Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

for

Rhodium Catalysts with Superbulky NHC Ligands for the Selective α-Hydrothiolation of Alkynes

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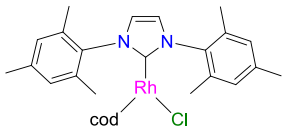
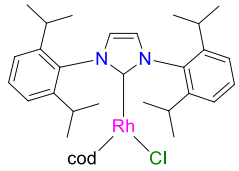
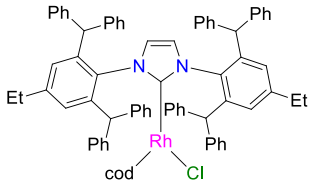
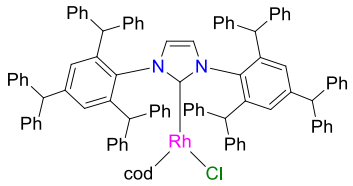
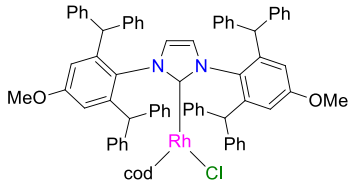
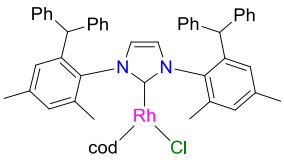
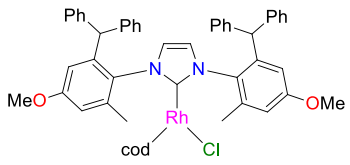
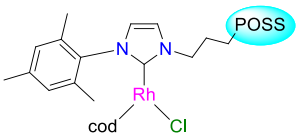
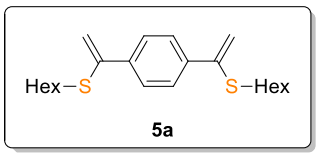
1. Analytical data of rhodium complexes I-VIII

 **Complex I** [RhCl(cod)(IMes)]	*Chloro(η^4-1,5-cyclooctadiene)(1,3-dimesitylimidazol-2-ylidene)rhodium(I),* Yellow solid, isolated yield: 90%, 99.2 mg (1.80×10^{-4} mmol); ^{1}H NMR ($CDCl_3$, δ, ppm): 1.49-1.56 (m, 4H, H_{COD}), 1.78 – 1.91 (m, 4H, H_{COD}), 2.11 (s, 6H, CH_3), 2.30 – 2.45 (m, 12H, CH_3), 3.26 – 3.32 (br, 2H, H_{COD}), 4.48 – 4.56 (br, 2H, H_{COD}), 6.96 (s, 2H, $CH^{4,5}$Im), 6.98 – 7.06 (m, 4H, CH_{Ar}); ^{13}C NMR ($CDCl_3$, δ, ppm): 18.12, 19.79, 21.13, 28.37, 32.69, 67.80 (d, J_{Rh-C} = 14.5 Hz), 96.08 (d, J_{Rh-C} = 7.5 Hz), 123.48, 128.08, 129.66, 134.32, 136.21, 137.56, 138.65, 183.46 (d, J_{Rh-C} = 52.4 Hz); MS (ESI): calcd. for $C_{29}H_{36}ClN_2Rh$: 515.1928; found: 515.1928. These spectroscopic data matched those reported in the literature.[1]
 **Complex II** [RhCl(cod)(IPr)]	*Chloro(η^4-1,5-cyclooctadiene)(1,3-bis(2,6-diisopropylphenylimidazol)-2-ylidene)rhodium(I),* Yellow solid, isolated yield: 92%, 116.9 mg (1.84×10^{-4} mmol); ^{1}H NMR ($CDCl_3$, δ, ppm): 1.09 (d, 12H, J_{HH} = 6.8 Hz, $CH(CH_3)_2$), 1.23 – 1.86 (m, 20H, H_{COD} and $CH(CH_3)_2$), 2.40 – 2.59 (br, 2H, $CH(CH_3)_2$), 3.20 – 3.28 (m, 2H, H_{COD}), 3.49 – 3.70 (br, 2H, $CH(CH_3)_2$), 4.51 – 4.61 (br, 2H, H_{COD}), 7.02 (s, 2H, $CH^{4,5}$Im), 7.26 – 7.46 (br, 4H, CH_{Ar}), 7.50 (t, 2H, J_{HH} = 7.7 Hz, CH_{Ar}); ^{13}C NMR ($CDCl_3$, δ, ppm): 26.54, 28.22, 28.79, 32.61, 67.76 (d, J_{Rh-C} = 14.3 Hz), 95.89 (d, J_{Rh-C} = 7.6 Hz), 122.84, 124.53, 129.74, 136.30, 185.97 (d, J_{Rh-C} = 52.0 Hz); MS (ESI): calcd. for $C_{35}H_{48}ClN_2Rh$: 599.2867; found: 599.2868. These spectroscopic data matched those reported in the literature.[2]
 **Complex III** [RhCl(cod)(IPr*^{Et})]	*Chloro(η^4-1,5-cyclooctadiene)(1,3-bis(4-ethyl-2,6-bis(diphenylmethyl)-phenylimidazol-2-ylidene)rhodium(I),* Yellow solid, isolated yield: 89%, 211.3 mg (1.78×10^{-4} mmol); ^{1}H NMR ($CDCl_3$, δ, ppm): 1.09 (t, 6H, J_{HH} = 7.6 Hz, CH_2CH_3), 1.44 - 1.55 (m, 2H, H_{COD}), 1.64 – 1.79 (m, 4H, H_{COD}), 1.97 – 2.08 (m, 2H, H_{COD}), 2.56 (q, 4H, J_{HH} = 7.5 Hz, CH_2CH_3), 3.58 (d, 2H, J_{HH} = 2.4 Hz, H_{COD}), 4.74 (s, 2H, $CH^{4,5}$Im), 4.92 – 5.01 (br, 2H, H_{COD}), 5.27 (s, 2H, $CHAr_3$), 6.69 (d, 4H, J_{HH} = 16.0 Hz, CH_{Ar}), 6.84 (d, 4H, J_{HH} = 16.1 Hz, CH_{Ar}), 6.91 – 7.30 (m, 27H, CH_{Ar}), 7.47 – 7.57 (m, 4H, CH_{Ar}); ^{13}C NMR ($CDCl_3$, δ, ppm): 15.57, 28.38, 28.77, 30.86, 32.44, 50.82, 51.53, 68.91 (d, J_{Rh-C} = 14.0 Hz), 78.70, 96.52 (d, J_{Rh-C} = 7.3 Hz), 123.54, 125.77, 126.40, 127.59, 127.86, 128.01, 129.16, 129.67, 130.15, 130.89, 136.33, 140.50, 143.20, 144.16, 144.31, 144.88, 183.84 (d, J_{Rh-C} = 51.6 Hz); MS (ESI): calcd. for $C_{79}H_{73}N_2Rh$: 1152.4829; found: 1152.4778; These spectroscopic data matched those reported in the literature.[3]

 **Complex IV** [RhCl(cod)(IPr*^{Ph2})]	*Chloro(η^4-1,5-cyclooctadiene)(1,3-bis(2,4,6-tris(diphenylmethyl)-phenylimidazol-2-ylidene)rhodium(I),* Yellow solid, isolated yield: 91%, 266. 4 mg (1.82×10^{-4} mmol); ^{1}H NMR ($CDCl_3$, δ, ppm): 1.44-1.56 (m, 2H, H_{COD}), 1.62 – 1.78 (m, 4H, H_{COD}), 1.94 – 2.10 (m, 2H, H_{COD}), 3.55 (br, 2H, H_{COD}), 4.84 (s, 2H, C$H^{4.5}$Im), 4.96 – 5.03 (br, 2H, H_{COD}), 5.19 (s, 2H, $CHAr_3$), 5.46 (s, 2H, $CHAr_3$), 6.62 – 6.73 (m, 6H, CH_{Ar}), 6.87 – 7.13 (m, 46H, CH_{Ar}), 7.15 – 7.21 (m, 10H, CH_{Ar}), 7.36 – 7.44 (m, 4H, CH_{Ar}); ^{13}C NMR ($CDCl_3$, δ, ppm): 28.44, 32.36, 50.84, 51.53, 56.33, 68.64 (d, J_{Rh-C} = 14.4 Hz), 96.65 (d, J_{Rh-C} = 8.0 Hz), 123.54, 125.67, 126.18, 126.33, 127.50, 127.88, 128.17, 129.09, 129.63, 129.90, 130.62, 131.33, 136.56, 143.45, 143.78, 144.38, 144.76, 184.20 (d, J_{Rh-C} = 51.9 Hz); MS (ESI): calcd. for $C_{101}H_{85}N_2Rh$: 1428.5768; found: 1428.5724. These spectroscopic data matched those reported in the literature.[3]
 **Complex V** [RhCl(cod)(IPr*^{OMe})]	*Chloro(η^4-1,5-cyclooctadiene)(1,3-bis(4-methoxy-2,6-bis(diphenyl-methyl)phenylimidazol-2-ylidene)rhodium(I),* Yellow solid, isolated yield: 86%, 204.9 mg (1.72×10^{-4} mmol); ^{1}H NMR ($CDCl_3$, δ, ppm): 1.50-1.58 (m, 2H, H_{COD}), 1.66 – 1.78 (m, 4H, H_{COD}), 2.01 – 2.11 (m, 2H, H_{COD}), 3.60 (s, 6H OCH_3), 3.47 – 3.65 (m, 2H, H_{COD}), 4.70 (s, 2H, C$H^{4.5}$Im), 4.96 – 5.01 (br, 2H, H_{COD}), 5.26 (s, 2H, $CHAr_3$), 6.53 – 6.84 (m, 12H, CH_{Ar}), 6.96 – 7.30 (m, 26H, CH_{Ar}), 7.45 – 7.60 (m, 4H, CH_{Ar}); ^{13}C NMR ($CDCl_3$, δ, ppm): 28.41, 30.85, 32.54, 50.93, 51.68, 55.11, 68.92 (d, J_{Rh-C} = 14.0 Hz), 78.62, 78.76, 96.63 (d, J_{Rh-C} = 7.4 Hz), 114.26, 115.23, 123.76, 125.83, 125.96, 126.44, 126.61, 127.70, 127.88, 128.09, 128.30, 129.07, 129.58, 130.07, 130.82, 131.76, 142.23, 142.89, 143.95, 144.03, 144.53, 146.03, 158.70, 184.43 (d, J_{Rh-C} = 52.1 Hz); MS (ESI): calcd. for $C_{77}H_{69}N_2O_2Rh$: 1156.4414; found: 1156.4364; e.a. calcd. for $C_{77}H_{69}ClN_2O_2Rh$ (%): C: 77.54, H: 5.83, N: 2.35; found: C: 77.33, H: 5.93, N: 2.33.
 **Complex VI** [RhCl(cod)(IPaul)]	*Chloro(η^4-1,5-cyclooctadiene)(1,3-Bis(2-diphenylmethyl-4,6-dimethyl-phenyl)imidazol-2-ylidene)rhodium(I),* Yellow solid, isolated yield: 90%, 153.9 mg (1.80×10^{-4} mmol); ^{1}H NMR ($CDCl_3$, δ, ppm): 1.50-1.66 (m, 4H, H_{COD}), 1.74 – 1.87 (m, 2H, H_{COD}), 1.92 (s, 3H, CH_3), 1.97 – 2.07 (m, 2H, H_{COD}), 2.21 (s, 3H, CH_3), 2.29 – 2.36 (m, 6H, CH_3), 3.32 – 3.40 (br, 1H, H_{COD}), 3.68 – 3.74 (br, 1H, H_{COD}), 4.84 – 4.89 (m, 1H, C$H^{4.5}$Im), 5.03 – 5.11 (m, 1H, C$H^{4.5}$Im), 5.55 (s, 1H, $CHAr_3$), 5.66 (s, 1H, CHAr_3), 6.04 (s, 1H, CH_{Ar}), 6.68 (s, 1H, CH_{Ar}), 6.76 (s, 3H, CH_{Ar}), 6.92 – 7.22 (m, 15H, CH_{Ar}), 7.28 – 7.33 (m, 4H, CH_{Ar}), 7.49 – 7.56 (m, 2H, CH_{Ar}); ^{13}C NMR ($CDCl_3$, δ, ppm): 1.01, 14.12, 14.19, 18.32, 18.44, 20.46, 21.45, 27.52, 28.39, 29.14, 29.35, 29.69, 31.91, 32.14, 32.67, 33.28, 50.17, 50.41, 51.47, 67.70, 67.89 (d, J_{Rh-C} = 14.1 Hz), 70.70 (d, J_{Rh-C} = 14.3 Hz), 96.09 (d, J_{Rh-C} = 6.9 Hz), 96.59 (d, J_{Rh-C} = 7.3 Hz), 97.10 (d, J_{Rh-C} = 7.6 Hz), 123.41, 123.62, 124.43, 125.79, 125.90, 126.35,

