

Supporting Information for
SYNTHESIS OF ISOQUINOLINIUM VIA RHODIUM(III)-
CATALYZED OXIDATIVE ANNULATION BETWEEN
ALDIMINES AND ALKYNES

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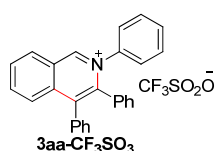
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1. General Methods

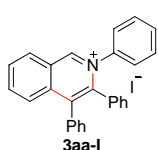
NMR data were obtained for ^1H at 400 MHz or 600 MHz, and for ^{13}C at 100 MHz. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in CDCl_3 solution. ESI HRMS was recorded on a Waters SYNAPT G2 and Water XEVO G2 Q-ToF. UV detection was monitored at 220 nm. TLC was performed on glass-backed silica plates. Column chromatography was performed on silica gel (200-300 mesh), eluting with dichloromethane and methanol. All aldehydes and anilines were commercially available. Substituted isoquinoliniums were prepared according to the literature procedures.

2. General procedure for synthesis of isoquinolinium salts derived fused compounds and Characterization data

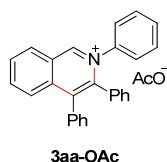
General procedure: (E)-*N*-benzylideneaniline **1a** (19.7 mg, 0.10 mmol), diphenylacetylene **2a** (26.7 mg, 0.15 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (3.1 mg, 5 mol%), additive (1 equiv) and acid (1 equiv) were stirred in solvent (1 mL) at Ar atmosphere at 90 °C for 1 h. After completion, the reaction mixture was purified by flash chromatography eluting with dichloromethane and methanol to give the desired product.



Procedure for synthesis of 2,3,4-Triphenylisoquinolinium trifluoromethanesulfonate (3aa- CF_3SO_3): (E)-*N*-benzylideneaniline **1a** (19.7 mg, 0.10 mmol), diphenylacetylene **2a** (26.7 mg, 0.15 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (3.1 mg, 5 mol%), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (20 mg, 1 equiv) and trifluoromethanesulfonic acid (15 mg, 1 equiv) were stirred in methanol (1 mL) at Ar atmosphere at 90 °C for 1 h. After completion, the reaction mixture was purified by flash chromatography eluting with dichloromethane and methanol (10:1) to give the desired product **3aa- CF_3SO_3** as a grey solid (42.6 mg, 82%). IR (KBr) 3565, 3499, 3062, 1625 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 9.93 (s, 1H), 8.68 (d, $J = 8.0$ Hz, 1H), 8.08 (t, $J = 8.0$ Hz, 1H), 7.98 (t, $J = 8.0$ Hz, 1H), 7.75 (d, $J = 8.0$ Hz, 1H), 7.55-7.53 (m, 2H), 7.37-7.32 (m, 6H), 7.28-7.27 (m, 2H), 7.08-7.03 (m, 5H). ^{13}C NMR (151 MHz, CDCl_3): δ 150.5, 142.1, 139.3, 138.8, 137.8, 133.1, 131.9, 131.3, 131.2, 131.0, 130.4, 130.3, 129.5, 129.1, 128.7, 128.4, 127.9, 126.9, 126.8, 126.5, 120.6, 119.4, 112.4. ESI HRMS: calcd. For $\text{C}_{27}\text{H}_{20}\text{N}^+$ 358.1590, found 358.1586.

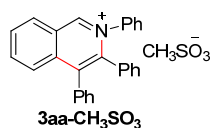


KI was added into isolated product **3aa- CF_3SO_3** (26 mg, 0.05 mmol) in methanol (0.5 mL), and then vigorously stirred overnight at room temperature. The reaction mixture was purified by flash chromatography eluting with dichloromethane and methanol (10:1) to isolated pure desired product **2,3,4-Triphenylisoquinolinium iodide (3aa-I)**. 99% yield; IR (KBr) 3422, 3062, 1622 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 10.09 (s, 1H), 8.74 (d, $J = 8.0$ Hz, 1H), 8.05 (t, $J = 8.0$ Hz, 1H), 7.94 (t, $J = 8.0$ Hz, 1H), 7.72 (d, $J = 8.0$ Hz, 1H), 7.66-7.64 (m, 2H), 7.33-7.29 (m, 8H), 7.13 (d, $J = 8.0$ Hz, 2H), 7.04-6.93 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 149.3, 143.3, 141.1, 138.4, 137.9, 136.8, 132.2, 130.9, 130.3, 130.3, 130.1, 129.4, 128.4, 128.2, 127.7, 127.4, 126.9, 126.0, 125.9, 125.6.

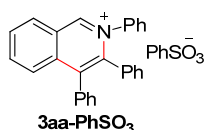


2,3,4-Triphenylisoquinolinium acetate (3aa-OAc), (see Table 1, entry 5). 42% yield; IR (KBr) 3453, 2960, 2926, 1713, 1625 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 11.09 (s, 1H), 9.29 (d, $J = 8.0$ Hz, 1H), 8.08 (t, $J = 8.0$ Hz, 1H), 8.01 (t, $J = 8.0$

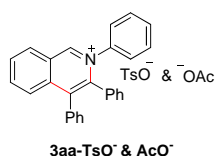
Hz, 1H), 7.75 (t, $J = 8.0$ Hz, 1H), 7.66-7.65 (m, 2H), 7.39-7.34 (m, 5H), 7.27-7.26 (m, 3H), 7.09-7.04 (m, 5H), 2.04 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3): δ 152.6, 138.8, 138.4, 137.8, 133.5, 133.2, 131.2, 131.2, 130.3, 129.5, 128.7, 128.5, 128.0, 127.2, 126.9, 126.1.



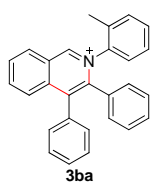
2,3,4-Triphenylisoquinolinium methanesulfonate (3aa-CH₃SO₃) (see Table 1, entry 8). 30% yield; IR (KBr) 3493, 3434, 3057, 1626 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 10.58 (s, 1H), 9.07 (s, 1H), 8.10-8.03 (m, 2H), 7.76 (t, $J = 8.0$ Hz, 1H), 7.62 (m, 2H), 7.38-7.34 (m, 6H), 7.28-7.25 (m, 2H), 7.05 (m, 5H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 152.7, 143.9, 142.1, 138.9, 138.6, 137.8, 133.3, 133.2, 131.3, 131.2, 130.4, 129.5, 129.2, 128.8, 128.6, 128.0, 127.2, 127.0, 126.3, 39.4.



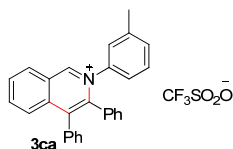
2,3,4-Triphenylisoquinolinium benzenesulfonate (3aa-PhSO₃) (see Table 1, entry 10). 33% yield; IR (KBr) 3427, 3054, 1627 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 10.48 (s, 1H), 8.94 (d, $J = 8.0$ Hz, 1H), 8.02 (t, $J = 8.4$ Hz, 1H), 7.92 (t, $J = 6.8$ Hz, 1H), 7.70 (d, $J = 8.4$ Hz, 1H), 7.64 (d, $J = 7.2$ Hz, 2H), 7.59 (d, $J = 7.2$ Hz, 2H), 7.31-7.27 (m, 6H), 7.22-7.18 (m, 5H), 7.06-7.00 (m, 5H).



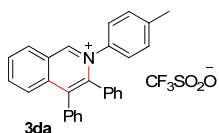
2,3,4-Triphenylisoquinolinium 4-methylbenzenesulfonate (3aa-TsO⁻ & OAc) (see Table 1, entry 11). 29% yield of acetate salt, 43% yield of tosylate salt; ^1H NMR (400 MHz, CDCl_3): δ 10.50 (s, 1H), 8.93 (d, $J = 8.0$ Hz, 1H), 7.95 (t, $J = 8.0$ Hz, 1H), 7.54 (t, $J = 6.8$ Hz, 1H), 7.48 (d, $J = 8.0$ Hz, 2H), 7.26-7.19 (m, 6H), 7.15-7.13 (m, 2H), 7.00-6.93 (m, 7H), 2.23 (s, 3H), 1.90 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 153.1, 144.1, 143.9, 142.1, 138.8, 138.5, 138.4, 137.6, 133.3, 133.2, 131.3, 131.3, 130.4, 130.2, 129.4, 129.1, 128.7, 128.5, 128.3, 127.9, 127.2, 127.1, 127.0, 126.1, 125.9, 21.3.



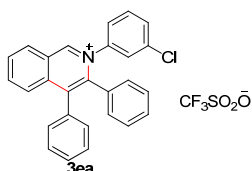
3,4-Diphenyl-2-o-tolylisoquinolinium trifluoromethanesulfonate (3ba). 85% yield; IR (KBr) 3436, 3057, 1627 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 9.93 (s, 1H), 8.69 (d, $J = 8.0$ Hz, 1H), 8.06 (t, $J = 8.0$ Hz, 1H), 7.97 (t, $J = 8.0$ Hz, 1H), 7.76 (d, $J = 8.4$ Hz, 1H), 7.37-7.32 (m, 4H), 7.26-7.17 (m, 5H), 7.05 (m, 5H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 150.0, 149.9, 143.4, 141.0, 139.2, 138.3, 137.7, 136.8, 132.2, 131.0, 131.0, 130.3, 130.2, 129.3, 128.2, 128.1, 127.7, 127.5, 126.9, 126.3, 126.0, 125.5, 122.7, 119.6 (q, $J = 319$ Hz), 21.2. ESI HRMS: calcd. For $\text{C}_{28}\text{H}_{22}\text{N}^+$ 372.1747, found 372.1747.



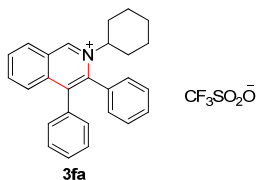
3,4-Diphenyl-2-m-tolylisoquinolinium trifluoromethanesulfonate (3ca). 80% yield; IR (KBr) 3440, 3069, 1622 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 9.93 (s, 1H), 8.78 (d, $J = 8.0$ Hz, 1H), 8.11 (t, $J = 8.0$ Hz, 1H), 8.02 (t, $J = 8.0$ Hz, 1H), 7.81 (d, $J = 8.4$ Hz, 1H), 7.66 (d, $J = 7.6$ Hz, 1H), 7.37-7.23 (m, 8H), 7.18-7.16 (m, 1H), 7.08-7.07 (m, 2H), 7.01-7.00 (m, 1H), 6.93-6.91 (m, 1H), 2.09 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3): δ 151.2, 144.5, 141.1, 139.6, 138.8, 138.0, 133.0, 132.3, 132.0, 131.4, 131.2, 130.9, 130.6, 130.5, 129.4, 129.3, 128.9, 128.8, 128.2, 127.9, 127.6, 127.3, 127.2, 126.5, 120.5 (q, $J = 318$ Hz), 17.6. For $\text{C}_{28}\text{H}_{22}\text{N}^+$ 372.1747, found 372.1748.



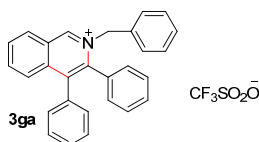
3,4-Diphenyl-2-p-tolyloisoquinolinium trifluoromethanesulfonate (3da). 79% yield; IR (KBr) 3482, 3060, 1626 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 9.93 (s, 1H), 8.69 (d, $J = 8.0$ Hz, 1H), 8.06 (t, $J = 8.0$ Hz, 1H), 7.97 (t, $J = 8.0$ Hz, 1H), 7.76 (d, $J = 8.0$ Hz, 1H), 7.37-7.26 (m, 4H), 7.26-7.17 (m, 5H), 7.05 (m, 5H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 151.1, 144.5, 140.8, 139.8, 139.3, 138.7, 137.8, 133.2, 132.0, 131.3, 131.2, 130.3, 130.1, 129.2, 128.7, 128.5, 128.0, 127.0, 126.5, 126.5, 120.6 (q, $J = 319$ Hz), 21.2. ESI HRMS: calcd. For $\text{C}_{28}\text{H}_{22}\text{N}^+$ 372.1747, found 372.1752.



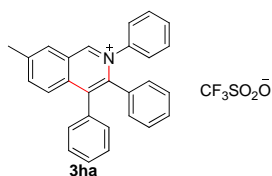
2-(3-Chlorophenyl)-3,4-diphenylisoquinolinium-trifluoromethanesulfonate (3ea). 77% yield; IR (KBr) 3468, 3240, 1624 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 9.88 (s, 1H), 8.62 (d, $J = 8.0$ Hz, 1H), 8.07 (t, $J = 8.0$ Hz, 1H), 7.95 (t, $J = 7.2$ Hz, 1H), 7.76 (d, $J = 8.8$ Hz, 1H), 7.58 (d, $J = 7.2$ Hz, 1H), 7.52 (s, 1H), 7.32-7.31 (m, 5H), 7.28-7.26 (m, 2H), 7.11-7.08 (m, 5H). ^{13}C NMR (100 MHz, CDCl_3): δ 150.9, 144.3, 142.7, 139.5, 139.0, 138.1, 135.0, 133.1, 132.0, 131.4, 131.2, 130.9, 130.8, 130.7, 130.3, 129.4, 128.8, 128.5, 128.1, 127.1, 127.0, 125.6, 120.4 (q, $J = 319$ Hz). ESI HRMS: calcd. for $\text{C}_{27}\text{H}_{19}\text{ClN}^+$ 392.1201, found 392.1119, 394.1229.



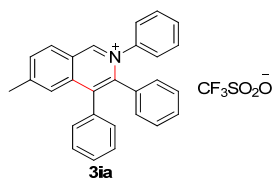
2-Cyclohexyl-3,4-diphenylisoquinolinium trifluoromethanesulfonate (3fa) 85% yield; IR (KBr) 3440, 3065, 3019, 1625 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 10.40 (s, 1H), 8.95 (d, $J = 7.2$ Hz, 1H), 8.00 (t, $J = 8.0$ Hz, 1H), 7.97 (t, $J = 7.6$ Hz, 1H), 7.61 (d, $J = 7.6$ Hz, 1H), 7.39 (m, 3H), 7.29-7.27 (m, 3H), 7.23 (m, 2H), 7.12 (m, 2H), 4.34 (m, 1H), 2.39-2.36 (m, 2H), 2.13 (m, 2H), 1.93-1.90 (m, 2H), 1.58-1.48 (m, 2H), 1.07-1.04 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 148.2, 143.9, 139.4, 137.6, 137.4, 133.3, 132.1, 131.2, 131.0, 130.3, 129.8, 129.0, 128.7, 128.5, 128.0, 120.8 (q, $J = 319$ Hz), 68.5, 33.6, 25.8, 23.9. ESI HRMS: calcd. for $\text{C}_{27}\text{H}_{26}\text{N}^+$ 364.2060, found 364.2058.



2-Benzyl-3,4-diphenylisoquinolinium trifluoromethanesulfonate (3ga). 52 % yield; IR (KBr) 3431, 3052, 1630 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 10.33 (s, 1H), 8.72 (d, $J = 8.0$ Hz, 1H), 8.02 (t, $J = 8.0$ Hz, 1H), 7.96 (t, $J = 8.0$ Hz, 1H), 7.65 (d, $J = 8.4$ Hz, 1H), 7.28-7.23 (m, 9H), 7.09-7.07 (m, 4H), 6.92 (d, $J = 7.2$ Hz, 2H), 5.89 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 151.3, 144.3, 139.8, 138.1, 137.5, 133.1, 131.9, 131.2, 130.7, 130.6, 130.1, 130.0, 129.3, 129.2, 128.7, 128.6, 128.4, 128.3, 127.3, 63.3. ESI HRMS: calcd. For $\text{C}_{28}\text{H}_{22}\text{N}^+$ 372.1747, found 372.1755.



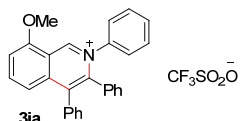
5-Methyl-2,3,4-triphenylisoquinolinium trifluoromethanesulfonate (3ha). 78% yield; IR (KBr) 3455, 3066, 1634 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 9.84 (s, 1H), 8.46 (s, 1H), 7.90 (t, $J = 8.8$ Hz, 1H), 7.67 (d, $J = 8.4$ Hz, 1H), 7.52-7.51 (m, 2H), 7.34-7.32 (m, 6H), 7.24 (m, 2H), 7.04 (m, 5H), 2.66 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 150.0, 143.7, 142.5, 142.2, 140.3, 139.1, 137.1, 133.3, 131.3, 131.2, 130.4, 130.3, 129.6, 129.2, 128.7, 128.5, 128.0, 127.3, 126.8, 126.3, 120.6 (q, $J = 319$ Hz), 21.8. ESI HRMS: calcd. For $\text{C}_{28}\text{H}_{22}\text{N}^+$ 372.1747, found 372.1746.



6-Methyl-2,3,4-triphenylisoquinolinium

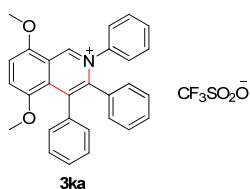
trifluoromethanesulfonate. (3ia) 93% yield; IR (KBr) 3476, 3245, 3061, 1626 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 9.83 (s, 1H), 8.55 (d, $J = 8.8$ Hz, 1H), 7.79 (d, $J = 8.0$ Hz, 1H), 7.51-7.49 (m, 3H), 7.34-7.31 (m, 6H), 7.26-7.23 (m, 2H), 7.03-6.99 (m, 5H), 2.58 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 150.5, 150.1, 144.4, 142.1, 139.0, 138.3, 133.7, 133.3, 131.7, 131.2, 130.4, 130.3, 129.5, 129.1, 128.7, 128.5, 127.9, 126.9, 125.5, 125.4, 120.6 (q, $J = 319$ Hz), 23.3. ESI HRMS: calcd. for $\text{C}_{28}\text{H}_{22}\text{N}^+$ 372.1747, found 372.1748.



8-Methoxy-2,3,4-triphenylisoquinolinium trifluoromethanesulfonate

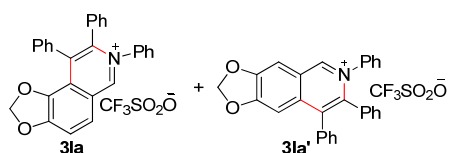
(3ja). 81% yield. IR (KBr) 3488, 3245, 3060, 1622 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 9.74 (s, 1H), 8.00 (d, $J = 8.0$ Hz, 1H), 7.56 (t, $J = 8.0$ Hz, 1H), 7.37-7.35 (m, 3H), 7.29-7.26 (m, 7H), 7.14-7.13 (m, 2H), 7.04-7.00 (m, 3H), 4.15 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 157.7, 144.5, 144.0, 141.6, 138.8, 138.7, 137.8, 132.5, 130.2, 130.2, 129.4, 129.3, 128.5, 128.1, 127.6, 127.4, 126.8, 125.9, 119.6 (q, $J = 319$ Hz), 118.6, 117.4, 108.2, 55.9. ESI HRMS: calcd. For $\text{C}_{28}\text{H}_{22}\text{NO}^+$ 388.1696, found 389.1693.



5,8-Dimethoxy-2,3,4-triphenylisoquinolinium

trifluoro-methanesulfonate (3ka). 75% yield; IR (KBr) 3062, 2920, 1650 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 9.69 (s, 1H), 9.51-9.49 (s, 2H), 7.44 (d, $J = 8.4$ Hz, 1H), 7.34-7.33 (m, 3H), 7.27-7.25 (m, 1H), 7.17-7.16 (m, 2H), 7.12-7.11 (m, 3H), 7.06-7.04 (m, 2H), 6.96-6.94 (m, 3H), 4.07 (s, 3H), 3.38 (s, 3H).

