

## Ruthenium-catalyzed *meta/ortho*-selective C-H alkylation of azoarenes with alkyl bromides

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#### 1. General Information

All commercial reagents and solvents were used directly without additional

purification. Column chromatography were performed on silica gel 200-300 mesh.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were registered on a Bruker Ascend<sup>TM</sup> 400 spectrometer (Germany). Chemical shifts were reported in units (ppm) referenced to 0.0 ppm of TMS in the  $^1\text{H}$  spectrum and 77.0 ppm of  $\text{CDCl}_3$  in the  $^{13}\text{C}$  spectrum. All coupling constants were reported in Hertz (Hz). HRMS data were obtained on a Waters LCT Premierxe<sup>TM</sup> (USA), Single-crystal X-ray crystallography was carried out on a Bruker Smart Apex II diffractometer system.

## 2. Experimental Section

### 2.1. General Procedure for the Synthesis of symmetrical Azobenzenes.<sup>1</sup>

A mixture of CuBr (4.2 mg, 0.03 mmol), pyridine (8.7 mg, 0.09 mmol), and arylamine (1 mmol) in toluene (4 mL) was stirred at 60 °C under air (1 atm) for 20 h and then cooled to room temperature and concentrated under vacuum. The residue was purified by flash chromatography on a short silica gel column, eluting with petroleum ether, to afford the desired products.

### 2.2. General Procedure for the Synthesis of Dissymmetric Azobenzenes.<sup>2</sup>

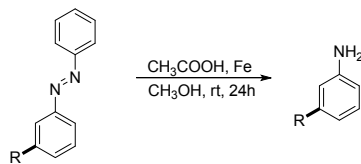
Nitrosobenzene derivative (0.80 mmol) was dissolved in glacial acetic acid (2 mL), and the amine (0.80 mmol) in EtOH (0.5 mL) was added to the solution. After being stirred for 6 h at 40 °C, the mixture was poured onto ice and filtered. The crude brown product was then purified by column chromatography with silica and ethyl acetate/petroleum ether.

### 2.3. Typical Experimental Procedure of the *meta*-Selective C-H Alkylation of Azoarenes

Azobenzenes (0.2 mmol), Alkyl bromide (0.6 mmol, 3.0 equiv.),  $[\text{Ru}(p\text{-Cymene})\text{Cl}_2]_2$  (0.01 mmol, 5 mol %),  $\text{K}_2\text{CO}_3$  (0.4 mmol, 2.0 equiv),  $t\text{BuCOOH}$  (30 mmol %), dry 1,4-dioxane (1.5 mL) were charged into a pre-dried 30-mL pressure tube sealed with rubber plugs under  $\text{N}_2$  atmosphere. The reaction mixture was stirred at 120 °C for 24 h. The reaction was cooled down to room temperature. The mixture was passed through a short pad of celite, washing with a mixture of EtOAc. The organic layer was concentrated under reduced pressure to give a crude oil, which was purified by column chromatography (*n*-hexane as eluent) on silica gel to afford the

desired products.

## 2.4. Experimental Procedure for the Reduction of Azobenzenes Product.



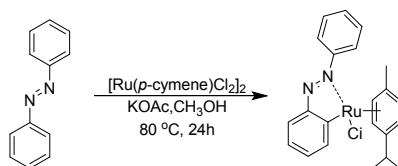
Azobenzenes, Fe powder (3.0 equiv.), CH<sub>3</sub>COOH, (6.0 equiv.), CH<sub>3</sub>OH (3 mL) were charged into a one-neck flask under N<sub>2</sub> atmosphere. The reaction mixture was stirred at room temperature for 24 h. The reaction was cooled down to room temperature. An aqueous solution of saturated Na<sub>2</sub>CO<sub>3</sub> was added to the mixture, and then stirred for additional 5 min. The aqueous layer was extracted with EtOAc (3 x 20 mL). The organic phase were combined and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated under reduced pressure to give crude product, which was purified by column chromatography (ethyl acetate/etroleum ether). The products were identified by NMR and MS spectra.

## 3. Mechanistic Studies

### 3.1 Isotope Labelling Studies in the Ruthenium-Catalyzed *meta*-Selective C-H Functionalization of Azoarenes

Under standard conditions, the ruthenium-catalyzed *meta*-selective C-H alkylation of isotope labelling azobenzene were characterized by <sup>1</sup>H NMR spectra respectively.

### 3.2. Preparation of Azoarene-Ruthenium Complex<sup>3</sup>



[RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> (0.5 mmol, 306 mg), KOAc (2 mmol, 196 mg), azobenzene (1 mmol, 182mg) and dry CH<sub>3</sub>OH (10 mL) were charged into a pre-dried 50-mL pressure tube sealed with rubber plugs under N<sub>2</sub> atmosphere. The reaction was stirred at 80 °C for 24h. The reaction was then concentrated to dryness, dissolved in a minimal amount of ethyl acetate and then purified through neutral alumina with EtOAc as the solvent to yield the complex as a dark red solid. And the structure was

definitely confirmed by single-crystal X-ray diffraction (Figure 2).

#### 4. References

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#### 5. Data and Spectra of <sup>1</sup>H NMR and <sup>13</sup>C NMR

**(E)-1-(3-(pentan-3-yl)phenyl)-2-phenyldiazene (3aa, red oil)** : <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.94-7.88 (m, 2H), 7.76-7.70 (m, 2H), 7.54-7.39 (m, 4H), 7.25 (s, 1H), 2.49-2.40 (m, 1H), 1.75 (ddd, J = 13.0, 7.2, 5.7 Hz, 2H), 1.66-1.59 (m, 2H), 0.81 (t, J = 7.4 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.79, 147.08, 130.76, 129.05, 128.82, 122.77, 119.92, 49.69, 29.26, 12.22. HRMS (ESI) Calcd. For C<sub>17</sub>H<sub>21</sub>N<sub>2</sub>: [M+H]<sup>+</sup>, 253.1705, Found: m/z 253.1708.

**(E)-1-(4-methyl-3-(pentan-3-yl)phenyl)-2-(p-tolyl)diazene (3ba, red oil)**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.81 (d, J = 8.3 Hz, 2H), 7.74 (d, J = 1.9 Hz, 1H), 7.61 (dd, J = 8.1, 2.1 Hz, 1H), 7.30 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 1.5 Hz, 1H), 2.81-2.73 (m, 1H), 2.42 (s, 3H), 2.38 (s, 3H), 1.81-1.72 (m, 2H), 1.65 (ddd, J = 13.6, 8.9, 7.3 Hz, 2H), 0.81 (t, J = 7.4 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 151.61, 150.95, 145.18, 141.00, 139.97, 130.69, 129.68, 122.67, 121.91, 118.26. HRMS (ESI) Calcd. For C<sub>19</sub>H<sub>24</sub>N<sub>2</sub>: [M+H]<sup>+</sup>, 280.1939, Found: m/z 280.1942.

**(E)-1-([1,1'-biphenyl]-4-yl)-2-(2-(pentan-3-yl)-[1,1'-biphenyl]-4-yl)diazene (3ca, red oil)**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.04 (d, J = 8.4 Hz, 1H), 7.93 (s, 1H), 7.82-7.75 (m, 3H), 7.72-7.69 (m, 1H), 7.50 (t, J = 7.7 Hz, 2H), 7.45 (dd, J = 10.9, 4.0 Hz, 3H), 7.42-7.38 (m, 2H), 7.36 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 7.2 Hz, 2H), 2.75-2.67 (m, 1H), 1.73-1.64 (m, 4H), 0.77 (t, J = 7.4 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.45, 151.98, 145.88, 144.83, 143.57, 141.66, 140.27, 130.64, 129.54, 128.89, 127.85, 127.20, 126.92, 123.32, 122.39, 118.02, 43.55, 29.75, 12.20. HRMS (ESI) Calcd. For C<sub>29</sub>H<sub>29</sub>N<sub>2</sub>: [M+H]<sup>+</sup>, 405.2331, Found: m/z 405.2338.

**(E)-1-(4-methoxy-3-(pentan-3-yl)phenyl)-2-(4-methoxyphenyl)diazene (3da, red**

oil):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (d,  $J = 8.9$  Hz, 2H), 7.76 (dd,  $J = 4.3, 2.2$  Hz, 2H), 7.02 (d,  $J = 8.9$  Hz, 2H), 6.97 (d,  $J = 9.3$  Hz, 1H), 3.90 (s, 6H), 3.00 (td,  $J = 8.5, 4.3$  Hz, 1H), 1.70 (ddd,  $J = 21.9, 14.3, 6.9$  Hz, 4H), 0.83 (t,  $J = 7.4$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.41, 160.04, 147.21, 146.92, 134.84, 124.25, 122.46, 121.34, 114.13, 110.43, 55.63, 41.02, 27.96, 12.05. HRMS (ESI) Calcd. For  $\text{C}_{19}\text{H}_{25}\text{N}_2\text{O}_2$ :  $[\text{M}+\text{H}]^+$ , 313.1916, Found:  $m/z$  313.1916

**(E)-1-(3-(pentan-3-yl)-4-(trifluoromethoxy)phenyl)-2-(4-**

**(trifluoromethoxy)phenyl)diazene (3ea, red oil):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01-7.95 (m, 2H), 7.87 (d,  $J = 2.4$  Hz, 1H), 7.78 (dd,  $J = 8.8, 2.4$  Hz, 1H), 7.38 (dd,  $J = 8.8, 2.0$  Hz, 3H), 2.99 (tt,  $J = 9.0, 5.6$  Hz, 1H), 1.86-1.76 (m, 2H), 1.66 (m,  $J = 8.8$  Hz, 2H), 0.85 (t,  $J = 7.4$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  151.02, 150.64, 139.32, 124.38, 123.74, 121.27, 120.55, 41.35, 28.60, 11.84. HRMS (ESI) Calcd. For  $\text{C}_{19}\text{H}_{19}\text{F}_6\text{N}_2\text{O}_2$ :  $[\text{M}+\text{H}]^+$ , 421.1351, Found:  $m/z$  421.1350.

**(E)-1-(4-fluoro-3-(pentan-3-yl)phenyl)-2-(4-fluorophenyl)diazene (3fa, red oil):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98-7.89 (m, 2H), 7.80 (dd,  $J = 6.8, 2.4$  Hz, 1H), 7.78-7.71 (m, 1H), 7.18 (dt,  $J = 18.2, 8.8$  Hz, 3H), 2.86 (td,  $J = 9.3, 4.7$  Hz, 1H), 1.85-1.75 (m, 2H), 1.72-1.64 (m, 2H), 0.86 (t,  $J = 7.4$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.52, 164.39, 163.02, 161.90, 149.05, 133.34, 124.71, 124.18, 121.20, 115.98, 41.88, 28.18, 12.07. HRMS (ESI) Calcd. For  $\text{C}_{17}\text{H}_{19}\text{F}_2\text{N}_2$ :  $[\text{M}+\text{H}]^+$ , 289.1516, Found:  $m/z$  289.1515.

**(E)-1-(4-chloro-3-(pentan-3-yl)phenyl)-2-(4-chlorophenyl)diazene (3ga, red oil):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91-7.85 (m, 2H), 7.81 (d,  $J = 2.3$  Hz, 1H), 7.68 (dd,  $J = 8.5, 2.4$  Hz, 1H), 7.51 (dd,  $J = 9.1, 2.1$  Hz, 3H), 3.17 (tt,  $J = 8.9, 5.6$  Hz, 1H), 1.81 (ddd,  $J = 13.2, 7.3, 5.8$  Hz, 2H), 1.73-1.63 (m, 2H), 0.86 (t,  $J = 7.4$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  151.23, 150.92, 144.33, 137.96, 137.02, 130.09, 129.37, 124.12, 123.70, 119.80, 44.30, 28.50, 11.80. HRMS (ESI) Calcd. For  $\text{C}_{17}\text{H}_{19}\text{Cl}_2\text{N}_2$ :  $[\text{M}+\text{H}]^+$ , 321.0925, Found:  $m/z$  321.0932.

**(E)-1-(4-bromo-3-(pentan-3-yl)phenyl)-2-(4-bromophenyl)diazene (3ha, red oil):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (dd,  $J = 14.1, 5.3$  Hz, 3H), 7.69 (dd,  $J = 16.3, 8.5$  Hz, 3H), 7.59 (dd,  $J = 8.2, 2.0$  Hz, 1H), 3.21-3.12 (m, 1H), 1.86-1.76 (m, 2H), 1.72-

1.63 (m, 2H), 0.86 (t,  $J = 7.4$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  133.42, 132.37, 124.36, 11.76. HRMS (ESI) Calcd. For  $\text{C}_{17}\text{H}_{19}\text{Br}_2\text{N}_2$ :  $[\text{M}+\text{H}]^+$ , 408.9915, Found:  $m/z$  408.9923.

**(E)-1-(3-(pentan-3-yl)phenyl)-2-(p-tolyl)diazene (3ia, red oil):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (d, 2H), 7.71 (d, 2H), 7.42 (t, 1H), 7.31 (d, 2H), 7.22 (d, 1H), 2.48-2.40 (m, 4H), 1.75 (m, 2H), 1.67-1.62 (m, 2H), 0.82 (m, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.89, 150.90, 147.02, 141.30, 130.41, 129.69, 128.75, 122.72, 119.75, 49.70, 29.24, 12.19. HRMS(ESI) Calcd. For  $\text{C}_{18}\text{H}_{23}\text{N}_2$ :  $[\text{M}+\text{H}]^+$ , 267.1861, Found:  $m/z$  267.1865.

**(E)-1-(4-(tert-butyl)phenyl)-2-(3-(pentan-3-yl)phenyl)diazene (3ja, red oil):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (d,  $J = 8.6$  Hz, 2H), 7.71 (d,  $J = 7.0$  Hz, 2H), 7.53 (d,  $J = 8.6$  Hz, 2H), 7.41 (t,  $J = 8.0$  Hz, 1H), 7.23 (d,  $J = 4.9$  Hz, 1H), 2.44 (dt,  $J = 14.4$ , 4.6 Hz, 1H), 1.79-1.70 (m, 2H), 1.67-1.59 (m, 2H), 1.37 (s, 9H), 0.81 (t,  $J = 7.4$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  154.35, 152.97, 150.75, 147.02, 130.39, 128.75, 125.96, 122.73, 122.48, 119.70, 49.69, 34.98, 31.27, 29.24, 12.20. HRMS(ESI) Calcd. For  $\text{C}_{21}\text{H}_{29}\text{N}_2$ :  $[\text{M}+\text{H}]^+$ , 309.2331, Found:  $m/z$  309.2322.

**(E)-1,2-bis(3-(pentan-3-yl)phenyl)diazene (3ka, red oil):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 (d,  $J = 1.2$  Hz, 4H), 7.42 (t,  $J = 8.1$  Hz, 2H), 7.27-7.23 (m, 2H), 2.48-2.40 (m, 2H), 1.80-1.70 (m, 4H), 1.63 (ddd,  $J = 13.7$ , 9.0, 7.3 Hz, 4H), 0.81 (t,  $J = 7.4$  Hz, 12H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.92, 147.02, 130.55, 128.78, 122.68, 119.86, 49.72, 29.28, 12.22. HRMS (ESI) Calcd. For  $\text{C}_{22}\text{H}_{31}\text{N}_2$ :  $[\text{M}+\text{H}]^+$ , 323.2487, Found:  $m/z$  323.2480.

**(E)-1,2-bis(4-methoxy-3-(pentan-3-yl)phenyl)diazene (3la, red oil):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79-7.69 (m, 4H), 6.95 (d, 2H), 3.88 (s, 6H), 2.99 (m, 2H), 1.70 (m, 8H), 0.81 (t,  $J = 7.4$  Hz, 12H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.89, 147.04, 134.78, 122.50, 121.14, 110.42, 55.71, 41.05, 27.98, 12.05. HRMS (ESI) Calcd. For  $\text{C}_{24}\text{H}_{35}\text{N}_2\text{O}_2$ :  $[\text{M}+\text{H}]^+$ , 383.2699, Found:  $m/z$  383.2699.

**(E)-1,2-bis(2-(pentan-3-yl)-[1,1'-biphenyl]-4-yl)diazene (3ma, red oil):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J = 1.8$  Hz, 2H), 7.78 (dd,  $J = 8.1$ , 1.8 Hz, 2H), 7.45 (t,  $J = 7.2$  Hz, 4H), 7.40 (d,  $J = 7.0$  Hz, 2H), 7.35 (d,  $J = 8.2$  Hz, 2H), 7.33-7.29 (m, 4H),

2.76-2.66 (m, 2H), 1.69 (dq, J = 14.2, 7.0 Hz, 8H), 0.77 (t, J = 7.4 Hz, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.51, 145.71, 144.76, 141.71, 130.61, 129.55, 127.93, 126.89, 122.24, 118.01, 43.56, 29.77, 12.21. HRMS(ESI) Calcd. For C<sub>34</sub>H<sub>39</sub>N<sub>2</sub>: [M+H]<sup>+</sup>, 475.3113, Found: m/z 475.3103.

**(R,E)-1-(3-(pentan-2-yl)phenyl)-2-phenyldiazene (3ab, red oil):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.97–7.90 (m, 2H), 7.80–7.72 (m, 2H), 7.57–7.42 (m, 4H), 7.33 (d, J = 7.6 Hz, 1H), 2.89 – 2.80 (m, 1H), 1.70–1.60 (m, 2H), 1.36–1.24 (m, 5H), 0.91 (t, J = 7.3 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.83, 149.14, 130.80, 129.87, 128.98, 122.77, 121.78, 120.06, 40.59, 39.67, 22.20, 20.79, 14.11. HRMS(ESI) Calcd. For C<sub>17</sub>H<sub>21</sub>N<sub>2</sub>: [M+H]<sup>+</sup>, 253.1705, Found: m/z 253.1700.

**(E)-1-(3-cyclohexylphenyl)-2-phenyldiazene (3ac, red oil):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.94 (dd, J = 7.0, 5.0 Hz, 2H), 7.81 (s, 1H), 7.76 (d, J = 7.8 Hz, 1H), 7.57 – 7.44 (m, 4H), 7.35 (d, J = 7.4 Hz, 1H), 2.65 (t, J = 11.6 Hz, 1H), 1.93 (dd, J = 30.4, 12.3 Hz, 4H), 1.79 (d, J = 12.6 Hz, 1H), 1.59 – 1.38 (m, 4H), 1.35 – 1.24 (m, 1H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.84, 149.22, 130.88, 129.73, 129.05, 122.80, 121.25, 120.41, 44.51, 34.37, 26.86, 26.12. HRMS (ESI) Calcd. For C<sub>18</sub>H<sub>21</sub>N<sub>2</sub>: [M+H]<sup>+</sup>, 265.1705, Found: m/z 265.1710.

**(E)-1-(3-cyclopentylphenyl)-2-phenyldiazene (3ad, red oil):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 – 7.88 (m, 2H), 7.81 (s, 1H), 7.76–7.70 (m, 1H), 7.55–7.41 (m, 4H), 7.36 (dd, J = 4.9, 2.7 Hz, 1H), 3.16–3.05 (m, 1H), 2.19–2.08 (m, 2H), 1.91–1.79 (m, 2H), 1.69 (tdd, J = 8.9, 6.6, 3.0 Hz, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.80, 147.77, 130.82, 129.99, 128.97, 122.78, 121.68, 120.15, 45.85, 34.59, 25.56. HRMS (ESI) Calcd. For C<sub>17</sub>H<sub>19</sub>N<sub>2</sub>: [M+H]<sup>+</sup>, 251.1548, Found: m/z 251.1547.

**(E)-1-phenyl-2-(3-(tetrahydro-2H-pyran-4-yl)phenyl)diazene (3ae, red oil):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 – 7.89 (m, 2H), 7.82 – 7.75 (m, 2H), 7.56 – 7.43 (m, 4H), 7.35 (d, J = 7.7 Hz, 1H), 4.16 – 4.07 (m, 2H), 3.56 (td, J = 11.5, 2.6 Hz, 2H), 2.93 – 2.83 (m, 1H), 1.89 (ddd, J = 24.2, 10.7, 7.9 Hz, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.93, 152.69, 147.00, 130.98, 129.47, 129.16, 122.82, 121.07, 68.34, 41.51, 33.85. HRMS (ESI) Calcd. For C<sub>17</sub>H<sub>19</sub>N<sub>2</sub>O: [M+H]<sup>+</sup>, 267.1497, Found: m/z 267.1494.

**(S,E)-methyl 2-(3-(phenyldiazenyl)phenyl)propanoate (3af, red oil):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 – 7.88 (m, 3H), 7.87 (s, 1H), 7.53 – 7.43 (m, 5H), 3.85 (dd,  $J = 14.5, 7.3$  Hz, 1H), 3.69 (s, 3H), 1.58 (d,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.68, 152.89, 141.64, 131.05, 130.07, 129.34, 129.08, 128.27, 122.86, 122.11, 121.66, 52.15, 45.34, 18.52. HRMS (ESI) Calcd. For  $\text{C}_{16}\text{H}_{17}\text{N}_2\text{O}_2$ :  $[\text{M}+\text{H}]^+$ , 269.1290, Found:  $m/z$  269.1297.

**(E)-1-(3-(tert-butyl)phenyl)-2-phenyldiazene (3ag, red oil):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (d,  $J = 1.5$  Hz, 1H), 7.94 (d,  $J = 7.1$  Hz, 3H), 7.75 (dd,  $J = 7.7, 1.2$  Hz, 1H), 7.54 (dd,  $J = 9.3, 3.2$  Hz, 4H), 1.43 (d,  $J = 1.2$  Hz, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.70, 152.39, 130.89, 129.08, 128.74, 128.13, 122.77, 120.94, 119.13, 34.93, 31.33. HRMS (ESI) Calcd. For  $\text{C}_{16}\text{H}_{19}\text{N}_2$ :  $[\text{M}+\text{H}]^+$ , 239.1548, Found:  $m/z$  239.1548.

**(E)-1-(3-((3r,5r,7r)-adamantan-1-yl)phenyl)-2-phenyldiazene (3ah, yellow solid):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 – 7.85 (m, 4H), 7.53 – 7.45 (m, 5H), 2.13 (s, 3H), 1.98 (dd,  $J = 14.2, 2.6$  Hz, 6H), 1.86 – 1.74 (m, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  154.75, 152.86, 150.67, 130.97, 130.68, 129.06, 128.75, 127.76, 125.60, 122.73, 120.45, 119.41, 43.11, 36.75, 28.92. HRMS (ESI) Calcd. For  $\text{C}_{22}\text{H}_{25}\text{N}_2$ :  $[\text{M}+\text{H}]^+$ , 317.2018, Found:  $m/z$  317.2011.

**(E)-methyl 2-methyl-2-(3-(phenyldiazenyl)phenyl)propanoate (3ai, red oil):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 – 7.94 (m, 2H), 7.93 (s, 1H), 7.81 (d,  $J = 6.8$  Hz, 1H), 7.56 – 7.47 (m, 5H), 3.70 (s, 3H), 1.68 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.96, 152.72 (d,  $J = 8.3$  Hz), 145.89, 131.00, 129.08, 128.47, 122.84, 121.05, 120.52, 52.32, 46.63, 26.56. HRMS (ESI) Calcd. For  $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_2$ :  $[\text{M}+\text{H}]^+$ , 283.1447, Found:  $m/z$  283.1448.

**(E)-1,2-bis(3-(s-pentan-2-yl)phenyl)diazene (3aj, red oil):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 – 7.68 (m, 4H), 7.42 (t,  $J = 7.7$  Hz, 2H), 7.29 (d,  $J = 7.6$  Hz, 2H), 2.82 (dd,  $J = 14.2, 7.0$  Hz, 2H), 1.65 – 1.58 (m, 4H), 1.31 – 1.29 (m, 6H), 0.89 (t,  $J = 7.3$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.96, 149.10, 129.72, 128.91, 121.73, 120.00, 40.61, 39.69, 22.23, 20.81, 14.13. HRMS (ESI) Calcd. For  $\text{C}_{22}\text{H}_{31}\text{N}_2$ :  $[\text{M}+\text{H}]^+$ , 323.2487, Found:  $m/z$  323.2488.



**(E)-1-(2-octylphenyl)-2-phenyldiazene (3ak, red oil):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J = 7.2$  Hz, 2H), 7.67 (d,  $J = 7.9$  Hz, 1H), 7.57 – 7.46 (m, 3H), 7.43 – 7.34 (m, 2H), 7.32 – 7.28 (m, 1H), 3.20 – 3.10 (m, 2H), 1.75 – 1.65 (m, 2H), 1.41 – 1.24 (m, 10H), 0.87 (t,  $J = 6.8$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.02, 150.37, 142.95, 130.97, 130.72, 130.49, 129.06, 126.44, 122.96, 115.31, 32.18, 31.88, 31.41, 29.67 – 29.07, 22.65, 14.09. HRMS (ESI) Calcd. For  $\text{C}_{20}\text{H}_{27}\text{N}_2$ :  $[\text{M}+\text{H}]^+$ , 295.2174, Found:  $m/z$  295.2172

**(E)-1-phenyl-2-(2-(3-phenylpropyl)phenyl)diazene (3al, red oil):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 – 7.83 (m, 2H), 7.68 (d,  $J = 8.0$  Hz, 1H), 7.52 (tdd,  $J = 6.7, 4.5, 2.4$  Hz, 3H), 7.43 – 7.35 (m, 2H), 7.30 (d,  $J = 1.5$  Hz, 2H), 7.20 (d,  $J = 6.7$  Hz, 4H), 3.22 – 3.15 (m, 2H), 2.75 – 2.70 (m, 2H), 2.07 – 2.00 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.94, 150.30, 142.30, 131.59 – 131.10 (m), 130.91 (d), 130.53, 129.06, 128.51, 128.27, 126.64, 125.67, 122.99, 120.66, 115.36, 35.76, 33.71, 31.09. HRMS (ESI) Calcd. For  $\text{C}_{21}\text{H}_{21}\text{N}_2$ :  $[\text{M}+\text{H}]^+$ , 301.1705, Found:  $m/z$  301.1703

**(E)-1-(2,6-dioctylphenyl)-2-phenyldiazene (3am, red oil):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (dd,  $J = 8.1, 1.5$  Hz, 2H), 7.59 – 7.51 (m, 3H), 7.20 (dd,  $J = 8.7, 6.1$  Hz, 1H), 7.16 – 7.11 (m, 2H), 2.69 – 2.60 (m, 4H), 1.57 – 1.51 (m, 4H), 1.30 – 1.21 (m, 20H), 0.87 (t,  $J = 6.9$  Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.81, 151.37, 135.11, 130.97, 129.11, 128.17, 127.83, 122.50, 31.94, 31.27, 29.78 – 29.02, 22.63, 14.09. HRMS (ESI) Calcd. For  $\text{C}_{28}\text{H}_{43}\text{N}_2$ :  $[\text{M}+\text{H}]^+$ , 407.3426, Found:  $m/z$  407.3428

**(E)-1-(2,6-bis(3-phenylpropyl)phenyl)-2-phenyldiazene (3an, red oil):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 – 7.73 (m, 2H), 7.51 (dd,  $J = 5.2, 1.9$  Hz, 3H), 7.22 – 7.16 (m, 5H), 7.12 (dt,  $J = 8.2, 5.0$  Hz, 8H), 2.73 – 2.67 (m, 4H), 2.61 (t,  $J = 7.6$  Hz, 4H), 1.92 – 1.82 (m, 4H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  152.79, 151.20, 142.29, 134.87, 131.04, 129.17, 128.44 (d), 128.15 (d), 125.62, 122.56, 35.85, 32.85, 31.84. HRMS (ESI) Calcd. For  $\text{C}_{30}\text{H}_{31}\text{N}_2$ :  $[\text{M}+\text{H}]^+$ , 419.2487, Found:  $m/z$  419.2485.

