Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Uncommon Carbene-to-Azole Ligand Rearrangement of N-heterocyclic Carbenes in a Ruthenium System

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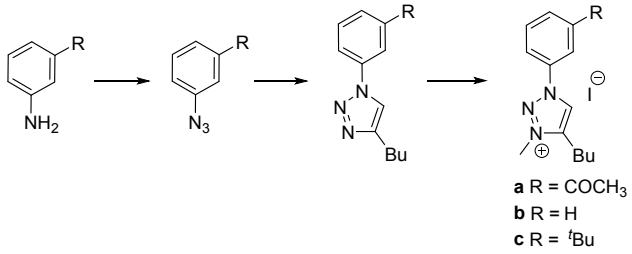
1. Experimental section for isolated compounds

General considerations. If not mentioned otherwise, all the manipulations were carried out without taking precautions to exclude air and moisture. All chemicals were used as received without further purification unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded on a 600 MHz spectrometer and calibrated using the solvent residual signals (δ_H = 7.26 ppm and δ_C = 77.16 ppm for $CDCl_3$). ESI mass spectra were measured using an Agilent 6540 or Waters Mass 3100 mass spectrometer. X-ray single crystal diffractions were done using a Rigaku XtaLAB P200 MM007 diffractometer. Elemental analyses were done on a vario EL analyzer of Elementar Analysensysteme GmbH.

General procedure for the syntheses of the triazolium salts a-b.

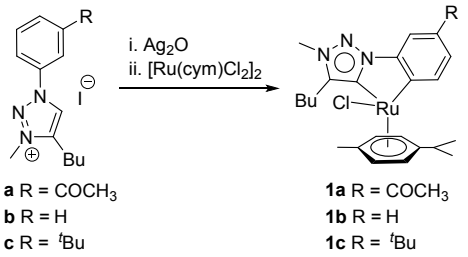


Scheme S1. Synthetic route of triazolium salts **a-b**.

A round-bottom flask was charged with amine (5 mmol) and HCl aqueous solution (3.2 ml, 6 M). The reaction mixture was cooled to 0 ℃, and an aqueous solution of $NaNO_2$ (350 mg, 5.13 mmol) was added. After 10 minutes, an aqueous solution of NaN_3 (330 mg, 5.1 mmol) was added dropwise. The mixture was stirred at the ambient temperature for 2 h and then diethyl ether was added. The organic phase was dried *in vacuo* affording the organic azide as oil. Then 1-hexyne (555 µL, 5 mmol), the copper carbene catalyst [CuCl(IPr)] (25 mg, 0.05 mmol) and the mixture of MeOH (2 mL)/H_2O (1 mL) were added. The mixture was stirred at 60 ℃ for 24 h. After cooling down to the ambient temperature, the resulting precipitate was collected and dried in *vacuo* affording the triazole as a dark oil. Then, CH_3I (3 ml) was added into a 25-mL Schlenk tube charged with triazole (without purification), and the reaction mixture was stirred and heated at 90 ℃ overnight. After cooling down to the ambient temperature, all the volatiles were removed *in vacuo* and the residue was washed with diethyl ether affording the triazolium salts as off-white solid. Compounds **a** and **b** have been reported in previous literatures, and the NMR data agrees with the reported.[1]

Compound c. 1634 mg (82%) ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.44 (s, 1H, Ar−H), 7.90 (s, 1H, Ar−H), 7.84 (d, 1H, Ar−H, $^{3}J_{H,H}$ = 7.8 Hz), 7.62 (d, 1H, Ar−H, $^{3}J_{H,H}$ = 7.8 Hz), 7.53 (t, 1H, Ar−H, $^{3}J_{H,H}$ = 7.8 Hz), 4.44 (s, 3H, N−CH_3), 3.11 (t, 2H, C$\underline{H_2}$$CH_2CH_2CH_3$, $^{3}J_{H,H}$ = 6.6 Hz), 1.87−1.85 (m, 2H, $CH_2C\underline{H_2}CH_2CH_3$), 1.49−1.46 (m, 2H, $CH_2CH_2C\underline{H_2}CH_3$), 1.38 (s, 9H, $C(CH_3)_3$), 0.96 (t, 3H, $CH_2CH_2CH_2C\underline{H_3}$, $^{3}J_{H,H}$ = 7.2 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 154.4, 146.0, 134.7, 130.1, 129.0, 127.5, 119.0, 118.6 (Ar−C), 39.5 (N−CH_3), 35.3 ($\underline{C}(CH_3)_3$), 31.2 ($C(\underline{C}H_3)_3$), 29.3 ($\underline{C}H_2CH_2CH_2CH_3$), 23.9 ($CH_2\underline{C}H_2CH_2CH_3$), 22.2 ($CH_2CH_2\underline{C}H_2CH_3$), 13.7 ($CH_2CH_2CH_2\underline{C}H_3$).

General procedure for the synthesis of the Ru complexes 1.
A round-bottom flask was charged with compound **a/b/c** (0.5 mmol, 1 eq.), Ag_2O (115.9 mg, 0.5 mmol, 1 eq.) and CH_2Cl_2 (10 mL). The reaction mixture was stirred at the ambient temperature for 16 h with the exclusion of light. A solution of $[RuCl_2(cym)]_2$ (153.1 mg, 0.25 mmol, 0.5 eq.) in CH_2Cl_2 was added. The mixture was stirred for additional 4 h. The precipitate was filtered off and the filtrate was dried *in vacuo*. The crude product was purified using column chromatography (SiO_2, CH_2Cl_2 : CH_3OH (v : v) = 30:1) affording the product as yellow powder.



Scheme S2. Synthetic route of Ru complexes.

Complex 1a. 113.3 mg (43%) ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.32 (d, 1H, Ar−H, $^3J_{H,H}$ = 7.8 Hz), 8.09 (d, 1H, Ar−H, $^4J_{H,H}$ = 1.8 Hz), 7.66 (dd, 1H, Ar−H, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.8 Hz), 5.68 (d, 1H, cym−H, $^3J_{H,H}$ = 6.0 Hz), 5.62 (d, 1H, cym−H, $^3J_{H,H}$ = 5.4 Hz), 5.32 (d, 1H, cym−H, $^3J_{H,H}$ = 6.0 Hz), 5.20 (d, 1H, cym−H, $^3J_{H,H}$ = 5.4 Hz), 4.07 (s, 3H, N−CH_3), 3.10−3.00 (m, 2H, C$\underline{H}_2$$CH_2CH_2CH_3$), 2.57 (s, 3H, $COCH_3$), 2.27−2.23 (m, 1H, $CHMe_2$), 2.00 (s, 3H, cym−CH_3), 1.92−1.89 (m, 1H, $CH_2C\underline{H}_2CH_2CH_3$), 1.74−1.70 (m, 1H, $CH_2C\underline{H}_2CH_2CH_3$), 1.59−1.54 (m, 2H, $CH_2CH_2C\underline{H}_2CH_3$), 1.06 (t, 3H, $CH_2CH_2CH_2C\underline{H}_3$, $^3J_{H,H}$ = 7.2 Hz), 0.93 (d, 3H, CH(C$\underline{H}_3$)$_2$, $^3J_{H,H}$ = 6.6 Hz), 0.74 (d, 3H, CH(C$\underline{H}_3$)$_2$, $^3J_{H,H}$ = 6.6 Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 197.7 (CO), 179.2, 170.7, 145.9, 145.3, 142.1, 132.4, 126.4, 112.6, 102.5, 100.8, 91.2, 89.6, 88.0, 83.5 (Ar−C), 36.2 (N−CH3), 31.6 ($\underline{C}H_2CH_2CH_2CH_3$), 30.9 ($CHMe_2$), 26.5 (CO$\underline{C}H_3$), 25.4 ($CH_2\underline{C}H_2CH_2CH_3$), 23.0, 23.0 (2 × CH($\underline{C}H_3$)$_2$), 21.8 ($CH_2CH_2\underline{C}H_2CH_3$), 18.9 (cym−$CH_3$), 13.9 ($CH_2CH_2CH_2\underline{C}H_3$). ESI−MS *m/z*: 533 [M-Cl+CH_3CN]$^+$. Anal. Calcd. for $C_{25}H_{32}ClN_3ORu$: C, 56.97; H, 6.12; N, 7.97%; Found: C, 56.58; H, 6.19; N, 7.72%.

Complex 1b. 109.2 mg (45%) ^{1}H NMR ($CDCl_3$, 600 MHz): 8.20 (dd, 1H, Ar−H, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.2 Hz), 7.51 (dd, 1H, Ar−H, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.2 Hz), 7.07 (td, 1H, Ar−H, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.2 Hz), 6.98 (td, 1H, Ar−H, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.2 Hz), 5.63 (d, 1H, cym−H, $^3J_{H,H}$ = 6.0 Hz), 5.55 (d, 1H, cym−H, $^3J_{H,H}$ = 6.0 Hz), 5.28 (d, 1H, cym−H, $^3J_{H,H}$ = 6.0 Hz), 5.17 (d, 1H, cym−H, $^3J_{H,H}$ = 6.0 Hz), 4.05 (s, 3H, NCH_3), 3.12−2.98 (m, 2H, C$\underline{H}_2$$CH_2CH_2CH_3$), 2.29−2.25 (m, 1H, C$\underline{H}$($CH_3$)$_2$), 1.99 (s, 3H, cym−$CH_3$), 1.96−1.88 (m, 1H, $CH_2C\underline{H}_2CH_2CH_3$), 1.76−1.69 (m, 1H, $CH_2C\underline{H}_2CH_2CH_3$), 1.61−1.55 (m, 2H, $CH_2CH_2C\underline{H}_2CH_3$), 1.07 (t, 3H, $CH_2CH_2CH_2C\underline{H}_3$, $^3J_{H,H}$ = 7.2 Hz), 0.94 (d, 3H, CH(C$\underline{H}_3$)$_2$, $^3J_{H,H}$ = 6.6 Hz), 0.76 (d, 3H, CH(C$\underline{H}_3$)$_2$, $^3J_{H,H}$ = 6.6 Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.8, 166.2, 145.7, 144.9, 142.1, 127.3, 122.4, 113.8, 90.7, 88.9, 87.3, 83.1 (Ar−C), 36.1 (N−CH3), 31.8, 31.0 ($\underline{C}H(CH_3)_2$ & $\underline{C}H_2CH_2CH_2CH_3$), 25.5 ($CH_2\underline{C}H_2CH_2CH_3$), 23.1, 23.1 (2 × CH($\underline{C}H_3$)$_2$), 21.9 ($CH_2CH_2\underline{C}H_2CH_3$), 19.1 (cym−$CH_3$), 14.0 ($CH_2CH_2CH_2\underline{C}H_3$). ESI−MS *m/z*: 450 [M-Cl]$^+$. Anal. Calcd. for $C_{23}H_{30}ClN_3Ru$: C, 56.96; H, 6.23; N, 8.66%; Found: C, 56.51; H, 6.46; N,8.64%.

Complex 1c. 129.9 mg (48%) ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.08 (d, 1H, Ar−H, $^3J_{H,H}$ = 7.8 Hz), 7.54 (d, 1H, Ar−H, $^4J_{H,H}$ = 1.8 Hz), 7.12 (dd, 1H, Ar−H, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.8 Hz), 5.57 (d, 1H, cym−H, $^3J_{H,H}$ = 5.4 Hz), 5.48 (d, 1H, cym−H, $^3J_{H,H}$ = 5.4 Hz), 5.29 (d, 1H, cym−H, $^3J_{H,H}$ = 6.0 Hz), 5.23 (d, 1H, cym−H, $^3J_{H,H}$ = 5.4 Hz), 4.03 (s, 3H, N−CH_3), 3.12−3.08 (m, 1H, C$\underline{H}_2$$CH_2CH_2CH_3$), 3.03−2.99 (m, 1H, C$\underline{H}_2$$CH_2CH_2CH_3$), 2.32−2.27 (m, 1H, CH(C$\underline{H}_3$)$_2$), 1.96 (s, 3H, cym−CH_3), 1.95−1.85 (m, 1H, $CH_2C\underline{H}_2CH_2CH_3$), 1.74−1.69 (m, 1H, $CH_2C\underline{H}_2CH_2CH_3$), 1.59−1.53 (m, 2H, $CH_2CH_2C\underline{H}_2CH_3$), 1.30 (s, 9H, C($CH_3$)$_3$), 1.05 (t, 3H, $CH_2CH_2CH_2C\underline{H}_3$, $^3J_{H,H}$ = 7.2 Hz), 0.94 (d, 3H, CH(C$\underline{H}_3$)$_2$, $^3J_{H,H}$ = 6.6 Hz), 0.79 (d, 3H, CH(C$\underline{H}_3$)$_2$, $^3J_{H,H}$ = 6.6 Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 170.6, 161.5, 145.6, 145.4, 144.6, 141.2, 124.6, 110.8, 100.3, 90.0, 88.5, 87.0, 83.4 (Ar−C), 35.9 (N−CH3), 34.2 (C(CH_3)$_3$), 31.6 ($\underline{C}H_2CH_2CH_2CH_3$), 31.6 (C($\underline{C}H_3$)$_3$), 30.9 (CH($\underline{C}H_3$)$_2$), 25.4 ($CH_2\underline{C}H_2CH_2CH_3$), 23.0, 22.9 (2 × CH($\underline{C}H_3$)$_2$), 21.9 ($CH_2CH_2\underline{C}H_2CH_3$), 18.9 (cym−$CH_3$), 13.9 ($CH_2CH_2CH_2\underline{C}H_3$). ESI−MS *m/z*: 547 [M-Cl+CH_3CN]$^+$. Anal. Calcd. for $C_{27}H_{38}ClN_3Ru$: C, 59.93; H, 7.08; N, 7.77%; Found: C, 59.63; H, 6.90; N,7.76%.

General procedure for the diphenylacetylene insertion reactions.
A Schlenk tube was charged with complex **1** (0.1 mmol, 1 equiv.), diphenylacetylene (39.2 mg, 0.22 mmol, 2.2 equiv.), and CH_3OH (1 mL). The tube was sealed and the reaction mixture was stirred and heated at 80 ℃ for 24 h. All the volatiles were removed *in vacuo*. The crude product was purified using column chromatography (SiO_2, CH_2Cl_2 : CH_3OH (v : v) = 30:1 and then CH_2Cl_2 : CH_3OH (v : v) = 5:1) .

Complex 2a. 21.9 mg (31%) ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.52 (s, 1H, Ar-H), 7.52 (d, 1H, Ar-H, $^3J_{H,H}$ = 7.8 Hz), 7.35-7.34 (m, 2H, Ar-H), 7.25-7.24 (m, 3H, Ar-H), 7.17-7.14 (m, 5H, Ar-H), 7.10 (d, 1H, Ar-H, $^3J_{H,H}$ = 7.8 Hz), 5.53 (d, 1H, cym-H, $^3J_{H,H}$ = 5.4 Hz), 5.27 (d, 1H, cym-H, $^3J_{H,H}$ = 5.4 Hz), 4.96 (d, 1H, cym-H, $^3J_{H,H}$ = 5.4 Hz), 4.72 (d, 1H, cym-H, $^3J_{H,H}$ = 5.4 Hz), 3.88 (s, 3H, N-CH_3), 2.56 (s, 3H, $COCH_3$), 2.55−2.51 (m, 1H, $CHMe_2$), 2.19−2.15 (m, 1H, C$\underline{H}_2$$CH_2CH_2CH_3$), 2.01 (s, 3H, cym−$CH_3$), 1.80−1.75 (m, 1H, C$\underline{H}_2$$CH_2CH_2CH_3$), 1.13 (d, 3H, CH(C$\underline{H}_3$)$_2$, $^3J_{H,H}$ = 6.6 Hz), 1.09−1.03 (m, 2H, $CH_2C\underline{H}_2CH_2CH_3$), 0.96 (d, 3H, CH(C$\underline{H}_3$)$_2$, $^3J_{H,H}$ = 7.2 Hz). 0.94−0.90 (m, 2H, $CH_2CH_2C\underline{H}_2CH_3$), 0.66 (t, 3H, $CH_2CH_2CH_2C\underline{H}_3$, $^3J_{H,H}$ = 7.2 Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 200.4 (CO), 169.5, 152.8, 148.6, 148.4, 142.5, 140.5, 137.1, 133.8, 130.5, 130.3, 128.9, 128.3, 127.8, 127.6, 127.6, 127.1, 120.7 (Ar-C), 88.9, 85.5, 80.4, 78.2 (cym-C), 35.7 (N−CH3), 31.7 ($\underline{C}H_2CH_2CH_2CH_3$), 31.0 ($\underline{C}H(CH_3)_2$), 27.0 (CO$\underline{C}H_3$), 23.3 ($CH_2\underline{C}H_2CH_2CH_3$), 22.8, 22.7 (CH($\underline{C}H_3$)$_2$), 21.9 ($CH_2CH_2\underline{C}H_2CH_3$), 18.9 (cym−$CH_3$), 14.2 ($CH_2CH_2CH_2\underline{C}H_3$). MS (ESI): *m/z* 670 [M-Cl]$^+$. Anal. Calcd. for $C_{39}H_{42}ClN_3ORu$: C, 66.42; H, 6.00; N, 5.96%; Found: C, 66.06; H, 5.55; N, 5.71%.

Complex 2b. 33.2 mg (50%) ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.86 (dd, 1H, Ar-H, $^3J_{H,H}$ = 7.8 Hz, $^3J_{H,H}$ = 1.2 Hz), 7.40-7.37 (m, 2H, Ar-H), 7.24-7.20 (m, 3H, Ar-H), 7.17-7.14 (m, 3H, Ar-H), 7.12-7.11 (m, 2H, Ar-H), 6.96 (dd, 1H, Ar-H, $^3J_{H,H}$ = 7.8 Hz, $^3J_{H,H}$ = 1.2 Hz), 6.86 (td, 1H, Ar-H, $^3J_{H,H}$ = 7.8 Hz, $^3J_{H,H}$ = 1.2 Hz), 6.82 (td, 1H, Ar-H, $^3J_{H,H}$ = 7.8 Hz, $^3J_{H,H}$ = 1.2 Hz), 5.37 (d, 1H, cym-H, $^3J_{H,H}$ = 5.4 Hz), 5.33 (d, 1H, cym-H, $^3J_{H,H}$ = 5.4 Hz), 4.82 (d, 1H, cym-H, $^3J_{H,H}$ = 5.4 Hz), 4.68 (d, 1H, cym-H, $^3J_{H,H}$ = 5.4 Hz), 3.82 (s, 3H, NCH_3), 2.56−2.51 (m, 1H, C$\underline{H}$(CH_3)$_2$), 2.23−2.180 (m, 1H, C$\underline{H}_2$$CH_2CH_2CH_3$), 1.98 (s, 3H, cym−$CH_3$), 1.91−1.86 (m, 1H, C$\underline{H}_2$$CH_2CH_2CH_3$), 1.12−1.02 (m, 5H, CH(C$\underline{H}_3$)$_2$ & $CH_2C\underline{H}_2CH_2CH_3$), 0.97−0.90 (m, 5H, CH(C$\underline{H}_3$)$_2$ & $CH_2CH_2C\underline{H}_2CH_3$), 0.65 (t, 3H, $CH_2CH_2CH_2C\underline{H}_3$, $^3J_{H,H}$ = 7.2 Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 169.7, 149.7, 148.8, 147.7, 141.7, 140.7, 140.4, 136.5, 130.7, 130.2, 128.7, 128.1, 127.6, 127.4, 127.3, 126.8, 125.4, 121.2, 87.5, 86.9, 78.9, 78.5 (Ar-C), 35.6 (NCH_3), 31.1, 29.8 ($\underline{C}H(CH_3)_2$ & $\underline{C}H_2CH_2CH_2CH_3$), 23.1, 22.9, 22.5, 21.9 (CH($\underline{C}H_3$)$_2$ & $CH_2\underline{C}H_2CH_2CH_3$ & $CH_2CH_2\underline{C}H_2CH_3$), 18.8 (cym−$CH_3$), 13.6 ($CH_2CH_2CH_2\underline{C}H_3$). MS (ESI): *m/z* 628 [M-Cl]$^+$. Anal. Calcd. for $C_{37}H_{40}ClN_3Ru$: C, 67.00; H, 6.08; N, 6.34%; Found: C, 66.80; H, 6.26; N, 5.81%.

