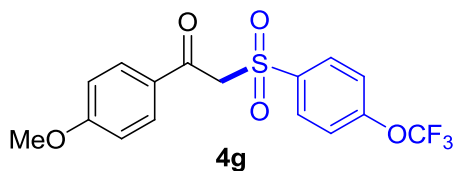
2-(4-tert-butylphenylsulfonyl)-1-(4-methoxyphenyl)ethanone (4d): ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 8.8$ Hz, 2H), 7.80 (d, $J = 8.4$ Hz, 2H), 7.54 (d, $J = 8.4$ Hz, 2H), 6.93 (d, $J = 8.8$ Hz, 2H), 4.67 (s, 2H), 3.87 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 186.2, 164.4, 158.0, 135.8, 131.8, 128.9, 128.3, 126.1, 113.9, 63.4, 55.5, 35.2, 30.9; HRMS calculated for $\text{C}_{19}\text{H}_{22}\text{NaO}_4\text{S}$ ($\text{M} + \text{Na}^+$): 369.1136, found: 369.1070. (White solid, 23.2 mg, 92% isolated yield).



1-(4-methoxyphenyl)-2-(4-methoxyphenylsulfonyl)ethanone (4e): ^1H NMR (400 MHz, CD_3COCD_3) δ 7.93 (d, J = 10.0 Hz, 2H), 7.79 (d, J = 9.6 Hz, 2H), 6.98 (d, J = 10.0 Hz, 2H), 6.94 (d, J = 10.8 Hz, 2H), 4.65 (s, 2H), 3.86 (s, 3H), 3.85 (s, 2H); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 186.5, 164.5, 164.1, 131.9, 130.8, 130.2, 128.9, 114.3, 114.1, 63.7, 55.7, 55.6; HRMS calculated for $\text{C}_{16}\text{H}_{16}\text{NaO}_5\text{S}$ ($\text{M} + \text{Na}^+$): 343.0616, found: 343.0606. (White solid, 19.4 mg, 83% isolated yield).

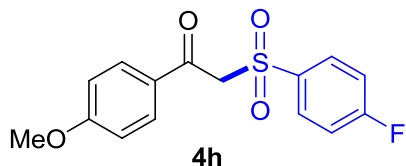


N-(4-(2-(4-methoxyphenyl)-2-oxoethylsulfonyl)phenyl)acetamide (4f): ^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, J = 6.8 Hz, 2H), 7.85-7.78 (m, 4H), 7.02 (d, J = 8.8 Hz, 2H), 4.91 (s, 2H), 3.89 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 205.4, 185.6, 163.8, 161.3, 141.4, 133.5, 131.7, 129.6, 129.3, 113.4, 113.8, 62.9, 55.2, 29.5, 29.3, 29.1, 29.0, 28.8, 28.6, 28.4, 23.5; HRMS calculated for $\text{C}_{17}\text{H}_{17}\text{NNaO}_5\text{S}$ ($\text{M} + \text{Na}^+$): 370.0725, found: 370.0705. (White solid, 22.3 mg, 88% isolated yield).

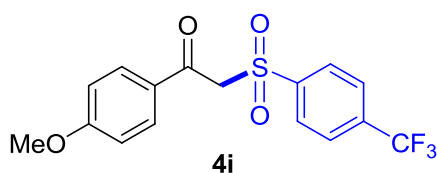


1-(4-methoxyphenyl)-2-(4-(trifluoromethoxy)phenylsulfonyl)ethanone (4g): ^1H NMR (400 MHz, CDCl_3) δ 7.95-7.90 (m, 4H), 7.36 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 4.70 (s, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 186.0, 164.7, 153.2, 136.8, 131.7, 130.9, 128.6, 120.6, 114.1, 63.2, 55.6; HRMS calculated for

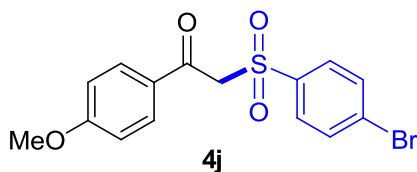
$C_{16}H_{13}F_3NaO_5S$ ($M + Na^+$): 397.0333, found: 397.0309. (White solid, 18.0 mg, 66% isolated yield).



