Electronic Supplementary Information

Synthesis, structural characterization, and coordination chemistry of imidazole-based alkylidene ketenes

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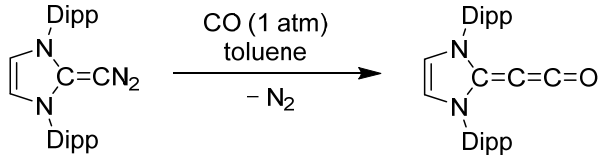
1. General

Unless stated otherwise, reactions were performed under an atmosphere of dry dinitrogen using either Schlenk techniques or a glove box. Solvents were purified and dried using an innovation technology SPS solvent system. The diazoolefins **1** and **2** were synthesized as described recently by our group.[1] If not stated otherwise, all reagents were obtained from commercial sources and used without further purification. Carbon monoxide (N47 Bt-S 10/200) was purchased from Carbagas. ^{13}C-enriched carbon monoxide (99 % ^{13}CO, < 2% ^{18}O) was purchased from Cambridge Isotope Laboratories Inc. NMR spectra were measured on a Bruker Avance DPX-400 (^{1}H: 400 MHz), Bruker Avance NEO-500 (^{1}H: 500 MHz) or Bruker Avance IIIHD-600 (^{1}H: 600 MHz) at 298 K if not stated otherwise. Chemical shifts are given in parts per million (ppm) relative to tetramethyl silane (TMS) for ^{13}C and ^{1}H. Mass spectra were recorded using Xevo G2-S QTOF mass spectrometer coupled to the Acquity UPLC Class Binary Solvent manager and BTN sample manager (Waters, Corporation, Milford, MA). The sample manager system temperature was maintained at 30 °C and the injection volume was 5 μL. Mass spectrometer detection was operated in positive ionization using the ZSpray™ dual-orthogonal multimode ESI/APCI/ESCi® source and a LTQ-Orbitrap ion trap mass analyzer. ToF mass spectra were acquired in the sensitive mode over the range of *m*/*z* 50–1200 at an acquisition rate of 0.036 sec/spectra. FT-IR spectra of powdered bulk samples were recorded on a Perkin-Elmer Spectrum One instrument using the ATR (attenuated total reflection) technique with diamond-anvil configuration.

2. Synthesis

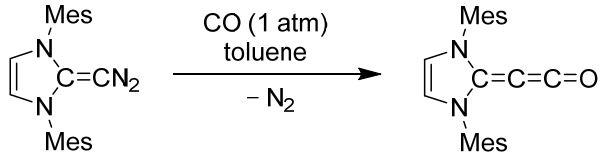


1 **4**

86%

Compound 4: Inside a 2 L Schlenk tube, 2-(diazomethylene)-1,3-bis(2,6-diisopropylphenyl)-2,3-dihydro-1*H*-imidazole (**1**, 1 g, 2.33 mmol, 1.0 eq.) was dissolved in toluene (100 ml). The solution was degassed by three freeze-pump-thaw cycles and then placed under an atmosphere of CO (1 atm, ca. 82 mmol). The resulting mixture was stirred at room temperature for 24 h. The mixture was filtered through a pad of celite® and the filtrate was evaporated to dryness to obtain a yellow solid. The latter was washed with diethyl ether (2 x 5 ml) and pentane (2 x 10 ml) and finally dried under vacuum to obtain 710 mg of alkylidene ketene **4** as a yellow solid. The ether washing solution was stored at −25 °C to obtain yellow crystals of **4** after three days. The crystals were separated, washed with pentane (2 x 2 ml), and dried under reduced pressure (150 mg, 860 mg in total, 86 %). The crystals obtained from cold ether were suitable for X-ray diffraction analysis.

^{1}H NMR (400 MHz, C_6D_6): δ = 7.24 (dd, *J* = 8.3 Hz, 7.2 Hz, 2H, CH_{arom}, Dipp, *para*), 7.11 (d, *J* = 7.7 Hz, 4H, CH_{arom}, Dipp, *meta*), 5.97 (s, 2H, CH, imidazole), 2.81 (sept, *J* = 6.8 Hz, 4H, C*H*$(CH_3)_2$), 1.37 (d, *J* = 6.9 Hz, 12H, CH(C*H*$_3)_2$), 1.11 (d, *J* = 6.9 Hz, 12H, CH(C*H*$_3)_2$). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ = 150.2 (C=*C*=O), 147.7 (C, imidazole), 147.0 (C_{arom}, Dipp, *ortho*), 133.2 (C_{arom}, Dipp, *ipso*), 130.6 (HC_{arom}, Dipp, *para*), 124.5 (HC_{arom}, Dipp, *meta*), 117.6 (HC, imidazole), 29.2 (*C*H$(CH_3)_2$), 23.99 (CH(*C*H$_3)_2$), 23.96 (CH(*C*H$_3)_2$), 15.0 (*C*=C=O). **IR:** $\tilde{\nu}$/cm^{-1} = 2106 ν(C=O) / 2055 ν(^{13}C=O). Compound **4** could not be detected by mass spectrometry.



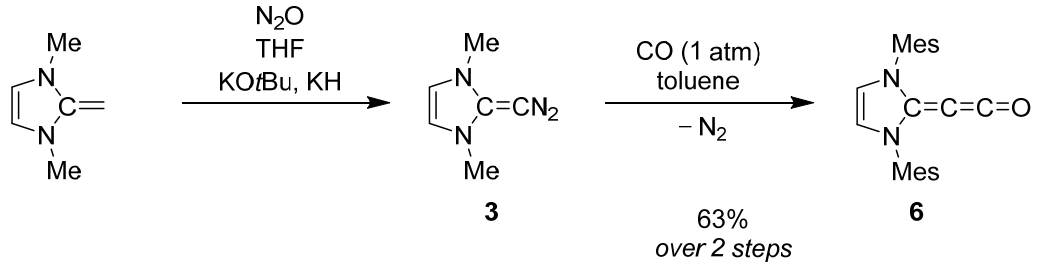
2 **5**

89%

Compound 5: Inside a 500 ml Schlenk tube, 2-(diazomethylene)-1,3-dimesityl-2,3-dihydro-1*H*-imidazole (**2**, 100 mg, 0.44 mmol, 1.0 eq.) was dissolved in toluene (20 ml). The solution was degassed by three freeze-pump-thaw cycles and then placed under an atmosphere of CO

(1 atm, ca. 20 mmol). The resulting mixture was stirred at room temperature for 24 h. Then, all volatiles were removed under reduced pressure and the residue washed with diethyl ether (2 x 3 ml) and pentane (2 x 3 ml). After drying under reduced pressure, **5** was obtained as a yellow powder (89 mg, 89%). Crystals suitable for X-ray diffraction analysis were obtained by storing a solution of **5** in toluene/pentane (v:v 2:1) at −40 °C.

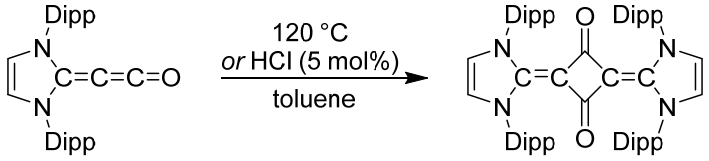
^{1}H NMR (400 MHz, C_6D_6): δ = 6.75 – 6.73 (m, 4H, CH_{arom}, Mes, *meta*), 5.71 (s, 2H, CH, imidazole), 2.08 (s, 6H, CH_3, Mes, *para*), 2.04 (s, 6H, CH_3, Mes, *ortho*). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ = 149.3 (C=*C*=O), 145.2 (C, imidazole), 139.3 (C_{arom}, Mes, *para*), 136.0 (C_{arom}, Mes, *ortho*), 133.5 (C_{arom}, Mes, *ipso*), 129.6 (HC_{arom}, Mes, *meta*), 116.4 (HC, imidazole), 21.1 (CH_3, *para*), 17.8 (CH_3, *ortho*), 12.0 (*C*=C=O). **IR:** $\tilde{\nu}$/cm^{-1} = 2066 *ν*(C=O) / 2018, 1994 *ν*(^{13}C=O). Compound **5** could not be detected by mass spectrometry.



Compound 6: 1,3-Dimethyl-2-methylene-2,3-dihydro-1*H*-imidazole (100 mg, 910 µmol, 1 eq.), potassium tert-butoxide (5 mg) and potassium hydride (40 mg, 1 mmol, 1.1 eq.) were placed in a 500 ml Schlenk tube. Tetrahydrofuran (20 mL) was added and the mixture was degassed by three freeze-pump-thaw cycles. Then, N_2O (1 atm, ca. 20 mmol) was added, and the mixture was stirred at room temperature for 2 h. The solution was filtered and all volatiles were removed under reduced pressure to obtain a yellow, crystalline solid. The latter was washed with diethyl ether (2 x 2 ml) and pentane (1 x 2 ml) and dried under vacuum. The solid was taken up in toluene (30 ml), filtered and, inside a 500 ml Schlenk tube, degassed by three freeze-pump-thaw cycles. The solution was placed under an atmosphere of CO (1 atm, ca. 20 mmol) and stirred at room temperature for 24 h. The solution was filtered and evaporated to dryness. The obtained light-yellow solid was washed with diethyl ether (2 ml) and pentane (2 ml) and finally dried under reduced pressure to obtain 78 mg of alkylideneketene **6** (63% over two steps). Crystals, suitable for X-ray diffraction analysis, were grown by vapor diffusion of pentane into a concentrated solution of **6** in toluene.

^{1}H NMR (400 MHz, C_6D_6): δ = 5.27 (s, 2H, CH, imidazole), 2.66 (s, 6H, CH_3). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ = 147.8(C=*C*=O), 143.9 (C, imidazole), 115.3 (HC, imidazole), 33.5

(CH_3), 9.5 (*C*=C=O). **IR:** $\tilde{\nu}$/cm^{-1} = 2098 ν(C=O) / 2045 ν(^{13}C=O). Compound **6** could not be detected by mass spectrometry.



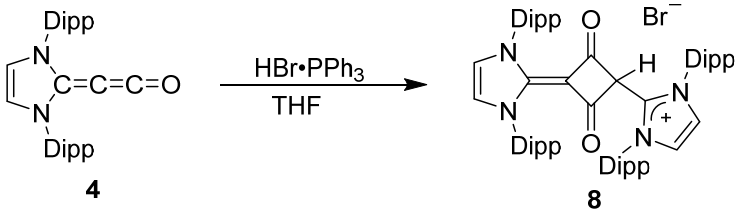
4 **7**

Dimerization of 4:

Heating: A solution of alkylidene ketene **4** (10 mg, 23 µmol) in toluene-d_8 (0.6 ml) in a J Young-type NMR tube was heated in an oil bath at 120 °C for 120 h. Analysis by ^{1}H NMR spectroscopy revealed that dimerization **7** had formed in a yield of ~ 80 %.

Catalytic amount HCl: HCl in diethyl ether (1.8 µl, 1 M, 0.05 eq.) was added to a solution of alkylidene ketene **4** (15 mg, 35 µmol) in C_6D_6. After 24 h, the quantitative consumption of **4** was observed by ^{1}H NMR spectroscopy. The solvent was removed under reduced pressure, and the yellow residue was dissolved in pentane (1 ml), filtered, and stored at −40 °C. After one week, small needle-like crystals of **7** formed, which were suitable for X-ray diffraction analysis (12 mg, 80%).

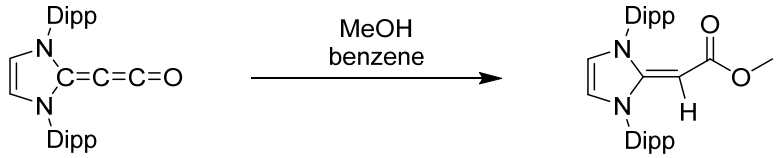
^{1}H NMR (400 MHz, C_6D_6): δ = 7.29 (t, *J* = 7.7 Hz, 4H, CH_{arom}, Dipp, *para*), 7.07 (d, *J* = 7.7 Hz, 8H, CH_{arom}, Dipp, *meta*), 5.78 (s, 4H, CH, imidazole), 2.89 (sept, *J* = 6.9 Hz, 8H, C*H*(CH_3)$_2$), 1.24 (d, *J* = 6.9 Hz, 24H, CH(C*H*$_3$)$_2$), 1.18 (d, *J* = 7.0 Hz, 24H, CH(C*H*$_3$)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ = 177.6 (C=O), 147.0 (C_{arom}, Dipp, *ortho*), 140.0 (C, imidazole), 135.2 (C_{arom}, Dipp, *ipso*), 128.7 (HC_{arom}, Dipp, *para*), 122.8 (HC_{arom}, Dipp, *meta*), 117.8 (HC, imidazole), 98.1 (*C*(CO)$_2$), 28.8 (*C*H(CH_3)$_2$), 24.3 (CH(*C*H$_3$)$_2$), 23.1 (CH(*C*H$_3$)$_2$). **IR:** $\tilde{\nu}$/cm^{-1} = 1643 ν(C=O). **HRMS** (ESI/QTOF) *m/z*: $[M + H]^+$ Calcd. for $C_{58}H_{73}N_4O_2^+$ 857.5728; Found 857.5752.



4 **8**

Compound 8: Alkylidene ketene **4** (50 mg, 117 µmol, 1.00 eq.) and HBr•PPh_3 (20 mg, 58 µmol, 0.50 eq) were dissolved in THF (3 ml) and stirred for 72 h at room temperature, resulting in the formation of a colorless precipitate. All volatiles were removed under vacuum and the residue was washed with diethyl ether (3 x 2 ml) and dried under reduced pressure to obtain 54 mg of **8** (99%). Single crystals, suitable for X-ray diffraction analysis, were obtained by layering a solution of in CH_2Cl_2 with pentane. **8** can be deprotonated to obtain **7** by stirring over excess NaH in THF for 24 h.

^{1}H NMR (400 MHz, CD_3CN): δ = 7.58 (s, 2H, CH, imidazole), 7.54 (t, *J* = 7.8 Hz, 2H, CH_{arom}, Dipp, *para*), 7.44 (t, *J* = 7.8 Hz, 2H, CH_{arom}, Dipp, *para*), 7.32 (s, 2H, CH, imidazole), 7.27 (d, *J* = 7.8 Hz, 4H, CH_{arom}, Dipp, *meta*), 7.19 (d, *J* = 7.8 Hz, 4H, CH_{arom}, Dipp, *meta*), 4.01 (s, 1H, $HC(CO)_2$), 2.29 (sept, *J* = 6.9, 4H, $CH(CH_3)_2$), 2.28 (sept, *J* = 6.8, 4H, $CH(CH_3)_2$), 1.03 (d, *J* = 6.9, 12H, $CH(CH_3)_2$), 1.02 (d, *J* = 6.9, 12H, $CH(CH_3)_2$), 0.97 (d, *J* = 6.8, 12H, $CH(CH_3)_2$), 0.96 (d, *J* = 6.8, 12H, $CH(CH_3)_2$). **^{13}C{^{1}H} NMR** (101 MHz, CD_3CN): δ = 172.1 (C=O), 146.6 (C_{arom}, Dipp, *ortho*), 146.4 (C_{arom}, Dipp, *ortho*), 144.5 (C, imidazole), 142.0 (C, imidazole), 133.0 (HC_{arom}, Dipp, *para*), 132.4 (C_{arom}, Dipp, *ipso*), 131.8 (HC_{arom}, Dipp, *para*), 130.6 (C_{arom}, Dipp, *ipso*), 126.3 (HC, imidazole), 125.7 (HC_{arom}, Dipp, *meta*), 125.0 (HC_{arom}, Dipp, *meta*), 124.3 (HC, imidazole), 94.8 ($C(CO)_2$), 60.7 ($HC(CO)_2$), 30.0 ($CH(CH_3)_2$), 29.7 ($CH(CH_3)_2$), 25.6 ($CH(CH_3)_2$), 25.2 ($CH(CH_3)_2$), 22.8 ($CH(CH_3)_2$), 22.7 ($CH(CH_3)_2$). **IR:** $\tilde{\nu}/cm^{-1}$ = 1659 *ν*(C=O). **HRMS** (ESI/QTOF) *m/z*: $[M]^+$ Calcd. for $C_{58}H_{73}N_4O_2^+$ 857.5728; Found 857.5724.

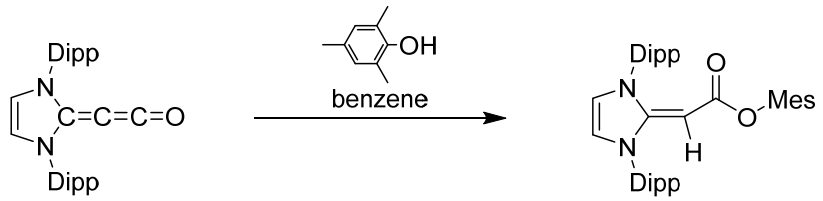


4 **9**

Compound 9: Alkylidene ketene **4** (50 mg, 117 µmol, 1.00 eq.) was dissolved in benzene (3 ml). MeOH (10 µl, 233 µmol, 2.00 eq.) was added, and the mixture was stirred at room temperature for 16 h. All volatiles were removed under vacuum and the residue was taken up in hexane (1 ml) and stored at −40 °C. After three days, yellowish crystals of **9** were obtained (53 mg, 99%). The crystals obtained were suitable for X-ray diffraction analysis.

^{1}H NMR (400 MHz, C_6D_6): δ = 7.22 (t, *J* = 7.7 Hz, 2H, CH_{arom}, Dipp, *para*), 7.10 (d, *J* = 7.7 Hz, 4H, CH_{arom}, Dipp, *meta*), 5.91 (s, 2H, CH, imidazole), 4.04 (s, 1H, $CH(CO_2CH_3)$), 3.22 (s, 3H, $CH(CO_2CH_3)$) 3.07 (pent, *J* = 6.9 Hz, 4H, $CH(CH_3)_2$), 1.36 (d, *J* = 6.9 Hz, 12H, $CH(CH_3)_2$), 1.16 (d, *J* = 6.9 Hz, 12H, $CH(CH_3)_2$). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ = 165.9 ($CO(OCH_3)$),

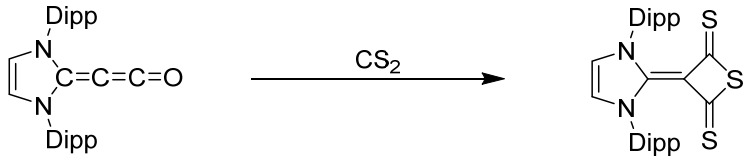
152.2 (C, imidazole), 146.9 (C_{arom}, Dipp, *ortho*), 129.8 (HC_{arom}, Dipp, *para*), 124.2 (HC_{arom}, Dipp, *meta*), 117.4 (broad, HC, imidazole), 60.6 (HC, *C*H(CO_2CH_3)), 49.0 (H_3C, CH(CO_2*C*H_3)), 29.1 (*C*H(CH_3)$_2$), 24.4 (CH(*C*H_3)$_2$), 23.6 (CH(*C*H_3)$_2$). The *ipso* C of the Dipp group could not be detected. **HRMS** (ESI/QTOF) *m/z*: $[M + H]^+$ Calcd. for $C_{30}H_{41}N_2O_2^+$ 461.3163; Found 461.3162.



4 **10**

Compound 10: Alkylidene ketene **4** (50 mg, 117 µmol, 1.00 eq.) was dissolved in benzene (3 ml). 2,4,6-Trimethylphenole (15.9 mg, 117 µmol, 1.00 eq.) was added, and the mixture was stirred at room temperature for 16 h. After that time, ester **10** formed quantitatively as evidenced by NMR spectroscopy. All volatiles were removed under reduced pressure and the residue was washed with hexane (1 ml), taken up in ether (1 ml) and stored at −40 °C. After one week, yellowish crystals of **10** were obtained (55 mg, 83%). The crystals were suitable for X-ray diffraction analysis.

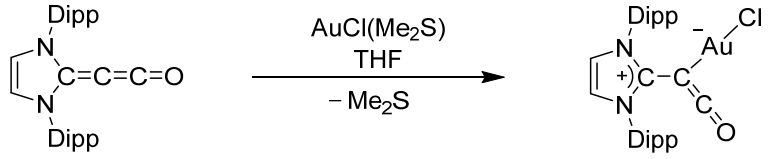
^{1}H NMR (400 MHz, C_6D_6): δ = 7.19 (dd, *J* = 8.4, 7.1 Hz, 2H, CH_{arom}, Dipp, *para*), 7.10 – 7.06 (m, 4H, CH_{arom}, Dipp, *meta*), 6.59 (s, 2H, CH_{arom}, Mes, *meta*) , 5.93 (s, 2H, CH, imidazole), 4.23 (s, 1H, C*H*(CO_2CH_3)), 3.06 (sept, *J* = 6.9 Hz, 4H, C*H*(CH_3)$_2$), 2.14 (s, 6H, Mes, *ortho*-CH_3), 2.04 (s, 3H, Mes, *para*-CH_3), 1.41 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.17 (d, *J* = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6): δ = 163.0 (*C*O(OCH_3)), 152.9 (C, imidazole), 148.2 (C_{arom}, Mes, *ipso*), 146.8 (C_{arom}, Dipp, *ortho*), 132.7 (C_{arom}, Mes, *para*), 131.2 (C_{arom}, Mes, *ortho*), 130.0 (HC_{arom}, Dipp, *para*), 128.9 (HC_{arom}, Mes, *meta*), 124.2 (HC_{arom}, Dipp, *meta*), 117.8 (broad, HC, imidazole), 59.6 (HC, *C*H(CO_2CH_3)), 29.2 (*C*H(CH_3)$_2$), 24.4 (CH(*C*H_3)$_2$), 23.6. (CH(*C*H_3)$_2$), 20.8 (CH_3, Mes, *para*), 16.8 (CH_3, Mes, *ortho*). The *ipso* C of the Dipp group could not be detected. **HRMS** (ESI/QTOF) *m/z*: $[M + H]^+$ Calcd. for $C_{38}H_{49}N_2O_2^+$ 565.3789; Found 565.3790.



4 **11**

Compound 11: Alkylidene ketene **4** (50 mg, 117 µmol, 1.00 eq.) was dissolved in CS_2 (2 ml). The solution was stirred at room temperature for 16 h. All volatiles were then removed under vacuum to obtain a yellow solid (60 mg, 98%). Crystals, suitable for X-ray diffraction analysis, were obtained by dissolving **4** in CS_2 and storing the solution at –40 °C for three days.

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.56 (t, *J* = 7.8 Hz, 2H, CH_{arom}, Dipp, *para*), 7.37 (d, *J* = 7.8 Hz, 4H, CH_{arom}, Dipp, *meta*), 6.91 (s, 2H, CH, imidazole), 2.62 (hept, *J* = 6.9 Hz, 4H, C*H*$(CH_3)_2$), 1.29 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3)_2$), 1.24 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3)_2$). **^{13}C{^{1}H} NMR** (101 MHz, CD_2Cl_2): δ = 146.3 (C_{arom}, Dipp, *ortho*), 144.4 (C, imidazole), 135.3 (C, C*C*$(CS)_2$, indirectly detected via ^{1}H/^{13}C-HMBC), 131.5 (C_{arom}, Dipp, *ipso*), 130.9 (HC_{arom}, Dipp, *para*), 124.4 (HC_{arom}, Dipp, *meta*), 119.6 (HC, imidazole), 29.1 (*C*H$(CH_3)_2$), 23.6 (CH(*C*H$_3)_2$), 23.6 (CH(*C*H$_3)_2$). The carbon atoms of the dithio thietane group could not be detected. **HRMS** (nanochip-ESI/LTQ-Orbitrap) *m/z*: $[M + H]^+$ Calcd. for $C_{30}H_{37}N_2S_3^+$ 521.2113; Found 521.2138.

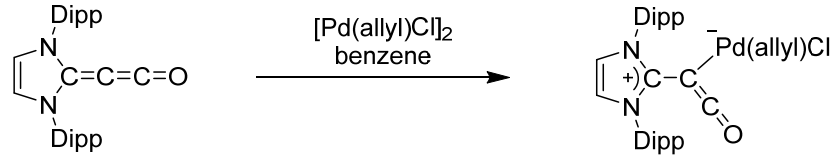


4 **12**

Complex 12: Alkylidene ketene **4** (68 mg, 158 µmol, 1.05 eq.) and $AuCl(Me_2S)$ (44 mg, 150 µmol, 1 eq.) were dissolved in THF (2 ml) and stirred at room temperature for 1 h. The solution was filtered using a syringe filter and then all volatiles were removed under reduced pressure. The residue was washed with diethyl ether (2 x 2 ml) and dried under vacuum to obtain an off-white solid (77 mg, 78 %). Crystals, suitable for X-ray diffraction analysis, were obtained by layering a solution of **12** in CH_2Cl_2 with pentane.

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.62 (t, *J* = 7.8 Hz, 2H, CH_{arom}, Dipp, *para*), 7.38 (d, *J* = 7.8 Hz, 4H, CH_{arom}, Dipp, *meta*), 7.07 (s, 2H, CH, imidazole), 2.53 (sept, *J* = 6.9 Hz, 4H, C*H*$(CH_3)_2$), 1.36 (d, *J* = 6.9 Hz, 12H, CH(C*H*$_3)_2$), 1.23 (d, *J* = 6.9 Hz, 12H, CH(C*H*$_3)_2$). **^{13}C{^{1}H} NMR** (101 MHz, CD_2Cl_2): δ = 165.8 (C=*C*=O), 150.2 (C, imidazole), 146.8 (C_{arom}, Dipp, *ortho*), 132.3 (HC_{arom}, Dipp, *para*), 131.3 (C_{arom}, Dipp, *ipso*), 125.4 (HC_{arom}, Dipp, *meta*),

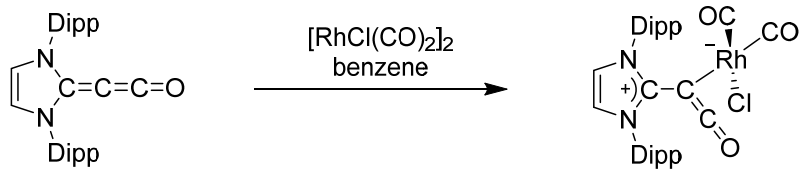
121.5 (HC, imidazole), 29.5 (*C*H(CH$_3$)$_2$), 24.6 (CH(*C*H$_3$)$_2$), 23.5 (CH(*C*H$_3$)$_2$), 12.8 (*C*=C=O). **IR:** $\tilde{\nu}$/cm^{-1} = 2060 *ν*(C=O). **HRMS** (nanochip-ESI/LTQ-Orbitrap) *m/z*: [M + Na]$^+$ Calcd. for $C_{29}H_{36}AuClN_2NaO^+$ 683.2074; Found 683.2074.



4 **13**

Complex 13: Alkylidene ketene **4** (100 mg, 233 µmol, 1.00 eq.) and [Pd(allyl)Cl]$_2$ (43 mg, 117 µmol, 0.5 eq.) were dissolved in benzene (1 ml) and stirred at room temperature for 16 h. The mixture was filtered using a syringe filter, and the filtrate was evaporated to dryness to obtain a yellow solid. The latter was washed with pentane (3 x 2 ml) and dried under vacuum (98 mg, 69%, unidentified impurities present). Pure **13** was obtained by repeated crystallization (3 x) by vapor diffusion of pentane into a toluene solution of **13** at –40 °C. The crystals obtained in this way were washed with diethyl ether and dried under vacuum for 24 h (34 mg, 24 %). Crystals, suitable for X-ray diffraction analysis, were obtained by layering a benzene solution of **13** with pentane. Complex **13** shows notable signs of decomposition in solution at room temperature over the course of several hours.

