Electronic Supporting Information

for

Efficient synthesis of small-sized phosphonated dendrons: potential organic coatings of iron oxide nanoparticles

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I.Synthetic Part

1.Part I: PEGylated dendrons

Compound 5: A solution of *para*-toluenesulfonyl chloride (22.3 g, 105 mM) in THF (35 mL) was added dropwise to a solution of tetraethyleneglycol monomethyl ether (20.0 g, 96 mM) and NaOH (6.7 g, 166 mM) in a mixture of THF/H_2O (135 mL/45 mL) kept at 0°C. After 1 hr stirring at 0°C, the reaction was allowed to warm to room temperature and stirred for 20 additional hours. The solution was then poured into 200 mL of brine and the volatiles were evaporated. The resulting mixture was extracted several times with CH_2Cl_2 and the combined organic layers were washed with brine, dried over $MgSO_4$ and filtered. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 98:2) to yield **5** (90.2 mmol., 94%). Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, J = 1.5 Hz, 2H, Ar-2,6-*H*), 7.28 (d, J = 1.5 Hz, 2H, Ar-3,5-*H*), 4.11-4.08 (m, 2H, $ArSO_2OCH_2$), 3.64-3.47 (m, 14H, OCH_2CH_2O), 3.31 (s, 3H, OCH_3), 2.39 (s, 3H, $ArCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.9 (Ar-S), 133.2 (Ar-CH_3), 130.0 (Ar), 72.1 (PEG), 70.9 (PEG), 70.7 (PEG), 70.6 (PEG), 69.5 (PEG), 68.8 (PEG), 59.1 (OCH_3), 21.8 (CH_3). MS (MALDI-TOF) m/z calculated for $C_{16}H_{26}NaO_5S$: 385.14, obtained: 385.13.

Compound 6: A solution of methyl gallate (20.0 g, 108.6 mmol), benzyl bromide (14.2 mL, 119.0 mmol, 1.1 equiv.), $KHCO_3$ (32.4 g, 324.0 mmol, 3.0 equiv.) and KI (0.1 g, 0.60 mmol) in DMF (100 mL) was stirred for 4 days at 30°C. The reaction mixture was then poured into 1 L of water and sulfuric acid was added until neutral pH was reached. The aqueous layer was extracted 3 times with CH_2Cl_2 (150 mL). The combined organic layers were washed three times with brine (50 mL), dried over $MgSO_4$ and filtered. The solvent was removed and the residue was purified by column chromatography (SiO_2, CH_2Cl_2 /MeOH 98:2) to provide a yellow oil, which was further washed with petroleum ether and afforded **6** (76.0 mmol, 70%). White foam. ^{1}H NMR (300 MHz, CD_3OD-*d*) δ 7.52 (d, J = 7.5 Hz, 2H, Ar^2-2,6-*H*), 7.31 (m, 3H, Ar^2-3,4,5-*H*), 7.13 (s, 2H, Ar^1-2,6-*H*), 5.18 (s, 2H, Ar^2OCH_2), 3.83 (s, 3H, $COOCH_3$); ^{13}C NMR (75 MHz, CD_3OD-*d*) δ 167.1 ($COOCH_3$), 150.5 (Ar-OH), 138.2 (Ar-O-CH_2), 137.2 (CH_2-Ar^{Bz}), 128.5 (Ar^{Bz}), 128.0 (Ar^{Bz}), 127.8 (Ar^{Bz}), 125.0 (Ar-$COOCH_3$), 108.8 (Ar), 73.8 (OCH_2), 51.2 ($COOCH_3$). MS (MALDI-TOF) m/z calculated for $C_{10}H_{12}NaO_5$: 225.20, obtained: 225.09.

Compound 7: A solution of **5** (26.9 g, 74.3 mmol, 2.2 equiv.), **6** (9.2 g, 33.4 mmol), K_2CO_3 (28.0 g, 200 mmol, 6.0 equiv.) and KI (0.6 g, 3.3 mM, 0.1 equiv.) in acetone (600 mL) was stirred 30 hrs at 65°C. The reaction mixture was filtered over Celite and the solvent was evaporated. The resulting crude product was diluted in CH_2Cl_2 (200 mL) and washed twice with an aqueous saturated solution of $NaHCO_3$ and with brine. After drying over $MgSO_4$, filtration and evaporation of the solvent, the crude product was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 95:5) to afford **7** (25.1 mmol, 75%). Colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, J = 7.7 Hz, 2H, Ar^2-2,6-*H*), 7.28 (m, 5H, Ar^2-3,4,5-*H* and Ar^1-2,6-*H*), 5.12 (s, 2H, Ar^2OCH_2), 4.20-4.17 (t, J = 4.8 Hz, 4H, Ar^1OCH_2), 3.90 (s, 3H, $COOCH_3$), 3.88-3.85 (t, J = 4.8 Hz, 4H, OCH_2CH_2O), 3.74-3.69 (m, 4H, OCH_2CH_2O), 3.67-3.60 (m, 16H, OCH_2CH_2O), 3.54-3.50 (m, 4H, OCH_2CH_2O), 3.35 (s, 6H, $OCH_2CH_2OCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9 ($COOCH_3$), 152.5 (Ar), 142.2 (Ar), 138.2 (CH_2-Ar^{Bz}), 128.2 (Ar^{Bz}), 128.0 (Ar^{Bz}), 127.8 (Ar^{Bz}), 125.3 (Ar-$COOCH_3$), 109.1 (Ar), 74.8 (OCH_2), 72.3 (PEG), 71.2 (PEG), 71.0 (PEG), 70.9 (PEG), 70.8 (PEG), 70.0 (PEG), 69.2 (PEG), 59.3 (OCH_3), 52.5 ($COOCH_3$). MS (MALDI-TOF) m/z calculated for $C_{33}H_{50}NaO_{13}$: 677.33, obtained: 677.03.

Compound 8: Sodium hydroxide (2.6 g, 63.5 mmol, 5 equiv.) was added to a solution of **7** (8.3 g, 12.7 mmol) in a mixture of MeOH/water 4/1 (150 mL). The reaction mixture was stirred 2 hrs at 70°C,

concentrated *in vacuo* and hydrolyzed (200 mL). The pH was adjusted to 3 by addition of HCl 12 N and the aqueous solution was extracted with CH_2Cl_2 (3 x 100 mL). The combined organic phases were washed with brine and water, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude material was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 95:5) to afford **8** (11.4 mM, 90%). Colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, J = 7.8 Hz, 2H, Ar^2-2,6-*H*), 7.38 (s, 2H, Ar^1-2,6-*H*), 7.35-7.28 (m, 3H, Ar^2-3,4,5-*H*), 5.13 (s, 2H, Ar^2OCH_2), 4.20-4.16 (t, J = 4.8 Hz, 4H, Ar^1OCH_2), 3.87-3.82 (t, J = 4.8 Hz, 4H, OCH_2CH_2O), 3.74-3.69 (m, 4H, OCH_2CH_2O), 3.67-3.61 (m, 16H, OCH_2CH_2O), 3.54-3.50 (m, 4H, OCH_2CH_2O), 3.37 (s, 6H, $OCH_2CH_2OCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6 (*C*OOH), 152.8 (Ar), 142.4 (Ar), 137.9 (CH_2-Ar^{Bz}), 128.2 (Ar^{Bz}), 128.0 (Ar^{Bz}), 127.8 (Ar^{Bz}), 124.8 (Ar-COOH), 109.2 (Ar), 74.8 (OCH_2), 72.3 (PEG), 71.2 (PEG), 71.0 (PEG), 70.9 (PEG), 70.8 (PEG), 70.0 (PEG), 69.2 (PEG), 59.1 (OCH_3). MS (MALDI-TOF) m/z calculated for $C_{32}H_{48}O_{13}$: 640.31, obtained: 640.24; calculated for $C_{29}H_{48}NaO_{13}$: 627.30, obtained: 627.13; calculated for $C_{29}H_{48}KO_{13}$: 643.27, obtained: 643.09.

Compound 9: 13.5 mL $LiAlH_4$ (1.0 M in THF) were slowly added to a solution of **7** (5.9 g, 9.0 mmol) in THF (100 mL) kept at 0°C. After 1 hr stirring at room temperature, the unreacted metal hydride was neutralized with ethyl acetate, MeOH and water and the mixture was evaporated under reduced pressure. The crude material was diluted with CH_2Cl_2 (100 mL). The organic phase was washed with a solution of HCl 1 N and brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford **9** (8.1 mM, 90%) which was used without further purification. Colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, J = 8.0 Hz, 2H, Ar^2-2,6-*H*), 7.36-7.30 (m, 3H, Ar^2-3,4,5-*H*), 6.62 (s, 2H, Ar^1-2,6-*H*), 5.02 (s, 2H, Ar^2OCH_2), 4.58 (d, J = 6.0 Hz, 2H, Ar^1CH_2OH), 4.18-4.14 (t, J = 4.8 Hz, 4H, Ar^1OCH_2), 3.86-3.81 (t, J = 4.8 Hz, 4H, OCH_2CH_2O), 3.71-3.68 (m, 4H, OCH_2CH_2O), 3.65-3.58 (m, 16H, OCH_2CH_2O), 3.55-3.50 (m, 4H, OCH_2CH_2O), 3.35 (s, 6H, $OCH_2CH_2OCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.8 (Ar), 138.2 (Ar), 137.4 (CH_2-Ar^{Bz}), 136.9 (Ar), 128.4 (Ar^{Bz}), 128.1 (Ar^{Bz}), 127.7 (Ar^{Bz}), 105.3 (Ar), 74.8 (OCH_2), 71.8 (PEG), 70.6 (PEG), 70.4 (PEG), 70.3 (PEG), 70.2 (PEG), 69.8 (PEG), 68.7 (PEG), 64.9 ($HOCH_2$), 58.9 (OCH_3). MS (MALDI-TOF) m/z calculated for $C_{32}H_{50}KO_{12}$: 665.23, obtained: 665.06.

Compound 10: Thionyl chloride (0.5 mL, 6.5 mmol, 1.5 equiv.) was slowly added to a solution of **9** (2.7 g, 4.3 mmol) in 50 mL CH_2Cl_2. After 2 hrs stirring under reflux, CH_2Cl_2 (50 mL) was added and the organic phase was washed with brine and water, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude oily mixture obtained was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 98:2) to afford **10** (3.0 mmol, 70%). Colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, J = 7.9 Hz, 2H, Ar^2-2,6-*H*), 7.36-7.28 (m, 3H, Ar^2-3,4,5-*H*), 6.62 (s, 2H, Ar^1-2,6-*H*), 5.01 (s, 2H, Ar^2OCH_2), 4.50 (s, 2H, Ar^1CH_2Cl), 4.18-4.13 (t, J = 4.9 Hz, 4H, Ar^1OCH_2), 3.88-3.82 (t, J = 4.8 Hz, 4H, OCH_2CH_2O), 3.73-3.68 (m, 4H, OCH_2CH_2O), 3.65-3.58 (m, 16H, OCH_2CH_2O), 3.56-3.51 (m, 4H, OCH_2CH_2O), 3.35 (s, 6H, $OCH_2CH_2OCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.8 (Ar), 138.2 (Ar), 138.0 (CH_2-Ar^{Bz}), 132.8 (Ar), 128.4 (Ar^{Bz}), 128.2 (Ar^{Bz}), 127.8 (Ar^{Bz}), 108.0 (Ar), 74.8 (OCH_2), 71.8 (PEG), 70.7 (PEG), 70.5 (PEG), 70.4 (PEG), 70.3 (PEG), 69.7 (PEG), 68.9 (PEG), 59.0 (OCH_3), 46.8 ($ClCH_2$). MS (MALDI-TOF) m/z calculated for $C_{32}H_{49}ClO_{11}$: 640.30, obtained: 640.24; calculated for $C_{28}H_{47}BrNaO_{11}$: 661.22, obtained: 661.00; calculated for $C_{28}H_{49}BrNaO_{11}$: 663.23, obtained: 663.00.

Compound 11: A solution of **10** (2.1 g, 3.3 mmol) in triethyl phosphite (3.0 mL) was stirred at 160°C for 2 hrs. The excess of solvent was evaporated under reduced pressure at 70°C. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 95:5) to afford **11** (2.8 mmol, 85%). Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, J = 7.8 Hz, 2H, Ar^2-2,6-*H*), 7.35-7.29 (m, 3H, Ar^2-3,4,5-*H*), 6.53 (d, J = 2.6 Hz, 2H, Ar^1-2,6-*H*), 5.01 (s, 2H, Ar^2OCH_2), 4.15-4.10 (t, J = 4.8 Hz, 4H, Ar^1OCH_2), 4.10-3.92 (m, 4H, $PO(OCH_2CH_3)_2$), 3.87-3.80 (t, J = 4.8 Hz, 4H, OCH_2CH_2O), 3.73-3.68 (m, 4H, OCH_2CH_2O), 3.66-3.59 (m, 16H, OCH_2CH_2O), 3.55-3.50 (m, 4H, OCH_2CH_2O), 3.36 (s, 6H, $OCH_2CH_2OCH_3$), 3.05 (d, J = 21.5 Hz, 2H, Ar^1CH_2P), 1.25 (t, J = 7.0 Hz, 6H, $PO(OCH_2CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.7 (J = 3.2 Hz) (Ar), 138.2 (CH_2-Ar^{Bz}), 137.0 (J = 3.8 Hz) (Ar), 128.2 (Ar^{Bz}), 128.0 (Ar^{Bz}), 126.9 (J = 8.8 Hz) (Ar^{Bz}), 109.1 (J = 6.5 Hz) (Ar), 74.8 (OCH_2), 71.9 (PEG), 70.8 (PEG), 70.7 (PEG), 70.6 (PEG), 70.5 (PEG), 69.7 (PEG), 68.8 (PEG), 62.1 (J = 6.8 Hz) (CH_2CH_3),

59.0 (OCH_3), 33.8 (J = 138.9 Hz) (CH-P), 16.4 (J = 6.0 Hz) (CH_2CH_3); ^{31}P NMR (81 MHz, $CDCl_3$) δ 26.32. MS (MALDI-TOF) m/z calculated for $C_{36}H_{59}O_{14}P$: 746.36, obtained: 746.31; calculated for $C_{32}H_{57}NaO_{14}P$: 719.34, obtained: 719.07; calculated for $C_{32}H_{57}KO_{14}P$: 735.31, obtained: 735.02.

Compound 13: A solution of 1-(benzyloxy)-4-(chloromethyl)benzene (2.0 g, 8.6 mmol) in $P(OEt)_3$ (3 mL) was stirred for 2 hrs at 160°C. The excess of $P(OEt)_3$ was evaporated under reduced pressure at 70°C. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 95:5) to afford **13** (7.9 mmol, 92%). White foam. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50-7.35 (m, 5H, Ar^2-*H*), 7.21 (d, J = 8.1 Hz 2H, Ar^1-2,6-*H*), 6.95 (d, J = 8.1 Hz 2H, Ar^1-3,5-*H*), 5.07 (s, 2H, Ar^1OCH_2), 4.02 (q, J = 7.1 Hz, 4H, $PO(OCH_2CH_3)_2$), 3.12 (d, J = 21.1 Hz, 2H, Ar^1CH_2P), 1.27 (t, J = 7.1 Hz, 6H, $PO(OCH_2CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.7 (J = 3.8 Hz) (Ar), 137.1 (CH_2-Ar^{Bz}), 130.8 (J = 6.0 Hz) (Ar), 128.6 (Ar^{Bz}), 128.0 (Ar^{Bz}), 127.5 (Ar^{Bz}), 123.7 (J = 9.3 Hz) (Ar), 115.0 (J = 2.7 Hz) (Ar), 70.0 (OCH_2), 62.1 (J = 6.5 Hz) (CH_2CH_3), 32.7 (J = 139.4 Hz) (CH-P), 16.4 (J = 6.0 Hz) (CH_2CH_3); ^{31}P NMR (81 MHz, $CDCl_3$) δ 26.79. MS (MALDI-TOF) m/z calculated for $C_{18}H_{24}O_4P$: 335.13, obtained: 335.16.

Compound 14: Palladium activated on carbon 10% (0.5 equiv.) was added to a solution of **13** (2.0 g, 6.0 mmol) in ethanol absolute (60 mL). The mixture was stirred under a hydrogen atmosphere at room temperature for 16 hrs. The crude mixture was filtered through a plug of Celite before being concentrated under reduced pressure. Phenol **14** (5.3 mmol, 89%) was used without further purification. White solid. Melting point: 93°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05 (dd, J = 2.8 and 8.0 Hz, 2H, Ar-2,6-*H*), 6.61 (d, J = 8.0 Hz 2H, Ar-3,5-*H*), 4.02 (q, J = 7.1 Hz, 4H, $PO(OCH_2CH_3)_2$), 3.08 (d, J = 21.0 Hz, 2H, Ar^1CH_2P), 1.27 (t, J = 7.1 Hz, 6H, $PO(OCH_2CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.1 (J = 3.8 Hz) (Ar), 130.6 (J = 6.6 Hz) (Ar), 121.0 (J = 9.3 Hz) (Ar), 116.0 (J = 3.2 Hz) (Ar), 62.4 (J = 7.1 Hz) (CH_2CH_3), 32.3 (J = 139.4 Hz) (CH-P), 16.4 (J = 6.0 Hz) (CH_2CH_3); ^{31}P NMR (81 MHz, $CDCl_3$) δ 27.58. MS (MALDI-TOF) m/z calculated for $C_{11}H_{18}O_4P$: 245.09, obtained: 245.13.

Compound 16: CBr_4 (14.2 g, 42.8 mmol, 1.2 equiv.) was added to a solution of 5-(hydroxymethyl)benzene-1,3-diol (5.0 g, 35.7 mmol) in THF (50 mL). The reaction mixture was cooled to 0°C and a solution of PPh_3 (11.2 g, 42.8 mM, 1.2 equiv.) in THF (10 mL) was added dropwise. After 2 hrs of stirring, water (100 mL) was added and THF was evaporated under reduced pressure. The aqueous phase was extracted three times with CH_2Cl_2. The combined organic phases were washed with brine and water, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, cyclohexane/EtOAc 70:30) to afford **16** (31.4 mmol, 88%). White foam. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.34 (br s, 2H, O*H*), 6.27 (d, J = 2.1 Hz, 2H, Ar-2,4-*H*), 6.14 (t, J = 2.1 Hz, 1H, Ar-6-*H*), 4.49 (s, 2H, $ArCH_2Br$); ^{13}C NMR (75 MHz, DMSO-d_6) δ 158.4 (Ar), 139.5 (Ar), 107.2 (Ar), 102.5 (Ar), 35.0 (CH_2Br).

Compound 17: A solution of **16** (1.00 g, 5.00 mM) in $P(OEt)_3$ (2.6 mL, 3.0 equiv.) was stirred for 2 hrs at 160°C. The excess of $P(OEt)_3$ was evaporated under reduced pressure at 70°C. The crude product was purified by recrystallization (EtOAc/cyclohexane) to afford **17** (3.75 mmol, 75%). White solid. Melting point: 145°C. ^{1}H NMR (300 MHz, CD_3OD) δ 6.74-6.68 (m, 3H, Ar-2,4,6-*H*), 4.05 (q, J = 7.1 Hz, 4H, $PO(OCH_2CH_3)_2$), 3.17 (d, J = 21.9 Hz, 2H, Ar^1CH_2P), 1.28 (t, J = 7.1 Hz, 6H, $PO(OCH_2CH_3)_2$); ^{13}C NMR (75 MHz, CD_3OD) δ 157.3 (Ar), 132.8 (Ar), 121.8 (Ar), 115.2 (Ar), 62.2 (J = 7.2 Hz) (CH_2CH_3), 32.2 (J = 138.3 Hz) (CH-P), 15.3 (J = 6.0 Hz) (CH_2CH_3); ^{31}P NMR (81 MHz, CD_3OD) δ 27.81. MS (MALDI-TOF) m/z calculated for $C_{11}H_{17}NaO_5P$: 283.08, obtained: 283.07; calculated for $C_{11}H_{34}NaO_{10}P$: 543.16, obtained: 543.15.

Compound 19: $LiAlH_4$ 0.5 M in THF (36.0 mmol, 1.8 equiv.) was added dropwise at 0°C to a solution of dimethyl 5-hydroxyisophtalate (4.20 g, 20.0 mmol) in anhydrous THF (21 mL). After 3 hrs stirring under reflux, the mixture was cooled to room temperature and acidified with H_2SO_4 (30 mL, 10%). The THF was evaporated under reduced pressure and the resulting aqueous phase was extracted several times (at least 6 times, TLC control) with ethyl acetate. The organic phase was dried over

$MgSO_4$, filtered and concentrated under reduced pressure to afford **19** (18.8 mmol, 94%). White foam. ^{1}H NMR (300 MHz, CD_3OD-*d*) δ 6.82 (s, 1H, Ar-4-*H*), 6.71 (s, 2H, Ar-2,6-*H*), 4.52 (d, J = 5.8 Hz, 4H, ArCH_2OH); ^{13}C NMR (75 MHz, CD_3OD-*d*) δ 157.2 (Ar), 143.7 (Ar), 115.1 (Ar), 112.1 (Ar), 63.0 (*C*H_2OH). MS (MALDI-TOF) m/z calculated for $C_{10}H_{12}NaO_5$: 225.20, obtained: 225.09.

Compound 20: A solution of HBr 30% in acetic acid (36.0 mmol, 1.8 equiv.) was added dropwise at 0°C to a solution of **19** (2.00 g, 13.0 mmol) in acetic acid (21 mL). The mixture was stirred 24 hrs at room temperature, and then 80 mL of distilled water were added. A white precipitate was formed and the mixture was stirred for additional 10 minutes. The resulting aqueous phase was extracted 3 times with CH_2Cl_2 (200 mL) and the organic layer was washed with distilled water (2 x 120 mL), a saturated solution of sodium hydrogenocarbonate (2 x 120 mL), and with brine (80 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure to afford **20** (12.5 mmol, 96%). White solid. Melting point: 93°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99 (t, J = 1.3 Hz, 1H, Ar-4-*H*), 6.04 (d, J = 1.3 Hz, 2H, Ar-2,6-*H*), 5.38 (br s, 1H, O*H*), 4.40 (s, 4H, ArCH_2Br); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.8 (Ar), 140.0 (Ar), 122.2 (Ar), 116.2 (Ar), 32.7 (*C*H_2Br).

Compound 21: A solution of **20** (2.24 g, 8.0 mmol) in $P(OEt)_3$ (4.0 equiv., 5.0 mL) was stirred 2 hrs at 160°C. The excess of $P(OEt)_3$ was evaporated under reduced pressure at 70°C. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 95:5) to afford **21** (7.6 mmol, 95%). White foam. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.82 (bs, 2H, Ar-2,6-*H*), 6.62 (bs, 1H, Ar-4-*H*), 3.99 (m, 8H, PO(OCH_2CH$_3$)$_2$), 3.49 (d, J = 21.9 Hz, 4H, ArCH_2P), 1.23 (t, J = 7.1 Hz, 12H, PO(OCH$_2$CH_3)$_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9 (Ar), 132.6 (J = 10.6 Hz) (Ar), 122.4 (J = 6.7 Hz) (Ar), 115.8 (Ar), 62.5 (J = 6.6 Hz) (*C*H_2CH$_3$), 33.6 (J = 138.8 Hz) (*C*H-P), 16.5 (J = 5.2 Hz) (CH$_2$*C*H$_3$); ^{31}P NMR (81 MHz, $CDCl_3$) δ 26.72. MS (MALDI-TOF) m/z calculated for $C_{16}H_{29}O_7P_2$: 395.14, obtained: 394.96.

Compound 23: was obtained following the same procedure as described for **18**. Starting from 3,5-dihydroxybenzoic methyl ester (0.7 g, 4.3 mmol), a white foam (2.8 mmol, 65%) was obtained after purification by column chromatography (SiO_2, CH_2Cl_2/MeOH 95:5). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (d, J = 2.5 Hz, 2H, Ar-2,6-*H*), 6.65 (t, J = 2.4 Hz, 1H, Ar-4-*H*), 4.98 (m, 2H, OCH$_2$CH$_2$N*H*), 4.04 (t, J = 5.0 Hz, 4H, OCH_2CH$_2$NH), 3.91 (s, 3H, COOCH_3), 3.56 (m, 4H, OCH$_2$CH_2NH), 1.45 (s, 18H, COOC(CH_3)); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.4 (*C*OOCH$_3$), 159.5 (*C*OO(CH$_3$)$_3$), 155.8 (Ar), 132.1 (Ar), 108.1 (Ar), 106.4 (Ar), 79.7 (*C*(CH$_3$)$_3$), 67.2 (O*C*H$_2$), 52.1 (COO*C*H$_3$), 39.9 (*C*H$_2$NH$_2$), 28.7 (C(*C*H$_3$)$_3$). MS (MALDI-TOF) m/z calculated for $C_{22}H_{34}NaN_2O_8$: 477.23, obtained: 477.22; $C_{44}H_{68}NaN_4O_{16}$: 931.46, obtained: 931.44.

Compound 24: was obtained following the same procedure as described for **8**. Starting from **23** (0.75 g, 1.7 mmol), a white foam (1.5 mmol, 86%) was obtained and used without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (s, 2H, Ar-2,6-*H*), 6.62 (s, 1H, Ar-4-*H*), 5.02 (m, 2H, OCH$_2$CH$_2$N*H*), 4.03 (t, J = 4.8 Hz, 4H, OCH_2CH$_2$NH), 3.52 (m, 4H, OCH$_2$CH_2NH), 1.48 (s, 18H, COOC(CH_3)); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.5 (*C*OOH), 159.4 (*C*OO(CH$_3$)$_3$), 156.1 (Ar), 136.1 (Ar), 108.2 (Ar), 106.4 (Ar), 79.7 (*C*(CH$_3$)$_3$), 67.3 (O*C*H$_2$), 39.9 (*C*H$_2$NH), 28.5 (C(*C*H$_3$)$_3$). MS (MALDI-TOF) m/z calculated for $C_{21}H_{32}NaN_2O_8$: 463.22, obtained: 463.20; $C_{42}H_{64}NaN_4O_{16}$: 903.44, obtained: 903.41.

Compound 25: BOP (0.5 g, 1.2 mmol, 1.3 equiv.) was added to an equimolar solution of **24** (0.4 g, 0.9 mmol) in anhydrous CH_2Cl_2 (20 mL) under argon. **22** (0.4 g, 0.9 mM) and *N,N*-diisopropylethylamine (0.45 mL, 2.7 mM, 3 equiv.) were then added and the reaction mixture was stirred overnight at room temperature. CH_2Cl_2 (20 mL) was added and the organic layer was washed with a solution of NaOH 1 N (2 x 20 mL), HCl 1 N (2 x 20 mL), brine (2 x 20 mL) and water (2 x 20 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 95:5) to afford **25** (0.6 mmol, 65%). Colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.95 (d, J = 2.4 Hz, 2H, Ar^1-2,6-*H*), 6.85-6.78 (m, 3H, Ar^2-2,4,6-*H*), 6.69 (t, J = 2.4 Hz, 1H, Ar^1-4-*H*), 6.57 (t, J = 2.0 Hz, 1H, Ar^{1}OCH$_2$CH$_2$N*H*), 5.02 (m, 2H, Ar^{2}OCH$_2$CH$_2$N*H*), 4.13 (t, J = 5.0 Hz, 2H, Ar^{1}OCH_2CH$_2$NH), 4.07-3.97 (m, 12H,

$Ar^2OCH_2CH_2NH$ and $PO(OCH_2CH_3)_2$), 3.82 (q, J = 5.0 Hz, 2H, $Ar^1OCH_2CH_2NH$), 3.55-3.50 (m, 4H, $Ar^2OCH_2CH_2NH$), 3.08 (d, J = 22.0 Hz, 4H, Ar^1CH_2P), 1.42 (s, 18H, $COOC(CH_3)$); 1.25 (t, J = 7.0 Hz, 12H, $PO(OCH_2CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2 (*C*ONH), 159.8 (Ar), 158.5 ($COO(CH_3)_3$), 155.8 (Ar), 136.8 (Ar), 133.1 (J = 6.0 Hz) (Ar), 124.0 (Ar), 114.8 (J = 4.5 Hz) (Ar), 106.0 (Ar), 104.7 (Ar), 79.8 ($C(CH_3)_3$), 67.5 (OCH_2CH_2NHBoc), 66.8 (OCH_2CH_2NH), 62.3 (J = 3.4 Hz) (CH_2CH_3), 39.5 (CH_2NHBoc), 36.8 (J = 4.0 Hz) ($CH_2NHCOAr$), 33.4 (J = 138.0 Hz) (*C*H-P), 28.4 ($C(CH_3)_3$), 16.4 (J = 2.7 Hz) (CH_2CH_3); ^{31}P NMR (81 MHz, $CDCl_3$) δ 26.10. MS (MALDI-TOF) m/z calculated for $C_{39}H_{63}NaN_3O_{14}P_2$: 882.38, obtained: 882.36.

1.1.General procedure for Steglich-type reaction with carboxylic acid 8 (27, 29, 31, 33)

BOP coupling reagent (1.3 equiv. per acid function) was added under argon to a solution **8** (1.0 equiv. per amine function) in distilled CH_2Cl_2. After 5 min of stirring, *N,N*-diisopropylethylamine (3 equiv. per amine function) and amine derivative (1.0 equiv.) were added. The reaction mixture was stirred overnight at room temperature. CH_2Cl_2 (50 mL) was added and the organic layer was washed with a solution of sodium hydroxide 1 N (2 x 20 mL), HCl 1 N (2 x 20 mL), brine (2 x 20 mL) and water (2 x 20 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure.

Compound 27: Starting from **15** (0.30 g, 0.45 mmol), **27** was obtained (0.31 mmol, 68%) as colourless oil after purification by column chromatography (SiO_2, CH_2Cl_2/MeOH 95:5). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, J = 8.1 Hz, 2H, $Ar^1$2,6-*H*), 7.35-7.25(m, 3H, Ar^3-3,4,5-*H*), 7.20 (dd, 2H, J = 2.4 and 8.5 Hz, Ar^3-2,6-*H*), 7.08 (s, 2H, Ar^2-2,6-*H*), 6.85 (d, J = 8.1 Hz, 3H, $Ar^1$3,5-*H* and $Ar^1OCH_2CH_2NH$), 5.08 (s, 2H, Ar^3OCH_2), 4.18 (t, 4H, J = 4.8 Hz, $Ar^2OCH_2CH_2O$), 4.11 (t, 2H, J = 5.3 Hz, $Ar^1OCH_2CH_2NH$), 4.08-3.96 (m, 4H, $PO(OCH_2CH_3)_2$), 3.85-3.78 (m, 6H, $Ar^1OCH_2CH_2NH$ and OCH_2CH_2O), 3.70-3.50 (m, 24H, OCH_2CH_2O), 3.33 (s, 6H, $OCH_2CH_2OCH_3$), 3.08 (d, J = 21.1 Hz, 2H, Ar^1CH_2P), 1.22 (t, J = 7.1 Hz, 6H, $PO(OCH_2CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2 (NH*C*O), 157.5 (J = 3.3 Hz) (Ar), 152.6 (Ar), 140.7 (Ar), 137.6 (Ar), 130.8 (J = 6.6 Hz) (Ar), 129.6 (Ar), 128.4 (Ar), 128.1 (Ar), 127.8 (Ar), 123.9 (J = 8.7 Hz) (Ar), 114.6 (J = 3.3 Hz) (Ar), 107.0 (Ar), 74.8 (OCH_2), 71.8 (PEG), 70.65 (PEG), 70.5 (PEG), 70.45 (PEG), 70.4 (PEG), 70.35 (PEG), 69.8 (PEG), 68.8 (PEG), 66.6 (OCH_2CH_2NH), 62.0 (J = 6.6 Hz) (CH_2CH_3), 58.9 (OCH_3), 39.5 ($CH_2NHCOAr$), 32.8 (J = 138.9 Hz) (*C*H-P), 16.3 (J = 6.0 Hz) (CH_2CH_3); ^{31}P NMR (81 MHz, $CDCl_3$) δ 26.63. MS (MALDI-TOF) m/z calculated for $C_{45}H_{69}NO_{16}P$: 910.43, obtained: 910.34; calculated for $C_{45}H_{68}NaNO_{16}P$: 932.43, obtained: 932.35; calculated for $C_{45}H_{68}KNO_{16}P$: 948.40, obtained: 948.30.

Compound 29: Starting from **22** (0.6 g, 1.4 mmol), **29** was obtained (1.2 mmol, 87%) as colourless oil after purification by column chromatography (SiO_2, CH_2Cl_2/MeOH 95:5). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, J = 7.7 Hz, 2H, Ar^3-2,6-*H*), 7.35-7.28 (m, 3H, Ar^3-3,4,5-*H*), 7.07 (s, 2H, Ar^2-2,6-*H*), 6.88 (t, J = 5.7 Hz, 1H, OCH_2CH_2NH), 6.85-6.78 (m, 3H, Ar^1-2,4,6-*H*), 5.07 (s, 2H, Ar^3OCH_2), 4.20-4.17 (t, J = 4.8 Hz, 4H, Ar^2OCH_2), 4.15-4.11 (t, J = 5.0 Hz, 2H, OCH_2CH_2NH), 4.08-3.96 (m, 8H, $PO(OCH_2CH_3)_2$), 3.88-3.78 (m, 6H, OCH_2CH_2NH and OCH_2CH_2O), 3.71-3.68 (m, 4H, OCH_2CH_2O), 3.65-3.58 (m, 16H, OCH_2CH_2O), 3.55-3.49 (m, 4H, OCH_2CH_2O), 3.35 (s, 6H, $OCH_2CH_2OCH_3$), 3.08 (d, J = 21.5 Hz, 4H, Ar^1CH_2P), 1.25 (t, J = 7.0 Hz, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2 (NH*C*O), 158.6 (J = 2.8 Hz) (Ar), 152.8 (Ar), 141.0 (Ar), 137.8 (Ar), 133.1 (J = 6.0 Hz) (Ar), 129.6 (Ar), 128.2 (Ar), 128.0 (Ar), 127.8 (Ar), 124.0 (J = 6.8 Hz) (Ar), 114.6 (J = 4.8 Hz) (Ar), 107.0 (Ar), 74.9 (OCH_2), 72.0 (PEG), 70.8 (PEG), 70.7 (PEG), 70.6 (PEG), 69.8 (PEG), 69.1 (PEG), 66.8 (OCH_2CH_2NH), 62.1 (J = 3.4 Hz) (CH_2CH_3), 58.9 (OCH_3), 39.5 ($CH_2NHCOAr$), 33.5 (J = 138.3 Hz) (*C*H-P), 16.5 (J = 2.7 Hz) (CH_2CH_3); ^{31}P NMR (81 MHz, $CDCl_3$) δ 26.08. MS (MALDI-TOF) m/z calculated for $C_{50}H_{79}NaNO_{19}P_2$: 1082.87, obtained: 1082.51.

Compound 31: Starting from **18** (0.9 g, 1.8 mmol), **31** was obtained (1.3 mmol, 70%) as colourless oil after purification by column chromatography (SiO_2, CH_2Cl_2/MeOH 95:5). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, J = 7.8 Hz, 2H, Ar^3-2,6-*H*), 7.35-7.28 (m, 3H, Ar^3-3,4,5-*H*), 7.08 (s, 4H, Ar^2-2,6-*H*), 6.88 (t, J = 7.2 Hz, 2H, CH_2NHCO), 6.48 (t, J = 1.7 Hz, 2H, Ar^1-2,4-*H*), 6.42 (m, 1H, Ar^1-6-*H*), 5.08 (s, 4H, Ar^3OCH_2), 4.20-4.15 (t, J = 4.8 Hz, 8H, Ar^1OCH_2), 4.14-4.10 (t, J = 4.8 Hz, 4H,

OC*H*$_2$CH$_2$NH), 4.08-3.93 (m, 4H, PO(OC*H*$_2$CH$_3$)$_2$), 3.87-3.77 (m, 12H, OCH$_2$C*H*$_2$NH and OCH$_2$CH$_2$O), 3.71-3.67 (m, 8H, OCH$_2$CH$_2$O), 3.65-3.56 (m, 32H, OCH$_2$CH$_2$O), 3.55-3.50 (m, 8H, OCH$_2$CH$_2$O), 3.33 (s, 12H, OCH$_2$CH$_2$OC*H*$_3$), 3.05 (d, *J* = 21.5 Hz, 2H, Ar^{1}C*H*$_2$P), 1.25 (t, *J* = 7.0 Hz, 6H, PO(OCH$_2$C*H*$_3$)$_2$); ^{13}C NMR (75 MHz, CDCl$_3$) δ 167.1 (NH*C*O), 159.5 (Ar), 146.6 (Ar), 141.2 (Ar), 133.9 (*J* = 5.8 Hz) (Ar), 128.4 (Ar), 128.2 (Ar), 127.8 (Ar), 124.8 (Ar), 108.7 (Ar), 101.1 (Ar), 74.7 (O*C*H$_2$), 71.9 (PEG), 70.8 (PEG), 70.7 (PEG), 70.6 (PEG), 69.8 (PEG), 69.5 (PEG), 66.8 (O*C*H$_2$CH$_2$NH), 62.3 (*J* = 7.0 Hz) (*C*H$_2$CH$_3$), 58.9 (O*C*H$_3$), 39.5 (*C*H$_2$NHCOAr), 33.4 (*J* = 137.5 Hz) (*C*H-P), 16.4 (*J* = 2.7 Hz) (CH$_2$*C*H$_3$); ^{31}P NMR (81 MHz, CDCl$_3$) δ 26.12. MS (MALDI-TOF) m/z calculated for C$_{79}$H$_{120}$N$_2$O$_{29}$P: 1591.76, obtained: 1591.74; calculated for C$_{79}$H$_{119}$NaN$_2$O$_{29}$P: 1623.76, obtained: 1623.76.

Compound 33: Starting from **26** (0.40 g, 0.45 mmol), **33** was obtained (0.32 mmol, 70%) as colourless oil after purification by column chromatography (SiO$_2$, CH$_2$Cl$_2$/MeOH 95:5). ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.50 (d, *J* = 7.7 Hz, 2H, Ar^3-2,6-*H*), 7.35-7.28 (m, 3H, Ar^3-3,4,5-*H*), 7.11 (s, 4H, Ar^2-2,6-*H*), 7.05 (t, *J* = 5.0 Hz, 2H, Ar^{2}OCH$_2$CH$_2$N*H*), 6.95 (d, *J* = 2.3 Hz, 2H, Ar^1-2,6-*H*), 6.69 (t, *J* = 2.4 Hz, 1H, Ar^1-4-*H*), 6.82-6.78 (m, 3H, Ar^2-2,4,6-*H*), 6.64 (t, *J* = 1.9 Hz, 1H, Ar^{1}OCH$_2$CH$_2$N*H*), 5.07 (s, 4H, Ar^{3}OC*H*$_2$), 4.20-4.17 (m, 14H, Ar^{2}OC*H*$_2$CH$_2$O, Ar^{1}OC*H*$_2$CH$_2$NH and Ar^{2}OC*H*$_2$CH$_2$NH), 4.08-3.96 (m, 8H, PO(OC*H*$_2$CH$_3$)$_2$), 3.83-3.78 (m, 14H, Ar^{1}OCH$_2$C*H*$_2$NH, Ar^{2}OCH$_2$C*H*$_2$NH and OCH$_2$CH$_2$O), 3.65-3.55 (m, 34H, OCH$_2$CH$_2$O), 3.55-3.48 (m, 8H, OCH$_2$CH$_2$O), 3.34 (s, 12H, OCH$_2$CH$_2$OC*H*$_3$), 3.08 (d, *J* = 22.0 Hz, 4H, Ar^{1}C*H*$_2$P), 1.23 (t, *J* = 7.0 Hz, 12H, PO(OCH$_2$C*H*$_3$)$_2$); ^{13}C NMR (75 MHz, CDCl$_3$) δ 167.2 (NH*C*O), 159.8 (Ar), 152.5 (Ar), 141.0 (Ar), 137.8 (Ar), 136.5 (Ar), 133.1 (*J* = 6.0 Hz) (Ar), 129.5 (Ar), 128.2 (Ar), 128.0 (Ar), 127.8 (Ar), 124.0 (Ar), 114.8 (*J* = 4.8 Hz) (Ar), 107.8 (Ar), 107.0 (Ar), 106.0 (Ar), 74.9 (O*C*H$_2$), 72.0 (PEG), 70.8 (PEG), 70.7 (PEG), 70.6 (PEG), 69.8 (PEG), 69.1 (PEG), 66.8 (O*C*H$_2$CH$_2$NH), 62.1 (*J* = 3.4 Hz) (*C*H$_2$CH$_3$), 58.9 (O*C*H$_3$), 39.5 (*C*H$_2$NHCOAr), 33.3 (*J* = 138.0 Hz) (*C*H-P), 16.4 (*J* = 2.7 Hz) (CH$_2$*C*H$_3$); ^{31}P NMR (81 MHz, CDCl$_3$) δ 26.18. MS (MALDI-TOF) m/z calculated for C$_{93}$H$_{169}$NaN$_3$O$_{34}$P$_2$: 1926.87, obtained: 1926.81.

1.2.General procedure for hydrogenation with palladium on carbon (28, 30, 32, 34)

Benzylated compound (**27**, **29**, **31** or **33**) was dissolved in ethanol absolute (20 mL) and palladium activated on carbon 10% (0.5 equiv.) was added. The mixture was stirred under a hydrogen atmosphere at room temperature for 16 hrs. The crude mixture was filtered through a plug of Celite, concentrated and purified by column chromatography.

Compound 28: Starting from **27** (0.6 g, 0.65 mmol), **28** was obtained (0.54 mmol, 83%) as a colourless oil after purification by column chromatography (SiO$_2$, CH$_2$Cl$_2$/MeOH 95:5). ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.21 (dd, *J* = 2.5 and 8.1 Hz, 2H, Ar^{1}2,6-*H*), 7.15 (s, 2H, Ar^2-2,6-*H*), 6.86 (d, *J* = 8.1 Hz, 2H, Ar^{1}3,5-*H*), 6.78 (t, *J* = 5.6 Hz, 1H, Ar^{1}OCH$_2$CH$_2$N*H*), 4.21 (t, 4H, *J* = 4.8 Hz, Ar^{2}OC*H*$_2$CH$_2$O), 4.11 (t, 2H, *J* = 5.2 Hz, Ar^{1}OC*H*$_2$CH$_2$NH), 4.05-3.95 (m, 4H, PO(OC*H*$_2$CH$_3$)$_2$), 3.88-3.80 (m, 6H, Ar^{1}OCH$_2$C*H*$_2$NH and OCH$_2$CH$_2$O), 3.72-3.50 (m, 24H, OCH$_2$CH$_2$O), 3.34 (s, 6H, OCH$_2$CH$_2$OC*H*$_3$), 3.07 (d, *J* = 21.1 Hz, 2H, Ar^{1}C*H*$_2$P), 1.22 (t, *J* = 7.0 Hz, 6H, PO(OCH$_2$C*H*$_3$)$_2$); ^{13}C NMR (75 MHz, CDCl$_3$) δ 168.1 (*C*ONH), 157.3 (*J* = 3.3 Hz) (Ar), 146.8 (Ar), 141.3 (Ar), 130.6 (*J* = 6.6 Hz) (Ar), 124.6 (Ar), 123.9 (*J* = 9.3 Hz) (Ar), 114.6 (*J* = 3.3 Hz) (Ar), 108.6 (Ar), 71.8 (PEG), 70.6 (PEG), 70.5 (PEG), 70.4 (PEG), 70.3 (PEG), 69.6 (*J* = 7.1 Hz) (PEG), 66.8 (O*C*H$_2$CH$_2$NH), 61.9 (*J* = 7.1 Hz) (*C*H$_2$CH$_3$), 58.9 (O*C*H$_3$), 39.4 (*C*H$_2$NHCOAr), 32.8 (*J* = 139.5 Hz) (*C*H-P), 16.3 (*J* = 6.0 Hz) (CH$_2$*C*H$_3$); ^{31}P NMR (81 MHz, CDCl$_3$) δ 26.64. MS (MALDI-TOF) m/z calculated for C$_{38}$H$_{63}$NO$_{16}$P: 820.38, obtained: 820.41; calculated for C$_{38}$H$_{62}$NaNO$_{16}$P: 842.38, obtained: 842.40.

Compound 30: Starting from **29** (0.8 g, 0.8 mmol), **30** was obtained (0.64 mmol, 80%) as a colourless oil after purification by column chromatography (SiO$_2$, CH$_2$Cl$_2$/MeOH 90:10). ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.16 (s, 2H, Ar^2-2,6-*H*), 6.85-6.78 (m, 3H, Ar^1-2,4,6-*H*), 6.65 (m, 1H, OCH$_2$CH$_2$N*H*), 4.27-4.21 (t, *J* = 4.7 Hz, 4H, Ar^{2}OC*H*$_2$), 4.15-4.10 (t, *J* = 5.0 Hz, 2H, OC*H*$_2$CH$_2$NH), 4.08-3.98 (m, 8H, PO(OC*H*$_2$CH$_3$)$_2$), 3.88-3.78 (m, 6H, OCH$_2$C*H*$_2$NH and OCH$_2$CH$_2$O), 3.75-3.60 (m, 20H, OCH$_2$CH$_2$O), 3.56-3.51 (m, 4H, OCH$_2$CH$_2$O), 3.35 (s, 6H, OCH$_2$CH$_2$OC*H*$_3$), 3.09 (d, *J* = 22.0 Hz, 4H, Ar^{1}C*H*$_2$P),

1.26 (t, J = 7.1 Hz, 12H, PO(OCH_2CH_3)$_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.3 (NH*C*O), 158.7 (J = 2.8 Hz) (Ar), 146.8 (Ar), 141.0 (Ar), 133.1 (J = 6.0 Hz) (Ar), 124.0 (Ar), 114.6 (Ar), 108.4 (Ar), 72.0 (PEG), 70.8 (PEG), 70.7 (PEG), 70.6 (PEG), 69.8 (PEG), 69.1 (PEG), 66.8 (O*C*H$_2$CH$_2$NH), 62.1 (J = 3.4 Hz) (*C*H$_2$CH$_3$), 58.9 (O*C*H$_3$), 39.5 (*C*H$_2$NHCOAr), 33.4 (J = 138.1 Hz) (*C*H-P), 16.4 (J = 2.7 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ 26.10. MS (MALDI-TOF) m/z calculated for $C_{43}H_{74}NO_{19}P_2$: 970.43, obtained: 970.44; calculated for $C_{43}H_{73}NaNO_{19}P_2$: 992.43, obtained: 992.44.

Compound 32: Starting from **31** (1.85 g, 1.2 mmol), **32** was obtained (1.0 mmol, 86%) as a colourless oil after purification by column chromatography (SiO_2, CH_2Cl_2/MeOH 90:10). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (br s, 2H, Ar^2-O*H*), 7.16 (s, 4H, Ar^2-2,6-*H*), 6.85 (t, J = 7.2 Hz, 2H, CH$_2$N*H*CO), 6.47 (t, J = 1.7 Hz, 1H, Ar^1-2,4-*H*), 6.40 (m, 1H, Ar^1-6-*H*), 4.22-4.17 (t, J = 4.9 Hz, 8H, Ar^{1}OC*H*$_2$), 4.12-4.08 (t, J = 4.8 Hz, 4H, OC*H*$_2$CH$_2$NH), 4.07-3.96 (m, 4H, PO(OC*H*$_2$CH$_3$)$_2$), 3.84-3.75 (m, 12H, OCH$_2$C*H*$_2$NH and OCH$_2$CH$_2$O), 3.71-3.67 (m, 40H, OCH$_2$CH$_2$O), 3.55-3.50 (m, 8H, OCH$_2$CH$_2$O), 3.35 (s, 12H, OCH$_2$CH$_2$OC*H*$_3$), 3.06 (d, J = 21.5 Hz, 2H, Ar^{1}C*H*$_2$P), 1.26 (t, J = 7.1 Hz, 6H, PO(OCH_2CH_3)$_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 159.7 (Ar), 146.6 (Ar), 141.2 (Ar), 133.9 (J = 6.0 Hz) (Ar), 124.8 (Ar), 108.7 (Ar), 101.1 (Ar), 71.9 (PEG), 70.8 (PEG), 70.7 (PEG), 70.6 (PEG), 69.8 (PEG), 69.5 (PEG), 66.7 (O*C*H$_2$CH$_2$NH), 62.3 (J = 7.0 Hz) (*C*H$_2$CH$_3$), 58.9 (O*C*H$_3$), 53.2, 39.5, 35.2, 33.4 (J = 137.5 Hz) (*C*H-P), 16.4 (J = 2.7 Hz) (CH$_2$*C*H$_3$); ^{31}P NMR (81 MHz, $CDCl_3$) δ 26.10. MS (MALDI-TOF) m/z calculated for $C_{65}H_{107}N_2O_{29}P$: 1411.56, obtained: 1411.55; calculated for $C_{65}H_{107}NaN_2O_{29}P$: 1433.67, obtained: 1433.56.

Compound 34: Starting from **33** (0.65 g, 0.34 mmol), **34** was obtained (0.26 mmol, 76%) as a colourless oil after purification by column chromatography (SiO_2, CH_2Cl_2/MeOH 95:5). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (br s, 2H, Ar^{2}O*H*), 7.20 (s, 4H, Ar^2-2,6-*H*), 7.11 (t, J = 5.5 Hz, 2H, Ar^{2}OCH$_2$CH$_2$N*H*), 6.96 (d, J = 1.7 Hz, 2H, Ar^1-2,6-*H*), 6.80-6.74 (m, 3H, Ar^2-2,4,6-*H*), 6.55 (t, J = 1.9 Hz, 1H, Ar^1-4-*H*), 6.44 (t, J = 5.3 Hz, 1H, Ar^{1}OCH$_2$CH$_2$N*H*), 4.17 (t, J = 4.8 Hz, 8H, Ar^{2}OC*H*$_2$), 4.11 (t, J = 4.6 Hz, 6H, Ar^{1}OC*H*$_2$CH$_2$NH and Ar^{2}OC*H*$_2$CH$_2$NH), 4.05-3.93 (m, 8H, PO(OC*H*$_2$CH$_3$)$_2$), 3.83-3.75 (m, 14H, Ar^{1}OCH$_2$C*H*$_2$NH, Ar^{2}OCH$_2$C*H*$_2$NH and OCH$_2$CH$_2$O), 3.70-3.60 (m, 34H, OCH$_2$CH$_2$O), 3.52-3.48 (m, 8H, OCH$_2$CH$_2$O), 3.34 (s, 12H, OCH$_2$CH$_2$OC*H*$_3$), 3.06 (d, J = 22.0 Hz, 4H, Ar^{1}C*H*$_2$P), 1.21 (t, J = 7.0 Hz, 12H, PO(OCH_2CH_3)$_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2 (NH*C*O), 159.8 (Ar), 152.5 (Ar), 140.8 (Ar), 136.5 (Ar), 133.1 (J = 6.0 Hz) (Ar), 129.5 (Ar), 124.5 (Ar), 114.8 (J = 4.8 Hz) (Ar), 108.7 (Ar), 106.0 (Ar), 104.8 (Ar), 71.9 (PEG), 70.8 (PEG), 70.7 (PEG), 70.6 (PEG), 69.8 (PEG), 69.1 (PEG), 66.8 (O*C*H$_2$CH$_2$NH), 62.1 (J = 7.0 Hz) (*C*H$_2$CH$_3$), 58.9 (O*C*H$_3$), 39.5 (*C*H$_2$NHCOAr), 33.4 (J = 137.5 Hz) (*C*H-P), 16.3 (J = 2.7 Hz) (CH$_2$*C*H$_3$); ^{31}P NMR (81 MHz, $CDCl_3$) δ 26.12. MS (MALDI-TOF) m/z calculated for $C_{79}H_{127}NaN_3O_{34}P_2$: 1746.78, obtained: 1746.79; calculated for $C_{79}H_{126}NaKN_3O_{34}P_2$: 1786.78, obtained: 1786.75.

1.3.General procedure for the Williamson [36] etherification with tosylated hydroxy-dPEG$^{TM}_8$-t-butyl ester 35 (36-39)

Compound 35: The synthesis and spectroscopic data of **35** are the same as those reported in the literature. [29].

K_2CO_3 (3 equiv. per phenol) and KI (0.3 equiv. per tosyl) were added to an equimolar solution of phenol (**28, 30, 32** or **34**) and **35** in acetone (15 mL). The reaction mixture was stirred at 60°C during 24 hrs, filtered over Celite, evaporated under reduced pressure and the crude was diluted in CH_2Cl_2 (50 mL). The organic layer was washed twice with a saturated solution of $NaHCO_3$, then with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography.

Compound 36: Starting from compound **28** (0.12 g, 0.15 mmol), compound **36** was obtained (0.13 mmol, 87%) as a colourless oil after purification by column chromatography (SiO_2, CH_2Cl_2/MeOH 95:5). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (dd, J = 2.5 and 8.1 Hz, 2H, Ar^1-2,6-*H*), 7.11 (s, 2H, Ar^2-2,6-*H*), 6.91 (t, J = 5.6 Hz, 1H, Ar^{1}OCH$_2$CH$_2$N*H*), 6.84 (d, J = 8.1 Hz, 2H, Ar^1-3,5-*H*), 4.20-4.15 (m,

6H, $Ar^2OCH_2CH_2O$), 4.11 (t, 2H, J = 5.1 Hz, $Ar^1OCH_2CH_2NH$), 4.05-3.95 (m, 4H, $PO(OCH_2CH_3)_2$), 3.85-3.77 (m, 8H, $Ar^1OCH_2CH_2NH$ and OCH_2CH_2O), 3.70-3.50 (m, 54H, OCH_2CH_2O), 3.33 (s, 6H, $OCH_2CH_2OCH_3$), 3.07 (d, J = 21.1 Hz, 2H, Ar^1CH_2P), 2.49 (t, 2H, J = 6.6 Hz, $Ar^2OCH_2CH_2COOC(CH_3)_3$), 1.43 (s, 9H, $Ar^2OCH_2CH_2COOC(CH_3)_3$), 1.22 (t, J = 7.1 Hz, 6H, $PO(OCH_2CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.0 ($COO(CH_3)_3$), 167.1 (NHCO), 157.6 (J = 3.3 Hz) (Ar), 152.5 (Ar), 141.6 (Ar), 130.8 (J = 6.6 Hz) (Ar), 129.5 (Ar), 124.1 (J = 9.3 Hz) (Ar), 114.6 (J = 2.7 Hz) (Ar), 107.4 (Ar), 80.3 ($C(CH_3)_3$), 72.2 (PEG), 71.9 (PEG), 70.7 (PEG), 70.6 (PEG), 70.5 (PEG), 70.55 (PEG), 70.4 (PEG), 70.3 (PEG), 69.7 (PEG), 69.1 (PEG), 66.8 (OCH_2CH_2NH), 66.6 (CH_2CH_2COO), 62.0 (J = 7.1 Hz) (CH_2CH_3), 58.9 (OCH_3), 39.8 ($CH_2NHCOAr$), 35.4 (CH_2COO), 32.8 (J = 138.9 Hz) (CH-P), 28.4 ($C(CH_3)_3$), 16.3 (J = 6.0 Hz) (CH_2CH_3); ^{31}P NMR (81 MHz, $CDCl_3$) δ 26.65. MS (MALDI-TOF) m/z calculated for $C_{61}H_{106}NaNO_{26}P$: 1322.60, obtained: 1322.58; calculated for calculated for $C_{61}H_{106}KNO_{26}P$: 1338.60, obtained: 1338.55.

Compound 37: Starting from **32** (0.3 g, 0.22 mmol), compound **37** was obtained (0.18 mmol, 82%) as a colourless oil after purification by column chromatography (SiO_2, CH_2Cl_2/MeOH 90:10). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 (s, 4H, Ar^2-2,6-*H*), 7.02 (t, J = 5.5 Hz, 2H, $Ar^1OCH_2CH_2NH$), 6.47 (t, 2H, J = 2.0 Hz, Ar^1-2,6-*H*), 6.41 (t, J = 2.0 Hz, 1H, Ar^1-4-*H*), 4.22-4.17 (m, J = 4.8 Hz, 12H, $Ar^2OCH_2CH_2O$), 4.11 (t, 4H, J = 5.1 Hz, $Ar^1OCH_2CH_2NH$), 4.05-3.95 (m, 4H, $PO(OCH_2CH_3)_2$), 3.85-3.75 (m, 16H, $Ar^1OCH_2CH_2NH$ and OCH_2CH_2O), 3.70-3.50 (m, 108H, OCH_2CH_2O), 3.35 (s, 12H, $OCH_2CH_2OCH_3$), 3.06 (d, J = 21.8 Hz, 2H, Ar^1CH_2P), 2.48 (t, 4H, J = 6.6 Hz, $Ar^2OCH_2CH_2COOC(CH_3)_3$), 1.41 (s, 9H, $Ar^2OCH_2CH_2COOC(CH_3)_3$), 1.21 (t, J = 7.0 Hz, 6H, $PO(OCH_2CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8 ($COO(CH_3)_3$), 167.1 (NHCO), 159.6 (J = 3.3 Hz) (Ar), 152.5 (Ar), 141.3 (Ar), 129.4 (Ar), 108.8 (J = 6.0 Hz) (Ar), 107.2 (Ar), 80.3 ($C(CH_3)_3$), 72.2 (PEG), 71.9 (PEG), 70.7 (PEG), 70.6 (PEG), 70.55 (PEG), 70.5 (PEG), 70.4 (PEG), 70.3 (PEG), 69.6 (PEG), 69.0 (PEG), 66.8 (OCH_2CH_2NH), 66.6 (CH_2CH_2COO), 62.2 (J = 6.6 Hz) (CH_2CH_3), 58.9 (OCH_3), 39.5 ($CH_2NHCOAr$), 36.4 (CH_2COO), 32.3 (J = 138.9 Hz) (CH-P), 28.2 ($C(CH_3)_3$), 16.3 (J = 6.0 Hz) (CH_2CH_3); ^{31}P NMR (81 MHz, $CDCl_3$) δ 26.08. MS (MALDI-TOF) m/z calculated for $C_{111}H_{195}NaN_2O_{49}P$: 2394.26 obtained: 2394.06.

Compound 38: Starting from compound **30** (0.3 g, 0.31 mmol), compound **38** was obtained (0.28 mmol, 90%) as a colourless oil after purification by column chromatography (SiO_2, CH_2Cl_2/MeOH 90:10). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 (s, 2H, Ar^2-2,6-*H*), 6.87 (t, J = 5.1 Hz, 1H, $Ar^1OCH_2CH_2NH$), 6.80 (t, 1H, J = 2.0 Hz, Ar^1-2-*H*), 6.76 (q, 2H, J = 2.0 Hz, Ar^1-4,6-*H*), 4.22-4.15 (m, 6H, $Ar^2OCH_2CH_2O$), 4.12 (t, 2H, J = 5.1 Hz, $Ar^1OCH_2CH_2NH$), 4.05-3.95 (m, 8H, J = 7.0 Hz, $PO(OCH_2CH_3)_2$), 3.85-3.75 (m, 8H, $Ar^1OCH_2CH_2NH$ and OCH_2CH_2O), 3.70-3.50 (m, 54H, OCH_2CH_2O), 3.33 (s, 6H, $OCH_2CH_2OCH_3$), 3.07 (d, J = 21.7 Hz, 4H, Ar^1CH_2P), 2.48 (t, 2H, J = 6.6 Hz, $Ar^2OCH_2CH_2COOC(CH_3)_3$), 1.42 (s, 9H, $Ar^2OCH_2CH_2COOC(CH_3)_3$), 1.22 (t, J = 7.0 Hz, 12H, $PO(OCH_2CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9 ($COO(CH_3)_3$), 167.1 (NHCO), 157.5 (Ar), 152.4 (Ar), 141.6 (Ar), 133.2 (J = 6.0 Hz) (Ar), 129.4 (Ar), 124.1 (Ar), 114.6 (J = 5.0 Hz) (Ar), 107.3 (Ar), 80.4 ($C(CH_3)_3$), 72.2 (PEG), 71.9 (PEG), 70.7 (PEG), 70.6 (PEG), 70.55 (PEG), 70.5 (PEG), 70.4 (PEG), 70.3 (PEG), 69.7 (PEG), 69.1 (PEG), 66.8 (OCH_2CH_2NH), 66.6 (CH_2CH_2COO), 62.1 (J = 7.0 Hz) (CH_2CH_3), 58.9 (OCH_3), 39.6 ($CH_2NHCOAr$), 35.2, (CH_2COO), 33.8 (J = 137.8 Hz) (CH-P), 27.9 ($C(CH_3)_3$), 16.4 (J = 6.0 Hz) (CH_2CH_3); ^{31}P NMR (81 MHz, $CDCl_3$) δ 26.06. MS (MALDI-TOF) m/z calculated for $C_{66}H_{117}NaNO_{29}P_2$: 1472.72, obtained: 1472.65.

Compound 39: Starting from **34** (0.11 g, 0.07 mmol), compound **39** was obtained (0.05 mmol, 70%) as a colourless oil after purification by column chromatography (SiO_2, CH_2Cl_2/MeOH 90:10). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (t, J = 5.5 Hz, 2H, $Ar^2OCH_2CH_2NH$), 7.17-7.10 (m, 5H, Ar^3-2,6-*H* and Ar^2-4-*H*), 7.02 (d, J = 1.7 Hz, 2H, Ar^2-2,6-*H*), 6.80-6.75 (m, 3H, Ar^1-2,4,6-*H*), 6.64 (t, J = 5.3 Hz, 1H, $Ar^1OCH_2CH_2NH$), 4.22-4.10 (m, 18H, $Ar^1OCH_2CH_2NH$, $Ar^2OCH_2CH_2NH$ and $Ar^3OCH_2CH_2O$), 4.05-3.95 (m, 8H, J = 7.0 Hz, $PO(OCH_2CH_3)_2$), 3.85-3.75 (m, 18H, $Ar^1OCH_2CH_2NH$, $Ar^2OCH_2CH_2NH$ and OCH_2CH_2O), 3.70-3.38 (m, 108H, OCH_2CH_2O), 3.33 (s, 12H, $OCH_2CH_2OCH_3$), 3.06 (d, J = 21.7 Hz, 4H, Ar^1CH_2P), 2.48 (t, 4H, J = 6.6 Hz, $Ar^3OCH_2CH_2COOC(CH_3)_3$), 1.43 (s, 18H, $Ar^2OCH_2CH_2COOC(CH_3)_3$), 1.24 (t, J = 7.0 Hz, 12H, $PO(OCH_2CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9 ($COO(CH_3)_3$), 167.1 (NHCO), 159.8 (Ar),

152.4 (Ar), 141.2 (Ar), 136.3 (Ar), 133.0 (Ar), 129.3 (Ar), 114.7 (Ar), 107.8 (Ar), 106.0 (Ar), 104.8 (Ar), 80.5 ($C(CH_3)_3$), 72.2 (PEG), 72.0 (PEG), 70.7 (PEG), 70.6 (PEG), 70.55 (PEG), 70.5 (PEG), 70.4 (PEG), 70.3 (PEG), 69.6 (PEG), 69.0 (PEG), 66.8 (OCH_2CH_2NH), 66.6 (CH_2CH_2COO), 62.1 (J = 6.5 Hz) (CH_2CH_3), 58.9 (OCH_3), 39.4 ($CH_2NHCOAr$), 36.2 (CH_2COO), 33.8 (J = 137.2 Hz) (CH-P), 28.1 ($C(CH_3)_3$), 16.4 (J = 6.0 Hz) (CH_2CH_3); ^{31}P NMR (81 MHz, $CDCl_3$) δ 26.08. MS (MALDI-TOF) m/z calculated for $C_{125}H_{215}NaN_3O_{54}P_2$: 2707.36, obtained: 2707.14.

1.4.General procedure for the Williamson [33] etherification with propargyl bromide (44-48)

A solution of phenolic (**12**, **28, 30, 32, 34**), propargyl bromide (80% in xylene) (1.2 equiv. per phenol) and K_2CO_3 (3 equiv. per phenol) in acetone (10 mL) was stirred during 2 hrs at 65°C. The reaction mixture was filtered over Celite and the solvent was evaporated. The resulting crude product was diluted in CH_2Cl_2 (30 mL), washed twice with an aqueous saturated solution of $NaHCO_3$ and with brine, dried over $MgSO_4$, filtered and evaporated to dryness. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 95:5).

Compound 44: Starting from **12** (0.30 g, 0.46 mmol), **44** was obtained (0.36 mmol, 79%) as a pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.54 (d, J = 2.5 Hz, 2H, Ar-2,6-*H*), 4.68 (d, J = 2.3 Hz, 2H, OCH_2CCH), 4.16 (t, J = 4.8 Hz, 4H, $ArOCH_2$), 4.04-3.93 (m, 4H, $PO(OCH_2CH_3)_2$), 3.85 (t, J = 4.8 Hz, 4H, OCH_2CH_2O), 3.75-3.62 (m, 20H, OCH_2CH_2O), 3.55-3.52 (m, 4H, OCH_2CH_2O), 3.33 (s, 6H, $OCH_2CH_2OCH_3$), 3.04 (d, J = 21.5 Hz, 2H, Ar^1CH_2P), 2.43 (t, J = 2.3 Hz, 1H, OCH_2CCH), 1.24 (t, J = 7.0 Hz, 6H, $PO(OCH_2CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.6 (J = 3.3 Hz) (Ar), 135.8 (J = 3.8 Hz) (Ar), 128.4 (J = 8.8 Hz) (Ar), 109.0 (J = 6.6 Hz) (Ar), 79.8 (CH_2CCH), 74.9 (CH_2CCH), 71.8 (PEG), 70.8 (PEG), 70.7 (PEG), 70.6 (PEG), 70.5 (PEG), 69.5 (PEG), 68.9 (PEG), 62.2 (J = 7.1 Hz) (CH_2CH_3), 59.7 (CH_2CCH), 59.0 (OCH_3), 33.7 (J = 139.8 Hz) (CH-P), 16.4 (J = 6.0 Hz) (CH_2CH_3); ^{31}P NMR (81 MHz, $CDCl_3$) δ 26.22. MS (MALDI-TOF) m/z calculated for $C_{32}H_{55}O_{14}P$: 695.33, obtained: 695.23, calculated for $C_{32}H_{54}NaO_{14}P$: 717.33 obtained: 717.22, calculated for $C_{32}H_{53}NaKO_{14}P$: 757.33 obtained: 757.27.

