Copper-Catalyzed Intramolecular Direct Amination of sp² C-H Bond for the Synthesis of N-Aryl Acridones

Supporting Information

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**General Remarks**

All manipulations were conducted with a standard Schlenk technique. $^1$H-NMR spectra were recorded on a Bruker AVIII-400 spectrometer. Chemical shifts (in ppm) were referenced to tetramethylsilane ($\delta = 0$ ppm) in CDCl$_3$ as an internal standard. $^{13}$C-NMR spectra were obtained by using the same NMR spectrometers and calibrated with CDCl$_3$. Mass spectra were recorded using an Agilent 5975 GC-MS. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.
Experimental Procedures

A Schlenk tube was charged with substrate 1 (0.3 mmol), CuI (0.06 mmol) and DMSO 1.6 mL. The mixture was stirred at 120 °C under air for 48 hours and monitored by TLC. The reaction was cooled down to room temperature, diluted with ethyl acetate, washed with brine (3×20 mL), dried over anhydrous Na₂SO₄, filtered, and dried under vaccum. The crude product was purified by column chromatography on silica gel to obtain the desired products 2.

Table S1

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^a Reaction conditions: substrate 1a (0.30 mmol), CuI (20 mol%), ligand (40 mol%), in DMSO (1.6 mL) stirred at 120 °C under air for 48 h. ^b Isolated yield.
Table S2

Table S2: Mechanism probing experiments

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^a Reaction conditions: substrate 1a (0.30 mmol), catalyst (20 mol%) in DMSO (1.6 mL) stirred at 120 °C under air for 48 h. ^b Isolated yield. ^c The reaction was carried out under N$_2$. 

Reaction conditions: substrate 1a (0.30 mmol), catalyst (20 mol%) in DMSO (1.6 mL) stirred at 120 °C under air for 48 h. Isolated yield. The reaction was carried out under N$_2$. 

Analytical Data of Compounds 2

1) 10-Phenyl-9(10H)-acridinon (2a)

The reaction of phenyl(2-(phenylamino)phenyl)methanone (1a, 0.3 mmol, 82.0 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under typical procedure afforded 63.4 mg (78%) of 2a as solid. m.p.: 286-288 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 8.59 (d, $J$ = 7.6 Hz, 2H), 7.80-7.43 (m, 5H), 7.37 (d, $J$ = 7.6 Hz, 2H), 7.32-7.20 (m, 2H), 6.75 (d, $J$ = 8.4 Hz, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ = 178.2, 143.2, 139.1, 133.3, 131.1, 130.1, 129.6, 127.4, 121.9, 121.6, 116.8 ppm; MS (70 eV): m/z (%) 271.1 (M$^+$, 100).

2) 10-(2-Methylphenyl)-9(10H)-acridinon (2b)

The reaction of phenyl(2-((2-methylphenyl)amino)phenyl)methanone (1b, 0.3 mmol, 86.1 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under typical procedure afforded 62 mg (73%) of 2b as solid. m.p.: 208-209 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 8.61 (d, $J$ = 7.6 Hz, 2H), 7.58-7.48 (m, 6H), 7.32-7.28 (m, 2H), 6.69 (d, $J$ = 8.4 Hz, 2H), 1.92 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ = 178.2, 142.4, 137.8, 137.5, 133.6, 132.4, 130.1, 129.9, 128.6, 127.5, 122.0, 121.7, 116.2, 17.0 ppm; MS (70 eV): m/z (%) 285.1 (M$^+$, 100). HRMS m/z (ESI) calcd for C$_{20}$H$_{16}$NO (M + H)$^+$: 286.1226, found
3) 10-(3-Methylphenyl)-9(10H)-acridinon (2c)

The reaction of phenyl(2-((3-methylphenyl)amino)phenyl)methanone (1c, 0.3 mmol, 86.2 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under typical procedure afforded 45 mg (53%) of 2c as solid. m.p.: 205-207 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 8.59 (d, $J$ = 6.4 Hz, 2H), 7.61-7.42 (m, 4H), 7.30-7.10 (m, 4H), 6.79 (d, $J$ = 10 Hz, 2H), 2.48 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ = 178.2, 143.2, 141.4, 139.0, 133.2, 130.8, 130.5, 130.3, 127.3, 126.9, 121.9, 121.5, 116.9, 21.4 ppm; HRMS m/z (ESI) calcd for C$_{20}$H$_{16}$NO (M + H)$^+$: 286.1226, found 286.1227.