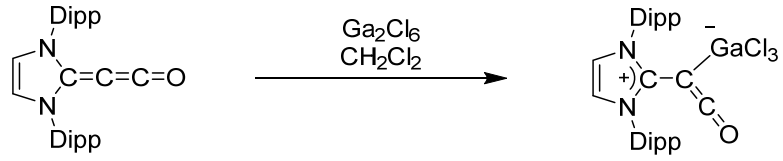
^{1}H NMR (400 MHz, CD_2Cl_2, 233 K): δ = 7.49 (t, *J* = 7.8 Hz, 2H, CH_{arom}, Dipp, *para*), 7.32 (d, *J* = 7.8 Hz, 4H, CH_{arom}, Dipp, *meta*), 6.97 (s, 2H, CH, imidazole), 4.70 (tt, *J'* = 12.8, *J''* = 6.9 Hz, 1H, C*H*(CH$_2$)$_2$), 3.81 (dd, *J'* = 7.0, *J''* = 2.2 Hz, 1H, , CH(C*H*$_2$)$_2$), 3.04 (dd, *J'* = 6.6, *J''* = 2.2 Hz, 1H, CH(C*H*$_2$)$_2$), 2.73 (br, 4H, C*H*(CH$_3$)$_2$), 2.38 (d, *J* = 12.8 Hz, 1H, CH(C*H*$_2$)$_2$), 1.34 (d, *J* = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.30 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.14 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.13 (d, *J* = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.11 (d, *J* = 11.5 Hz, 1H, CH(C*H*$_2$)$_2$, indirectly detected by ^{1}H/^{1}H-COSY). **^{13}C{^{1}H} NMR** (101 MHz, CD_2Cl_2, 233 K): δ = 151.3 (C, imidazole), 147.0 (C_{arom}, Dipp, *ortho*), 146.8 (C=*C*=O), 131.5 (C_{arom}, Dipp, *ipso*), 131.0 (HC_{arom}, Dipp, *para*), 124.5 (HC_{arom}, Dipp, *meta*), 124.2 (HC_{arom}, Dipp, *meta*), 120.4 (HC, imidazole), 112.0 (*C*H(CH$_2$)$_2$), 67.3 (CH(*C*H$_2$)$_2$), 55.5 (CH(*C*H$_2$)$_2$), 28.7 (*C*H(CH$_3$)$_2$), 28.6 (*C*H(CH$_3$)$_2$), 25.2 (CH(*C*H$_2$)$_2$), 24.9 (CH(*C*H$_2$)$_2$), 23.0 (CH(*C*H$_3$)$_2$), 22.9 (CH(*C*H$_3$)$_2$), 1.9 (*C*=C=O). **IR:** $\tilde{\nu}$/cm^{-1} = 2045 *ν*(C=O). Complex **13** could not be detected by mass spectrometry.



4 **14**

Complex 14: A solution of alkylidene ketene **4** (50 mg, 117 µmol, 1.00 eq.) and $[RhCl(CO)_2]_2$ (23 mg, 58 µmol, 0.5 eq.) in benzene (1 ml) was stirred at room temperature for 16 h. The mixture was filtered using a syringe filter, and the filtrate was evaporated to dryness to obtain a brown solid. The latter was washed with pentane (2 x 1 ml) and dried under vacuum (52 mg, 71%, unidentified impurities present). Pure **14** was obtained by crystallization (vapor diffusion of pentane into a toluene solution at –40 °C). The crystals obtained in this way were suitable for X-ray diffraction analysis. Complex **14** shows notable signs of decomposition in solution at room temperature over the course of several hours.

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.59 (t, *J* = 7.8 Hz, 2H, CH_{arom}, Dipp, *para*), 7.39 (d, *J* = 7.8 Hz, 4H, CH_{arom}, Dipp, *meta*), 7.02 (s, 2H, CH, imidazole), 2.76 (sept, *J* = 6.8 Hz, 4H, C*H*$(CH_3)_2$), 1.39 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3)_2$), 1.17 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3)_2$). **^{13}C{^{1}H} NMR** (101 MHz, CD_2Cl_2): δ = 183.3 (d, $^1J_{CRh}$ = 63.9 Hz, OC_{Rh}), 182.3 (d, $^1J_{CRh}$ = 70.5 Hz, OC_{Rh}), 155.0 (C=*C*=O), 152.9 (C, imidazole), 147.4 (C_{arom}, Dipp, *ortho*), 132.0 (HC_{arom}, Dipp, *para*), 131.8 (C_{arom}, Dipp, *ipso*), 125.1 (HC_{arom}, Dipp, *meta*), 121.4 (HC, imidazole), 29.4 (*C*H$(CH_3)_2$), 25.7 (CH(*C*H$_3)_2$), 23.1 (CH(*C*H$_3)_2$), 6.2 (d, $^1J_{CRh}$ = 20.9 Hz, *C*=C=O). **IR:** $\tilde{\nu}$/cm^{-1} = 2067 *ν*(*cis* OC_{Rh}), 2052 *ν*(C=O) / 2005 *ν*(^{13}C=O), 1991 *ν*(*trans* OC_{Rh}). Complex **14** could not be detected by mass spectrometry.



4 **15**

Complex 15: A solution of alkylidene ketene **4** (50 mg, 117 µmol, 1.00 eq.) and Ga_2Cl_6 (22 mg, 61 µmol, 0.53 eq.) in CH_2Cl_2 (2 ml) was stirred at room temperature for 24 h. All volatiles were removed under reduced pressure, and the residue was washed with diethyl ether (1 x 1 ml) and hexane (3 x 2 ml) to obtain a colorless solid (65 mg, 92%). Crystals, suitable for X-ray diffraction analysis, were obtained by layering a solution of **4** in toluene (20 mg in 0.5 ml) with a solution of Ga_2Cl_6 in hexane (9 mg in 0.5 ml).

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.62 (t, *J* = 7.8 Hz, 2H, CH_{arom}, Dipp, *para*), 7.41 (d, *J* = 7.8 Hz, 4H, CH_{arom}, Dipp, *meta*), 7.26 (s, 2H, CH, imidazole), 2.61 (sept, *J* = 6.8 Hz, 4H, C*H*$(CH_3)_2$), 1.38 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3)_2$), 1.19 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3)_2$). **^{13}C{^{1}H} NMR** (101 MHz, CD_2Cl_2): δ = 168.1 (C, imidazole), 147.7 (C=*C*=O), 146.4 (C_{arom}, Dipp, *ortho*), 132.8 (HC_{arom}, Dipp, *para*), 130.4 (C_{arom}, Dipp, *ipso*), 125.9 (HC_{arom}, Dipp, *meta*), 123.8 (HC, imidazole), 29.5 (*C*H$(CH_3)_2$), 25.9 (CH(*C*H$_3)_2$), 23.1 (CH(*C*H$_3)_2$), 21.5 (*C*=C=O). **IR:** $\tilde{\nu}/cm^{-1}$ = 2099 *ν*(C=O). Complex **15** could not be detected by mass spectrometry.

3. NMR spectra

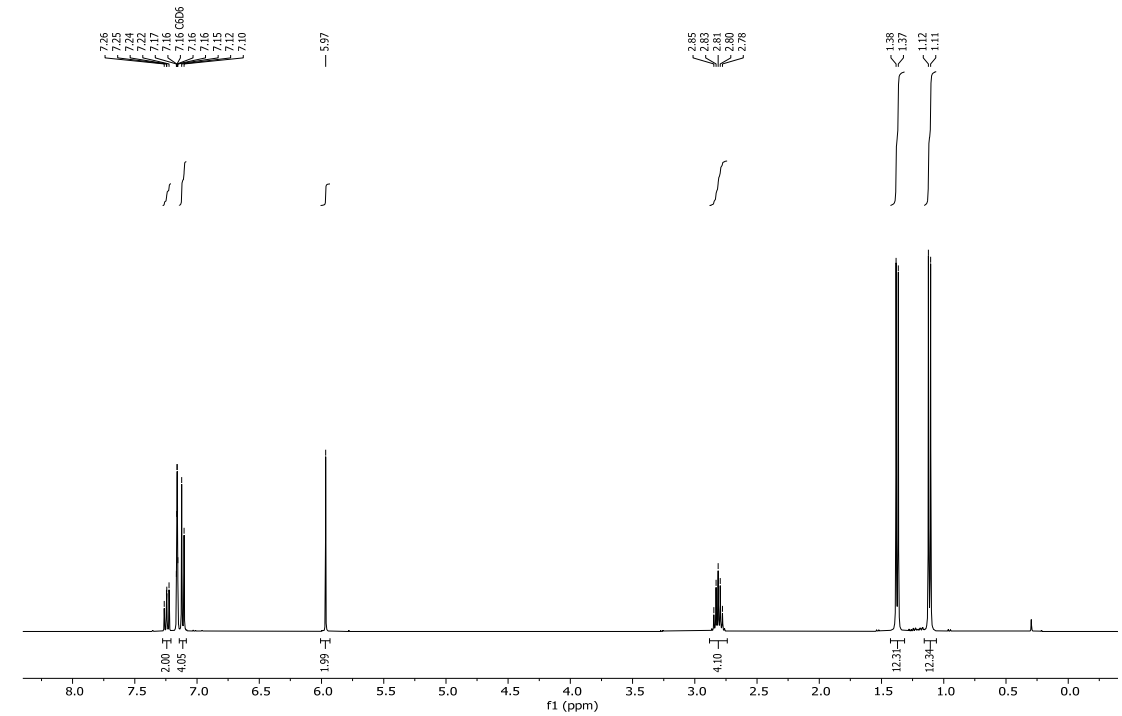


Figure S1. ^{1}H NMR (400 MHz, C_6D_6) spectrum of compound **4**.

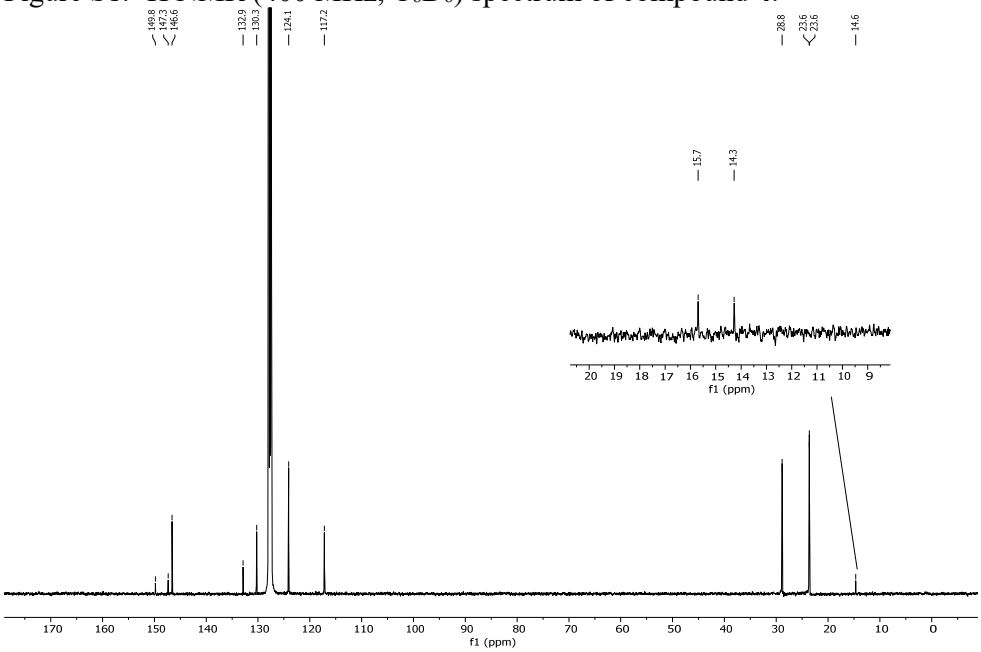


Figure S2. ^{13}C NMR (101 MHz, C_6D_6) spectrum of compound **4**. The inset shows the coupling of *C*CO in ^{13}C labeled **4**^{13C}.

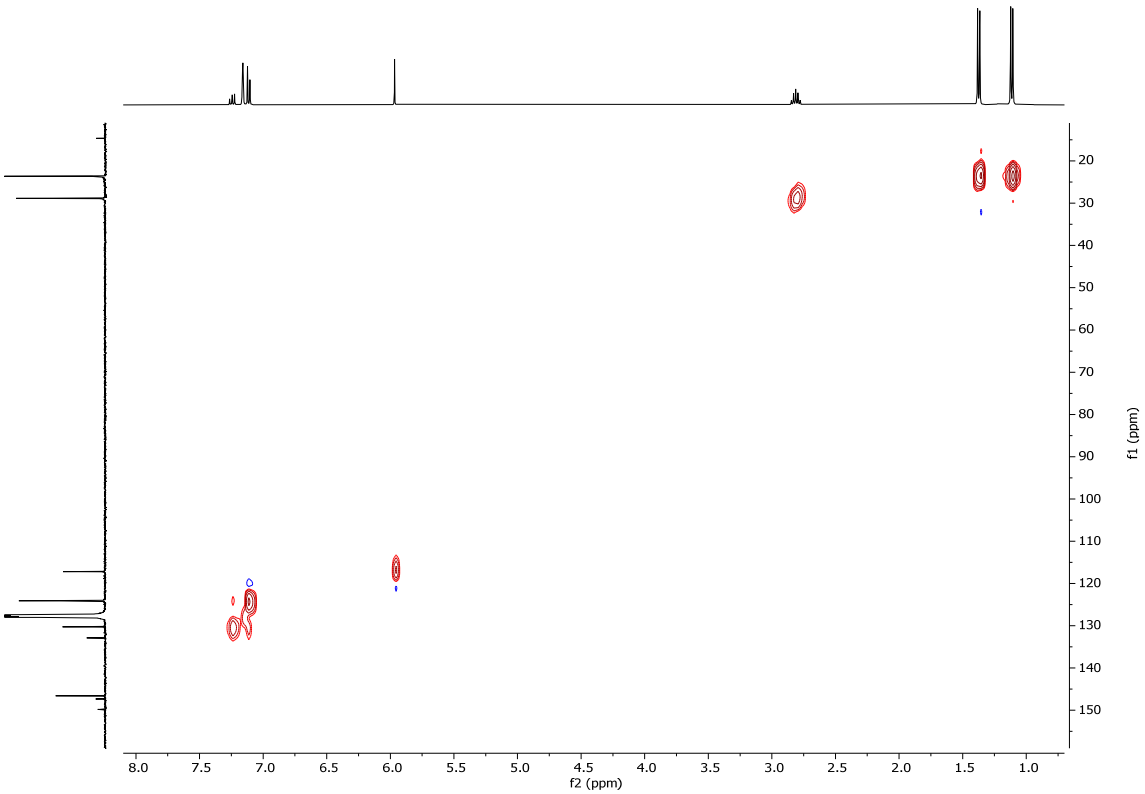


Figure S3. $^{1}H/^{13}C$ HSQC NMR spectrum of **4** in C_6D_6.

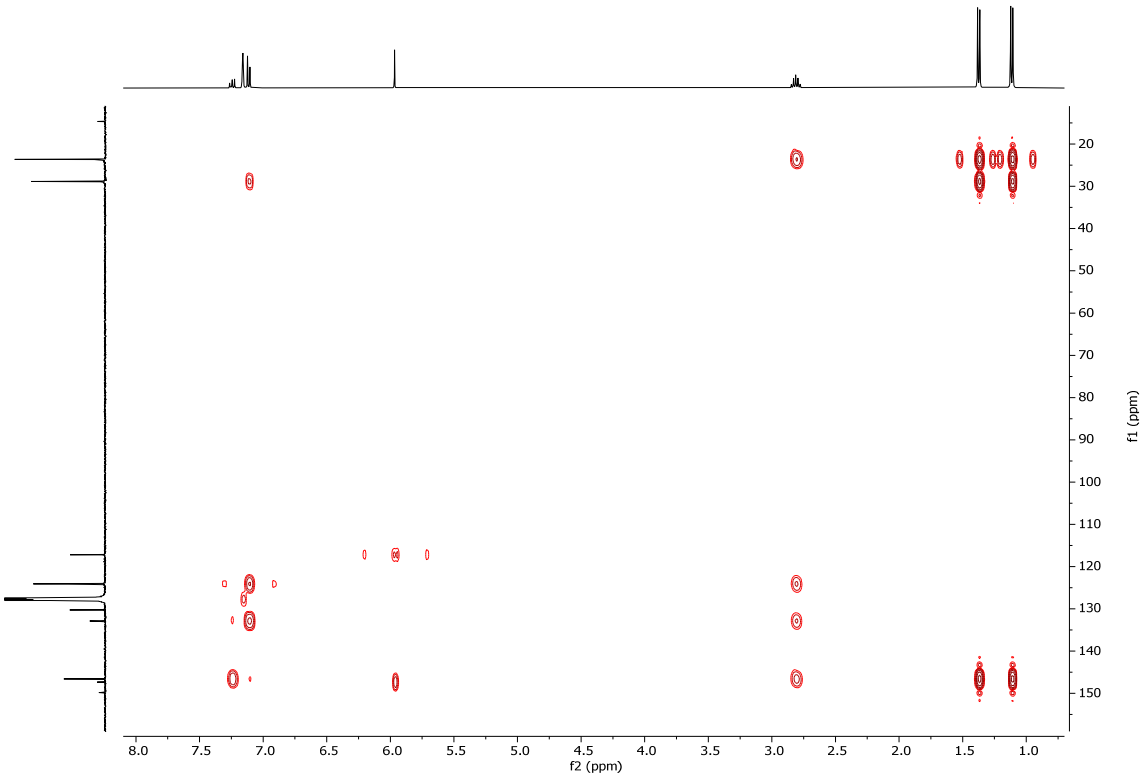


Figure S4. $^{1}H/^{13}C$ HMBC NMR spectrum of **4** in C_6D_6.

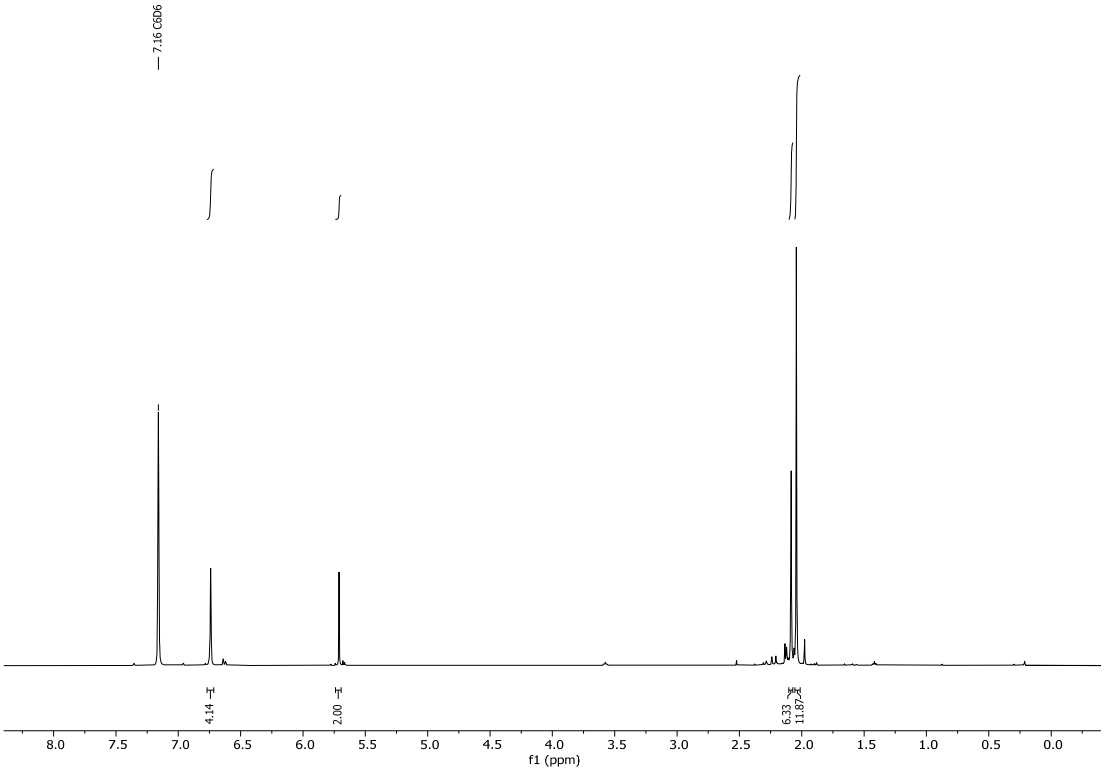


Figure S5. ^{1}H NMR (400 MHz, C_6D_6) spectrum of compound **5**.

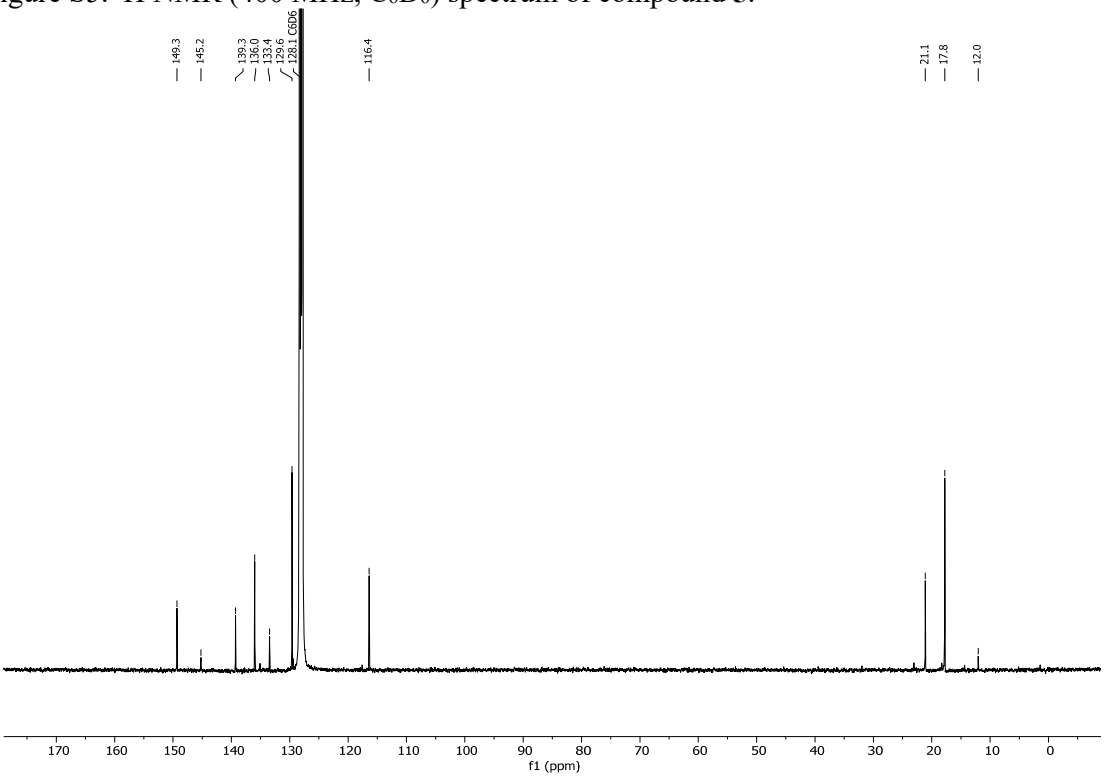


Figure S6. ^{13}C NMR (101 MHz, C_6D_6) spectrum of compound **5**.

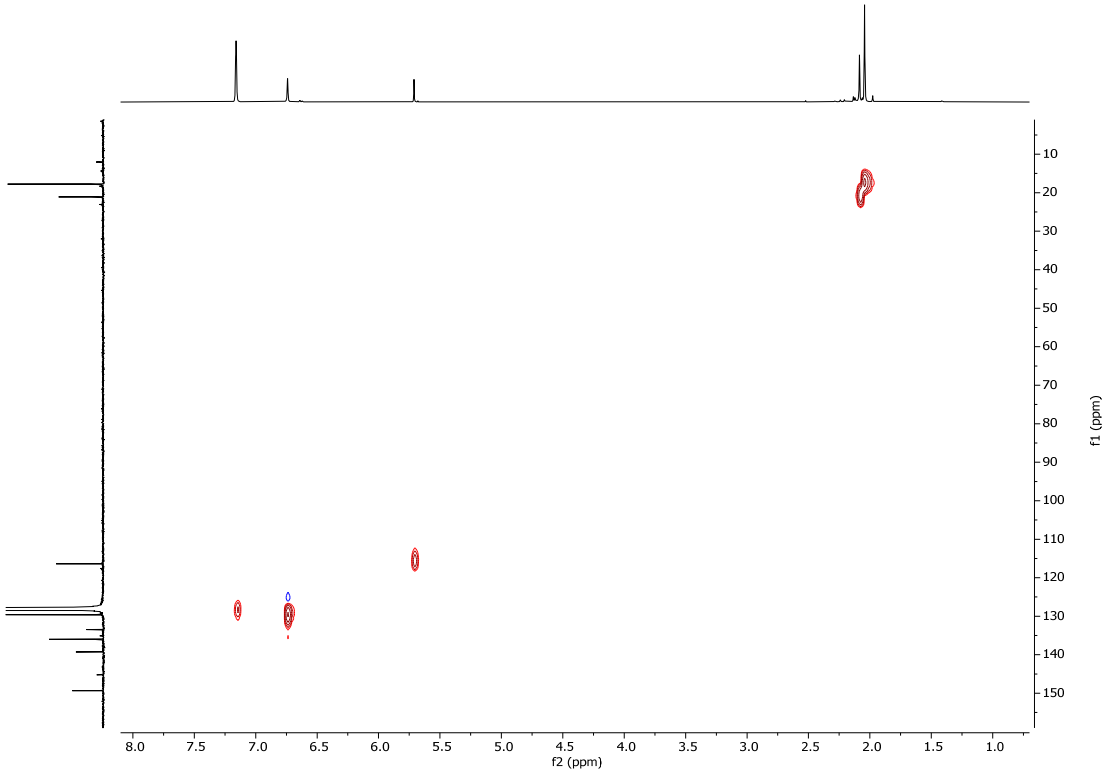


Figure S7. $^{1}H/^{13}C$ HSQC NMR spectrum of **5** in C_6D_6.

