Supporting Information

Specialized Ruthenium Olefin Metathesis Catalysts Bearing Bulky Unsymmetrical NHC Ligands: Computations, Synthesis and Application

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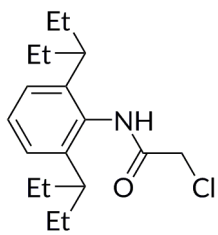
General remarks

All reagents were purchased from Sigma-Aldrich, Strem, TCI, Alfa Aesar, and Apeiron Synthesis and used without further purification. All reactions involving the synthesis of metal complexes were carried out in oven-dried glassware with magnetic stirring under an argon atmosphere with anhydrous solvents, using standard Schlenk techniques. Ethenolysis was conducted in Carl Roth autoclave, using ethylene of purity N4.5. Toluene and diethyl ether were distilled over K, while DMF was distilled over CaH_2 under an atmosphere of argon. CH_2Cl_2 and toluene used for reactions were purified using mBraun's SPS (solvent purification system). Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 pre-coated plates (0.25 mm thickness) with a fluorescent indicator. Visualization of TLC plates was performed by UV light or by $KMnO_4$ water solution. Flash chromatography was performed using silica gel 60 (230–400 mesh). NMR spectra were recorded on an Agilent 400-MR DD2 400 MHz spectrometer. NMR chemical shifts are reported in ppm and referred to residual solvent peaks at 7.26 and 77.16 ppm for ^1H and ^{13}C in $CDCl_3$, 5.32 and 53.84 ppm for ^1H and ^{13}C in CD_2Cl_2, and 3.31 and 49.00 ppm ^1H and ^{13}C in CD_3OD, respectively. The following abbreviations are used in reporting NMR data: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). Coupling constants (*J*) are in Hz. Spectra are reported as follows: chemical shift (δ, ppm), multiplicity, coupling constants (Hz), integration. IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer with a diamond ATR accessory. Wavenumbers are given in cm^{-1}. GC analyses were performed using Clarus 580 chromatograph using durene as an internal standard. Microanalyses were made using Vario EL III apparatus. Melting points were recorded on an OptiMelt SRS apparatus with a heating rate of 10 °C/min. High-resolution electrospray mass spectra (ESI-HRMS) were recorded on a Quattro LC triple-quadrupole mass spectrometer. The mass spectrometer was calibrated with an internal standard solution of sodium formate or sodium iodide in MeOH.

General procedure for the preparation of amides

In a round bottom flask K_2CO_3 (2 equiv.) and corresponding amine (1 equiv.) were dissolved in a mixture of DCM and MeCN (1 : 1). The vigorously stirred suspension was cooled to 0 °C and chloroacetyl chloride (1.1 equiv.) was added dropwise for 15 min. The reaction mixture was left for 2 h allowing to heat up to RT. Saturated aqueous solution of $NaHCO_3$ was added. Water phase was extracted with DCM and the resulting organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated under vacuum. The crude mixture was purified by column chromatography (*c*-Hex/EtOAc).

Synthesis of *N*-chloroacetyl-2,6-bis(3-pentyl)aniline



Following the general procedure 2,6-bis(3-pentyl)aniline (1.00 g, 4.3 mmol), K_2CO_3 (1.20 g, 8.6 mmol), chloroacetyl chloride (0.53 g, 4.7 mmol) and a mixture of DCM and MeCN (1 : 1, 20 mL) were used. *N*-chloroacetyl-2,6-bis(3-pentyl)aniline (1.30 g, 98%) was obtained as a colorless powder (Mp = 173-175 °C).

^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.09 (d, *J* =

7.7 Hz, 2H), 4.23 (s, 2H), 2.55 (tt, J = 8.6, 5.8 Hz, 2H), 1.77 – 1.62 (m, 4H), 1.60 – 1.43 (m, 4H), 0.78 (t, J = 7.4 Hz, 12H).

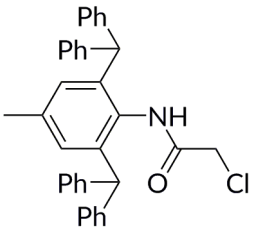
^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 143.5, 133.4, 128.6, 124.2, 43.4, 42.9, 29.2, 12.4.

HRMS (ESI): *m/z* calcd. for $C_{18}H_{29}NOCl$ [M+H$^+$] 310.1932, found 302.1947.

Anal. Calcd. for $C_{18}H_{28}NOCl$: C, 69.77; H, 9.11; N, 4.52. Found: C, 69.82; H, 9.12; N, 4.66.

ATR-IR: ν = 681, 714, 758, 782, 799, 985, 1225, 1261, 1328, 1353, 1378, 1454, 1522, 1590, 1657, 1683, 2873, 2930, 2961, 3022, 3226.

Synthesis of *N*-chloroacetyl-2,6-bis(diphenylmethyl)-4-methylaniline



Following the general procedure 2,6-bis(diphenylmethyl)-4-methylaniline (1.00 g, 2.3 mmol), K_2CO_3 (0.63 g, 4.9 mmol), chloroacetyl chloride (0.28 g, 2.5 mmol), and a mixture of DCM and MeCN (1 : 1, 20 mL) were used. *N*-Chloroacetyl-2,6-di(3-pentyl)aniline (1.10 g, 94%) was obtained as a colorless powder (Mp = 226-228 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.23 (m, 12H), 7.16 – 7.07 (m, 8H), 6.98 (s, 1H), 6.66 (s, 2H), 5.60 (s, 2H), 3.95 (s, 2H), 2.19 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$)δ 165.1, 143.2, 142.5, 138.0, 130.5, 129. 9, 129.7, 128.9, 126.9, 52.6, 42.3, 21.5.

HRMS (ESI): *m/z* calcd. for $C_{35}H_{31}NOCl$: [M+H$^+$] 516.2089, found 516.2101.

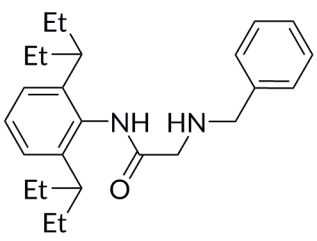
Anal. Calcd. for $C_{35}H_{30}NOCl$: C, 81.46; H, 5.86; N, 2.71. Found: C, 81.67; H, 6.06; N, 2.74.

ATR-IR: ν = 459, 482, 503, 546, 607, 623, 700, 711, 753, 768, 782, 858, 1030, 1079, 1241, 1263, 1409, 1446, 1495, 1598, 1674, 3024, 3056, 3381.

General procedure for the preparation of aminoamides

To a suspension of appropriate chloramide (1 equiv.) and K_2CO_3 (2 equiv.) in a mixture of toluene and MeCN (1 : 1), benzylamine (1 equiv.) was added. The reaction mixture was refluxed under Ar atmosphere for 24 h. The solvents were evaporated, the residue was dissolved in DCM and washed with brine. The water phases was washed with DCM and combined organic phases were dried under $MgSO_4$, filtered and concentrated under vacuum. The crude mixture was purified by column chromatography (*c*-Hex/EtOAc).

Synthesis of *N*-2,6-bis(3-pentyl)phenyl-2-benzylaminoacetamide



Following the general procedure *N*-chloroacetyl-2,6-bis(3-pentyl) aniline (1.00 g, 3.2 mmol), K_2CO_3 (0.90 g, 6.4 mmol), benzylamine (0.35 g, 3.2 mmol), and a mixture of toluene and MeCN (1 : 1, 20 mL) were used. *N*-(2,6-bis-(diphenylmethyl)-4-methylphenyl)-2-benzylaminoacetamide (0.77 g, 63%) was obtained as a yellowish sticky oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.45 – 7.21 (m, 5H), 7.07 (d, *J* = 7.7 Hz, 2H), 3.94 (s, 2H), 3.49 (s, 2H), 2.58 (tt, *J* = 8.4, 5.9 Hz, 2H), 1.74 – 1.60 (m, 4H), 1.60 – 1.46 (m, 4H), 0.77 (t, *J* = 7.4 Hz, 12H).

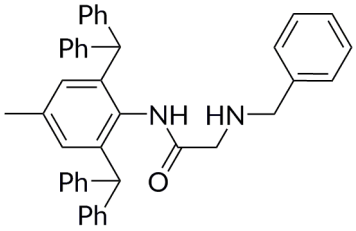
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 143.3, 139.3, 134.3, 128.8, 128.1, 127.8, 127.6, 124.0, 77.5, 77.2, 76.8, 54.4, 52.1, 43.3, 12.4.

HRMS (ESI): *m/z* calcd. for $C_{25}H_{37}N_2O$: [M+H$^+$] 381.2900, found 381.2915.

Anal. Calcd. for $C_{25}H_{36}N_2O$: C, 78.90; H, 9.54; N, 7.36. Found: C, 78.99; H, 9.52; N, 7.30.

ATR-IR: ν = 697, 743, 781, 797, 1120, 1264, 1334, 1355, 1376, 1454, 1495, 1667, 2872, 2929, 2958, 3027, 3063, 3301.

Synthesis of *N*-(2,6-bis(diphenylmethyl)-4-methylphenyl)-2-benzylaminoacetamide



Following the general procedure *N*-Chloroacetyl-2,6-bis-(diphenylmethyl)-4-methylaniline (1.00 g, 1.9 mmol), K_2CO_3 (0.54 g, 3.9 mmol) and benzylamine (0.21 g, 1.9 mmol), and a mixture of toluene and MeCN (1 : 1, 20 mL) were used, *N*-(2,6-bis-(diphenylmethyl)-4-methylphenyl)-2-benzyl-aminoacetamide (0.95 g, 84%) was obtained as a yellowish sticky oil solidifying during storage (Mp = 172-175 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.31 – 7.21 (m, 11H), 7.20 – 7.12 (m, 4H), 7.11 – 7.01 (m, 8H), 6.86 – 6.78 (m, 2H), 6.59 (s, 2H), 5.64 (s, 2H), 3.31 (s, 2H), 3.20 (s, 2H), 2.14 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 143.7, 142.0, 139.5, 137.2, 131. 7, 129.8, 129.7, 128.7, 128.6, 128.3, 127.4, 126.8, 53.6, 52.6, 51.9, 21.4.

HRMS (ESI): *m/z* calcd. for $C_{42}H_{39}N_2O$: [M+H$^+$] 587.3057, found 587.3066.

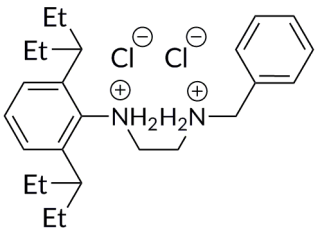
Anal. Calcd. for $C_{42}H_{38}N_2O$: C, 85.97; H, 6.53; N, 4.77. Found: C, 86.10; H, 6.63; N, 4.76.

ATR-IR: ν = 460, 514, 602, 675, 746, 822, 856, 907, 935, 988, 1033, 1114, 1148, 1196, 1216, 1282, 1366, 1417, 1449, 1465, 1508, 1602, 1762, 2840, 2935.

General procedure for the preparation of diamine dihydrochloride

In the oven-dried round bottom flask to the efficiently stirred solution of LAH (3 equiv.) in dry THF at −20 °C under Ar atmosphere, corresponding aminoamides solution in dry THF was added dropwise during 30 min. Cooling bath was removed, the mixture was allowed to heat up to RT, and then was refluxing for 8 h. The reaction mixture was cooled to −20 °C and water was added dropwise. An excess of potassium sodium tartrate was added and the mixture was vigorously stirred overnight. THF was evaporated and Et_2O was added. Phases were separated and the water phase was washed with Et_2O. Combined organic phases were dried under Na_2SO_4 and filtered. Diamine dihydrochloride, as a white powder, was precipitated using 1M HCl solution in Et_2O (2.5 equiv.) at −40 °C, filtered, washed with cold Et_2O and dried in high vacuum.

Synthesis of 1-benzyl-3-(2,6-bis(3-pentyl)phenyl)-1,2-diaminoethane dihydrochloride (2a)



Following the general procedure *N*-2,6-bis(3-pentyl)phenyl-2-benzylaminoacetamide (2.00 g, 5,3 mmol), LAH (0.60 g, 15,9 mmol), dry THF (40 mL) and 1M HCl solution in Et_2O (14 mL) were used. 1-Benzyl-3-(2,6-bis(3-pentyl)phenyl)-1,2-diaminoethane dihydrochloride (2.10 g, 91%) was obtained as a colorless powder (Mp = 259-260 °C).

^{1}H NMR (400 MHz, CD_3OD) δ 7.65 – 7.58 (m, 2H), 7.53 – 7.41 (m, 4H), 7.32 – 7.25 (m, 2H), 4.35 (s, 2H), 3.77 – 3.65 (m, 2H), 3.63 – 3.47 (m, 2H), 2.92 – 2.79 (m, 2H), 1.93 – 1.75 (m, 5H), 1.71 – 1.51 (m, 4H), 0.86 (t, *J* = 7.4 Hz, 12H).

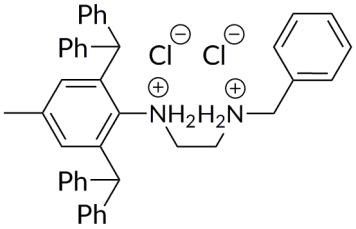
^{13}C NMR (100 MHz, CD_3OD) δ 141.1, 132.0, 131.2, 130.9, 130.8, 130.4, 127.2, 52.9, 50.5, 45.0, 43.0, 30.4, 12.2.

HRMS (ESI): *m/z* calcd. for $C_{25}H_{39}N_2$: [M+H$^+$] 367.3125, found 367.3108.

Anal. Calcd. for $C_{25}H_{40}N_2Cl_2 \times ½H_2O$: C, 66.95; H, 9.21; N, 6.25. Found: C, 66.60; H, 9.16; N, 6.09.

ATR-IR: ν = 699, 747, 780, 1038, 1128, 1187, 1260, 1377, 1449, 1585, 2474, 2555, 2679, 2776, 2855, 2872, 2928, 2959.

Synthesis of 1-benzyl-3-(2,6-bis(diphenylmethyl)-4-methylphenyl)-1,2-diaminoethane dihydrochloride (2b)



Following the general procedure (2,6-bis(diphenylmethyl)-4-methylphenyl)-2-benzyl-aminoacetamide (2.00 g, 3.4 mmol), LAH (0.39 g, 10,2 mmol) in dry THF (40 mL) and 1M HCl solution in Et_2O (9 mL) were used. 1-Benzyl-3-(2,6-bis(diphenylmethyl)-4-methylphenyl)-1,2-diaminoethane dihydrochloride (2.03 g, 92%) was obtained as a colorless powder.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 11.38 (s, 2H), 10.27 (s, 2H), 7.43 – 7.36 (m, 2H), 7.34 – 7.08 (m, 25H), 6.83 (s, 2H), 4.02 (s, 2H), 3.07 (s, 2H), 2.56 – 2.40 (m, 2H), 2.18 (s, 3H).

^{13}C NMR (100 MHz, CD_2Cl_2) δ 143.3, 139.8, 138.9, 132.5, 132.0, 130.9, 130.5, 130.2, 129.8, 129.4, 129.2, 127.4, 50.4, 50.2, 48.3, 42.4, 21.7.

HRMS (ESI): *m/z* calcd. for $C_{42}H_{41}N_2$: [M+H$^+$] 573.3264, found 573.3282.

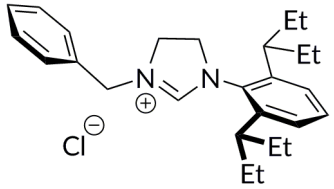
Anal. Calcd. for $C_{42}H_{42}N_2Cl_2$: C, 78.12; H, 6.56; N, 4.34. Found: C, 77.90; H, 6.68; N, 4.23.

ATR-IR: ν = 567, 606, 622, 691, 734, 764, 980, 1032, 1064, 1081, 1347, 1363, 1444, 1463, 1493, 1557, 1597, 2654, 3024.

General procedure for the preparation of imidazolinium salts

To the corresponding diamine dihydrochloride (1 equiv.) and freshly distilled triethyl orthoformate (10 equiv.) was heated at 120 °C overnight under Ar atmosphere. The reaction mixture was cooled to RT, precipitate was filtered off, washed with Et_2O and dried in high vacuum.

Synthesis of 1-benzyl-3-(2,6-bis(3-pentyl)phenyl)-4,5-dihydro-1*H*-imidazolinium chloride (3a)



Following the general procedure 1-benzyl-3-(2,6-bis(3-pentyl)phenyl)-1,2-diaminoethane dihydrochloride (0.70 g, 1.8 mmol) and triethyl orthoformate (2.76 g, 18.3 mmol were used. 1-Benzyl-3-(2,6-bis(3-pentyl)phenyl)-4,5-dihydro-1*H*-imidazolinium chloride (0.50 g, 78%) was obtained as a colorless powder (Mp = 167-169 °C).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (s, 1H), 7.58 – 7.49 (m, 2H), 7.43 – 7.30 (m, 4H), 7.10 (d, *J* = 7.8 Hz, 2H), 5.25 (s, 2H), 4.33 – 4.15 (m, 2H), 4.15 – 3.97 (m, 2H), 2.36 – 2.25 (m, 2H), 1.84 – 1.43 (m, 8H), 0.78 (t, *J* = 7.3 Hz, 6H), 0.71 (t, *J* = 7.3 Hz, 6H).

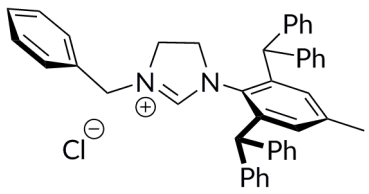
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 144.0, 133.3, 133.0, 130.9, 129.5, 129.4, 129.2, 125.3, 77.5, 77.2, 76.8, 53.7, 52.2, 48.5, 43.4, 30.4, 28.3, 12.7, 12.6.

HRMS (ESI): *m/z* calcd. for $C_{26}H_{37}N_2$ [M+H$^+$] 377.2951, found 377.2967.

Anal. Calcd. for $C_{26}H_{37}N_2Cl\times½H_2O$: C, 73.99; H, 9.08; N, 6.64. Found: C, 74.25; H, 9.15; N, 6.63.

ATR-IR: ν = 484, 711, 755, 771, 807, 1147, 1179, 1222, 1265, 1295, 1369, 1444, 1457, 1497, 1587, 1628, 2870, 2931, 2954.

Synthesis of 1-benzyl-3-(2,6-bis(diphenylmethyl)-4-methylphenyl)-4,5-dihydro-1*H*-imidazolinium chloride (3b)



Following the general procedure 1-benzyl-3-(2,6-bis-(diphenylmethyl)-4-methylphenyl)-1,2-diaminoethane dihydrochloride (0.70 g, 1.8 mmol) and triethyl orthoformate (2.76 g, 18.3 mmol) were used. 1-Benzyl-3-(2,6-bis(diphenylmethyl)-4-methylphenyl)-4,5-dihydro-1*H*-imidazolinium chloride (0.50 g, 79%) was obtained as a colorless powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.48 – 7.41 (m, 2H), 7.41 – 7.36 (m, 3H), 7.36 – 7.29 (m, 4H), 7.25 – 7.21 (m, 6H), 7.20 – 7.14 (m, 6H), 7.08 – 7.00 (m, 4H), 6.63 (s, 2H), 5.74 (s, 2H), 4.81 (s, 2H), 3.42 – 3.24 (m, 2H), 3.05 – 2.88 (m, 2H), 2.12 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 142.6, 142.5, 142.1, 140.1, 132.7, 130.7, 130.5, 129.7, 129.6, 129.6, 129.3, 129.3, 129.0, 128.9, 127.1, 127.1, 52.4, 52.3, 50.2, 47.9, 21.8.

HRMS (ESI): *m/z* calcd. for $C_{43}H_{39}N_2$: [M+H$^+$] 583.3108, found 583.3129.

Anal. Calcd. for $C_{43}H_{39}N_2Cl$: C, 83.40; H, 6.35; N, 4.52. Found: C, 83.13; H, 6.30; N, 4.44.

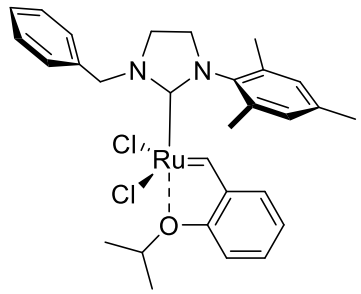
ATR-IR: ν = 471, 546, 568, 594, 607, 702, 744, 783, 1030, 1080, 1131, 1218, 1276, 1305, 1371, 1441, 1495, 1633, 3028.

General procedure for the preparation of Ru7 and Ru8 catalysts

Corresponding imidazolinium salt (1.5 equiv.) was dried in a preheated Schlenk flask under high vacuum for 30 minutes. After that dry and degassed hexane was added under nitrogen atmosphere. To this vigorously stirred suspension potassium *tert*-pentoxide (1.5 equiv.) was added. After 5 minutes Schlenk flask was placed in preheated (65 °C) oil bath and Hoveyda-Grubbs first generation catalyst **Ru12** (1 equiv.) was added at once. During progress of the reaction precipitation of green-brown solid was observed. After 25 minutes the reaction mixture was cool down to RT, precipitate was filtrated and washed with pentane. Crude product was dissolved in DCM, filtered through short silica pad and crystallized from DCM/MeOH (1:3).

Synthesis of complex Ru7

Following the general procedure 1-benzyl-3-(2,4,6-trimethylphenyl)-4,5-dihydro-1*H*-imidazolinium chloride (150 mg, 0.476 mmol), **Ru12** (191 mg, 0.310 mmol) and potassium *tert*-pentoxide solution (0.267 mL, 0.476 mmol) in dry hexane (15 mL) were used. Product was obtained as green solid (89 mg, 0.149 mmol, 47%).



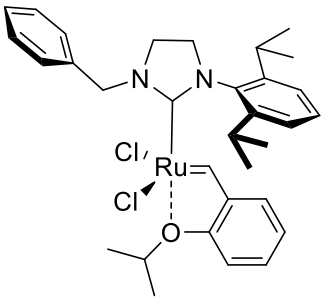
^{1}H NMR (400 MHz, $CDCl_3$): δ 16.24 (s, 1H), 7.72 (d, *J* = 6.8 Hz, 2H), 7.53-7.37 (m, 4H), 7.09 (s, 2H), 6.97-6.93 (m, 3H), 5.64 (s, 2H), 5.18 (sept, *J* = 6.0 Hz, 1H), 3.94-3.89 (m, 2H), 3.66-3.62 (m, 2H), 2.47 (s, 3H), 2.28 (s, 6H), 1.75 (d, *J* = 6.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 291.6, 209.9, 152.6, 144.1, 138.9, 138.2, 137.8, 136.2, 129.7, 129.4, 128.9, 128.4, 123.6, 122.7, 122.6, 112.9, 75.2, 56.1, 52.0, 47.9, 22.0, 21.3, 18.3.

^{1}H and ^{13}C NMR spectra are in agreement with those previously reported.[1]

Synthesis of complex Ru8

Following the general procedure 1-benzyl-3-(2,6-diisopropylphenyl)-4,5-dihydro-1*H*-imidazolinium chloride (180 mg, 0.504 mmol), **Ru12** (202 mg, 0.336 mmol) and potassium *tert*-pentoxide solution (0.283 mL, 0.504 mmol) in dry hexane (15 mL) were used. Product was obtained as green solid (130 mg, 0.203 mmol, 60%).



^{1}H NMR (400 MHz, CD_2Cl_2): δ 16.21 (s, 1H), 7.77–7.71 (m, 2H), 7.63 (t, *J* = 7.7 Hz, 1H), 7.55 (ddd, *J* = 8.3, 7.0, 2.0 Hz, 1H), 7.51–7.44 (m, 2H), 7.44–7.36 (m, 3H), 5.64 (s, 2H), 5.16 (hept, *J* = 6.1 Hz, 1H), 3.97–3.86 (m, 2H), 3.71–3.59 (m, 2H), 3.16 (hept, *J* = 6.8 Hz, 2H), 1.73 (d, *J* = 6.2 Hz, 6H), 1.22 (d, *J* = 6.9 Hz, 6H), 0.87 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (100 MHz, CD_2Cl_2): δ = 290.0, 289.9, 211.2, 153.6, 149.5, 144.2, 138.4, 137.3, 130.6, 130.3, 130.1, 129.6, 129.1, 125.8, 123.3, 122.8, 113.8, 75.9, 56.8, 55.8, 48.2, 28.3, 25.8, 24.0, 22.4 ppm.

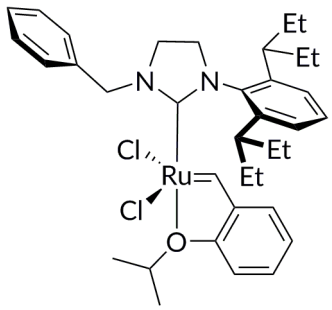
^{1}H and ^{13}C NMR spectra are in agreement with those previously reported.[1]

General procedure for the preparation of Ru9 and Ru10 catalysts

Corresponding imidazolinium salt (1.2 equiv.) was dried in preheated Schlenk flask at 60 °C for 2 h under high vacuum. After cooling down, toluene was added under argon atmosphere to obtain 0.02M final carbene concentration. To a vigorously stirred suspension, potassium *tert*-pentoxide (1.7M in toluene, 1.2 equiv.) was added and left until become clear (usually 2 min). Schlenk flask was placed in preheated (75 °C) oil bath and Hoveyda-Grubbs first generation catalyst **Ru12** (1 equiv.) was added at once. Progress of the reaction was monitored by TLC (*c*-Hex/EtOAc). After full consumption of **Ru12** catalyst (around 5 minutes) the reaction mixture was cooled in water bath and purified by column chromatography (c-Hex/EtOAc). Than solvent was evaporated, product was crystallized from DCM/MeOH mixture and dried in vacuum.

Synthesis of complex Ru9

Following the general procedure 1-benzyl-3-(2,6-bis(3-pentyl)phenyl)-4,5-dihydro-1*H*-imidazolinium chloride (173 mg, 0.42 mmol), Hoveyda-Grubbs first generation catalyst **Ru12** (210 mg, 0.35 mmol) and potassium *tert*-pentoxide solution (0.25 mL, 0.42 mmol) in dry toluene (21 mL) were used. Desired product was obtained as a dark green crystals (155 mg, 63%).



^{1}H NMR (400 MHz, CD_2Cl_2) δ 16.23 (s, 1H), 7.78 – 7.71 (m, 2H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.53 (ddd, *J* = 8.7, 6.4, 2.6 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.43 – 7.37 (m, 1H), 7.32 (d, *J* = 7.7 Hz, 2H), 7.01 (d, *J* = 8.3 Hz, 1H), 6.97 – 6.89 (m, 2H), 5.67 (s, 2H), 5.16 (hept, *J* = 6.1 Hz, 1H), 3.99 (dd, *J* = 10.7, 8.4 Hz, 2H), 3.61 (dd, *J* = 10.6, 8.4 Hz, 2H), 2.84 – 2.70 (m, 2H), 1.73 (d, *J* = 6.1 Hz, 6H), 1.77 – 1.64 (m, 2H), 1.61 – 1.48 (m, 2H), 1.48 – 1.34 (m, 2H), 1.25 (ddd, *J* = 13.5, 7.5, 5.8 Hz, 2H), 0.81 (t, *J* = 7.4 Hz, 6H), 0.64 (t, *J* = 7.3 Hz, 6H).

^{13}C NMR (100 MHz, CD_2Cl_2) δ 289.7, 289.6, 211.5, 211.5, 153.7, 147.4, 143.6, 140.6, 137.6, 130.1, 130.0, 129.7, 129.5, 129.0, 126.6, 123.2, 122.9, 113.7, 75.9, 56.8, 56,0, 48,0, 41.4, 28.7, 28.5, 22.4, 12.1, 12.0.

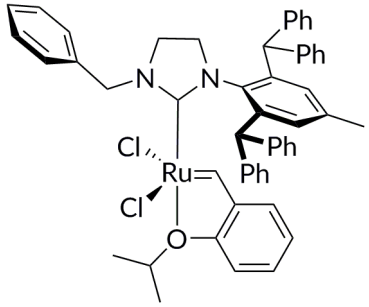
HRMS (ESI): *m/z* calcd. for $C_{36}H_{48}N_2OClRu$: $[M+H^+]$ 661.2500, found 661.2512.

Anal. Calcd. for $C_{36}H_{48}N_2OCl_2Ru$: C, 62.06; H, 6.94; N, 4.02. Found: C, 61.65; H, 6.77; N, 3.92.

ATR-IR: ν = 751, 800, 936, 1091, 1109, 1221, 1264, 1293, 1321, 1353, 1383, 1421, 1454, 1474, 1490, 2871, 2933, 2962.

Synthesis of complex Ru10

Following the general procedure 1-benzyl-3-(2,6-bis(diphenylmethyl)-4-methylphenyl)-4,5-dihydro-1*H*-imidazolinium chloride (300 mg, 0.48 mmol), Hoveyda-Grubbs first generation catalyst **Ru12** (242 mg, 0.40 mmol) and potassium *tert*-pentoxide solution (0.28 mL, 0.48 mmol) in dry toluene (24 mL) were used. Desired product was obtained as a greenish powder (160 mg, 68%).



^{1}H NMR (400 MHz, CD_2Cl_2) δ 16.96 (s, 1H), 7.81 – 7.74 (m, 2H), 7.71 – 7.65 (m, 1H), 7.49 – 7.43 (m, 2H), 7.42 – 7.37 (m, 1H), 7.28 (d, *J* = 7.2 Hz, 4H), 7.20 (dt, *J* = 8.7, 7.4 Hz, 5H), 7.15 – 7.09 (m, 2H), 7.08 – 6.95 (m, 7H), 6.94 – 6.89 (m, 1H), 6.83 (s, 2H), 6.70 – 6.64 (m, 4H), 6.13 (s, 2H), 5.67 (s, 2H), 5.34 (hept, *J* = 6.2 Hz, 1H), 2.81 – 2.73 (m, 2H), 2.29 (s, 3H), 2.03 – 1.96 (m, 2H), 1.87 (d, *J* = 6.1 Hz, 6H).

^{13}C NMR (100 MHz, CD_2Cl_2) δ 290.6, 290.2, 209.5, 154.1, 154.1, 145.3, 145.1, 144.6, 144.3, 139.2, 139.0, 137.3, 131.5, 130.6, 130.5, 130.5, 130.1, 129.5, 129.4, 129.1, 128.8, 127.3, 126.8, 123.4, 123.2, 114.0, 76.2, 56.5, 52.7, 50.8, 47.9, 22.5, 21.9.

HRMS (ESI): *m/z* calcd. for $C_{53}H_{50}N_2OClRu$: $[M+H^+]$ 867.2661, found 867.2673.

Anal. Calcd. for $C_{53}H_{50}N_2OCl_2Ru$: C, 70.50; H, 5.58; N, 3.10; Cl, 7.85. Found: C, 70.64; H, 5.54; N, 3.15; Cl, 7.72.

ATR-IR: ν = 603, 699, 757, 804, 842, 936, 1030, 1114, 1216, 1264, 1295, 1327, 1383, 1420, 1445, 1474, 1493, 1592, 3021.

General procedure for thermal stability studies

In a Young NMR tube corresponding Hoveyda-type catalyst (12.8 μmol) was dissolved in 0.65 mL of CD_2Cl_2 followed by addition of 0.13 M solution of 1,3,5-trimethoxybenzene in CD_2Cl_2 (internal standard, 50 μL, 6.4 μmol) in glove box. An NMR tube was removed from glove box and placed in preheated (40 °C) water batch. ^{1}H NMR spectra were recorded in convenient time intervals. Degradation of catalyst was calculated by comparing the integration of benzylidene signal in complexes and 9 protons from methoxy groups in internal standard.

General procedure for time-conversions studies (Figure 8)

All manipulation were carried out in glove box. An NMR tube was filled with 117mM stock solution of appropriate substrate (0.6 mL, 70 μmol) in toluene-*d*$_8$. A solution was heated to corresponding temperature and equilibrated for 10 min. Catalyst (0.1 mL, 0.7 μmol) was taken from the 7 mM stock solution in toluene-*d*$_8$ and injected into preheated NMR tube. Process was monitored using Agilent array function over an appropriate time. Conversion was calculated by comparing the integration of methylene protons in substrate and product, based on equation Yield (%) = ([P] × 100%)/([P]+[S]).

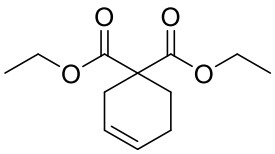
General procedure for DRRM reaction (Table 1)

An NMR tube was charged with substrate (0.1 mL, 14 μmol), taken from 0.14 M stock solution in $CDCl_3$ and durene (internal standard, 0.5 mL, 7 μmol), taken from 14 mM stock solution in $CDCl_3$, under argon atmosphere. Mixture was cooled with ice bath and saturated with ethylene. The reaction mixture was allowed to warm to RT, 7 mM catalyst solution in $CDCl_3$ was added (0.1 mL, 0.7 μmol) and rapidly immersed in 60 °C water bath for 14h. After this time conversion and diastereomeric excess was determined by GC.

General procedure for preparative RCM reactions (Table 2)

An oven dried reaction tube was charged with 0.14 M solution of substrate in dry toluene (0.7 mmol, 5 mL), placed in the Radleys Carousel Reaction Station, and equilibrated at 80 °C for 10 min under argon atmosphere. After that 3.5 mM solution of catalyst in dry toluene (7 μmol, 2 mL) was added and the reaction mixture was allowed to stir at 80 °C for 20 h. After cooling down the reaction mixture was quenched by 35 mM SnatchCat solution (35 μmol, 1 mL) and purified by column chromatography on CombiFlash system.

Diethyl cyclohex-3-ene-1,1-dicarboxylate (9)

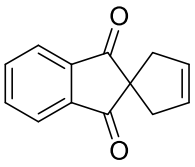


^{1}H NMR (400 MHz, $CDCl_3$): δ 5.68 – 5.65 (m, 2H), 4.18 (q, J = 7.1, 4H), 2.57 – 2.53 (m, 2H), 2.17 – 2.05 (m, 4H), 1.24 (t, J = 7.1 Hz, 6H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.8, 126.2, 124.1, 61.4, 53.1, 30.6, 27.5, 22.7, 14.2.

^{1}H and ^{13}C NMR spectra are in agreement with those previously reported.[2]

Spiro[cyclopent[3]ene-1,2'-indene]-1',3'-dione (11)

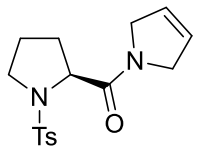


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 – 7.96 (m, 2H), 7.88 – 7.81 (m, 2H), 5.77 – 5.69 (m, 2H), 2.78 – 2.74 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 203.5, 141.7, 135.7, 128.3, 123.5, 77.0, 57.7, 41.7.

^{1}H and ^{13}C NMR spectra are in agreement with those previously reported.[3]

(*S*)-1-(Tosylprolyl)-2,5-dihydro-1H-pyrrole (13)

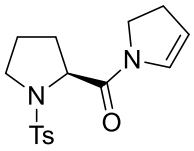


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H), 5.90 – 5.77 (m, 2H), 4.65 – 4.53 (m, 2H), 4.36 – 4.10 (m, 3H), 3.52 – 3.35 (m, 2H), 2.41 (d, J = 1.3 Hz, 3H), 2.41 (s, 3H), 2.21 – 1.90 (m, 3H), 1.86 – 1.73 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 143.5, 136.0, 129.7, 127.7, 127.7, 126.0, 125.1, 59.3, 53.6, 53.3, 48.5, 30.5, 25.0, 21.7.

^{1}H and ^{13}C NMR spectra are in agreement with those previously reported.[4,5]

(*S*)-1-(Tosylprolyl)-2,3-dihydro-1H-pyrrole (13')



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 6.92 – 6.73 (m, 1H), 5.33 – 5.25 (m, 1H), 4.65 – 4.48 (m, 1H), 4.21 – 3.83 (m, 1H), 3.83 – 3.76 (m, 1H), 3.52 – 3.30 (m, 2H), 2.88 – 2.54 (m, 1H), 2.41 (s, 3H), 2.23 – 1.93 (m, 2H), 1.87 – 1.73 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ main conformer: 167,0, 143,6, 135,8, 129,6, 128,4, 127,7, 112,8, 111,7, 59,5, 48,5, 45,7, 30,6, 24,9, 21,7; second conformer: 167,4, 143,6, 135,9, 129,5, 128,4, 127,7, 112,8, 111,7, 59,4, 48,4, 45,6, 30,6, 25,1, 21,7.

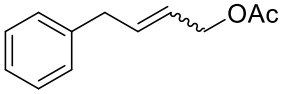
Anal. Calcd. for $C_{16}H_{20}N_2O_3S$: C, 59,98; H, 6,29; N, 8,74; O, 14,98; S, 10,01; found: C, 59,80, H, 6,37; N, 8,60; S, 9,85.

HRMS (ESI): *m/z* calcd. for $C_{16}H_{21}N_2O_3S$: 321,1267; found: 321,1268.

General procedure for preparative CM reactions (Table 2, Scheme 2 & 3 and Chart 1)

An oven dried reaction tube was charged with a solution of the corresponding substrate in dry toluene (1 equiv.) and a solution of cross partner (3 equiv.). A tube was placed in the Radleys Carousel Reaction Station and equilibrated in appropriate temperature for 10 min under argon atmosphere. After that a stock solution of catalyst in dry toluene (1 mol %) was added and the reaction mixture was allowed to stir in adequate temperature for appropriate time. After cooling down the reaction mixture was quenched with 35 mM SnatchCat solution (5 mol %) and purified by column chromatography on the CombiFlash system.

4-Phenylbut-2-en-1-yl acetate (16)

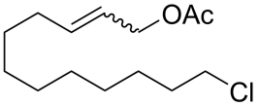


^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 7.23 – 7.15 (m, 5H), 5.97 –5.87 (m, 1H), 5.70 – 5.58 (m, 1H), 4.54 (dd, *J* = 6.3, 0.9 Hz, 2H), 3.39 (d, *J* = 6.8 Hz, 2H), 2.07 (s,3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 170.8, 139.5, 134.5,128.5, 128.4, 126.2, 125.1, 124.1, 64.8, 38.6, 20.9.

^{1}H and ^{13}C NMR spectra are in agreement with those previously reported.[6]

12-Chlorododec-2-en-1-yl acetate (18) (mixture of *E* and *Z* isomers)



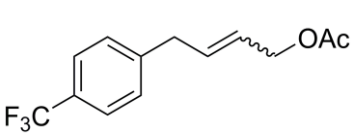
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 – 5.47 (m, 2H), 4.61 (d, *J* = 6.8 Hz, 0.35H, *Z*), 4.50 (d, *J* = 6.5 Hz, 1.6H, *E*), 3.52 (t, *J* = 6.8 Hz, 2H), 2.14 – 1.99 (m, 2H), 2.05 (s, 3H), 1.76 (p, *J* = 6.9 Hz, 2H), 1.49 – 1.21 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 171.0, 136.8, 135.6, 123.8, 123.4, 65.5, 60.6, 45.3, 32.8, 32.4, 29.5, 29.5, 29.3, 29.2, 29.0, 29.0, 27.7, 27.0, 21.2, 21.2.

HRMS (ESI): *m/z* calcd. for $C_{14}H_{25}O_2ClNa$: [M+Na$^+$] 283.1441, found 283.1441

ATR-IR: ν = 607, 650, 723, 969, 1025, 1079, 1228, 1365, 1445, 1461, 1739, 2855, 2927, 3464.

4-(4-(Trifluoromethyl)phenyl)but-2-en-1-yl acetate (20) (mixture of *E* and *Z* isomers)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.9 Hz, 2H), 7.33 – 7.27 (m, 2H), 5.96 – 5.59 (m, 2H), 4.73 (d, *J* = 6.5 Hz, 0.55H, *Z*), 4.55 (d, *J* = 6.2 Hz, 1.60H, *E*), 3.54 (d, *J* = 7.2 Hz, 0.55H, *Z*), 3.45 (d, *J* = 6.7 Hz, 1.6H, *E*), 2.08 (s, 0.8H, *Z*), 2.07 (s, 2.2H, *E*).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 170.9, 144.0 (q, *J* = 1.4 Hz), 143.8 (q, *J* = 1.3 Hz), 133.3, 132.1, 129.1, 128.8, 128.8 (q, *J* = 32.3 Hz), 126.3, 125.6 (q, *J* = 3.9 Hz), 125.3, 124.4 (q, *J* = 271.7 Hz), 64.8, 60.2, 38.5, 33.7, 21.1.

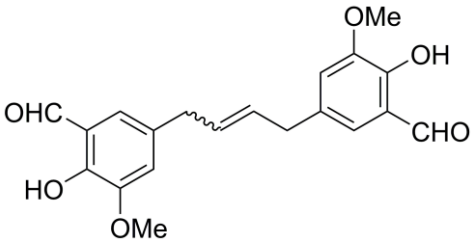
^{19}F NMR (376 MHz, $CDCl_3$) δ 62.4.

LRMS (ESI): *m/z* calcd. for $C_{13}H_{13}O_2F_3$: [M+Na$^+$] 281.1, found 281.2.

ATR-IR: ν = 596, 622, 734, 820, 847, 918, 969, 1018, 1065, 1117, 1161, 1227, 1322, 1364, 1382, 1418, 1618, 1738, 2943, 3023.

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5 (q, *J* = 1.4 Hz), 130.3, 128.8, 128.5 (q, *J* = 32.2 Hz), 125.37 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 271.9 Hz), 38.67.

5,5'-(But-2-ene-1,4-diyl)bis(2-hydroxy-3-methoxybenzaldehyde) (22) (mixture of *E* and *Z* isomers)

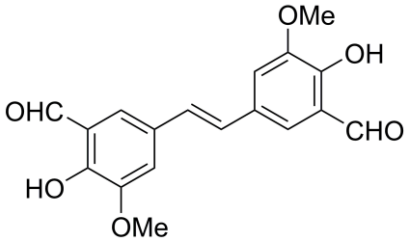


^{1}H NMR (400 MHz, $CDCl_3$) δ 10.95 (d, *J* = 0.7 Hz, 1H), 9.88 (s, 1H), 7.01 – 6.97 (s, 1H), 6.93 (d, *J* = 2.0 Hz, 1H), 5.77 (ddd, *J* = 5.8, 4.6, 1.1 Hz, 0.1H), 5.67 (td, *J* = 3.7, 1.8 Hz, 0.8H), 3.89 (s, 3H), 3.50 (d, *J* = 5.5 Hz, 0.2H), 3.37 (d, *J* = 5.2 Hz, 1.8H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 196.6, 150.2, 148.4, 132.0, 130z.6, 129.3, 123.7, 123.3, 120.6, 118.7, 118.5, 56.4, 56.4, 38.3, 32.8.

^{1}H and ^{13}C NMR spectra are in agreement with those previously reported.[7]

5,5'-(Ethene-1,2-diyl)bis(2-hydroxy-3-methoxybenzaldehyde) (23)



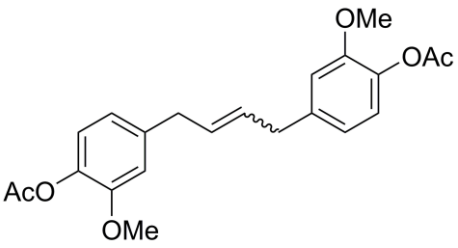
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.10 (s, 1H), 9.96 (s, 1H), 7.31 – 7.27 (m, 2H), 6.97 (s, 1H), 4.00 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 151.6, 148.8, 129.3, 126.6, 122.9, 120.8, 115.0, 56.5.

HRMS (ESI): *m/z* calcd. for $C_{18}H_{17}O_6$: [M+H$^+$] 329.1020, found 329.1011.

ATR-IR: ν = 562, 641, 738, 863, 942, 955, 995, 1092, 1171, 1196, 1246, 1277, 1330, 1379, 1398, 1457, 1475, 1592, 1642.

But-2-ene-1,4-diylbis(2-methoxy-4,1-phenylene) diacetate (25a) (mixture of *E* and *Z* isomers)



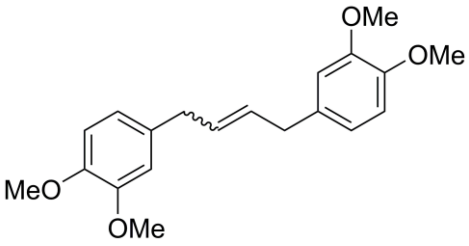
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 – 6.93 (m, 1H), 6.83 – 6.76 (m, 2H), 5.76 (ddd, *J* = 5.8, 4.6, 1.1 Hz, 0.2H), 5.70 (td, *J* = 3.8, 1.9 Hz, 0.8H), 3.80 (s, 3H), 3.51 (d, *J* = 5.7 Hz, 0.4H), 3.40 – 3.34 (m, 1.6H), 2.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 151.0, 150.9, 139.7, 139.6, 137.9, 137.9, 130.5, 129.1, 122.6, 122.5, 120.5, 120.4, 112.7, 112.5, 55.8, 38.9, 33.3, 20.7.