Compound 45: Starting from **28** (0.15 g, 0.18 mmol), **45** was obtained (0.16 mmol, 89%) was a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (dd, J = 2.6 and 8.3 Hz, 2H, Ar^1-2,6-*H*), 7.11 (s, 2H, Ar^2-2,6-*H*), 6.88-6.83 (m, 3H, $Ar^1OCH_2CH_2NH$ and Ar^1-3,5-*H*), 4.78 (d, J = 2.4 Hz, 2H, OCH_2CCH), 4.22 (t, 4H, J = 4.7 Hz $Ar^2OCH_2CH_2O$), 4.12 (t, 2H, J = 5.2 Hz, $Ar^1OCH_2CH_2NH$), 4.05-3.95 (m, 4H, $PO(OCH_2CH_3)_2$), 3.78-3.88 (m, 6H, $Ar^1OCH_2CH_2NH$ and OCH_2CH_2O), 3.72-3.50 (m, 24H, OCH_2CH_2O), 3.34 (s, 6H, $OCH_2CH_2OCH_3$), 3.06 (d, J = 21.3 Hz, 2H, Ar^1CH_2P), 2.43 (t, J = 2.4 Hz, 1H, OCH_2CCH), 1.24 (t, J = 7.0 Hz, 6H, $PO(OCH_2CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1 (NHCO), 157.4 (J = 3.7 Hz) (Ar), 152.5 (Ar), 139.4 (Ar), 130.8 (J = 6.6 Hz) (Ar), 130.0 (Ar), 123.8 (J = 9.3 Hz) (Ar), 114.5 (J = 3.3 Hz) (Ar), 107.1 (Ar), 79.2 (CH_2CCH), 74.9 (CH_2CCH), 71.9 (PEG), 70.7 (PEG), 70.6 (PEG), 70.55 (PEG), 70.45 (PEG), 70.4 (PEG), 69.6 (PEG), 69.1 (PEG), 66.8 (OCH_2CH_2NH), 62.1 (J = 7.1 Hz) (CH_2CH_3), 59.8 (CH_2CCH), 58.8 (OCH_3), 39.6 ($CH_2NHCOAr$), 32.9 (J = 139.4 Hz) (CH-P), 16.3 (J = 6.0 Hz) (CH_2CH_3); ^{31}P NMR (81 MHz, $CDCl_3$) δ 26.58. MS (MALDI-TOF) m/z calculated for $C_{41}H_{65}NO_{16}P$: 858.40, obtained: 858.32; MS (MALDI-TOF) m/z calculated for $C_{41}H_{64}NaNO_{16}P$: 880.40, obtained: 880.30.

Compound 46: Starting from **32** (0.2 g, 0.14 mmol), **46** was obtained (0.12 mmol, 85%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09 (s, 4H, Ar^2-2,6-*H*), 6.93 (t, J = 5.6 Hz, 2H, $Ar^1OCH_2CH_2NH$), 6.51 (m, 2H, Ar^1-2,6-*H*), 6.41 (m, 1H, Ar^1-4-*H*), 4.78 (d, J = 2.5 Hz, 4H, OCH_2CCH), 4.22-4.18 (t, J = 4.5 Hz, 8H, Ar^2OCH_2), 4.11 (t, J = 5.3 Hz, 4H, $Ar^1OCH_2CH_2NH$), 4.05-3.95 (m, 4H, $PO(OCH_2CH_3)_2$), 3.88-3.84 (t, J = 4.5 Hz, 8H, Ar^2OCH_2), 3.78 (q, J = 5.3 Hz, 4H, $Ar^1OCH_2CH_2NH$), 3.68-3.52 (m, 40H, OCH_2CH_2O), 3.50-3.45 (m, 8H, OCH_2CH_2O), 3.33 (s, 12H, $OCH_2CH_2OCH_3$), 3.05 (d, J = 21.5 Hz, 2H, Ar^1CH_2P), 2.46 (t, J = 2.4 Hz, 2H, OCH_2CCH), 1.25 (t, J = 7.1 Hz, 6H, $PO(OCH_2CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2 (NHCO), 159.7 (Ar), 152.6 (Ar), 139.5 (Ar), 133.9 (J = 8.2 Hz) (Ar), 130.1 (Ar), 108.7 (J = 6.6 Hz) (Ar), 106.9 (Ar), 101.1 (Ar), 79.2 (CH_2CCH), 75.2 (CH_2CCH), 71.7 (PEG), 70.7 (PEG), 70.55 (PEG), 70.5 (PEG), 70.45 (PEG), 70.4 (PEG), 69.6 (PEG), 69.2 (PEG), 66.8 (OCH_2CH_2NH), 62.3 (J = 7.1 Hz) (CH_2CH_3), 60.0 (CH_2CCH),

58.9 (O*C*H$_3$), 39.5 (*C*H$_2$NHCOAr), 33.4 (*J* = 138.3 Hz) (*C*H-P), 16.4 (*J* = 6.0 Hz) (CH$_2$*C*H$_3$); ^{31}P NMR (81 MHz, CDCl$_3$) δ 26.12. MS (MALDI-TOF) m/z calculated for $C_{71}H_{112}N_2O_{29}P$: 1487.70, obtained: 1487.70; calculated for $C_{71}H_{112}NaN_2O_{29}P$: 1509.70, obtained: 1509.68.

Compound 47: Starting from **30** (0.37 g, 0.38 mmol), **47** was obtained (0.35 mmol, 91%) as a colourless oil. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.08 (s, 2H, Ar^2-2,6-*H*), 7.02 (t, *J* = 5.6 Hz, 1H, Ar^{1}OCH$_2$CH$_2$N*H*), 6.78 (m, 1H, Ar^1-2-*H*), 6.72 (m, 2H, Ar^1-4,6-*H*), 4.78 (d, *J* = 2.4 Hz, 2H, OC*H*$_2$CCH), 4.25-4.20 (t, *J* = 4.7 Hz, 4H, Ar^{2}OC*H*$_2$), 4.15-4.10 (t, *J* = 5.0 Hz, 2H, Ar^{1}OC*H*$_2$CH$_2$NH), 4.10-3.95 (m, 8H, *J* = 7.0 Hz, PO(OC*H*$_2$CH$_3$)$_2$), 3.82 (t, 4H, *J* = 4.7 Hz, OCH$_2$CH$_2$O), 3.78 (q, 2H, *J* = 5.3 Hz, Ar^{1}OCH$_2$C*H*$_2$NH), 3.68-3.50 (m, 20H, OCH$_2$CH$_2$O), 3.55-3.51 (m, 4H, OCH$_2$CH$_2$O), 3.35 (s, 6H, OCH$_2$CH$_2$OC*H*$_3$), 3.08 (d, *J* = 22.0 Hz, 4H, Ar^{1}C*H*$_2$P), 2.44 (t, *J* = 2.4 Hz, 1H, OCH$_2$CC*H*), 1.24 (t, *J* = 7.1 Hz, 12H, PO(OCH$_2$C*H*$_3$)$_2$); ^{13}C NMR (75 MHz, CDCl$_3$) δ 167.1 (NH*C*O), 158.5 (*J* = 2.8 Hz) (Ar), 152.7 (Ar), 139.5 (Ar), 133.1 (*J* = 6.0 Hz) (Ar), 130.2 (Ar), 124.0 (*J* = 6.8 Hz) (Ar), 114.6 (*J* = 5.0 Hz) (Ar), 107.0 (Ar), 79.2 (CH$_2$*C*CH), 74.9 (CH$_2$C*C*H), 71.8 (PEG), 70.65 (PEG), 70.55 (PEG), 70.5 (PEG), 70.4 (PEG), 70.35 (PEG), 69.6 (PEG), 69.0 (PEG), 66.6 (O*C*H$_2$CH$_2$NH), 62.1 (*J* = 6.6 Hz) (*C*H$_2$CH$_3$), 59.8 (*C*H$_2$CCH), 58.9 (O*C*H$_3$), 39.5 (*C*H$_2$NHCOAr), 33.8 (*J* = 137.8 Hz) (*C*H-P), 16.4 (*J* = 2.7 Hz) (CH$_2$*C*H$_3$); ^{31}P NMR (81 MHz, CDCl$_3$) δ 26.08. MS (MALDI-TOF) m/z calculated for $C_{46}H_{75}NaNO_{19}P_2$: 1030.44, obtained: 1030.41.

Compound 48: Starting from **34** (0.29 g, 0.17 mmol), **48** was obtained (0.15 mmol, 86%) as a colourless oil. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.18 (t, *J* = 5.7 Hz, 2H, Ar^{2}OCH$_2$CH$_2$N*H*), 7.11 (s, 4H, Ar^3-2,6-*H*), 7.02 (t, *J* = 5.5 Hz, 1H, Ar^{1}OCH$_2$CH$_2$N*H*), 6.95 (d, *J* = 1.7 Hz, 2H, Ar^2-2,6-*H*), 6.78-6.71 (m, 3H, Ar^2-2,4,6-*H*), 6.58 (t, *J* = 1.9 Hz, 1H, Ar^2-4-*H*), 4.78 (d, *J* = 2.4 Hz, 4H, OC*H*$_2$CCH), 4.17 (t, *J* = 4.6 Hz, 8H, Ar^{2}OC*H*$_2$), 4.15-4.10 (m, 6H, Ar^{1}OC*H*$_2$CH$_2$NH and Ar^{2}OC*H*$_2$CH$_2$NH), 4.05-3.93 (m, 8H, PO(OC*H*$_2$CH$_3$)$_2$), 3.85-3.75 (m, 14H, OCH$_2$CH$_2$O, Ar^{1}OC*H*$_2$CH$_2$NH and Ar^{2}OC*H*$_2$CH$_2$NH), 3.70-3.60 (m, 34H, OCH$_2$CH$_2$O), 3.53-3.48 (m, 8H, OCH$_2$CH$_2$O), 3.34 (s, 12H, OCH$_2$CH$_2$OC*H*$_3$), 3.06 (d, *J* = 22.0 Hz, 4H, Ar^{1}C*H*$_2$P), 2.45 (t, *J* = 2.4 Hz, 2H, OCH$_2$CC*H*), 1.23 (t, *J* = 7.0 Hz, 12H, PO(OCH$_2$C*H*$_3$)$_2$); ^{13}C NMR (75 MHz, CDCl$_3$) δ 167.2 (NH*C*O), 159.8 (Ar), 158.5 (Ar), 152.6 (Ar), 139.8 (Ar), 136.6 (Ar), 133.1 (*J* = 6.0 Hz) (Ar), 130.1 (Ar), 124.2 (Ar), 114.8 (*J* = 4.8 Hz) (Ar), 107.2 (Ar), 106.1 (Ar), 104.8 (Ar), 79.2 (CH$_2$*C*CH), 75.1 (CH$_2$C*C*H), 71.9 (PEG), 70.7 (PEG), 70.6 (PEG), 70.55 (PEG), 70.5 (PEG), 70.45 (PEG), 70.4 (PEG), 69.7 (PEG), 69.1 (PEG), 66.8 (O*C*H$_2$CH$_2$NH), 62.1 (*J* = 7.0 Hz) (*C*H$_2$CH$_3$), 60.0 (*C*H$_2$CCH), 58.9 (O*C*H$_3$), 39.5 (*C*H$_2$NHCOAr), 33.5 (*J* = 137.5 Hz) (*C*H-P), 16.3 (*J* = 2.7 Hz) (CH$_2$*C*H$_3$); ^{31}P NMR (81 MHz, CDCl$_3$) δ 26.18. MS (MALDI-TOF) m/z calculated for $C_{85}H_{132}N_3O_{34}P_2$: 1800.81, obtained: 1800.68; calculated for $C_{85}H_{131}NaN_3O_{34}P_2$: 1822.81, obtained: 1822.67.

Compound 49: A solution of Patent Blue VF (5.7 g, 10.0 mmol) in POCl$_3$ (19 ml, 200 mmol, 20.0 equiv.) was cooled at 0°C. After 1 hr of stirring, the solution was allowed to warm up to room temperature and was further stirred for 3 days. The reaction mixture was then added dropwise to an ice bath. The obtained aqueous phase was extracted three times with CH$_2$Cl$_2$ (200 mL) and the resulting organic phase was washed with brine, dried over MgSO$_4$, filtered and concentrated under reduced pressure. Sulfonylchloride derivative **49** was obtained as a dark green foam (9.0 mmol, 90%) and was directly used without further purification.

Compound 50: Azido-dPEG$^{TM}_7$-amine (0.7 g, 1.77 mmol) was dissolved, under an argon atmosphere, in CH$_2$Cl$_2$ (6 mL) followed by the addition of NEt$_3$ (718 µL, 5.32 mmol, 3.0 equiv.) and 4-DMAP (22 mg, 0.1 mmol). The resulting mixture was stirred at 0°C for 15 min. Patent Blue VF sulfonyl chloride **49** (1.5 g, 2.66 mmol, 1.5 equiv.) dissolved in a mixture of CH$_2$Cl$_2$/DMF (10 mL / 1.5 mL) was then added dropwise. The solution was allowed to warm up to room temperature and stirred overnight. The crude reaction mixture was concentrated under reduced pressure and purified by column chromatography (SiO$_2$, CH$_2$Cl$_2$/MeOH 90:10) to afford **50** (0.89 mmol, 50%) as a dark blue foam. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$) δ 8.57 (d, *J* = 1.9 Hz, 1H, Ar^1-2-*H*), 7.87 (dd, *J* = 1.9 and 7.9 Hz, 1H, Ar^1-6-*H*), 7.45 (m, 4H, Ar^2-2,6-*H*), 7.14 (d, *J* = 7.9 Hz, 1H, Ar^1-5-*H*), 6.80 (m, 4H, Ar^2-3,5-*H*), 5.98 (t, *J* = 5.9 Hz, 1H, CH$_2$N*H*O$_2$), 3.66-3.55 (m, 36H, OCH$_2$CH$_2$O and N(C*H*$_2$CH$_3$)$_2$), 3.37 (t, *J* = 4.8 Hz, 2H,

$CH_2CH_2N_3$), 3.21 (q, J = 5.5 Hz, 2H, CH_2NHO_2), 1.29 (t, J = 7.1 Hz, 12H, $N(CH_2CH_3)_2$); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 176.4 (Ar), 155.7 (Ar=N), 149.4 (Ar), 142.3 (Ar), 141.3 (Ar), 141.0 (Ar), 132.0 (Ar), 127.5 (Ar), 126.9 (Ar), 113.5 (Ar), 71.1 (PEG), 70.9 (PEG), 70.4 (PEG), 70.0 (PEG), 51.3 (CH_2N_3), 46.4 ($N(CH_2CH_3)_2$), 43.7 (CH_2NH), 13.1 ($N(CH_2CH_3)_2$). MS (MALDI-TOF) m/z calculated for $C_{43}H_{65}N_6O_{12}S_2$: 921.41, obtained: 921.37; calculated for $C_{43}H_{64}N_6NaO_{12}S_2$: 943.39, obtained: 943.35; calculated for $C_{43}H_{64}KN_6O_{12}S_2$: 959.36, obtained: 959.33.

1.5.General procedure for the "Click chemistry" reaction with azide derivative 50 (51, 53, 55, 57, 59)

A 0.1 M aqueous solution of $CuSO_4.5H_2O$ (0.05 equiv. per azide) and a 0.1 M aqueous solution of sodium ascorbate (0.1 equiv. per azide) were added at room temperature to an equimolar solution of propargyl derivative (**44-48**) and azide **50** in a mixture of DMSO:H_2O 4:1 (8 mL). The reaction mixture was stirred at room temperature overnight. 20 mL of brine were then added to quench the reaction and the resulting aqueous phase was extracted several times with CH_2Cl_2. The organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography.

Compound 51: Starting from **44** (0.19 g, 0.27 mmol), **51** was obtained (0.14 mmol, 52%) as a dark blue foam after purification by column chromatography (SiO_2, CH_2Cl_2/MeOH 90:10). ^1H NMR (300 MHz, $CDCl_3$) δ 8.69 (d, J = 1.9 Hz, 1H, Ar^{dye}-2-*H*), 7.92 (s, 1H, $Ar^{Triazole}$-*H*), 7.81 (dd, J = 1.9 and 7.9 Hz, 1H, Ar^{dye}-6-*H*), 7.40 (d, 4H, J = 9.4 Hz, Ar^{dye}-AA'-*H*), 7.08 (d, J = 7.9 Hz, 1H, Ar^{dye}-5-*H*), 6.71 (d, 4H, J = 9.4 Hz, Ar^{dye}-BB'-*H*), 6.49 (d, J = 2.4 Hz, 2H, Ar^1-2,6-*H*), 5.82 (t, J = 5.8 Hz, 1H, CH_2NHO_2), 5.12 (s, 2H, $OCH_2Ar^{Triazole}$-CH_2), 4.48 (t, J = 5.2 Hz, 2H, $OCH_2Ar^{Triazole}$-CH_2), 4.10 (t, J = 4.8 Hz, 4H, $Ar^1OCH_2CH_2$), 4.00-3.92 (m, 4H, $PO(OCH_2CH_3)_2$), 3.82-3.75 (m, 6H, OCH_2CH_2O and $CH_2CH_2NHO_2$), 3.70-3.45 (m, 58H, OCH_2CH_2O and $N(CH_2CH_3)_2$), 3.31 (s, 6H, $OCH_2CH_2OCH_3$), 3.18 (q, J = 5.5 Hz, 2H, $CH_2CH_2NHO_2$), 3.01 (d, J = 21.5 Hz, 2H, Ar^1CH_2P), 1.22 (t, J = 7.1 Hz, 18H, $N(CH_2CH_3)_2$ and $PO(OCH_2CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.2 (Ar), 155.1 (Ar^{dye}=N), 152.5 (Ar), 148.7 (Ar), 144.9 (Ar), 141.8 ($Ar^{Triazole}$), 141.1 (Ar), 140.6 (Ar), 136.6 (Ar), 131.2 (Ar), 127.3 ($Ar^{Triazole}$), 127.2 (Ar), 127.1 (Ar), 126.3 (Ar), 124.2 (Ar), 113.0 (Ar), 109.1 (Ar), 71.9 (OCH_2-$Ar^{Triazole}$), 70.8 (PEG), 70.7 (PEG), 70.6 (PEG), 70.5 (PEG), 70.4 (PEG), 69.7 (PEG), 68.6 (PEG), 62.1 (CH_2CH_3), 58.9 (OCH_3), 50.1 ($Ar^{Triazole}$-CH_2), 45.8 ($N(CH_2CH_3)_2$), 42.9 (CH_2NHSO_2), 33.8 (J = 138.5 Hz) (*C*H-P), 16.4 (J = 5.5 Hz) (CH_2CH_3), 12.8 ($N(CH_2CH_3)_2$). ^{31}P NMR (81 MHz, $CDCl_3$) δ 26.23. MS (MALDI-TOF) m/z calculated for $C_{75}H_{120}N_6O_{26}PS_2$: 1615.74, obtained: 1615.59; calculated for C $C_{75}H_{119}NaN_6O_{26}PS_2$: 1637.74, obtained: 1637.59.

Compound 53: Starting from **45** (0.12 g, 0.14 mmol), **53** was obtained (0.1 mmol, 68%) as a dark blue foam after purification by column chromatography (SiO_2, CH_2Cl_2/MeOH 90:10). ^1H NMR (300 MHz, $CDCl_3$) δ 8.74 (d, J = 1.8 Hz, 1H, Ar^{dye}-2-*H*), 7.94 (s, 1H, $Ar^{Triazole}$-*H*), 7.89 (dd, J = 1.8 and 7.9 Hz, 1H, Ar^{dye}-6-*H*), 7.58 (t, 1H, J = 5.3 Hz, $Ar^1OCH_2CH_2NH$), 7.41 (d, 4H, J = 9.2 Hz, Ar^{dye}-AA'-*H*), 7.19-7.08 (m, 6H, Ar^{dye}-5-*H*, Ar^1-2,6-*H* and Ar^2-2,6-*H*), 6.83 (d, 2H, J = 8.5 Hz, Ar^1-3,5-*H*), 6.70 (d, 4H, J = 9.2 Hz, Ar^{dye}-BB'-*H*), 6.38 (t, J = 5.8 Hz, 1H, CH_2NHO_2), 5.22 (s, 2H, $OCH_2Ar^{Triazole}$-CH_2), 4.49 (t, J = 5.1 Hz, 2H, $OCH_2Ar^{Triazole}$-CH_2), 4.17 (t, J = 4.8 Hz, 4H, $Ar^2OCH_2CH_2$), 4.06 (t, 2H, J = 5.1 Hz, $Ar^1OCH_2CH_2NH$), 4.00-3.92 (m, 4H, $PO(OCH_2CH_3)_2$), 3.85-3.78 (m, 8H, OCH_2CH_2O, $Ar^1OCH_2CH_2NH$ and $CH_2CH_2NHO_2$), 3.70-3.45 (m, 58H, OCH_2CH_2O and $N(CH_2CH_3)_2$), 3.32 (s, 6H, $OCH_2CH_2OCH_3$), 3.22 (q, J = 5.5 Hz, 2H, $CH_2CH_2NHO_2$), 3.05 (d, J = 21.1 Hz, 2H, Ar^1CH_2P), 1.23 (t, J = 7.1 Hz, 18H, $N(CH_2CH_3)_2$ and $PO(OCH_2CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.1 (Ar), 166.8 (NH*C*O), 157.9 (Ar), 155.0 (Ar^{dye}=N), 152.1 (Ar), 148.2 (Ar), 144.7 (Ar), 141.8 ($Ar^{Triazole}$), 141.0 (Ar), 140.6 (Ar), 139.5 (Ar), 138.2 (Ar), 131.1 (Ar), 130.5 (J = 6.6 Hz) (Ar), 129.6 (Ar), 127.1 ($Ar^{Triazole}$), 126.8 (Ar), 126.4 (Ar), 124.7 (Ar), 122.3 (Ar), 114.8 (Ar), 113.2 (Ar), 106.7 (Ar), 72.1 (OCH_2-$Ar^{Triazole}$), 70.7 (PEG), 70.6 (PEG), 70.5 (PEG), 70.4 (PEG), 69.4 (PEG), 69.2 (PEG), 68.8 (PEG), 66.2 (OCH_2CH_2NH), 62.0 (J = 7.0 Hz) (CH_2CH_3), 58.9 (OCH_3), 50.3 ($Ar^{Triazole}$-CH_2), 45.6 ($N(CH_2CH_3)_2$), 42.9 (CH_2NHSO_2), 39.4 ($CH_2NHCOAr$), 32.6 (J = 138.9 Hz) (*C*H-P), 16.5 (J = 6.0 Hz) (CH_2CH_3), 12.8 ($N(CH_2CH_3)_2$); ^{31}P NMR (81 MHz, $CDCl_3$) δ 26.72. MS (MALDI-TOF) m/z

calculated for $C_{84}H_{128}N_7O_{28}PS_2$: 1778.80, obtained: 1778.69; calculated for $C_{84}H_{128}NaN_7O_{28}PS_2$: 1800.80, obtained: 1800.65; calculated for $C_{84}H_{128}Na_2N_7O_{28}PS_2$: 1823.80, obtained: 1823.64.

Compound 55: Starting from **46** (0.1 g, 0.07 mmol), **55** was obtained (0.035 mmol, 50%) as a dark blue foam after purification by column chromatography (SiO_2, CH_2Cl_2/MeOH 85:15). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68 (d, J = 1.4 Hz, 2H, Ar^{dye}-2-*H*), 7.97 (s, 2H, $Ar^{Triazole}$-*H*), 7.90 (dd, J = 1.6 and 8.1 Hz, 2H, Ar^{dye}-6-*H*), 7.78 (t, J = 5.7 Hz, 2H, $Ar^2OCH_2CH_2NH$), 7.40-7.34 (d, 8H, J = 9.2 Hz, Ar^{dye}-AA'-*H*), 7.17 (s, 4H, Ar^2-2,6-*H*), 7.11 (d, 2H, J = 8.0 Hz, Ar^{dye}-5-*H*), 6.65 (d, 8H, J = 9.2 Hz, Ar^{dye}-BB'-*H*), 6.40-6.35 (m, 3H, Ar^1-2,4,6-*H*), 6.25 (t, J = 5.7 Hz, 2H, CH_2NHO_2), 5.22 (s, 4H, $OCH_2Ar^{Triazole}$-CH_2), 4.51 (t, J = 5.0 Hz, 4H, $OCH_2Ar^{Triazole}$-CH_2), 4.17 (t, J = 4.7 Hz, 8H, $Ar^2OCH_2CH_2$), 4.05-3.95 (m, 8H, $Ar^1OCH_2CH_2NH$, and $PO(OCH_2CH_3)_2$), 3.88-3.80 (m, 14H, OCH_2CH_2O, $Ar^1OCH_2CH_2NH$ and $CH_2CH_2NHO_2$), 3.72-3.40 (m, 116H, OCH_2CH_2O and $N(CH_2CH_3)_2$), 3.35 (s, 12H, $OCH_2CH_2OCH_3$), 3.20 (m, 4H, $CH_2CH_2NHO_2$), 3.02 (d, J = 21.5 Hz, 2H, Ar^1CH_2P), 1.25 (t, J = 7.0 Hz, 30H, $N(CH_2CH_3)_2$ and $PO(OCH_2CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.3 (Ar), 166.8 (NH*C*O), 159.9 (Ar), 155.0 (Ar^{dye}=N), 152.3 (Ar), 148.2 (Ar), 144.5 (Ar), 142.1 ($Ar^{Triazole}$), 140.8 (Ar), 140.3 (Ar), 139.6 (Ar), 133.2 (Ar), 131.4 (Ar), 129.6 (Ar), 127.1 ($Ar^{Triazole}$), 126.9 (Ar), 126.6 (Ar), 124.8 (Ar), 113.2 (Ar), 109.1 (Ar), 106.8 (Ar), 71.8 (OCH_2-$Ar^{Triazole}$), 70.7 (PEG), 70.6 (PEG), 70.55 (PEG), 70.5 (PEG), 70.45 (PEG), 70.4 (PEG), 69.5 (PEG), 69.3 (PEG), 68.6 (PEG), 66.3 (OCH_2CH_2NH), 62.2 (J = 7.1 Hz) (CH_2CH_3), 58.9 (OCH_3), 50.2 ($Ar^{Triazole}$-CH_2), 45.8 ($N(CH_2CH_3)_2$), 43.1 (CH_2NHSO_2), 39.3 ($CH_2NHCOAr$), 33.4 (J = 137.5 Hz) (*C*H-P), 16.3 (J = 6.0 Hz) (CH_2CH_3), 12.8 ($N(CH_2CH_3)_2$); ^{31}P NMR (81 MHz, $CDCl_3$) δ 26.24. MS (MALDI-TOF) m/z calculated for $C_{157}H_{239}N_{14}O_{53}PS_4$: 3329.87, obtained: 3329.28.

Compound 57: Starting from **47** (0.29 g, 0.29 mmol), **57** was obtained (0.26 mmol, 88%) as a dark blue foam after purification by column chromatography (SiO_2, CH_2Cl_2/MeOH 85:15). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.73 (d, J = 1.7 Hz, 1H, Ar^{dye}-2-*H*), 7.95 (s, 1H, $Ar^{Triazole}$-*H*), 7.89 (dd, J = 1.8 and 7.9 Hz, 1H, Ar^{dye}-6-*H*), 7.42 (d, 4H, J = 9.2 Hz, Ar^{dye}-AA'-*H*), 7.15 (s, 2H, Ar^2-2,6-*H*), 7.11 (d, 1H, J = 8.1 Hz, Ar^{dye}-5-*H*), 6.80 (m, 1H, Ar^1-2-*H*), 6.76 (m, 2H, Ar^1-4,6-*H*), 6.70 (d, 4H, J = 9.2 Hz, Ar^{dye}-BB'-*H*), 6.18 (t, J = 5.8 Hz, 1H, CH_2NHO_2), 5.22 (s, 2H, $OCH_2Ar^{Triazole}$-CH_2), 4.52 (t, J = 5.2 Hz, 2H, $OCH_2Ar^{Triazole}$-CH_2), 4.19 (t, J = 5 Hz, 4H, $Ar^2OCH_2CH_2$), 4.08 (t, 2H, J = 5.0 Hz, $Ar^1OCH_2CH_2NH$), 4.05-3.95 (m, 8H, $PO(OCH_2CH_3)_2$), 3.88-3.82 (m, 8H, OCH_2CH_2O, $Ar^1OCH_2CH_2NH$ and $CH_2CH_2NHO_2$), 3.70-3.45 (m, 58H, OCH_2CH_2O and $N(CH_2CH_3)_2$), 3.34 (s, 6H, $OCH_2CH_2OCH_3$), 3.22 (q, J = 5.3 Hz, 2H, $CH_2CH_2NHO_2$), 3.07 (d, J = 21.7 Hz, 4H, Ar^1CH_2P), 1.25 (t, J = 7.1 Hz, 24H, $N(CH_2CH_3)_2$ and $PO(OCH_2CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.1 (Ar), 166.8 (NH*C*O), 158.9 (Ar), 155.1 (Ar^{dye}=N), 152.3 (Ar), 148.9 (Ar), 142.1 ($Ar^{Triazole}$), 140.9 (Ar), 140.5 (Ar), 133.2 (Ar), 131.4 (Ar), 129.8 (Ar), 127.6 (Ar), 127.4 ($Ar^{Triazole}$), 126.3 (Ar), 124.8 (Ar), 123.8 (Ar), 114.6 (Ar), 113.1 (Ar), 106.9 (Ar), 72.0 (OCH_2-$Ar^{Triazole}$), 70.7 (PEG), 70.6 (PEG), 70.5 (PEG), 70.4 (PEG), 69.4 (PEG), 68.9 (PEG), 66.3 (OCH_2CH_2NH), 62.2 (CH_2CH_3), 58.8 (OCH_3), 50.4 ($Ar^{Triazole}$-CH_2), 46.1 ($N(CH_2CH_3)_2$), 43.2 (CH_2NHSO_2), 39.4 ($CH_2NHCOAr$), 33.3 (J = 137.5 Hz) (*C*H-P), 16.4 (CH_2CH_3), 12.8 ($N(CH_2CH_3)_2$); ^{31}P NMR (81 MHz, $CDCl_3$) δ 26.60. MS (MALDI-TOF) m/z calculated for $C_{89}H_{140}N_7O_{31}P_2S_2$: 1928.84, obtained: 1928.70; calculated for $C_{89}H_{139}NaN_7O_{31}P_2S_2$: 1950.84, obtained: 1950.71.

Compound 59: Starting from **48** (0.25 g, 0.14 mmol), **59** was obtained (0.07 mmol, 50%) as a dark blue foam after purification by column chromatography (SiO_2, CH_2Cl_2/MeOH 85:15). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68 (d, J = 1.4 Hz, 2H, Ar^{dye}-2-*H*), 7.95 (s, 2H, $Ar^{Triazole}$-*H*), 7.88 (dd, J = 1.7 and 8.1 Hz, 2H, Ar^{dye}-6-*H*), 7.82 (t, J = 5.7 Hz, 2H, $Ar^2OCH_2CH_2NH$), 7.30-7.22 (d, 8H, J = 9.2 Hz, Ar^{dye}-AA'-*H*), 7.14 (s, 4H, Ar^3-2,6-*H*), 7.07 (d, 2H, J = 8.0 Hz, Ar^{dye}-5-*H*), 6.97 (m, 2H, Ar^2-2,6-*H*), 6.58 (m, 1H, Ar^2-4-*H*),), 6.64 (t, J = 5.7 Hz, 2H, CH_2NHO_2), 6.62-6.55 (m, 3H, Ar^1-2,4,6-*H*), 6.52 (d, 8H, J = 9.2 Hz, Ar^{dye}-BB'-*H*), 6.43 (m, 1H, $Ar^1OCH_2CH_2NH$), 5.18 (s, 4H, $OCH_2Ar^{Triazole}$-CH_2), 4.47 (t, J = 5.0 Hz, 4H, $OCH_2Ar^{Triazole}$-CH_2), 4.12 (m, 8H, $Ar^2OCH_2CH_2$), 4.05-3.87 (m, 14H, $Ar^1OCH_2CH_2NH$, $Ar^2OCH_2CH_2NH$ and $PO(OCH_2CH_3)_2$), 3.80-3.73 (m, 14H, OCH_2CH_2O, $Ar^1OCH_2CH_2NH$ and $Ar^2OCH_2CH_2NH$), 3.68-3.33 (m, 120H, OCH_2CH_2O, $CH_2CH_2NHO_2$ and $N(CH_2CH_3)_2$), 3.28 (s, 12H, $OCH_2CH_2OCH_3$), 3.12 (q, J = 5.4 Hz, 4H, $CH_2CH_2NHO_2$), 2.98 (d, J = 21.7 Hz, 4H, Ar^1CH_2P), 1.13 (t, J = 7.0 Hz, 36H, $N(CH_2CH_3)_2$ and $PO(OCH_2CH_3)_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.2 (Ar),

166.8 (J = 7.7 Hz) (NH*C*O), 159.6 (Ar), 158.8 (Ar), 154.8 (Ar^{dye}=N), 152.3 (Ar), 147.9 (Ar), 144.6 (Ar), 142.2 ($Ar^{Triazole}$), 140.6 (Ar), 139.4 (Ar), 136.1 (Ar), 133.2 (J = 12 Hz) (Ar), 131.6 (Ar), 129.4 (Ar), 127.1 ($Ar^{Triazole}$), 126.9 (Ar), 124.8 (Ar), 123.8 (Ar), 114.7 (Ar), 113.2 (Ar), 106.6 (Ar), 105.9 (Ar), 105.2 (Ar), 71.8 (O*C*H_2-$Ar^{Triazole}$), 70.7 (PEG), 70.6 (PEG), 70.55 (PEG), 70.5 (PEG), 70.45 (PEG), 70.4 (PEG), 69.5 (PEG), 68.7 (PEG), 66.3 (O*C*H_2CH_2NH), 62.2 (J = 7.1 Hz) (*C*H_2CH_3), 58.8 (O*C*H_3), 50.2 ($Ar^{Triazole}$-*C*H_2), 45.8 (N(*C*$H_2CH_3)_2$), 43.0 (*C*H_2NHSO_2), 39.3 (*C*H_2NHCOAr), 33.4 (J = 137.5 Hz) (*C*H-P), 16.4 (J = 6.0 Hz) (CH_2*C*H_3), 12.7 (N(CH_2*C*$H_3)_2$); ^{31}P NMR (81 MHz, $CDCl_3$) δ 26.08. MS (MALDI-TOF) m/z calculated for $C_{171}H_{259}N_{15}O_{58}P_2S_4$: 3643.16, obtained: 3643.78.

2.Part II: PAMAM-PEG dendrons

Compound 61: A solution of sodium trimethylsilanolate (TMSONa, 1 M) in CH_2Cl_2 (66 mL, 66 mmol) was added to a solution of G0.5 PAMAM dendron (5 g, 22 mmol) in CH_2Cl_2 (90 mL). The mixture was stirred for 16 hrs at room temperature. The solvent was then evaporated *in vacuo* and the residue was precipitated in EtOAc. The solid was filtered and **61** was obtained (22 mmol, quant). Yellow solid. Melting point: 250°C. ^{1}H NMR (300 MHz, D_2O) δ 3.36 (s, 2H, CH_2 alkyne), 2.38 (dd, 4H, J = 10.6 Hz and 11.9 Hz, NCH_2), 1.63 (dd, 4H, J = 12.2 Hz and 10.6 Hz, CH_2COONa), 0.84 (s, 1H, CH alkyne); ^{13}C NMR (75 MHz, D_2O) δ 181.1 (COO), 77.9 (C alkyne), 74.5 (CH alkyne), 49.7 (NCH_2), 41.1 (alkyne-*C*H_2), 34.9 (CH_2COONa). MS (MALDI-TOF) m/z calculated for $C_9H_{11}NNa_2O_4$ 243.05, obtained $[M-H]^-$ = 242.28.

Compound 62: TBDPSCl (1.6 mL, 6.27 mmol) was added to a solution of amino-dPEG®$_4$-alcohol (1.05 g, 5.45 mmol) and imidazole (0.85 g, 12.5 mmol) in CH_2Cl_2 (35 mL). The mixture was stirred for 3 hrs at room temperature and then diluted with CH_2Cl_2 (20 mL). The resulting mixture was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH/NH_4OH 80:20:0.25) to yield **62** (4.3 mmol, 80%). Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (m, 4H, Ar), 7.40 (m, 6H, Ar), 3.83 (dd, 2H, J = 4.2 Hz and 4.6 Hz, CH_2OSi), 3.68-3.60 (m, 10H, PEG), 3.51 (dd, 2H, J = 4.2 Hz, J = 4.4 Hz, $H_2NCH_2CH_2O$), 2.83 (dd, 2H, J = 4.4 Hz and 4.2 Hz, NH_2CH_2), 1.06 (s, 9H, *t*Bu); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.5 (Ar), 133.6 (Ar), 129.6 (Ar), 127.6 (Ar), 72.5 and 72.4 (*C*H_2CH_2OSi, $H_2NCH_2CH_2$), 70.7 (PEG), 70.6 (PEG), 70.5 (PEG), 70.2 (PEG), 63.4 (CH_2OSi), 41.4 (C^{IV} *t*Bu), 26.8 (CH_3 *t*Bu), 19.1 (H_2NCH_2). MS (MALDI-TOF) m/z calculated for $C_{24}H_{37}NO_4Si$ 431.25, obtained $[M+H]^+$ = 432.21.

Compound 63: N,N'-Diisopropylcarbodiimide (DIC, 1.2 mL, 7.54 mmol) and HOBt (1.02 g, 7.54 mmol) were added to a solution of **61** (0.46 g, 1.88 mmol) and **62** (1.63 g, 3.77 mmol) in DMF (7 mL). The mixture was stirred at 60°C for 24 hrs then quenched at room temperature with an ammonium chloride aqueous saturated solution. The aqueous phase was extracted with ether and the organic phase was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude mixture was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 95:5) to yield **63** (1.33 mmol, 70%). Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, 8H, Ar), 7.40 (m, 12H, Ar), 3.80 (dd, 4H, J = 2.49 Hz and 2.46 Hz, CH_2OSi), 3.66-3.39 (m, 30H, PEG, CH_2 alkyne), 2.80 (dd, 4H, J = 6.36 Hz and 6.12 Hz, CONHCH_2), 2.30 (dd, 4H, J = 6.36 Hz and 6.36 Hz, CH_2CONH), 2.17 (dd, 1H, J = 2 Hz and 1.8 Hz, H alkyne), 1.04 (s, 18H, *t*Bu); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.1 (CONH), 135.4 (Ar TBDPS), 133.4 (Ar TBDPS), 129.5 (Ar TBDPS), 127.5 (Ar TBDPS), 77.2 (C alkyne), 73.4 (CH alkyne), 71.9 (O*C*H_2CH_2OTBDPS), 70.2 (PEG), 70.0 (PEG), 69.7 (PEG), 69.3 (PEG), 69.2 (PEG), 62.8 (OCH_2*C*H_2OTBDPS), 48.8 (NCH_2 PAMAM), 40.7 (CH_2N next to alkyne), 38.6 (C^{IV} *t*Bu), 38.4 ($CONHCH_2$), 33.0 (CH_2CONH), 26.1 (*t*Bu); MS (MALDI-TOF) m/z calculated for $C_{57}H_{83}N_3O_{10}Si_2$ 1025.56, obtained $[M+H]^+$ = 1026.52.

Compound 64: amino-dPEG®$_3$-*tert*butylester is a commercially available product purchased from Quanta Design.

Compound 65: N-(3-Dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDCI, 0.38 g, 1.97 mmol), HOBt (0.05 g, 0.33 mmol) and DIPEA (0.31 mL, 1.8 mmol) were added to a suspension of **61** (0.2 g, 0.82 mmol) and **64** (0.58 g, 1.8 mmol) in CH_3CN (9 mL). The mixture was stirred at room

temperature for 16 h and then the solvent was evaporated. The crude mixture was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 90:10) to yield **65** (1.05 mmol, 67%) as yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (m, 2H, NH), 3.70-3.42 (m, 34H, CH_2O PEG, CH_2 alkyne), 3.39 (m, 4H, NCH_2 PAMAM), 2.81 (dd, 4H, J = 6.36 Hz and 6.36 Hz, CONHCH_2CH$_2$O), 2.48 (dd, 4H, J = 6.57 Hz and 6.57 Hz, NCH_2CH_2CONH PAMAM), 2.36 (dd, 4H, J = 6.12 and 6.36 Hz, 2 CH_2COO*t*Bu), 2.23 (dd, 1H, J = 2.2 Hz and 2.4 Hz, H alkyne), 1.45 (s, 18H, 2 *t*Bu); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9 (CONH), 170.8 (COO*t*Bu), 80.5 (C^{IV} tBu), 77.8 (C Alkyne), 73.6 (CH Alkyne), 70.6 (PEG), 70.5 (PEG), 70.4 (PEG), 70.3 (PEG), 70.2 (PEG), 69.9 (PEG), 66.8 (OCH_2CH_2COO*t*Bu), 49.5 (NCH_2CH_2), 41.5 (Alkyne-CH_2), 39.1 (CONHCH_2CH_2O), 36.2 (CH_2COO*t*Bu), 33.9 (CH_2CONH), 27.9 (CH_3 *t*Bu). MS (MALDI-TOF) m/z calculated for $C_{39}H_{71}N_30_{14}$ 805.49, obtained $[M+H]^+$ = 806.55.

Compound 66 [37]: 1,4-Bis(chloromethyl)benzene (5 g, 28.6 mmol) was heated at 120°C until its total dissolution. After dropwise addition of triethylphosphite (2.5 mL, 14.3 mmol), the reaction mixture was stirred for 2 h. The excess of triethylphosphite was then removed *in vacuo*, and the crude mixture was purified by column chromatography (SiO_2, EtOAc/CH 80:20) to yield **66** (6.94 mmol, 48%) as a viscous colourless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (m, 4H, H Ar), 4.58 (s, 2H, CH_2Cl), 4.07 (qt, 2H, J = 7.02 Hz, CH_2CH_3), 3.18 (d, 2H, J= 21.7 Hz, CH_2PO(OEt)$_2$), 1.33 (dd, 3H, J=7.02 and 7.23 Hz, CH_3).

Compounds 68-69: The preparation procedures and analytical data similar to those reported in the literature.[29a].

Compound 70: The preparation procedure and analytical data similar to those reported in the literature. [29b].

Compounds 71-72: The preparation procedures and analytical data similar to those reported in the literature.[22c]

2.1.General procedure for the "Click chemistry" reaction with azide derivatives 63 or 65 (73, 74 and 75)

A mixture of azide (**67** or **72**) (1.1 equiv.) and propargyl derivative (**63** or **65**) (1 equiv.) in THF/H_2O (4/1, v/v, in mL) in the presence of 5% mol of $CuSO_4.5H_2O$ and 10% mol of sodium ascorbate was stirred at room temperature for 16 hrs. The reaction mixture was then quenched with brine and the aqueous phase extracted with EtOAc. The organic phase was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude mixture was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 90:10).

Compound 73: Starting from **65** (0.070 g, 0.25 mmol) and **67** (0.2 g, 0.27 mmol), **73** was obtained (0.15 mmol, 60%). Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (s, 1H, CH triazole), 7.35 (bs, 2H, NH), 7.15-7.04 (m, 3H, H Ar), 5.34 (s, 2H, CH_2N next to triazole), 3.86 (qt, 4H, J = 7.23 Hz, CH_2CH_3), 3.64 (bs, 2H, CH_2N PAMAM next to triazole), 3.53 (dd, 4H, J = 6.36 and 6.57 Hz, $CONHCH_2CH_2O$), 3.46-3.19 (m, 32H, PEG, NCH_2 PAMAM), 3.01 (d, 2H, J = 21.7 Hz, CH_2PO(OEt)$_2$), 2.60 (bs, 4H, CONHCH_2CH_2O), 2.32 (dd, 4H, J = 6.36 and 6.57 Hz, CH_2CONH), 2.24 (bs, 4H, CH_2COO*t*Bu), 1.28 (s, 18H, *t*Bu), 1.09 (dd, 3H, J = 6.99 and 7.23 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0 (CONH), 170.6 (COO*t*Bu), 143.9 (C triazole), 133.5 (J = 3.82 Hz, C Ar next to triazole), 132.2 (J = 9.27 Hz, C Ar next to CH_2PO(OEt)$_2$), 130.3 (J = 6.54 Hz, CH Ar next to CH_2PO(OEt)$_2$), 128.0 (J = 2.73 Hz, CH Ar next to triazole), 122.8 (CH triazole), 80.5 (C^{IV} *t*Bu), 70.4 (PEG), 70.3 (PEG), 70.1 (PEG), 70.0 (PEG), 69.9 (PEG), 66.7 (CH_2CH_2COO*t*Bu), 62.0 (J = 6.54 Hz, CH_2CH_3), 53.4 (CH_2N next to triazole), 49.3 (NCH_2 PAMAM), 47.8 (CH_2N PAMAM next to triazole), 38.9 (CONHCH_2CH_2O), 36.1 (CH_2COO*t*Bu), 34.1, 32.3 (d, J = 137.5 Hz, CH_2PO(OEt)$_2$), 33.5 (CH_2CONH), 27.9 (*t*Bu), 16.2 (J = 6.00 Hz, CH_3); ^{31}P NMR (81 MHz, $CDCl_3$) δ 25.87; MS (MALDI-TOF) m/z calculated for $C_{51}H_{89}N_6O_{17}P$ 1088.60, obtained $[M+H]^+$ =1089.62.

Compound 74: The preparation procedure and analytical data are reported in the literature.[22c]

Compound 75: Starting from **63** (1.3 g, 1.28 mmol) and **72** (0.55 g, 1.30 mmol), **75** was obtained (0.79 mmol, 62%). Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (m, 8H, Ar TBDPS), 7.67 (s, 1H, H triazole), 7.66 to 7.28 (m, 12H, Ar TBDPS), 7.21-7.10 (m, 3H, Ar), 5.45 (s, 2H, CH_2 next to triazole), 4.00 (quint, 8H, J = 7.23 Hz, CH_2CH$_3$), 3.81-3.49 (m, 30H, PEG), 3.38 (q, 4H, J = 5.04 and 10.53 Hz, CH_2 PAMAM), 3.14, 3.07 (d, 4H, J = 21.9 Hz, CH_2PO(OEt)$_2$), 2.73 (dd, 4H, J = 6.12 and 6.15 Hz, NHCH_2CH$_2$O), 2.37 (dd, 4H, J = 6.12 and 6.36 Hz, CH$_2$CONH), 1.23 (t, 12H, J = 7.02 Hz, CH$_3$), 1.03 (s, 18H, *t*Bu); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0 (CONH), 144.0 (C Ar next to triazole), 135.4 (Ar TBDPS), 133.5 (Ar TBDPS), 133.0 (C triazole, J = 6.00 Hz Ar next to CH$_2$PO(OEt)$_2$), 131.3 (J = 6.54 Hz, C Ar next to CH$_2$PO(OEt)$_2$), 129.5 (Ar TBDPS), 127.8 (J = 4.91 Hz, CH Ar next to triazole), 127.5 (Ar TBDPS), 122.8 (CH triazole), 72.3 (PEG *C*H$_2$CH$_2$OSi), 70.6 (PEG), 70.5 (PEG), 70.4 (PEG), 70.0 (PEG), 69.7 (PEG), 63.3 (CH$_2$OSi), 62.1 (*C*H$_2$CH$_3$), 53.4 (CH$_2$ triazole), 49.4 (NCH$_2$), 47.9 (CH$_2$N triazole), 38.9 (CONHCH$_2$), 34.2, 32.4 (J = 136.9 Hz, *C*H$_2$PO(OEt)$_2$), 33.7 (CH$_2$CONH), 26.7 (*t*Bu), 19.0 (C^{IV} *t*Bu), 16.15 (J = 6.00 Hz, CH$_3$); ^{31}P NMR (81 MHz, $CDCl_3$) δ 26.32; MS (MALDI-TOF) m/z calculated for $C_{74}H_{112}N_6O1_6P_2Si_2$ 1458.71, obtained $[M+H]^+$ = 1459.57.

3.Part III: linear phosphonates

Compound 77 [31]: A solution of dPEG$_4$-di-alcohol (21.4 g, 76.0 mmol) and KOH (1.2 g, 20.9 mmol) in THF (7 mL) was refluxed until KOH was dissolved. The solution was cooled to room temperature and TsO-PEG$_3$-Me [25] (6 g, 19.0 mmol) was added. The mixture was refluxed for 18 hrs then $CHCl_3$ was added. The organic layer was washed with water, dried over $MgSO_4$, filtered and evaporated *in vacuo* to yield **77** (12.3 mmol, 65%). Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.37-3.73 (m, 36H, PEG), 3.36 (s, 3H, CH$_3$).

3.1.General procedure for the "Click chemistry" reaction with propargyl bromide (76,78) [32]

A suspension of potassium tert-butoxide (1.14 equiv.) in THF (25 mL) was added to a solution of PEG-alcohol (1 equiv.) dissolved in THF (3 mL) and cooled to 0°C. Propargyl bromide (2 equiv.) in THF (50 mL) was then added dropwise and the reaction mixture was stirred for 1 hr at 0°C and for one week at room temperature. EtOAc (200 mL) was added and the organic layer was washed with brine (3 x 75 mL), dried over $MgSO_4$, filtered and evaporated *in vacuo*. No further purification was necessary to yield the desired compound.

Compound 76 [33]: Starting from triethyleneglycol monomethyl ether (2 g, 12.2 mmol), **76** was obtained (12.1 mmol, 99%). Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.21 (d, 2H, J =2.4 Hz, CH$_2$ alkyne), 3.71-3.53 (m, 12H, PEG), 3.38 (s, 3H, CH$_3$), 2.42 (dd, 1H, J = 2.43 and 2.19 Hz, H alkyne).

Compound 78: Starting from **77** (5.26 g, 12.3 mmol), **78** was obtained (4.15 mmol, 34%). Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (m, 8H), 4.20 (d, 2H, J = 1.53 Hz, CH$_2$ alkyne), 3.80-3.55 (m, 37H, PEG, 1H alkyne), 3.38 (s, 3H, CH$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 79.5 (CH alkyne), 74.8 (C alkyne), 71.5 (CH_2OCH$_3$), 70.2 (PEG), 70.1 (PEG), 69.9 (PEG), 68.6 (alkyne-CH$_2$O*C*H$_2$CH$_2$O) 58.4 (alkyne-*C*H$_2$), 57.8 (CH$_3$). MS (MALDI-TOF) m/z calculated for $C_{22}H_{42}O_{10}$ 466.27, obtained $[M+Na]^+$ = 489.21, $[M+K]^+$ = 505.17.

Compound 79: Same procedure as described for **73-75**. After column chromatography (SiO_2, CH_2Cl_2/MeOH 95:5), **79** was obtained (0.31 mmol, 65%). Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (s, 1H, H triazole), 7.10 (s, 1H, Ar), 7.01 (s, 2H, Ar), 5.36 (s, 2H, CH$_2$N next to triazole), 4.53 (s, 2H, CH$_2$O next to triazole), 3.88 (qt, 2H, J = 7.02 Hz, CH_2CH$_3$), 3.58-3.40 (m, 12H, PEG), 3.24 (s,

3H, OCH_3), 3.03, 2.95 (d, 4H, J = 21.93 Hz, $CH_2PO(OEt)_2$), 1.11 (dd, 3H, J = 7.02 and 7.23 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.5 (C triazole), 135.1 (C Ar next to triazole), 133.1 (J = 5.45 Hz, C Ar next to $CH_2PO(OEt)_2$), 131.5 (J = 7.08 Hz, CH Ar next to $CH_2PO(OEt)_2$), 128.0 (J = 4.36 Hz, CH Ar next to triazole), 122.4 (CH triazole), 71.8 (CH_2OCH_3), 70.4 (PEG), 70.3 (PEG), 69.8 (PEG), 69.6 (PEG), 64.5 (CH_2O next to triazole), 62.0 (J = 7.09 Hz, CH_2CH_3), 58.8 (OCH_3), 53.6 (CH_2N next to triazole), 34.2, 32.4 (d, J = 137.46 Hz, $CH_2PO(OEt)_2$), 16.2 (J = 6.0 Hz, CH_3); ^{31}P NMR (81 MHz, $CDCl_3$) δ 26.26; MS (MALDI-TOF) m/z calculated for $C_{27}H_{47}N_3O_{10}P_2$ 635.27, obtained $[M+H]^+$ = 636.06, $[M+Na]^+$ = 650.02, $[M+K]^+$ = 673.98.

Compound 80: Same procedure as described for **73-75**. After column chromatography (SiO_2, CH_2Cl_2/MeOH 95:5), compound **80** was obtained (0.57 mmol, 61%). Yellow oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.42 (s, 1H, H triazole), 7.10 (s, 1H, Ar), 7.01 (s, 2H, Ar), 5.35 (s, 2H, CH_2N next to triazole), 4.51 (s, 2H, CH_2O next to triazole), 3.87 (qt, 2H, J = 7.02 Hz, CH_2CH_3), 3.59-3.40 (m, 36H, PEG), 3.24 (s, 3H, OCH3), 3.02, 2.95 (d, 4H, J = 21.9 Hz, $CH_2PO(OEt)_2$), 1.10 (dd, 3H, J = 6.99 and 7.23 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.6 (C triazole), 135.3 (J = 6.03 Hz, C Ar next to triazole), 133.2 (J = 12.06 Hz, C Ar next to $CH_2PO(OEt)_2$), 131.5 (J = 6.58 Hz, CH Ar next to $CH_2PO(OEt)_2$), 128.0 (J = 10.42 Hz, CH Ar next to triazole), 122.4 (CH triazole), 71.5 (CH_2OCH_3), 70.2 (PEG), 70.1 (PEG), 69.4 (PEG), 64.2 (CH_2O next to triazole), 61.7 (J = 6.58 Hz, CH_2CH_3), 58.5 (OCH_3), 53.2 (CH_2N next to triazole), 33.7, 31.9 (d, J = 137.46 Hz, $CH_2PO(OEt)_2$), 15.7 (J = 6.0 Hz, CH_3); ^{31}P NMR (81 MHz, $CDCl_3$) δ 26.25; MS (MALDI-TOF) m/z calculated for $C_{39}H_{71}N_3O_{16}P_2$ 899.43, obtained $[M+H]^+$ = 900.43, $[M+Na]^+$ = 922.43, $[M+K]^+$ = 938.40.

Compound 82: The preparation procedure and analytical data similar to those reported in the literature [31a].

Compound 83: The preparation procedure and analytical data similar to those reported in the literature [31b].

Compound 84: The preparation procedure and analytical data similar to those reported in the literature [31a].

Compound 85: Same procedure as described for **72**. Starting from **83** (0.7 g, 1.07 mmol), **85** was obtained (1.07 mmol, quant). Yellow oil. ^1H NMR (300 MHz, $CDCl_3$) δ 3.73-3.59 (m, 32H, PEG), 3.38 (dd, 2H, J = 4.80 and 5.28 Hz, $CH_2COOtBu$), 2.50 (t, 2H, J = 6.57 Hz, CH_2N_3), 1.45 (s, 9H, tBu); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.0 ($COOtBu$), 80.1 (C^{IV} tBu), 70.5 (PEG), 70.4 (PEG), 70.3 (PEG), 70.2 (PEG), 69.8 (PEG), 66.7 ($OCH_2CH_2N_3$), 50.5 (CH_2N_3), 36.1 ($CH_2COOtBu$), 27.9 (tBu). MS (MALDI-TOF) m/z calculated for $C_{23}H_{45}N_3O_{10}$ 523.31, obtained $[M+Na]^+$ = 546.28.

Compound 86: Same procedure as described for **73-75**. Starting from **81** (1.18 g, 2.74 mmol) and **84** (1 g, 2.88 mmol), **86** was obtained (0.87 mmol, 32%). Burgundy oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.86 (s, 1H, CH triazole), 6.78 (m, 3H, Ar), 5.16 (s, 2H, OCH_2 triazole), 4.55 (dd, 2H, J = 5.04 and 5.28 Hz, NCH_2 triazole), 4.02 (qt, 8H, J = 7.02 Hz, CH_2CH_3), 3.89 (dd, J = 5.04 and 5.25 Hz, 2H, NCH_2CH_2O), 3.72-3.59 (m, 14H, PEG), 3.13, 3.06 (d, 4H, J = 21.93 Hz, $CH_2PO(OEt)_2$), 2.48 (dd, 2H, J = 6.57 and 6.57 Hz, $CH_2COOtBu$), 1.43 (s, 9H, tBu), 1.22 (t, 12H, J = 7.02 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5 ($COOtBu$), 158.3 (C Ar next to triazole), 143.3 (C triazole), 133.1 (J = 9.27 Hz, C Ar next to $CH_2PO(OEt)_2$), 124.3 (J = 7.08 Hz, CH Ar next to $CH_2PO(OEt)_2$), 123.9 (CH triazole), 115.4 (CH Ar next to triazole), 80.1 (C^{IV} tBu), 70.4 (PEG), 70.3 (PEG), 70.2 (PEG), 70.1 (PEG), 69.1 (PEG), 68.6 (NCH_2CH_2O next to triazole), 66.3 (OCH_2 next to triazole), 61.9 (J = 6.54 Hz, CH_2CH_3), 61.6 (NCH_2CH_2O), 50.1 ($CH_2CH_2COOtBu$), 36.1 ($CH_2COOtBu$), 34.3, 32.5 (J = 137.46 Hz, $CH_2PO(OEt)_2$), 27.9 (tBu), 16.2 (J = 6 Hz, CH_3); ^{31}P NMR (81 MHz, $CDCl_3$) δ 26.78; MS (MALDI-TOF) m/z calculated for $C_{34}H_{59}N_3O_{13}P_2$ 779.35, obtained $[M+H]^+$ = 780.19, $[M+Na]^+$ = 802.15, $[M-tBu]^+$ = 724.18.

Compound 87: Same procedure as described for **73-75**. Starting from **81** (0.35 g, 0.82 mmol) and **85** (0.45 g, 0.86 mmol), **87** was obtained (0.57 mmol, 69%). Burgundy oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (s, 1H, CH triazole), 6.85 (bs, 3H, Ar), 5.16 (s, 2H, OCH_2 triazole), 4.55 (dd, 2H, J = 5.04 and 5.25 Hz, NCH_2 triazole), 4.02 (qt, 8H, J = 7.23 Hz, CH_2CH_3), 3.89 (dd, 2H, J = 5.04 and 5.25 Hz, NCH_2CH_2O), 3.70 (dd, 2H, J = 6.36 and 6.78 Hz, $CH_2CH_2COOtBu$), 3.63-3.59 (m, 28H, PEG), 3.13, 3.06 (d, 4H, J = 21.9 Hz, $CH_2PO(OEt)_2$), 2.49 (t, 2H, J = 6.57 Hz, $CH_2COOtBu$), 1.44 (s, 9H, *t*Bu), 1.25 (t, J = 7.02 Hz, 12H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ. 170.5 ($COOtBu$), 158.2 (C Ar next to triazole), 143.0 (C triazole), 133.1 (J = 9.27 Hz, C Ar next to $CH_2PO(OEt)_2$), 124.1 (CH triazole), 123.8 (J = 6.54 Hz, CH Ar next to $CH_2PO(OEt)_2$), 114.7 (J = 9.27 Hz, CH Ar next to triazole), 80.1 (C^{IV} *t*Bu), 70.3 (PEG), 70.2 (PEG), 70.1 (PEG), 69.1 (NCH_2CH_2O next to triazole),66.6 (OCH_2 next to triazole), 61.9 (J = 6.54 Hz, CH_2CH_3), 61.6 (NCH_2CH_2O), 50.0 ($CH_2CH_2COOtBu$), 36.0 ($CH_2COOtBu$), 34.3, 32.5 (J = 136.91 Hz, $CH_2PO(OEt)_2$), 27.8 (*t*Bu), 16.2 (J = 6 Hz, CH_3); ^{31}P NMR (81 MHz, $CDCl_3$) δ 26.74; MS (MALDI-TOF) m/z calculated for $C_{42}H_{75}N_3O_{17}P_2$ 955.45, obtained $[M-tBu]^+$ = 900.43.

3.2.General procedure for bromination of 88 and 89

To obtain compound **88** or **89**, compound **82** or **83** respectively (1 equiv.) was dissolved in acetone (5 mL). After addition of lithium bromide (2 equiv.), the solution was stirred at reflux for 16 hrs. After addition of water (20 mL) and EtOAc (10 mL), the organic layer was washed, dried over $MgSO_4$, filtered and evaporated *in vacuo*.

Compound 88: Starting from **82** (0.5 g, 1.25 mmol) and after purification by column chromatography (SiO_2, CH_2Cl_2/MeOH 96:4), compound **88** was obtained (0.9 mmol, 72%). Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.81 (dd, 2H, J = 6.39 and 6.42 Hz, $BrCH_2CH_2O$), 3.71 (dd, 2H, J = 6.57 and 6.6 Hz, $CH_2CH_2COOtBu$), 3.68-3.58 (m, 12H, PEG), 3.47 (dd, 2H, J = 6.21 and 6.42 Hz, $BrCH_2CH_2O$), 2.50 (dd, 2H, J = 6.6 and 6.6 Hz, $CH_2COOtBu$), 1.44 (s, 9H, *t*Bu); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8 ($COOtBu$), 80.4 (C^{IV} *t*Bu), 71.1 ($BrCH_2CH_2O$), 70.6 (PEG), 70.5 (PEG), 70.4 (PEG), 70.3 ($BrCH_2CH_2OCH_2$), 66.8 ($CH_2CH_2COOtBu$), 36.2 ($CH_2COOtBu$), 30.2 ($BrCH_2CH_2O$), 28.0 (*t*Bu). MS (MALDI-TOF) m/z calculated for $C_{15}H_{29}BrO_6$ 384.11, obtained $[M+Na]^+$ = 407.11.

Compound 89: Starting from **83** (0.2 g, 0.31 mmol), **89** was obtained and used in the next step without further purification (0.21 mmol, 70%). Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.81 (dd, 2H, J = 6.36 and 6.36 Hz, $BrCH_2CH_2O$), 3.71 (dd, 2H, J = 6.57 and 6.6 Hz, $CH_2CH_2COOtBu$), 3.68-3.59 (m, 28H, PEG), 3.47 (dd, 2H, J = 6.36 and 6.36 Hz, $BrCH_2CH_2O$), 2.50 (dd, 2H, J = 6.57 and 6.57 Hz, $CH_2COOtBu$), 1.45 (s, 9H, *t*Bu); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7 ($COOtBu$), 80.2 (C^{IV} *t*Bu), 71.0 ($BrCH_2CH_2O$), 70.5 (PEG), 70.4 (PEG), 70.3 (PEG), 70.2 ($BrCH_2CH_2OCH_2$), 66.7 ($CH_2CH_2COOtBu$), 36.1 ($CH_2COOtBu$), 30.2 ($BrCH_2CH_2O$), 27.9 (*t*Bu). MS (MALDI-TOF) m/z calculated for $C_{23}H_{45}BrO_{10}$ 560.22, obtained $[M+Na]^+$ = 583.12, $[M+K]^+$ = 599.08.

Compounds **90** and **91** were prepared following the same procedure as described for **70**.

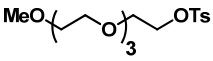
Compound 90: Starting from **88** (0.31 g, 0.82 mmol), **90** was obtained (0.82 mmol, quant). Colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.94 (m, 4H, CH_2CH_3), 3.65-3.43 (m, 16H, PEG), 2.33 (dd, 2H, J = 6.36 and 6.57 Hz, $CH_2COOtBu$), 1.95 (m, 2H, $CH_2PO(OEt)_2$), 1.28 (s, 9H, *t*Bu), 1.16 (dd, 6H, J = 7.02 and 7.02 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6 ($COOtBu$), 80.2 (C^{IV} *t*Bu), 70.5 (PEG), 70.4 (PEG), 70.3 (PEG), 70.2 (PEG), 70.0 ($CH_2CH_2COOtBu$), 66.7 (CH_2CH_3), 64.9 ($OCH_2CH_2PO(OEt)_2$), 61.4 (J = 6 Hz, $CH_2PO(OEt)_2$), 36.1 ($CH_2COOtBu$), 27.7 (*t*Bu), 16.3 (J = 6.54 Hz, CH_3); ^{31}P NMR (81 MHz, $CDCl_3$) δ 29.29; MS (MALDI-TOF) m/z calculated for $C_{19}H_{39}O_9P$ 442.23, obtained $[M+Na]^+$ = 465.19, $[M+K]^+$ = 481.15.