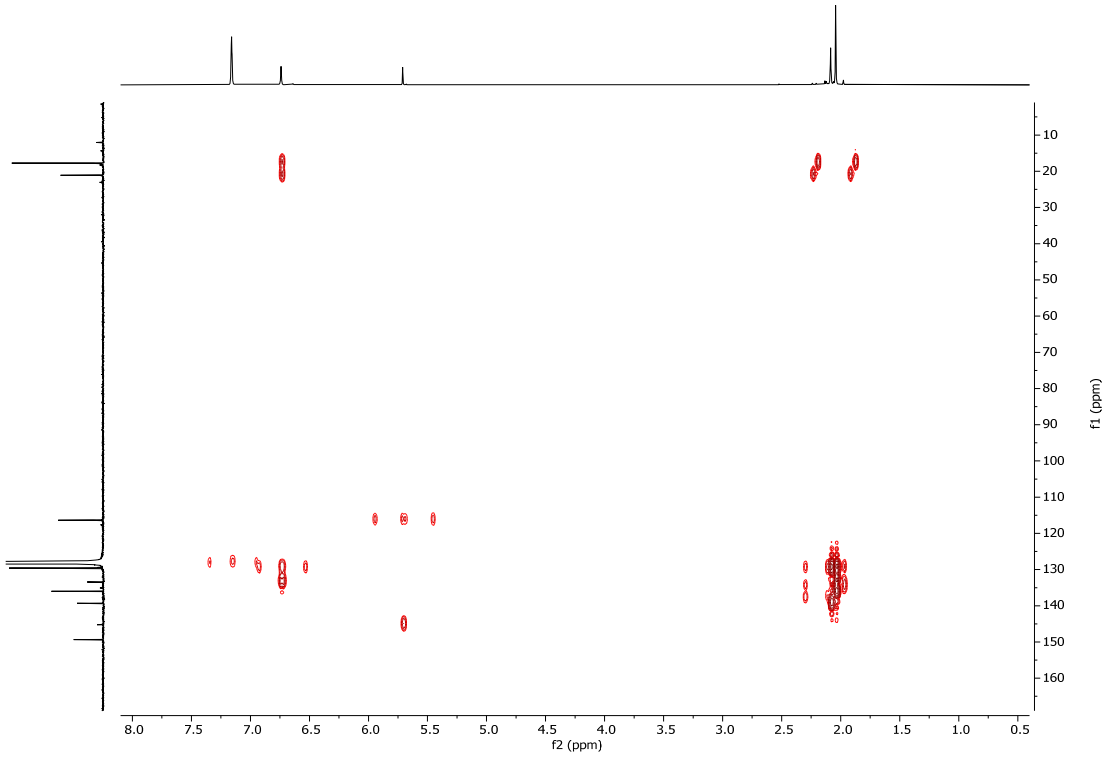


Figure S 8. $^{1}H/^{13}C$ HMBC NMR spectrum of **5** in C_6D_6.

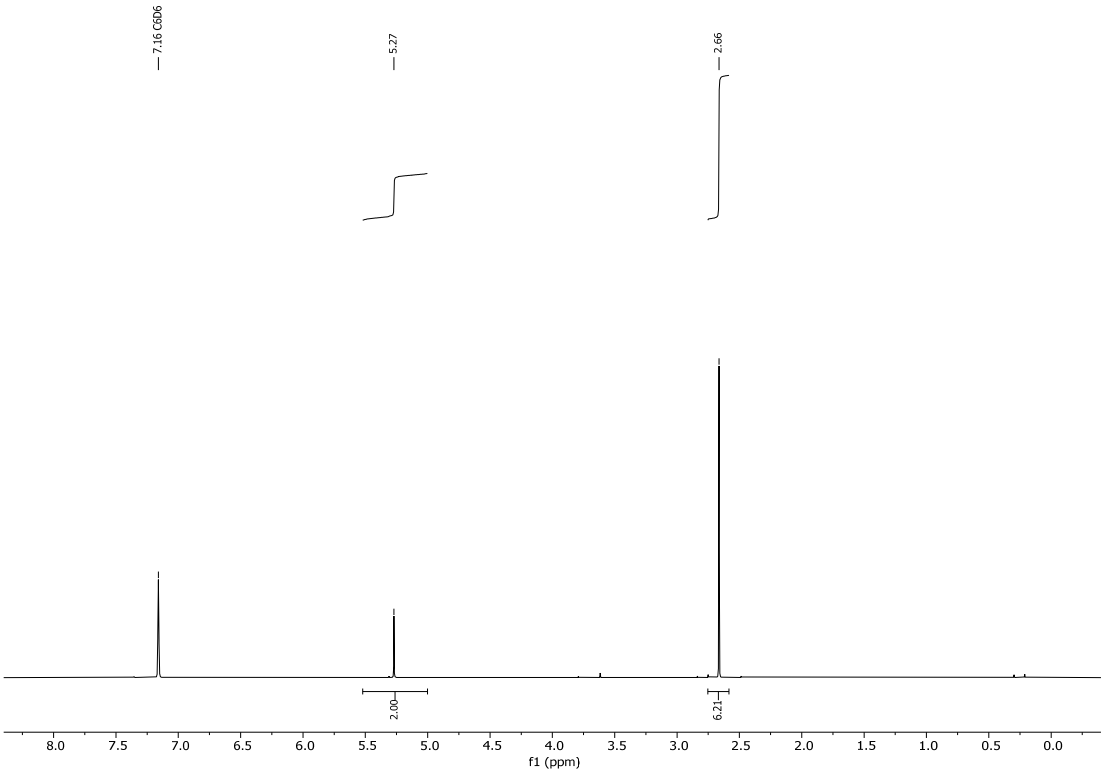


Figure S 9. ^{1}H NMR (400 MHz, C_6D_6) spectrum of compound **6**.

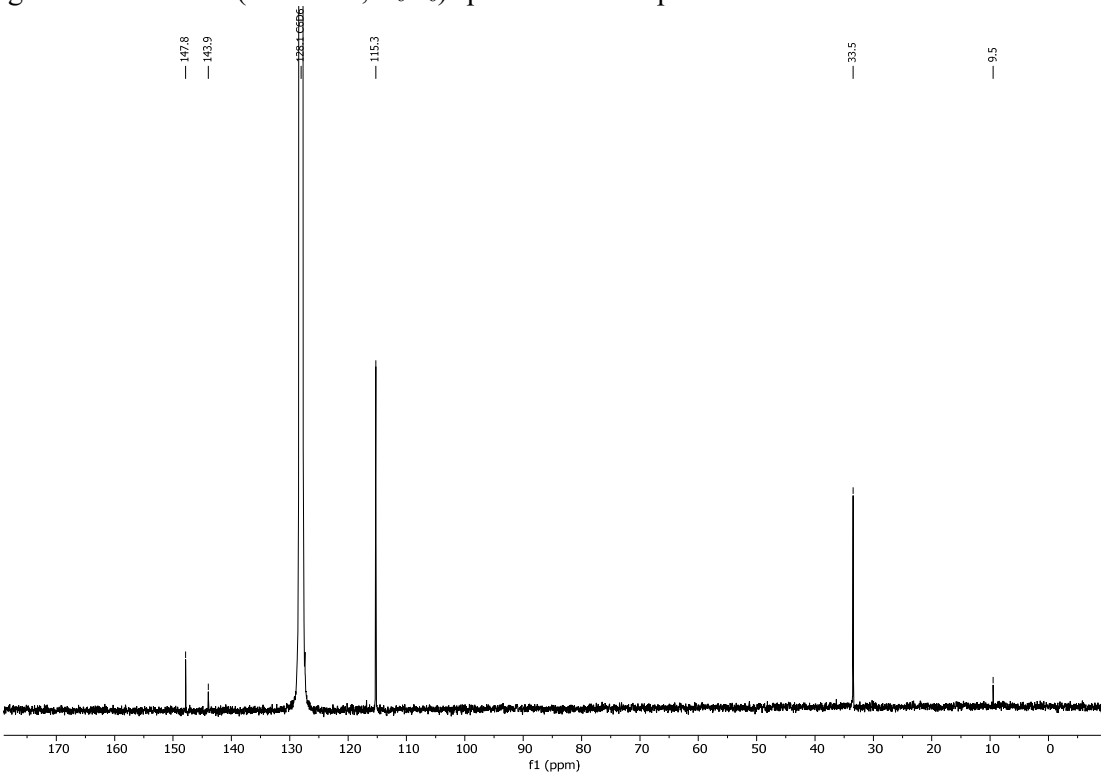


Figure S 10. ^{13}C NMR (101 MHz, C_6D_6) spectrum of compound **6**.

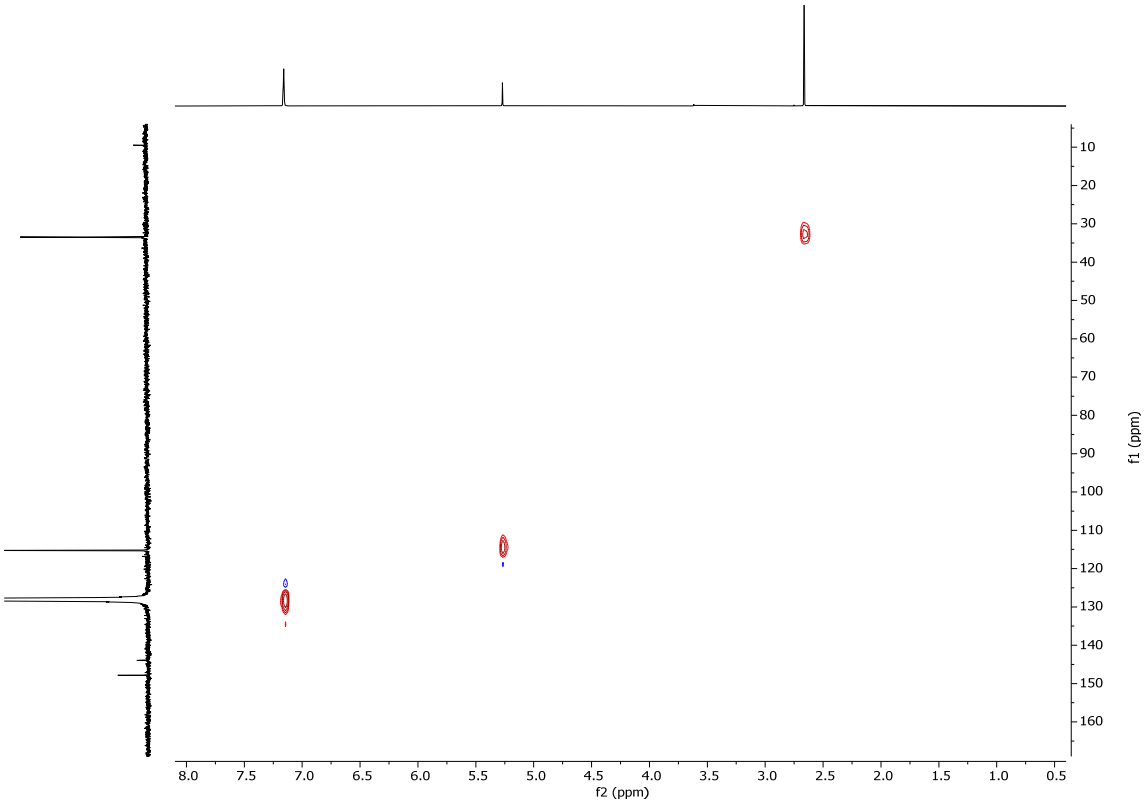


Figure S 11. $^{1}H/^{13}C$ HSQC NMR spectrum of **6** in C_6D_6.

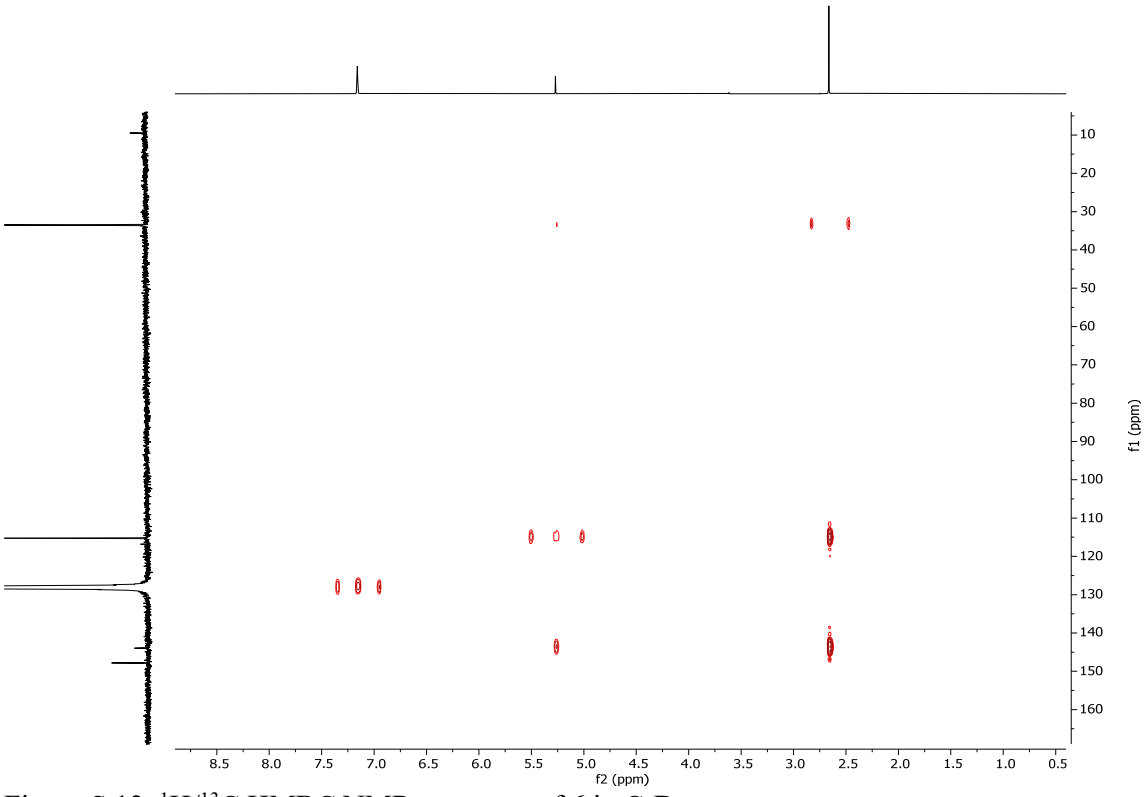


Figure S 12. $^{1}H/^{13}C$ HMBC NMR spectrum of **6** in C_6D_6.

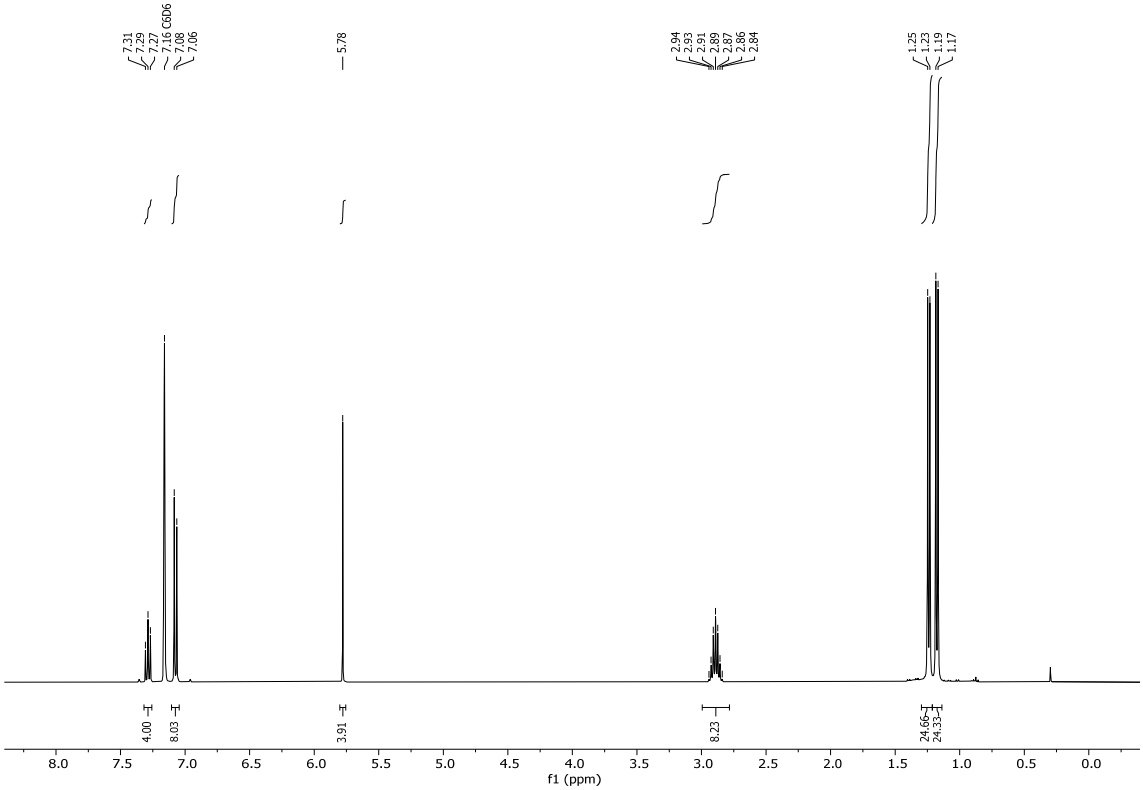


Figure S13. ^{1}H NMR (400 MHz, C_6D_6) spectrum of compound **7**.

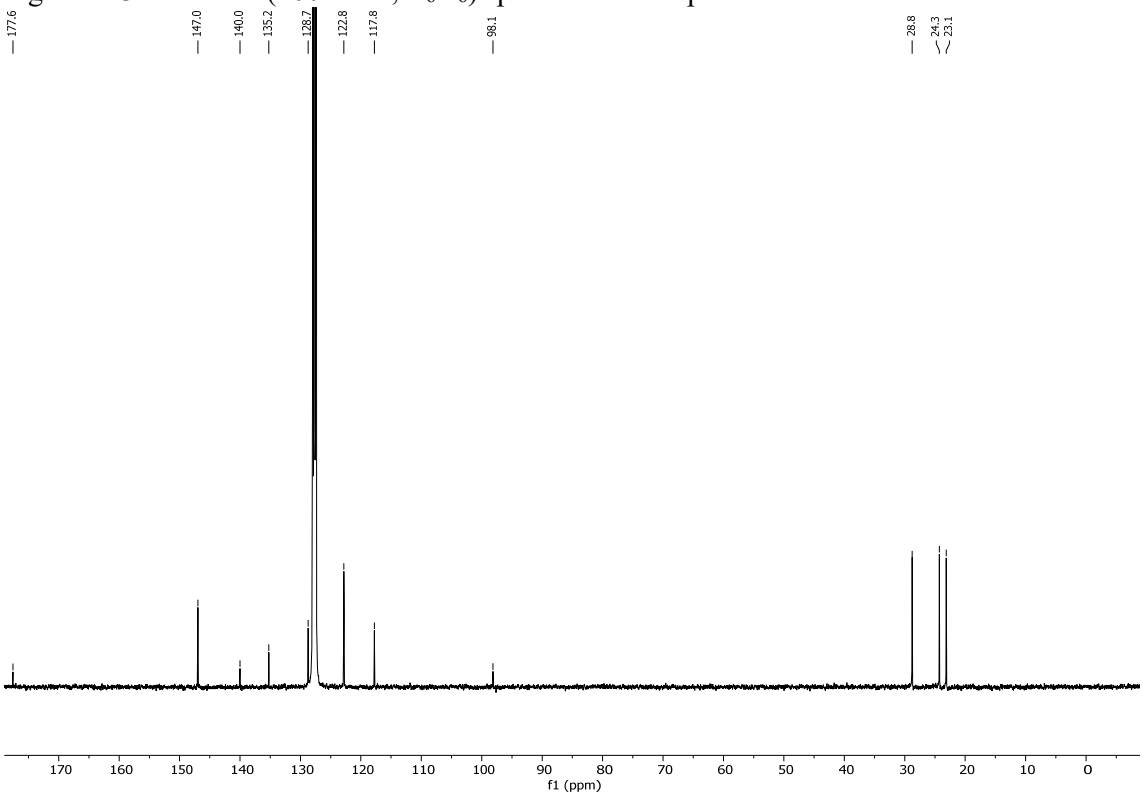


Figure S14. ^{13}C NMR (101 MHz, C_6D_6) spectrum of compound **7**.

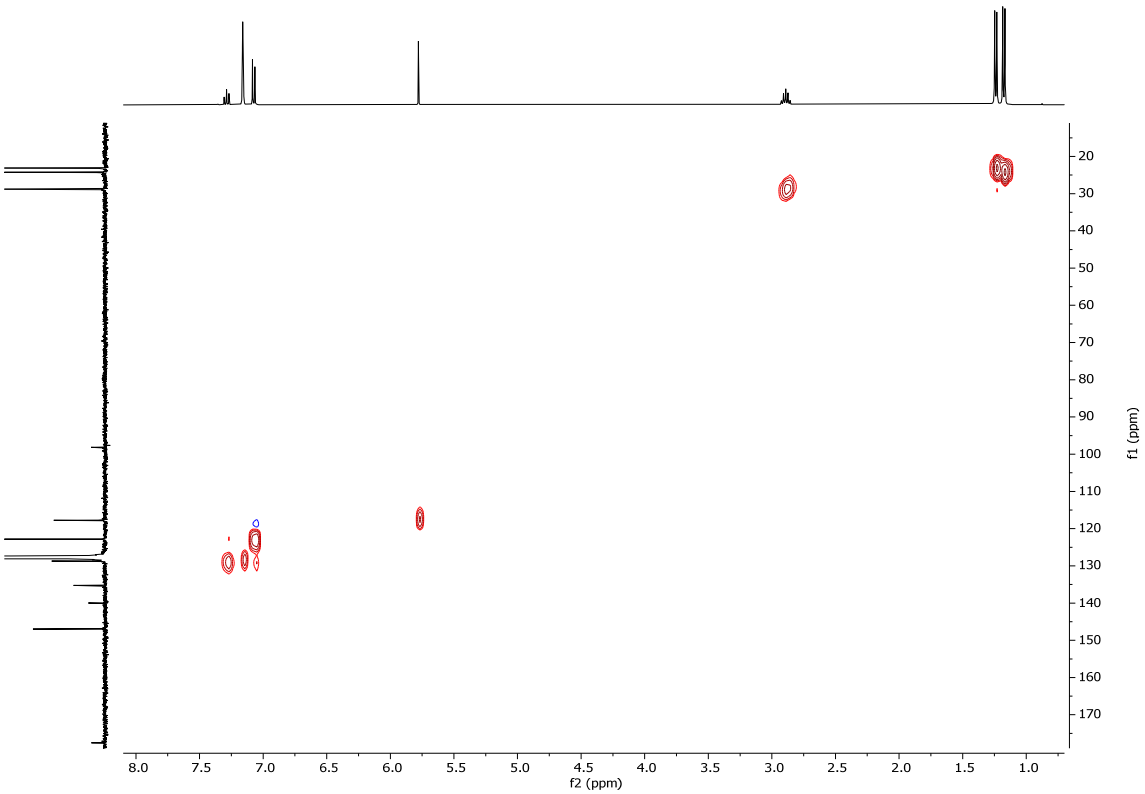


Figure S15. $^{1}H/^{13}C$ HSQC NMR spectrum of **7** in C_6D_6.

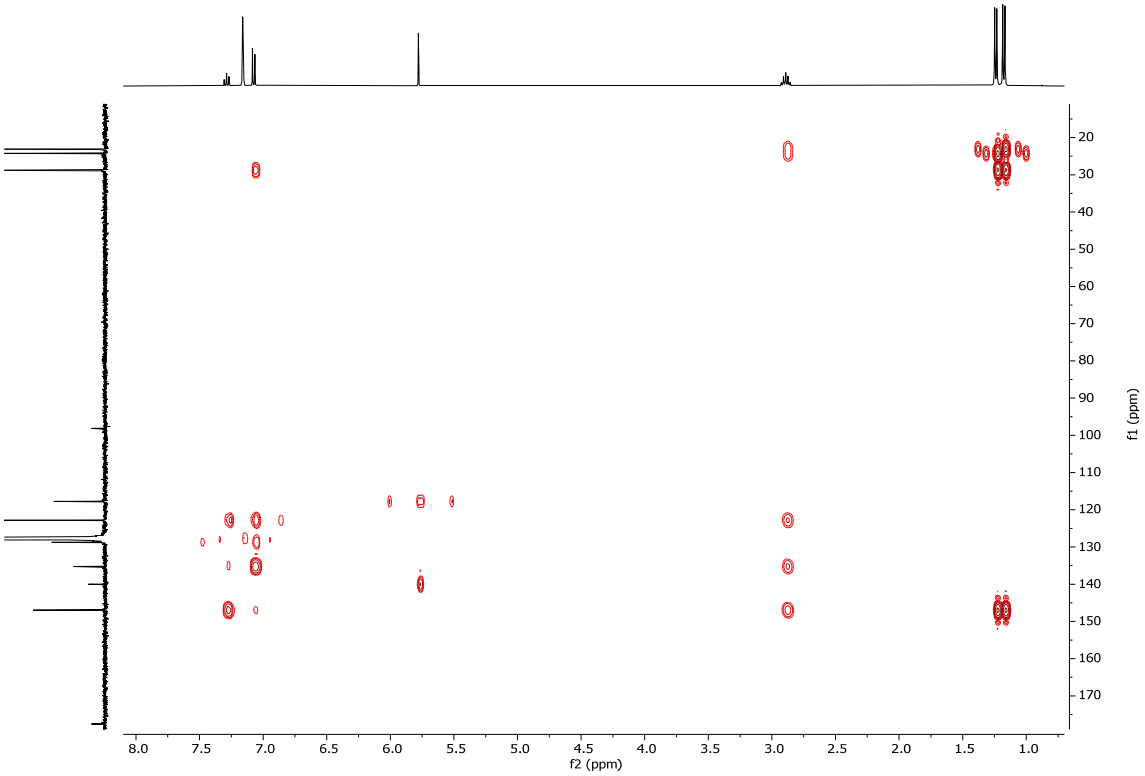


Figure S16. $^{1}H/^{13}C$ HMBC NMR spectrum of **7** in C_6D_6.

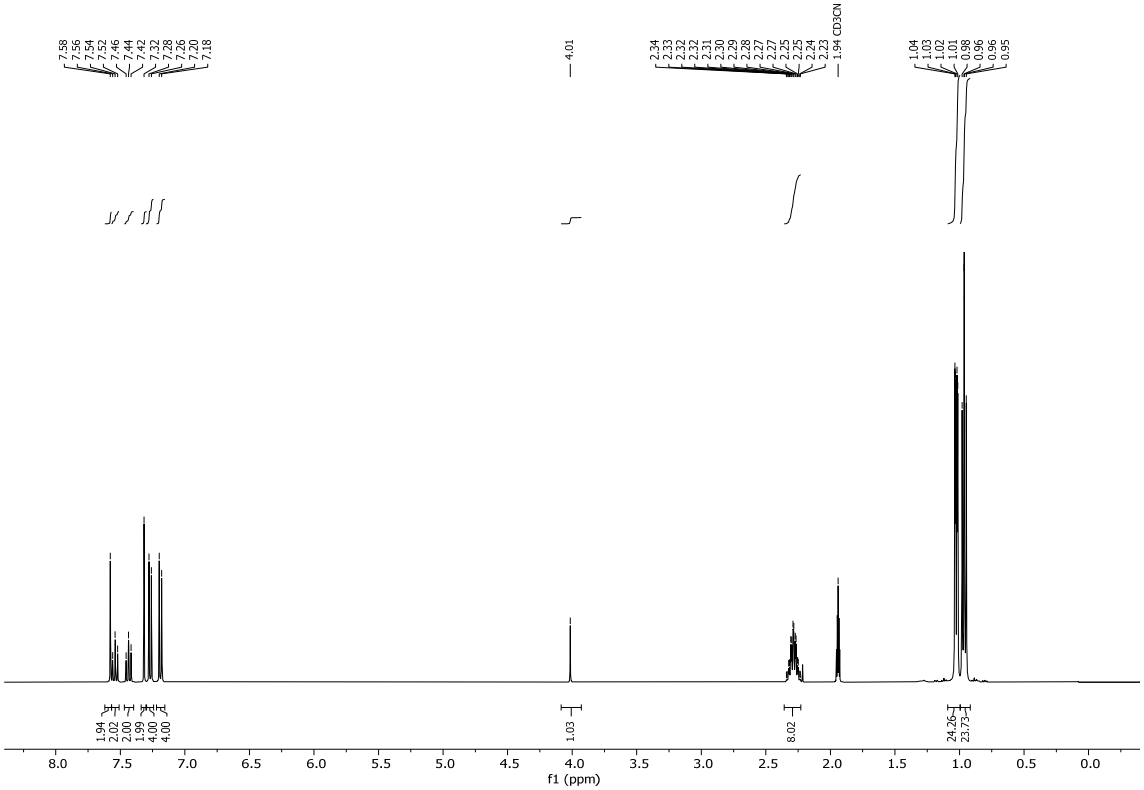


Figure S17. ^{1}H NMR (400 MHz, MeCN-d_3) spectrum of compound **8**.