Complex 2c. 28.8 mg (40%) ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.93 (d, 1H, Ar-H, $^4J_{H,H}$ = 1.8 Hz), 7.36-7.35 (m, 2H, Ar-H), 7.21-7.13 (m, 6H, Ar-H), 7.05-7.04 (m, 2H, Ar-H), 6.99 (d, 1H, Ar-H, $^3J_{H,H}$ = 8.4 Hz), 6.81 (dd, 1H, Ar-H, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,H}$ = 1.8 Hz), 5.50 (d, 1H, cym-H, $^3J_{H,H}$ = 5.4 Hz), 5.37 (d, 1H, cym-H, $^3J_{H,H}$ = 5.4 Hz), 4.91 (d, 1H, cym-H, $^3J_{H,H}$ = 5.4 Hz), 4.69 (d, 1H, cym-H, $^3J_{H,H}$ = 5.4 Hz),

3.85 (s, 3H, NCH_3), 2.58−2.53 (m, 1H, C*H*$(CH_3)_2$), 2.26−2.20 (m, 1H, C*H*$_2CH_2CH_2CH_3$), 1.98−1.93 (m, 4H, C*H*$_2CH_2CH_2CH_3$ & cym−CH_3), 1.26 (s, 9H, C(C*H*$_3)_3$), 1.15−0.90 (m, 4H, CH_2C*H*$_2CH_2CH_3$ & CH_2CH_2C*H*$_2CH_3$), 1.10 (d, 3H, CH(C*H*$_3)_2$, $^3J_{H,H}$ = 6.8 Hz), 0.96 (d, 3H, CH(C*H*$_3)_2$, $^3J_{H,H}$ = 6.8 Hz), 0.66 (t, 3H, $CH_2CH_2CH_2$C*H*$_3$, $^3J_{H,H}$ = 6.8 Hz). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 168.5, 150.2, 148.8, 146.6, 144.5, 143.0, 141.2, 138.2, 136.4, 130.7, 130.3, 128.4, 128.1, 127.2, 127.0, 127.0, 126.0, 118.6, 88.5, 86.4, 80.0, 77.6 (Ar-C), 35.7 (NCH_3), 34.9 (*C*$(CH_3)_3$), 31.7 (C(*C*$H_3)_3$, 30.7, 29.7 (*C*H$(CH_3)_2$ & *C*$H_2CH_2CH_2CH_3$), 23.2, 23.2, 22.7, 22.0 (CH(*C*$H_3)_2$ & CH_2*C*$H_2CH_2CH_3$ & CH_2CH_2*C*H_2CH_3), 18.8 (cym−CH_3), 13.6 ($CH_2CH_2CH_2$*C*H_3). MS (ESI): ***m/z*** 684 $[M\text{-}Cl]^+$. Anal. Calcd. for $C_{41}H_{48}ClN_3Ru$: C, 68.46; H, 6.73; N, 5.84%; Found: C, 67.85; H, 6.26; N, 5.82%.

Complex 3a^{Cl}. 16.0 mg (34%) ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.27 (d, 1H, Ar−H, $^4J_{H,H}$ = 1.8 Hz), 8.24 (dd, 1H, Ar-H, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,H}$ = 1.8 Hz), 7.69 (d, 1H, Ar-H, $^3J_{H,H}$ = 8.4 Hz), 7.34-7.29 (brs, 8H, Ar-H), 7.13-7.11 (m, 2H, Ar-H), 4.80 (s, 3H, N−CH_3), 2.81 (s, 3H, $COCH_3$), 2.75-2.72 (m, 2H, C*H*$_2CH_2CH_2CH_3$), 1.25-1.21 (m, 2H, CH_2C*H*$_2CH_2CH_3$), 1.02-0.96 (m, 2H, CH_2CH_2C*H*$_2CH_3$), 0.66 (t, 3H, $CH_2CH_2CH_2$C*H*$_3$, $^3J_{H,H}$ = 7.2 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 195.8 (CO), 141.0, 140.8, 138.5, 133.5, 132.0, 131.8, 130.2, 130.0, 129.8, 129.5, 129.3, 129.1, 128.8, 128.7, 128.6, 117.3 (Ar-C), 40.2 (N−CH_3), 30.7 (*C*$H_2CH_2CH_2CH_3$), 27.2 ($COCH_3$), 24.5 (CH_2*C*$H_2CH_2CH_3$), 22.6 (CH_2CH_2*C*H_2CH_3), 13.5 ($CH_2CH_2CH_2$*C*H_3).

Complex 3b^{Cl}. 13.7 mg (32%) ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.70 (d, 1H, Ar-H, $^3J_{H,H}$ = 8.4 Hz), 7.90-7.87 (m, 1H, Ar-H), 7.71-7.68 (m, 1H, Ar-H), 7.56-7.55 (m, 1H, Ar-H), 7.27-7.24 (m, 6H, Ar-H), 7.21-7.19 (m, 2H, Ar-H), 7.08-7.06 (m, 2H, Ar-H), 4.74 (s, 3H, N−CH_3), 2.66-2.63 (m, 2H, C*H*$_2CH_2CH_2CH_3$), 1.20-1.15 (m, 2H, CH_2C*H*$_2CH_2CH_3$), 0.96-0.90 (m, 2H, CH_2CH_2C*H*$_2CH_3$), 0.61 (t, 3H, $CH_2CH_2CH_2$C*H*$_3$, $^3J_{H,H}$ = 7.2 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 141.5, 139.9, 133.7, 132.1, 131.6, 131.3, 130.6, 130.2, 130.1, 129.4, 129.1, 129.1, 128.5, 128.5, 128.3, 127.5, 126.4, 116.8 (Ar-C), 39.8 (N−CH_3), 30.6 (*C*$H_2CH_2CH_2CH_3$), 24.0 (CH_2*C*$H_2CH_2CH_3$), 22.4 (CH_2CH_2*C*H_2CH_3), 13.3 ($CH_2CH_2CH_2$*C*H_3).

Complex 3c^{Cl}. 13.1 mg (27%) ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.68 (d, 1H, Ar−H,$^4J_{H,H}$ = 1.8 Hz), 7.77 (dd, 1H, Ar-H, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,H}$ = 1.8 Hz), 7.53 (d, 1H, Ar-H, $^3J_{H,H}$ = 8.4 Hz), 7.31-7.27 (m, 6H, Ar-H), 7.24-7.22 (m, 2H, Ar-H), 7.11-7.10 (m, 2H, Ar-H), 4.82 (s, 3H, N−CH_3), 2.74-2.72 (m, 2H, C*H*$_2CH_2CH_2CH_3$), 1.46 (s, 9H, C$(CH_3)_3$), 1.23-1.18 (m, 2H, CH_2C*H*$_2CH_2CH_3$), 1.01-0.95 (m, 2H, CH_2CH_2C*H*$_2CH_3$), 0.65 (t, 3H, $CH_2CH_2CH_2$C*H*$_3$, $^3J_{H,H}$ = 7.2 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 156.3, 141.3, 139.9, 134.1, 132.4, 131.4, 130.4, 130.2, 129.2, 129.2, 128.9, 128.8, 128.6, 128.5, 128.4, 126.8, 124.3, 113.0 (Ar-C), 40.2 (N−CH_3), 35.9 (CMe_3), 31.2 (C(*C*$H_3)_3$), 30.8 (*C*$H_2CH_2CH_2CH_3$), 24.3 (CH_2*C*$H_2CH_2CH_3$), 22.6 (CH_2CH_2*C*H_2CH_3), 13.5 ($CH_2CH_2CH_2$*C*H_3).

The compounds **3^{PF6}** were synthesized using $AgPF_6$ (55.6 mg, 0.22 mmol, 2.2 eq.) as an additive.

Complex 3a^{PF6}. 48.1 mg (83%) ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.28 (s, 1H, Ar−H), 8.21 (dd, 1H, Ar-H, $^3J_{H,H}$ = 8.4 Hz, $^4J_{H,H}$ = 1.2 Hz), 7.66 (d, 1H, Ar-H, $^3J_{H,H}$ = 8.4 Hz), 7.29 (brs, 8H, Ar-H), 7.12-7.10 (m, 2H, Ar-H), 4.72 (s, 3H, N−CH_3), 2.79 (s, 3H, $COCH_3$), 2.63 (t, 2H, C*H*$_2CH_2CH_2CH_3$, $^3J_{H,H}$ = 8.0 Hz), 1.25-1.16 (m, 2H, CH_2C*H*$_2CH_2CH_3$), 1.00-0.91 (m, 2H, CH_2CH_2C*H*$_2CH_3$), 0.63 (t, 3H, $CH_2CH_2CH_2$C*H*$_3$, $^3J_{H,H}$ = 7.2 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 196.1 (CO), 140.8, 140.6, 138.4, 133.5, 132.0, 131.8, 130.2, 129.9, 129.4, 129.4, 129.2, 129.0, 128.7, 128.6, 128.5, 117.4 (Ar-C), 39.9 (N−CH_3), 30.6 (*C*$H_2CH_2CH_2CH_3$), 27.2 ($COCH_3$), 24.1 (CH_2*C*$H_2CH_2CH_3$), 22.5 (CH_2CH_2*C*H_2CH_3), 13.4 ($CH_2CH_2CH_2$*C*H_3).

Complex 3b^{PF6}. 16.7 mg (31%) ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.77 (d, 1H, Ar-H, $^3J_{H,H}$ = 8.4 Hz), 7.93-7.90 (m, 1H, Ar-H), 7.74-7.71 (m, 1H, Ar-H), 7.60 (dd, 1H, Ar-H, $^3J_{H,H}$ = 9.0 Hz, $^4J_{H,H}$ = 1.2 Hz), 7.32-7.28 (m, 8H, Ar-H), 7.16-7.14 (m, 2H, Ar-H), 4.52 (s, 3H, N−CH_3), 2.54-2.51 (m, 2H, C*H*$_2CH_2CH_2CH_3$), 1.23-1.18 (m, 2H, CH_2C*H*$_2CH_2CH_3$), 0.98-0.93 (m, 2H, CH_2CH_2C*H*$_2CH_3$), 0.66 (t, 3H, $CH_2CH_2CH_2$C*H*$_3$, $^3J_{H,H}$ = 7.2 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 141.4, 139.6, 134.1, 132.5, 131.5, 131.5, 130.5, 130.5, 130.3, 129.4, 129.1, 129.1, 128.6, 128.5, 128.4, 127.8, 126.7, 117.0 (Ar-C), 38.6 (N−CH_3), 30.6 (*C*$H_2CH_2CH_2CH_3$), 23.7 (CH_2*C*$H_2CH_2CH_3$), 22.6 (CH_2CH_2*C*H_2CH_3), 13.4 ($CH_2CH_2CH_2$*C*H_3).

Complex 3c^{PF6}. 49.8 mg (84%) ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.68 (s, 1H, Ar−H), 7.75 (d, 1H, Ar-H, $^3J_{H,H}$ = 8.4 Hz), 7.52 (d, 1H, Ar-H, $^3J_{H,H}$ = 8.4 Hz), 7.29-7.27 (m, 6H, Ar-H), 7.23-7.22 (m, 2H, Ar-H), 7.10-7.09 (m, 2H, Ar-H), 4.77 (s, 3H, N−CH_3), 2.67 (t, 2H, C*H*$_2CH_2CH_2CH_3$, $^3J_{H,H}$ = 6.0 Hz), 1.45 (s, 9H, C$(CH_3)_3$), 1.22-1.18 (m, 2H, CH_2C*H*$_2CH_2CH_3$), 0.98-0.95 (m, 2H, CH_2CH_2C*H*$_2CH_3$), 0.64 (t, 3H, $CH_2CH_2CH_2$C*H*$_3$, $^3J_{H,H}$ = 6.6 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 156.3, 141.4, 139.8, 134.0, 132.4, 131.4, 130.4, 130.2, 129.2, 129.1, 128.9, 128.8, 128.6, 128.5, 128.4, 126.8, 124.8, 124.3, 112.9 (Ar-C), 39.9 (N−CH_3), 35.9 (CMe_3), 31.2 (C(*C*$H_3)_3$), 30.8 (*C*$H_2CH_2CH_2CH_3$), 24.1 (CH_2*C*$H_2CH_2CH_3$), 22.5 (CH_2CH_2*C*H_2CH_3), 13.5 ($CH_2CH_2CH_2$*C*H_3).

General procedure for the dimethyl acetylenedicarboxylate insertion reactions

A Schlenk tube was charged with complex **2b/c** (0.1 mmol, 1 eq.), dimethyl acetylenedicarboxylate (0.22 mmol, 28 µL, 2.2 eq.) and CH_3OH (1 mL). The tube was sealed and the reaction mixture was stirred at the ambient temperature for 24 h. All the volatiles were removed *in vacuo*. The crude product was purified using column chromatography (SiO_2, CH_2Cl_2:CH_3OH (v:v)=30:1 and CH_2Cl_2:CH_3OH (v:v)=5:1).

Compound **5b.** 31.4 mg (50%) ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.44-7.41 (m, 1H, Ar−H), 7.38 (dd, 1H, Ar−H, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.2 Hz), 7.34-7.29 (m, 2H, Ar−H), 5.14 (d, 1H, cym−H, $^3J_{H,H}$ = 6.0 Hz), 4.55 (d, 1H, cym−H, $^3J_{H,H}$ = 4.8 Hz), 4.39 (d, 1H, cym−H, $^3J_{H,H}$ = 3.6 Hz), 4.00 (s, 3H, NCH_3), 3.65 (br s, 3H, $COOCH_3$), 3.57 (s, 3H, $COOCH_3$), 3.35−3.31 (m, 1H, C*H*$_2CH_2CH_2CH_3$), 2.98 (br s, 1H, C*H*$_2CH_2CH_2CH_3$), 2.53 (br s, 1H, C*H*$(CH_3)_2$), 1.93 (s, 3H, cym−CH_3), 1.73−1.70 (m, 1H), 1.49−1.39 (m, 3H), 1.06-1.04 (m, 6H,

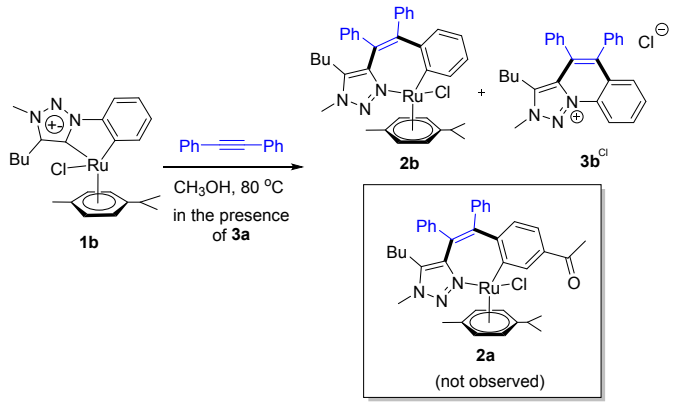
$CH(C\underline{H}_3)_2$), 0.94 (t, 3H, $CH_2CH_2CH_2C\underline{H}_3$, $^3J_{H,H}$ = 7.2 Hz). One of the resonances arising from cymene ligand is missing, despite several attempts. ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.4, 165.0, 147.3, 138.5, 137.7, 132.7, 128.9, 126.8, 126.4, 90.0, 85.0, 51.6, 36.4, 32.2, 31.0, 25.4, 22.9, 18.8, 14.0. MS (ESI): *m/z* 592 $[M\text{-}Cl]^+$. Anal. Calcd. for $C_{29}H_{36}ClN_3O_4Ru$: C, 55.54; H, 5.79; N, 6.70%; Found: C, 54.86; H, 6.16; N, 6.34%.

Compound **5c.** 32.8 mg (48%) ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.45 (dd, 1H, Ar−H, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.8 Hz), 7.31 (d, 1H, Ar−H, $^3J_{H,H}$ = 7.8 Hz), 7.26 (d, 1H, Ar−H, $^4J_{H,H}$ = 1.8 Hz), 5.19 (d, 1H, cym−H, $^3J_{H,H}$ = 6.0 Hz), 4.66 (d, 1H, cym−H, $^3J_{H,H}$ = 6.0 Hz), 4.40 (d, 1H, cym−H, $^3J_{H,H}$ = 4.8 Hz), 4.05 (s, 3H, NCH_3), 3.67 (br s, 3H, $COOCH_3$), 3.60 (s, 3H, $COOCH_3$), 3.49−3.44 (m, 1H, $C\underline{H}_2CH_2CH_2CH_3$), 2.95−2.91 (m, 1H, $C\underline{H}_2CH_2CH_2CH_3$), 2.35 (m, 1H, $C\underline{H}(CH_3)_2$), 1.94 (s, 3H, cym−CH_3), 1.76−1.72 (m, 1H), 1.57−1.41 (m, 3H), 1.36 (s, 9H, $C(CH_3)_3$), 1.03 (d, 3H, $CH(C\underline{H}_3)_2$, $^3J_{H,H}$ = 6.6 Hz), 1.00 (d, 3H, $CH(C\underline{H}_3)_2$, $^3J_{H,H}$ = 6.6 Hz), 0.97 (t, 3H, $CH_2CH_2CH_2C\underline{H}_3$, $^3J_{H,H}$ = 7.2 Hz). One of the resonances arising from cymene ligand is missing, despite several attempts. ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.5, 165.0, 150.2, 147.3, 137.2, 135.5, 132.3, 130.6, 125.9, 123.7, 109.4, 88.8, 86.6, 51.6, 36.4, 34.8, 32.2, 31.3, 31.0, 25.5, 22.9, 18.6, 14.1. MS (ESI): *m/z* 648 $[M\text{-}Cl]^+$. Anal. Calcd. for $C_{33}H_{44}ClN_3O_4Ru$: C, 58.01; H, 6.49; N, 6.15%; Found: C, 57.00; H, 6.78; N, 5.76%.

Compound **6b.** 12.5 mg (32%) ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.73 (d, 1H, Ar−H, $^3J_{H,H}$ = 8.4 Hz), 8.14 (d, 1H, Ar−H, $^3J_{H,H}$ = 8.4 Hz), 8.06 (t, 1H, Ar−H, $^3J_{H,H}$ = 7.2 Hz), 7.93 (t, 1H, Ar−H, $^3J_{H,H}$ = 7.2 Hz), 4.87 (s, 3H, NCH_3), 4.07 (s, 3H, $COOCH_3$), 4.03 (s, 3H, $COOCH_3$), 3.44−3.41 (m, 2H, $C\underline{H}_2CH_2CH_2CH_3$), 1.73−1.68 (m, 2H, $CH_2C\underline{H}_2CH_2CH_3$), 1.55−1.49 (m, 2H, $CH_2CH_2C\underline{H}_2CH_3$), 0.99 (t, 3H, $CH_2CH_2CH_2C\underline{H}_3$, $^3J_{H,H}$ = 7.2 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.4, 162.7, 142.0, 134.4, 134.2, 131.8, 130.3, 128.6, 121.6, 120.0, 117.6, 116.6, 54.2, 54.1, 40.9, 30.6, 25.1, 22.9, 13.9.

Compound **6c.** 7.7 mg (17%) ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.66 (d, 1H, Ar−H, $^4J_{H,H}$ = 1.8 Hz), 8.08 (d, 1H, Ar−H, $^3J_{H,H}$ = 7.8 Hz), 7.97 (dd, 1H, Ar−H, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.8 Hz), 4.93 (s, 3H, NCH_3), 4.06 (s, 3H, $COOCH_3$), 4.01 (s, 3H, $COOCH_3$), 3.47−3.45 (m, 2H, $C\underline{H}_2CH_2CH_2CH_3$), 1.73−1.68 (m, 2H, $CH_2C\underline{H}_2CH_2CH_3$), 1.55−1.49 (m, 2H, $CH_2CH_2C\underline{H}_2CH_3$), 1.46 (s, 9H, $C(CH_3)_3$), 0.98 (t, 3H, $CH_2CH_2CH_2C\underline{H}_3$, $^3J_{H,H}$ = 7.2 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.6, 162.6, 159.5, 141.6, 134.4, 130.3, 129.9, 128.2, 128.2, 119.3, 118.8, 113.6, 54.1, 53.9, 36.3, 31.1, 31.0, 30.6, 25.0, 22.8, 13.8.

2. Cross-over experiment for mechanism study



Scheme S3. Cross-over experiments for mechanism study.

In a 25-mL Schlenk tube, compound **1b** (24.3 mg, 0.05 mmol), diphenylacetylene (19.6 mg, 0.11 mmol) and $\mathbf{3a}^{PF_6}$ (29.0 mg, 0.05 mmol) were mixed in CH_3OH (1 mL). The reaction mixture was stirred and heated at 80℃ for 24 h. Then, all the volatiles were removed *in vacuo*. The crude product was subjected to ^{1}H NMR and ESI mass spectrometry. No signals corresponding to **2a** was observed. By carrying out this experiment, the reaction pathway, which involves the oxidative addition of **3b** with the *in situ* generated Ru^0 species yielding **2b**, can be ruled out.

