

•Electronic Supplementary Information

Transition metal-free access to 3,4-Dihydro-1,2-oxaphosphinine-2-oxides from Phosphonochloridates and Chalcones through tandem Michael addition and nucleophilic substitution

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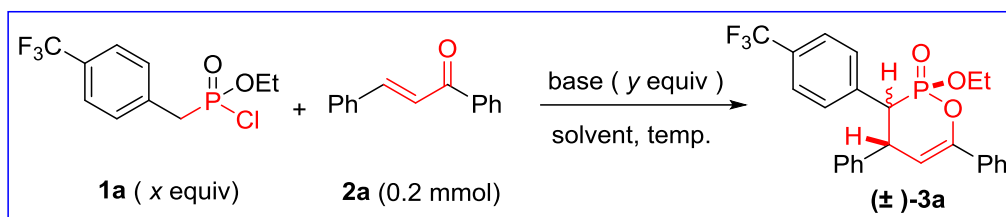
1. General information

All reactions were carried out under anhydrous conditions employing standard techniques unless otherwise noted. Tetrahydrofuran was refluxed over LiAlH₄, and freshly distilled prior to use. ¹H (400 MHz), ¹³C (100 MHz), and ¹⁹F NMR (376 MHz) spectra were recorded on a Bruker AMX 400 NMR spectrometer with TMS as an internal standard in CDCl₃ solution. Chemical shifts for ¹H NMR are reported as follows: chemical shift in reference to residual CHCl₃ at 7.26 ppm (δ ppm), multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet), coupling constant (Hz), and integration. Chemical shifts for ¹³C NMR are reported in terms of chemical shift in reference to the CDCl₃ solvent signal (77.16 ppm, middle peak). IR spectra (ν/cm⁻¹) were taken on a Nicolet 5700 FT-IR spectrometer (neat or KBr pellets). Melting points were obtained on a Yanaco M500 melting point apparatus and are uncorrected. High resolution mass spectra were obtained via an Agilent LC/MSD TOF mass spectrometer. Products were purified on column chromatography with silica gel (200–300 mesh). Thin-layer chromatography (TLC) separations were performed on silica gel GF₂₅₄ plates with a mixture of petroleum ether (PE) and ethyl acetate (EA) as eluent, and the plates were visualized with UV light. Substituted chalcones and phosphonochloridates, which were freshly synthesized prior to use by reaction of ethyl hydrogen alkylphosphonates and thionyl chloride, were known and prepared according to published procedures,^{1,2} unless otherwise noted. Others were commercially available and used as received.

¹ (a) J. X. Xu, Q. H. Zhang, L. B. Chen and H. Chen, *J. Chem. Soc. Perkin. Trans. 1*, 2001, **(18)**, 2266; (b) J. X. Xu, L. G. Ma and P. Jiao, *Chem. Commun.*, 2004, **(14)**, 1616; (c) L. G. Ma, D. M. Du and J. X. Xu, *J. Org. Chem.*, 2005, **70**, 10155. (d) J. X. Xu, C. F. Xia, L. Yu and Q. Z. Zhou, *Phosphorus Sulfur Silicon Relat. Elem.*, 1999, **152**, 35.

² Y. Yu and F. Sun, *Ind. Eng. Chem. Res.*, 2014, **53**, 16135.

Table S1. Optimization of reaction conditions^a



Entry	Solvent	Temp. (°C)	Base	x:y	Time (h)	Total yield ^b (%)	Cis:Trans ratio ^c
1	THF	39	NaH	1.5:1.5	6	NR	-
2	THF	39	NaO ^t Bu	1.5:1.5	6	Trace	-
3	THF	39	LDA	1.5:1.5	6	55	55:45
4	THF	39	NaHMDS	1.5:1.5	6	63	21:79
5	THF	39	KHMDS	1.5:1.5	6	61	39:61
6	PhMe	39	NaHMDS	1.5:1.5	6	35	52:48
7	Et ₂ O	39	NaHMDS	1.5:1.5	6	41	65:35
8	DMF	39	NaHMDS	1.5:1.5	6	33	1:99
9	THF	39	NaHMDS	1.5:1.5	12	44	19:81
10	THF	25	NaHMDS	1.5:1.5	12	44	61:39
11	THF	0	NaHMDS	1.5:1.5	12	59	25:75
12	THF	-78-rt	NaHMDS	1.5:1.5	12	73	30:70
13	THF	-78-rt	NaHMDS	3.0:3.0	12	78	53:47
14	THF	-78-rt	NaHMDS	4.1:4.1	12	98	60:40
15	THF	-78-rt	NaHMDS	4.5:4.5	12	82	49:51
16	THF	-78-rt	NaHMDS	4.1:5.0	12	76	22:78
17	THF	-78-rt	NaHMDS	3.2:4.1	12	60	1:99
18	THF	-78-rt	NaHMDS	2.0:4.1	12	16	1:99
19	THF	-78-rt	LiHMDS	4.1:4.1	12	98	89:11
20	THF	-78-rt	LiHMDS	4.1:4.1	6	98	83:17
21	THF	-78-rt	LiHMDS	4.1:4.1	24	98	90:10
22^d	THF	-78-rt	LiHMDS	4.1:4.1	12	99	92:8
23	PhMe	-78-rt	LiHMDS	4.1:4.1	12	67	81:19
24	Et ₂ O	-78-rt	LiHMDS	4.1:4.1	12	83	36:64
25	DMF	-78-rt	LiHMDS	4.1:4.1	12	64	48:52
26	CH ₃ CN	-78-rt	LiHMDS	4.1:4.1	12	90	68:22
27	1,4-dioxane	-78-rt	LiHMDS	4.1:4.1	12	51	83:17
28	THF	39	LiHMDS	4.1:4.1	12	60	64:36
29	THF	25	LiHMDS	4.1:4.1	12	70	74:26
30	THF	0	LiHMDS	4.1:4.1	12	66	67:33

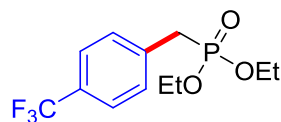
^aReactions were conducted on a 0.2 mmol scale in THF. ^b Isolated yields. ^c Ratios were determined by ¹H NMR spectroscopy of the crude reaction mixtures. ^d 4Å MS was added as additive.

2. General procedure for the preparation of ethyl hydrogen alkylphosphonates 8.

P(OEt)₃ (6.0 mmol, 1.2 mL) and alkyl halide (5.0 mmol) were stirred and refluxed in a flask at 140 °C for 12 h. Diethyl alkylphosphonate was obtained by reduced distillation under vacuum (< 1 mmHg pressure). Then, 3 equivalents sodium hydroxide and diethyl alkylphosphonate in EtOH were stirred and refluxed at 85 °C for 12 h. After washing sequentially with HCl (1.0 mol/L), aqueous phase was extracted with dichloromethane (15 mL × 3). The combined organic layer was washed with brine (20 mL × 3), dried over Na₂SO₄, and concentrated under vacuum to get the desired product 8.

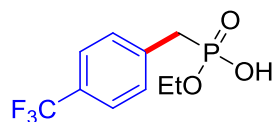
3. Characterization data of compounds 6 and 8

Diethyl (4-(trifluoromethyl)benzyl)phosphonate (6)



Colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 6.5 Hz, 2H), 4.06 (dq, *J* = 7.1, 8.0 Hz, 2H), 4.06 (dq, *J* = 6.8, 7.2 Hz, 2H), 3.19 (d, *J* = 22.0 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 136.0 (dd, *J* = 9.0, 1.2 Hz), 130.2 (d, *J* = 6.5 Hz), 129.2 (dq, *J* = 32.5, 3.7 Hz), 125.6 (dq, *J* = 3.6, 3.5 Hz), 124.2 (dq, *J* = 271.9, 1.2 Hz), 62.4 (d, *J* = 6.8 Hz), 33.9 (d, *J* = 138.2 Hz), 16.5 (d, *J* = 6.0 Hz). ³¹P NMR (162 MHz, CDCl₃) δ: 25.1 (dd, *J* = 5.2, 2.5 Hz).

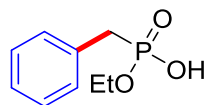
Ethyl hydrogen (4-(trifluoromethyl)benzyl)phosphonate (8a)



White solid. M.p. 145–147 °C. ¹H NMR (400 MHz, CDCl₃): 10.77 (s, 1H), 7.55 (d, *J* = 7.9 Hz, 2H), 7.38 (d, *J* = 7.4 Hz, 2H), 3.86 (dq, *J* = 7.2, 7.6 Hz, 2H), 3.09 (d, *J* = 22.5 Hz, 2H), 1.20 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz,

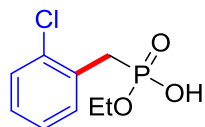
CDCl₃): 135.7 (dd, $J = 9.2$ Hz, $J = 1.1$ Hz), 130.2 (d, $J = 6.5$ Hz), 129.2 (dq, $J = 32.4$ Hz, $J = 3.3$ Hz), 125.5 (dq, $J = 3.6$, 3.6 Hz), 124.9 (dq, $J = 271.9$, 1.1 Hz), 61.9 (d, $J = 7.1$ Hz), 33.8 (d, $J = 140.6$ Hz), 16.2 (d, $J = 6.4$ Hz). ³¹P NMR (162 MHz, CDCl₃) 27.86 (d, $J = 2.5$ Hz). IR (KBr, cm⁻¹): 3406, 2993, 2285, 1682, 1419, 1339, 1119, 986, 852, 631. HRMS (ESI) calcd. for C₁₀H₁₂F₃O₃P (M + H⁺) m/z 269.0549, found 269.0551.

Ethyl hydrogen benzylphosphonate (8b)



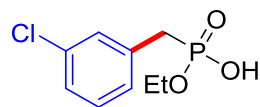
Yellow solid. M.p. 66–67 °C. ¹H NMR (400 MHz, CDCl₃): 10.56 (s, 1H), 7.38 – 7.21 (m, 5H), 3.91 (dq, $J = 7.1$, 7.1 Hz, 2H), 3.06 (d, $J = 22$ Hz, 2H), 1.23 (t, $J = 7.0$ Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): 131.5 (d, $J = 9.2$ Hz), 129.9 (d, $J = 6.6$ Hz), 128.4 (d, $J = 3.1$ Hz), 126.8 (d, $J = 3.7$ Hz), 61.6 (d, $J = 7.0$ Hz), 33.7 (d, $J = 140.6$ Hz), 16.2 (d, $J = 6.4$ Hz). ³¹P NMR (162 MHz, CDCl₃) 29.0. IR (KBr, cm⁻¹): 3404, 2990, 2276, 1680, 1410, 1339, 1117, 986, 852, 631. HRMS (ESI) calcd. for C₉H₁₃O₃P (M + H⁺) m/z 201.0675, found 201.0683.

Ethyl hydrogen (2-chlorobenzyl)phosphonate (8c)



White solid. M.p. 59–61 °C. ¹H NMR (400 MHz, CDCl₃): 11.96 (s, 1H), 7.41–7.34 (m, 2H), 7.23–7.13 (m, 2H), 3.95 (dq, $J = 7.2$, 7.2 Hz, 2H), 3.29 (d, $J = 22.5$ Hz, 2H), 1.23 (t, $J = 7.1$ Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): 134.6 (d, $J = 8.4$ Hz), 131.9 (d, $J = 5.3$ Hz), 130.0 (d, $J = 9.1$ Hz), 129.7 (d, $J = 3.1$ Hz), 128.4 (d, $J = 3.7$ Hz), 126.9 (d, $J = 3.5$ Hz), 62.0 (d, $J = 7.0$ Hz), 31.0 (d, $J = 141.9$ Hz), 16.3 (d, $J = 6.5$ Hz). ³¹P NMR (162 MHz, CDCl₃) 28.1. IR (KBr, cm⁻¹): 3406, 2984, 1650, 1478, 1443, 1209, 1037, 992, 754. HRMS (ESI) calcd. for C₉H₁₂ClO₃P (M + H⁺) m/z 235.0285, found 235.0286.

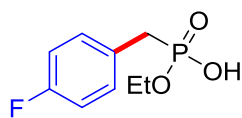
Ethyl hydrogen (3-chlorobenzyl)phosphonate (8d)



Yellow solid. M.p. 80–83 °C. ¹H NMR (400 MHz, CDCl₃): 12.48 (s, 1H), 7.29–7.10 (m, 4H), 3.91 (dq, $J = 14.3$, 7.1 Hz, 2H), 3.01 (d, $J = 22.2$ Hz, 2H),

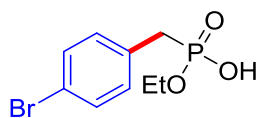
1.22 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 134.2 (d, $J = 3.3$ Hz), 133.6 (d, $J = 9.1$ Hz), 129.9 (d, $J = 6.6$ Hz), 129.7 (d, $J = 2.7$ Hz), 128.2 (d, $J = 6.5$ Hz), 127.1 (d, $J = 3.4$ Hz), 61.9 (d, $J = 7.0$ Hz), 33.4 (d, $J = 141.0$ Hz), 16.2 (d, $J = 6.3$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 27.88. IR (KBr, cm^{-1}): 3409, 2984, 2281, 1650, 1478, 1443, 1037, 992, 837, 754. HRMS (ESI) calcd. for $\text{C}_9\text{H}_{12}\text{ClO}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 235.0285, found 235.0293.

Ethyl hydrogen (4-fluorobenzyl)phosphonate (8e)



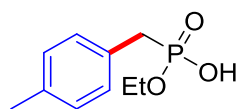
Yellow solid. M.p. 101–103 °C. ^1H NMR (400 MHz, CDCl_3): 8.62 (s, 1H), 7.22 (ddd, $J = 8.1, 5.2, 2.6$ Hz, 2H), 6.98 (t, $J = 8.6$ Hz, 2H), 3.88 (dq, $J = 6.8, 7.6$ Hz, 2H), 3.02 (d, $J = 21.8$ Hz, 2H), 1.21 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 162.1 (dd, $J = 245.3, 4.0$ Hz), 131.5 (dd, $J = 7.9, 6.7$ Hz), 127.2 (dd, $J = 9.2, 3.3$ Hz), 115.5 (dd, $J = 21.5, 3.1$ Hz), 61.8 (d, $J = 7.1$ Hz), 33.0 (d, $J = 141.7$ Hz), 16.3 (d, $J = 6.4$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 28.92 (d, $J = 5.9$ Hz). IR (KBr, cm^{-1}): 3408, 2984, 2282, 1650, 1478, 1443, 1037, 993, 837, 754. HRMS (ESI) calcd. for $\text{C}_9\text{H}_{12}\text{FO}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 219.0581, found 219.0582.

Ethyl hydrogen (4-bromobenzyl)phosphonate (8f)



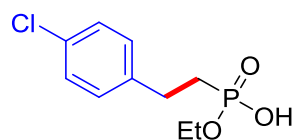
Yellow solid. M.p. 95–98 °C. ^1H NMR (400 MHz, CDCl_3): 11.73 (s, 1H), 7.42 (d, $J = 8.0$ Hz, 2H), 7.19–7.02 (m, 2H), 3.88 (dq, $J = 7.2, 7.6$ Hz, 2H), 2.99 (d, $J = 22.1$ Hz, 2H), 1.23 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 131.8, 131.7 (d, $J = 3.5$ Hz), 130.6 (d, $J = 9.3$ Hz), 121.1 (d, $J = 4.7$ Hz), 61.9 (d, $J = 7.1$ Hz), 33.4 (d, $J = 141.1$ Hz), 16.4 (d, $J = 6.5$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 28.18. IR (KBr, cm^{-1}): 3406, 2984, 2282, 1650, 1478, 1443, 1037, 993, 837, 754. HRMS (ESI) calcd. for $\text{C}_9\text{H}_{12}\text{BrO}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 278.9780, found 278.9789.

Ethyl hydrogen (4-methylbenzyl)phosphonate (8g)



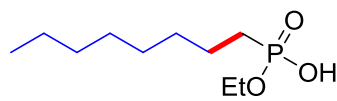
Yellow solid. M.p. 74–77 °C. ^1H NMR (400 MHz, CDCl_3): 12.20 (s, 1H), 7.15 (dd, $J = 8.1, 2.1$ Hz, 2H), 7.09 (d, $J = 7.9$ Hz, 2H), 3.88 (dq, $J = 7.1, 7.1$ Hz, 2H), 2.99 (d, $J = 21.9$ Hz, 2H), 2.29 (d, $J = 2.1$ Hz, 3H), 1.21 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 136.3 (d, $J = 3.9$ Hz), 129.8 (d, $J = 6.6$ Hz), 129.2 (d, $J = 3.2$ Hz), 128.3 (d, $J = 9.3$ Hz), 61.5 (d, $J = 7.1$ Hz), 33.3 (d, $J = 140.9$ Hz), 21.1 (d, $J = 1.2$ Hz), 16.2 (d, $J = 6.5$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 29.46. IR (KBr, cm^{-1}): 3407, 2984, 2282, 1650, 1478, 1443, 1037, 993, 837, 754. HRMS (ESI) calcd. for $\text{C}_{10}\text{H}_{15}\text{O}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 215.0832, found 215.0832.

Ethyl hydrogen (4-chlorophenylethyl)phosphonate (8h)



Yellow oil liquid. ^1H NMR (400 MHz, CDCl_3): 10.32 (s, 1H), 7.24 (d, $J = 8.0$ Hz, 2H), 7.12 (d, $J = 7.9$ Hz, 2H), 4.08 (dq, $J = 6.4, 7.2$ Hz, 2H), 2.92–2.85 (m, 2H), 2.11–1.91 (m, 2H), 1.31 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 139.5 (d, $J = 18.0$ Hz), 132.2, 129.5, 128.8, 61.4 (d, $J = 6.4$ Hz), 27.8 (d, $J = 142.0$ Hz), 28.0 (d, $J = 3.2$ Hz), 16.4 (d, $J = 6.1$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 31.96. IR (KBr, cm^{-1}): 3402, 2994, 2287, 1683, 1419, 1339, 1123, 986, 852, 631. HRMS (ESI) calcd. for $\text{C}_{10}\text{H}_{14}\text{ClO}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 249.0442, found 249.0443.

Ethyl hydrogen octylphosphonate (8i)



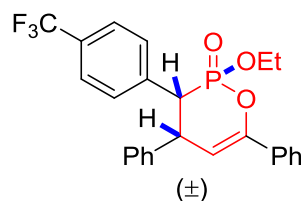
Yellow oil liquid. ^1H NMR (400 MHz, CDCl_3): 11.93 (s, 1H), 4.07 (dq, $J = 7.2, 7.2$ Hz, 2H), 1.78–1.53 (m, 4H), 1.41–1.22 (m, 13H), 0.87 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 61.0 (d, $J = 6.8$ Hz), 31.9, 30.7 (d, $J = 17.2$ Hz), 29.2 (d, $J = 2.8$ Hz), 26.7, 25.3, 22.8, 22.3 (d, $J = 5.0$ Hz), 16.5 (d, $J = 6.4$ Hz), 14.20. ^{31}P NMR (162 MHz, CDCl_3) 35.50. IR (KBr, cm^{-1}): 3400, 2995, 2288, 1680, 1415, 1330, 1119, 987, 852. HRMS (ESI) calcd. for $\text{C}_{10}\text{H}_{23}\text{O}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 223.1458, found 223.1451.

4. General procedure for the preparation of 3,4-dihydro-1,2-oxaphosphinine-2-oxides 3.

Ethyl hydrogen alkylphosphonate **8** (1.0 mmol) and thionyl chloride (1 mL) were added into a two-neck flask under an argon atmosphere. The mixture was refluxed at 80 °C for 12 h. After removal of HCl and residual SOCl₂ through addition of CaCl₂-dried, EtOH-free distilled chloroform and concentration, a 0.5 mmol/mL solution of the corresponding phosphonochloridate **1** in dry THF was prepared. A solution of phosphonochloridate **1** (0.82 mmol, 1.64 mL) and α,β -unsaturated ketone **2** (0.2 mmol) were added into an oven-dried tube followed by 1.0 mol/L solution of LiHMDS (0.82 mmol, 0.82 mL) in THF. The mixture was stirred at -78 °C, then allowed to warm slowly to ambient temperature for 12 h. After quenching with saturated NH₄Cl, the mixture was extracted with dichloromethane (10 mL $\times$ 3). The combined organic layer was washed with brine (15 mL $\times$ 3), dried over Na₂SO₄, and concentrated under vacuum. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10/1 to 5/1, v/v) to afford the desired product **3**.

5. Characterization data of compounds 3, 4, and 7

rel-(2*R*,3*R*,4*R*)-2-Ethoxy-4,6-diphenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3a)

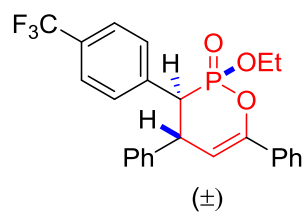


Yellow oil liquid (85 mg, 91 %). ¹H NMR (400 MHz, CDCl₃):

7.76 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.48–7.39 (m, 3H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.18–7.11 (m, 3H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.93 (dd, *J* = 6.5, 2.8 Hz, 2H), 5.88 (d, *J* = 0.7 Hz, 1H), 4.59 (dt, *J* = 2.8, 6.7 Hz, 1H), 4.44–4.28 (m, 2H), 3.66 (dd, *J* = 21.8, 6.7 Hz, 1H), 1.41 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): 149.9 (d, *J* = 7.4 Hz), 139.0 (d, *J* = 10.9 Hz), 136.4, 133.7 (d, *J* = 6.4 Hz), 130.5 (d, *J* = 8.4 Hz), 130.0 (q, *J* = 32.3 Hz),

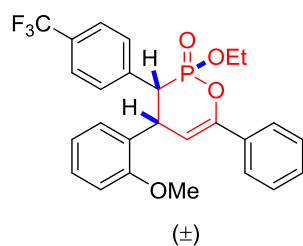
129.5, 128.8, 128.6, 128.4, 127.4, 127.0 (q, $J = 272.1$ Hz), 125.4 (d, $J = 3.1$ Hz) 124.8, 105.0 (d, $J = 12.1$ Hz), 63.1 (d, $J = 7.0$ Hz), 45.7 (d, $J = 5.4$ Hz), 43.6 (d, $J = 124.7$ Hz), 16.7 (d, $J = 5.2$ Hz). ^{19}F NMR (376 MHz, CDCl_3) 62.7. IR (KBr, cm^{-1}): 2984, 1618, 1326, 1166, 1124, 1069, 762, 700. ^{31}P NMR (162 MHz, CDCl_3) 18.14. HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{22}\text{F}_3\text{O}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 459.1331, found 459.1332.

***rel*-(2*R*,3*S*,4*R*)-2-Ethoxy-4,6-diphenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*trans,trans*)-3a)**



White solid (7 mg, 8 %). M.p. 199–201 °C. ^1H NMR (400 MHz, CDCl_3): 7.66 (dd, $J = 7.4$ Hz, 2.0 Hz, 2H), 7.51 (d, $J = 8.1$ Hz, 2H), 7.43–7.34 (m, 5H), 7.24–7.15 (m, 3H), 7.09–7.03 (m, 2H), 5.74 (t, $J = 1.9$ Hz, 1H), 4.35–4.21 (m, 2H), 3.57 (dd, $J = 21.6, 12.2$ Hz, 1H), 1.37 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ : 148.6 (d, $J = 7.1$ Hz), 141.1 (d, $J = 14.0$ Hz), 137.1 (d, $J = 7.7$ Hz), 133.6 (d, $J = 6.7$ Hz), 130.2 (d, $J = 3.8$ Hz), 129.8 (d, $J = 6.5$ Hz), 129.3, 129.0, 128.7, 128.0, 127.7, 125.7, 124.2 (q, $J = 269.2$ Hz), 107.0 (d, $J = 9.2$ Hz), 63.1 (d, $J = 7.6$ Hz), 45.6 (d, $J = 5.2$ Hz), 46.3 (d, $J = 122.7$ Hz), 16.6 (d, $J = 5.3$ Hz). ^{19}F NMR (376 MHz, CDCl_3) 62.7. ^{31}P NMR (162 MHz, CDCl_3) 17.17. IR (KBr, cm^{-1}): 2984, 1618, 1326, 1166, 1124, 1069, 762, 700. HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{22}\text{F}_3\text{O}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 459.1331, found 459.1332.

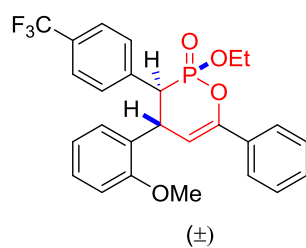
***rel*-(2*R*,3*R*,4*R*)-2-Ethoxy-4-(2-methoxyphenyl)-6-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3b)**



Yellow oil liquid (92 mg, 93 %). ^1H NMR (400 MHz, CDCl_3): 7.81–7.71 (m, 2H), 7.49–7.38 (m, 3H), 7.32 (d, $J = 8.2$ Hz, 2H), 7.17–7.05 (m, 3H),

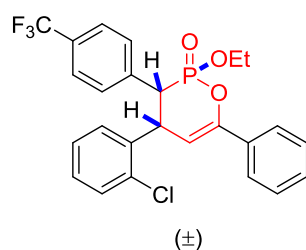
6.84–6.73 (m, 2H), 6.65 (t, $J = 7.4$ Hz, 1H), 5.87 (t, 1H), 5.01 (dt, $J = 2.8, 6.9$ Hz, 1H), 4.42–4.31 (m, 2H), 3.96 (dd, $J = 15.9, 8.0$ Hz, 1H), 3.84 (s, 3H), 1.42 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 156.5, 149.9 (d, $J = 7.2$ Hz), 137.3, 133.9 (d, $J = 6.3$ Hz), 130.1 (d, $J = 8.3$ Hz), 129.6, 129.3, 128.8, 128.5, 127.2 (d, $J = 10.7$ Hz), 125.5, 125.1 (d, $J = 3.0$ Hz), 124.7, 122.8, 120.5, 110.0, 105.5 (d, $J = 12.3$ Hz), 62.9 (d, $J = 6.9$ Hz), 55.5, 40.2 (d, $J = 124.4$ Hz), 39.1 (d, $J = 5.1$ Hz), 16.7 (d, $J = 5.1$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 19.0 (d, $J = 0.9$ Hz). IR (KBr, cm^{-1}): 2924, 2360, 1494, 1274, 1124, 1069, 914, 772. HRMS (ESI) calcd. for $\text{C}_{26}\text{H}_{24}\text{F}_3\text{O}_4\text{P}$ ($\text{M} + \text{H}^+$) m/z 489.1437, found 489.1447.

***rel*-(2*R*,3*S*,4*R*)-2-Ethoxy-4-(2-methoxyphenyl)-6-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*trans,trans*)-3b)**



White solid (6 mg, 6 %), M.p. 143–145 °C. ^1H NMR (400 MHz, CDCl_3): 7.64 (dd, $J = 7.5$ Hz, 1.5 Hz, 2H), 7.47 (d, $J = 8.0$ Hz, 2H), 7.43–7.33 (m, 5H), 7.16 (t, $J = 7.4$ Hz, 2H), 6.86 (t, $J = 7.4$ Hz, 1H), 6.73 (d, $J = 8.2$ Hz, 1H), 5.65 (m, 1H), 4.83–4.74 (m, 1H), 4.35–4.21 (m, 2H), 3.79 (dd, $J = 20.1, 10.0$ Hz, 1H), 3.61 (s, 3H), 1.35 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR data could not be obtained because of less amount. ^{31}P NMR (162 MHz, CDCl_3) 18.14 (d, $J = 1.9$ Hz). IR (KBr, cm^{-1}): 2930, 1619, 1326, 1271, 1114, 1009, 772. HRMS (ESI) calcd. for $\text{C}_{26}\text{H}_{24}\text{F}_3\text{O}_4\text{P}$ ($\text{M} + \text{H}^+$) m/z 489.1437, found 489.1447.

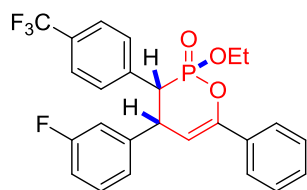
***rel*-(2*R*,3*R*,4*R*)-4-(2-Chlorophenyl)-2-ethoxy-6-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3c)**



Colorless liquid (93 mg, 95 %). ^1H NMR (400 MHz, CDCl_3):

7.80–7.72 (m, 2H), 7.50–7.41 (m, 3H), 7.33 (d, $J = 8.1$ Hz, 3H), 7.12–7.04 (m, 3H), 6.89 (t, $J = 7.6$ Hz, 1H), 6.68 (d, $J = 7.7$ Hz, 1H), 5.79 (m, 1H), 5.07 (dt, $J = 3.2, 6.4$ Hz, 1H), 4.47–4.32 (m, 2H), 3.99 (dd, $J = 22.0, 6.7$ Hz, 1H), 1.43 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 150.4 (d, $J = 7.3$ Hz), 136.6 (d, $J = 11.7$ Hz), 133.6 (d, $J = 6.3$ Hz), 133.3, 130.4, 130.1 (d, $J = 6.6$ Hz), 130.0, 129.6 (d, $J = 8.9$ Hz), 129.3 (q, $J = 10.4$ Hz), 128.8 (q, $J = 7.1$ Hz), 128.1, 126.8, 125.5 (d, $J = 3.3$ Hz), 124.8, 122.7, 104.4 (d, $J = 12.2$ Hz), 63.2 (d, $J = 6.9$ Hz), 42.5 (d, $J = 4.9$ Hz), 39.6 (d, $J = 125.2$ Hz), 16.7 (d, $J = 5.2$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 17.93. IR (KBr, cm^{-1}): 2985, 1619, 1332, 1166, 1124, 1069, 763, 700. HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{21}\text{ClF}_3\text{O}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 493.0942, found 493.0938.

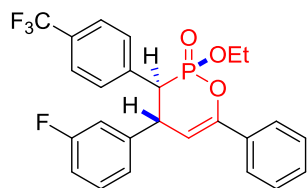
***rel*-(2*R*,3*R*,4*R*)-2-Ethoxy-4-(3-fluorophenyl)-6-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3d)**



(±)

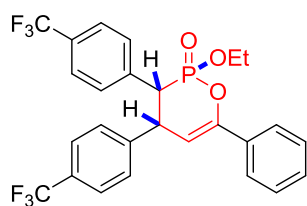
Colorless oil liquid (73 mg, 77 %). ^1H NMR (400 MHz, CDCl_3): 7.77–7.74 (m, 2H), 7.50–7.35 (m, 5H), 7.13–7.08 (m, 3H), 6.84 (dt, $J = 1.8, 8.3$ Hz, 1H), 6.70 (dd, $J = 19.2, 8.7$ Hz, 2H), 5.84 (m, 1H), 4.58 (dt, $J = 2.6, 6.7$ Hz, 1H), 4.42–4.30 (m, 2H), 3.67 (dd, $J = 21.9, 6.7$ Hz, 1H), 1.39 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 162.3 (d, $J = 246.8$ Hz), 150.2 (d, $J = 7.4$ Hz), 141.6 (q, $J = 10.9$ Hz), 136.2, 133.5 (d, $J = 6.4$ Hz), 130.4, (d, $J = 8.4$ Hz), 130.1, (d, $J = 1.6$ Hz), 129.8 (d, $J = 8.2$ Hz), 129.7 (d, $J = 2.0$ Hz), 129.6, 129.4, 128.8, 125.5 (q, $J = 7.2$ Hz), 124.9, 124.3 (d, $J = 2.7$ Hz), 114.4 (d, $J = 21$ Hz), 104.2 (d, $J = 12.2$ Hz), 63.2 (d, $J = 7.1$ Hz), 42.5 (d, $J = 4.6$ Hz), 43.3 (d, $J = 125.2$ Hz), 16.6 (d, $J = 5.4$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 17.65. IR (KBr, cm^{-1}): 3100, 1532, 1352, 1187, 982, 747, 614. HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{21}\text{F}_3\text{O}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 477.1237, found 477.1233.

***rel*-(2*R*,3*S*,4*R*)-2-Ethoxy-4-(3-fluorophenyl)-6-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*trans,trans*)-3d)**



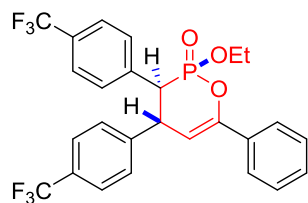
(±) White solid (19 mg, 20 %). M.p. 173–174 °C. ^1H NMR (400 MHz, CDCl_3): 7.69–7.63 (m, 2H), 7.53 (d, $J = 8.0$ Hz, 2H), 7.48–7.33 (m, 6H), 7.17 (dd, $J = 14.1, 7.9$ Hz, 1H), 6.90–6.78 (m, 3H), 5.70 (m, 1H), 4.35–4.21 (m, 3H), 3.53 (dd, $J = 21.7, 12.3$ Hz, 1H), 1.36 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR data could not be obtained because of less amount. ^{31}P NMR (162 MHz, CDCl_3) 16.66. IR (KBr, cm^{-1}): 3108, 1534, 1352, 1187, 982, 747, 612. HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{21}\text{F}_3\text{O}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 477.1237, found 477.1233.

***rel*-(2*R*,3*R*,4*R*)-2-Ethoxy-6-phenyl-3,4-bis(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3e)**



(±) Colorless oil liquid (56 mg, 53 %). ^1H NMR (400 MHz, CDCl_3): 7.76–7.71 (m, 2H), 7.50–7.35 (m, 7H), 7.11–7.03 (m, 4H), 5.83 (m, 1H), 4.65–4.58 (m, 1H), 4.46–4.25 (m, 2H), 3.71 (dd, $J = 22.0, 6.7$ Hz, 1H), 1.39 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 150.5 (d, $J = 7.4$ Hz), 150.0 (d, $J = 10.2$ Hz), 136.0 (d, $J = 2.8$ Hz), 133.4 (d, $J = 6.5$ Hz), 130.4 (q, $J = 20.2$ Hz), 129.2, 128.9, 125.6 (q, $J = 6.9$ Hz), 125.3 (q, $J = 3.8$ Hz), 124.9, 103.9 (d, $J = 12.2$ Hz), 63.3 (d, $J = 7.0$ Hz), 45.7 (d, $J = 5.4$ Hz), 43.3 (d, $J = 125.8$ Hz), 16.6 (d, $J = 5.3$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 17.35. IR (KBr, cm^{-1}): 2925, 1619, 1167, 1069, 1011, 771. HRMS (ESI) calcd. for $\text{C}_{26}\text{H}_{21}\text{F}_6\text{O}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 527.1205, found 527.1207.

***rel*-(2*R*,3*S*,4*R*)-2-Ethoxy-6-phenyl-3,4-bis(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*trans,trans*)-3e)**

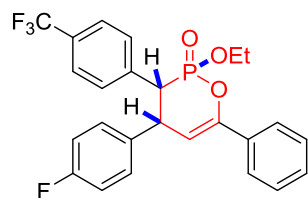


(±)

White solid (44 mg, 42 %). ¹H NMR (400 MHz, CDCl₃): 7.66

(dd, *J* = 6.5, 3.2 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.44–7.34 (m, 5H), 7.19 (d, *J* = 8.1 Hz, 2H), 5.70–5.67 (m, 1H), 4.41–4.22 (m, 3H), 3.55 (dd, *J* = 21.8, 11.2 Hz, 1H), 1.37 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): 149.3 (d, *J* = 7.5 Hz), 145.2 (d, *J* = 1.7 Hz), 136.6 (dd, *J* = 7.8, 0.9 Hz), 133.3 (d, *J* = 6.8 Hz), 130.2 (dq, *J* = 32.1 Hz), 129.8 (d, *J* = 6.5 Hz), 129.6, 128.8, 126.0 (m), 125.3 (dq, *J* = 271.0 Hz), 125.9, 105.2 (d, *J* = 9.4 Hz), 63.4 (d, *J* = 7.6 Hz), 47.3 (d, *J* = 5.1 Hz), 46.1 (d, *J* = 123.5 Hz), 16.6 (d, *J* = 5.4 Hz). ³¹P NMR (162 MHz, CDCl₃) 16.35 (d, *J* = 1.9 Hz). IR (KBr, cm⁻¹): 2925, 1619, 1167, 1069, 1011, 771. HRMS (ESI) calcd. for C₂₆H₂₁F₆O₃P (M + H⁺) *m/z* 527.1205, found 527.1207.

***rel*-(2*R*,3*R*,4*R*)-2-Ethoxy-4-(4-fluorophenyl)-6-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3f)**



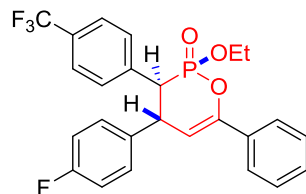
(±)

White solid (68 mg, 71 %). M.p. 135–136 °C ¹H NMR (400

MHz, CDCl₃): 7.81–7.68 (m, 2H), 7.45–7.37 (m, 5H), 7.11–7.03 (m, 2H), 6.91–6.81 (m, 4H), 5.82 (m, 1H), 4.59–4.51 (m, 1H), 4.39–4.28 (m, 2H), 3.65 (dd, *J* = 21.8, 6.7 Hz, 1H), 1.38 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): 162.0 (d, *J* = 246.6 Hz), 150.0 (d, *J* = 7.3 Hz), 136.3, 134.6 (dd, *J* = 10.2, 2.7 Hz), 130.5 (d, *J* = 8.5 Hz), 130.3 (d, *J* = 8.0 Hz), 130.0, 129.6 (d, *J* = 13.1 Hz), 129.3, 128.8, 115.2 (d, *J* = 21.4 Hz), 104.7 (d, *J* = 12 Hz), 63.1 (d, *J* = 7.0 Hz), 45.2 (d, *J* = 5.2 Hz), 43.5 (d, *J* = 125.0 Hz), 16.6 (d, *J* = 5.2 Hz). ³¹P NMR (162 MHz, CDCl₃) 17.85. IR (KBr, cm⁻¹): 3443, 1620, 1509, 1326, 1010, 772. HRMS (ESI) calcd. for C₂₅H₂₁F₄O₃P (M + H⁺) *m/z*

477.1237, found 477.1239.

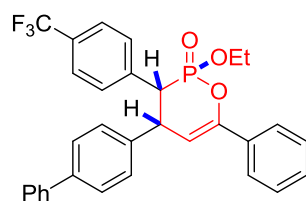
***rel*-(2*R*,3*S*,4*R*)-2-Ethoxy-4-(4-fluorophenyl)-6-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*trans,trans*)-3f)**



(±)

Colorless oil liquid (19 mg, 20 %). ¹H NMR (400 MHz, DMSO-*d*₆): 7.72–7.53 (m, 6H), 7.45–7.28 (m, 5H), 7.01 (t, *J* = 8.7 Hz, 2H), 5.82 (m, 1H), 4.49–4.46 (m, 1H), 4.25–4.07 (m, 3H), 1.22 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆): 161.1 (d, *J* = 242.7 Hz), 146.7 (d, *J* = 7.2 Hz), 138.2, (d, *J* = 7.8 Hz), 137.3 (d, *J* = 14.2 Hz), 133.3, (d, *J* = 6.5 Hz), 130.2 (q, *J* = 11.4 Hz), 129.0, 128.7 (d, *J* = 9.1 Hz), 128.0, 127.7 (d, *J* = 3.6 Hz), 125.1, 124.4, 122.8, 115.2 (d, *J* = 21.2 Hz), 107.7 (d, *J* = 8.5 Hz), 62.4 (d, *J* = 7.4 Hz), 44.9 (d, *J* = 4.6 Hz), 43.7 (d, *J* = 120.7 Hz), 16.2 (d, *J* = 4.4 Hz). ³¹P NMR (162 MHz, DMSO-*d*₆) 17.54. IR (KBr, cm⁻¹): 3443, 1620, 1509, 1326, 1010, 772. HRMS (ESI) calcd. for C₂₅H₂₁F₄O₃P (M + H⁺) *m/z* 477.1237, found 477.1239.

***rel*-(2*R*,3*R*,4*R*)-4-([1,1'-Biphenyl]-4-yl)-2-ethoxy-6-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3g)**

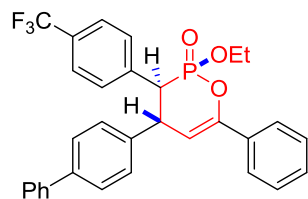


(±)

Colorless oil liquid (47 mg, 44 %). ¹H NMR (400 MHz, CDCl₃): 7.77 (dd, *J* = 7.9 Hz, 1.6 Hz, 2H), 7.56–7.29 (m, 12H), 7.14 (d, *J* = 7.9 Hz, 2H), 7.01 (d, *J* = 8.2 Hz, 2H), 5.92 (m, 1H), 4.63 (dt, *J* = 2.9, 7.1 Hz, 1H), 4.44–4.30 (m, 2H), 3.71 (dd, *J* = 21.8, 6.7 Hz, 1H), 1.41 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): 150.0 (d, *J* = 7.4 Hz), 140.3 (d, *J* = 17.8 Hz), 138.0 (d, *J* = 10.6 Hz), 136.4, 133.7 (d, *J* = 6.4 Hz), 130.6, (d, *J* = 8.4 Hz), 130.3, 130.0, 129.6, 129.5, 129.4, 129.1, 128.9 (d, *J* = 8.9 Hz), 127.3 (q, *J* = 44.4 Hz), 127.0 (d, *J* = 8.2 Hz), 125.4 (d, *J* = 3.1

Hz), 124.9, 105.0 (d, $J = 11.9$ Hz), 63.1 (d, $J = 7.0$ Hz), 45.5 (d, $J = 5.4$ Hz), 43.5 (d, $J = 124.6$ Hz), 16.7 (d, $J = 5.2$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 18.09 (d, $J = 1.1$ Hz). IR (KBr, cm^{-1}): 3030, 1654, 1487 1269, 1124, 1009, 765. HRMS (ESI) calcd. for $\text{C}_{31}\text{H}_{26}\text{F}_3\text{O}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 535.1644, found 535.1649.

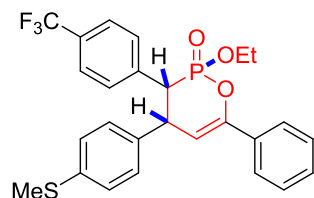
***rel*-(2*R*,3*S*,4*R*)-4-([1,1'-Biphenyl]-4-yl)-2-ethoxy-6-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*trans,trans*)-3g)**



(±)

Colorless oil liquid (43 mg, 40 %). ^1H NMR (400 MHz, CDCl_3): 7.59 (d, $J = 8.5$ Hz, 2H), 7.50 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 8.3$ Hz, 4H), 7.27–7.16 (m, 4H), 7.04 (d, $J = 7.0$ Hz, 2H), 5.72 (m, 1H), 4.33–4.22 (m, 3H), 3.56 (dd, $J = 21.6, 12.2$ Hz, 1H), 1.36 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 147.7 (d, $J = 7.1$ Hz), 140.8 (d, $J = 13.6$ Hz), 136.9, 135.3, 132.1 (d, $J = 6.4$ Hz), 129.8 (d, $J = 6.4$ Hz), 129.08 (d, $J = 7.9$ Hz), 127.8 (d, $J = 11.5$ Hz), 127.4, 127.0 (d, $J = 5.1$ Hz), 126.7 (d, $J = 9.3$ Hz), 126.1, 125.6 (d, $J = 31.3$ Hz), 125.4 (d, $J = 9.2$ Hz), 123.3, 107.4 (d, $J = 9.2$ Hz), 63.3 (d, $J = 7.5$ Hz), 47.5 (d, $J = 5.0$ Hz), 46.2 (d, $J = 122.6$ Hz), 16.6 (d, $J = 5.2$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 17.15. IR (KBr, cm^{-1}): 3030, 1654, 1487 1269, 1124, 1009, 765. HRMS (ESI) calcd. for $\text{C}_{31}\text{H}_{26}\text{F}_3\text{O}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 535.1644, found 535.1649.

***rel*-(2*R*,3*R*,4*R*)-2-Ethoxy-4-(4-(methylthiophenyl)-6-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3h)**

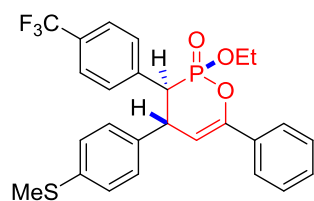


(±)

Colorless oil liquid (48 mg, 47 %). ^1H NMR (400 MHz, CDCl_3): 7.74 (dd, $J = 7.7, 1.7$ Hz, 2H), 7.47–7.37 (m, 5H), 7.11 (d, $J = 7.9$ Hz, 2H), 7.02 (d, $J = 8.3$ Hz, 2H), 6.84 (d, $J = 8.3$ Hz, 2H), 5.83 (m, 1H), 4.52 (dt, $J = 2.9, 7.4$

Hz, 1H), 4.39–4.28 (m, 2H), 3.65 (dd, $J = 21.8, 6.7$ Hz, 1H), 2.41 (s, 3H), 1.38 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 149.9 (d, $J = 7.3$ Hz), 137.7, 136.4, 135.6 (d, $J = 10.7$ Hz), 133.6 (d, $J = 6.4$ Hz), 130.5, (d, $J = 8.4$ Hz), 129.9, 129.5 (d, $J = 12.3$ Hz), 129.2, 128.8 126.3, 125.4 (d, $J = 3.2$ Hz), 124.8, 122.7, 104.9 (d, $J = 12.0$ Hz), 63.1 (d, $J = 7.0$ Hz), 45.3 (d, $J = 5.2$ Hz), 43.5 (d, $J = 124.5$ Hz), 16.7 (d, $J = 5.2$ Hz), 15.8. IR (KBr, cm^{-1}): 2984, 1619, 1326, 1269, 1166, 1010. ^{31}P NMR (162 MHz, CDCl_3) 18.03 (d, $J = 1.0$ Hz). HRMS (ESI) calcd. for $\text{C}_{26}\text{H}_{24}\text{F}_3\text{O}_3\text{PS}$ ($\text{M} + \text{H}^+$) m/z 505.1209, found 505.1208.

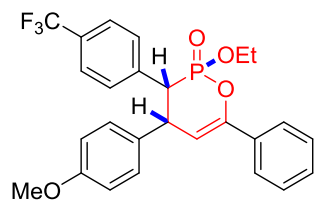
***rel*-(2*R*,3*S*,4*R*)-2-Ethoxy-4-(4-(methylthiophenyl)-6-phenyl-3-(4-(trifluoromethyl)phenyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*trans,trans*)-3h)**



(±)

Yellow solid (41 mg, 41 %). M.p. 172–174 °C. ^1H NMR (400 MHz, CDCl_3): 7.65 (dd, $J = 7.4, 2.1$ Hz, 2H), 7.52 (d, $J = 8.2$ Hz, 2H), 7.42–7.37 (m, 5H), 7.10–7.07 (m, 2H), 6.97 (d, $J = 8.3$ Hz, 2H), 5.71–5.69 (m, 2H), 4.31–4.22 (m, 3H), 3.53 (dd, $J = 21.6, 12.2$ Hz, 1H), 2.41 (s, 3H), 1.36 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 148.7 (d, $J = 7.2$ Hz), 138.0, 137.7 (d, $J = 13.9$ Hz), 137.0 (d, $J = 7.3$ Hz), 133.5 (d, $J = 6.7$ Hz), 130.8 (d, $J = 6.5$ Hz), 129.8 (d, $J = 6.4$ Hz), 129.4 (d, $J = 13.6$ Hz), 128.9, 128.7, 128.3, 126.8, 125.6 (q, $J = 35.2$ Hz), 124.8, 122.7, 106.9 (d, $J = 9.1$ Hz), 63.1 (d, $J = 7.5$ Hz), 47.0 (d, $J = 5.0$ Hz), 46.2 (d, $J = 122.3$ Hz), 16.5 (d, $J = 5.3$ Hz), 15.6. ^{31}P NMR (162 MHz, CDCl_3) 17.09 (d, $J = 2.1$ Hz). IR (KBr, cm^{-1}): 2924, 1618, 1493, 1274, 1122, 1014, 814. HRMS (ESI) calcd. for $\text{C}_{26}\text{H}_{24}\text{F}_3\text{O}_3\text{PS}$ ($\text{M} + \text{H}^+$) m/z 505.1209, found 505.1208.

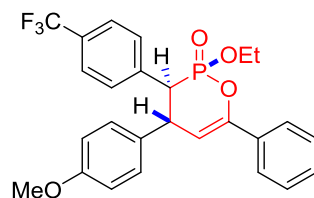
***rel*-(2*R*,3*R*,4*R*)-2-Ethoxy-4-(4-(methoxy)-phenyl)-6-phenyl-3-(4-(trifluoromethyl)phenyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3i)**



(±)

Colorless oil liquid (63 mg, 65 %). ^1H NMR (400 MHz, CDCl_3): 7.75 (d, $J = 6.6$ Hz, 2H), 7.49–7.33 (m, 5H), 7.11 (d, $J = 7.9$ Hz, 2H), 6.84 (d, $J = 8.5$ Hz, 2H), 6.67 (d, $J = 8.5$ Hz, 2H), 5.85 (m, 1H), 4.53 (dt, $J = 2.6, 7.5$ Hz, 1H), 4.39–4.29 (m, 2H), 3.73 (s, 3H), 3.64 (dd, $J = 21.7, 6.7$ Hz, 1H), 1.39 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 158.8, 149.6 (d, $J = 7.2$ Hz), 136.6, 133.7 (d, $J = 6.4$ Hz), 130.9 (d, $J = 10.6$ Hz), 130.6 (d, $J = 8.4$ Hz), 129.8, 129.4 (d, $J = 7.2$ Hz), 128.8, 125.5, 125.3 (d, $J = 3.0$ Hz), 124.8, 122.8, 113.7, 105.4 (d, $J = 11.8$ Hz), 63.0 (d, $J = 7.0$ Hz), 55.3, 45.1 (d, $J = 5.3$ Hz), 43.7 (d, $J = 124.1$ Hz), 16.6 (d, $J = 5.2$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 18.33. IR (KBr, cm^{-1}): 2933, 1724, 1611, 1512, 1326, 1257, 1010. HRMS (ESI) calcd. for $\text{C}_{26}\text{H}_{24}\text{F}_3\text{O}_4\text{P}$ ($\text{M} + \text{H}^+$) m/z 489.1437, found 489.1444.

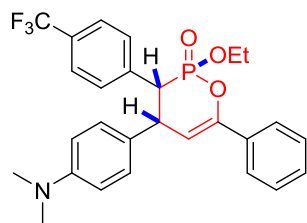
***rel*-(2*R*,3*S*,4*R*)-2-Ethoxy-4-(4-(methoxy)-phenyl)-6-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*trans,trans*)-3i)**



(±)

Yellow solid (11 mg, 11 %). M.p. 134–136 °C. ^1H NMR (400 MHz, CDCl_3): 7.69–7.63 (m, 2H), 7.51 (d, $J = 8.0$ Hz, 2H), 7.44–7.34 (m, 5H), 6.96 (d, $J = 8.4$ Hz, 2H), 6.73 (d, $J = 8.4$ Hz, 2H), 5.72 (m, 1H), 4.31–4.22 (m, 3H), 3.73 (s, 3H), 3.52 (dd, $J = 21.4, 12.2$ Hz, 1H), 1.36 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR data could not be obtained because of less amount. ^{31}P NMR (162 MHz, CDCl_3) 17.37. IR (KBr, cm^{-1}): 2936, 1724, 1611, 1512, 1326, 1155, 1032. HRMS (ESI) calcd. for $\text{C}_{26}\text{H}_{24}\text{F}_3\text{O}_4\text{P}$ ($\text{M} + \text{H}^+$) m/z 489.1437, found 489.1444.

***rel*-(2*R*,3*R*,4*R*)-4-(4-(Dimethylamino)-phenyl)-2-ethoxy-6-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3j)**

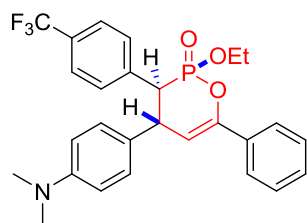


(±)

Yellow oil liquid (58 mg, 57 %). ¹H NMR (400 MHz, CDCl₃):

7.75 (d, *J* = 7.4 Hz, 2H), 7.46–7.34 (m, 5H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.76 (d, *J* = 8.2 Hz, 2H), 6.49 (d, *J* = 8.2 Hz, 2H), 5.86 (m, 1H), 4.48 (t, *J* = 5.6 Hz, 1H), 4.38–4.27 (m, 2H), 3.63 (dd, *J* = 21.6, 6.6 Hz, 1H), 3.63 (s, 6H), 1.39 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): 149.8, 149.3 (d, *J* = 7.2 Hz), 136.9, 133.9 (d, *J* = 6.5 Hz), 130.6 (d, *J* = 8.4 Hz), 129.7, 129.3 (d, *J* = 12.5 Hz), 128.8, 126.4 (d, *J* = 11.0 Hz), 125.6, 125.3 (d, *J* = 2.9 Hz), 124.8, 122.8, 112.7, 106.0 (d, *J* = 11.6 Hz), 62.9 (d, *J* = 7.0 Hz), 45.1 (d, *J* = 5.3 Hz), 43.8 (d, *J* = 123.1 Hz), 40.6, 16.7 (d, *J* = 5.3 Hz). ³¹P NMR (162 MHz, CDCl₃) 18.75. IR (KBr, cm⁻¹): 2928, 1679, 1523, 1326, 1269, 1222, 1010. HRMS (ESI) calcd. for C₂₇H₂₇F₃NO₃P (M + H⁺) *m/z* 502.1753, found 502.1757.

***rel*-(2*R*,3*S*,4*R*)-4-(4-(Dimethylamino)-phenyl)-2-ethoxy-6-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*trans,trans*)-3j)**



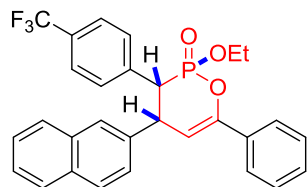
(±)

Yellow solid (24 mg, 24 %). M.p. 133–134 °C. ¹H NMR (400

MHz, CDCl₃): 7.65 (d, *J* = 7.4 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.41–7.35 (m, 5H), , 6.91 (d, *J* = 8.3 Hz, 2H), 6.55 (d, *J* = 8.3 Hz, 2H), 5.74 (m, 1H), 4.35–4.07 (m, 3H), 3.54 (dd, *J* = 21.4, 12.1 Hz, 1H), 2.88 (s, 6H), 1.35 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): 149.7, 147.9 (d, *J* = 7.0 Hz), 137.4 (d, *J* = 18.1 Hz), 133.6 (d, *J* = 6.9 Hz), 130.7 (d, *J* = 6.5 Hz), 130.3 (d, *J* = 18.1 Hz), 129.8 (d, *J* = 6.4 Hz), 128.9 (d, *J* = 24.0 Hz), 128.5 (d, *J* = 9.4 Hz), 129.8 (d, *J* = 6.4 Hz), 125.4, 112.5, 111.6, 107.9 (d, *J* = 8.8 Hz), 62.8 (d, *J* = 7.5 Hz), 46.5 (d, *J* = 5.0 Hz), 46.3 (d, *J* = 120.9 Hz), 40.4, 16.4 (d, *J* = 5.3 Hz). ³¹P NMR (162 MHz, CDCl₃) 17.84 (d, *J* = 2.0 Hz). IR (KBr, cm⁻¹): 2936, 1613, 1326, 1269, 1110. HRMS (ESI) calcd. for C₂₇H₂₇F₃NO₃P (M + H⁺) *m/z*

502.1753, found 502.1757.

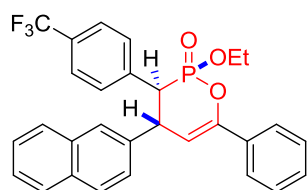
***rel*-(2*R*,3*R*,4*R*)-2-Ethoxy-4-(naphthalen-2-yl)-6-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3k)**



(±) Colorless oil liquid (75 mg, 74 %). ¹H NMR (400 MHz,

CDCl₃): 7.81–7.72 (m, 3H), 7.66–7.59 (m, 2H), 7.50–7.40 (m, 6H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.99 (dd, *J* = 8.5, 1.5 Hz, 1H), 5.97 (m, 1H), 4.76 (dt, *J* = 2.7, 6.6 Hz, 1H), 4.46–4.32 (m, 2H), 3.76 (dd, *J* = 21.9, 6.6 Hz, 1H), 1.43 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): 148.5 (d, *J* = 7.2 Hz), 133.4 (d, *J* = 6.8 Hz), 133.3, 132.6, 129.7 (d, *J* = 6.6 Hz), 129.2, 128.8, 128.6, 127.7 (d, *J* = 3.5 Hz), 126.9, 126.4, 126.1, 125.6 (q, *J* = 2.9 Hz), 125.4, 124.7, 106.9 (d, *J* = 9.3 Hz), 63.1 (d, *J* = 7.4 Hz), 47.5 (d, *J* = 5.3 Hz), 45.9 (d, *J* = 122.6 Hz), 16.5 (d, *J* = 5.4 Hz). ³¹P NMR (162 MHz, CDCl₃) 18.08. IR (KBr, cm⁻¹): 2971, 1394, 1219, 1066, 913, 773, 747. HRMS (ESI) calcd. for C₂₉H₂₄F₃O₃P (M + H⁺) *m/z* 509.1488, found 509.1487.

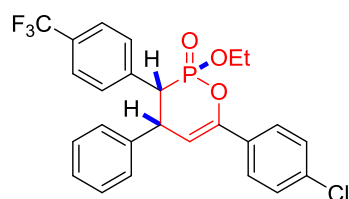
***rel*-(2*R*,3*S*,4*R*)-2-ethoxy-4-(naphthalen-2-yl)-6-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*trans,trans*)-3k)**



(±) Yellow oil (10 mg, 9 %). ¹H NMR (400 MHz, CDCl₃) 7.78–

7.65 (m, 5H), 7.52–7.37 (m, 10H), 7.20 (dd, *J* = 8.5, 1.6 Hz, 1H), 5.79 (m, 1H), 4.47 (dt, *J* = 3.2, 5.6 Hz, 1H), 3.71 (dd, *J* = 21.7, 12.2 Hz, 1H), 1.38 (t, *J* = 7.1 Hz, 3H). ¹³C NMR data could not be obtained because of less amount. ³¹P NMR (162 MHz, CDCl₃) 17.09 (d, *J* = 1.6 Hz). IR (KBr, cm⁻¹): 2971, 1394, 1219, 1066, 913, 773, 747. HRMS (ESI) calcd. for C₂₉H₂₄F₃O₃P (M + H⁺) *m/z* 509.1488, found 509.1487.

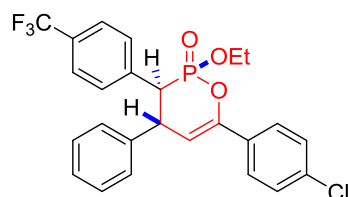
***rel*-(2*R*,3*R*,4*R*)-6-(4-Chlorophenyl)-2-ethoxy-4-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3l)**



(±)

Colorless oil liquid (73 mg, 74%). ¹H NMR (400 MHz, CDCl₃): 7.68 (d, *J* = 8.5 Hz, 2H), 7.38 (dd, *J* = 21.7, 8.3 Hz, 4H), 7.18–7.11 (m, 3H), 7.06 (d, *J* = 7.9 Hz, 2H), 6.96–6.88 (m, 2H), 5.86 (m, 1H), 4.57 (dt, *J* = 2.7, 7.0 Hz, 1H), 4.40–4.29 (m, 2H), 3.67 (dd, *J* = 21.8, 6.7 Hz, 1H), 1.39 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): 149.0 (d, *J* = 7.2 Hz), 138.7 (d, *J* = 10.6 Hz), 136.3, 135.4, 132.1 (d, *J* = 6.5 Hz), 130.4 (d, *J* = 8.5 Hz), 129.7 (d, *J* = 32.4 Hz), 129.0, 128.6, 128.4, 127.5, 125.9 (d, *J* = 32.7 Hz), 125.3 (d, *J* = 3.1 Hz), 122.7, 105.4 (d, *J* = 9.3 Hz), 63.2 (d, *J* = 7.0 Hz), 45.8 (d, *J* = 5.3 Hz), 43.5 (d, *J* = 124.7 Hz), 16.6 (d, *J* = 5.2 Hz). ³¹P NMR (162 MHz, CDCl₃) 18.11. IR (KBr, cm⁻¹): 2930, 1615, 1491, 1325, 1125, 1020, 764. HRMS (ESI) calcd. for C₂₅H₂₁ClF₃O₃P (M + H⁺) *m/z* 493.0942, found 493.0947.

***rel*-(2*R*,3*S*,4*R*)-6-(4-Chlorophenyl)-2-ethoxy-4-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*trans,trans*)-3l)**

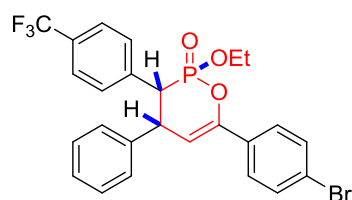


(±)

Yellow oil liquid (13 mg, 13%). ¹H NMR (400 MHz, CDCl₃): 7.59 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 4H), 7.24–7.16 (m, 3H), 7.04 (d, *J* = 7.0 Hz, 2H), 5.72 (m, 1H), 4.36–4.22 (m, 3H), 3.56 (dd, *J* = 21.6, 12.2 Hz, 1H), 1.36 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): 147.2 (d, *J* = 7.1 Hz), 140.8 (d, *J* = 13.6 Hz), 136.9 (d, *J* = 8.0 Hz), 135.3, 132.1 (d, *J* = 6.4 Hz), 129.9 (dq, *J* = 70.9 Hz), 129.8 (d, *J* = 6.4 Hz), 129.0 (d, *J* = 7.4 Hz), 127.8 (d, *J* = 11.5 Hz), 125.4 (dq, *J* = 271.0 Hz), 126.1, 125.7, 107.4 (d, *J* = 9.2 Hz), 63.2 (d, *J* = 7.5

Hz), 47.5 (d, $J = 5.0$ Hz), 46.2 (d, $J = 122.6$ Hz), 16.6 (d, $J = 5.2$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 17.14. IR (KBr, cm^{-1}): 2930, 1615, 1491, 1325, 1125, 1020, 764. HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{21}\text{ClF}_3\text{O}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 493.0942, found 493.0947.

***rel*-(2*R*,3*R*,4*R*)-6-(4-Bromophenyl)-2-ethoxy-4-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3m)**

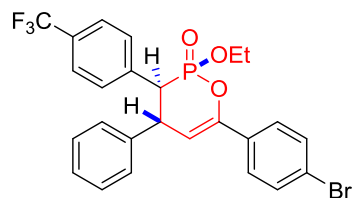


(±)

Colorless oil (86 mg, 81 %). ^1H NMR (400 MHz, CDCl_3):

7.62–7.55 (m, 4H), 7.35 (d, $J = 8.1$ Hz, 2H), 7.15–7.11 (m, 3H), 7.06 (d, $J = 7.9$ Hz, 2H), 6.92–6.90 (m, 2H), 5.88 (d, $J = 1.1$ Hz, 1H), 4.55 (td, $J = 7.0$ Hz, 2.9 Hz, 1H), 4.43–4.27 (m, 2H), 3.67 (dd, $J = 21.8$, 6.7 Hz, 1H), 1.39 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 149.0 (d, $J = 7.2$ Hz), 138.6 (d, $J = 10.7$ Hz), 136.3, 132.6 (d, $J = 6.6$ Hz), 132.0, 130.4 (d, $J = 8.5$ Hz), 129.9 (d, $J = 1.8$ Hz), 129.6 (d, $J = 2.0$ Hz), 128.5 (d, $J = 22.8$ Hz), 127.5, 126.3, 125.3 (d, $J = 3.5$ Hz), 122.7, 105.5 (d, $J = 12.1$ Hz), 63.2 (d, $J = 7.0$ Hz), 45.8 (d, $J = 5.5$ Hz), 43.5 (d, $J = 124.7$ Hz), 16.6 (d, $J = 5.3$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 18.11. IR (KBr, cm^{-1}): 2998, 1619, 1489, 1326, 1270, 761, 607. HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{21}\text{BrF}_3\text{O}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 537.0437, found 537.0436.

***rel*-(2*R*,3*S*,4*R*)-6-(4-Bromophenyl)-2-ethoxy-4-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*trans,trans*)-3m)**



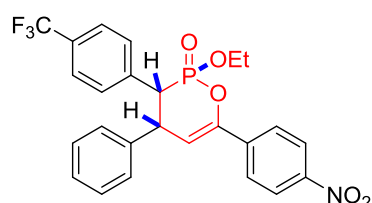
(±)

Yellow oil (15 mg, 14 %). ^1H NMR (400 MHz, CDCl_3):

7.52–7.49 (m, 6H), 7.35 (d, $J = 7.0$ Hz, 2H), 7.25–7.17 (m, 3H), 7.06–7.02 (m, 2H), 5.78–5.70 (m, 1H), 4.33–4.21 (m, 3H), 3.56 (dd, $J = 21.6$, 12.3 Hz, 1H), 1.36 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 147.7 (d, $J = 7.3$ Hz), 140.8 (d, $J = 13.9$ Hz),

136.9 (d, $J = 8.8$ Hz), 132.5 (d, $J = 6.9$ Hz), 131.9, 129.8 (d, $J = 6.6$ Hz), 129.0, 127.9, 127.8, 126.4, 125.7 (dt, $J = 3.2, 3.2$ Hz), 125.4, 123.5, 122.7, 107.5 (d, $J = 9.2$ Hz), 63.3 (d, $J = 7.5$ Hz), 47.5 (d, $J = 5.2$ Hz), 46.1 (d, $J = 122.8$ Hz), 16.6 (d, $J = 5.4$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 17.13 (d, $J = 2.0$ Hz). IR (KBr, cm^{-1}): 2998, 1619, 1489, 1326, 1270, 761, 607. HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{21}\text{ClF}_3\text{O}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 493.0942, found 493.0947.

***rel*-(2*R*,3*R*,4*R*)-6-(4-Nitrophenyl)-2-ethoxy-4-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide (*cis,cis*)-3n)**

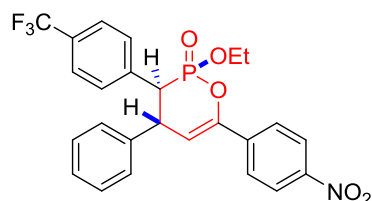


(±)

Yellow oil (42 mg, 42 %). ^1H NMR (400 MHz, CDCl_3):

8.28 (d, $J = 8.9$ Hz, 2H), 7.90 (d, $J = 8.9$ Hz, 2H), 7.36 (d, $J = 8.1$ Hz, 2H), 7.20–7.13 (m, 3H), 7.05 (d, $J = 7.9$ Hz, 2H), 6.95–6.87 (m, 2H), 6.09 (d, $J = 1.6$ Hz, 1H), 4.60 (dt, $J = 3.0, 8.4$ Hz, 1H), 4.42–4.28 (m, 2H), 3.71 (dd, $J = 21.9, 6.8$ Hz, 1H), 1.39 (t, $J = 7.1, 3\text{H}$). ^{13}C NMR (101 MHz, CDCl_3): 148.2, 148.0 (d, $J = 7.0$ Hz), 139.5 (d, $J = 6.4$ Hz), 138.0 (d, $J = 10.2$ Hz), 136.0, 130.4 (d, $J = 8.5$ Hz), 128.6 (d, $J = 20.3$ Hz), 127.8, 125.5, 125.4 (d, $J = 3.1$ Hz), 124.1, 122.7, 109.2 (d, $J = 12.0$ Hz), 63.5 (d, $J = 6.9$ Hz), 46.1 (d, $J = 5.3$ Hz), 43.4 (d, $J = 124.9$ Hz), 16.7 (d, $J = 5.1$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 17.98. IR (KBr, cm^{-1}): 1621, 1504, 1336, 1148, 913, 878, 747. HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{21}\text{F}_3\text{NO}_5\text{P}$ ($\text{M} + \text{H}^+$) m/z 504.1182, found 504.1188.

***rel*-(2*R*,3*R*,4*R*)-6-(4-Nitrophenyl)-2-ethoxy-4-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide (*trans,trans*)-3n)**

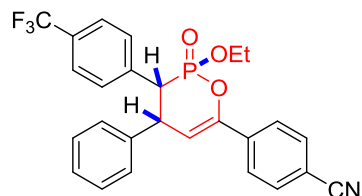


(±)

Yellow oil (1 mg, 1 %). NMR data could not be obtained.

because of its less amount.

***rel*-4-((2*R*,3*R*,4*R*)-2-Ethoxy-2-oxido-4-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinin-6-yl)benzonitrile ((*cis,cis*)-3o)**

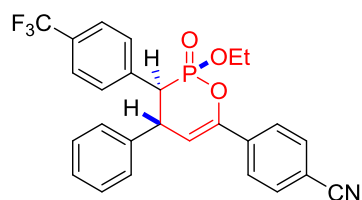


(±)

Colorless oil (35 mg 36 %). ¹H NMR (400 MHz, CDCl₃):

7.84 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.17–7.11 (m, 3H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.94–6.87 (m, 2H), 6.02 (m, 1H), 4.61–4.55 (m, 1H), 4.40–4.30 (m, 2H), 3.70 (dd, *J* = 21.9, 6.7 Hz, 1H), 1.38 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): 148.2 (d, *J* = 7.0 Hz), 138.2 (d, *J* = 10.2 Hz), 137.7 (d, *J* = 6.4 Hz), 136.0, 132.6, 130.4 (d, *J* = 8.5 Hz), 130.1, 129.7, 128.6 (d, *J* = 19.4 Hz), 127.7, 125.4 (d, *J* = 3.2 Hz), 125.3, 122.7, 118.5, 112.9, 108.4 (d, *J* = 12.1 Hz), 63.4 (d, *J* = 7.0 Hz), 46.0 (d, *J* = 5.3 Hz), 43.5 (d, *J* = 124.9 Hz), 16.7 (d, *J* = 5.1 Hz). ³¹P NMR (162 MHz, CDCl₃) 18.00. IR (KBr, cm⁻¹): 3005, 2228, 1325, 1275, 1010, 750. HRMS (ESI) calcd. for C₂₆H₂₁F₃NO₃P (M + H⁺) *m/z* 484.1284, found 484.1286.

***rel*-4-((2*R*,3*S*,4*R*)-2-Ethoxy-2-oxido-4-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinin-6-yl)benzonitrile ((*trans,trans*)-3o)**



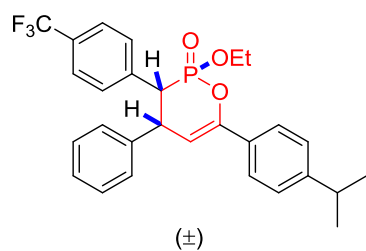
(±)

Colorless oil (27 mg, 28 %). ¹H NMR (400 MHz, CDCl₃):

7.79–7.65 (m, 4H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.37 (t, *J* = 8.3 Hz, 2H), 7.24–7.15 (m, 3H), 7.04 (d, *J* = 7.3 Hz, 2H), 5.88 (s, 1H), 4.36–4.21 (m, 3H), 3.59 (dd, *J* = 21.6, 12.3 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): 147.0 (d, *J* = 7.0 Hz), 140.3 (d, *J* = 13.9 Hz), 137.7 (d, *J* = 6.9 Hz), 136.5 (d, *J* = 7.4 Hz), 132.6 (d, *J* = 14.4 Hz), 130.8 (d, *J* = 6.4 Hz), 130.4, 129.8 (d, *J* = 6.4 Hz), 129.1 (d, *J* = 10.0 Hz), 128.9

(d, $J = 3.9$ Hz), 127.9 (d, $J = 9.2$ Hz), 125.8, 125.3 (d, $J = 8.5$ Hz), 122.7, 118.5, 112.8, 110.2 (d, $J = 9.1$ Hz), 63.5 (d, $J = 7.5$ Hz), 47.5 (d, $J = 5.2$ Hz), 46.0 (d, $J = 122.8$ Hz), 16.6 (d, $J = 5.2$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 17.01. IR (KBr, cm^{-1}): 3005, 2228, 1325, 1275, 1010, 750. HRMS (ESI) calcd. for $\text{C}_{26}\text{H}_{21}\text{F}_3\text{NO}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 484.1284, found 484.1286.

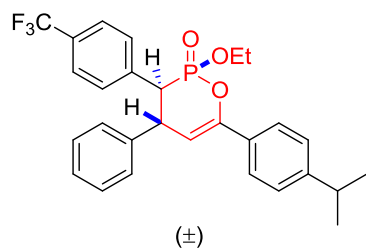
***rel*-(2*R*,3*R*,4*R*)-6-(4-Isopropenyl)-2-ethoxy-4-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3p)**



Colorless oil (78 mg, 78 %). ^1H NMR (400 MHz, CDCl_3):

7.70 (d, $J = 8.3$ Hz, 2H), 7.33 (dd, $J = 12.2, 8.3$ Hz, 4H), 7.17–7.06 (m, 5H), 6.92 (dd, $J = 6.4, 2.9$ Hz, 2H), 5.84 (s, 1H), 4.59 (dt, $J = 2.8, 6.4$ Hz, 1H), 4.43–4.30 (m, 2H), 3.65 (dd, $J = 21.8, 6.7$ Hz, 1H), 3.04–2.91 (m, 1H), 1.41 (t, $J = 7.1$ Hz, 3H), 1.30 (d, $J = 6.9$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3): 150.5, 145.0 (d, $J = 7.4$ Hz), 139.2 (d, $J = 11.1$ Hz), 136.5, 131.3 (d, $J = 6.5$ Hz), 130.5 (d, $J = 8.4$ Hz), 129.8 (d, $J = 2.0$ Hz), 129.5 (d, $J = 1.9$ Hz), 128.5 (d, $J = 22.3$ Hz), 127.4, 126.9, 125.3 (q, $J = 3.4$ Hz), 124.8, 122.8, 104.1 (d, $J = 12.1$ Hz), 63.0 (d, $J = 7.1$ Hz), 45.7 (d, $J = 5.6$ Hz), 43.6 (d, $J = 124.6$ Hz), 34.1, 24.0 (d, $J = 2.7$ Hz), 16.7 (d, $J = 5.4$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 18.13 (d, $J = 1.0$ Hz). IR (KBr, cm^{-1}): 2963, 1326, 1271, 1166, 1125, 1007, 763. HRMS (ESI) calcd. for $\text{C}_{28}\text{H}_{28}\text{F}_3\text{O}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 501.1801, found 501.1807.

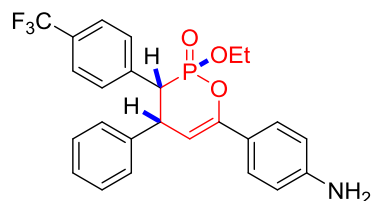
***rel*-(2*R*,3*S*,4*R*)-6-(4-Isopropenyl)-2-ethoxy-4-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*trans,trans*)-3p)**



Colorless liquid (20 mg, 20 %). ^1H NMR (400 MHz,

CDCl₃): 7.61 (d, $J = 8.3$ Hz, 2H), 7.52 (d, $J = 8.2$ Hz, 2H), 7.38 (d, $J = 7.0$ Hz, 2H), 7.29–7.15 (m, 5H), 7.06 (dd, $J = 7.5, 1.5$ Hz, 5H), 5.73–5.69 (m, 1H), 4.37–4.23 (m, 3H), 3.57 (dd, $J = 21.5, 12.2$ Hz, 1H), 3.02–2.88 (m, 1H), 1.38 (t, $J = 7.1$ Hz, 3H), 1.29 (d, $J = 6.9$ Hz, 6H). ¹³C NMR (101 MHz, CDCl₃): 150.4, 148.7 (d, $J = 7.3$ Hz), 141.2 (d, $J = 13.9$ Hz), 137.2 (d, $J = 7.8$ Hz), 131.1 (d, $J = 6.7$ Hz), 129.8 (d, $J = 6.6$ Hz), 128.9, 128.7 (d, $J = 2.6$ Hz), 127.9, 127.6, 126.8, 125.7 (q, $J = 3.0$ Hz), 124.8, 122.8, 106.1 (d, $J = 9.3$ Hz), 63.1 (d, $J = 7.5$ Hz), 47.6 (d, $J = 5.3$ Hz), 46.4 (d, $J = 122.7$ Hz), 34.1, 24.0 (d, $J = 2.7$ Hz), 16.6 (d, $J = 5.5$ Hz). ³¹P NMR (162 MHz, CDCl₃) 17.18 (d, $J = 1.9$ Hz). IR (KBr, cm⁻¹): 2971, 1618 1326, 1271, 1124, 1007, 763. HRMS (ESI) calcd. for C₂₈H₂₈F₃O₃P (M + H⁺) m/z 501.1801, found 501.1807.

***rel*-(2*R*,3*R*,4*R*)-6-(4-Aminopropenyl)-2-ethoxy-4-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3q)**

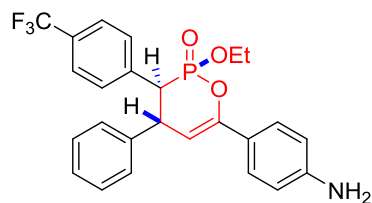


(±)

Yellow oil (54 mg, 57 %). ¹H NMR (400 MHz, CDCl₃):

7.54 (d, $J = 8.6$ Hz, 2H), 7.33 (d, $J = 8.2$ Hz, 2H), 7.16–7.04 (m, 5H), 6.95–6.89 (m, 2H), 6.71 (d, $J = 8.6$ Hz, 2H), 5.65 (m, 1H), 4.56 (dt, $J = 2.8, 6.4$ Hz, 1H), 4.41–4.29 (m, 2H), 3.81 (s, 2H), 3.62 (dd, $J = 21.7, 6.6$ Hz, 1H), 1.40 (t, $J = 7.1$ Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): 150.1 (d, $J = 7.4$ Hz), 146.7, 139.4 (d, $J = 11.2$ Hz), 136.6, 130.5 (d, $J = 8.3$ Hz), 128.6, 128.3, 128.2, 127.3, 126.2, 125.3 (d, $J = 3.0$ Hz), 124.5 (d, $J = 6.3$ Hz), 122.8, 115.5, 101.9 (d, $J = 12.0$ Hz), 62.9 (d, $J = 7.0$ Hz), 45.6 (d, $J = 5.2$ Hz), 43.6 (d, $J = 124.6$ Hz), 16.7 (d, $J = 5.3$ Hz). ³¹P NMR (162 MHz, CDCl₃) 18.31. IR (KBr, cm⁻¹): 2961, 1756, 1355, 1225, 913, 773. HRMS (ESI) calcd. for C₂₅H₂₃F₃NO₃P (M + H⁺) m/z 474.1440, found 474.1447.

***rel*-(2*R*,3*R*,4*R*)-6-(4-Aminopropenyl)-2-ethoxy-4-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*trans,trans*)-3q)**

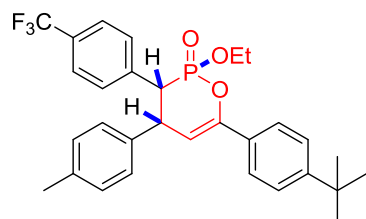


(±)

Yellow oil (1 mg, 1 %). NMR data could not be obtained

because of its less amount. It was observed in the reaction mixture.

***rel*-(2*R*,3*R*,4*R*)-6-(4-(*tert*-Butyl)phenyl)-2-ethoxy-4-(*p*-tolyl)-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3r)**

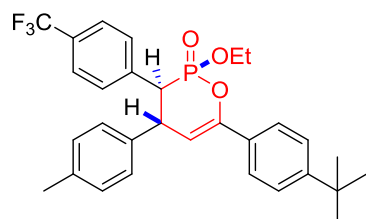


(±)

Colorless oil liquid (62 mg, 58 %). ¹H NMR (400 MHz,

CDCl₃): 7.70 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.95 (d, *J* = 7.8 Hz, 2H), 6.81 (d, *J* = 7.8 Hz, 2H), 5.84 (s, 1H), 4.59–4.52 (m, 1H), 4.46–4.28 (m, 2H), 3.64 (dd, *J* = 21.8, 6.6 Hz, 1H), 2.25 (s, 3H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.37 (s, 9H). ¹³C NMR (101 MHz, CDCl₃): 152.7, 149.8 (d, *J* = 7.3 Hz), 137.0, 136.6, 136.1 (d, *J* = 11.3 Hz), 130.9 (d, *J* = 6.6 Hz), 130.5 (d, *J* = 8.3 Hz), 129.0, 128.5, 125.7, 125.3 (d, *J* = 2.8 Hz), 124.5, 122.8, 104.5 (d, *J* = 12.0 Hz), 62.9 (d, *J* = 7.0 Hz), 45.3 (d, *J* = 5.4 Hz), 43.6 (d, *J* = 124.0 Hz), 34.9, 31.3, 16.7 (d, *J* = 5.3 Hz). ³¹P NMR (162 MHz, CDCl₃) 18.29. IR (KBr, cm⁻¹): 2964, 1514, 1326, 1270, 1126, 1020, 748. HRMS (ESI) calcd. for C₃₀H₃₂F₃O₃P (M + H⁺) *m/z* 529.2114, found 529.2120.

***rel*-(2*R*,3*S*,4*R*)-6-(4-(*tert*-Butyl)phenyl)-2-ethoxy-4-(*p*-tolyl)-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*trans,trans*)-3r)**

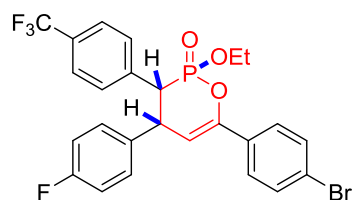


(±)

Colorless oil (26 mg, 25 %). ¹H NMR (400 MHz, CDCl₃)

7.59 (d, $J = 8.3$ Hz, 2H), 7.51 (d, $J = 8.1$ Hz, 2H), 7.45–7.35 (m, 4H), 7.00 (d, $J = 7.8$ Hz, 2H), 6.92 (d, $J = 7.8$ Hz, 2H), 5.68 (m, 1H), 4.34–4.15 (m, 3H), 3.53 (dd, $J = 21.5$, 12.2 Hz, 1H), 2.26 (s, 3H), 1.38–1.30 (m, 12H). ^{13}C NMR (101 MHz, CDCl_3): 152.4, 148.4 (d, $J = 7.0$ Hz), 138.1 (d, $J = 13.9$ Hz), 137.5 (d, $J = 4.2$ Hz), 137.3, 137.2, 135.3, 130.7 (d, $J = 6.4$ Hz), 129.7 (d, $J = 6.5$ Hz), 129.5, 127.6, 125.5, 124.4, 123.5, 106.4 (d, $J = 9.2$ Hz, 1H), 62.9 (d, $J = 7.6$ Hz), 47.0 (d, $J = 5.0$ Hz), 46.2 (d, $J = 122.3$ Hz), 34.7, 31.2, 21.0, 16.4 (d, $J = 5.4$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 17.34 (d, $J = 1.6$ Hz). IR (KBr, cm^{-1}): 2870, 1514, 1326, 1270, 1166, 1070, 812. HRMS (ESI) calcd. for $\text{C}_{30}\text{H}_{32}\text{F}_3\text{O}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 529.2114, found 529.2120.

***rel*-(2*R*,3*R*,4*R*)-6-(4-Bromophenyl)-2-ethoxy-4-(4-fluorophenyl)-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3s)**

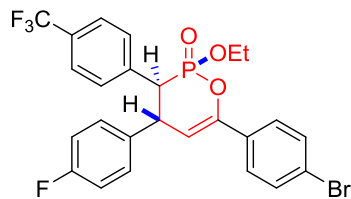


(±)

Colorless oil (72 mg, 64 %). ^1H NMR (400 MHz, CDCl_3):

7.80 (s, 1H), 7.57 (d, $J = 7.9$ Hz, 1H), 7.45 (d, $J = 7.9$ Hz, 1H), 7.31 (d, $J = 8.1$ Hz, 2H), 7.21 (dd, $J = 15.4$, 7.4 Hz, 1H), 6.99 (d, $J = 7.9$ Hz, 2H), 6.81–6.72 (m, 4H), 5.75 (m, 1H), 4.51–4.41 (m, 1H), 4.31–4.19 (m, 2H), 3.57 (dd, $J = 21.9$, 6.8 Hz, 1H), 1.29 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 162.0 (d, $J = 247$ Hz), 148.5 (d, $J = 6.8$ Hz), 136.1, 135.5 (d, $J = 6.3$ Hz), 134.2 (d, $J = 7.6$ Hz), 132.4, 130.5, 130.4, 130.3, 127.9, 125.4, 123.2 (d, $J = 33.1$ Hz), 122.7 (d, $J = 13.3$ Hz), 115.3 (q, $J = 21.5$ Hz), 106.0 (d, $J = 11.8$ Hz), 63.3 (d, $J = 6.7$ Hz), 45.2 (d, $J = 4.7$ Hz), 43.5 (d, $J = 125.1$ Hz), 16.6 (d, $J = 4.8$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 17.76. IR (KBr, cm^{-1}): 2931, 1724, 1510, 1326, 1271, 1165, 1019, 823. HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{20}\text{BrF}_4\text{O}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 555.0342, found 555.0342.

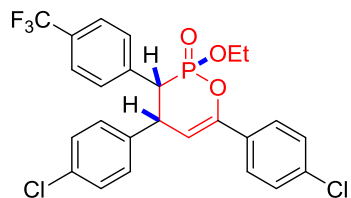
***rel*-(2*R*,3*S*,4*R*)-6-(4-Bromophenyl)-2-ethoxy-4-(4-fluorophenyl)-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*trans,trans*)-3s)**



(±)

Yellow oil (22 mg, 20 %). ^1H NMR (400 MHz, DMSO- d_6): 7.86 (s, 1H), 7.72–7.53 (m, 6H), 7.44–7.31 (m, 3H), 7.03 (t, $J = 8.7$ Hz, 2H), 6.01 (m, 1H), 4.50 (d, $J = 12.6$ Hz, 1H), 4.28–4.07 (m, 3H), 1.23 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, DMSO- d_6): 158.0 (d, $J = 490.1$ Hz), 145.6 (d, $J = 7.0$ Hz), 138.5 (d, $J = 6.7$ Hz), 137.5, 136.1, 132.2, 132.0, 131.3, 130.7 (d, $J = 7.2$ Hz), 127.4, 125.6, 123.9, 122.6, 115.6 (d, $J = 21.1$ Hz), 109.7 (d, $J = 8.8$ Hz), 63.1 (d, $J = 7.6$ Hz), 45.3 (d, $J = 5.3$ Hz), 44.0 (d, $J = 120.4$ Hz), 16.70 (d, $J = 4.3$ Hz). ^{31}P NMR (162 MHz, DMSO- d_6) 17.48. IR (KBr, cm^{-1}): 2931, 1724, 1510, 1326, 1271, 1165, 1019, 823. HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{20}\text{BrF}_4\text{O}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 555.0342, found 555.0342.

***rel*-(2*R*,3*R*,4*R*)-4,6-Bis(4-chlorophenyl)-2-ethoxy-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis*,*cis*)-3*t*)**

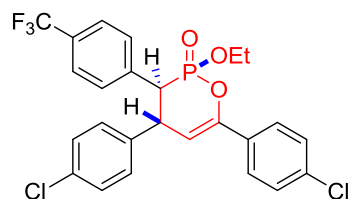


(±)

Colorless oil (63 mg, 60 %). ^1H NMR (400 MHz, CDCl_3): 7.66 (d, $J = 8.6$ Hz, 2H), 7.41–7.39 (m, 4H), 7.13–7.08 (m, 4H), 6.86 (d, $J = 8.4$ Hz, 2H), 5.78 (m, 1H), 4.56–4.46 (m, 1H), 4.36–4.28 (m, 2H), 3.66 (dd, $J = 21.9, 6.7$ Hz, 1H), 1.36 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 149.2 (d, $J = 7.2$ Hz), 137.1 (d, $J = 10.2$ Hz), 136.1, 135.6, 133.5, 132.0 (d, $J = 6.6$ Hz), 130.5 (d, $J = 8.5$ Hz), 130.1, 129.9 (d, $J = 2.0$ Hz), 129.1, 128.5, 126.2, 125.3 (q, $J = 3.4$ Hz), 122.7, 104.9 (d, $J = 12.0$ Hz), 63.4 (d, $J = 7.0$ Hz), 45.4 (d, $J = 5.4$ Hz), 43.4 (d, $J = 125.2$ Hz), 16.6 (d, $J = 5.3$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 17.66. IR (KBr, cm^{-1}): 2926, 1619, 1491, 1326, 1273, 1165, 1019, 817. HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{20}\text{Cl}_2\text{F}_3\text{O}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 527.0552, found 527.0561.

***rel*-(2*R*,3*S*,4*R*)-4,6-Bis(4-chlorophenyl)-2-ethoxy-3-(4-(trifluoromethyl)phenyl)-**

3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*trans,trans*)-3t)

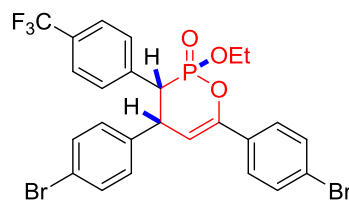


(±)

White solid (14 mg, 13 %). M.p. 205–208 °C. ¹H NMR

(400 MHz, CDCl₃): 7.59–7.52 (m, 4H), 7.38–7.34 (m, 4H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 5.67–5.65 (m, 1H), 4.34–4.21 (m, 3H), 3.50 (dd, *J* = 21.7, 12.3 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ: 148.1 (d, *J* = 7.2 Hz), 139.3 (d, *J* = 14.2 Hz), 136.6 (d, *J* = 6.7 Hz), 135.5, 134.2 (d, *J* = 3.1 Hz), 133.6, 133.1, 131.9 (d, *J* = 6.9 Hz), 129.8 (d, *J* = 6.5 Hz), 129.2 (d, *J* = 3.8 Hz), 129.0, 126.2, 125.9 (q, *J* = 4.6 Hz), 106.8 (d, *J* = 9.2 Hz), 63.4 (d, *J* = 7.6 Hz), 47.0 (d, *J* = 5.1 Hz), 46.2 (d, *J* = 123.0 Hz), 16.6 (d, *J* = 5.3 Hz). ³¹P NMR (162 MHz, CDCl₃) 16.64 (d, *J* = 1.7 Hz). IR (KBr, cm⁻¹): 2927, 1619, 1491, 1326, 1273, 1165, 1125, 817. HRMS (ESI) calcd. for C₂₅H₂₀Cl₂F₃O₃P (M + H⁺) *m/z* 527.0552, found 527.0561.

***rel*-(2*R*,3*R*,4*R*)-4,6-Bis(4-bromophenyl)-2-ethoxy-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3u)**



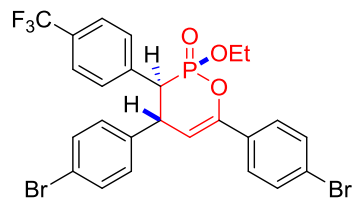
(±)

Colorless oil (76 mg, 70 %). ¹H NMR (400 MHz, CDCl₃):

7.60–7.54 (m, 4H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 5.79 (m, 1H), 4.53–4.45 (m, 1H), 4.36–4.28 (m, 2H), 3.66 (dd, *J* = 21.9, 6.7 Hz, 1H), 1.36 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): 149.3 (d, *J* = 7.2 Hz), 137.6 (d, *J* = 10.2 Hz), 136.0 (q, *J* = 3.7 Hz), 132.4 (d, *J* = 6.6 Hz), 132.0, 131.5, 130.5 (t, *J* = 4.2 Hz), 130.2 (d, *J* = 2.0 Hz), 129.9 (d, *J* = 2.0 Hz), 126.4, 125.5 (d, *J* = 3.3 Hz), 123.8, 122.6, 121.6, 104.9 (d, *J* = 12.0 Hz), 63.4 (d, *J* = 7.0 Hz), 45.4 (d, *J* = 5.4 Hz), 43.3 (d, *J* = 125.2 Hz), 16.6 (d, *J* = 5.3 Hz). ³¹P NMR (162 MHz, CDCl₃) 17.61. IR (KBr, cm⁻¹): 2926, 1488, 1397, 1326, 1269, 1166, 1019, 772

HRMS (ESI) calcd. for C₂₅H₂₀Br₂F₃O₃P (M + H⁺) *m/z* 616.9521, found 616.9526.

***rel*-(2*R*,3*S*,4*R*)-4,6-Bis(4-bromophenyl)-2-ethoxy-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*trans,trans*)-3u)**

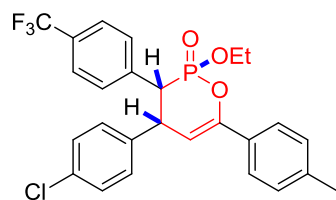


(±)

Colorless oil (21 mg, 18 %). ¹H NMR (400 MHz, CDCl₃):

7.59–7.47 (m, 5H), 7.39–7.31 (m, 4H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.57–5.47 (m, 1H), 4.33–4.20 (m, 3H), 3.50 (dd, *J* = 21.7, 12.2 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): 148.2 (d, *J* = 7.3 Hz), 139.8 (d, *J* = 14.0 Hz), 136.57 (q, *J* = 7.8 Hz), 132.4, 132.3, 132.2, 132.0, 129.8 (d, *J* = 6.5 Hz), 129.5, 126.4, 125.9, 123.7, 121.7, 106.8 (d, *J* = 9.2 Hz), 63.4 (d, *J* = 7.6 Hz), 47.0 (d, *J* = 5.2 Hz), 46.0 (d, *J* = 122.9 Hz), 16.6 (d, *J* = 5.3 Hz). ³¹P NMR (162 MHz, CDCl₃) 16.58 (d, *J* = 2.0 Hz). IR (KBr, cm⁻¹): 2926, 1488, 1326, 1269, 1126, 1018, 1019, 772. HRMS (ESI) calcd. for C₂₅H₂₀Br₂F₃O₃P (M + H⁺) *m/z* 616.9521, found 616.9526.

***rel*-(2*R*,3*R*,4*R*)-4-(4-Chlorophenyl)-2-ethoxy-6-(4-tolyl)-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3v)**



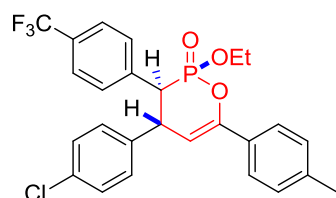
(±)

Colorless oil (72 mg, 71 %). ¹H NMR (400 MHz, CDCl₃):

7.65 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 2H), 7.15–7.12 (m, 4H), 6.89 (d, *J* = 8.4 Hz, 2H), 5.77 (d, *J* = 1.2 Hz, 1H), 4.55 (dt, *J* = 2.6, 7.6 Hz, 1H), 4.41–4.32 (m, 2H), 3.66 (dd, *J* = 21.9, 6.7 Hz, 1H), 2.44 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): 150.3 (d, *J* = 7.3 Hz), 139.8, 137.6 (d, *J* = 10.7 Hz), 136.2, 130.8 (d, *J* = 6.5 Hz), 130.5 (d, *J* = 8.3 Hz), 129.9 (d, *J* = 32.8 Hz), 129.3 (d, *J* = 37.4 Hz), 129.1, 128.7 (d, *J* = 8.5 Hz), 128.5, 125.5 (d, *J* = 2.9 Hz), 124.9 (d, *J* = 15.9 Hz), 122.7, 103.5 (d, *J* = 12.0 Hz), 45.3 (d, *J* = 5.1 Hz), 43.4 (d, *J* = 125.1 Hz), 21.4,

16.7 (d, $J = 5.2$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 17.70 (d, $J = 0.9$ Hz). IR (KBr, cm^{-1}): 2926, 1618, 1491, 1326, 1269, 1125, 1008, 772. HRMS (ESI) calcd. for $\text{C}_{26}\text{H}_{23}\text{ClF}_3\text{O}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 507.1098, found 507.1110.

***rel*-(2*R*,3*S*,4*R*)-4-(4-Chlorophenyl)-2-ethoxy-6-(*p*-tolyl)-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*trans,trans*)-3v)**

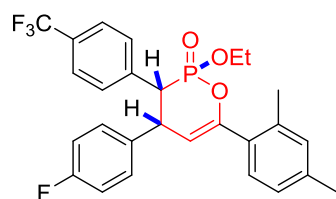


(±)

Colorless oil (10 mg, 10 %). ^1H NMR (400 MHz, CDCl_3):

7.53 (t, $J = 7.7$ Hz, 4H), 7.35 (d, $J = 6.9$ Hz, 2H), 7.22–7.14 (m, 4H), 6.98 (d, $J = 8.4$ Hz, 2H), 5.63–5.60 (m, 1H), 4.34–4.21 (m, 2H), 3.48 (dd, $J = 21.6, 12.2$ Hz, 1H), 2.38 (s, 3H), 1.35 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 150.3 (d, $J = 7.3$ Hz), 139.8, 137.6 (d, $J = 10.7$ Hz), 136.2, 133.3, 130.8 (d, $J = 6.5$ Hz), 130.5 (d, $J = 8.3$ Hz), 129.9 (d, $J = 32.8$ Hz), 129.3 (d, $J = 37.4$ Hz), 128.7 (d, $J = 8.5$ Hz), 128.5, 125.5 (d, $J = 2.9$ Hz), 124.8, 122.7, 103.5 (d, $J = 12.0$ Hz), 63.2 (d, $J = 7.0$ Hz), 45.3 (d, $J = 5.1$ Hz), 43.4 (d, $J = 125.1$ Hz), 16.7 (d, $J = 5.2$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 16.71 (d, $J = 2.0$ Hz). IR (KBr, cm^{-1}): 2360, 1326, 1219, 914, 772. HRMS (ESI) calcd. for $\text{C}_{26}\text{H}_{23}\text{ClF}_3\text{O}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 507.1098, found 507.1110.

***rel*-(2*R*,3*R*,4*R*)-6-(2,4-Dimethylphenyl)-2-ethoxy-4-(4-fluorophenyl)-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3w)**



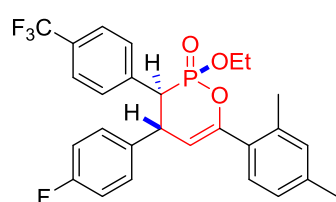
(±)

Colorless oil (62 mg, 62 %). ^1H NMR (400 MHz, CDCl_3):

7.40 (dd, $J = 20.6, 7.9$ Hz, 3H), 7.18 (d, $J = 7.9$ Hz, 2H), 7.11–7.04 (m, 2H), 6.96–6.91 (m, 2H), 6.83 (t, $J = 8.5$ Hz, 2H), 5.35 (m, 1H), 4.51 (ddd, $J = 9.9, 7.1, 2.7$ Hz, 1H), 4.38–4.25 (m, 2H), 3.67 (dd, $J = 21.9, 6.8$ Hz, 1H), 2.53 (s, 3H), 2.37 (s, 3H), 1.37 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 162.0 (d, $J = 246.4$ Hz), 151.6 (d, $J = 7.9$

Hz), 139.6, 136.6, 136.3, 134.5 (d, $J = 6.7$ Hz), 131.9, 131.8, 130.5 (dd, $J = 12.3, 8.4$ Hz), 130.0, 129.7, 129.1, 126.7, 125.3 (d, $J = 3.1$ Hz), 122.7, 115.1 (d, $J = 21.4$ Hz), 108.4 (d, $J = 11.7$ Hz), 63.2 (d, $J = 6.8$ Hz), 45.4 (d, $J = 5.0$ Hz), 43.5 (d, $J = 124.7$ Hz), 21.3, 20.8, 16.7 (d, $J = 5.4$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 17.41. IR (KBr, cm^{-1}): 2926, 2360, 1617, 1509, 1326, 1266, 1165, 1126, 1002, 814. HRMS (ESI) calcd. for $\text{C}_{27}\text{H}_{25}\text{F}_4\text{O}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 505.1548, found 505.1549.

***rel*-(2*R*,3*S*,4*R*)-6-(2,4-Dimethylphenyl)-2-ethoxy-4-(4-fluorophenyl)-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*trans,trans*)-3w)**

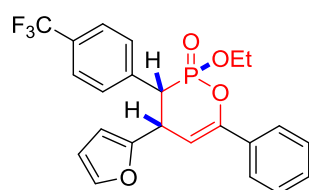


(±)

Colorless oil (27 mg, 26 %). ^1H NMR (400 MHz, CDCl_3):

7.52 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 7.8$ Hz, 2H), 7.28 (s, 1H), 7.07–6.98 (m, 4H), 6.88 (t, $J = 8.5$ Hz, 2H), 5.21 (m, 1H), 4.32–4.22 (m, 3H), 3.49 (dd, $J = 21.4, 12.2$ Hz, 1H), 2.47 (s, 3H), 2.34 (s, 3H), 1.39 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 162.0 (d, $J = 246.6$ Hz), 150.7 (d, $J = 8.0$ Hz), 142.6, 137.2 (d, $J = 6.6$ Hz), 136.7 (dd, $J = 14.2, 2.9$ Hz), 131.8 (d, $J = 6.3$ Hz), 131.7, 129.8 (d, $J = 6.3$ Hz), 129.3 (d, $J = 8.1$ Hz), 129.1, 126.6, 125.8, 122.7, 115.8 (d, $J = 21.5$ Hz), 110.4 (d, $J = 9.0$ Hz), 63.3 (d, $J = 7.4$ Hz), 46.8 (d, $J = 4.8$ Hz), 46.6 (d, $J = 121.9$ Hz). 21.3, 20.6, 16.7 (d, $J = 5.3$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 16.42. IR (KBr, cm^{-1}): 2926, 1617, 1509, 1326, 1273, 1221, 1126, 1005, 772. HRMS (ESI) calcd. for $\text{C}_{27}\text{H}_{25}\text{F}_4\text{O}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 505.1548, found 505.1549.

***rel*-(2*R*,3*R*,4*R*)-6-(2,4-Dimethylphenyl)-2-ethoxy-4-(furan-2-yl)-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3x)**

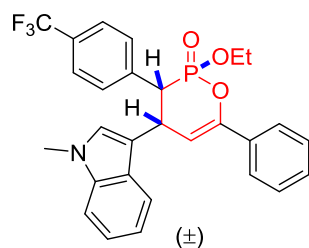


(±)

Colorless oil (57 mg, 63 %). ^1H NMR (400 MHz, CDCl_3):

7.78–7.69 (m, 2H), 7.47–7.37 (m, 5H), 7.29–7.18 (m, 2H), 6.14 (dd, $J = 2.8, 1.8$ Hz, 1H), 5.92 (d, $J = 3.1$ Hz, 1H), 5.89 (m, 1H), 4.71–4.67 (m, 1H), 4.41–4.27 (m, 2H), 3.88 (dd, $J = 22.4, 6.6$ Hz, 1H), 1.38 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 152.0 (d, $J = 13.0$ Hz), 150.0 (d, $J = 7.4$ Hz), 141.9, 136.5, 133.5 (d, $J = 6.4$ Hz), 129.9 (d, $J = 7.6$ Hz), 129.6, 128.8, 125.7 (d, $J = 48.6$ Hz), 124.9, 122.8, 110.5, 107.9, 102.0 (d, $J = 12.5$ Hz), 63.1 (d, $J = 7.1$ Hz), 41.3 (d, $J = 124.9$ Hz), 39.4 (d, $J = 5.1$ Hz), 16.6 (d, $J = 5.4$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 17.37. IR (KBr, cm^{-1}): 2918, 1619, 1509, 1326, 1275, 1123, 749. HRMS (ESI) calcd. for $\text{C}_{23}\text{H}_{20}\text{F}_3\text{O}_4\text{P}$ ($\text{M} + \text{H}^+$) m/z 449.1124, found 449.1124.

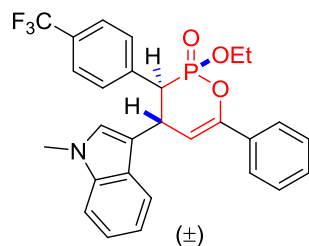
***rel*-(2*R*,3*R*,4*R*)-2-Ethoxy-4-(1-methyl-1*H*-indol-3-yl)-6-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3y)**



Yellow oil (60 mg, 60 %). ^1H NMR (400 MHz, CDCl_3) 7.78–

7.72 (m, 2H), 7.48–7.38 (m, 3H), 7.34–7.17 (m, 5H), 7.12 (d, $J = 7.9$ Hz, 2H), 7.07–7.02 (m, 1H), 6.53 (s, 1H), 5.93 (d, $J = 1.4$ Hz, 1H), 4.93 (dt, $J = 3.0, 7.6$ Hz, 1H), 4.45–4.30 (m, 2H), 3.83 (dd, $J = 21.6, 6.5$ Hz, 1H), 3.60 (s, 3H), 1.43 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 149.1 (d, $J = 7.3$ Hz), 137.5 (d, $J = 2.5$ Hz), 136.7, 133.9 (d, $J = 6.6$ Hz), 130.3 (d, $J = 8.4$ Hz), 129.3, 128.8, 128.1, 126.9, 125.6 (d, $J = 2.5$ Hz), 125.5 (d, $J = 3.4$ Hz), 125.1, 124.8, 121.9, 119.4, 118.1, 112.2 (d, $J = 11.7$ Hz), 109.6, 106.2 (d, $J = 11.6$ Hz), 63.0 (d, $J = 7.0$ Hz), 42.6 (d, $J = 123.7$ Hz), 37.4 (d, $J = 5.4$ Hz), 32.8, 16.8 (d, $J = 5.3$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 18.76 (d, $J = 0.9$ Hz). IR (KBr, cm^{-1}): 2930, 1617, 11472, 1326, 1262, 1123, 749. HRMS (ESI) calcd. for $\text{C}_{28}\text{H}_{25}\text{F}_3\text{NO}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 512.1597, found 512.1599.

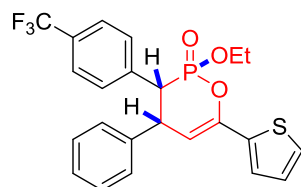
***rel*-(2*R*,3*S*,4*R*)-2-Ethoxy-4-(1-methyl-1*H*-indol-3-yl)-6-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*trans,trans*)-3y)**



Red solid (20 mg, 19 %). M.p. 113–115 °C. ^1H NMR (400

MHz, CDCl_3) 7.69–7.67 (m, 2H), 7.60 (d, $J = 8.0$ Hz, 1H), 7.51 (d, $J = 8.2$ Hz, 2H), 7.42–7.38 (m, 5H), 7.30–7.20 (m, 2H), 7.13–7.07 (m, 1H), 6.66 (s, 1H), 5.92–5.90 (m, 1H), 4.59 (ddd, $J = 12.1, 4.1, 2.7$ Hz, 1H), 4.36–4.25 (m, 2H), 3.90 (dd, $J = 21.3, 12.1$ Hz, 1H), 3.66 (s, 3H), 1.39 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 147.5 (d, $J = 7.0$ Hz), 137.9 (d, $J = 1.4$ Hz), 137.3, 133.6 (d, $J = 7.0$ Hz), 129.8 (d, $J = 2.6$ Hz), 129.6 (d, $J = 6.5$ Hz), 129.0, 128.5, 126.9, 126.1, 125.5, 124.7, 122.0, 119.2 (d, $J = 35.1$ Hz), 113.3, 113.2, 109.6, 107.8 (d, $J = 8.9$ Hz), 62.9 (d, $J = 7.5$ Hz), 44.5 (d, $J = 121.2$ Hz), 39.1 (d, $J = 5.2$ Hz), 32.7, 16.5 (d, $J = 5.4$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 17.85 (d, $J = 2.1$ Hz). IR (KBr, cm^{-1}): 3058, 2360, 1618, 1474, 1326, 1270, 1120, 1010, 772. HRMS (ESI) calcd. for $\text{C}_{28}\text{H}_{25}\text{F}_3\text{NO}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 512.1597, found 512.1599.

***rel*-(2*R*,3*R*,4*R*)-2-Ethoxy-4-phenyl-6-(thiophen-2-yl)-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3*z*)**

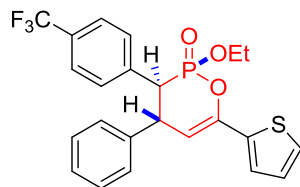


Yellow solid (44 mg, 47 %). M.p. 156–158 °C. ^1H NMR (400

MHz, CDCl_3) 7.68 (s, 1H), 7.39–7.27 (m, 4H), 7.17–7.04 (m, 5H), 6.92–6.91 (m, 2H), 5.72 (s, 1H), 4.57 (t, $J = 5.9$ Hz, 1H), 4.43–4.28 (m, 2H), 3.64 (dd, $J = 21.9, 6.6$ Hz, 1H), 1.40 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 145.6 (d, $J = 7.0$ Hz), 141.0 (d, $J = 13.9$ Hz), 137.1 (d, $J = 7.3$ Hz), 135.9 (d, $J = 7.3$ Hz), 130.8 (d, $J = 6.3$ Hz), 129.8 (d, $J = 6.5$ Hz), 128.9, 128.7 (d, $J = 6.2$ Hz), 127.8 (d, $J = 22.9$ Hz), 126.8, 125.9, 125.3, 124.4 (d, $J = 16.4$ Hz), 122.5, 106.5 (d, $J = 9.3$ Hz), 63.2 (d, $J = 7.5$ Hz), 47.4 (d, $J = 5.2$ Hz), 46.4 (d, $J = 122.6$ Hz), 16.5 (d, $J = 5.2$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 17.95. IR (KBr, cm^{-1}): 2983, 1618, 1419, 1326, 1274, 1122, 1023, 701. HRMS (ESI)

calcd. for C₂₃H₂₀F₃O₃P (M + H⁺) *m/z* 465.0896, found 465.0896.

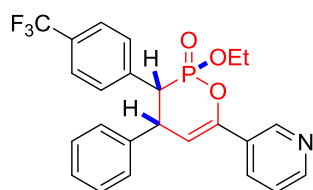
***rel*-(2*R*,3*S*,4*R*)-2-Ethoxy-4-phenyl-6-(thiophen-2-yl)-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*trans,trans*)-3z)**



(±) Colorless oil (22 mg, 24 %). ¹H NMR (400 MHz, CDCl₃): 7.60

(s, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.40–7.29 (m, 3H), 7.24–7.17 (m, 4H), 7.04 (d, *J* = 7.1 Hz, 2H), 5.59 (m, 1H), 4.33–4.22 (m, 3H), 3.54 (dd, *J* = 21.5, 12.2 Hz, 1H), 1.37 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): 146.8 (d, *J* = 6.8 Hz), 139.0 (d, *J* = 10.9 Hz), 136.4, 136.0 (d, *J* = 7.0 Hz), 130.5 (d, *J* = 8.4 Hz), 129.7 (d, *J* = 30.6 Hz), 128.9, 128.5 (d, *J* = 20.6 Hz), 127.5, 126.9, 125.4 (d, *J* = 3.1 Hz), 124.3, 122.6, 104.4 (d, *J* = 12.2 Hz), 63.1 (d, *J* = 7.0 Hz), 45.6 (d, *J* = 5.4 Hz), 43.7 (d, *J* = 124.5 Hz), 16.7 (d, *J* = 5.2 Hz). ³¹P NMR (162 MHz, CDCl₃) 17.05 (d, *J* = 1.4 Hz). IR (KBr, cm⁻¹): 2929, 1656, 1326, 1274, 1122, 1123, 858, 701. HRMS (ESI) calcd. for C₂₃H₂₀F₃O₃P (M + H⁺) *m/z* 465.0896, found 465.0896.

