Supporting Information for:

Exploiting Phosphonate Chemistry in Metal-Mediated Dearomatization: Stereoselective Construction of Functionalized Spirolactams from Arene Ruthenium Complexes

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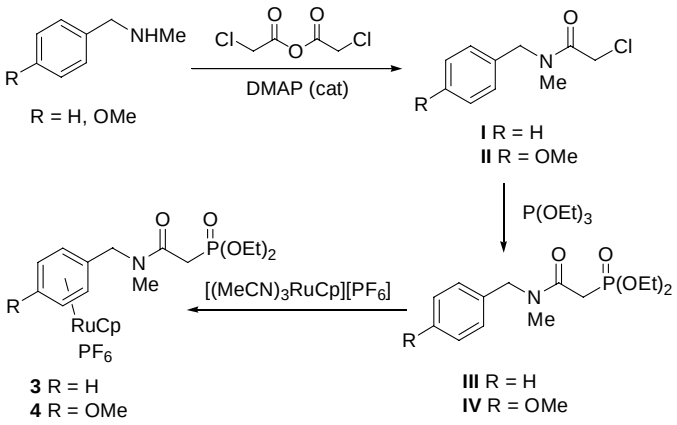
General Experimental. All commercially available reagents and solvents were used as received unless otherwise noted. Tetrahydrofuran was either distilled from Na-benzophenone or passed through an activated alumina column, DMF was distilled from CaH_2 or passed through a column of activated molecular sieves. All reactions were performed in oven-dried glassware under a blanket of dry argon unless otherwise noted. Thin-layer chromatography was performed on silica gel 60 glass-backed TLC plates (250 μm). All reactions were monitored by TLC for consumption of starting substrate. Radial chromatography was performed using 2 mm plates coated with TLC grade silica. ^{1}H- and ^{13}C-NMR spectra were obtained at 300 or 500 MHz as indicated. Chemical shifts (δ) are reported relative to residual solvent peaks or TMS. IR spectra were recorded on an FT-IR spectrophotometer equipped with an ATR attachment. Melting points were determined using a capillary melting point apparatus and are uncorrected. High resolution mass spectra were obtained using electron impact ionization (EI), fast atom bombardment (FAB), or electrospray ionization (ESI).

Stereochemical Assignments. Olefin stereochemistry (*Z*) of spirocyclic compounds was determined experimentally for cyclohexadienyl complexes **5** and **9** *via* 2D NOESY NMR spectroscopy. Olefin geometry for the remaining compounds was assigned by analogy. The NOESY spectrum was also obtained for dienol **(-)-22** in order to determine the regio- and stereochemistry of hydroxyl addition. The structural assignment of this latter compound along with dienol **19** were confirmed by single crystal X-ray diffractometry.[1] Stereochemical assignments for **16** and **18** were made by analogy.

Preparation of η^6-arene ruthenium complexes:



N-Benzyl-N-methyl chloroacetamide (I) and N-4-methoxybenzyl-N-methyl chloroacetamide (II). To a mixture of chloroacetic anhydride (2.79 g, 15.8 mmol) and DMAP (catalytic amount) in ~10 mL THF was added dropwise a solution of N-methylbenzylamine (1.32 g, 10.6 mmol) in 5 mL THF. Once the addition was complete the reaction was maintained at rt for ~10 min. The solvent was removed *in vacuo* and the resulting yellow oil was partitioned between CH_2Cl_2 and saturated aqueous $NaHCO_3$. The organic phase was separated and dried over anhyd. $MgSO_4$. Filtration and removal of the solvent gave a dark yellow oil that was further purified by flash column chromatography (1:1 EtOAc:Hexanes) to afford **I** as a light yellow oil (2.09 g, 100%). ^{1}H-NMR (300 MHz, $CDCl_3$, mixture of rotamers) δ 2.96 (s, 1.2H), 2.99 (s, 1.8H), 4.11 (s, 0.8H), 4.14 (s, 1.2H), 4.59 (s, 2H), 7.20-7.35 (m, 5H). ^{13}C-NMR (75 MHz, $CDCl_3$, mixture of rotamers) δ 34.6, 35.2, 41.1, 41.3, 51.5, 53.9, 126.6, 127.8, 128.1, 128.9, 129.2, 135.7, 136.3, 167.3, 167.5, 169.3. The methoxybenzyl derivative **II** was prepared similarly in 90% yield from 2.37 g of 4-methoxy-N-methylbenzylamine. ^{1}H-NMR (300 MHz, $CDCl_3$, mixture of rotamers) δ 2.94 (s, 1H), 2.97 (s, 2H), 3.80 (s, 2H), 3.81 (s, 1H), 4.12 (s, 2H), 4.53 (s, 2H), 6.84-6.91 (m, 2H), 7.10-7.20 (m, 2H). ^{13}C-

NMR (75 MHz, $CDCl_3$, mixture of rotamers) δ 34.3, 35.0, 41.3, 41.6, 50.9, 53.3, 55.48, 55.5, 114.3, 114.6, 127.8, 128.0, 128.7, 129.7, 159.3, 166.7. IR (neat) ν (cm^{-1}) 1657.

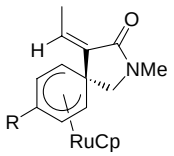
β-Amidophosphonates III and IV. Arbuzov reaction of **I** and **II** afforded phosphonates **III** and **IV**, respectively. The preparation of **III** is representative. Chloroacetamide **I** (5.54 g, 23.8 mmol) was mixed with $P(OEt)_3$ (6.5 mL) and heated to 100 ºC for 12 h. After cooling to rt, excess $P(OEt)_3$ was removed *in vacuo* and the remaining residue was purified by flash column chromatography (EtOAc) to afford **III** as colorless oil (5.34 g, 75%). ^{1}H-NMR (300 MHz, $CDCl_3$, mixture of rotamers) δ 1.34 (t, J = 7.1 Hz, 6H), 2.98 (s, 1.1H), 3.07 (d, J_{PH} = 22.1 Hz, 0.8H), 3.05 (s, 1.9H), 3.13 (d, J_{PH} = 22.1 Hz, 1.2H), 4.13-4.24 (m, 4H), 4.62 (s, 1.2H), 4.70 (s, 0.8H), 7.17-7.39 (m, 5H). ^{13}C-NMR (125 MHz, $CDCl_3$, mixture of rotamers) δ 16.3, 16.4, 33.0, 33.1, 34.1, 34.1, 34.6, 36.1, 51.1, 54.3, 62.6, 62.6, 62.7, 126.3, 127.4, 127.9, 128.6, 129.0, 136.3, 136.9, 165.1, 165.2, 165.3, 165.4. IR (neat) ν (cm^{-1}) 1642, 1021. HRMS (EI) calcd for $C_{14}H_{22}NO_4P$ 299.1286 $[M]^+$, found 299.1287.

Phosphonate **IV** was prepared in 93% yield from 1.0 g of **II** using an identical procedure. ^{1}H-NMR (300 MHz, $CDCl_3$, mixture of rotamers) δ 1.33 (t, J = 7.5 Hz, 6H), 2.95 (d, J = 1.2 Hz, 1H), 3.02 (s, 2H), 3.08 (d J_{PH} = 21.0 Hz, 1.2H), 3.11 (d, J_{PH} = 21.0 Hz, 0.8H), 3.80 (d, J = 3.0 Hz, 3H), 4.12- 4.23 (m, 4H), 4.5 (s, 1.2H), 4.6 (s, 0.8 H), 6.83-6.90 (m, 2H), 7.18-7.21 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$, mixture of rotamers) δ 16.4, 16.5, 32.7, 32.8, 34.2, 34.5, 34.6, 36.0, 50.6, 53.9, 55.4, 62.7, 62.8, 62.8, 114.1, 114.5, 127.8, 128.2, 129.1, 129.4, 159.1, 159.3, 165.0, 165.3, 165.4. IR (neat) ν (cm^{-1}) 1649, 1027. HRMS (EI) calcd for $C_{15}H_{24}NO_5P$ 329.1391 $[M]^+$, found 329.1395.

General procedure of the preparation of η^6-Arene ruthenium complexes Arene complexes were prepared by treatment of arene ligands with equimolar amounts of $[(MeCN)_3RuCp][PF_6]$ in 1,2-dichloroethane according to previously reported procedures.[2] Complex **3** (5.29 g, 82%) was obtained as a brown viscous semi-solid from 3.16 g (10.6 mmol) of **III** after filtration of the crude

product through a short plug of neutral alumina (acetone). ^{1}H-NMR (500 MHz, acetone-d_6) δ 1.31 (t, J = 7.0 Hz, 6H), 3.22 (d, J_{PH} = 21.7 Hz, 2H), 3.35 (s, 3H), 4.09-4.18 (m, 4H), 4.63 (s, 2H), 5.53 (s, 5H), 6.25-6.33 (m, 3H), 6.44 (d, J = 6.0 Hz, 2H). ^{13}C-NMR (125 MHz, acetone-d_6) δ 16.7, 33.1, 34.1, 38.1, 50.3, 63.0, 82.1, 85.8, 86.2, 87.1, 103.3, 166.9. HRMS (FAB, NBA) calcd for $C_{19}H_{27}NO_4PRu$ 466.0721 $[M]^+$, found 466.0718. Complex **4** (1.60 g, 92%) was obtained as pale brown solid from 0.90 g (2.72 mmol) of **IV**. Mp = 82-84 ^{o}C. ^{1}H-NMR (300 MHz, acetone-d_6) δ 1.31 (t, J = 7.5 Hz, 6H), 3.21 (d, J_{PH} = 21.0 Hz, 2H), 3.32 (s, 3H), 3.86 (s, 3H), 4.10-4.20 (m, 4H), 4.55 (s, 2H), 5.53 (s, 5H), 6.38-6.41 (m, 4H). ^{13}C-NMR (75 MHz, acetone-d_6) δ 17.1, 33.1, 34.9, 38.3, 50.2, 58.2, 63.4, 75.2, 82.1, 84.7, 86.2, 100.5, 135.6, 167.2. HRMS (FAB, NBA) calcd for $C_{20}H_{29}NO_5PRu$ 496.0826 $[M]^+$, found 496.0832. Anal. Calcd for $C_{20}H_{29}NO_3Ru{\cdot}PF_6$: C 37.44, H 4.55, N 2.18. Found: C 37.68, H 4.49, N 2.30.

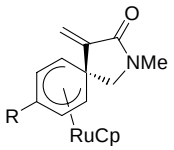
General procedure for the preparation of spirolactam complexes 5-14. The preparation of **5** is representative. A solution of **3** (341 mg, 0.56 mmol) in ~4 mL THF was added to NaH (60%, 78.2 mg, 1.2 mmol) at rt. The resulting mixture was maintained for 30 min, during which time the reaction turned golden yellow. Acetaldehyde (123 mg, 2.8 mmol) was added *via* syringe and the reaction was stirred at rt for another 30 min. The reaction was quenched with a few drops of H_2O and the solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2, washed with brine, dried over anhyd. $MgSO_4$, filtered, and concentrated to afford a yellow solid. Purification by flash column chromatography gave **5** (138 mg, 70%). Spirocyclizations involving complex **4** were performed in a similar fashion except that DMF was used as the solvent.



5 (R = H)
6 (R = OMe)

Complex 5. 70%. Mp 189-190 ºC. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.99 (d, *J* = 7.3 Hz, 3H), 2.63 (d, *J* = 5.3 Hz, 2H), 2.86 (s, 3H), 3.25 (s, 2H), 4.46 (t, *J* = 5.3 Hz, 2H), 4.80 (s, 5H), 5.55 (q, *J* = 7.3 Hz, 1H), 5.76 (t, *J* = 5.3 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 13.2, 29.7, 38.1, 45.9, 64.9, 75.5, 76.2, 79.6, 132.5, 142.4, 168.1. IR (neat) ν (cm^{-1}) 1672. HRMS (EI) calcd for $C_{17}H_{19}NORu$ 355.0510 $[M]^+$, found 355.0513. Anal. Calcd for $C_{17}H_{19}NORu$: C 57.61, H 5.40, N 3.95. Found: C 57.55, H 5.44, N 3.98.

Complex 6. 71%. Mp 148-149 ºC. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.91 (d, *J* = 7.3 Hz, 3H), 2.39 (dd, *J* = 5.1, 1.3 Hz, 2H), 2.78 (s, 3H), 3.29 (s, 2H), 3.63 (s, 3H), 4.66 (dd, *J* = 5.1, 1.3 Hz, 2H), 4.89 (s, 5H), 5.54 (q *J* = 7.26, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 13.1, 29.6, 32.2, 47.4, 57.6, 63.9, 65.6, 76.1, 132.2, 132.7, 141.6, 168.0. IR (neat) ν (cm^{-1}) 1678. HRMS (FAB, NBA) calcd for $C_{18}H_{21}NO_2Ru$·Na 408.0513 $[M+Na]^+$, found 408.0519. Anal. Calcd for $C_{18}H_{21}NO_2Ru$: C 56.24, H 5.51, N 3.64. Found: C 56.46, H 5.56, N 3.58.

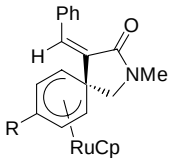


7 (R = H)
8 (R = OMe)

Complex 7. From **3** and paraformaldehyde, 74%. Mp 157-158 ºC. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.61 (d, *J* = 6.1 Hz, 2H), 2.91 (s, 3H), 3.30 (s, 2H), 4.48 (dd, *J* = 6.1, 4.8 Hz, 2H), 4.82 (s, 5H), 4.98 (d, *J* = 1.0 Hz, 1H), 5.65 (d, *J* = 1.0 Hz, 1H), 5.83 (t, *J* = 4.8 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$)

δ 30.0, 36.4, 45.4, 64.6, 75.7, 76.1, 80.1, 115.6, 150.9, 167.3. IR (neat) ν (cm^{-1}) 1678. HRMS (EI) calcd for $C_{16}H_{17}NORu$ 341.0353 $[M]^+$, found 341.0352. Anal. Calcd for $C_{16}H_{17}NORu$: C 56.46, H 5.03, N 4.11. Found: C 56.73, H 4.98, N 4.13.

Complex 8. From **4** and paraformaldehyde, 70%. Mp 135-136 ºC. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.38 (d, *J* = 6.0 Hz, 2H), 2.95 (s, 3H), 3.28 (s, 2H), 3.74 (s, 3H), 4.65 (d, *J* = 6.0 Hz, 2H), 4.87 (s, 5H), 5.05 (s, 1H), 5.66 (s, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 30.1, 30.7, 46.9, 57.7, 63.7, 65.5, 76.3, 115.6, 133.3, 150.0, 167.3. IR (neat) ν (cm^{-1}) 1687. HRMS (FAB, NBA) calcd for $C_{17}H_{19}NO_2Ru{\cdot}Na$ 394.0357 $[M+Na]^+$, found 394.0356. Anal. Calcd for $C_{17}H_{19}NO_2Ru$: C 55.12, H 5.17, N 3.78. Found: C 55.14, H 5.40, N 3.64.

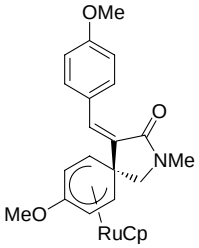


9 (R = H)
10 (R = OMe)

Complex 9. From **3** and benzaldehyde, 59%. Mp 196-198 ºC. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.73 (d, *J* = 6.1 Hz, 2H), 2.91 (s, 3H), 3.37 (s, 2H), 4.55 (t, *J* = 5.5 Hz, 2H), 4.83 (s, 5H), 5.82 (t, *J* = 4.5 Hz, 1H), 6.24 (s, 1H), 7.18-7.28 (m, 3H), 7.80 (d, *J* = 7.6 Hz, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 30.2, 37.9, 47.5, 65.1, 76.0, 76.5, 79.6, 127.8, 128.2, 130.8, 134.5, 135.2, 141.8, 166.4. IR (neat) ν (cm^{-1}) 1669. HRMS (EI) calcd for $C_{22}H_{21}NORu$ 417.0666 $[M]^+$, found 417.0674. Anal. Calcd for $C_{22}H_{21}NORu$: C 63.45, H 5.08, N 3.36. Found: C 63.22, H 5.14, N 3.12.