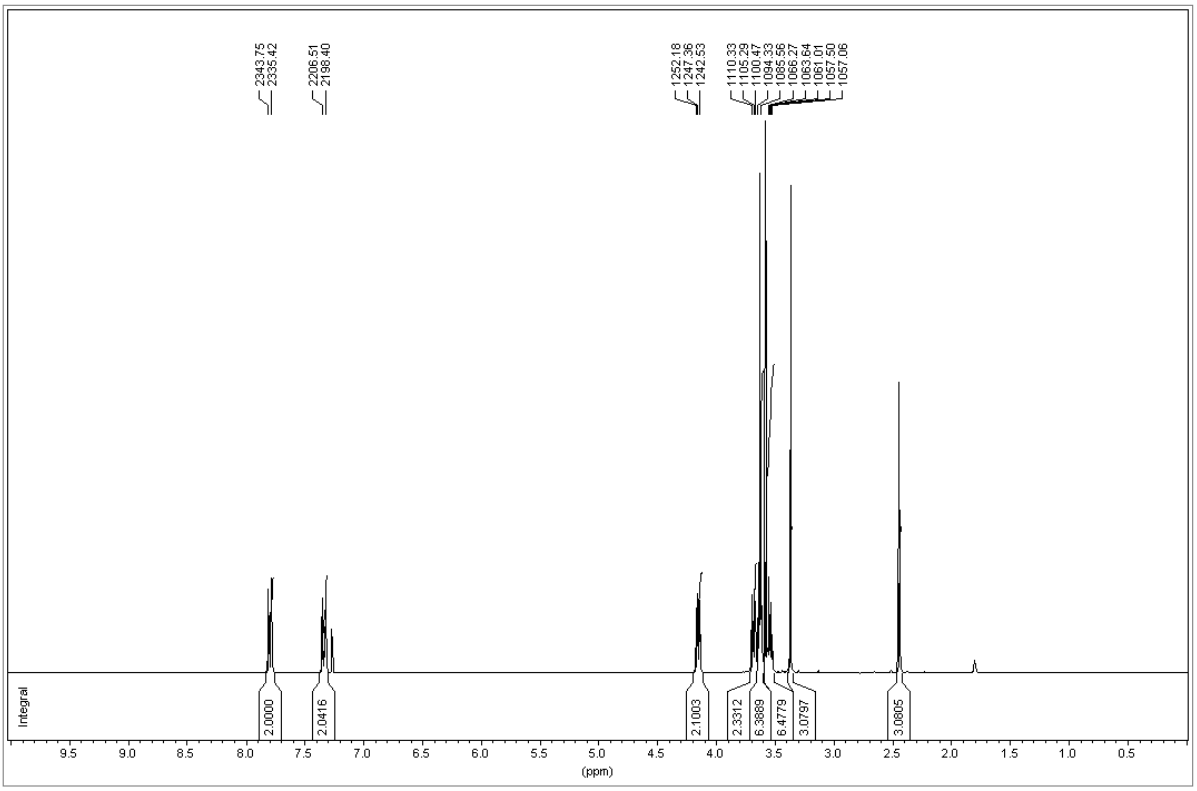
Compound 91: Starting from **89** (0.1 g, 0.18 mmol), compound **91** was obtained (0.16 mmol, 92%). Colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.10 (m, 4H, CH_2CH_3), 3.72-3.57 (m, 32H, PEG), 2.49 (t, 2H, J = 6.6 Hz, $CH_2COOtBu$), 2.11 (m, 2H, $CH_2PO(OEt)_2$), 1.43 (s, 9H, *t*Bu), 1.31 (dd, 6H, J =

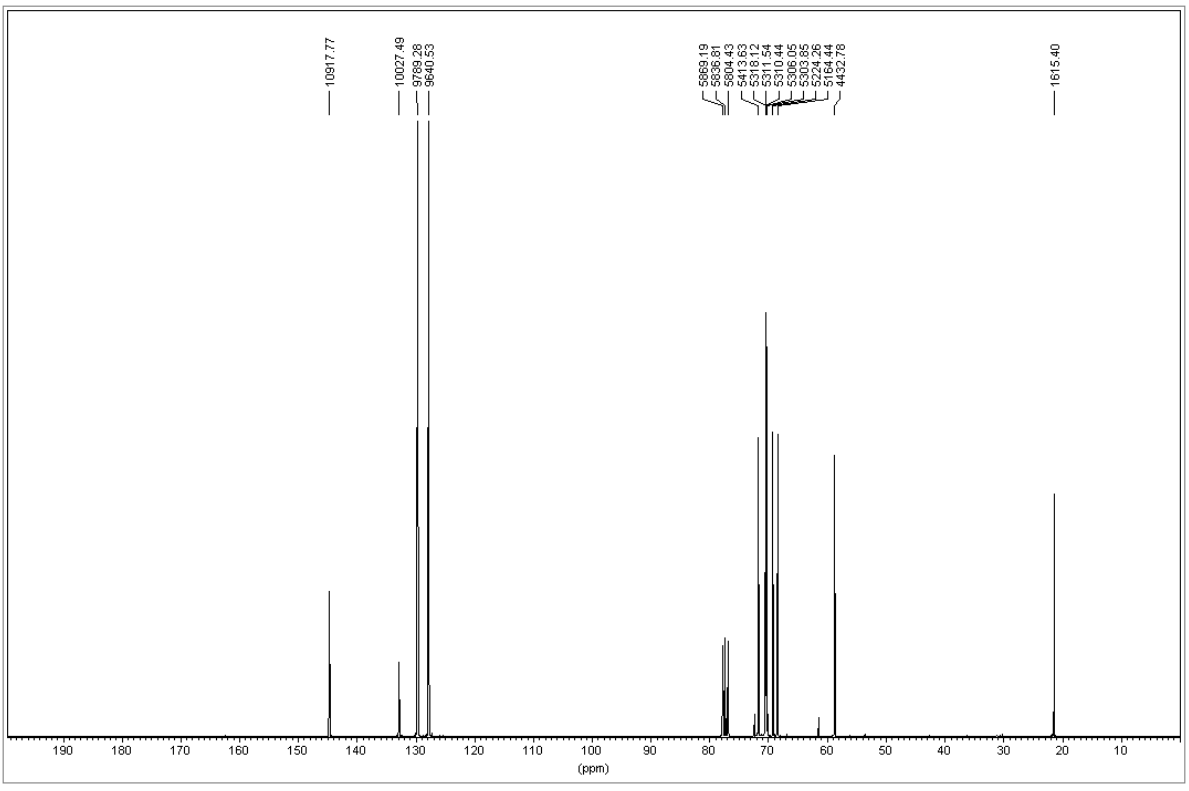
6.96 and 7.20 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4 (COO*t*Bu), 79.9 (C^{IV} *t*Bu), 70.3 (PEG), 70.2 (PEG), 70.1 (PEG), 69.9 ($CH_2CH_2COOtBu$), 66.5 (CH_2CH_3), 64.8 ($OCH_2CH_2PO(OEt)_2$), 61.2 (J = 6.54 Hz, $CH_2PO(OEt)_2$), 35.9 ($CH_2COOtBu$), 27.8 (*t*Bu), 16.2 (J = 6 Hz, CH_3); ^{31}P NMR (81 MHz, $CDCl_3$) δ 29.35; MS (MALDI-TOF) m/z calculated for $C_{27}H_{55}O_{13}P$ 618.33, obtained $[M+Na]^+$ = 641.10, $[M+K]^+$ = 657.08.

II.NMR spectra of the different synthesized compounds

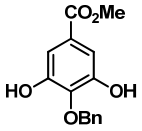
Compound 5 (^{1}H and ^{13}C, $CDCl_3$)

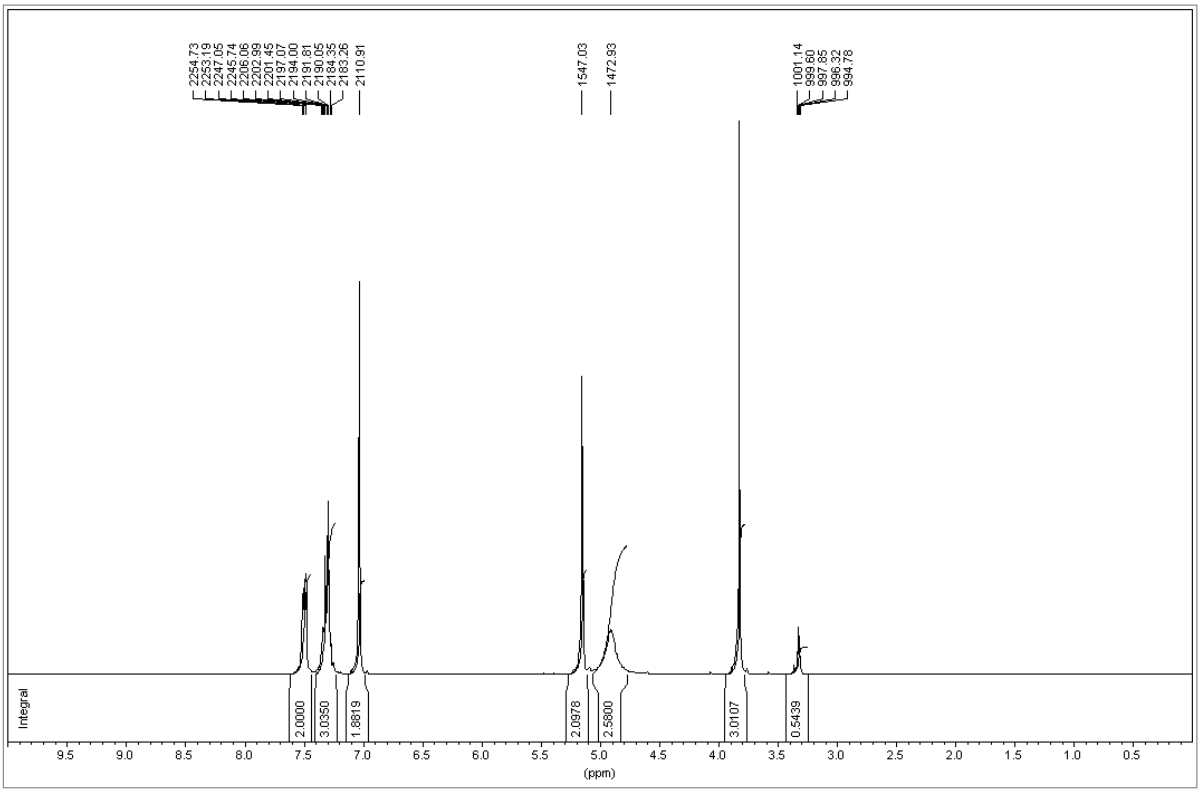


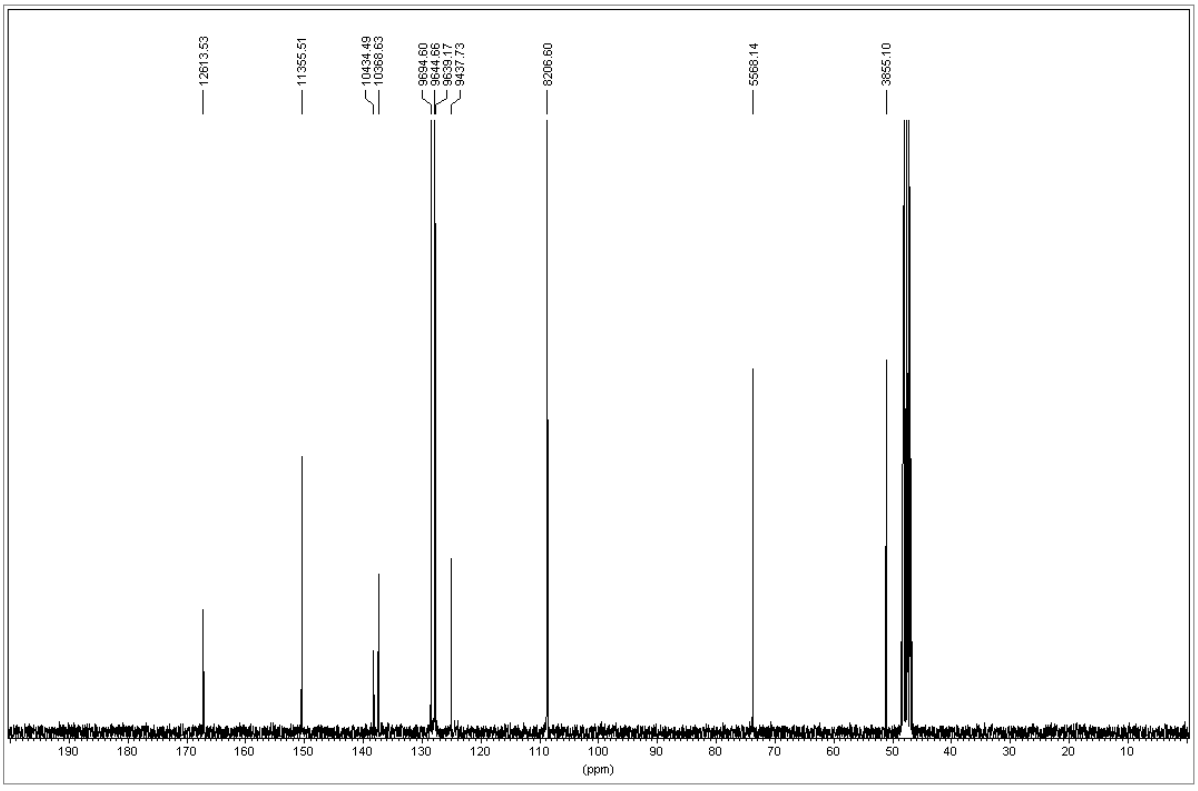




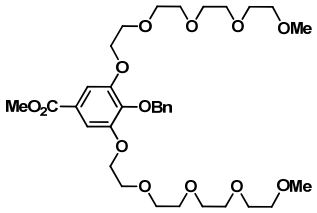
Compound 6 (^{1}H and ^{13}C, CD_3OD)

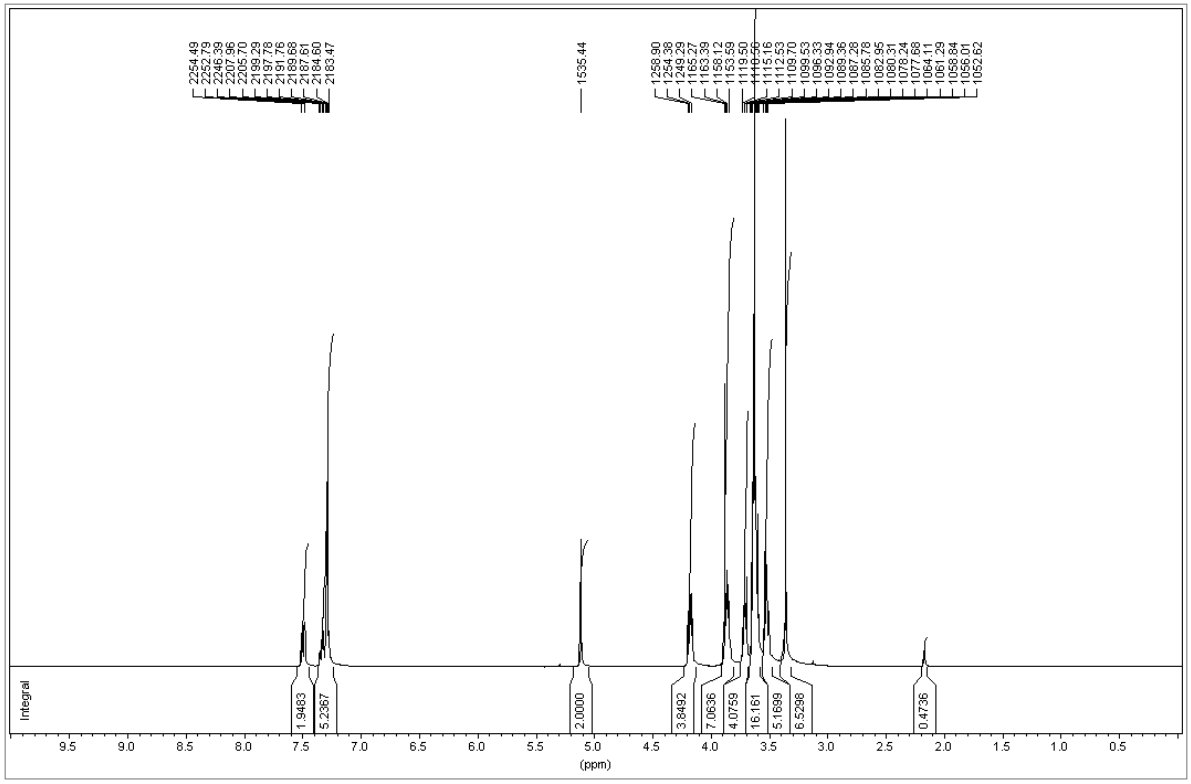


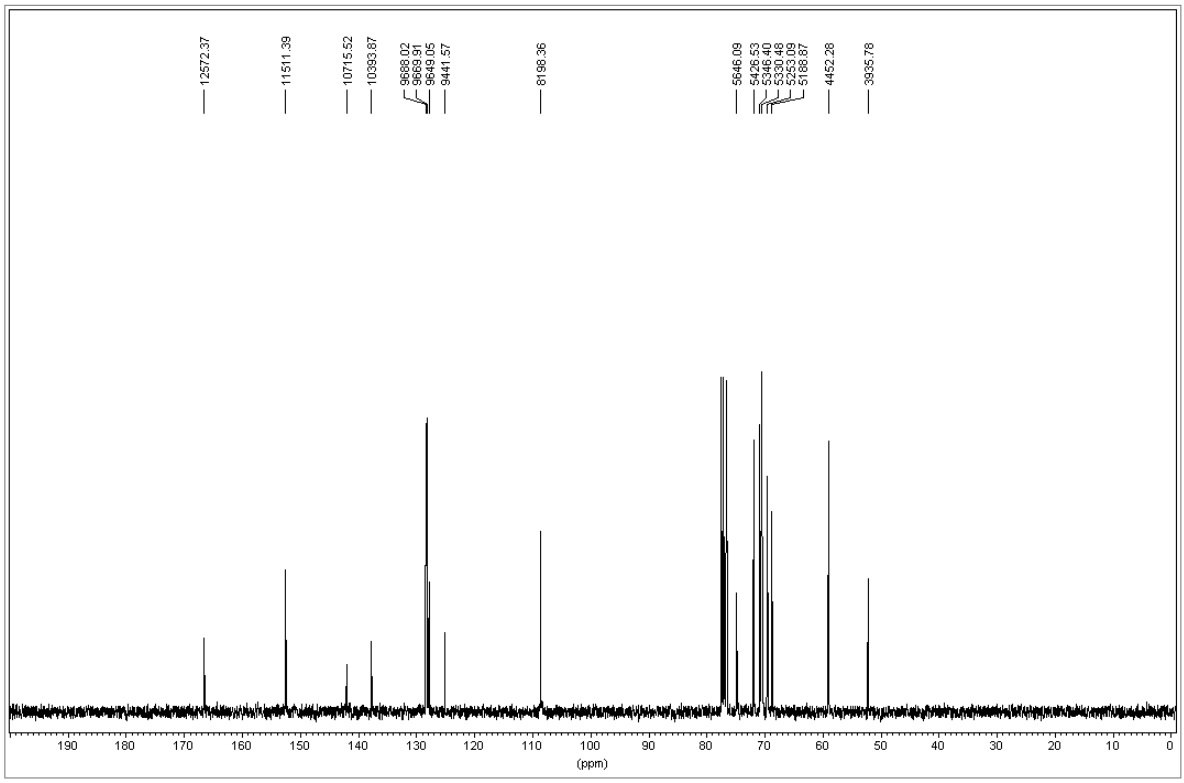




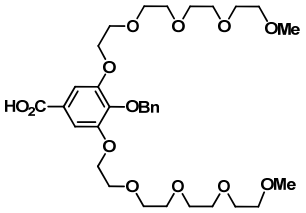
Compound 7 (^{1}H and ^{13}C, $CDCl_3$)

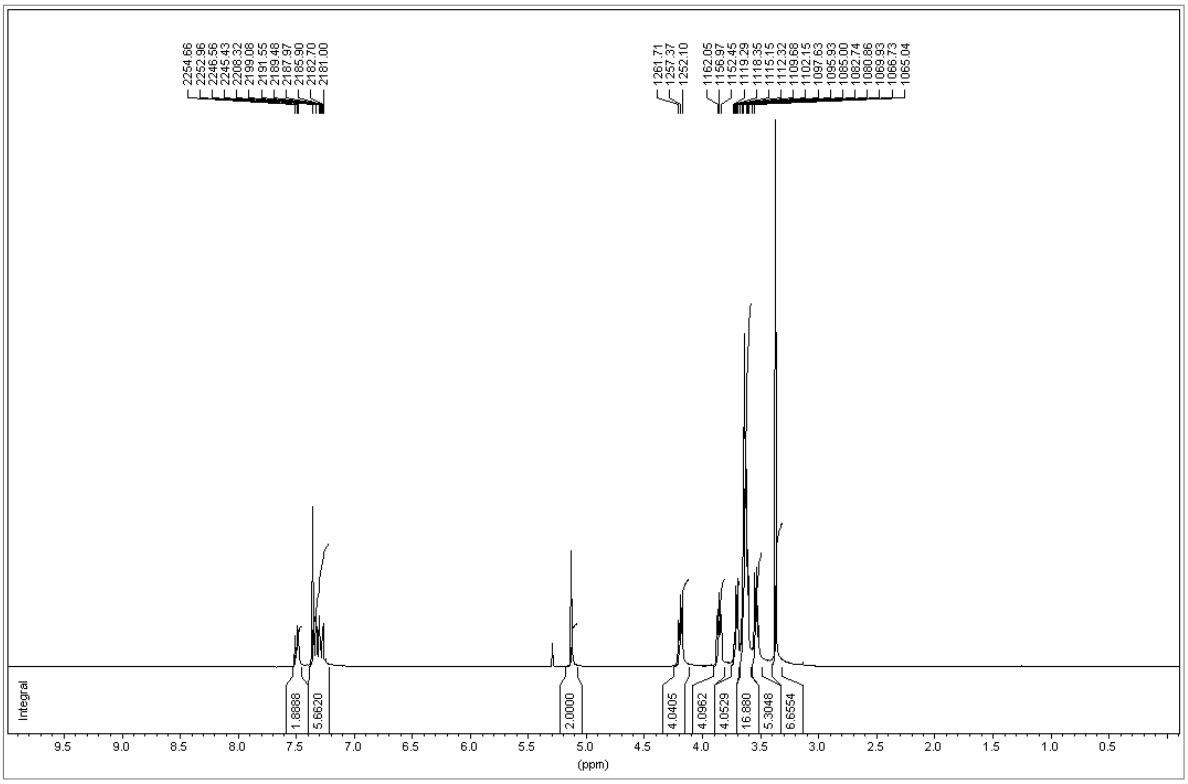


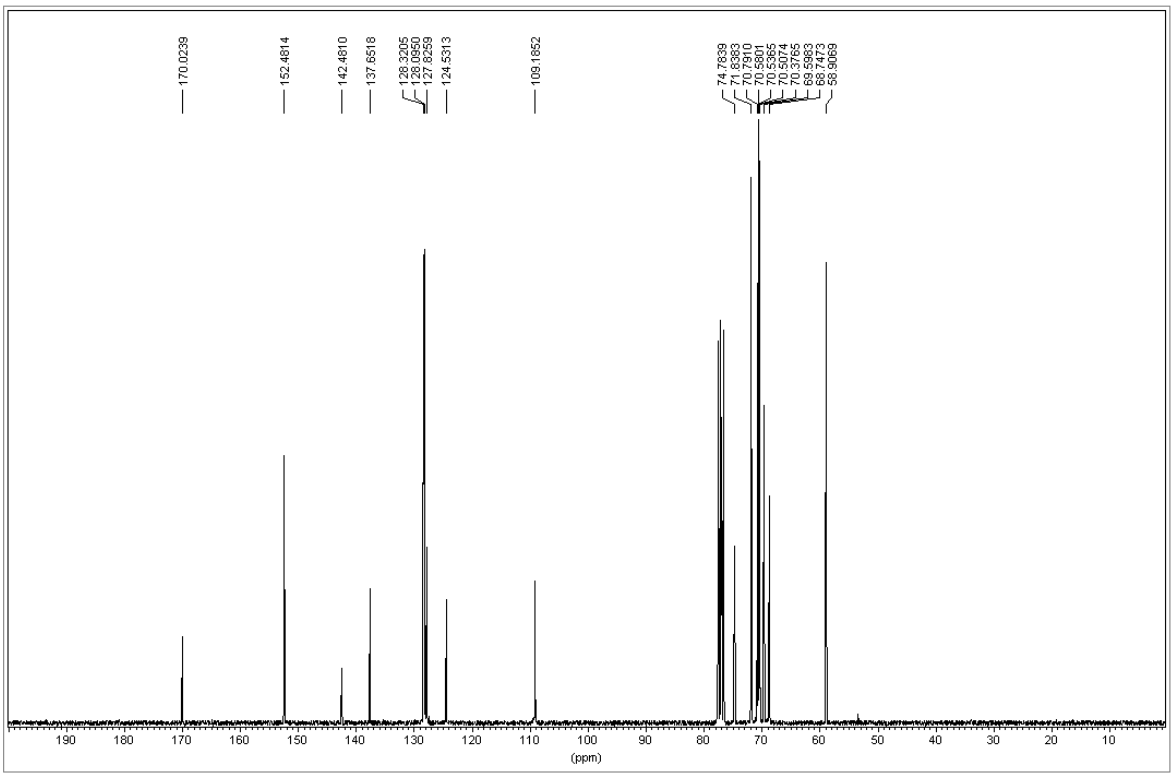




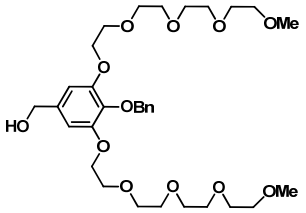
Compound 8 (^{1}H and ^{13}C, $CDCl_3$)

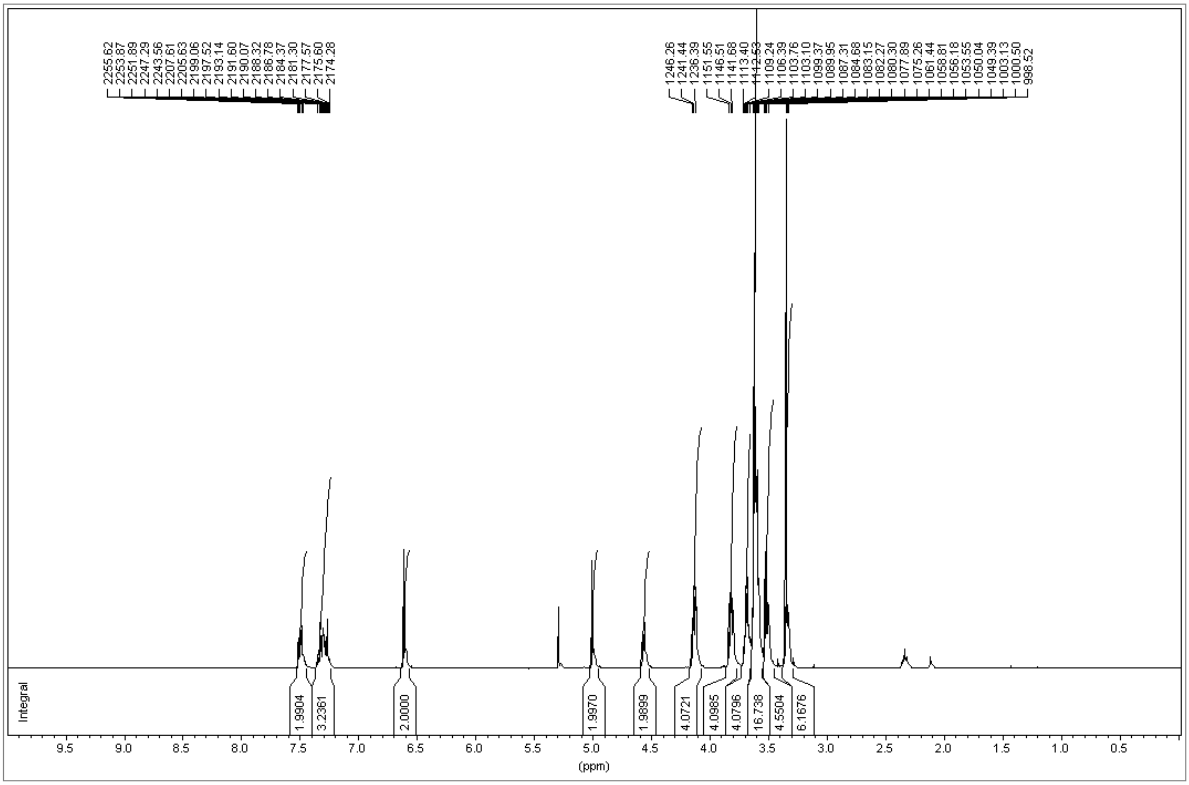


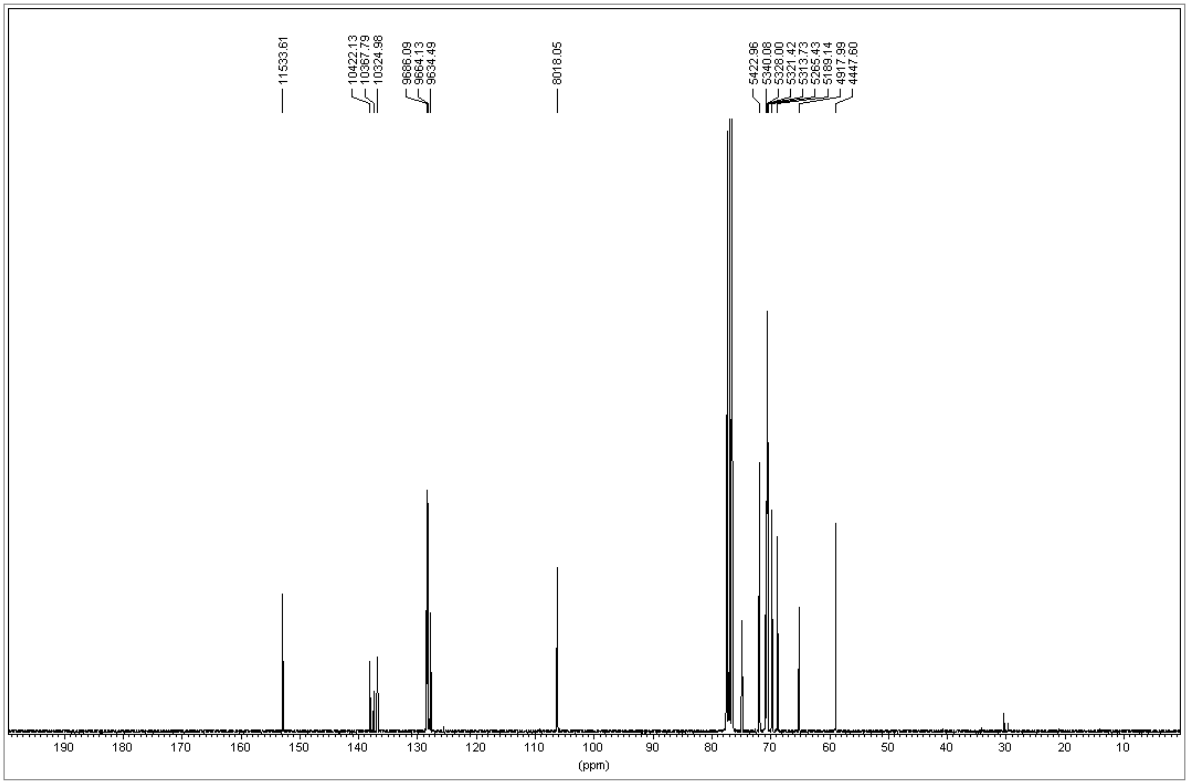




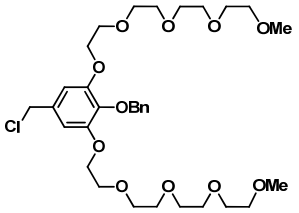
Compound 9 (^{1}H and ^{13}C, $CDCl_3$)

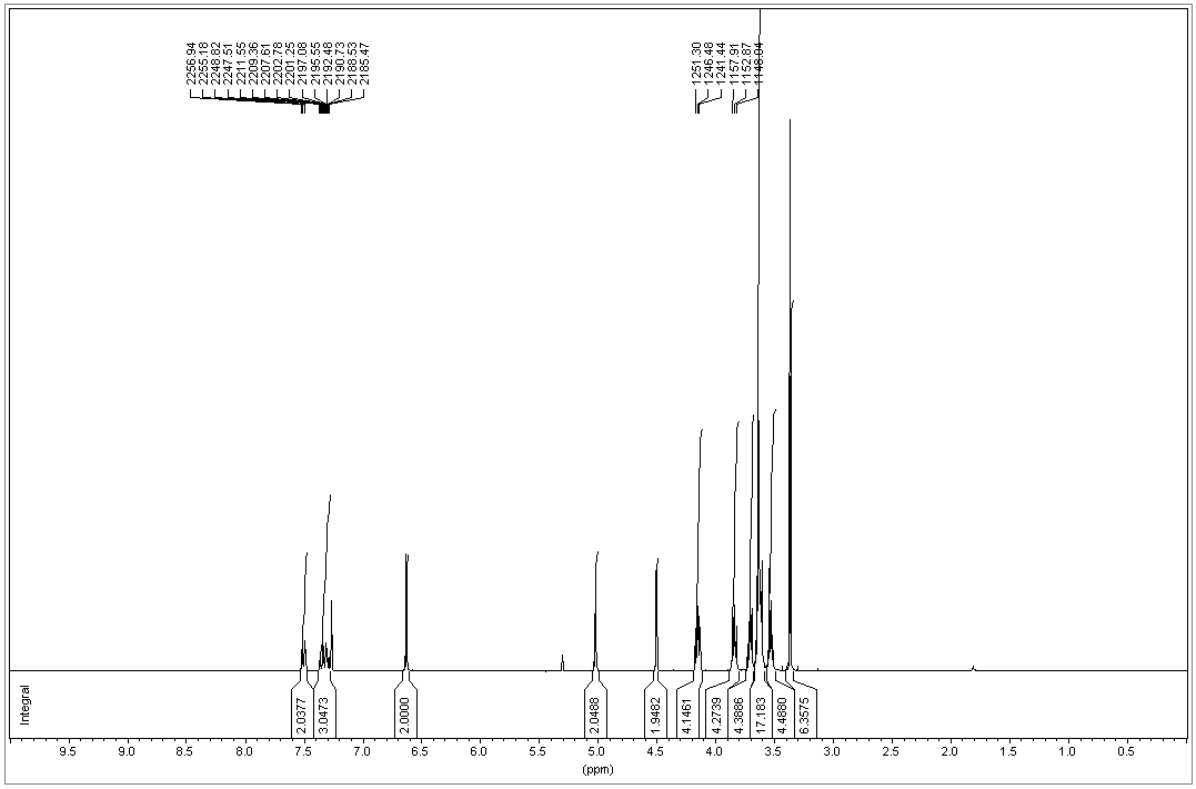


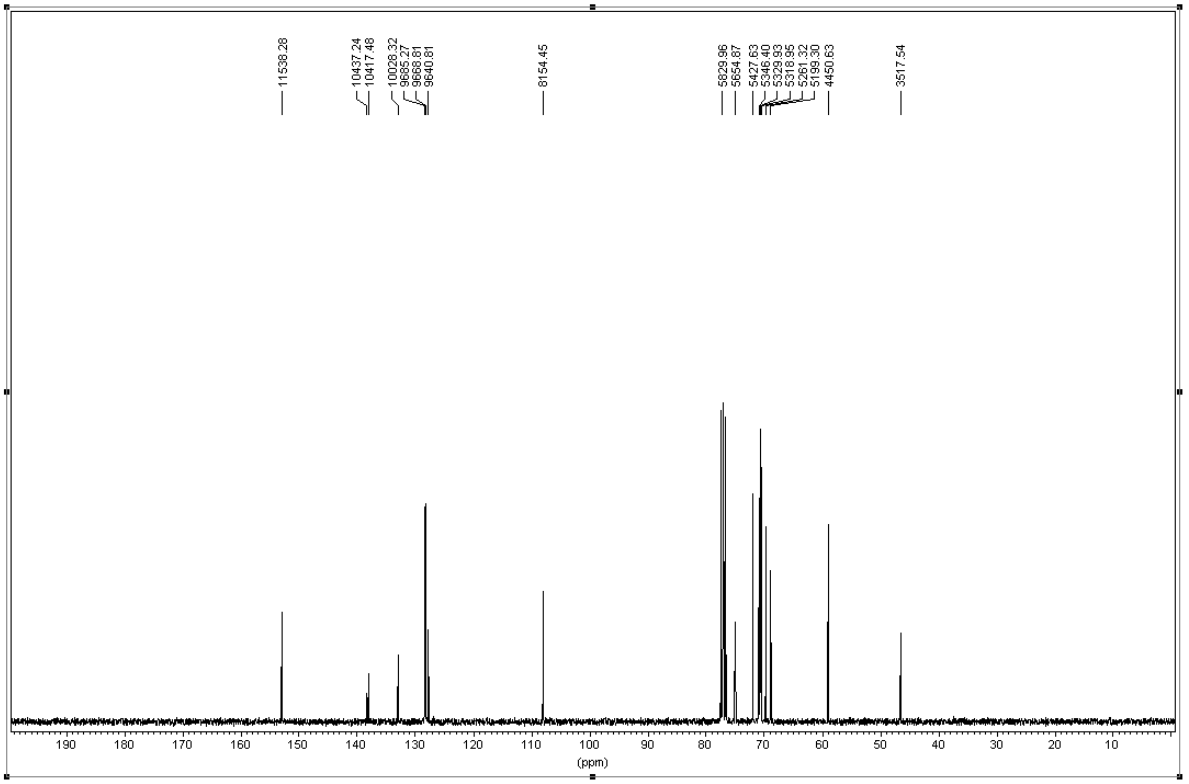




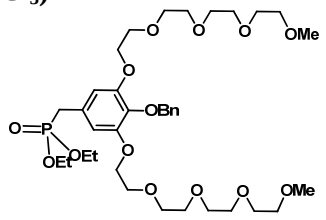
Compound 10 (^{1}H and ^{13}C, $CDCl_3$)

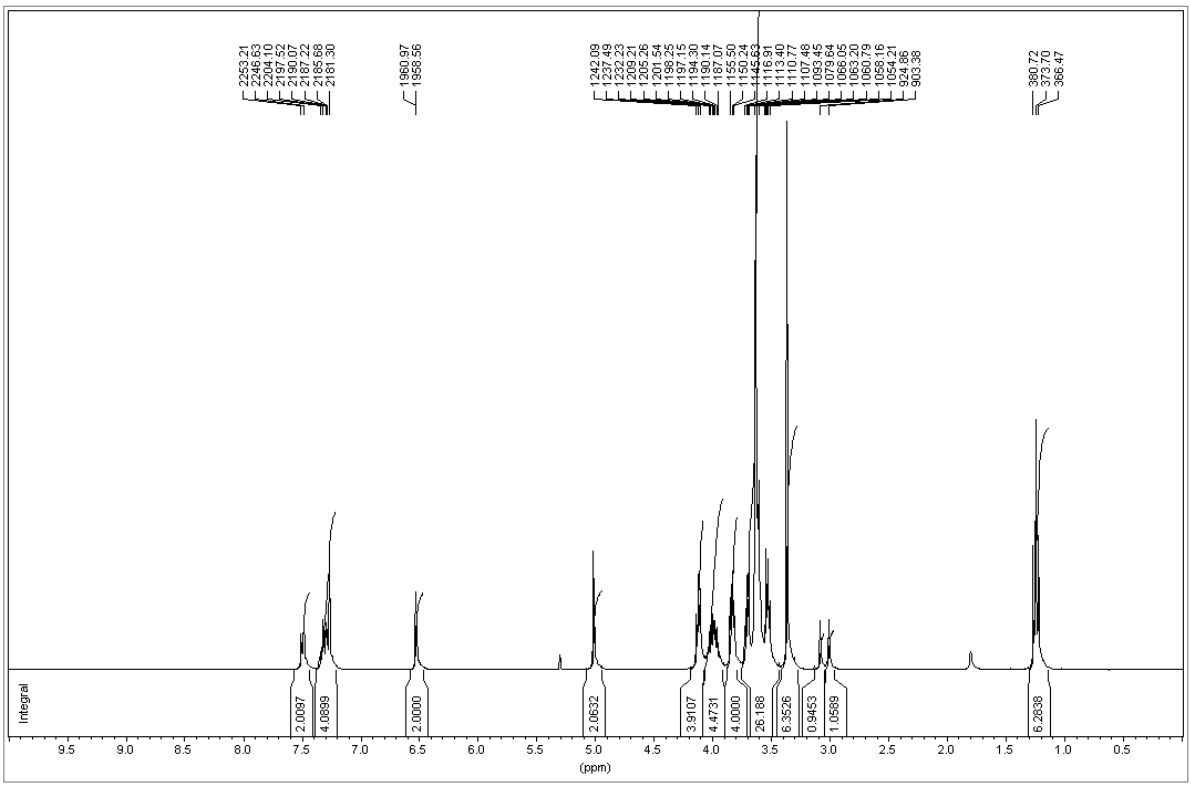


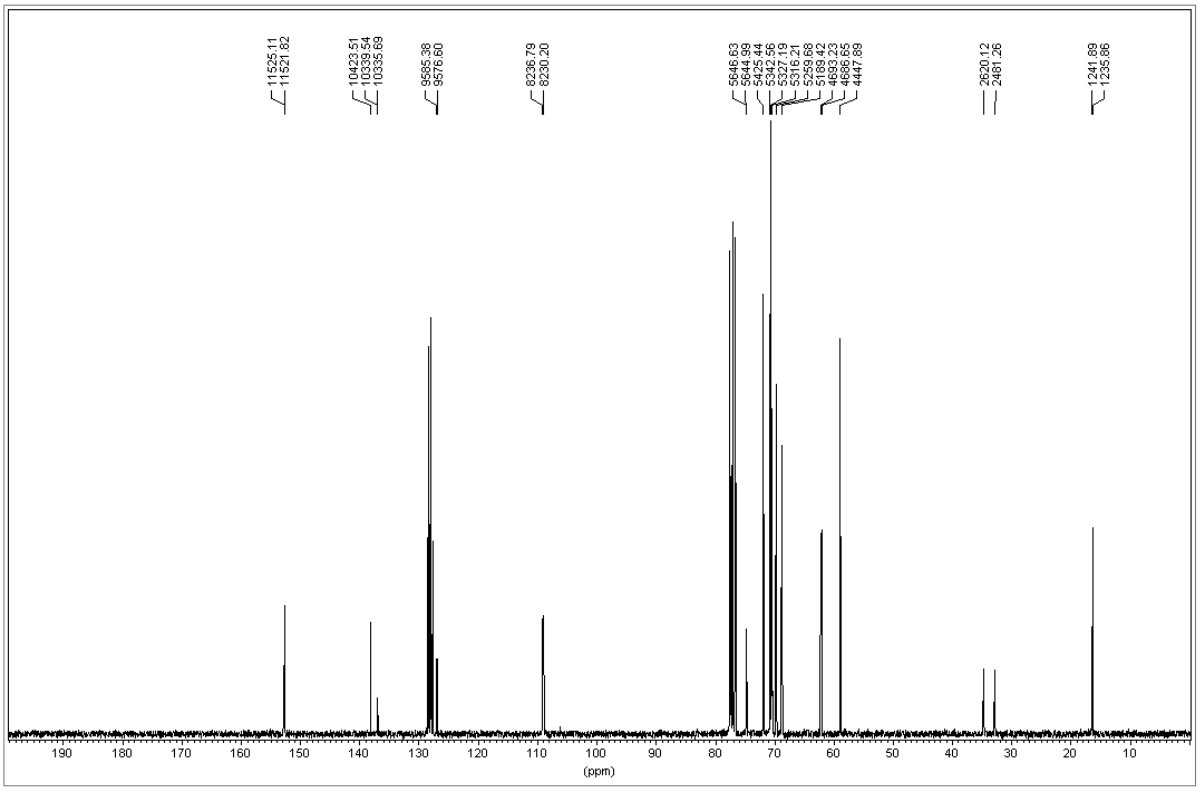


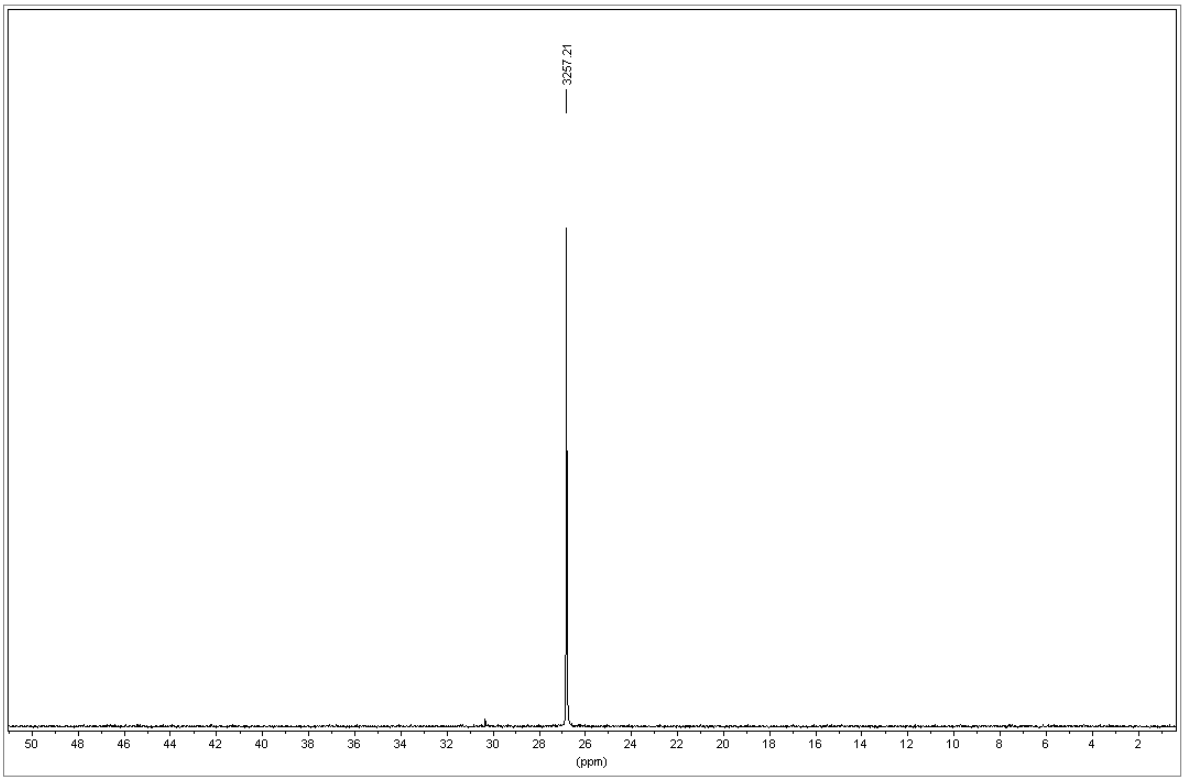


Compound 11 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

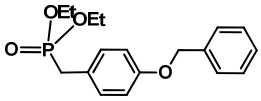


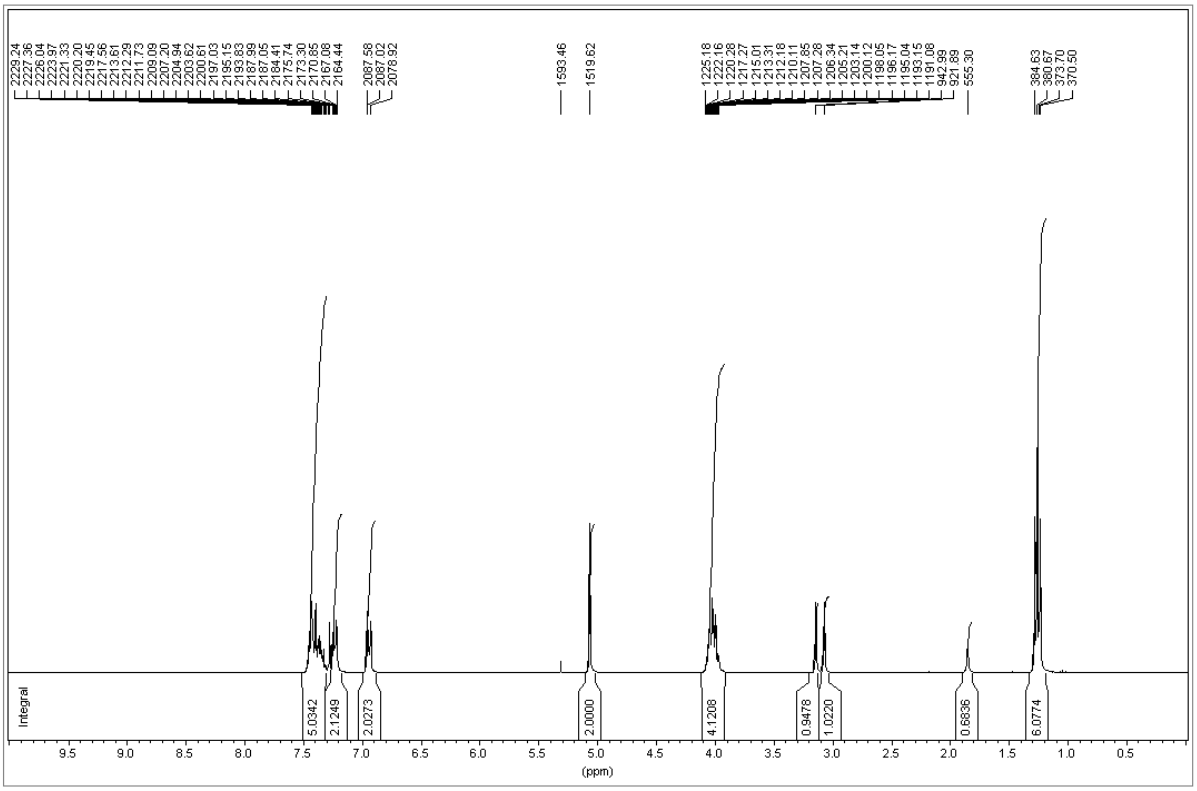


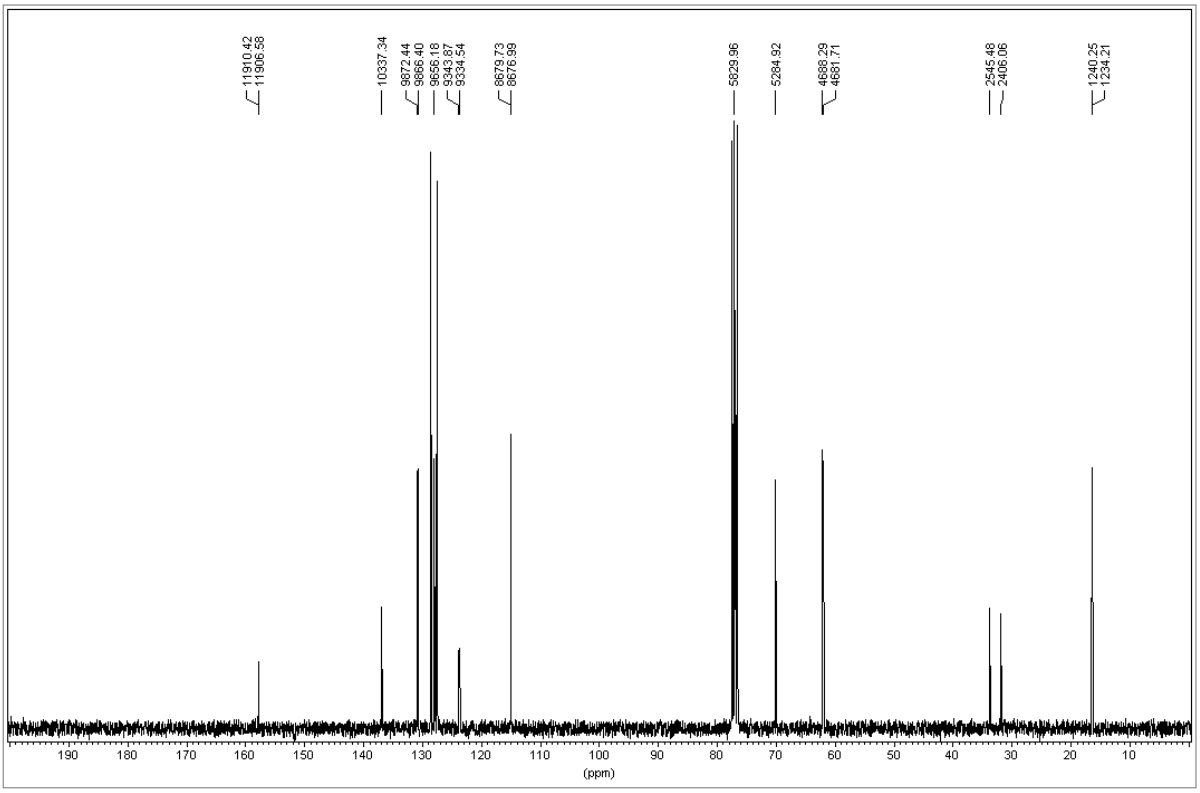


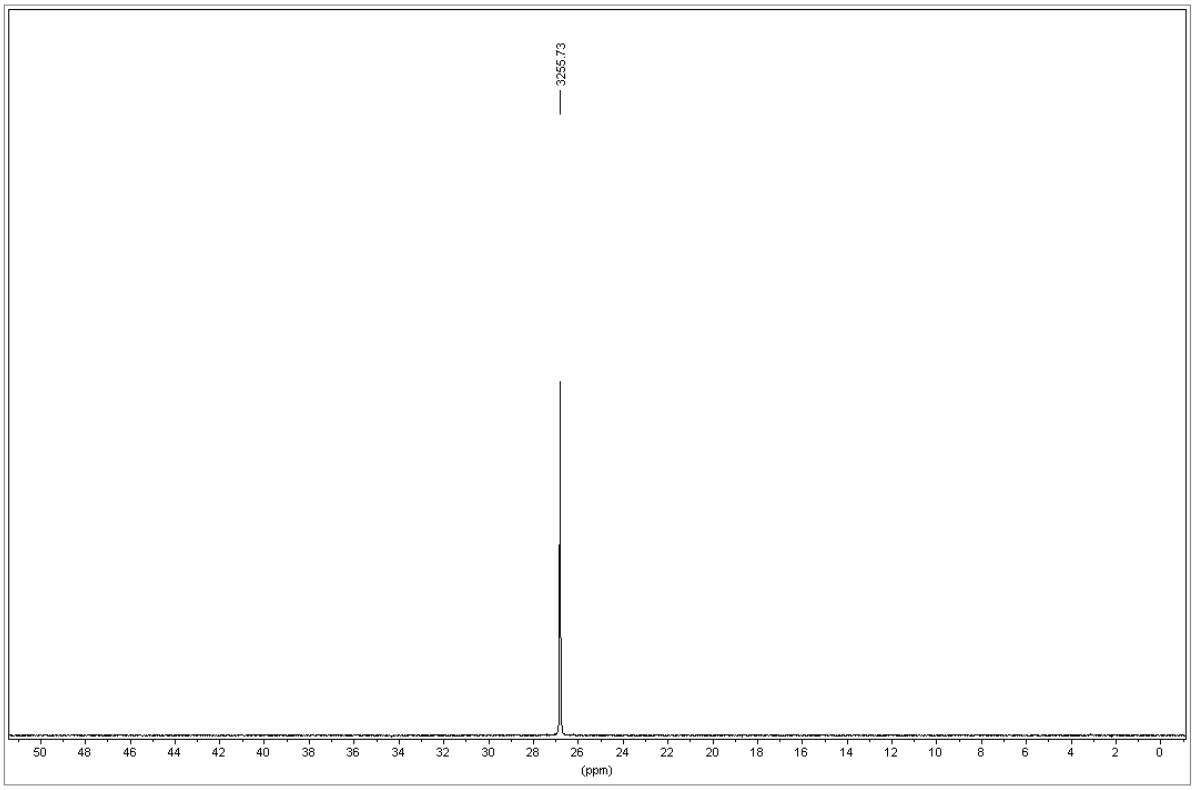


Compound 13 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

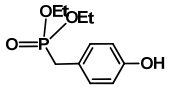


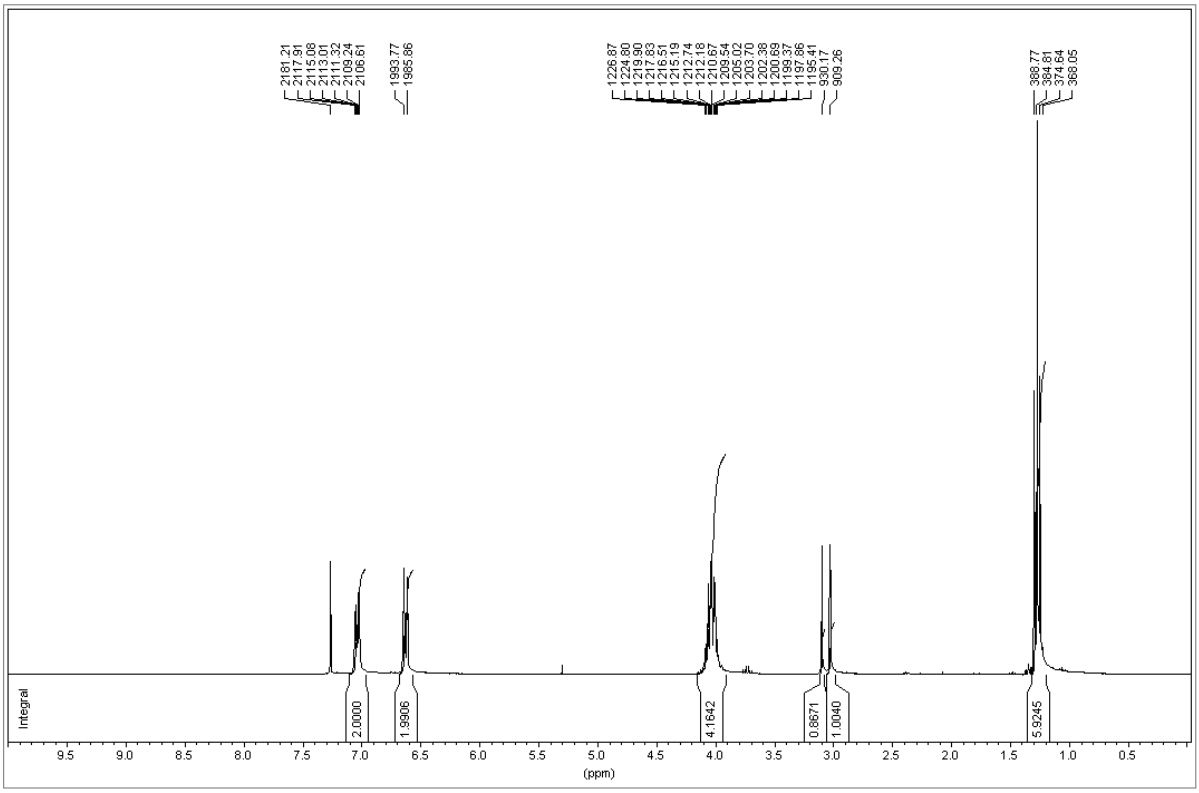


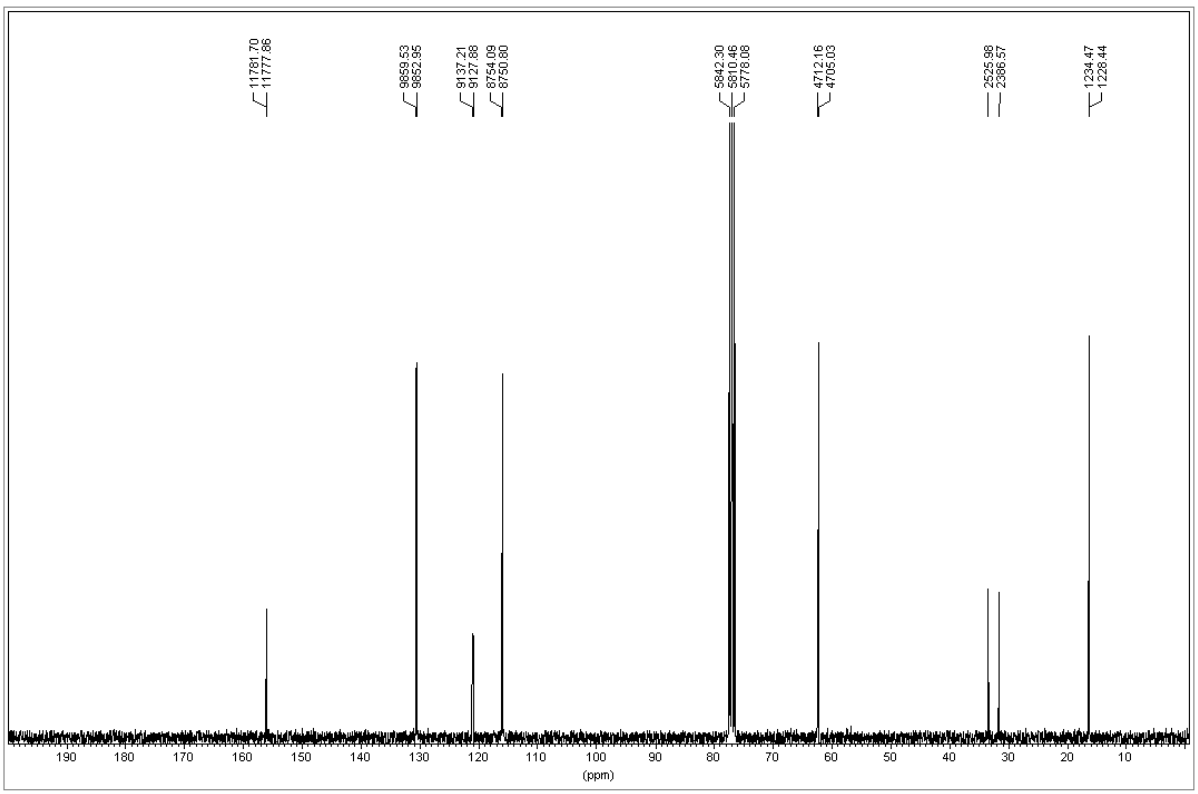

11910.42
11906.58
10337.34
9872.44
9866.40
9656.18
9343.87
9334.54
8679.73
8676.99
5829.96
5284.92
4688.29
4681.71
2545.48
2406.06
1240.25
1234.21
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

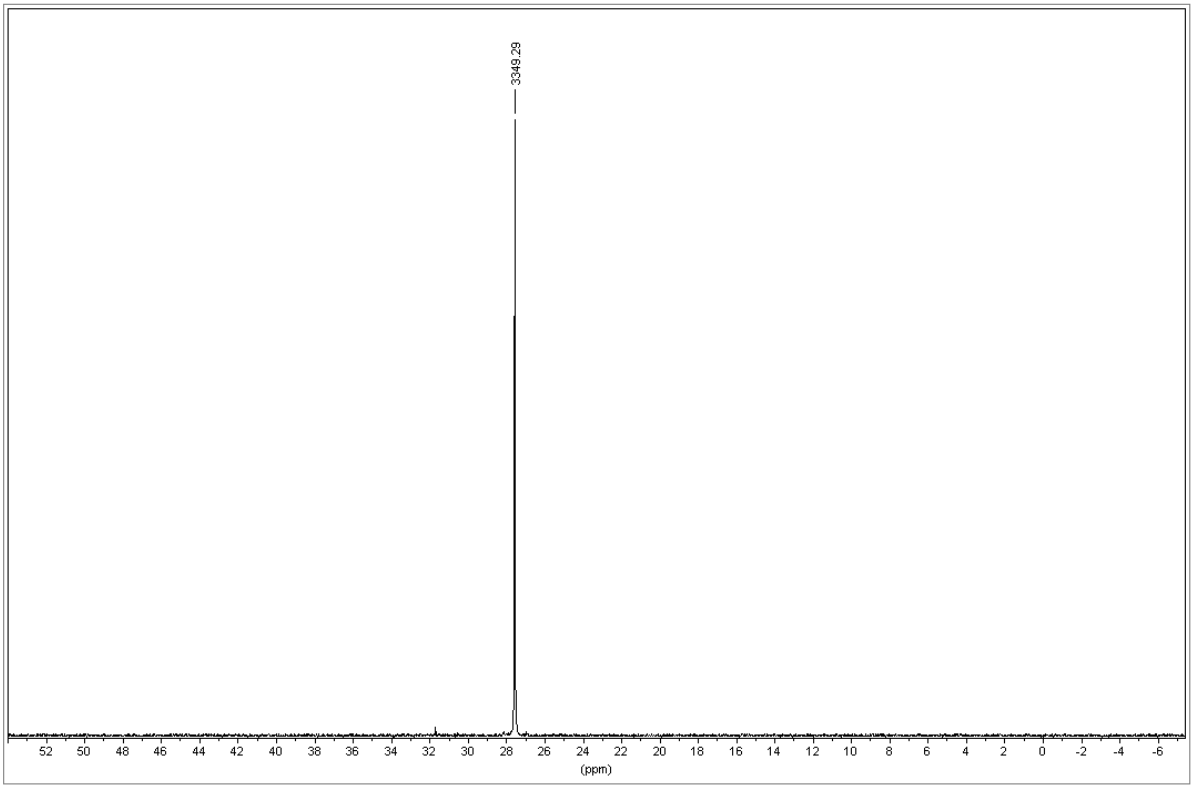

3255.73
50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0
(ppm)