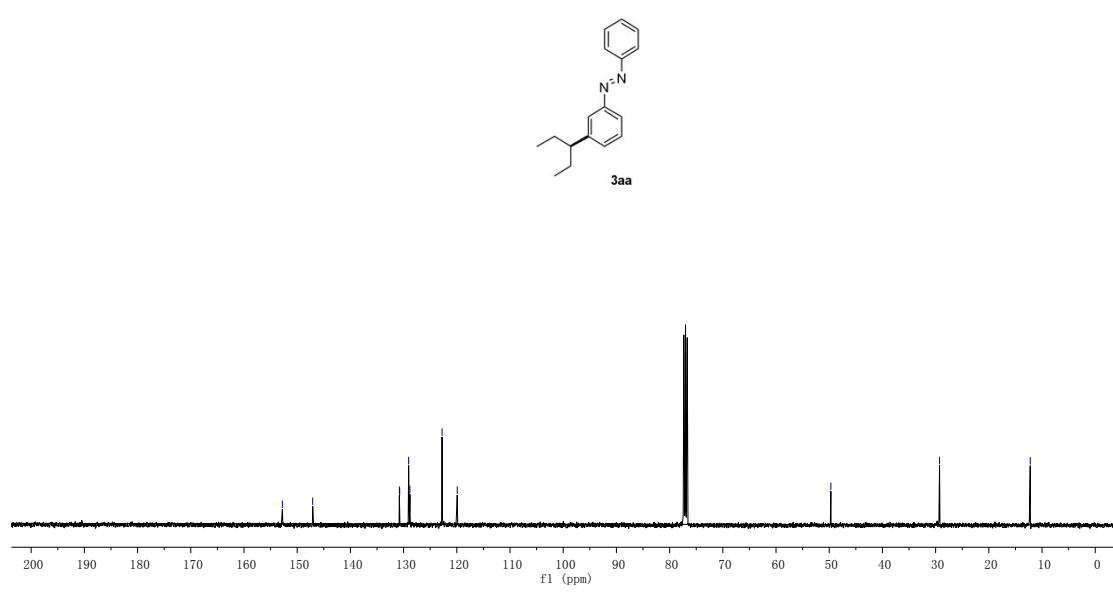
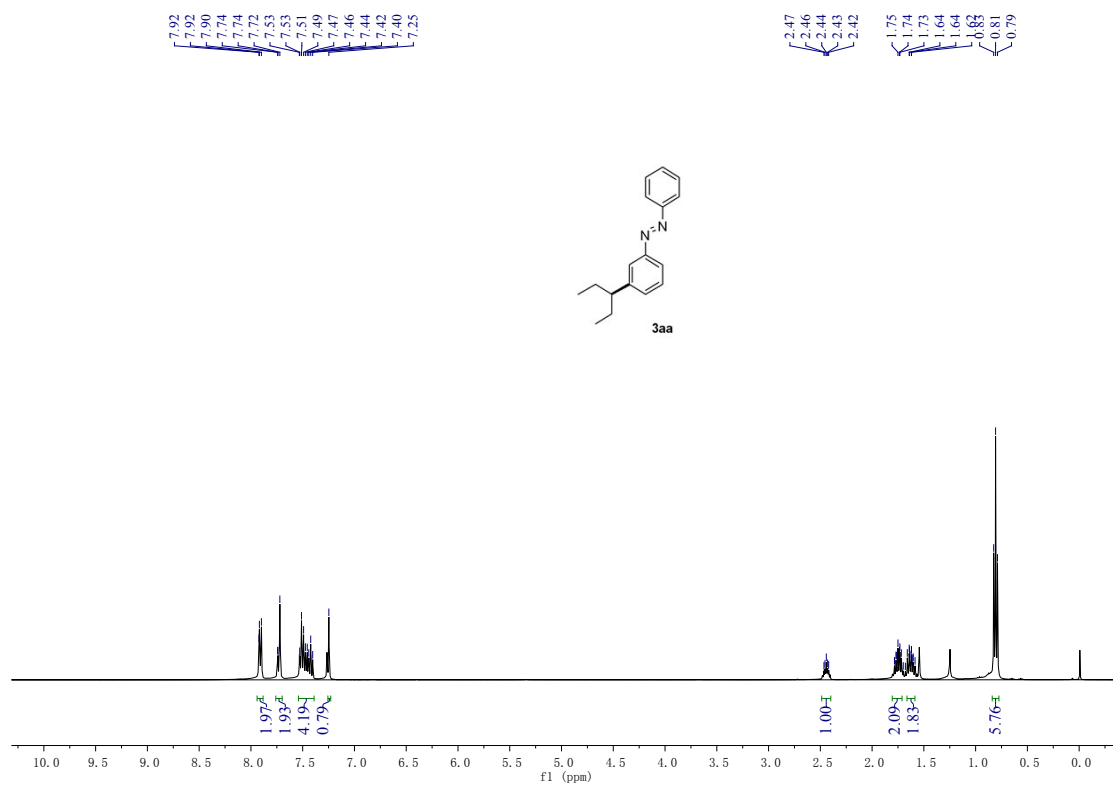
**(E)-1-(3-(pentan-3-yl)phenyl)-2-(3-tosylphenyl)diazene (6, orange red solid):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.48 (s, 1H), 8.10 (d,  $J = 8.2$  Hz, 1H), 8.03 (d,  $J = 7.8$  Hz, 1H), 7.90 (d,  $J = 8.3$  Hz, 2H), 7.77 (d,  $J = 8.3$  Hz, 2H), 7.67 (d,  $J = 7.8$  Hz, 1H), 7.46 (t,  $J = 7.6$  Hz, 1H), 7.34 – 7.30 (m, 3H), 2.49 – 2.45 (m, 1H), 2.42 (s, 3H), 1.77 (dd,  $J$

= 14.1, 6.5 Hz, 2H), 1.67 – 1.62 (m, 2H), 0.83 (t, J = 7.4 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.90, 152.43, 147.28, 144.39, 143.29, 138.39, 131.65, 130.03 (d), 128.99 (d), 127.87, 127.22, 122.89, 121.62, 120.47, 49.65, 29.23, 21.57, 12.17. HRMS (ESI) Calcd. For C<sub>24</sub>H<sub>27</sub>N<sub>2</sub>O<sub>2</sub>S: [M+H]<sup>+</sup>, 407.1793, Found: *m/z* 407.1795.

**2-octylaniline (7, colorless oil):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.04 (t, J = 7.9 Hz, 2H), 6.75 (t, J = 7.4 Hz, 1H), 6.70 (d, J = 7.8 Hz, 1H), 3.73 (s, 2H), 2.55 – 2.44 (m, 2H), 1.62 (d, J = 7.7 Hz, 2H), 1.29 (s, 10H), 0.90 (t, J = 6.8 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.88, 129.41, 127.07, 126.79, 118.81, 115.58, 31.87, 31.30, 29.71, 29.50, 29.26, 28.77, 22.64, 14.06. HRMS (ESI) Calcd. For C<sub>14</sub>H<sub>24</sub>N: [M+H]<sup>+</sup>, 206.1909, Found: *m/z* 206.1905.

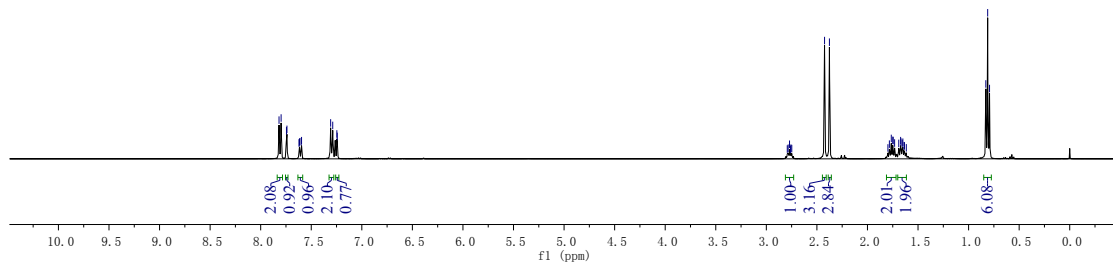
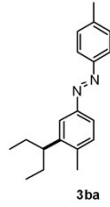
**3-(pentan-3-yl)aniline (8, colorless oil):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.09 (t, J = 7.7 Hz, 1H), 6.58 (d, J = 7.5 Hz, 1H), 6.56 – 6.52 (m, 1H), 6.51 (s, 1H), 3.47 (s, 2H), 2.28 – 2.17 (m, 1H), 1.67 (ddd, J = 13.0, 7.3, 5.6 Hz, 2H), 1.58 – 1.49 (m, 2H), 0.81 (t, J = 7.4 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 147.22, 128.94, 118.43, 114.74, 112.79, 49.76, 29.20, 12.27. HRMS (ESI) Calcd. For C<sub>11</sub>H<sub>18</sub>N: [M+H]<sup>+</sup>, 164.1439, Found: *m/z* 164.1432.

**Complex I (brown black solid):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.35 - 8.27 (m, 1H), 8.22 - 8.18 (m, 2H), 7.51 (d, J = 6.8 Hz, 4H), 7.24-7.15 (m, 2H), 5.70 (d, J = 6.2 Hz, 1H), 5.55 (d, J = 6.0 Hz, 1H), 5.18 (d, J = 6.2 Hz, 1H), 5.07 (d, J = 6.0 Hz, 1H), 2.29 (m, 1H), 2.12 (s, 3H), 0.91 (d, J = 6.9 Hz, 3H), 0.74 (d, J = 6.9 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 139.33, 130.64, 129.89, 128.37, 123.71, 123.08, 92.62, 86.59, 86.17, 30.90, 22.82, 21.27.

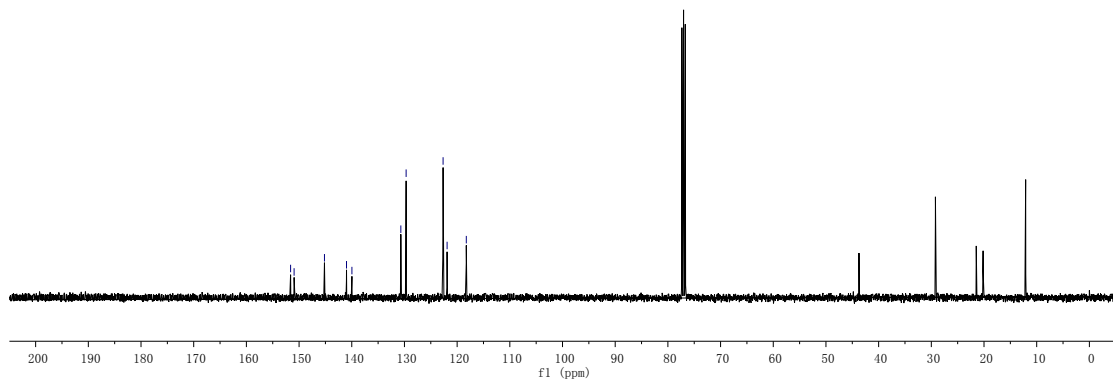
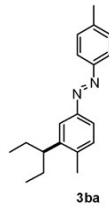


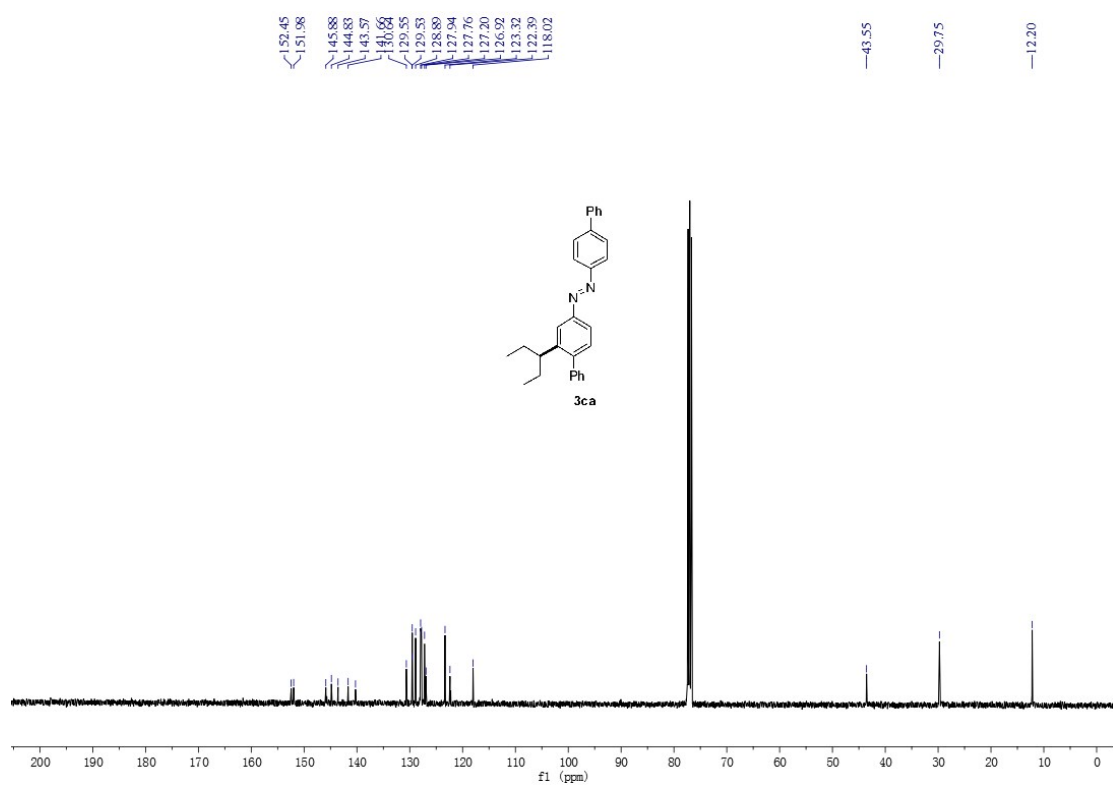
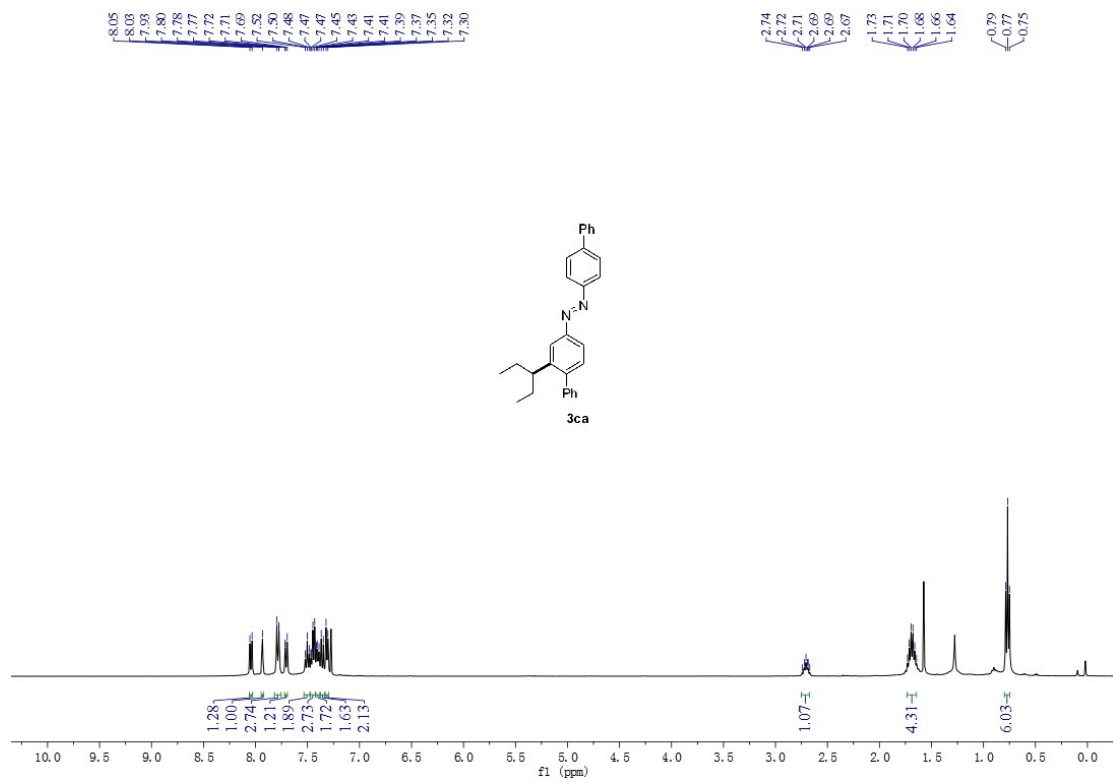
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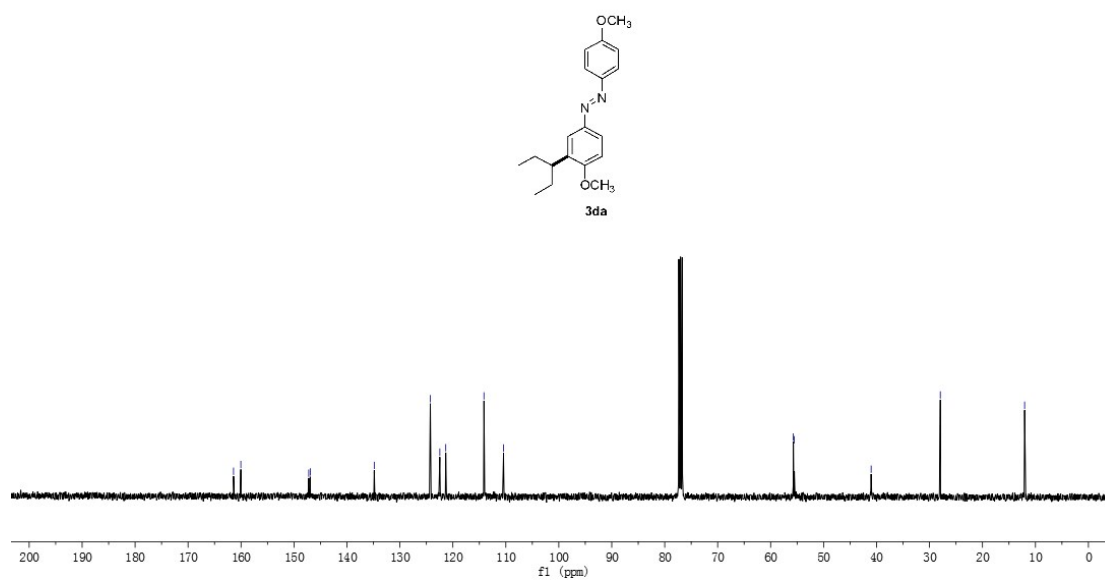
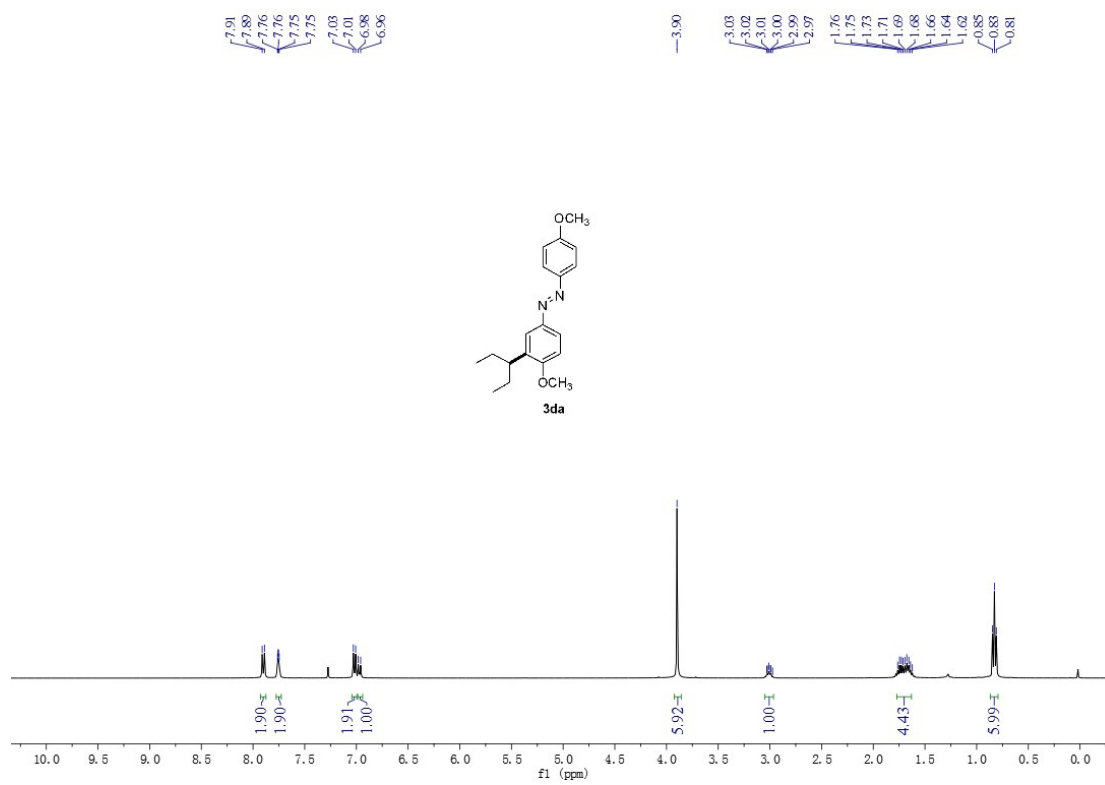
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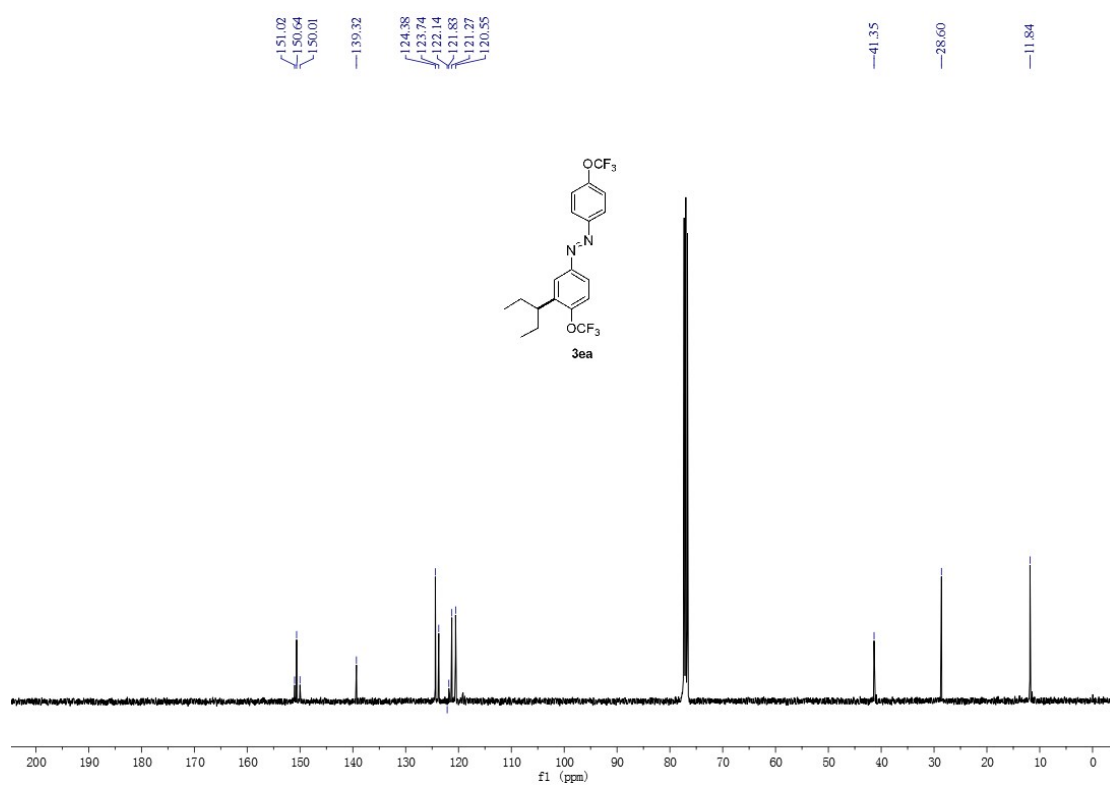
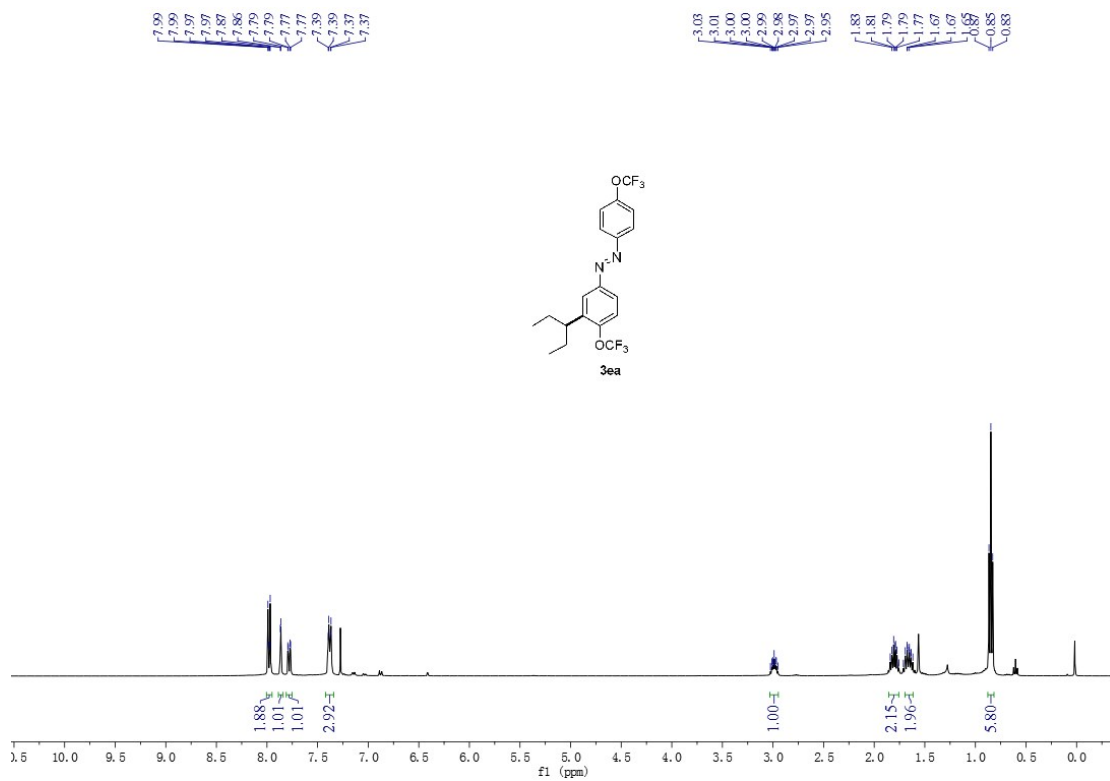