Complex 10. From **4** and benzaldehyde, 80%. Mp 197-200 ^{0}C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.45 (d, *J* = 6.3 Hz, 2 H), 2.91 (s, 3H), 3.36 (s, 2H), 3.67 (s, 3H), 4.73 (d, *J* = 6.3 Hz, 2H), 4.89 (s,

5H), 6.30 (s, 1H), 7.25 (m, 3H), 7.79 (d, J = 7.0 Hz, 2H).^{13}C-NMR (75 MHz, $CDCl_3$) δ 30.2, 32.1, 49.0, 57.7, 64.2, 66.0, 76.4, 127.2, 130.8, 132.9, 134.3, 135.1, 141.2, 166.4. IR (neat) ν (cm^{-1}) 1677. HRMS (FAB, NBA) calcd for $C_{23}H_{23}NO_2Ru{\cdot}Na$ 470.0670, $[M+Na]^+$, found 470.0676. Anal. Calcd for $C_{23}H_{23}NO_2Ru$: C 61.87, H 5.19, N 3.14. Found: C 62.15, H 5.22, N 3.22



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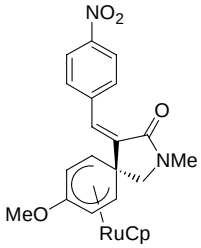
Complex 11. From **4** and *p*-anisaldehyde, 81%. Mp 190-191 ºC. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.49 (d, J = 6.0 Hz, 2H), 2.90 (s, 3H), 3.35 (s, 2H), 3.67 (s, 3H), 3.79 (s, 3H), 4.72 (d, J = 6.0 Hz, 2 H), 4.88 (s, 5H), 6.22 (s, 1H), 6.81 (d, J = 9.0 Hz, 2H), 7.87 (d, J = 9.0 Hz,2H).^{13}C-NMR (75 MHz, $CDCl_3$) δ 30.2, 32.5, 48.9, 55.4, 57.7, 64.3, 66.0, 76.2, 113.2, 127.9, 132.7, 132.8, 134.1, 139.3, 159.7, 166.7. IR (neat) ν (cm^{-1}) 1666. HRMS (FAB, NBA) calcd for $C_{24}H_{25}NO_3Ru{\cdot}Na$ 500.0776 $[M+Na]^+$, found 500.0782. Anal calcd for $C_{24}H_{25}NO_3Ru$: C 60.49, H 5.29, N 2.94. Found: C 60.51, H 5.25, N 2.89.



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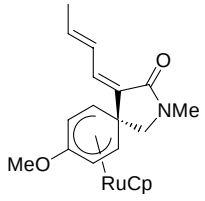
Complex 12. From **4** and *p*-nitrobenzaldehyde, 55%. Mp 189-190 ºC. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.48 (d, J = 9.0Hz, 2H), 2.92 (s, 3H), 3.40 (s, 2H), 3.68 (s, 3H), 4.74 (d, J = 9.0 Hz, 2H),

4.92 (s, 5H), 6.31 (s, 1H), 7.87(d, *J* = 9.0 Hz, 2H), 8.11 (d, *J* = 9.0 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 30.3, 31.1, 49.1, 57.7, 64.0, 65.8, 76.6, 122.9, 131.3, 131.3, 133.05, 141.7, 144.3, 147.0, 165.7. IR (neat) ν (cm^{-1}) 1677. HRMS (FAB, NBA) calcd for $C_{23}H_{22}N_2O_4Ru{\cdot}Na$ 515.0521 $[M+Na]^+$, found 515.0527. Anal. Calcd for $C_{23}H_{22}N_2O_4Ru$: C 56.21, H 4.51, N 5.70. Found: C 56.56, H 4.91, N 5.28.



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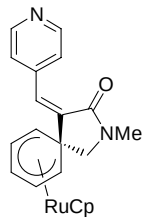
Complex 13. From **4** and crotonaldehyde, 76%. Mp 182-184 ºC. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.77 (d, *J* = 9.0 Hz, 3H), 2.38 (d, *J* = 7.5 Hz, 2H), 2.87 (s, 3H), 3.26 (s, 2H), 3.68 (s, 3H), 4.65 (d, *J* = 7.5 Hz, 2H), 4.88 (s, 5H), 5.92 (m, 1H), 5.95 (d, *J* = 12.0 Hz, 1H), 7.46 (m, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ.14.3, 29.8, 32.1, 47.3, 57.7, 64.1, 65.8, 76.2, 127.6, 132.9, 134.0, 135.5, 137.9, 167.7. IR (neat) ν (cm^{-1}) 1672. HRMS (ESI) calcd for $C_{20}H_{24}NO_2Ru$ 412.0851 $[M+H]^+$, found 412.0856.



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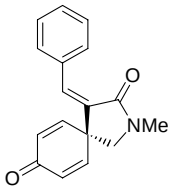
Complex 14. From **3** and 4-pyridylcarboxaldehyde, 74%. Mp 191-192 ºC. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.71 (d, *J* = 6.0 Hz, 2H), 2.92 (s, 3H), 3.40 (s, 2H), 4.56 (dd, *J* = 6.0, 4.8 Hz, 2H), 4.85 (s, 5H), 5.84 (t, *J* = 4.8 Hz, 1H), 6.13 (s, 1H), 7.59 (dd, *J* = 4.6, 1.6 Hz, 2H), 8.49 (dd, *J* = 4.6, 1.6 Hz,

2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 30.2, 36.8, 47.4, 64.7, 75.6, 76.3, 79.8, 124.6, 131.0, 142.5, 145.4, 149.3, 165.6. IR (neat) ν (cm^{-1}) 1668. HRMS (EI) calcd for $C_{21}H_{20}N_2ORu$ 418.0618 $[M]^+$, found 418.0619. Anal. Calcd for $C_{21}H_{20}N_2ORu$: C 60.42, H 4.83, N 6.71. Found: C 60.60, H 4.81, N 6.72.



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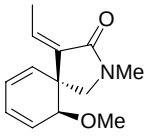
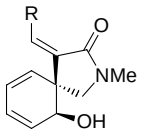
Dienone 15. To a stirred solution of **10** (50 mg, 0.11 mmol) in ~5mL THF, $CuCl_2$ (45 mg, 0.33 mmol) was added at rt. A dark brown solid formed in the reaction. The reaction was stirred for 30 min, after which time TLC indicated complete consumption of starting material. Solids were removed by gravity filtration and the filtrate was partitioned between CH_2Cl_2 and water. The layers were separated and the organic phase was washed with brine, dried over anhyd. $MgSO_4$, and concentrated *in vacuo* to afford yellow oil which was then subjected to flash column chromatography (EtOAc:Hexanes, 1:1) to give **15** (24 mg, 79 %) as a white solid. Mp 155-156 ^oC. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 3.03 (s, 3H), 3.57 (s, 2H), 6.37 (d, J = 10.0 Hz, 2H), 6.46 (s, 1H), 6.94 (d, J = 10.0Hz, 2 H), 7.33 (m, 3H), 7.89 (dd, J = 7.5, 2.1, Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 30.6, 47.0, 54.4, 128.2, 128.7, 129.7, 131.4, 133.5, 138.0, 149.8, 165.6, 185.5. IR (neat) ν (cm^{-1}) 1677, 1666. HRMS (FAB, NBA) calcd for $C_{17}H_{16}NO_2$ 266.1181 $[M+H]^+$, found 266.1181. Anal. Calcd for $C_{17}H_{15}NO_2$: C 76.96, H 5.70, N 5.28. Found: C 76.69, H 5.84, N 5.04.



16

Methoxy diene 16. To a stirred solution of **5** (200 mg, 0.564 mmol) in ~5 mL methanol under 1 atm of CO (balloon), $CuBr_2$ (0.34 g, 1.55 mmol) in 1 mL methanol was added dropwise *via* syringe. The reaction initially turned dark red, then gradually changed to pale yellow over a period of 2 h. The solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2, washed with brine, dried over anhyd. $MgSO_4$, filtered and concentrated to give a yellow oil. Purification by flash column chromatography gave **16** (76 mg, 62%) as a colorless oil along with $RuCp(CO)_2Br$ (**17**, 60%) as yellow needles whose spectral properties matched those previously reported.[3] ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.23 (d, *J* = 9.0 Hz, 3H), 2.88 (s, 3H), 3.17 (d, *J* = 10.5 Hz, 1H), 3.30 (d, *J* = 10.5 Hz, 1H), 3.34 (s, 3H), 3.71 (d, *J* = 6.0 Hz, 1H), 5.63 (m, 1H), 5.90 (m, 1H), 6.01 (m, 2H), 6.11 (q, *J* = 7.0 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 13.6, 29.7, 46.2, 55.7, 58.4, 80.6, 124.2, 124.9, 125.07, 131.1, 134.2, 135.1, 168.6. IR (neat) ν (cm^{-1}) 1665. HRMS (ESI) calcd for $C_{13}H_{18}NO_2$ 220.1338 $[M+H]^+$, found 220.1338.



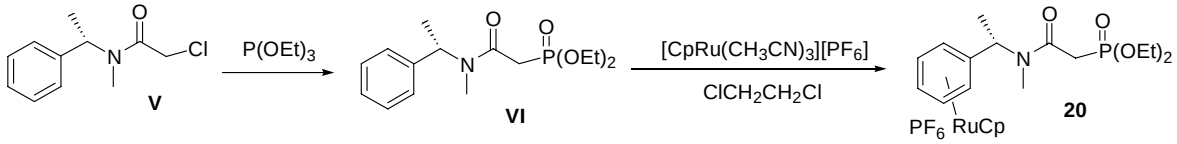
18 R = CH_3
19 R = Ph

Dienol 18. To a stirred solution of **5** (50 mg, 0.14 mmol) in 4 mL THF under 1 atm of CO (balloon), $CuBr_2$ (85 mg, 0.38 mmol) in 1 mL of H_2O was added *via* syringe. The reaction became dark red, then pale yellow over a period of 2 h. Workup of the reaction as described for **16** above and purification by flash column chromatography (1:1 Hexanes:EtOAc) gave **18** (19 mg, 65%) as a white crystalline solid along with $RuCp(CO)_2Br$ (62%) as yellow needles. Mp 105-107 ^{o}C. ^{1}H-NMR

(300 MHz, $CDCl_3$) δ 2.25 (d, *J* = 9.0 Hz, 3H), 2.88 (s, 3H), 3.21 (d, *J* = 10.5 Hz, 1H), 3.36 (d, *J* = 10.5 Hz, 1H), 4.12 (d, *J* = 3.0Hz, 1H), 5.62 (m, 1H), 5.82 (m, 1H), 6.01 (m, 2H), 6.18 (q, *J* = 9.0 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 13.6, 29.8, 47.0, 55.3, 70.9, 124.4, 125.0, 127.3, 131.0, 133.5, 168.2. IR (neat) ν (cm^{-1}) 1677, 3377. Anal. Calcd for $C_{12}H_{15}NO_2$: C 70.22, H 7.37, N 6.82. Found: C 69.70 H 7.21, N 6.68.

Dienol 19. Dienol **19** was prepared from **9** using the procedure described above. 70%. Mp 130–132 °C. ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.87 (s, 3H), 3.28 (d, *J* = 9.0 Hz, 1H), 3.39 (d, *J* = 9.0 Hz, 1H), 4.04 (d, *J* = 6.0 Hz, 1H), 5.74 (d, *J* = 7.5 Hz, 1H), 5.86 (m, 1H), 6.12 (m, 2H), 6.82 (s, 1H), 7.31 (m, 3H), 7.91 (d, *J* = 9.0 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 30.1, 48.1, 54.2, 70.1, 124.8, 126.6, 127.8, 128.7, 131.0, 131.4, 132.8, 134.2, 137.1, 166.4. IR (neat) ν (cm^{-1}) 1665, 3300. Anal. Calcd for $C_{17}H_{17}NO_2$: C 76.38, H 6.41, N 5.24. Found: C 75.66, H 6.64, N 4.98.

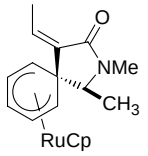
Preparation of η^6-arene ruthenium complex 20:



β-Amidophosphonate VI Arbuzov reaction of **V** [4] afforded phosphonate **VI**. Chloroacetamide **V** (2.51 g, 11.8 mmol) was mixed with $P(OEt)_3$ (3.14 mL, 17.8 mmol) and heated to 100 ºC for 12 h. After cooling to rt, excess $P(OEt)_3$ was removed *in vacuo* and the remaining oily residue was purified by flash column chromatography (EtOAc) to afford **VI** as colorless oil (3.55 g, 96%). $[\alpha]_D$ = – 96.8 (*c* = 0.008, MeOH). ^{1}H-NMR (300 MHz, $CDCl_3$, mixture of rotamers) δ 1.34 (m, 6H), 1.50 (d, *J* = 9.0 Hz, 2H), 1.64 (d, *J* = 6.0 Hz, 1H), 2.70 (s, 1H), 2.77 (s, 2H), 3.53 (m, 2H), 4.19 (m, 4H), 5.32 (q, *J* = 9.0 Hz, 0.3H), 6.05 (q, *J* = 6.0 Hz, 0.7H), 7.30 (m, 5H). ^{13}C-NMR (75 MHz, $CDCl_3$,

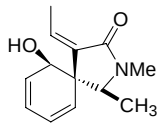
mixture of rotamers) δ 15.5, 16.2, 16.3, 16.3, 17.7, 28.3, 30.6, 32.9, 34.4, 34.7, 50.6, 55.7, 62.5, 126.4, 127.1, 127.2, 127.4, 128.3, 128.6, 139.9, 140.1, 164.9, 164.9. IR (neat) ν (cm^{-1}) 1641. HRMS (FAB, NBA) calcd for $C_{15}H_{25}NOP$ 314.1521 $[M+H]^+$, found 314.1521.

η^6-Arene ruthenium complex 20. The η^6-arene complex was prepared by using the general procedure given previously. Complex **20** (1.54 g. 82%) was obtained as a brown viscous semi-solid from 0.93 g (2.99 mmol) of **VI** after filtration of the crude product through a short plug of neutral alumina (acetone). $[\alpha]_D$ = + 78.4 (*c* = 0.006, MeOH). ^{1}H-NMR (500 MHz, acetone-d_6) δ 1.31 (t, *J* = 7.5 Hz, 6H), 1.58 (d, *J* = 9.0 Hz, 3H), 2.93 (m, 1H), 3.16 (s, 3H), 3.35 (m, 1H), 4.14 (m, 4 H), 5.5 (s, 5H), 5.75 (q, *J* = 9.0 Hz, 1H), 6.33 (m, 4H), 6.53 (d, *J* = 3.0 Hz,1H). ^{13}C-NMR (75 MHz, acetone-d_6) δ 16.7, 32.1, 33.1, 34.8, 51.2, 63.1, 62.9, 82.1, 85.2, 85.6, 86.0, 86.3, 107.5, 166.6. HRMS (FAB, NBA) calcd for $C_{20}H_{29}NO_4PRu$ 480.0878 $[M]^+$, found 480.0883.



21

Complex 21. This complex was prepared using the general spirocyclization procedure. 74%. Mp 202-204 °C. $[\alpha]_D$ = – 77.2 (*c* = 0.002, MeOH). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.08 (d, *J* = 9.0 Hz, 3H), 1.97 (d, *J* = 6. 0 Hz, 3H), 2.46 (d, *J* = 6.0 Hz, 1H), 2.72 (d, *J* = 6.0 Hz, 1H), 2.87 (s, 3H), 3.36 (q, *J* = 6.0 Hz, 1H), 4.24 (t, *J* = 4.5 Hz, 1H), 4.71 (t, *J* = 6.0 Hz, 1H), 4.80 (s, 5H), 5.43 (q, *J* = 6.0 Hz, 1H), 5.72 (t, *J* = 4.5 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 13.2, 14.4, 28.0, 30.1, 41.5, 50.3, 67.7, 75.6, 79.6, 131.8, 140.3, 167.1. IR (neat) ν (cm^{-1}) 1665. Anal. Calcd. for $C_{18}H_{21}NORu$: C 58.68, H 5.74, N 3.80. Found: C 59.01, H 5.90, N 3.70.



(-)-22

Dienol (-)-22. This material was obtained from **21** using the procedures described for the preparation of **18**-**19**. 55%. Mp 155-157 ^{o}C. $[\alpha]_D = -186.1$ ($c = 0.003$, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.04 (d, $J = 9.0$ Hz, 3H), 2.29 (d, $J = 9.0$ Hz, 3H), 2.89 (s, 3H), 3.47 (q, $J = 6.0$ Hz, 1H), 3.80 (d, $J = 3.0$ Hz, 1H), 5.60 (d, 9.0 Hz, 1H), 5.95 (m, 1H), 6.13 (m, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 13.8, 16.7, 28.2, 51.7, 57.2, 68.4, 125.8, 125.9, 126.0, 130.7, 131.9, 135.9, 168.1. IR (neat) ν (cm^{-1}) 1663, 3412. HRMS (ESI) calcd for $C_{13}H_{18}NO_2$ 220.1338 $[M+H]^+$, found 220.1336.