HRMS (ESI): *m/z* calcd. for $C_{22}H_{25}O_6$: [M+H$^+$] 407.1471, found 407.1468.

ATR-IR: ν = 602, 675, 746, 822, 856, 907, 935, 988, 1033, 1063, 1114, 1148, 1196, 1215, 1260, 1282, 1314, 1366, 1417, 1449, 1464, 1508, 1602, 1761, 2840, 2913, 2935, 3001.

1,4-Bis(3,4-dimethoxyphenyl)but-2-ene (25b) (mixture of *E* and *Z* isomers)

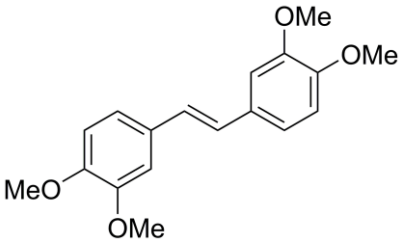


^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 – 6.63 (m, 3H), 5.72 (ddd, *J* = 5.8, 4.6, 1.2 Hz, 0.2H), 5.66 (ddd, *J* = 5.3, 3.7, 1.5 Hz, 0.8H), 3.87 – 3.83 (m, 6H), 3.47 (d, *J* = 5.8 Hz, 0.4H), 3.32 (d, *J* = 5.4 Hz, 1.6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 148.9, 147.4, 133.4, 130.6, 129.2, 120.3, 120.2, 111.9, 111.7, 111.3, 111.3, 56.0, 56.0, 55.8, 55.8, 38.6, 33.0.

^{1}H and ^{13}C NMR spectra are in agreement with those previously reported.[8]

(*E*)-1,2-Bis(3,4-dimethoxyphenyl)ethane

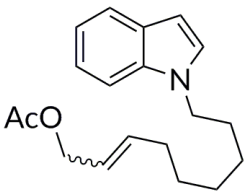


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 – 7.00 (m, 2H), 6.93 (s, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 3.95 (s, 3H), 3.90 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 148.8, 130.8, 126.7, 119.7, 111.3, 108.6, 56.1, 56.0.

^{1}H and ^{13}C NMR spectra are in agreement with those previously reported.[9]

9-(1*H*-Indol-1-yl)non-2-en-1-yl acetate (29) (mixture of *E* and *Z* isomers)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (ddd, *J* = 7.9, 1.3, 0.7 Hz, 1H), 7.38 (d, *J* = 8.3 Hz, 1H), 7.27 – 7.22 (m, 1H), 7.17 – 7.13 (m, 1H), 7.12 (d, *J* = 3.1 Hz, 1H), 6.53 (dd, *J* = 3.1, 0.9 Hz, 1H), 5.83 – 5.52 (m, 2H), 4.64 (dd, *J* = 6.7, 1.0 Hz, 1H), 4.54 (dd, *J* = 6.5, 1.0 Hz, 1H), 4.13 (t, *J* = 7.1 Hz, 2H), 2.17 – 2.02 (m, 5H), 1.86 (p, *J* = 7.3 Hz, 1H), 1.45 – 1.29 (m, 6H).

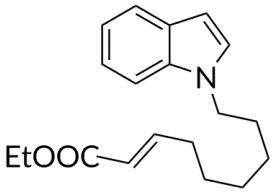
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 170.9, 136.4, 136.0, 135.2, 128.6, 127.8, 127.8, 124.0, 123.5, 121.3, 121.0, 119.2, 109.4, 100.9, 100.9, 65.3, 60.4, 46.4, 32.2, 30.2, 30.2, 29.3, 28.8, 28.8, 28.7, 27.5, 26.9, 26.9, 21.1, 21.1.

HRMS (ESI): *m/z* calcd. for $C_{19}H_{26}NO_2$: [M+H$^+$] 300.1958, found 300.1952.

ATR-IR: ν = 607, 738, 763, 965, 1023, 1159, 1226, 1315, 1336, 1362, 1399, 1463, 1485, 1511, 1611, 1734, 2855, 2929, 3023, 3051.

Ethyl 9-(1*H*-indol-1-yl)non-2-enoate (30)

E isomer



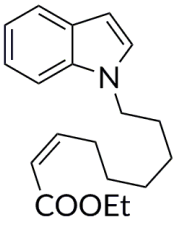
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (ddd, *J* = 7.9, 0.8 Hz, 1H), 7.39 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.16 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.13 (d, *J* = 3.1 Hz, 1H), 6.99 (dt, *J* = 15.6, 7.0 Hz, 1H), 6.55 (dd, *J* = 3.1, 0.9 Hz, 1H), 5.86 (dt, *J* = 15.6, 1.6 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.14 (t, *J* = 7.1 Hz, 2H), 2.26 – 2.15 (m, 1H), 1.87 (p, *J* = 7.2 Hz, 2H), 1.53 – 1.42 (m, 2H), 1.42 – 1.28 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 149.1, 135.9, 128.6, 127.8, 121.4, 121.3, 121.0, 119.2, 109.4, 100.9, 60.2, 46.3, 32.0, 30.1, 28.7, 27.9, 26.8, 14.3.

HRMS (ESI): *m/z* calcd. for $C_{19}H_{25}NO_2Na$: [M+Na$^+$] 322.1783, found 322.1782.

ATR-IR: ν = 741, 980, 1042, 1095, 1181, 1267, 1366, 1465, 1486, 1610, 1652, 1712, 2857, 2930.

Z isomer

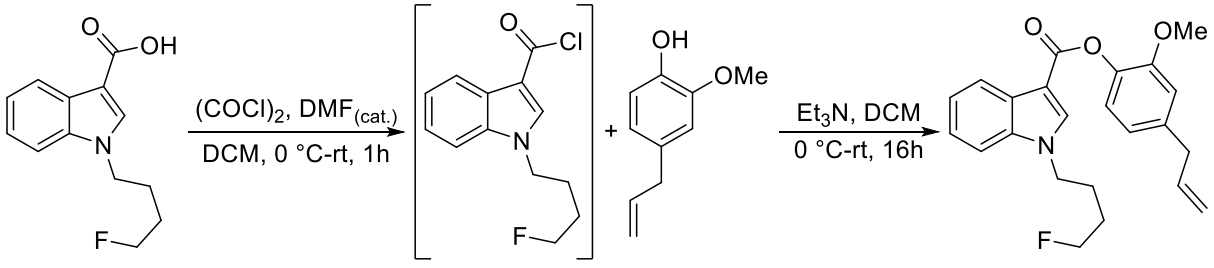


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (ddd, *J* = 7.9, 1.2, 0.8 Hz, 1H), 7.35 (dq, *J* = 8.2, 0.9 Hz, 1H), 7.24 – 7.18 (m, 1H), 7.13 – 7.08 (m, 2H), 6.49 (dd, *J* = 3.1, 0.9 Hz, 1H), 6.18 (dt, *J* = 11.5, 7.5 Hz, 1H), 5.76 (dt, *J* = 11.5, 1.7 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 4.12 (t, *J* = 7.1 Hz, 2H), 2.64 (qd, *J* = 7.4, 1.7 Hz, 2H), 1.84 (p, *J* = 7.3 Hz, 2H), 1.47 – 1.32 (m, 6H), 1.29 (t, *J* = 7.1 Hz, 3H).

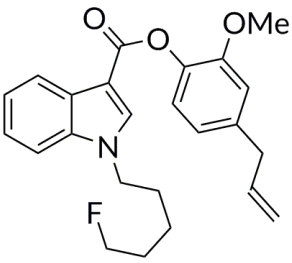
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 150.4, 136.0, 128.7, 127.9, 121.4, 121.0, 119.9, 119.3, 109.5, 101.0, 59.9, 46.5, 30.3, 29.0, 29.0, 28.9, 26.9, 14.4.

ATR-IR: ν = 741, 1042, 1095, 1181, 1267, 1366, 1465, 1486, 1610, 1652, 1712, 2857, 2930.

Synthesis of 4-allyl-2-methoxyphenyl 1-(5-fluoropentyl)-1*H*-indole-3-carboxylate



To a cold (0 °C) solution of 1-(5-fluoropentyl)indole-3-carboxylic acid (2.5 g, 10 mmol, 1equiv.) in DCM (25 mL) oxalyl chloride (1.7 mL, 20 mmol, 2equiv.) was added dropwise followed by two drops of DMF. The reaction mixture was warmed to RT during 1 h and afterwards solvent was evaporated. Residue was dissolved in DCM (40 mL) and TEA (1.75 mL, 12.5 mmol, 1.25 equiv.) was added. The mixture was cooled to 0 °C and solution of eugenol (1.7 mL, 11 mmol, 1.1 equiv.) in DCM (10 mL) was added. Cooling bath was removed and the reaction mixture was stirred at RT for 16 h. After that time water (30 mL) was added and the layers were separated. Organic layer was washed with brine and dried over $MgSO_4$. Product was purified on CombiFlash (Teledyne ISCO) using 20% EtOAc in hexane as a eluent. Further crystallization from hexane allowed to obtain 3.3 g (83%) of the desired product as a colorless crystals.



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.23 (m, 1H), 8.01 (s, 1H), 7.43 – 7.38 (m, 1H), 7.35 – 7.27 (m, 2H), 7.12 (d, *J* = 7.9 Hz, 1H), 6.87 – 6.81 (m, 2H), 6.00 (ddt, *J* = 16.8, 10.0, 6.7 Hz, 1H), 5.18 – 5.08 (m, 2H), 4.45 (dt, *J* = 47.2, 5.9 Hz, 2H), 4.20 (t, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 3.42 (dt, *J* = 6.7, 1.5 Hz, 2H), 1.97 (dt, *J* = 15.2, 7.3 Hz, 2H), 1.83 – 1.66 (m, 2H), 1.56 – 1.45 (m, 2H).

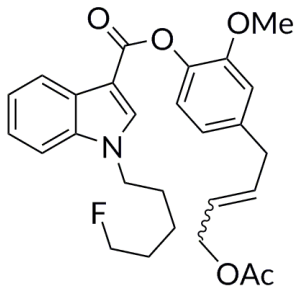
^{13}C NMR (100z MHz, $CDCl_3$) δ 163.0, 151.7, 138.7, 138.3, 137.4, 136.7, 135.1, 127.2, 123.3, 123.0, 122.2, 122.2, 120.8, 116.1, 113.0, 110.1, 106.3, 83.8 (d, *J* = 165.1 Hz),56.1, 47.1, 40.3, 30.1 (d, *J* = 19.8 Hz), 29.7, 23.0 (d, *J* = 5.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ 218.62(tt, *J* = 47.2, 25.9 Hz).

HRMS (ESI): *m/z* calcd. for $C_{24}H_{26}NO_3FNa$: [M+Na^+] 418.1789, found 418.1774.

ATR-IR: ν = 602, 675, 747, 822, 856, 907, 935, 988, 1032, 1114, 1149, 1196, 1216, 1261, 1283, 1315, 1366, 1417, 1449, 1465, 1508, 1603, 1762, 2935, 2958.

4-(4-Acetoxybut-2-en-1-yl)-2-methoxyphenyl 1-(4-fluorobutyl)-1*H*-indole-3- carboxylate (31) (mixture of *E* and *Z* isomers)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 8.24 (m, 1H), 8.01 (s, 1H), 7.42 – 7.38 (m, 1H), 7.34 – 7.27 (m, 2H), 7.12 (d, *J* = 7.7 Hz, 1H), 6.86 – 6.79 (m, 2H), 6.01 – 5.63 (m, 2H), 4.76 (dd, *J* = 6.9, 1.3 Hz, 0.47H), 4.58 (dq, *J* = 6.3, 1.1 Hz, 1.6H), 4.44 (dt, *J* = 47.2, 5.9 Hz, 2H), 4.20 (t, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 3.52 – 3.47 (m, 0.45H), 3.45 – 3.38 (m, 1.6H), 2.08 (s, 3H), 1.96 (dt, *J* = 15.0, 7.3 Hz, 2H), 1.81 – 1.68 (m, 2H), 1.55 – 1.45 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 170.9, 162.9, 151.7, 151.7, 138.4, 138.4, 138.3, 138.2, 136.7, 135.2, 134.4, 133.4, 127.1, 125.5, 124.5, 123.4, 123.3, 123.0, 122.2, 122.1, 120.8, 120.6, 112.9, 112.8, 110.1, 106.2, 83.7 (d, *J* = 165.0 Hz), 64.9, 60.3, 56.0, 56.0, 47.1, 38.6, 33.7, 30.0 (d, *J* = 19.8 Hz), 29.7, 23.0 (d, *J* = 4.9 Hz), 21.1.

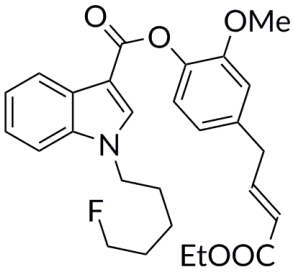
^{19}F NMR (376 MHz, $CDCl_3$) δ -218.58 (tt, *J* = 47.2, 25.9 Hz).

HRMS (ESI): *m/z* calcd. for $C_{27}H_{30}NO_5FNa$: [M+Na^+] 490.2000, found 490.1990.

ATR-IR: ν = 748, 973, 1032, 1066, 1106, 1122, 1149, 1198, 1228, 1381, 1418, 1465, 1486, 1508, 1531, 1603, 1716, 2940.

4-(4-Ethoxy-4-oxobut-2-en-1-yl)-2-methoxyphenyl 1-(4-fluorobutyl)-1*H*-indole-3- carboxylate (32)

***E* isomer**



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 – 8.21 (m, 1H), 8.01 (s, 1H), 7.44 – 7.37 (m, 1H), 7.36 – 7.26 (m, 2H), 7.18 – 7.06 (m, 2H), 6.85 – 6.77 (m, 2H), 5.87 (dt, *J* = 15.6, 1.6 Hz, 1H), 4.44 (dt, *J* = 47.2, 5.9 Hz, 2H), 4.20 (t, *J* = 7.1 Hz, 3H), 4.20 (q, *J* = 7.1 Hz, 1H), 3.54 (dd, *J* = 6.8, 1.7 Hz, 2H), 1.97 (p, *J* = 7.3 Hz, 2H), 1.82 – 1.66 (m, 2H), 1.55 – 1.45 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H).

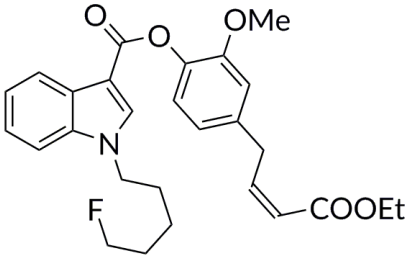
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 162.8, 151.9, 147.1, 138.7, 136.7, 136.4, 135.2, 127.2, 123.6, 123.1, 122.6, 122.3, 122.1, 121.1, 113.1, 110.1, 106.1, 83.7 (d, *J* = 164.9 Hz), 60.4, 56.1, 47.1, 38.5, 30.1 (d, *J* = 19.8 Hz), 29.7, 23.0 (d, *J* = 5.0 Hz), 14.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -218.62 (tt, *J* = 47.2, 25.9 Hz).

HRMS (ESI): *m/z* calcd. for $C_{27}H_{30}NO_5FNa$: [M+Na$^+$] 490.2000, found 490.1987.

ATR-IR: ν = 748, 974, 1033, 1149, 1197, 1265, 1382, 1465, 1508, 1531, 1602, 1713, 2968.

***Z* isomer**



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.23 (m, 1H), 8.01 (s, 1H), 7.42 – 7.38 (m, 1H), 7.34 – 7.27 (m, 2H), 7.12 (d, *J* = 7.9 Hz, 1H), 6.90 – 6.84 (m, 2H), 6.39 (dt, *J* = 11.4, 7.5 Hz, 1H), 5.88 (dt, *J* = 11.4, 1.8 Hz, 1H), 4.44 (dt, *J* = 47.3, 5.9 Hz, 2H), 4.22 (p, *J* = 7.1 Hz, 4H), 4.04 (dd, *J* = 7.5, 1.8 Hz, 2H), 3.81 (s, 3H), 1.97 (p, *J* = 7.3 Hz, 2H), 1.82 – 1.66 (m, 2H), 1.55 – 1.45 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).

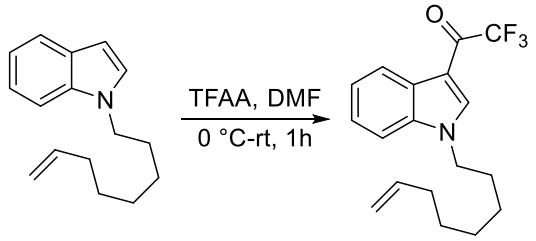
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 162.8, 151.7, 147.8, 138.4, 138.0, 136.6, 135.1, 127.0, 123.3, 122.9, 122.1, 122.0, 120.7, 120.0, 112.9, 110.0, 106.1, 83.7 (d, *J* = 165.1 Hz), 60.1, 56.0, 47.0, 35.1, 30.0 (d, *J* = 19.9 Hz), 29.6, 22.9 (d, *J* = 4.9 Hz), 14.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -218.63 (tt, *J* = 47.2, 25.9 Hz).

HRMS (ESI): *m/z* calcd. for $C_{27}H_{30}NO_5FNa$: [M+Na$^+$] 490.2000, found 490.1987.

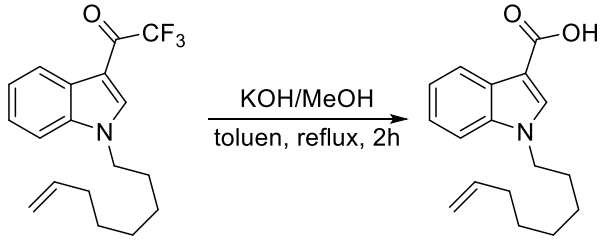
ATR-IR: ν = 750, 973, 1032, 1066, 1123, 1157, 1198, 1266, 1382, 1414, 1465, 1486, 1506, 1531, 1600, 1718, 2940.

Synthesis of 1-(oct-7-en-1-yl)-3-trifuoroacetyl-indole



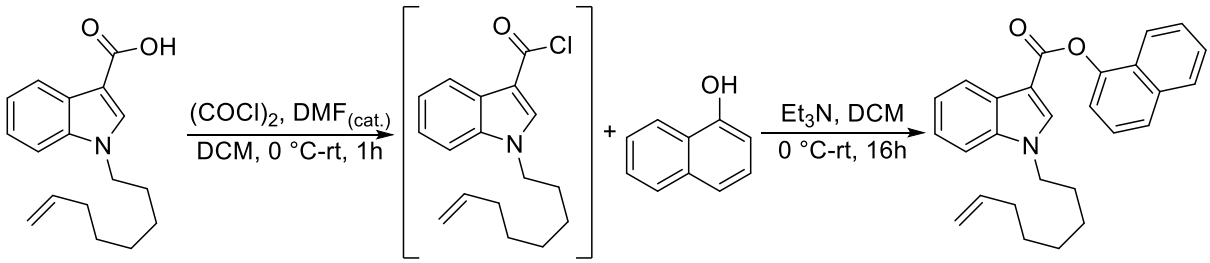
To a cold (0 °C) solution of 1-(oct-7-en-1-yl)indole (2 g, 8.8 mmol, 1equiv.) in DMF (20 mL) TFAA (2.75 mL, 19.8 mmol, 2.2 equiv.) was added dropwise. The reaction mixture was allowed to reach room temperature and was stirred for 1 h. Afterwards the reaction mixture was poured into ice and the pinkish precipitate (1-(oct-7-en-1-yl)-3-trifuoroacetyl-indole) was separated by filtration and dried on air. The product was used without further purification.

Synthesis of 1-(oct-7-en-1-yl)-indole-3-carboxylic acid



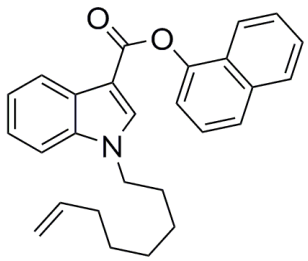
A solution of 1-(oct-7-en-1-yl)-3-trifuoroacetyl-indole dissolved in toluene (5 mL) was added to a boiling solution of KOH (1.75 g, 30.8 mmol, 3.5 equiv.) in methanol (10 mL). The reaction was stirring under reflux for 2 h. The mixture was cooled, methanol was evaporated, and water (50 mL) and toluene (10 mL) were added. Layers are separated. Water phase was acidified to pH = 1 using 6M HCl and extracted with DCM. Organic layer was dried under $MgSO_4$. Drying agent was filtered, mixture was concentrated and product was precipitated with hexane. The product was used without further purification.

Synthesis of naphthalen-1-yl 1-(oct-7-en-1-yl)-1H-indole-3-carboxylate



To a cold (0 °C) solution of 1-(oct-7-en-1-yl)-indole-3-carboxylic acid (2.2 g, 8.1 mmol, 1 equiv.) in DCM (25 mL) oxalyl chloride (1.4 mL, 16.2 mmol, 2 equiv.) was added dropwise followed by two drops of DMF. The reaction mixture was warmed to RT during 1 h and afterwards solvent was evaporated. Residue was dissolved in DCM (40 mL) and TEA (1.40 mL, 10.1 mmol, 1.25 equiv.) was added. Mixture was cooled to 0 °C and a solution of 2-naphthol (1.23 g, 8.5 mmol, 1.05 equiv.) in DCM (10 mL) was added. Cooling bath was removed and the

reaction mixtures stirred for 16 h. After that water (30 mL) was added and layers were separated. Organic layer was washed with brine and dried over $MgSO_4$. Product was purified using flash chromatography on CombiFlash (Teledyne ISCO) using 10% EtOAc in hexane as an eluent. Further crystallization from EtOAc hexane mixture allowed to obtain 2.7g (80% over 3 steps) of desired product as a colorless crystals.



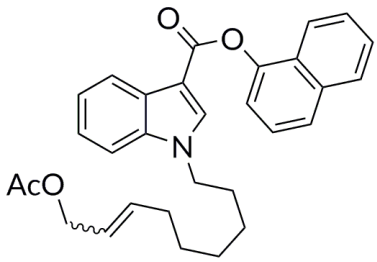
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.30 (m, 1H), 8.13 (s, 1H), 8.07 – 8.02 (m, 1H), 7.94 – 7.89 (m, 1H), 7.79 (dt, *J* = 8.4, 1.0 Hz, 1H), 7.57 – 7.44 (m, 4H), 7.42 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.41 – 7.29 (m, 2H), 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.01 (dq, *J* = 17.1, 1.6 Hz, 1H), 4.96 (ddt, *J* = 10.2, 2.3, 1.2 Hz, 1H), 4.23 (t, *J* = 7.2 Hz, 2H), 2.13 – 2.02 (m, 2H), 2.01 – 1.88 (m, 2H), 1.48 – 1.32 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 147.0, 138.9, 136.9, 135.5, 134.9, 128.1, 127.7, 127.1, 126.5, 125.8, 125.7, 123.2, 122.4, 122.1, 121.8, 118.8, 114.7, 110.4, 106.1, 47.4, 33.7, 30.0, 28.8, 28.7, 26.9.

HRMS (ESI): *m/z* calcd. for $C_{54}H_{54}N_2O_4Na$: [2M+Na$^+$] 817.3976, found 817.3973.

ATR-IR: ν =744, 768, 788, 908, 964, 1012, 1081, 1110, 1147, 1198, 1258, 1375, 1391, 1464, 1485, 1508, 1529, 1598, 1614, 1654, 1714, 2855, 2928, 3054.

Naphthalen-1-yl 1-(9-acetoxynon-7-en-1-yl)-1*H*-indole-3-carboxylate (33) (mixture of *E* and *Z* isomers)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 – 8.31 (m, 1H), 8.13 (d, *J* = 1.5 Hz, 1H), 8.08 – 8.02 (m, 1H), 7.94 – 7.89 (m, 1H), 7.79 (dt, *J* = 8.3, 1.0 Hz, 1H), 7.58 – 7.40 (m, 5H), 7.40 – 7.31 (m, 2H), 5.82 – 5.32 (m, 2H), 4.63 (dd, *J* = 6.6, 1.1 Hz, 0.6H), 4.52 (dt, *J* = 6.5, 1.1 Hz, 1.2H), 4.22 (t, *J* = 7.1 Hz, 2H), 2.18 – 2.02 (m, 5H), 1.95 (p, *J* = 7.1 Hz, 2H), 1.48 – 1.32 (m, 6H).

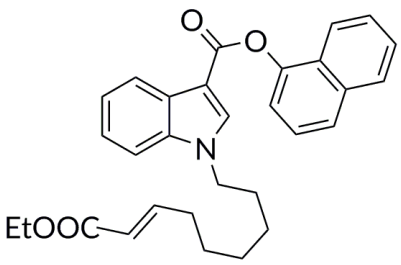
^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 171.0, 163.4, 147.0, 136.8, 136.2, 135.5, 135.0, 134.8, 128.1, 127.7, 127.1, 126.4, 125.8, 125.7, 124.2, 123.7, 123.2, 123.1, 122.4, 122.4, 122.1, 121.7, 118.7, 110.3, 106.1, 65.3, 60.4, 47.3, 32.2, 30.0, 29.9, 29.3, 28.8, 28.8, 27.5, 26.8, 26.8, 21.2, 21.1.

HRMS (ESI): *m/z* calcd. for $C_{30}H_{31}NO_4Na$: [M+Na$^+$] 492.2145, found 492.2127.

ATR-IR: ν = 563, 748, 770, 790, 869, 965, 1013, 1081, 1148, 1224, 1376, 1462, 1486, 1508, 1529, 1598, 1716, 2855, 2930, 3054.

Naphthalen-1-yl 1-(9-ethoxy-9-oxonon-7-en-1-yl)-1*H*-indole-3-carboxylate (34)

***E* isomer**



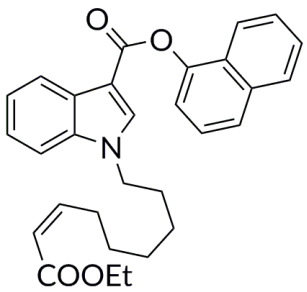
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 – 8.29 (m, 1H), 8.13 (s, 1H), 8.06 – 8.01 (m, 1H), 7.93 – 7.88 (m, 1H), 7.78 (dt, *J* = 8.3, 1.0 Hz, 1H), 7.56 – 7.44 (m, 4H), 7.41 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.39 – 7.30 (m, 2H), 6.20 (dt, *J* = 11.5, 7.6 Hz, 1H), 5.77 (dt, *J* = 11.5, 1.7 Hz, 1H), 4.23 (t, *J* = 7.2 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.67 (qd, *J* = 7.3, 1.7 Hz, 2H), 1.95 (td, *J* = 11.0, 9.0, 5.5 Hz, 2H), 1.54 – 1.36 (m, 6H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 163.4, 150.2, 147.0, 136.9, 135.5, 134.9, 128.1, 127.7, 127.1, 126.4, 125.8, 125.7, 123.2, 122.4, 122.1, 121.8, 120.1, 118.8, 110.4, 106.1, 59.9, 47.4, 30.0, 28.9, 28.9, 26.8, 14.4.

HRMS (ESI): *m/z* calcd. for $C_{30}H_{31}NO_4Na$: [M+Na$^+$] 492.2145, found 492.2124.

ATR-IR: ν = 749, 771, 967, 1013, 1083, 1148, 1259, 1376, 1463, 1530, 1652, 1715, 2857, 2932.

***Z* isomer**



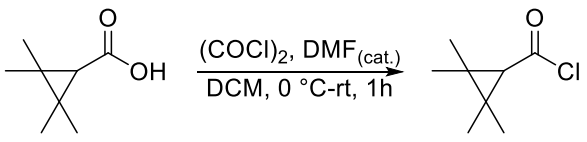
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 – 8.32 (m, 1H), 8.13 (s, 1H), 8.09 – 8.04 (m, 1H), 7.94 – 7.89 (m, 1H), 7.80 (dt, *J* = 8.3, 1.1 Hz, 1H), 7.58 – 7.41 (m, 5H), 7.40 – 7.31 (m, 2H), 6.97 (dt, *J* = 15.6, 6.9 Hz, 1H), 5.84 (dt, *J* = 15.6, 1.5 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 4.20 (t, *J* = 7.2 Hz, 2H), 2.20 (qd, *J* = 7.1, 1.6 Hz, 2H), 1.99 – 1.87 (m, 2H), 1.54 – 1.34 (m, 6H), 1.31 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 163.4, 148.9, 147.0, 136.8, 135.4, 134.8, 128.1, 127.6, 127.1, 126.4, 125.8, 125.6, 123.2, 122.4, 122.0, 121.7, 121.6, 118.7, 110.3, 106.0, 60.3, 47.2, 32.1, 29.9, 28.8, 27.9, 26.8, 14.4.

HRMS (ESI): *m/z* calcd. for $C_{30}H_{31}NO_4Na$: [M+Na$^+$] 492.2145, found 492.2122.

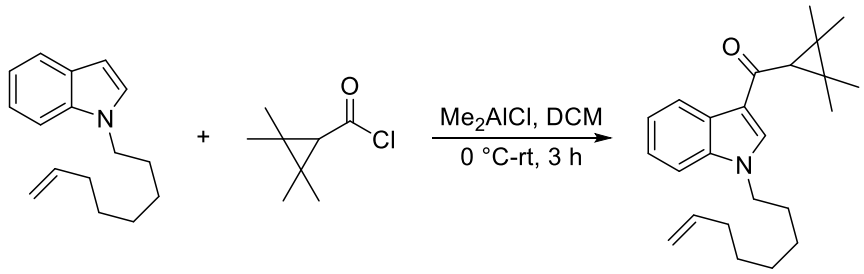
ATR-IR: ν = 749, 771, 967, 1083, 1190, 1377, 1464, 1530, 1716, 2857, 2931.

Synthesis of 2,2,3,3-tetramethylcyclopropyl carboxylic acid chloride

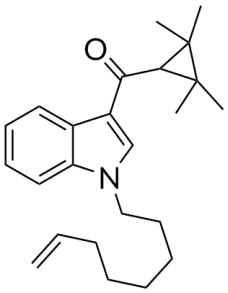


To a cold (0 °C) solution of 2,2,3,3-tetramethylcyclopropyl carboxylic acid (1.44 g, 10.2 mmol, 1.05 equiv.) in DCM (20 mL) oxalyl chloride (1.75 mL, 20.3 mmol, 2.1 equiv.) was added dropwise followed by two drops of DMF. The reaction mixture was warmed to room temperature during 1 h and afterwards solvent was evaporated. The product was used without further purification.

Synthesis of (1-(oct-7-en-1-yl)-1H-indol-3-yl)(2,2,3,3-tetramethylcyclopropyl)methanone



To a cold (0 °C) solution of 1-(oct-7-en-1-yl)indole (2.2 g, 9.7 mmol, 1equiv.) in dry DCM (20 mL), dimethyl aluminum chloride (1M solution in hexane, 12.1 mL, 12.1 mmol, 1.25 equiv.) was added. The reaction was stirred for 15 min at 0 °C and acid chloride in dry DCM (5 mL) was added dropwise. The reaction was allowed to reach RT and stirred for additional 3 h. After cooled to 0 °C 1.5 mL of water was added slowly followed by 15% NaOH solution (1.5 mL) and water (3 mL). $MgSO_4$ was added and the mixture was stirred at RT for 1 h. Drying agent was filtered and crude product was purified on CombiFlash (Teledyne ISCO) using 5% EtOAc in hexane as a eluent. Further crystallization from EtOAc hexane mixture allowed to obtain 2.4 g (73%) of the desired product as a colorless crystals.



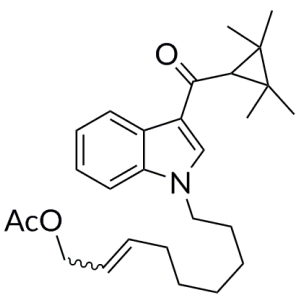
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 – 8.37 (m, 1H), 7.66 (s, 1H), 7.36 – 7.32 (m, 1H), 7.30 – 7.26 (m, 1H), 7.25 (d, *J* = 1.9 Hz, 1H), 5.78 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 5.03 – 4.89 (m, 2H), 4.15 (t, *J* = 7.2 Hz, 2H), 2.03 (q, *J* = 6.7, 2H), 1.95 (s, 1H), 1.89 (dd, *J* = 9.4, 4.2 Hz, 2H), 1.42 – 1.34 (m, 6H), 1.35 (s, 6H), 1.31 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 138.9, 136.7, 133.6, 126.5, 123.0, 122.8, 122.2, 119.7, 114.6, 109.8, 47.1, 41.8, 33.8, 31.7, 30.1, 28.8, 28.7, 26.9, 24.2, 17.2.

HRMS (ESI): *m/z* calcd. for $C_{24}H_{33}NONa$: [M+Na$^+$] 352.2635, found 352.2619.

ATR-IR: ν = 741, 754, 815, 842, 907, 971, 1109, 1146, 1175, 1213, 1371, 1391, 1411, 1464, 1481, 1522, 1610, 2925, 3108.

9-(3-(2,2,3,3-Tetramethylcyclopropane-1-carbonyl)-1*H*-indol-1-yl)non-2-en-1-yl acetate (35) (mixture of *E* and *Z* isomers)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 – 8.38 (m, 1H), 7.66 (s, 1H), 7.36 – 7.31 (m, 1H), 7.30 – 7.23 (m, 2H), 5.80 – 5.48 (m, 2H), 4.60 (dd, *J* = 6.7, 1.1 Hz, 0.4H), 4.50 (dq, *J* = 6.5, 1.0 Hz, 1.6H), 4.15 (t, *J* = 7.2 Hz, 2H), 2.16 – 2.00 (m, 2H), 2.05 (s, 3H), 1.95 (s, 1H), 1.92 – 1.83 (m, 2H), 1.43 – 1.32 (m, 6H), 1.35 (s, 6H), 1.31 (s, 6H).

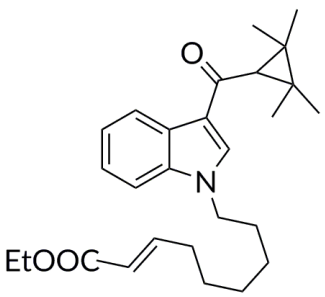
^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 171.1, 171.0, 136.7, 136.3, 135.1, 133.6, 126.5, 124.1, 123.7, 123.0, 122.8, 122.2, 119.7, 109.7, 77.5, 77.2, 76.8, 65.4, 60.5, 47.1, 41.8, 41.7, 32.2, 31.7, 30.1, 30.1, 29.3, 28.8, 28.8, 28.8, 27.5, 26.9, 26.9, 24.2, 21.2, 21.2, 17.2.

HRMS (ESI): *m/z* calcd. for $C_{27}H_{38}NO_3$: [M+H$^+$] 424.2846, found 424.2827.

ATR-IR: ν = 742, 962, 1014, 1024, 1109, 1145, 1227, 1376, 1391, 1413, 1464, 1523, 1612, 1628, 1735, 2858, 2926.

Ethyl 9-(3-(2,2,3,3-tetramethylcyclopropane-1-carbonyl)-1*H*-indol-1-yl)non-2-enoate (36)

E isomer



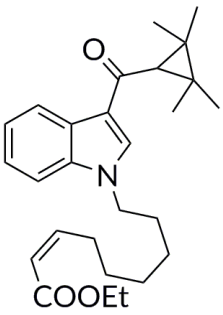
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 – 8.37 (m, 1H), 7.65 (s, 1H), 7.36 – 7.30 (m, 1H), 7.30 – 7.21 (m, 2H), 6.93 (dt, *J* = 15.6, 7.0 Hz, 1H), 5.80 (dt, *J* = 15.7, 1.6 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 4.14 (t, *J* = 7.2 Hz, 2H), 2.18 (qd, *J* = 7.1, 1.6 Hz, 2H), 1.94 (s, 1H), 1.88 (t, *J* = 7.1 Hz, 2H), 1.52 – 1.41 (m, 2H), 1.35 (s, 6H), 1.30 (s, 6H), 1.28 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 166.8, 149.0, 136.7, 133.5, 126.5, 123.0, 122.8, 122.2, 121.6, 119.8, 109.7, 60.3, 47.1, 41.8, 32.1, 31.7, 30.0, 28.8, 28.0, 26.9, 24.2, 17.2, 14.4.

HRMS (ESI): *m/z* calcd. for $C_{27}H_{38}NO_3$: [M+H$^+$] 424.2846, found 424.2834.

ATR-IR: ν = 742, 1041, 1106, 1143, 1180, 1267, 1368, 1391, 1413, 1464, 1523, 1628, 1714, 2861, 2930.

Z isomer



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 – 8.37 (m, 1H), 7.66 (s, 1H), 7.36 – 7.31 (m, 1H), 7.30 – 7.22 (m, 2H), 6.18 (dt, *J* = 11.5, 7.5 Hz, 1H), 5.76 (dt, *J* = 11.5, 1.7 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 4.14 (t, *J* = 7.2 Hz, 2H), 2.65 (qd, *J* = 7.4, 1.7 Hz, 2H), 1.95 (s, 1H), 1.89 (p, *J* = 7.2 Hz, 2H), 1.51 – 1.34 (m, 6H), 1.35 (s, 6H), 1.31 (s, 6H), 1.28 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 166.6, 150.2, 136.7, 133.6, 126.5, 123.0, 122.8, 122.2, 120.0, 119.7, 109.7, 59.9, 47.1, 41.7, 31.7, 30.0, 28.9, 28.9, 28.9, 26.8, 24.2, 17.2, 14.4.

HRMS (ESI): *m/z* calcd. for $C_{27}H_{38}NO_3$: [M+H$^+$] 424.2846, found 424.2836.

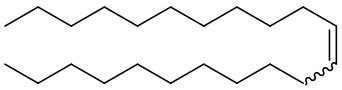
ATR-IR: ν = 743, 1105, 1144, 1182, 1377, 1391, 1414, 1464, 1523, 1634, 1715, 2860, 2928, 2980.

Self-cross metathesis of 1-octene (37)

To a mixture of 1-octene (1.5 mL, 9.4 mmol) and tetradecane (0.5 mL, 1.9 mmol) used as an internal standard, catalyst (500 ppm) was added. The resulting mixture was stirred at 80 °C under an argon atmosphere. Samples were taken at appropriate time intervals and quenched with SnatchCat solution (35 μmol, 1 mL). Conversion and selectivity were determined by GC measurement.

Preparative self-cross metathesis of 1-dodecene

In 250 mL two-neck flask, 1-dodecene (45.5 g, 60.0 mL, 270 mmol) was heated to 70 °C. After temperature equilibration, **Ru9** (50 ppm, 9.4 mg, 13.5 µmol, dissolved in 0.5 mL of DCM) was added. The reaction mixture was stirred for 2 hours. Second portion of catalyst (50 ppm, 9.4 mg, 13.5 µmol, dissolved in 0.5 mL of DCM) was added and stirred for another 2 hours. After that SnatchCat (solution in DCM, 400ppm) was added in one portion and the reaction mixture was stirred at RT for 20 minutes. The reaction mixture was filtered through a short pad with silica gel (5 g) using hexane (10 mL). The mixture was distilled to yield colorless oil (35.5 g, 115 mmol, yield 85%, 96% purity).



^{1}H NMR (400 MHz, $CDCl_3$) δ 5.45 – 5.29 (m, 2H), 2.08 – 1.87 (m, 4H), 1.41 – 1.15 (m, 32H), 0.95 – 0.80 (m, 6H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 130.5, 130.0, 77.5, 77.2, 76.8, 32.8, 32.1, 29.9, 29.8, 29.8, 29.7, 29.7, 29.5, 29.5, 29.3, 27.4, 22.9, 14.3.

^{1}H and ^{13}C NMR spectra are in agreement with those previously reported.[10]

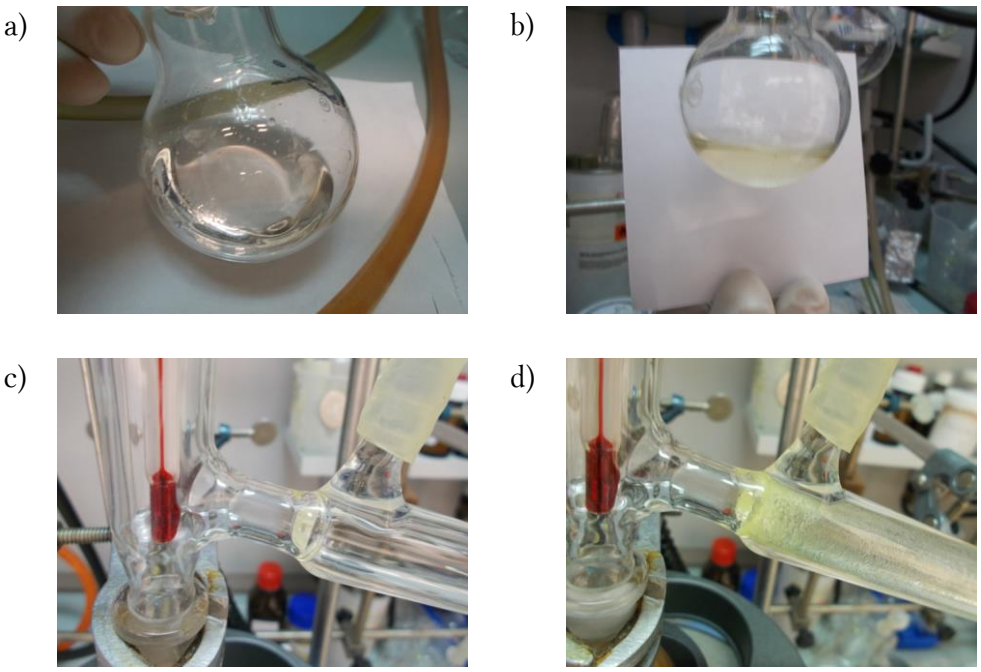


Fig S1. a) Pure colorless product obtained in the presence of **Ru9**. b) Yellowish product obtained in the presence of **Ru7** and tetrafluoro-1,4-benzoquinone (added to avoid migration of double bond). c) Distillation of the reaction mixture after self-CM with **Ru9**. d) Distillation of the reaction mixture after self-CM with **Ru7** and tetrafluoro-1,4-benzoquinone (added to avoid migration of double bond). The yellow crystals are subliming tetrafluoro-1,4-benzoquinone.

General procedure for stability studies in presence of ethylene

In a Young NMR tube corresponding Hoveyda type catalyst (12.8 µmol) was dissolved in 0.65 mL of CD_2Cl_2 and 0.13 M solution of 1,3,5-trimethoxybenzene in CD_2Cl_2 (internal standard, 50 µL, 6.4 µmol) was added in glove box. A Young tube valve was partially open and immediately placed inside an autoclave. Autoclave was purged 3 times with argon and 2 times

with ethylene. Then sample was pressurized to 20 bar for 20 min with ethylene, removed from autoclave. Degradation of catalyst was monitored overnight using Agilent Array function by comparing the integration of benzylidene signal in complexes and 9 protons from methoxy groups in internal standard.

General procedure for ethenolysis reaction

Into a dry autoclave tube charged with ethyl oleate (**39**) (purified by passing through an Al_2O_3 pad, 4.66 g, 15 mmol) and tetradecane (internal standard, 0.61g, 3 mmol), catalyst was added in 0.1 mL of HPLC grade DCM. Autoclave was closed, purged with ethylene (3 times) and stirring at 50 °C for 3h with 20 bar continuous ethylene pressure. After this time reaction was quenched by ethyl-vinyl ether addition. Conversion and selectivity was determined by GC measurement.

Crystallographic information

The single crystal diffraction data for **Ru9** and **Ru10** were collected on a SuperNova diffractometers with mirror-monochromated MoKα radiation. The diffractometers were equipped with an Oxford Cryosystems nitrogen gas-flow apparatus and measurements were conducted at 100K. In the case of **Ru9,** the analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid was used.[11] In the case of **Ru10** also empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm was used.
The CrysAlis PRO program was applied for the data collection and its further reduction.[12] The structures were solved by direct methods and refined using SHELXL[13] program in cooperation with the Olex2 program.[14] The refinements were based on F^2. In the case of **Ru9**, the positions of all the hydrogen atoms were found from Fourier map and its parameters were refined, whereas in the case of **Ru10** most of hydrogen atoms were constrained.
In the case of **Ru10**, where positional disorder of phenyl rings is observed, for this particular ring where disorder was so significant that it was possible to model it, the carbon atoms were refined isotropically (for one of two possible positions). In this structure some significant voids filled in with highly disordered molecules of dichloromethane are present this is why the solvent mask calculated by Olex2 was used.

The lattice parameters and the final *R*-indices obtained for the refinement of the structures of **Ru9** and **Ru10** are presented in Table S1. Selected geometrical parameters are shown in Table S2 and Table S3.