3. The diphenylacetylene insertion reaction using $NaBAr^F_4$ as an additive

In a 25-mL Schlenk tube, compound **1a** (52.7 mg, 0.1 mmol), diphenylacetylene (39.2 mg, 0.22 mmol) and $NaBAr^F_4$ (Ar^F = 3,5-bis(trifluoromethyl)phenyl) (195.0 mg, 0.22 mmol) were mixed in CH_3OH (1 mL). The reaction mixture was stirred and heated at 80 ℃ for 24 h. Then, all the volatiles were removed *in vacuo*. The residue was dissolved in CH_2Cl_2 and washed with H_2O. The organic phase was collected, dried *in vacuo* and washed with Et_2O (to remove the released free cymene). ^{1}H NMR spectroscopic analysis of

the crude product (see Figure S1) revealed the formation of **3a** (BAr^F_4 as the anion). Also similar to the case with $AgPF_6$ as the halide scavenger, the formation of rearrangement product **2a** was not observed.

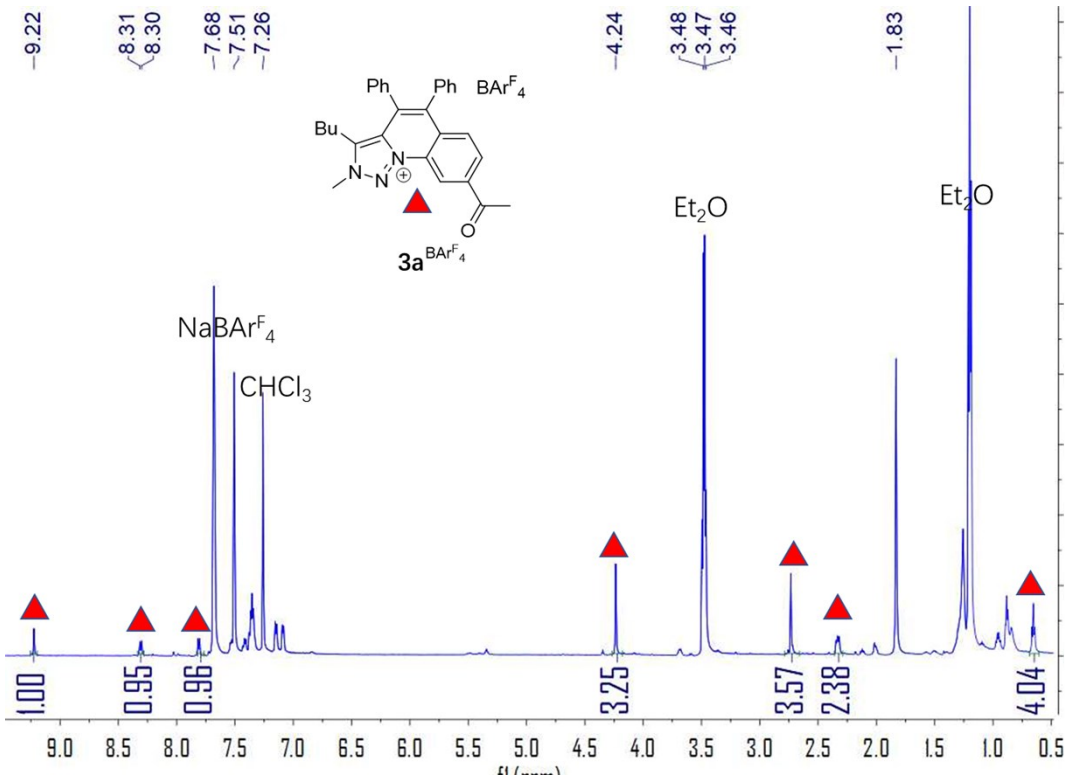
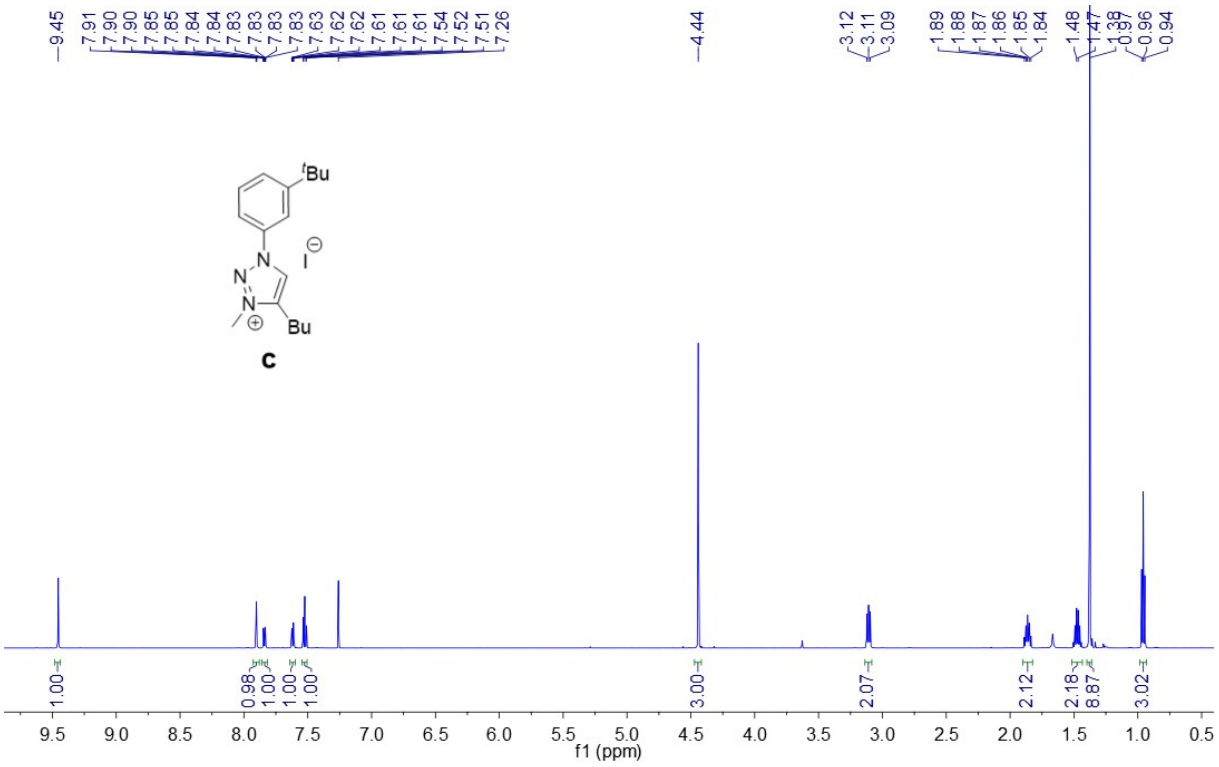
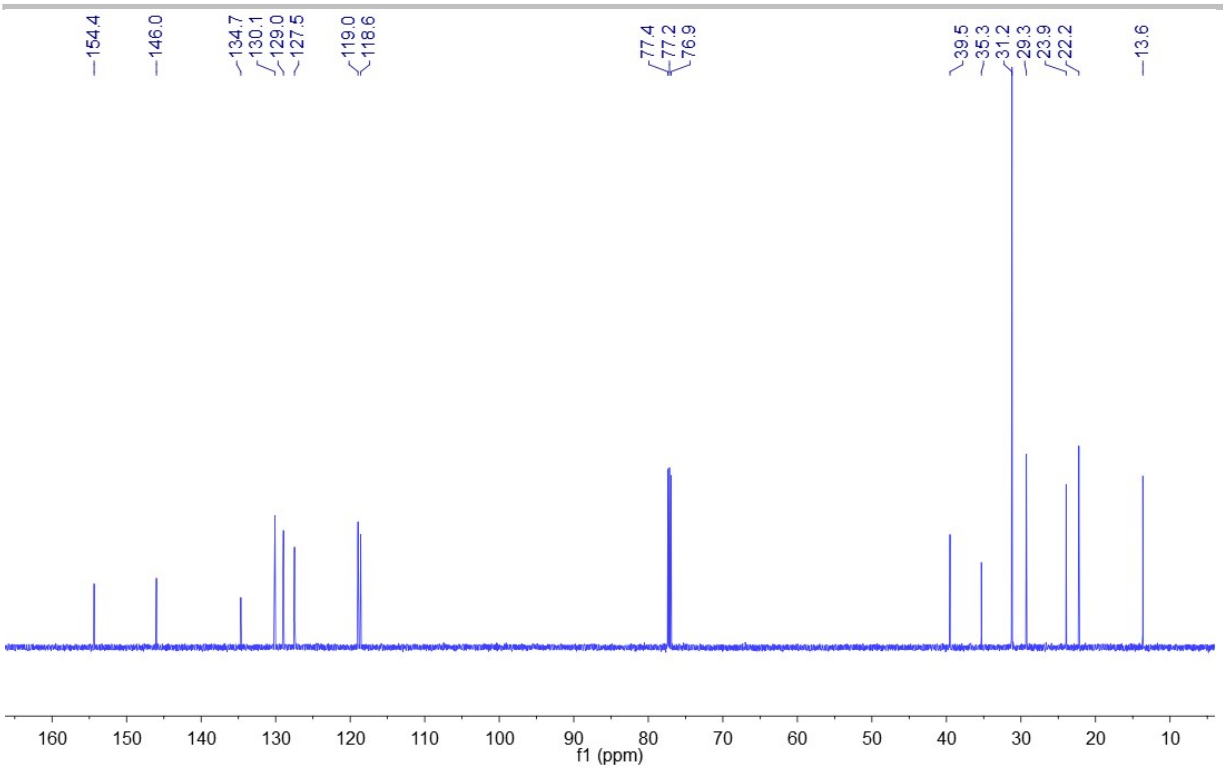


Figure S1. ^{1}H NMR spectrum of the crude product for the reaction of **1a**, diphenylacetylene and $NaBAr^F_4$.

4. NMR spectra of isolated compounds

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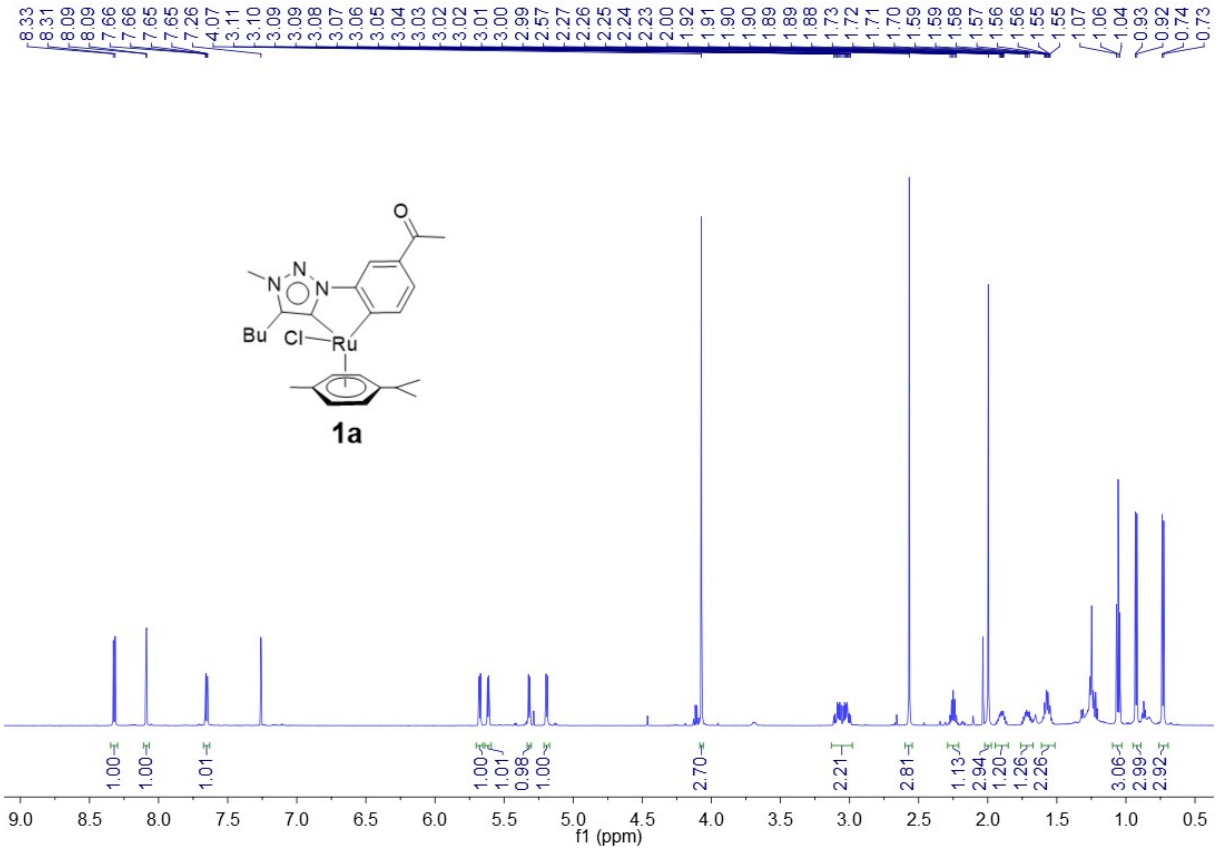
31.2
29.3
23.9
22.2
13.6
f1 (ppm)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8.09
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7.65
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3.09
3.08
3.07
3.06
3.05
3.04
3.03
3.02
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3.01
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1.70
1.59
1.59
1.58
1.57
1.56
1.56
1.55
1.55
1.07
1.06
1.04
0.93
0.92
0.74
0.73
O
N
N
N
Bu
Cl
Ru
1a
1.00
1.00
1.01
1.00
1.01
0.98
1.00
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1.20
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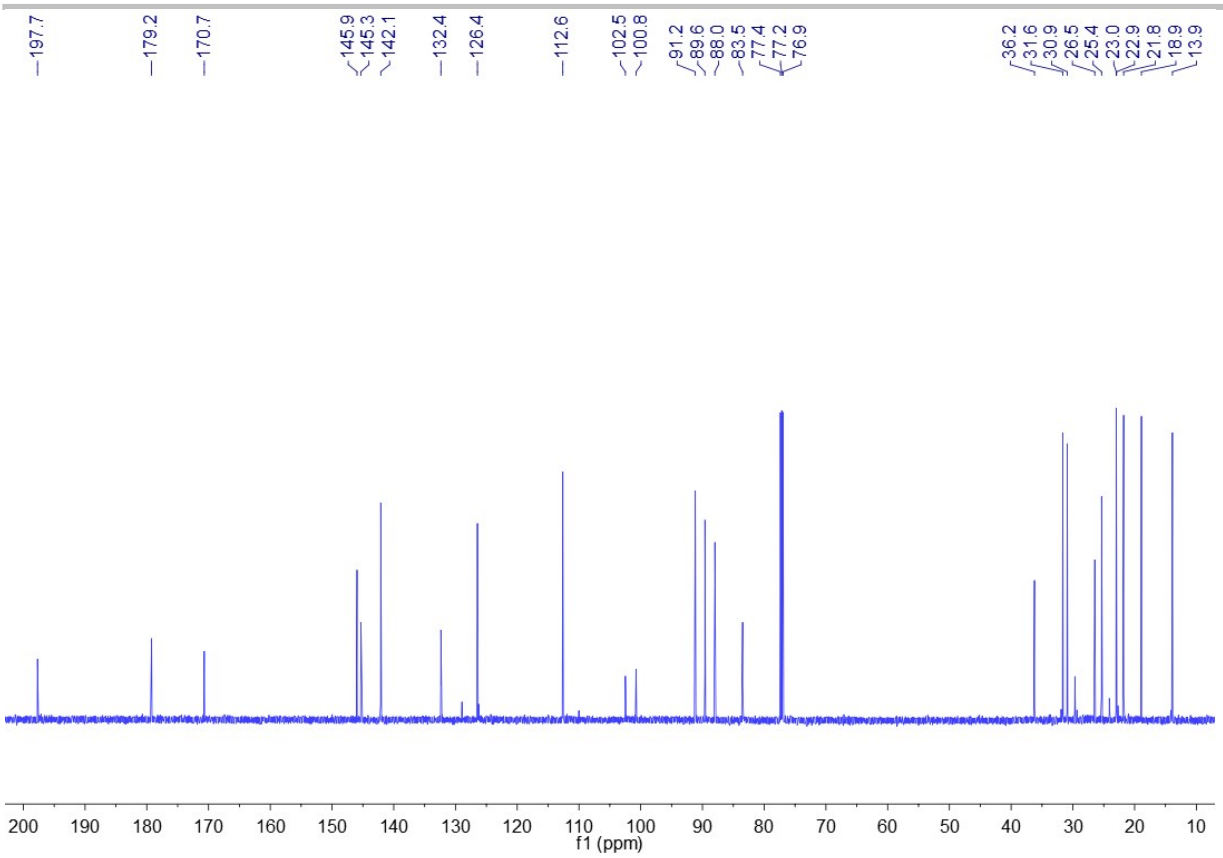
2.26
3.06
2.99
2.92
f1 (ppm)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88.0
83.5
77.4
77.2
76.9
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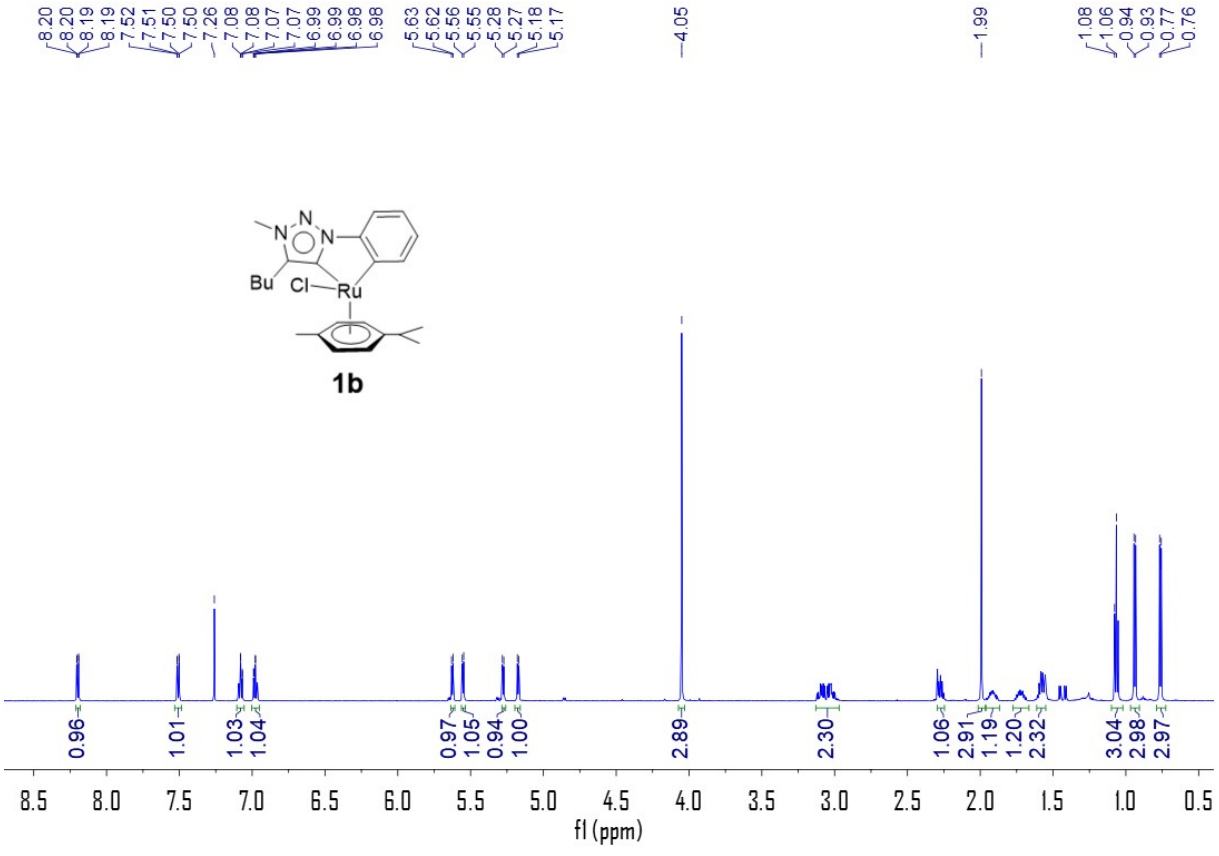
25.4
23.0
22.9
21.8
18.9
13.9
f1 (ppm)