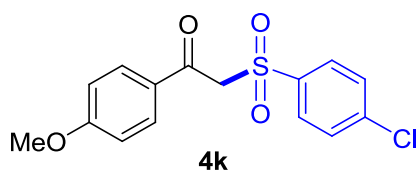
2-(4-fluorophenylsulfonyl)-1-(4-methoxyphenyl)ethanone (4h): 1H NMR (400 MHz, $CDCl_3$) δ 7.93-7.88 (m, 4H), 7.26-7.18 (m, 2H), 6.96 (d, $J = 10.8$ Hz, 2H), 4.69 (s, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.2, 167.4, 164.7, 134.7, 131.9, 131.7, 131.6, 128.7, 116.6, 116.4, 114.2, 63.4, 55.6; HRMS calculated for $C_{15}H_{13}FNaO_4S$ ($M + Na^+$): 331.0416, found: 331.0404. (White solid, 19.6 mg, 87% isolated yield).



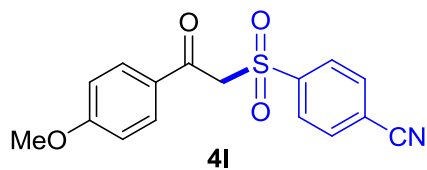
1-(4-methoxyphenyl)-2-(4-(trifluoromethyl)phenylsulfonyl)ethanone (4i): 1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, $J = 8.4$ Hz, 2H), 7.92 (d, $J = 6.8$ Hz, 2H), 7.82 (d, $J = 8.4$ Hz, 2H), 6.96 (d, $J = 6.8$ Hz, 2H), 4.73 (s, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9, 164.8, 131.8, 129.4, 128.8, 128.6, 127.0, 126.3, 126.2, 126.1, 114.2, 63.0, 55.7; HRMS calculated for $C_{16}H_{14}F_3O_4S$ ($M + H^+$): 359.0565, found: 359.0547. (White solid, 21.4 mg, 82% isolated yield).



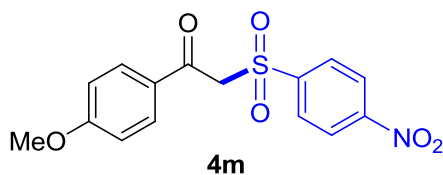
2-(4-bromophenylsulfonyl)-1-(4-methoxyphenyl)ethanone (4j): ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, J = 7.2 Hz, 2H), 7.75 (d, J = 8.8 Hz, 2H), 7.69 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 7.2 Hz, 2H), 4.68 (s, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 186.1, 164.7, 137.5, 132.5, 131.9, 130.2, 129.6, 128.7, 114.2, 63.3, 55.7; HRMS calculated for $\text{C}_{15}\text{H}_{13}\text{BrNaO}_4\text{S}$ ($\text{M} + \text{Na}^+$): 390.9616, found: 390.9611. (White solid, 21.0 mg, 78% isolated yield).



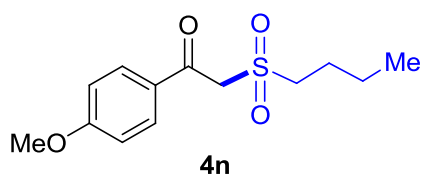
2-(4-chlorophenylsulfonyl)-1-(4-methoxyphenyl)ethanone (4k): ^1H NMR (300 MHz, CDCl_3) δ 7.94 (d, J = 6.9 Hz, 2H), 7.83 (d, J = 6.6 Hz, 2H), 7.53 (d, J = 6.6 Hz, 2H), 6.97 (d, J = 6.9 Hz, 2H), 4.69 (s, 2H), 3.89 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 186.1, 164.7, 141.1, 137.0, 131.9, 130.2, 129.5, 128.6, 114.2, 63.3, 55.7; HRMS calculated for $\text{C}_{15}\text{H}_{13}\text{ClNaO}_4\text{S}$ ($\text{M} + \text{Na}^+$): 347.0121, found: 347.0126. (White solid, 19.4 mg, 82% isolated yield).



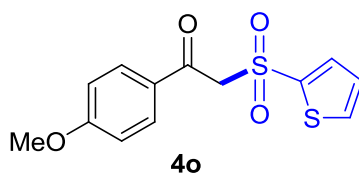
4-(2-(4-methoxyphenyl)-2-oxoethylsulfonyl)benzonitrile (4l): ^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, J = 8.4 Hz, 2H), 7.91 (d, J = 8.8 Hz, 2H), 7.85 (d, J = 8.4 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 4.73 (s, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 185.8, 164.9, 142.6, 132.9, 131.8, 129.5, 128.4, 127.0, 117.9, 117.1, 114.3, 62.9, 55.7; HRMS calculated for $\text{C}_{16}\text{H}_{13}\text{NNaO}_4\text{S}$ ($\text{M} + \text{Na}^+$): 338.0463, found: 338.0452. (Yellow solid, 16.3 mg, 71% isolated yield).