Compound 14 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

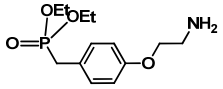


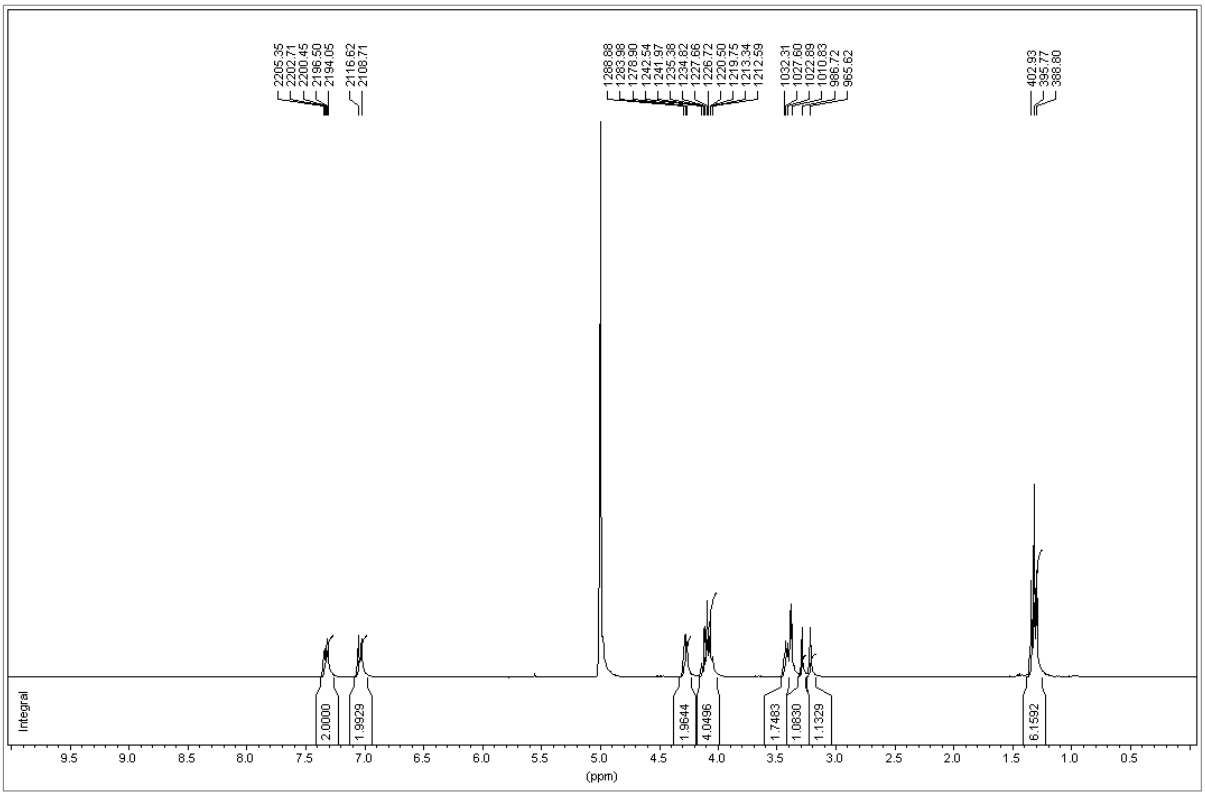


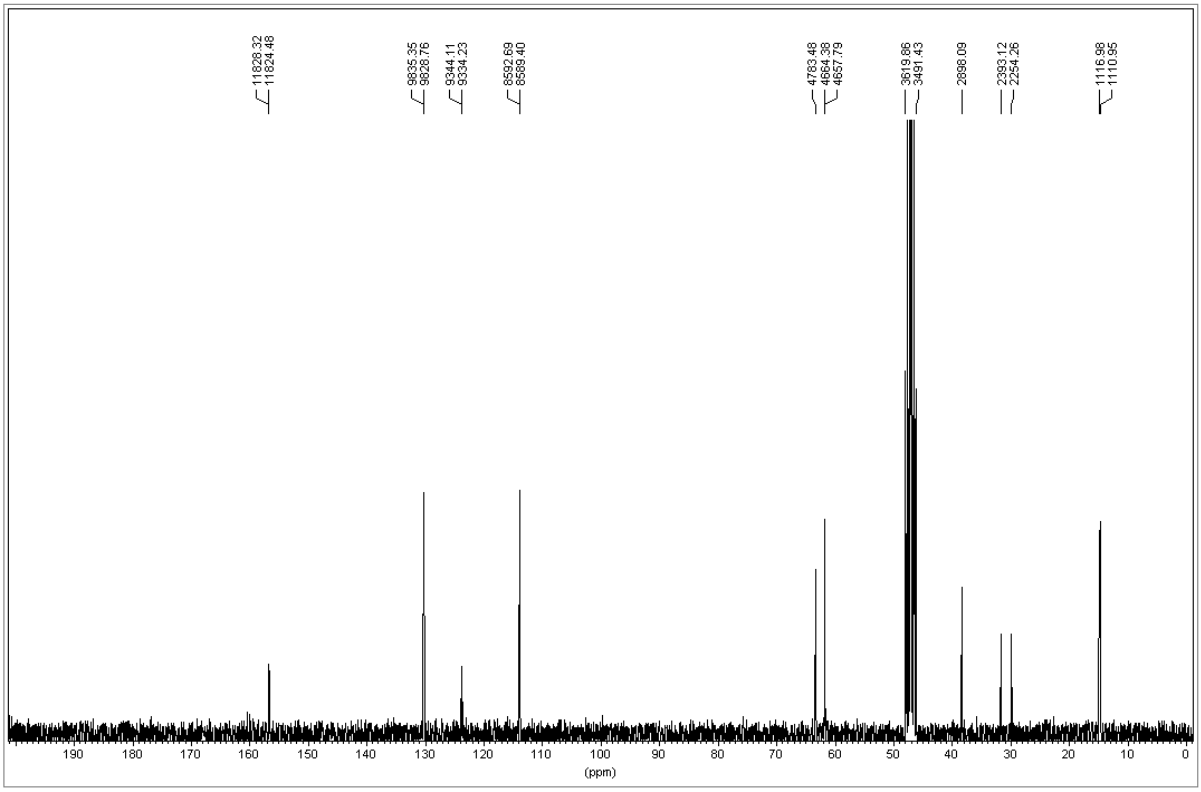


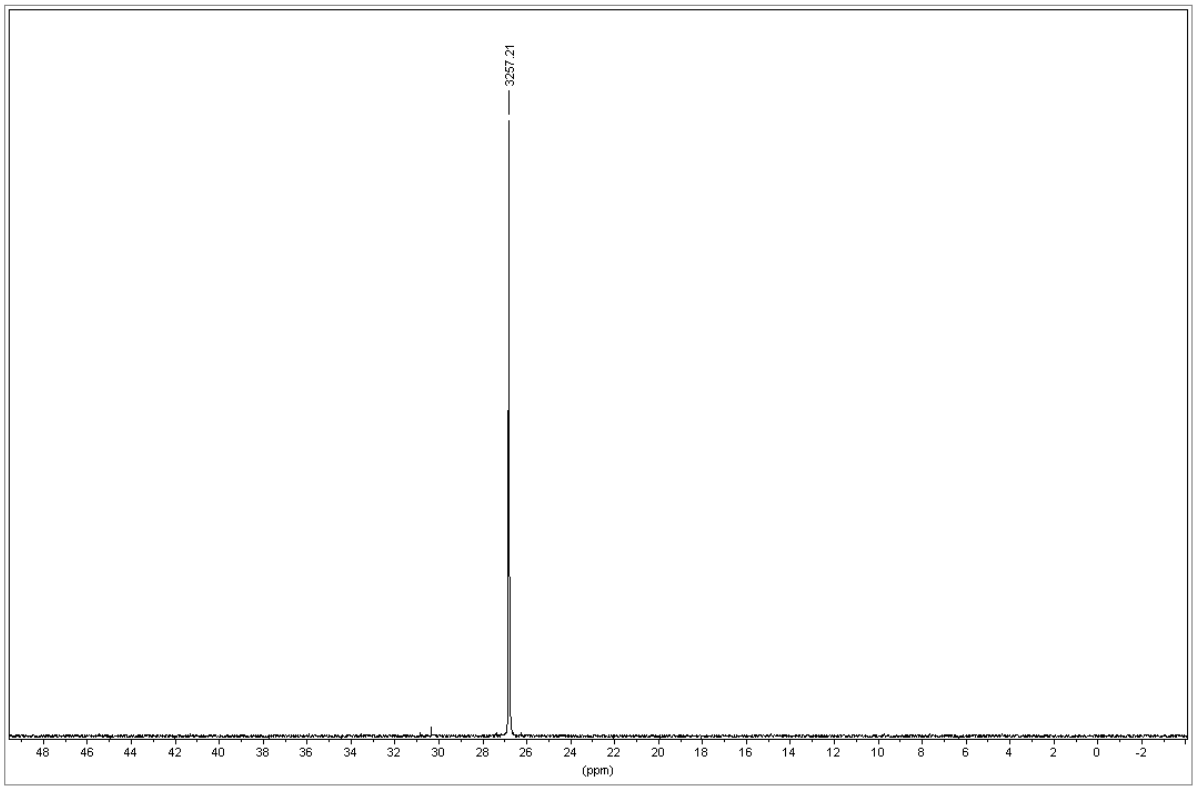


Compound 15 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

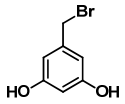


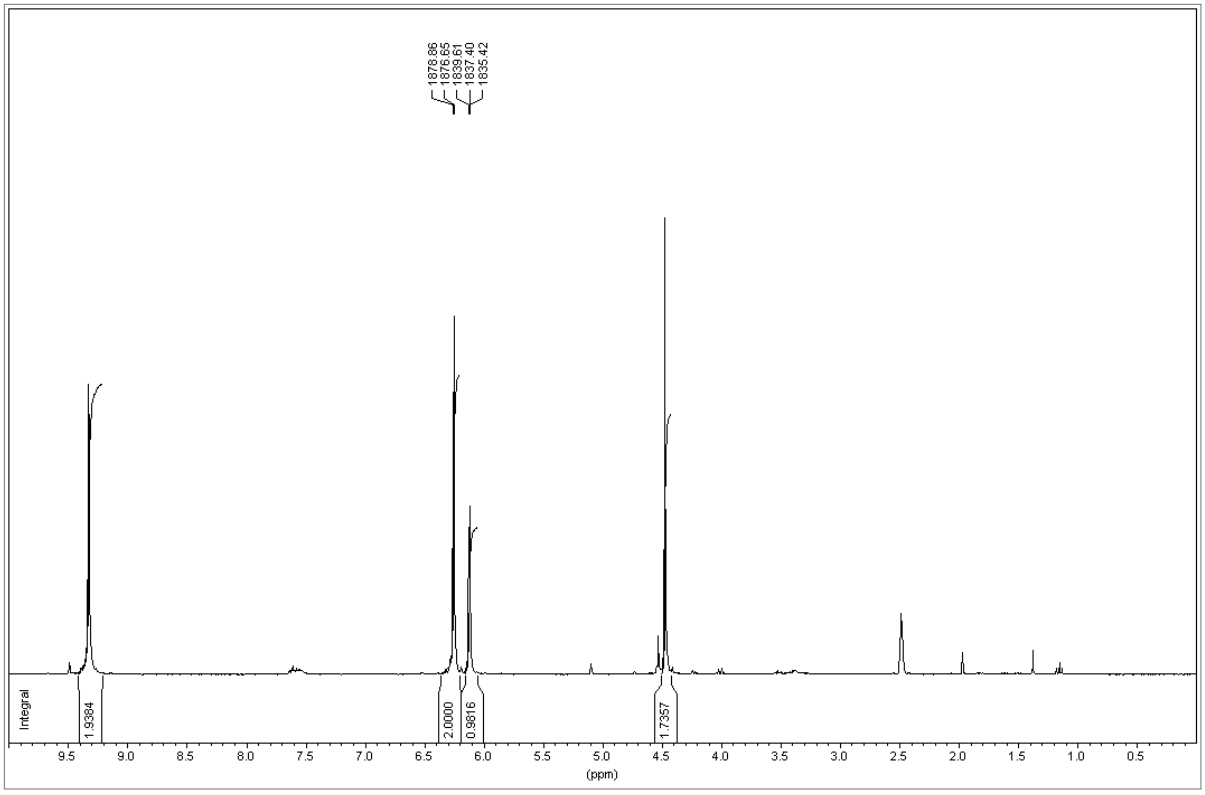


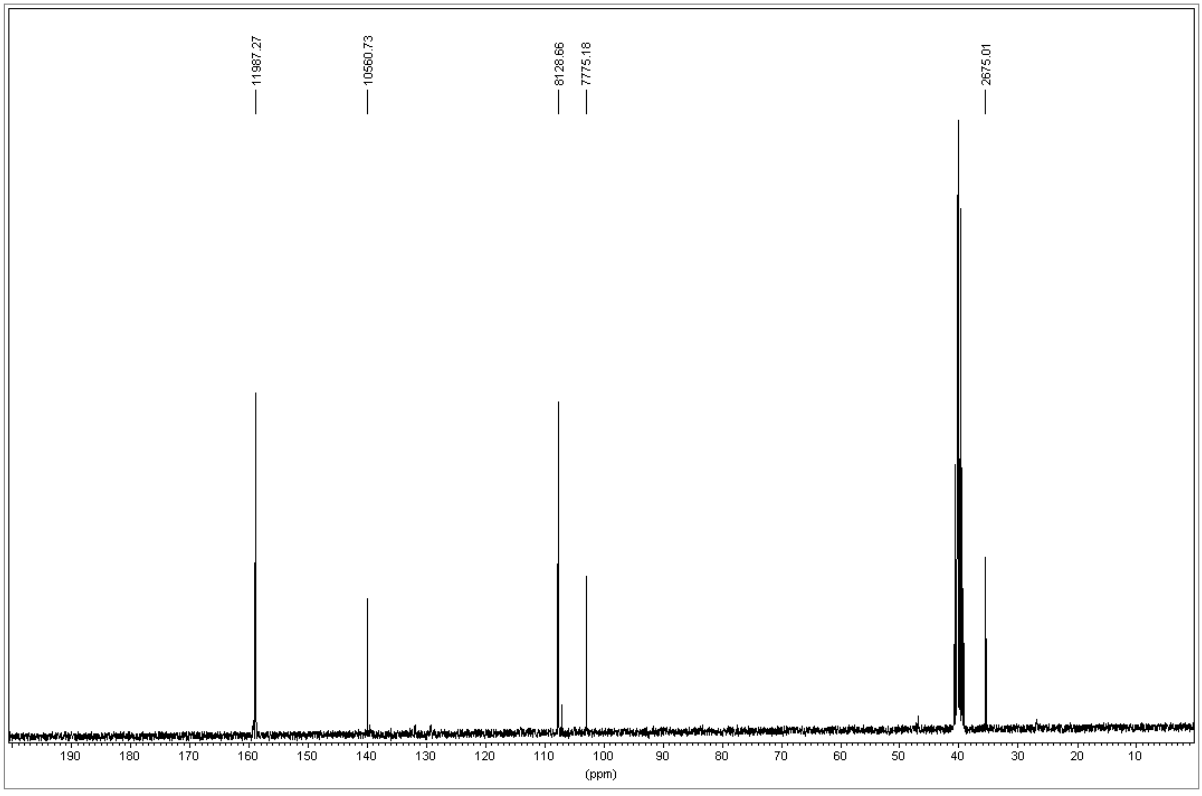

11828.32
11824.48
9835.35
9826.76
9344.11
9334.23
8592.69
8589.40
4783.48
4664.38
4657.79
3619.86
3491.43
2898.09
2393.12
2254.26
1116.98
1110.95
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)


3257.21
48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0 -2
(ppm)

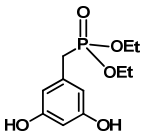
Compound 16 (^{1}H and ^{13}C, DMSO-d_6)

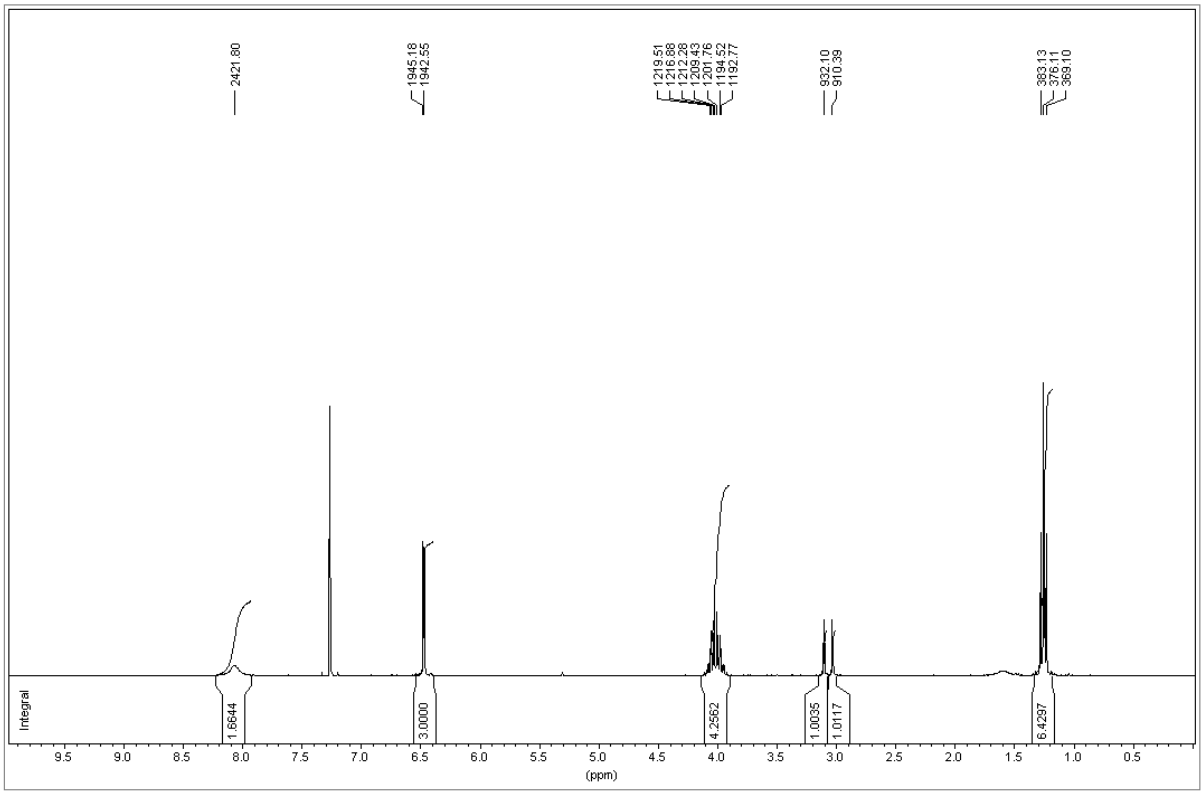


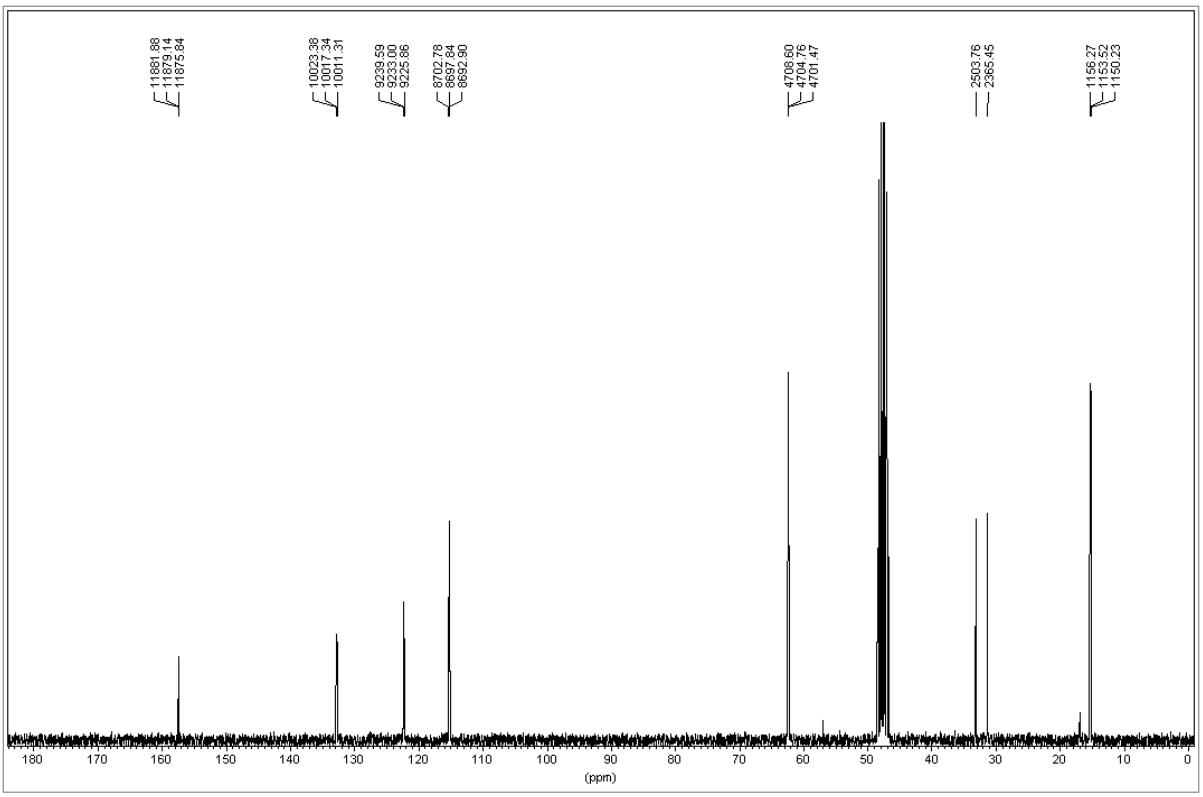


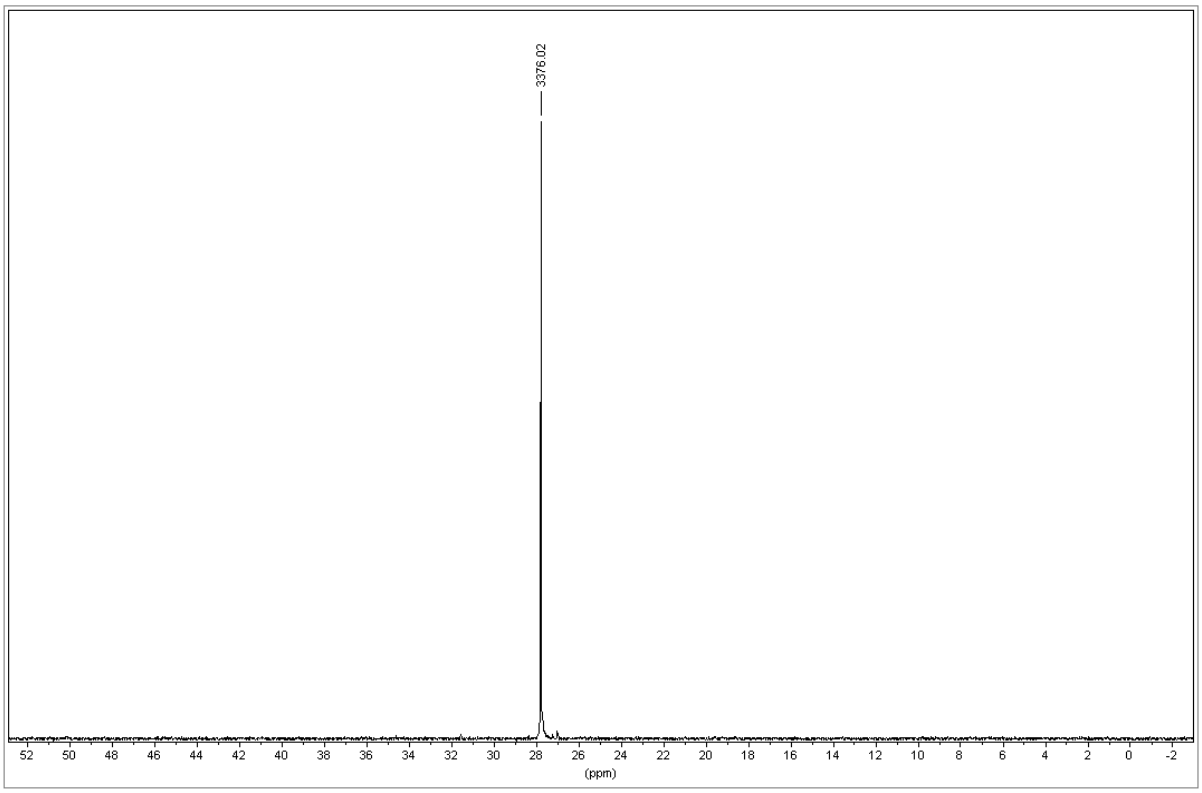


Compound 17 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$ and CD_3OD)

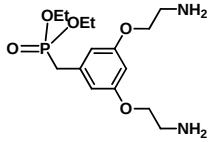


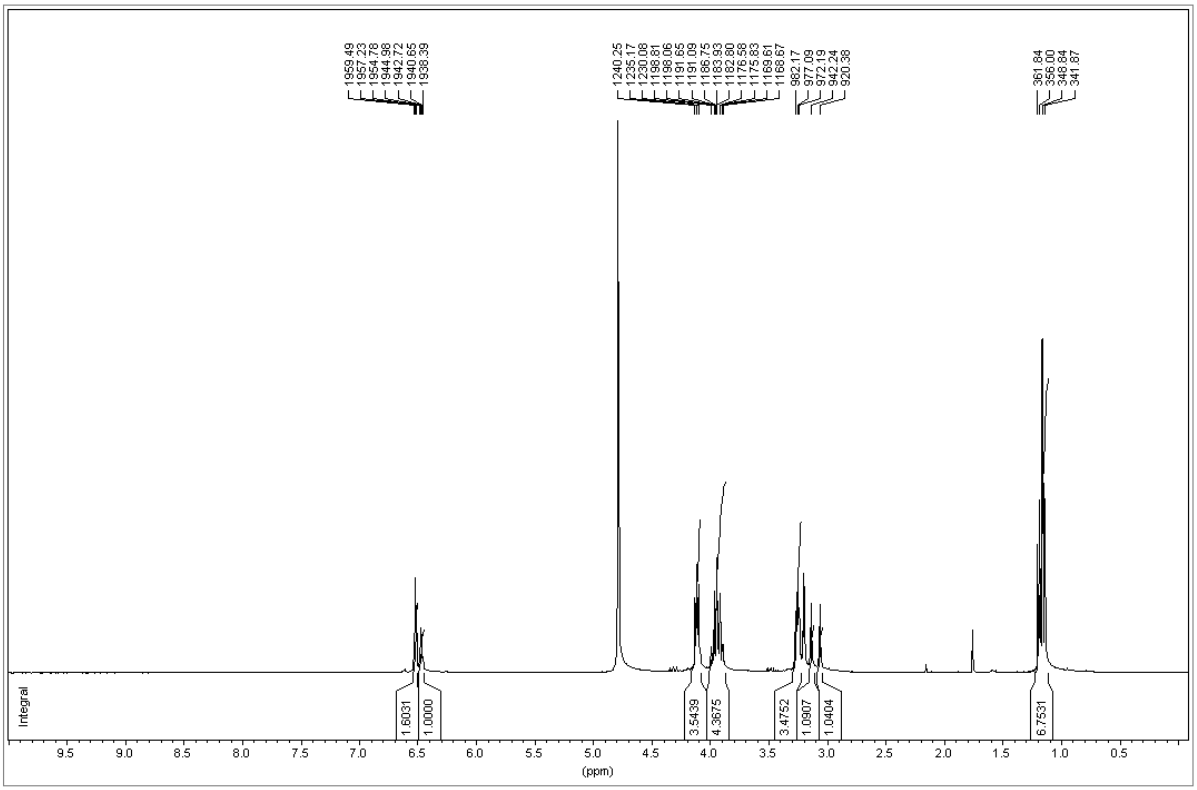


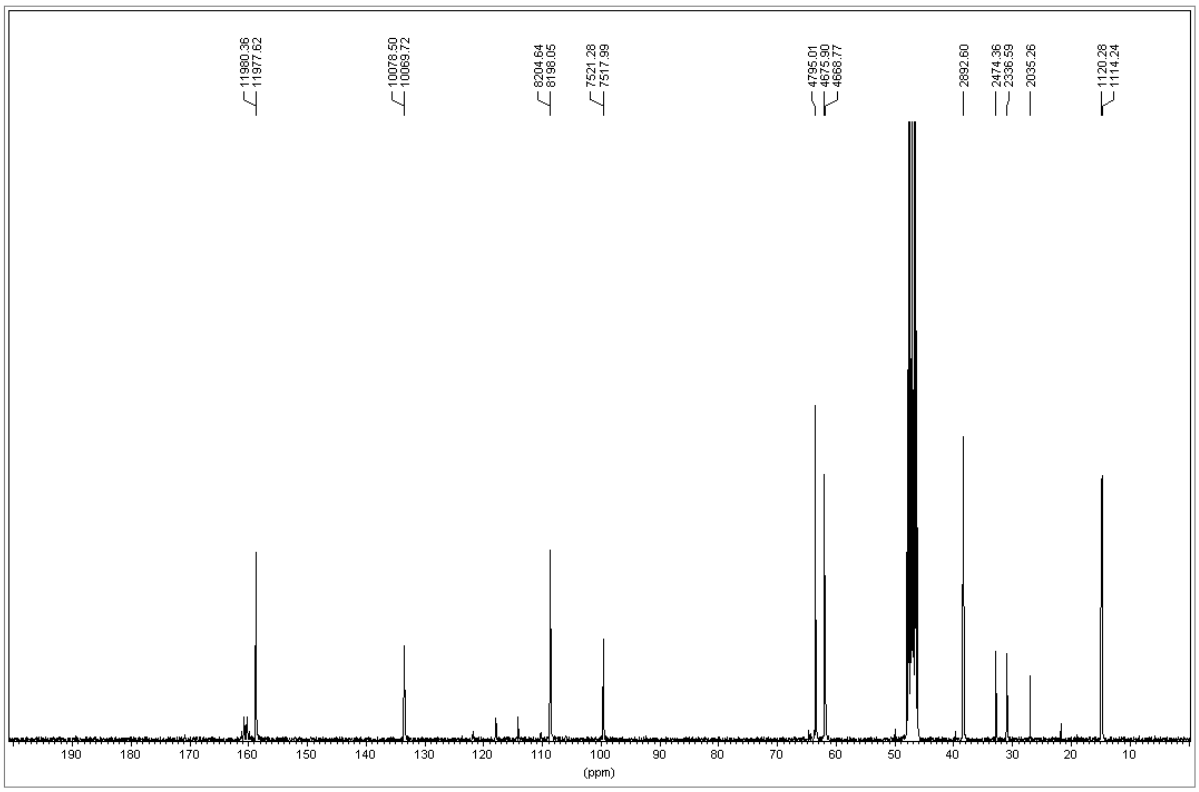


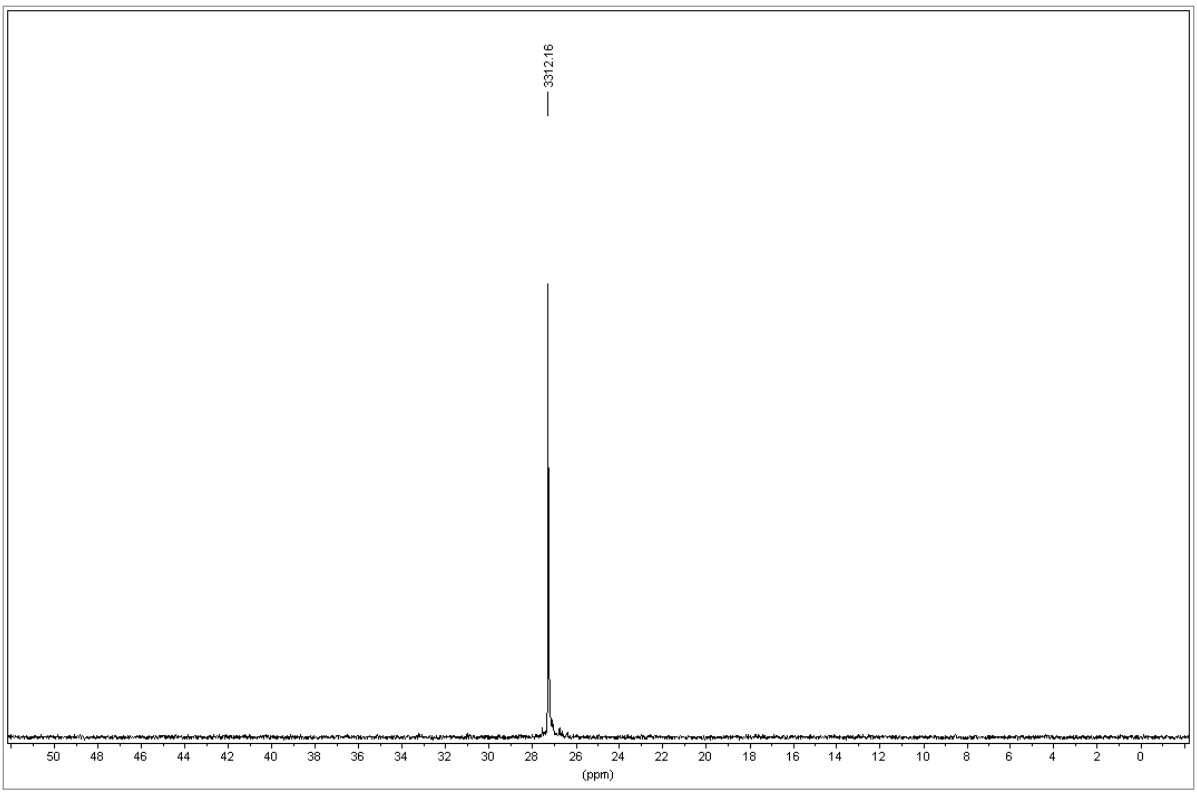


Compound 18 (^{1}H, ^{13}C and ^{31}P, CD_3OD)

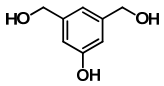


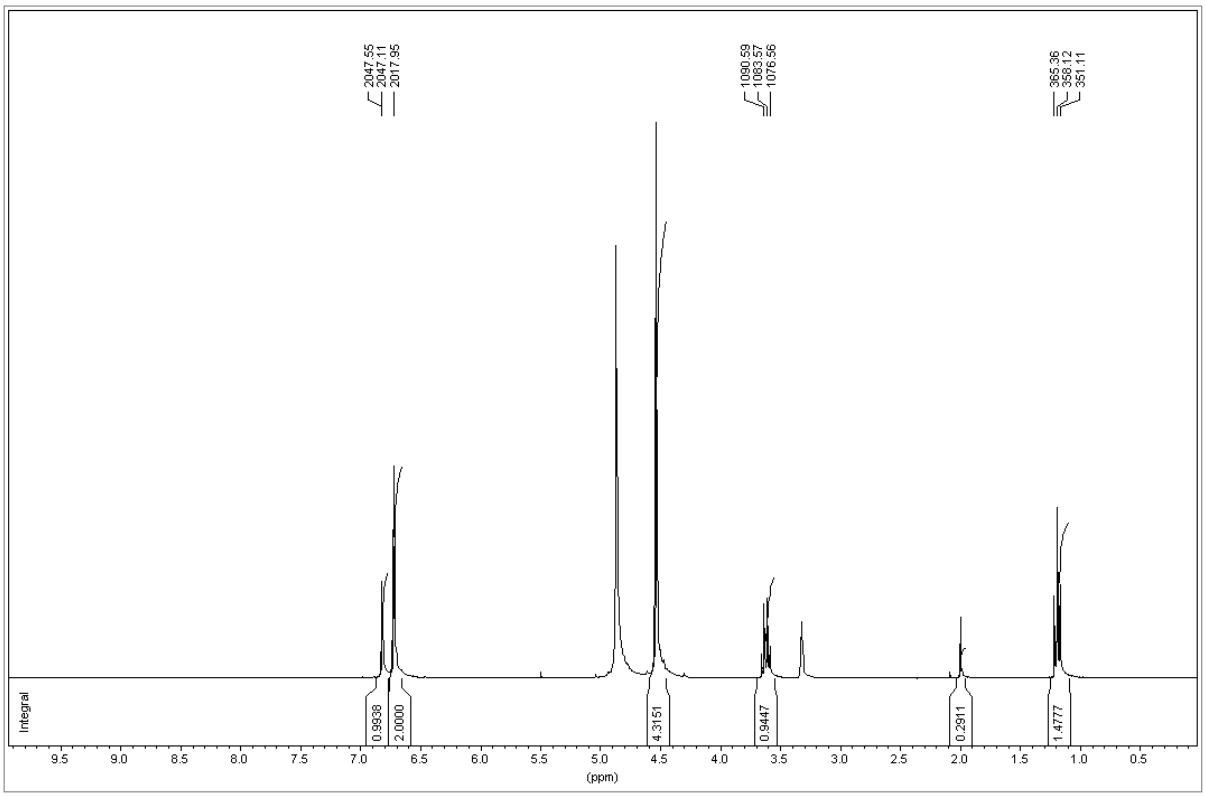


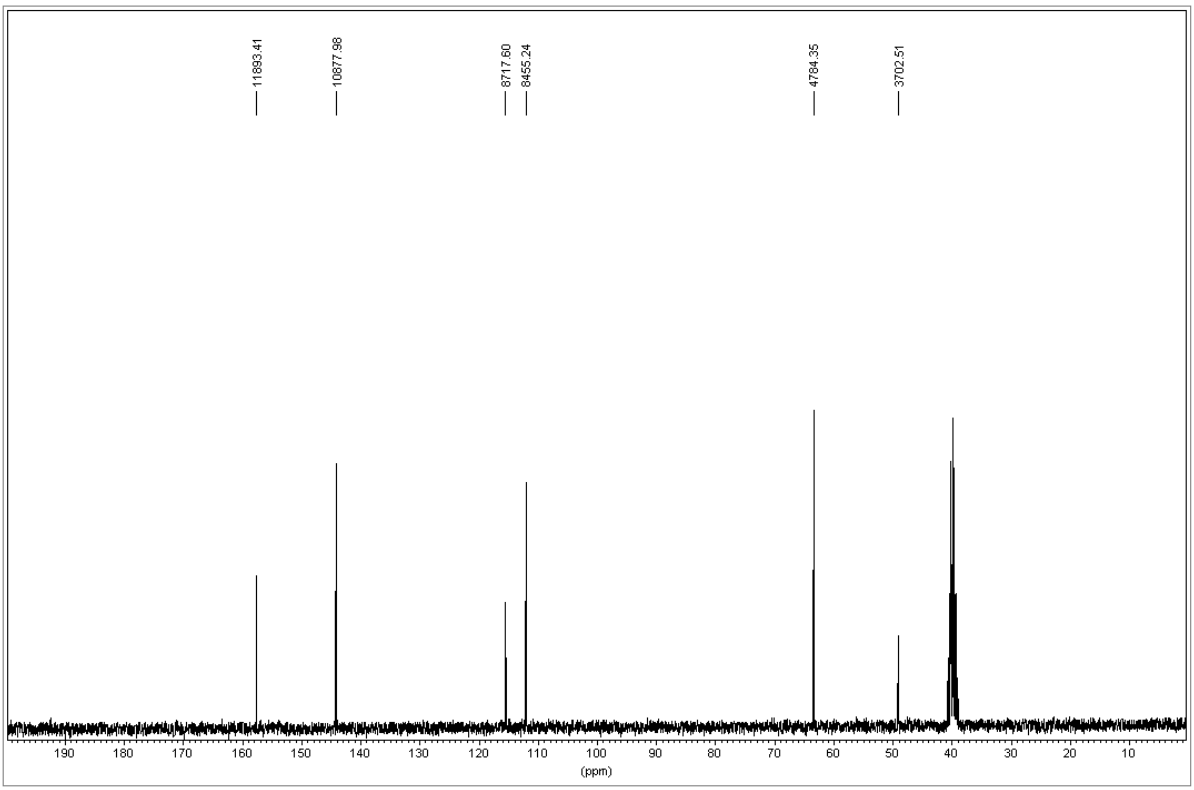

11960.36
11977.62
10078.50
10069.72
8204.64
8198.05
7521.28
7517.99
4795.01
4675.90
4668.77
2892.60
2474.36
2336.59
2035.26
1120.28
1114.24
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)


3312.16
50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0
(ppm)

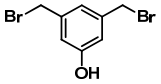
Compound 19 (^{1}H and ^{13}C, CD_3OD)

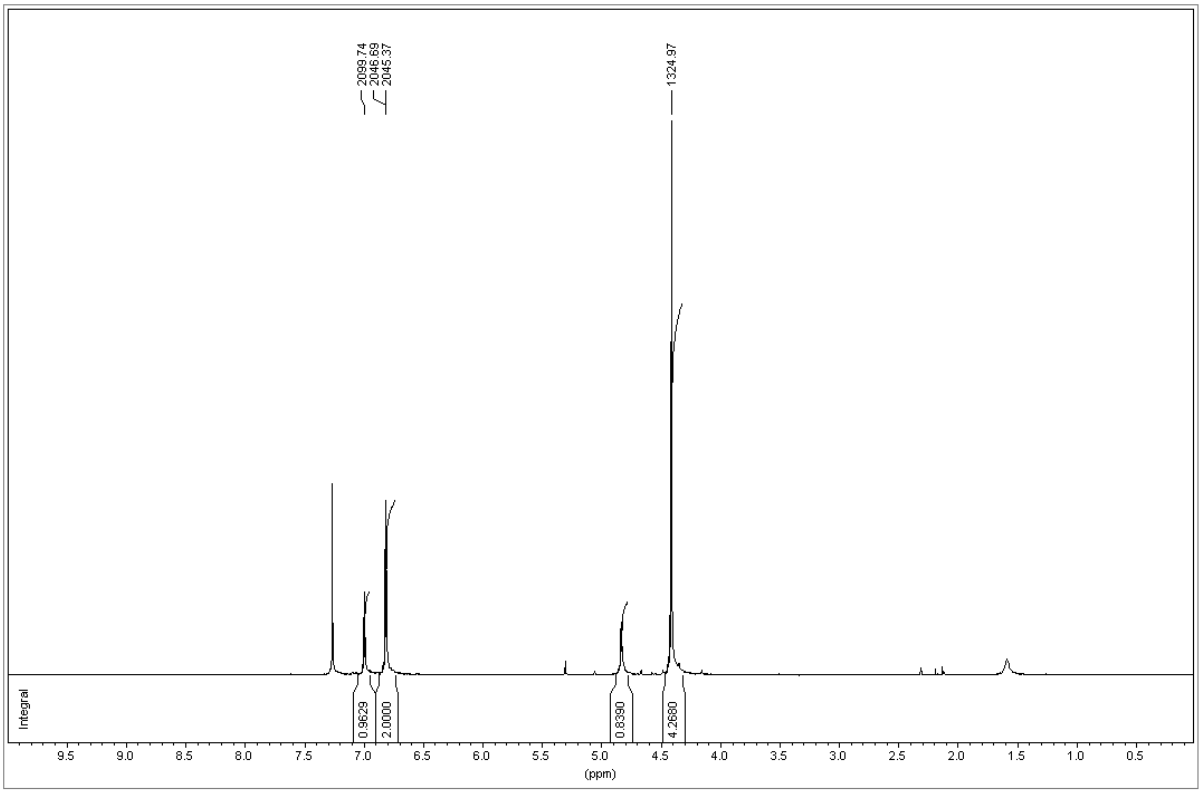


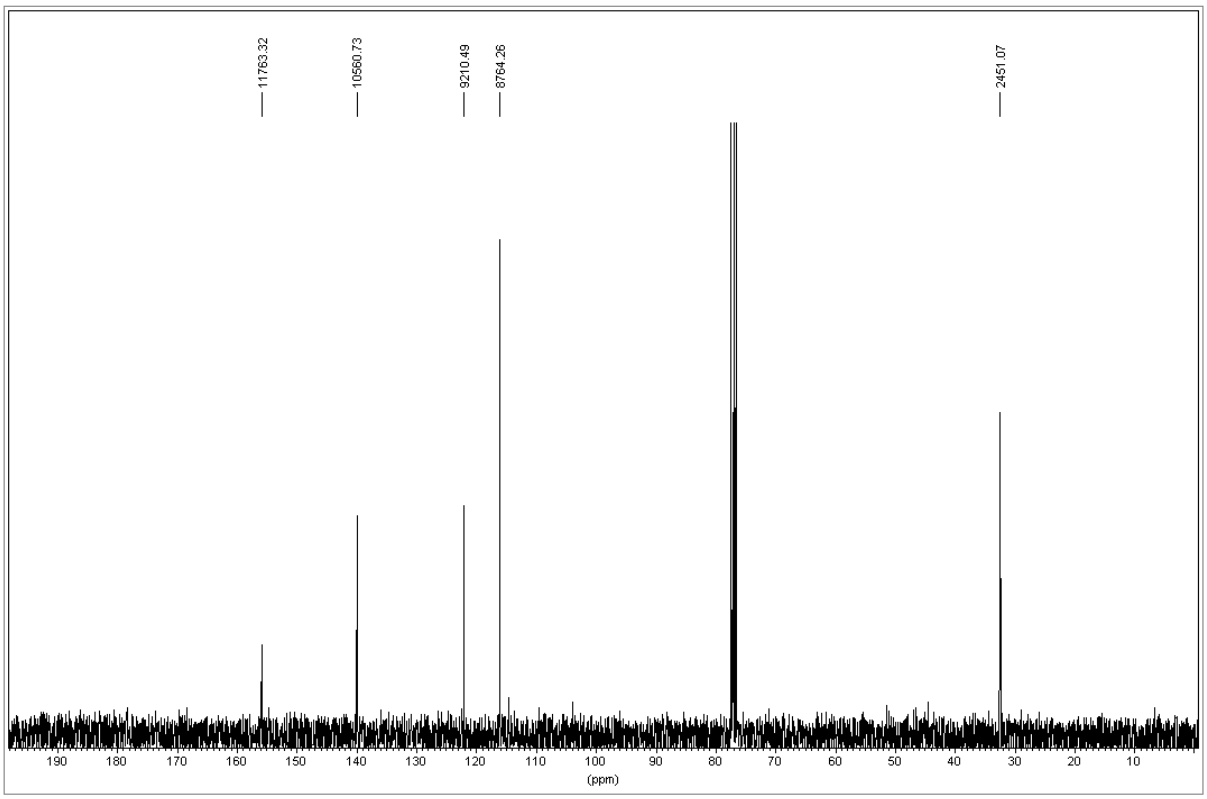




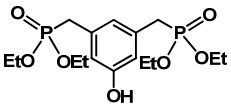
Compound 20 (^{1}H and ^{13}C, $CDCl_3$)

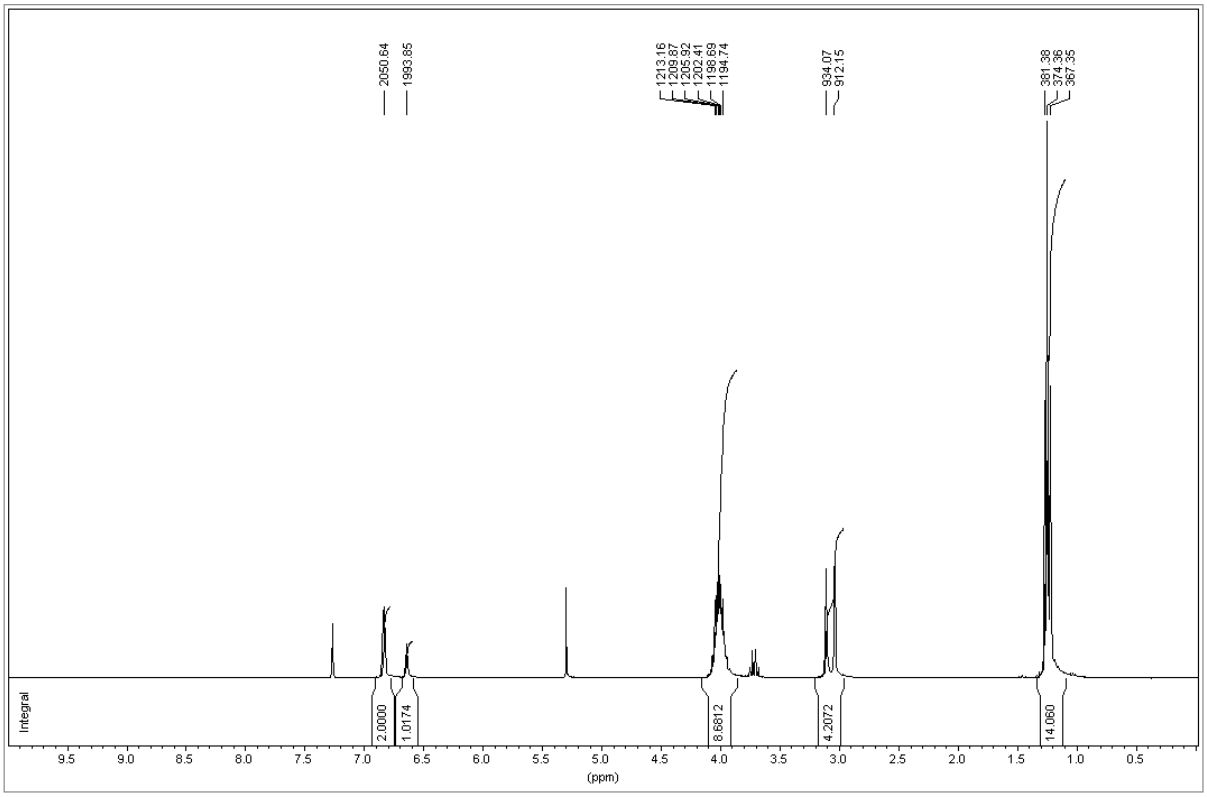


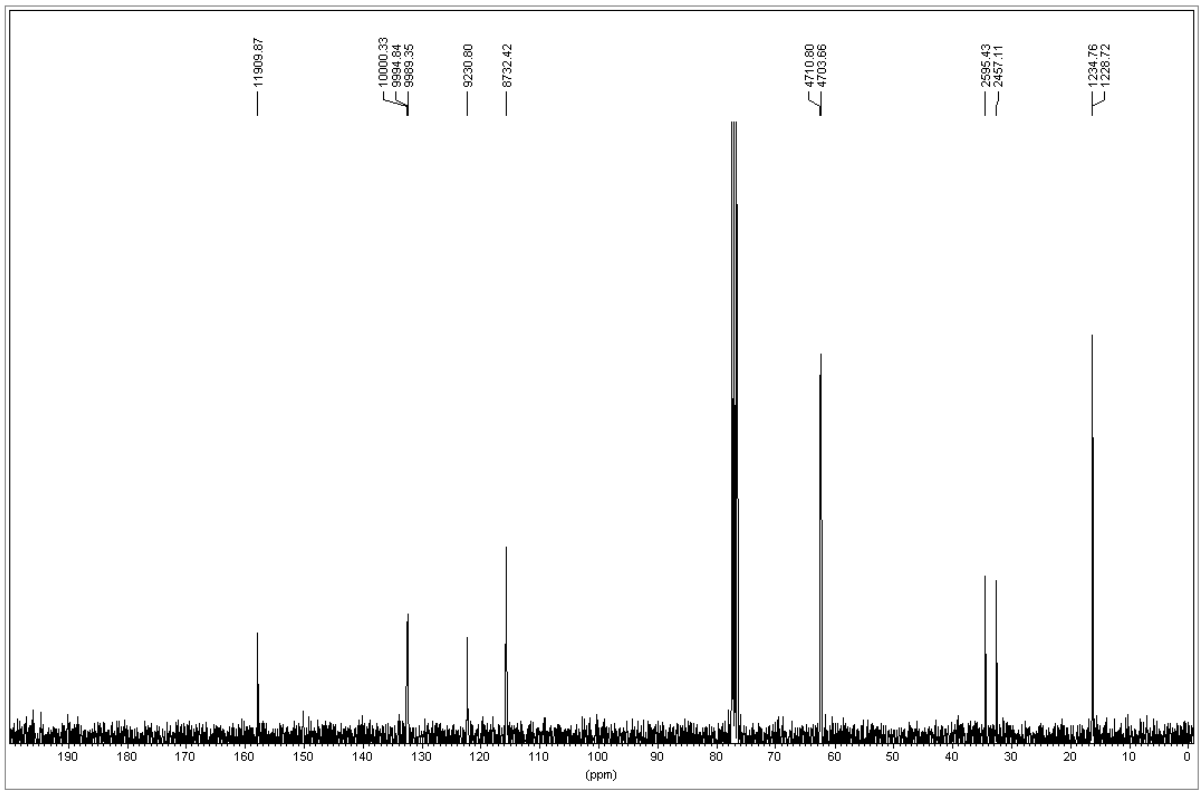


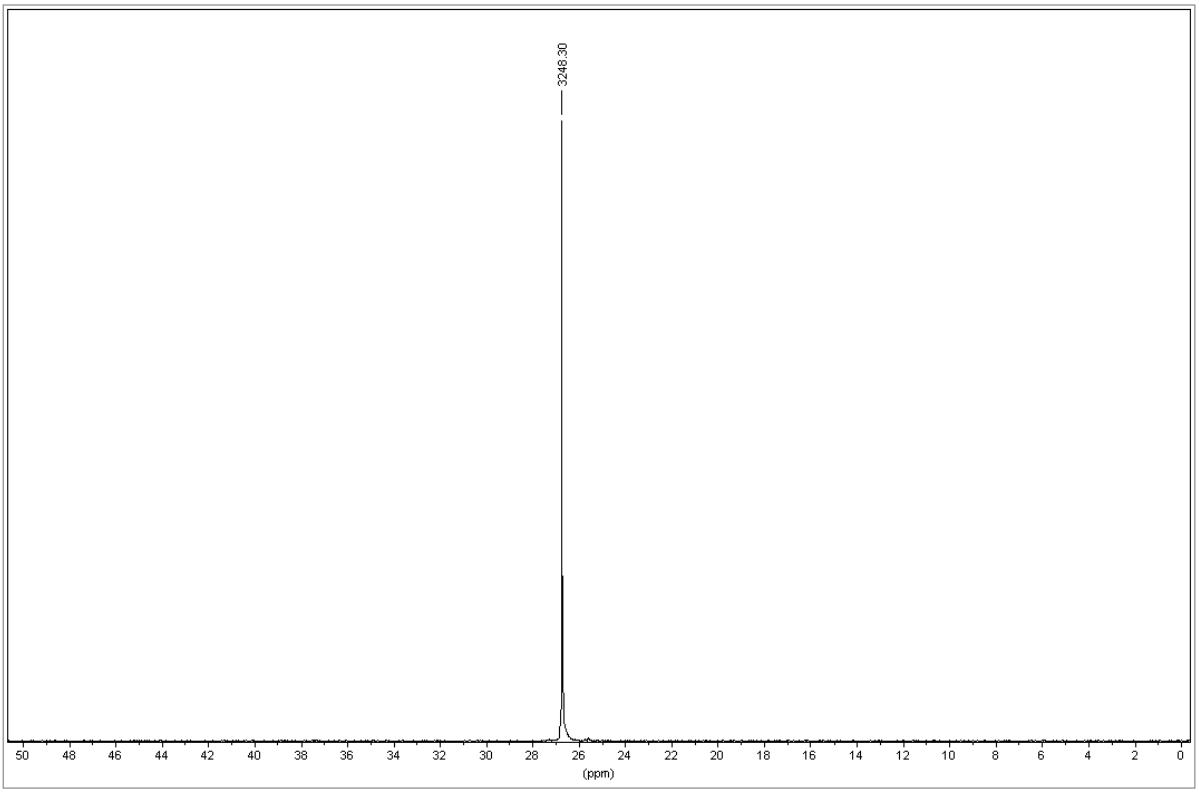


Compound 21 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

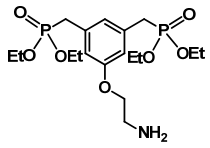


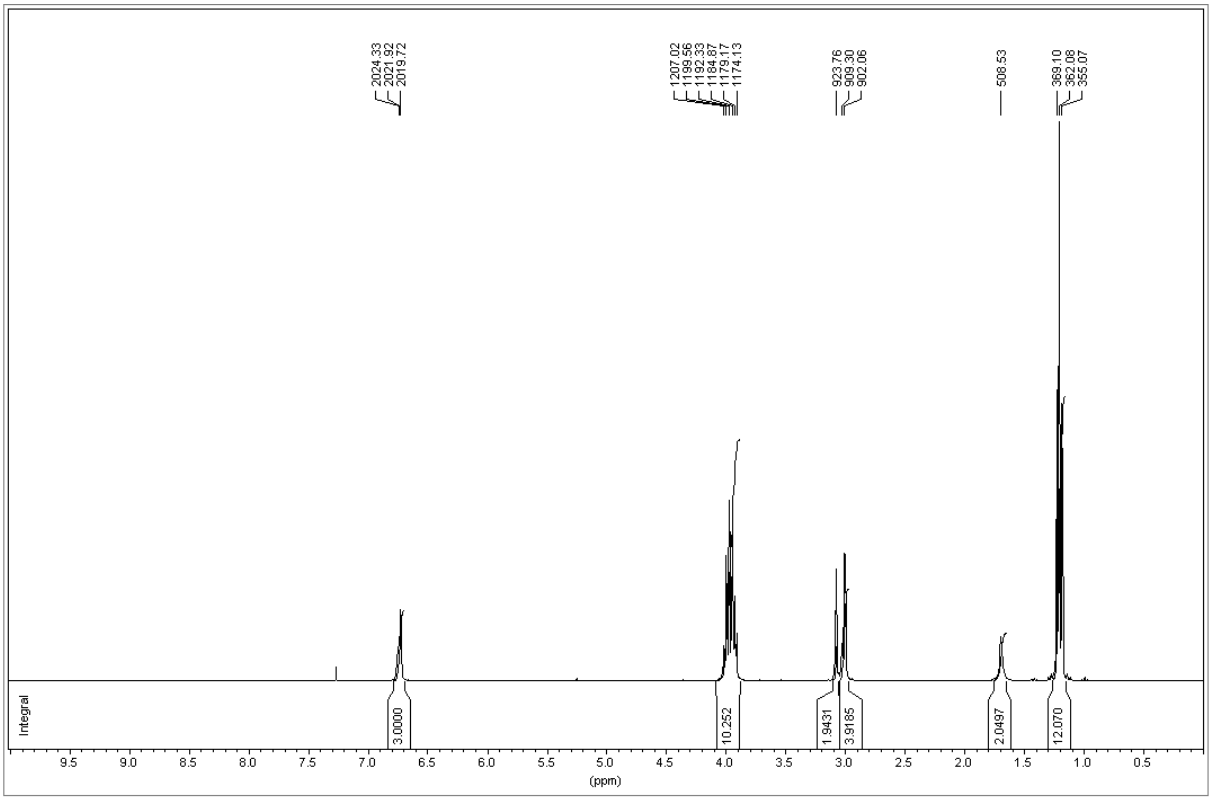


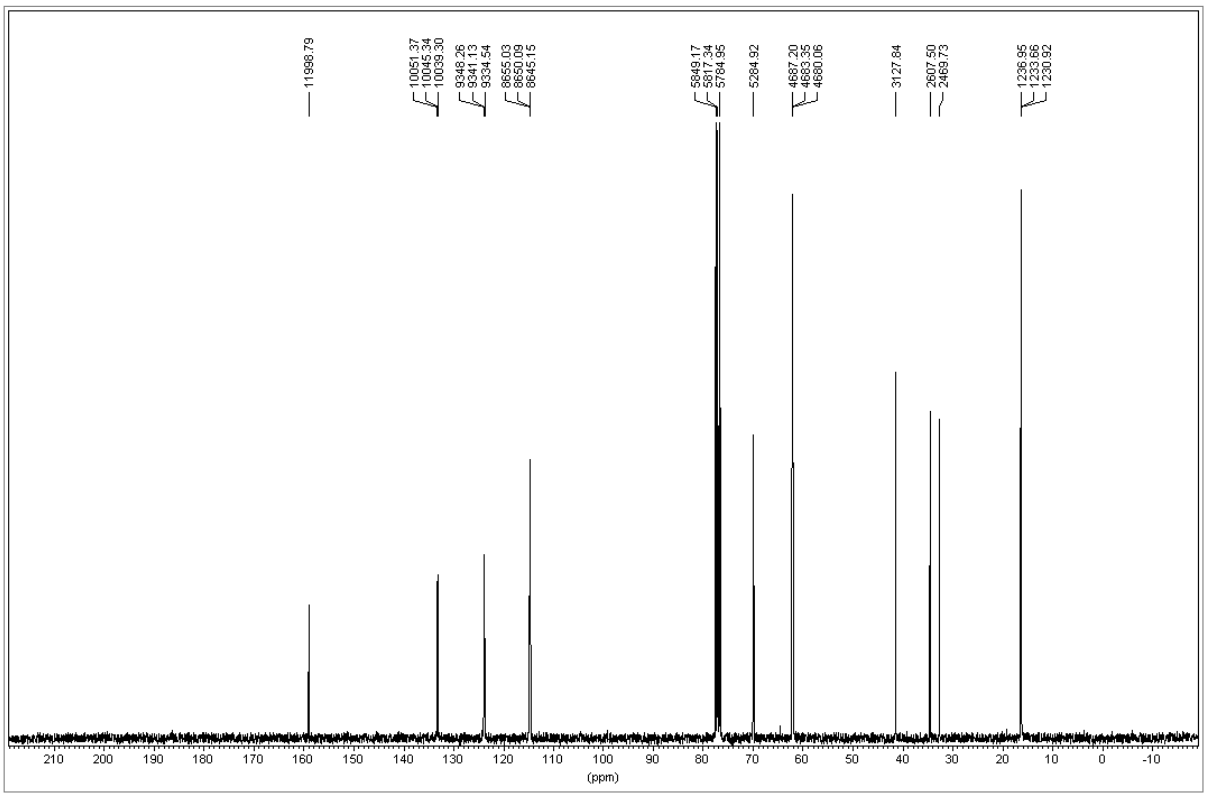


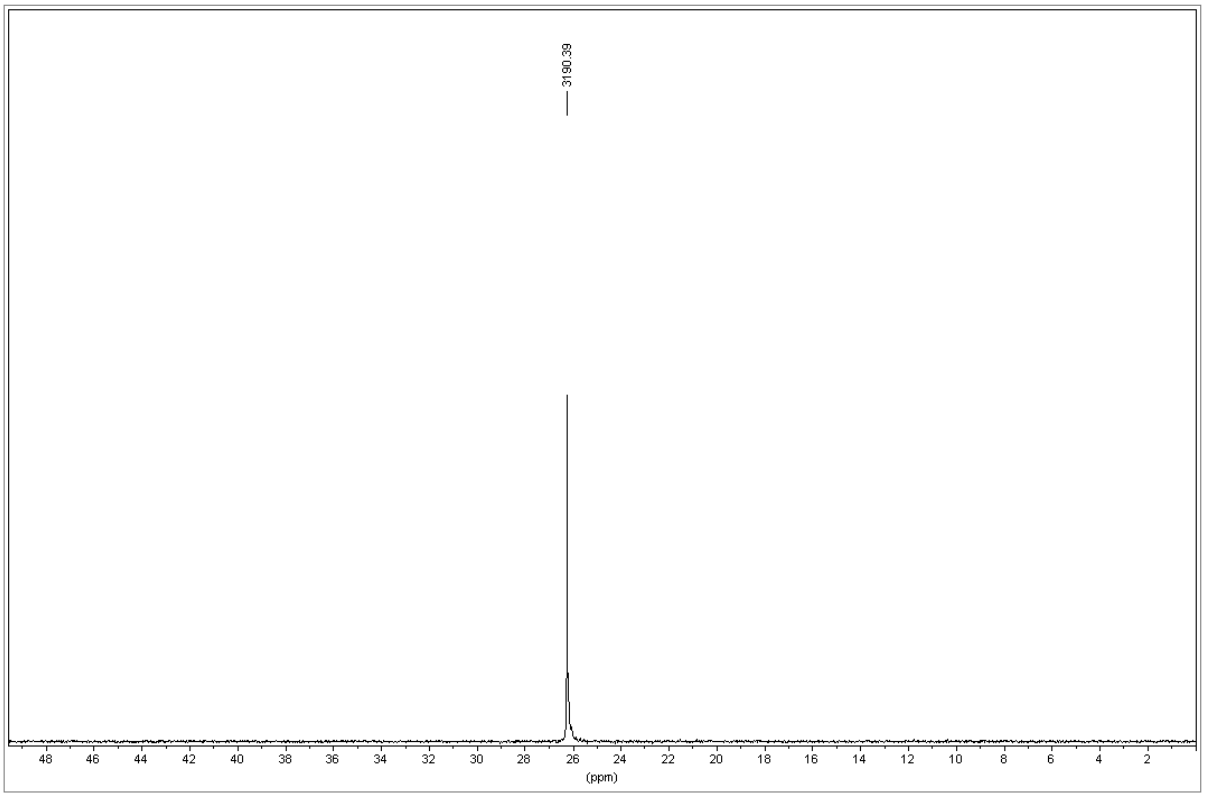


Compound 22 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

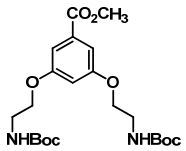


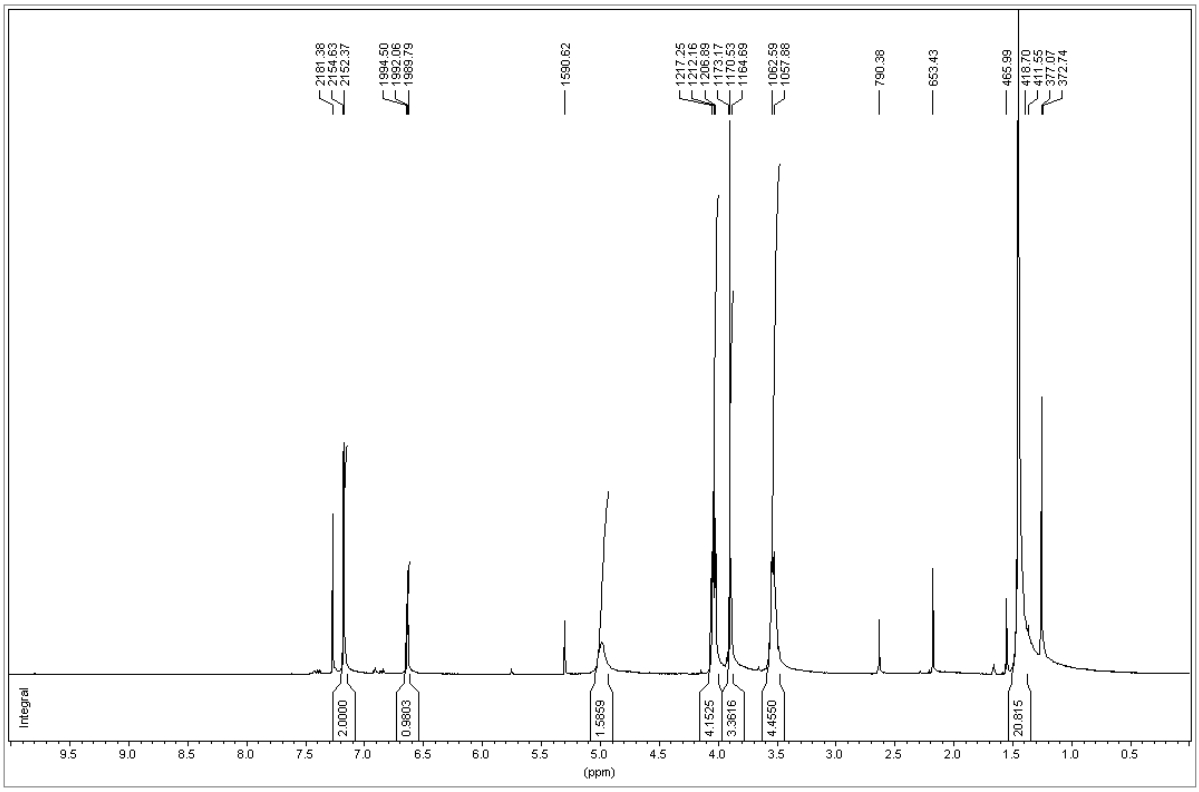


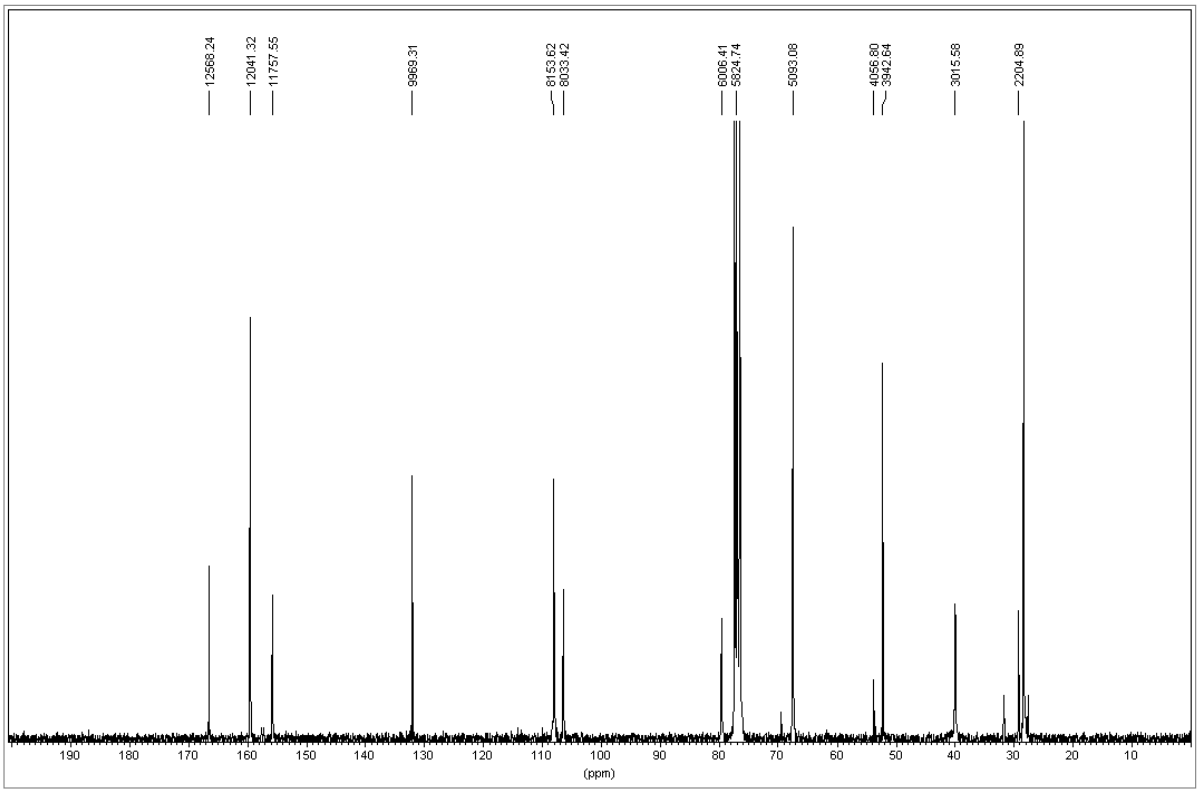

11998.79
10051.37
10045.34
10039.30
9348.26
9341.13
9334.54
8655.03
8650.09
8645.15
5849.17
5817.34
5764.95
5284.92
4687.20
4663.35
4660.06
3127.84
2607.50
2468.73
1236.95
1233.66
1230.92
(ppm)


