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Supporting Information

For

Iron-Catalyzed Radical Aryldifluoromethylation of Activated Alkenes to Difluoromethyl Oxindoles

Jian-Yong Wang, Xin Zhang, Yan Bao, Yue-Ming Xu, Xiu-Fen Cheng, and Xi-Sheng Wang*

Department of Chemistry, University of Science and Technology of China, 96 Jinzhai Road, Hefei, Anhui 230026, China

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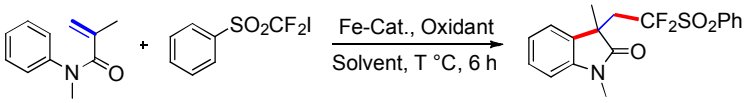
General Information:

NMR spectra were recorded on Bruker-400 (400 MHz for ^{1}H; 100 MHz for ^{13}C and 100 MHz for ^{19}F {^{1}H decoupled}) instruments. High resolution mass spectra were recorded on P-SIMS-Gly of Bruker Daltonics Inc. using ESI-TOF (electrospray ionization-time of flight). $FeCp_2$ was obtained from Adamas and used as received. H_2O_2 and solvents were purchased from Sinopharm and used as received.

Tables of the Optimization of Reaction Conditions

Table 1. Optimization of Reaction Conditions

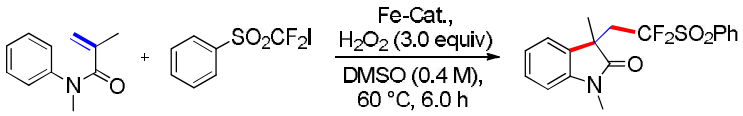


1a **2a**

Run	Solvent (mL)	Oxidant (equiv)	T (°C)	Yield (%)
1[c]	DMSO (0.5)	H_2O_2 (5.0)	40	50
2[c]	DMSO (0.5)	H_2O_2 (5.0)	60	55
3[c]	DMSO (0.5)	H_2O_2 (5.0)	80	46
4[c]	$CHCl_3$ (0.5)	H_2O_2 (5.0)	60	N.R.
5[c]	DMA (0.5)	H_2O_2 (5.0)	60	Trace
6[c]	DMF (0.5)	H_2O_2 (5.0)	60	5
7	DMSO (0.5)	H_2O_2 (5.0)	60	56
8	DMSO (0.5)	H_2O_2 (5.0)	60	56
9	DMSO (0.5)	DTBP (5.0)	60	N.R.
10	DMSO (0.5)	TBHP (5.0)	60	N.R.
11	DMSO (0.5)	DDQ (5.0)	60	N.R.
12	DMSO (0.5)	BQ (5.0)	60	N.R.
13	DMSO (0.5)	$K_2S_2O_8$ (5.0)	60	Trace
14	DMSO (0.5)	$PhI(OAc)_2$ (5.0)	60	N.R.
15	DMSO (0.5)	NFSI (5.0)	60	N.R.
16	DMSO (0.5)	BPO (5.0)	60	N.R.
17	DMSO (0.5)	TBPB (5.0)	60	N.R.
18	DMSO (0.5)	H_2O_2 (2.0)	60	56
19	DMSO (0.5)	H_2O_2 (3.0)	60	57

[a] Reaction conditions:**1a** (0.2 mmol, 1.0 equiv), $FeSO_4 \cdot 7H_2O$ (20 mol%), $PhSO_2CF_2I$ (0.3 mmol, 1.5 equiv) and solvent (0.5 mL) at 60 °C. [b] Isolated yield. [c] N_2.

Table 2. Catalysts Screening

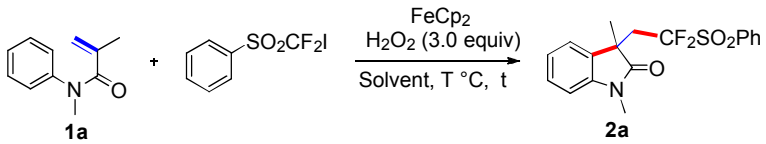


1a **2a**

Run	Fe-Cat. (mol%)	Yield (%)	run	Fe-Cat. (mol%)	Yield (%)
1	$FeBr_2$ (20)	63	9	$FeBr_3$ (20)	50
2	$FeCl_2$ (20)	67	10	$Fe_2(SO_4)_3 \cdot xH_2O$ (20)	63
3	$FeC_2O_4 \cdot 2H_2O$ (20)	55	11	$Fe(DBM)_3$ (20)	72
4	FeF_2 (20)	72	12	FeF_3 (20)	44
5	$Fe(OAc)_2$ (20)	73	13	$Fe_2(C_2O_4)_3 \cdot 6H_2O$ (20)	25
6	$FeCp_2$ (20)	75	14	$Fe(NO_3)_3 \cdot 9H_2O$ (20)	66
7	$FeCl_3$ (20)	74	15	$Fe(acac)_3$ (20)	72
8	$FeCl_3 \cdot 6H_2O$ (20)	49			

[a] Reaction conditions:**1a** (0.2 mmol, 1.0 equiv.), $FeCp_2$ (20 mol%), $PhSO_2CF_2I$ (0.3 mmol, 1.5 equiv) and DMSO (0.5 mL) at 60 °C. [b] Isolated yield.