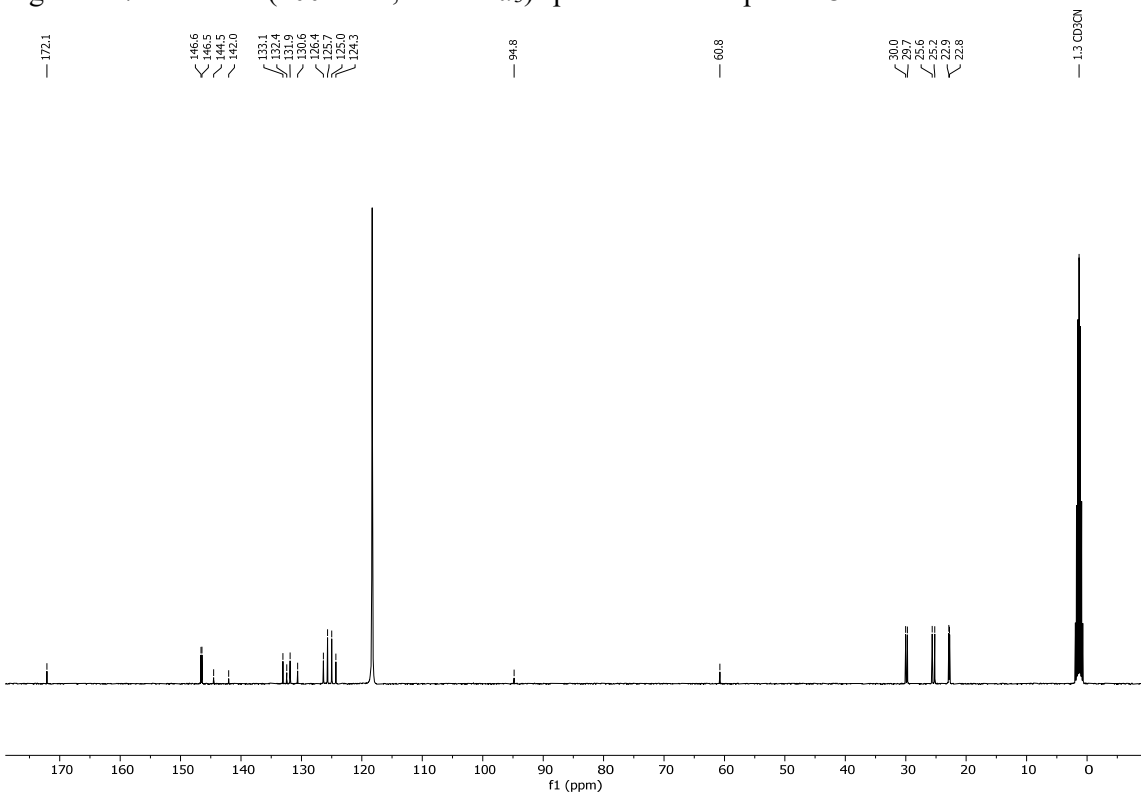


Figure S18. ^{13}C NMR (101 MHz, MeCN-d_3) spectrum of compound **8**.

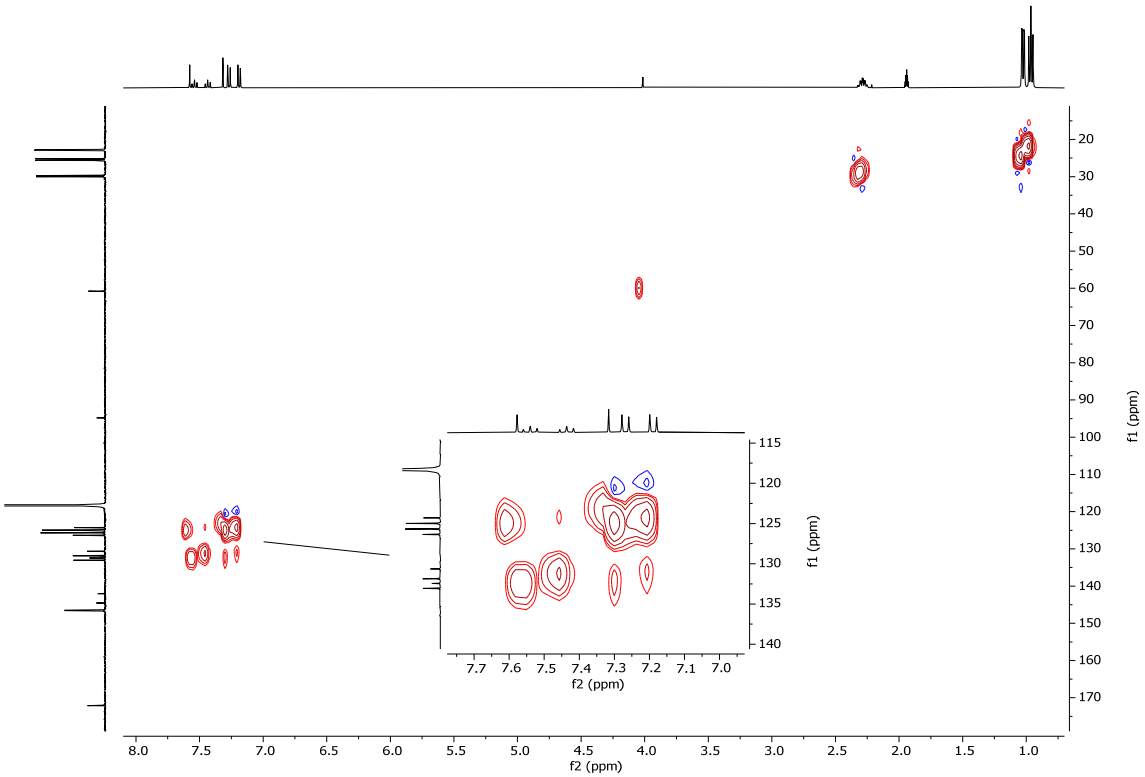


Figure S19. $^{1}H/^{13}C$ HSQC NMR spectrum of **8** in MeCN-d_3.

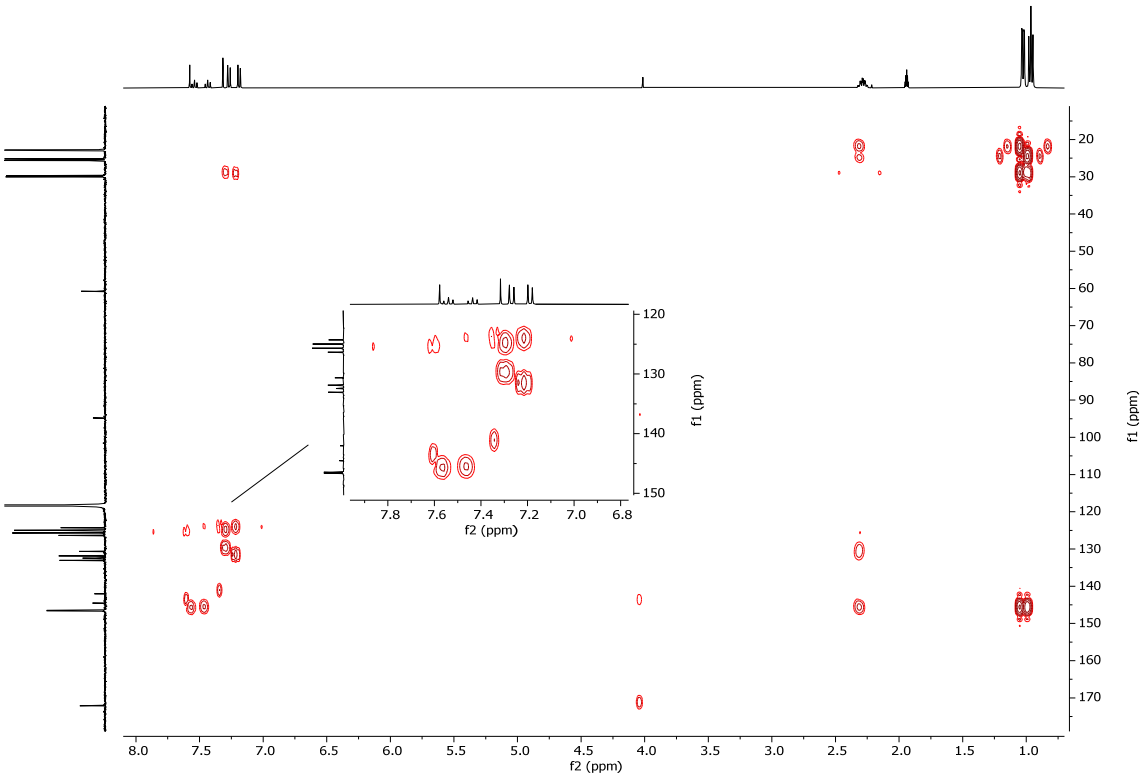


Figure S20. $^{1}H/^{13}C$ HMBC NMR spectrum of **8** in MeCN-d_3.

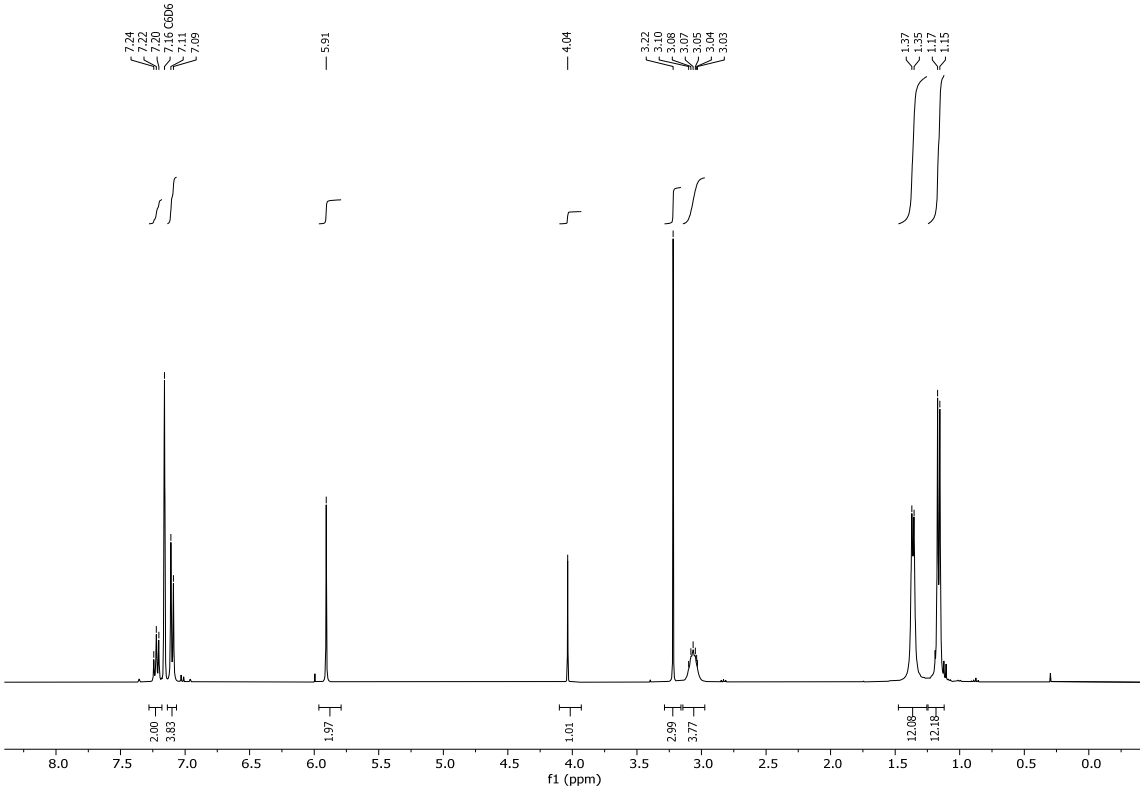


Figure S21. ^{1}H NMR (400 MHz, C_6D_6) spectrum of compound **9**.

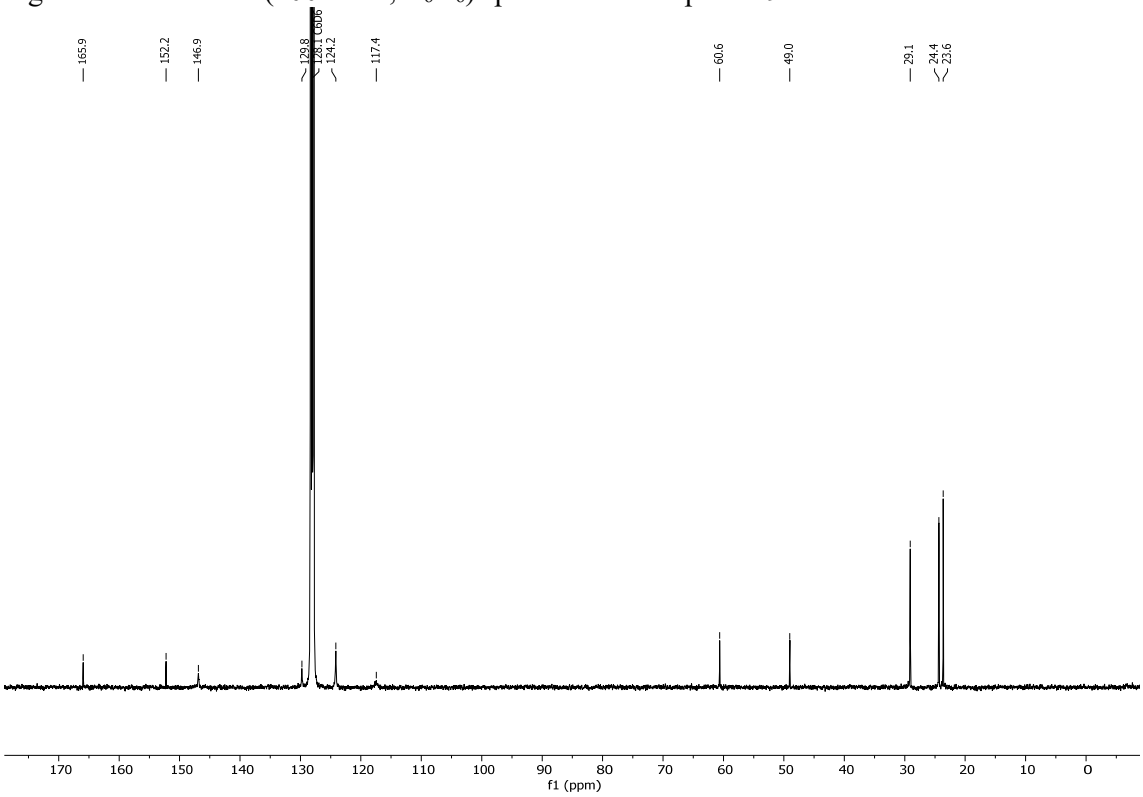


Figure S22. ^{13}C NMR (101 MHz, C_6D_6) spectrum of compound **9**.

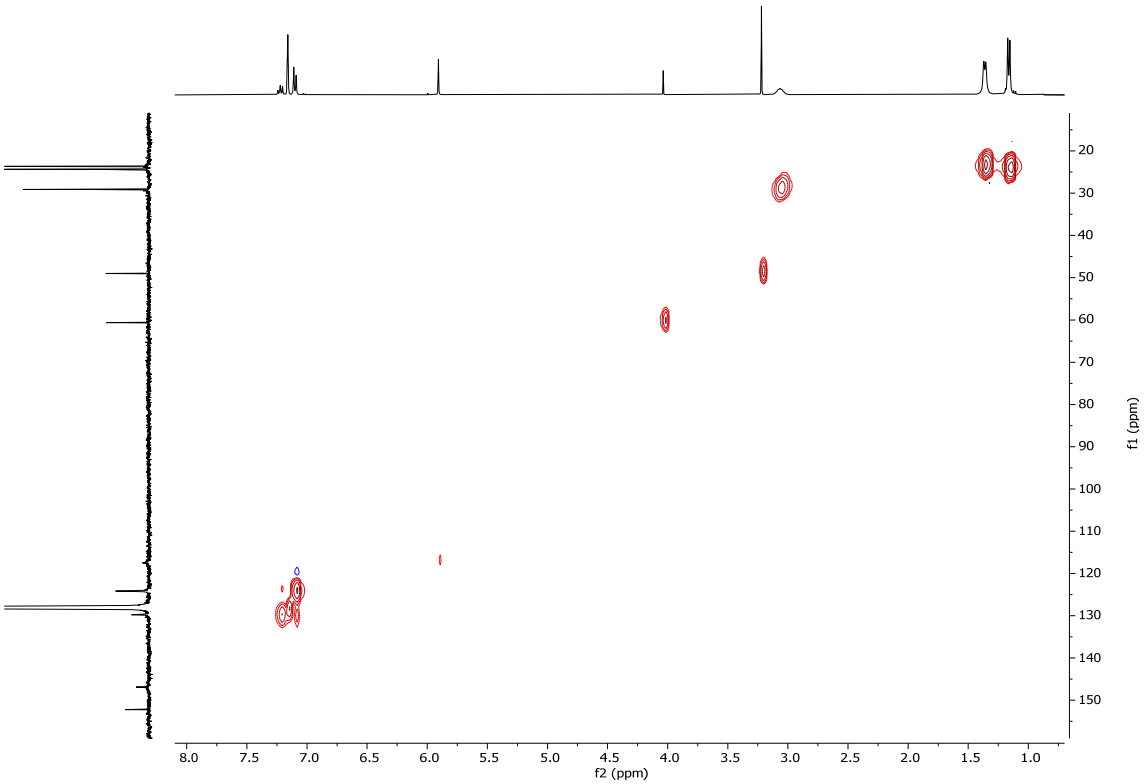


Figure S23. $^{1}H/^{13}C$ HSQC NMR spectrum of **9** in C_6D_6.

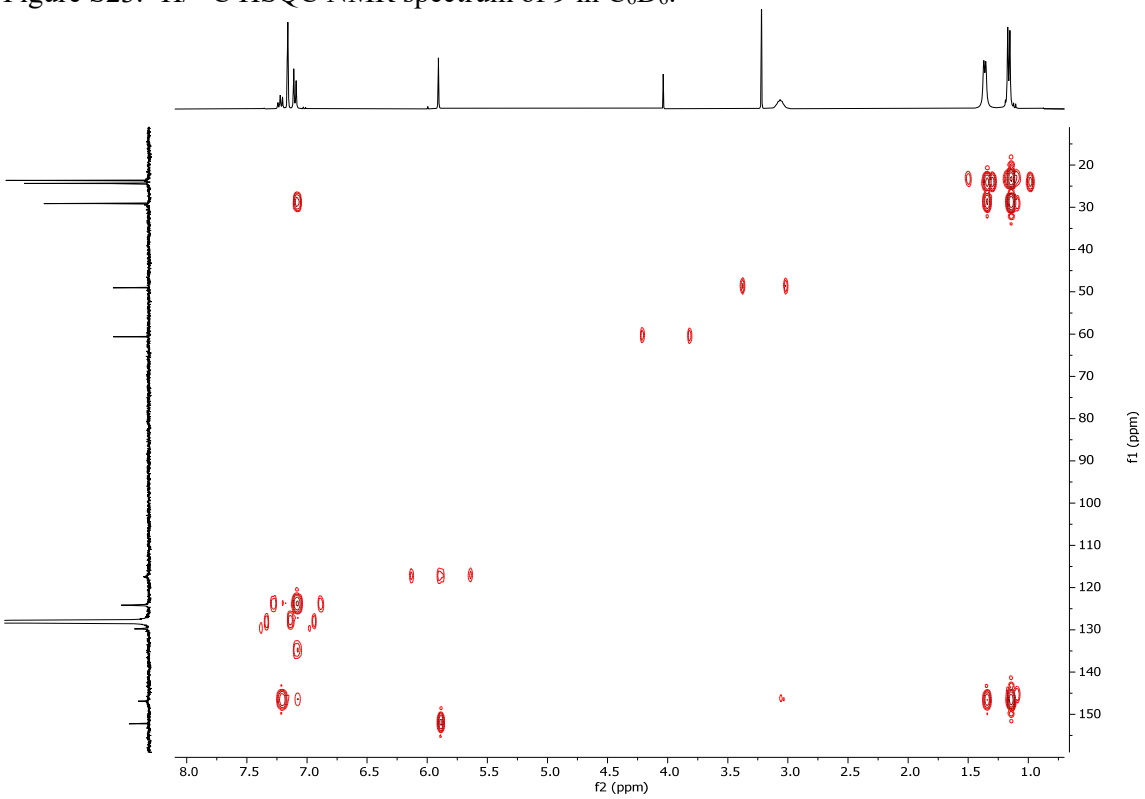


Figure S24. $^{1}H/^{13}C$ HMBC NMR spectrum of **9** in C_6D_6.

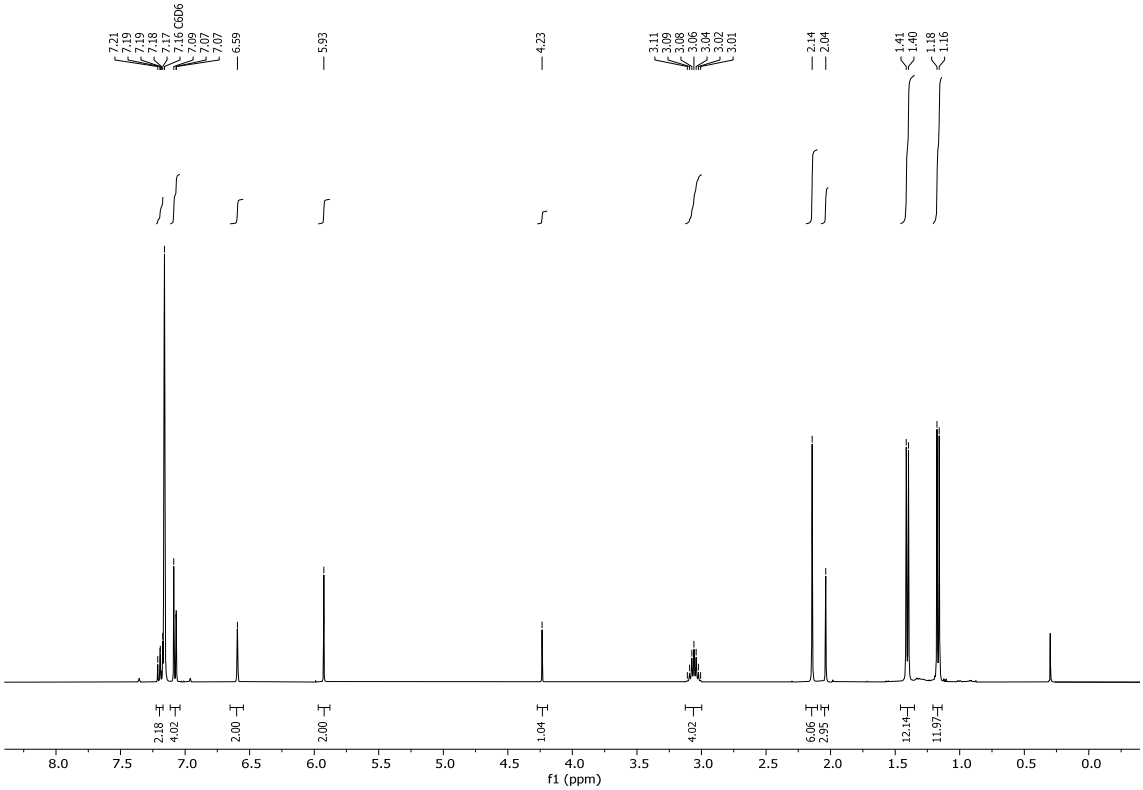


Figure S25. ^{1}H NMR (400 MHz, C_6D_6) spectrum of compound **10**.

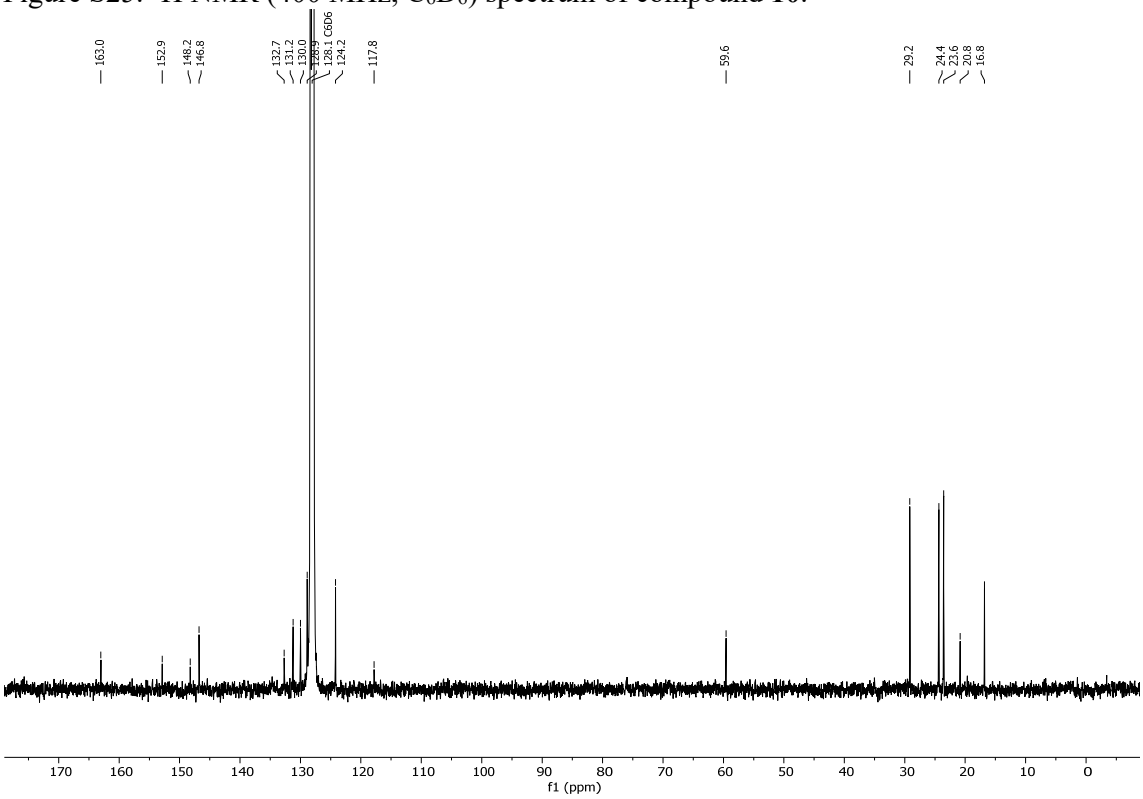


Figure S26. ^{13}C NMR (101 MHz, C_6D_6) spectrum of compound **10**.