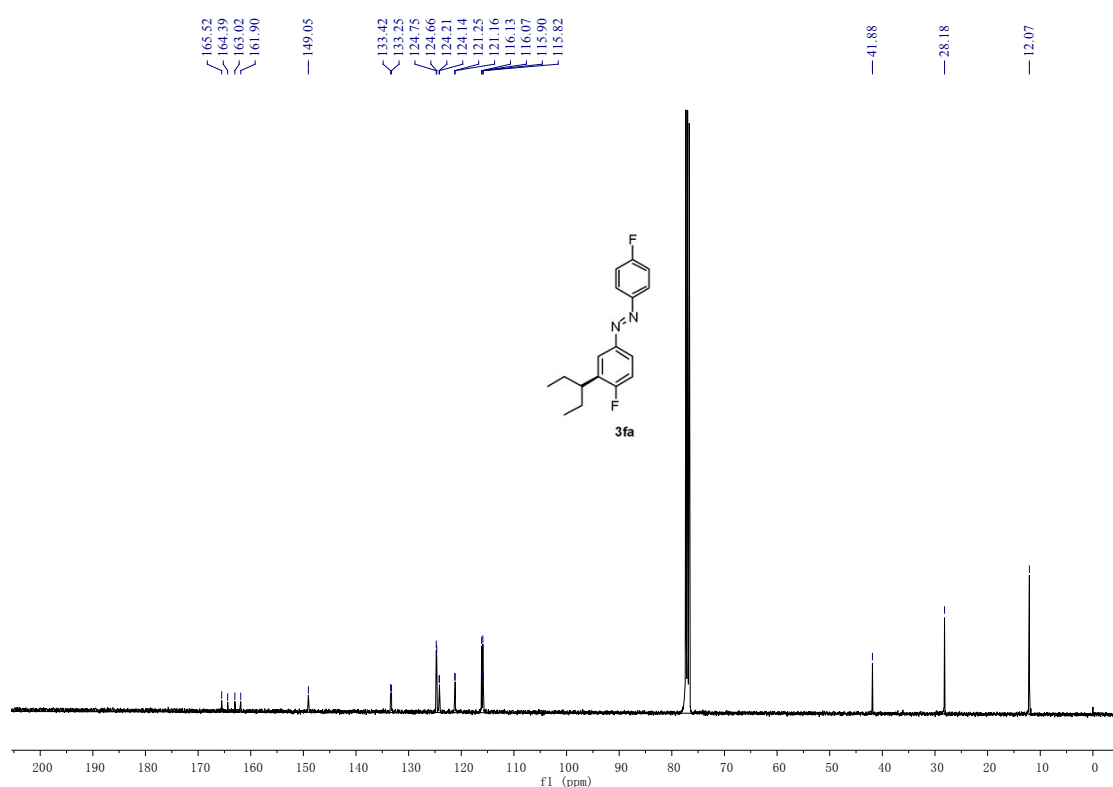
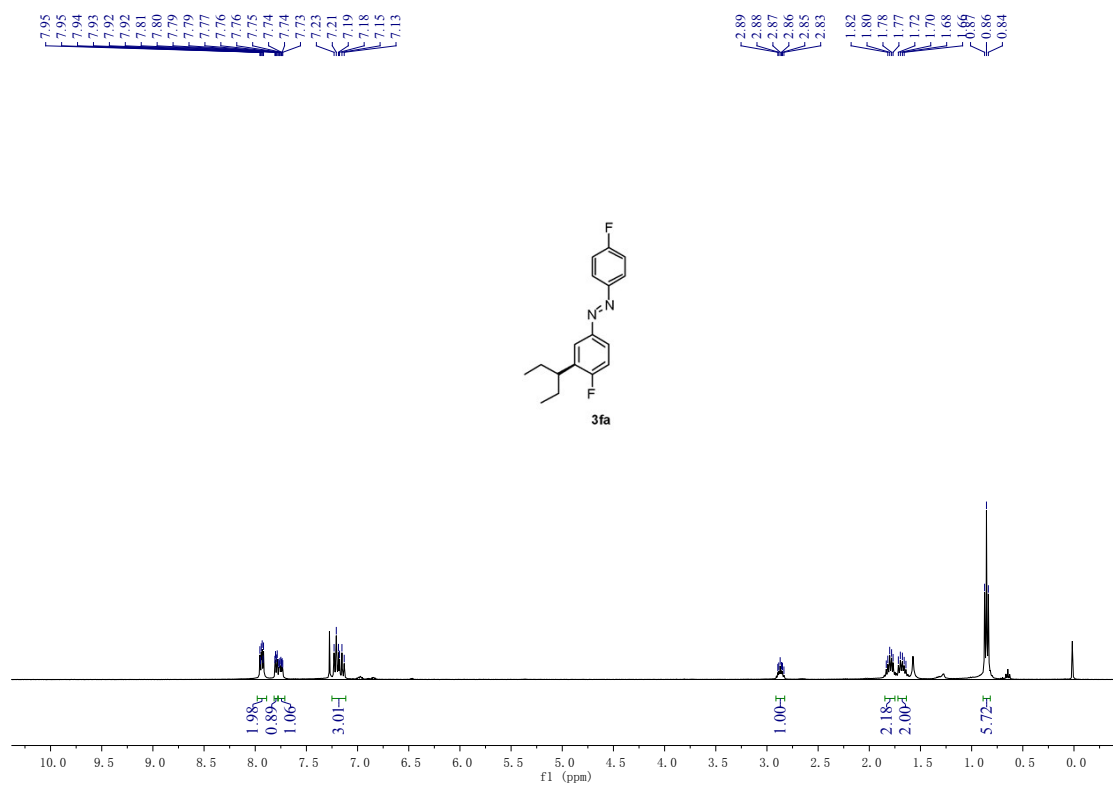
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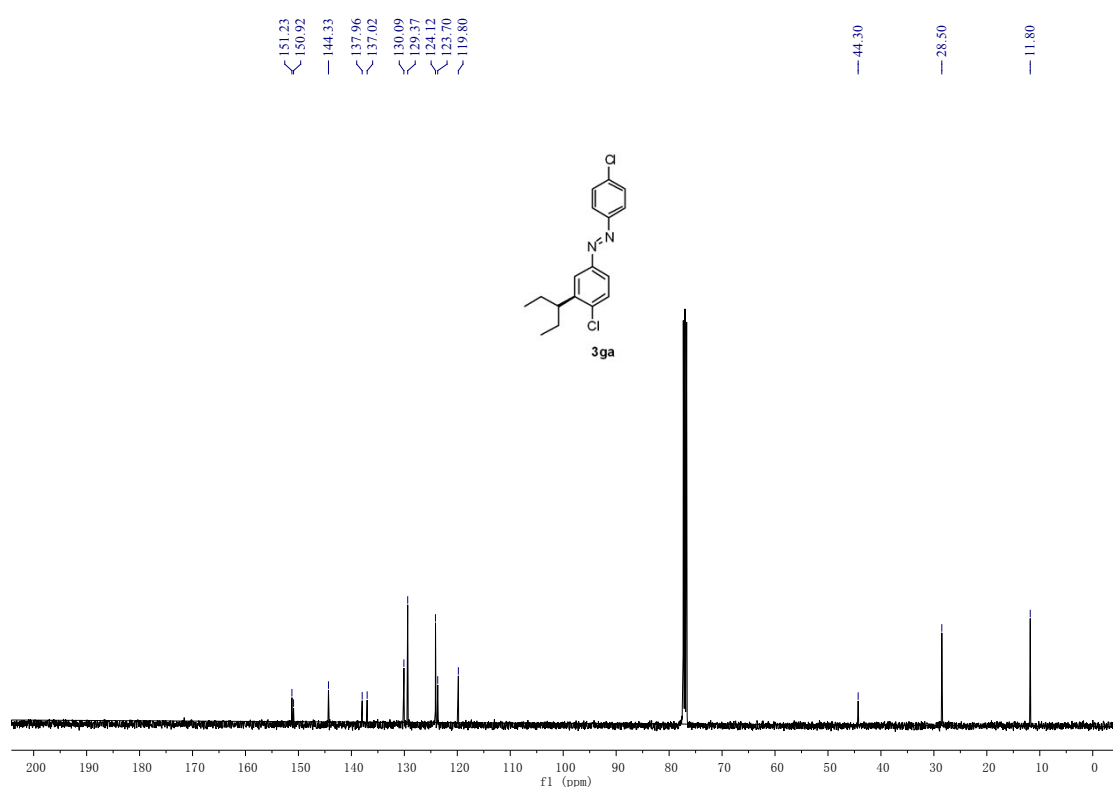
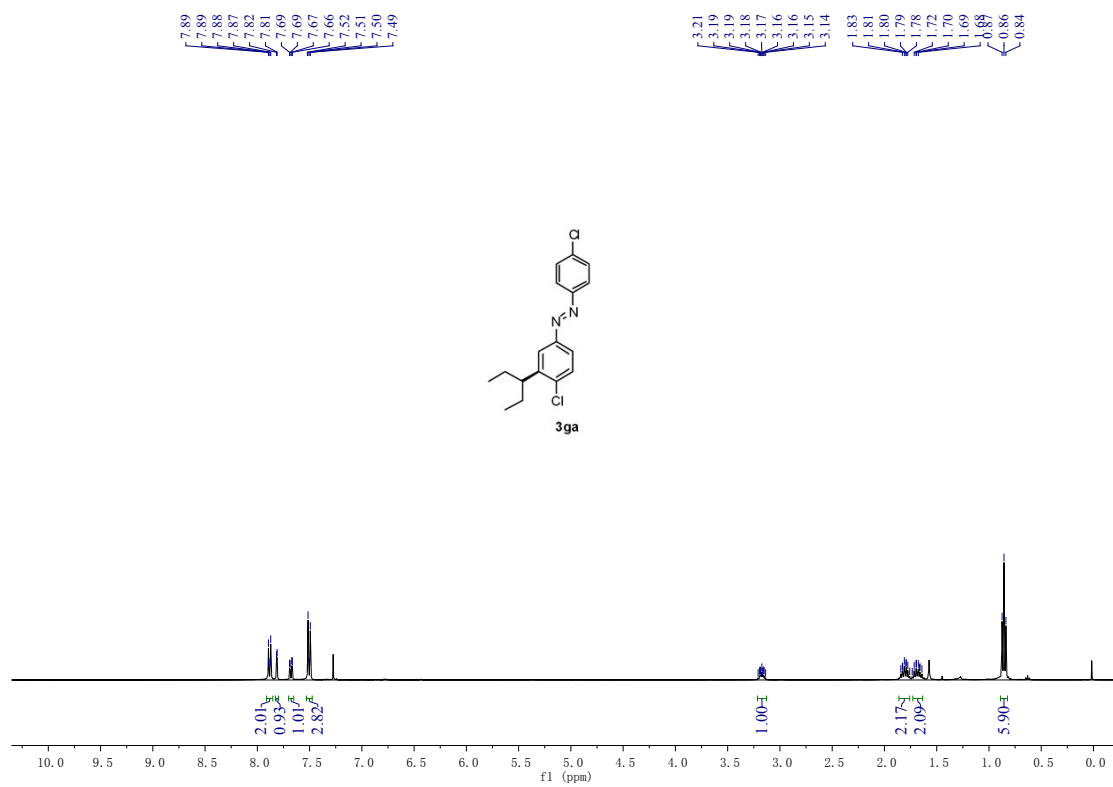






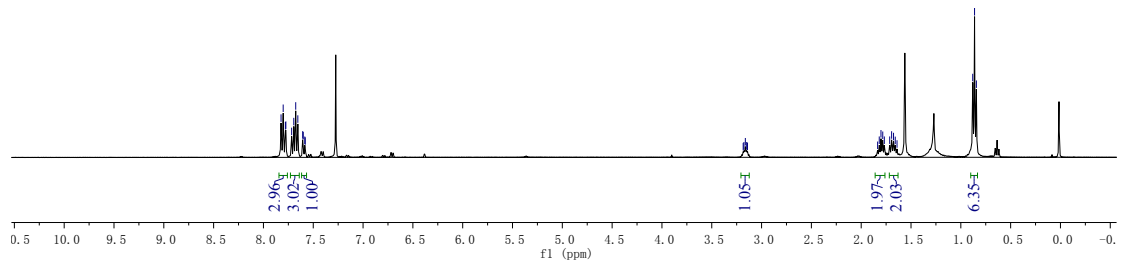
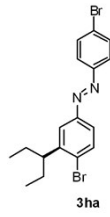






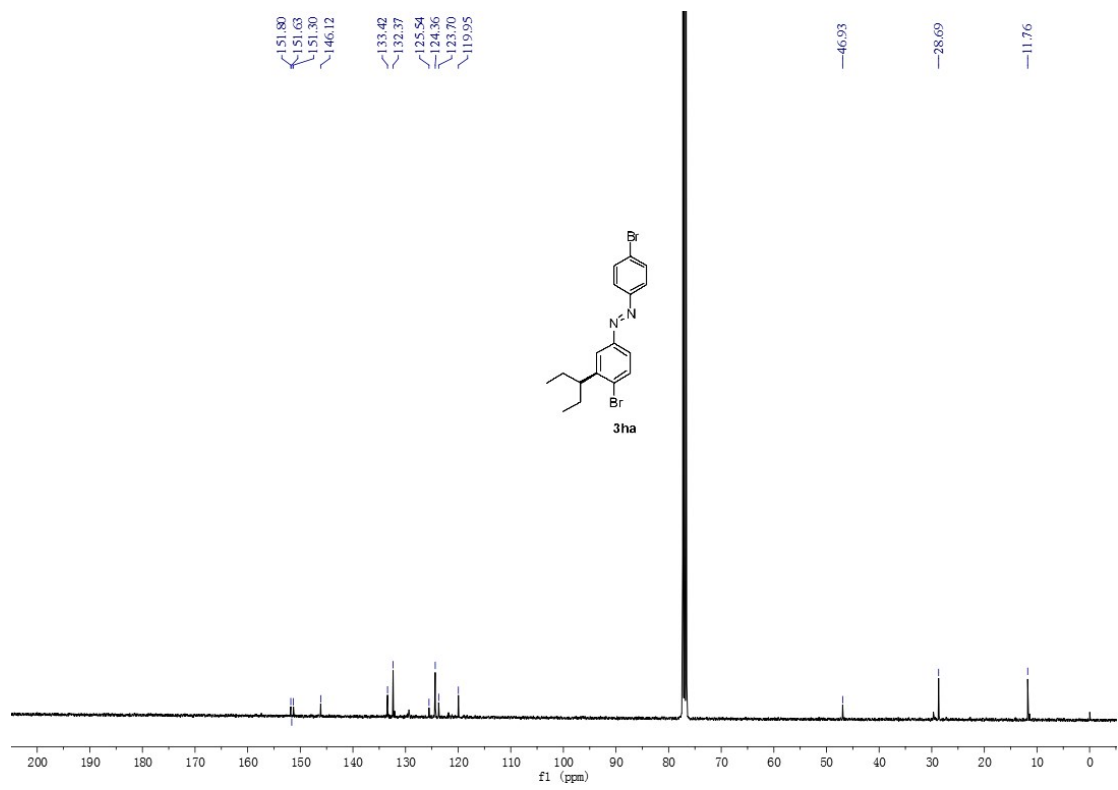
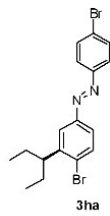
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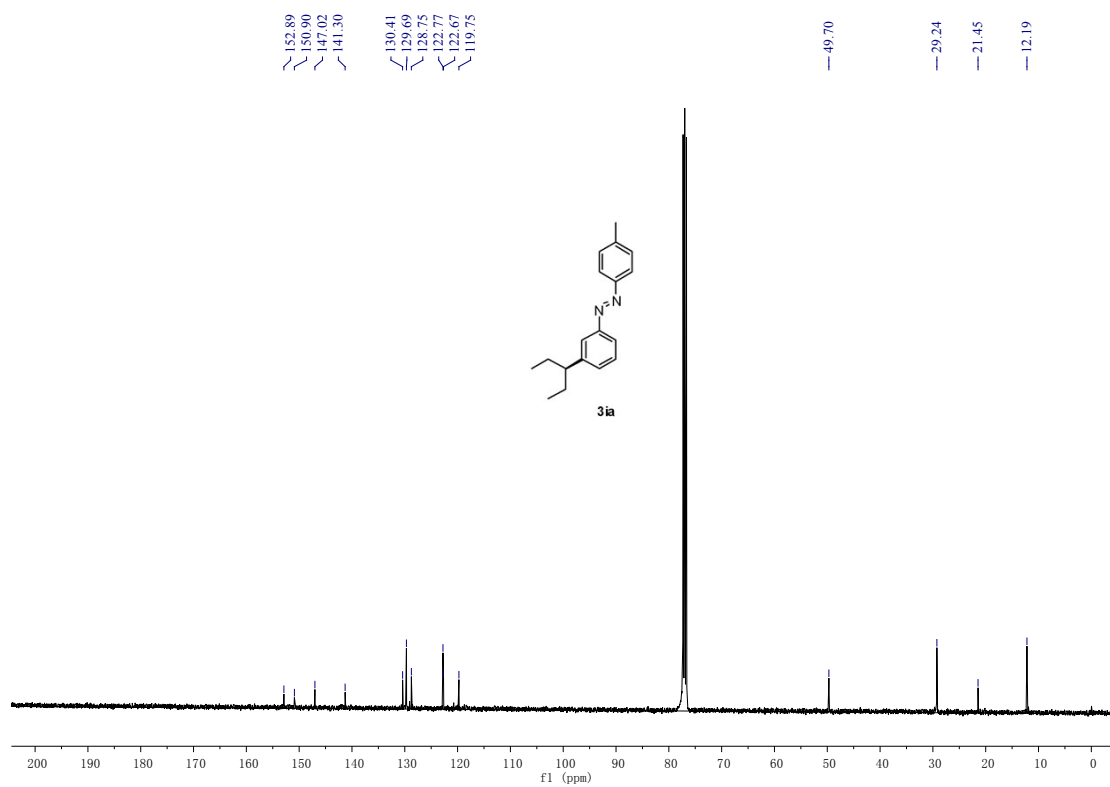
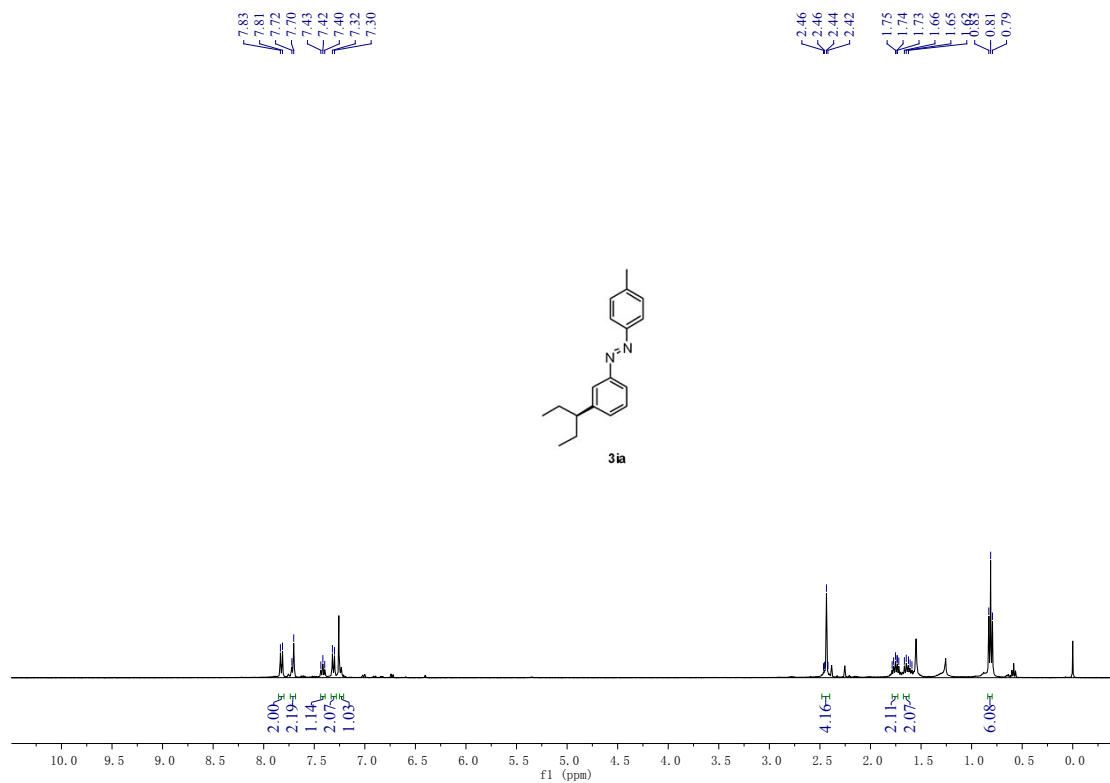
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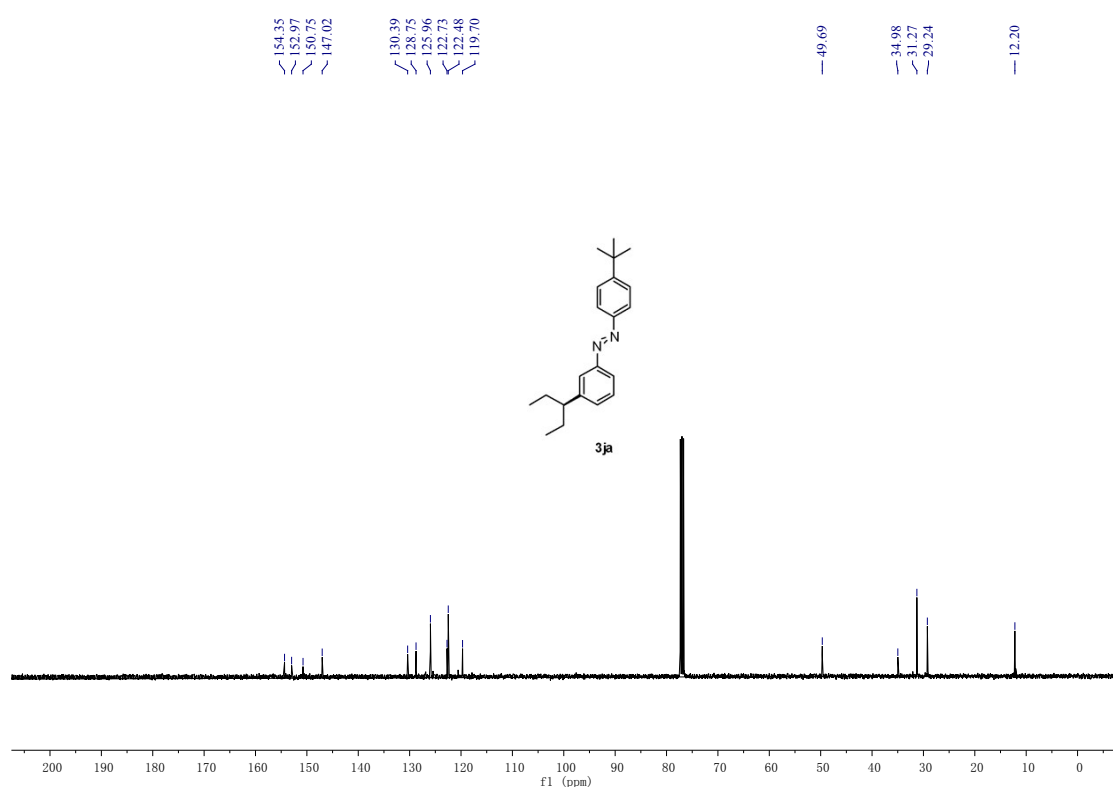
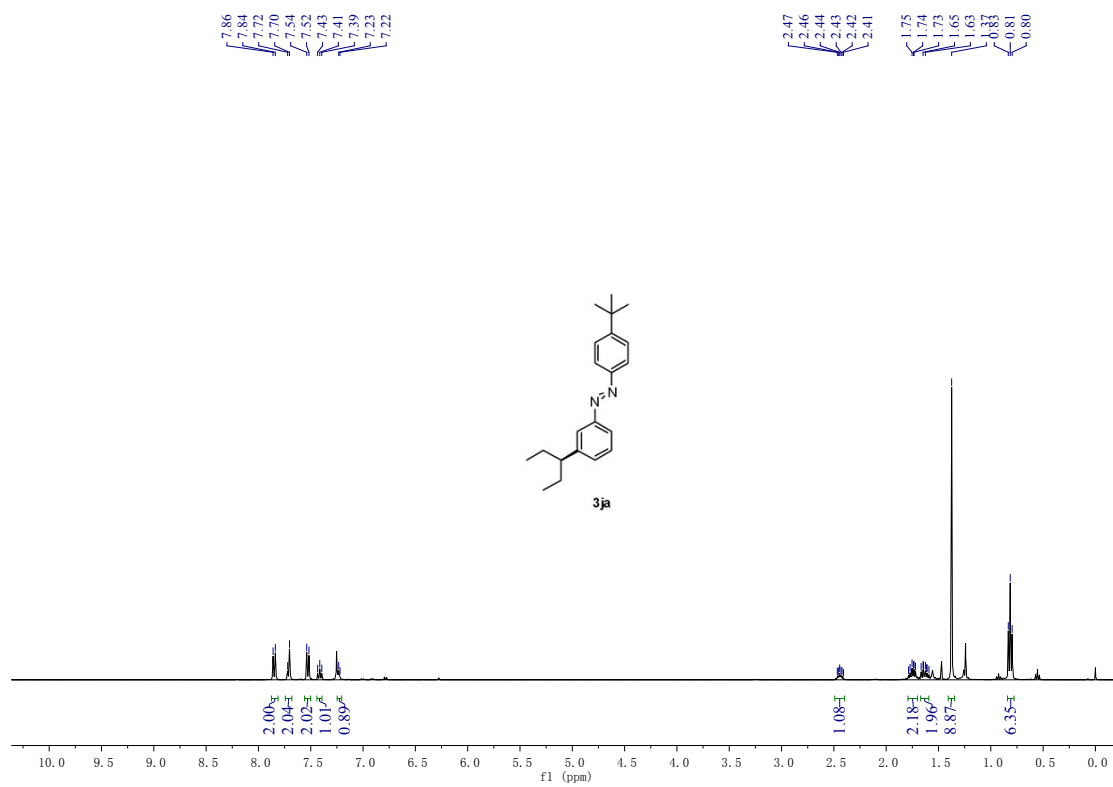


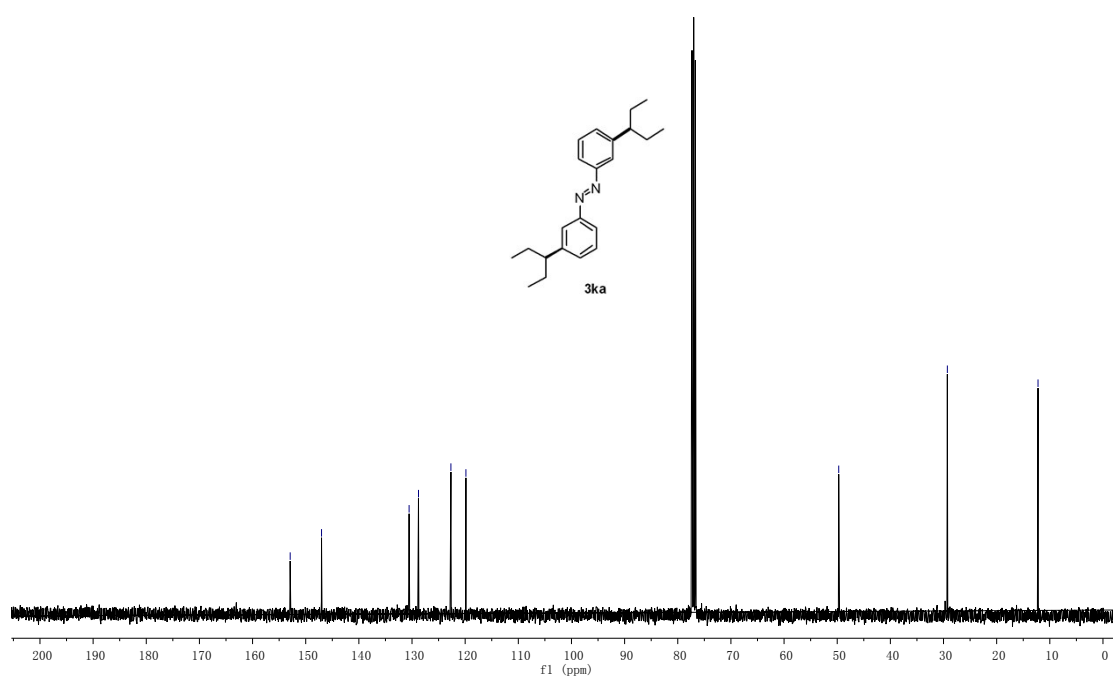
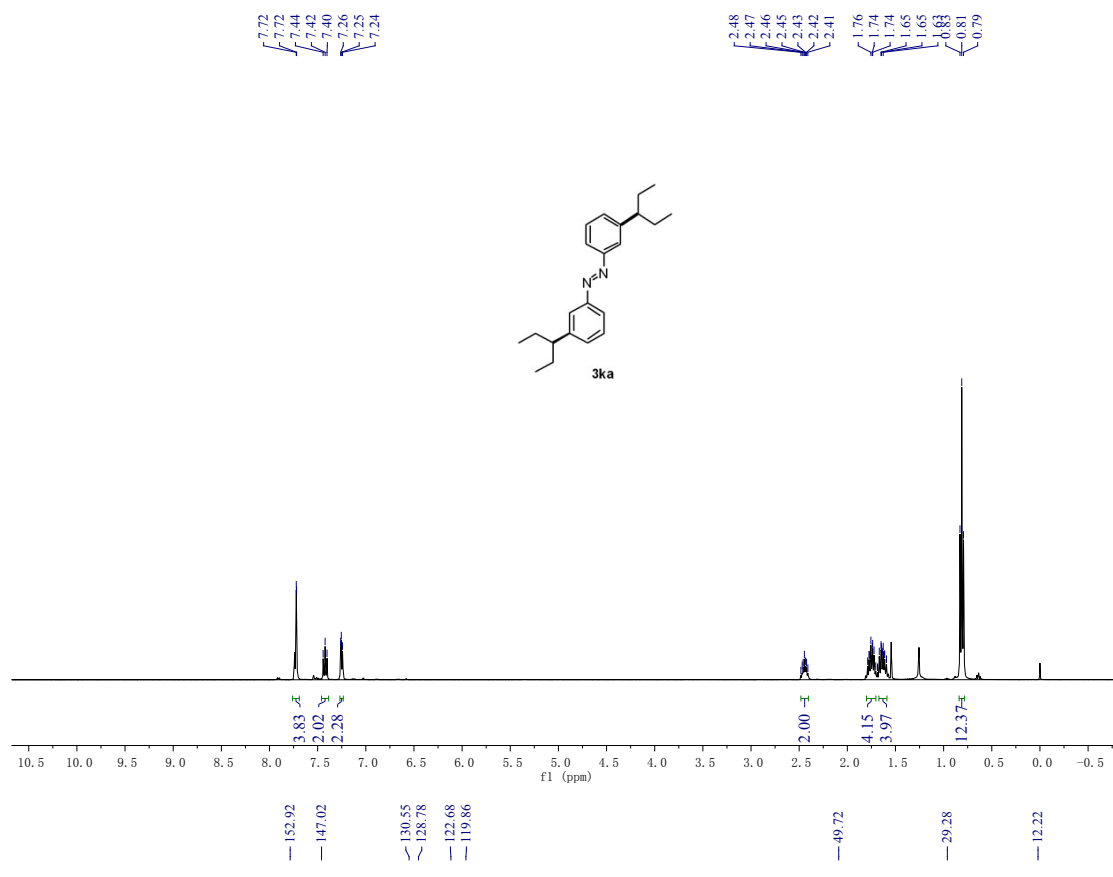
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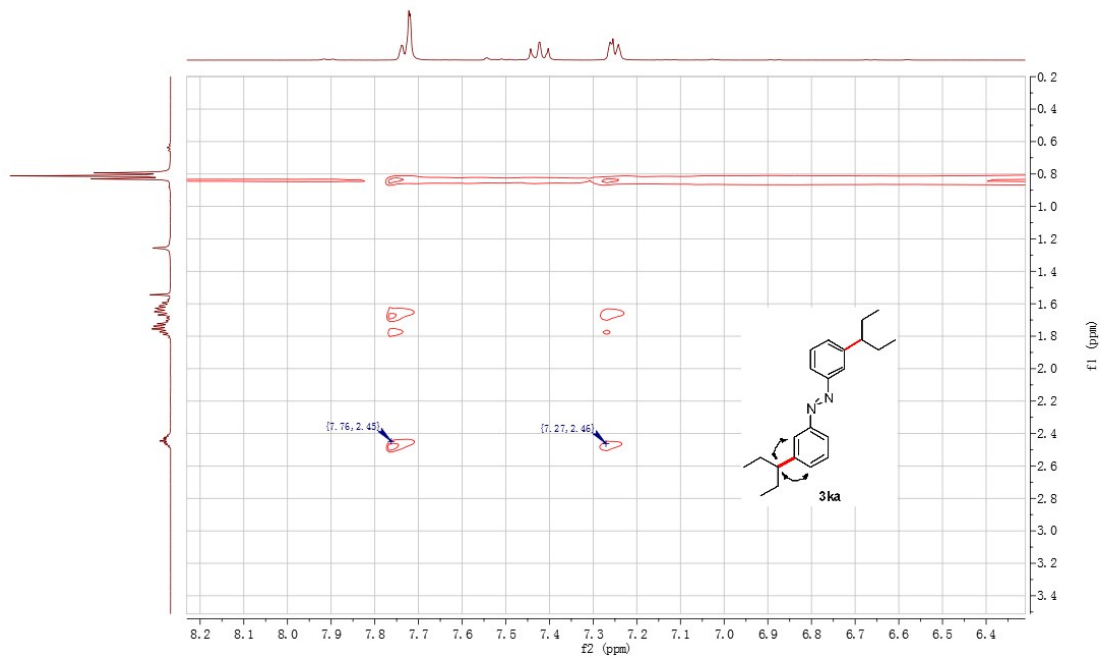
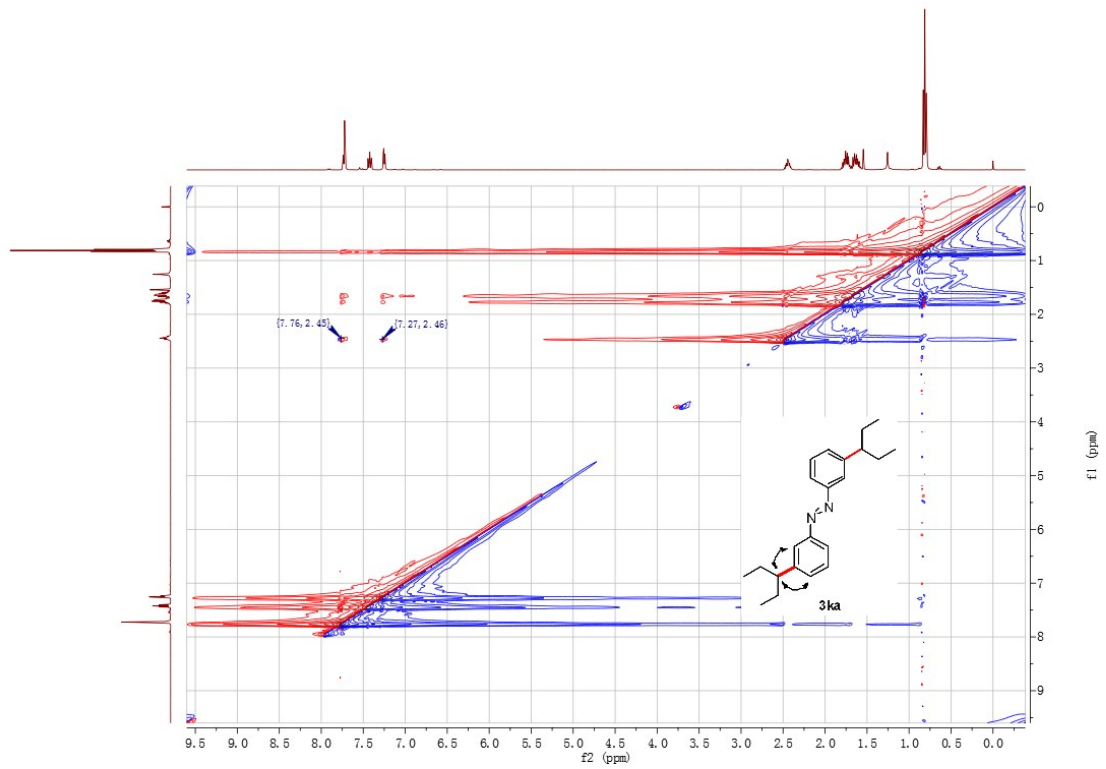
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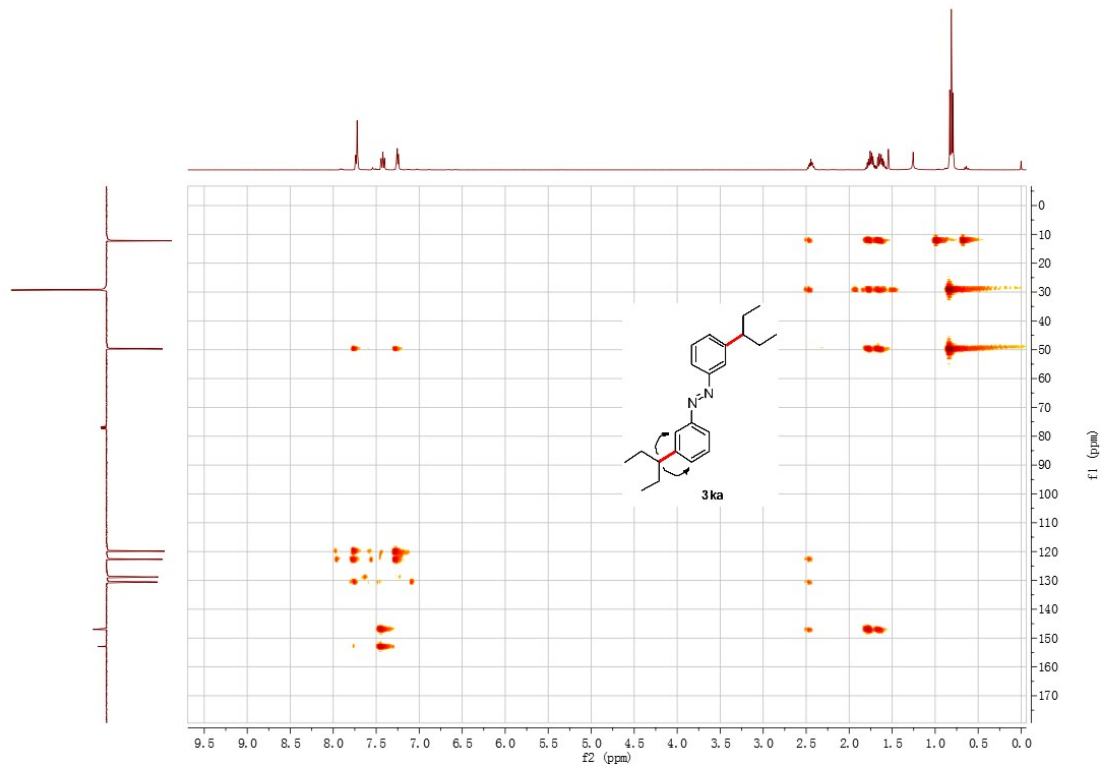