Table 3. Solvent Screening



Run	Fe-Cat. (mol%)	Solvent (mL)	T (°C)	t (h)	Yield (%)
1	$FeCP_2$ (0.2)	DMSO (42.6 μL) + DCE (0.5)	60	6	3
2	$FeCP_2$ (0.2)	DMSO (71 μL) + DCE (0.5)	60	6	24
3	$FeCP_2$ (0.2)	DMSO (0.1) + DCE (0.4)	60	6	31
4	$FeCP_2$ (0.2)	DMSO (0.1) + DCE (0.4)	60	8	78
5	$FeCP_2$ (0.2)	DMSO (0.1) + Dioxane (0.4)	60	8	81
6	$FeCP_2$ (0.2)	DMSO (0.1) + ^{t}BuOH (0.4)	60	8	75
7	$FeCP_2$ (0.2)	DMSO (0.1) + $CHCl_3$ (0.4)	60	8	77
8	$FeCP_2$ (0.2)	DMSO (0.1) + DCM (0.4)	60	8	79
9	$FeCP_2$ (0.2)	DMSO (0.1) + Tol (0.4)	60	8	64
10	$FeCP_2$ (0.2)	DMSO (0.1) + THF (0.4)	60	8	87
11	$FeCP_2$ (0.2)	DMSO (0.1) + $Cl_2CHCHCl_2$ (0.4)	60	8	78
12	$FeCP_2$ (0.2)	DMSO (0.1) +Et_2O (0.4)	60	8	83
13	$FeCP_2$ (0.2)	DMSO (0.1) + THF (0.9)	60	8	79
14	$FeCP_2$ (0.2)	DMSO (0.2) + THF (0.8)	60	8	73
15	$FeCP_2$ (0.2)	DMSO (0.1) + THF (0.4)	60	10	82
16[c]	$FeCP_2$ (0.2)	DMSO (0.1) + THF (0.4)	60	8	71
17[d]	$FeCP_2$ (0.2)	DMSO (0.1) + THF (0.4)	60	8	92
18	$FeCP_2$ (0.2)	DMSO (0.1) + THF (0.4)	40	8	82
19	$FeCP_2$ (0.2)	DMSO (0.1) + THF (0.4)	80	8	86
20	$FeCP_2$ (0.05)	DMSO (0.1) + THF (0.4)	60	8	87
21	$FeCP_2$ (0.1)	DMSO (0.1) + THF (0.4)	60	8	89
22	$FeCP_2$ (0.3)	DMSO (0.1) + THF (0.4)	60	8	84

[a] Reaction conditions:**1a** (0.2 mmol, 1.0 equiv), $FeCp_2$ (20 mol%), $PhSO_2CF_2I$ (0.3 mmol, 1.5 equiv) and solvent at 60 °C. [b] Isolated yield. [c] $PhSO_2CF_2I$ (0.24 mmol, 1.2 equiv). [d] $PhSO_2CF_2I$ (0.40 mmol, 2.0 equiv).

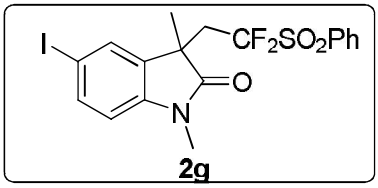
Preparation of Substrates:

$PhSO_2CF_2I$ was synthesized through the known method.[S1] All acrylamides **1** were prepared following the procedure reported.[S2,S3]

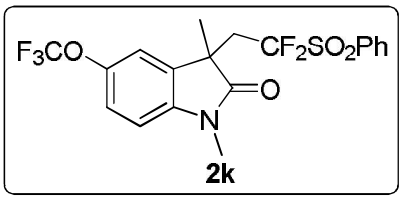
General Procedure of Difluoromethylation of Acrylamides 1:

Acrylamides **1** (0.2 mmol), $FeCp_2$ (3.7 mg, 0.02 mmol), and $PhSO_2CF_2I$ (95.4 mg, 0.3 mmol) were combined in an oven-dried Schlenk tube, and DMSO/THF (v/v = 1/4, 0.5 mL) was added *via* syringe. The reaction mixture was then placed into a preheated oil bath at 60 °C with vigorous stirring and Hydrogen peroxide was added drop by drop *via* syringe. The reaction mixture was stirred for another 6 hours, then cooled to

room temperature and filtered through a plug of silica (eluted with EtOAc). The filtrate was concentrated, and the residue was purified by column chromatography on silica gel (petroleum ether: EtOAc = 5:1) to give product **2**.