***rel*-(2*R*,3*R*,4*R*)-2-ethoxy-4-phenyl-6-(pyridin-3-yl)-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3aa)**

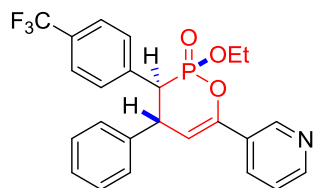


(±) Yellow solid (50 mg, 54 %). M.p. 62–65 °C. ¹H NMR (400

MHz, CDCl₃): 8.99 (s, 1H), 8.65 (s, 1H), 8.09(d, *J* = 7.7 Hz), 7.46–7.40 (m, 1H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.15(d, *J* = 4.3 Hz, 3H), 7.06(d, *J* = 7.7 Hz, 2H), 6.93–6.90(m, 2H), 5.59 (m, 1H), 4.58 (td, *J* = 6.1, 2.5 Hz, 1H), 4.42–4.30 (dq, *J* = 7.5, 8.0 Hz, 2H), 3.70 (dd, *J* = 22.0, 6.6 Hz, 1H), 1.39 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): 149.5, 147.3 (d, *J* = 5.8 Hz), 145.6 (d, *J* = 6.2 Hz), 138.2 (d, *J* = 10.3 Hz), 136.1, 132.9, 130.5 (d, *J* = 8.4 Hz), 128.6 (d, *J* = 22.6 Hz), 127.7, 125.4 (d, *J* = 3.3 Hz), 123.9, 107.2 (d, *J* =

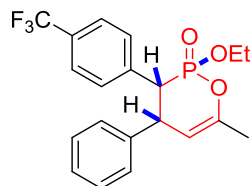
12.0 Hz), 63.5 (d, $J = 7.0$ Hz), 46.0 (d, $J = 5.3$ Hz), 43.6 (d, $J = 125.0$ Hz), 16.7 (d, $J = 5.2$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 18.03. IR (KBr, cm^{-1}): 2925, 2360, 1657, 1326, 1271, 1124, 1006, 703. HRMS (ESI) calcd. for $\text{C}_{24}\text{H}_{21}\text{F}_3\text{NO}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 460.1284, found 460.1291.

***rel*-(2*R*,3*R*,4*R*)-2-ethoxy-4-phenyl-6-(pyridin-3-yl)-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*trans,trans*)-3aa)**



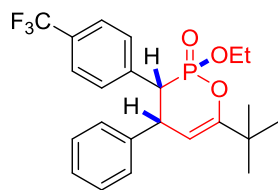
(±) Yellow oil liquid (4 mg, 5 %). NMR data could not be obtained because of less amount. However, We can found chemical shift δ 3.59 (dd, $J = 21.6, 12.3$ Hz, 1H) in mixture ^1H NMR spectrum

***rel*-(2*R*,3*R*,4*R*)-2-ethoxy-6-methyl-4-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3ab)**



(±) Yellow oil liquid (32 mg, 40 %). ^1H NMR (400 MHz, CDCl_3): 7.35 (d, $J = 8.2$ Hz, 2H), 7.13–7.09 (m, 3H), 7.02 (d, $J = 7.9$ Hz, 2H), 6.86 (dd, $J = 6.5, 2.8$ Hz, 2H), 5.02 (m, 1H), 4.37–4.20 (m, 3H), 3.53 (dd, $J = 21.8, 6.7$ Hz, 1H), 2.08 (s, 3H), 1.39 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 149.6 (d, $J = 8.0$ Hz), 139.0 (d, $J = 10.4$ Hz), 136.6, 130.5 (d, $J = 8.5$ Hz), 128.6, 128.2, 127.3, 126.3 (d, $J = 4.2$ Hz), 125.5 (d, $J = 1.4$ Hz), 125.3 (m), 104.7 (d, $J = 12.1$ Hz), 62.9 (d, $J = 6.9$ Hz), 45.3 (d, $J = 5.7$ Hz), 45.30 (d, $J = 124.5$ Hz), 21.2 (d, $J = 6.1$ Hz), 16.7 (d, $J = 5.3$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 17.98. IR (KBr, cm^{-1}): 3442, 2925, 1685, 1618, 1326, 1263, 960, 755. HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{20}\text{F}_3\text{O}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 397.1175, found 397.1184.

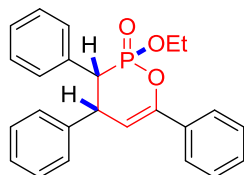
***rel*-(2*R*,3*R*,4*R*)-6-(tert-butyl)-2-ethoxy-4-phenyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3ac)**



(±) Colorless oil liquid (64 mg, 73 %). ^1H NMR (400 MHz, CDCl_3):

7.34 (d, $J = 8.2$ Hz, 2H), 7.14–7.07 (m, 3H), 7.00 (d, $J = 7.9$ Hz, 2H), 6.90–6.79 (m, 2H), 5.07 (m, 1H), 4.46–4.21 (m, 3H), 3.50 (dd, $J = 21.6, 6.6$ Hz, 1H), 1.42 (t, $J = 7.1$ Hz, 3H), 1.27 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3): 160.1 (d, $J = 9.5$ Hz), 139.5 (d, $J = 11.3$ Hz), 136.7, 130.4 (d, $J = 8.5$ Hz), 129.6 (q, $J = 32.0$ Hz), 128.3 (d, $J = 19.1$ Hz), 127.8, 125.1 (d, $J = 3.3$ Hz), 125.0 (q, $J = 27.1$ Hz), 101.0 (d, $J = 12.0$ Hz), 62.5 (d, $J = 6.9$ Hz), 45.0 (d, $J = 5.4$ Hz), 43.30 (d, $J = 124.7$ Hz), 36.5 (d, $J = 5.1$ Hz), 27.7, 26.2, 16.7 (d, $J = 5.5$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 18.10. IR (KBr, cm^{-1}): 3440, 2920, 1685, 1614, 1323, 1261, 959, 753. HRMS (ESI) calcd. for $\text{C}_{23}\text{H}_{26}\text{F}_3\text{O}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 439.1644, found 439.1650.

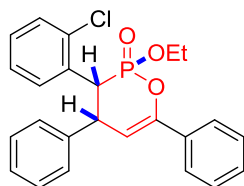
***rel*-(2*R*,3*R*,4*R*)-2-Ethoxy-3,4,6-triphenyl-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3ad)**



(±) Yellow solid (42 mg, 54 %). M.p. 150–151 °C. ^1H NMR (400 MHz,

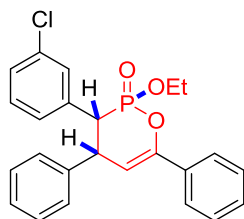
CDCl_3): 7.77–7.76 (m, 2H), 7.47–7.38 (m, 3H), 7.13–7.07 (m, 6H), 6.99–6.90 (m, 4H), 5.87 (m, 1H), 4.55 (dt, $J = 2.8, 6.9$ Hz, 1H), 4.40–4.29 (m, 2H), 3.60 (dd, $J = 21.9, 6.7$ Hz, 1H), 1.39 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 149.7 (d, $J = 7.3$ Hz), 139.5 (d, $J = 11.0$ Hz), 134.0 (d, $J = 6.5$ Hz), 132.0 (d, $J = 4.0$ Hz), 130.2 (d, $J = 8.6$ Hz), 129.2, 128.8, 128.7, 128.4, 128.1, 127.5 (d, $J = 1.9$ Hz), 127.1, 124.8, 105.4 (d, $J = 12.2$ Hz), 62.7 (d, $J = 7.1$ Hz), 46.0 (d, $J = 5.3$ Hz), 43.6 (d, $J = 124.4$ Hz), 16.7 (d, $J = 5.4$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 19.44. IR (KBr, cm^{-1}): 3061, 1495, 1453, 1269, 1009, 762, 698, 568. HRMS (ESI) calcd. for $\text{C}_{24}\text{H}_{23}\text{O}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 391.1458, found 391.1459.

***rel*-(2*R*,3*R*,4*R*)-3-(2-Chlorophenyl)-2-ethoxy-4,6-diphenyl-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3ae)**



(±) Colorless oil (50 mg, 59 %). ¹H NMR (400 MHz, CDCl₃): 7.76–7.72 (m, 2H), 7.46–7.35 (m, 4H), 7.23–7.19 (m, 1H), 7.15–6.96 (m, 7H), 5.88–5.85 (m, 1H), 4.54 (ddd, *J* = 27.8, 16.6, 5.4 Hz, 2H), 4.31 (dq, *J* = 9.0, 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) 149.5, 133.9 (d, *J* = 5.8 Hz), 133.7 (d, *J* = 9.7 Hz), 130.9 (d, *J* = 5.4 Hz), 130.5, 129.6, 129.3 (d, *J* = 4.2 Hz), 128.8 (d, *J* = 9.2 Hz), 128.0, 127.3, 126.9, 124.9, 105.7 (d, *J* = 12.4 Hz), 45.2 (d, *J* = 5.1 Hz), 38.3 (d, *J* = 127.2 Hz), 16.6 (d, *J* = 5.5 Hz). ³¹P NMR (162 MHz, CDCl₃) 18.44. IR (KBr, cm⁻¹): 2926, 1269, 1009, 761. HRMS (ESI) calcd. for C₂₄H₂₂ClO₃P (M + H⁺) *m/z* 425.1068, found 425.1072.

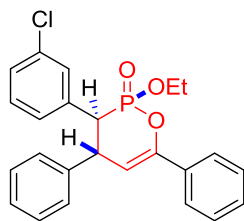
***rel*-(2*R*,3*R*,4*R*)-3-(3-Chlorophenyl)-2-ethoxy-4,6-diphenyl-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3af)**



(±) Colorless oil liquid (23 mg, 27 %). ¹H NMR (400 MHz, CDCl₃): 7.76–7.73 (m, 2H), 7.48–7.39 (m, 3H), 7.19–7.08 (m, 4H), 7.03 (t, *J* = 8.1 Hz, 1H), 6.97–6.87 (m, 4H), 5.86 (m, 1H), 4.54 (dt, *J* = 2.9, 6.9 Hz, 1H), 4.40–4.28 (m, 2H), 3.55 (dd, *J* = 22.1, 6.7 Hz, 1H), 1.39 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): 149.9 (d, *J* = 7.3 Hz), 139.1 (d, *J* = 10.6 Hz), 134.2, 133.8 (d, *J* = 6.7 Hz), 130.4 (d, *J* = 9.4 Hz), 129.6, 129.5, 129.4, 129.3, 128.8 (d, *J* = 4.6 Hz), 128.3, 128.2 (d, *J* = 7.9 Hz), 127.8, 127.4, 124.9, 105.1 (d, *J* = 12.2 Hz), 63.0 (d, *J* = 7.0 Hz), 45.9 (d, *J* = 5.3 Hz), 43.4 (d, *J* = 124.9 Hz), 16.7 (d, *J* = 5.3 Hz). ³¹P NMR (162 MHz, CDCl₃) 18.31. IR (KBr, cm⁻¹): 2923, 1655, 1326, 1269, 1031, 691. HRMS (ESI) calcd. for C₂₄H₂₂ClO₃P

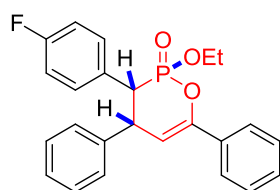
(M + H⁺) *m/z* 425.1068, found 425.1076.

***rel*-(2*R*,3*S*,4*R*)-3-(3-Chlorophenyl)-2-ethoxy-4,6-diphenyl-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*trans,trans*)-3af)**



(±) White solid (40 mg, 47 %). M.p. 178–180 °C ¹H NMR (400 MHz, CDCl₃): 7.68–7.63 (m, 2H), 7.42–7.35 (m, 3H), 7.36–7.30 (m, 1H), 7.24–7.12 (m, 5H), 7.08–7.03 (m, 3H), 5.75–5.72 (m, 1H), 4.36–4.19 (m, 3H), 3.45 (dd, *J* = 21.3, 12.2 Hz, 1H), 1.38 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): 148.6 (d, *J* = 7.3 Hz), 141.2 (d, *J* = 13.9 Hz), 134.9 (d, *J* = 7.7 Hz), 134.5, 133.6 (d, *J* = 6.7 Hz), 129.9, 129.3 (d, *J* = 7.2 Hz), 128.8 (d, *J* = 18.3 Hz), 128.7, 128.1, 128.0, 127.9, 127.6, 124.8, 107.0 (d, *J* = 9.1 Hz), 63.1 (d, *J* = 7.5 Hz), 47.7 (d, *J* = 5.0 Hz), 46.1 (d, *J* = 123.2 Hz), 16.5 (d, *J* = 5.3 Hz). ³¹P NMR (162 MHz, CDCl₃) 17.48. IR (KBr, cm⁻¹): 2923, 1655, 1326, 1269, 1031, 691. HRMS (ESI) calcd. for C₂₄H₂₂ClO₃P (M + H⁺) *m/z* 425.1068, found 425.1076.

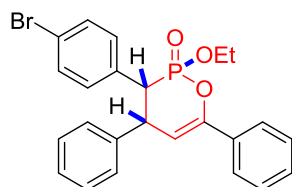
***rel*-(2*R*,3*R*,4*R*)-2-Ethoxy-3-(4-fluorophenyl)-4,6-diphenyl-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3ag)**



(±) Yellow solid (41 mg, 50 %). M.p. 188–190 °C. ¹H NMR (400 MHz, CDCl₃): 7.81–7.72 (m, 2H), 7.47–7.38 (m, 3H), 7.18–7.11 (m, 3H), 6.95–6.89 (m, 4H), 6.78 (t, *J* = 8.6 Hz, 2H), 5.86 (d, *J* = 0.8 Hz, 1H), 4.53 (dt, *J* = 2.9, 6.8 Hz, 1H), 4.41–4.29 (m, 2H), 3.58 (dd, *J* = 22.2, 6.7 Hz, 1H), 1.43–1.35 (m, 3H). ¹³C NMR (101 MHz, CDCl₃): 162.3 (d, *J* = 247.0 Hz), 149.7 (d, *J* = 7.3 Hz), 139.3 (d, *J* = 10.9 Hz), 133.8 (d, *J* = 6.4 Hz), 131.7 (t, *J* = 8.3 Hz), 131.0, 129.3, 128.8, 128.3, 127.9, 127.3, 124.8, 115.4 (d, *J* = 21.4 Hz), 105.1 (d, *J* = 12.0 Hz), 62.9 (d, *J* = 6.9 Hz), 45.9

(d, $J = 4.8$ Hz), 42.8 (d, $J = 125.0$ Hz), 16.7 (d, $J = 5.3$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 19.07 (d, $J = 2.5$ Hz). IR (KBr, cm^{-1}): 2982, 1724, 1509, 1270, 1031, 1010, 761, 697. HRMS (ESI) calcd. for $\text{C}_{24}\text{H}_{22}\text{FO}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 409.1363, found 409.1367.

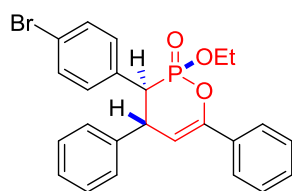
***rel*-(2*R*,3*R*,4*R*)-2-Ethoxy-3-(4-bromophenyl)-4,6-diphenyl-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3ah)**



(±) White solid (35 mg, 37 %). M.p. 218–220 °C. ^1H NMR (400

MHz, CDCl_3): 7.78–7.71 (m, 2H), 7.48–7.38 (m, 3H), 7.25–7.13 (m, 5H), 6.94 (dd, $J = 6.3, 2.7$ Hz, 2H), 6.83 (d, $J = 7.2$ Hz, 2H), 5.86 (m, 1H), 4.54 (dt, $J = 2.8, 6.9$ Hz, 1H), 4.41–4.28 (m, 2H), 3.56 (dd, $J = 22.0, 6.7$ Hz, 1H), 1.39 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 149.8 (d, $J = 7.4$ Hz), 139.2 (d, $J = 10.8$ Hz), 133.8 (d, $J = 6.4$ Hz), 131.8 (d, $J = 8.5$ Hz), 131.6, 131.2 (d, $J = 3.9$ Hz), 129.7 (d, $J = 7.2$ Hz), 129.4, 128.8 (d, $J = 2.7$ Hz), 128.4, 127.4, 124.8, 121.8, 105.1 (d, $J = 12.0$ Hz), 63.0 (d, $J = 7.0$ Hz), 45.7 (d, $J = 5.2$ Hz), 43.2 (d, $J = 124.8$ Hz), 16.7 (d, $J = 5.3$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 18.52. IR (KBr, cm^{-1}): 2980, 1649, 1489, 1269, 1032, 1010, 761. HRMS (ESI) calcd. for $\text{C}_{24}\text{H}_{22}\text{BrO}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 469.0553, found 469.0557.

***rel*-(2*R*,3*S*,4*R*)-2-Ethoxy-3-(4-bromophenyl)-4,6-diphenyl-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*trans,trans*)-3ah)**

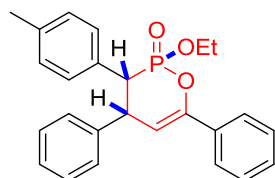


(±) White solid (25 mg, 27 %). M.p. 225–227 °C. ^1H NMR (400

MHz, CDCl_3): 7.67–7.64 (m, 2H), 7.39–7.34 (m, 5H), 7.24–7.15 (m, 3H), 7.13–7.02 (m, 4H), 5.74–5.71 (m, 1H), 4.34–4.13 (m, 3H), 3.45 (dd, $J = 21.5, 12.2$ Hz, 1H), 1.36 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) 148.6 (d, $J = 7.4$ Hz), 141.3 (d, $J = 13.8$ Hz), 133.6, 131.9, 131.6, 131.1 (d, $J = 6.8$ Hz), 129.3, 129.0 (d, $J = 10.5$ Hz), 128.7,

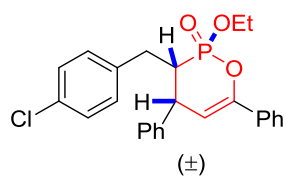
127.8 (d, $J = 40.0$ Hz), 127.6, 124.8, 121.9, 107.1 (d, $J = 8.9$ Hz), 63.1 (d, $J = 7.6$ Hz), 47.6 (d, $J = 4.9$ Hz), 45.8 (d, $J = 123.3$ Hz), 16.6 (d, $J = 5.2$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 17.54. IR (KBr, cm^{-1}): 3061, 1649, 1489, 1269, 1010, 761. HRMS (ESI) calcd. for $\text{C}_{24}\text{H}_{22}\text{BrO}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 469.0553, found 469.0557.

***rel*-(2*R*,3*R*,4*R*)-2-Ethoxy-3-(4-methylphenyl)-4,6-diphenyl-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3ai)**



($\pm$) Yellow oil (41mg, 51 %). ^1H NMR (400 MHz, CDCl_3): 7.77–7.75 (m, 2H), 7.47–7.38 (m, 3H), 7.17–7.11 (m, 3H), 7.00–6.81 (m, 6H), 5.87 (m, 1H), 4.53 (dt, $J = 2.9, 7.0$ Hz, 1H), 4.39–4.29 (m, 2H), 3.57 (dd, $J = 22.1, 6.6$ Hz, 1H), 2.21 (s, 1H), 1.39 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 149.6 (d, $J = 7.3$ Hz), 139.6 (d, $J = 11.1$ Hz), 137.0 (d, $J = 2.2$ Hz), 134.1 (d, $J = 6.5$ Hz), 123.0 (d, $J = 8.5$ Hz), 129.2, 128.9, 128.8, 128.7, 128.7, 128.1, 127.0, 124.8, 105.4 (d, $J = 12.1$ Hz), 21.1, 16.7 (d, $J = 5.4$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 19.78. IR (KBr, cm^{-1}): 1219, 1009, 772. HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{25}\text{O}_3\text{P}$ ($\text{M} + \text{H}^+$) m/z 405.1614, found 405.1604.

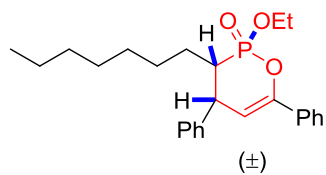
***rel*-(2*R*,3*S*,4*R*)-3-(4-Chlorobenzyl)-2-ethoxy-4,6-diphenyl-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3aj)**



($\pm$) Yellow oil (21 mg, 24 %). ^1H NMR (400 MHz, CDCl_3): 7.72–7.68 (m, 2H), 7.43–7.31 (m, 8H), 7.11–7.06 (m, 2H), 6.77 (d, $J = 8.4$ Hz, 2H), 5.84 (dd, $J = 2.6, 1.4$ Hz, 1H), 4.38–4.32 (m, 1H), 4.24 (dq, $J = 8.9, 7.1$ Hz, 2H), 2.98–2.84 (m, 1H), 2.64–2.48 (m, 2H), 1.33 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 149.7 (d, $J = 7.6$ Hz), 139.6 (d, $J = 11.1$ Hz), 138.4 (d, $J = 6.1$ Hz), 133.9 (d, $J = 2.2$ Hz), 133.9, 132.0, 130.3, 129.2, 128.9 (d, $J = 3.4$ Hz), 128.7, 128.4, 127.7, 124.8, 104.1 (d, $J = 11.4$ Hz), 62.6 (d, $J = 7.2$ Hz), 44.0 (d, $J = 5.2$ Hz), 38.2 (d, $J = 123.8$ Hz), 29.35 (d, $J = 1.3$ Hz), 16.6 (d, $J = 5.3$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 23.55. IR (KBr, cm^{-1}):

2925, 1492, 1262, 1093, 1015, 762. HRMS (ESI) calcd. for $C_{25}H_{24}ClO_3P$ ($M + H^+$) m/z 439.1224, found 439.1221.

***rel*-(2*R*,3*S*,4*R*)-2-Ethoxy-3-heptyl-4,6-diphenyl-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-3ak)**

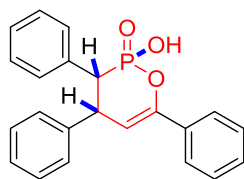


(±)

Colorless liquid (12mg, 15 %). 1H NMR (400 MHz, $CDCl_3$):

7.53 (d, $J = 7.1$ Hz, 2H), 7.31–7.16 (m, 8H), 5.47 (m, 1H), 4.35–4.09 (m, 2H), 3.53 (d, $J = 11.5$ Hz, 1H), 2.21–2.03 (m, 1H), 1.28 (t, $J = 7.0$ Hz, 3H), 1.24–0.99 (m, 12H), 0.76 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 147.7 (d, $J = 7.2$ Hz), 142.3 (d, $J = 14.1$ Hz), 133.8 (d, $J = 6.4$ Hz), 128.8 (d, $J = 8.8$ Hz), 128.3 (d, $J = 15.8$ Hz), 127.4, 124.6, 107.3 (d, $J = 10.2$ Hz), 61.8 (d, $J = 7.5$ Hz), 46.9 (d, $J = 4.7$ Hz), 37.5 (d, $J = 124.9$ Hz), 31.7, 29.1 (d, $J = 66.2$ Hz), 27.8 (d, $J = 2.8$ Hz), 26.9 (d, $J = 4.4$ Hz), 22.6, 16.5 (d, $J = 5.2$ Hz), 14.0. ^{31}P NMR (162 MHz, $CDCl_3$) 25.25. IR (KBr, cm^{-1}): 2925, 1619, 1325, 1261, 1046, 761. HRMS (ESI) calcd. for $C_{25}H_{33}O_3P$ ($M + H^+$) m/z 413.2240, found 413.2245.

***rel*-(2*R*,3*R*,4*R*)-2-Hydroxy-3,4,6-triphenyl-3,4-dihydro-1,2-oxaphosphinine 2-oxide ((*cis,cis*)-4)**

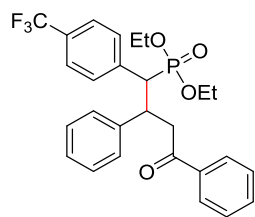


(±)

Colorless oil (15 mg, 20 %). 1H NMR (400 MHz, $CDCl_3$): 7.81–

7.71 (m, 2H), 7.50–7.42 (m, 3H), 7.20–7.08 (m, 6H), 7.03–6.91 (m, 4H), 6.01 (m, 1H), 4.76 (dt, $J = 2.5, 6.3$ Hz, 1H), 3.91 (dd, $J = 21.1, 6.7$ Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): 149.9 (d, $J = 9.3$ Hz), 138.4, 138.3, 138.2, 132.8 (d, $J = 6.6$ Hz), 129.8, 128.8, 128.7 (d, $J = 1.3$ Hz), 128.5, 128.3, 128.2 (d, $J = 2.7$ Hz), 127.4, 124.9, 105.7 (d, $J = 13.7$ Hz), 50.9 (d, $J = 98.8$ Hz), 45.4 (d, $J = 3.6$ Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 31.02. IR (KBr, cm^{-1}): 3372, 2975, 1618, 1498, 1048. HRMS (ESI) calcd. for $C_{22}H_{19}O_3P$ ($M + H^+$) m/z 363.1145, found 363.1142.

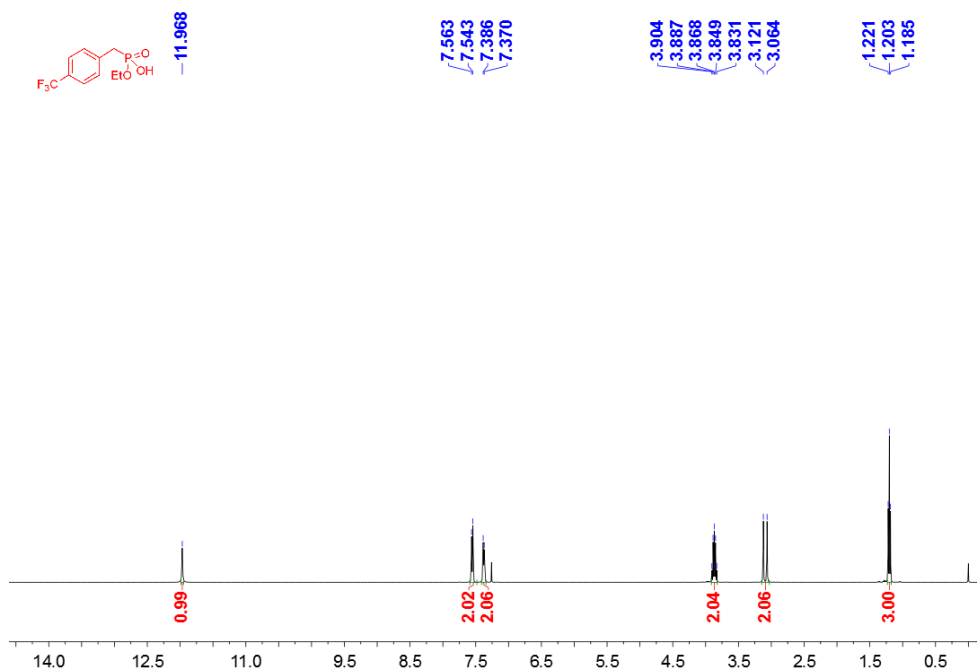
Diethyl (4-oxo-2,4-diphenyl-1-(4-(trifluoromethyl)phenyl)butyl)phosphonate (7)



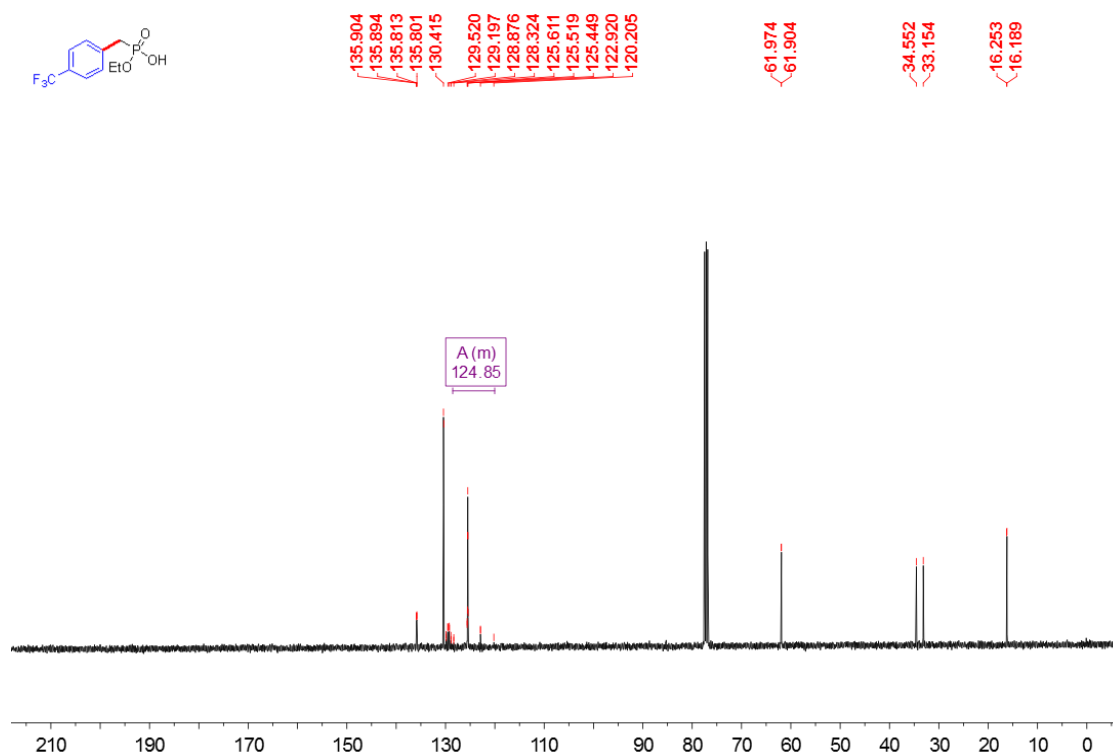
White solid (22 mg 22 %). M.p. 140–142 °C. ^1H NMR (400 MHz, CDCl_3): 7.91 (d, $J = 7.4$ Hz, 2H), 7.53 (t, $J = 7.4$ Hz, 1H), 7.48–7.33 (m, 4H), 7.27–7.19 (m, 2H), 7.11–6.95 (m, 5H), 4.21–3.91 (m, 5H), 3.82–3.51 (m, 3H), 1.23 (t, $J = 7.1$ Hz, 3H), 1.12 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3): 198.2, 141.4 (d, $J = 14.6$ Hz), 140.3 (d, $J = 6.4$ Hz), 137.2, 133.1, 130.4 (d, $J = 6.6$ Hz), 129.3 (d, $J = 1.5$ Hz), 129.1, 128.9, 128.6 (d, $J = 14.9$ Hz), 128.2, 126.7, 125.5, 125.1, 122.8, 50.0 (d, $J = 135.4$ Hz), 44.1, 43.1, 16.4 (d, $J = 6.1$ Hz), 16.3 (d, $J = 5.8$ Hz). ^{31}P NMR (162 MHz, CDCl_3) 26.27 (d, $J = 1.6$ Hz). IR (KBr, cm^{-1}): 2984, 1687, 1618, 1326, 1248, 1021. HRMS (ESI) calcd. for $\text{C}_{27}\text{H}_{28}\text{F}_3\text{O}_4\text{P}$ ($\text{M} + \text{H}^+$) m/z 505.1750, found 505.1760.

6. Copies of Spectra of Products 8, 3, 4, 6, and 7

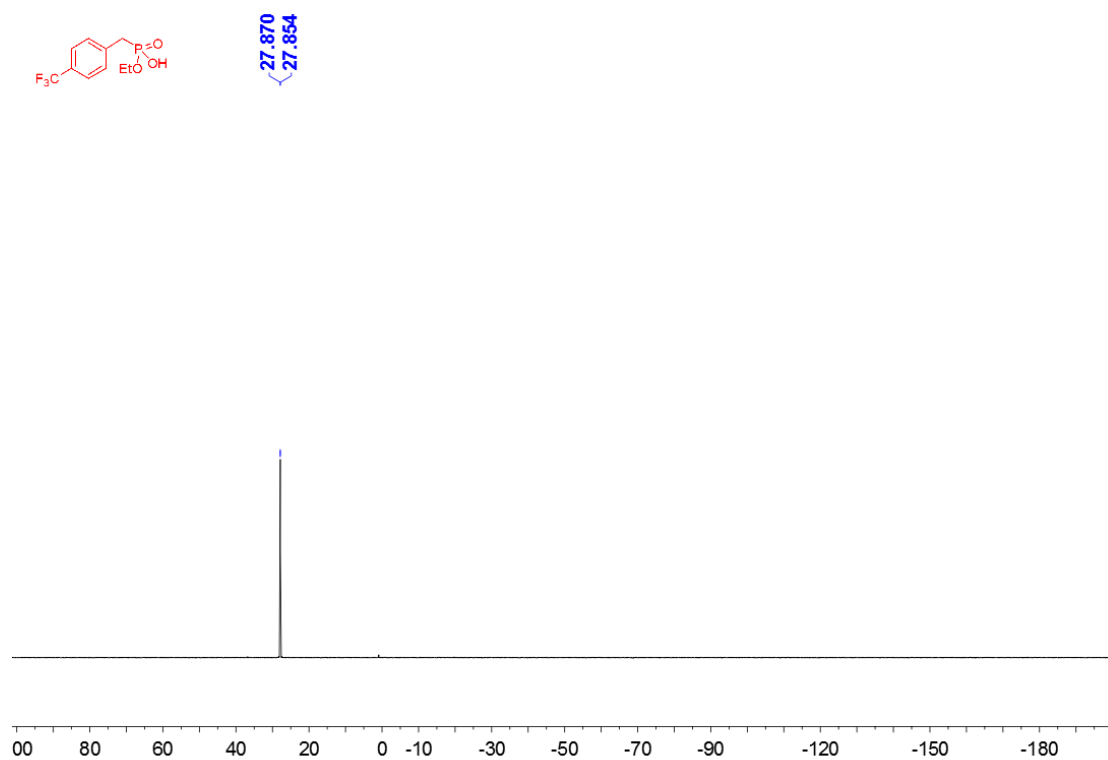
6.1. Copies of ^1H , ^{13}C , and ^{31}P NMR spectra of products 8



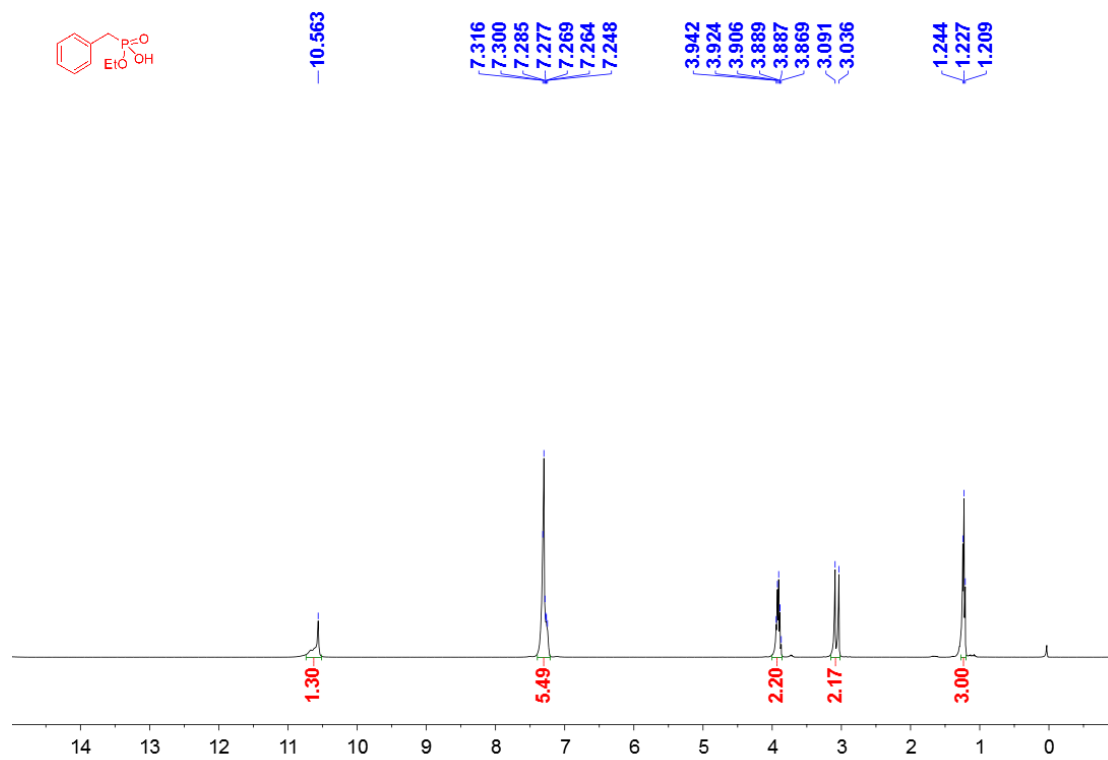
^1H NMR Spectrum of Compound 8a



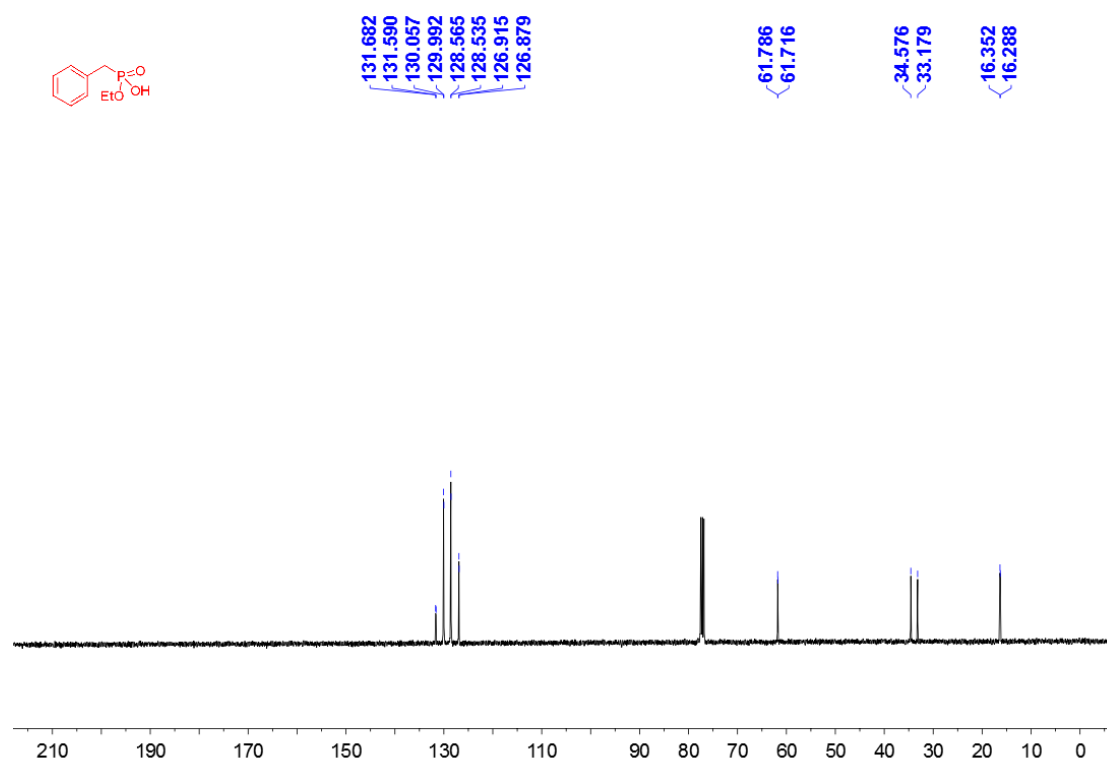
¹³C NMR Spectrum of Compound **8a**



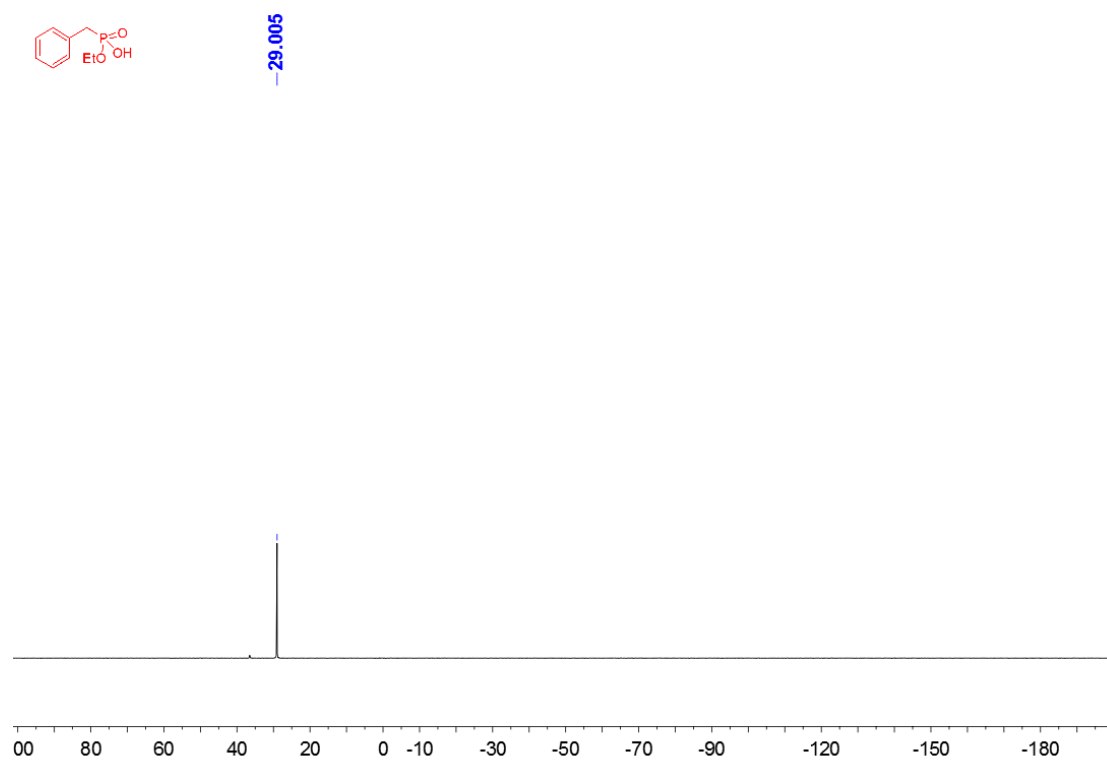
³¹P NMR Spectrum of Compound **8a**



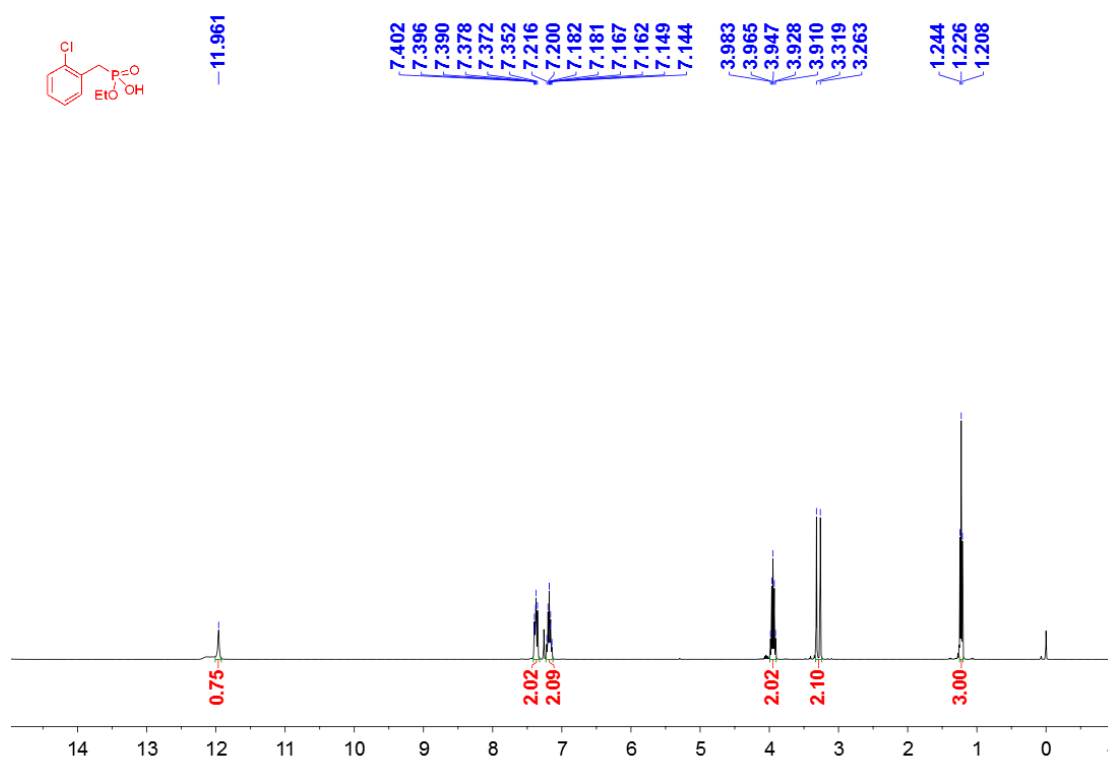
^1H NMR Spectrum of Compound **8b**



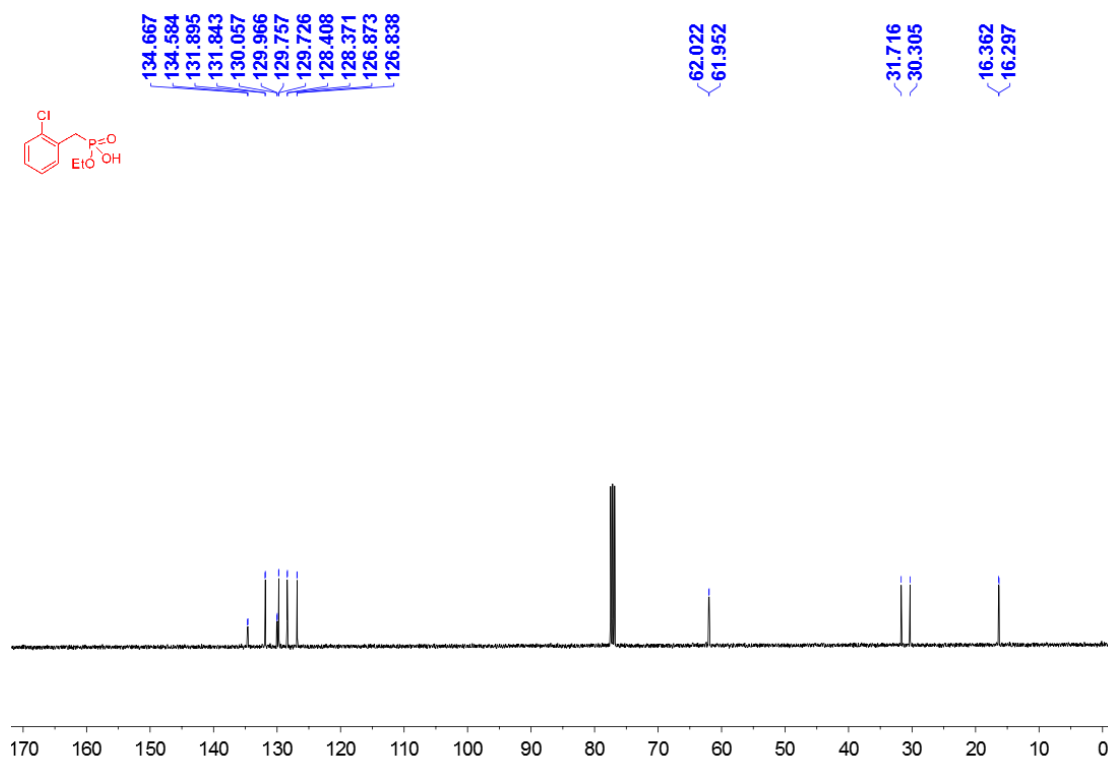
^{13}C NMR Spectrum of Compound **8b**



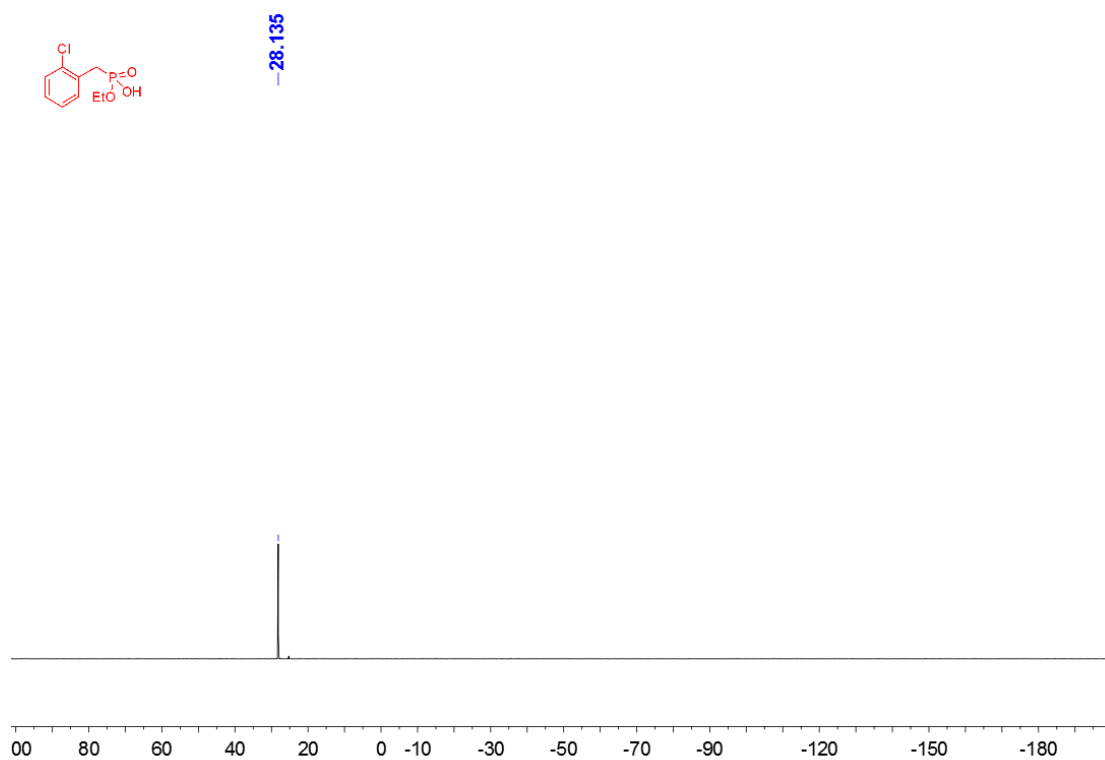
³¹P NMR Spectrum of Compound **8b**



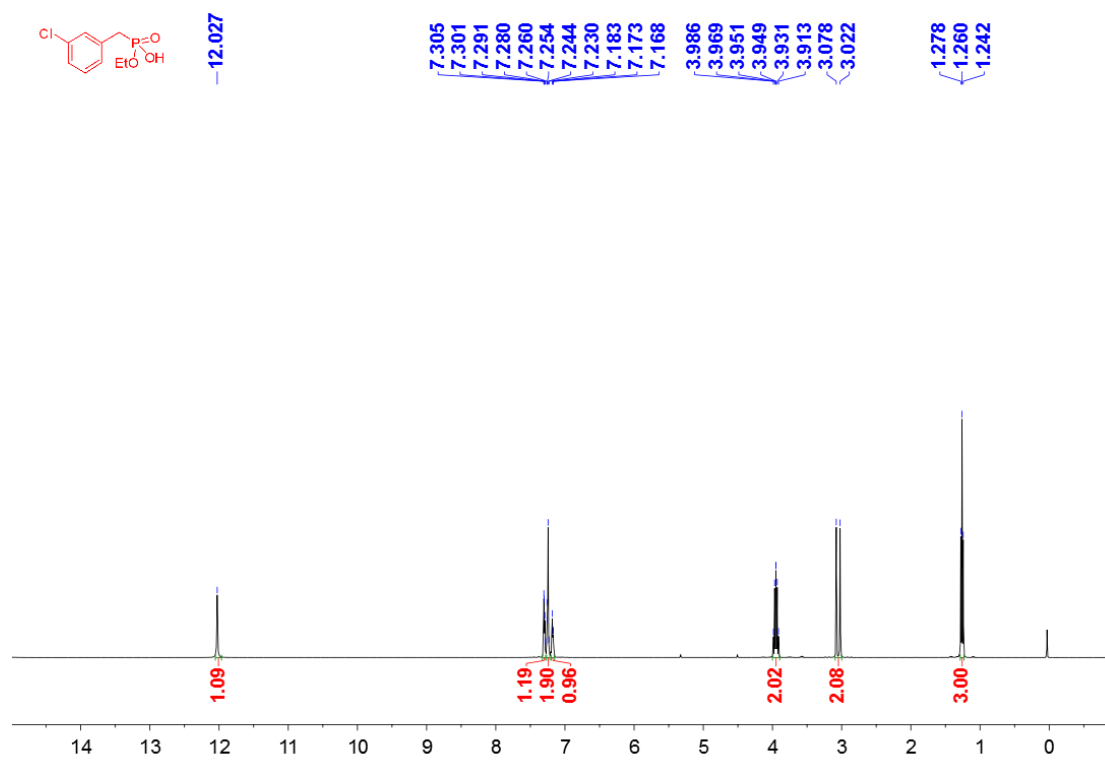
¹H NMR Spectrum of Compound **8c**



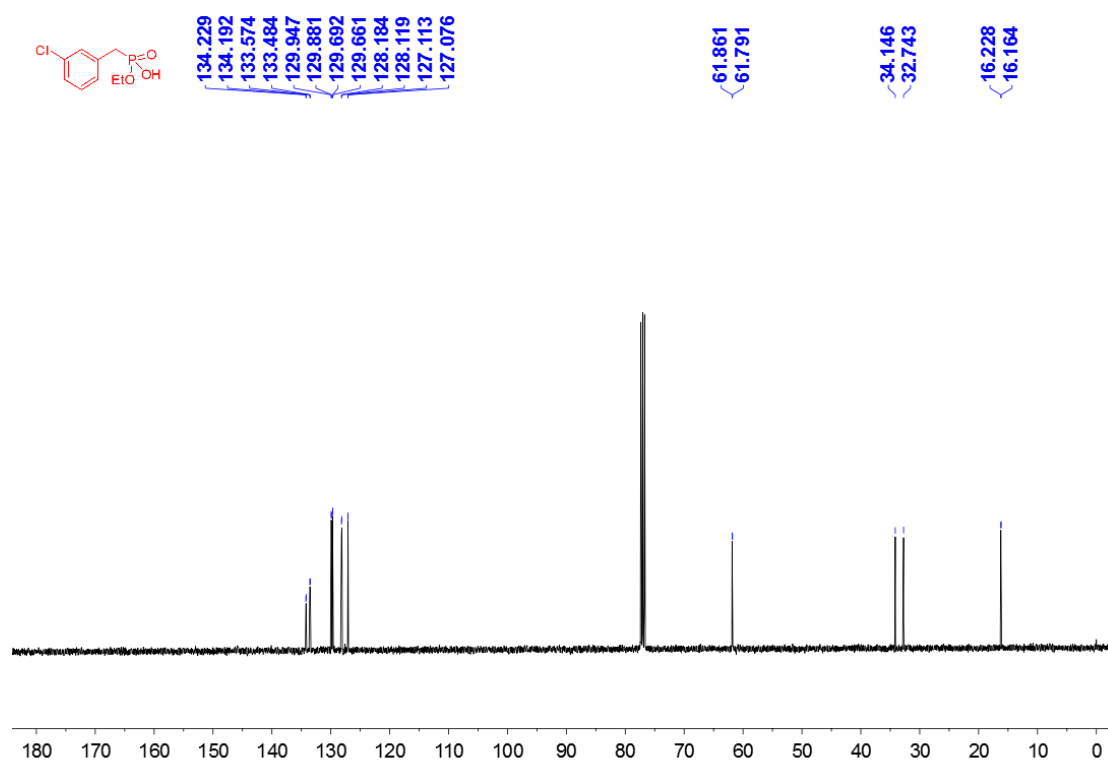
¹³C NMR Spectrum of Compound **8c**



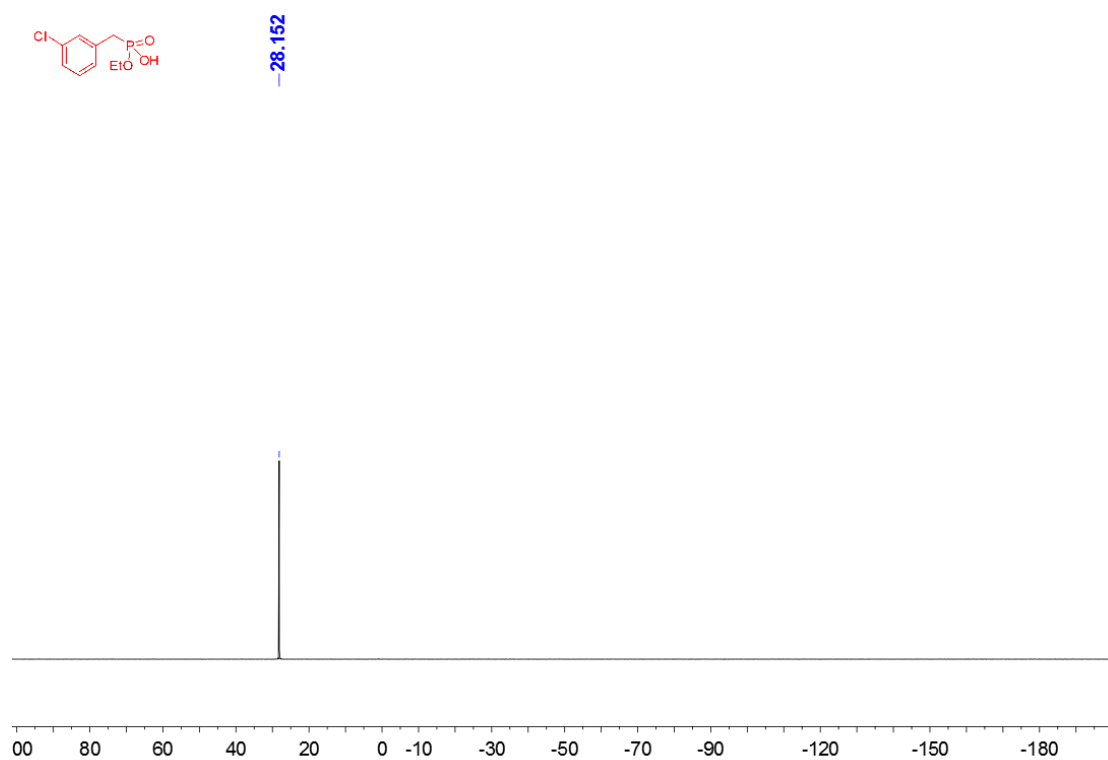
³¹P NMR Spectrum of Compound **8c**



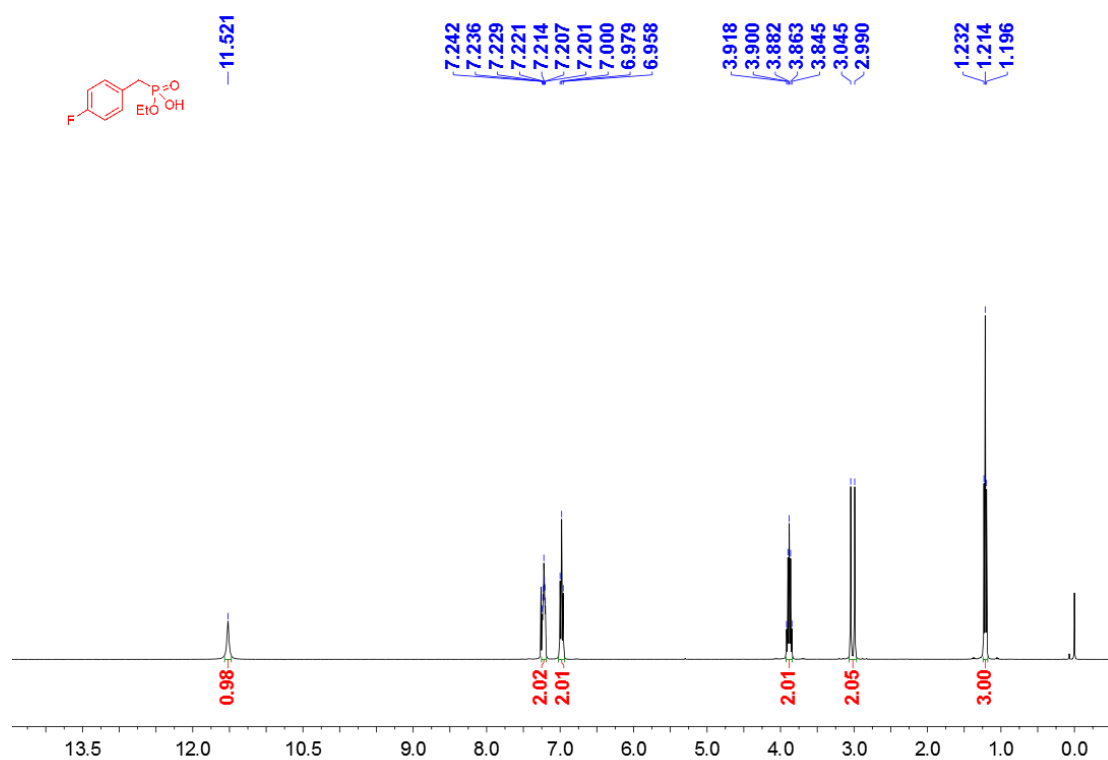
¹H NMR Spectrum of Compound **8d**



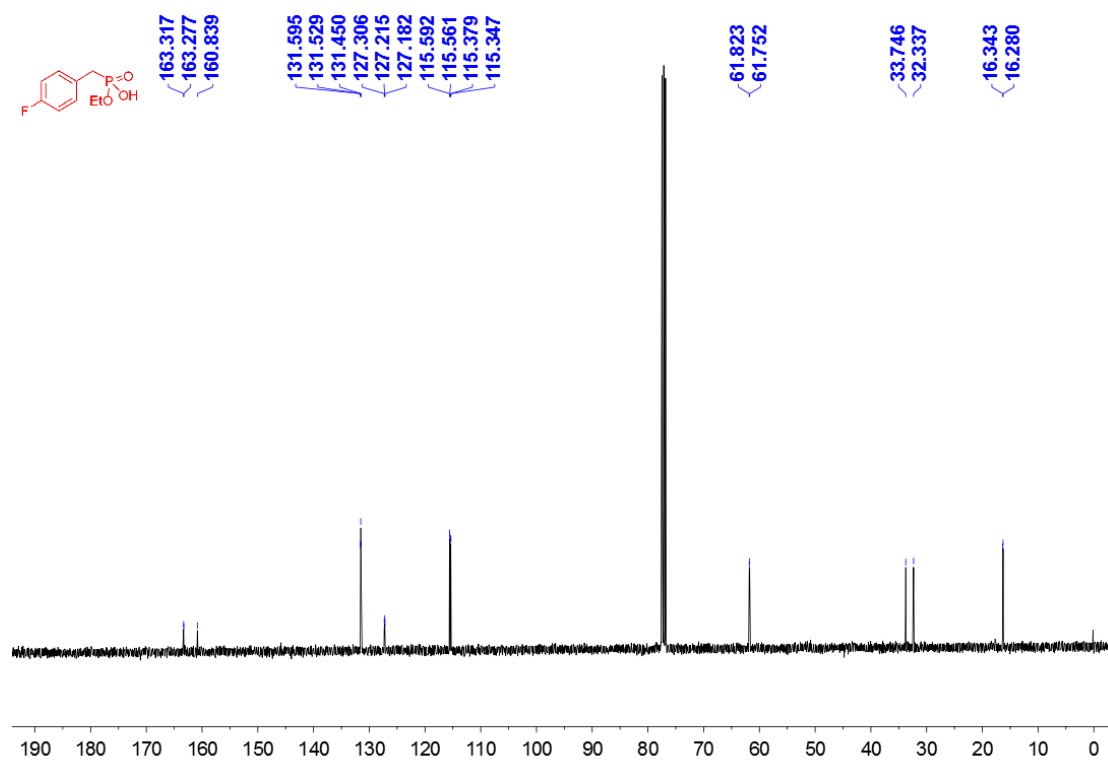
¹³C NMR Spectrum of Compound **8d**



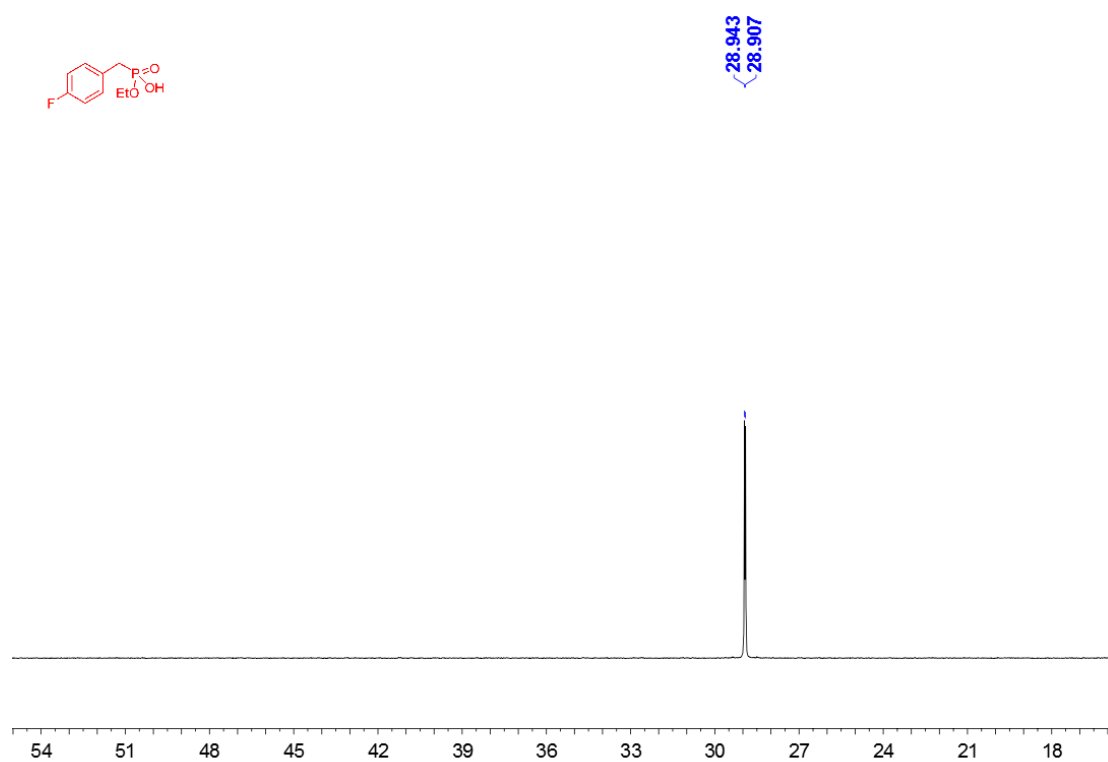
³¹P NMR Spectrum of Compound **8d**



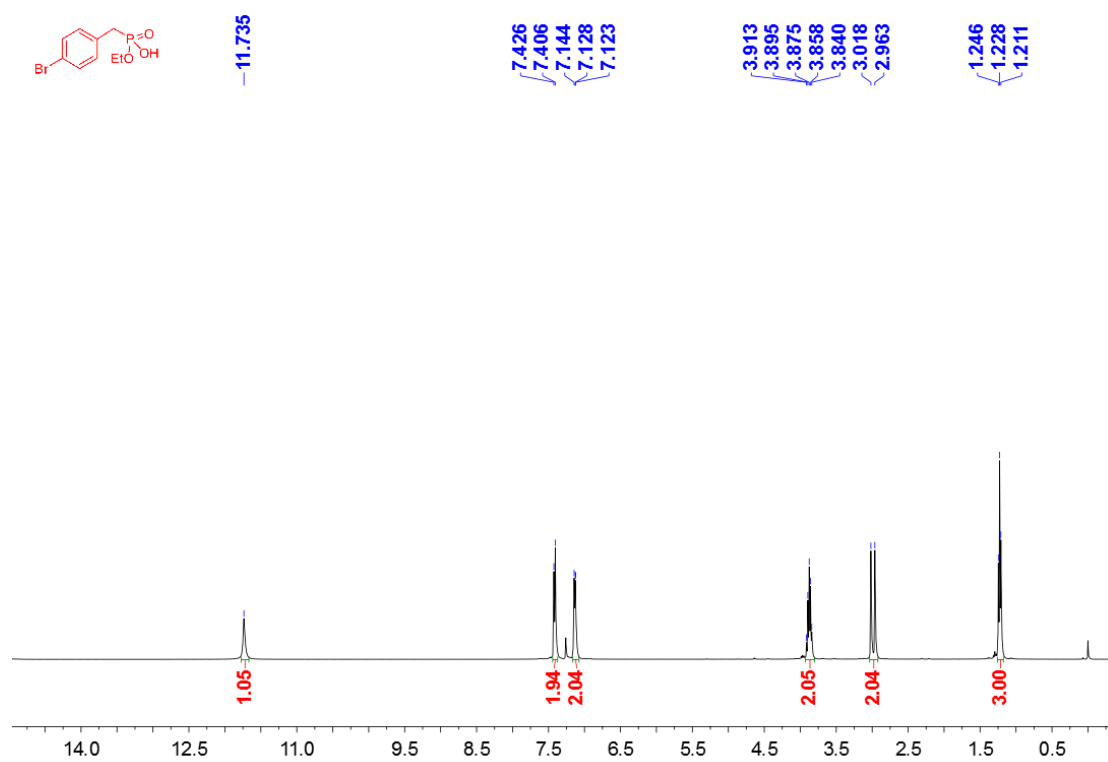
¹H NMR Spectrum of Compound 8e



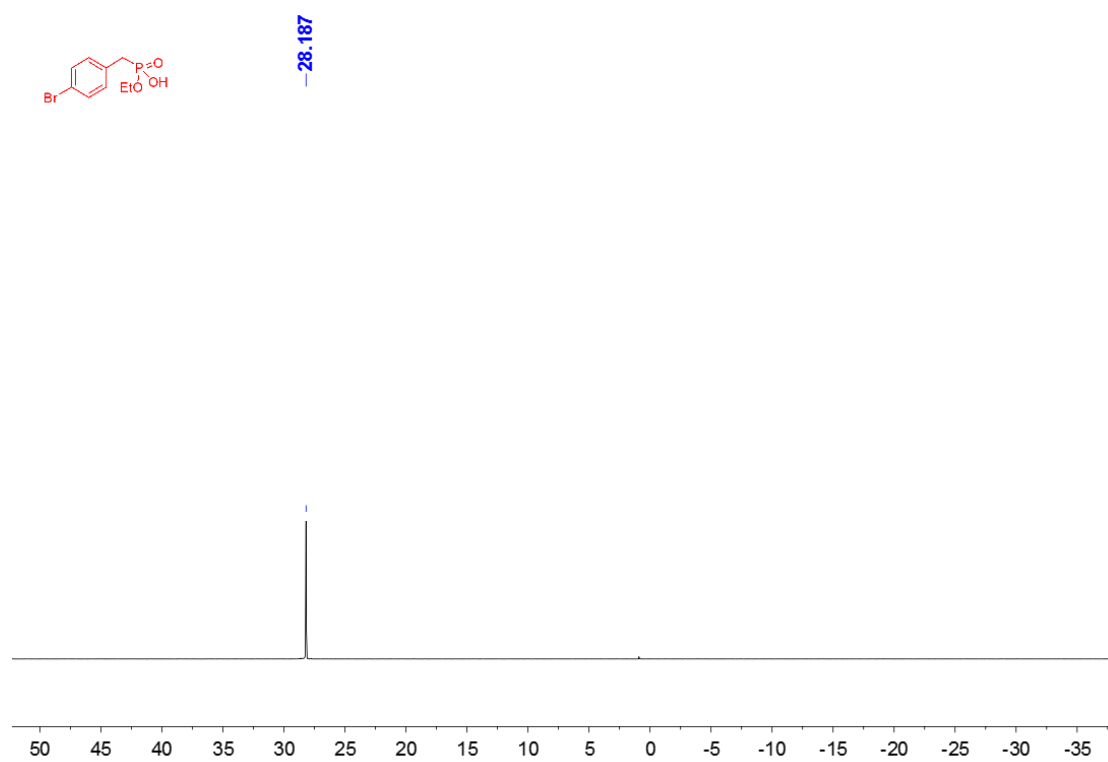
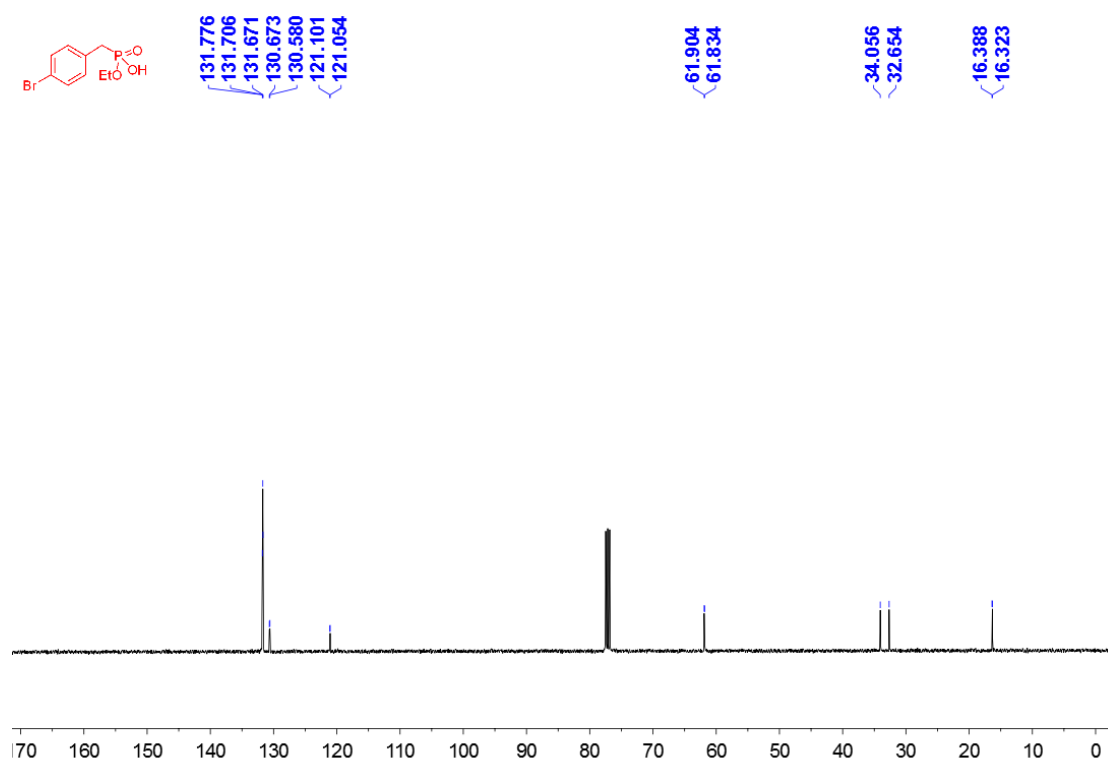
¹³C NMR Spectrum of Compound 8e

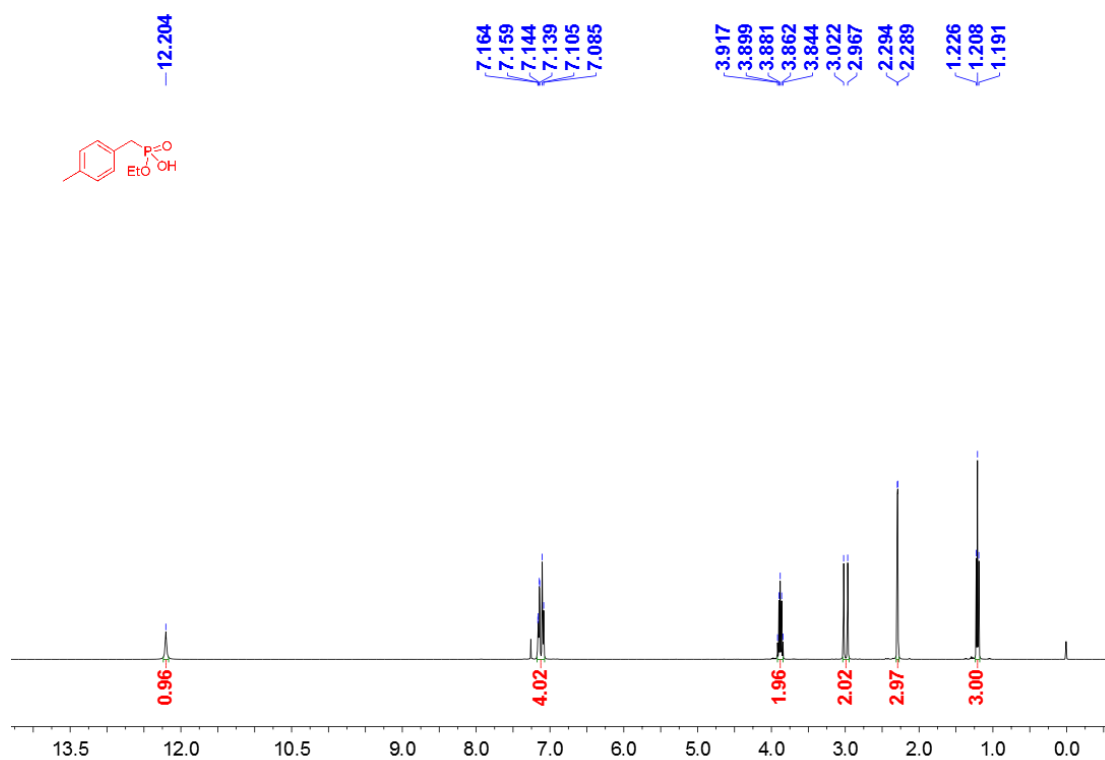


^{31}P NMR Spectrum of Compound 8e

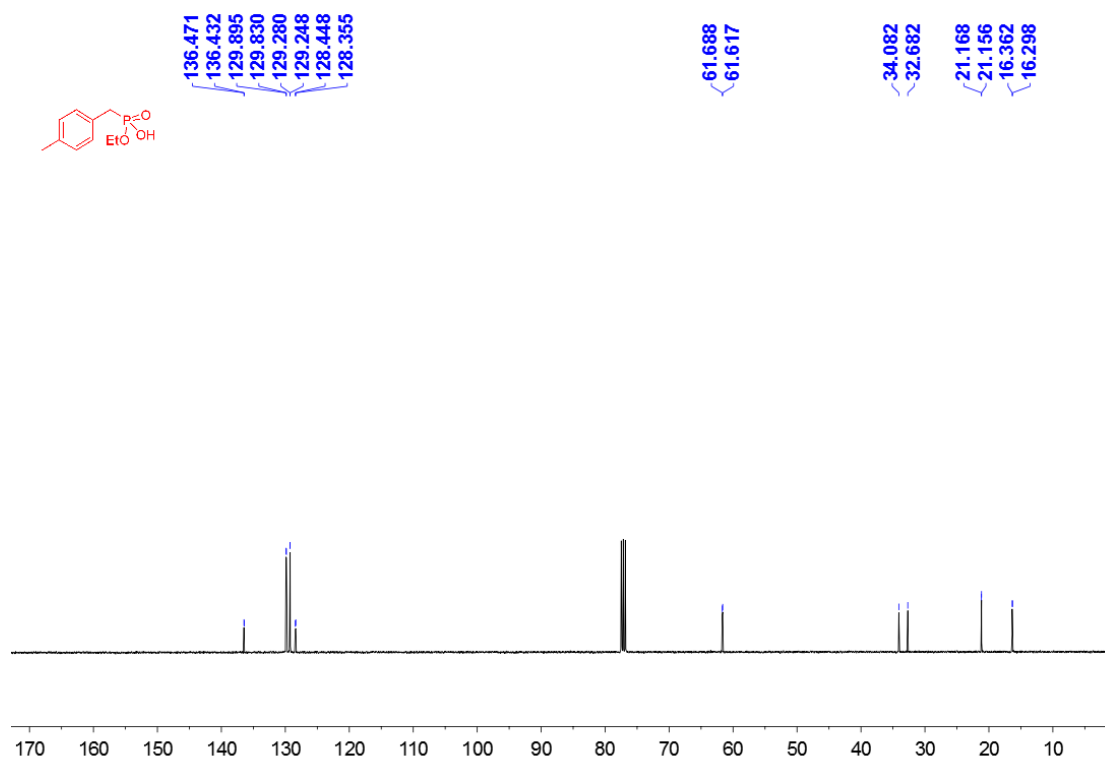


^1H NMR Spectrum of Compound 8f

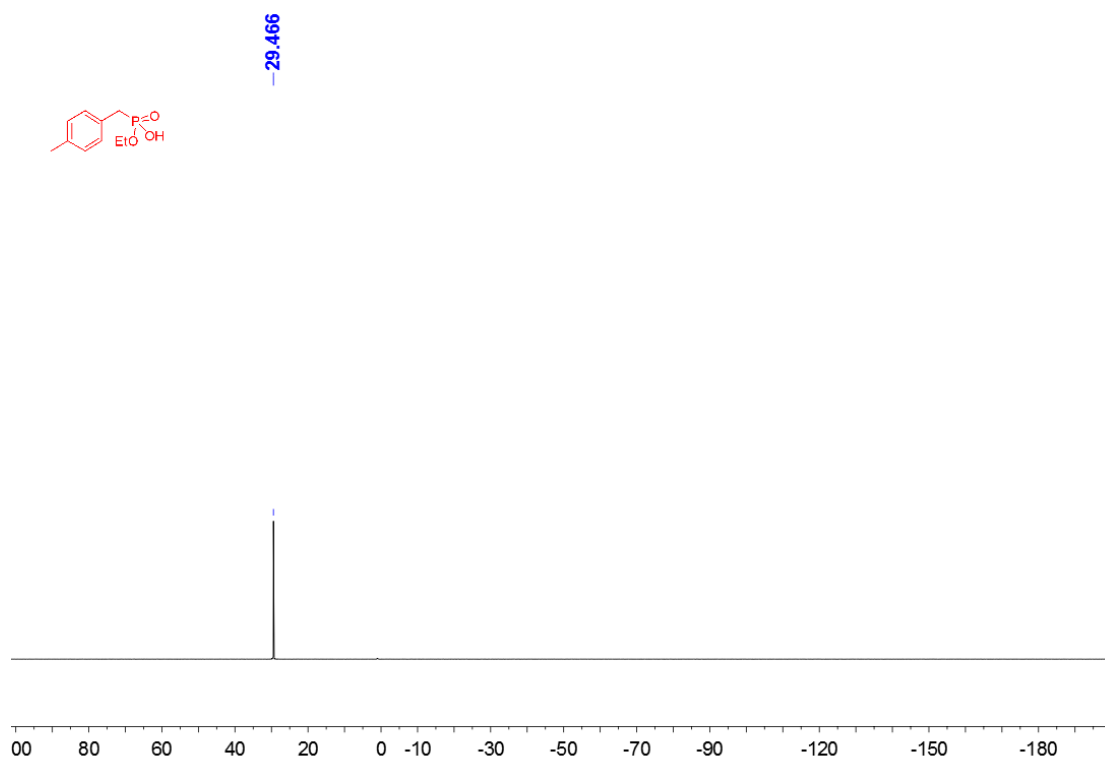




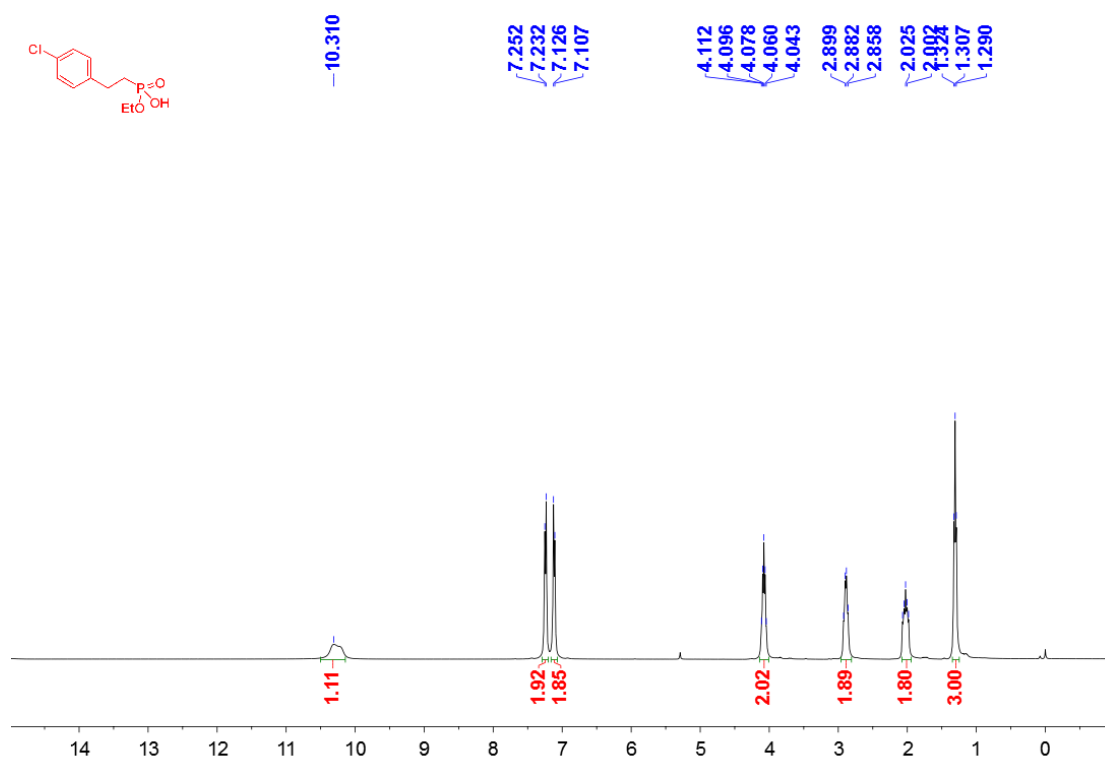
¹H NMR Spectrum of Compound **8g**



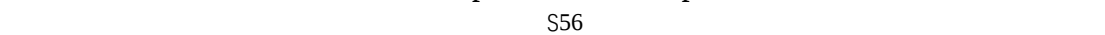
¹³C NMR Spectrum of Compound **8g**

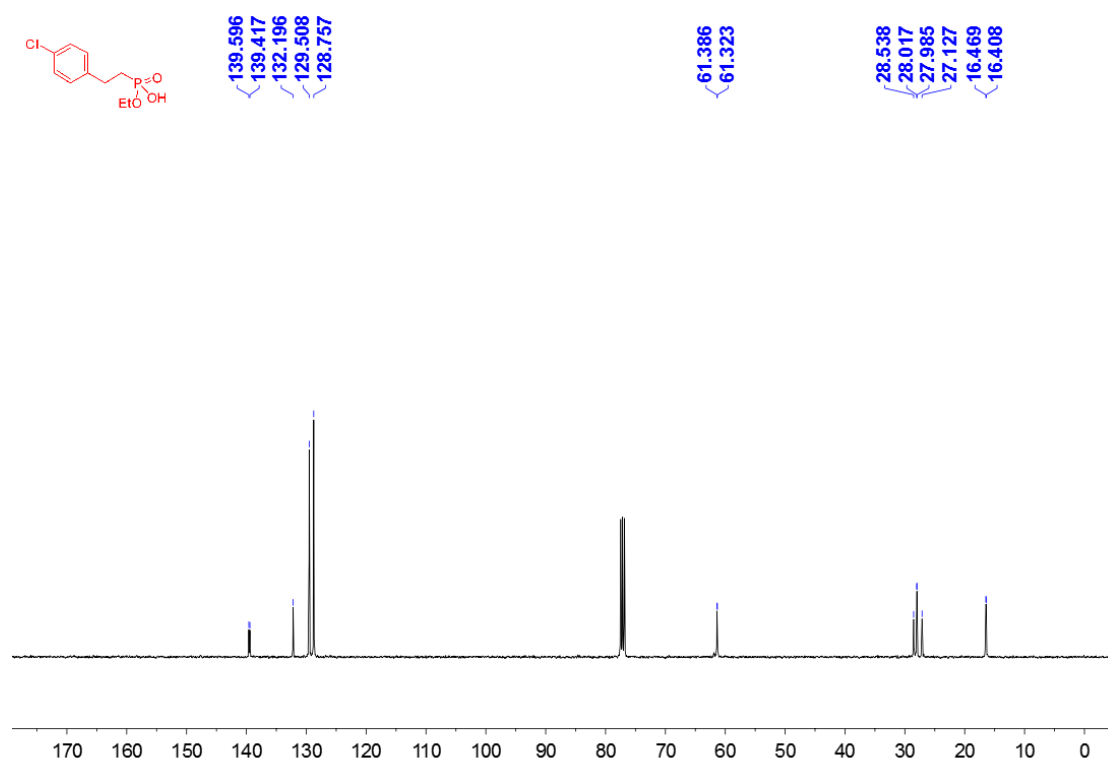


³¹P NMR Spectrum of Compound **8g**

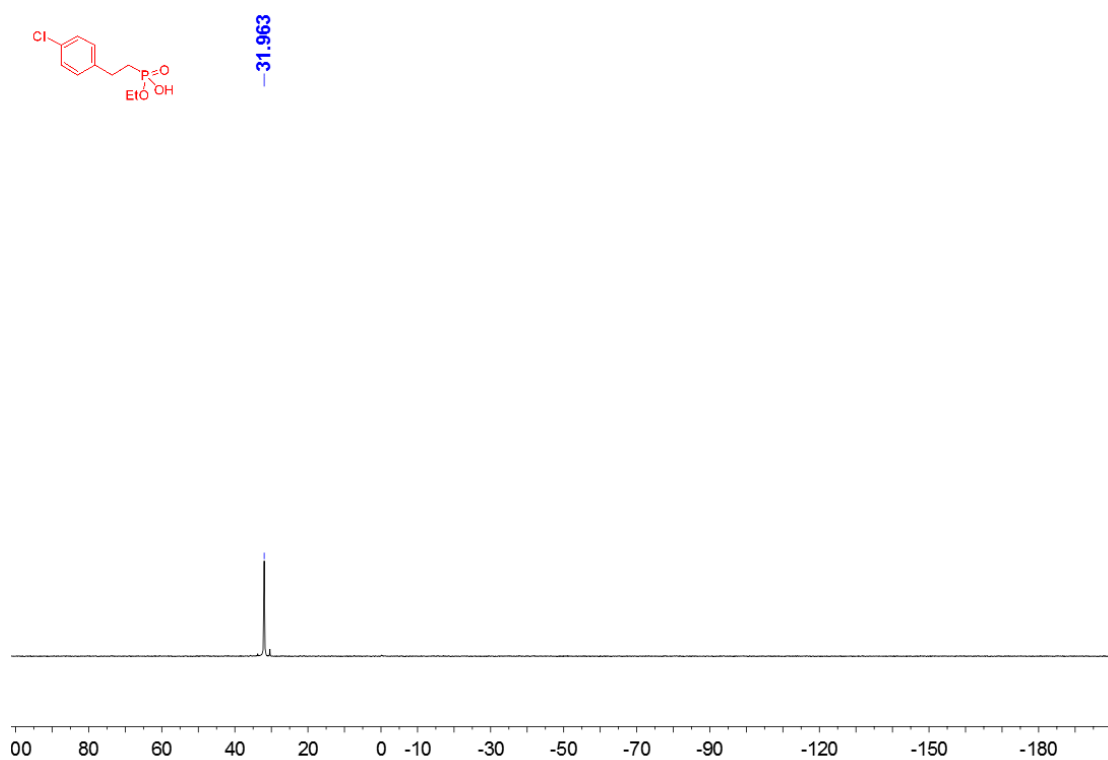


¹H NMR Spectrum of Compound **8h**

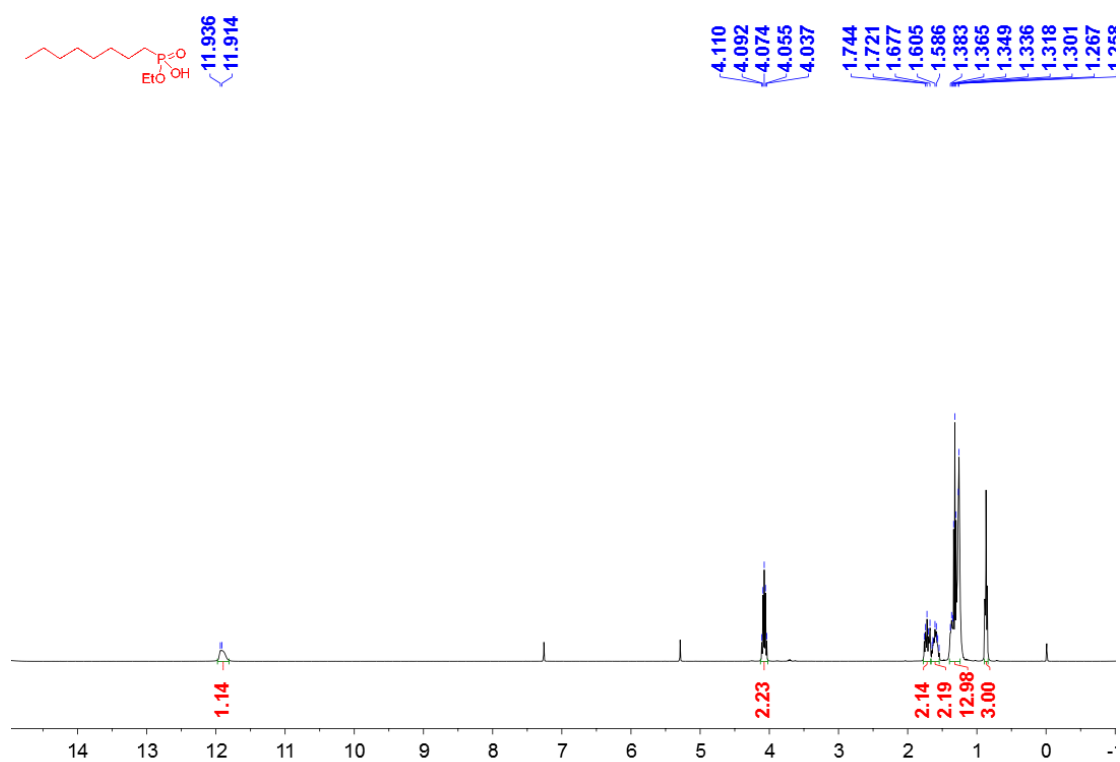




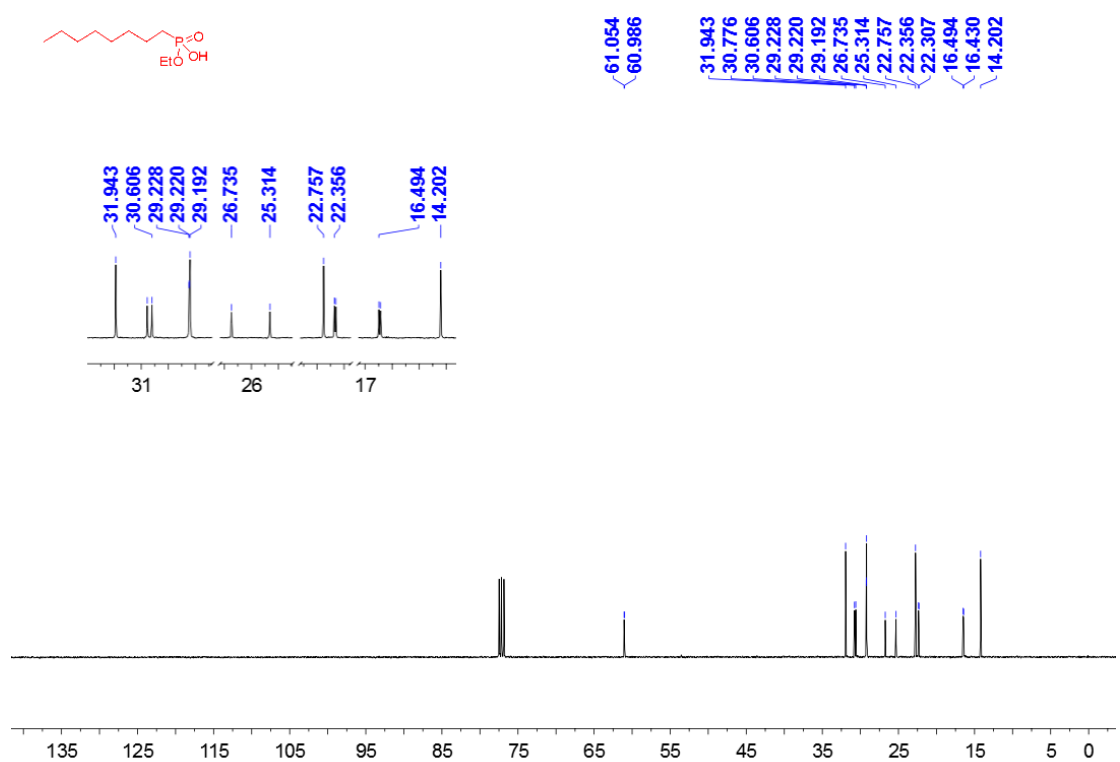
¹³C NMR Spectrum of Compound **8h**



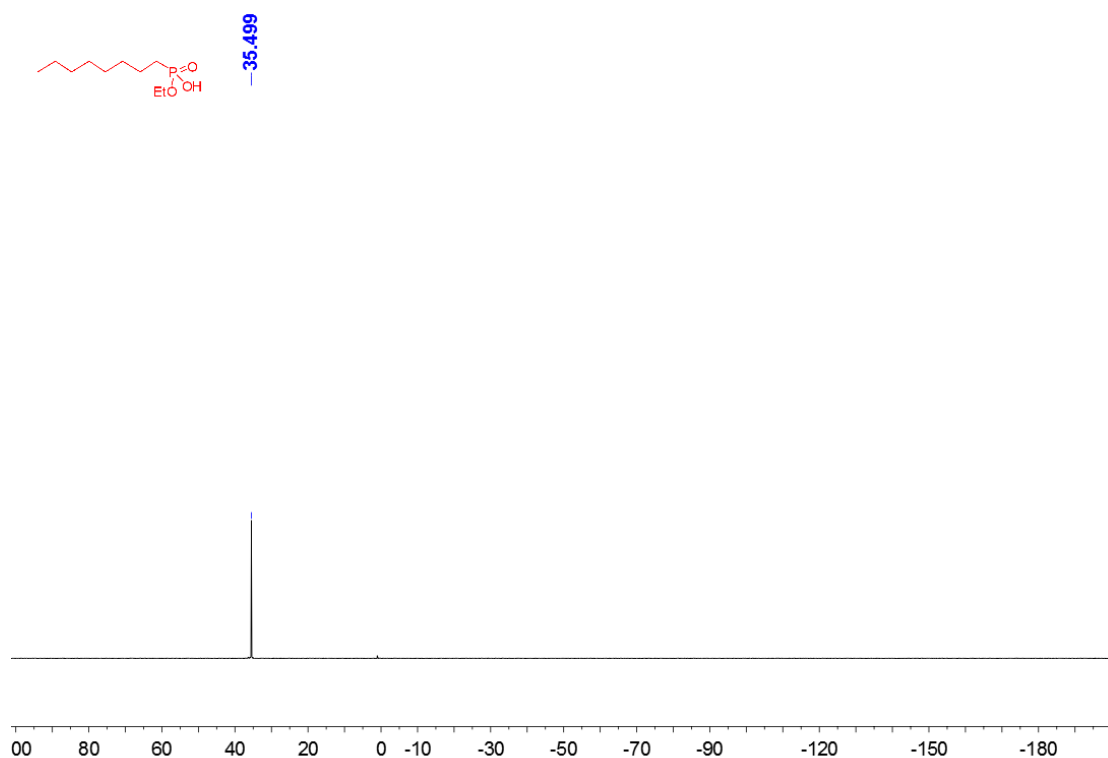
³¹P NMR Spectrum of Compound **8h**



¹H NMR Spectrum of Compound **8i**

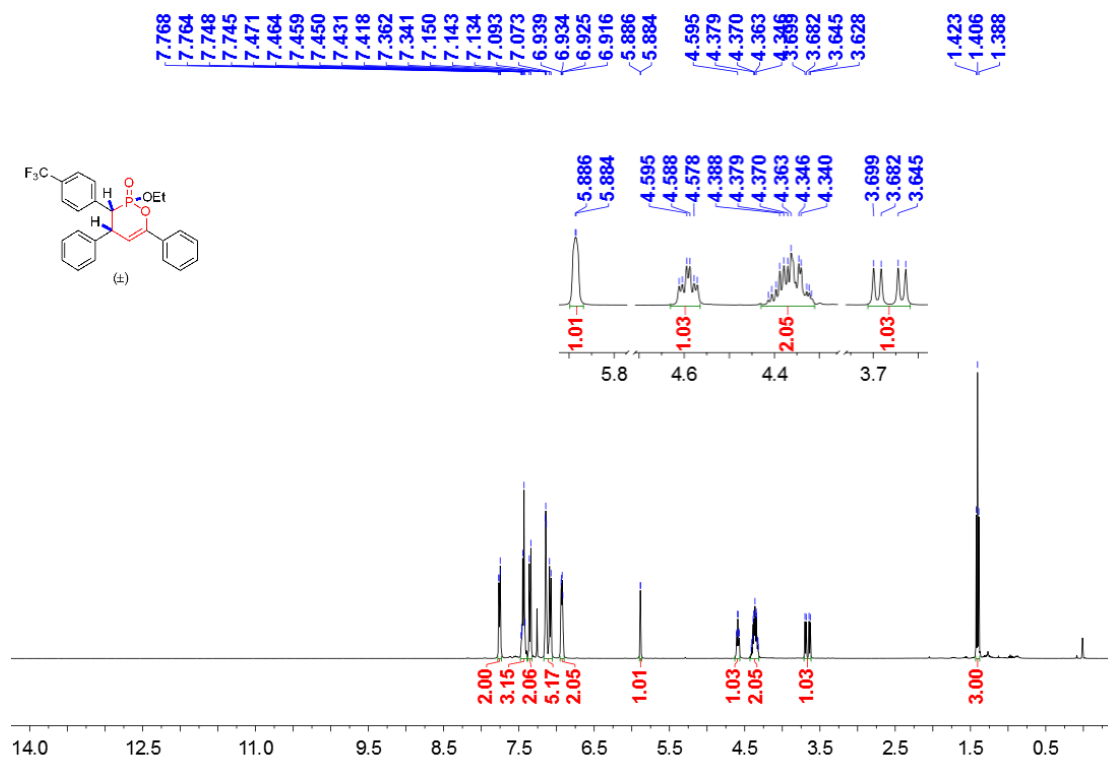


¹³C NMR Spectrum of Compound **8i**

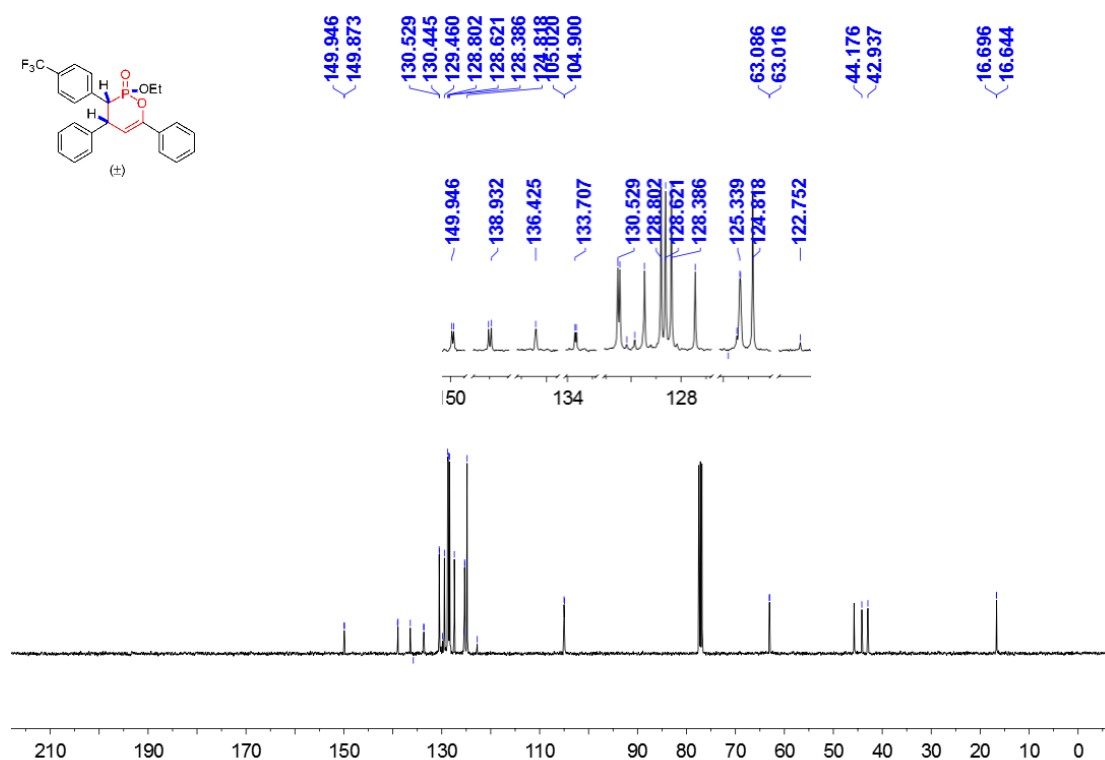


^{31}P NMR Spectrum of Compound 8i

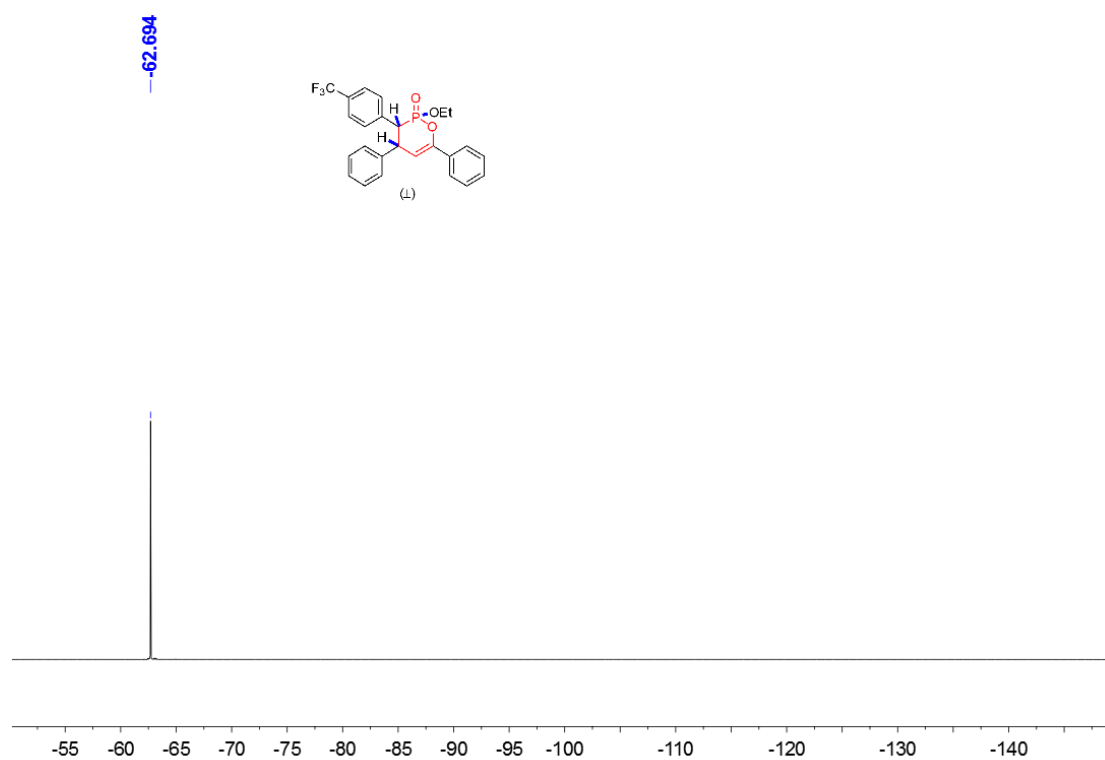
6.2. Copies of ^1H , ^{13}C , ^{31}P , and ^{19}F NMR spectra of products 3