1-(4-methoxyphenyl)-2-(4-nitrophenylsulfonyl)ethanone (4m): ^1H NMR (400 MHz, CDCl_3) δ 8.39 (d, $J = 6.8$ Hz, 2H), 8.11 (d, $J = 6.8$ Hz, 2H), 7.92 (d, $J = 8.8$ Hz, 2H), 6.97 (d, $J = 8.8$ Hz, 2H), 4.76 (s, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 185.8, 164.9, 151.0, 144.1, 131.8, 130.3, 128.4, 124.3, 114.3, 62.9, 55.7; HRMS calculated for $\text{C}_{15}\text{H}_{13}\text{NNaO}_6\text{S}$ ($\text{M} + \text{Na}^+$): 358.0361, found: 358.0385. (White solid, 15.7 mg, 32% isolated yield).



2-(butylsulfonyl)-1-(4-methoxyphenyl)ethanone (4n): ^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 8.8$ Hz, 2H), 6.98 (d, $J = 8.8$, 2H), 4.51 (s, 2H), 3.88 (s, 3H), 3.25 (t, $J = 8.0$ Hz, 2H), 1.90-1.83 (m, 2H), 1.51-1.46 (m, 2H), 0.98-0.94 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 187.5, 164.8, 131.9, 128.8, 114.2, 59.4, 55.7, 53.4, 23.8, 21.6, 13.5; HRMS calculated for $\text{C}_{13}\text{H}_{19}\text{O}_4\text{S}$ ($\text{M} + \text{H}^+$): 271.1004, found: 271.0991. (Pale yellow oil, 17.0 mg, 86% isolated yield).

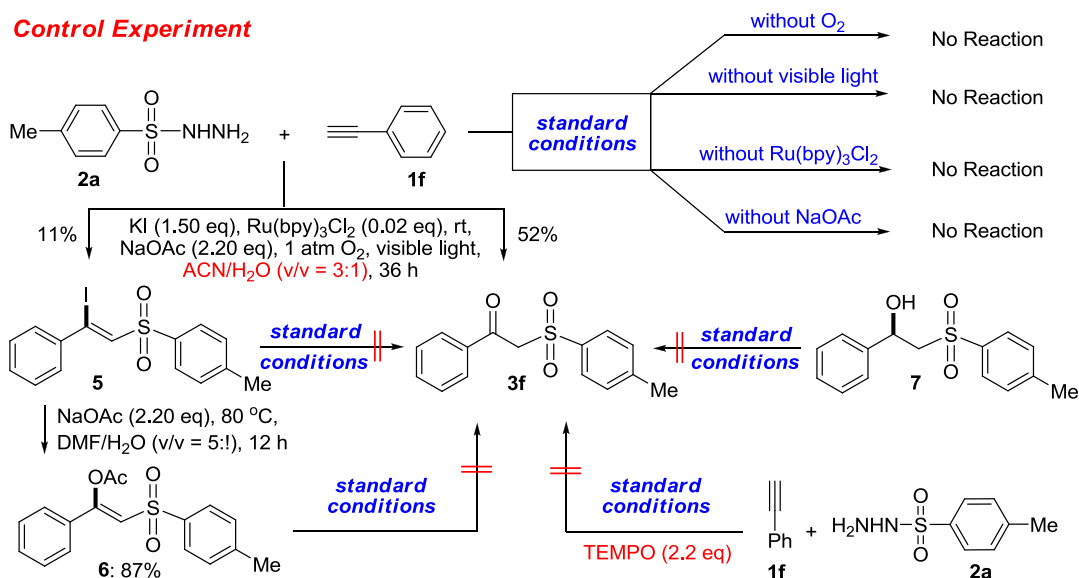


1-(4-methoxyphenyl)-2-(thiophen-2-ylsulfonyl)ethanone (4o): ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 7.2$ Hz, 2H), 7.74-7.21 (m, 1H), 7.68-7.67 (m, 1H), 7.14-7.11 (m, 1H), 6.96 (d, $J = 6.8$ Hz, 2H), 4.77 (s, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz,

CDCl₃) δ 186.0, 164.6, 139.4, 135.4, 134.9, 131.8, 128.7, 127.9, 114.1, 64.3, 55.6; HRMS calculated for C₁₃H₁₂NaO₄S₂ (M + Na⁺): 319.0075, found: 319.0046. (Pale yellow oil, 14.5 mg, 67% isolated yield).