3190.39
(ppm)

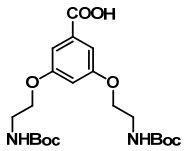
Compound 23 (^{1}H and ^{13}C, $CDCl_3$)

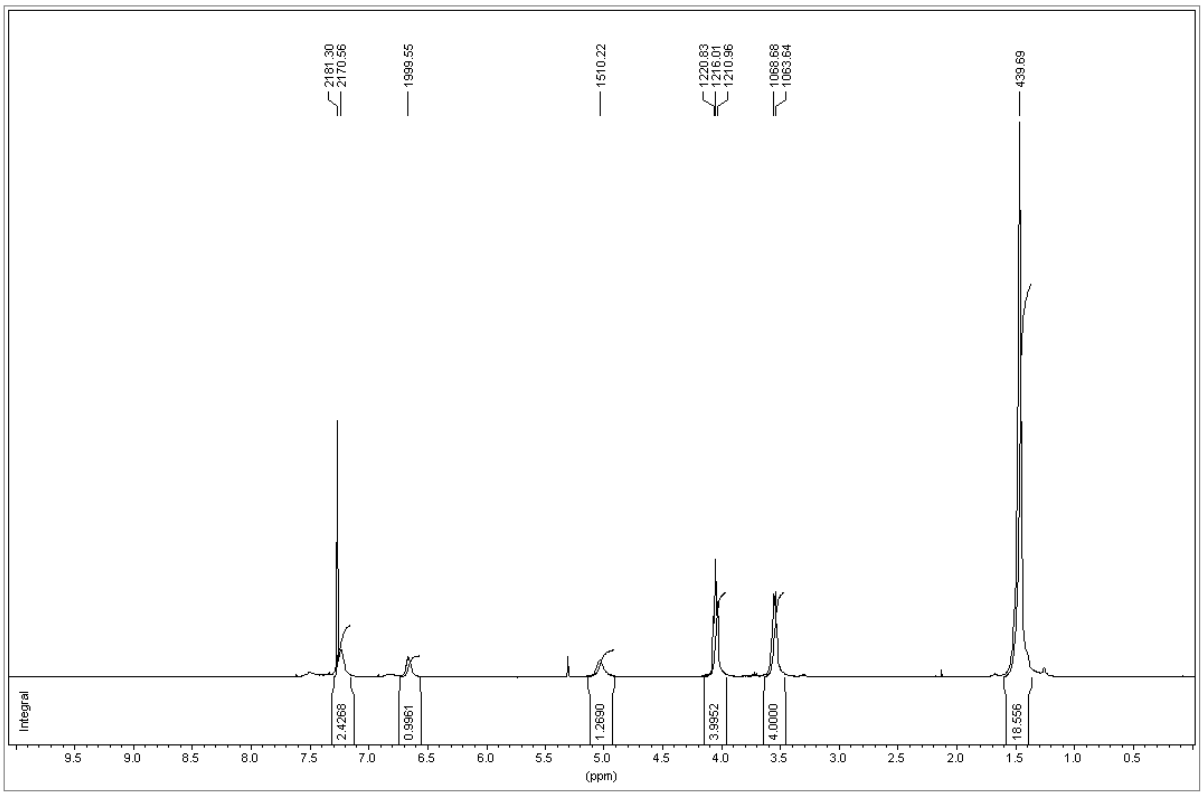


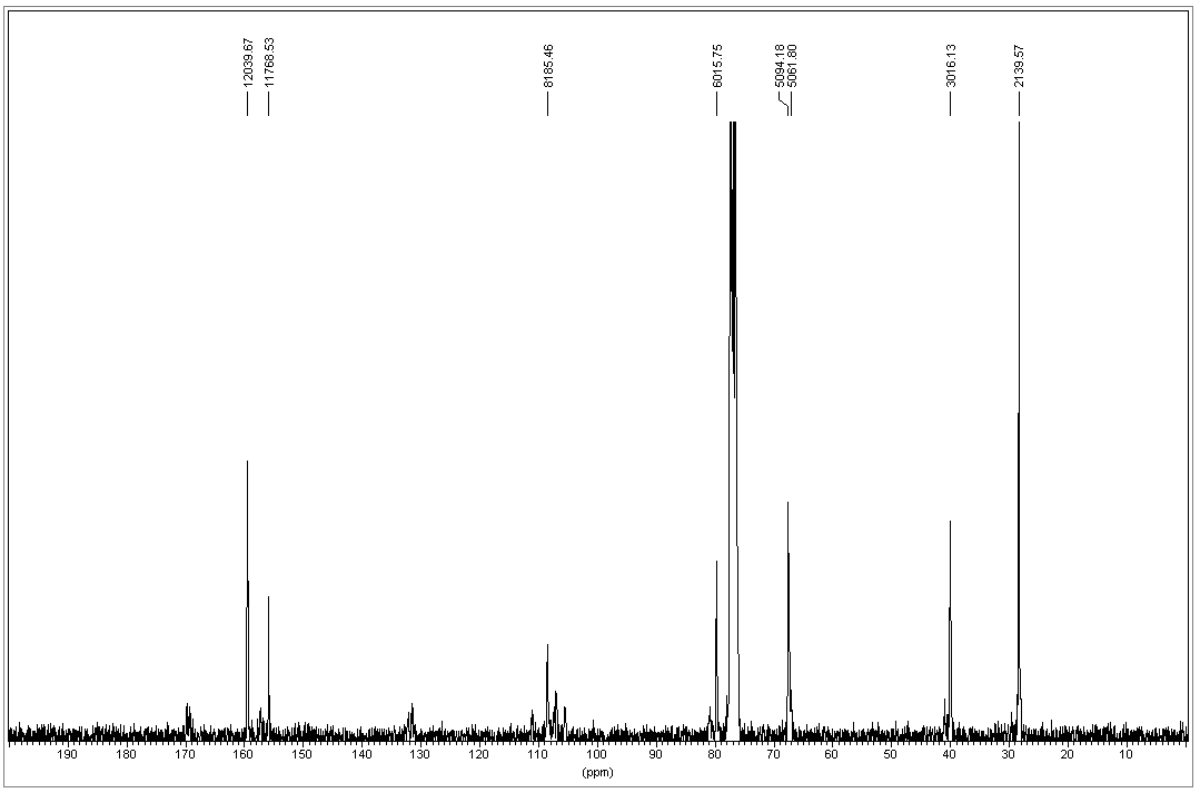




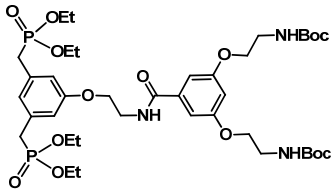
Compound 24 (^{1}H and ^{13}C, $CDCl_3$)

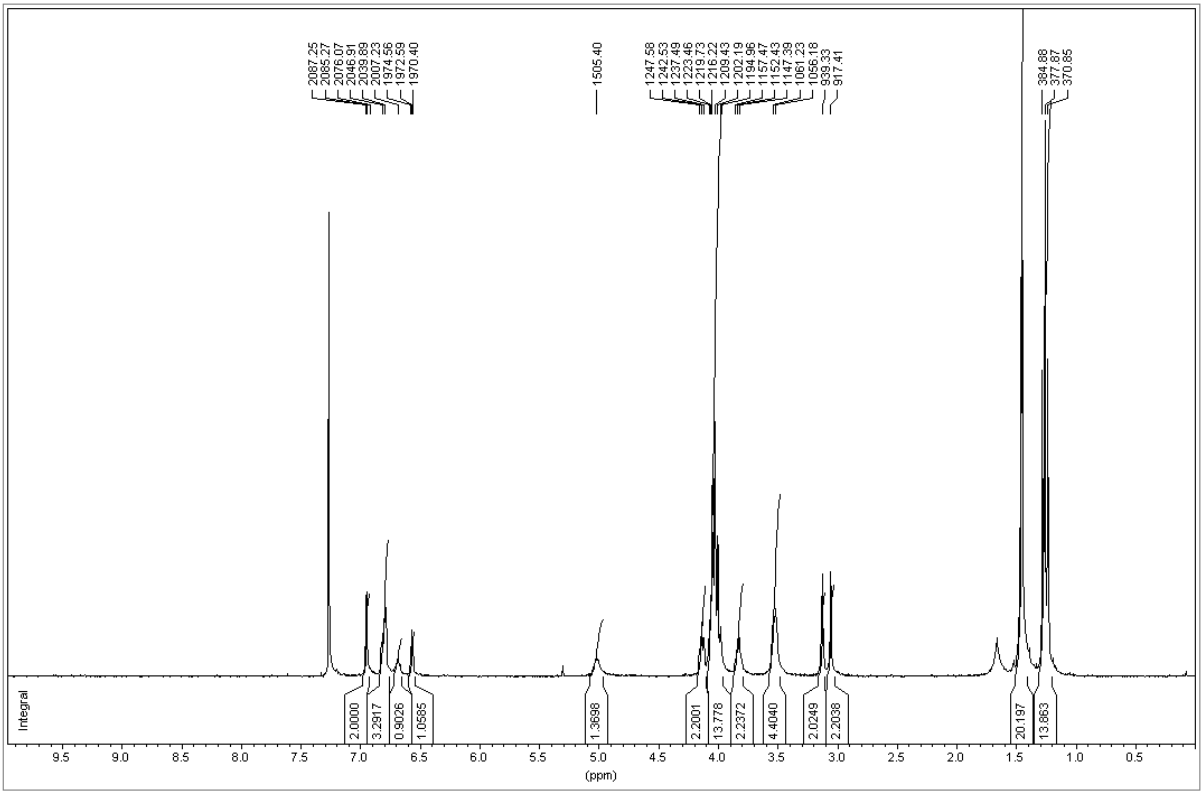


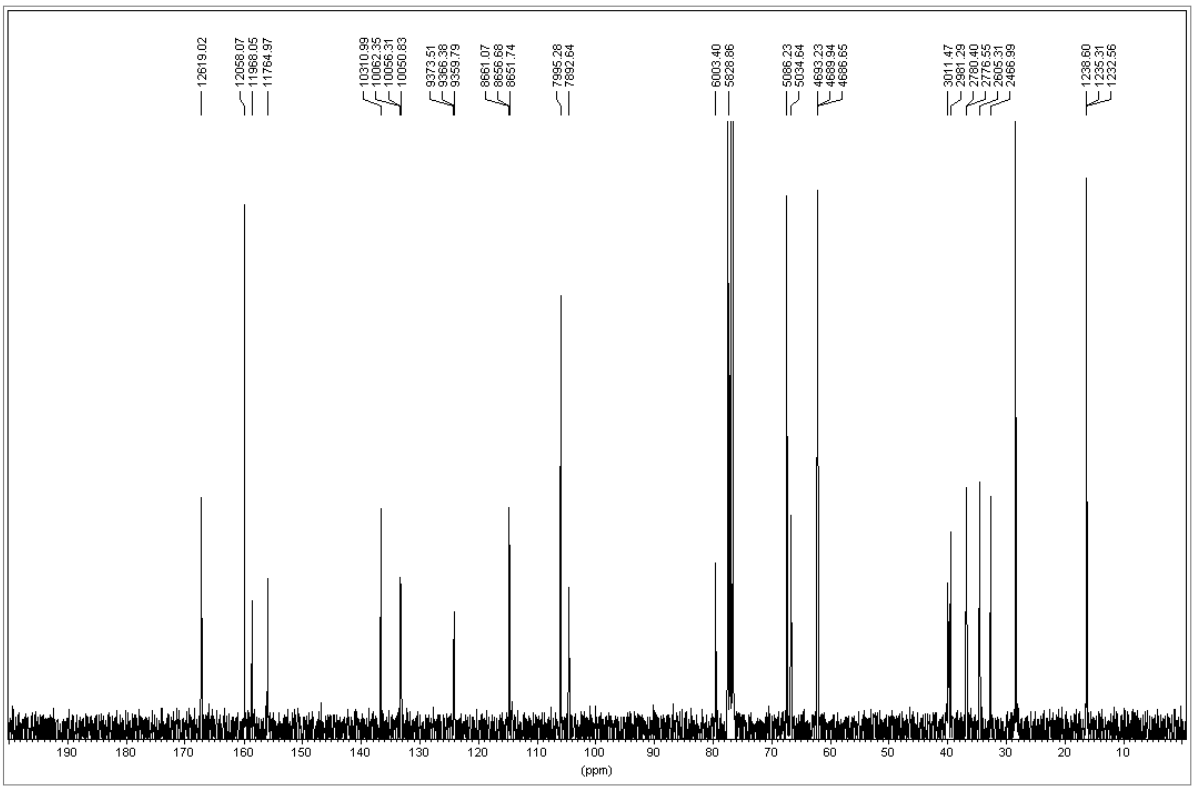


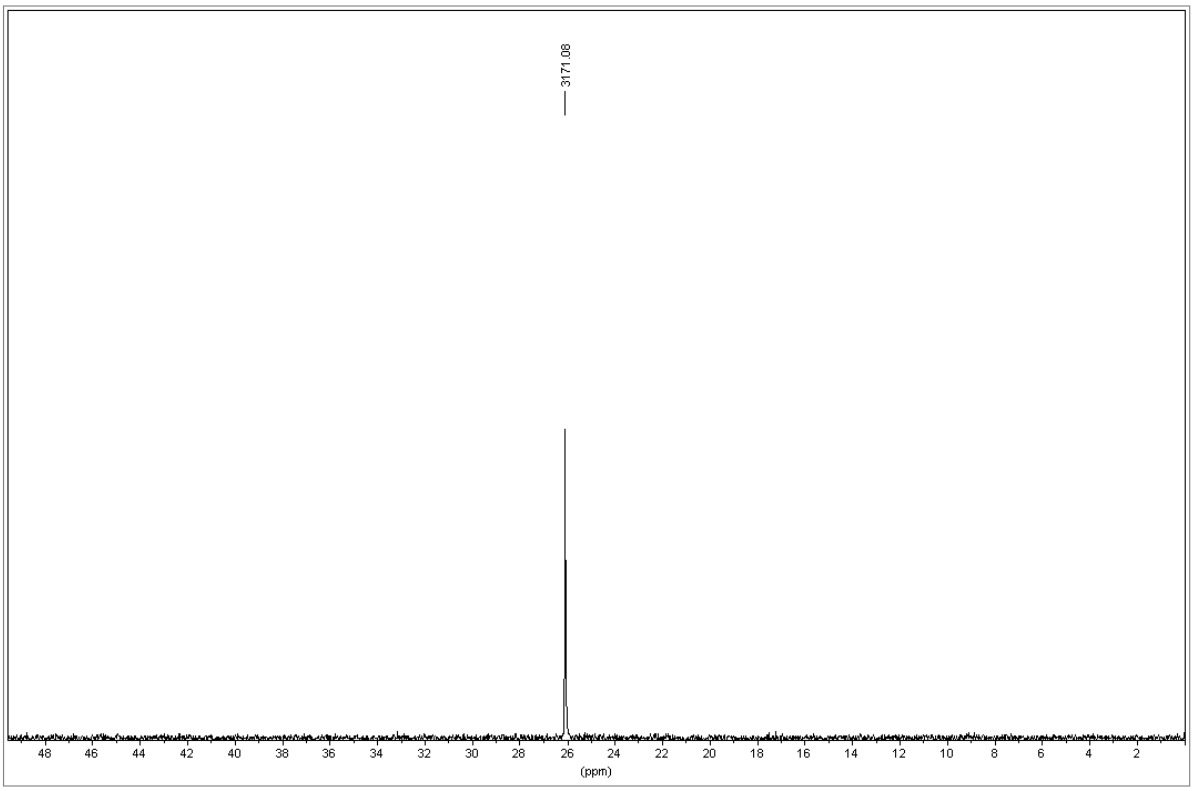


Compound 25 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

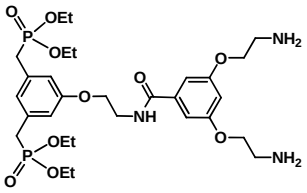


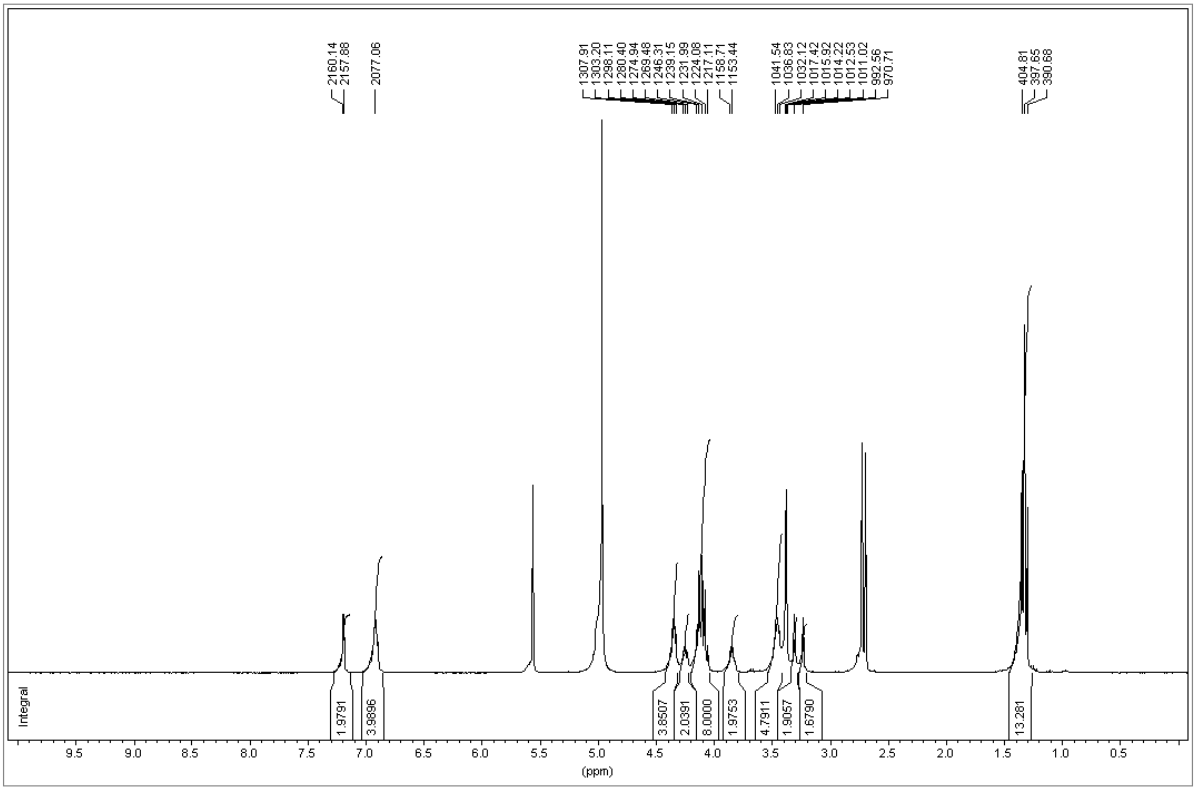


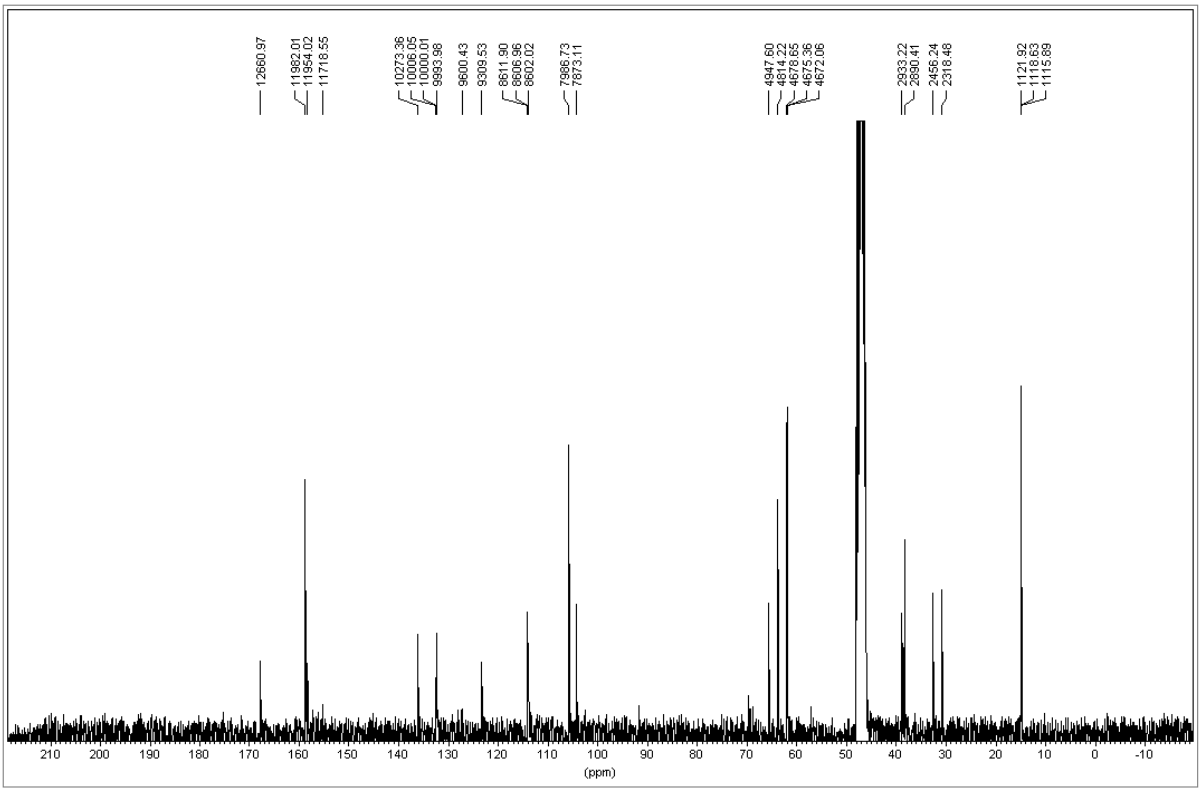

12619.02
12058.07
11968.05
11764.97
10310.99
10062.35
10056.31
10050.83
9373.51
9366.38
9359.79
8861.07
8856.68
8851.74
7995.28
7892.64
6903.40
6828.86
5086.23
5034.64
4693.23
4689.94
4686.85
3011.47
2981.29
2780.40
2776.55
2605.31
2466.99
1238.60
1235.31
1232.56
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

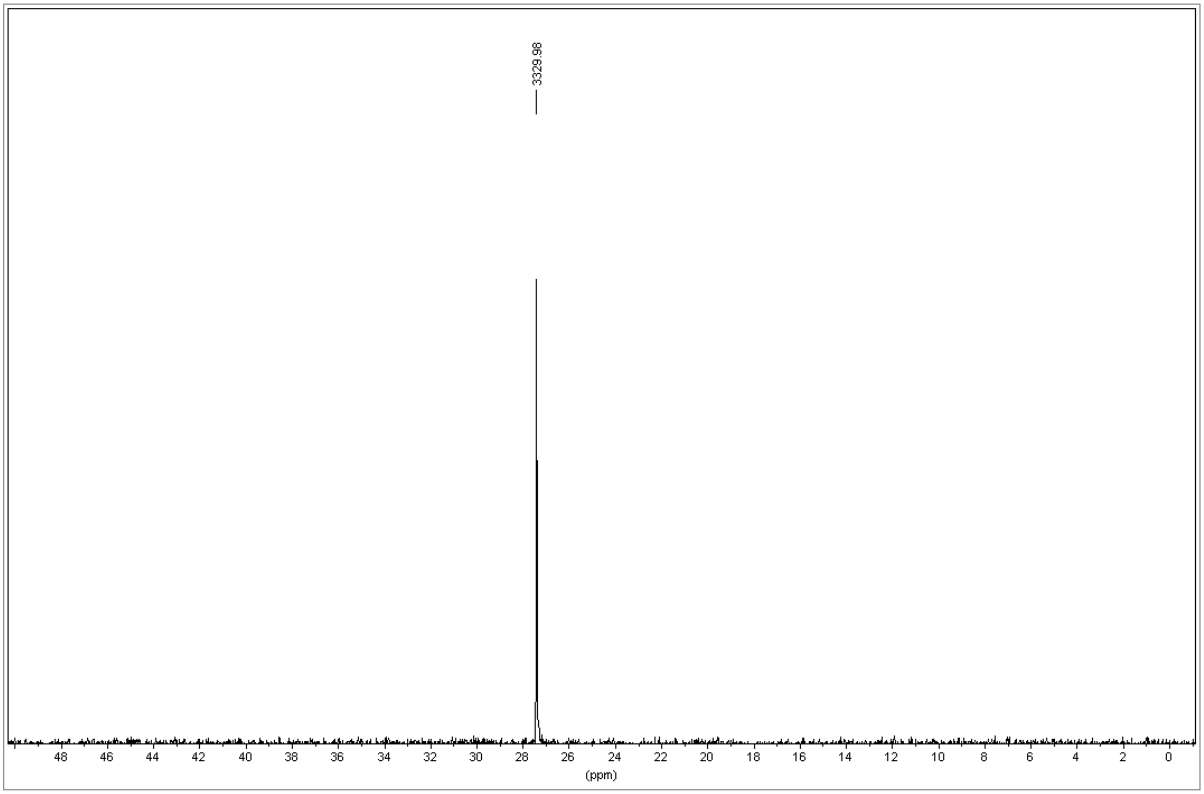

3171.08
48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2
(ppm)

Compound 26 (^{1}H, ^{13}C and ^{31}P, CD_3OD)

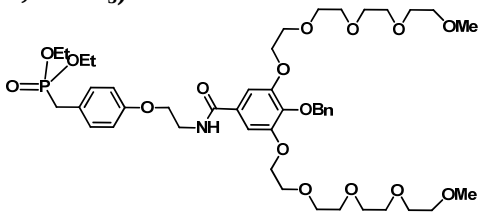


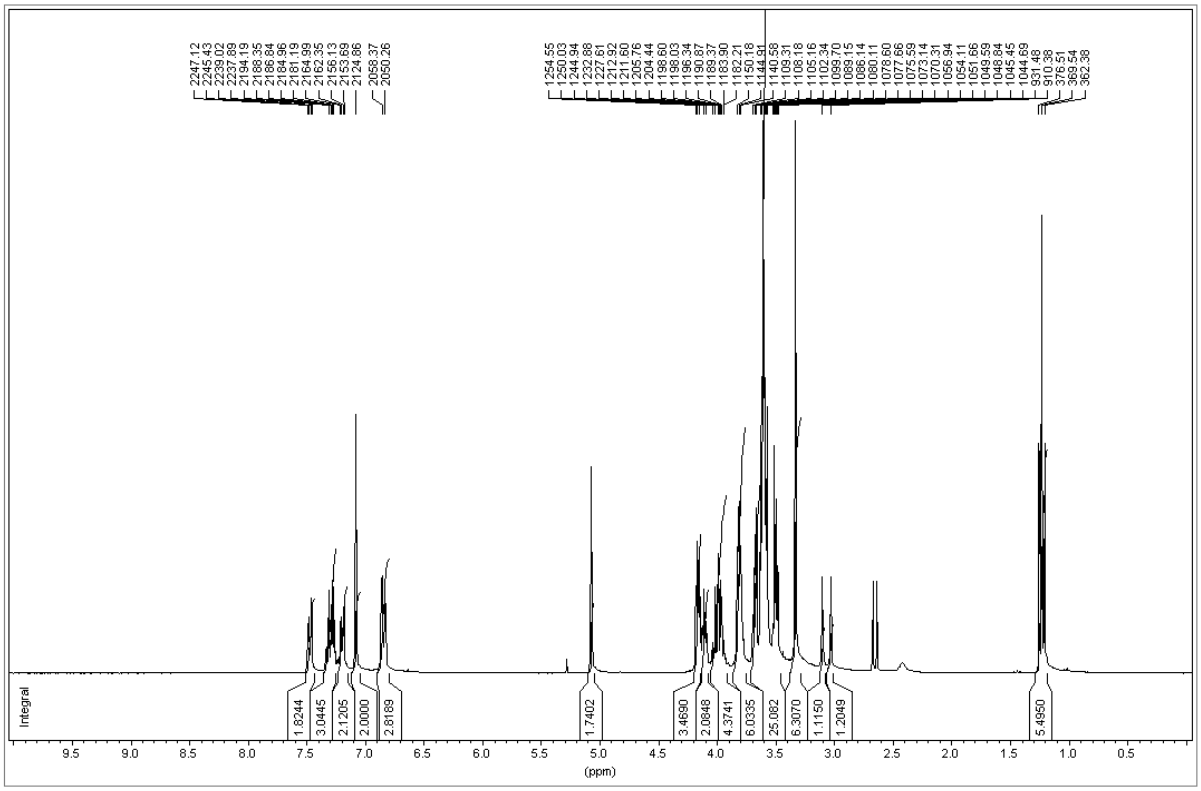


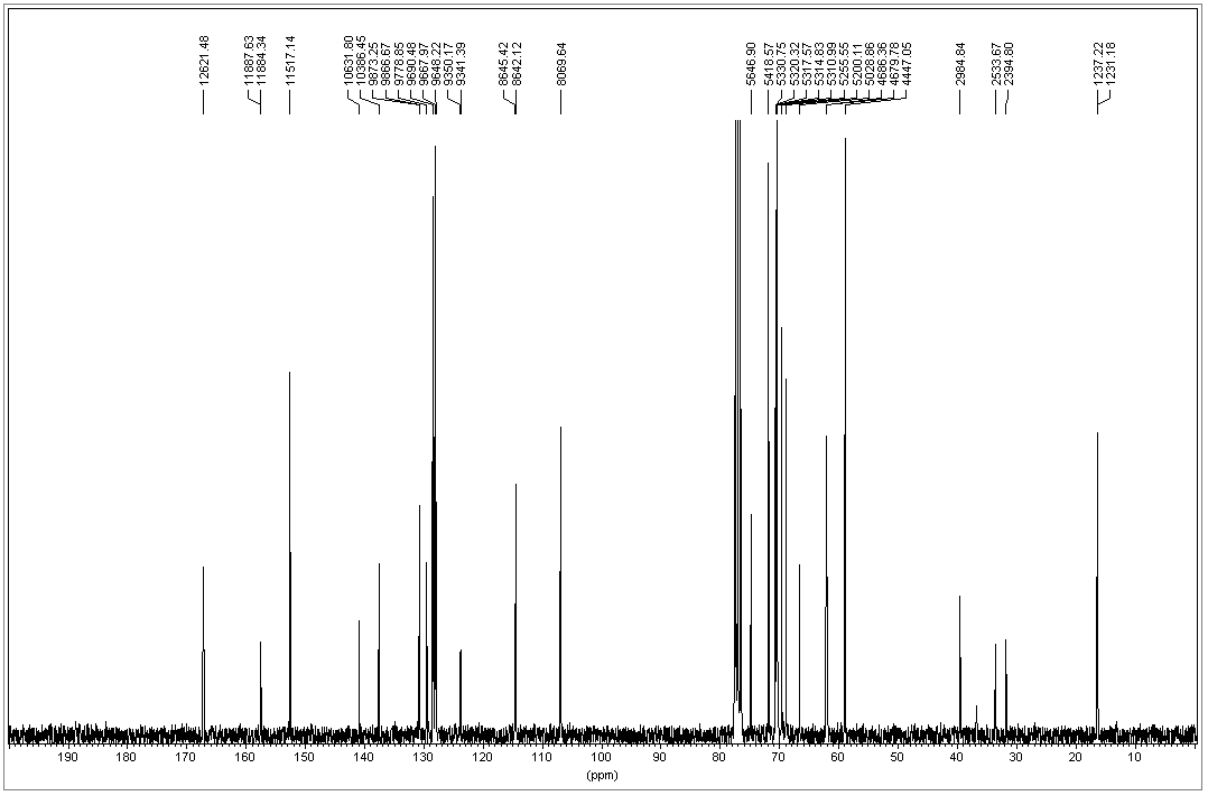


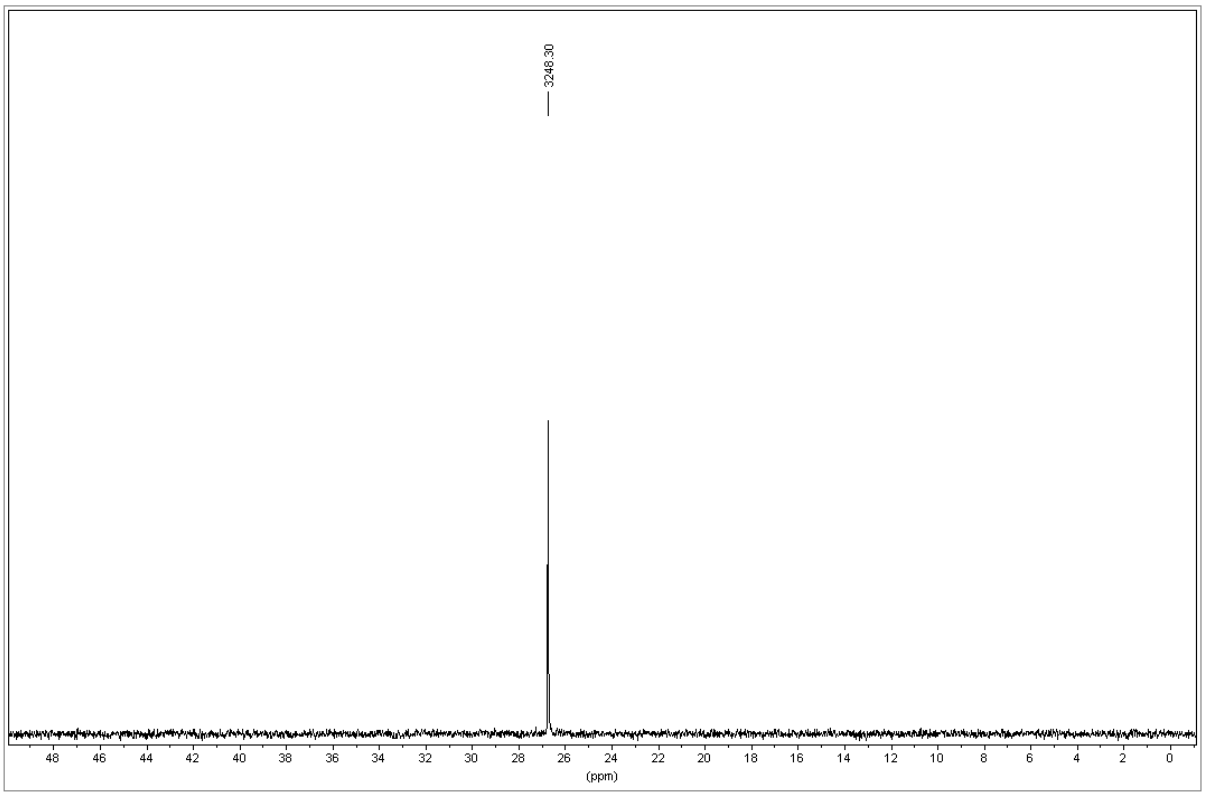


Compound 27 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

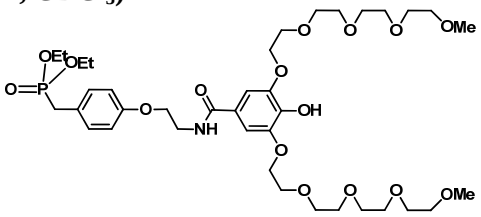


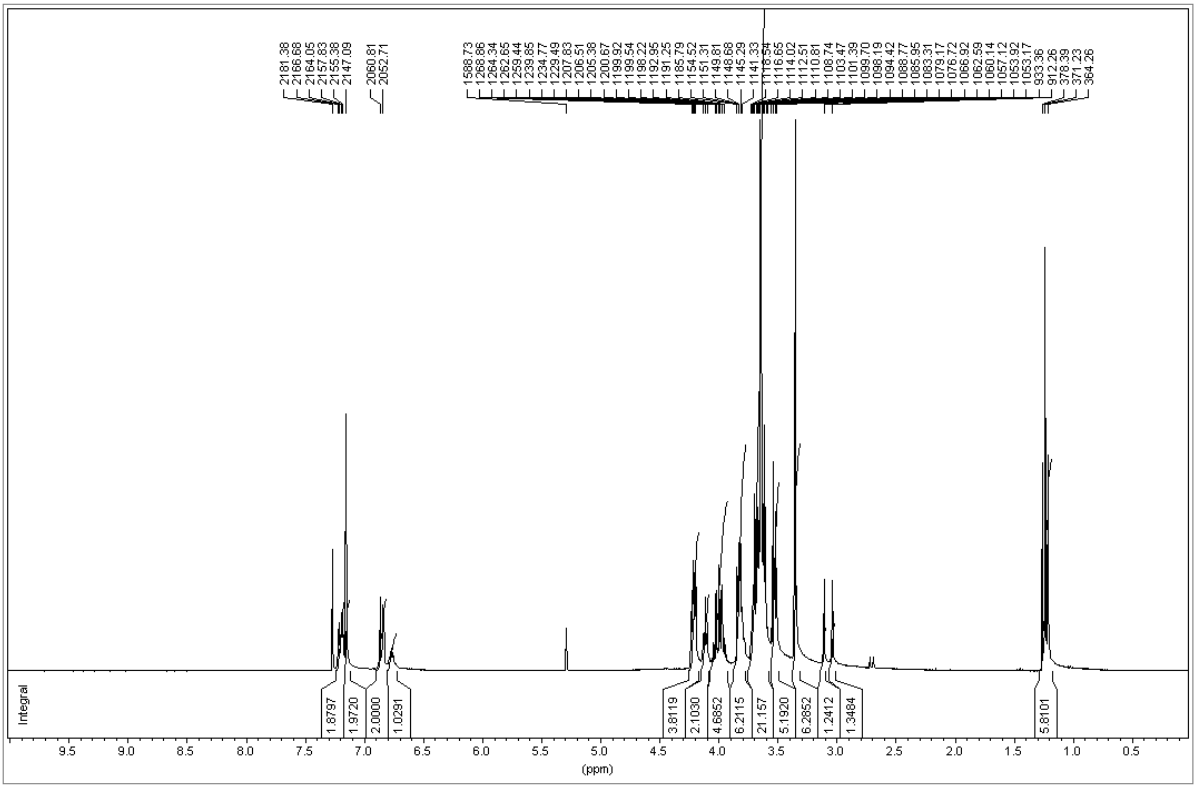


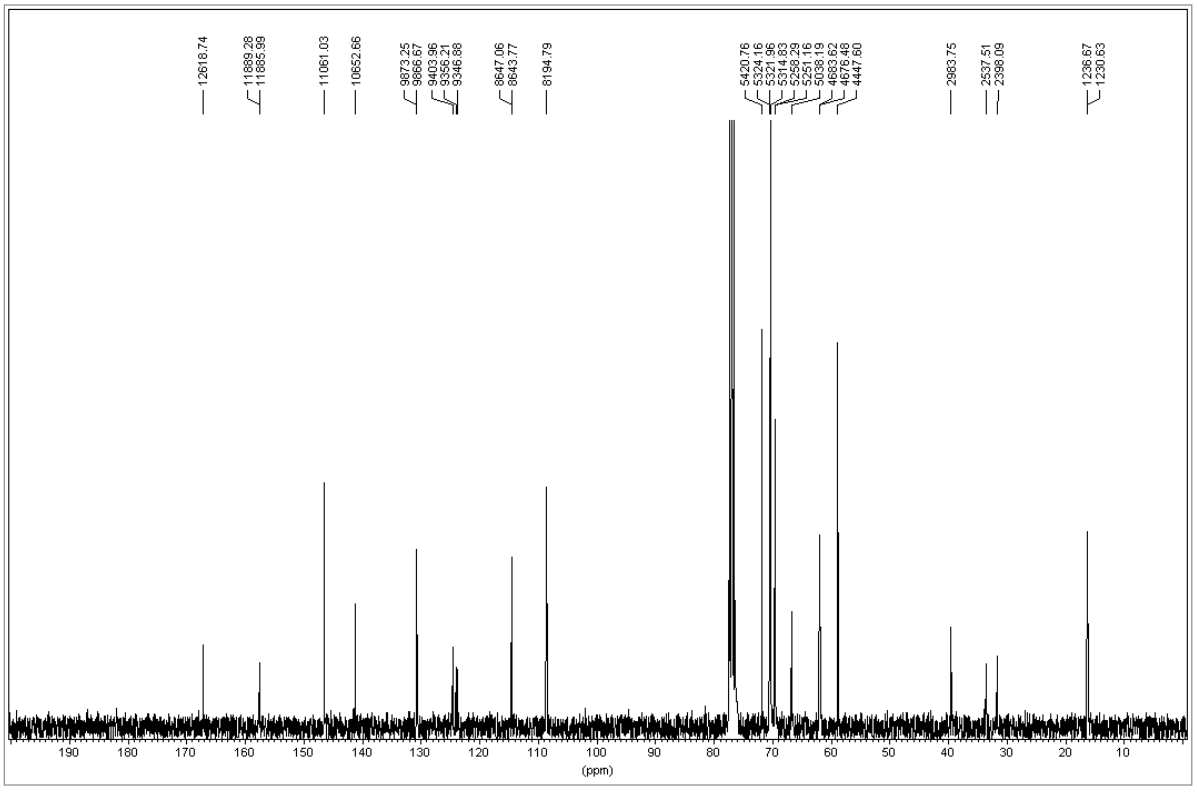

12621.48
11887.63
11684.34
11517.14
10631.80
10386.45
9973.25
9864.67
9778.85
9690.48
9667.97
9648.22
9350.17
9341.39
8645.42
8642.12
8069.64
5846.90
5418.57
5330.75
5320.32
5317.57
5314.83
5310.99
5255.55
5200.11
5028.86
4686.36
4679.78
4447.05
2964.64
2533.67
2394.80
1237.22
1231.18
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

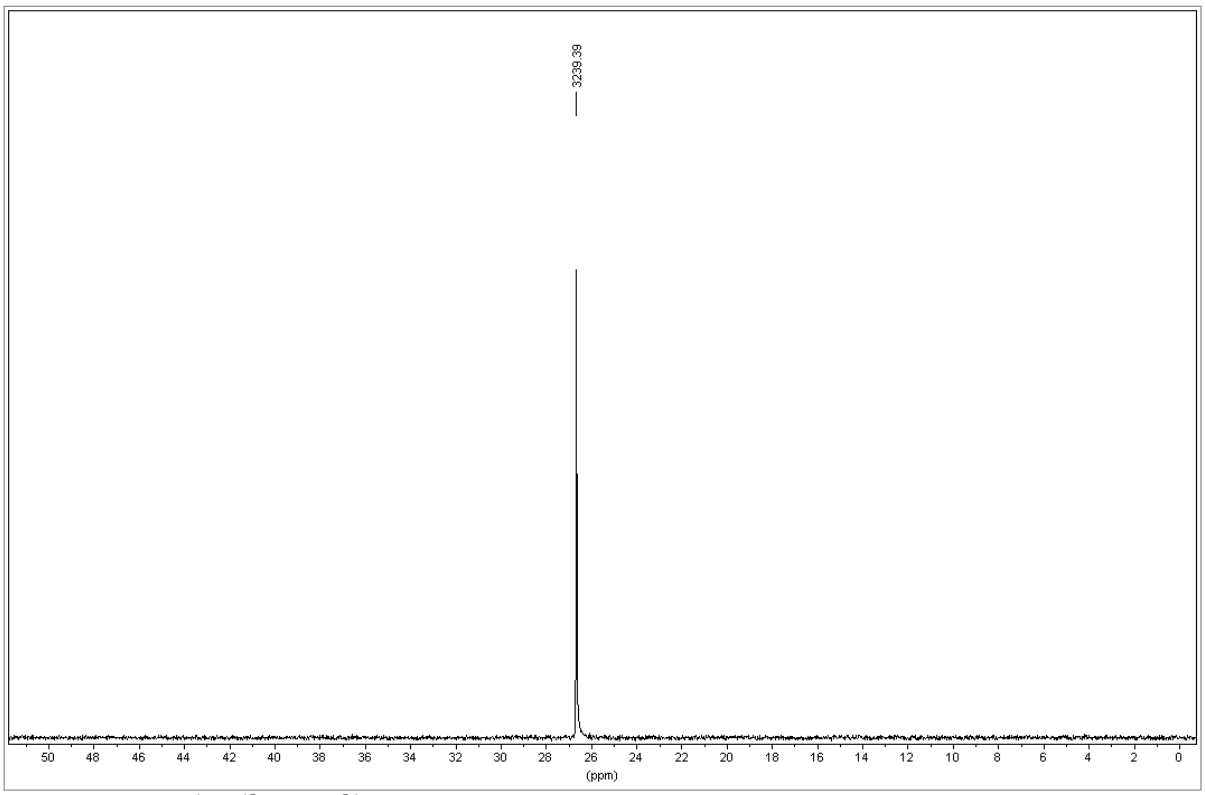

3248.30
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
(ppm)

Compound 28 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

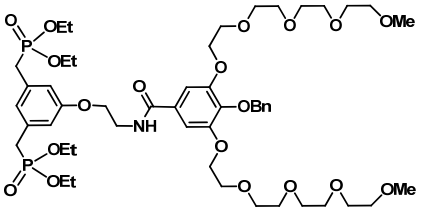


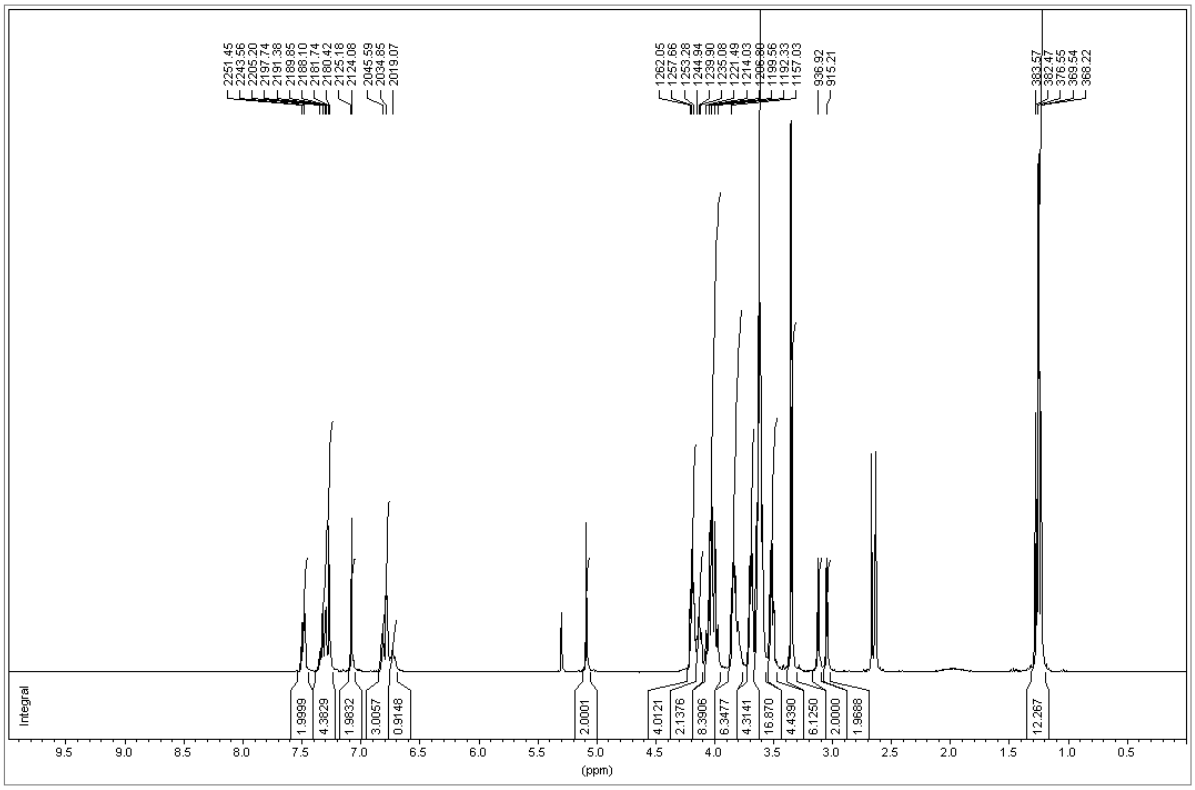


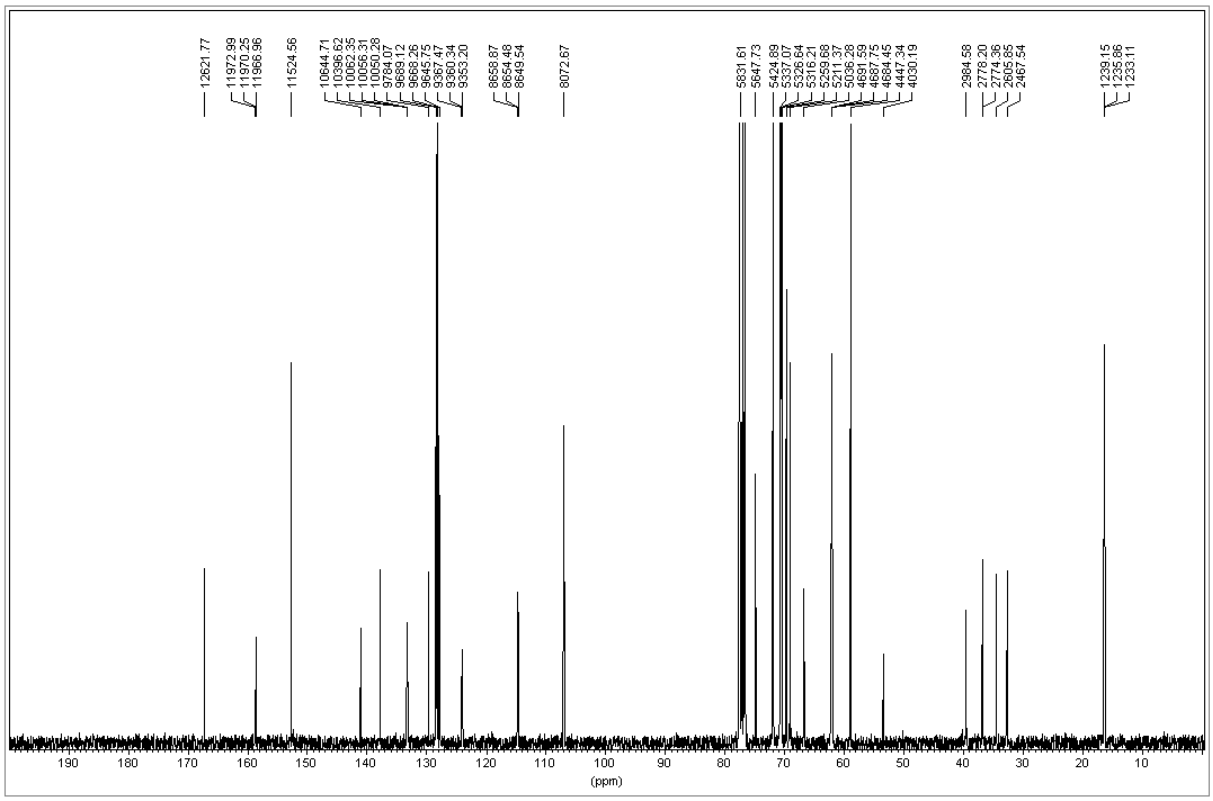


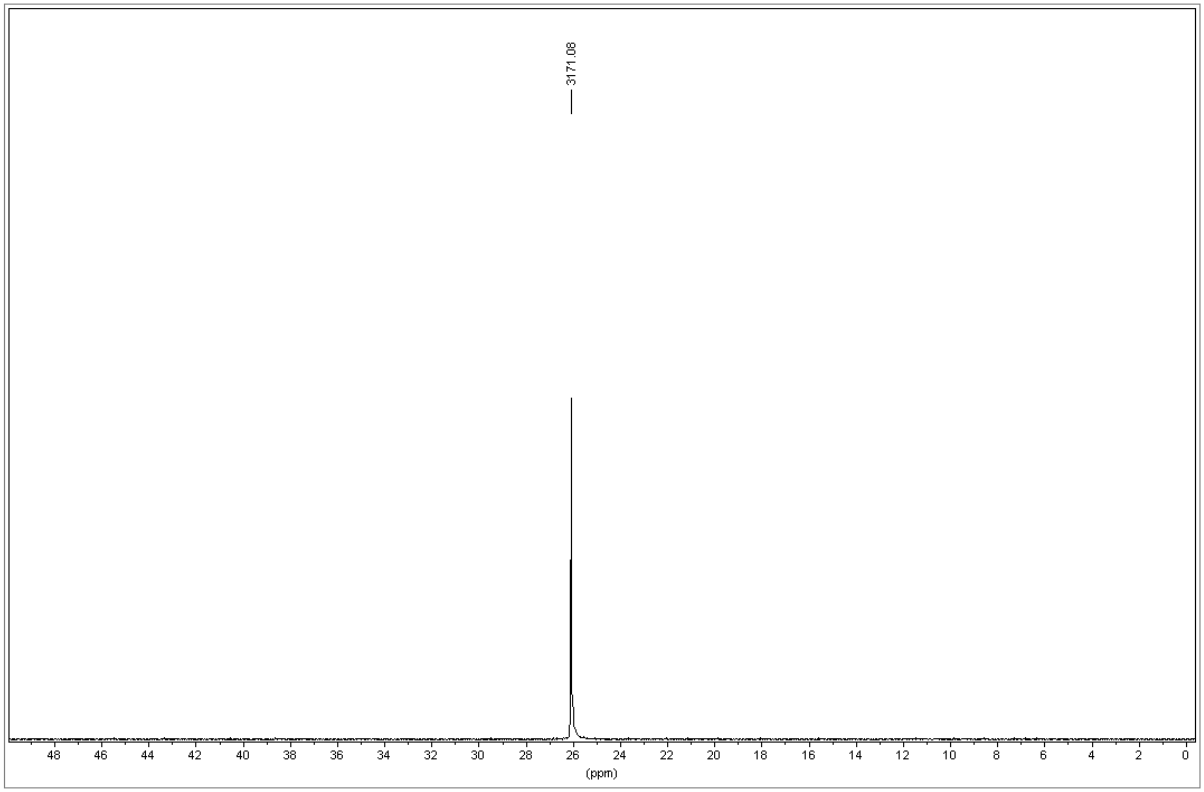


Compound 29 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

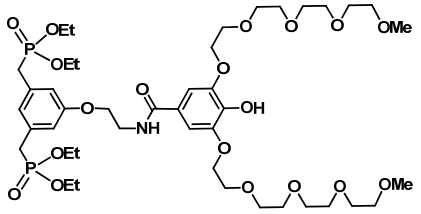


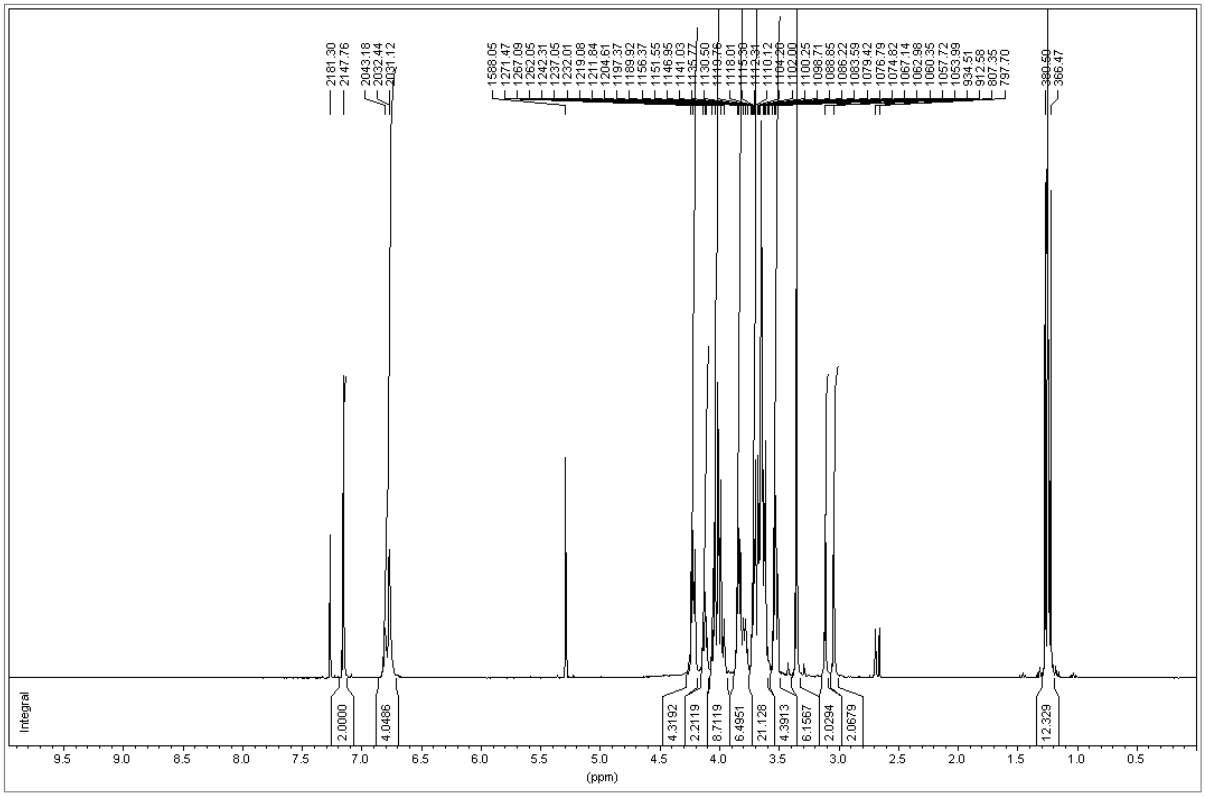


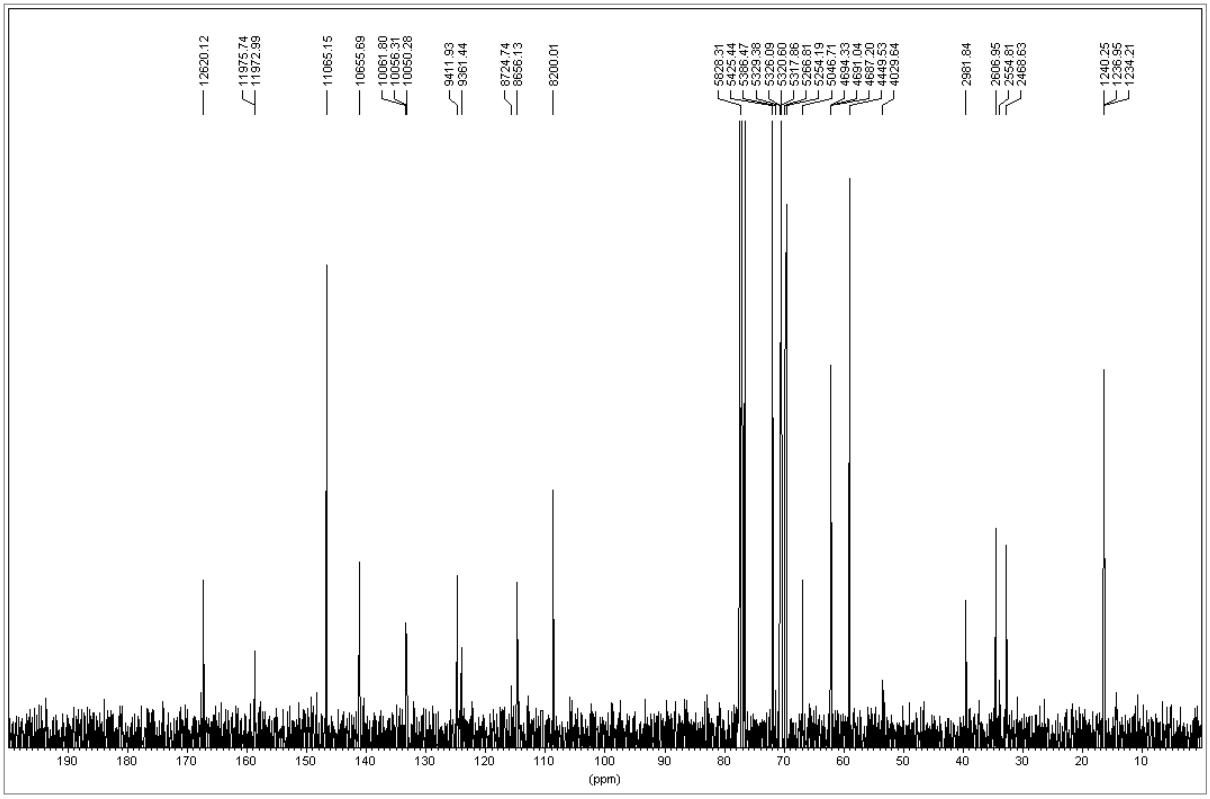

12621.77
11972.99
11970.25
11966.96
11524.56
10644.71
10396.62
10062.35
10056.31
10050.28
9784.07
9683.12
9645.75
9367.47
9360.34
9353.20
8658.87
8654.48
8649.54
8072.67
5831.61
5647.73
5424.89
5337.07
5326.64
5316.21
5259.68
5211.37
5036.28
4691.59
4687.75
4684.45
4447.34
4030.19
2984.58
2778.20
2774.36
2605.85
2467.54
1239.15
1235.86
1233.11
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