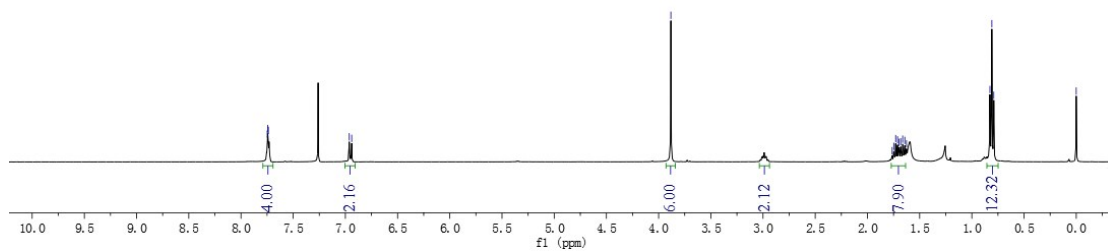
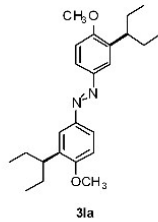


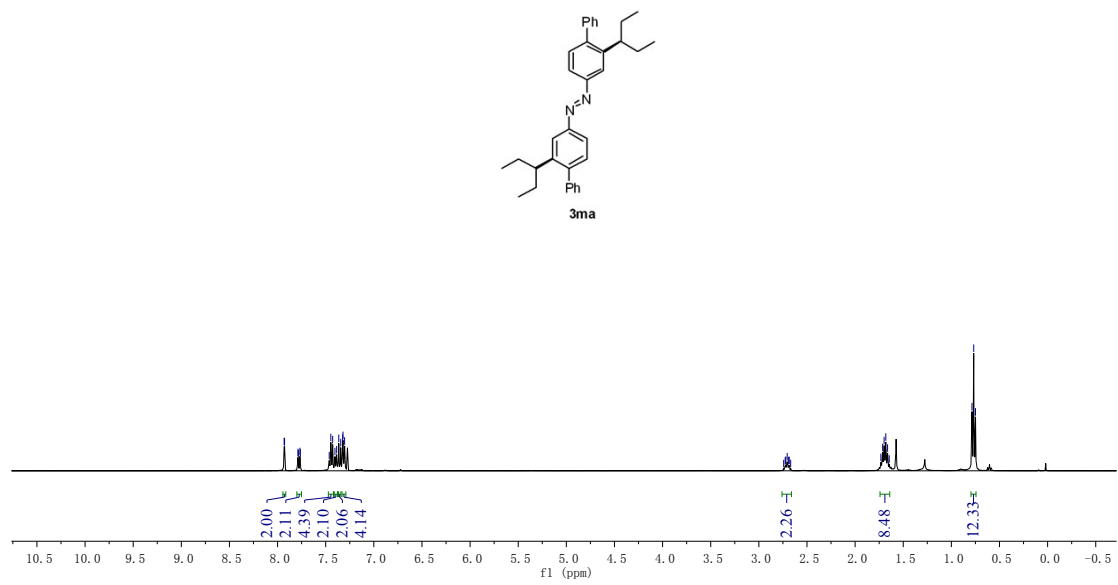
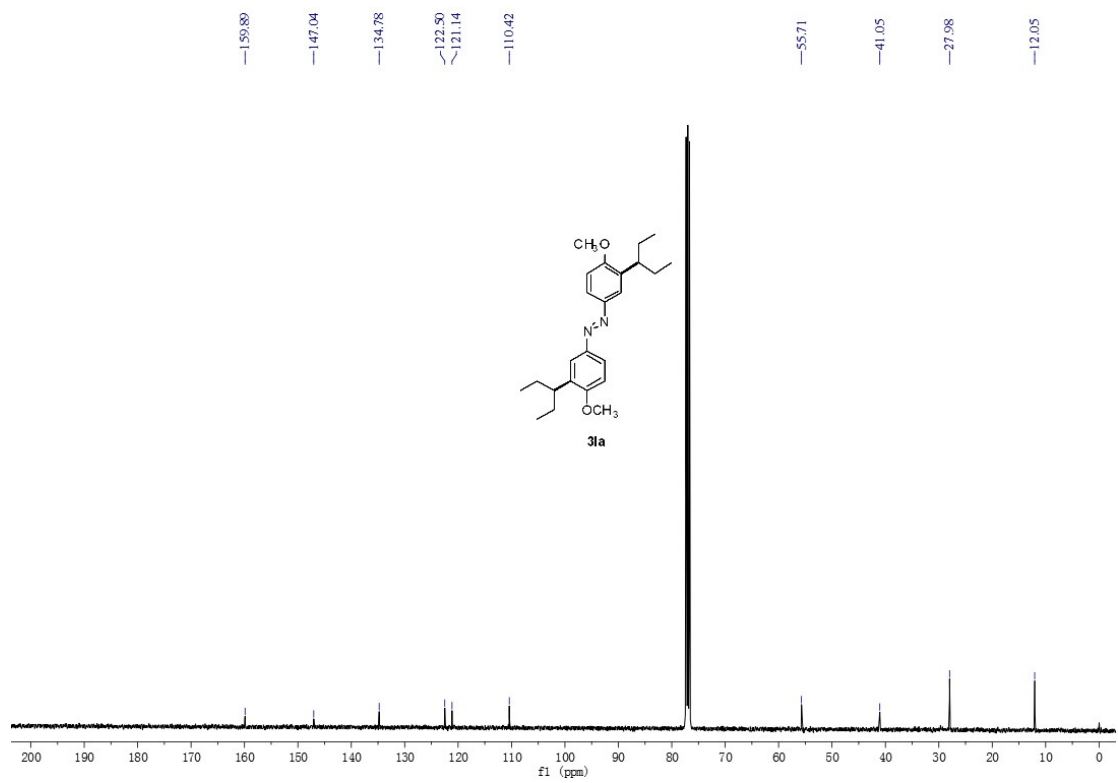




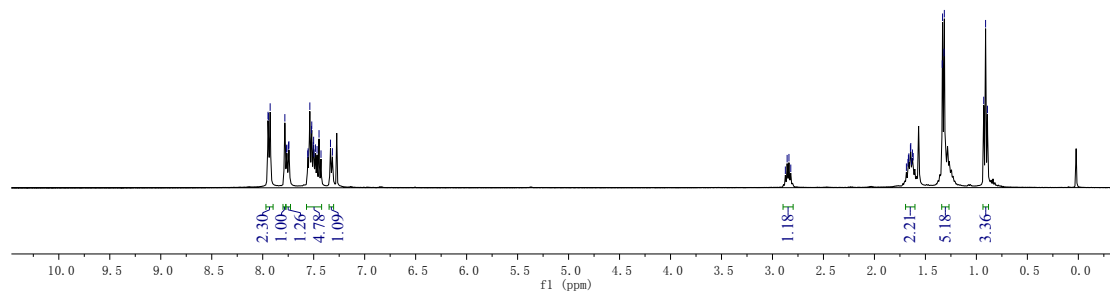
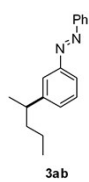
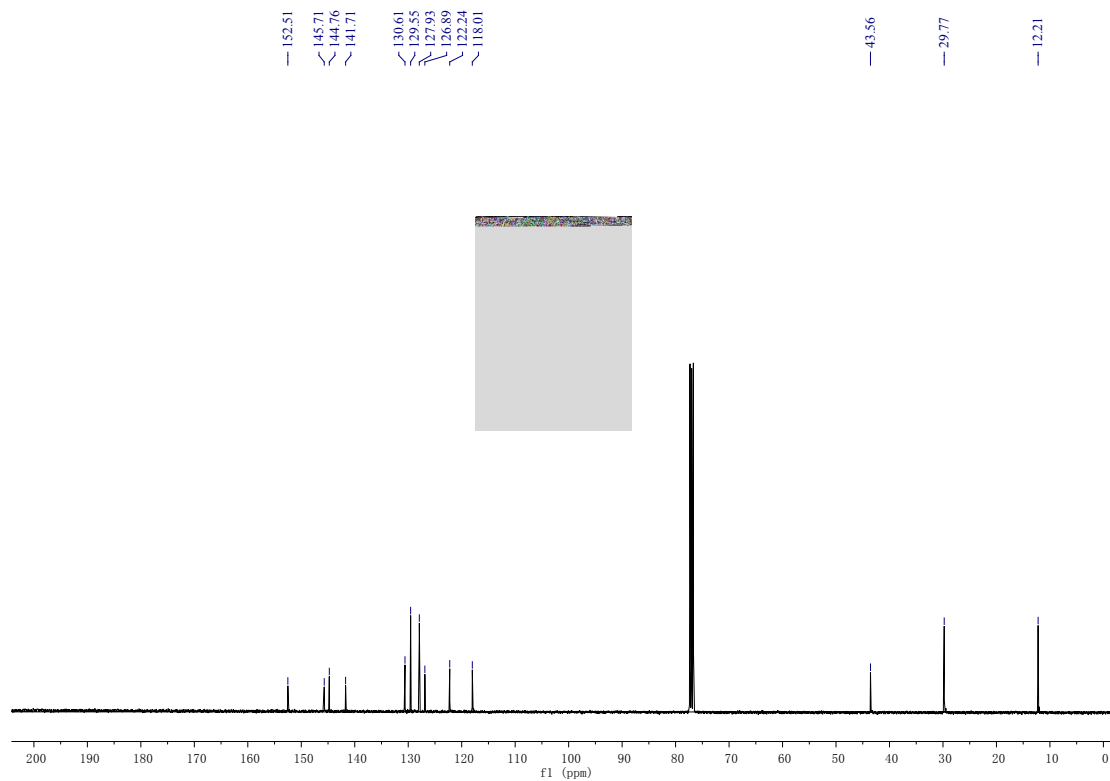


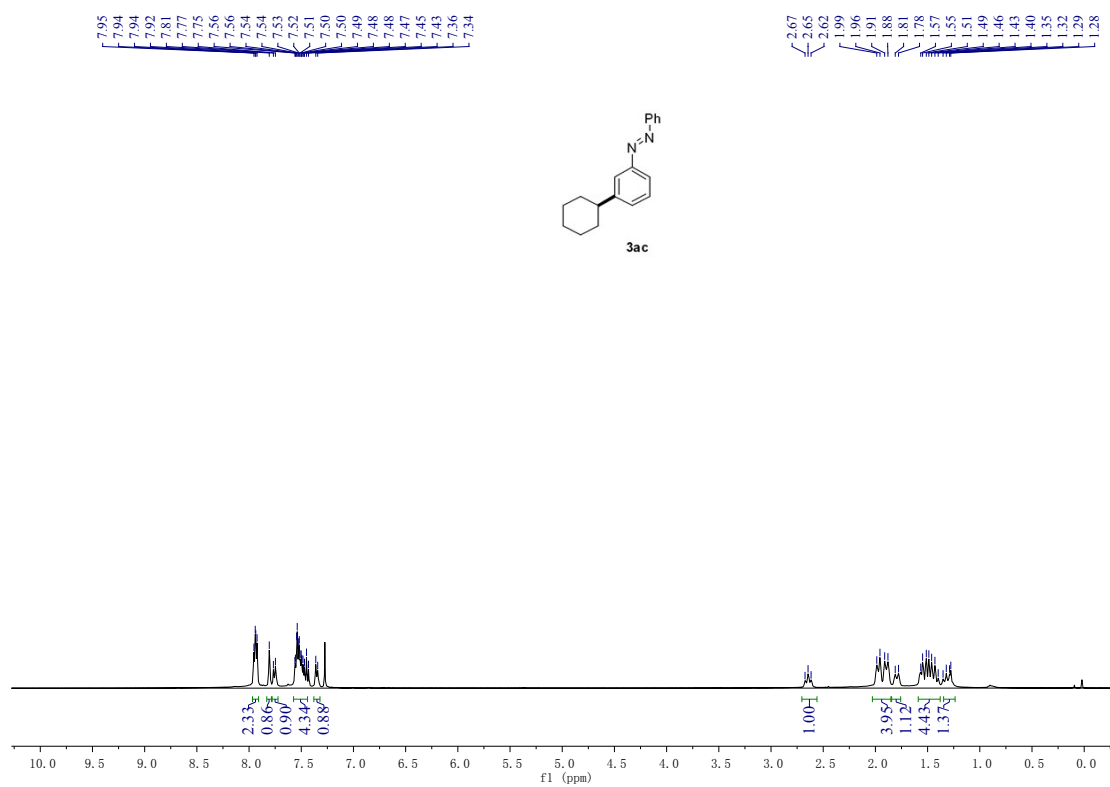
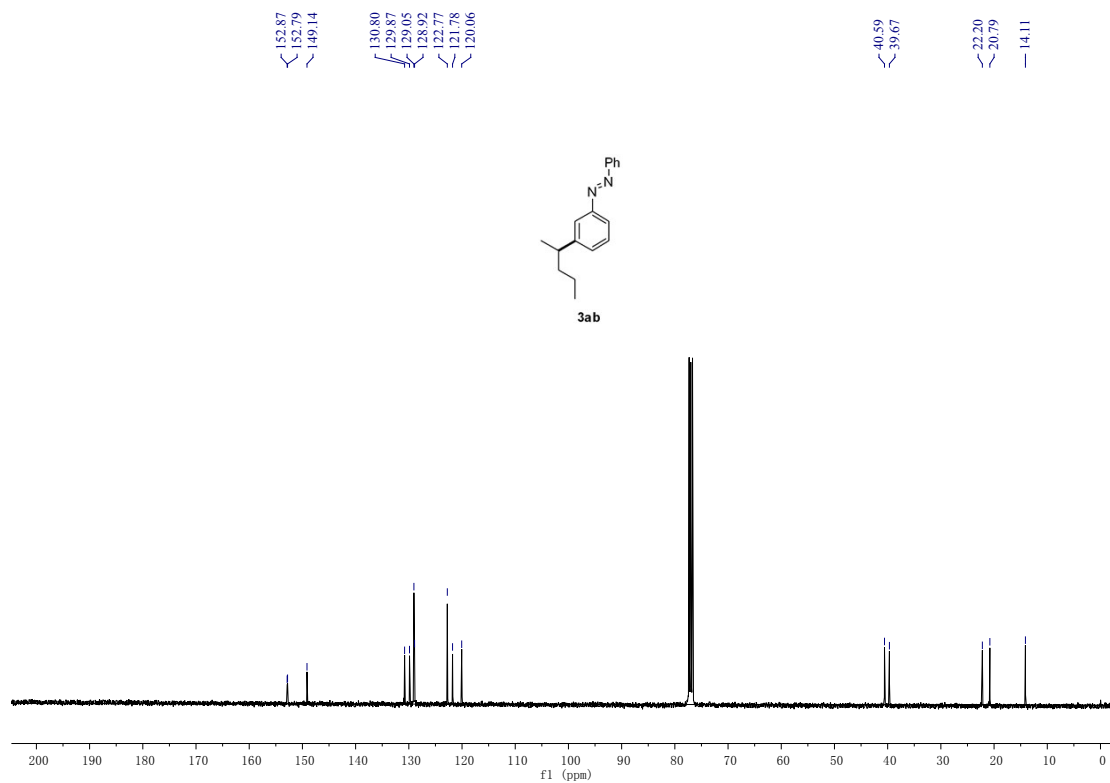
$\left\{ \begin{array}{l} 7.75 \\ 7.74 \\ 7.74 \end{array} \right.$ 
 $\left\{ \begin{array}{l} 6.96 \\ 6.94 \end{array} \right.$ 
 $\left\{ \begin{array}{l} 3.88 \end{array} \right.$ 
 $\left\{ \begin{array}{l} 1.76 \\ 1.75 \\ 1.73 \\ 1.71 \\ 1.70 \\ 1.68 \\ 1.66 \\ 1.64 \\ 1.63 \end{array} \right.$ 
 $\left\{ \begin{array}{l} 0.88 \\ 0.81 \\ 0.79 \end{array} \right.$ 
 $\left\{ \begin{array}{l} 0.00 \end{array} \right.$

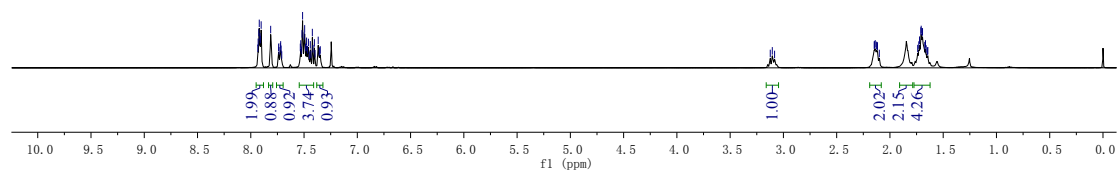
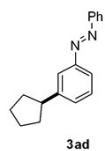
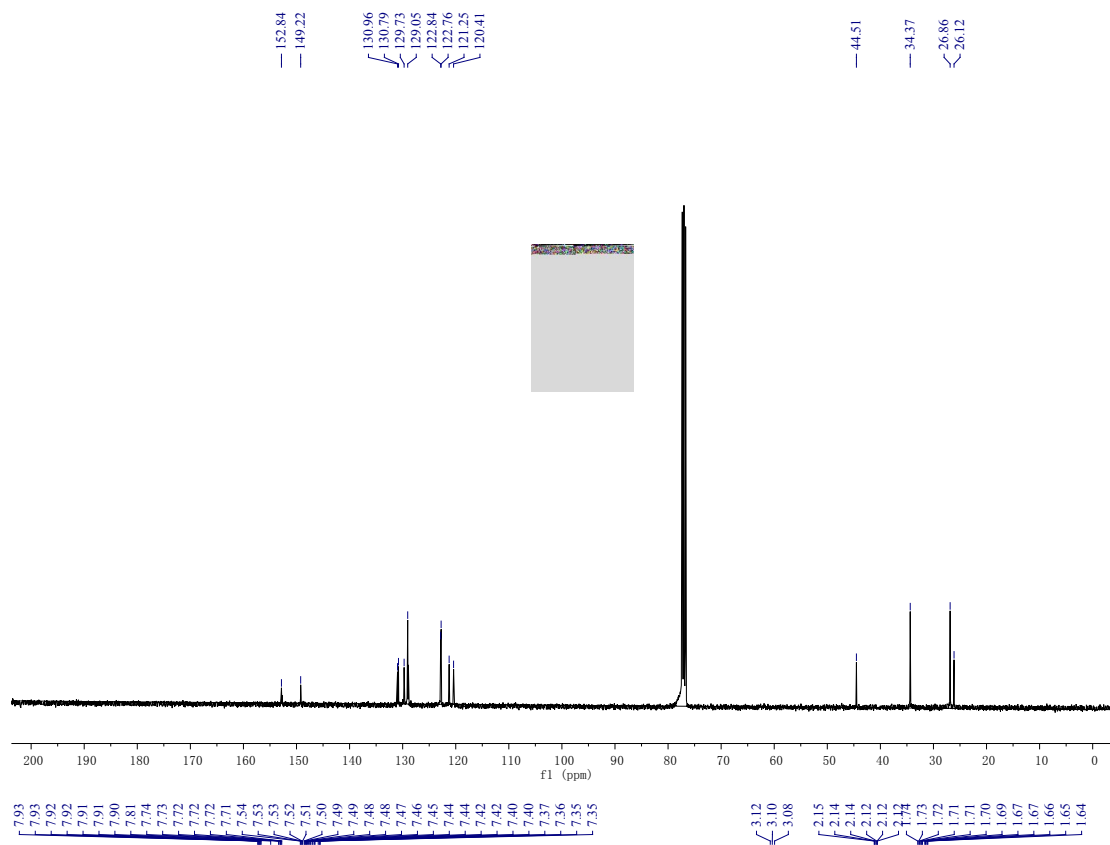


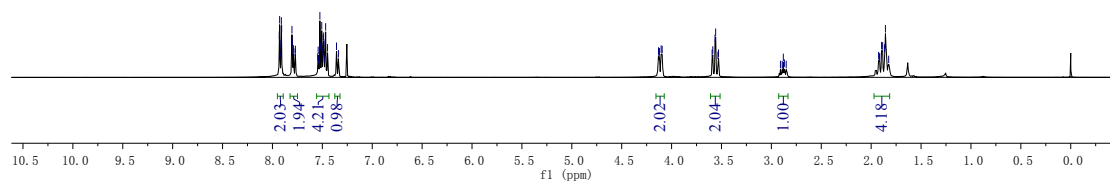
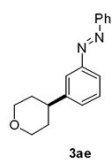
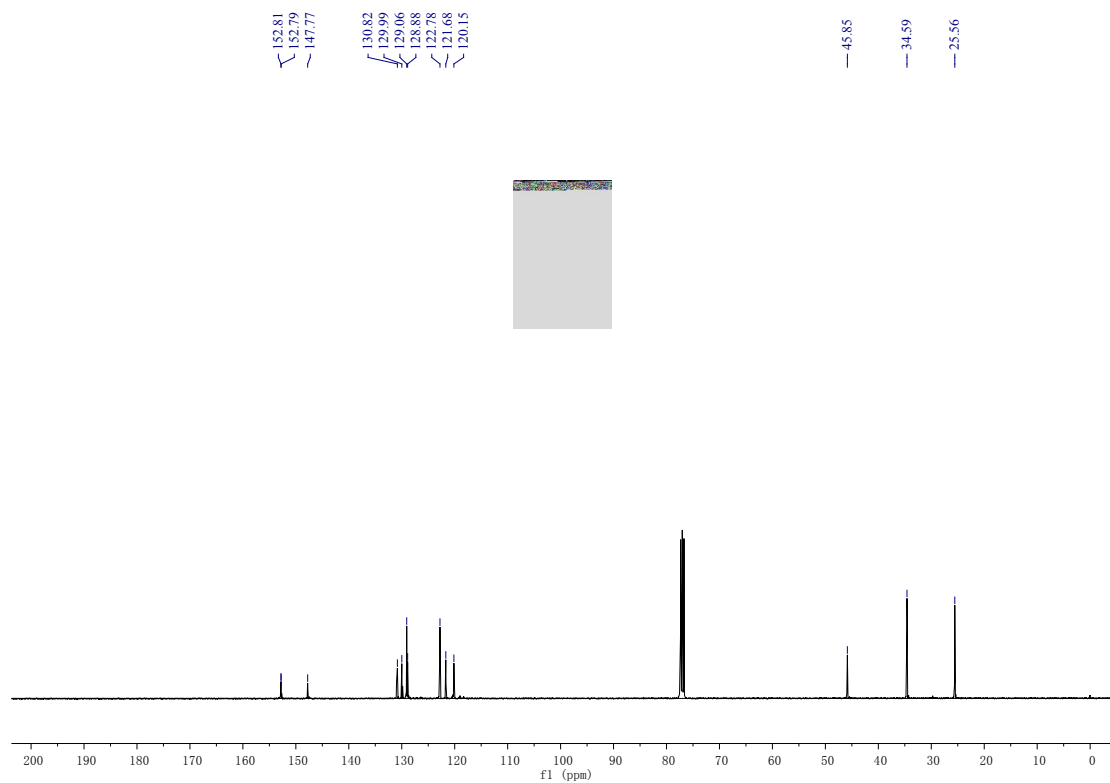












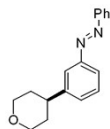
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152.69  
147.00

130.98  
129.47  
129.23  
129.10  
122.82  
121.08  
121.06

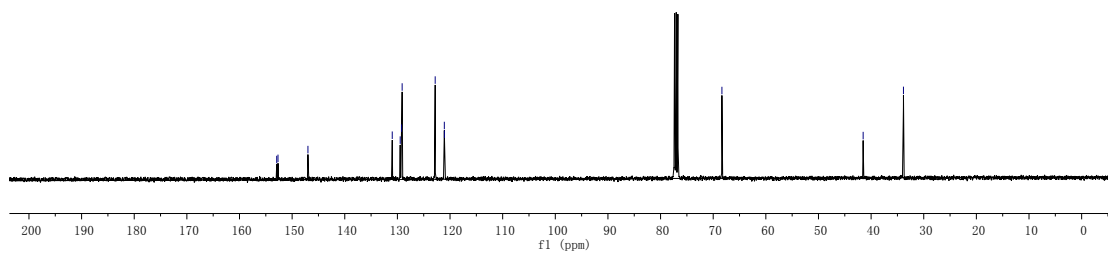
68.34

41.51

33.85



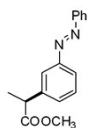
3ae



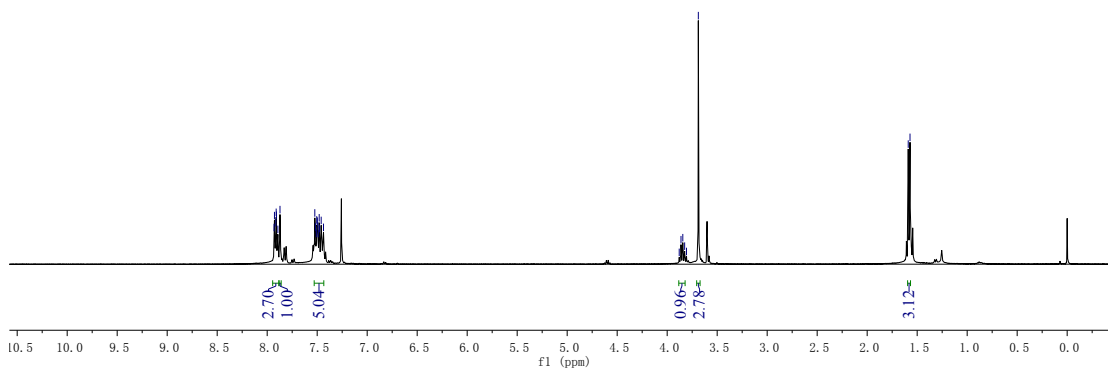
7.93  
7.93  
7.91  
7.91  
7.89  
7.87  
7.52  
7.51  
7.51  
7.50  
7.49  
7.49  
7.48  
7.48  
7.46  
7.44