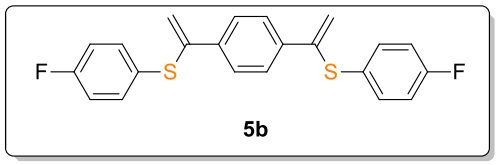
	127.66, 127.82, 127.92, 128.01, 128.10, 128.23, 129.13, 129.22, 129.41, 129.62, 129.70, 129.91, 130.49, 130.64,130.83, 135.21, 135.75, 136.29, 136.88, 138.10, 138.34, 138.57, 140.54, 142.70, 143.19, 143.44, 143.60, 144.00, 144.72, 180.79 (d, $J_{Rh\text{-}C}$ = 52.0 Hz); MS (ESI): calcd. for $C_{53}H_{53}ClN_2Rh$: 819.3186; found: 819.3167
 **Complex VII** [RhCl(cod)(IPaul^{OMe})]	*Chloro(η^4-1,5-cyclooctadiene)(1,3-Bis(2-diphenylmethyl-4-methyl-6-methoxyphenyl)-imidazol-2-ylidene)rhodium(I),* Yellow solid, isolated yield: 85%, 150.8 mg (1.70×10^{-4} mmol); ^{1}H NMR ($CDCl_3$, δ, ppm): 1.55-1.69 (m, 4H, H_{COD}), 1.78 – 1.88 (m, 2H, H_{COD}), 1.93 (s, 3H, CH_3), 1.98 – 2.12 (m, 2H, H_{COD}), 2.24 (s, 3H, CH_3), 2.29 – 2.38 (m, 1H, H_{COD}), 3.36 – 3.42 (br, 1H, H_{COD}), 3.72 – 3.78 (m, 6H, OCH_3), 4.83 – 4.90 (m, 1H, $CH^{4.5}$Im), 5.04 – 5.10 (m, 1H, $CH^{4.5}$Im), 5.51 (s, 1H, $CHAr_3$), 5.62 (s, 1H, $CHAr_3$), 5.97 (s, 1H, CH_{Ar}), 6.42 – 6.52 (m, 2H, 4H, CH_{Ar}), 6.68 – 6.83 (m, 4H, CH_{Ar}), 6.95 – 7.00 (m, 2H, CH_{Ar}), 7.02 – 7.14 (m, 7H, CH_{Ar}), 7.16 – 7.25 (m, 4H, CH_{Ar}), 7.26 – 7.32 (m, 4H, CH_{Ar}), 7.48 – 7.54 (m, 2H, CH_{Ar}); ^{13}C NMR ($CDCl_3$, δ, ppm): 18.85, 20.99, 27.61, 29.12, 32.22, 33.43, 50.58, 51.70, 55.22 (d, $J_{Rh\text{-}C}$ = 23.1 Hz), 67.75 (d, $J_{Rh\text{-}C}$ = 14.2 Hz), 70.47, 96.60 (d $J_{Rh\text{-}C}$ = 7.7 Hz), 97.17 (d $J_{Rh\text{-}C}$ = 7.2 Hz), 112.71, 113.47, 114.54, 115.21, 123.57, 124.55, 125.86, 126.07, 126.46, 127.94, 128.00, 128.12, 129.34, 129.58, 129.68, 129.86, 130.28, 130.38, 132.40, 132.49, 136.85, 140.22, 142.33, 142.54, 143.14, 143.32, 143.72, 145.20, 158.96, 181.78 (d, $J_{Rh\text{-}C}$ = 52.5 Hz); MS (ESI): calcd. for $C_{53}H_{53}N_2O_2Rh$: 852.3162; found: 852.3120.
 **Complex VIII** [RhCl(cod)(IMes-POSS)]	*Chloro(η^4-1,5-cyclooctadiene)(3-(3-heptaisobutylPOSS(T8)-propyl)-1-mesitylimidazol-2-ylidene)rhodium(I),* Yellow solid, isolated yield: 86%, 221.8 mg (1.72×10^{-4} mmol); ^{1}H NMR ($CDCl_3$, δ, ppm): 0.59 – 0.65 (m, 14H, CH_2), 0.70 – 0.79 (m, 2H, CH_{COD}), 0.96 (dd, 44H, J_{HH} = 6.6, 1.0 Hz, $CH(CH_3)_2$), 1.24 – 1.46 (m, 2H, CH_{COD}), 1.62 – 1.74 (m, 2H, CH_{COD}), 1.79 (s, 3H, CH_3), 1.82 – 1.90 (m, 7H, $CH_2CH(CH_3)_2$), 1.90 – 2.17 (m, 4H, CH_2, CH_{COD}), 2.28 – 2.37 (m, 1H, CH_{COD}), 2.37 (s, 3H, CH_3), 2.49 (s, 3H, CH_3), 3.19-3.26 (m, 1H, CH_{COD}), 3.60 – 3.65 (m, 1H, CH_{COD}), 4.13 – 4.21 (m, 1H, NCH_2), 4.97 – 5.03 (m, 1H, NCH_2), 5.06 – 5.12 (m, 1H, CH_{COD}), 5.20 – 5.29 (m, 1H, CH_{COD}), 6.79 (d, 1H, J_{HH} = 1.9 Hz, $CH^{4.5}$Im), 6.90 (s, 1H, CH_{Ar}), 6.99 (d, 1H, J_{HH} = 1.9 Hz, $CH^{4.5}$Im), 7.06 (s, 1H, CH_{Ar}); ^{13}C NMR ($CDCl_3$, δ, ppm): 9.66, 17.70, 21.05, 21.79, 22.47, 22.48, 23.85, 23.93, 24.10, 25.09, 28.37, 30.22, 30.58, 33.88, 55.40, 70.69 (d, $J_{Rh\text{-}C}$ = 14.2 Hz), 71.16 (d, $J_{Rh\text{-}C}$ = 14.3 Hz), 94.75 (d, $J_{Rh\text{-}C}$ = 7.5 Hz), 94.85 (d, $J_{Rh\text{-}C}$ = 7.1 Hz), 120.28, 123.96, 128.02, 129.70, 134.67, 136.11, 137.03, 138.66, 181.27 (d, $J_{Rh\text{-}C}$ = 50.1 Hz); ^{29}Si NMR ($CDCl_3$, δ, ppm): -67.65, -67.85, -68.17; MS (ESI): calcd. for $C_{51}H_{95}N_2O_{12}RhSi_8$: 1254.4094; found: 1254.4062.

2. Analytical data of isolated products 5a-5e



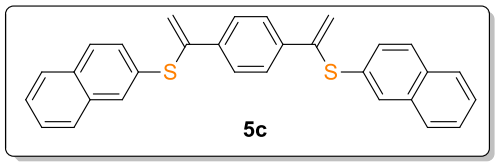
5a

^{1}H NMR ($CDCl_3$, δ, ppm): 0.88 (t, 6H, J_{HH} = 6.9 Hz, CH_3), 1.20-1.47 (m, 12H, CH_2), 1.58-1.69 (m, 4H, CH_2), 2.68-2.72 (m, 4H, CH_2), 5.17 (s, 2H, =CH_2), 5.47 (s, 2H, =CH_2), 7.39-7.53 (m, 4H, -C$_6H_4$-); ^{13}C NMR ($CDCl_3$, δ, ppm): 14.00, 22.49, 28.41, 28.58, 31.34, 32.16, 110.41, 126.98, 139.71, 144.71; MS m/z (rel, intensity): 59.10 (27), 115.00 (49), 128.00 (12), 161.00 (28), 163.20 (22) 179.00 (22), 194.10 (100), 219.20 (13), 245.20 (11), 263.20 (80), 278.10 (75), 347.10 (49), 361.80 (15, M^+)



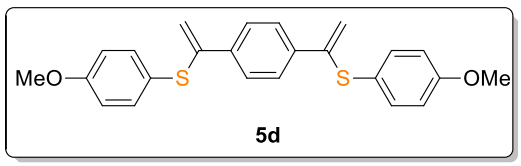
5b

^{1}H NMR ($CDCl_3$, δ, ppm): 5.18 (s, 2H, =CH_2), 5.59 (s, 2H, =CH_2), 6.94 – 7.00 (m, 2H, -C$_6H_4$-), 7.30 - 7.41 (m, 2H, -C$_6H_4$-), 7.51 (s, 8H, -C$_6H_4$-);^{13}C NMR ($CDCl_3$, δ, ppm): 115.04, 116.28 (d, $J_{C\text{-}F}$ = 22Hz), 127.07, 128.33 (d, $J_{C\text{-}F}$ = 3.4 Hz), 134.53 (d, $J_{C\text{-}F}$ = 8.3 Hz), 138.65, 144.44, 162.41 (d, $J_{C\text{-}F}$ = 248Hz); MS m/z (rel, intensity): 83.20 (4), 101.90 (7), 127.00 (10), 146.20 (11), 255.40 (43), 273.30 (27), 382.10 (100, M^+).



5c

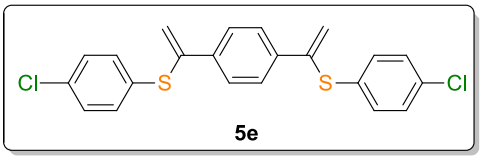
^{1}H NMR ($CDCl_3$, δ, ppm): 5.33 (s, 2H, =CH_2), 5.69 (s, 2H, =CH_2), 7.39 (d, 1H, J_{HH} = 1.8 Hz, naphthalene), 7.41 (d, 1H, J_{HH} = 1.8 Hz, naphthalene), 7.44-7.46 (m, 4H, naphthalene), 7.59 (s, 4H, -C$_6H_4$-), 7.68-7.73 (m, 4H, naphthalene), 7.75-7.88 (m, 2H, naphthalene), 7.84-7.86 (m, 2H, naphthalene); ^{13}C NMR ($CDCl_3$, δ, ppm): 116.55, 126.24, 126.46, 127.09, 127.43, 127.69, 128.66, 128.79, 128.85, 129.01, 130.73, 131.15, 132.34, 133.70, 138.85, 143.70; MS m/z (rel, intensity): 115.20 (15), 127.20 (11), 141.20 (12), 145.20 (5), 159.00 (5), 287.50 (15), 305.30 (55), 414.40 (5), 446.20 (100, M^+).



5d

^{1}H NMR (C_6D_6, δ, ppm): 3.15 (s, 6H, OCH_3), 5.07 (s, 2H, =CH_2), 5.41 (s, 2H, =CH_2), 6.60 (d, 4H, J_{HH} = 8.9 Hz, -C$_6H_4$-OMe), 7.38 (d, 4H, J_{HH} = 8.9 Hz, -C$_6H_4$-OMe), 7.64 (s, 4H, -C$_6H_4$-); ^{13}C NMR (C_6D_6, δ, ppm): 55.07

(OCH_3), 112.60, 115.62, 124.08, 127.83, 136.27, 140.03, 147.17, 160.71; MS m/z (rel, intensity): 121.20 (14), 127.00 (6), 267.30 (14), 285.20 (16), 406.20 (100, M^+).



5e

^{1}H NMR ($CDCl_3$, δ, ppm): 5.38 (s, 2H, =CH_2), 5.69 (s, 2H, =CH_2), 7.19-7.25 (m, 8H, -C_6H_4-Cl), 7.50 (s, 4H, -C_6H_4-); ^{13}C NMR ($CDCl_3$, δ, ppm): 117.37, 127.16, 129.21, 132.36, 132.69, 133.30, 138.51, 143.18; MS m/z (rel, intensity): 50.20 (8), 75.20 (9), 102.10 (14), 108.00 (12), 127.20 (22), 146.00 (13), 236.20 (23), 271.50 (58), 289.20 (46), 291.10 (23), 379.30 (12), 414.20 (100, M^+),

3. NMR spectra of rhodium complexes I-VIII

[RhCl(cod)(IMes)]

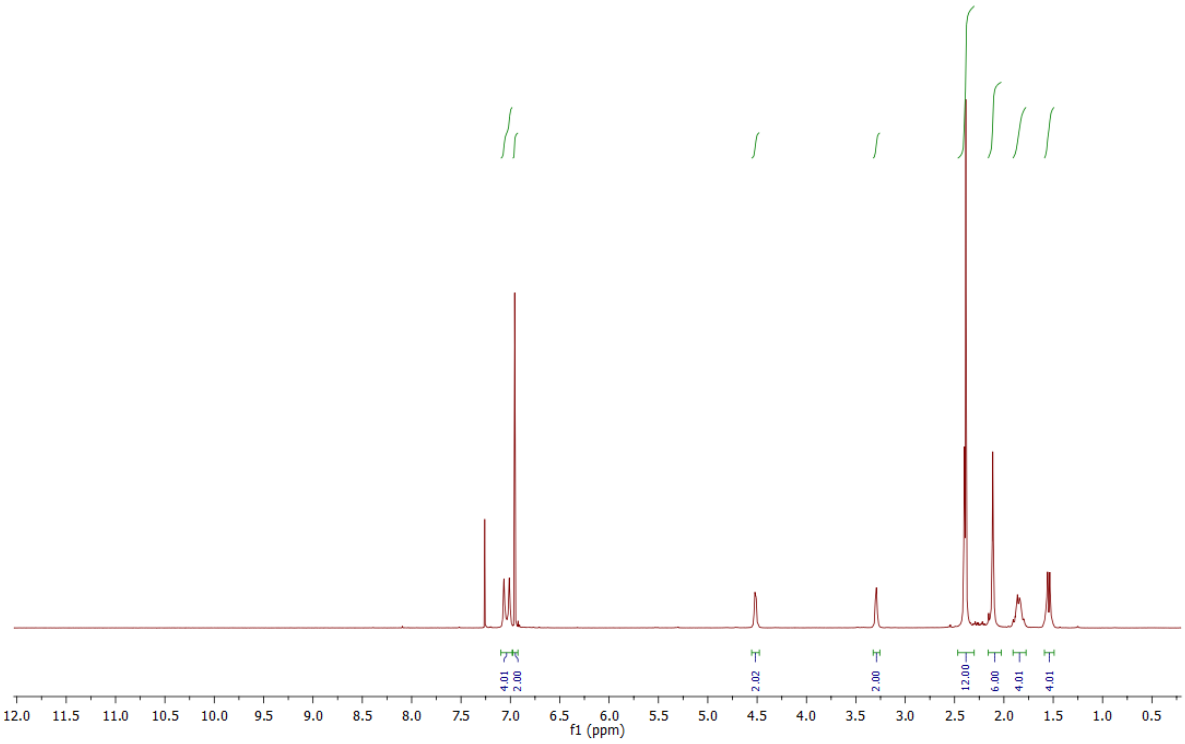


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) of [RhCl(cod)(IMes)]