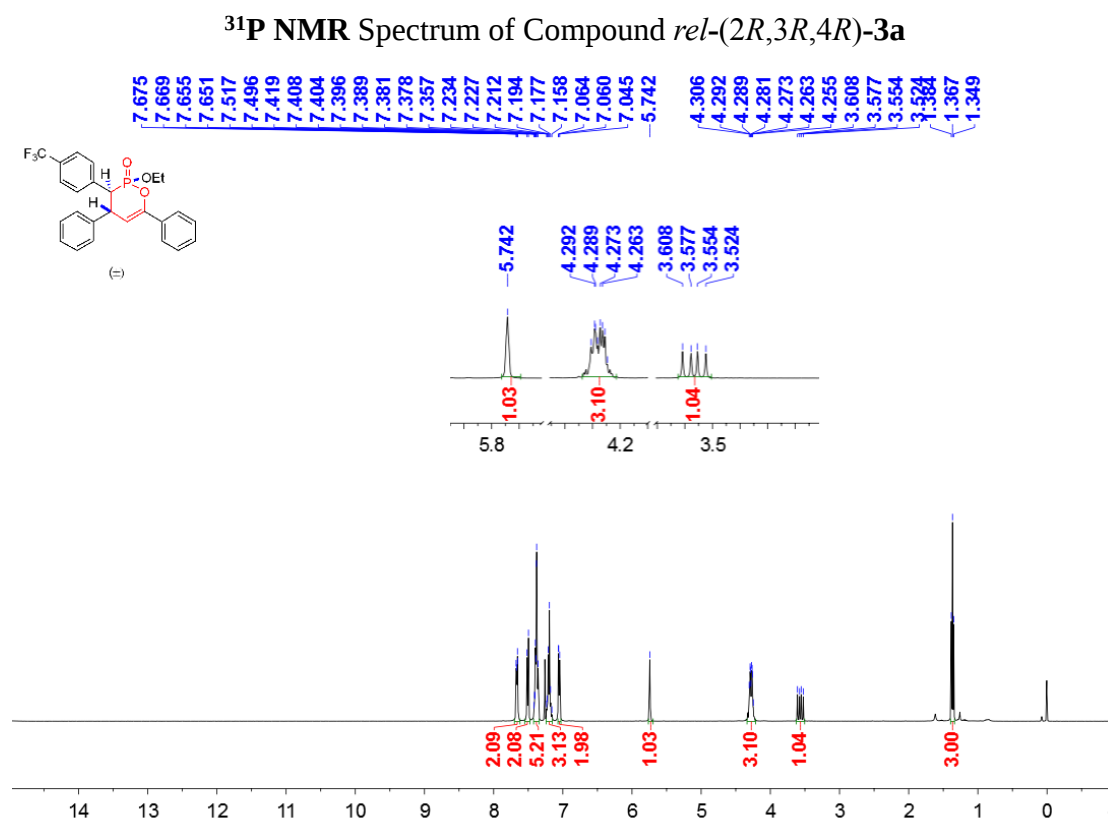
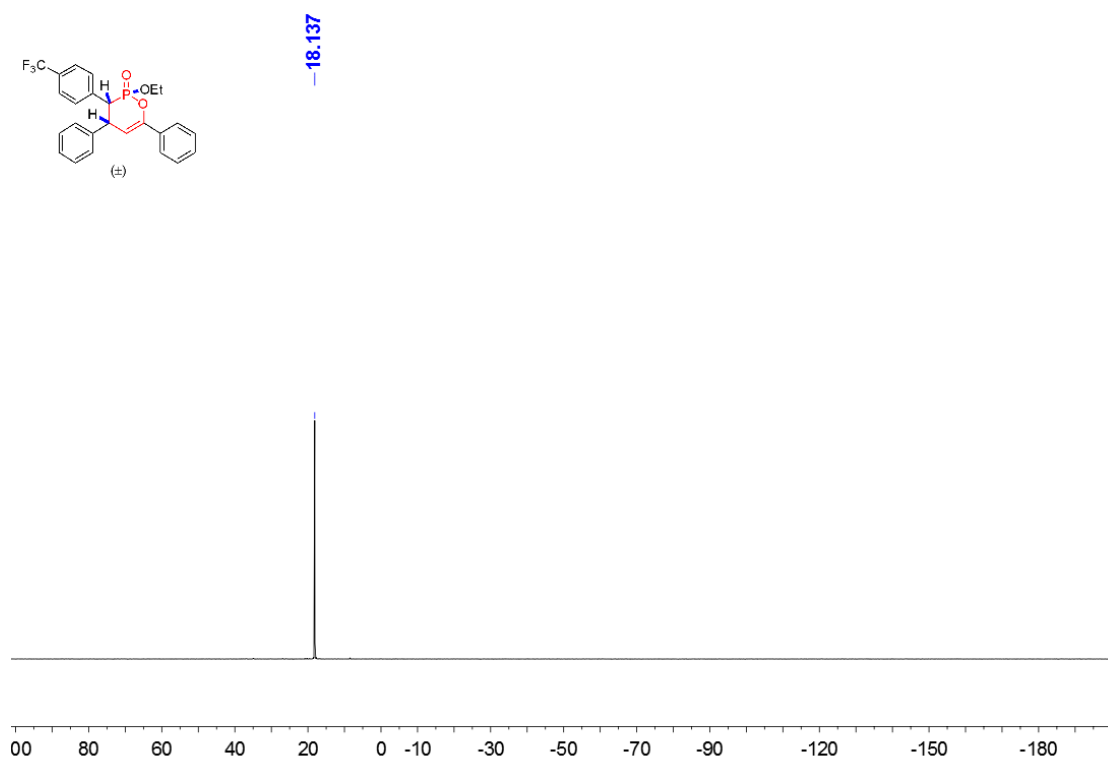
^1H NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3a

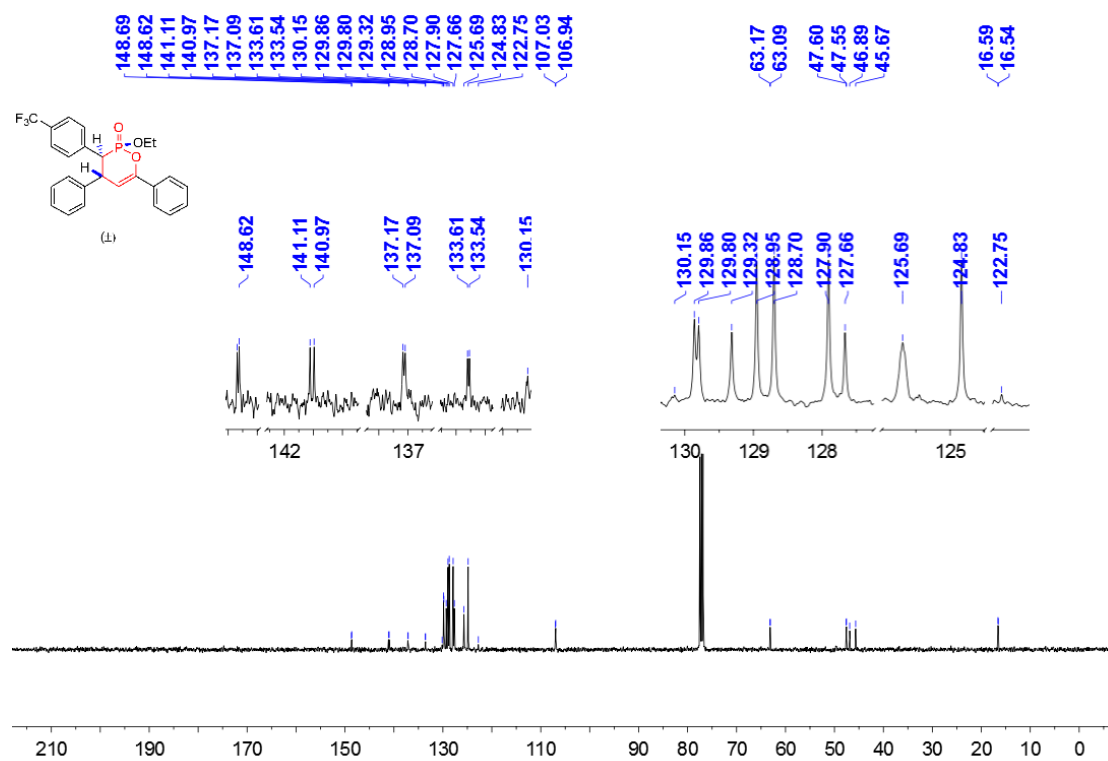


^{13}C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3a

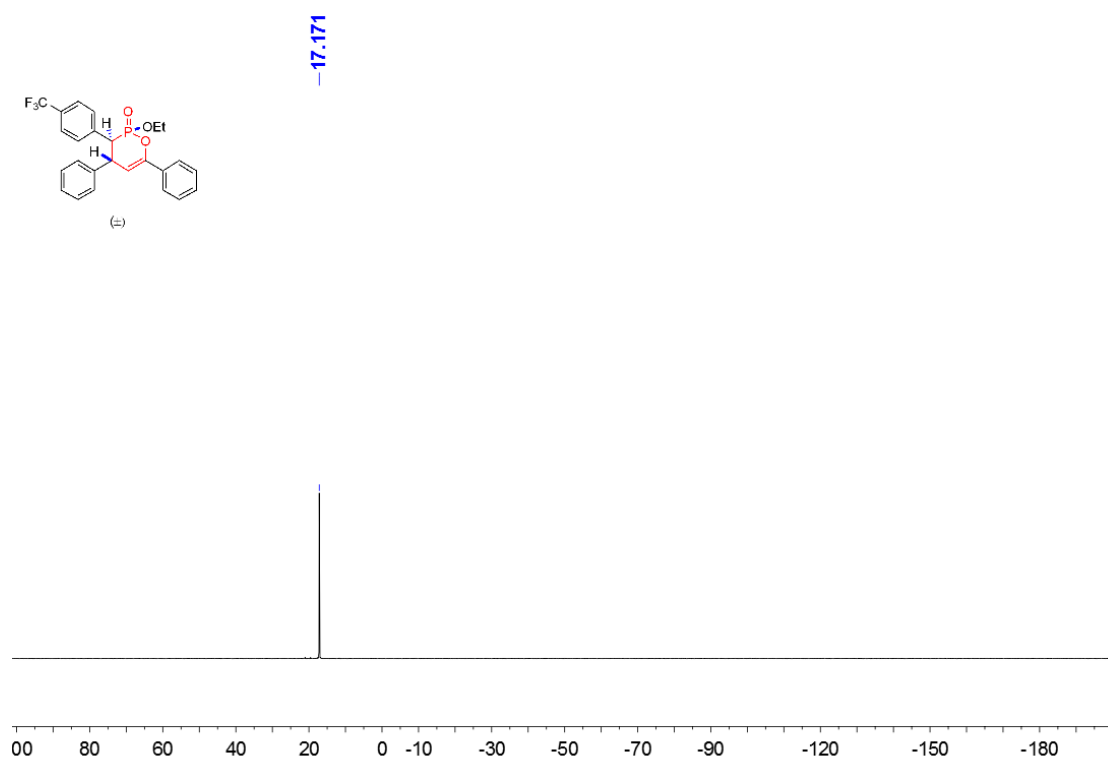


^{19}F NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3a

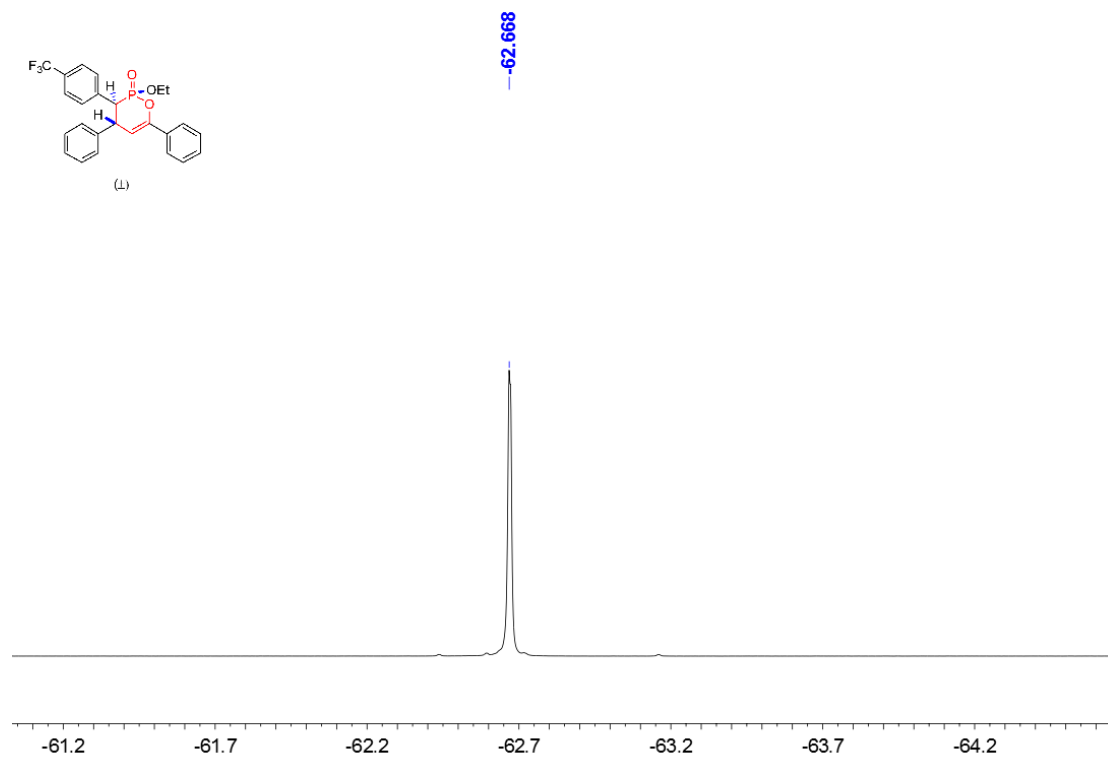




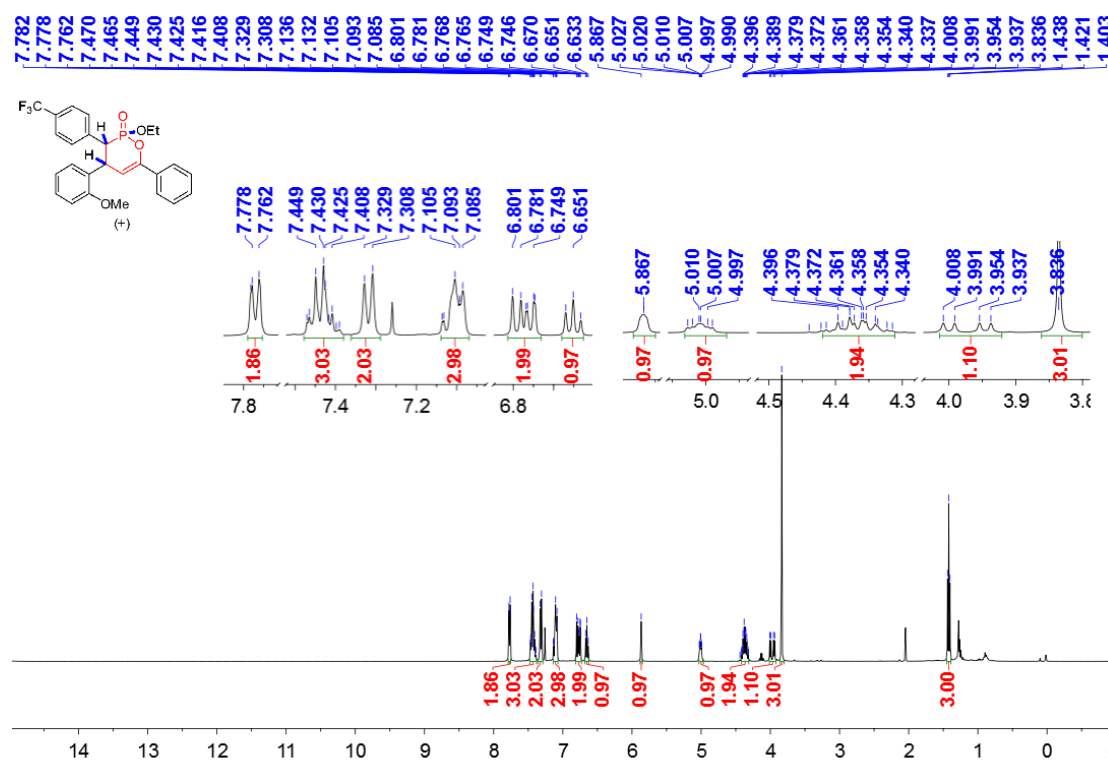
¹³C NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-3a



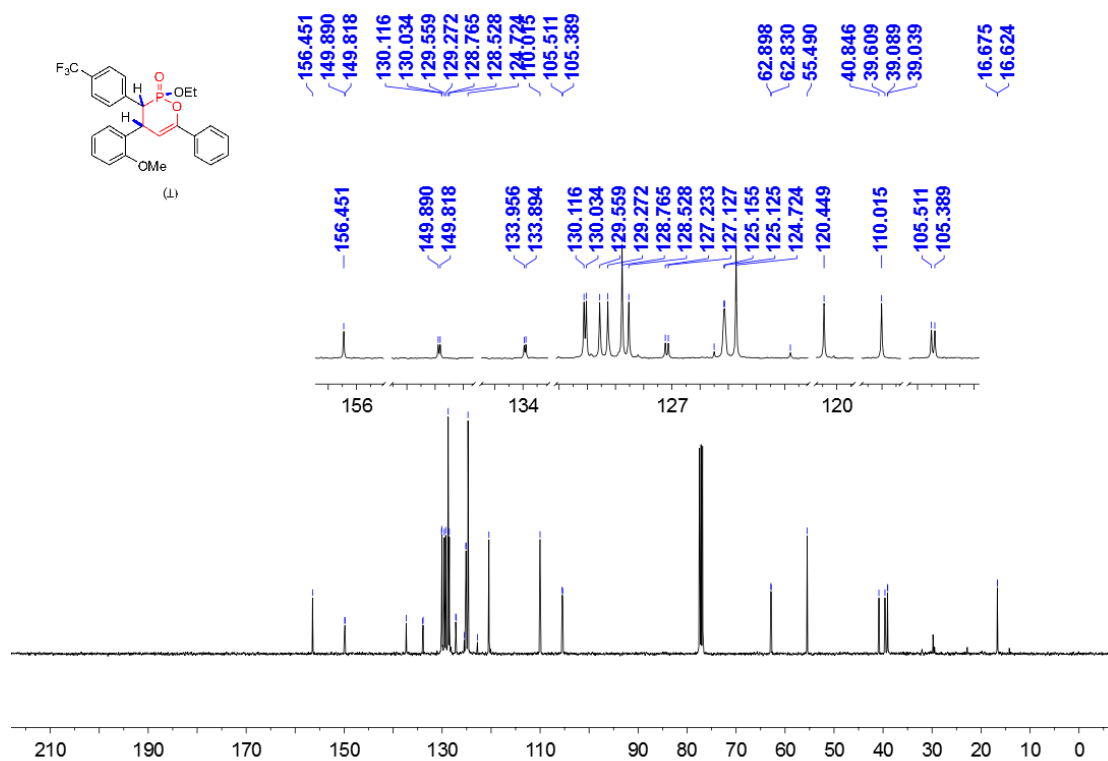
³¹P NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-3a



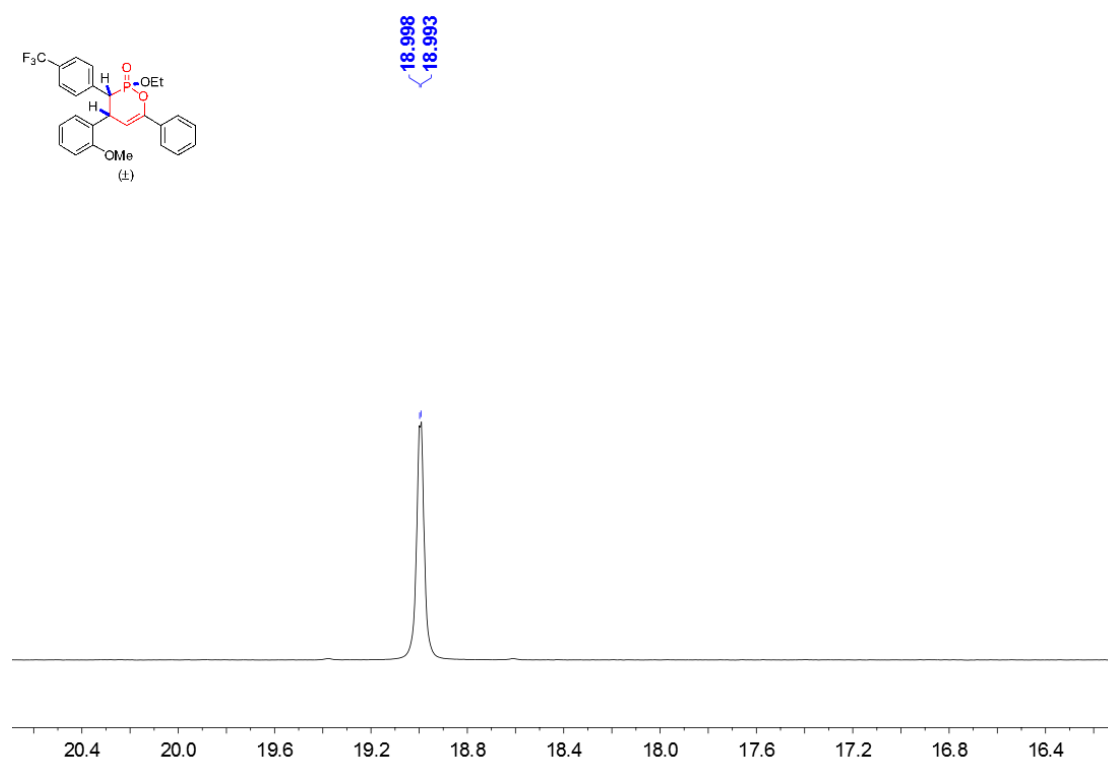
¹⁹F NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-3a



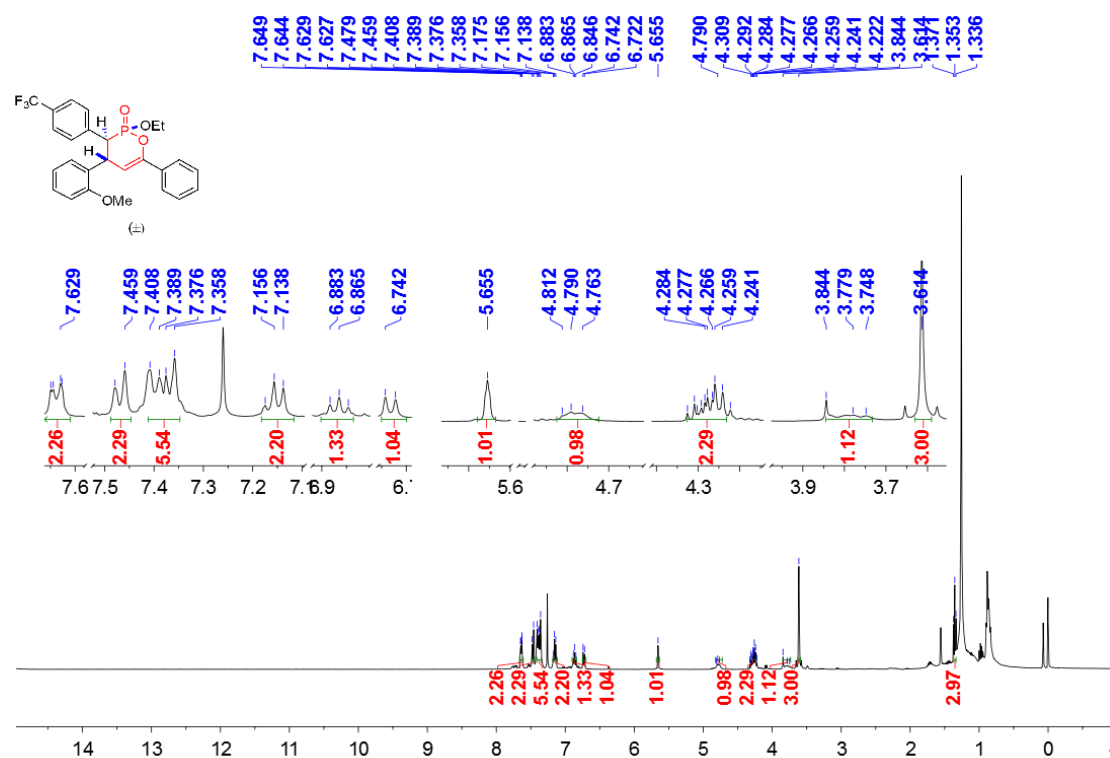
¹H NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3b



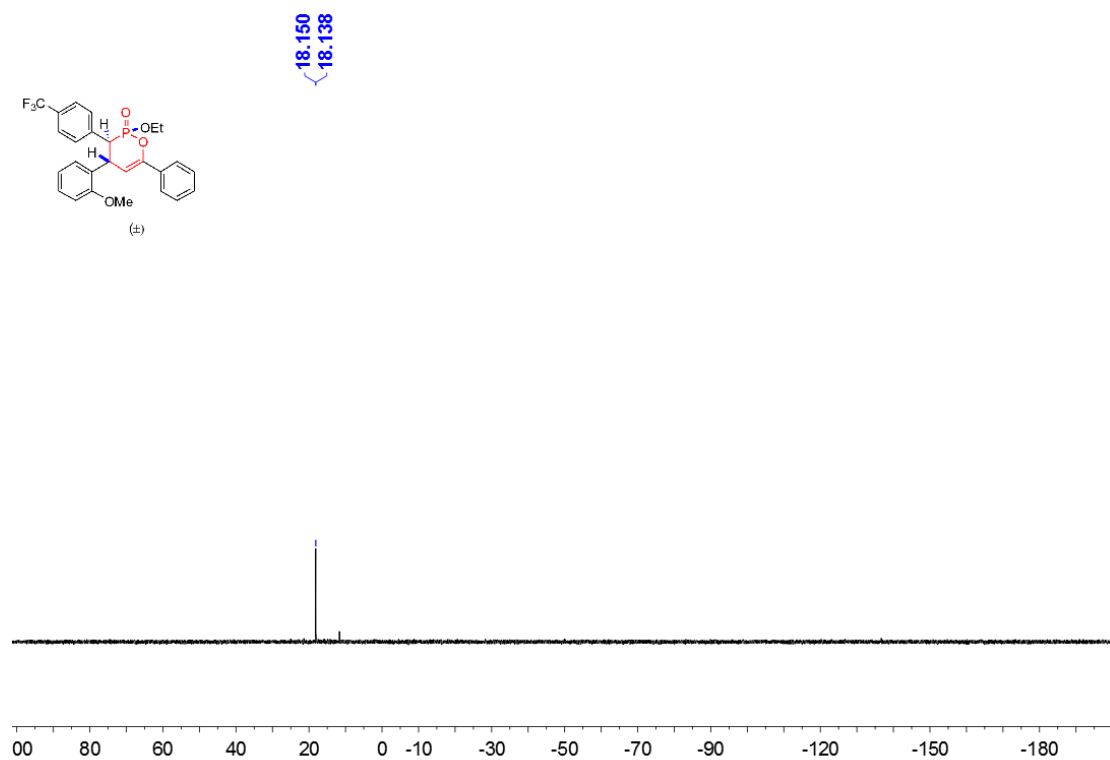
¹³C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3b**



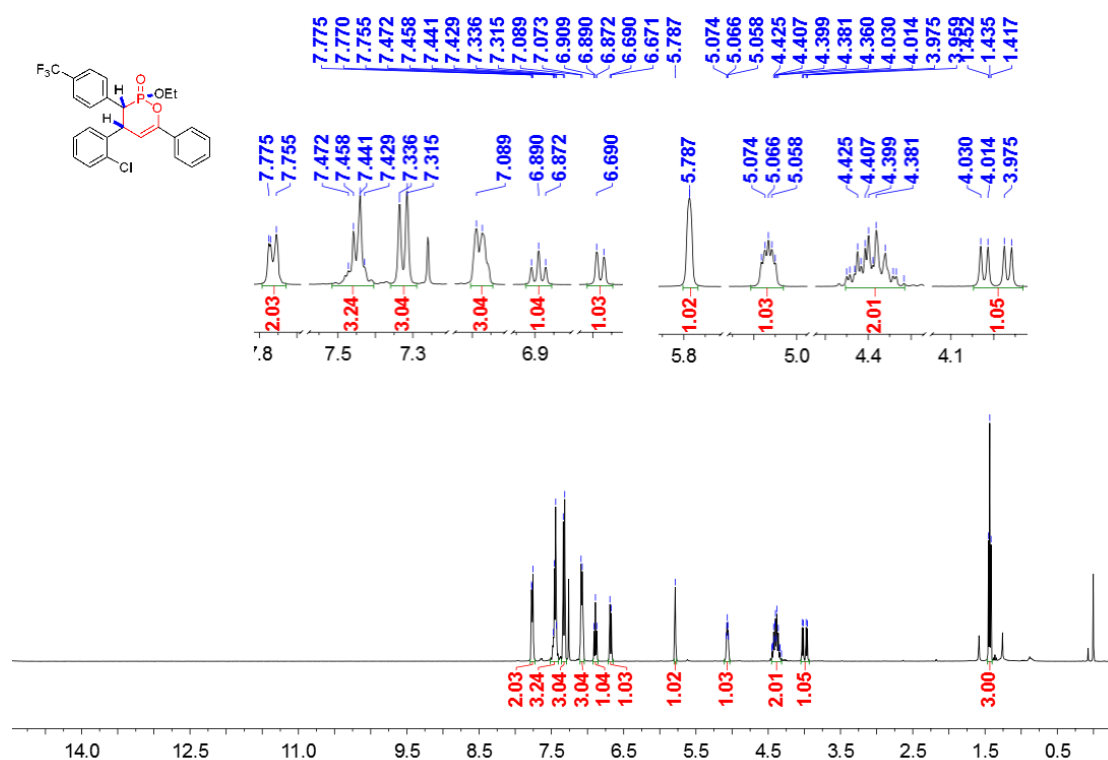
³¹P NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3b**



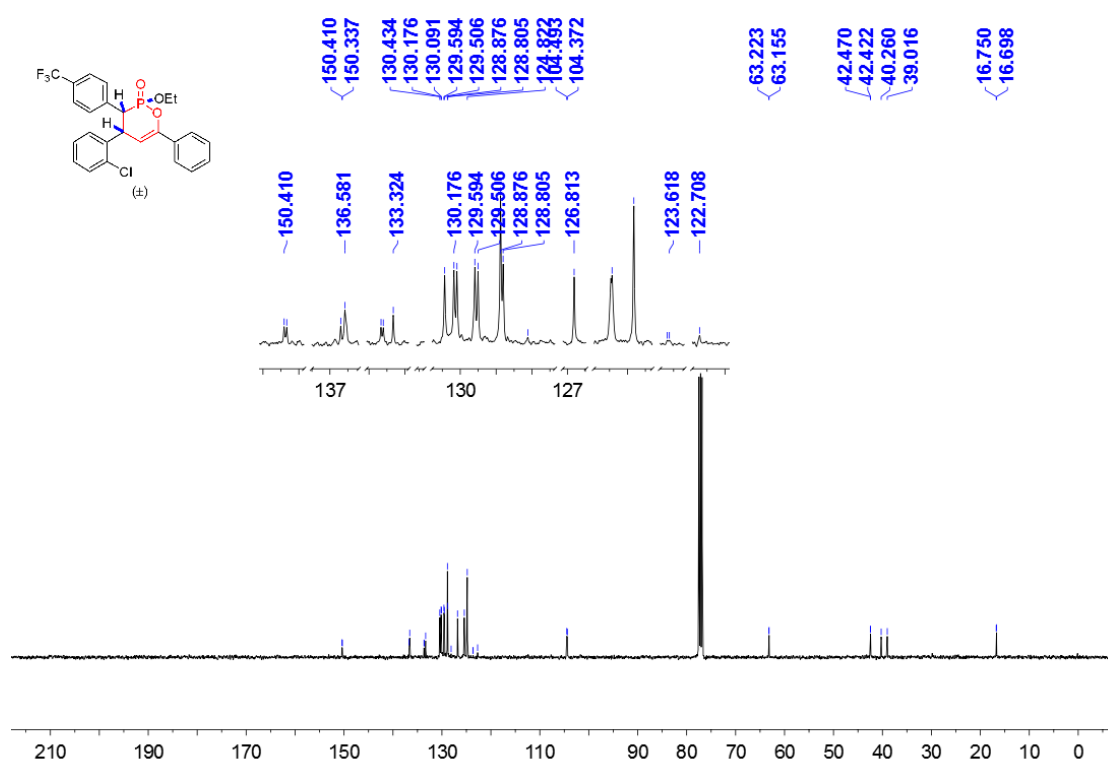
¹H NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3b**



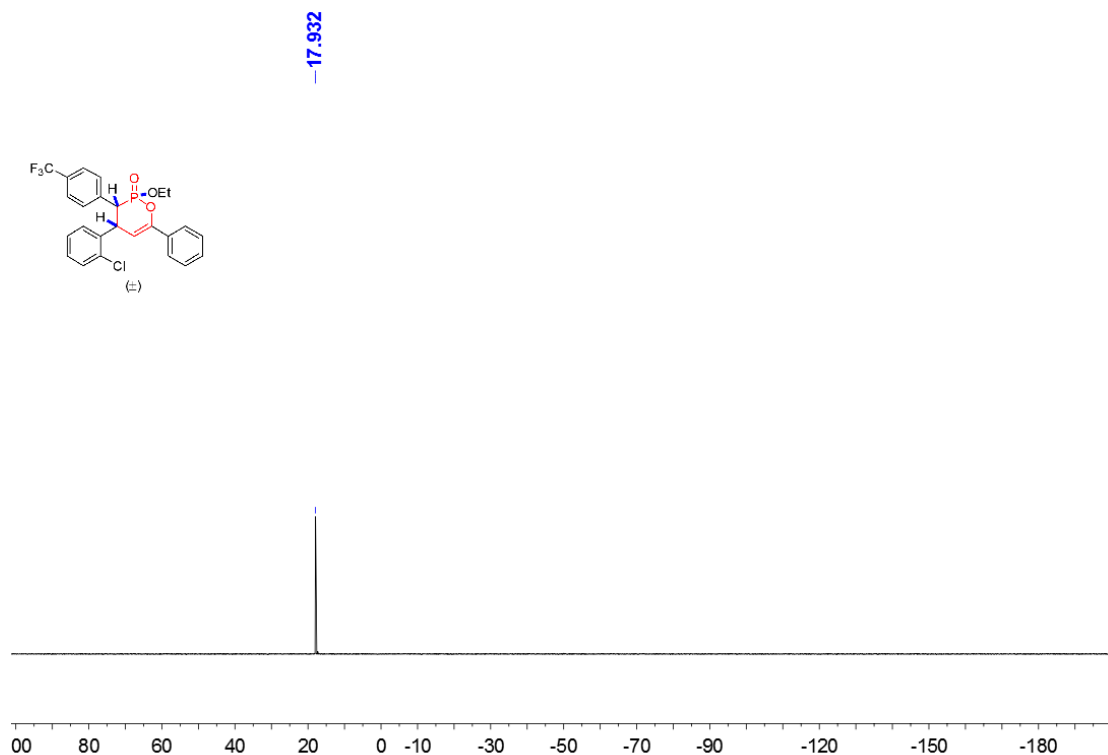
³¹P NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3b**



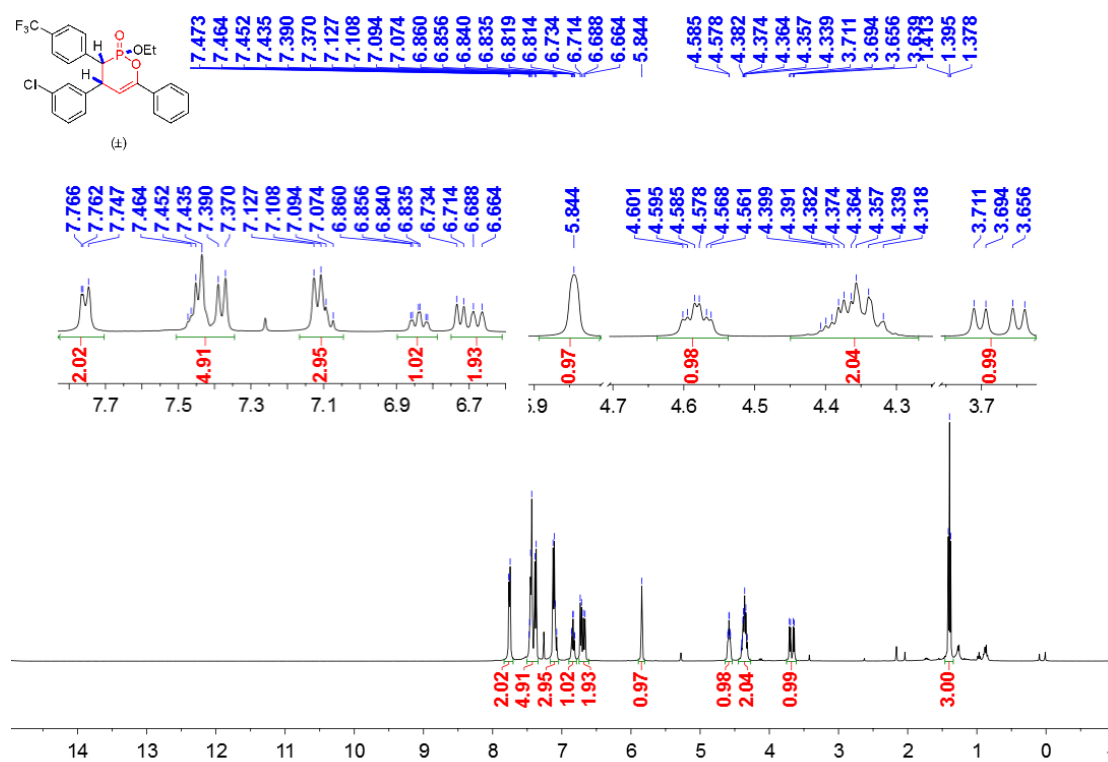
¹H NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3c**



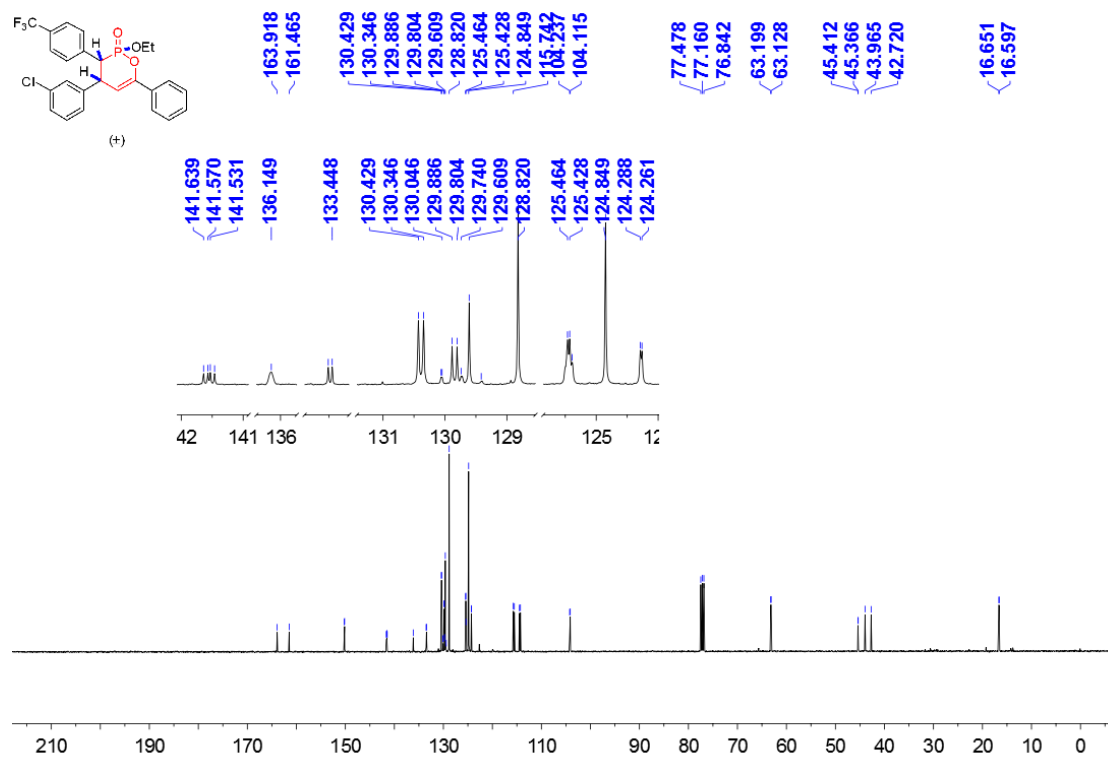
¹³C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3c**



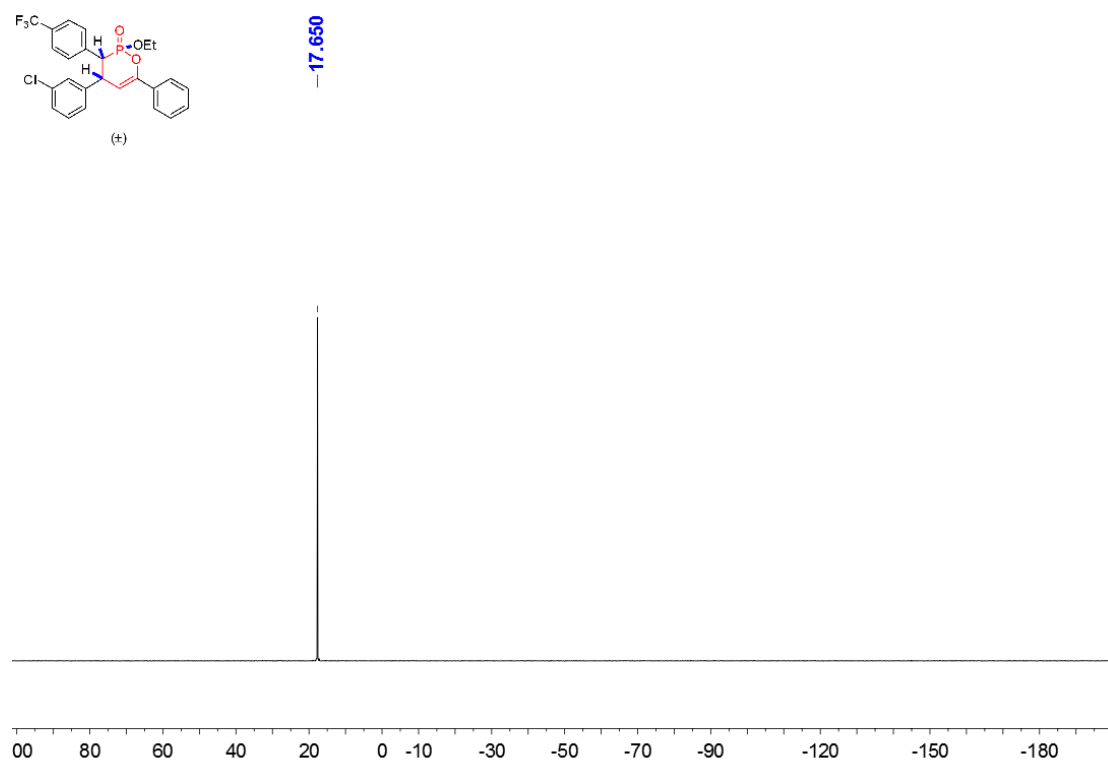
³¹P NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3c



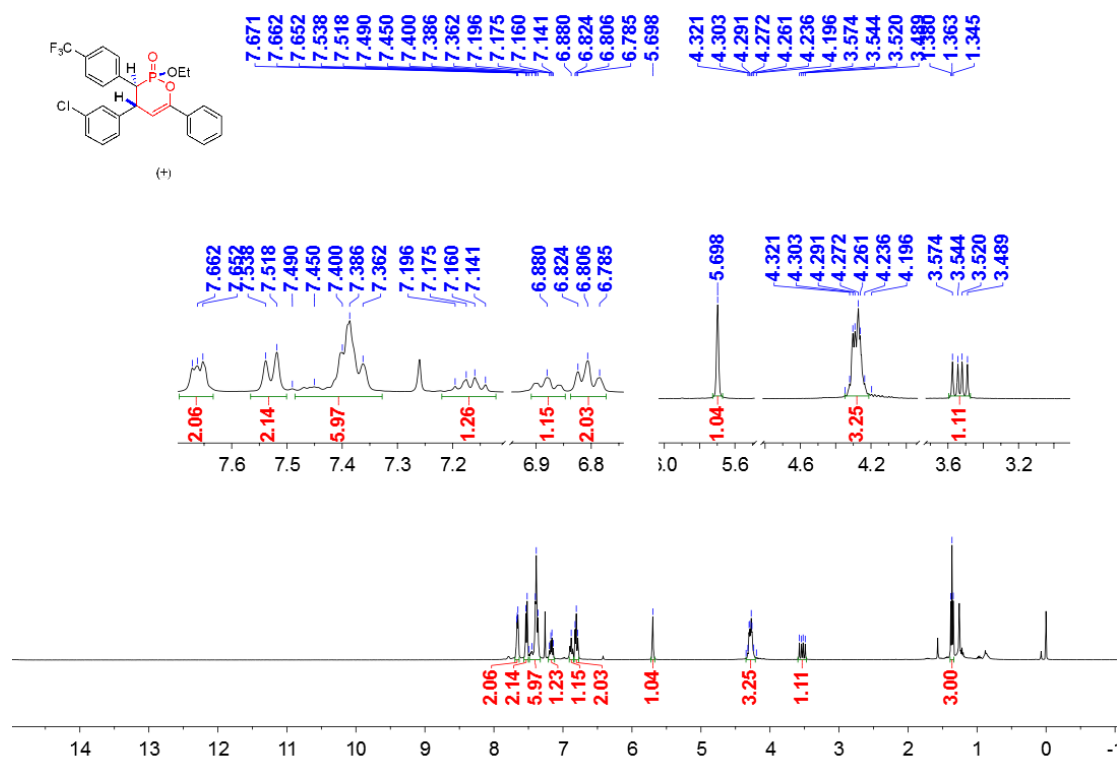
¹H NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3d



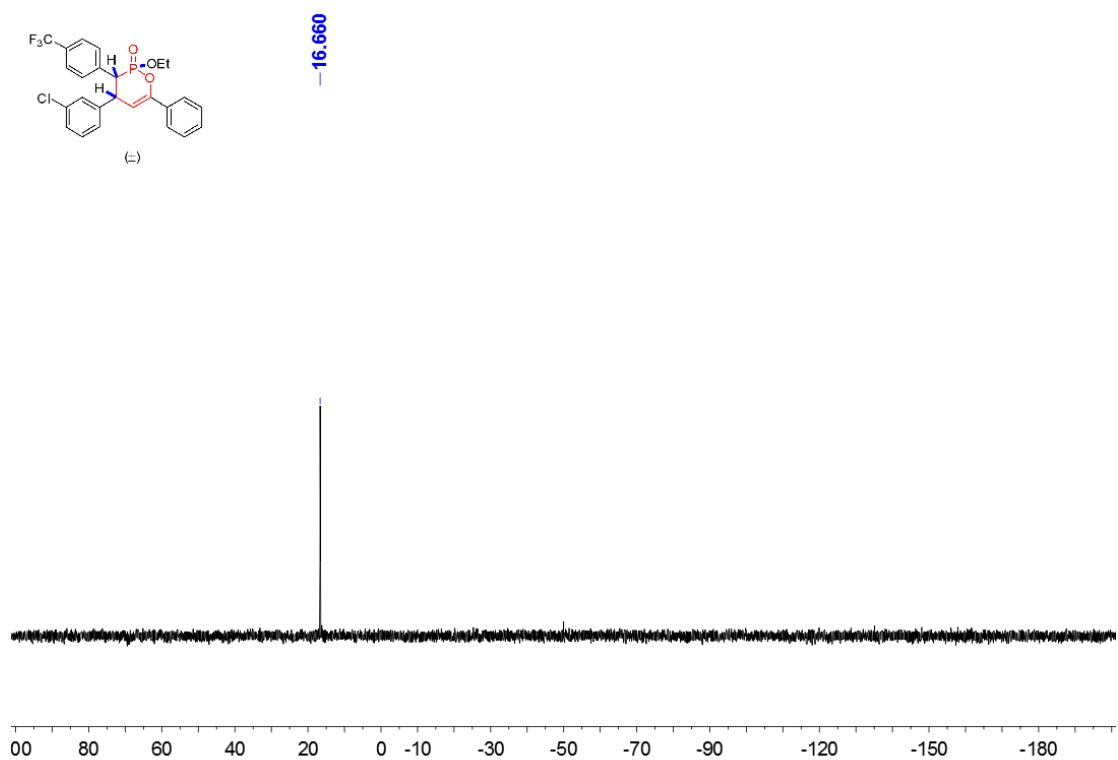
^{13}C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3d**



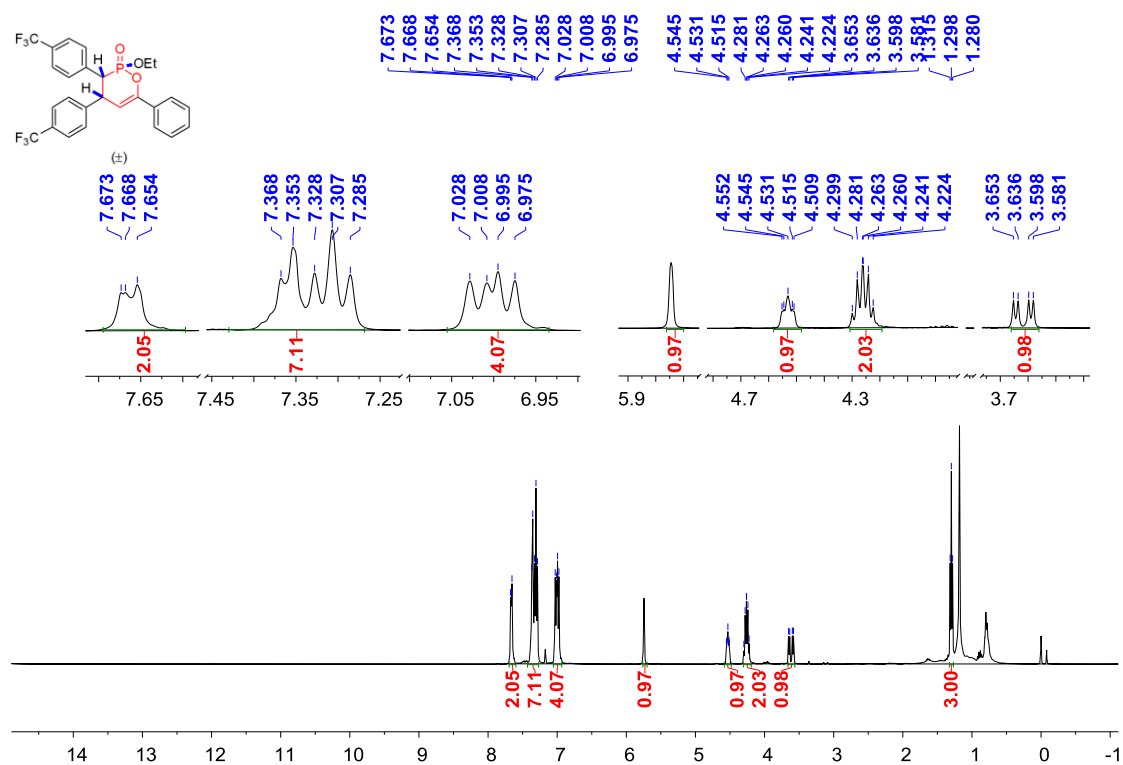
^{31}P NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3d**



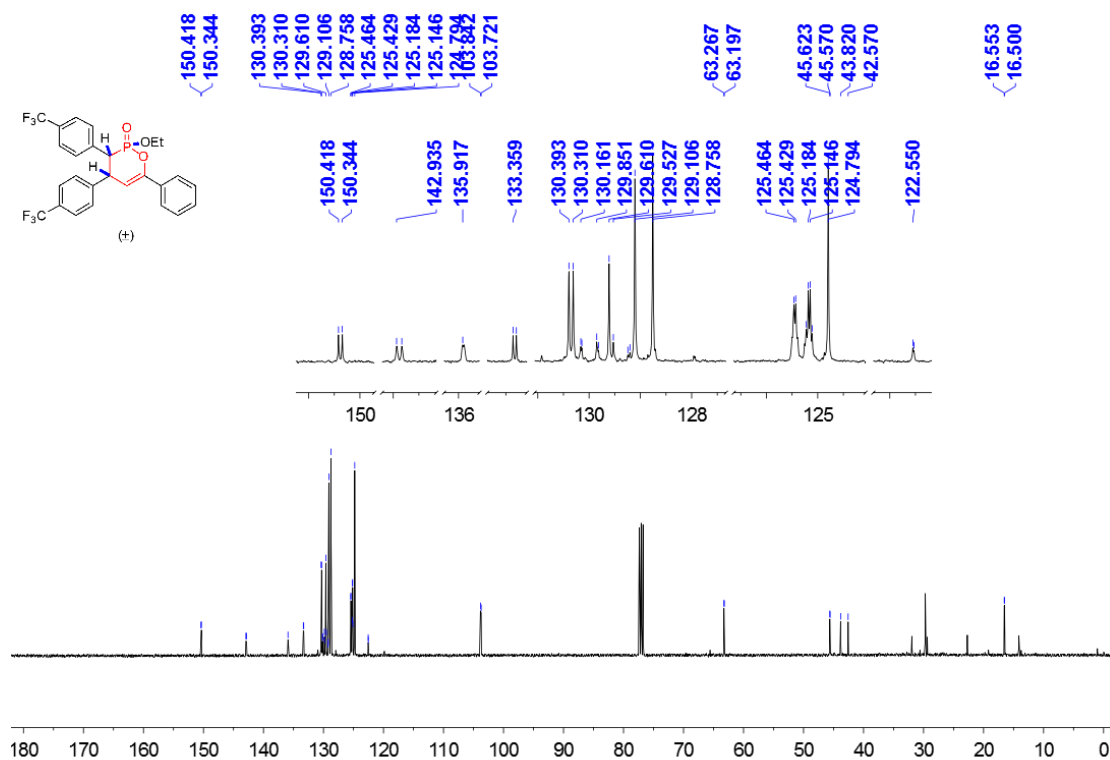
¹H NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-3d



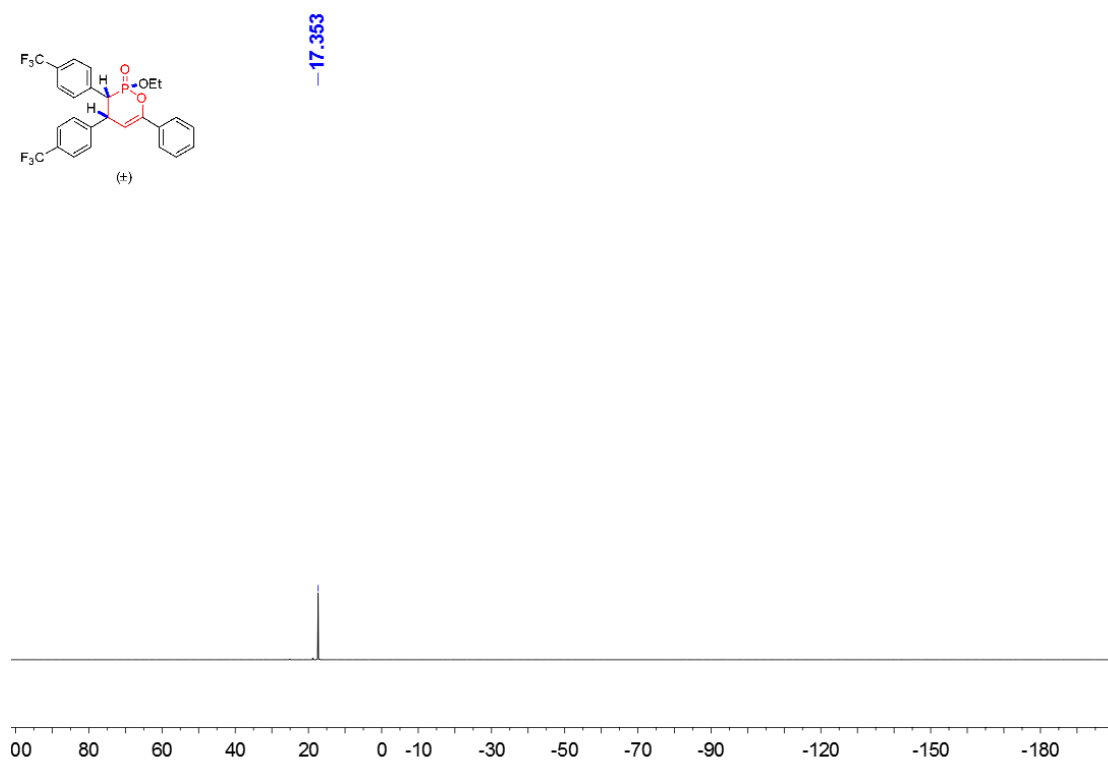
³¹P NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-3d



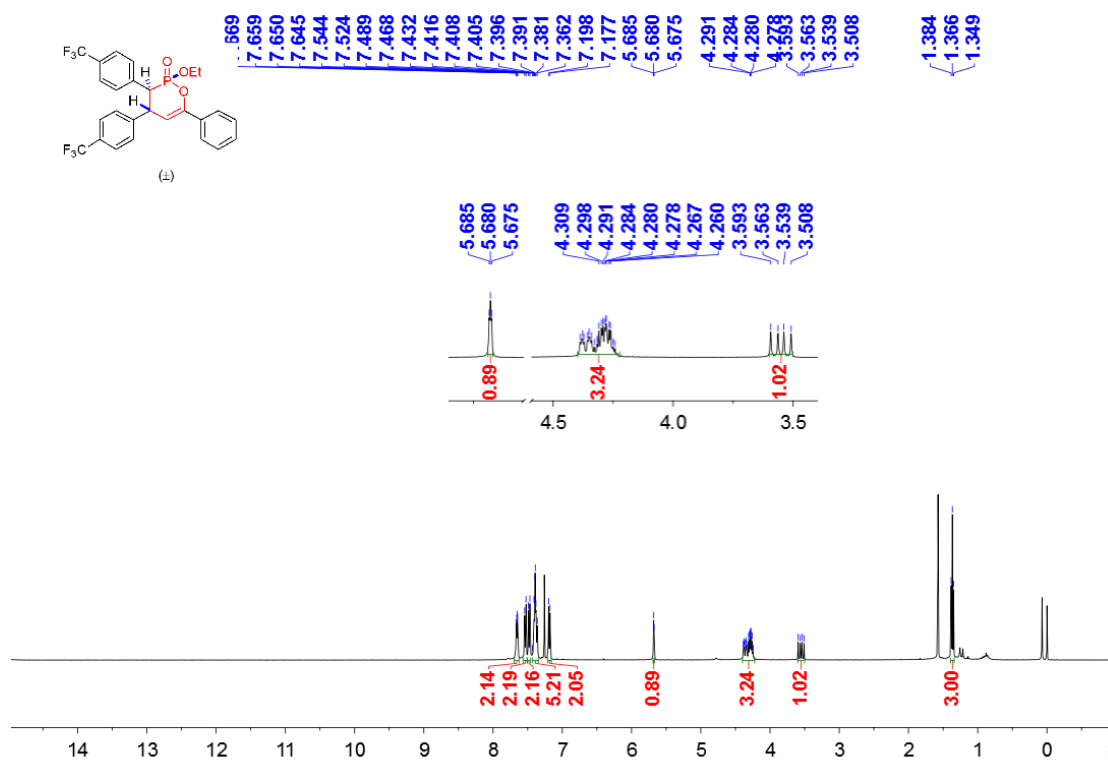
¹H NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3e**



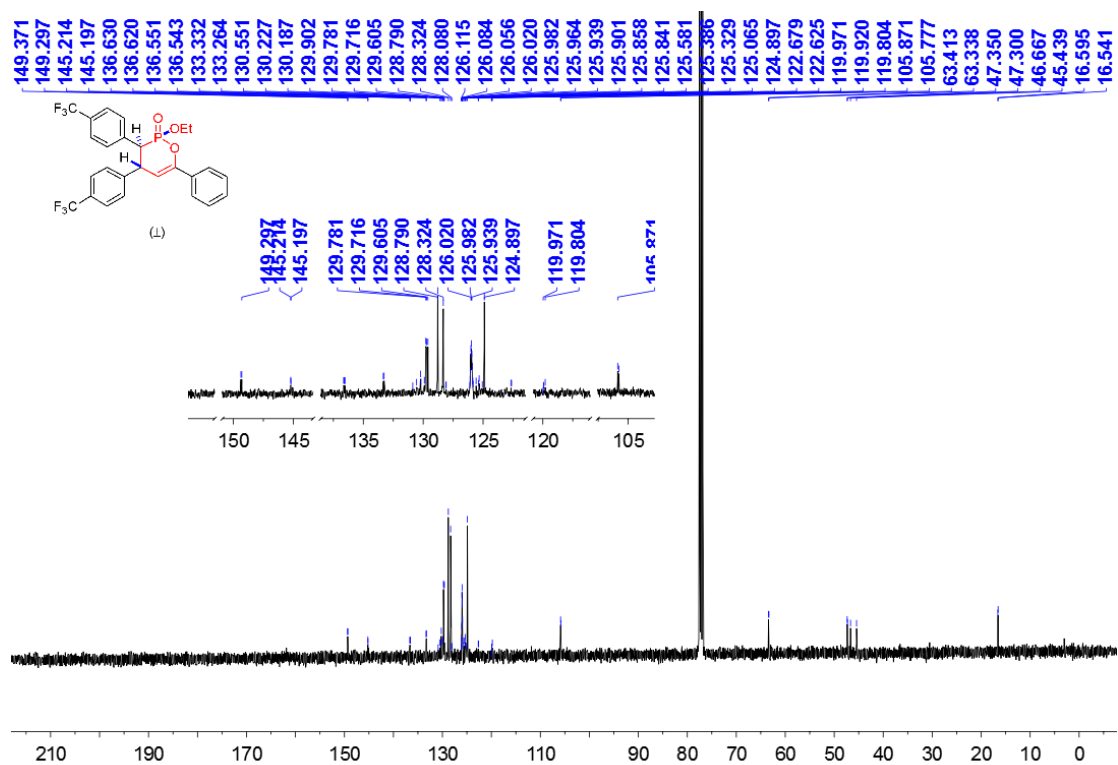
¹³C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3e**



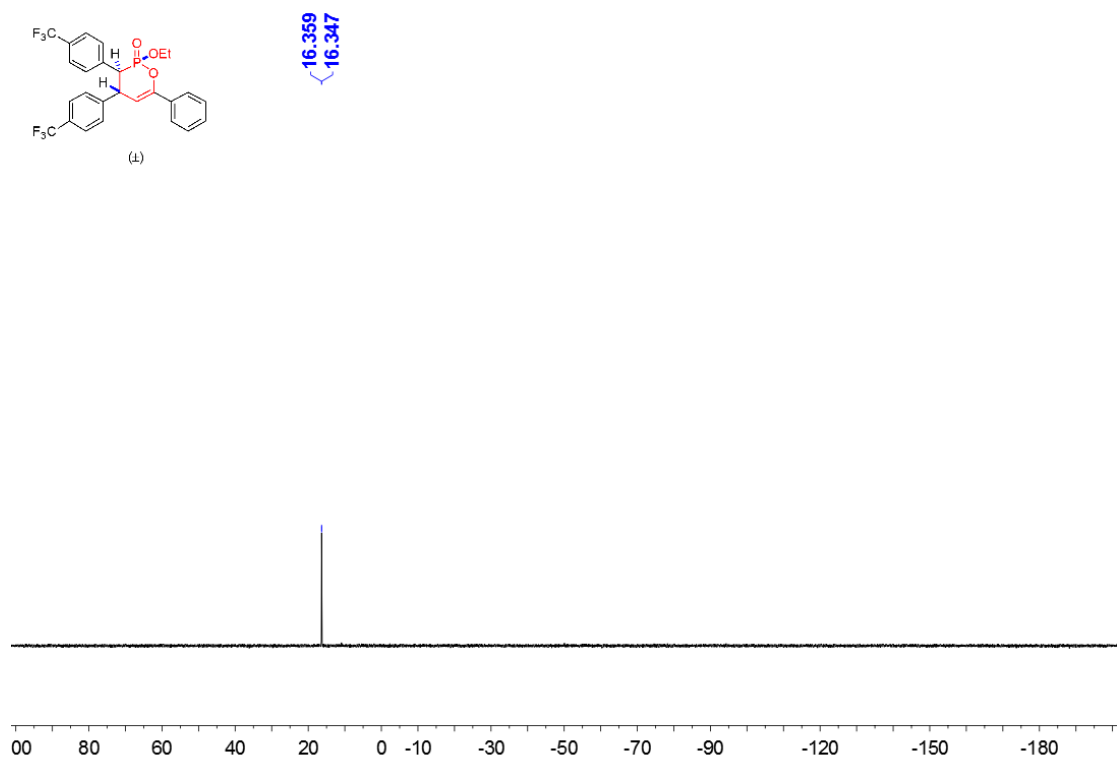
³¹P NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3e**



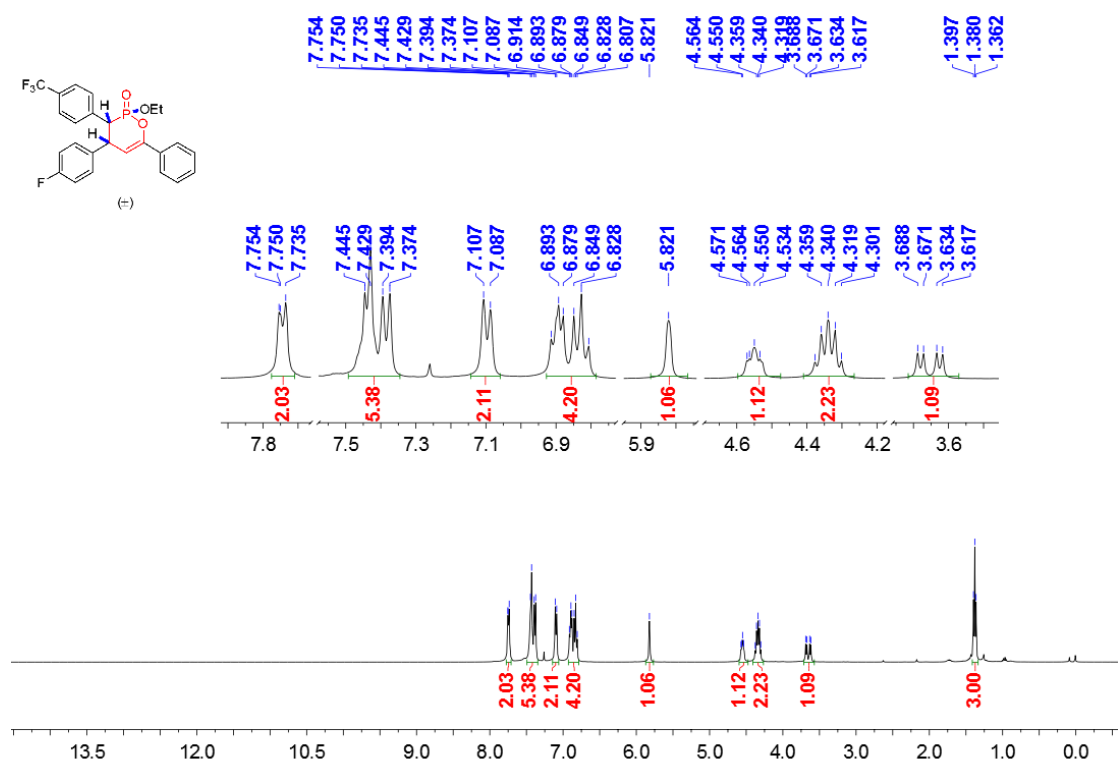
¹H NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3e**



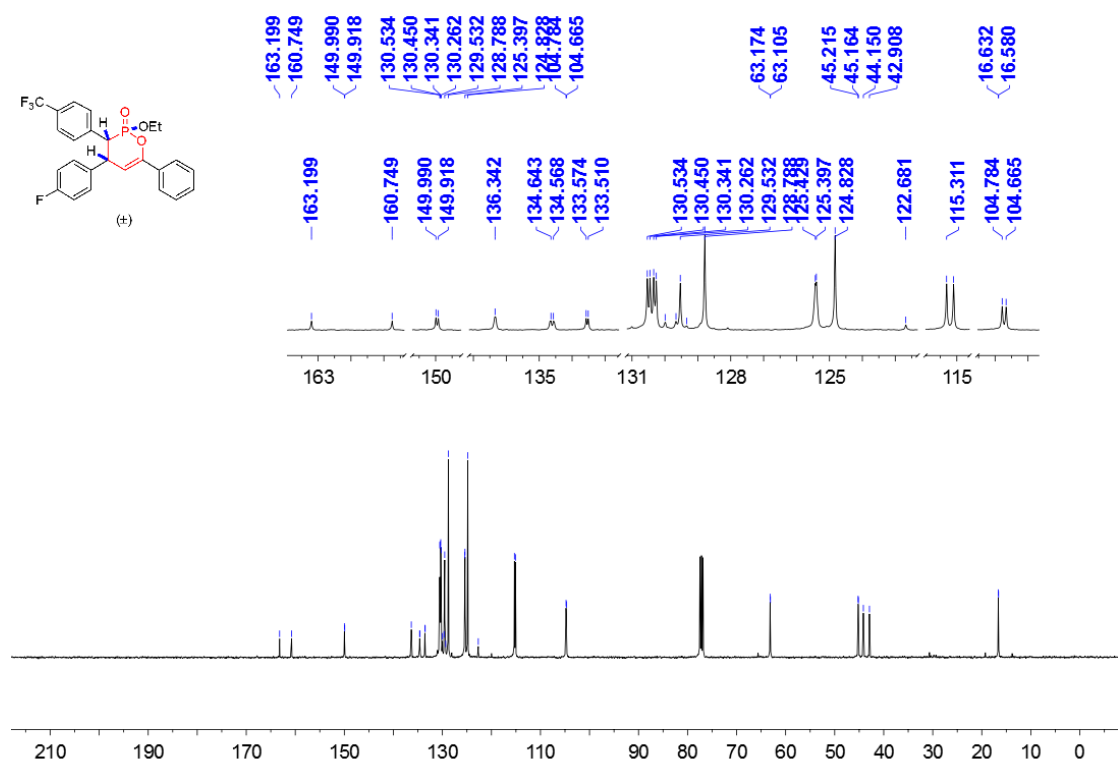
¹³C NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3e**



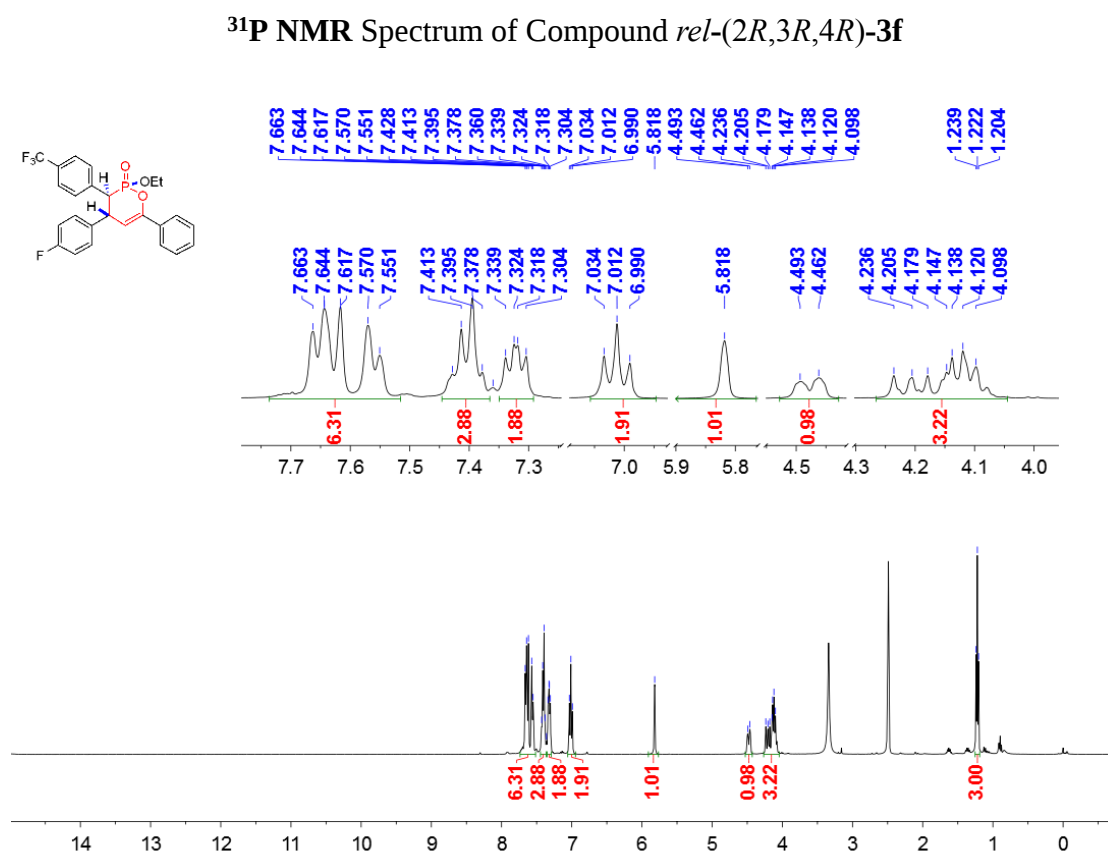
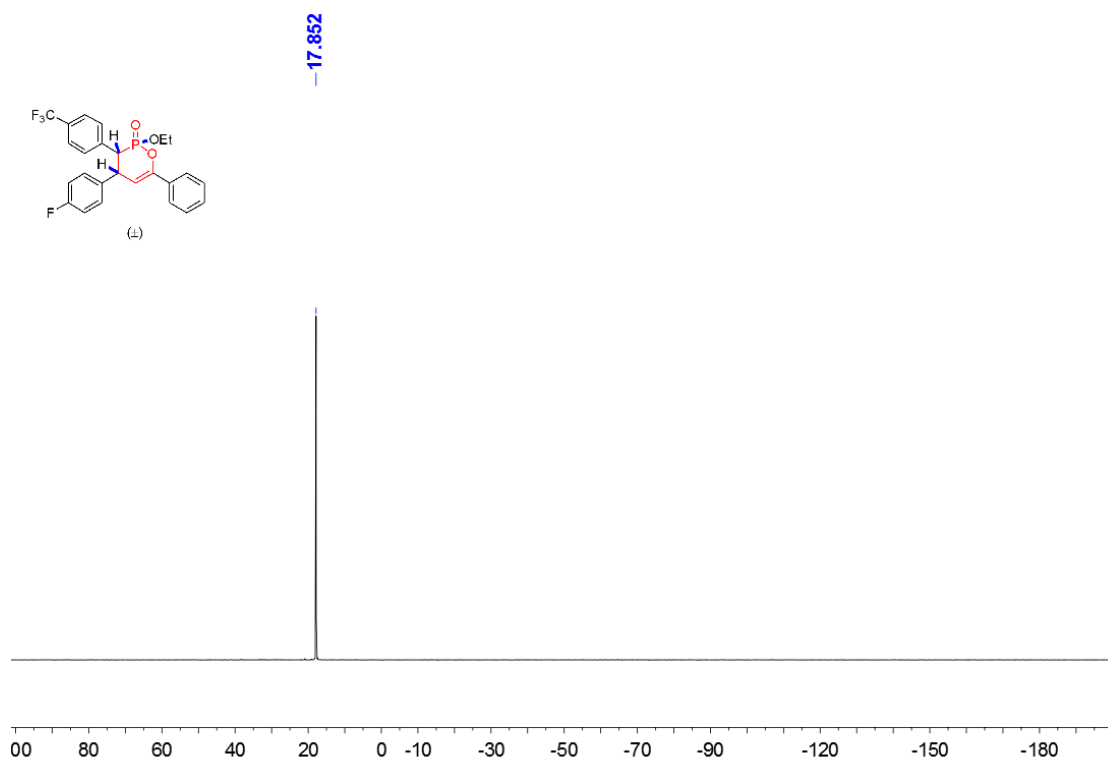
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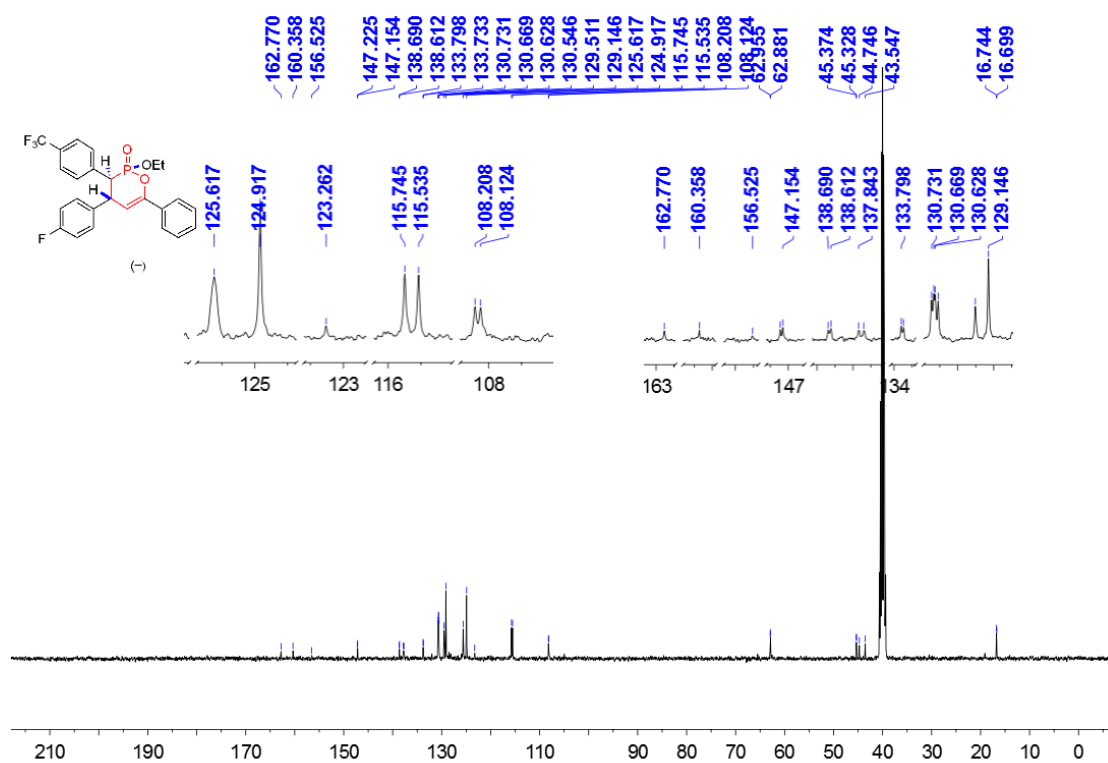


^1H NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3f

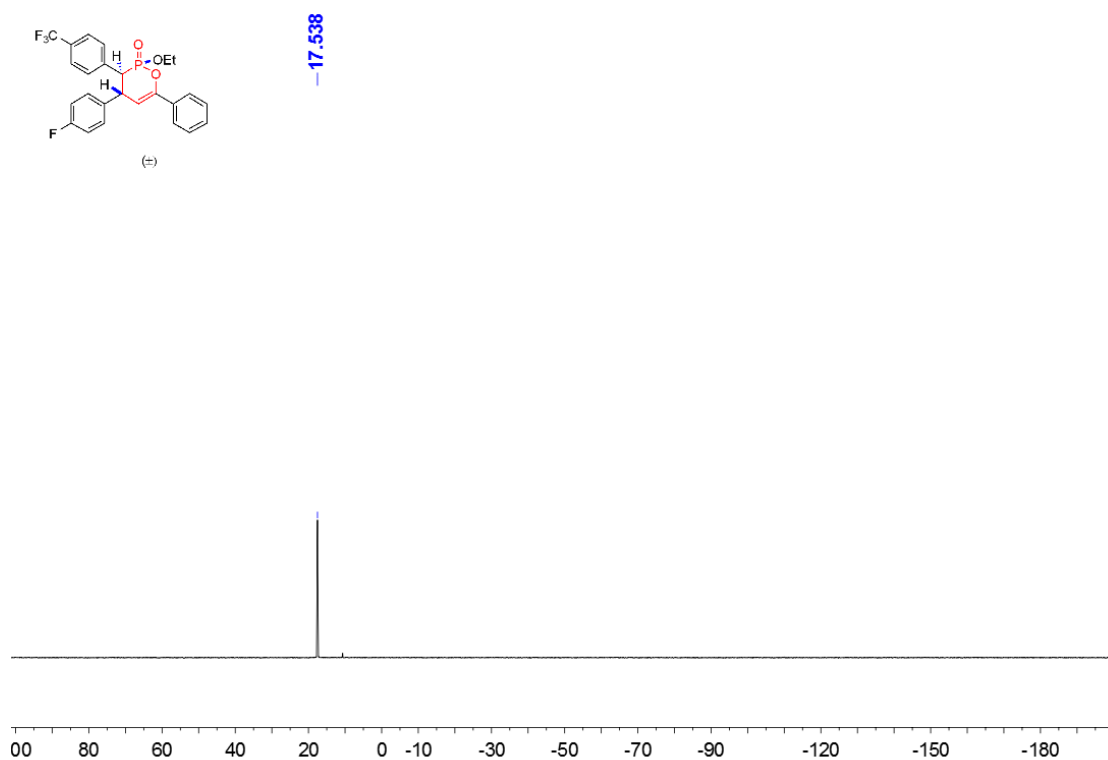


^{13}C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3f

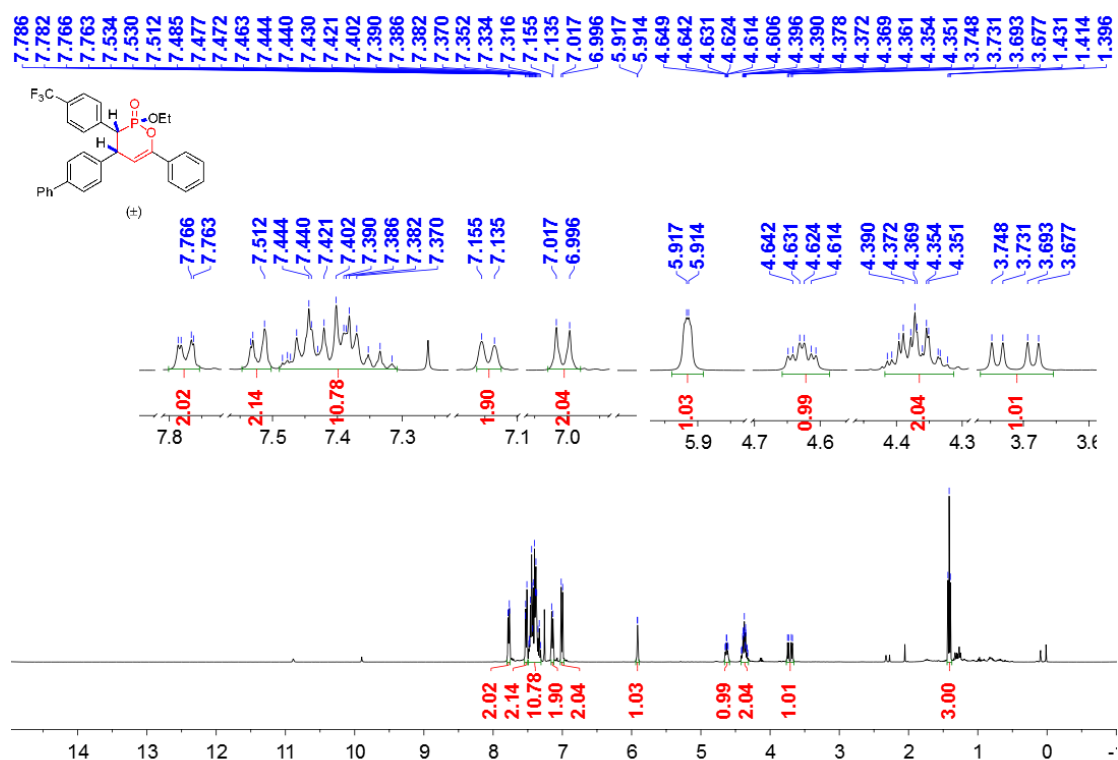




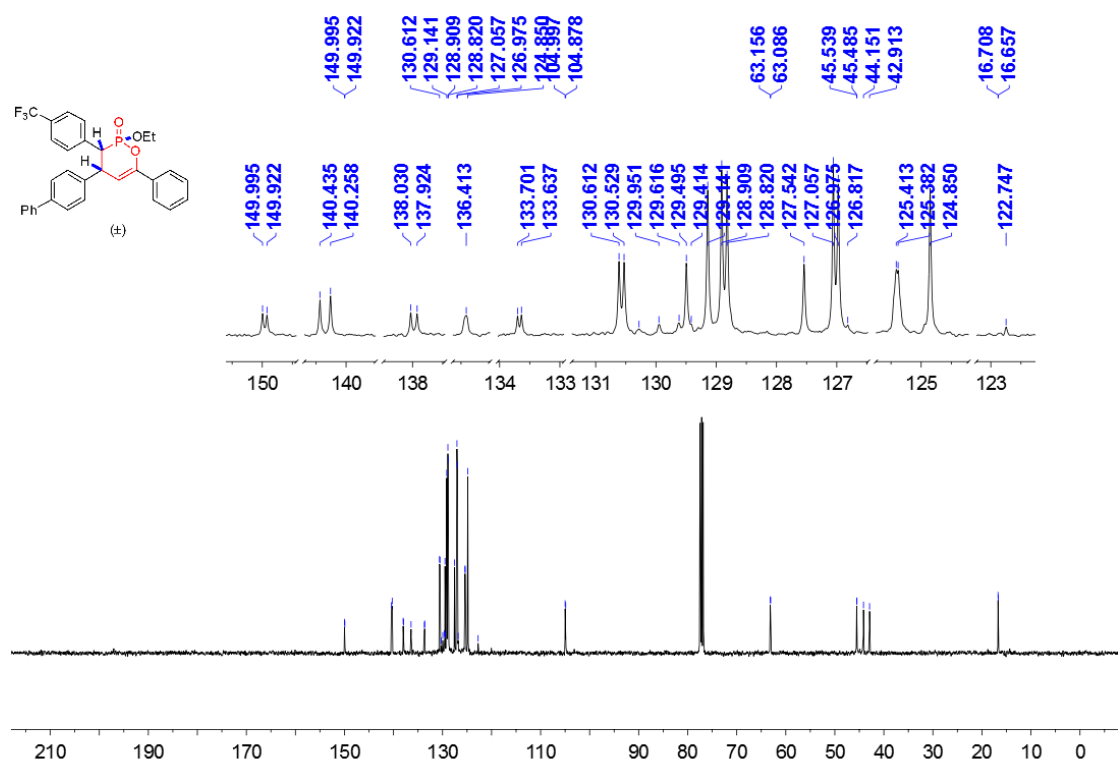
¹³C NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-3f



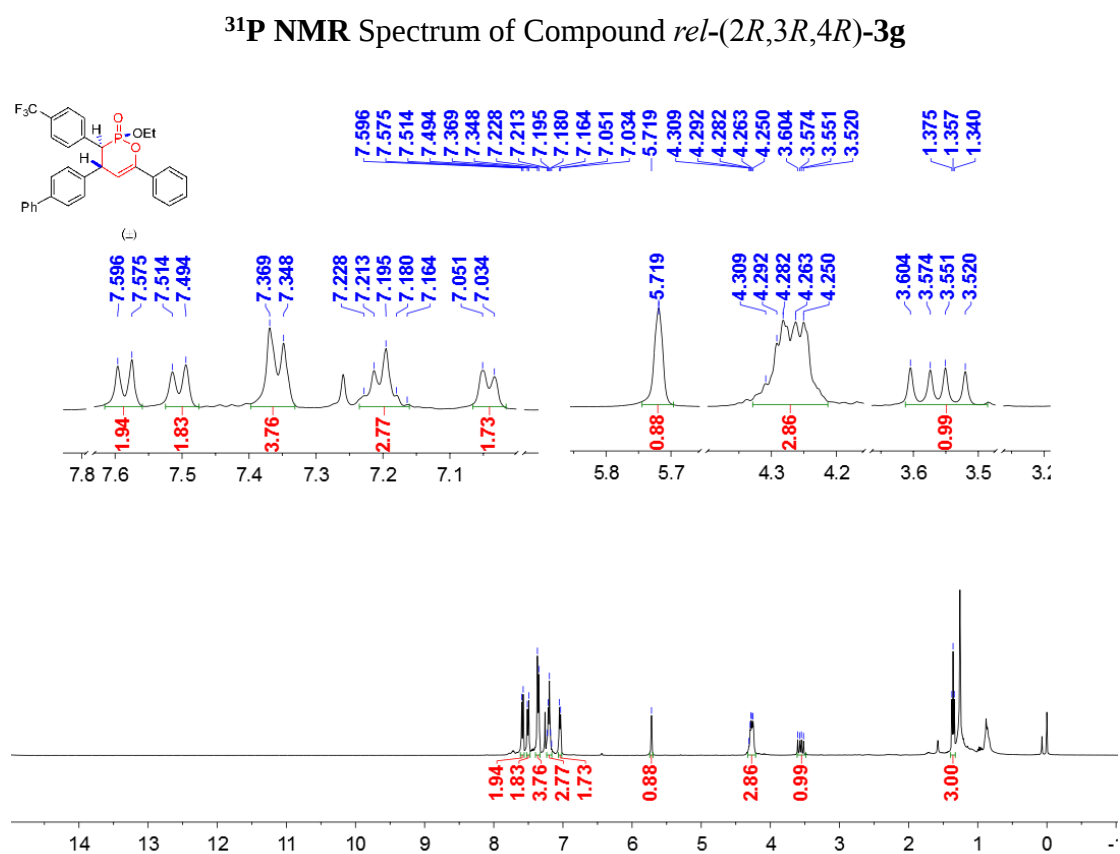
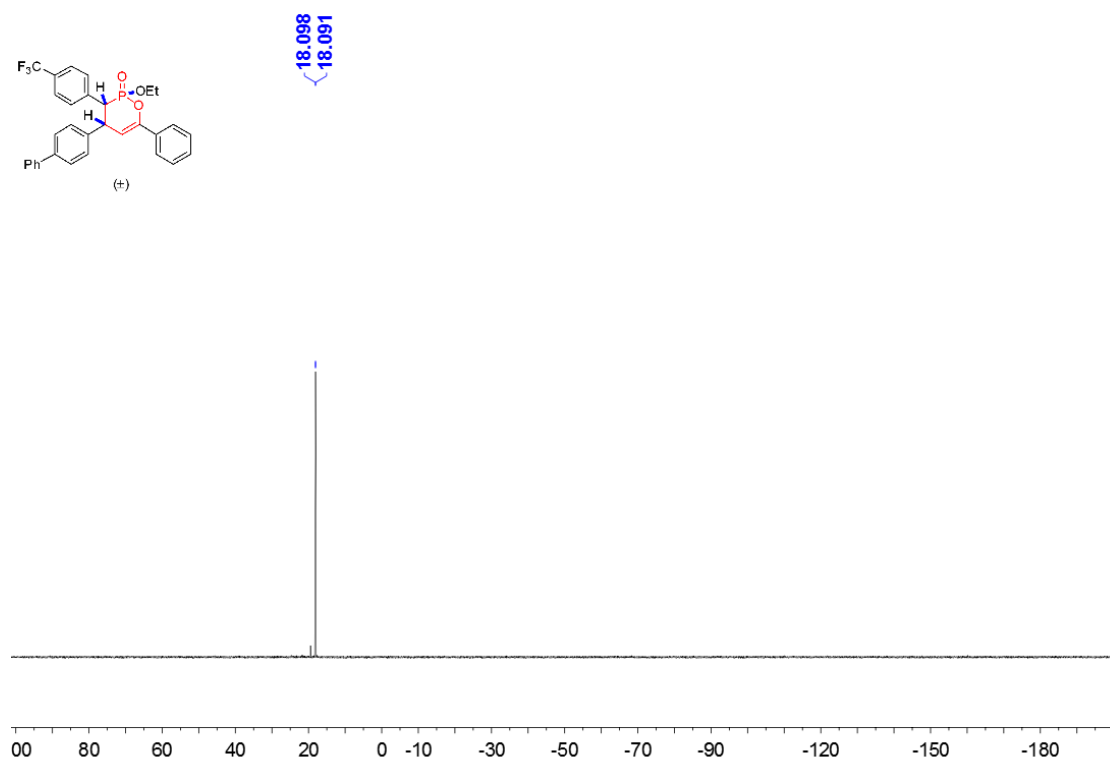
³¹P NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-3f

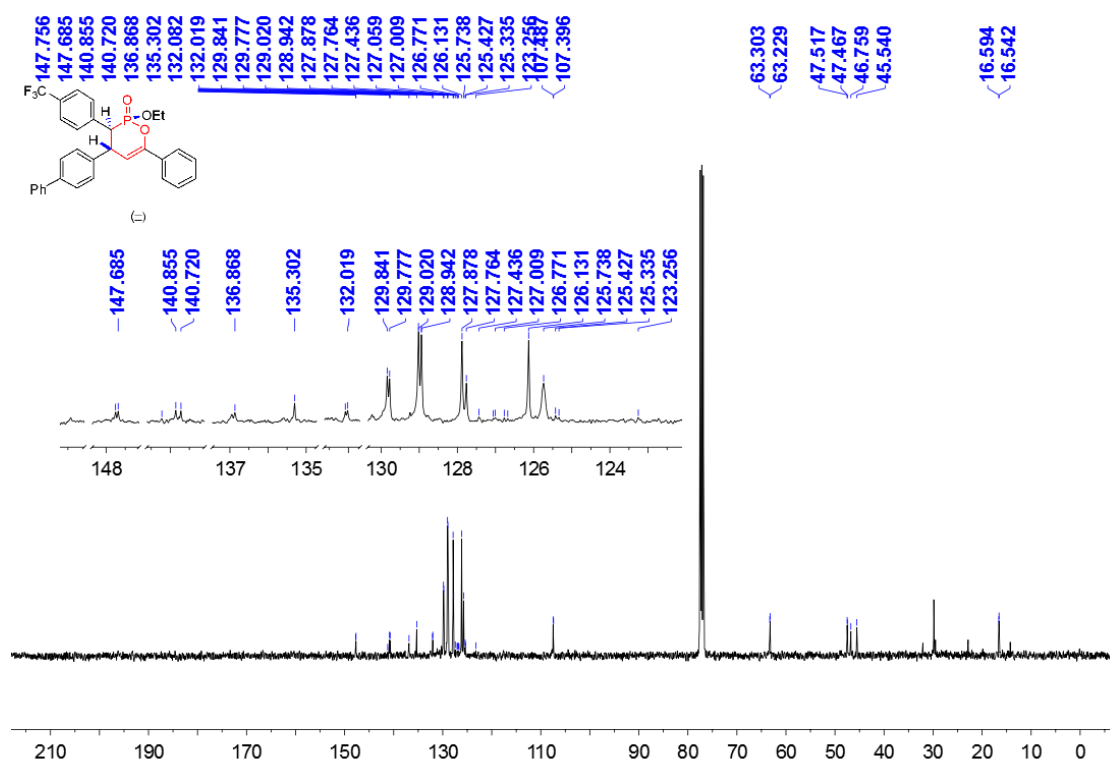


¹H NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3g

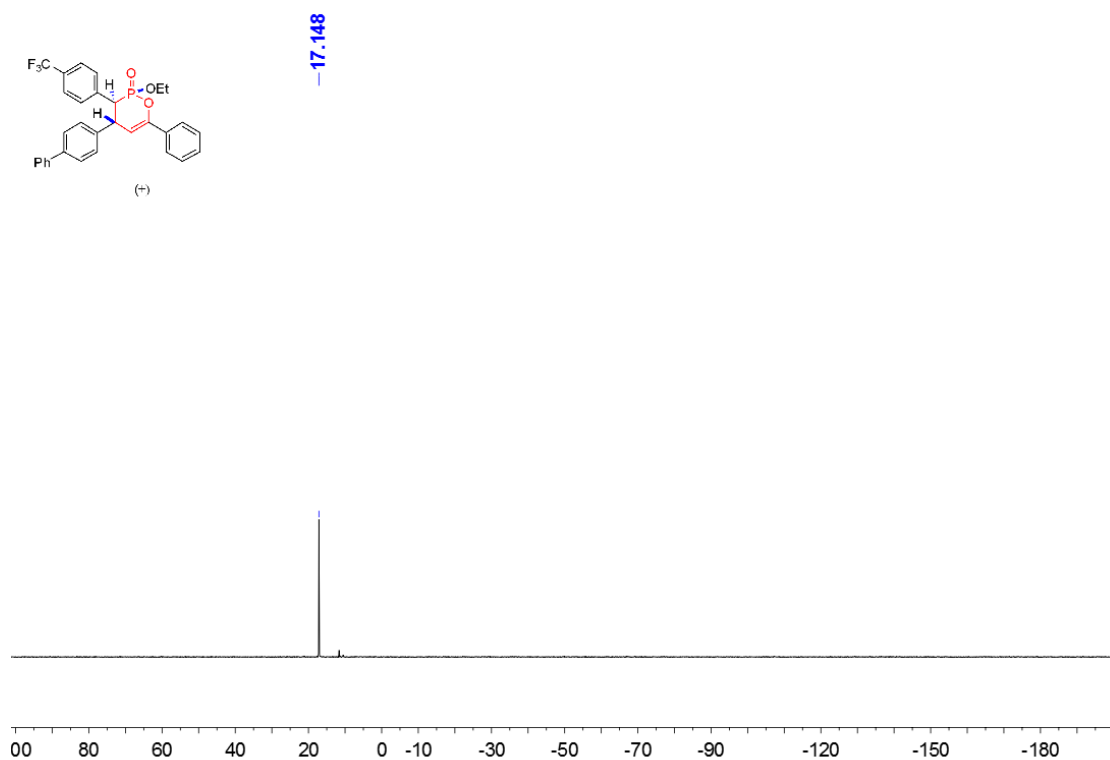


¹³C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3g

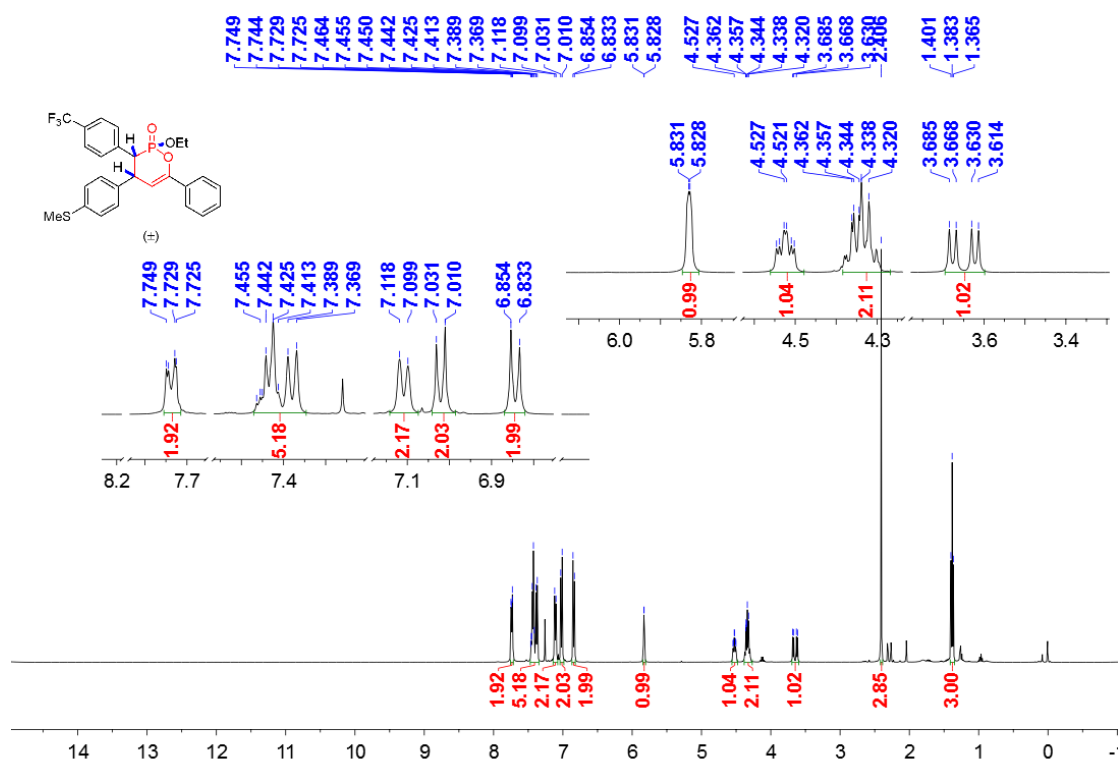




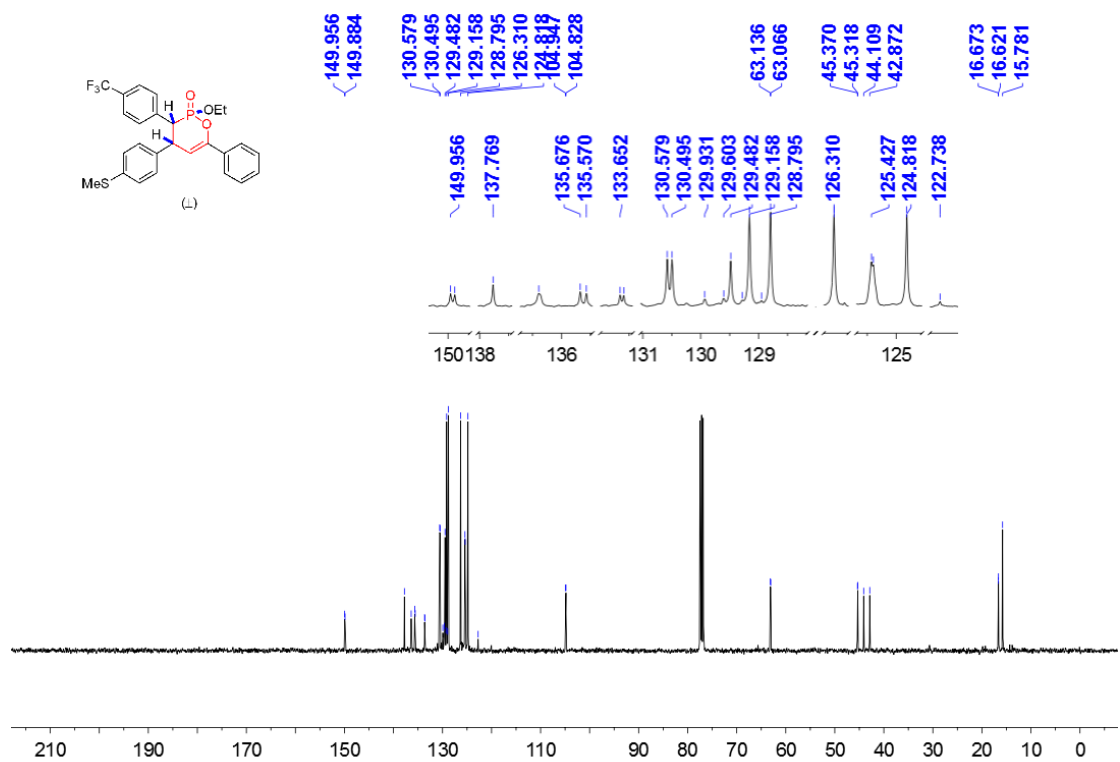
¹³C NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3g**



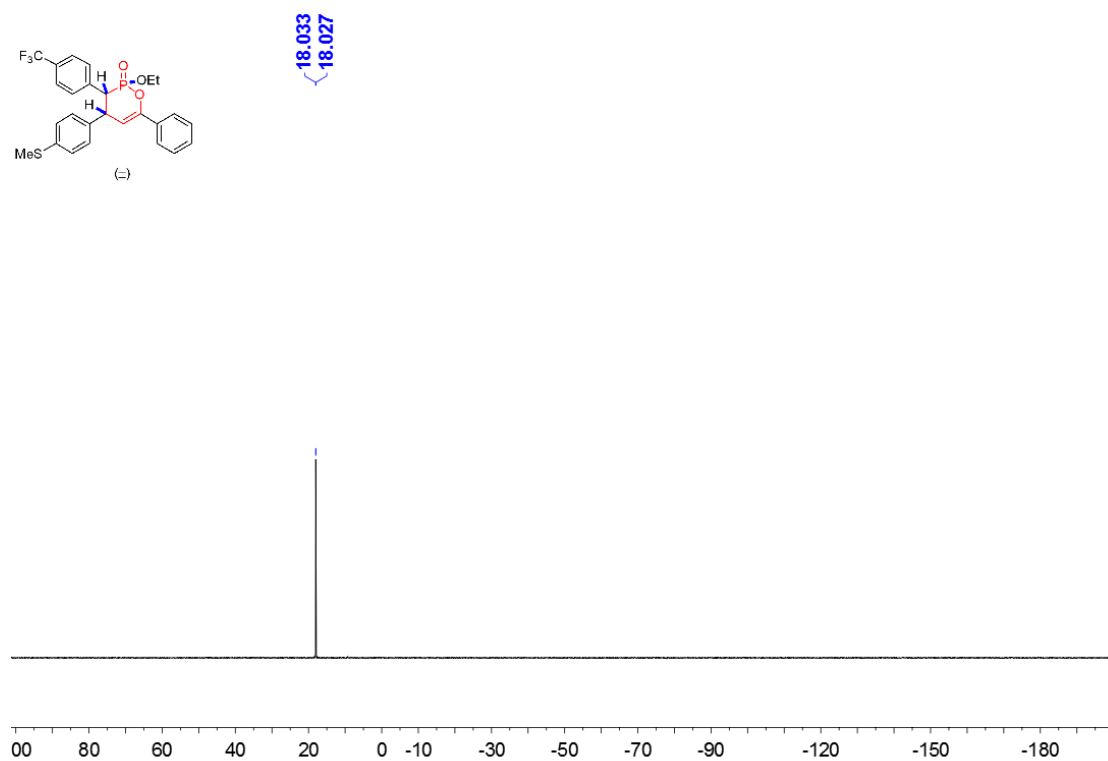
³¹P NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3g**



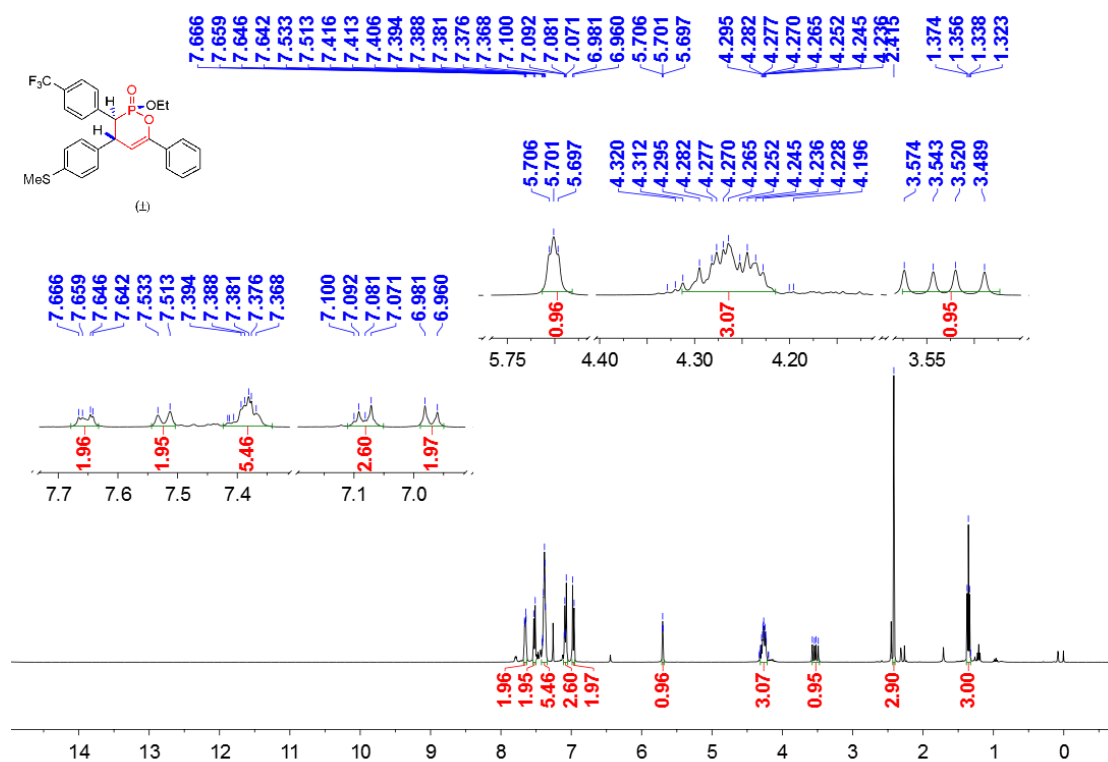
¹H NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3h



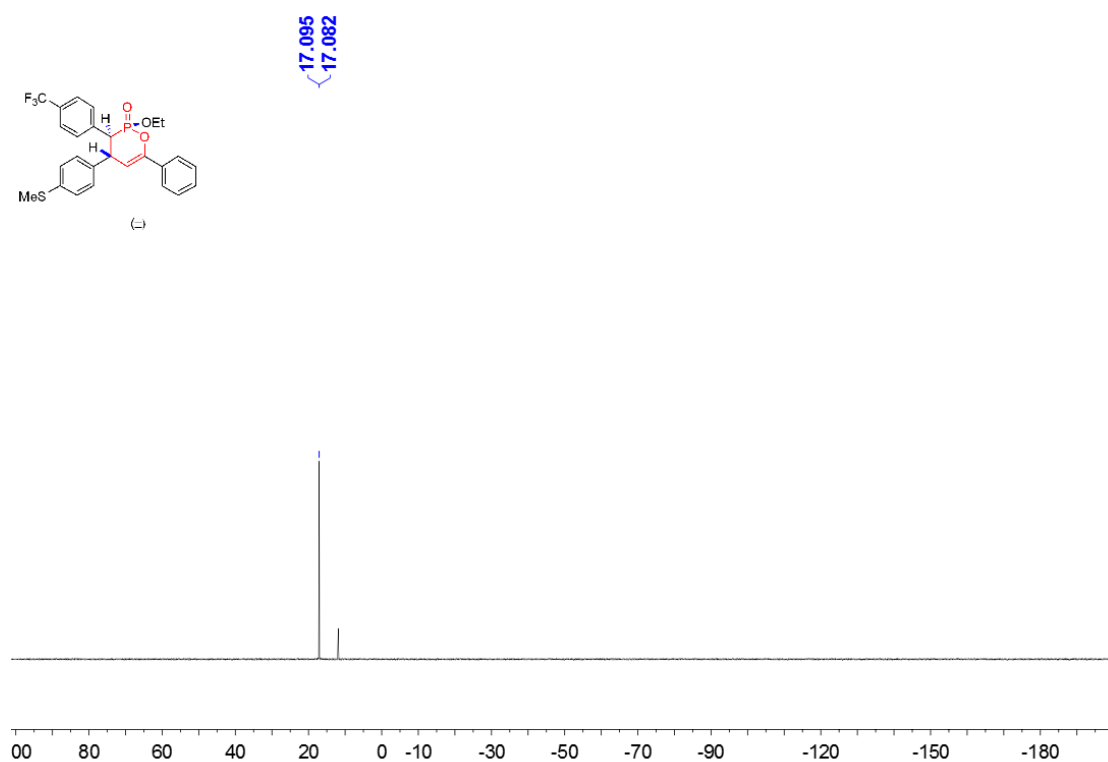
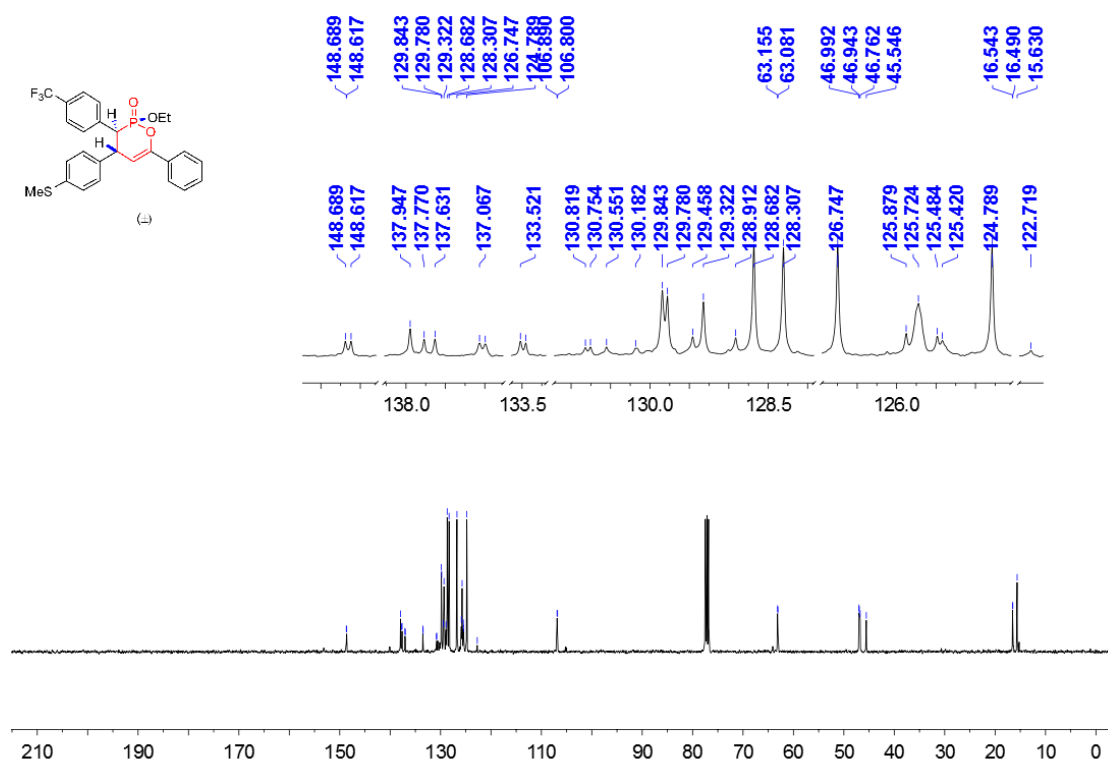
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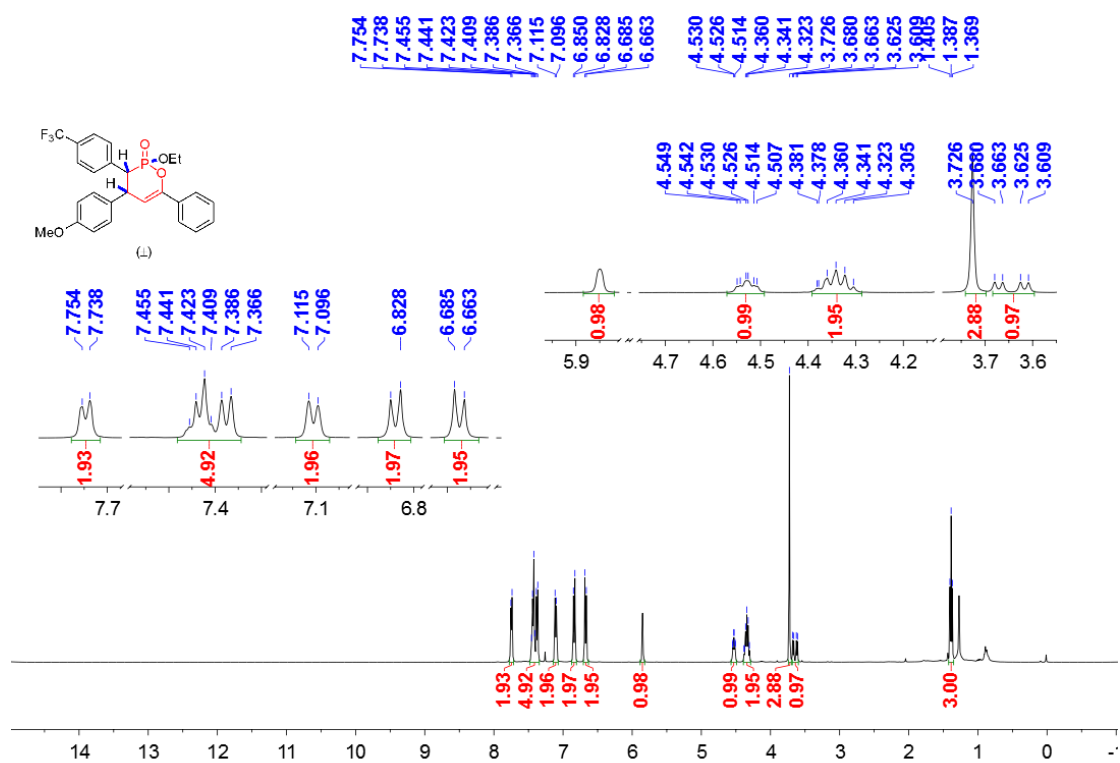


