

Supporting Information

Catalyst-free, visible-light-induced direct radical cross-coupling perfluoroalkylation of the imidazo[1,2-*a*]-pyridines with perfluoroalkyl iodides

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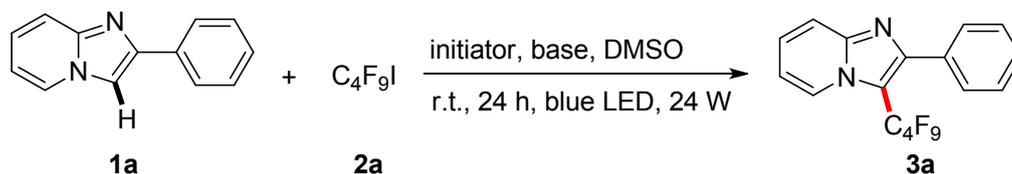
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1. General Information

All reagents were used as purchased from the supplier without further purification unless otherwise noted. Reactions were monitored by using thin-layer chromatography (TLC) on commercial silica gel plates (GF 254). Visualization of the developed plates was performed under UV lights (GF 254 nm). Solvents for flash column chromatography (FC), crystallization and extractions have been distilled once. Flash column chromatography was performed on silica gel (200-300 mesh). ^1H , ^{13}C and ^{19}F NMR spectra were recorded on a Bruker AV500 or 600 MHz spectrometer. Chemical shifts (δ) were reported in ppm referenced to an internal TMS standard or the DMSO- d_6 residual peak (δ 2.50) for ^1H NMR. Chemical shifts of ^{13}C NMR were reported relative to CDCl_3 (δ 77.0) or DMSO- d_6 (δ 39.5). The following abbreviations were used to describe peak splitting patterns when appropriate: br s = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constant, J , was reported in Hertz unit (Hz). High resolution mass spectra (HRMS) were obtained on an ESI-LC-MS/MS spectrometer. All imidazo[1,2-*a*]pyridines were prepared according to the reported method.^[1]

2. Optimization of the Reaction Conditions

Table S1 Optimization of the reaction conditions of visible-light-induced perfluoroalkylation of the imidazo[1,2-*a*]pyridines with perfluoroalkyl iodides^a

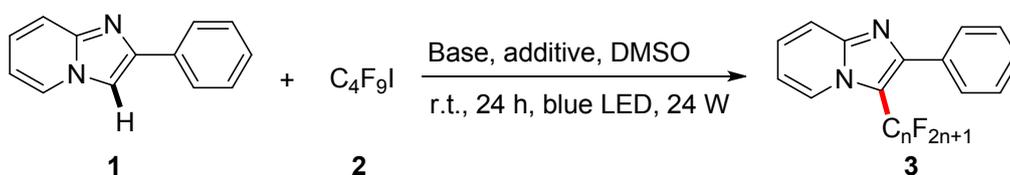


Entry	Base	Solvent	Additive	Yield [%] ^b
1 ^c	DIPEA	DCM		40
2	DIPEA	MeOH		trace
3	Pyridine	DMSO		trace
4	Pyrrolidine	DMF		37
5 ^d	PMDETA	DMSO		60
6	TMEDA	DMSO	TFA(20%)	45
7 ^e	TMEDA	DMSO	K_2HPO_4 (20%)	70
8	TMEDA	DMSO	KH_2PO_4 (20%)	66
9	TMEDA	DMSO	KHCO_3 (20%)	65
10 ^f	TMEDA	DMSO	K_3PO_4 (20%)	trace

^a Reaction conditions: **1a** (0.2 mmol), $\text{C}_4\text{F}_9\text{I}$ (**2a**, 0.42 mmol), initiator (0.4 mmol), additive (20

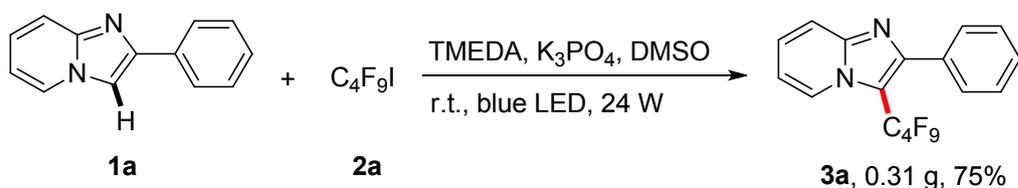
mmol%), solvent (2 mL), rt, Ar (balloon), 24 h, 24 W blue LED, in Schlenk tubes. ^b NMR yields of **3a** determined by using 1-iodo-4-(trifluoromethyl)benzene as an internal standard. ^c 40 h. ^d 36 h. ^e 48 h. ^f In air.

3. General Procedure for the Synthesis of **3**



To a solution of imidazo[1,2-*a*]pyridines (0.20 mmol) and K_3PO_4 (0.04 mmol, 20 mol%) in DMSO (2 mL) was added $\text{C}_n\text{F}_{2n+1}\text{I}$ (0.21 mmol, 1.1 equiv) and TMEDA (0.2 mmol) under an argon atmosphere. The vial was stirred under blue LED (24 W) irradiation at room temperature for 12 h after which a second portion of $\text{C}_n\text{F}_{2n+1}\text{I}$ (0.21 mmol, 1.1 equiv) and TMEDA (0.2 mmol) was added. The solution was stirred under blue LED irradiation for another 12 h. The reaction was monitored by TLC until the starting material was completely consumed. The reaction mixture was diluted with EtOAc (5 mL \times 3) and washed with brine (5 mL \times 3). The organic layer was dried over MgSO_4 , and concentrated under vacuum. The residue was purified by column chromatography to give the corresponding products.

4. Scale-UP Synthesis of **3a**



In a 25 mL flask, a mixture of **1a** (1 mmol, 1.0 equiv), K_3PO_4 (0.2 mmol, 0.2 equiv) were added and charged with argon more than three times. A solution of $\text{C}_4\text{F}_9\text{I}$ **2a** (1.1 mmol, 1.0 equiv) and TMEDA (1 mmol) in DMSO (10 mL) was injected into the above tube. The resulting suspension was stirred vigorously at room temperature for 10 minutes before being irradiated in reactor with cooling device using a blue LED (24 W) for 20 hours, after which a second portion of **2a** (1.1 mmol, 1.1 equiv) and TMEDA (1 mmol) was added. The solution was stirred under blue LED irradiation for another 16 h. After the reaction was completed, the solvents were evaporated under reduced pressure, and the residue was purified with chromatography column on silica gel or preparative TLC (PE/EA = 4:1) to give **3a** (0.31 g) in 75% yield.

4. Free-radical Inhibition Experiment

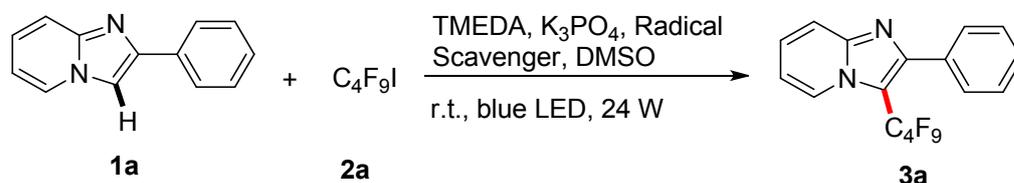


Table S2 Effects of Radical Inhibitor on the Reaction Efficiency^a

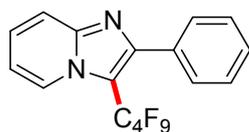
Entry	Radical Scavenger	Yield of 3a ^b
1	-	90%
2	TEMPO	trace
3	hydroquinone	n.d.
4	1,1-diphenylethene	2%

^a Reaction conditions: **1a** (0.2 mmol), **2a** (0.42 mmol), K_3PO_4 (20 mol%), TMEDA (0.4 mmol), radical scavenger (3.0 equiv), and DMSO (2 mL) at r.t. under an argon atmosphere and 24 W blue LED irradiation for 24 h. ^b NMR yield of **3a**.

Procedure: To a solution of **1a** (0.20 mmol) and K_3PO_4 (0.04 mmol, 20 mol%) in DMSO (2 mL) was added **2a** (0.42 mmol, 1.1 equiv), radical scavenger (0.6 mmol) and TMEDA (0.4 mmol) under an argon atmosphere. The vial was stirred under blue LED (24 W) irradiation at room temperature for 24 h. The reaction was monitored by TLC until the starting material was completely consumed. The residue was used to determine NMR yield of **3a** by using 1-iodo-4-(trifluoromethyl)benzene as an internal standard without further purification.

7. Product Characterization

3-(perfluorobutyl)-2-phenylimidazo[1,2-a]pyridine (**3a**)

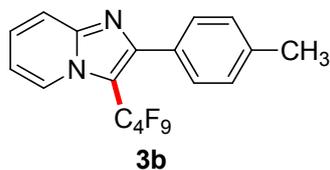


3a

Colloidal solid, 73 mg; yield: 89%. ¹H NMR (600 MHz, $CDCl_3$): δ = 8.36 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.64-7.66 (m, 2H), 7.47-7.49 (m, 4H), 7.06 (t, J = 6.2 Hz, 1H); ¹³C NMR (125 MHz, $CDCl_3$): δ = 149.9, 146.3, 132.3, 129.6, 129.1, 128.1, 128.0, 127.9, 126.0-126.1 (m), 118.2-118.3 (m), 117.9, 116.3-116.4 (m), 114.6-114.7 (m), 114.5, 107.7-107.8 (m); ¹⁹F NMR (470 MHz, $CDCl_3$): δ = -80.9 to -80.8 (m, 3F), -106.2 to -106.1 (m, 2F), -121.7 to -

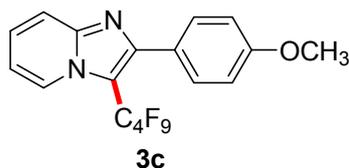
121.6 (m, 2F), -125.9 to -125.8 (m, 2F) ; HRMS (ESI): Exact mass calcd for $C_{17}H_{10}F_9N_2^+$ $[M+1]^+$ 413.0695, found 413.0696.

3-(perfluorobutyl)-2-(p-tolyl)imidazo[1,2-a]pyridine (3b)



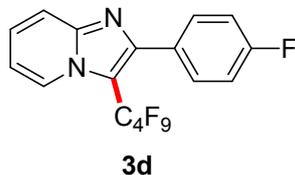
Colloidal solid, 68 mg; yield: 80%. 1H NMR (600 MHz, $CDCl_3$): δ = 8.35 (d, J = 7.8 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.54-7.55 (m, 2H), 7.46-7.47 (m, 1H), 7.27-7.29 (m, 2H), 7.03-7.05 (m, 1H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.1, 148.3, 139.1, 129.4, 128.8, 127.7, 127.8, 126.0-126.1 (m), 118.2-118.3 (m), 117.8, 116.3-116.4 (m), 114.6-114.7 (m), 114.3, 106.6-106.7 (m), 21.4; ^{19}F NMR (470 MHz, $CDCl_3$): δ = -80.9 to -80.8 (m, 3F), -106.2 to -106.1 (m, 2F), -121.6 to -121.5 (m, 2F), -125.9 to -125.8 (m, 2F); HRMS (ESI): Exact mass calcd for $C_{18}H_{12}F_9N_2^+$ $[M+1]^+$ 427.0851, found 427.0853.

2-(4-methoxyphenyl)-3-(perfluorobutyl)imidazo[1,2-a]pyridine (3c)



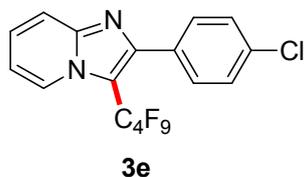
Colloidal solid, 66 mg; yield: 75%. 1H NMR (600 MHz, $CDCl_3$): δ = 8.35 (d, J = 7.8 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.54-7.55 (m, 2H), 6.99-7.04 (m, 3H), 3.89 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.4, 149.8, 146.3, 130.9, 127.8, 126.0-126.1 (m), 124.6, 118.2-118.3 (m), 117.7, 114.5-114.6 (m), 114.6-114.8 (m), 113.5, 109.6-109.8 (m), 107.4-107.5 (m), 55.3; ^{19}F NMR (470 MHz, $CDCl_3$): δ = -80.9 to -80.8 (m, 3F), -106.2 to -106.1 (m, 2F), -121.7 to -121.6 (m, 2F), -125.9 to -125.8 (m, 2F); HRMS (ESI): Exact mass calcd for $C_{18}H_{12}F_9N_2O^+$ $[M+1]^+$ 443.0800, found 443.0801.

2-(4-fluorophenyl)-3-(perfluorobutyl)imidazo[1,2-a]pyridine (3d)



Colloidal solid, 77 mg; yield: 90%. 1H NMR (600 MHz, $CDCl_3$): δ = 8.34 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.61-7.64 (m, 2H), 7.45-7.48 (m, 1H), 7.14-7.17 (m, 2H), 7.04 (t, J = 6.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.2 (d, J = 247.5 Hz), 149.3, 146.5, 131.4 (d, J = 9.0 Hz), 128.8, 127.8, 126.0-126.1 (m), 118.2-118.3 (m), 118.0, 116.4-116.5 (m), 115.2, 115.0, 114.6-114.7 (m), 114.4, 107.8-107.9 (m); ^{19}F NMR (470 MHz, $CDCl_3$): δ = -80.9 to -80.8 (m, 3F), -106.1 to -106.0 (m, 2F), -112.4 (s, 1F), -121.8 to -121.7 (m, 2F), -125.9 to -125.8 (m, 2F); HRMS (ESI): Exact mass calcd for $C_{17}H_9F_{10}N_2^+$ $[M+1]^+$ 431.0601, found 431.0603.

2-(4-chlorophenyl)-3-(perfluorobutyl)imidazo[1,2-a]pyridine (3e)



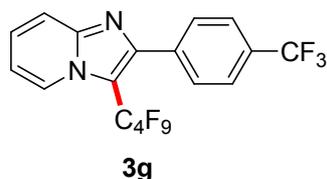
Colloidal solid, 82 mg; yield: 92%. ¹H NMR (600 MHz, CDCl₃): δ = 8.35 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 6.8 Hz, 1H), 7.59 (d, J = 7.2 Hz, 2H); 7.49-7.50 (m, 1H), 7.29 (d, J = 7.2 Hz, 1H), 7.06 (t, J = 6.8 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ = 148.8, 146.5, 135.4, 130.9, 128.3, 128.1, 126.0-126.1 (m), 124.4, 123.9, 118.2-118.3 (m), 117.9, 116.3-116.4 (m), 114.6, 112.8-112.9 (m), 108.0-108.1 (m); ¹⁹F NMR (470 MHz, CDCl₃): δ = -80.9 to -80.8 (m, 3F), -106.1 to -106.0 (m, 2F), -121.7 to -121.6 (m, 2F), -125.9 to -125.8 (m, 2F); HRMS (ESI): Exact mass calcd for C₁₉H₉ClF₉N₂⁺ [M+1]⁺ 447.0305, found 447.0306.

2-(4-bromophenyl)-3-(perfluorobutyl)imidazo[1,2-a]pyridine (3f)



Colloidal solid, 89 mg; yield: 92%. ¹H NMR (600 MHz, CDCl₃): δ = 8.36 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.61-7.62 (m, 2H); 7.50-7.54 (m, 3H), 7.08 (t, J = 6.4 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ = 148.6, 148.3, 131.3, 131.2, 128.3, 126.1, 124.4, 123.8, 118.2-118.3 (m), 117.9, 116.3-116.4 (m), 114.7, 114.5-114.6 (m), 112.7-112.8 (m), 111.1-111.2 (m), 108.0-108.1 (m); ¹⁹F NMR (470 MHz, CDCl₃): δ = -80.9 to -80.8 (m, 3F), -106.2 to -106.1 (m, 2F), -121.7 to -121.6 (m, 2F), -125.9 to -125.8 (m, 2F); HRMS (ESI): Exact mass calcd for C₁₇H₉BrF₉N₂⁺ [M+1]⁺ 490.9800, found 490.9800.

3-(perfluorobutyl)-2-(4-(trifluoromethyl)phenyl)imidazo[1,2-a]pyridine (3g)



Colloidal solid, 81 mg; yield: 84%. ¹H NMR (600 MHz, CDCl₃): δ = 8.35 (d, J = 8.0 Hz, 1H), 7.72-7.80 (m, 5H), 7.47 (t, J = 6.4 Hz, 1H), 7.05 (t, J = 6.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ = 149.1, 146.9, 136.7, 130.6 (q, J = 235.4 Hz), 127.7, 126.0-126.1 (m), 124.8-124.9 (m), 123.1, 120.1, 118.4, 116.2-116.3 (m), 114.8-114.9 (m), 116.3-116.4 (m), 114.8-114.9 (m), 114.4, 113.0-113.1 (m), 111.1-111.2 (m), 108.2-108.3 (m); ¹⁹F NMR (470 MHz, CDCl₃): δ = -62.7 (s, 3F), -80.9 to -80.8 (m, 3F), -106.1 to -106.0 (m, 2F), -121.8 to -121.7 (m, 2F), -125.9 to -125.8 (m, 2F); HRMS (ESI): Exact mass calcd for C₁₈H₉F₁₂N₂⁺ [M+1]⁺ 481.0569, found 481.0570.

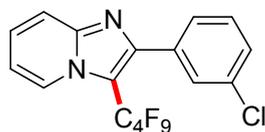
2-(3-methoxyphenyl)-3-(perfluorobutyl)imidazo[1,2-a]pyridine (3h)



3h

Colloidal solid, 79mg; yield: 90%. ¹H NMR (600 MHz, CDCl₃): δ = 8.32-8.34 (m, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.42-7.43 (m, 1H), 7.35-7.37 (m, 1H), 7.23 (d, J = 8.2 Hz, 1H), 7.19 (s, 1H), 6.98-7.02 (m, 2H), 3.86 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ = 159.1, 150.4, 146.7, 134.3, 129.0, 127.3, 126.0-126.1 (m), 122.1, 118.3-118.4 (m), 118.1, 115.1, 114.7-114.8 (m), 114.6, 114.1, 113.0-113.1 (m), 111.3-111.4 (m), 107.6-107.8 (m), 55.2; ¹⁹F NMR (470 MHz, CDCl₃): δ = -80.9 to -80.8 (m, 3F), -106.1 to -106.0 (m, 2F), -121.7 to -121.6 (m, 2F), -125.9 to -125.8 (m, 2F); HRMS (ESI): Exact mass calcd for C₁₈H₁₂F₉N₂O⁺ [M+1]⁺ 443.0800, found 443.0801.