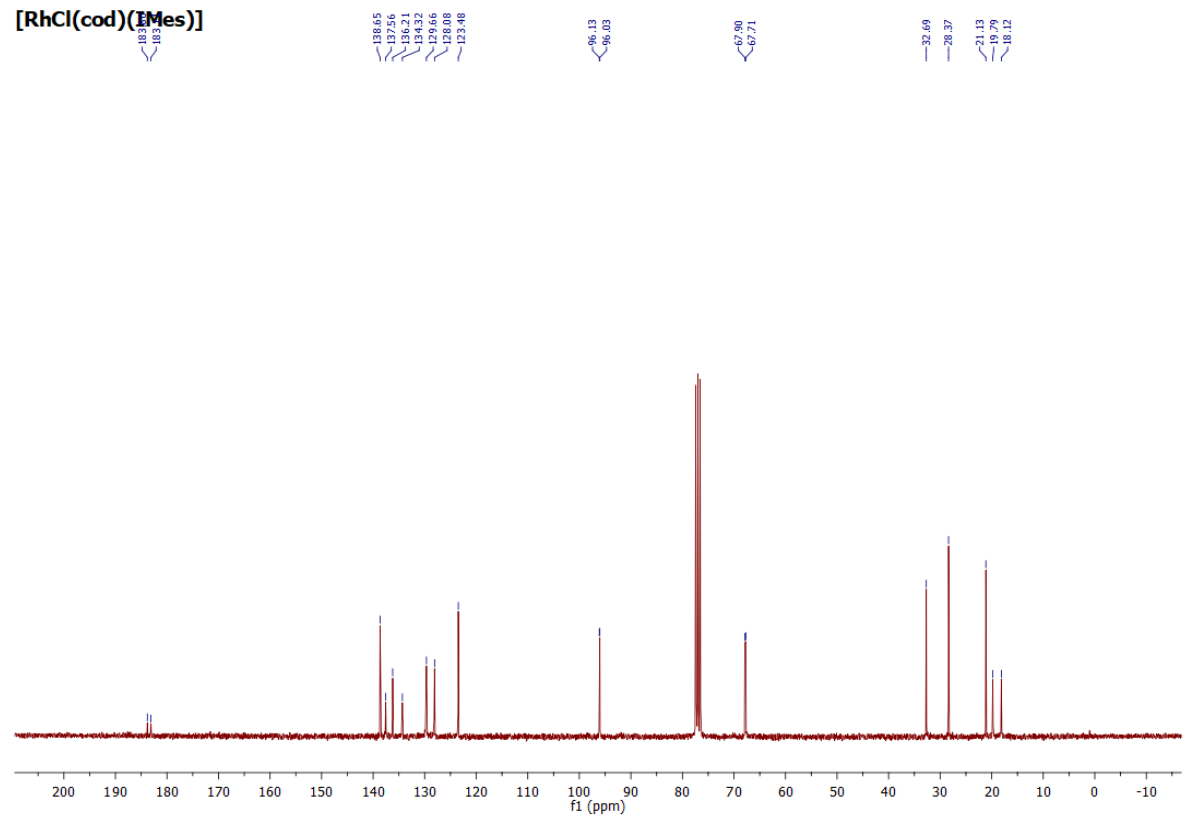


Figure S2. ^{13}C NMR (101 MHz, $CDCl_3$) of [RhCl(cod)(IMes)]

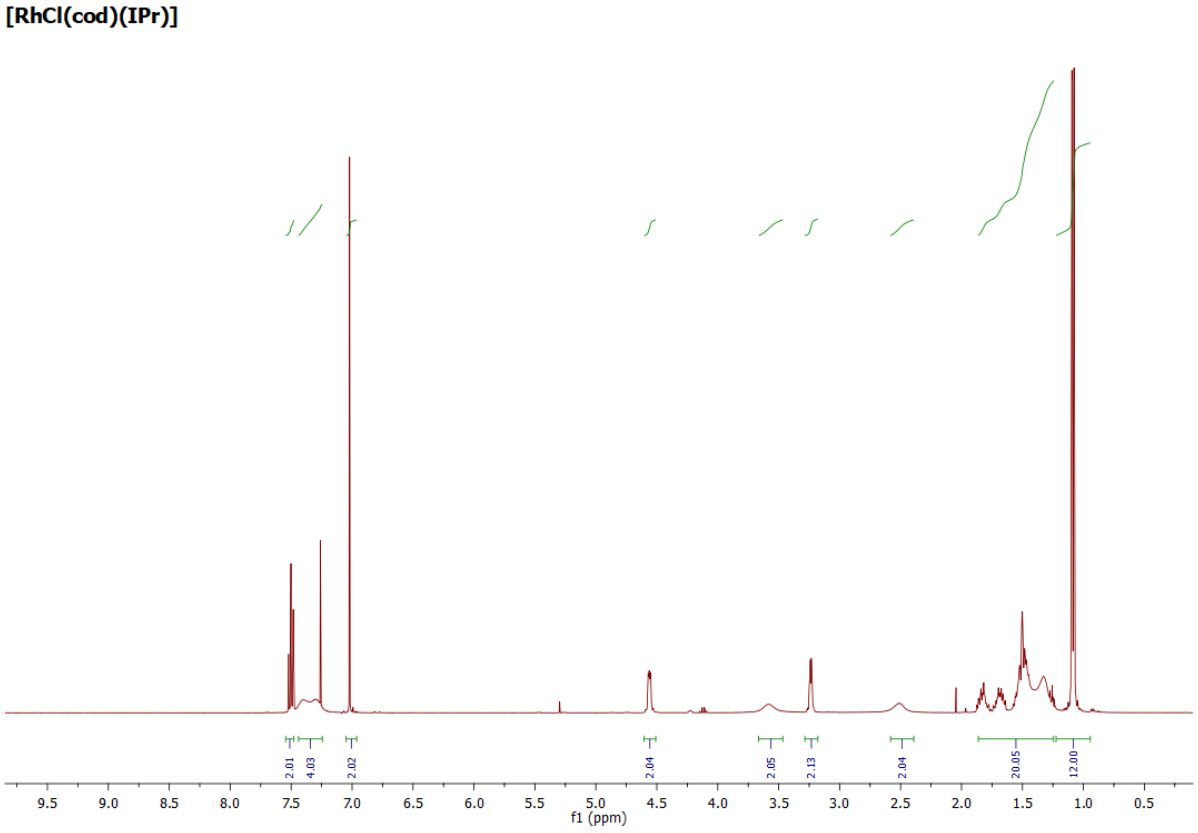


Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) of [RhCl(cod)(IPr)]

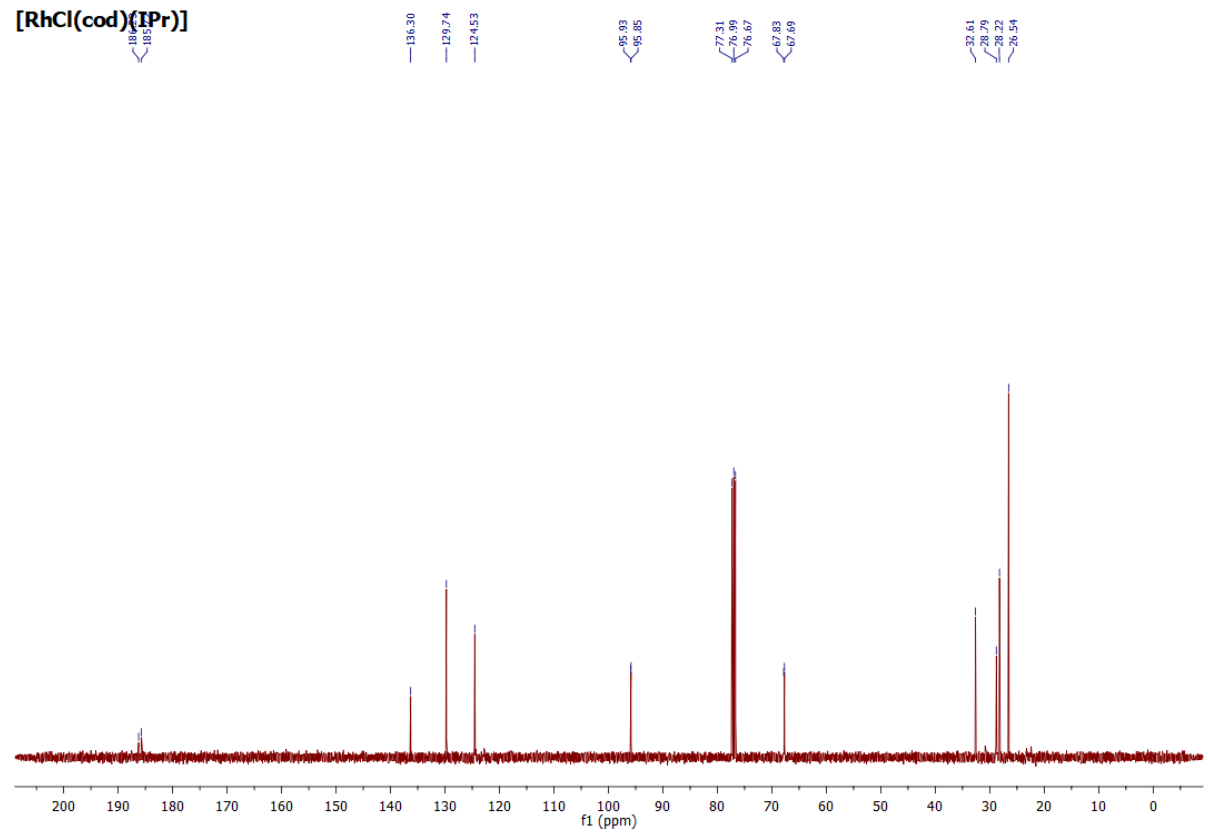


Figure S4. ^{13}C NMR (101 MHz, $CDCl_3$) of [RhCl(cod)(IPr)]

[RhCl(cod)(IPr*Et)]

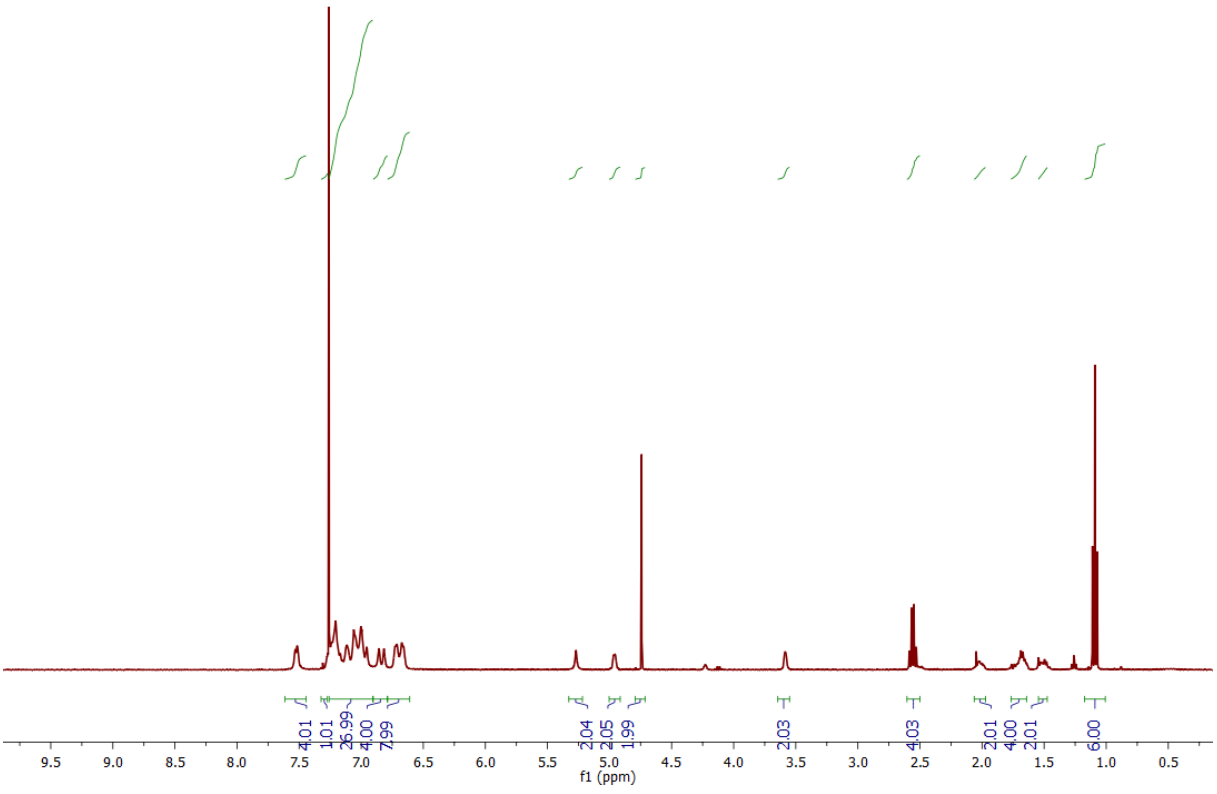


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) of [RhCl(cod)(IPr*^{Et})]