³¹P NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3h

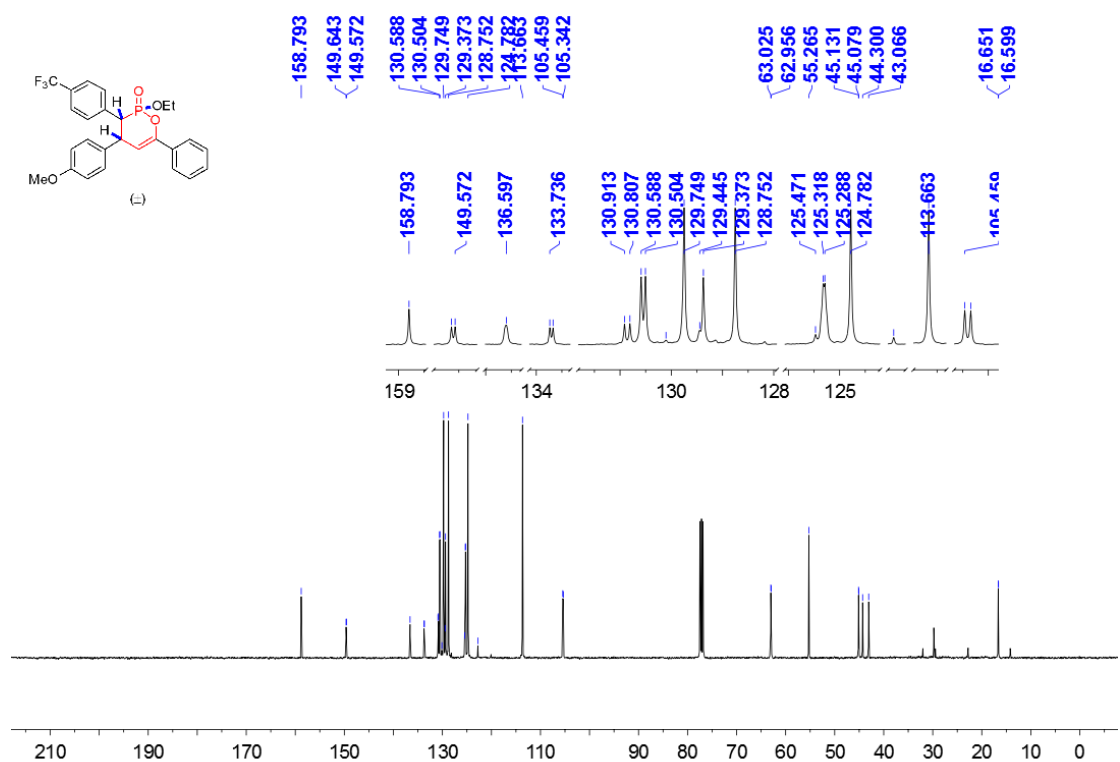


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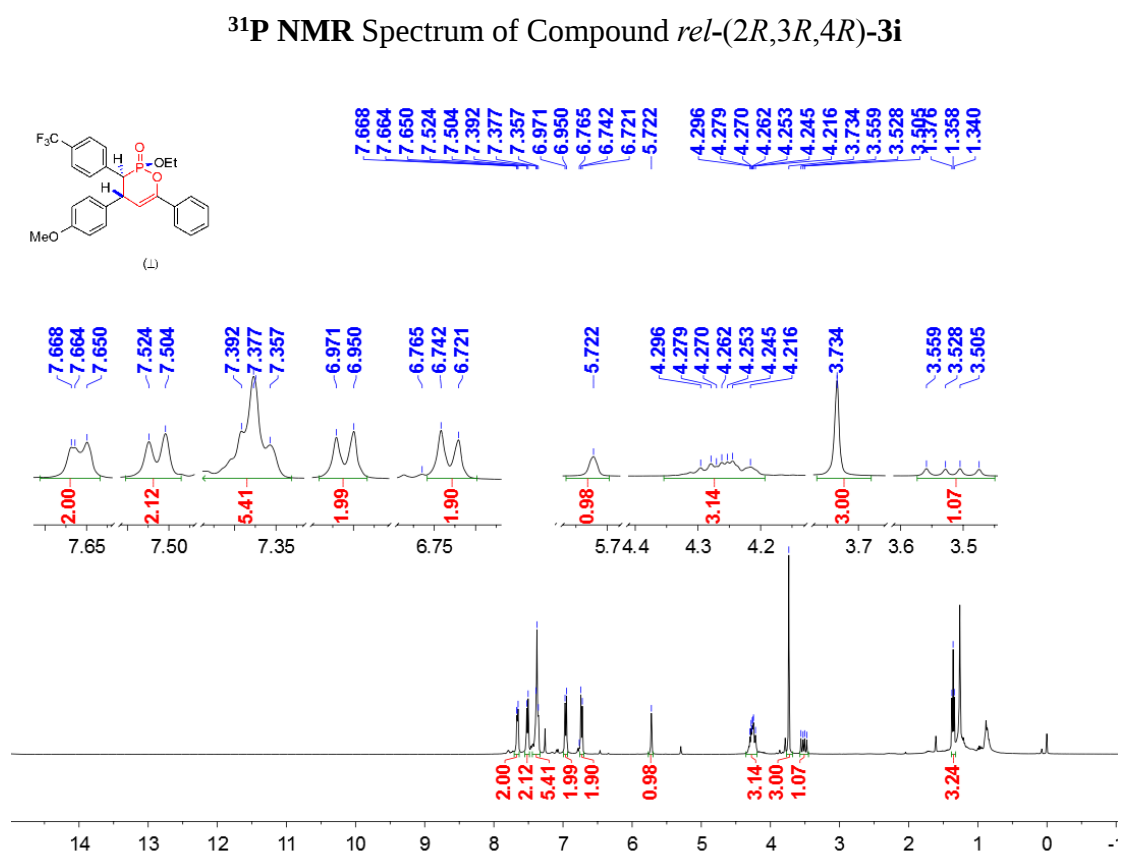
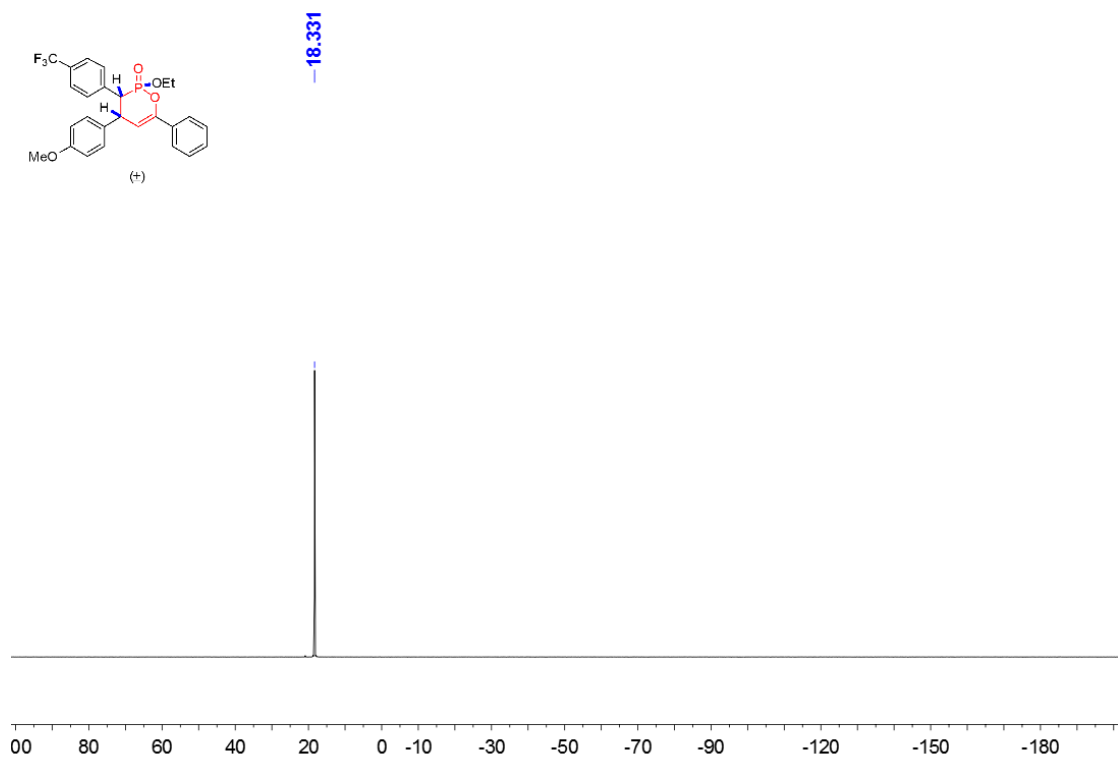


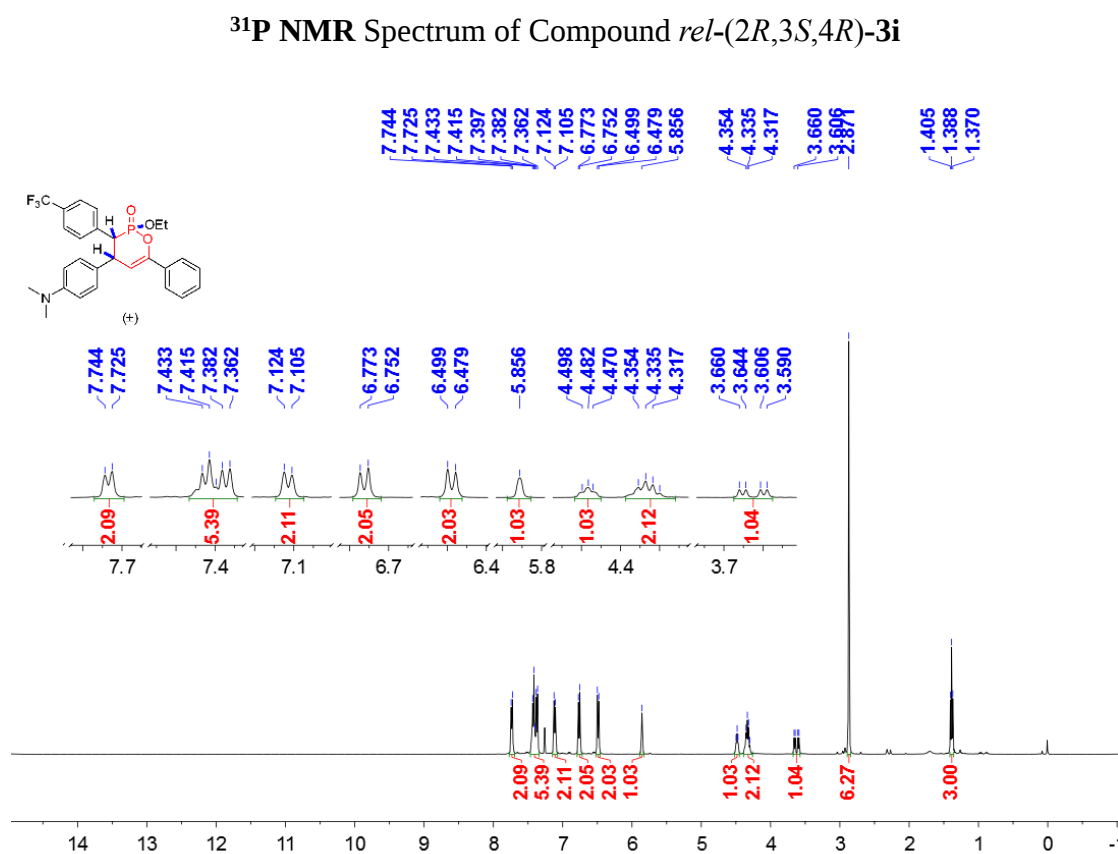
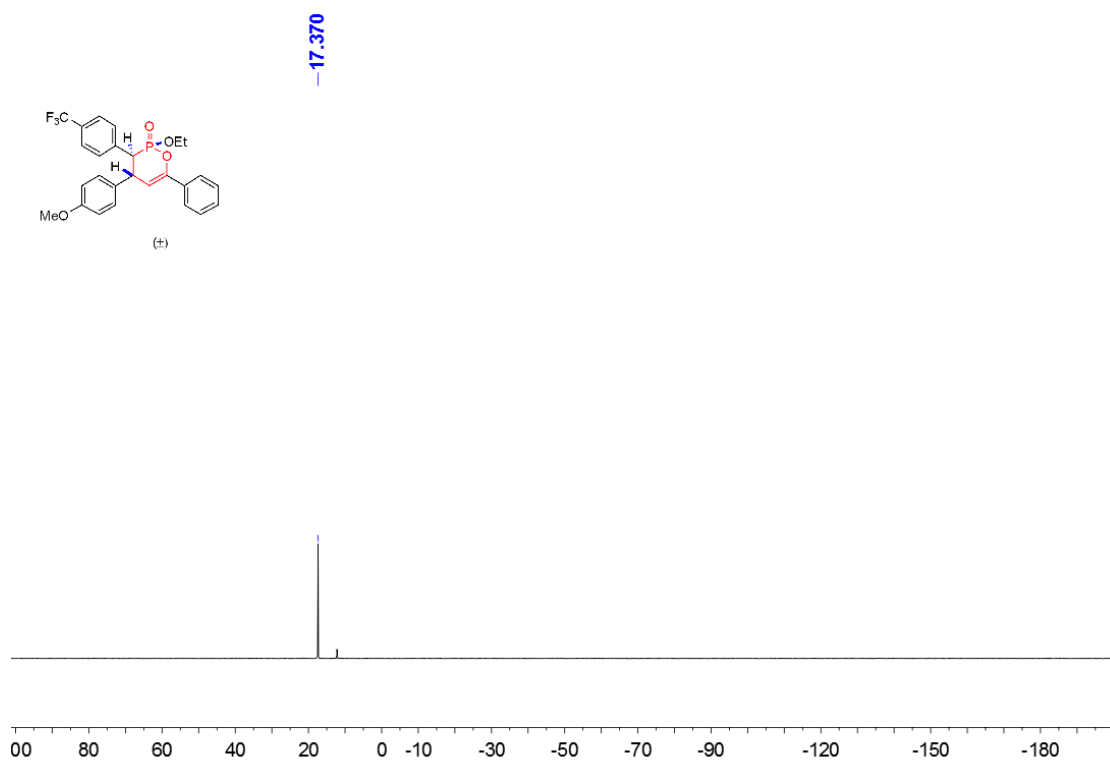


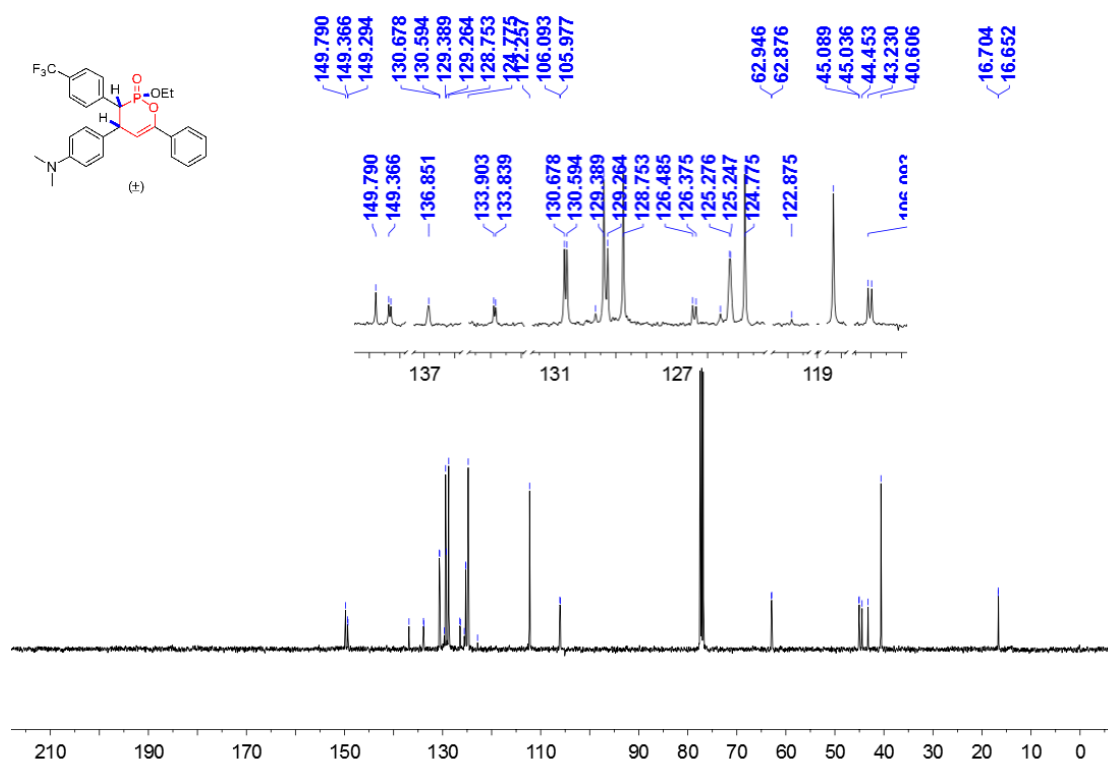
¹H NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3i**



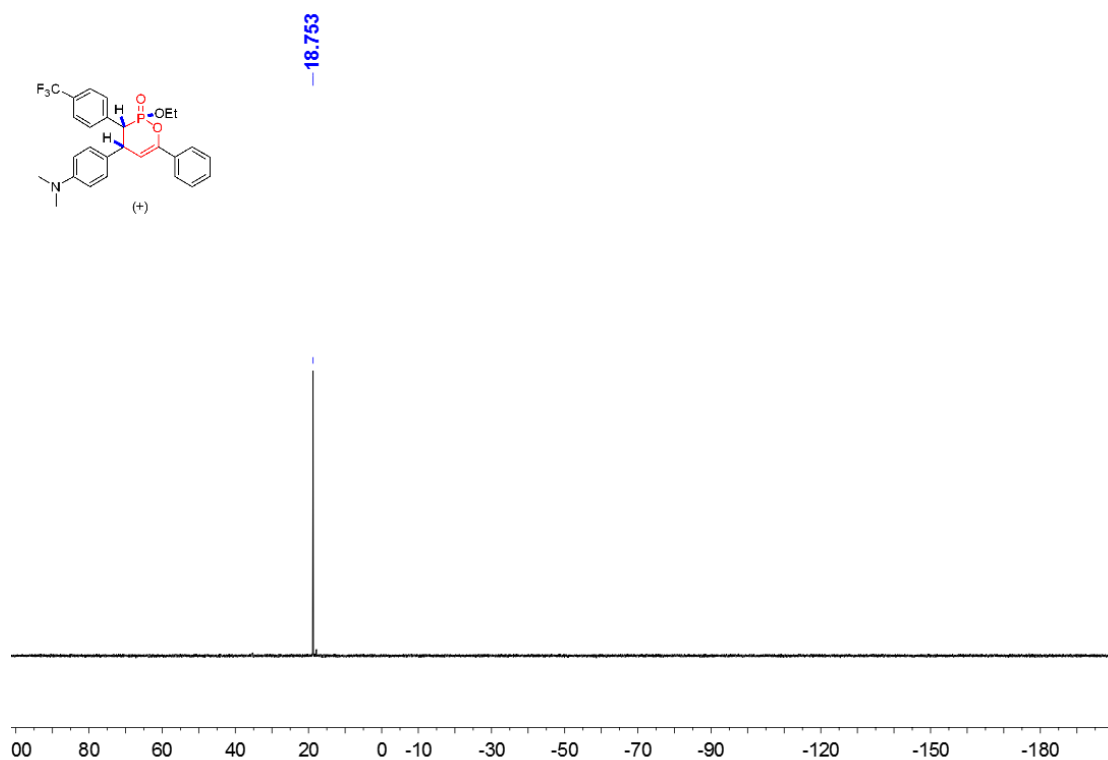
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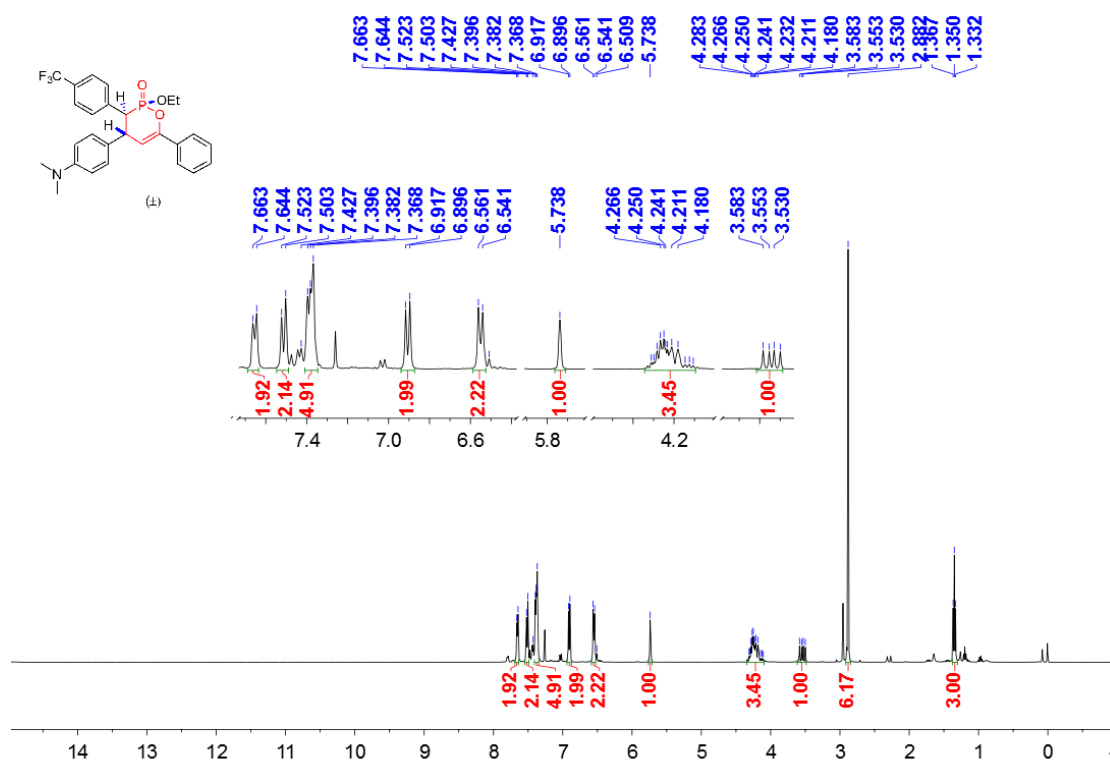




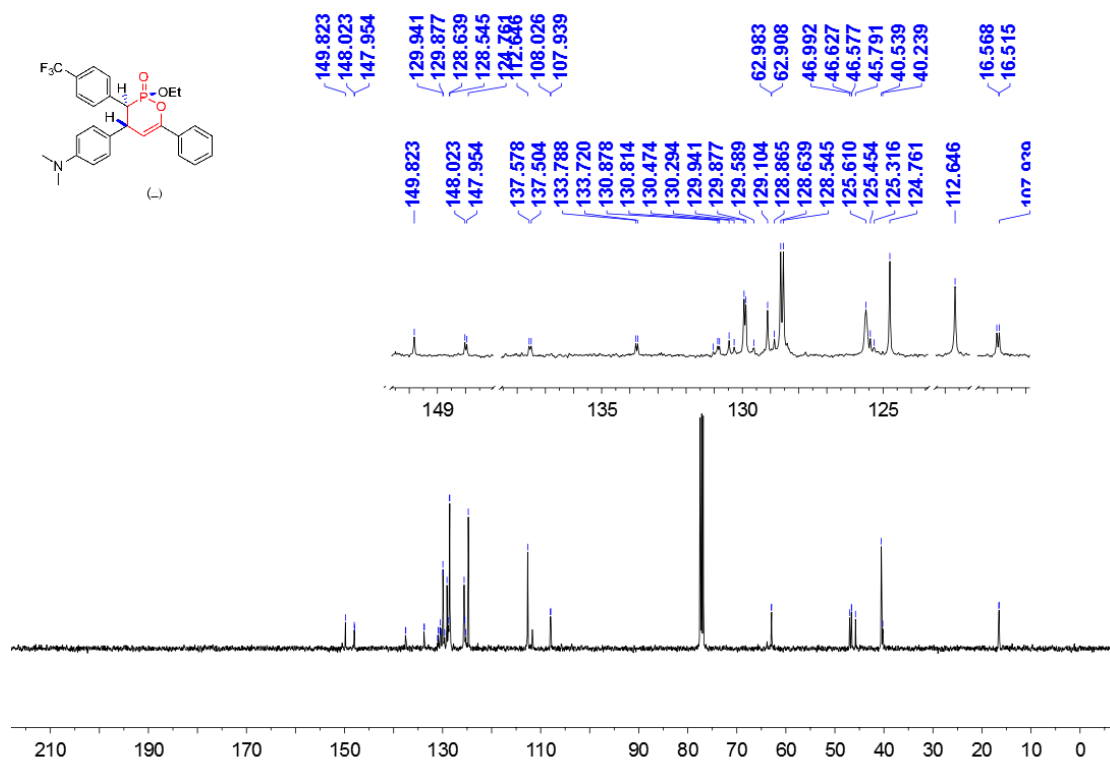
¹³C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3j**



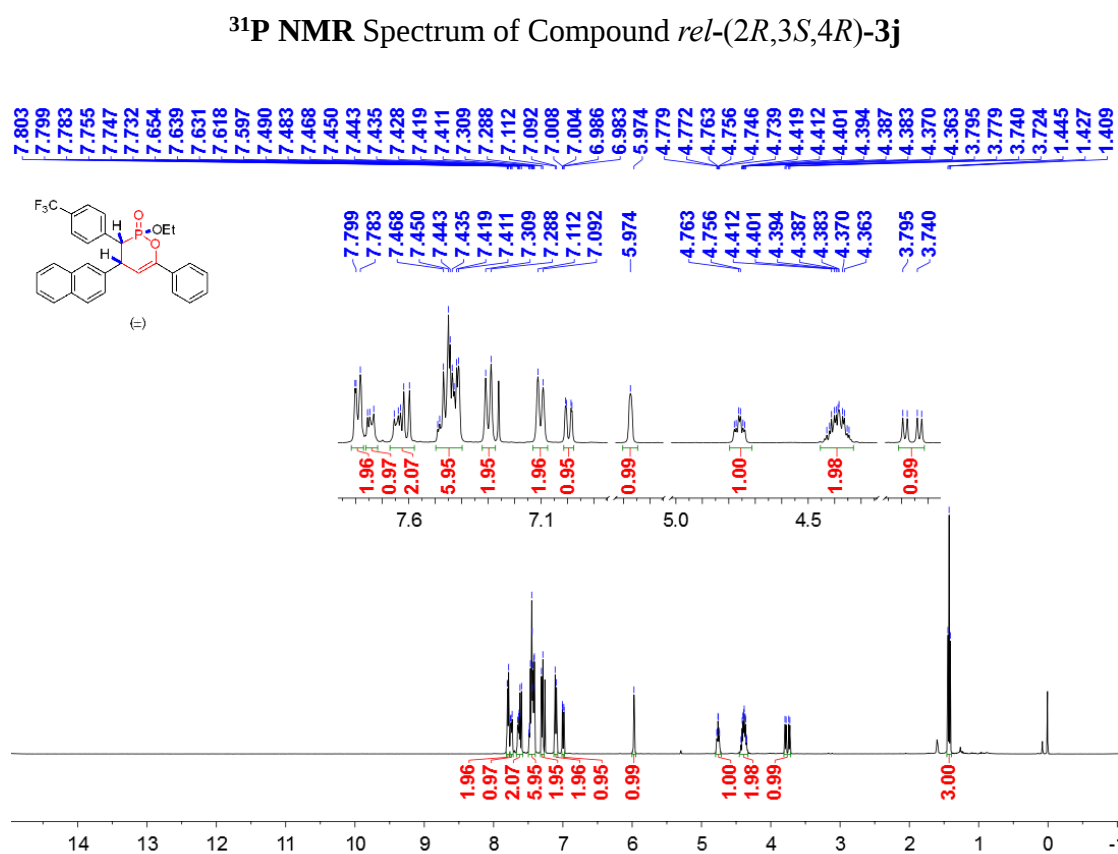
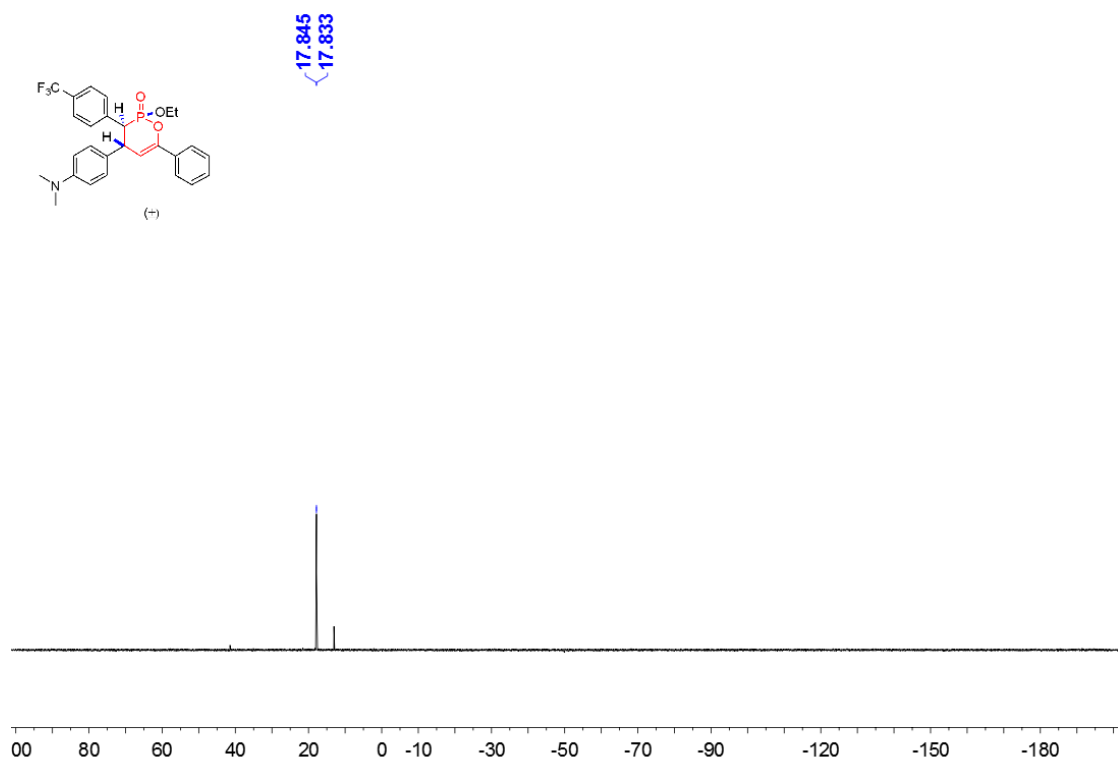
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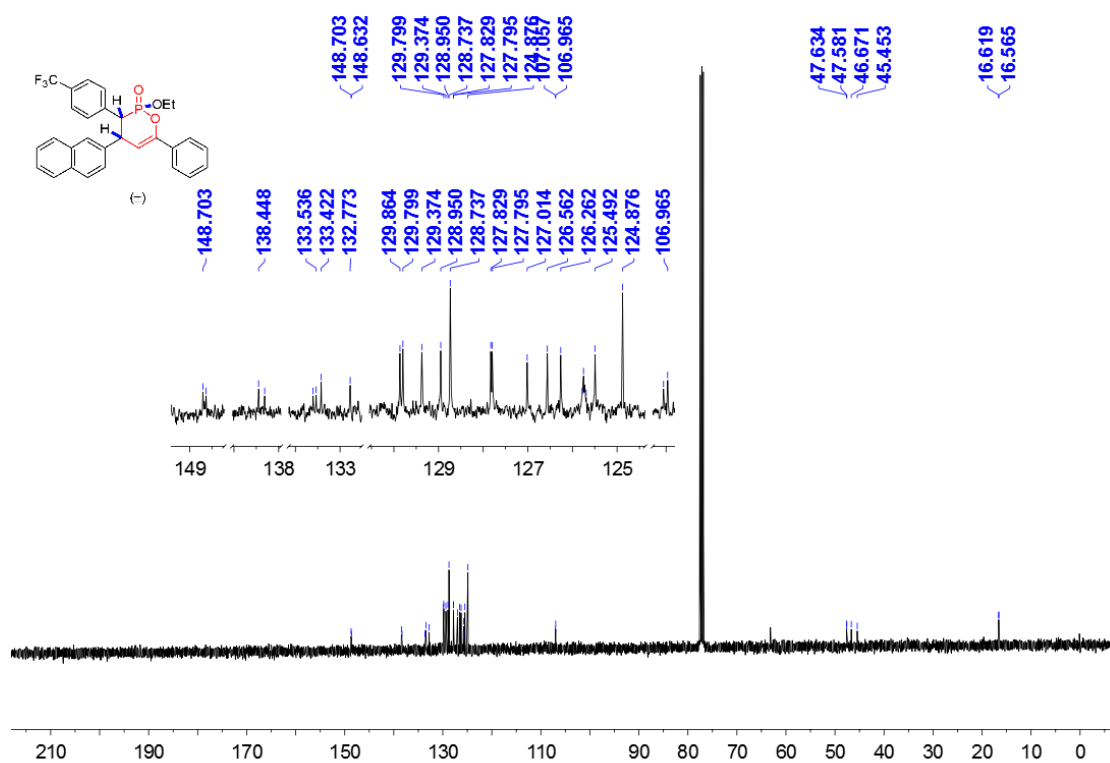


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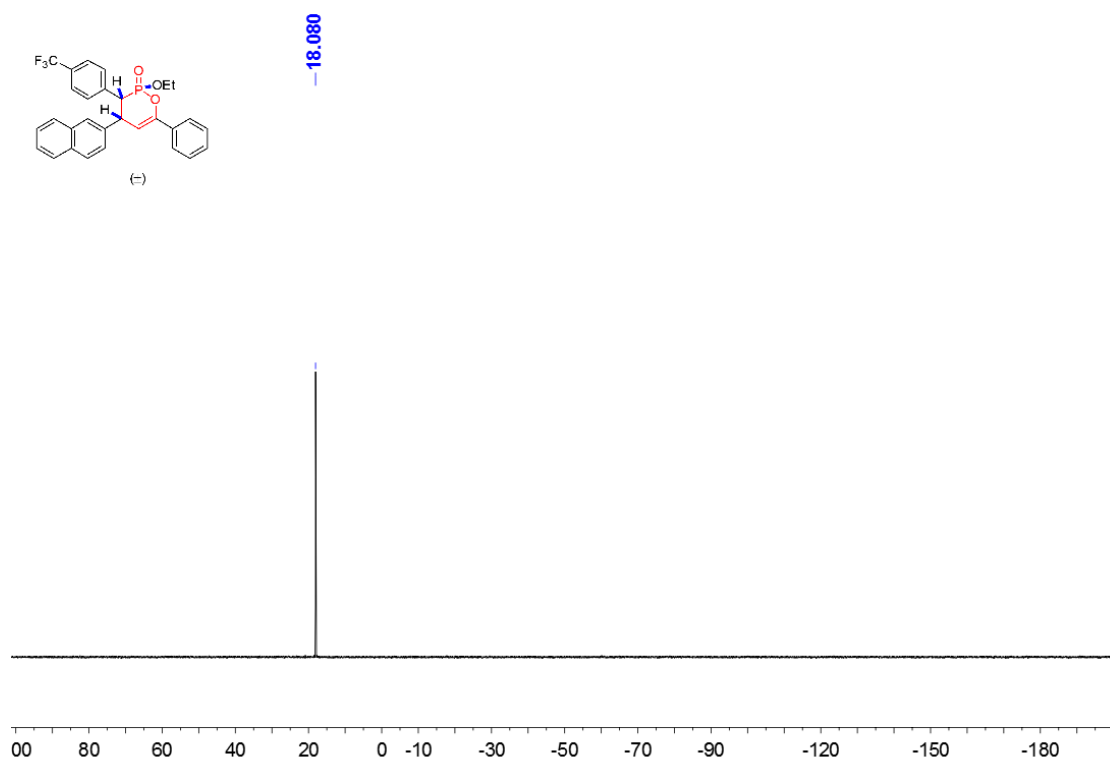


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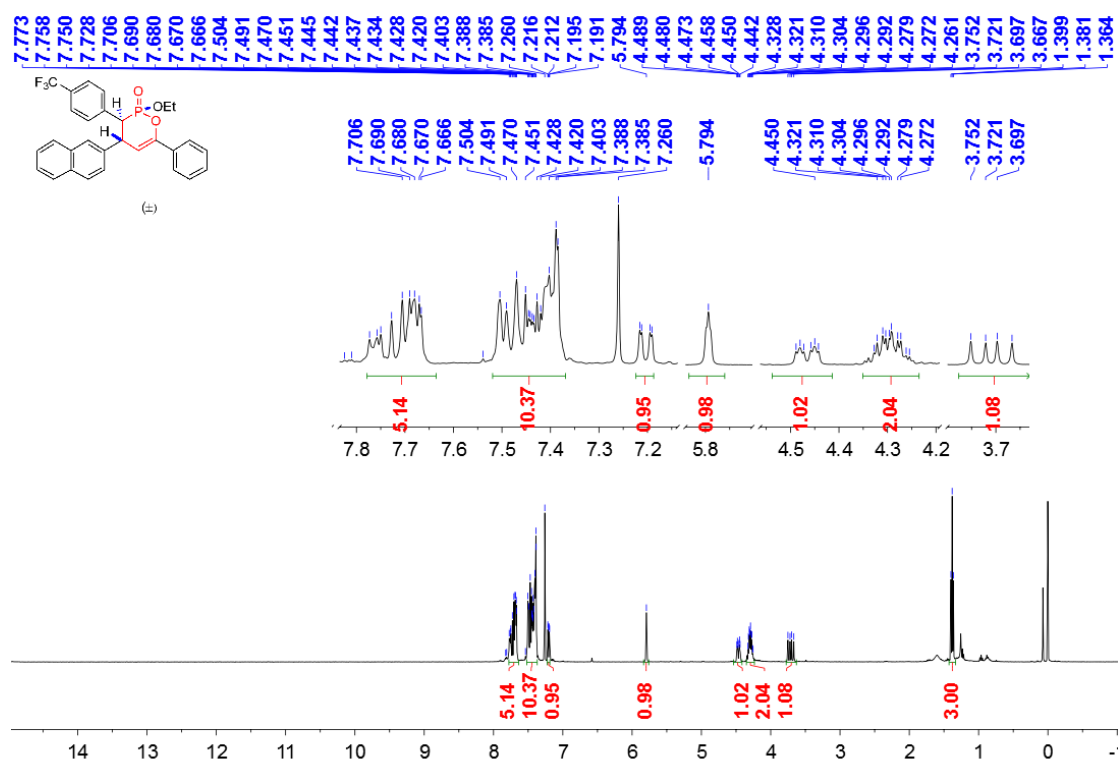




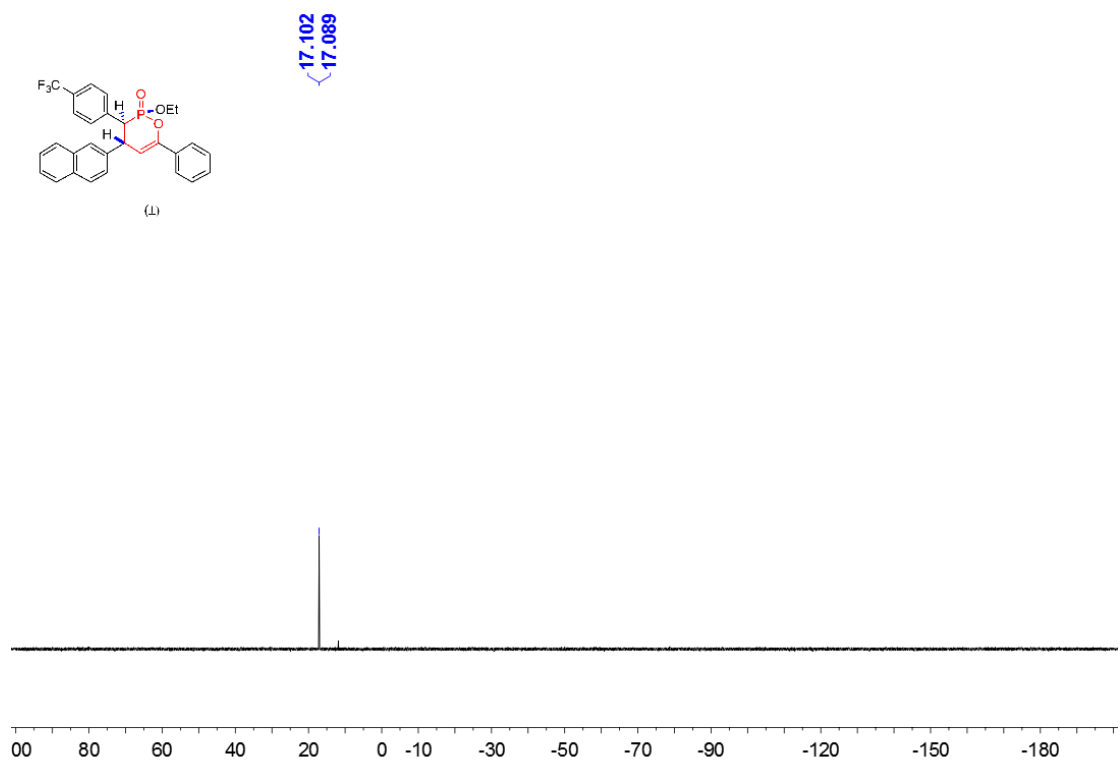
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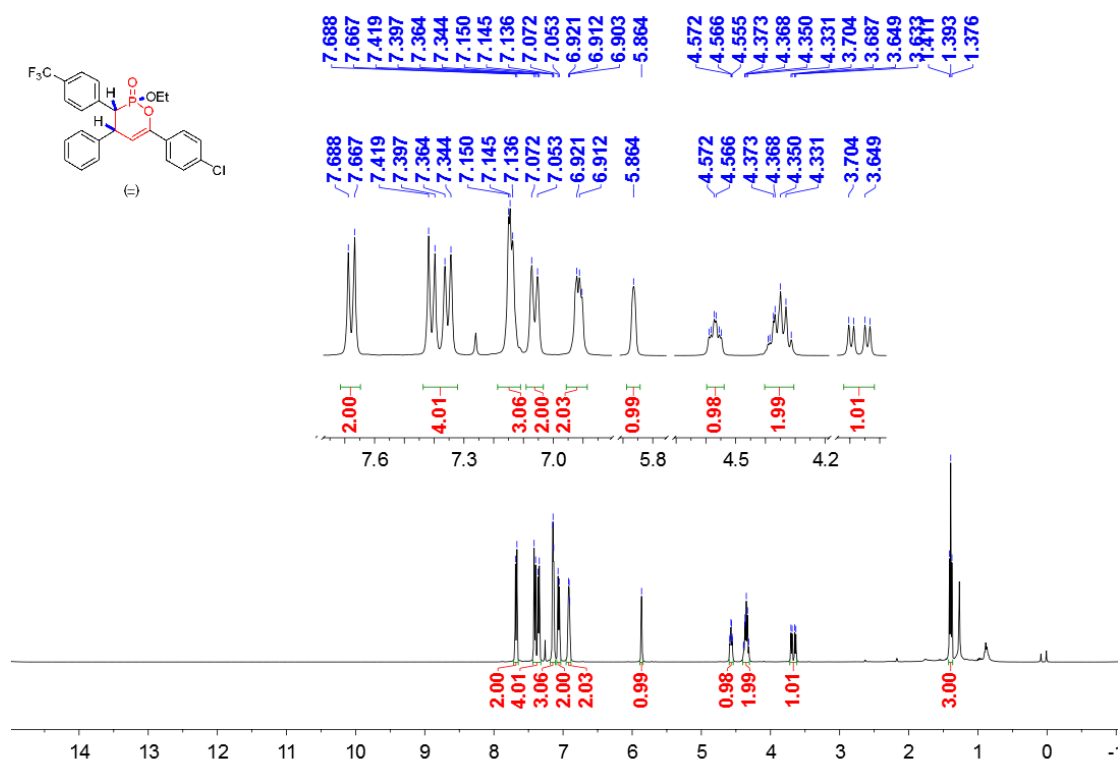
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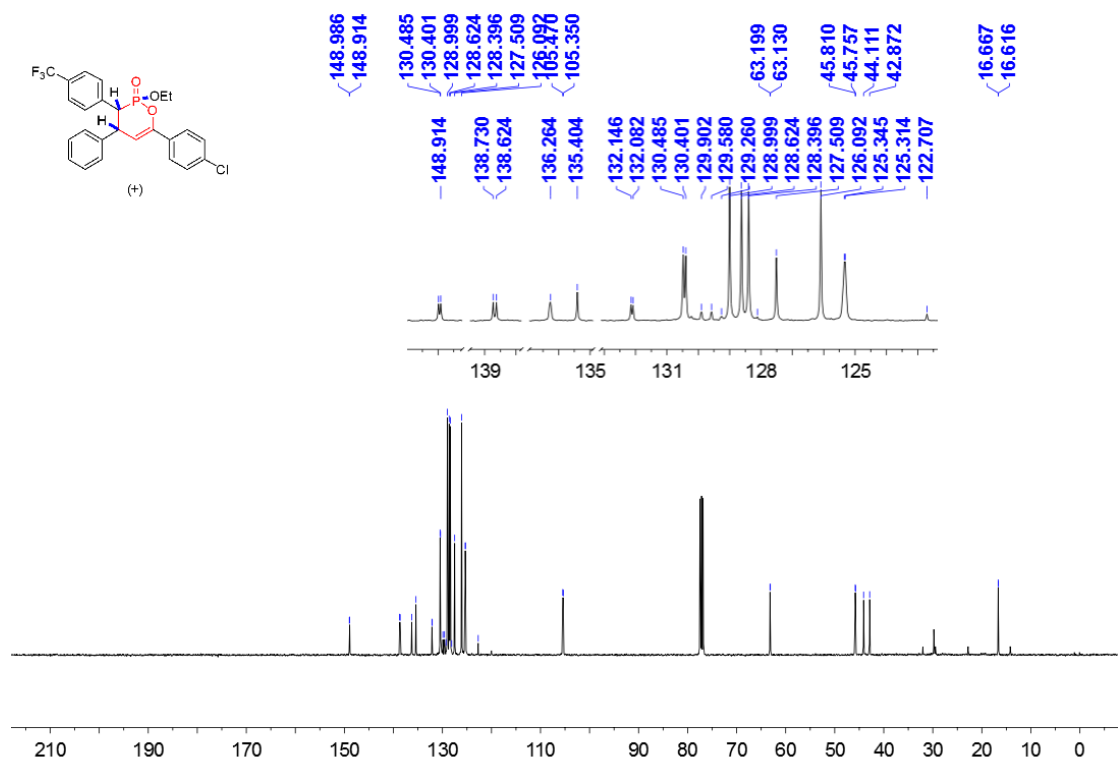
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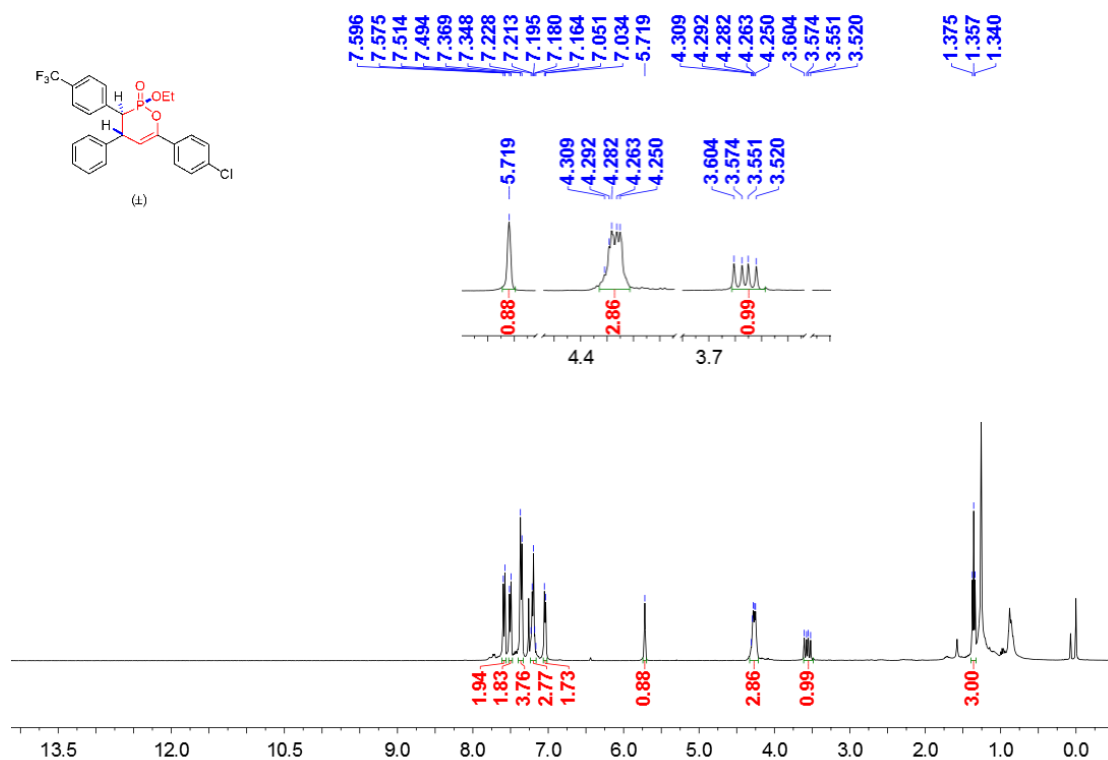
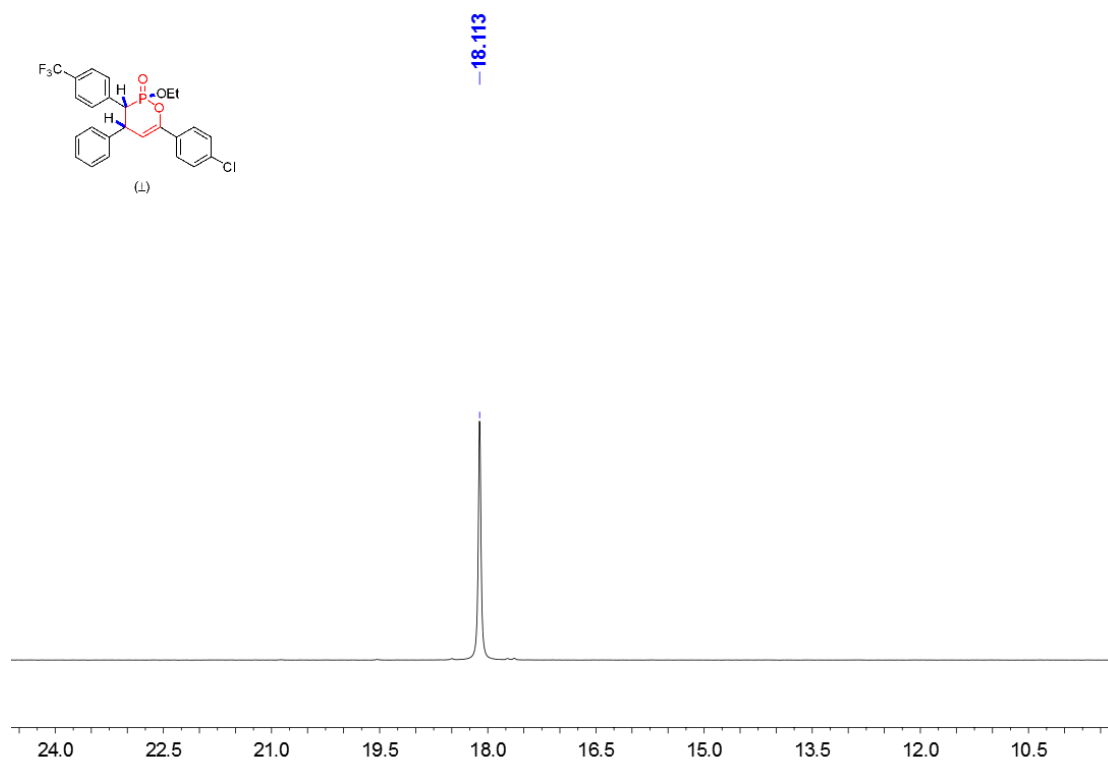
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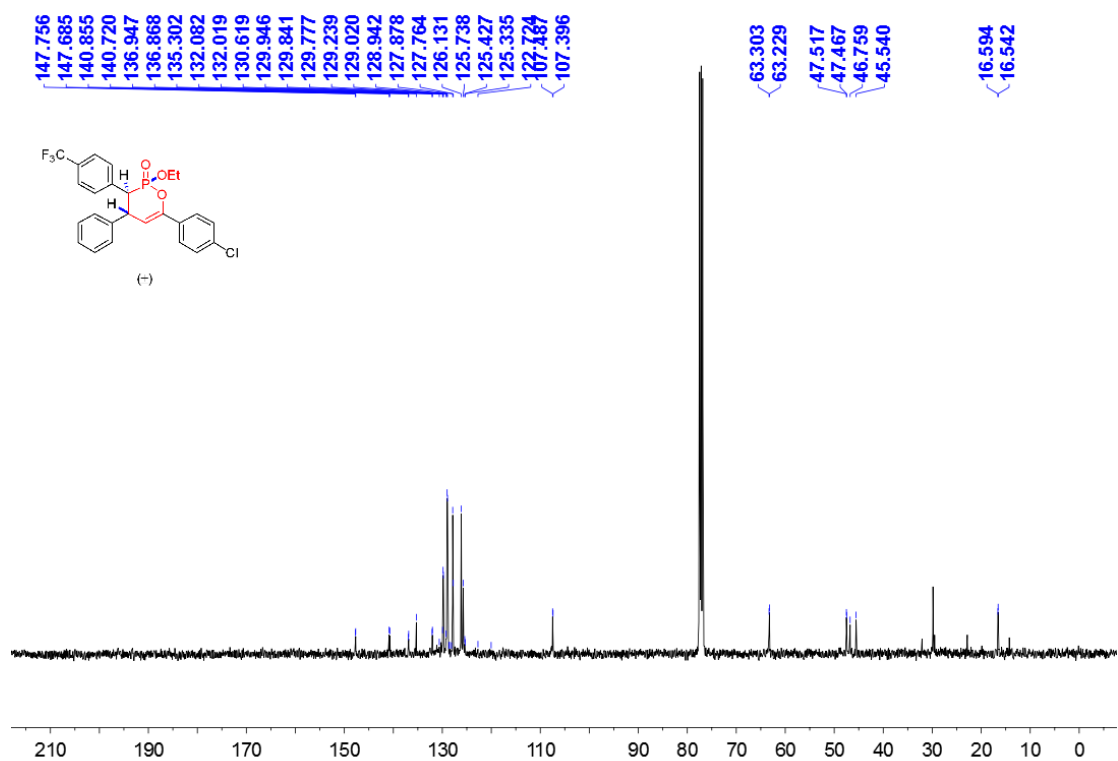


¹H NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**31**



¹³C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**31**

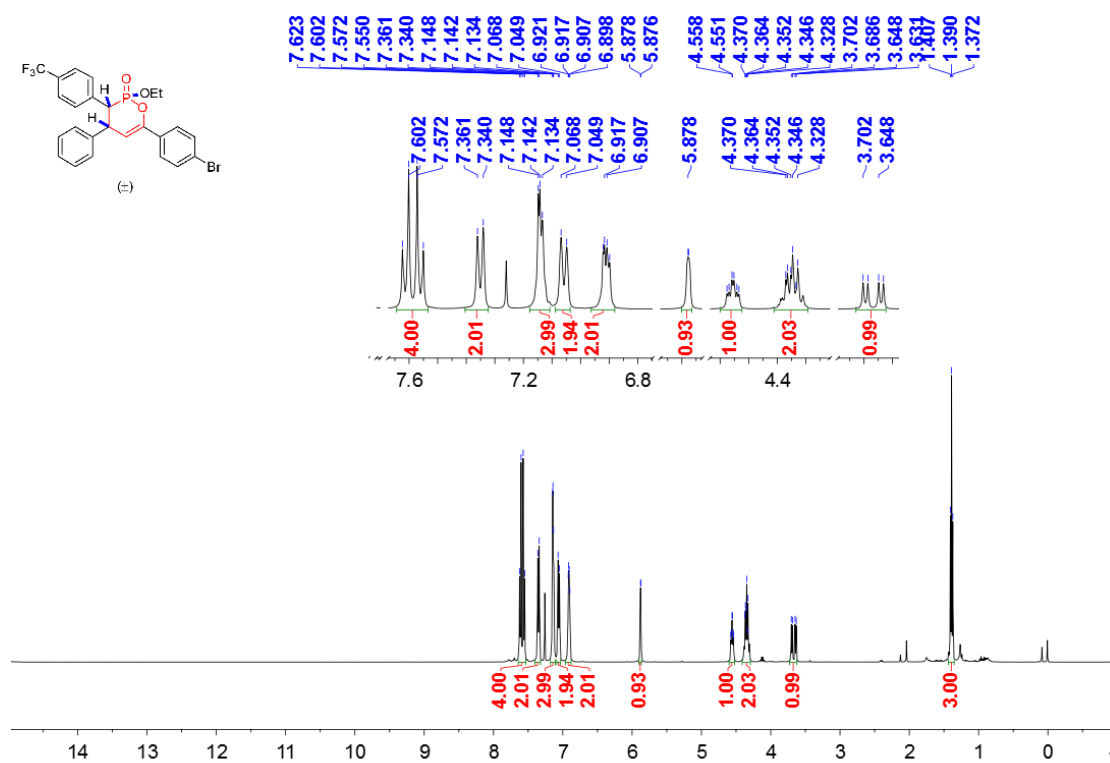




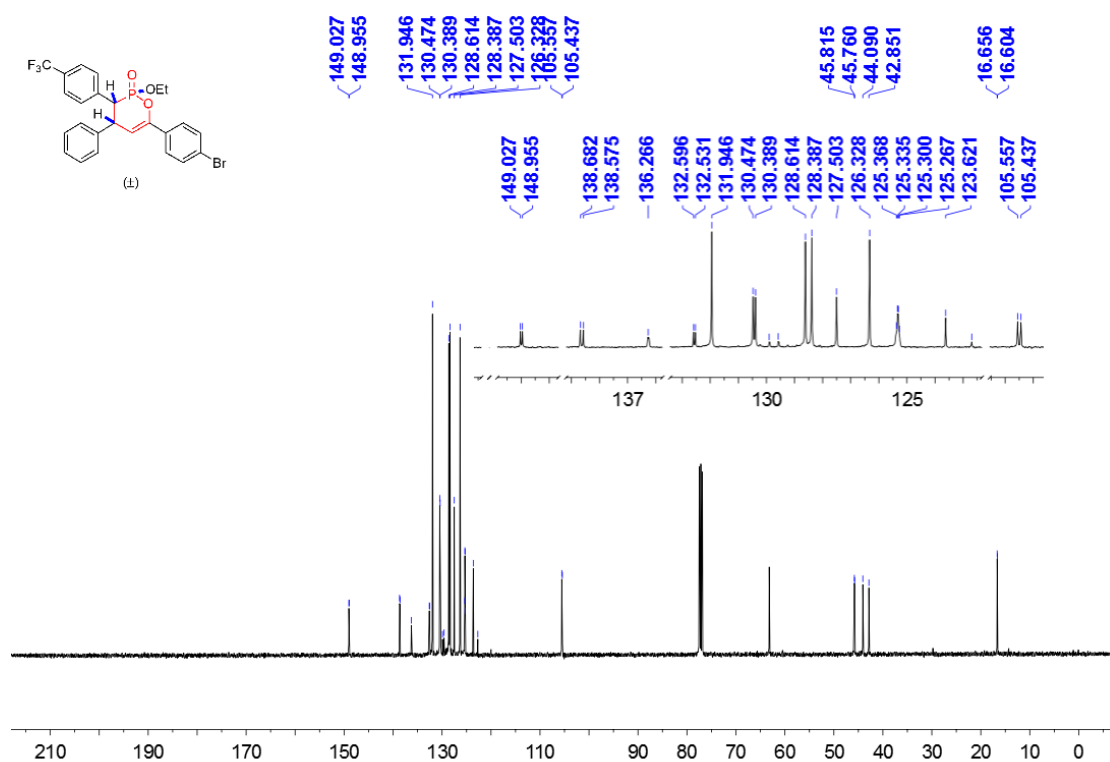
¹³C NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3I**



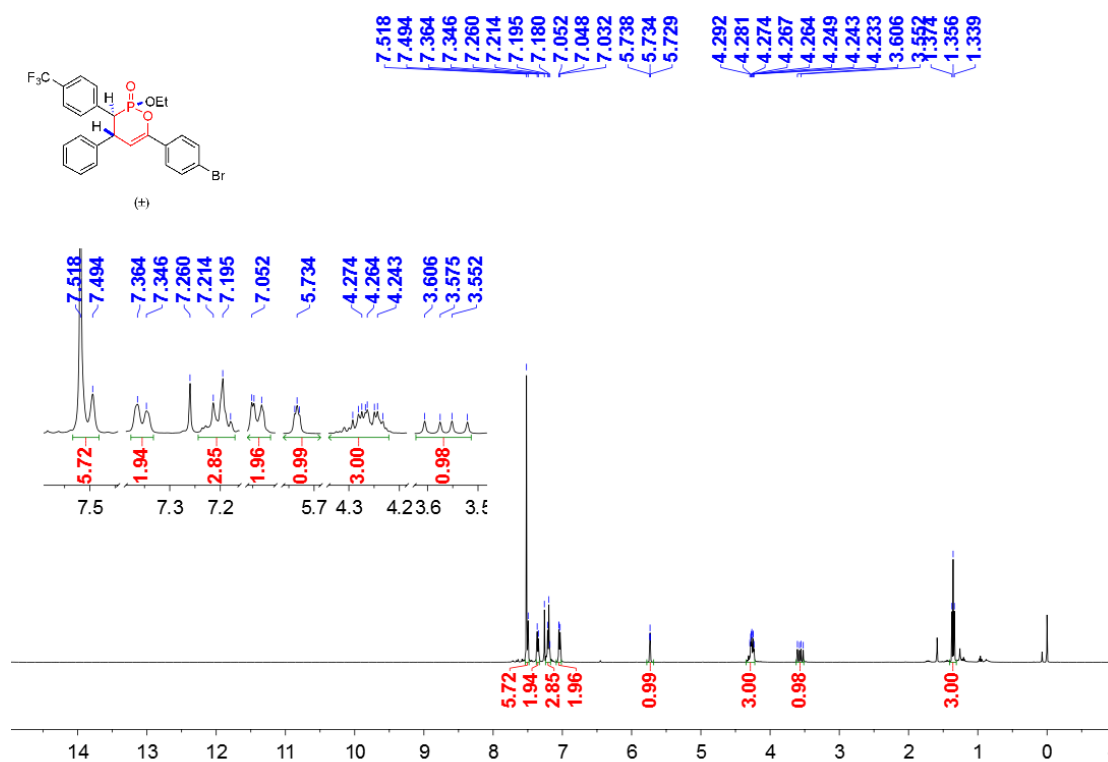
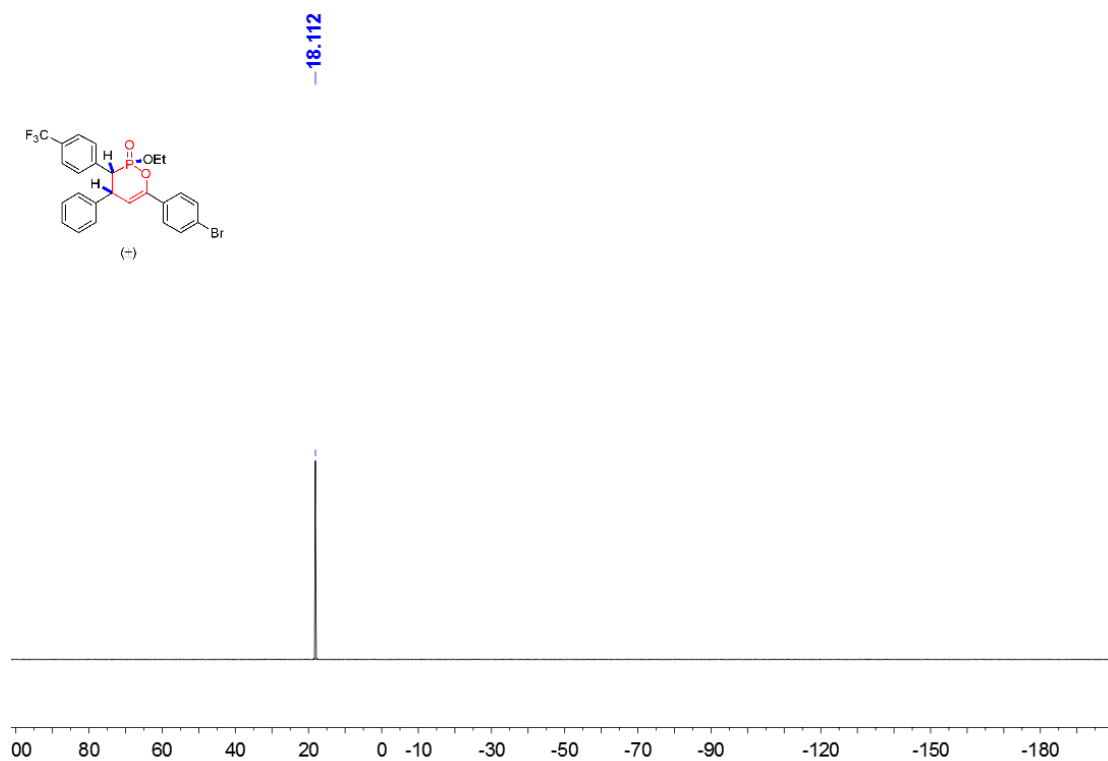
³¹P NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3I**

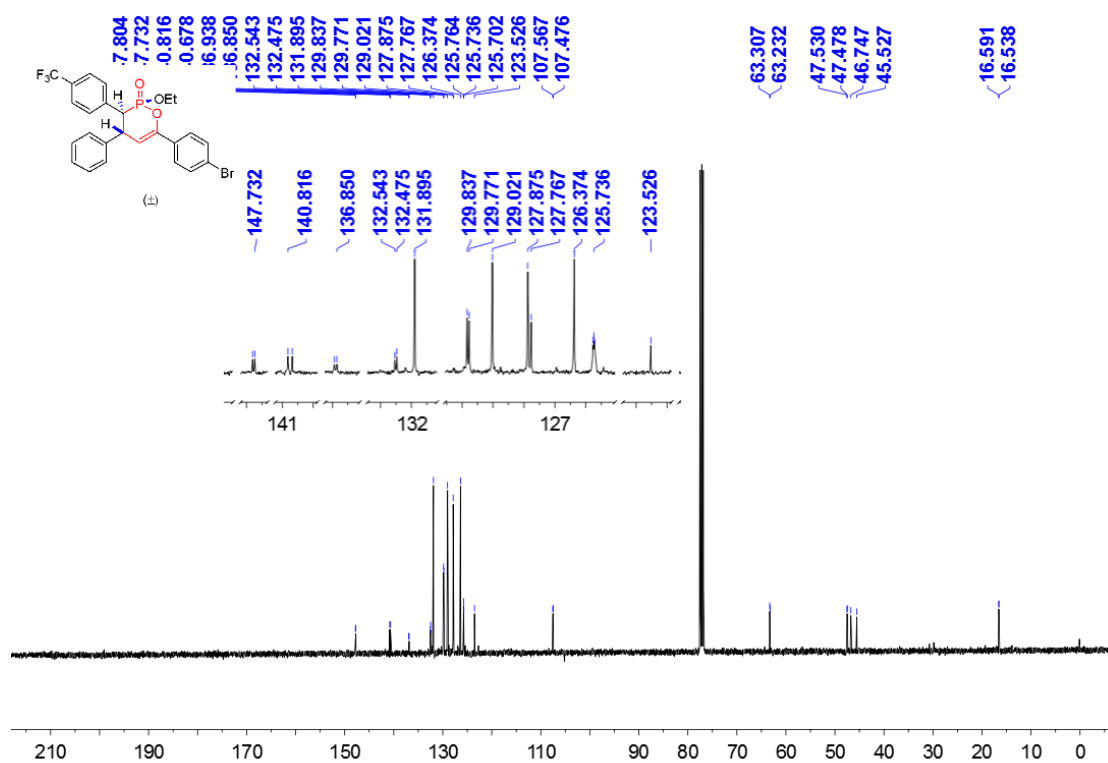


¹H NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3m



¹³C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3m

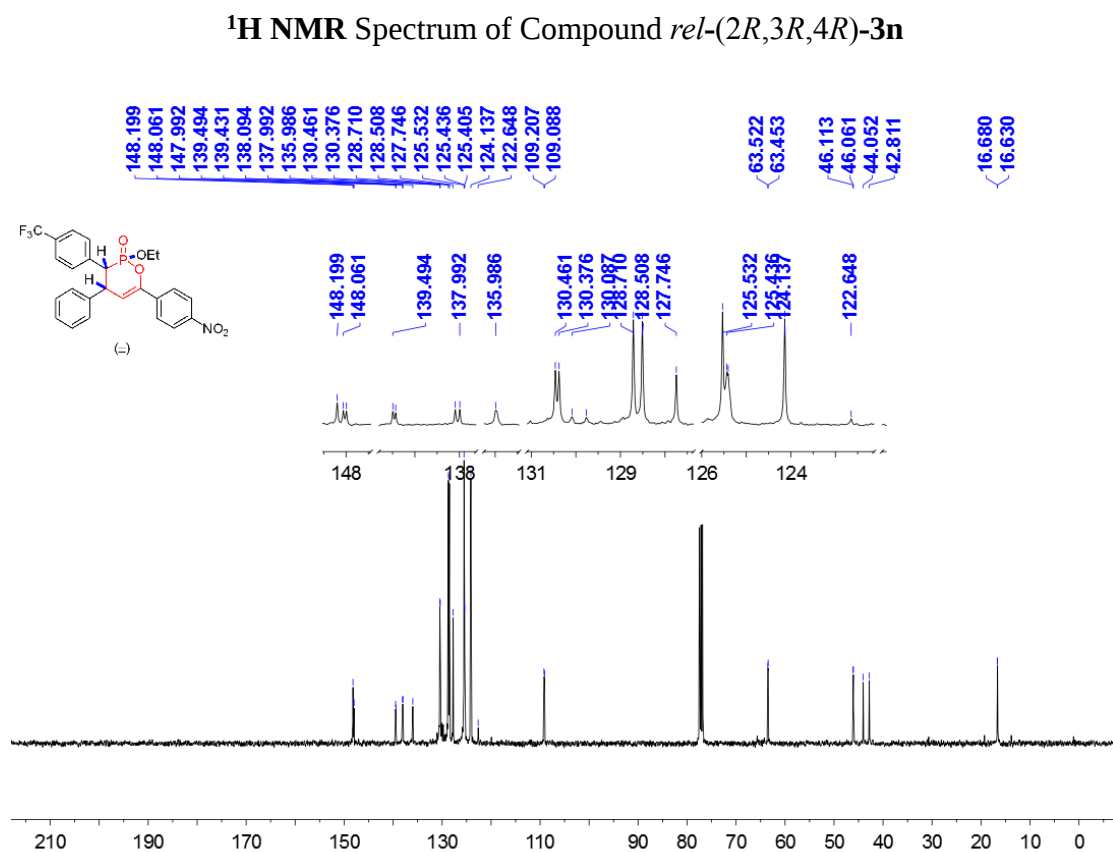
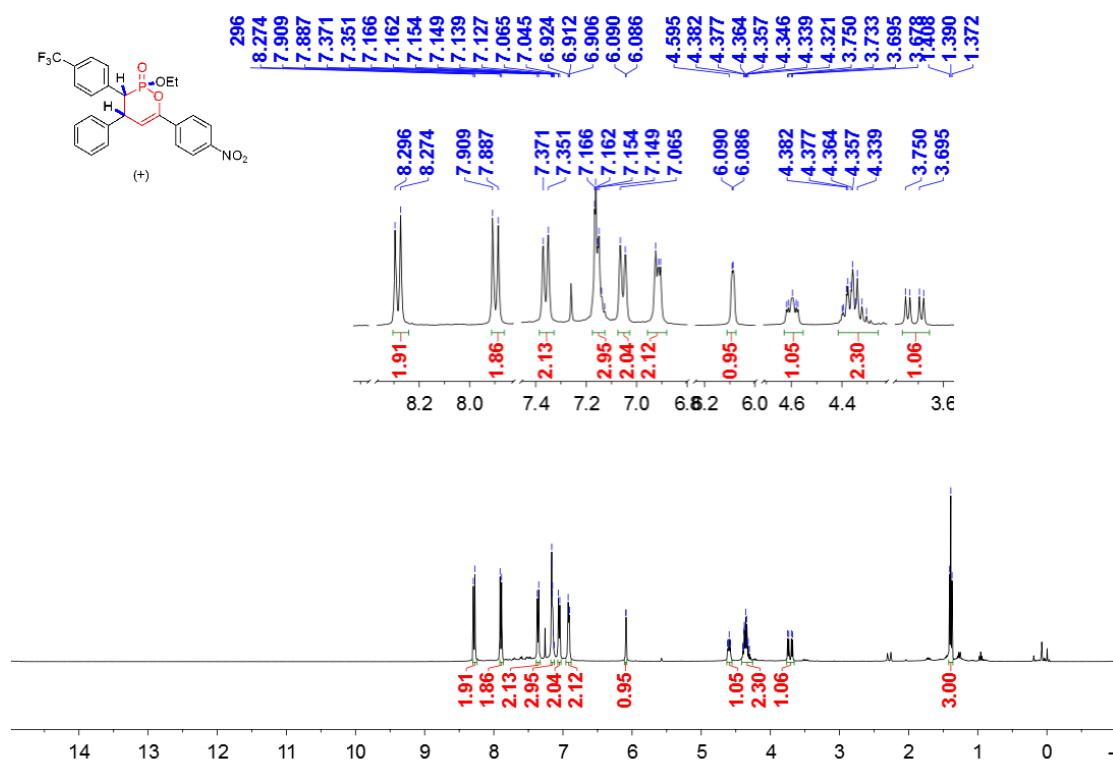


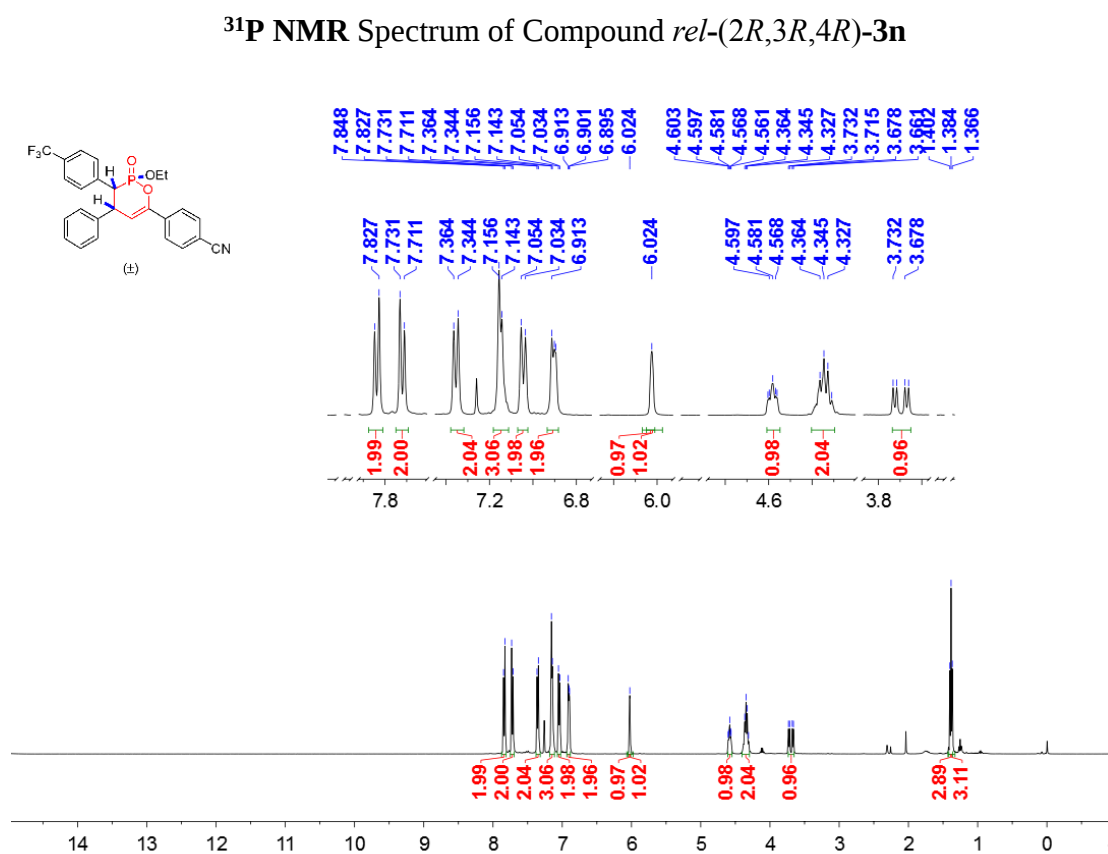
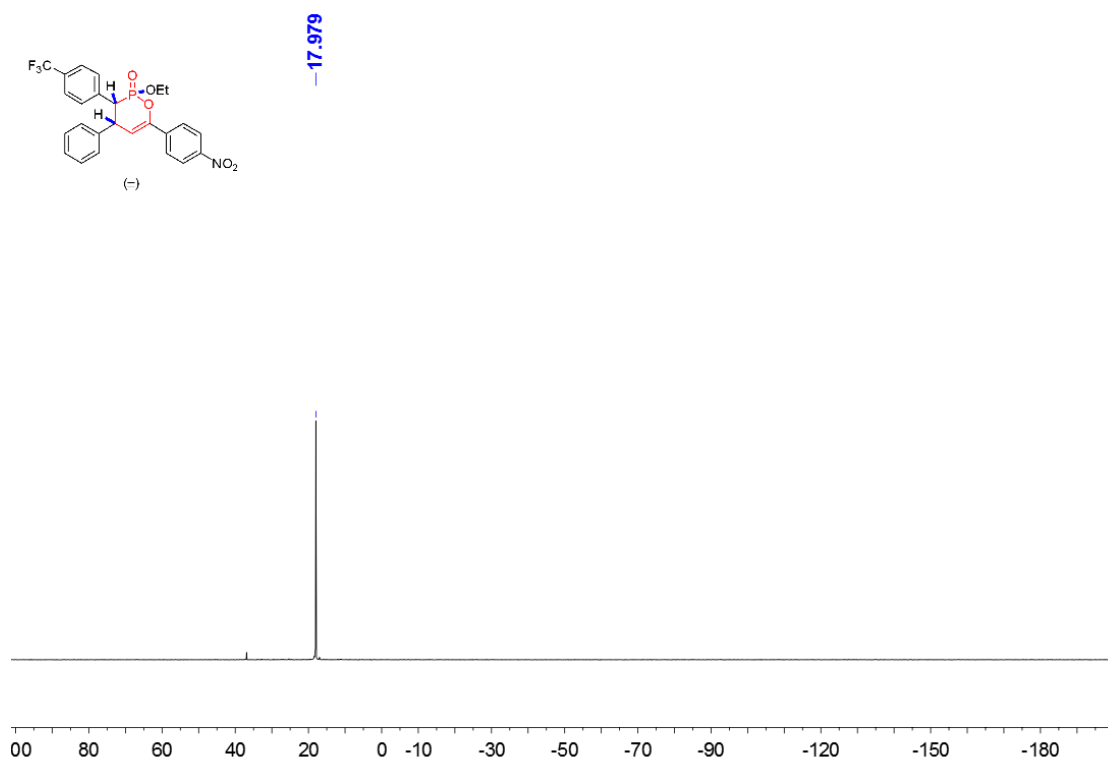


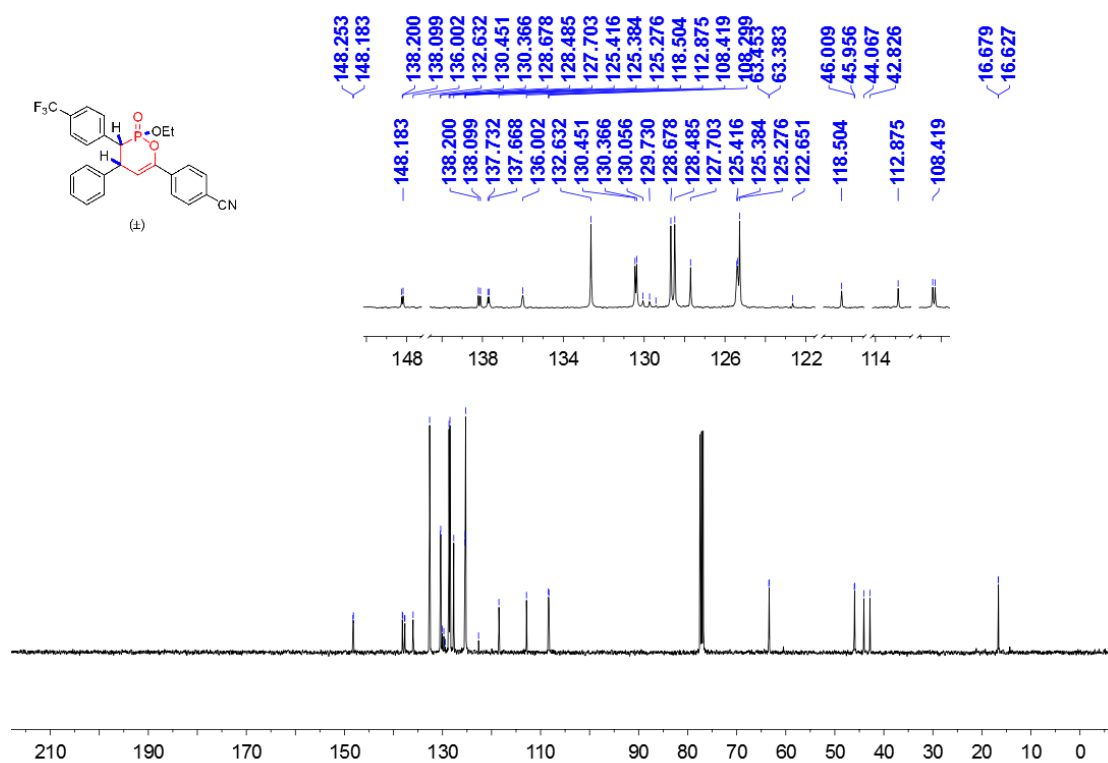
¹³C NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3m**



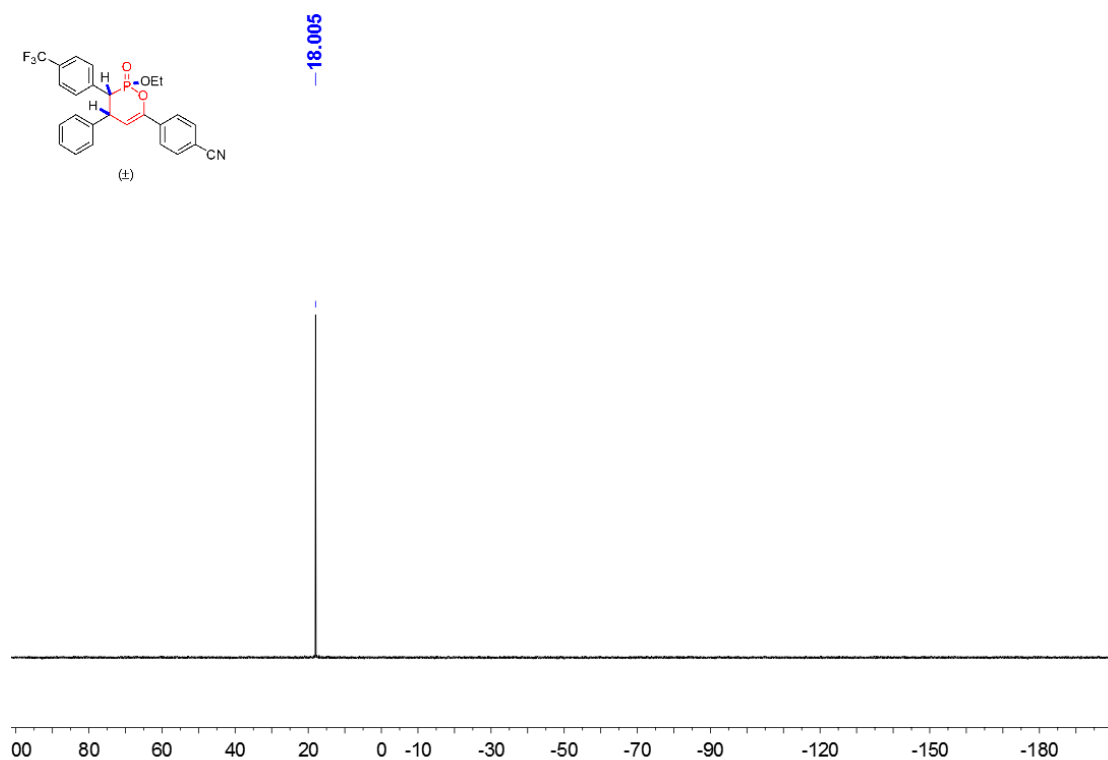
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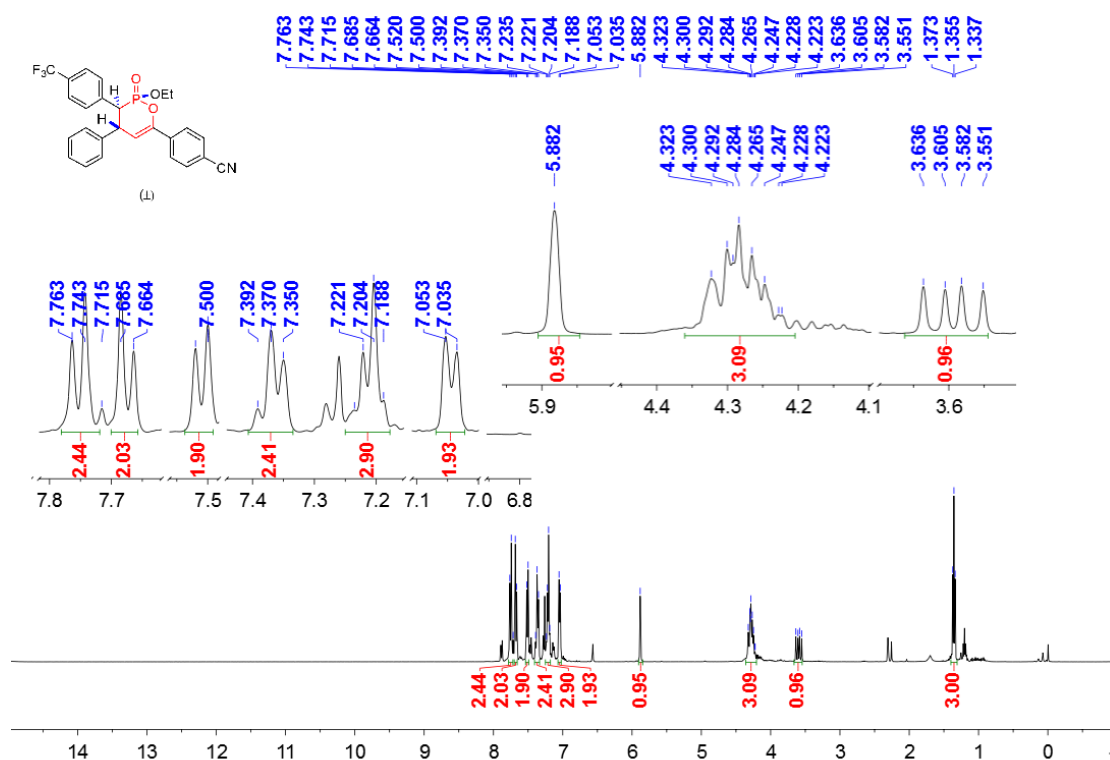




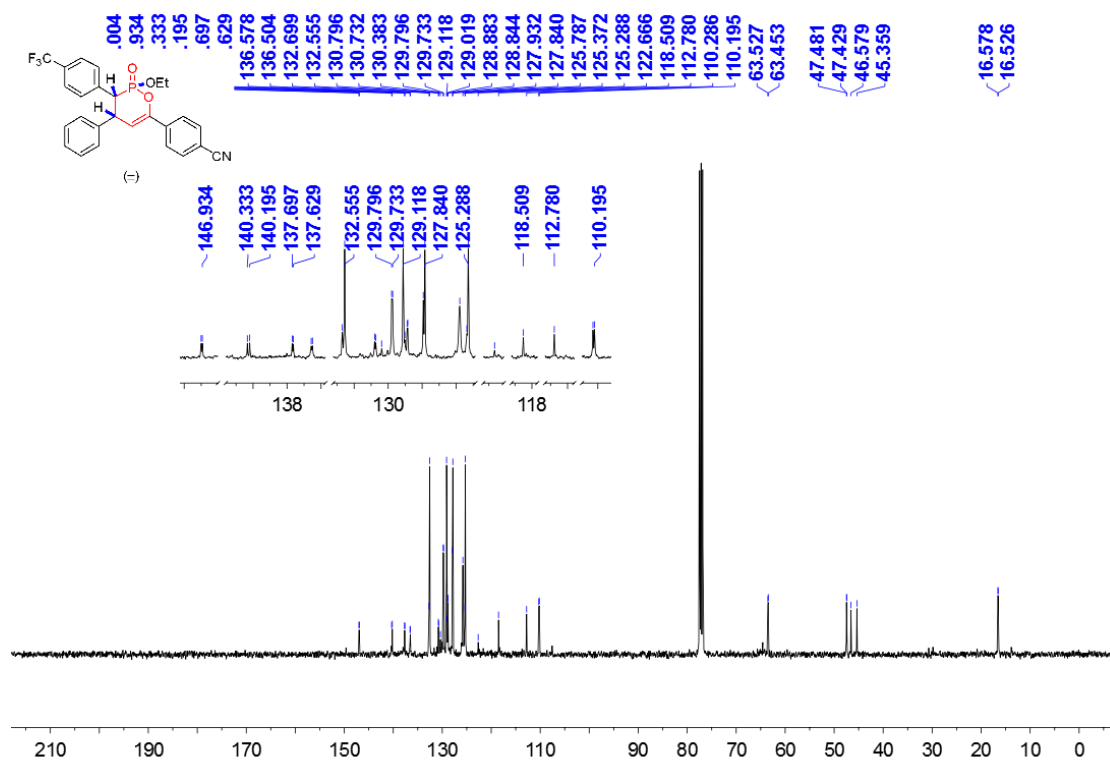
^{13}C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3o**



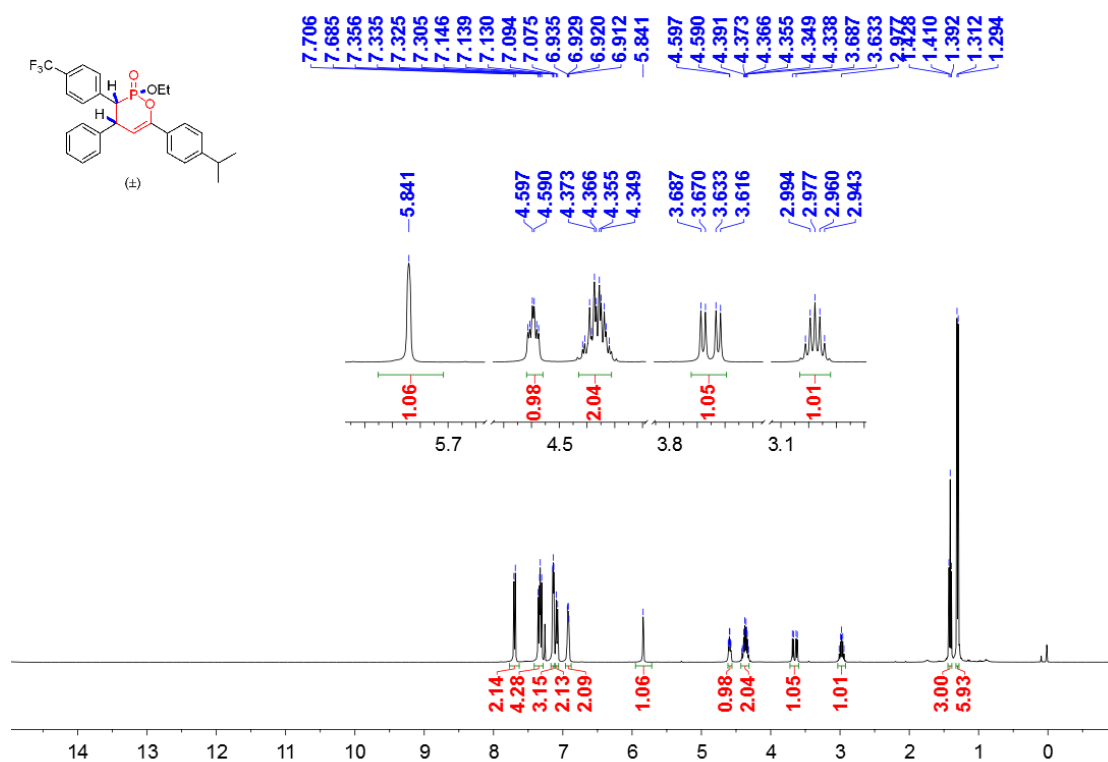
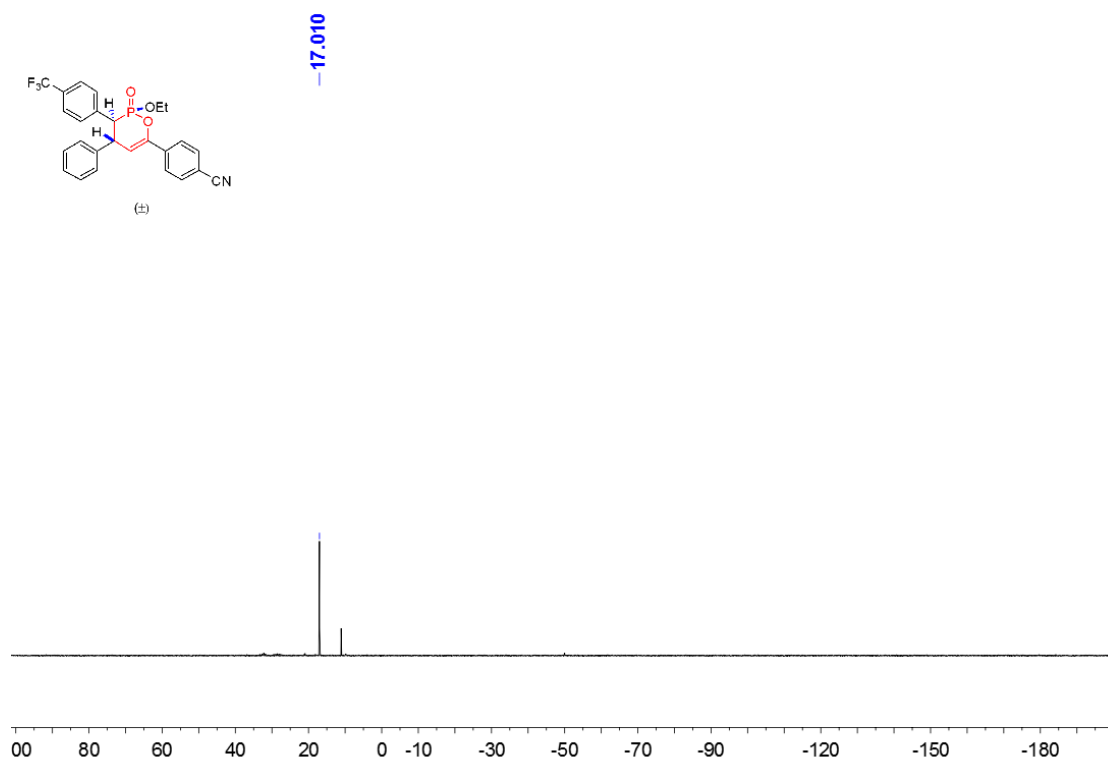
^{31}P NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3o**

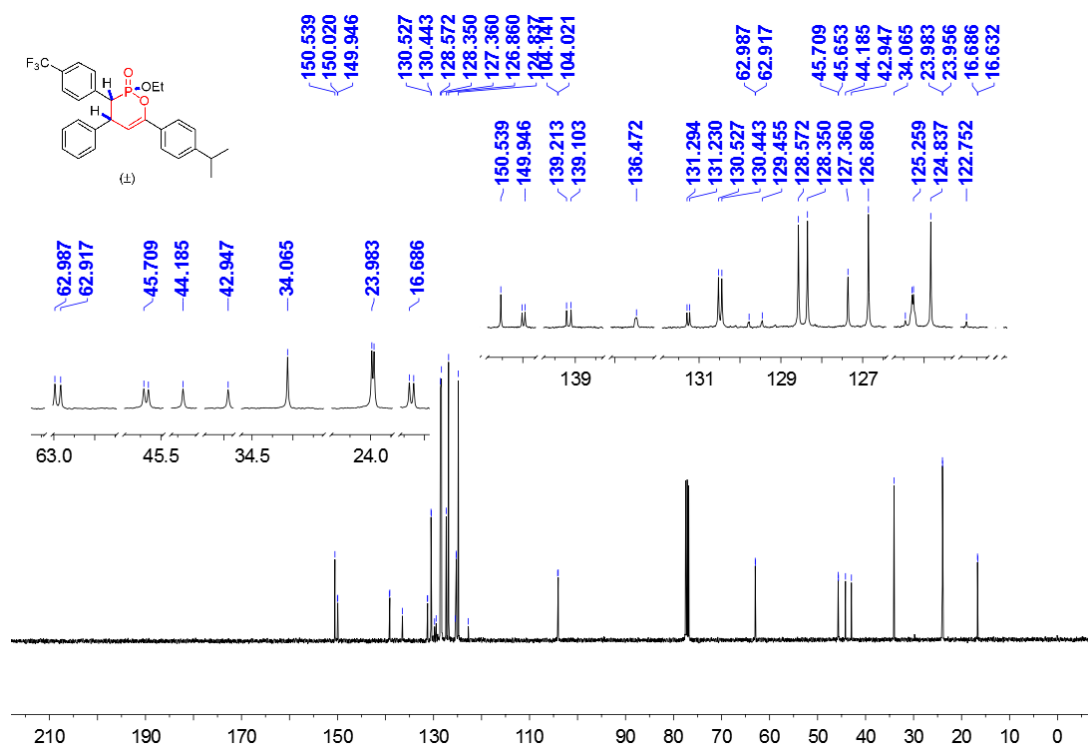


¹H NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3o**

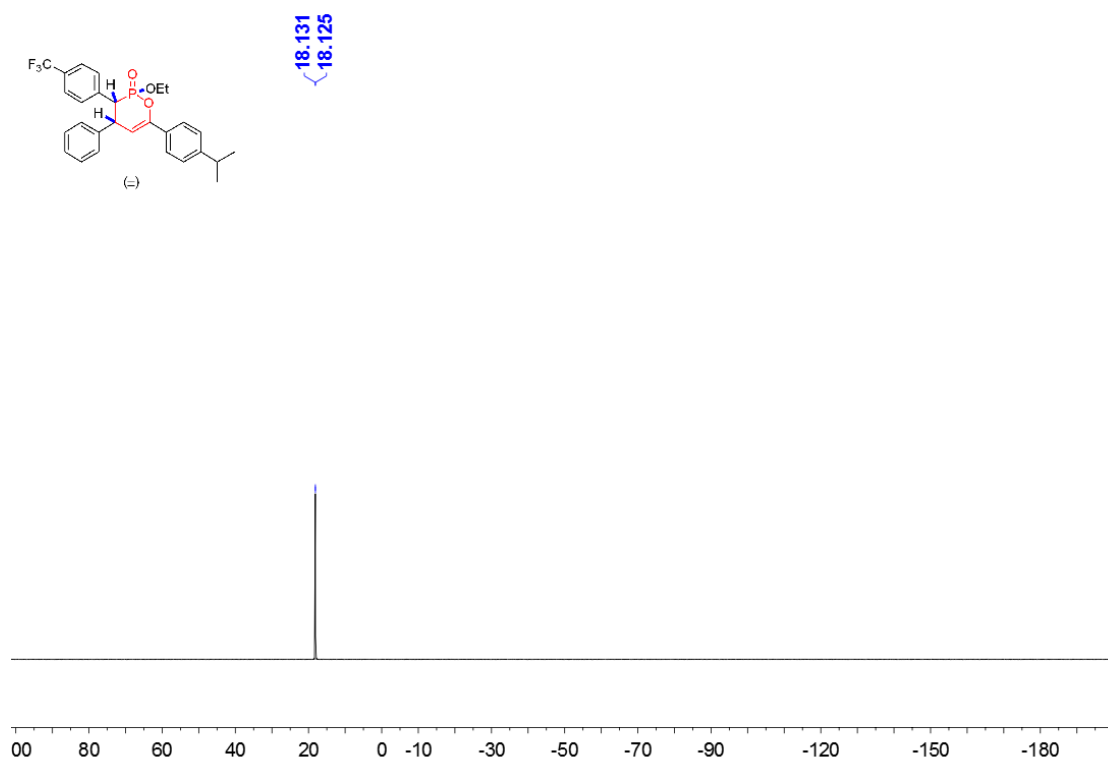


¹³C NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3o**

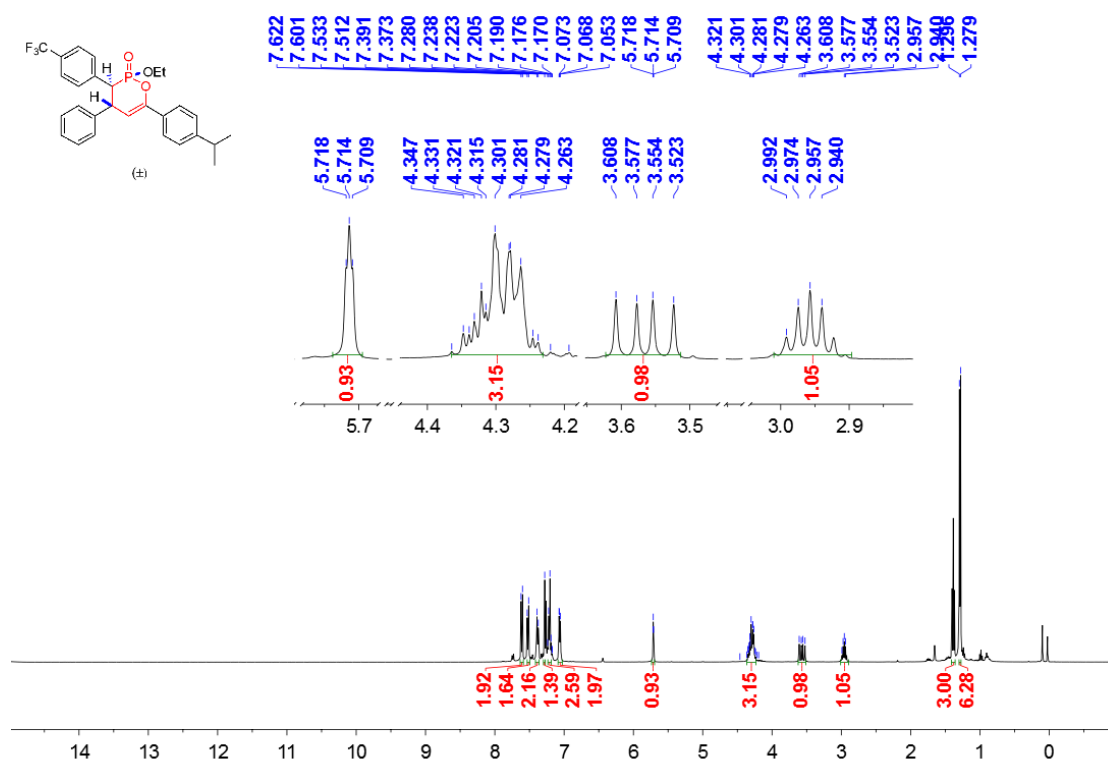




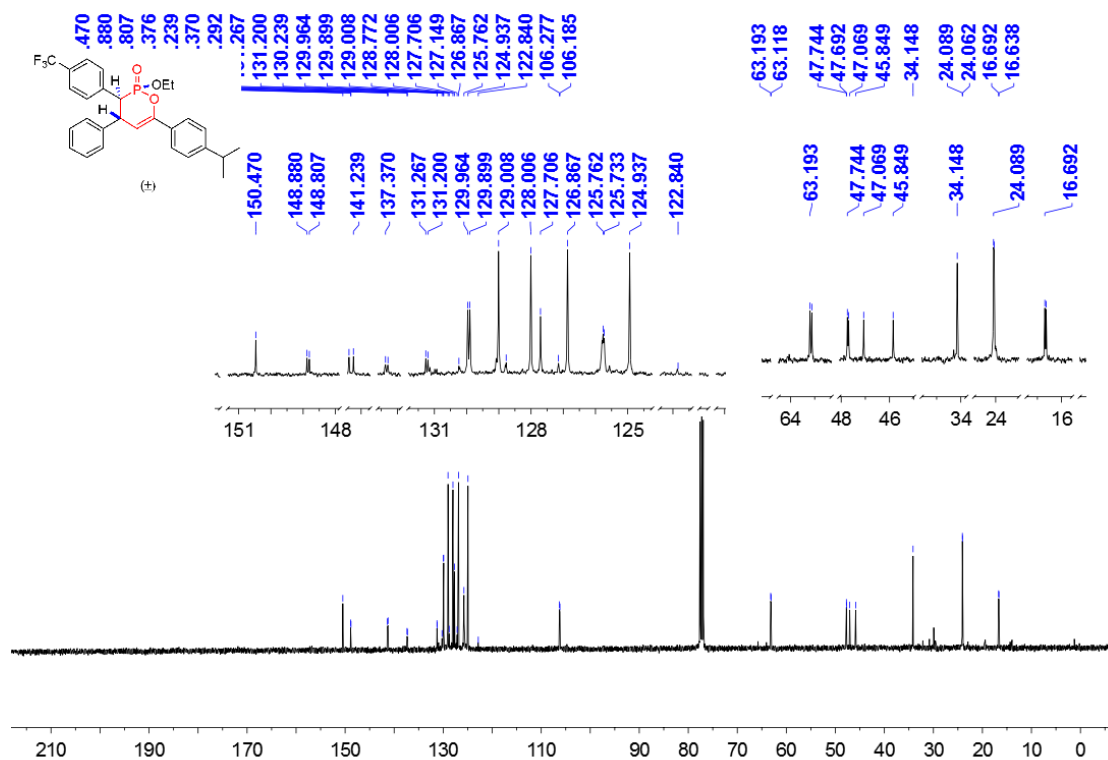
¹³C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3p