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1. Pigge, F. C.; Coniglio, J. J.; Dalvi, R.; Rath, N. P. unpublished results.
2. Gill, T. P.; Mann, K. R. *Organometallics* **1982**, *1*, 485. Kündig, E. P.; Monnier, F. R. *Adv. Synth. Catal.* **2004**, *346*, 901.
3. Haines, R. J.; du Preez, A. L. *J. Chem. Soc., Dalton Trans.* **1972**, 944.
4. Pallavicini, M.; Valoti, E.; Villa, L.; Resta, I. *Tetrahedron: Asymmetry* **1994**, *5*, 363.


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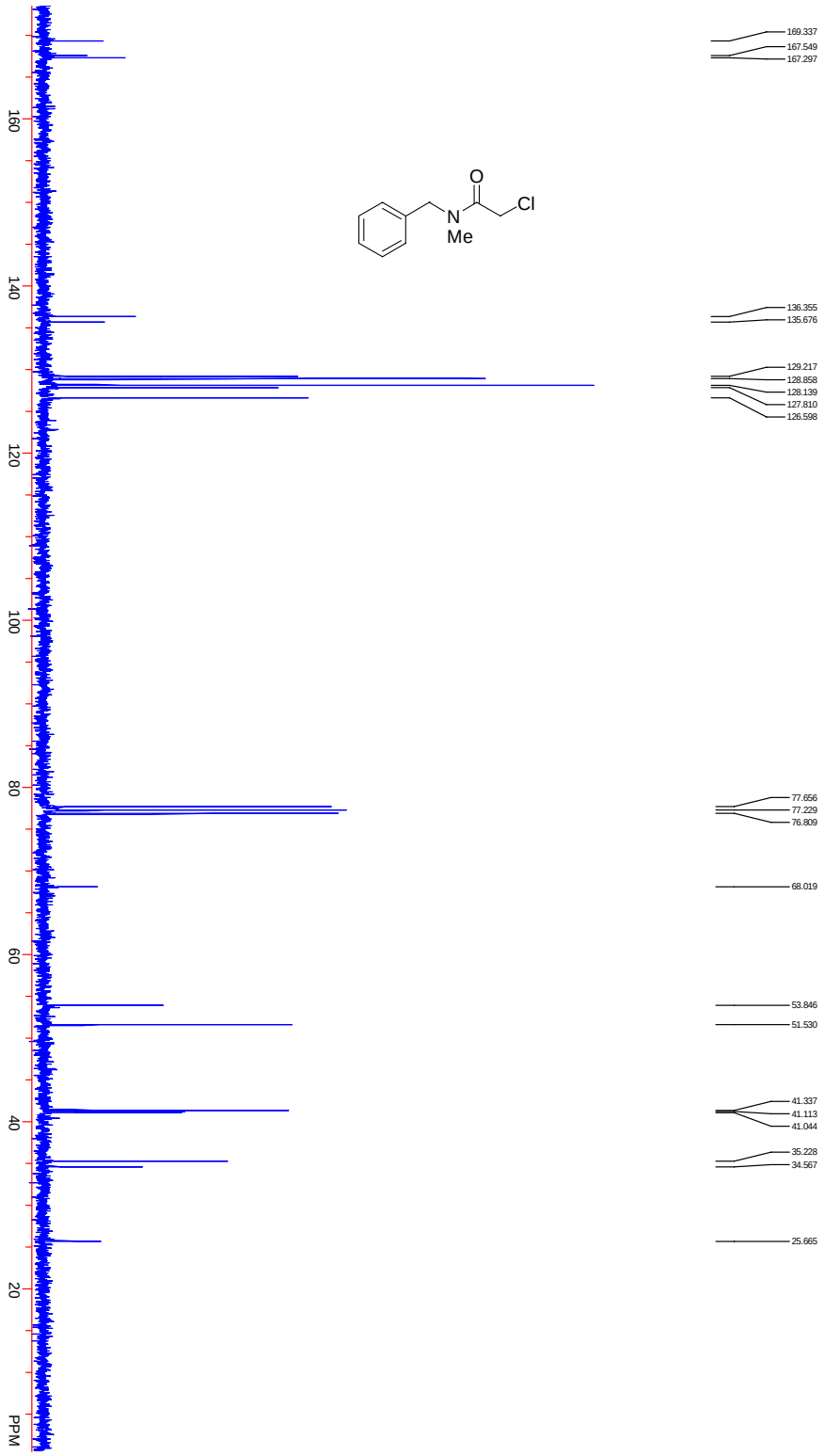