Table S1. X-ray experimental details for Ru9 and Ru10

	Ru9	Ru10
Crystal data		
Chemical formula	$C_{36}H_{48}Cl_2N_2ORu$	$C_{53}H_{50}Cl_2N_2ORu$
M_r	696.73	902.92
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
Temperature (K)	100	100
a (Å)	19.3364 (2)	13.1600 (2)
b (Å)	10.4303 (1)	10.1269 (1)
c (Å)	16.5865 (2)	37.8176 (6)
β (°)	95.737 (1)	98.138 (2)
V (Å^3)	3328.48 (6)	4989.2 (1)
Z	4	4
F(000)	1456	1872
D_x (Mg m^{-3})	1.390	1.202
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.66	0.46
Crystal size (mm)	0.39 × 0.16 × 0.08	0.18 × 0.10 × 0.08
Data collection		
Diffractometer	SuperNova, Dual, Cu at zero, Atlas	SuperNova, Dual, Cu at zero, Atlas
Absorption correction	Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid.	Analytical numeric absorption correction using a multifaceted crystal model based on expressions derived by R.C. Clark & J.S. Reid. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.954, 0.989	0.939, 0.974
No. of measured, independent and observed [I > 2σ(I)] reflections	205909, 16967, 14828	180470, 15249, 13139
R_{int}	0.083	0.075
θ values (°)	θ_{max} = 37.0, θ_{min} = 2.1	θ_{max} = 30.5, θ_{min} = 1.6

Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.028, 0.070, 1.11	0.075, 0.156, 1.20
No. of reflections	16967	15249
No. of parameters	571	564
No. of restraints	0	12
H-atom treatment	All H-atom parameters refined	H atoms treated by a mixture of independent and constrained refinement
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0214P)^2 + 1.7749P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + 29.2521P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.001	0.001
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	1.31, -0.60	1.30, -2.75

Table S2. Selected geometric parameters Ru9 (Å, °)

Ru1—Cl1	2.3327 (3)	C12—C17	1.4116 (13)
Ru1—Cl2	2.3311 (3)	C13—C14	1.4005 (14)
Ru1—O1	2.2948 (8)	C13—C23	1.5194 (14)
Ru1—C1	1.8334 (10)	C14—C15	1.3865 (16)
Ru1—C2	1.9766 (9)	C15—C16	1.3910 (16)
O1—C33	1.3667 (12)	C16—C17	1.3978 (14)
O1—C34	1.4742 (13)	C17—C18	1.5224 (14)
N1—C2	1.3490 (12)	C18—C19	1.5503 (15)
N1—C3	1.4700 (14)	C18—C21	1.5379 (15)
N1—C5	1.4485 (13)	C19—C20	1.5237 (19)
N2—C2	1.3550 (12)	C21—C22	1.5276 (17)
N2—C4	1.4759 (13)	C23—C24	1.5445 (15)
N2—C12	1.4309 (12)	C23—C26	1.5383 (15)
C1—C28	1.4531 (13)	C24—C25	1.5234 (15)
C3—C4	1.5268 (15)	C26—C27	1.5229 (18)
C5—C6	1.5191 (15)	C28—C29	1.4034 (14)
C6—C7	1.3951 (17)	C28—C33	1.4083 (14)
C6—C11	1.3957 (15)	C29—C30	1.3930 (15)
C7—C8	1.3926 (17)	C30—C31	1.3962 (17)
C8—C9	1.394 (2)	C31—C32	1.3951 (15)

C9—C10	1.391 (2)	C32—C33	1.3908 (14)
C10—C11	1.3953 (17)	C34—C35	1.5164 (18)
C12—C13	1.4067 (13)	C34—C36	1.5095 (17)
Cl2—Ru1—Cl1	150.728 (10)	C13—C12—C17	122.24 (8)
O1—Ru1—Cl1	89.33 (2)	C17—C12—N2	118.79 (8)
O1—Ru1—Cl2	88.96 (2)	C12—C13—C23	122.71 (8)
C1—Ru1—Cl1	103.74 (3)	C14—C13—C12	117.87 (9)
C1—Ru1—Cl2	104.55 (3)	C14—C13—C23	119.32 (9)
C1—Ru1—O1	78.69 (4)	C15—C14—C13	120.94 (10)
C1—Ru1—C2	100.20 (4)	C14—C15—C16	120.20 (10)
C2—Ru1—Cl1	90.13 (3)	C15—C16—C17	121.31 (10)
C2—Ru1—Cl2	92.14 (3)	C12—C17—C18	121.83 (8)
C2—Ru1—O1	178.61 (3)	C16—C17—C12	117.43 (9)
C33—O1—Ru1	110.19 (6)	C16—C17—C18	120.74 (9)
C33—O1—C34	119.14 (8)	C17—C18—C19	112.37 (9)
C34—O1—Ru1	129.59 (6)	C17—C18—C21	112.97 (8)
C2—N1—C3	114.11 (8)	C21—C18—C19	110.45 (9)
C2—N1—C5	126.07 (9)	C20—C19—C18	115.59 (10)
C5—N1—C3	119.60 (8)	C22—C21—C18	114.18 (9)
C2—N2—C4	112.53 (8)	C13—C23—C24	109.31 (8)
C2—N2—C12	129.33 (8)	C13—C23—C26	112.26 (8)
C12—N2—C4	117.79 (8)	C26—C23—C24	111.83 (9)
C28—C1—Ru1	119.27 (7)	C25—C24—C23	113.84 (9)
N1—C2—Ru1	119.79 (7)	C27—C26—C23	113.62 (10)
N1—C2—N2	107.05 (8)	C29—C28—C1	122.62 (9)
N2—C2—Ru1	133.06 (7)	C29—C28—C33	118.66 (9)
N1—C3—C4	101.61 (8)	C33—C28—C1	118.72 (8)
N2—C4—C3	102.87 (8)	C30—C29—C28	120.50 (10)
N1—C5—C6	113.71 (9)	C29—C30—C31	119.55 (10)
C7—C6—C5	121.29 (9)	C32—C31—C30	121.08 (10)
C7—C6—C11	119.24 (10)	C33—C32—C31	118.82 (10)
C11—C6—C5	119.36 (10)	O1—C33—C28	112.93 (8)
C8—C7—C6	120.38 (11)	O1—C33—C32	125.86 (9)
C7—C8—C9	119.96 (13)	C32—C33—C28	121.20 (9)

C10—C9—C8	120.09 (11)	O1—C34—C35	108.88 (9)
C9—C10—C11	119.72 (12)	O1—C34—C36	106.28 (9)
C10—C11—C6	120.54 (12)	C36—C34—C35	113.87 (10)
C13—C12—N2	118.86 (8)		
Ru1—O1—C33—C28	-3.92 (10)	C11—C6—C7—C8	1.66 (18)
Ru1—O1—C33—C32	176.81 (8)	C12—N2—C2—Ru1	-17.33 (16)
Ru1—O1—C34—C35	-89.07 (11)	C12—N2—C2—N1	166.26 (9)
Ru1—O1—C34—C36	33.98 (13)	C12—N2—C4—C3	-161.27 (8)
Ru1—C1—C28—C29	175.89 (8)	C12—C13—C14—C15	-0.99 (16)
Ru1—C1—C28—C33	-3.70 (12)	C12—C13—C23—C24	-100.82 (11)
Cl1—Ru1—C1—C28	-85.54 (8)	C12—C13—C23—C26	134.49 (10)
Cl2—Ru1—C1—C28	86.88 (8)	C12—C17—C18—C19	-86.28 (11)
O1—Ru1—C1—C28	0.95 (7)	C12—C17—C18—C21	147.94 (9)
N1—C3—C4—N2	-12.57 (10)	C13—C12—C17—C16	0.21 (14)
N1—C5—C6—C7	-44.32 (15)	C13—C12—C17—C18	-178.96 (9)
N1—C5—C6—C11	139.31 (11)	C13—C14—C15—C16	0.80 (19)
N2—C12—C13—C14	176.67 (9)	C13—C23—C24—C25	178.80 (9)
N2—C12—C13—C23	-6.91 (14)	C13—C23—C26—C27	-56.82 (13)
N2—C12—C17—C16	-175.98 (9)	C14—C13—C23—C24	75.56 (12)
N2—C12—C17—C18	4.86 (14)	C14—C13—C23—C26	-49.14 (13)
C1—C28—C29—C30	178.27 (10)	C14—C15—C16—C17	-0.07 (19)
C1—C28—C33—O1	5.07 (13)	C15—C16—C17—C12	-0.42 (16)
C1—C28—C33—C32	-175.63 (9)	C15—C16—C17—C18	178.75 (11)
C2—Ru1—C1—C28	-178.19 (8)	C16—C17—C18—C19	94.59 (12)
C2—N1—C3—C4	10.01 (11)	C16—C17—C18—C21	-31.20 (13)
C2—N1—C5—C6	128.55 (11)	C17—C12—C13—C14	0.48 (14)
C2—N2—C4—C3	12.69 (11)	C17—C12—C13—C23	176.91 (9)
C2—N2—C12—C13	105.57 (12)	C17—C18—C19—C20	-51.66 (13)
C2—N2—C12—C17	-78.11 (13)	C17—C18—C21—C22	-57.89 (12)
C3—N1—C2—Ru1	-179.50 (7)	C19—C18—C21—C22	175.30 (10)
C3—N1—C2—N2	-2.52 (12)	C21—C18—C19—C20	75.48 (12)
C3—N1—C5—C6	-57.17 (13)	C23—C13—C14—C15	-177.54 (10)
C4—N2—C2—Ru1	169.58 (8)	C24—C23—C26—C27	179.89 (11)
C4—N2—C2—N1	-6.83 (11)	C26—C23—C24—C25	-56.25 (12)

C4—N2—C12—C13	-81.65 (11)	C28—C29—C30—C31	-1.56 (16)
C4—N2—C12—C17	94.66 (11)	C29—C28—C33—O1	-174.53 (9)
C5—N1—C2—Ru1	-4.94 (14)	C29—C28—C33—C32	4.77 (15)
C5—N1—C2—N2	172.03 (10)	C29—C30—C31—C32	2.80 (17)
C5—N1—C3—C4	-164.92 (9)	C30—C31—C32—C33	-0.24 (16)
C5—C6—C7—C8	-174.71 (12)	C31—C32—C33—O1	175.61 (10)
C5—C6—C11—C10	174.06 (11)	C31—C32—C33—C28	-3.59 (15)
C6—C7—C8—C9	0.6 (2)	C33—O1—C34—C35	77.79 (12)
C7—C6—C11—C10	-2.38 (18)	C33—O1—C34—C36	-159.15 (10)
C7—C8—C9—C10	-2.1 (2)	C33—C28—C29—C30	-2.14 (15)
C8—C9—C10—C11	1.4 (2)	C34—O1—C33—C28	-173.17 (9)
C9—C10—C11—C6	0.88 (19)	C34—O1—C33—C32	7.57 (15)

Table S3. Selected geometric parameters R10 (Å, °)

Ru1—Cl1	2.3273 (10)	C22—C23	1.383 (7)
Ru1—Cl2	2.3402 (9)	C23—C24	1.391 (6)
Ru1—O1	2.272 (3)	C25—C26	1.398 (5)
Ru1—C1	1.829 (4)	C25—C30	1.390 (5)
Ru1—C2	1.969 (4)	C26—C27	1.387 (6)
O1—C50	1.377 (5)	C27—C28	1.388 (7)
O1—C51	1.472 (4)	C28—C29	1.385 (6)
N1—C2	1.352 (5)	C29—C30	1.397 (6)
N1—C3	1.469 (5)	C31—C32	1.538 (11)
N1—C5	1.468 (5)	C31—C32A	1.49 (3)
N2—C2	1.351 (4)	C31—C38	1.529 (5)
N2—C4	1.488 (5)	C32—C33	1.369 (14)
N2—C12	1.445 (4)	C32—C37	1.390 (12)
C1—C45	1.453 (5)	C33—C34	1.390 (10)
C3—C4	1.515 (5)	C34—C35	1.361 (14)
C5—C6	1.516 (6)	C35—C36	1.378 (14)
C6—C7	1.393 (6)	C36—C37	1.389 (11)
C6—C11	1.386 (6)	C32A—C33A	1.387 (19)
C7—C8	1.394 (6)	C32A—C37A	1.393 (19)
C8—C9	1.390 (6)	C33A—C34A	1.402 (19)
C9—C10	1.395 (6)	C34A—C35A	1.377 (18)

C10—C11	1.390 (6)	C35A—C36A	1.375 (17)
C12—C13	1.398 (5)	C36A—C37A	1.405 (18)
C12—C17	1.402 (5)	C38—C39	1.392 (5)
C13—C14	1.399 (5)	C38—C43	1.392 (5)
C13—C31	1.530 (5)	C39—C40	1.400 (6)
C14—C15	1.382 (5)	C40—C41	1.384 (7)
C15—C16	1.401 (5)	C41—C42	1.385 (6)
C15—C44	1.516 (5)	C42—C43	1.395 (5)
C16—C17	1.392 (5)	C45—C46	1.393 (5)
C17—C18	1.534 (5)	C45—C50	1.413 (5)
C18—C19	1.520 (5)	C46—C47	1.386 (6)
C18—C25	1.522 (5)	C47—C48	1.399 (6)
C19—C20	1.395 (6)	C48—C49	1.390 (6)
C19—C24	1.392 (6)	C49—C50	1.388 (5)
C20—C21	1.398 (7)	C51—C52	1.510 (7)
C21—C22	1.386 (8)	C51—C53	1.520 (6)
Cl1—Ru1—Cl2	153.56 (4)	C22—C21—C20	120.0 (5)
O1—Ru1—Cl1	88.98 (8)	C23—C22—C21	119.8 (4)
O1—Ru1—Cl2	89.00 (7)	C22—C23—C24	120.1 (5)
C1—Ru1—Cl1	103.10 (11)	C23—C24—C19	121.0 (4)
C1—Ru1—Cl2	102.40 (11)	C26—C25—C18	119.5 (3)
C1—Ru1—O1	79.22 (13)	C30—C25—C18	122.0 (3)
C1—Ru1—C2	101.54 (15)	C30—C25—C26	118.5 (4)
C2—Ru1—Cl1	88.46 (10)	C27—C26—C25	120.9 (4)
C2—Ru1—Cl2	93.23 (10)	C26—C27—C28	119.9 (4)
C2—Ru1—O1	177.43 (12)	C29—C28—C27	120.0 (4)
C50—O1—Ru1	110.1 (2)	C28—C29—C30	119.9 (4)
C50—O1—C51	119.2 (3)	C25—C30—C29	120.8 (4)
C51—O1—Ru1	130.4 (3)	C13—C31—C32	112.2 (6)
C2—N1—C3	113.9 (3)	C32A—C31—C13	119.6 (17)
C2—N1—C5	125.0 (3)	C32A—C31—C38	112 (3)
C5—N1—C3	120.7 (3)	C38—C31—C13	111.2 (3)
C2—N2—C4	112.3 (3)	C38—C31—C32	113.4 (7)
C2—N2—C12	126.9 (3)	C33—C32—C31	125.5 (9)

C12—N2—C4	120.5 (3)	C33—C32—C37	116.4 (9)
C45—C1—Ru1	119.3 (3)	C37—C32—C31	118.1 (9)
N1—C2—Ru1	118.8 (3)	C32—C33—C34	121.8 (12)
N2—C2—Ru1	133.6 (3)	C35—C34—C33	120.4 (10)
N2—C2—N1	107.4 (3)	C34—C35—C36	119.9 (7)
N1—C3—C4	102.4 (3)	C35—C36—C37	118.6 (8)
N2—C4—C3	103.1 (3)	C36—C37—C32	122.8 (9)
N1—C5—C6	110.6 (3)	C33A—C32A—C31	119 (2)
C7—C6—C5	120.4 (4)	C33A—C32A—C37A	121 (2)
C11—C6—C5	120.4 (4)	C37A—C32A—C31	120 (2)
C11—C6—C7	119.2 (4)	C32A—C33A—C34A	119 (2)
C6—C7—C8	120.1 (4)	C35A—C34A—C33A	120.7 (19)
C9—C8—C7	120.3 (4)	C36A—C35A—C34A	121 (2)
C8—C9—C10	119.9 (4)	C35A—C36A—C37A	119.8 (19)
C11—C10—C9	119.2 (4)	C32A—C37A—C36A	119.2 (18)
C6—C11—C10	121.4 (4)	C39—C38—C31	122.6 (3)
C13—C12—N2	119.6 (3)	C43—C38—C31	118.5 (3)
C13—C12—C17	121.3 (3)	C43—C38—C39	118.9 (4)
C17—C12—N2	119.1 (3)	C38—C39—C40	120.0 (4)
C12—C13—C14	118.0 (3)	C41—C40—C39	120.3 (4)
C12—C13—C31	121.5 (3)	C40—C41—C42	120.2 (4)
C14—C13—C31	120.2 (3)	C41—C42—C43	119.4 (4)
C15—C14—C13	121.9 (3)	C38—C43—C42	121.2 (4)
C14—C15—C16	118.8 (3)	C46—C45—C1	122.9 (3)
C14—C15—C44	121.1 (3)	C46—C45—C50	118.9 (3)
C16—C15—C44	120.0 (3)	C50—C45—C1	118.2 (3)
C17—C16—C15	121.0 (3)	C47—C46—C45	121.3 (4)
C12—C17—C18	120.1 (3)	C46—C47—C48	118.9 (4)
C16—C17—C12	118.8 (3)	C49—C48—C47	121.1 (4)
C16—C17—C18	121.2 (3)	C50—C49—C48	119.5 (4)
C19—C18—C17	111.0 (3)	O1—C50—C45	113.0 (3)

C19—C18—C25	111.8 (3)	O1—C50—C49	126.6 (3)
C25—C18—C17	114.2 (3)	C49—C50—C45	120.3 (4)
C20—C19—C18	119.7 (4)	O1—C51—C52	106.3 (3)
C24—C19—C18	121.9 (3)	O1—C51—C53	110.0 (3)
C24—C19—C20	118.4 (4)	C52—C51—C53	112.2 (4)
C19—C20—C21	120.7 (5)		

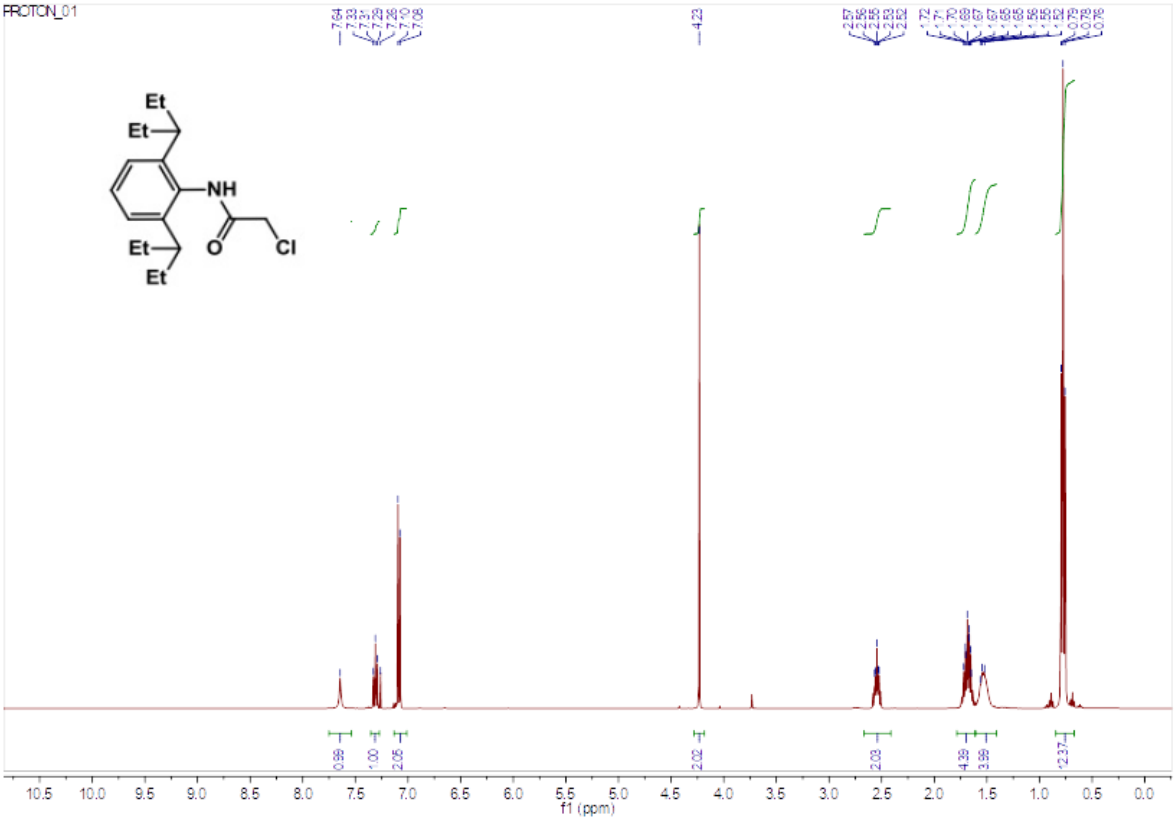
Ru1—O1—C50—C45	3.3 (4)	C17—C18—C19—C24	-37.7 (5)
Ru1—O1—C50—C49	-174.8 (3)	C17—C18—C25—C26	-79.7 (4)
Ru1—O1—C51—C52	18.7 (5)	C17—C18—C25—C30	102.9 (4)
Ru1—O1—C51—C53	-102.9 (4)	C18—C19—C20—C21	179.3 (4)
Ru1—C1—C45—C46	176.1 (3)	C18—C19—C24—C23	-178.5 (4)
Ru1—C1—C45—C50	-3.1 (4)	C18—C25—C26—C27	-176.6 (4)
Cl1—Ru1—C1—C45	-82.8 (3)	C18—C25—C30—C29	175.9 (4)
Cl2—Ru1—C1—C45	90.2 (3)	C19—C18—C25—C26	153.3 (4)
O1—Ru1—C1—C45	3.6 (3)	C19—C18—C25—C30	-24.1 (5)
N1—C3—C4—N2	-9.0 (4)	C19—C20—C21—C22	-0.9 (7)
N1—C5—C6—C7	-80.3 (5)	C20—C19—C24—C23	-0.1 (6)
N1—C5—C6—C11	97.6 (4)	C20—C21—C22—C23	0.1 (7)
N2—C12—C13—C14	175.3 (3)	C21—C22—C23—C24	0.6 (7)
N2—C12—C13—C31	-9.6 (5)	C22—C23—C24—C19	-0.7 (6)
N2—C12—C17—C16	-177.0 (3)	C24—C19—C20—C21	0.8 (6)
N2—C12—C17—C18	4.4 (5)	C25—C18—C19—C20	-87.3 (4)
C1—C45—C46—C47	-178.3 (4)	C25—C18—C19—C24	91.1 (4)
C1—C45—C50—O1	-0.8 (5)	C25—C26—C27—C28	0.8 (7)
C1—C45—C50—C49	177.5 (3)	C26—C25—C30—C29	-1.5 (6)
C2—Ru1—C1—C45	-173.9 (3)	C26—C27—C28—C29	-1.8 (7)
C2—N1—C3—C4	6.8 (4)	C27—C28—C29—C30	1.1 (7)
C2—N1—C5—C6	142.2 (4)	C28—C29—C30—C25	0.5 (7)
C2—N2—C4—C3	9.4 (4)	C30—C25—C26—C27	0.9 (6)
C2—N2—C12—C13	103.6 (4)	C31—C13—C14—C15	-173.1 (3)
C2—N2—C12—C17	-76.6 (5)	C31—C32—C33—C34	-177.4 (12)
C3—N1—C2—Ru1	-176.6 (2)	C31—C32—C37—C36	176.9 (10)
C3—N1—C2—N2	-1.1 (4)	C31—C32A—C33A—C34A	-178 (5)
C3—N1—C5—C6	-45.6 (5)	C31—C32A—C37A—C36A	176 (4)

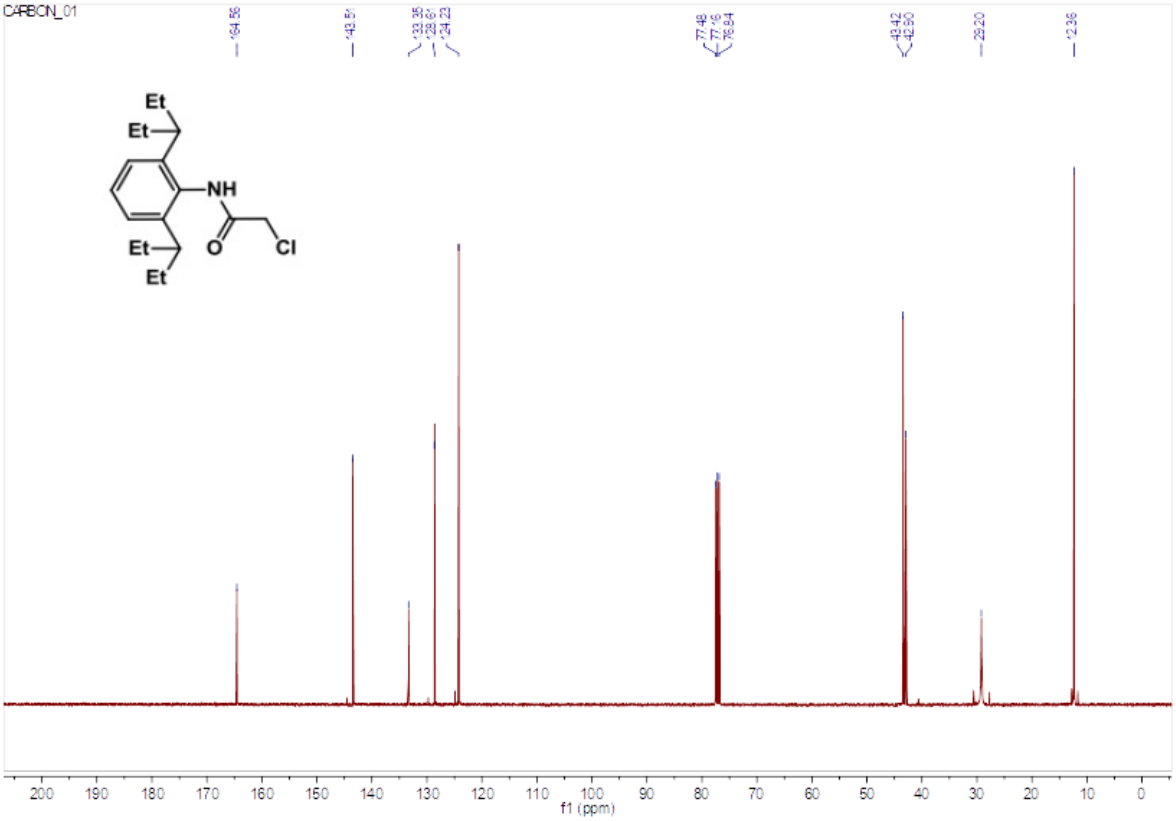
C4—N2—C2—Ru1	169.1 (3)	C31—C38—C39—C40	178.9 (4)
C4—N2—C2—N1	-5.5 (4)	C31—C38—C43—C42	-178.5 (3)
C4—N2—C12—C13	-84.1 (4)	C32—C31—C32A—C33A	-4 (17)
C4—N2—C12—C17	95.8 (4)	C32—C31—C32A—C37A	174 (26)
C5—N1—C2—Ru1	-4.0 (5)	C32—C31—C38—C39	13.6 (8)
C5—N1—C2—N2	171.5 (3)	C32—C31—C38—C43	-165.6 (8)
C5—N1—C3—C4	-166.2 (3)	C32—C33—C34—C35	1 (2)
C5—C6—C7—C8	179.0 (4)	C33—C32—C37—C36	-2 (2)
C5—C6—C11—C10	-178.3 (3)	C33—C34—C35—C36	-2.8 (16)
C6—C7—C8—C9	-1.6 (7)	C34—C35—C36—C37	2.2 (14)
C7—C6—C11—C10	-0.3 (6)	C35—C36—C37—C32	0.1 (16)
C7—C8—C9—C10	1.4 (7)	C37—C32—C33—C34	1 (2)
C8—C9—C10—C11	-0.7 (6)	C32A—C31—C32—C33	172 (23)
C9—C10—C11—C6	0.1 (6)	C32A—C31—C32—C37	-7 (20)
C11—C6—C7—C8	1.0 (6)	C32A—C31—C38—C39	23.1 (15)
C12—N2—C2—Ru1	-18.1 (6)	C32A—C31—C38—C43	-156.1 (15)
C12—N2—C2—N1	167.4 (3)	C32A—C33A—C34A—C35A	-2 (8)
C12—N2—C4—C3	-164.0 (3)	C33A—C32A—C37A—C36A	-7 (8)
C12—C13—C14—C15	2.1 (5)	C33A—C34A—C35A—C36A	0 (6)
C12—C13—C31—C32	83.7 (8)	C34A—C35A—C36A—C37A	-2 (6)
C12—C13—C31—C32A	78 (3)	C35A—C36A—C37A—C32A	5 (6)
C12—C13—C31—C38	-148.0 (3)	C37A—C32A—C33A—C34A	5 (9)
C12—C17—C18—C19	-73.9 (4)	C38—C31—C32—C33	-102.8 (15)
C12—C17—C18—C25	158.7 (3)	C38—C31—C32—C37	78.7 (13)
C13—C12—C17—C16	2.8 (5)	C38—C31—C32A—C33A	-102 (5)
C13—C12—C17—C18	-175.7 (3)	C38—C31—C32A—C37A	75 (5)
C13—C14—C15—C16	2.1 (6)	C38—C39—C40—C41	1.1 (7)
C13—C14—C15—C44	179.0 (4)	C39—C38—C43—C42	2.3 (6)
C13—C31—C32—C33	24.2 (18)	C39—C40—C41—C42	-0.6 (8)
C13—C31—C32—C37	-154.3 (10)	C40—C41—C42—C43	1.0 (7)
C13—C31—C32A—C33A	31 (7)	C41—C42—C43—C38	-1.8 (6)

C13—C31—C32A—C37A	-152 (4)	C43—C38—C39—C40	-1.9 (6)
C13—C31—C38—C39	-114.0 (4)	C44—C15—C16—C17	179.1 (4)
C13—C31—C38—C43	66.8 (4)	C45—C46—C47—C48	-0.5 (6)
C14—C13—C31—C32	-101.2 (8)	C46—C45—C50—O1	-179.9 (3)
C14—C13—C31—C32A	-107 (3)	C46—C45—C50—C49	-1.7 (5)
C14—C13—C31—C38	27.0 (4)	C46—C47—C48—C49	1.0 (7)
C14—C15—C16—C17	-4.0 (6)	C47—C48—C49—C50	-1.8 (6)
C15—C16—C17—C12	1.5 (5)	C48—C49—C50—O1	-179.8 (4)
C15—C16—C17—C18	-179.9 (3)	C48—C49—C50—C45	2.2 (6)
C16—C17—C18—C19	107.6 (4)	C50—O1—C51—C52	-168.0 (3)
C16—C17—C18—C25	-19.8 (5)	C50—O1—C51—C53	70.3 (5)
C17—C12—C13—C14	-4.6 (5)	C50—C45—C46—C47	0.8 (6)
C17—C12—C13—C31	170.5 (3)	C51—O1—C50—C45	-171.2 (3)
C17—C18—C19—C20	143.9 (4)	C51—O1—C50—C49	10.7 (6)

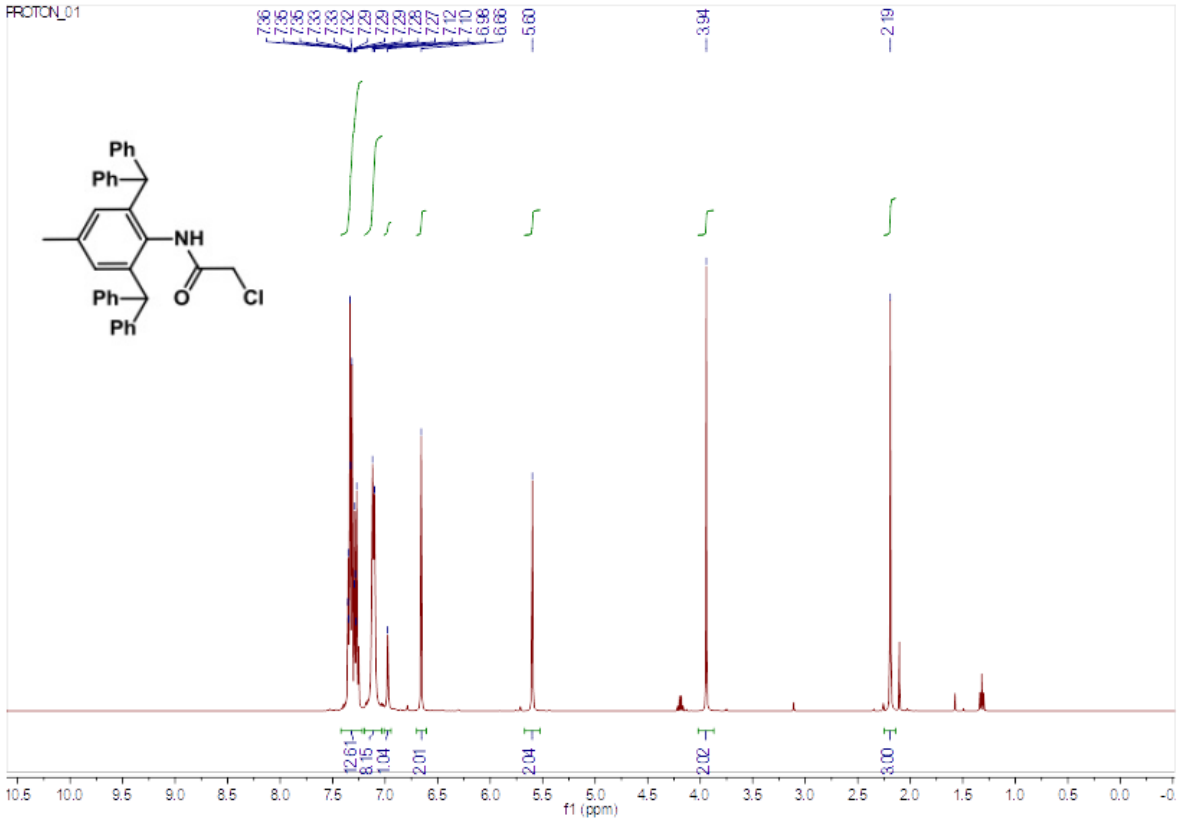
^{1}H and ^{13}C NMR Spectra

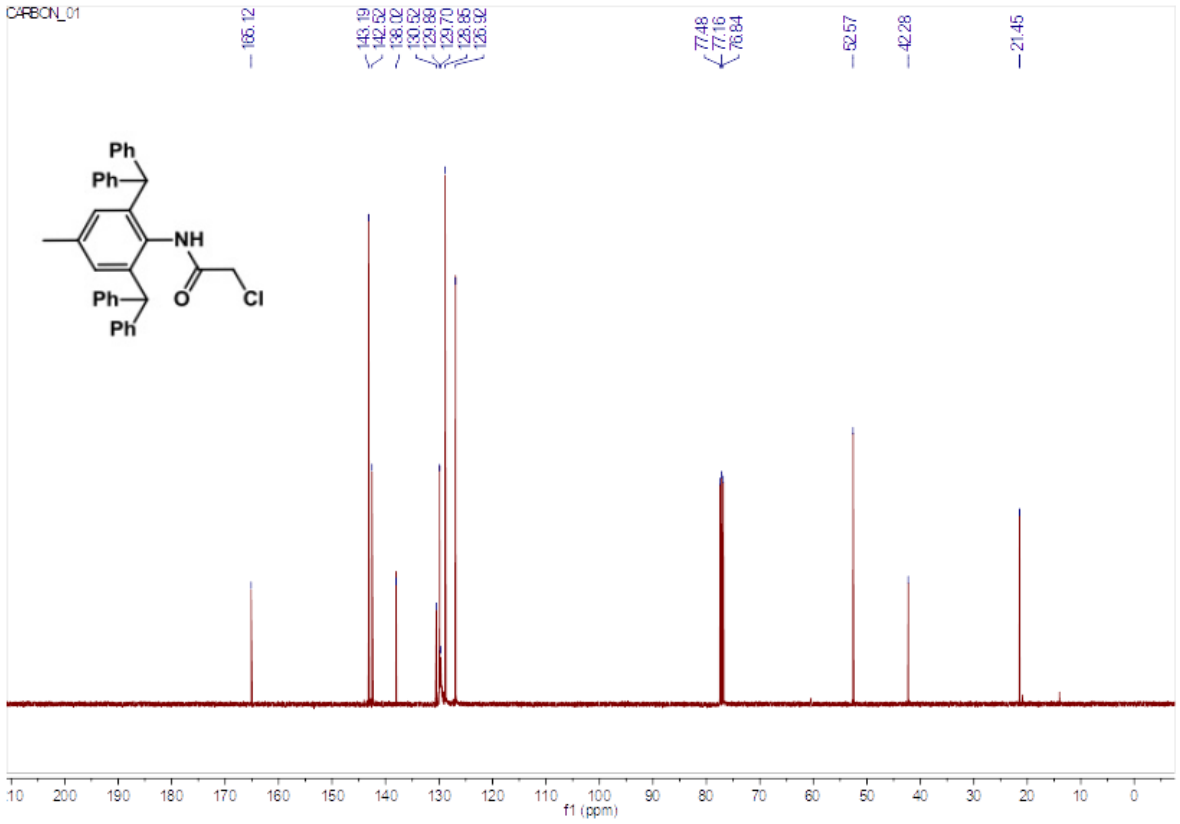
N-Chloroacetyl-2,6-bis(3-pentyl)aniline



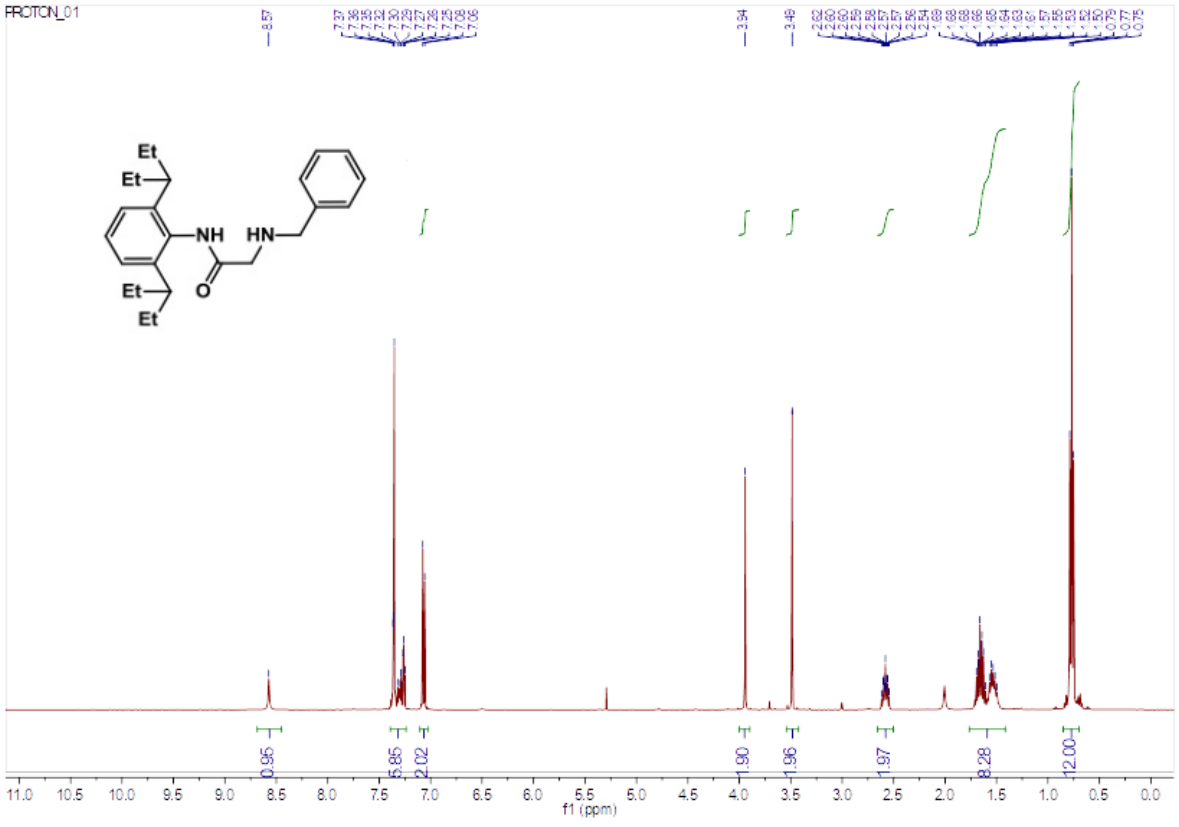


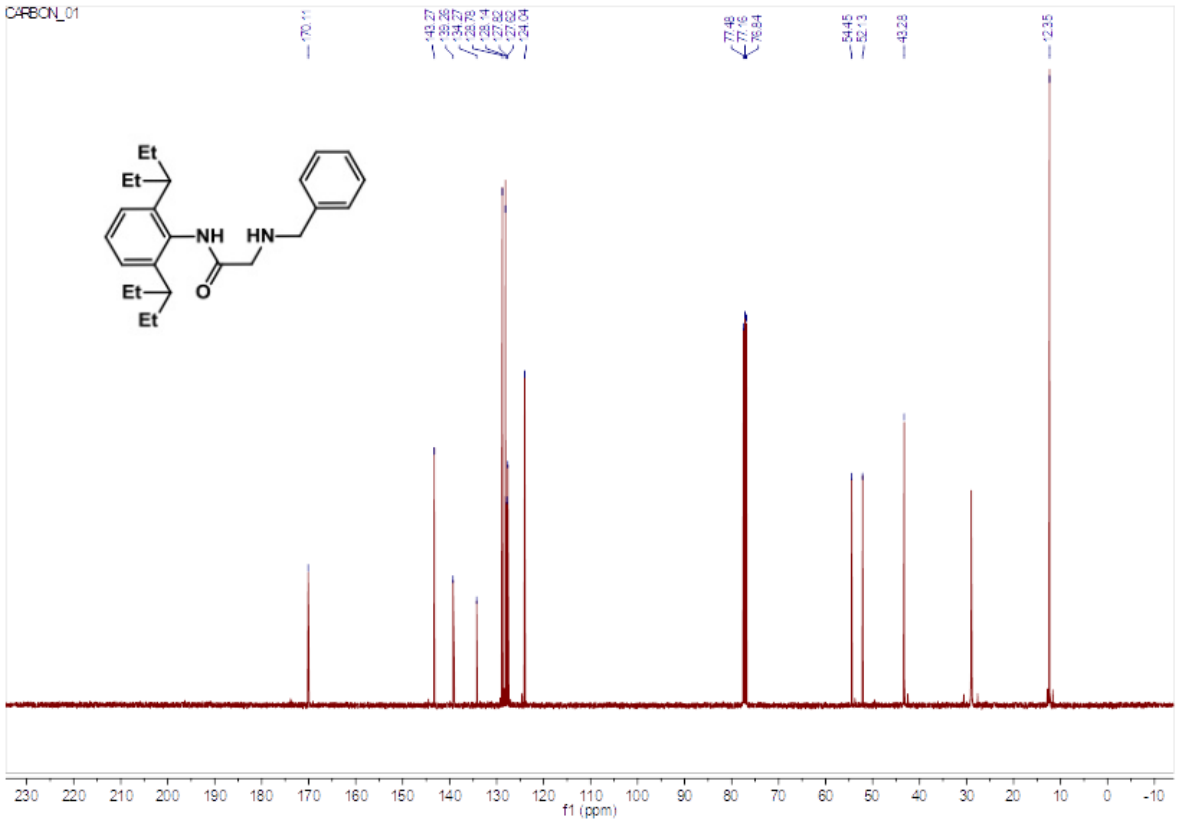
N-Chloroacetyl-2,6-bis(diphenylmethyl)-4-methylaniline