4) 10-(4-Methylphenyl)-9(10H)-acridinon (2d)

The reaction of phenyl(2-((4-methylphenyl)amino)phenyl)methanone (1d, 0.3 mmol, 86.2 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under typical procedure afforded 80 mg (93%) of 2d as solid. m.p.: 281-283 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 8.59 (d, $J$ = 8.4 Hz, 2H), 7.53-7.48 (m, 4H), 7.29-7.22 (m, 4H), 6.80 (d, $J$ = 8.4 Hz, 2H), 2.54 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ = 178.3, 143.3, 140.0, 136.4, 133.1,
5) 10-(4-Phenylphenyl)-9(10H)-acridinon (2e)

The reaction of phenyl(2-((4-phenylphenyl)amino)phenyl)methanone (1e, 0.3 mmol, 104.8 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under typical procedure afforded 76 mg (73%) of 2e as solid. m.p.: 268-269 °C; ¹H NMR (CDCl₃, 400 MHz): δ = 8.61 (d, J = 7.6 Hz, 2H), 7.92 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 6.8 Hz, 2H), 7.56-7.50 (m, 5H), 7.45 (d, J = 8.0 Hz, 2H), 7.32-7.24 (m, 2H), 6.87 (d, J = 8.4 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 178.1, 143.3, 142.7,139.7, 138.1, 133.4, 130.4, 129.7, 129.1, 128.2, 127.4, 127.3, 121.9, 121.6, 116.9 ppm; MS (70 eV): m/z (%) 347.1 (M⁺, 100). HRMS m/z (ESI) calcd for C₂₅H₁₈NO (M + H)⁺: 348.1383, found 348.1381.

6) 10-(4-Iodophenyl)-9(10H)-acridinon (2f)

The reaction of phenyl(2-((4-iodophenyl)amino)phenyl)methanone (1f, 0.3 mmol, 119.8 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under typical procedure...
afforded 95 mg (80 %) of 2f as solid. m.p.: 286-287 °C; $^1$H NMR (CDCl$_3$, 400 MHz): δ = 8.59 (d, $J$ = 8.0 Hz, 2H), δ = 8.06 (d, $J$ = 8.0 Hz, 2H), 7.56-7.49 (m, 2H), 7.34-7.22 (m, 4H), 7.14 (d, $J$ = 7.6 Hz, 2H), 6.76 (d, $J$ = 8.4 Hz, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): δ = 178.0, 142.9, 140.5, 138.8, 133.4, 132.2, 127.5, 122.0, 121.8, 116.5, 95.3 ppm; MS (70 eV): m/z (%) 397.0 (M$^+$, 100). HRMS m/z (ESI) calcd for C$_{19}$H$_{13}$INO (M + H)$^+$: 398.0036, found 398.0039.

7) 10-(4-Bromophenyl)-9(10H)-acridinon (2g)

The reaction of phenyl(2-((4-bromophenyl)amino)phenyl)methanone (1g, 0.3 mmol, 105.7 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under typical procedure afforded 85 mg (81 %) of 2g as solid. m.p.: 259-260 °C; $^1$H NMR (CDCl$_3$, 400 MHz): δ = 8.59 (d, $J$ = 7.6 Hz, 2H), δ = 7.85 (d, $J$ = 8.4 Hz, 2H), 7.59-7.51 (m, 2H), 7.40-7.25 (m, 4H), 6.75 (d, $J$ = 8.4 Hz, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): δ = 178.1, 143.0, 140.5, 138.1, 134.5, 133.4, 132.0, 127.5, 123.8, 121.8, 116.5 ppm; MS (70 eV): m/z (%) 349.0 (M$^+$, 80Br , 100), 351.0 (M$^+$, 82Br, 100). HRMS m/z (ESI) calcd for C$_{19}$H$_{13}$BrNO (M + H)$^+$: 350.0175, found 350.0172.