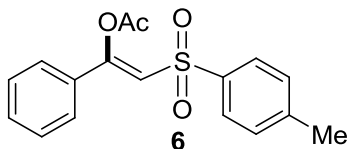
It should be noted that some of compound **3** and **4** have been prepared by other research groups, see: (a) A. K. Singh, R. Chawla, T. Keshari, V. K. Yadav and L. D. S. Yadav, *Org. Biomol. Chem.*, 2014, **12**, 8550; (b) H. Jiang, Y. Cheng, Y. Zhang and S. Yu, *Eur. J. Org. Chem.*, 2013, 5485; (c) S. Handa, J. C. Fennwald, and B. H. Lipshutz, *Angew. Chem. Int. Ed.*, 2014, **53**, 3432; (d) W. Wei, C. Liu, D. Yang, J. Wen, J. You, Y. Suo and H. Wang, *Chem. Commun.*, 2013, **49**, 10239; (e) Q. Lu, J. Zhang, G. Zhao, Y. Qi, H. Wang and A. W. Lei, *J. Am. Chem. Soc.*, 2013, **135**, 11481.

Control experiments on reaction parameters



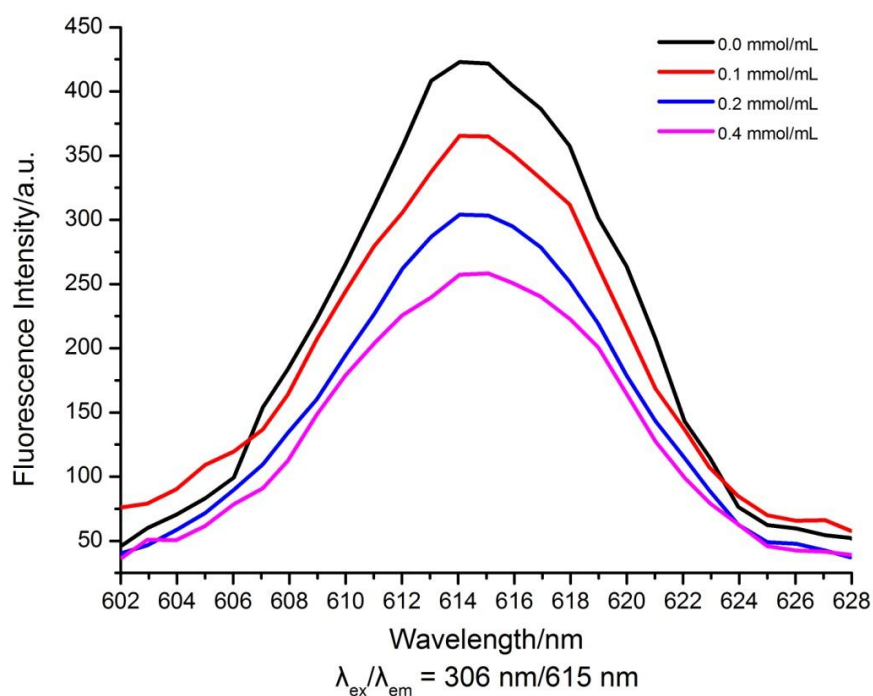
Compound **5** and **7** were prepared according to the reported literature, see: (a) Li, X.; Xu, X.; Shi, X. *Tetrahedron Lett.* **2013**, **54**, 3071. (b) Nair, V.; Augustine, A.; Suja, T. D. *Synthesis* **2002**, 2259. (c) Kariya, A.; Yamaguchi, T.; Nobuta, T.; Tada, N.; Miura, T.; Itoh, A. *RSC Adv.* **2014**, **4**, 13191.

¹H NMR and ¹³C NMR spectra data of compound 6



1-phenyl-2-tosylvinyl acetate (6): ¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.47-7.45 (m, 3H), 7.44 (d, *J* = 7.2, 2H), 7.39-7.34 (m, 2H), 6.64 (s, 1H), 2.44 (s, 3H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 167.8, 156.2, 144.7, 138.6, 132.2, 131.6, 129.9, 129.0, 127.6, 126.1, 117.3, 21.7, 20.9; HRMS calculated for C₁₇H₁₆NaO₄S (M + Na⁺): 339.0667, found: 339.0619.

Fluorescence spectra of Ru(bpy)₃Cl₂ with different concentration of KI



Concentration of Ru(bpy)₃Cl₂ : 1.1 μmol/L;
Concentration of KI : 0.0; 0.1; 0.2; 0.4 mmol/mL.

Copies of ¹H NMR and ¹³C NMR spectra