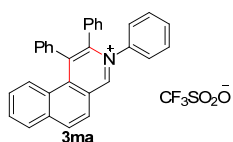
^{13}C NMR (100 MHz, CDCl_3): δ 152.3, 149.9, 145.6, 145.1, 142.6, 137.7, 137.1, 131.5, 131.2, 130.3, 129.8, 129.5, 129.4, 128.8, 127.5, 127.1, 126.9, 126.8, 120.9, 120.7 (q, $J = 319$ Hz), 120.1, 110.3, 57.1, 56.8. ESI HRMS: calcd. For $\text{C}_{29}\text{H}_{24}\text{NO}_2^+$ 418.1802, found 418.1807.



6,7,8-Triphenyl-[1,3]dioxolo[4,5-g]isoquinolin-6-ium trifluoromethanesulfonate (3la);

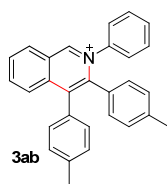
6,7,8-Triphenyl-[1,3]dioxolo[4,5-g]isoquinolin-6-ium trifluoromethanesulfonate (3la'); (3la:3la' = 10:1). 74%

yield; IR (KBr) 3470, 3062, 1630 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 9.74 (s, 1H), 8.43 (d, $J = 8.0$ Hz, 1H), 7.62 (d, $J = 8.8$ Hz, 1H), 7.45 (t, $J = 8.0$ Hz, 2H), 7.34 (m, 3H), 7.21 (m, 5H), 7.00 (m, 5H), 6.05 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 155.4, 151.4, 143.8, 142.1, 141.9, 131.3, 130.3, 130.1, 129.5, 129.1, 128.3, 127.8, 127.6, 126.8, 122.7, 122.6, 120.6 (q, $J = 319$ Hz), 116.0, 103.9. ESI HRMS: calcd. For $\text{C}_{28}\text{H}_{20}\text{NO}_2^+$ 402.1489, found 402.1493.

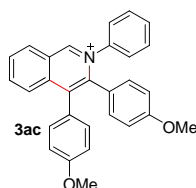


1,2,3-Triphenylbenzo[f]isoquinolinium trifluoromethanesulfonate

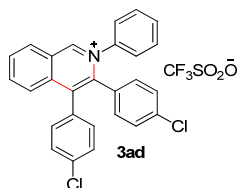
(3ma). 80% yield; IR (KBr) 3463, 3062, 1613 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 10.12 (s, 1H), 8.85 (d, $J = 7.6$ Hz, 1H), 8.25 (t, $J = 9.2$ Hz, 1H), 8.03 (d, $J = 7.6$ Hz, 1H), 7.87 (t, $J = 7.6$ Hz, 1H), 7.82 (t, $J = 7.6$ Hz, 1H), 7.62-7.57 (m, 3H), 7.37-7.36 (m, 3H), 7.32 (m, 5H), 7.15-7.13 (m, 2H), 7.06-7.00 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 147.3, 143.5, 142.6, 140.7, 139.7, 139.3, 133.5, 132.4, 131.1, 130.5, 129.7, 129.6, 129.3, 128.8, 128.6, 127.9, 127.1, 123.5, 122.8, 120.5 (q, $J = 319$ Hz). ESI HRMS: calcd. For $\text{C}_{31}\text{H}_{22}\text{N}^+$ 408.1747, found 408.1749.



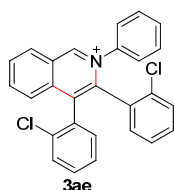
2-Phenyl-3,4-dip-tolyloisoquinolinium trifluoromethanesulfonate (3ab). 72 % yield; IR (KBr) 3564, 3492, 3066, 1625, 1491 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 9.96 (s, 1H), 8.70 (d, $J = 8.0$ Hz, 1H), 8.05 (t, $J = 8.0$ Hz, 1H), 7.97 (t, $J = 8.0$ Hz, 1H), 7.70 (d, $J = 8.0$ Hz, 1H), 7.50-7.48 (m, 2H), 7.37 (m, 3H), 7.15-7.09 (m, 4H), 6.91-6.89 (m, 2H), 6.84-6.82 (s, 2H), 2.34 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 150.9, 144.6, 142.3, 139.5, 139.3, 139.0, 138.6, 137.7, 132.0, 131.2, 131.0, 130.4, 130.2, 129.5, 129.3, 128.7, 128.2, 126.9, 126.8, 126.6, 120.6 (q, $J = 319$ Hz), 21.32, 21.27. ESI HRMS: calcd. For $\text{C}_{29}\text{H}_{24}\text{N}^+$ 386.1903, found 386.1898.



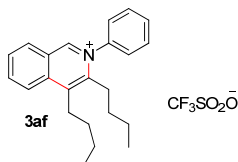
3,4-Bis(4-methoxyphenyl)-2-phenylisoquinolinium trifluoromethanesulfonate (3ac). 75% yield; IR (KBr) 3561, 3500, 3066, 1611 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 9.83 (s, 1H), 8.61 (d, $J = 8.0$ Hz, 1H), 8.04 (t, $J = 8.0$ Hz, 1H), 7.93 (t, $J = 7.6$ Hz, 1H), 7.79 (d, $J = 8.4$ Hz, 1H), 7.50-7.48 (m, 2H), 7.37-7.35 (m, 3H), 7.15 (d, $J = 8.4$ Hz, 2H), 6.95 (d, $J = 8.4$ Hz, 2H), 6.85 (d, $J = 8.4$ Hz, 2H), 6.54 (d, $J = 7.6$ Hz, 2H), 3.79 (s, 3H), 3.64 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 159.7, 159.6, 150.6, 144.7, 142.4, 139.5, 139.2, 137.6, 132.7, 131.9, 131.7, 131.1, 130.4, 129.6, 126.9, 126.7, 126.6, 125.3, 123.3, 120.6 (d, $J = 31.9$ Hz), 114.1, 113.5, 55.3, 55.1. ESI HRMS: calcd. For $\text{C}_{29}\text{H}_{24}\text{NO}_2^+$ 418.1802, found 418.1798.



3,4-Bis(4-chlorophenyl)-2-phenylisoquinolinium trifluoromethanesulfonate (3ad). 65% yield; IR (KBr) 3564, 3242, 3064, 2924, 1626 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 9.75 (s, 1H), 8.55 (d, $J = 8.0$ Hz, 1H), 8.09 (t, $J = 8.0$ Hz, 1H), 7.96 (t, $J = 8.0$ Hz, 1H), 7.72 (d, $J = 8.0$ Hz, 1H), 7.56-7.55 (m, 2H), 7.42-7.35 (m, 5H), 7.27-7.25 (m, 2H), 7.11-7.09 (m, 2H), 7.05-7.03 (m, 2H). ^{13}C NMR (151 MHz, CDCl_3): δ 150.9, 134.5, 141.9, 138.7, 138.4, 138.0, 135.7, 135.2, 132.6, 131.7, 131.7, 131.5, 131.5, 130.7, 129.7, 129.4, 129.0, 128.4, 127.0, 126.8, 126.4, 121.4, 120.4, 119.1 (q, $J = 259$ Hz). ESI HRMS: calcd. For $\text{C}_{27}\text{H}_{18}\text{Cl}_2\text{N}^+$ 426.0811, found 426.0815, 428.0798, 430.0801.

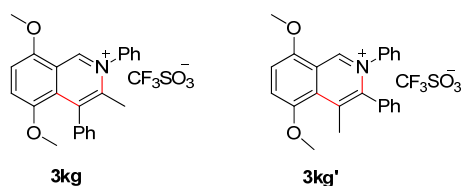


3,4-Bis(2-chlorophenyl)-2-phenylisoquinolinium trifluoromethanesulfonate (3ae). 64% yield; IR (KBr) 3563, 3490, 3069, 1624 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 9.80 (s, 1H), 8.58 (d, $J = 8.4$ Hz, 1H), 8.10 (t, $J = 7.6$ Hz, 1H), 7.96 (t, $J = 7.6$ Hz, 1H), 7.72 (d, $J = 8.4$ Hz, 1H), 7.57 (d, $J = 7.6$ Hz, 2H), 7.39-7.35 (m, 3H), 7.32-7.27 (m, 4H), 7.11-7.03 (m, 3H), 7.03-7.01 (m, 1H). ^{13}C NMR (151 MHz, CDCl_3): δ 151.3, 142.9, 141.8, 138.5, 138.1, 137.9, 134.7, 134.5, 133.9, 132.5, 131.9, 131.5, 130.7, 130.0, 129.6, 129.4, 129.2, 127.0, 126.8, 126.3, 120.4 (q, $J = 318$ Hz). ESI HRMS: calcd. For $\text{C}_{27}\text{H}_{18}\text{Cl}_2\text{N}^+$ 426.0811, found 426.0824, 426.0841, 430.0847.



3,4-Dibutyl-2-phenylisoquinolinium trifluoromethanesulfonate (3af). 49 % yield; IR (KBr) 3446, 3066, 1631 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 9.73 (s, 1H), 8.59 (d, $J = 8.0$ Hz, 1H), 8.22-8.16 (m, 2H), 7.92 (t, $J = 7.2$

Hz, 1H), 7.69-7.68 (m, 3H), 7.63 (m, 2H), 3.20 (t, $J = 8.0$ Hz, 2H), 2.86 (t, $J = 8.0$ Hz, 2H), 1.75-1.71 (m, 2H), 1.65-1.59 (m, 2H), 1.48 (t, $J = 8.0$ Hz, 2H), 1.24-1.18 (m, 2H), 1.05 (t, $J = 7.2$ Hz, 3H), 0.73 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 149.2, 144.2, 140.1, 137.2, 136.7, 136.3, 131.6, 130.5, 129.6, 129.3, 125.1, 125.0, 122.6, 119.6 (q, $J = 319$ Hz), 31.7, 30.4, 28.6, 27.5, 22.2, 21.6, 12.7, 12.0. ESI HRMS: calcd. For $\text{C}_{23}\text{H}_{28}\text{N}^+$ 318.2216, found 318.2219.



$3\text{kg}:3\text{kg}' = 1.8:1$

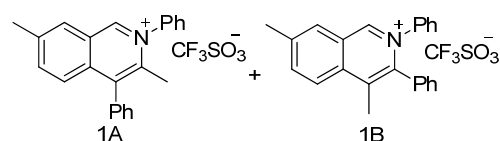
5,8-Dimethoxy-3-methyl-2,4-diphenylisoquinolin-2-ium trifluoromethanesulfonate (3kg).

5,8-Dimethoxy-4-methyl-2,3-diphenylisoquinolin-2-ium trifluoromethanesulfonate (3kg'). ($3\text{kg}:3\text{kg}' = 1.8:1$), 82% yield; IR (KBr) 3059, 2941, 2839, 1622,

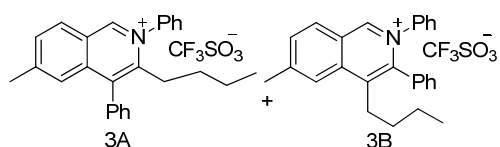
1600 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 9.53 (s, 1H), 9.52 (s, 1H), 7.71-7.68 (m, 7H), 7.60 (d, $J = 8.0$ Hz, 1H), 7.45-7.42 (m, 5H), 7.38-7.36 (m, 8H), 7.31-7.29 (m, 4H), 7.25-7.24 (m, 2H), 7.17 (d, $J = 8.4$ Hz, 2H), 4.05 (s, 3H), 4.03 (s, 4H), 4.00 (s, 3H), 3.38 (s, 4H), 2.75 (s, 2H), 2.18 (s, 5H).

3. Substrate scope of unsymmetrically disubstituted alkynes

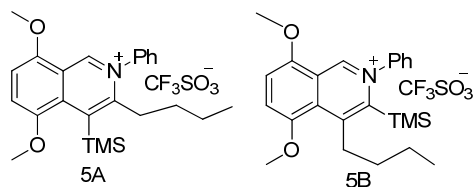
Unfortunately, asymmetric disubstituted alkynes as coupling partners can be employed in the reaction but giving the two isomers which were very hard to separate and confirm the structure. Only the structure of **3kg** and **3kg'** can be confirmed in 82% yield but albeit with poor regioselectivity.



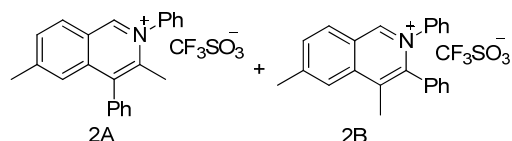
67% $1\text{A}:1\text{B}$ or $1\text{B}:1\text{A} = 2.4:1$



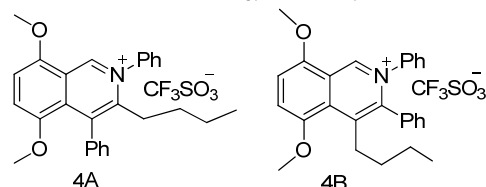
42% $3\text{A}:3\text{B}$ or $3\text{B}:3\text{A} = 5.8:1$



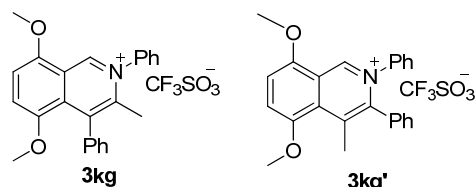
48% $5\text{A}:5\text{B}$ or $5\text{B}:5\text{A} = 1:1$



70% $2\text{A}:2\text{B}$ or $2\text{B}:2\text{A} = 3.1:1$

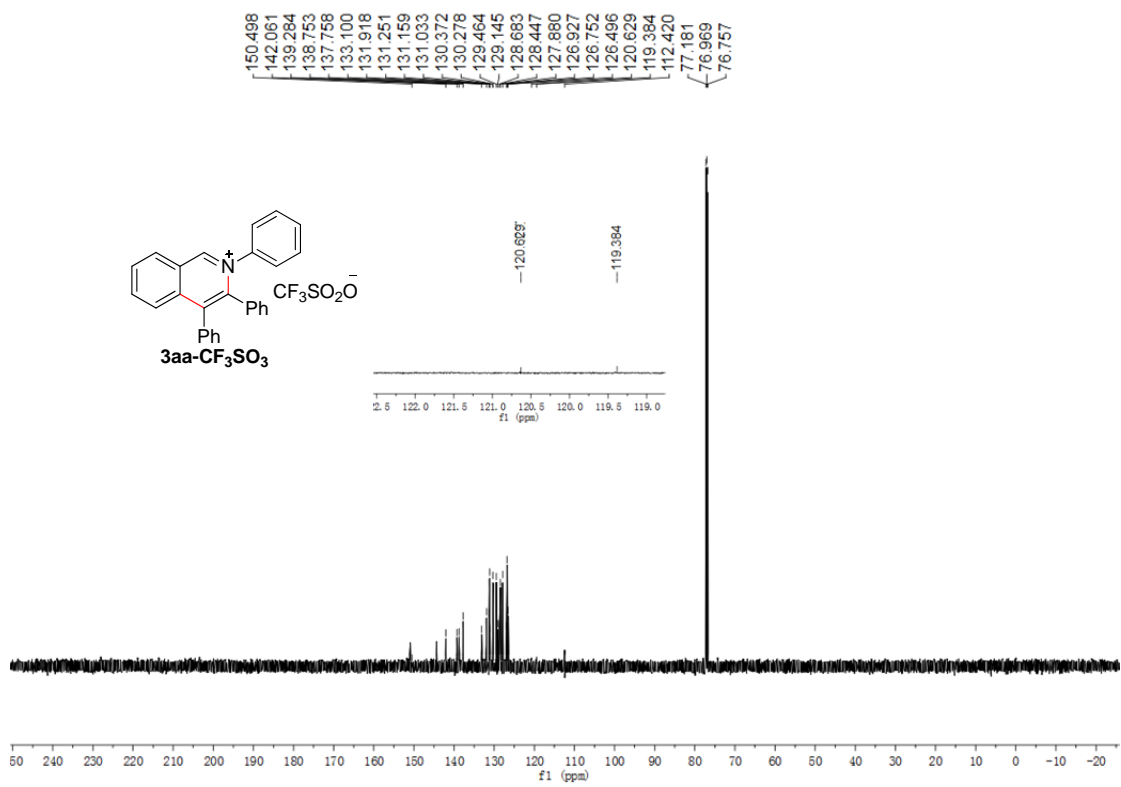
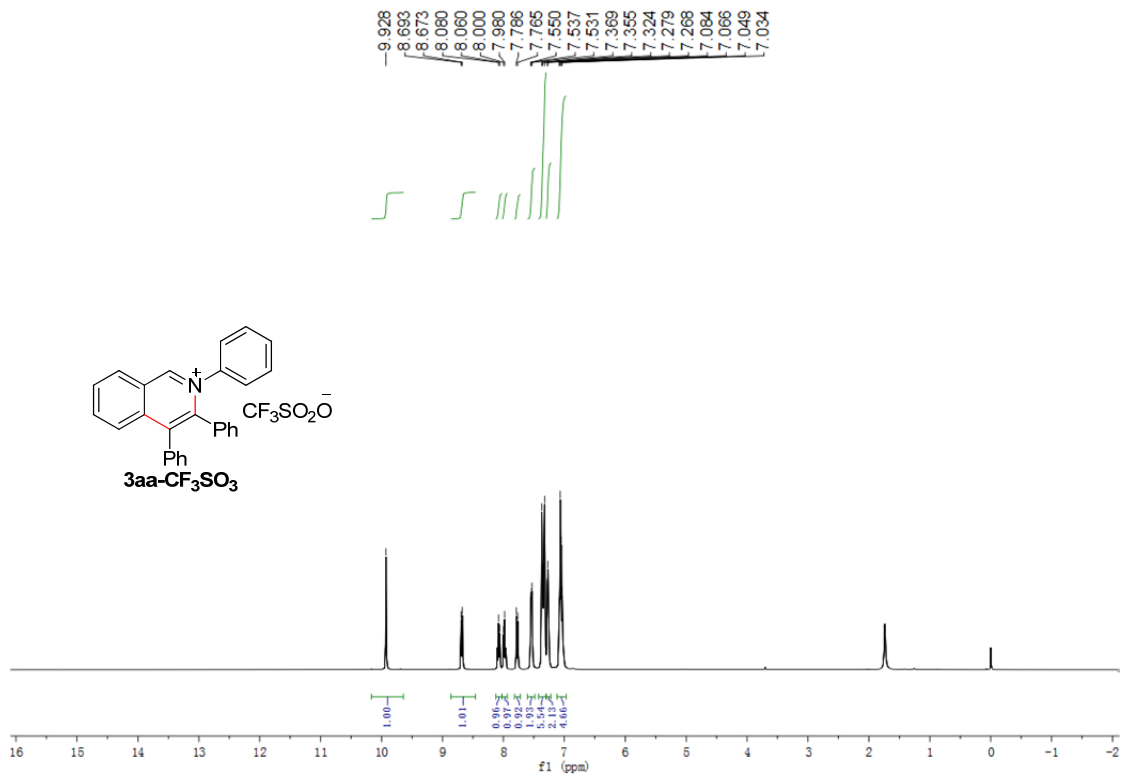


