

## Electronic Supplementary Information

### Visible-light-initiated nickel-catalyzed amination of aryl halides using thioxanthen-9-one as a photocatalyst

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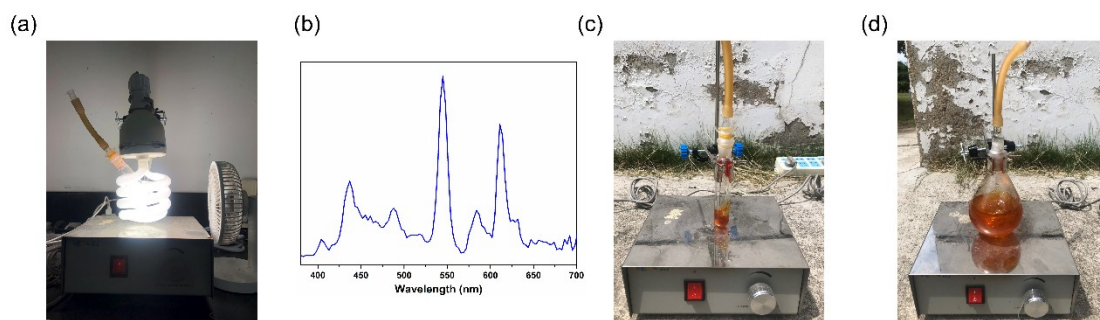
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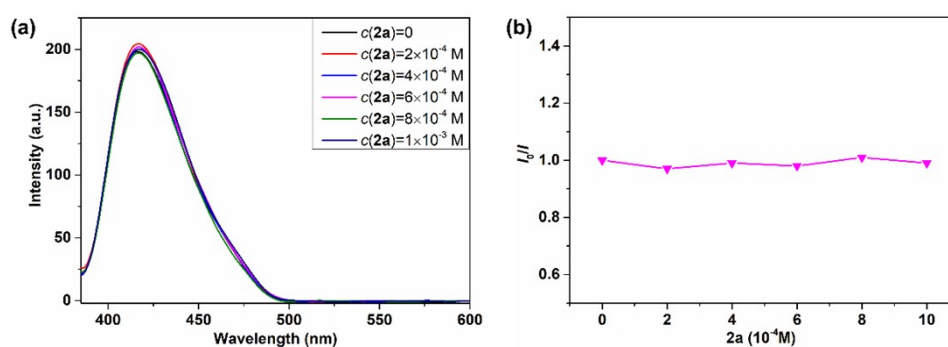
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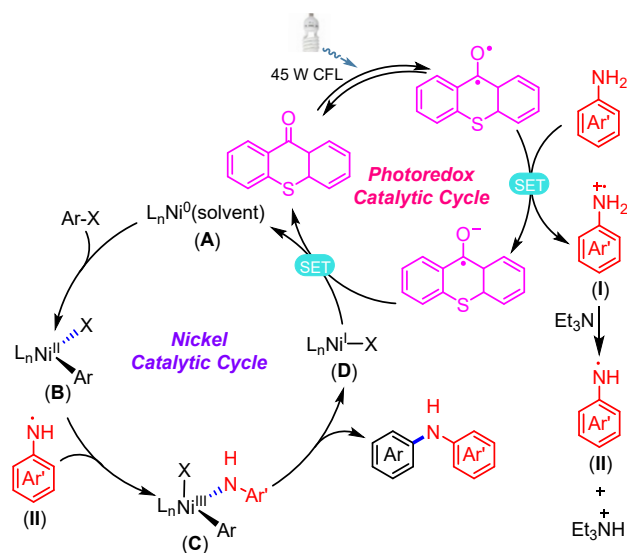
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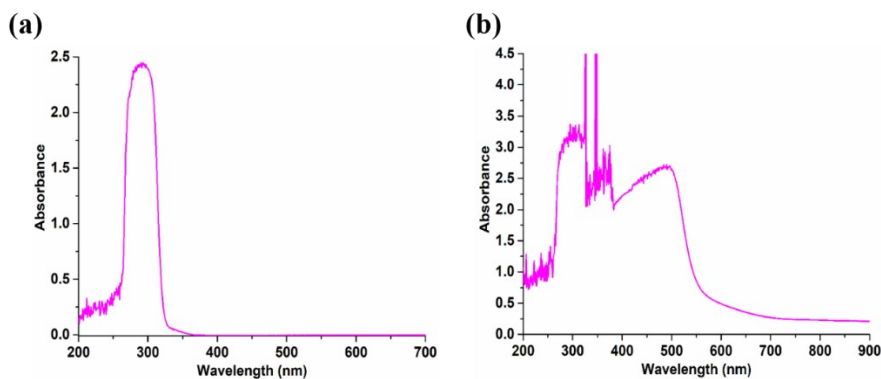
**Fig. S1.** The reaction set-up with 45 W CFL (the power density is about  $0.81 \text{ mW cm}^{-2}$ ) (a), emission spectra of the 45 W CFL (b), the reaction set-up under sunlight (c) and gram scale reaction set-up (d)



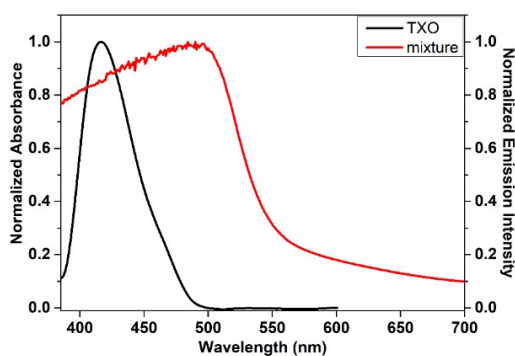
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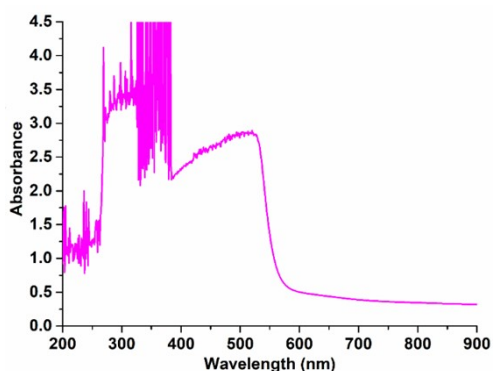
**Scheme S1.** The electron transfer mechanism.



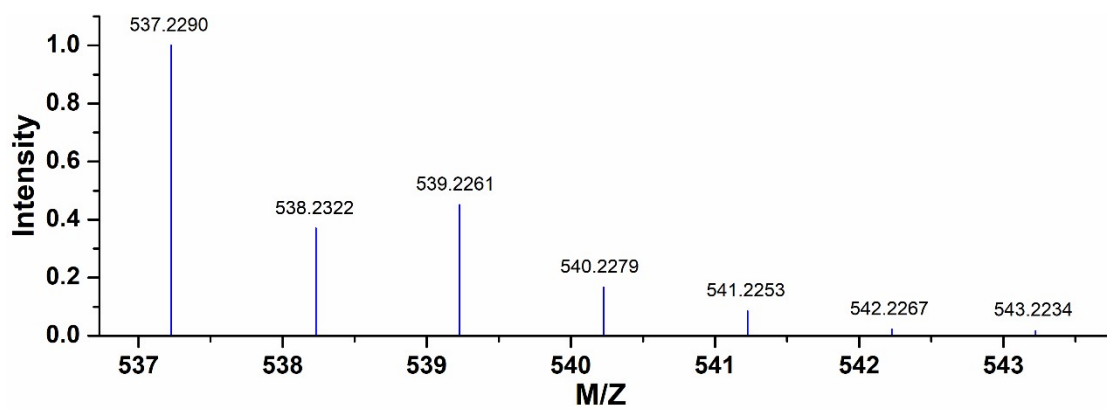
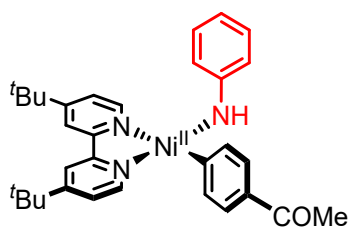
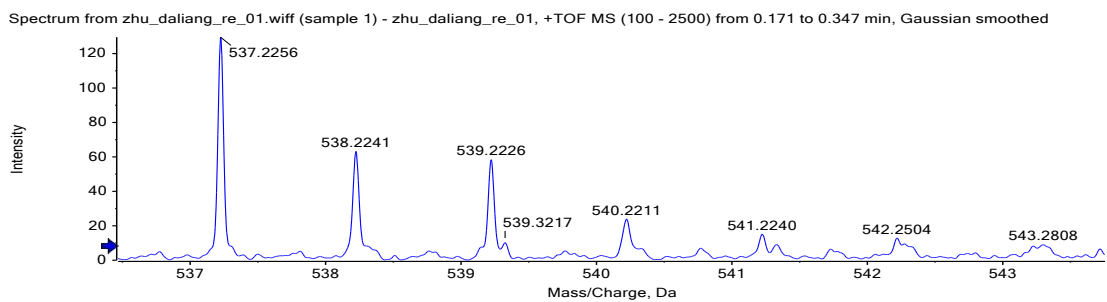
**Fig. S3.** UV-visible spectrum of the DMAC solution of **1a** (0.001 M), **2a** (0.002 M), Et<sub>3</sub>N (0.002 M) (a); the reaction mixture of **1a** (0.1 M), **2a** (0.2 M), Et<sub>3</sub>N (0.2 M), dtbbpy (0.012 M) and Ni(cod)<sub>2</sub> (0.01 M) in DMAC (b) under a nitrogen atmosphere.



**Fig. S4.** The emission spectra of TXO and absorbance spectrum of the reaction mixture of **1a** (0.1 M), **2a** (0.2 M), Et<sub>3</sub>N (0.2 M), dtbbpy (0.012 M) and Ni(cod)<sub>2</sub> (0.01 M) in DMAC under a nitrogen atmosphere.



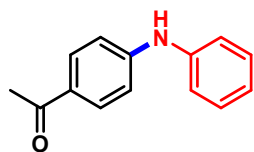
**Fig. S5.** UV-visible spectrum of the reaction mixture of **1a** (0.1 M), **2a** (0.2 M), Et<sub>3</sub>N (0.2 M), dtbbpy (0.012 M) and Ni(cod)<sub>2</sub> (0.01 M) in DMAC after the 12 h irradiation of 45 W CFL.



**Fig. S6.** The ESI-MS spectrum of (dtbbpy)-4-acetylphenyl-nickel(II)-NHPH. The calculated isotope patterns (bottom) and observed patterns (upper).

## NMR Data of Products

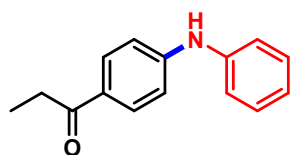
### 1-(4-phenoxyphenyl)ethan-1-one (3aa)<sup>S1</sup>



Following the General Procedure with the corresponding 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and aniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the colorless solid **3aa** (37.6mg, 89% for 1-(4-bromophenyl)ethan-1-one; 13.1 mg, 31% for 1-(4-chlorophenyl)ethan-1-one).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 7.87 (d,  $J$  = 8.8 Hz, 2H), 7.35 (t,  $J$  = 7.9 Hz, 2H), 7.19 (d,  $J$  = 7.6 Hz, 2H), 7.08 (t,  $J$  = 7.4 Hz, 1H), 6.99 (d,  $J$  = 8.8 Hz, 2H), 2.53 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 196.6, 148.6, 140.8, 130.8, 129.7, 129.2, 123.6, 120.9, 114.6, 26.4. QTOF-MS  $m/z$  [M + H]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>14</sub>NO<sup>+</sup> 212.1070; Found 212.1064.

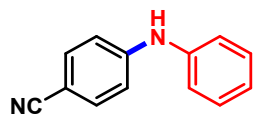
### 1-(4-(phenylamino)phenyl)propan-1-one (3ba)<sup>S2</sup>



Following the General Procedure with the corresponding 1-(4-bromophenyl)propan-1-one (0.2 mmol) and aniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the yellow solid **3ba** (40.5 mg, 90%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 7.88 (d,  $J$  = 8.7 Hz, 2H), 7.34 (t,  $J$  = 7.9 Hz, 2H), 7.18 (d,  $J$  = 7.7 Hz, 2H), 7.08 (t,  $J$  = 7.4 Hz, 1H), 7.00 (d,  $J$  = 8.7 Hz, 2H), 6.12 (s, 1H), 2.93 (q,  $J$  = 7.3 Hz, 2H), 1.21 (t,  $J$  = 7.3 Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 199.4, 148.3, 140.9, 130.5, 129.7, 128.9, 123.4, 120.7, 114.7, 31.4, 8.8. QTOF-MS  $m/z$  [M + H]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>16</sub>NO<sup>+</sup> 226.1226; Found 226.1213.

### 4-(phenylamino)benzotrile (3ca)<sup>S1</sup>

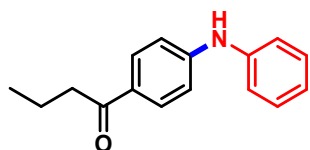


Following the General Procedure with the corresponding 4-bromobenzotrile (0.2 mmol) and

aniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the colorless solid **3ca** (35.7 mg, 92% for 4-bromobenzonitrile; 13.2 mg, 34% for 4-chlorobenzonitrile).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.47 (d,  $J$  = 8.7 Hz, 2H), 7.36 (t,  $J$  = 7.8 Hz, 2H), 7.17 (d,  $J$  = 7.9 Hz, 2H), 7.12 (t,  $J$  = 7.4 Hz, 1H), 6.98 (d,  $J$  = 8.7 Hz, 2H), 6.17 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 148.2, 140.2, 133.9, 129.8, 124.1, 121.4, 120.2, 115.1, 101.5. QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{13}\text{H}_{11}\text{N}_2^+$  195.0917; Found 195.0908.

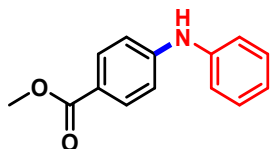
#### 1-(4-(phenylamino)phenyl)butan-1-one (3da)



Following the General Procedure with the corresponding 1-(4-bromophenyl)butan-1-one (0.2 mmol) and aniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the white solid **3da** (41.6 mg, 87%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.88 (d,  $J$  = 8.8 Hz, 2H), 7.40–7.29 (m, 2H), 7.18 (d,  $J$  = 7.5 Hz, 2H), 7.07 (t,  $J$  = 7.4 Hz, 1H), 7.00 (d,  $J$  = 8.8 Hz, 2H), 6.25 (s, 1H), 2.87 (t,  $J$  = 7.4 Hz, 2H), 1.84–1.68 (m, 2H), 1.00 (t,  $J$  = 7.4 Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 199.1, 148.4, 140.9, 130.5, 129.7, 128.9, 123.4, 120.7, 114.6, 40.2, 18.4, 14.2. m.p. = 91.2–91.9 °C. IR (KBr disk,  $\text{cm}^{-1}$ ) 3331, 2972, 2960, 2926, 2867, 1657, 1585, 1524, 1494, 1448, 1413, 1367, 1326, 1300, 1222, 1177, 1121, 1012, 896, 844, 806, 750, 695, 636, 595, 568, 501. QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{18}\text{NO}^+$  240.1383; Found 240.1388.

#### methyl 4-(phenylamino)benzoate (3ea)<sup>S1</sup>

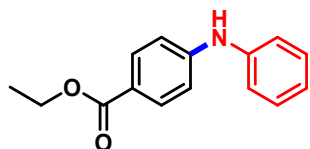


Following the General Procedure with the corresponding methyl 4-bromobenzoate (0.2 mmol) and aniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the colorless oil **3ea** (40.0 mg, 88%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.92 (d,  $J$  = 8.7 Hz, 2H), 7.34 (t,  $J$  = 7.9 Hz, 2H), 7.17 (d,  $J$

= 8.3 Hz, 2H), 7.07 (t,  $J = 7.4$  Hz, 1H), 6.99 (d,  $J = 8.7$  Hz, 2H), 6.05 (s, 1H), 3.88 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta = 167.2, 148.3, 141.1, 131.7, 129.7, 123.3, 121.3, 120.6, 114.8, 51.9$ . QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{14}\text{H}_{14}\text{NO}_2^+$  228.1019; Found 228.1032.

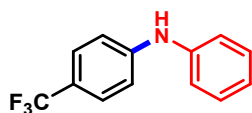
#### ethyl 4-(phenylamino)benzoate (**3fa**)<sup>S3</sup>



Following the General Procedure with the corresponding ethyl 4-bromobenzoate (0.2 mmol) and aniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the pale yellow solid **3fa** (41.5 mg, 86%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta = 7.92$  (d,  $J = 8.8$  Hz, 2H), 7.38–7.30 (m, 2H), 7.17 (d,  $J = 7.5$  Hz, 2H), 7.06 (t,  $J = 7.4$  Hz, 1H), 6.99 (d,  $J = 8.8$  Hz, 2H), 6.03 (s, 1H), 4.34 (q,  $J = 7.1$  Hz, 2H), 1.37 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta = 166.7, 148.1, 141.1, 131.6, 129.7, 123.3, 121.7, 120.5, 114.8, 60.7, 14.6$ . QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{16}\text{NO}_2^+$  242.1176; Found 242.1185.

#### N-phenyl-4-(trifluoromethyl)aniline (**3ga**)<sup>S1</sup>

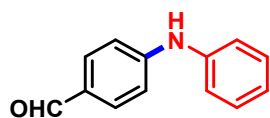


Following the General Procedure with the corresponding 1-bromo-4-(trifluoromethyl)benzene (0.2 mmol) and aniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the colorless oil **3ga** (42.2 mg, 89%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta = 7.49$  (d,  $J = 8.6$  Hz, 2H), 7.36 (t,  $J = 7.8$  Hz, 2H), 7.17 (d,  $J = 7.8$  Hz, 2H), 7.07 (dd,  $J = 13.8, 7.9$  Hz, 3H), 5.93 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta = 146.9, 141.3, 129.7, 126.9$  (q,  $J = 3.8$  Hz), 124.8 (q,  $J = 270.8$  Hz), 123.1, 121.8 (q,  $J = 32.7$  Hz), 120.2, 115.5.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta = -61.35$ . QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{13}\text{H}_{11}\text{F}_3\text{N}^+$  238.0838; Found 238.0855.

#### 4-(phenylamino)benzaldehyde (**3ha**)<sup>S1</sup>

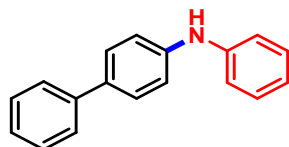




Following the General Procedure with the corresponding 4-bromobenzaldehyde (0.2 mmol) and aniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the pale colorless solid **3ha** (33.1 mg, 84%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 9.79 (s, 1H), 7.74 (d,  $J$  = 8.7 Hz, 2H), 7.41–7.32 (m, 2H), 7.21 (d,  $J$  = 7.6 Hz, 2H), 7.12 (t,  $J$  = 7.4 Hz, 1H), 7.03 (d,  $J$  = 8.7 Hz, 2H), 6.36 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 190.6, 150.1, 140.3, 132.3, 129.8, 128.7, 124.1, 121.5, 114.7. QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{13}\text{H}_{12}\text{NO}^+$  198.0913; Found 198.0900.

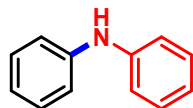
#### N-phenyl-[1,1'-biphenyl]-4-amine (**3ia**)<sup>S4</sup>



Following the General Procedure with the corresponding 4-bromo-1,1'-biphenyl (0.2 mmol) and aniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the white solid **3ia** (34.8 mg, 71%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.59 (d,  $J$  = 7.3 Hz, 2H), 7.55 – 7.50 (m, 2H), 7.44 (t,  $J$  = 7.7 Hz, 2H), 7.35–7.27 (m, 3H), 7.14 (t,  $J$  = 8.1 Hz, 4H), 6.97 (t,  $J$  = 7.3 Hz, 1H), 5.80 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 143.0, 142.7, 141.0, 133.9, 129.6, 128.9, 128.2, 126.8, 126.7, 121.4, 118.3, 117.9. QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{18}\text{H}_{16}\text{N}^+$  246.1277; Found 246.1275.

#### diphenylamine (**3ja**)<sup>S1</sup>

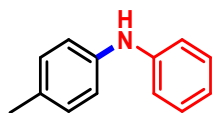


Following the General Procedure with the corresponding bromobenzene (0.2 mmol) and aniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the white solid **3ja** (14.5 mg, 43% for bromobenzene; 23.3 mg, 69% for iodobenzene).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.29 (dd,  $J$  = 14.6, 7.4 Hz, 4H), 7.09 (dd,  $J$  = 11.4, 8.4 Hz,

4H), 7.02 – 6.89 (m, 2H), 5.70 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 143.3, 129.6, 129.6, 121.2, 118.0, 118.0. QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{12}\text{H}_{12}\text{N}^+$  170.0964; Found 170.0986.

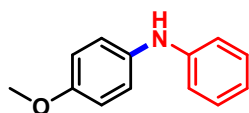
#### 4-methyl-N-phenylaniline (**3ka**)<sup>S1</sup>



Following the General Procedure with the corresponding 1-bromo-4-methylbenzene (0.2 mmol) and aniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 50/1) as an eluent, to yield the colorless solid **3ka** (16.1 mg, 44% for 1-bromo-4-methylbenzene; 24.9 mg, 68% for 1-iodo-4-methylbenzene).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.23 (d,  $J$  = 7.6, 2H), 7.09 (d,  $J$  = 8.2, 2H), 7.01 (dd,  $J$  = 8.3, 2.5, 4H), 6.88 (t,  $J$  = 7.3, 1H), 2.30 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 144.1, 140.5, 131.1, 130.1, 129.5, 120.5, 119.1, 117.0, 20.9. QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{13}\text{H}_{14}\text{N}^+$  184.1121; Found 184.1110.

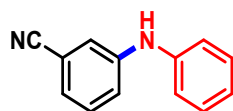
#### 4-methoxy-N-phenylaniline (**3la**)<sup>S3</sup>



Following the General Procedure with the corresponding 1-bromo-4-methoxybenzene (0.2 mmol) and aniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the white solid **3la** (16.3 mg, 41% for 1-bromo-4-methoxybenzene; 25.1 mg, 63% for 1-iodo-4-methoxybenzene).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.25–7.18 (m, 2H), 7.12–7.05 (m, 2H), 6.96–6.78 (m, 5H), 5.84–5.07 (m, 1H), 3.81 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 155.5, 145.4, 135.9, 129.5, 122.4, 119.8, 115.8, 114.8, 55.8. QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{13}\text{H}_{14}\text{NO}^+$  200.1070; Found 200.1068.

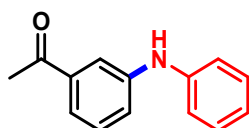
#### 3-(phenylamino)benzonitrile (**3ma**)<sup>S5</sup>



Following the General Procedure with the corresponding 3-bromobenzonitrile (0.2 mmol) and aniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the pale yellow solid **3ma** (31.4 mg, 81%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ = 7.38–7.26 (m, 4H), 7.20 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.12 (t, *J* = 8.8 Hz, 3H), 7.06 (t, *J* = 7.3 Hz, 1H), 5.85 (s, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, ppm) δ = 144.8, 141.2, 130.4, 129.9, 123.8, 123.3, 120.8, 119.9, 119.2, 119.0, 113.4. QTOF-MS *m/z* [M + H]<sup>+</sup> Calcd for C<sub>13</sub>H<sub>11</sub>N<sub>2</sub><sup>+</sup> 195.0917; Found 195.0920.

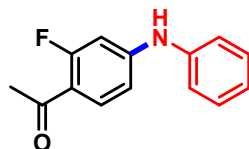
### 1-(3-(phenylamino)phenyl)ethan-1-one (**3na**)<sup>S5</sup>



Following the General Procedure with the corresponding 1-(3-bromophenyl)ethan-1-one (0.2 mmol) and aniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the pale yellow solid **3na** (33.8 mg, 80%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ = 7.65–7.59 (m, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.37–7.24 (m, 4H), 7.09 (d, *J* = 7.6 Hz, 2H), 6.98 (t, *J* = 7.4 Hz, 1H), 5.86 (s, 1H), 2.57 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, ppm) δ = 198.4, 144.0, 142.5, 138.6, 129.7, 122.1, 121.8, 121.0, 118.7, 116.7, 26.9. QTOF-MS *m/z* [M + H]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>14</sub>NO<sup>+</sup> 212.1070; Found 212.1063.

### 1-(2-fluoro-4-(phenylamino)phenyl)ethan-1-one (**3oa**)

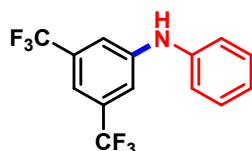


Following the General Procedure with the corresponding 1-(4-bromo-2-fluorophenyl)ethan-1-one (0.2 mmol) and aniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the pale yellow solid **3oa** (38.0 mg, 83%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ = 7.82 (t, *J* = 8.6 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.19 (d, *J* =

7.7 Hz, 2H), 7.13 (t,  $J = 7.4$  Hz, 1H), 6.69 (ddd,  $J = 16.0, 11.3, 2.2$  Hz, 2H), 6.31 (s, 1H), 2.57 (d,  $J = 5.2$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta = 194.4$  (d,  $J = 3.9$  Hz), 164.6 (d,  $J = 254.0$  Hz), 150.7 (d,  $J = 12.0$  Hz), 140.0, 132.5 (d,  $J = 4.4$  Hz), 129.8, 124.4, 121.7, 116.9 (d,  $J = 13.1$  Hz), 111.3 (d,  $J = 1.9$  Hz), 101.0 (d,  $J = 28.8$  Hz), 31.3 (d,  $J = 7.8$  Hz).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta = -106.26$ . m.p. = 99.4-100.3 °C. IR (KBr disk,  $\text{cm}^{-1}$ ) 3328, 3201, 3125, 3083, 3001, 1662, 1607, 1592, 1527, 1510, 1498, 1454, 1417, 1370, 1347, 1298, 1274, 1177, 1133, 1061, 965, 856, 743, 704, 591, 502. QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{14}\text{H}_{13}\text{FNO}^+$  230.0976; Found 230.0977.

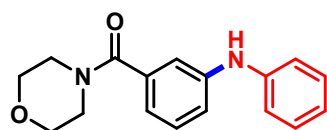
### N-phenyl-3,5-bis(trifluoromethyl)aniline (3pa)<sup>S1</sup>



Following the General Procedure with the corresponding 1-bromo-3,5-bis(trifluoromethyl)benzene (0.2 mmol) and aniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA ( $v/v = 20/1$ ) as an eluent, to yield the white solid **3pa** (50.6 mg, 83%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta = 7.41\text{--}7.35$  (m, 4H), 7.32 (s, 1H), 7.13 (dd,  $J = 12.1, 7.6$  Hz, 3H), 6.01 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta = 145.5, 140.5, 132.9$  (q,  $J = 33.0$  Hz), 130.1, 124.0, 123.6 (q,  $J = 272.7$  Hz), 120.6, 115.3 (q,  $J = 3.0$  Hz), 113.2 (dt,  $J = 7.8, 3.9$  Hz).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta = -63.19$ . QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{14}\text{H}_{10}\text{F}_6\text{N}^+$  306.0712; Found 306.0723.

### morpholino(3-(phenylamino)phenyl)methanone (3qa)

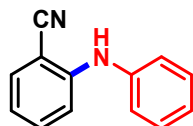


Following the General Procedure with the corresponding (3-bromophenyl)(morpholino)methanone (0.2 mmol) and aniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA ( $v/v = 10/1$ ) as an eluent, to yield the white solid **3qa** (42.9 mg, 76%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta = 7.33\text{--}7.23$  (m, 4H), 7.13–7.04 (m, 4H), 6.98 (t,  $J = 7.4$  Hz, 1H), 6.88 (d,  $J = 7.5$  Hz, 1H), 51.84 (s, 1H), 3.81–3.44 (m, 8H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta = 170.6, 144.1, 142.3, 136.7, 129.8, 129.7, 122.2, 119.0, 118.9, 118.4, 115.4, 67.1$ . m.p. =

113.3-114.2 °C. IR (KBr disk,  $\text{cm}^{-1}$ ) 3279, 3118, 3049, 3002, 2968, 2922, 2852, 1623, 1580, 1530, 1497, 1447, 1435, 1365, 1319, 1303, 1274, 1260, 1222, 1166, 1142, 1110, 1069, 1030, 993, 960, 884, 838, 801, 761, 728, 701, 627, 574, 486. QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_2^+$  283.1441; Found 283.1453.

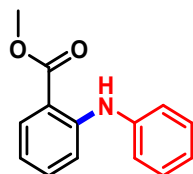
### 2-(phenylamino)benzonitrile (**3ra**)<sup>S4</sup>



Following the General Procedure with the corresponding 2-bromobenzonitrile (0.2 mmol) and aniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the slightly yellow solid **3ra** (26.0 mg, 67%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.50 (dd,  $J$  = 7.8, 1.5 Hz, 1H), 7.37 (t,  $J$  = 7.9 Hz, 3H), 7.24–7.18 (m, 3H), 7.14 (t,  $J$  = 7.4 Hz, 1H), 6.89–6.81 (m, 1H), 6.35 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 147.5, 140.1, 134.1, 133.2, 129.8, 124.4, 121.9, 119.4, 117.8, 114.3, 98.6. QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{13}\text{H}_{11}\text{N}_2^+$  195.0917; Found 195.0934.

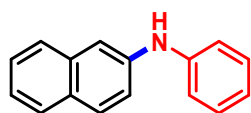
### methyl 2-(phenylamino)benzoate (**3sa**)<sup>S6</sup>



Following the General Procedure with the corresponding methyl 2-bromobenzoate (0.2 mmol) and aniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the pale yellow oil **3sa** (28.6 mg, 63%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 9.47 (s, 1H), 7.96 (dd,  $J$  = 8.1, 1.4 Hz, 1H), 7.34 (dd,  $J$  = 11.1, 4.6 Hz, 2H), 7.29 (dd,  $J$  = 6.9, 1.6 Hz, 1H), 7.27–7.22 (m, 3H), 7.11–7.04 (m, 1H), 6.72 (ddd,  $J$  = 8.1, 6.8, 1.4 Hz, 1H), 3.89 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 169.1, 148.1, 140.9, 134.3, 131.8, 129.5, 129.3, 123.7, 122.7, 117.3, 114.2, 112.1, 52.0. QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{14}\text{H}_{14}\text{NO}_2^+$  228.1019; Found 228.1027.

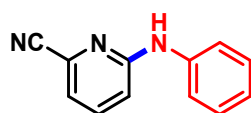
### N-phenylnaphthalen-2-amine (**3ta**)<sup>S7</sup>



Following the General Procedure with the corresponding 2-bromonaphthalene (0.2 mmol) and aniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the colorless solid **3ta** (30.7 mg, 70%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 7.79–7.68 (m, 2H), 7.62 (d,  $J$  = 8.2 Hz, 1H), 7.38 (dd,  $J$  = 11.2, 3.9 Hz, 2H), 7.34–7.25 (m, 3H), 7.18 (dd,  $J$  = 8.8, 2.2 Hz, 1H), 7.13 (d,  $J$  = 7.7 Hz, 2H), 6.96 (t,  $J$  = 7.3 Hz, 1H), 5.81 (s, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 143.1, 141.0, 134.8, 129.6, 129.4, 127.8, 126.7, 126.6, 123.7, 121.6, 120.2, 118.4, 111.7. QTOF-MS  $m/z$  [M + H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>14</sub>N<sup>+</sup> 220.1121; Found 220.1113.

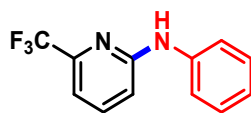
### 6-(phenylamino)picolinonitrile (**3ua**)



Following the General Procedure with the corresponding 6-bromopicolinonitrile (0.2 mmol) and aniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 10/1) as an eluent, to yield the yellow solid **3ua** (32.4 mg, 83% for 6-bromopicolinonitrile; 20.7 mg, 53% for 6-chloropicolinonitrile).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 7.55 (dd,  $J$  = 8.6, 7.3 Hz, 1H), 7.37 (d,  $J$  = 4.3 Hz, 4H), 7.18–7.09 (m, 2H), 6.99 (d,  $J$  = 8.6 Hz, 1H), 6.73 (s, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 156.8, 139.1, 138.3, 132.0, 129.7, 124.4, 121.4, 120.0, 117.8, 112.5. m.p. = 119.0–119.9 °C. IR (KBr disk, cm<sup>-1</sup>) 3361, 3026, 2920, 2850, 2240, 1621, 1591, 1537, 1499, 1481, 1467, 1450, 1384, 1368, 1310, 1249, 1195, 1077, 794, 753, 719, 691, 624, 553, 503. QTOF-MS  $m/z$  [M + H]<sup>+</sup> Calcd for C<sub>12</sub>H<sub>10</sub>N<sub>3</sub><sup>+</sup> 196.0869; Found 196.0864.

### N-phenyl-6-(trifluoromethyl)pyridin-2-amine (**3va**)

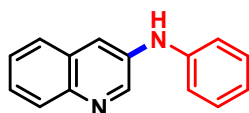


Following the General Procedure with the corresponding 2-bromo-6-(trifluoromethyl)pyridine (0.2

mmol) and aniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 10/1) as an eluent, to yield the pale yellow oil **3va** (38.1 mg, 80% for 2-bromo-6-(trifluoromethyl)pyridine; 26.2 mg, 55% for 2-chloro-6-(trifluoromethyl)pyridine).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.60 (t,  $J$  = 7.9 Hz, 1H), 7.36 (d,  $J$  = 4.2 Hz, 4H), 7.16–7.06 (m, 2H), 6.99 (d,  $J$  = 8.5 Hz, 1H), 6.75 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 156.3, 146.9 (q,  $J$  = 34.2 Hz), 139.6, 138.8, 129.7, 124.0, 121.7 (q,  $J$  = 274.0 Hz), 121.1, 111.3 (dd,  $J$  = 3.1 Hz), 111.2, 111.2.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  = -68.61. IR (KBr disk,  $\text{cm}^{-1}$ ) 3405, 3039, 2926, 2854, 1612, 1596, 1579, 1530, 1498, 1455, 1419, 1370, 1350, 1319, 1284, 1187, 1135, 1082, 986, 934, 895, 802, 737, 693, 655, 596, 528, 494. QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{12}\text{H}_{10}\text{F}_3\text{N}_2^+$  239.0791; Found 239.0788.

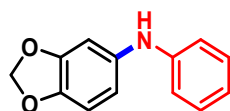
#### N-phenylquinolin-3-amine (**3wa**)<sup>S8</sup>



Following the General Procedure with the corresponding 3-bromoquinoline (0.2 mmol) and aniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 10/1) as an eluent, to yield the colorless oil **3wa** (27.3 mg, 62%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 8.70 (d,  $J$  = 2.7 Hz, 1H), 8.01 (d,  $J$  = 8.2 Hz, 1H), 7.73 (d,  $J$  = 2.6 Hz, 1H), 7.63 (dd,  $J$  = 8.0, 1.3 Hz, 1H), 7.49 (dtd,  $J$  = 14.7, 6.9, 1.4 Hz, 2H), 7.35 (dd,  $J$  = 8.3, 7.5 Hz, 2H), 7.23–7.15 (m, 2H), 7.05 (t,  $J$  = 7.4 Hz, 1H), 6.09 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 145.2, 143.8, 142.0, 137.2, 129.8, 129.2, 129.0, 127.4, 126.7, 126.7, 122.5, 118.8, 117.1. QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{13}\text{N}_2^+$  221.1073; Found 221.1090.