8.20
8.20
8.19
8.19
7.52
7.51
7.50
7.50
7.26
7.08
7.08
7.07
7.07
6.99
6.98
6.98
5.63
5.62
5.56
5.55
5.28
5.27
5.18
5.17
4.05
1.99
1.08
1.06
0.94
0.93
0.77
0.76
Bu
Cl
Ru
1b
0.96
1.01
1.03
1.04
0.97
1.05
0.94
1.00
2.89
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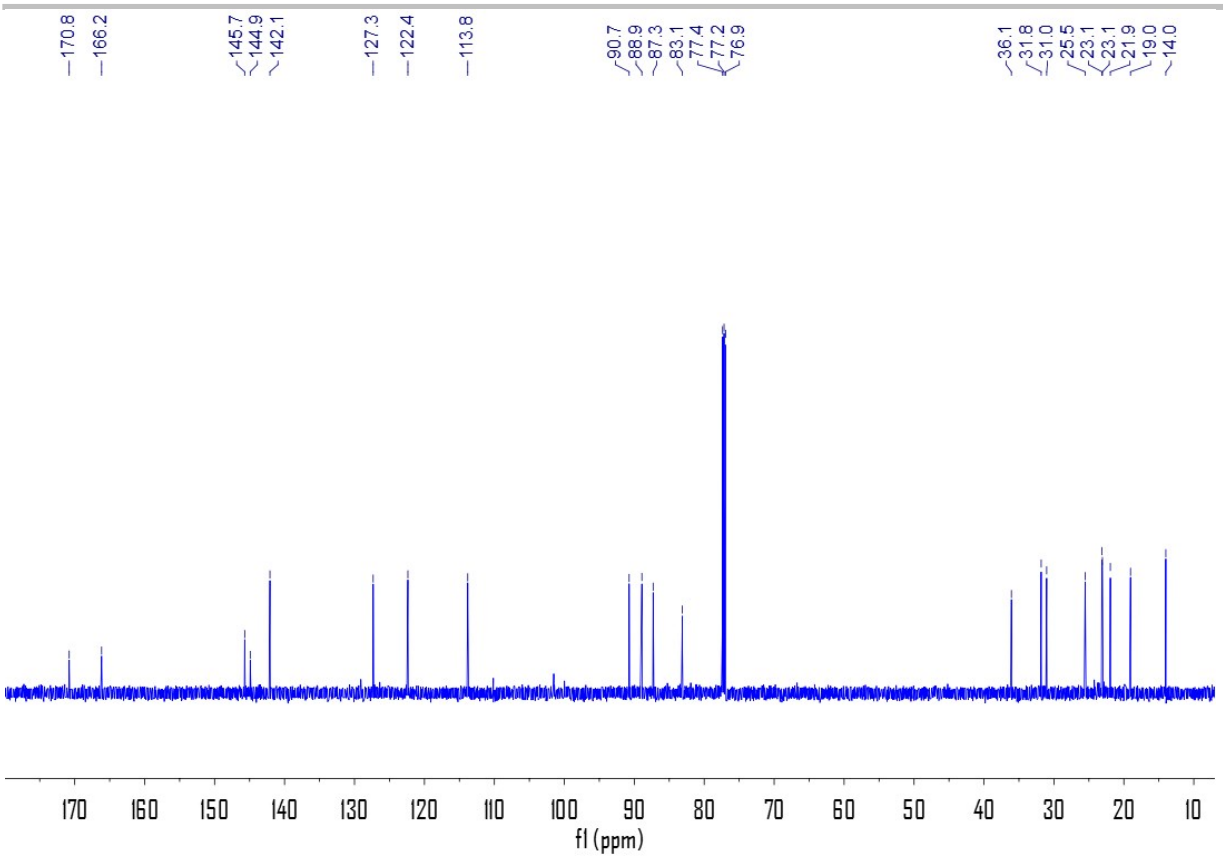
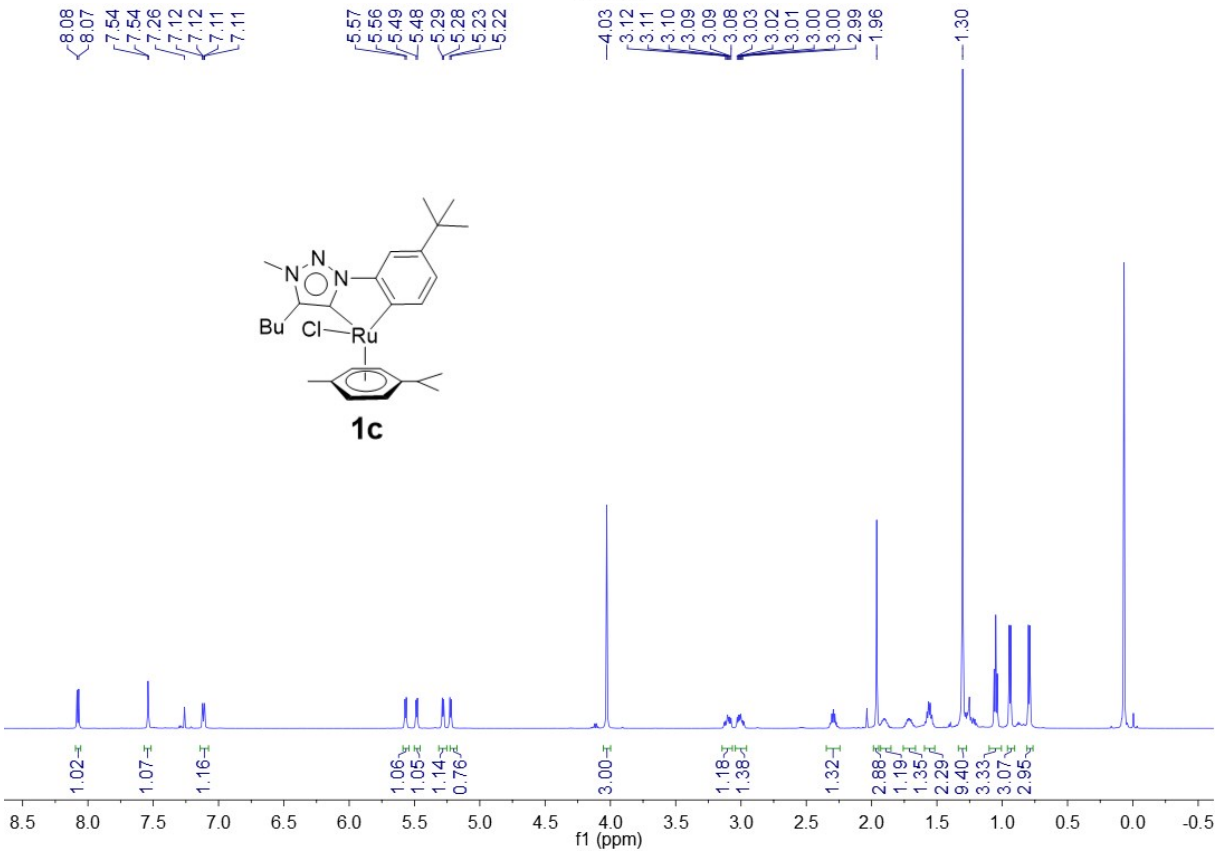
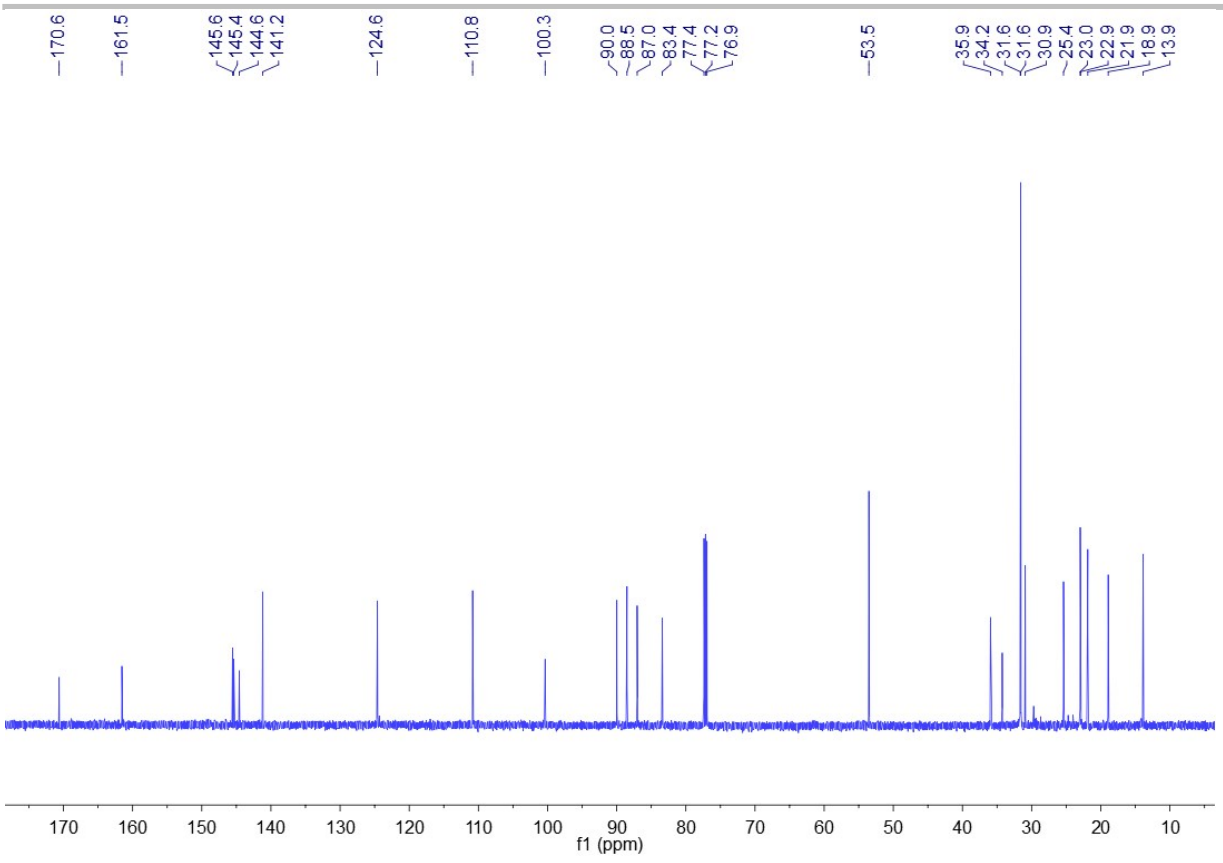
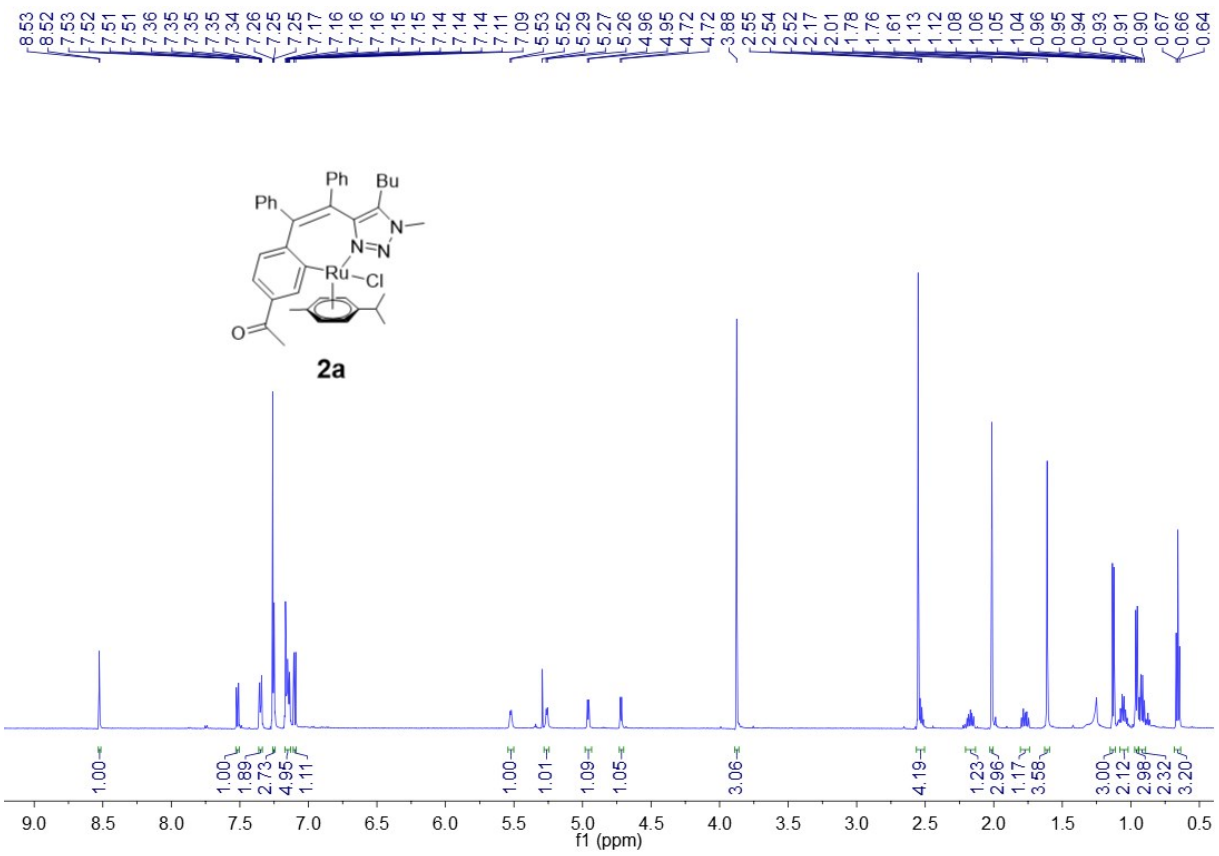
1.06
2.91
1.19
1.20
2.32
3.04
2.98
2.97
f1 (ppm)

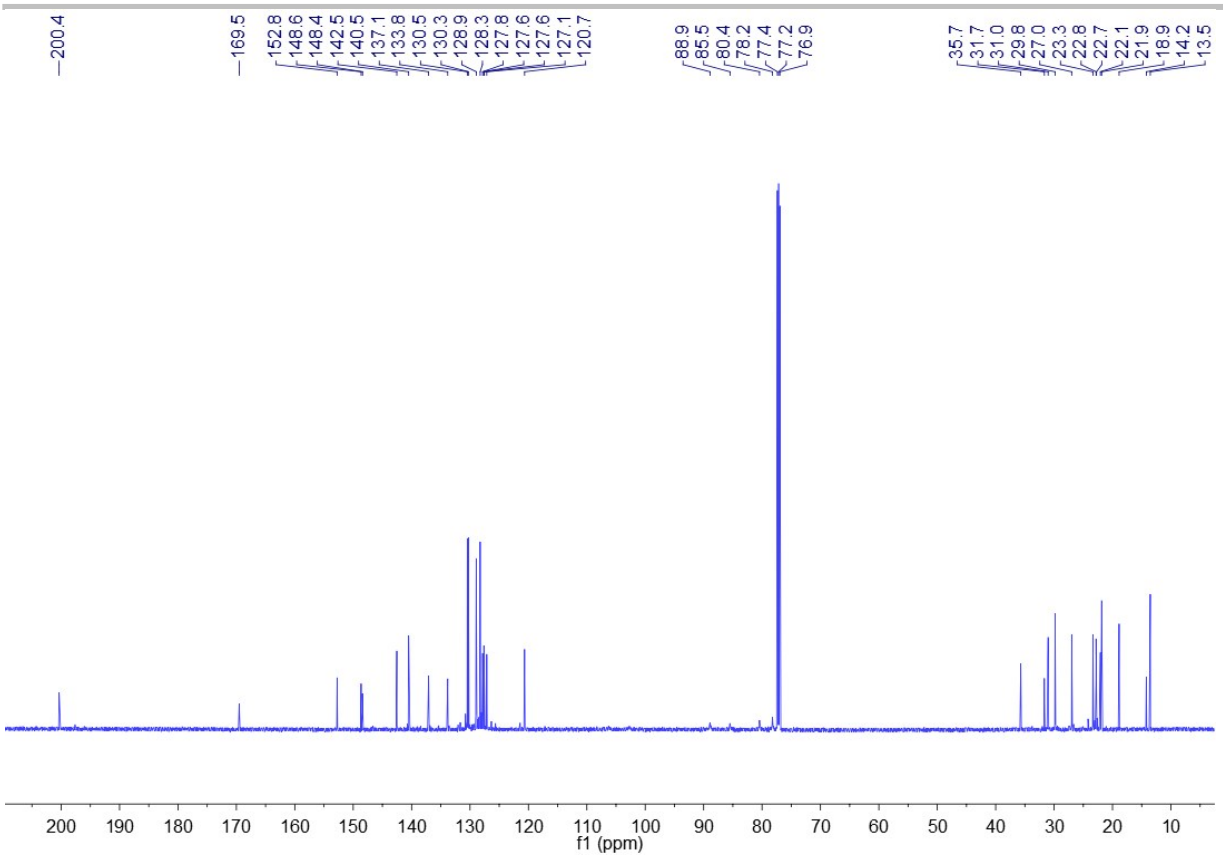

170.8
166.2
145.7
144.9
142.1
127.3
122.4
113.8
90.7
88.9
87.3
83.1
77.4
77.2
76.9
36.1
31.8
31.0
25.5
23.1
23.1
21.9
19.0
14.0
f1 (ppm)


8.08
8.07
7.54
7.54
7.26
7.12
7.12
7.11
7.11
5.57
5.56
5.49
5.48
5.29
5.28
5.23
5.22
4.03
3.12
3.11
3.10
3.09
3.09
3.08
3.03
3.02
3.01
3.00
3.00
2.99
1.96
1.30
Bu
Cl
Ru
1.02
1.07
1.16
1.06
1.05
1.14
0.76
3.00
1.18
1.38
1.32
2.88
1.19
1.35
2.29
9.40
3.33
3.07
2.95
f1 (ppm)

1c


170.6
161.5
145.6
145.4
144.6
141.2
124.6
110.8
100.3
90.0
88.5
87.0
83.4
77.4
77.2
76.9
53.5
35.9
34.2
31.6
31.6
30.9
25.4
23.0
22.9
21.9
18.9
13.9
f1 (ppm)