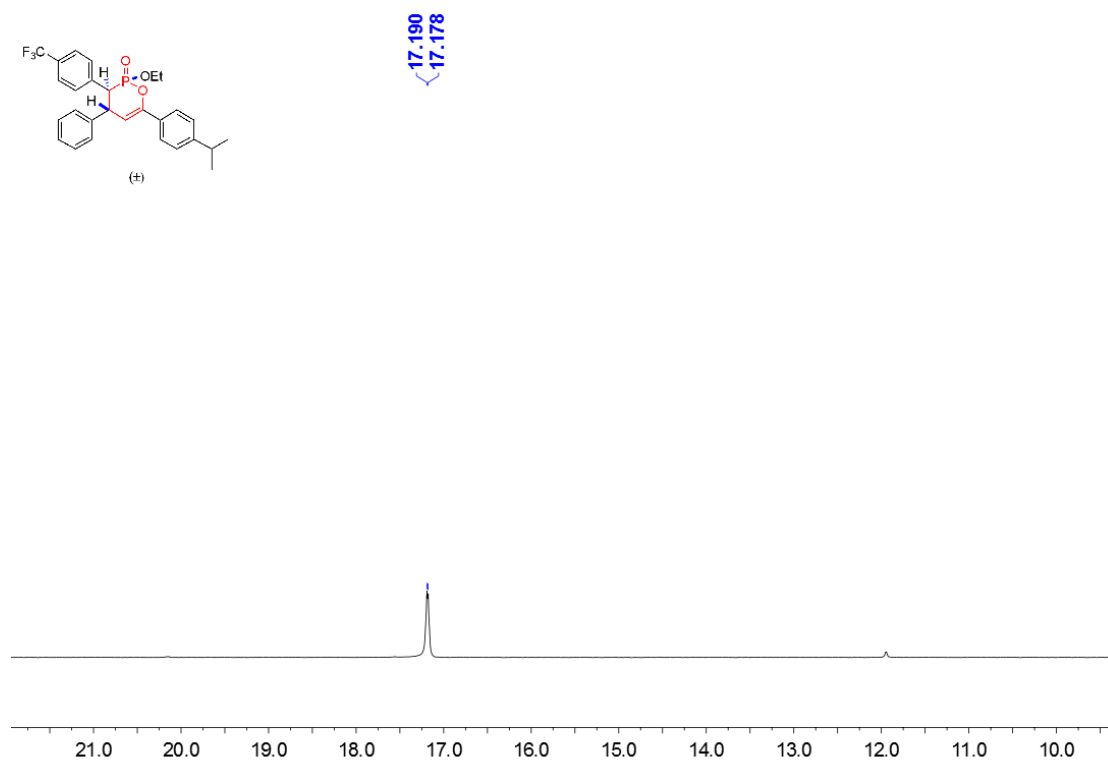
³¹P NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3p



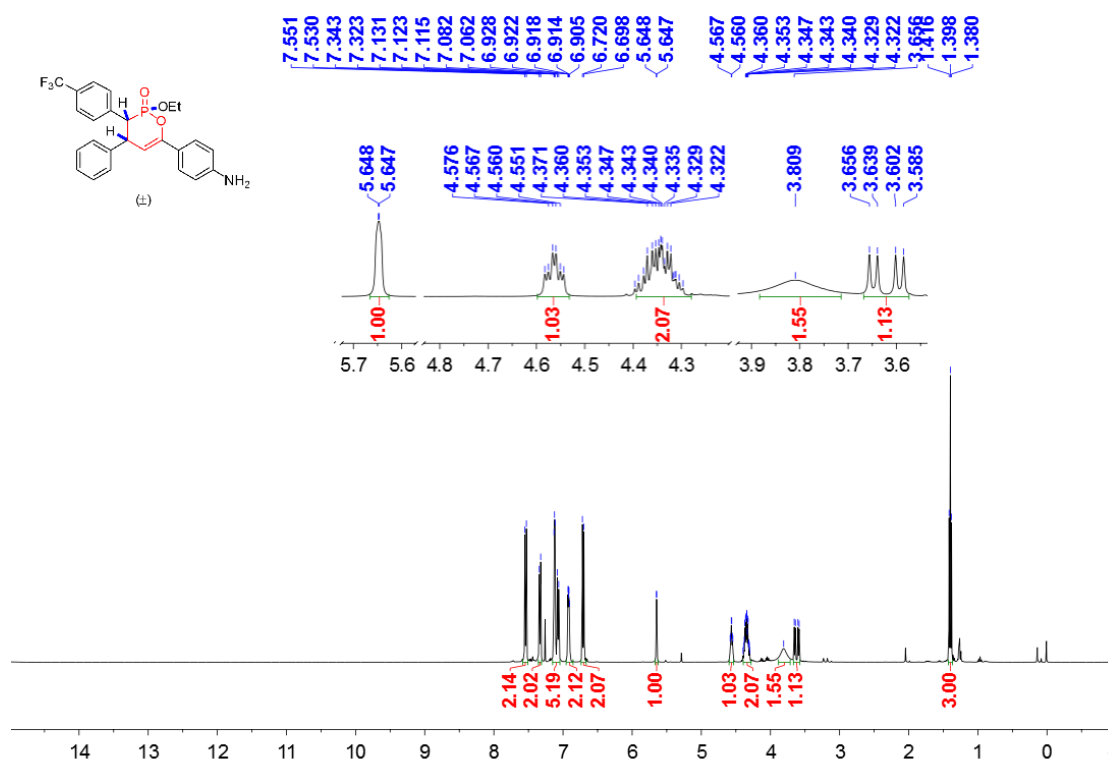
¹H NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3p**



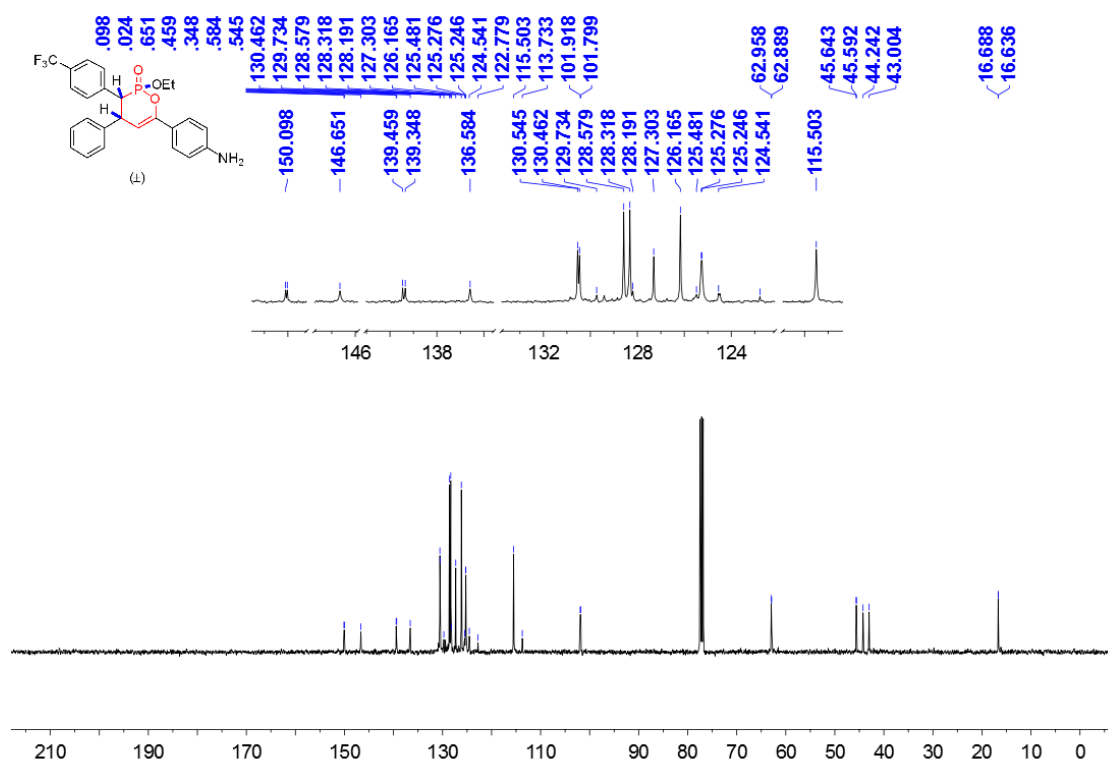
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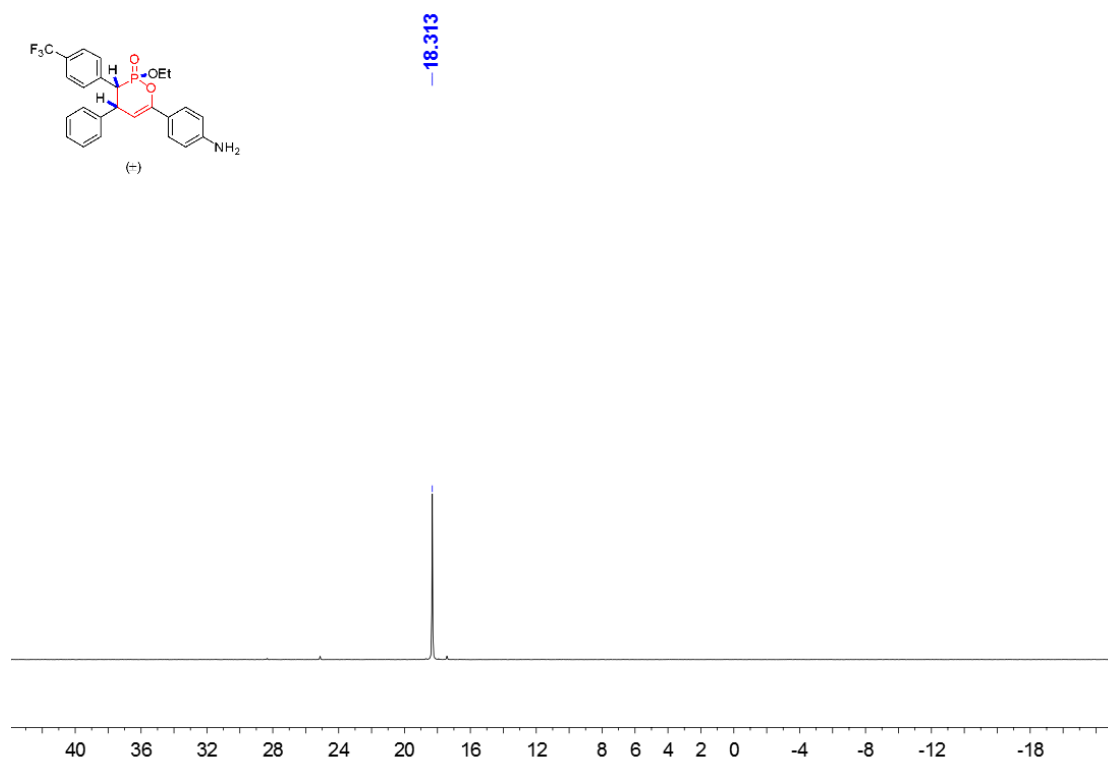
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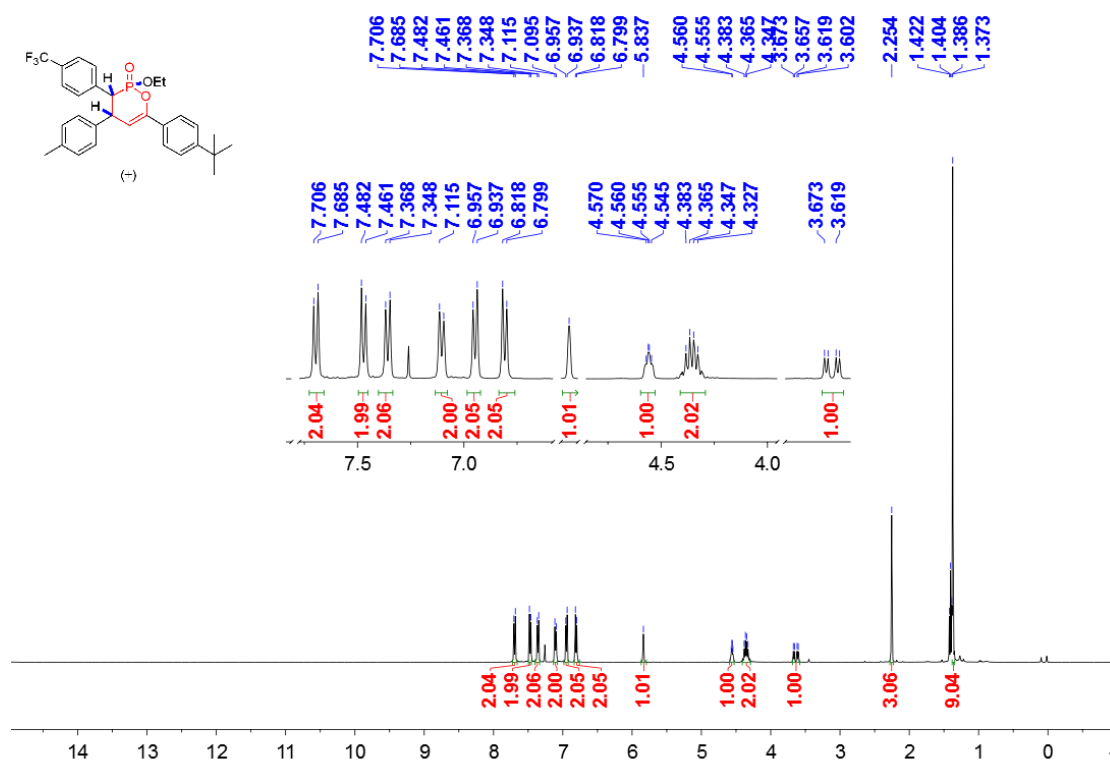
¹H NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3q



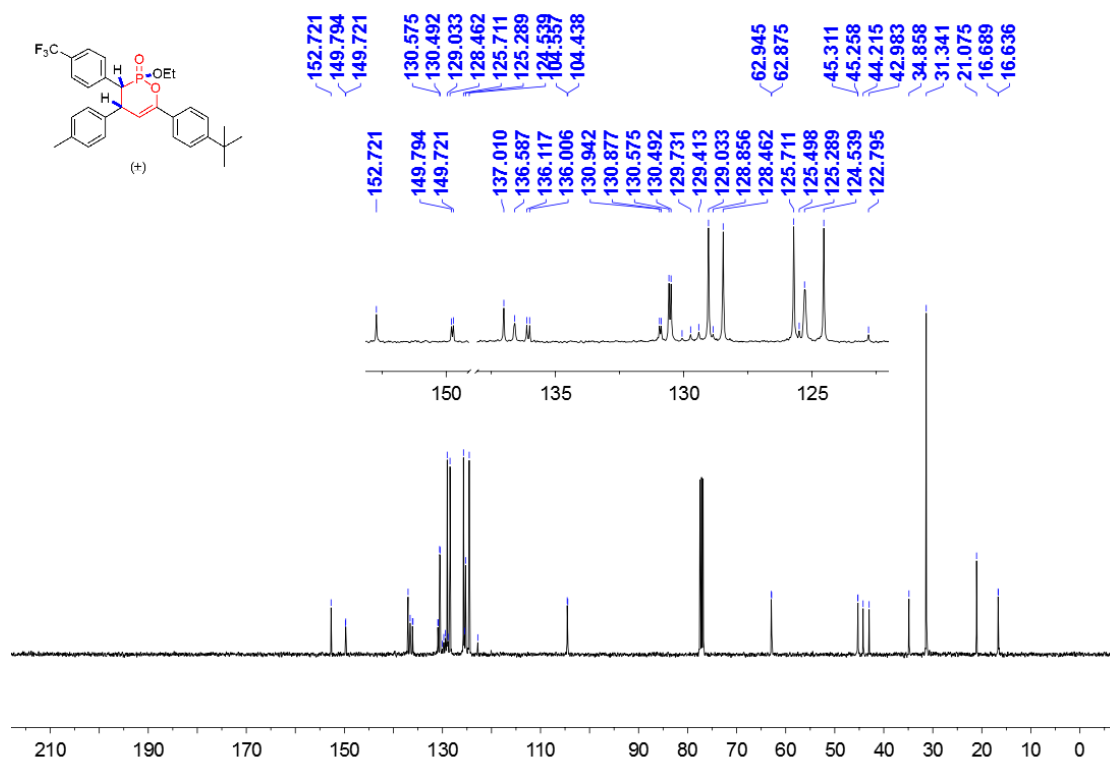
¹³C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3q



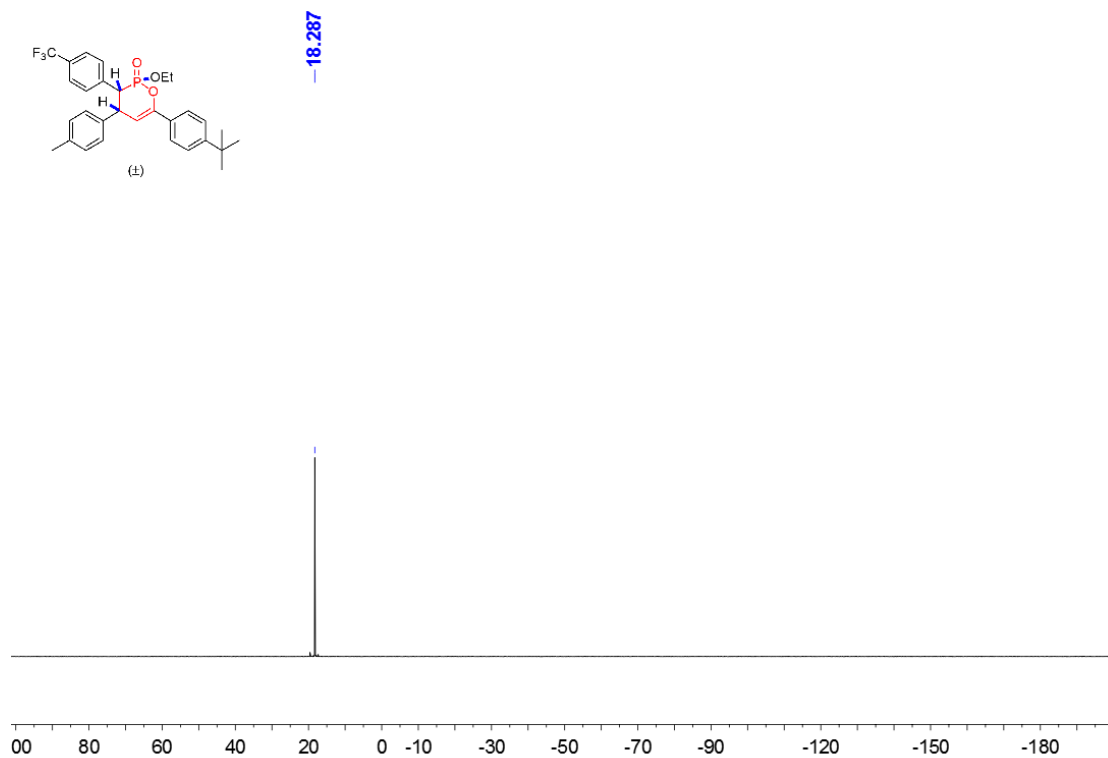
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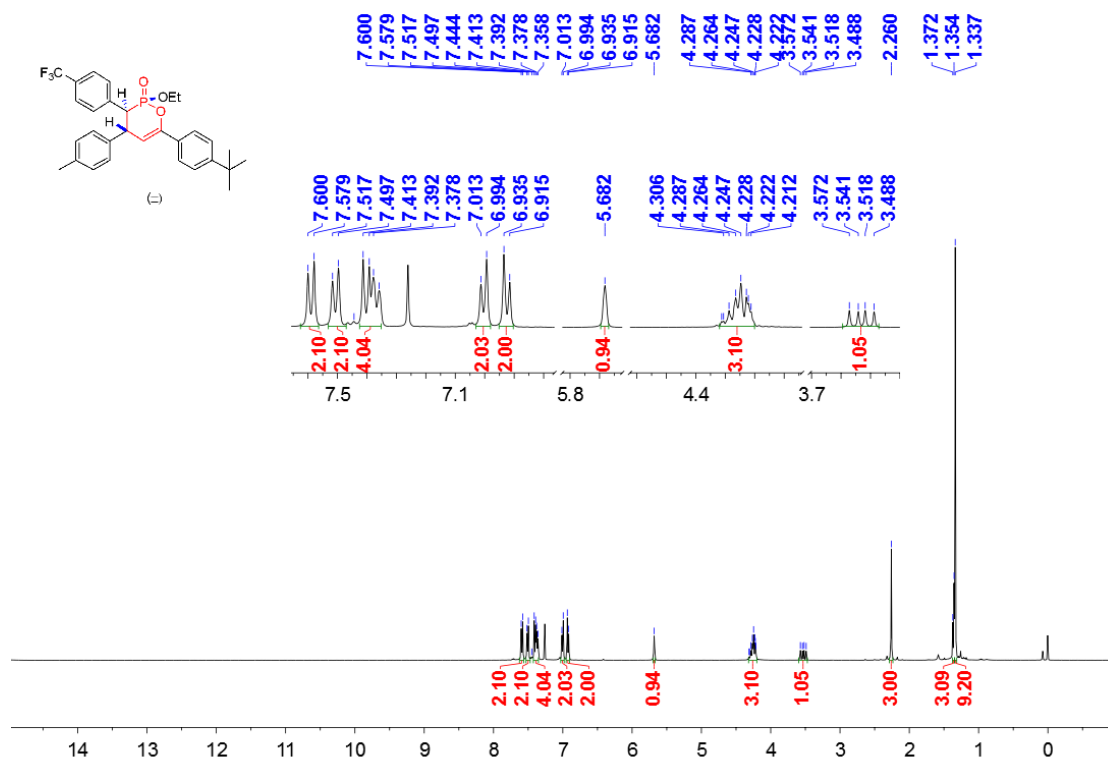
¹H NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3r**



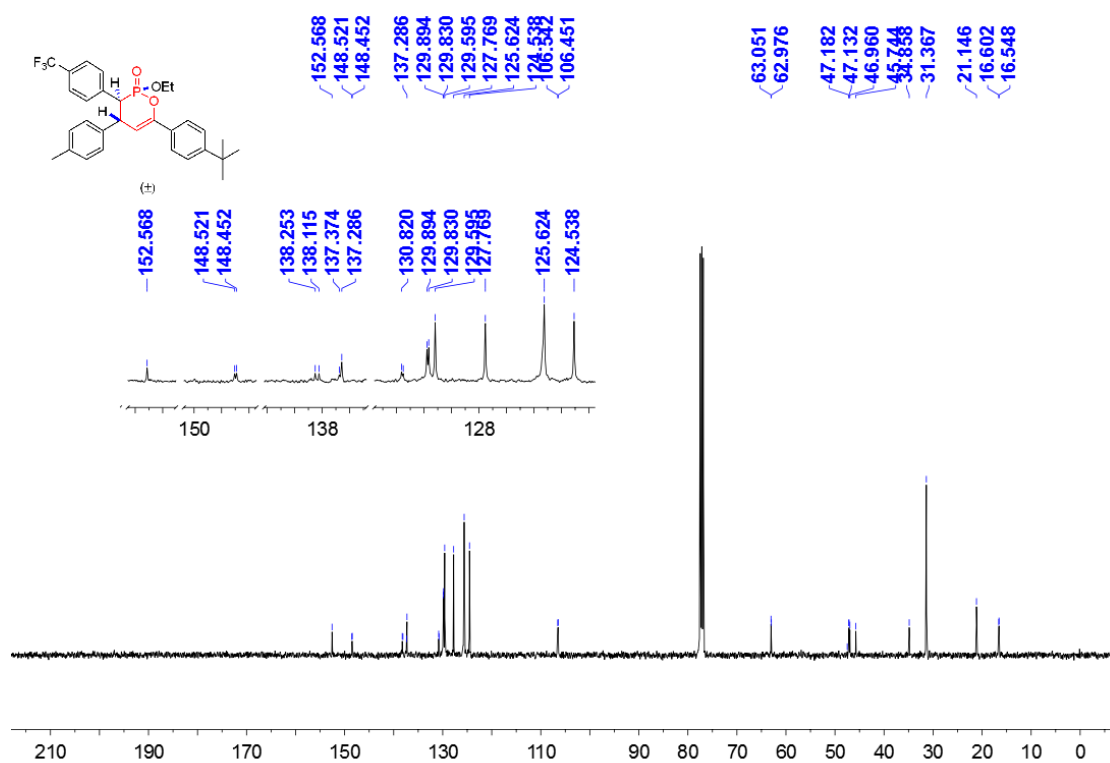
¹³C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3r**



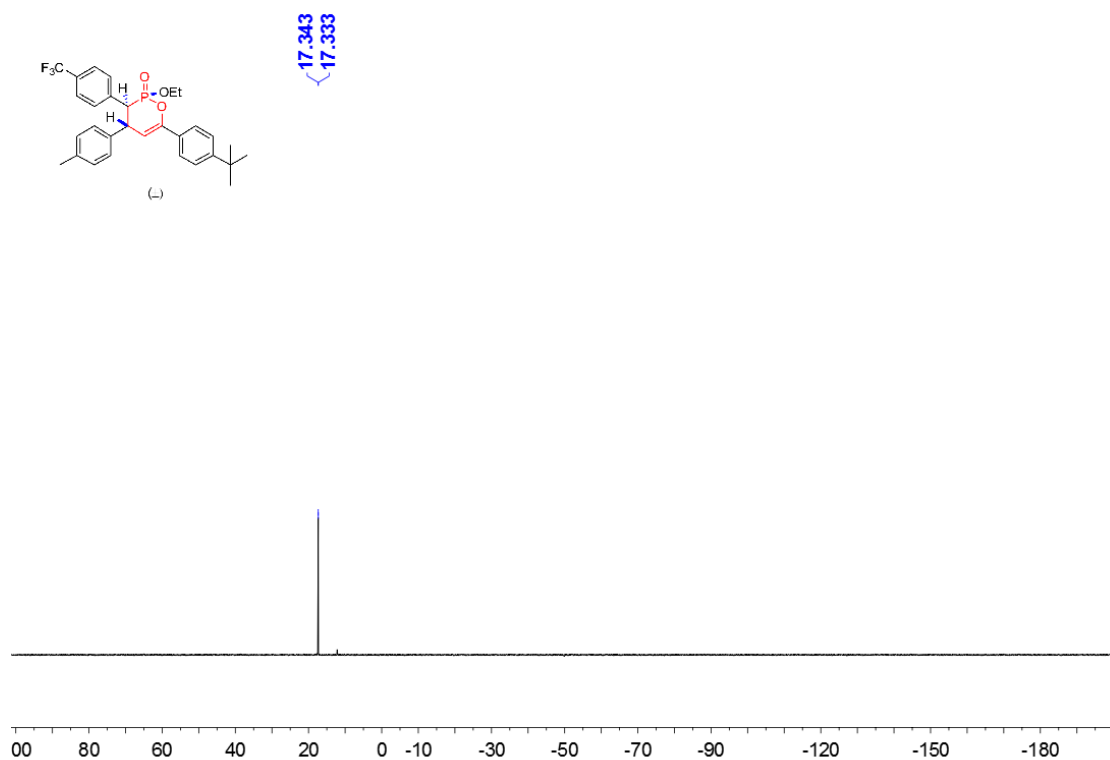
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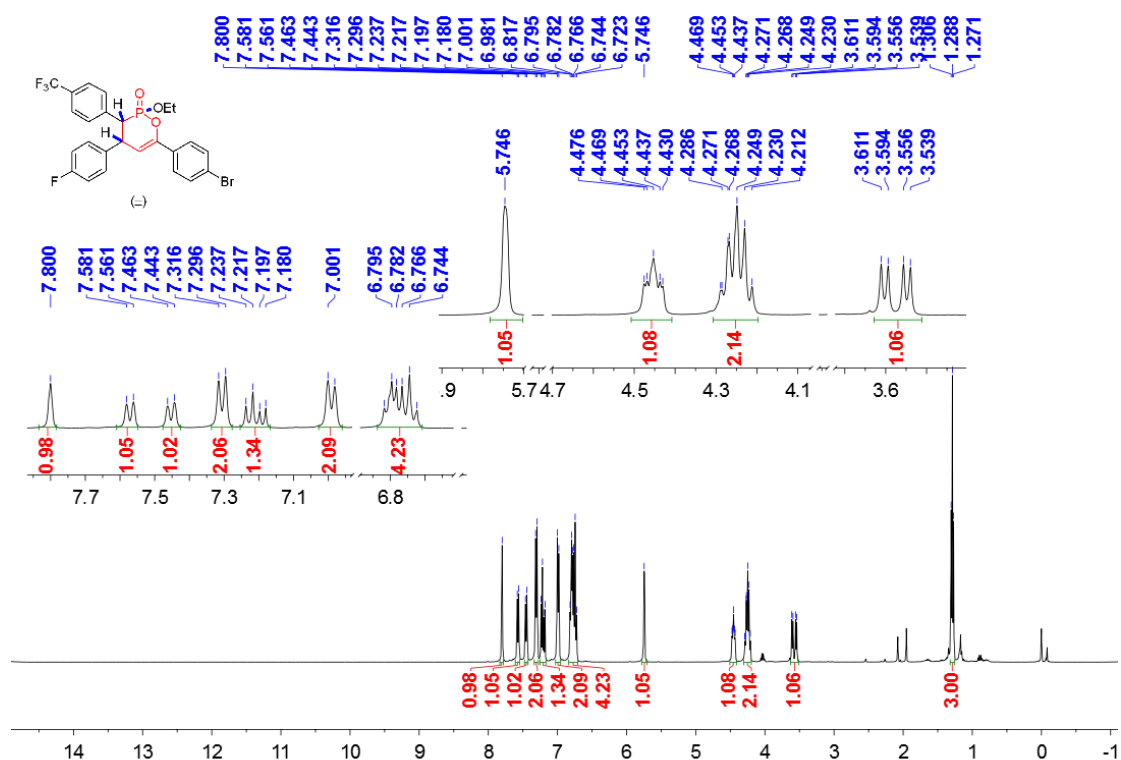
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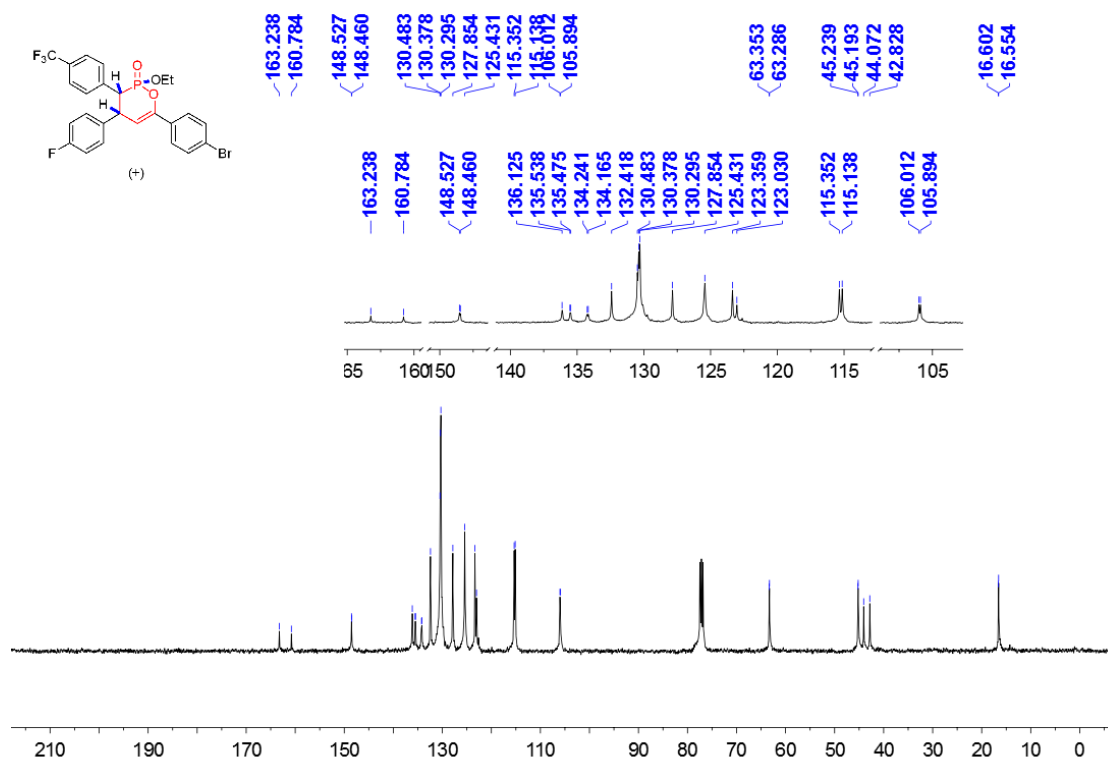
^{13}C NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3r**



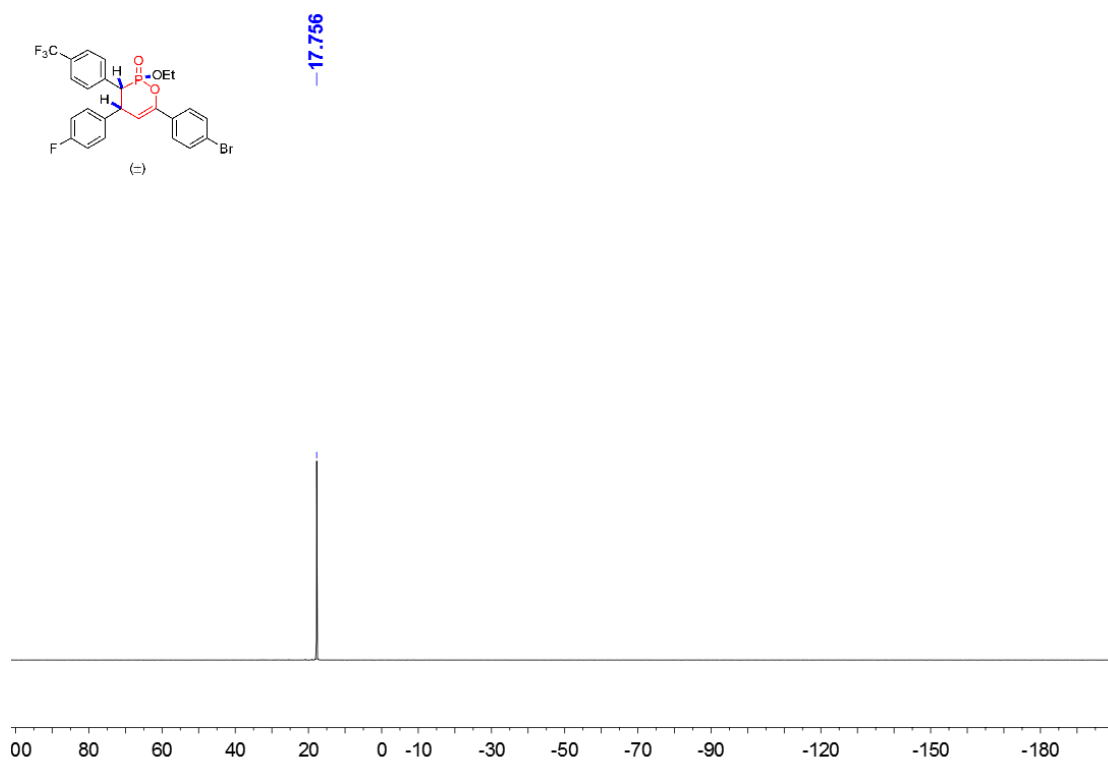
^{31}P NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3r**



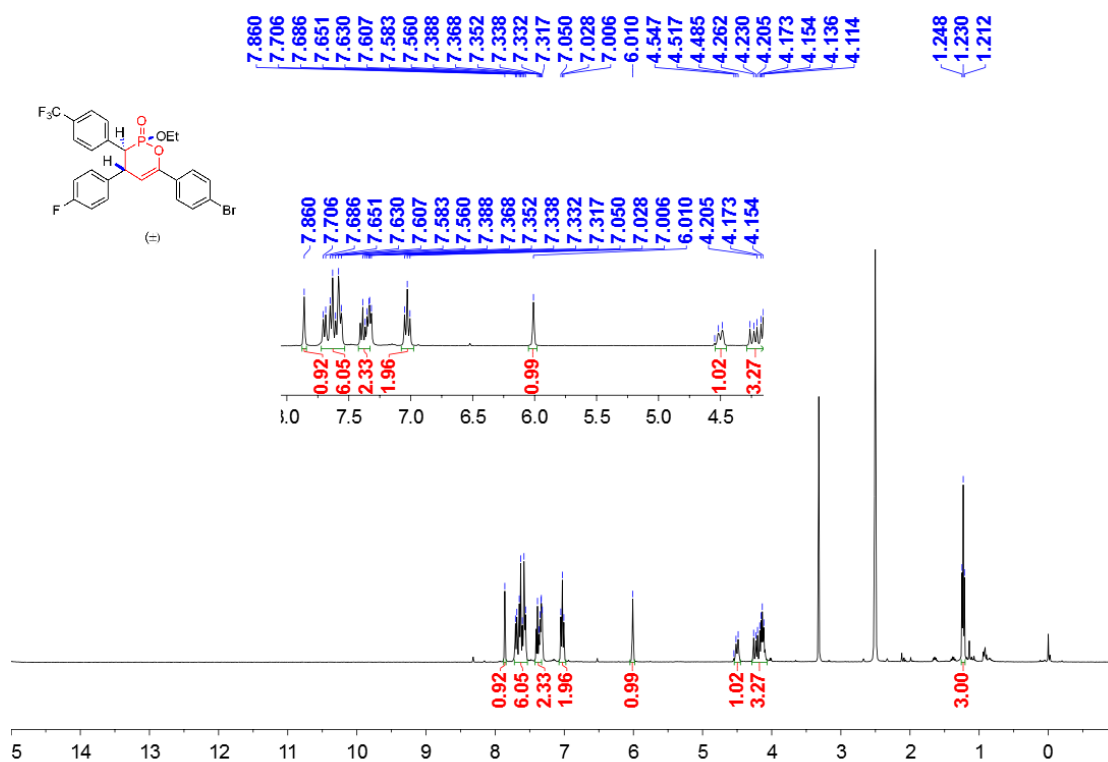
¹H NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3s**



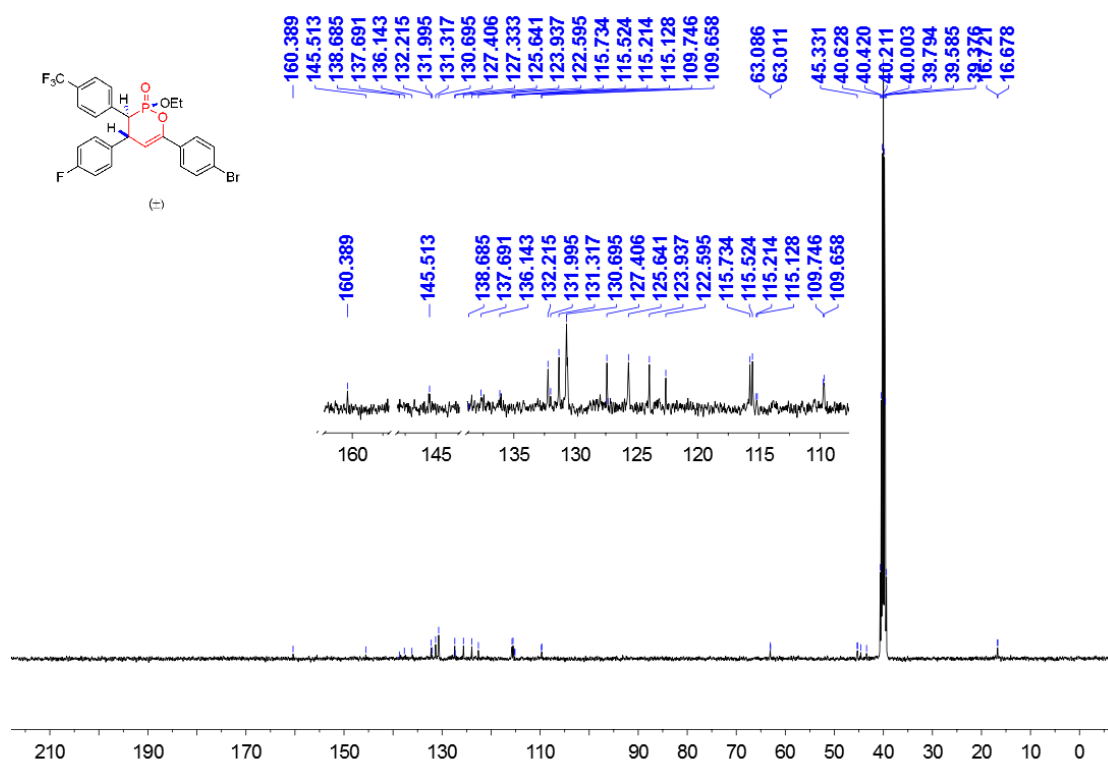
¹³C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3s**



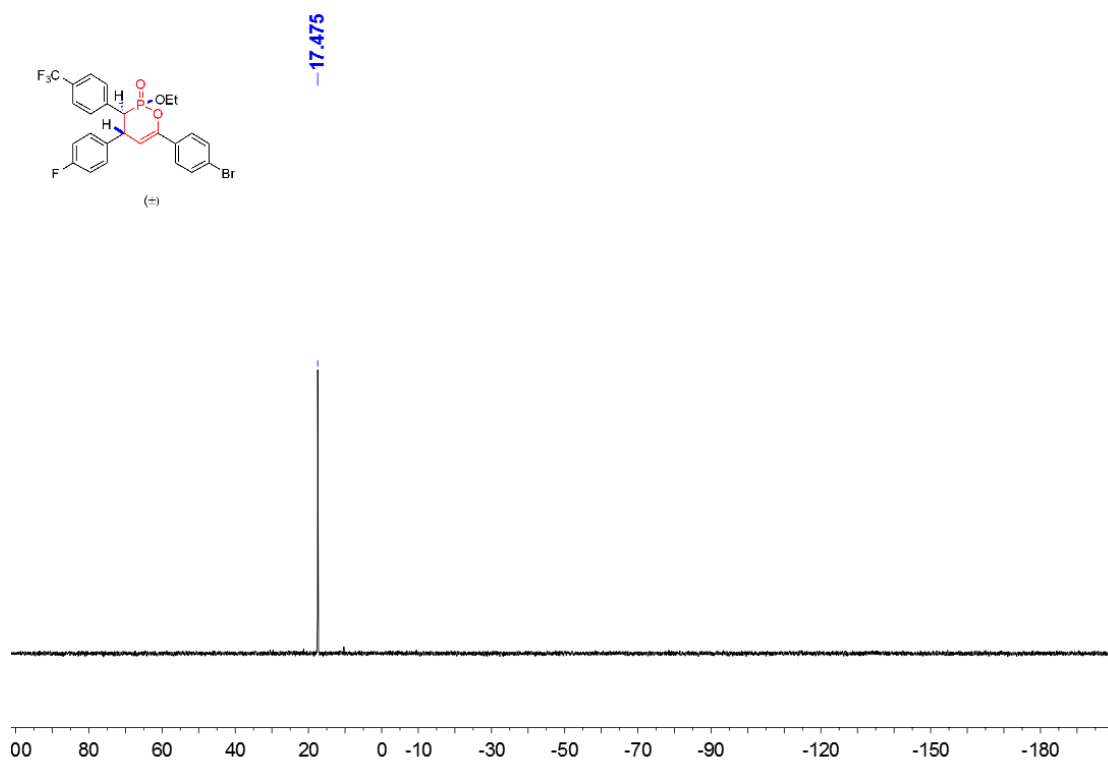
³¹P NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3s



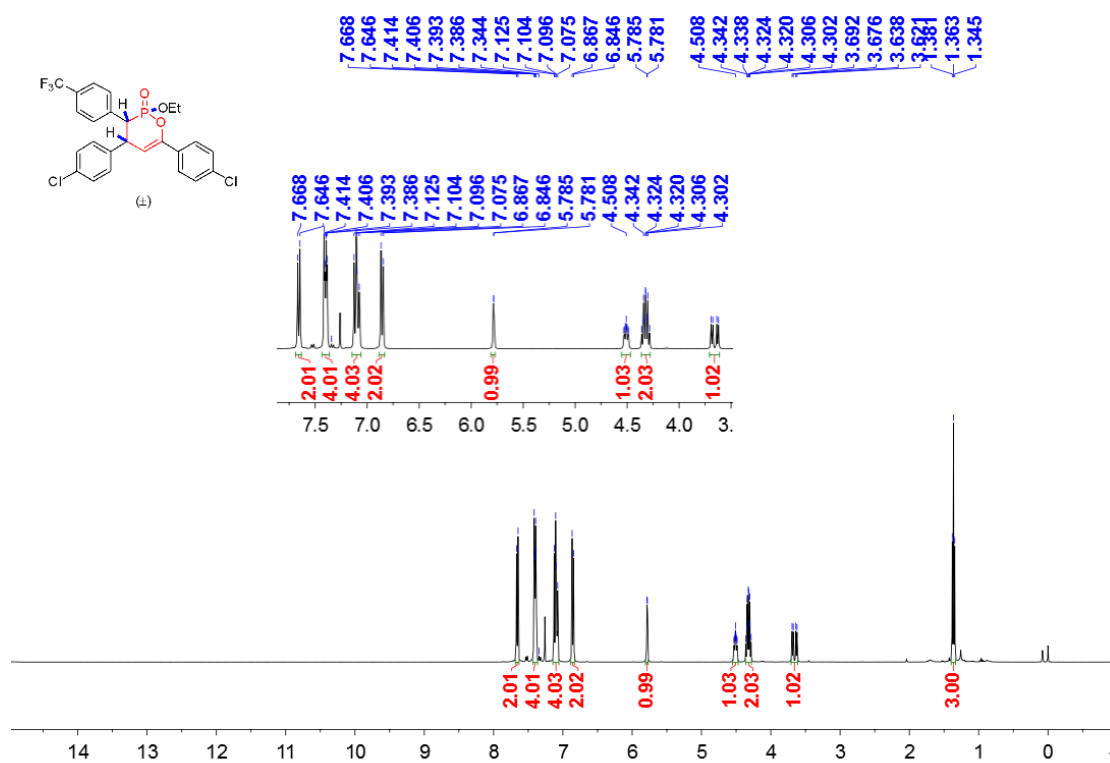
¹H NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-3s



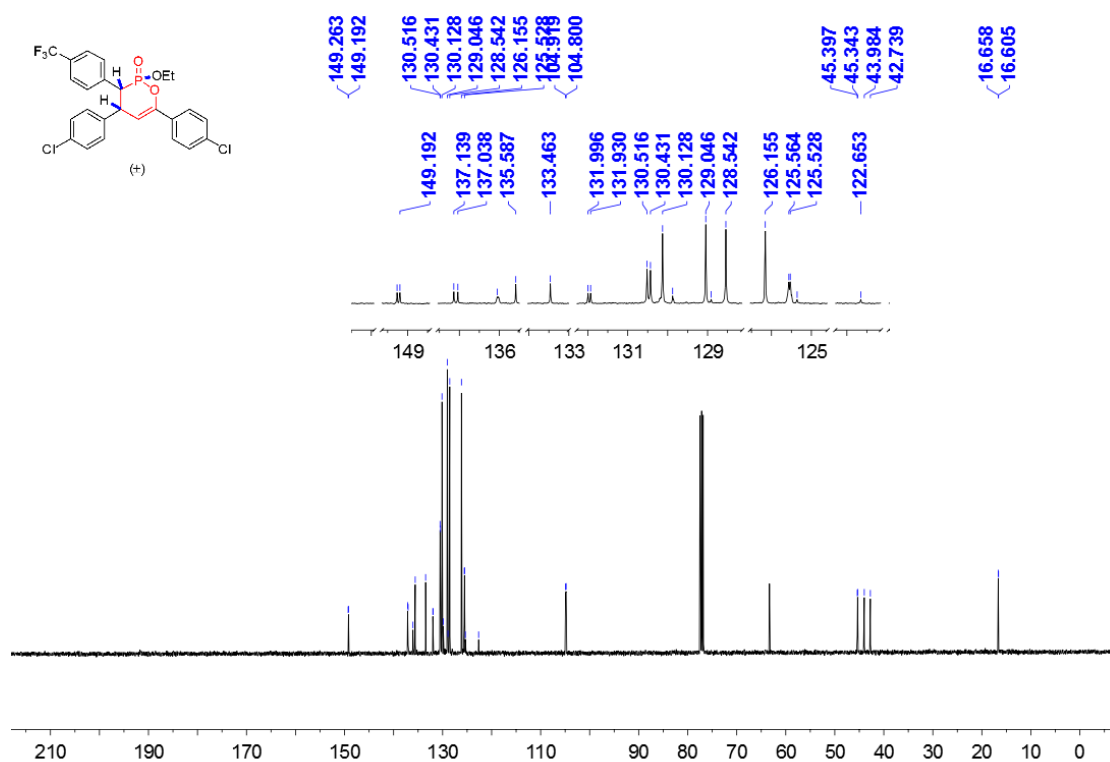
¹³C NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3s**



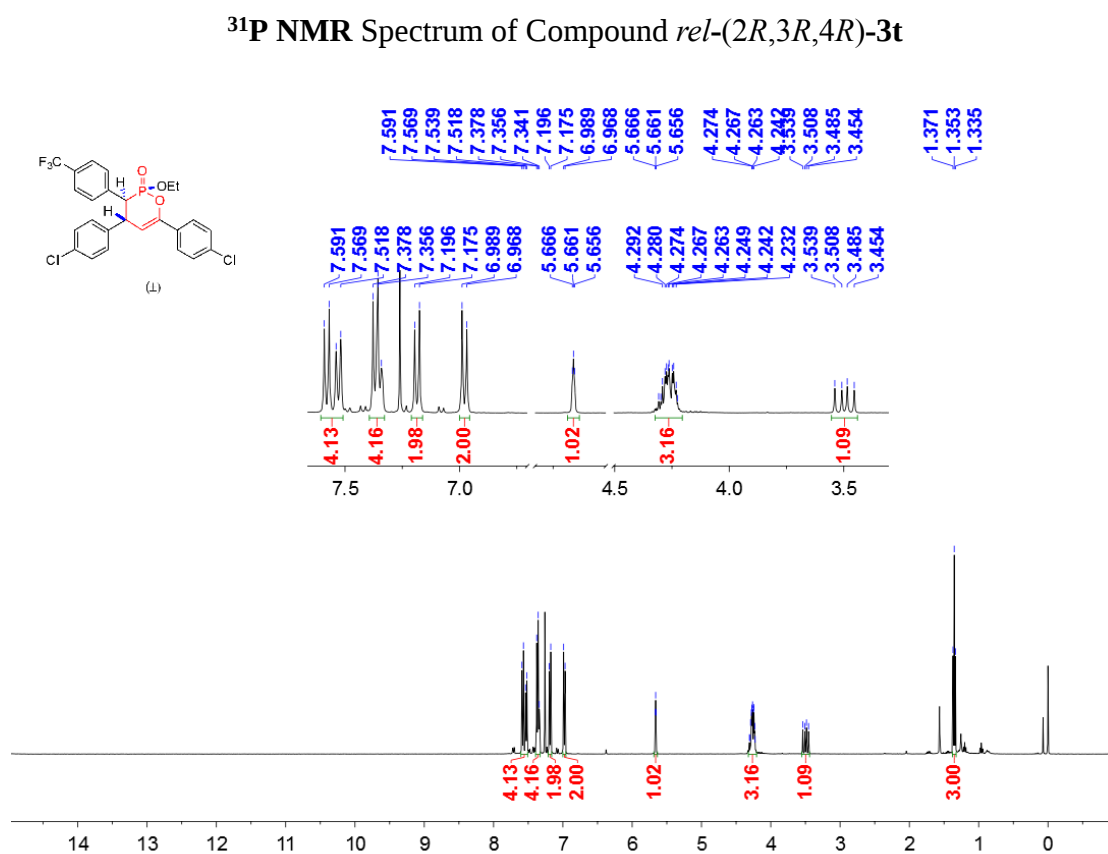
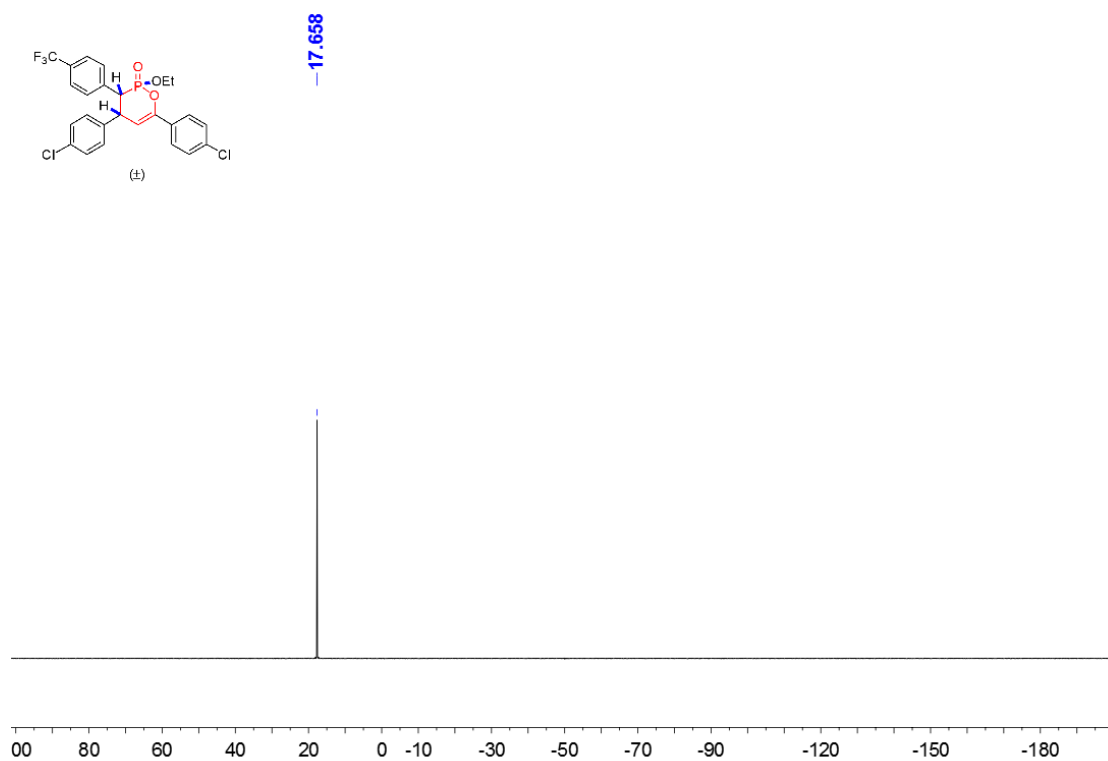
³¹P NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3s**

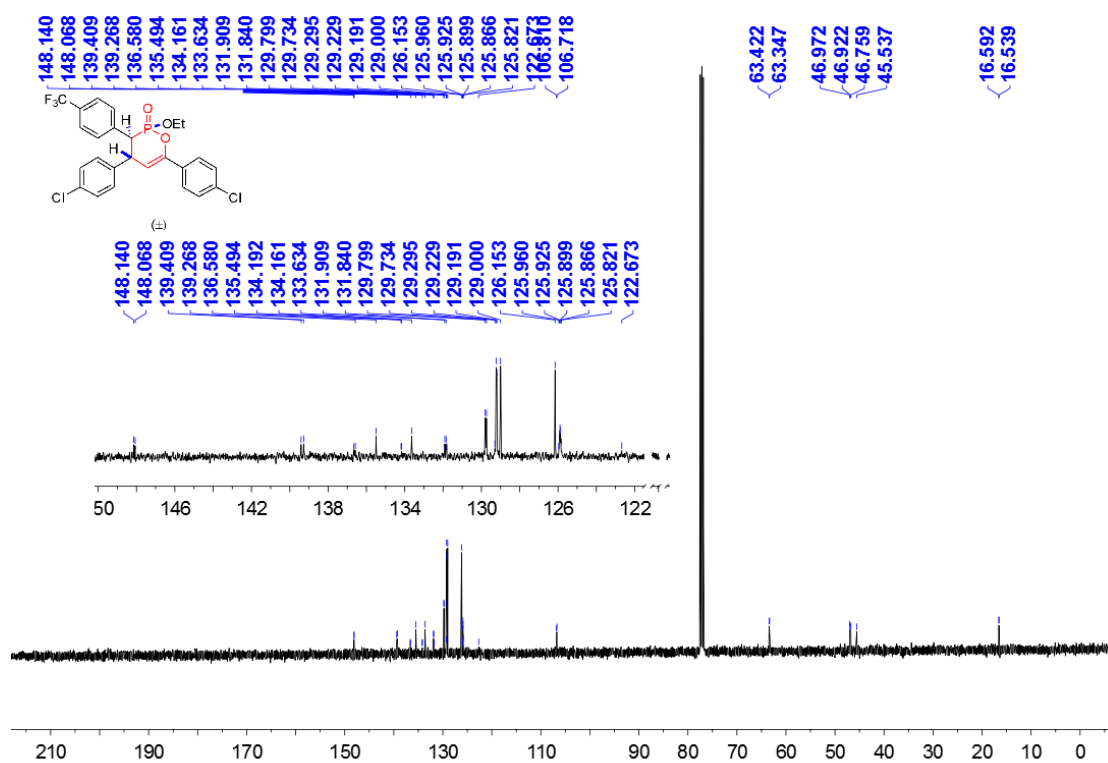


¹H NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3t**

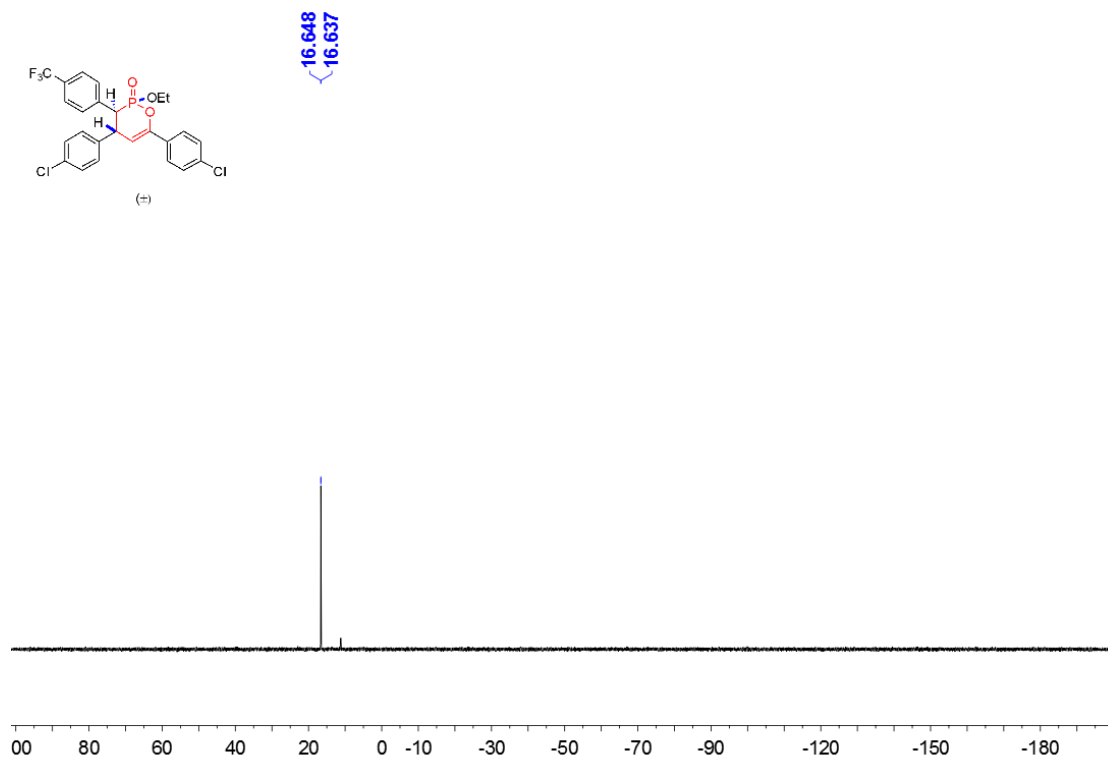


¹³C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3t**

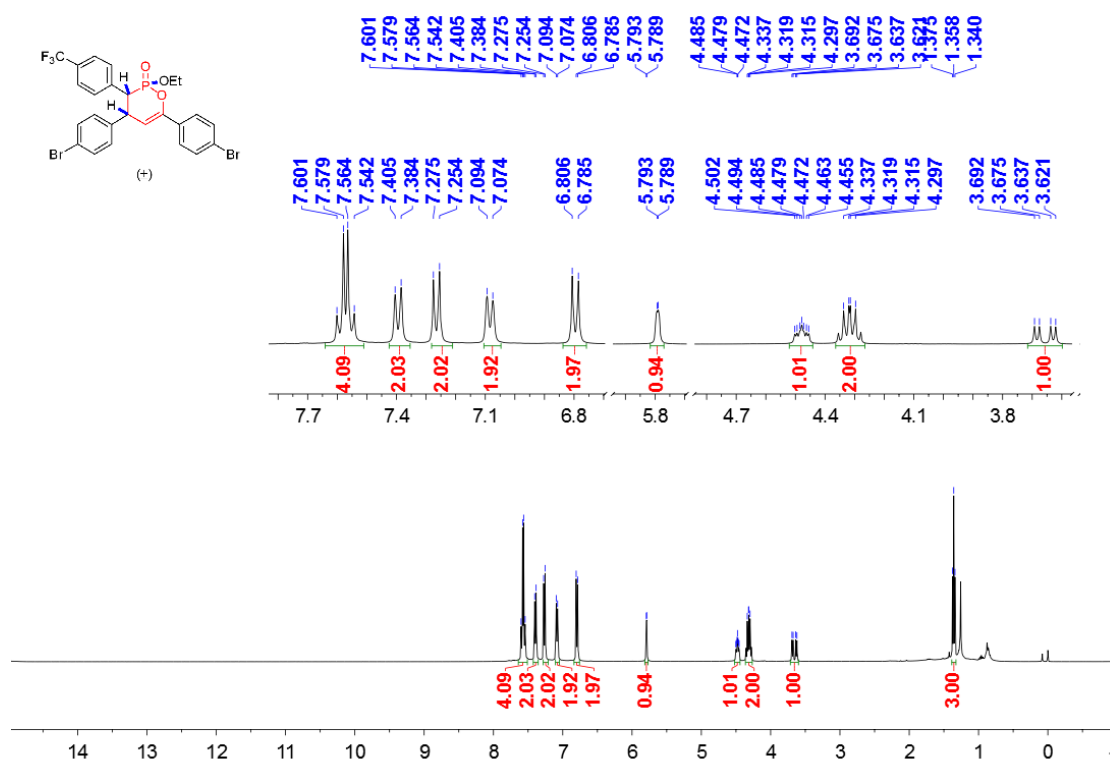




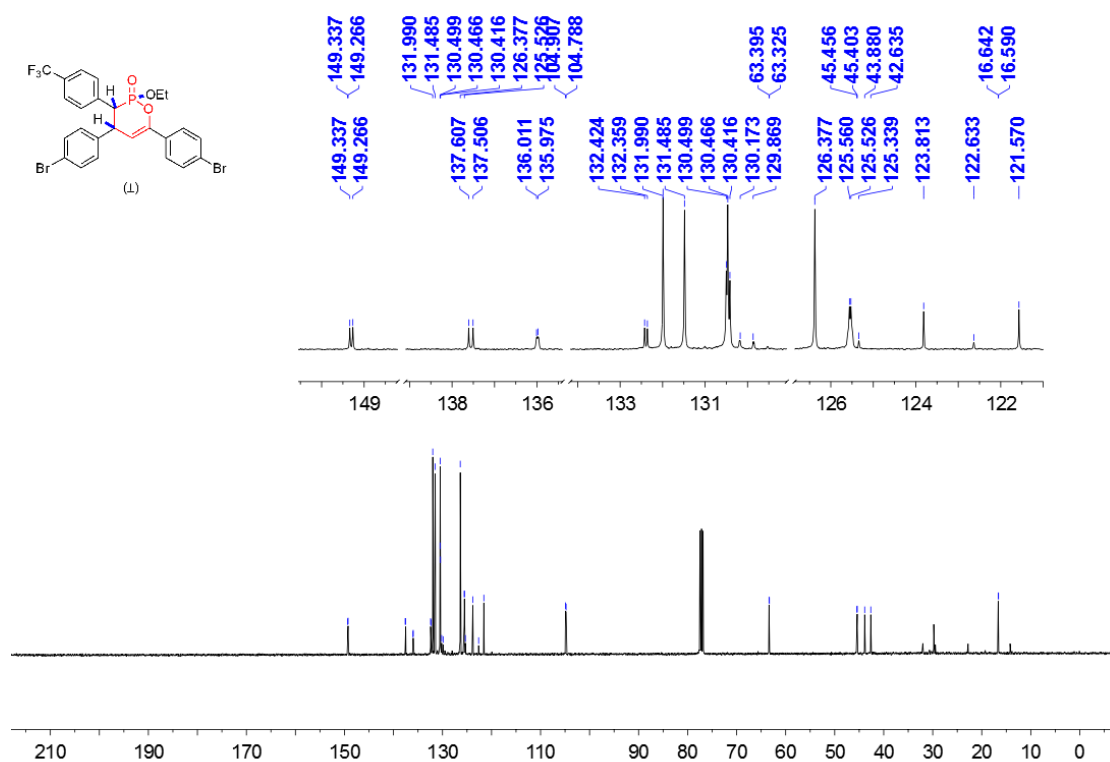
¹³C NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3t**



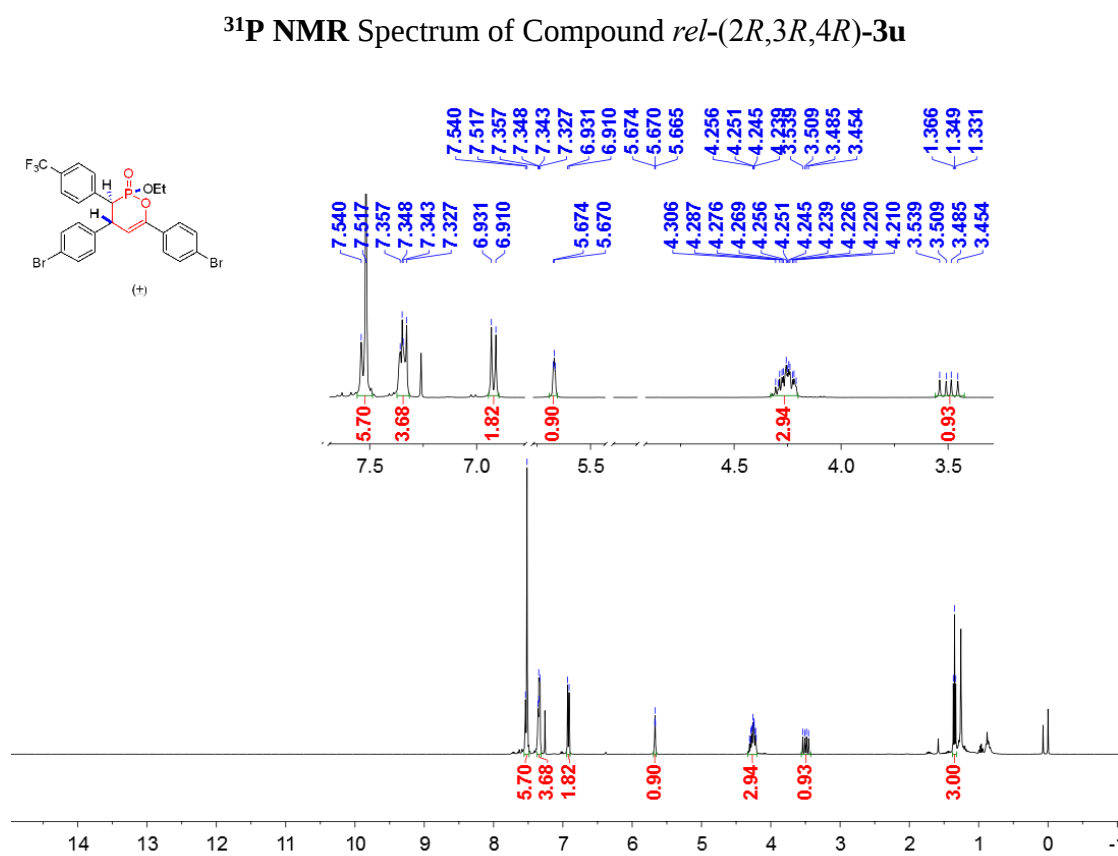
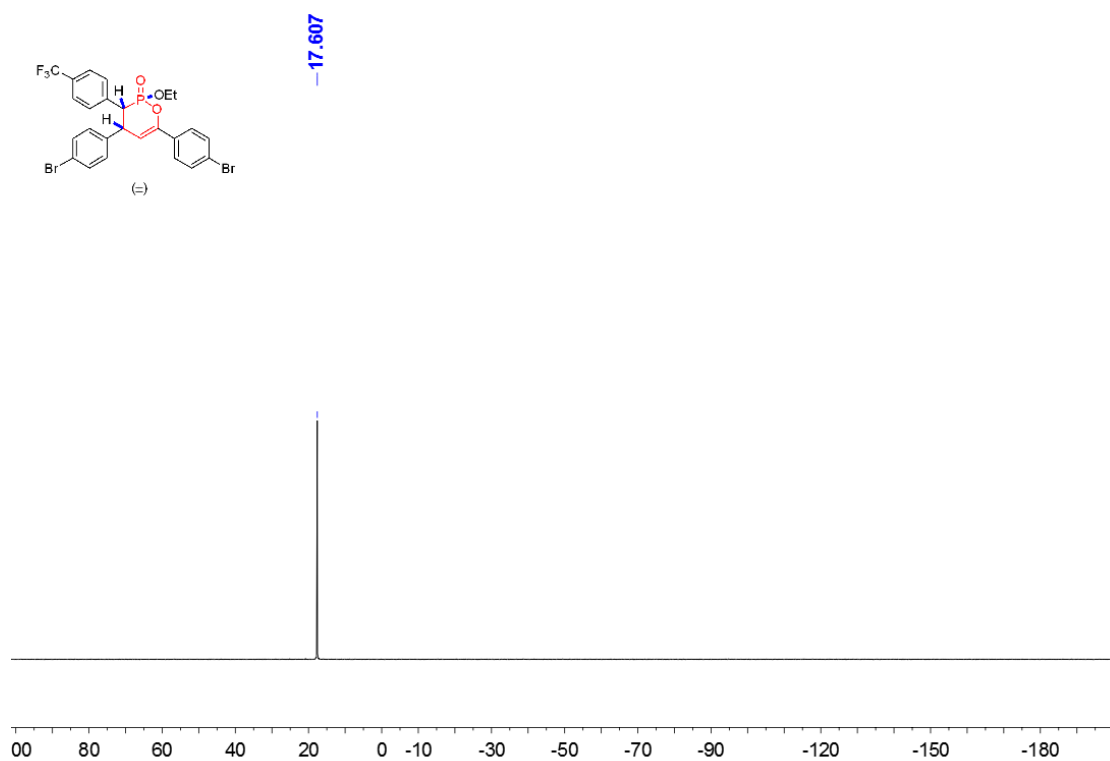
³¹P NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3t**

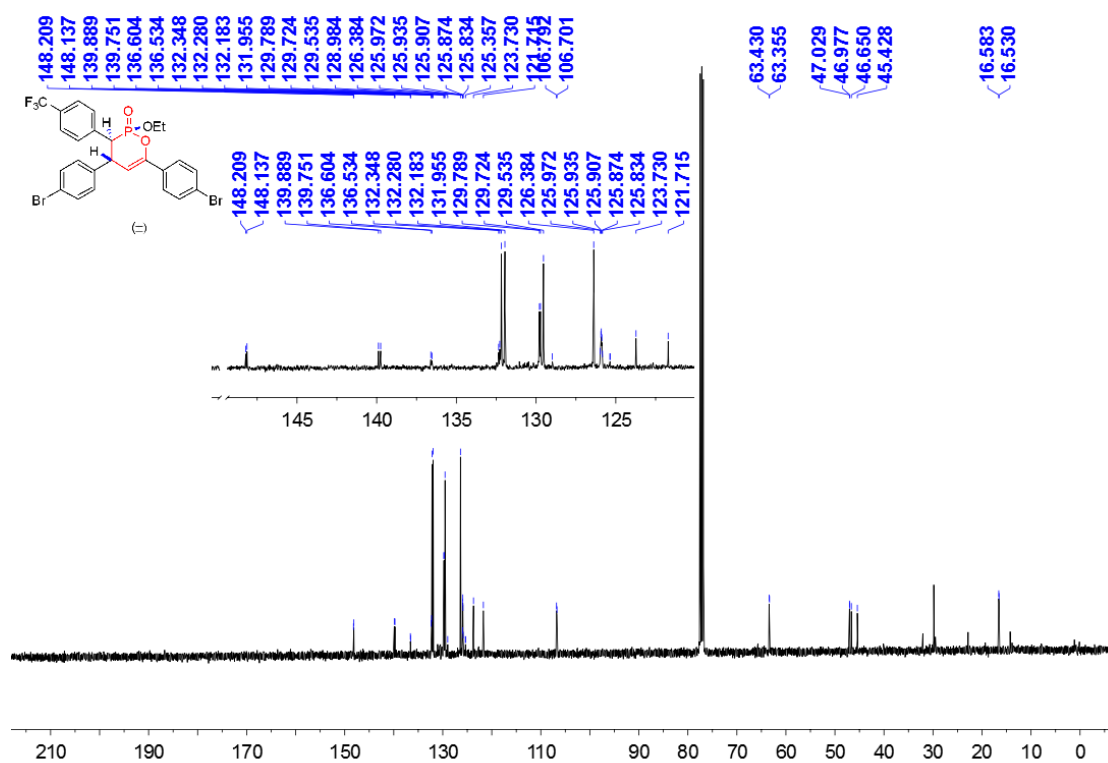


¹H NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3u

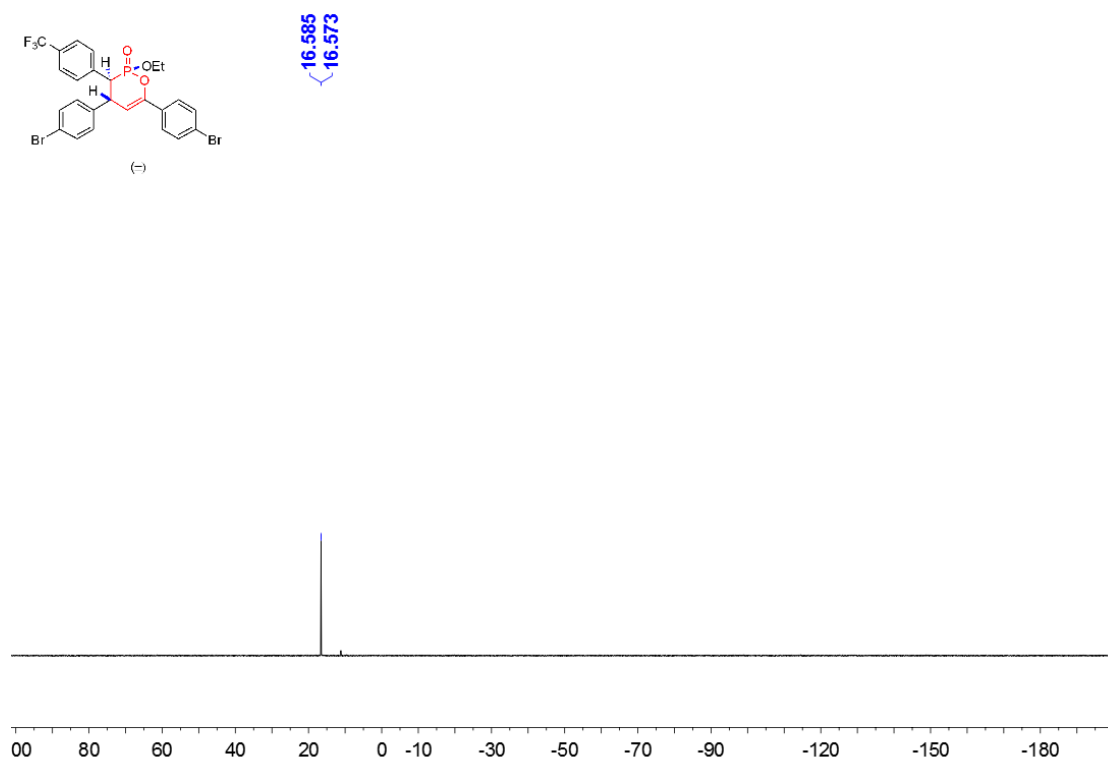


¹³C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3u

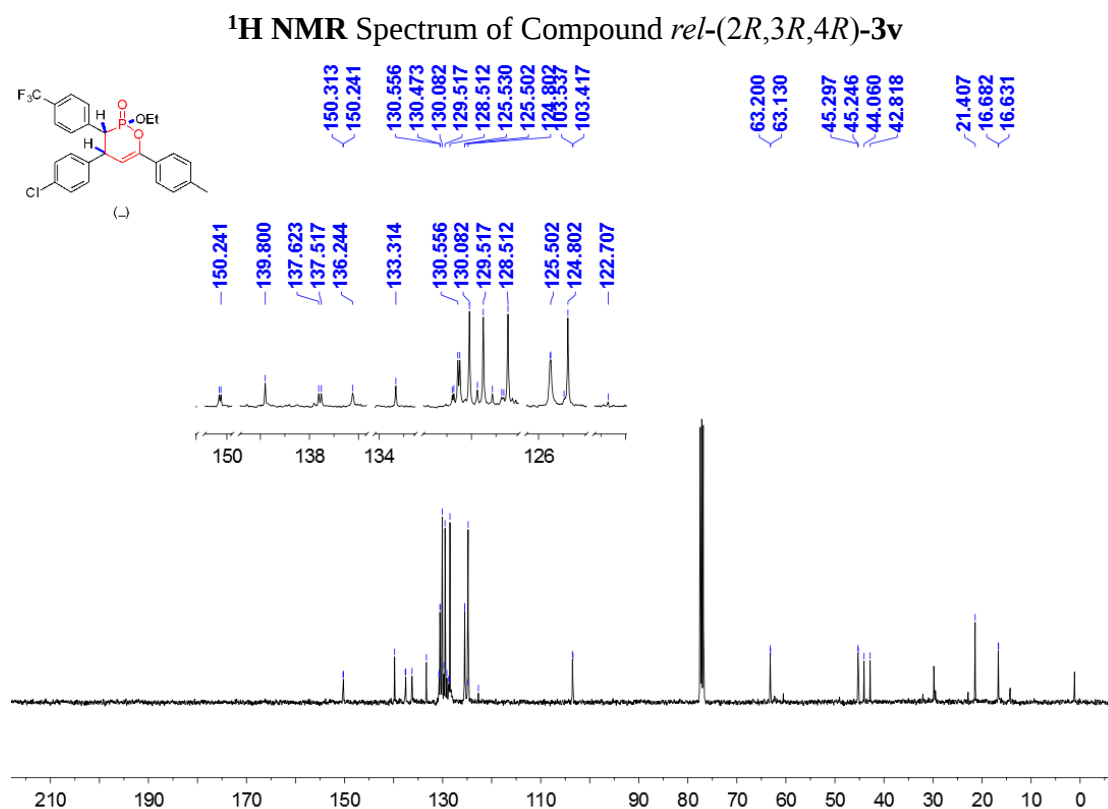
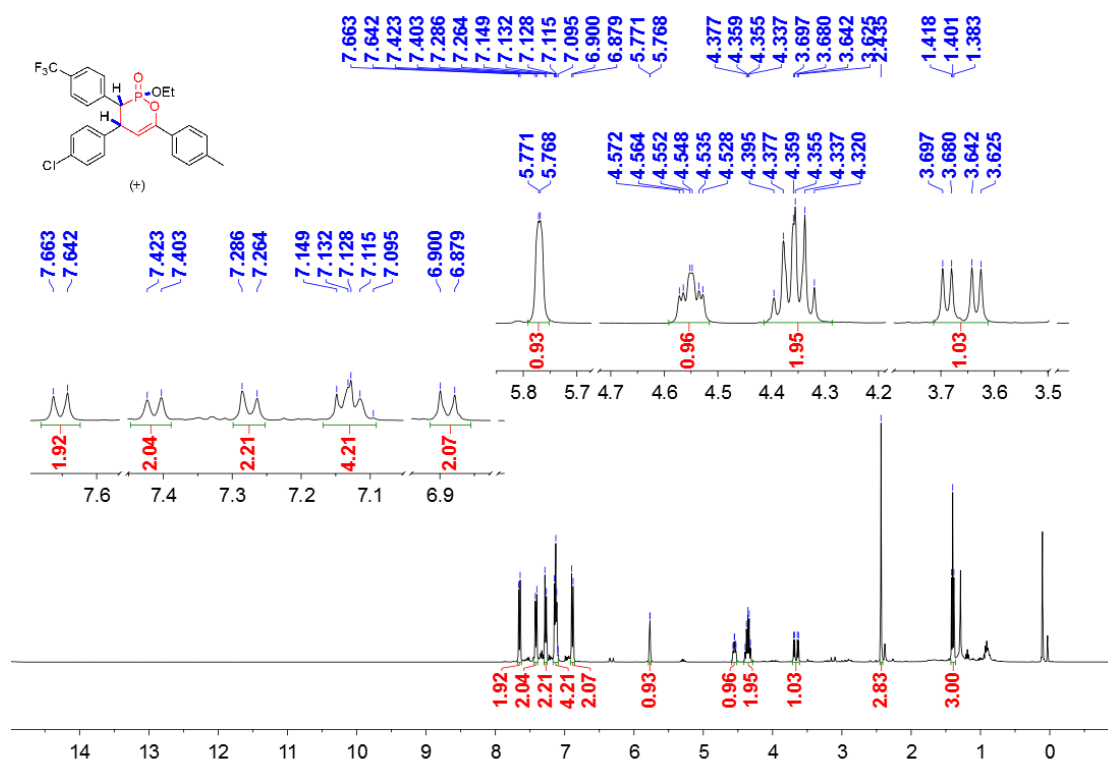


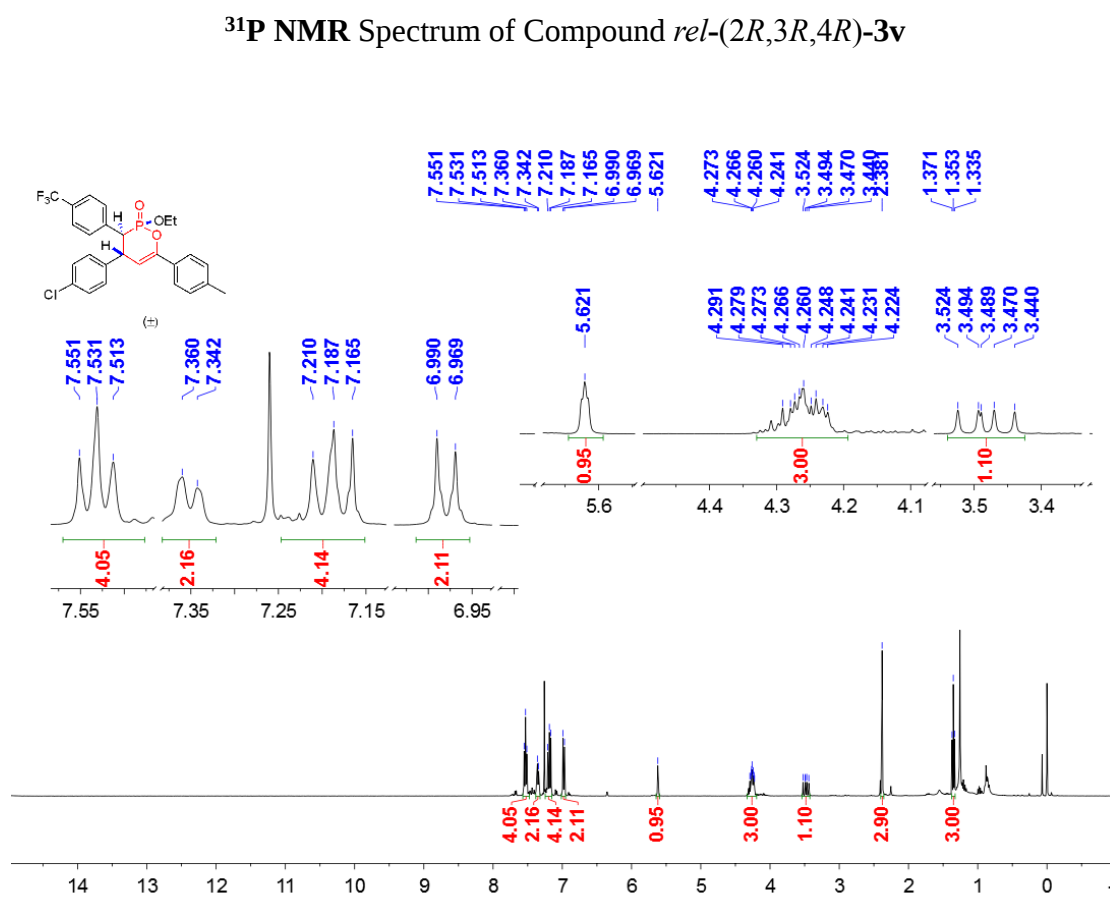
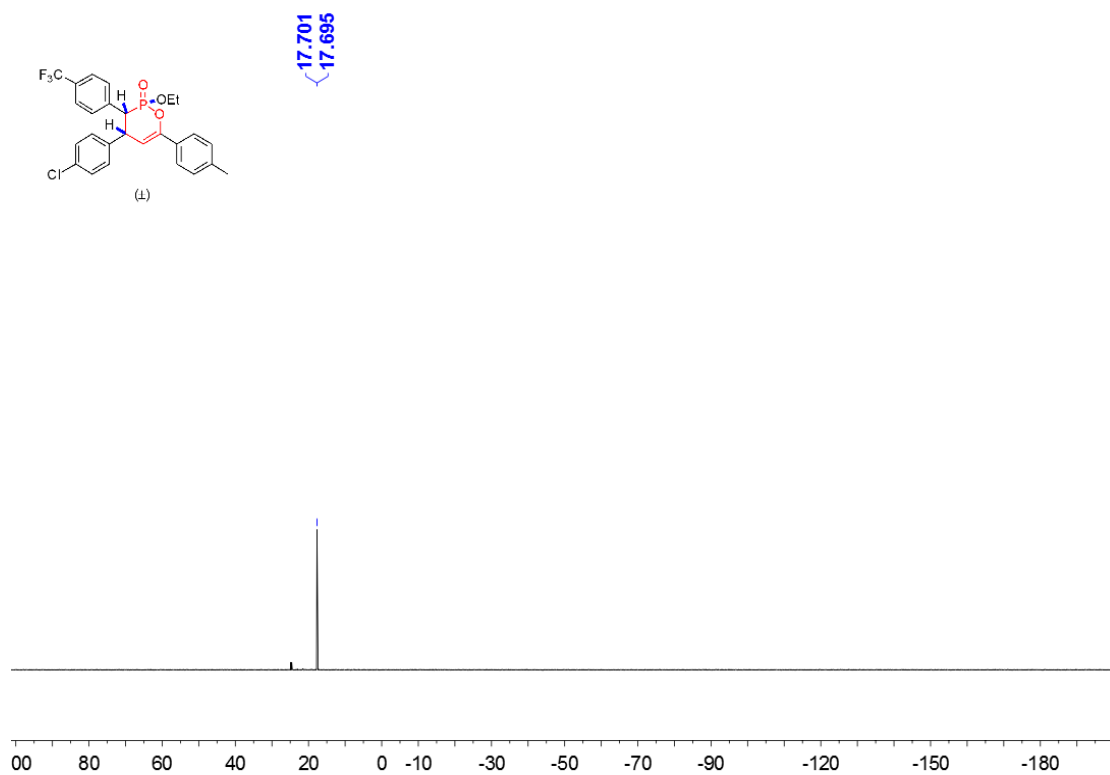


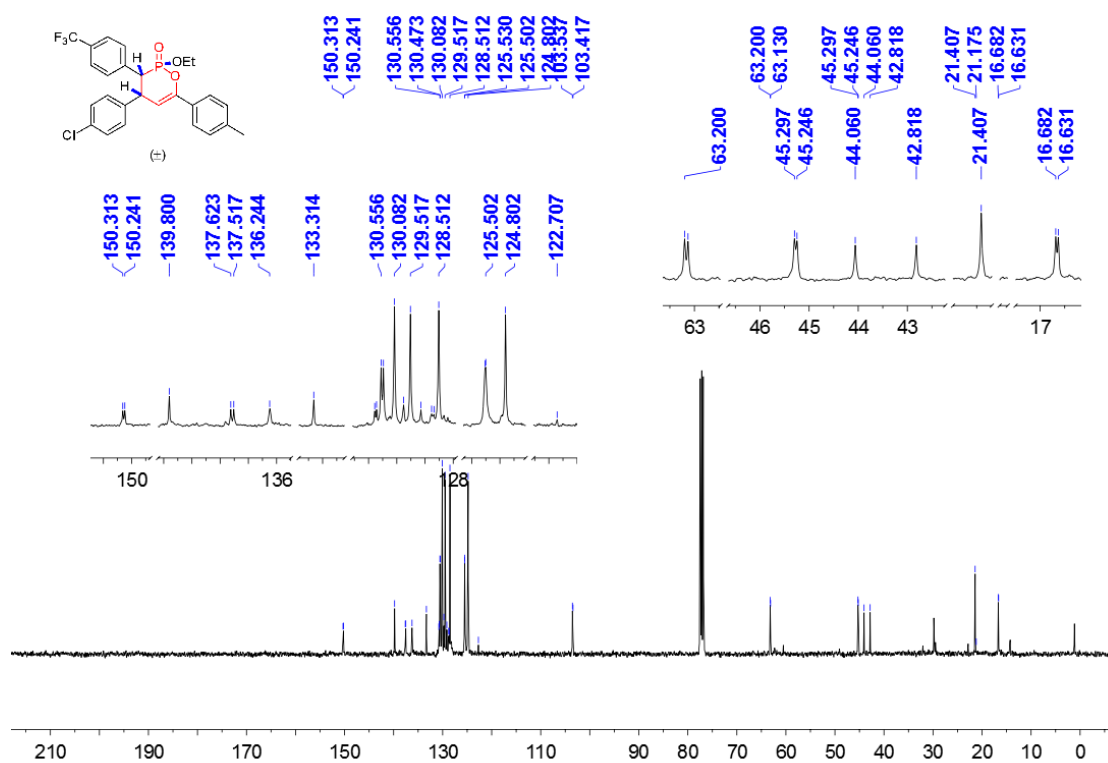
¹³C NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3u**



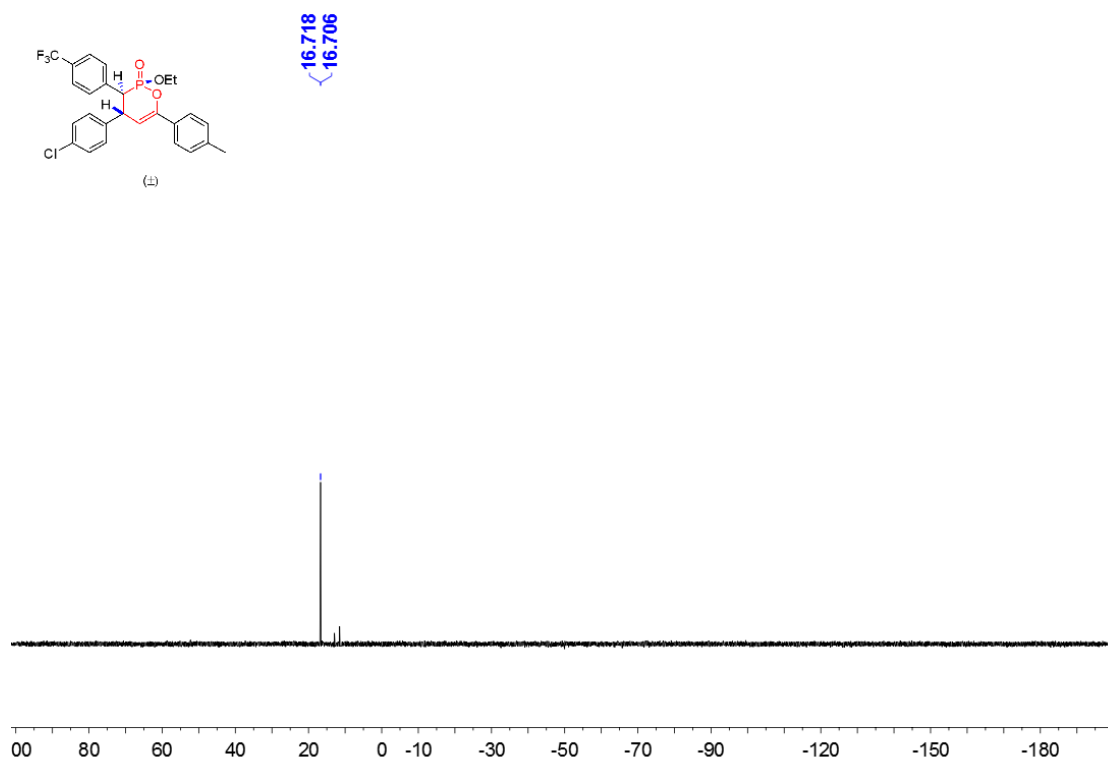
³¹P NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3u**



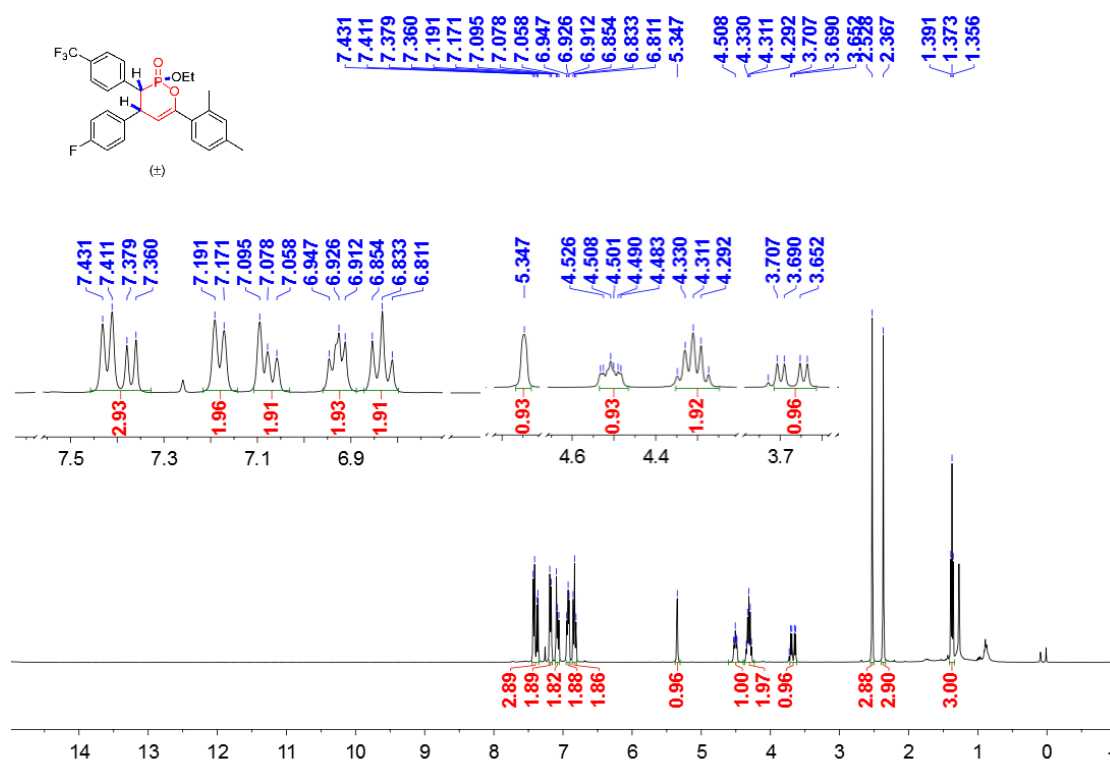




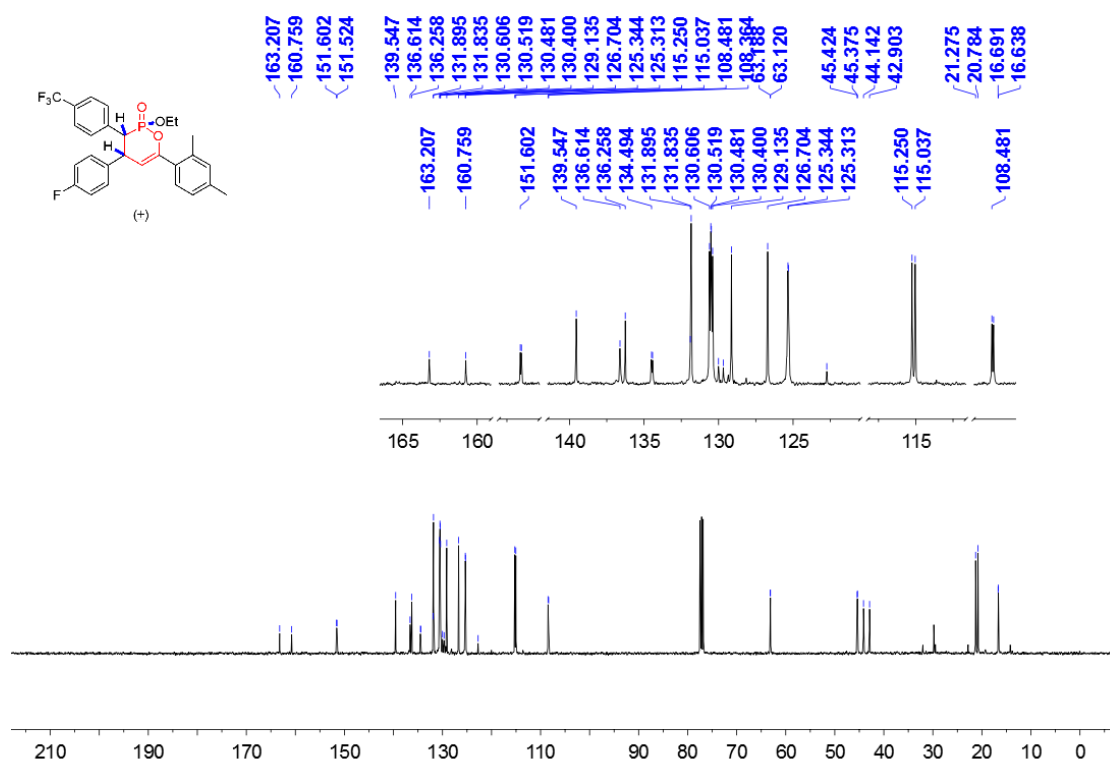
¹³C NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3v**



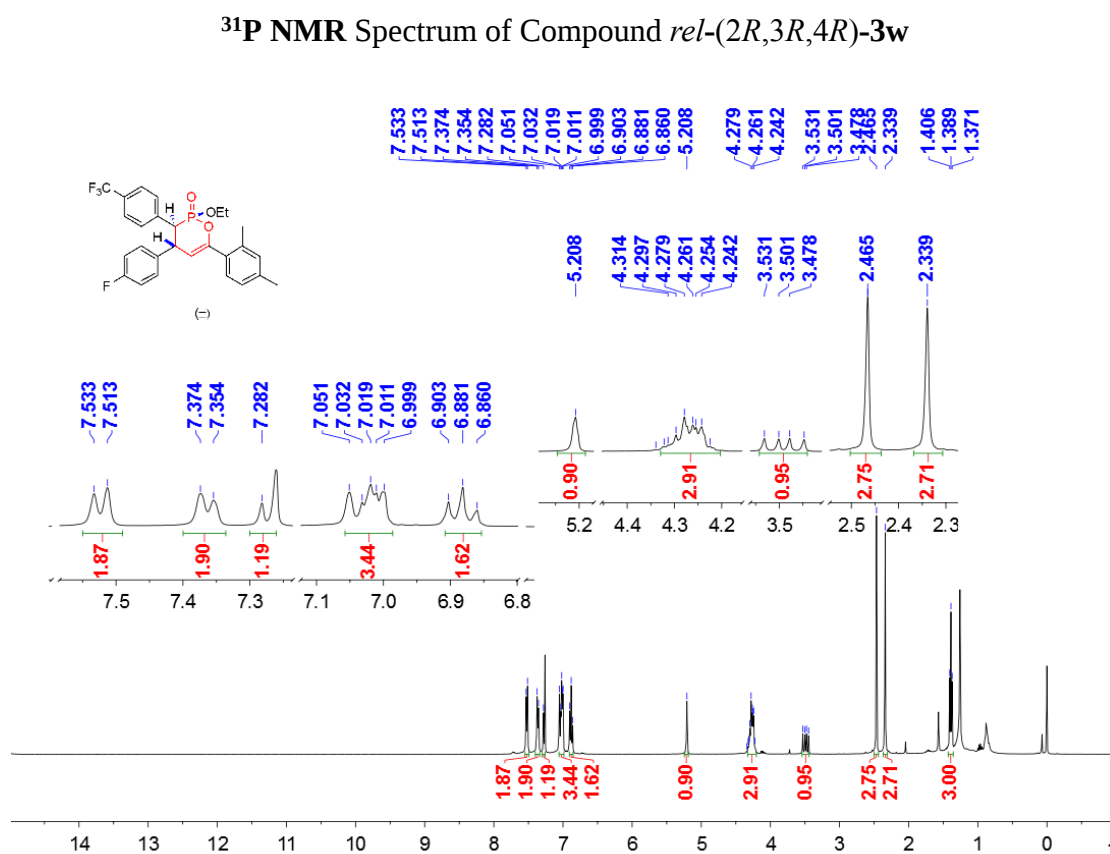
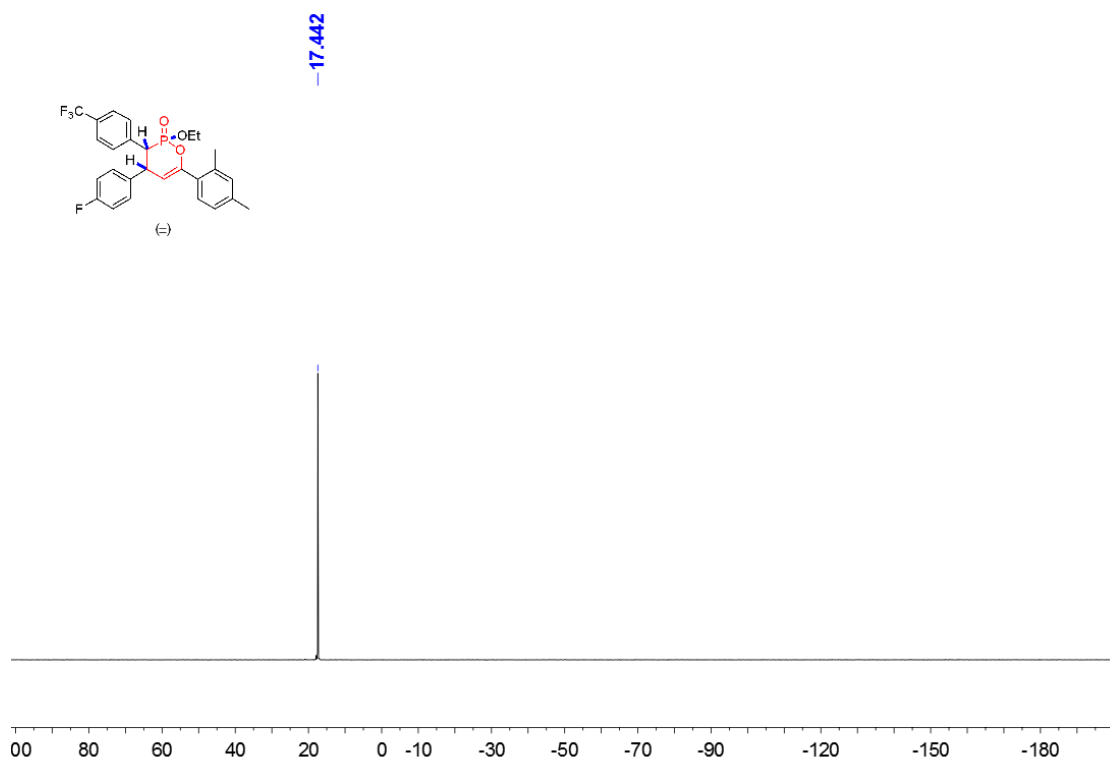
³¹P NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3v**

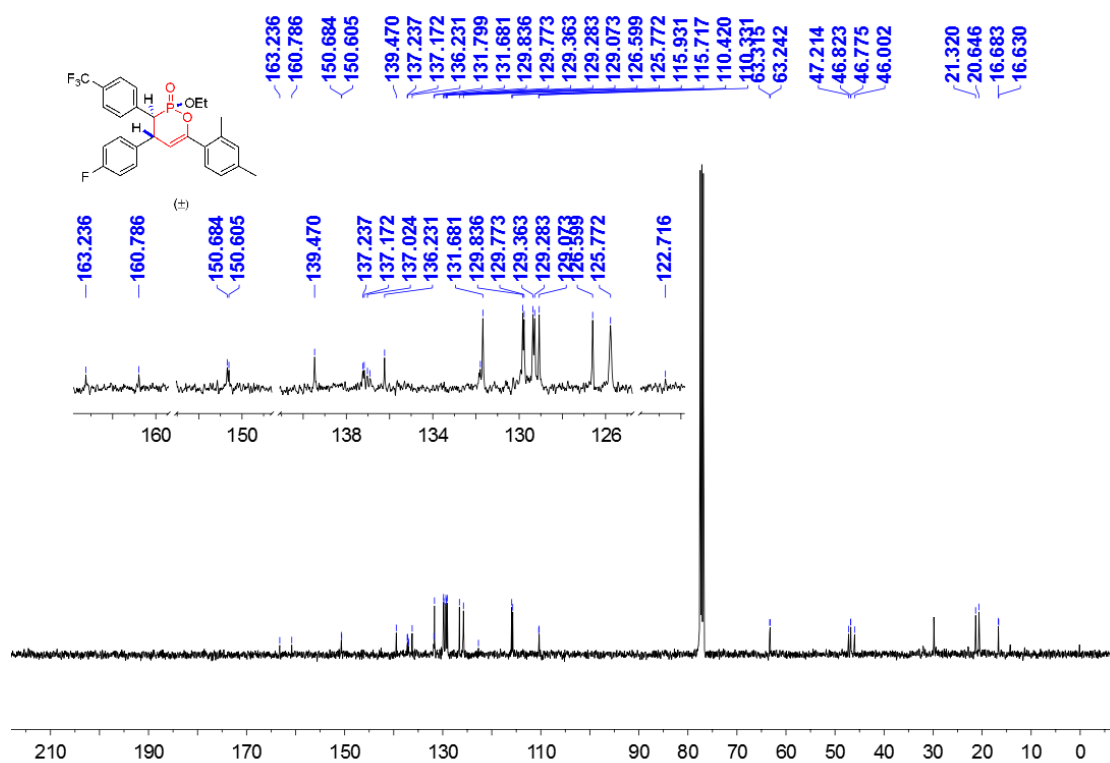


¹H NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3w

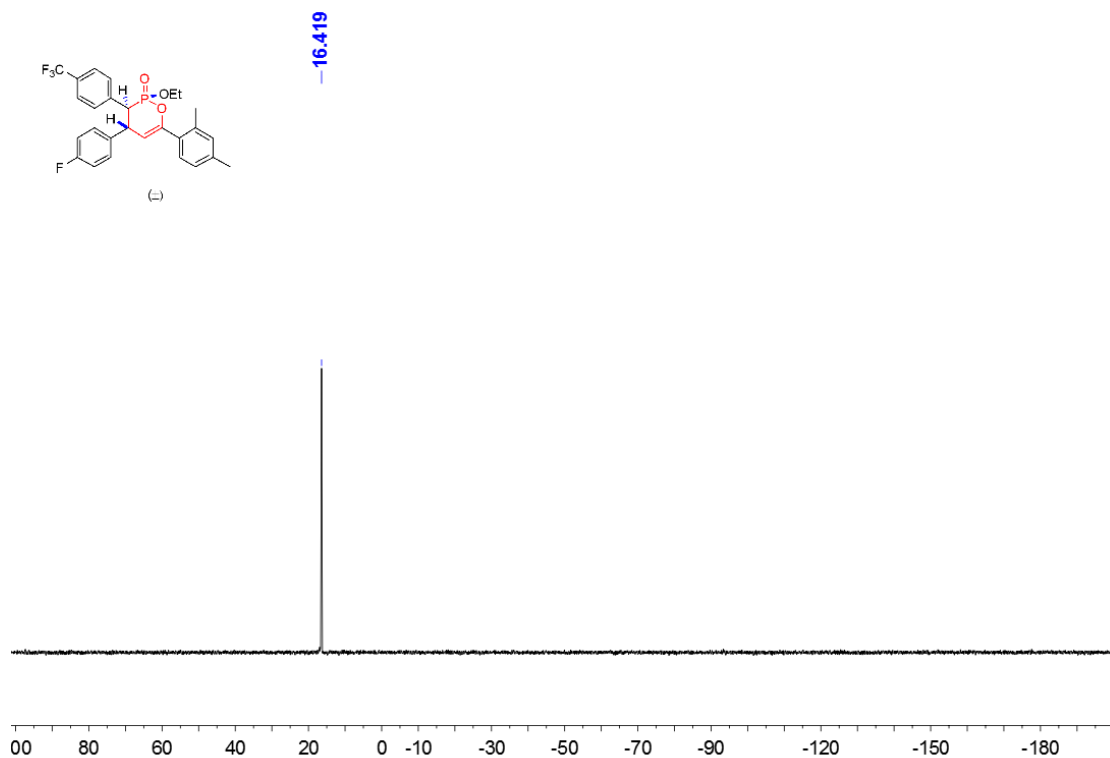


¹³C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3w

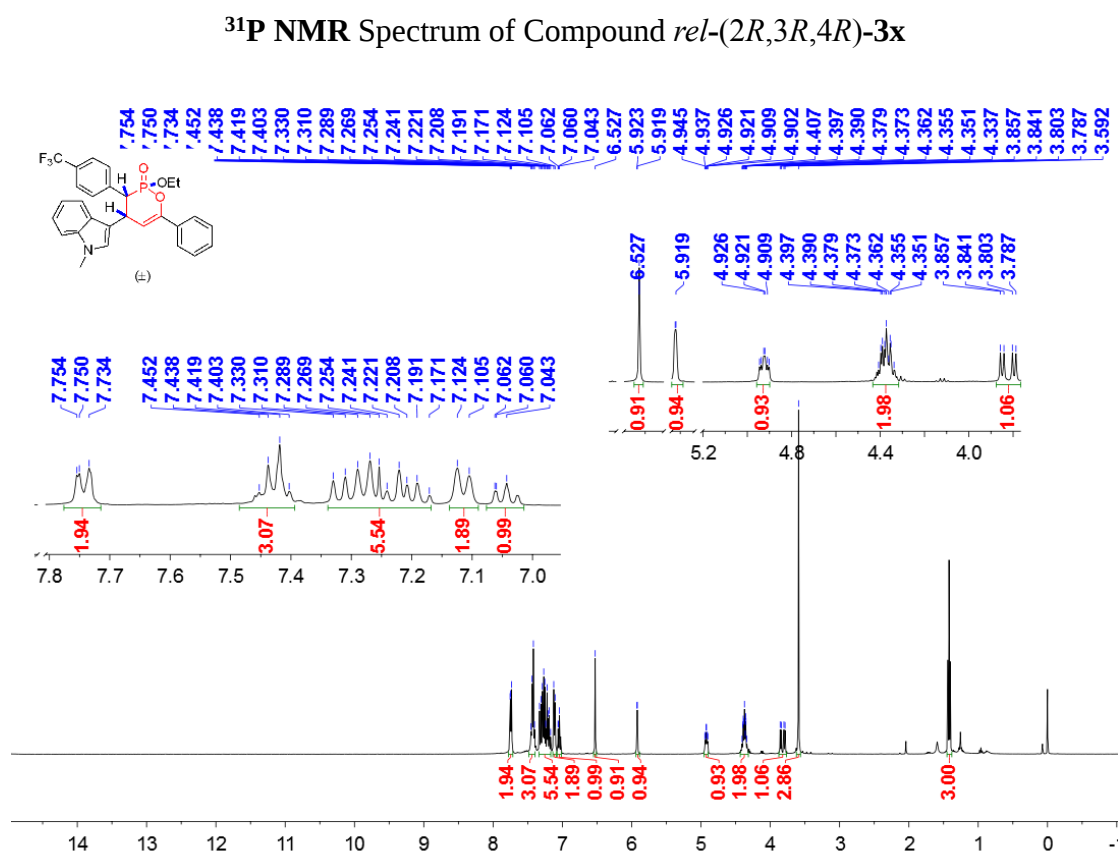
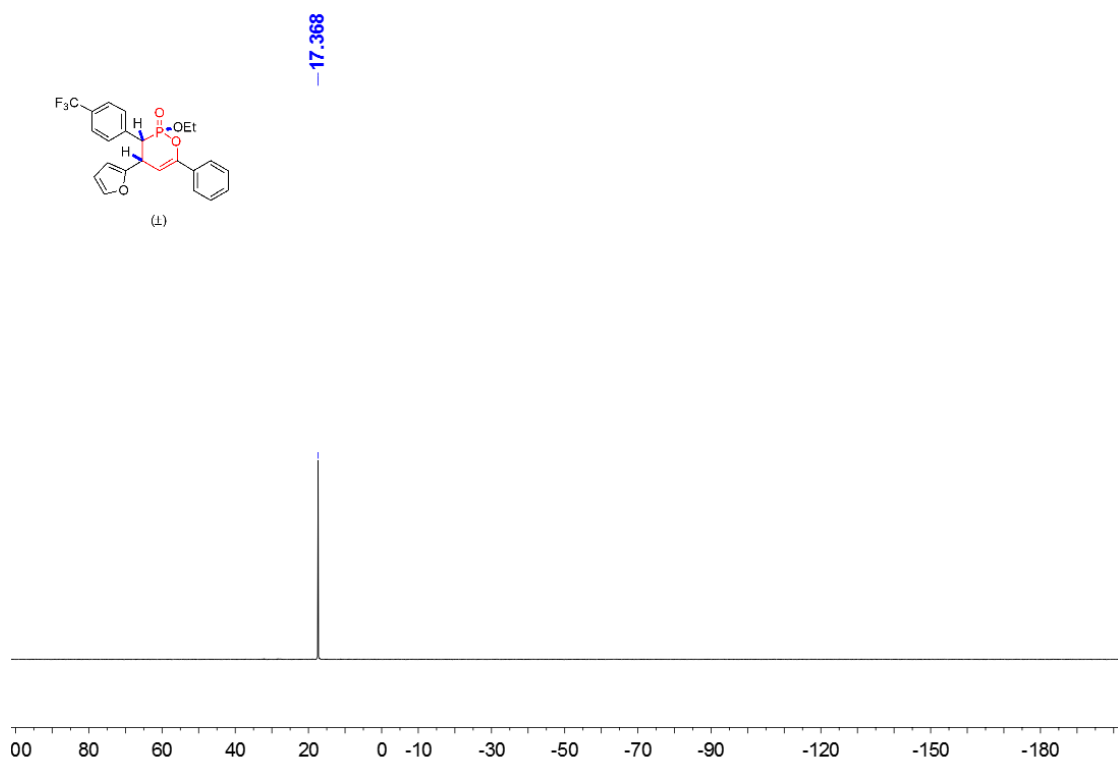