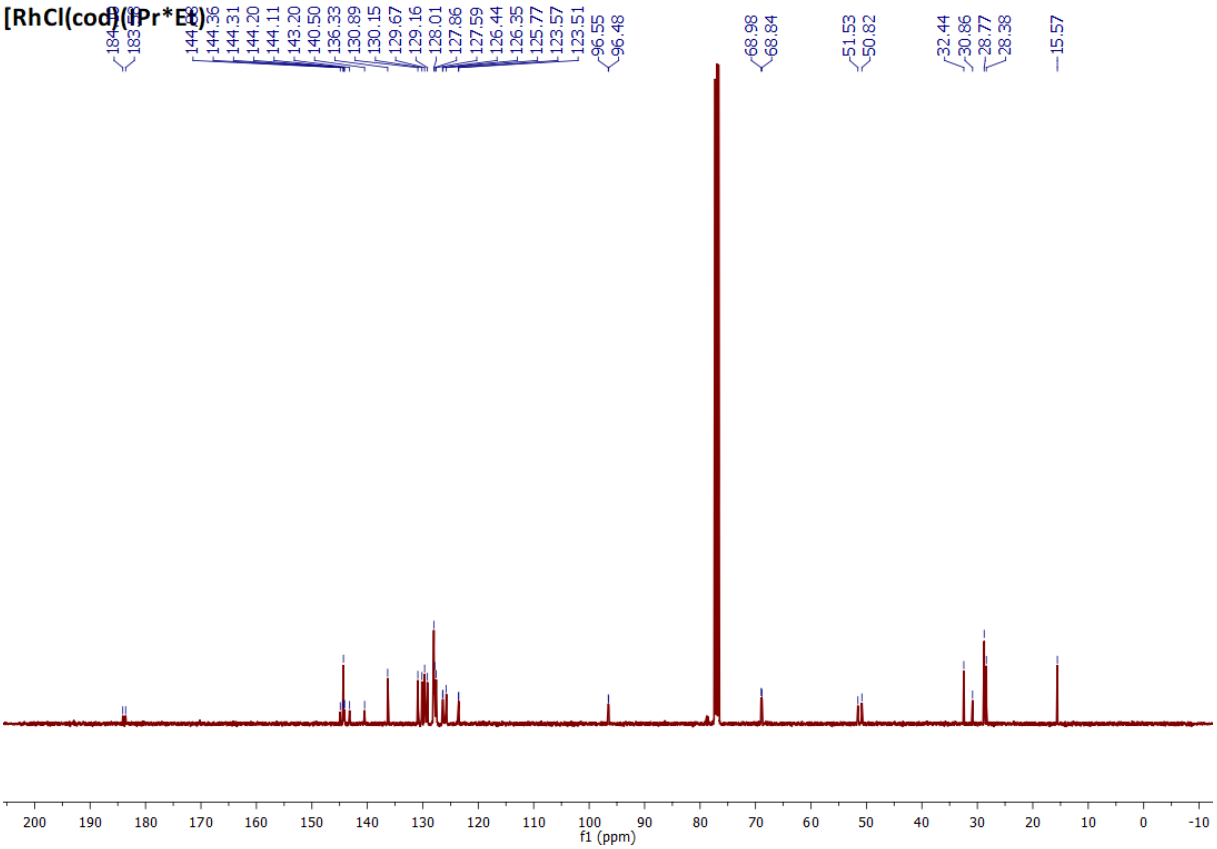


Figure S6. ^{13}C NMR (101 MHz, $CDCl_3$) of [RhCl(cod)(IPr*^{Et})]

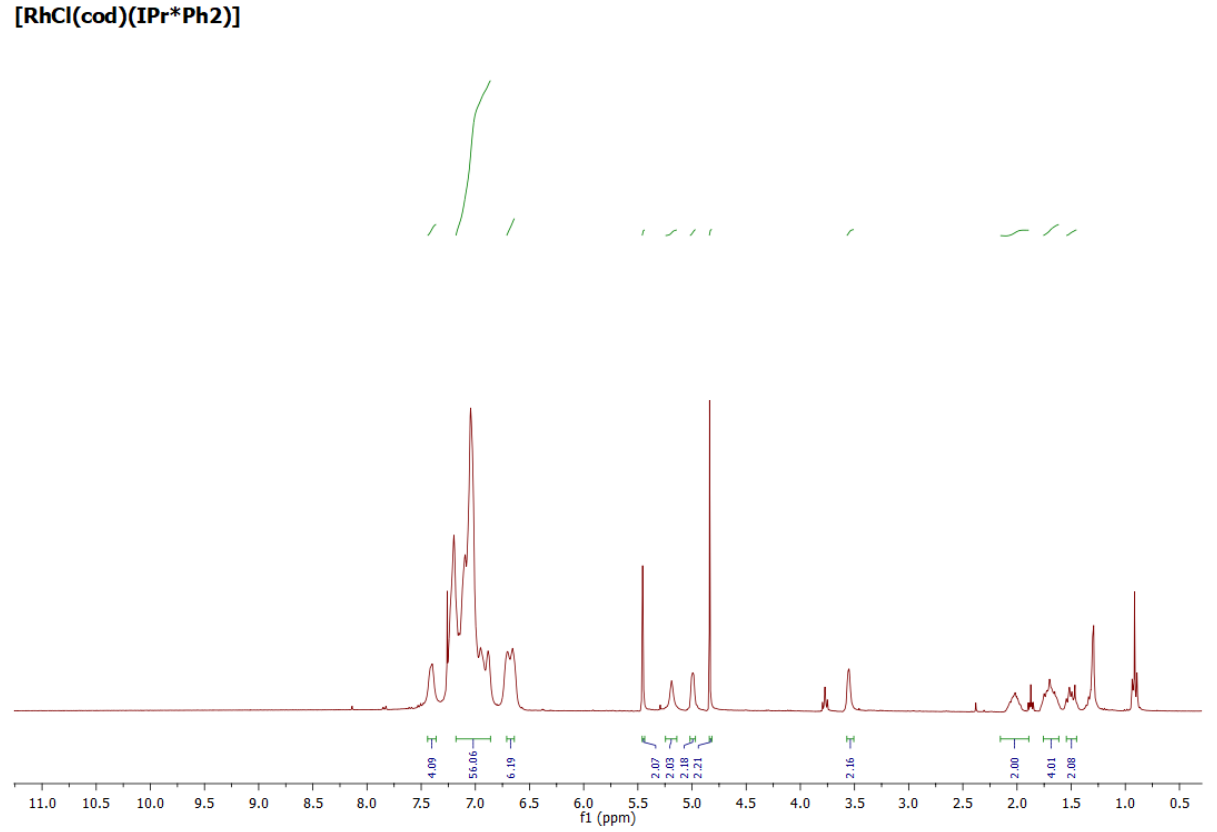


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) of [RhCl(cod)(IPr*^{Ph2})]

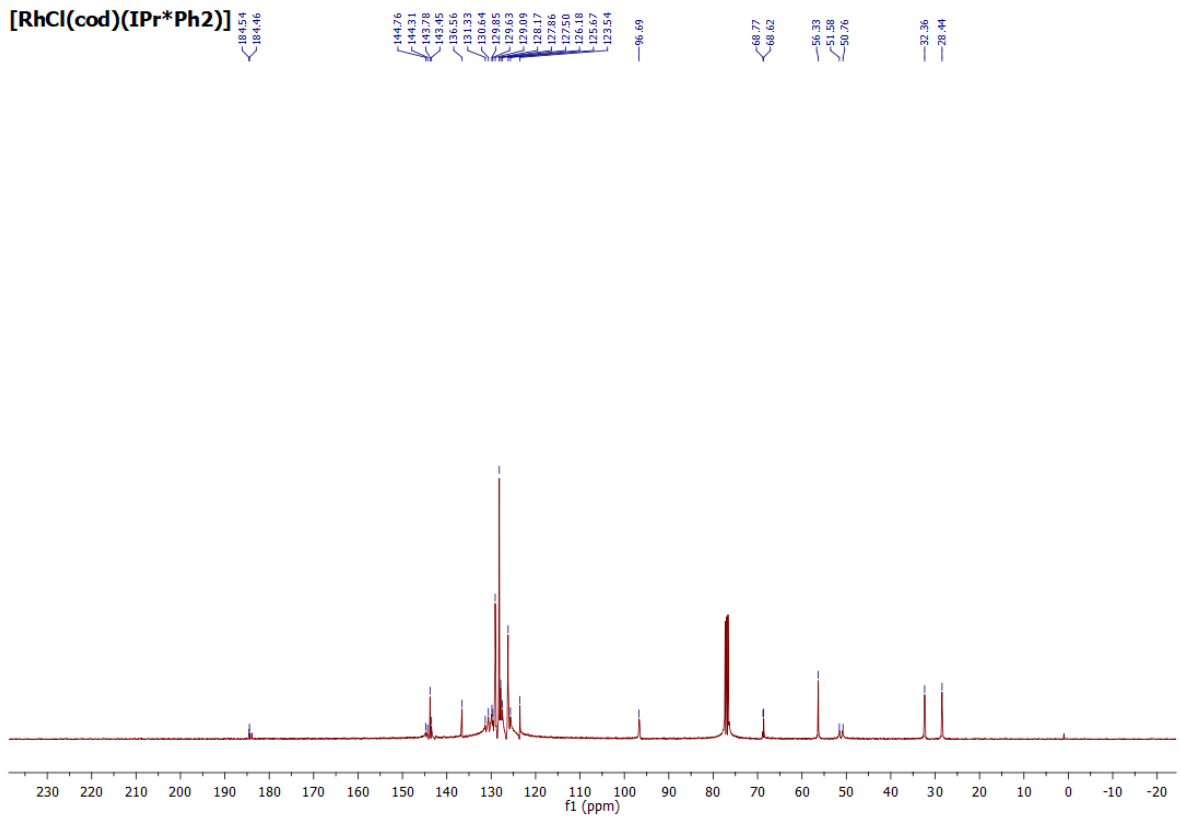


Figure S8. ^{13}C NMR (101 MHz, $CDCl_3$) of [RhCl(cod)(IPr*^{Ph2})]

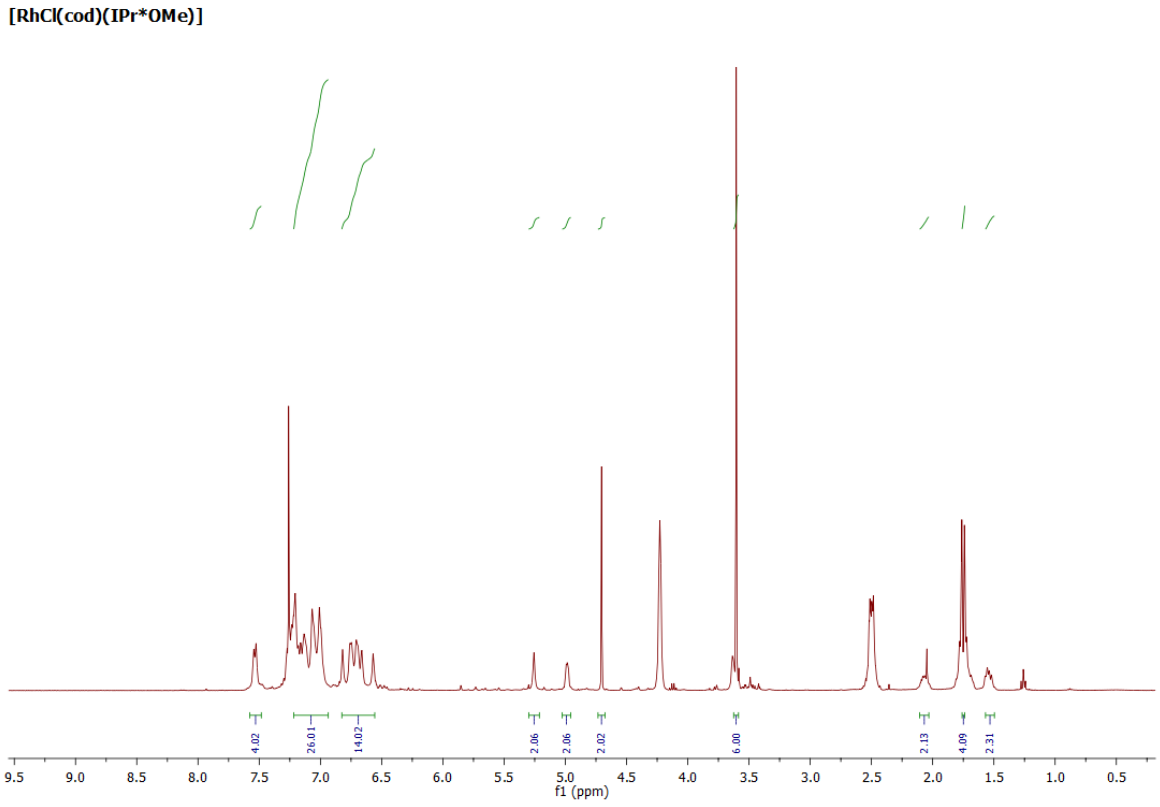


Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) of [RhCl(cod)(IPr*^{OMe})]

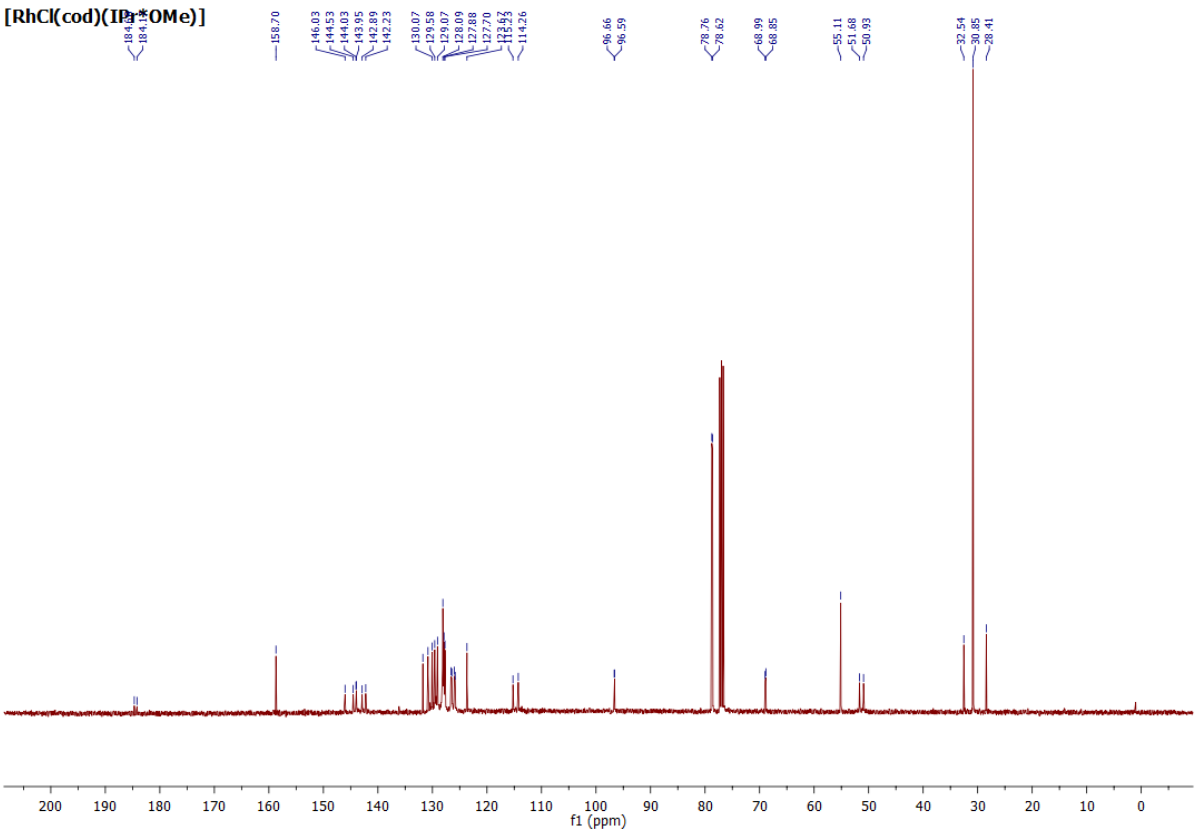


Figure S10. ^{13}C NMR (101 MHz, $CDCl_3$) of [RhCl(cod)(IPr*^{OMe})]