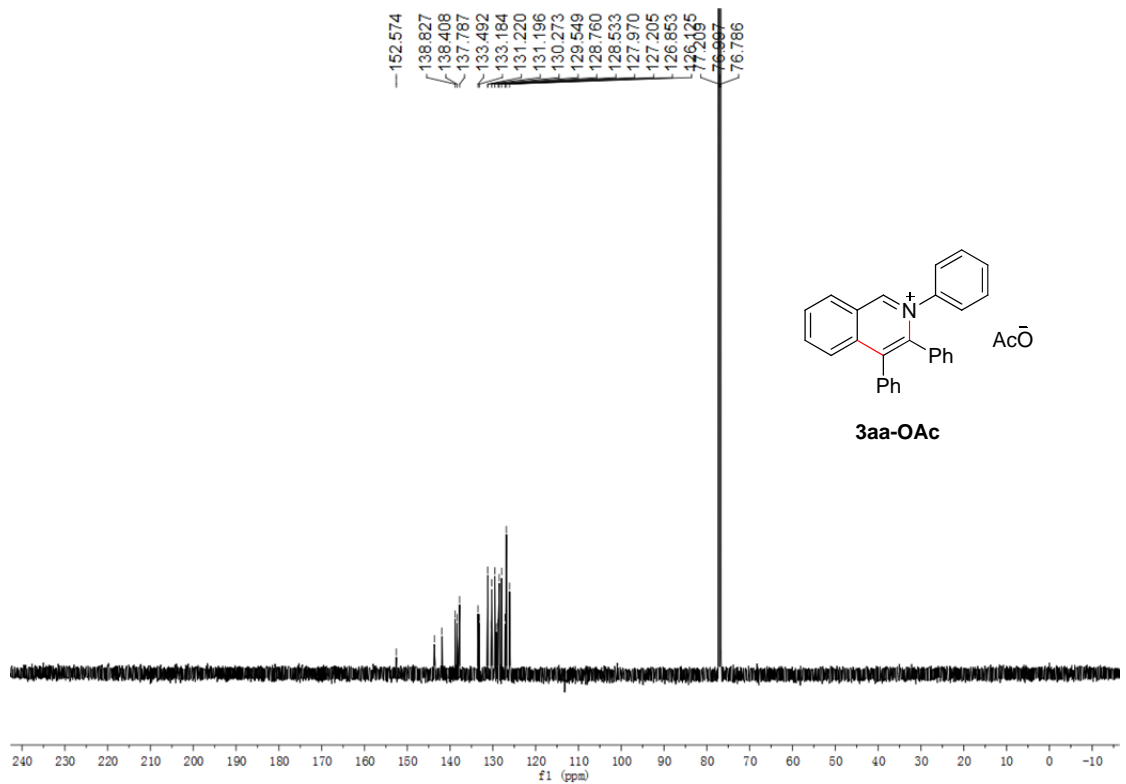
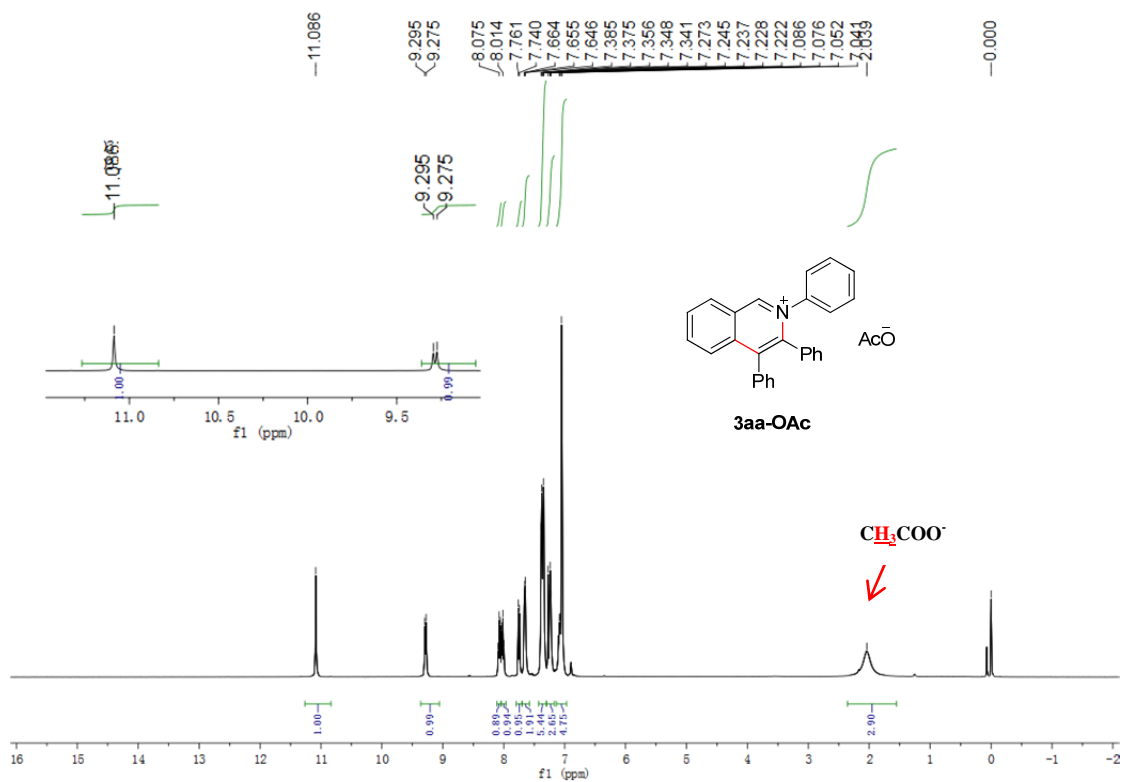
89% $4\text{A}:4\text{B}$ or $4\text{B}:4\text{A} = 2.1:1$

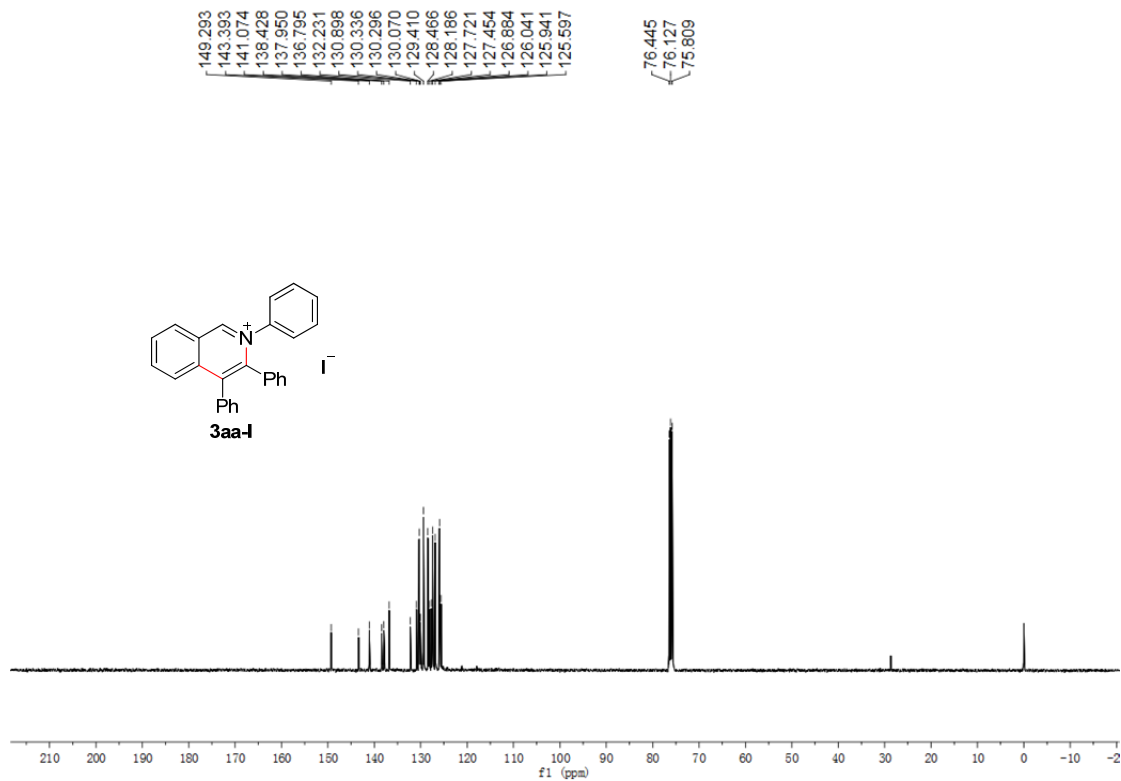
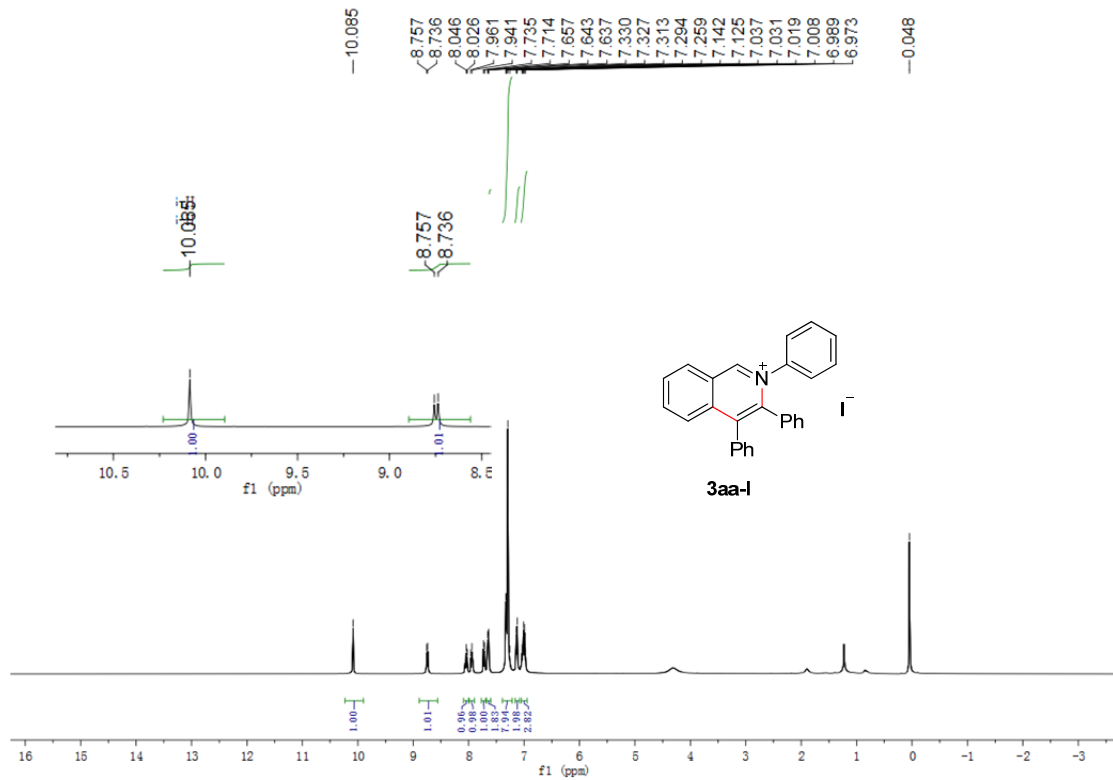


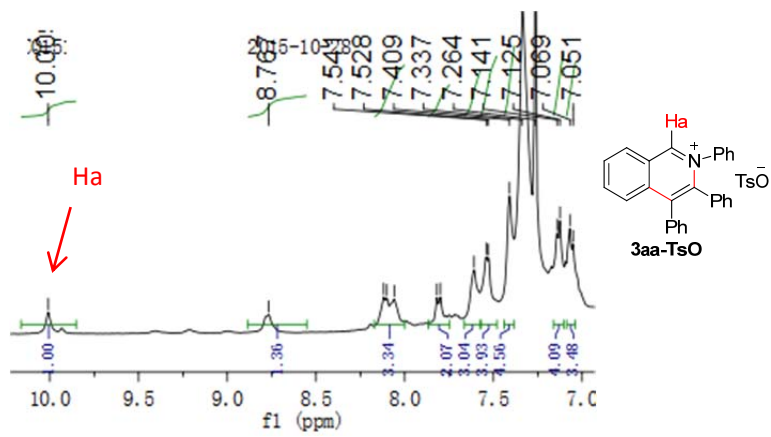
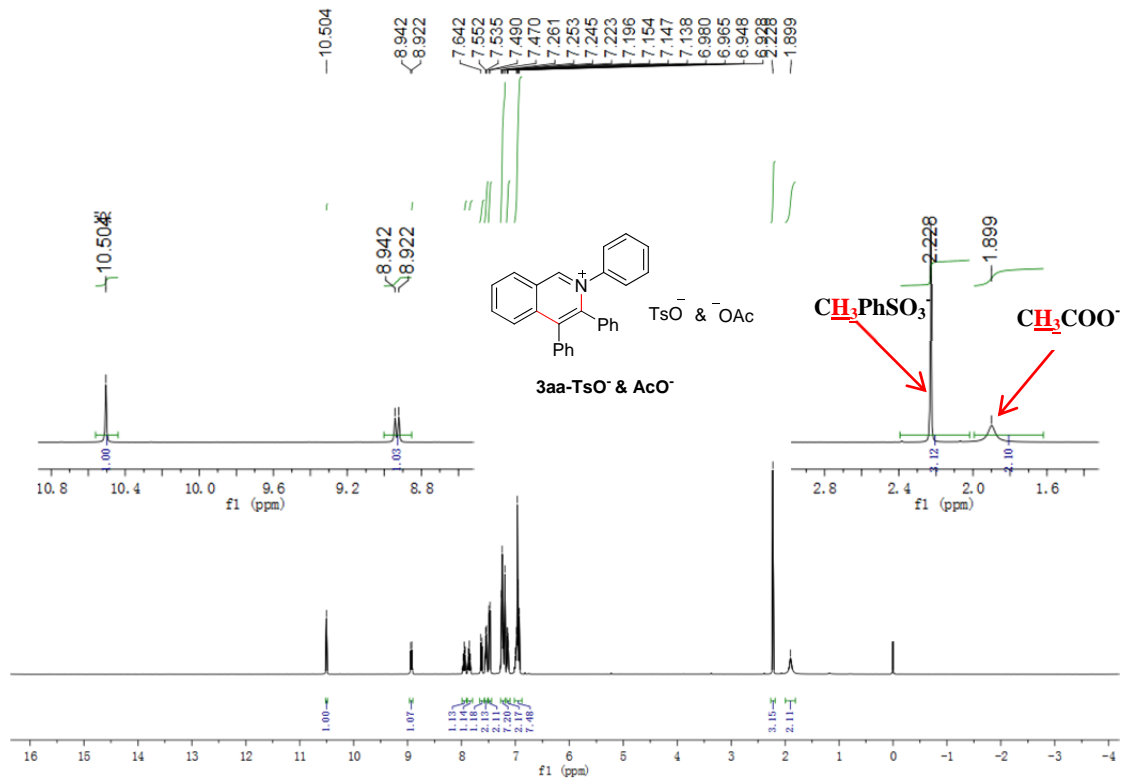
82% $3\text{kg}:3\text{kg}' = 1.8:1$

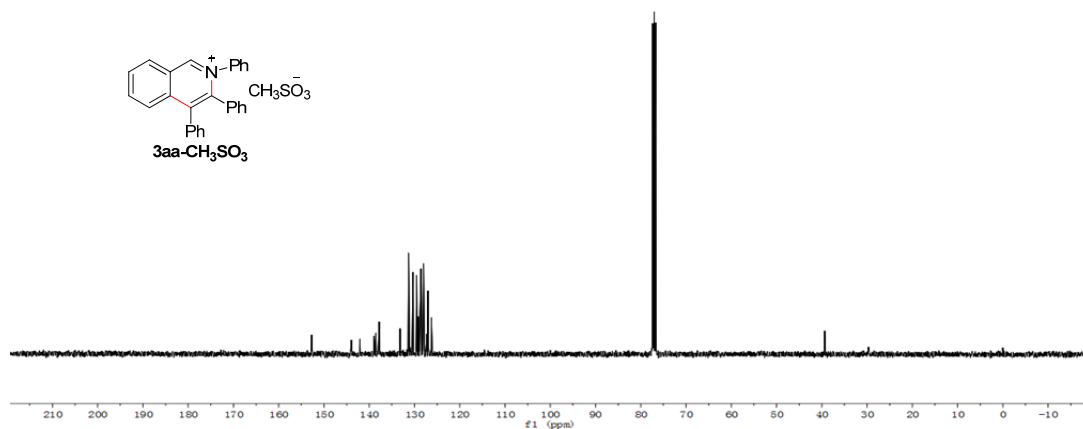
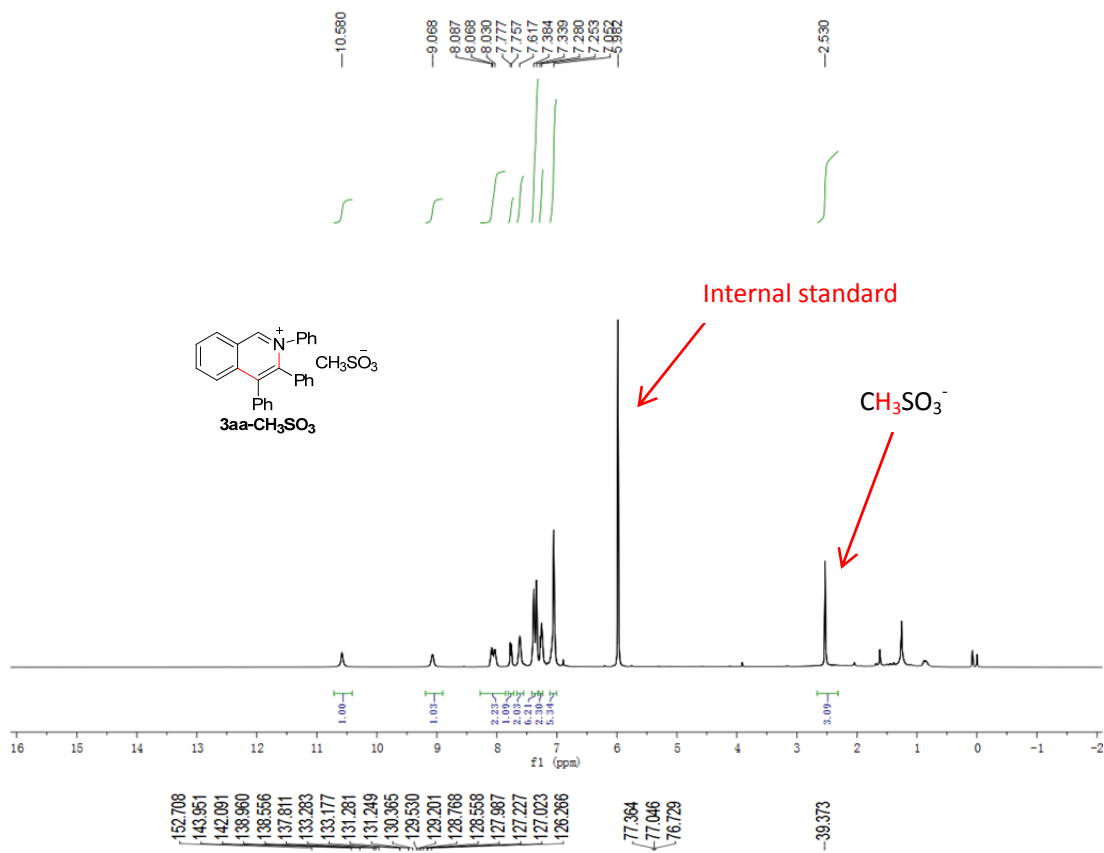
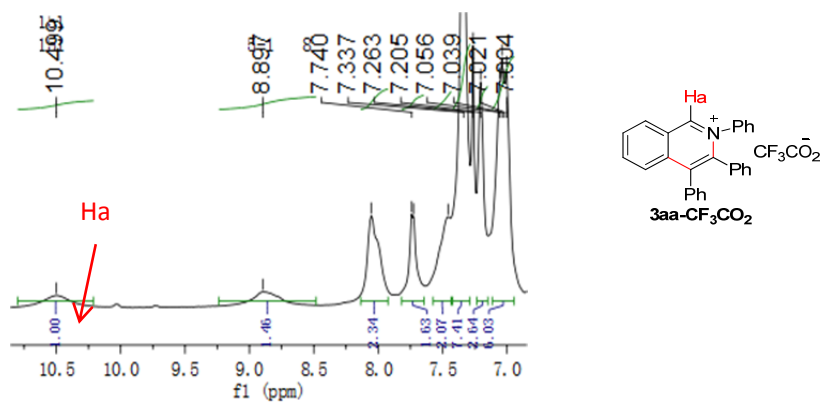
4. NMR spectra of isoquinolinium salts derived fused compounds and structure determination