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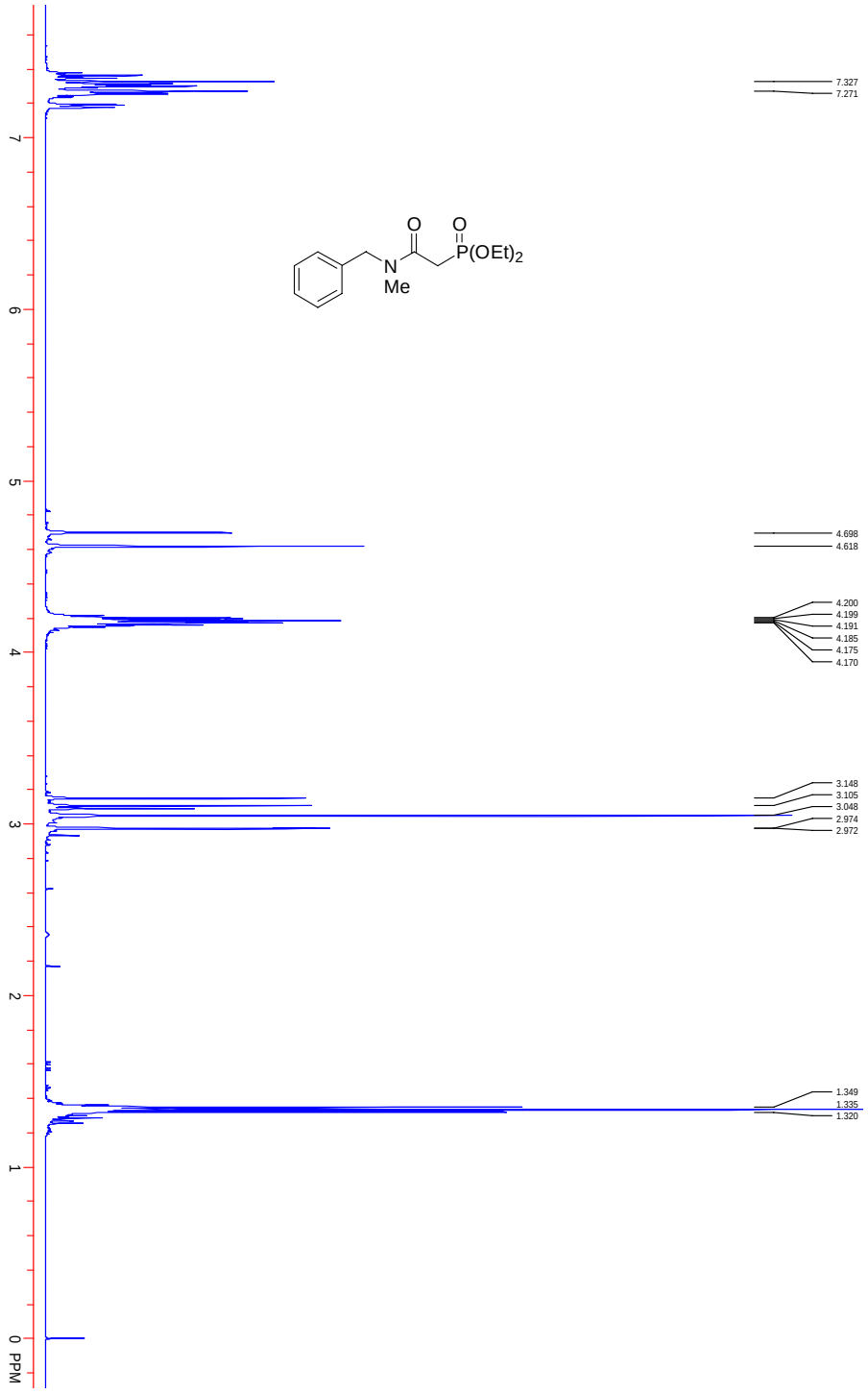
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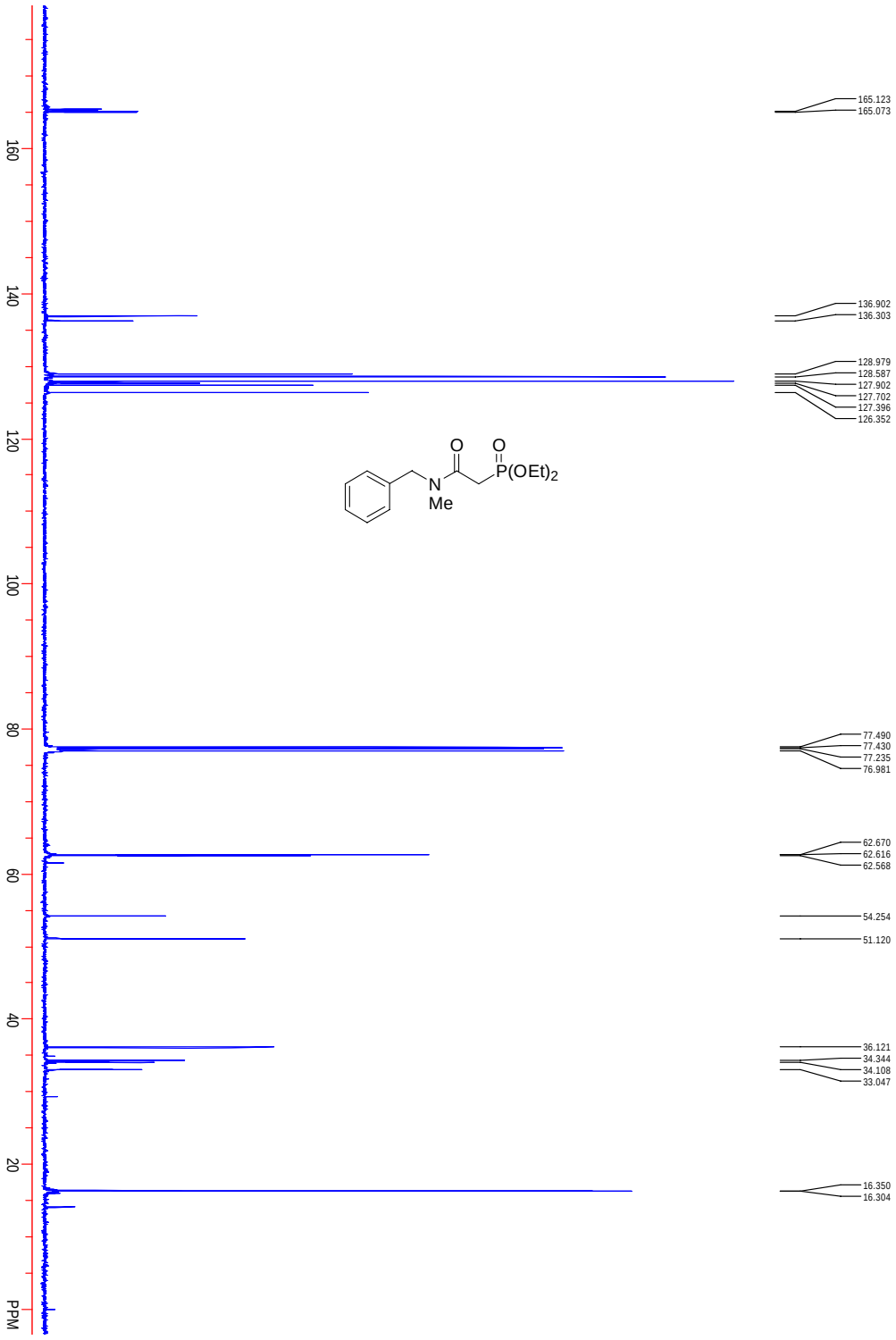
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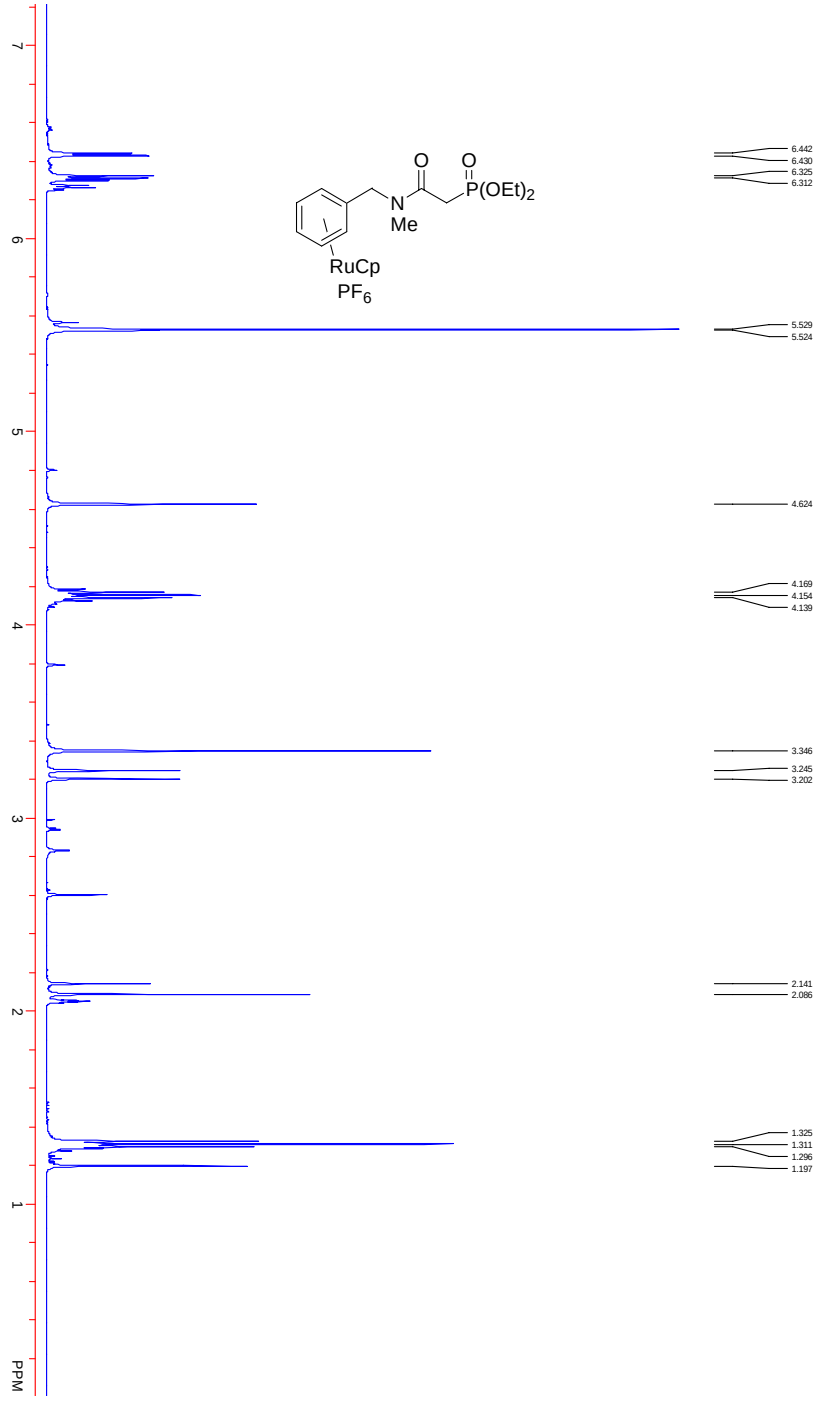
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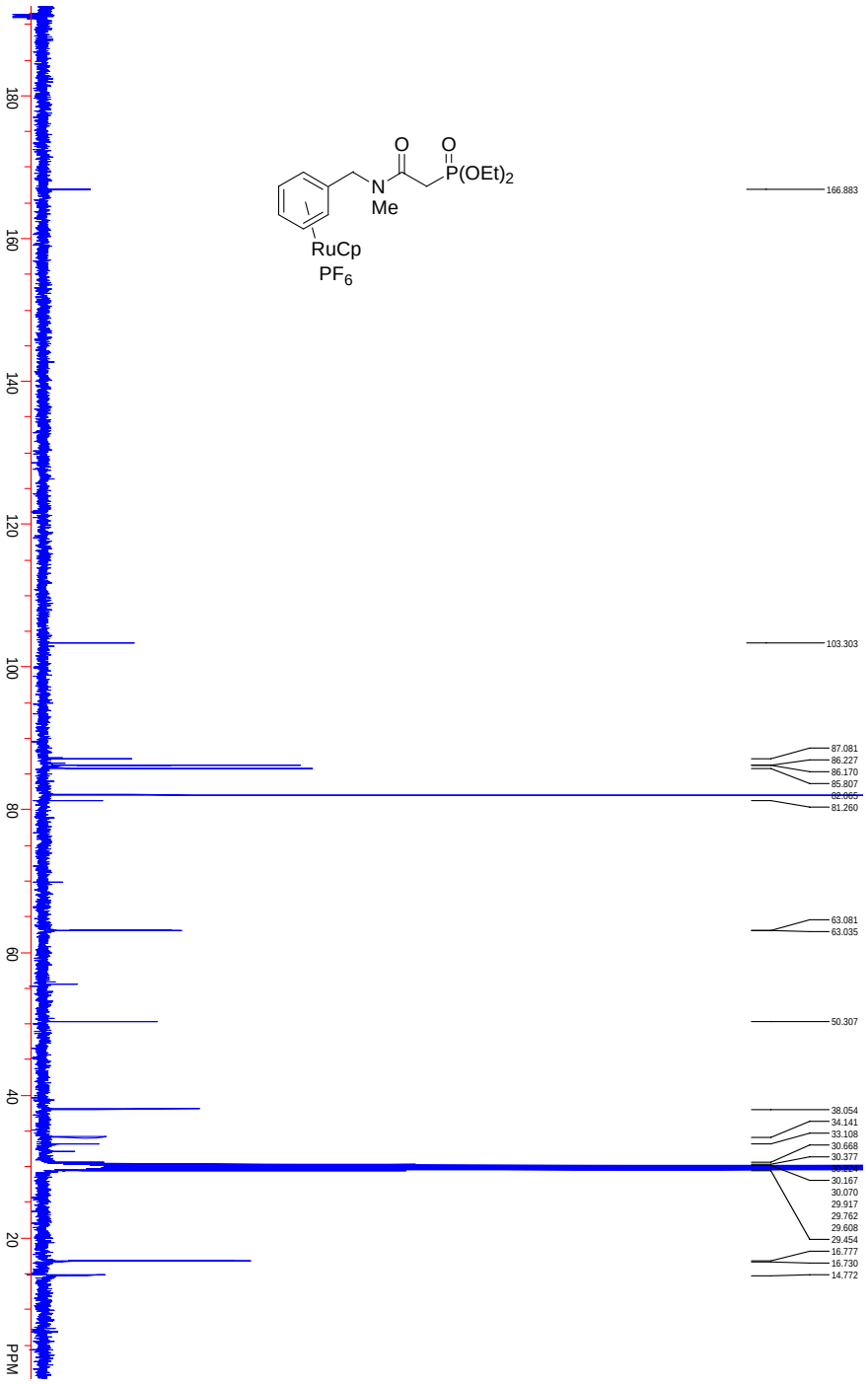
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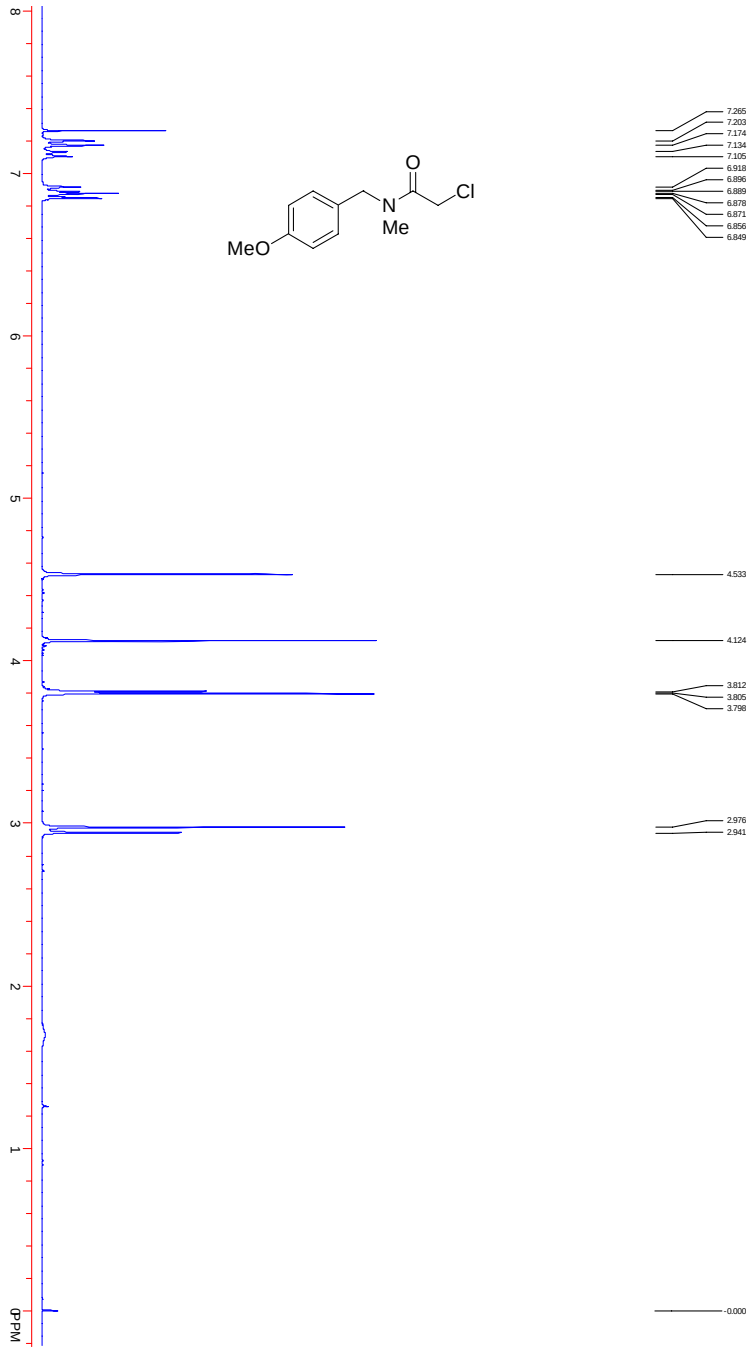
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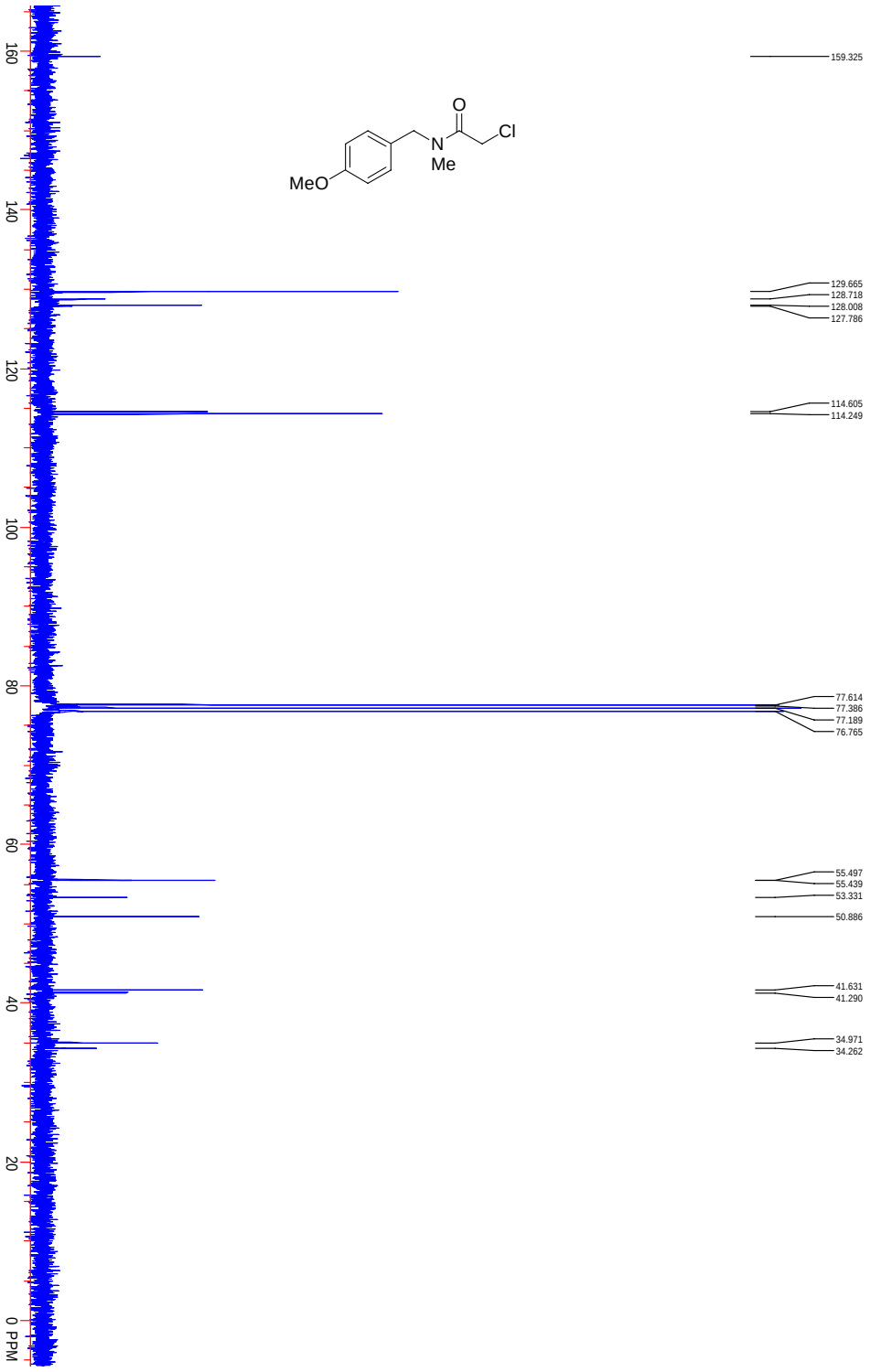