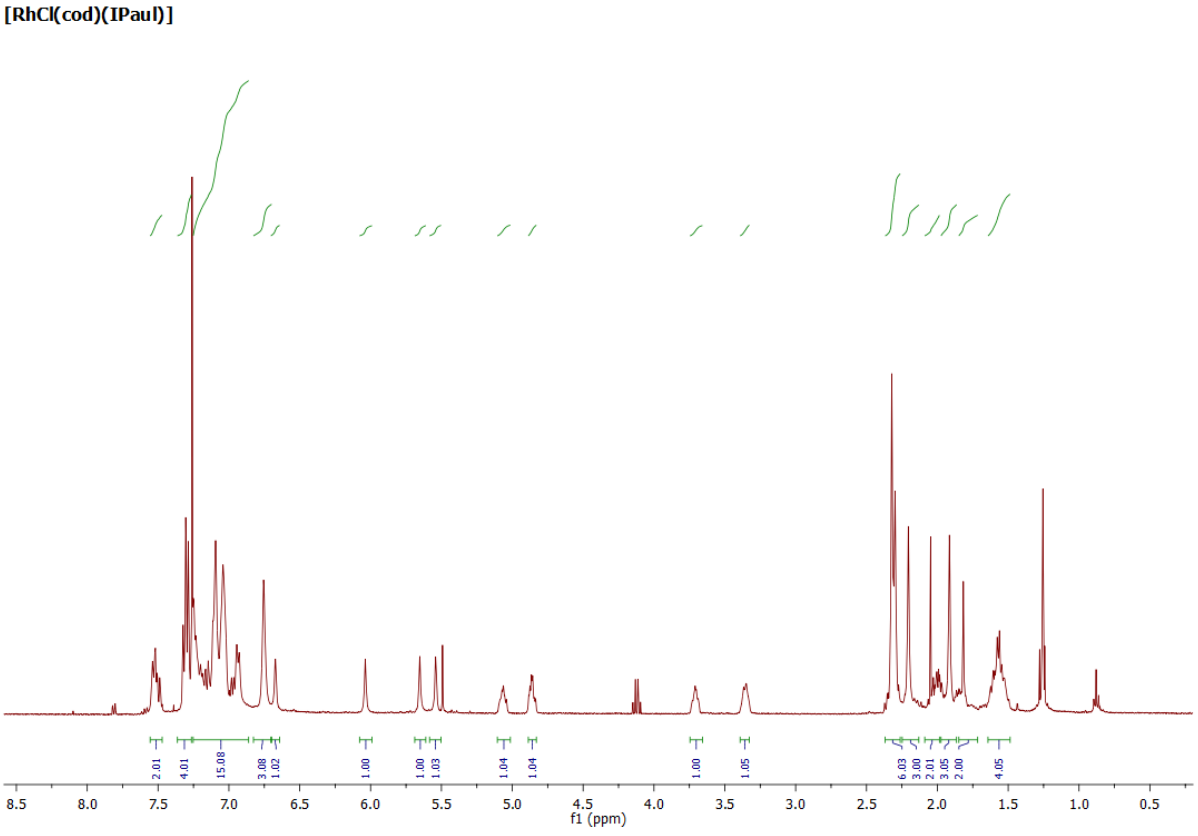


Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) of [RhCl(cod)(IPaul)]

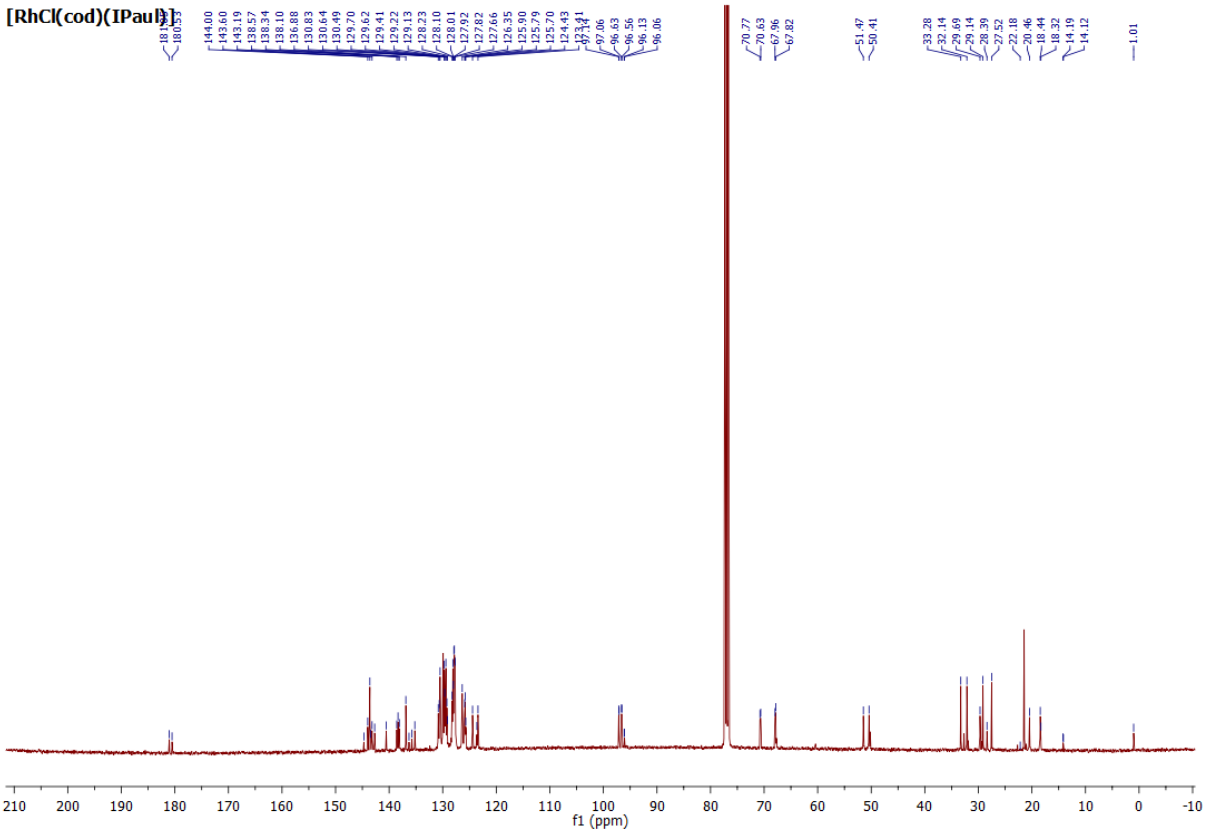


Figure S12. ^{13}C NMR (101 MHz, $CDCl_3$) of [RhCl(cod)(IPaul)]

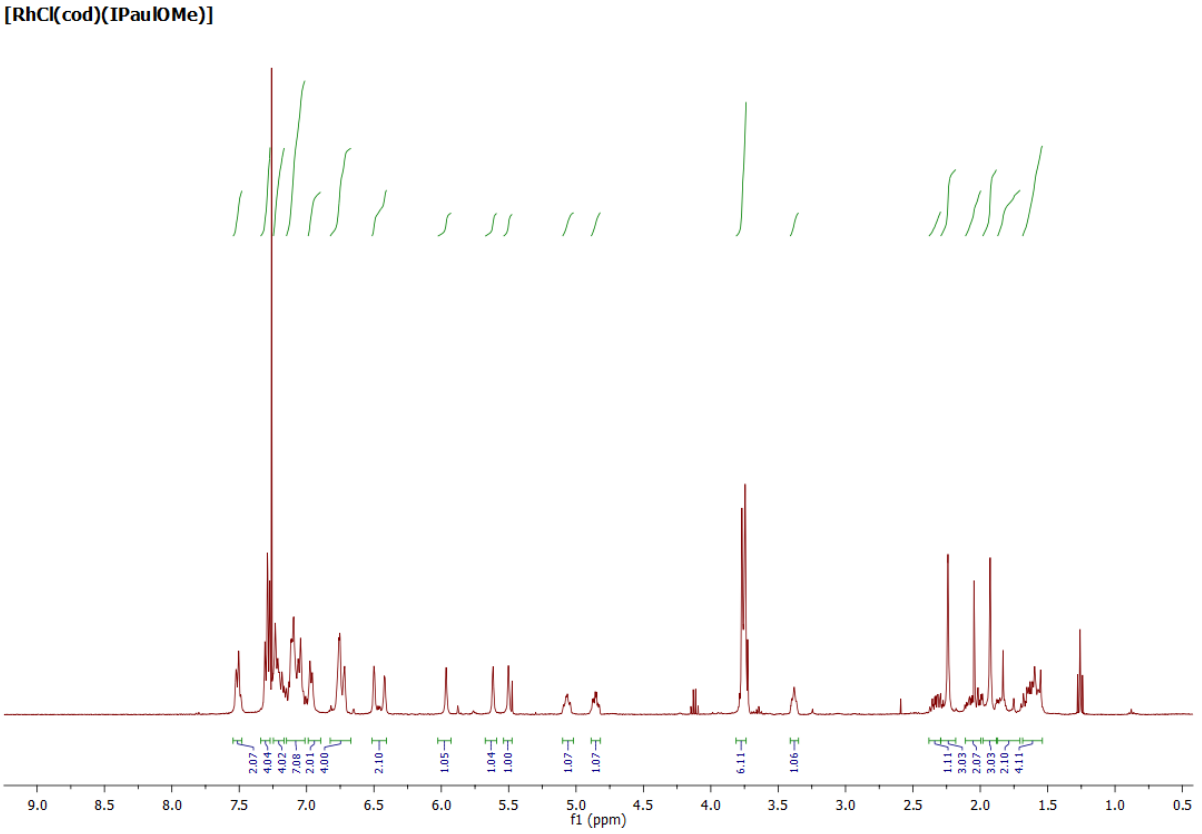


Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) of [RhCl(cod)($IPaul^{OMe}$)]

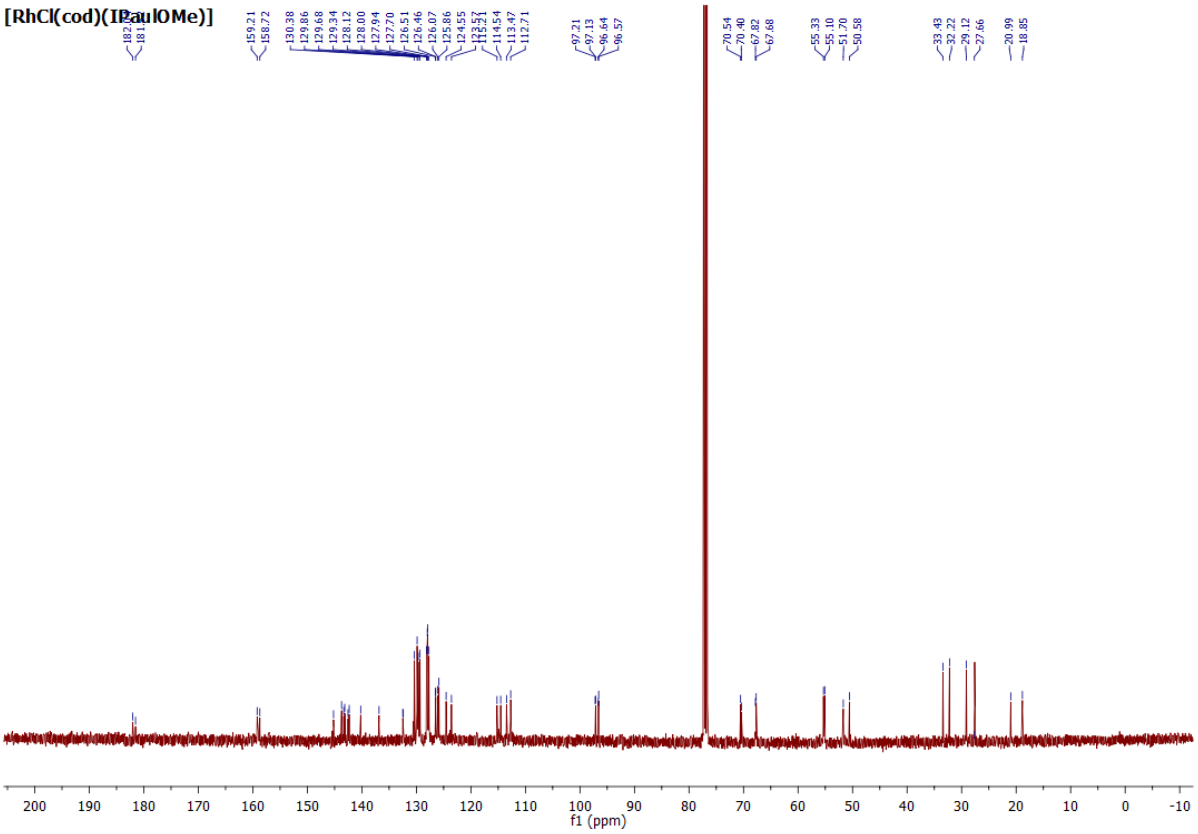


Figure S14. ^{13}C NMR (101 MHz, $CDCl_3$) of [RhCl(cod)(IPaul^{OMe})]