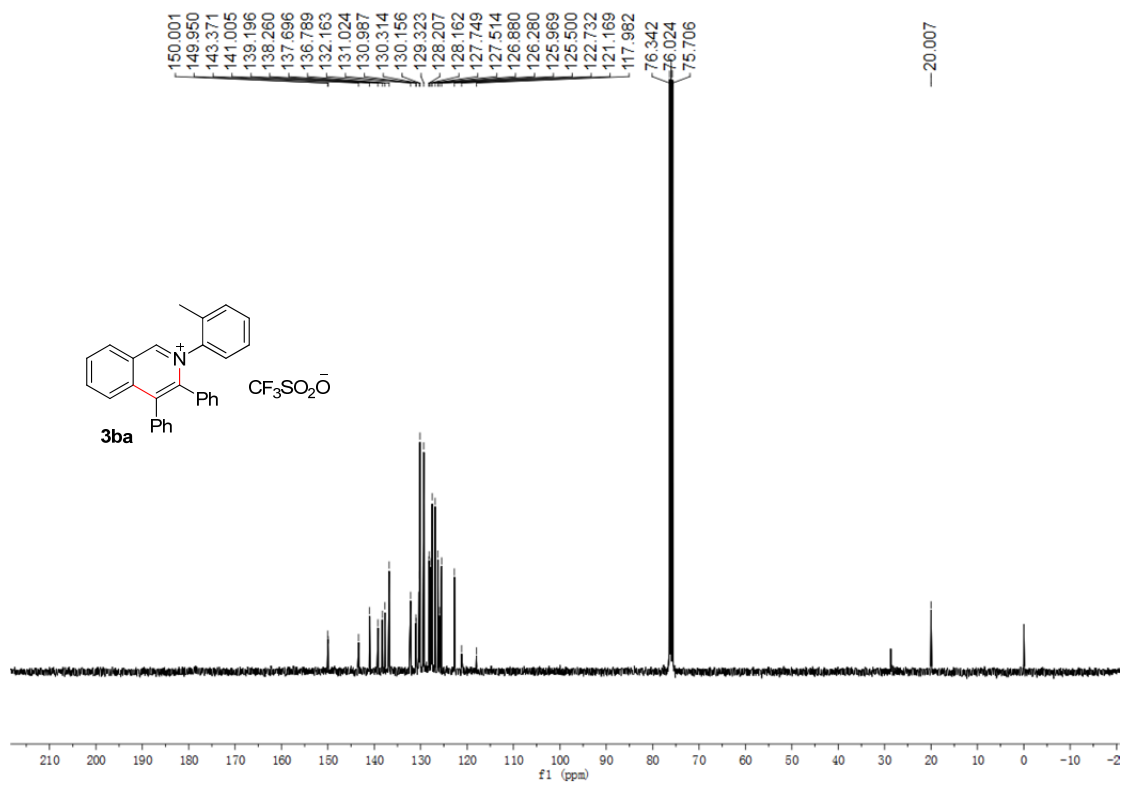
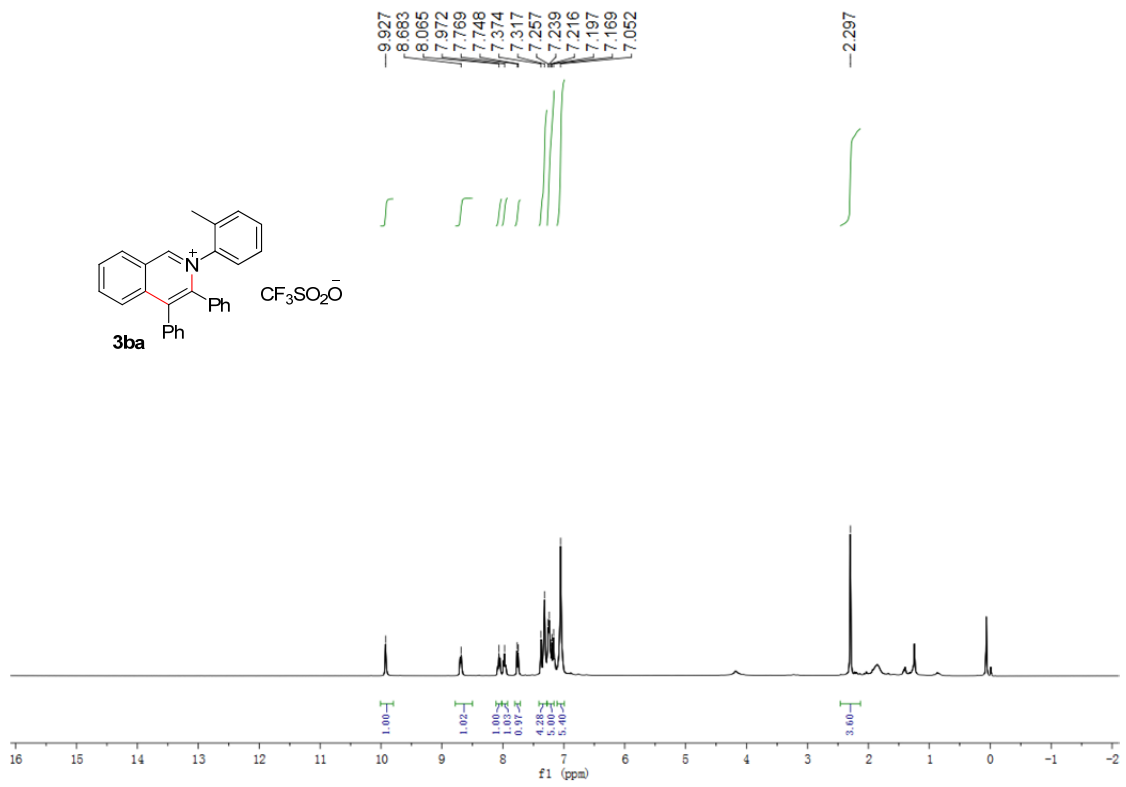




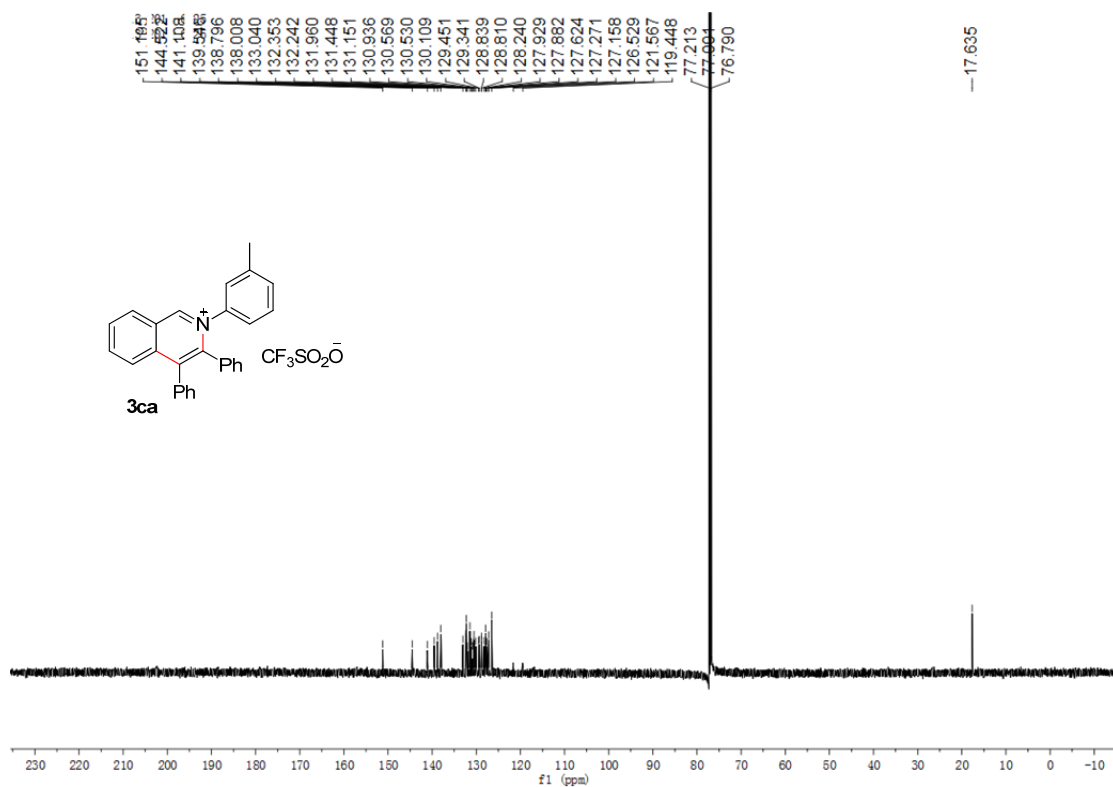
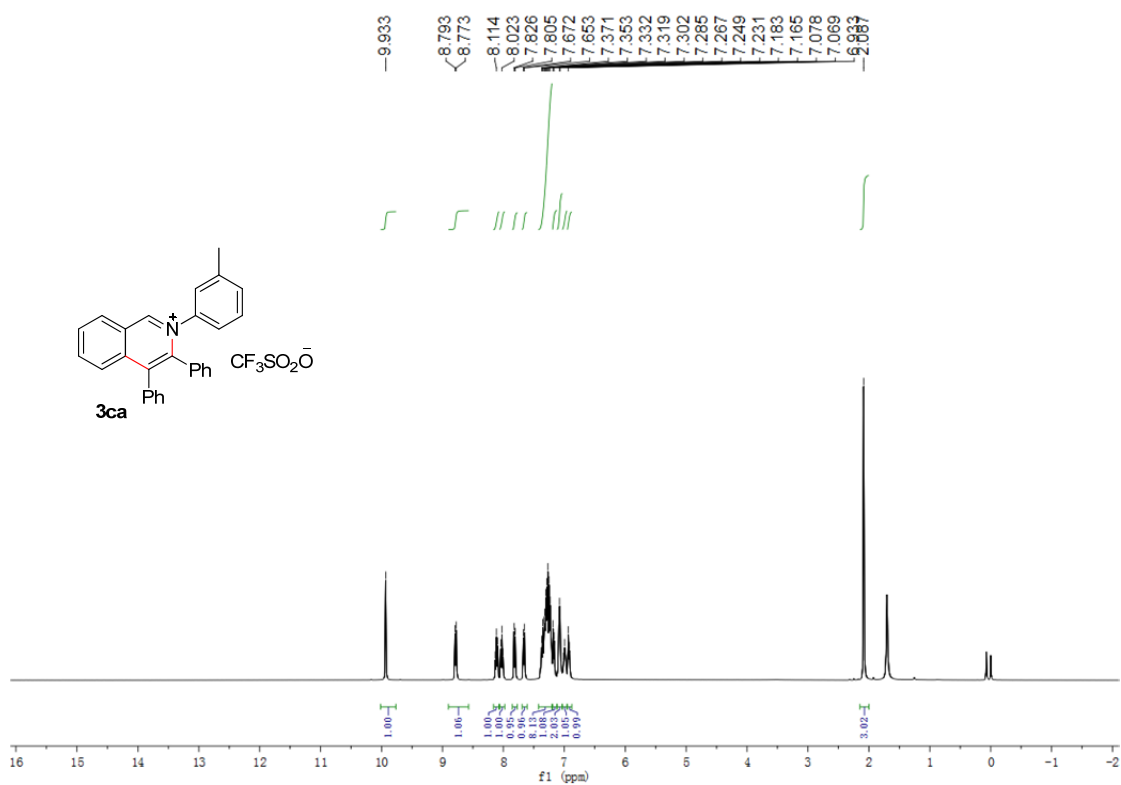




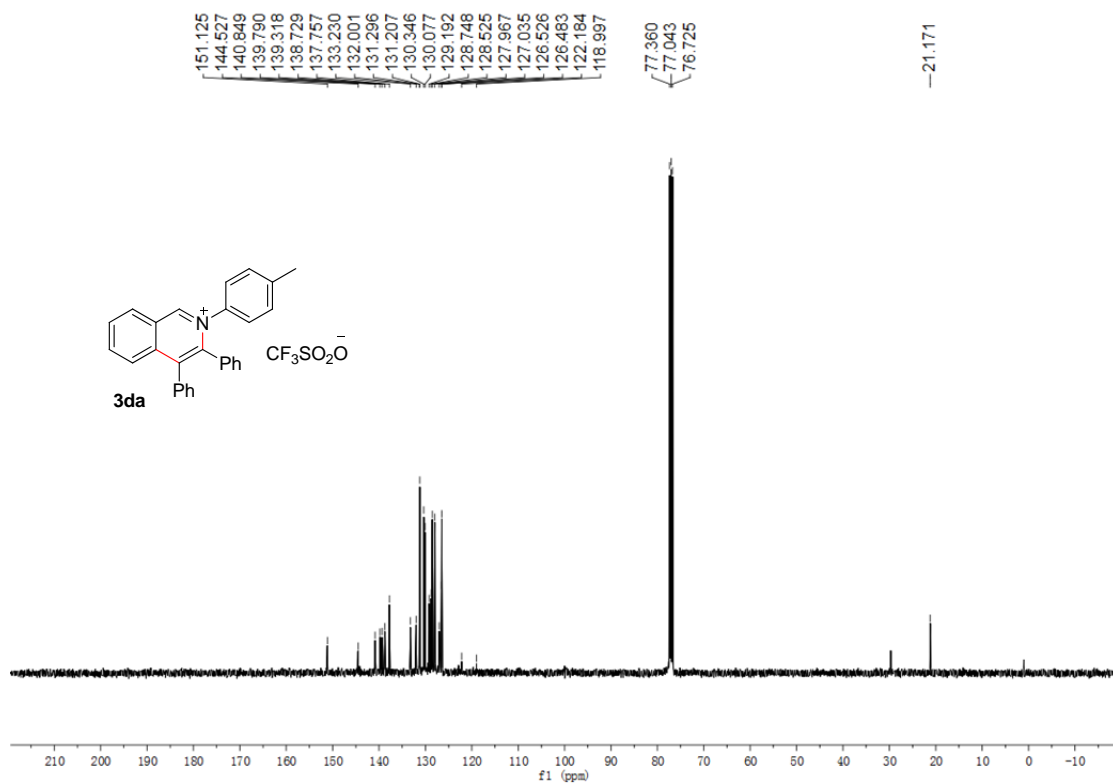
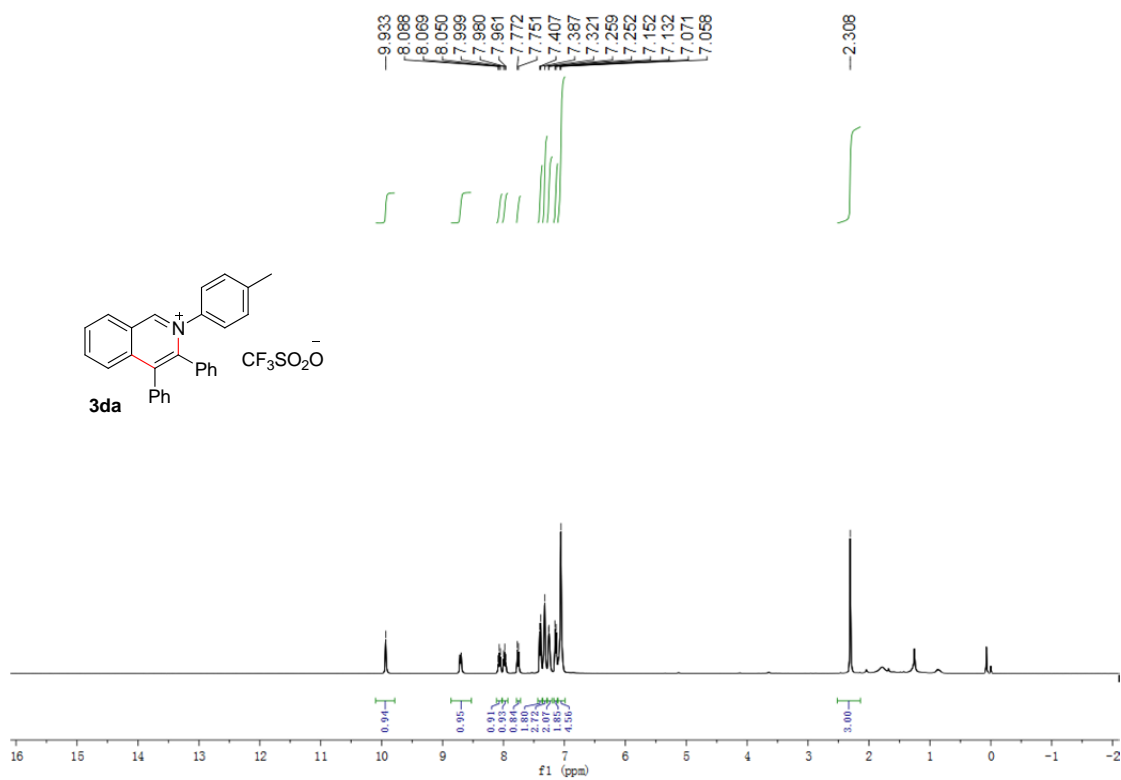