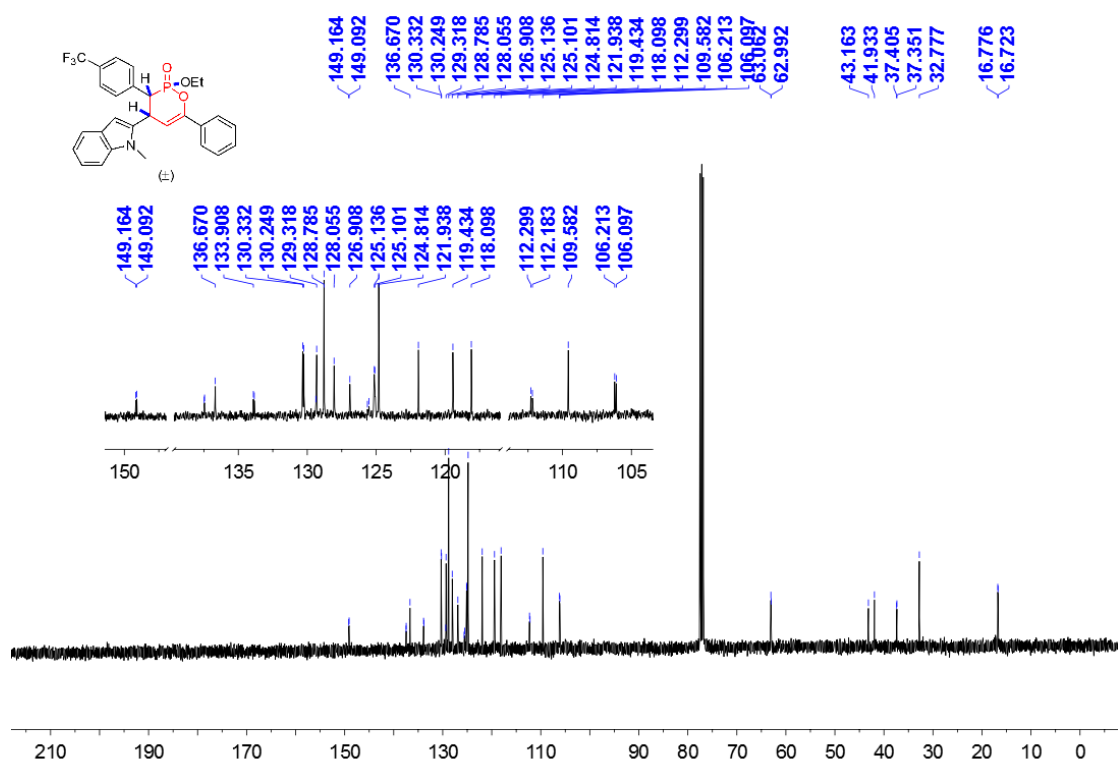


¹³C NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3w**

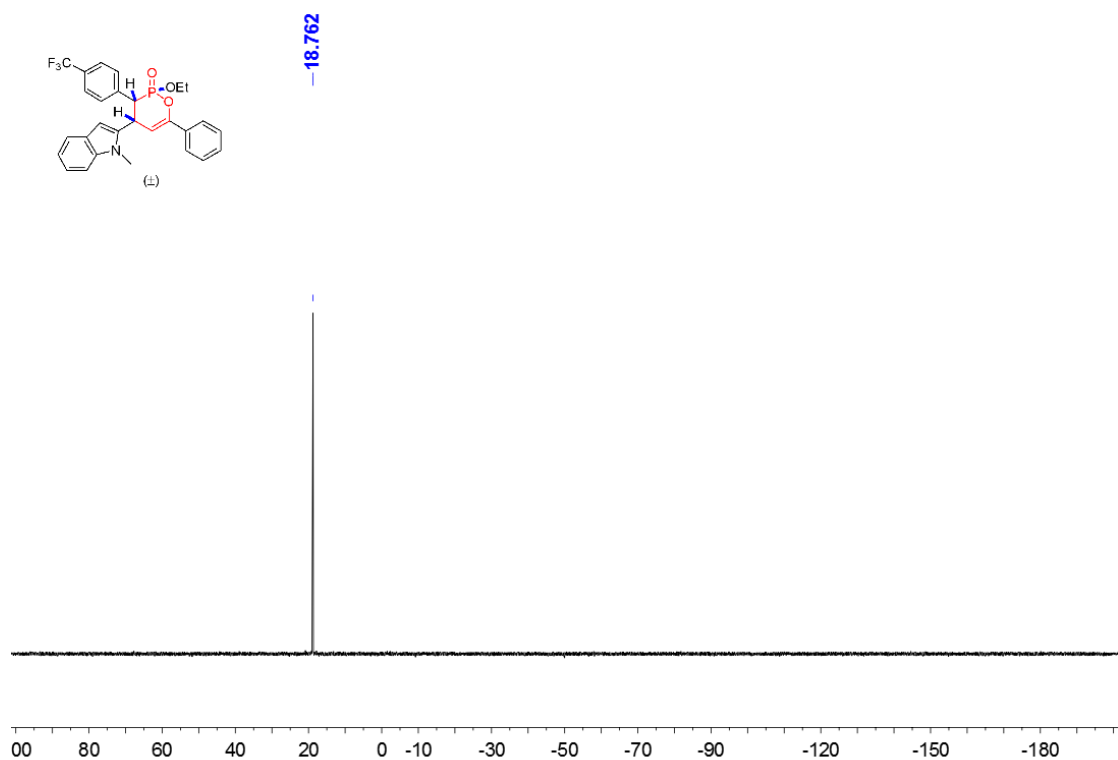


³¹P NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3w**

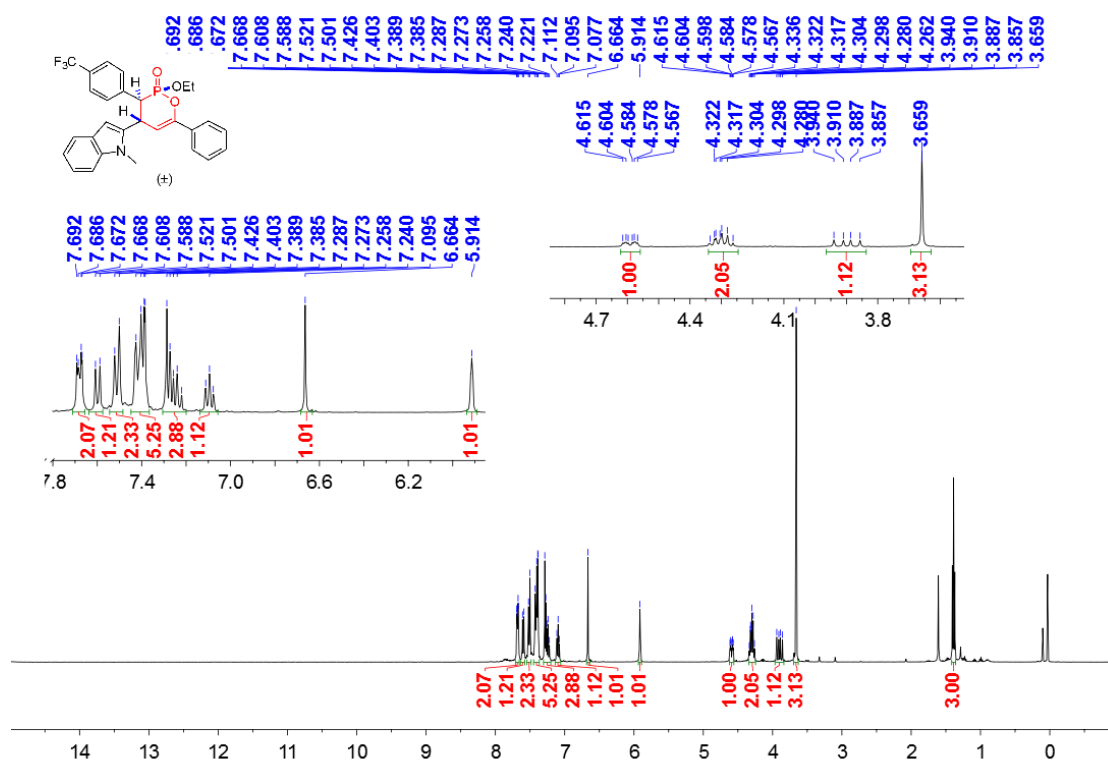




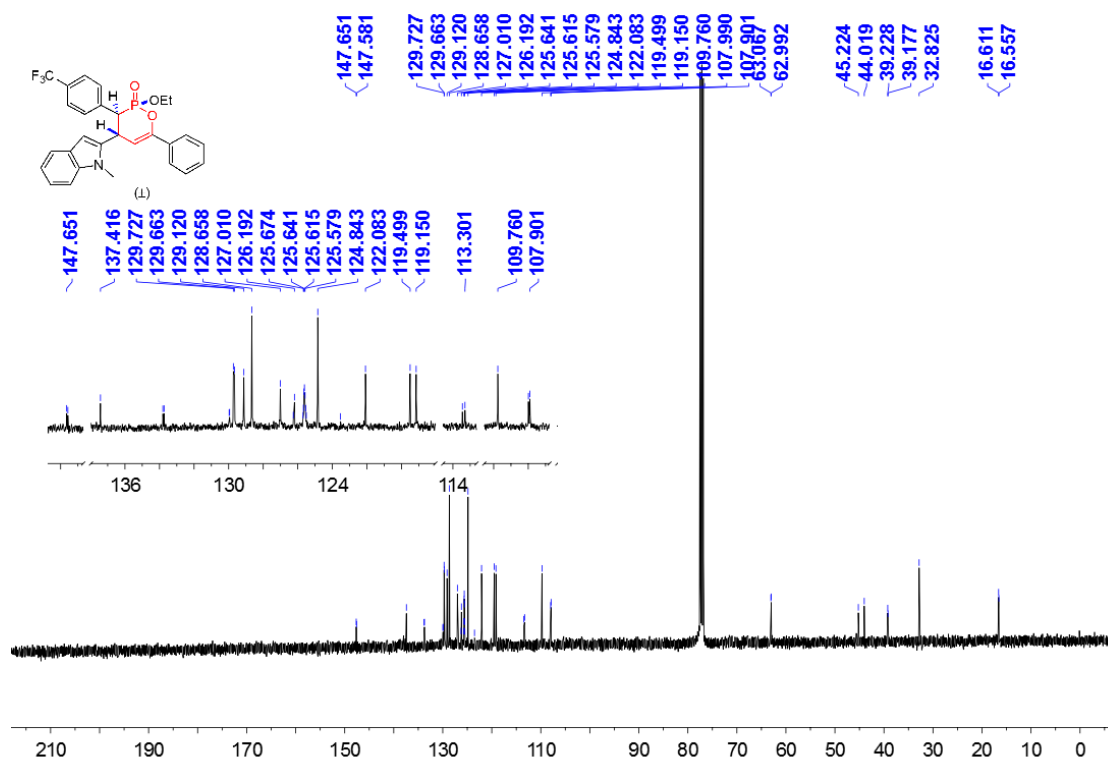
¹³C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3y**



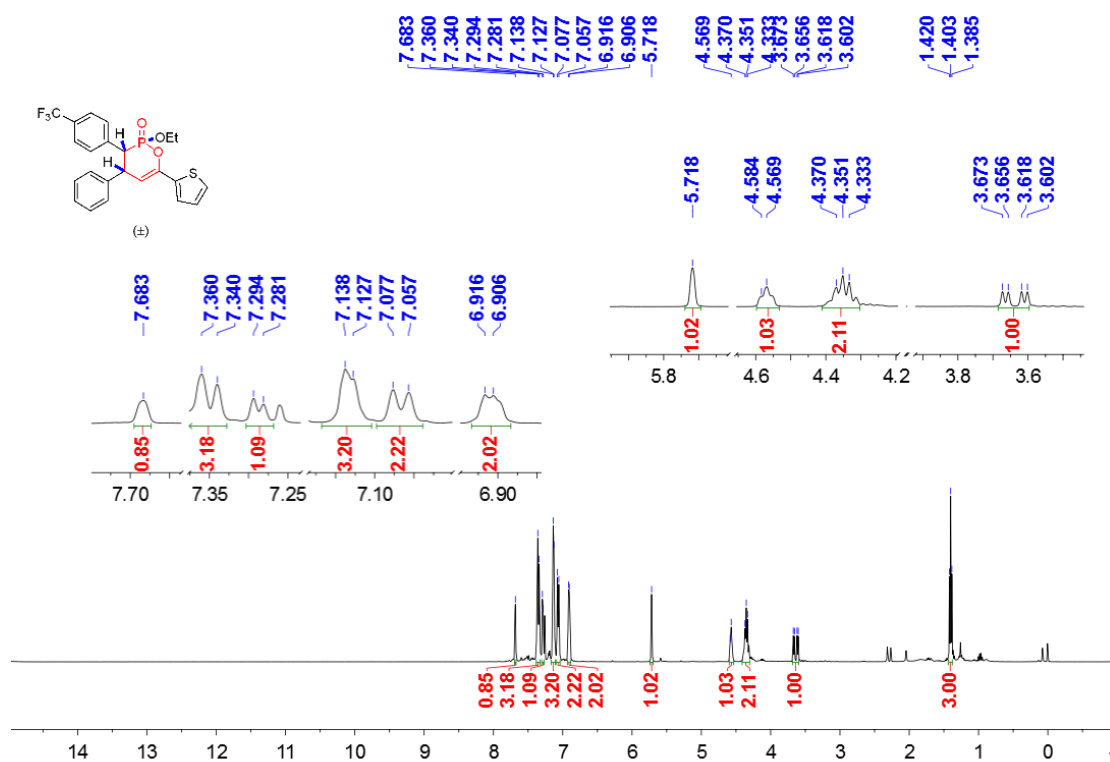
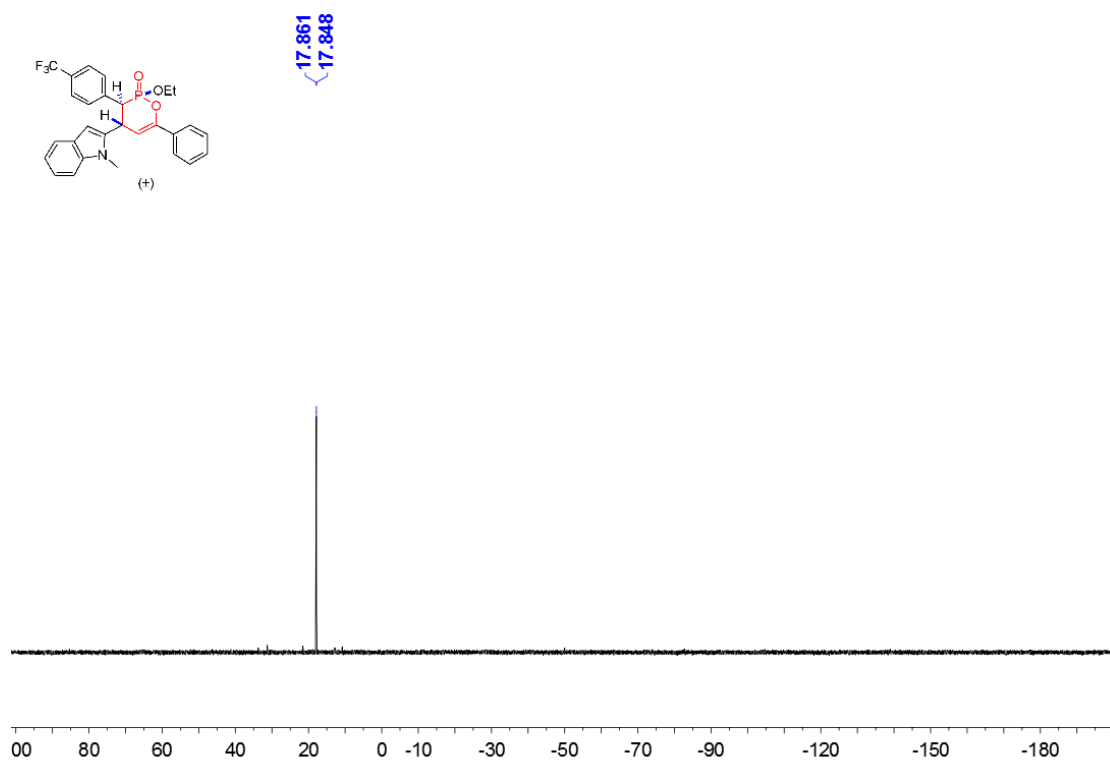
³¹P NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3y**

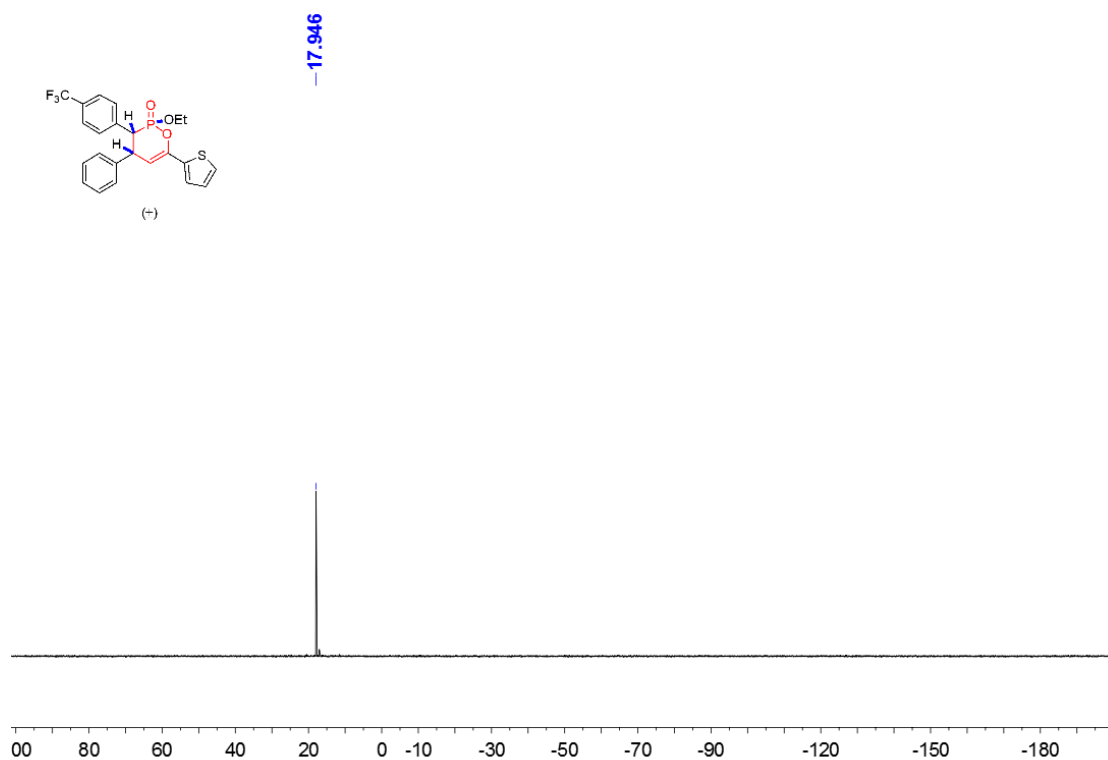
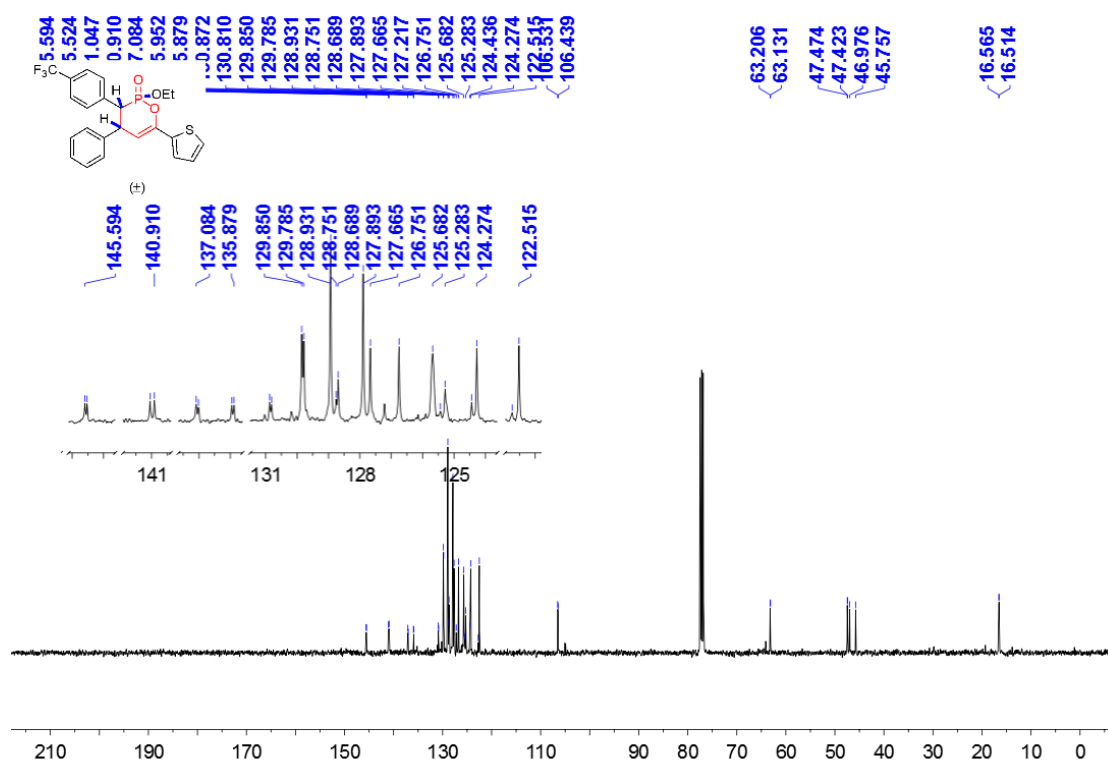


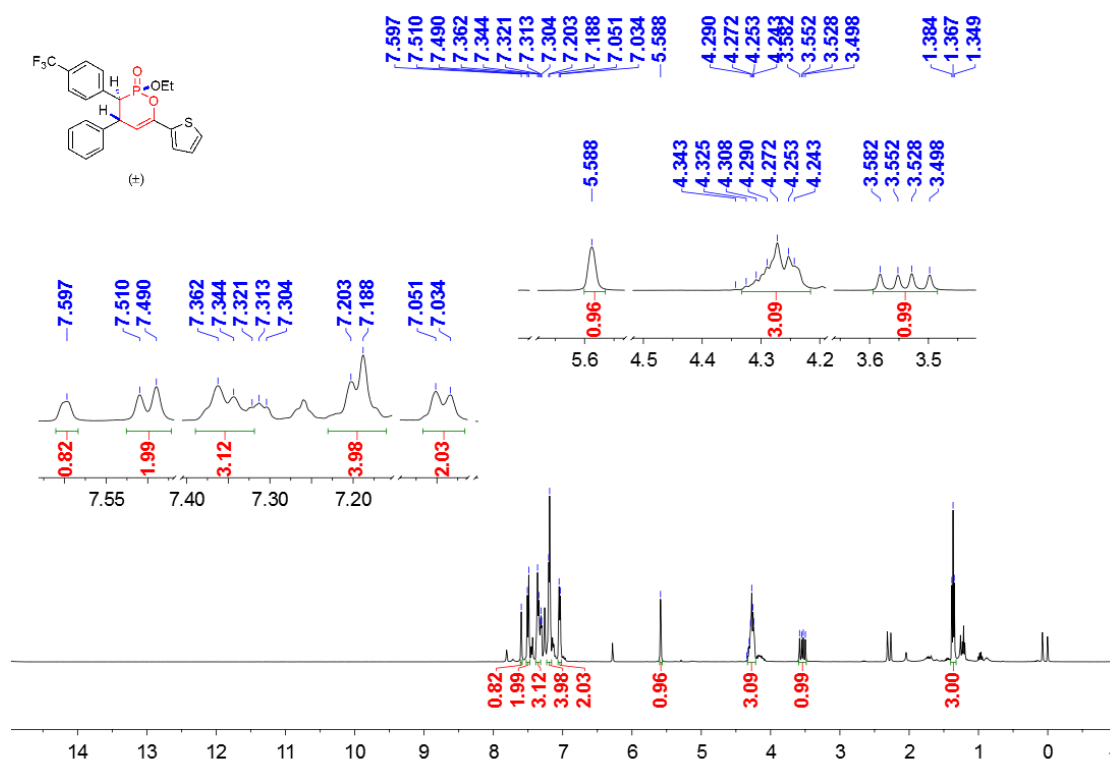
¹H NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3y**



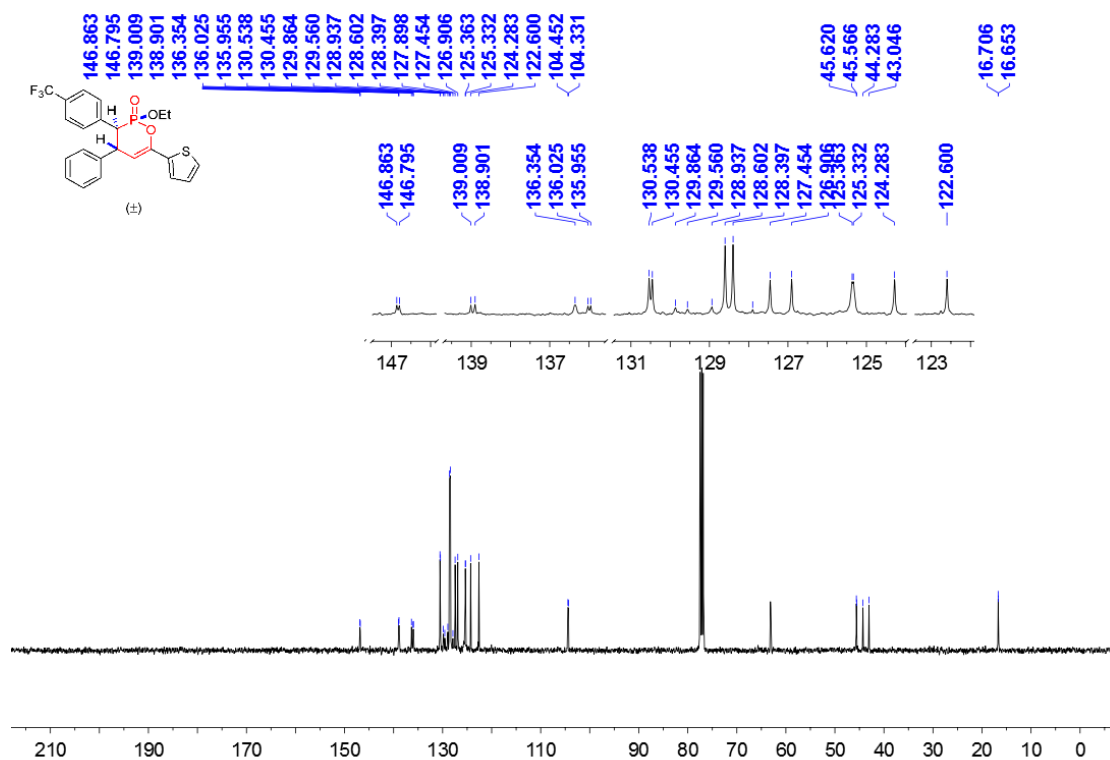
¹³C NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3y**



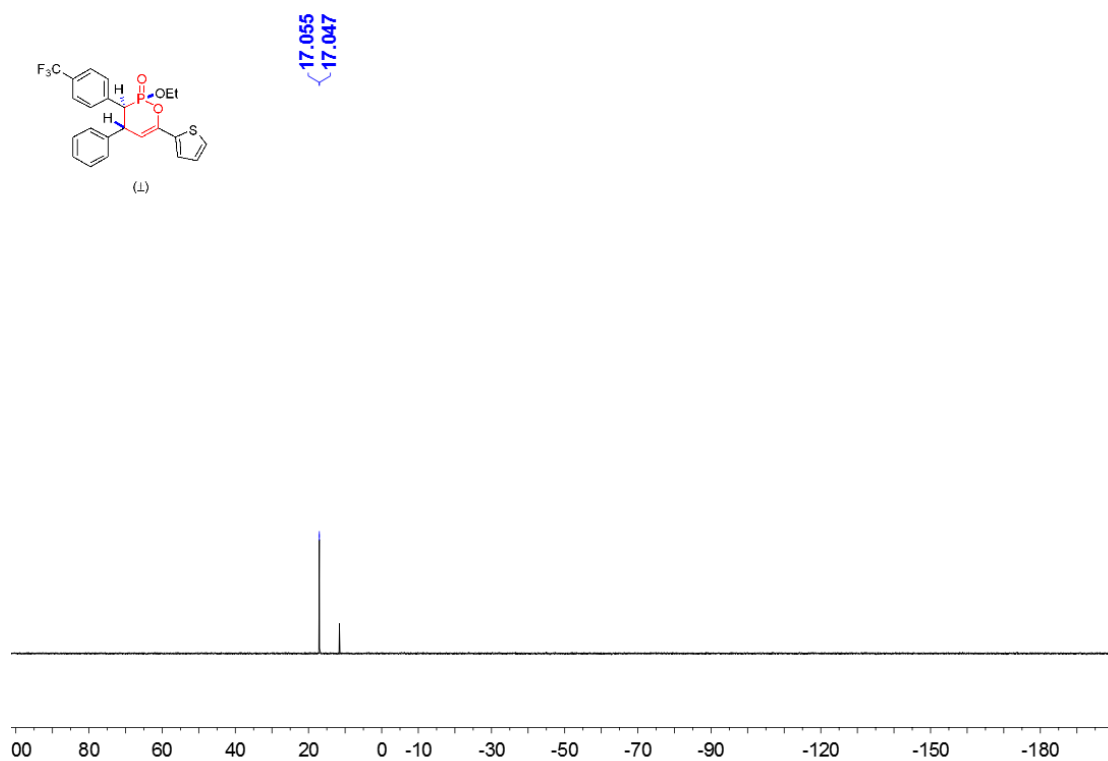




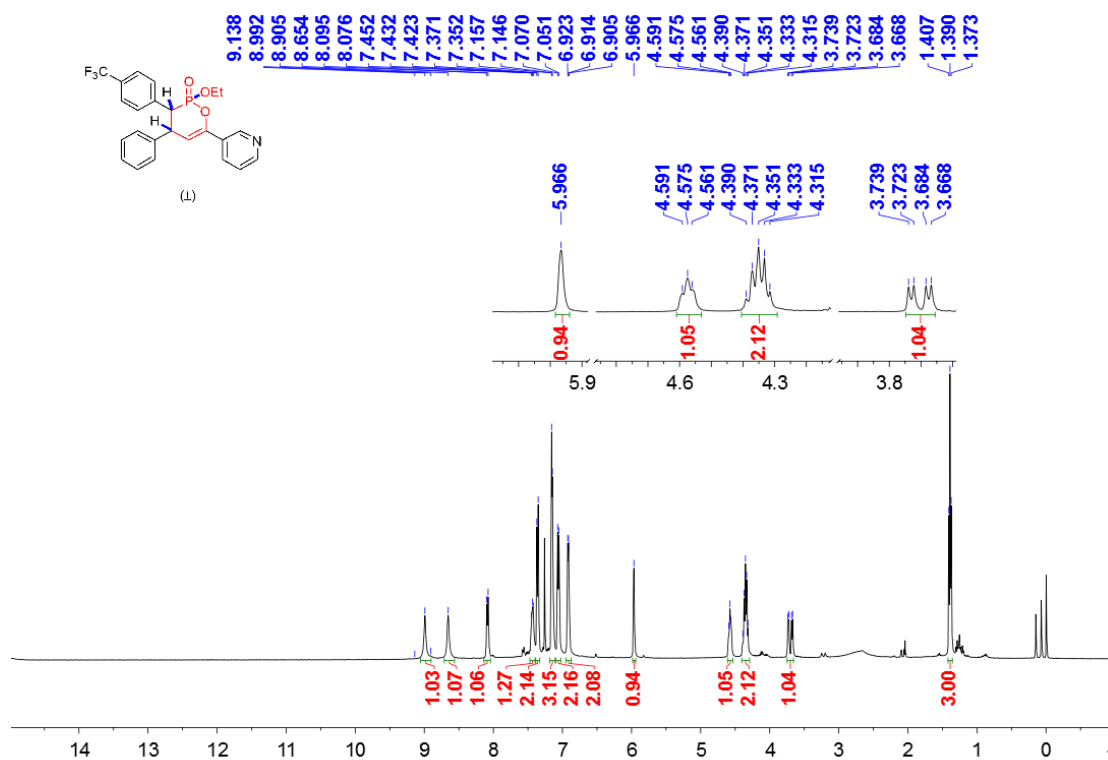
¹H NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3z**



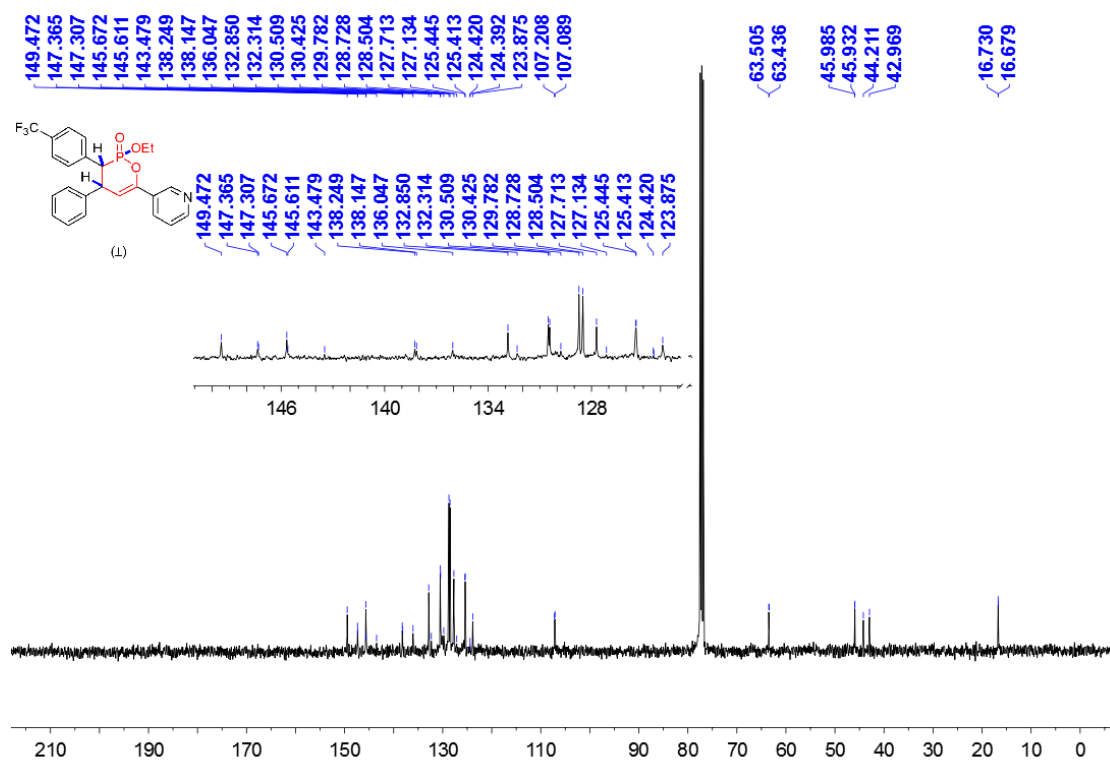
¹³C NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3z**



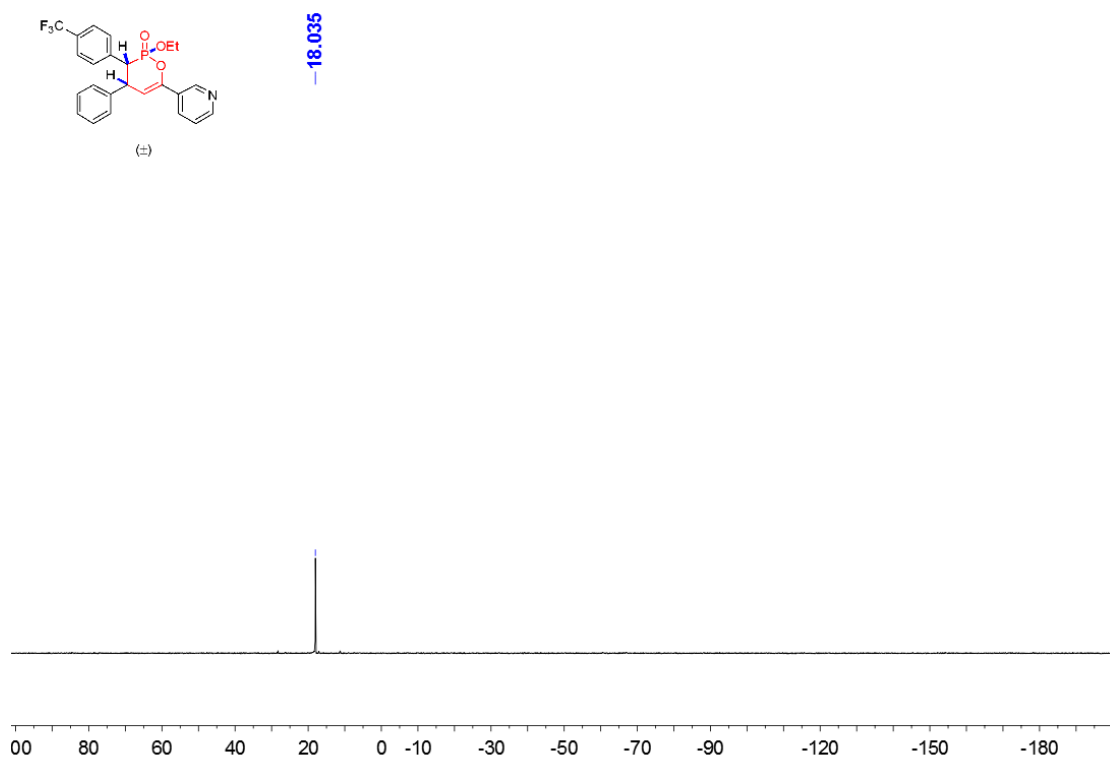
^{31}P NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3z**



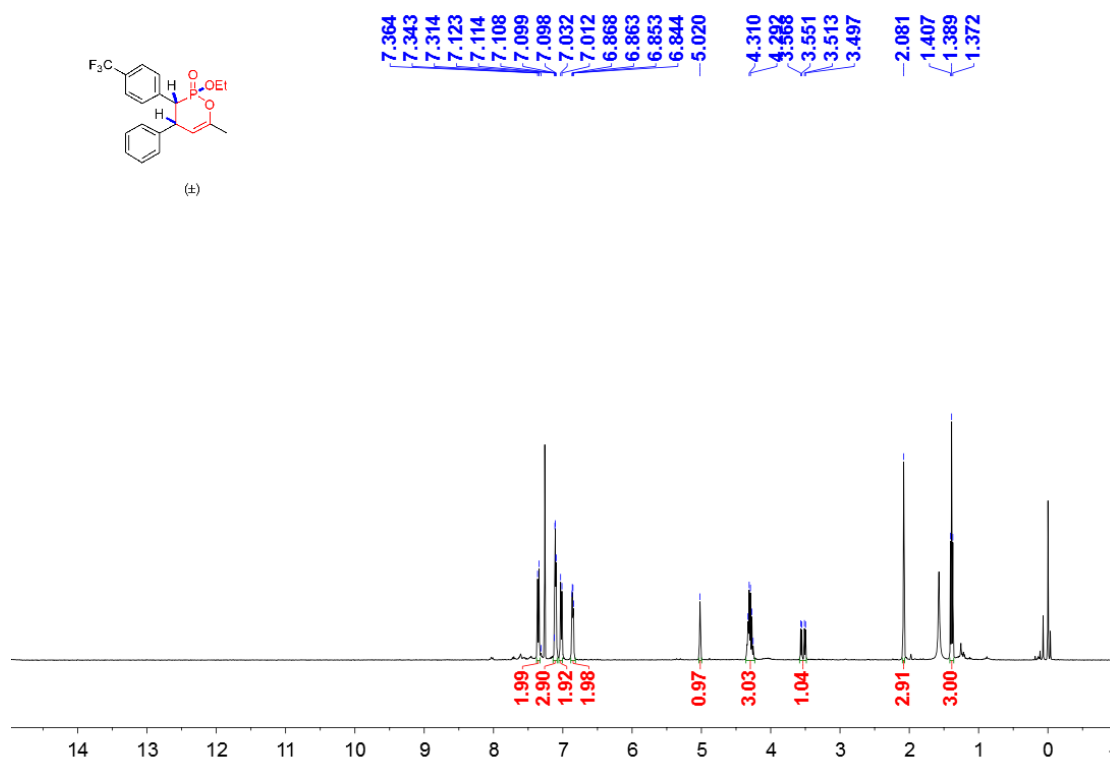
^1H NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3aa**



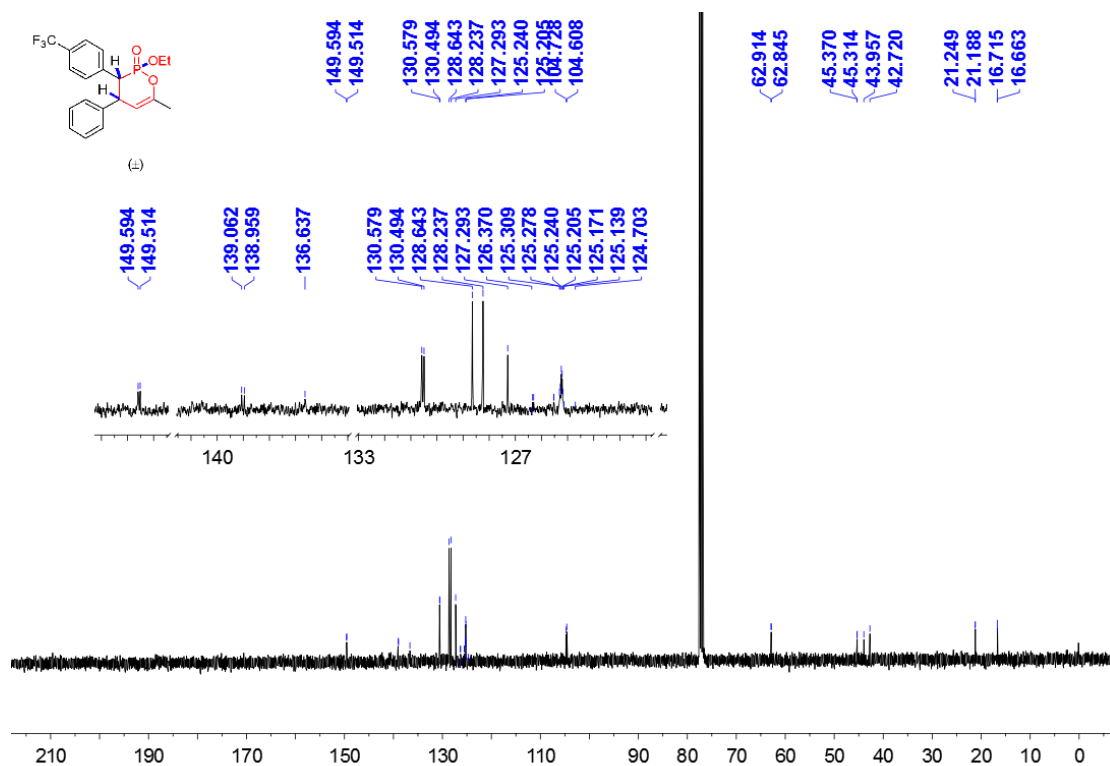
¹³C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3aa**



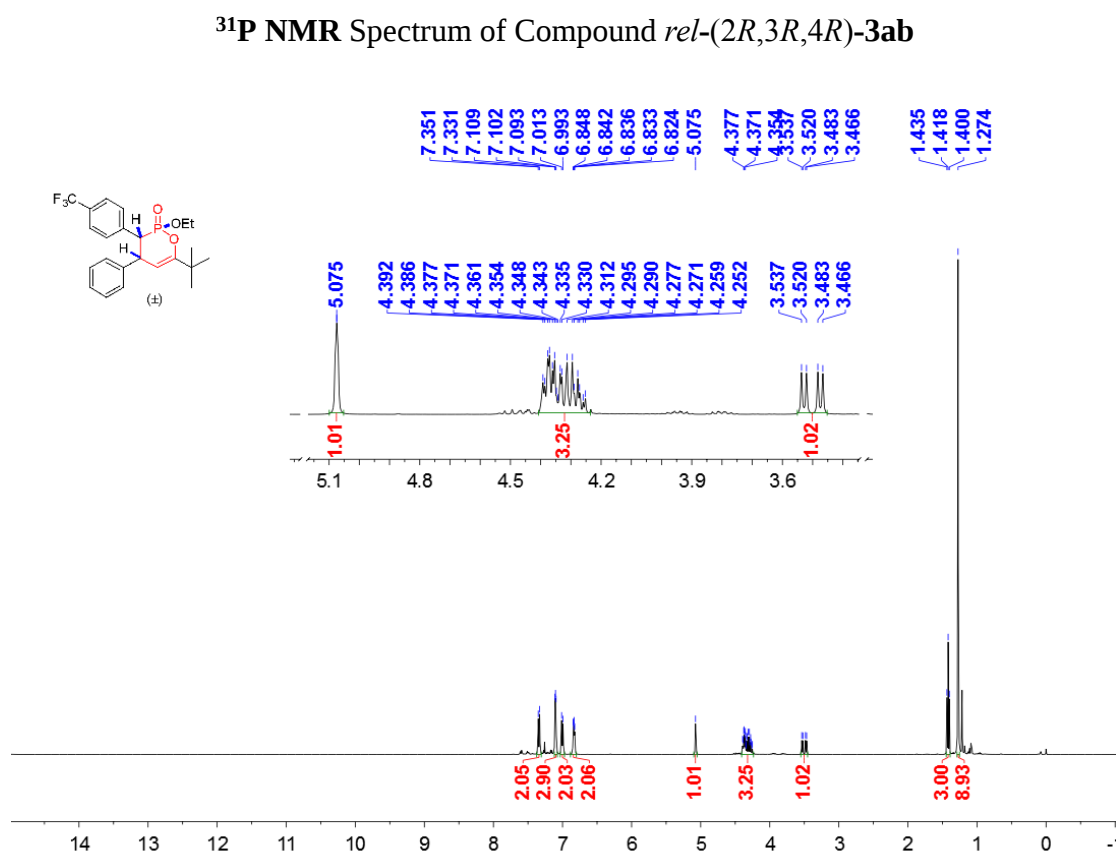
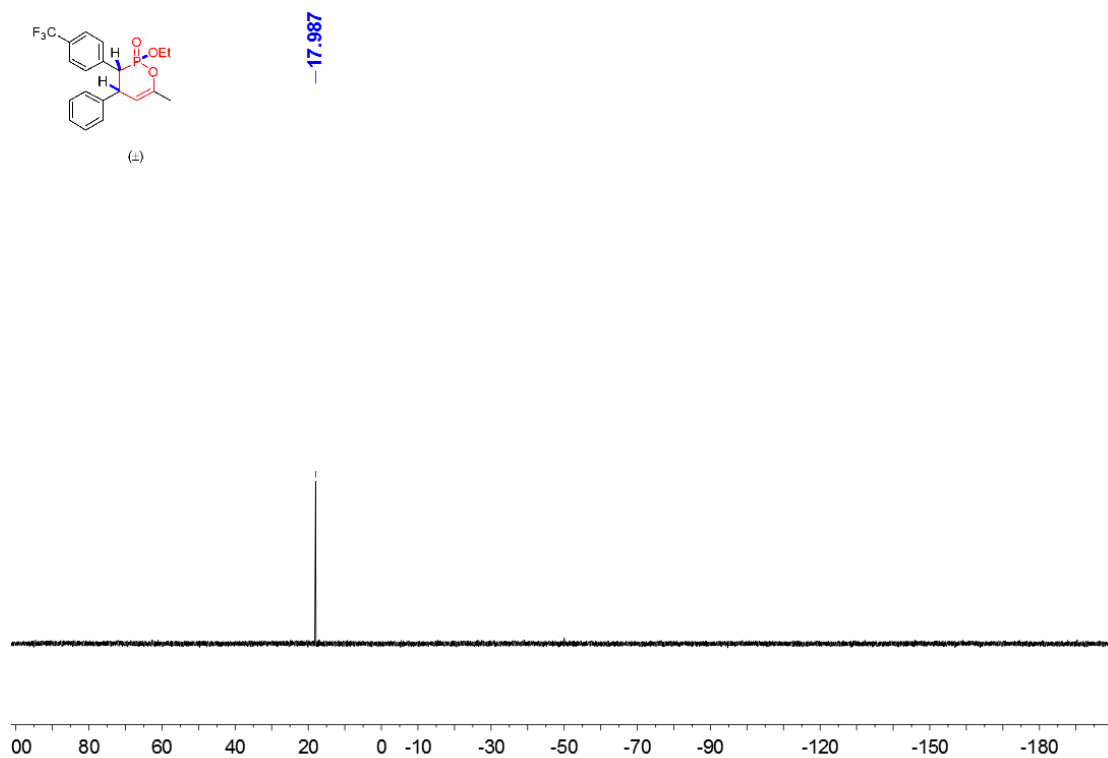
³¹P NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3aa**

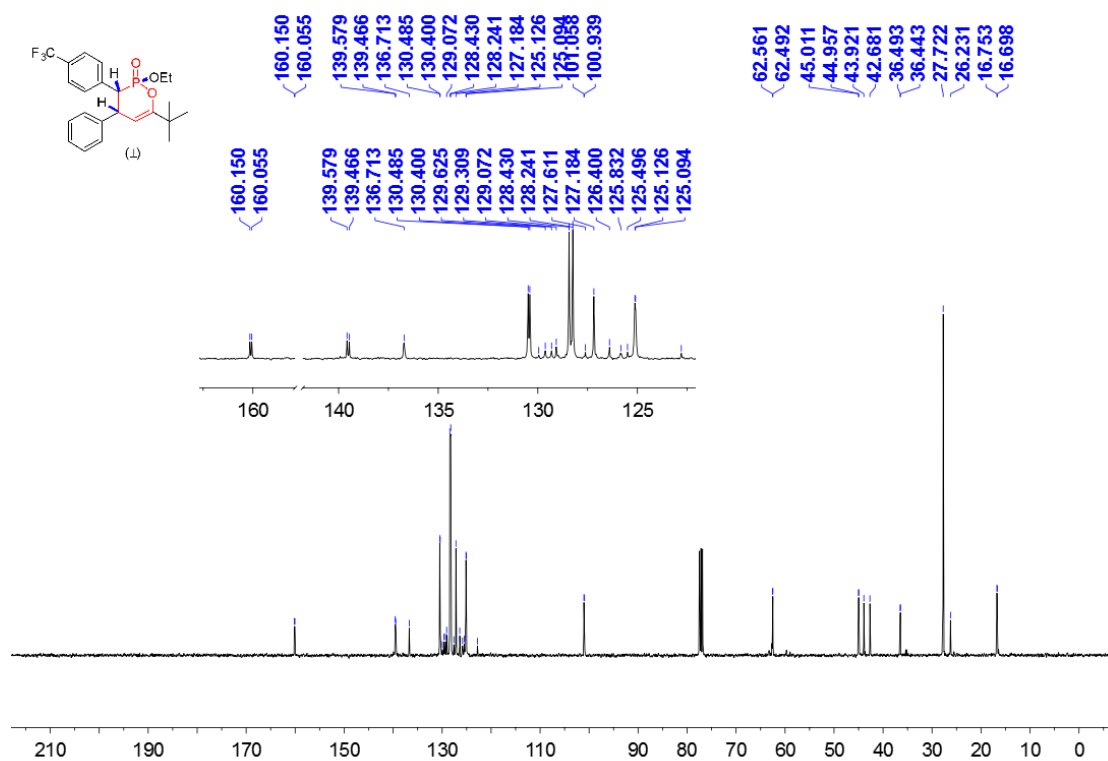


¹H NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3ab**

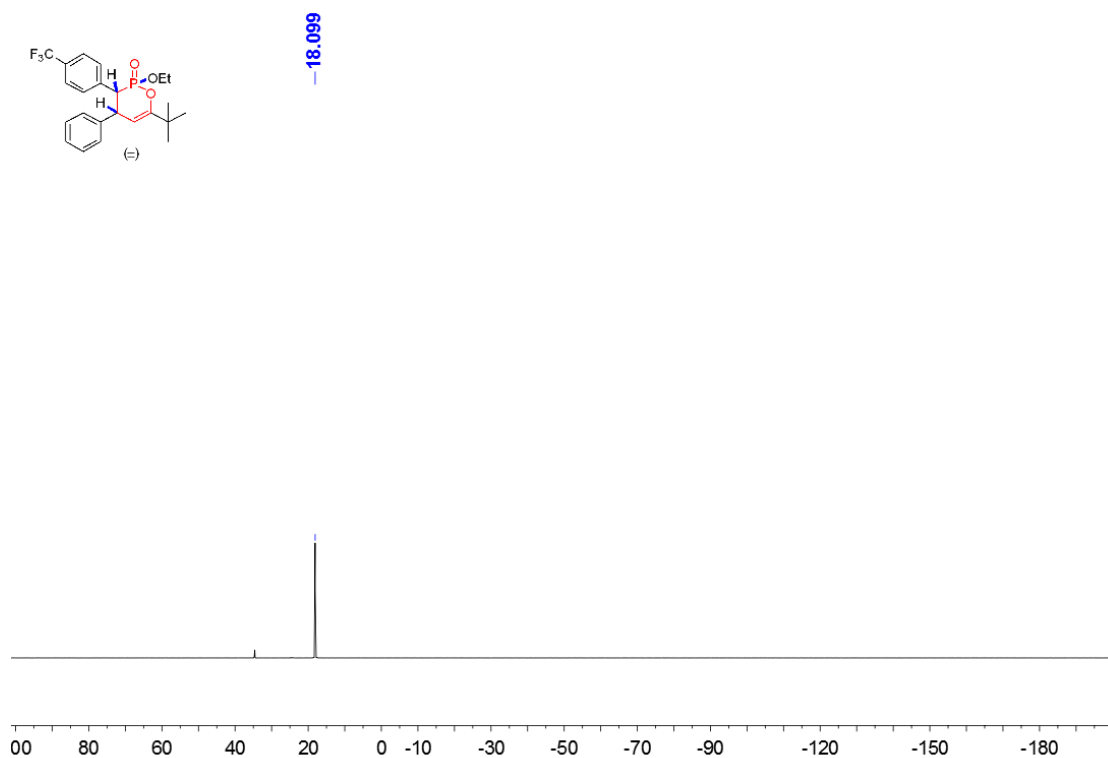


¹³C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3ab**

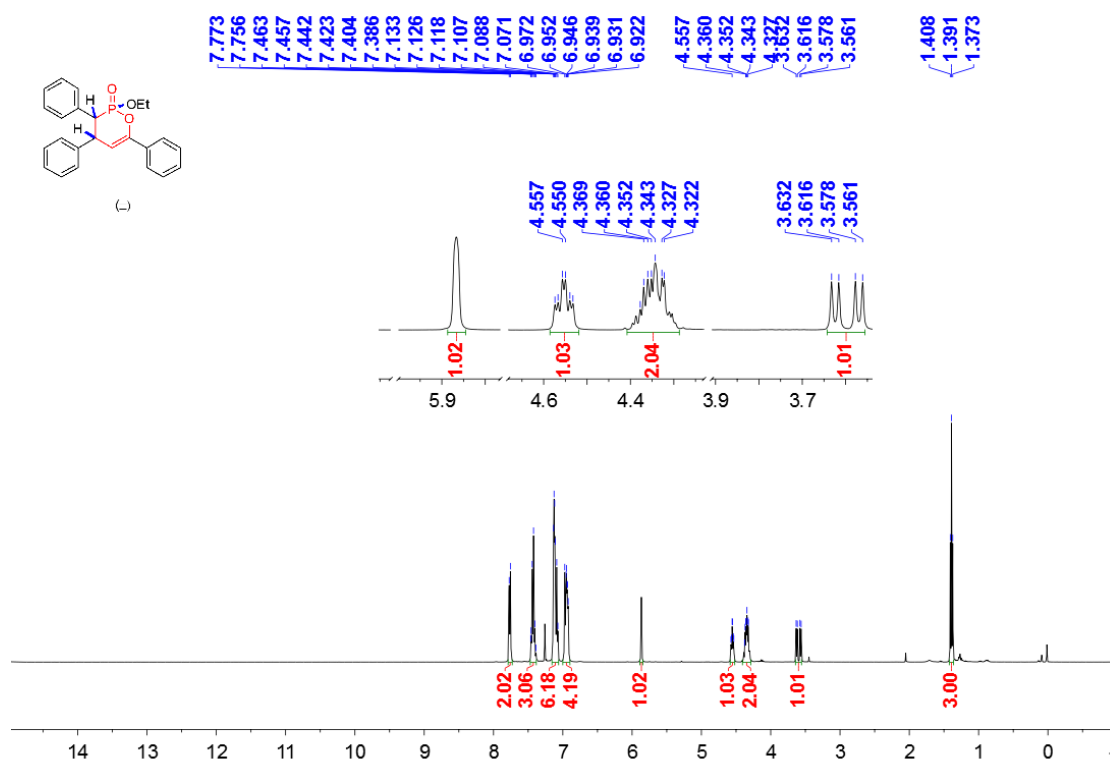




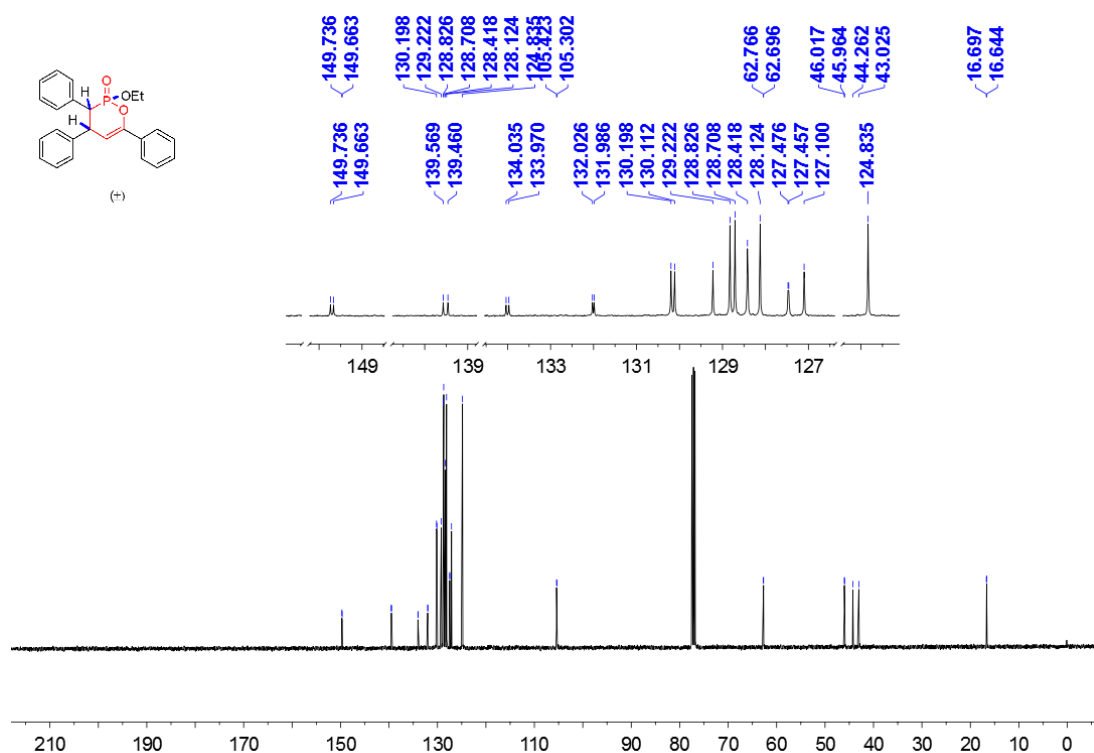
¹³C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3ac**



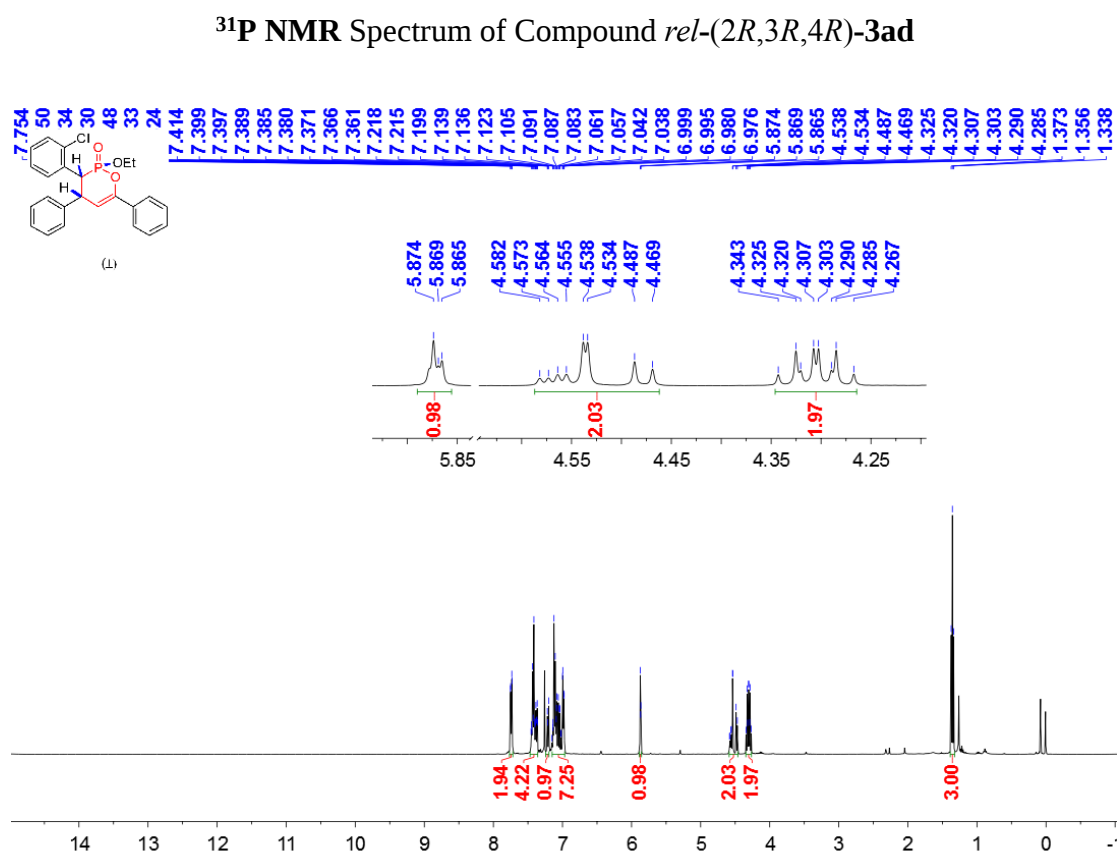
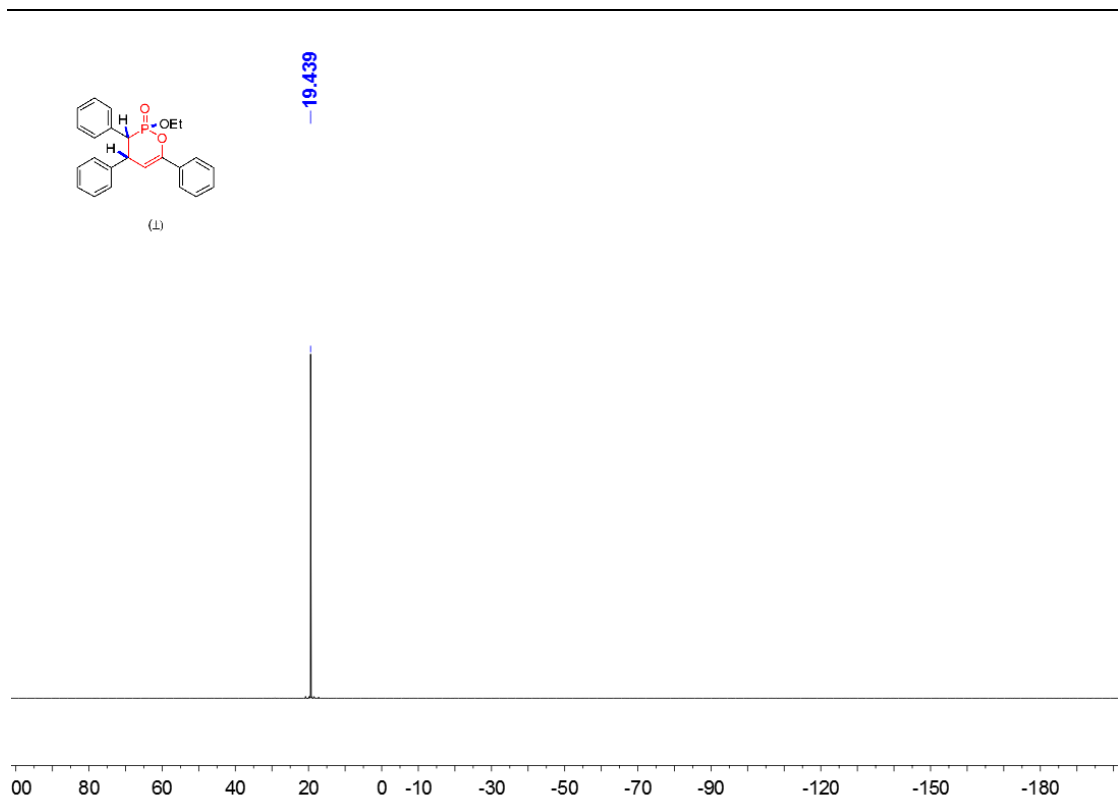
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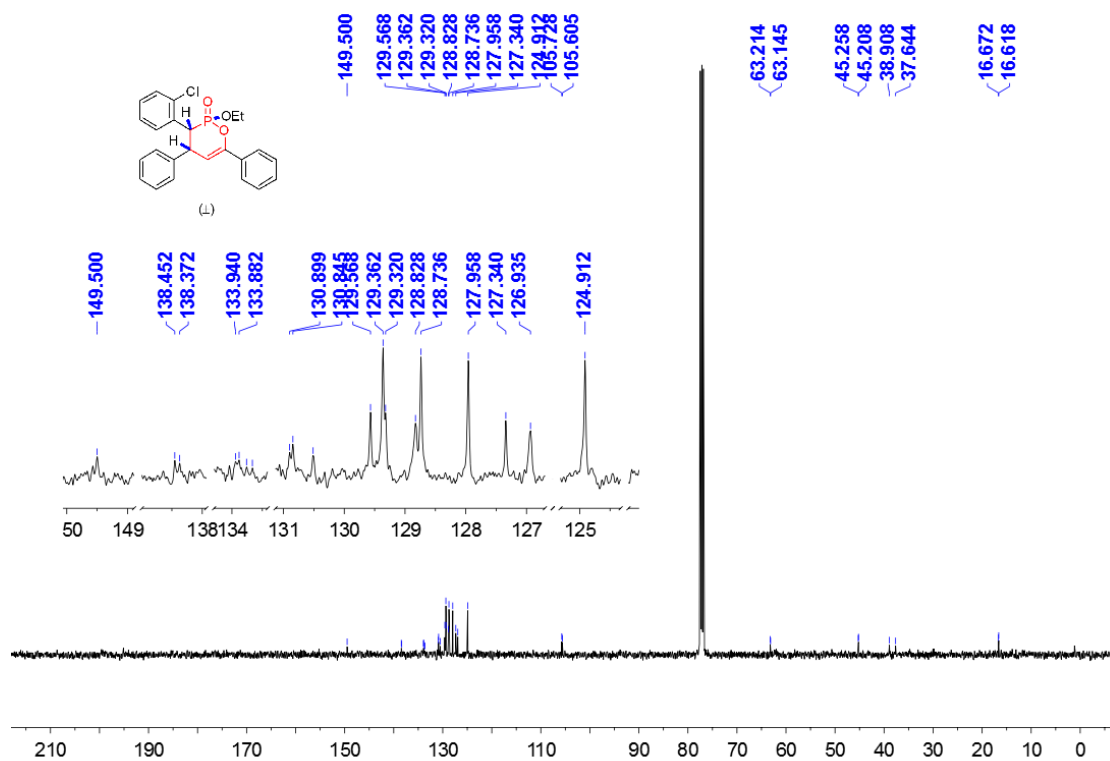


¹H NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3ad

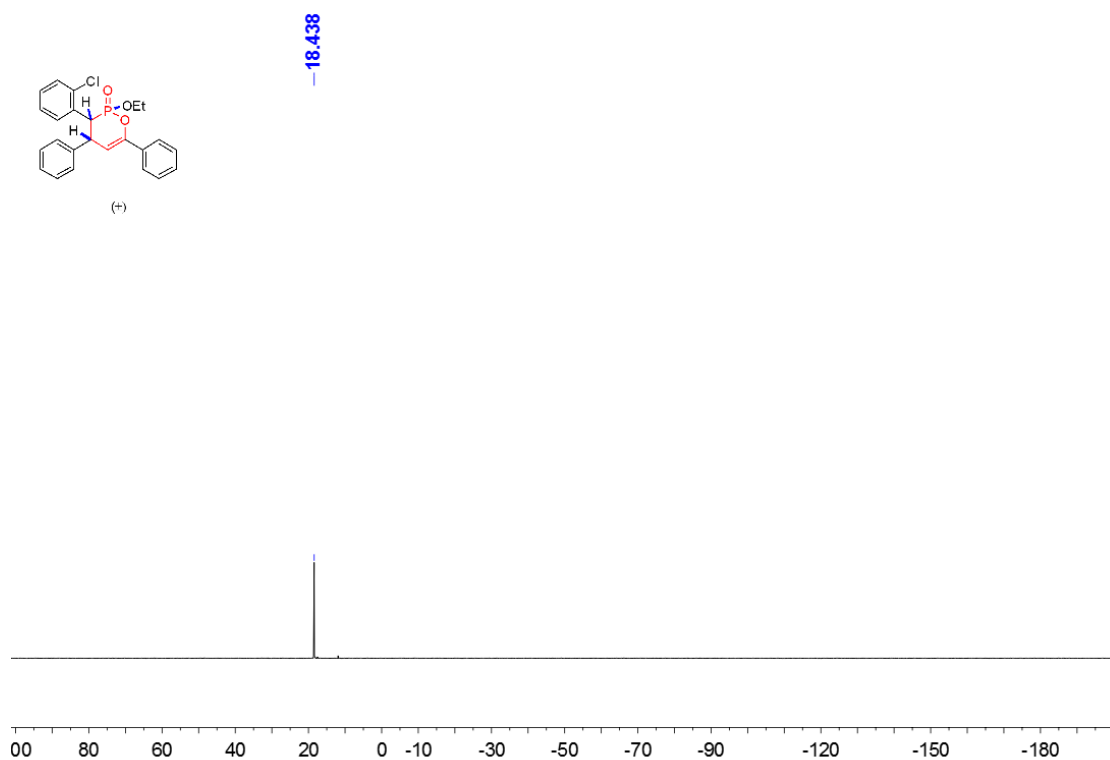


¹³C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3ad

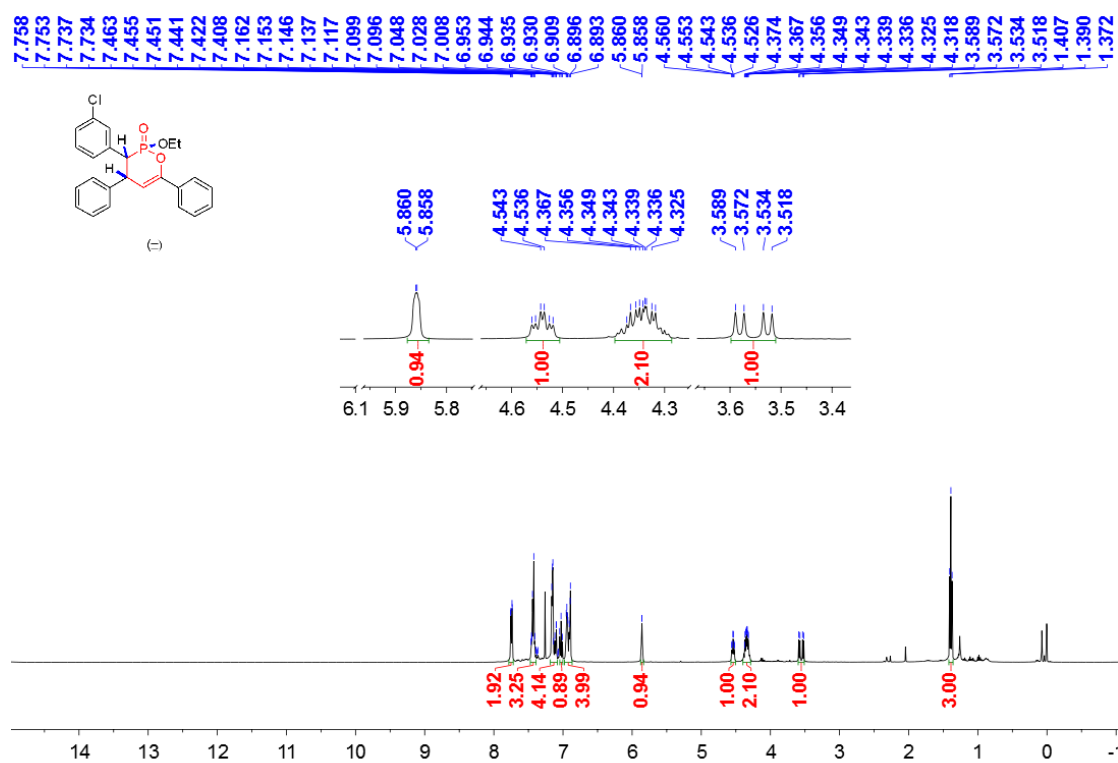




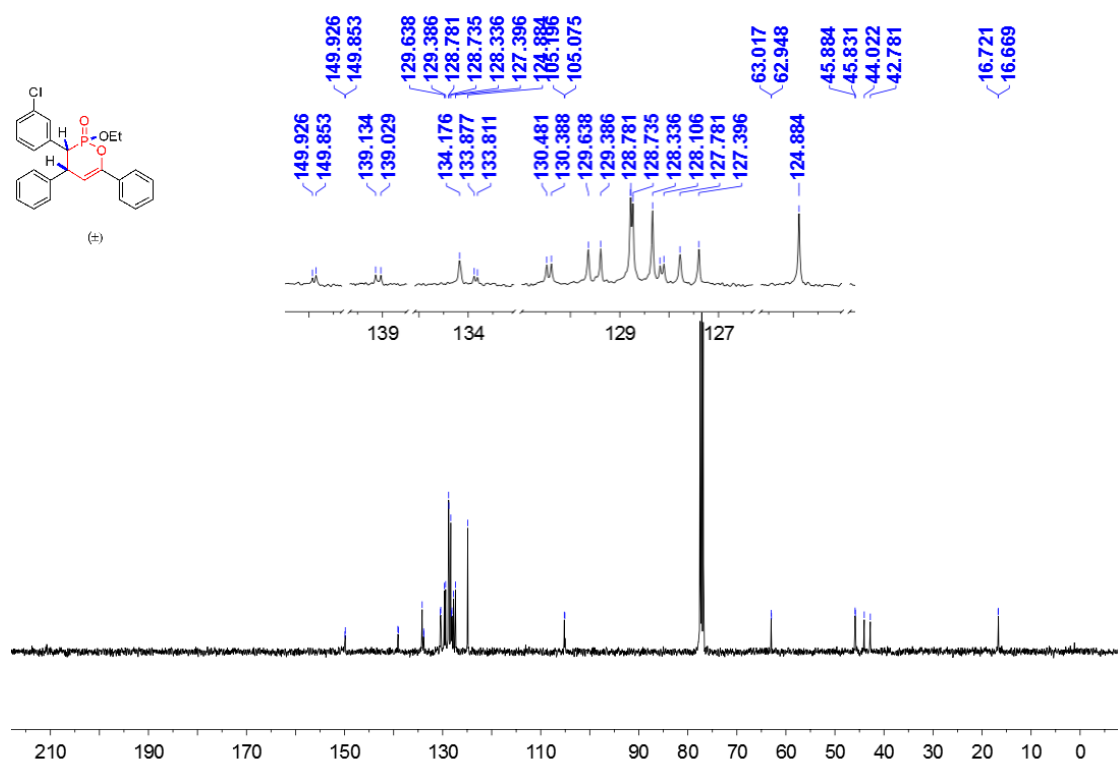
¹³C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3ae**



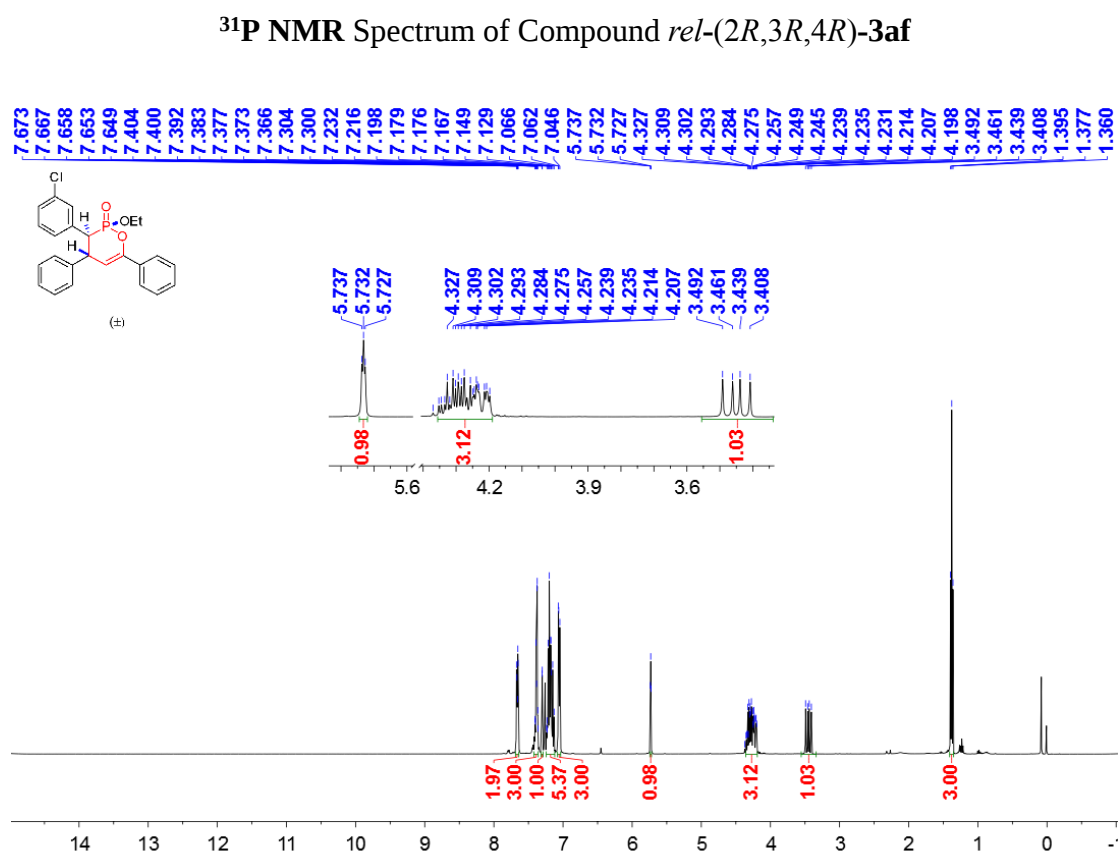
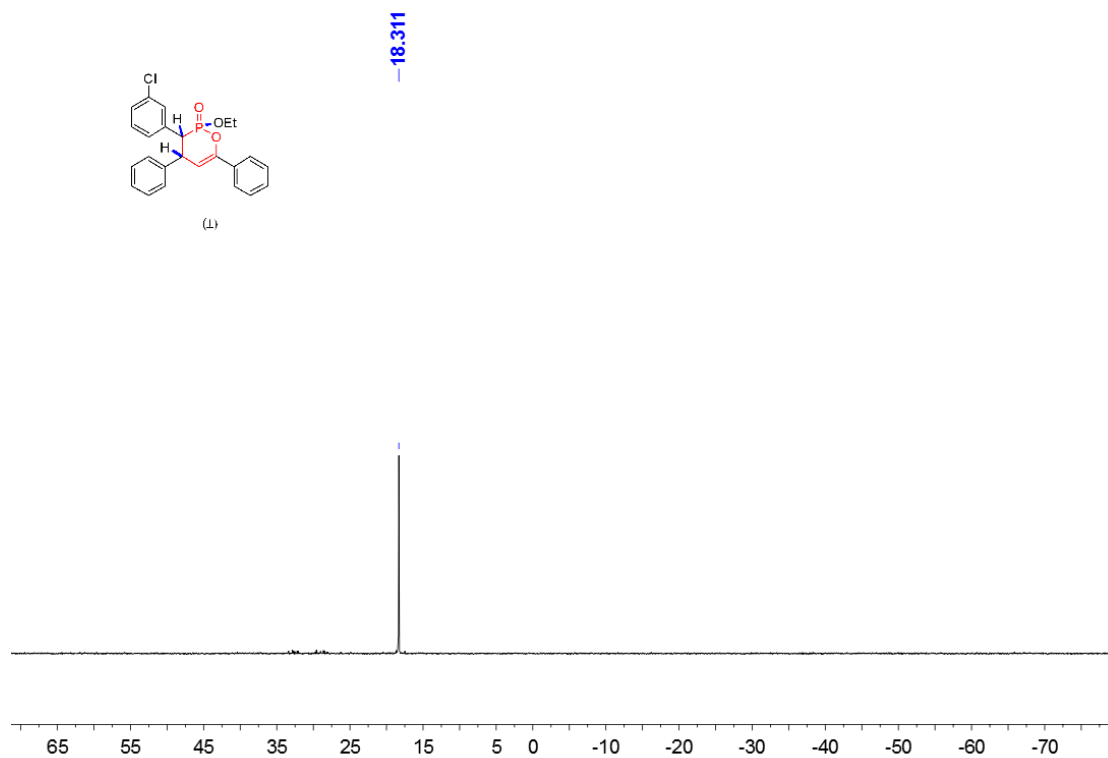
³¹P NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3ae**

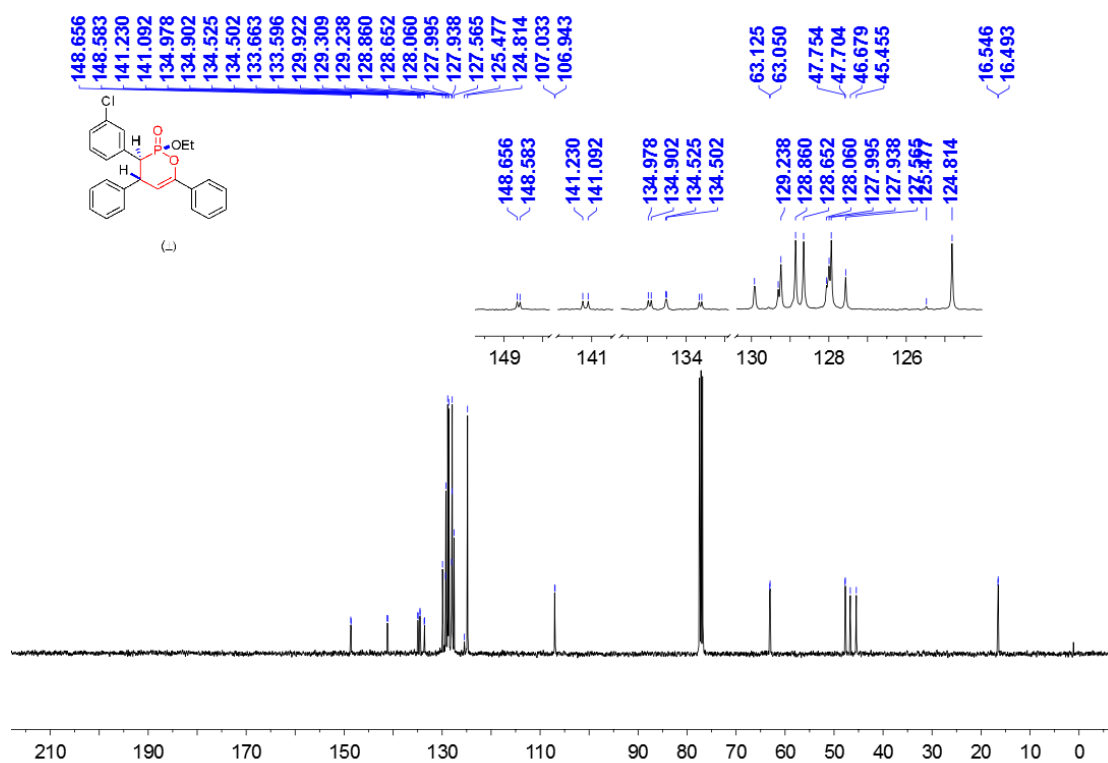


¹H NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3af

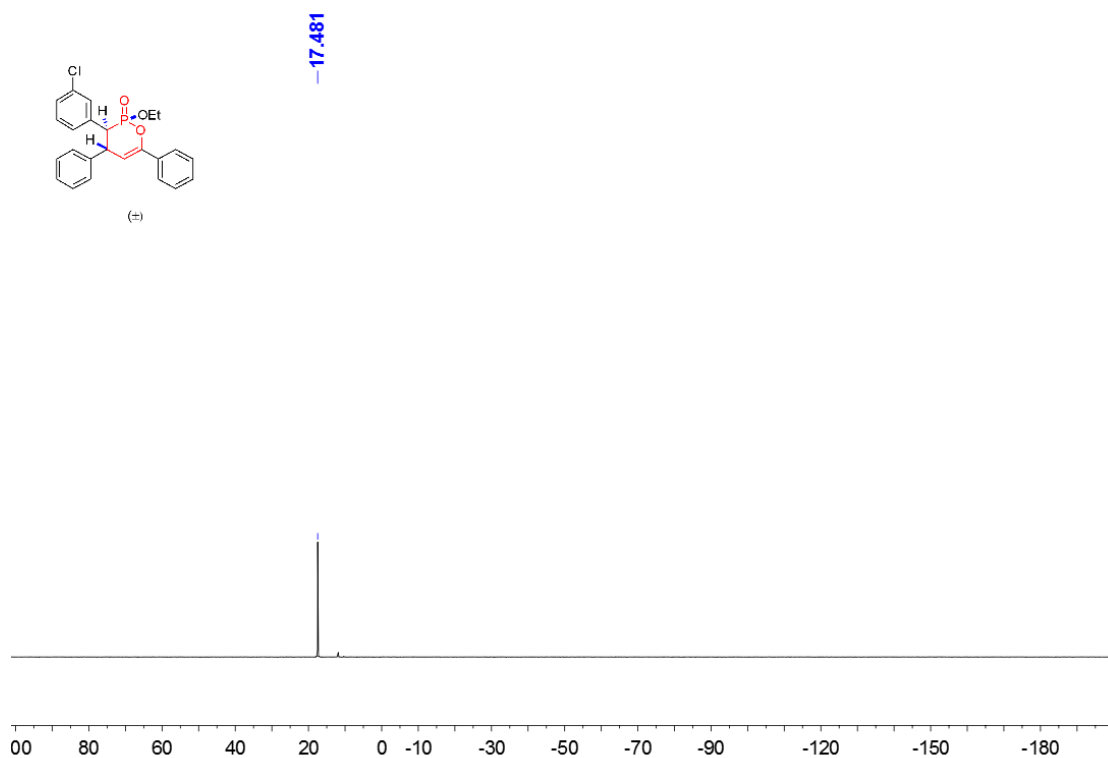


¹³C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3af

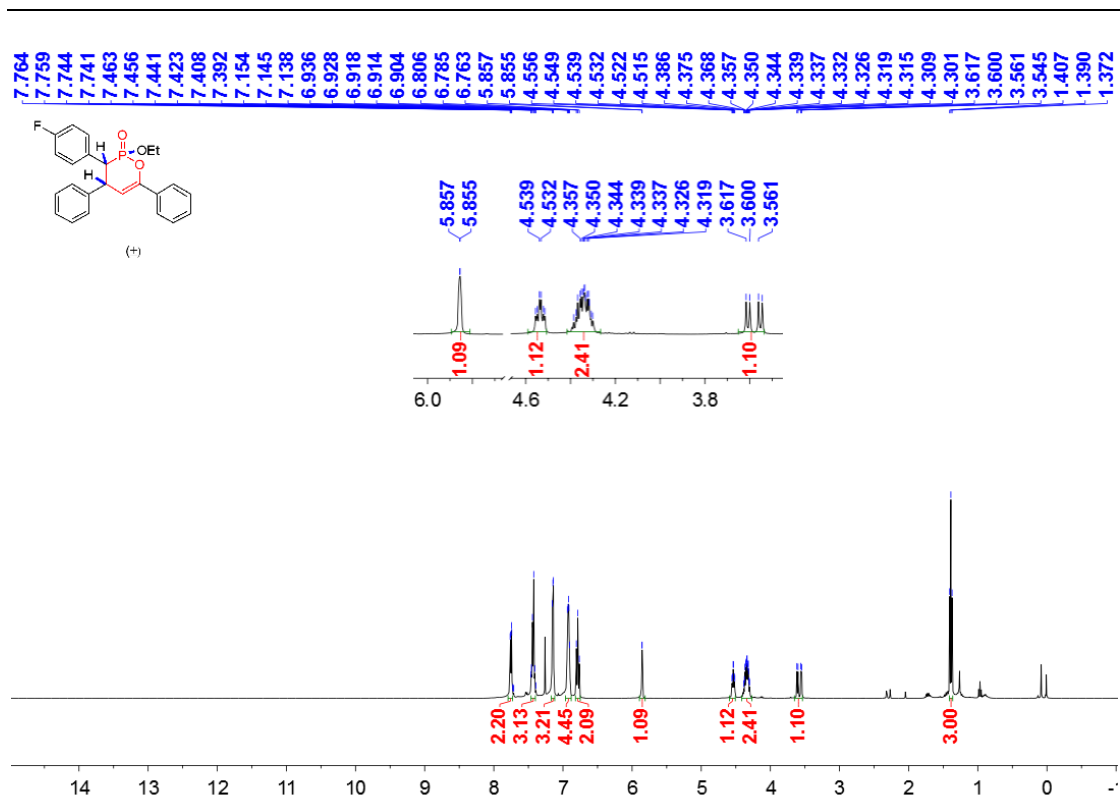




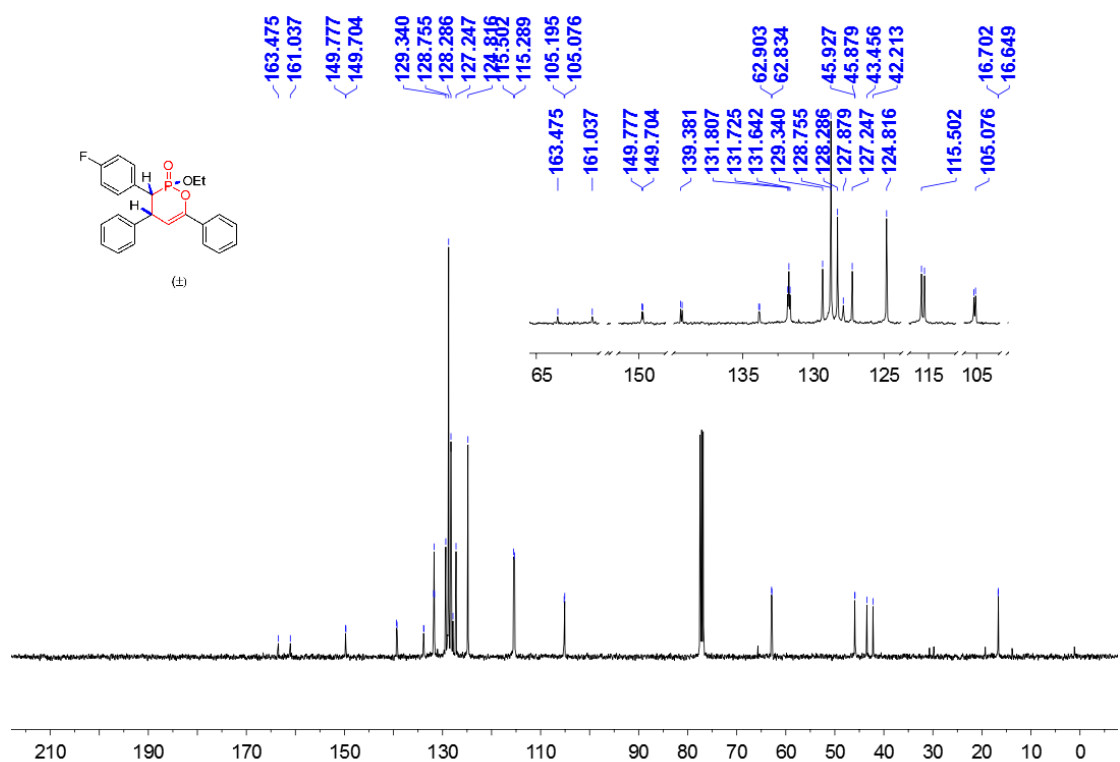
¹³C NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3af**



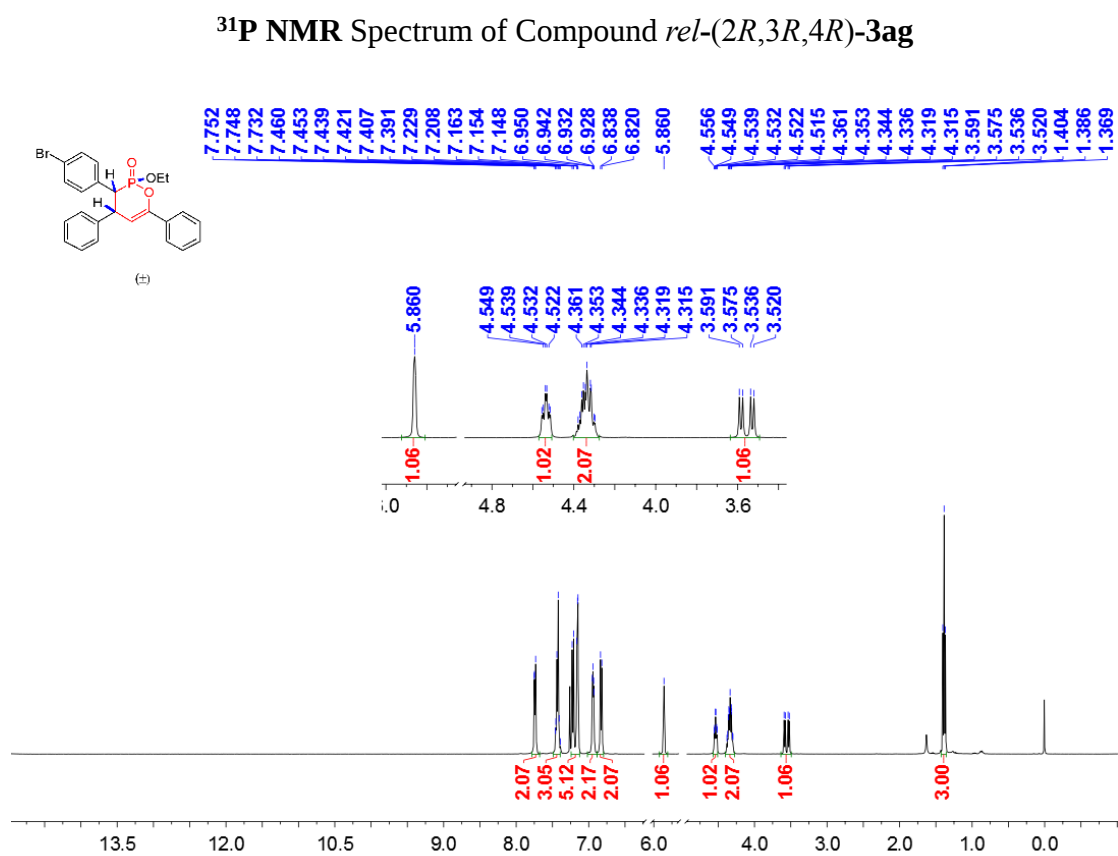
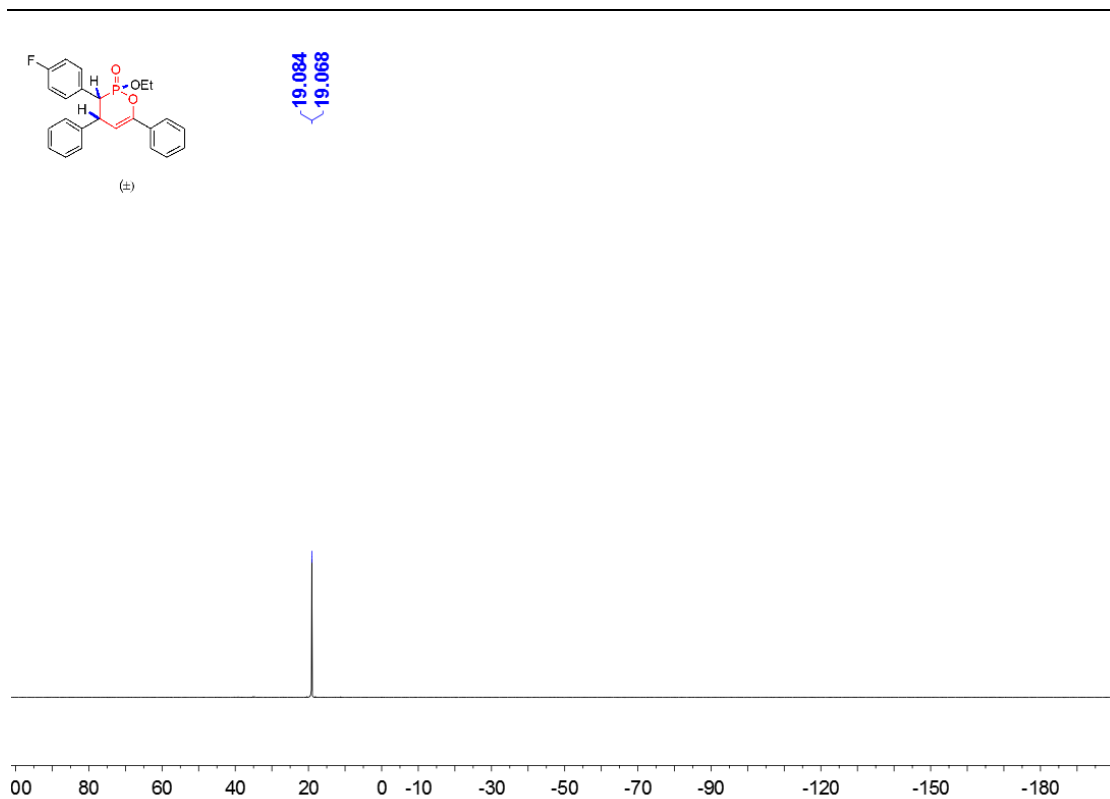
³¹P NMR Spectrum of Compound *rel*-(2*R*,3*S*,4*R*)-**3af**

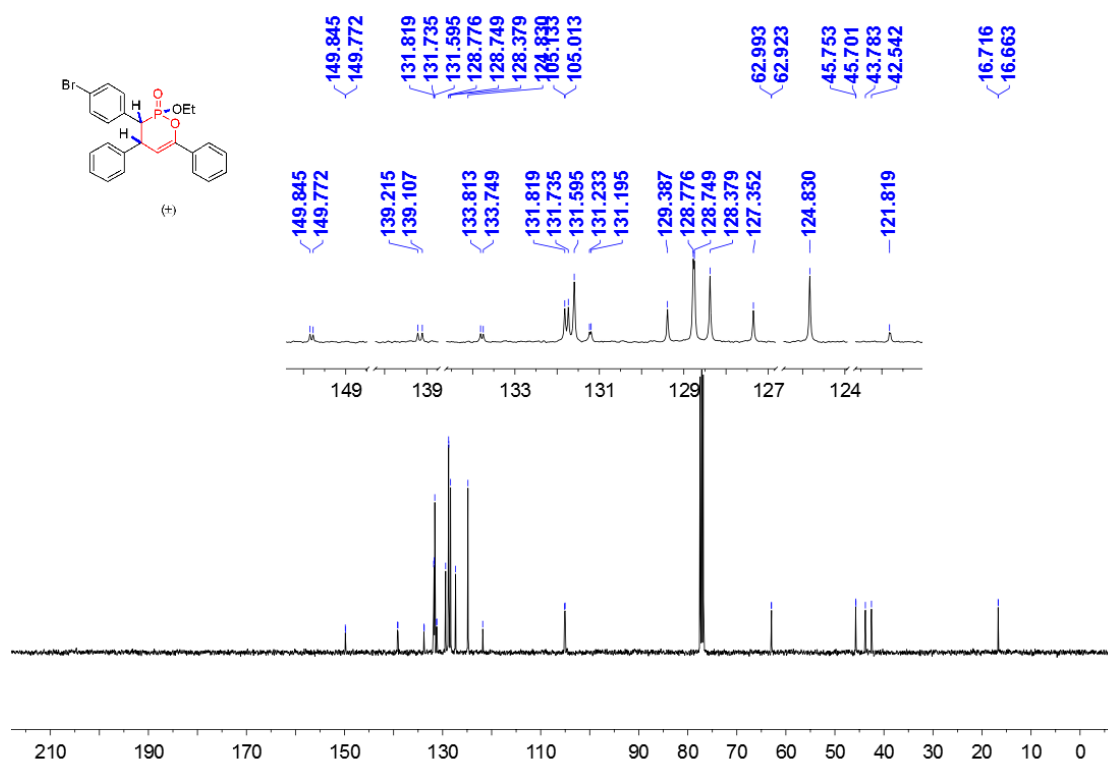


¹H NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3ag

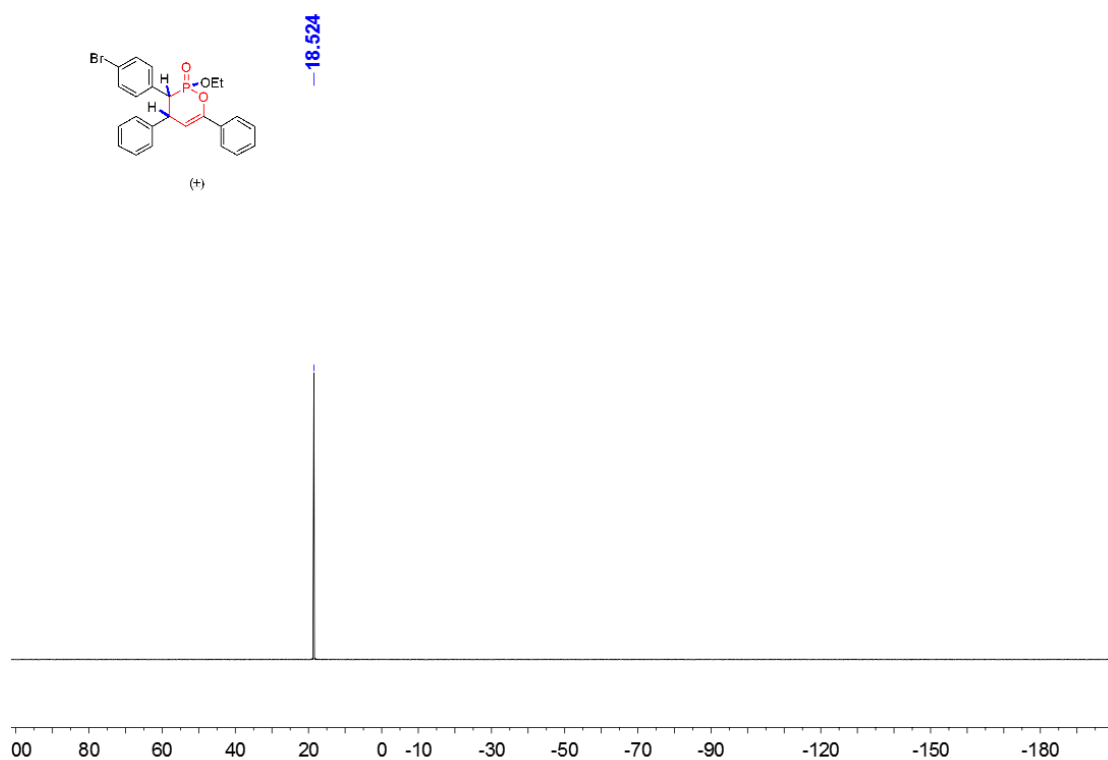


¹³C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3ag





^{13}C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-**3ah**



Chemical structure of compound 10 (a phosphonate ester) is shown. The structure is a phosphonate ester derivative of a chiral phosphine oxide, featuring a central phosphorus atom bonded to an ethoxy group, a phenyl group, and a chiral center. The chiral center is also bonded to a phenyl group and a 4-bromophenyl group.

¹H NMR spectrum (CDCl₃) of compound 10. The spectrum shows peaks corresponding to the structure, with integration values provided below the peaks. The chemical shifts (δ) are listed at the top of the spectrum.

Chemical shifts (δ) listed at the top of the spectrum:

- 7.665, 7.659, 7.646, 7.642, 7.398, 7.386, 7.379, 7.372, 7.368, 7.360, 7.234, 7.228, 7.212, 7.194, 7.175, 7.166, 7.156, 7.148, 7.124, 7.118, 7.102, 7.097, 7.058, 7.054, 7.038, 5.726, 5.722, 5.717, 4.309, 4.291, 4.284, 4.284, 4.277, 4.273, 4.266, 4.257, 4.248, 4.240, 4.232, 4.222, 4.216, 4.202, 4.195, 4.186, 3.491, 3.461, 3.438, 3.407, 1.356, 1.338.

Integration values (red numbers) are provided below the peaks:

- 1.87, 4.67, 3.29, 2.10, 1.94, 0.95, 3.30, 1.00, 3.00.