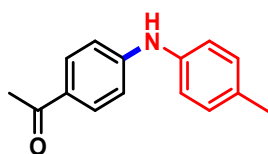
#### N-phenylbenzo[*d*][1,3]dioxol-5-amine (**3xa**)<sup>S9</sup>



Following the General Procedure with the corresponding 5-bromobenzo[*d*][1,3]dioxole (0.2 mmol) and aniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the colorless oil **3xa** (20.9 mg, 49% for 5-bromobenzo[*d*][1,3]dioxole; 25.6 mg, 60% for 5-iodobenzo[*d*][1,3]dioxole).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.15 (t,  $J$  = 7.9 Hz, 2H), 6.86 (d,  $J$  = 7.9 Hz, 2H), 6.78 (t,  $J$  = 7.3 Hz, 1H), 6.67 (d,  $J$  = 8.2 Hz, 1H), 6.63 (d,  $J$  = 2.1 Hz, 1H), 6.48 (dd,  $J$  = 8.2, 2.2 Hz, 1H), 5.87 (s, 2H), 5.44 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 148.4, 144.9, 143.1, 137.5, 129.5, 120.2, 116.4, 113.2, 108.8, 102.8, 101.3. QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{13}\text{H}_{12}\text{NO}_2^+$  214.0863; Found 214.0855.

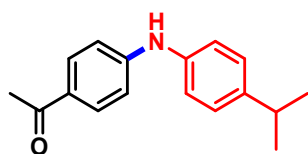
### 1-(4-(*p*-tolylamino)phenyl)ethan-1-one (**3ab**)<sup>S10</sup>



Following the General Procedure with the corresponding 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and *p*-toluidine (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the pale yellow solid **3ab** (41.0 mg, 91%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.85 (d,  $J$  = 8.6 Hz, 2H), 7.16 (d,  $J$  = 8.1 Hz, 2H), 7.09 (d,  $J$  = 8.2 Hz, 2H), 6.92 (d,  $J$  = 8.6 Hz, 2H), 6.06 (s, 1H), 2.52 (s, 3H), 2.34 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 196.6, 149.3, 138.0, 133.6, 130.9, 130.3, 128.8, 121.8, 114.0, 26.3, 21.1. QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{16}\text{NO}^+$  226.1226; Found 226.1210.

### 1-(4-((4-isopropylphenyl)amino)phenyl)ethan-1-one (**3ac**)<sup>S11</sup>

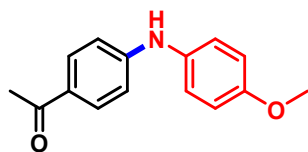


Following the General Procedure with the corresponding 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and 4-isopropylaniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the white solid **3ac** (45.5 mg, 90%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.85 (d,  $J$  = 8.7 Hz, 2H), 7.21 (d,  $J$  = 8.4 Hz, 2H), 7.12 (d,  $J$  = 8.4 Hz, 2H), 6.94 (d,  $J$  = 8.7 Hz, 2H), 6.03 (s, 1H), 2.91 (dt,  $J$  = 13.8, 6.9 Hz, 1H), 2.52 (s, 3H), 1.27 (s, 7H), 1.25 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 196.6, 149.2, 144.7, 138.3, 130.9, 128.8, 127.6, 121.6, 114.1, 33.8, 26.3, 24.3. QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{20}\text{NO}^+$  254.1539; Found 254.1538.



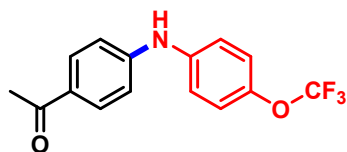
### 1-(4-((4-methoxyphenyl)amino)phenyl)ethan-1-one (**3ad**)<sup>S11</sup>



Following the General Procedure with the corresponding 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and 4-methoxyaniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the white solid **3ad** (44.8 mg, 93%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 7.83 (d,  $J$  = 8.7 Hz, 2H), 7.14 (d,  $J$  = 8.8 Hz, 2H), 6.91 (d,  $J$  = 8.8 Hz, 2H), 6.81 (d,  $J$  = 8.7 Hz, 2H), 5.92 (s, 1H), 3.82 (s, 3H), 2.51 (s, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 196.6, 156.9, 150.3, 133.4, 131.0, 128.4, 124.9, 115.0, 113.4, 55.8, 26.3. QTOF-MS  $m/z$  [M + H]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>16</sub>NO<sub>2</sub><sup>+</sup> 242.1176; Found 242.1153.

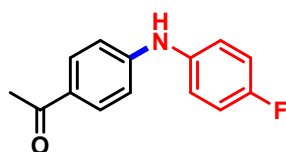
### 1-(4-((4-(trifluoromethoxy)phenyl)amino)phenyl)ethan-1-one (**3ae**)<sup>S11</sup>



Following the General Procedure with the corresponding 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and 4-(trifluoromethoxy)aniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the white solid **3ae** (40.7, 69%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 7.88 (d,  $J$  = 8.7 Hz, 2H), 7.19 (s, 4H), 6.99 (d,  $J$  = 8.7 Hz, 2H), 6.21 (s, 1H), 2.54 (s, 3H). <sup>13</sup>C {<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 196.7, 148.1, 144.7, 139.8, 130.9, 129.8, 122.6, 121.6, 120.7 (q,  $J$  = 256.7 Hz), 114.9, 26.4. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = -58.18. QTOF-MS  $m/z$  [M + H]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>13</sub>F<sub>3</sub>NO<sub>2</sub><sup>+</sup> 296.0893; Found 296.0899.

### 1-(4-((4-fluorophenyl)amino)phenyl)ethan-1-one (**3af**)<sup>S12</sup>

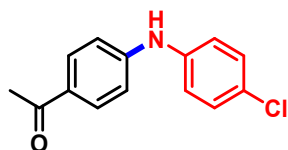


Following the General Procedure with the corresponding 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and 4-fluoroaniline (0.4 mmol). The crude product was purified by preparative TLC, using

PE and EA (v/v = 20/1) as an eluent, to yield the yellow solid **3af** (28.4 mg, 62%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.85 (d,  $J$  = 8.7 Hz, 2H), 7.16 (dd,  $J$  = 8.8, 4.7 Hz, 2H), 7.05 (t,  $J$  = 8.5 Hz, 2H), 6.88 (d,  $J$  = 8.7 Hz, 2H), 6.04 (s, 1H), 2.52 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 196.6, 159.6 (d,  $J$  = 243.3 Hz), 149.3, 136.7 (d,  $J$  = 2.8 Hz), 130.9, 129.1, 123.8 (d,  $J$  = 8.1 Hz), 116.5 (d,  $J$  = 22.6 Hz), 114.0, 26.3.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = -118.54. QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{14}\text{H}_{13}\text{FNO}^+$  230.0976; Found 230.0979.

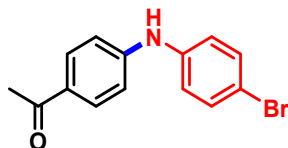
#### 1-(4-((4-chlorophenyl)amino)phenyl)ethan-1-one (**3ag**)<sup>S11</sup>



Following the General Procedure with the corresponding 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and 4-chloroaniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the white solid **3ag** (30.9 mg, 63%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.87 (d,  $J$  = 8.6 Hz, 2H), 7.29 (d,  $J$  = 8.6 Hz, 2H), 7.11 (d,  $J$  = 8.6 Hz, 2H), 6.97 (d,  $J$  = 8.6 Hz, 2H), 6.12 (s, 1H), 2.53 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 196.6, 148.1, 139.6, 130.8, 129.8, 129.7, 128.4, 122.0, 114.9, 26.4. QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{14}\text{H}_{13}\text{ClNO}^+$  246.0680; Found 246.0669.

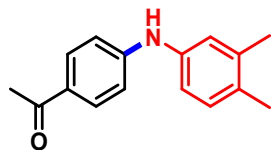
#### 1-(4-((4-bromophenyl)amino)phenyl)ethan-1-one (**3ah**)<sup>S13</sup>



Following the General Procedure with the corresponding 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and 4-bromoaniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the white solid **3ah** (38.1 mg, 66%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.87 (d,  $J$  = 8.7 Hz, 2H), 7.44 (d,  $J$  = 8.7 Hz, 2H), 7.06 (d,  $J$  = 8.7 Hz, 2H), 6.98 (d,  $J$  = 8.7 Hz, 2H), 6.10 (s, 1H), 2.53 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 196.6, 147.9, 140.1, 132.7, 130.8, 129.8, 122.2, 115.7, 115.0, 26.4. QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{14}\text{H}_{13}\text{BrNO}^+$  290.0175; Found 290.0191.

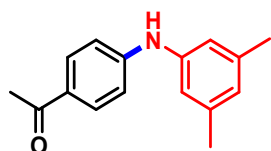
### 1-(4-((3,4-dimethylphenyl)amino)phenyl)ethan-1-one (**3ai**)



Following the General Procedure with the corresponding 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and 3,4-dimethylaniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the white solid **3ai** (40.6 mg, 85%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.85 (d,  $J$  = 8.8 Hz, 2H), 7.11 (d,  $J$  = 8.0 Hz, 1H), 7.02–6.87 (m, 4H), 6.02 (s, 1H), 2.52 (s, 3H), 2.26 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 196.6, 149.4, 138.3, 138.1, 132.4, 130.8, 130.7, 128.7, 123.2, 119.2, 114.0, 26.3, 20.1, 19.3. m.p. = 144.0–144.8 °C. IR (KBr disk,  $\text{cm}^{-1}$ ) 3321, 2974, 2934, 1919, 1649, 1588, 1565, 1521, 1504, 1424, 1383, 1358, 1330, 1278, 1251, 1180, 1120, 1072, 1024, 955, 873, 848, 830, 802, 785, 699, 628, 591, 472. QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{18}\text{NO}^+$  240.1383; Found 240.1375.

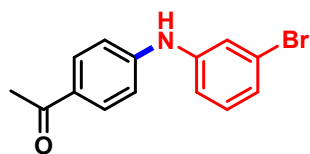
### 1-(4-((3,5-dimethylphenyl)amino)phenyl)ethan-1-one (**3aj**)<sup>S14</sup>



Following the General Procedure with the corresponding 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and 3,5-dimethylaniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the yellow solid **3aj** (40.2 mg, 84%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.86 (d,  $J$  = 8.7 Hz, 2H), 6.98 (d,  $J$  = 8.7 Hz, 2H), 6.81 (s, 2H), 6.74 (s, 1H), 6.13 (s, 1H), 2.53 (s, 3H), 2.31 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 196.7, 148.8, 140.6, 139.4, 130.8, 128.9, 125.4, 118.6, 114.6, 26.3, 21.6. QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{18}\text{NO}^+$  240.1383; Found 240.1385.

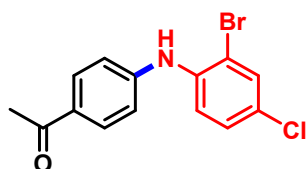
### 1-(4-((3-bromophenyl)amino)phenyl)ethan-1-one (**3ak**)<sup>S15</sup>



Following the General Procedure with the corresponding 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and 3-bromoaniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the pale yellow solid **3ak** (34.7 mg, 60%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.89 (d,  $J$  = 8.7 Hz, 2H), 7.33 (s, 1H), 7.18 (d,  $J$  = 6.5 Hz, 2H), 7.11–7.06 (m, 1H), 7.02 (d,  $J$  = 8.7 Hz, 2H), 6.11 (s, 1H), 2.54 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 196.6, 147.5, 142.6, 131.0, 130.8, 130.2, 126.1, 123.4, 122.9, 118.7, 115.5, 26.4. QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{14}\text{H}_{13}\text{BrNO}^+$  290.0175; Found 290.0164.

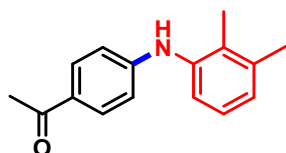
#### 1-(4-((2-bromo-4-chlorophenyl)amino)phenyl)ethan-1-one (3al)



Following the General Procedure with the corresponding 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and 2-bromo-4-chloroaniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the pale grey solid **3al** (34.2 mg, 53%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.91 (d,  $J$  = 8.7 Hz, 2H), 7.59 (d,  $J$  = 2.3 Hz, 1H), 7.35 (d,  $J$  = 8.7 Hz, 1H), 7.24 (dd,  $J$  = 8.7, 2.3 Hz, 1H), 7.06 (d,  $J$  = 8.7 Hz, 2H), 6.22 (s, 1H), 2.56 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 196.6, 146.6, 138.2, 132.9, 130.9, 130.8, 128.6, 127.7, 119.9, 116.6, 115.1, 26.5. m.p. = 94.7–95.5 °C. IR (KBr disk,  $\text{cm}^{-1}$ ) 3402, 3071, 2952, 2917, 2849, 1673, 1604, 1585, 1520, 1498, 1459, 1416, 1380, 1356, 1325, 1280, 1226, 1180, 1144, 1123, 1102, 1032, 956, 925, 868, 849, 816, 735, 656, 591, 542, 491. QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{14}\text{H}_{12}\text{BrClNO}^+$  323.9785; Found 323.9790.

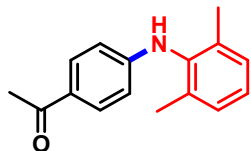
#### 1-(4-((2,3-dimethylphenyl)amino)phenyl)ethan-1-one (3am)



Following the General Procedure with the corresponding 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and 2,3-dimethylaniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the pale yellow solid **3am** (33.0 mg, 69%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.83 (d,  $J$  = 8.7 Hz, 2H), 7.15 – 7.10 (m, 2H), 7.07–7.01 (m, 1H), 6.70 (d,  $J$  = 8.7 Hz, 2H), 5.80 (s, 1H), 2.51 (s, 3H), 2.33 (s, 3H), 2.15 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 196.6, 150.4, 138.6, 138.5, 132.0, 130.9, 128.3, 127.3, 126.4, 122.6, 113.6, 26.3, 20.8, 14.19. m.p. = 120.5-121.1 °C. IR (KBr disk,  $\text{cm}^{-1}$ ) 3321, 2913, 2852, 1661, 1599, 1572, 1524, 1468, 1424, 1384, 1334, 1277, 1175, 1119, 1091, 1020, 961, 826, 808, 777, 748, 699, 606, 576, 490. QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{18}\text{NO}^+$  240.1383; Found 240.1368.

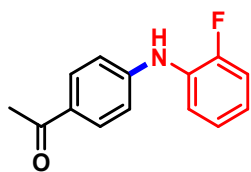
#### 1-(4-((2,6-dimethylphenyl)amino)phenyl)ethan-1-one (**3an**)



Following the General Procedure with the corresponding 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and 2,6-dimethylaniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the white solid **3an** (32.0 mg, 67%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.81 (d,  $J$  = 8.8 Hz, 2H), 7.15 (s, 3H), 6.46 (d,  $J$  = 8.7 Hz, 2H), 5.60 (s, 1H), 2.50 (s, 3H), 2.20 (s, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 196.6, 150.9, 136.8, 136.6, 131.1, 128.9, 128.0, 127.2, 112.3, 26.3, 18.5. m.p. = 110.1-110.8 °C. IR (KBr disk,  $\text{cm}^{-1}$ ) 3374, 2921, 2851, 1651, 1602, 1586, 1515, 1478, 1377, 1361, 1333, 1276, 1176, 1163, 1121, 1071, 1033, 956, 831, 779, 688, 594, 552, 503. QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{18}\text{NO}^+$  240.1383; Found 240.1374.

#### 1-(4-((2-fluorophenyl)amino)phenyl)ethan-1-one (**3ao**)<sup>S16</sup>

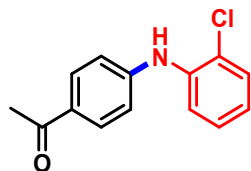


Following the General Procedure with the corresponding 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and 2-fluoroaniline (0.4 mmol). The crude product was purified by preparative TLC, using

PE and EA (v/v = 20/1) as an eluent, to yield the yellow oil **3ao** (22.9 mg, 50%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.90 (d,  $J$  = 8.8 Hz, 2H), 7.47–7.37 (m, 1H), 7.19–7.08 (m, 2H), 7.03 (d,  $J$  = 8.7 Hz, 3H), 6.12 (s, 1H), 2.55 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 196.7, 154.5 (d,  $J$  = 243.6 Hz), 147.6, 130.7, 129.9, 129.2 (d,  $J$  = 11.3 Hz), 124.7 (d,  $J$  = 3.8 Hz), 123.6 (d,  $J$  = 7.5 Hz), 121.0 (d,  $J$  = 1.4 Hz), 116.3 (d,  $J$  = 19.4 Hz), 115.3, 26.4.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = -128.68. QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{14}\text{H}_{13}\text{FNO}^+$  230.0976; Found 230.0976.

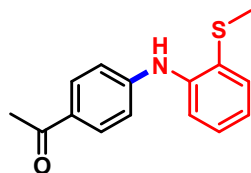
### 1-(4-((2-chlorophenyl)amino)phenyl)ethan-1-one (**3ap**)<sup>S11</sup>



Following the General Procedure with the corresponding 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and 2-chloroaniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the pale yellow solid **3ap** (25.5 mg, 52%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.91 (d,  $J$  = 8.6 Hz, 2H), 7.43 (t,  $J$  = 8.5 Hz, 2H), 7.23 (t,  $J$  = 7.7 Hz, 1H), 7.09 (d,  $J$  = 8.6 Hz, 2H), 6.97 (t,  $J$  = 7.6 Hz, 1H), 6.32 (s, 1H), 2.55 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 196.6, 147.0, 138.1, 130.7, 130.5, 130.3, 127.7, 124.5, 123.3, 119.4, 116.3, 26.4. QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{14}\text{H}_{13}\text{ClNO}^+$  246.0680; Found 246.0682.

### 1-(4-((2-(methylthio)phenyl)amino)phenyl)ethan-1-one (**3aq**)

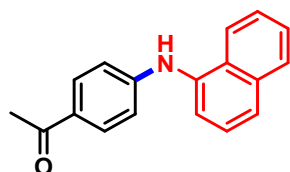


Following the General Procedure with the corresponding 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and 2-(methylthio)aniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the pale yellow solid **3aq** (36.0 mg, 70%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  = 7.89 (d,  $J$  = 8.7 Hz, 2H), 7.41 (dd,  $J$  = 18.5, 4.7 Hz, 2H), 7.25–7.18 (m, 1H), 7.05 (dd,  $J$  = 13.2, 5.0 Hz, 3H), 6.57 (s, 1H), 2.54 (s, 3H), 2.39 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR

(101 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 196.7, 148.1, 140.3, 131.3, 130.8, 129.7, 128.7, 127.7, 123.7, 119.7, 115.4, 26.4, 17.5. m.p. = 83.6-84.5 °C. IR (KBr disk, cm<sup>-1</sup>) 3301, 3079, 2911, 1659, 1596, 1576, 1523, 1462, 1431, 1414, 1384, 1332, 1306, 1276, 1252, 1179, 1122, 1070, 1023, 962, 829, 748, 734, 677, 640, 592, 491, 447. QTOF-MS  $m/z$  [M + H]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>16</sub>NOS<sup>+</sup> 258.0947; Found 258.0936.

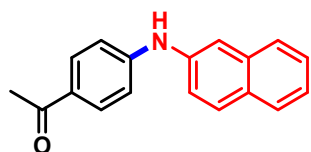
### 1-(4-(naphthalen-1-ylamino)phenyl)ethan-1-one (**3ar**)<sup>S15</sup>



Following the General Procedure with the corresponding 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and naphthalen-1-amine (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the pale yellow solid **3ar** (31.8 mg, 61%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 7.97 (d,  $J$  = 8.1 Hz, 1H), 7.93–7.89 (m, 1H), 7.85 (d,  $J$  = 8.8 Hz, 2H), 7.77–7.71 (m, 1H), 7.57–7.45 (m, 4H), 6.84 (d,  $J$  = 8.8 Hz, 2H), 2.52 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 196.6, 150.5, 136.4, 135.0, 130.9, 129.5, 128.8, 126.7, 126.6, 126.1, 125.9, 122.5, 121.0, 114.3, 26.3. QTOF-MS  $m/z$  [M + H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>16</sub>NO<sup>+</sup> 262.1226; Found 262.1239.

### 1-(4-(naphthalen-2-ylamino)phenyl)ethan-1-one (**3as**)<sup>S15</sup>

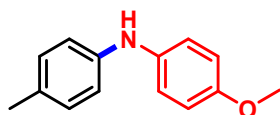


Following the General Procedure with the corresponding 1-(4-bromophenyl)ethan-1-one (0.2 mmol) and naphthalen-2-amine (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the pale yellow solid **3as** (33.9 mg, 65%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 7.91 (d,  $J$  = 8.7 Hz, 2H), 7.81 (t,  $J$  = 8.4 Hz, 2H), 7.72 (d,  $J$  = 8.1 Hz, 1H), 7.59 (d,  $J$  = 1.5 Hz, 1H), 7.47 (t,  $J$  = 7.4 Hz, 1H), 7.40 (t,  $J$  = 7.5 Hz, 1H), 7.31 (dd,  $J$  = 8.7, 2.1 Hz, 1H), 7.08 (d,  $J$  = 8.7 Hz, 2H), 6.30 (s, 1H), 2.55 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 196.6, 148.4, 138.5, 134.5, 130.9, 130.5, 129.7, 129.6, 127.9, 127.1, 126.9, 124.9,

121.6, 116.2, 115.0, 26.4. QTOF-MS  $m/z$   $[M + H]^+$  Calcd for  $C_{18}H_{16}NO^+$  262.1226; Found 262.1210.

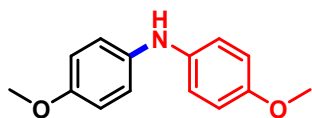
**4-methoxy-N-(p-tolyl)aniline (3k'd)**<sup>S17</sup>



Following the General Procedure with the corresponding 1-iodo-4-methylbenzene (0.2 mmol) and 4-methoxyaniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the brown solid **3k'd** (32.4 mg, 76%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 7.05 (dd,  $J$  = 10.4, 3.8 Hz, 4H), 6.94–6.80 (m, 4H), 5.42 (s, 1H), 3.81 (s, 3H), 2.30 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 154.9, 142.6, 136.8, 130.0, 129.5, 121.3, 116.7, 114.8, 55.8, 20.6. QTOF-MS  $m/z$   $[M + H]^+$  Calcd for  $C_{14}H_{16}NO^+$  214.1226; Found 214.1230.

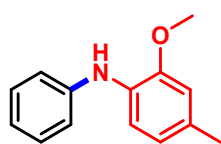
**bis(4-methoxyphenyl)amine (3l'd)**<sup>S17</sup>



Following the General Procedure with the corresponding 1-iodo-4-methoxybenzene (0.2 mmol) and 4-methoxyaniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 10/1) as an eluent, to yield the brownish white solid **3l'd** (35.7 mg, 78%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 6.98–6.92 (m, 4H), 6.87–6.80 (m, 4H), 5.32 (s, 1H), 3.79 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 154.3, 138.1, 119.7, 114.9, 55.8. QTOF-MS  $m/z$   $[M + H]^+$  Calcd for  $C_{14}H_{16}NO_2^+$  230.1176; Found 230.1195.

**2-methoxy-4-methyl-N-phenylaniline (3j't)**<sup>S17</sup>



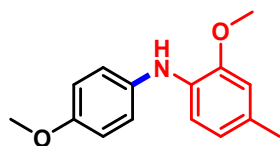
Following the General Procedure with the corresponding iodobenzene (0.2 mmol) and 2-methoxy-4-methylaniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA



(v/v = 20/1) as an eluent, to yield the white solid **3j't** (26.4 mg, 62%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ = 7.34–7.25 (m, 3H), 7.14 (dd, *J* = 8.5, 1.0, 2H), 6.95 (t, *J* = 7.3, 1H), 6.76 (d, *J* = 7.1, 2H), 6.06 (s, 1H), 3.88 (s, 3H), 2.38 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, ppm) δ = 148.8, 143.6, 130.2, 130.1, 129.4, 121.0, 120.6, 117.7, 116.0, 111.8, 55.6, 21.3. QTOF-MS *m/z* [M + H]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>16</sub>NO<sup>+</sup> 214.1226; Found 214.1211.

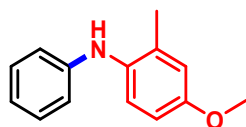
#### 2-methoxy-N-(4-methoxyphenyl)-4-methylaniline (**3l't**)<sup>S18</sup>



Following the General Procedure with the corresponding 1-iodo-4-methoxybenzene (0.2 mmol) and 2-methoxy-4-methylaniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 10/1) as an eluent, to yield the yellow oil **3l't** (29.2 mg, 60%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ = 7.12–7.05 (m, 2H), 6.97 (d, *J* = 8.0, 1H), 6.88–6.82 (m, 2H), 6.70 (d, *J* = 1.3, 1H), 6.65 (dd, *J* = 8.0, 0.8, 1H), 5.83 (s, 1H), 3.88 (s, 3H), 3.80 (s, 3H), 2.31 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, ppm) δ = 155.0, 147.9, 136.4, 132.4, 128.8, 122.0, 121.2, 114.8, 113.6, 111.6, 55.8, 55.7, 21.3. QTOF-MS *m/z* [M + H]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>18</sub>NO<sub>2</sub><sup>+</sup> 244.1332; Found 244.1343.

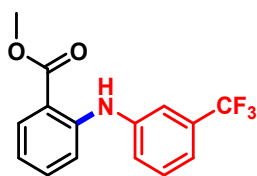
#### 4-methoxy-2-methyl-N-phenylaniline (**3j'u**)<sup>S19</sup>



Following the General Procedure with the corresponding iodobenzene (0.2 mmol) and 4-methoxy-2-methylaniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the white solid **3j'u** (**MMDPA**) (30.2 mg, 71%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm) δ = 7.21–7.12 (m, 3H), 6.79 (dd, *J* = 11.2, 4.8, 2H), 6.73 (dd, *J* = 10.0, 4.9, 3H), 5.19 (s, 1H), 3.80 (s, 3H), 2.22 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, ppm) δ = 156.5, 146.4, 134.2, 133.7, 129.5, 125.2, 118.9, 116.5, 115.0, 112.0, 55.7, 18.4. QTOF-MS *m/z* [M + H]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>16</sub>NO<sup>+</sup> 214.1226; Found 214.1223.

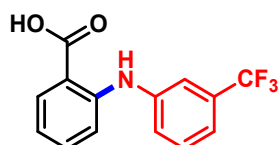
**methyl 2-((3-(trifluoromethyl)phenyl)amino)benzoate (3sv)<sup>S20</sup>**



Following the General Procedure with the corresponding methyl 2-bromobenzoate (0.2 mmol) and 3-(trifluoromethyl)aniline (0.4 mmol). The crude product was purified by preparative TLC, using PE and EA (v/v = 20/1) as an eluent, to yield the colourless oil **3sv** (36.0 mg, 61%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 9.52 (s, 1H), 7.90 (dd,  $J$  = 8.0, 1.5 Hz, 1H), 7.40 (s, 1H), 7.36–7.25 (m, 3H), 7.22–7.14 (m, 2H), 6.72 (ddd,  $J$  = 8.1, 7.2, 1.1 Hz, 1H), 3.81 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = 169.0, 146.9, 141.8, 134.5, 132.0 (q,  $J$  = 32.2 Hz), 131.9, 130.1, 124.7, 124.2 (q,  $J$  = 272.5 Hz), 119.7 (q,  $J$  = 3.9 Hz), 118.5, 118.2 (q,  $J$  = 3.8 Hz), 114.5, 113.1, 52.1. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  = -62.79. QTOF-MS  $m/z$  [M + H]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>13</sub>F<sub>3</sub>NO<sub>2</sub><sup>+</sup> 296.0893; Found 296.0890.

**2-((3-(trifluoromethyl)phenyl)amino)benzoic acid (Flufenamic Acid)<sup>S21</sup>**



The 100 mL round bottom flask containing a stirring bar was charged with methyl 2-((3-(trifluoromethyl)phenyl)amino)benzoate (29.5 mg, 0.2 mmol) in EtOH (2 mL) and KOH (11.2 mg, 0.2 mmol) in water (2 mL), which was stirred for 24 h at 100 °C. After that, EtOH was evaporated from the reaction mixture and the resultant solution was acidified to pH 2 by HCl (2M). Next, 4 mL of water was added, and the mixture was extracted three times with DCM. The combined organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The pure product was obtained by TLC using PE and EA as the eluent, to yield the white solid **Flufenamic Acid** (50.6 mg, 90%).

<sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO, ppm)  $\delta$  = 13.21 (s, 1H), 9.70 (s, 1H), 7.93 (d,  $J$  = 7.9 Hz, 1H), 7.52 (s, 3H), 7.45 (t,  $J$  = 7.1 Hz, 1H), 7.39–7.23 (m, 2H), 6.88 (t,  $J$  = 7.3 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, *d*<sub>6</sub>-DMSO, ppm)  $\delta$  = 169.7, 145.5, 142.0, 134.2, 132.0, 130.6, 130.3 (q,  $J$  = 31.5 Hz), 124.1

(q,  $J = 272.3$  Hz), 123.7, 118.9, 118.6 (q,  $J = 3.7$  Hz), 116.4 (q,  $J = 3.8$  Hz), 114.9, 114.4.  $^{19}\text{F}$  NMR (376 MHz,  $d_6$ -DMSO, ppm)  $\delta = -61.36$ . QTOF-MS  $m/z$   $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{14}\text{H}_{11}\text{F}_3\text{NO}_2^+$  282.0736; Found 282.0719.

## References

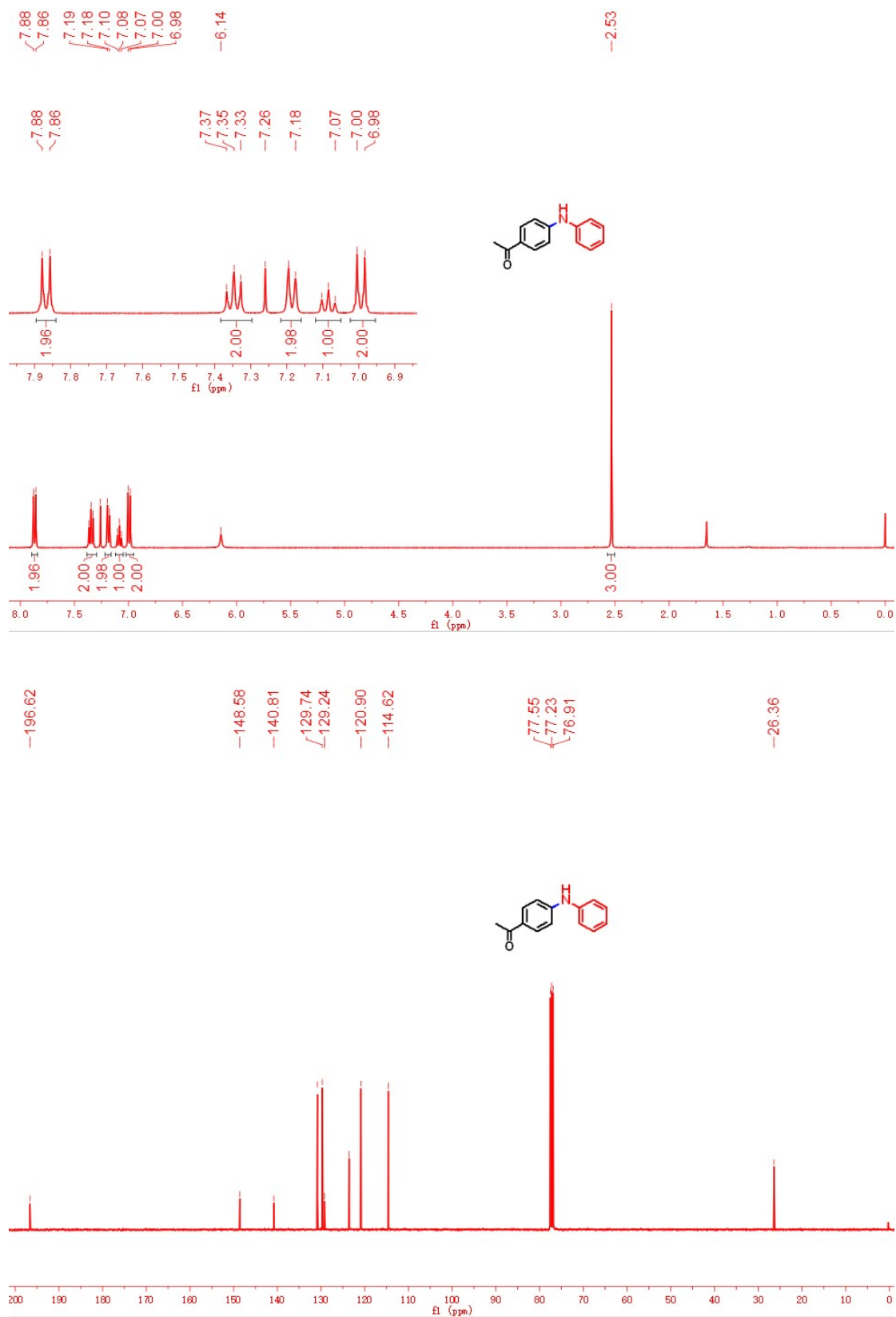
- S1 H. Song, Y. Shen, H. Zhou, D. Ding, F. Yang, Y. Wang, C. Xu and X. Cai, Light-promoted low-valent-tungsten-catalyzed ambient temperature amination of boronic acids with nitroaromatics, *J. Org. Chem.*, 2022, **87**, 5303–5314.
- S2 J. Yu, Y. Wang, P. Zhang and J. Wu, Direct amination of phenols under metal-free conditions, *Synlett*, 2013, **24**, 1448–1454.
- S3 Y. Xie, S. Liu, Y. Liu, Y. Wen and G.-J. Deng, Palladium-catalyzed one-pot diarylamine formation from nitroarenes and cyclohexanones, *Org. Lett.*, 2012, **14**, 1692–1695.
- S4 B. R. Walker, S. Manabe, A. T. Brusoe and C. S. Sevov, Mediator-enabled electrocatalysis with ligandless copper for anaerobic Chan–Lam coupling reactions, *J. Am. Chem. Soc.*, 2021, **143**, 6257–6265.
- S5 T. Ichitsuka, I. Takahashi, N. Koumura, K. Sato and S. Kobayashi, Continuous synthesis of aryl amines from phenols utilizing integrated packed-bed flow systems, *Angew. Chem., Int. Ed.*, 2020, **59**, 15891–1589.
- S6 J. C. Yang, D. Niu, B. P. Karsten, F. Lima and S. L. Buchwald, Use of a “catalytic” cosolvent, N,N-dimethyl octanamide, allows the flow synthesis of imatinib with no solvent switch, *Angew. Chem., Int. Ed.*, 2016, **55**, 2531–2535.
- S7 J. C. Vantourout, R. P. Law, A. Isidro-Llobet, S. J. Atkinson and A. J. B. Watson, Chan–Evans–Lam amination of boronic acid pinacol (BPin) esters: overcoming the aryl amine problem, *J. Org. Chem.*, 2016, **81**, 3942–3950.
- S8 R. Pratap and H. Yorimitsu, Palladium-catalyzed amination of aryl sulfides and sulfoxides with azarylamines of poor nucleophilicity, *Synthesis*, 2019, **51**, 2705–2712.
- S9 X. Ding, M. Huang, Z. Yi, D. Du, X. Zhu and Y. Wan, Room-temperature CuI-catalyzed amination of aryl iodides and aryl bromides, *J. Org. Chem.*, 2017, **82**, 5416–5423.
- S10 V. Semeniuchenko, W. M. Braje and M. G. Organ, Sodium butylated hydroxytoluene: a functional group tolerant, eco-friendly base for solvent-free, Pd-catalysed amination, *Chem. Eur. J.*, 2021, **27**, 12535–12539.
- S11 P. Wang, C. Wang, Z. Zhu, S. Xu, Y. Hou and Y. Zhao, A novel and unusual method for C–N bond formation between benzene ring and various amines, *Tetrahedron Lett.*, 2021, **81**, 153355.
- S12 B. H. Lipshutz and D. W. Chung and B. Rich, Aminations of aryl bromides in water at room temperature. *Adv. Synth. Catal.*, 2009, **351**, 1717–1721.