2-(3-chlorophenyl)-3-(perfluorobutyl)imidazo[1,2-a]pyridine (3i)



3i

Colloidal solid, 76 mg; yield: 85%. ¹H NMR (600 MHz, CDCl₃): δ = 8.33-8.35 (m, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.65 (s, 1H), 7.52 (d, J = 8.1 Hz, 1H), 7.43-7.47 (m, 2H), 7.38-7.40 (m, 1H), 7.02-7.05 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ = 148.9, 146.7, 134.7, 133.9, 129.7, 129.2, 129.1, 127.7, 127.6, 126.0-126.1 (m), 117.9-118.1 (m), 116.3, 114.7-114.8 (m), 114.4, 112.6-112.8 (m), 111.3-111.4 (m), 107.9-108.1 (m); ¹⁹F NMR (470 MHz, CDCl₃): δ = -80.9 to -80.8 (m, 3F), -106.1 to -106.0 (m, 2F), -121.7 to -121.6 (m, 2F), -125.9 to -125.8 (m, 2F); HRMS (ESI): Exact mass calcd for C₁₇H₉ClF₉N₂⁺ [M+1]⁺ 447.0305, found 447.0307.

2-(3-bromophenyl)-3-(perfluorobutyl)imidazo[1,2-a]pyridine (3j)



3j

Colloidal solid, 78 mg; yield: 80%. ¹H NMR (600 MHz, CDCl₃): δ = 8.25 (d, J = 7.8 Hz, 1H), 7.71-7.73 (m, 2H), 7.47-7.52 (m, 2H), 7.37-7.40 (m, 1H), 7.23-7.26 (m, 1H), 6.94-6.97 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ = 148.7, 146.6, 134.7, 132.6, 132.1, 129.5, 128.2, 127.8, 126.0-126.1 (m), 122.0, 118.0-118.3 (m), 118.1, 116.2-116.3 (m), 114.6, 113.0-113.1 (m), 111.2-111.4 (m), 107.9-108.1 (m); ¹⁹F NMR (470 MHz, CDCl₃): δ = -80.9 to -80.8 (m, 3F), -106.1 to -106.0 (m, 2F), -121.7 to -121.6 (m, 2F), -125.9 to -125.8 (m, 2F); HRMS (ESI): Exact mass calcd for C₁₇H₉BrF₉N₂⁺ [M+1]⁺ 490.9800, found 490.9802.

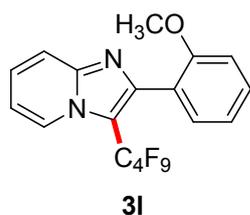
3-(perfluorobutyl)-2-(3-(trifluoromethyl)phenyl)imidazo[1,2-a]pyridine (3k)



3k

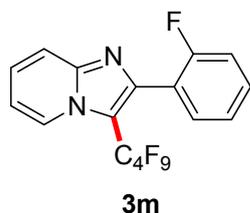
Colloidal solid, 72 mg; yield: 76%. ^1H NMR (600 MHz, CDCl_3): δ = 8.36 (d, J = 7.8 Hz, 1H), 7.93 (s, 1H), 7.80-7.85 (m, 2H), 7.72-7.74 (m, 1H), 7.60 (t, J = 6.8 Hz, 1H), 7.46-7.49 (m, 1H), 7.05 (t, J = 6.4 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ = 148.8, 146.8, 133.7, 132.8, 130.6 (q, J = 236.1 Hz), 128.5, 127.8, 126.6, 126.0-126.1 (m), 125.6-125.7 (m), 124.8, 123.0, 118.2, 116.2-116.3 (m), 114.5, 112.7-112.9 (m), 111.2-111.4 (m), 108.1-108.3 (m); ^{19}F NMR (470 MHz, CDCl_3): δ = -62.8 (s, 3F), -80.9 to -80.8 (m, 3F), -106.2 to -106.1 (m, 2F), -121.7 to -121.6 (m, 2F), -125.9 to -125.8 (m, 2F); HRMS (ESI): Exact mass calcd for $\text{C}_{18}\text{H}_9\text{F}_{12}\text{N}_2^+$ $[\text{M}+1]^+$ 481.0569, found 481.0570.

2-(2-methoxyphenyl)-3-(perfluorobutyl)imidazo[1,2-a]pyridine (3l)



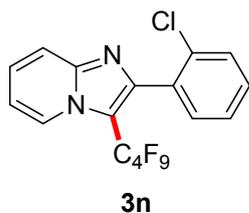
Colloidal solid, 65 mg; yield: 74%. ^1H NMR (600 MHz, CDCl_3): δ = 8.32-8.35 (m, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.41-7.43 (m, 1H), 7.35-7.37 (m, 1H), 7.19-7.23 (m, 1H), 7.98-7.02 (m, 2H), 3.86 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ = 159.2, 150.5, 146.7, 134.5, 129.3, 127.6, 122.4, 118.3-118.5 (m), 118.2, 116.0, 114.7-114.9 (m), 114.6, 114.3, 113.0-113.2 (m), 111.4-111.5 (m), 107.8-107.9 (m), 55.3; ^{19}F NMR (470 MHz, CDCl_3): δ = -80.9 to -80.8 (m, 3F), -107.9 to -107.8 (m, 2F), -122.3 to -122.2 (m, 2F), -126.1 to -126.0 (m, 2F); HRMS (ESI): Exact mass calcd for $\text{C}_{18}\text{H}_{12}\text{F}_9\text{N}_2\text{O}^+$ $[\text{M}+1]^+$ 443.0800, found 443.0802.

2-(2-fluorophenyl)-3-(perfluorobutyl)imidazo[1,2-a]pyridine (3m)



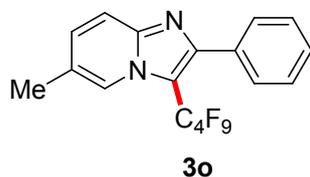
Colloidal solid, 65 mg; yield: 76%. ^1H NMR (600 MHz, CDCl_3): δ = 8.42-8.45 (m, 1H), 8.09-8.22 (m, 1H), 7.76-7.84 (m, 1H), 7.29-7.46 (m, 4H), 6.90-7.20 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ = 163.6 (d, J = 246.8 Hz), 149.5, 146.8, 131.5 (d, J = 10.2 Hz), 128.9, 127.9, 126.3-126.4 (m), 118.3-118.4 (m), 118.3, 116.4-116.5 (m), 115.4, 114.9, 113.8-113.9 (m), 113.8, 113.7, 111.4-111.7 (m), 107.8-107.9 (m); ^{19}F NMR (470 MHz, CDCl_3): δ = -80.9 to -80.8 (m, 3F), -106.1 to -106.0 (m, 2F), -112.4 (s, 1F), -121.8 to -121.7 (m, 2F), -125.9 to -125.8 (m, 2F); HRMS (ESI): Exact mass calcd for $\text{C}_{17}\text{H}_9\text{F}_{10}\text{N}_2^+$ $[\text{M}+1]^+$ 431.0601, found 431.0601.

2-(2-chlorophenyl)-3-(perfluorobutyl)imidazo[1,2-a]pyridine (3n)



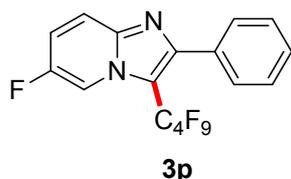
Colloidal solid, 67 mg; yield: 75%. ¹H NMR (600 MHz, CDCl₃): δ = 8.35 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.46-7.52 (m, 2H), 7.40-7.42 (m, 2H), 7.33-7.36 (m, 1H), 7.06 (t, J = 6.4 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ = 147.2, 146.5, 134.3, 131.9, 131.6, 130.4, 129.4, 127.6, 126.0, 125.8-125.9 (m), 118.3, 116.3-116.4 (m), 114.5, 112.4-112.6 (m), 112.5-112.6 (m), 111.0-111.2 (m), 111.3-111.4 (m), 109.3-109.5 (m); ¹⁹F NMR (470 MHz, CDCl₃): δ = -80.9 to -80.8 (m, 3F), -105.9 to -105.8 (m, 2F), -121.6 to -121.5 (m, 2F), -125.9 to -125.8 (m, 2F); HRMS (ESI): Exact mass calcd for C₁₇H₉ClF₉N₂⁺ [M+1]⁺ 447.0305, found 447.0306.

6-methyl-3-(perfluorobutyl)-2-phenylimidazo[1,2-a]pyridine (3o)



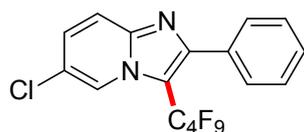
Colloidal solid, 69 mg; yield: 81%. ¹H NMR (600 MHz, CDCl₃): δ = 8.19 (s, 1H), 7.70 (d, J = 7.9 Hz, 1H), 7.61-7.63 (m, 2H), 7.44-7.46 (m, 3H), 7.29 (s, 1H), 2.43 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ = 150.1, 145.6, 133.1, 130.6, 129.5, 128.8, 127.9, 127.6, 124.1, 123.5-123.6 (m), 118.3-118.4 (m), 117.2, 116.0-116.1 (m), 114.5-114.7 (m), 111.2-111.4 (m), 107.4-107.6 (m), 18.5; ¹⁹F NMR (470 MHz, CDCl₃): δ = -80.9 to -80.8 (m, 3F), -105.9 to -105.8 (m, 2F), -121.6 to -121.5 (m, 2F), -125.9 to -125.8 (m, 2F); HRMS (ESI): Exact mass calcd for C₁₈H₁₂F₉N₂⁺ [M+1]⁺ 427.0851, found 427.0852.

6-fluoro-3-(perfluorobutyl)-2-phenylimidazo[1,2-a]pyridine (3p)



Colloidal solid, 65 mg; yield: 76%. ¹H NMR (600 MHz, CDCl₃): δ = 8.28-8.29 (m, 1H), 7.74-7.76 (m, 1H), 7.61-7.63 (m, 2H), 7.45-7.47 (m, 3H), 7.28-7.37 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ = 153.7 (d, J = 237.1 Hz), 151.6, 144.5, 132.8, 129.4, 129.0, 128.0, 119.6, 119.4, 118.7, 116.3-116.4 (m), 114.4-114.6 (m), 113.2-113.3 (m), 111.0-111.2 (m), 109.2-109.3 (m), 18.5; ¹⁹F NMR (470 MHz, CDCl₃): δ = -80.9 to -80.8 (m, 3F), -106.7 to -106.6 (m, 2F), -121.8 to -121.7 (m, 2F), -126.0 to -125.9 (m, 2F), -136.9 to -136.8 (s, 1F); HRMS (ESI): Exact mass calcd for C₁₇H₉F₁₀N₂⁺ [M+1]⁺ 431.0601, found 431.0603.

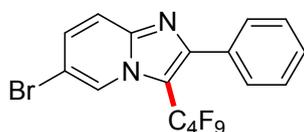
6-chloro-3-(perfluorobutyl)-2-phenylimidazo[1,2-a]pyridine (3q)



3q

Colloidal solid, 81 mg; yield: 91%. ^1H NMR (600 MHz, CDCl_3): δ = 8.37 (s, 1H), 7.78-7.80 (m, 1H), 7.62-7.63 (m, 2H), 7.44-7.49 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3): δ = 150.7, 144.7, 131.9, 129.5, 129.3, 129.2, 128.1, 123.6-123.8 (m), 122.9, 120.7-120.8 (m), 118.3, 115.9-116.0 (m), 114.0-114.2 (m), 111.2-111.3 (m), 108.4-108.6 (m); ^{19}F NMR (470 MHz, CDCl_3): δ = -80.9 to -80.8 (m, 3F), -106.3 to -106.2 (m, 2F), -121.8 to -121.7 (m, 2F), -126.0 to -125.9 (m, 2F); HRMS (ESI): Exact mass calcd for $\text{C}_{17}\text{H}_9\text{ClF}_9\text{N}_2^+$ $[\text{M}+1]^+$ 447.0305, found 447.0306.

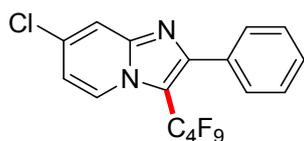
6-bromo-3-(perfluorobutyl)-2-phenylimidazo[1,2-a]pyridine (3r)



3r

Colloidal solid, 90 mg; yield: 92%. ^1H NMR (600 MHz, CDCl_3): δ = 8.45 (s, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.61-7.63 (m, 2H), 7.50-7.51 (m, 1H), 7.45-7.48 (m, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ = 151.1, 145.1, 132.5, 131.0, 129.5, 129.1, 128.0, 125.7-125.9 (m), 118.7, 118.3-118.4 (m), 116.2-116.3 (m), 114.4-114.5 (m), 111.2-111.4 (m), 109.0, 108.2-108.6 (m); ^{19}F NMR (470 MHz, CDCl_3): δ = -80.9 to -80.8 (m, 3F), -106.2 to -106.1 (m, 2F), -121.6 to -121.5 (m, 2F), -125.9 to -125.8 (m, 2F); HRMS (ESI): Exact mass calcd for $\text{C}_{17}\text{H}_9\text{BrF}_9\text{N}_2^+$ $[\text{M}+1]^+$ 490.9800, found 490.9802.

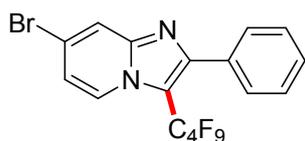
7-chloro-3-(perfluorobutyl)-2-phenylimidazo[1,2-a]pyridine (3s)



3s

Colloidal solid, 71 mg; yield: 80%. ^1H NMR (600 MHz, CDCl_3): δ = 8.24 (d, J = 8.0 Hz, 1H), 7.77 (s, 1H), 7.61-7.63 (m, 2H), 7.45-7.48 (m, 3H), 6.98-7.00 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ = 151.5, 146.7, 134.1, 132.6, 129.5, 129.1, 128.0, 126.1-126.3 (m), 118.3-118.4 (m), 116.9, 116.2-116.4 (m), 115.7, 114.4-114.6 (m), 111.2-111.4 (m), 108.2-108.6 (m); ^{19}F NMR (470 MHz, CDCl_3): δ = -80.9 to -80.8 (m, 3F), -106.1 to -106.0 (m, 2F), -121.7 to -121.6 (m, 2F), -125.9 to -125.8 (m, 2F); HRMS (ESI): Exact mass calcd for $\text{C}_{17}\text{H}_9\text{ClF}_9\text{N}_2^+$ $[\text{M}+1]^+$ 447.0305, found 447.0306.

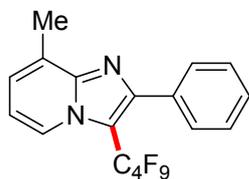
7-bromo-3-(perfluorobutyl)-2-phenylimidazo[1,2-a]pyridine (3t)



3t

Colloidal solid, 74 mg; yield: 75%. ^1H NMR (600 MHz, CDCl_3): δ = 8.17 (d, J = 7.6 Hz, 1H), 7.95 (s, 1H), 7.61-7.63 (m, 2H), 7.45-7.47 (m, 3H), 7.09-7.10 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ = 151.4, 146.9, 132.6, 129.5, 129.1, 128.0, 126.1-126.2 (m), 121.5, 120.4, 118.3-118.5 (m), 118.0, 116.3-116.5 (m), 114.4-114.6 (m), 111.2-111.3 (m), 108.2-108.4 (m); ^{19}F NMR (470 MHz, CDCl_3): δ = -80.9 to -80.8 (m, 3F), -106.1 to -106.0 (m, 2F), -121.7 to -121.6 (m, 2F), -125.9 to -125.8 (m, 2F); HRMS (ESI): Exact mass calcd for $\text{C}_{17}\text{H}_9\text{BrF}_9\text{N}_2^+$ $[\text{M}+1]^+$ 490.9800, found 490.9802.

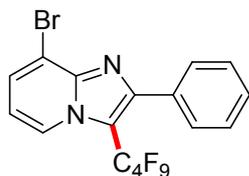
8-methyl-3-(perfluorobutyl)-2-phenylimidazo[1,2-a]pyridine (3u)



3u

Colloidal solid, 64 mg; yield: 75%. ^1H NMR (600 MHz, CDCl_3): δ = 8.20 (d, J = 7.8 Hz, 1H), 7.62-7.64 (m, 2H), 7.44-7.46 (m, 3H), 7.21-7.22 (m, 1H), 6.89-6.92 (m, 1H), 2.71 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ = 150.1, 147.2, 133.4, 129.7, 128.7, 128.3, 127.9, 126.1, 123.6-123.8 (m), 118.1-118.3 (m), 116.3-116.5 (m), 114.7-114.8 (m), 113.9, 113.6, 111.2-111.3 (m), 17.2; ^{19}F NMR (470 MHz, CDCl_3): δ = -80.9 to -80.8 (m, 3F), -106.1 to -106.0 (m, 2F), -121.7 to -121.6 (m, 2F), -125.9 to -125.8 (m, 2F); HRMS (ESI): Exact mass calcd for $\text{C}_{18}\text{H}_{12}\text{F}_9\text{N}_2^+$ $[\text{M}+1]^+$ 427.0851, found 427.0852.

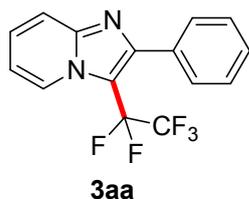
8-bromo-3-(perfluorobutyl)-2-phenylimidazo[1,2-a]pyridine (3v)



3v

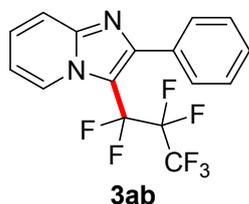
Colloidal solid, 64 mg; yield: 66%. ^1H NMR (600 MHz, CDCl_3): δ = 8.32 (d, J = 7.8 Hz, 1H), 7.68-7.70 (m, 1H), 7.62-7.64 (m, 2H), 7.44-7.46 (m, 3H), 6.87-6.89 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ = 151.3, 144.8, 132.8, 129.8, 129.6, 129.0, 127.9, 125.2-125.3 (m), 118.1-118.3 (m), 116.2-116.4 (m), 114.4-114.6 (m), 114.0, 112.7-112.8 (m), 112.3, 109.6-109.7 (m); ^{19}F NMR (470 MHz, CDCl_3): δ = -80.9 to -80.8 (m, 3F), -106.3 to -106.2 (m, 2F), -121.7 to -121.6 (m, 2F), -125.9 to -125.8 (m, 2F); HRMS (ESI): Exact mass calcd for $\text{C}_{17}\text{H}_9\text{BrF}_9\text{N}_2^+$ $[\text{M}+1]^+$ 490.9800, found 490.9802.