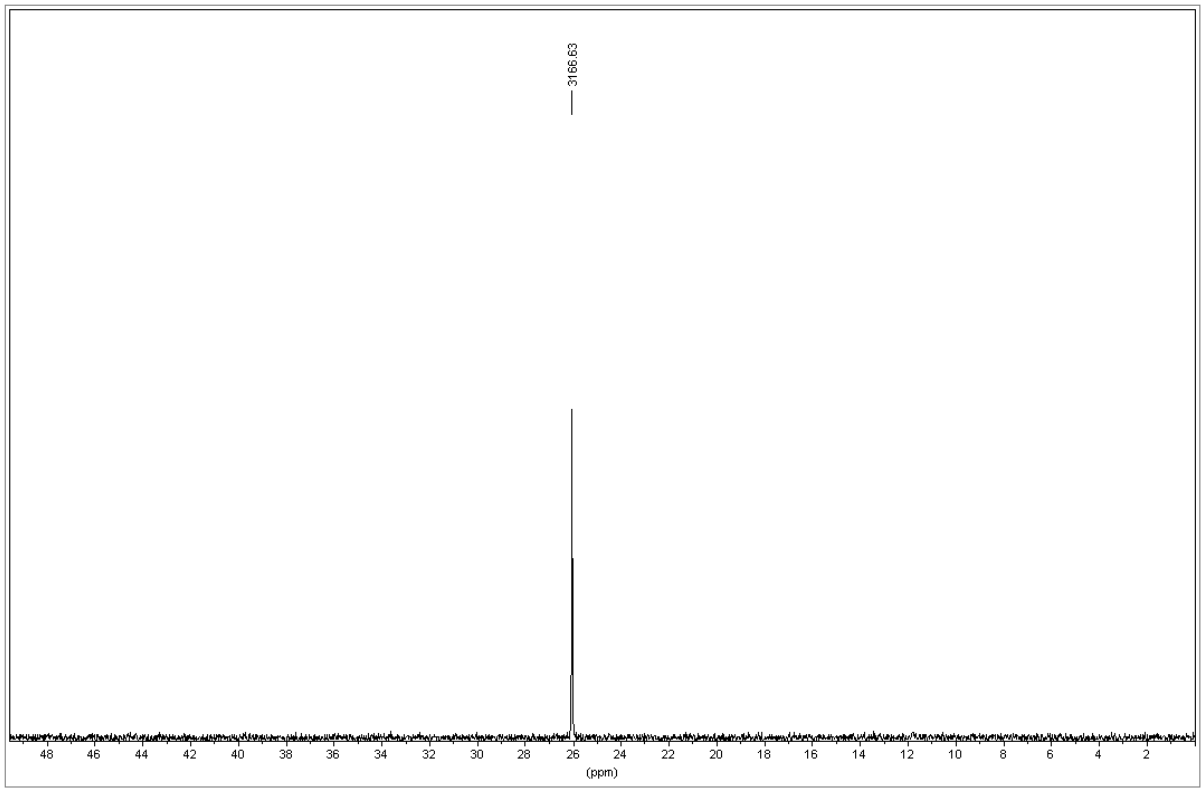

3171.08
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
(ppm)

Compound 30 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

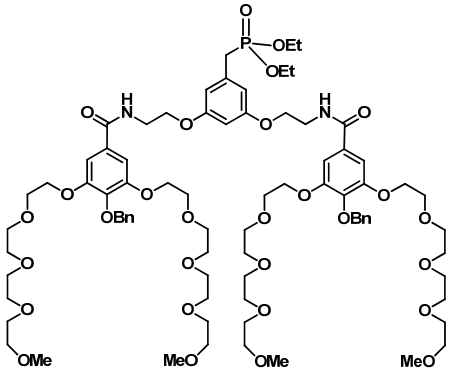


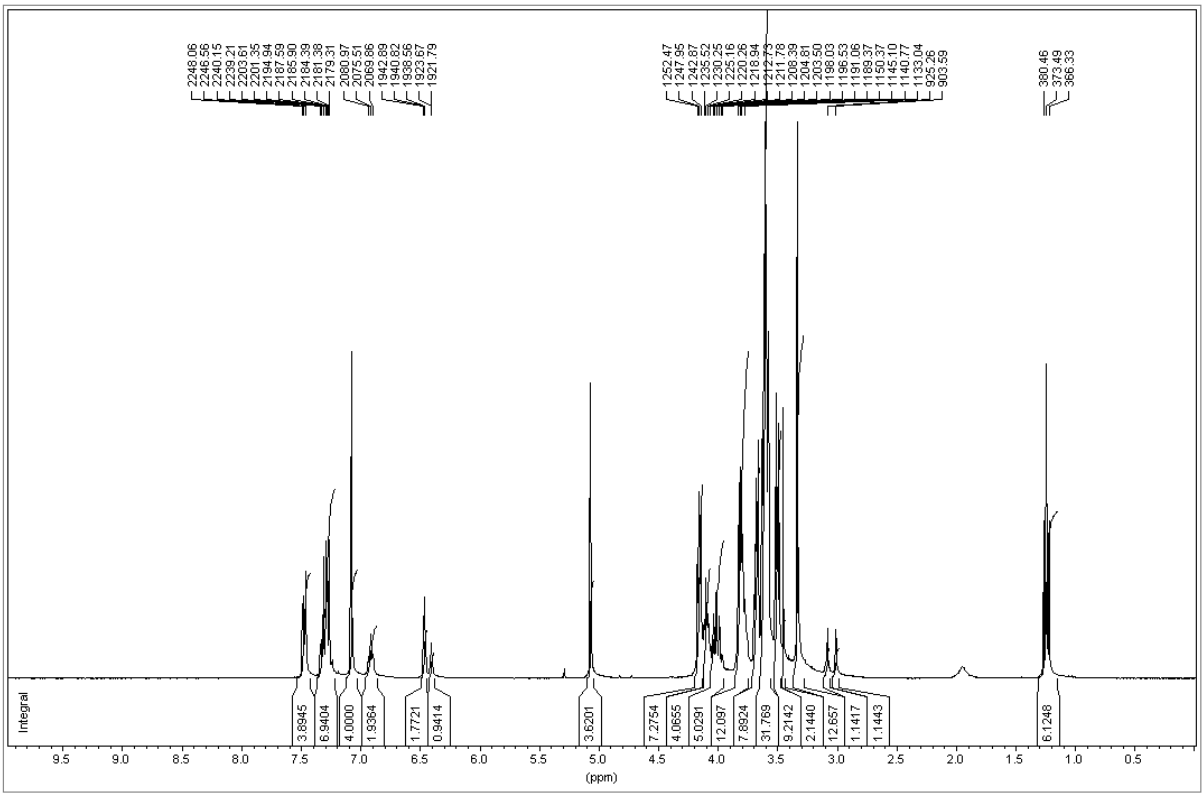


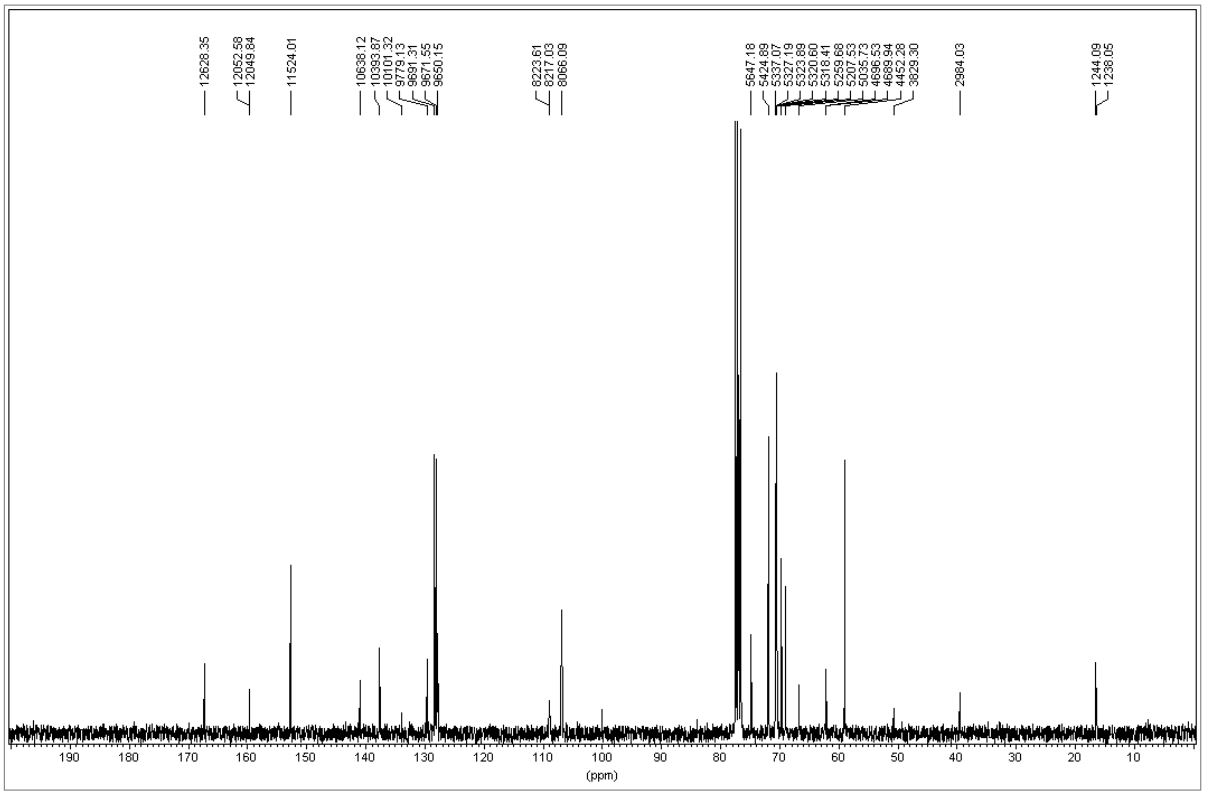

12620.12
11975.74
11972.99
11065.15
10655.69
10061.80
10056.31
10050.28
9411.93
9361.44
8724.74
8656.13
8200.01
5828.31
5425.44
5386.47
5329.38
5326.09
5320.60
5317.86
5266.81
5264.19
5246.71
4694.33
4691.04
4687.20
4449.53
4029.64
2981.84
2606.95
2554.81
2468.63
1240.25
1236.95
1234.21
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

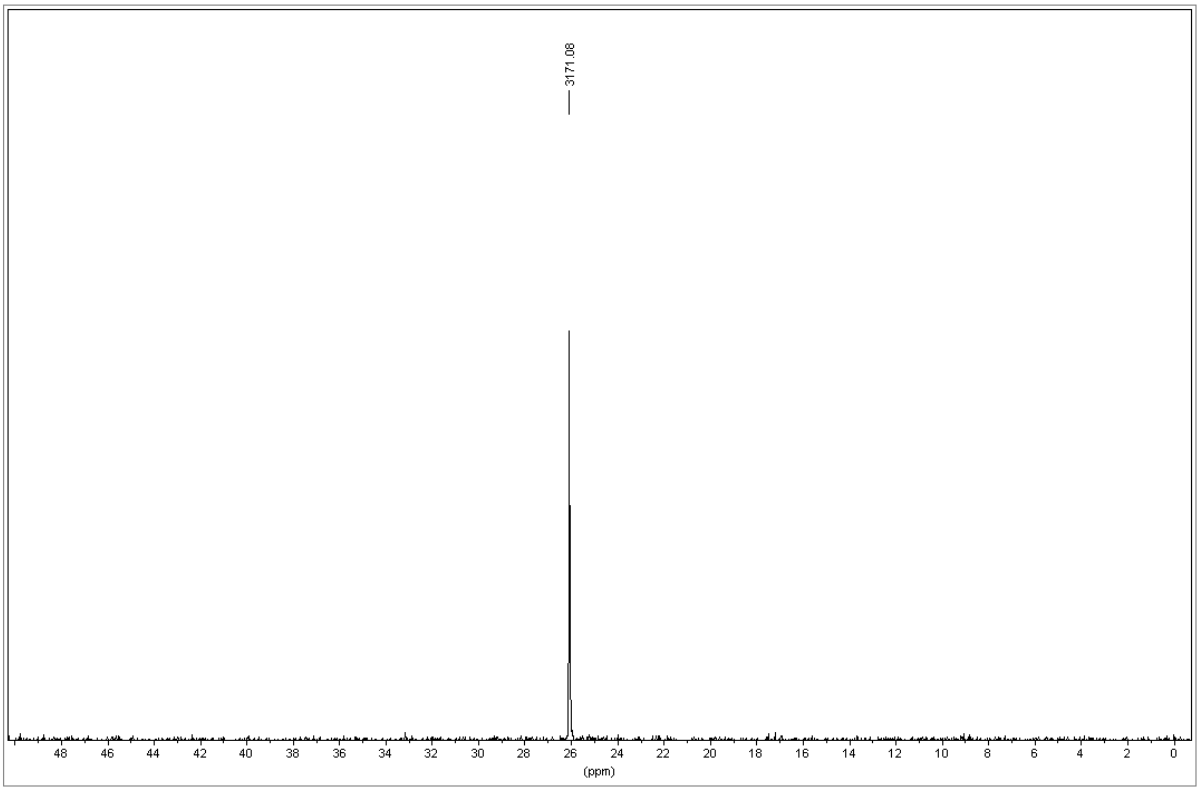

3166.63
48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2
(ppm)

Compound 31 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

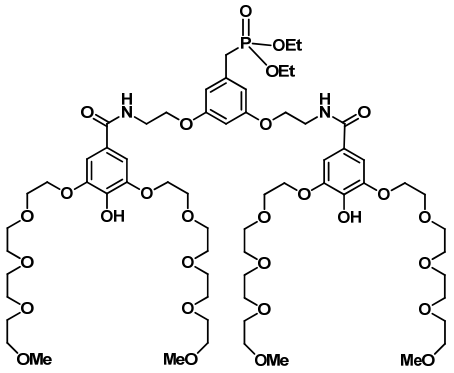


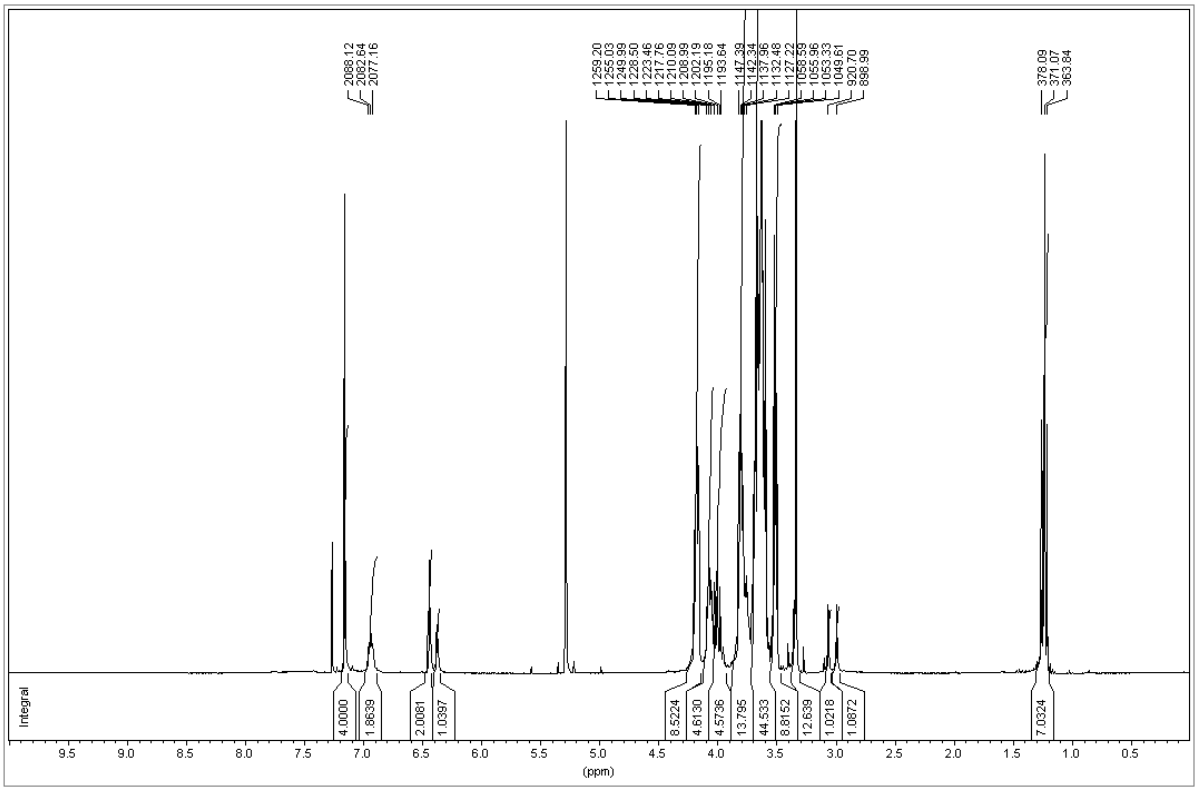


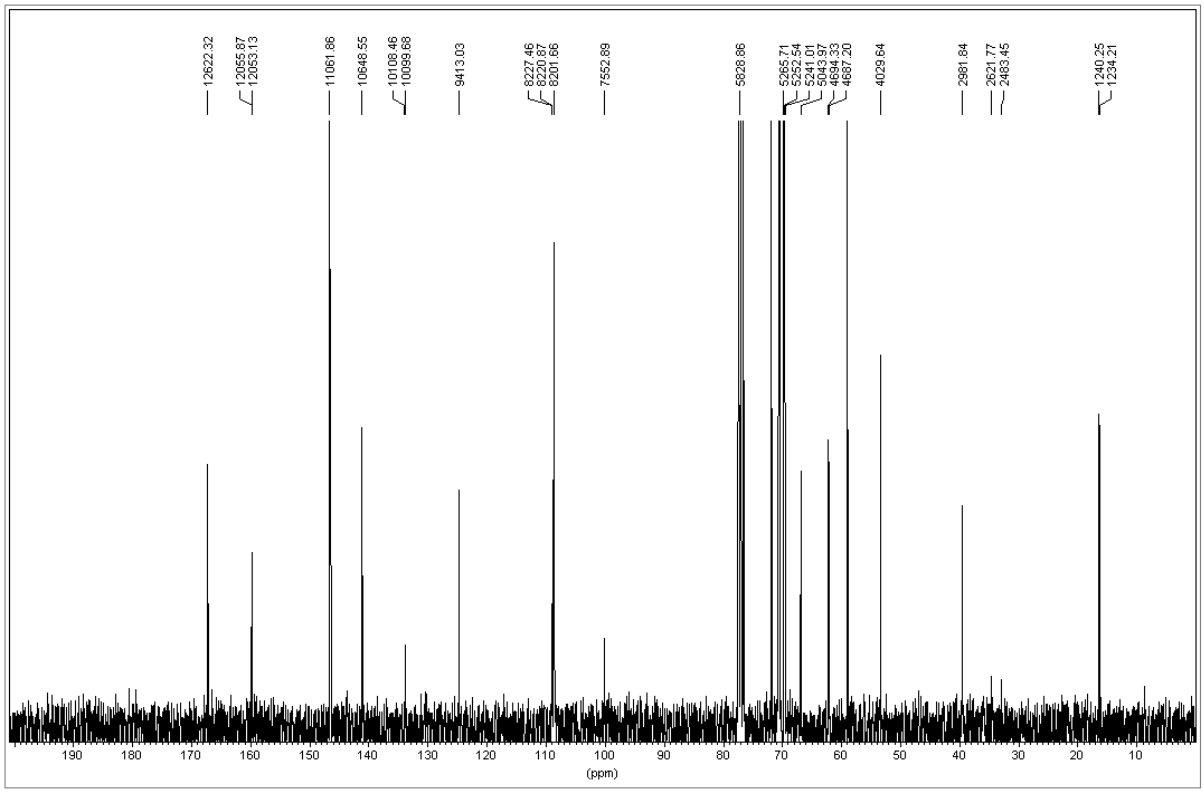

12628.35
12052.58
12049.84
11524.01
10638.12
10393.87
10101.32
9779.13
9691.31
9671.55
9650.15
8323.61
8277.03
8066.09
5647.18
5424.89
5337.07
5327.19
5323.89
5320.60
5318.41
5259.68
5207.53
5035.73
4696.53
4689.94
4452.28
3029.30
2984.03
1244.09
1238.05
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

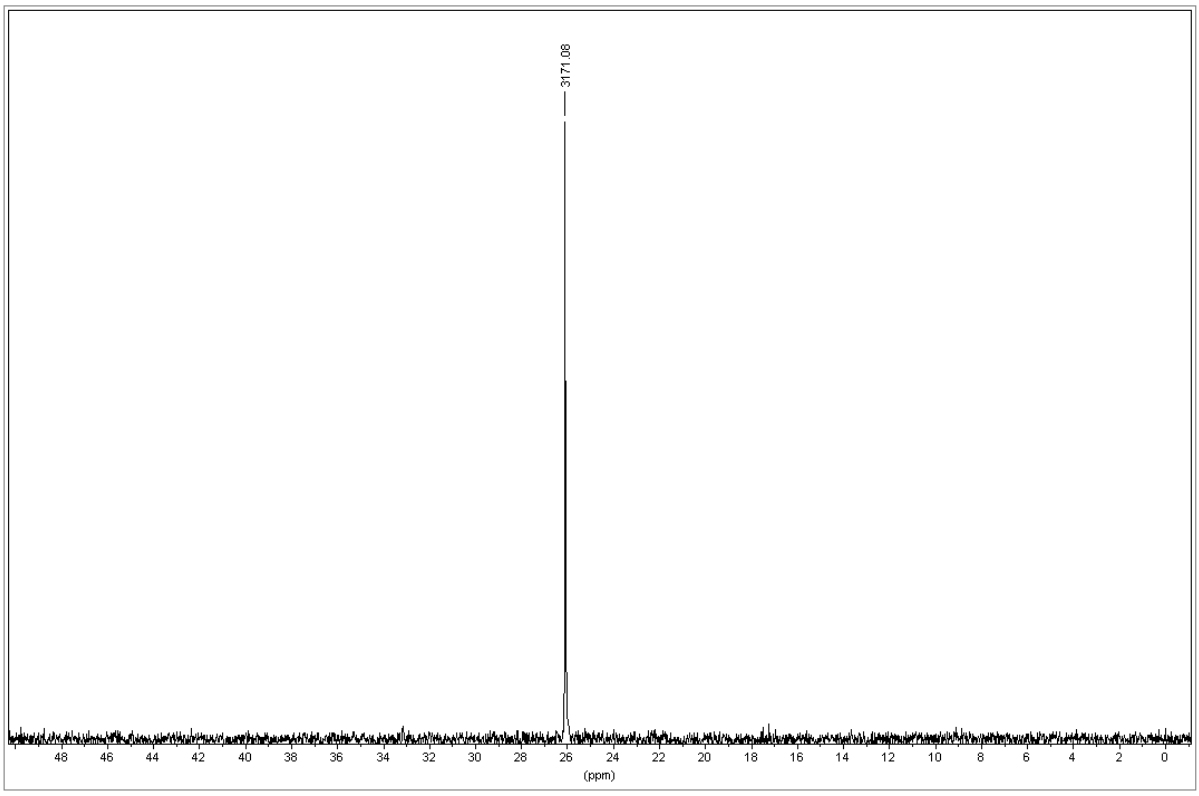

3171.08
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
(ppm)

Compound 32 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

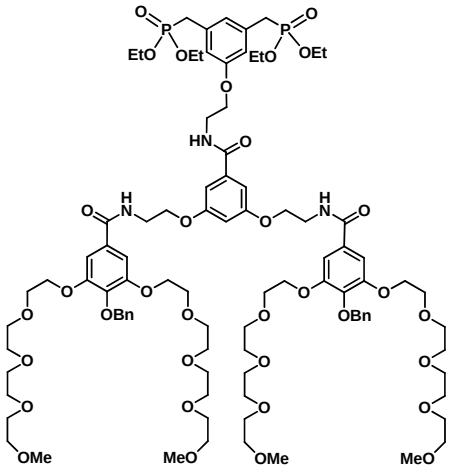


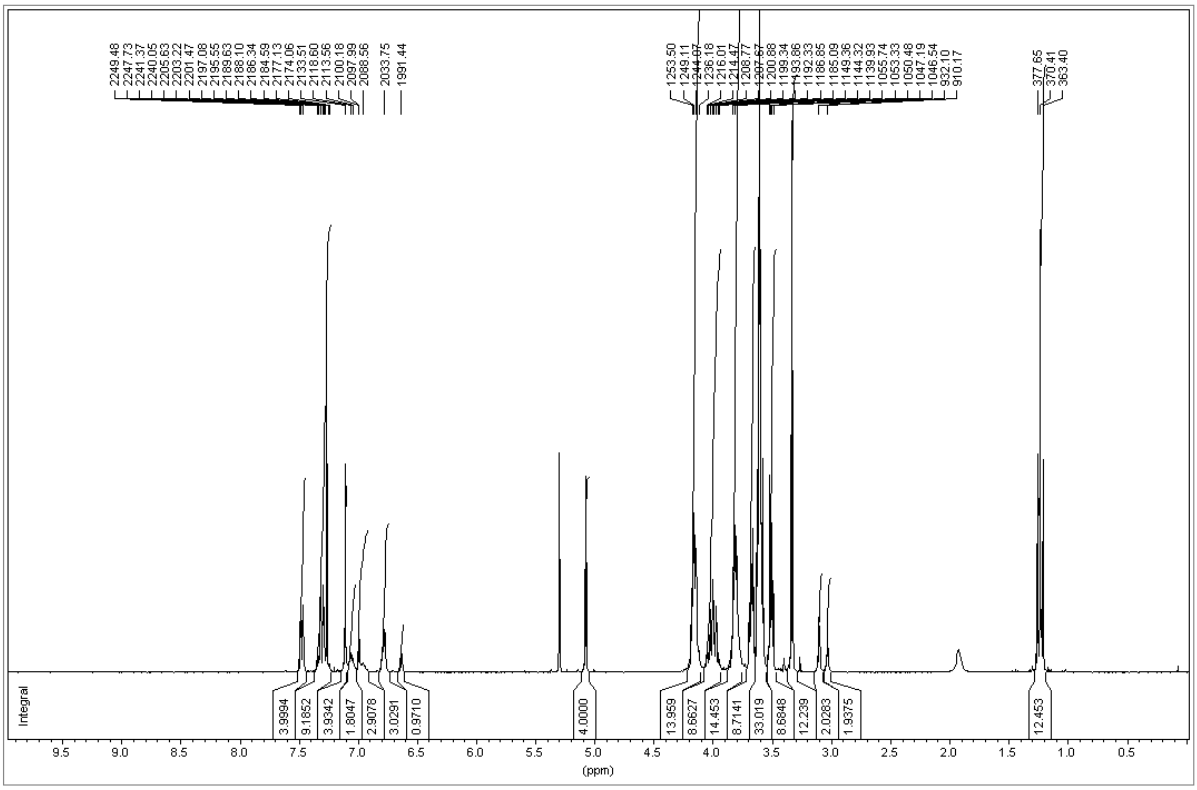


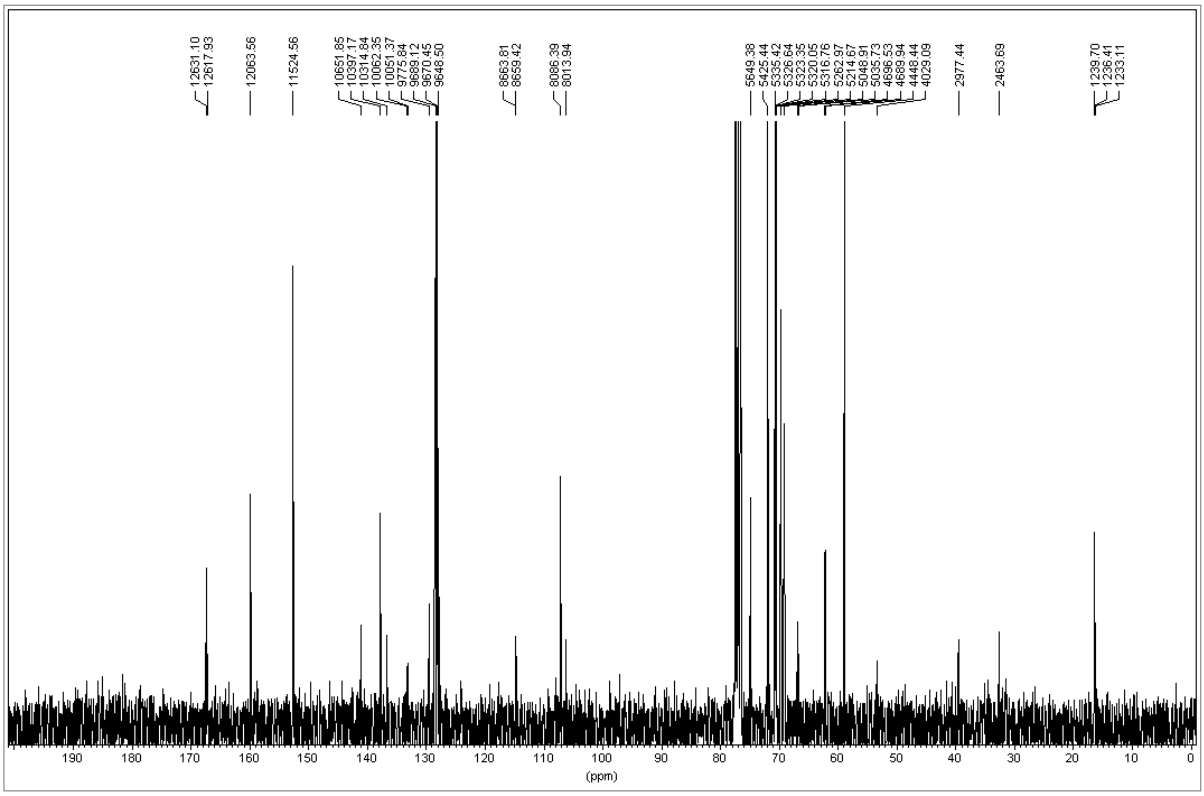

12622.32
12055.87
12053.13
11061.86
10648.55
10108.46
10099.68
9413.03
8227.46
8220.87
8201.66
7552.89
5828.86
5265.71
5252.54
5241.01
5043.97
4694.33
4687.20
4029.64
2981.84
2621.77
2483.45
1240.25
1234.21
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

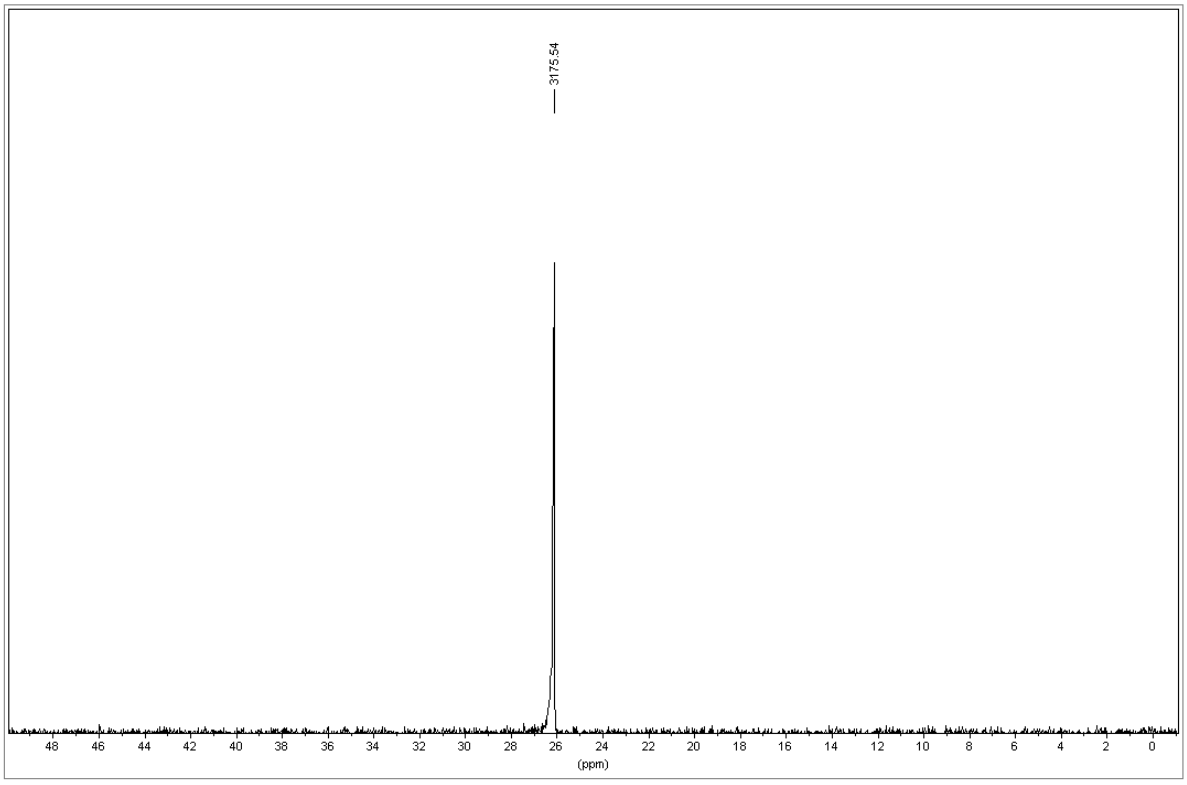

3171.08
48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0
(ppm)

Compound 33 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

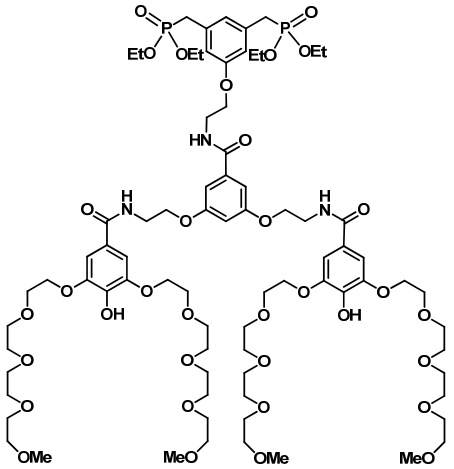


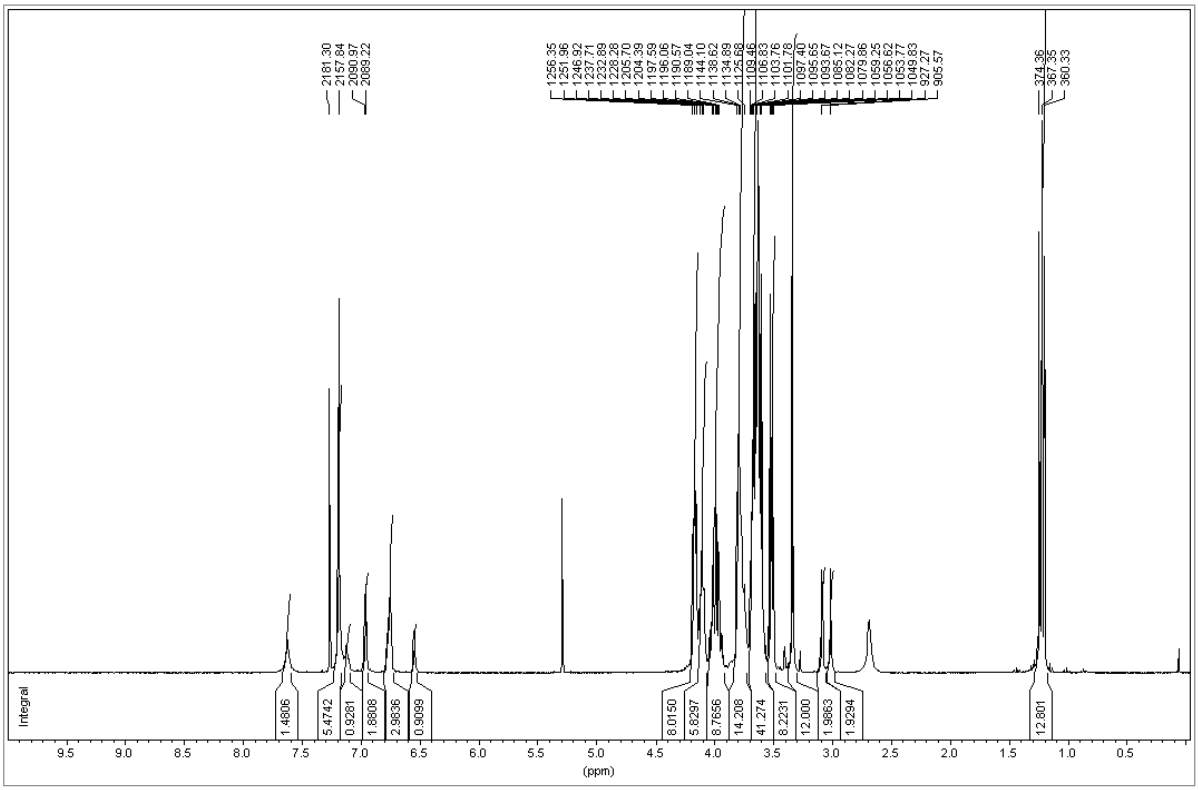


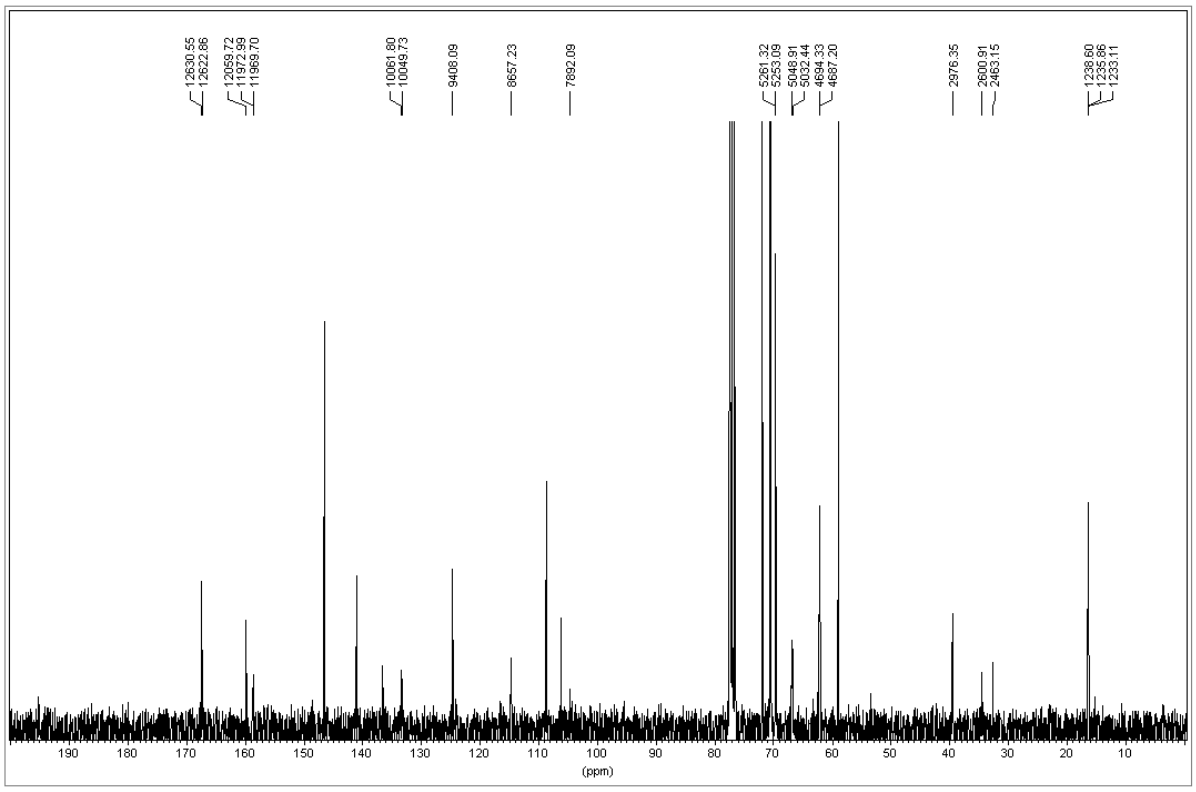

12631.10
12617.93
12063.56
11524.56
10651.85
10397.17
10314.84
10062.35
10051.37
9775.84
9699.12
9670.45
9648.50
8663.81
8659.42
8086.39
8013.94
5549.38
5425.44
5335.42
5326.64
5323.35
5320.05
5316.76
5262.97
5214.67
5046.91
5005.73
4696.53
4689.94
4448.44
4029.09
2977.44
2463.69
1239.70
1236.41
1233.11
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

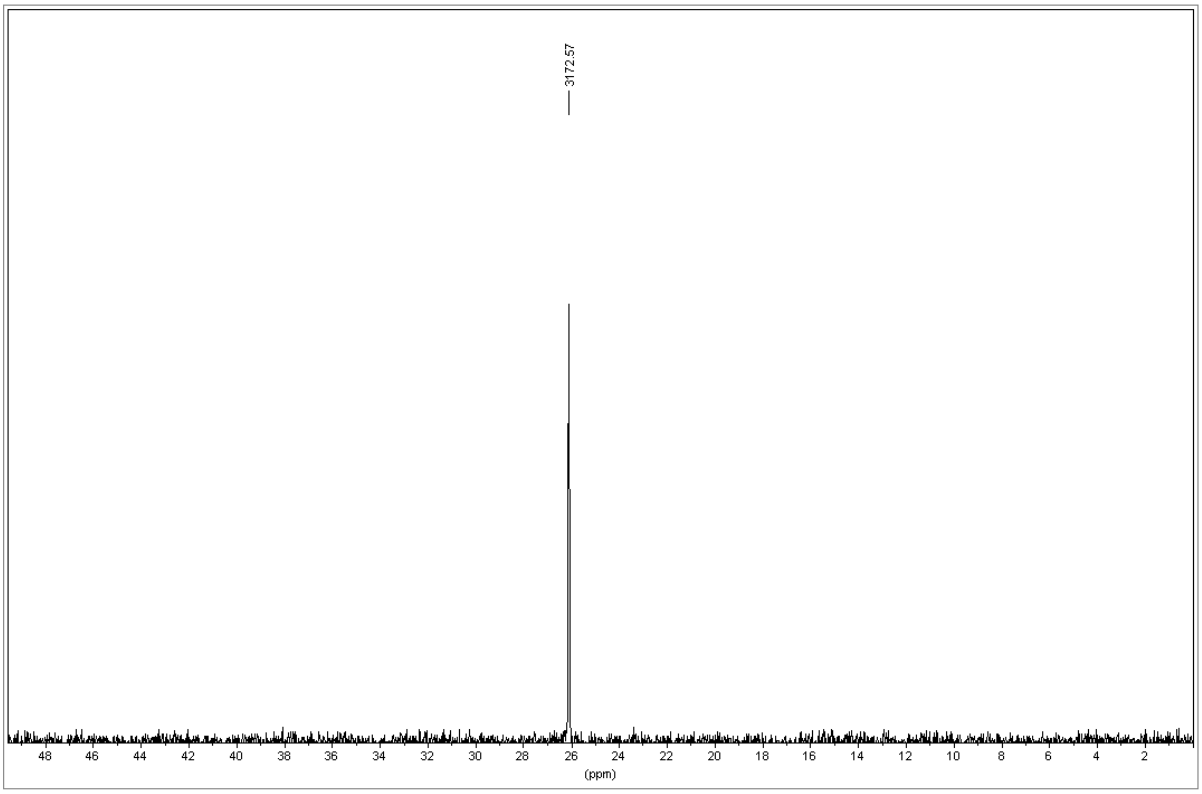

3175.54
48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0
(ppm)

Compound 34 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

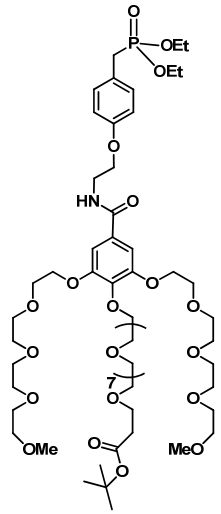


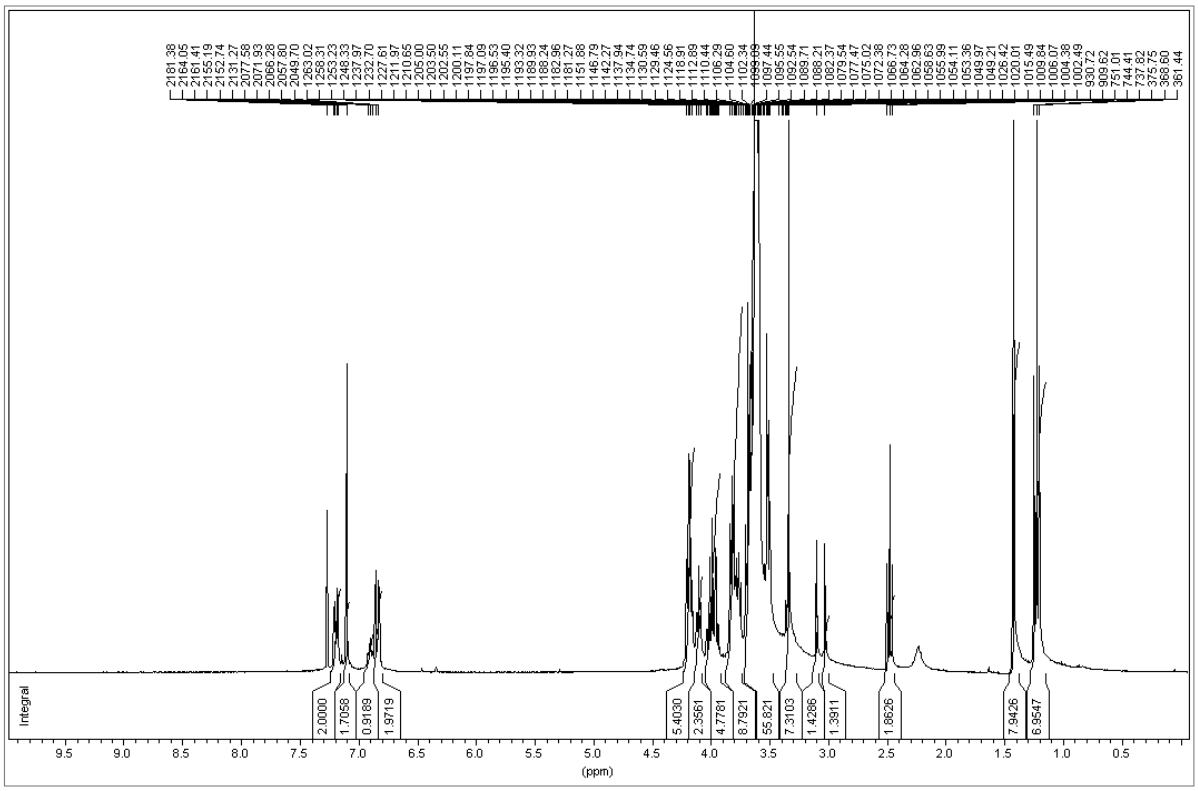


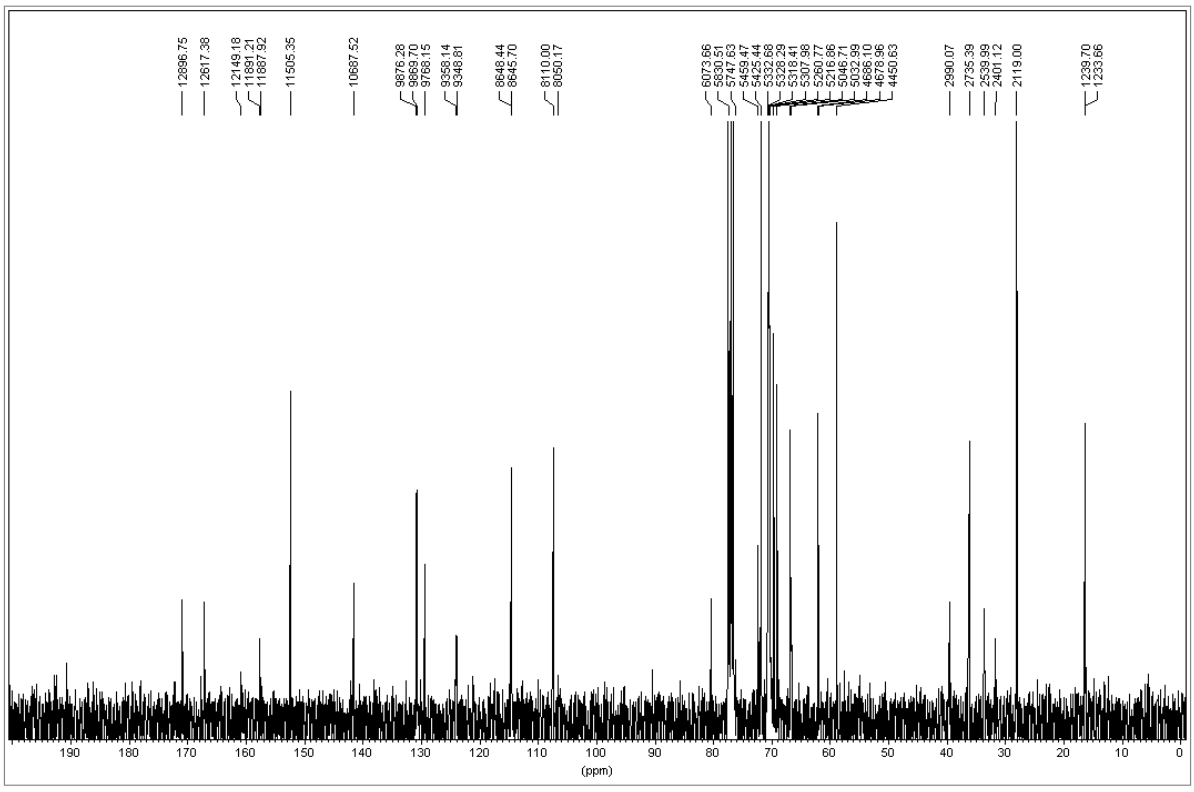

12630.55
12622.86
12059.72
11972.99
11969.70
10061.80
10049.73
9408.09
8657.23
7892.09
5261.32
5253.09
5048.91
5032.44
4694.33
4687.20
2976.35
2600.91
2463.15
1238.60
1235.86
1233.11
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

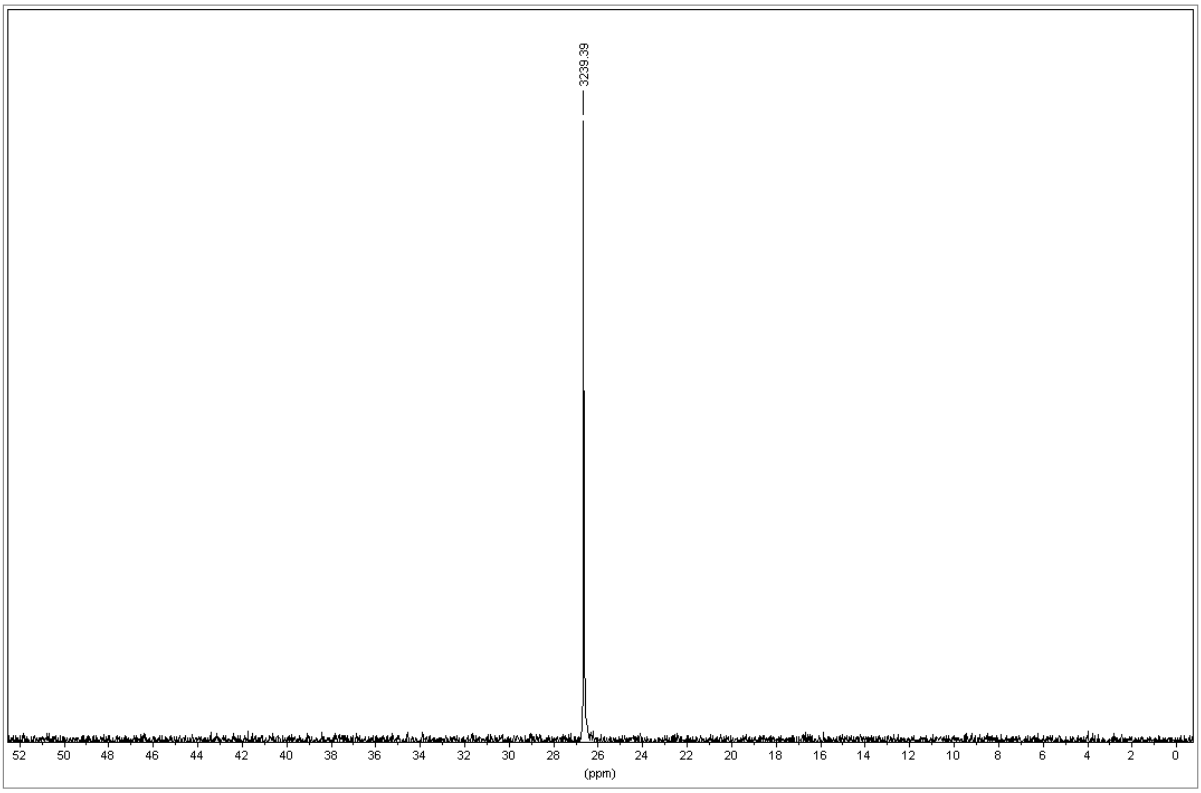

3172.57
48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2
(ppm)

Compound 36 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

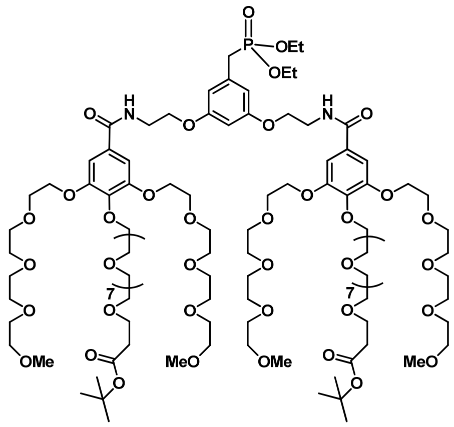


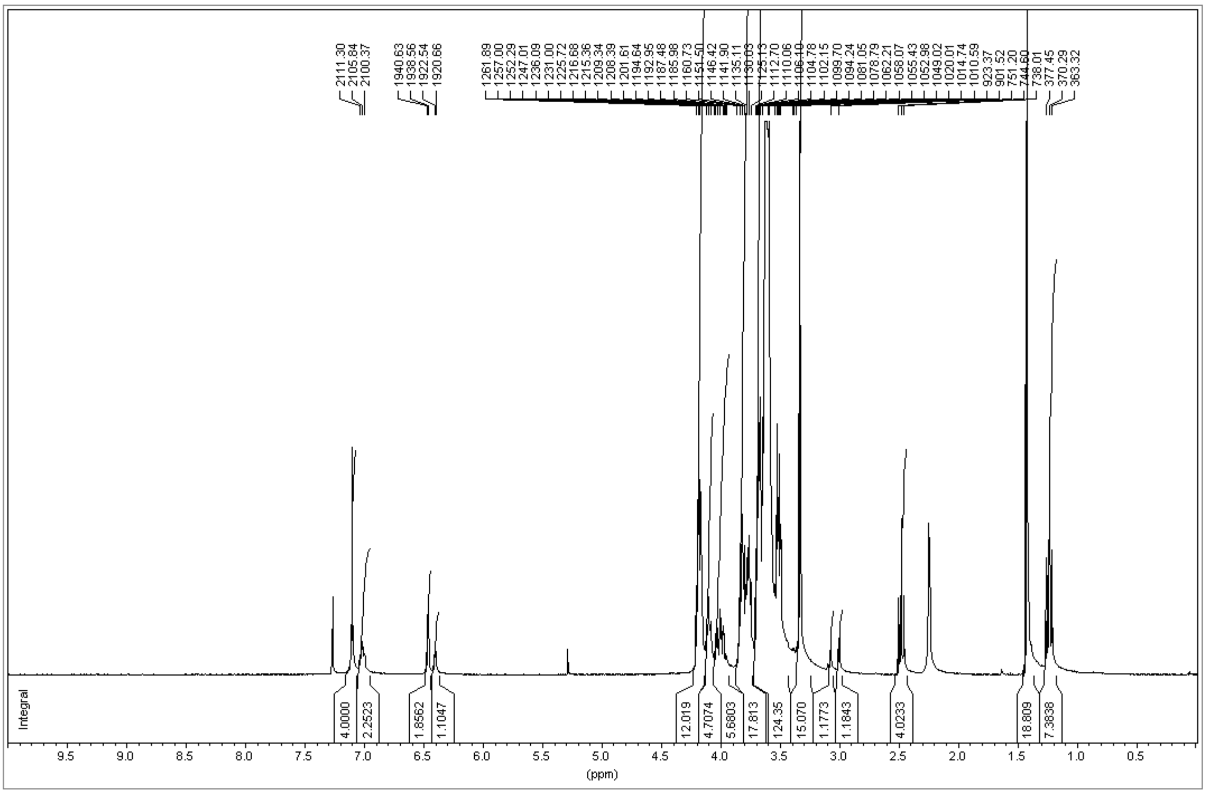


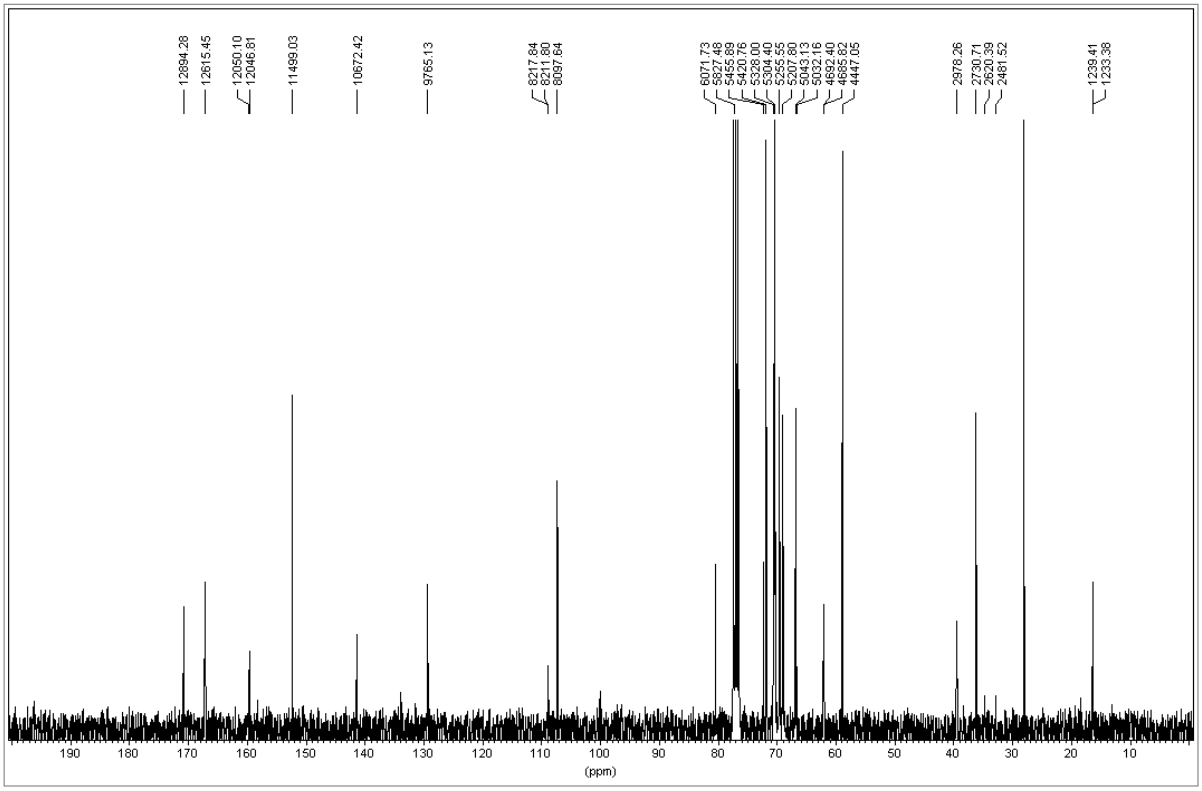

12896.75
12617.38
12149.18
11891.21
11887.92
11505.35
10687.52
9876.28
9869.70
9768.15
9358.14
9348.81
8648.44
8645.70
8110.00
8050.17
6073.66
5930.51
5747.63
5446.47
5425.44
5332.68
5328.29
5318.41
5307.98
5260.77
5216.86
5046.71
5032.99
4686.10
4678.96
4450.63
2990.07
2735.39
2539.99
2401.12
2119.00
1239.70
1233.66
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

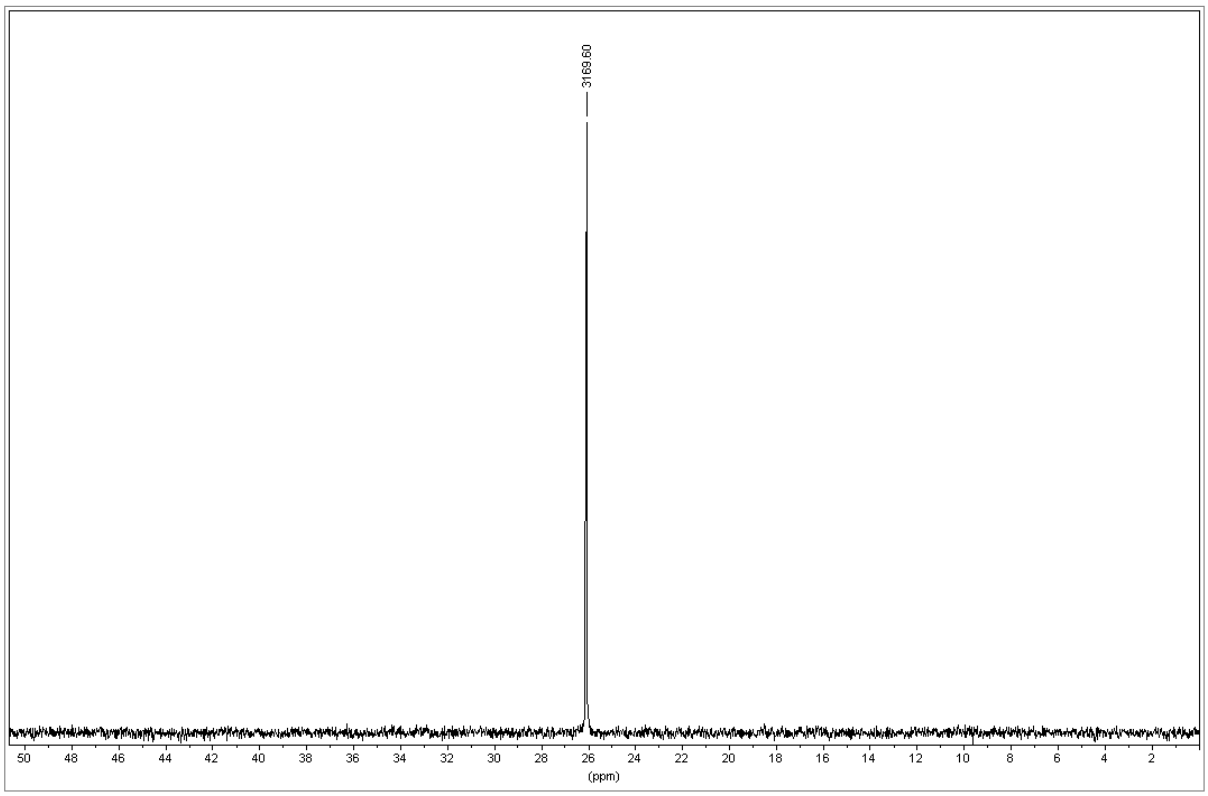

3239.39
52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0
(ppm)