- S13 H. Rao, H. Fu, Y. Jiang and Y. Zhao, Copper-catalyzed arylation of amines using diphenyl pyrrolidine-2-phosphonate as the new ligand, *J. Org. Chem.*, 2005, **70**, 8107–8109.
- S14 R. A. Altman, K. W. Anderson and S. L. Buchwald, Pyrrole-2-carboxylic acid as a ligand for the Cu-catalyzed reactions of primary anilines with aryl halides, *J. Org. Chem.*, 2008, **73**, 5167–5169.
- S15 K. Manna, T. Ganguly, S. Baitalik and R. Jana, Visible-light- and PPh<sub>3</sub>-mediated direct C–N coupling of nitroarenes and boronic acids at ambient temperature, *Org. Lett.*, 2021, **23**, 8634–8639.
- S16 L. Ackermann, R. Sandmann and W. Song, Palladium- and nickel-catalyzed aminations of aryl imidazolylsulfonates and sulfamates, *Org. Lett.*, 2011, **13**, 1784–1786.
- S17 G. Chakraborti, S. Paladhi, T. Mandal and J. Dash, “On water” promoted ullmann-type C–N bond-forming reactions: application to carbazole alkaloids by selective N-arylation of aminophenols, *J. Org. Chem.*, 2018, **83**, 7347–7359.
- S18 B. Liégault, D. Lee, M. P. Huestis, D. R. Stuart and K. Fagnou, Intramolecular Pd(II)-catalyzed oxidative biaryl synthesis under air: reaction development and scope, *J. Org. Chem.*, 2008, **73**, 5022–5028.
- S19 Z. Yi, M. Huang, Y. Wan and X. Zhu. An effective heterogeneous copper catalyst system for C–N coupling and its application in the preparation of 2-methyl-4-methoxydiphenylamine (MMDPA), *Synthesis*, 2018, **50**, 3911–3920.
- S20 S. A. Worlikar and R. C. Larock, Palladium-catalyzed one-step synthesis of isoindole-1,3-diones by carbonylative cyclization of o-halobenzoates and primary amines, *J. Org. Chem.*, 2008, **73**, 7175–7180.
- S21 A. O. Adeniji, B. M. Twenter, M. C. Byrns, Y. Jin, M. Chen, J. D. Winkler and T. M. Penning, Development of potent and selective inhibitors of aldo-keto reductase 1C3 (Type 5 17 $\beta$ -hydroxysteroid dehydrogenase) based on N-phenyl-aminobenzoates and their structure-activity relationships. *J. Med. Chem.* **2012**, *55*, 2311–2323.

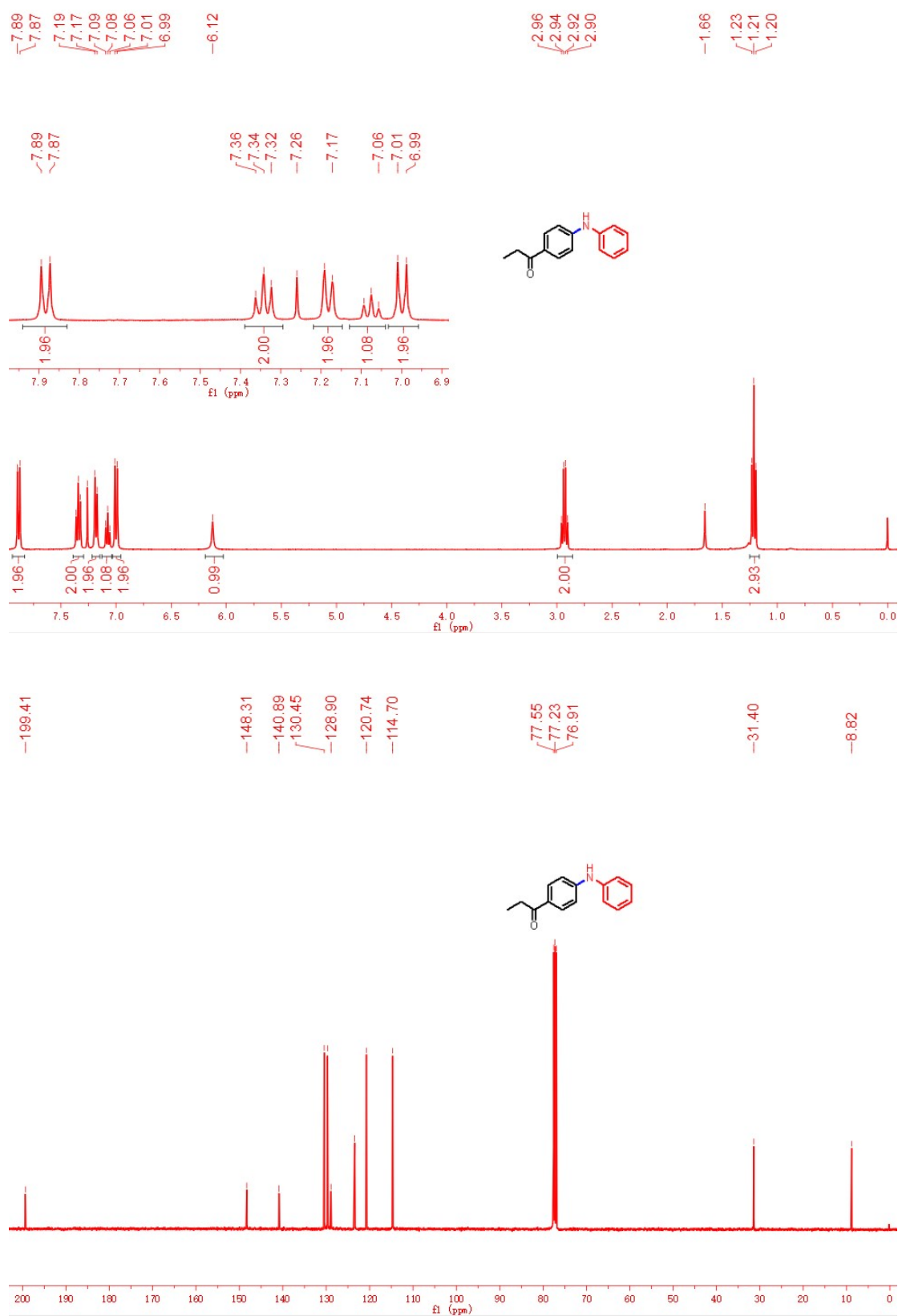
## NMR Spectra

**Fig. S7.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 1-(4-phenoxyphenyl)ethan-

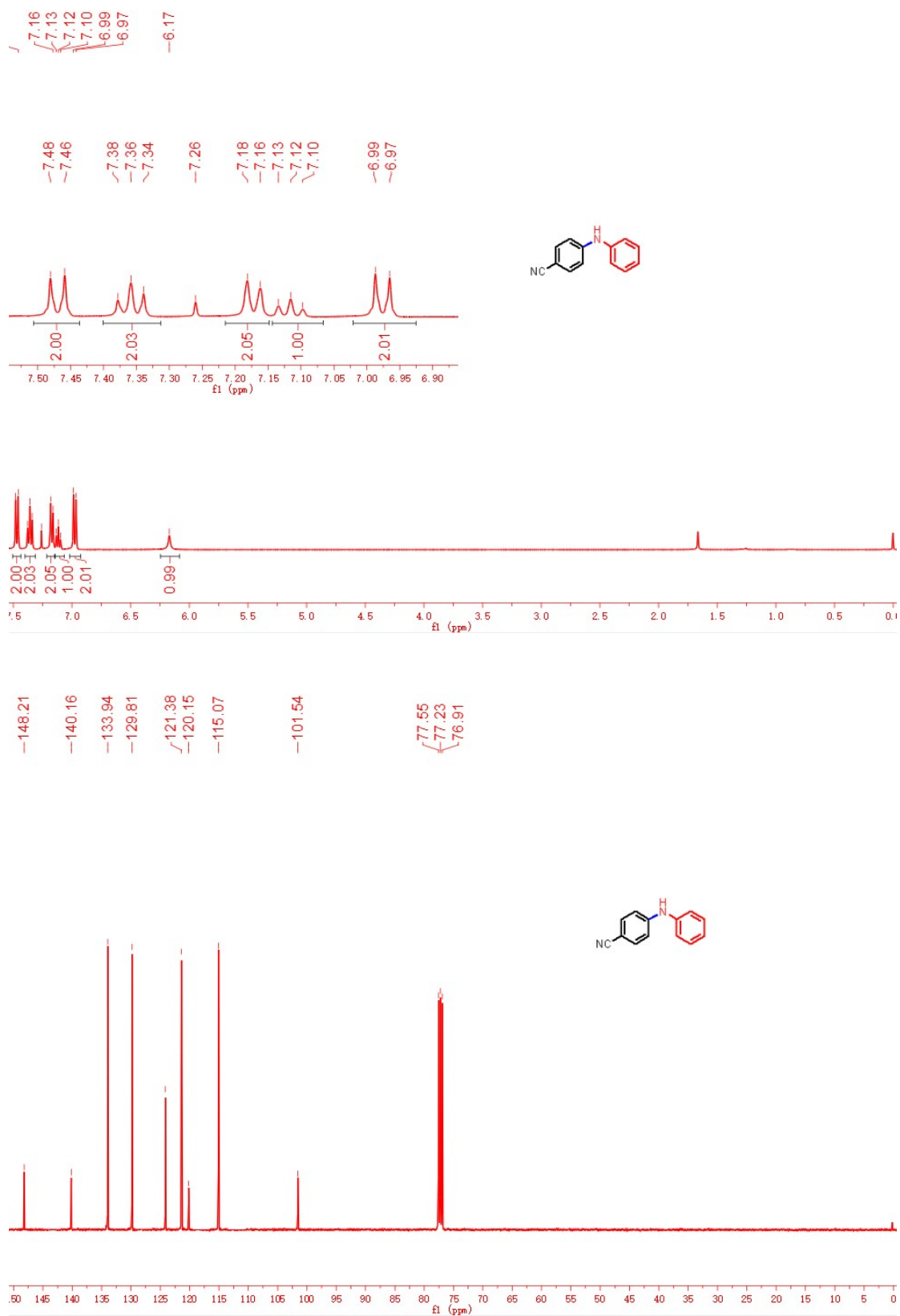
1-one (**3aa**) in  $\text{CDCl}_3$



**Fig. S8.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 1-(4-(phenylamino)phenyl)propan-1-one (**3ba**) in  $\text{CDCl}_3$

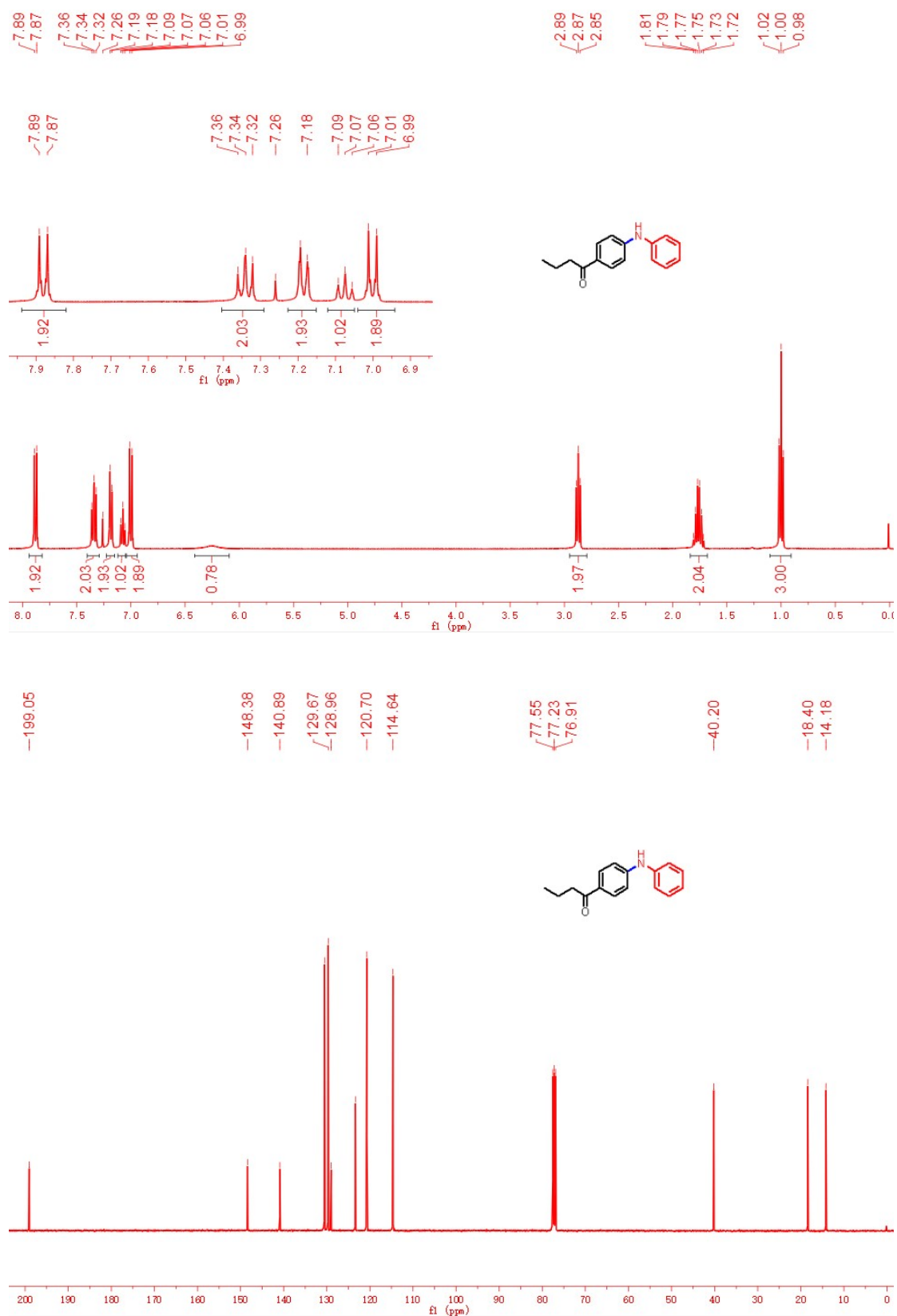


**Fig. S9.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 4-(phenylamino)benzonitrile (**3ca**) in  $\text{CDCl}_3$

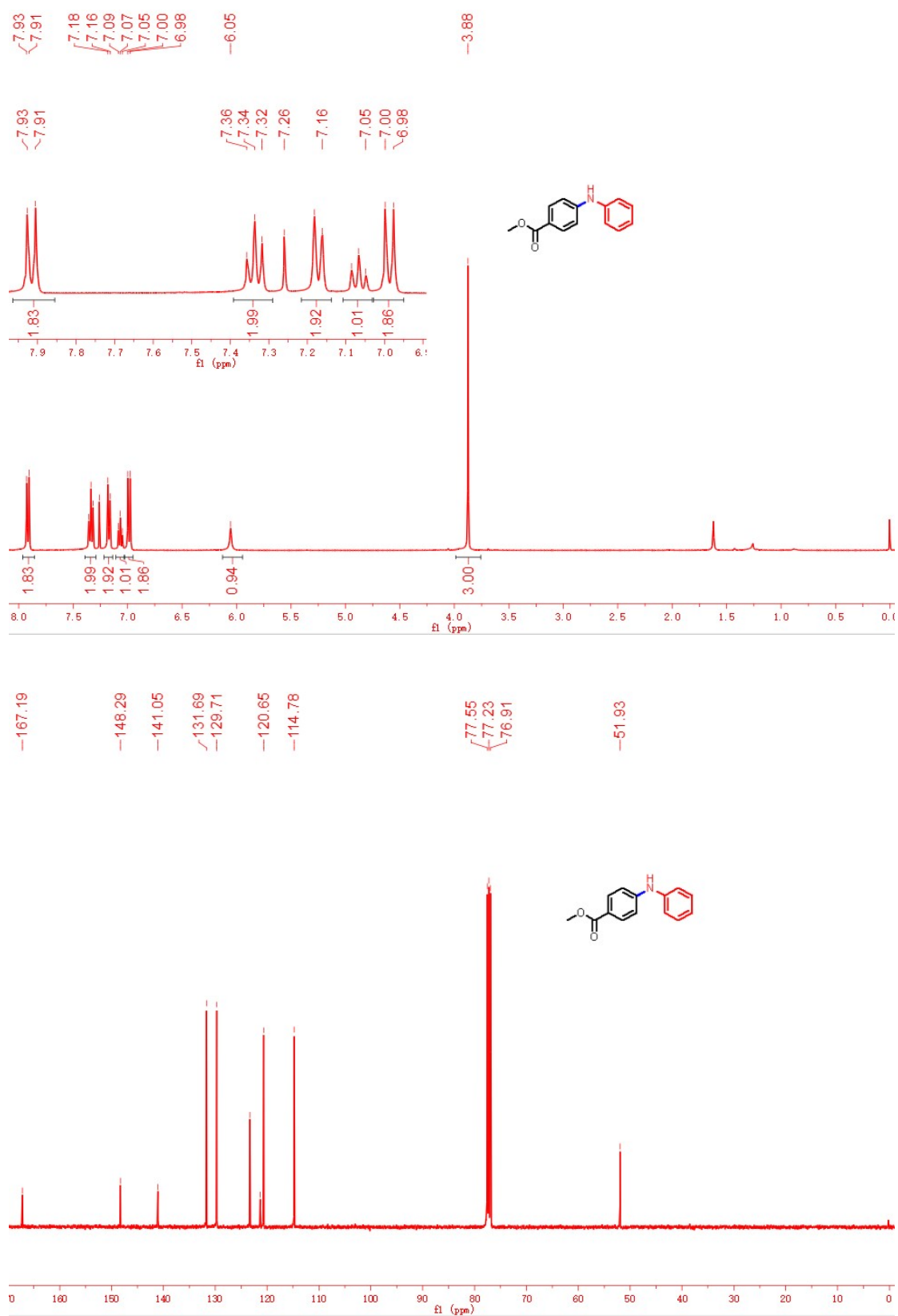




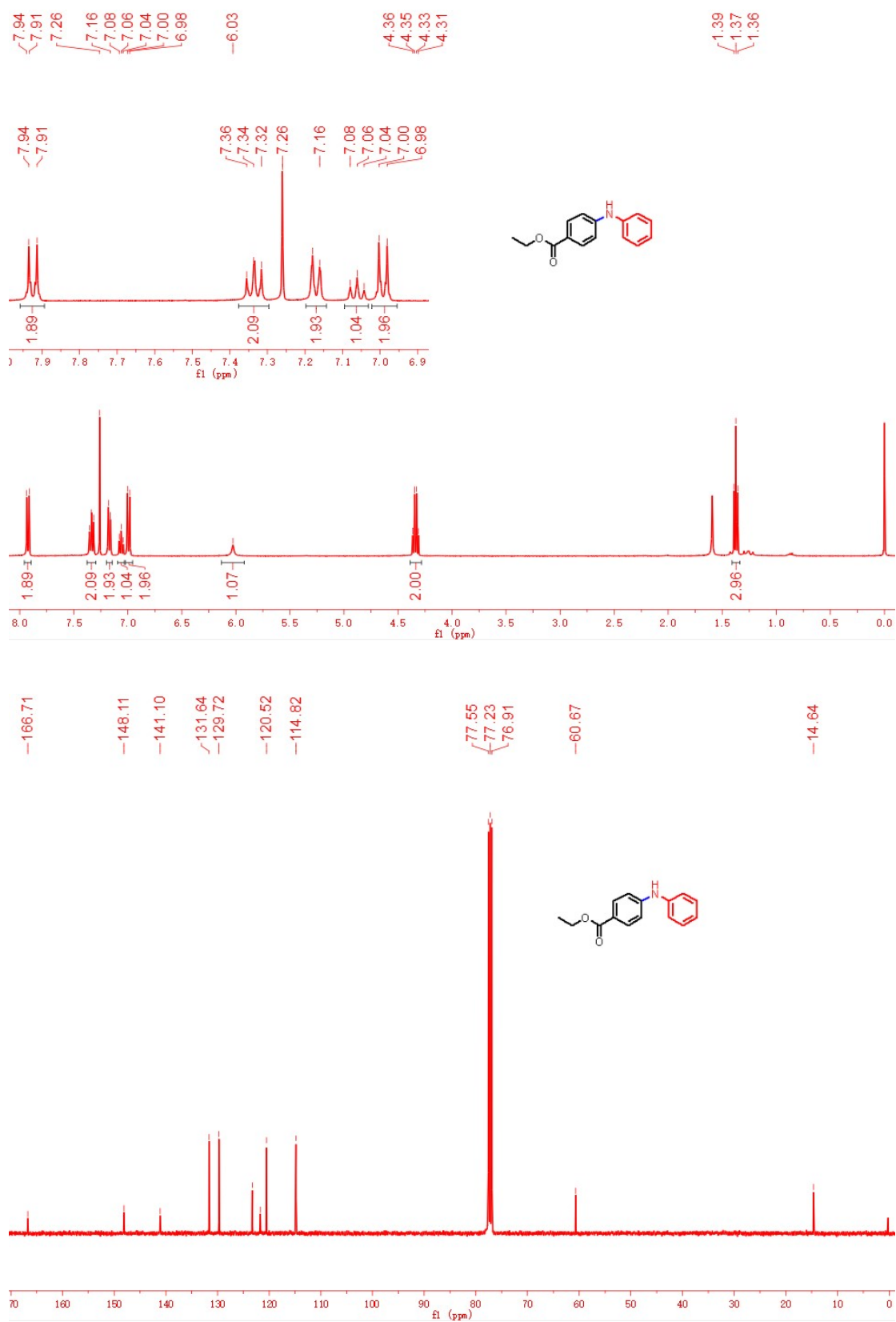
**Fig. S10.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 1-(4-(phenylamino)phenyl)butan-1-one (**3da**) in  $\text{CDCl}_3$



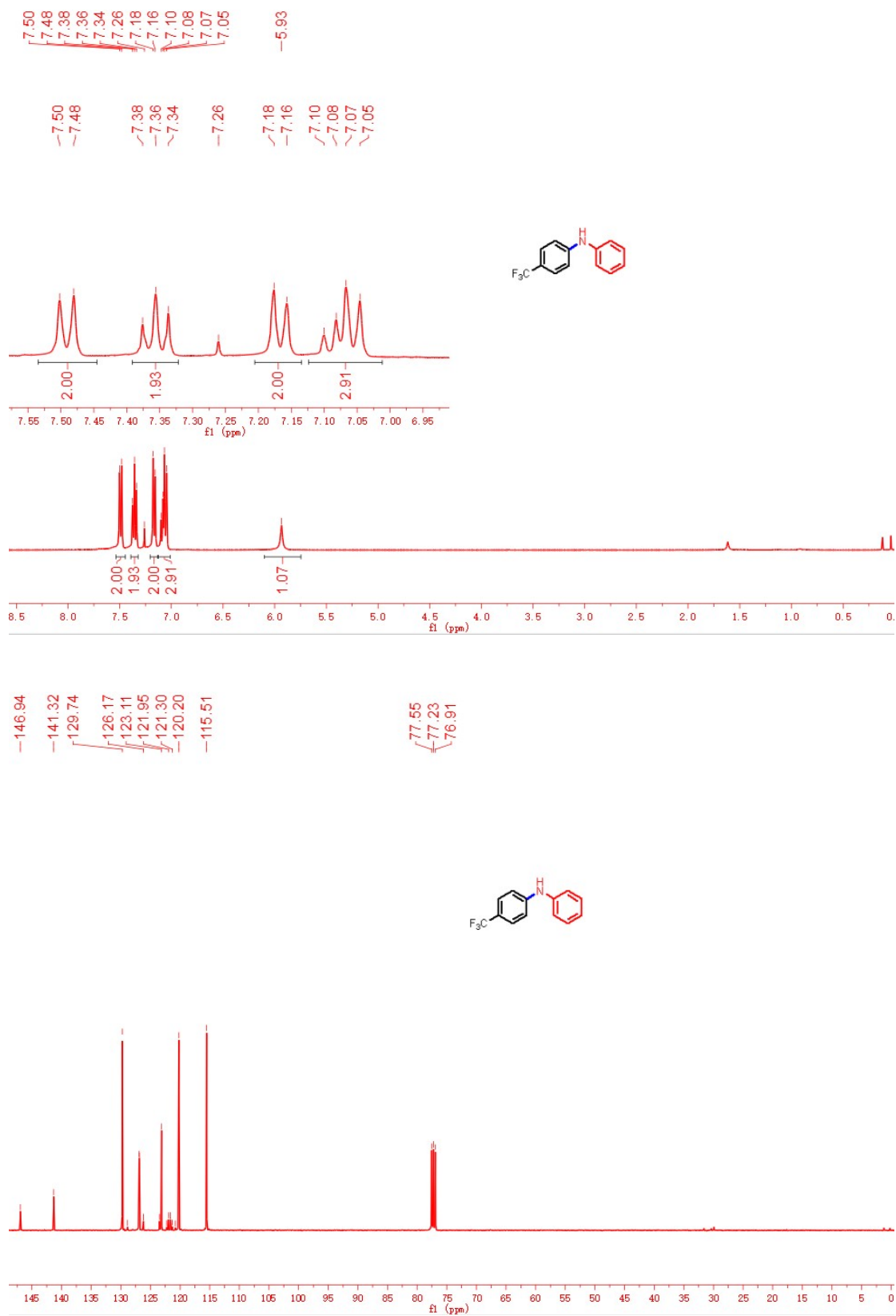
**Fig. S11.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for methyl 4-(phenylamino)benzoate (**3ea**) in  $\text{CDCl}_3$

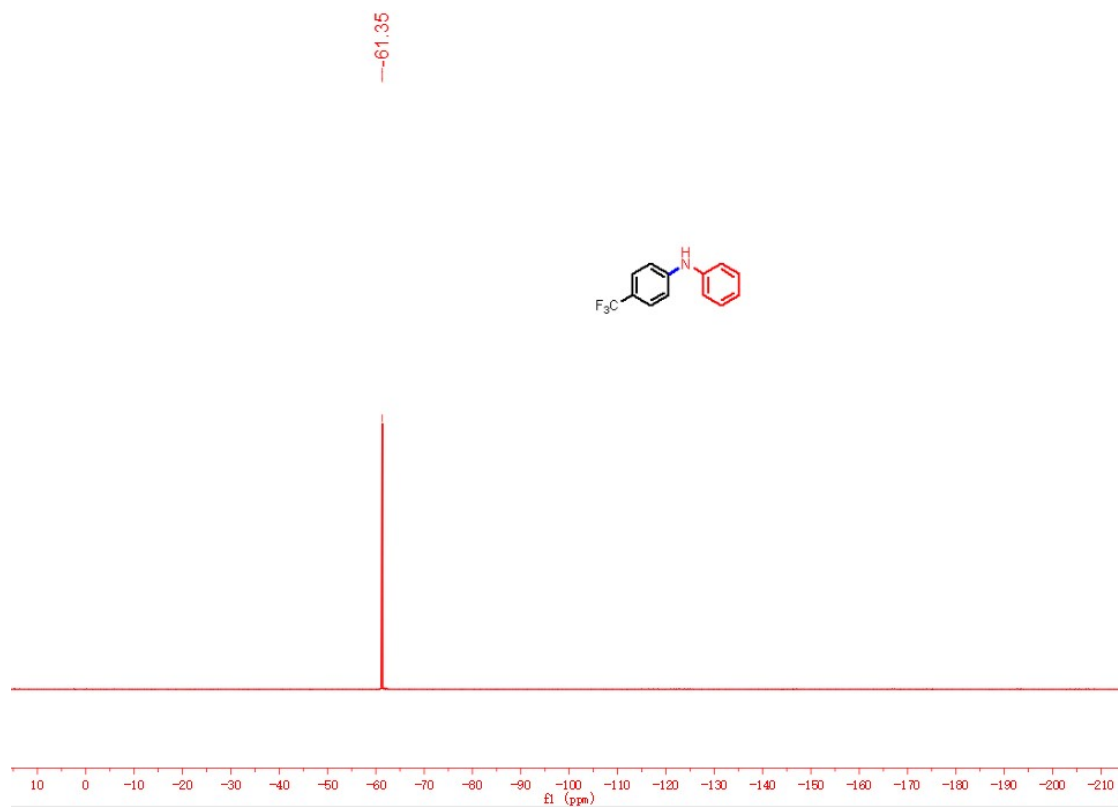


**Fig. S12.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for ethyl 4-(phenylamino)benzoate (**3fa**) in  $\text{CDCl}_3$

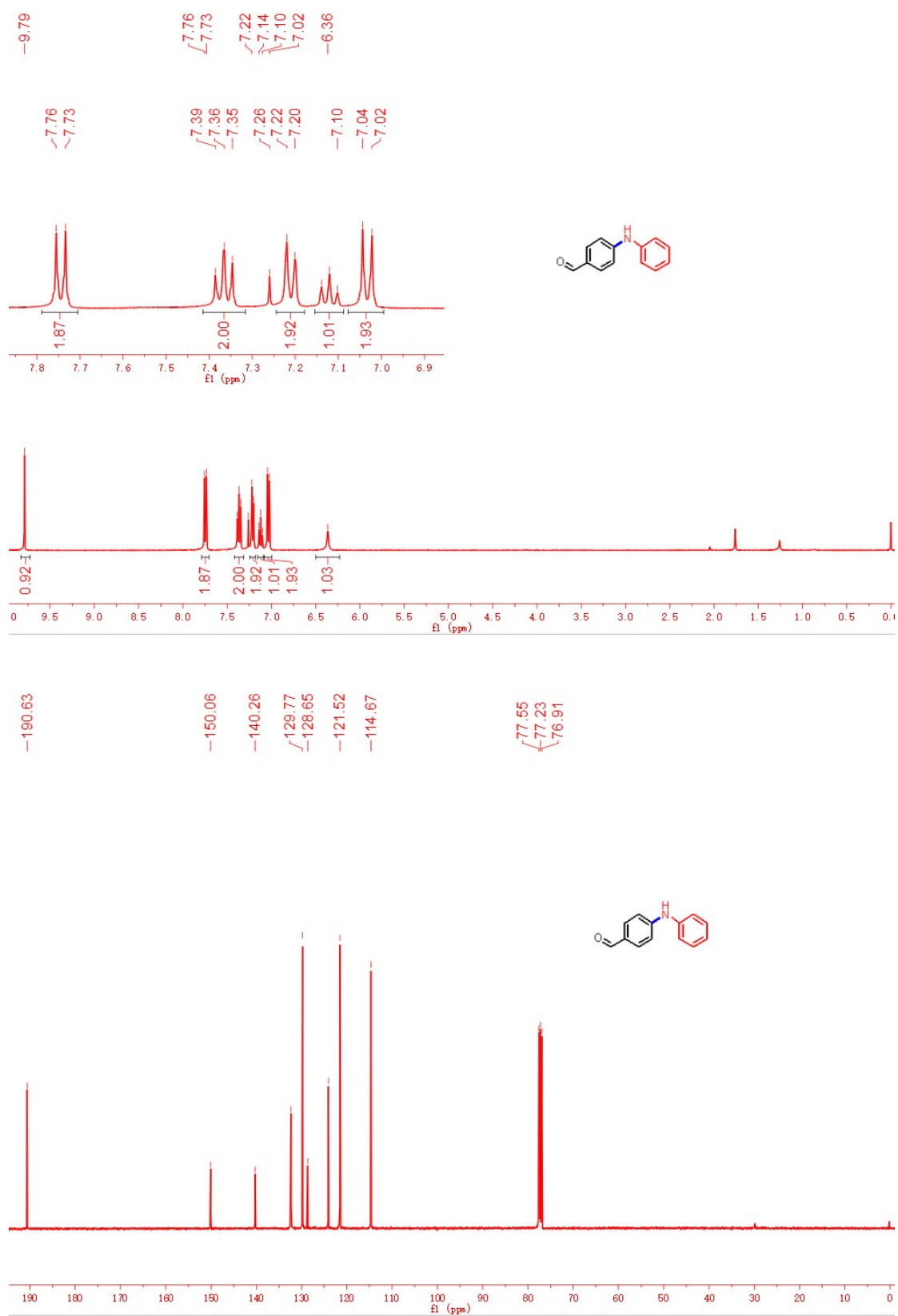


**Fig. S13.** The  $^1\text{H}$  (400 MHz),  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) and  $^{19}\text{F}$  NMR (377 MHz) NMR spectra for N-phenyl-4-(trifluoromethyl)aniline (**3ga**) in  $\text{CDCl}_3$