8) 10-(4-Chlorophenyl)-9(10H)-acridinon (2h)
The reaction of phenyl(2-((4-chlorophenyl)amino)phenyl)methanone (1h, 0.3 mmol, 92.3 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under typical procedure afforded 78 mg (85 %) of 2h as solid. m.p.: 233-234 °C; $^1$H NMR (CDCl$_3$, 400 MHz): \( \delta = 8.59 \) (d, \( J = 8.0 \) Hz, 2H), 7.70 (d, \( J = 8.4 \) Hz, 2H), 7.55-7.49 (m, 2H), 7.35-7.27 (m, 4H), 6.75 (d, \( J = 8.4 \) Hz, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): \( \delta = 178.1, 143.0, 137.6, 135.8, 133.4, 131.6, 131.5, 127.5, 122.0, 121.8, 116.5 \) ppm; MS (70 eV): m/z (%) 305.1 (M$^+$, $^{35}$Cl, 100), 307.0 (M$^+$, $^{37}$Cl, 35). HRMS m/z (ESI) calcd for C$_{19}$H$_{14}$ClNO (M + H)$^+$: 306.0680, found 306.0679.

9) 10-(4-Fluorophenyl)-9(10$H$)-acridinon (2i)

The reaction of phenyl(2-((4-fluorophenyl)amino)phenyl)methanone (1i, 0.3 mmol, 87.4 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under typical procedure afforded 62 mg (71 %) of 2i as solid. m.p.: 271-272 °C; $^1$H NMR (CDCl$_3$, 400 MHz): \( \delta = 8.59 \) (d, \( J = 7.6 \) Hz, 2H), 7.55-7.49 (m, 2H), 7.47-7.35 (m, 4H), 7.31-7.25 (m, 2H), 6.75 (d, \( J = 8.4 \) Hz, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): \( \delta = 178.1, 162.9 \) (d, \( J = 250 \) Hz), 143.2, 134.9 (d, \( J = 3.2 \) Hz), 133.4, 132.0 (d, \( J = 8.7 \) Hz), 127.4, 121.9, 121.7, 118.2 (d, \( J = 22.6 \) Hz), 116.6 ppm; $^{19}$F NMR: (376 MHz, CDCl$_3$): \( \delta = -109.4 \) ppm;
MS (70 eV): m/z (%) 289.1 (M⁺, 100). HRMS m/z (ESI) calcd for C₁₉H₁₃FNO (M + H)⁺: 290.0976, found 290.0975.

10) 10-(4-Ethoxycarbonylphenyl)-9(10H)-acridinon (2j)

The reaction of phenyl(2-((4-ethoxycaronylphenyl)amino)phenyl)methanone (1j, 0.3 mmol, 103.6 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under typical procedure afforded 57 mg (58 %) of 2j as solid. m.p.: 219-220 ºC; ¹H NMR (CDCl₃, 400 MHz): δ = 8.61 (d, J = 8.4 Hz, 2H), 8.40 (d, J = 8.0 Hz, 2H), 7.56-7.46 (m, 4H), 7.33-7.25 (m, 2H), 6.72 (d, J = 8.4 Hz, 2H), 4.49 (q, J = 6.8 Hz, 2H), 1.47 (t, J = 6.8 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ = 178.1, 165.5, 143.1, 142.8, 133.4, 132.4, 132.0, 130.4, 127.5, 121.8, 116.5, 61.6, 14.3 ppm; MS (70 eV): m/z (%) 344.2 (100), 345.2 (M⁺, 90). HRMS m/z (ESI) calcd for C₂₂H₁₈NO₃ (M + H)⁺: 344.1281, found 344.1280.