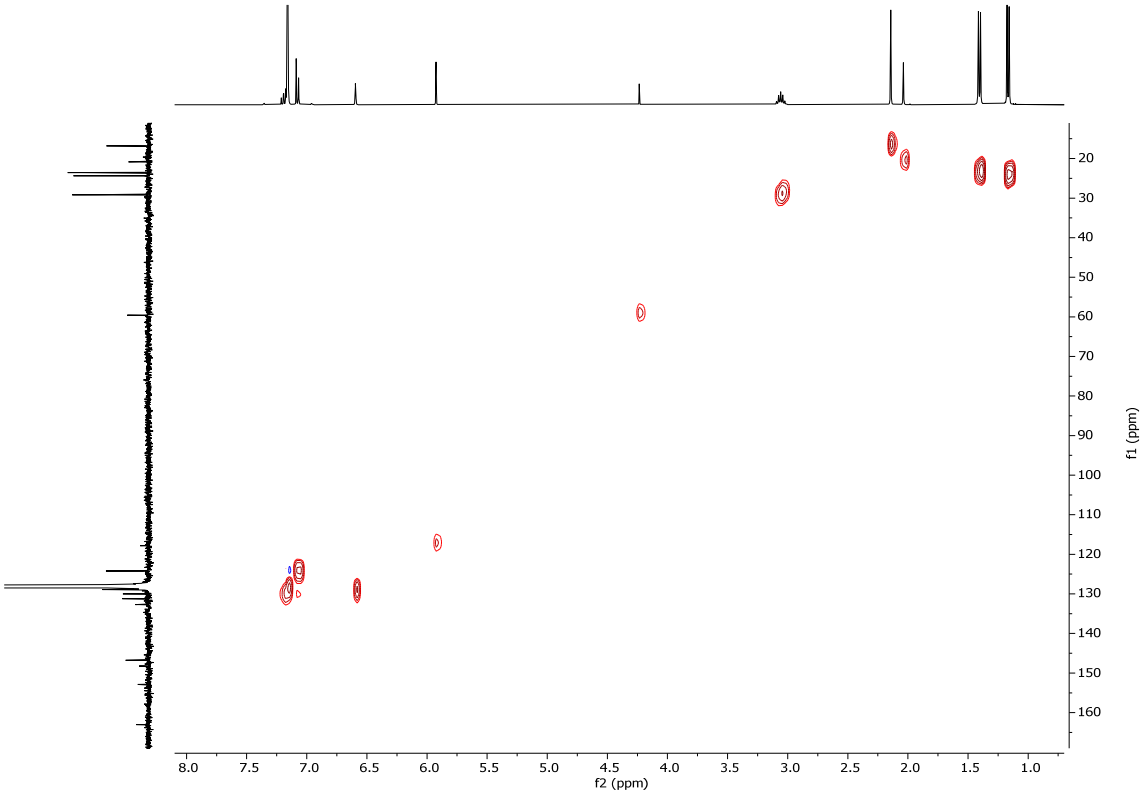


Figure S27. $^{1}H/^{13}C$ HSQC NMR spectrum of **10** in C_6D_6.

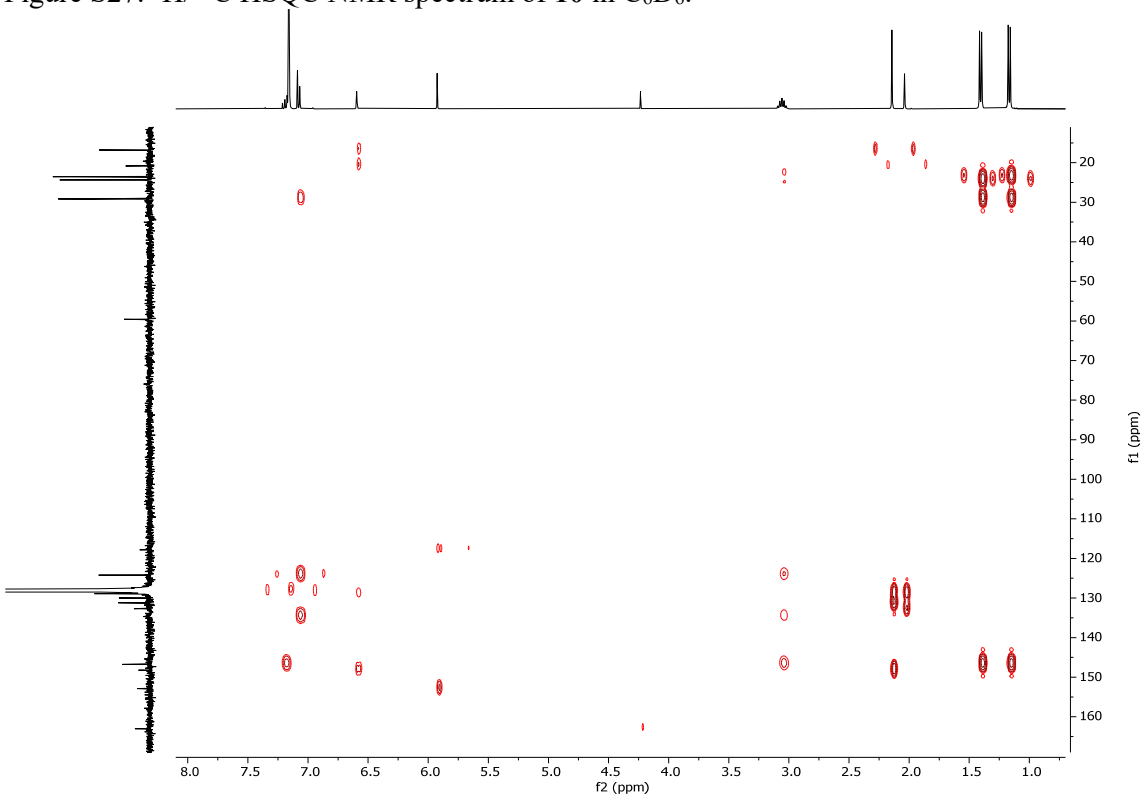


Figure S28. $^{1}H/^{13}C$ HMBC NMR spectrum of **10** in C_6D_6.

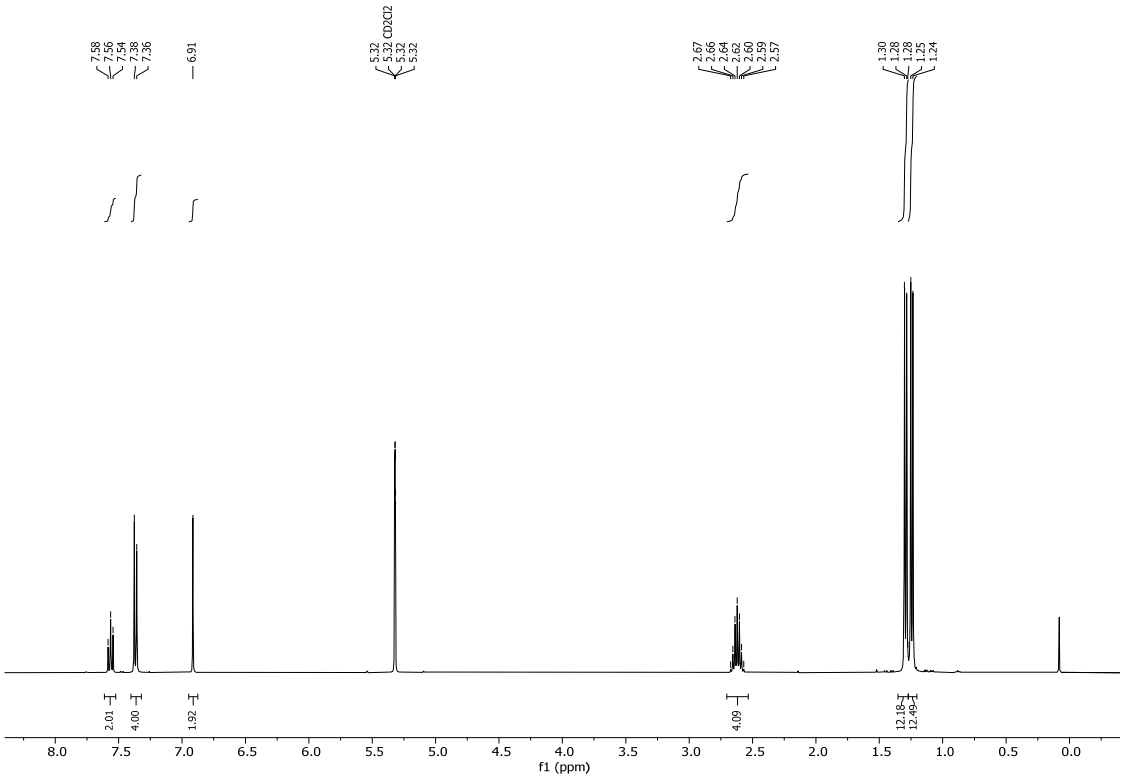


Figure S29. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of compound **11**.

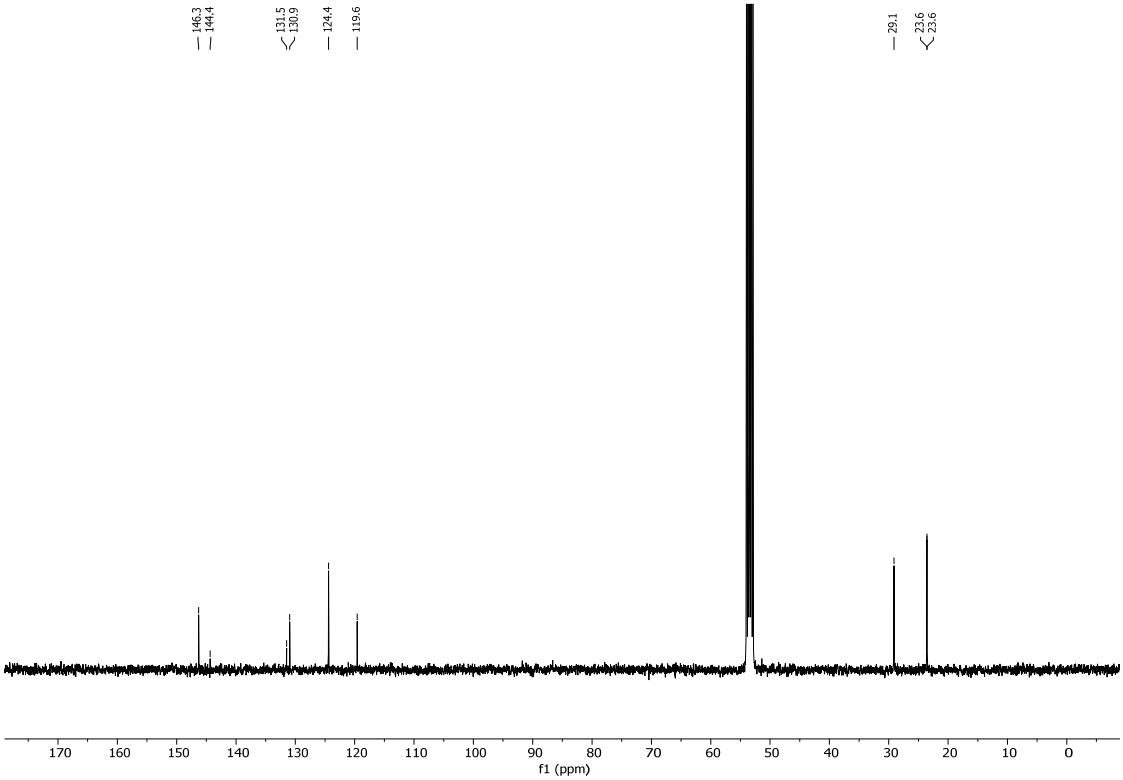


Figure S30. ^{13}C NMR (101 MHz, CD_2Cl_2) spectrum of compound **11**.

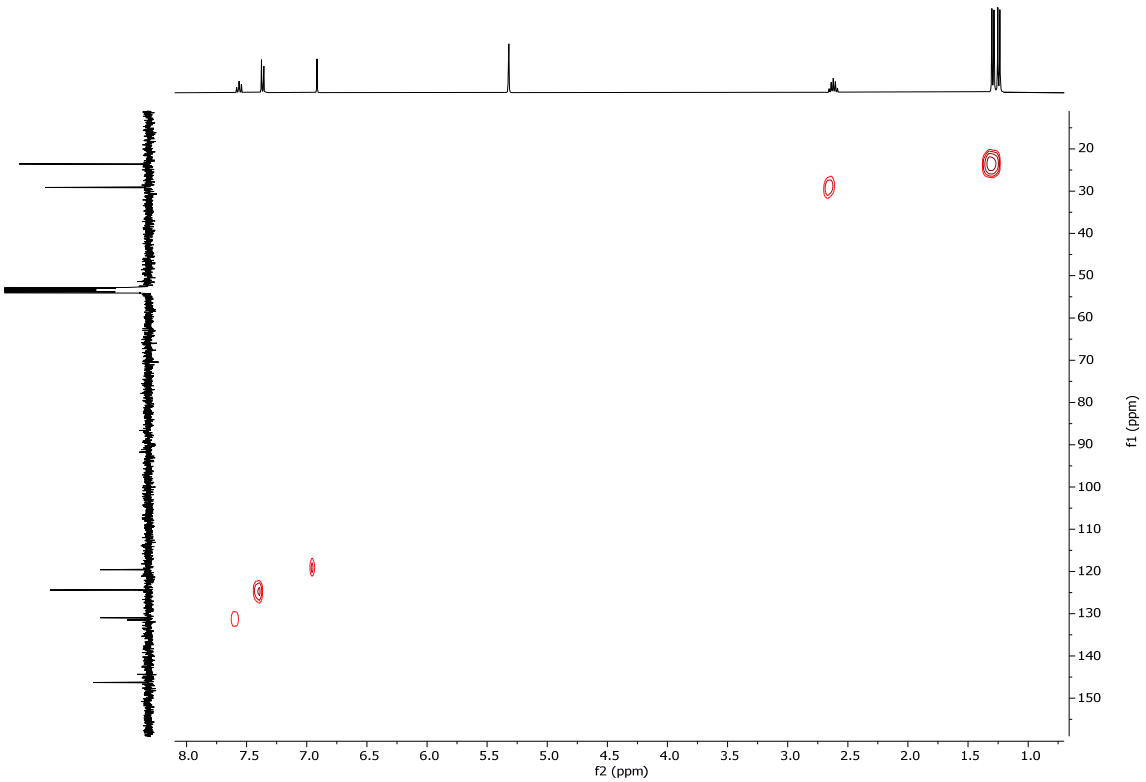


Figure S31. $^{1}H/^{13}C$ HSQC NMR spectrum of **11** in C_6D_6.

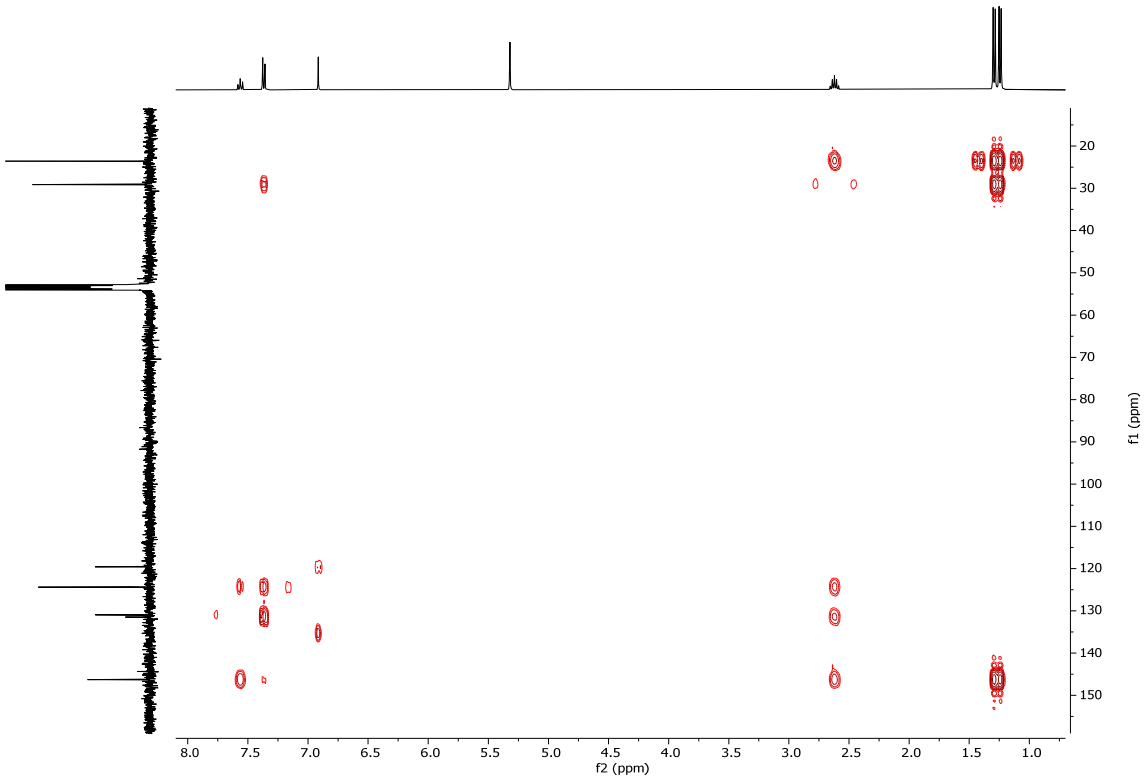


Figure S32. $^{1}H/^{13}C$ HMBC NMR spectrum of **11** in C_6D_6.

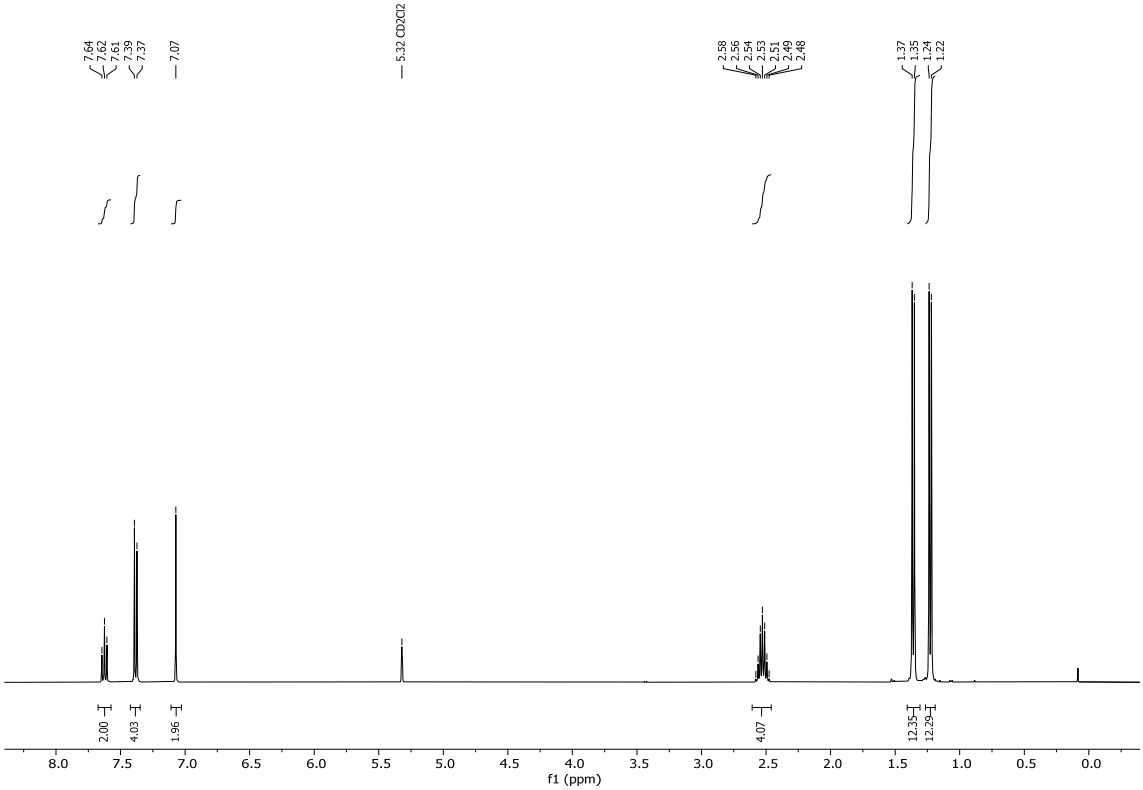


Figure S33. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of complex **12**.

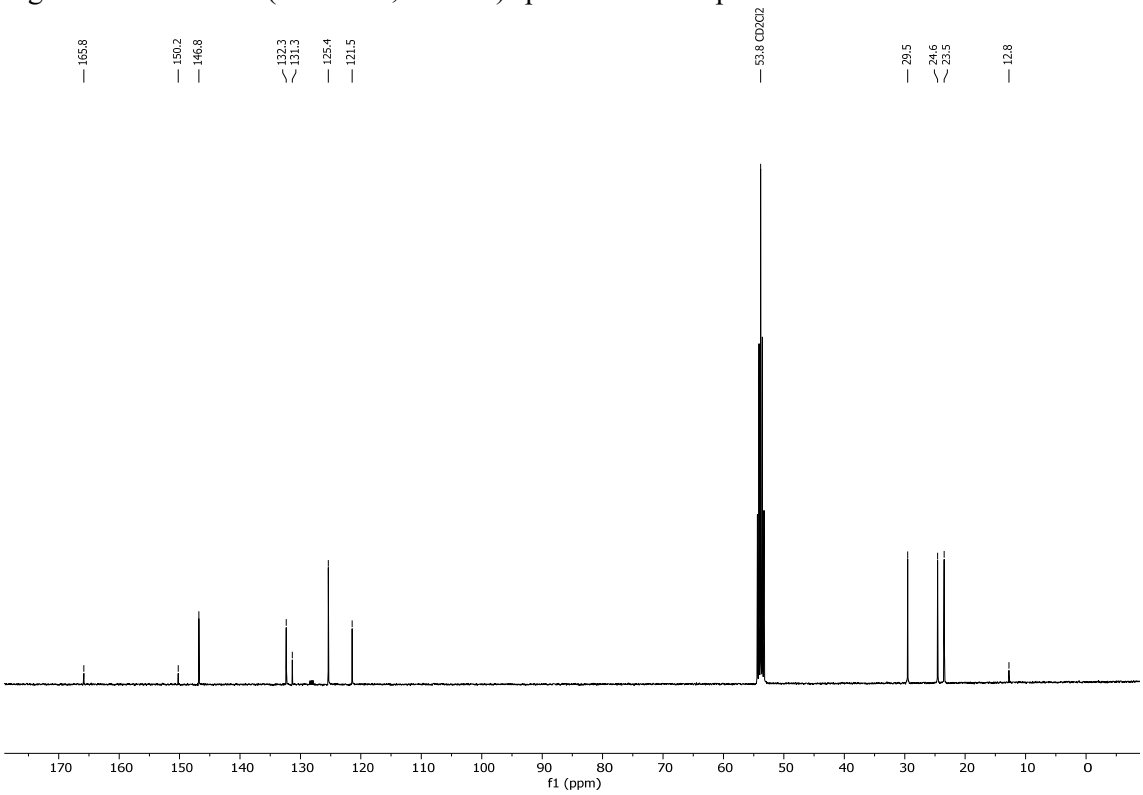


Figure S34. ^{13}C NMR (101 MHz, CD_2Cl_2) spectrum of complex **12**.

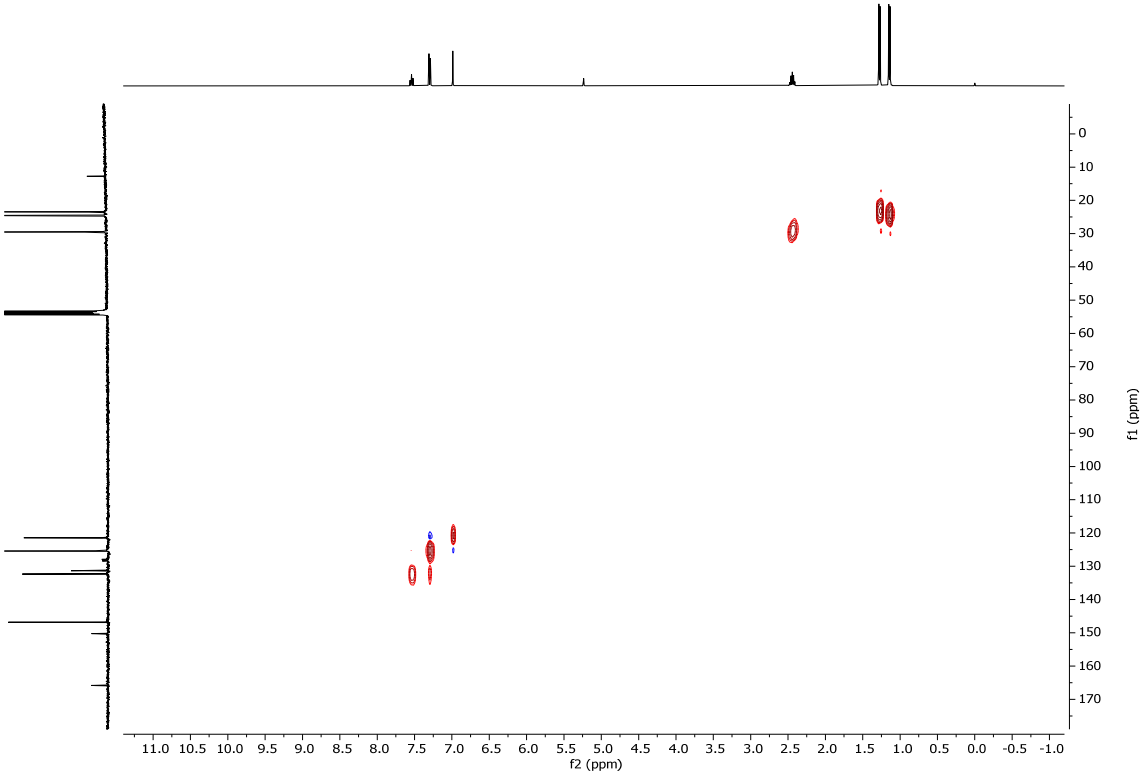


Figure S35. $^{1}H/^{13}C$ HSQC NMR spectrum of **12** in CD_2Cl_2.