3-(perfluoroethyl)-2-phenylimidazo[1,2-a]pyridine (3aa)



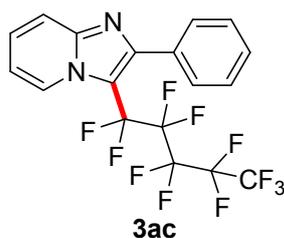
Colloidal solid, 51 mg; yield: 83%. ^1H NMR (600 MHz, CDCl_3): δ = 8.23 (d, J = 7.4 Hz, 1H), 7.67-7.69 (m, 1H), 7.54-7.56 (m, 2H), 7.31-7.38 (m, 4H), 6.89-6.92 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ = 150.2, 146.7, 133.1, 129.5, 128.8, 128.0, 127.1, 125.9-126.0 (m), 127.6-127.8 (m), 118.1, 114.0, 111.7-111.9 (m), 107.4-107.6 (m); ^{19}F NMR (470 MHz, CDCl_3): δ = -83.8 to -83.7 (m, 3F), -110.5 to -110.4 (m, 2F); HRMS (ESI): Exact mass calcd for $\text{C}_{15}\text{H}_{10}\text{F}_5\text{N}_2^+$ $[\text{M}+1]^+$ 313.0759, found 313.0760.

3-(perfluoropropyl)-2-phenylimidazo[1,2-a]pyridine (3ab)



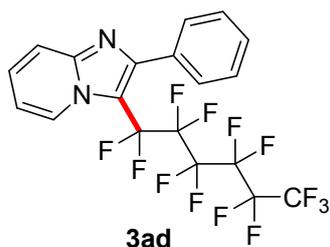
Colloidal solid, 61 mg; yield: 85%. ^1H NMR (600 MHz, CDCl_3): δ = 8.35 (d, J = 7.4 Hz, 1H), 7.82-7.84 (m, 1H), 7.63-7.65 (m, 2H), 7.44-7.48 (m, 4H), 7.02-7.04 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ = 150.1, 146.5, 132.6, 129.6, 128.0, 127.6, 125.9-126.1 (m), 118.6-118.7 (m), 118.0, 116.6-116.8 (m), 115.6-115.7 (m), 114.2, 107.6-107.7 (m); ^{19}F NMR (470 MHz, CDCl_3): δ = -80.1 to -80.0 (m, 3F), -106.6 to -106.7 (m, 2F), -125.1 to -125.2 (m, 2F); HRMS (ESI): Exact mass calcd for $\text{C}_{16}\text{H}_{10}\text{F}_7\text{N}_2^+$ $[\text{M}+1]^+$ 563.0727, found 563.0727.

3-(perfluoropentyl)-2-phenylimidazo[1,2-a]pyridine (3ac)



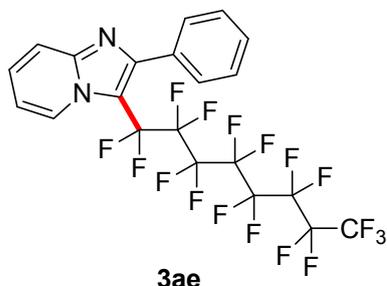
Colloidal solid, 73 mg; yield: 80%. ^1H NMR (600 MHz, CDCl_3): δ = 8.33 (d, J = 7.9 Hz, 1H), 7.77-7.79 (m, 1H), 7.61-7.63 (m, 2H), 7.41-7.45 (m, 4H), 6.98-7.01 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ = 150.6, 146.7, 132.9, 129.6, 128.9, 128.0, 127.5, 125.9-126.0 (m), 118.1, 116.2-116.3 (m), 114.9-115.0 (m), 114.1, 113.0-113.1 (m), 111.9-112.0 (m), 110.4-110.5 (m), 107.7-108.0 (m); ^{19}F NMR (470 MHz, CDCl_3): δ = -62.7 (s, 3F), -80.8 to -80.9 (m, 2F), -106.1 to -106.2 (m, 2F), -121.6 to -121.7 (m, 2F), -125.8 to -125.9 (m, 2F); HRMS (ESI): Exact mass calcd for $\text{C}_{18}\text{H}_{10}\text{F}_7\text{N}_2^+$ $[\text{M}+1]^+$ 463.0663, found 463.0665.

3-(perfluorohexyl)-2-phenylimidazo[1,2-a]pyridine (3ad)



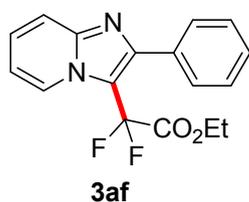
Colloidal solid, 74 mg; yield: 73%. ¹H NMR (600 MHz, CDCl₃): δ = 8.23 (d, J = 7.9 Hz, 1H), 7.66-7.68 (m, 1H), 7.53-7.54 (m, 2H), 7.18-7.36 (m, 4H), 6.87-6.90 (m, 1H); ¹³C NMR (125 MHz, CDCl₃): δ = 150.7, 146.8, 133.1, 129.5, 128.8, 127.9, 127.3, 125.9-126.0 (m), 118.1, 116.1-116.2 (m), 114.9-115.0 (m), 114.0-114.1 (m), 113.1-113.2 (m), 111.9-112.0 (m), 111.0-111.1 (m), 110.1-110.2 (m), 107.8-108.0 (m); ¹⁹F NMR (470 MHz, CDCl₃): δ = -80.8 to -80.7 (t, J = 14.1 Hz, 3F), -105.9 to -105.8 (m, 2F), -120.8 to -120.7 (m, 2F), -121.8 to -121.7 (m, 2F), -122.7 to -122.6 (m, 2F), -126.1 to -126.0 (m, 2F); HRMS (ESI): Exact mass calcd for C₁₉H₁₀F₁₃N₂⁺ [M+1]⁺ 513.0631, found 513.0633.

3-(perfluorooctyl)-2-phenylimidazo[1,2-a]pyridine (3ae)



Colloidal solid, 86 mg; yield: 71%. ¹H NMR (600 MHz, CDCl₃): δ = 8.37 (d, J = 7.6 Hz, 1H), 7.90-7.92 (m, 1H), 7.64-7.68 (m, 2H), 7.47-7.52 (m, 4H), 7.08 (t, J = 5.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ = 150.7, 146.6, 133.1, 129.4, 128.8, 127.9, 127.5, 125.9-126.1 (m), 118.3, 116.1-116.3 (m), 114.9-115.1 (m), 114.0-114.1 (m), 113.0-113.2 (m), 111.9-112.1 (m), 111.0-111.2 (m), 110.1-110.2 (m), 107.8-108.2 (m); ¹⁹F NMR (470 MHz, CDCl₃): δ = -80.7 to -80.5 (t, J = 14.9 Hz, 3F), -106.0 to -106.9 (m, 2F), -120.6 to -120.5 (m, 2F), -121.8 to -121.4 (m, 2F), -122.6 to -122.5 (m, 2F), -126.1 to -126.0 (m, 2F); HRMS (ESI): Exact mass calcd for C₂₁H₁₀F₁₇N₂⁺ [M+1]⁺ 613.0567, found 613.0568.

ethyl 2,2-difluoro-2-(2-phenylimidazo[1,2-a]pyridin-3-yl)acetate (3af)



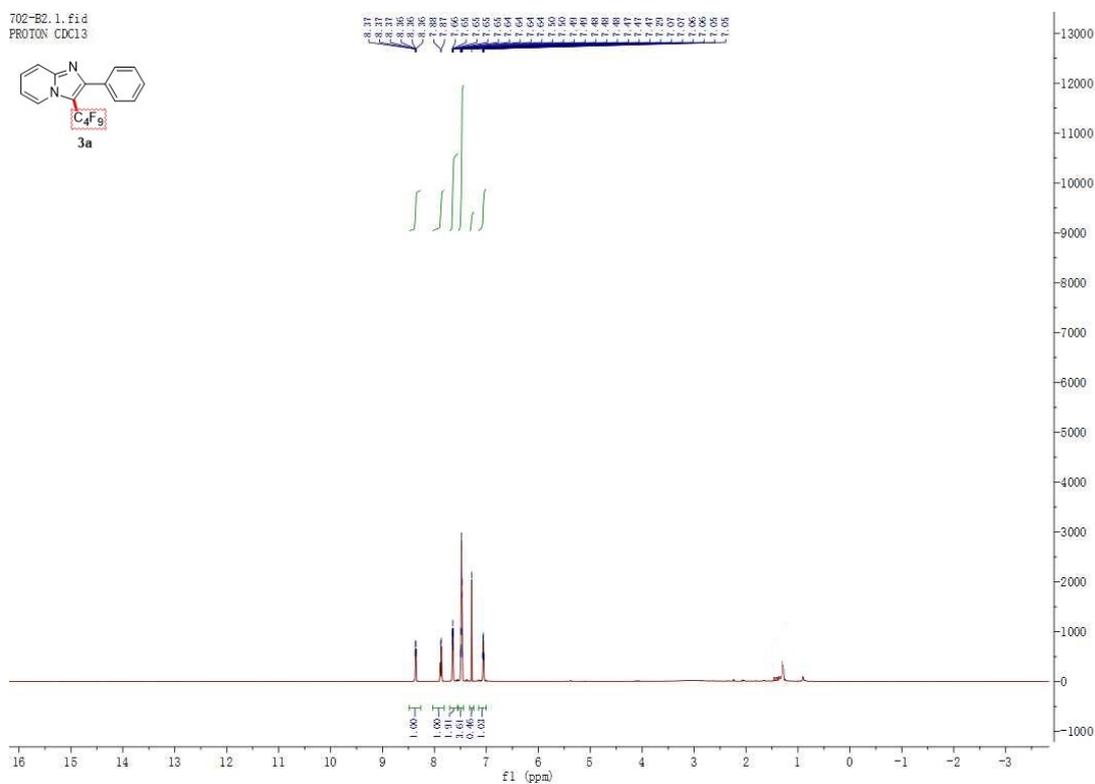
Colloidal solid, 38 mg; yield: 61%. ¹H NMR (600 MHz, CDCl₃): δ = 8.56 (d, J = 7.4 Hz, 1H), 7.77-7.79 (m, 1H), 7.66-7.68 (m, 2H), 7.40-7.49 (m, 4H), 6.99-7.02 (m, 1H), 4.00 (t, J = 4.0 Hz, 2H), 1.17 (t, J 4.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ = 162.3 (t, J_{F-C} = 126.9 Hz), 145.9, 132.9, 129.6, 128.9, 128.1, 127.0, 126.6 (t, J_{F-C} = 23.5 Hz), 117.7, 113.6, 111.3, 109.4, 99.9, 63.7, 13.6; ¹⁹F NMR (470 MHz, CDCl₃): δ = -98.6 (s, 2F); HRMS (ESI): Exact mass

calcd for $C_{21}H_{10}F_{17}N_2^+$ $[M+1]^+$ 613.0567, found 613.0568.

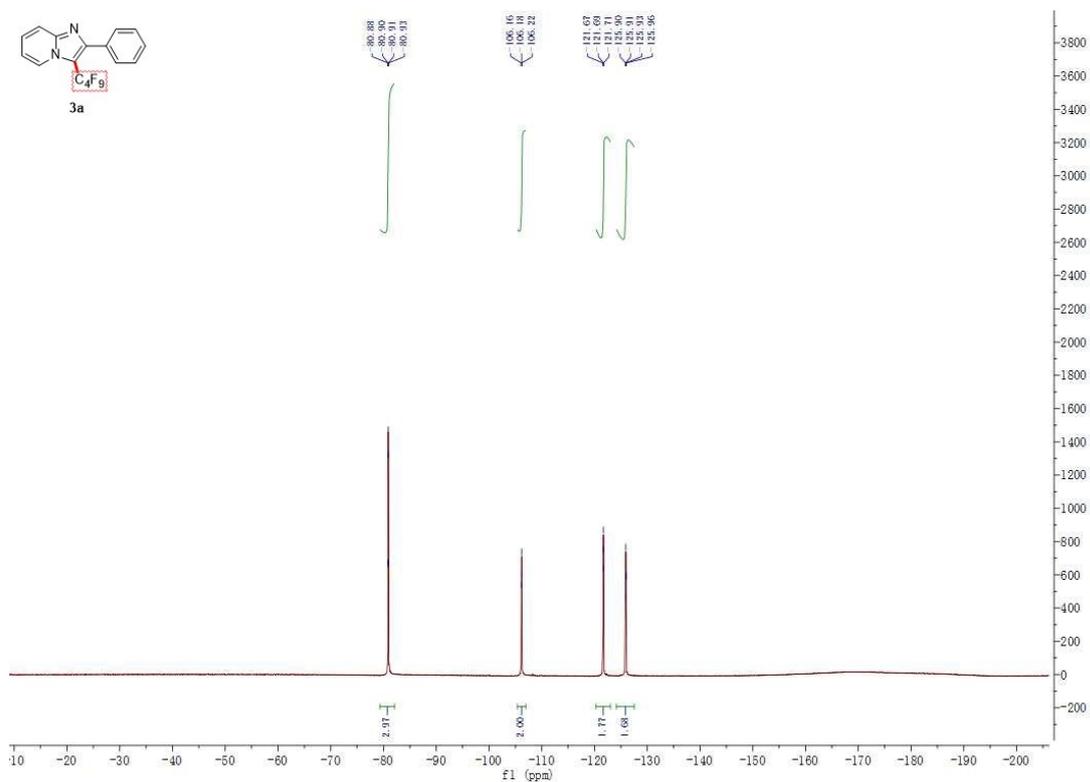
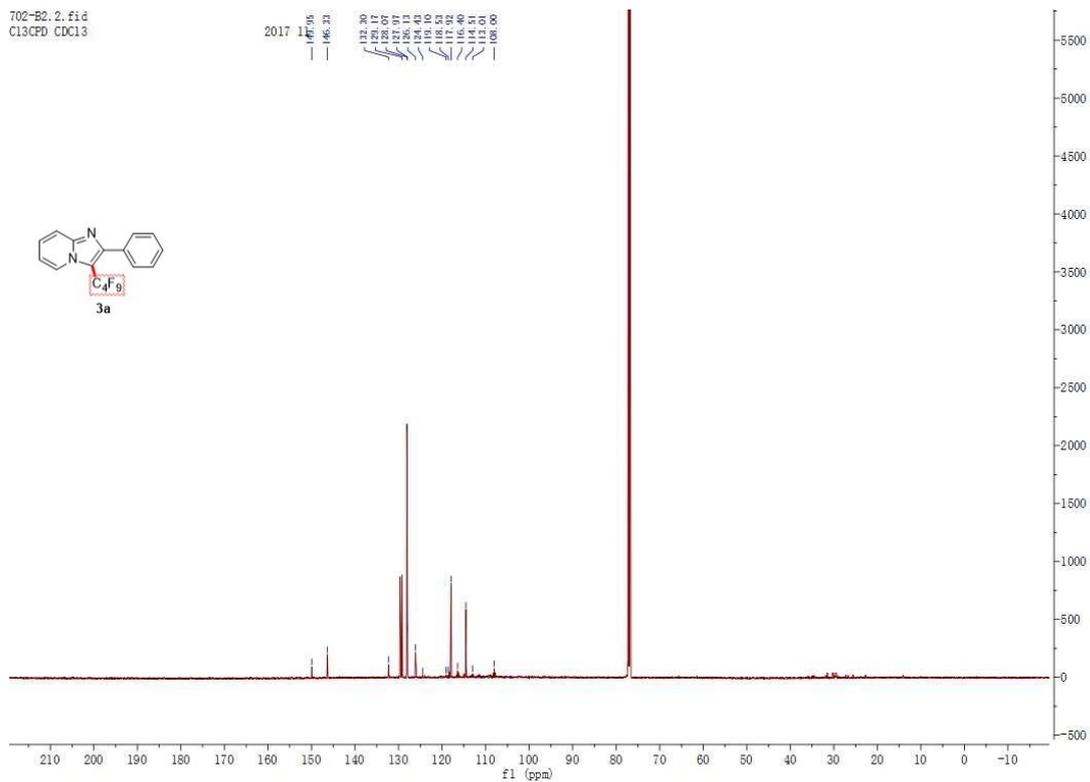
8. References

- [1] (a) S.-Y. Takizawa, J.-I. Nishida, T. Tsuzuki, S. Tokito and Y. Ymashita, *Inorg. Chem.*, 2007, **46**, 4308; (b) G. S. Kumar, S. P. Ragini, A. S. Kumar and H. M. Meshram, *RSC Adv.*, 2015, **5**, 51576; (c) A. K. Bagdi, M. Rahman, S. Santra, A. Majee and A. Hajra, *Adv. Synth. Catal.*, 2013, **355**, 1741.