2g: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.6 Hz, 2H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.59-7.53 (m, 4H), 6.61 (d, *J* = 8.0 Hz, 1H), 3.17 (ddd, *J* = 34.8, 15.6, 2.4 Hz, 1H), 3.16 (s, 3H), 2.87 (ddd, *J* = 32.0, 15.6, 6.4 Hz, 1H), 1.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.6, 142.6, 137.4, 135.6, 132.4, 131.5, 131.0, 129.4, 123.3 (dd, *J* = 290.1, 289.2 Hz), 110.5, 85.1, 44.5 (d, *J* = 0.9 Hz), 35.1 (t, *J* = 18.6 Hz), 26.6, 25.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.4 (d, *J* = 225.6 Hz, 1F), -103.8 (d, *J* = 225.6 Hz, 1F). HRMS ESI (m/z): $[M+H]^+$ calcd for $C_{18}H_{17}F_2NIO_3S$: 491.9936, found: 491.9920.



2k: δ 7.88 (d, *J* = 7.6 Hz, 2H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 1H), 3.21 (s, 3H), 3.19 (ddd, J = 34.8, 15.4, 2.8 Hz, 1H), 2.90 (ddd, *J* = 32.0, 15.6, 6.8 Hz, 1H), 1.48 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 178.1, 144.8 (q, *J* = 1.9 Hz), 141.6, 135.1, 132.8, 131.5, 121.0, 129.4, 123.3 (dd, *J* = 290.0, 289.2 Hz), 121.7, 120.6 (q, *J* = 257.8 Hz), 117.9 (br), 108.9, 44.9 (d, *J* = 1.1 Hz), 35.1 (t, *J* = 18.6 Hz), 26.7, 25.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.4, -99.6 (d, *J* = 226.2 Hz, 1F), -104.0 (d, *J* = 226.2 Hz, 1F). HRMS ESI (m/z): $[M+H]^+$ calcd for $C_{19}H_{17}F_5NO_4S$: 450.0793, found: 450.0795.

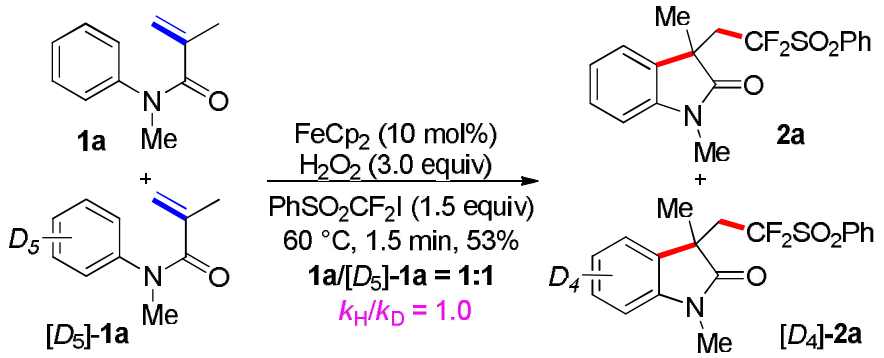
Mechanism Studies:

Intermolecular KIE Experiment:

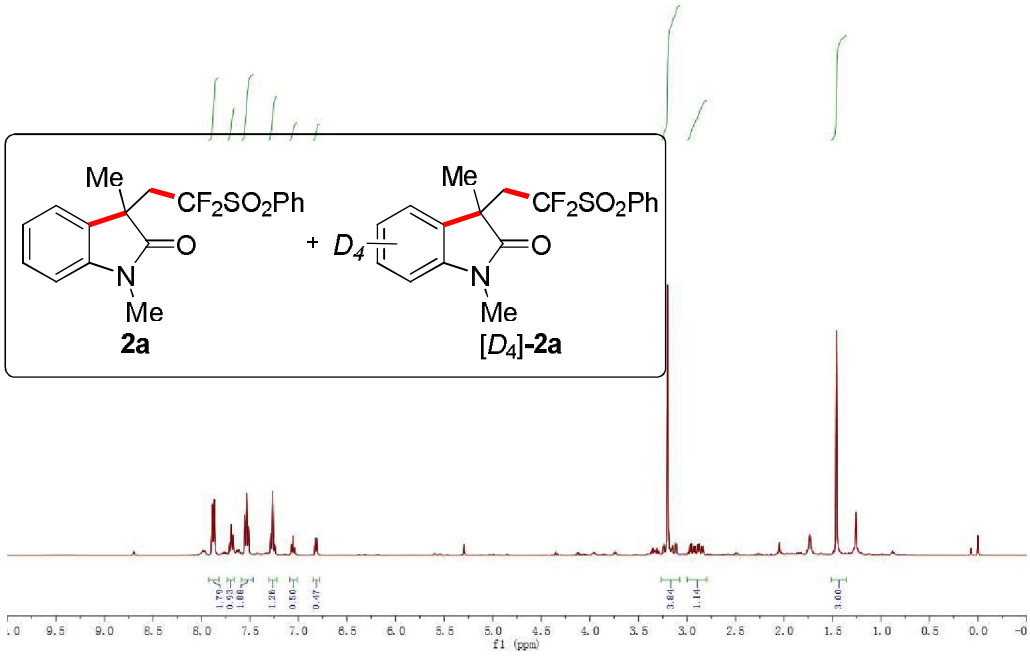
1a-d_5 was synthesized according to the known method above.[S3,S4]

Acrylamides **1a** (0.2 mmol) [or **1a** (0.1 mmol) and **1a**-d_5 (0.1 mmol)], $FeCp_2$ (3.7 mg, 0.02 mmol), and $PhSO_2CF_2I$ (95.4 mg, 0.3 mmol) were combined in an oven-dried Schlenk tube，and DMSO/THF (v/v = 1/4, 0.5 mL) was added *via* syringe.