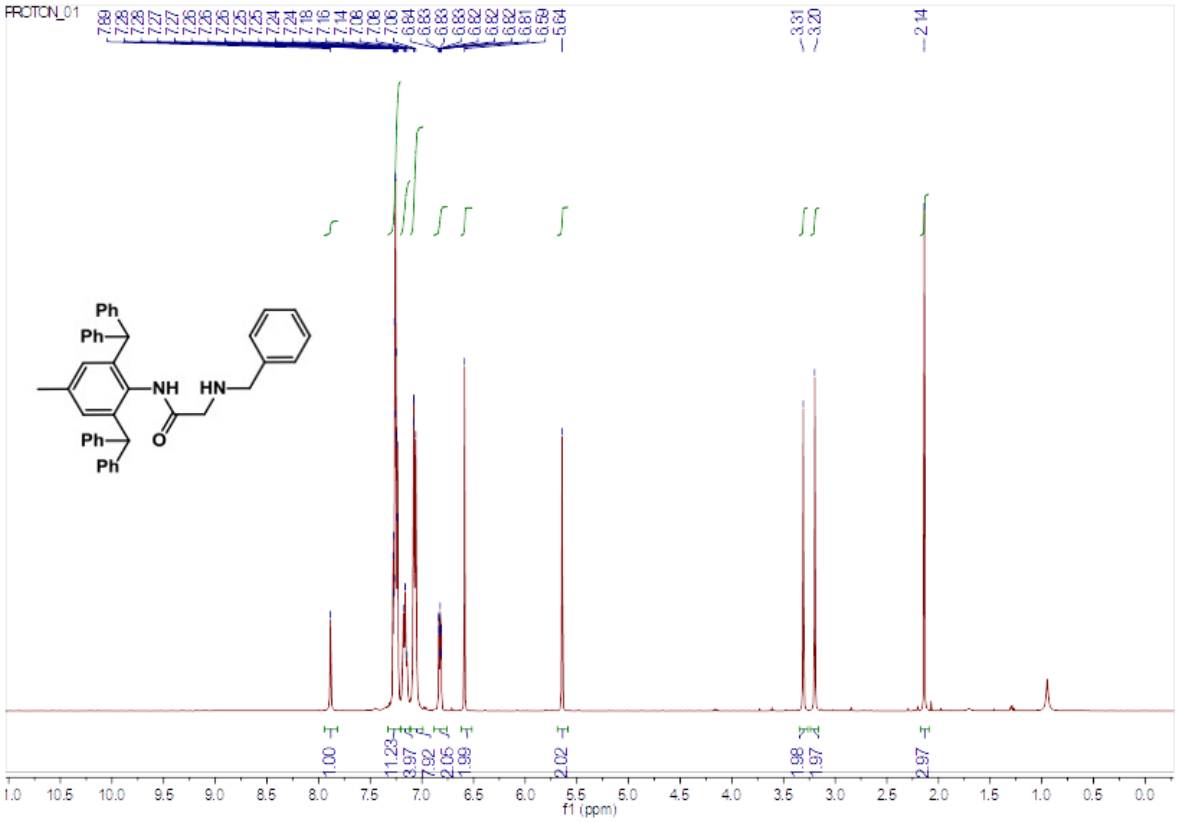


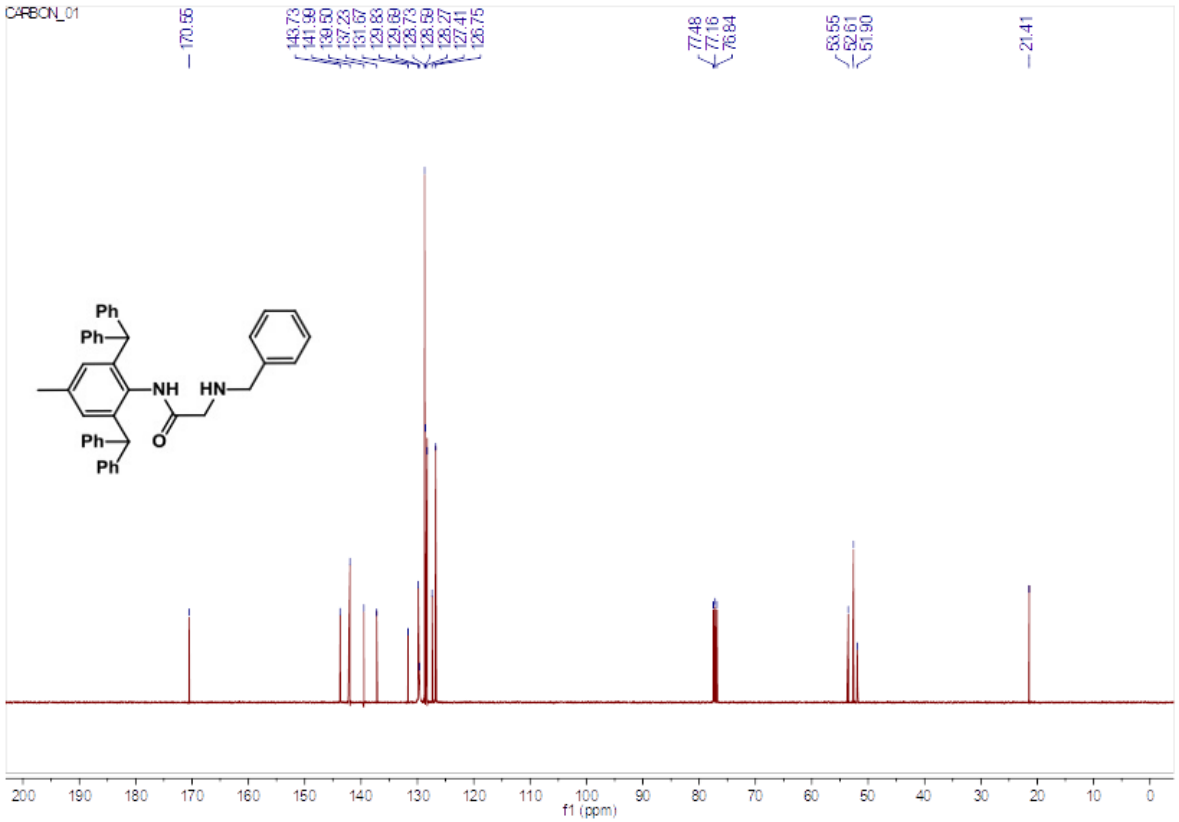
N-2,6-Bis(3-pentyl)phenyl-2-benzylaminoacetamide



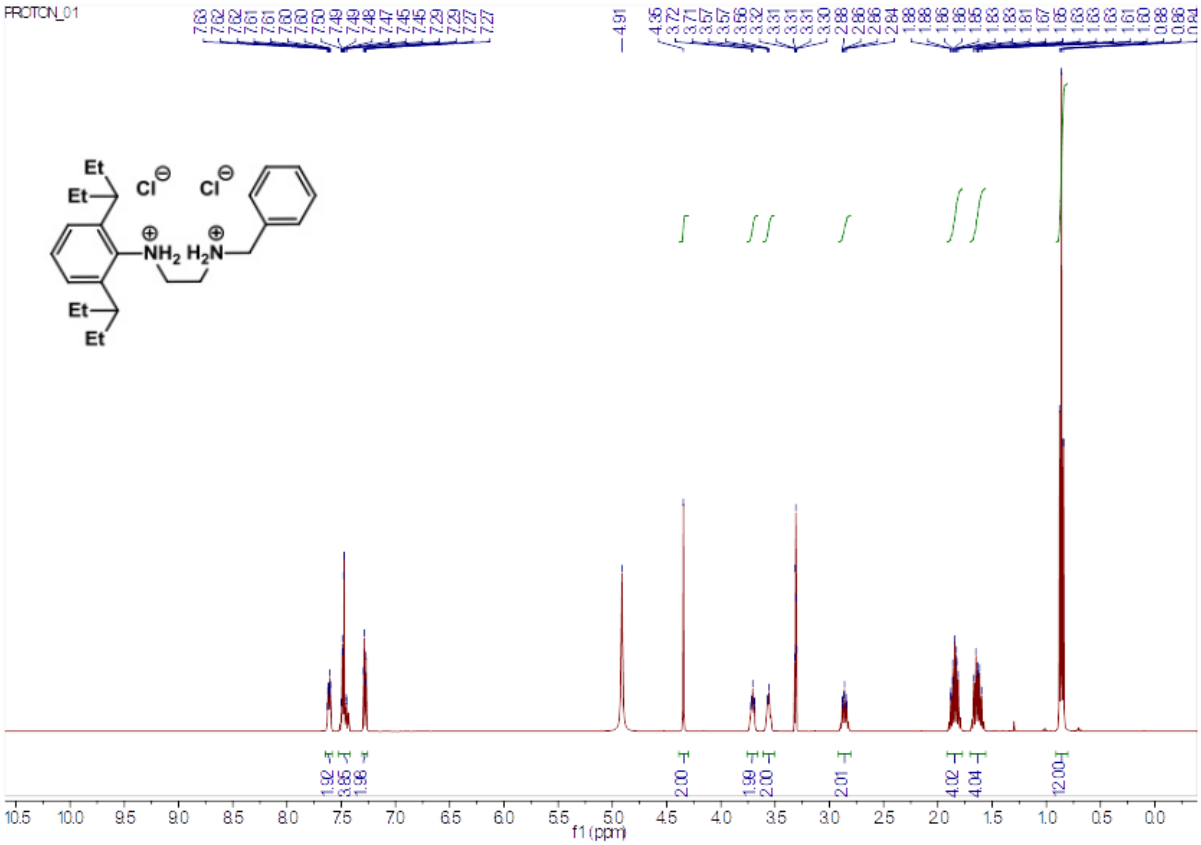


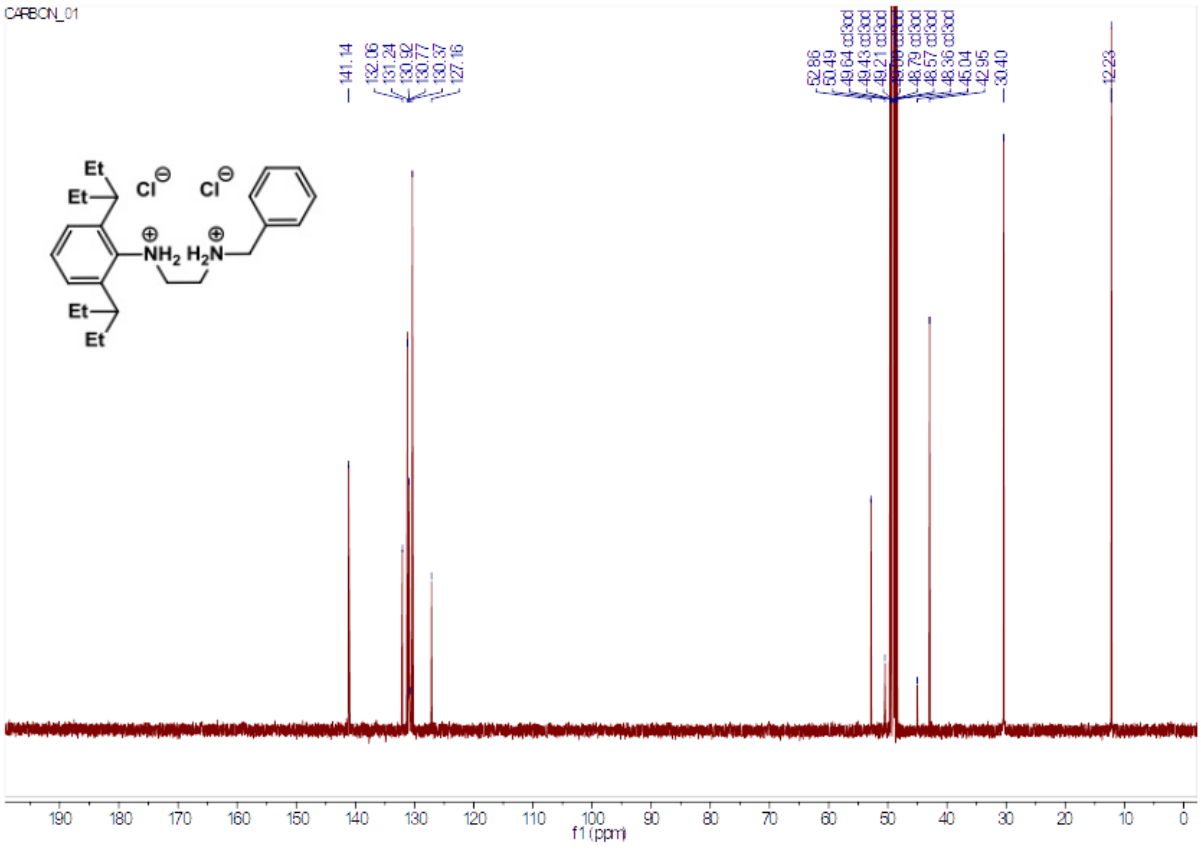
N-(2,6-Bis(diphenylmethyl)-4-methylphenyl)-2-benzylaminoacetamide



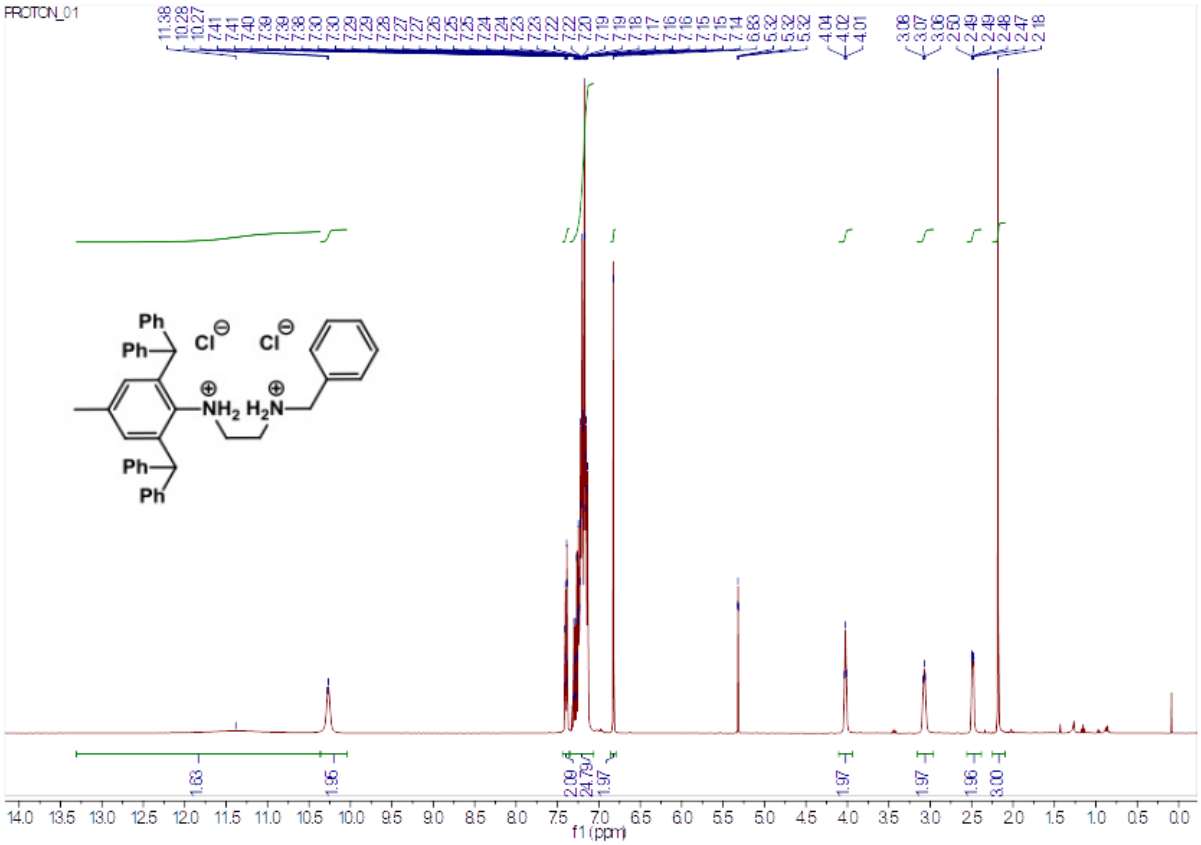


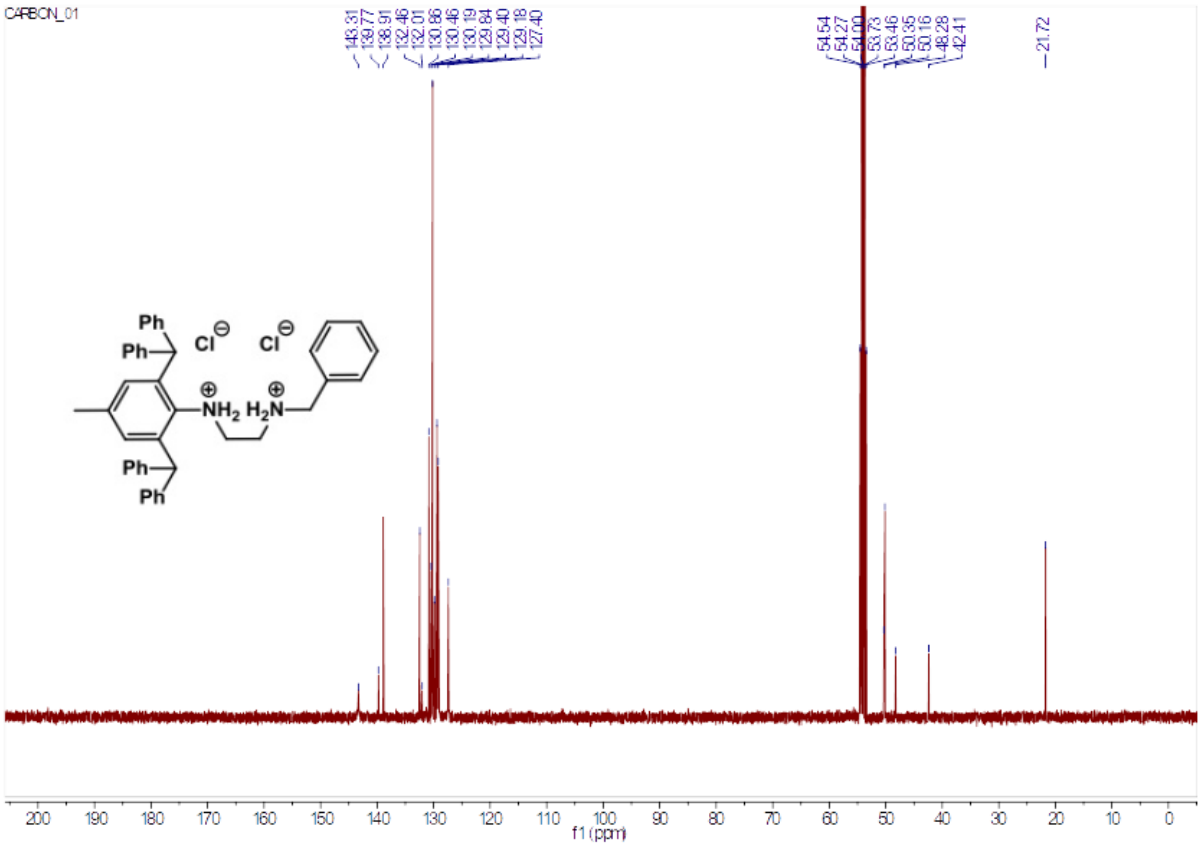
1-Benzyl-3-(2,6-bis(3-pentyl)phenyl)-1,2-diaminoethane dihydrochloride (2a)



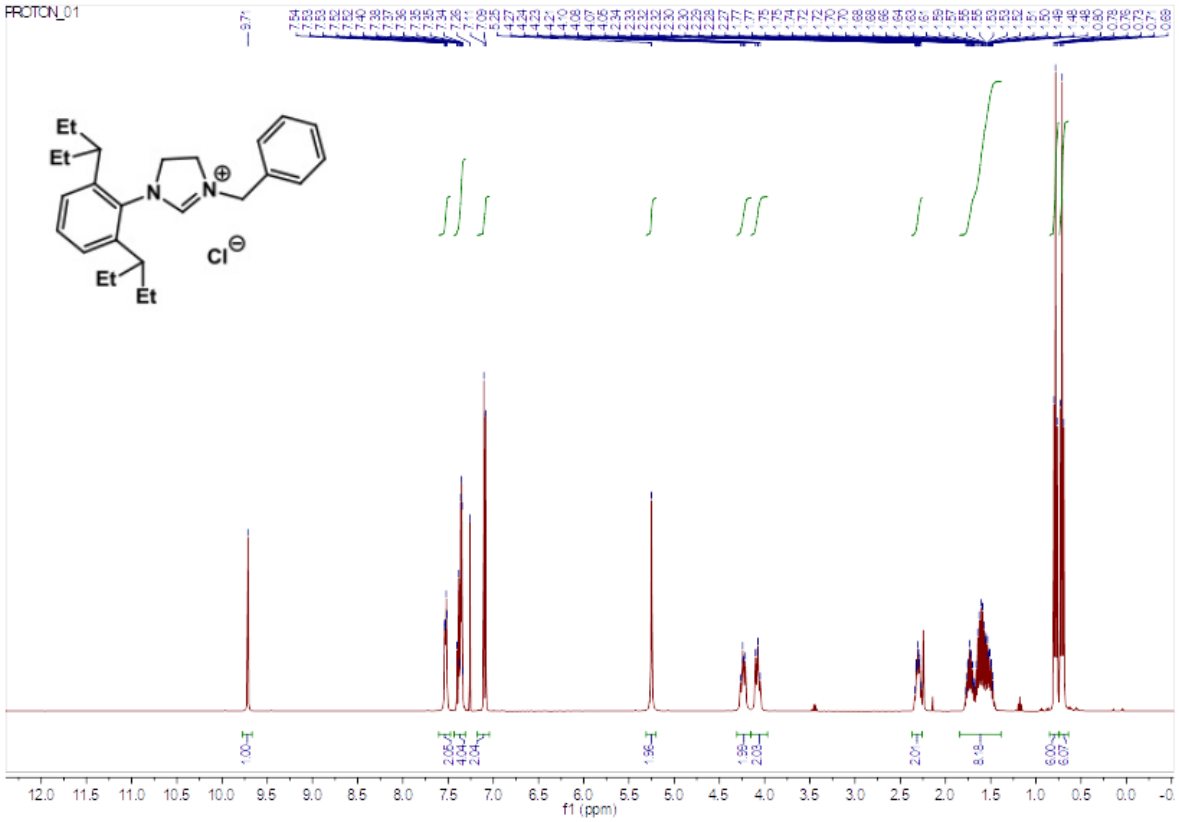


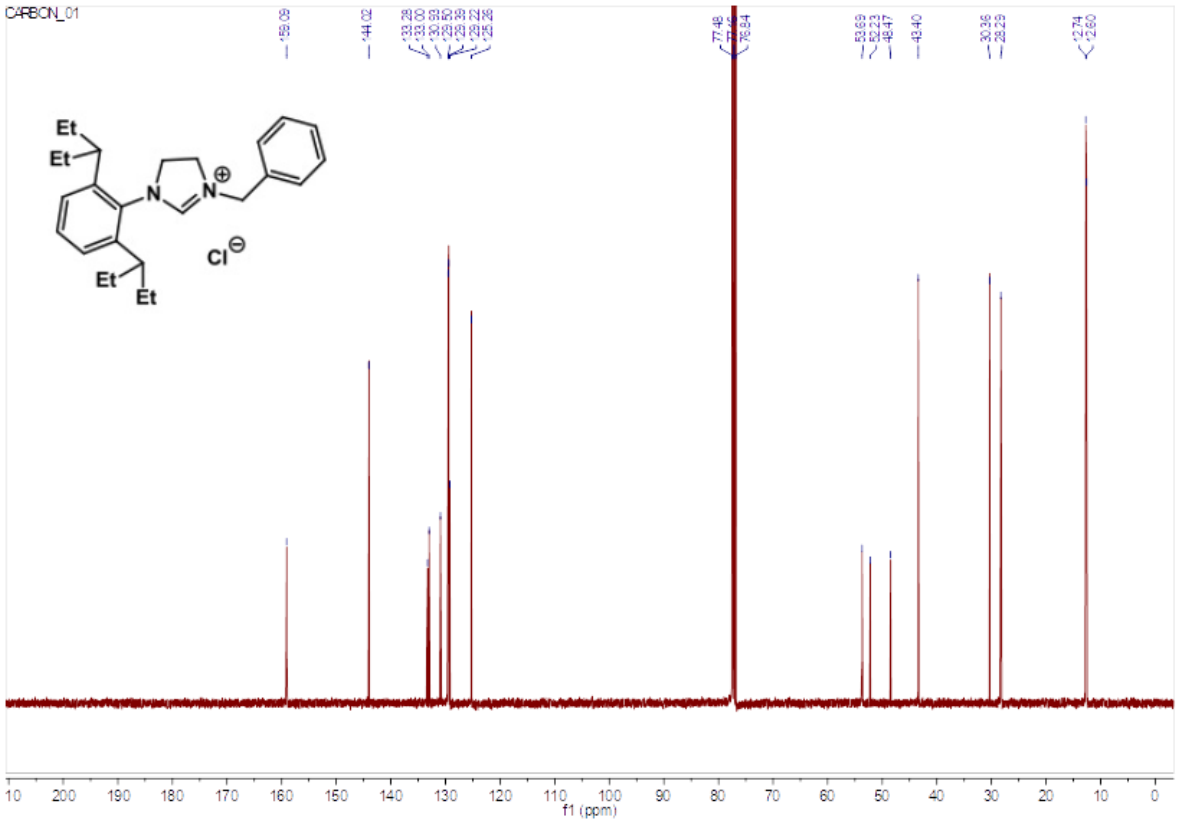
1-Benzyl-3-(2,6-bis(diphenylmethyl)-4-methylphenyl)-1,2-diaminoethane dihydrochloride (2b)



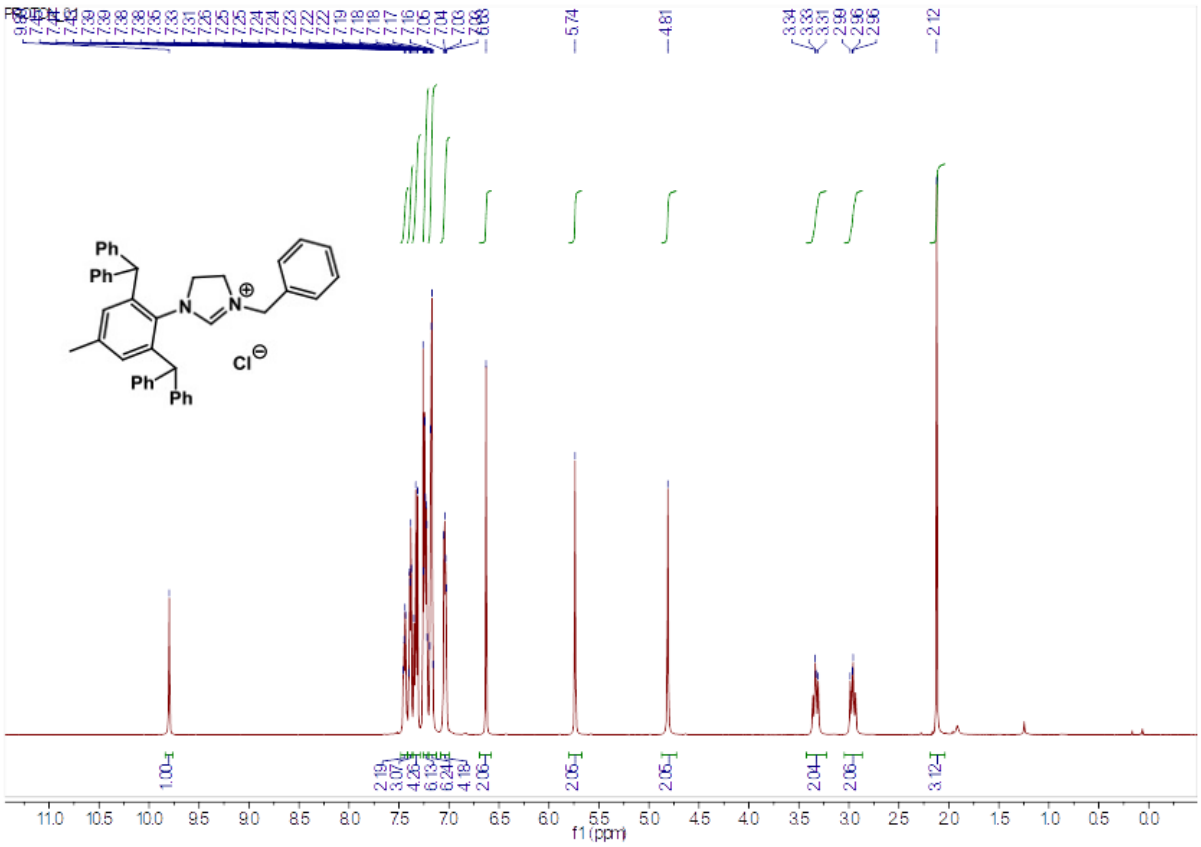


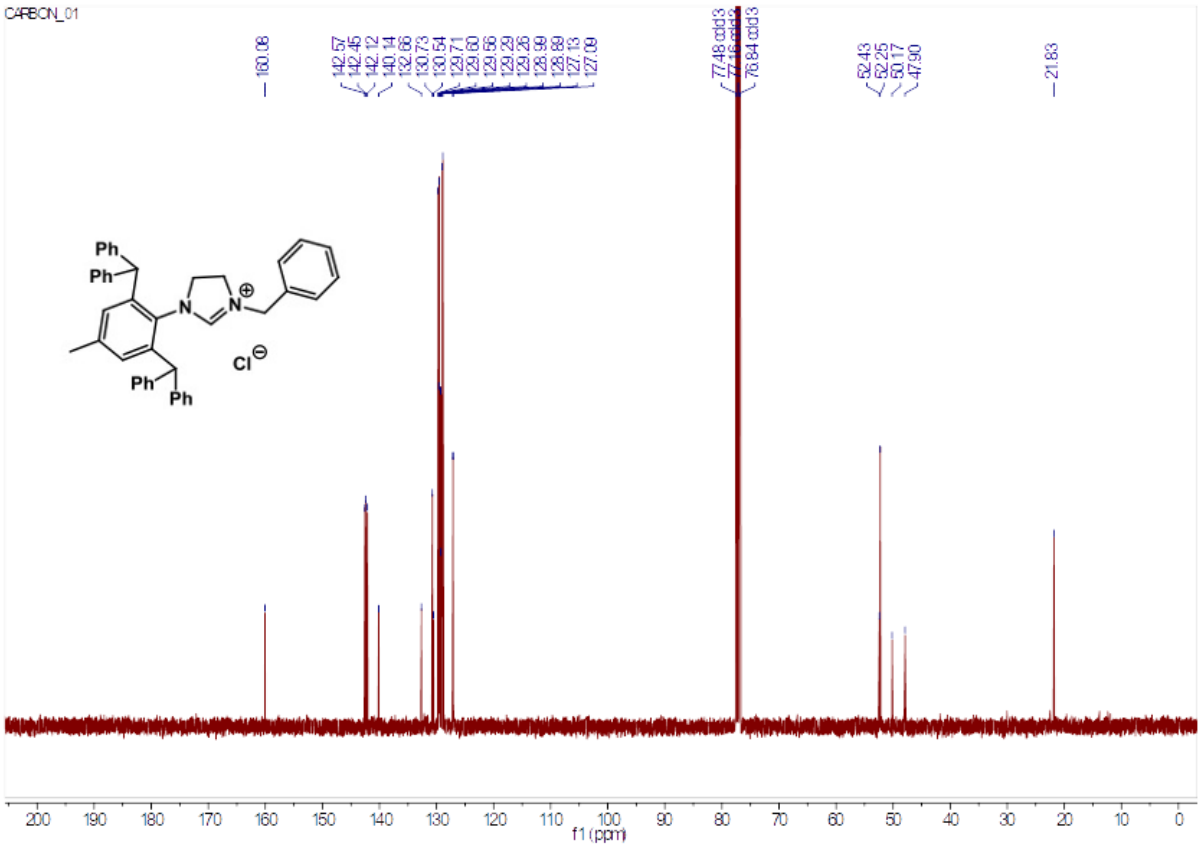
1-Benzyl-3-(2,6-bis(3-pentyl)phenyl)-4,5-dihydro-1*H*-imidazolinium chloride (3a)



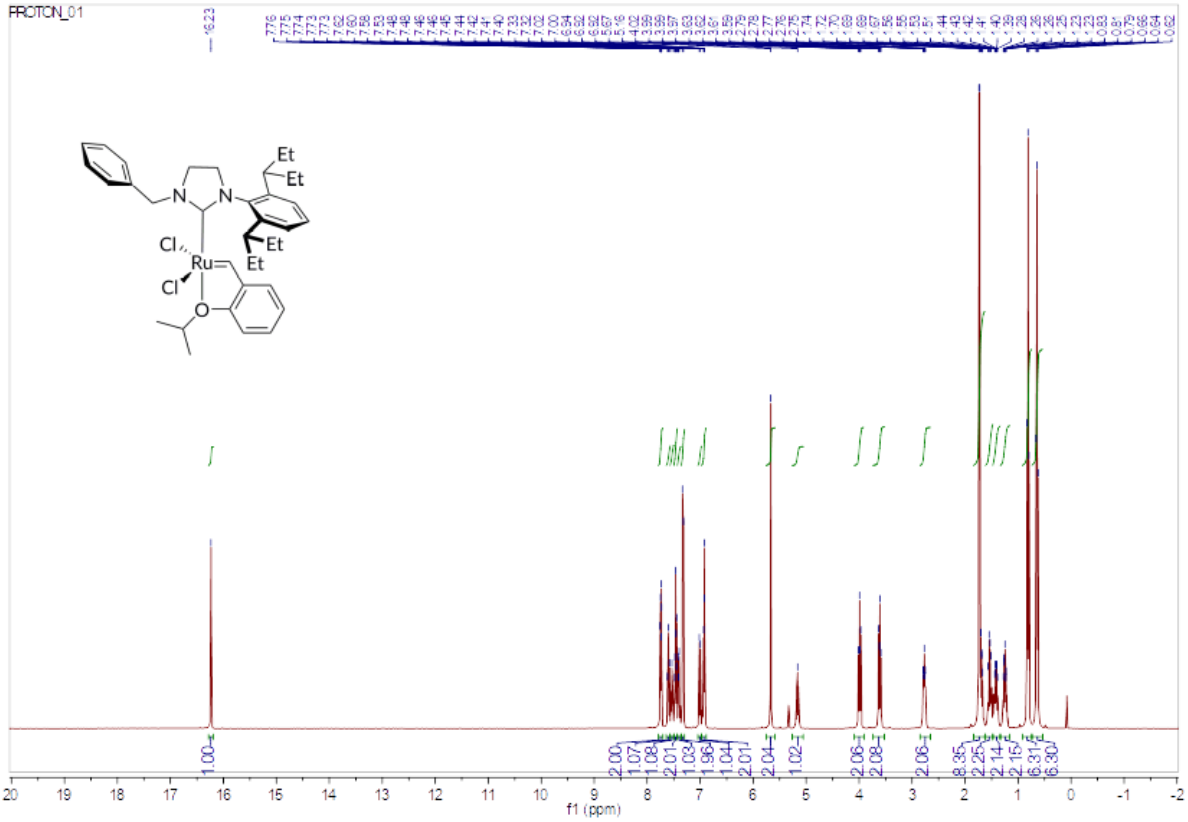


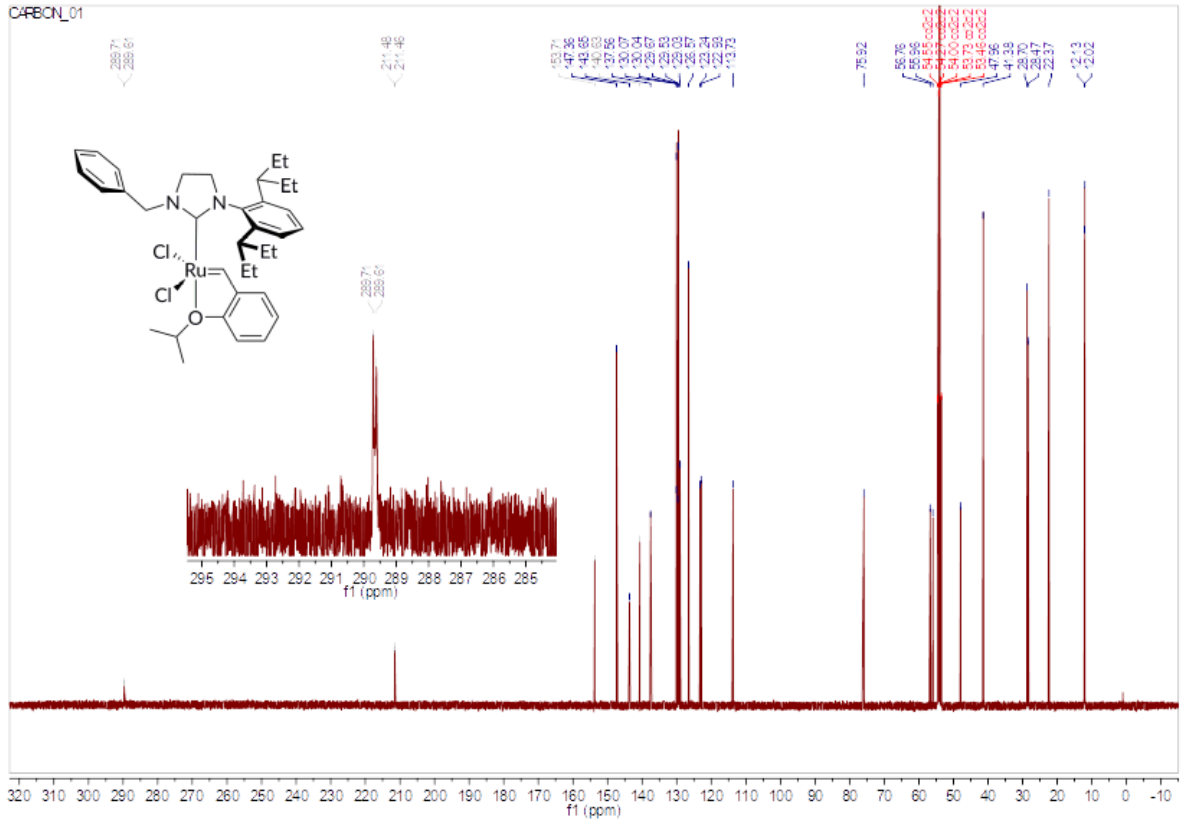
1-Benzyl-3-(2,6-bis(diphenylmethyl)-4-methylphenyl)-4,5-dihydro-1*H*-imidazolinium chloride (3b)