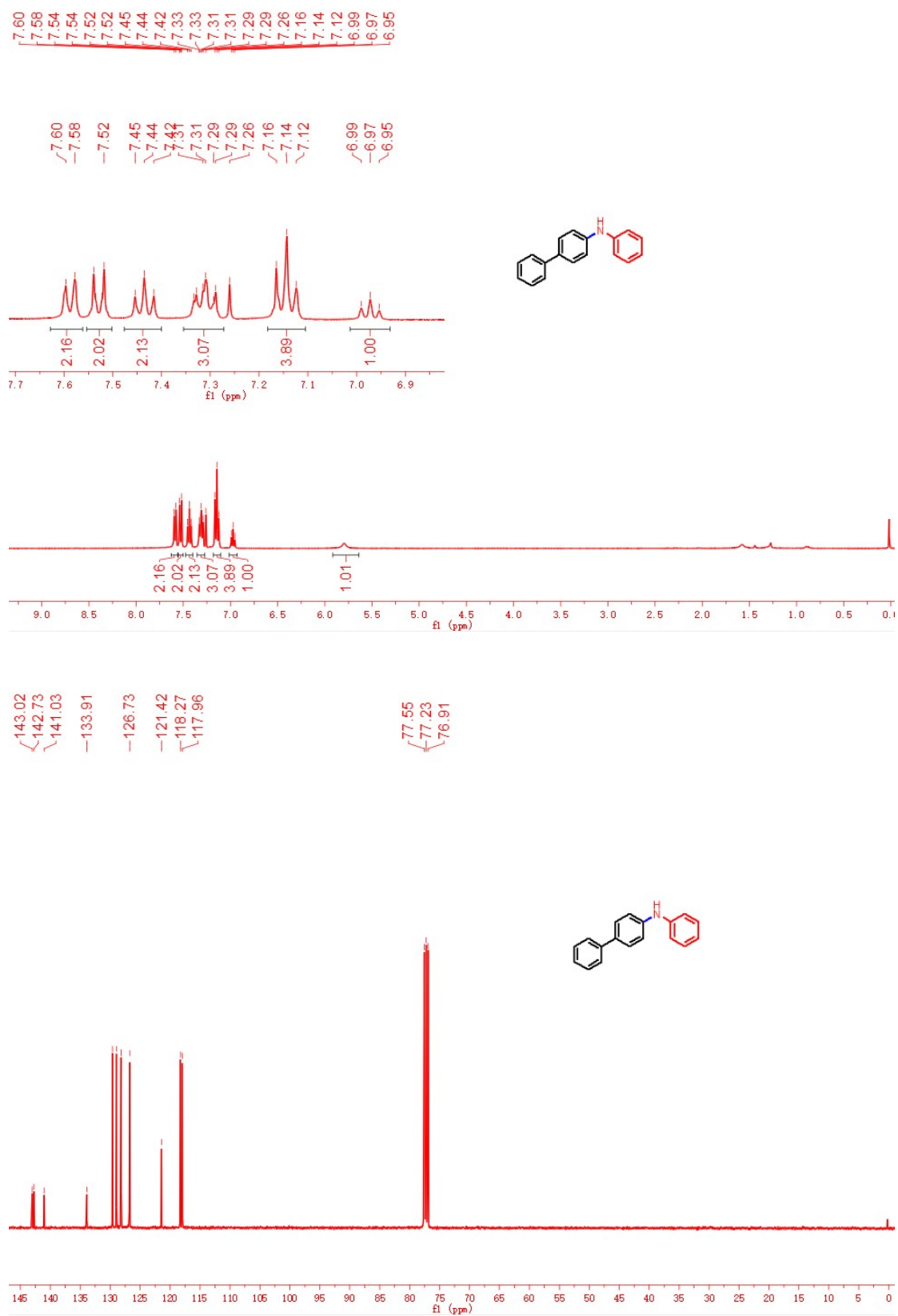




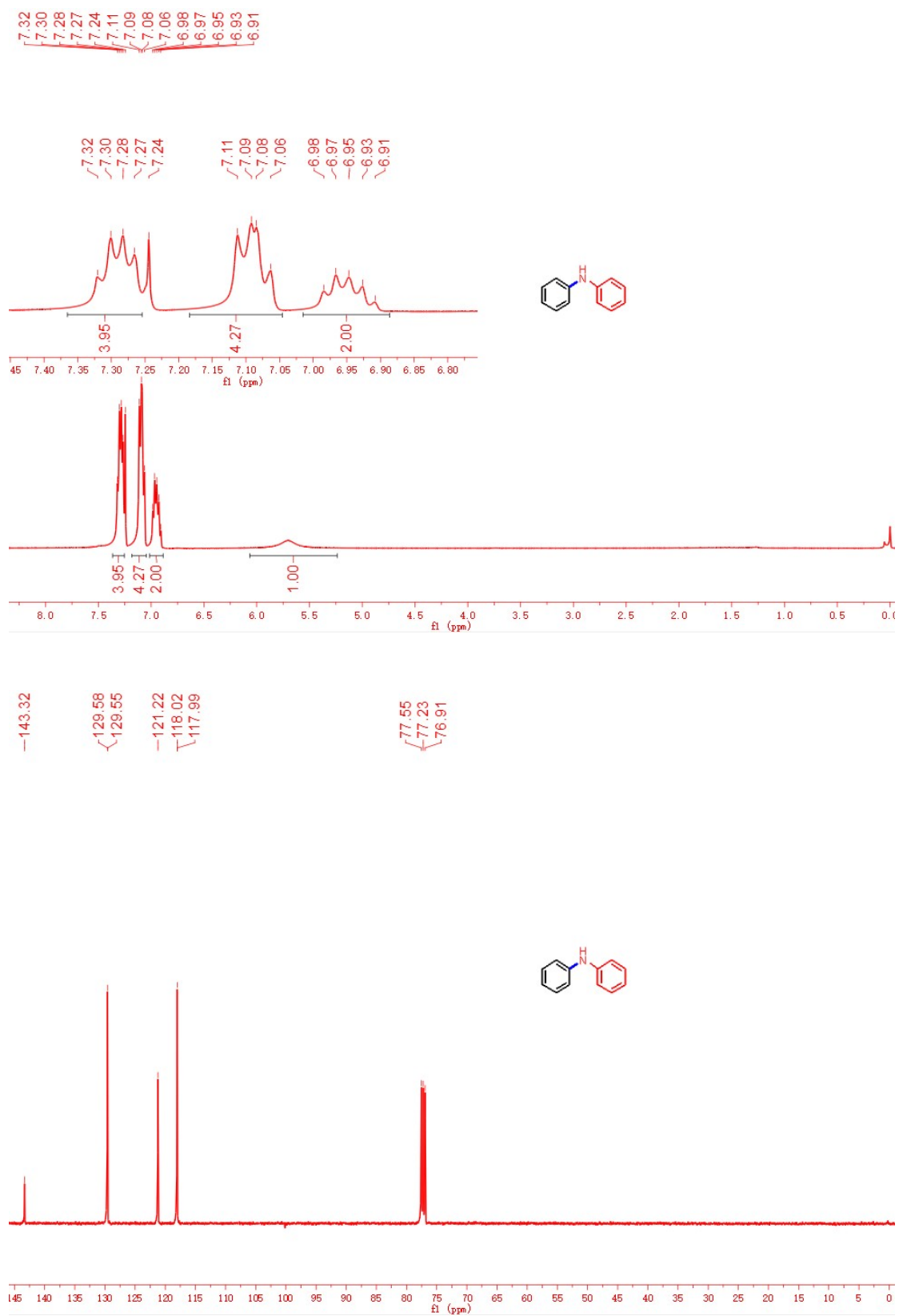
**Fig. S14.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 4-(phenylamino)benzaldehyde (**3ha**) in  $\text{CDCl}_3$



**Fig. S15.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for N-phenyl-[1,1'-biphenyl]-4-amine (**3ia**) in  $\text{CDCl}_3$

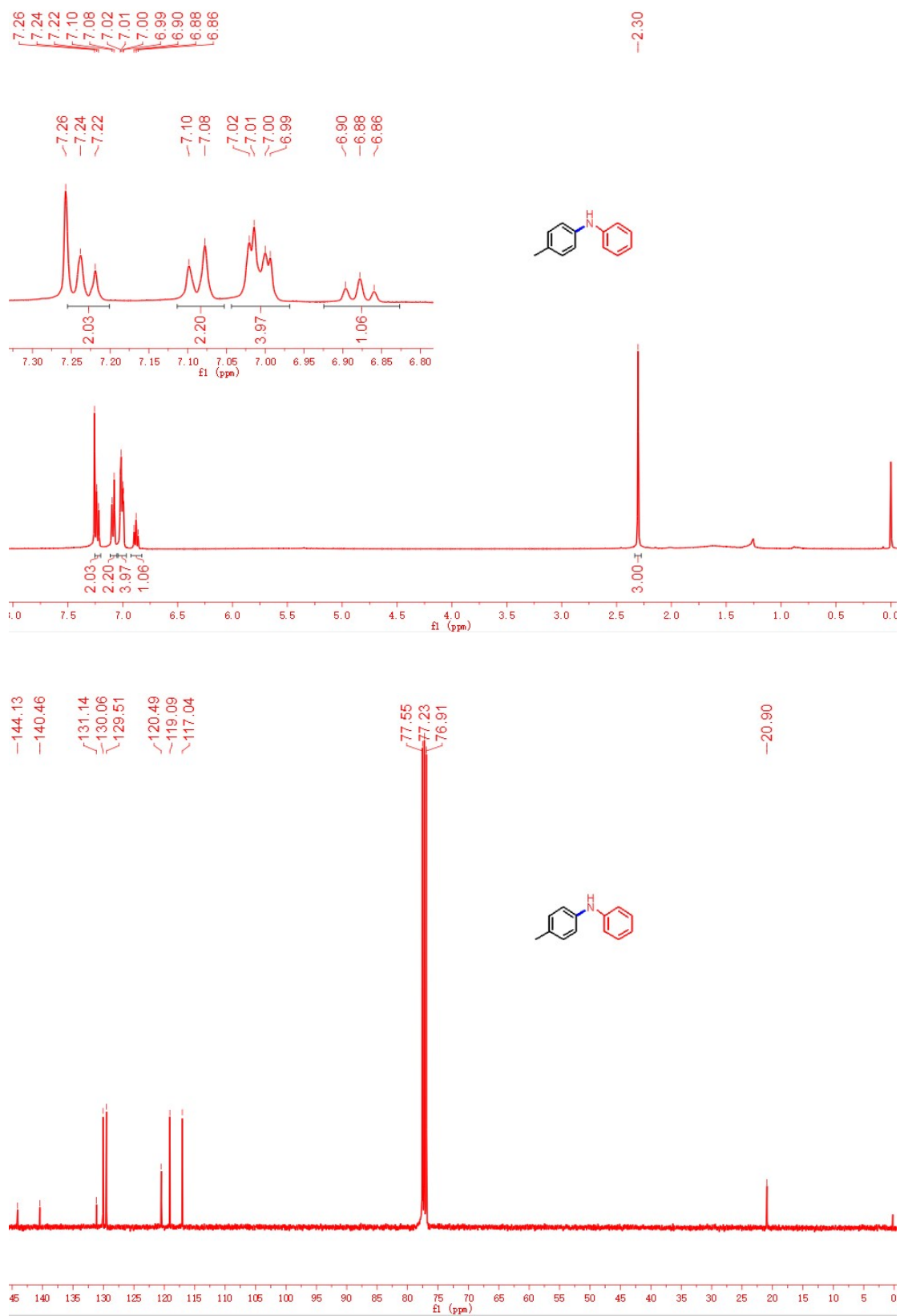


**Fig. S16.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for diphenylamine (**3ja**) in  $\text{CDCl}_3$

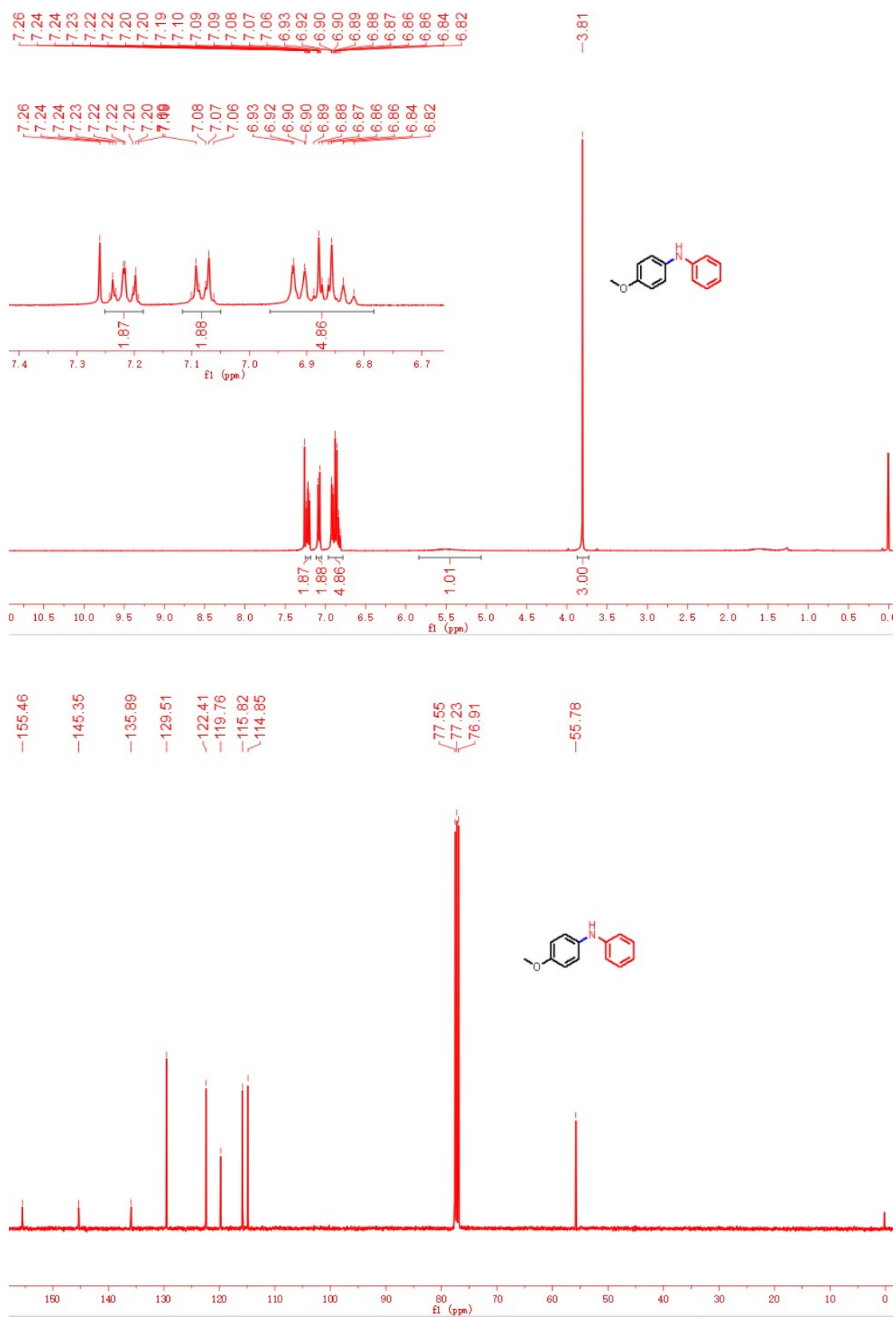




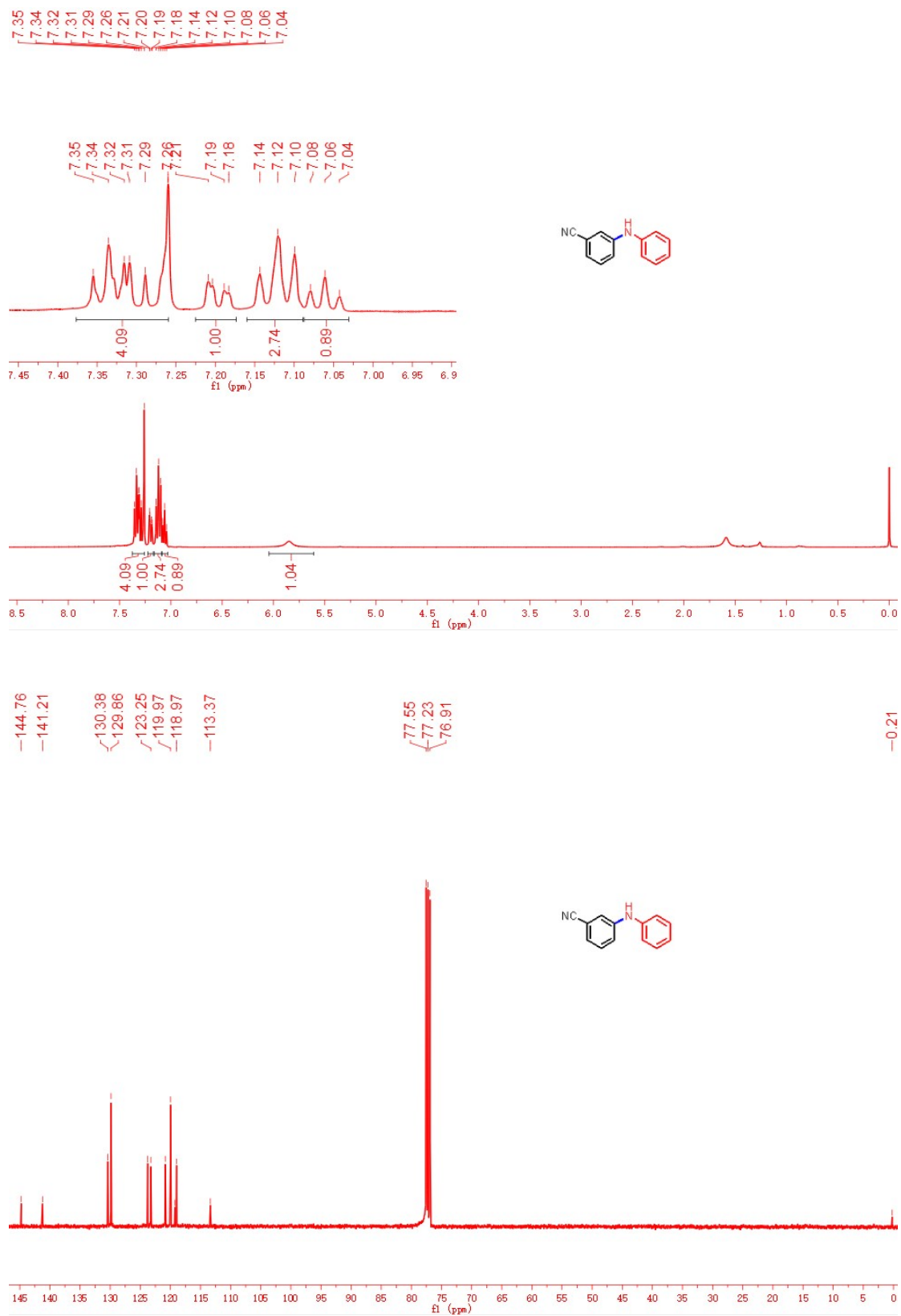
**Fig. S17.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 4-methyl-N-phenylaniline (**3ka**) in  $\text{CDCl}_3$



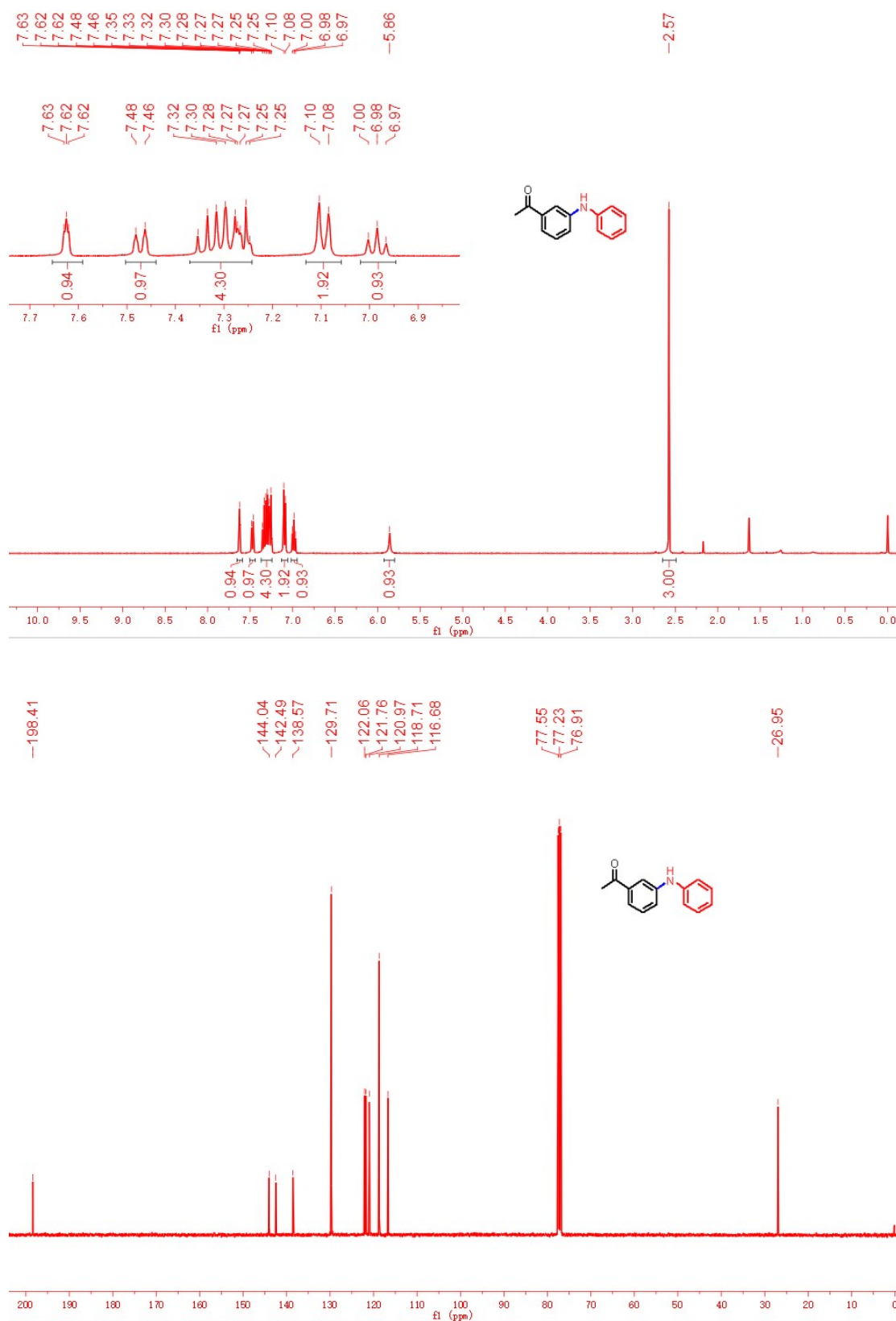
**Fig. S18.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 4-methoxy-N-phenylaniline (**31a**) in  $\text{CDCl}_3$



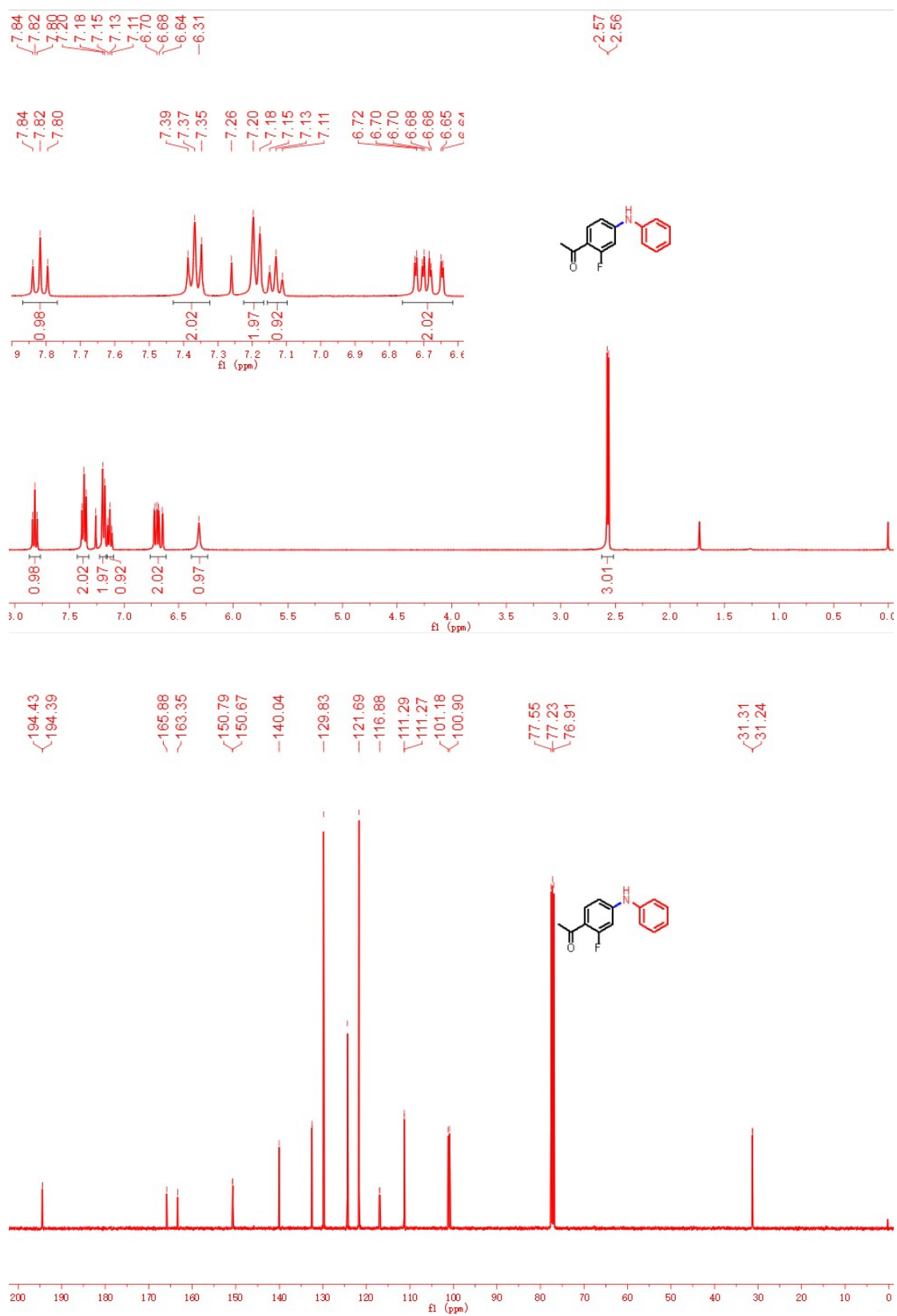
**Fig. S19.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 3-(phenylamino)benzonitrile (**3ma**) in  $\text{CDCl}_3$

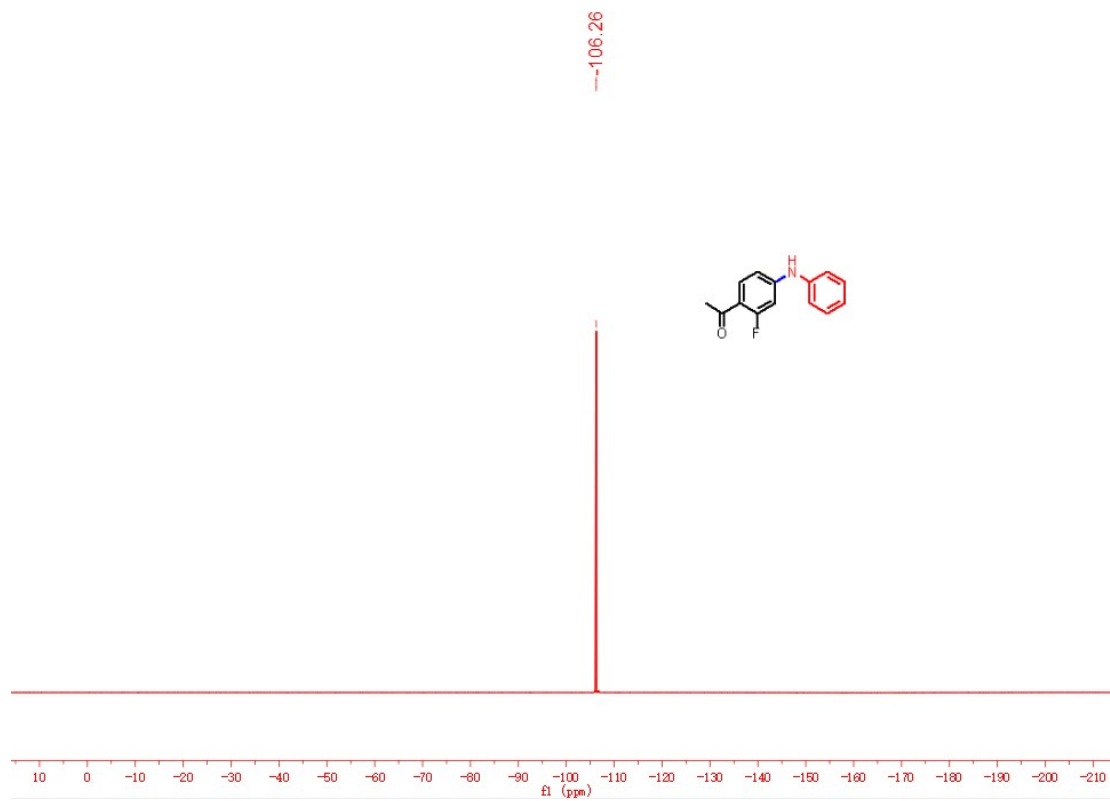


**Fig. S20.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 1-(3-(phenylamino)phenyl)ethan-1-one (**3na**) in  $\text{CDCl}_3$

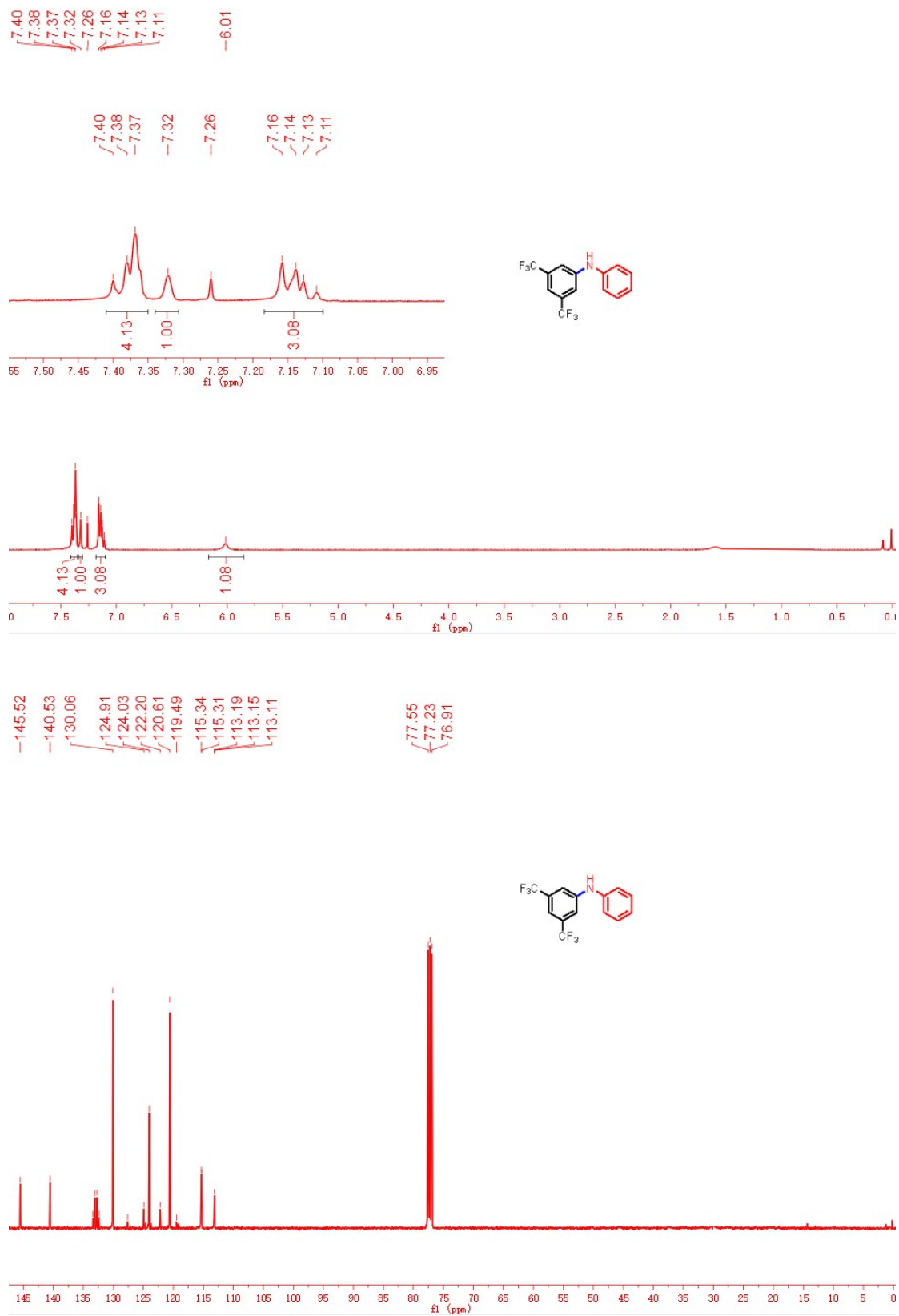


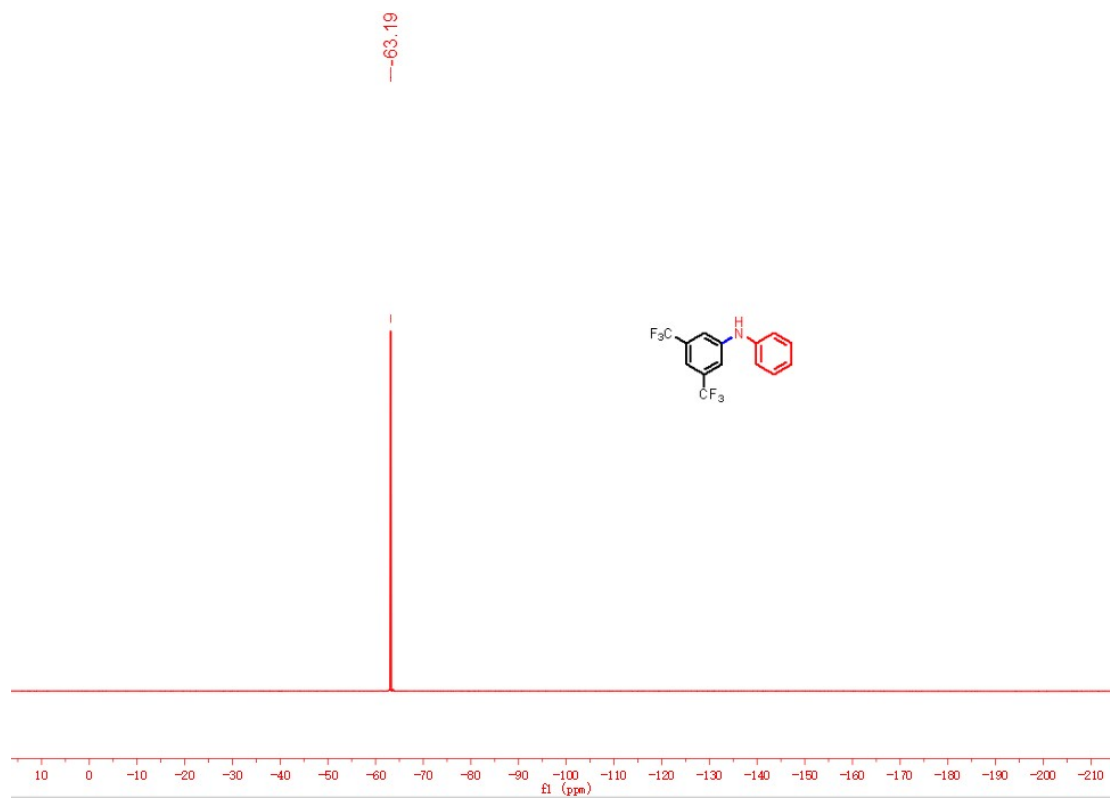
**Fig. S21.** The  $^1\text{H}$  (400 MHz),  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) and  $^{19}\text{F}$  NMR (377 MHz) NMR spectra for 1-(2-fluoro-4-(phenylamino)phenyl)ethan-1-one (**30a**) in  $\text{CDCl}_3$