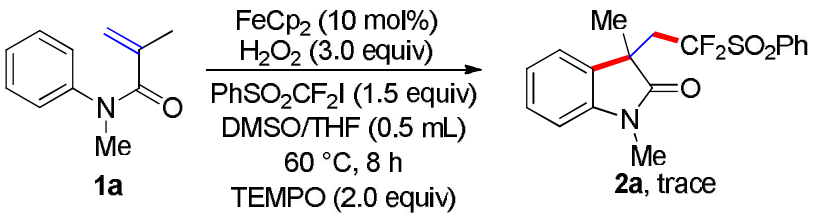
The reaction mixture was then placed into a preheated oil bath at 60 °C with vigorous stirring and Hydrogen peroxide was added drop by drop *via* syringe. The reaction mixture was stirred for another 1.5 minutes, and filtered through a plug of silica (eluted with EtOAc) immediately. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel (petroleum ether: EtOAc = 5:1) to give product **2a** and **2a**-d_4.



(1)

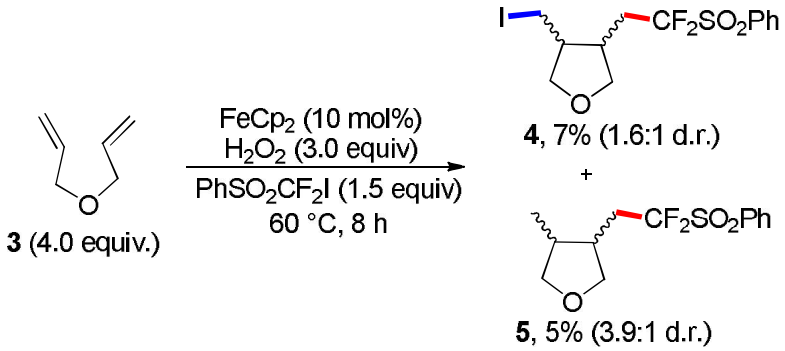


Radical Trapping Experiment with TEMPO:



Acrylamides **1** (0.2 mmol), $FeCp_2$ (3.7 mg, 0.02 mmol), and $PhSO_2CF_2I$ (95.4 mg, 0.30 mmol) and TEMPO (62.6 mg, 0.4 mmol) were combined in an oven-dried Schlenk tube, and DMSO/THF (v/v = 1/4, 0.5 mL) was added via syringe. The reaction mixture was then placed into a preheated oil bath at 60 °C with vigorous stirring and Hydrogen peroxide was added drop by drop via syringe. The reaction mixture was stirred for another 6 hours, then cooled to room temperature and filtered through a plug of silica (eluted with EtOAc). Only trace of **2a** was detected by GC-MS.

Procedure of Difluoromethylation of Allyl Ether:



$FeCp_2$ (3.7 mg, 0.02 mmol), $PhSO_2CF_2I$ (95.4 mg, 0.30 mmol) and allyl ether **3** (78.5 mg, 0.8 mmol) were combined in an oven-dried Schlenk tube, and DMSO/THF (v/v = 1/4, 0.5 mL) was added *via* syringe. The reaction mixture was then placed into a preheated oil bath at 60 °C with vigorous stirring and Hydrogen peroxide was added drop by drop *via* syringe. The reaction mixture was stirred for another 8 hours, then cooled to room temperature and filtered through a plug of silica (eluted with EtOAc). The filtrate was concentrated, and the residue was purified by column chromatography on silica gel (petroleum ether: EtOAc = 5:1). Compounds **4** and **5** were obtained as an unseparated mixture, and determined by ^{1}H NMR and LC-MS. (**4**:**5** = 1.46:1, **4**: HRMS ESI (m/z): $[M+H]^+$ calcd for $C_{13}H_{16}F_2O_3SI$: 416.9822, found: 416.9817; **5**: HRMS ESI (m/z): $[M+H]^+$ calcd for $C_{13}H_{17}F_2O_3S$: 291.0866, found: 4291.0864).