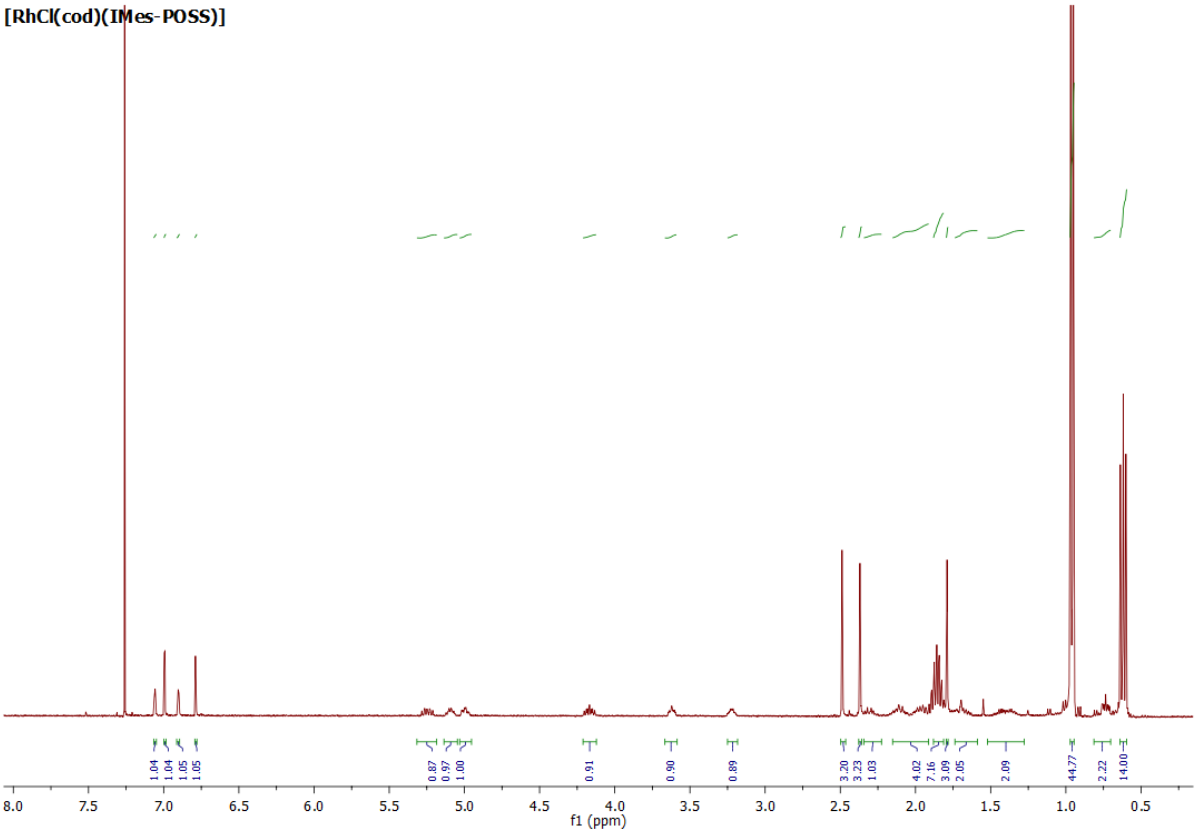


Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$) of [RhCl(cod)(IMes-POSS)]

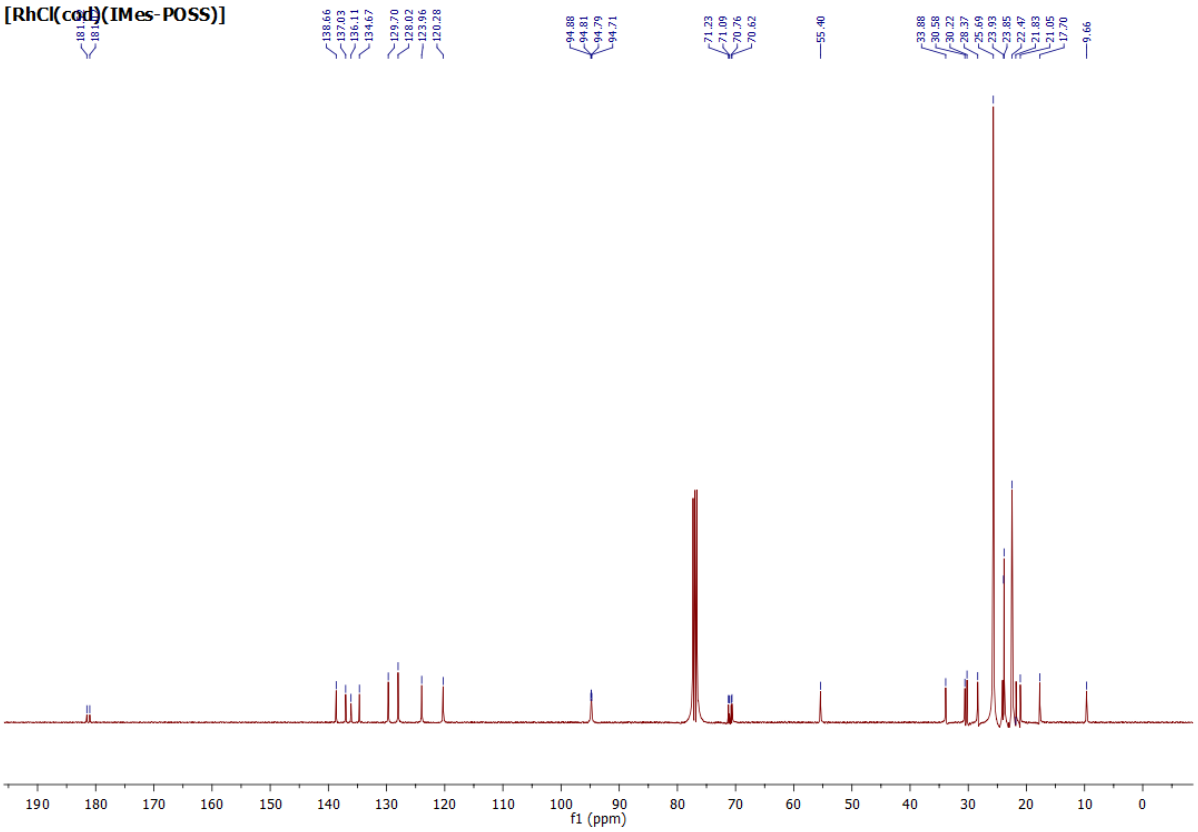


Figure S16. ^{13}C NMR (101 MHz, $CDCl_3$) of [RhCl(cod)(IMes-POSS)]

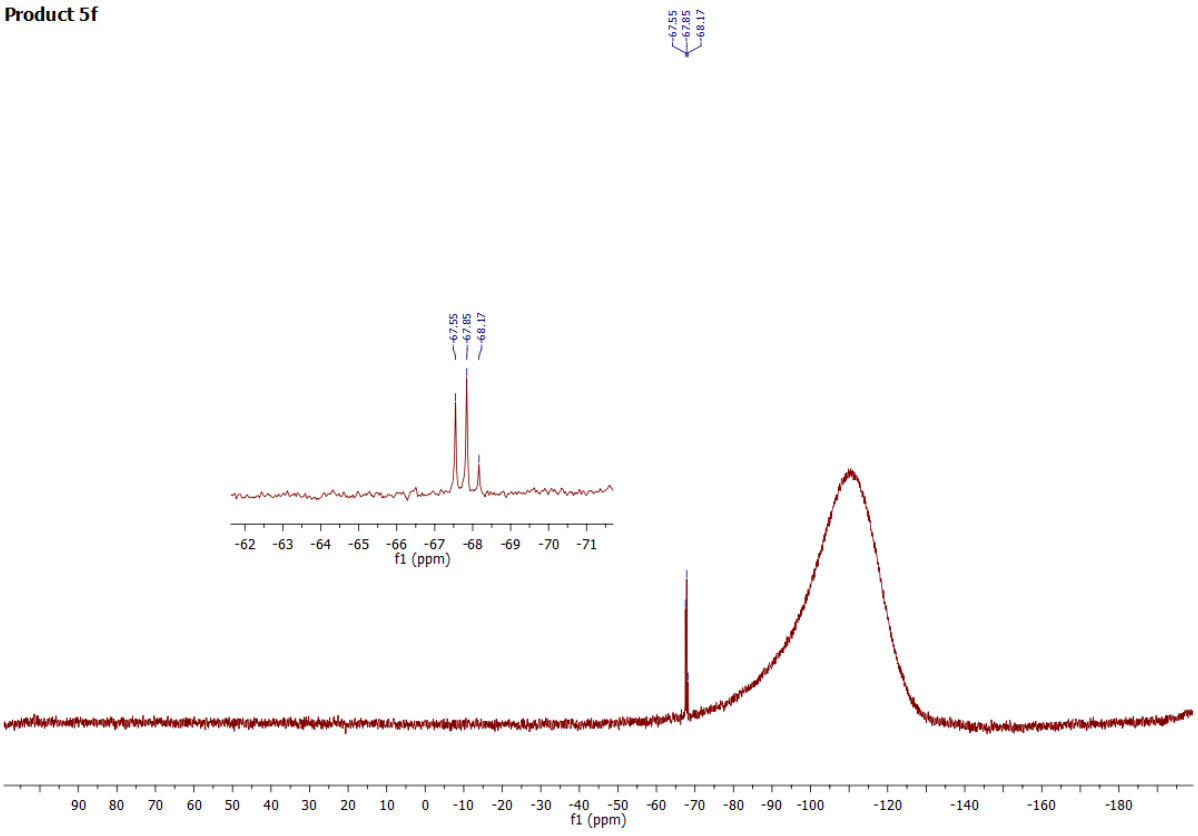


Figure S17. ^{29}Si NMR (79 MHz, $CDCl_3$) of [RhCl(cod)(IMes-POSS)]