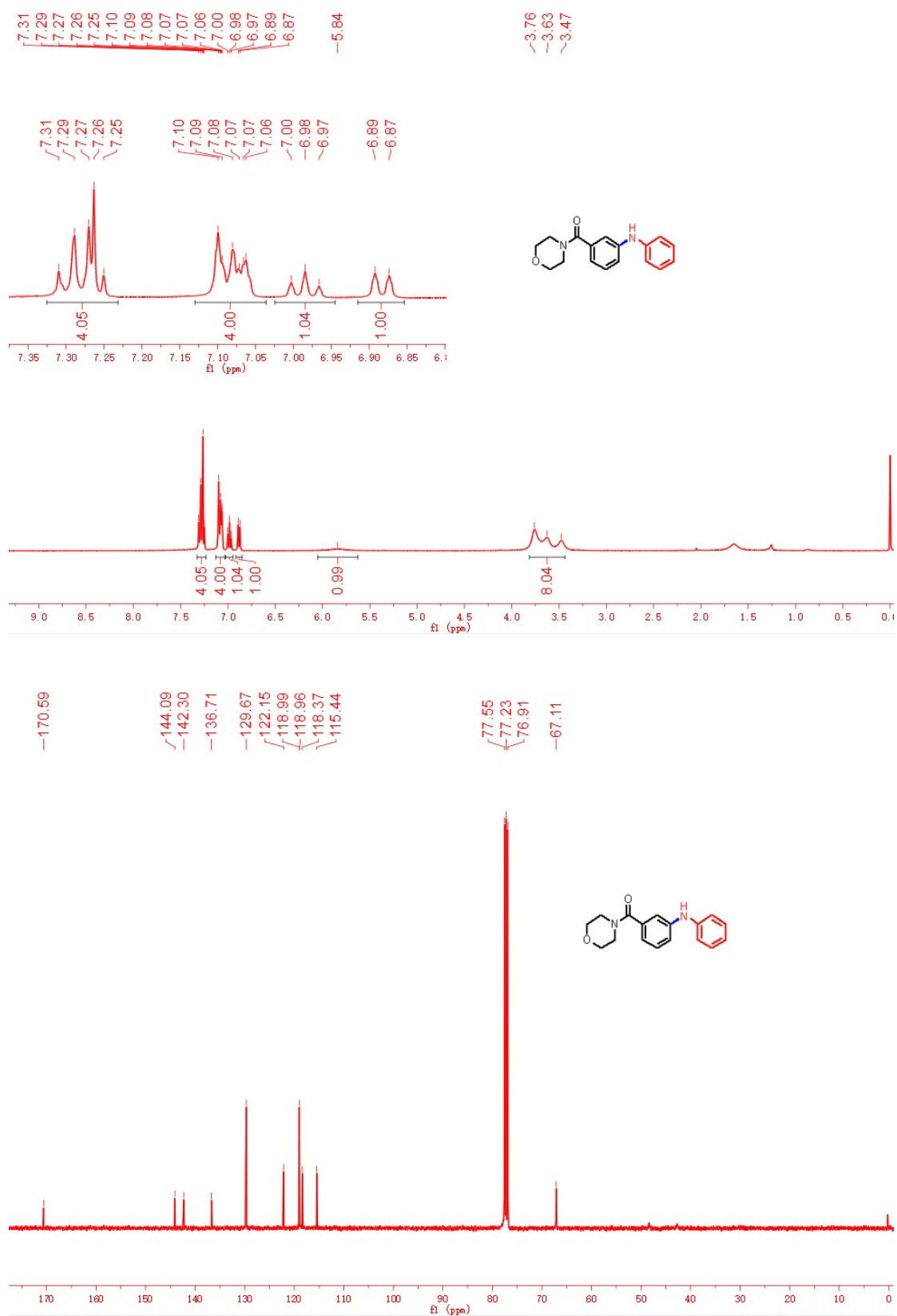
**Fig. S22.** The  $^1\text{H}$  (400 MHz),  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) and  $^{19}\text{F}$  NMR (377 MHz) NMR spectra for N-phenyl-3,5-bis(trifluoromethyl)aniline (**3pa**) in  $\text{CDCl}_3$



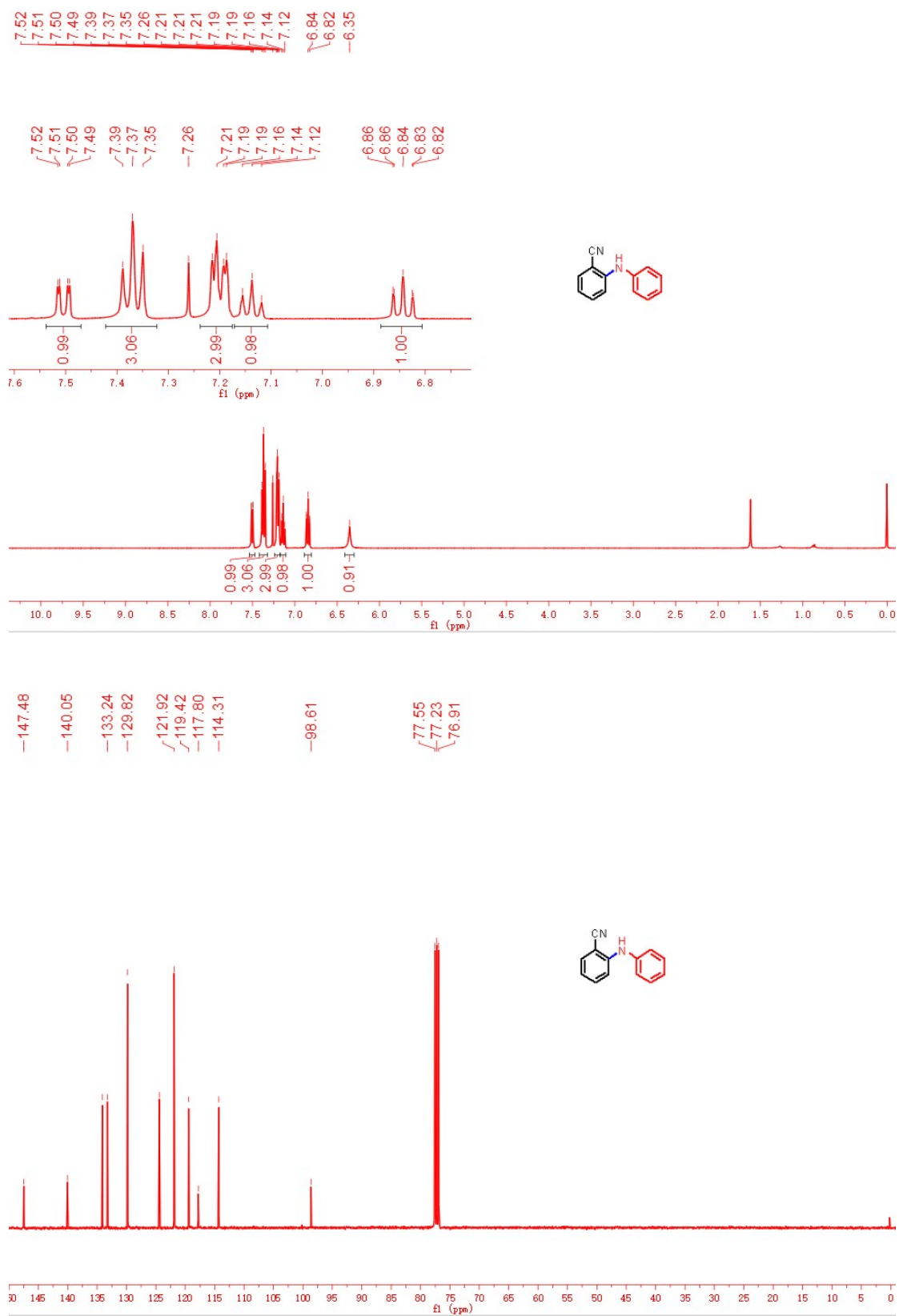




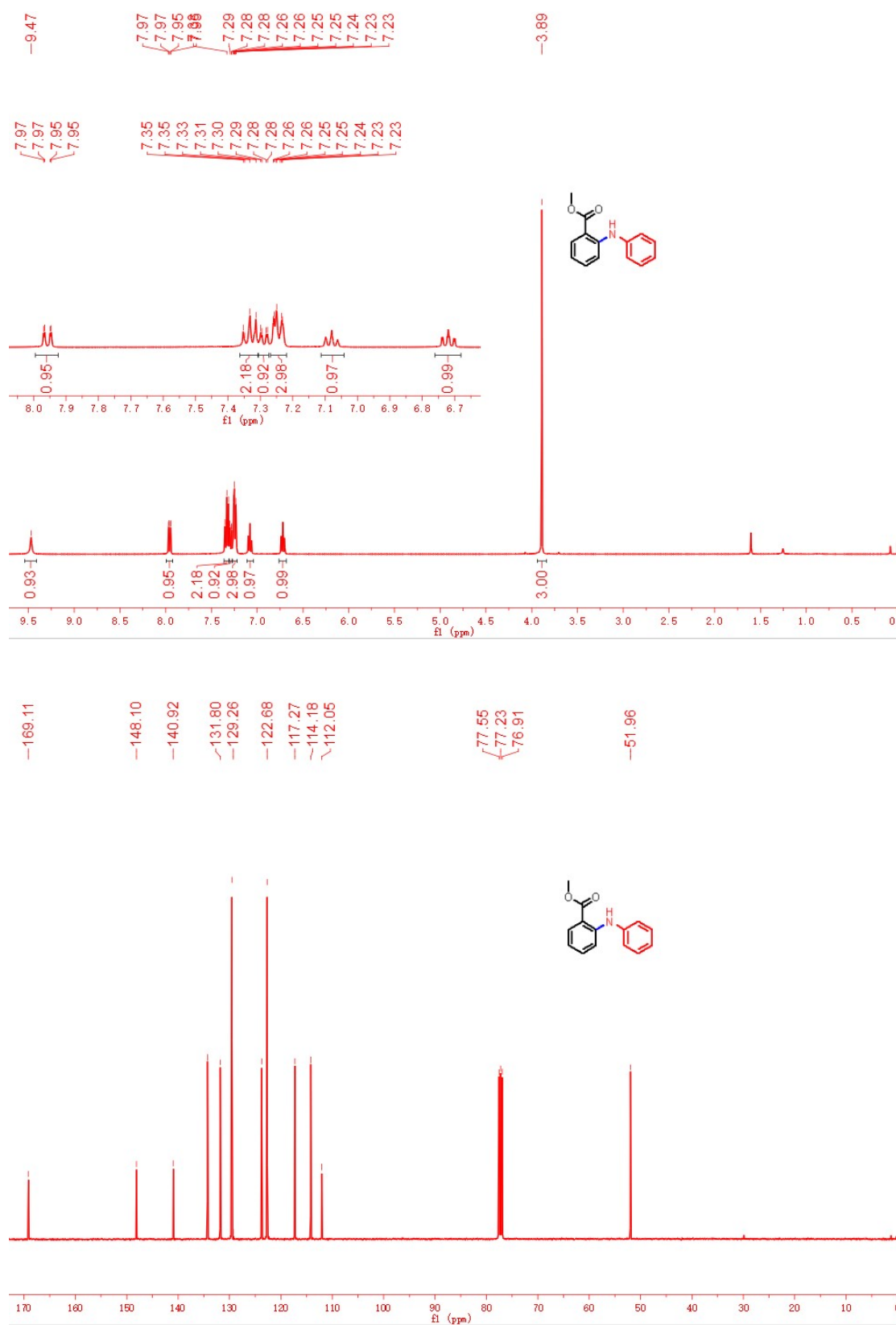
**Fig. S23.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for morpholino(3-(phenylamino)phenyl)methanone (**3qa**) in  $\text{CDCl}_3$



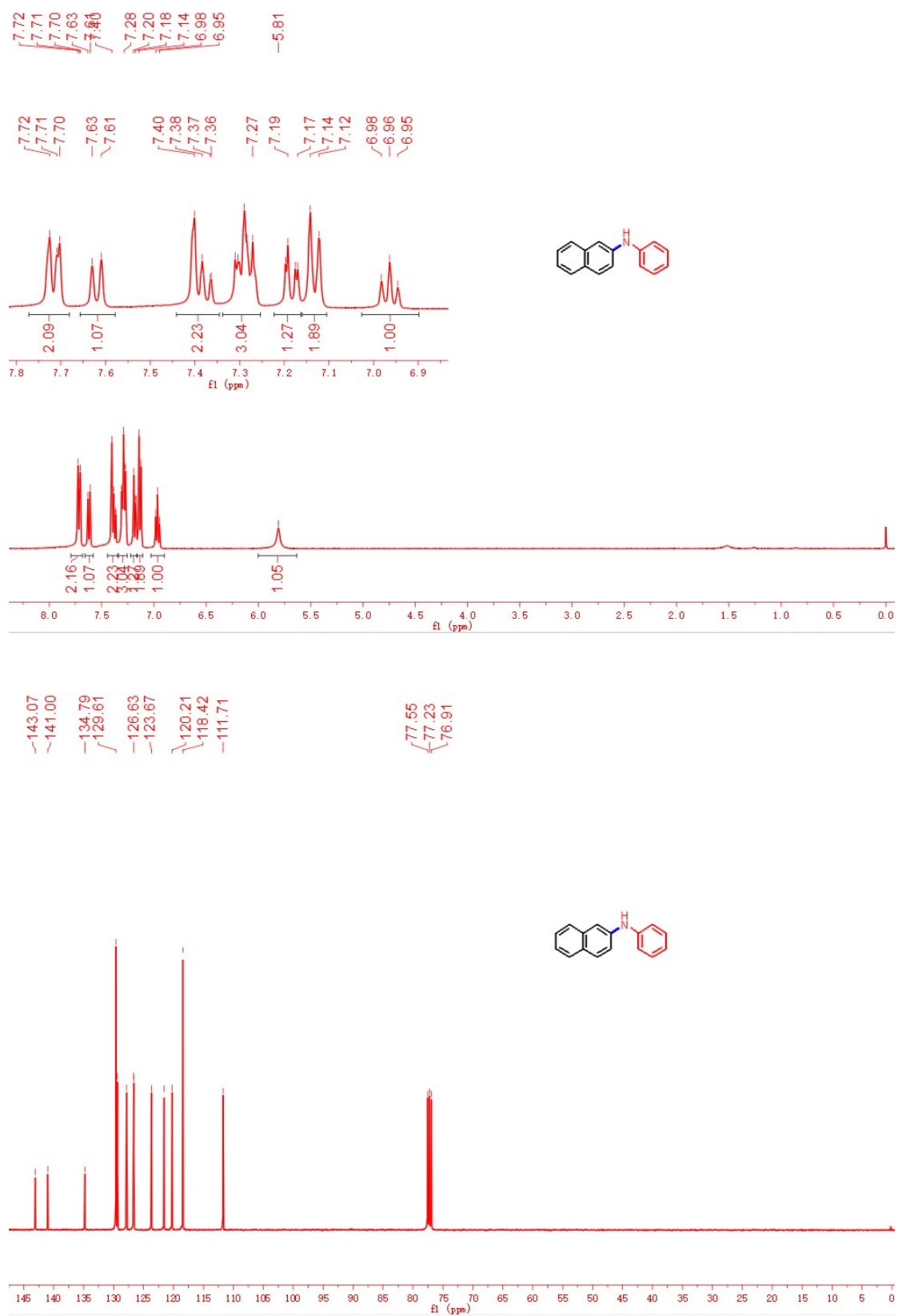
**Fig. S24.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 2-(phenylamino)benzonitrile (**3ra**) in  $\text{CDCl}_3$



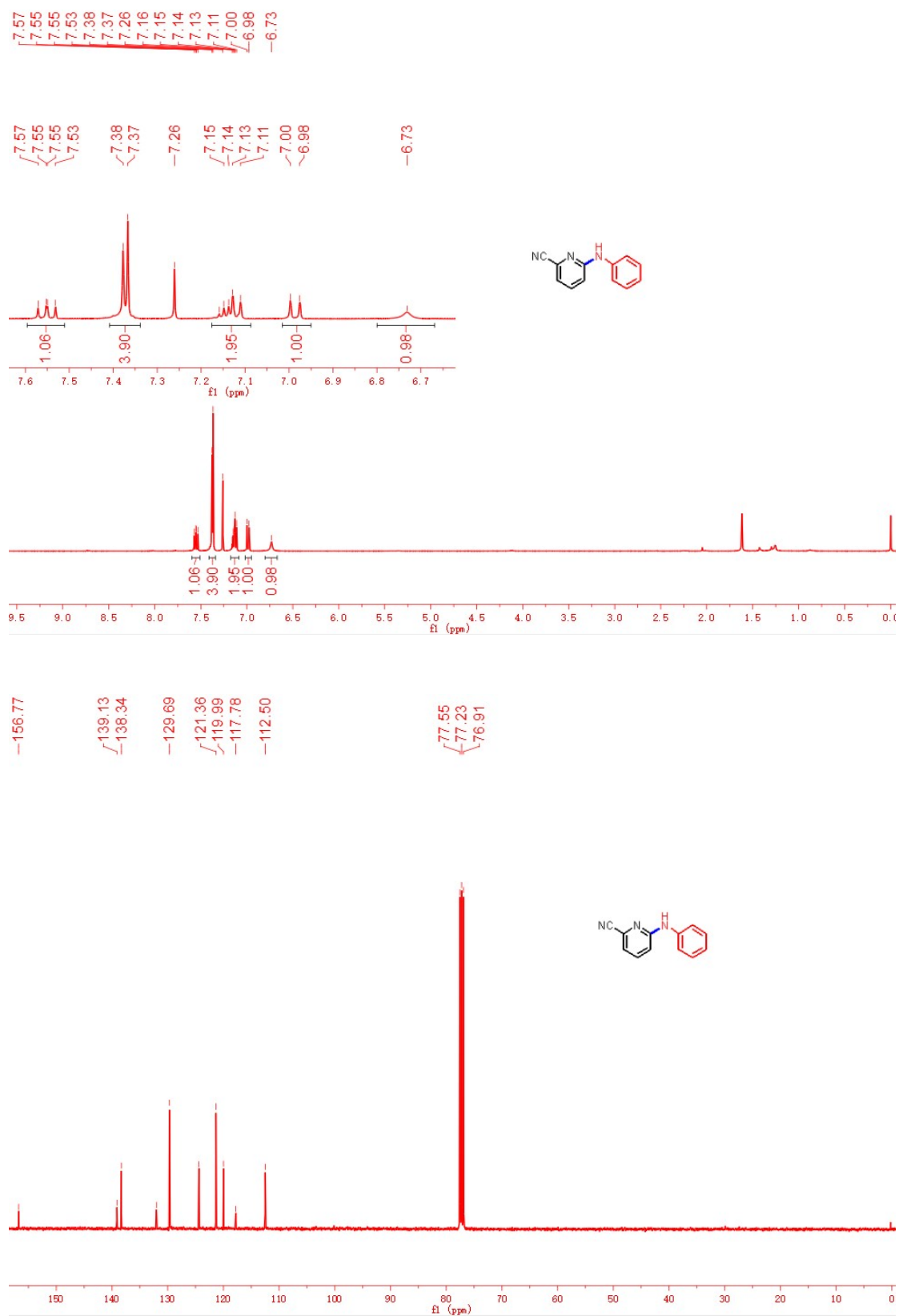
**Fig. S25.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for methyl 2-(phenylamino)benzoate (**3sa**) in  $\text{CDCl}_3$



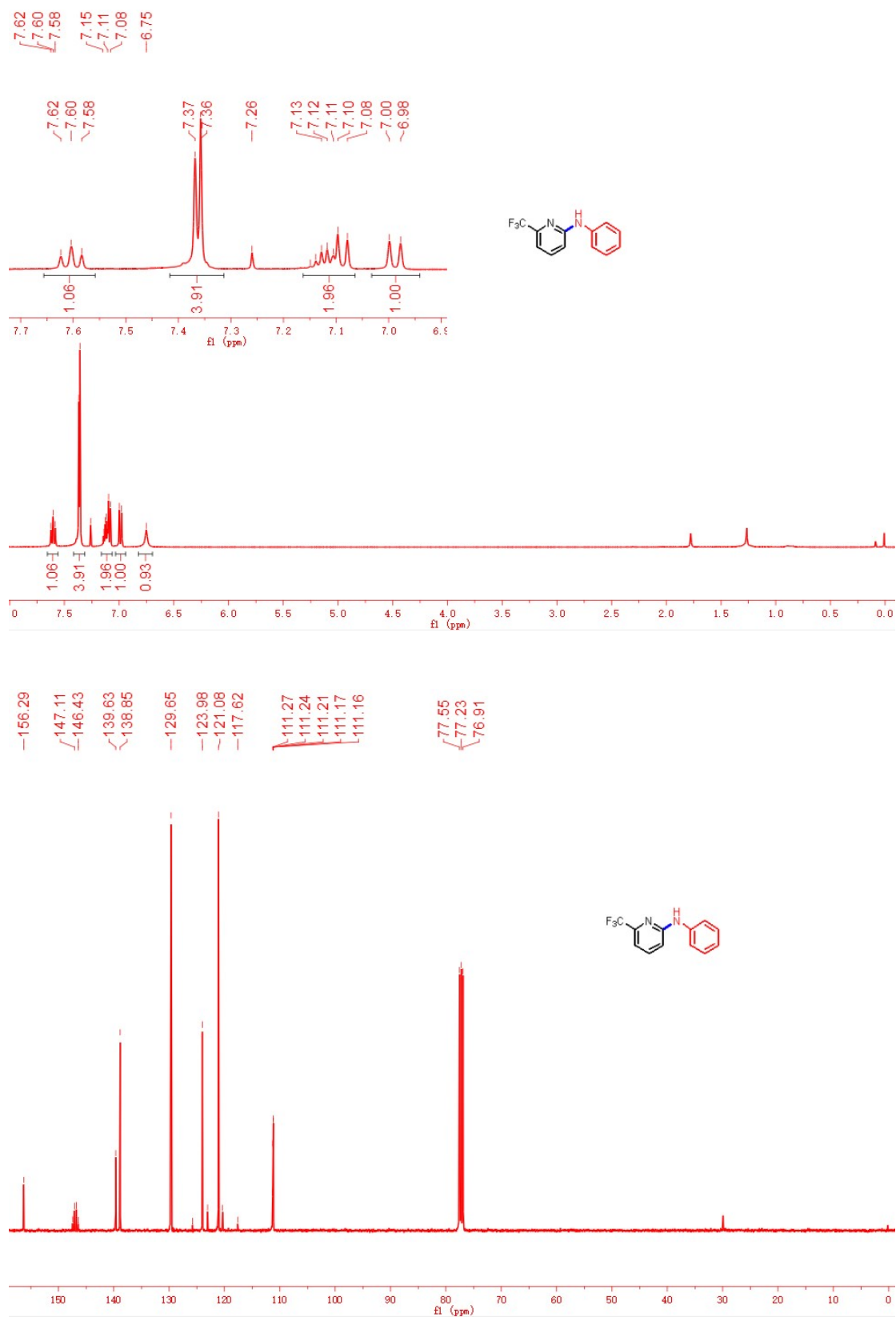
**Fig. S26.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for N-phenylnaphthalen-2-amine (**3ta**) in  $\text{CDCl}_3$

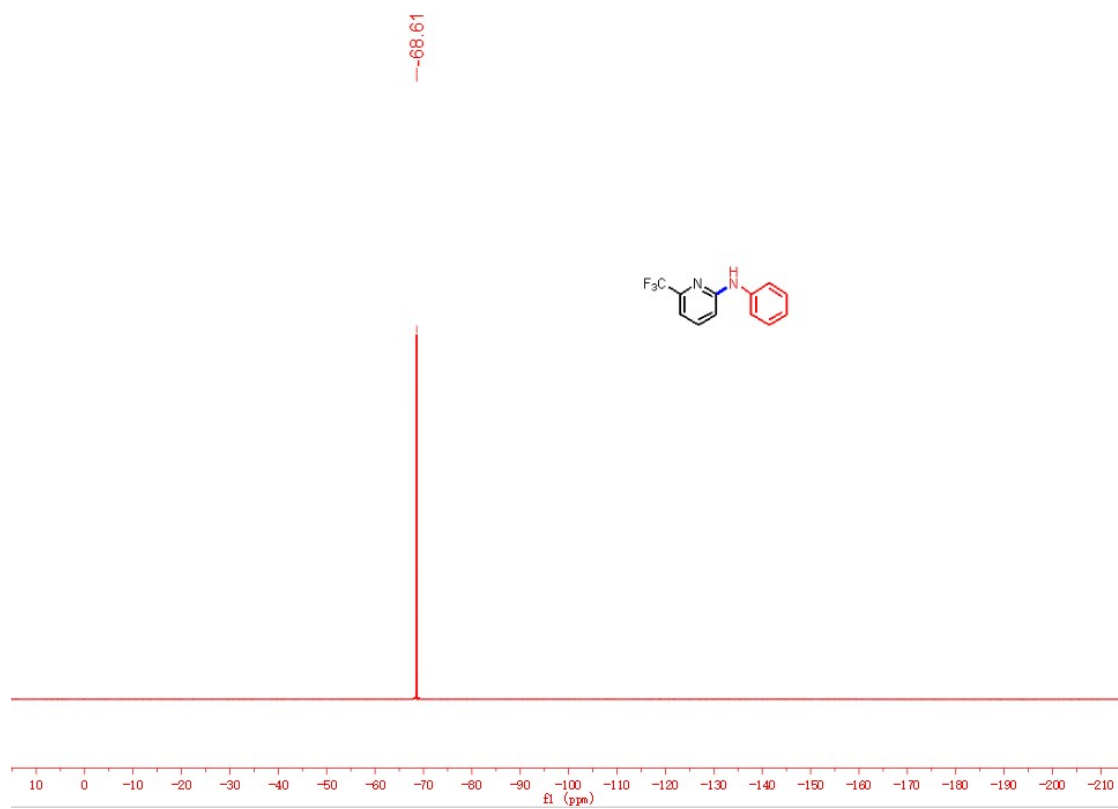


**Fig. S27.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 6-(phenylamino)picolinonitrile (**3ua**) in  $\text{CDCl}_3$

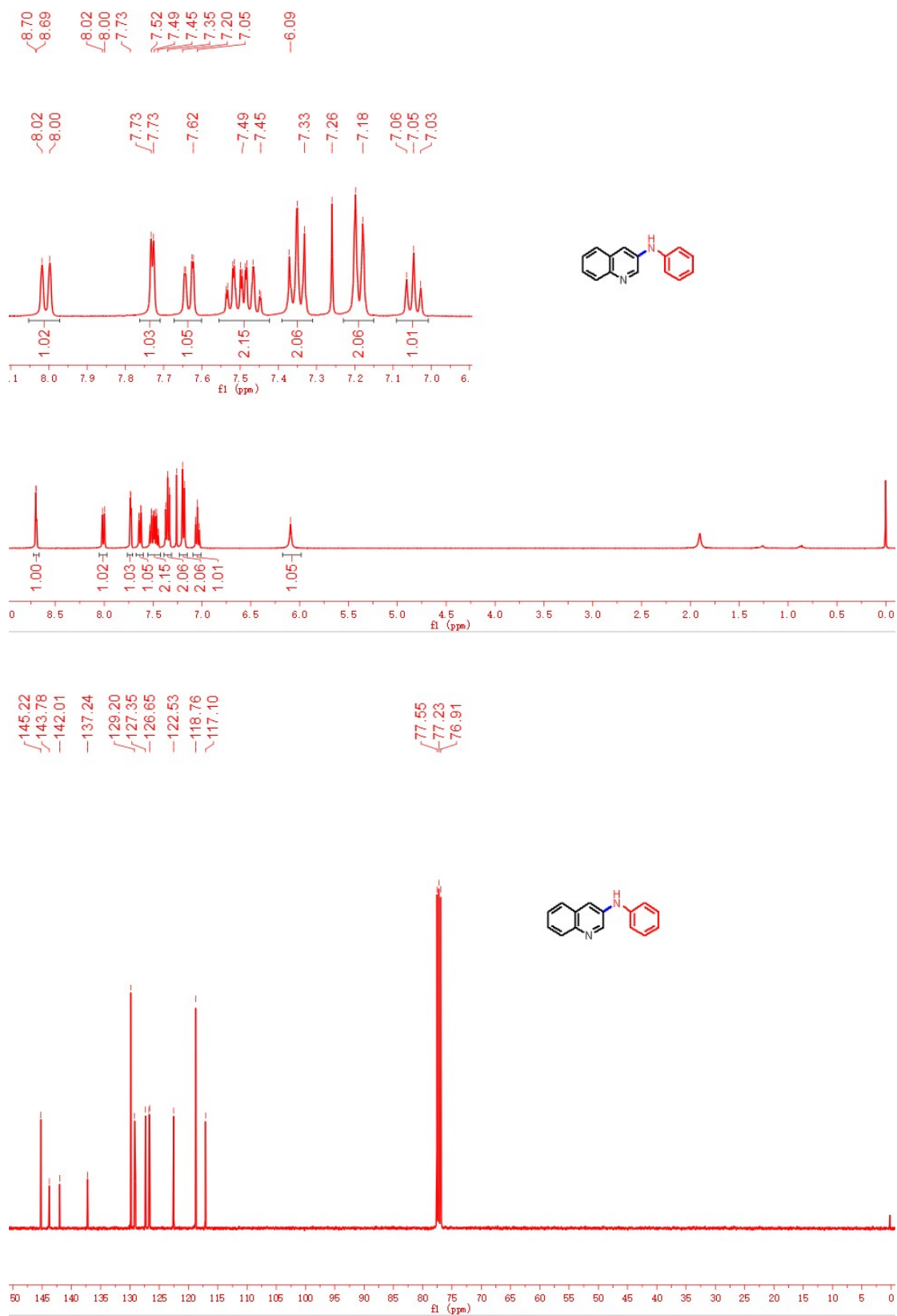


**Fig. S28.** The  $^1\text{H}$  (400 MHz),  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) and  $^{19}\text{F}$  NMR (377 MHz) NMR spectra for N-phenyl-6-(trifluoromethyl)pyridin-2-amine (**3va**) in  $\text{CDCl}_3$



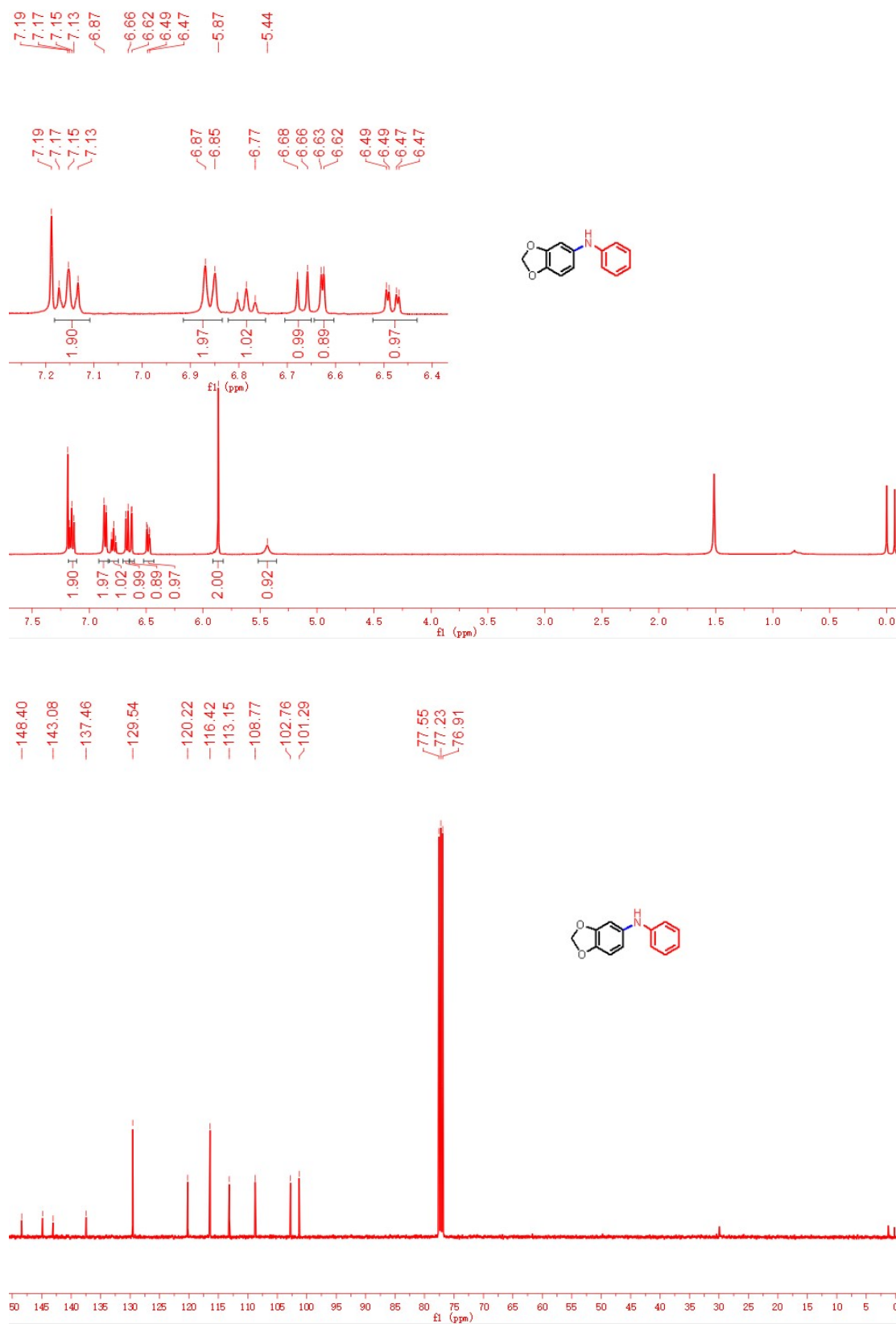


**Fig. S29.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for N-phenylquinolin-3-amine (**3wa**) in  $\text{CDCl}_3$