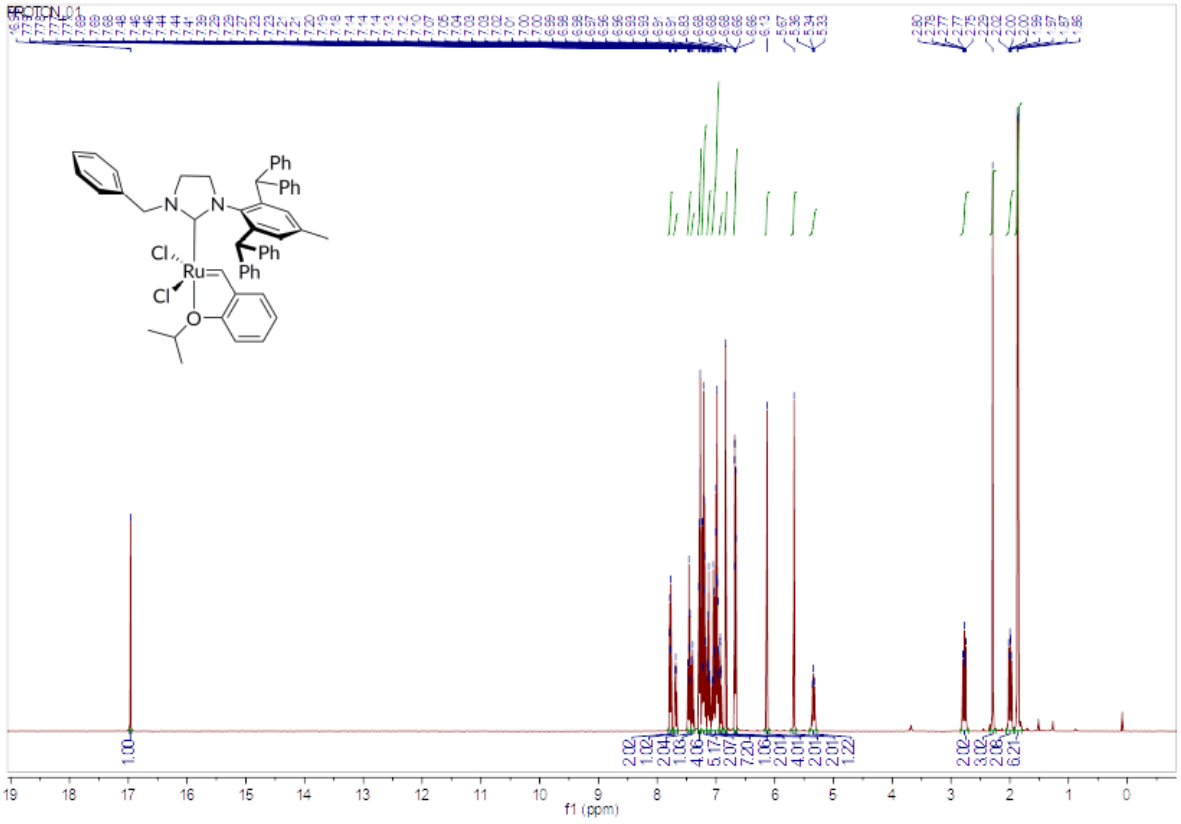


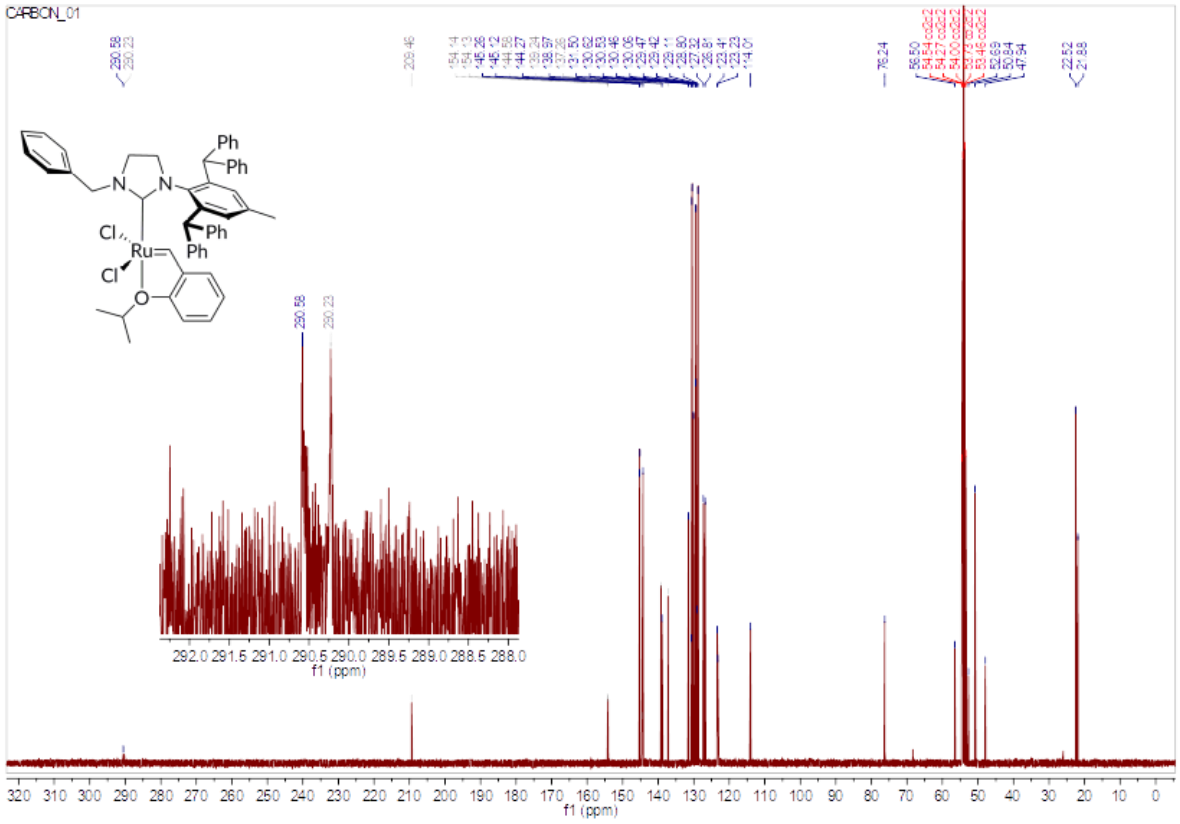
Complex Ru9



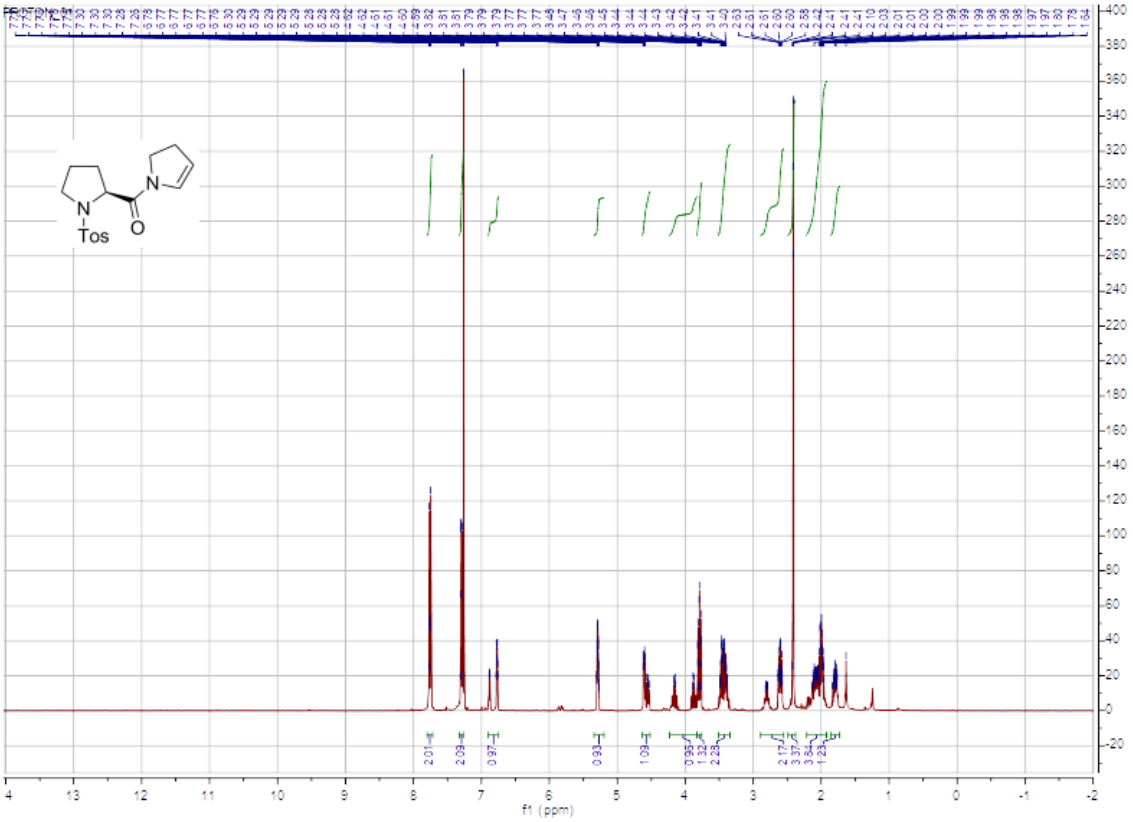


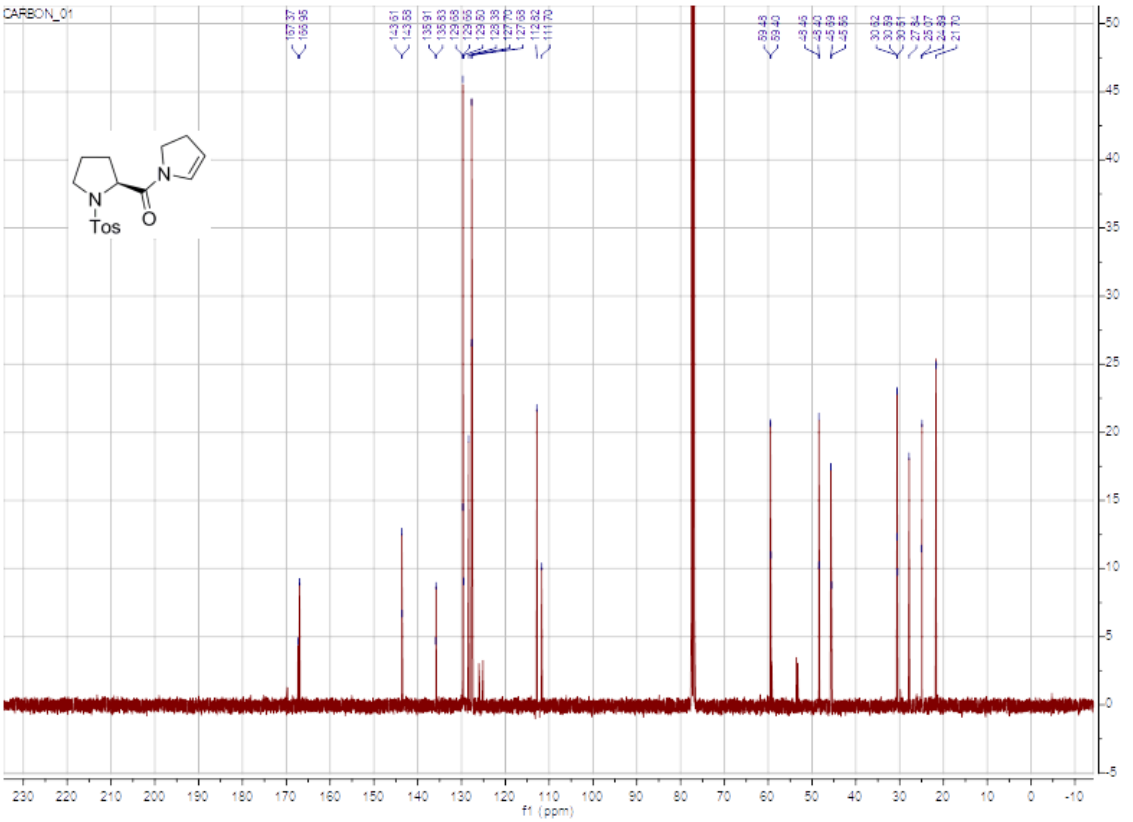
Complex Ru10



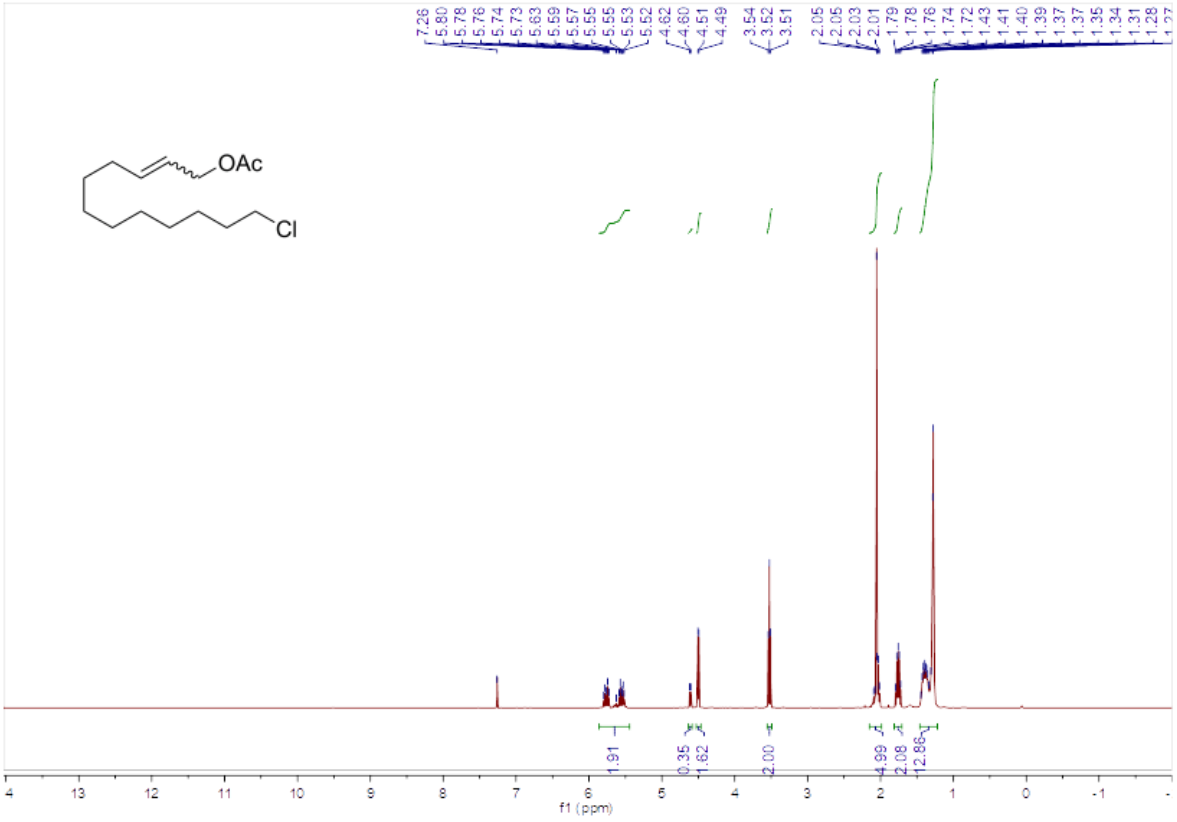


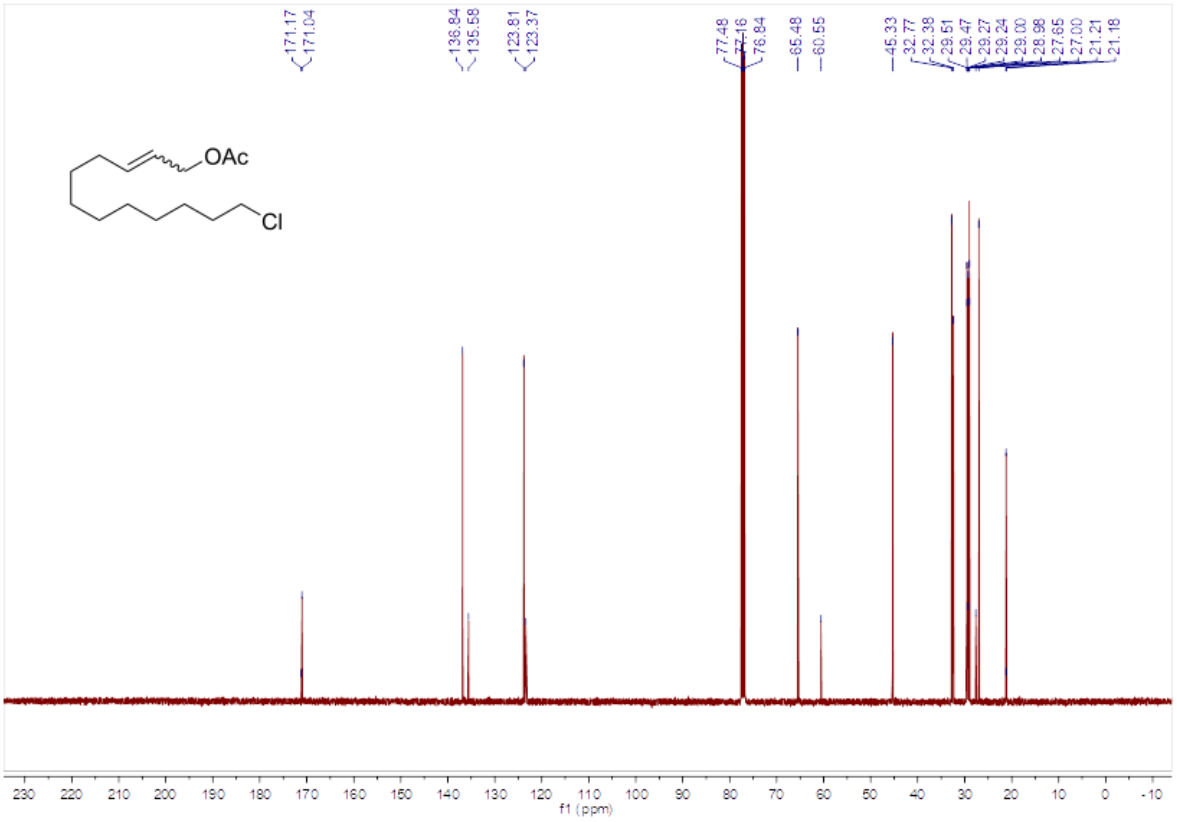
(*S*)-1-(Tosylprolyl)-2,3-dihydro-1*H*-pyrrole (13')



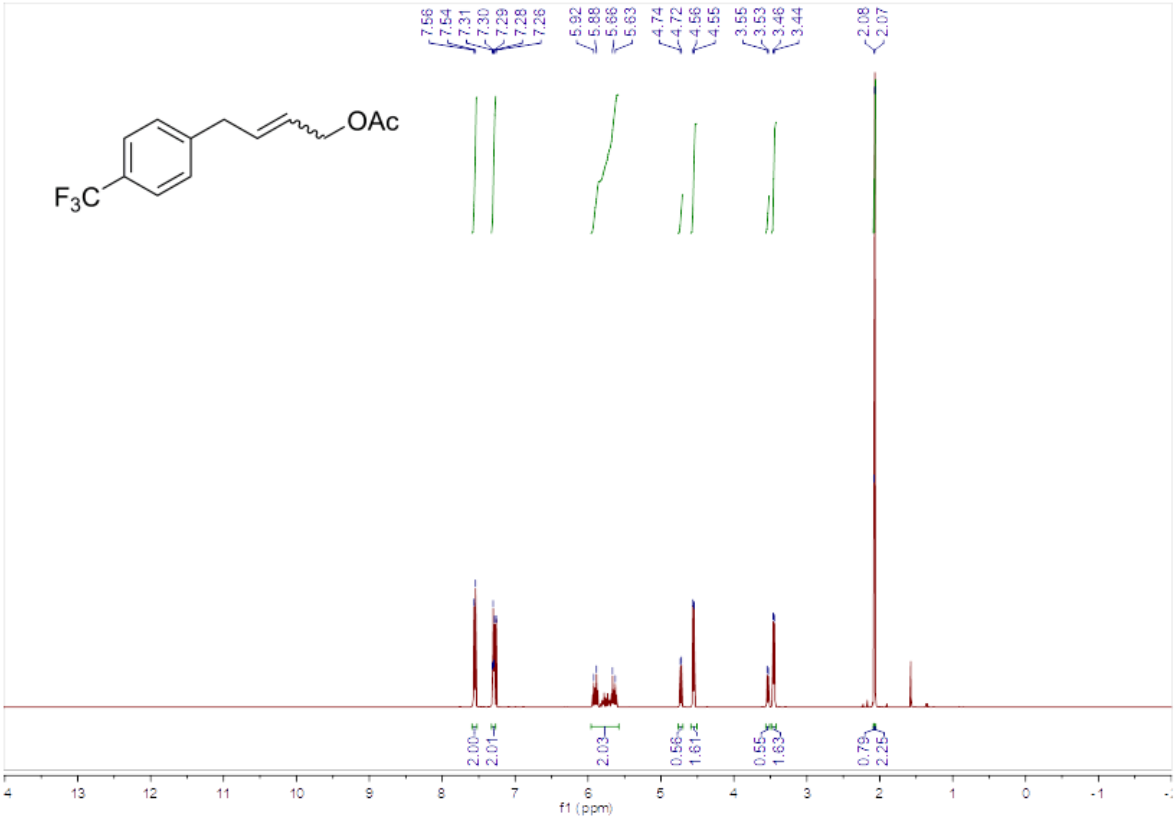


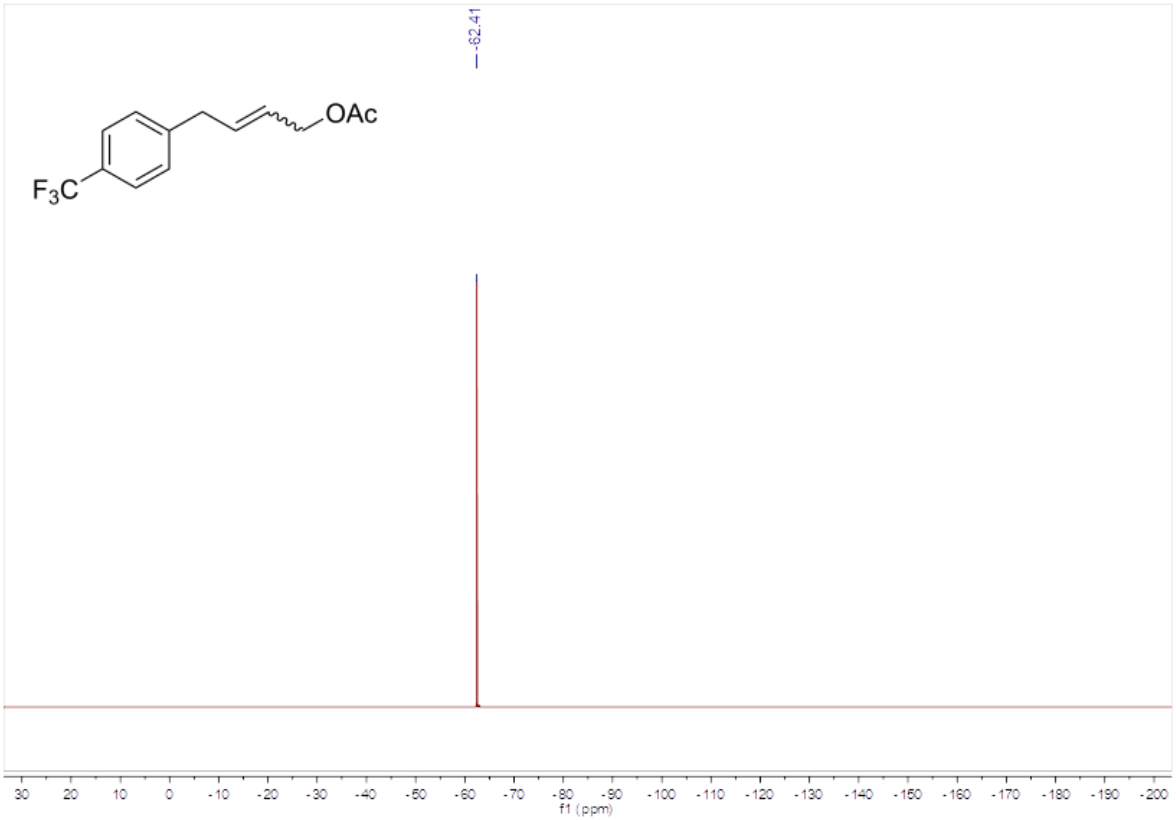
12-Chlorododec-2-en-1-yl acetate (18)

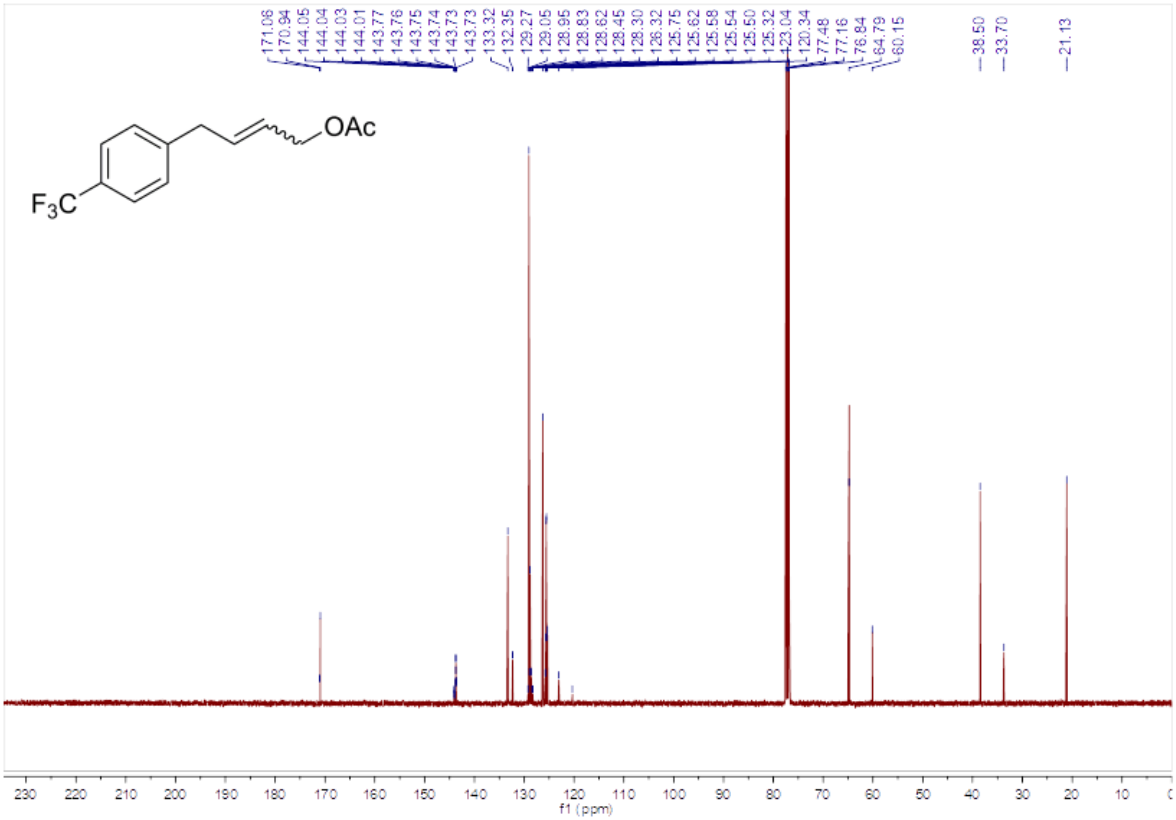




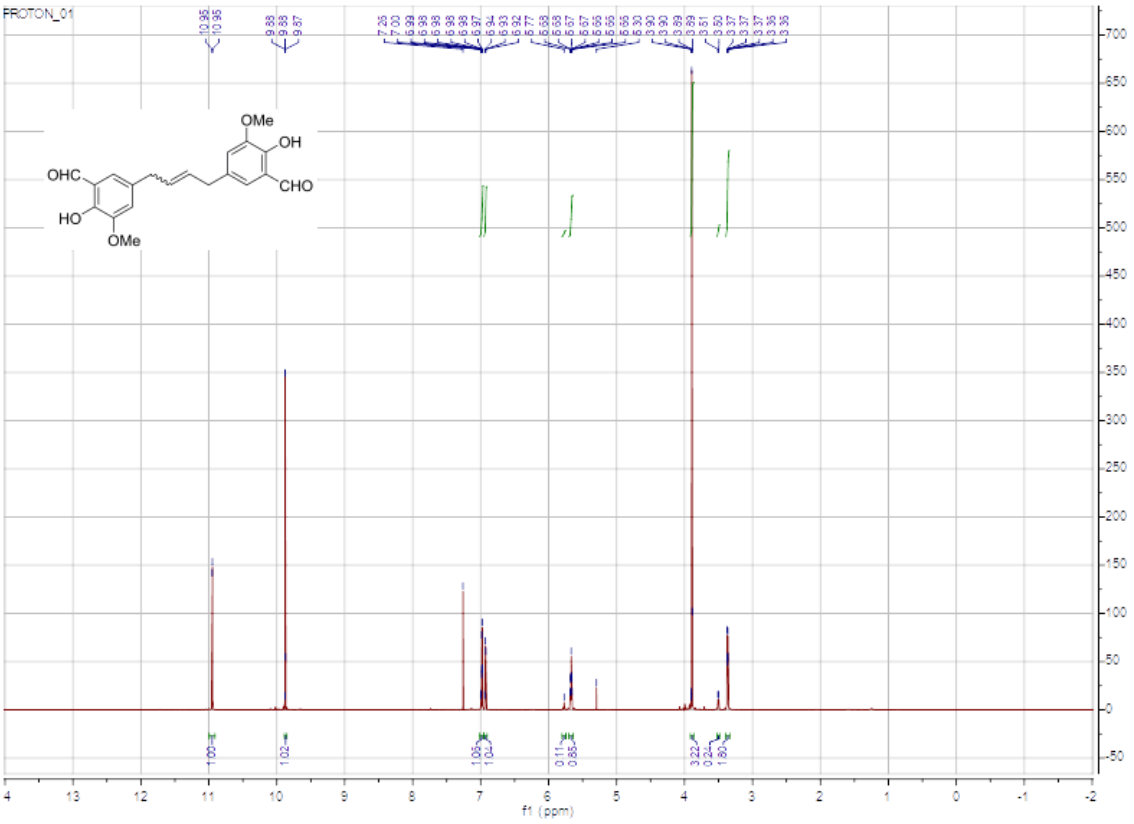
4-(4-(Trifluoromethyl)phenyl)but-2-en-1-yl acetate

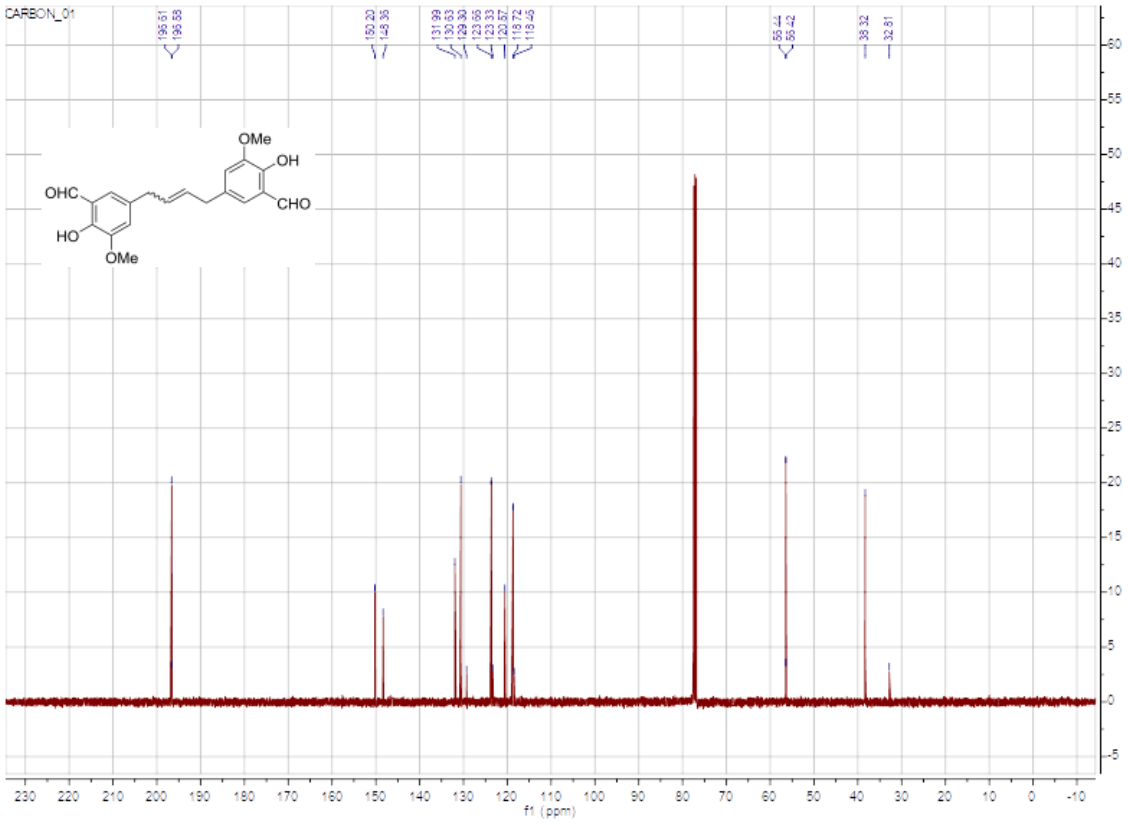




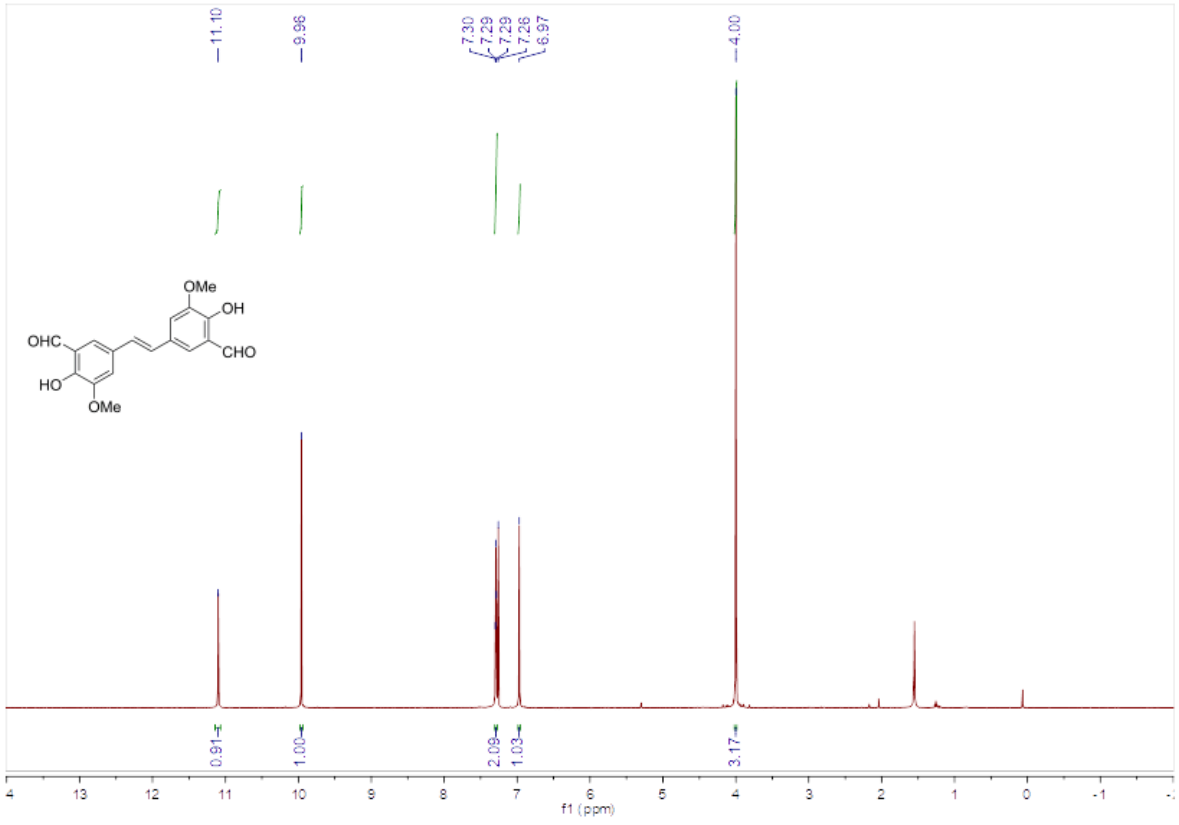


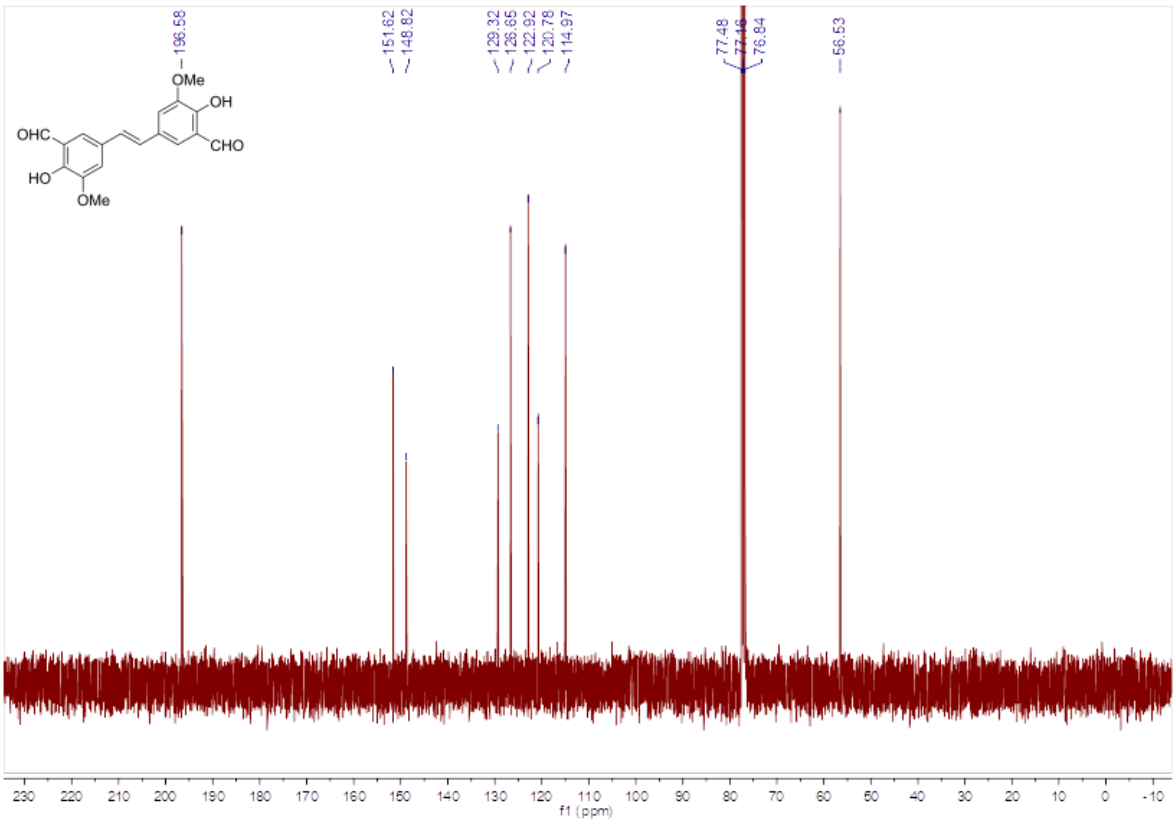
5,5'-(But-2-ene-1,4-diyl)bis(2-hydroxy-3-methoxybenzaldehyde)



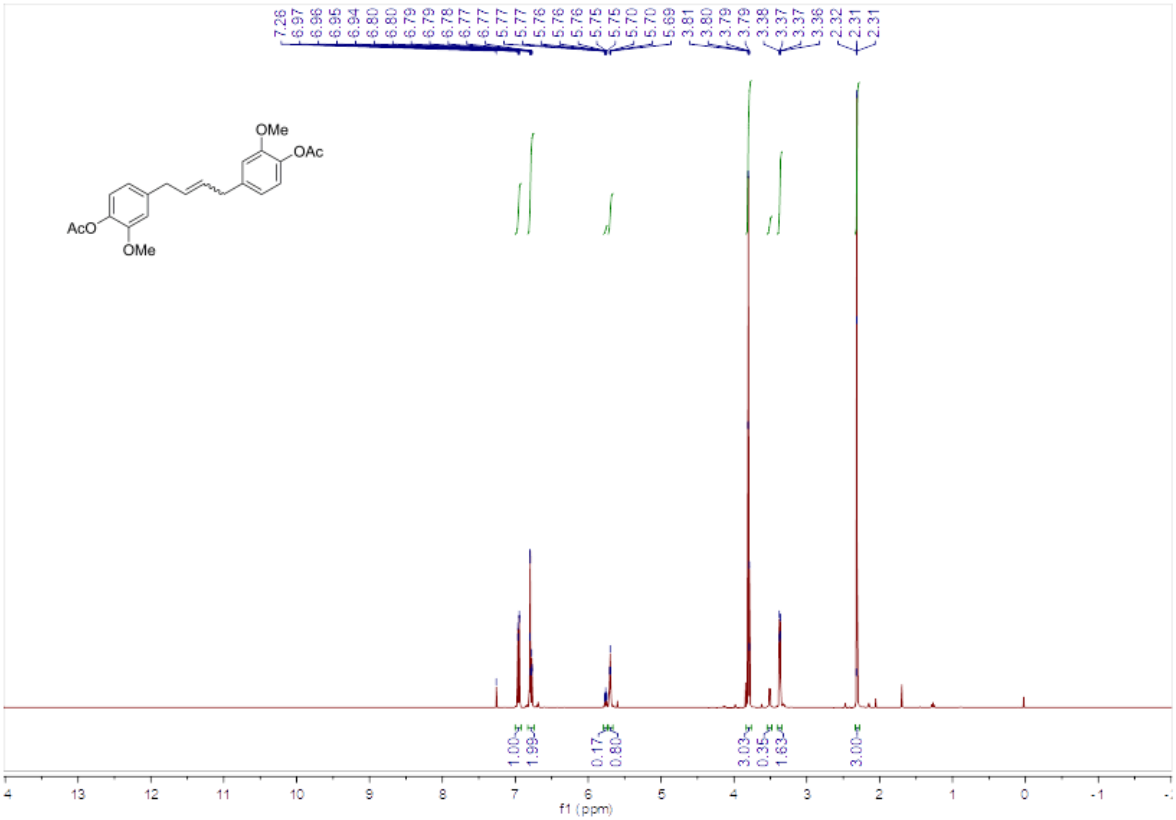


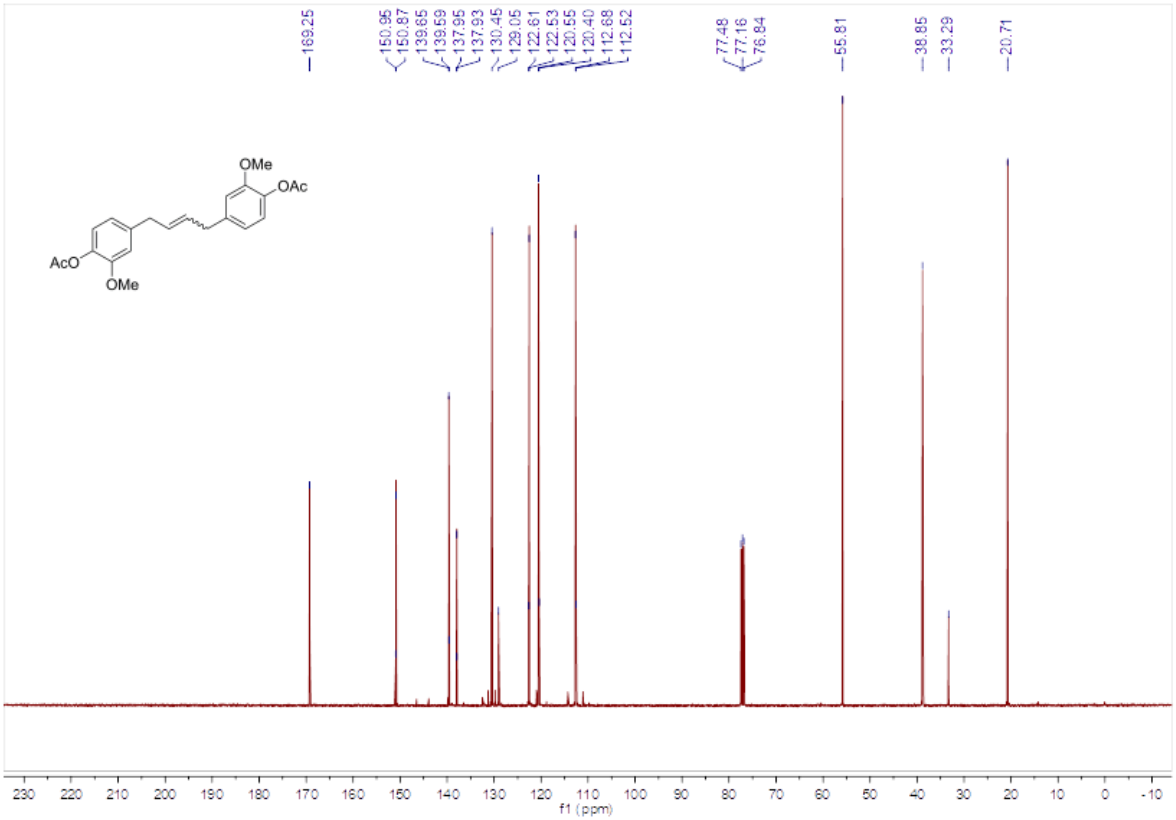
5,5'-(Ethene-1,2-diyl)bis(2-hydroxy-3-methoxybenzaldehyde)



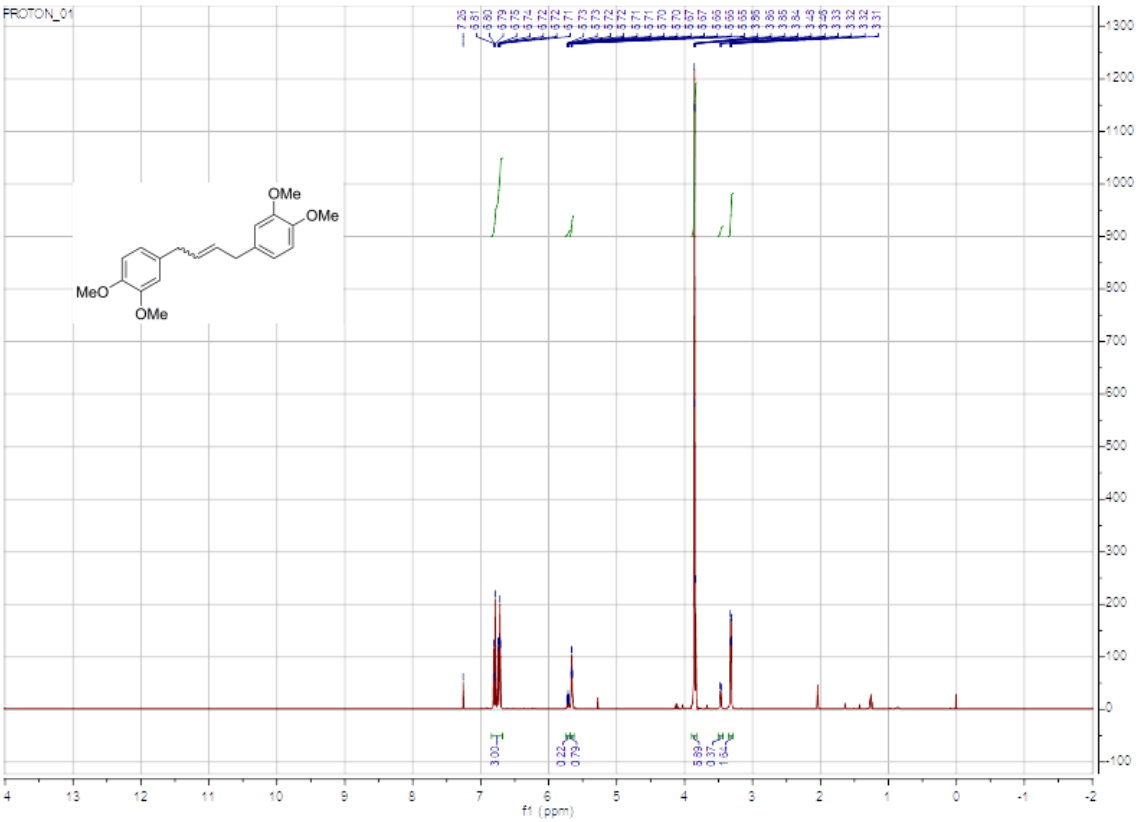


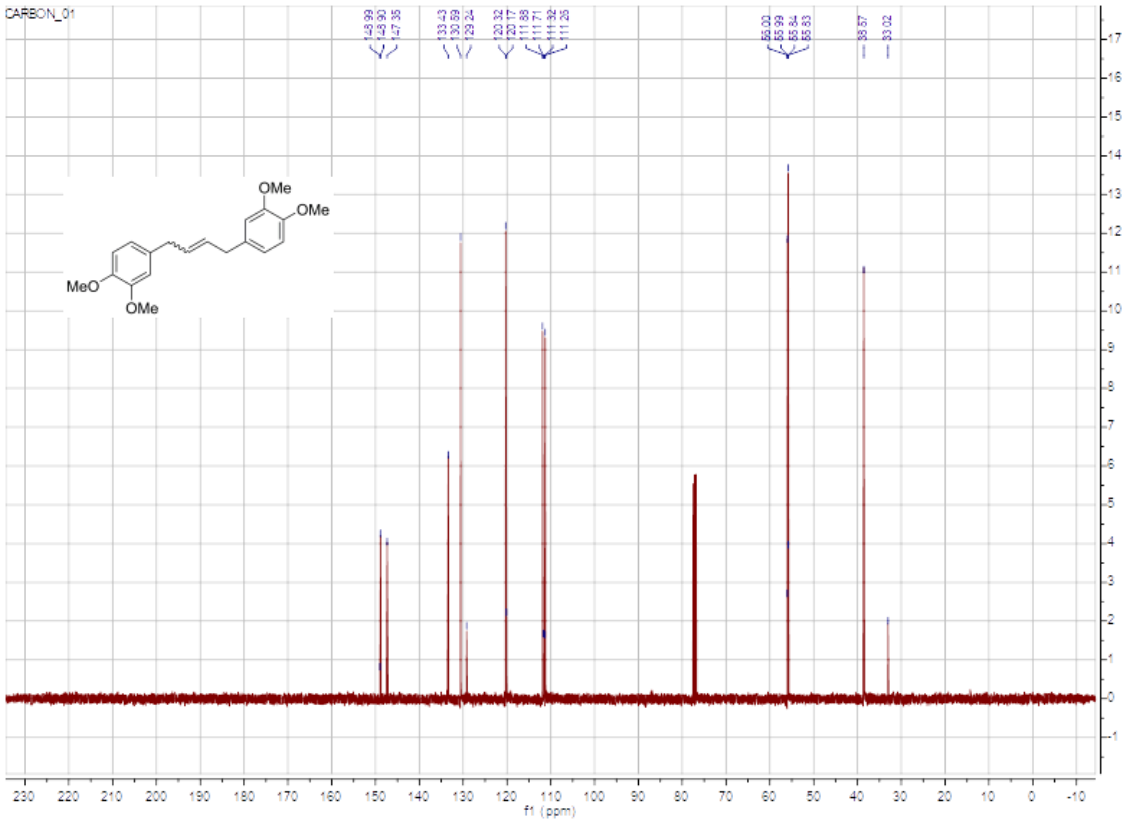
But-2-ene-1,4-diylbis(2-methoxy-4,1-phenylene) diacetate