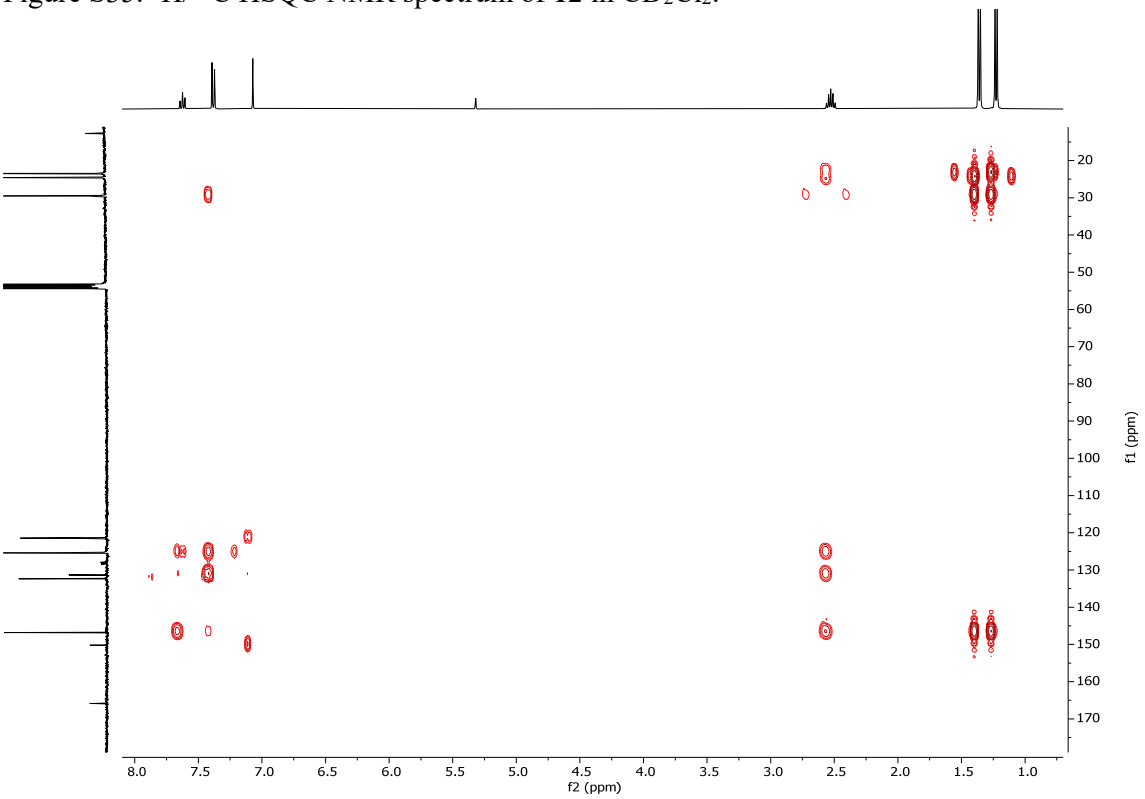


Figure S36. $^{1}H/^{13}C$ HMBC NMR spectrum of **12** in CD_2Cl_2.

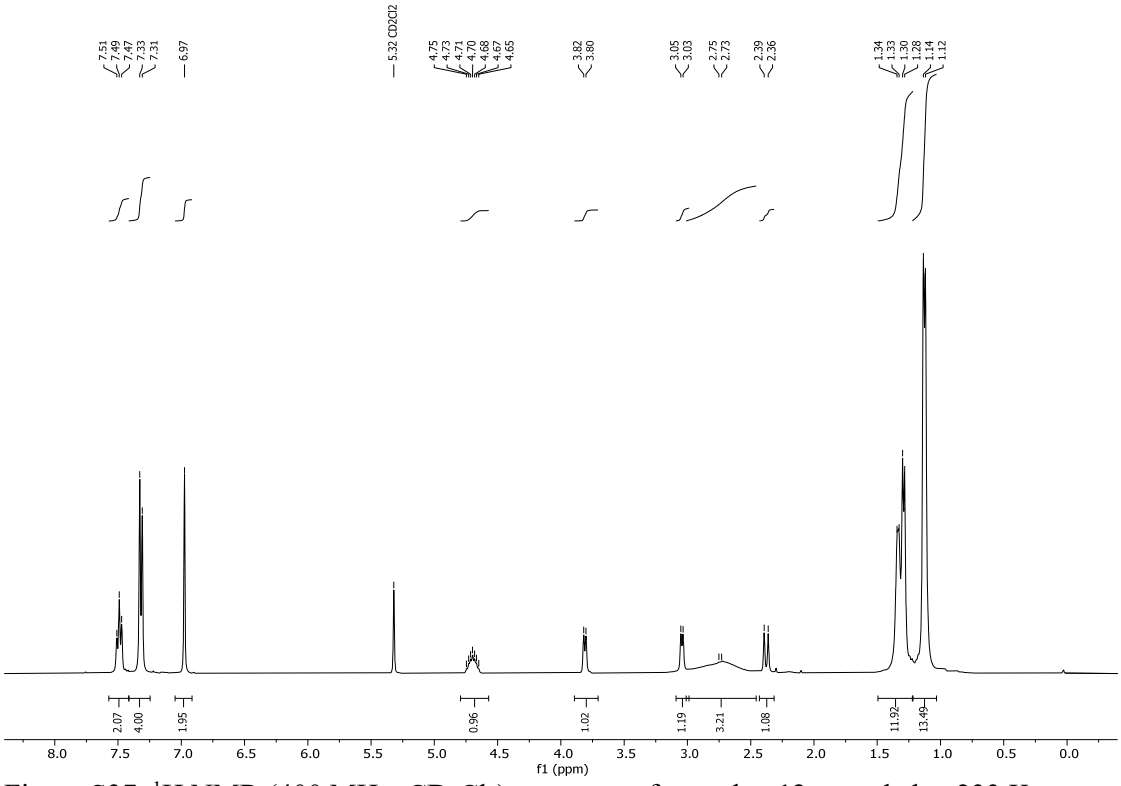


Figure S37. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of complex **13** recorded at 233 K.

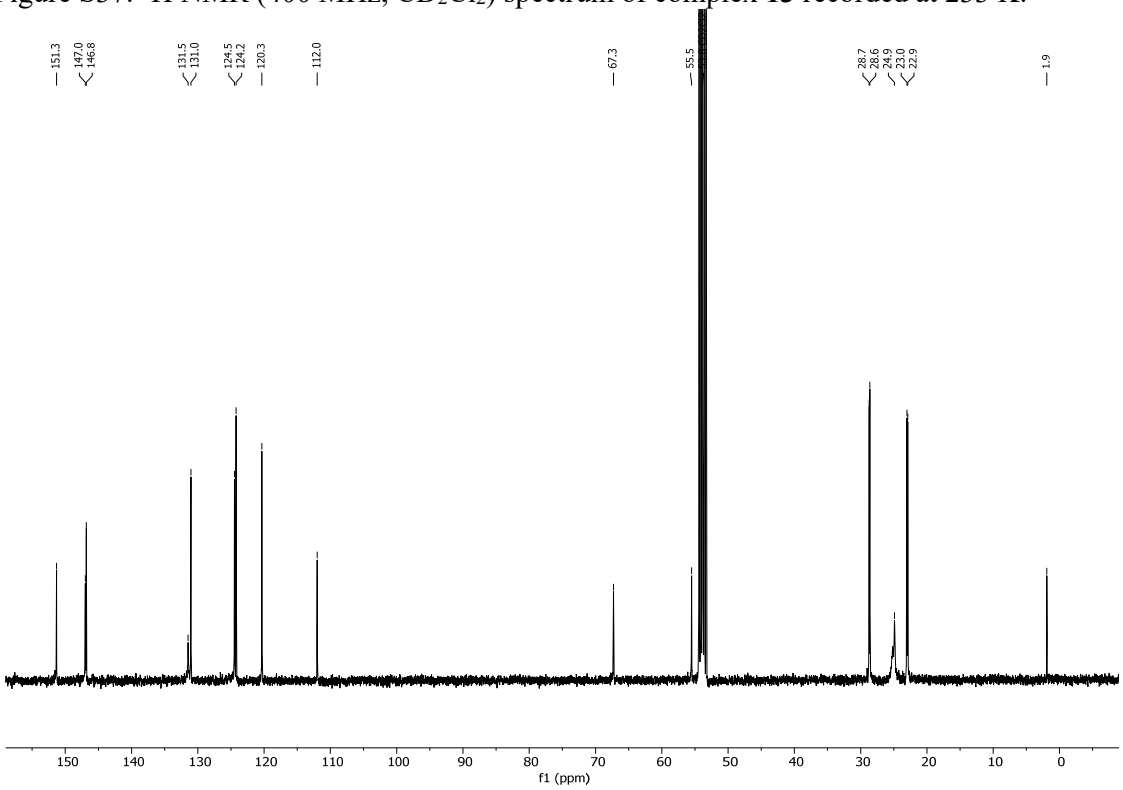


Figure S38. ^{13}C NMR (101 MHz, CD_2Cl_2) spectrum of complex **13** recorded at 233 K.

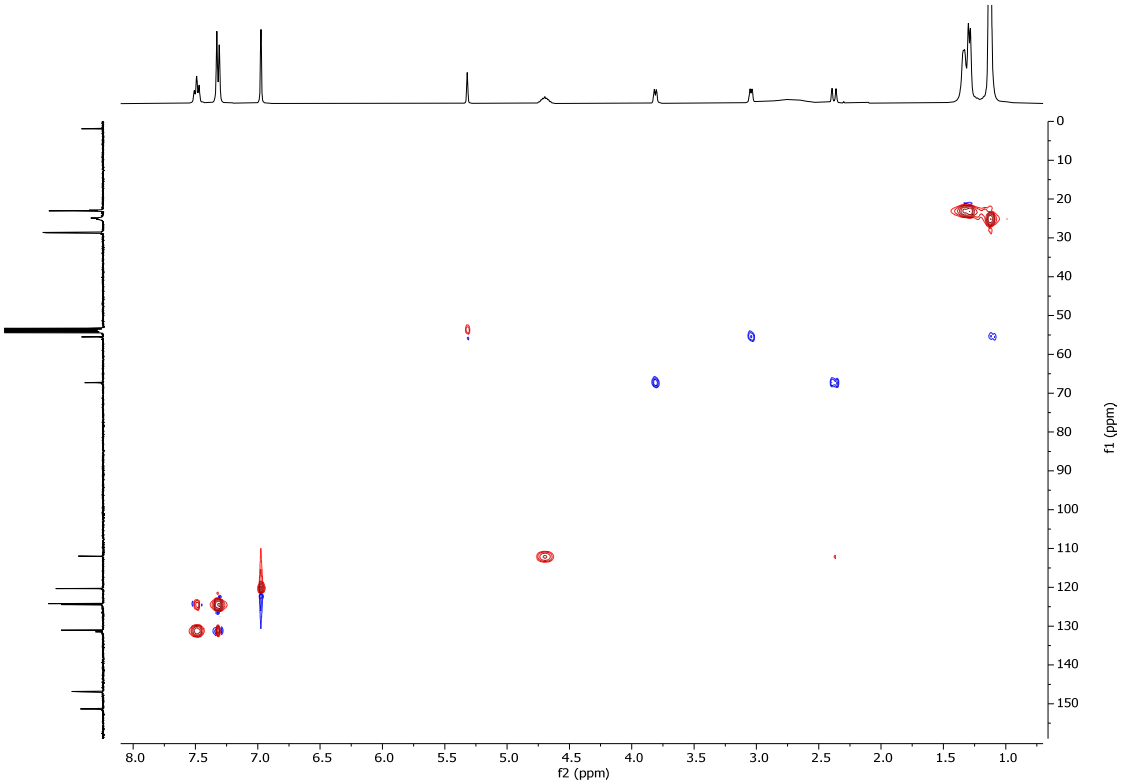


Figure S39. $^{1}H/^{13}C$ HSQC NMR spectrum of **13** in CD_2Cl_2 recorded at 233 K.

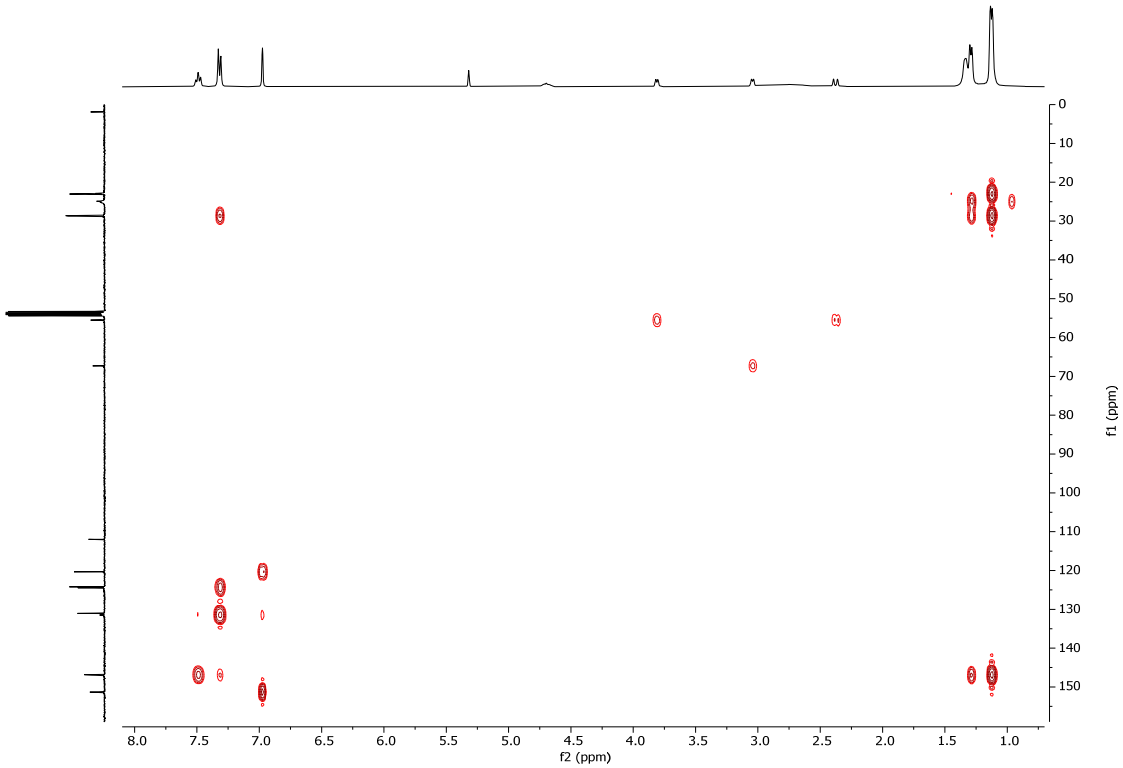


Figure S40. $^{1}H/^{13}C$ HMBC NMR spectrum of **13** in CD_2Cl_2 recorded at 233 K.

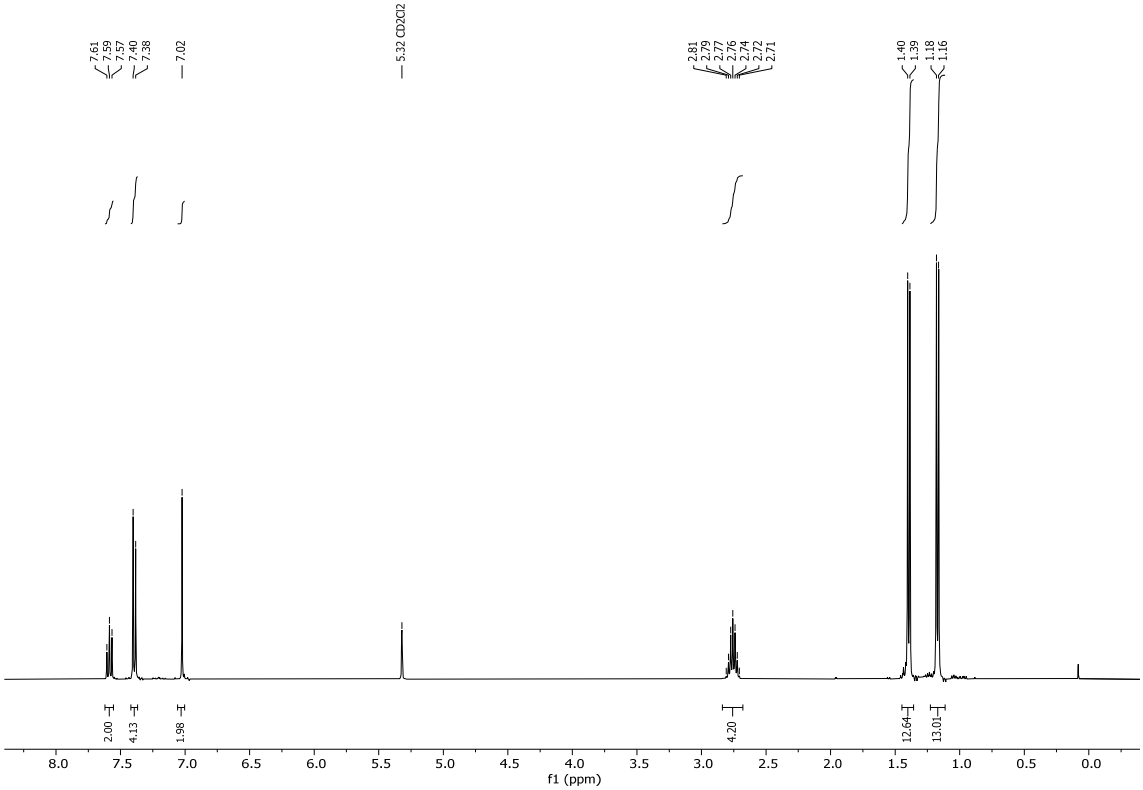


Figure S41. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of complex **14**.

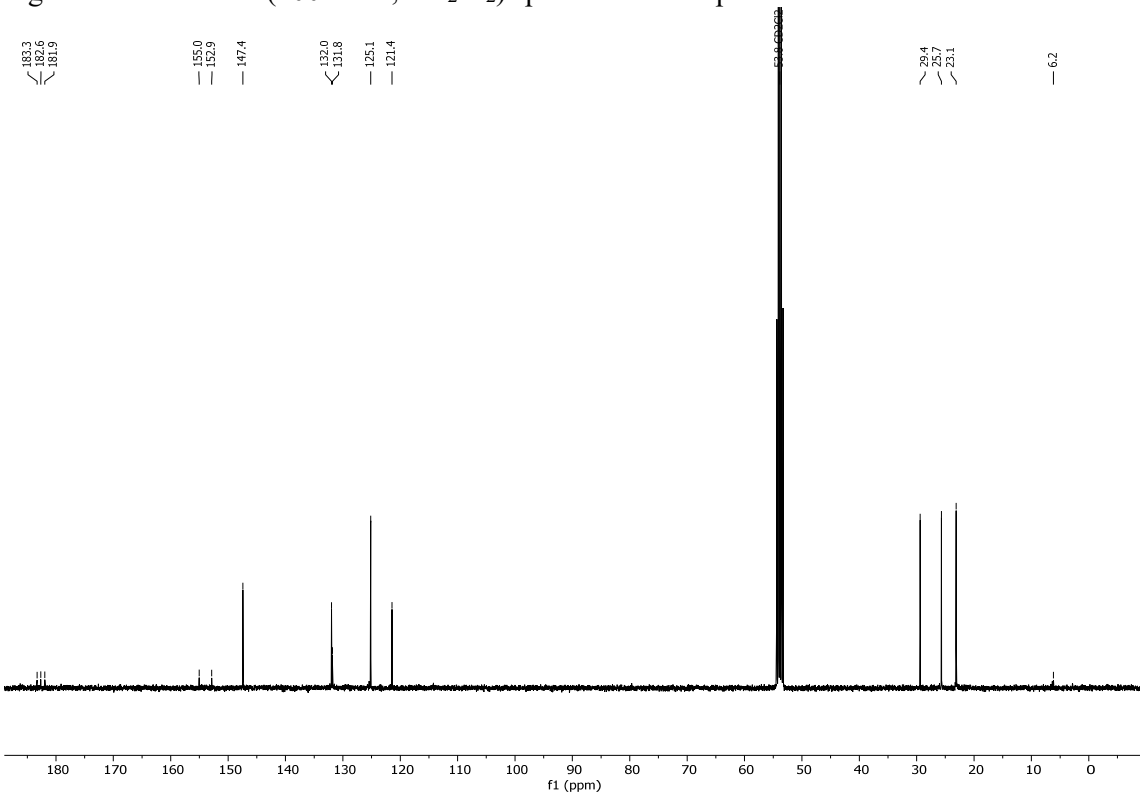


Figure S42. ^{13}C NMR (101 MHz, CD_2Cl_2) spectrum of complex **14**.

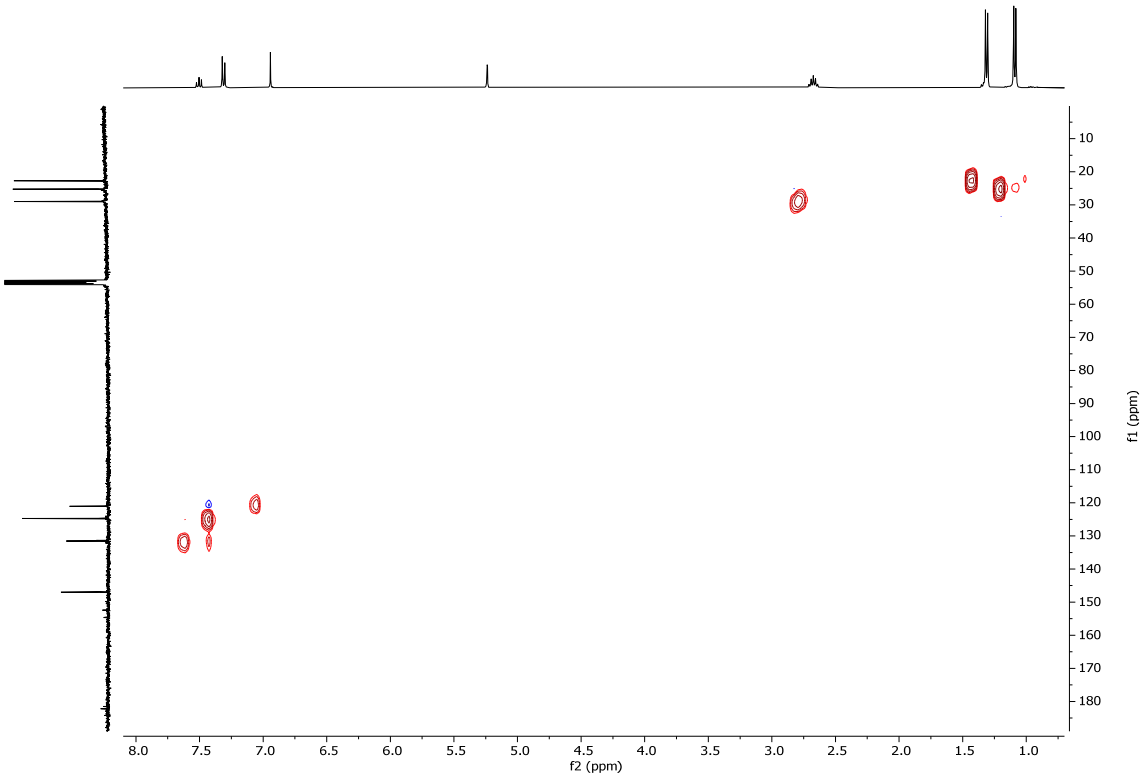


Figure S43. $^{1}H/^{13}C$ HSQC NMR spectrum of **14** in CD_2Cl_2.

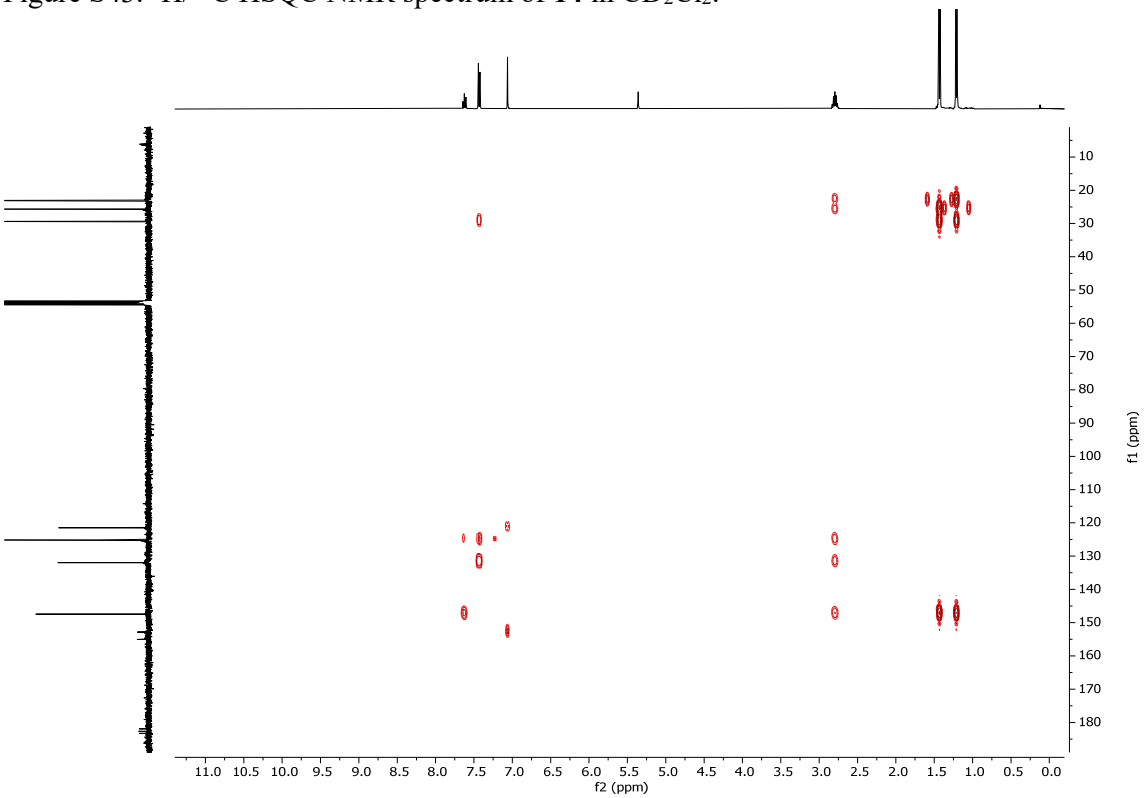


Figure S44. $^{1}H/^{13}C$ HMBC NMR spectrum of **14** in CD_2Cl_2.

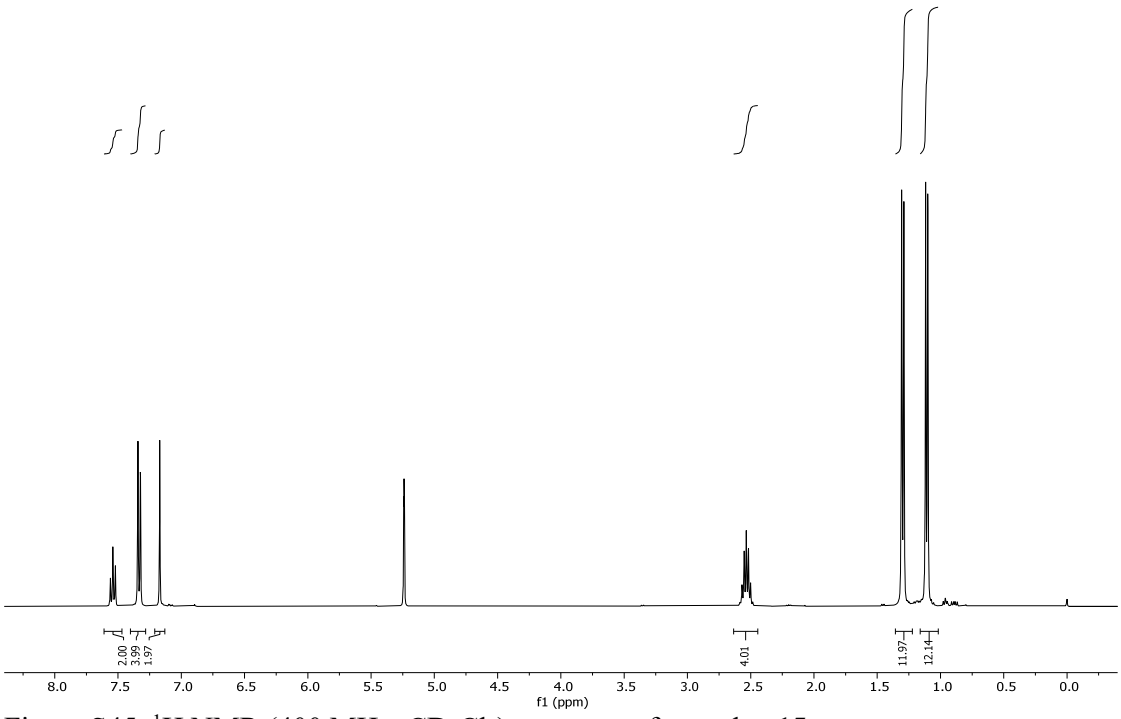


Figure S45. ^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of complex **15**.