References:

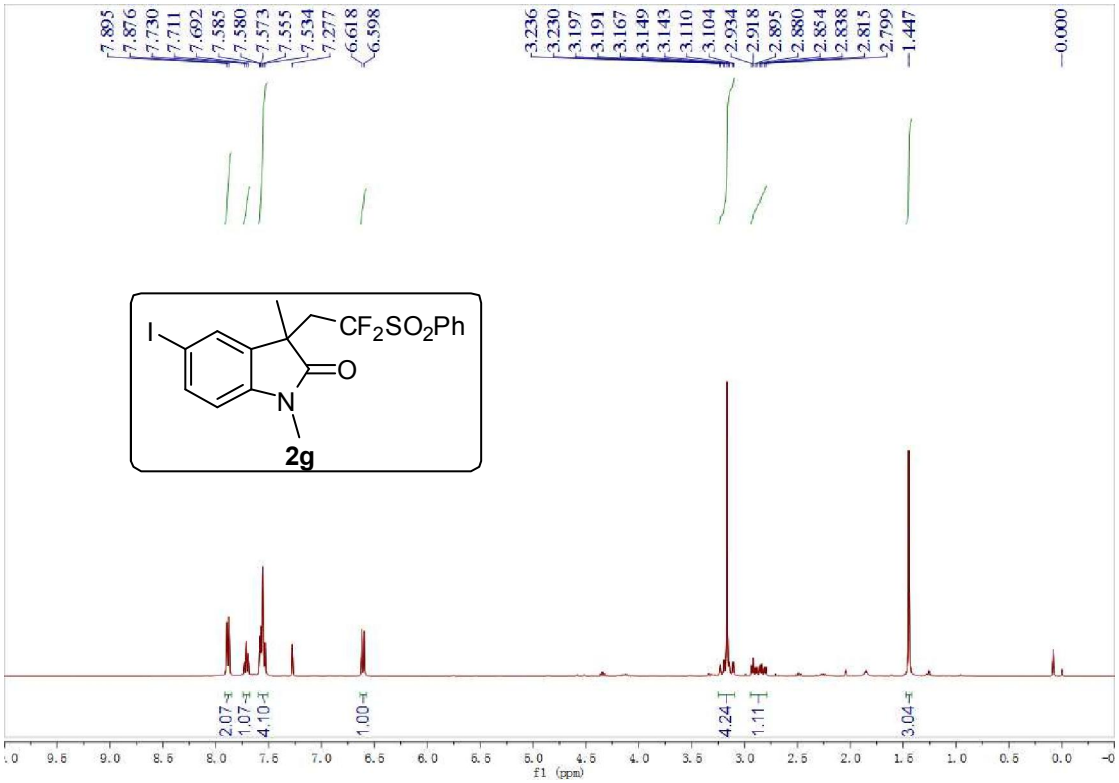
[S1] a) G. K. S. Prakash, J. Hu, G. A. Olah, *Org. Lett*. **2004**, *6*, 4315; b) Y. Li, J. Liu, L. Zhang, L. Zhu, J. Hu, *J. Org. Chem.* **2007**, *72*, 5824.

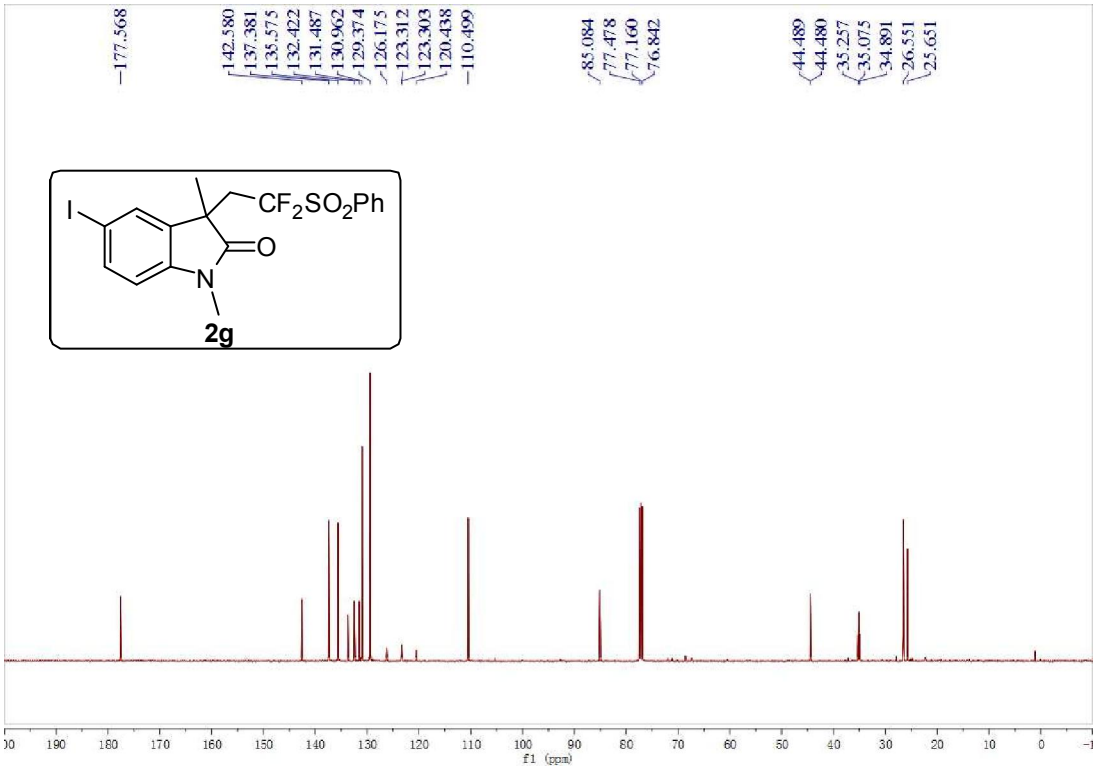
[S2] a) A. Pinto, Y. Jia, L. Neuville, J. Zhu, *Chem. Eur. J.* **2007**, *13*, 961; b) K. Jones, M. Thompson, C. Wright, *J. Chem. Soc., Chem. Commun.* **1986**, 715; c) H. Wei, T. Piou, J. Dufour, L. Neuville, J. Zhu, *Org. Lett.*, **2011**, *13*, 2244-2247.