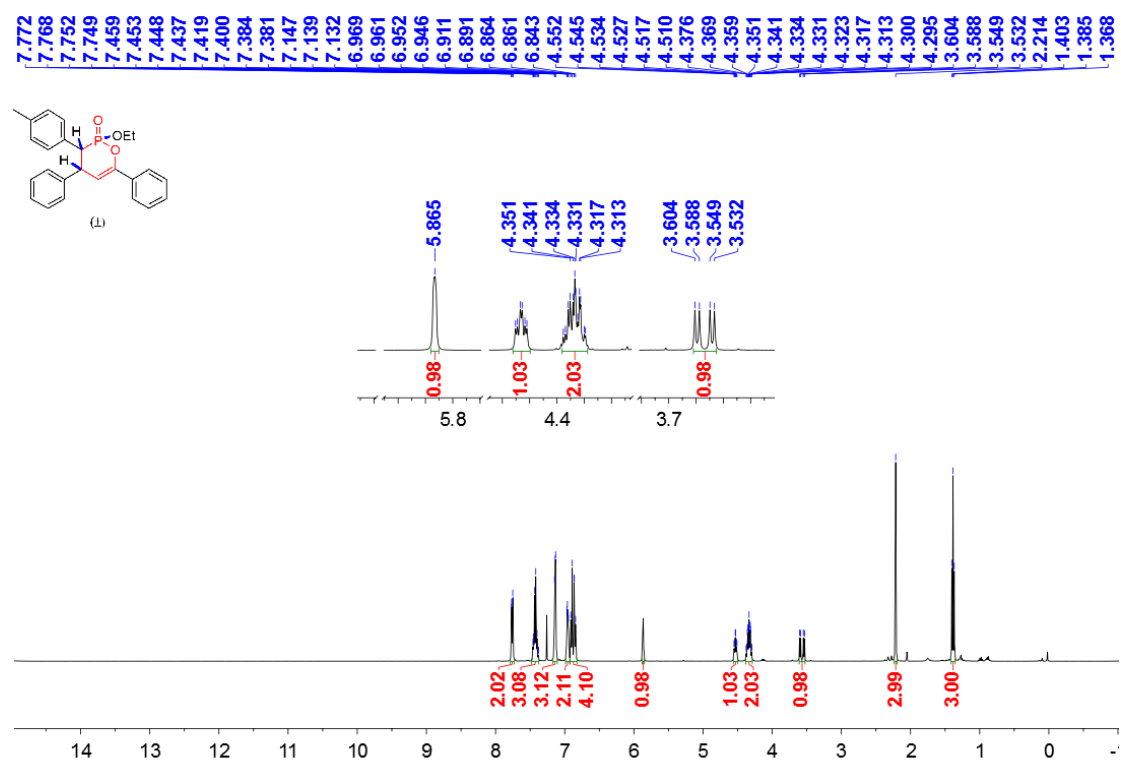
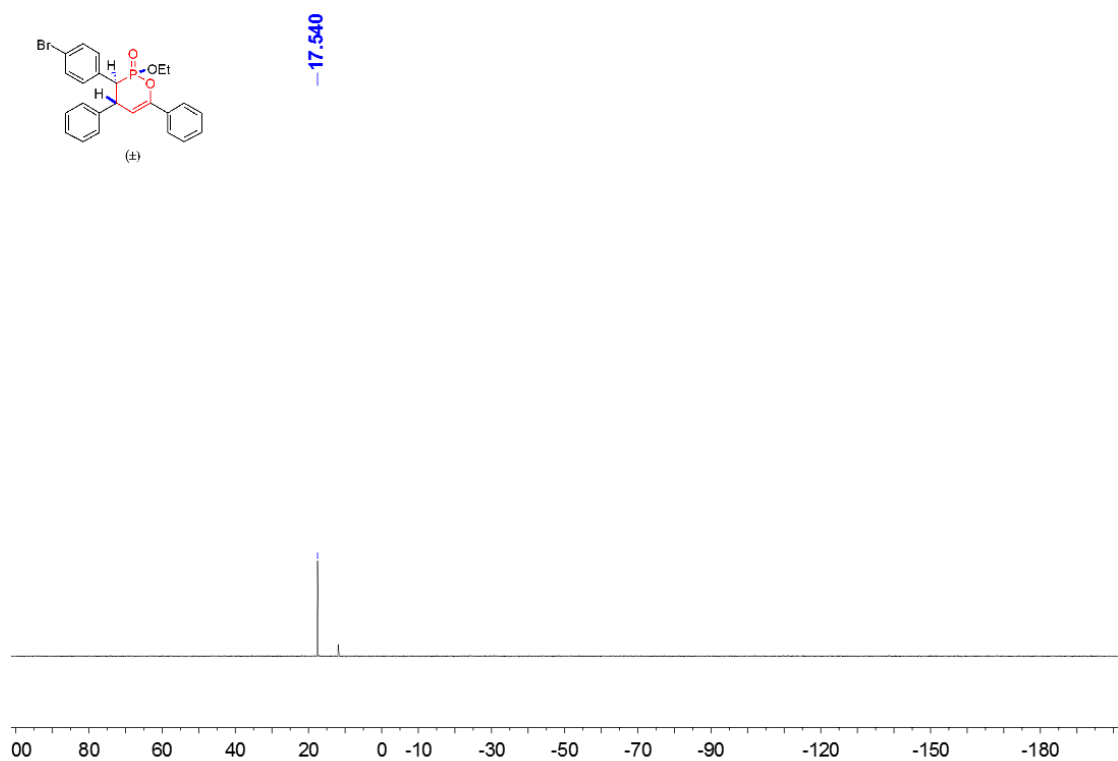
Chemical structure (L) and its corresponding ¹³C NMR spectrum (CDCl₃) are shown. The structure is a phosphonate derivative of a brominated phenol. The spectrum displays peaks for the compound, with chemical shifts (ppm) labeled above the peaks:

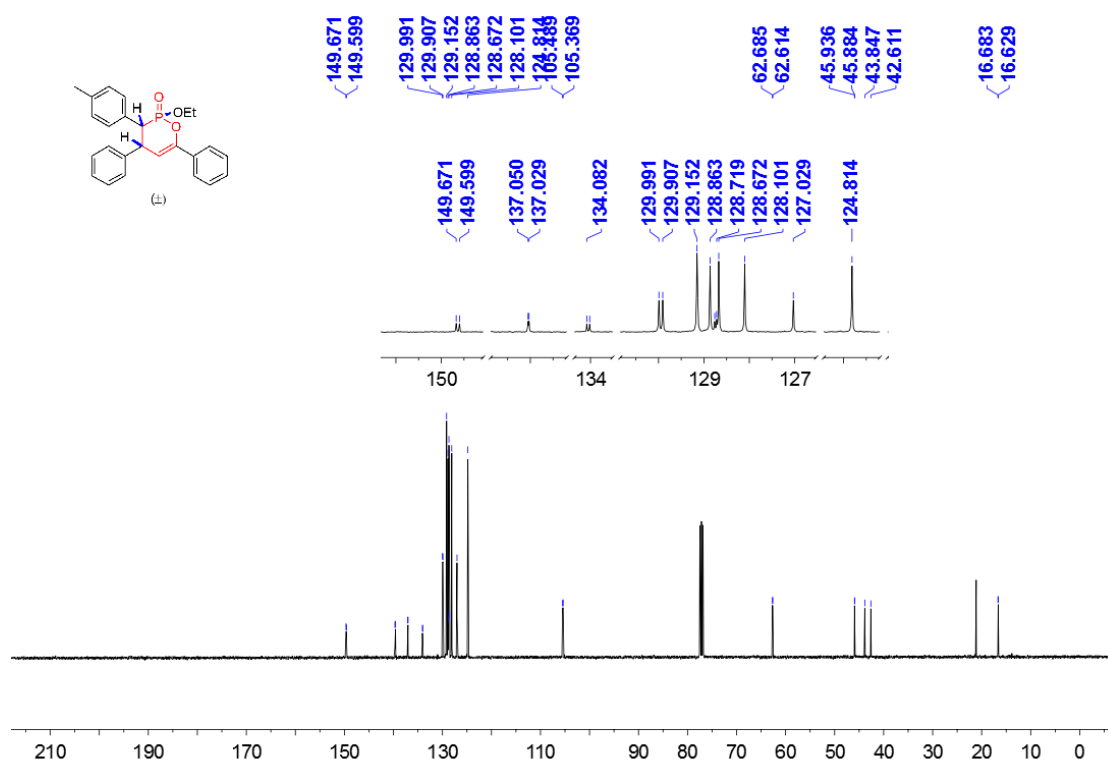
Chemical structure (L): CCOP(=O)(c1ccccc1)c2ccccc2C3=CC=C(C=C3)C4=CC=C(C=C4)C5=CC=C(C=C5)Br

¹³C NMR peaks (ppm):

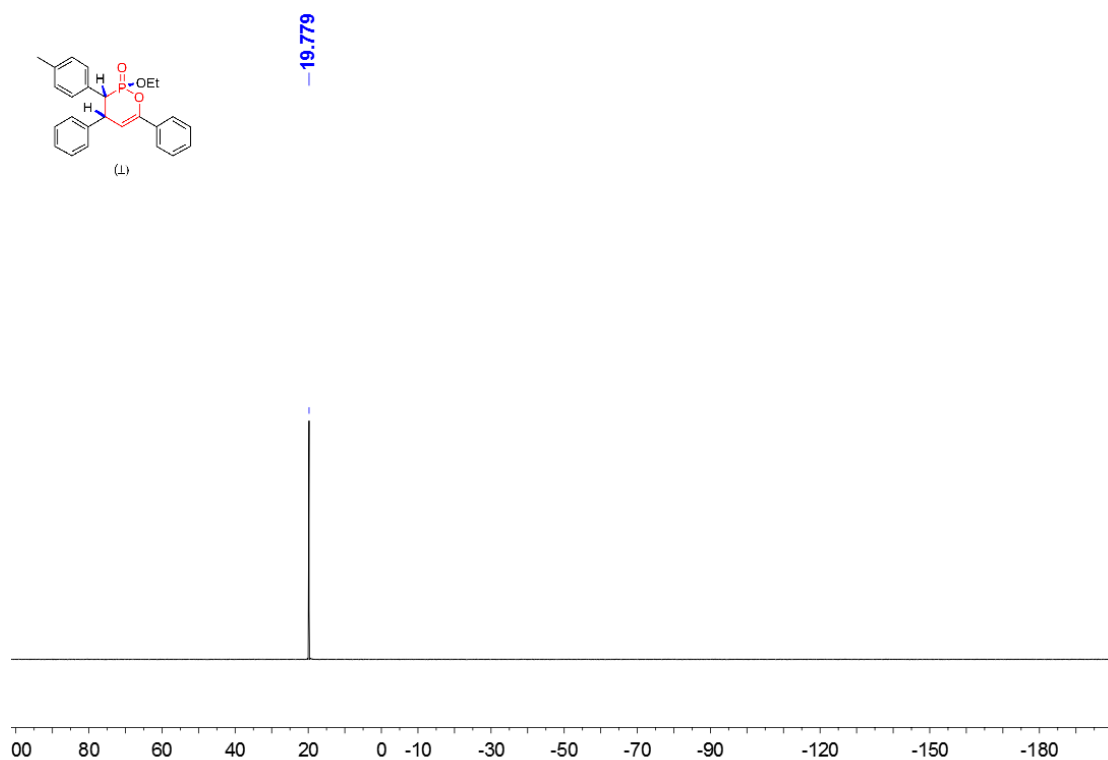
- 148.654, 148.581, 141.324, 141.186, 133.635, 131.934, 131.133, 131.066, 129.258, 129.013, 128.908, 128.682, 127.972, 127.574, 124.840, 121.938
- 63.086, 63.010, 47.613, 47.565, 46.443, 45.218
- 16.611, 16.559

S144

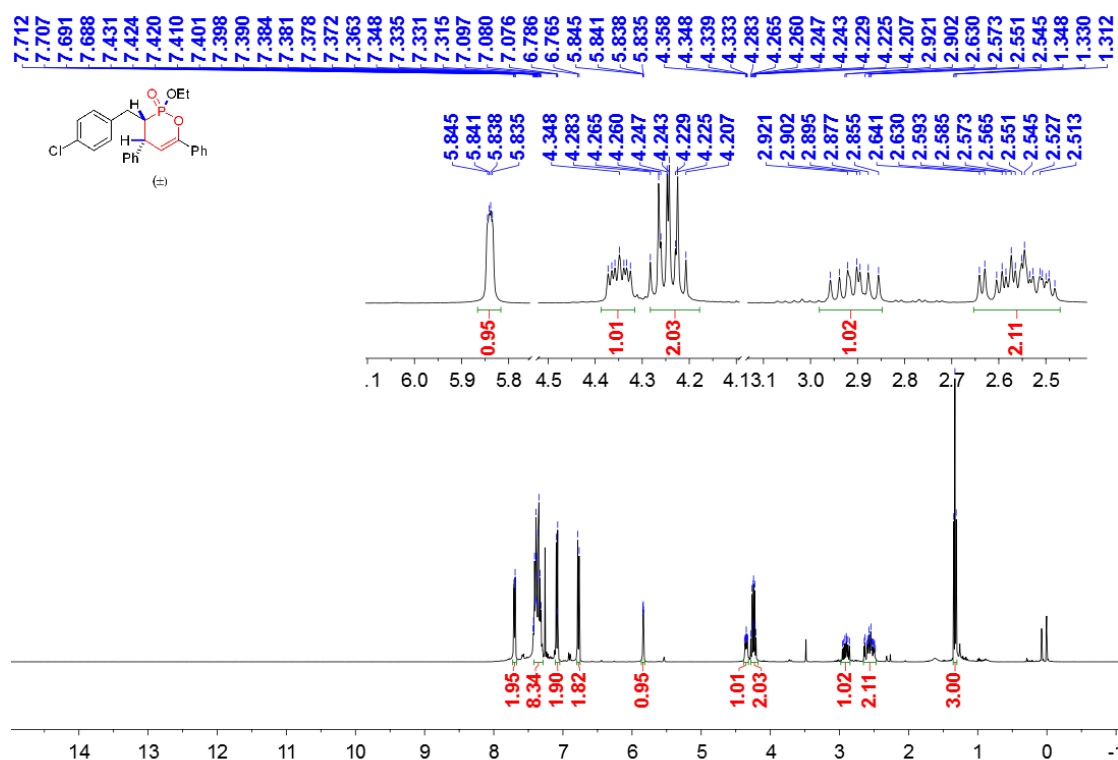




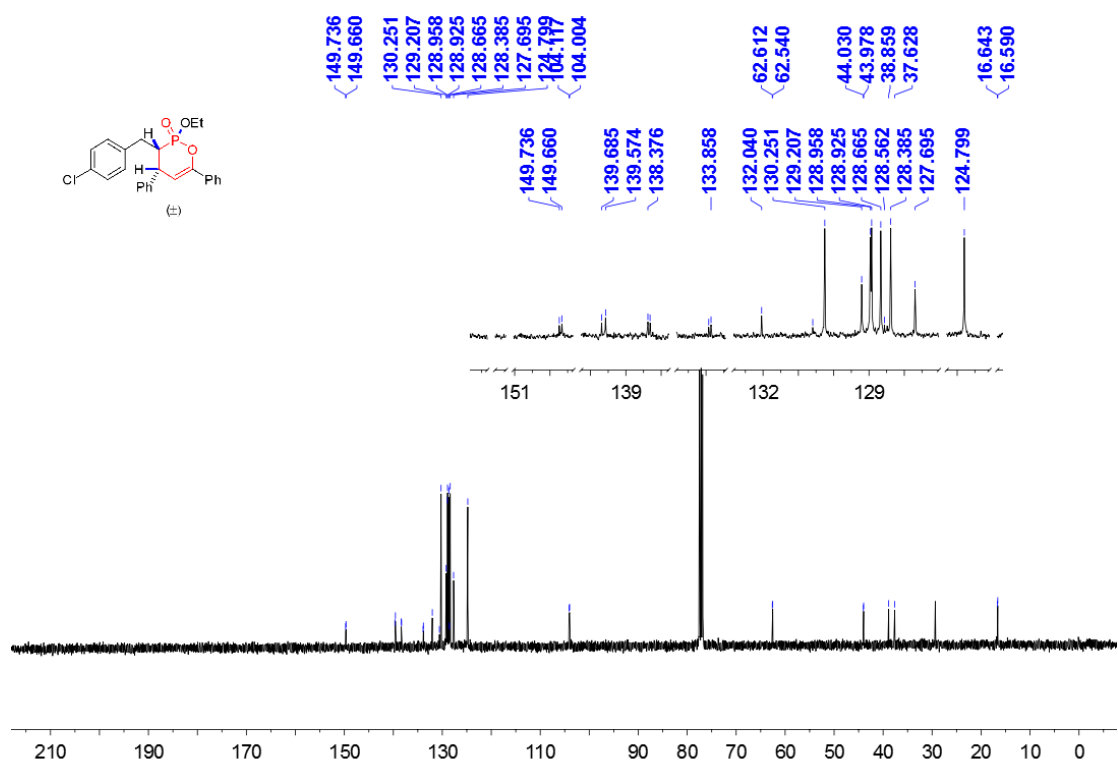
¹³C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3ai



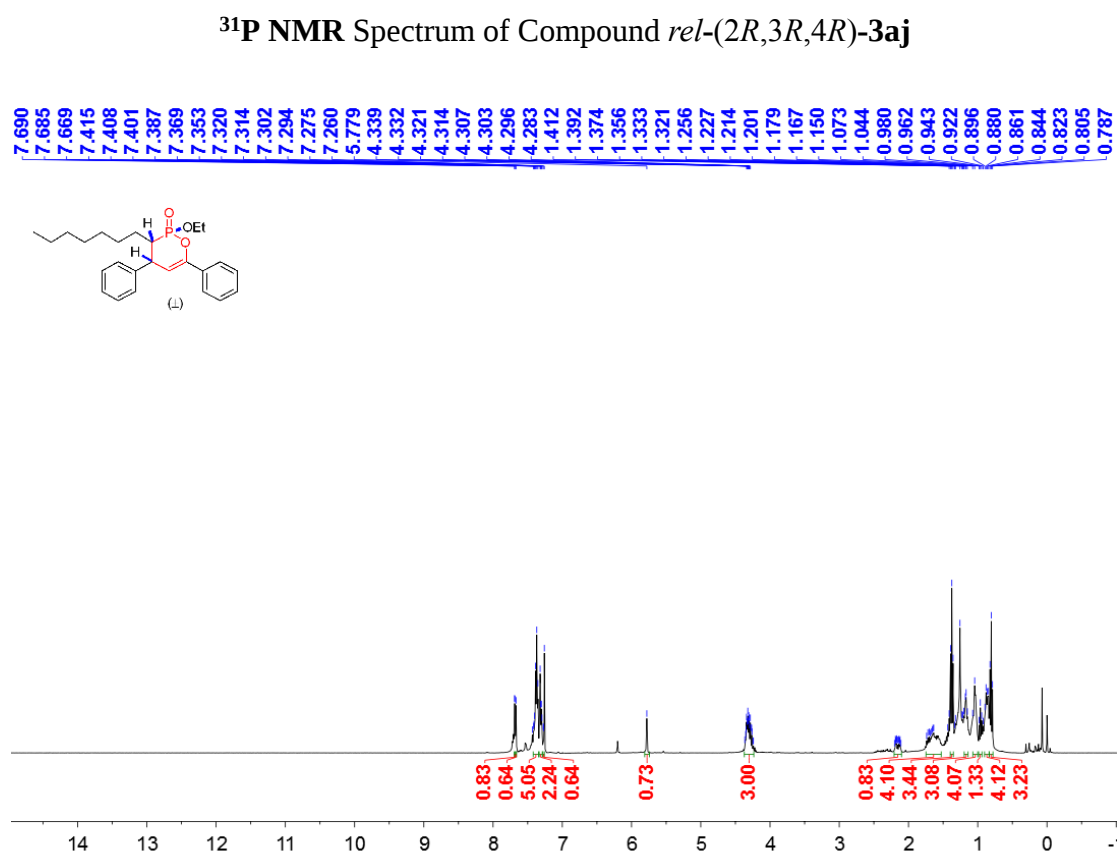
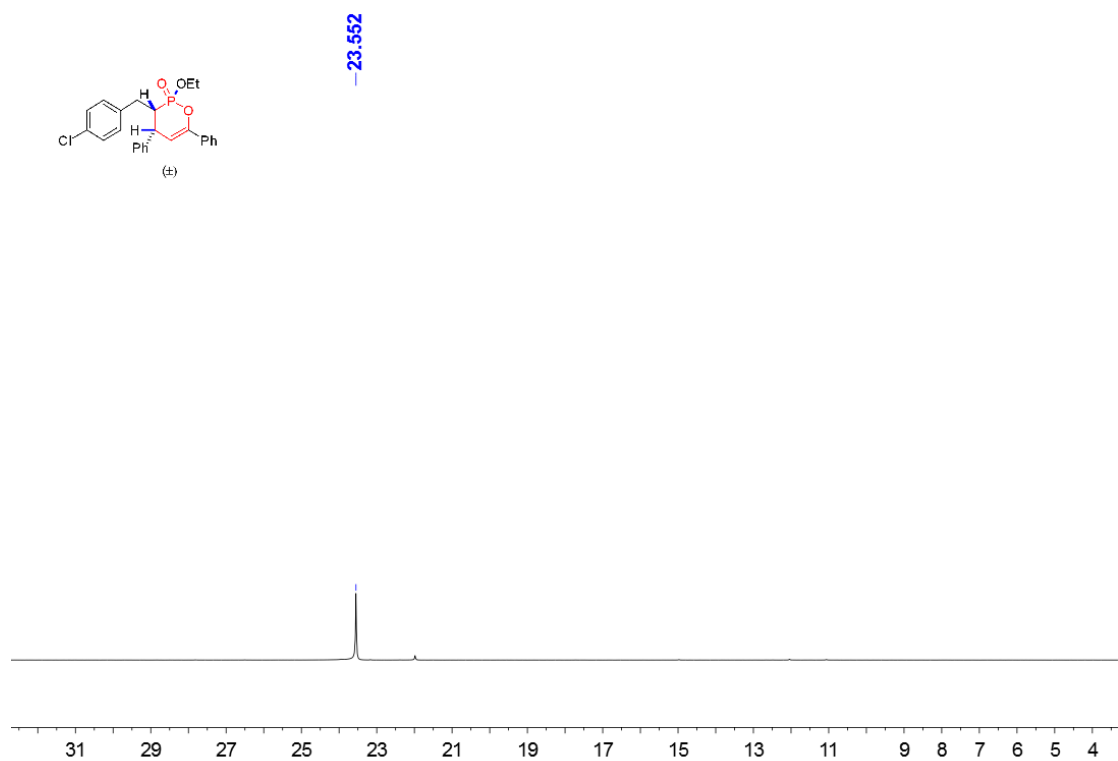
³¹P NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3ai

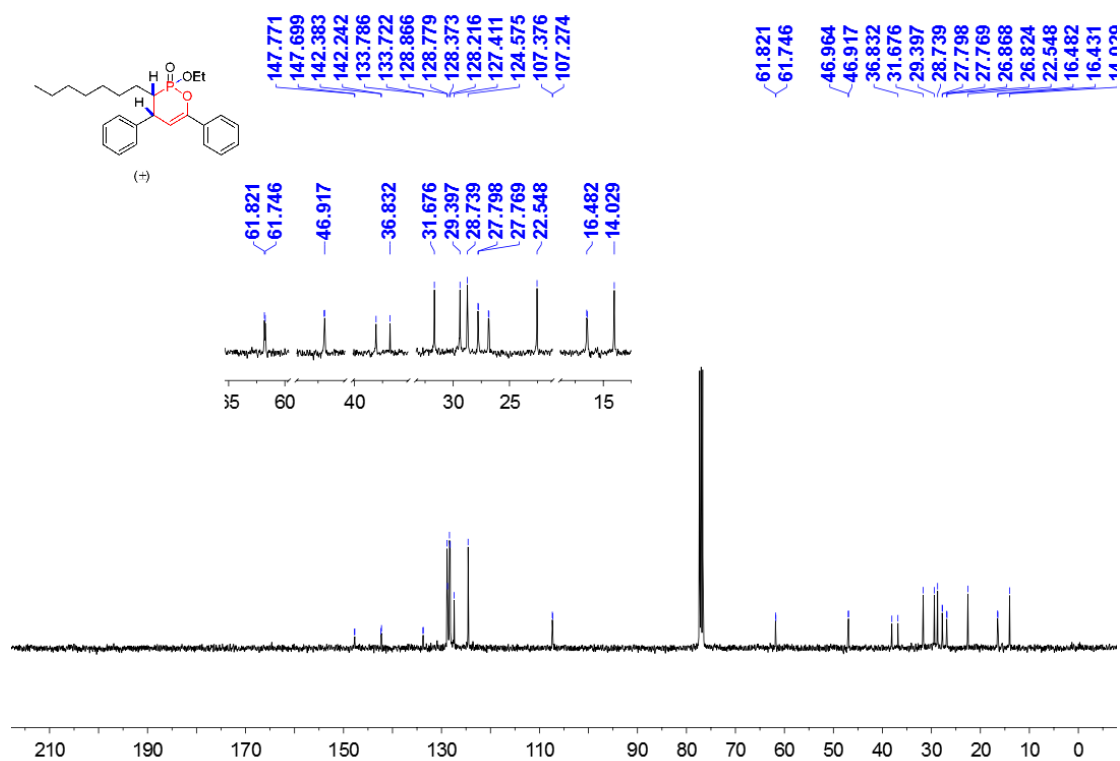


¹H NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3aj

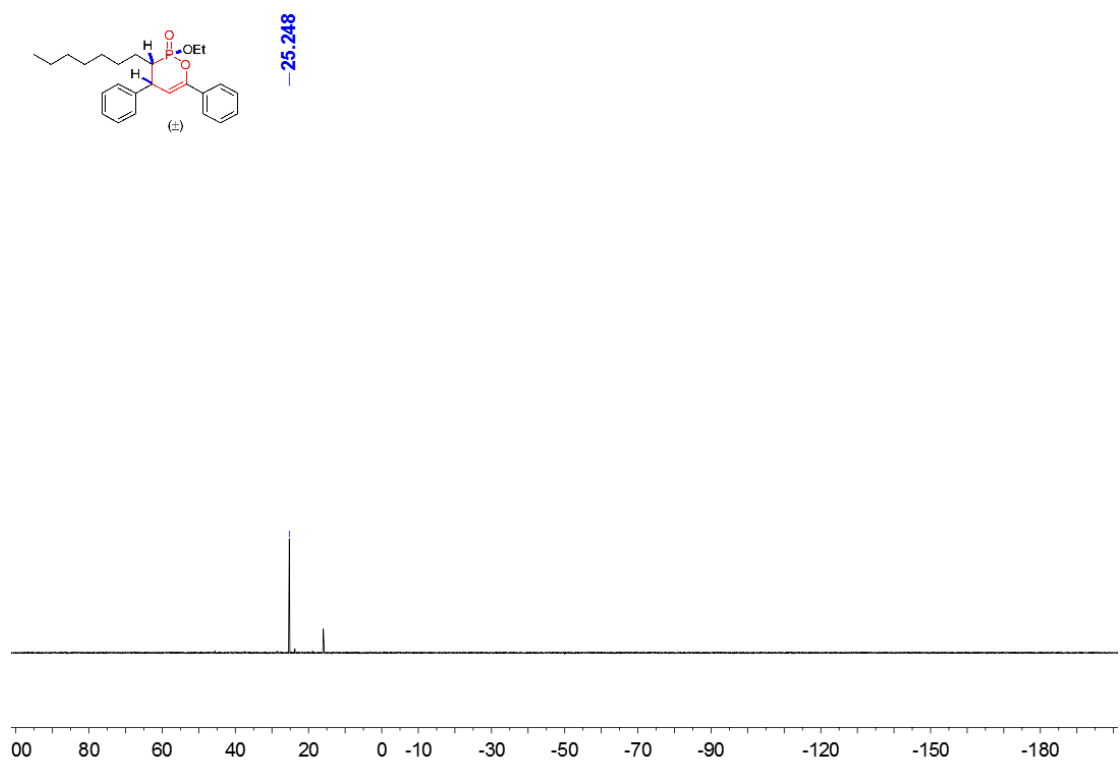


¹³C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3aj



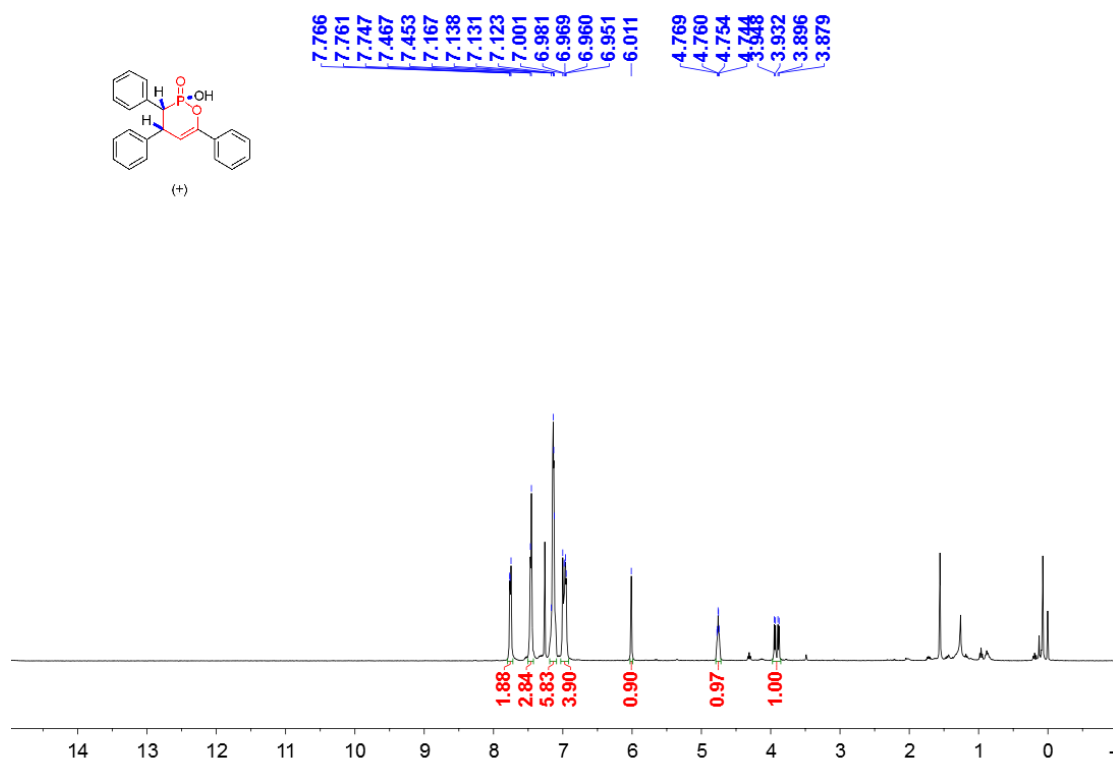


¹³C NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3ak

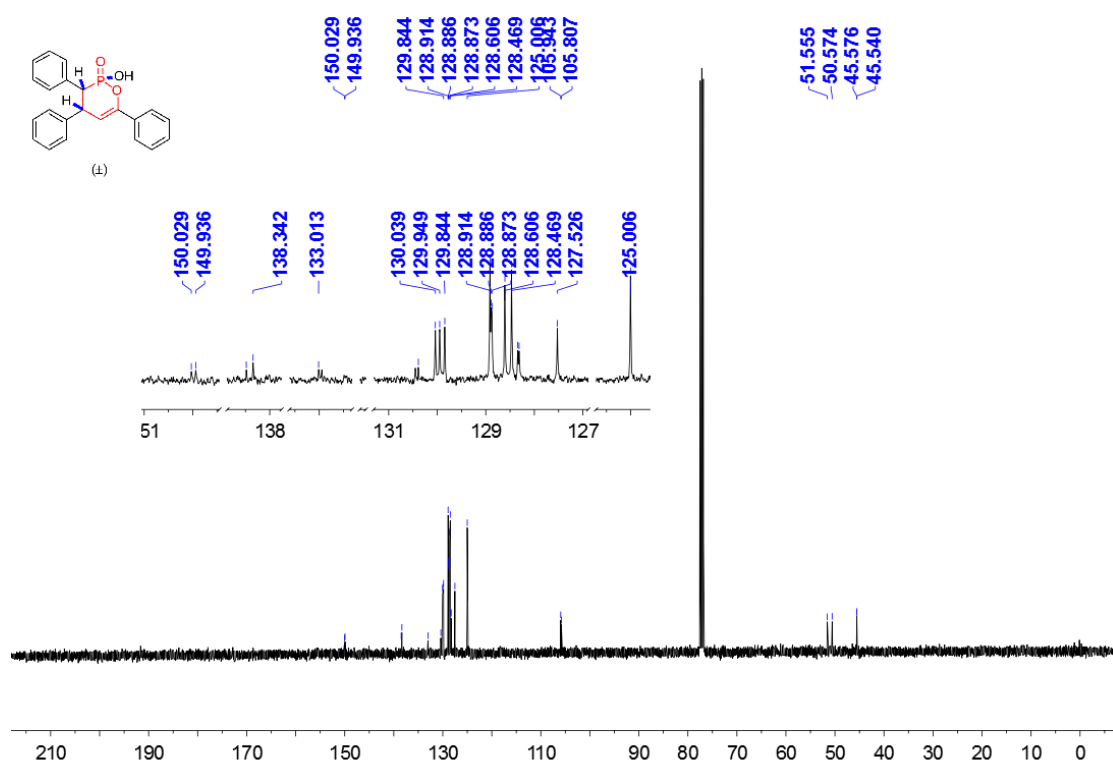


³¹P NMR Spectrum of Compound *rel*-(2*R*,3*R*,4*R*)-3ak

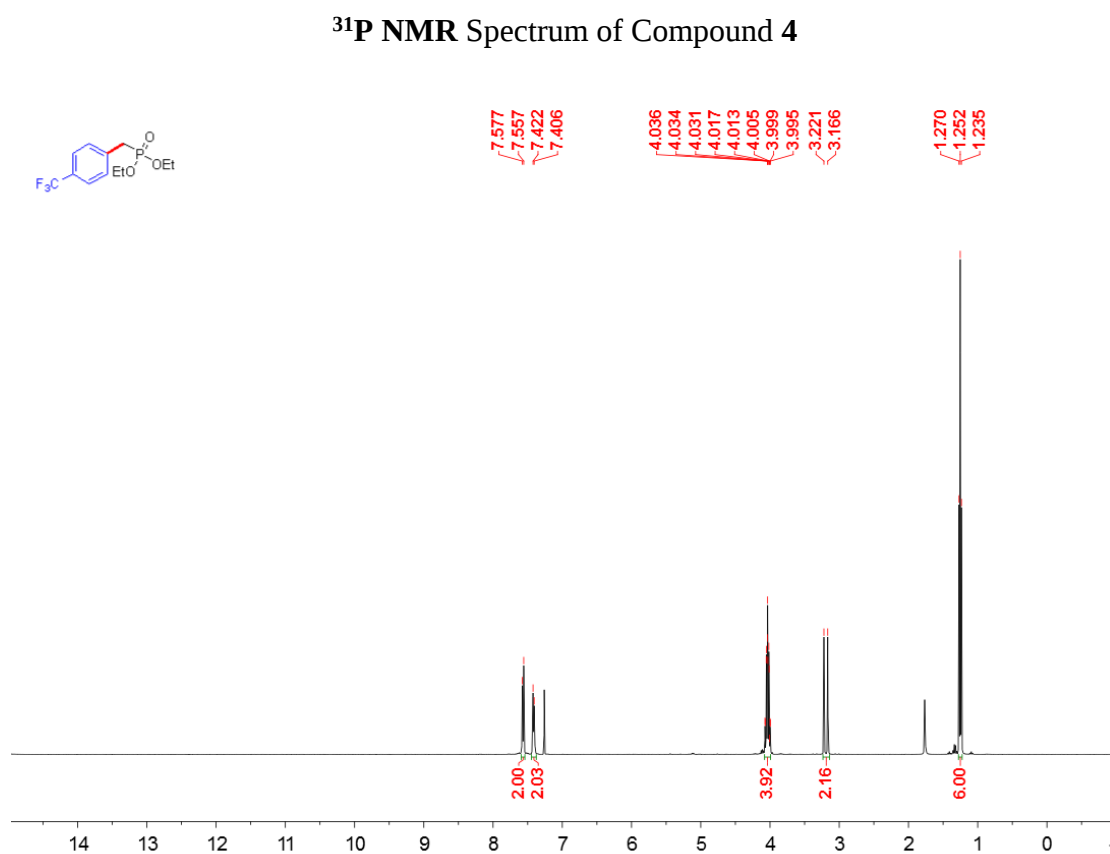
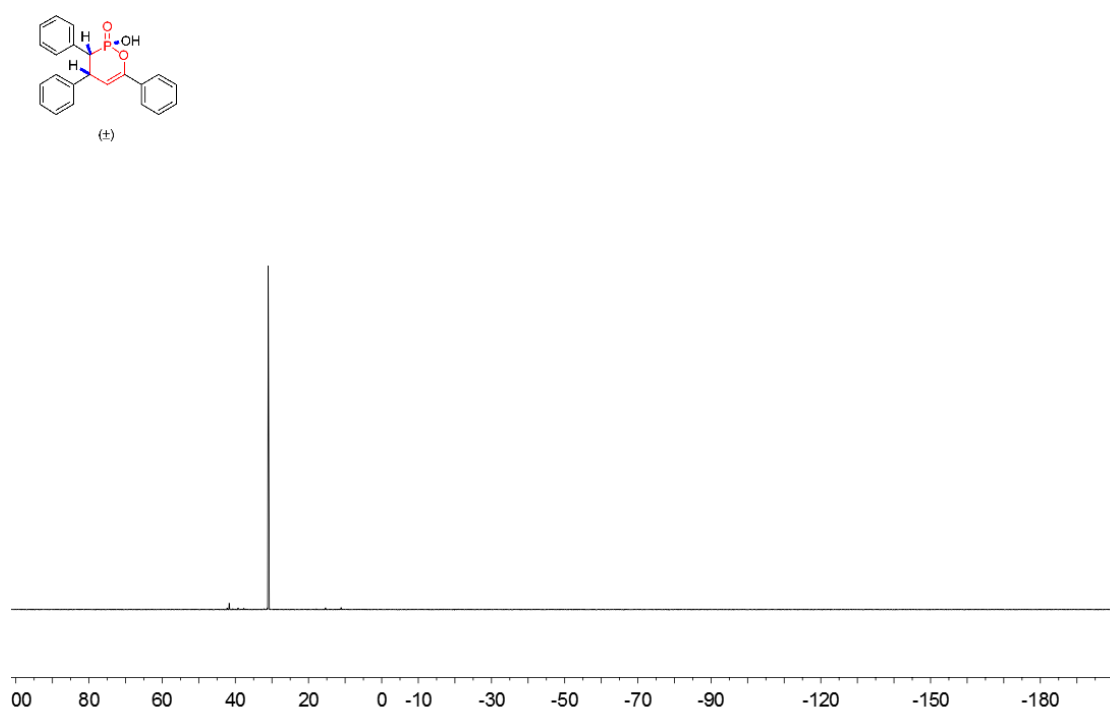
6.3. Copies of ^1H , ^{13}C , and ^{31}P spectra of products 4, 6 and 7

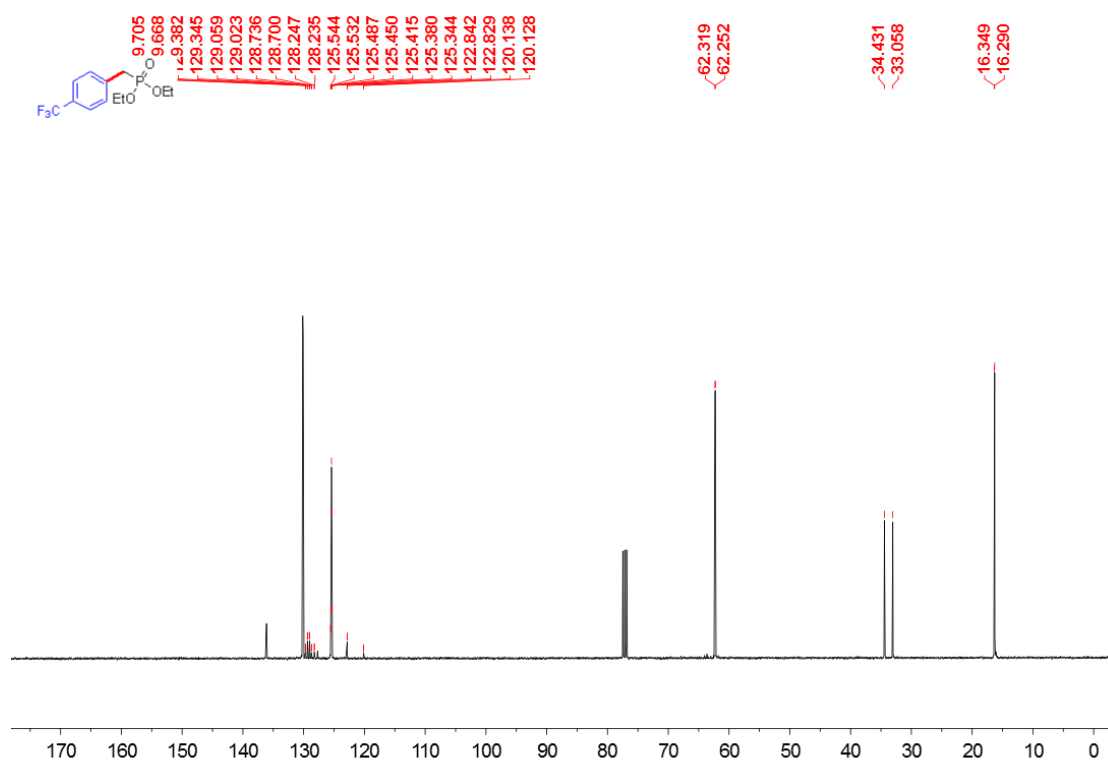


^1H NMR Spectrum of Compound 4

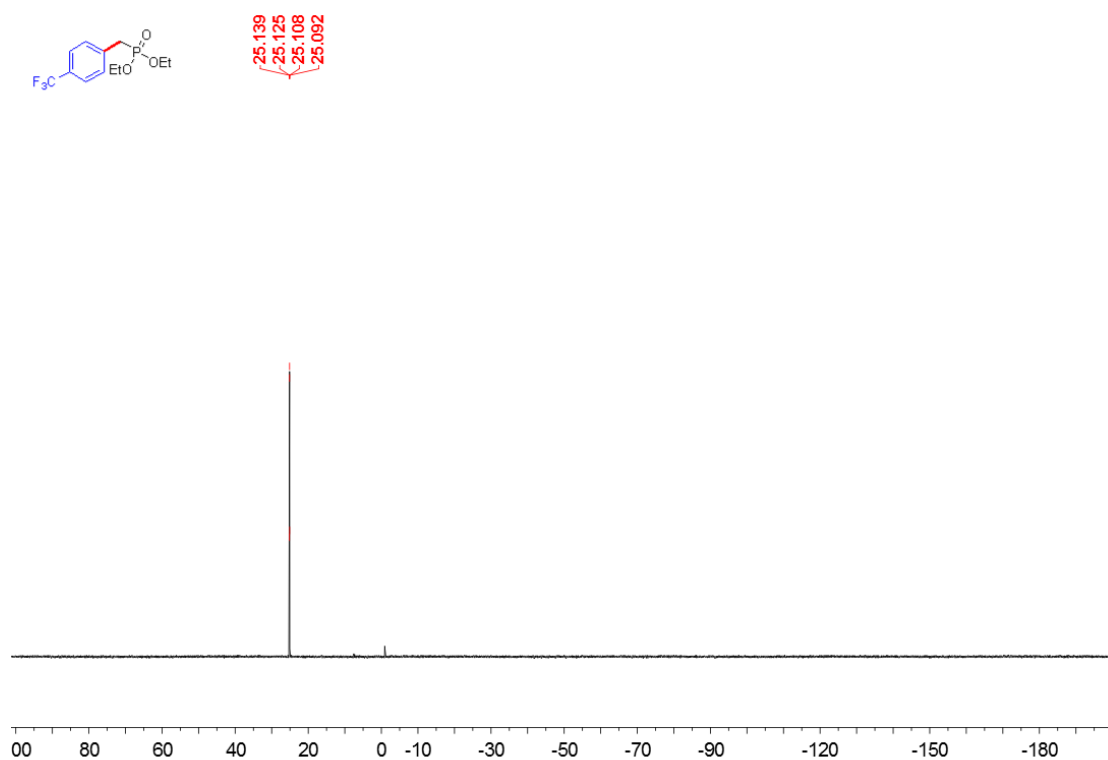


^{13}C NMR Spectrum of Compound 4

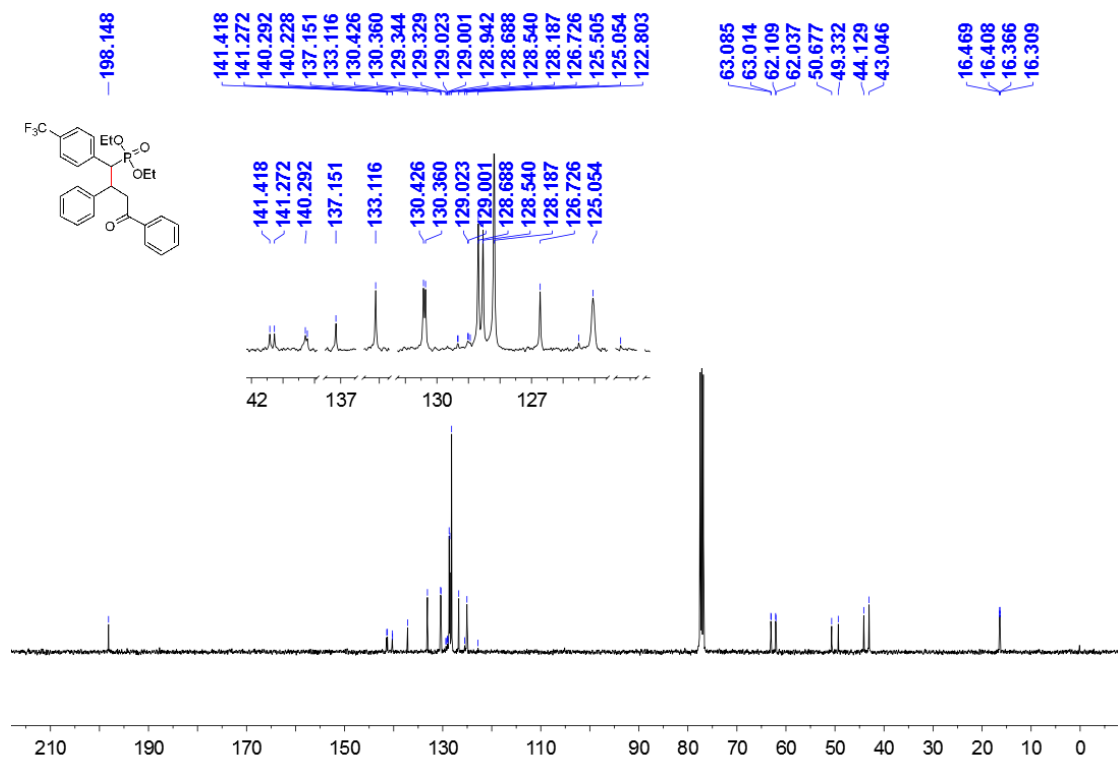
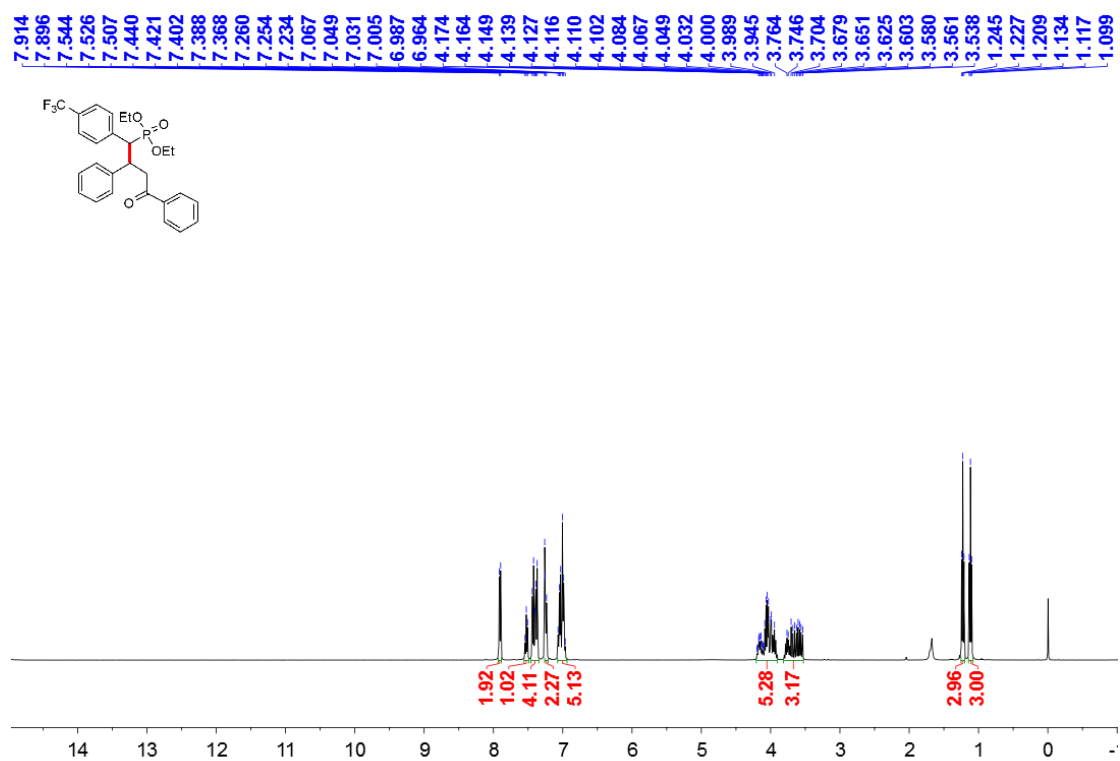


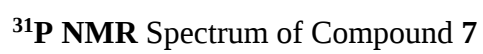


¹³C NMR Spectrum of Compound 6

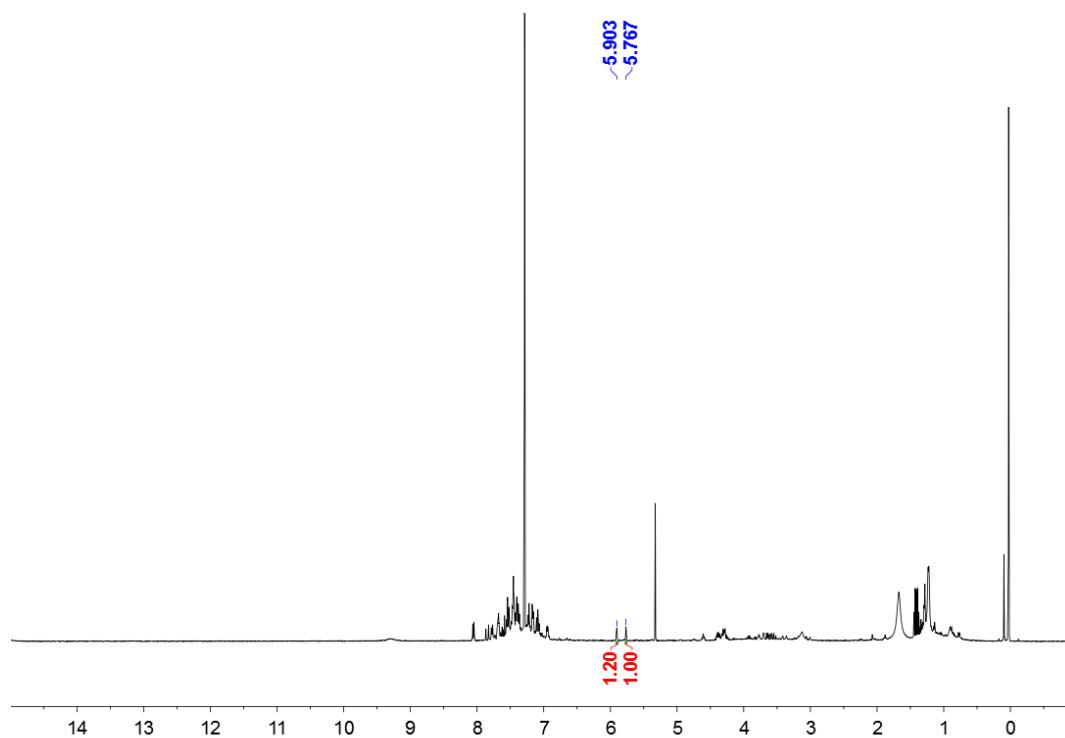


³¹P NMR Spectrum of Compound 6

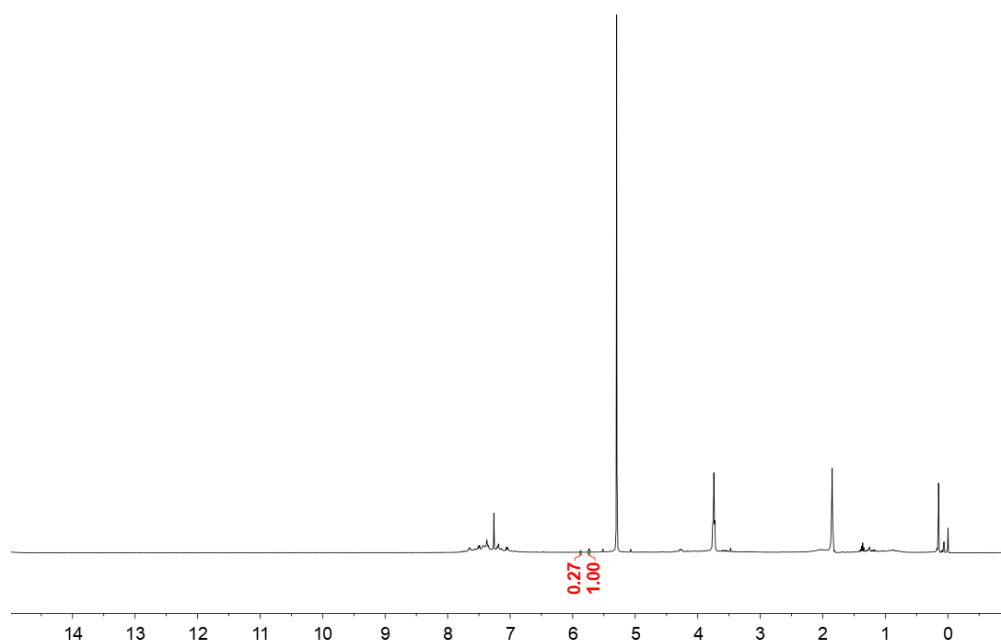




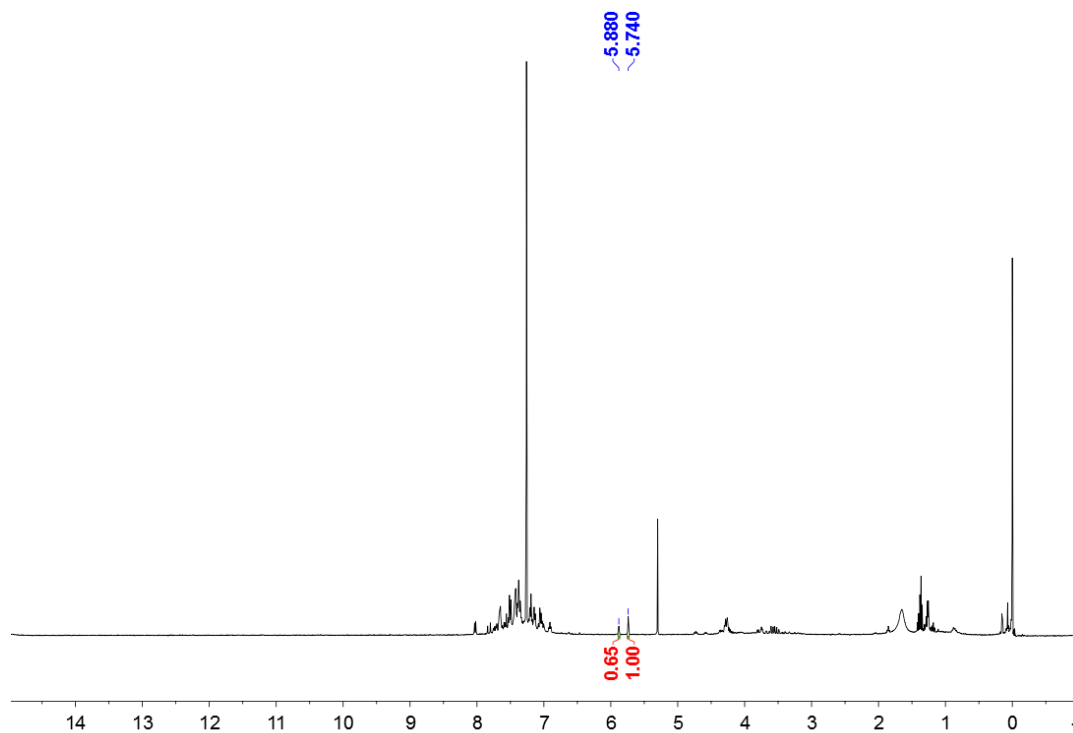
6.4. Copies of ^1H NMR spectra of the crude reaction mixtures in optimization of the reaction conditions