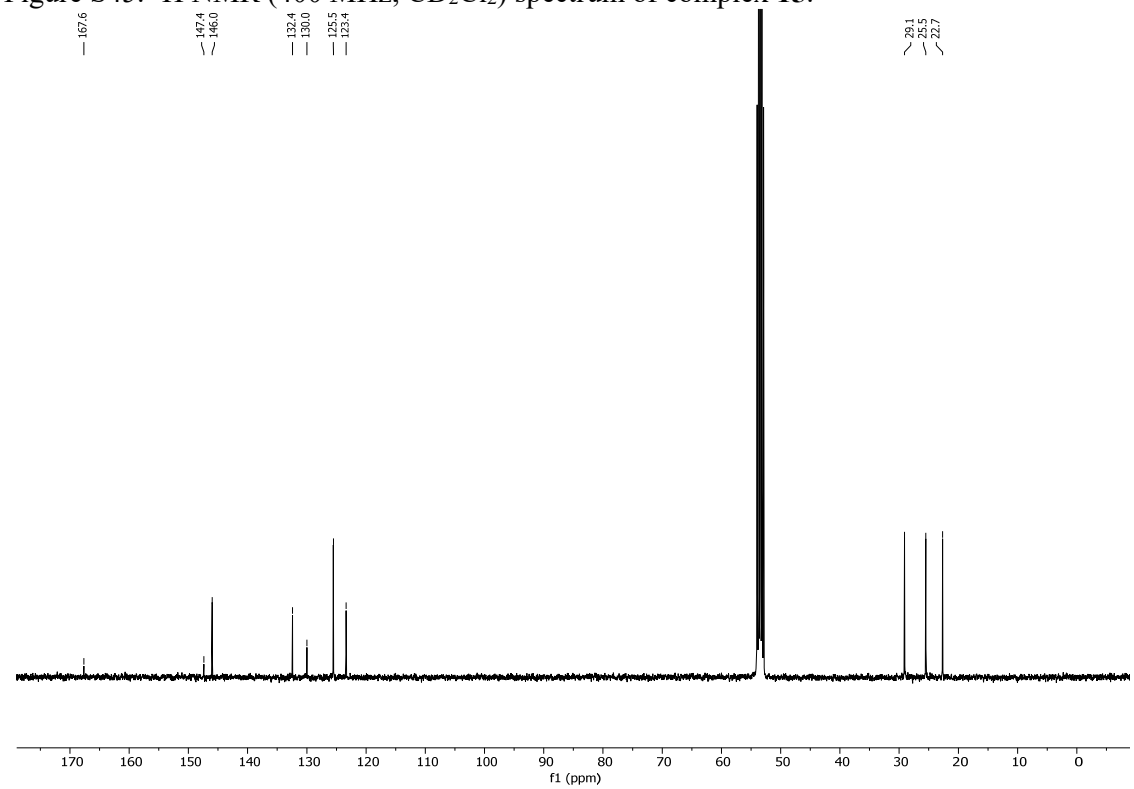


Figure S46. ^{13}C NMR (101 MHz, CD_2Cl_2) spectrum of complex **15**.

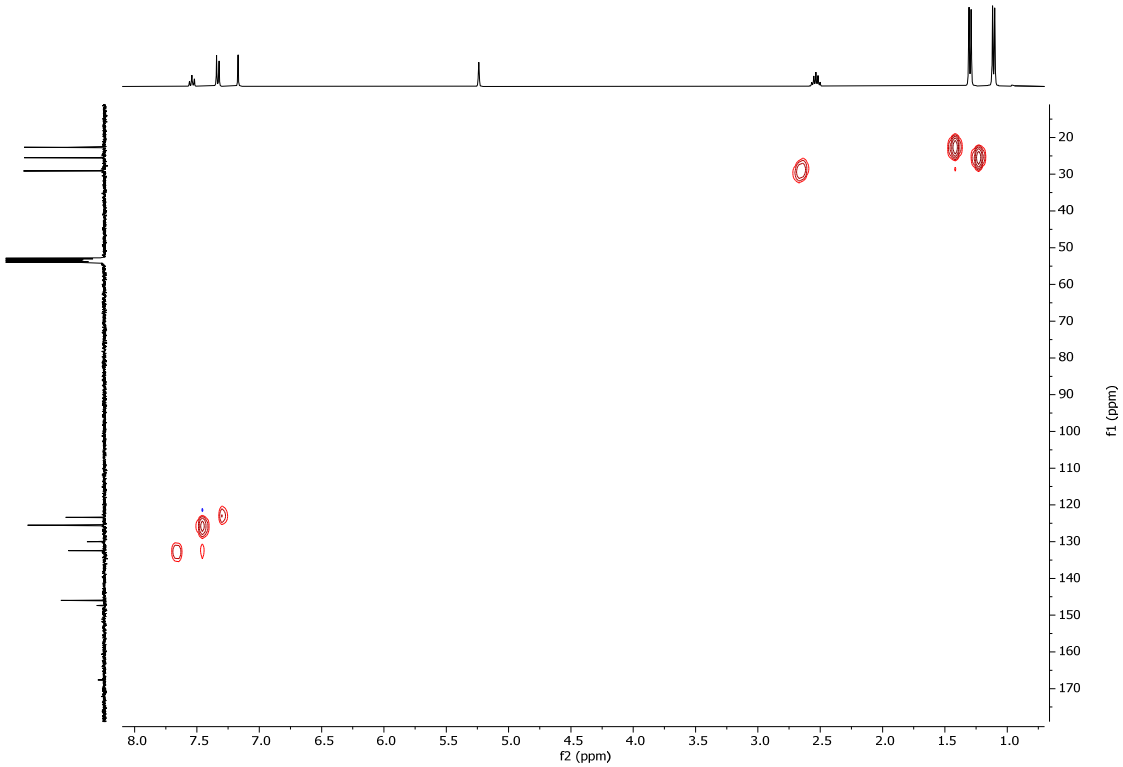


Figure S47. $^{1}H/^{13}C$ HSQC NMR spectrum of **15** in CD_2Cl_2.

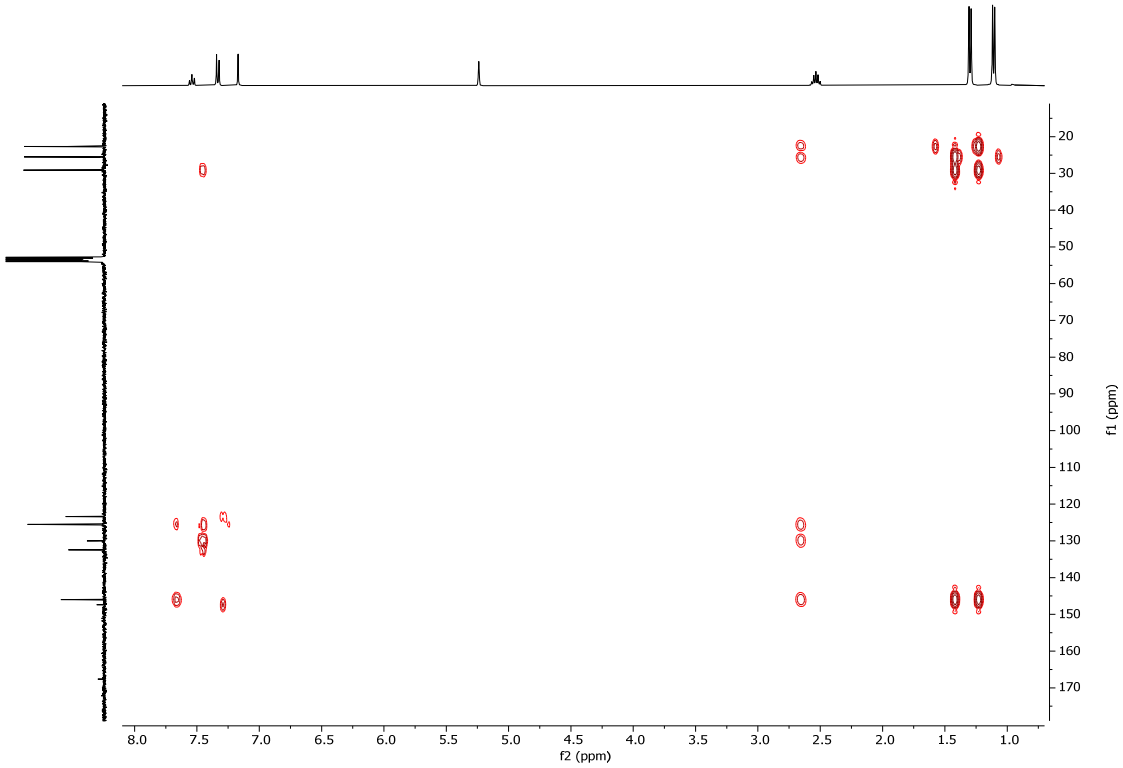


Figure S48. $^{1}H/^{13}C$ HMBC NMR spectrum of **15** in CD_2Cl_2.

4. Dimerization of 4

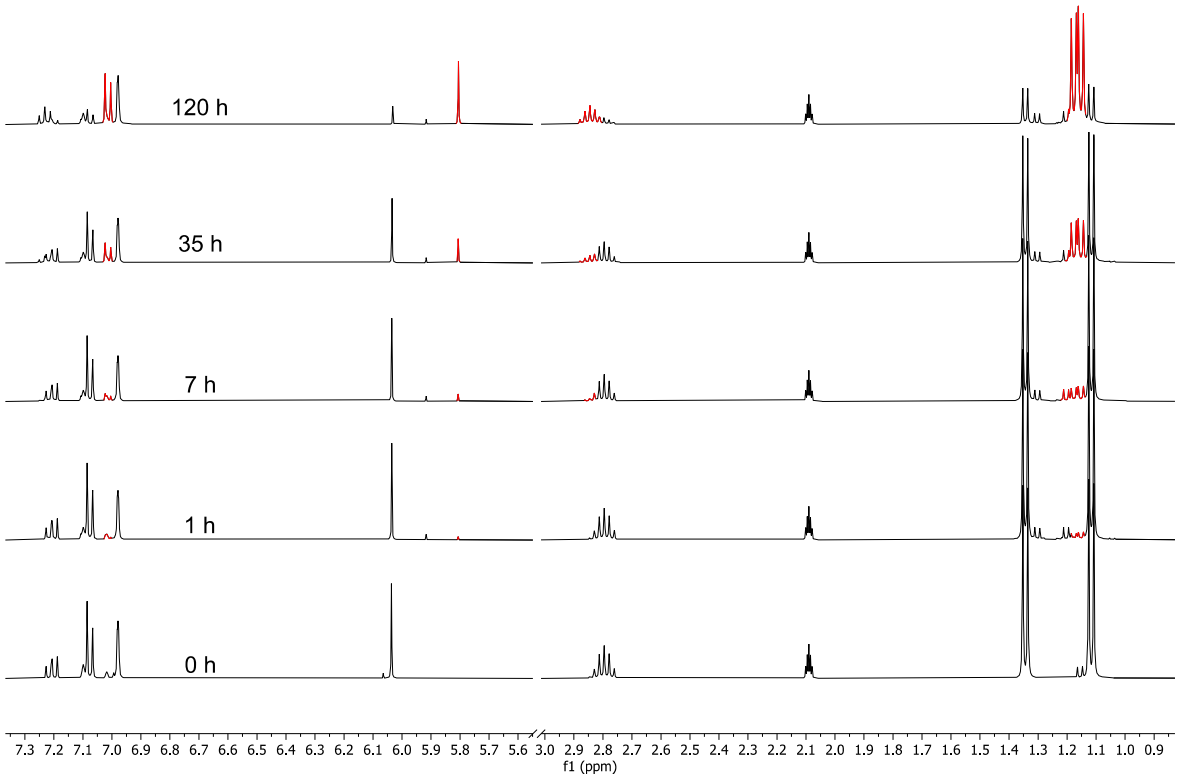
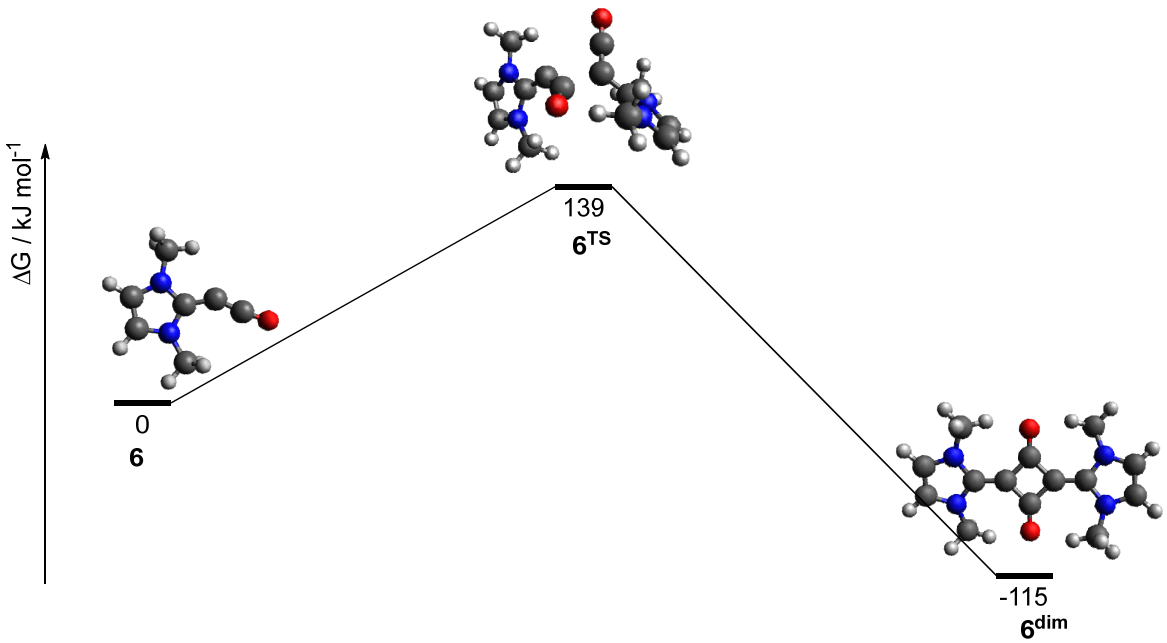


Figure S49. Heating of **4** in toluene-d_8 at 120 °C at different times monitored by ^{1}H NMR (400 MHz). The signals of the newly formed dimer **7** are colored in red.



Scheme S1. Gibbs free energy Δ*G* of the dimerization of alkylidene ketene **6** calculated at the BP86/def2-SVP level of theory including D3 dispersion correction[2] and Becke-Johnson damping.[3] The dimerization is thermodynamically favored, however, kinetically inhibited as evidenced from the high transition state barrier. Since **6** does not exhibit any steric bulk, the kinetic stability of the alkylidene ketenes **4**–**6** is rooted in their electronic properties. The higher tendency of **4** to dimerize, in spite of its larger steric bulk, is possible due to attractive dispersion interactions which were already found to be responsible for the dimerization of other bulky compounds.[4]

5. Isotopic shift of CO stretching vibration in complex 14

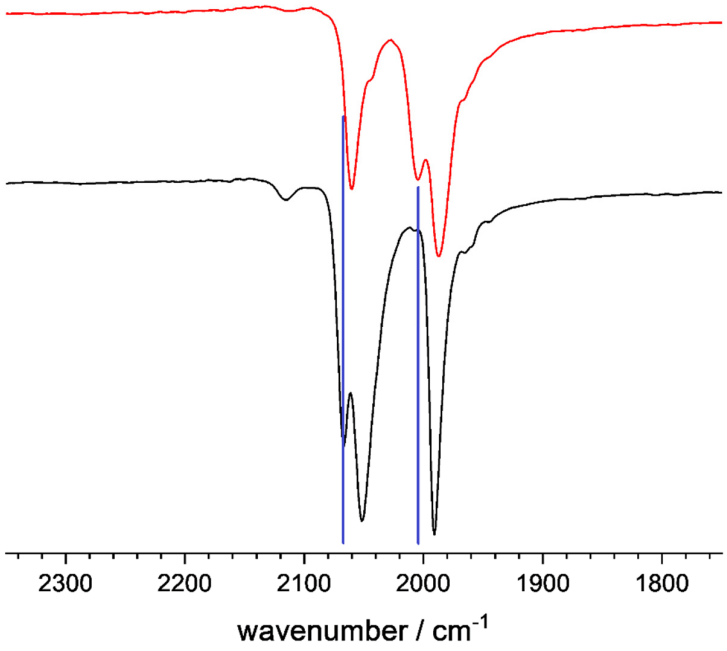


Figure S50. IR spectrum of complex **14** prepared with unlabeled methyleneketene **4** (black line) and ^{13}C labeled **4**^{13C} (red line). The isotopic shift of the C=O stretching is indicated by blue bars.

6. Single crystal X-ray analyses

Bragg-intensities of **4**, **5**, **6**, **7**, **8**, **9**, **10**, **11**, **12, 13, 14** and **15** were collected at 140.00(10) K using Cu*Kα* radiation. A Rigaku SuperNova dual system diffractometer with an Atlas S2 CCD detector was used for compounds **4**, **5**, **10**, **11**, **12** and **14**, and one equipped with an Atlas CCD detector for compounds **6**, **8**, **9**, **13** and **15**. A suitable crystal was selected and mounted on a XtaLAB Synergy R, DW system, HyPix-Arc 150 diffractometer. The datasets were reduced and corrected for absorption, with the help of a set of faces enclosing the crystals as snugly as possible, with *CrysAlis*^{Pro}.[5] The solutions and refinements of the structures were performed by the latest available version of *ShelXT*[6] and *ShelXL*.[7] All non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on $|F|^2$. The hydrogen atoms were placed at calculated positions by means of the "riding" model in which each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent C-atom (1.5 U_{eq} for the methyl groups). Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif. The CCDC codes of each compound are given in Table S2 containing the X-ray diffraction data (see below).

The C_2O group of compound **4** is disordered across a two-fold rotation axis (Figure S51). Based on the bond lengths, it is evident that C4 is connected to O4, and C4' to O4'. However, there is some ambiguity regarding the connectivity between C3 and C4. Model A assumes that C3 is bound to C4', whereas Model B assumes that C3 is bound to C4. The geometric parameters of Model A are closer to what was found for the structurally related compounds **5** and **6**. Furthermore, Model A represents a better match with the calculated structure of **4** (see below, Table S1). Therefore, Model A is preferred over Model B.

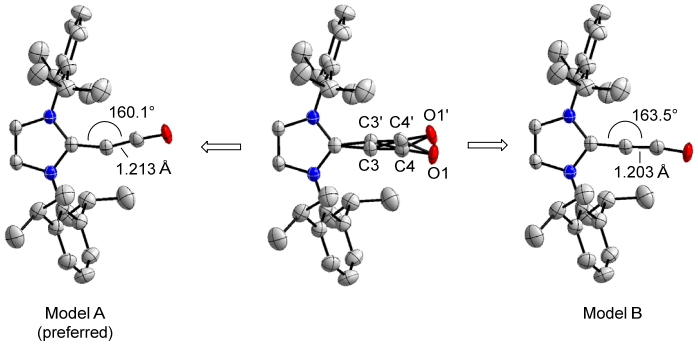


Figure S51. Disorder of the C_2O group in compound **4**.

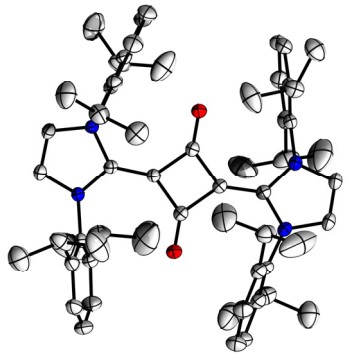


Figure S52. Molecular structure of dimer **7** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

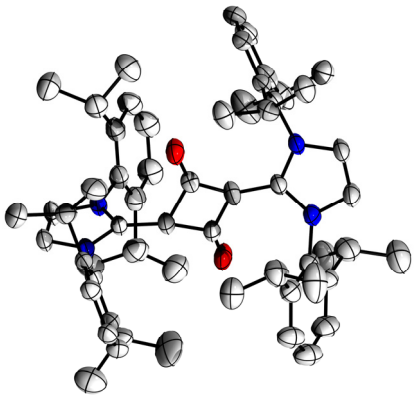


Figure S53. Molecular structure of dimer **8** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and the bromide anion are omitted for clarity. The isopropyl group and the cyclobutene dione ring are disordered. Only one molecule of the asymmetric unit is shown.

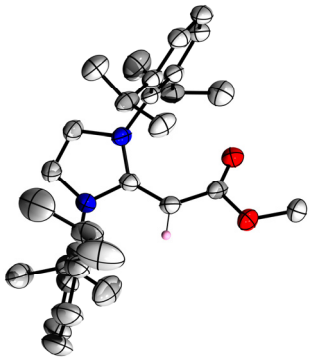


Figure S54. Molecular structure of the methanol adduct **9** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms (except for C2) are omitted for clarity. The isopropyl groups are disordered. Only one molecule of the asymmetric unit is shown.

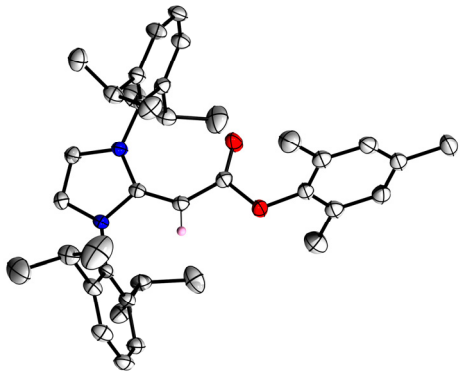


Figure S55. Molecular structure of the mesitol adduct **10** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms (except for C2) are omitted for clarity. The isopropyl groups are disordered.

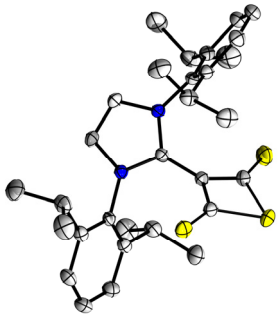


Figure S56. Molecular structure of the CS_2 adduct **11** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. The asymmetric unit contains one molecule CS_2 (not shown).

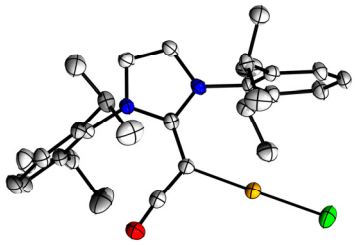


Figure S57. Molecular structure of the AuCl complex **12** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

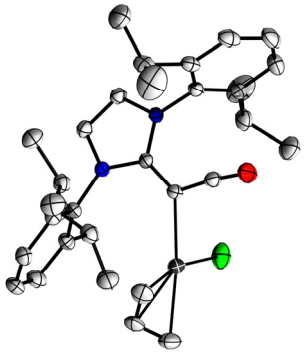


Figure S58. Molecular structure of the Pd(allyl)Cl complex **13** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. The asymmetric unit contains one solvent molecule benzene (not shown). The allyl ligand is disordered.

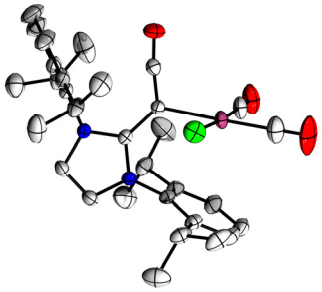


Figure S59. Molecular structure of the $RhCl(CO)_2$ complex **14** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

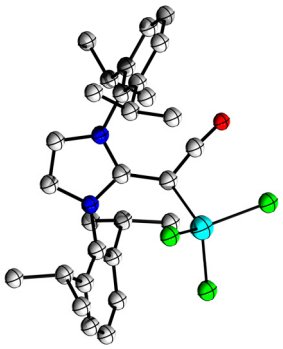


Figure S60. Molecular structure of the $GaCl_3$ complex **15** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. The $GaCl_3$ moiety is disordered.

Table S1. Characteristic bond lengths (pm) as well as C–C–CO bent angle (°) of **4**–**6** and of complexes **12**–**15** as determined by X-ray diffraction analysis. Structural parameters of **4** calculated on the BP86/def2-SVP (**4**$_{BP86}$) or M062X/6-311+G(d,p) (**4**$_{M062X}$) level of theory are shown as well. The DFT methods were chosen to be the same as the ones used by Tonner and Frenking[8] for the investigation of divalent carbon(0) compounds and by us for the calculation of diazoolefins, respectively.[1]

	C–C_2O	C–CO	C–O	C–M	C–C–CO
4	137.6(3)	121.3(5)	120.4(3)	--	160.1(12)
4$_{BP86}$ (bent)	137.0	129.0	119.6	--	146.2
4$_{BP86}$ (linear)	135.8	127.6	119.9	--	179.5
4$_{M062X}$ (bent)	137.6	128.1	117.9	--	137.1
5	137.45(17)	123.41(18)	118.18(17)	--	136.14(13)
6	138.6(2)	123.9(2)	120.63(14)	--	149.51(12)
12 (M = Au)	141.8(6)	131.7(8)	115.6(8)	203.8(5)	123.1(5)
13 (M = Pd)	140.2(3)	130.2(3)	117.0(3)	214.4(2)	123.9(2)
14 (M = Rh)	140.7(3)	129.7(3)	116.7(3)	213.3(2)	126.17(19)
15 (M = Ga)	143.7(2)	131.7(3)	115.6(2)	200.92(17)	119.80(16)

Table S2. Crystallographic data for the compounds **4**–**15**.