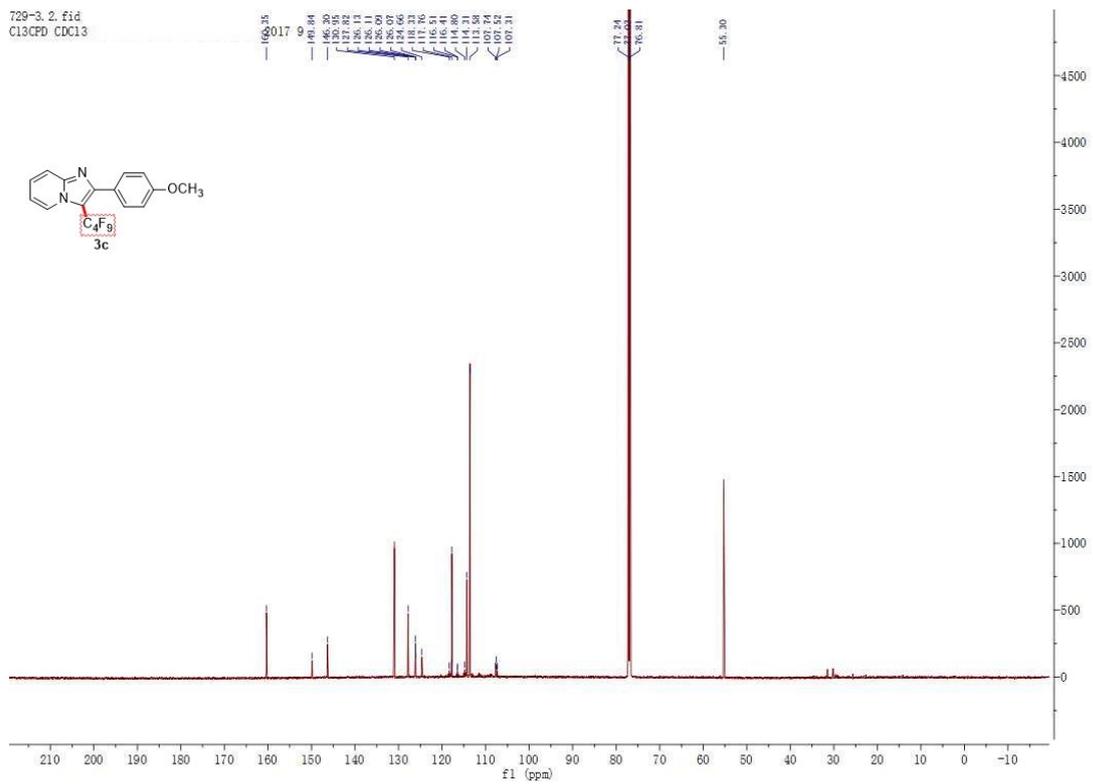
9. Copies of 1H NMR, ^{13}C NMR and ^{19}F NMR Spectra



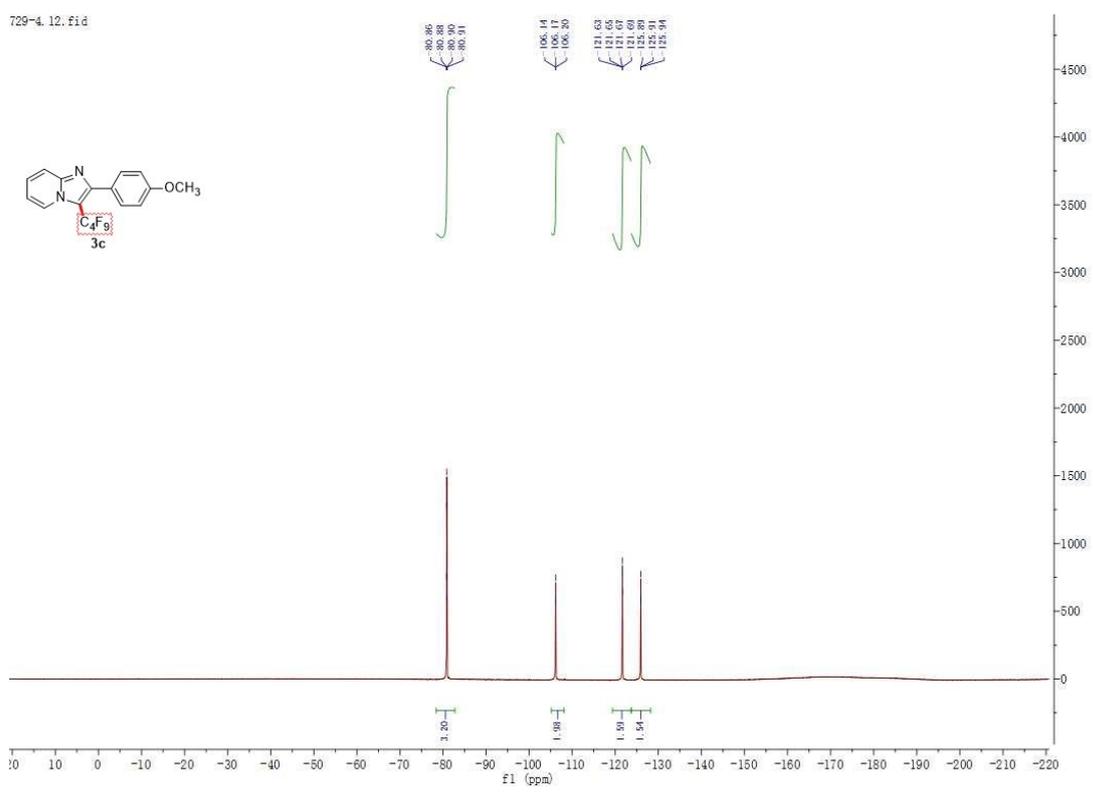
702-B2.2.Fid
C13CPD CDC13



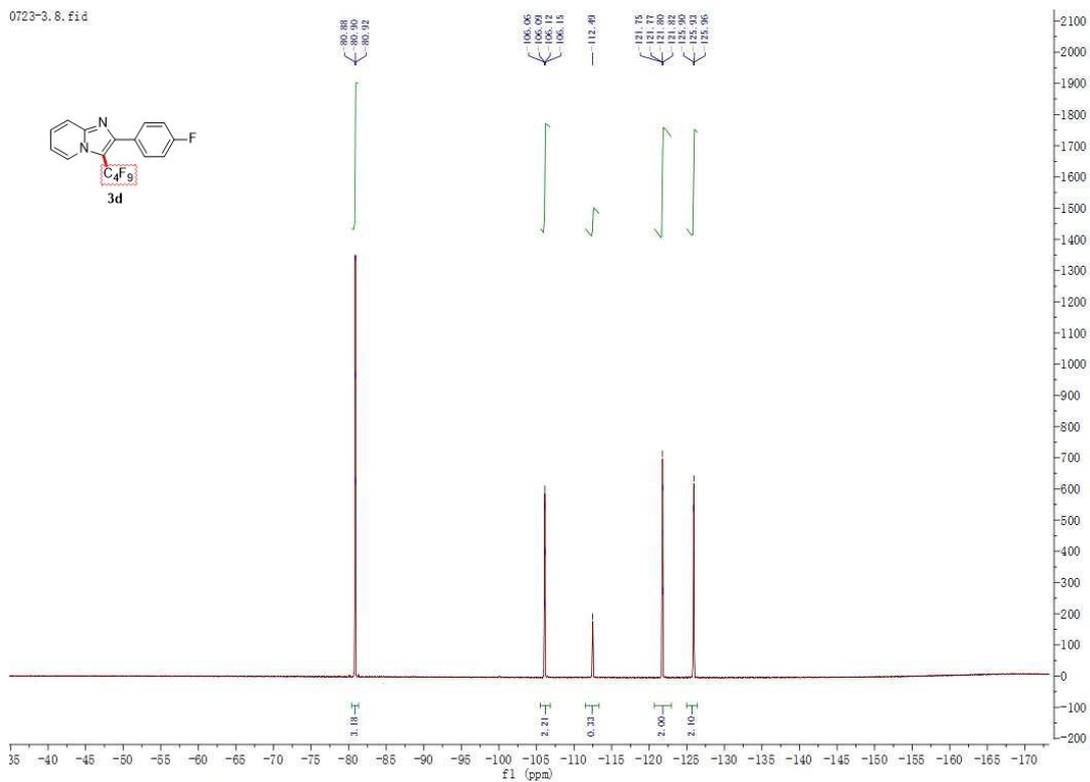
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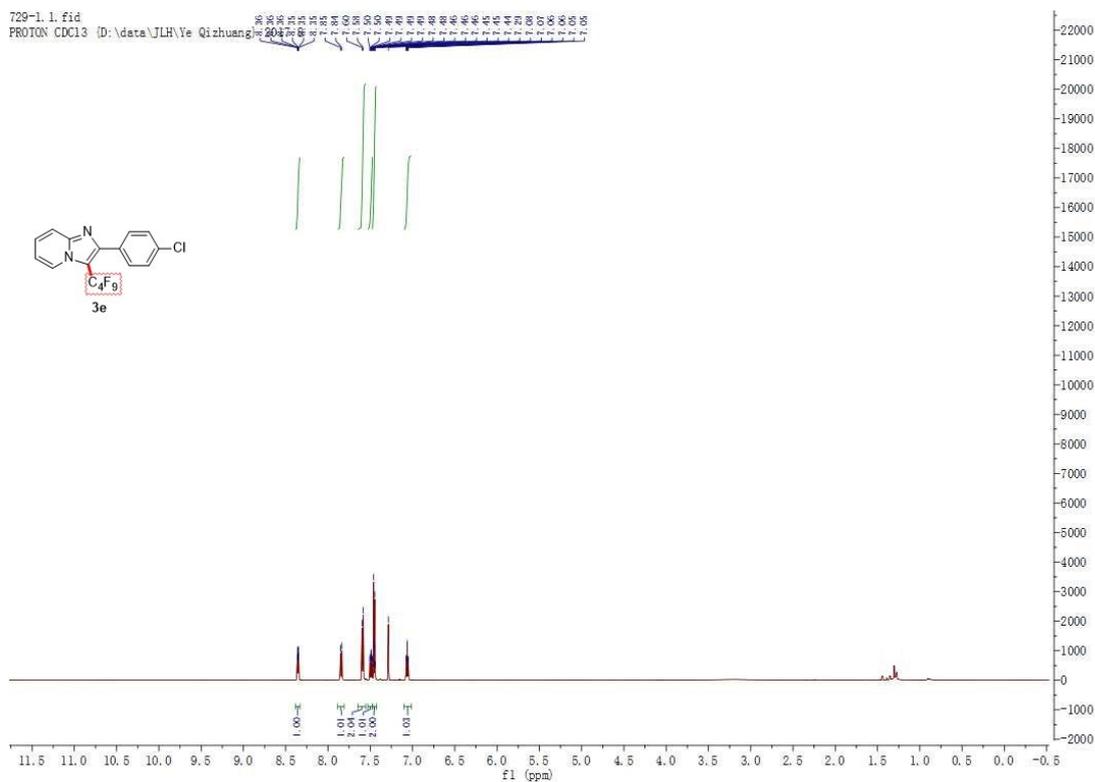
729-4. 12.fid



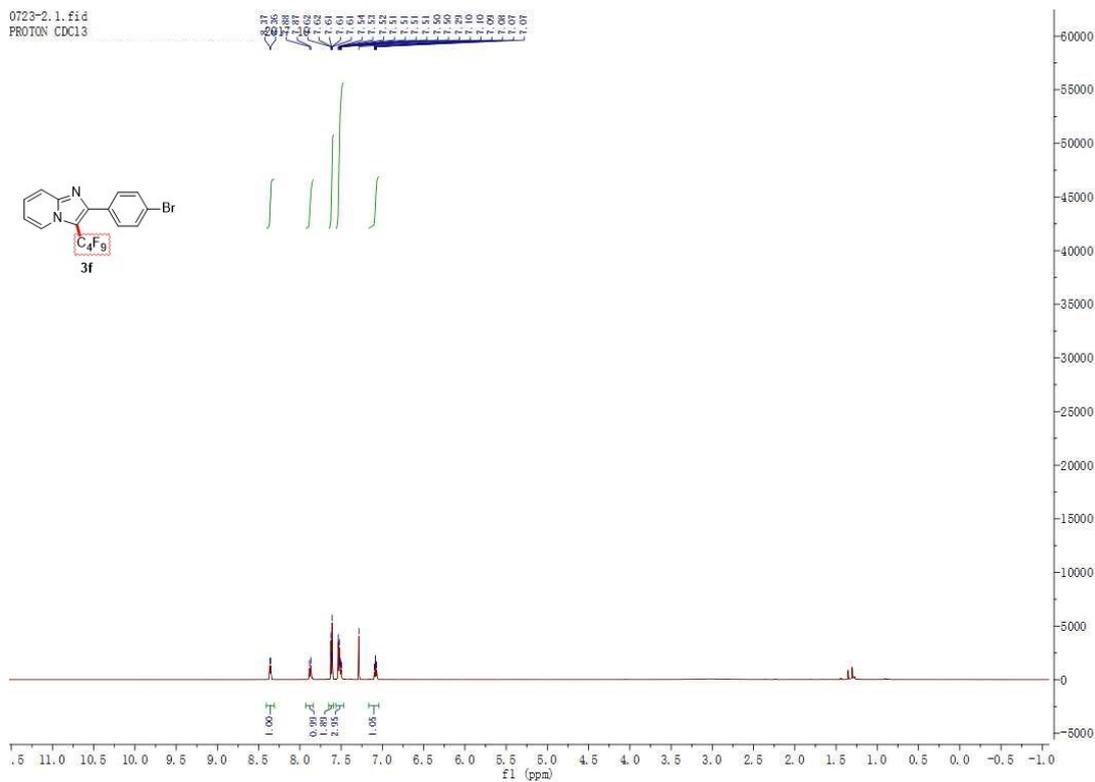
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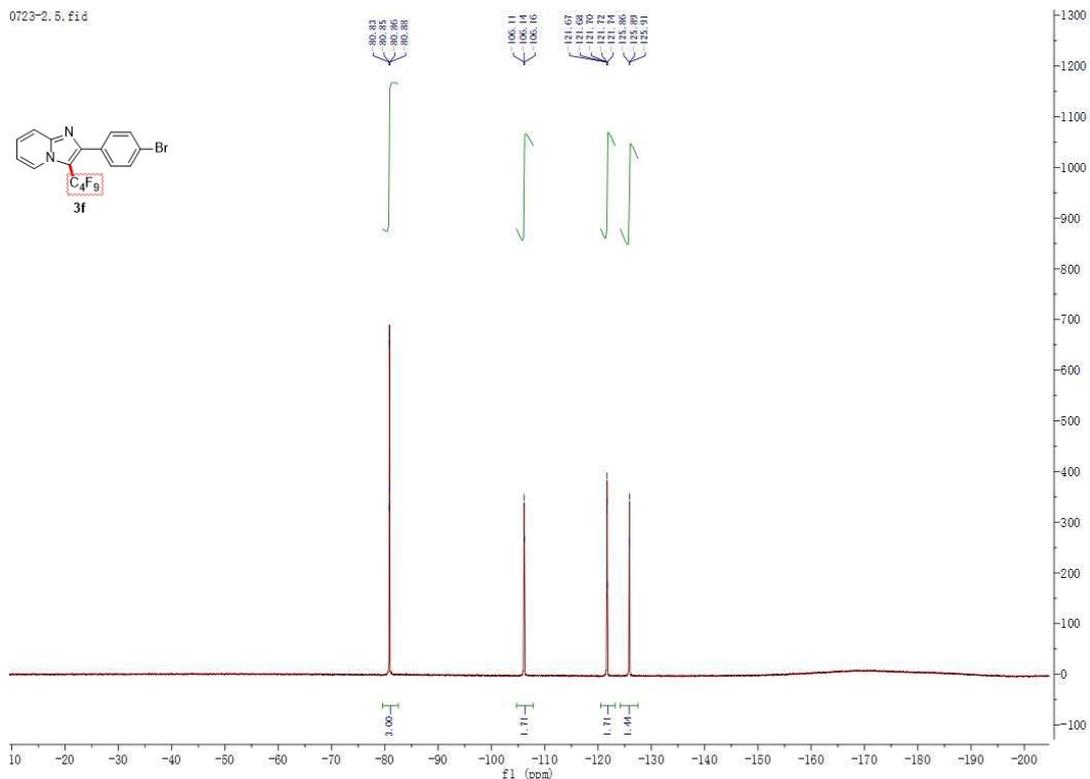
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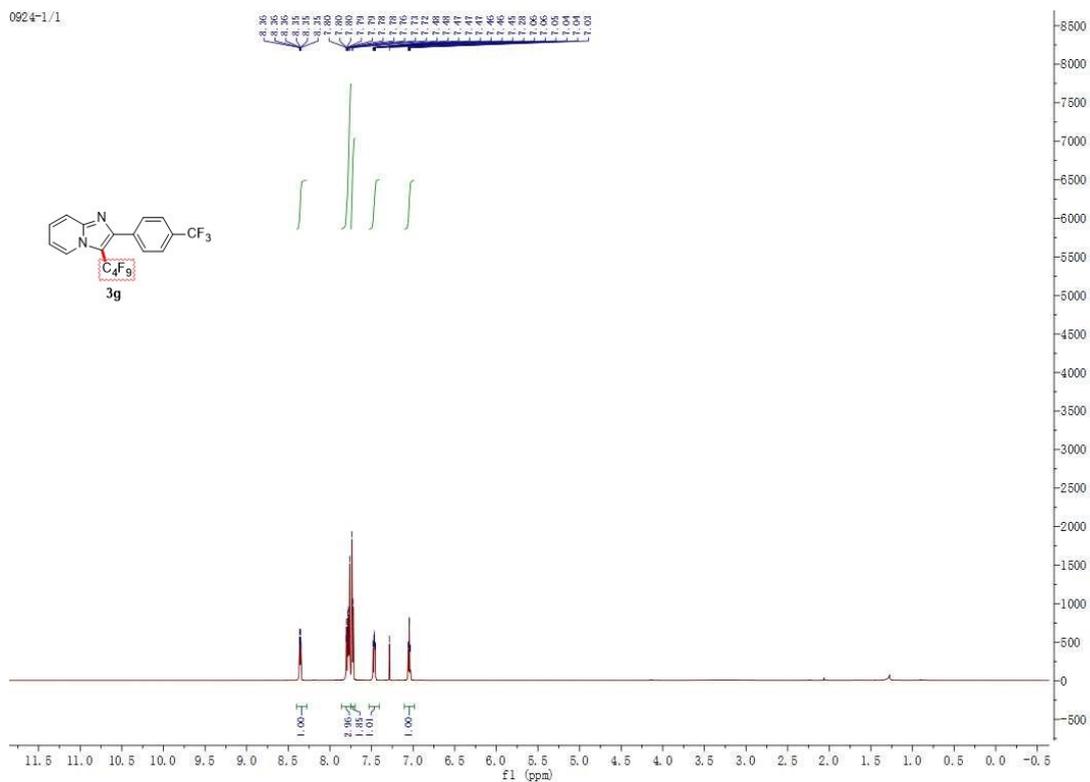
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PROTON CDCl3