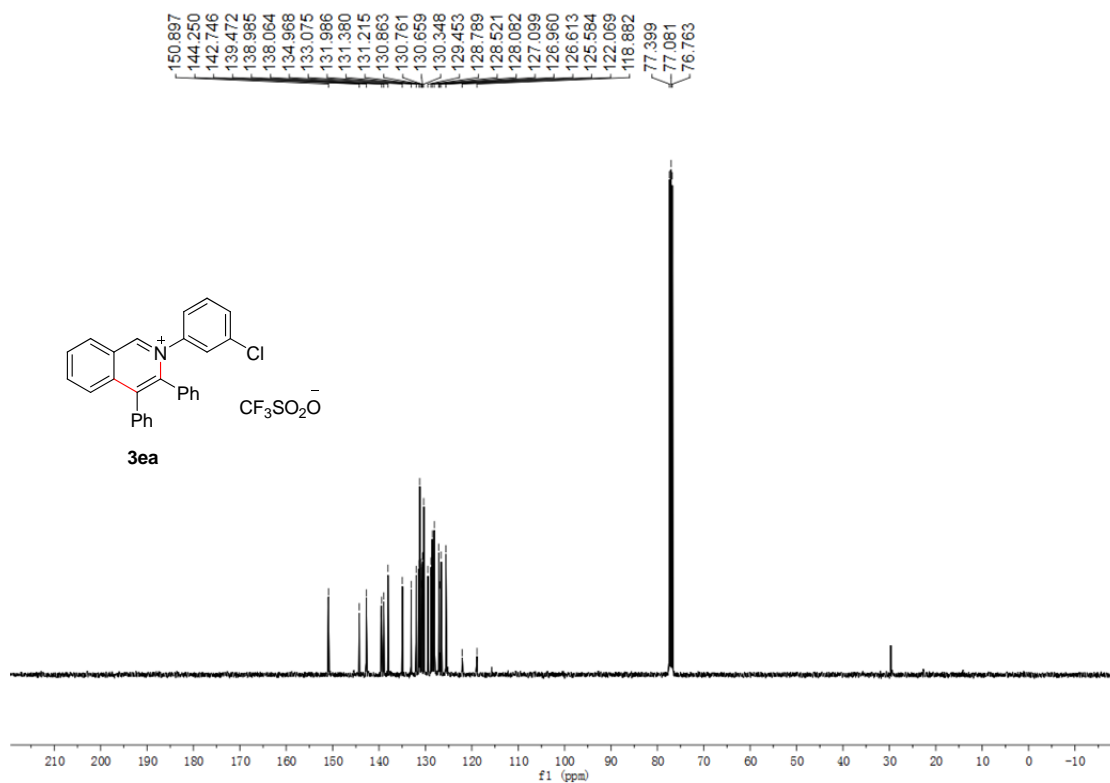
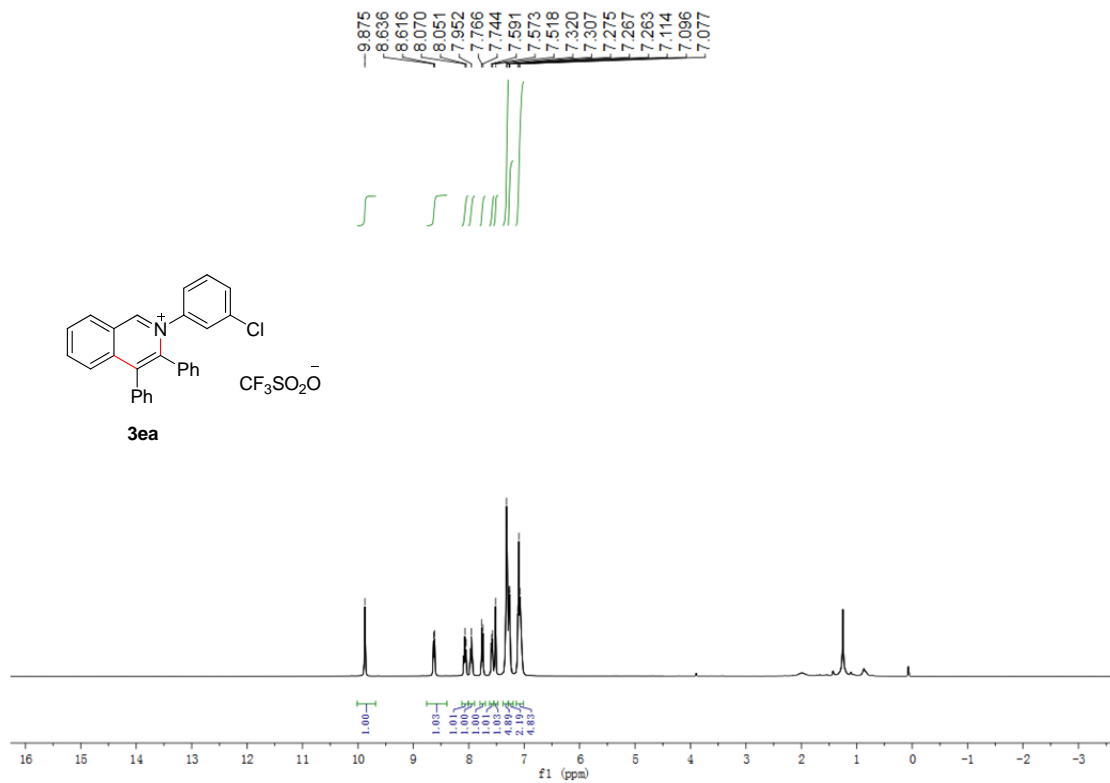
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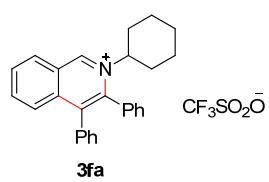
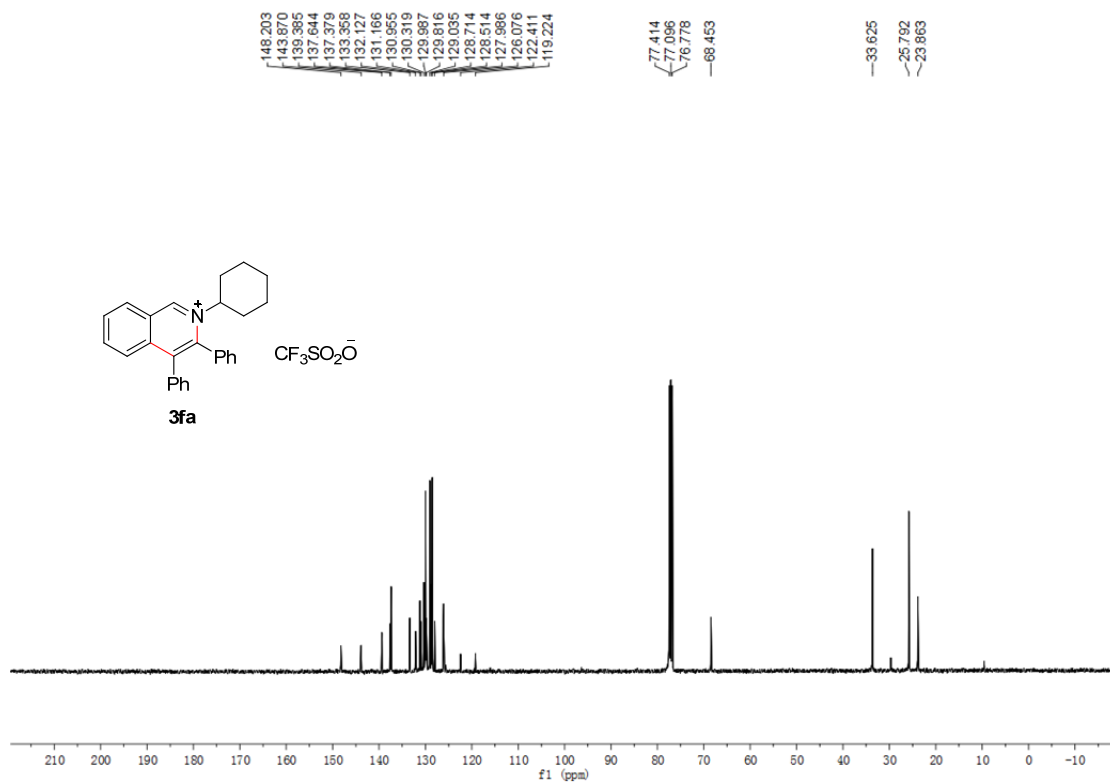
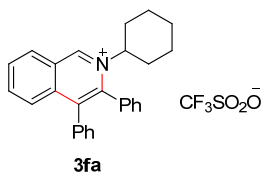
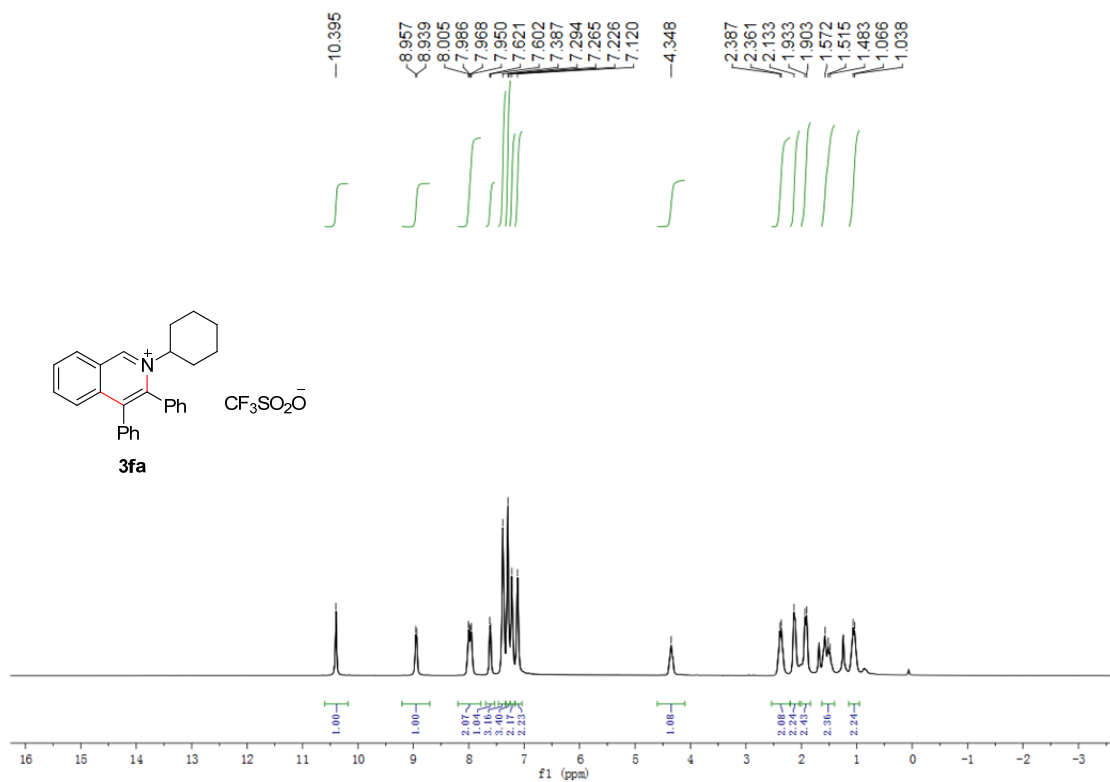
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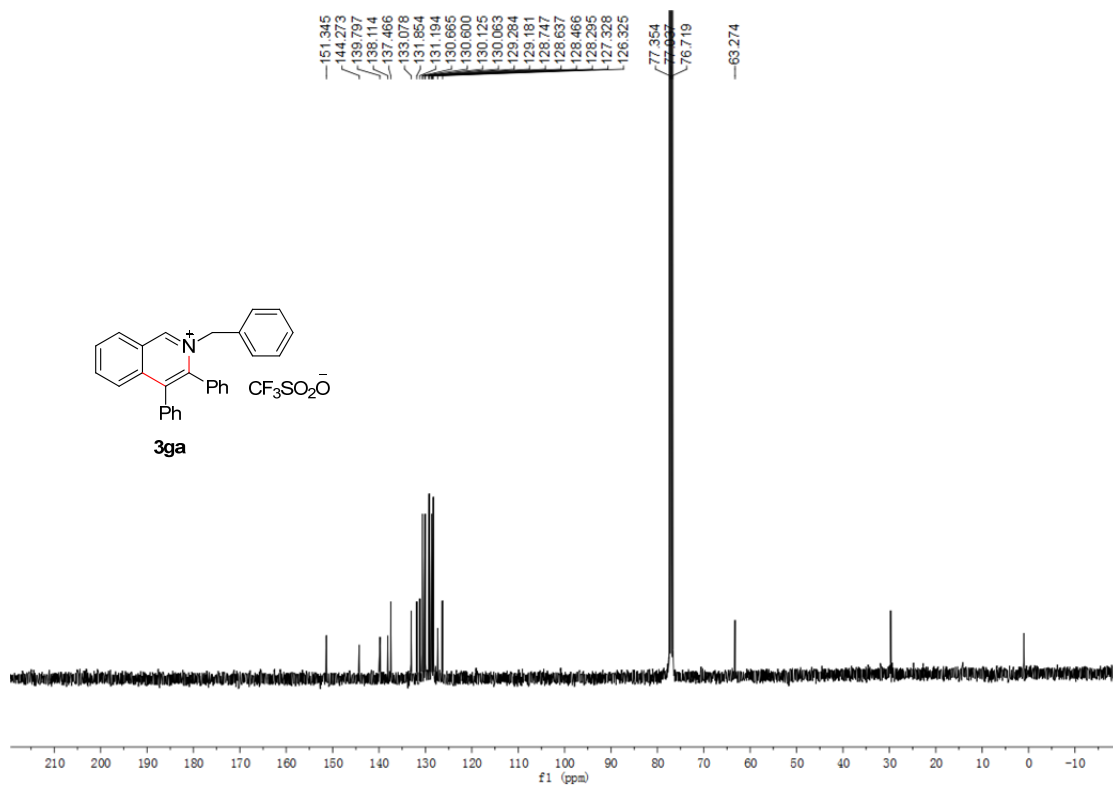
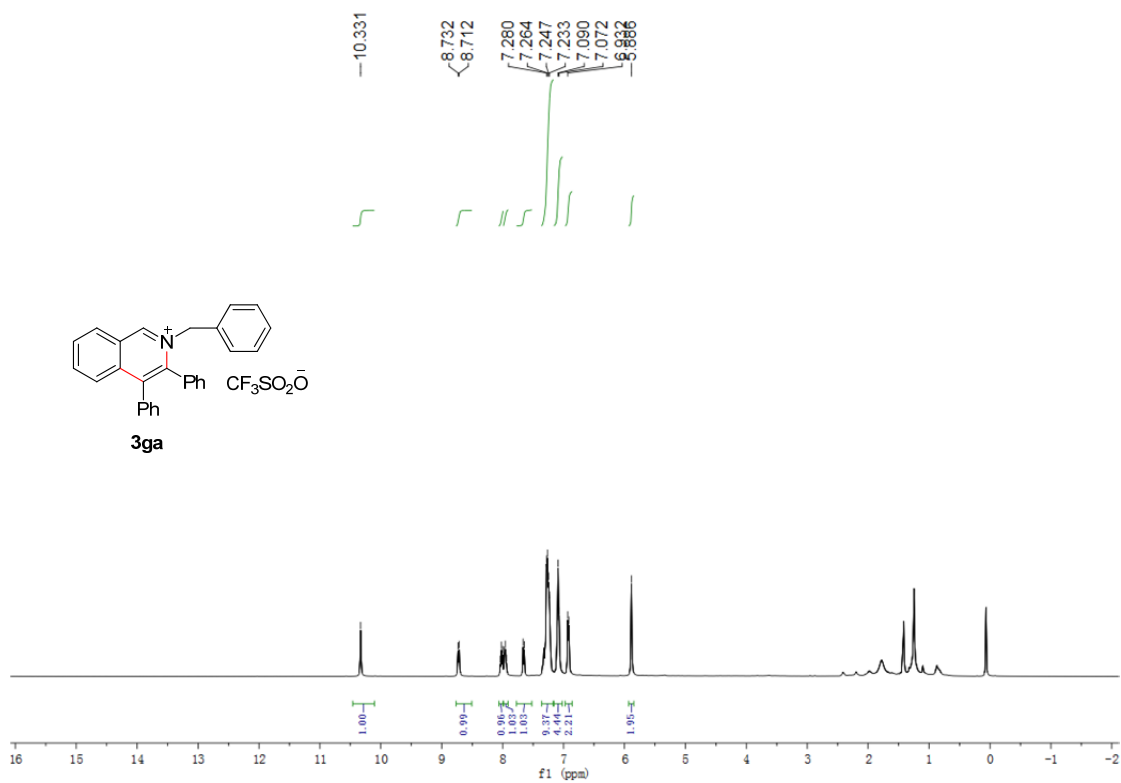
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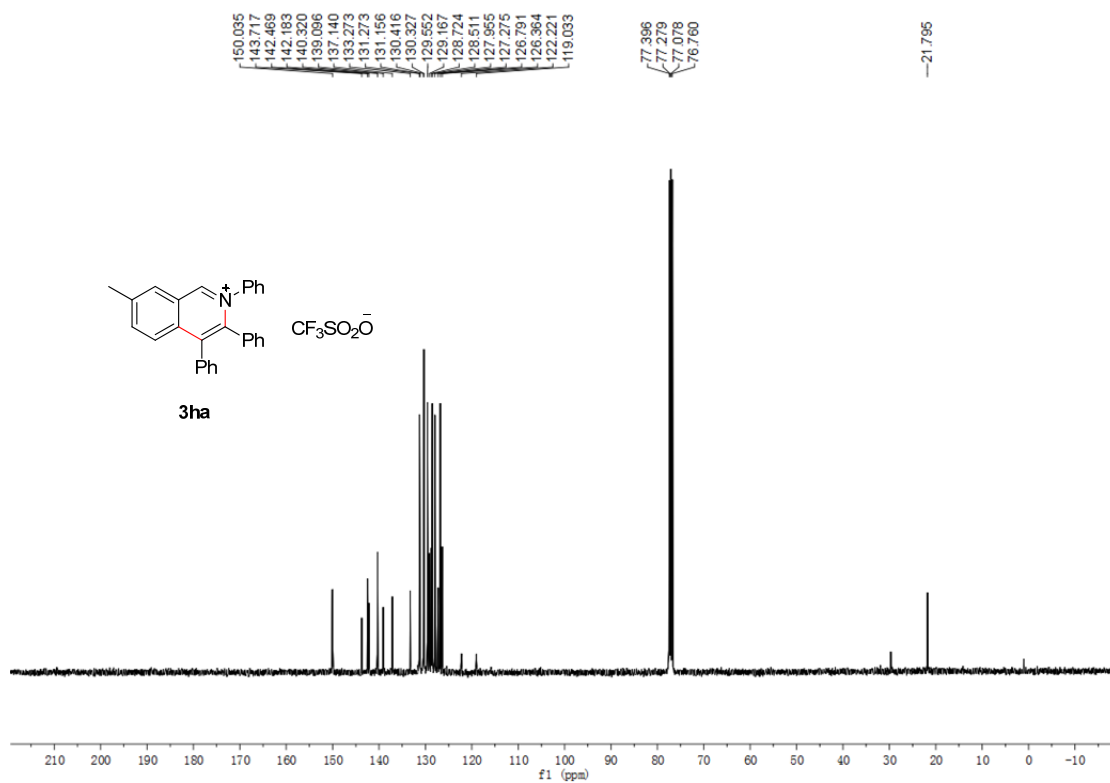
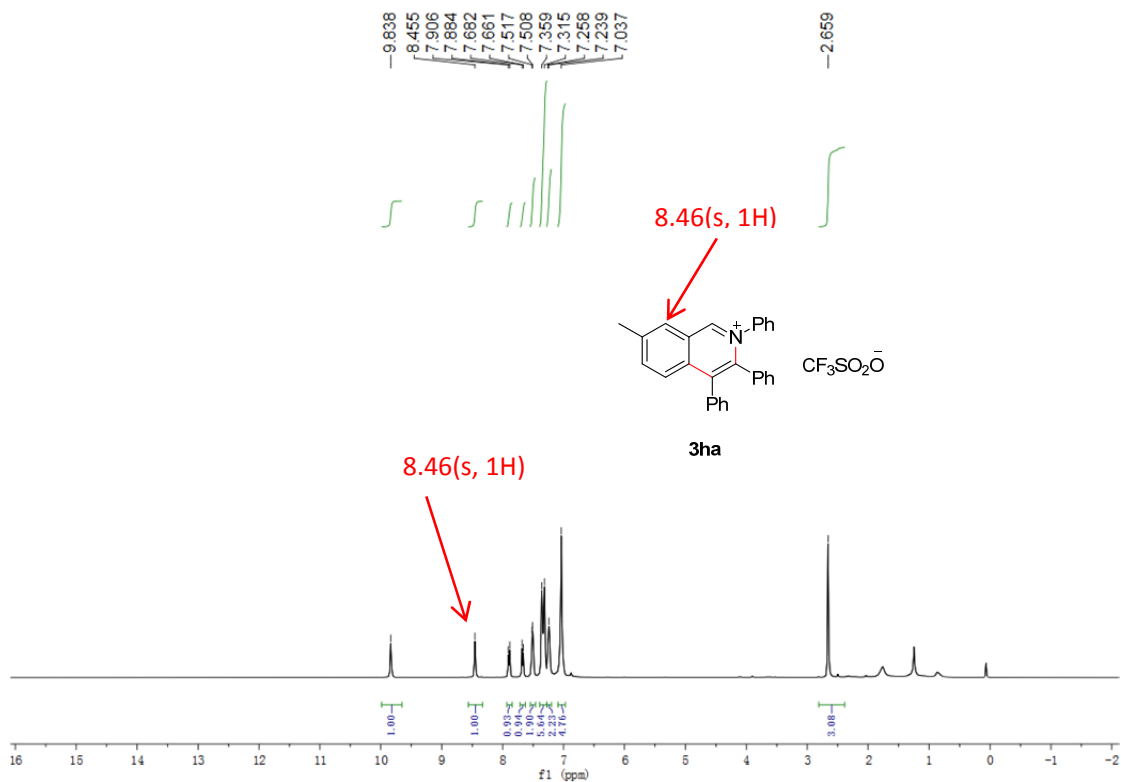
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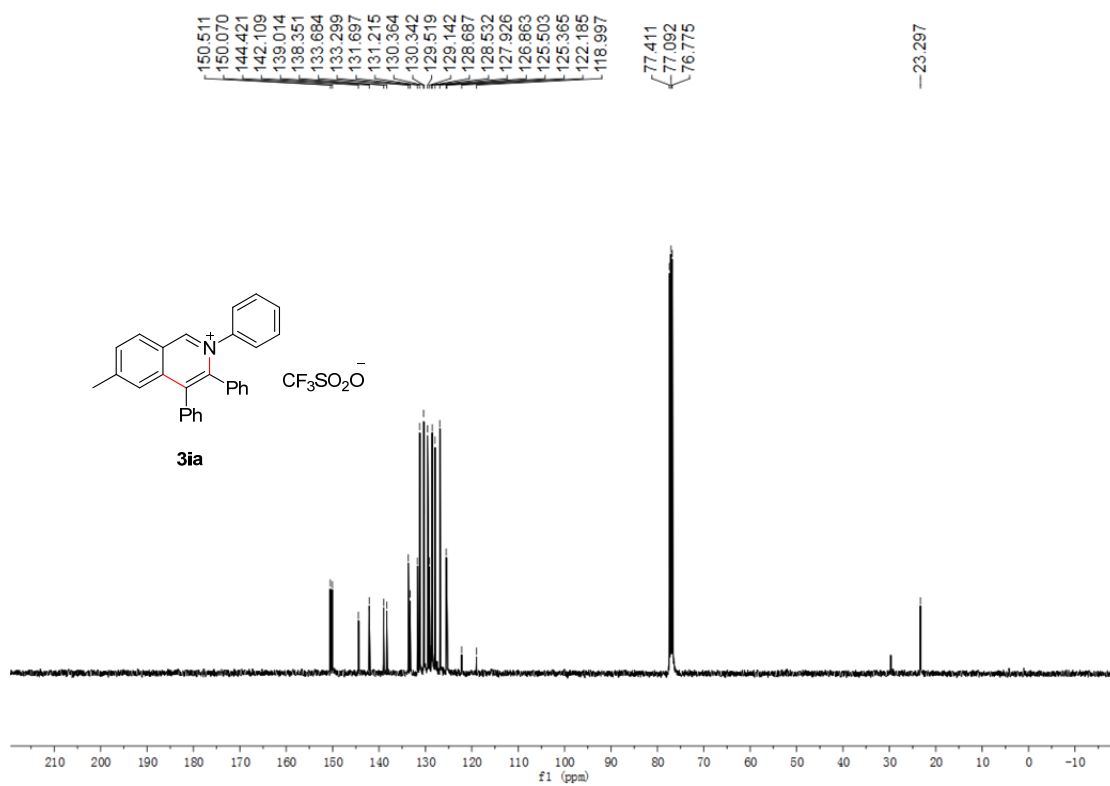
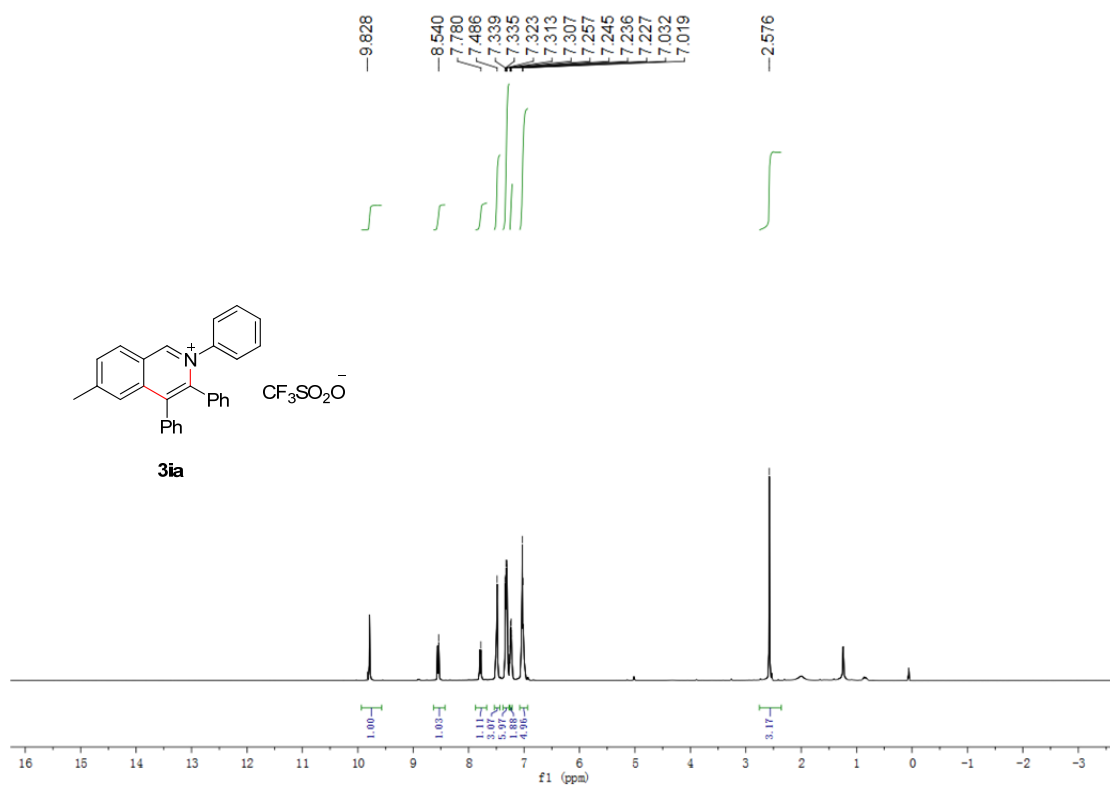
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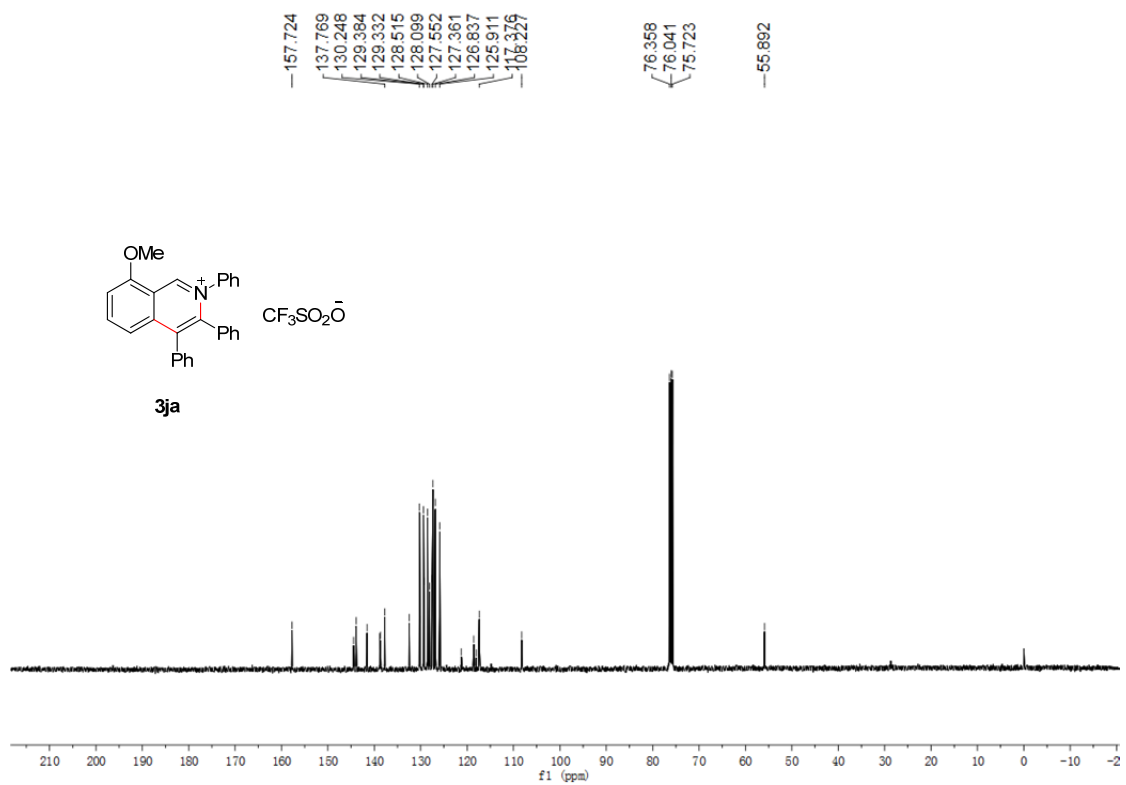
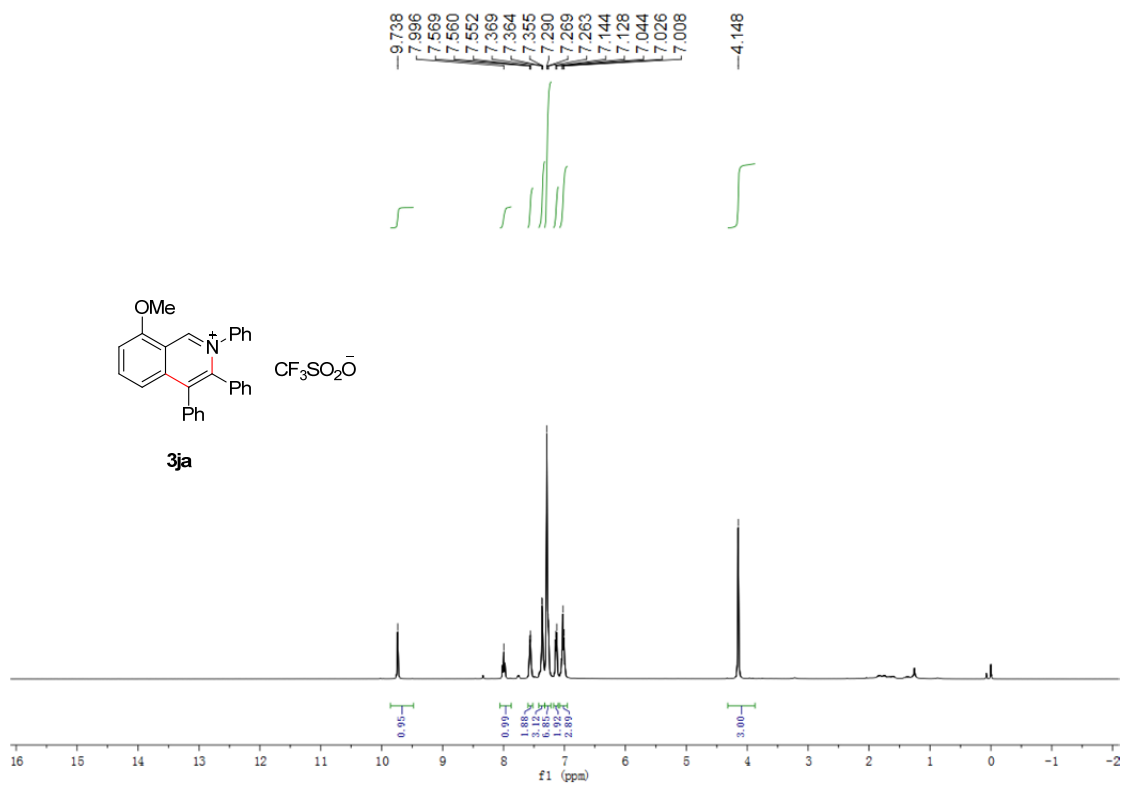
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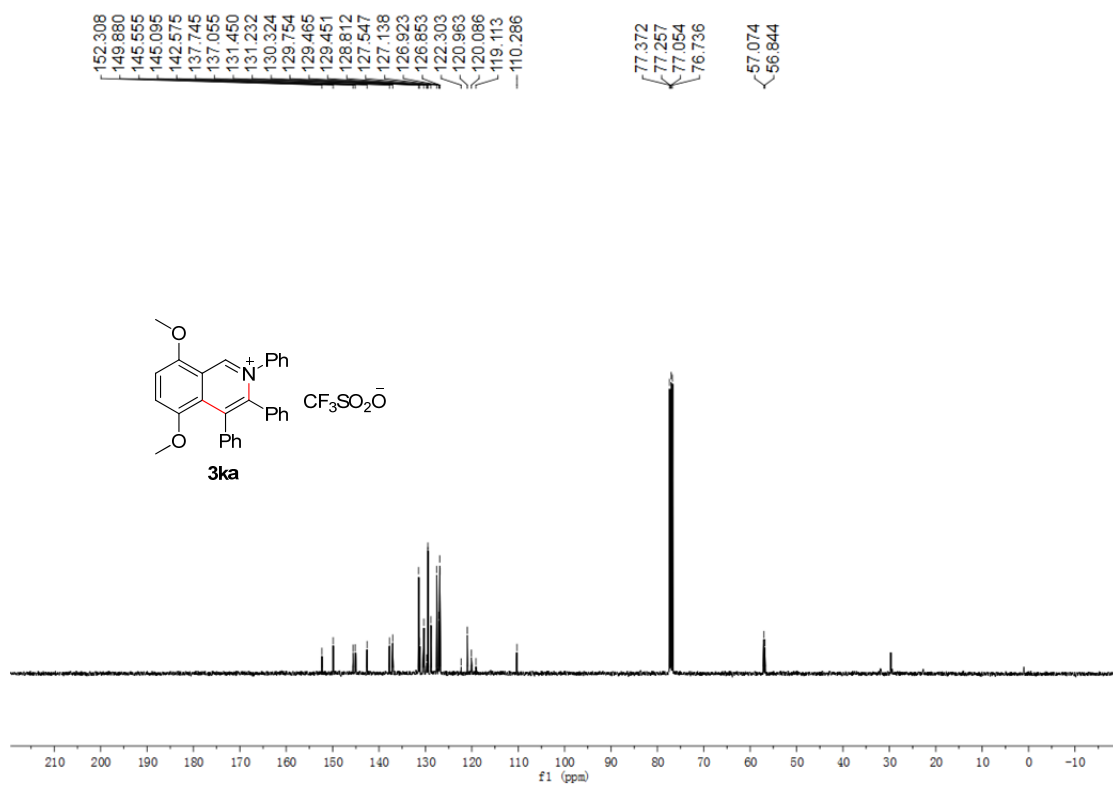
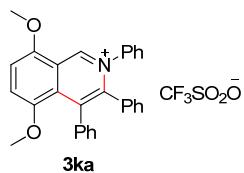
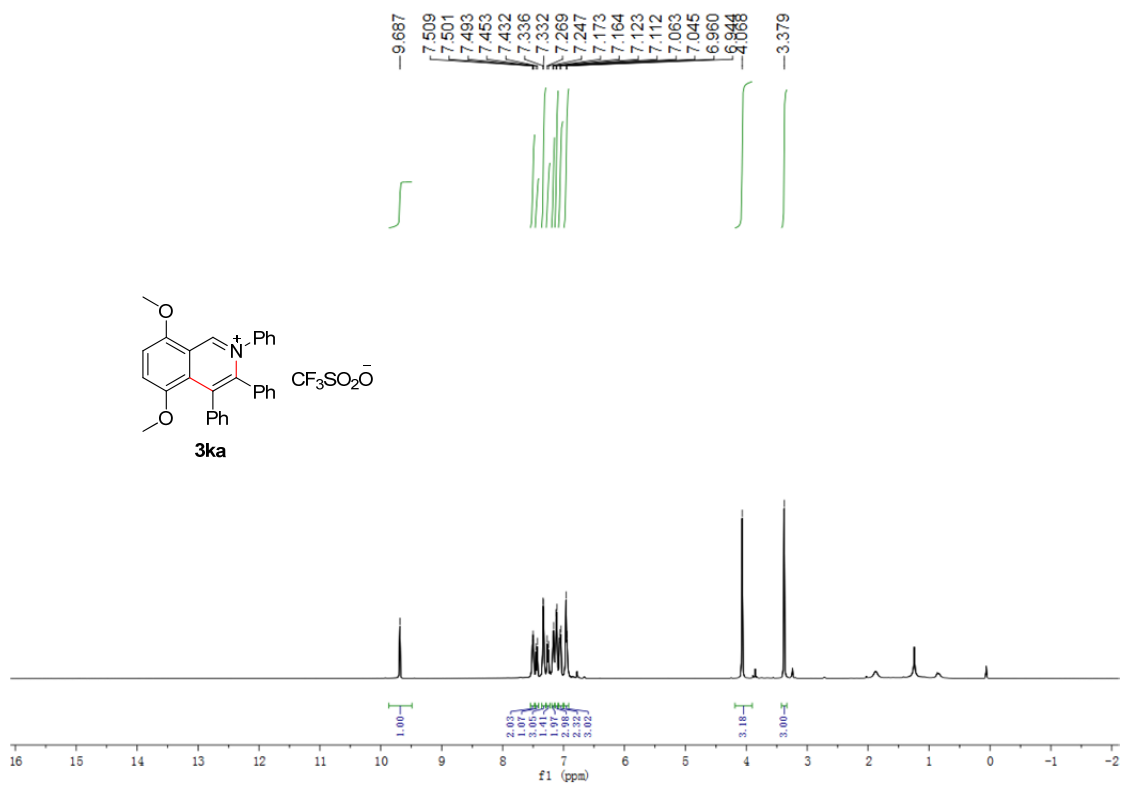
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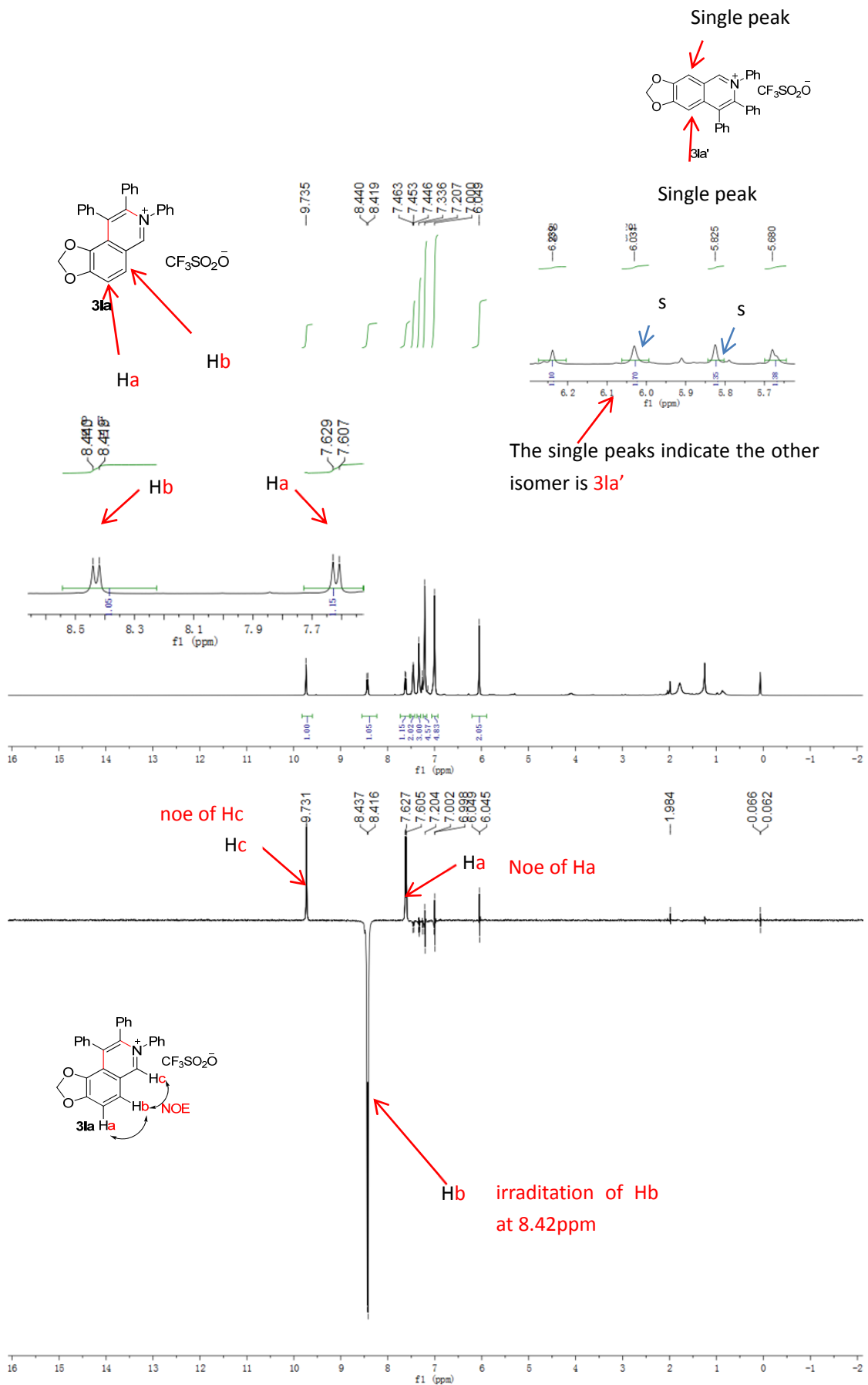