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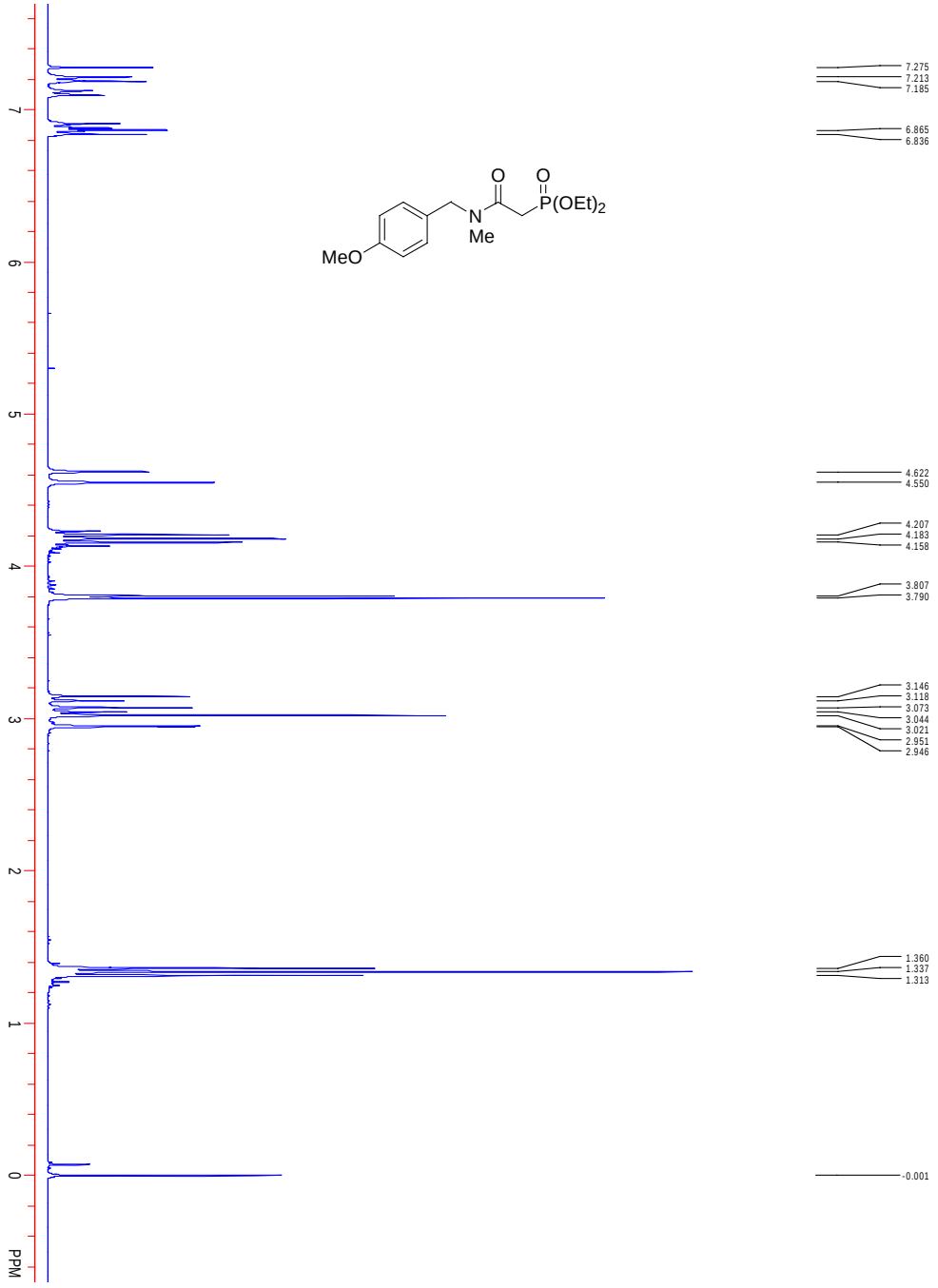
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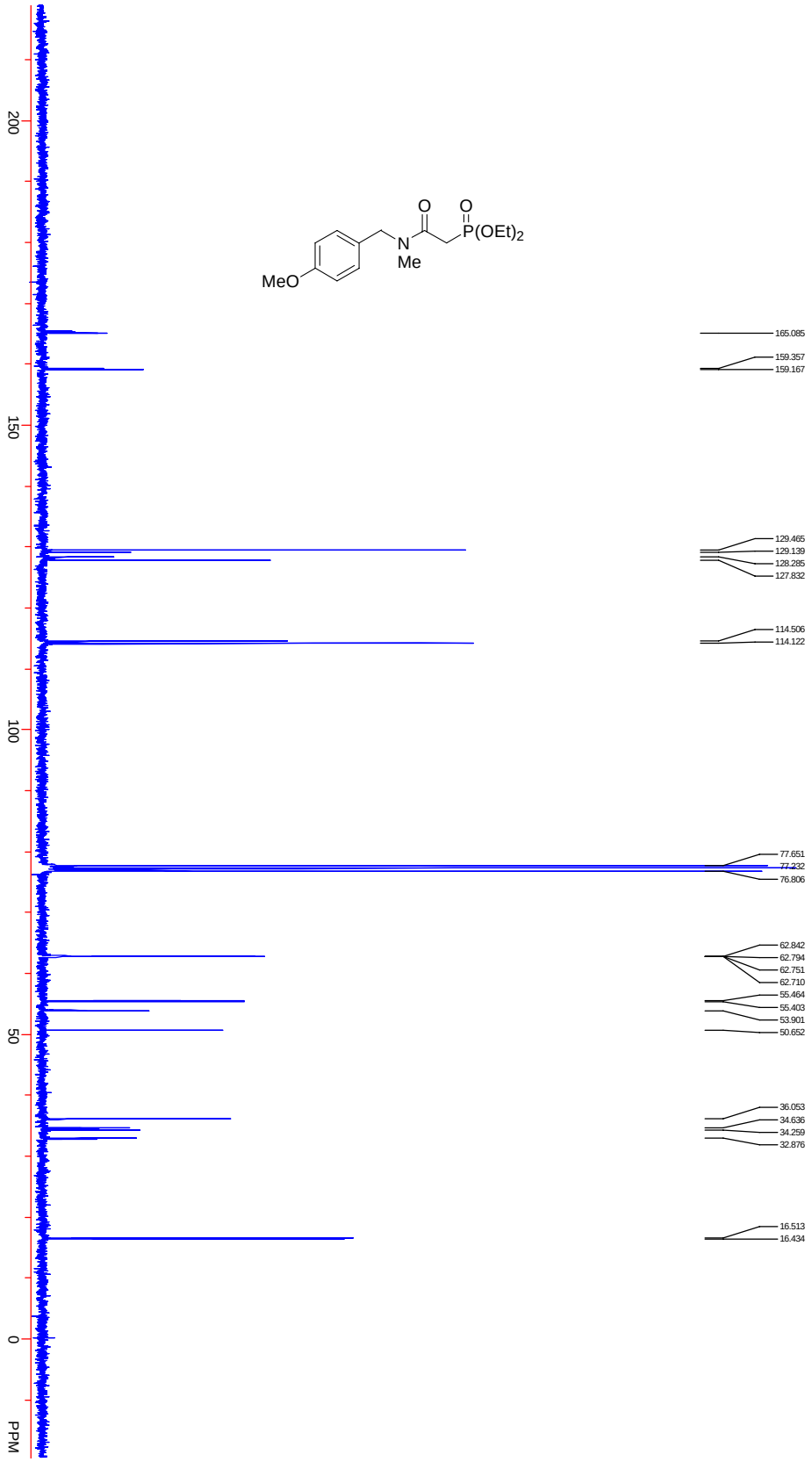
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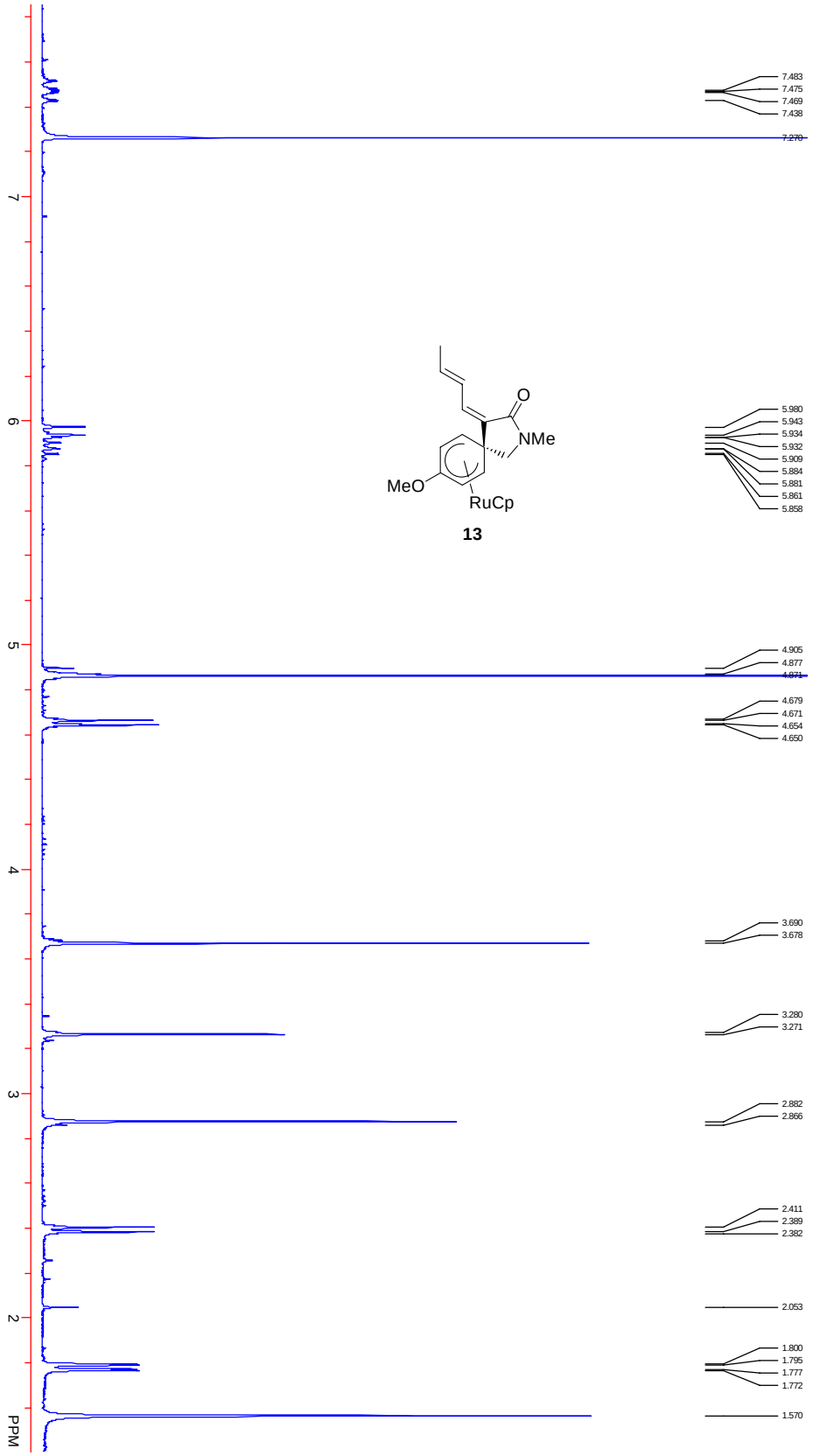
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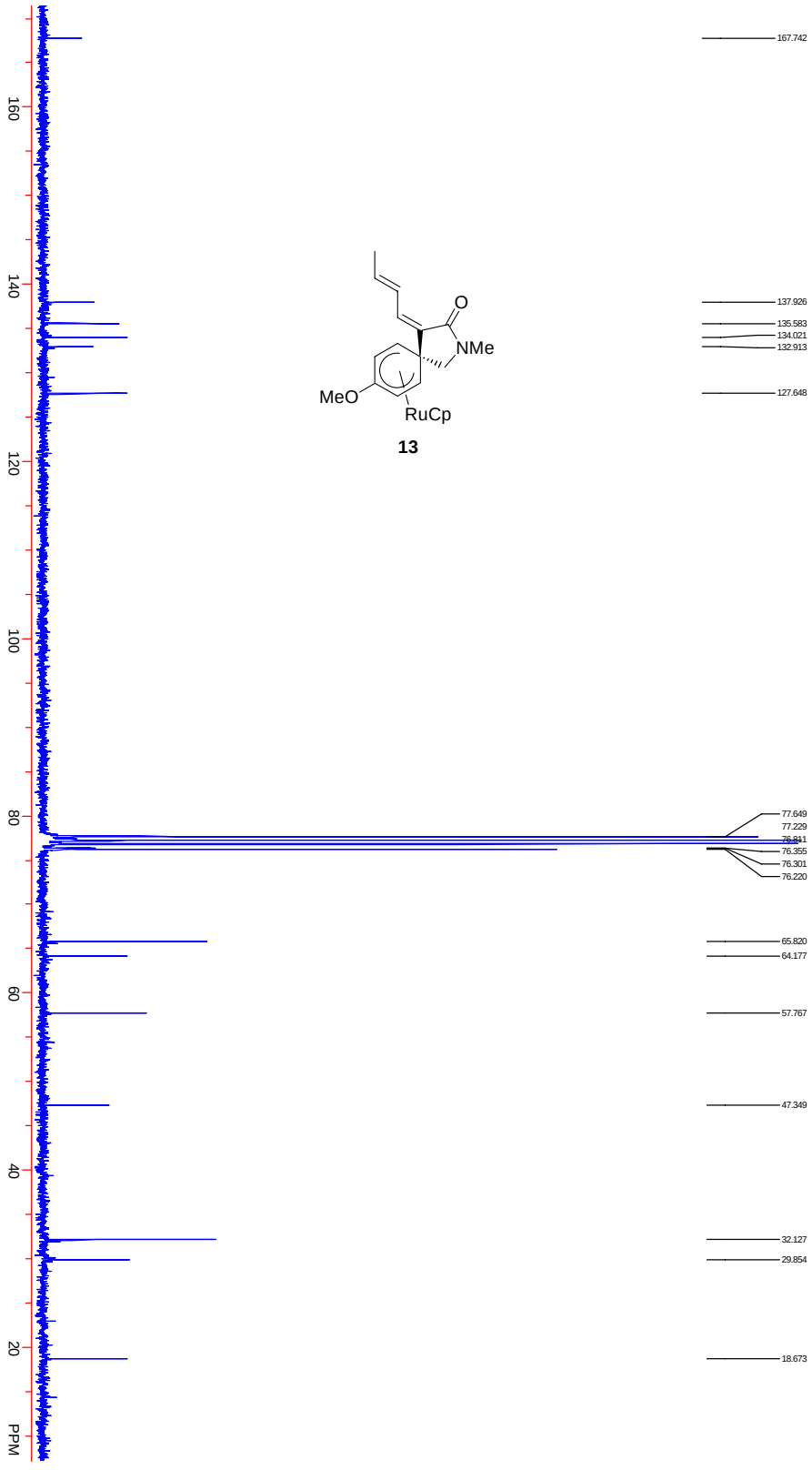
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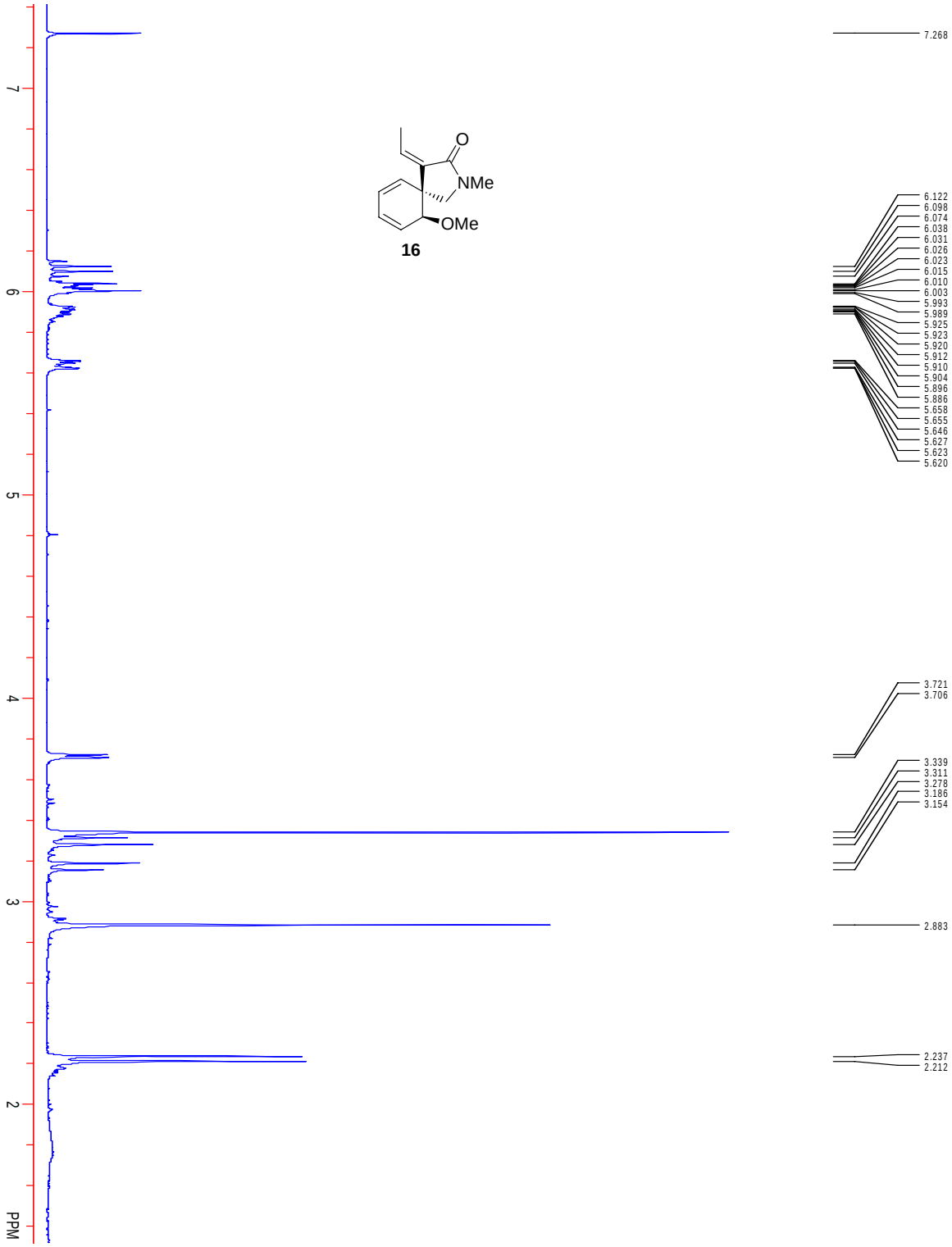