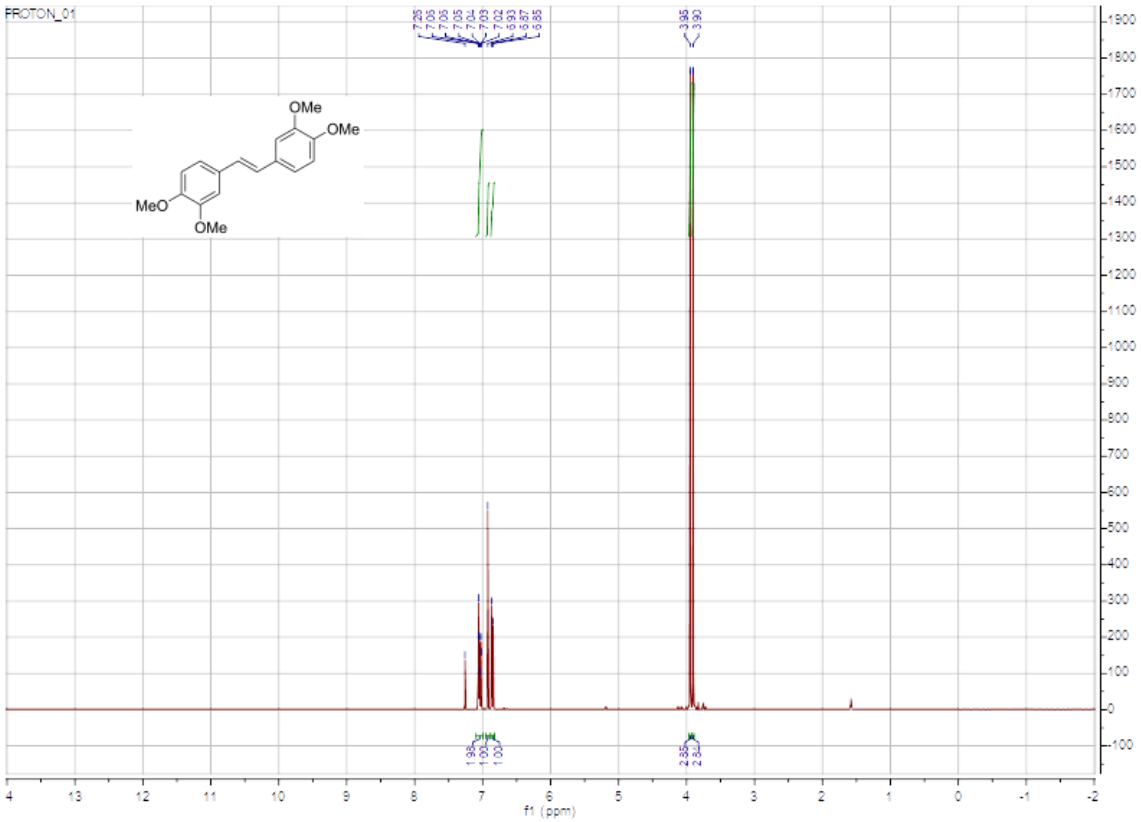


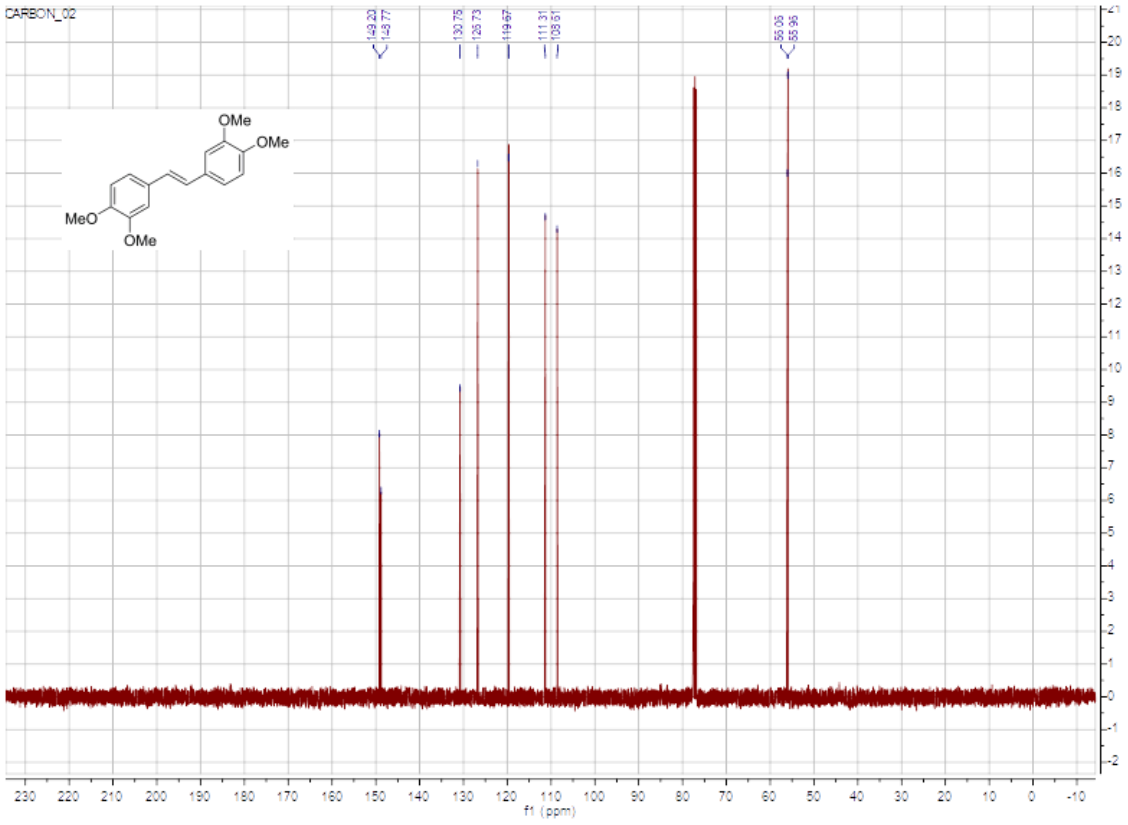
1,4-Bis(3,4-dimethoxyphenyl)but-2-ene (25b)



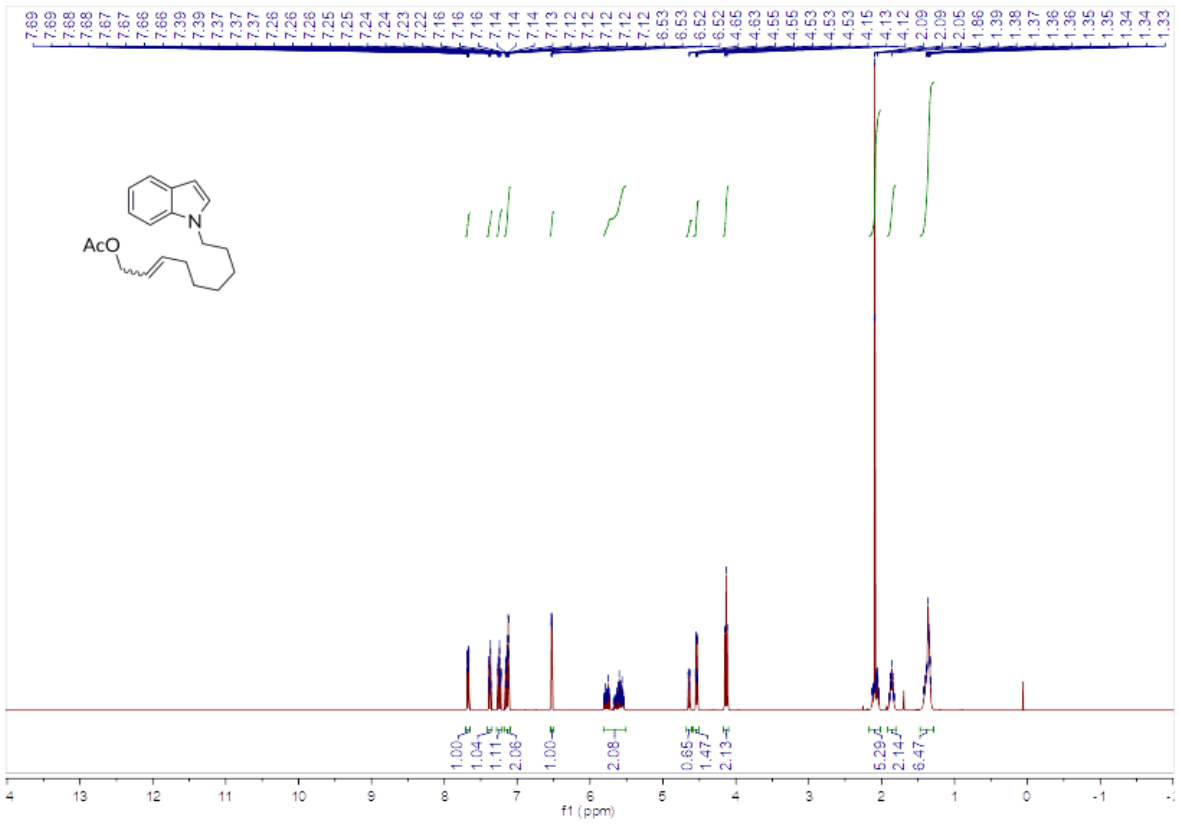


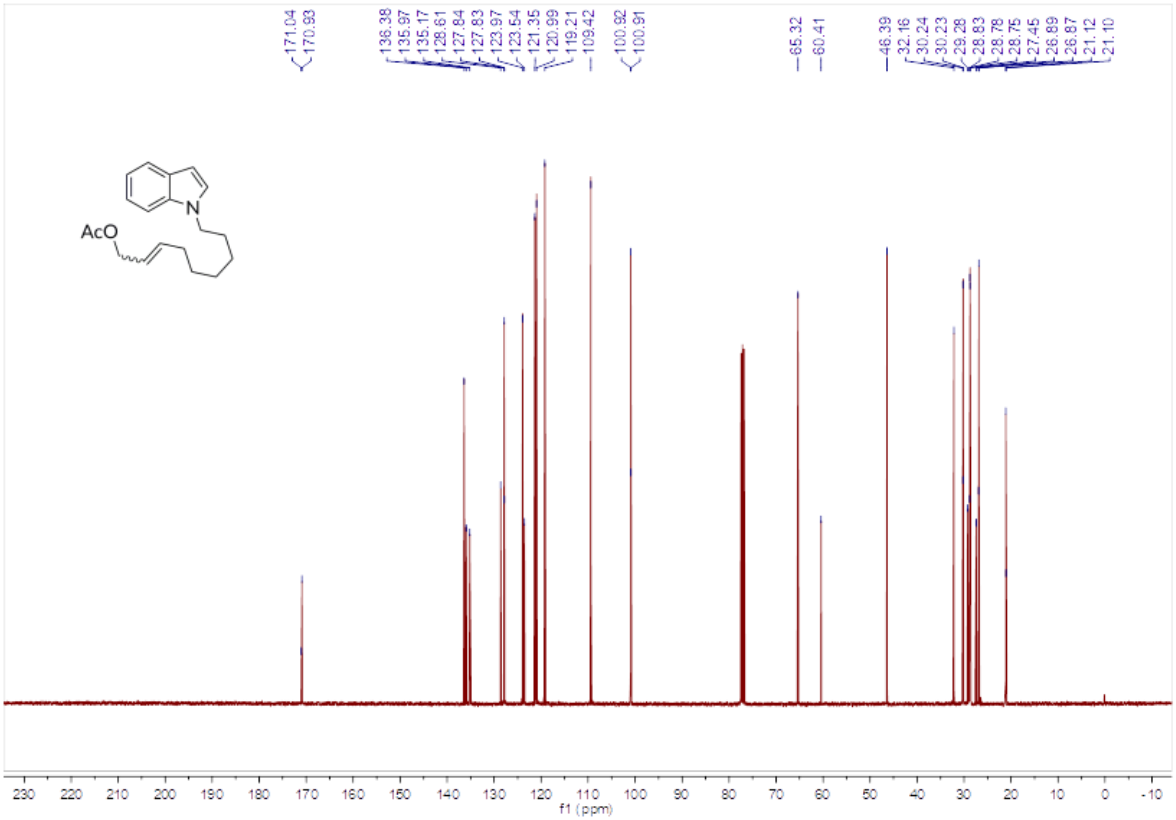
(*E*)-1,2-Bis(3,4-dimethoxyphenyl)ethane



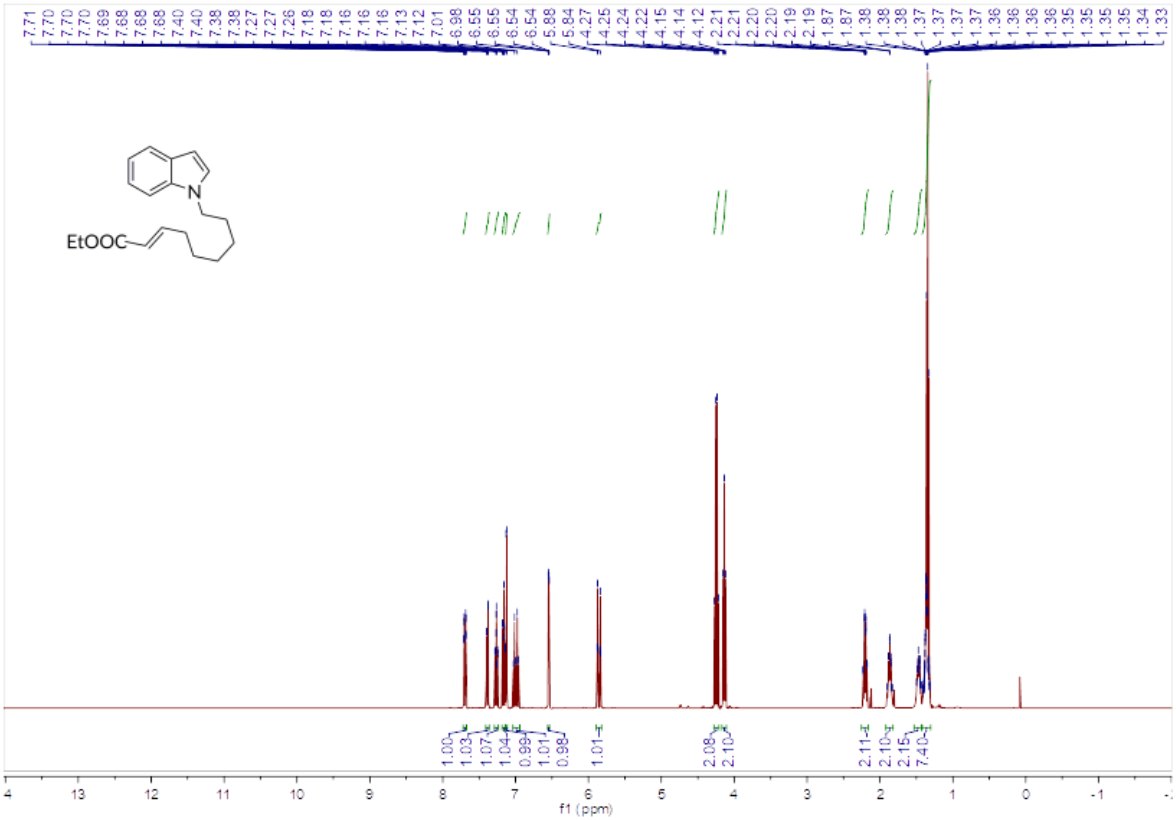


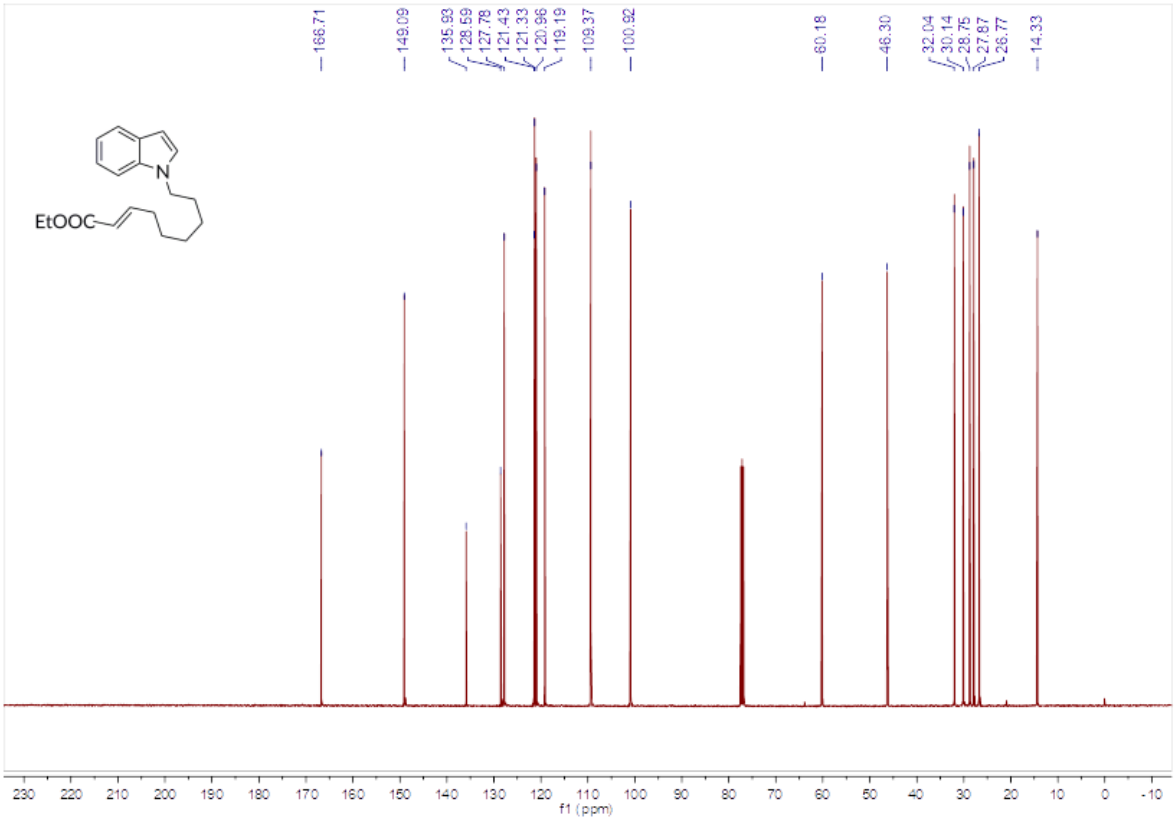
9-(1*H*-Indol-1-yl)non-2-en-1-yl acetate (29)



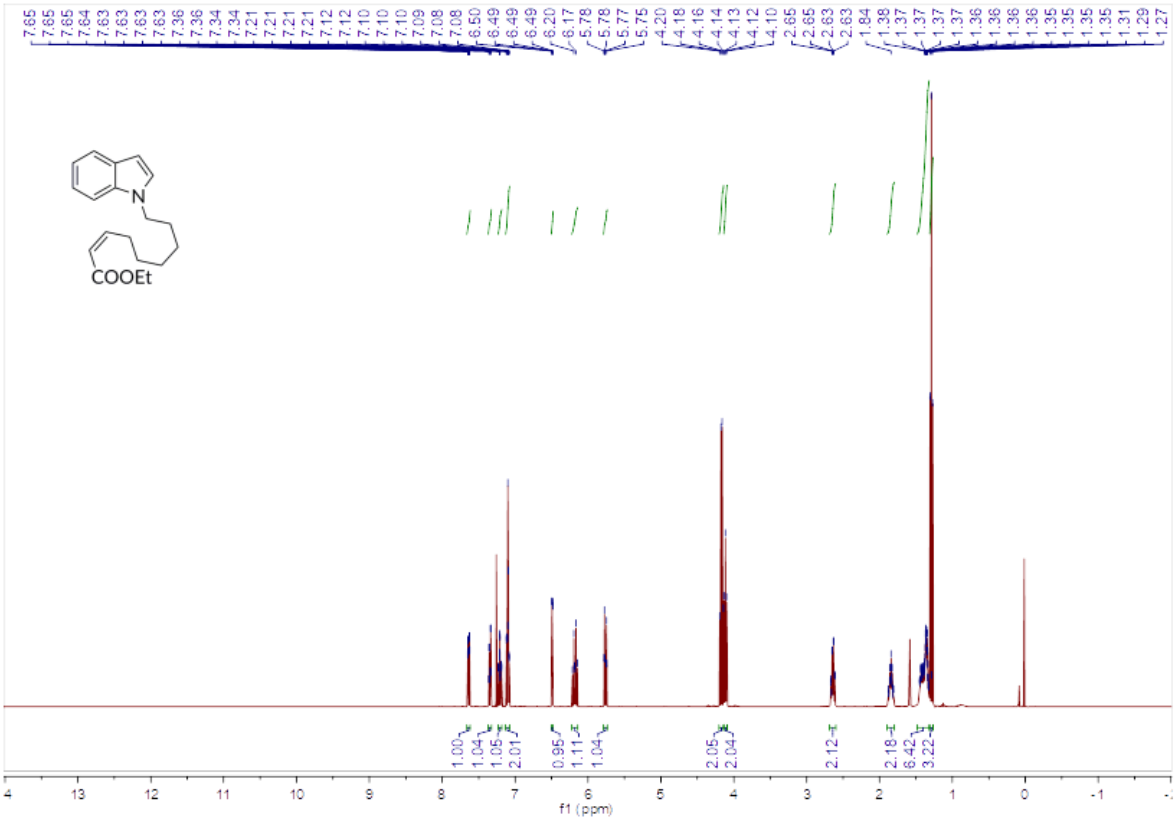


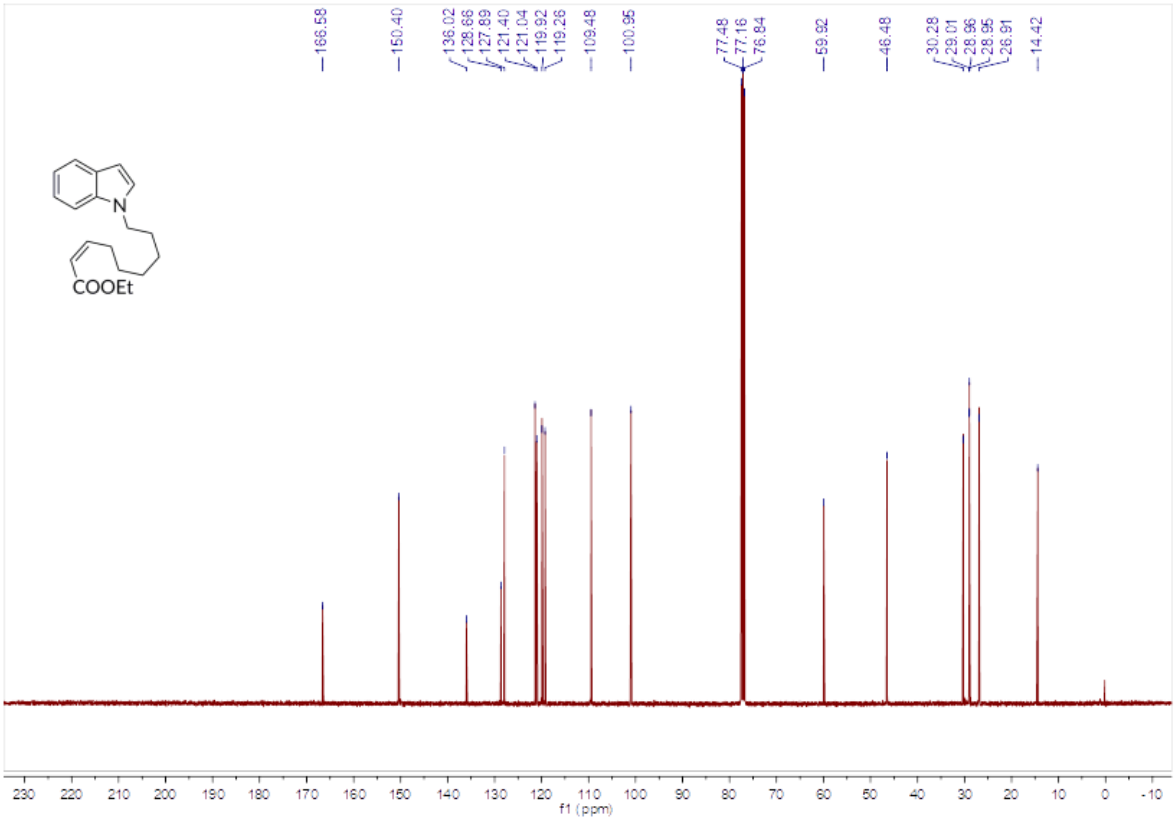
Ethyl (*E*)-9-(1*H*-indol-1-yl)non-2-enoate (30)



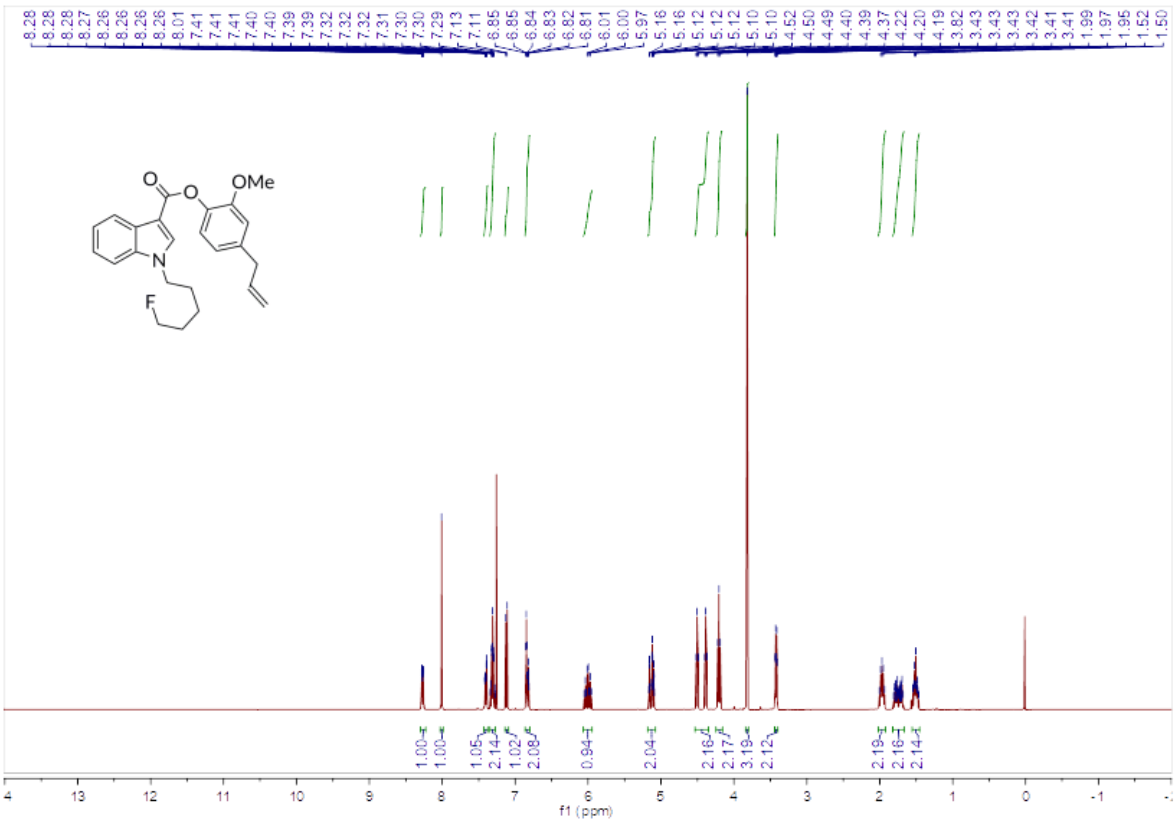


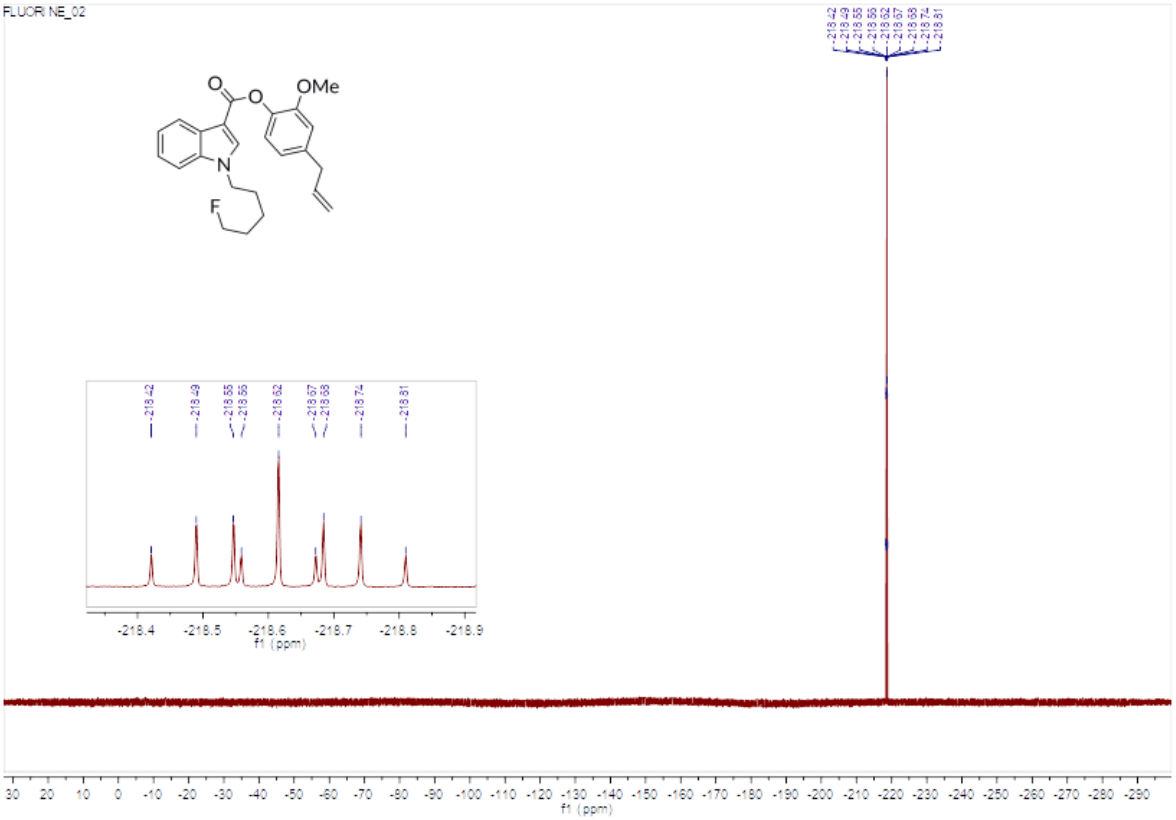
Ethyl (*Z*)-9-(1*H*-indol-1-yl)non-2-enoate (30)

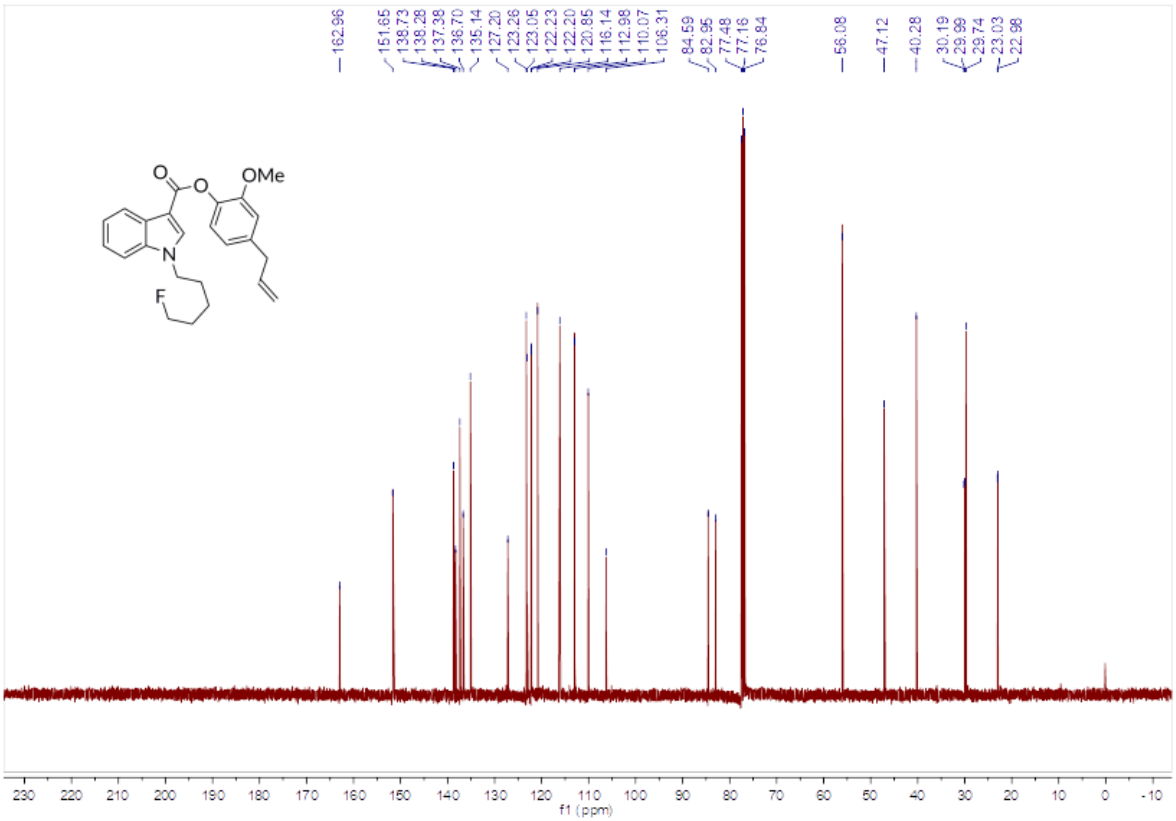




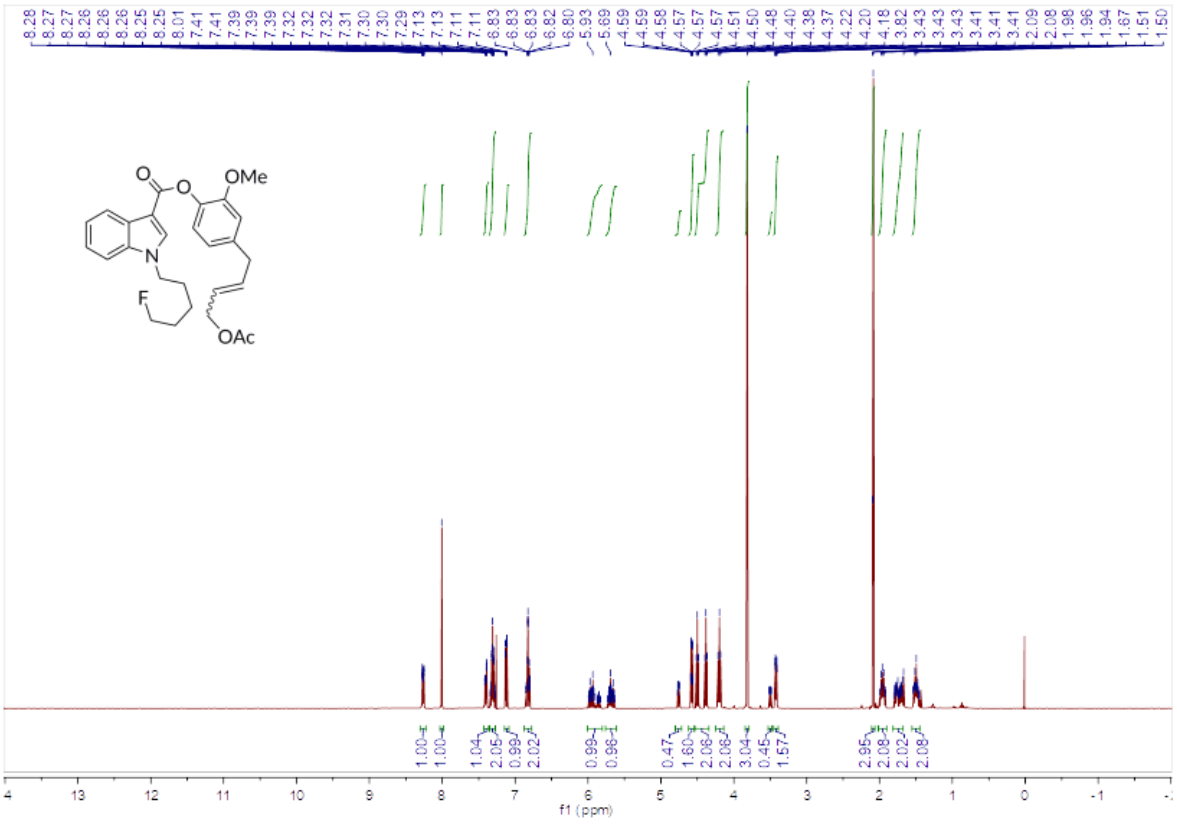
4-Allyl-2-methoxyphenyl 1-(5-fluoropentyl)-1*H*-indole-3-carboxylate

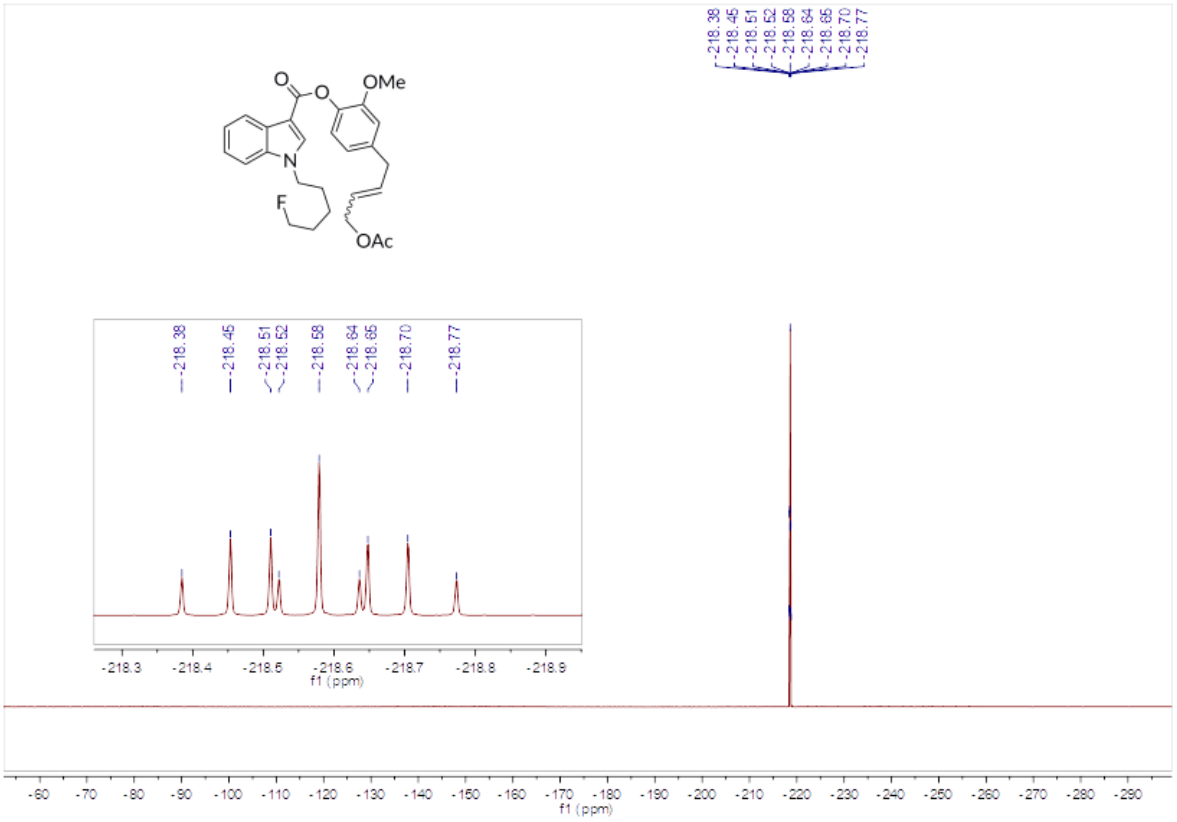


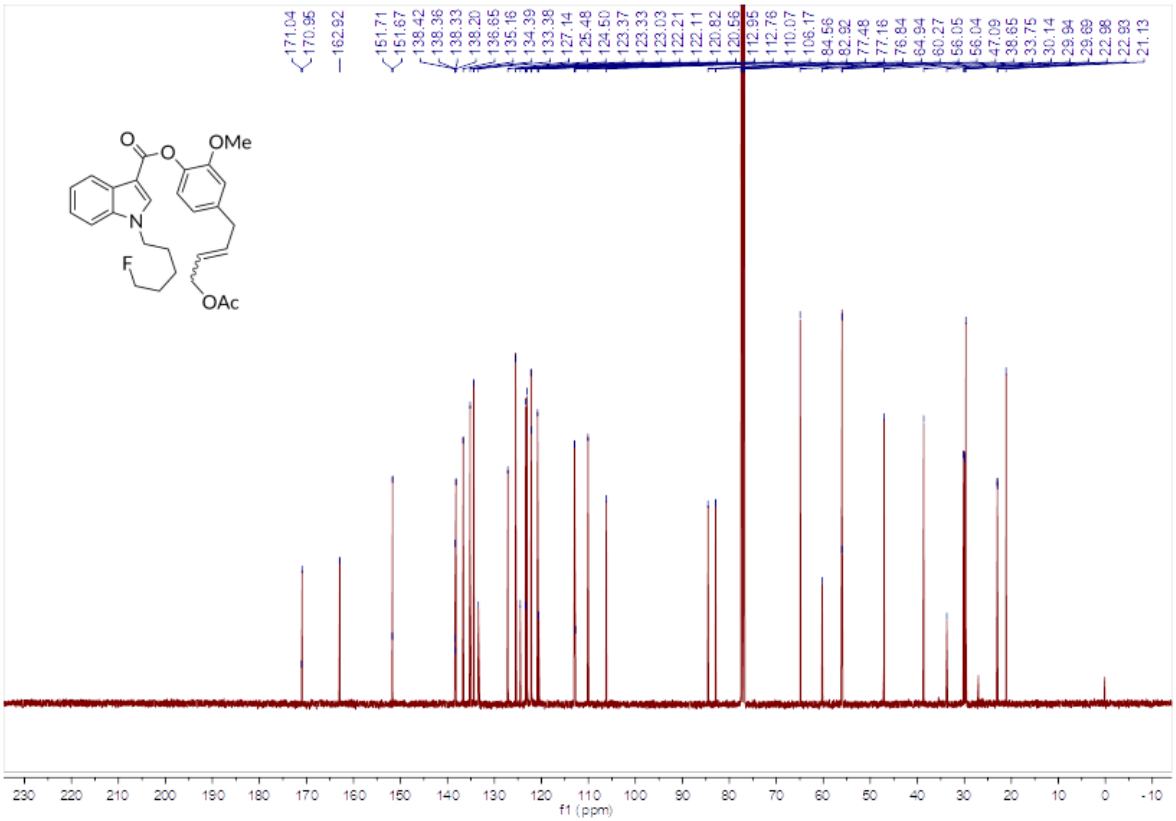

FLUORINE_02
-218.42
-218.49
-218.55
-218.55
-218.62
-218.67
-218.68
-218.74
-218.81
OMe
O
O
N
F
f1 (ppm)


162.96
151.65
138.73
138.28
137.38
136.70
135.14
127.20
123.26
123.05
122.23
122.20
120.85
116.14
112.98
110.07
106.31
84.59
82.95
77.48
77.16
76.84
56.08
47.12
40.28
30.19
29.99
29.74
23.03
22.98
OMe
O
O
N
F
f1 (ppm)