Compound 37 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

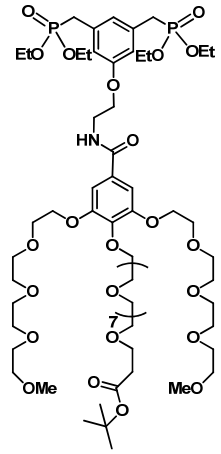


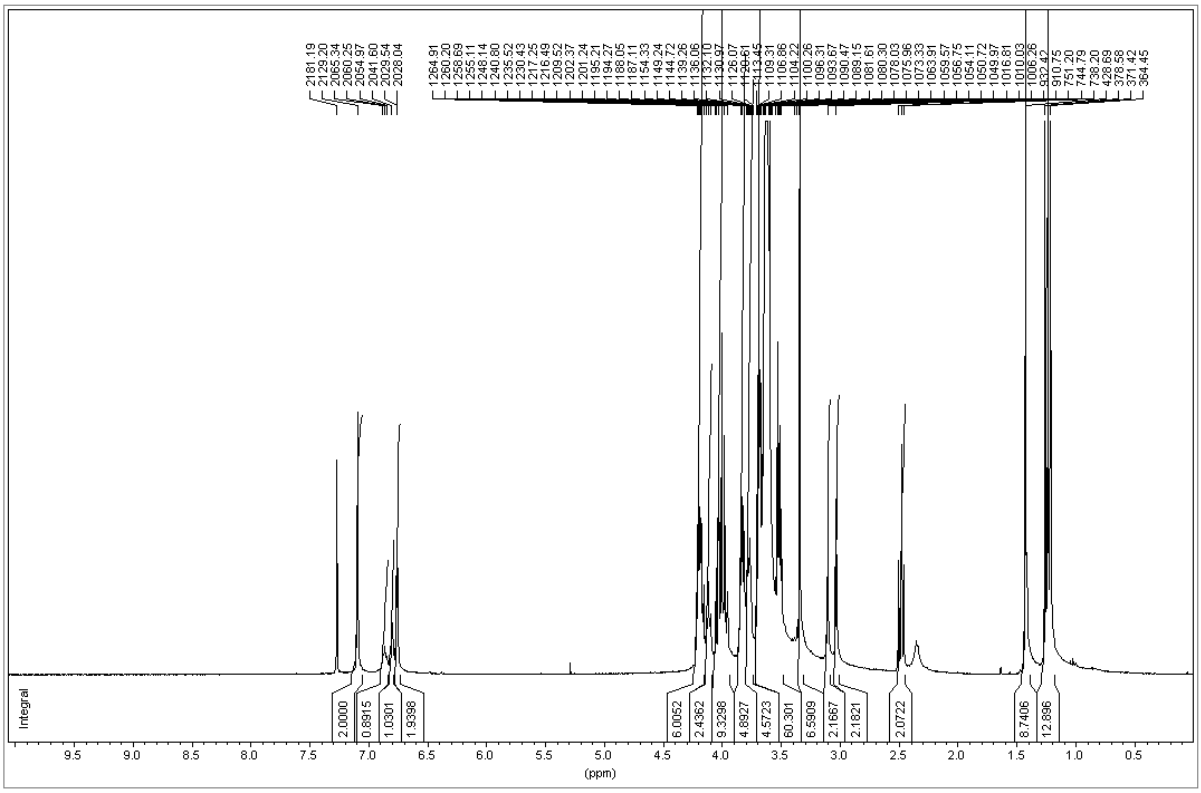


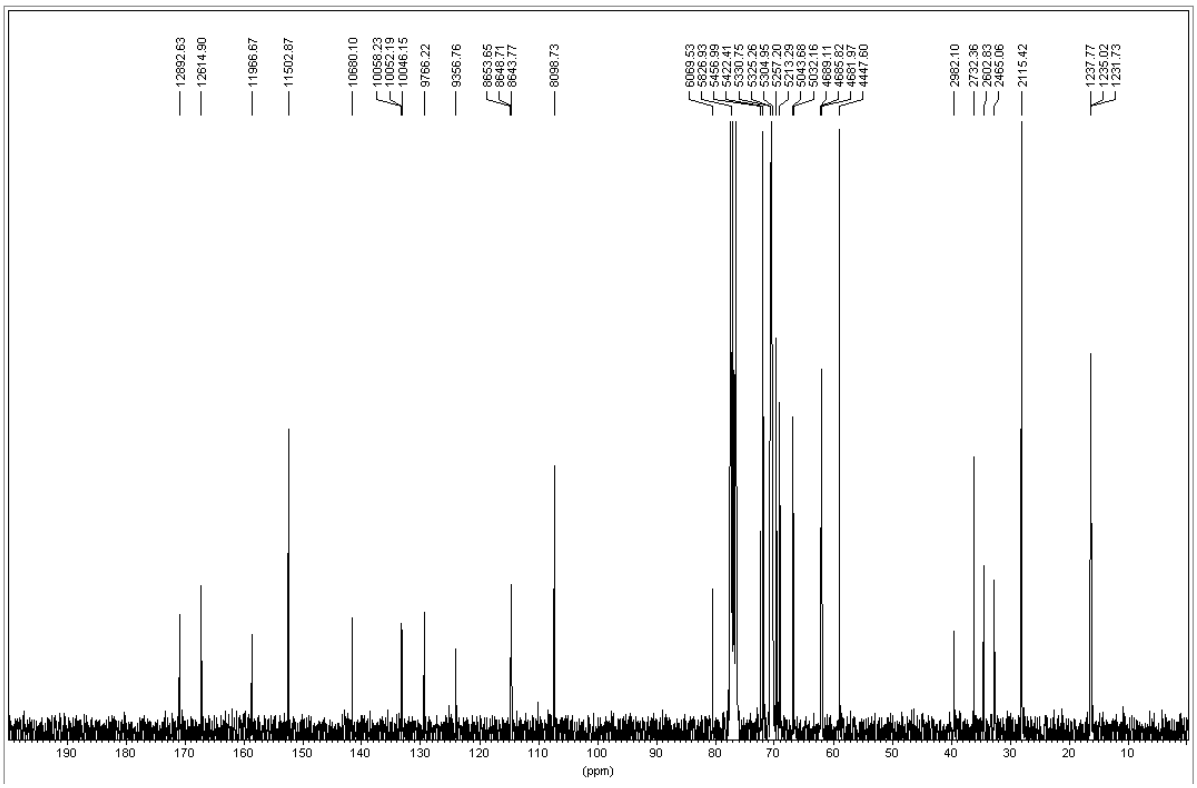

12894.28
12615.45
12050.10
12046.81
11499.03
10672.42
9765.13
8217.84
8211.80
8097.64
6071.73
5827.46
5455.89
5420.76
5328.00
5304.40
5255.55
5207.80
5043.13
5032.15
4692.40
4685.82
4447.05
2978.26
2730.71
2620.39
2481.52
1239.41
1233.38
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

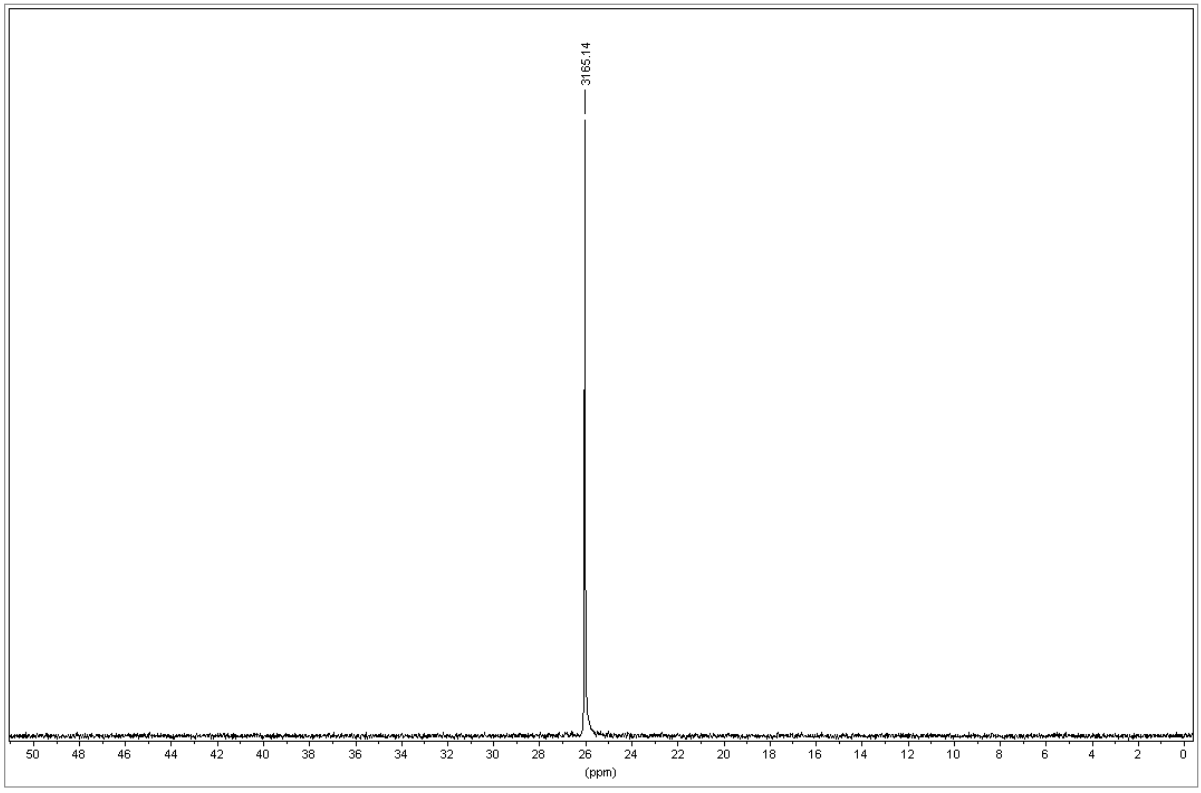

3169.60
50
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
(ppm)

Compound 38 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

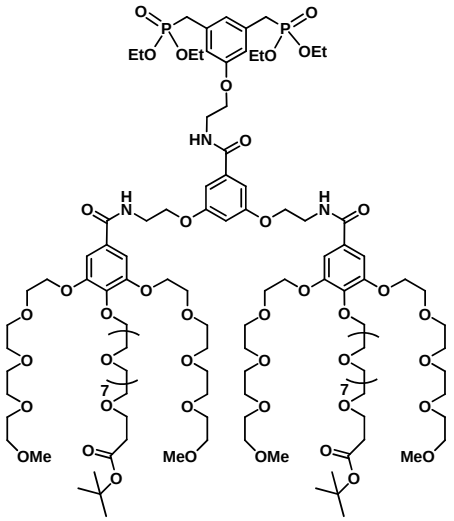


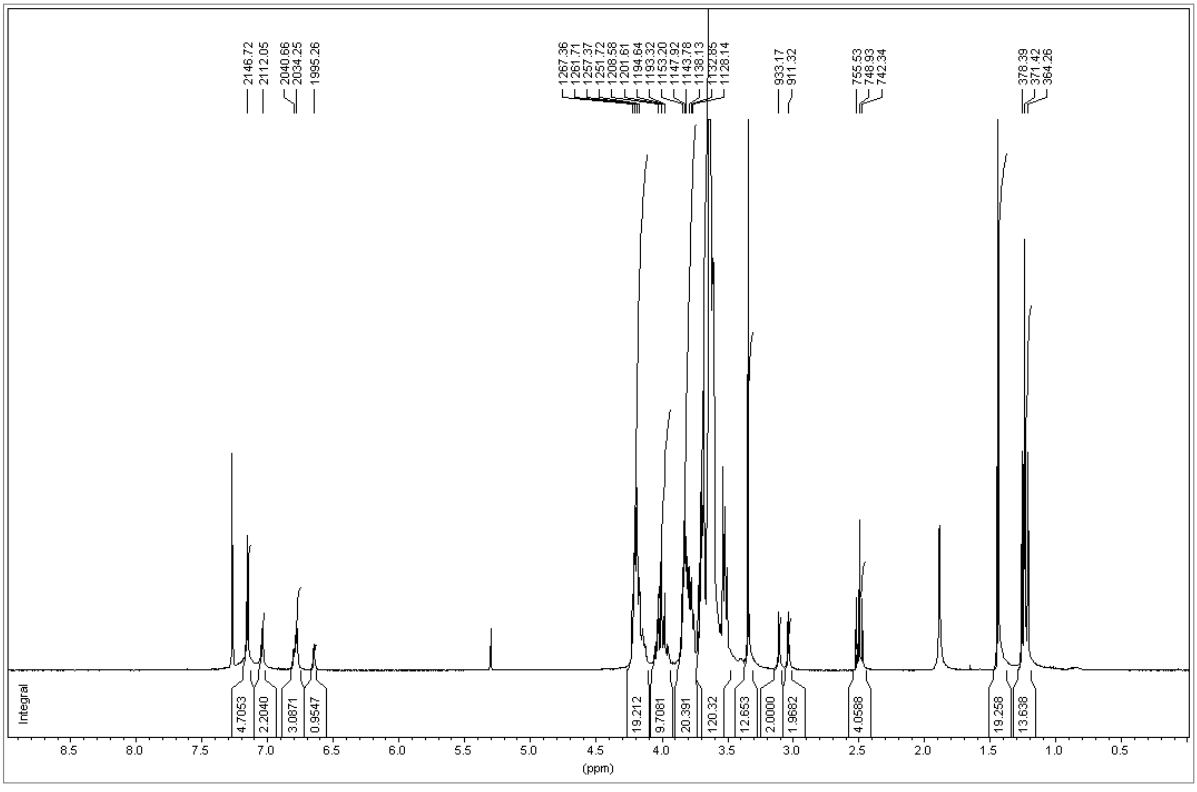


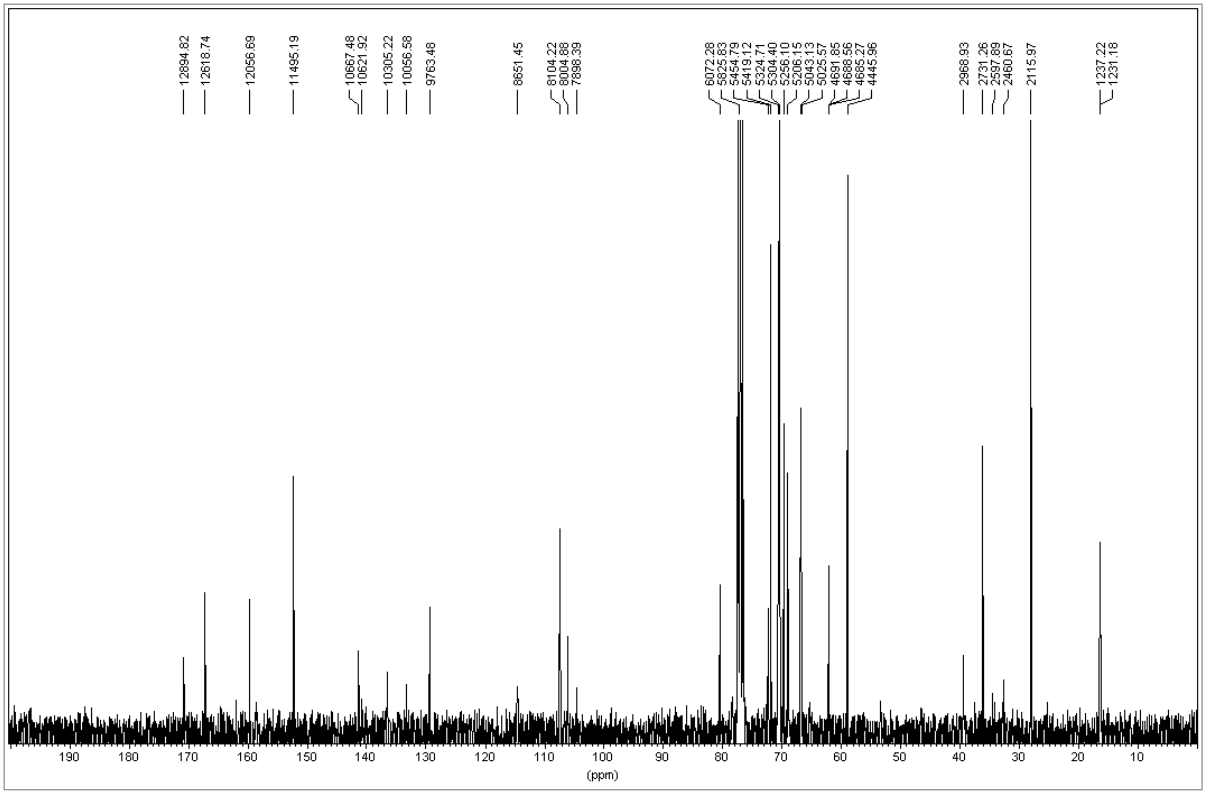

12892.63
12614.90
11966.67
11502.87
10680.10
10058.23
10052.19
10046.15
9766.22
9356.76
8653.65
8648.71
8643.77
8098.73
6069.53
5826.93
5456.99
5422.41
5330.75
5325.26
5304.95
5237.20
5231.29
5043.68
5032.16
4689.11
4685.82
4681.97
4447.60
2982.10
2732.36
2602.83
2465.06
2115.42
1237.77
1235.02
1231.73
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

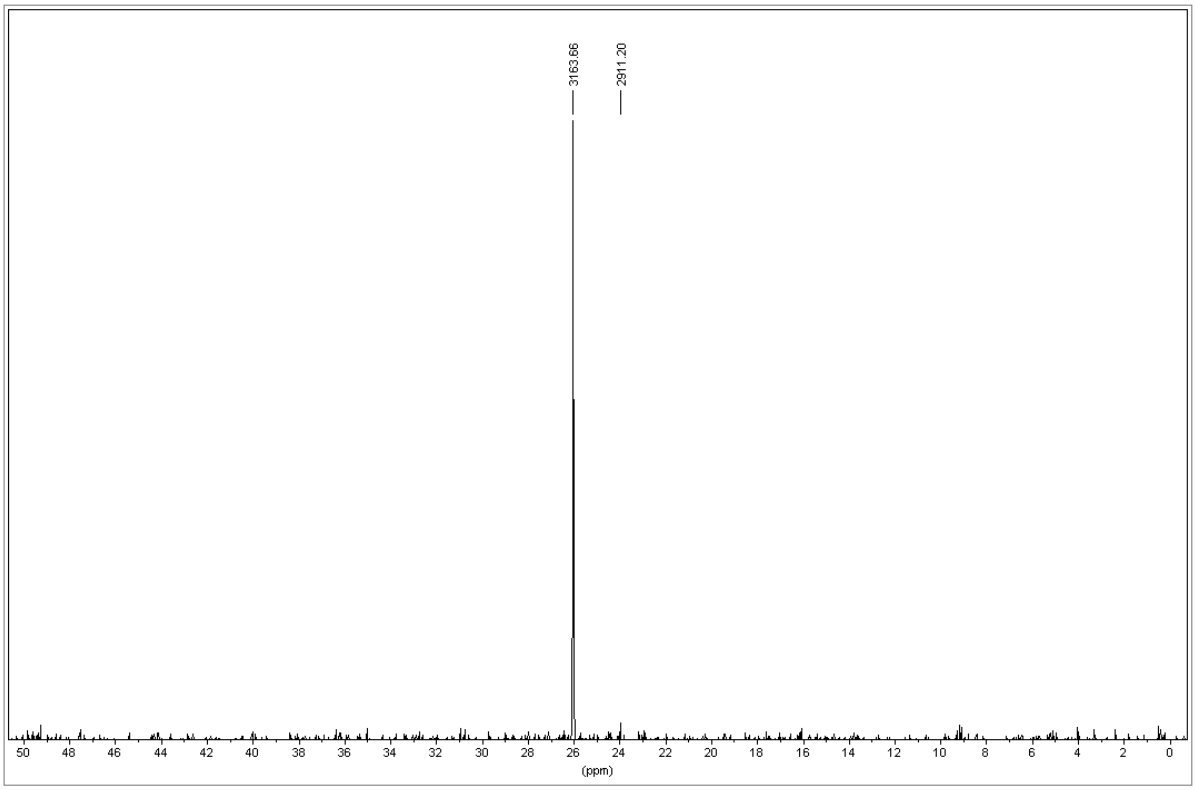

3165.14
50
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
(ppm)

Compound 39 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

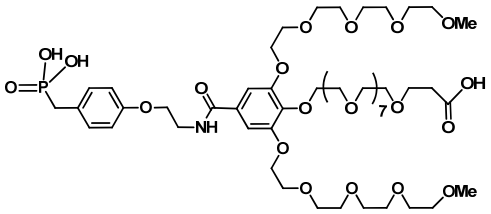


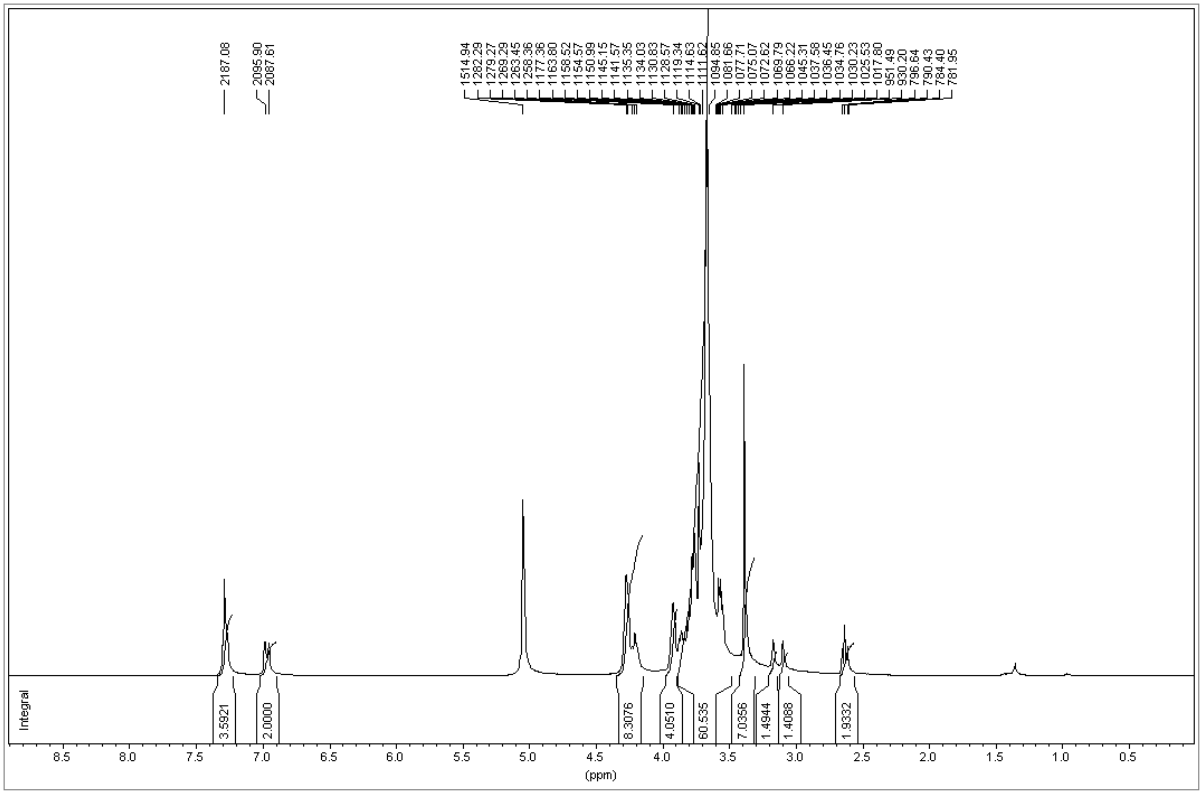


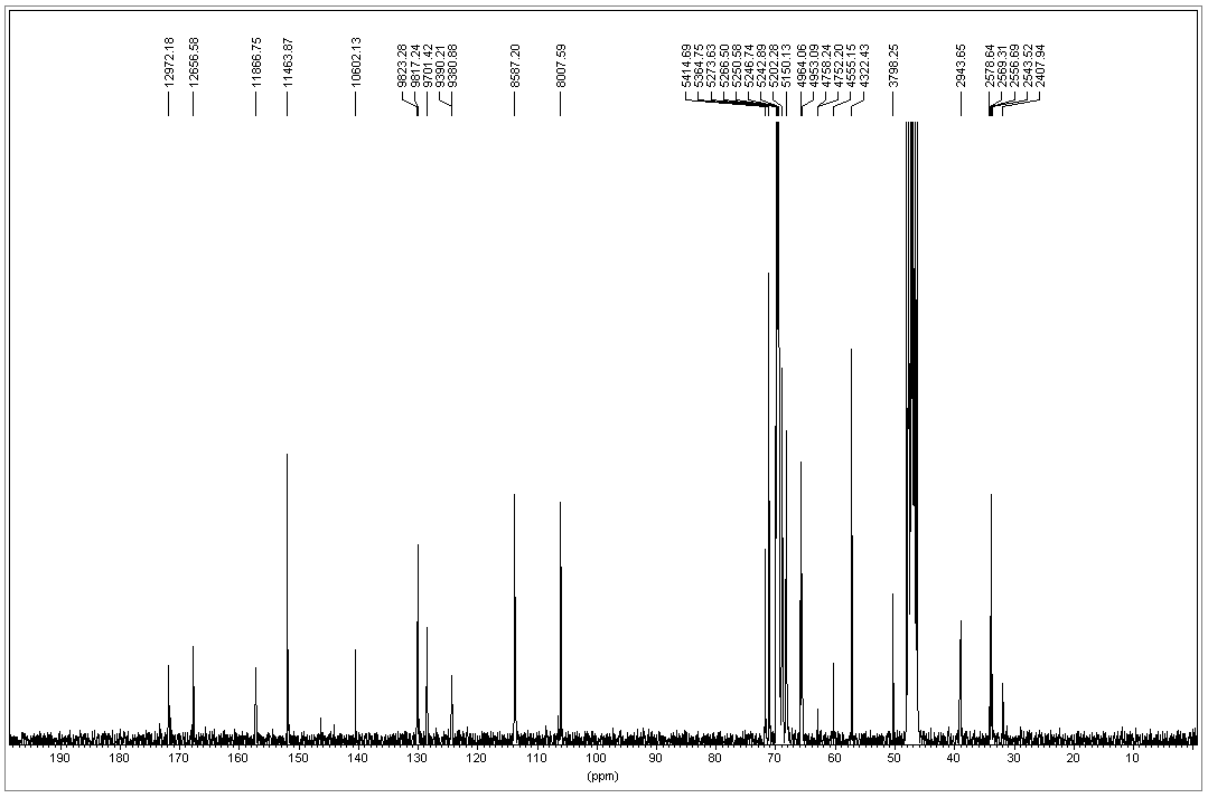

12894.82
12618.74
12056.69
11495.19
10667.48
10621.92
10305.22
10056.58
9763.48
8651.45
8104.22
8004.68
7898.39
6072.28
5925.83
5451.79
5419.12
5324.71
5304.40
5256.10
5206.15
5043.13
5025.57
4691.85
4668.56
4655.27
4445.96
2968.93
2731.26
2597.89
2460.67
2115.97
1237.22
1231.18
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

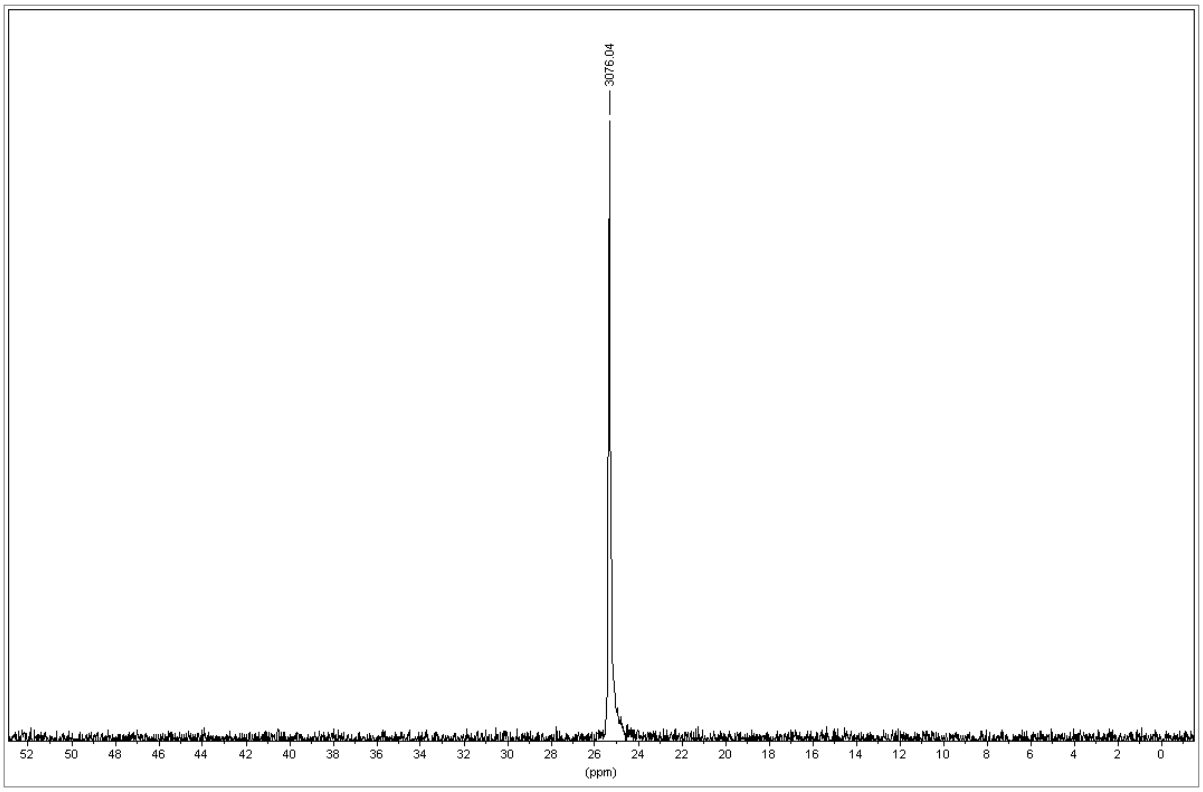

3163.66
2911.20
50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0
(ppm)

Compound 40 (^{1}H, ^{13}C and ^{31}P, CD_3OD)

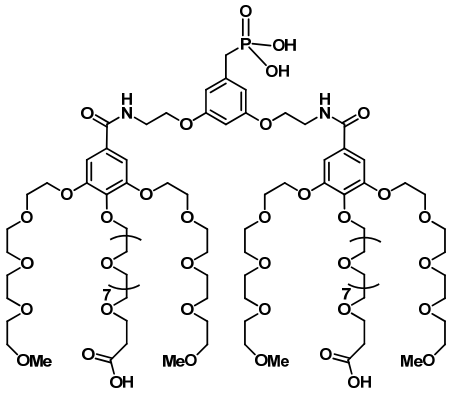


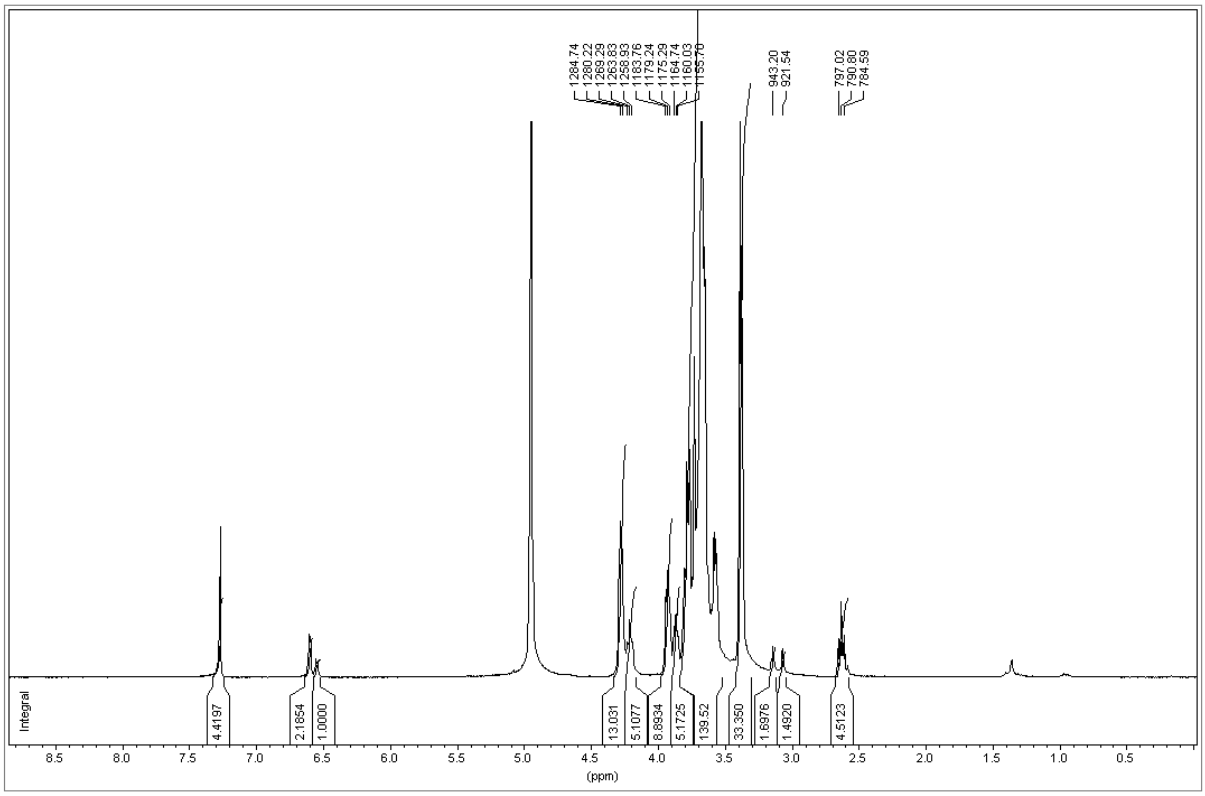


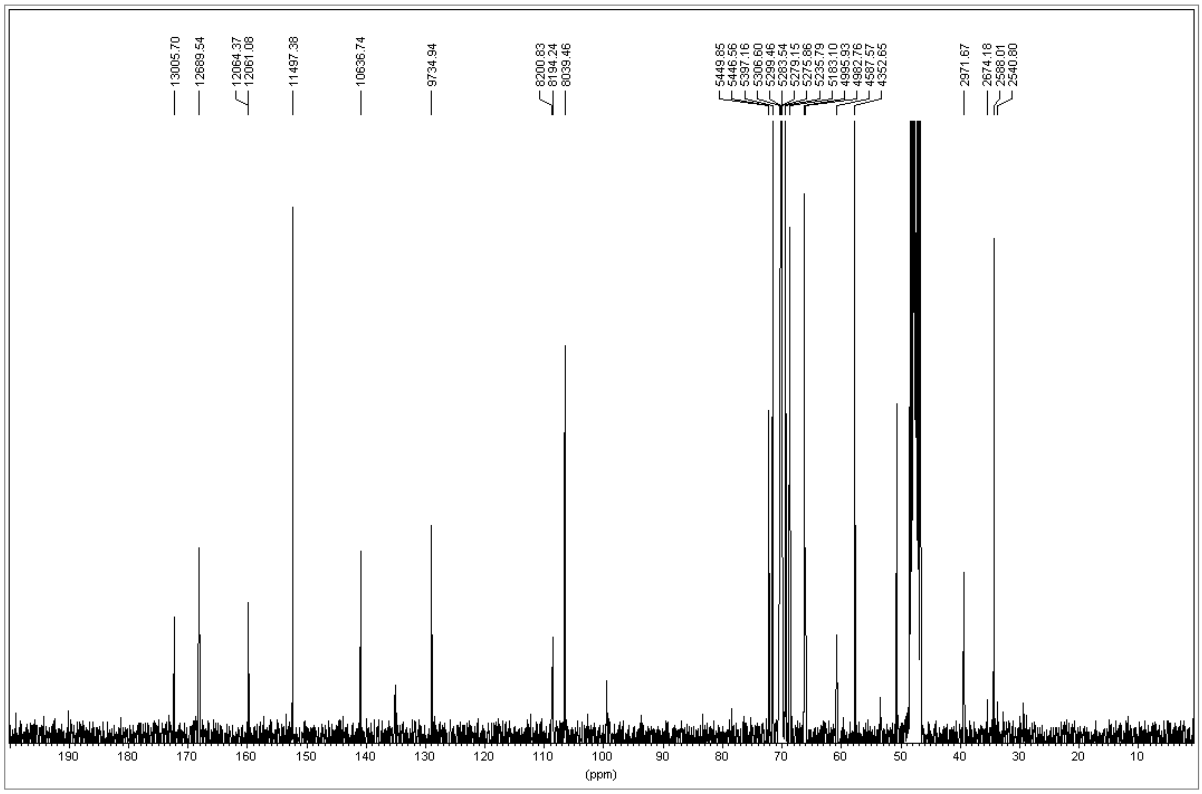

12972.18
12656.58
11866.75
11463.67
10602.13
9823.28
9617.24
9470.42
9390.21
9380.88
8587.20
8007.59
5414.69
5364.75
5273.63
5266.50
5236.58
5234.74
5242.89
5202.28
5150.13
4964.06
4953.09
4758.24
4752.20
4555.15
4322.43
3798.25
2943.65
2578.64
2568.31
2558.69
2543.52
2407.94
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

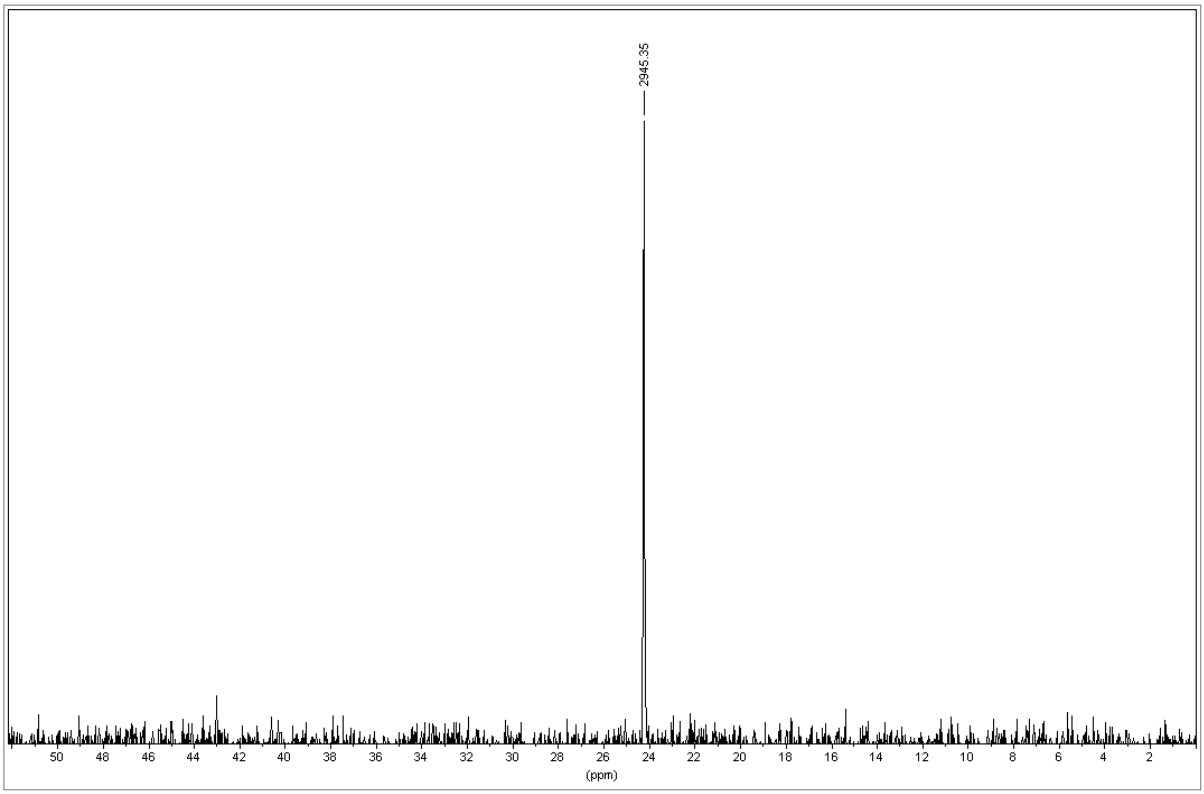

3076.04
52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0
(ppm)

Compound 41 (^{1}H, ^{13}C and ^{31}P, CD_3OD)

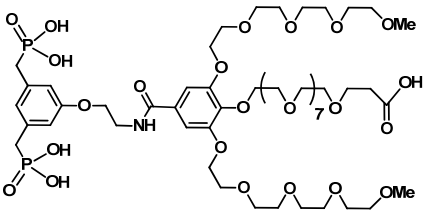


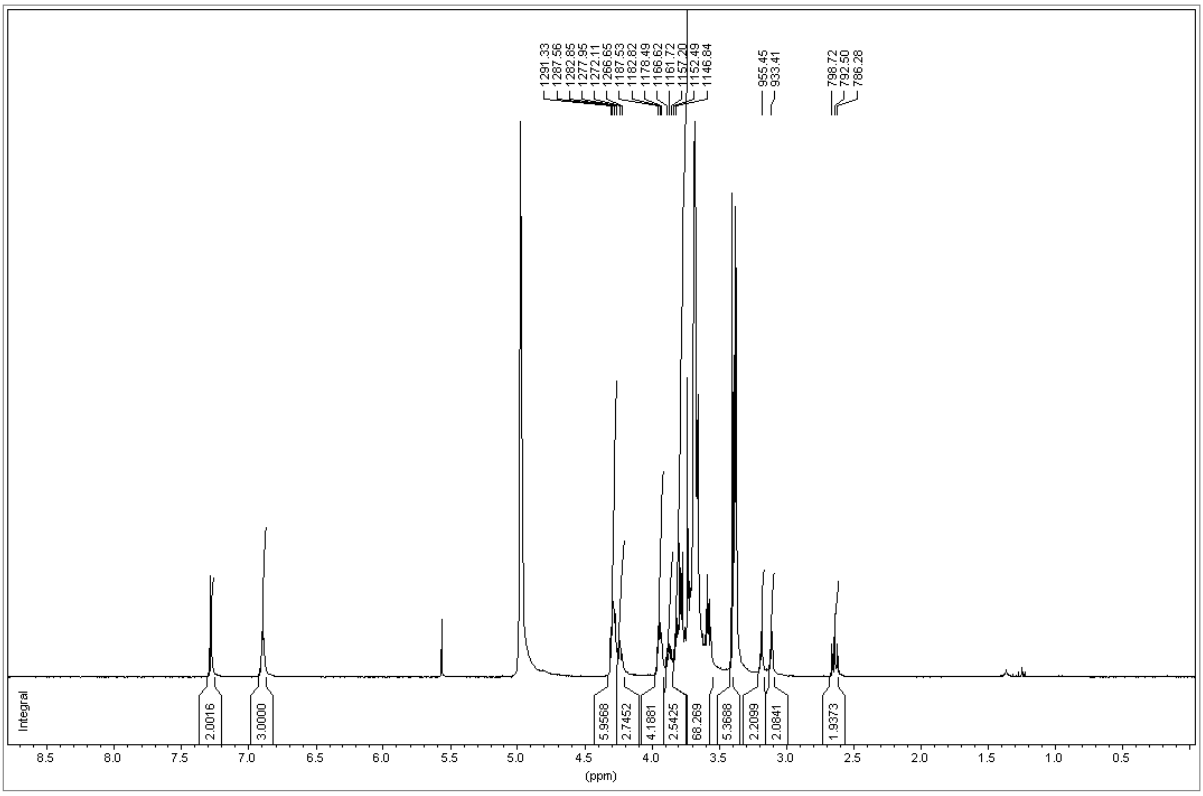


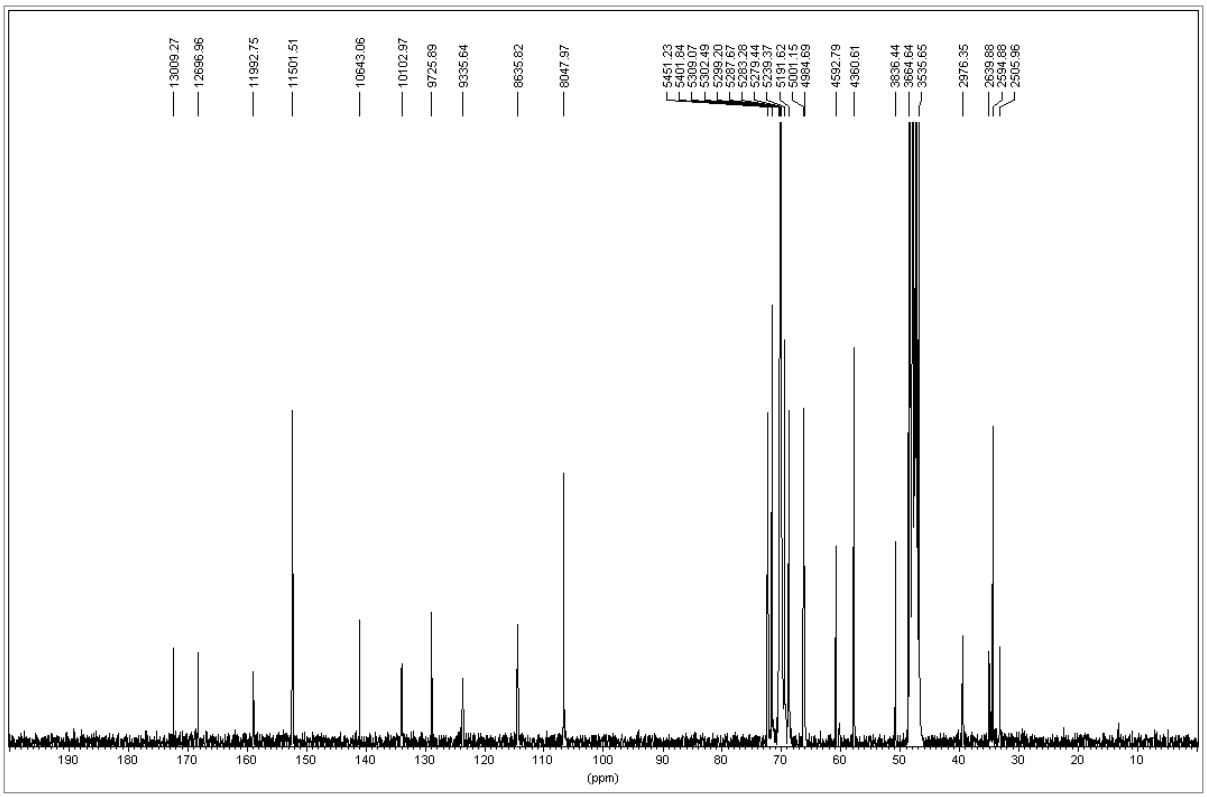

13005.70
12689.54
12064.37
12061.08
11497.38
10636.74
9734.94
8200.83
8194.24
8039.46
5449.85
5446.56
5397.16
5306.60
5288.46
5283.54
5279.15
5275.86
5235.79
5183.10
4995.93
4982.76
4587.57
4552.65
2971.67
2674.18
2568.01
2540.80
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

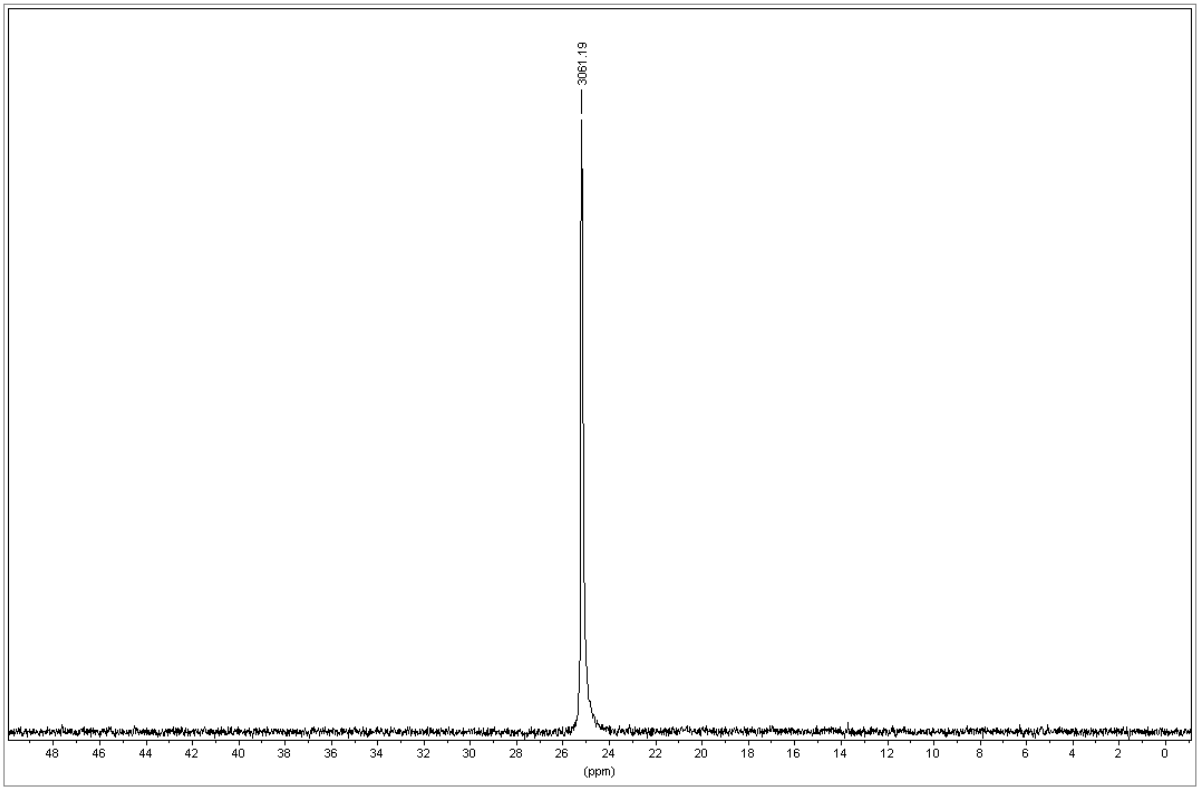

2945.35
50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2
(ppm)

Compound 42 (^{1}H, ^{13}C and ^{31}P, CD_3OD)

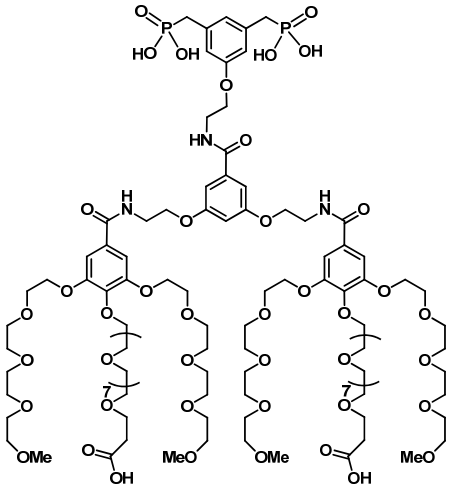


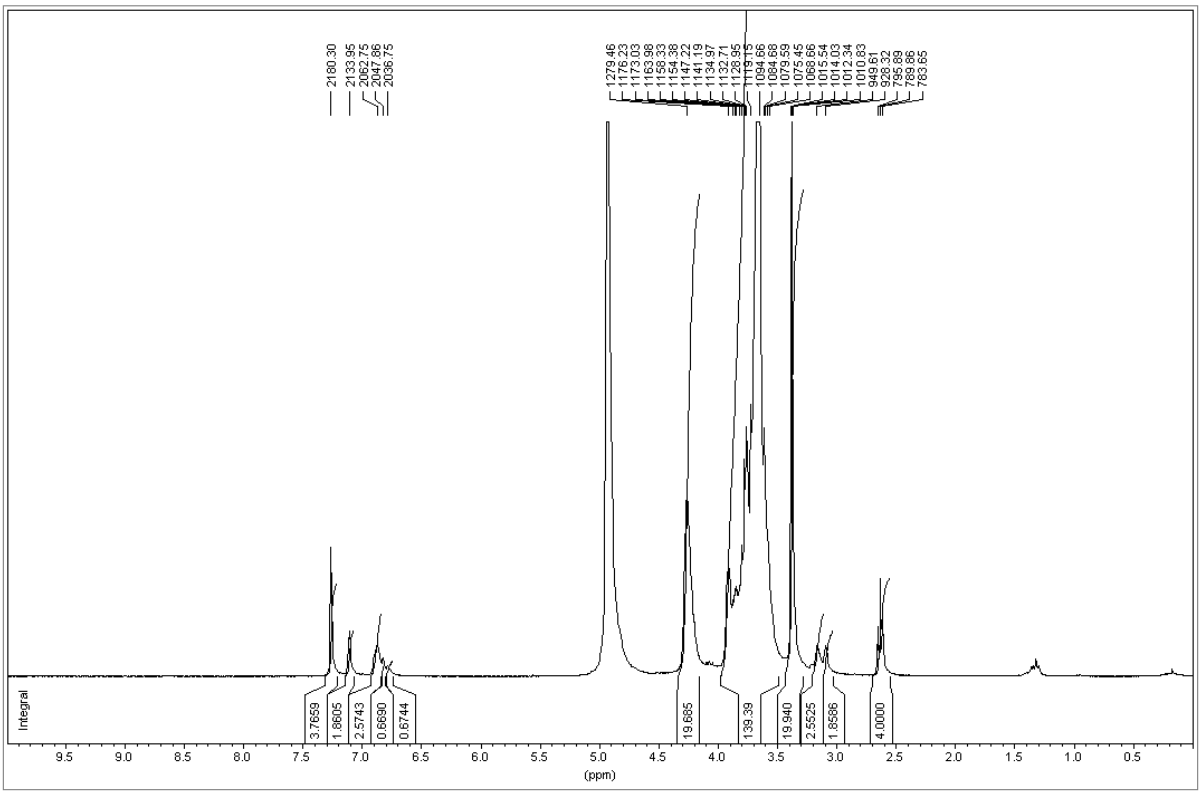


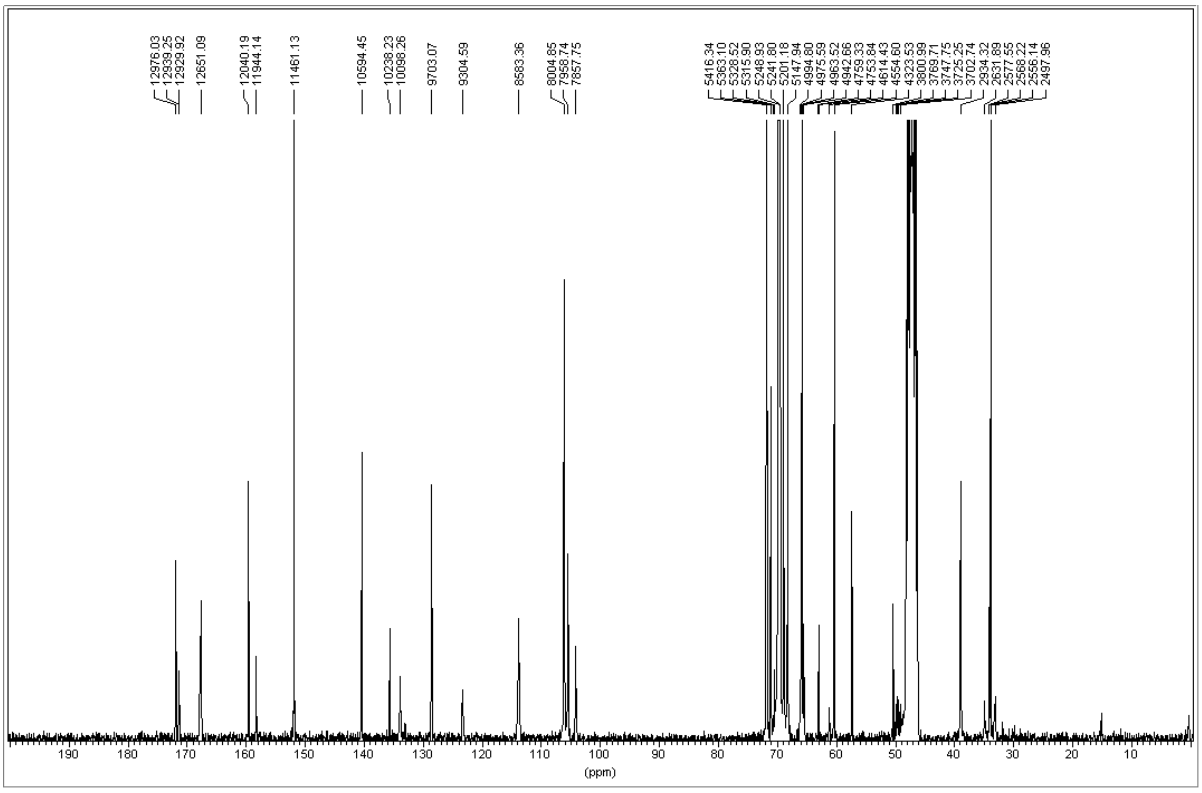

13009.27
12696.96
11992.75
11501.51
10643.06
10102.97
9725.89
9335.64
8635.82
8047.97
5451.23
5401.84
5369.07
5302.49
5298.20
5287.67
5283.28
5279.44
5239.37
5191.62
5001.15
4964.69
4592.79
4360.61
3838.44
3664.64
3535.65
2976.35
2639.88
2594.88
2505.96
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

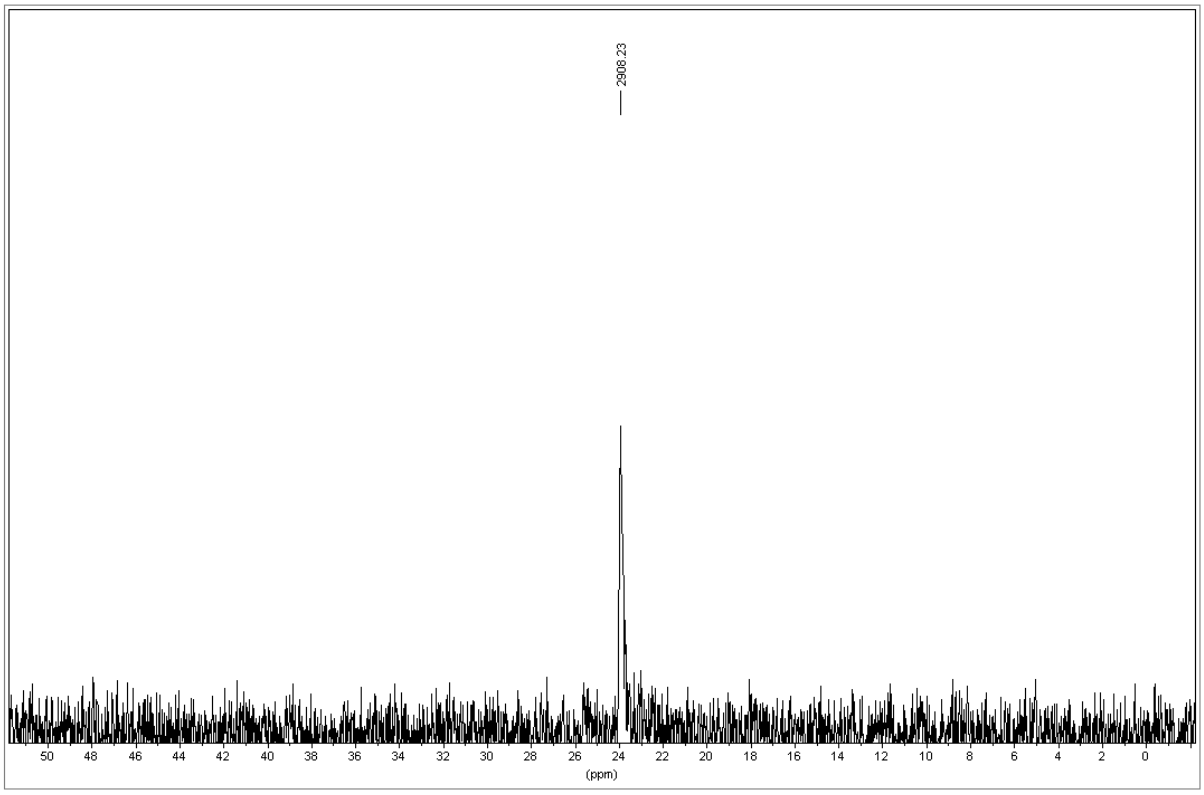

3061.19
48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0
(ppm)

Compound 43 (^{1}H, ^{13}C and ^{31}P, CD_3OD)

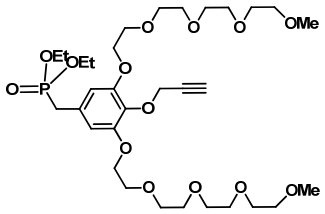


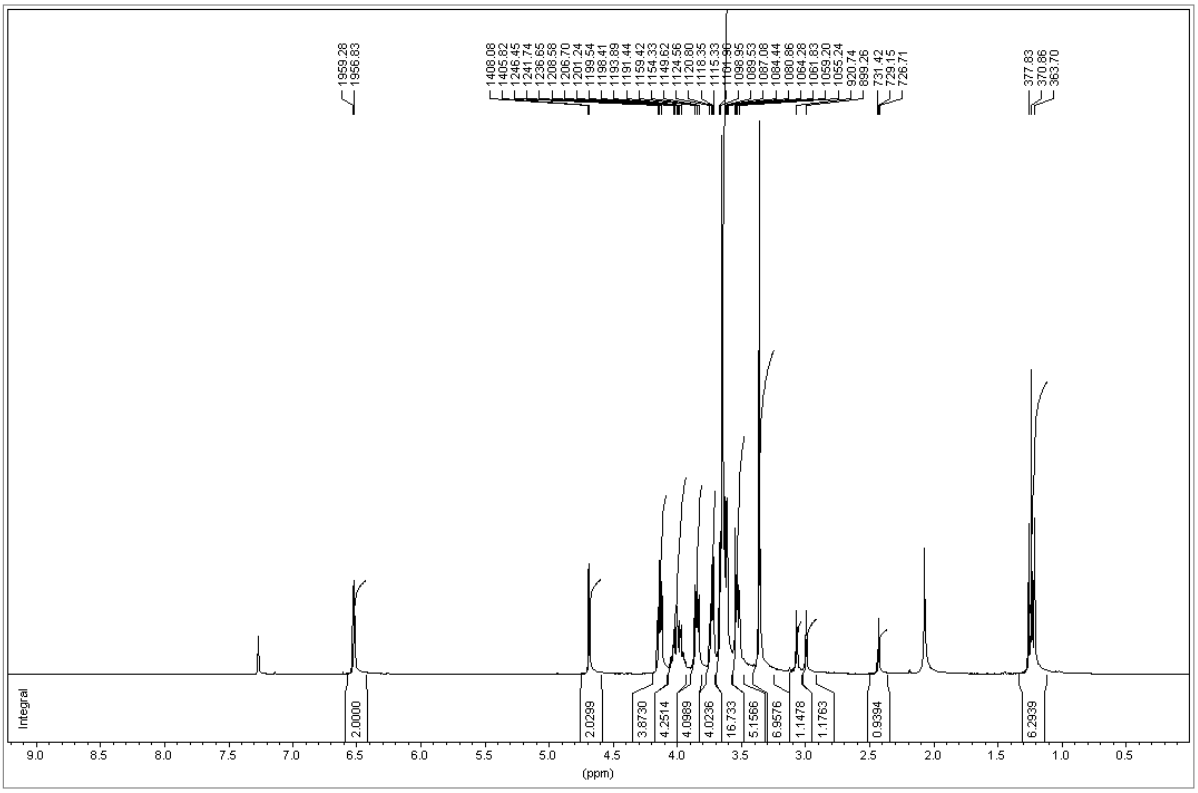


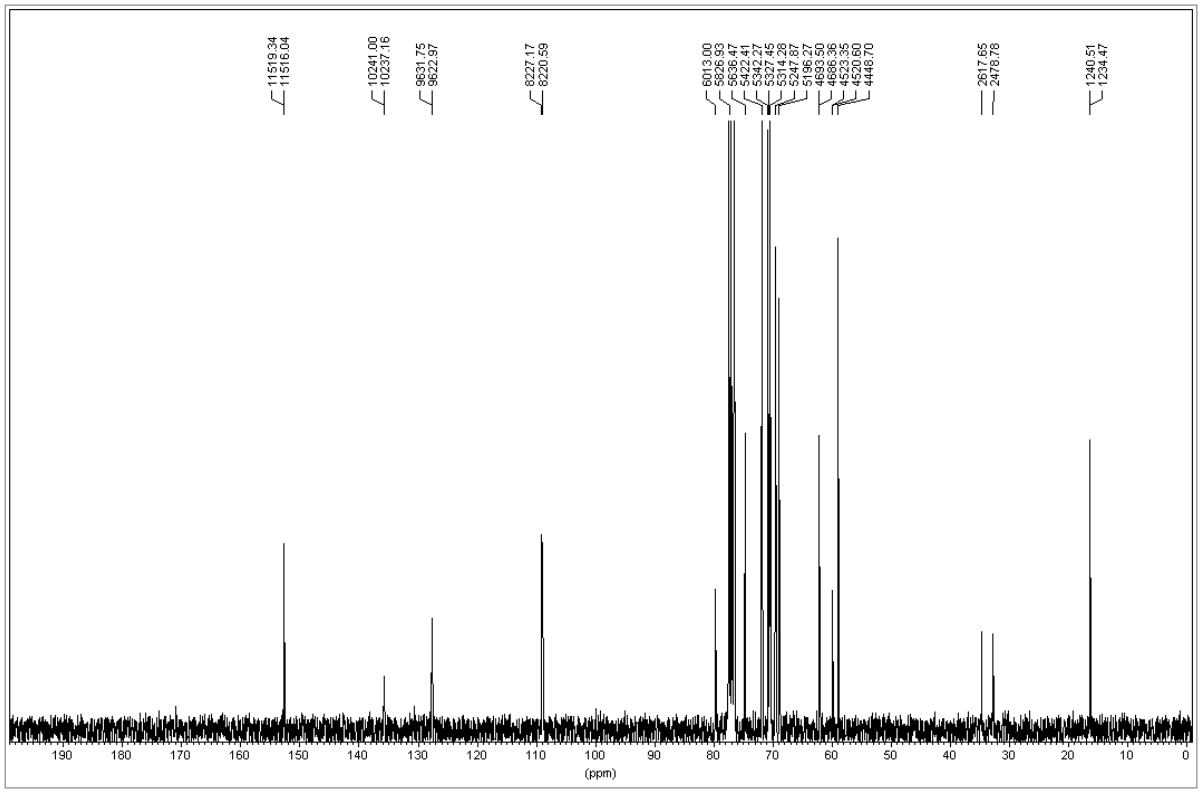

12976.03
12939.25
12929.92
12651.09
12040.19
11944.14
11461.13
10594.45
10238.23
10098.26
9703.07
9304.59
8583.36
8004.85
7958.74
7857.75
5416.34
5363.10
5328.52
5315.90
5248.93
5241.80
5201.18
5147.94
5084.60
4975.59
4963.52
4942.66
4759.33
4753.84
4614.43
4554.60
4323.53
3980.39
3969.71
3747.75
3725.25
3702.74
2934.32
2631.89
2577.55
2568.22
2555.14
2497.96
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