3.88  
3.86  
3.84  
3.83  
3.81  
3.69

1.59  
1.57



3af

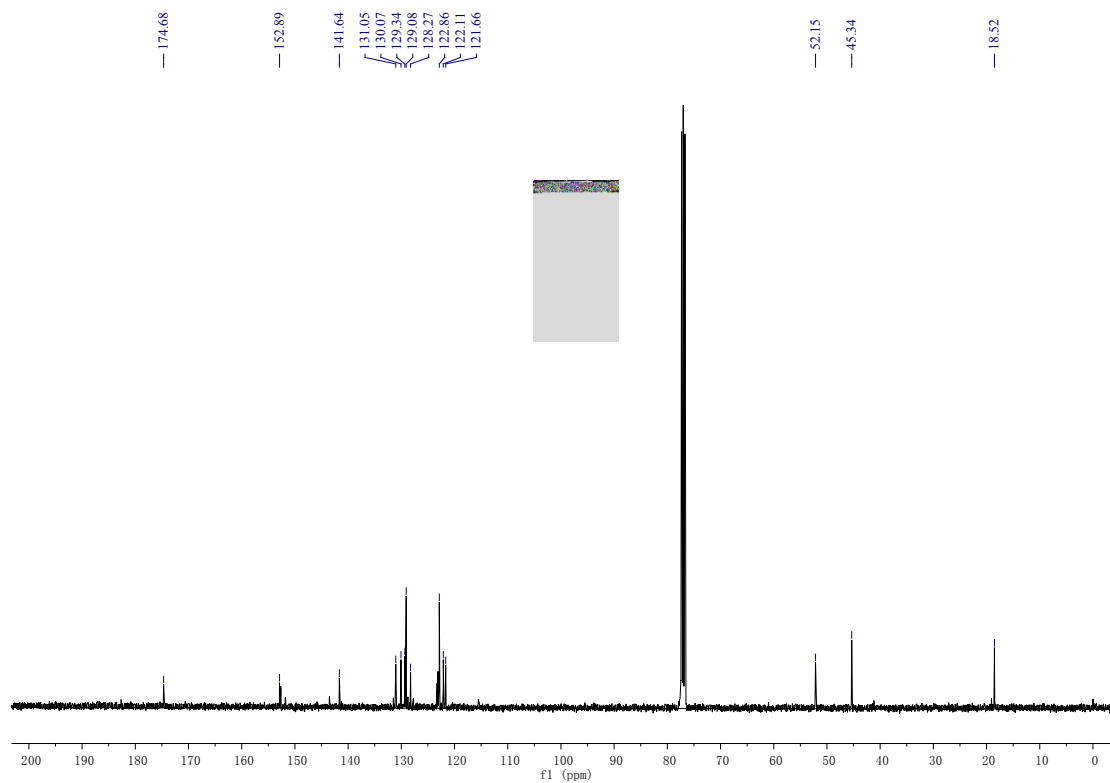


2.70  
1.00

5.04

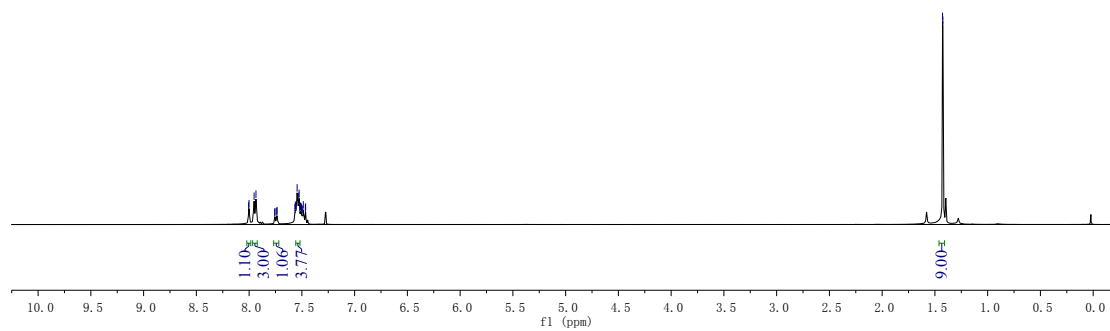
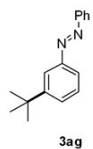
0.96  
2.78

3.12



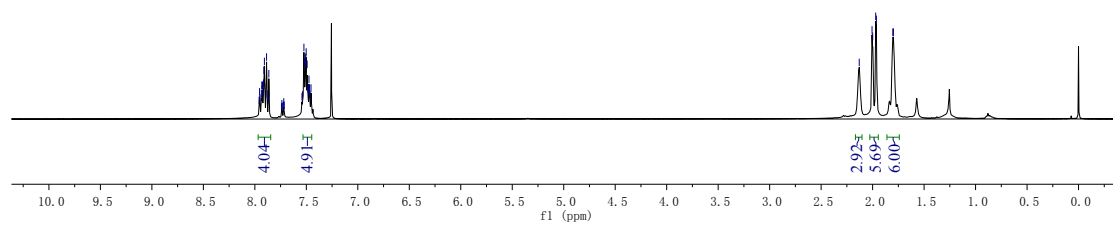
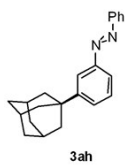
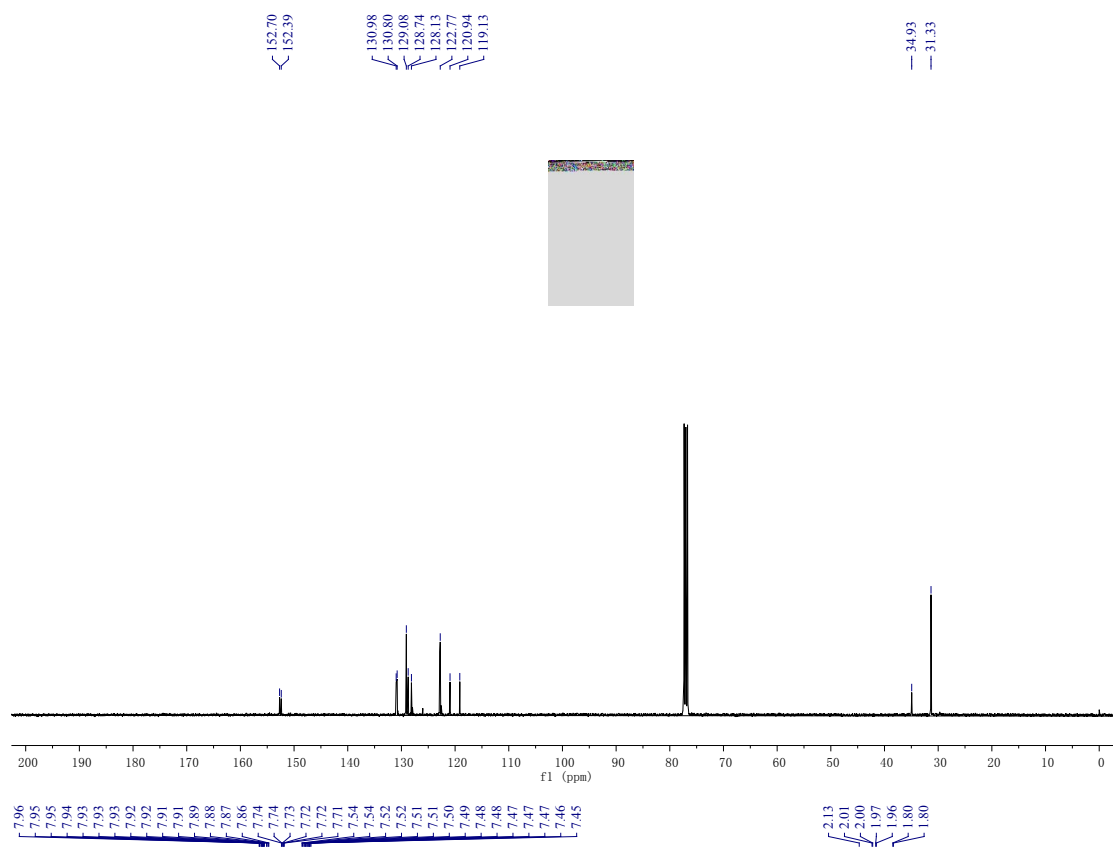
8.00  
7.95  
7.94  
7.76  
7.75  
7.74  
7.74  
7.57  
7.56  
7.54  
7.53  
7.53  
7.52  
7.51  
7.51  
7.50  
7.50  
7.49  
7.47  
7.46

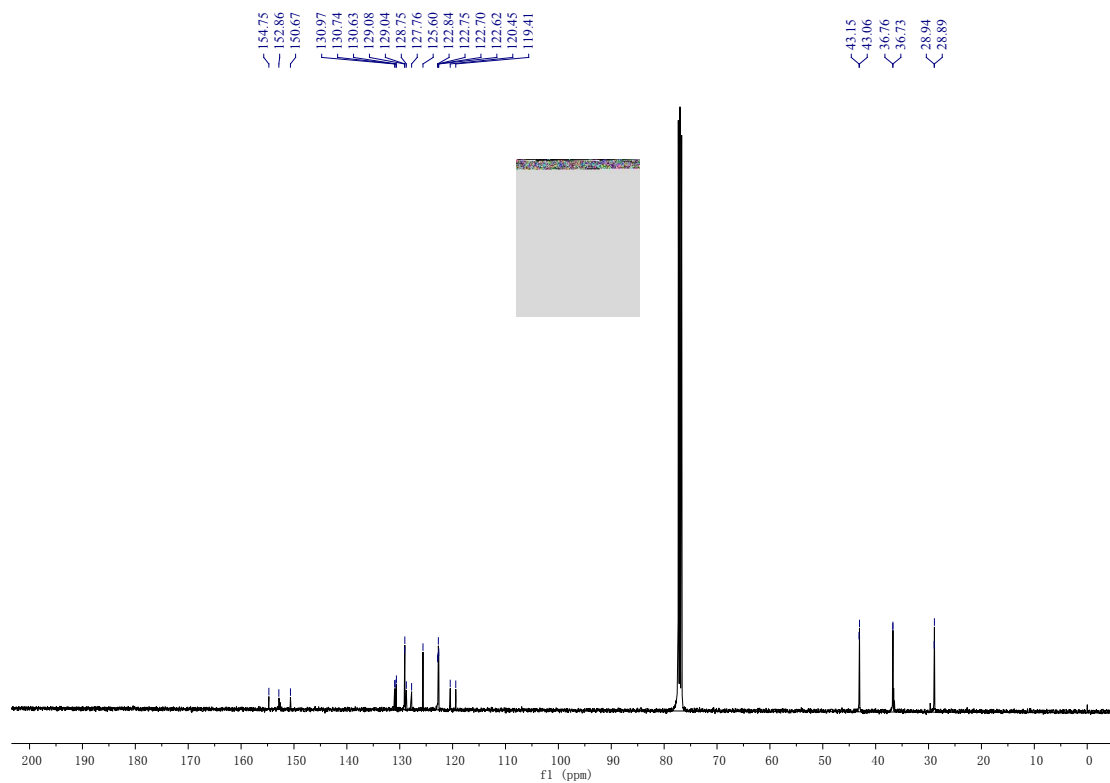
1.43  
1.42



1.10  
3.00  
1.06  
3.77

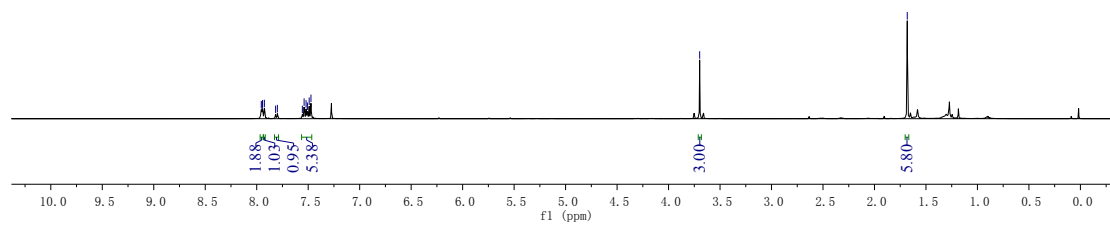
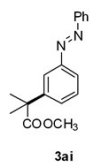
9.00





7.96  
7.95  
7.94  
7.93  
7.83  
7.80  
7.56  
7.54  
7.52  
7.51  
7.49  
7.47

43.15  
43.06  
36.76  
36.73  
28.94  
28.89

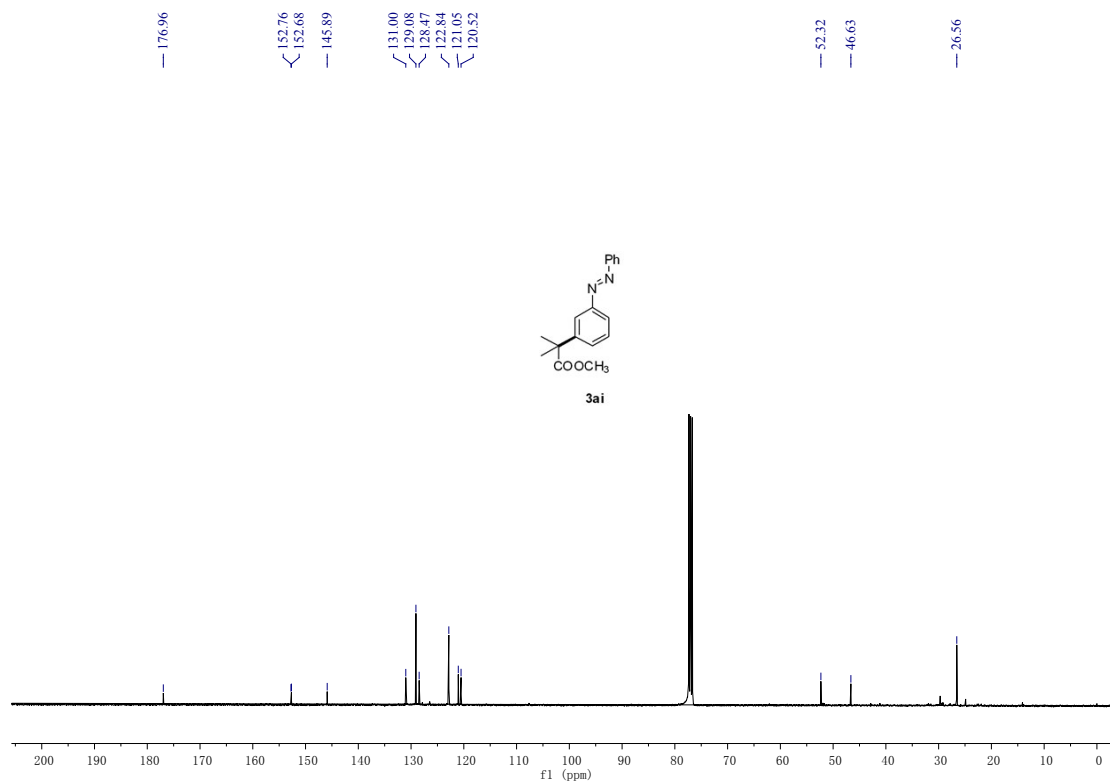


1.88  
1.03  
0.95  
5.38

3.00

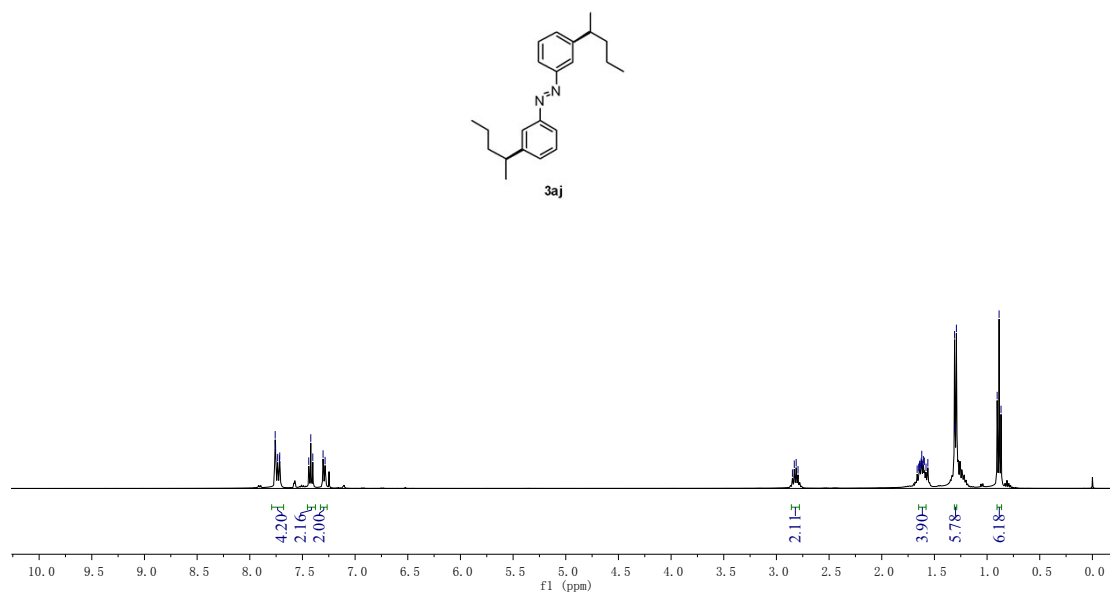
5.80

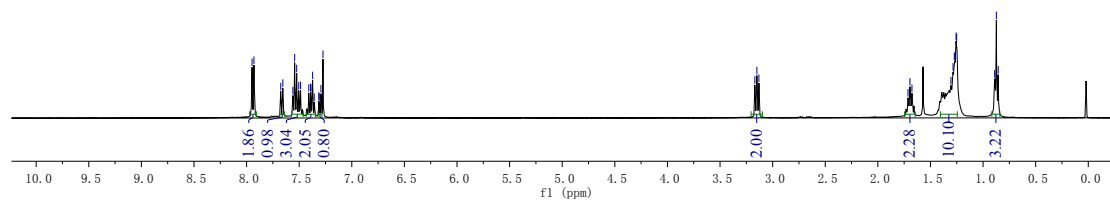
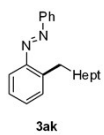
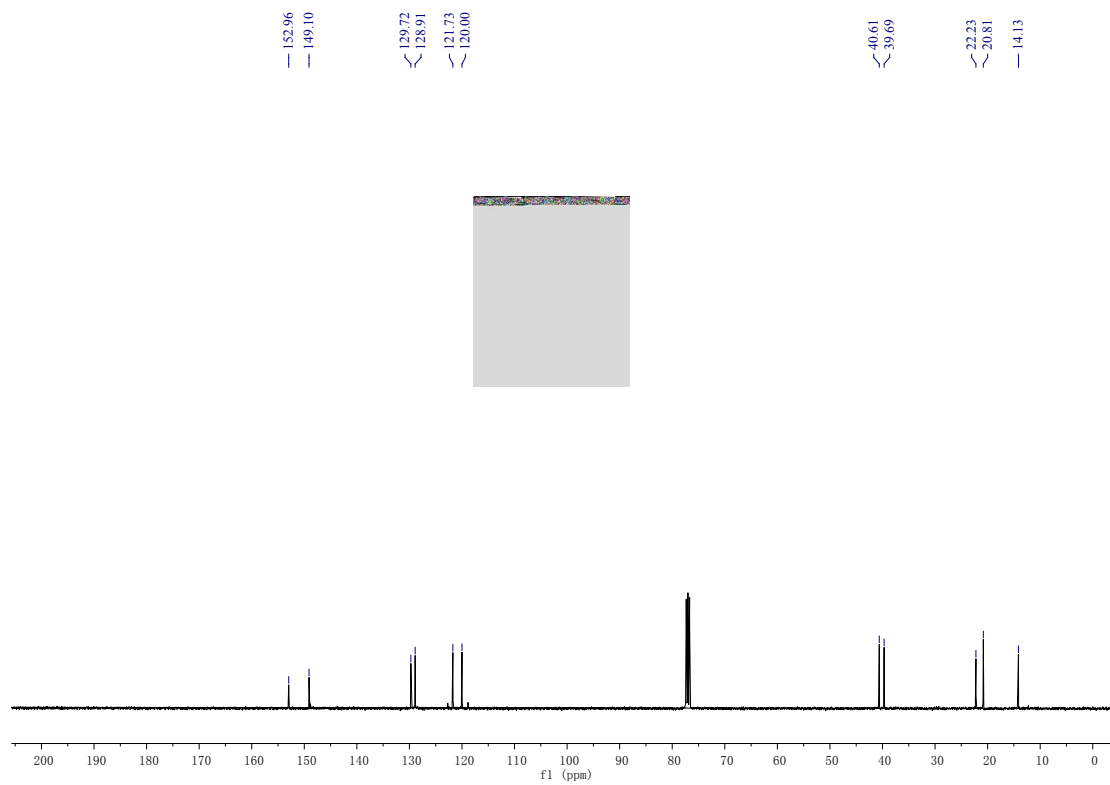


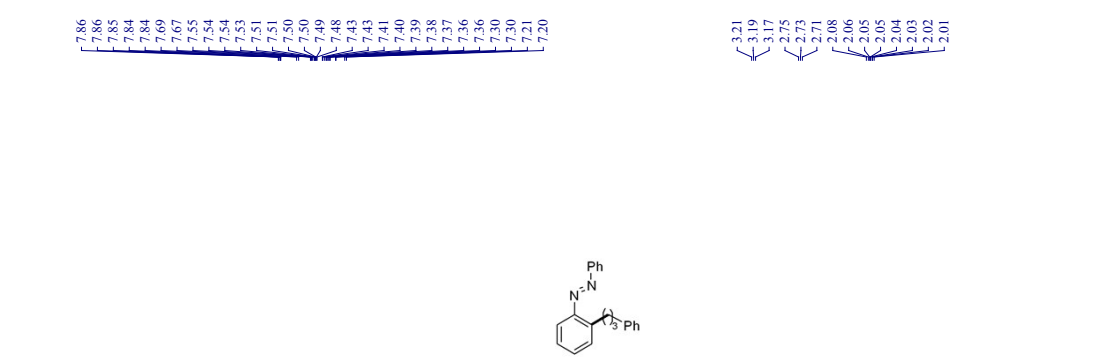
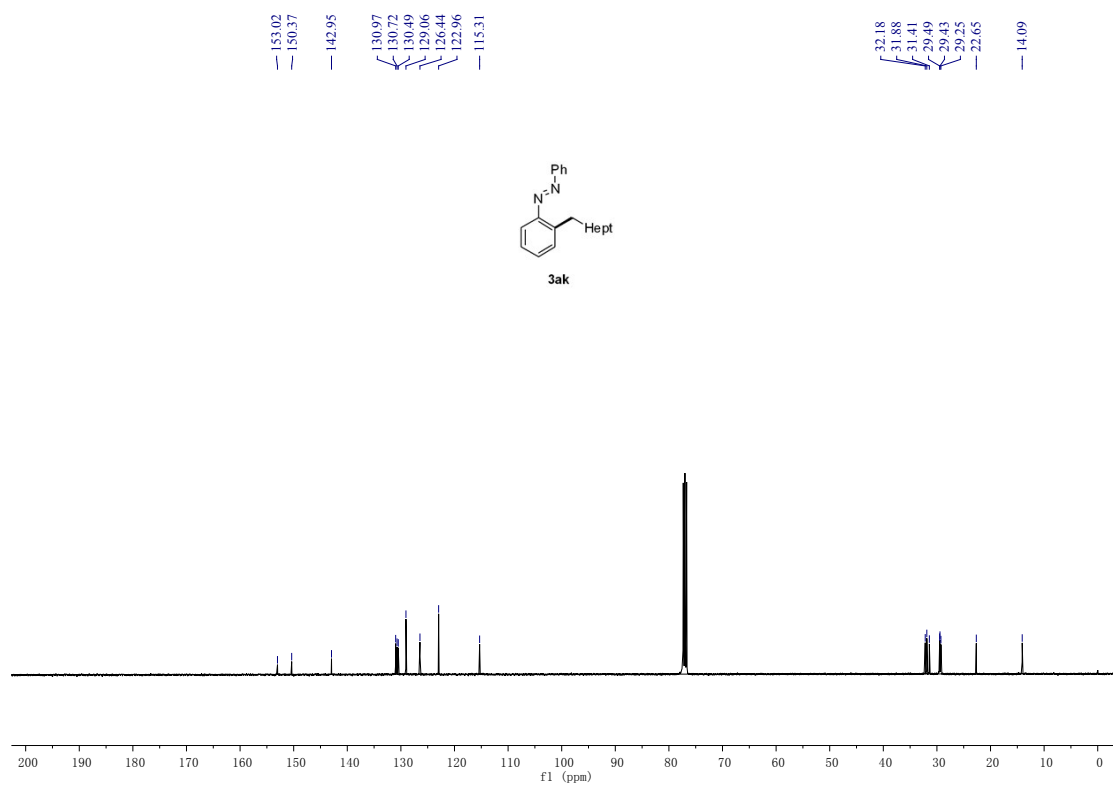


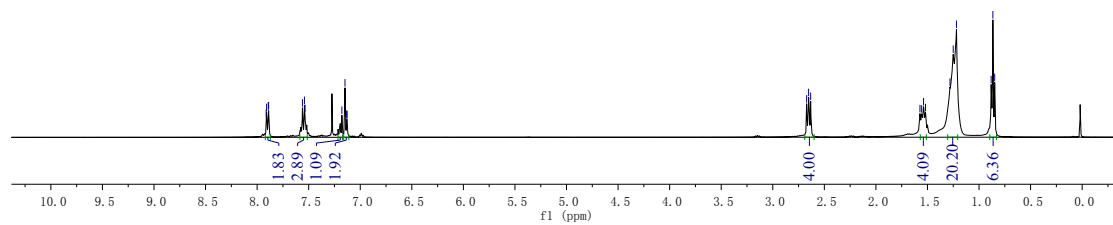
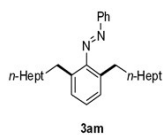
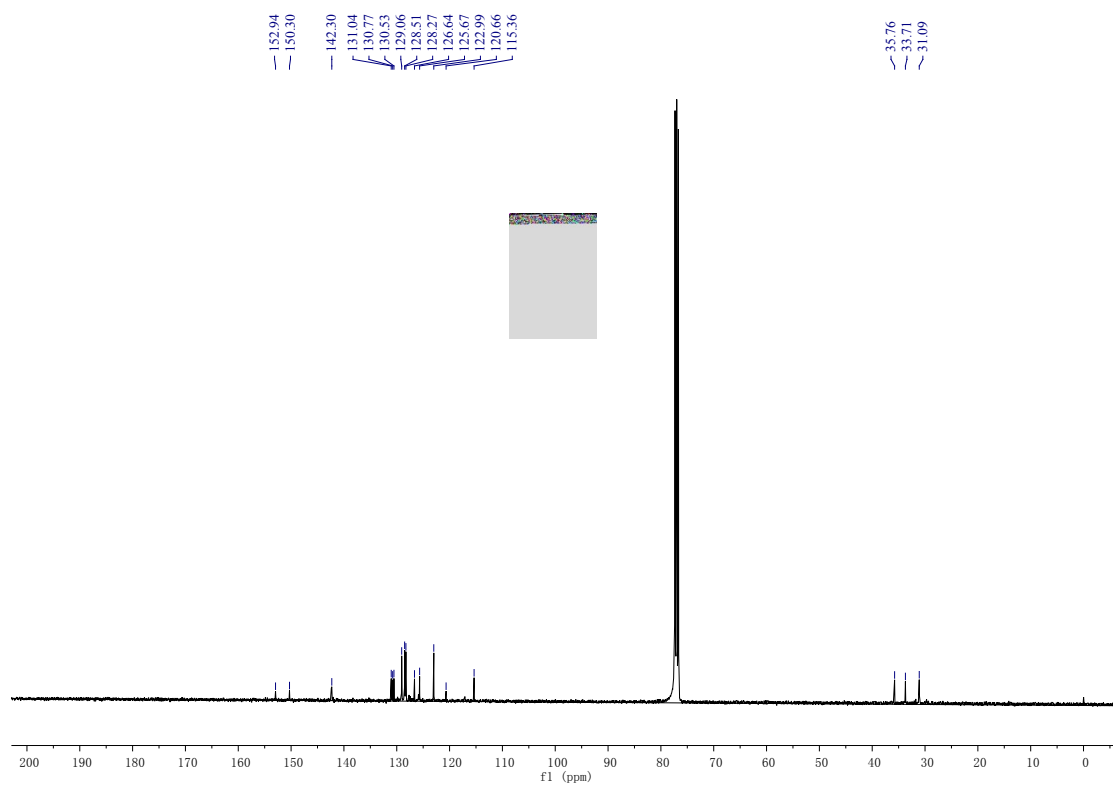
7.76  
7.75  
7.74  
7.72  
7.44  
7.42  
7.40  
7.30  
7.29

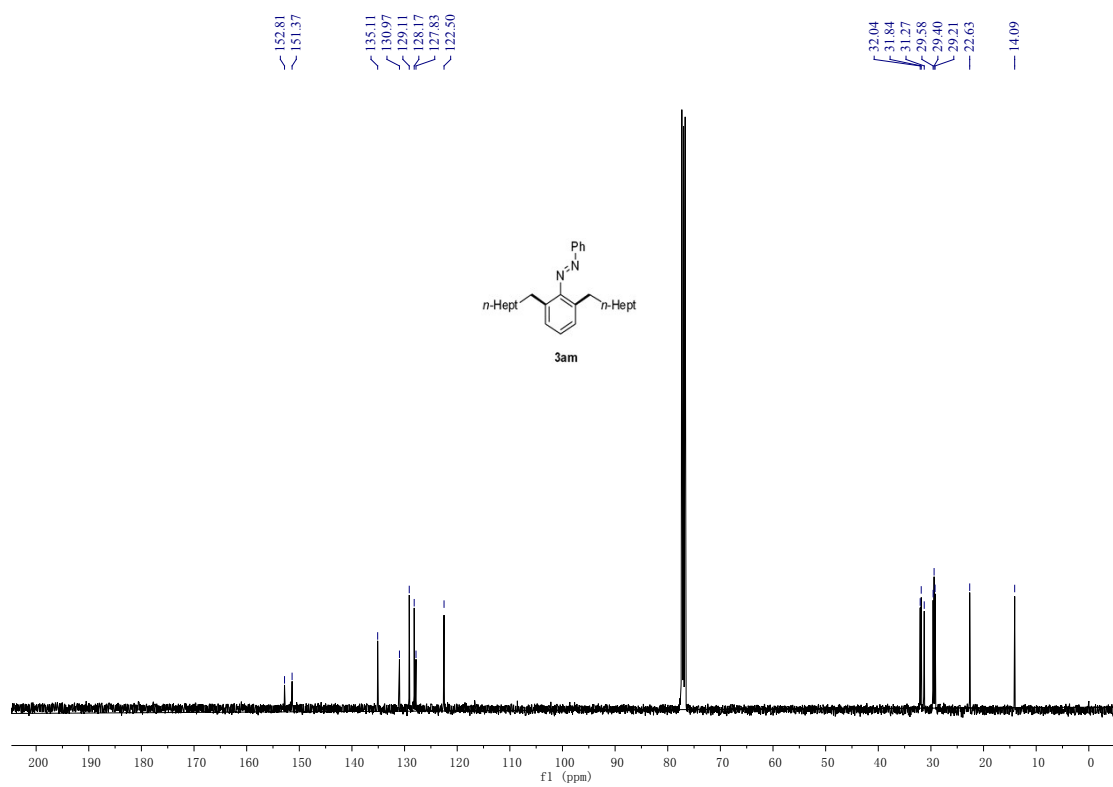
2.85  
2.83  
2.81  
2.79  
1.63  
1.62  
1.60  
1.60  
1.56  
1.31  
1.30  
0.99  
0.89  
0.87