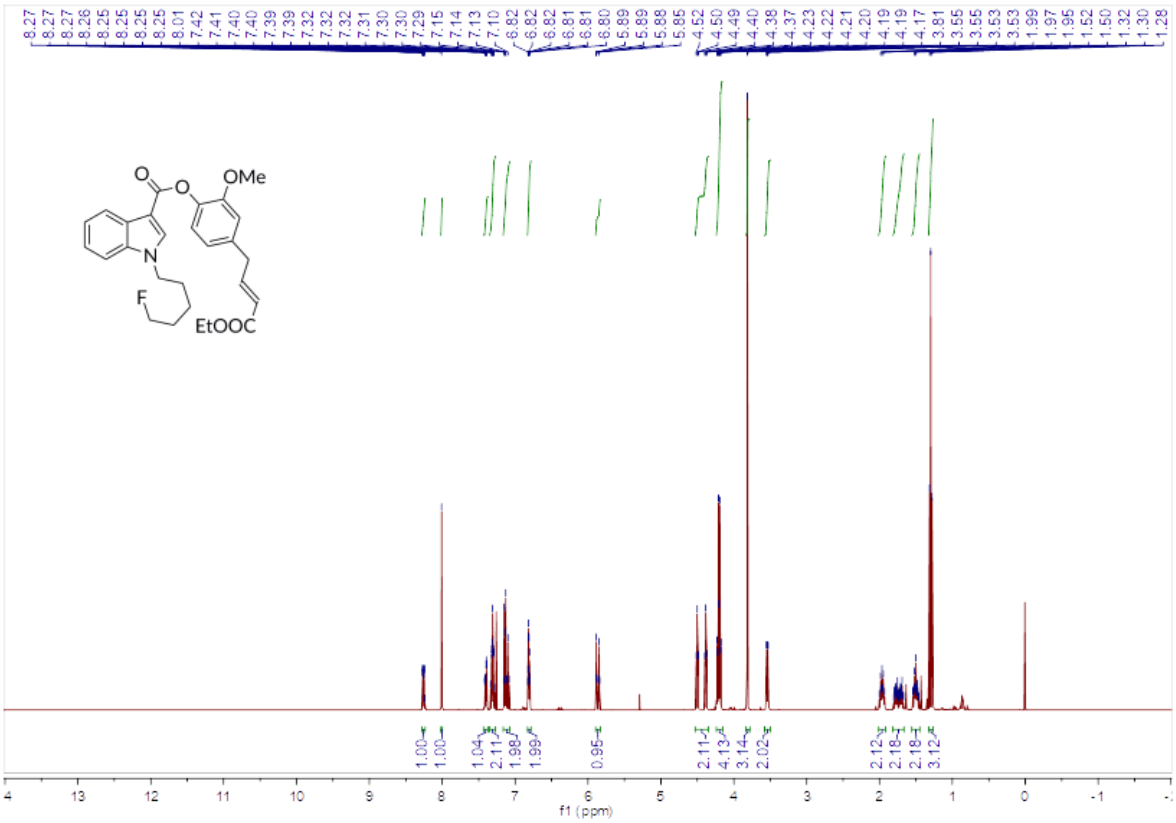
4-(4-Acetoxybut-2-en-1-yl)-2-methoxyphenyl 1-(4-fluorobutyl)-1*H*-indole-3-carboxylate (31)

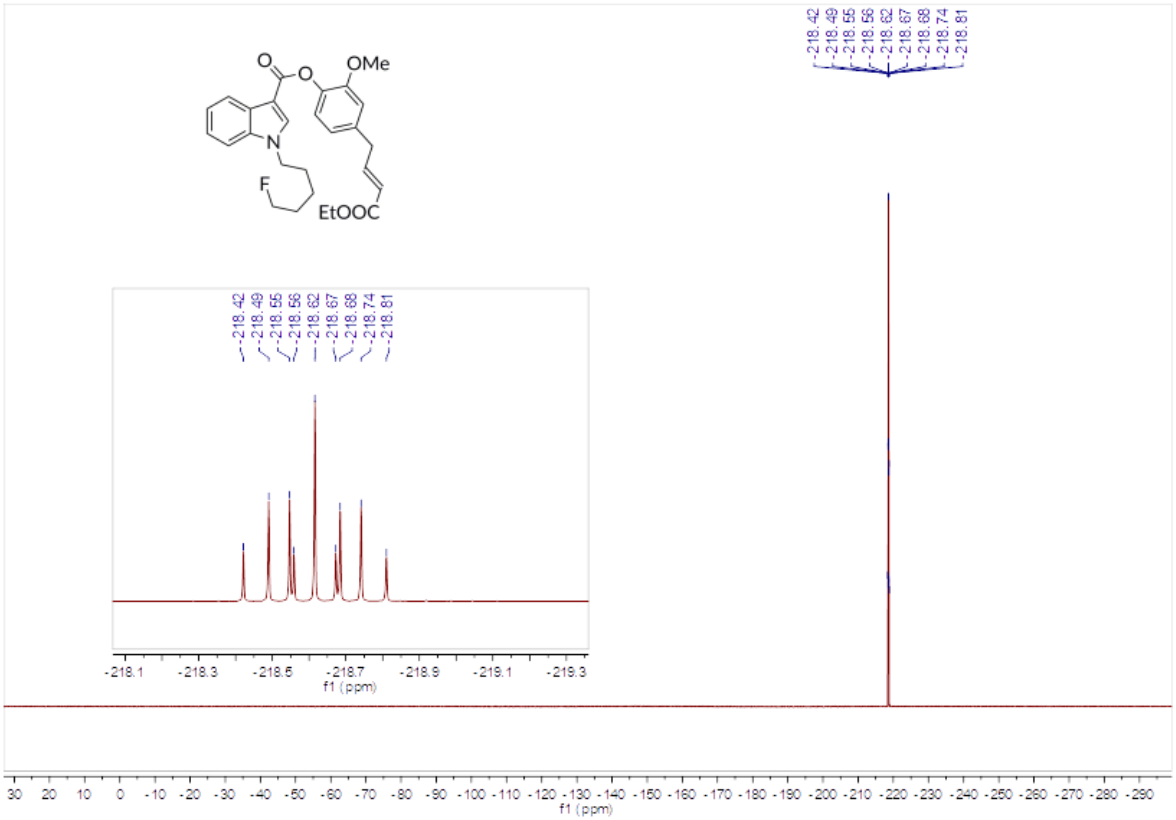


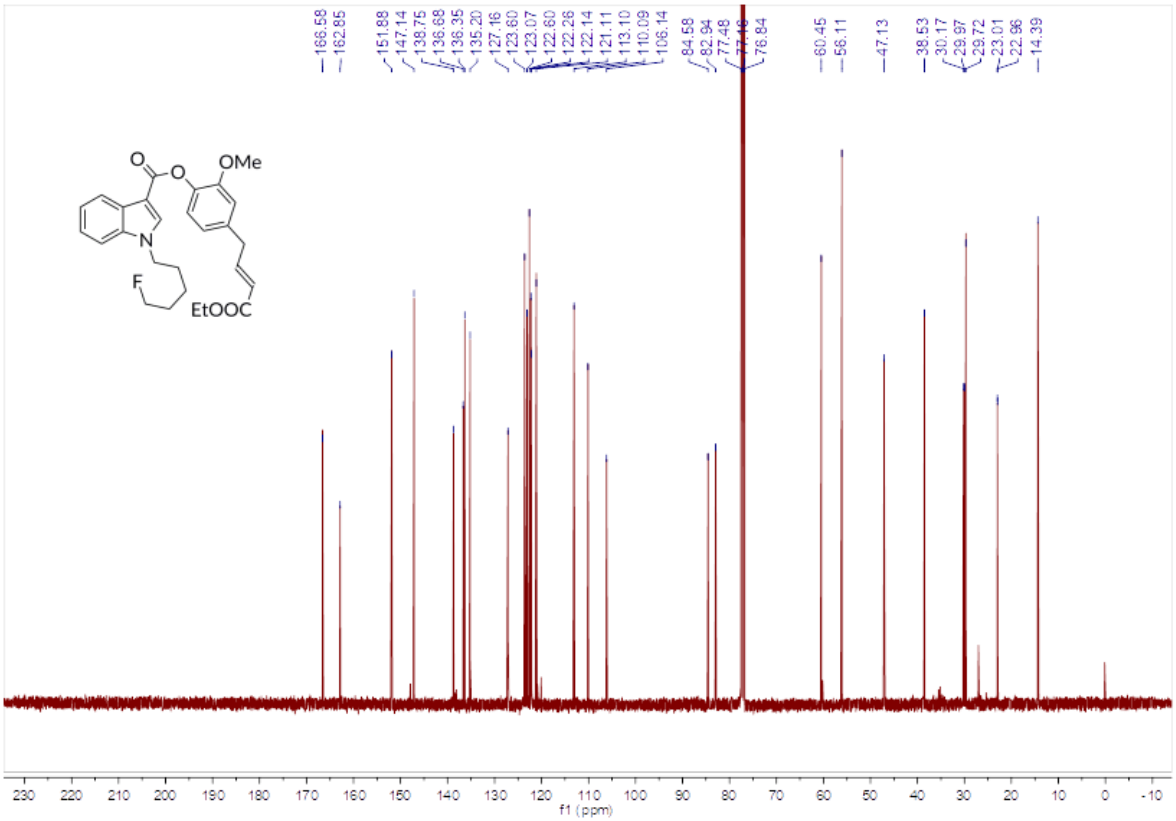




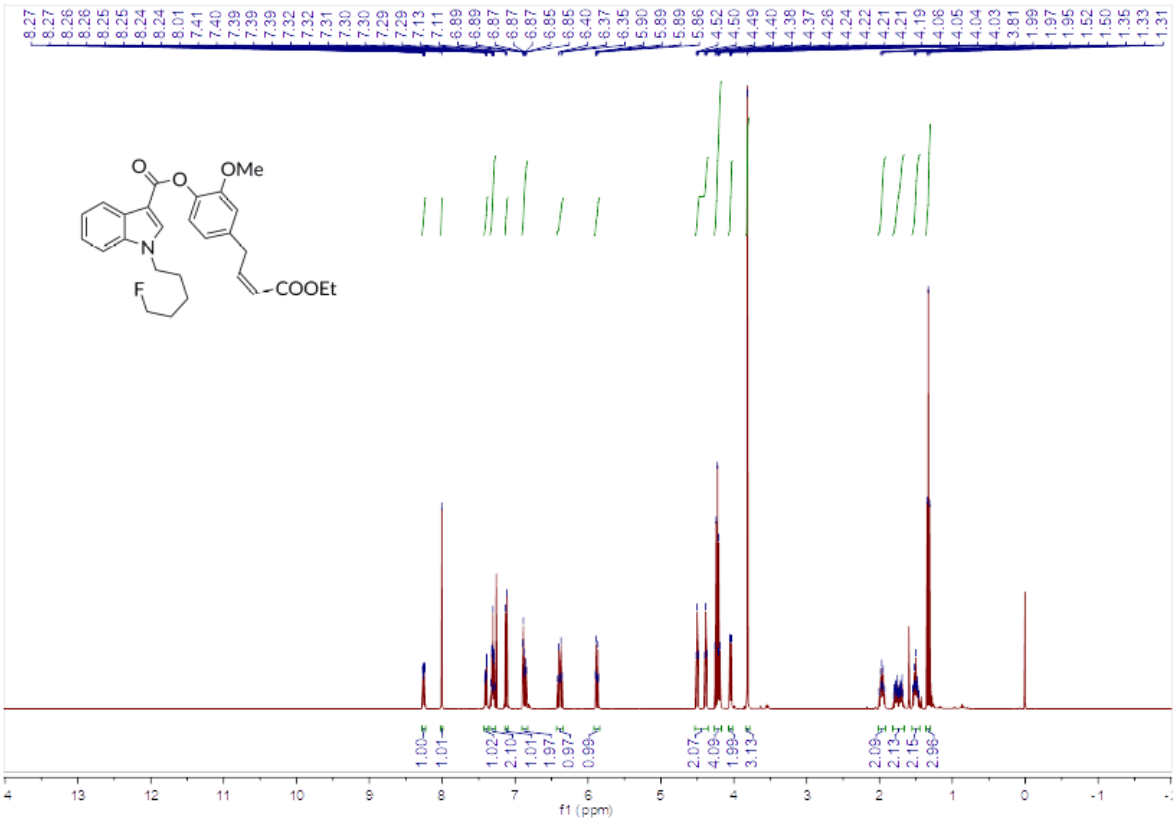
(*E*)-4-(4-Ethoxy-4-oxobut-2-en-1-yl)-2-methoxyphenyl 1-(4-fluorobutyl)-1*H*-indole-3-carboxylate (32)

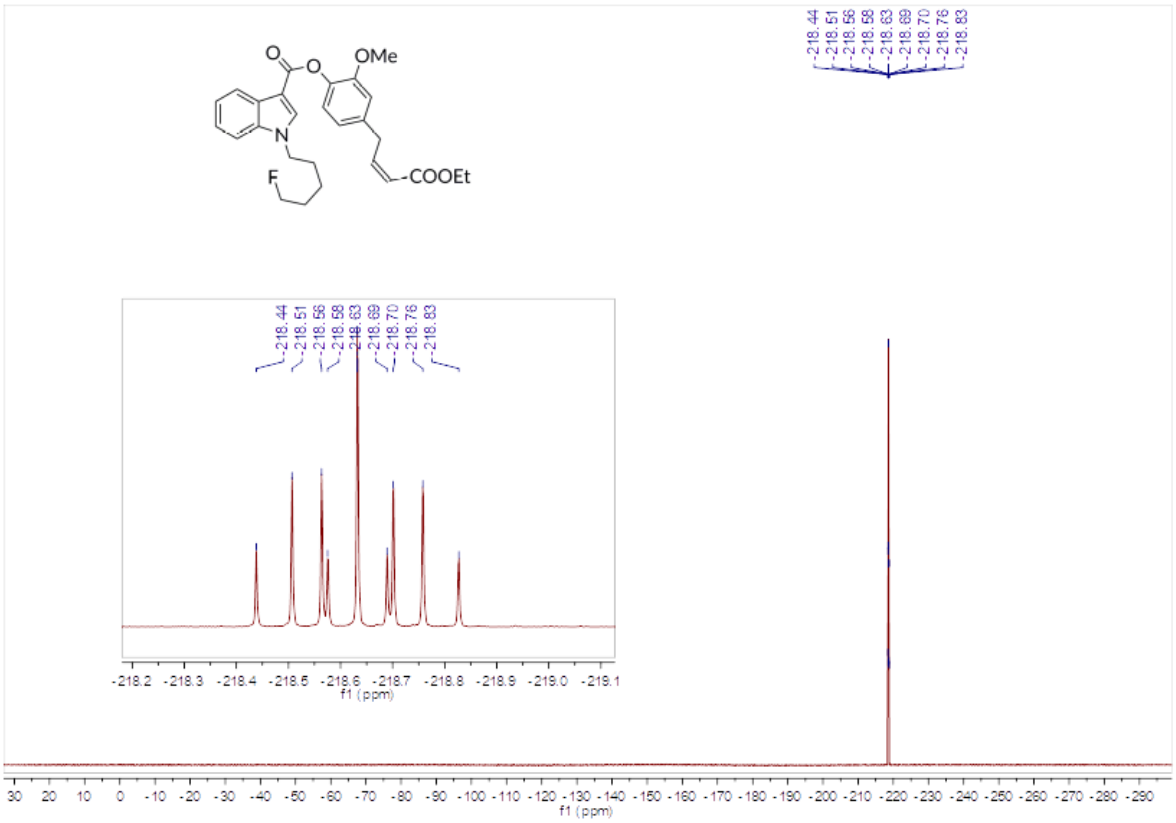


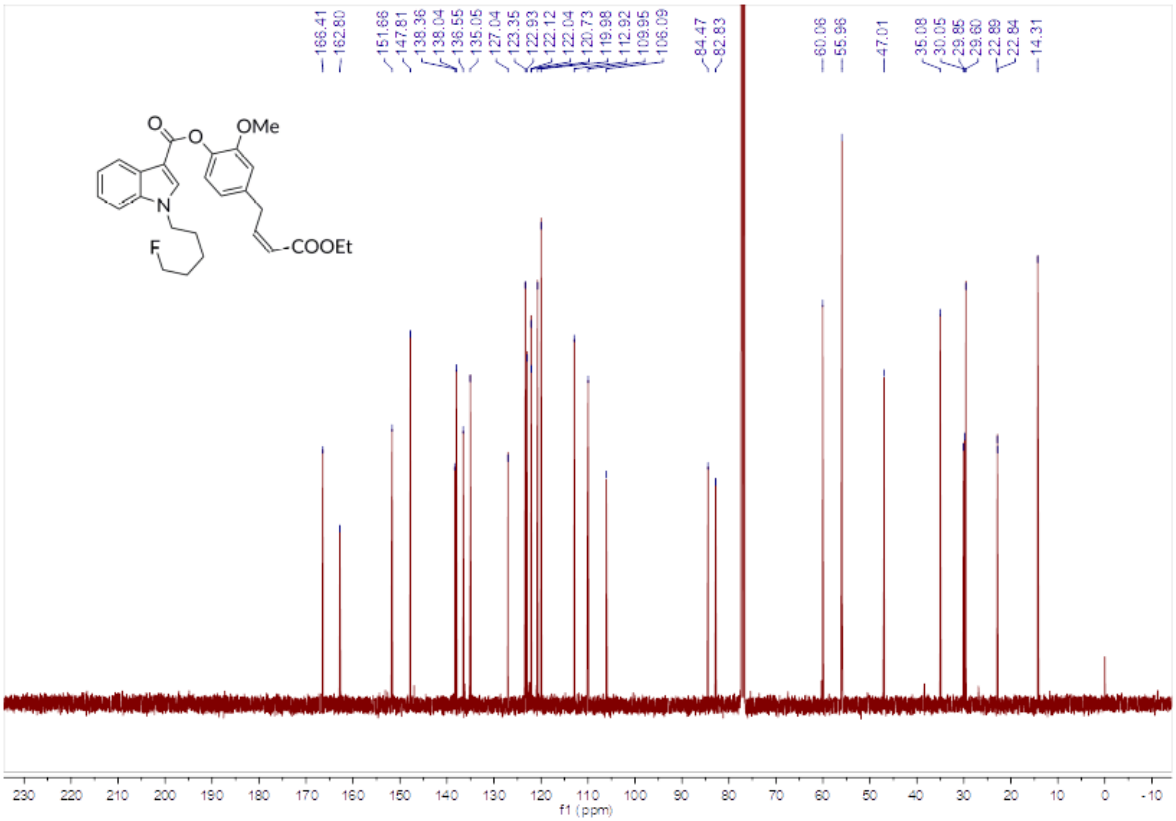

-218.42
-218.49
-218.55
-218.56
-218.62
-218.67
-218.68
-218.74
-218.81
OMe
O
O
N
F
EtOOC
-218.1
-218.3
-218.5
-218.7
-218.9
-219.1
-219.3
f1 (ppm)
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290
f1 (ppm)


166.58
162.85
151.88
147.14
138.75
136.68
136.35
135.20
127.16
123.60
123.07
122.60
122.26
122.14
121.11
113.10
110.09
106.14
84.58
82.94
77.48
77.16
76.84
60.45
56.11
47.13
38.53
30.17
29.97
29.72
23.01
22.96
14.39
OMe
O
O
N
F
EtOOC
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

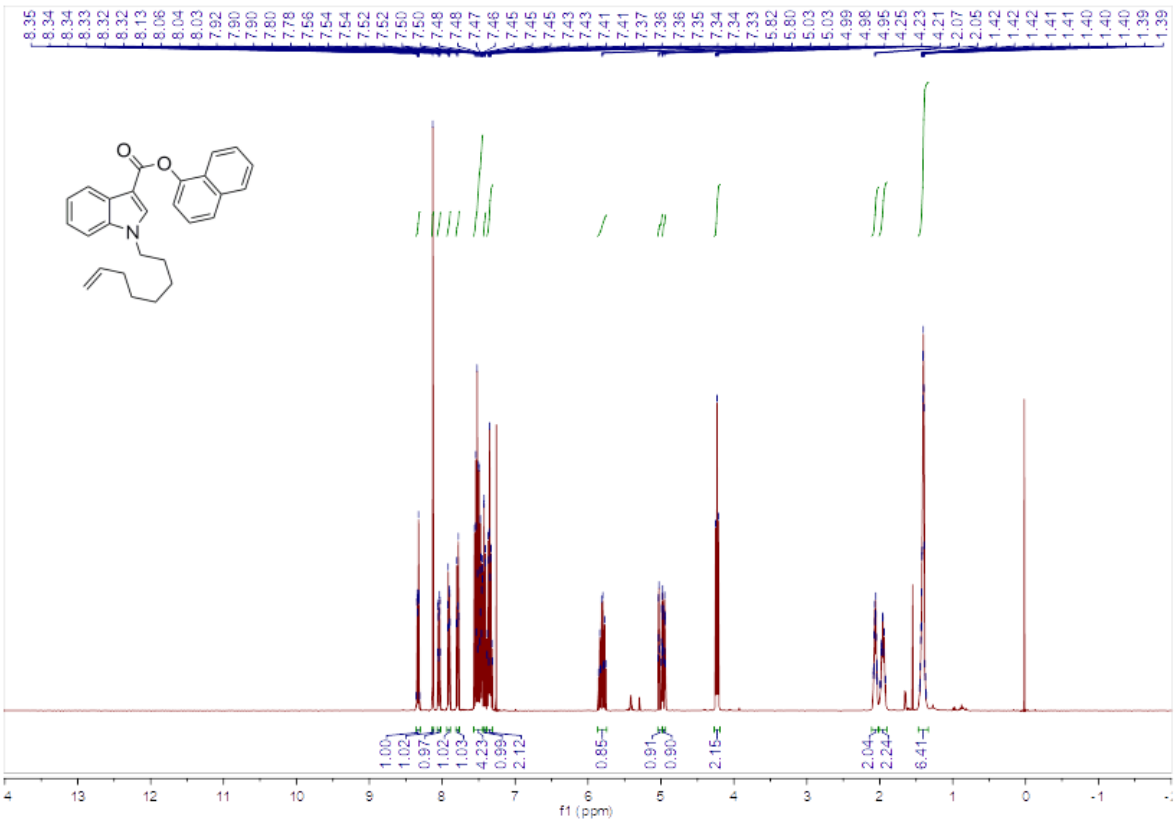
(*Z*)-4-(4-Ethoxy-4-oxobut-2-en-1-yl)-2-methoxyphenyl 1-(4-fluorobutyl)-1*H*-indole-3-carboxylate (32)

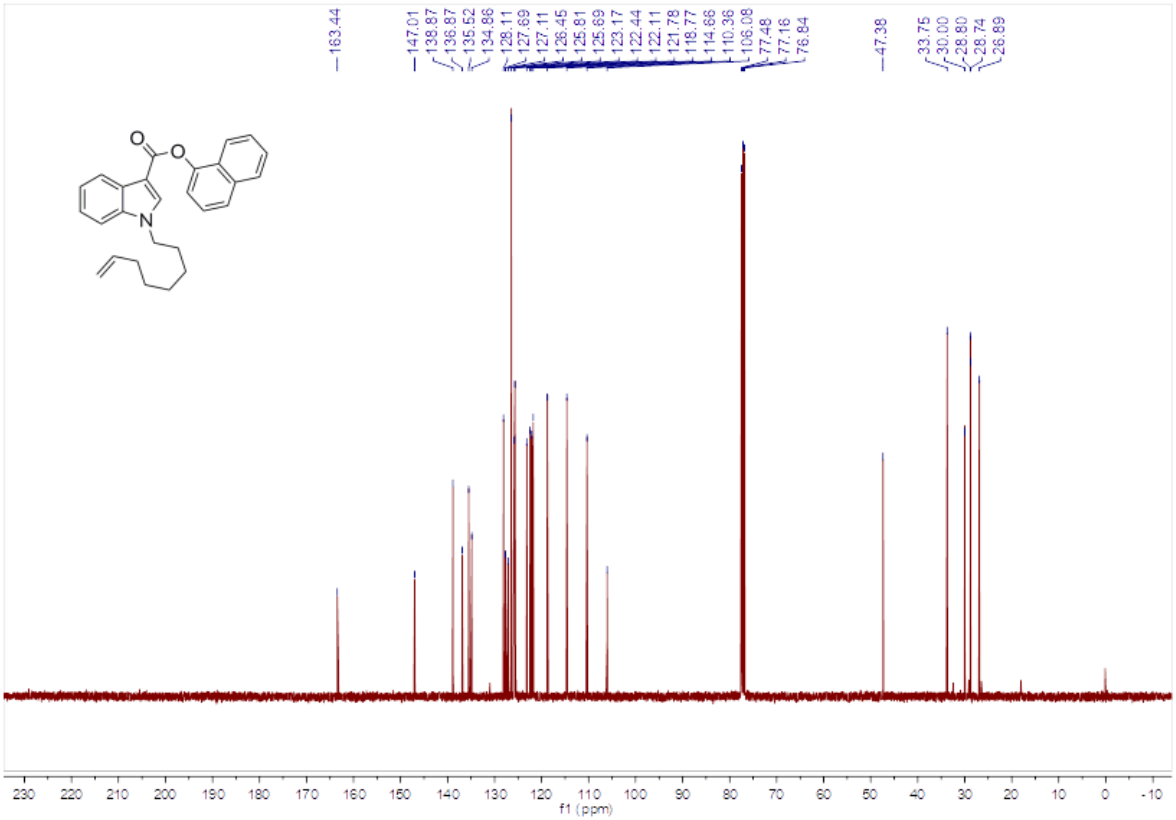




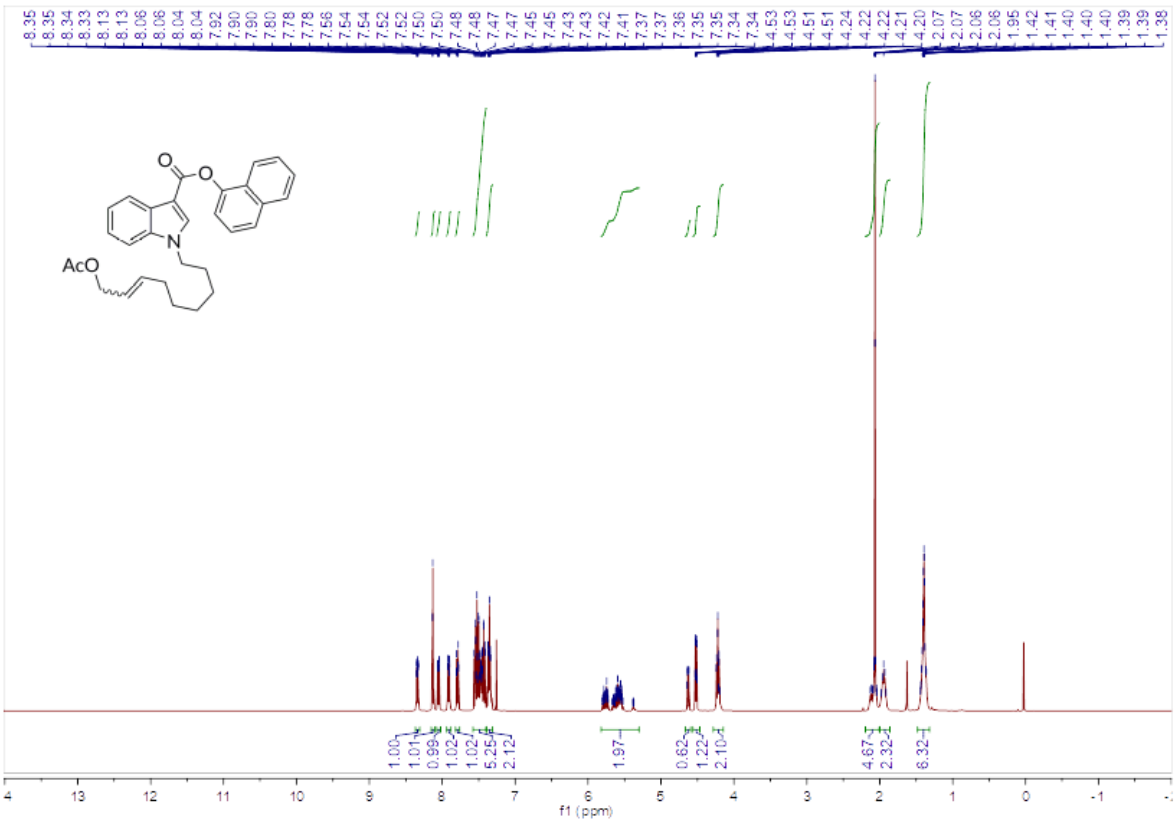


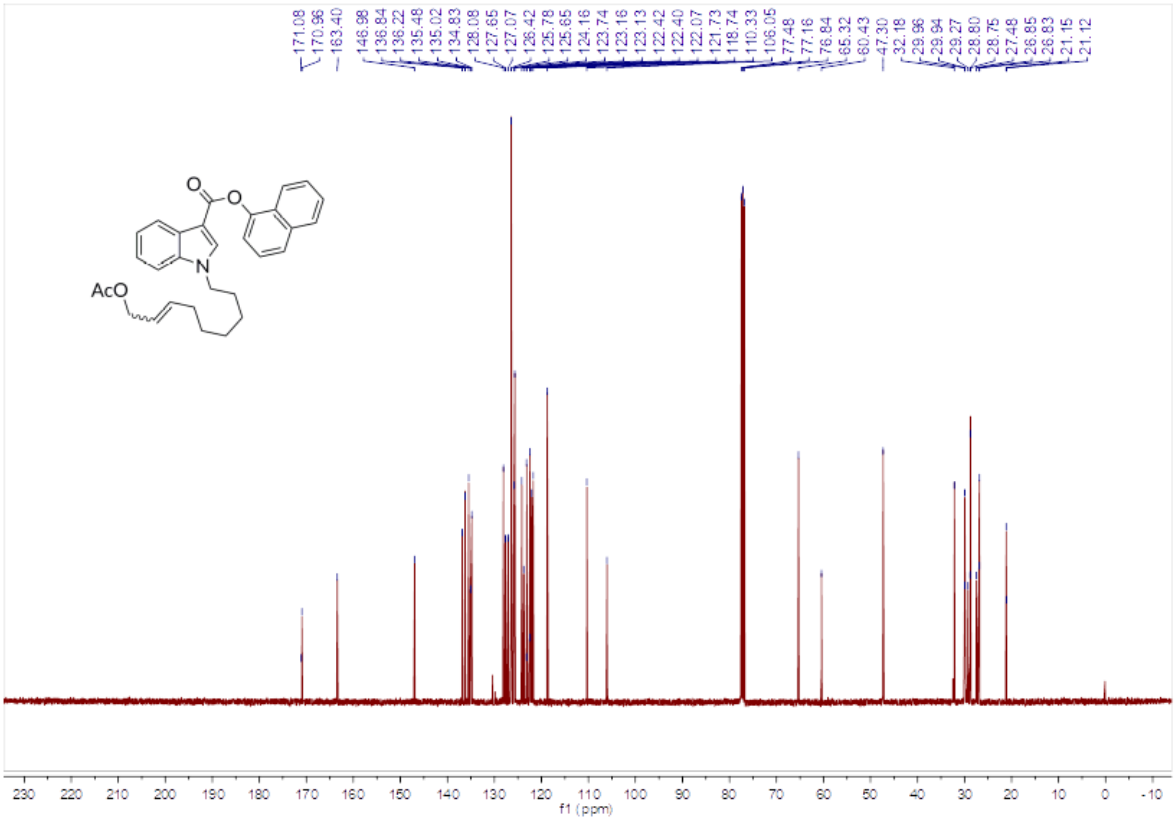
Naphthalen-1-yl 1-(oct-7-en-1-yl)-1*H*-indole-3-carboxylate



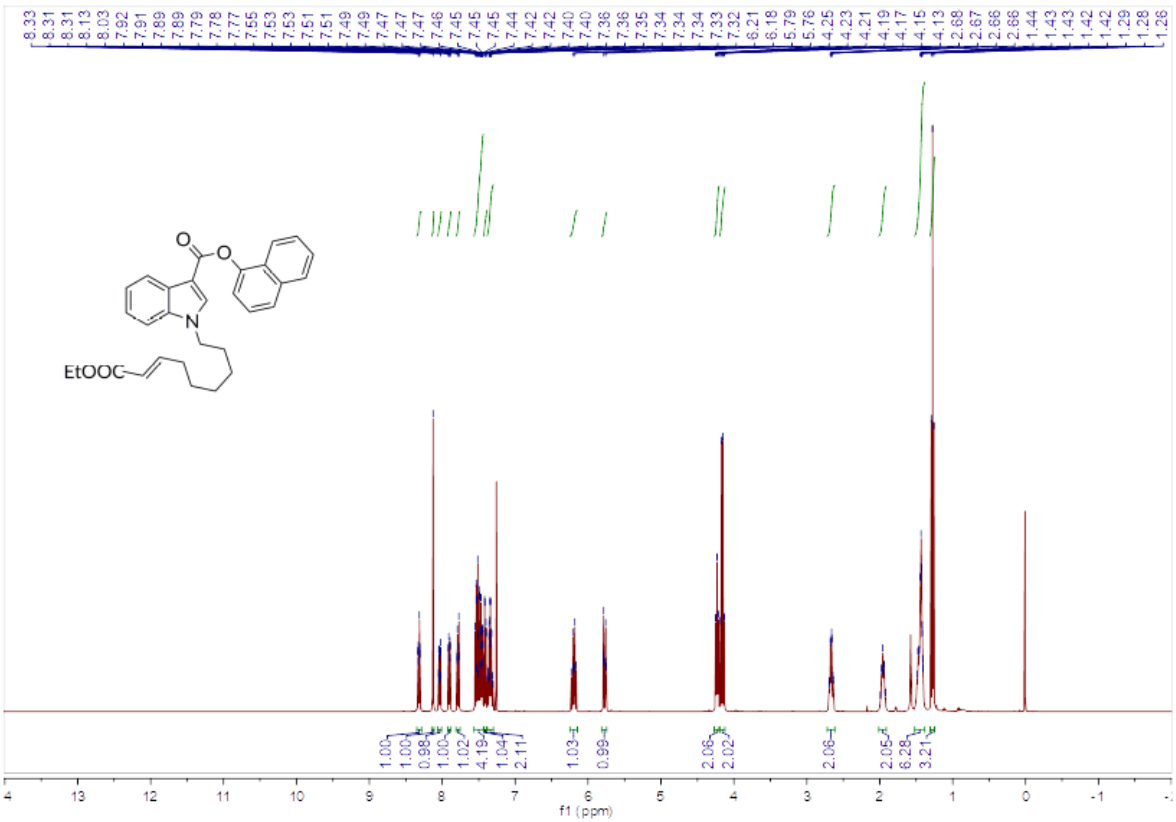


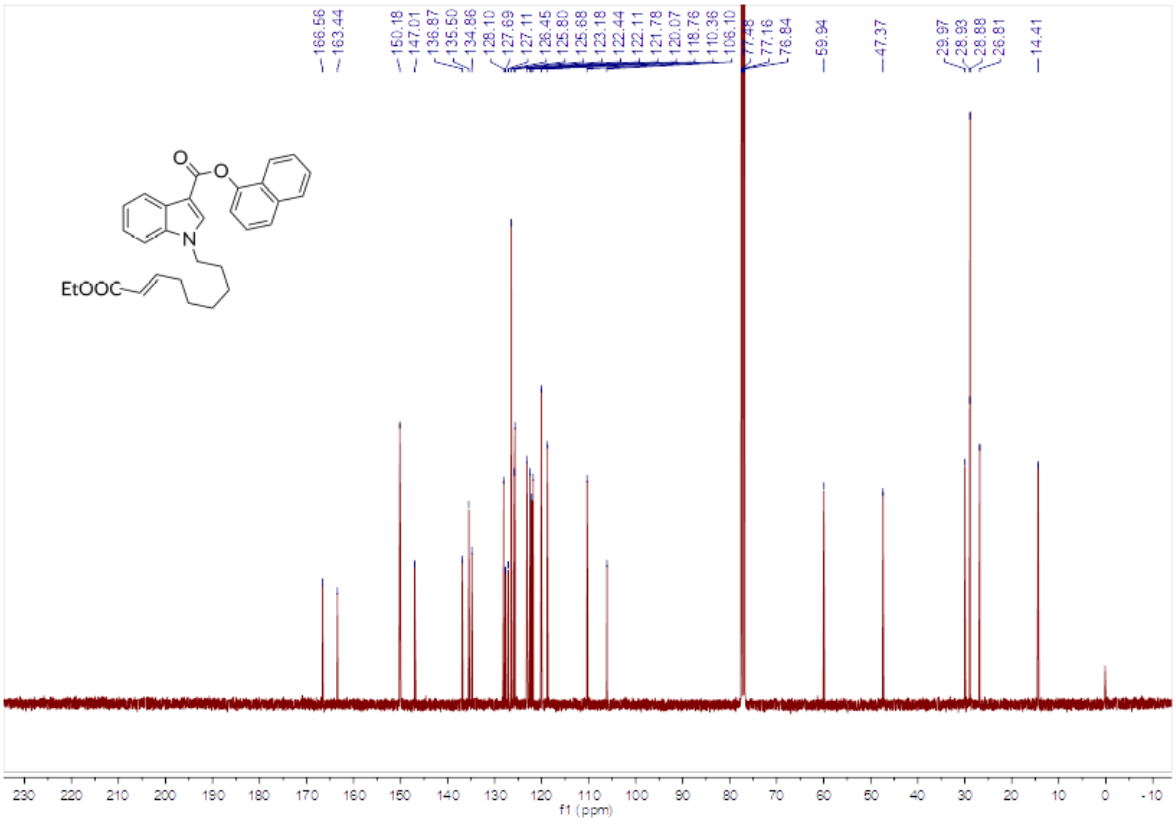
Naphthalen-1-yl 1-(9-acetoxynon-7-en-1-yl)-1*H*-indole-3-carboxylate (33)



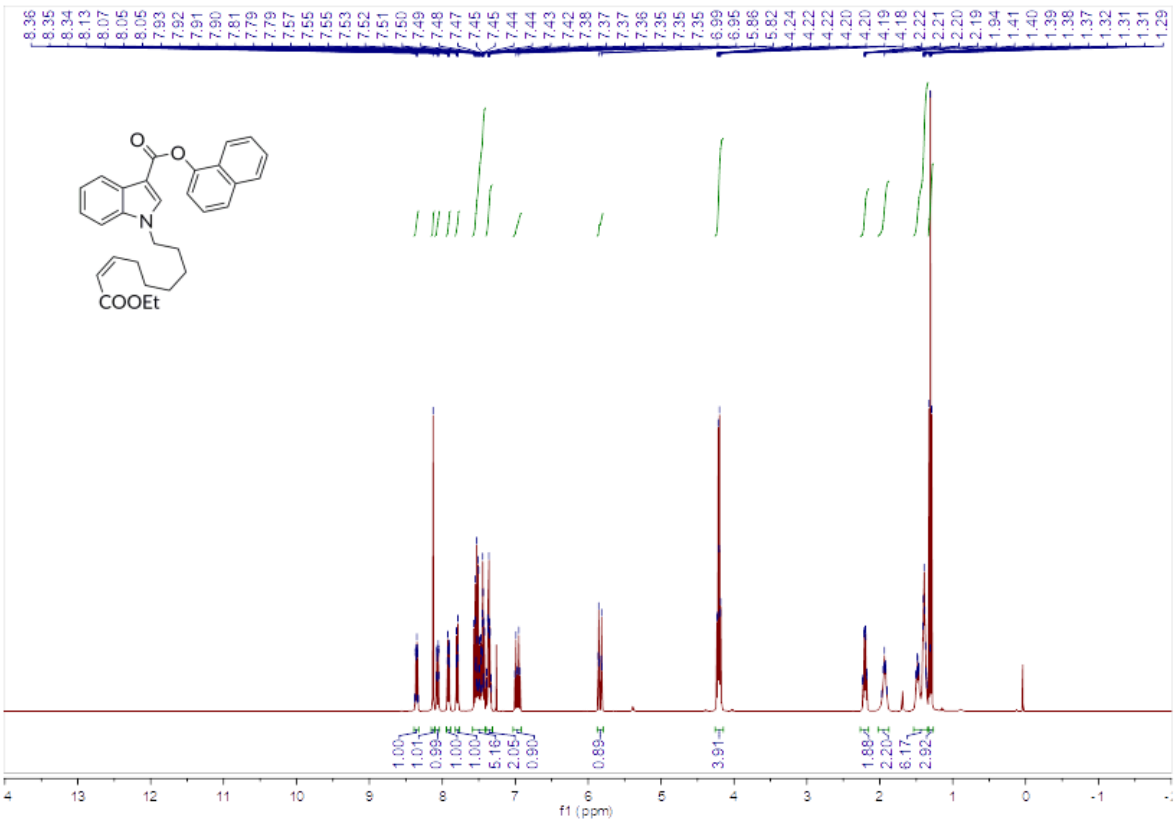


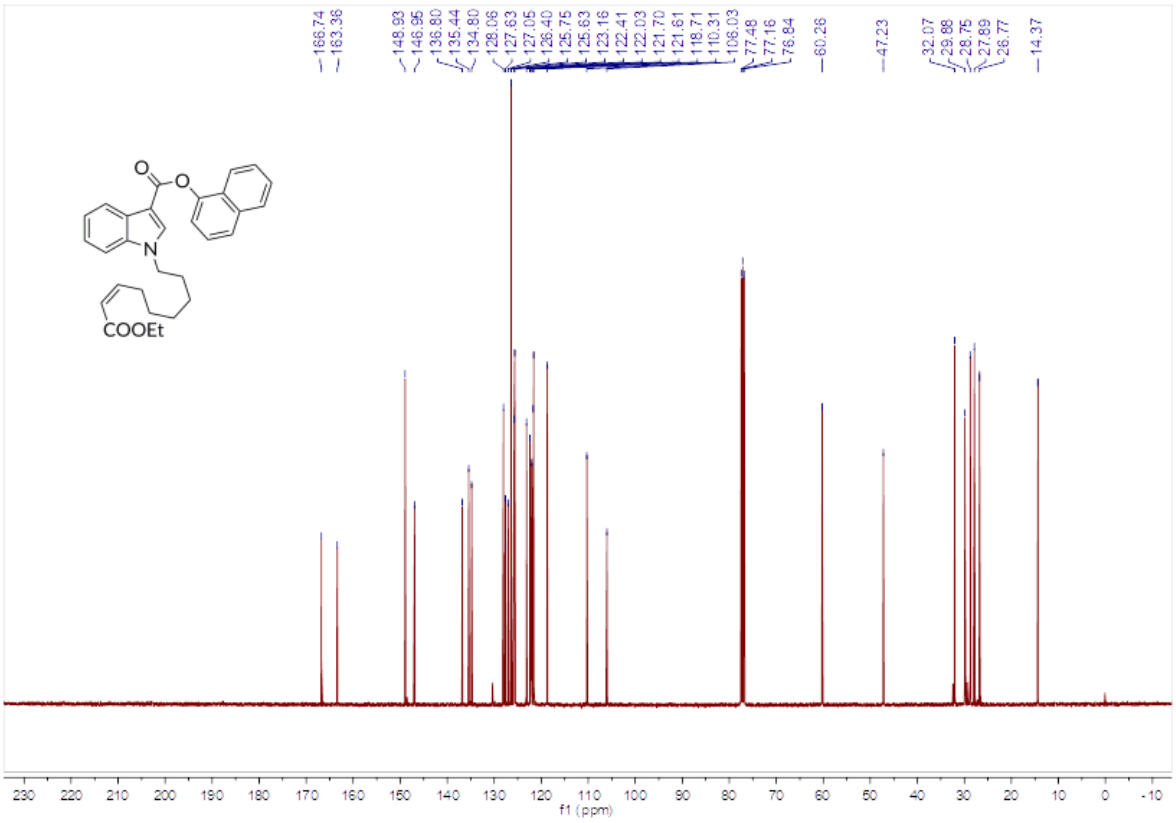
Naphthalen-1-yl (*E*)-1-(9-ethoxy-9-oxonon-7-en-1-yl)-1*H*-indole-3-carboxylate (34)