11) 10-(4-Cyanophenyl)-9(10H)-acridinon (2k)

The reaction of phenyl(2-((4-cyanophenyl)amino)phenyl)methanone (1k, 0.3 mmol, 89.5 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under typical procedure afforded 27 mg (30 %) of 2k as solid. m.p.: 330-332 ºC; ¹H NMR (CDCl₃, 400 MHz):
$\delta = 8.6$ (d, $J = 8.0$ Hz, 2H), $8.05$ (d, $J = 7.6$ Hz, 2H), $7.60$-$7.50$ (m, 4H), $7.36$-$7.30$ (m, 2H), $6.64$ (d, $J = 8.4$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 177.9$, $143.3$, $142.5$, $135.1$, $133.6$, $131.7$, $127.7$, $122.1$, $122.0$, $117.5$, $116.0$, $114.1$ ppm; MS (70 eV): m/z (%) 297.1 (100), 298.1 (M$^+$, 55). HRMS m/z (ESI) calcd for C$_{20}$H$_{13}$N$_2$O (M + H)$^+$: 297.1023, found 297.1023.

11) 10-((4-Trifluoromethylphenyl)-9(10$H$)-acridinon (2l)

The reaction of phenyl(2-((4-trifluoromethylphenyl)amino)phenyl)methanone (1l, 0.3 mmol, 102.4 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under typical procedure afforded 43 mg (42 %) of 2l as solid. m.p.: 330-331 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 8.60$ (d, $J = 8.0$ Hz, 2H), $8.01$ (d, $J = 7.6$ Hz, 2H), $7.59$-$7.51$ (m, 4H), $7.36$-$7.30$ (m, 2H), $6.68$ (d, $J = 8.8$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 178.0$, $142.7$, $142.4$, $133.5$, $132.2$, $131.9$, $131.0$, $128.4$ (q, $J = 3.6$ HZ), $126.6$ (q, $J = 286$ HZ), $125.0$, $121.9$, $116.3$ ppm; $^{19}$F NMR: (376 MHz, CDCl$_3$): $\delta = - 61.5$ ppm; MS (70 eV): m/z (%) 339.1 (M$^+$, 100). HRMS m/z (ESI) calcd for C$_{20}$H$_{13}$F$_3$NO (M + H)$^+$: 340.0944, found 340.0943.

12) 3-Methyl-10- phenyl-9(10$H$)-acridinon (2m)
The reaction of (2-phenylamino)phenyl(p-tolyl)methanone (1m, 0.24 mmol, 69 mg) and CuI (0.048 mmol, 9.4 mg) in DMSO 1.6 mL under typical procedure afforded 46 mg (67 %) of 2m as solid. m.p.: 263-264 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 8.58\) (d, \(J = 8.0\) Hz, 1H), 8.48 (d, \(J = 8.8\) Hz, 1H), 7.75-7.65 (m, 3H), 7.50-7.45 (m, 1H), 7.37 (d, \(J = 7.2\) Hz, 2H), 7.34-7.25 (m, 1H), 7.11 (d, \(J = 7.6\) Hz, 1H), 6.72 (d, \(J = 8.8\) Hz, 1H), 6.51 (s, 1H), 2.33 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 177.9, 144.3, 143.4, 143.2, 139.2, 133.0, 131.1, 130.1, 129.6, 127.3, 127.28, 123.4, 121.9, 121.4, 120.0, 116.8, 116.4, 22.3 ppm; MS (70 eV): m/z (%) 285.1 (M\(^+\), 100). HRMS m/z (ESI) calcd for C\(_{20}\)H\(_{16}\)NO (M + H\(^+\)): 286.1226, found 286.1226.