Ph
Bu
Ph
N
N=N
Ru
Cl
O
2a
1.00
1.00
1.89
2.73
4.95
1.11
1.00
1.01
1.09
1.05
3.06
4.19
1.23
2.96
1.17
3.58
3.00
2.12
2.98
2.32
3.20
f1 (ppm)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152.8
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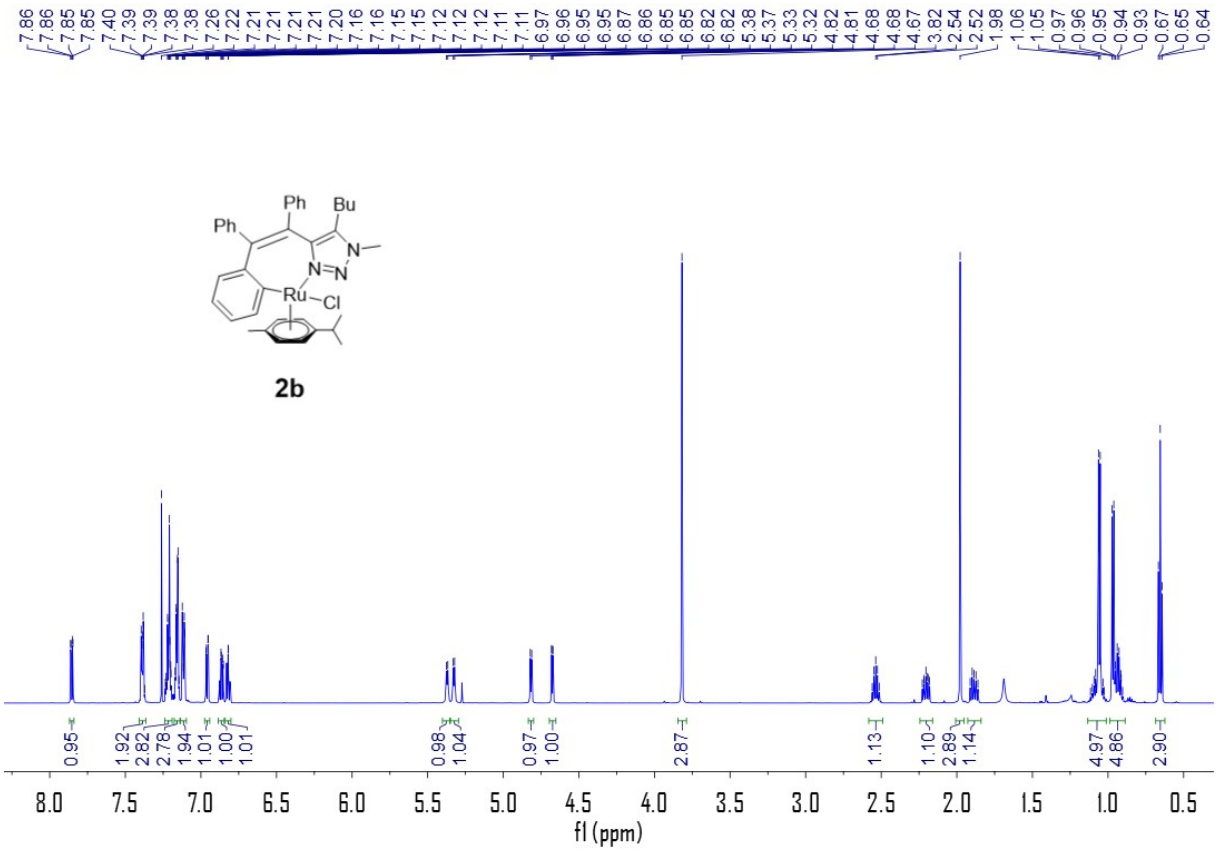
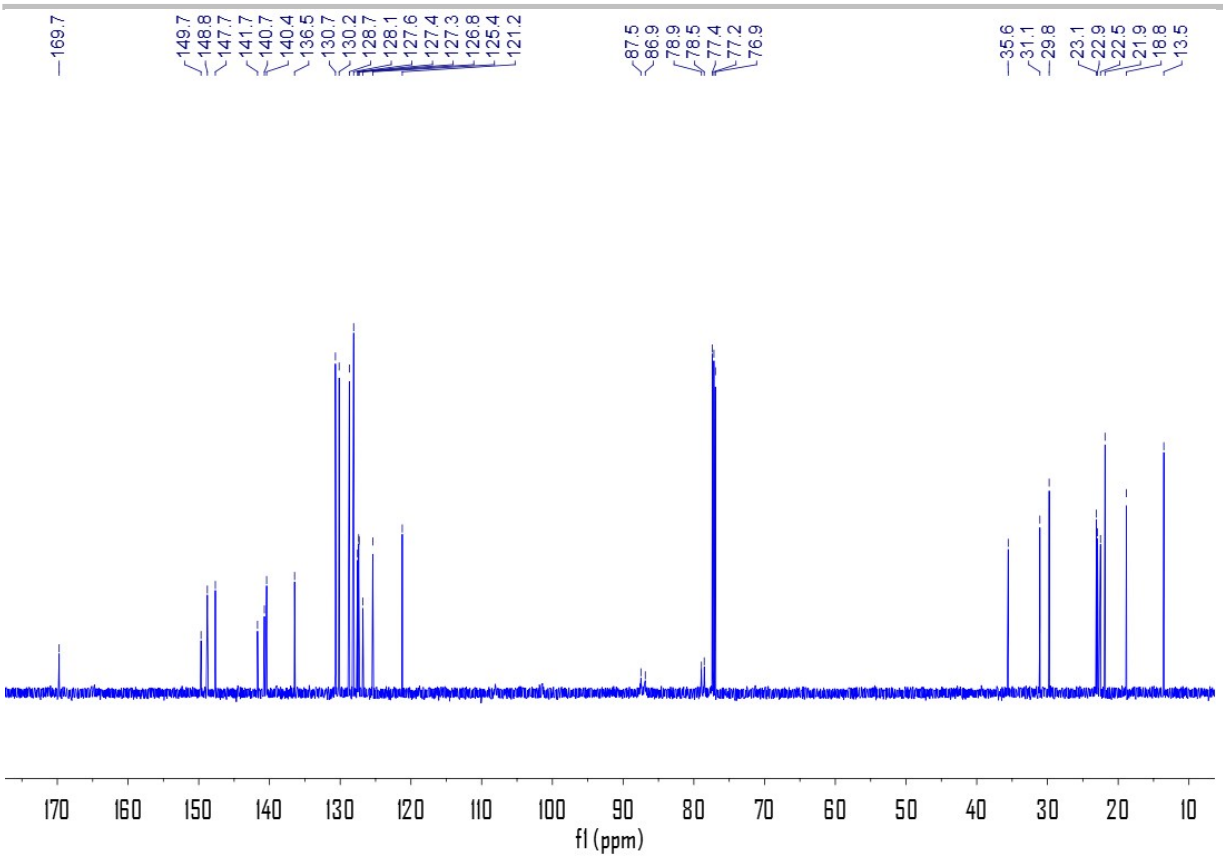
148.4
142.5
140.5
137.1
133.8
130.5
130.3
128.9
128.3
127.8
127.6
127.6
127.1
120.7
88.9
85.5
80.4
78.2
77.4
77.2
76.9
35.7
31.7
31.0
29.8
27.0
23.3
22.8
22.7
22.1
21.9
18.9
14.2
13.5
f1 (ppm)


Ph
Bu
Ph
N
N=N
Ru
Cl
2b
0.95
1.92
2.82
2.78
1.94
1.01
1.00
1.01
0.98
1.04
0.97
1.00
2.87
1.13
1.10
2.89
1.14
4.97
4.86
2.90
f1 (ppm)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149.7
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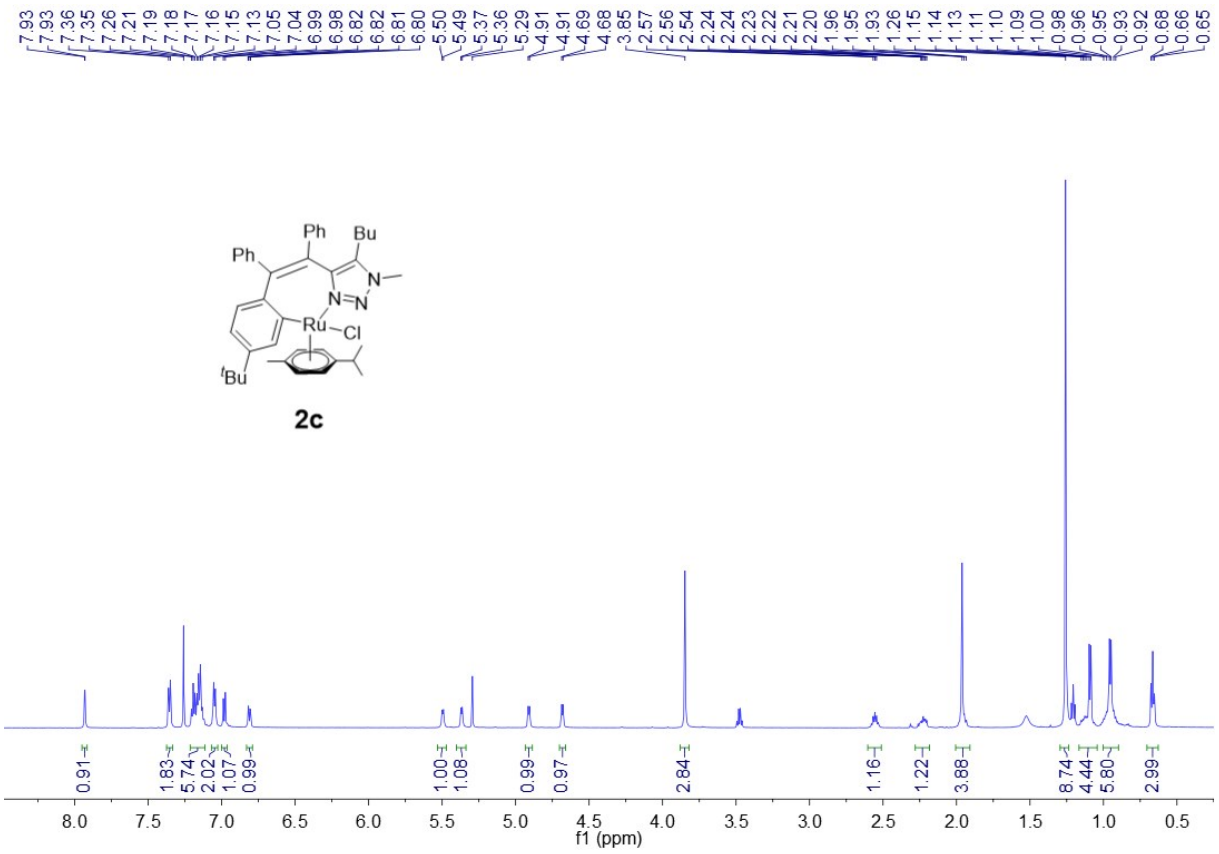
147.7
141.7
140.7
140.4
136.5
130.7
130.2
128.7
128.1
127.6
127.4
127.3
126.8
125.4
121.2
87.5
86.9
78.9
78.5
77.4
77.2
76.9
35.6
31.1
29.8
23.1
22.9
22.5
21.9
18.8
13.5
f1 (ppm)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7.93
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7.26
7.21
7.19
7.18
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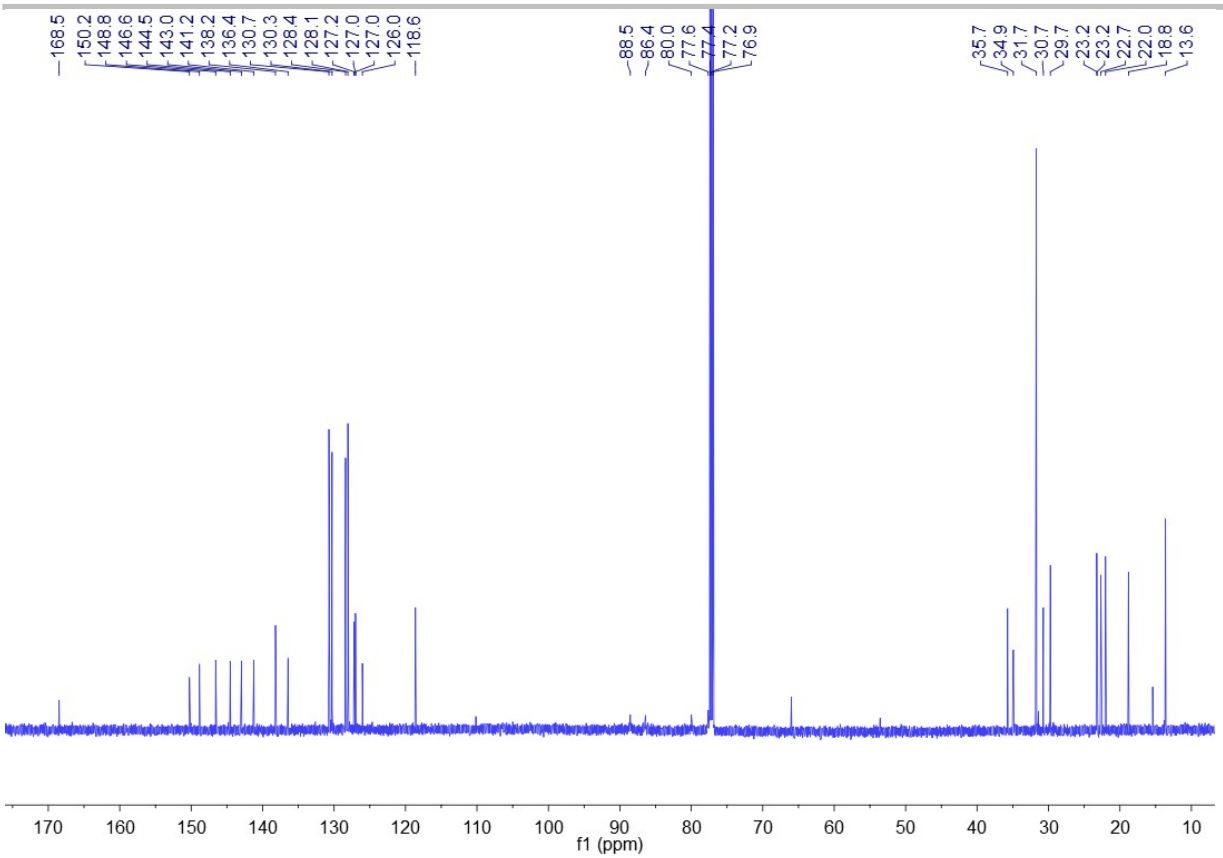
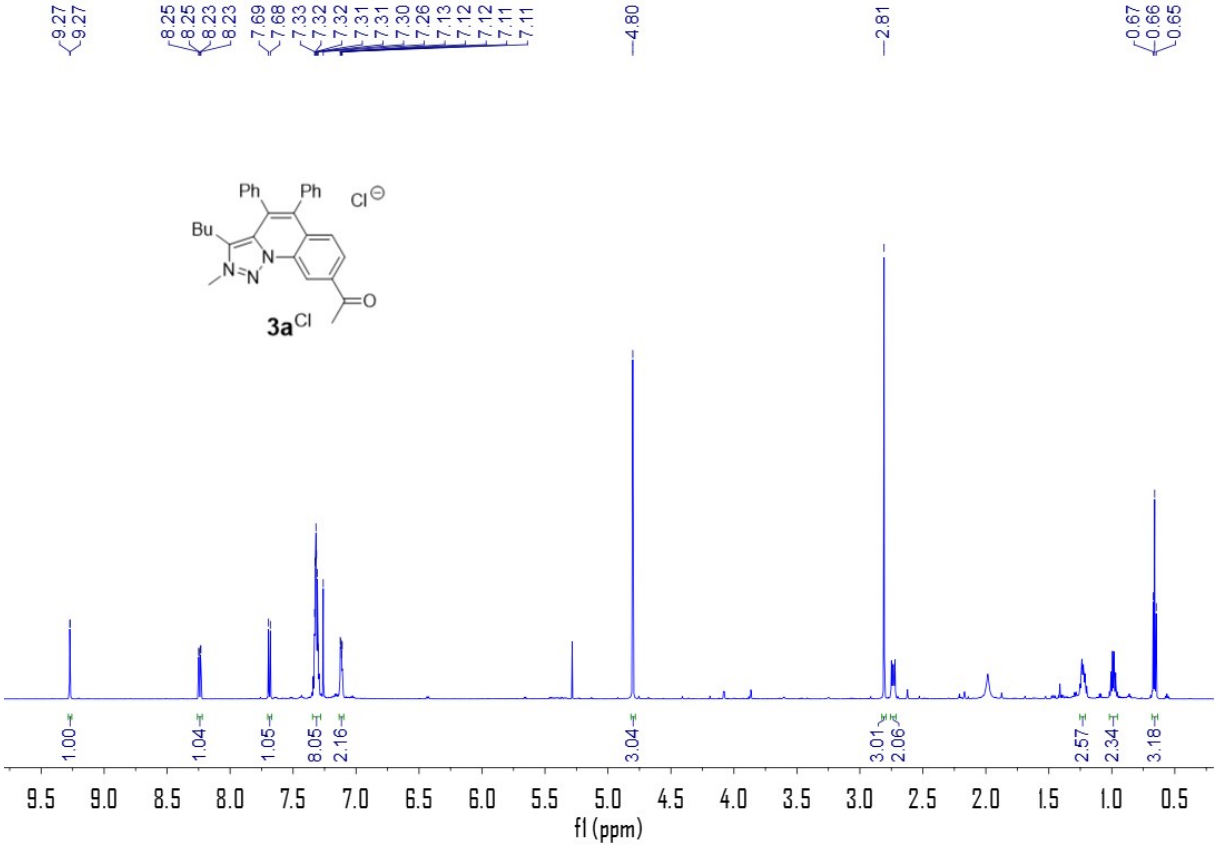
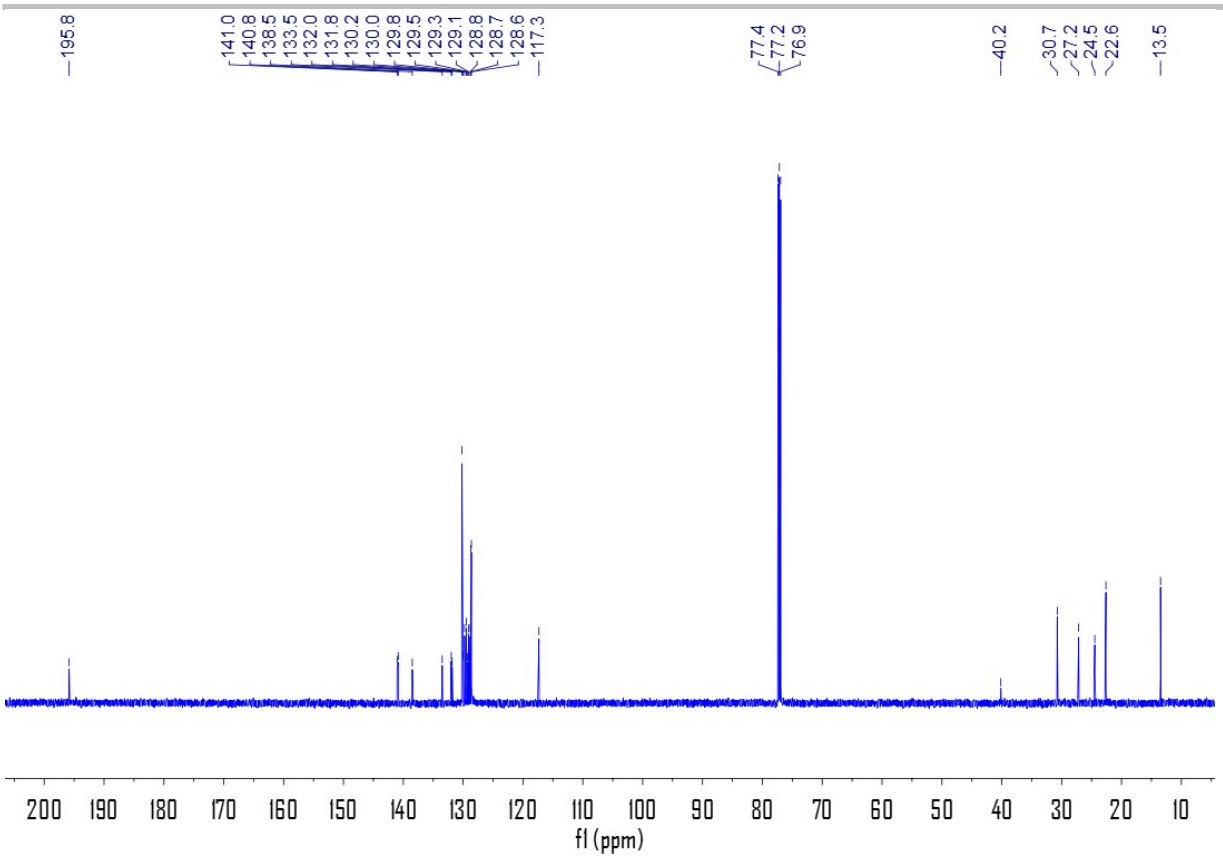
7.16
7.15
7.13
7.05
7.04
6.99
6.98
6.82
6.82
6.81
6.80
5.50
5.49
5.37
5.36
5.29
4.91
4.91
4.69
4.68
3.85
2.57
2.56
2.54
2.24
2.24
2.23
2.22
2.21
2.20
1.96
1.95
1.93
1.26
1.15
1.14
1.13
1.11
1.10
1.09
1.00
0.98
0.96
0.95
0.93
0.92
0.68
0.66
0.65
0.91
1.83
5.74
2.02
1.07
0.99
1.00
1.08
0.99
0.97
2.84
1.16
1.22
3.88
8.74
4.44
5.80
2.99
f1 (ppm)

Ph
Ph
Bu
N
N
Ru
Cl
tBu

2c


168.5
150.2
148.8
146.6
144.5
143.0
141.2
138.2
136.4
130.7
130.3
128.4
128.1
127.2
127.0
127.0
126.0
118.6
88.5
86.4
80.0
77.6
77.4
77.2
76.9
35.7
34.9
31.7
30.7
29.7
23.2
23.2
22.7
22.0
18.8
13.6
f1 (ppm)