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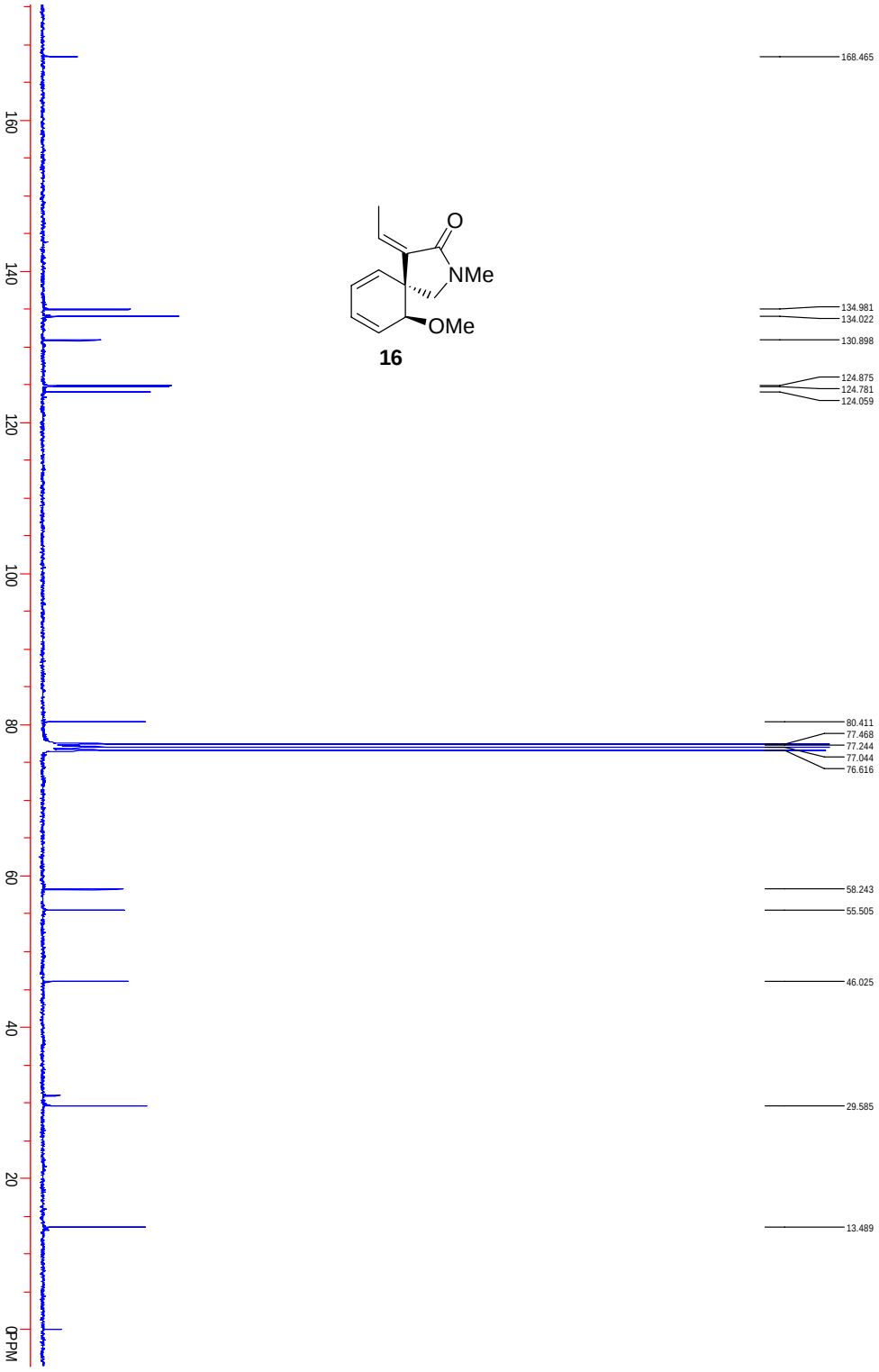
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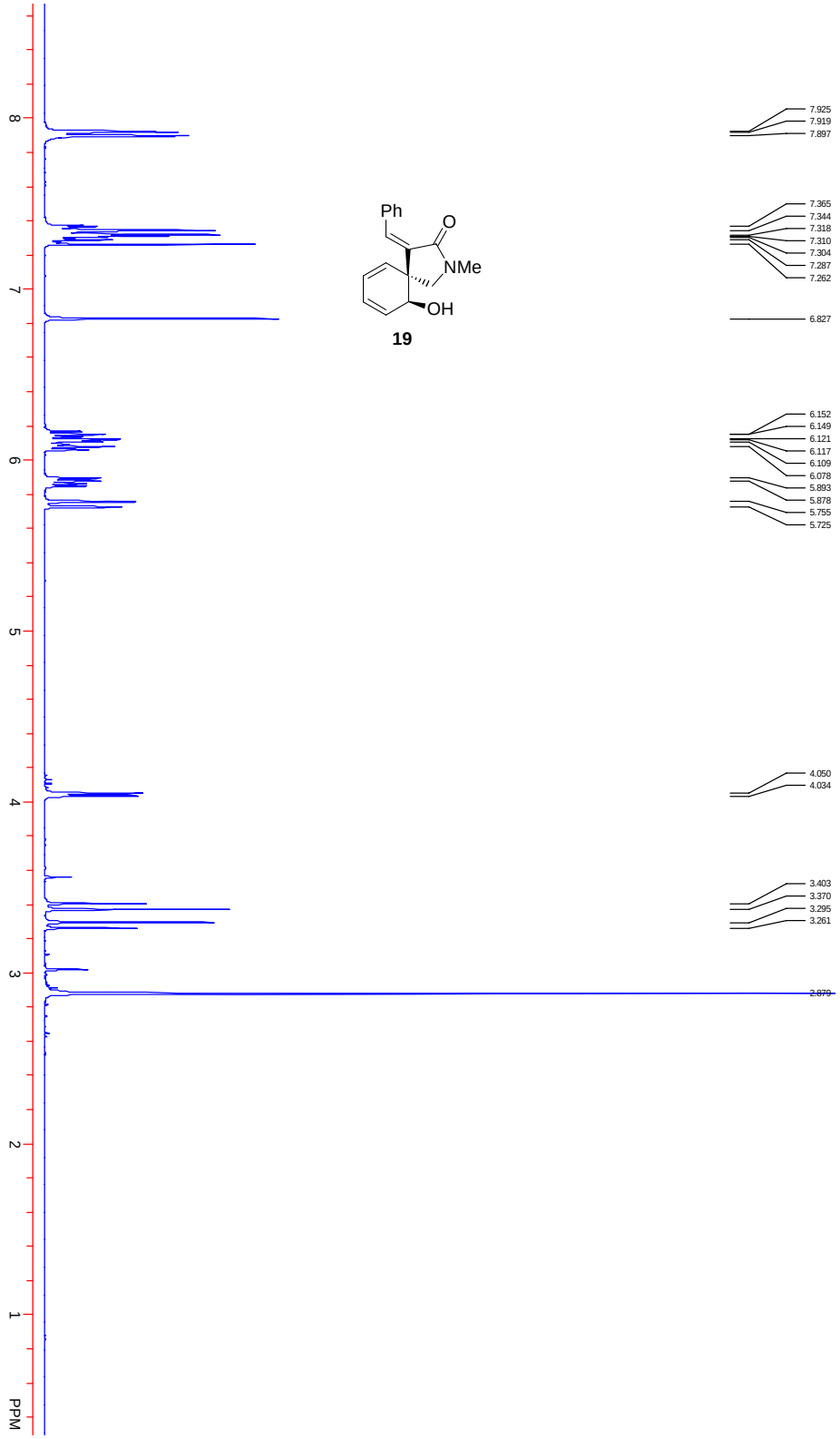
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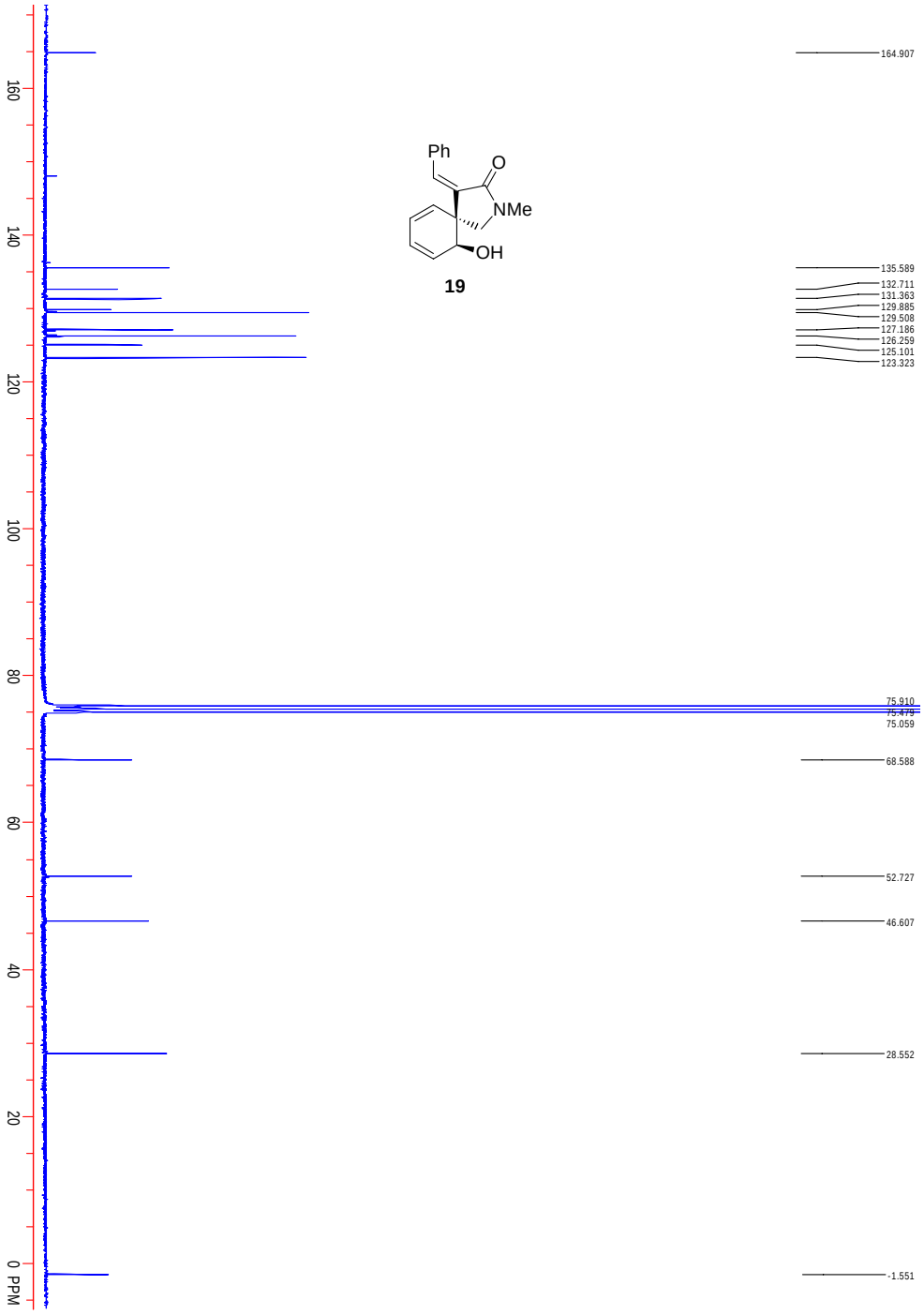
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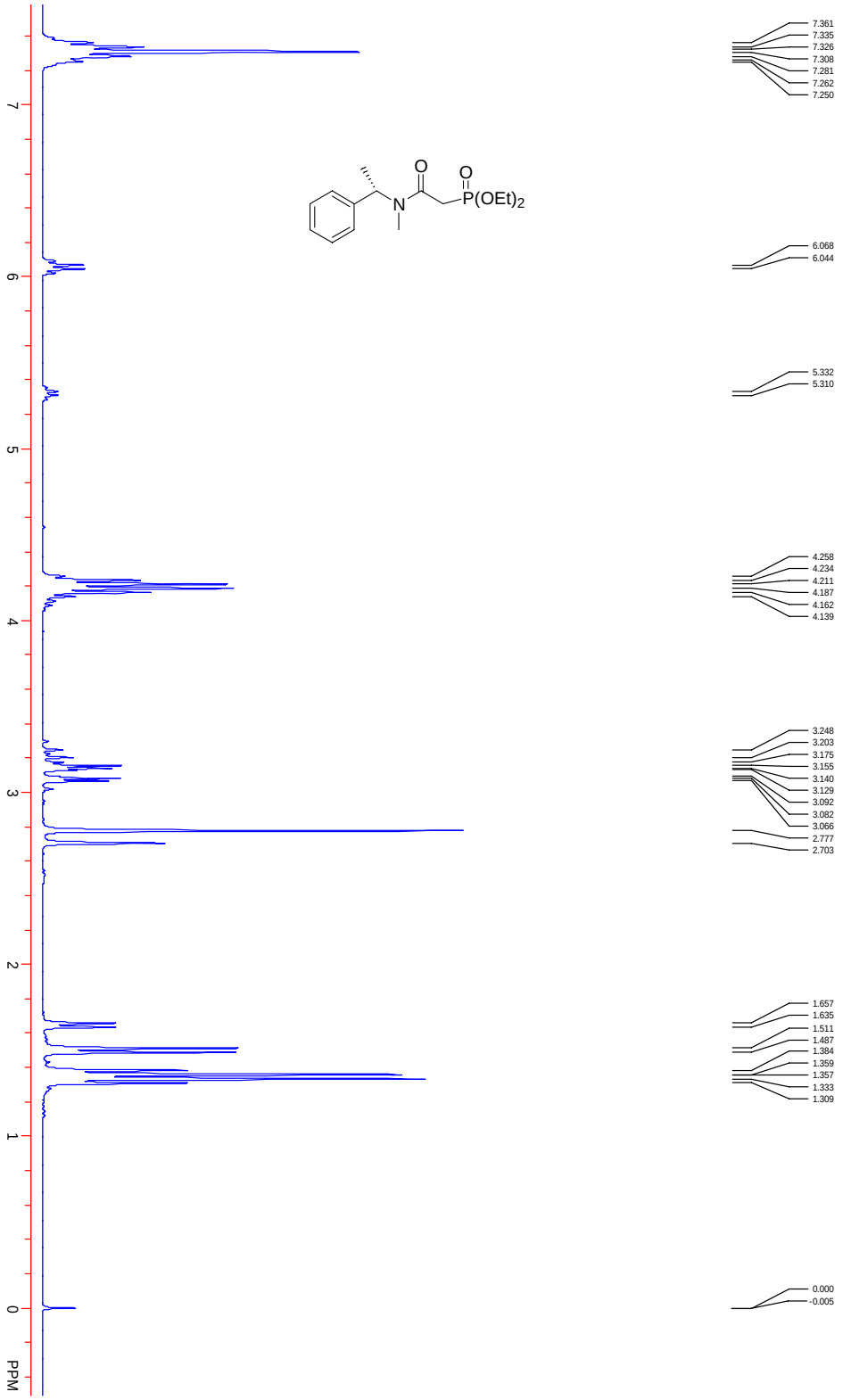
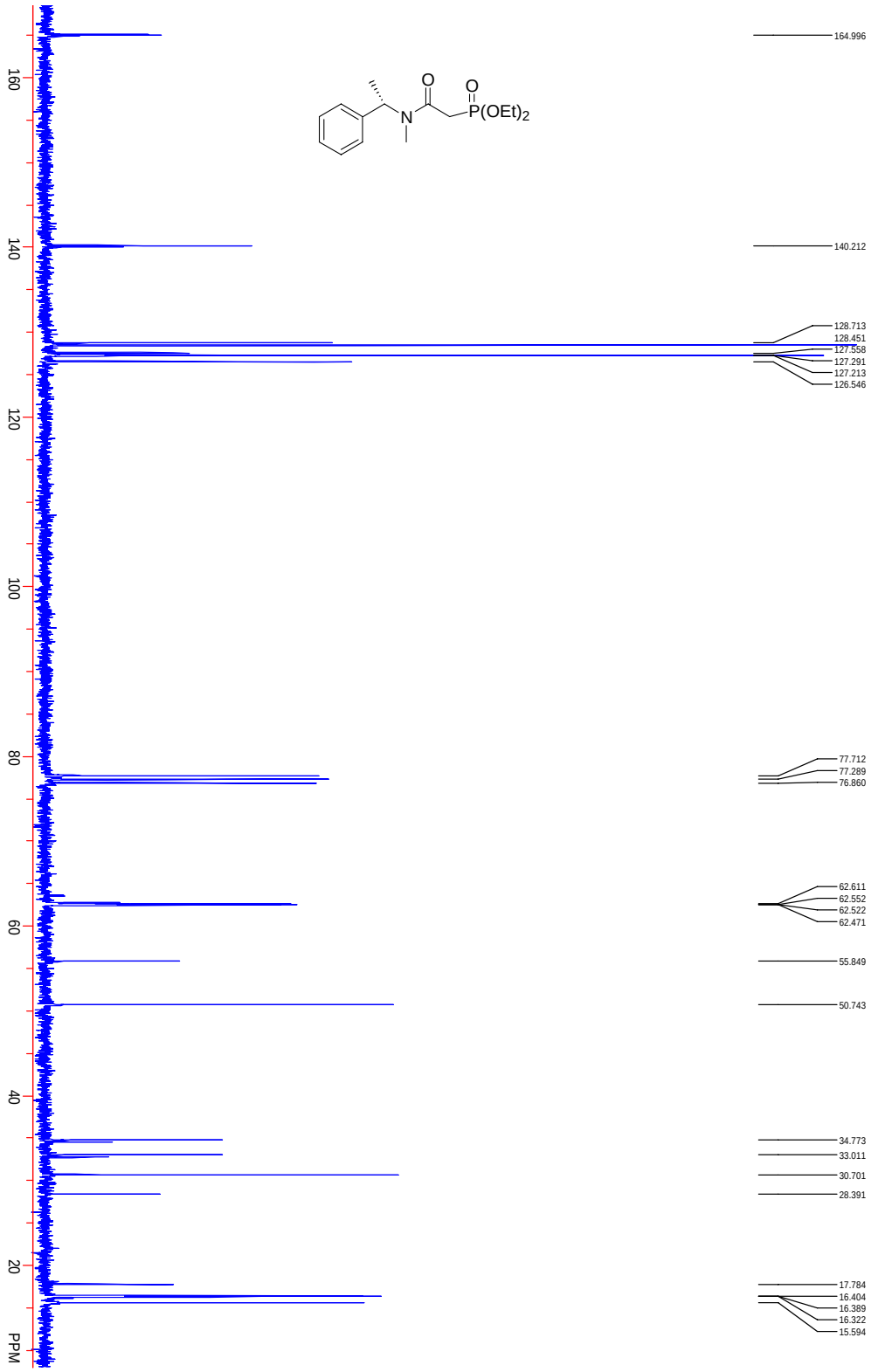
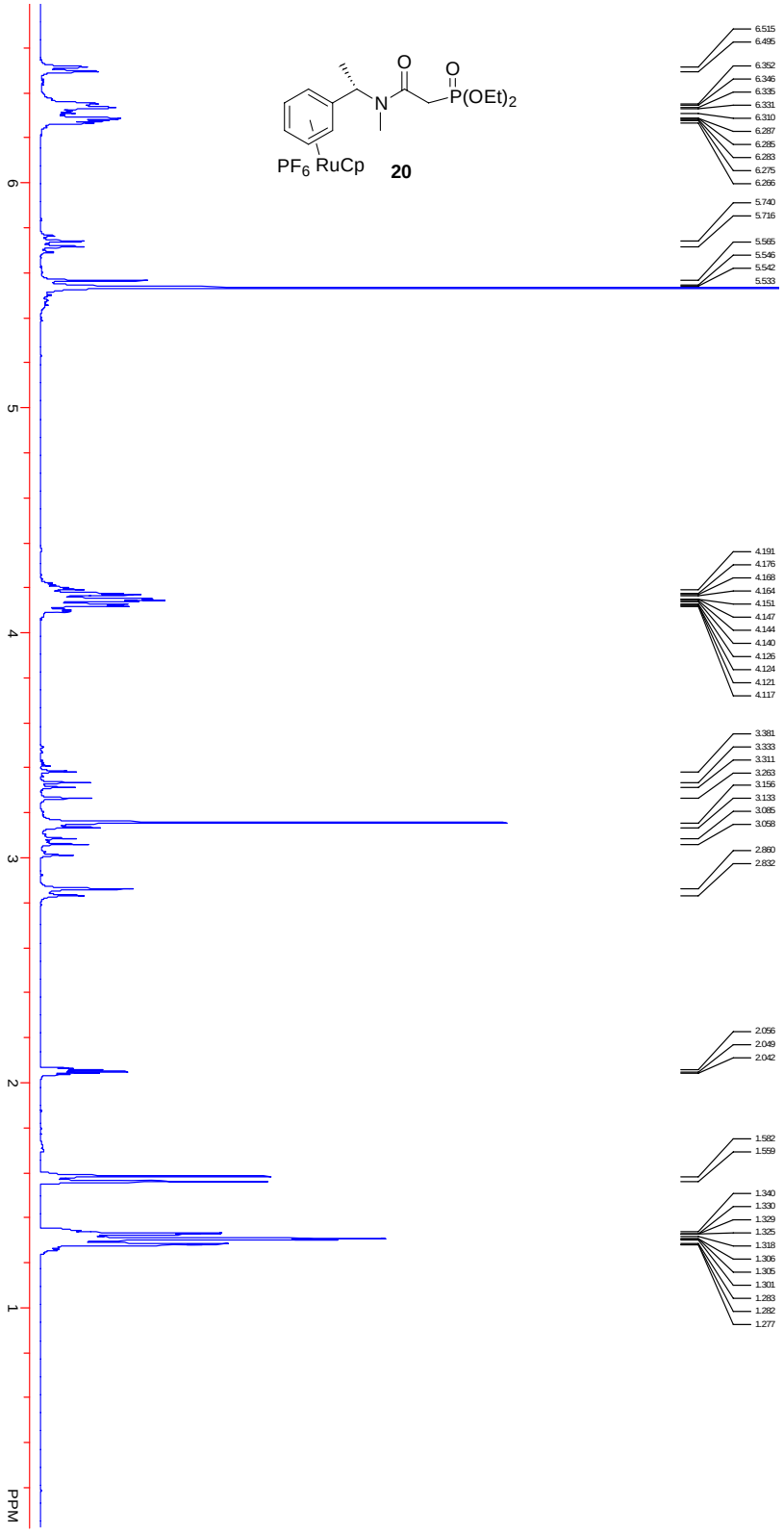
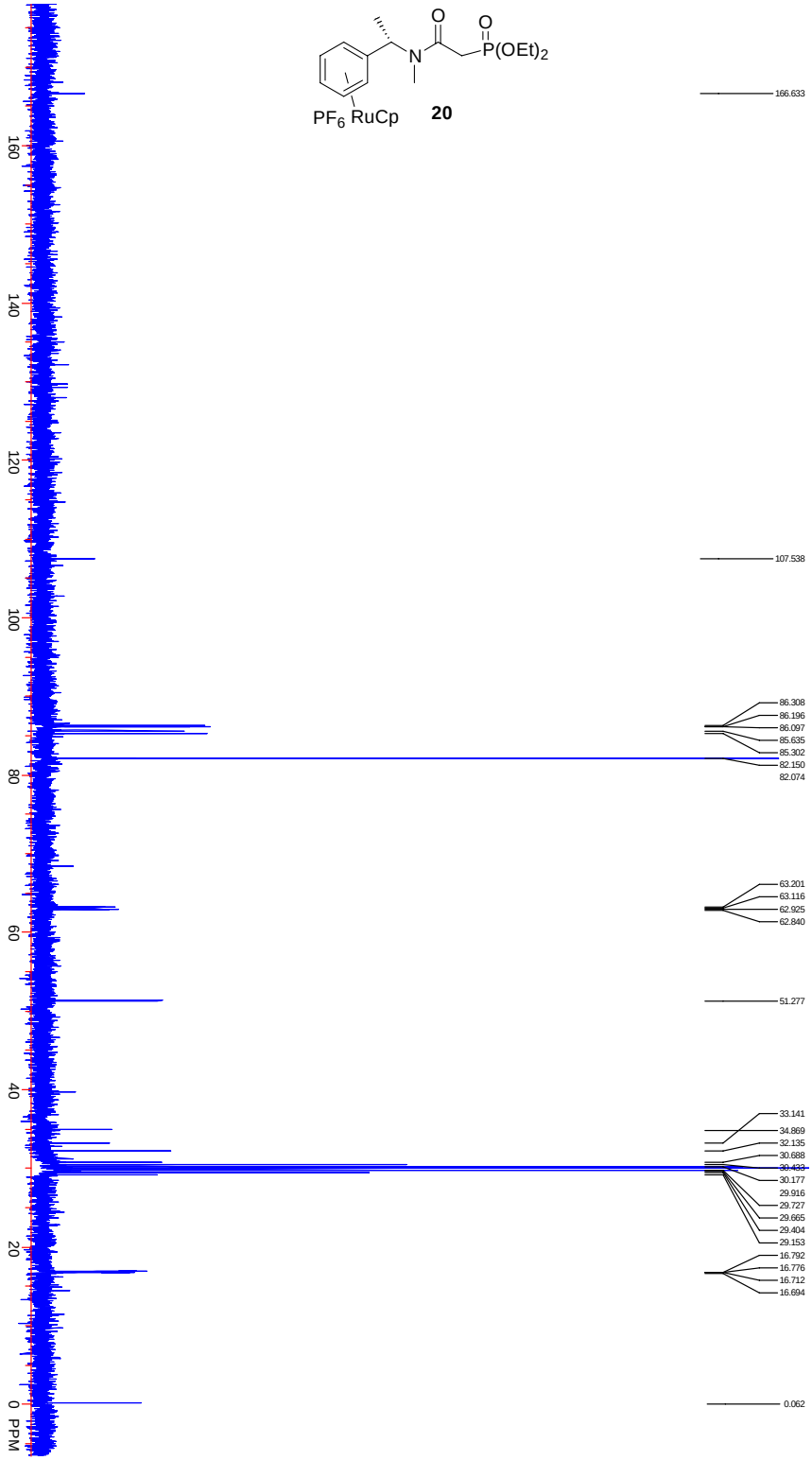
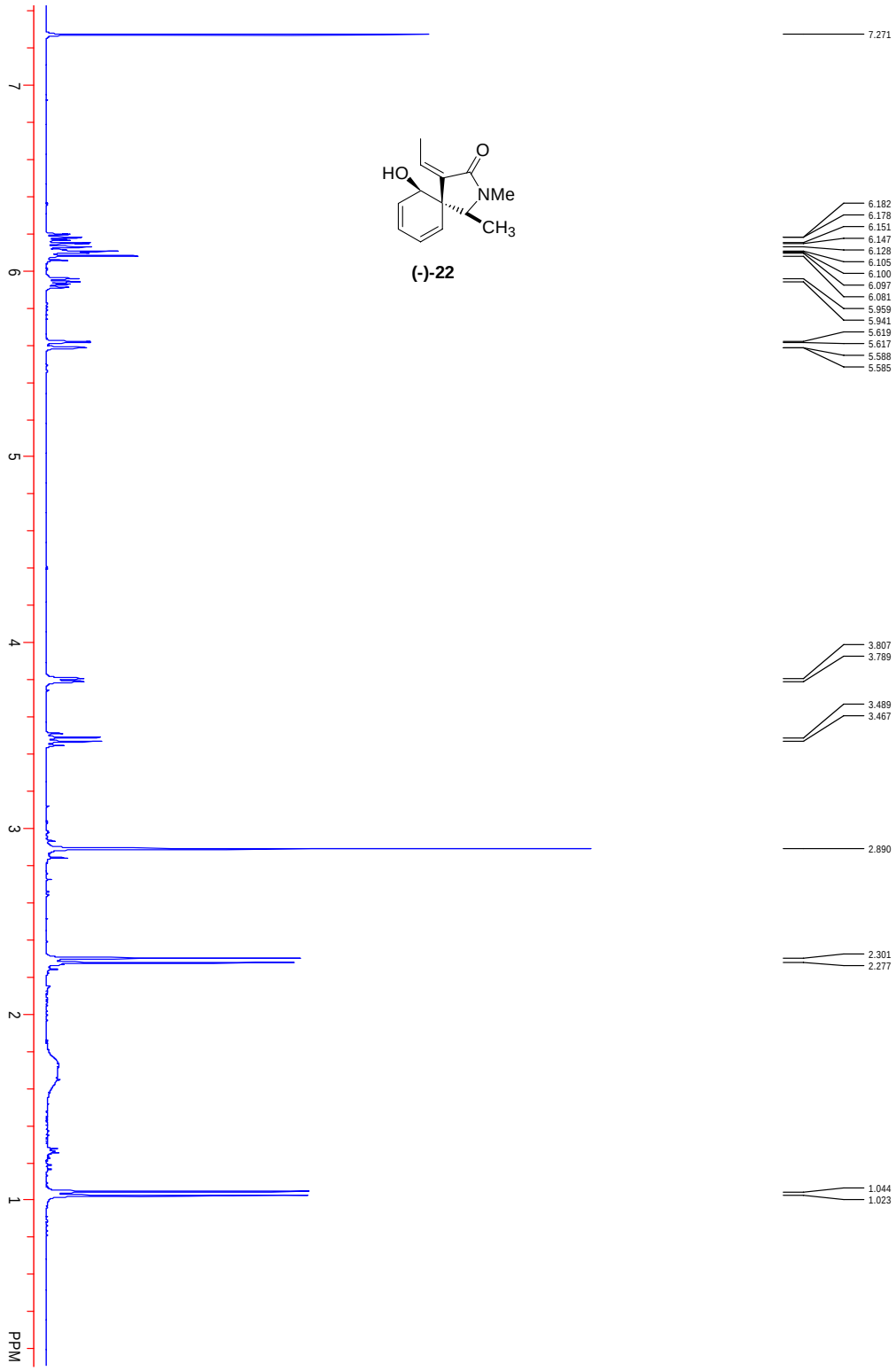
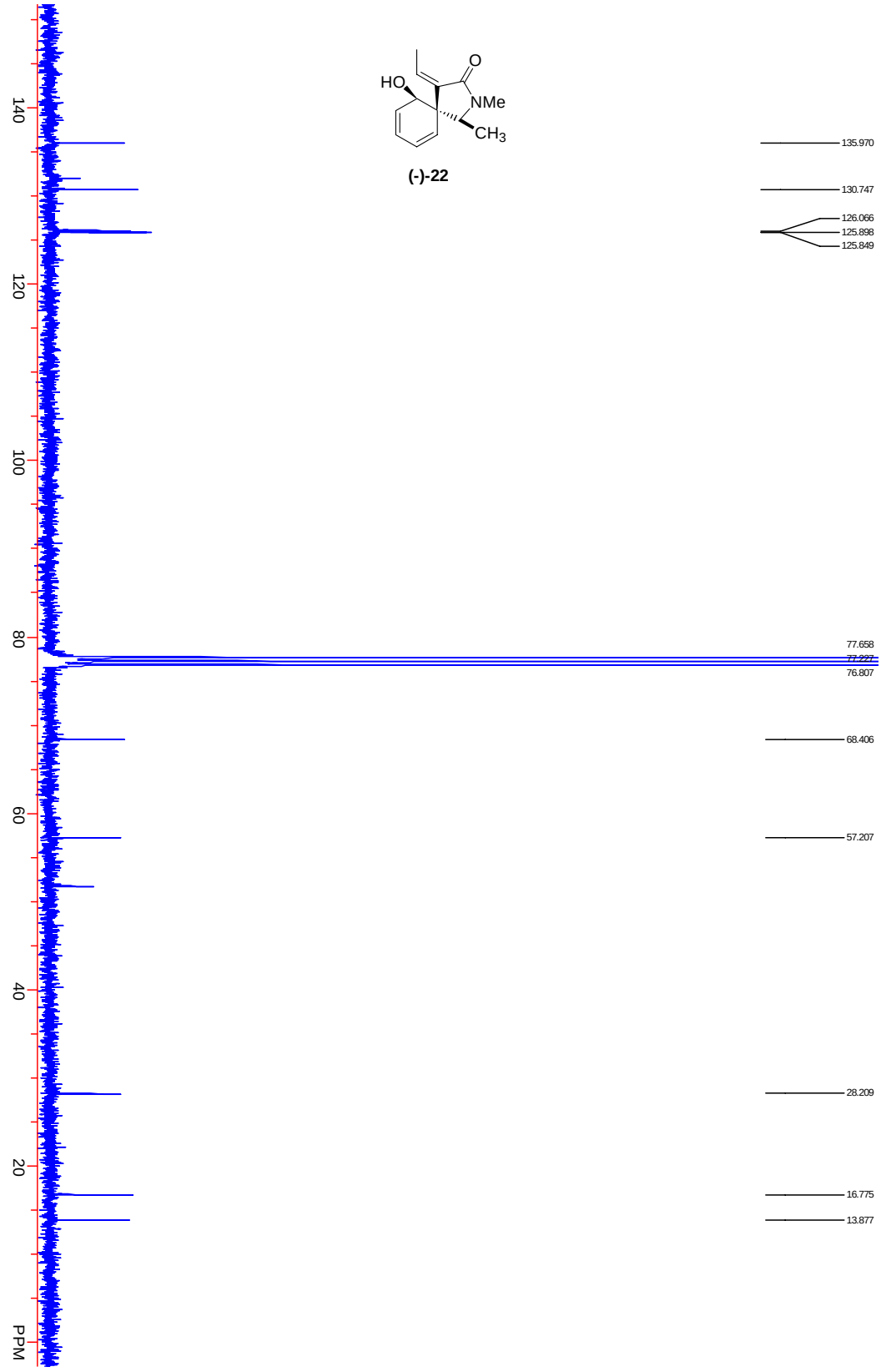