13) 3-tert-Butyl-10-phenyl-9(10H)-acridinon (2n)

![3-tert-Butyl-10-phenyl-9(10H)-acridinon](image)

The reaction of (4-tert-butylphenyl)(2-phenylamino)phenyl)methanone (1n, 0.3 mmol, 98.8 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under typical procedure afforded 69 mg (70 %) of 2n as solid. m.p.: 284-285 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 8.59\) (d, \(J = 7.6\) Hz, 1H), 8.52 (d, \(J = 8.8\) Hz, 1H), 7.78-7.62 (m, 3H), 7.50-7.45 (m, 1H), 7.40-7.22 (m, 4H), 6.77 (d, \(J = 8.4\) Hz, 1H), 6.71 (s, 1H), 1.19 (s, 9H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 157.1, 143.3, 143.2, 139.2, 132.9, 131.0, 130.1, 129.5, 127.2, 126.9, 121.3, 119.8, 116.7, 113.0, 35.3, 30.8 ppm; MS (70 eV): m/z (%) 327.2 (M\(^+\), 100). HRMS m/z (ESI) calcd for C\(_{23}\)H\(_{22}\)NO (M + H\(^+\)): 328.1696, found 328.1698.

14) 3-Methoxy-10-phenyl-9(10H)-acridinon (2o)
The reaction of (4-methoxyphenyl)(2-(phenylamino)phenyl)methanone (1o, 0.25 mmol, 76.0 mg) and CuI (0.05 mmol, 9.5 mg) in DMSO 1.6 mL under typical procedure afforded 22 mg (29 %) of 2o as solid. m.p.: 202-203 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 8.59$-$8.51$ (m, 2H), 7.75-$7.61$ (m, 3H), 7.49-$7.43$ (m, 1H), 7.37 (d, $J = 7.2$ Hz, 2H), 7.28-$7.24$ (m, 1H), 6.88 (d, $J = 8.0$ Hz, 1H), 6.71 (d, $J = 8.8$ Hz, 1H), 6.1 (s, 1H), 3.7 (s, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 177.3$, 163.8, 145.2, 143.4, 139.2, 132.8, 131.1, 130.1, 129.61, 129.56, 127.3, 122.1, 121.5, 116.62, 116.58, 110.3, 99.7, 55.3 ppm; MS (70 eV): m/z (%) 301.1 (M$^+$, 100). HRMS m/z (ESI) calcd for C$_{20}$H$_{16}$NO$_2$ (M + H)$^+$: 302.1176, found 302.1174

15) 3-Trifluoromethoxy-10-phenyl-9(10H)-acridinon (2p)

The reaction of (4-trifluoromethoxy)(2-(phenylamino)phenyl)methanone (1p, 0.3 mmol, 107.2 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under typical procedure afforded 49 mg (46 %) of 2p as solid. m.p.: 223-224 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 8.64$-$8.55$ (m, 2H), 7.76-$7.67$ (m, 3H), 7.55-$7.49$ (m, 1H), 7.37 (d, $J = 7.2$ Hz, 2H), 7.34-$7.28$ (m, 1H), 7.12 (d, $J = 8.4$ Hz, 1H), 6.76 (d, $J = 8.4$ Hz, 1H), 6.53 (s, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 177.2$, 152.8, 144.3, 143.4, 140.8, 138.5, 133.6, 131.4, 130.0, 129.99, 129.8, 127.3, 122.1, 120.3 (q, $J = 257$ Hz) 120.1
116.9, 113.8, 108.0 ppm; $^{19}$F NMR: (376 MHz, CDCl$_3$): $\delta = \text{-56.3 ppm}$; MS (70 eV): m/z (%) 355.1 (M$^+$, 100). HRMS m/z (ESI) calcd for C$_{20}$H$_{13}$F$_3$NO (M + H)$^+$: 356.0893, found 356.0894

16) 3-Chloro-10-phenyl-9(10H)-acridinon (2q)

The reaction of (4-chloro)(2-(phenylamino)phenyl)methanone (1q, 0.3 mmol, 92.3 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under typical procedure afforded 70 mg (76 %) of 2q as solid. m.p.: 261-262 °C; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 8.58$-$8.49$ (m, 2H), 7.76-$7.64$ (m, 3H), 7.55-$7.48$ (m, 1H), 7.37 (d, $J = 7.2$ Hz, 2H), 7.32-$7.21$ (m, 2H), 6.74-$6.70$ (m, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 177.4$, 143.8, 143.3, 139.8, 138.5, 133.5, 131.3, 129.97, 129.92, 129.1, 127.3, 122.3, 122.1, 120.3, 118.6, 116.9, 116.3 ppm; MS (70 eV): m/z (%) 305.1 (M$^+$, $^{35}$Cl, 100), 307.0 (M$^+$, $^{37}$Cl, 35). HRMS m/z (ESI) calcd for C$_{19}$H$_{14}$ClNO (M + H)$^+$: 306.0680, found 306.0680.