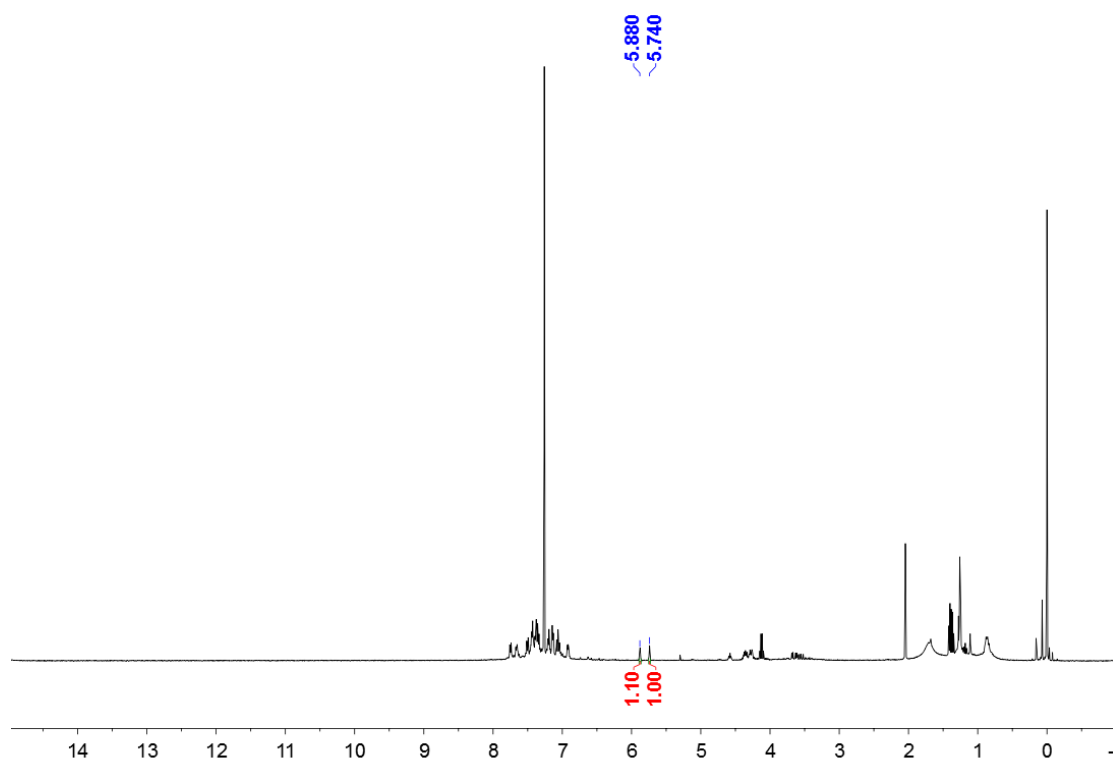
^1H NMR Spectrum of Entry 3



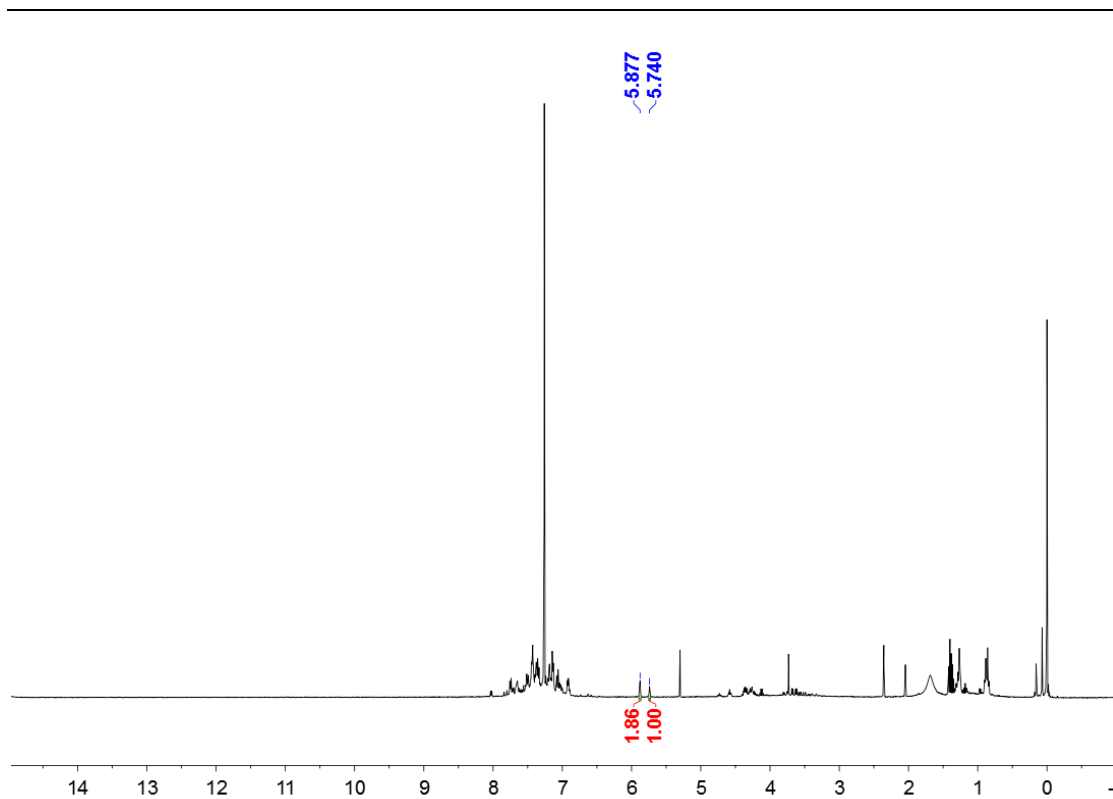
^1H NMR Spectrum of Entry 4



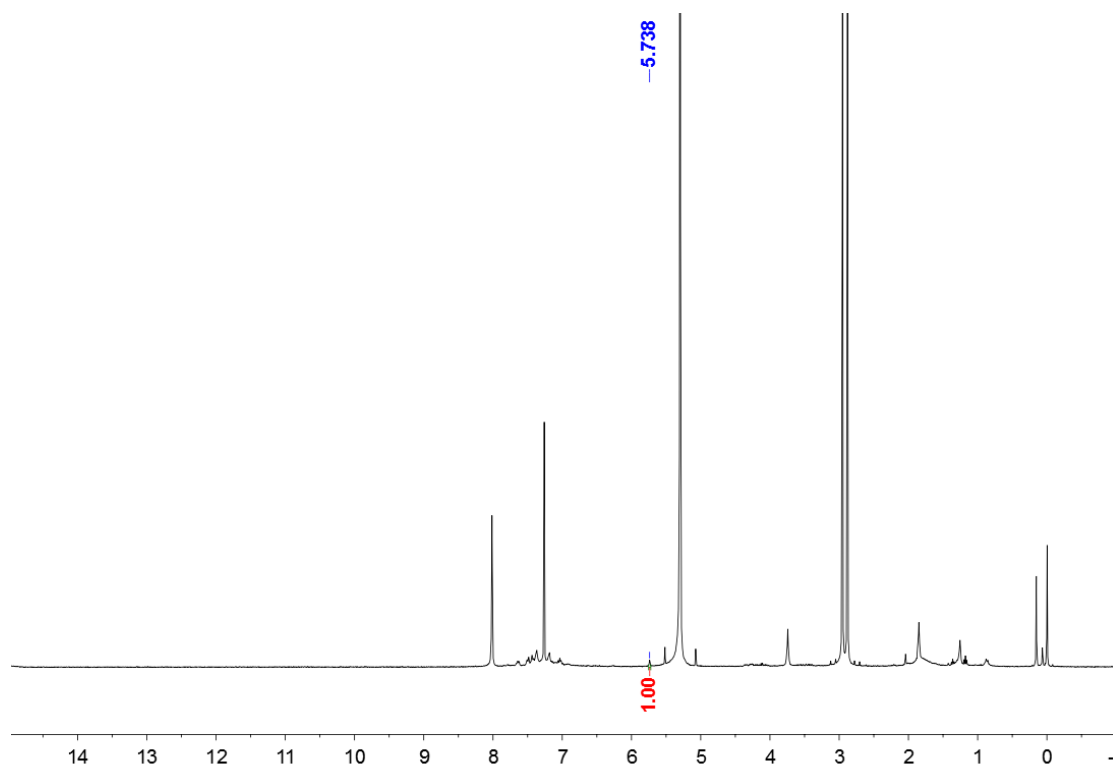
¹H NMR Spectrum of Entry 5



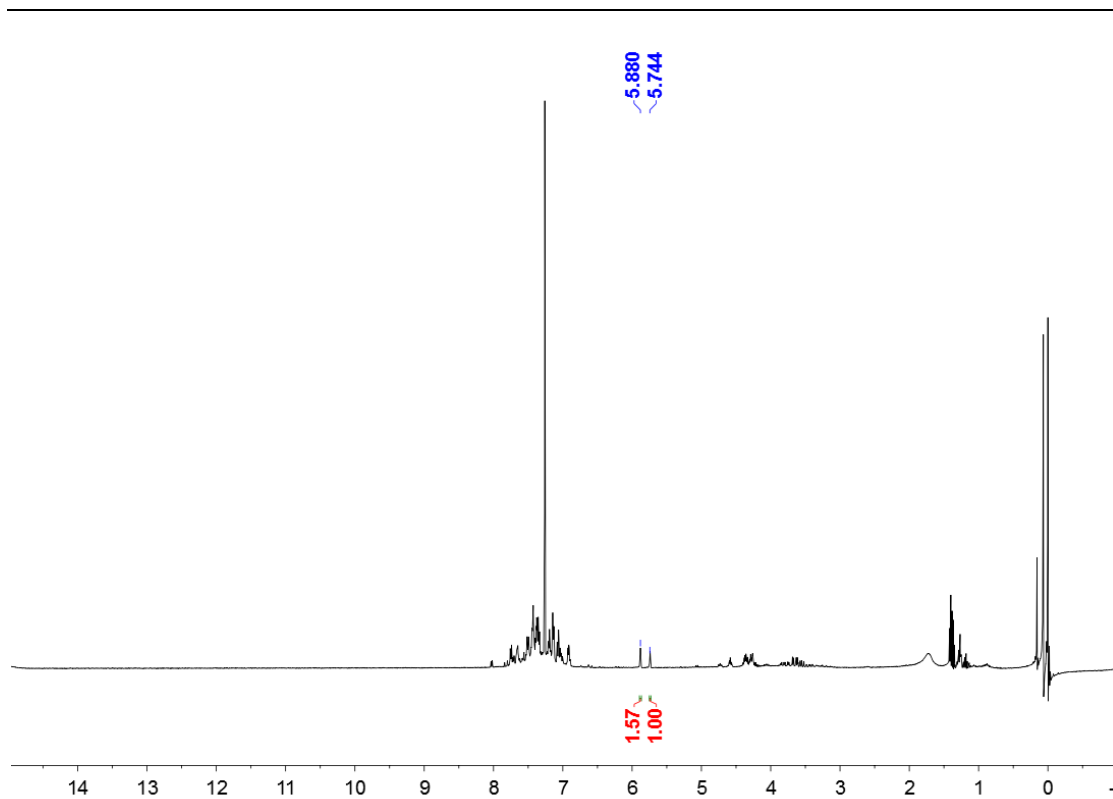
¹H NMR Spectrum of Entry 6



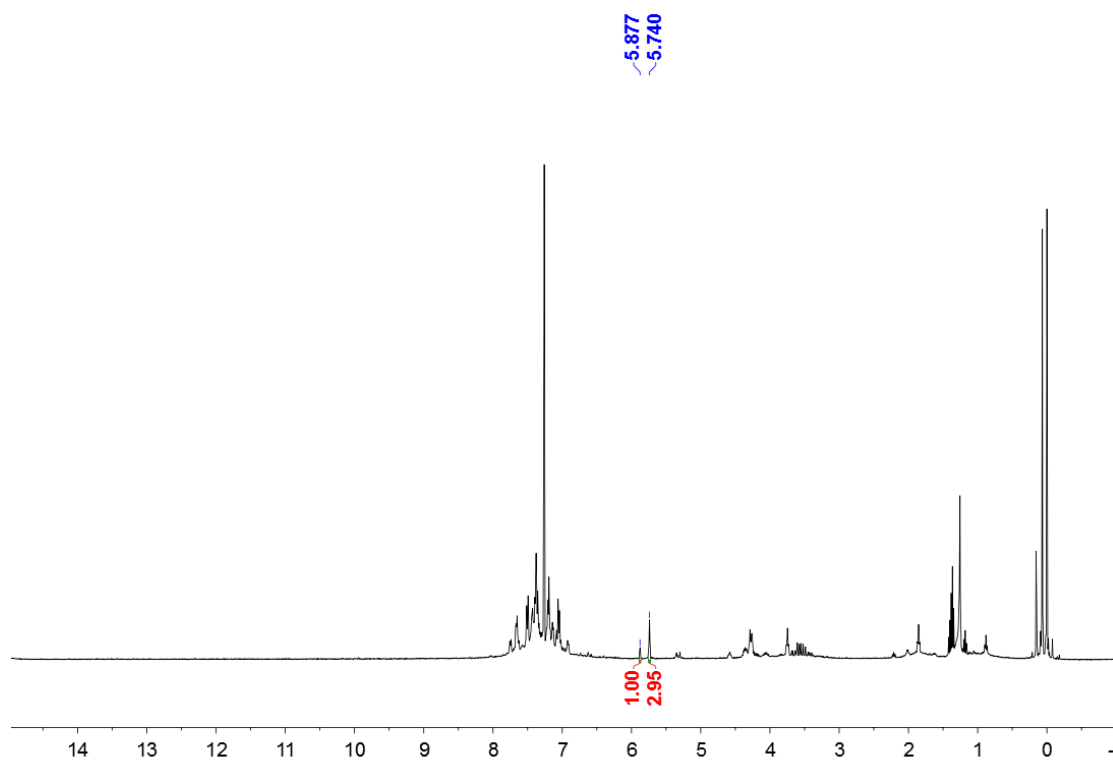
¹H NMR Spectrum of Entry 7



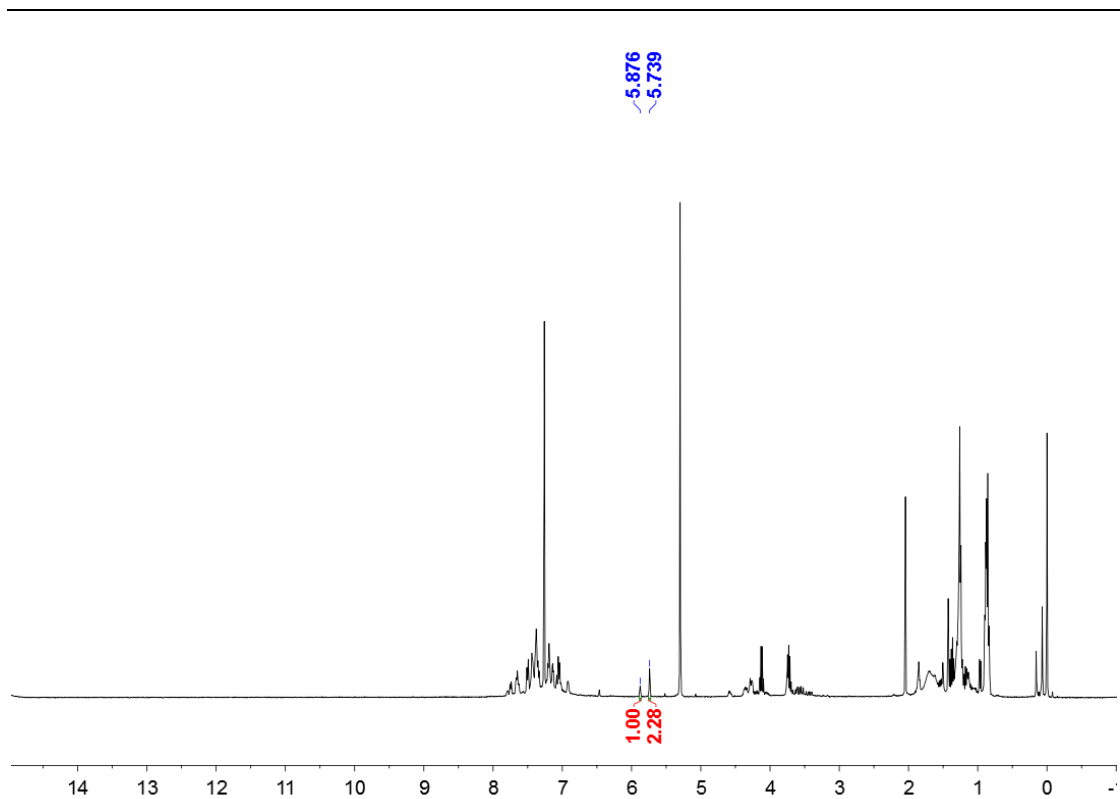
¹H NMR Spectrum of Entry 8



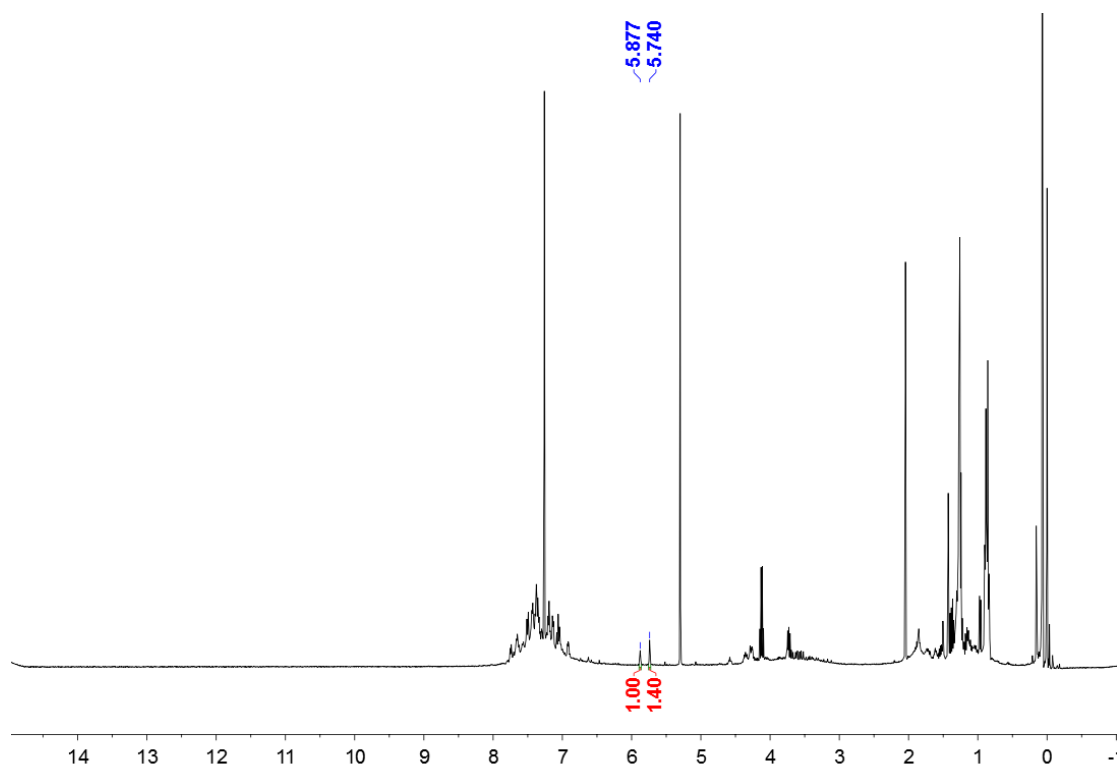
¹H NMR Spectrum of Entry 10



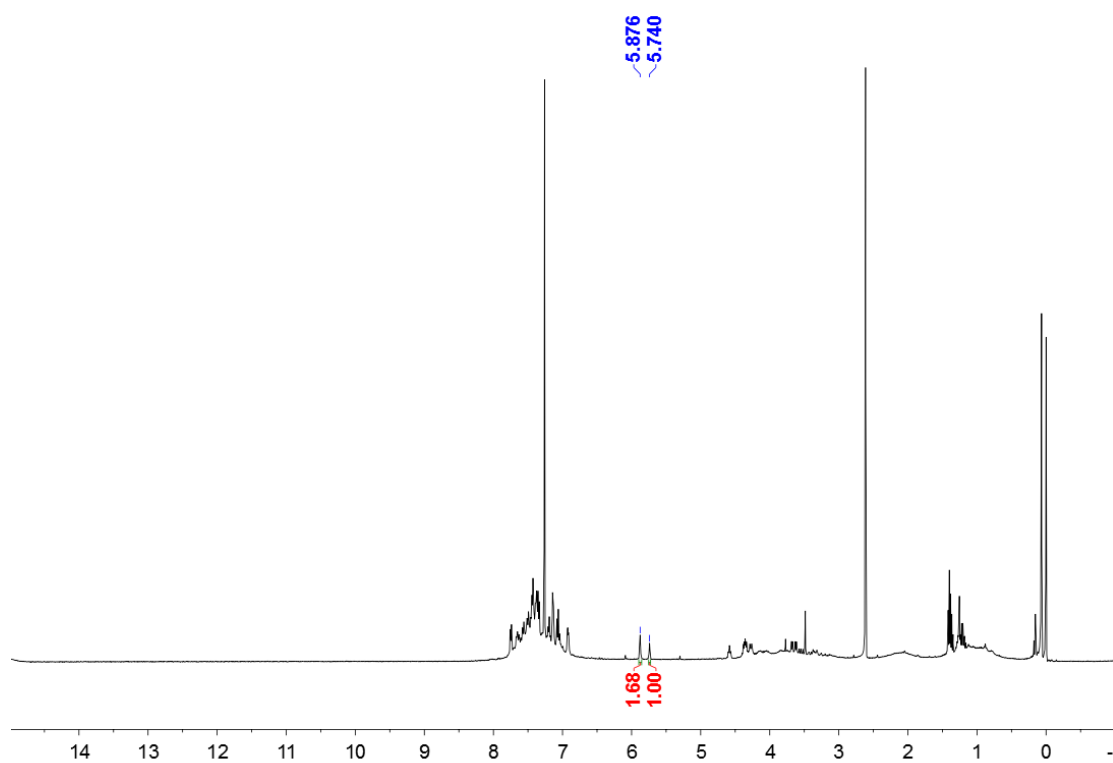
¹H NMR Spectrum of Entry 11



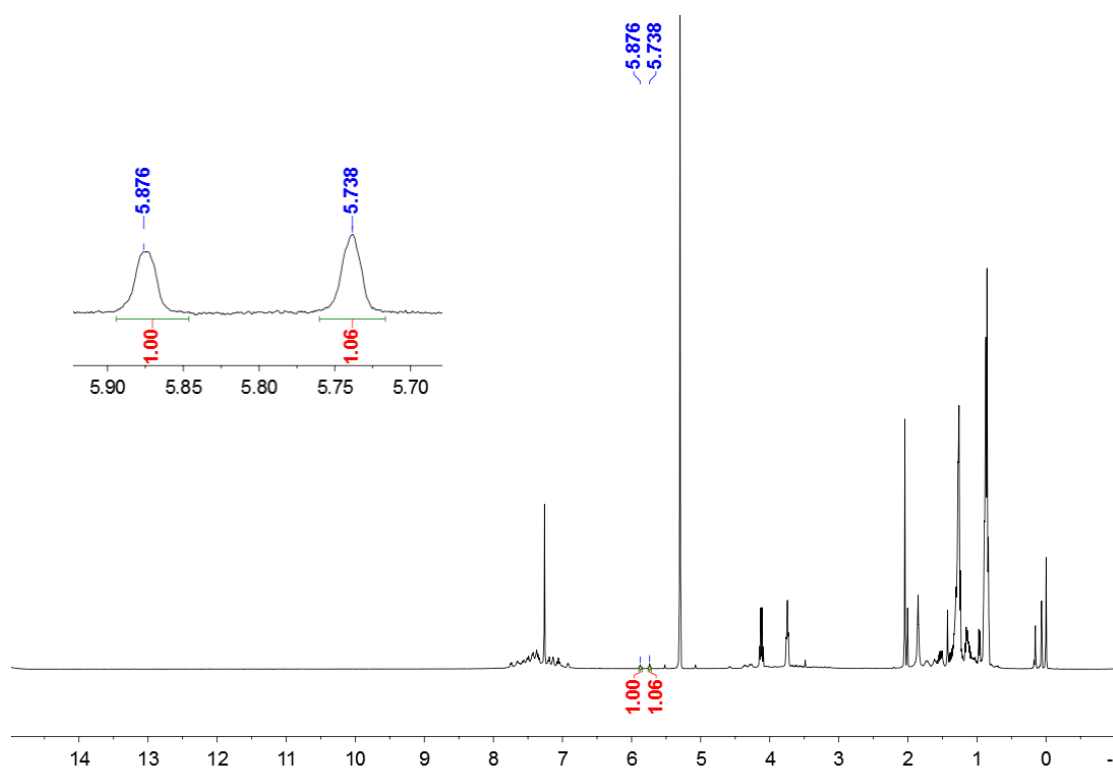
¹H NMR Spectrum of Entry 12



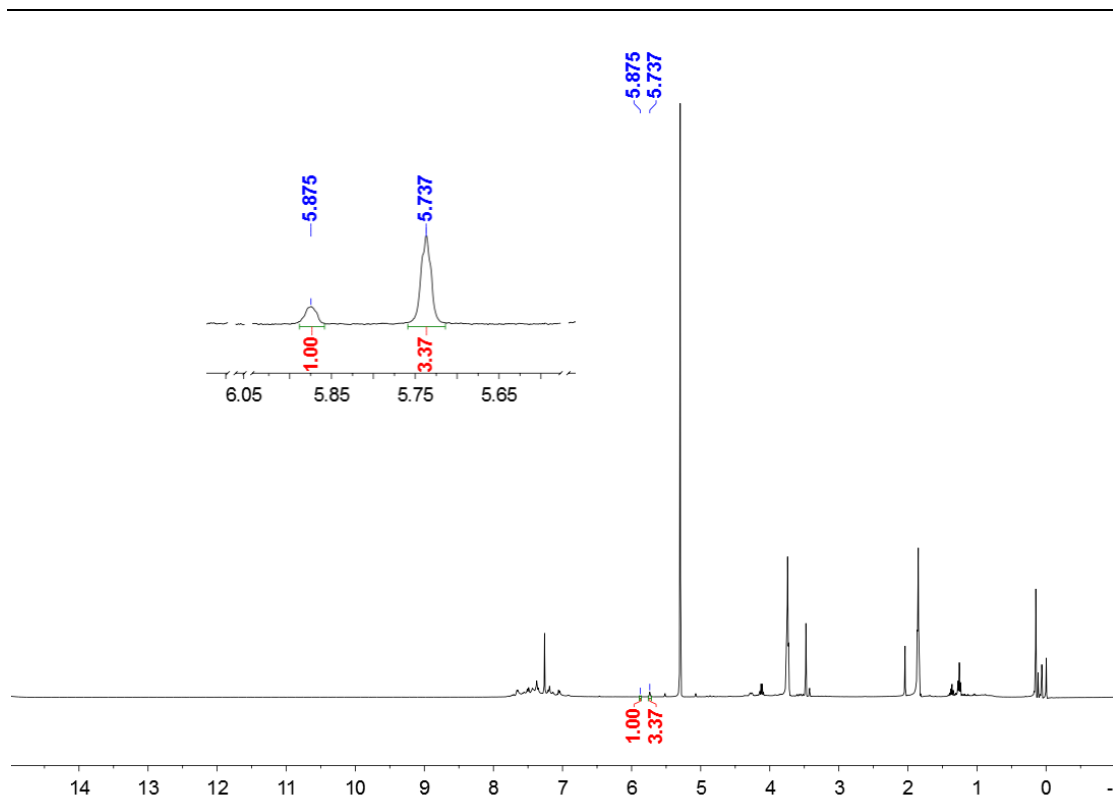
¹H NMR Spectrum of Entry 13



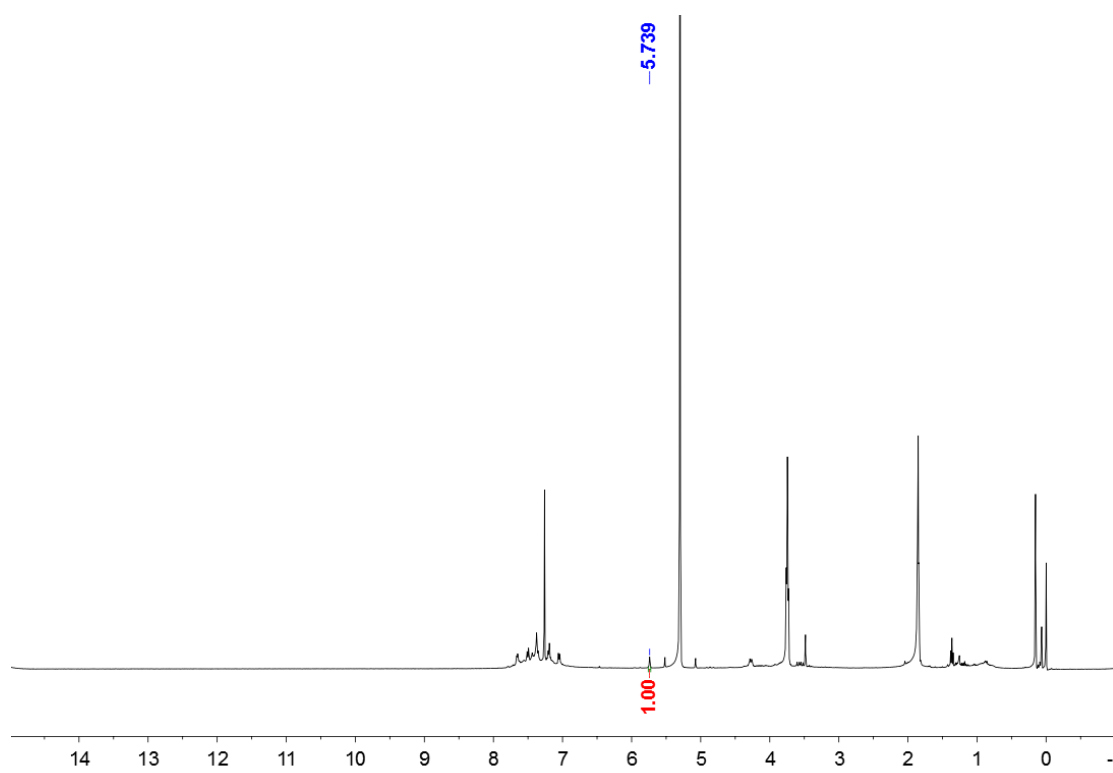
¹H NMR Spectrum of Entry 14



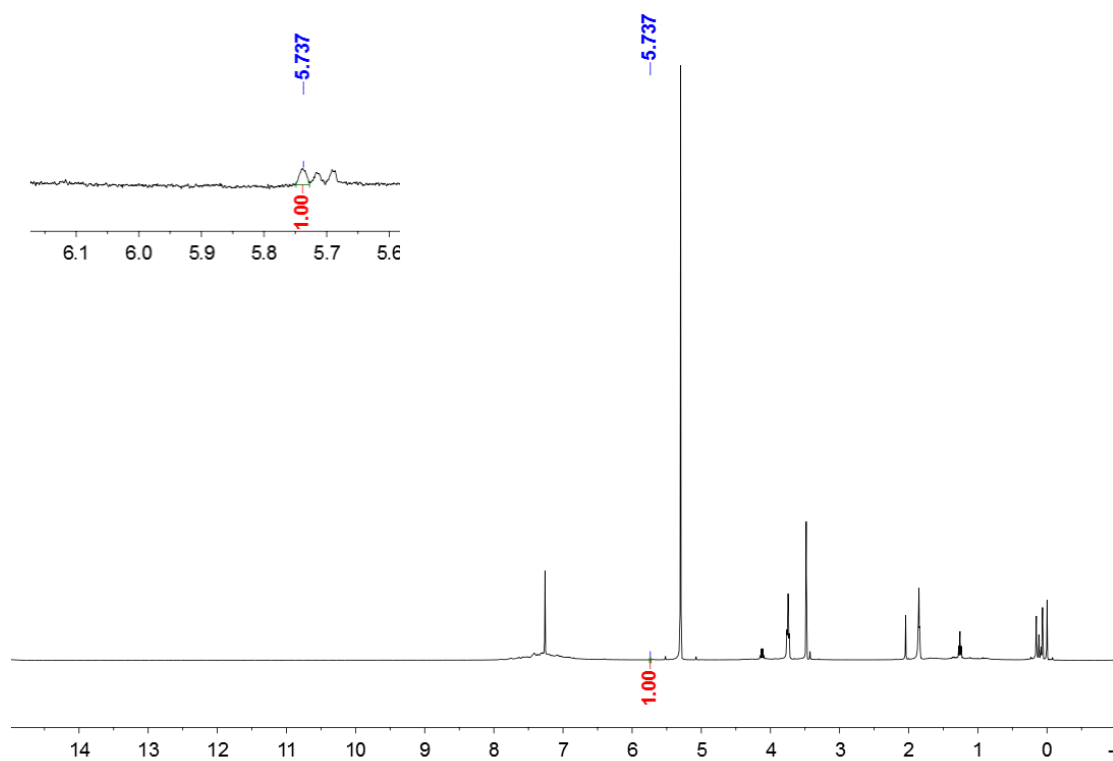
¹H NMR Spectrum of Entry 15



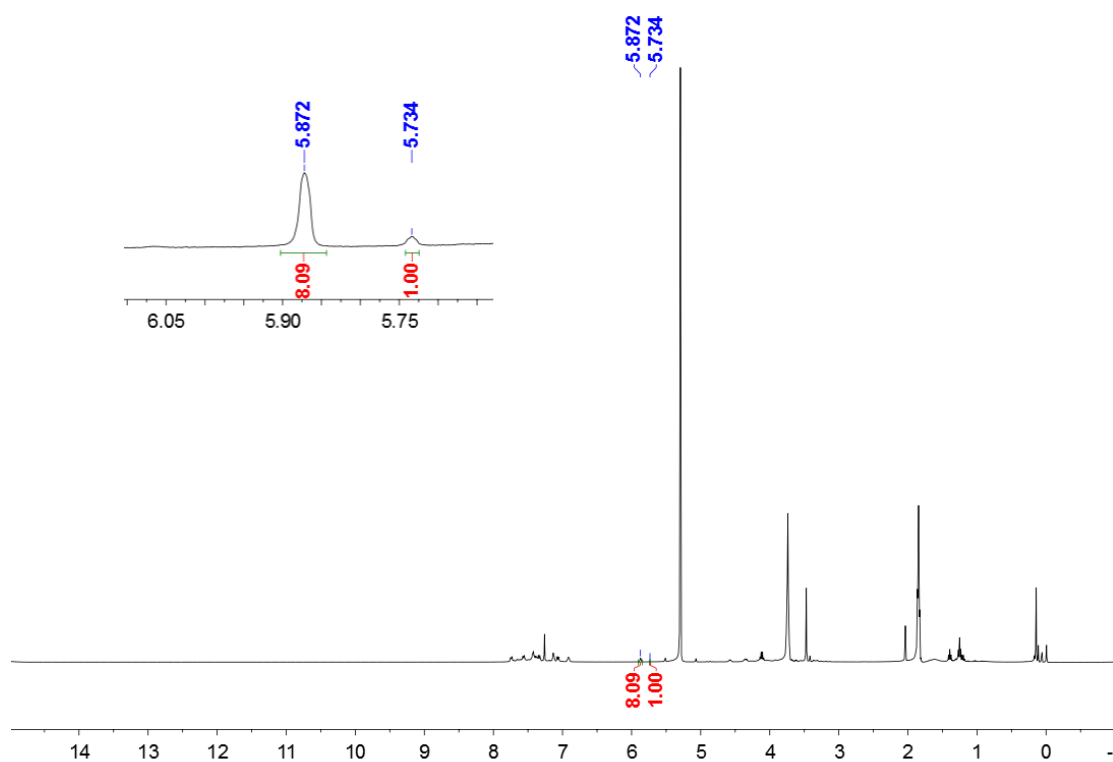
^1H NMR Spectrum of Entry 16



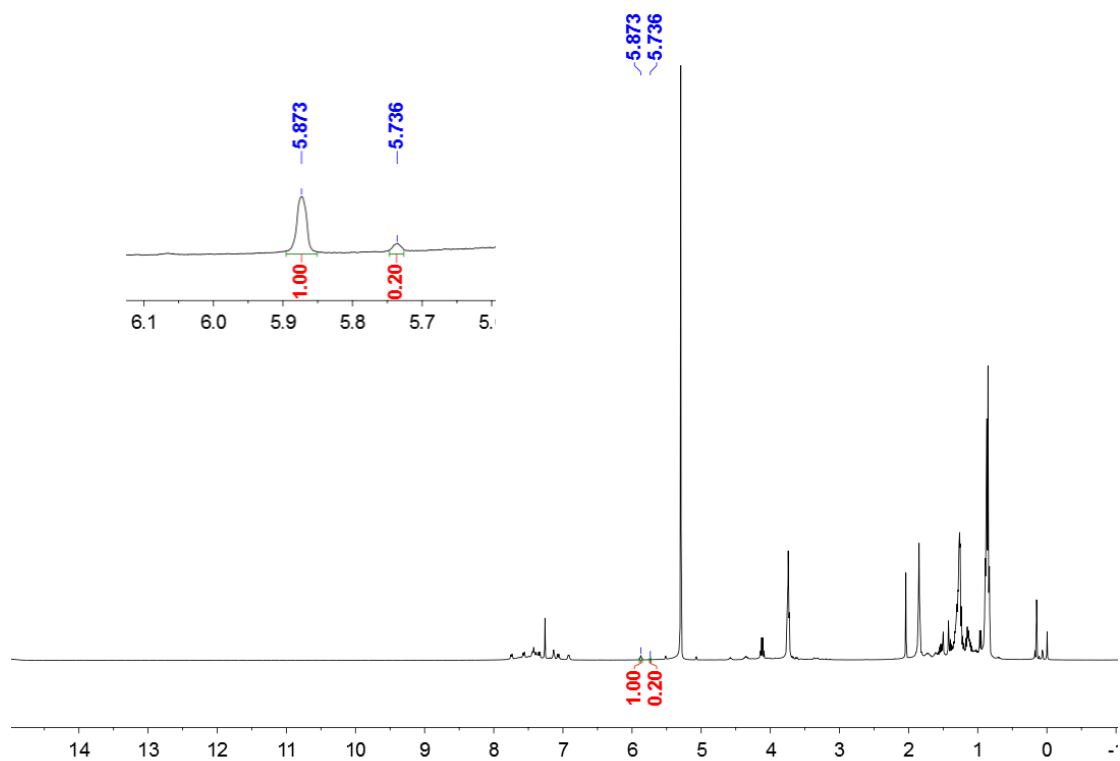
^1H NMR Spectrum of Entry 17



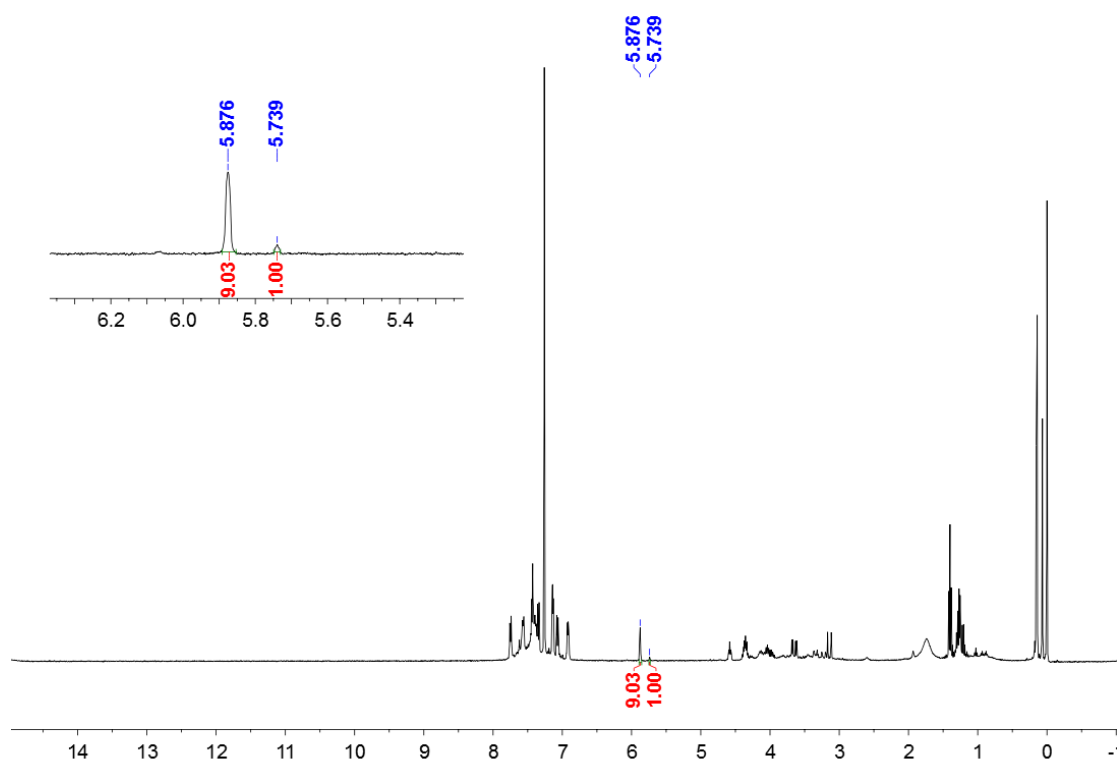
¹H NMR Spectrum of Entry 18



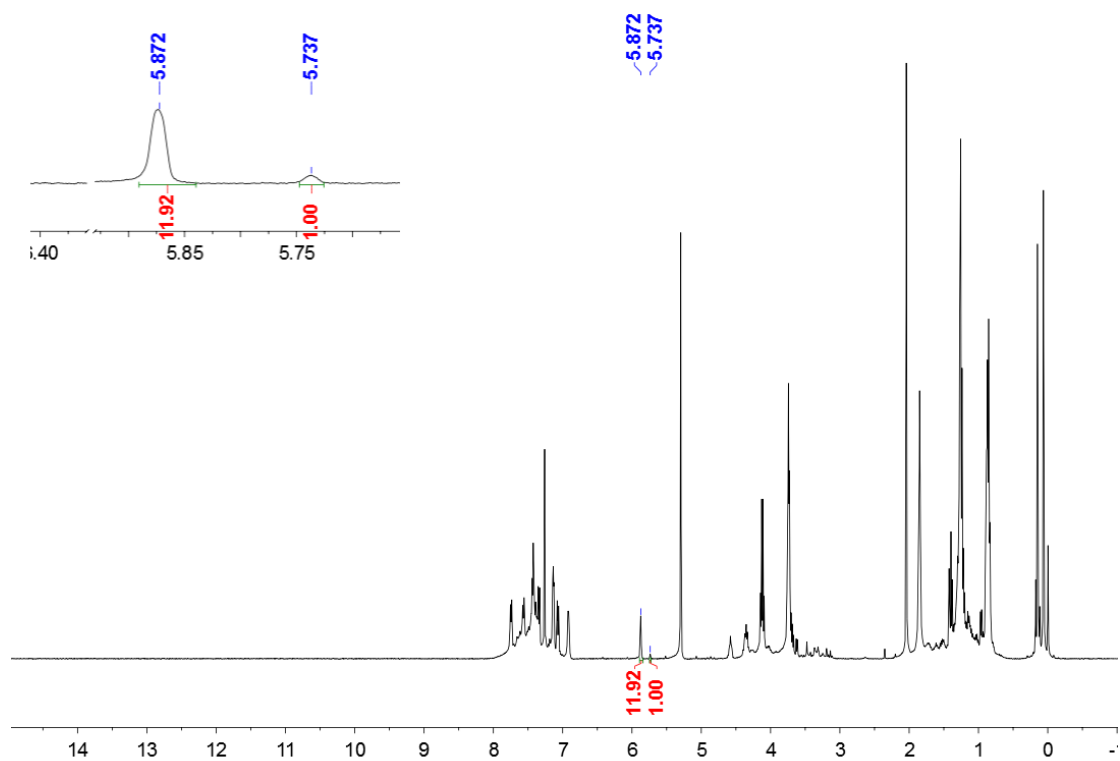
¹H NMR Spectrum of Entry 19



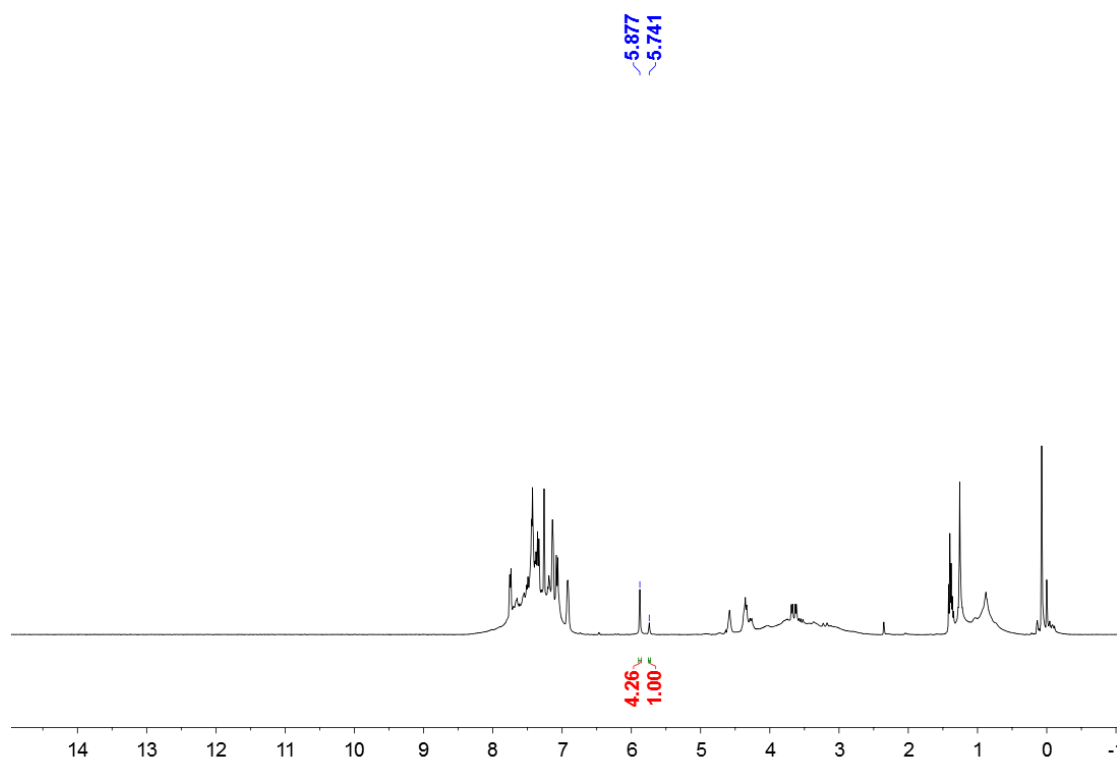
¹H NMR Spectrum of Entry 20



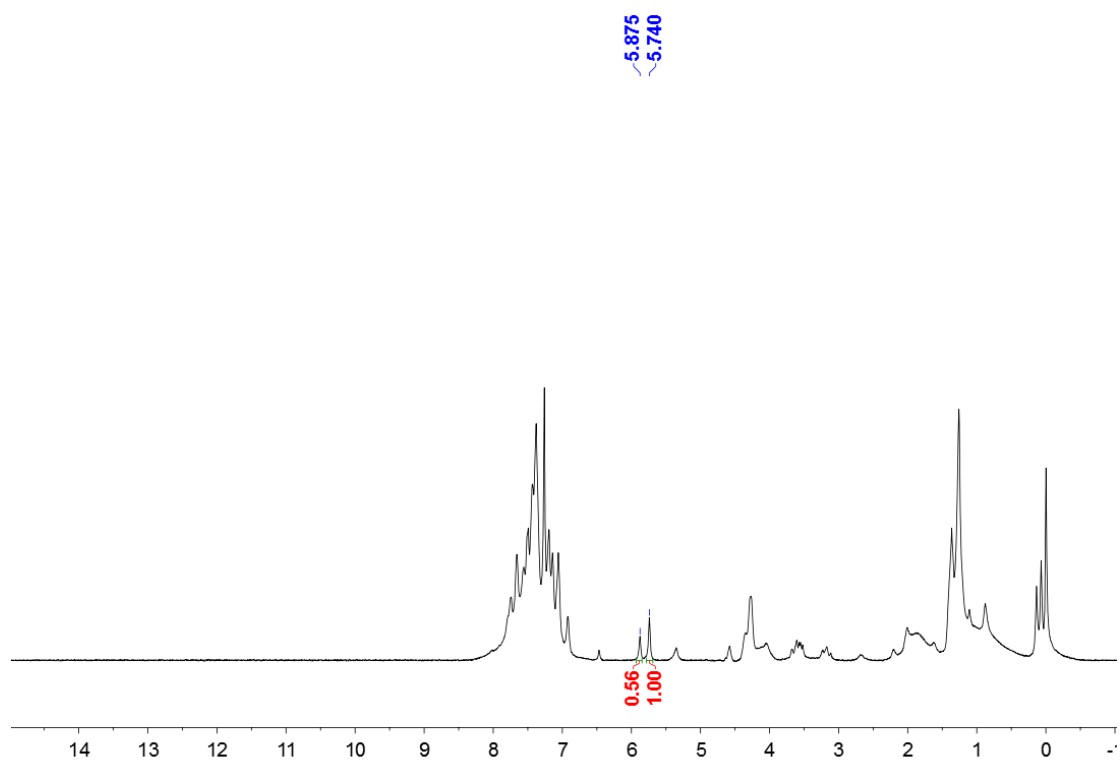
¹H NMR Spectrum of Entry 21



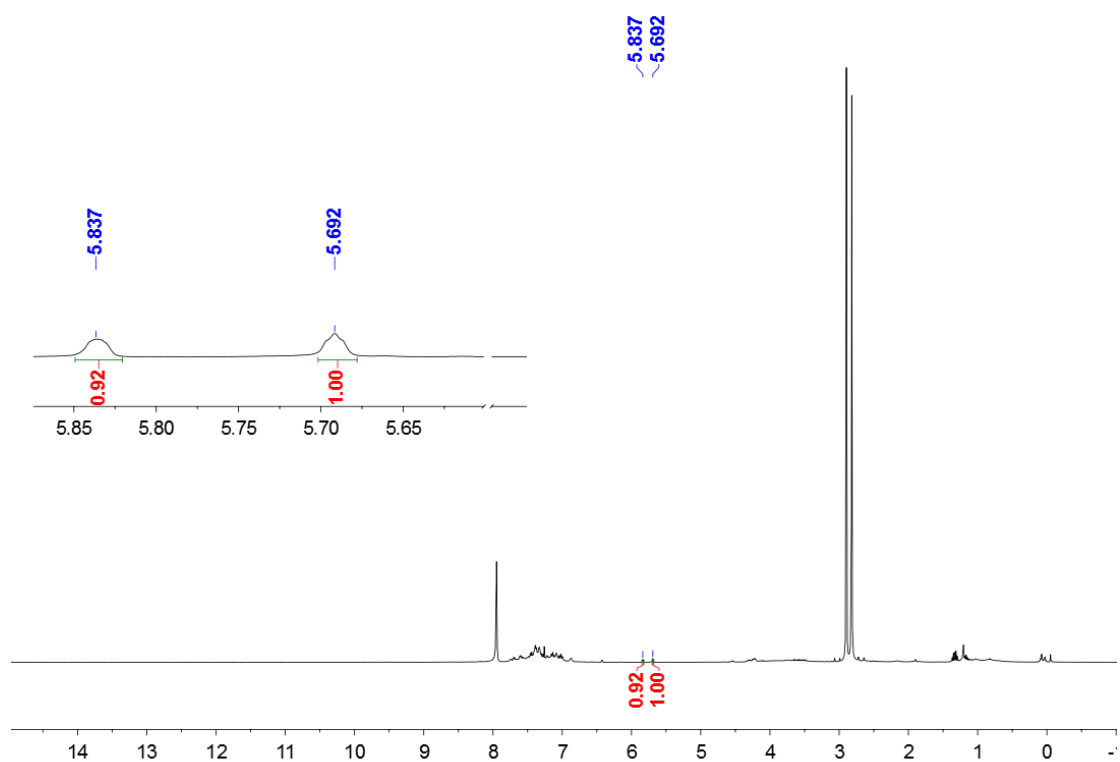
^1H NMR Spectrum of Entry 22



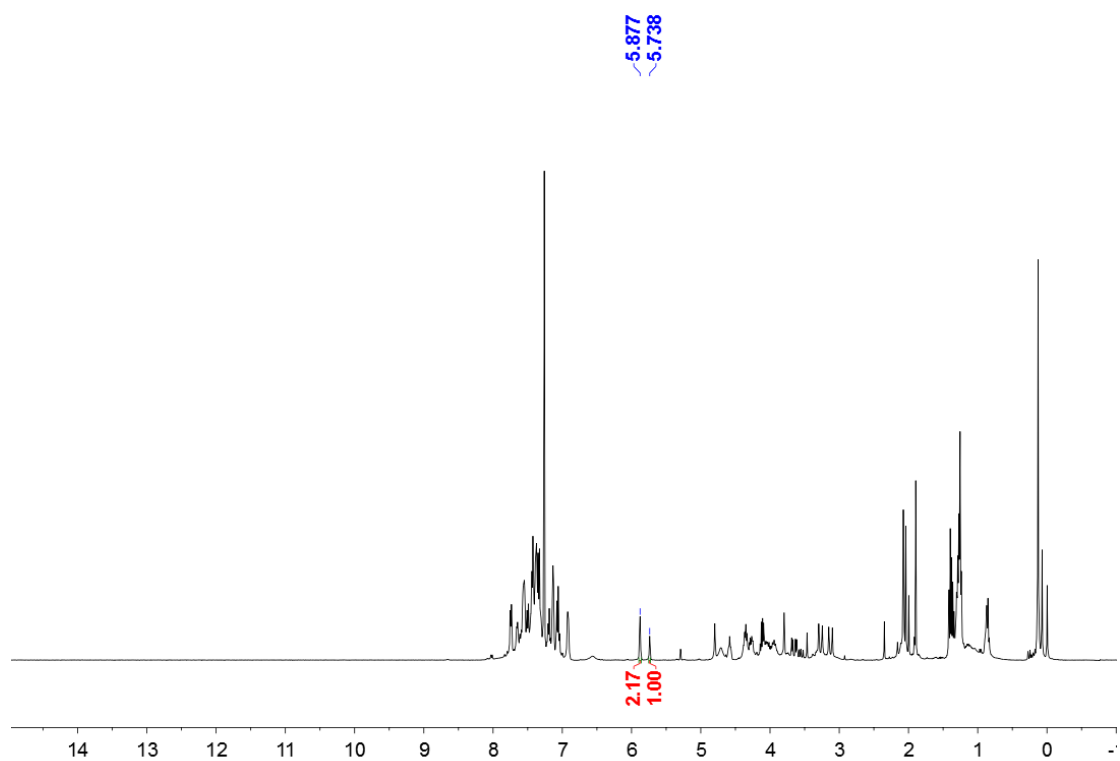
^1H NMR Spectrum of Entry 23



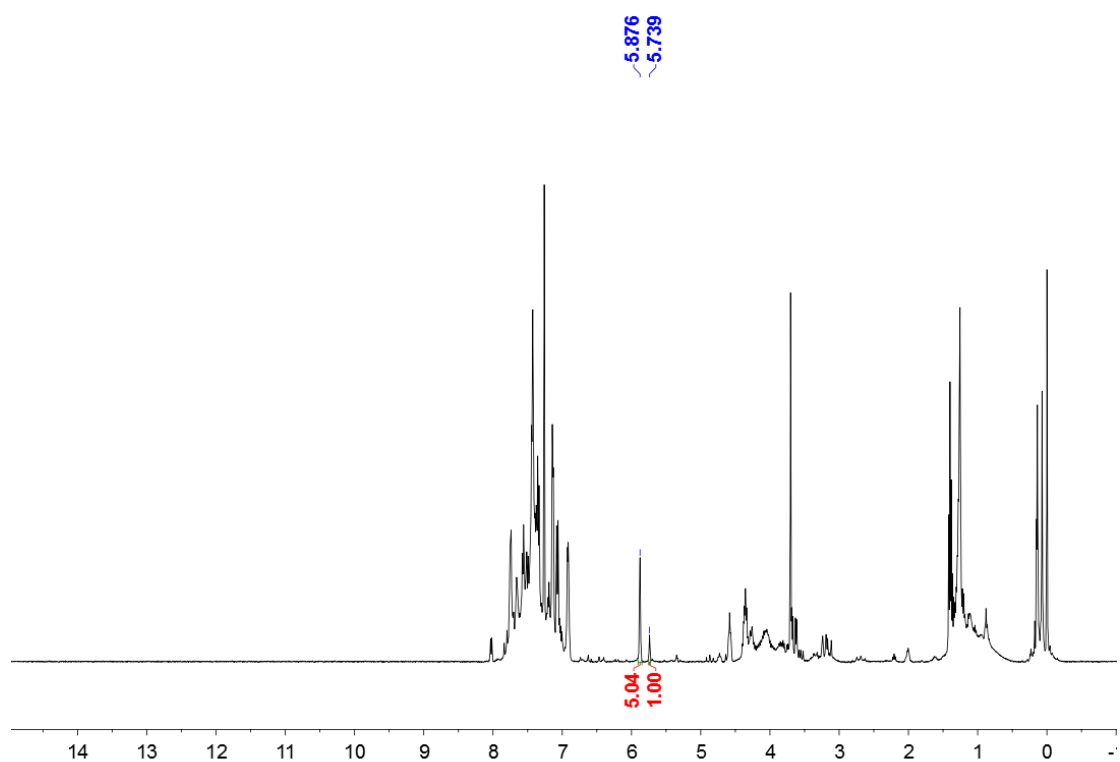
¹H NMR Spectrum of Entry 24



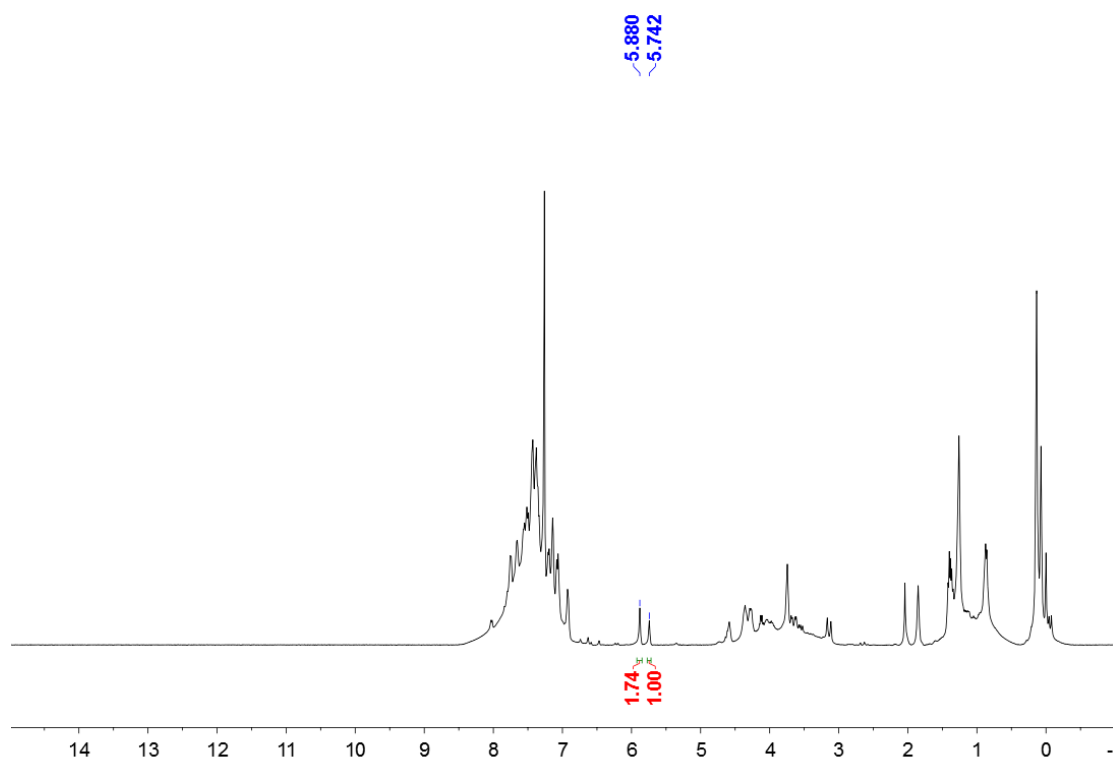
¹H NMR Spectrum of Entry 25



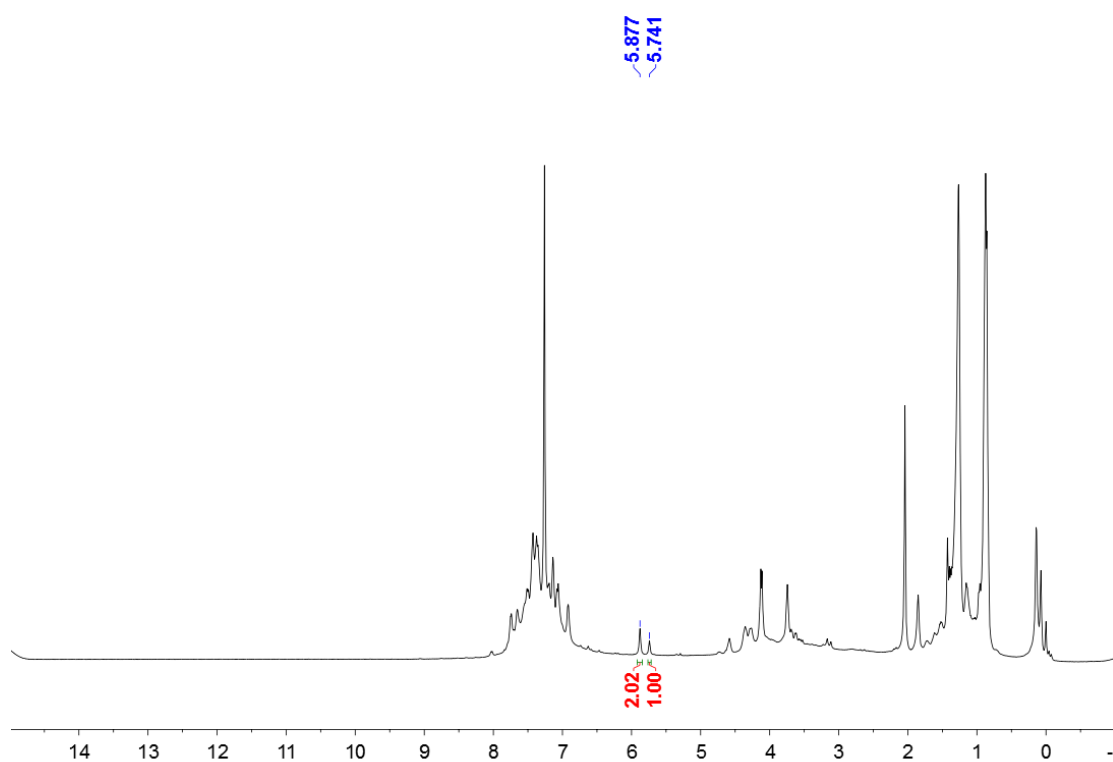
¹H NMR Spectrum of Entry 26



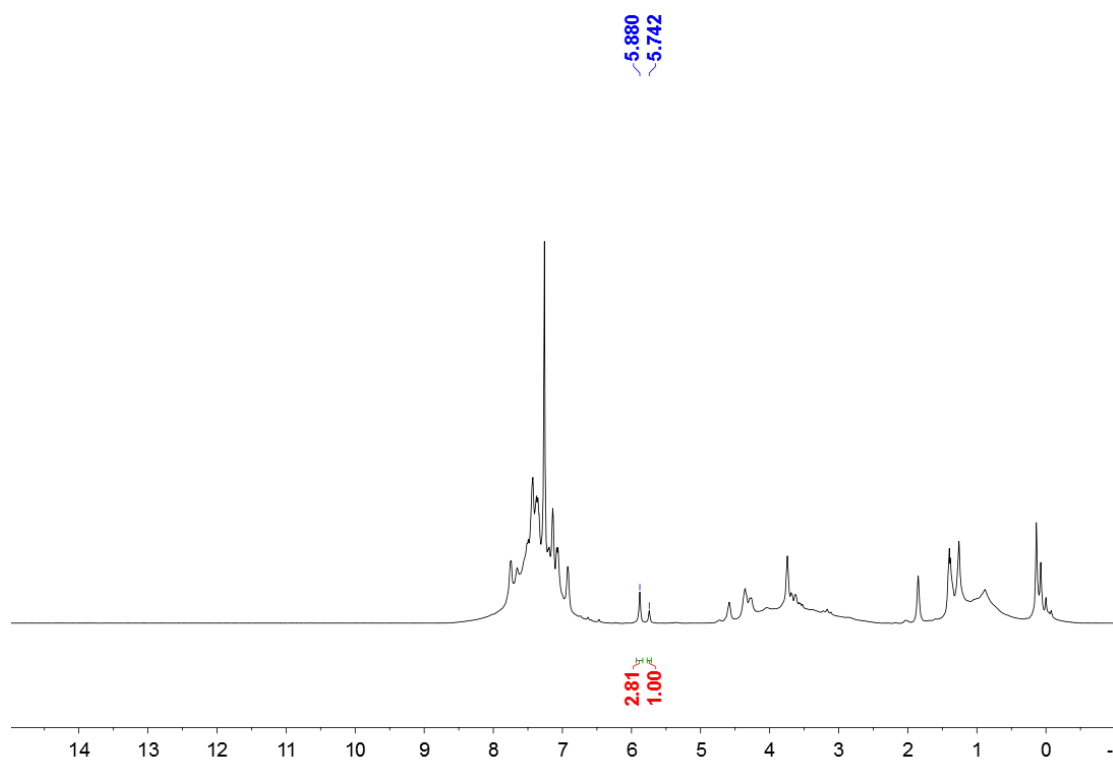
¹H NMR Spectrum of Entry 27



¹H NMR Spectrum of Entry 28

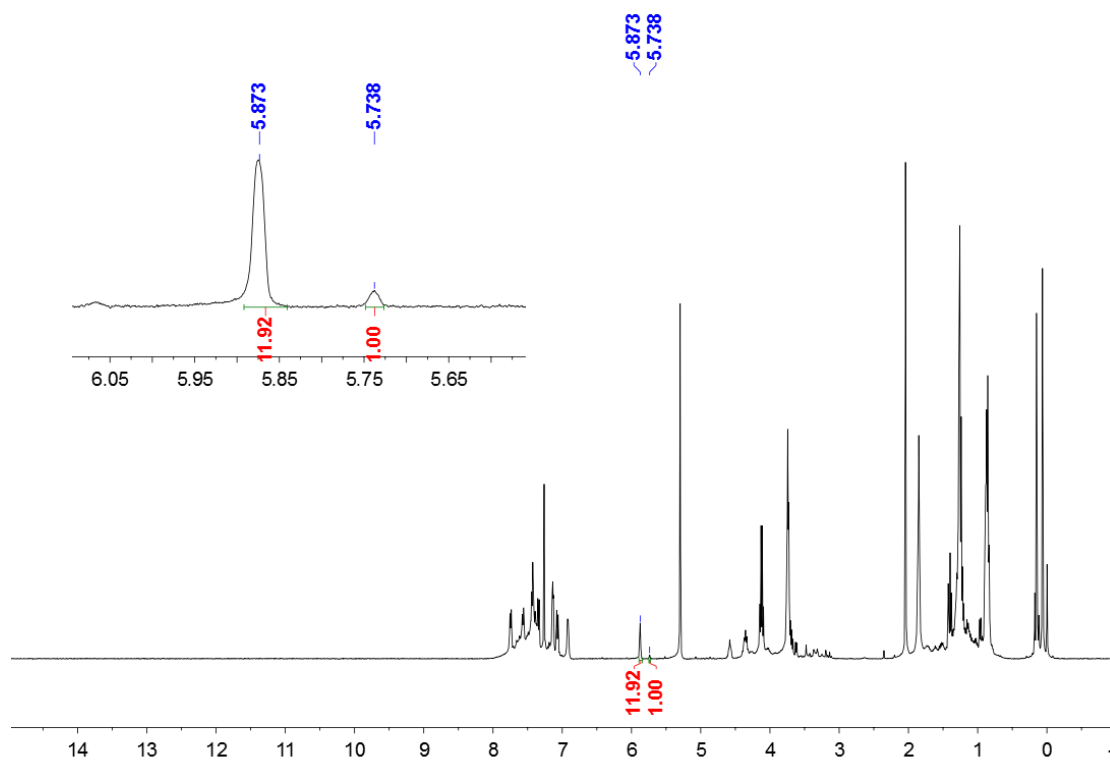


¹H NMR Spectrum of Entry 29

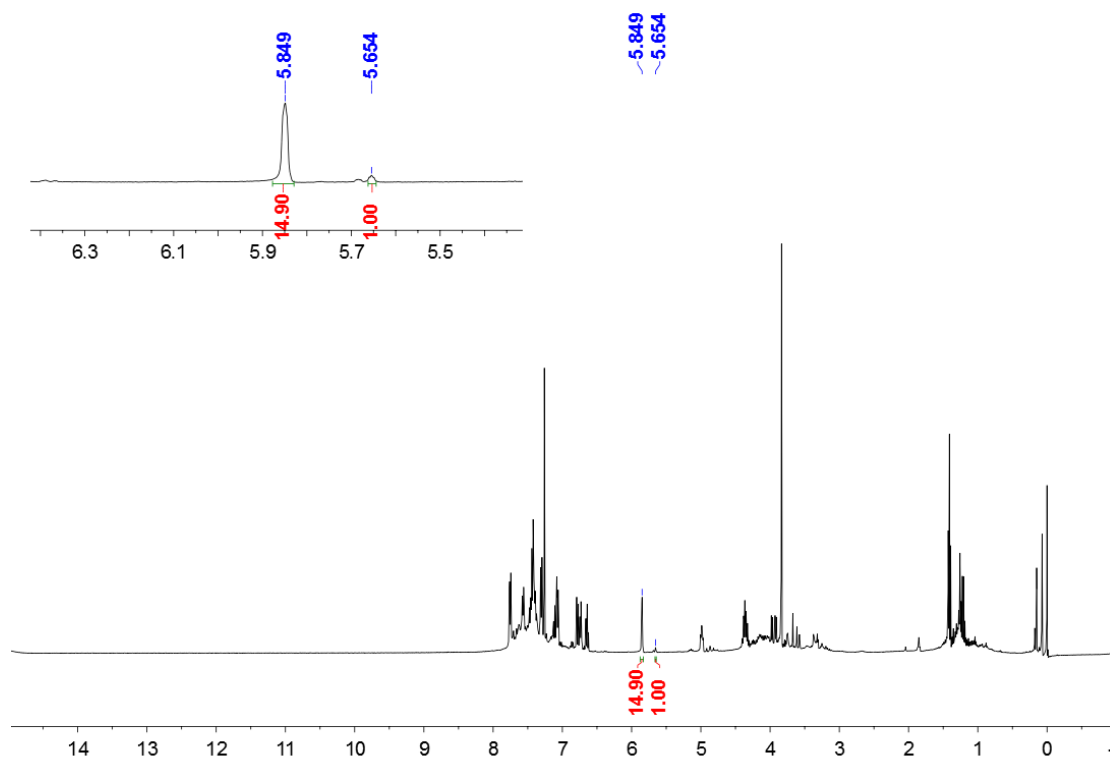


^1H NMR Spectrum of Entry 30

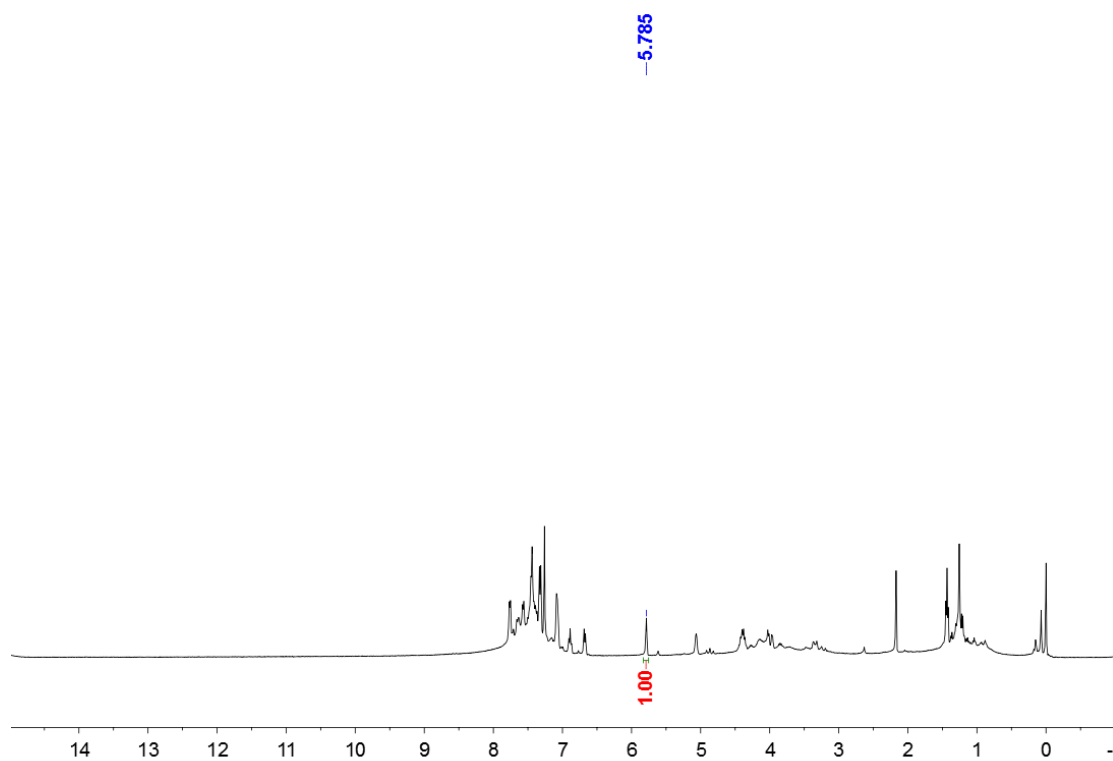
6.5. Copies of ^1H NMR spectra of the crude reaction mixtures of compounds 3



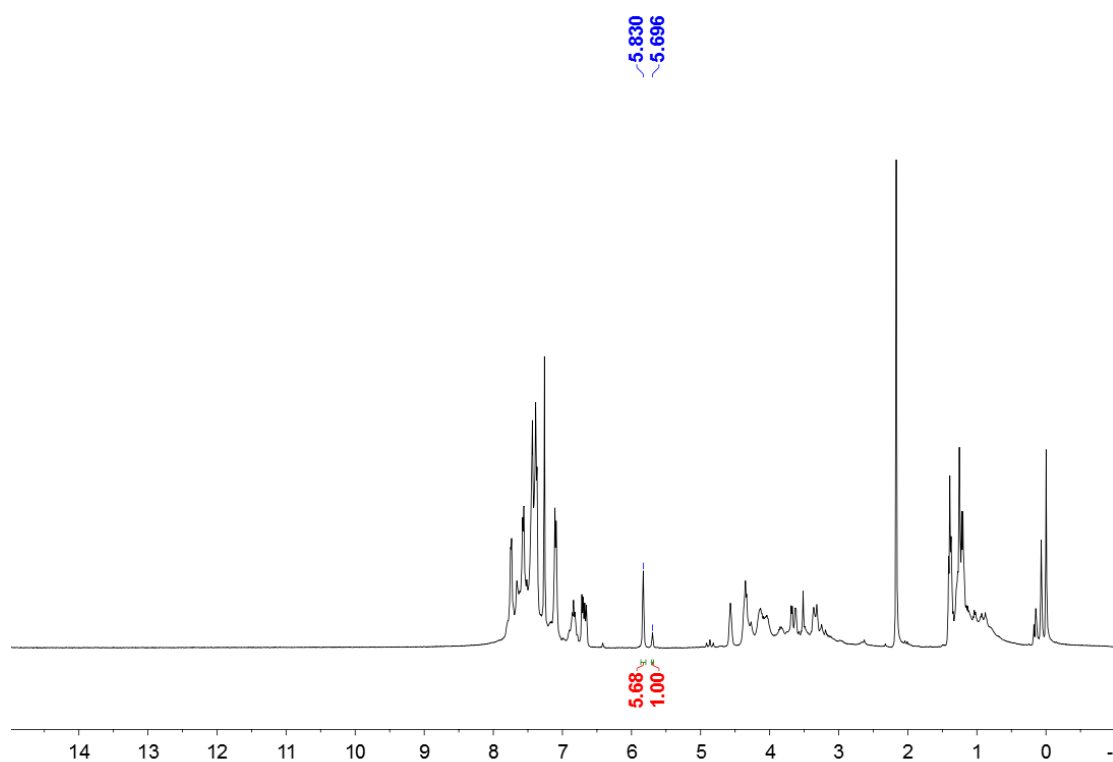
^1H NMR Spectrum of the Crude Reaction Mixture 3a



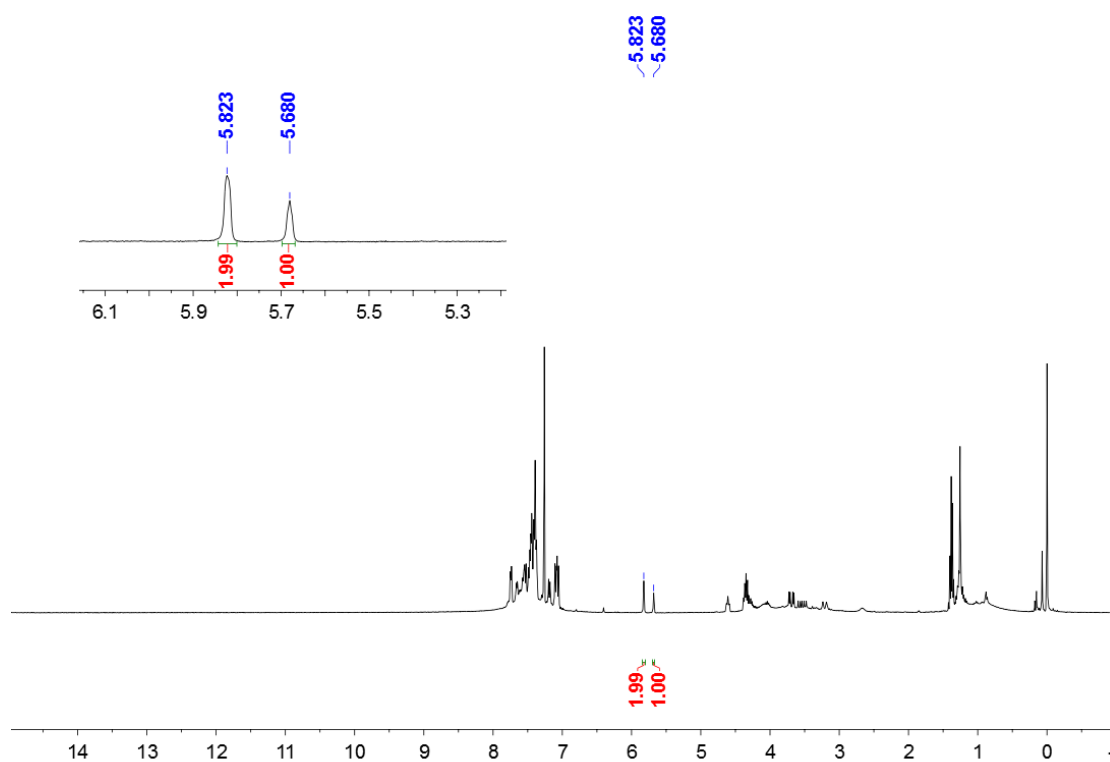
^1H NMR Spectrum of the Crude Reaction Mixture 3b



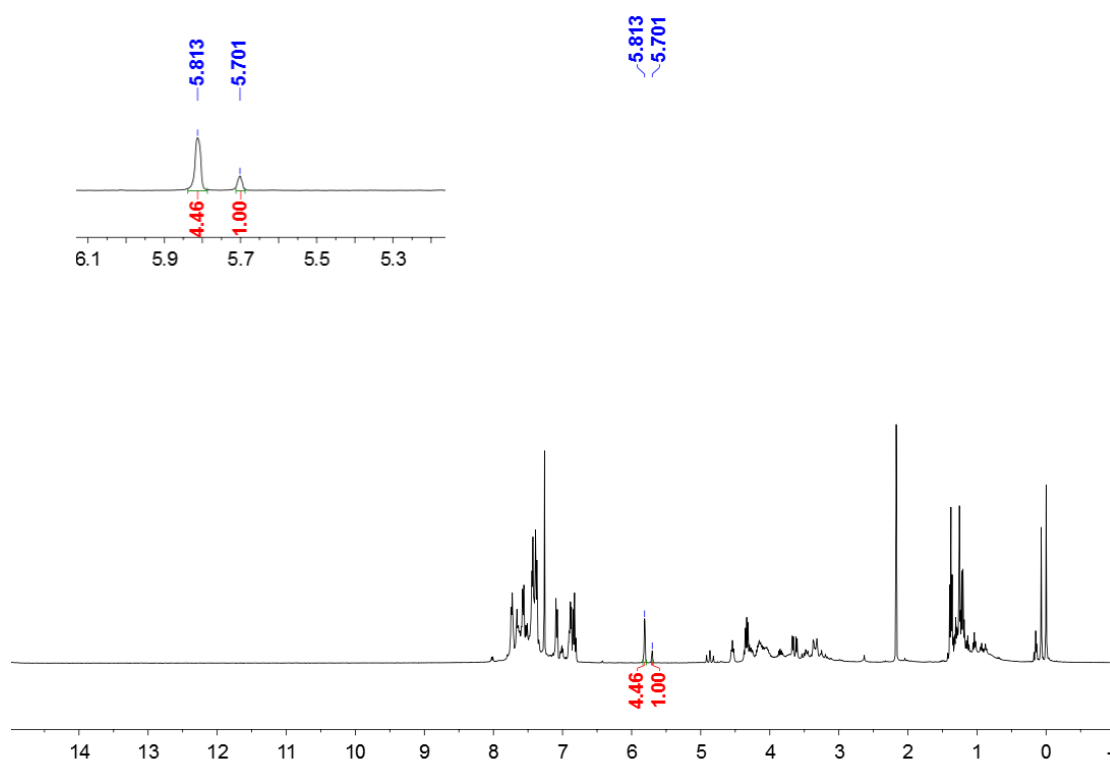
¹H NMR Spectrum of the Crude Reaction Mixture **3c**



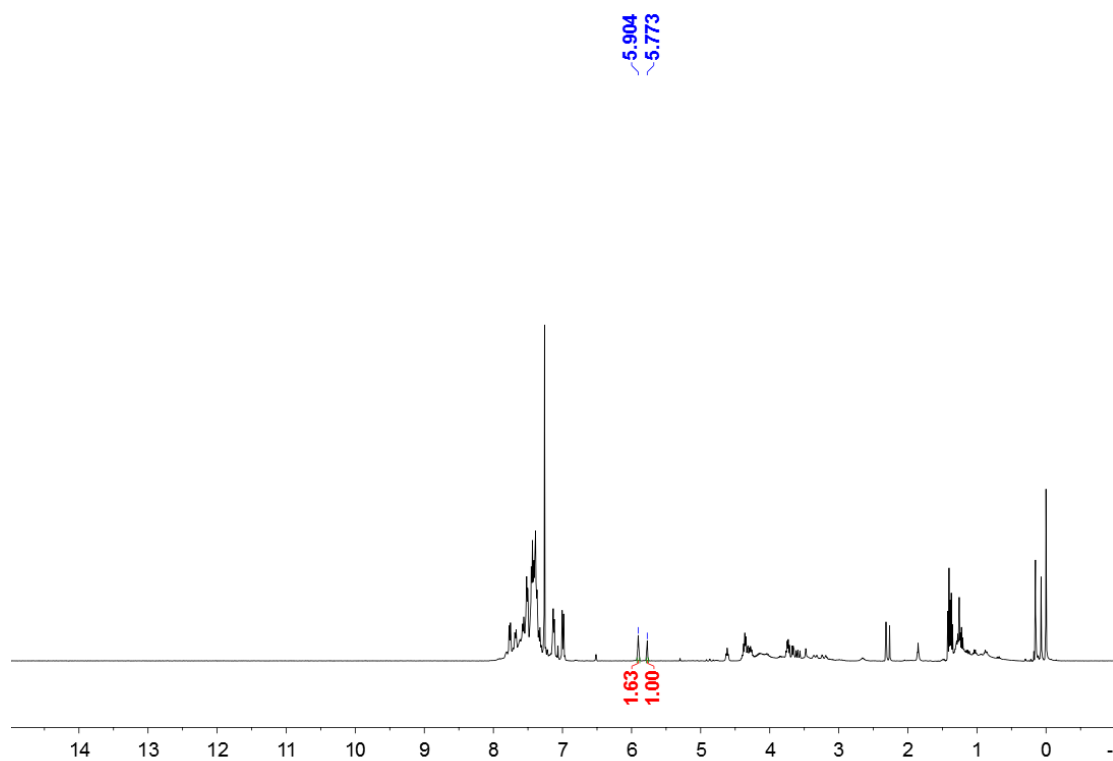
¹H NMR Spectrum of the Crude Reaction Mixture **3d**



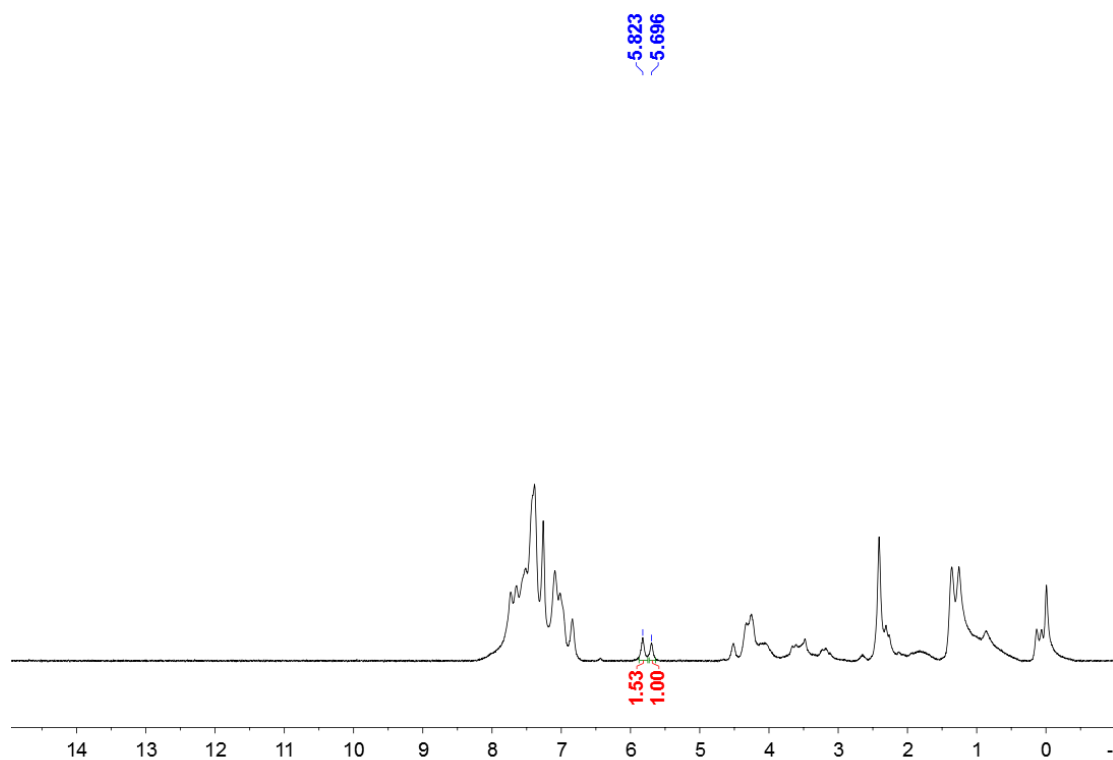
^1H NMR Spectrum of the Crude Reaction Mixture 3e



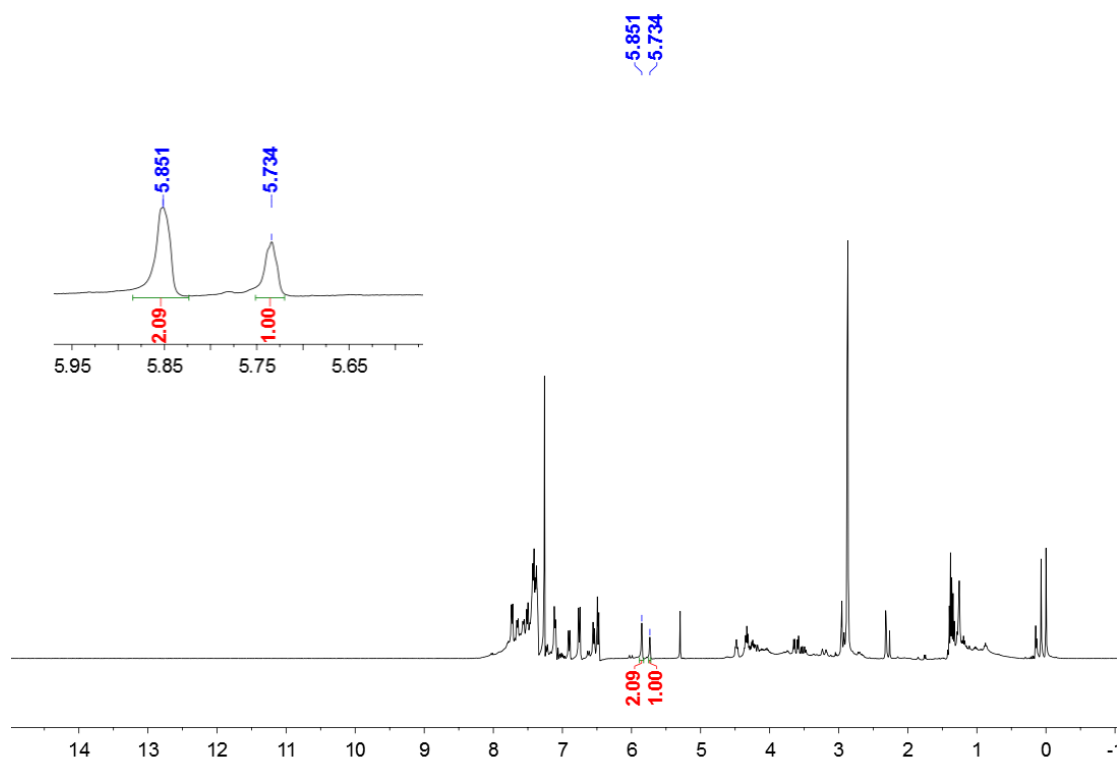
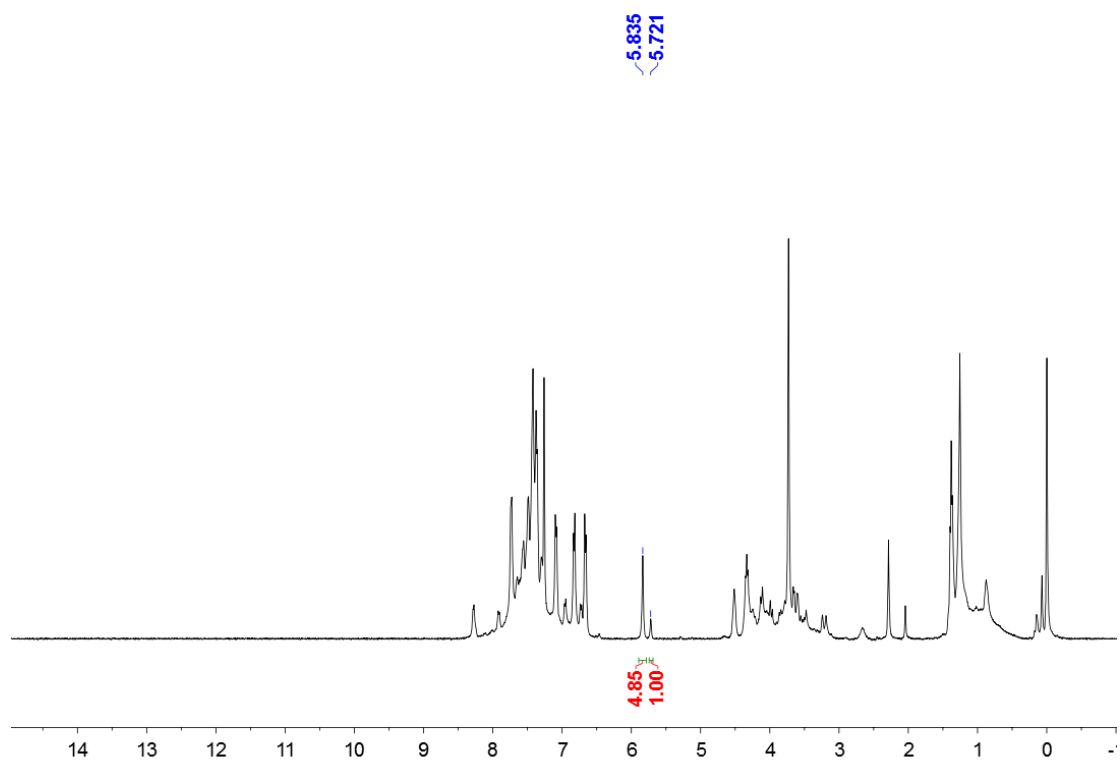
^1H NMR Spectrum of the Crude Reaction Mixture 3f

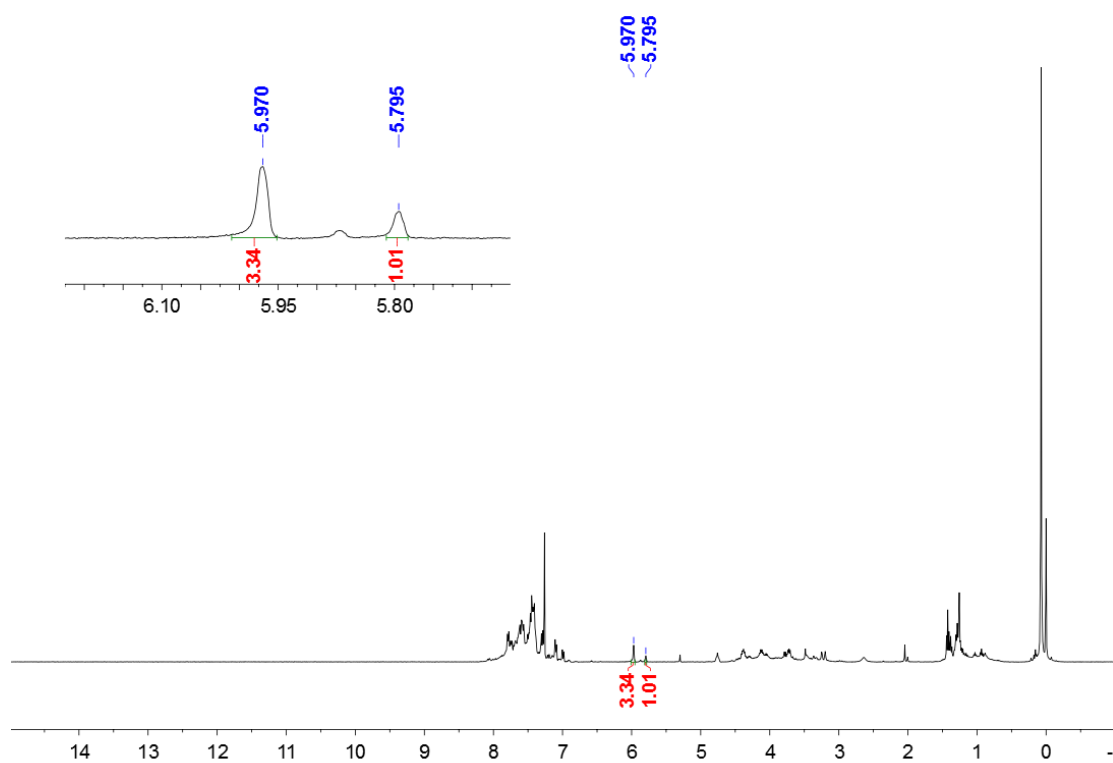


¹H NMR Spectrum of the Crude Reaction Mixture **3g**

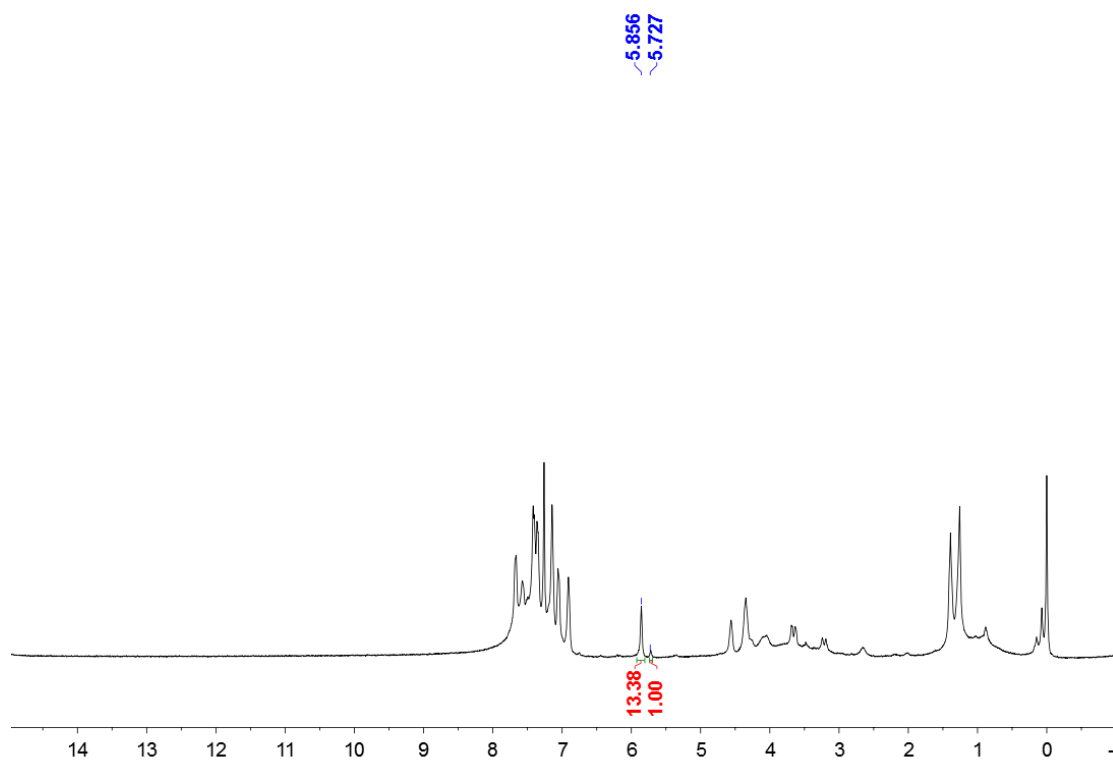


¹H NMR Spectrum of the Crude Reaction Mixture **3h**

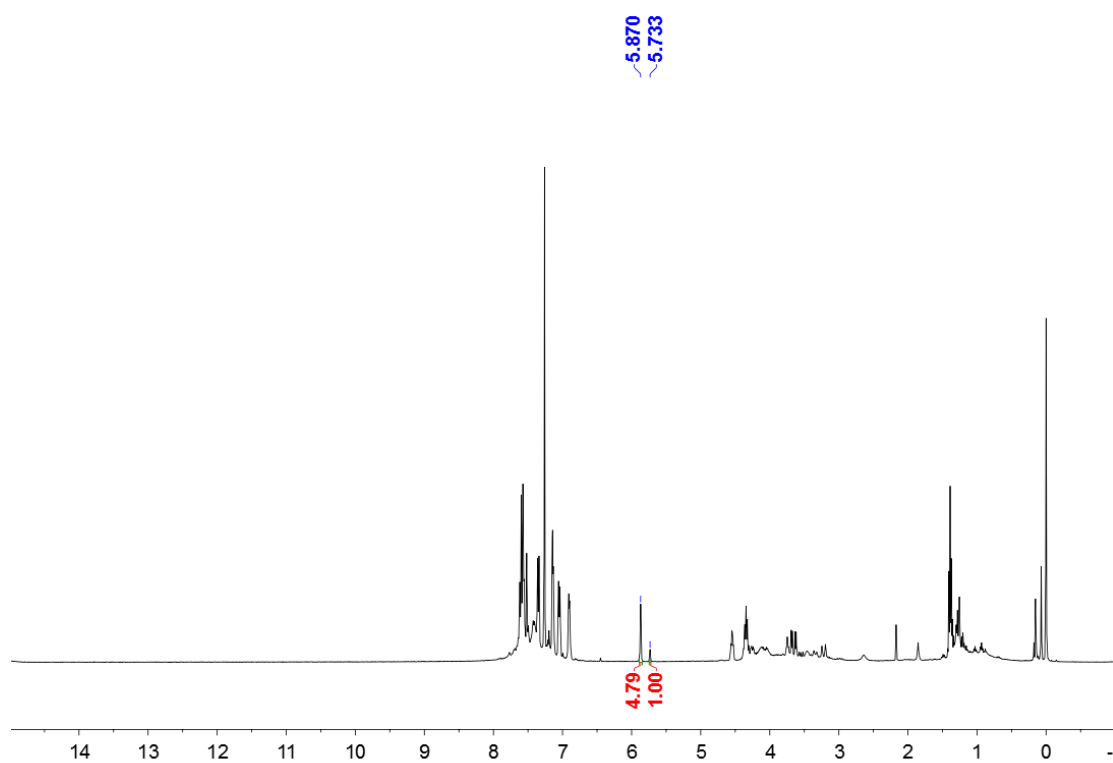




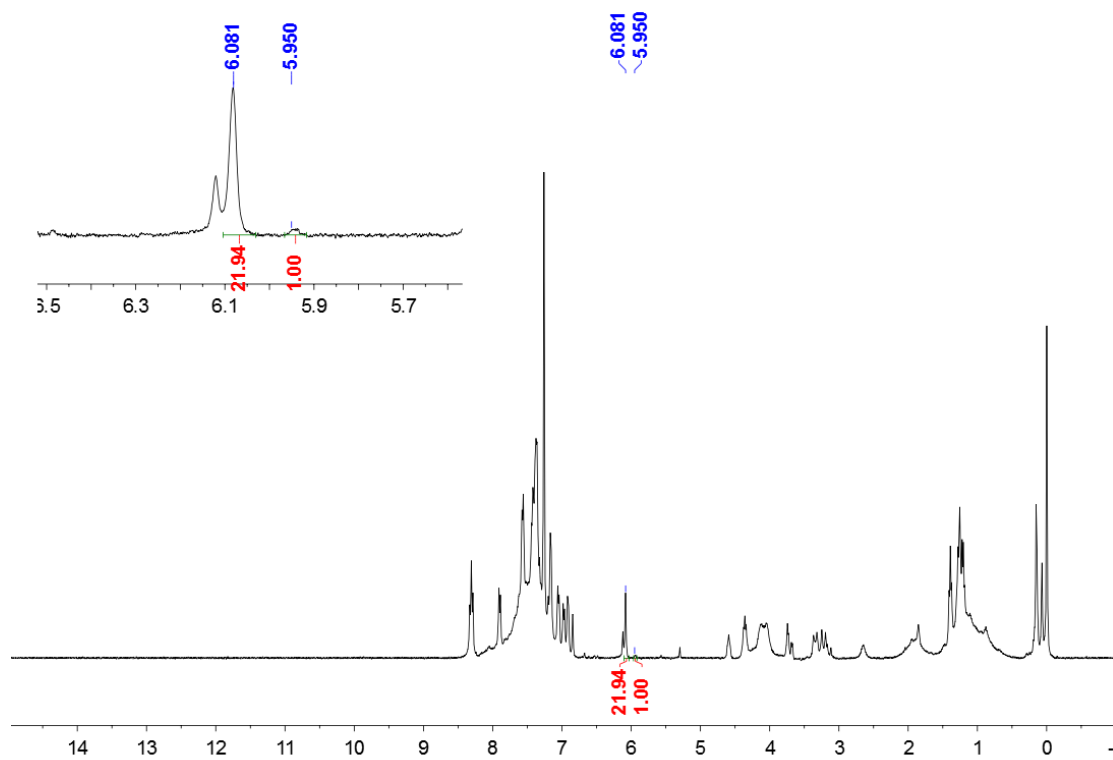
^1H NMR Spectrum of the Crude Reaction Mixture **3k**



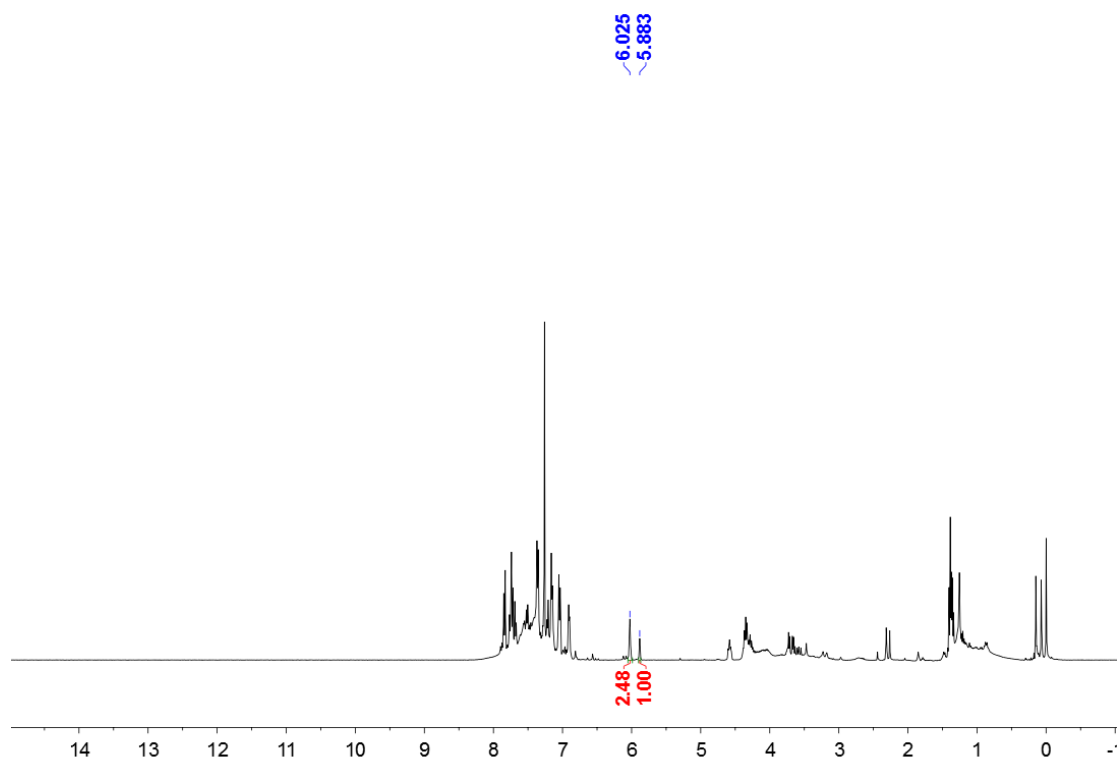
^1H NMR Spectrum of the Crude Reaction Mixture **3l**



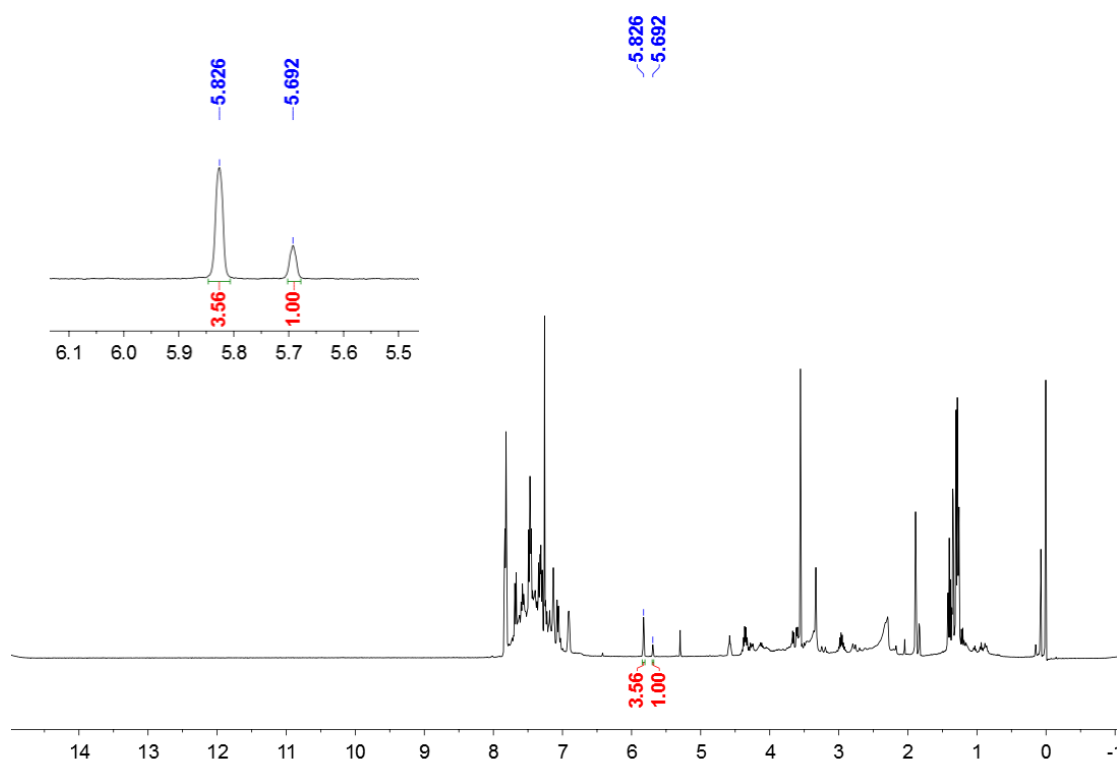
¹H NMR Spectrum of the Crude Reaction Mixture **3m**



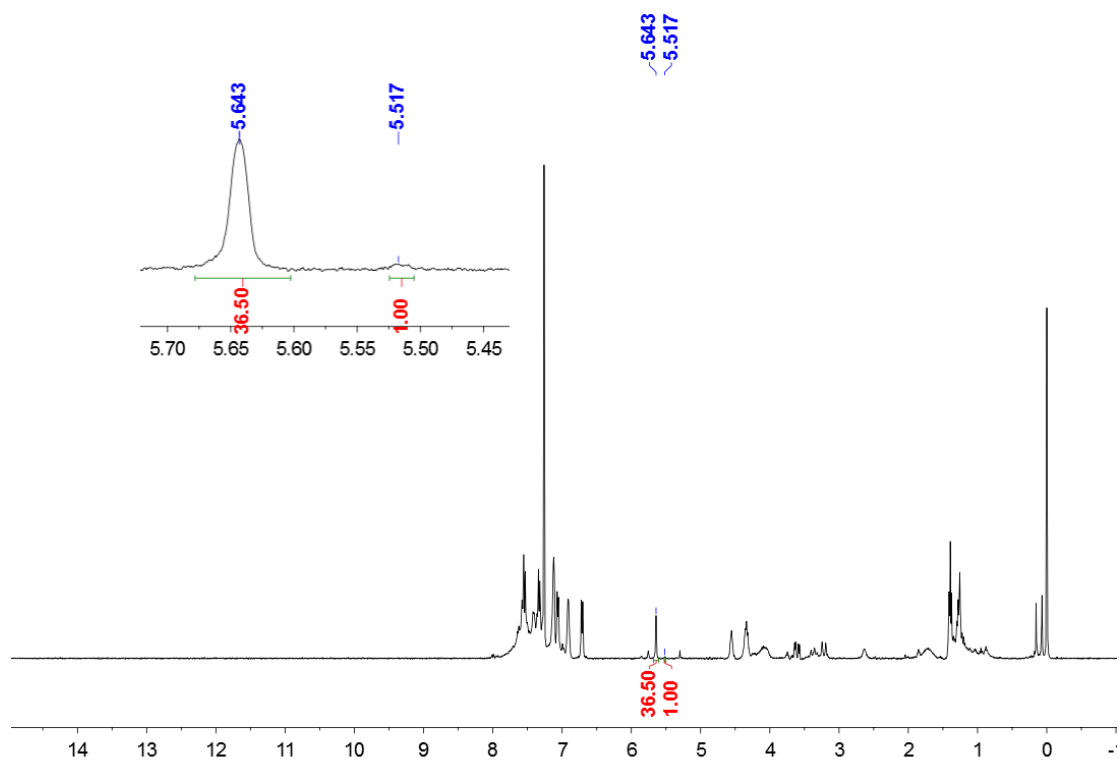
¹H NMR Spectrum of the Crude Reaction Mixture **3n**



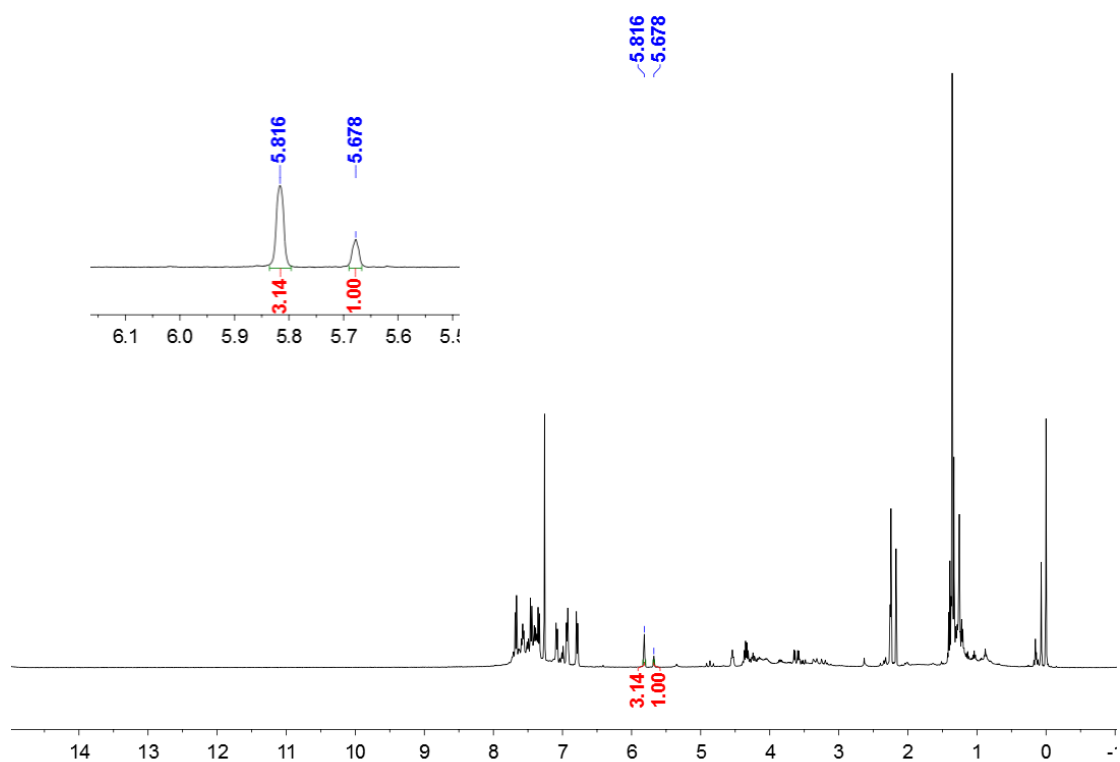
^1H NMR Spectrum of the Crude Reaction Mixture **3o**



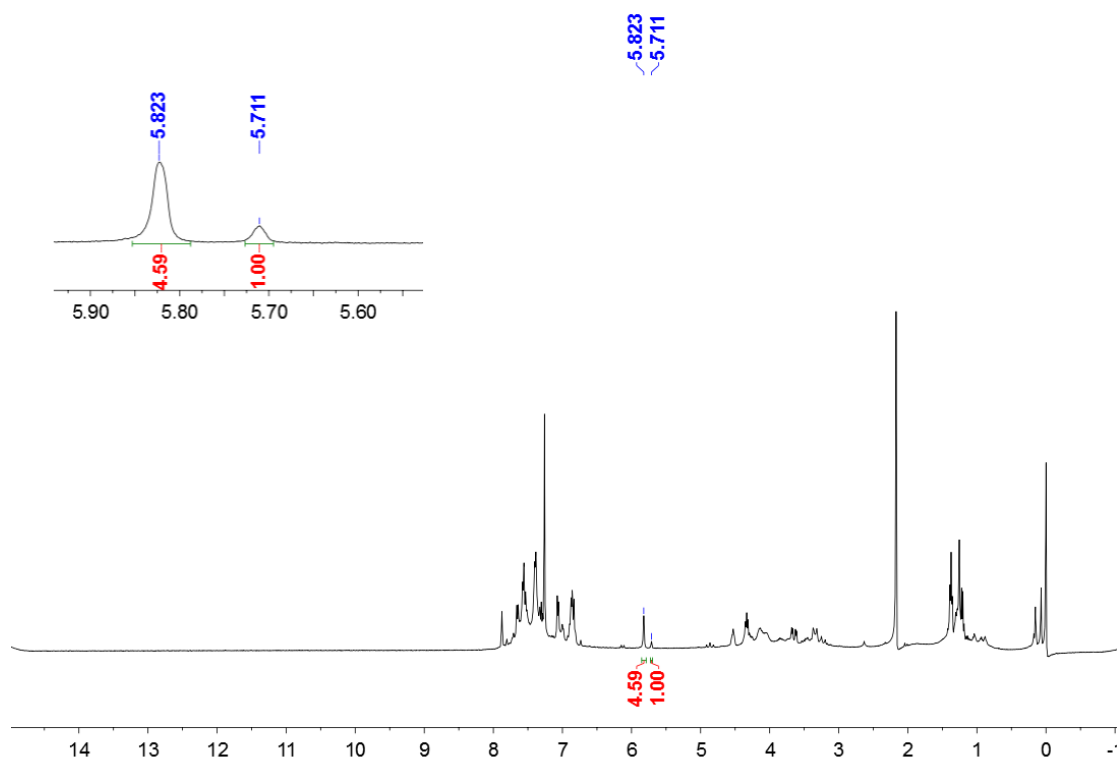
^1H NMR Spectrum of the Crude Reaction Mixture **3p**



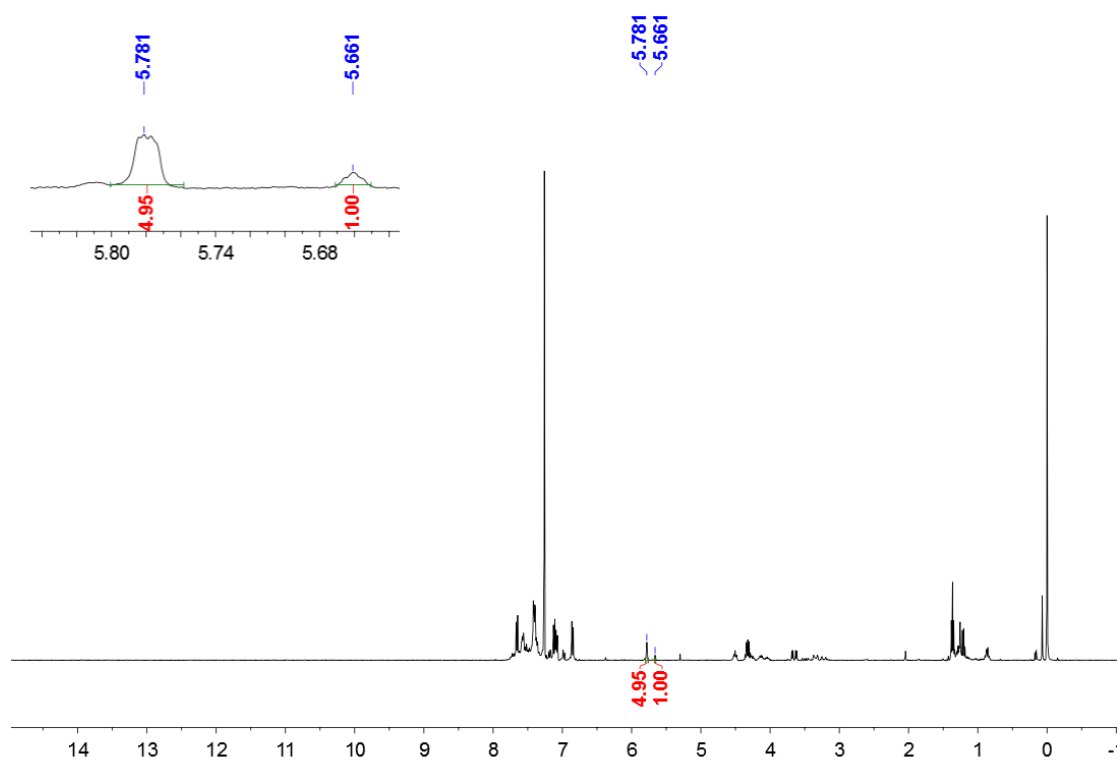
¹H NMR Spectrum of the Crude Reaction Mixture **3q**



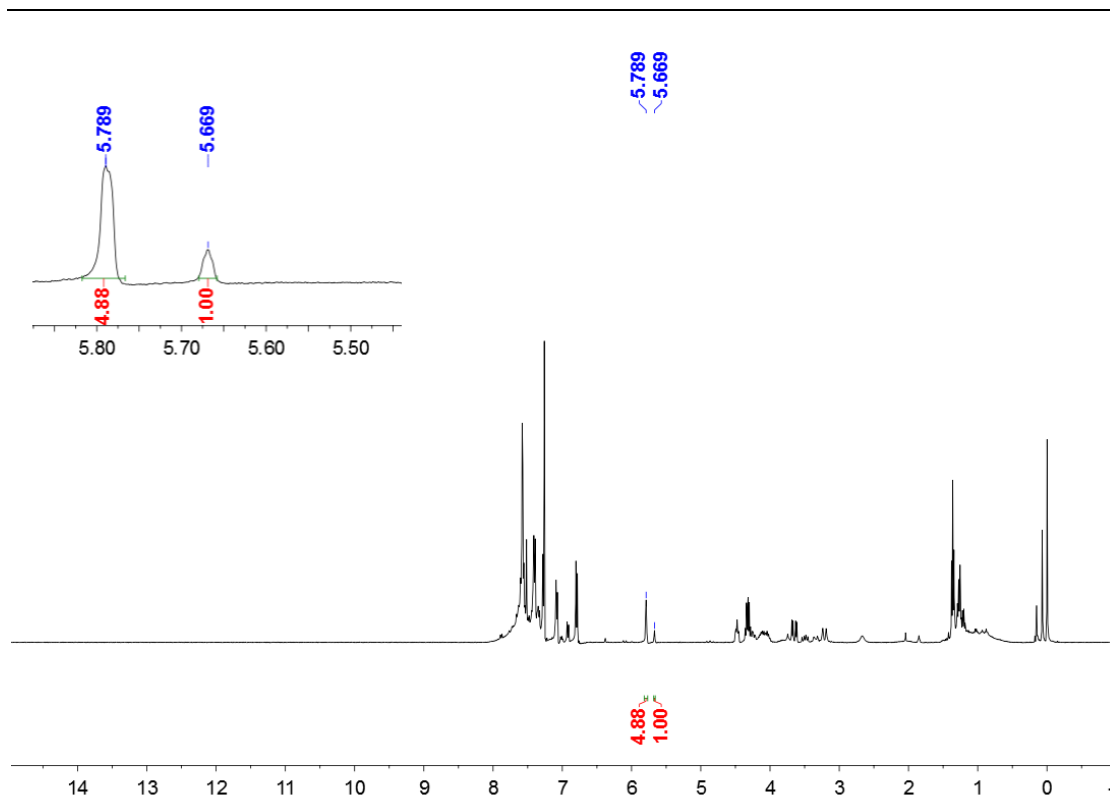
¹H NMR Spectrum of the Crude Reaction Mixture **3r**



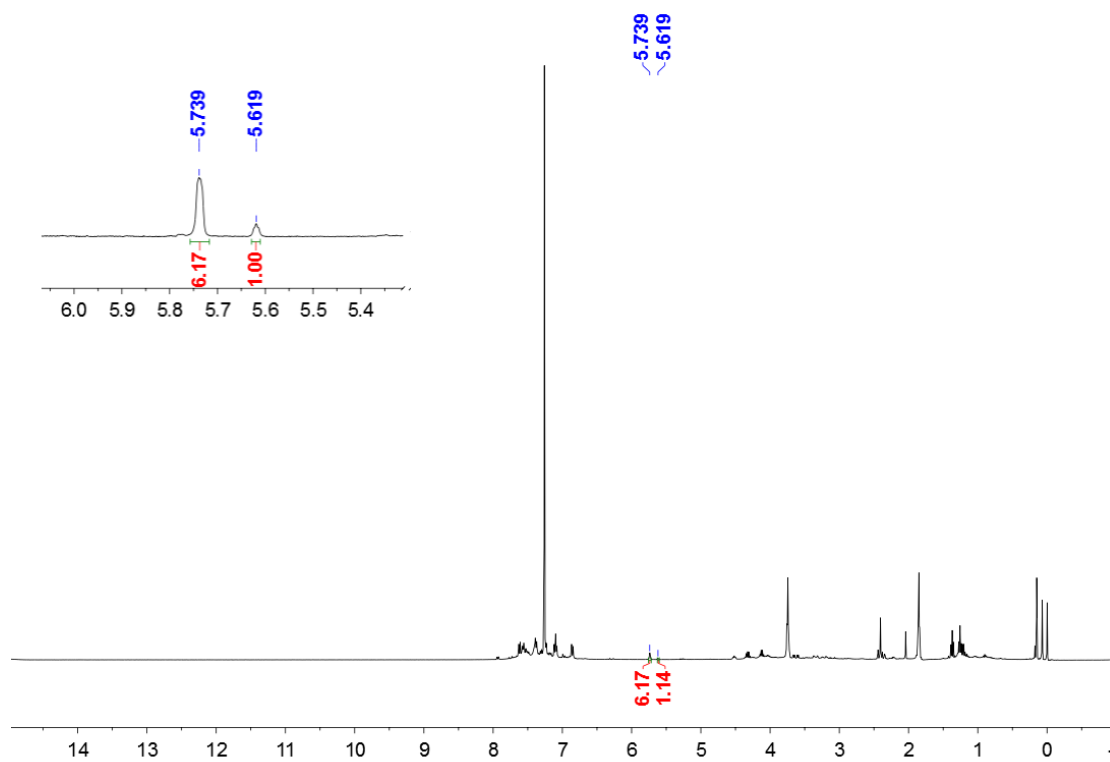
¹H NMR Spectrum of the Crude Reaction Mixture **3s**



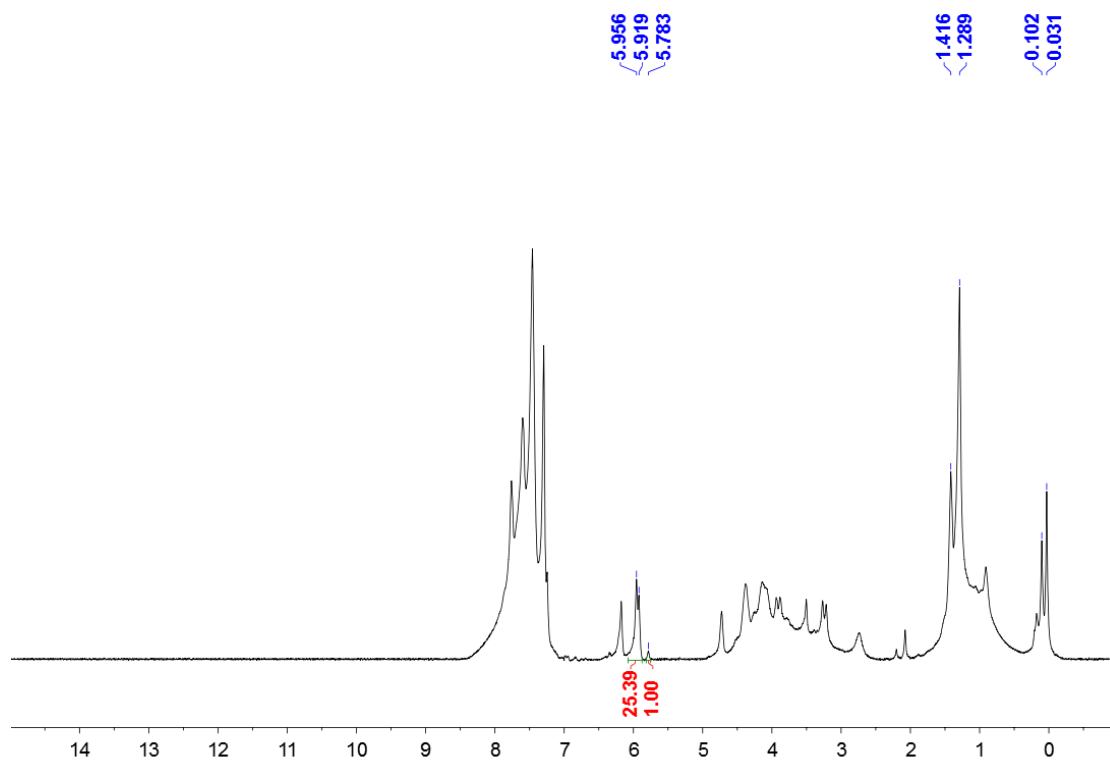
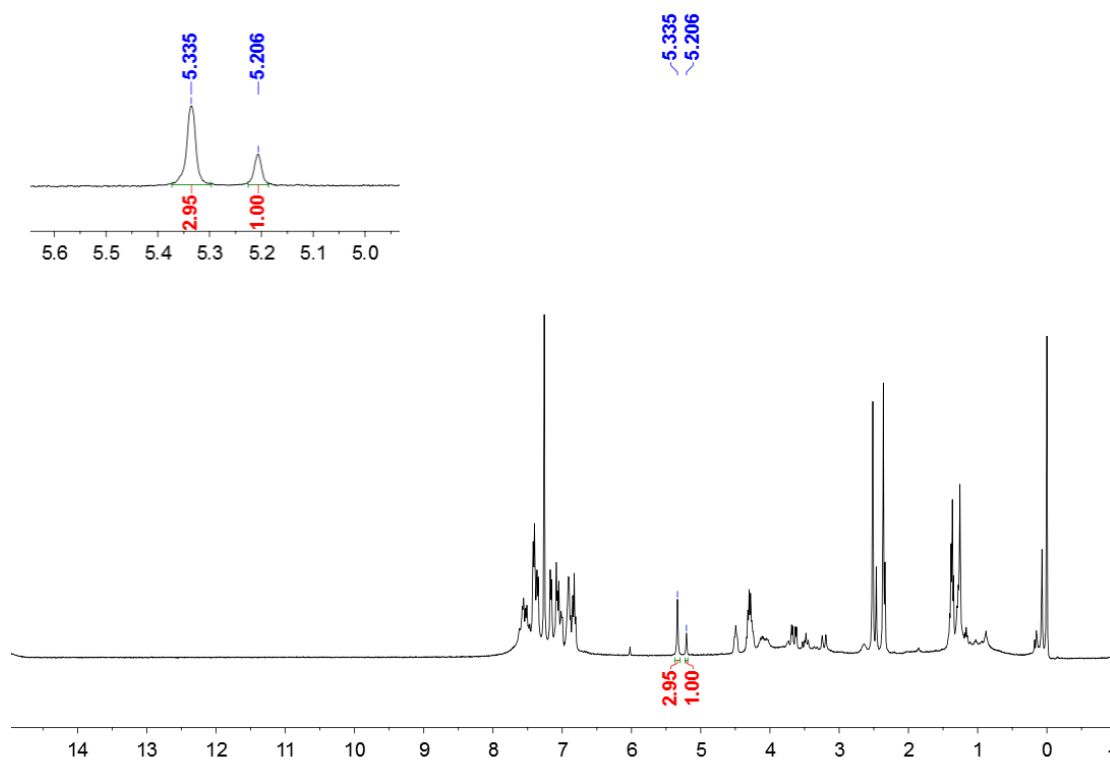
¹H NMR Spectrum of the Crude Reaction Mixture **3t**

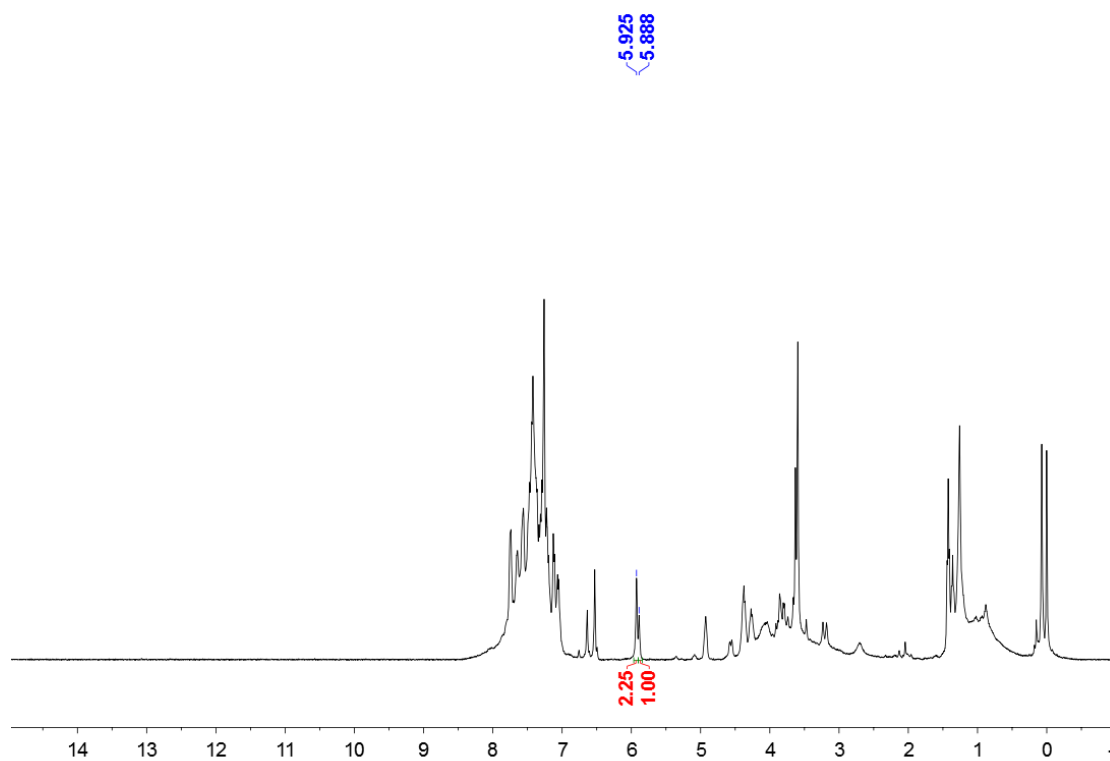


¹H NMR Spectrum of the Crude Reaction Mixture **3u**



¹H NMR Spectrum of the Crude Reaction Mixture **3v**

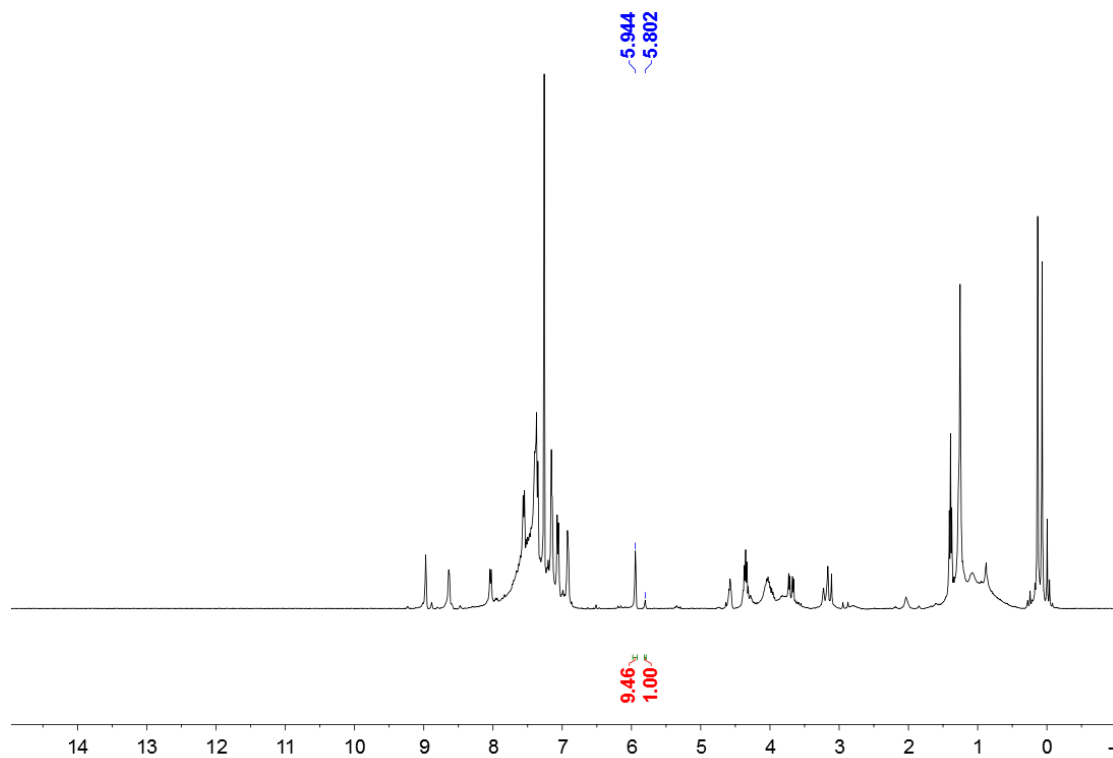




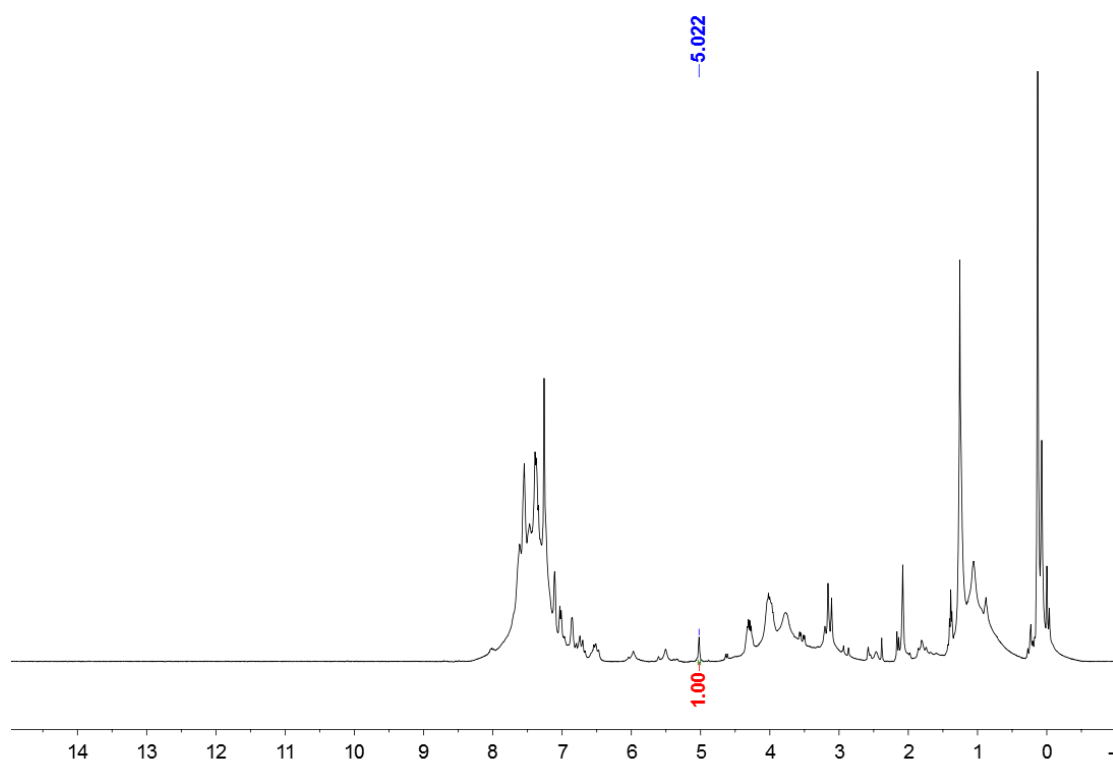
^1H NMR Spectrum of the Crude Reaction Mixture **3y**



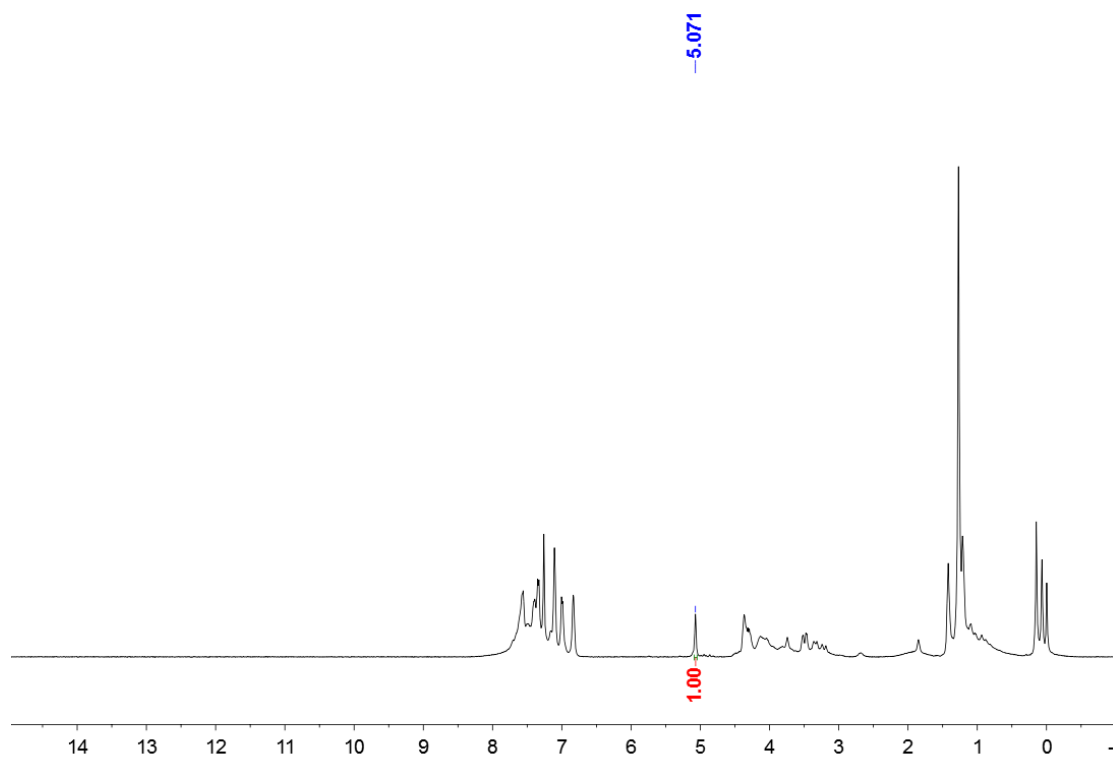
^1H NMR Spectrum of the Crude Reaction Mixture **3z**



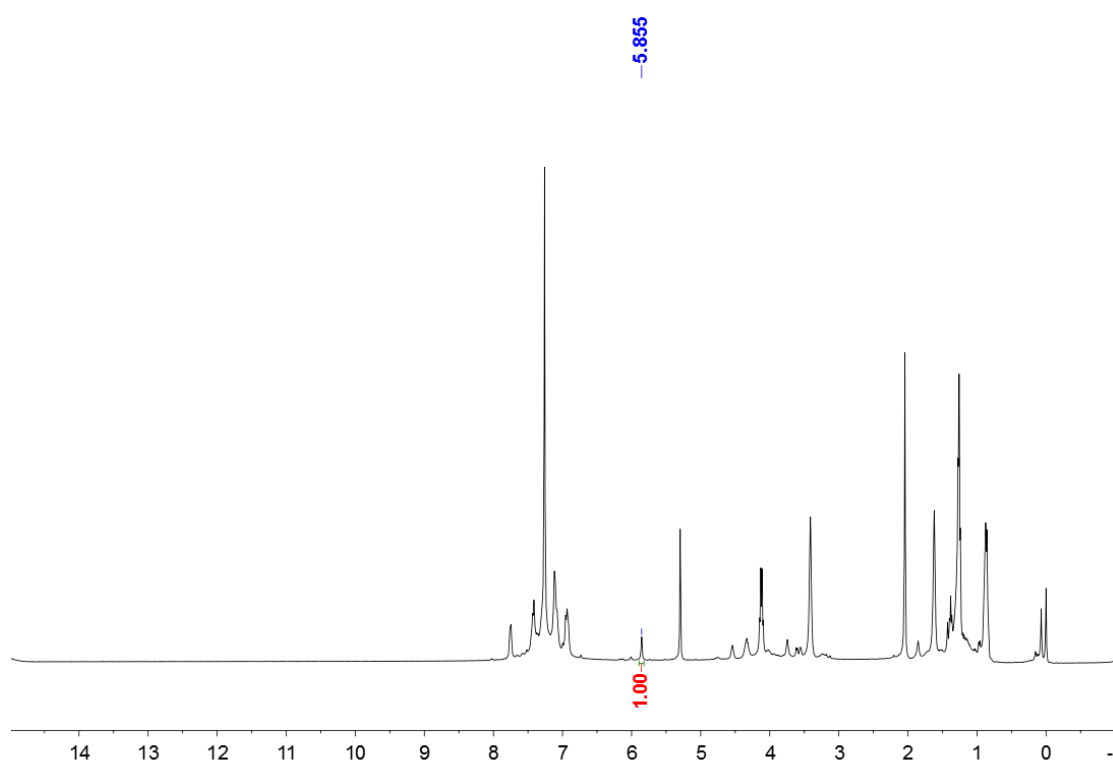
¹H NMR Spectrum of the Crude Reaction Mixture **3aa**



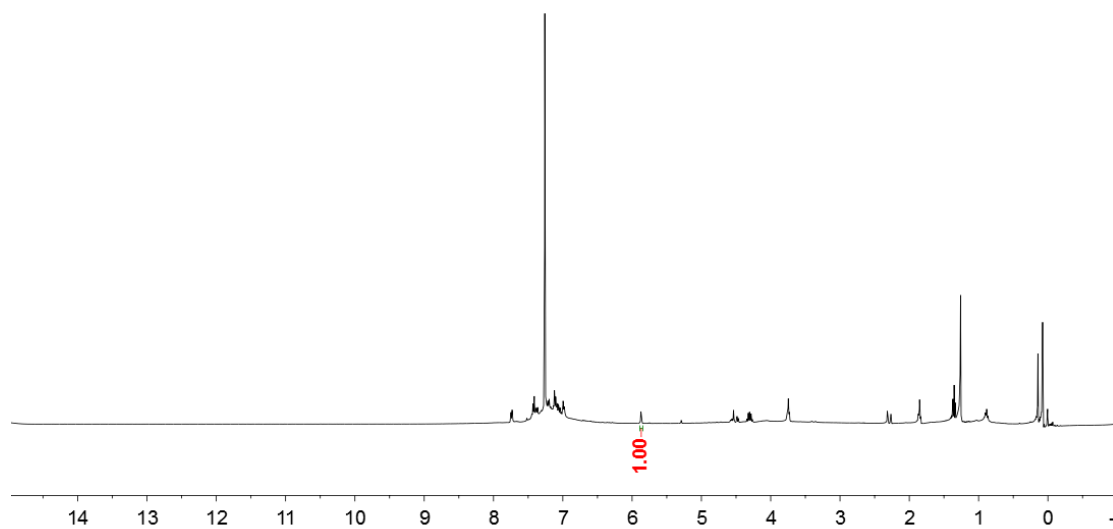
¹H NMR Spectrum of the Crude Reaction Mixture **3ab**



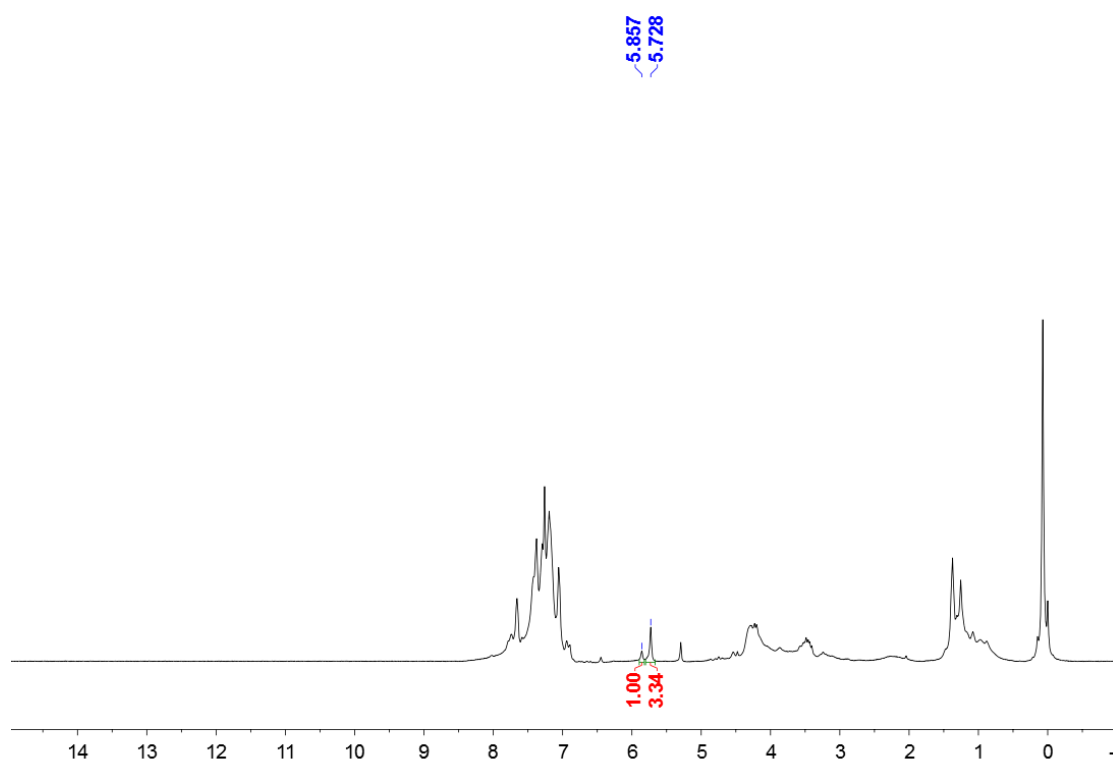
¹H NMR Spectrum of the Crude Reaction Mixture **3ac**



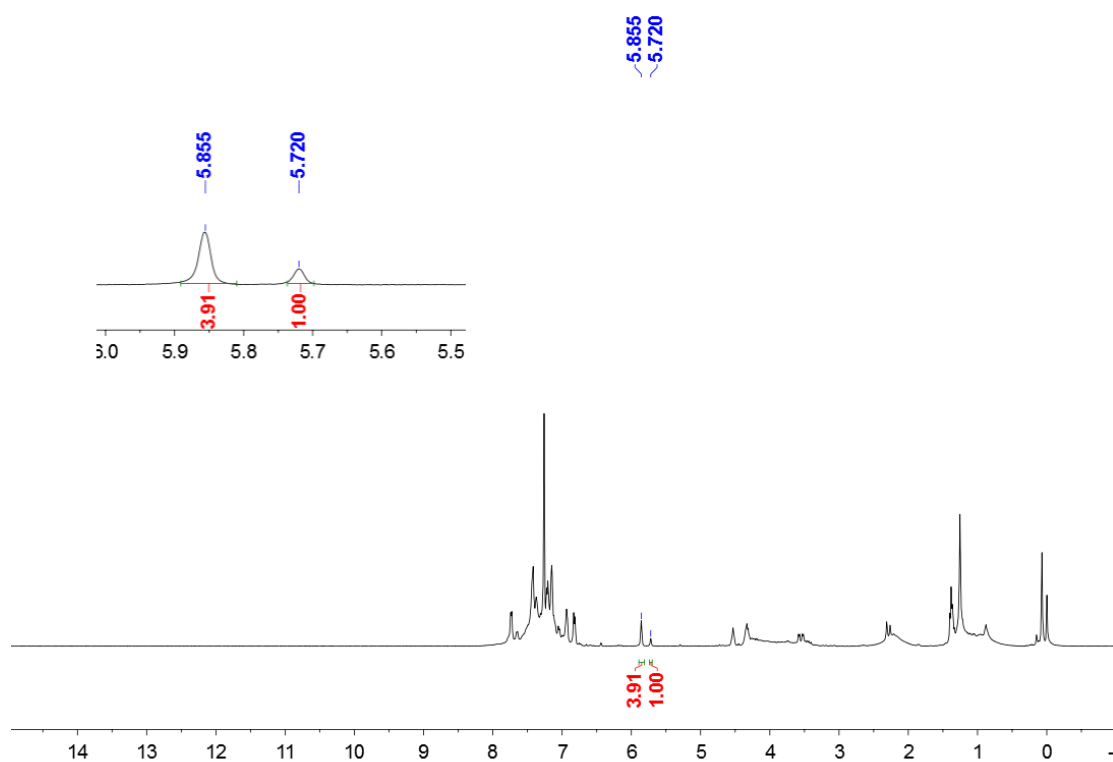
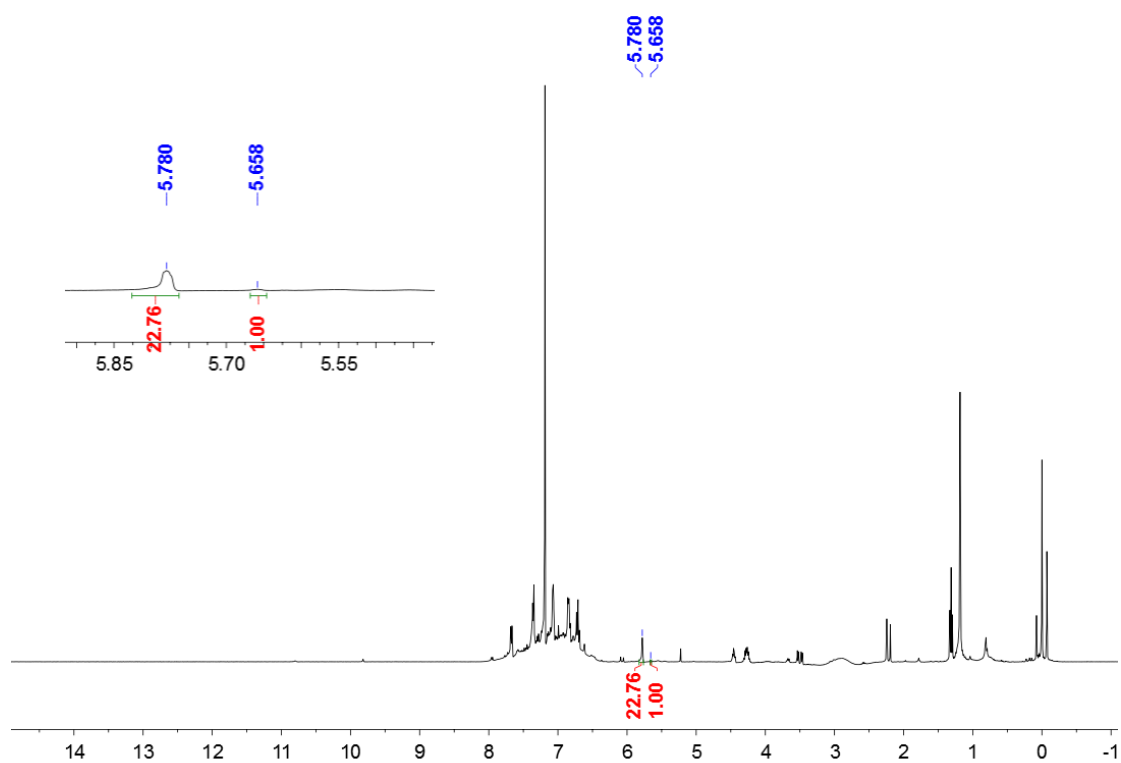
¹H NMR Spectrum of the Crude Reaction Mixture **3ad**

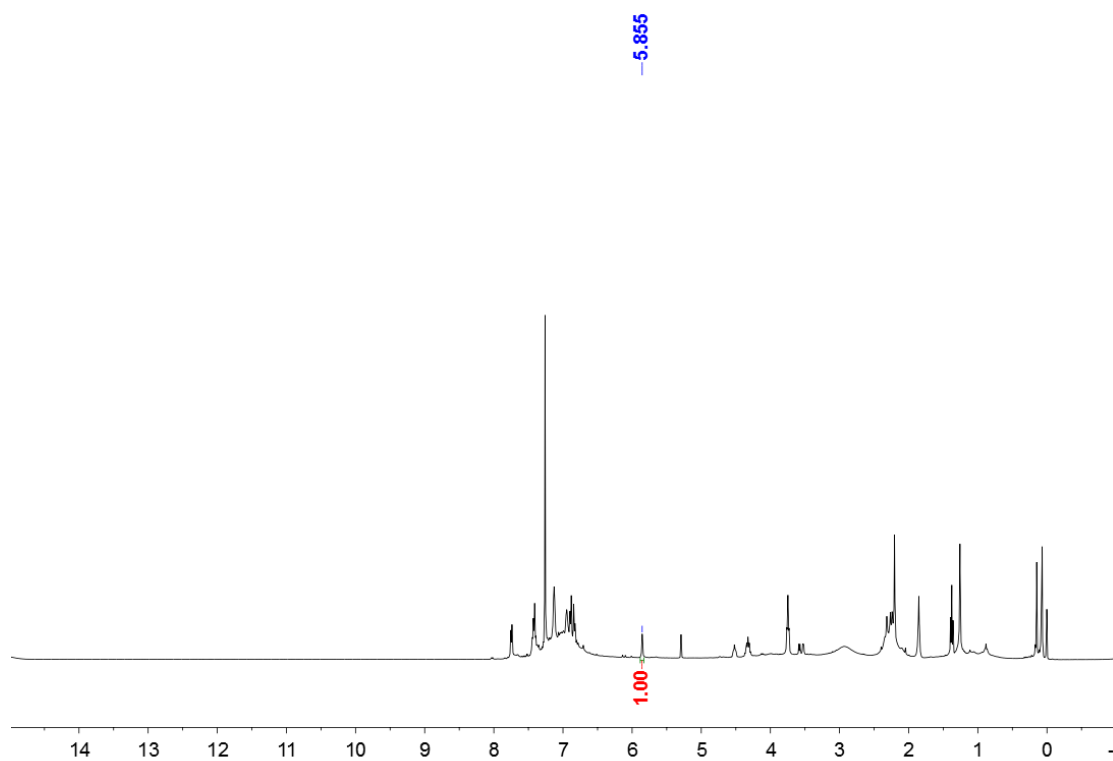


^1H NMR Spectrum of the Crude Reaction Mixture **3ae**

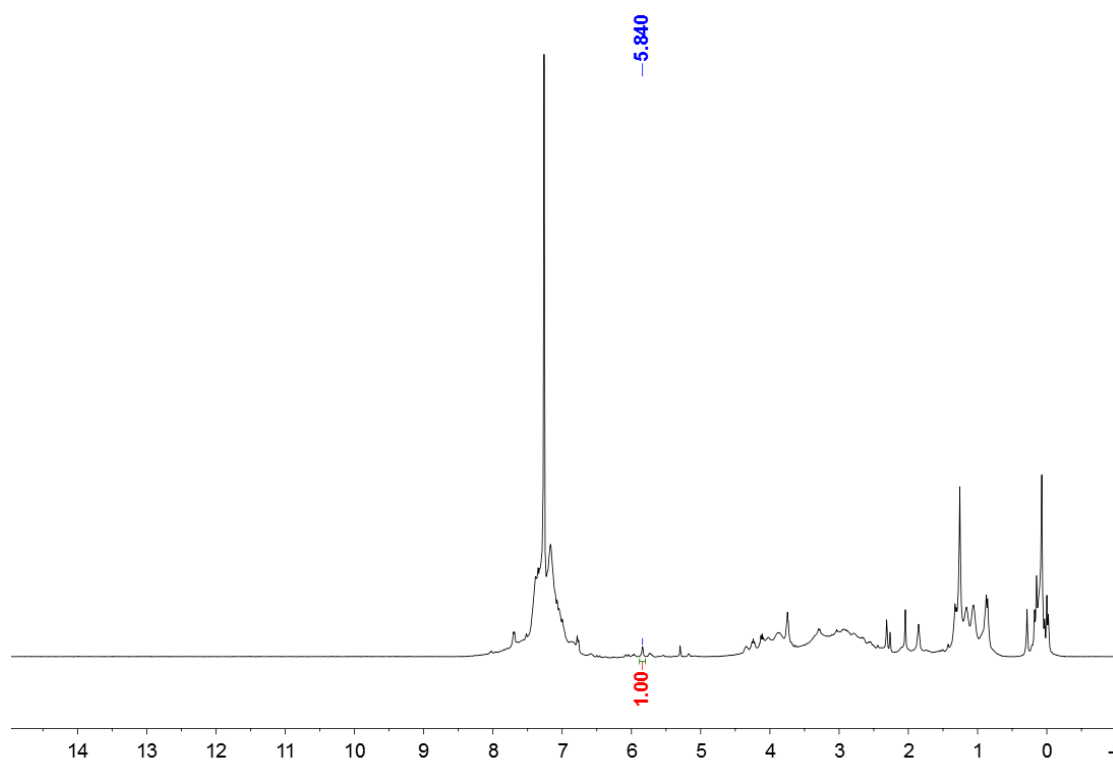


^1H NMR Spectrum of the Crude Reaction Mixture **3af**

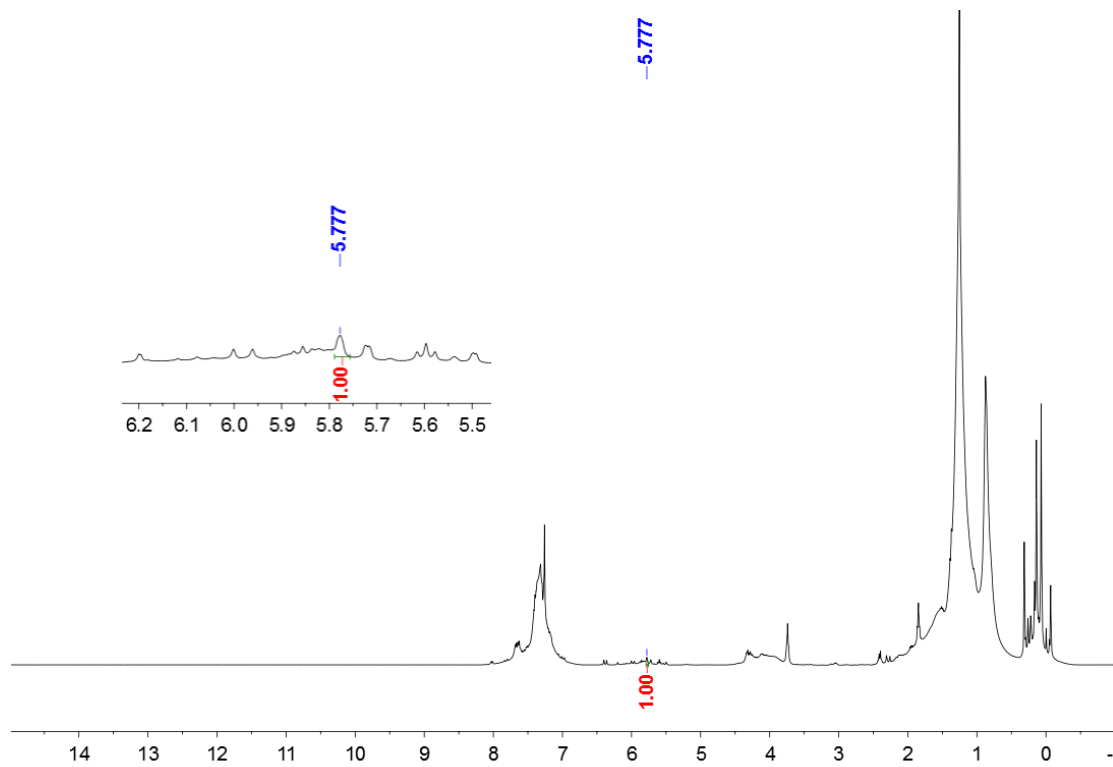




¹H NMR Spectrum of the Crude Reaction Mixture **3ai**



¹H NMR Spectrum of the Crude Reaction Mixture **3aj**



^1H NMR Spectrum of the Crude Reaction Mixture **3ak**