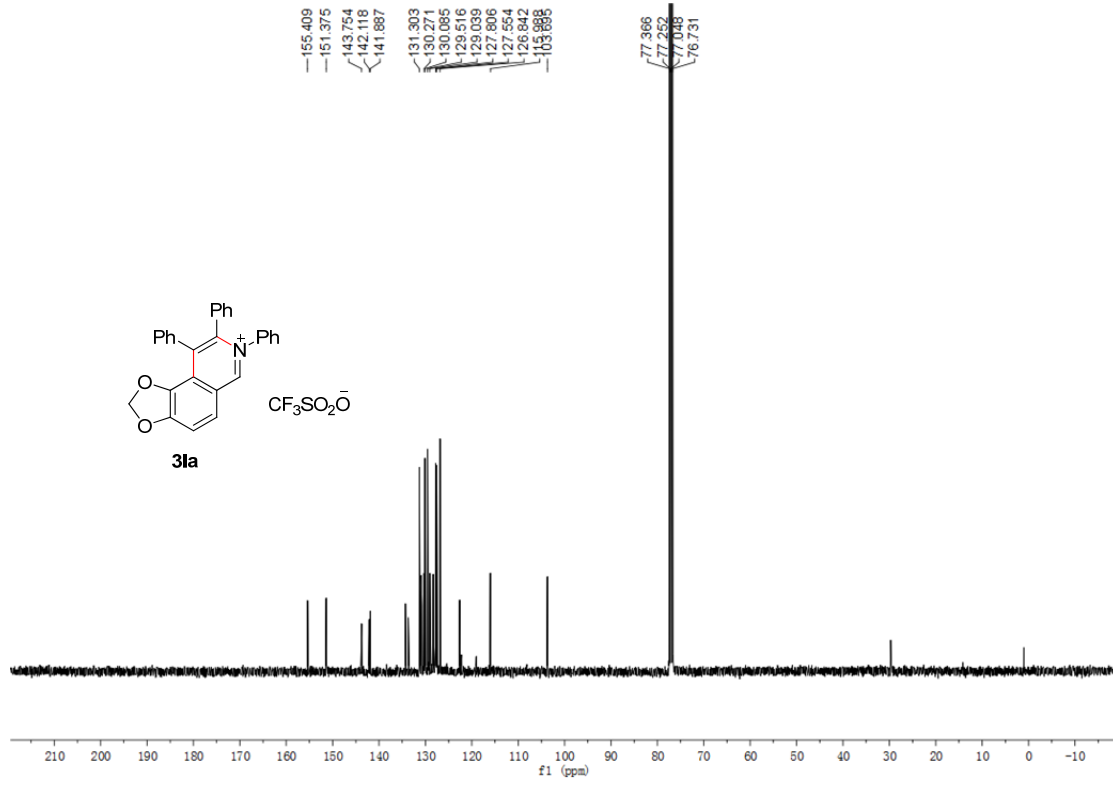
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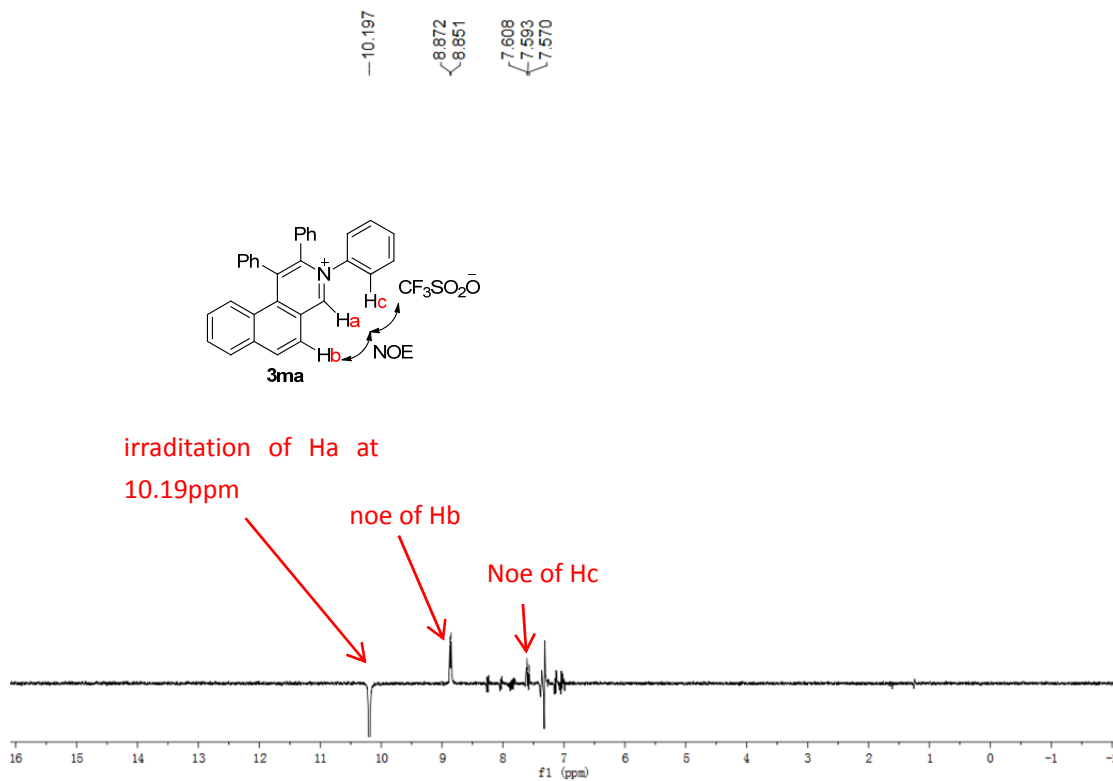
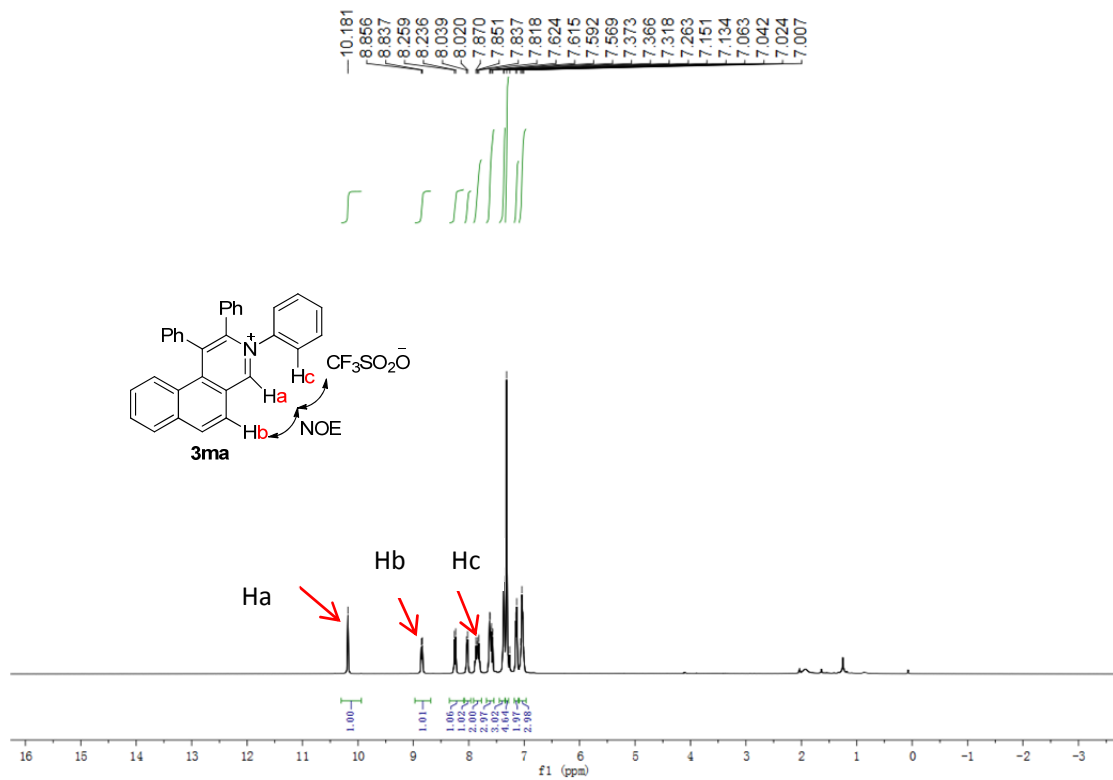
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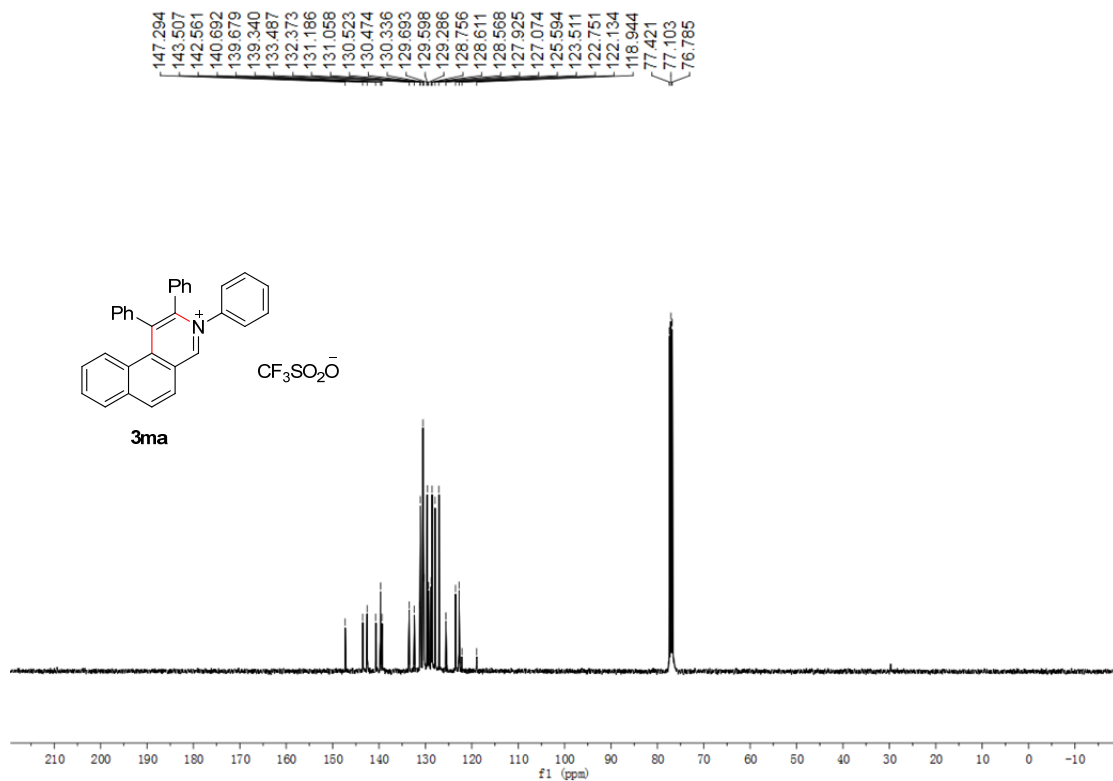