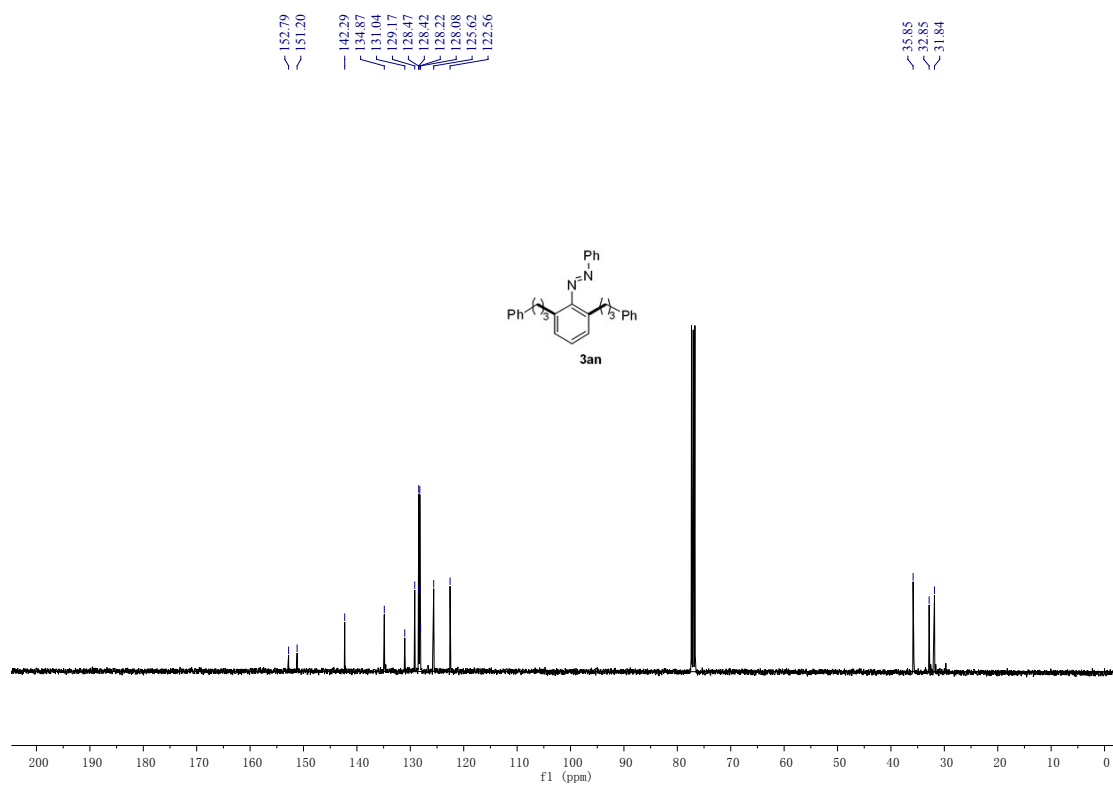


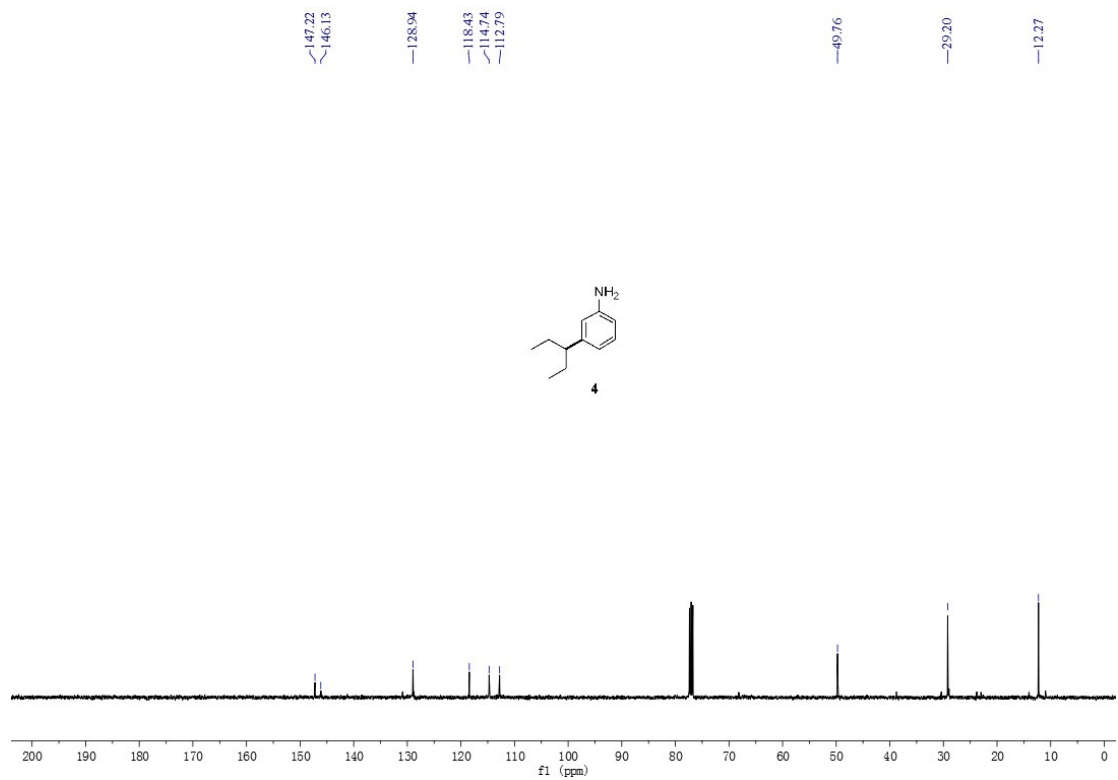
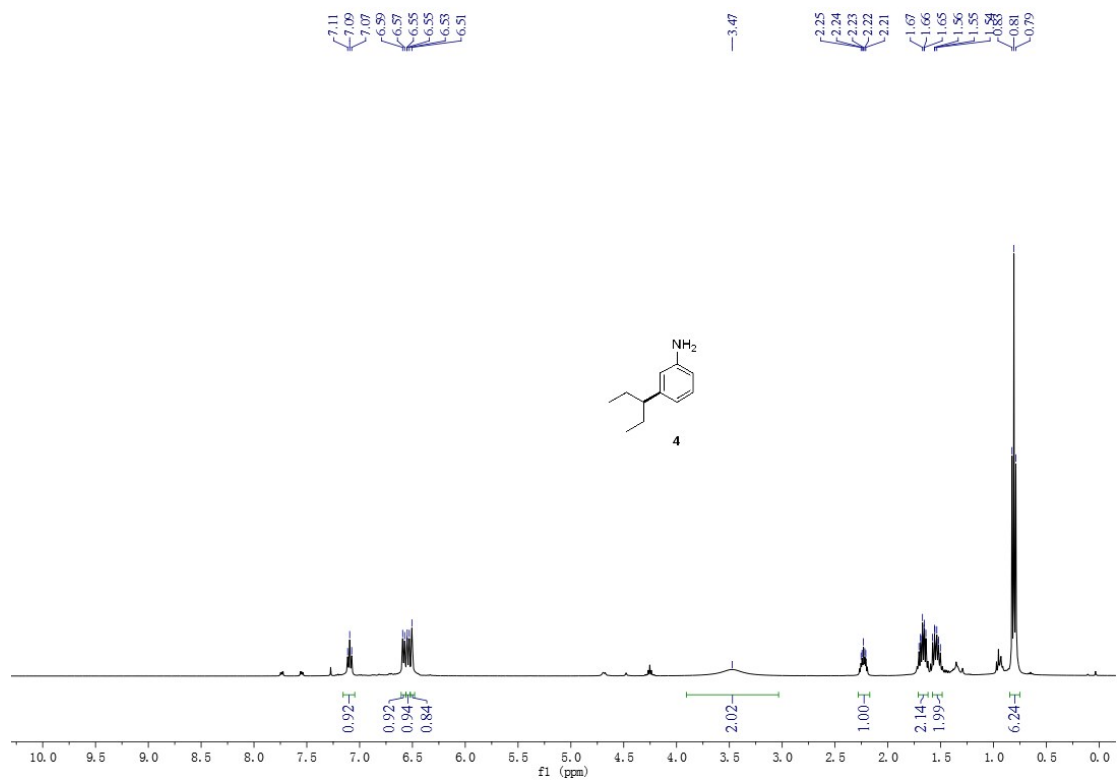


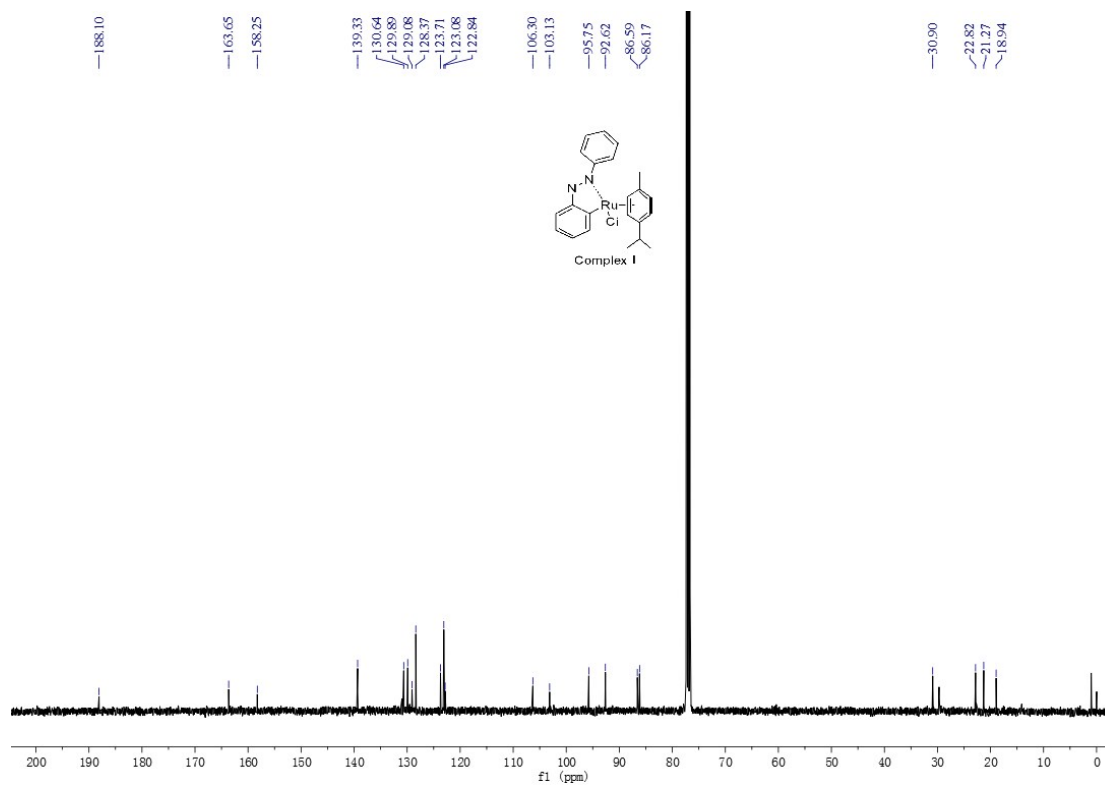
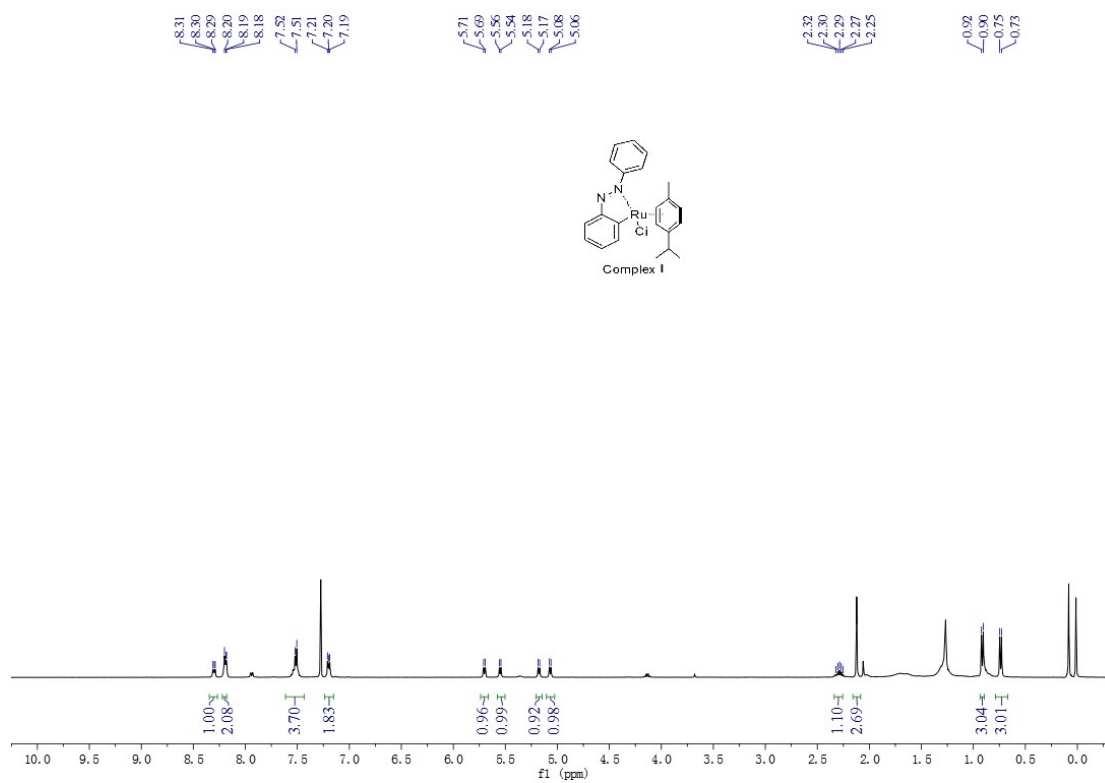




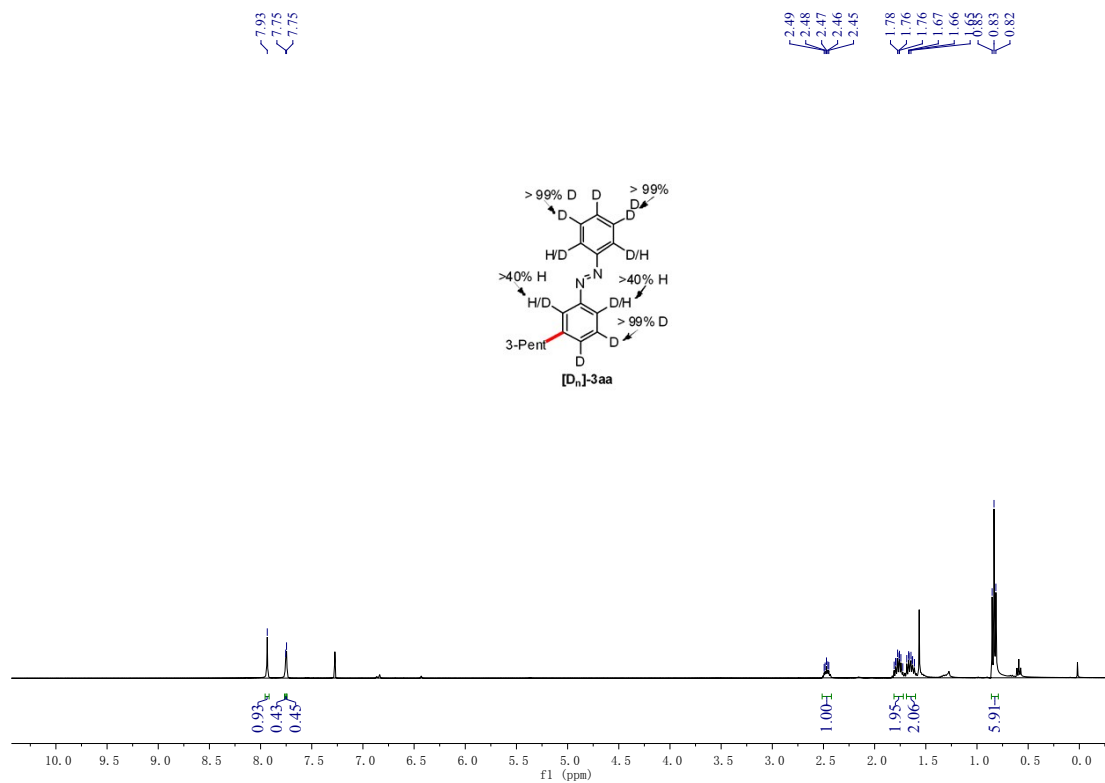




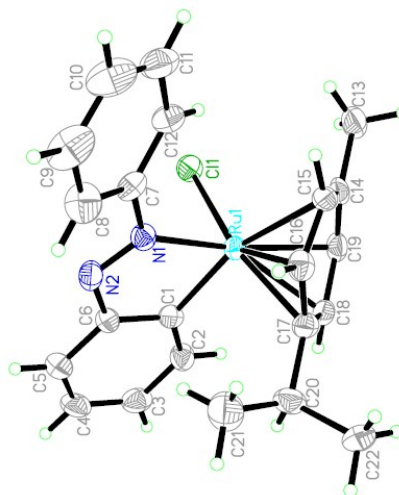








## 6.1 X-ray crystal structure and data for ruthenium-azobenzene complex



**Table 1.** Crystal data and structure refinement for ruthenium-azobenzene complex.

|                     |                       |
|---------------------|-----------------------|
| Identification code | 1501752               |
| Empirical formula   | $C_{22}H_{23}ClN_2Ru$ |
| Formula weight      | 451.94                |
| Temperature         | 293(2) K              |
| Wavelength          | 0.71073 Å             |

|                                   |   |
|-----------------------------------|---|
| Crystal system, space group       | Triclinic, P-1  |
| Unit cell dimensions              | a = 10.445(2) Å    alpha = 82.53(3) deg.<br>b = 14.347(3) Å    beta = 85.30(3) deg.<br>c = 14.407(3) Å    gamma = 74.55(3) deg. |
| Volume                            | 2060.8(7) Å <sup>3</sup>  |
| Z, Calculated density             | 4, 1.457 Mg/m <sup>3</sup>  |
| Absorption coefficient            | 0.898 mm <sup>-1</sup>  |
| F(000)                            | 920   |
| Crystal size                      | 0.20 x 0.20 x 0.20 mm   |
| Theta range for data collection   | 3.12 to 25.01 deg.  |
| Limiting indices                  | -12 ≤ h ≤ 12, -17 ≤ k ≤ 17, -17 ≤ l ≤ 17  |
| Reflections collected / unique    | 20937 / 7196 [R(int) = 0.0450]  |
| Completeness to theta = 25.01     | 99.1 %  |
| Absorption correction             | None  |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup>   |
| Data / restraints / parameters    | 7196 / 0 / 469  |
| Goodness-of-fit on F <sup>2</sup> | 1.105   |
| Final R indices [I > 2σ(I)]       | R1 = 0.0695, wR2 = 0.1802   |
| R indices (all data)              | R1 = 0.0817, wR2 = 0.1846   |
| Largest diff. peak and hole       | 2.247 and -0.948 e.Å <sup>-3</sup>  |

**Table 2.** Atomic coordinates ( × 10<sup>4</sup>) and equivalent isotropic displacement parameters (Å<sup>2</sup> × 10<sup>3</sup>) for 1501752. U(eq) is defined as one third of the trace of the orthogonalized U<sub>ij</sub> tensor.

|       | x        | y       | z       | U(eq) |
|-------|----------|---------|---------|-------|
| Ru(1) | 2209(1)  | 6796(1) | 1235(1) | 36(1) |
| Ru(2) | -3187(1) | 6893(1) | 4565(1) | 32(1) |
| Cl(2) | -4375(3) | 6085(2) | 3720(2) | 49(1) |
| Cl(1) | 768(3)   | 5949(2) | 2181(2) | 50(1) |

|       |           |          |          |       |
|-------|-----------|----------|----------|-------|
| C(21) | 3149(15)  | 9017(10) | -15(12)  | 94(5) |
| N(2)  | -110(8)   | 8458(6)  | 958(6)   | 49(2) |
| N(3)  | -4981(7)  | 7777(5)  | 4962(5)  | 36(2) |
| C(13) | 3425(13)  | 4310(9)  | 1093(13) | 92(5) |
| N(4)  | -5512(8)  | 8571(6)  | 4447(6)  | 41(2) |
| N(1)  | 529(8)    | 7677(6)  | 639(6)   | 43(2) |
| C(1)  | 1591(10)  | 7893(7)  | 2061(7)  | 40(2) |
| C(23) | -3541(9)  | 7976(7)  | 3498(7)  | 38(2) |
| C(29) | -5728(9)  | 7617(7)  | 5804(7)  | 38(2) |
| C(17) | 3981(10)  | 7231(7)  | 647(7)   | 44(2) |
| C(38) | -2241(10) | 6982(8)  | 5815(7)  | 44(2) |
| C(20) | 4221(12)  | 8232(8)  | 501(9)   | 58(3) |
| C(28) | -4740(9)  | 8694(7)  | 3643(7)  | 42(2) |
| C(34) | -5843(10) | 6680(8)  | 6116(9)  | 54(3) |
| C(24) | -2826(10) | 8121(8)  | 2666(7)  | 47(2) |
| C(40) | -1009(9)  | 6623(7)  | 4367(7)  | 39(2) |
| C(36) | -2019(10) | 5407(7)  | 5309(8)  | 46(2) |
| C(6)  | 476(10)   | 8589(7)  | 1758(7)  | 45(2) |
| C(2)  | 2130(11)  | 8037(8)  | 2861(8)  | 52(3) |
| C(39) | -1471(9)  | 7277(7)  | 5047(6)  | 38(2) |
| C(3)  | 1619(13)  | 8871(9)  | 3289(9)  | 63(3) |
| C(25) | -3242(12) | 8924(8)  | 2032(8)  | 56(3) |
| C(33) | -6581(13) | 6545(10) | 6867(7)  | 71(4) |
| C(42) | -1120(12) | 8244(8)  | 4922(8)  | 56(3) |
| C(31) | -7120(13) | 8185(11) | 7124(9)  | 77(4) |
| C(15) | 3361(10)  | 5898(8)  | 54(8)    | 51(3) |
| C(27) | -5190(11) | 9508(8)  | 2994(8)  | 55(3) |
| C(35) | -2365(12) | 4438(8)  | 5403(11) | 76(4) |
| C(7)  | 9(10)     | 7504(8)  | -190(7)  | 47(2) |
| C(5)  | -69(12)   | 9435(8)  | 2188(9)  | 61(3) |

|       |           |          |           |       |
|-------|-----------|----------|-----------|-------|
| C(26) | -4429(13) | 9619(9)  | 2187(9)   | 68(3) |
| C(12) | 144(11)   | 6545(9)  | -364(8)   | 59(3) |
| C(41) | -1329(10) | 5716(7)  | 4490(8)   | 47(3) |
| C(30) | -6360(12) | 8377(8)  | 6331(8)   | 56(3) |
| C(19) | 4095(9)   | 5703(7)  | 1630(8)   | 49(3) |
| C(37) | -2456(10) | 6025(8)  | 5972(7)   | 51(3) |
| C(14) | 3651(10)  | 5316(7)  | 916(9)    | 53(3) |
| C(32) | -7270(13) | 7270(11) | 7394(9)   | 70(4) |
| C(16) | 3414(10)  | 6860(8)  | -30(7)    | 49(3) |
| C(4)  | 509(13)   | 9562(9)  | 2965(10)  | 68(4) |
| C(18) | 4320(9)   | 6632(7)  | 1497(7)   | 44(2) |
| C(8)  | -598(13)  | 8281(11) | -832(9)   | 73(4) |
| C(11) | -331(13)  | 6367(11) | -1176(10) | 73(4) |
| C(44) | -2200(14) | 9080(9)  | 5254(12)  | 89(5) |
| C(9)  | -1077(15) | 8090(14) | -1637(9)  | 88(5) |
| C(43) | 136(12)   | 8133(9)  | 5446(9)   | 64(3) |
| C(22) | 5582(13)  | 8188(10) | 2(11)     | 79(4) |
| C(10) | -910(17)  | 7142(14) | -1795(10) | 90(5) |