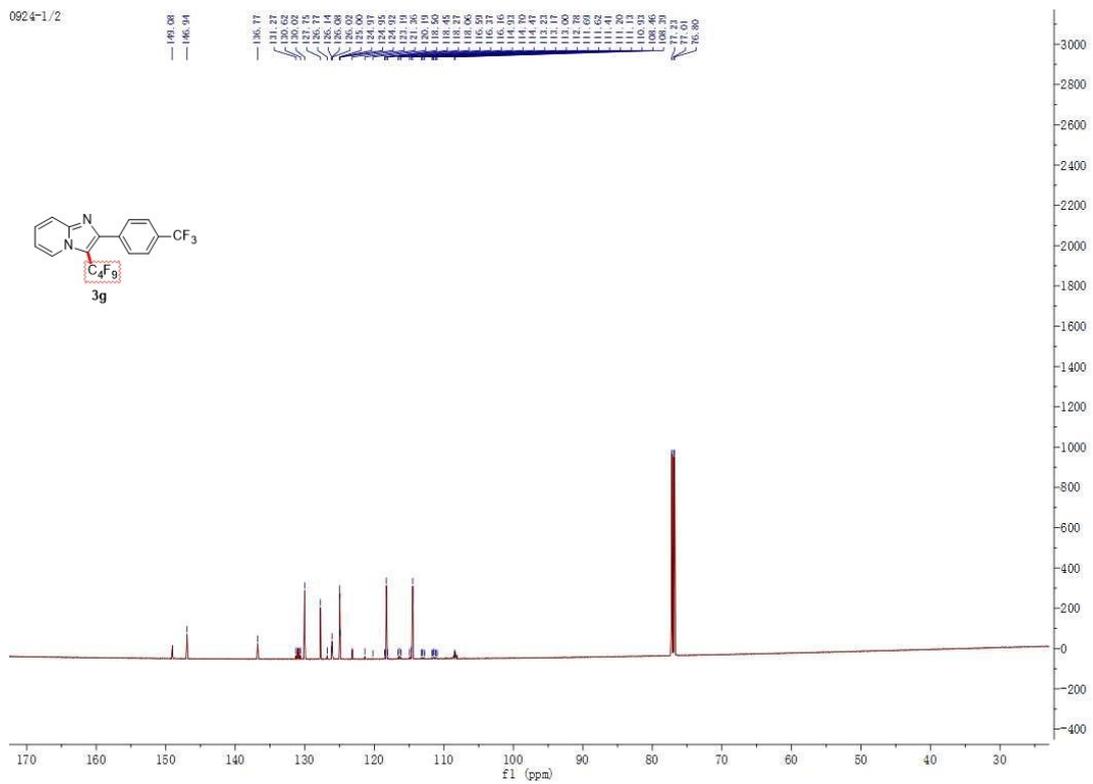
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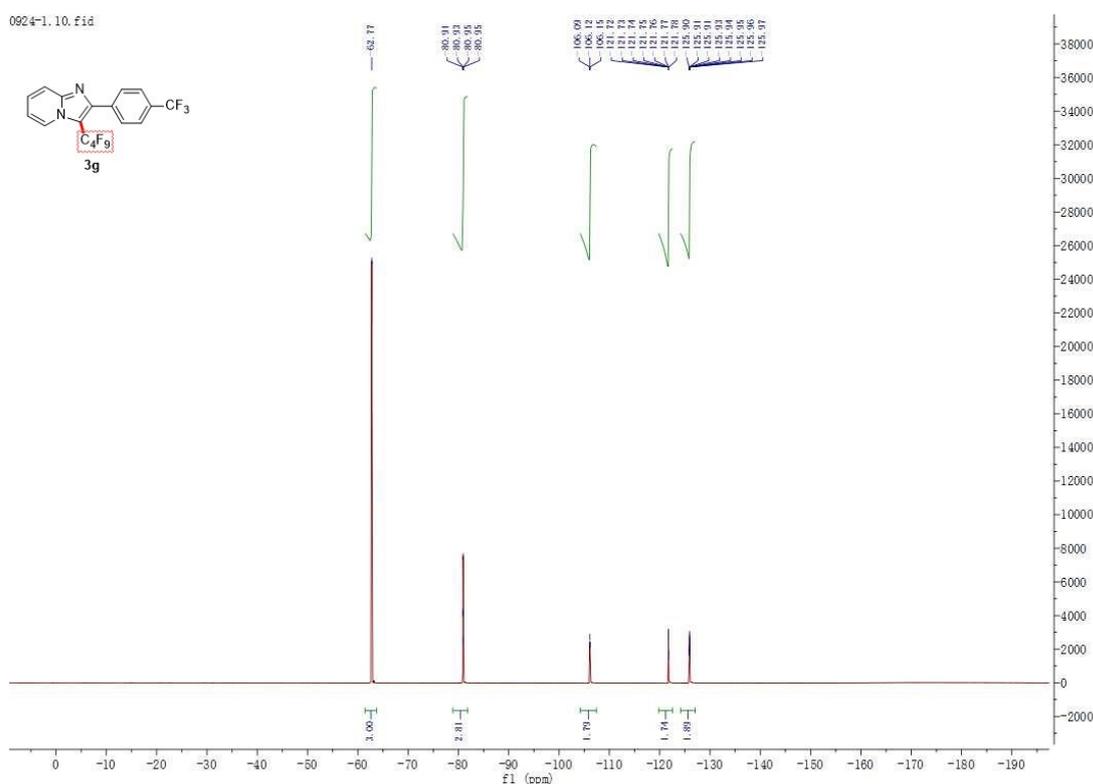
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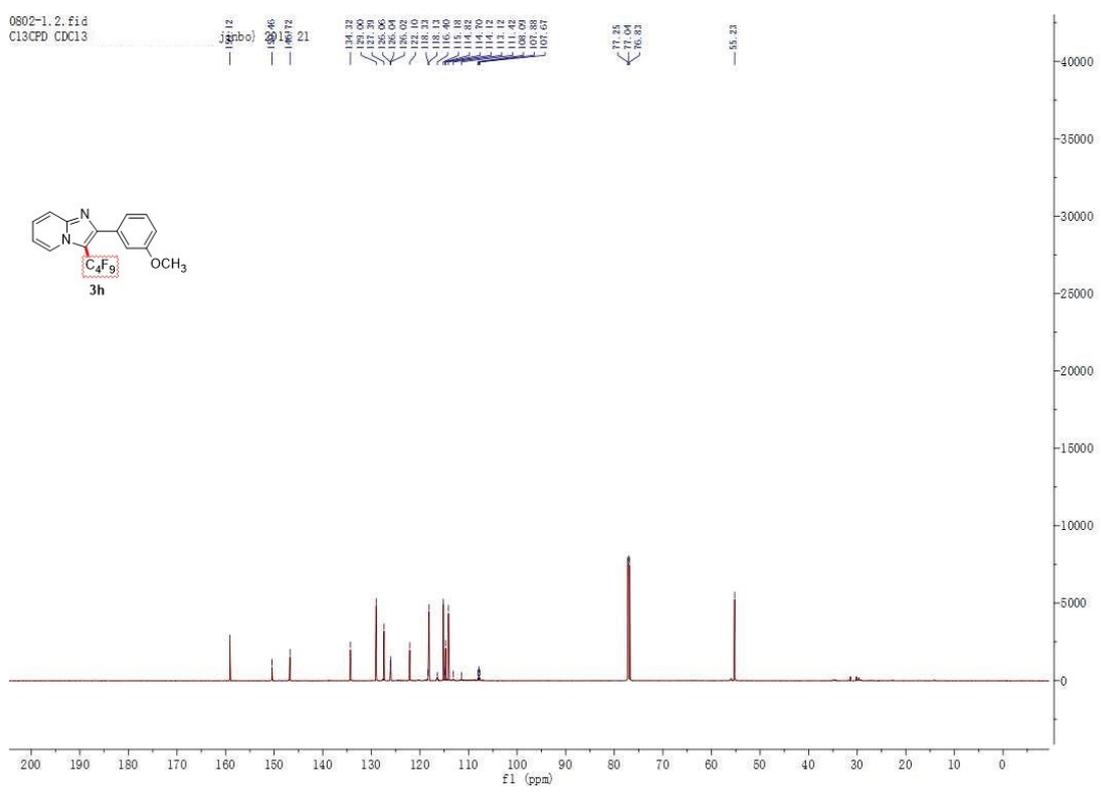
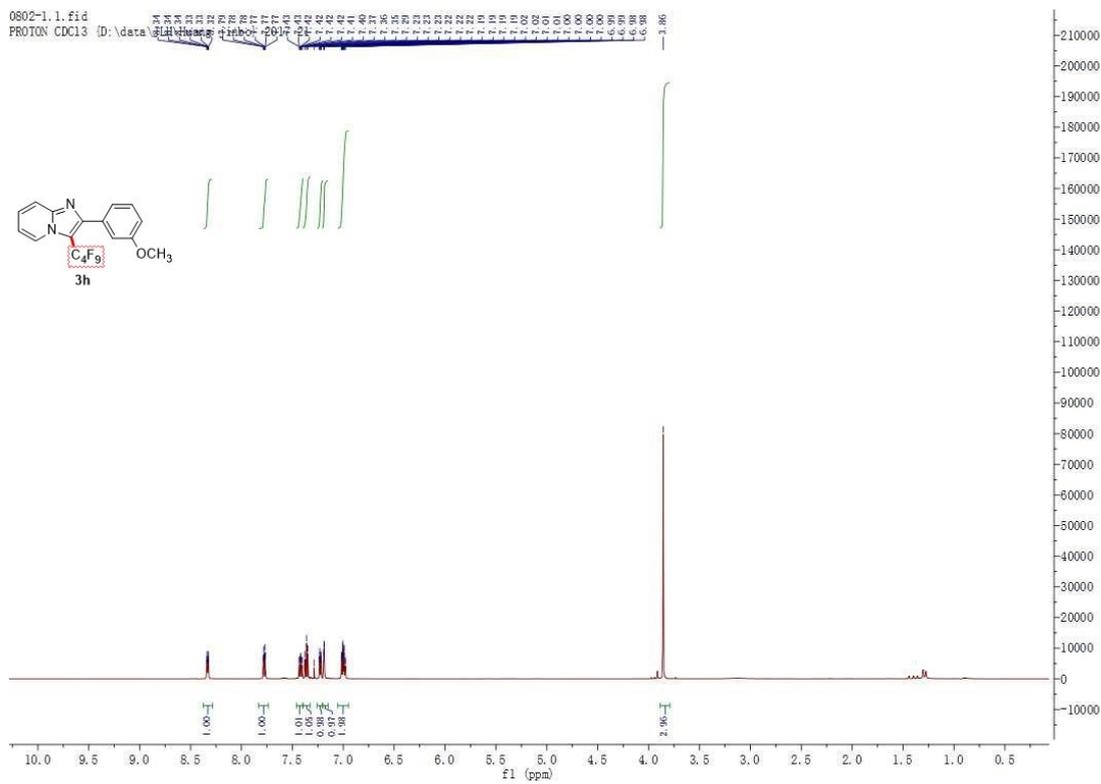


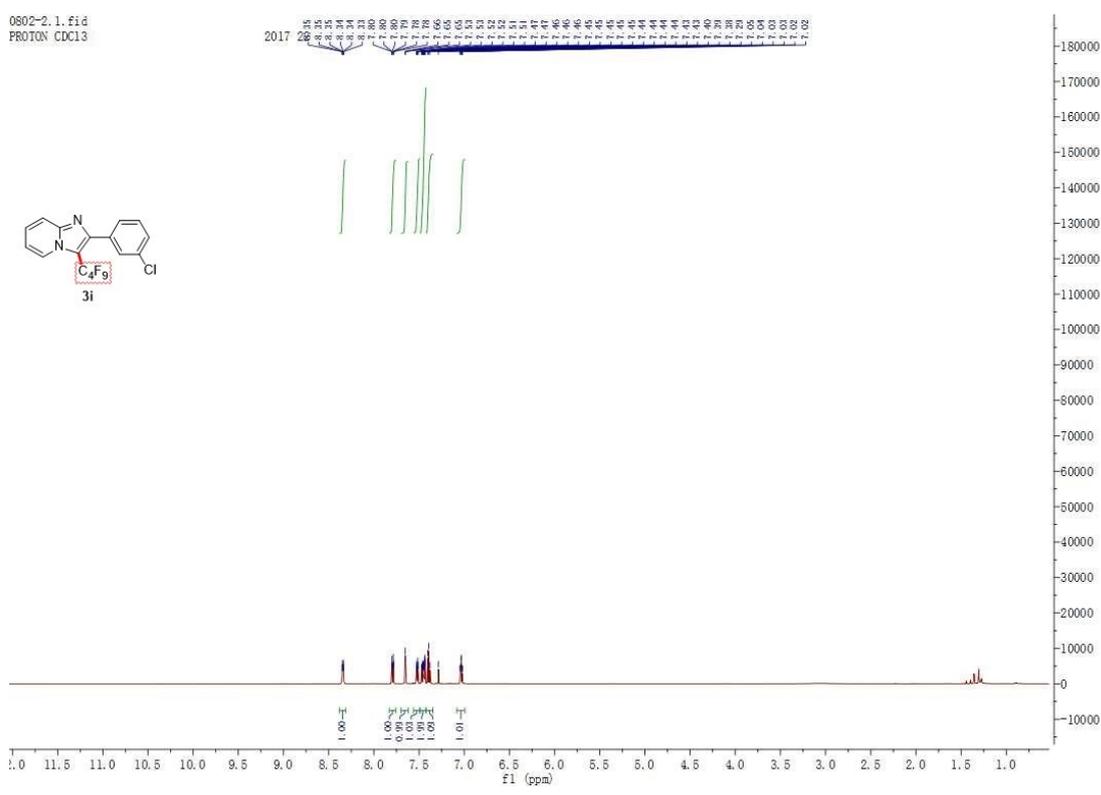
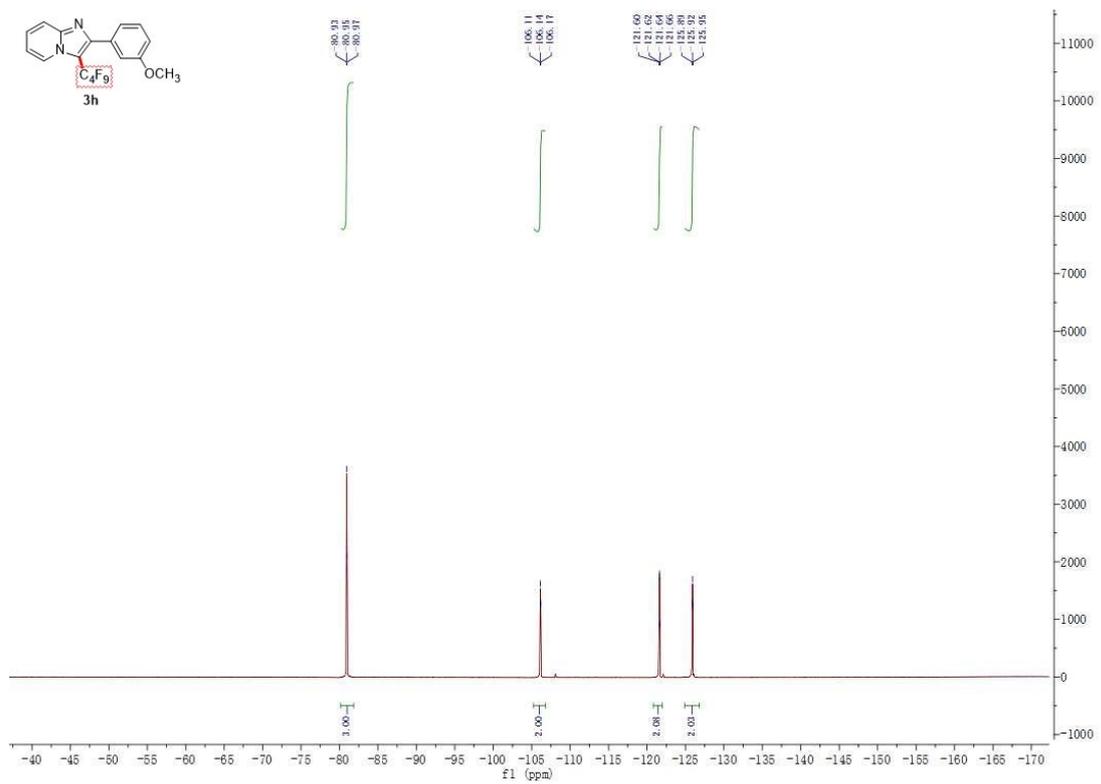
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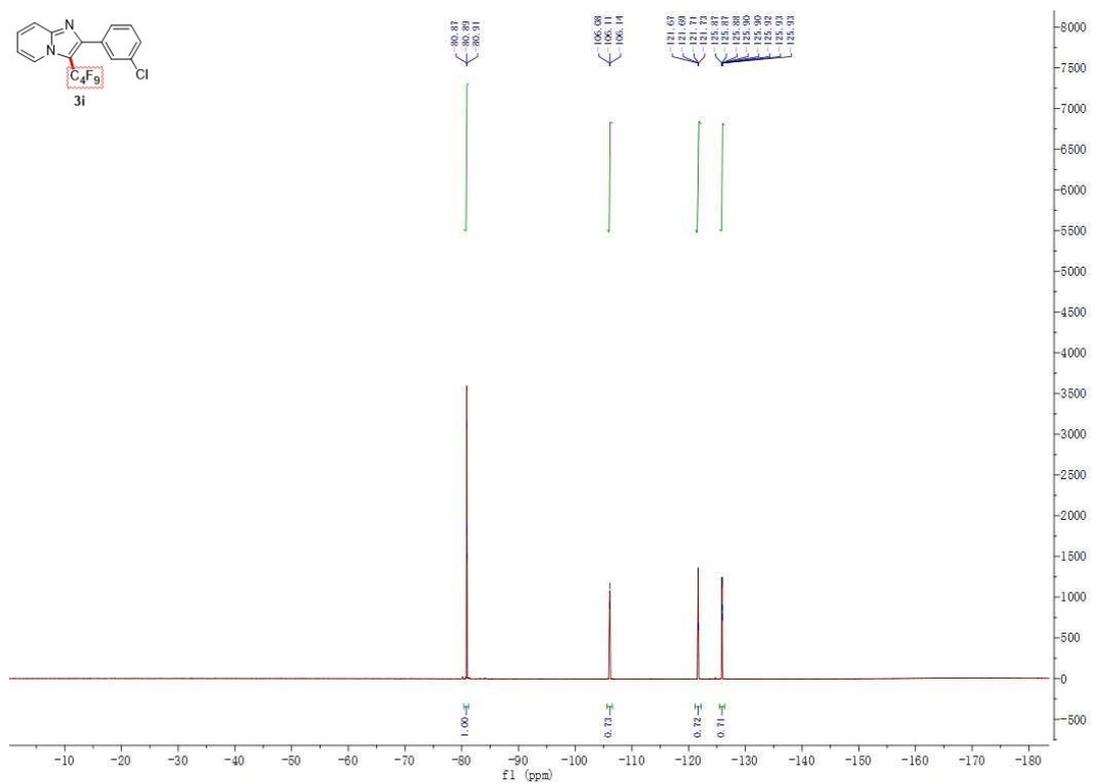
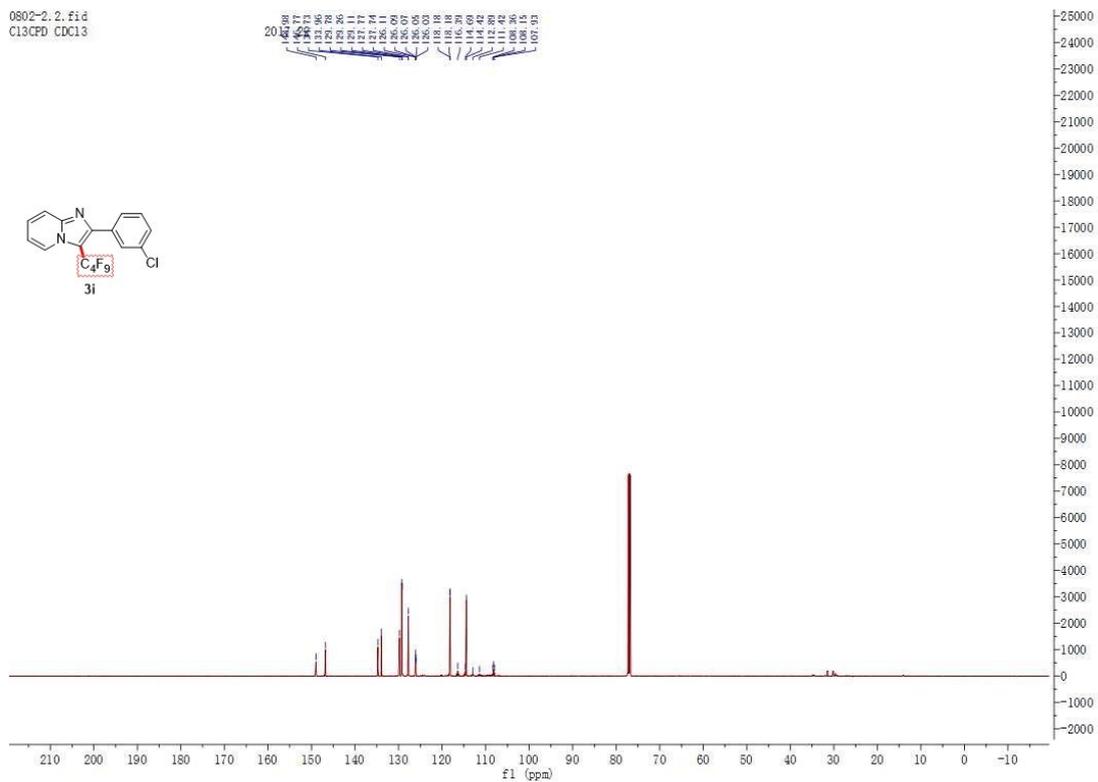
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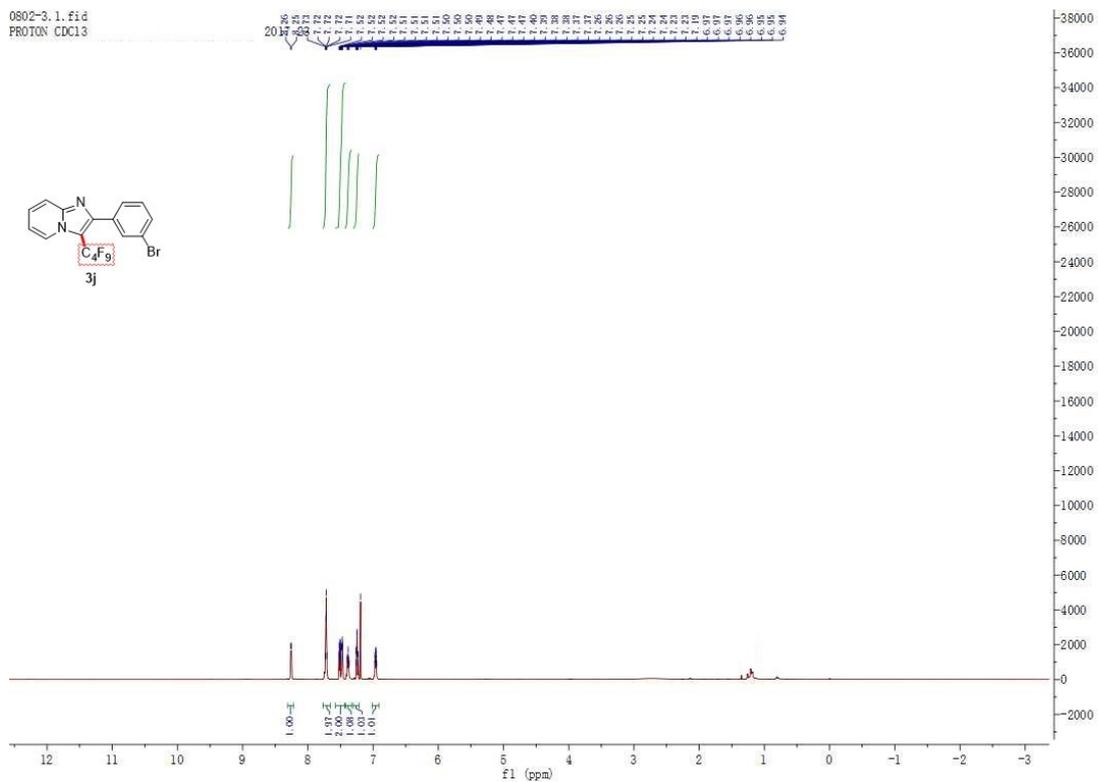