Compound	**4**	**5**	**6**
Empirical Formula	$C_{29}H_{36}N_2O$	$C_{23}H_{24}N_2O$	$C_7H_8N_2O$
$\rho_{calc.}$ / g cm^{-3}	0.928	1.180	1.323
μ / mm^{-1}	0.428	0.564	0.752
Formula Weight	428.60	344.44	136.15
Colour	colourless	clear light orange	clear light yellow
Shape	plate-shaped	prism-shaped	plate-shaped
Size/mm^3	0.28×0.13×0.04	0.14×0.06×0.05	0.22×0.17×0.03
Temperature / K	140.00(10)	140.00(10)	140.00(10)
Crystal System	monoclinic	monoclinic	monoclinic
Space Group	$I2/a$	$P2_1/c$	$P2_1/c$
a/Å	16.8250(4)	9.28771(11)	6.2198(3)
b/Å	8.93762(18)	13.5951(2)	15.0126(7)
c/Å	21.4865(4)	15.3562(3)	7.3727(3)
α/°	90	90	90
β/°	108.212(2)	90.7900(15)	96.876(4)
γ/°	90	90	90
V/Å^3	3069.19(12)	1938.80(5)	683.47(6)
Z	4	4	4
Z'	0.5	1	1
Wavelength / Å	1.54184	1.54184	1.54184
Radiation type	Cu$K\alpha$	Cu$K\alpha$	Cu$K\alpha$
Θ_{min} / °	4.332	4.344	5.895
Θ_{max} / °	72.721	76.060	72.347
Measured Reflections	3163	40503	3278
Independent Reflections	3163	3989	1312
Reflections [I ≥ 2σ(I)]	2346	3238	1156
R_{int}	n/a	0.0211	0.0119
Parameters	165	247	95
Restraints	18	0	0
Larges Peak / e · A^3	0.130	0.203	0.127
Deepest Hole / e · A^3	-0.201	-0.199	-0.230
GooF	0.996	1.016	1.068
wR_2 (all data)	0.1035	0.1086	0.0891
wR_2	0.1002	0.1019	0.0849
R_1 (all data)	0.0493	0.0489	0.0372
R_1	0.0379	0.0385	0.0321
CCDC number	2094730	2097046	2108061

Compound	**7**	**8**	**9**
Empirical Formula	$C_{58}H_{72}N_4O_2$	$C_{59}H_{75}Br_{0.47}Cl_{2.53}N_4O_2$	$C_{30}H_{40}N_2O_2$
$\rho_{calc.}$ / g cm^{-3}	1.110	1.107	1.098
μ / mm^{-1}	0.512	1.867	0.528
Formula Weight	857.19	999.53	460.64
Colour	clear intense yellow	clear light yellow	clear pale colourless
Shape	prism-shaped	prism-shaped	irregular
Size/mm^3	0.59×0.39×0.12	0.60×0.36×0.09	0.20×0.16×0.10
Temperature / K	140.00(10)	140.00(10)	140.00(10)
Crystal System	monoclinic	monoclinic	triclinic
Space Group	$I2/a$	$P2_1/c$	$P\bar{1}$
a/Å	21.7877(2)	24.5239(7)	11.8074(4)
b/Å	12.66021(12)	29.6444(9)	16.1835(6)
c/Å	37.7430(4)	16.5867(5)	16.6250(7)
α/°	90	90	62.421(4)
β/°	99.9129(10)	95.752(3)	83.645(3)
γ/°	90	90	82.289(3)
V/Å^3	10255.47(18)	11997.8(6)	2786.1(2)
Z	8	8	4
Z'	1	2	2
Wavelength / Å	1.54184	1.54184	1.54184
Radiation type	Cu$K\alpha$	Cu$K\alpha$	Cu$K\alpha$
Θ_{min} / °	3.688	2.981	3.003
Θ_{max} / °	76.063	72.610	72.806
Measured Reflections	60758	61782	11529
Independent Reflections	10659	23200	11529
Reflections [I ≥ 2σ(I)]	9079	12412	7996
R_{int}	0.0392	0.0860	n/a
Parameters	666	1356	695
Restraints	160	1203	708
Larges Peak / e · A^3	0.480	0.746	0.343
Deepest Hole / e · A^3	-0.313	-0.495	-0.267
GooF	1.029	0.996	0.995
wR_2 (all data)	0.1232	0.2142	0.1521
wR_2	0.1164	0.1748	0.1407
R_1 (all data)	0.0525	0.1362	0.0739
R_1	0.0448	0.0727	0.0523
CCDC number	2094061	2094753	2094754

Compound	**10**	**11**	**12**
Empirical Formula	$C_{38}H_{48}N_2O_2$	$C_{31}H_{36}N_2S_5$	$C_{29}H_{36}AuClN_2O$
$\rho_{calc.}$ / g cm^{-3}	1.140	1.225	1.617
μ / mm^{-1}	0.535	3.462	11.258
Formula Weight	564.78	596.92	661.01
Colour	clear intense yellow	clear intense orange	clear intense orange
Shape	prism-shaped	prism-shaped	prism
Size/mm^3	0.24×0.19×0.07	0.41×0.27×0.16	0.75×0.51×0.13
Temperature / K	140.00(10)	140.00(10)	140.00(10)
Crystal System	monoclinic	monoclinic	orthorhombic
Space Group	$P2_1/n$	$P2_1/c$	$Pna2_1$
a/Å	20.58217(16)	8.29535(12)	20.61099(13)
b/Å	16.76993(7)	10.67345(16)	12.54486(9)
c/Å	20.98706(16)	36.5755(5)	10.50093(7)
α/°	90	90	90
β/°	114.7272(9)	92.0920(11)	90
γ/°	90	90	90
V/Å^3	6579.72(9)	3236.24(8)	2715.14(3)
Z	8	4	4
Z'	2	1	1
Wavelength / Å	1.54184	1.54184	1.54184
Radiation type	Cu$K\alpha$	Cu$K\alpha$	Cu$K\alpha$
Θ_{min} / °	3.510	4.315	4.125
Θ_{max} / °	72.739	72.679	72.750
Measured Reflections	54913	17191	47677
Independent Reflections	12907	6219	5359
Reflections [I ≥ 2σ(I)]	11527	5654	5353
R_{int}	0.0222	0.0205	0.0740
Parameters	780	371	316
Restraints	0	43	1
Larges Peak / e · A^3	0.281	0.265	1.960
Deepest Hole / e · A^3	-0.207	-0.374	-0.926
GooF	1.027	1.028	1.099
wR_2 (all data)	0.1017	0.0832	0.0827
wR_2	0.0982	0.0806	0.0827
R_1 (all data)	0.0441	0.0356	0.0309
R_1	0.0391	0.0321	0.0309
CCDC number	2094465	2094043	2094751

Compound	**13**	**14**	**15**
Empirical Formula	$C_{38}H_{47}ClN_2OPd$	$C_{31}H_{36}ClN_2O_3Rh$	$C_{32.5}H_{39.5}Cl_3GaN_2O$
$\rho_{calc.}$ / g cm^{-3}	1.321	1.338	1.315
μ / mm^{-1}	5.254	5.509	3.593
Formula Weight	689.62	622.98	650.23
Colour	clear intense yellow	clear pale yellow	clear pale yellow
Shape	prism	prism	plate
Size/mm^3	0.27×0.09×0.05	0.19×0.17×0.15	0.17×0.11×0.03
Temperature / K	140.00(10)	140.00(10)	140.00(10)
Crystal System	triclinic	monoclinic	monoclinic
Space Group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a/Å	8.2887(3)	10.32987(14)	10.39335(14)
b/Å	12.5359(4)	14.7730(2)	19.4815(2)
c/Å	16.8607(5)	20.5303(3)	16.5164(2)
α/°	86.331(3)	90	90
β/°	82.998(3)	99.0954(13)	100.7901(13)
γ/°	86.923(3)	90	90
V/Å^3	1733.45(9)	3093.59(7)	3285.08(7)
Z	2	4	4
Z'	1	1	1
Wavelength / Å	1.54184	1.54184	1.54184
Radiation type	Cu$K\alpha$	Cu$K\alpha$	Cu$K\alpha$
Θ_{min} / °	3.537	3.702	3.545
Θ_{max} / °	72.576	72.620	72.609
Measured Reflections	14148	15548	28001
Independent Reflections	6693	6015	6441
Reflections [I ≥ 2σ(I)]	6159	5408	5515
R_{int}	0.0288	0.0265	0.0304
Parameters	449	351	386
Restraints	212	0	39
Larges Peak / e · A^3	0.365	0.387	0.719
Deepest Hole / e · A^3	-0.586	-0.622	-0.504
GooF	1.104	1.044	1.030
wR_2 (all data)	0.0685	0.0683	0.0877
wR_2	0.0637	0.0660	0.0826
R_1 (all data)	0.0339	0.0322	0.0397
R_1	0.0290	0.0278	0.0320
CCDC number	2094755	2094731	2094752

7. Quantum chemical calculations

All quantum chemical calculations were done using the ORCA 4.2.0 program package[9] using the BP86 exchange-correlation functional[10] in combination with the Karlsruhe def2-SVP basis set.[11] An integration grid of 4 was chosen for the evaluation of gradients and final energies, an integration grid of 2 was chosen for SCF iterations. Orbitals were visualized using the AVOGADRO 1.2.0 software.[12]

Cartesian Coordinates of Computed Structures

Compound **4**, BP86/def2-SVP

N	-0.78396248915839	-0.02089136336318	1.00380721791890
C	0.37304007671019	0.03311525467306	0.22232492708961
N	-0.10043775020437	0.04295171135702	-1.09641885944732
C	-1.49627745454245	-0.00397187683103	-1.10830577612546
C	-1.91868073981400	-0.04307642492773	0.19189181316548
C	1.66247752767957	0.07147796206326	0.68450947500354
H	-2.05990633133745	-0.00482278692061	-2.04517867327505
H	-2.92513149199922	-0.08408428581972	0.61710550852235
C	2.91171304851386	0.15276639803114	0.37253853933106
O	4.09479888071314	0.23263831192007	0.21654522124337
C	-0.79747605183633	-0.04236189165705	2.44365787257359
C	-0.85777828871082	1.18951187325722	3.14577289763049
C	-0.89660309442462	1.13766740242892	4.55382079196784
C	-0.87605821413905	-0.08670900598514	5.23449861849605
C	-0.80932605124075	-1.28894709755202	4.51768363345026
C	-0.76598664320414	-1.29596218022737	3.10890289413602
C	-0.84703185191242	2.53876284142510	2.42951559885597
H	-0.93908955451504	2.07740195988426	5.12592910100255
H	-0.90790700514769	-0.10447704381326	6.33554065278745
H	-0.78397607118832	-2.24556186254703	5.06213596627039
C	-0.64137136128652	-2.61662964995833	2.35114585778695
C	0.73124861282770	0.05928752734904	-2.27057788875179
C	1.07460178279262	-1.17683456363710	-2.88063904845034
C	1.84433885003871	-1.13241402181489	-4.06050870950923
C	2.26516772402809	0.08707680090186	-4.60622818565546
C	1.93270626534481	1.29140626701384	-3.97268097647011
C	1.16358848936359	1.30759514531605	-2.79166119603314
C	0.66187220560875	-2.52447011281336	-2.29090190588374
H	2.12375104477341	-2.07434486094432	-4.55710454431710
H	2.86355589434776	0.09873797562810	-5.53034240901425
H	2.27913465527655	2.24431938082713	-4.40149408386609
C	0.82748645030253	2.63764668291615	-2.12038156499501
C	-0.08458021750400	3.50633093463108	-3.01275272966935
C	2.10441333209661	3.39835438678299	-1.70671139282543
H	0.26493175095666	2.41100076303951	-1.19143549076533
H	0.05986570776513	-2.32313506026660	-1.38076913491470
C	1.89630683592338	-3.33786886284942	-1.84840420348881
C	-0.22769474178960	-3.32830216974356	-3.26193850121086
C	0.49115317144842	3.27110628278862	2.66810670643673
C	-2.05471154831365	3.41553859297177	2.81819806652877
H	-0.92193337641324	2.34002236221950	1.34063462282219
C	-1.74158037163538	-3.62464888167415	2.73848585972424
C	0.77044291857599	-3.21351535422221	2.53681411892350
H	-0.76294097189607	-2.39425748858567	1.27076918900178

H	-3.01688561542984	2.89711609291266	2.62592970682737
H	-2.05377839216848	4.35898225309503	2.23495669857678
H	-2.03455473552185	3.69361956093924	3.89246419702764
H	0.63322407784218	3.51160740061579	3.74255206144279
H	0.52033274312173	4.22475457615355	2.10215152019137
H	1.34551619161984	2.64556080593271	2.34082016307635
H	-1.65786533838646	-3.93927207245166	3.79961346492792
H	-1.66374615997499	-4.54127581365509	2.11848248350477
H	-2.75700720925664	-3.20091073838240	2.59448708365660
H	0.95968063289889	-3.47178922850361	3.59990516602347
H	0.88390264375196	-4.14057174130866	1.93794763332966
H	1.54774165342602	-2.49174011317544	2.21560920923614
H	-0.56230808210384	-4.27605145142239	-2.79190400388707
H	0.31801080801601	-3.59592062872024	-4.19083182671814
H	-1.13141131975935	-2.75803727498144	-3.55835624424872
H	2.51236243863727	-2.76838841214147	-1.12420686028113
H	1.58366576986289	-4.28704761720507	-1.36605163180651
H	2.54294065896781	-3.59997306336709	-2.71210978521458
H	-0.36158731524926	4.44643781082011	-2.49224736433811
H	-1.02137350061670	2.97670729800942	-3.28000918255960
H	0.42164663704256	3.78765818074584	-3.95983114428171
H	1.84283162628219	4.32188106375203	-1.15001144086932
H	2.70239454857726	3.70320950994900	-2.59132341934607
H	2.75266668554678	2.77588963111730	-1.05846136027049

Compound **4**, M06-2X/6-311+G(d,p)

N	-0.62008884582766	0.08933236951512	1.00599932948643
C	0.45963885251710	0.21897895197952	0.15812262402269
N	-0.08934472767452	0.07324754889998	-1.09869193823395
C	-1.46664985518537	-0.09751309095146	-1.02555579041490
C	-1.79484160202853	-0.09405967732258	0.27936017981133
C	1.77160748424109	0.47680172574633	0.48304927801171
H	-2.06884929806016	-0.20776266551847	-1.91151970208497
H	-2.74405344050840	-0.20617181867962	0.77433502914585
C	2.87105864509659	0.67689132765451	-0.14319065751051
O	3.93733603748733	0.88420943452945	-0.60278742570531
C	-0.60205632200790	-0.02652259532008	2.44388108296424
C	-0.59234275482257	1.13564942674312	3.21321476614025
C	-0.70747945506835	0.97992141068445	4.59629904373538
C	-0.84317900577365	-0.27967989755018	5.16441192829022
C	-0.83874990008346	-1.41585838001841	4.36636929810889
C	-0.70888189280917	-1.31328310049532	2.98131966455403
C	-0.44530179611644	2.51668338566123	2.59556984515915
H	-0.70400755043958	1.85677486129428	5.23458583501399
H	-0.95282756975938	-0.37683687648087	6.23887650980249
H	-0.94562955172614	-2.39383886464585	4.82298160968118
C	-0.70275676449055	-2.56925952931048	2.11530710351540
C	0.68262367357817	0.06430262204426	-2.31032242155693
C	1.02175687670653	-1.18239966981066	-2.85133982953211
C	1.78548748863500	-1.16478805612021	-4.01684434043331
C	2.18123156386150	0.03798179100078	-4.59271710179555
C	1.82214394708619	1.25183947565509	-4.02398838804005
C	1.06145480314408	1.29192925581979	-2.85527156021274
C	0.59867685181424	-2.48139280243647	-2.17219049522905
H	2.07694266697349	-2.09801866950582	-4.48399018930083
H	2.77912872325291	0.02544626878257	-5.49659562419601
H	2.14137262192962	2.17810209242931	-4.48752421864261
C	0.64211951277654	2.61125560262413	-2.22009372377572
C	-0.48940059771456	3.25191948805822	-3.04074524711137
C	1.82905731409191	3.56884918974174	-2.04983466293432

H	0.25257575963689	2.39818610436305	-1.22282987580977
H	-0.36370786766703	-2.30360458390340	-1.68303970594998
C	1.61012430230545	-2.87746066772775	-1.08225470176365
C	0.39931015054009	-3.63510229335182	-3.16261609669052
C	0.90498648364344	3.13067278711862	2.99647323525701
C	-1.61949847556306	3.42813345469823	2.98266286981234
H	-0.44936174243619	2.40380196939640	1.50932810376958
C	-2.06392771326759	-3.28141799016490	2.17265724102844
C	0.43016073409970	-3.51906813878360	2.53075297384715
H	-0.51814645984889	-2.27498916023739	1.07925150486695
H	-2.57587567883026	2.99485347178344	2.68050652068728
H	-1.51571004931300	4.40187568545792	2.49981072575723
H	-1.65259983674770	3.59565407740646	4.06209989498545
H	0.96213219056407	3.25926920874168	4.08071784229723
H	1.02661690234861	4.11158042389931	2.53176876153524
H	1.72337080393736	2.48528880249911	2.67428565014443
H	-2.28020437775206	-3.62710565036502	3.18660899140195
H	-2.06754951931241	-4.15146400953188	1.51168148037083
H	-2.87496667257458	-2.61648407786110	1.86674960290615
H	0.29041416102771	-3.87769084590680	3.55350453683994
H	0.44834616973440	-4.39071182378549	1.87236424625494
H	1.39773598113890	-3.01771064149834	2.47128290746101
H	-0.05853121250893	-4.48336960077356	-2.64919632835710
H	1.35143684788074	-3.98061542283680	-3.57208942399097
H	-0.24803888380454	-3.34646974659646	-3.99308013009214
H	1.71459206099984	-2.10291265928496	-0.31922149154740
H	1.29073837228399	-3.80399517432621	-0.59651003539471
H	2.59493819646195	-3.04388361634239	-1.52596664343543
H	-0.81262343149110	4.18909113313744	-2.58134934978065
H	-1.35327797303156	2.58594560232139	-3.10636346922227
H	-0.15253875891932	3.46915894360828	-4.05781546836773
H	1.51019004006854	4.45527421894301	-1.49684007508235
H	2.21427970116672	3.90315329951598	-3.01616788080162
H	2.64196666213379	3.08926238569016	-1.50217122366994

Compound **4** (linear), BP86/def2-SVP

N	-0.76291250309538	-0.02252029738270	1.03090008480238
C	0.39506673214334	0.01249929663599	0.23979718937840
N	-0.09116402307250	0.03373747221367	-1.07552332538984
C	-1.48621064728128	0.01225055544250	-1.07816606569534
C	-1.90159466381791	-0.02231474576715	0.22477834954270
C	1.68886736107688	0.02359139714587	0.65131754778642
H	-2.05599367449901	0.02338649314433	-2.01112487141776
H	-2.90686211840667	-0.04672661647447	0.65455516523050
C	2.90796676149670	0.03482572440960	1.02726600919349
O	4.05301059447486	0.04552107141186	1.38195262986991
C	-0.76750827312879	-0.04952425076234	2.46962771383905
C	-0.79238431490633	1.18082353159968	3.17729448918126
C	-0.82508039514121	1.12468630136646	4.58521574405818
C	-0.82719458536199	-0.10223723319614	5.26170451650186
C	-0.79044221260637	-1.30257172463709	4.53991686934887
C	-0.75657313742061	-1.30564781721467	3.13093931933022
C	-0.77210144986571	2.53335411382967	2.46707192812816
H	-0.84399592773437	2.06320468952762	5.16074557123994
H	-0.85229877143106	-0.12342797769794	6.36281506796450
H	-0.78149044551132	-2.26197740942066	5.08044389208257
C	-0.69252537332036	-2.62941904676823	2.37098126740117
C	0.73690273721244	0.06386751331204	-2.25190711226720
C	1.12935668587038	-1.16554758050773	-2.84379860080645
C	1.90390166984935	-1.10731415553227	-4.01999163595250

C	2.28018940664798	0.12045461525081	-4.57991712745406
C	1.89615096368140	1.31939713885074	-3.96544645085955
C	1.12096015962846	1.32095870605943	-2.78827561841781
C	0.75939524207289	-2.51893863653561	-2.23982777036882
H	2.22132999801366	-2.04433557475613	-4.50296708983690
H	2.88281329050987	0.14327597117780	-5.50113906315124
H	2.20810238807855	2.27896896459263	-4.40584753640518
C	0.74196676099602	2.64430054174445	-2.12656174142198
C	-0.10996041992913	3.52930386697928	-3.06027582468999
C	1.99472351875517	3.39211842032342	-1.62303020797959
H	0.12234495402210	2.40939665085657	-1.23650882592270
H	0.14253998762823	-2.32609562782977	-1.33780622667340
C	2.01740651381110	-3.28243991070730	-1.77528640426588
C	-0.09276070577613	-3.36509434709428	-3.20845938022742
C	0.51126862334465	3.32110417069049	2.80476808175945
C	-2.04307578606001	3.35559334407121	2.76771285390647
H	-0.75755935073070	2.33773147697116	1.37530591151744
C	-1.92610008776496	-3.51277717521083	2.65205421339940
C	0.62442580722844	-3.37715270460121	2.66868964629618
H	-0.69648655238622	-2.39323629427710	1.28725634660411
H	-2.96303042551917	2.80418580493202	2.48321405301287
H	-2.03240213088750	4.31103132530656	2.20428133221376
H	-2.12482590641597	3.60675849673616	3.84566580464282
H	0.56522453942224	3.56989054340092	3.88502413300896
H	0.54130542954970	4.27537671412732	2.24029052890715
H	1.41608798807333	2.73670603414774	2.54332166115480
H	-1.98539812598830	-3.80764541010770	3.72029269702855
H	-1.88371675292127	-4.44545699420957	2.05296534465908
H	-2.87078968130357	-2.98891578495049	2.39815041819926
H	0.69548880578751	-3.66713628433359	3.73765106954880
H	0.68927747361917	-4.30543593441327	2.06510950263675
H	1.50237772925823	-2.74527161517657	2.42743849646488
H	-0.39826284059713	-4.31844093832456	-2.72986403133079
H	0.47037638728545	-3.62417046267040	-4.12932675816614
H	-1.01312157742087	-2.83016595127587	-3.51890790602675
H	2.60274096570549	-2.68220309263259	-1.05016467367051
H	1.73399920157978	-4.23728731235753	-1.28591388496134
H	2.68254536204027	-3.53027442585284	-2.62929912073096
H	-0.41904511285623	4.46024417854885	-2.54146407298989
H	-1.02821988713443	3.00594727927034	-3.39561145874323
H	0.45450499357399	3.82954664214497	-3.96778787822340
H	1.70478030160599	4.32263552250664	-1.09231294955734
H	2.66195846334994	3.68017063799249	-2.46258241862723
H	2.57964306289888	2.76268412595729	-0.92280041760917

Compound **6**, BP86-D3BJ/def2-SVP

N	-0.65669025608100	0.01131863739404	0.99536633250515
C	0.40842811844304	0.20205422434411	0.11913365368471
N	-0.14198106364037	0.02586037950198	-1.14725064102755
C	-1.49900020330735	-0.26394840999159	-1.04691312242909
C	-1.81832363746244	-0.27272515621698	0.28617393910251
C	1.70397148341040	0.49895678939375	0.46154689312002
H	-2.12213236188852	-0.44192448093578	-1.92778242964109
H	-2.77295320158231	-0.46092619523715	0.78508744659733
C	2.88562830102195	0.72765531529150	-0.00616668765340
O	4.01880608163969	0.95383469773909	-0.31296381627561
C	-0.52106067078265	0.10547499346006	2.43503010172447
C	0.64546848083492	0.13717629443571	-2.35760932998745

H	0.53956959667960	0.35148082247135	2.64055088361112
H	-0.77596815514033	-0.85792103132870	2.92274695781896
H	-1.17091360029439	0.90559309004680	2.84415155094540
H	1.45878806544648	-0.61754767005277	-2.36451505515164
H	-0.00976140819833	-0.02003355763444	-3.23363572486947
H	1.11383643090163	1.14017425731903	-2.42284095207436

Compound **6**^{TS}, BP86-D3BJ/def2-SVP

O	0.33942437349928	2.03538961169704	-2.50681719205595
C	-0.15712062604680	1.15119743445898	-1.90180773869778
C	1.60283748312983	-0.55773137026652	-0.71173710861672
C	-0.72330531033835	0.11945780547523	-1.28876344442459
C	2.62710269433311	-0.85875603038746	0.14366075827137
C	0.40207906354913	-1.13734823476014	-0.98431649648123
C	-1.94896447410850	0.15363117337862	-0.57410133917277
N	3.93058960343447	-0.33088330896247	0.07765723751427
N	2.64239461755418	-1.64947815561647	1.30853178359098
O	-0.10160431481079	-2.27116513078880	-1.13482205882970
N	-2.31627389581454	1.07952858735021	0.38231786426037
N	-2.94591461160238	-0.79378988925415	-0.58720077589151
C	4.32362531466718	0.60621464394378	-0.94644097158211
C	4.68450392210316	-0.76065963218988	1.16525586920343
C	1.49616172799192	-2.39751131177215	1.77166411648719
C	3.88554919584689	-1.56289262522712	1.93568924258068
C	-3.53499553412892	0.71304255022736	0.94388801157178
C	-1.46704502352789	2.18649520857302	0.79309828425264
C	-3.92350212935122	-0.45582698353782	0.33755370810389
C	-2.99583620276827	-1.89008934012088	-1.55873884423828
H	5.72699336706738	-0.46015870932982	1.30392012473893
H	4.10043260552278	-2.08379824236801	2.87339602848498
H	-4.01328093940775	1.30561467445069	1.72862444444353
H	-4.81844774047706	-1.06909384982771	0.47594302787321
H	-1.28238265737326	2.88006561634894	-0.05101745720301
H	-0.49102039718451	1.80222355539139	1.15042153469975
H	-1.97058388511396	2.74170550932258	1.60497031986887
H	-1.98088231290258	-2.34012132138105	-1.60502632401615
H	-3.28314476198450	-1.49382420389264	-2.55430170100191
H	-3.75144513797121	-2.62031189472393	-1.21716307110610
H	4.85098731737631	1.47685982887331	-0.50302820584474
H	3.38298686796936	0.93986436053405	-1.43632148560762
H	4.97777451244583	0.14192069481273	-1.71662298119654
H	0.90173243960804	-2.73061209104352	0.89666293983032
H	1.83551503424352	-3.28671617302857	2.33801278213547
H	0.83502281457001	-1.78721375635865	2.42987011805493

Compound **6**^{dim}, BP86-D3BJ/def2-SVP

O	0.43088401759319	2.23905295712972	-0.41875602109262
C	0.20628656561494	1.03196940884544	-0.22493466727467
C	1.06164058356311	-0.15116702754198	0.07126356606452
C	-1.02516284234317	0.19380706758218	-0.19807316323838
C	2.43488507234679	-0.37973439719242	0.24115394265851
C	-0.16986139600275	-0.98959046101786	0.09889286060737
C	-2.39713459630980	0.42048366640383	-0.38045593332044
N	3.48061368103077	0.48500317022681	-0.06821782927123
N	3.04393875228750	-1.52173685789206	0.75297351919856
O	-0.39487003480370	-2.19645201613785	0.29259770358776
N	-3.05348992809653	1.64750037074121	-0.41149447333124
N	-3.39367590893598	-0.53238905772546	-0.57079509899446
C	3.36407832905486	1.72346245468777	-0.82461444588577

C	4.69728693104399	-0.11882619136104	0.24265280702358
C	2.36193925148639	-2.62475244338208	1.41452098154917
C	4.42737897093015	-1.35485001994677	0.75697705114280
C	-4.41744542898161	1.44566199246650	-0.61338308923949
C	-2.47233691788319	2.93044271018220	-0.04294420069782
C	-4.62636826392495	0.10033169418410	-0.71957252495985
C	-3.17728907367170	-1.95011294204718	-0.82127888181336
H	5.64854527631761	0.38714808142218	0.05515733424811
H	5.09372791288195	-2.13392409168806	1.13731798620293
H	-5.11728253298152	2.28497968346301	-0.65478862057467
H	-5.54096172875080	-0.47050782720665	-0.90349192382963
H	-1.39061182839964	2.94177060702513	-0.29464710447258
H	-2.58970121437945	3.11435020789029	1.04739001602839
H	-2.99263732133809	3.73265542722418	-0.60016513064778
H	-2.25100787354404	-2.28677446442598	-0.30950260639070
H	-3.07647398186002	-2.14467455091767	-1.91100478172240
H	-4.04402384848848	-2.51942397920773	-0.43349636614774
H	4.15971927805073	2.41990067326369	-0.49629821120419
H	2.36820072094623	2.18282766416643	-0.64743929837861
H	3.48131931763045	1.53000701098729	-1.91351486022473
H	1.34659385530021	-2.75396976533588	0.98419537835338
H	2.95032305135717	-3.55100933108785	1.26510905599962
H	2.26787015325941	-2.43010342377739	2.50513203004763

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