9.27
9.27
8.25
8.25
8.23
8.23
7.69
7.68
7.33
7.32
7.32
7.31
7.31
7.30
7.26
7.13
7.12
7.12
7.11
7.11
4.80
2.81
0.67
0.66
0.65
Ph
Ph
Cl
Bu
N
N
O
3a Cl
1.00
1.04
1.05
8.05
2.16
3.04
3.01
2.06
2.57
2.34
3.18
f1 (ppm)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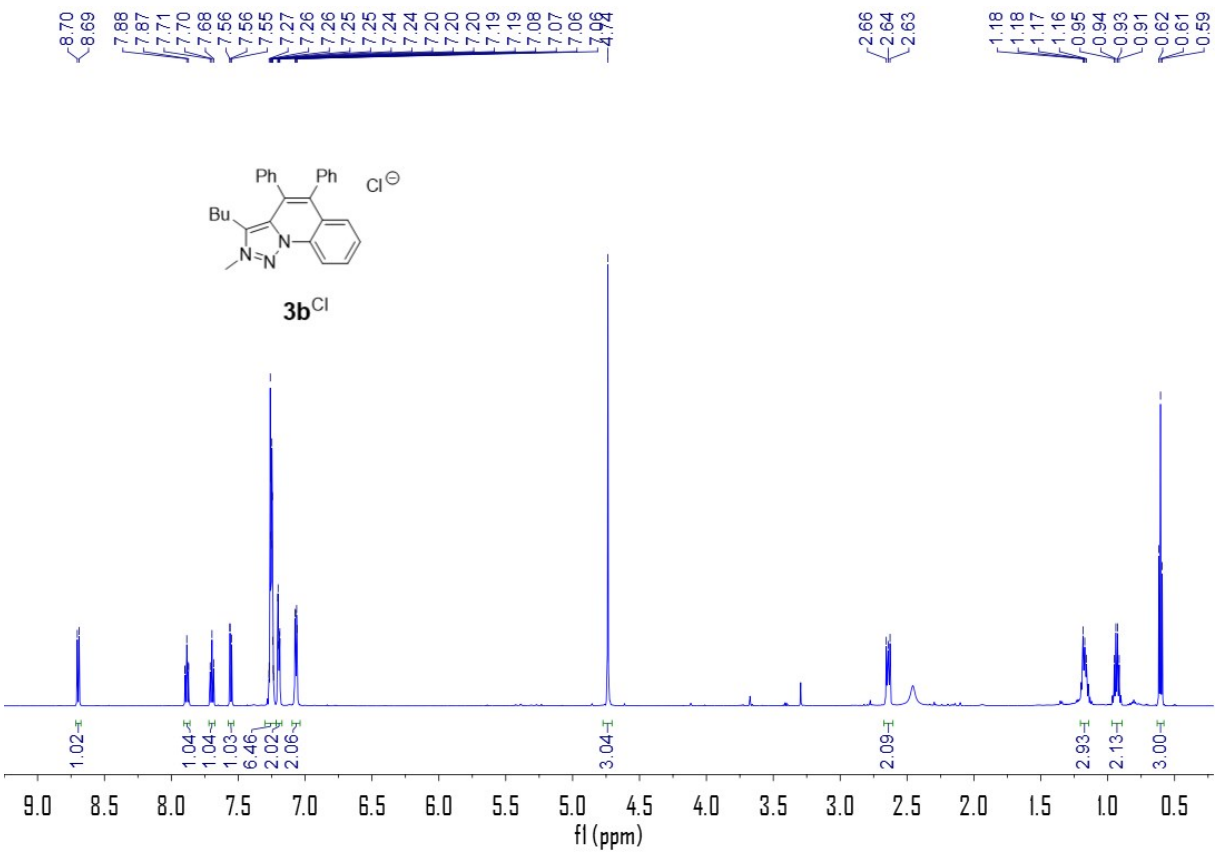
138.5
133.5
132.0
131.8
130.2
130.0
129.8
129.5
129.3
129.1
128.8
128.7
128.6
117.3
77.4
77.2
76.9
40.2
30.7
27.2
24.5
22.6
13.5
f1 (ppm)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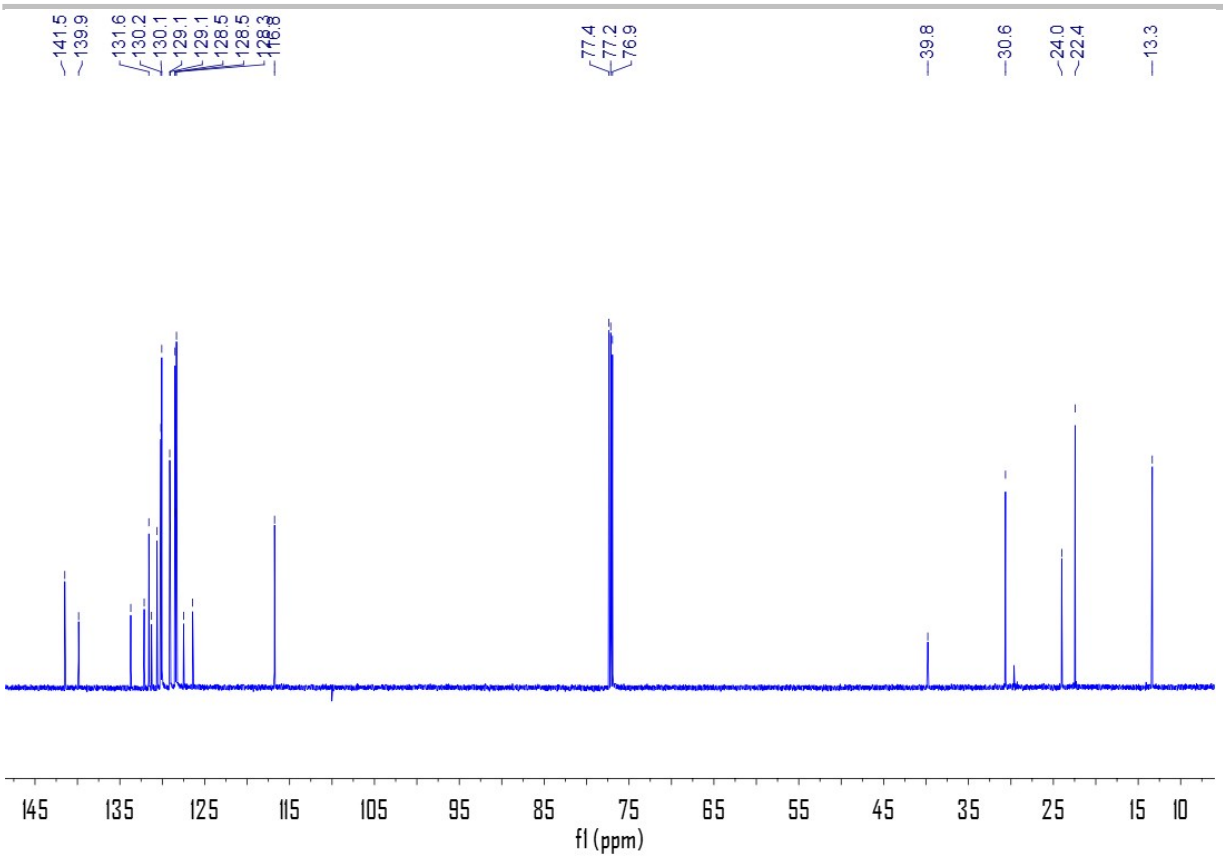
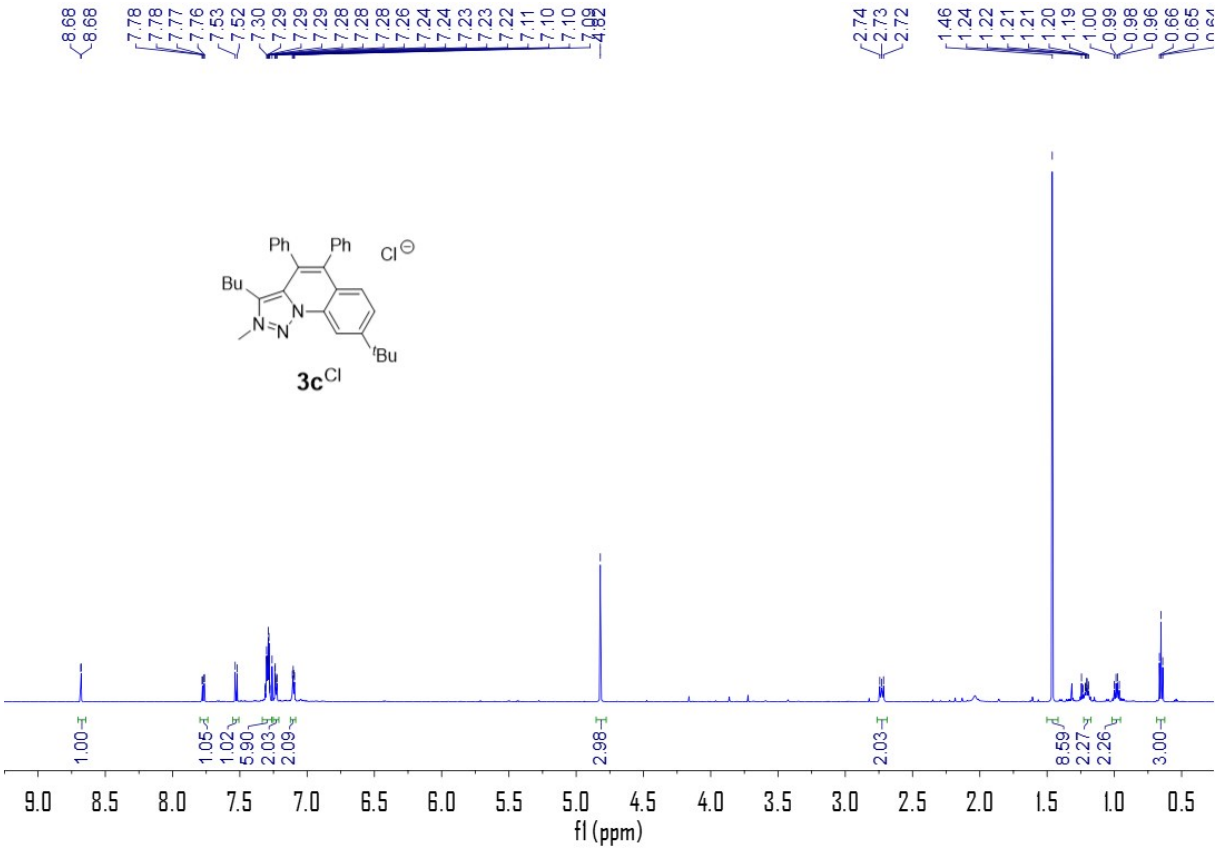
7.71
7.70
7.68
7.56
7.56
7.55
7.27
7.26
7.26
7.25
7.25
7.24
7.24
7.20
7.20
7.20
7.19
7.19
7.08
7.07
7.06
4.96
4.74
2.66
2.64
2.63
1.18
1.18
1.17
1.16
0.95
0.94
0.93
0.91
0.62
0.61
0.59
Ph
Ph
Cl⊖
Bu
N
N
N
3bCl
1.02
1.04
1.04
1.03
6.46
2.02
2.06
3.04
2.09
2.93
2.13
3.00
f1 (ppm)


141.5
139.9
131.6
130.2
130.1
129.1
129.1
128.5
128.5
77.4
77.2
76.9
39.8
30.6
24.0
22.4
13.3
f1 (ppm)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8.68
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7.78
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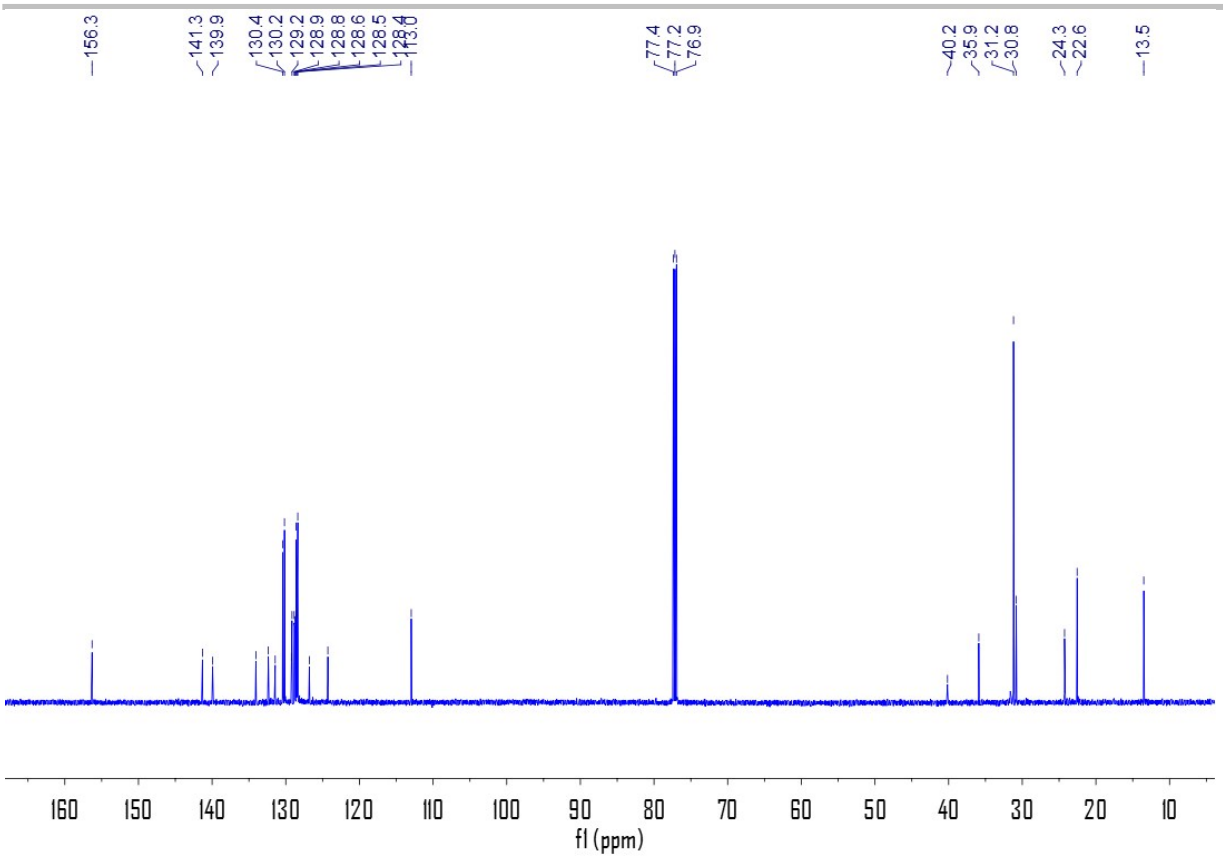
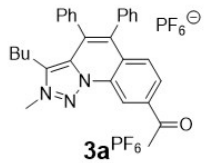
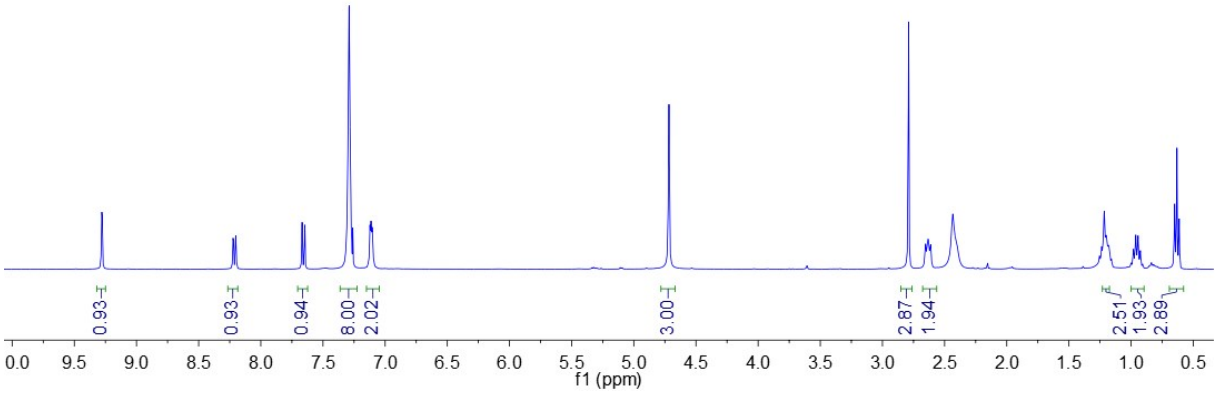
7.76
7.53
7.52
7.30
7.29
7.29
7.29
7.28
7.28
7.28
7.26
7.24
7.24
7.23
7.23
7.22
7.11
7.10
7.10
7.09
4.82
2.74
2.73
2.72
1.46
1.24
1.22
1.21
1.21
1.20
1.19
1.00
0.99
0.98
0.96
0.66
0.65
Ph
Ph
Cl⊖
Bu
tBu
3cCl
1.00
1.05
1.02
5.90
2.03
2.09
2.98
2.03
8.59
2.27
2.26
3.00
f1 (ppm)


156.3
141.3
139.9
130.4
130.2
129.2
128.9
128.8
128.6
128.5
128.4
113.0
77.4
77.2
76.9
40.2
35.9
31.2
30.8
24.3
22.6
13.5
f1 (ppm)


9.28
8.22
8.22
8.20
8.20
7.67
7.65
7.29
7.26
7.12
7.11
7.11
7.10
7.10
4.72
2.79
2.65
2.63
2.61
1.25
1.24
1.22
1.20
1.18
1.16
1.00
0.96
0.94
0.65
0.63


Ph
Ph
PF6
Bu
N
N
N
O

3a^{PF_6}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0.93
0.94
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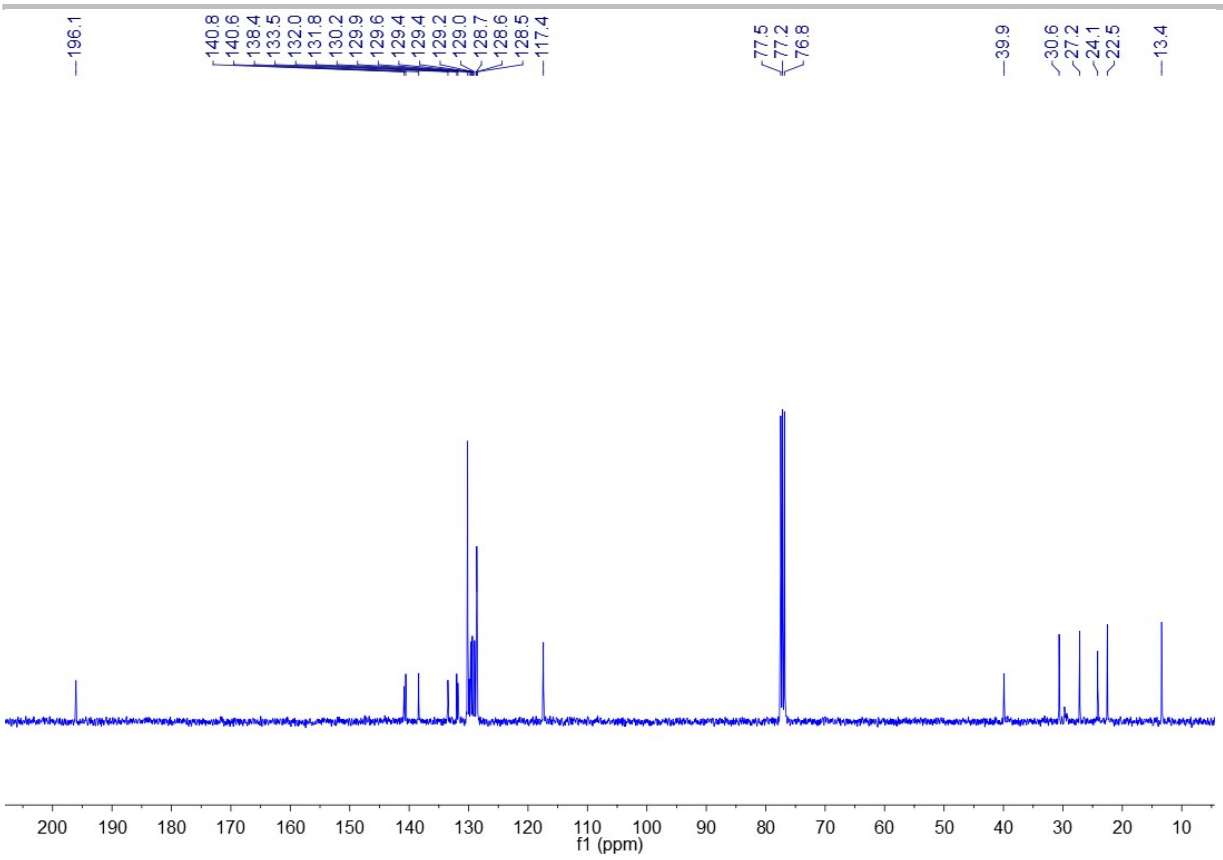
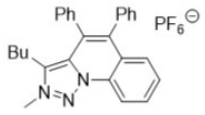
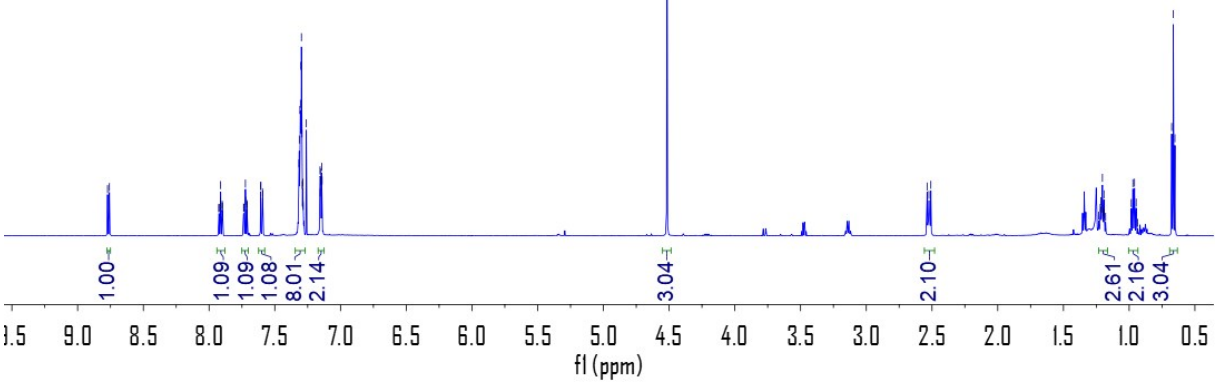
2.02
3.00
2.87
1.94
2.51
1.93
2.89
f1 (ppm)