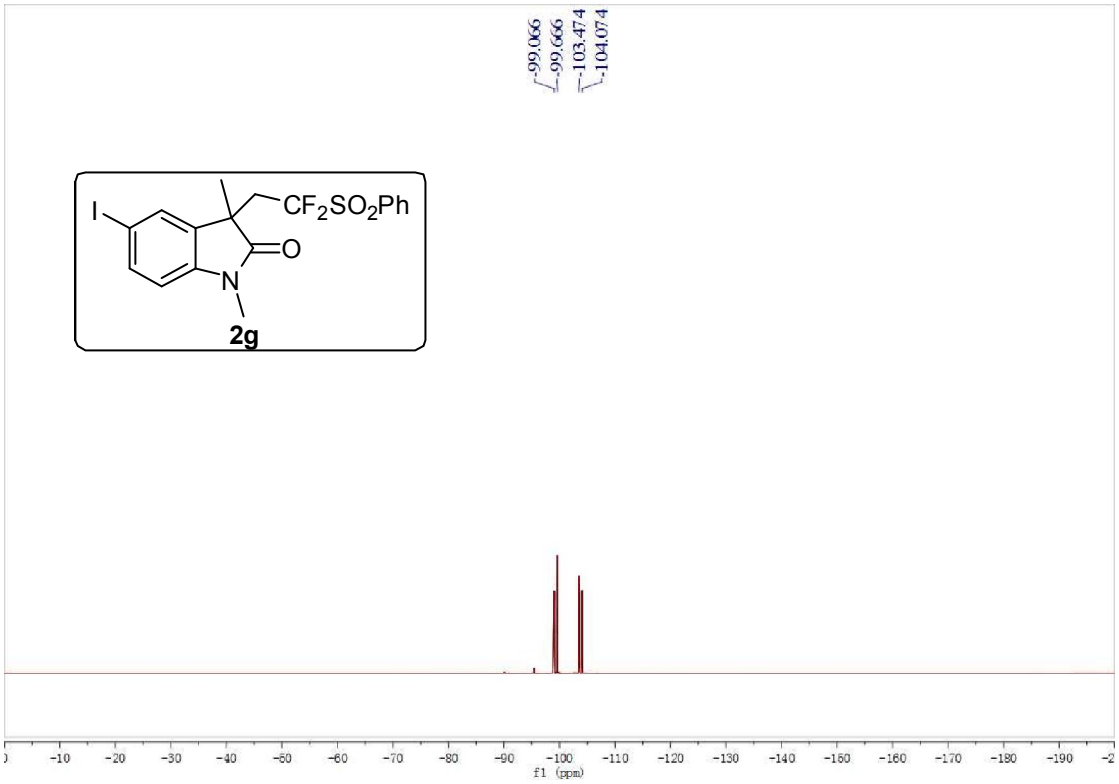
[S3] X. Mu, T. Wu, H.-Y. Wang , Y.-L.Guo, G. Liu, *J. Am. Chem. Soc.* **2012**, *134*, 878-881.

[S4] J.-Y. Wang, Y.-M. Su, F. Yin, B. Yan, X. Zhang, Y.-M. Xu, X.-S. Wang, *Chem. Commun.* **2014**, *50*, 4108.

Copies of ^{1}H, ^{13}C and ^{19}F {^{1}H decoupled} NMR Spectra of New Coumpounds:



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N
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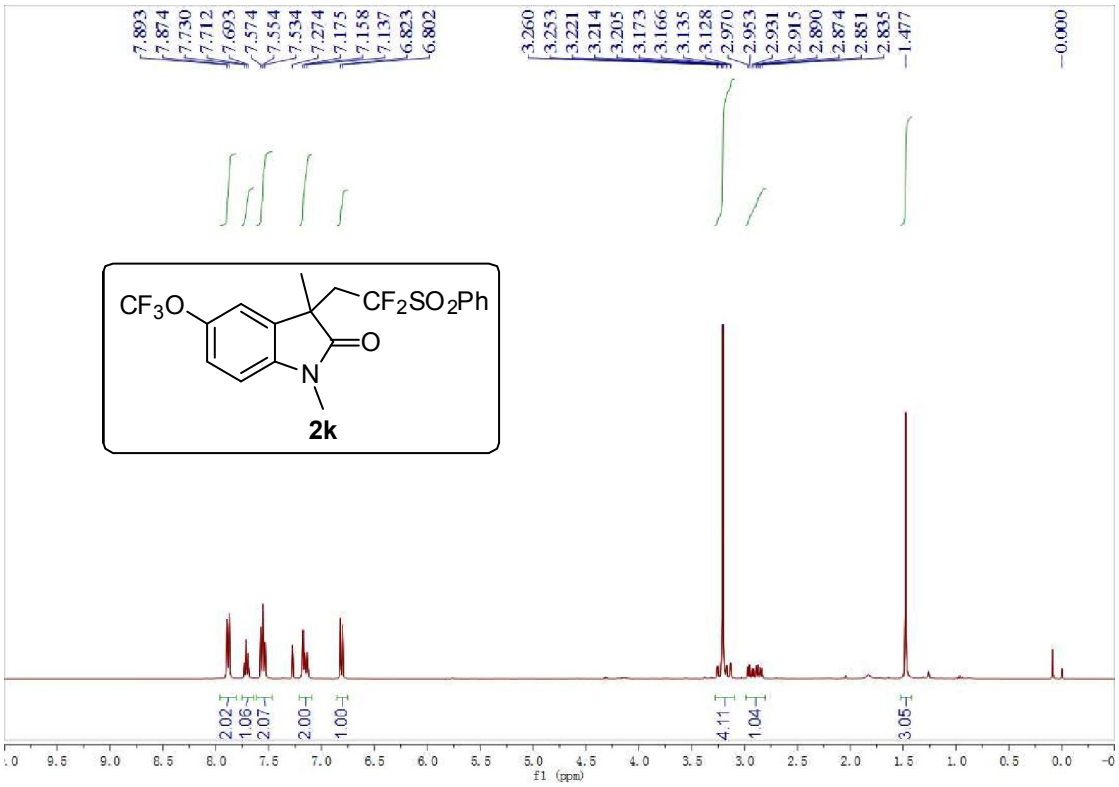
f1 (ppm)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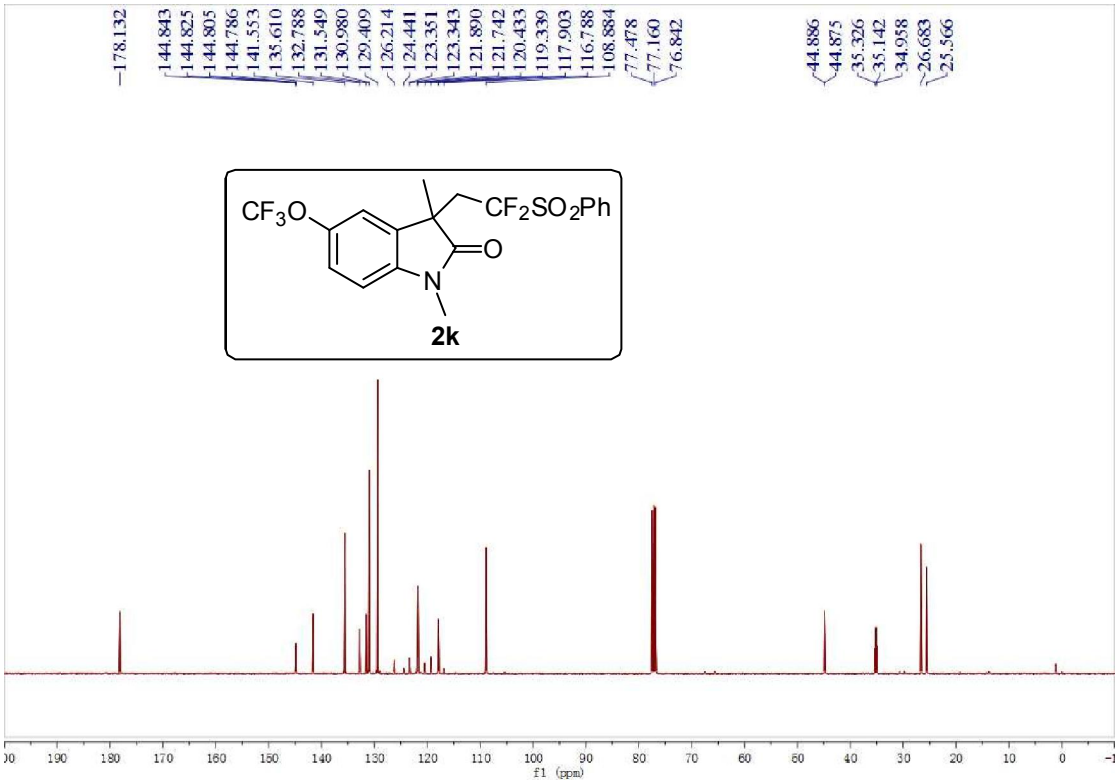