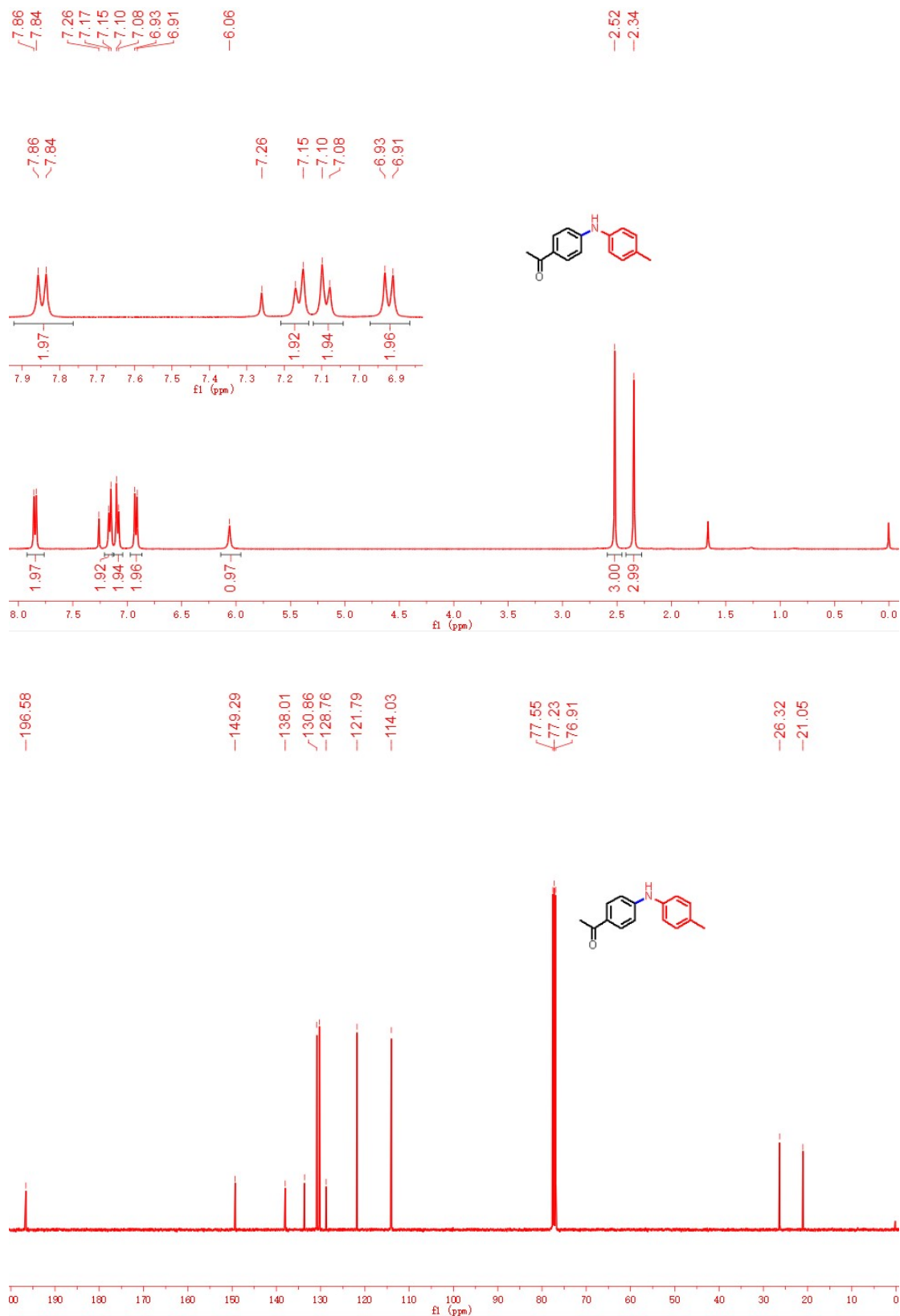




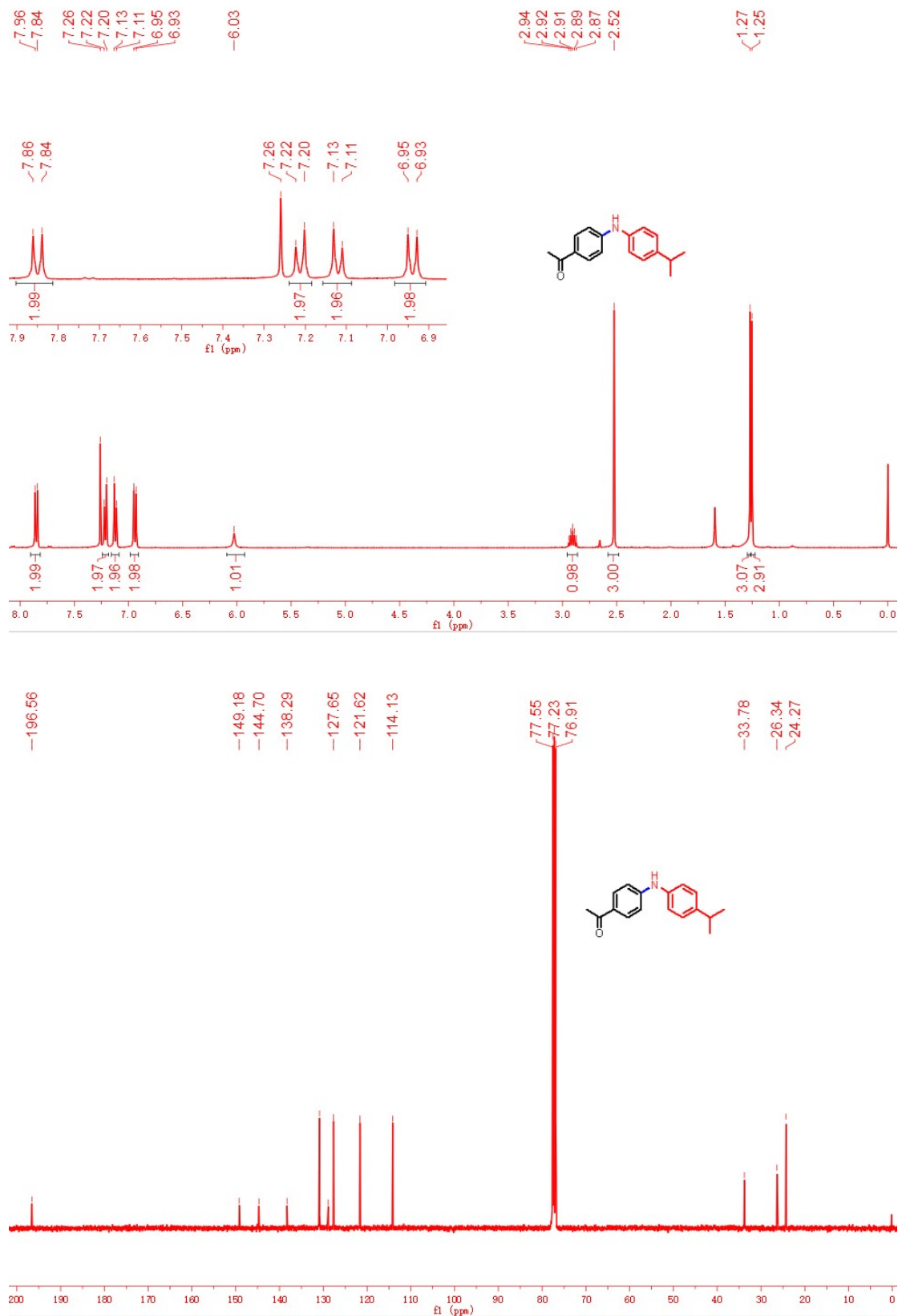
**Fig. S30.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for N-phenylbenzo[d][1,3]dioxol-5-amine (**3xa**) in  $\text{CDCl}_3$



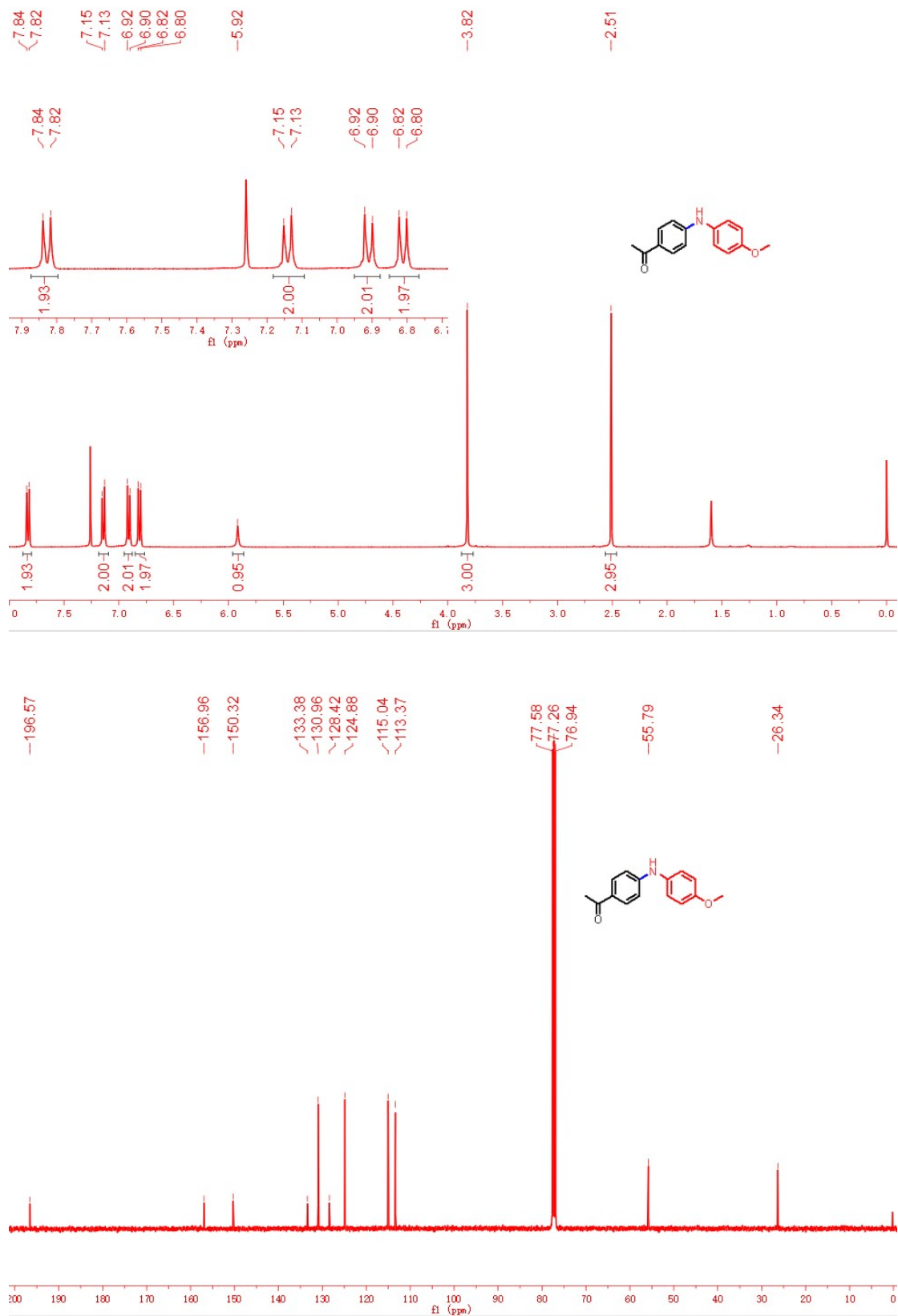
**Fig. S31.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 1-(4-(*p*-tolylamino)phenyl)ethan-1-one (**3ab**) in  $\text{CDCl}_3$



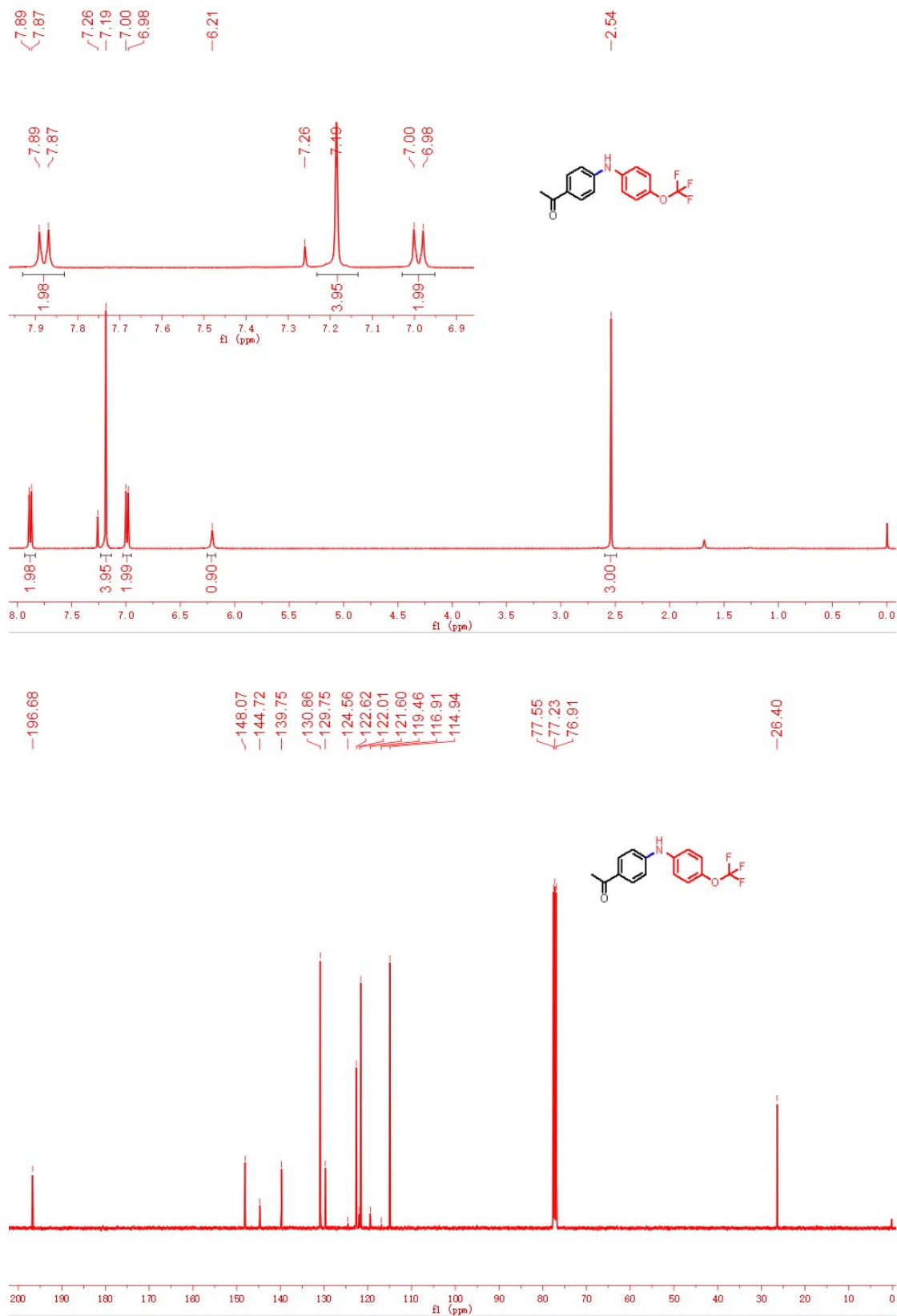
**Fig. S32.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 1-(4-((4-isopropylphenyl)amino)phenyl)ethan-1-one (**3ac**) in  $\text{CDCl}_3$

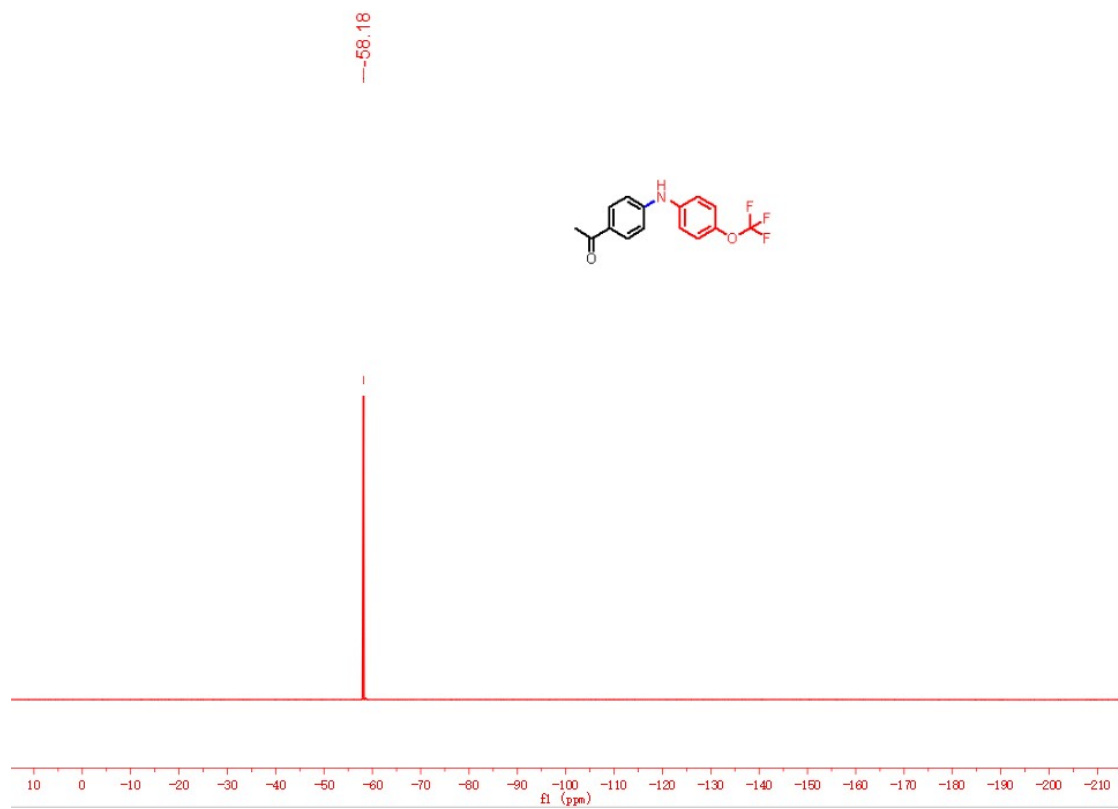


**Fig. S33.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 1-(4-((4-methoxyphenyl)amino)phenyl)ethan-1-one (**3ad**) in  $\text{CDCl}_3$

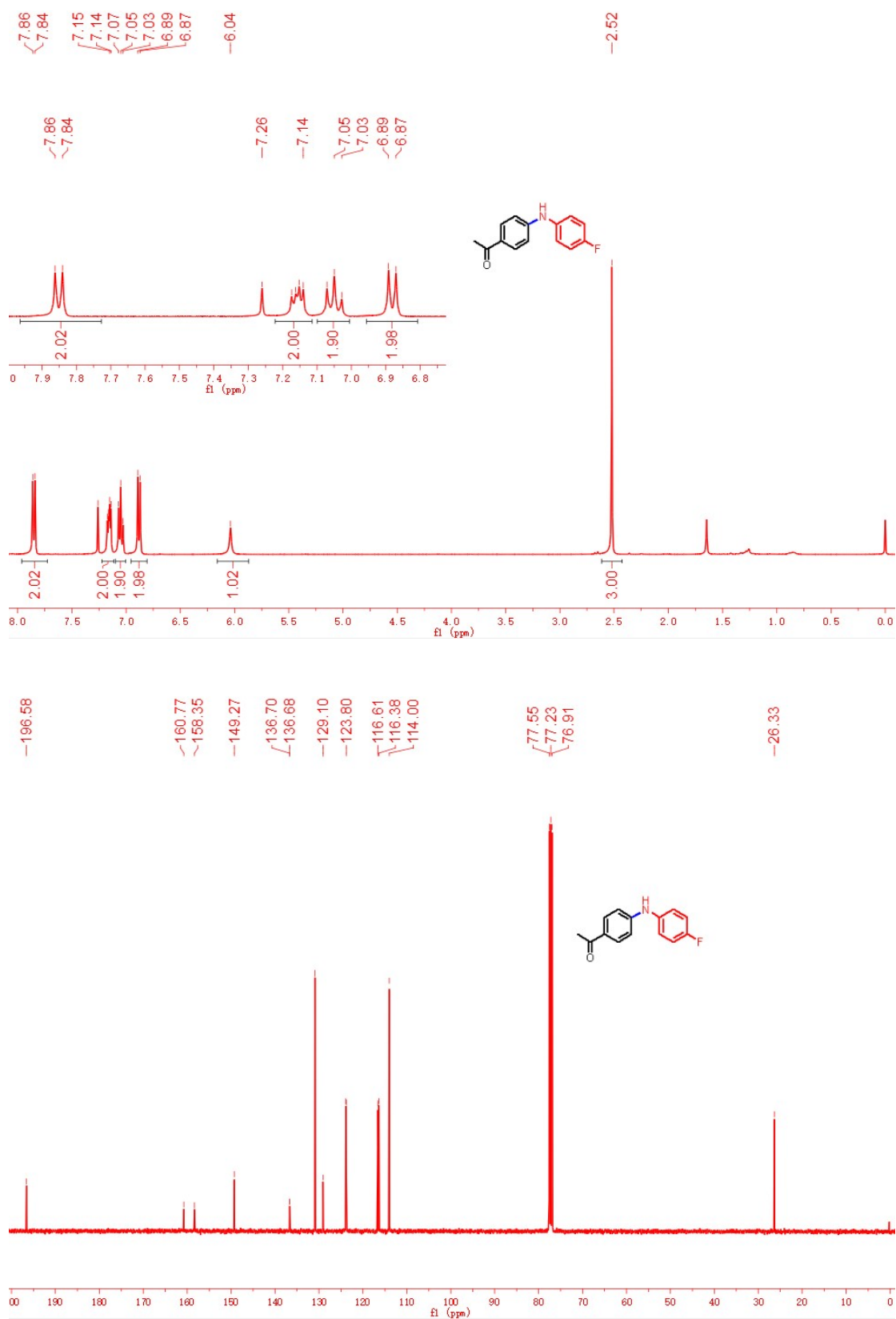


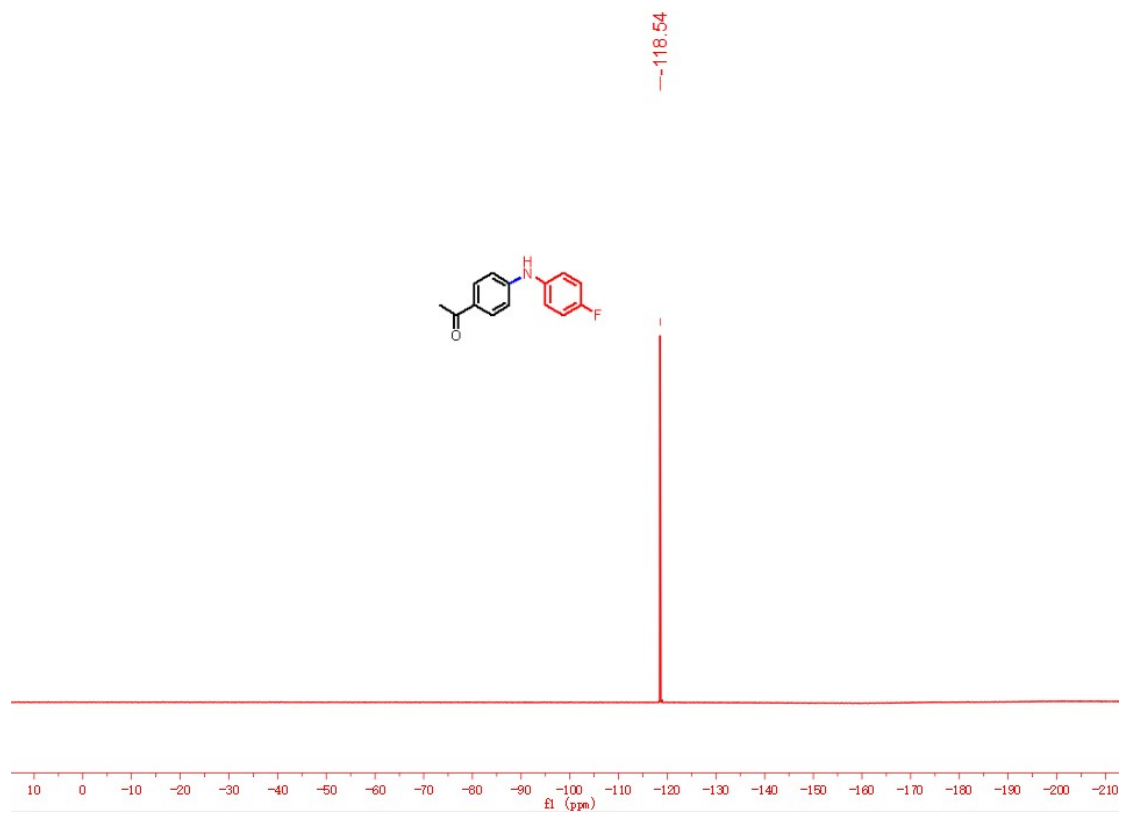
**Fig. S34.** The  $^1\text{H}$  (400 MHz),  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) and  $^{19}\text{F}$  NMR (377 MHz) NMR spectra for 1-(4-((4-(trifluoromethoxy)phenyl)amino)phenyl)ethan-1-one (**3ae**) in  $\text{CDCl}_3$





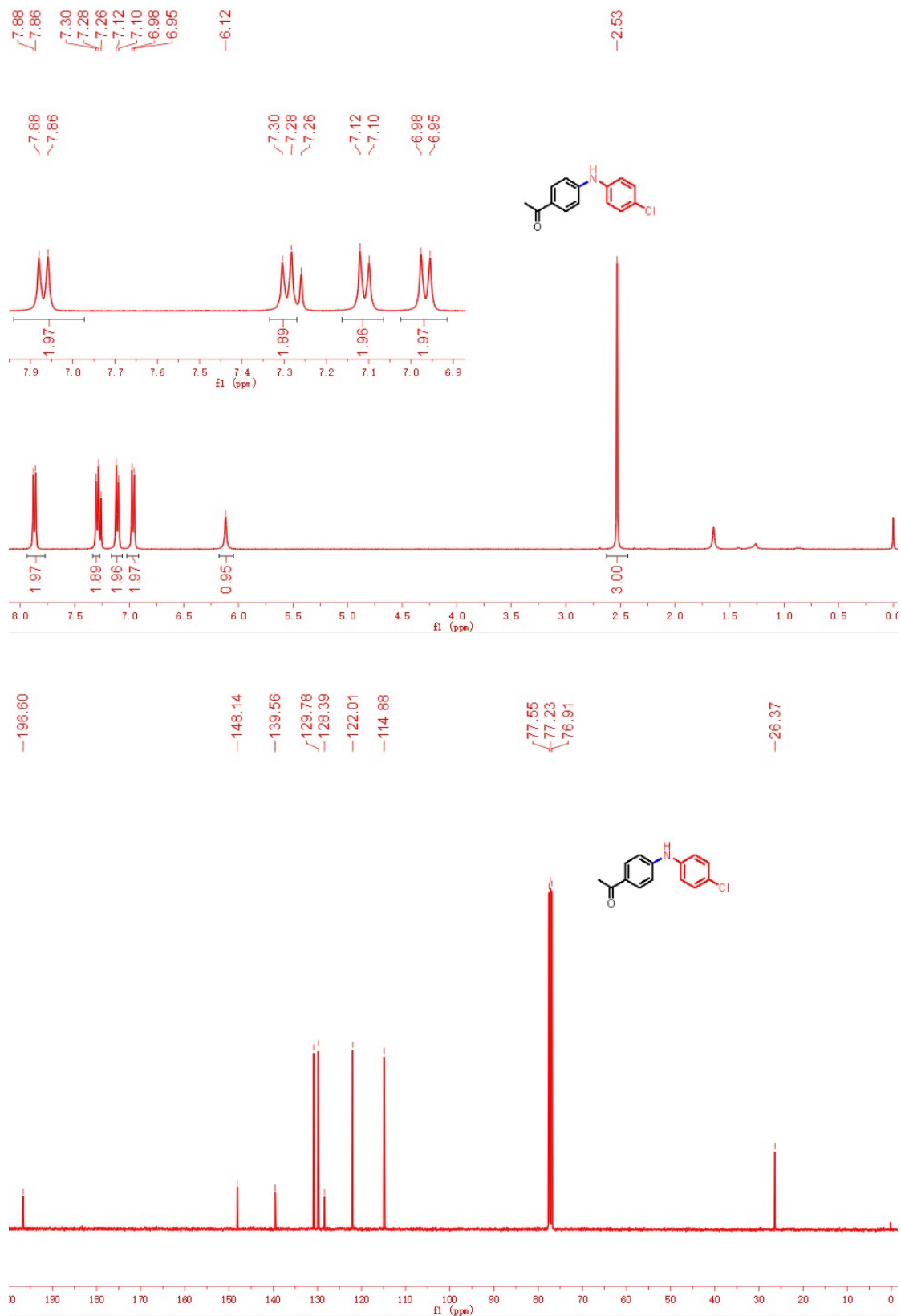
**Fig. S35.** The  $^1\text{H}$  (400 MHz),  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) and  $^{19}\text{F}$  NMR (377 MHz) NMR spectra for 1-(4-((4-fluorophenyl)amino)phenyl)ethan-1-one (**3af**) in  $\text{CDCl}_3$



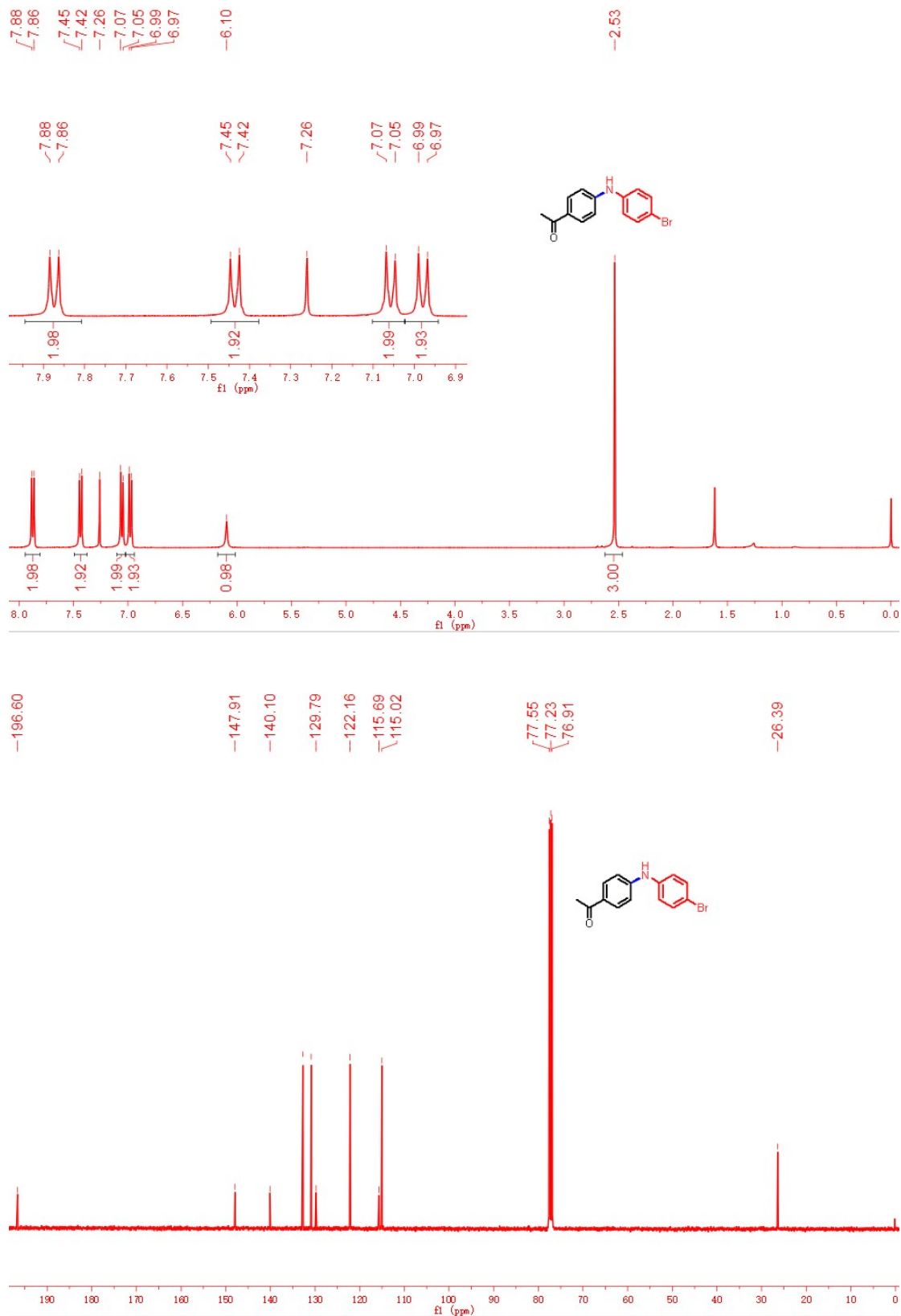




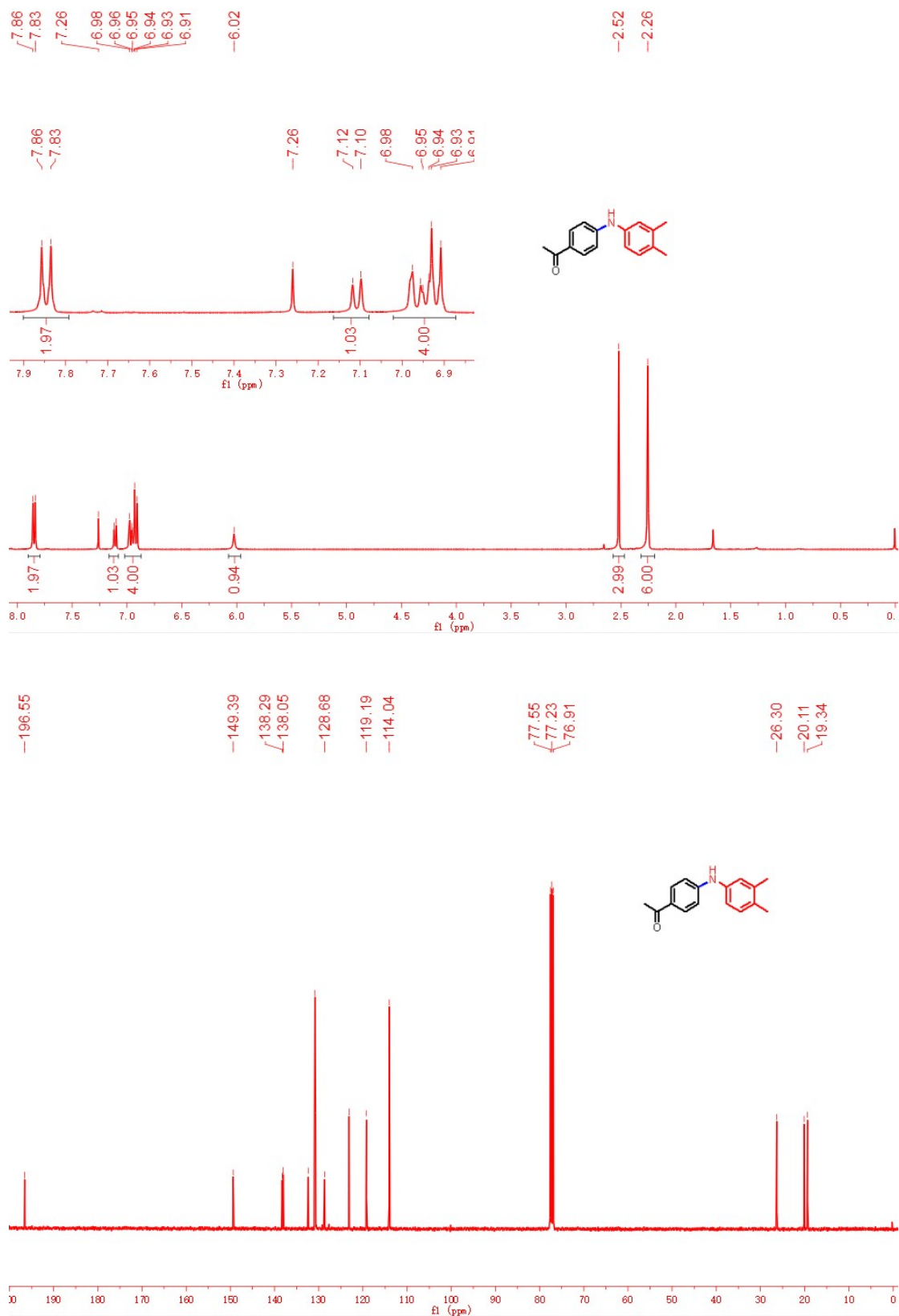
**Fig. S36.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 1-(4-((4-chlorophenyl)amino)phenyl)ethan-1-one (**3ag**) in  $\text{CDCl}_3$