4. NMR spectra of isolated products 5a-5e

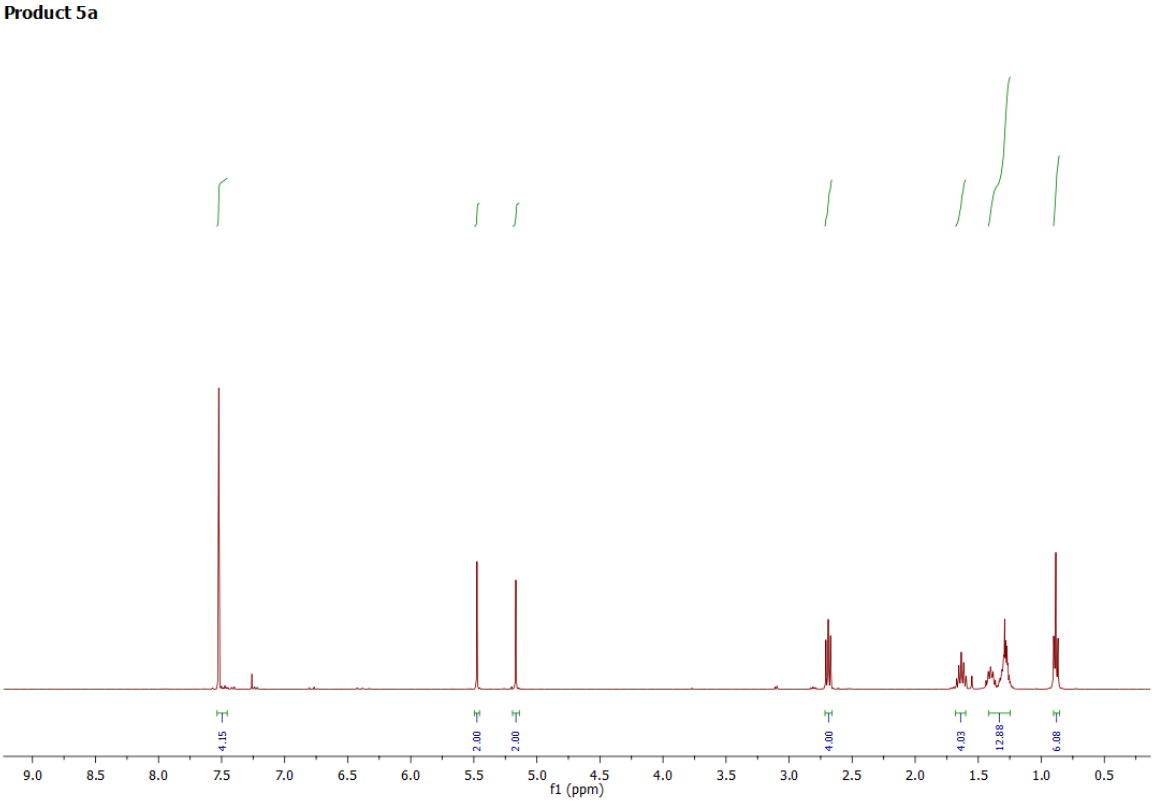


Figure S18. ^{1}H NMR (400 MHz, $CDCl_3$) of product **5a**

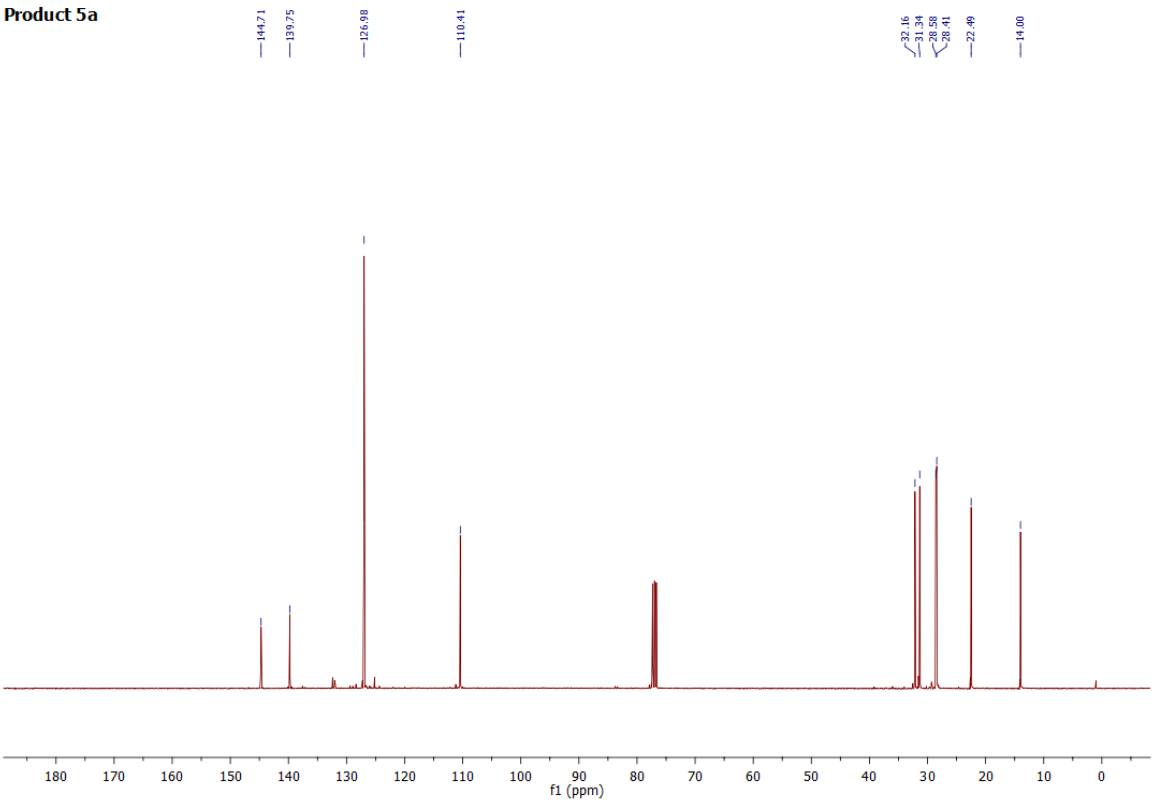


Figure S19. ^{13}C NMR (101 MHz, $CDCl_3$) of product **5a**

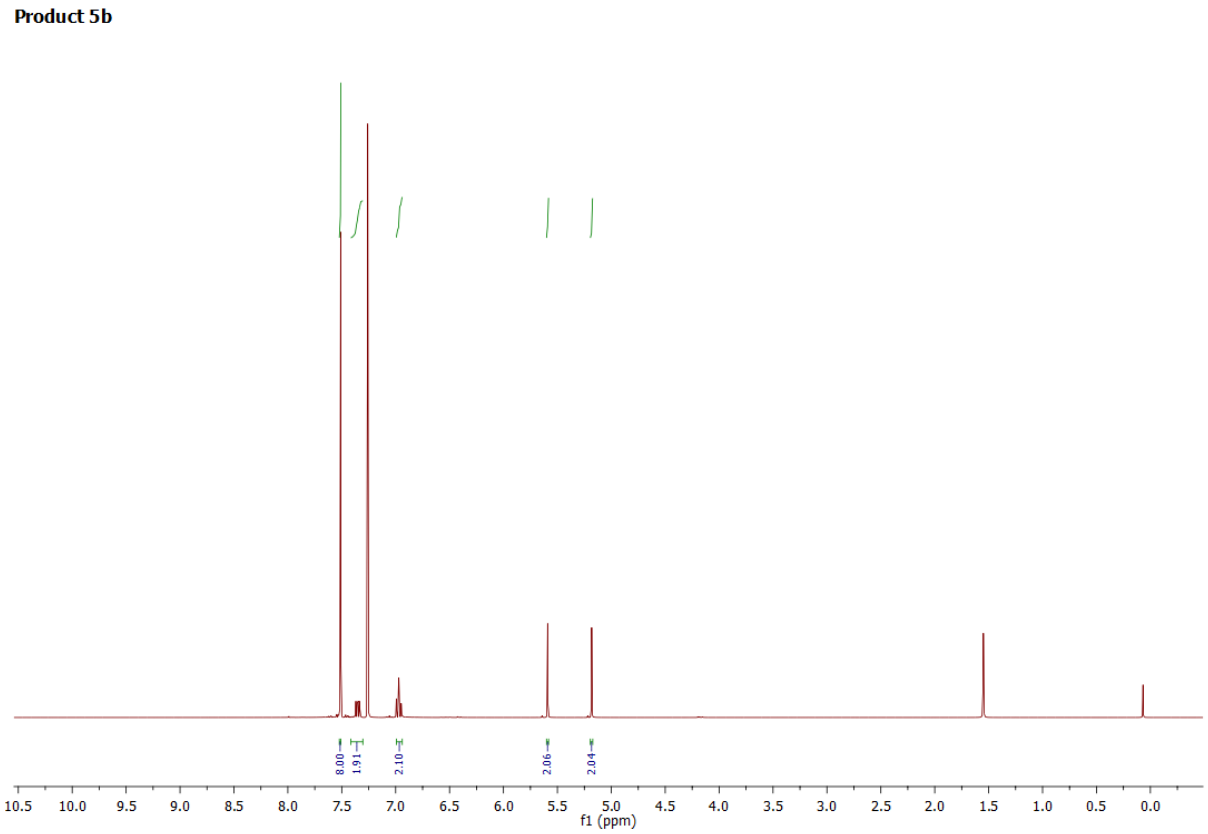


Figure S20. ^{1}H NMR (400 MHz, $CDCl_3$) of product **5b**

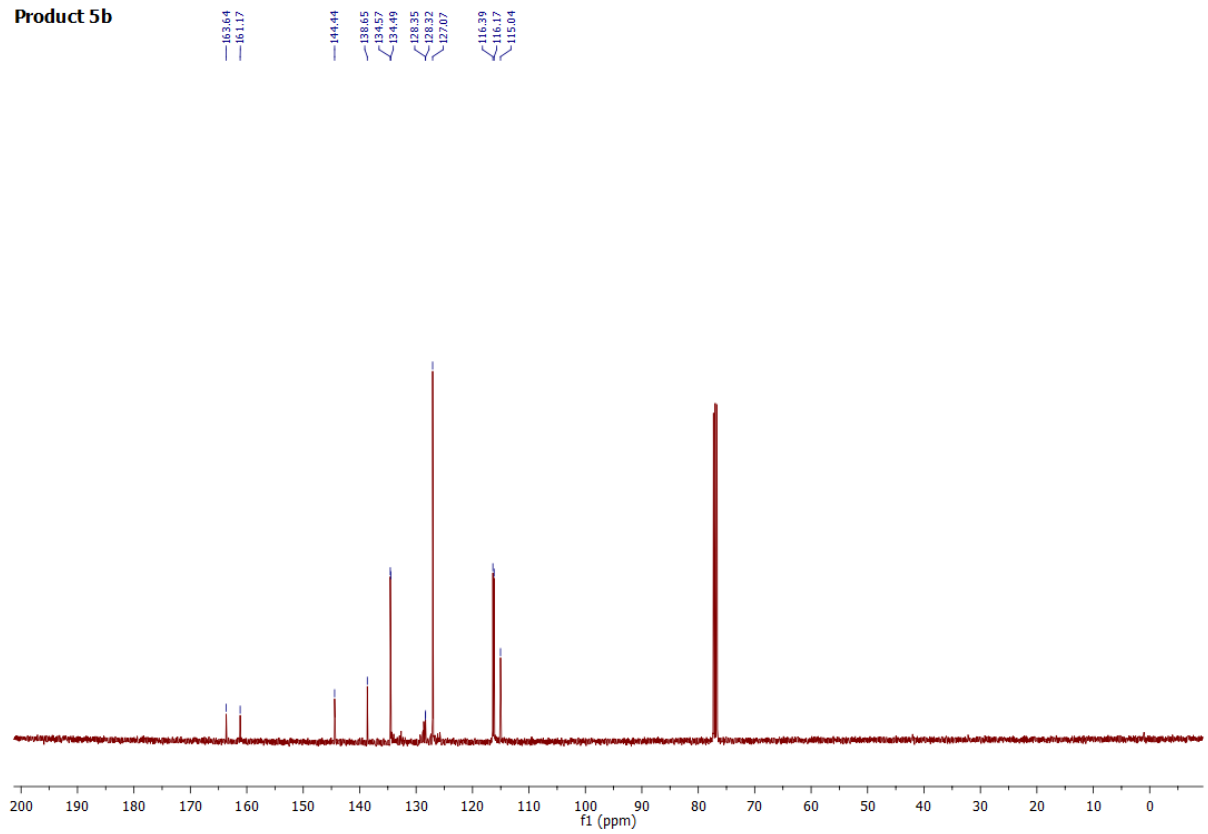


Figure S21. ^{13}C NMR (101 MHz, $CDCl_3$) of product **5b**

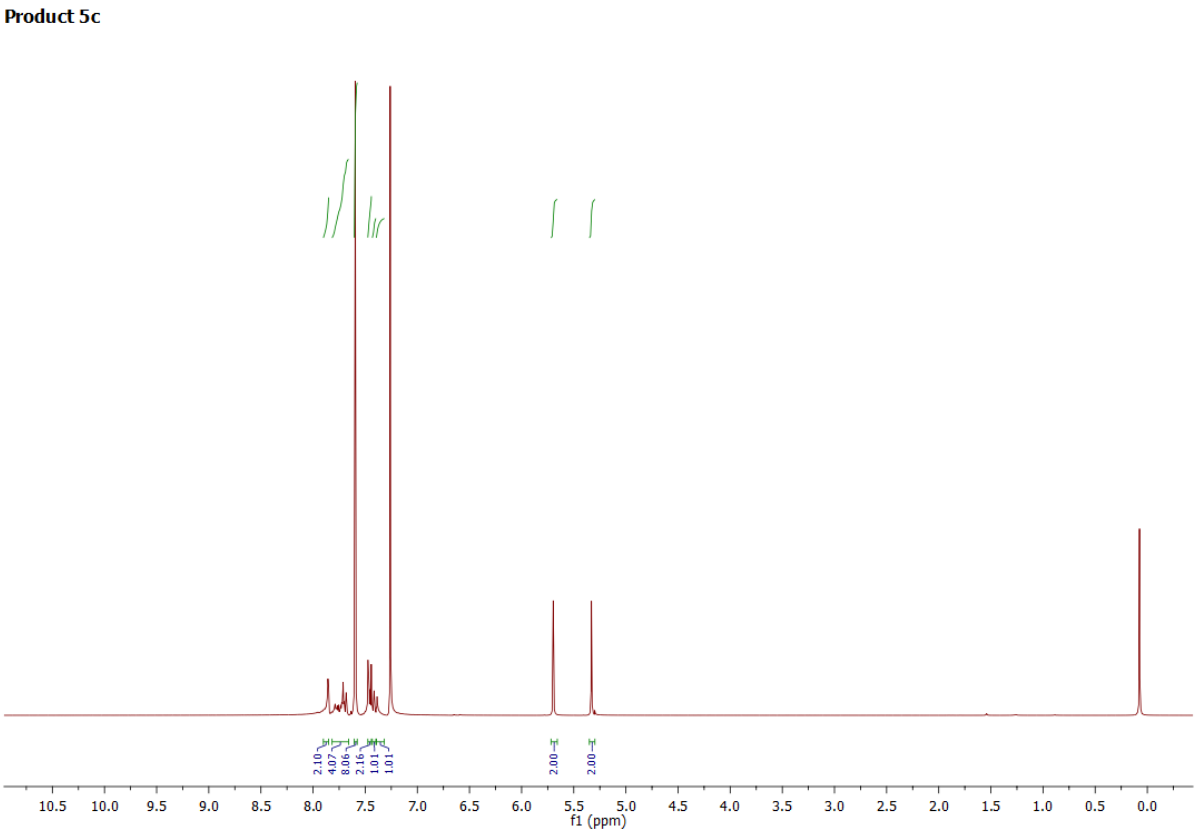


Figure S22. ^{1}H NMR (400 MHz, $CDCl_3$) of product **5c**

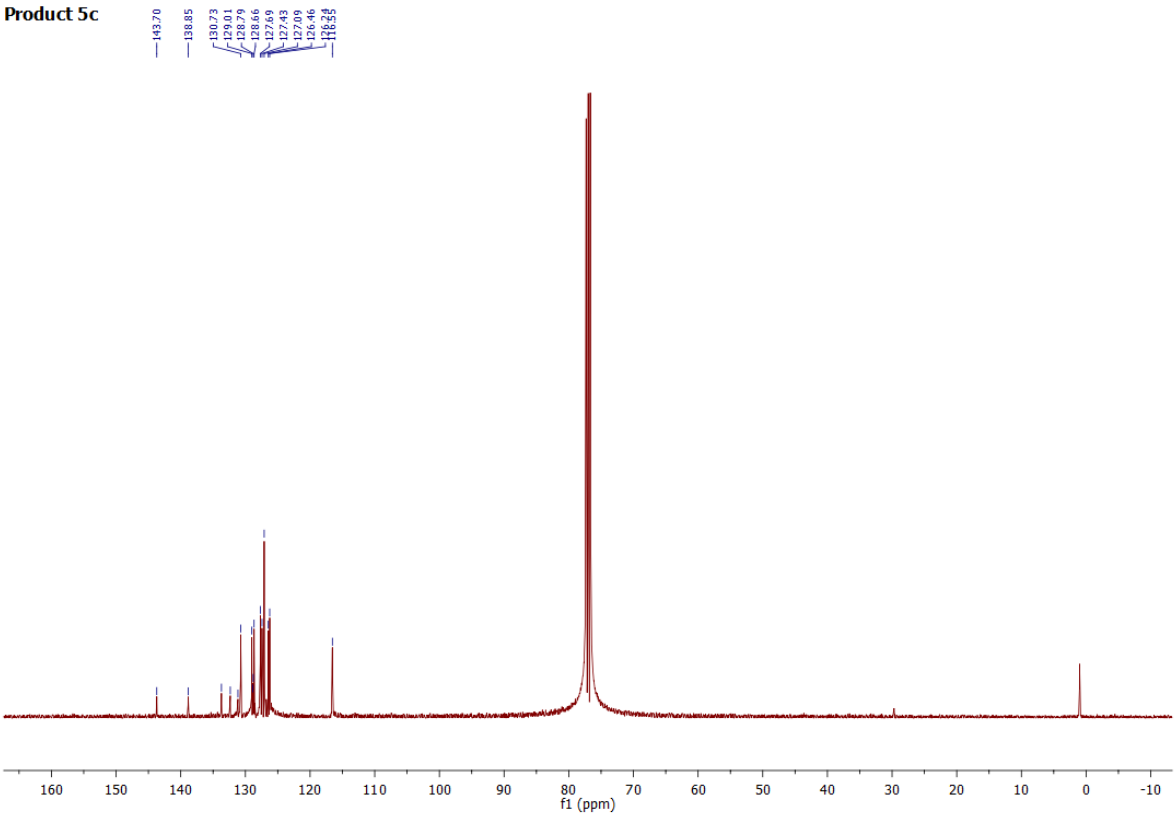


Figure S23. ^{13}C NMR (101 MHz, $CDCl_3$) of product **5c.** (Signals at 1.04 and 29.76 ppm derives from grease acc . *J. Org. Chem. Vol. No. 21, 1997).*