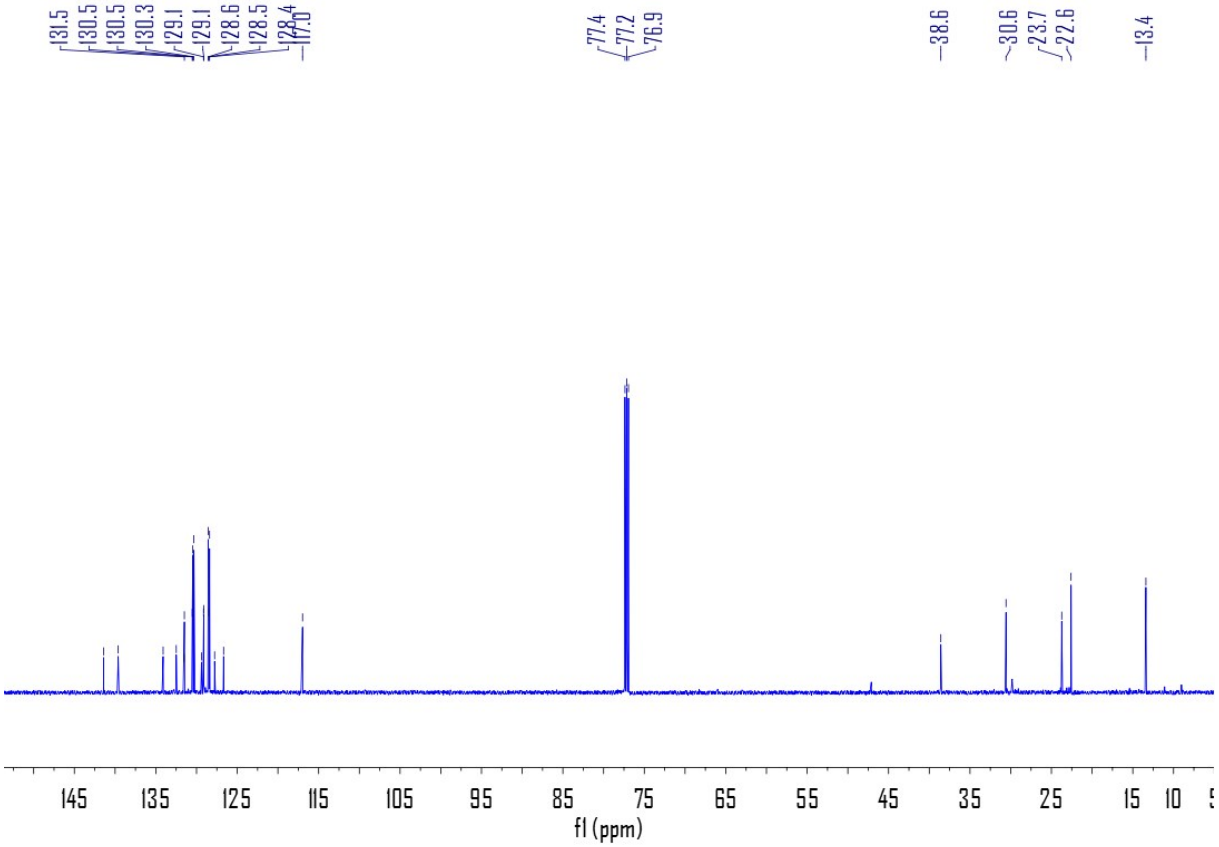

196.1
140.8
140.6
138.4
133.5
132.0
131.8
130.2
129.9
129.6
129.4
129.4
129.2
129.0
128.7
128.6
128.5
117.4
77.5
77.2
76.8
39.9
30.6
27.2
24.1
22.5
13.4
f1 (ppm)

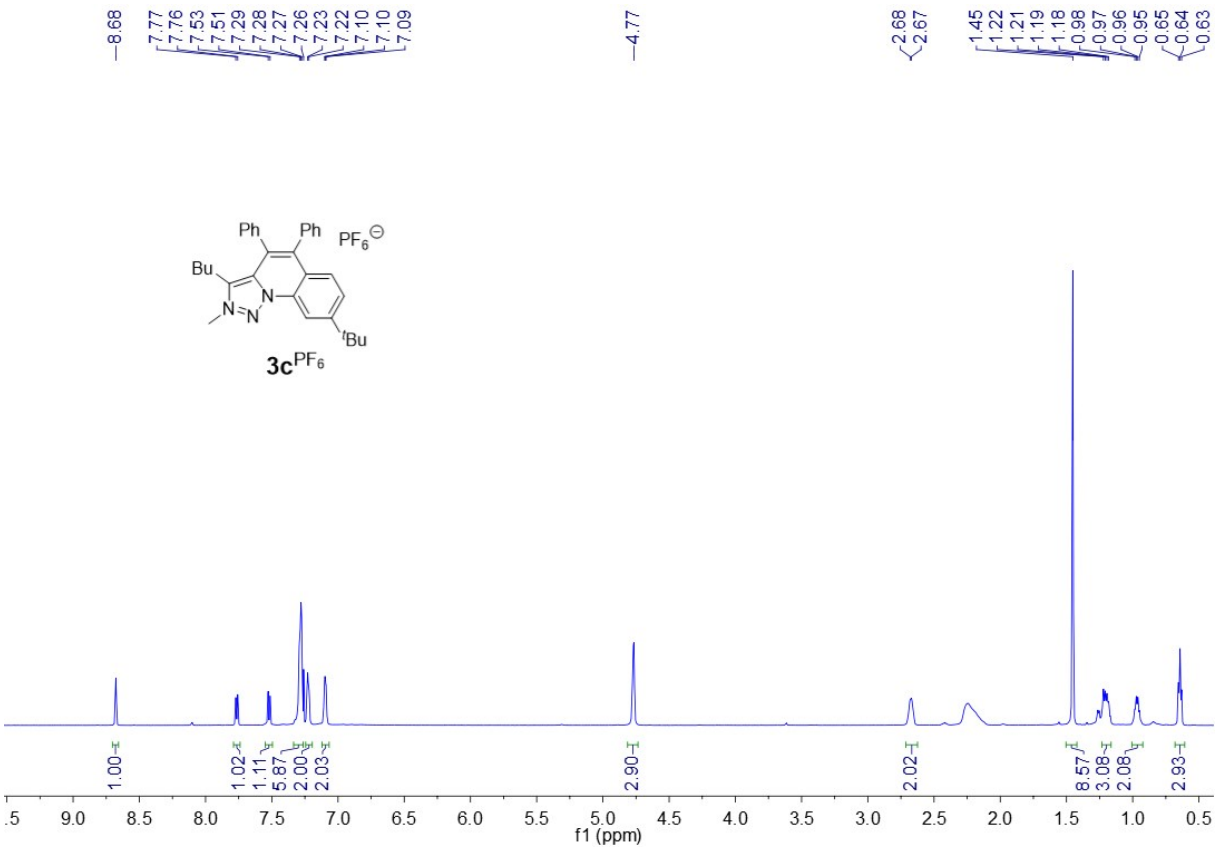

8.77
8.76
7.91
7.91
7.90
7.72
7.72
7.71
7.61
7.61
7.59
7.59
7.32
7.31
7.31
7.31
7.30
7.30
7.29
7.29
7.29
7.26
7.16
7.15
7.15
7.15
7.14
7.14
4.52
2.54
2.52
2.51
1.22
1.20
1.19
0.98
0.97
0.96
0.95
0.68
0.66
0.65


Ph
Ph
PF6
Bu
N
N

3b^{PF_6}


1.00
1.09
1.09
1.08
8.01
2.14
3.04
2.10
2.61
2.16
3.04
f1 (ppm)


131.5
130.5
130.5
130.3
129.1
129.1
128.6
128.5
128.4
117.0
77.4
77.2
76.9
38.6
30.6
23.7
22.6
13.4
f1 (ppm)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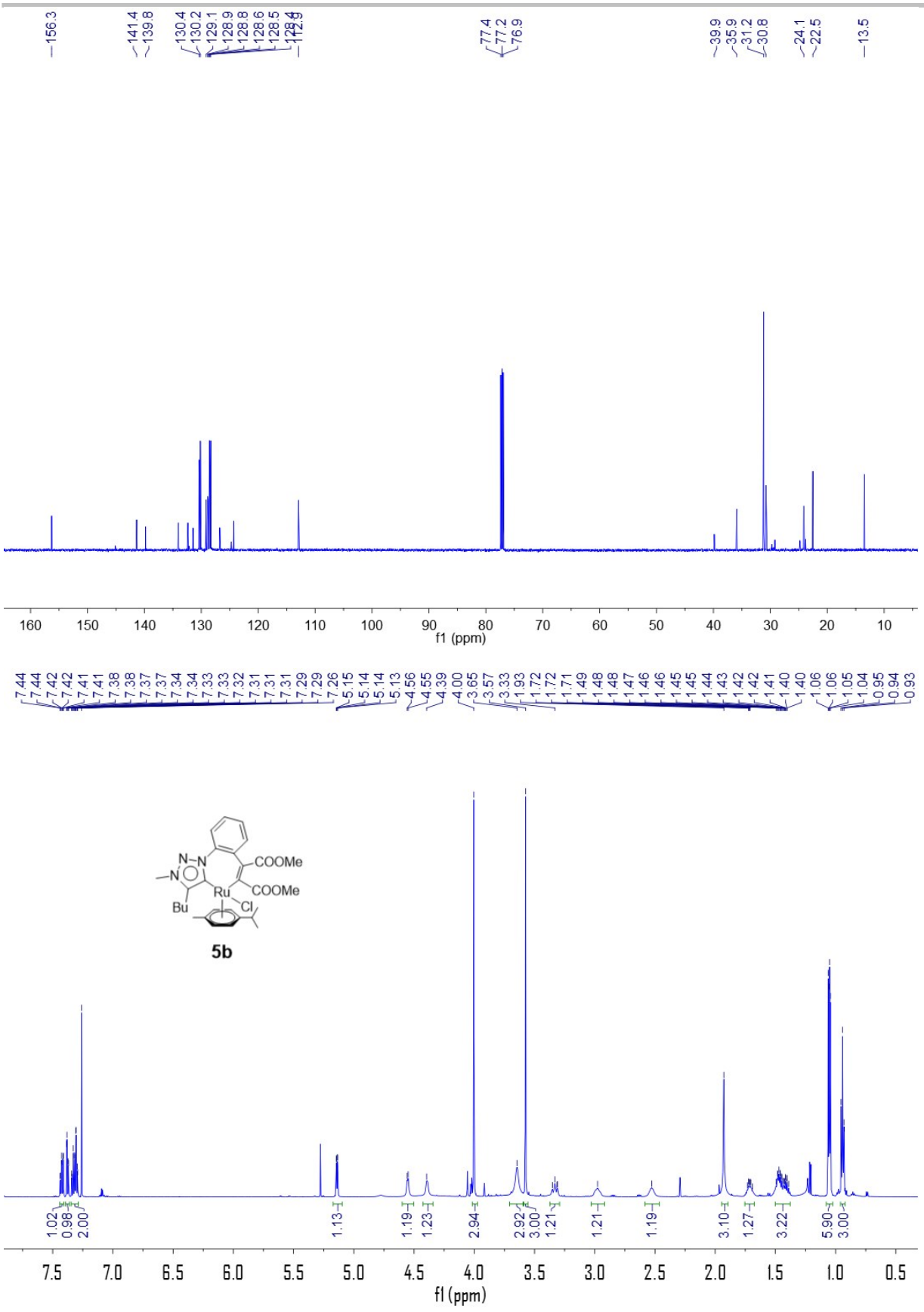
7.29
7.28
7.27
7.26
7.23
7.22
7.10
7.09
4.77
2.68
2.67
1.45
1.22
1.21
1.19
1.18
0.98
0.97
0.96
0.95
0.65
0.64
0.63
1.00
1.02
1.11
5.87
2.00
2.03
2.90
2.02
8.57
3.08
2.08
2.93
f1 (ppm)

Ph
Ph
PF6
Bu
N
N
tBu

3c^{PF_6}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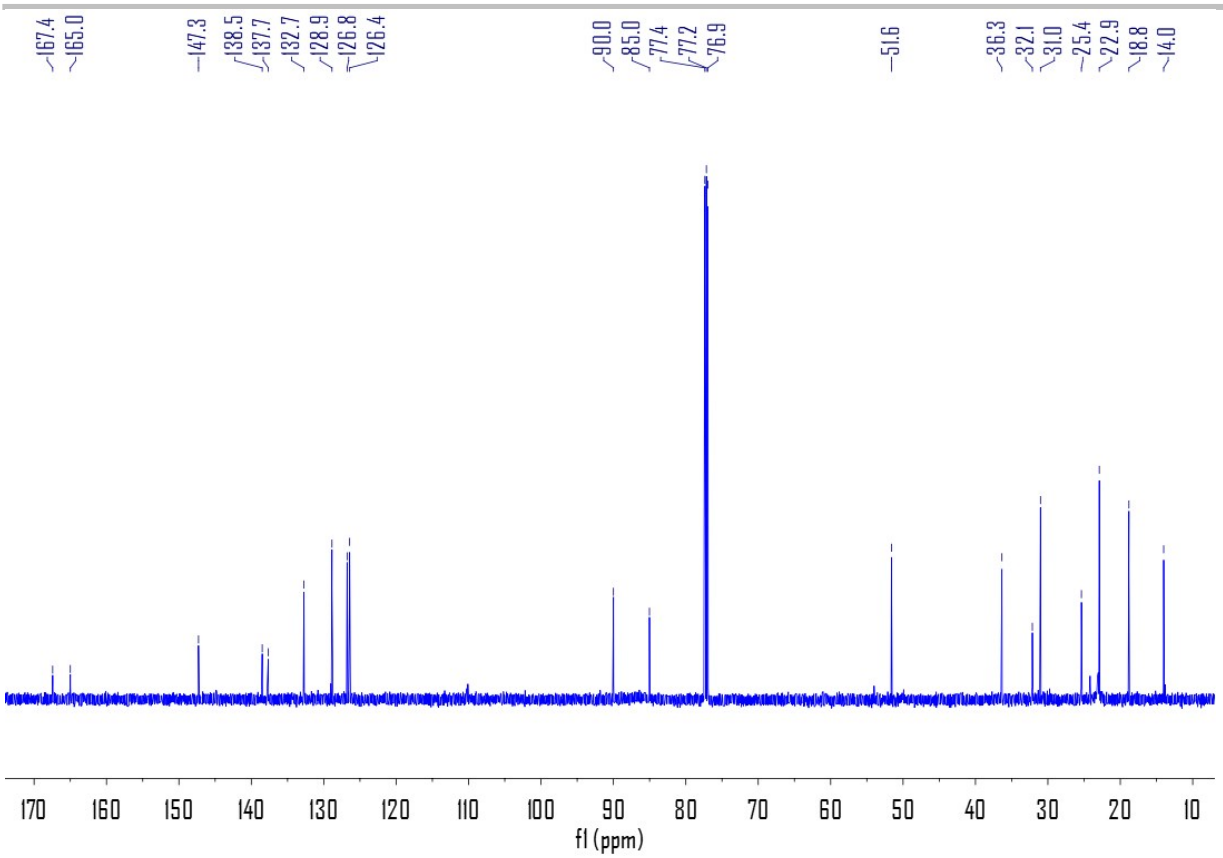
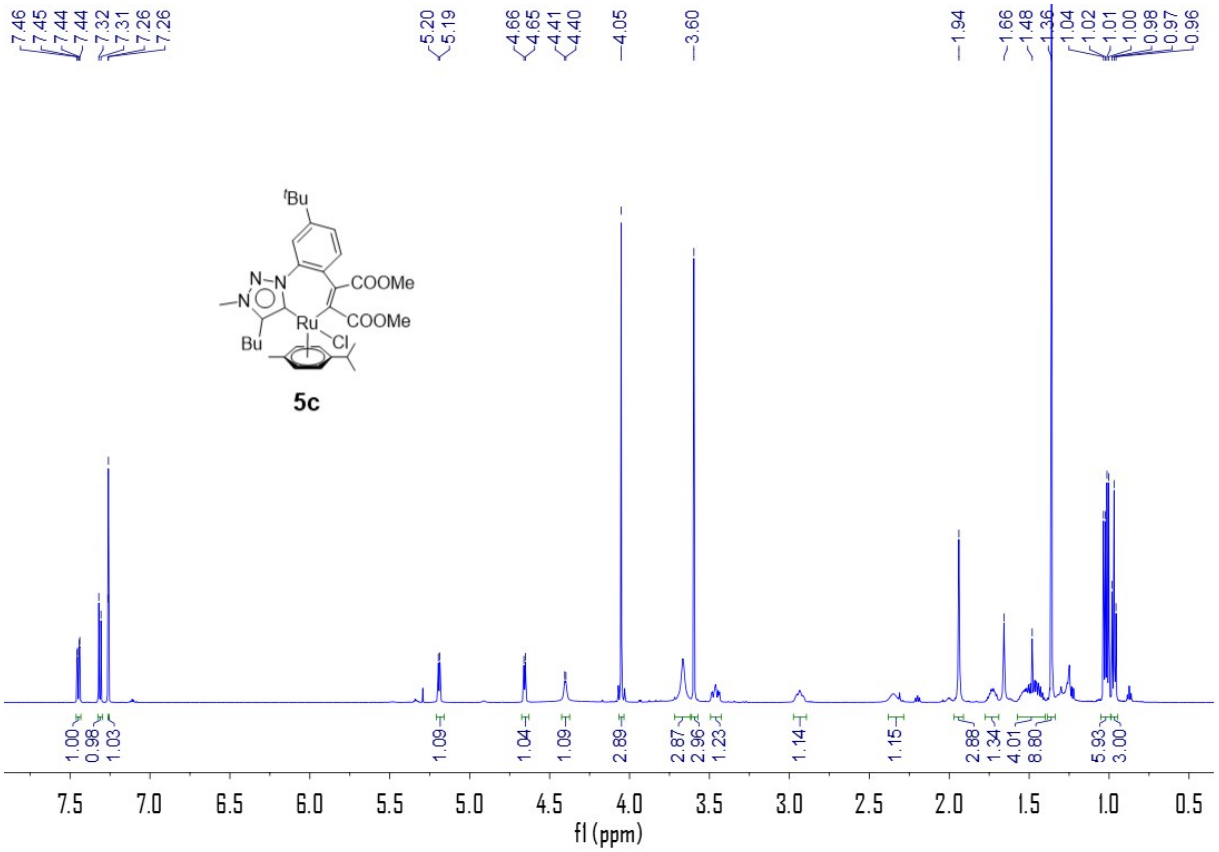
130.4
130.2
129.1
128.9
128.8
128.6
128.5
128.4
127.9
77.4
77.2
76.9
39.9
35.9
31.2
30.8
24.1
22.5
13.5
f1 (ppm)
7.44
7.44
7.42
7.42
7.41
7.41
7.38
7.38
7.37
7.37
7.34
7.34
7.33
7.33
7.32
7.31
7.31
7.31
7.29
7.29
7.26
5.15
5.14
5.13
4.56
4.55
4.39
4.00
3.65
3.57
3.33
1.93
1.72
1.72
1.71
1.49
1.48
1.48
1.47
1.46
1.46
1.45
1.45
1.44
1.43
1.42
1.42
1.41
1.40
1.40
1.06
1.06
1.05
1.04
0.95
0.94
0.93
COOMe
COOMe
Ru
Cl
Bu
5b
1.02
0.98
2.00
1.13
1.19
1.23
2.94
2.92
3.00
1.21
1.21
1.19
3.10
1.27
3.22
5.90
3.00
f1 (ppm)