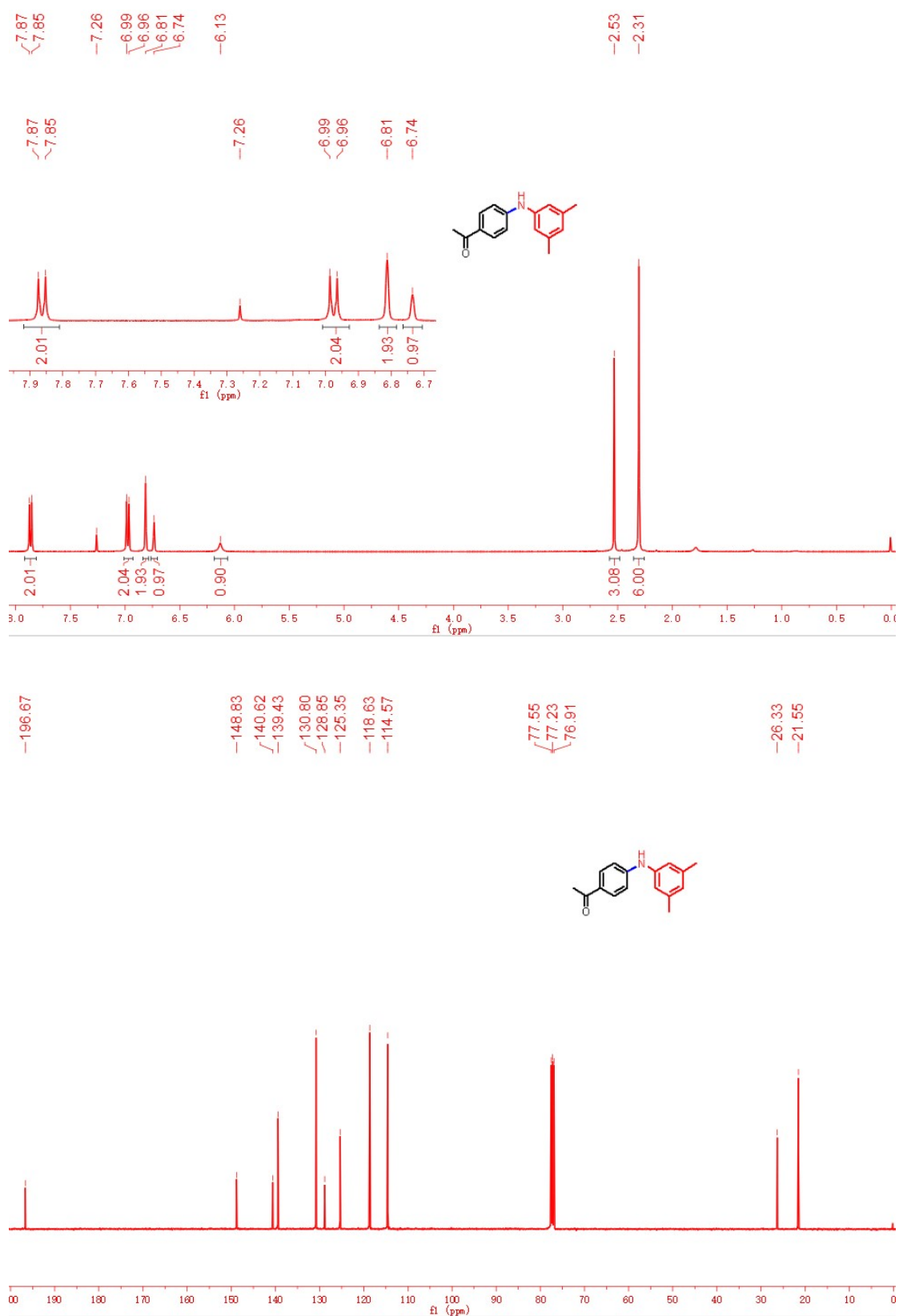
**Fig. S37.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 1-(4-((4-bromophenyl)amino)phenyl)ethan-1-one (**3ah**) in  $\text{CDCl}_3$



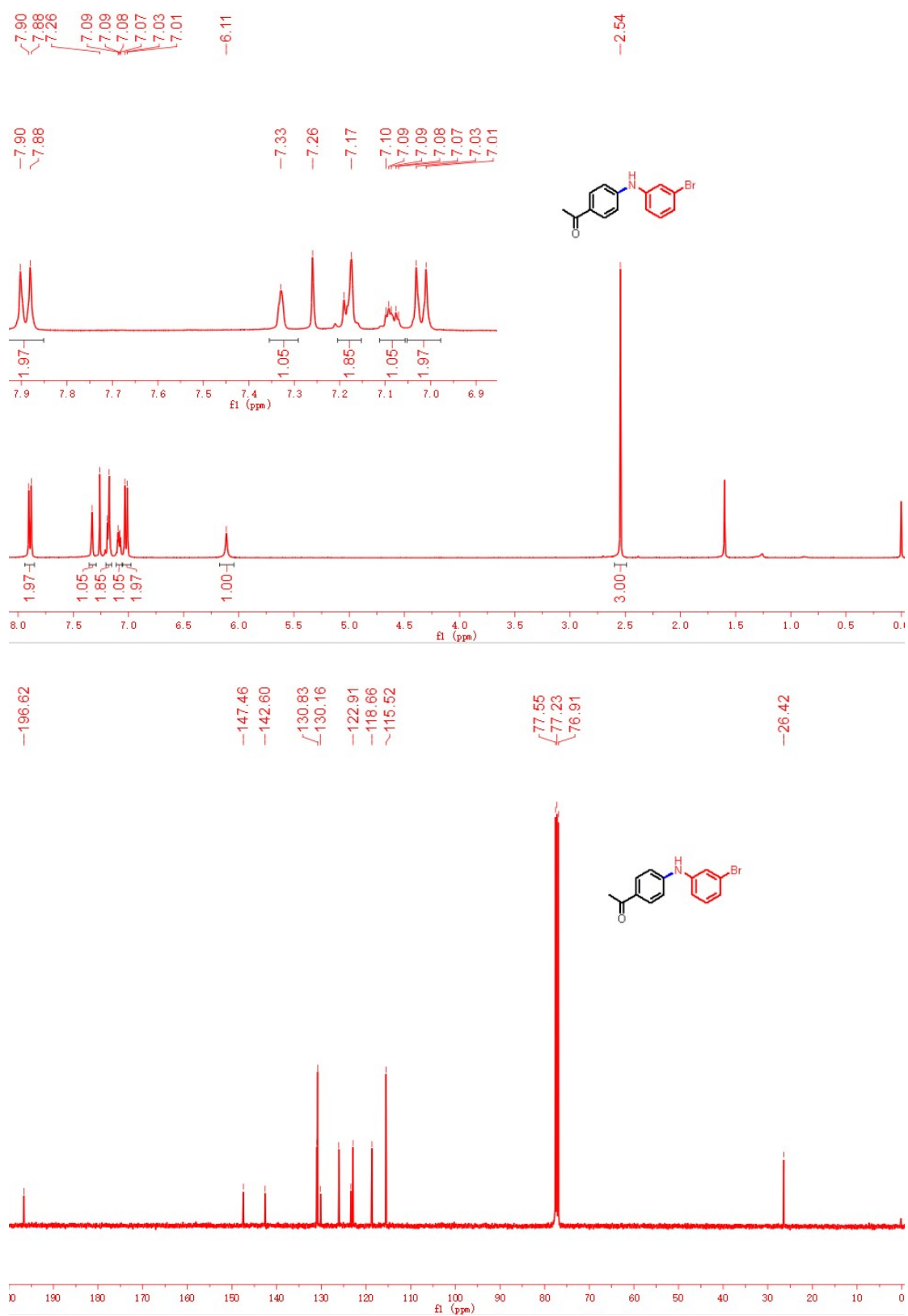
**Fig. S38.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 1-(4-((3,4-dimethylphenyl)amino)phenyl)ethan-1-one (**3ai**) in  $\text{CDCl}_3$



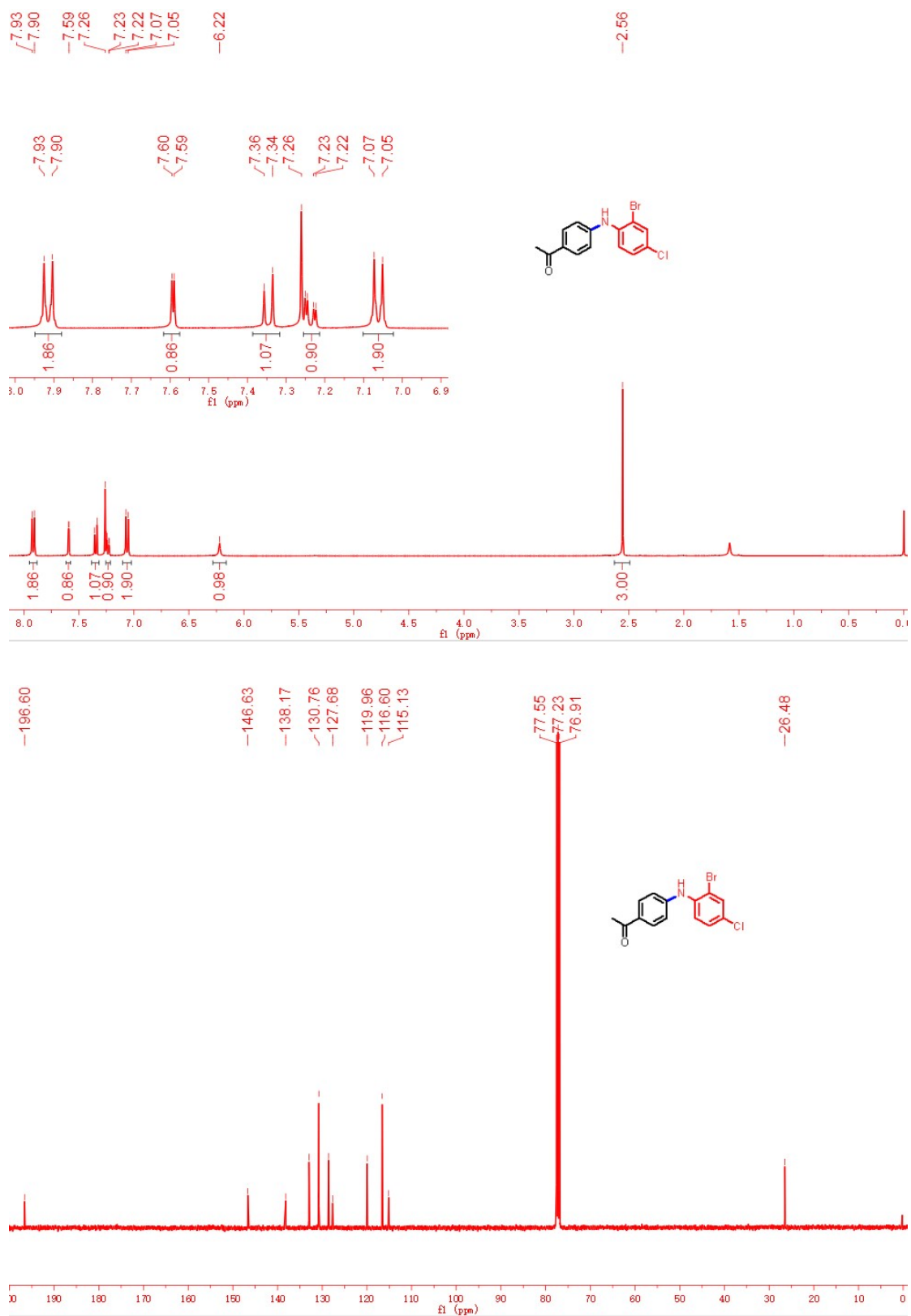
**Fig. S39.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 1-(4-((3,5-dimethylphenyl)amino)phenyl)ethan-1-one (**3aj**) in  $\text{CDCl}_3$



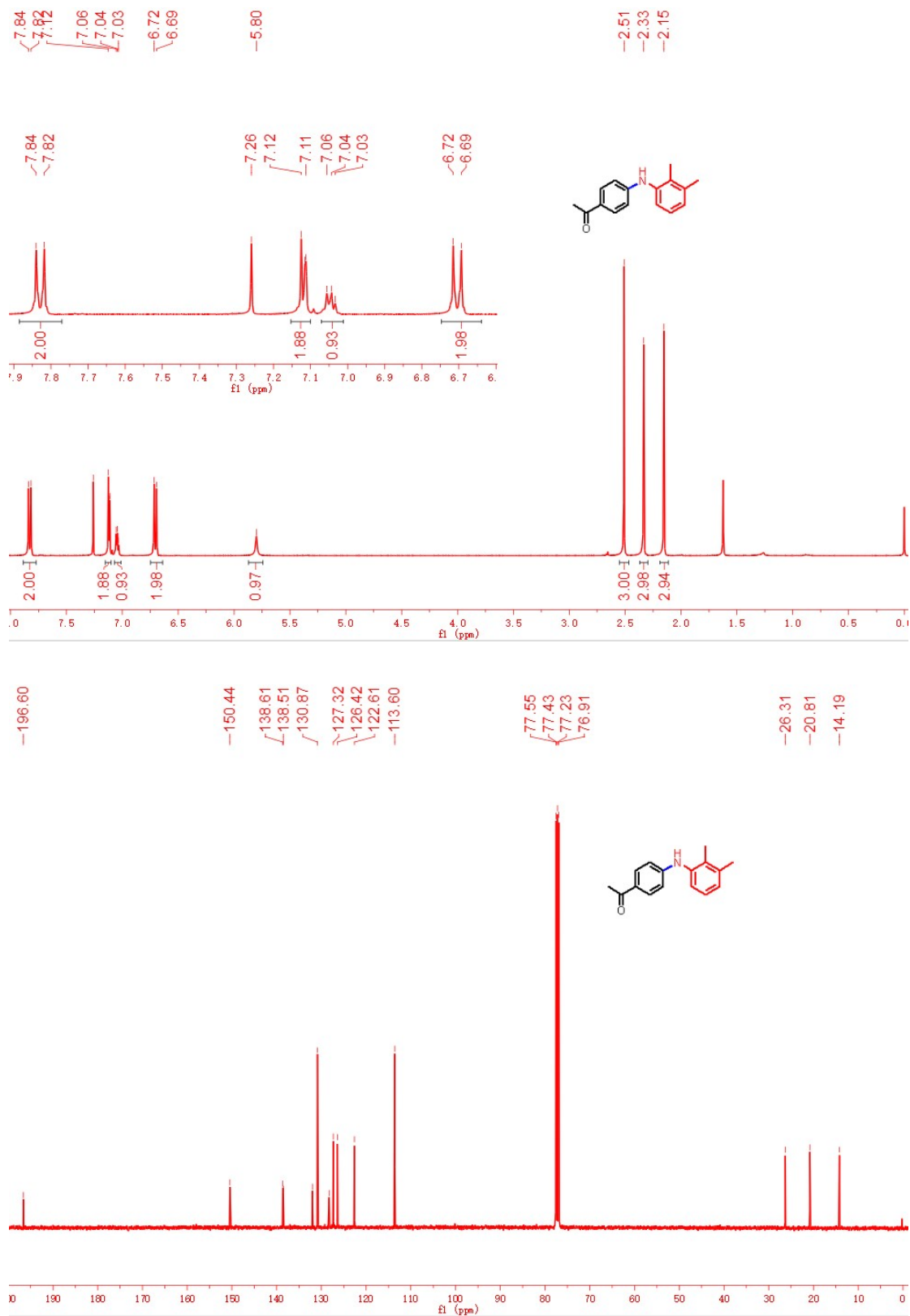
**Fig. S40.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 1-(4-((3-bromophenyl)amino)phenyl)ethan-1-one (**3ak**) in  $\text{CDCl}_3$



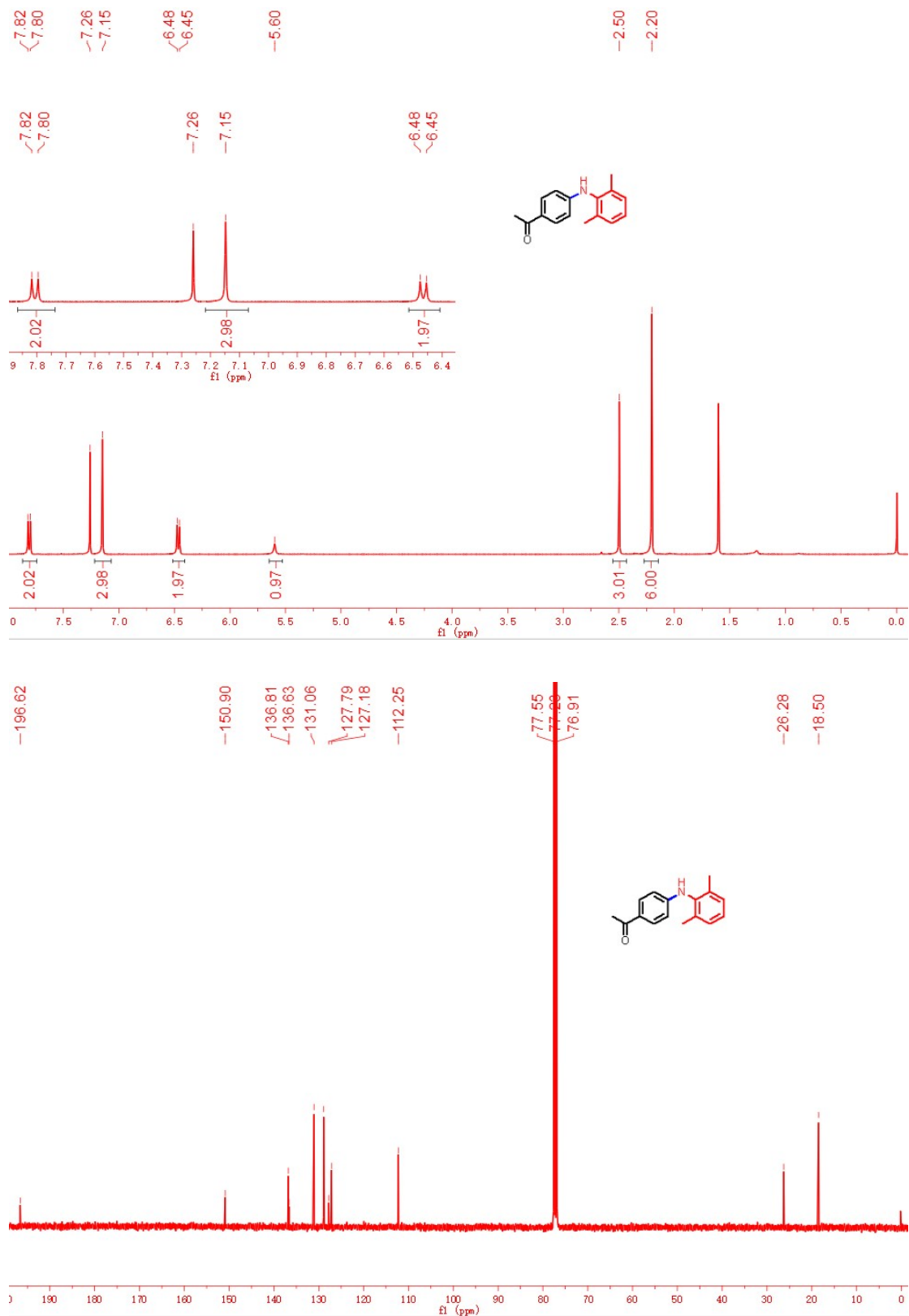
**Fig. S41.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 1-(4-((2-bromo-4-chlorophenyl)amino)phenyl)ethan-1-one (**3al**) in  $\text{CDCl}_3$



**Fig. S42.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 1-(4-((2,3-dimethylphenyl)amino)phenyl)ethan-1-one (**3am**) in  $\text{CDCl}_3$

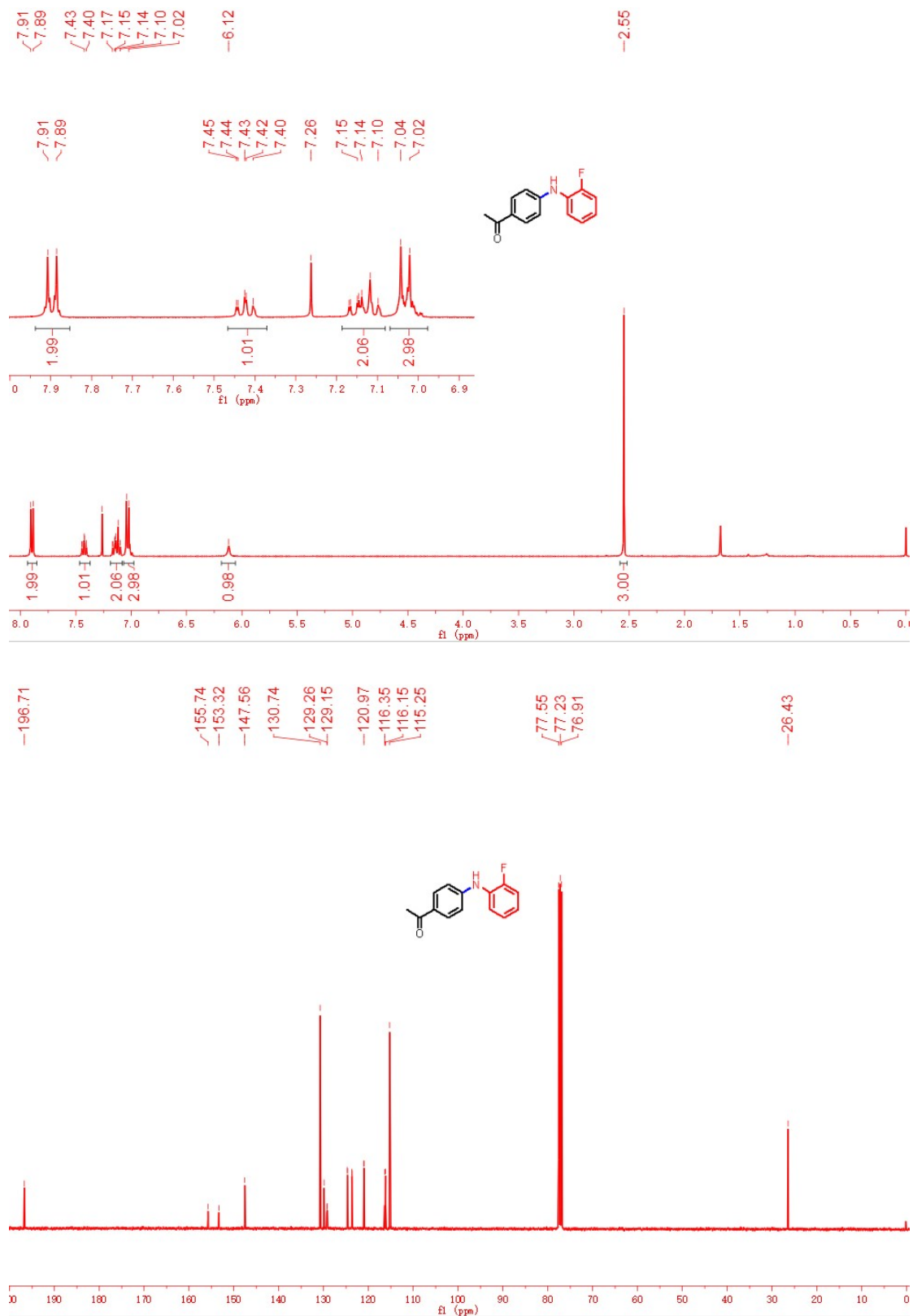


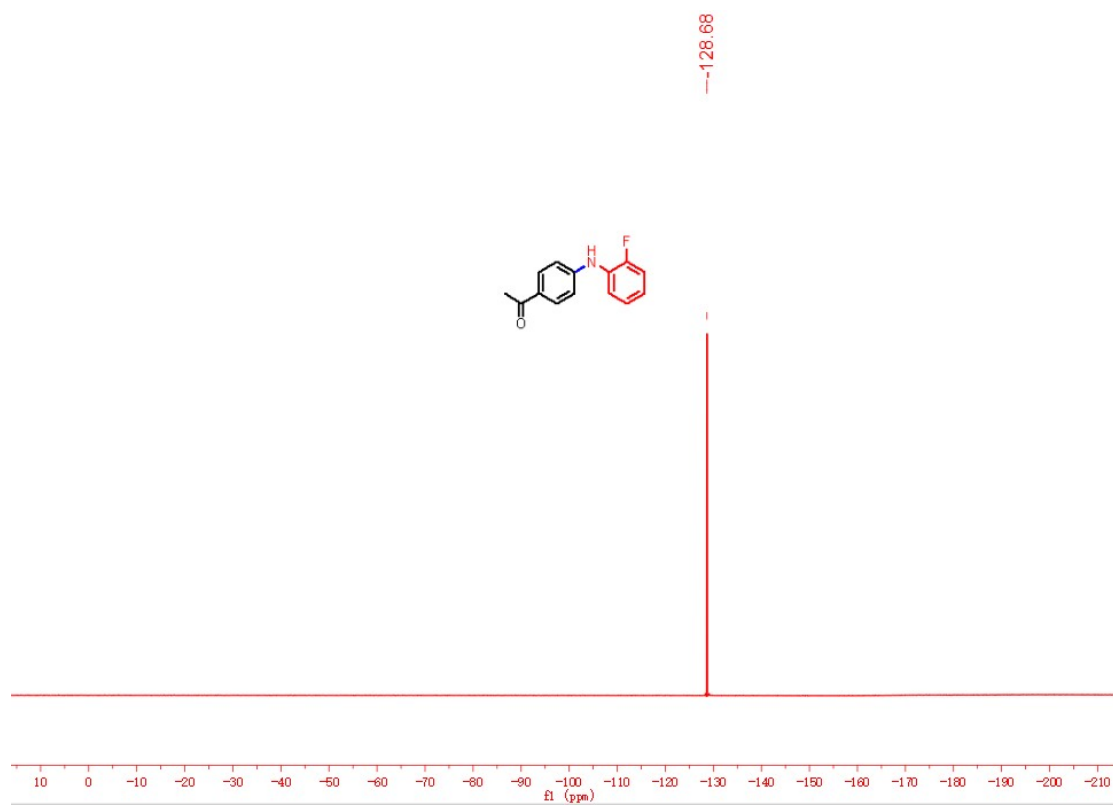
**Fig. S43.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 1-(4-((2,6-dimethylphenyl)amino)phenyl)ethan-1-one (**3an**) in  $\text{CDCl}_3$



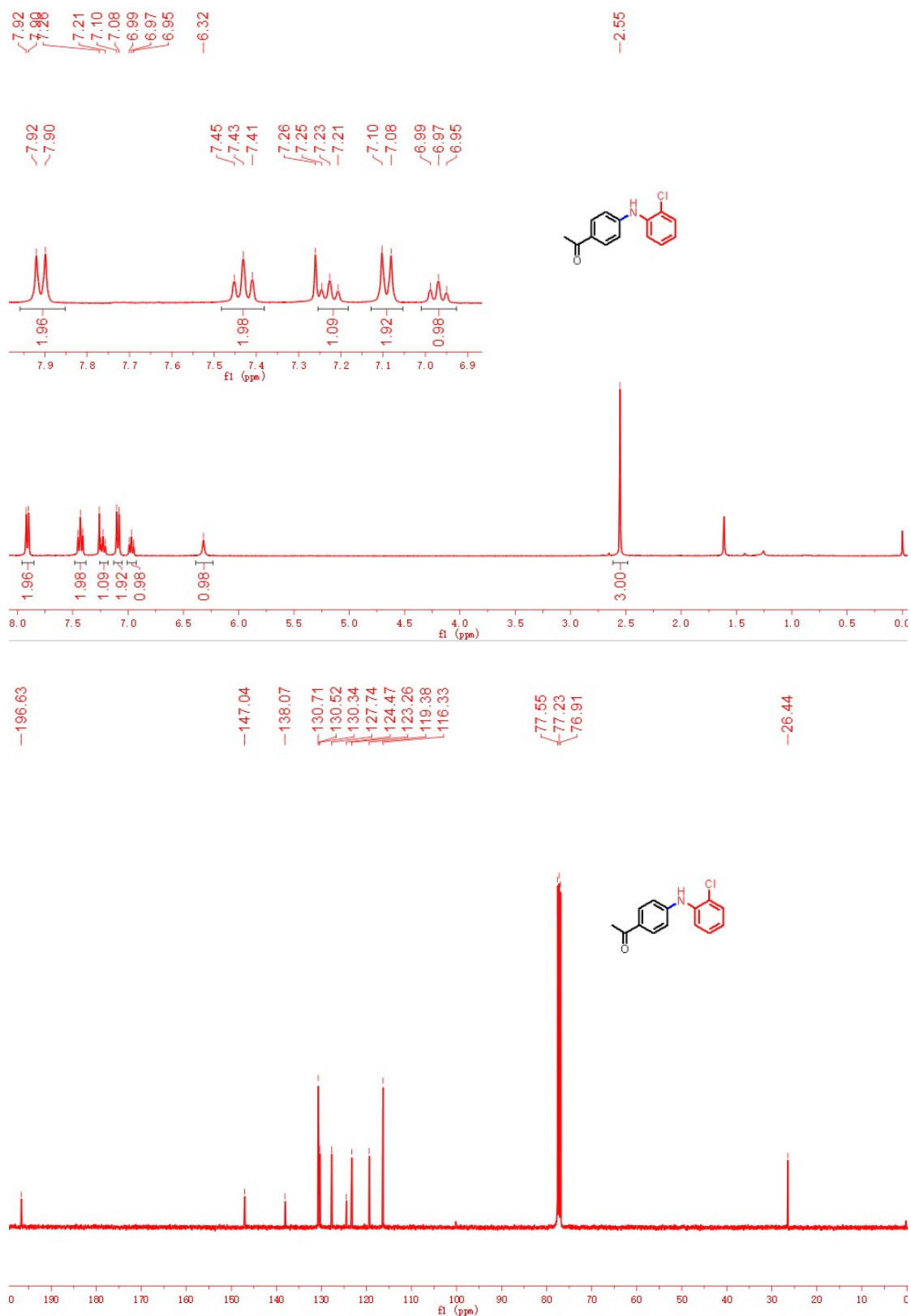


**Fig. S44.** The  $^1\text{H}$  (400 MHz),  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) and  $^{19}\text{F}$  NMR (377 MHz) NMR spectra for 1-(4-((2-fluorophenyl)amino)phenyl)ethan-1-one (**3ao**) in  $\text{CDCl}_3$