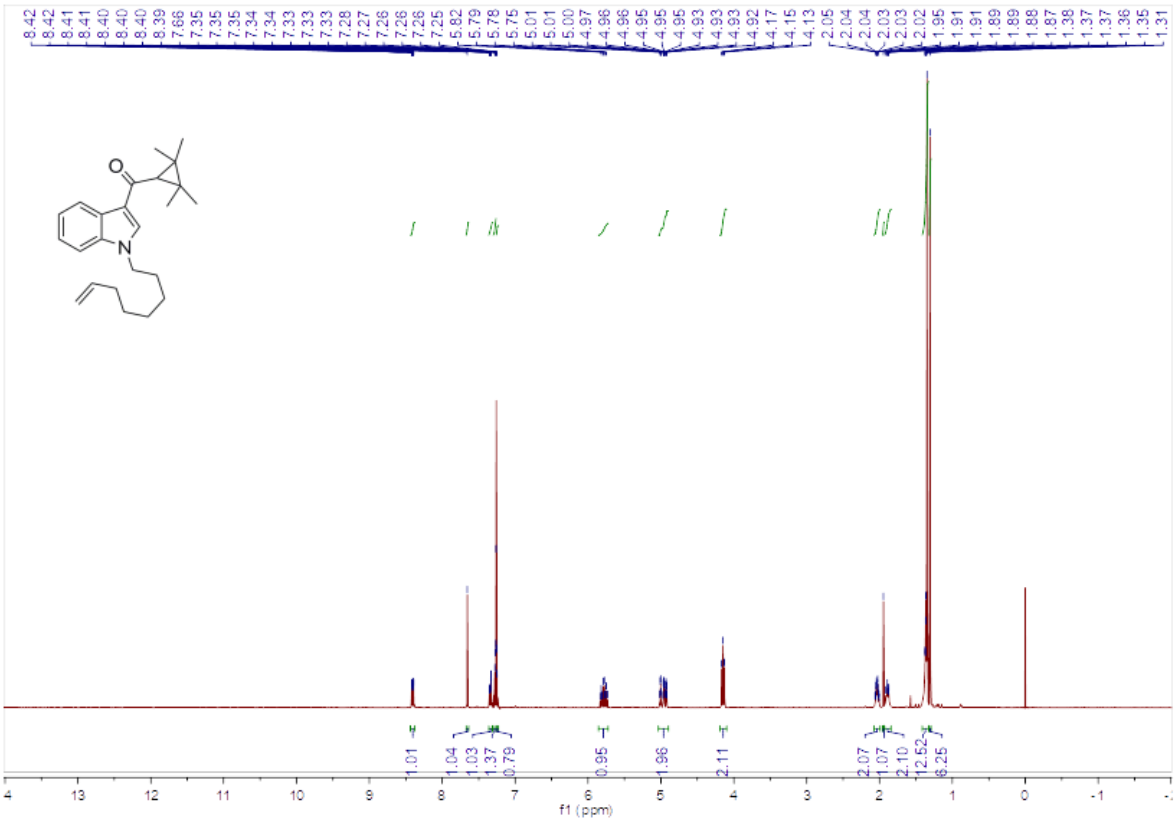


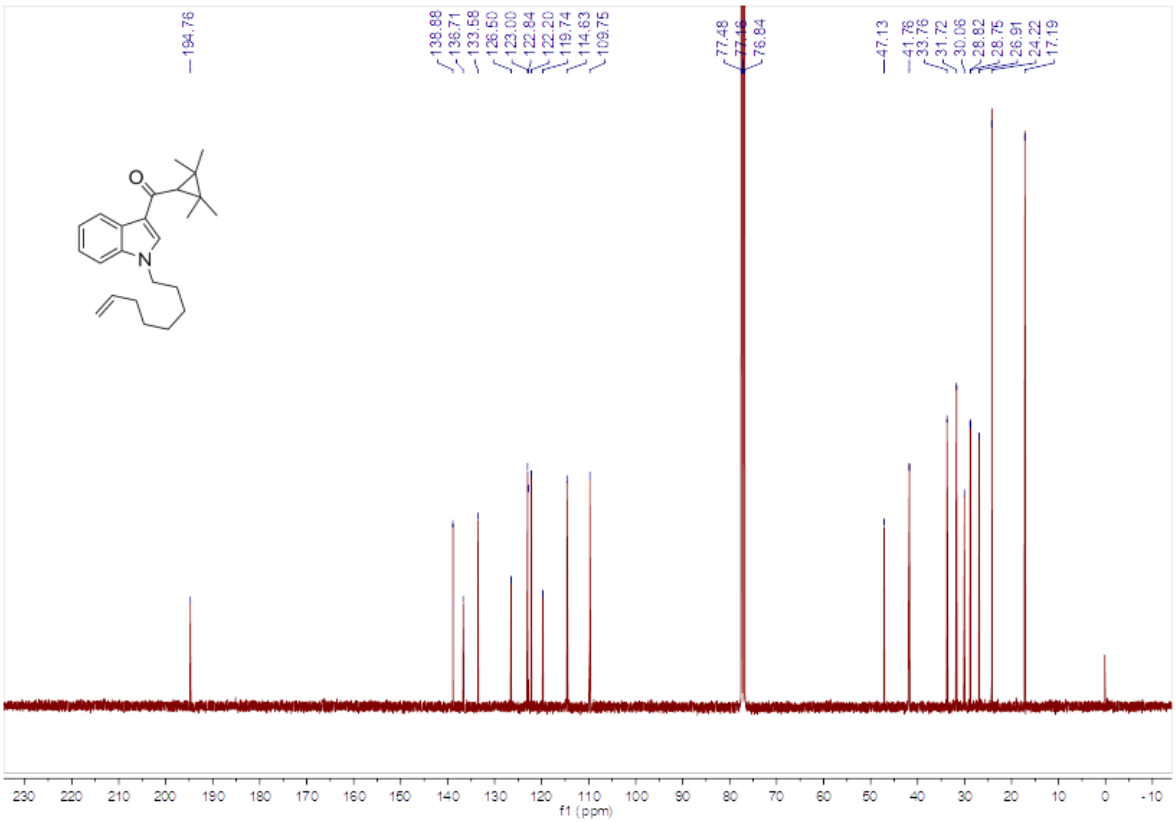
Naphthalen-1-yl (*Z*)-1-(9-ethoxy-9-oxonon-7-en-1-yl)-1*H*-indole-3-carboxylate (34)



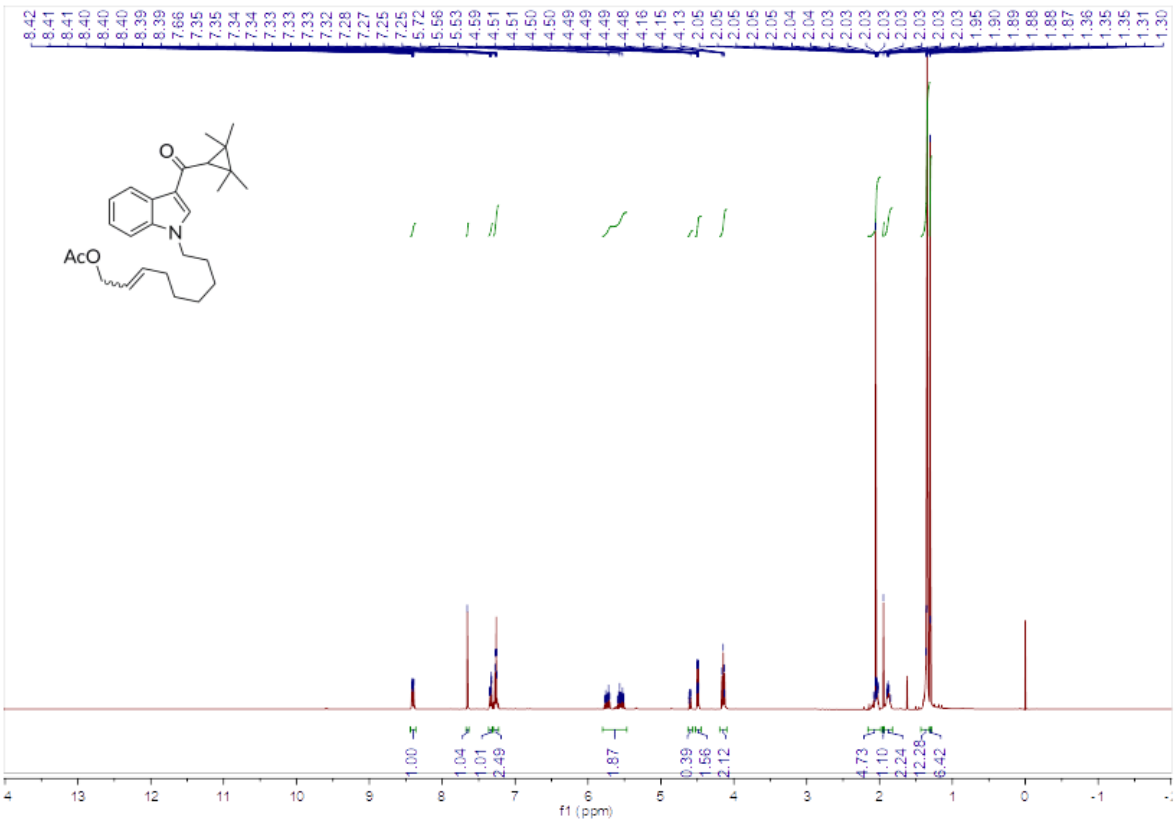


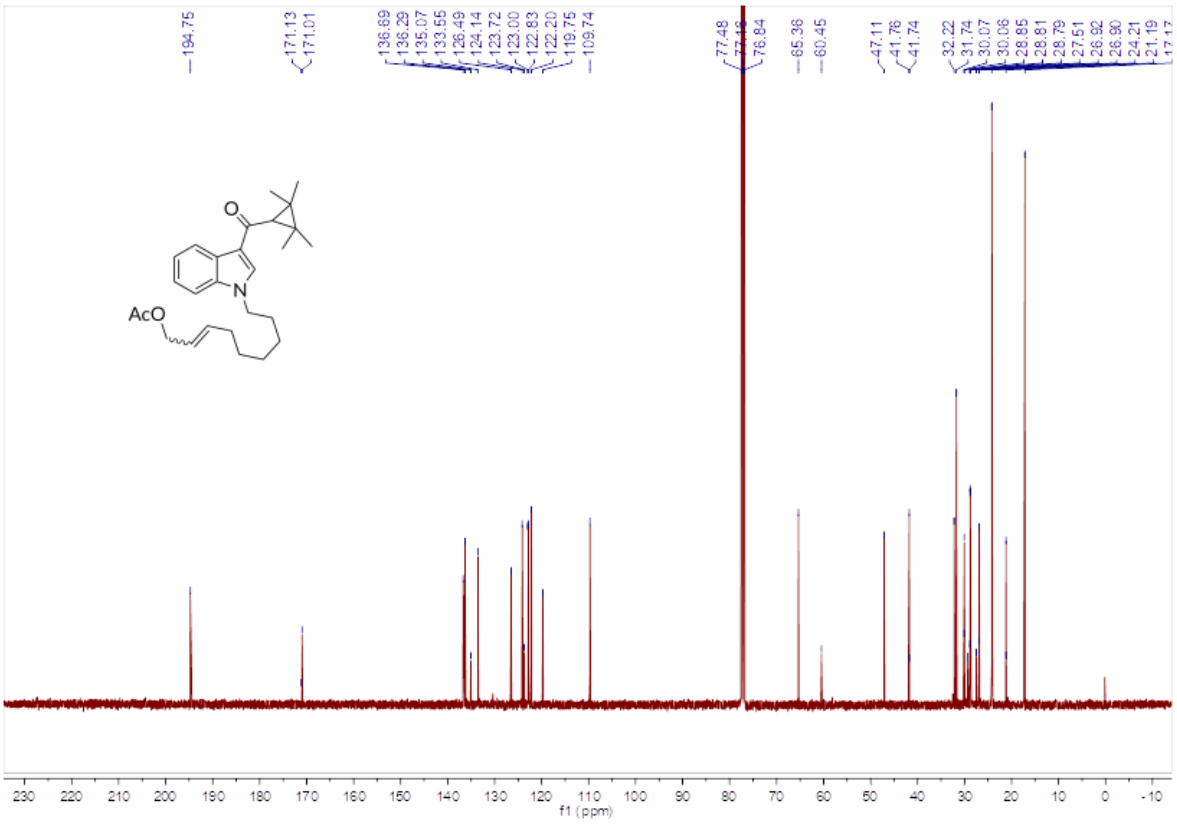
(1-(Oct-7-en-1-yl)-1*H*-indol-3-yl)(2,2,3,3-tetramethylcyclopropyl)methanone



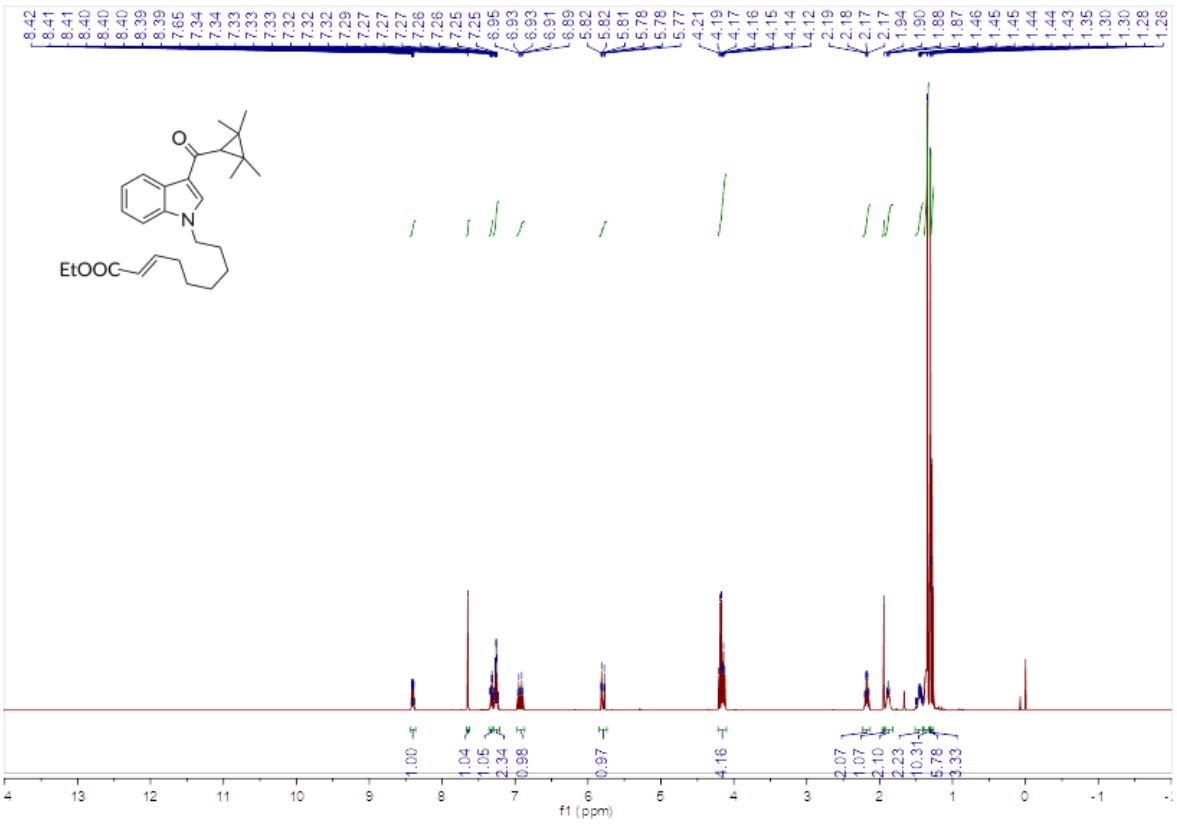


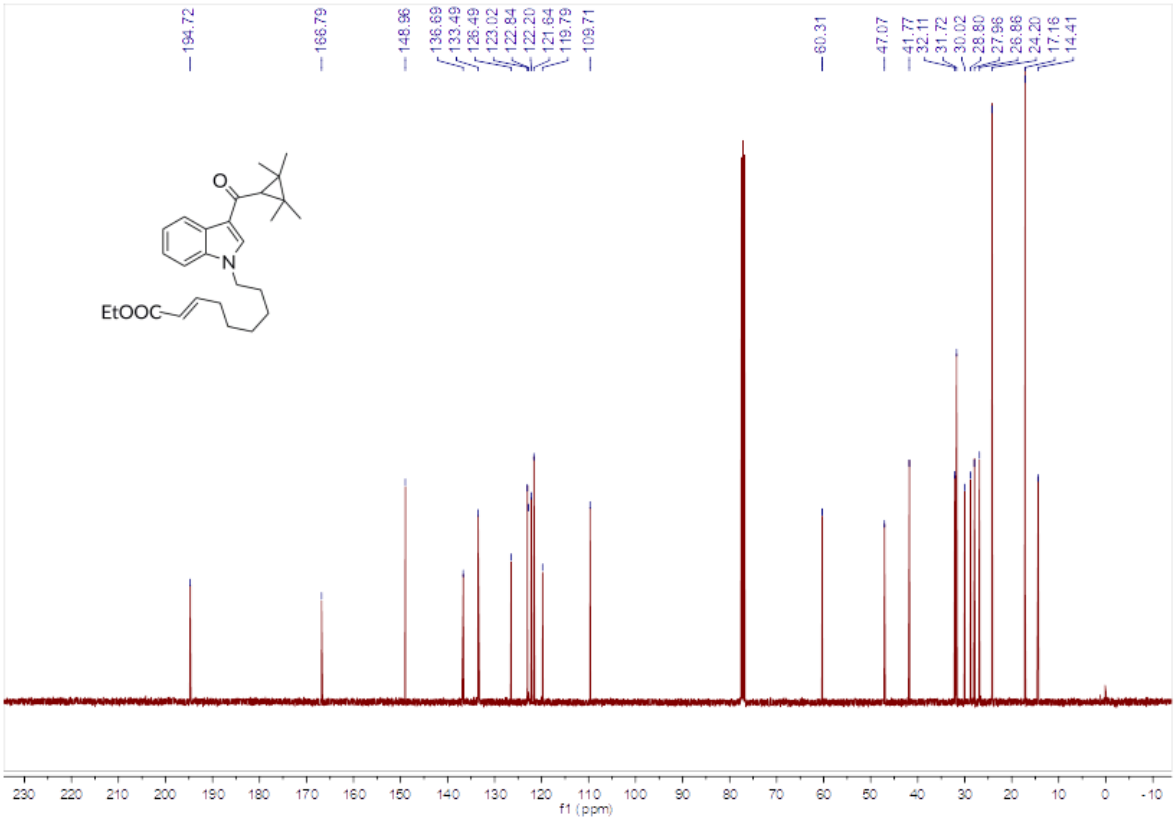
9-(3-(2,2,3,3-Tetramethylcyclopropane-1-carbonyl)-1*H*-indol-1-yl)non-2-en-1-yl acetate (35)



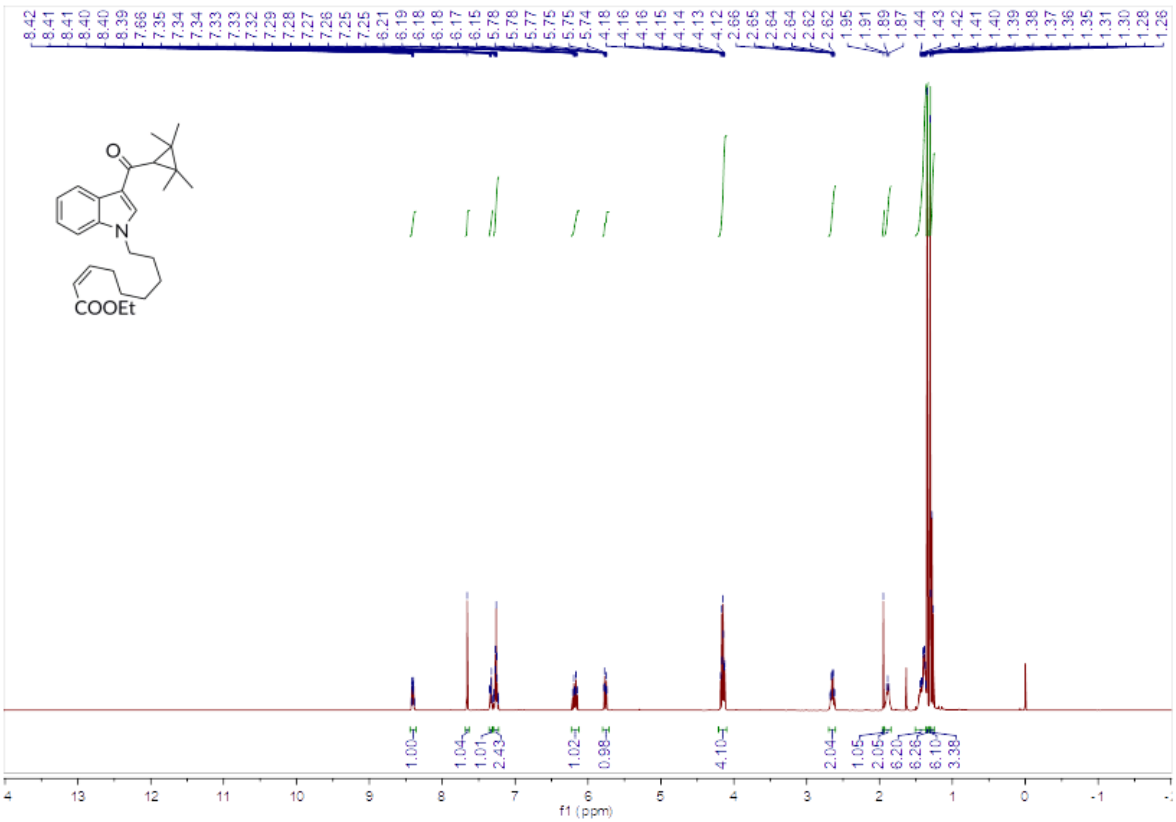


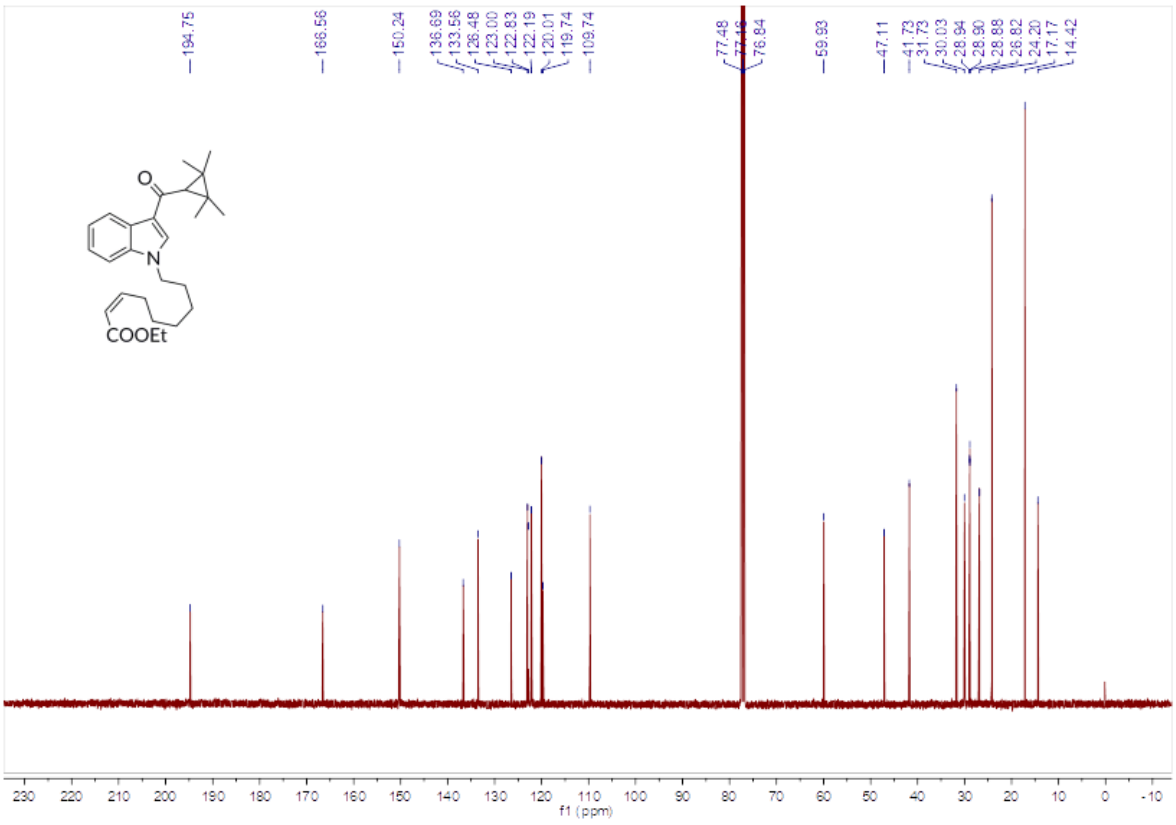
Ethyl (*E*)-9-(3-(2,2,3,3-tetramethylcyclopropane-1-carbonyl)-1*H*-indol-1-yl)non-2-enoate (36)





Ethyl (*Z*)-9-(3-(2,2,3,3-tetramethylcyclopropane-1-carbonyl)-1*H*-indol-1-yl)non-2-enoate (36)





Computational details

In this work we have used a computational protocol similar to our previous computational investigations, shown earlier to be a good choice for studying ruthenium catalysts of olefin metathesis.[15] Starting models of precatalysts were prepared on the basis of the crystal structure of Hoveyda-Grubbs catalyst. For each stationary point we have confirmed that all vibration frequencies are positive for minima and that only one is imaginary for transition states. We have initially considered two rotamers for each new catalyst (**Ru7**-**Ru10**), one with the bulky group above the benzylidene part of the catalyst and one with the methylphenyl moiety above the benzylidene part of the catalyst. In each case the energy difference between two rotamers was above 4 kcal/mol in favor of the first rotamer, suggesting that the second roatmer is not likely to be of importance. This results was later shown to be in agreement with experimental data, where the X-ray analysis showed only one monomer for each new catalyst.

For the geometry optimization step we used the 6-31G** basis set for C, N, O, Cl and H atoms, while the Ru atom was described by the Los Alamos angular momentum projected effective core potential (ECP) using the double-z contraction of valence functions (denoted as LACVP**). All calculations used the standard energy convergence criterion of $5x10^{-5}$ Hartree. Additionally, for each stationary point we performed solvation calculations using the Poisson-Boltzmann self-consistent polarizable continuum method as implemented in Jaguar v.7.9 (Schrodinger, 2013) to represent toluene, using the dielectric constant of 2.379 and the effective radius 2.762 Å. We also performed single-point energy calculations using the DLPNO-CCSD(T) method and def2-svp basis set. Free energies were defined as the sum of electronic

energy (from single-point DLPNO-CCSD(T) calculations), solvation energy, zero-point energy correction, thermal correction to enthalpy, and the negative product of temperature and entropy (at 323.15 K), all from B3LYP calculations. All DFT calculations have been performed in Jaguar v.7.9,[16] while DLPNO-CCSD(T) calculations have been performed in the Orca v. 4.0.0.1.[17]

The mechanism of the entire catalytic cycle of olefin metathesis for Hoveyda-Grubbs-like catalysts has been explored thoroughly and it was found that the dissociative mechanism is the most favorable option for the case of large and moderate olefins, but for smaller olefins the initiation may follow either the dissociative, interchange or both mechanisms in parallel.[18] As a result, for most cases one need only consider the dissociative mechanism as the likely initiation pathway for any new, hypothetical precatalysts, particularly for ruthenium complexes that are structurally similar to Hoveyda-Grubbs catalyst, as in this case.

To better quantify the intramolecular interactions between the benzyl group and ruthenium core of the complexes we have used the very accurate SAPT0 method and the functional-group SAPT partition scheme, as implemented in PSI4 software.[19] In this part of the study we used B3LYP-optimized geometries of catalyst and performed SAPT0 intramolecular calculations in the cc-pVTZ-DK basis set for Ru and cc-pVTZ-MINAO basis set for all other atoms.[20] The partition of the system was performed in such way that the -CH_2- group was defined as a linker, while the interaction energy was calculated between the phenyl ring and the remaining part of the catalyst.

Computational results

Table S4. Total energy values (E) and Gibbs free energy values (G; as defined in the manuscript) for complexes Ru7-Ru10.

structure	DLPNO E (Hartrees)	solvation E in CH_2Cl_2 (Hartrees)	zero-point E (kcal/mol)	entropy E (cal/mol)	thermal correction to enthalpy (kcal/mol)	G (Hartrees)
Ru7 – pre	-2319.1667	-0.002	356.82	243.54	27.37	-2318.6721
Ru7 – ts	-2319.1360	-0.002	355.96	242.53	27.13	-2318.6418
Ru7 – act	-2319.1384	-0.003	356.38	248.60	27.65	-2318.6475
Ru7 – act2	-2319.1327	-0.004	356.65	236.16	26.79	-2318.6375
Ru8 – pre	-2436.6720	-0.001	410.96	258.59	29.94	-2436.0928
Ru8 – ts	-2436.6382	-0.001	410.25	256.80	29.63	-2436.0601
Ru8 – act	-2436.6424	-0.002	410.64	264.13	30.19	-2436.0671
Ru8 – act2	-2436.6354	-0.003	410.78	260.40	30.06	-2436.0587
Ru9 – pre	-2593.3408	0.001	482.97	283.53	33.69	-2592.6510
Ru9 – ts	-2593.3073	0.001	482.38	279.70	33.30	-2592.6173
Ru9 – act	-2593.3124	-0.001	482.50	288.30	33.95	-2592.6264
Ru9 – act2	-2593.3056	-0.001	482.69	284.72	33.79	-2592.6178
Ru10 – pre	-3240.0274	-0.001	561.53	331.13	39.94	-3239.2264
Ru10 – ts	-3239.9952	0.000	560.80	336.88	40.28	-3239.1972

Ru10 – act	-3239.9991	-0.002	561.25	333.55	40.14	-3239.2002
Ru10 – act2	-3239.9945	-0.002	561.45	329.46	39.98	-3239.1936

Cartesian coordinates of DFT-optimized complexes

```
69
Ru7 - pre
 C1 12.641 10.388 3.514
 C2 13.850 8.743 2.339
 H2A 14.940 8.845 2.441
 H2B 13.638 8.202 1.413
 C3 13.209 8.101 3.574
 H3A 12.405 7.404 3.311
 H3B 13.926 7.573 4.208
 C4 12.064 9.067 5.577
 C5 12.884 9.196 6.715
 C6 12.325 8.923 7.966
 H6 12.949 9.023 8.852
 C7 10.990 8.527 8.107
 C8 10.207 8.408 6.956
 H8 9.167 8.104 7.048
 C9 10.719 8.671 5.679
 C10 14.322 9.642 6.593
 H10A 14.782 9.731 7.580
 H10B 14.401 10.610 6.086
 H10C 14.920 8.929 6.013
 C11 10.413 8.248 9.476
 H11A 10.268 9.176 10.043
 H11B 11.080 7.613 10.068
 H11C 9.442 7.749 9.408
 C12 9.833 8.556 4.461
 H12A 9.775 9.503 3.915
 H12B 8.820 8.267 4.752
 H12C 10.201 7.799 3.758
 C14 13.541 11.009 1.261
 H14A 14.611 11.255 1.294
 H14B 12.999 11.939 1.456
 C15 13.153 10.479 -0.107
 C16 11.810 10.196 -0.395
 H16 11.055 10.372 0.368
 C17 11.449 9.712 -1.651
 H17 10.405 9.500 -1.866
 C18 12.421 9.506 -2.633
 H18 12.136 9.128 -3.611
 C19 13.758 9.789 -2.354
 H19 14.519 9.632 -3.114
 C20 14.121 10.273 -1.095
 H20 15.164 10.493 -0.880
 C22 11.387 12.230 5.513
 H22 11.372 11.336 6.137
 C23 10.841 13.429 6.110
 C24 10.837 14.638 5.369
 C25 10.311 15.808 5.914
 H25 10.306 16.736 5.357
 C26 9.784 15.778 7.208
 H26 9.376 16.692 7.630
 C27 9.778 14.601 7.961
 H27 9.368 14.596 8.966
 C28 10.304 13.437 7.411
 H28 10.309 12.509 7.977
 C29 11.575 15.693 3.273
 H29 10.658 16.291 3.337
 C31 12.785 16.480 3.767
 H31A 12.655 16.830 4.794
 H31B 12.942 17.355 3.127
 H31C 13.675 15.846 3.729
 C30 11.735 15.192 1.845
 H30A 12.667 14.627 1.741
 H30B 11.779 16.050 1.166
 H30C 10.897 14.552 1.560
 N1 13.221 10.068 2.330
 N2 12.652 9.273 4.286
 O1 11.368 14.516 4.118
 Cl1 10.049 11.918 2.488
 Cl2 14.333 12.943 4.086
 Ru1 12.039 12.271 3.791
69
Ru7 - ts
 C1 12.611 10.396 3.514
 C2 13.967 8.862 2.365
 H2A 15.041 9.025 2.531
 H2B 13.838 8.340 1.415
 C3 13.298 8.148 3.544
 H3A 12.542 7.424 3.216
 H3B 14.007 7.632 4.196
 C4 12.037 9.013 5.533
 C5 12.824 9.149 6.693
 C6 12.239 8.849 7.926
 H6 12.836 8.957 8.829
 C7 10.910 8.423 8.028
 C8 10.163 8.293 6.854
 H8 9.128 7.963 6.916
 C9 10.701 8.580 5.594
 C10 14.252 9.635 6.614
 H10A 14.682 9.731 7.614
 H10B 14.317 10.608 6.116
 H10C 14.887 8.943 6.048
 C11 10.297 8.139 9.379
 H11A 10.047 9.071 9.901
 H11B 10.988 7.584 10.023
 H11C 9.376 7.556 9.287
 C12 9.852 8.455 4.351
 H12A 9.774 9.409 3.820
 H12B 8.843 8.124 4.609
 H12C 10.268 7.725 3.647
 C14 13.564 11.128 1.306
 H14A 14.605 11.460 1.404
 H14B 12.931 12.004 1.470
 C15 13.309 10.568 -0.082
 C16 12.021 10.148 -0.446
 H16 11.209 10.245 0.270
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 C17 11.785 9.629 -1.717
 H17 10.783 9.310 -1.991
 C18 12.828 9.524 -2.641
 H18 12.641 9.118 -3.631
 C19 14.110 9.944 -2.287
 H19 14.926 9.867 -3.001
 C20 14.348 10.462 -1.012
 H20 15.349 10.788 -0.738
 C22 11.226 12.111 5.562
 H22 11.222 11.224 6.196
 C23 10.858 13.422 6.137
 C24 9.675 14.096 5.745
 C25 9.383 15.358 6.283
 H25 8.491 15.894 5.983
 C26 10.250 15.936 7.209
 H26 10.012 16.917 7.613
 C27 11.410 15.276 7.616
 H27 12.083 15.735 8.334
 C28 11.707 14.027 7.078
 H28 12.620 13.512 7.362
 C29 7.661 13.984 4.380
 H29 7.163 14.505 5.208
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 H31B 7.012 15.387 2.863
 H31C 8.439 14.421 2.416
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 H30B 5.837 13.159 3.569
 H30C 6.608 12.138 4.800
 N1 13.263 10.151 2.352
 N2 12.650 9.266 4.262
 O1 8.895 13.414 4.872
 Cl1 10.099 11.855 2.296
 Cl2 14.047 13.079 4.210
 Ru1 11.865 12.190 3.863
69
Ru7 - act
 C1 12.658 10.389 3.485
 C2 13.934 8.866 2.235
 H2A 15.016 9.052 2.301
 H2B 13.732 8.325 1.308
 C3 13.389 8.157 3.481
 H3A 12.625 7.410 3.233
 H3B 14.167 7.668 4.074
 C4 12.274 9.024 5.556
 C5 13.125 9.232 6.657
 C6 12.640 8.923 7.930
 H6 13.285 9.085 8.791
 C7 11.351 8.415 8.126
 C8 10.538 8.215 7.007
 H8 9.533 7.821 7.143
 C9 10.973 8.516 5.712
 C10 14.516 9.790 6.476
 H10A 15.017 9.895 7.442
 H10B 14.494 10.771 5.990
 H10C 15.136 9.137 5.850
 C11 10.847 8.118 9.519
 H11A 10.555 9.041 10.036
 H11B 11.620 7.641 10.130
 H11C 9.974 7.460 9.500
 C12 10.051 8.331 4.530
 H12A 9.919 9.266 3.976
 H12B 9.067 7.990 4.861
 H12C 10.434 7.586 3.822
 C14 13.418 11.125 1.210
 H14A 14.461 11.465 1.228
 H14B 12.790 11.995 1.426
 C15 13.057 10.571 -0.157
 C16 11.734 10.197 -0.434
 H16 10.973 10.331 0.331
 C17 11.399 9.675 -1.682
 H17 10.370 9.392 -1.888
 C18 12.378 9.523 -2.667
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H30 3.724 -0.181 13.734
H31 3.660 -2.641 13.334
H32 4.032 -3.549 11.089
H34 4.872 -4.019 9.312
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H35B 2.382 -3.576 9.195
H35C 2.872 -4.804 8.015
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H36B 6.338 -3.339 7.461
H36C 4.928 -2.929 6.460
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Ru9 - act
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Cl1 3.685 -0.646 6.888
Cl2 1.513 2.523 9.372
O1 6.773 -0.285 10.503
N1 2.894 2.758 5.988
N2 4.725 3.443 6.989
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C2 3.699 2.555 7.062
C3 3.497 3.652 4.994
C4 4.563 4.358 5.833
C5 1.714 1.969 5.634
C6 0.557 2.850 5.197
C7 0.027 3.802 6.079
C8 -1.029 4.619 5.679
C9 -1.568 4.494 4.395
C10 -1.049 3.546 3.516
C11 0.011 2.728 3.916
C12 5.872 3.593 7.848
C13 7.077 2.958 7.456
C14 8.208 3.145 8.261
C15 8.157 3.937 9.401
C16 6.969 4.567 9.759
C17 5.802 4.424 8.997
C18 4.533 5.176 9.403
C19 4.470 6.599 8.767
C20 5.545 7.600 9.210
C21 4.313 5.277 10.934
C22 4.224 3.943 11.679
C23 7.192 2.058 6.224
C24 7.347 0.575 6.657
C25 7.206 -0.440 5.516
C26 8.343 2.490 5.282
C27 8.230 3.909 4.716
C28 4.464 0.176 10.657
C29 3.217 -0.055 11.276
C30 3.073 -0.986 12.299
C31 4.186 -1.710 12.723
C32 5.438 -1.504 12.143
C33 5.594 -0.563 11.119
C34 7.964 -1.038 10.817
C35 7.944 -2.381 10.087
C36 9.137 -0.158 10.403
H1 5.549 1.584 9.374
H3A 2.754 4.338 4.582
H3B 3.927 3.065 4.168
H4A 5.513 4.488 5.312
H4B 4.219 5.338 6.179
H5A 1.417 1.384 6.509
H5B 1.973 1.250 4.847
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H8 -1.435 5.351 6.371
H9 -2.391 5.133 4.086
H10 -1.465 3.442 2.517
H11 0.416 1.991 3.226
H14 9.141 2.659 7.990
H15 9.046 4.069 10.013
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H18 3.678 4.620 9.006
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H19B 4.518 6.510 7.677
H20A 5.494 7.814 10.282
H20B 5.414 8.552 8.684
H20C 6.553 7.235 8.988
H21A 3.375 5.828 11.079
H21B 5.091 5.901 11.393
H22A 5.160 3.379 11.616
H22B 3.424 3.320 11.269
H22C 4.012 4.111 12.741
H23 6.256 2.126 5.660
H24A 8.324 0.452 7.144
H24B 6.589 0.350 7.414
H25A 7.254 -1.460 5.910
H25B 7.993 -0.341 4.762
H25C 6.235 -0.335 5.022
H26A 9.301 2.384 5.808
H26B 8.385 1.781 4.447
H27A 9.096 4.151 4.091
H27B 7.338 4.018 4.087
H27C 8.176 4.660 5.512
H29 2.367 0.545 10.965
H30 2.105 -1.138 12.765
H31 4.089 -2.445 13.518
H32 6.282 -2.087 12.492
H34 8.009 -1.193 11.902
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H35B 7.072 -2.978 10.365
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H36A 10.082 -0.657 10.637
H36B 9.106 0.799 10.931
H36C 9.104 0.041 9.329
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Cl2 1.839 2.502 9.841
O1 7.066 -0.122 10.512
N1 2.938 2.630 6.053
N2 4.697 3.397 7.135
C1 4.708 0.963 9.523
C2 3.712 2.455 7.167
C3 3.556 3.551 5.092
C4 4.518 4.321 5.989
C5 1.939 1.671 5.557
C6 0.783 1.426 6.507
C7 0.386 0.120 6.826
C8 -0.747 -0.101 7.615
C9 -1.491 0.977 8.091
C10 -1.093 2.281 7.784
C11 0.039 2.501 7.006
C12 5.898 3.539 7.925
C13 7.085 2.941 7.426
C14 8.280 3.182 8.115
C15 8.310 3.984 9.250
C16 7.136 4.556 9.726
C17 5.906 4.359 9.082
C18 4.649 5.037 9.630
C19 4.429 6.453 9.018
C20 5.507 7.504 9.309
C21 4.600 5.117 11.177
C22 4.703 3.777 11.912

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 C26 8.179 2.443 5.159
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 C30 3.485 -1.201 12.364
 C31 4.683 -1.761 12.806
 C32 5.895 -1.425 12.205
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 C35 8.523 -2.058 10.231
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 H4A 5.477 4.539 5.518
 H4B 4.077 5.261 6.337
 H5A 2.426 0.724 5.305
 H5B 1.552 2.109 4.630
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 H21B 5.371 5.801 11.553
 H22A 5.666 3.287 11.736
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 H24B 6.657 0.314 7.470
 H25A 7.306 -1.510 5.989
 H25B 7.954 -0.406 4.773
 H25C 6.209 -0.450 5.115
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 H27C 8.017 4.616 5.360
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 H32 6.806 -1.882 12.571
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 H35B 7.738 -2.756 10.535
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 H36B 9.225 1.293 10.899
 H36C 9.362 0.449 9.347
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 N2 0.207 2.751 4.548
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 C2 -0.510 2.801 5.699
 C3 -0.395 0.537 5.058
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 H3B 0.403 -0.011 5.579
 C4 0.145 1.403 3.918
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 H4B -0.536 1.431 3.063
 C5 -1.645 1.139 7.180
 H5A -2.006 2.039 7.689
 H5B -0.919 0.671 7.857
 C6 -2.815 0.207 6.928
 C7 -3.881 0.615 6.113
 H7 -3.858 1.606 5.665
 C8 -4.961 -0.237 5.894
 H8 -5.785 0.089 5.263
 C9 -4.992 -1.503 6.485
 H9 -5.836 -2.165 6.311
 C10 -3.937 -1.913 7.299
 H10 -3.954 -2.896 7.762
 C11 -2.853 -1.060 7.517
 H11 -2.029 -1.383 8.150
 C12 0.971 3.790 3.916
 C13 2.329 3.951 4.284
 C14 3.095 4.898 3.600
 H14 4.133 5.039 3.888
 C15 2.561 5.679 2.571
 C16 1.210 5.524 2.254
 H16 0.771 6.156 1.488
 C17 0.395 4.588 2.903
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 C19 -1.331 3.351 1.475
 C20 -2.596 2.742 1.433
 H20 -3.352 3.044 2.153
 C21 -2.890 1.765 0.484
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 H22 -2.151 0.613 -1.186
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C47 0.490 9.297 7.285
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C52 -2.881 4.485 9.952
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H52C -1.932 4.015 10.219
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N2 0.258 2.674 4.544
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H3B 0.201 -0.132 5.464
C4 0.075 1.364 3.862
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H4B -0.596 1.482 3.008
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H5B -1.071 0.525 7.755
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C7 -4.037 0.930 6.060
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C8 -5.199 0.216 5.774
H8 -5.994 0.688 5.203
C9 -5.349 -1.099 6.226
H9 -6.257 -1.653 6.003
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H11 -2.369 -1.447 7.830
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C23 -0.455 2.166 -0.639
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 H53C -0.050 5.153 11.044
 H1 0.820 5.554 5.485
109
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 N2 0.333 2.683 4.607
 C1 0.076 5.578 6.486
 C2 -0.406 2.698 5.745
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 H3B 0.461 -0.116 5.538
 C4 0.252 1.363 3.924
 H4A 1.239 1.050 3.582
 H4B -0.419 1.439 3.064
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 H53C 4.013 7.029 8.752
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109
Ru10 - act2
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 Cl2 -3.041 5.115 6.164
 O1 0.977 8.144 5.000
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H3B -1.089 -0.083 5.061
C4 0.201 1.456 4.174
H4A 1.048 0.883 4.561
H4B 0.240 1.467 3.085
C5 -2.596 1.733 6.623
H5A -2.930 0.702 6.457
H5B -3.358 2.402 6.213
C6 -2.449 1.966 8.114
C7 -1.518 1.226 8.856
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H11 -4.014 3.444 8.217
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C13 2.495 3.872 4.421
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C22 -2.112 1.216 -0.044
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C28 -2.498 8.184 1.045
H28 -2.925 9.110 0.669
C29 -1.872 7.292 0.172
H29 -1.811 7.519 -0.889
C30 -1.342 6.093 0.652
H30 -0.897 5.390 -0.046
C31 3.028 3.179 5.683
H31 2.222 3.217 6.422
C32 3.365 1.702 5.487
C33 3.864 1.185 4.285
H33 3.977 1.839 3.424
C34 4.212 -0.165 4.179
H34 4.598 -0.549 3.238
C35 4.064 -1.017 5.273
H35 4.334 -2.067 5.189
C36 3.565 -0.512 6.475
H36 3.444 -1.167 7.334
C37 3.220 0.835 6.580
H37 2.833 1.228 7.517
C38 4.204 3.937 6.314
C39 5.540 3.602 6.063
H39 5.773 2.756 5.423
C40 6.581 4.331 6.641
H40 7.611 4.053 6.436
C41 6.301 5.404 7.487
H41 7.111 5.968 7.942
C42 4.972 5.739 7.753
H42 4.740 6.563 8.423
C43 3.933 5.012 7.173
H43 2.903 5.261 7.406
C44 3.853 6.068 1.590
H44A 3.435 7.030 1.278
H44B 4.075 5.503 0.675
H44C 4.803 6.258 2.097
C45 0.346 7.068 7.013
C46 0.144 7.147 8.413
H46 -0.166 6.253 8.945
C47 0.389 8.309 9.128
H47 0.233 8.335 10.201
C48 0.864 9.435 8.452
H48 1.075 10.351 8.998
C49 1.088 9.403 7.077
H49 1.466 10.291 6.587
C50 0.825 8.239 6.343
C51 1.560 9.231 4.242
H51 1.143 10.177 4.609
C52 1.111 9.028 2.802
H52A 1.469 8.066 2.424
H52B 1.515 9.826 2.170
H52C 0.022 9.036 2.724
C53 3.081 9.220 4.399
H53A 3.385 9.338 5.442
H53B 3.528 10.034 3.818
H53C 3.485 8.270 4.034
H1 0.426 5.833 5.253

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