17) 3-Fluoro-10-phenyl-9(10H)-acridinon (2r)

The reaction of (4-fluoro)(2-(phenylamino)phenyl)methanone (1r, 0.3 mmol, 87.4 mg)
and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under typical procedure afforded 29 mg (33 %) of \( \text{2r} \) as solid. m.p.: 275-276 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz): \( \delta = 8.62-8.55 \) (m, 2H), 7.75-7.61 (m, 3H), 7.53-7.47 (m, 3H), 7.37 (d, \( J = 7.2 \) Hz, 2H), 7.32-7.21 (m, 1H), 7.01-6.95 (m, 1H), 6.74 (d, \( J = 8.8 \) Hz, 1H), 6.41-6.36 (m, 2H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \( \delta = 177.2, 165.9 \) (d, \( J = 250.9 \) Hz), 144.9 (d, \( J = 11.8 \) Hz), 143.4, 140.7, 138.7, 133.4, 131.3, 130.5 (d, \( J = 10.8 \) Hz), 129.93, 129.86, 127.3, 122.0, 118.7, 116.8, 110.4 (d, \( J = 23.1 \) Hz), 102.7 (d, \( J = 27.0 \) Hz) ppm; \(^{19}\)F NMR: (376 MHz, CDCl\(_3\)): \( \delta = -102.1 \) ppm; MS (70 eV): m/z (%) 289.1 (M\(^+\), 100). HRMS m/z (ESI) calcd for C\(_{19}\)H\(_{13}\)FNO (M + H): 290.0976, found 290.0975.

18) 3-Fluoro-10-phenyl-9(10H)-acridinon (2r)

![Structure of 2r]

The reaction of (4-fluoro-2-(phenylamino)phenyl)(phenyl)methanone (\( \text{1s} \), 0.3 mmol, 87.3 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under typical procedure afforded 72 mg (83 %) of \( \text{2r} \) as solid.

19) 2-Chloro-10-phenyl-9(10H)-acridinon (2s)

![Structure of 2s]

The reaction of (5-chloro-2-(phenylamino)phenyl)(phenyl)methanone (\( \text{1t} \), 0.3 mmol, 92.3 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL under typical procedure
afforded 78 mg (85 %) of 2s as solid. m.p.: 230-231°C; $^1$H NMR (CDCl$_3$, 400 MHz):
$\delta = 8.65-8.52$ (m, 2H), 7.76-7.67 (m, 3H), 7.55-7.49 (m, 5H), 6.79-6.71 (m, 2H); $^{13}$C
NMR (CDCl$_3$, 100 MHz): $\delta = 177.0, 143.1, 141.6, 138.8, 133.5, 133.4, 131.2, 129.9,$
129.8, 127.6, 127.4, 126.4, 122.7, 121.9, 121.8, 118.6, 116.9 ppm; MS (70 eV): m/z
(%) 305.1 (M$^+$, $^{35}$Cl, 100), 307.0 (M$^+$, $^{37}$Cl, 35). HRMS m/z (ESI) calcd for
C$_{19}$H$_{14}$ClNO (M + H)$^+$: 306.0680, found 306.0681.