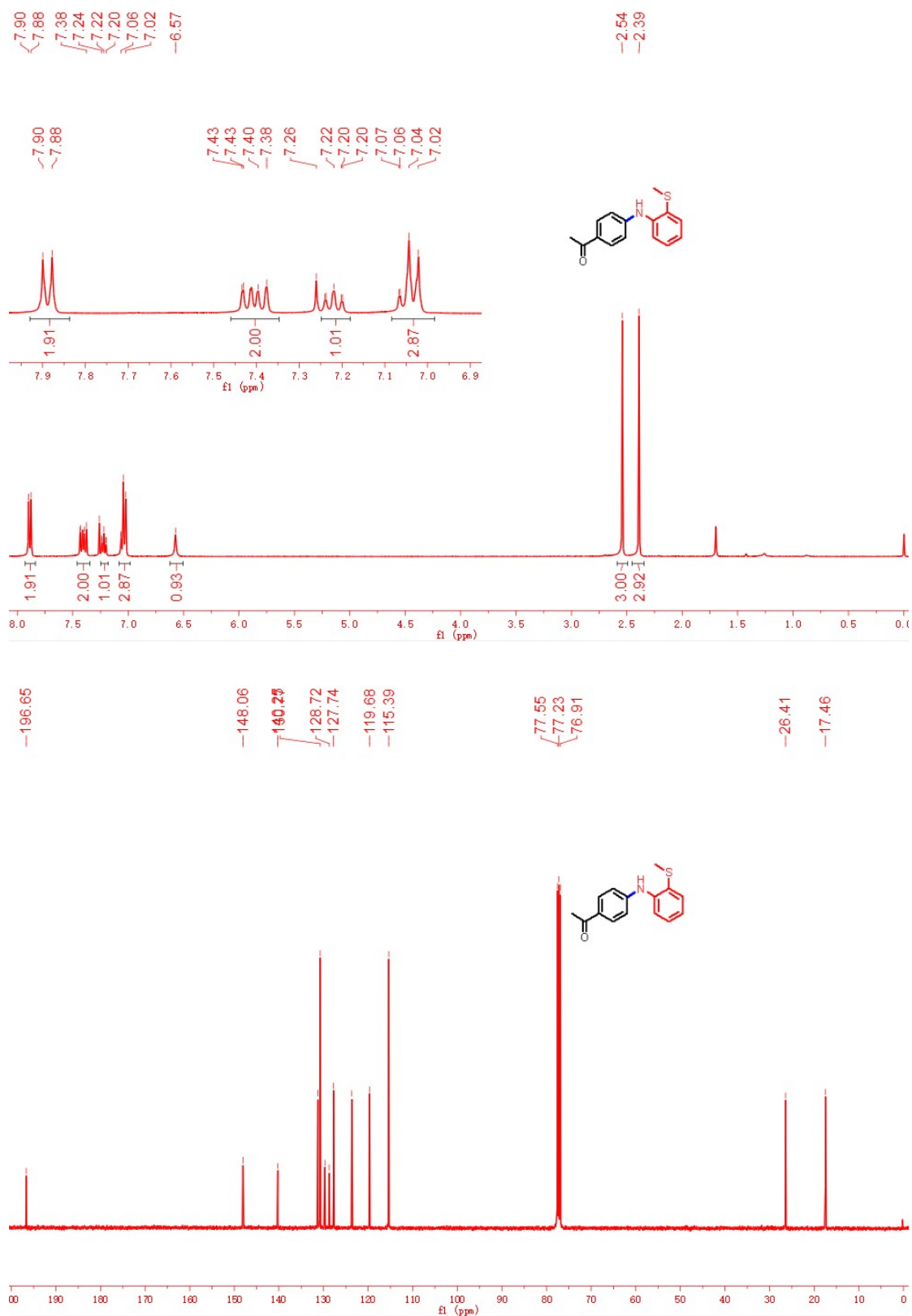




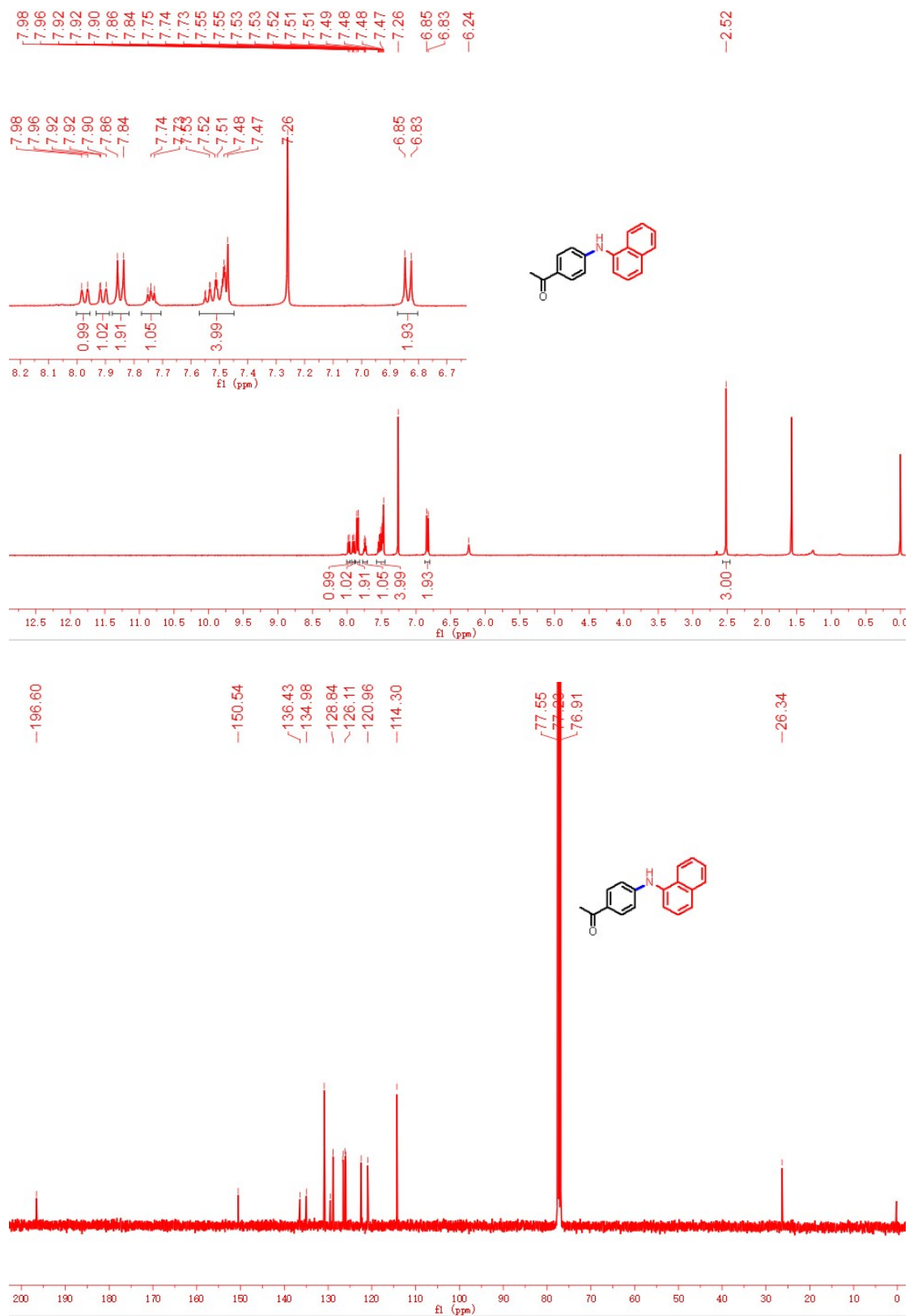
**Fig. S45.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 1-(4-((2-chlorophenyl)amino)phenyl)ethan-1-one (**3ap**) in  $\text{CDCl}_3$



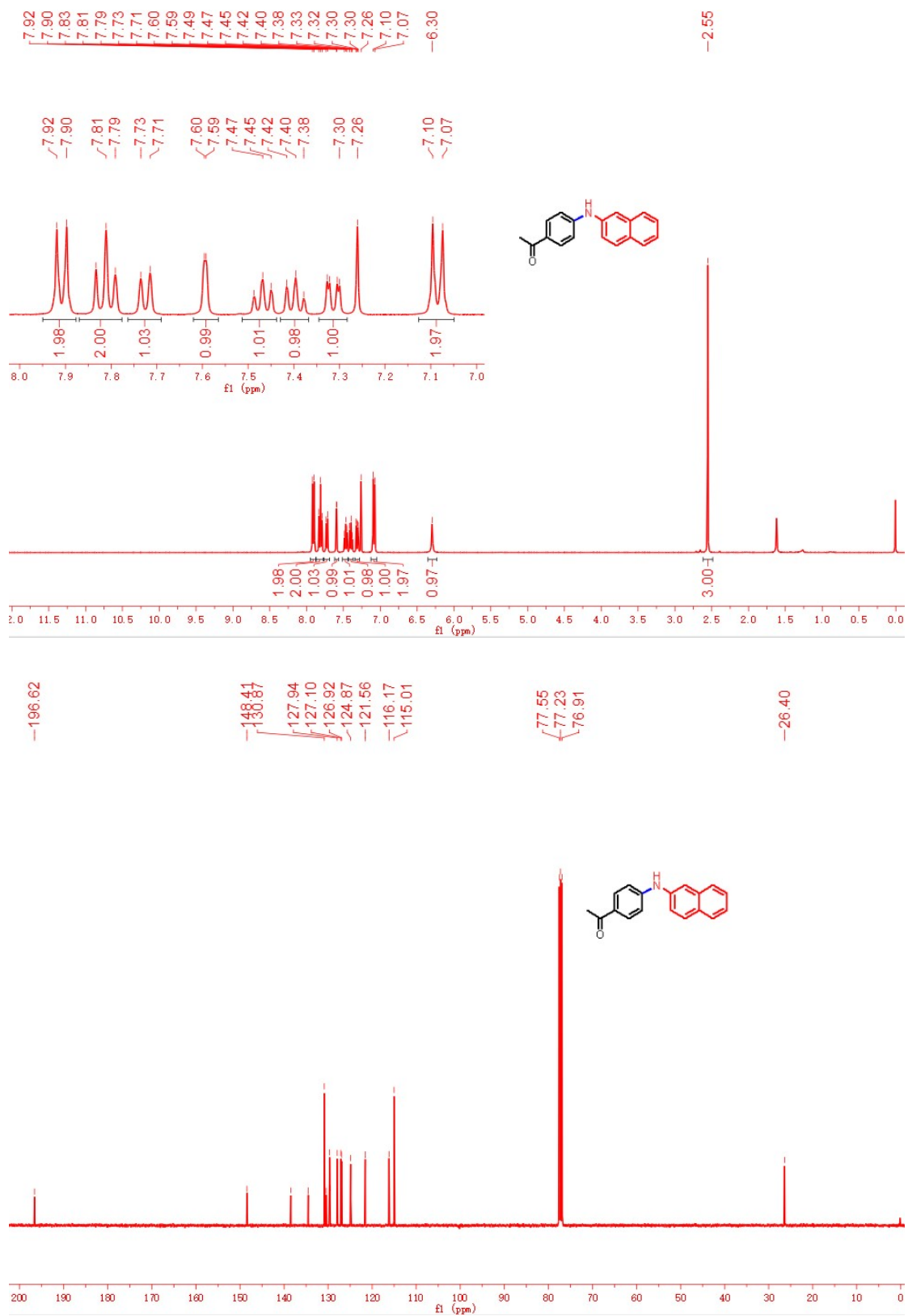
**Fig. S46.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 1-(4-((2-(methylthio)phenyl)amino)phenyl)ethan-1-one (**3aq**) in  $\text{CDCl}_3$



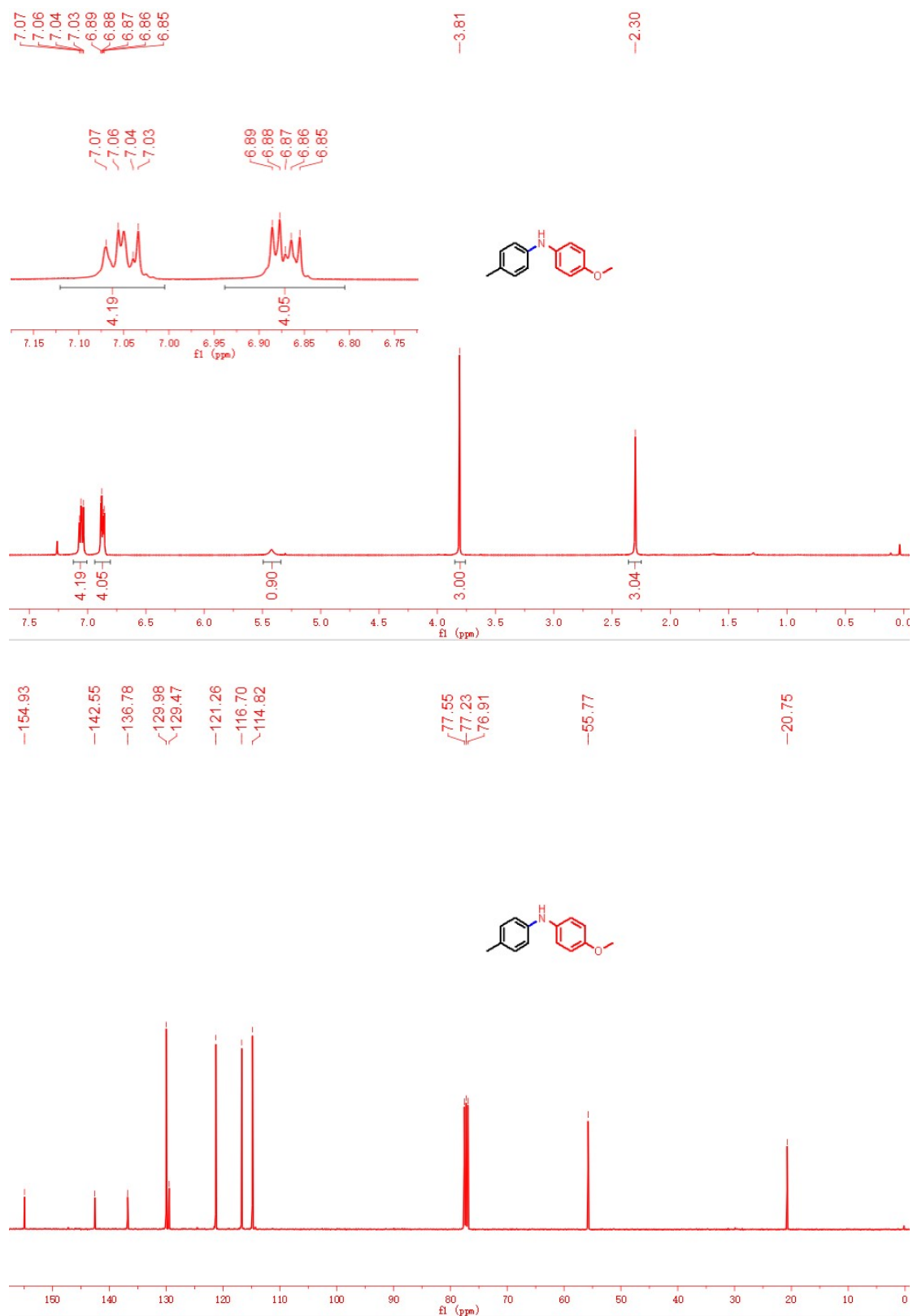
**Fig. S47.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 1-(4-(naphthalen-1-ylamino)phenyl)ethan-1-one (**3ar**) in  $\text{CDCl}_3$



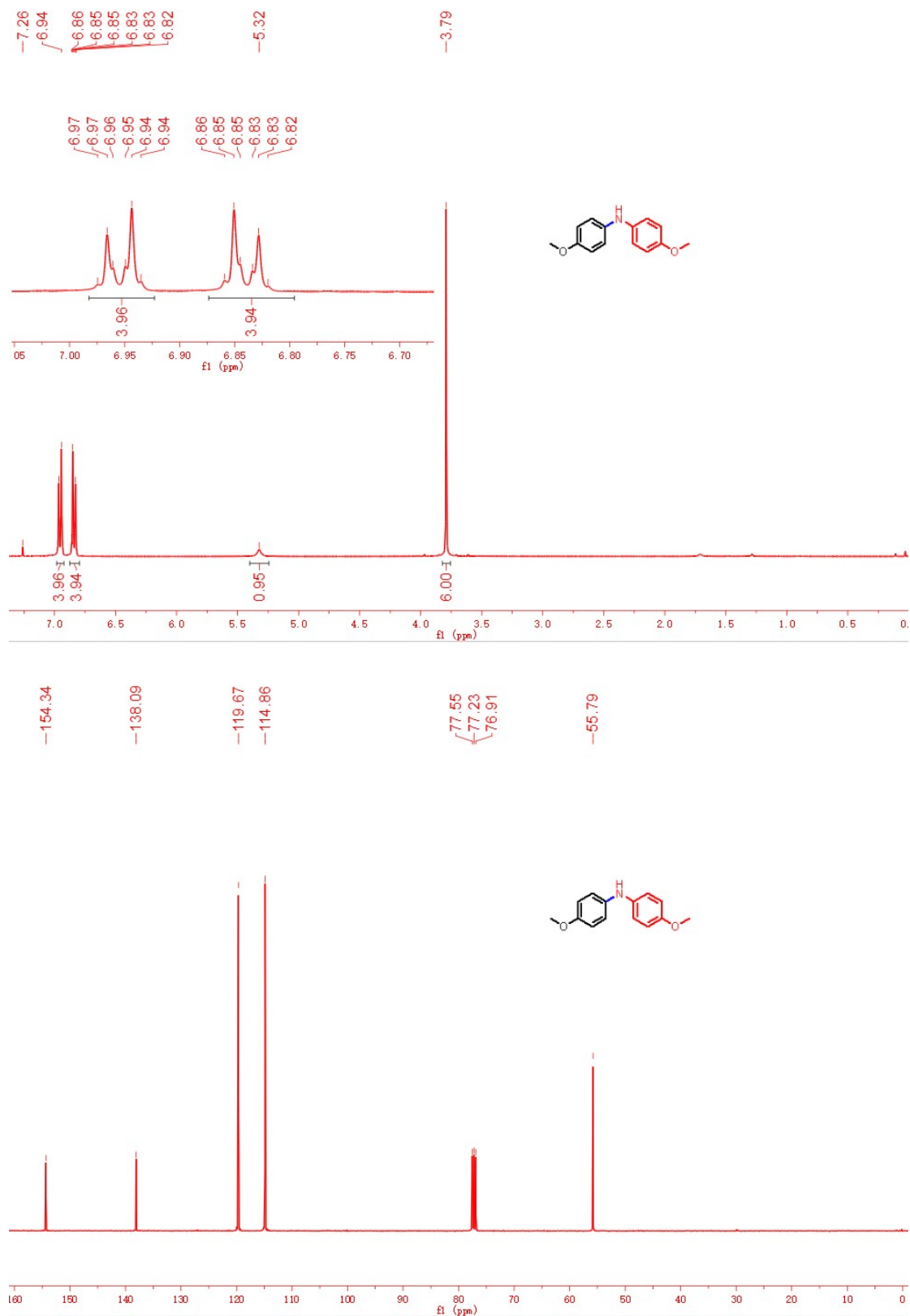
**Fig. S48.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 1-(4-(naphthalen-2-ylamino)phenyl)ethan-1-one (**3as**) in  $\text{CDCl}_3$



**Fig. S49.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 4-methoxy-N-(*p*-tolyl)aniline (**3k'd**) in  $\text{CDCl}_3$

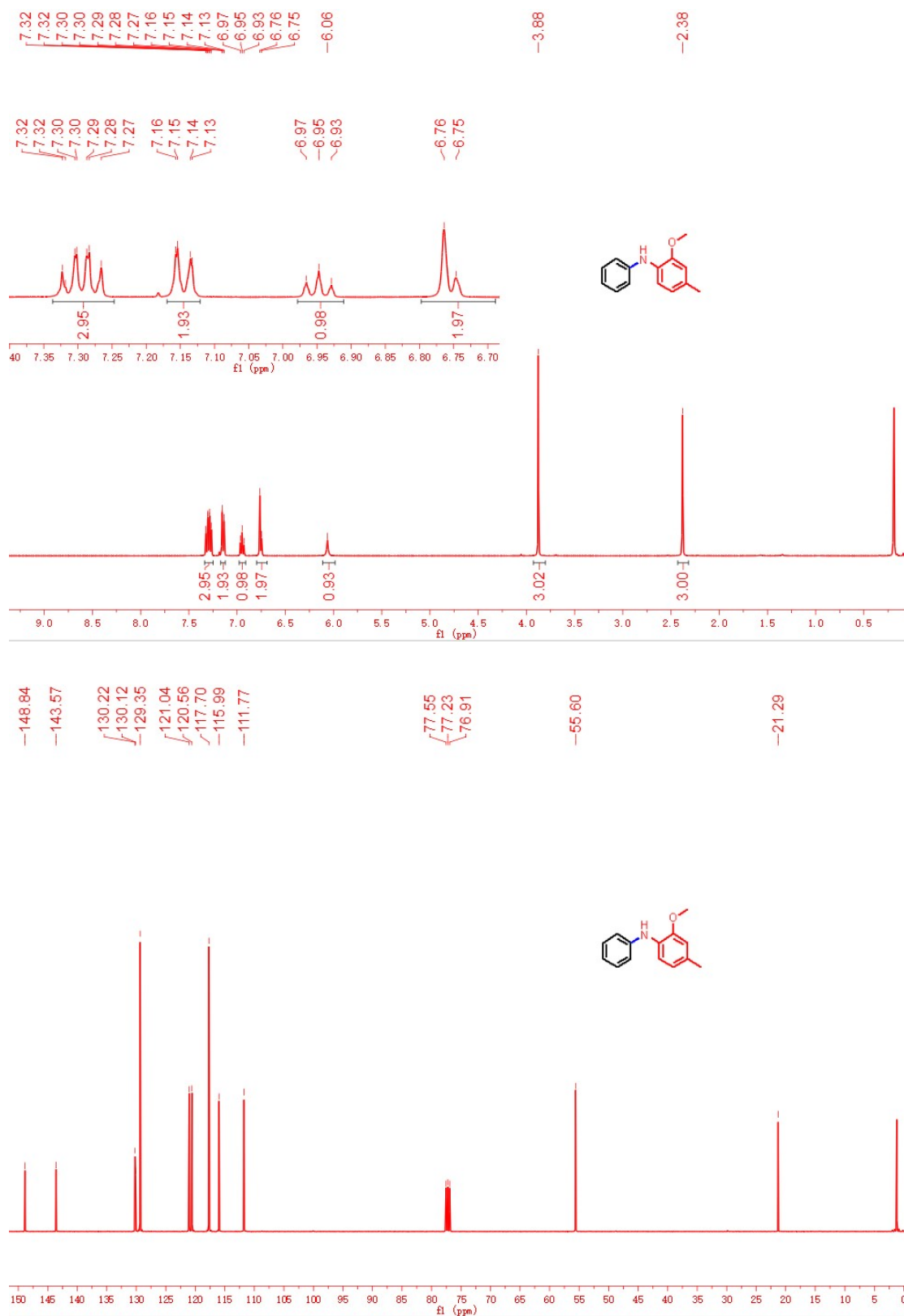


**Fig. S50.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for bis(4-methoxyphenyl)amine (**31'd**) in  $\text{CDCl}_3$

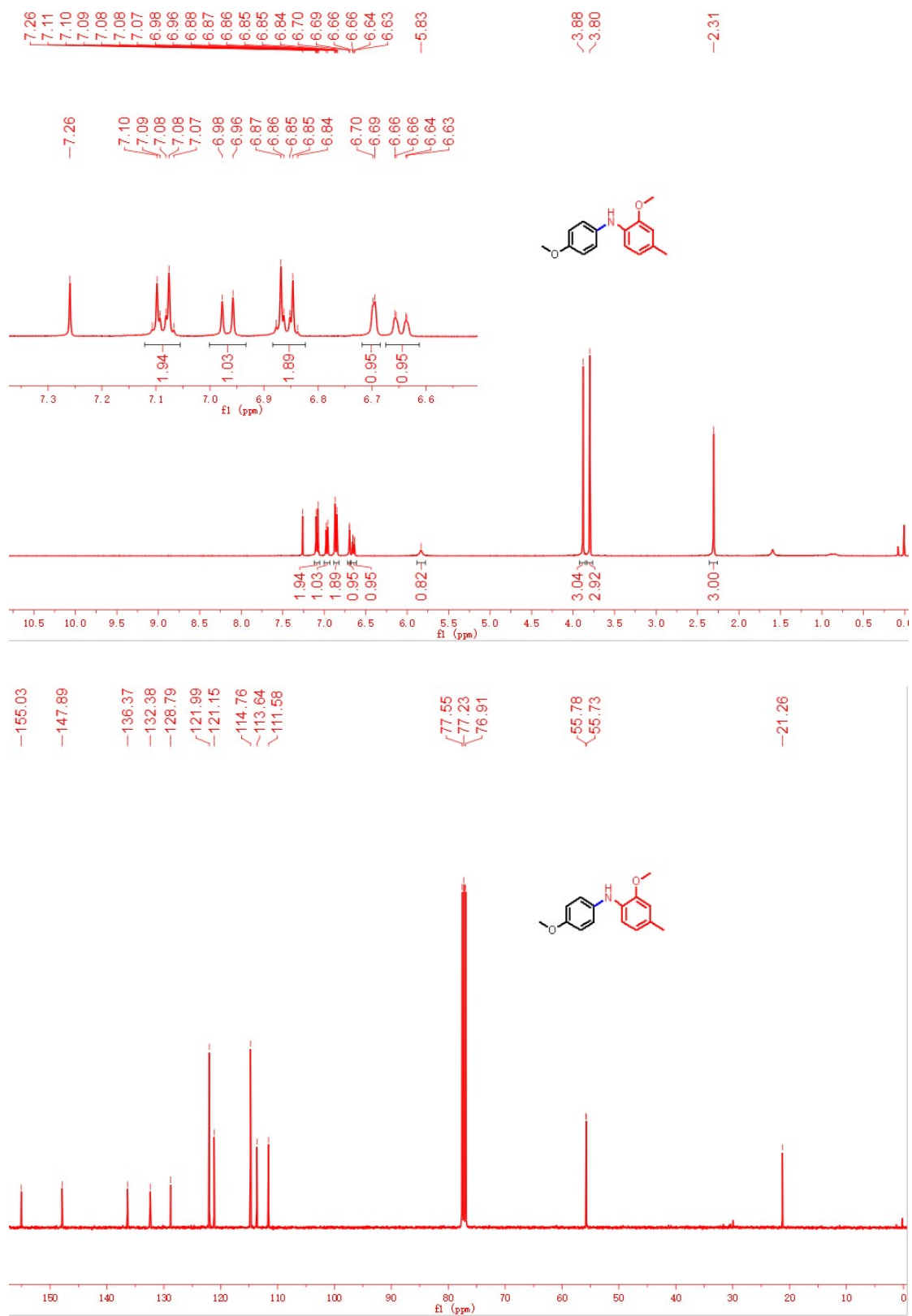




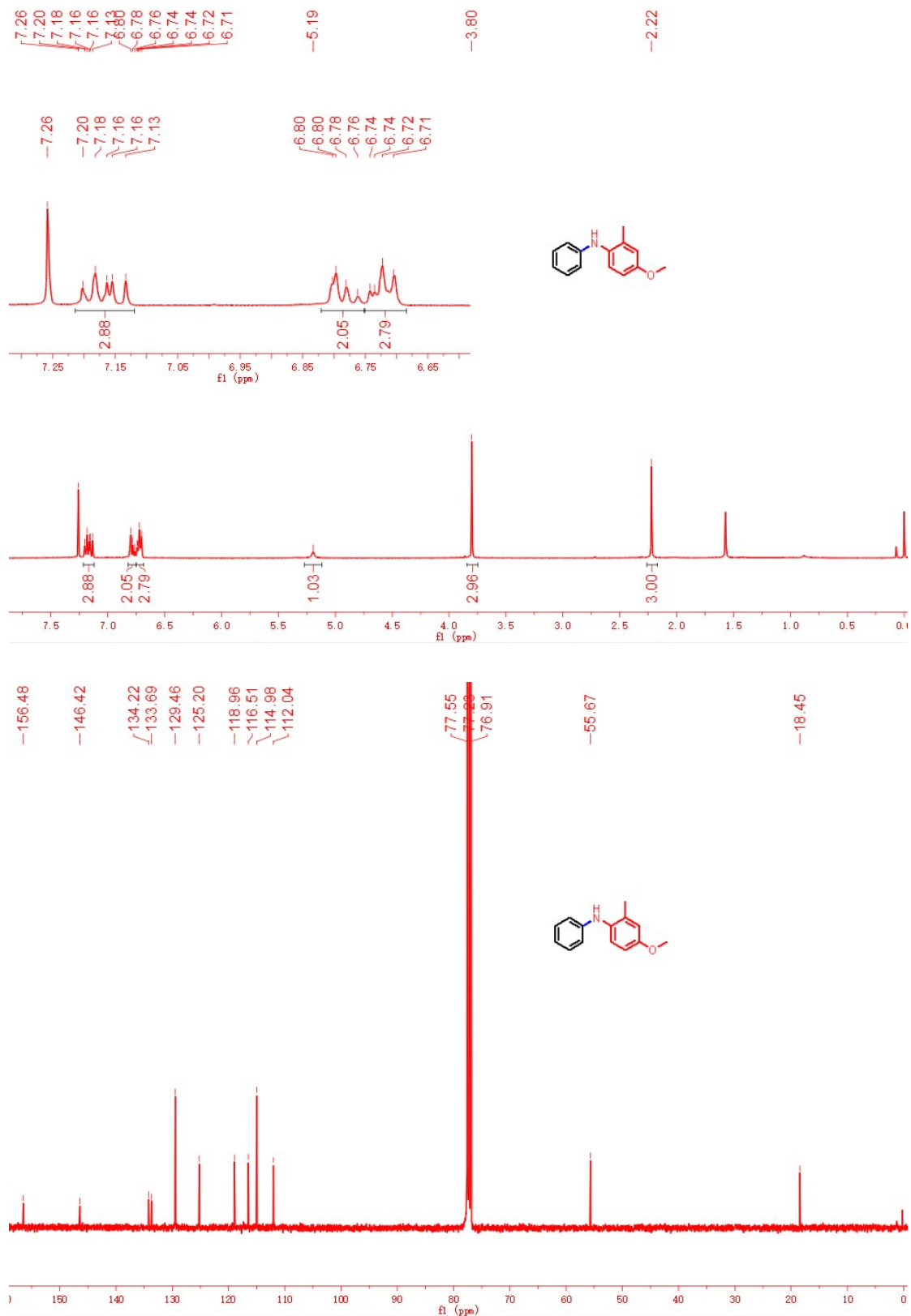
**Fig. S51.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 2-methoxy-4-methyl-N-phenylaniline (**3j't**) in  $\text{CDCl}_3$



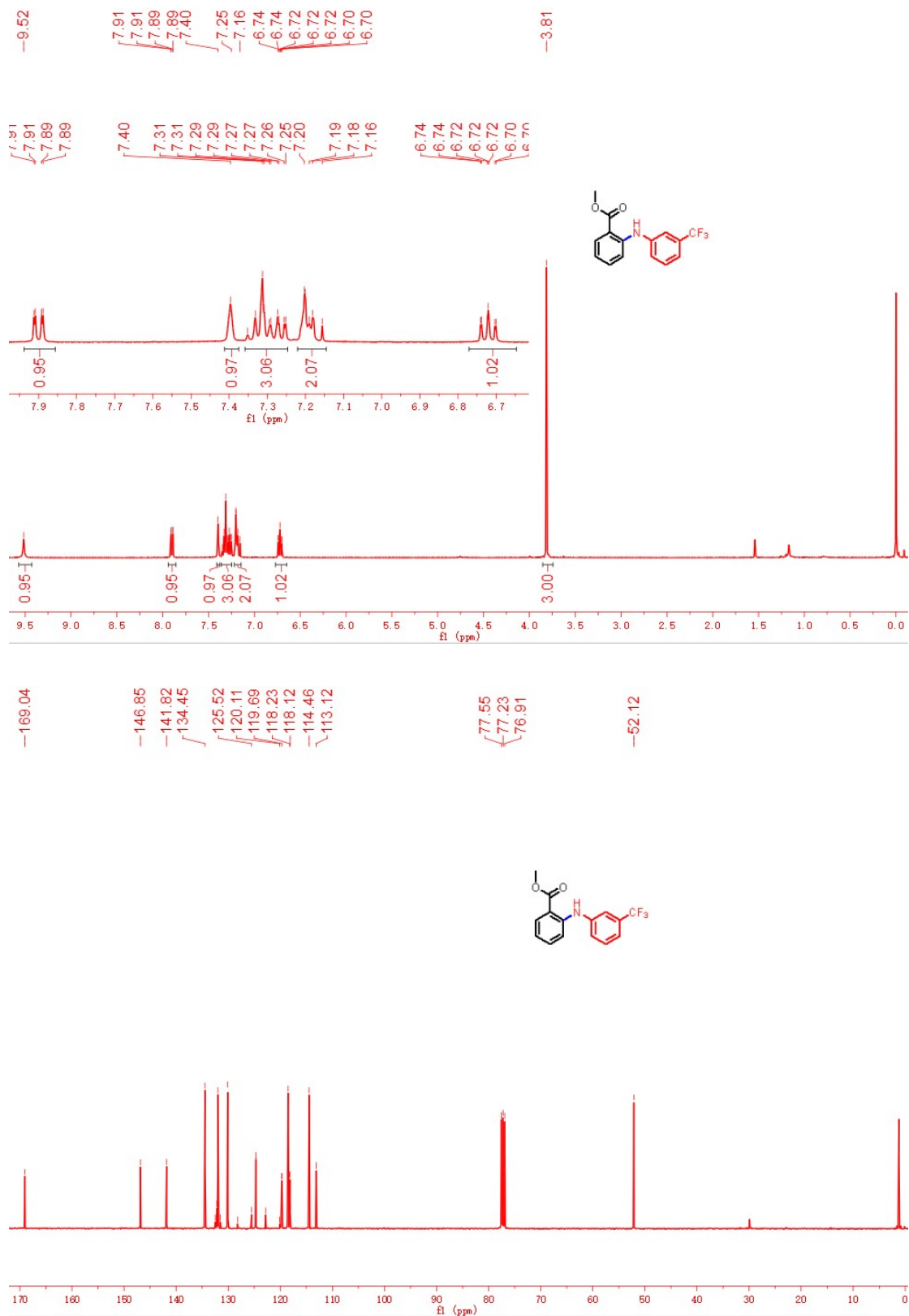
**Fig. S52.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 2-methoxy-N-(4-methoxyphenyl)-4-methylaniline (**31't**) in  $\text{CDCl}_3$

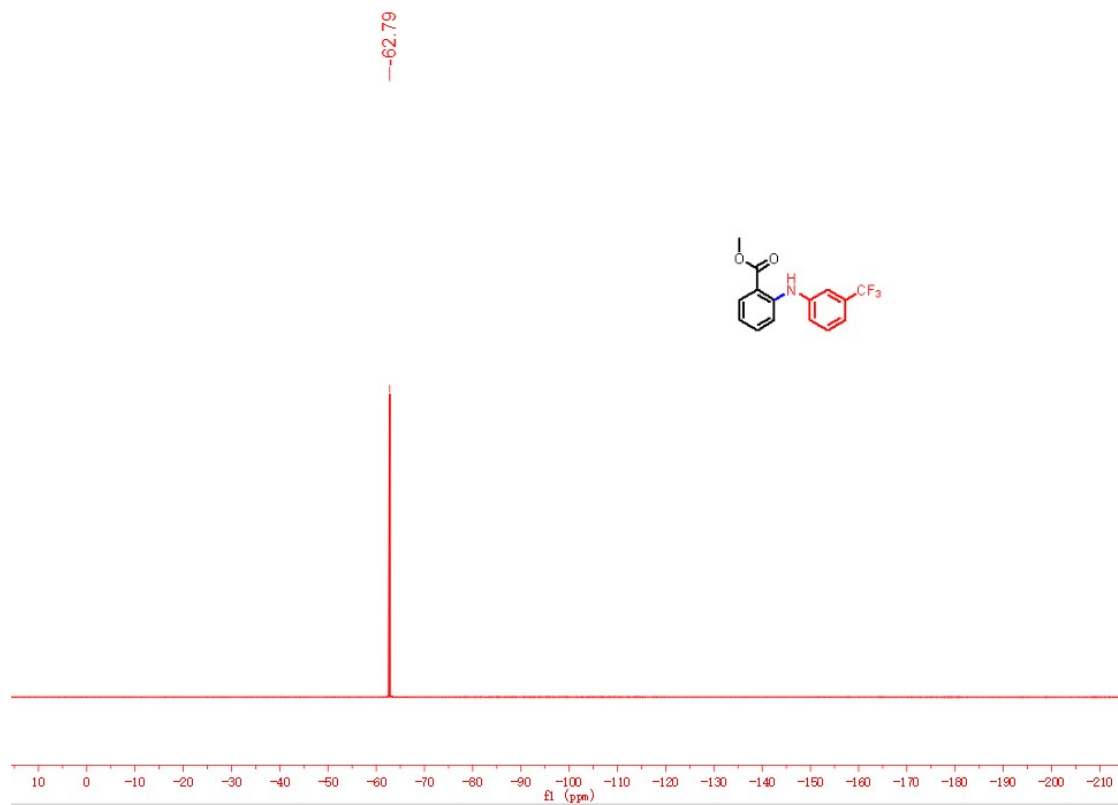


**Fig. S53.** The  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) NMR spectra for 4-methoxy-2-methyl-N-phenylaniline (**3j'u**) in  $\text{CDCl}_3$



**Fig. S54.** The  $^1\text{H}$  (400 MHz),  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) and  $^{19}\text{F}$  NMR (377 MHz) NMR spectra for methyl 2-((3-(trifluoromethyl)phenyl)amino)benzoate (**3sv**) in  $\text{CDCl}_3$





**Fig. S55.** The  $^1\text{H}$  (400 MHz),  $^{13}\text{C}\{^1\text{H}\}$  (101 MHz) and  $^{19}\text{F}$  NMR (377 MHz) NMR spectra for 2-((3-(trifluoromethyl)phenyl)amino)benzoic acid (Flufenamic Acid) in  $d_6$ -DMSO