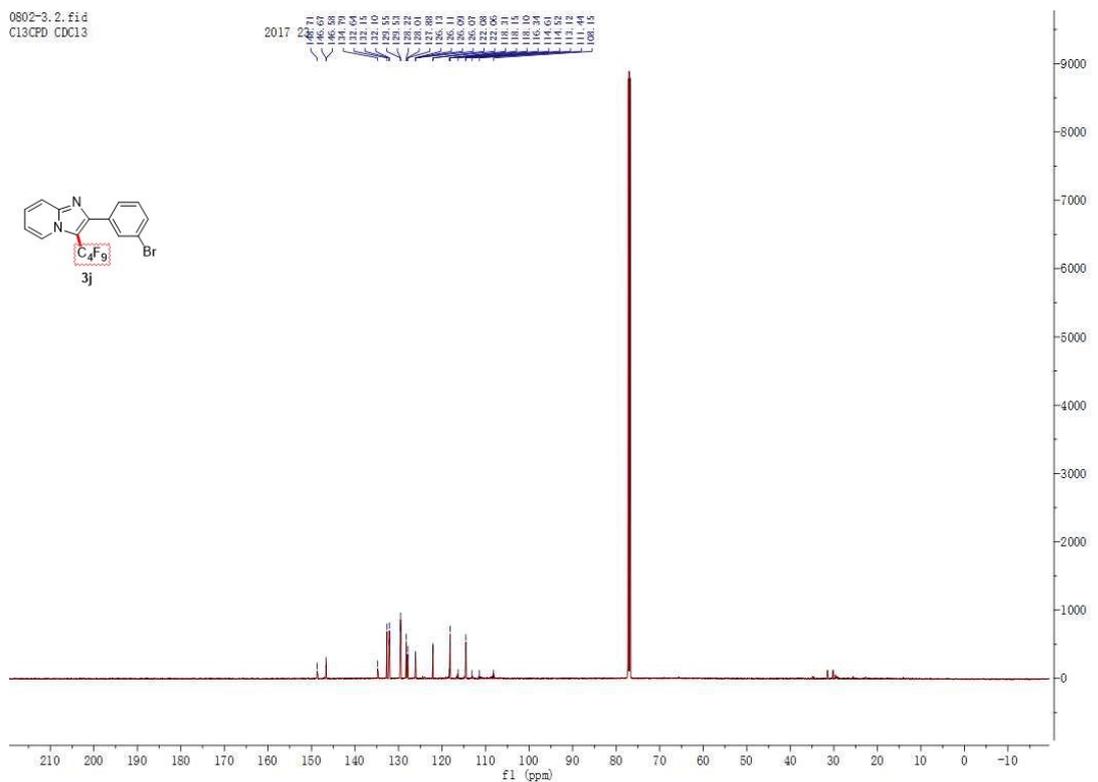
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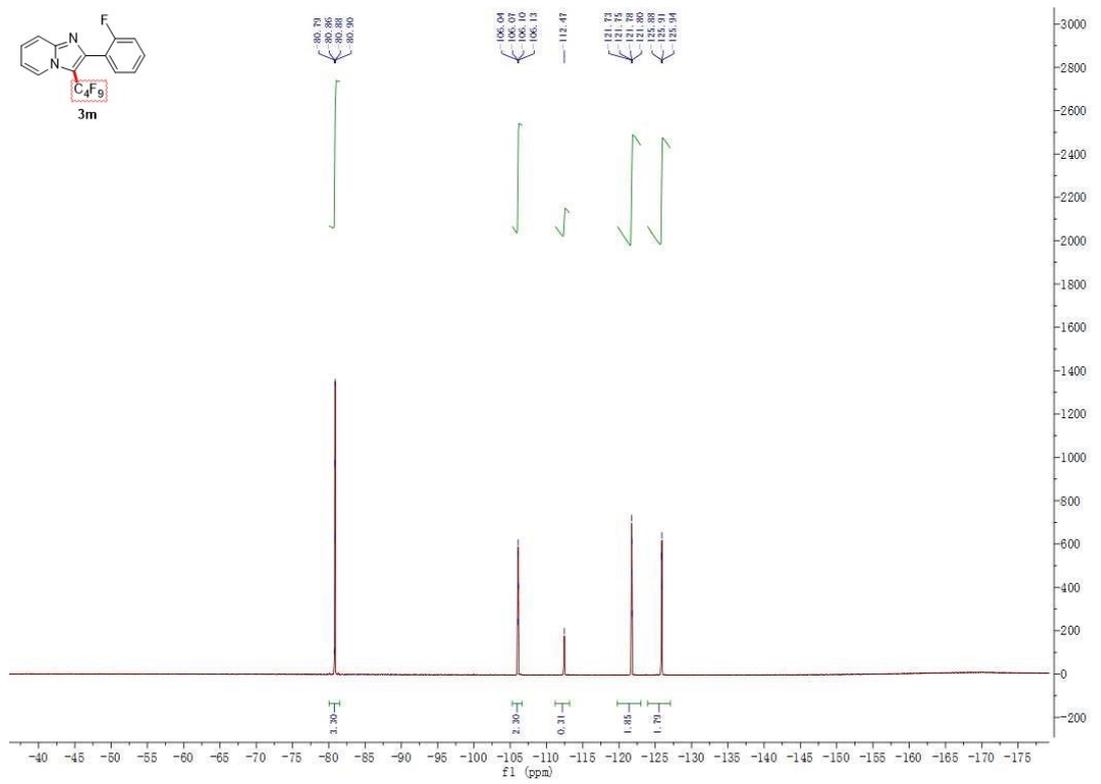
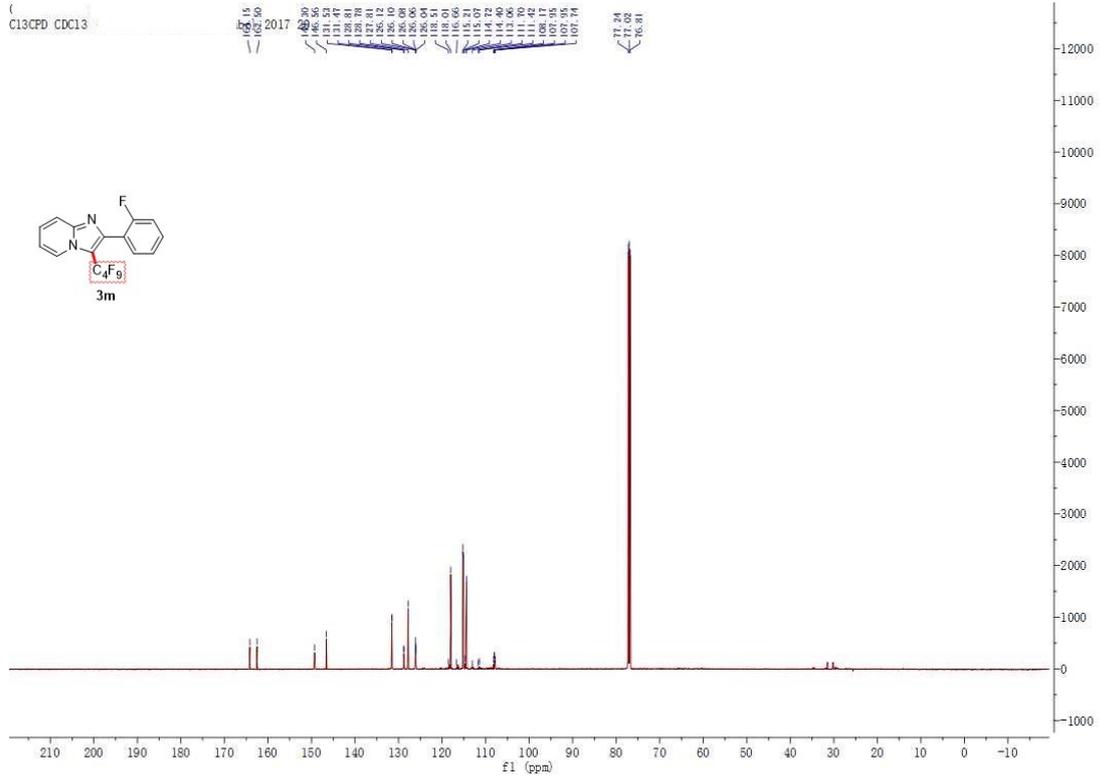
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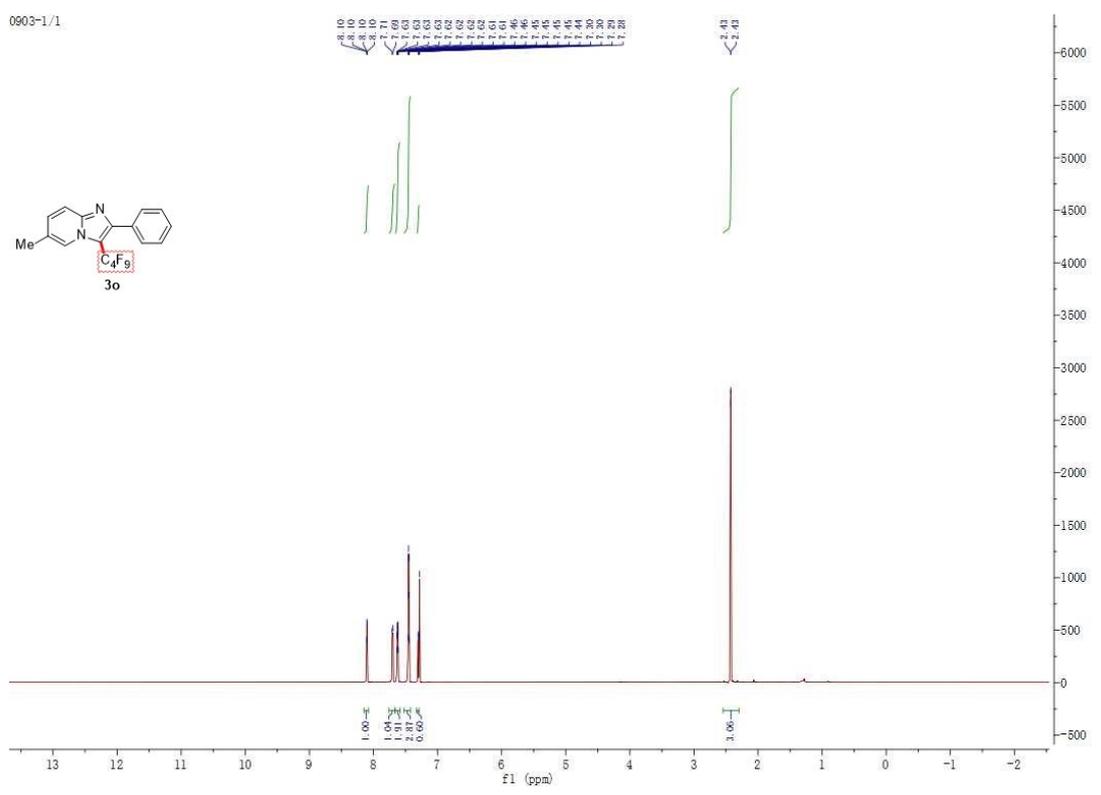
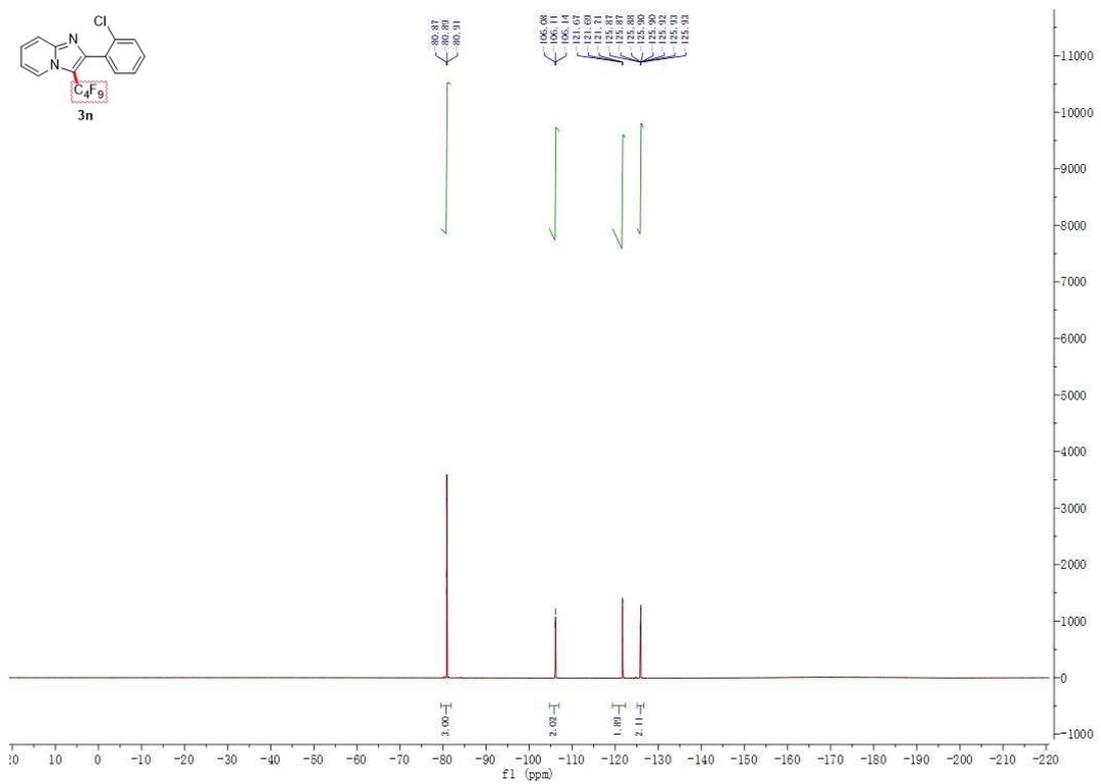