20) 10H-Acrinid-9-one (5)$^2$

![Chemical Structure Image]

The reaction of 4 (0.3 mmol, 90 mg) and CuI (0.06 mmol, 11.4 mg) in DMSO 1.6 mL
under typical procedure afforded 30.5 mg (52 %) of 5 as solid. m.p. (acetic acid):
346-348°C; $^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta = 11.7$ (br s, 1H), 8.23 (d, $J = 8.0$ Hz,
2H), 7.80-7.65 (m, 2H), 7.54 (d, $J = 8.0$ Hz, 2H), 7.30-7.20 (m, 2H); $^{13}$C NMR
(DMSO-$d_6$, 100 MHz): $\delta = 176.8, 140.9, 133.4, 126.0, 121.0, 120.6, 117.3$ ppm; MS
(70 eV): m/z (%) 195.1 (M$^+$, 100).

References
2. A. Pintér, A. Sud, D. Sureshkumar, M. Klussmann, Angew. Chem., Int. Ed. 2010,
49, 5004.
Peking University Mass Spectrometry Sample Analysis Report

Analysis Info
Analysis Name: 12070710_20120724_000002.d
Sample: L130-3
Comment: ESI Positive

Acquisition Date: 7/24/2012 1:28:54 PM
Instrument: Bruker Apex IV FTMS
Operator: Peking University

Electronic Supplementary Material (ESI) for Chemical Communications
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Peking University Mass Spectrometry Sample Analysis Report

Analysis Info
Analyst Name: 12070710_20120724_000006.d
Sample: L144-2
Comment: ESI Positive

Acquisition Date: 7/24/2012 1:32:37 PM
Instrument: Bruker Apex IV FTMS
Operator: Peking University

Electronic Supplementary Material (ESI) for Chemical Communications
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Peking University Mass Spectrometry Sample Analysis Report

Analysis Info
Analysis Name: 12070710_20120724_000003.d
Sample: L130-1
Comment: ESI Positive

Acquisition Date: 7/24/2012 1:20:50 PM
Instrument: Bruker Apex IV FTMS
Operator: Peking University

![Mass Spectra](image)

**Molecular Formula:** C20H18N2O
**Exact Mass:** 266.12261
**Mass Resolution:** 1292437.4
**Mass Accuracy:** 0.1 ppm

---

Bruker Compass DataAnalysis 4.0

Printed: 7/24/2012 1:30:52 PM

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Peking University Mass Spectrometry Sample Analysis Report

Analysis Info
Analysis Name: 12070710_20120724_000005.d
Sample: L141-2
Comment: ESI Positive

Acquisition Date: 7/24/2012 1:31:31 PM
Instrument: Bruker Apex IV FTMS
Operator: Peking University

![Mass Spectrometry Chart]

Mass, m/z | Formula | Score | m/z | err [Da] | err [ppm] | mSigma | rpb | e- | Conf | N-Rule
--- | --- | --- | --- | --- | --- | --- | --- | --- | --- | ---
398.00385 | C18H13N3O | 100.00 | 398.00385 | -0.2 | -0.8 | 2.5 | 13.5 | even | ok

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### Peking University Mass Spectrometry Sample Analysis Report

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<td>Sample: L141-1</td>
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<td>Acquisition Date: 7/24/2012 1:36:30 PM</td>
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<td>Instrument: Bruker Apex IV FTMS</td>
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<td>Operator: Peking University</td>
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![Mass Spectrometry Graph]

**M/z** 350.01772 352.01548 351.02116 355.18006 354.28927

**Mean m/z** 350.01772

**Formula** C19H13BrN0

**Score** 100.063

**err [mDa]** -0.2

**err [ppm]** -0.6

**m/z** 348.13826 350.01772 352.01548 351.02116 355.18006 354.28927

**Mz** 348 357 354 355 356 300

**Bruker Compass DataAnalysis 4.0**

**Printed:** 7/24/2012 1:36:08 PM

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# Peking University Mass Spectrometry Sample Analysis Report

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**Acquisition Date:** 7/24/2012 1:35:43 PM  
**Instrument:** Bruker Apex IV FTMS  
**Operator:** Peking University

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**Diagram:**

![Mass Spectrometry Graph](image)

---

**Bruker Compass Data/Analysis 4.0**  
**Printed:** 7/24/2012 1:36:41 PM  
**Page 1 of 1**
Peking University Mass Spectrometry Sample Analysis Report