**Table 3.** Bond lengths [Å] and angles [deg] for 1501752.

|             |           |
|-------------|-----------|
| Ru(1)-C(1)  | 2.032(9)  |
| Ru(1)-N(1)  | 2.049(8)  |
| Ru(1)-C(16) | 2.135(10) |
| Ru(1)-C(17) | 2.181(10) |
| Ru(1)-C(18) | 2.213(10) |
| Ru(1)-C(19) | 2.229(9)  |
| Ru(1)-C(15) | 2.326(9)  |
| Ru(1)-C(14) | 2.330(9)  |
| Ru(1)-Cl(1) | 2.409(3)  |
| Ru(2)-C(23) | 2.020(10) |

|              |           |
|--------------|-----------|
| Ru(2)-N(3)   | 2.048(7)  |
| Ru(2)-C(38)  | 2.157(9)  |
| Ru(2)-C(39)  | 2.197(9)  |
| Ru(2)-C(40)  | 2.204(9)  |
| Ru(2)-C(41)  | 2.212(9)  |
| Ru(2)-C(37)  | 2.309(10) |
| Ru(2)-C(36)  | 2.327(9)  |
| Ru(2)-Cl(2)  | 2.397(3)  |
| C(21)-C(20)  | 1.524(18) |
| C(21)-H(21A) | 0.9600    |
| C(21)-H(21B) | 0.9600    |
| C(21)-H(21C) | 0.9600    |
| N(2)-N(1)    | 1.264(11) |
| N(2)-C(6)    | 1.404(13) |
| N(3)-N(4)    | 1.291(10) |
| N(3)-C(29)   | 1.415(12) |
| C(13)-C(14)  | 1.510(15) |
| C(13)-H(13A) | 0.9600    |
| C(13)-H(13B) | 0.9600    |
| C(13)-H(13C) | 0.9600    |
| N(4)-C(28)   | 1.376(12) |
| N(1)-C(7)    | 1.428(12) |
| C(1)-C(6)    | 1.376(14) |
| C(1)-C(2)    | 1.385(14) |
| C(23)-C(24)  | 1.382(13) |
| C(23)-C(28)  | 1.414(13) |
| C(29)-C(34)  | 1.395(14) |
| C(29)-C(30)  | 1.396(13) |
| C(17)-C(16)  | 1.408(14) |
| C(17)-C(18)  | 1.414(14) |

|              |           |
|--------------|-----------|
| C(17)-C(20)  | 1.507(14) |
| C(38)-C(39)  | 1.401(14) |
| C(38)-C(37)  | 1.436(15) |
| C(38)-H(38A) | 0.9800    |
| C(20)-C(22)  | 1.529(16) |
| C(20)-H(20A) | 0.9800    |
| C(28)-C(27)  | 1.398(14) |
| C(34)-C(33)  | 1.301(16) |
| C(34)-H(34A) | 0.9300    |
| C(24)-C(25)  | 1.370(15) |
| C(24)-H(24A) | 0.9300    |
| C(40)-C(39)  | 1.411(13) |
| C(40)-C(41)  | 1.414(14) |
| C(40)-H(40A) | 0.9800    |
| C(36)-C(37)  | 1.357(15) |
| C(36)-C(41)  | 1.416(15) |
| C(36)-C(35)  | 1.513(14) |
| C(6)-C(5)    | 1.396(14) |
| C(2)-C(3)    | 1.377(15) |
| C(2)-H(2A)   | 0.9300    |
| C(39)-C(42)  | 1.512(14) |
| C(3)-C(4)    | 1.379(18) |
| C(3)-H(3A)   | 0.9300    |
| C(25)-C(26)  | 1.391(16) |
| C(25)-H(25A) | 0.9300    |
| C(33)-C(32)  | 1.376(17) |
| C(33)-H(33A) | 0.9300    |
| C(42)-C(44)  | 1.510(17) |
| C(42)-C(43)  | 1.529(15) |
| C(42)-H(42A) | 0.9800    |

|              |           |
|--------------|-----------|
| C(31)-C(32)  | 1.366(19) |
| C(31)-C(30)  | 1.378(17) |
| C(31)-H(31A) | 0.9300    |
| C(15)-C(16)  | 1.386(15) |
| C(15)-C(14)  | 1.409(16) |
| C(15)-H(15A) | 0.9800    |
| C(27)-C(26)  | 1.370(16) |
| C(27)-H(27A) | 0.9300    |
| C(35)-H(35A) | 0.9600    |
| C(35)-H(35B) | 0.9600    |
| C(35)-H(35C) | 0.9600    |
| C(7)-C(8)    | 1.396(16) |
| C(7)-C(12)   | 1.398(16) |
| C(5)-C(4)    | 1.369(17) |
| C(5)-H(5A)   | 0.9300    |
| C(26)-H(26A) | 0.9300    |
| C(12)-C(11)  | 1.385(16) |
| C(12)-H(12A) | 0.9300    |
| C(41)-H(41A) | 0.9800    |
| C(30)-H(30A) | 0.9300    |
| C(19)-C(14)  | 1.395(16) |
| C(19)-C(18)  | 1.400(14) |
| C(19)-H(19A) | 0.9800    |
| C(37)-H(37A) | 0.9800    |
| C(32)-H(32A) | 0.9300    |
| C(16)-H(16A) | 0.9800    |
| C(4)-H(4A)   | 0.9300    |
| C(18)-H(18A) | 0.9800    |
| C(8)-C(9)    | 1.387(18) |
| C(8)-H(8A)   | 0.9300    |

|                   |          |
|-------------------|----------|
| C(11)-C(10)       | 1.37(2)  |
| C(11)-H(11A)      | 0.9300   |
| C(44)-H(44A)      | 0.9600   |
| C(44)-H(44B)      | 0.9600   |
| C(44)-H(44C)      | 0.9600   |
| C(9)-C(10)        | 1.37(2)  |
| C(9)-H(9A)        | 0.9300   |
| C(43)-H(43A)      | 0.9600   |
| C(43)-H(43B)      | 0.9600   |
| C(43)-H(43C)      | 0.9600   |
| C(22)-H(22A)      | 0.9600   |
| C(22)-H(22B)      | 0.9600   |
| C(22)-H(22C)      | 0.9600   |
| C(10)-H(10A)      | 0.9300   |
|                   |          |
| C(1)-Ru(1)-N(1)   | 75.5(4)  |
| C(1)-Ru(1)-C(16)  | 124.6(4) |
| N(1)-Ru(1)-C(16)  | 93.7(4)  |
| C(1)-Ru(1)-C(17)  | 95.2(4)  |
| N(1)-Ru(1)-C(17)  | 111.2(4) |
| C(16)-Ru(1)-C(17) | 38.1(4)  |
| C(1)-Ru(1)-C(18)  | 91.8(4)  |
| N(1)-Ru(1)-C(18)  | 146.0(4) |
| C(16)-Ru(1)-C(18) | 67.4(4)  |
| C(17)-Ru(1)-C(18) | 37.5(4)  |
| C(1)-Ru(1)-C(19)  | 115.2(4) |
| N(1)-Ru(1)-C(19)  | 169.0(4) |
| C(16)-Ru(1)-C(19) | 78.3(4)  |
| C(17)-Ru(1)-C(19) | 66.9(4)  |
| C(18)-Ru(1)-C(19) | 36.7(4)  |



|                   |          |
|-------------------|----------|
| C(1)-Ru(1)-C(15)  | 160.0(4) |
| N(1)-Ru(1)-C(15)  | 105.2(4) |
| C(16)-Ru(1)-C(15) | 35.9(4)  |
| C(17)-Ru(1)-C(15) | 65.7(4)  |
| C(18)-Ru(1)-C(15) | 76.5(4)  |
| C(19)-Ru(1)-C(15) | 63.9(4)  |
| C(1)-Ru(1)-C(14)  | 150.4(4) |
| N(1)-Ru(1)-C(14)  | 133.9(4) |
| C(16)-Ru(1)-C(14) | 65.2(4)  |
| C(17)-Ru(1)-C(14) | 77.7(4)  |
| C(18)-Ru(1)-C(14) | 65.0(4)  |
| C(19)-Ru(1)-C(14) | 35.6(4)  |
| C(15)-Ru(1)-C(14) | 35.2(4)  |
| C(1)-Ru(1)-Cl(1)  | 88.5(3)  |
| N(1)-Ru(1)-Cl(1)  | 86.9(2)  |
| C(16)-Ru(1)-Cl(1) | 146.0(3) |
| C(17)-Ru(1)-Cl(1) | 161.8(3) |
| C(18)-Ru(1)-Cl(1) | 124.7(3) |
| C(19)-Ru(1)-Cl(1) | 95.5(3)  |
| C(15)-Ru(1)-Cl(1) | 111.4(3) |
| C(14)-Ru(1)-Cl(1) | 90.3(3)  |
| C(23)-Ru(2)-N(3)  | 76.5(3)  |
| C(23)-Ru(2)-C(38) | 123.1(4) |
| N(3)-Ru(2)-C(38)  | 94.1(3)  |
| C(23)-Ru(2)-C(39) | 95.2(4)  |
| N(3)-Ru(2)-C(39)  | 113.6(3) |
| C(38)-Ru(2)-C(39) | 37.5(4)  |
| C(23)-Ru(2)-C(40) | 93.7(4)  |
| N(3)-Ru(2)-C(40)  | 149.3(3) |
| C(38)-Ru(2)-C(40) | 66.7(4)  |

|                     |          |
|---------------------|----------|
| C(39)-Ru(2)-C(40)   | 37.4(3)  |
| C(23)-Ru(2)-C(41)   | 118.5(4) |
| N(3)-Ru(2)-C(41)    | 165.0(4) |
| C(38)-Ru(2)-C(41)   | 77.8(4)  |
| C(39)-Ru(2)-C(41)   | 67.2(4)  |
| C(40)-Ru(2)-C(41)   | 37.3(4)  |
| C(23)-Ru(2)-C(37)   | 160.4(4) |
| N(3)-Ru(2)-C(37)    | 102.2(4) |
| C(38)-Ru(2)-C(37)   | 37.3(4)  |
| C(39)-Ru(2)-C(37)   | 67.0(4)  |
| C(40)-Ru(2)-C(37)   | 77.4(4)  |
| C(41)-Ru(2)-C(37)   | 63.7(4)  |
| C(23)-Ru(2)-C(36)   | 154.4(4) |
| N(3)-Ru(2)-C(36)    | 128.8(4) |
| C(38)-Ru(2)-C(36)   | 64.9(4)  |
| C(39)-Ru(2)-C(36)   | 78.4(4)  |
| C(40)-Ru(2)-C(36)   | 66.2(4)  |
| C(41)-Ru(2)-C(36)   | 36.2(4)  |
| C(37)-Ru(2)-C(36)   | 34.0(4)  |
| C(23)-Ru(2)-Cl(2)   | 86.3(3)  |
| N(3)-Ru(2)-Cl(2)    | 88.1(2)  |
| C(38)-Ru(2)-Cl(2)   | 150.2(3) |
| C(39)-Ru(2)-Cl(2)   | 158.1(3) |
| C(40)-Ru(2)-Cl(2)   | 120.7(3) |
| C(41)-Ru(2)-Cl(2)   | 92.8(3)  |
| C(37)-Ru(2)-Cl(2)   | 113.3(3) |
| C(36)-Ru(2)-Cl(2)   | 90.8(3)  |
| C(20)-C(21)-H(21A)  | 109.5    |
| C(20)-C(21)-H(21B)  | 109.5    |
| H(21A)-C(21)-H(21B) | 109.5    |

|                     |           |
|---------------------|-----------|
| C(20)-C(21)-H(21C)  | 109.5     |
| H(21A)-C(21)-H(21C) | 109.5     |
| H(21B)-C(21)-H(21C) | 109.5     |
| N(1)-N(2)-C(6)      | 110.5(8)  |
| N(4)-N(3)-C(29)     | 113.8(7)  |
| N(4)-N(3)-Ru(2)     | 120.9(6)  |
| C(29)-N(3)-Ru(2)    | 125.4(6)  |
| C(14)-C(13)-H(13A)  | 109.5     |
| C(14)-C(13)-H(13B)  | 109.5     |
| H(13A)-C(13)-H(13B) | 109.5     |
| C(14)-C(13)-H(13C)  | 109.5     |
| H(13A)-C(13)-H(13C) | 109.5     |
| H(13B)-C(13)-H(13C) | 109.5     |
| N(3)-N(4)-C(28)     | 111.3(8)  |
| N(2)-N(1)-C(7)      | 113.8(9)  |
| N(2)-N(1)-Ru(1)     | 122.1(7)  |
| C(7)-N(1)-Ru(1)     | 124.1(7)  |
| C(6)-C(1)-C(2)      | 116.8(9)  |
| C(6)-C(1)-Ru(1)     | 113.6(7)  |
| C(2)-C(1)-Ru(1)     | 129.6(8)  |
| C(24)-C(23)-C(28)   | 115.9(9)  |
| C(24)-C(23)-Ru(2)   | 131.2(7)  |
| C(28)-C(23)-Ru(2)   | 112.9(7)  |
| C(34)-C(29)-C(30)   | 119.0(10) |
| C(34)-C(29)-N(3)    | 119.4(9)  |
| C(30)-C(29)-N(3)    | 121.6(9)  |
| C(16)-C(17)-C(18)   | 117.6(10) |
| C(16)-C(17)-C(20)   | 122.7(10) |
| C(18)-C(17)-C(20)   | 119.6(9)  |
| C(16)-C(17)-Ru(1)   | 69.2(6)   |

|                    |           |
|--------------------|-----------|
| C(18)-C(17)-Ru(1)  | 72.5(6)   |
| C(20)-C(17)-Ru(1)  | 128.9(7)  |
| C(39)-C(38)-C(37)  | 122.7(9)  |
| C(39)-C(38)-Ru(2)  | 72.8(5)   |
| C(37)-C(38)-Ru(2)  | 77.1(6)   |
| C(39)-C(38)-H(38A) | 118.6     |
| C(37)-C(38)-H(38A) | 118.6     |
| Ru(2)-C(38)-H(38A) | 118.6     |
| C(17)-C(20)-C(21)  | 115.1(11) |
| C(17)-C(20)-C(22)  | 109.9(9)  |
| C(21)-C(20)-C(22)  | 110.1(11) |
| C(17)-C(20)-H(20A) | 107.1     |
| C(21)-C(20)-H(20A) | 107.1     |
| C(22)-C(20)-H(20A) | 107.1     |
| N(4)-C(28)-C(27)   | 118.7(9)  |
| N(4)-C(28)-C(23)   | 118.4(9)  |
| C(27)-C(28)-C(23)  | 122.9(9)  |
| C(33)-C(34)-C(29)  | 119.1(12) |
| C(33)-C(34)-H(34A) | 120.4     |
| C(29)-C(34)-H(34A) | 120.4     |
| C(25)-C(24)-C(23)  | 121.8(10) |
| C(25)-C(24)-H(24A) | 119.1     |
| C(23)-C(24)-H(24A) | 119.1     |
| C(39)-C(40)-C(41)  | 119.5(9)  |
| C(39)-C(40)-Ru(2)  | 71.1(5)   |
| C(41)-C(40)-Ru(2)  | 71.7(5)   |
| C(39)-C(40)-H(40A) | 119.8     |
| C(41)-C(40)-H(40A) | 119.8     |
| Ru(2)-C(40)-H(40A) | 119.8     |
| C(37)-C(36)-C(41)  | 118.9(9)  |

|                    |           |
|--------------------|-----------|
| C(37)-C(36)-C(35)  | 120.6(11) |
| C(41)-C(36)-C(35)  | 120.3(11) |
| C(37)-C(36)-Ru(2)  | 72.3(6)   |
| C(41)-C(36)-Ru(2)  | 67.4(5)   |
| C(35)-C(36)-Ru(2)  | 128.1(7)  |
| C(1)-C(6)-C(5)     | 123.1(10) |
| C(1)-C(6)-N(2)     | 118.3(9)  |
| C(5)-C(6)-N(2)     | 118.5(10) |
| C(3)-C(2)-C(1)     | 121.0(11) |
| C(3)-C(2)-H(2A)    | 119.5     |
| C(1)-C(2)-H(2A)    | 119.5     |
| C(38)-C(39)-C(40)  | 117.1(9)  |
| C(38)-C(39)-C(42)  | 123.3(9)  |
| C(40)-C(39)-C(42)  | 119.6(9)  |
| C(38)-C(39)-Ru(2)  | 69.7(5)   |
| C(40)-C(39)-Ru(2)  | 71.5(5)   |
| C(42)-C(39)-Ru(2)  | 129.6(7)  |
| C(2)-C(3)-C(4)     | 120.9(11) |
| C(2)-C(3)-H(3A)    | 119.5     |
| C(4)-C(3)-H(3A)    | 119.5     |
| C(24)-C(25)-C(26)  | 121.2(10) |
| C(24)-C(25)-H(25A) | 119.4     |
| C(26)-C(25)-H(25A) | 119.4     |
| C(34)-C(33)-C(32)  | 124.5(14) |
| C(34)-C(33)-H(33A) | 117.8     |
| C(32)-C(33)-H(33A) | 117.8     |
| C(44)-C(42)-C(39)  | 114.7(10) |
| C(44)-C(42)-C(43)  | 109.1(10) |
| C(39)-C(42)-C(43)  | 108.6(9)  |
| C(44)-C(42)-H(42A) | 108.1     |

|                     |           |
|---------------------|-----------|
| C(39)-C(42)-H(42A)  | 108.1     |
| C(43)-C(42)-H(42A)  | 108.1     |
| C(32)-C(31)-C(30)   | 121.1(12) |
| C(32)-C(31)-H(31A)  | 119.5     |
| C(30)-C(31)-H(31A)  | 119.5     |
| C(16)-C(15)-C(14)   | 119.1(10) |
| C(16)-C(15)-Ru(1)   | 64.5(5)   |
| C(14)-C(15)-Ru(1)   | 72.5(6)   |
| C(16)-C(15)-H(15A)  | 119.0     |
| C(14)-C(15)-H(15A)  | 119.0     |
| Ru(1)-C(15)-H(15A)  | 119.0     |
| C(26)-C(27)-C(28)   | 118.5(10) |
| C(26)-C(27)-H(27A)  | 120.7     |
| C(28)-C(27)-H(27A)  | 120.7     |
| C(36)-C(35)-H(35A)  | 109.5     |
| C(36)-C(35)-H(35B)  | 109.5     |
| H(35A)-C(35)-H(35B) | 109.5     |
| C(36)-C(35)-H(35C)  | 109.5     |
| H(35A)-C(35)-H(35C) | 109.5     |
| H(35B)-C(35)-H(35C) | 109.5     |
| C(8)-C(7)-C(12)     | 120.3(11) |
| C(8)-C(7)-N(1)      | 120.5(11) |
| C(12)-C(7)-N(1)     | 119.2(10) |
| C(4)-C(5)-C(6)      | 118.4(11) |
| C(4)-C(5)-H(5A)     | 120.8     |
| C(6)-C(5)-H(5A)     | 120.8     |
| C(27)-C(26)-C(25)   | 119.6(10) |
| C(27)-C(26)-H(26A)  | 120.2     |
| C(25)-C(26)-H(26A)  | 120.2     |
| C(11)-C(12)-C(7)    | 119.7(12) |

|                    |           |
|--------------------|-----------|
| C(11)-C(12)-H(12A) | 120.1     |
| C(7)-C(12)-H(12A)  | 120.1     |
| C(40)-C(41)-C(36)  | 122.1(9)  |
| C(40)-C(41)-Ru(2)  | 71.0(5)   |
| C(36)-C(41)-Ru(2)  | 76.3(6)   |
| C(40)-C(41)-H(41A) | 118.7     |
| C(36)-C(41)-H(41A) | 118.7     |
| Ru(2)-C(41)-H(41A) | 118.7     |
| C(31)-C(30)-C(29)  | 118.9(11) |
| C(31)-C(30)-H(30A) | 120.5     |
| C(29)-C(30)-H(30A) | 120.5     |
| C(14)-C(19)-C(18)  | 121.8(10) |
| C(14)-C(19)-Ru(1)  | 76.2(6)   |
| C(18)-C(19)-Ru(1)  | 71.0(5)   |
| C(14)-C(19)-H(19A) | 118.9     |
| C(18)-C(19)-H(19A) | 118.9     |
| Ru(1)-C(19)-H(19A) | 118.9     |
| C(36)-C(37)-C(38)  | 119.3(10) |
| C(36)-C(37)-Ru(2)  | 73.7(6)   |
| C(38)-C(37)-Ru(2)  | 65.6(5)   |
| C(36)-C(37)-H(37A) | 119.3     |
| C(38)-C(37)-H(37A) | 119.3     |
| Ru(2)-C(37)-H(37A) | 119.3     |
| C(19)-C(14)-C(15)  | 118.7(9)  |
| C(19)-C(14)-C(13)  | 119.8(12) |
| C(15)-C(14)-C(13)  | 121.4(12) |
| C(19)-C(14)-Ru(1)  | 68.3(5)   |
| C(15)-C(14)-Ru(1)  | 72.2(6)   |
| C(13)-C(14)-Ru(1)  | 128.8(7)  |
| C(31)-C(32)-C(33)  | 117.2(12) |

|                     |           |
|---------------------|-----------|
| C(31)-C(32)-H(32A)  | 121.4     |
| C(33)-C(32)-H(32A)  | 121.4     |
| C(15)-C(16)-C(17)   | 122.2(10) |
| C(15)-C(16)-Ru(1)   | 79.6(6)   |
| C(17)-C(16)-Ru(1)   | 72.8(6)   |
| C(15)-C(16)-H(16A)  | 118.9     |
| C(17)-C(16)-H(16A)  | 118.9     |
| Ru(1)-C(16)-H(16A)  | 118.9     |
| C(5)-C(4)-C(3)      | 119.7(11) |
| C(5)-C(4)-H(4A)     | 120.1     |
| C(3)-C(4)-H(4A)     | 120.1     |
| C(19)-C(18)-C(17)   | 119.5(10) |
| C(19)-C(18)-Ru(1)   | 72.3(6)   |
| C(17)-C(18)-Ru(1)   | 70.0(6)   |
| C(19)-C(18)-H(18A)  | 119.7     |
| C(17)-C(18)-H(18A)  | 119.7     |
| Ru(1)-C(18)-H(18A)  | 119.7     |
| C(9)-C(8)-C(7)      | 119.3(14) |
| C(9)-C(8)-H(8A)     | 120.4     |
| C(7)-C(8)-H(8A)     | 120.4     |
| C(10)-C(11)-C(12)   | 118.6(14) |
| C(10)-C(11)-H(11A)  | 120.7     |
| C(12)-C(11)-H(11A)  | 120.7     |
| C(42)-C(44)-H(44A)  | 109.5     |
| C(42)-C(44)-H(44B)  | 109.5     |
| H(44A)-C(44)-H(44B) | 109.5     |
| C(42)-C(44)-H(44C)  | 109.5     |
| H(44A)-C(44)-H(44C) | 109.5     |
| H(44B)-C(44)-H(44C) | 109.5     |
| C(10)-C(9)-C(8)     | 119.0(14) |



|                     |           |
|---------------------|-----------|
| C(10)-C(9)-H(9A)    | 120.5     |
| C(8)-C(9)-H(9A)     | 120.5     |
| C(42)-C(43)-H(43A)  | 109.5     |
| C(42)-C(43)-H(43B)  | 109.5     |
| H(43A)-C(43)-H(43B) | 109.5     |
| C(42)-C(43)-H(43C)  | 109.5     |
| H(43A)-C(43)-H(43C) | 109.5     |
| H(43B)-C(43)-H(43C) | 109.5     |
| C(20)-C(22)-H(22A)  | 109.5     |
| C(20)-C(22)-H(22B)  | 109.5     |
| H(22A)-C(22)-H(22B) | 109.5     |
| C(20)-C(22)-H(22C)  | 109.5     |
| H(22A)-C(22)-H(22C) | 109.5     |
| H(22B)-C(22)-H(22C) | 109.5     |
| C(11)-C(10)-C(9)    | 123.0(13) |
| C(11)-C(10)-H(10A)  | 118.5     |
| C(9)-C(10)-H(10A)   | 118.5     |

**Table 4.** Anisotropic displacement parameters ( $\text{Å}^2 \times 10^3$ ) for 1501752. The anisotropic displacement factor exponent takes the form:  $-2 \pi^2 [ h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12} ]$

|       | U11    | U22   | U33     | U23    | U13    | U12    |
|-------|--------|-------|---------|--------|--------|--------|
| Ru(1) | 33(1)  | 37(1) | 36(1)   | -6(1)  | 2(1)   | -7(1)  |
| Ru(2) | 28(1)  | 33(1) | 31(1)   | -3(1)  | -5(1)  | -3(1)  |
| Cl(2) | 51(2)  | 48(1) | 51(2)   | -9(1)  | -15(1) | -11(1) |
| Cl(1) | 49(1)  | 51(2) | 50(2)   | -6(1)  | 12(1)  | -17(1) |
| C(21) | 82(10) | 64(9) | 123(13) | 18(9)  | 17(9)  | -16(8) |
| N(2)  | 37(5)  | 48(5) | 57(6)   | -2(4)  | 0(4)   | -4(4)  |
| N(3)  | 31(4)  | 34(4) | 42(4)   | -4(3)  | -2(3)  | -4(3)  |
| C(13) | 59(8)  | 47(7) | 167(16) | -25(9) | 50(9)  | -21(6) |

|       |       |        |         |        |        |        |
|-------|-------|--------|---------|--------|--------|--------|
| N(4)  | 39(4) | 33(4)  | 44(5)   | 4(4)   | -6(4)  | 1(3)   |
| N(1)  | 40(4) | 44(5)  | 43(5)   | -5(4)  | 4(4)   | -10(4) |
| C(1)  | 44(5) | 42(5)  | 36(5)   | -8(4)  | 6(4)   | -15(4) |
| C(23) | 33(5) | 42(5)  | 42(5)   | -6(4)  | -8(4)  | -11(4) |
| C(29) | 33(5) | 38(5)  | 39(5)   | -2(4)  | -3(4)  | -5(4)  |
| C(17) | 45(6) | 49(6)  | 42(6)   | -10(5) | 9(4)   | -18(5) |
| C(38) | 44(6) | 53(6)  | 37(5)   | -14(5) | -8(4)  | -7(5)  |
| C(20) | 70(8) | 42(6)  | 65(7)   | -3(5)  | 7(6)   | -24(6) |
| C(28) | 37(5) | 41(5)  | 45(6)   | -2(4)  | 2(4)   | -7(4)  |
| C(34) | 35(5) | 44(6)  | 78(8)   | 13(6)  | 1(5)   | -11(5) |
| C(24) | 35(5) | 58(7)  | 44(6)   | -2(5)  | -1(4)  | -9(5)  |
| C(40) | 28(5) | 45(6)  | 42(5)   | -6(4)  | -8(4)  | -3(4)  |
| C(36) | 36(5) | 31(5)  | 66(7)   | 8(5)   | -16(5) | -6(4)  |
| C(6)  | 41(5) | 43(6)  | 51(6)   | -16(5) | 3(5)   | -9(4)  |
| C(2)  | 47(6) | 57(7)  | 52(6)   | -17(5) | -3(5)  | -7(5)  |
| C(39) | 37(5) | 43(5)  | 36(5)   | -8(4)  | -10(4) | -6(4)  |
| C(3)  | 66(8) | 72(8)  | 63(8)   | -29(7) | 12(6)  | -33(7) |
| C(25) | 58(7) | 61(7)  | 51(7)   | 8(6)   | 2(5)   | -27(6) |
| C(33) | 87(9) | 77(9)  | 28(6)   | -12(6) | -17(6) | 24(7)  |
| C(42) | 68(7) | 46(6)  | 60(7)   | -6(5)  | -21(6) | -20(6) |
| C(31) | 73(9) | 98(11) | 56(8)   | -41(8) | 14(7)  | -3(8)  |
| C(15) | 42(6) | 61(7)  | 58(7)   | -36(6) | 11(5)  | -18(5) |
| C(27) | 56(7) | 42(6)  | 58(7)   | 9(5)   | -6(5)  | 0(5)   |
| C(35) | 48(7) | 38(6)  | 142(13) | 12(7)  | -32(8) | -13(5) |
| C(7)  | 40(5) | 65(7)  | 39(5)   | -2(5)  | -4(4)  | -20(5) |
| C(5)  | 57(7) | 48(7)  | 80(9)   | -21(6) | 1(6)   | -12(5) |
| C(26) | 81(9) | 54(7)  | 56(7)   | 21(6)  | 0(6)   | -11(6) |
| C(12) | 55(7) | 68(8)  | 61(7)   | -13(6) | -15(6) | -20(6) |
| C(41) | 41(5) | 41(6)  | 58(7)   | -15(5) | -15(5) | 2(4)   |
| C(30) | 69(7) | 41(6)  | 53(7)   | -11(5) | 4(6)   | -2(5)  |

|       |         |         |         |        |         |         |
|-------|---------|---------|---------|--------|---------|---------|
| C(19) | 34(5)   | 40(6)   | 63(7)   | 4(5)   | -1(5)   | 2(4)    |
| C(37) | 39(6)   | 66(7)   | 44(6)   | 12(5)  | -11(5)  | -16(5)  |
| C(14) | 37(5)   | 33(5)   | 83(8)   | -14(5) | 27(5)   | -6(4)   |
| C(32) | 70(8)   | 88(10)  | 49(7)   | 8(7)   | 9(6)    | -27(7)  |
| C(16) | 47(6)   | 58(7)   | 41(6)   | -10(5) | 0(5)    | -8(5)   |
| C(4)  | 72(8)   | 55(7)   | 87(9)   | -39(7) | 17(7)   | -24(7)  |
| C(18) | 33(5)   | 49(6)   | 49(6)   | -11(5) | 2(4)    | -8(4)   |
| C(8)  | 78(9)   | 83(10)  | 52(7)   | 0(7)   | -13(7)  | -12(7)  |
| C(11) | 68(8)   | 94(10)  | 72(9)   | -27(8) | -2(7)   | -39(8)  |
| C(44) | 81(10)  | 46(7)   | 142(14) | -21(8) | -35(10) | -8(7)   |
| C(9)  | 92(11)  | 125(14) | 53(8)   | 28(9)  | -31(7)  | -45(10) |
| C(43) | 62(7)   | 61(7)   | 78(9)   | -14(6) | -23(6)  | -24(6)  |
| C(22) | 63(8)   | 63(8)   | 119(12) | -16(8) | 23(8)   | -37(7)  |
| C(10) | 107(12) | 123(14) | 57(9)   | 0(9)   | -27(8)  | -57(11) |

**Table 5.** Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for 1501752.

|        | x     | y    | z    | U(eq) |
|--------|-------|------|------|-------|
| H(21A) | 2304  | 9053 | 314  | 141   |
| H(21B) | 3112  | 8860 | -638 | 141   |
| H(21C) | 3357  | 9634 | -47  | 141   |
| H(13A) | 4213  | 3841 | 901  | 138   |
| H(13B) | 2695  | 4286 | 741  | 138   |
| H(13C) | 3224  | 4162 | 1749 | 138   |
| H(38A) | -2706 | 7464 | 6234 | 53    |
| H(20A) | 4252  | 8429 | 1124 | 70    |
| H(34A) | -5397 | 6158 | 5792 | 65    |
| H(24A) | -2040 | 7660 | 2532 | 56    |
| H(40A) | -614  | 6843 | 3766 | 47    |
| H(2A)  | 2848  | 7563 | 3113 | 62    |

|        |       |       |       |     |
|--------|-------|-------|-------|-----|
| H(3A)  | 2029  | 8970  | 3804  | 75  |
| H(25A) | -2722 | 9006  | 1487  | 67  |
| H(33A) | -6649 | 5915  | 7061  | 85  |
| H(42A) | -920  | 8406  | 4253  | 67  |
| H(31A) | -7538 | 8686  | 7481  | 93  |
| H(15A) | 2857  | 5696  | -392  | 61  |
| H(27A) | -5988 | 9964  | 3108  | 66  |
| H(35A) | -1697 | 3952  | 5744  | 114 |
| H(35B) | -2403 | 4254  | 4791  | 114 |
| H(35C) | -3213 | 4494  | 5734  | 114 |
| H(5A)  | -807  | 9900  | 1952  | 73  |
| H(26A) | -4703 | 10157 | 1746  | 81  |
| H(12A) | 552   | 6029  | 63    | 71  |
| H(41A) | -1167 | 5326  | 3961  | 57  |
| H(30A) | -6268 | 9004  | 6149  | 68  |
| H(19A) | 4146  | 5350  | 2261  | 59  |
| H(37A) | -3110 | 5888  | 6463  | 61  |
| H(32A) | -7814 | 7143  | 7912  | 84  |
| H(16A) | 3034  | 7300  | -575  | 59  |
| H(4A)  | 154   | 10112 | 3272  | 81  |
| H(18A) | 4546  | 6909  | 2029  | 52  |
| H(8A)  | -681  | 8918  | -719  | 88  |
| H(11A) | -258  | 5733  | -1297 | 88  |
| H(44A) | -2988 | 9161  | 4920  | 133 |
| H(44B) | -1906 | 9666  | 5139  | 133 |
| H(44C) | -2393 | 8946  | 5913  | 133 |
| H(9A)  | -1505 | 8598  | -2065 | 106 |
| H(43A) | 828   | 7604  | 5235  | 96  |
| H(43B) | -48   | 8002  | 6106  | 96  |
| H(43C) | 418   | 8724  | 5324  | 96  |

|        |       |      |       |     |
|--------|-------|------|-------|-----|
| H(22A) | 6251  | 7699 | 338   | 118 |
| H(22B) | 5774  | 8809 | -21   | 118 |
| H(22C) | 5574  | 8029 | -624  | 118 |
| H(10A) | -1205 | 7020 | -2348 | 108 |