7.361
7.335
7.326
7.308
7.281
7.262
7.250
6.068
6.044
5.332
5.310
4.258
4.234
4.211
4.187
4.162
4.139
3.248
3.203
3.175
3.155
3.140
3.129
3.092
3.082
3.066
2.777
2.703
1.657
1.635
1.511
1.487
1.384
1.359
1.357
1.333
1.309
0.000
-0.005
O
O
P(OEt)2
N
7
6
5
4
3
2
1
0
PPM

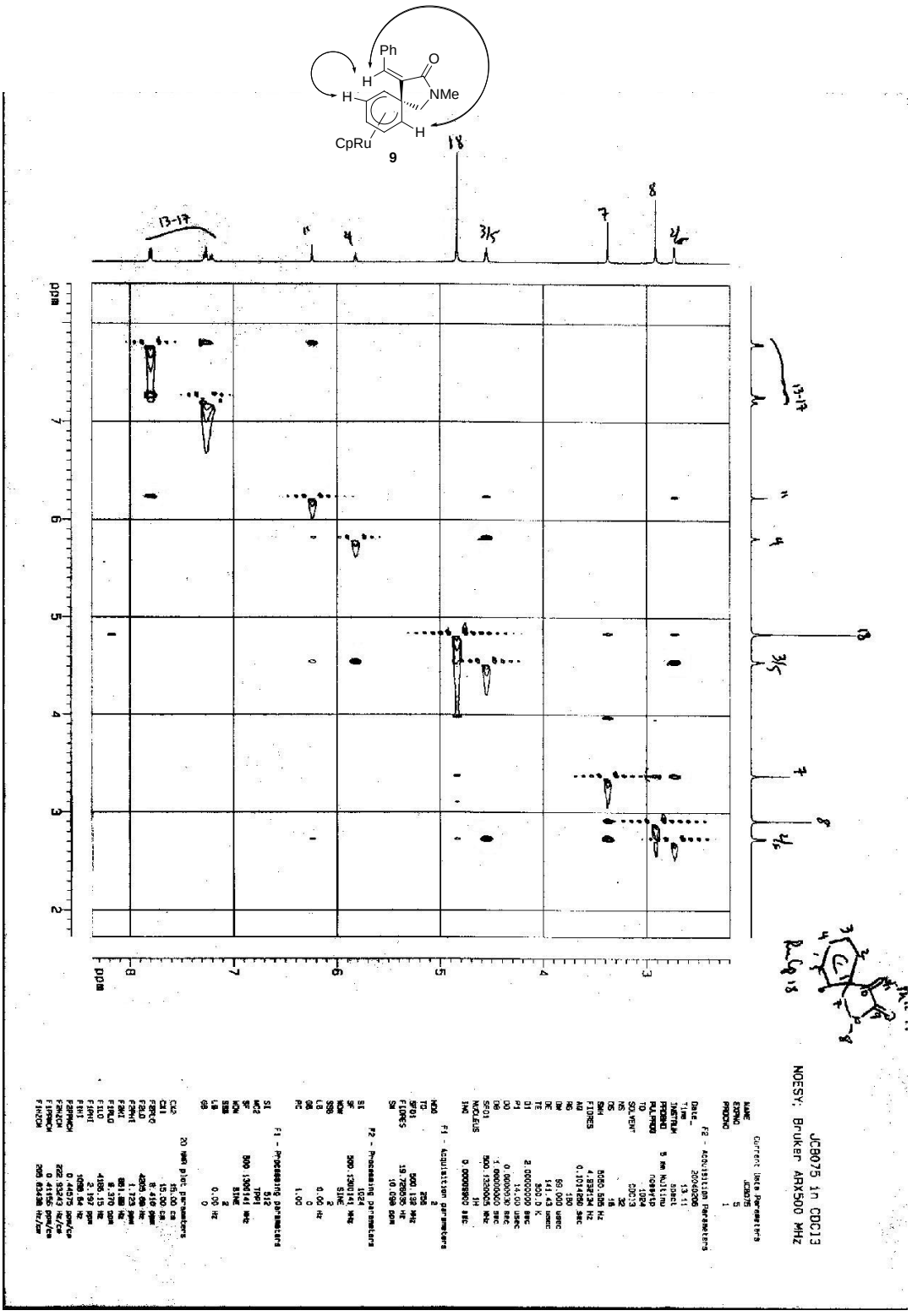

O
O
N
P(OEt)2
164.996
140.212
128.713
128.451
127.558
127.291
127.213
126.546
77.712
77.289
76.860
62.611
62.552
62.522
62.471
55.849
50.743
34.773
33.011
30.701
28.391
17.784
16.404
16.389
16.322
15.594
160
140
120
100
80
60
40
20
PPM