Analysis Info
Analysis Name: 12070710_20120724_000007.d
Sample: L137-2
Comment: ESI Positive

Acquisition Date: 7/24/2012 1:33:38 PM
Instrument: Bruker Apex IV FTMS
Operator: Peking University

Electronic Supplementary Material (ESI) for Chemical Communications
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Peking University Mass Spectrometry Sample Analysis Report

Analysis Info
Analysis Name: 12070710_20120724_000012.d
Sample: L139-3
Comment: ESI Positive

Acquisition Date: 7/24/2012 1:39:32 PM
Instrument: Bruker Apex IV FTMS
Operator: Peking University

Chemical structure image

2k
**Peking University Mass Spectrometry Sample Analysis Report**

**Analysis Info**
- **Analysis Name**: 12070710_20120724_000016
- **Sample**: L142-4
- **Comment**: ESI Positive

**Acquisition Date**: 7/24/2012 1:43:40 PM
- **Instrument**: Bruker Apex IV FTMS
- **Operator**: Peking University

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<th>Formulas</th>
<th>Score</th>
<th>m/z</th>
<th>err [mDa]</th>
<th>err [ppm]</th>
<th>mSigma</th>
<th>nHb</th>
<th>c-Conf</th>
<th>n-Rule</th>
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<td>288.12264</td>
<td>0.0</td>
<td>0.1</td>
<td>15.9</td>
<td>13.5</td>
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**Graph**: Mass spectrum with peaks at m/z 268.12261, 270.12785, 308.10506, and 358.21197.

**Software**: Bruker Compass DataAnalysis 4.0

**Printed**: 7/24/2012 1:44:45 PM

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Peking University Mass Spectrometry Sample Analysis Report

Analysis Info
Analysis Name 12070710_20120724_000019.d
Sample L142-1
Comment ESI Positive

Acquisition Date 7/24/2012 1:46:45 PM
Instrument Bruker Apex IV FTMS
Operator Peking University

![Mass Spectrogram](image)

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<tr>
<th>Meas. m/z &amp; Formula</th>
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<th>m/z</th>
<th>err [mDa]</th>
<th>err [ppm]</th>
<th>mSigma</th>
<th>rdb</th>
<th>e°</th>
<th>Conf</th>
<th>N-Rule</th>
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<td>-0.8</td>
<td>7.0</td>
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<td>ok</td>
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Peking University Mass Spectrometry Sample Analysis Report

Analysis Info
Analysis Name: 12070710_20120724_000015.d
Sample: L142-2
Comment: ESI Positive

Acquisition Date: 7/24/2012 1:42:45 PM
Instrument: Bruker Apex IV FTMS
Operator: Peking University

Chemical structure of 2q

MZ: 306.06796
Score: 100.03
m/z: 306.06602
err (mDa): 0.1
err (ppm): 2.2
mSigma: 8.3
p-value: 0.0015
Compounds identified:

C19H13ClN3O 306.06796

Printed: 7/24/2012 1:47:42 PM
Peking University Mass Spectrometry Sample Analysis Report

Analysis Info
Analysis Name: 12070710_20120724_000014.dat
Sample: L146-2
Comment: ESI Positive

Acquisition Date: 7/24/2012 1:41:52 PM
Instrument: Bruker Apex IV FTMS
Operator: Peking University

![Mass Spectrum Graph]

**Formula:** C19H13F1NO
**Score:** 100.00
**m/z:** 290.09745
**err (mDa):** 0.1
**err (ppm):** 0.4
**mSigma:** 13.3
**rdb:** 13.5
**e:** ok

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printed: 7/24/2012 1:42:48 PM
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Peking University Mass Spectrometry Sample Analysis Report

Analysis Info
Analyst Name: 12070710_20120724_000020.d
Sample: L139-1
Comment: ESI Positive

Acquisition Date: 7/24/2012 1:47:37 PM
Instrument: Bruker Apex IV FTMS
Operator: Peking University