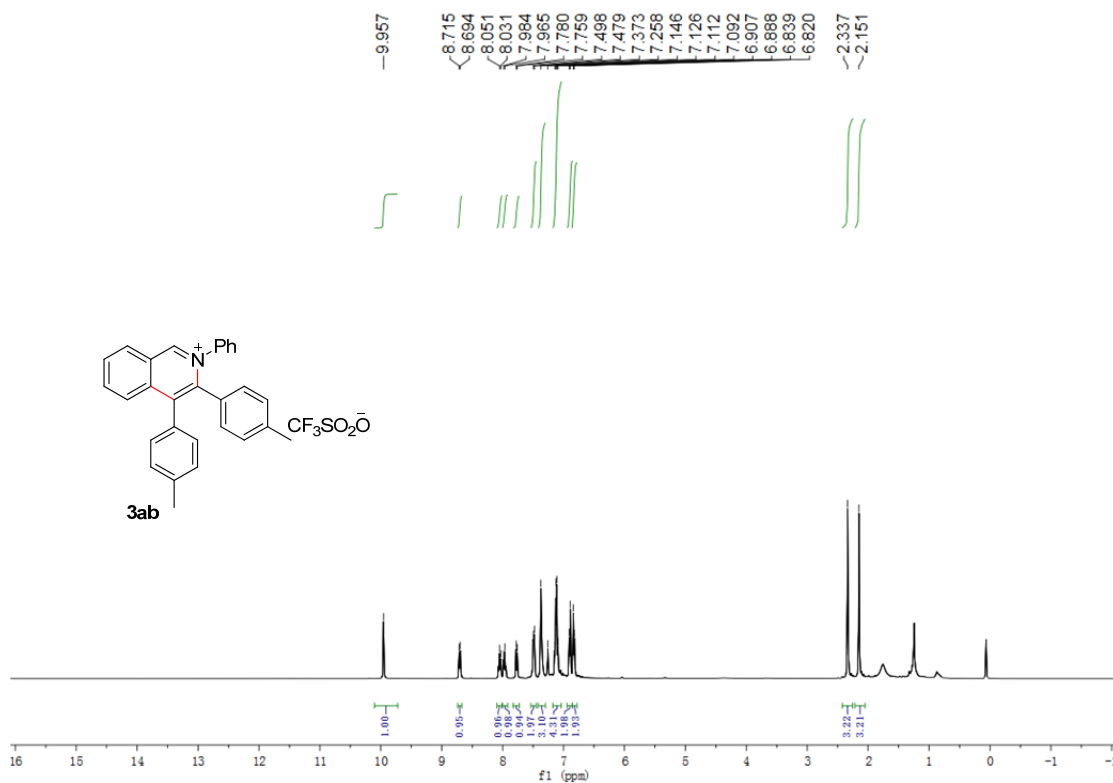


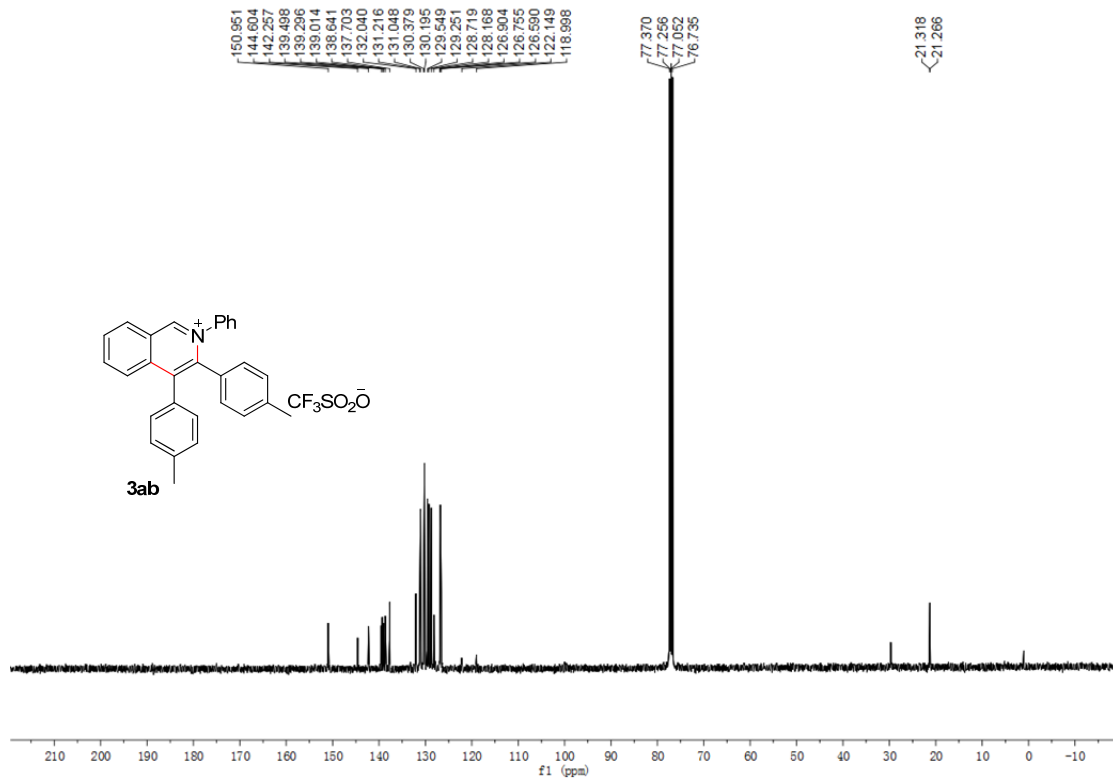
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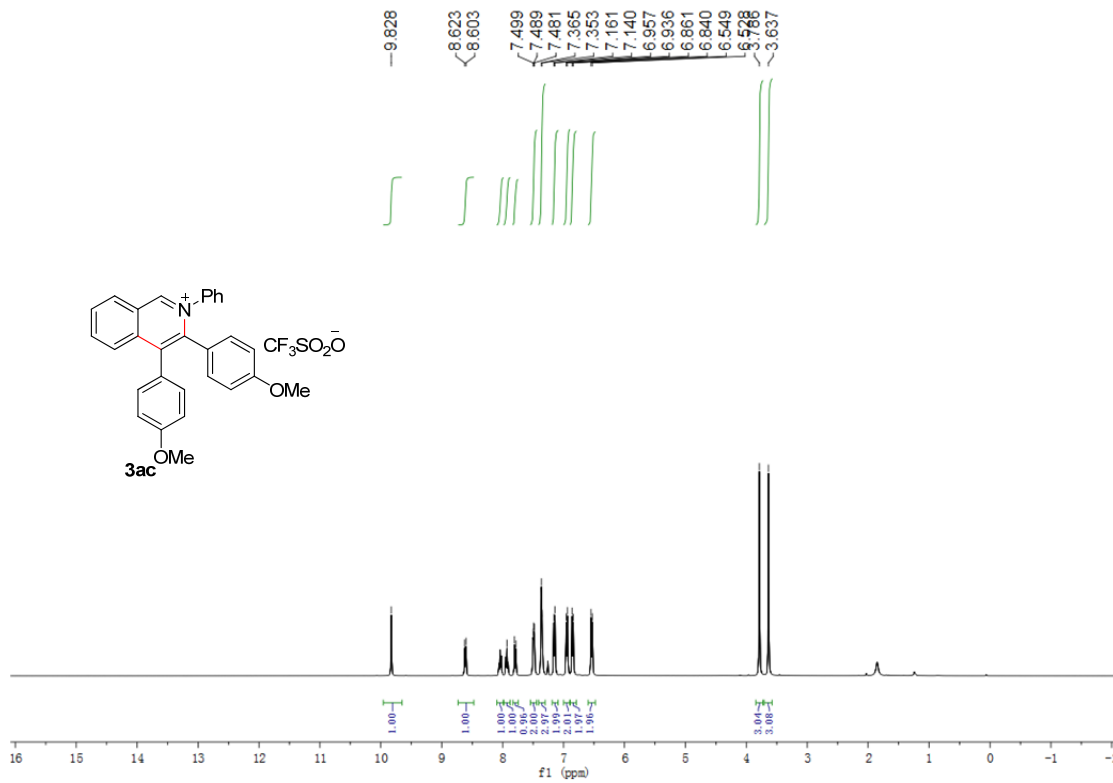