**Table 6.** Torsion angles [deg] for 1501752.

|                        |           |
|------------------------|-----------|
| C(23)-Ru(2)-N(3)-N(4)  | -1.7(7)   |
| C(38)-Ru(2)-N(3)-N(4)  | 121.4(7)  |
| C(39)-Ru(2)-N(3)-N(4)  | 88.2(7)   |
| C(40)-Ru(2)-N(3)-N(4)  | 72.4(10)  |
| C(41)-Ru(2)-N(3)-N(4)  | 177.9(11) |
| C(37)-Ru(2)-N(3)-N(4)  | 158.2(7)  |
| C(36)-Ru(2)-N(3)-N(4)  | -177.8(7) |
| Cl(2)-Ru(2)-N(3)-N(4)  | -88.3(7)  |
| C(23)-Ru(2)-N(3)-C(29) | -179.5(8) |
| C(38)-Ru(2)-N(3)-C(29) | -56.4(8)  |
| C(39)-Ru(2)-N(3)-C(29) | -89.7(8)  |
| C(40)-Ru(2)-N(3)-C(29) | -105.5(9) |
| C(41)-Ru(2)-N(3)-C(29) | 0.0(18)   |
| C(37)-Ru(2)-N(3)-C(29) | -19.6(8)  |
| C(36)-Ru(2)-N(3)-C(29) | 4.3(9)    |
| Cl(2)-Ru(2)-N(3)-C(29) | 93.8(7)   |
| C(29)-N(3)-N(4)-C(28)  | 179.5(8)  |
| Ru(2)-N(3)-N(4)-C(28)  | 1.4(11)   |
| C(6)-N(2)-N(1)-C(7)    | -178.6(8) |
| C(6)-N(2)-N(1)-Ru(1)   | -1.7(11)  |
| C(1)-Ru(1)-N(1)-N(2)   | 2.0(8)    |
| C(16)-Ru(1)-N(1)-N(2)  | -122.8(8) |
| C(17)-Ru(1)-N(1)-N(2)  | -88.0(8)  |
| C(18)-Ru(1)-N(1)-N(2)  | -69.1(10) |

|                         |            |
|-------------------------|------------|
| C(19)-Ru(1)-N(1)-N(2)   | -165.9(17) |
| C(15)-Ru(1)-N(1)-N(2)   | -157.3(8)  |
| C(14)-Ru(1)-N(1)-N(2)   | 178.7(7)   |
| Cl(1)-Ru(1)-N(1)-N(2)   | 91.3(8)    |
| C(1)-Ru(1)-N(1)-C(7)    | 178.7(8)   |
| C(16)-Ru(1)-N(1)-C(7)   | 53.8(8)    |
| C(17)-Ru(1)-N(1)-C(7)   | 88.6(8)    |
| C(18)-Ru(1)-N(1)-C(7)   | 107.5(9)   |
| C(19)-Ru(1)-N(1)-C(7)   | 11(2)      |
| C(15)-Ru(1)-N(1)-C(7)   | 19.3(8)    |
| C(14)-Ru(1)-N(1)-C(7)   | -4.7(10)   |
| Cl(1)-Ru(1)-N(1)-C(7)   | -92.1(7)   |
| N(1)-Ru(1)-C(1)-C(6)    | -1.7(7)    |
| C(16)-Ru(1)-C(1)-C(6)   | 82.7(8)    |
| C(17)-Ru(1)-C(1)-C(6)   | 108.9(8)   |
| C(18)-Ru(1)-C(1)-C(6)   | 146.3(8)   |
| C(19)-Ru(1)-C(1)-C(6)   | 175.7(7)   |
| C(15)-Ru(1)-C(1)-C(6)   | 92.9(14)   |
| C(14)-Ru(1)-C(1)-C(6)   | -176.9(7)  |
| Cl(1)-Ru(1)-C(1)-C(6)   | -89.0(7)   |
| N(1)-Ru(1)-C(1)-C(2)    | 178.8(10)  |
| C(16)-Ru(1)-C(1)-C(2)   | -96.7(10)  |
| C(17)-Ru(1)-C(1)-C(2)   | -70.5(10)  |
| C(18)-Ru(1)-C(1)-C(2)   | -33.1(10)  |
| C(19)-Ru(1)-C(1)-C(2)   | -3.7(11)   |
| C(15)-Ru(1)-C(1)-C(2)   | -86.5(15)  |
| C(14)-Ru(1)-C(1)-C(2)   | 3.7(14)    |
| Cl(1)-Ru(1)-C(1)-C(2)   | 91.6(10)   |
| N(3)-Ru(2)-C(23)-C(24)  | -177.8(10) |
| C(38)-Ru(2)-C(23)-C(24) | 96.1(10)   |

|                         |           |
|-------------------------|-----------|
| C(39)-Ru(2)-C(23)-C(24) | 69.1(10)  |
| C(40)-Ru(2)-C(23)-C(24) | 31.7(10)  |
| C(41)-Ru(2)-C(23)-C(24) | 2.3(11)   |
| C(37)-Ru(2)-C(23)-C(24) | 93.5(14)  |
| C(36)-Ru(2)-C(23)-C(24) | -4.8(15)  |
| Cl(2)-Ru(2)-C(23)-C(24) | -88.9(9)  |
| N(3)-Ru(2)-C(23)-C(28)  | 1.4(7)    |
| C(38)-Ru(2)-C(23)-C(28) | -84.6(8)  |
| C(39)-Ru(2)-C(23)-C(28) | -111.6(7) |
| C(40)-Ru(2)-C(23)-C(28) | -149.1(7) |
| C(41)-Ru(2)-C(23)-C(28) | -178.4(7) |
| C(37)-Ru(2)-C(23)-C(28) | -87.2(13) |
| C(36)-Ru(2)-C(23)-C(28) | 174.5(7)  |
| Cl(2)-Ru(2)-C(23)-C(28) | 90.4(7)   |
| N(4)-N(3)-C(29)-C(34)   | 139.8(9)  |
| Ru(2)-N(3)-C(29)-C(34)  | -42.2(12) |
| N(4)-N(3)-C(29)-C(30)   | -39.9(13) |
| Ru(2)-N(3)-C(29)-C(30)  | 138.1(8)  |
| C(1)-Ru(1)-C(17)-C(16)  | -143.9(7) |
| N(1)-Ru(1)-C(17)-C(16)  | -67.5(7)  |
| C(18)-Ru(1)-C(17)-C(16) | 129.8(9)  |
| C(19)-Ru(1)-C(17)-C(16) | 100.8(7)  |
| C(15)-Ru(1)-C(17)-C(16) | 30.2(6)   |
| C(14)-Ru(1)-C(17)-C(16) | 65.2(7)   |
| Cl(1)-Ru(1)-C(17)-C(16) | 114.9(9)  |
| C(1)-Ru(1)-C(17)-C(18)  | 86.2(6)   |
| N(1)-Ru(1)-C(17)-C(18)  | 162.7(6)  |
| C(16)-Ru(1)-C(17)-C(18) | -129.8(9) |
| C(19)-Ru(1)-C(17)-C(18) | -29.0(6)  |
| C(15)-Ru(1)-C(17)-C(18) | -99.7(7)  |

|                         |            |
|-------------------------|------------|
| C(14)-Ru(1)-C(17)-C(18) | -64.7(6)   |
| Cl(1)-Ru(1)-C(17)-C(18) | -14.9(12)  |
| C(1)-Ru(1)-C(17)-C(20)  | -28.1(10)  |
| N(1)-Ru(1)-C(17)-C(20)  | 48.4(10)   |
| C(16)-Ru(1)-C(17)-C(20) | 115.9(13)  |
| C(18)-Ru(1)-C(17)-C(20) | -114.3(12) |
| C(19)-Ru(1)-C(17)-C(20) | -143.3(11) |
| C(15)-Ru(1)-C(17)-C(20) | 146.0(11)  |
| C(14)-Ru(1)-C(17)-C(20) | -179.0(11) |
| Cl(1)-Ru(1)-C(17)-C(20) | -129.2(10) |
| C(23)-Ru(2)-C(38)-C(39) | -47.9(7)   |
| N(3)-Ru(2)-C(38)-C(39)  | -124.4(6)  |
| C(40)-Ru(2)-C(38)-C(39) | 30.7(6)    |
| C(41)-Ru(2)-C(38)-C(39) | 68.3(6)    |
| C(37)-Ru(2)-C(38)-C(39) | 130.6(9)   |
| C(36)-Ru(2)-C(38)-C(39) | 104.2(6)   |
| Cl(2)-Ru(2)-C(38)-C(39) | 142.3(5)   |
| C(23)-Ru(2)-C(38)-C(37) | -178.6(6)  |
| N(3)-Ru(2)-C(38)-C(37)  | 104.9(6)   |
| C(39)-Ru(2)-C(38)-C(37) | -130.6(9)  |
| C(40)-Ru(2)-C(38)-C(37) | -99.9(7)   |
| C(41)-Ru(2)-C(38)-C(37) | -62.3(6)   |
| C(36)-Ru(2)-C(38)-C(37) | -26.4(6)   |
| Cl(2)-Ru(2)-C(38)-C(37) | 11.6(9)    |
| C(16)-C(17)-C(20)-C(21) | 37.5(15)   |
| C(18)-C(17)-C(20)-C(21) | -141.8(11) |
| Ru(1)-C(17)-C(20)-C(21) | -51.1(15)  |
| C(16)-C(17)-C(20)-C(22) | -87.5(14)  |
| C(18)-C(17)-C(20)-C(22) | 93.2(13)   |
| Ru(1)-C(17)-C(20)-C(22) | -176.0(9)  |



|                         |            |
|-------------------------|------------|
| N(3)-N(4)-C(28)-C(27)   | 178.4(9)   |
| N(3)-N(4)-C(28)-C(23)   | 0.0(13)    |
| C(24)-C(23)-C(28)-N(4)  | 178.1(9)   |
| Ru(2)-C(23)-C(28)-N(4)  | -1.3(12)   |
| C(24)-C(23)-C(28)-C(27) | -0.3(15)   |
| Ru(2)-C(23)-C(28)-C(27) | -179.7(9)  |
| C(30)-C(29)-C(34)-C(33) | 3.0(16)    |
| N(3)-C(29)-C(34)-C(33)  | -176.8(10) |
| C(28)-C(23)-C(24)-C(25) | 1.5(15)    |
| Ru(2)-C(23)-C(24)-C(25) | -179.3(8)  |
| C(23)-Ru(2)-C(40)-C(39) | 93.8(6)    |
| N(3)-Ru(2)-C(40)-C(39)  | 24.3(10)   |
| C(38)-Ru(2)-C(40)-C(39) | -30.8(6)   |
| C(41)-Ru(2)-C(40)-C(39) | -131.4(9)  |
| C(37)-Ru(2)-C(40)-C(39) | -68.5(6)   |
| C(36)-Ru(2)-C(40)-C(39) | -102.5(6)  |
| Cl(2)-Ru(2)-C(40)-C(39) | -178.3(5)  |
| C(23)-Ru(2)-C(40)-C(41) | -134.8(6)  |
| N(3)-Ru(2)-C(40)-C(41)  | 155.7(6)   |
| C(38)-Ru(2)-C(40)-C(41) | 100.6(7)   |
| C(39)-Ru(2)-C(40)-C(41) | 131.4(9)   |
| C(37)-Ru(2)-C(40)-C(41) | 62.9(6)    |
| C(36)-Ru(2)-C(40)-C(41) | 29.0(6)    |
| Cl(2)-Ru(2)-C(40)-C(41) | -46.9(7)   |
| C(23)-Ru(2)-C(36)-C(37) | 143.6(8)   |
| N(3)-Ru(2)-C(36)-C(37)  | -45.1(8)   |
| C(38)-Ru(2)-C(36)-C(37) | 28.8(6)    |
| C(39)-Ru(2)-C(36)-C(37) | 65.9(6)    |
| C(40)-Ru(2)-C(36)-C(37) | 103.2(7)   |
| C(41)-Ru(2)-C(36)-C(37) | 133.0(9)   |

|                         |            |
|-------------------------|------------|
| Cl(2)-Ru(2)-C(36)-C(37) | -133.3(6)  |
| C(23)-Ru(2)-C(36)-C(41) | 10.6(12)   |
| N(3)-Ru(2)-C(36)-C(41)  | -178.1(5)  |
| C(38)-Ru(2)-C(36)-C(41) | -104.1(7)  |
| C(39)-Ru(2)-C(36)-C(41) | -67.1(6)   |
| C(40)-Ru(2)-C(36)-C(41) | -29.8(6)   |
| C(37)-Ru(2)-C(36)-C(41) | -133.0(9)  |
| Cl(2)-Ru(2)-C(36)-C(41) | 93.7(6)    |
| C(23)-Ru(2)-C(36)-C(35) | -101.1(13) |
| N(3)-Ru(2)-C(36)-C(35)  | 70.2(12)   |
| C(38)-Ru(2)-C(36)-C(35) | 144.2(12)  |
| C(39)-Ru(2)-C(36)-C(35) | -178.7(12) |
| C(40)-Ru(2)-C(36)-C(35) | -141.5(12) |
| C(41)-Ru(2)-C(36)-C(35) | -111.7(14) |
| C(37)-Ru(2)-C(36)-C(35) | 115.4(14)  |
| Cl(2)-Ru(2)-C(36)-C(35) | -18.0(11)  |
| C(2)-C(1)-C(6)-C(5)     | 3.5(16)    |
| Ru(1)-C(1)-C(6)-C(5)    | -176.0(9)  |
| C(2)-C(1)-C(6)-N(2)     | -178.9(9)  |
| Ru(1)-C(1)-C(6)-N(2)    | 1.6(12)    |
| N(1)-N(2)-C(6)-C(1)     | 0.0(13)    |
| N(1)-N(2)-C(6)-C(5)     | 177.7(10)  |
| C(6)-C(1)-C(2)-C(3)     | -4.2(16)   |
| Ru(1)-C(1)-C(2)-C(3)    | 175.1(8)   |
| C(37)-C(38)-C(39)-C(40) | 6.2(14)    |
| Ru(2)-C(38)-C(39)-C(40) | -55.3(7)   |
| C(37)-C(38)-C(39)-C(42) | -173.7(9)  |
| Ru(2)-C(38)-C(39)-C(42) | 124.8(9)   |
| C(37)-C(38)-C(39)-Ru(2) | 61.5(8)    |
| C(41)-C(40)-C(39)-C(38) | -0.4(13)   |

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| Ru(2)-C(40)-C(39)-C(38) | 54.4(7)    |
| C(41)-C(40)-C(39)-C(42) | 179.5(9)   |
| Ru(2)-C(40)-C(39)-C(42) | -125.7(8)  |
| C(41)-C(40)-C(39)-Ru(2) | -54.8(8)   |
| C(23)-Ru(2)-C(39)-C(38) | 141.3(6)   |
| N(3)-Ru(2)-C(39)-C(38)  | 63.8(6)    |
| C(40)-Ru(2)-C(39)-C(38) | -129.5(9)  |
| C(41)-Ru(2)-C(39)-C(38) | -99.9(7)   |
| C(37)-Ru(2)-C(39)-C(38) | -30.0(6)   |
| C(36)-Ru(2)-C(39)-C(38) | -63.7(6)   |
| Cl(2)-Ru(2)-C(39)-C(38) | -125.5(7)  |
| C(23)-Ru(2)-C(39)-C(40) | -89.2(6)   |
| N(3)-Ru(2)-C(39)-C(40)  | -166.7(5)  |
| C(38)-Ru(2)-C(39)-C(40) | 129.5(9)   |
| C(41)-Ru(2)-C(39)-C(40) | 29.6(6)    |
| C(37)-Ru(2)-C(39)-C(40) | 99.5(7)    |
| C(36)-Ru(2)-C(39)-C(40) | 65.8(6)    |
| Cl(2)-Ru(2)-C(39)-C(40) | 4.0(11)    |
| C(23)-Ru(2)-C(39)-C(42) | 24.3(10)   |
| N(3)-Ru(2)-C(39)-C(42)  | -53.2(10)  |
| C(38)-Ru(2)-C(39)-C(42) | -117.0(12) |
| C(40)-Ru(2)-C(39)-C(42) | 113.5(12)  |
| C(41)-Ru(2)-C(39)-C(42) | 143.1(10)  |
| C(37)-Ru(2)-C(39)-C(42) | -147.0(10) |
| C(36)-Ru(2)-C(39)-C(42) | 179.3(10)  |
| Cl(2)-Ru(2)-C(39)-C(42) | 117.5(9)   |
| C(1)-C(2)-C(3)-C(4)     | 3.8(18)    |
| C(23)-C(24)-C(25)-C(26) | -1.8(18)   |
| C(29)-C(34)-C(33)-C(32) | -0.4(19)   |
| C(38)-C(39)-C(42)-C(44) | -36.1(15)  |

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| C(40)-C(39)-C(42)-C(44) | 144.0(11)  |
| Ru(2)-C(39)-C(42)-C(44) | 54.2(14)   |
| C(38)-C(39)-C(42)-C(43) | 86.2(12)   |
| C(40)-C(39)-C(42)-C(43) | -93.7(11)  |
| Ru(2)-C(39)-C(42)-C(43) | 176.5(8)   |
| C(1)-Ru(1)-C(15)-C(16)  | -14.5(15)  |
| N(1)-Ru(1)-C(15)-C(16)  | 74.9(7)    |
| C(17)-Ru(1)-C(15)-C(16) | -31.9(6)   |
| C(18)-Ru(1)-C(15)-C(16) | -70.1(7)   |
| C(19)-Ru(1)-C(15)-C(16) | -106.9(7)  |
| C(14)-Ru(1)-C(15)-C(16) | -135.6(10) |
| Cl(1)-Ru(1)-C(15)-C(16) | 167.6(6)   |
| C(1)-Ru(1)-C(15)-C(14)  | 121.1(12)  |
| N(1)-Ru(1)-C(15)-C(14)  | -149.5(6)  |
| C(16)-Ru(1)-C(15)-C(14) | 135.6(10)  |
| C(17)-Ru(1)-C(15)-C(14) | 103.7(7)   |
| C(18)-Ru(1)-C(15)-C(14) | 65.5(6)    |
| C(19)-Ru(1)-C(15)-C(14) | 28.7(6)    |
| Cl(1)-Ru(1)-C(15)-C(14) | -56.8(6)   |
| N(4)-C(28)-C(27)-C(26)  | -179.0(11) |
| C(23)-C(28)-C(27)-C(26) | -0.6(18)   |
| N(2)-N(1)-C(7)-C(8)     | 32.0(14)   |
| Ru(1)-N(1)-C(7)-C(8)    | -144.8(9)  |
| N(2)-N(1)-C(7)-C(12)    | -149.5(10) |
| Ru(1)-N(1)-C(7)-C(12)   | 33.7(13)   |
| C(1)-C(6)-C(5)-C(4)     | -2.1(18)   |
| N(2)-C(6)-C(5)-C(4)     | -179.7(11) |
| C(28)-C(27)-C(26)-C(25) | 0.4(19)    |
| C(24)-C(25)-C(26)-C(27) | 1(2)       |
| C(8)-C(7)-C(12)-C(11)   | -0.2(17)   |

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| N(1)-C(7)-C(12)-C(11)   | -178.7(10) |
| C(39)-C(40)-C(41)-C(36) | -4.7(14)   |
| Ru(2)-C(40)-C(41)-C(36) | -59.3(8)   |
| C(39)-C(40)-C(41)-Ru(2) | 54.5(8)    |
| C(37)-C(36)-C(41)-C(40) | 4.1(14)    |
| C(35)-C(36)-C(41)-C(40) | 178.8(9)   |
| Ru(2)-C(36)-C(41)-C(40) | 56.8(8)    |
| C(37)-C(36)-C(41)-Ru(2) | -52.7(9)   |
| C(35)-C(36)-C(41)-Ru(2) | 122.0(9)   |
| C(23)-Ru(2)-C(41)-C(40) | 53.7(7)    |
| N(3)-Ru(2)-C(41)-C(40)  | -125.7(13) |
| C(38)-Ru(2)-C(41)-C(40) | -67.5(6)   |
| C(39)-Ru(2)-C(41)-C(40) | -29.6(6)   |
| C(37)-Ru(2)-C(41)-C(40) | -104.3(7)  |
| C(36)-Ru(2)-C(41)-C(40) | -131.4(9)  |
| Cl(2)-Ru(2)-C(41)-C(40) | 141.1(6)   |
| C(23)-Ru(2)-C(41)-C(36) | -174.8(6)  |
| N(3)-Ru(2)-C(41)-C(36)  | 5.7(17)    |
| C(38)-Ru(2)-C(41)-C(36) | 64.0(6)    |
| C(39)-Ru(2)-C(41)-C(36) | 101.8(7)   |
| C(40)-Ru(2)-C(41)-C(36) | 131.4(9)   |
| C(37)-Ru(2)-C(41)-C(36) | 27.2(6)    |
| Cl(2)-Ru(2)-C(41)-C(36) | -87.5(6)   |
| C(32)-C(31)-C(30)-C(29) | 0(2)       |
| C(34)-C(29)-C(30)-C(31) | -2.5(17)   |
| N(3)-C(29)-C(30)-C(31)  | 177.2(10)  |
| C(1)-Ru(1)-C(19)-C(14)  | 173.7(6)   |
| N(1)-Ru(1)-C(19)-C(14)  | -19(2)     |
| C(16)-Ru(1)-C(19)-C(14) | -63.4(7)   |
| C(17)-Ru(1)-C(19)-C(14) | -101.6(7)  |

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| C(18)-Ru(1)-C(19)-C(14) | -131.2(10) |
| C(15)-Ru(1)-C(19)-C(14) | -28.4(6)   |
| Cl(1)-Ru(1)-C(19)-C(14) | 82.8(6)    |
| C(1)-Ru(1)-C(19)-C(18)  | -55.1(7)   |
| N(1)-Ru(1)-C(19)-C(18)  | 111.9(19)  |
| C(16)-Ru(1)-C(19)-C(18) | 67.8(7)    |
| C(17)-Ru(1)-C(19)-C(18) | 29.6(6)    |
| C(15)-Ru(1)-C(19)-C(18) | 102.7(7)   |
| C(14)-Ru(1)-C(19)-C(18) | 131.2(10)  |
| Cl(1)-Ru(1)-C(19)-C(18) | -146.0(6)  |
| C(41)-C(36)-C(37)-C(38) | 1.7(14)    |
| C(35)-C(36)-C(37)-C(38) | -173.1(9)  |
| Ru(2)-C(36)-C(37)-C(38) | -48.8(8)   |
| C(41)-C(36)-C(37)-Ru(2) | 50.5(8)    |
| C(35)-C(36)-C(37)-Ru(2) | -124.2(9)  |
| C(39)-C(38)-C(37)-C(36) | -7.0(15)   |
| Ru(2)-C(38)-C(37)-C(36) | 52.5(9)    |
| C(39)-C(38)-C(37)-Ru(2) | -59.5(8)   |
| C(23)-Ru(2)-C(37)-C(36) | -130.3(11) |
| N(3)-Ru(2)-C(37)-C(36)  | 145.6(6)   |
| C(38)-Ru(2)-C(37)-C(36) | -133.9(9)  |
| C(39)-Ru(2)-C(37)-C(36) | -103.8(7)  |
| C(40)-Ru(2)-C(37)-C(36) | -65.9(6)   |
| C(41)-Ru(2)-C(37)-C(36) | -28.8(6)   |
| Cl(2)-Ru(2)-C(37)-C(36) | 52.4(7)    |
| C(23)-Ru(2)-C(37)-C(38) | 3.6(15)    |
| N(3)-Ru(2)-C(37)-C(38)  | -80.5(6)   |
| C(39)-Ru(2)-C(37)-C(38) | 30.1(6)    |
| C(40)-Ru(2)-C(37)-C(38) | 68.0(6)    |
| C(41)-Ru(2)-C(37)-C(38) | 105.1(7)   |

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| C(36)-Ru(2)-C(37)-C(38) | 133.9(9)   |
| Cl(2)-Ru(2)-C(37)-C(38) | -173.7(5)  |
| C(18)-C(19)-C(14)-C(15) | -3.2(14)   |
| Ru(1)-C(19)-C(14)-C(15) | 53.6(8)    |
| C(18)-C(19)-C(14)-C(13) | 179.9(9)   |
| Ru(1)-C(19)-C(14)-C(13) | -123.3(9)  |
| C(18)-C(19)-C(14)-Ru(1) | -56.9(8)   |
| C(16)-C(15)-C(14)-C(19) | -5.5(14)   |
| Ru(1)-C(15)-C(14)-C(19) | -51.8(8)   |
| C(16)-C(15)-C(14)-C(13) | 171.3(9)   |
| Ru(1)-C(15)-C(14)-C(13) | 125.1(9)   |
| C(16)-C(15)-C(14)-Ru(1) | 46.3(8)    |
| C(1)-Ru(1)-C(14)-C(19)  | -11.6(11)  |
| N(1)-Ru(1)-C(14)-C(19)  | 175.0(6)   |
| C(16)-Ru(1)-C(14)-C(19) | 105.3(7)   |
| C(17)-Ru(1)-C(14)-C(19) | 67.2(7)    |
| C(18)-Ru(1)-C(14)-C(19) | 29.8(6)    |
| C(15)-Ru(1)-C(14)-C(19) | 132.1(9)   |
| Cl(1)-Ru(1)-C(14)-C(19) | -99.0(6)   |
| C(1)-Ru(1)-C(14)-C(15)  | -143.7(8)  |
| N(1)-Ru(1)-C(14)-C(15)  | 42.8(8)    |
| C(16)-Ru(1)-C(14)-C(15) | -26.9(6)   |
| C(17)-Ru(1)-C(14)-C(15) | -64.9(6)   |
| C(18)-Ru(1)-C(14)-C(15) | -102.4(7)  |
| C(19)-Ru(1)-C(14)-C(15) | -132.1(9)  |
| Cl(1)-Ru(1)-C(14)-C(15) | 128.8(6)   |
| C(1)-Ru(1)-C(14)-C(13)  | 99.9(14)   |
| N(1)-Ru(1)-C(14)-C(13)  | -73.5(14)  |
| C(16)-Ru(1)-C(14)-C(13) | -143.2(15) |
| C(17)-Ru(1)-C(14)-C(13) | 178.7(14)  |

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| C(18)-Ru(1)-C(14)-C(13) | 141.3(14)  |
| C(19)-Ru(1)-C(14)-C(13) | 111.5(16)  |
| C(15)-Ru(1)-C(14)-C(13) | -116.4(16) |
| Cl(1)-Ru(1)-C(14)-C(13) | 12.5(13)   |
| C(30)-C(31)-C(32)-C(33) | 3(2)       |
| C(34)-C(33)-C(32)-C(31) | -3(2)      |
| C(14)-C(15)-C(16)-C(17) | 12.1(15)   |
| Ru(1)-C(15)-C(16)-C(17) | 61.8(9)    |
| C(14)-C(15)-C(16)-Ru(1) | -49.8(9)   |
| C(18)-C(17)-C(16)-C(15) | -9.5(15)   |
| C(20)-C(17)-C(16)-C(15) | 171.2(10)  |
| Ru(1)-C(17)-C(16)-C(15) | -65.2(9)   |
| C(18)-C(17)-C(16)-Ru(1) | 55.7(8)    |
| C(20)-C(17)-C(16)-Ru(1) | -123.6(10) |
| C(1)-Ru(1)-C(16)-C(15)  | 174.1(6)   |
| N(1)-Ru(1)-C(16)-C(15)  | -111.0(7)  |
| C(17)-Ru(1)-C(16)-C(15) | 128.6(10)  |
| C(18)-Ru(1)-C(16)-C(15) | 98.2(7)    |
| C(19)-Ru(1)-C(16)-C(15) | 61.4(7)    |
| C(14)-Ru(1)-C(16)-C(15) | 26.4(6)    |
| Cl(1)-Ru(1)-C(16)-C(15) | -21.0(10)  |
| C(1)-Ru(1)-C(16)-C(17)  | 45.4(8)    |
| N(1)-Ru(1)-C(16)-C(17)  | 120.4(6)   |
| C(18)-Ru(1)-C(16)-C(17) | -30.4(6)   |
| C(19)-Ru(1)-C(16)-C(17) | -67.3(7)   |
| C(15)-Ru(1)-C(16)-C(17) | -128.6(10) |
| C(14)-Ru(1)-C(16)-C(17) | -102.2(7)  |
| Cl(1)-Ru(1)-C(16)-C(17) | -149.6(5)  |
| C(6)-C(5)-C(4)-C(3)     | 1.4(19)    |
| C(2)-C(3)-C(4)-C(5)     | -2.2(19)   |



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| C(14)-C(19)-C(18)-C(17) | 5.7(14)   |
| Ru(1)-C(19)-C(18)-C(17) | -53.6(8)  |
| C(14)-C(19)-C(18)-Ru(1) | 59.3(9)   |
| C(16)-C(17)-C(18)-C(19) | 0.5(14)   |
| C(20)-C(17)-C(18)-C(19) | 179.9(9)  |
| Ru(1)-C(17)-C(18)-C(19) | 54.7(8)   |
| C(16)-C(17)-C(18)-Ru(1) | -54.1(8)  |
| C(20)-C(17)-C(18)-Ru(1) | 125.3(9)  |
| C(1)-Ru(1)-C(18)-C(19)  | 132.1(7)  |
| N(1)-Ru(1)-C(18)-C(19)  | -161.5(7) |
| C(16)-Ru(1)-C(18)-C(19) | -100.9(7) |
| C(17)-Ru(1)-C(18)-C(19) | -131.8(9) |
| C(15)-Ru(1)-C(18)-C(19) | -64.3(7)  |
| C(14)-Ru(1)-C(18)-C(19) | -28.9(6)  |
| Cl(1)-Ru(1)-C(18)-C(19) | 42.6(7)   |
| C(1)-Ru(1)-C(18)-C(17)  | -96.2(6)  |
| N(1)-Ru(1)-C(18)-C(17)  | -29.7(9)  |
| C(16)-Ru(1)-C(18)-C(17) | 30.8(6)   |
| C(19)-Ru(1)-C(18)-C(17) | 131.8(9)  |
| C(15)-Ru(1)-C(18)-C(17) | 67.5(6)   |
| C(14)-Ru(1)-C(18)-C(17) | 102.9(7)  |
| Cl(1)-Ru(1)-C(18)-C(17) | 174.4(5)  |
| C(12)-C(7)-C(8)-C(9)    | 0.6(19)   |
| N(1)-C(7)-C(8)-C(9)     | 179.1(11) |
| C(7)-C(12)-C(11)-C(10)  | 0.8(19)   |
| C(7)-C(8)-C(9)-C(10)    | -2(2)     |
| C(12)-C(11)-C(10)-C(9)  | -2(2)     |
| C(8)-C(9)-C(10)-C(11)   | 2(3)      |