167.4
165.0
147.3
138.5
137.7
132.7
128.9
126.8
126.4
90.0
85.0
77.4
77.2
76.9
51.6
36.3
32.1
31.0
25.4
22.9
18.8
14.0
f1 (ppm)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7.44
7.44
7.32
7.31
7.26
7.26
5.20
5.19
4.66
4.65
4.41
4.40
4.05
3.60
1.94
1.66
1.48
1.36
1.04
1.02
1.01
1.00
0.98
0.97
0.96
tBu
COOMe
COOMe
Ru
Cl
Bu
5c
1.00
0.98
1.03
1.09
1.04
1.09
2.89
2.87
2.96
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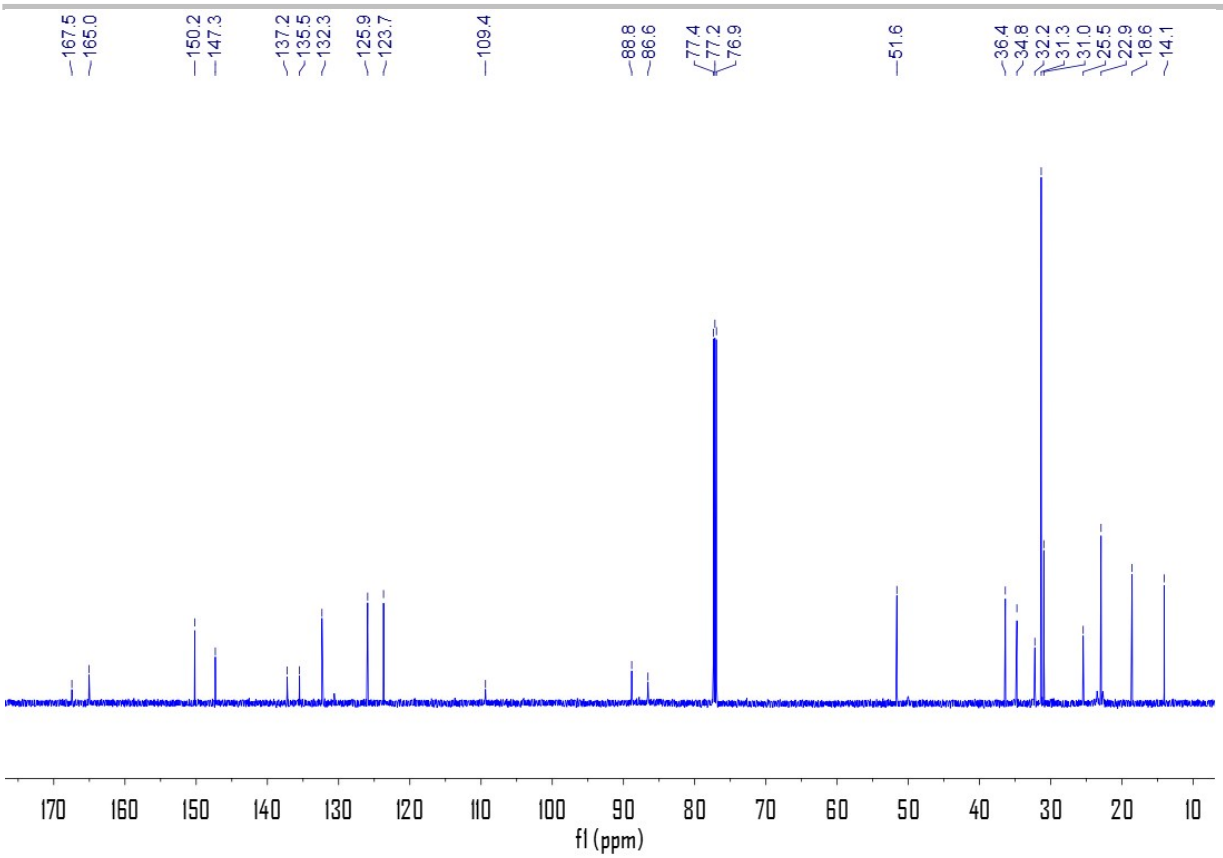
1.14
1.15
2.88
1.34
4.01
8.80
5.93
3.00
f1 (ppm)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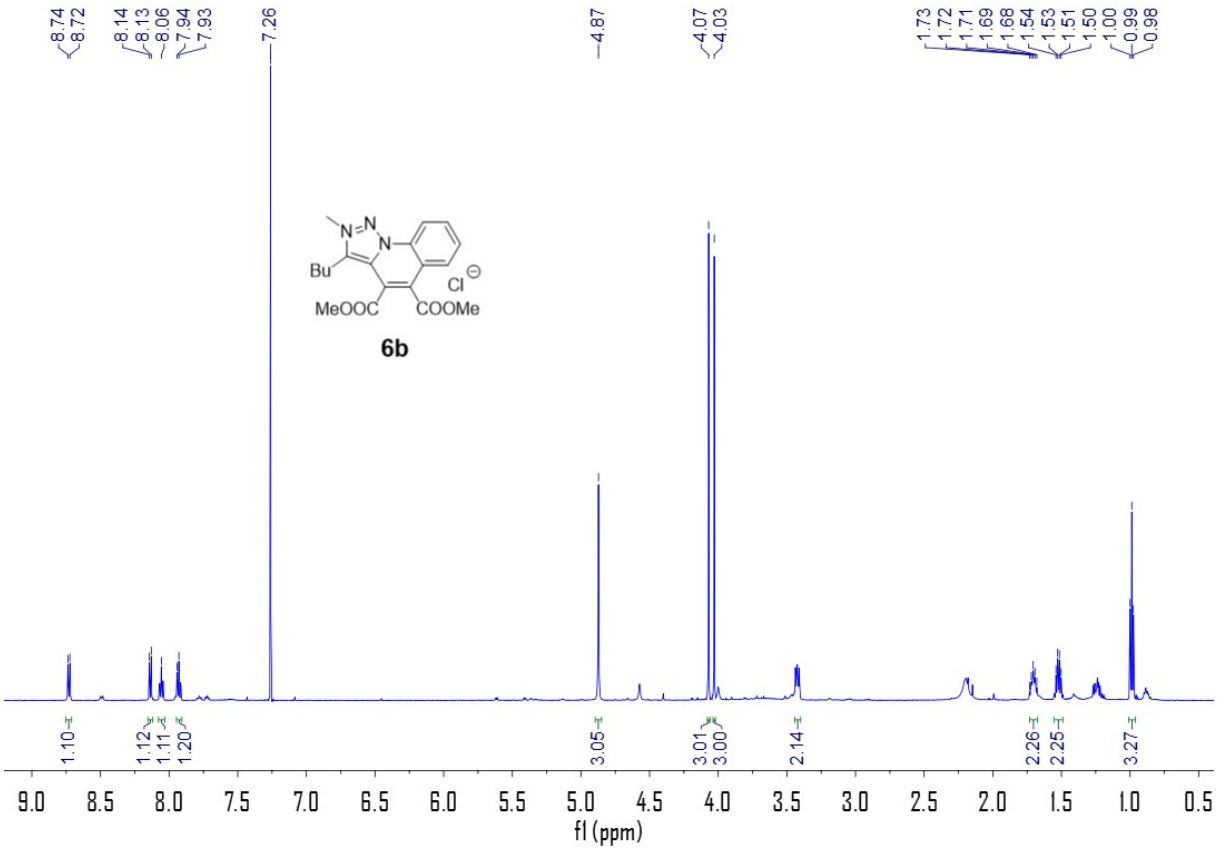
165.0
150.2
147.3
137.2
135.5
132.3
125.9
123.7
109.4
88.8
86.6
77.4
77.2
76.9
51.6
36.4
34.8
32.2
31.3
31.0
25.5
22.9
18.6
14.1
f1 (ppm)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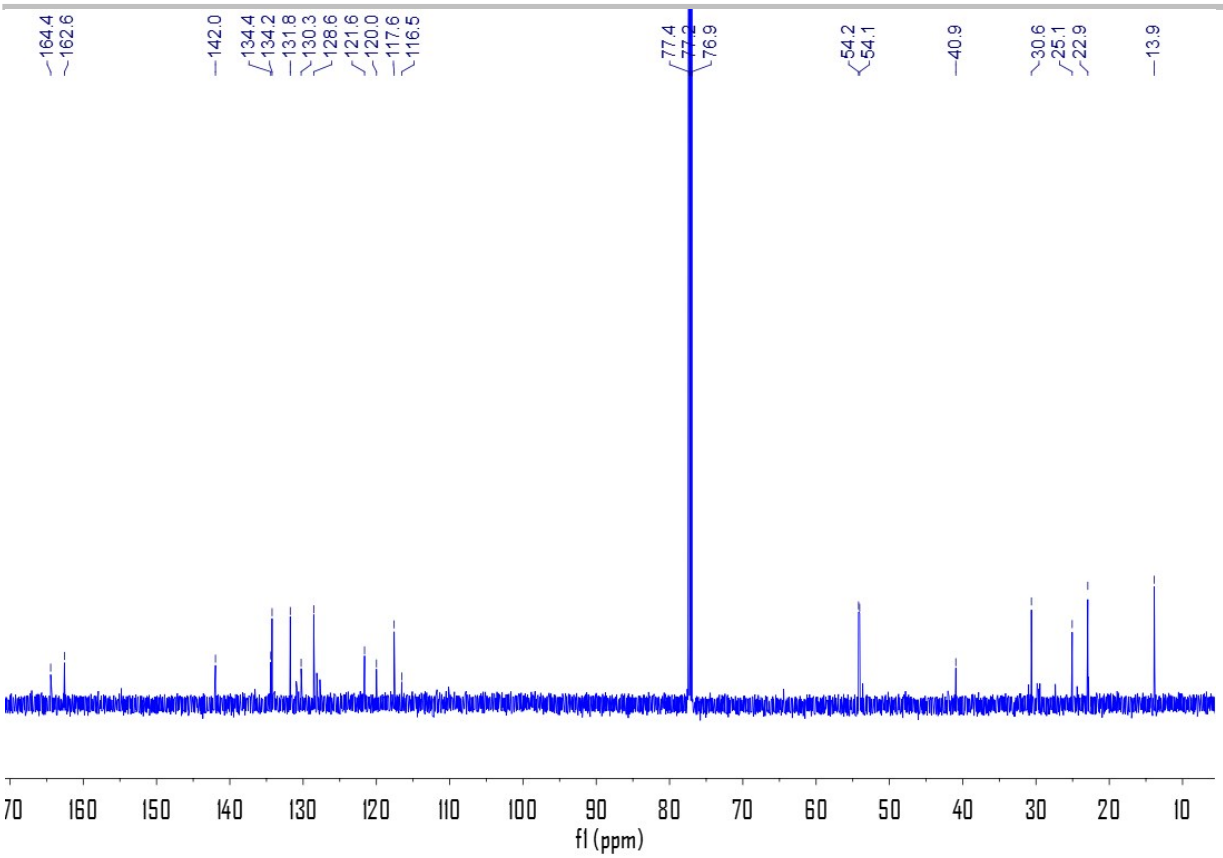
8.72
8.14
8.13
8.06
7.94
7.93
7.26
4.87
4.07
4.03
1.73
1.72
1.71
1.69
1.68
1.54
1.53
1.51
1.50
1.00
0.99
0.98
Bu
Cl
MeOOC
COOMe
6b
1.10
1.12
1.11
1.20
3.05
3.01
3.00
2.14
2.26
2.25
3.27
f1 (ppm)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134.4
134.2
131.8
130.3
128.6
121.6
120.0
117.6
116.5
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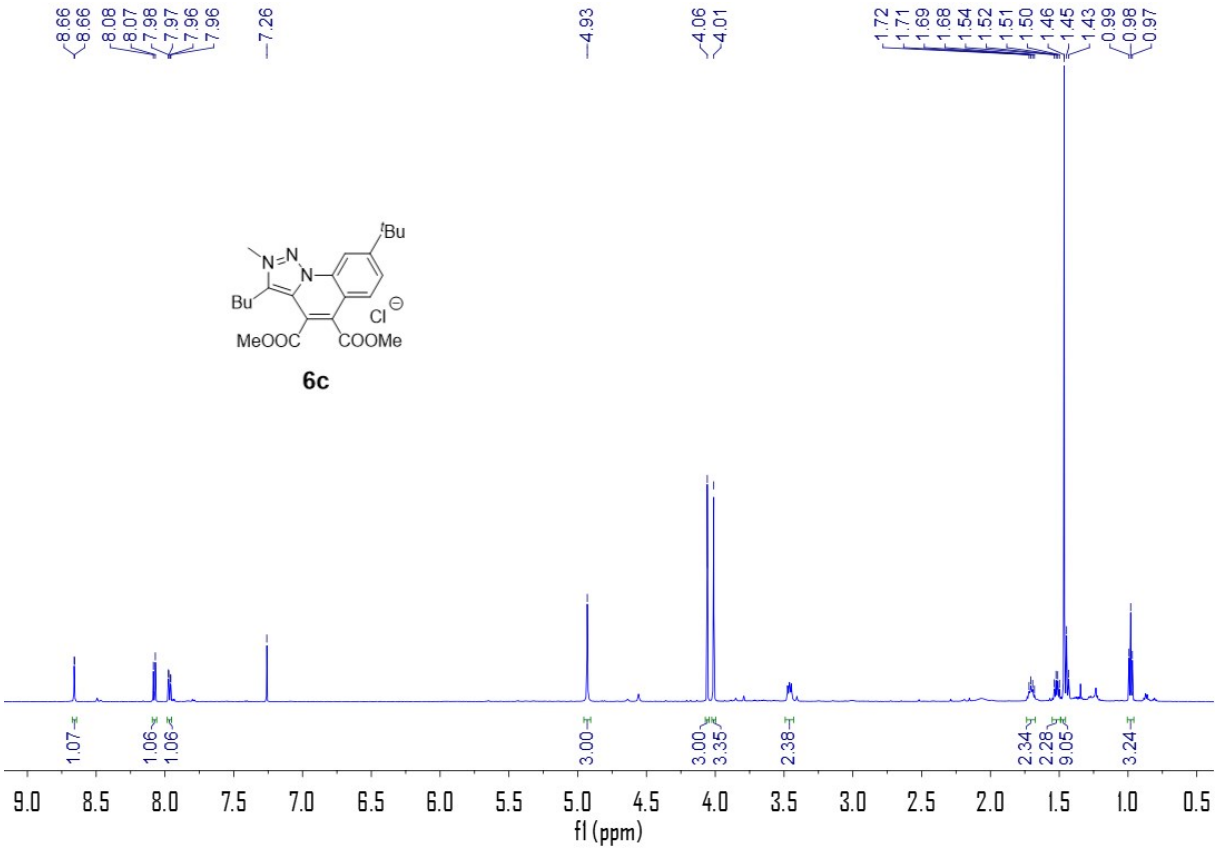
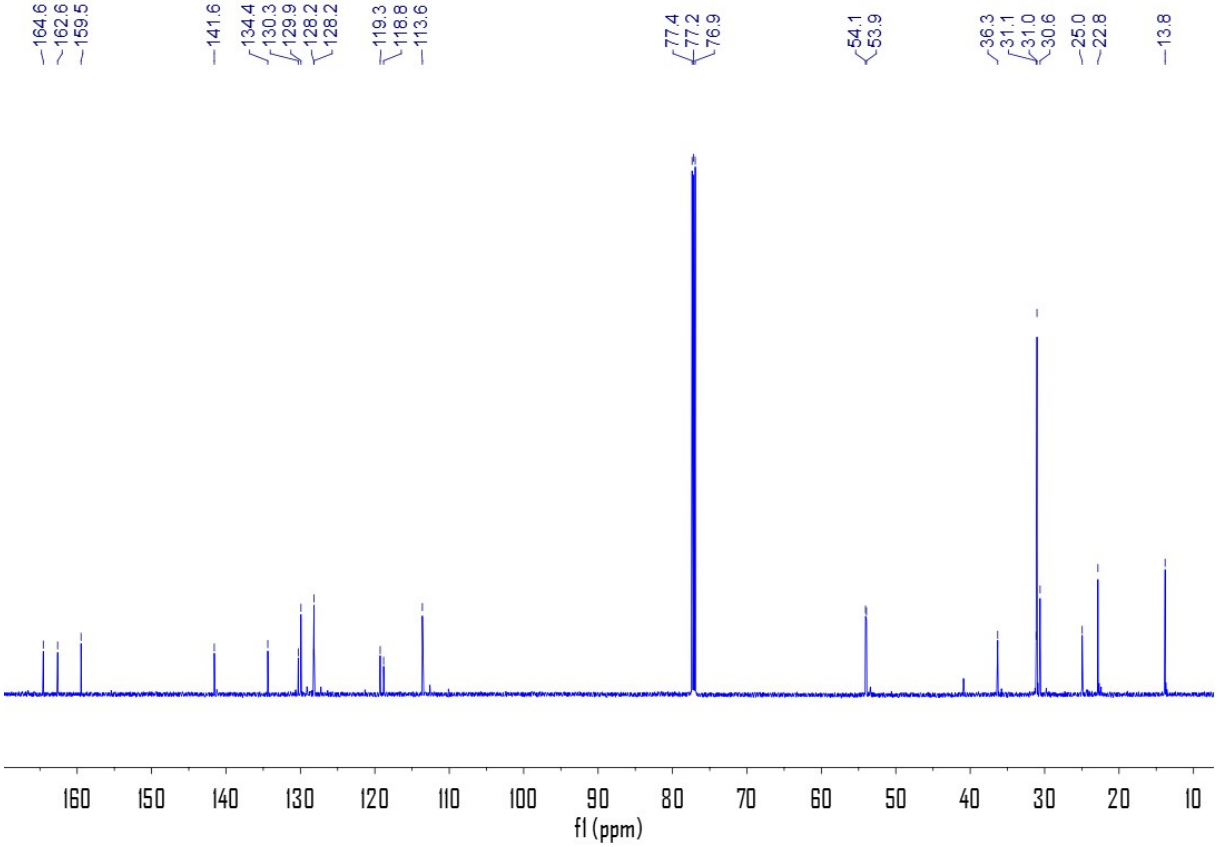
77.2
76.9
54.2
54.1
40.9
30.6
25.1
22.9
13.9
f1 (ppm)


8.66
8.66
8.08
8.07
7.98
7.97
7.96
7.96
7.26
4.93
4.06
4.01
1.72
1.71
1.69
1.68
1.54
1.52
1.51
1.50
1.46
1.45
1.43
0.99
0.98
0.97
1.07
1.06
1.06
3.00
3.00
3.35
2.38
2.34
2.28
9.05
3.24
f1 (ppm)

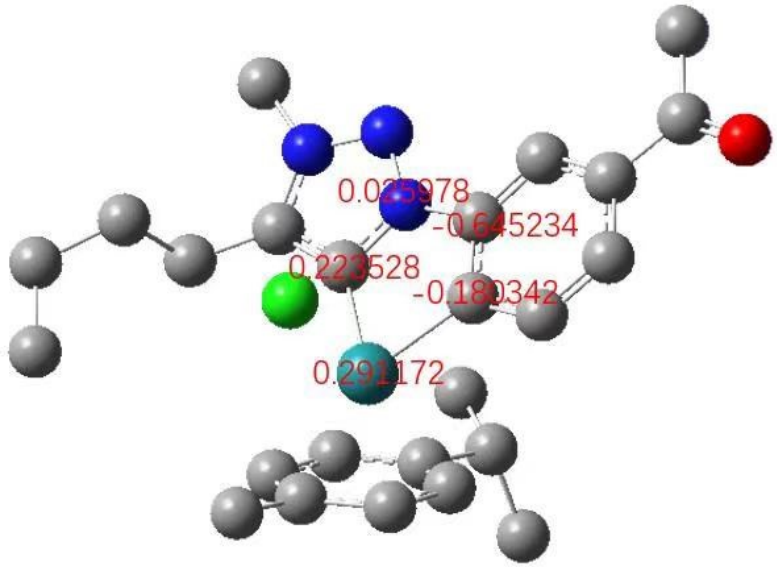
tBu
Bu
Cl
MeOOC
COOMe

6c



5. Computational study.

Gaussian 09 software was used to carry out the computational study[2]. The Mulliken charges of **1a** were obtained by density functional theory (DFT) calculations at the hybrid functional B3LYP level. The 6-311++g** basis sets for C, H, O, N, Cl atoms and the LANL2DZ for Ru atom were selected. The solvent effect of methanol was taken into account by means of the default polarizable continuum model (PCM)[3]. The Grimme's version 3 dispersion corrections were introduced to consider the dispersion effects[4].



Reference

[1] X. Zhang, X. Yan, B. Zhang, R. Wang, S. Guo, S. Peng, *Transit. Met. Chem.* 2019, **44**, 39-48.

[2] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman; G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson et al. Gaussian 09, Gaussian, Inc., Wallingford, CT, 2009.

[3] J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* 2005, **105**, 2999-3094.

[4] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* 2010, **132**, 154104.