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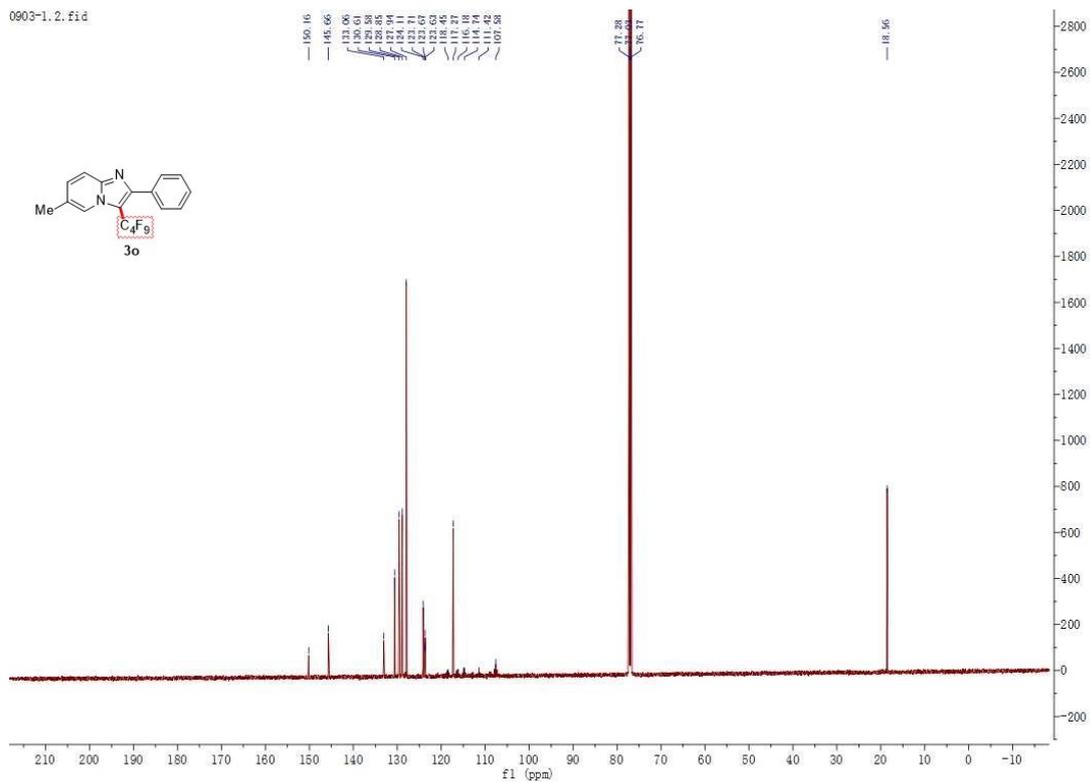


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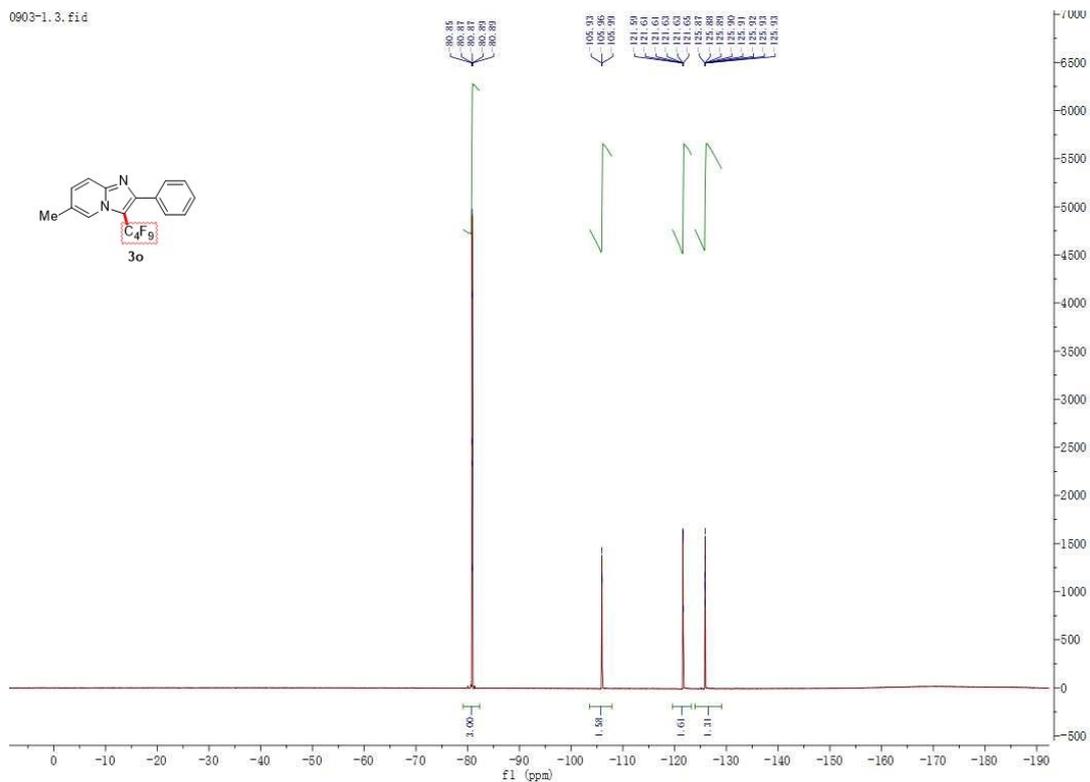