f1 (ppm)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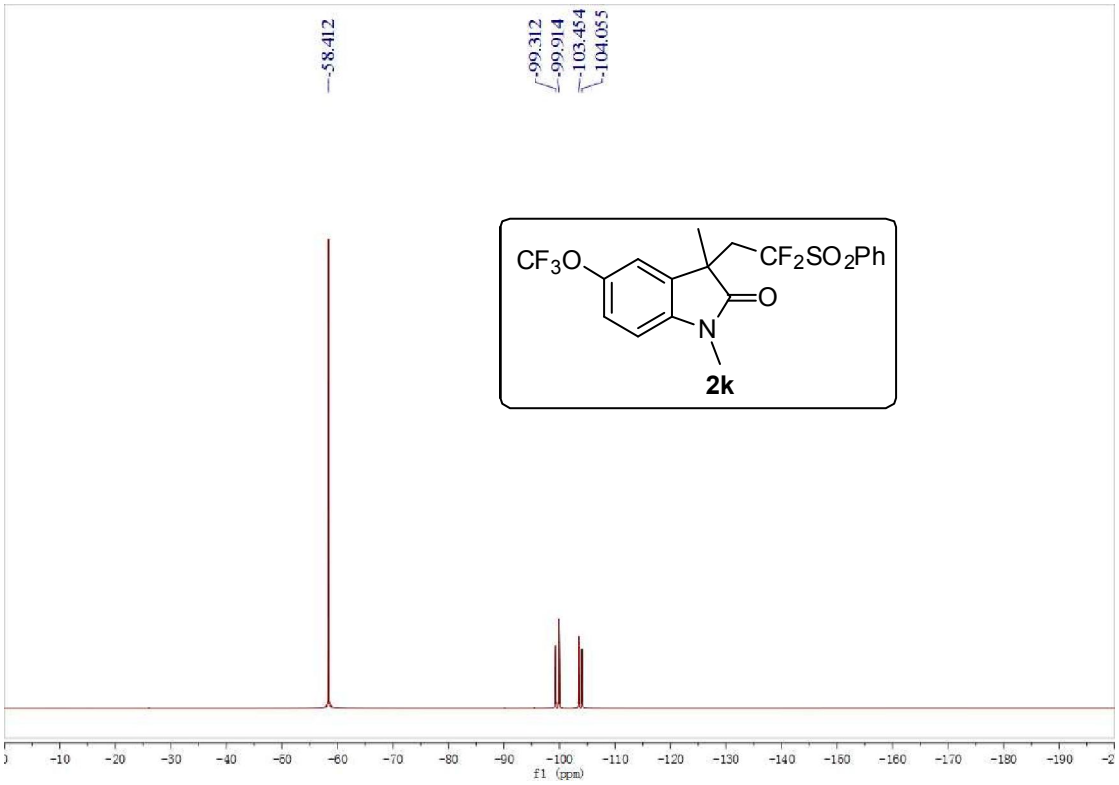
f1 (ppm)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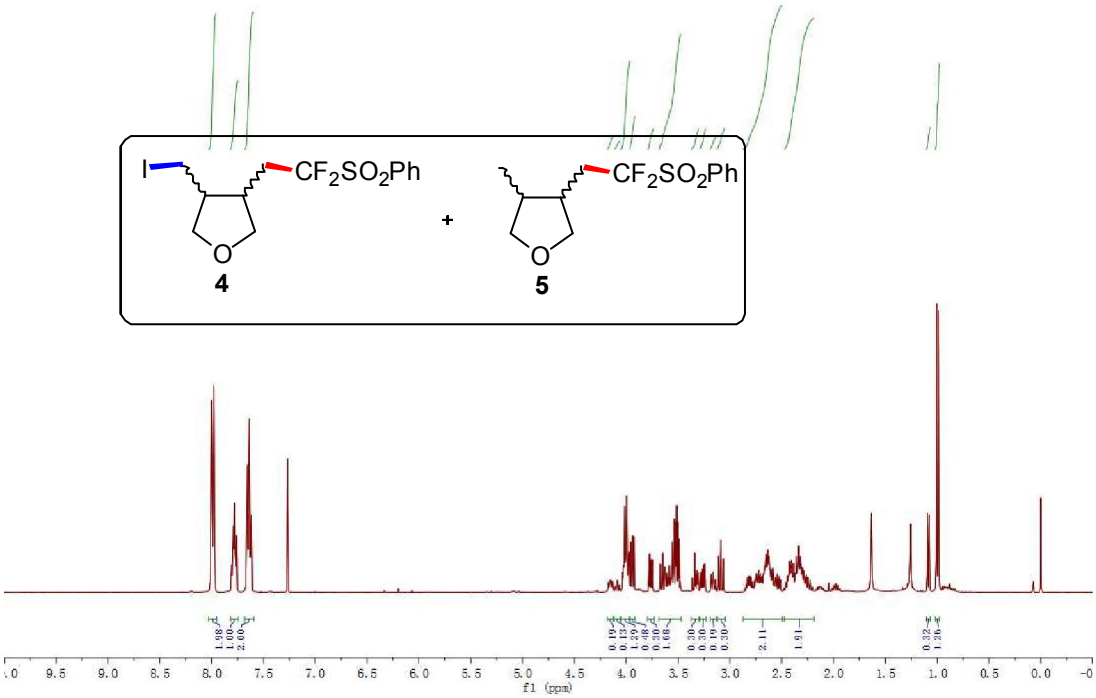
f1 (ppm)


I
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O
4
+
CF2SO2Ph
O
5
f1 (ppm)