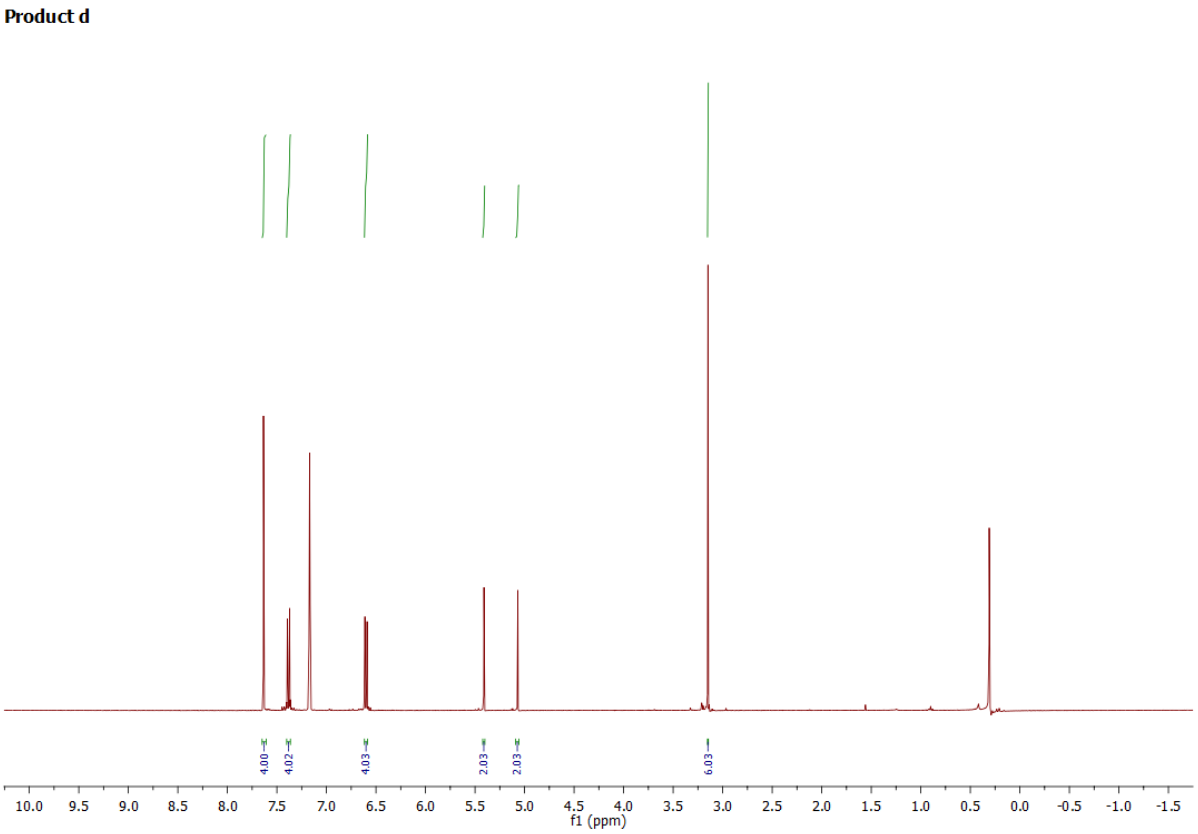


Figure S24. ^{1}H NMR (400 MHz, C_6D_6) of product **5d**

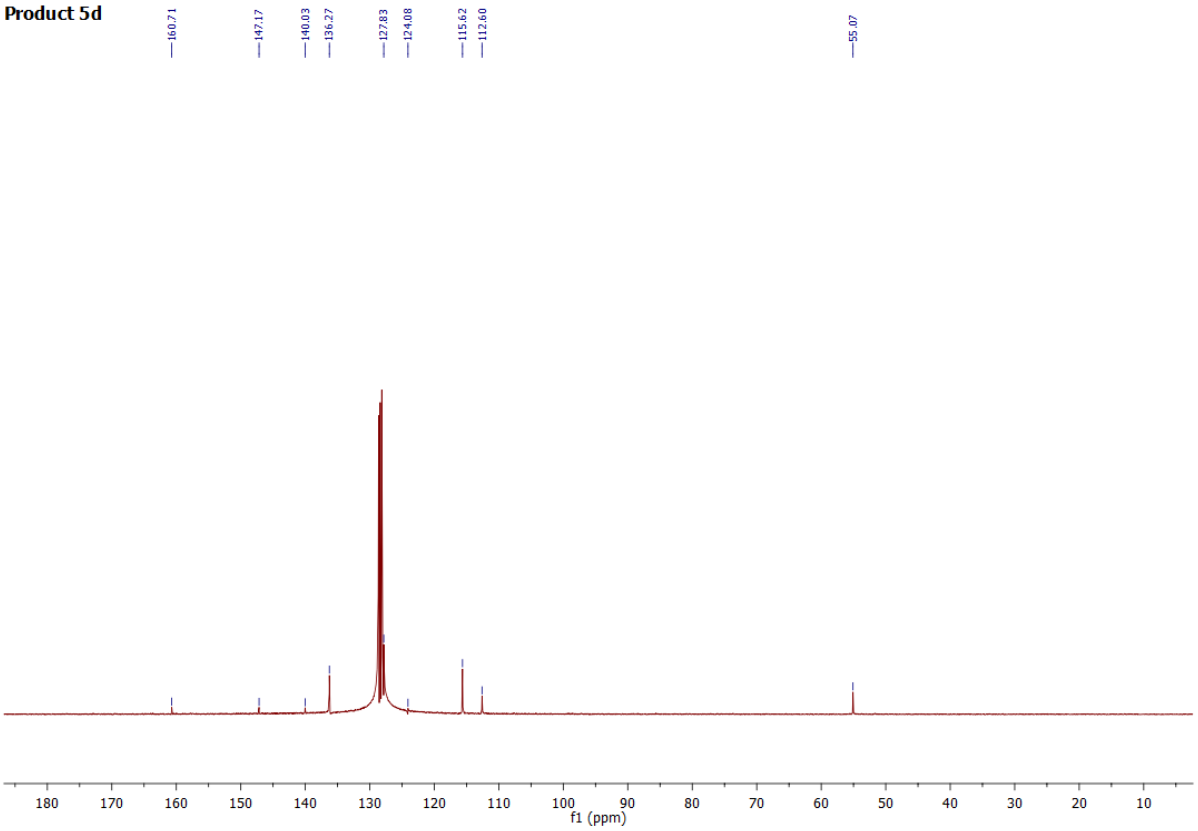


Figure S25. ^{13}C NMR (101 MHz, C_6D_6) of product **5d**

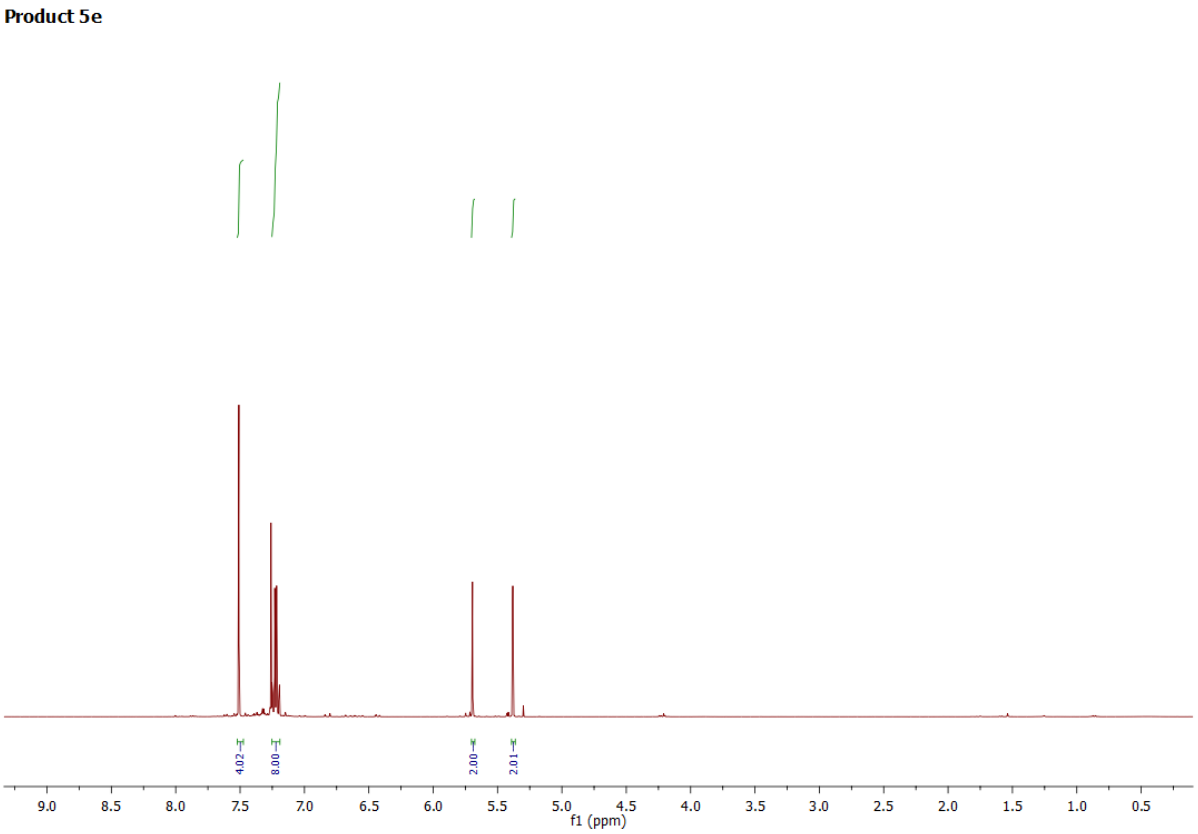


Figure S26. ^{1}H NMR (400 MHz, $CDCl_3$) of product **5e**

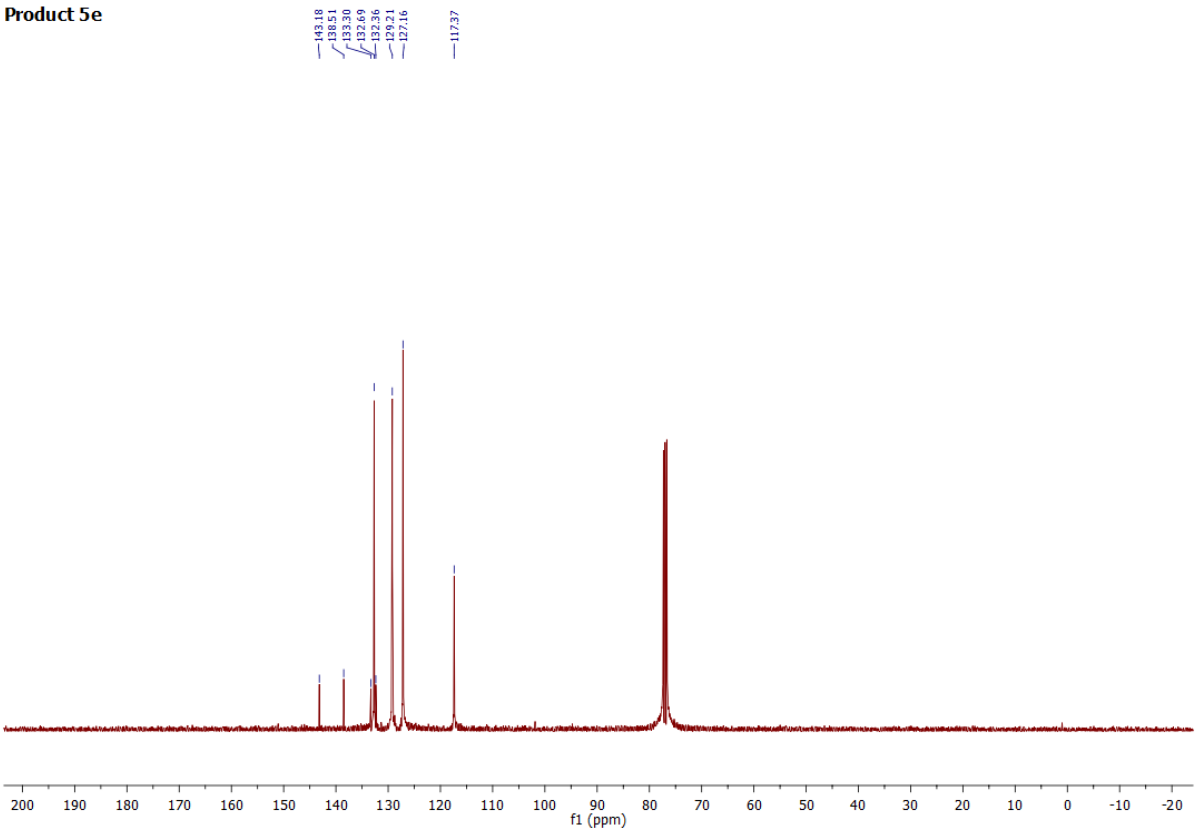


Figure S27. ^{13}C NMR (101 MHz, $CDCl_3$) of product **5e**

5. References

[1] A. M. Seayad, K. Selvakumar, M. Ahmed, M. Beller, *Tetrahedron Lett.* **2003**, *44*, 1679–1683.

[2] S. I. Lee, S. Y. Park, J. H. Park, I. G. Jung, S. Y. Choi, Y. K. Chung, B. Y. Lee, *J. Org. Chem.* **2006**, *71*, 91–96.

[3] M. Bołt, P. Żak, *Inorg. Chem*. **2021**, *60*, 17579–17585.