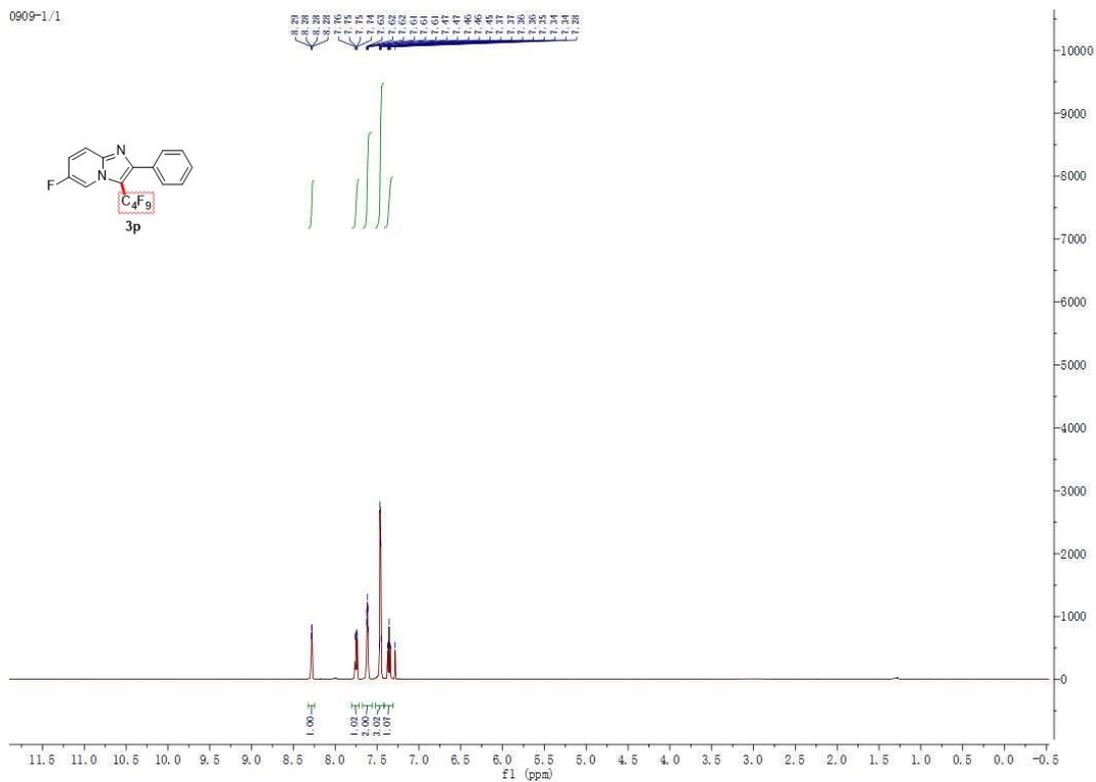
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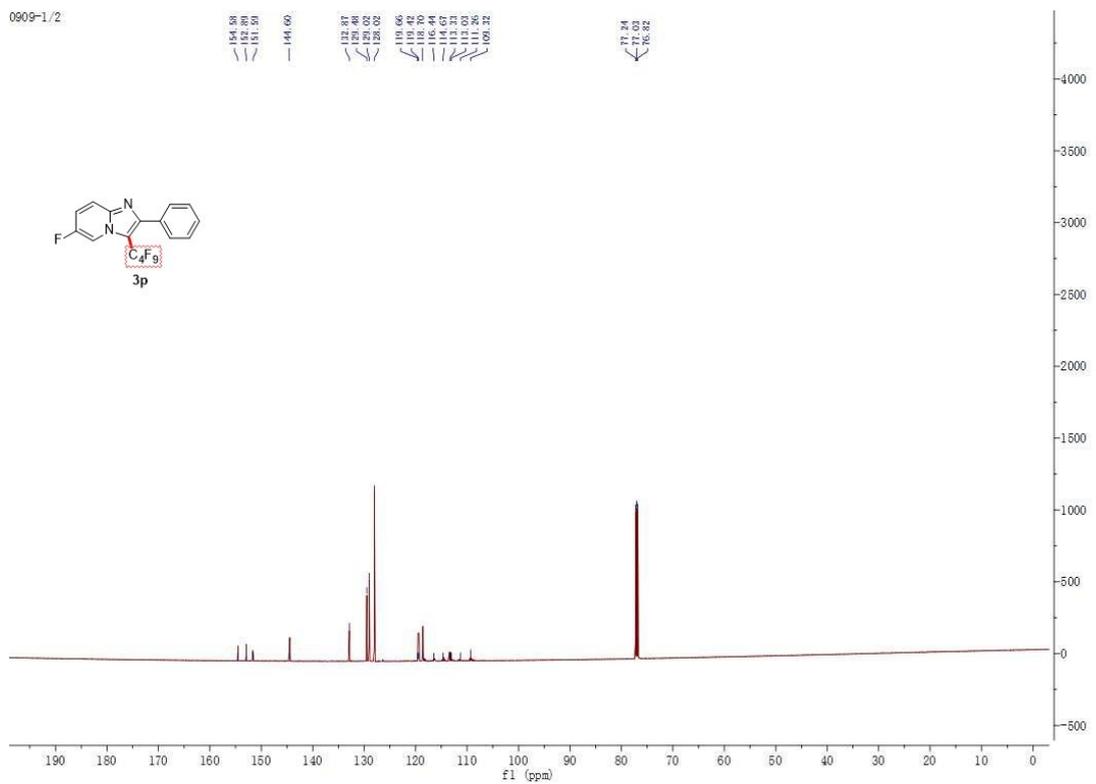
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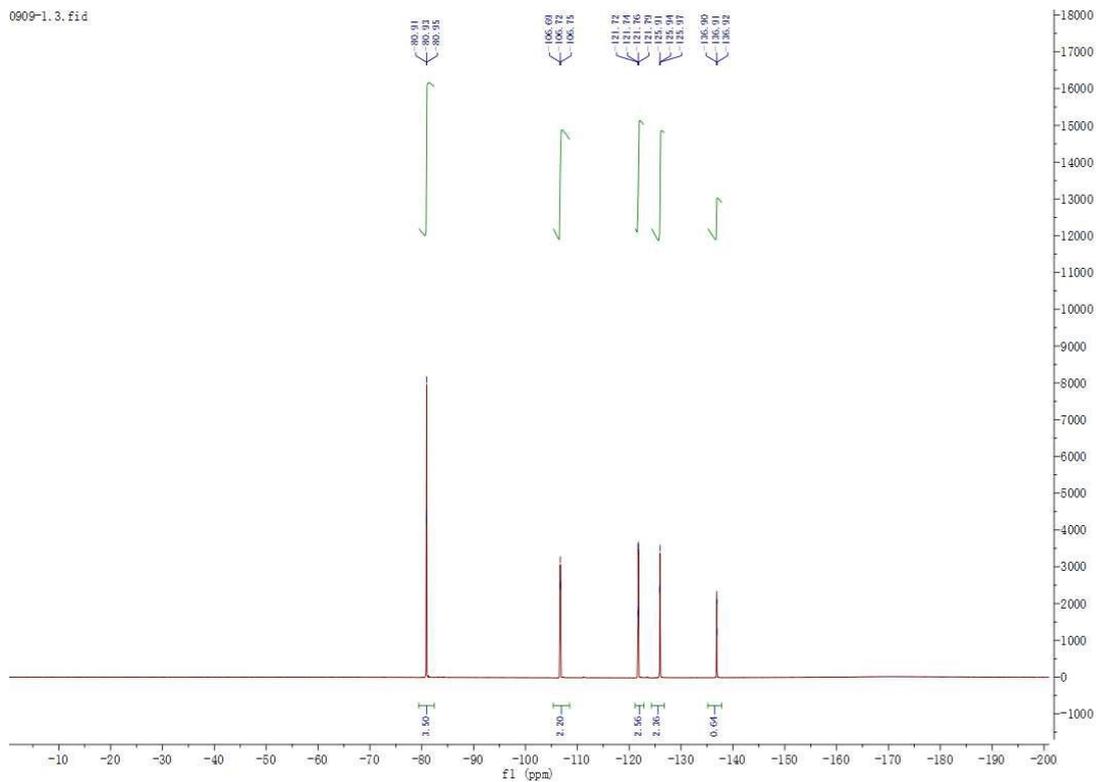
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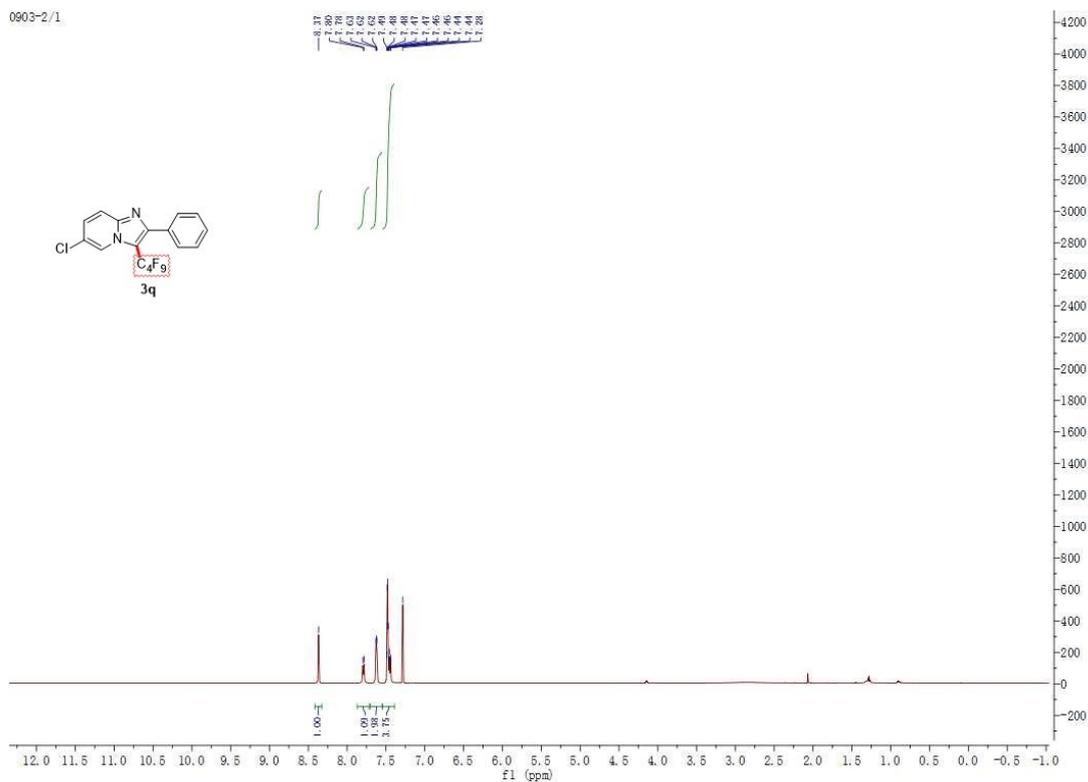
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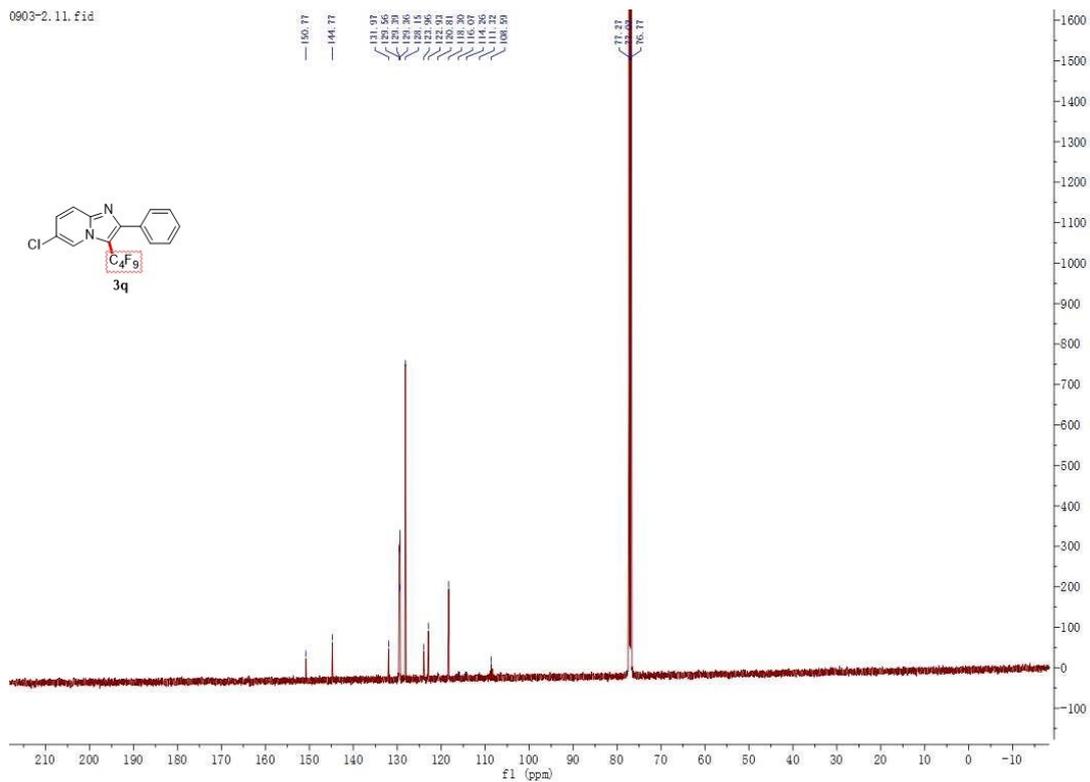
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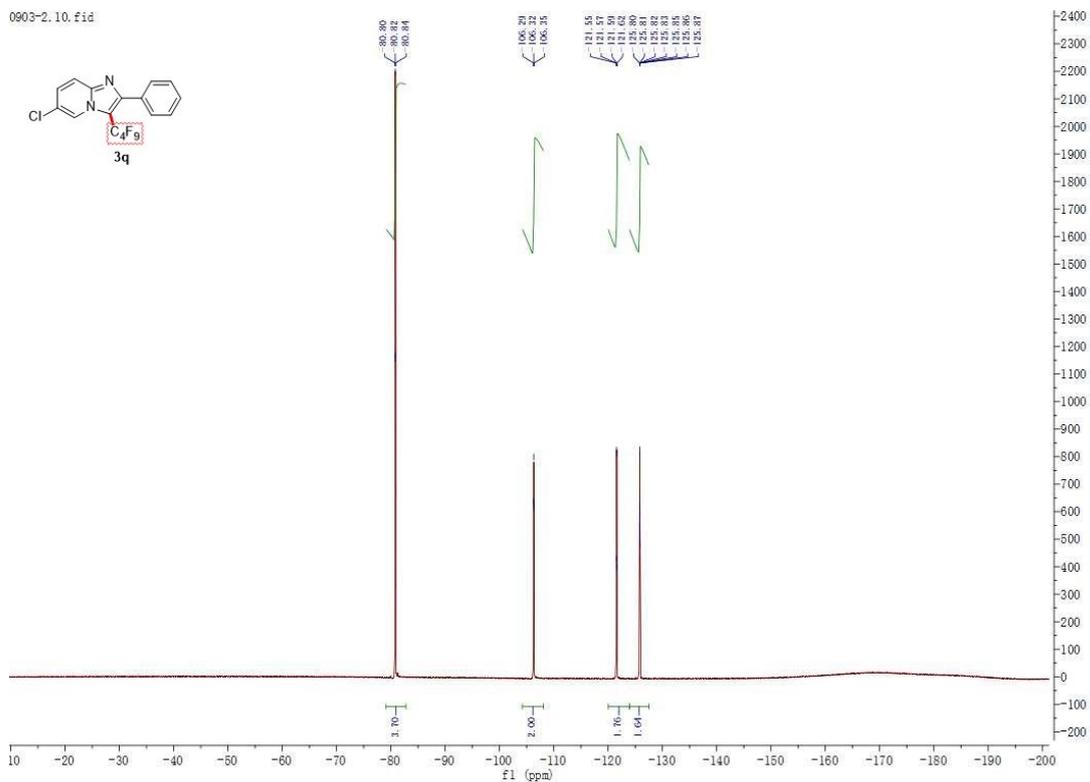
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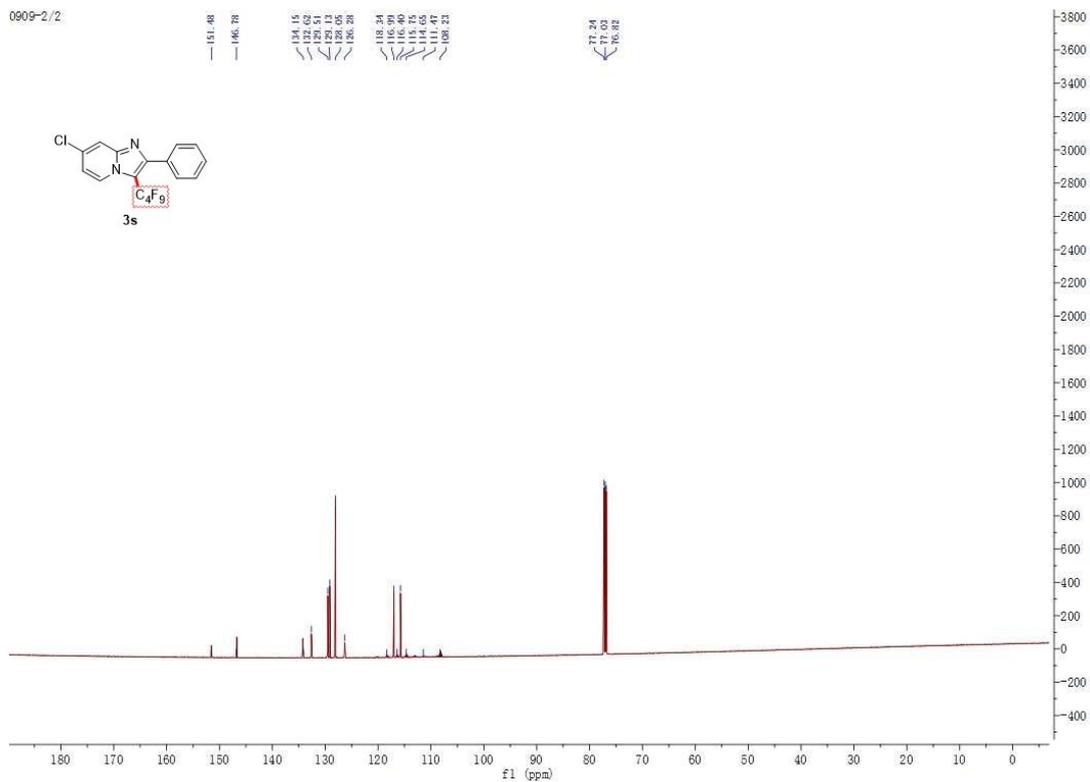
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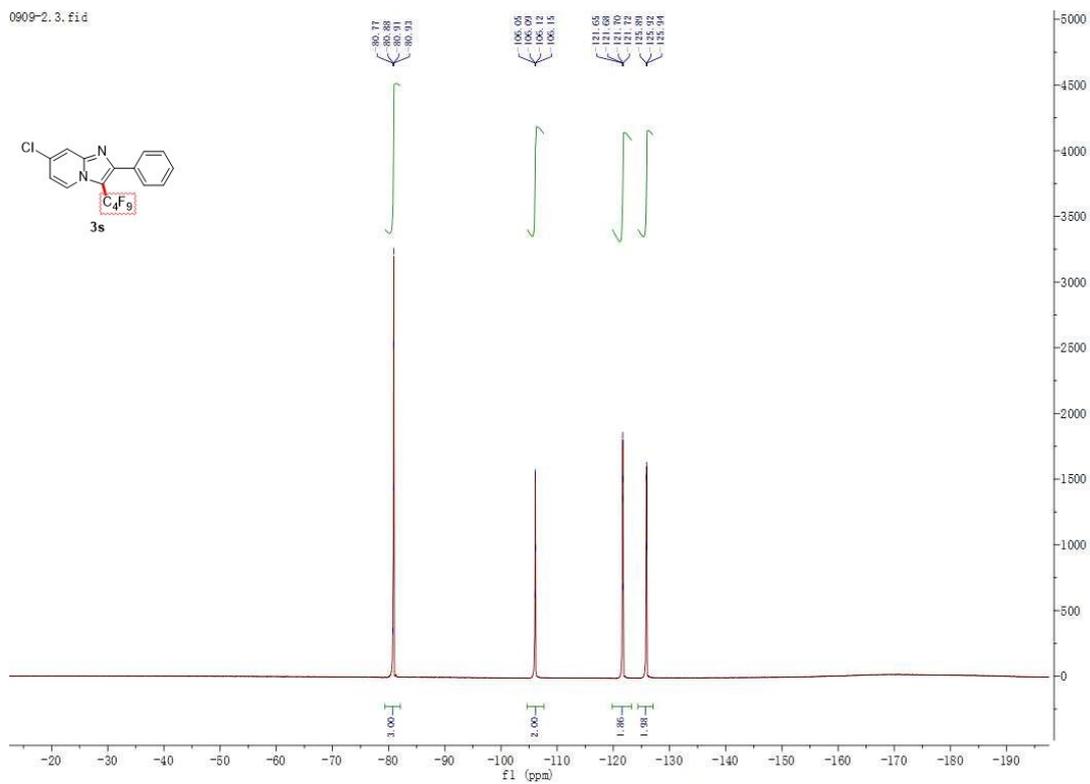
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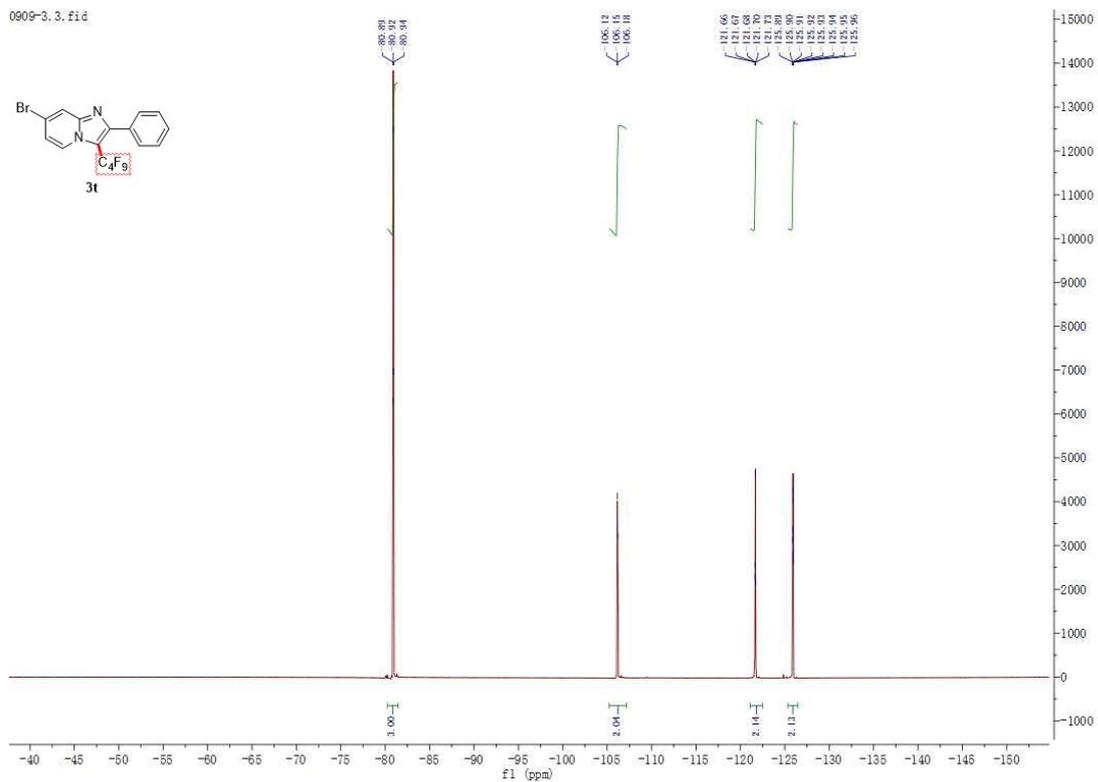
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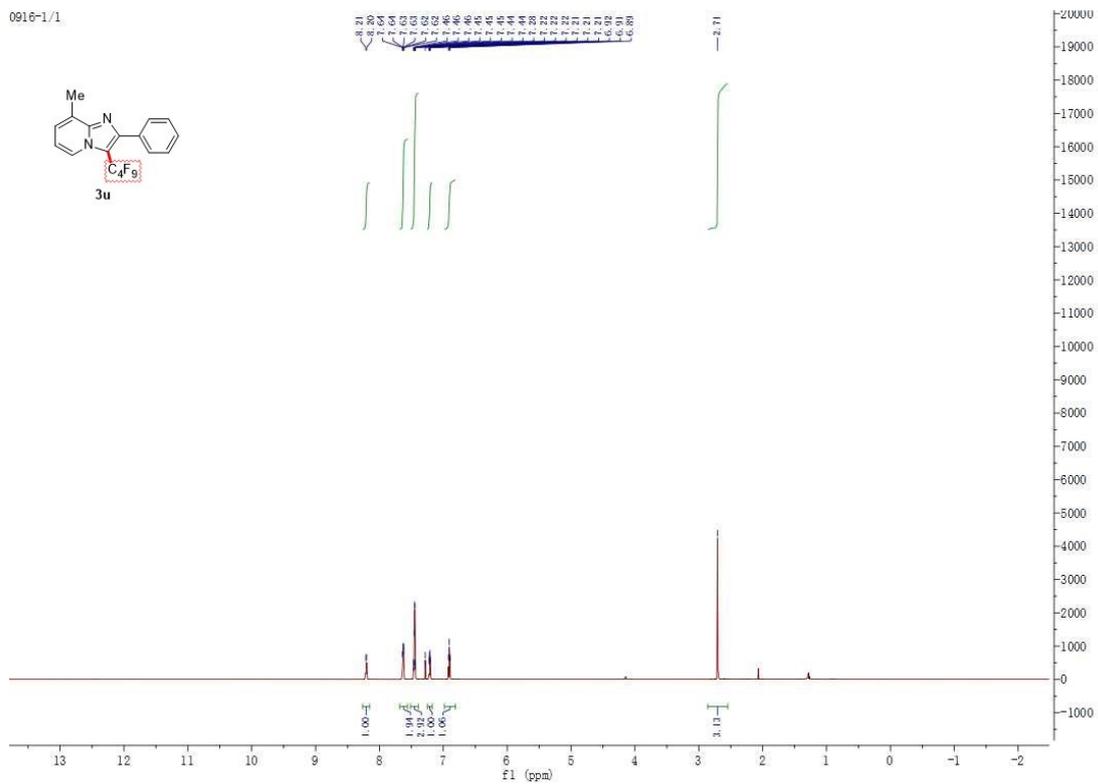
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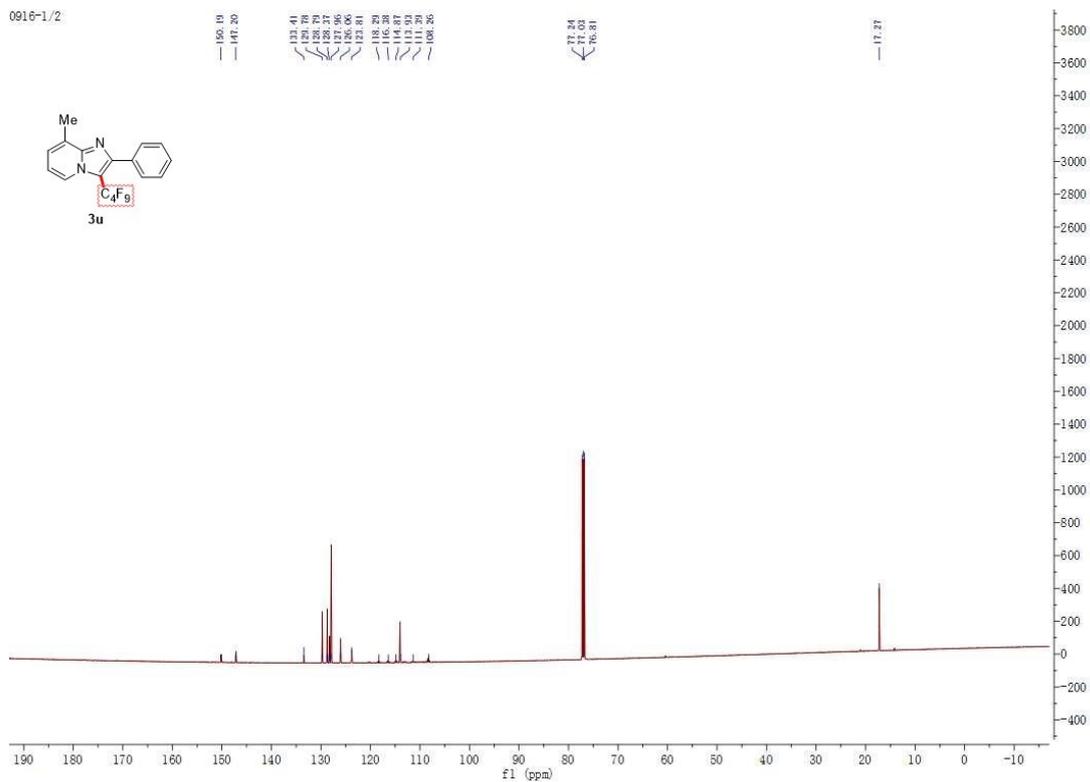
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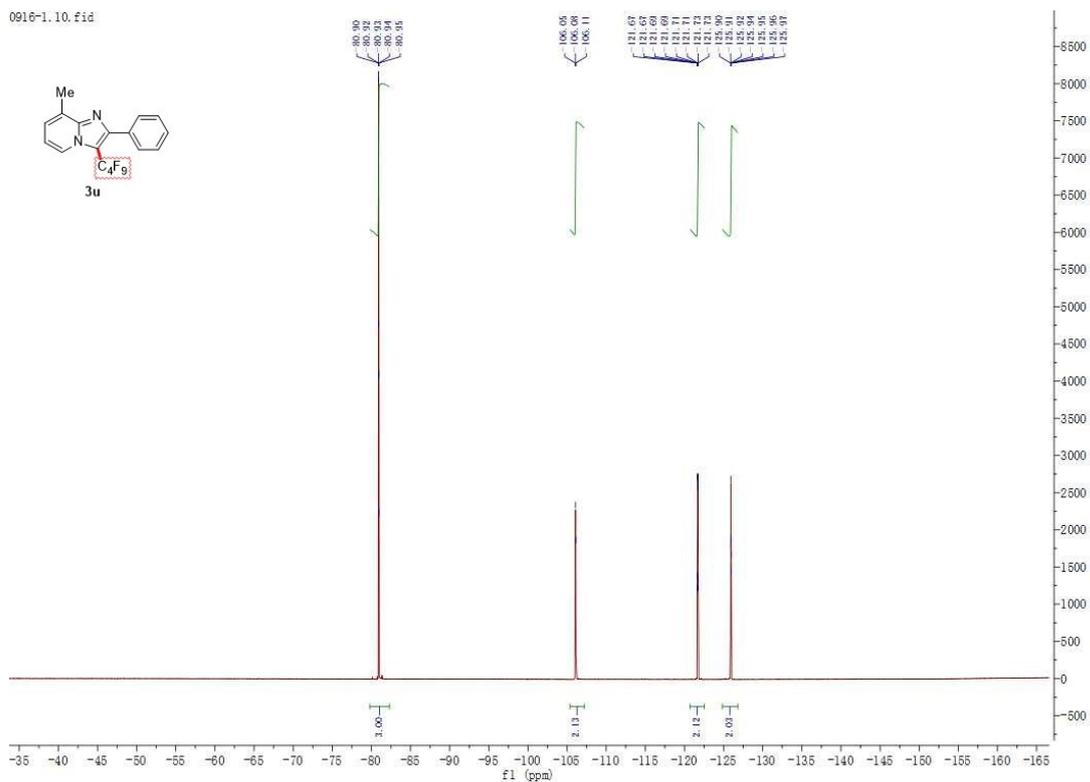
0916-1/1



0916-1/2



0916-1.10.fid



0916-2.10.fid