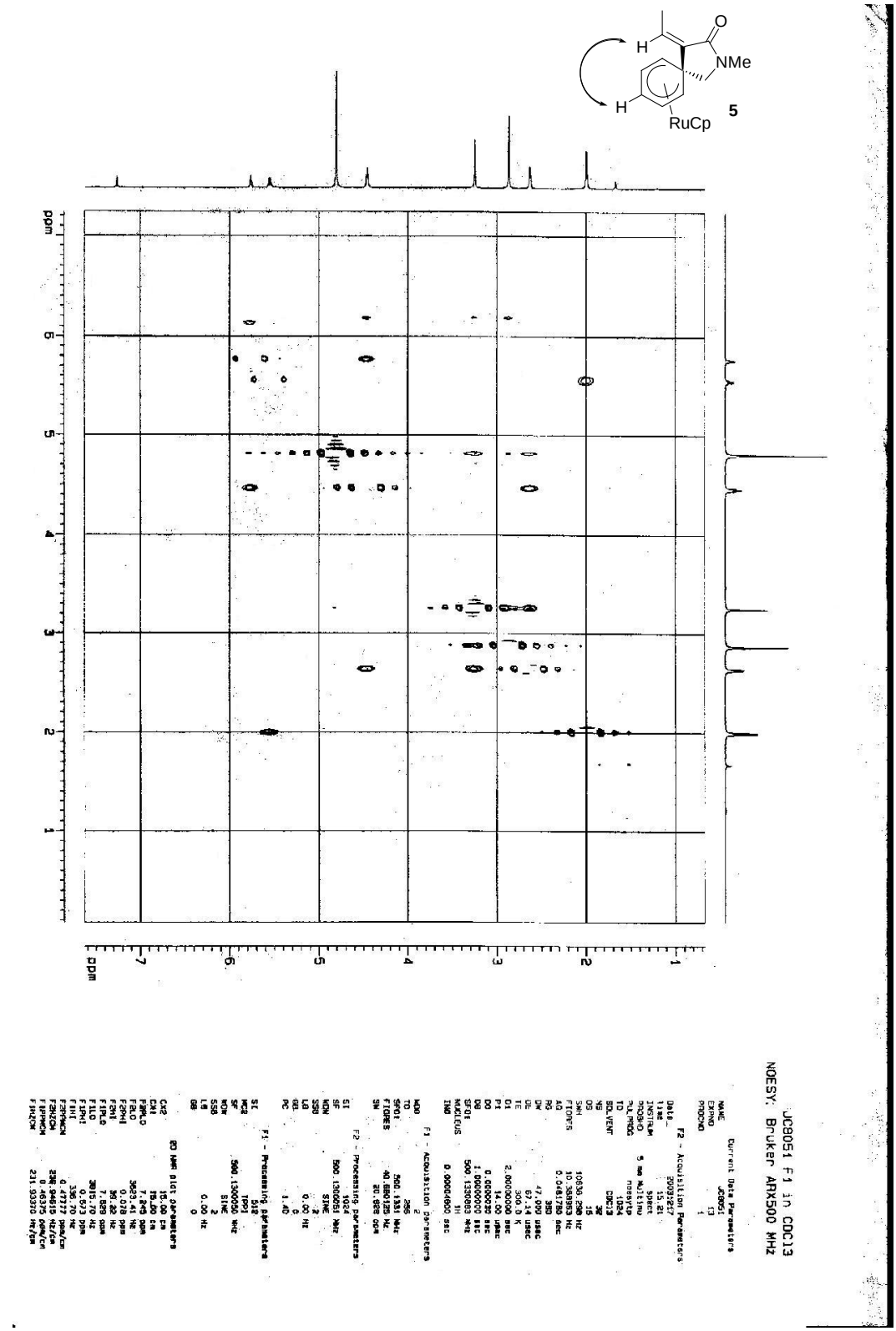

6.515
6.495
6.352
6.346
6.335
6.331
6.310
6.287
6.285
6.283
6.275
6.266
5.740
5.716
5.565
5.546
5.542
5.533
4.191
4.176
4.168
4.164
4.151
4.147
4.144
4.140
4.126
4.124
4.121
4.117
3.381
3.333
3.311
3.263
3.156
3.133
3.085
3.058
2.860
2.832
2.056
2.049
2.042
1.582
1.559
1.340
1.330
1.329
1.325
1.318
1.306
1.305
1.301
1.283
1.282
1.277
6
5
4
3
2
1
PPM
O
O
N
P(OEt)2
PF6 RuCp
20


O
O
P(OEt)2
N
PF6 RuCp
20
166.633
107.538
86.308
86.196
86.097
85.635
85.302
82.150
82.074
63.201
63.116
62.925
62.840
51.277
33.141
34.869
32.135
30.688
30.433
30.177
29.916
29.727
29.665
29.404
29.153
16.792
16.776
16.712
16.694
0.062
160
140
120
100
80
60
40
20
0
PPM


HO
O
NMe
CH3
(-)-22
7.271
6.182
6.178
6.151
6.147
6.128
6.105
6.100
6.097
6.081
5.959
5.941
5.619
5.617
5.588
5.585
3.807
3.789
3.489
3.467
2.890
2.301
2.277
1.044
1.023
7
6
5
4
3
2
1
PPM


HO
O
NMe
CH3
(-)-22
140
120
100
80
60
40
20
PPM
135.970
130.747
126.066
125.898
125.849
77.658
77.227
76.807
68.406
57.207
28.209
16.775
13.877


Ph
H
O
NMe
H
H
CpRu
9
JCB075 in CDCl3
NOESY; Bruker ARX500 MHz



JC8051 F1 in CDCl3
NOESY: Bruker ARX500 MHz

Current Data Parameters
NAME JC8051
EXPNO 13
PROCNO 1

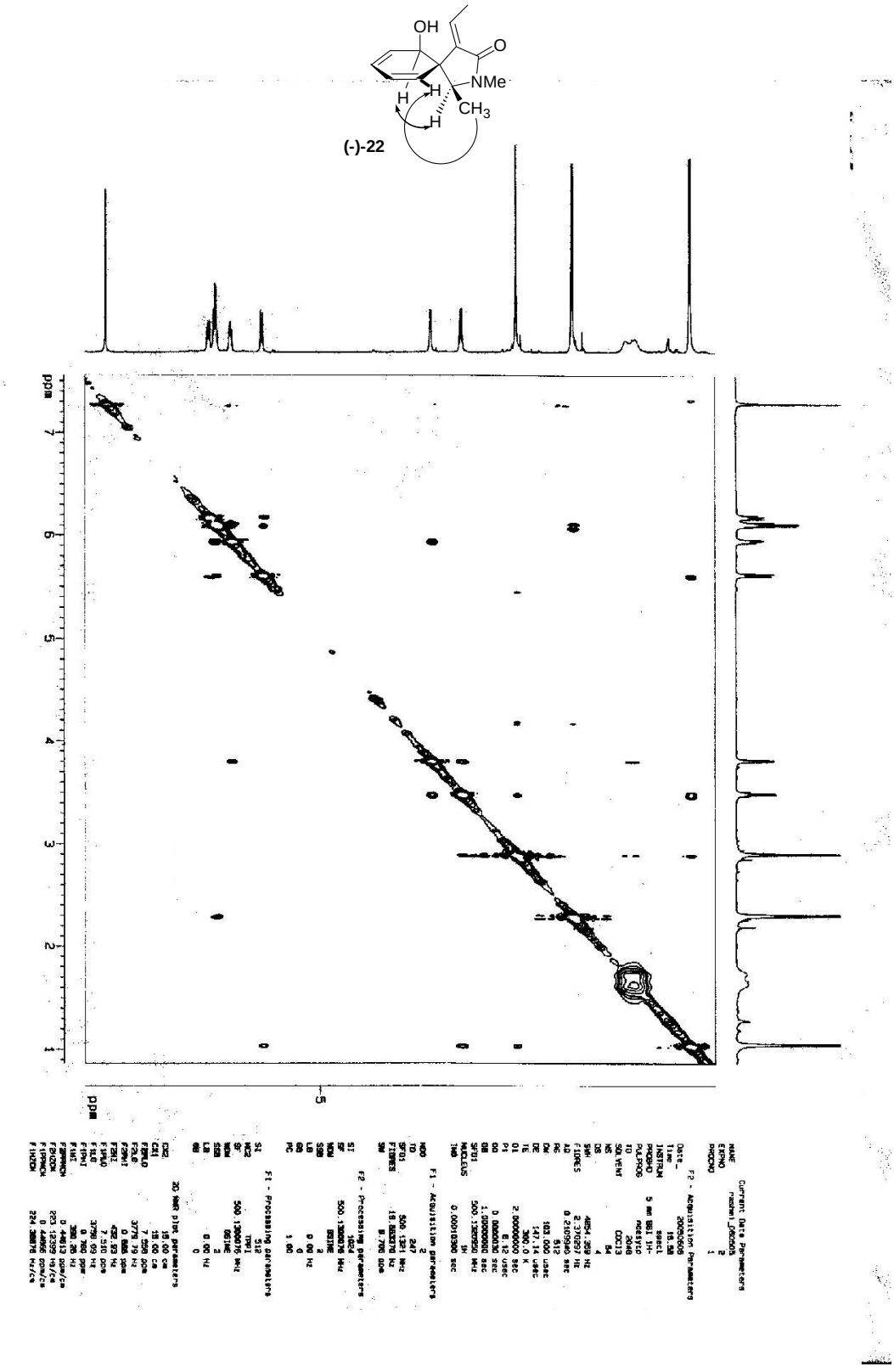
F2 - Acquisition Parameters
Date_ 20031221
Time 15:47
INSTRUM 5 mm Multinu
PROBHD
PULPROG noesytp
TD 1024
SOLVENT CDCl3
NS 32
DS 16
SWH 10638.298 Hz
FIDRES 10.388863 Hz
AQ 0.0481780 sec
RG 380
DW 47.000 usec
DE 6.50 usec
TE 297.1 K
D0 2.00000000 sec
D1 14.00 usec
D8 0.00000032 sec
D9 1.00000000 sec
SFO1 500.1330883 MHz
NUCLEUS 1H
IN0 0.00004800 sec

F1 - Acquisition parameters
NDM
TD 256
SFO1 500.1351 MHz
FIDRES 40.880125 Hz
SW 20.952 ppm

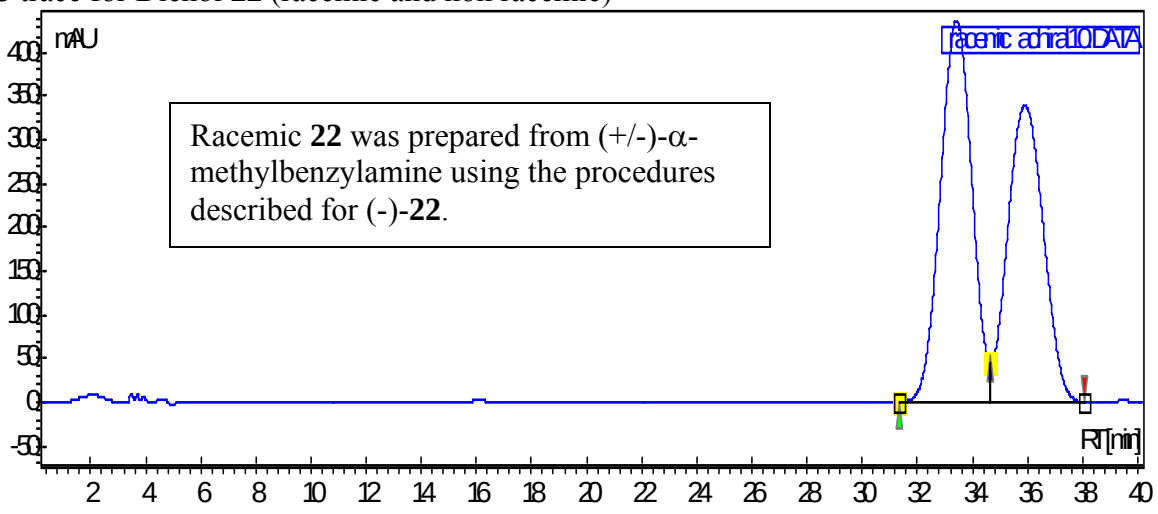
F2 - Processing parameters
SI 1024
SF 500.1300051 MHz
WDW SINE
SSB 2
LB 0.00 Hz
GB
PC 1.40

F1 - Processing parameters
SI 512
MC2 TPPI
SF 500.1300090 MHz
WDW SINE
SSB 2
LB 0.00 Hz
GB
PC

2D NMR plot parameters
CX 15.00 cm
CY 15.00 cm
F1PLO 7.240 ppm
F1PHI 0.018 ppm
F2PLO 7.839 ppm
F2PHI 0.922 ppm
F1LO 3815.70 Hz
F1HI 335.70 Hz
F1PPCM 0.573 ppm/cm
F1HZCM 286.584615 Hz/cm
F2PPCM 0.46375 ppm/cm
F2HZCM 231.93370 Hz/cm


OH
O
NMe
H
H
H
CH3
(-)-22
ppm
1
2
3
4
5
6
7
ppm
1
5

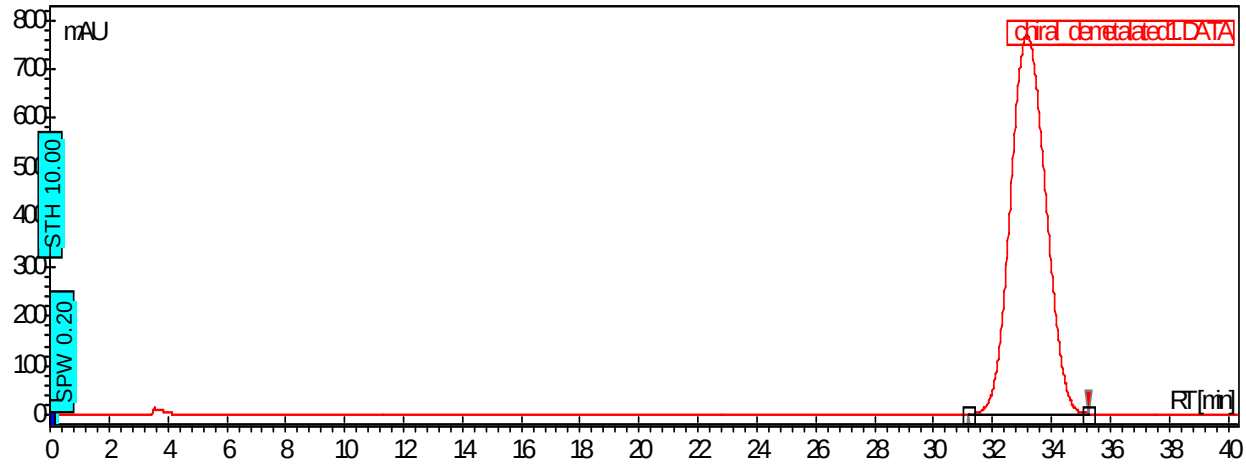
HPLC trace for Dienol **22** (racemic and non racemic)



Racemic **22** was prepared from (+/-)-α-methylbenzylamine using the procedures described for (-)-**22**.

#	Name	Area % [%]	Time [Min]
1	Peak 1	53.090	33.41
2	Peak 2	46.910	35.91

Total 100.000



#	Name	Time [Min]	Area % [%]
1	Peak	33.16	100.000

Total 100.000

Column: ChiralPak AD-H 4.6 x 250 mm
Eluent: 96:4 Hexanes:IPA