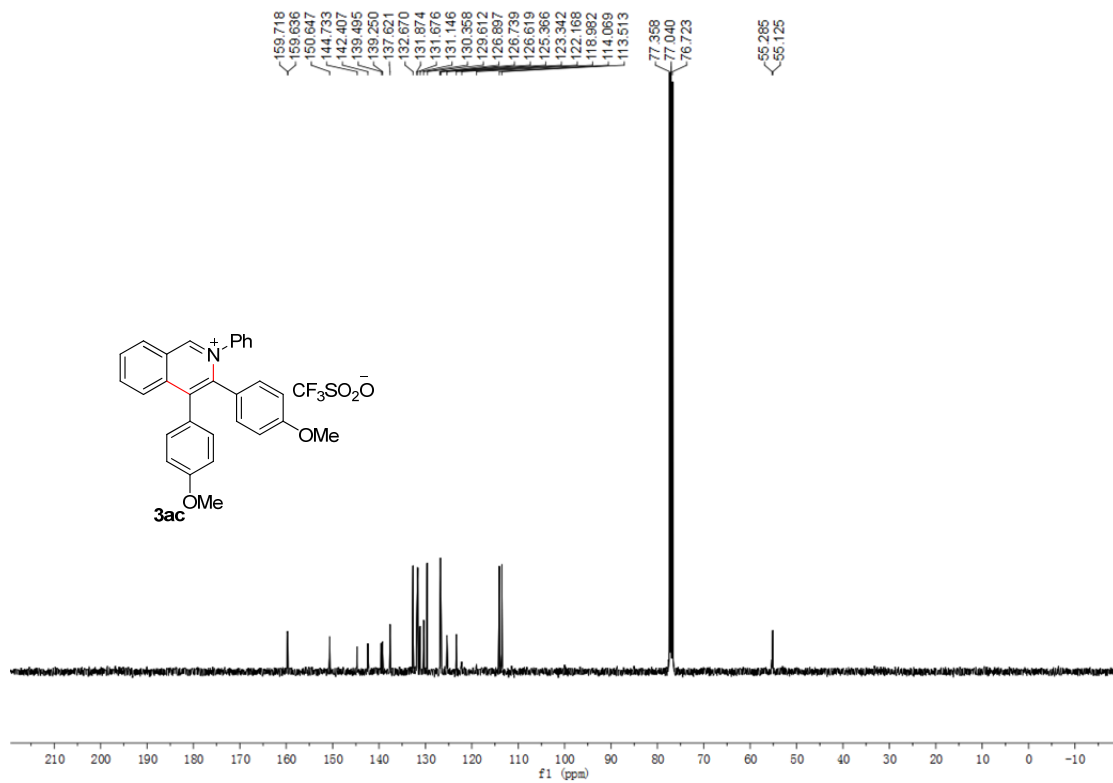
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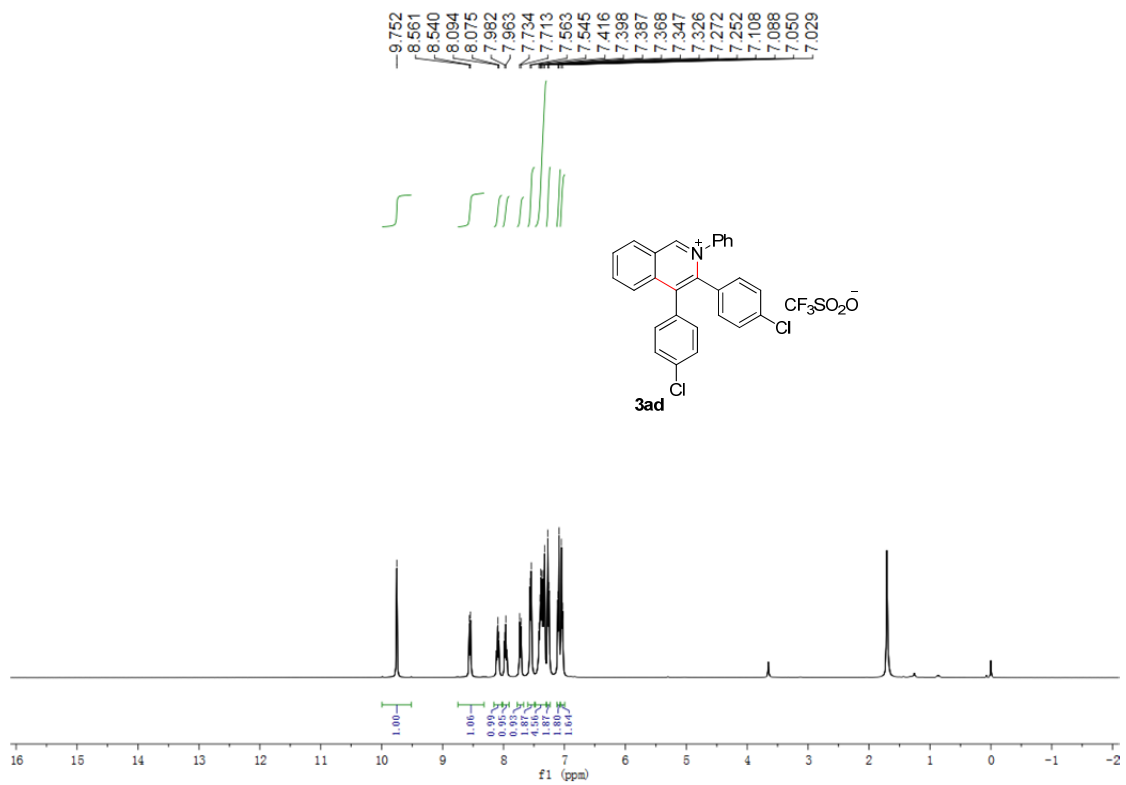


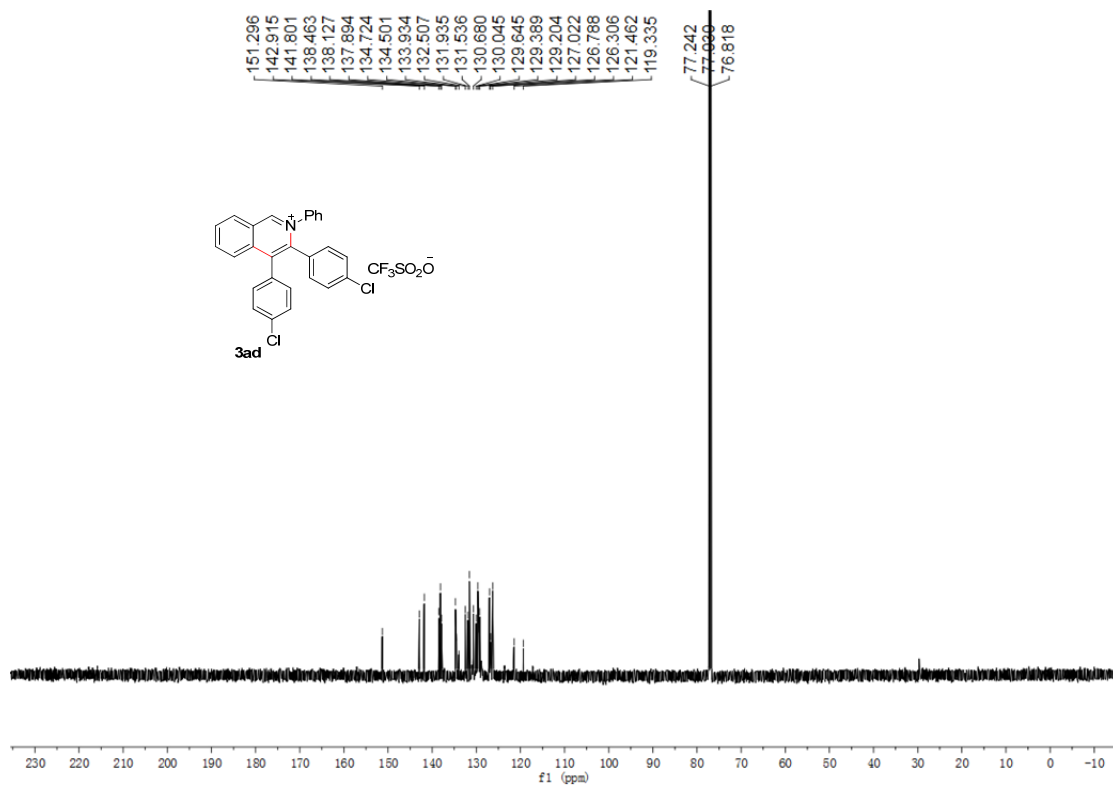
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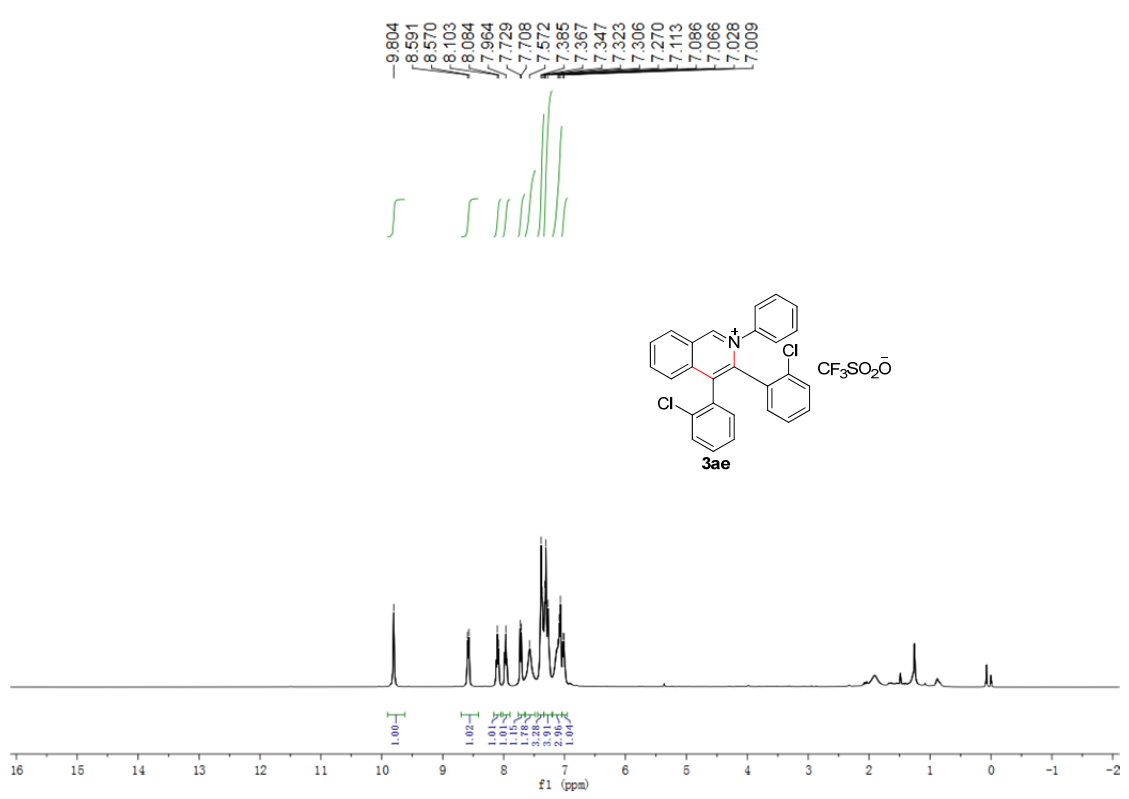


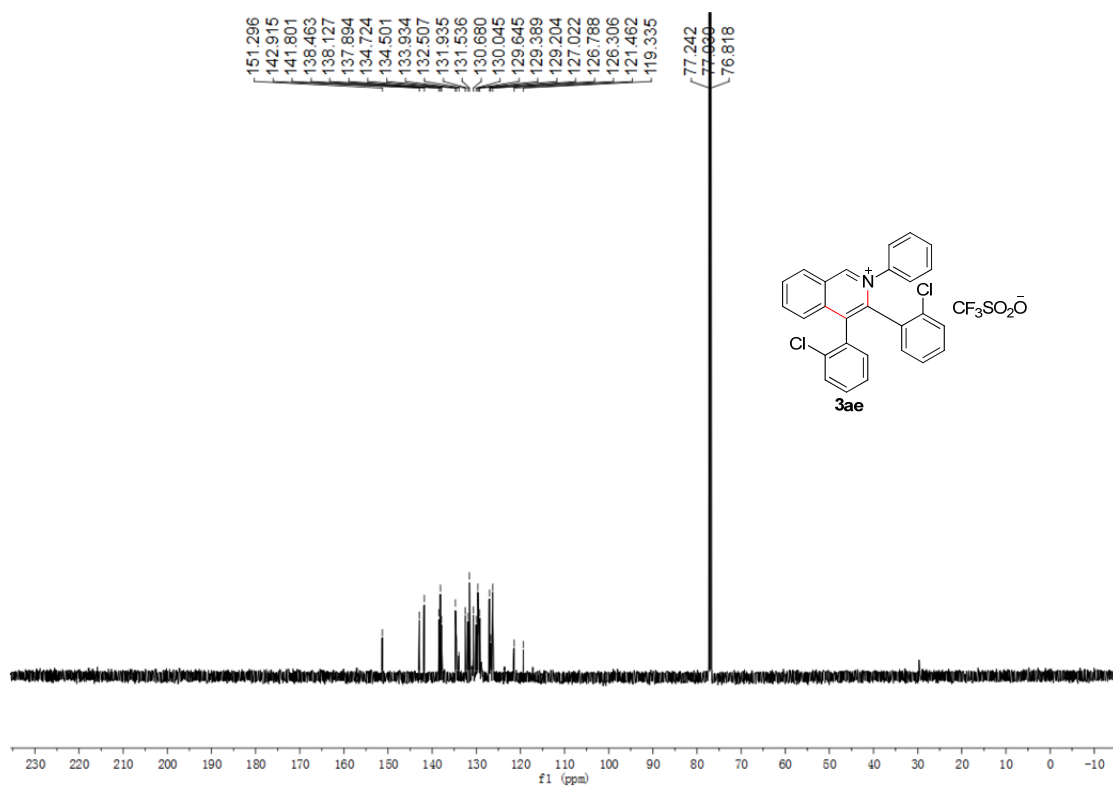
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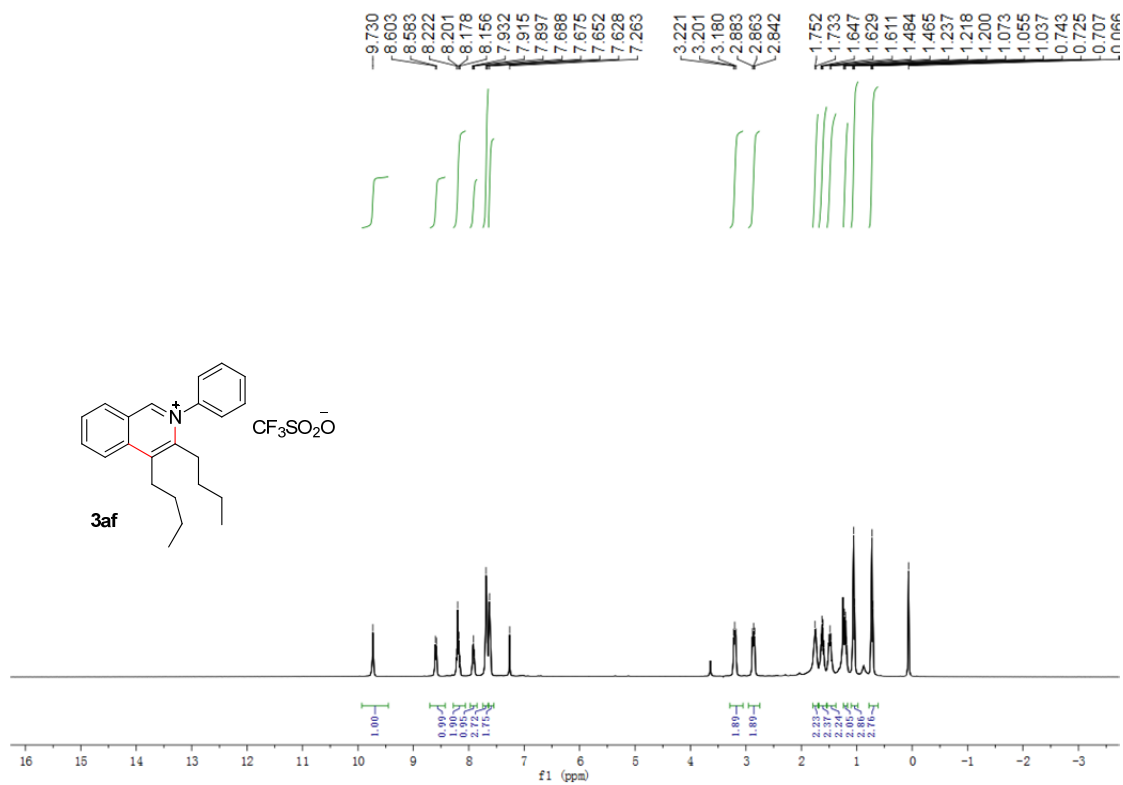


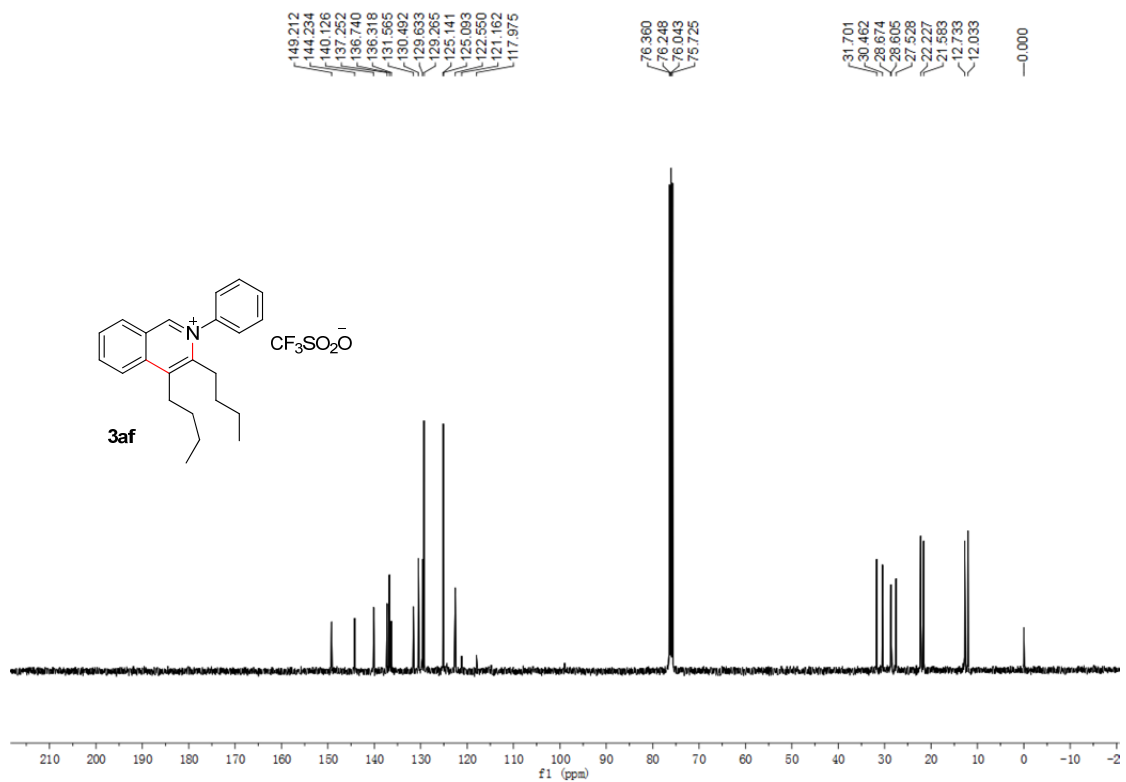
3ae





3af





3ag:3ag'