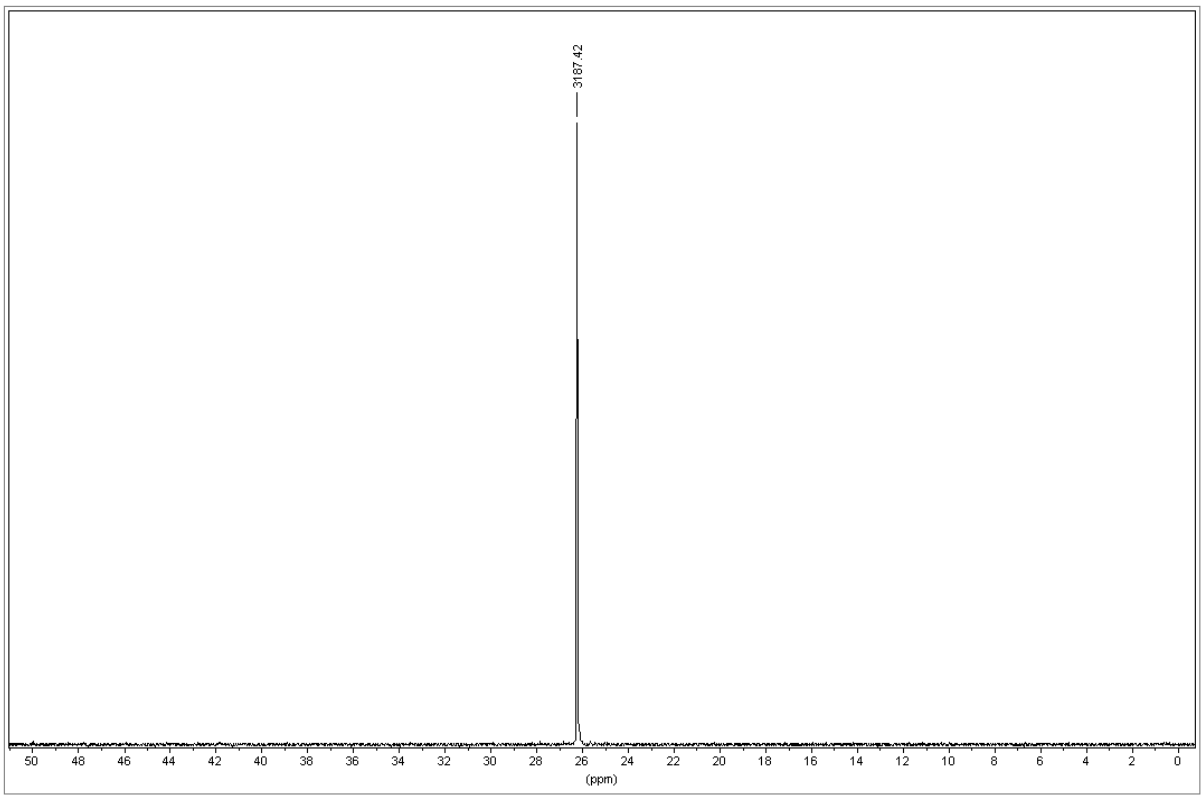

2908.23
50
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
(ppm)

Compound 44 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

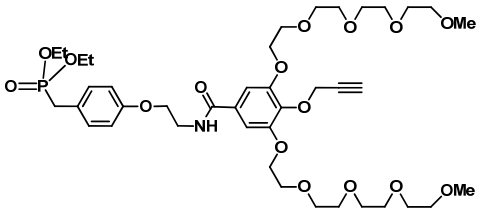


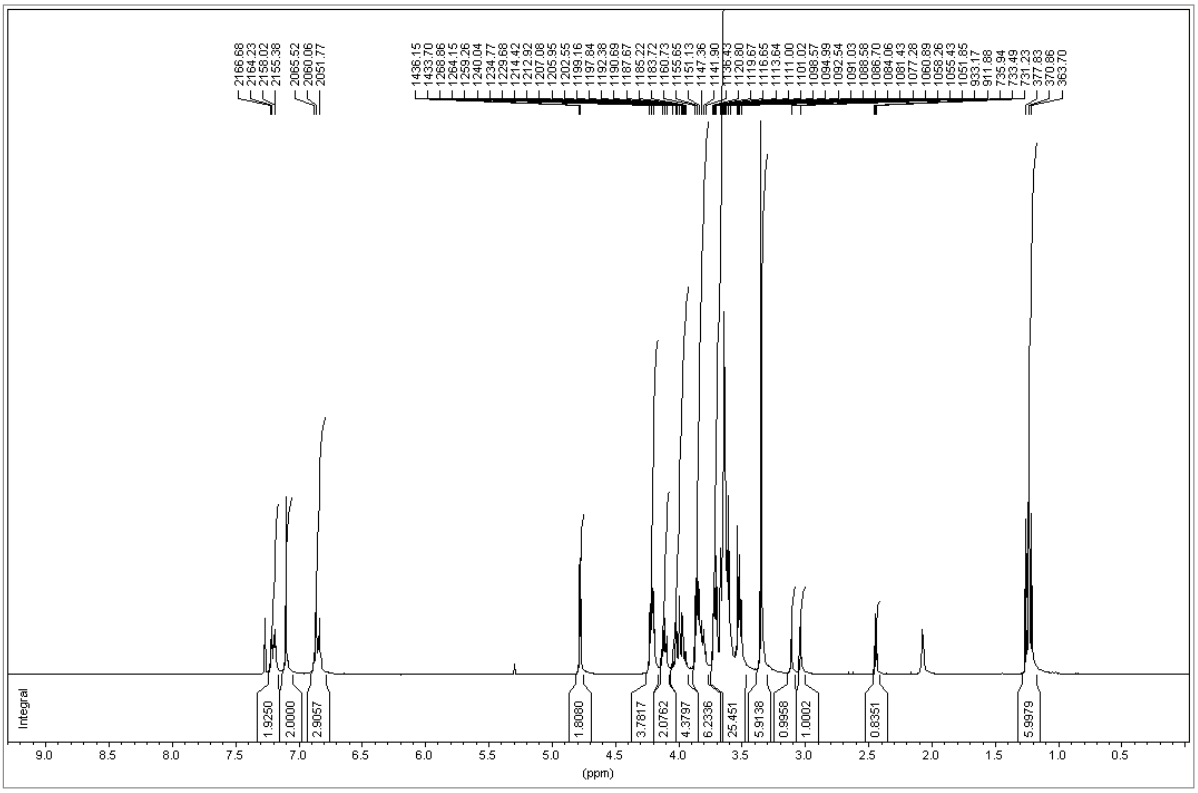


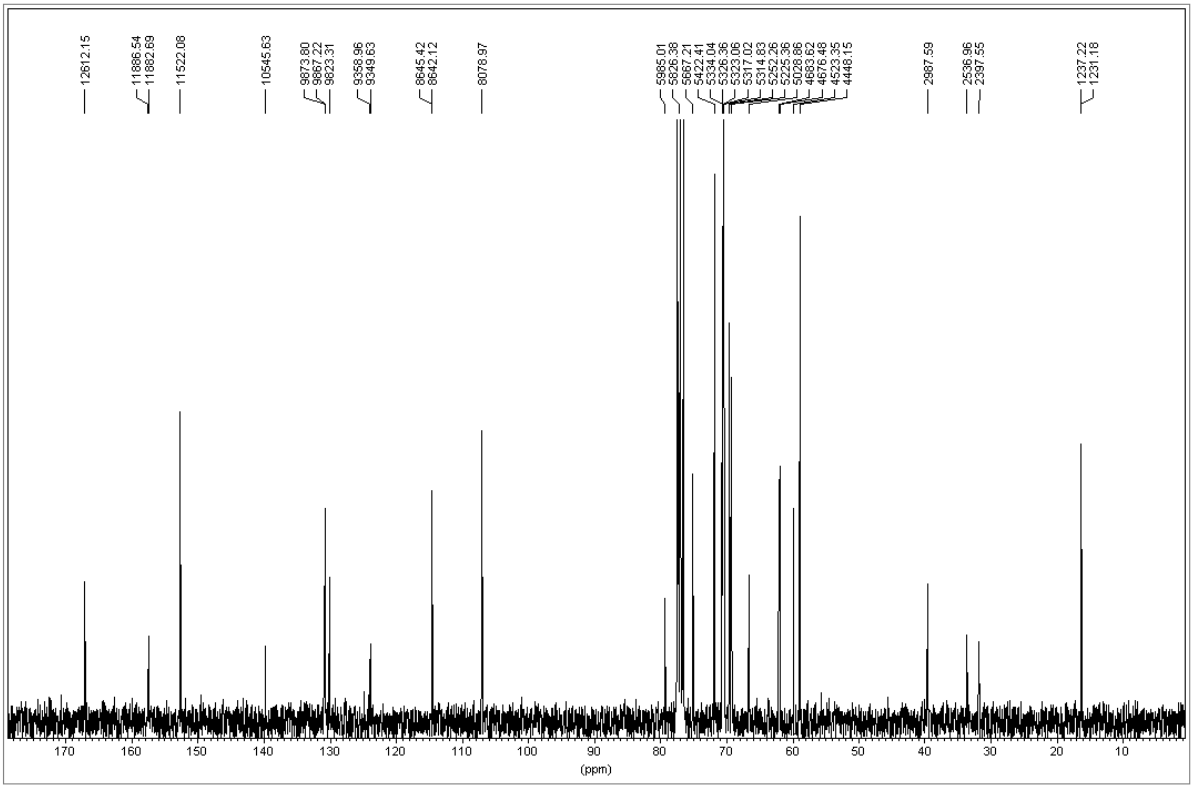

11519.34
11516.04
10241.00
10237.16
9631.75
9622.97
8227.17
8220.59
6013.00
5816.93
5636.47
5422.41
5342.27
5327.45
5314.28
5247.87
5196.27
4693.50
4553.36
4520.60
4448.70
2617.65
2478.76
1240.51
1234.47
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

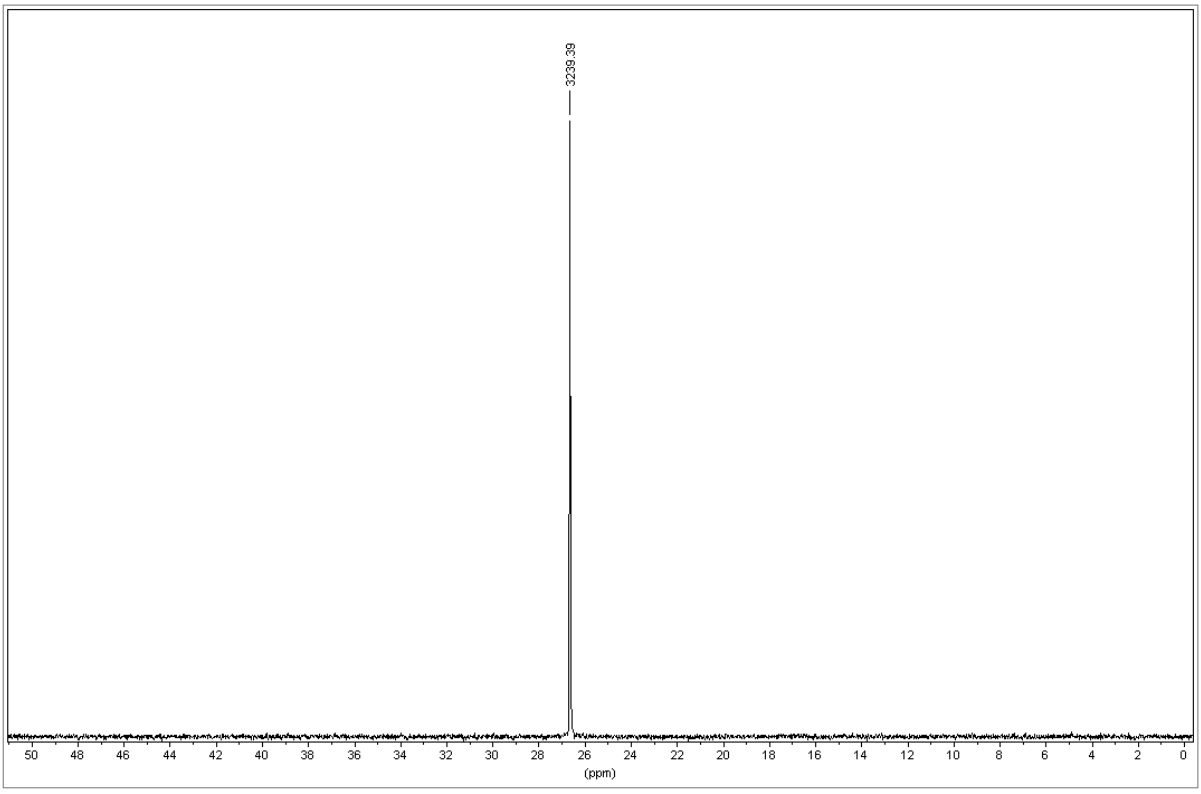

3187.42
50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0
(ppm)

Compound 45 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

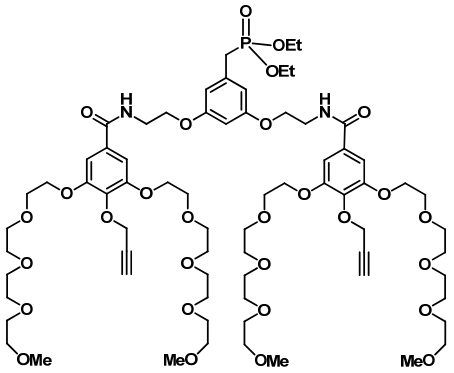


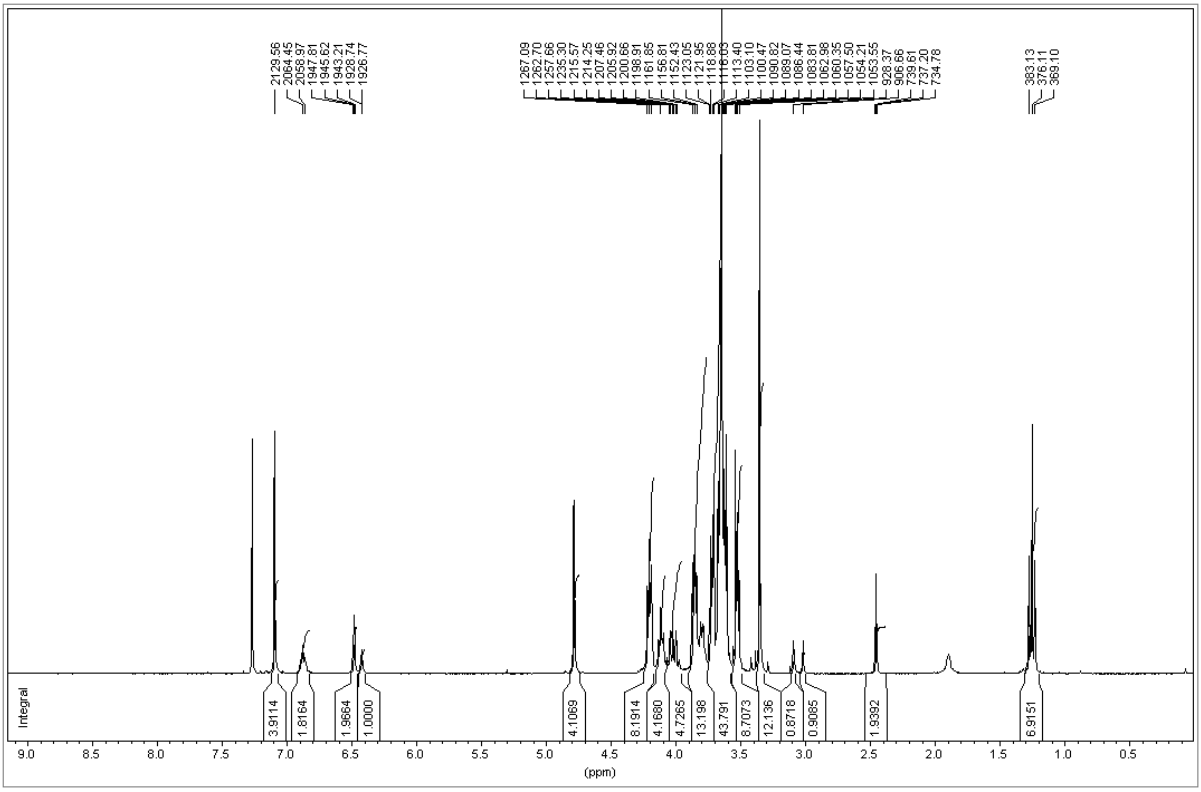


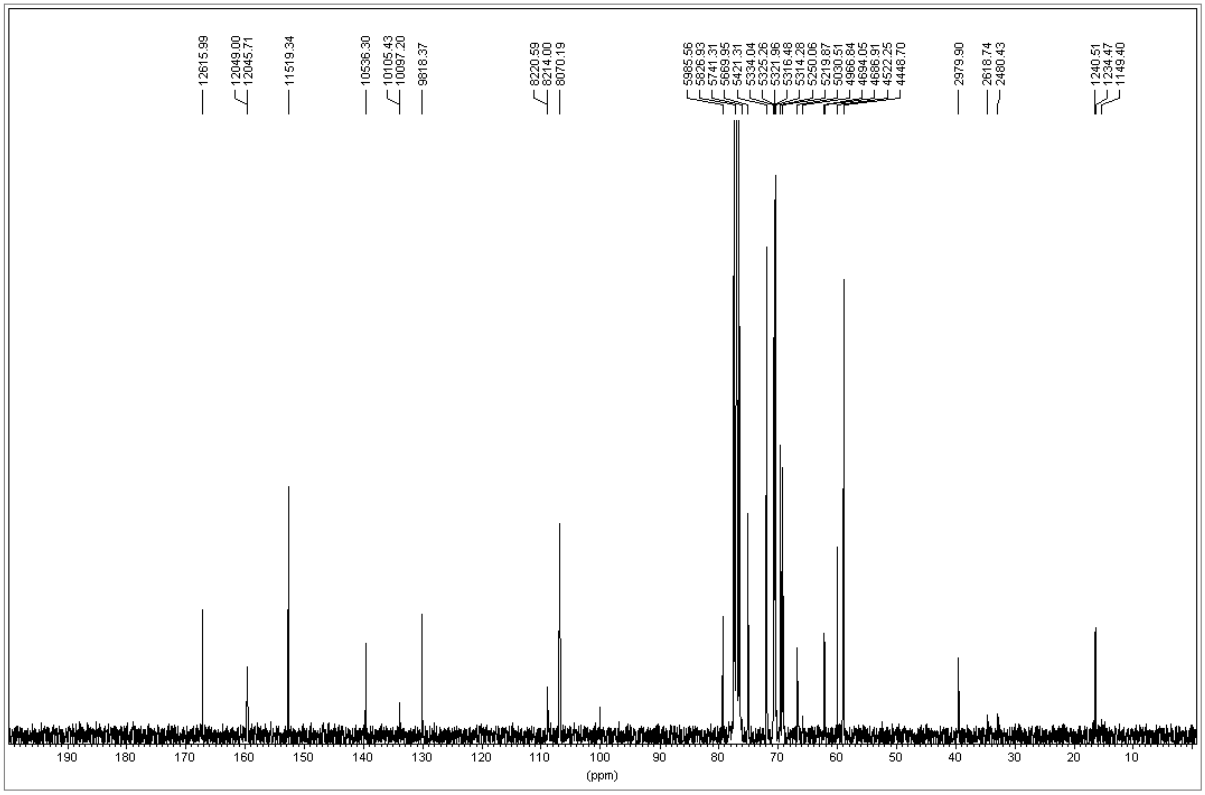

12612.15
11886.54
11882.69
11522.08
10545.63
9873.80
9867.22
9823.31
9358.96
9349.63
8645.42
8642.12
8078.97
5985.01
5685.38
5667.71
5422.41
5334.04
5326.36
5323.06
5317.02
5314.83
5252.26
5226.86
5026.86
4683.62
4676.48
4523.35
4448.15
2987.59
2536.96
2397.55
1237.22
1231.18
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

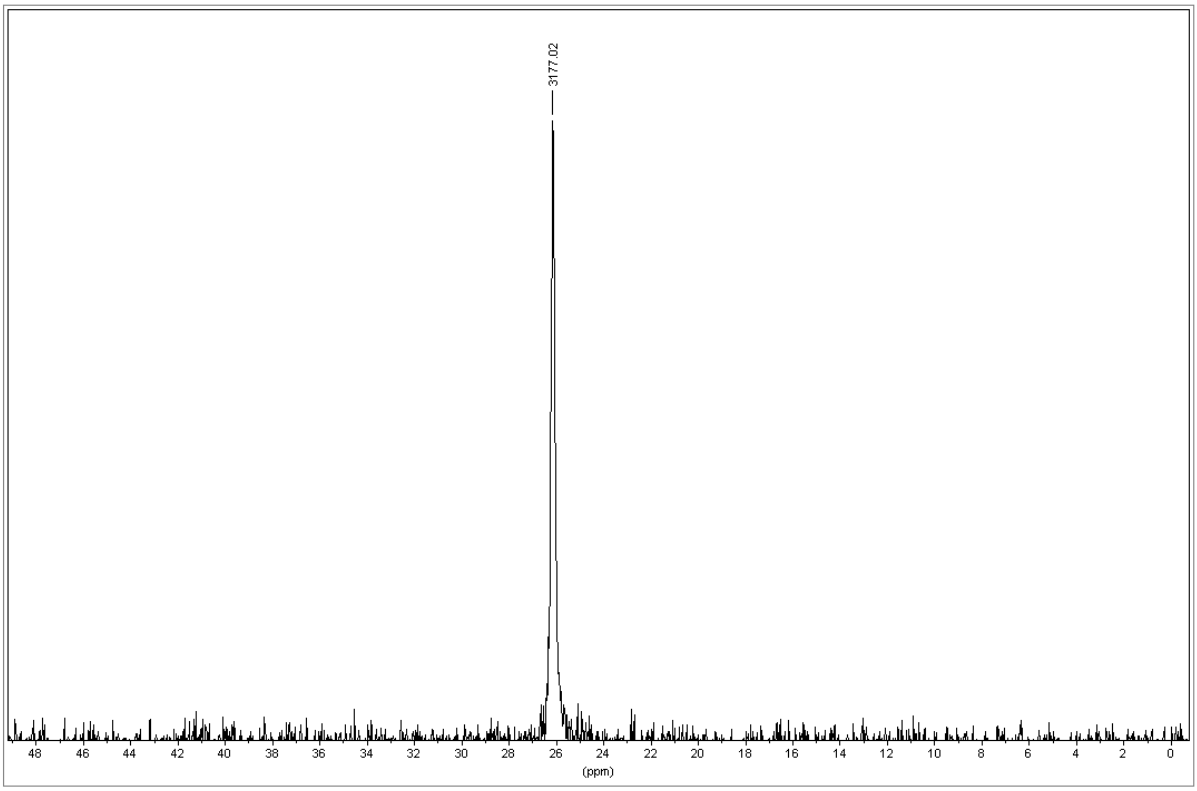

3239.39
50
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
(ppm)

Compound 46 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

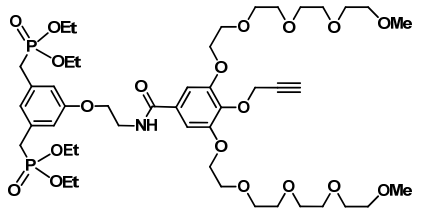


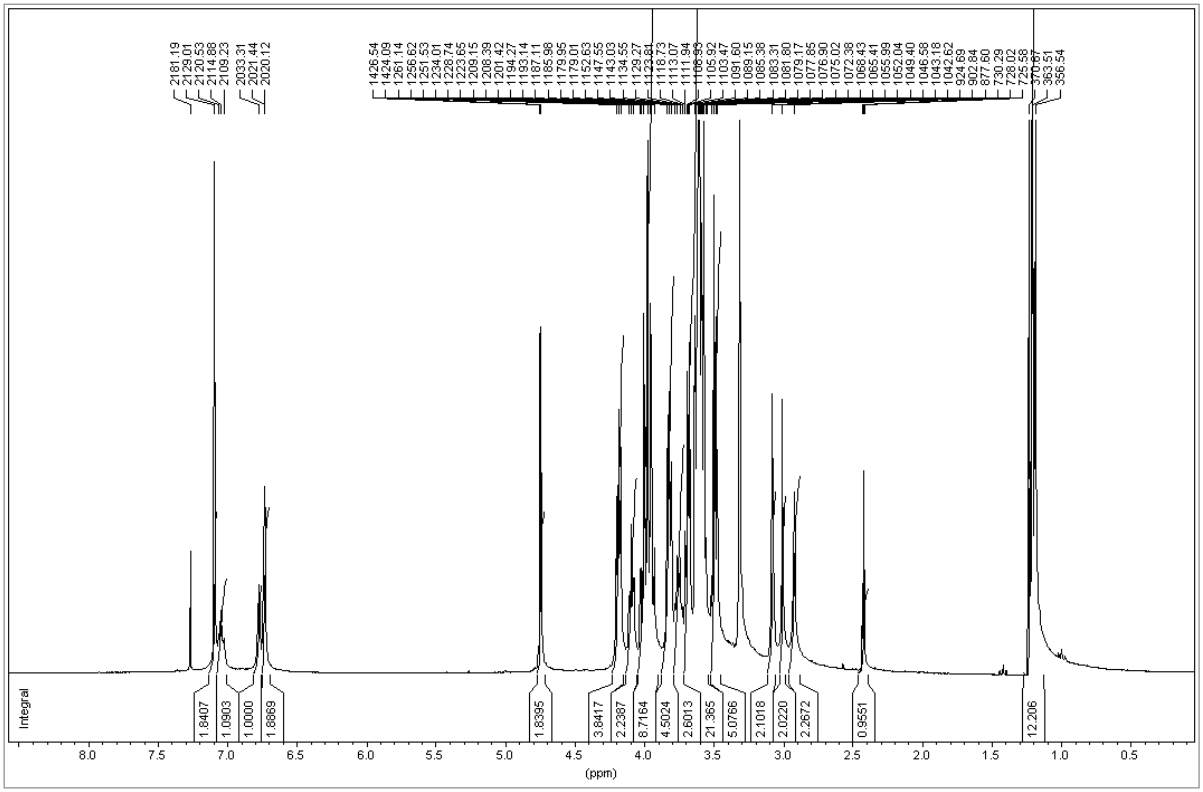


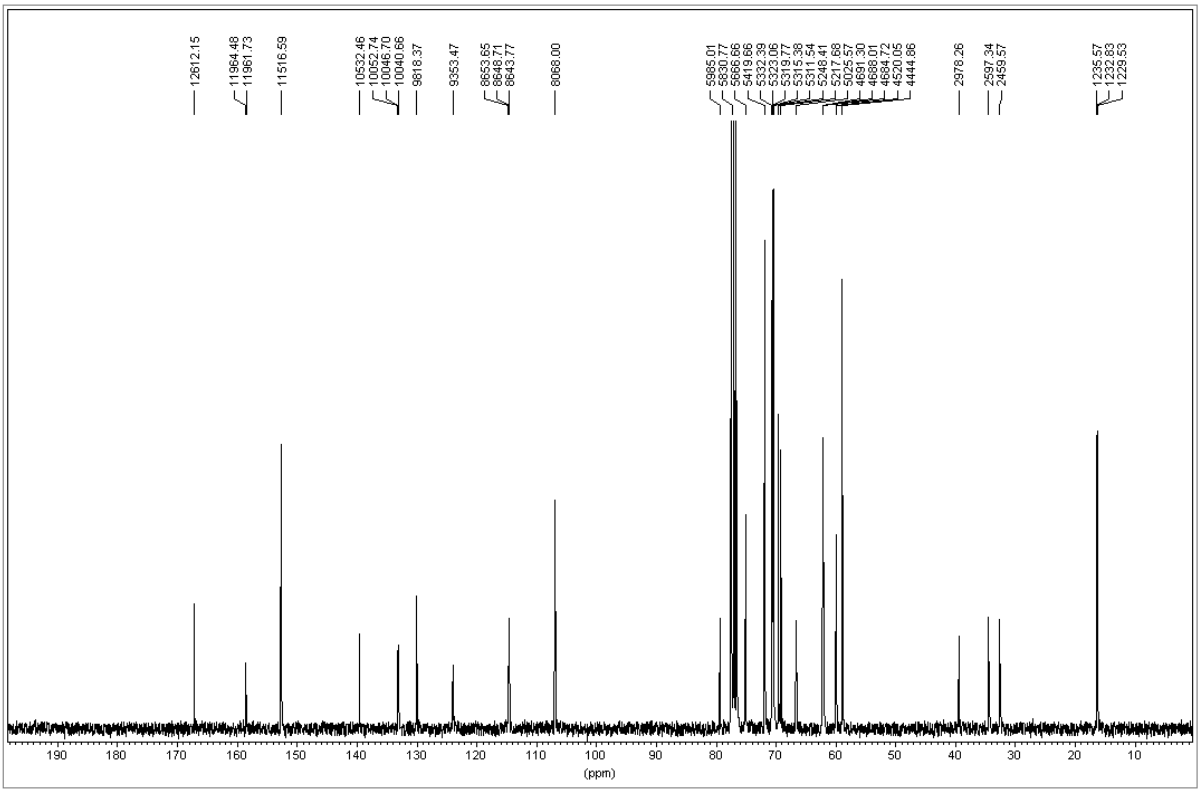

12615.99
12049.00
12045.71
11519.34
10536.30
10105.43
10097.20
9818.37
8220.59
8214.00
8070.19
5985.56
5826.93
5741.31
5669.95
5421.31
5334.04
5325.26
5321.96
5315.48
5314.28
5250.06
5219.87
5030.51
4966.84
4694.05
4686.91
4522.25
4446.70
2979.90
2618.74
2480.43
1240.51
1234.47
1149.40
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

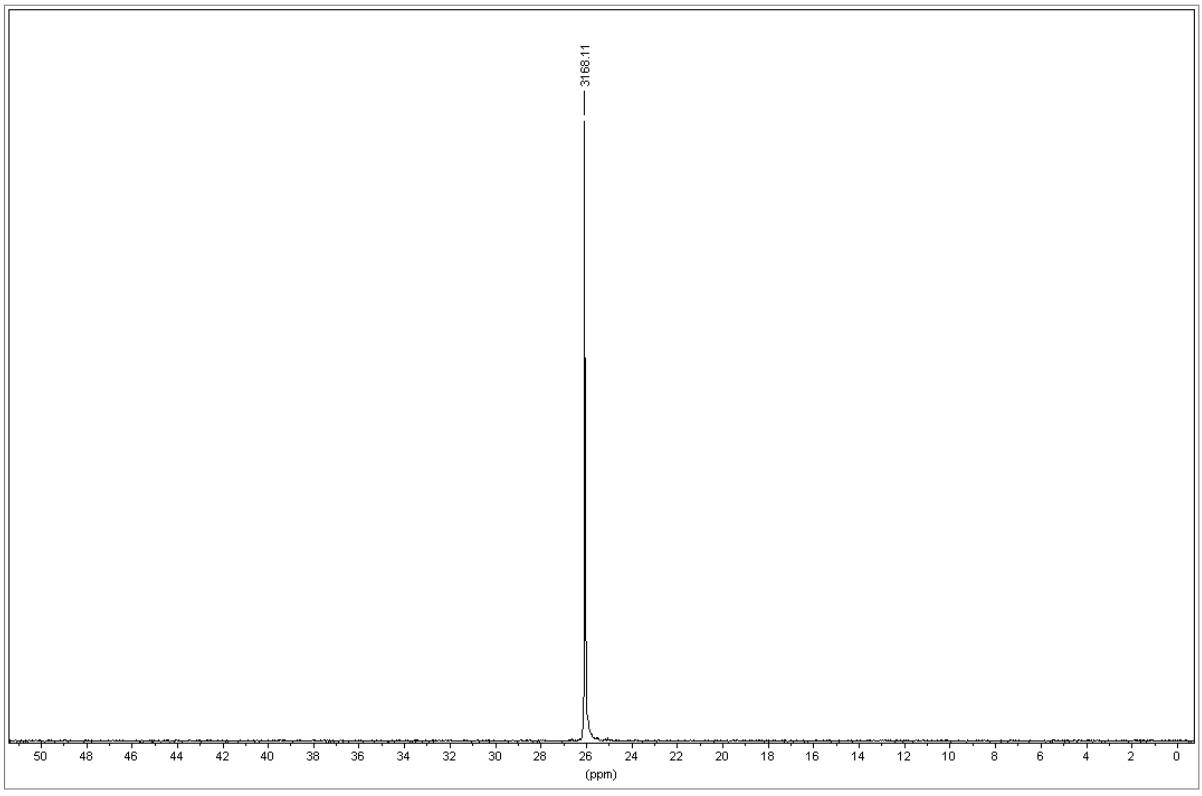

3177.02
48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0
(ppm)

Compound 47 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

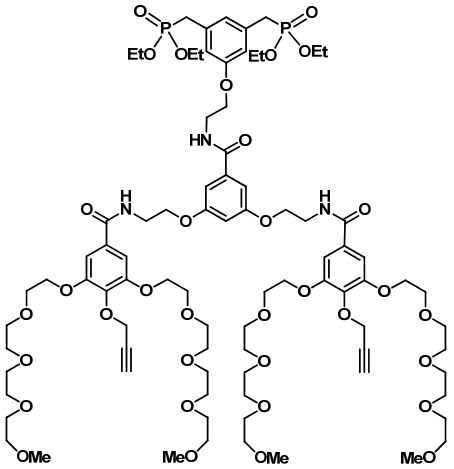


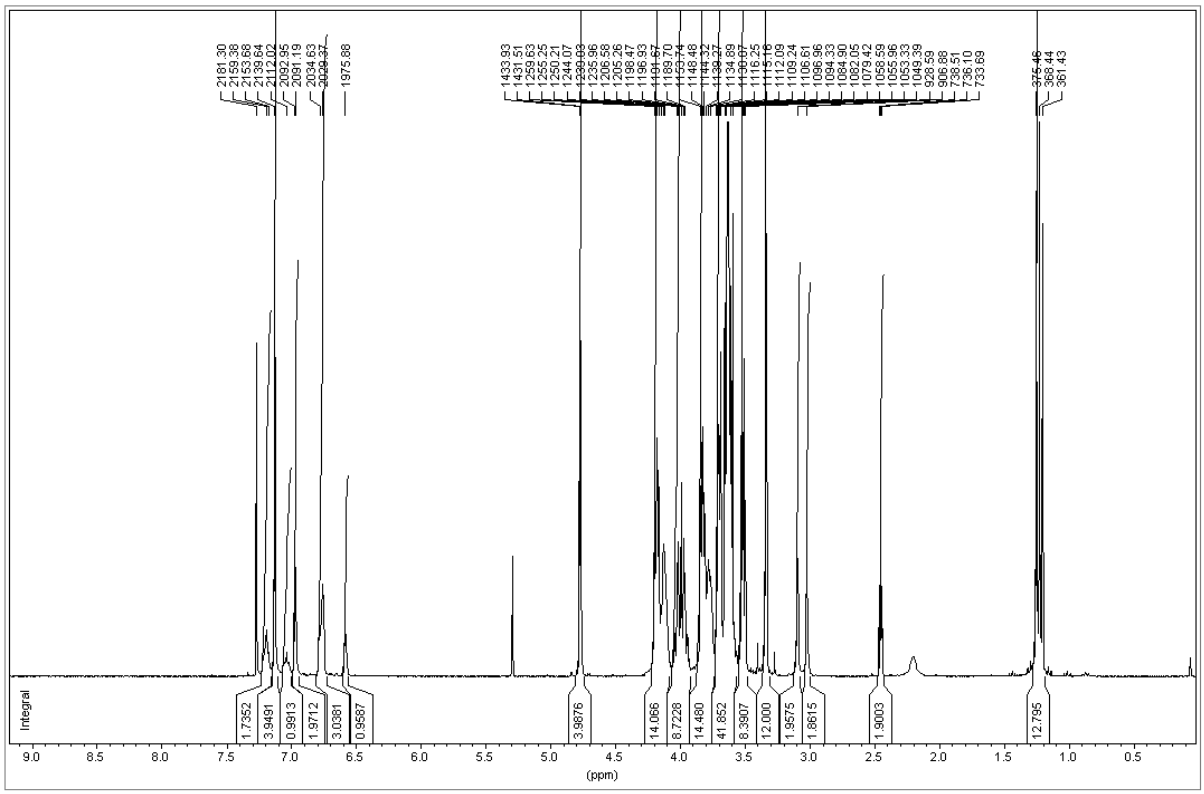


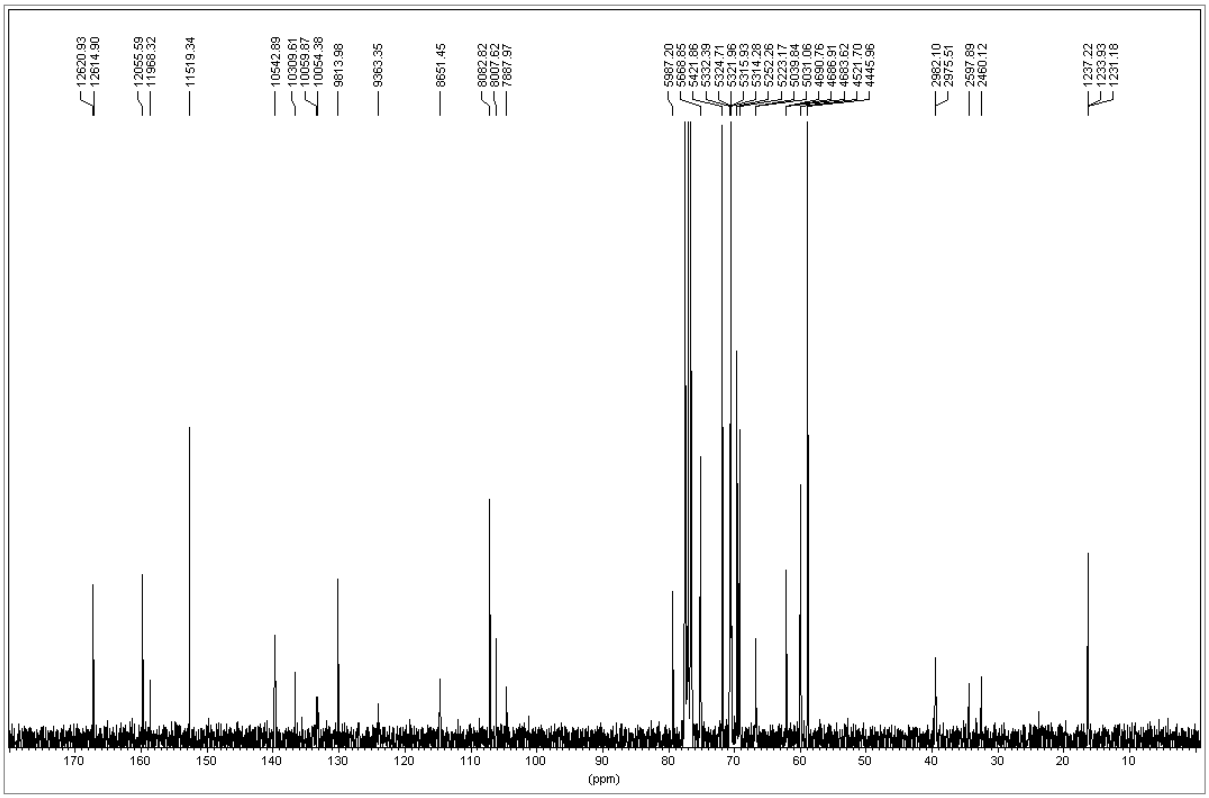

12612.15
11964.48
11961.73
11516.59
10532.46
10052.74
10046.70
10040.66
9818.37
9353.47
8653.65
8648.71
8643.77
8068.00
5985.01
5830.77
5666.66
5419.66
5332.39
5323.06
5319.77
5315.36
5311.54
5248.41
5217.68
5025.57
4691.30
4689.01
4684.72
4520.05
4444.86
2978.26
2597.34
2459.57
1235.57
1233.63
1228.53
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

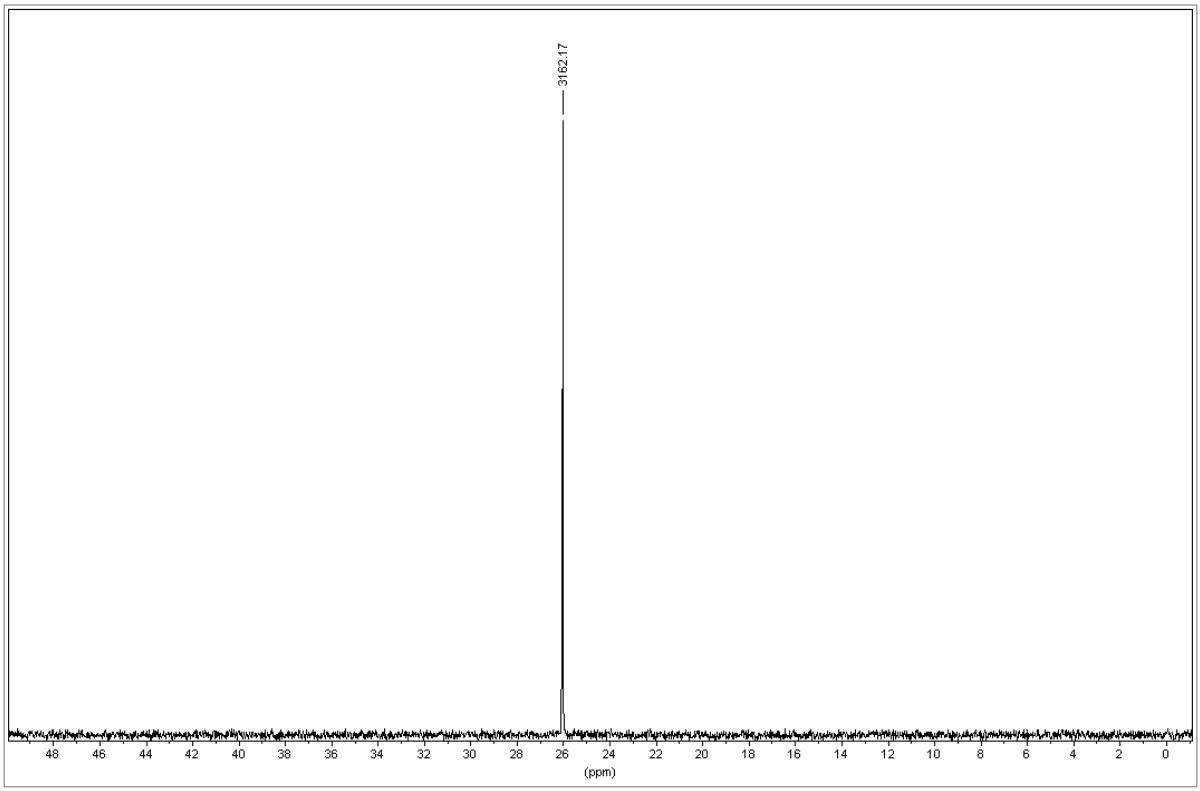

3168.11
50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0
(ppm)

Compound 48 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

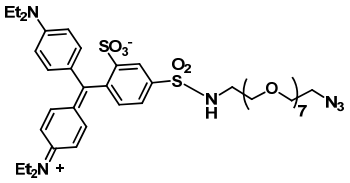


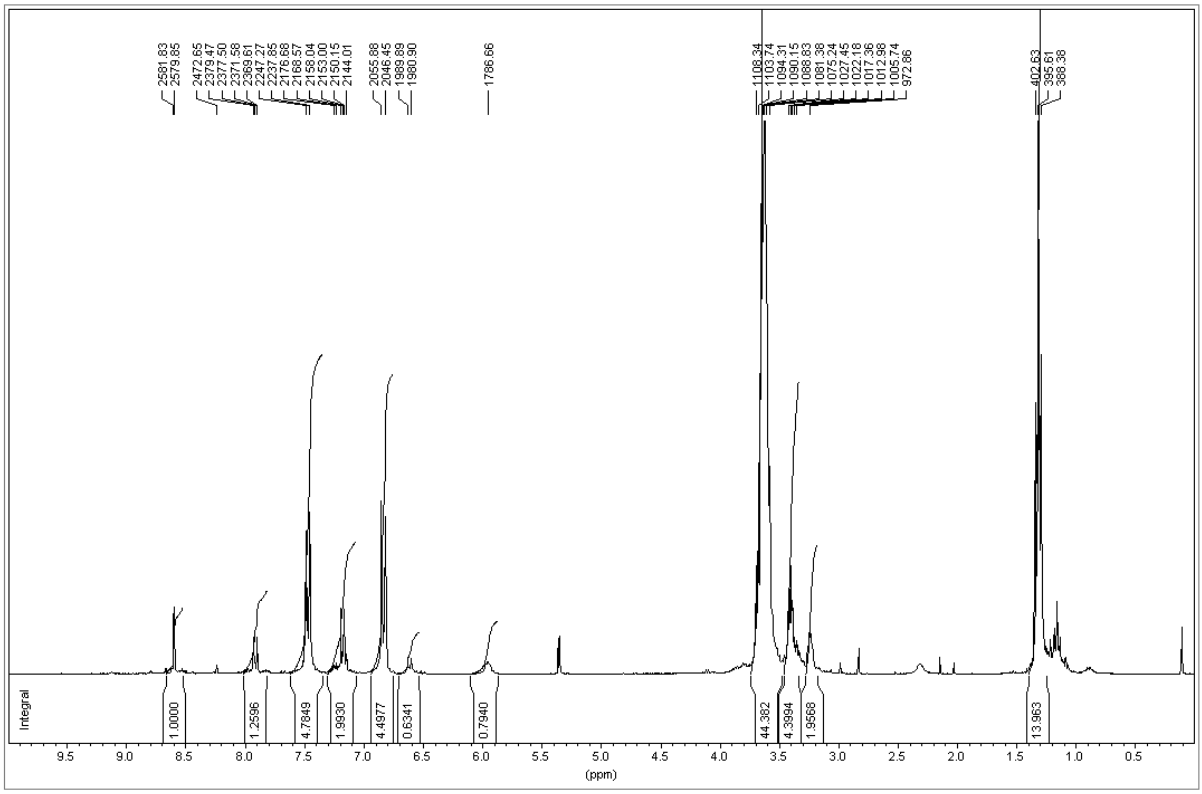


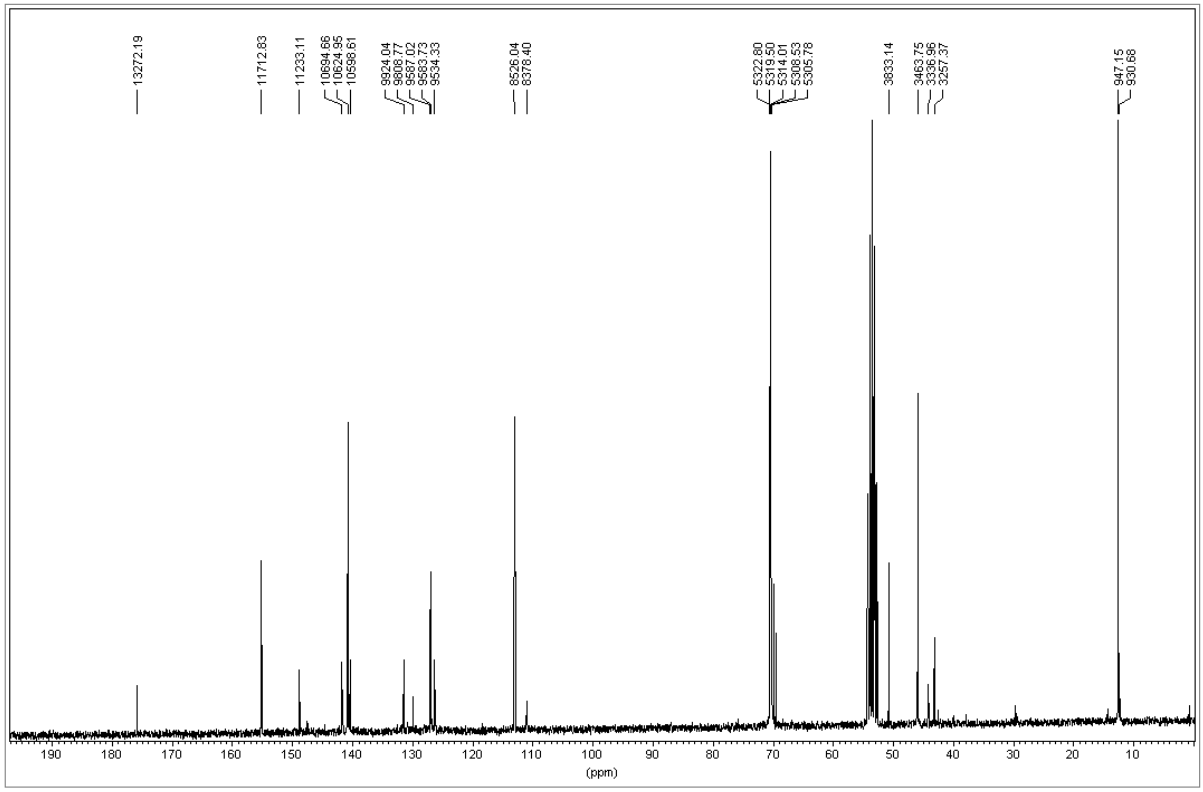

12620.93
12614.90
12055.59
11968.32
11519.34
10542.89
10309.61
10059.87
10054.38
9813.98
9363.35
8651.45
8082.82
8007.62
7887.97
5987.20
5868.85
5421.86
5324.71
5321.96
5315.93
5314.28
5252.26
5223.17
5039.84
5031.06
4690.76
4685.91
4683.62
4521.70
4445.96
2982.10
2975.51
2597.89
2460.12
1237.22
1233.93
1231.16
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)


3162.17
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
(ppm)

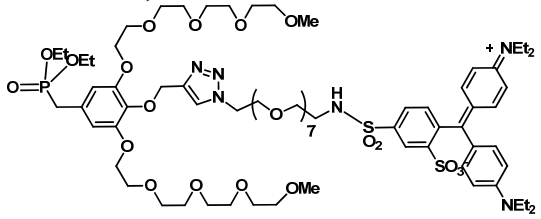
Compound 50 (^{1}H and ^{13}C, CD_2Cl_2)

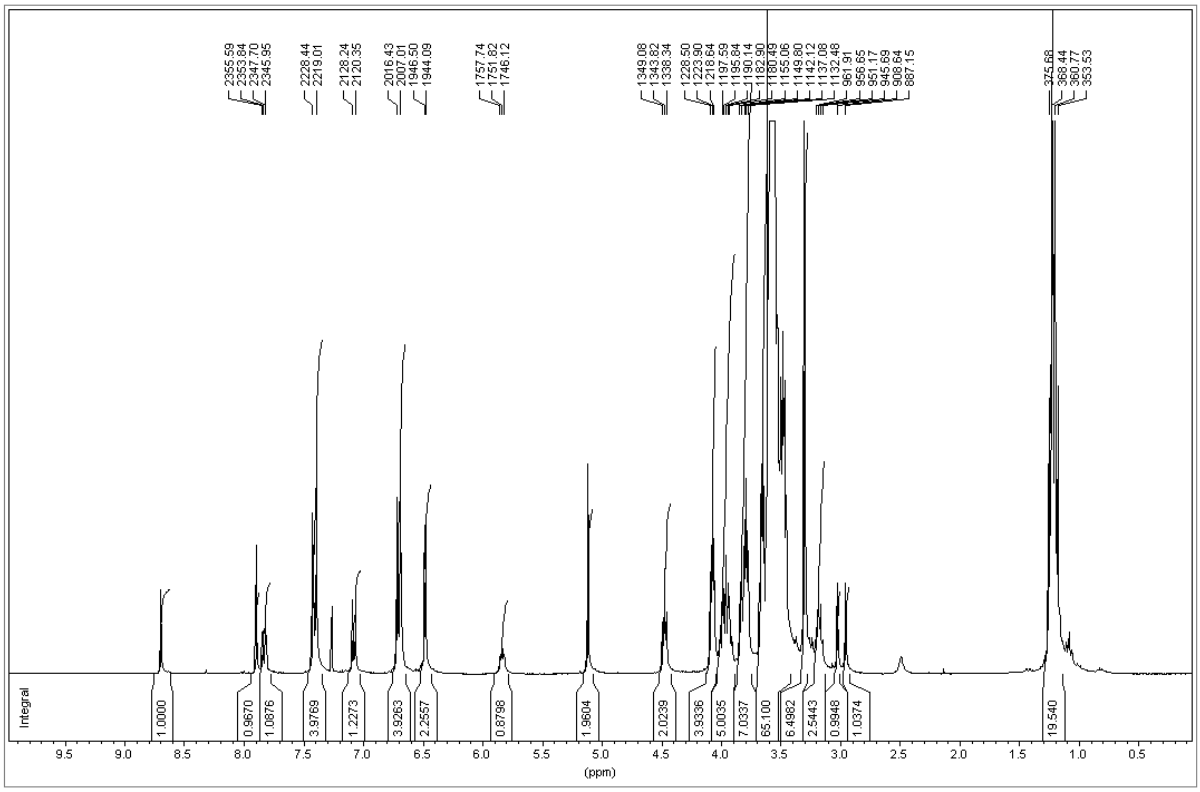


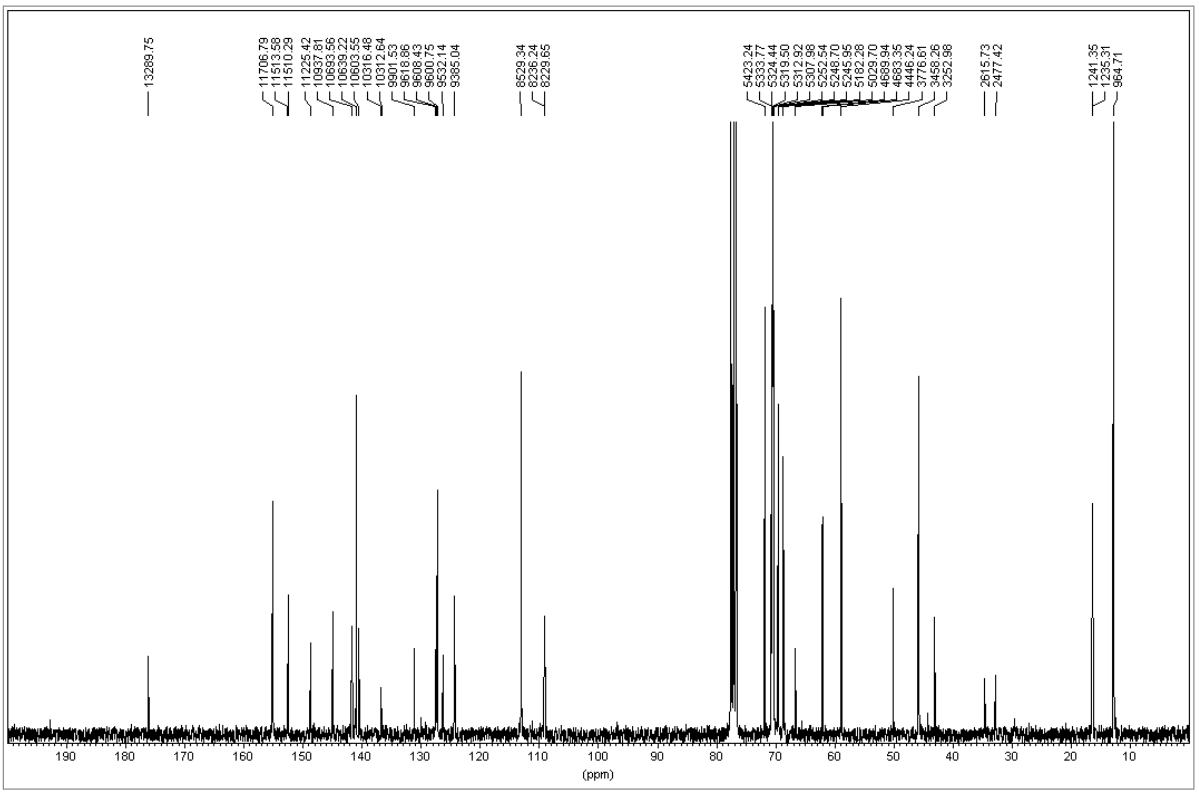


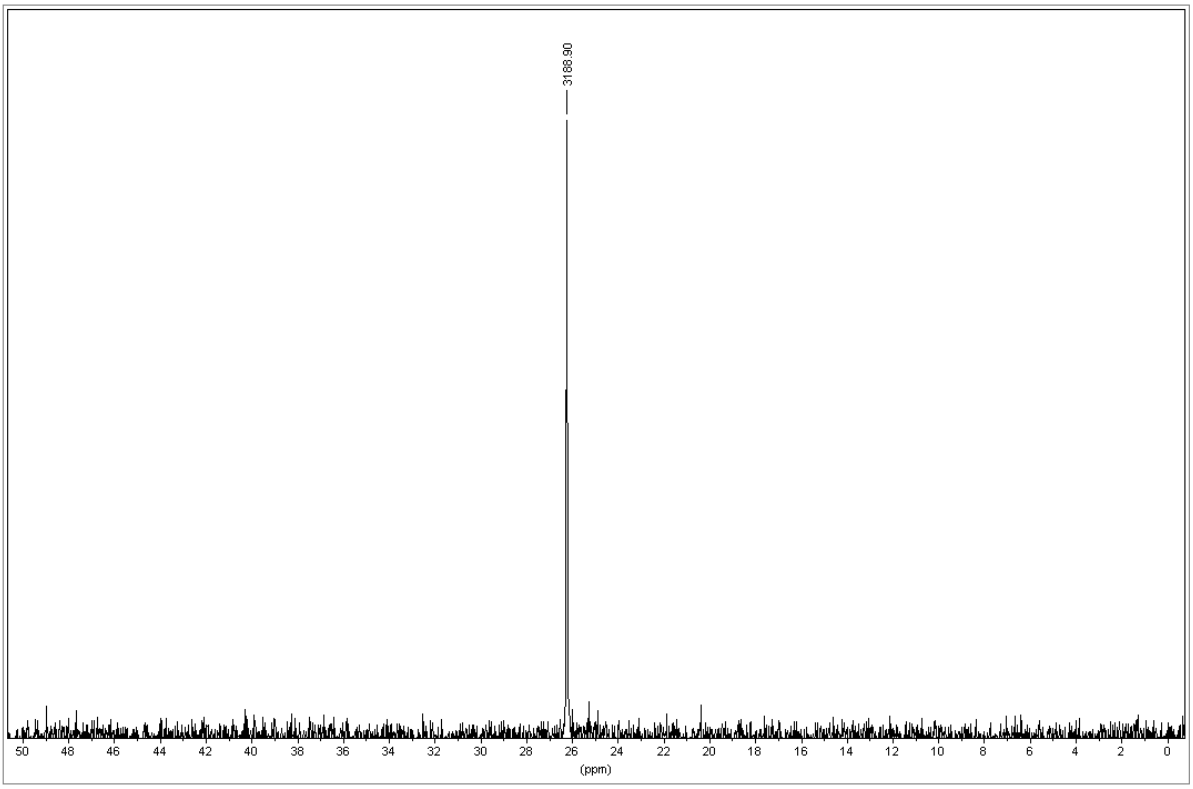

1327.19
1171.83
1123.11
1069.66
1062.95
1059.81
992.77
986.07
958.73
953.33
852.04
837.40
532.80
531.95
531.40
530.85
530.53
530.78
383.14
346.75
333.96
325.37
94.15
93.68
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

Compound 51 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

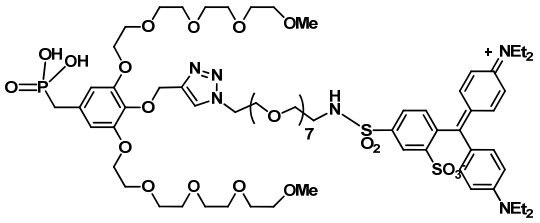


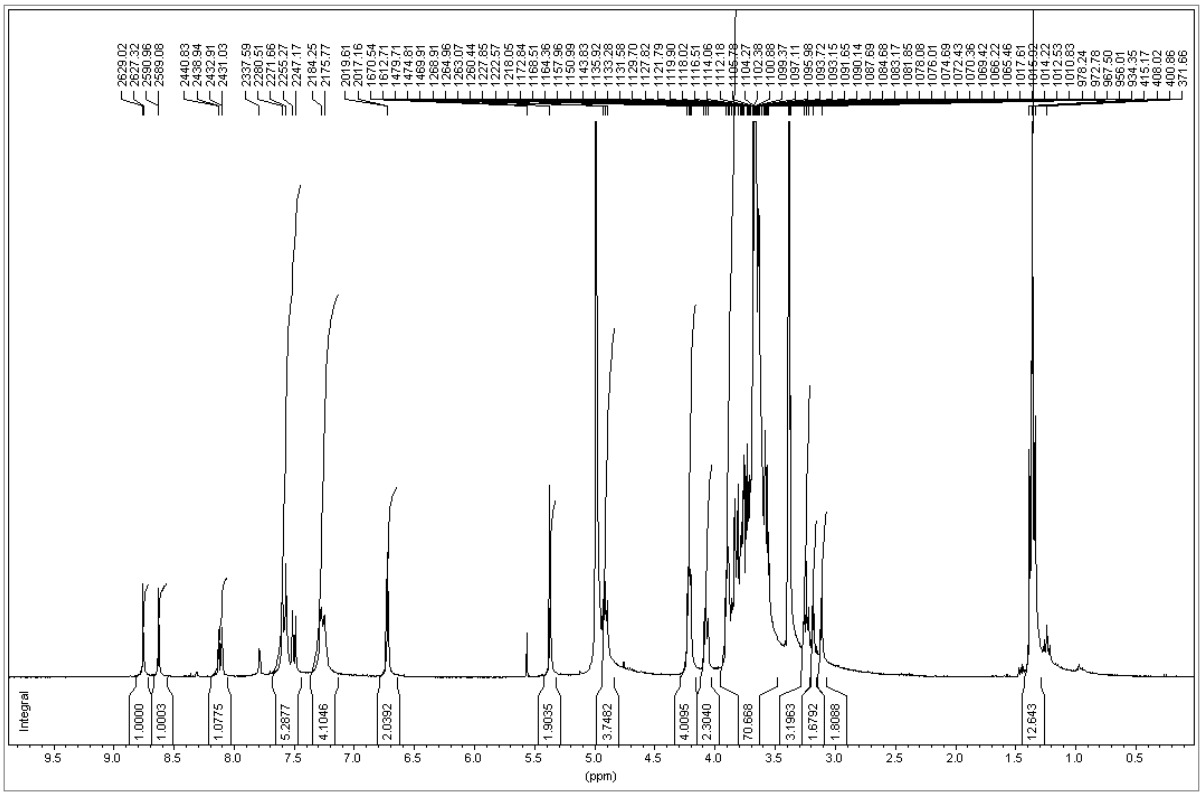


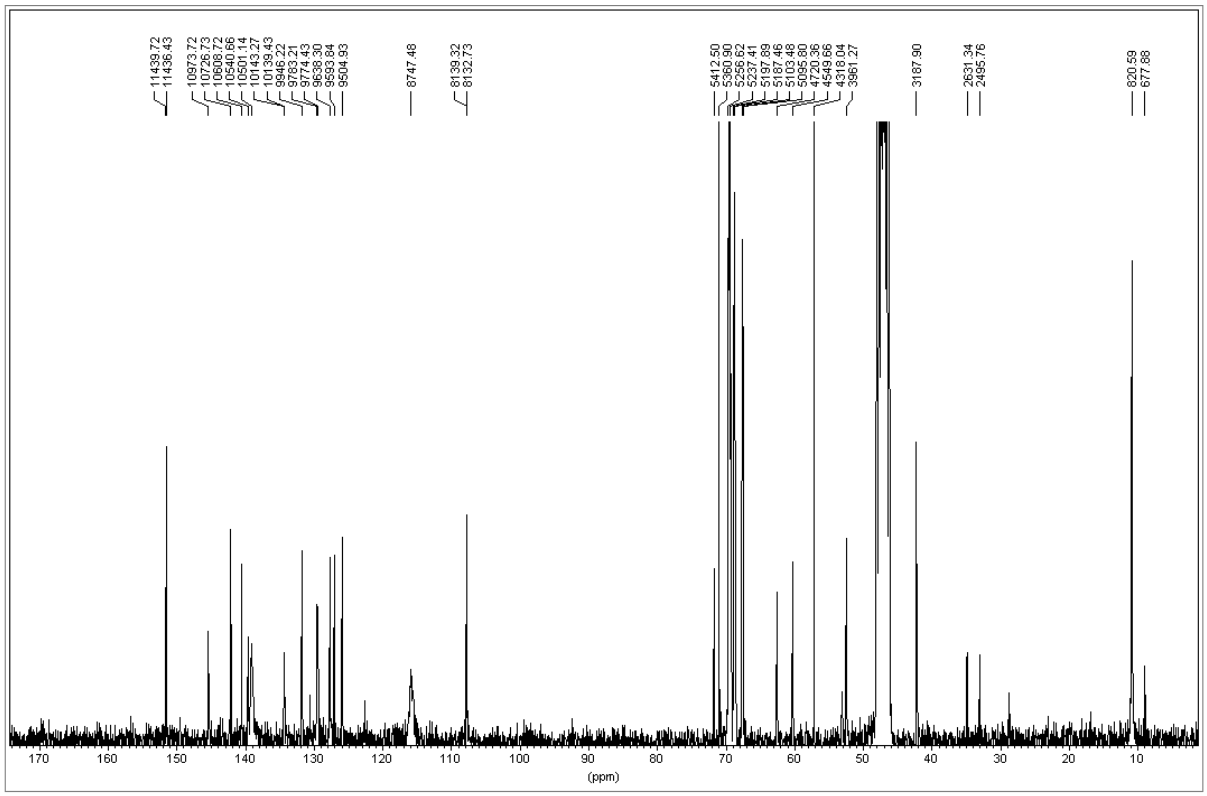


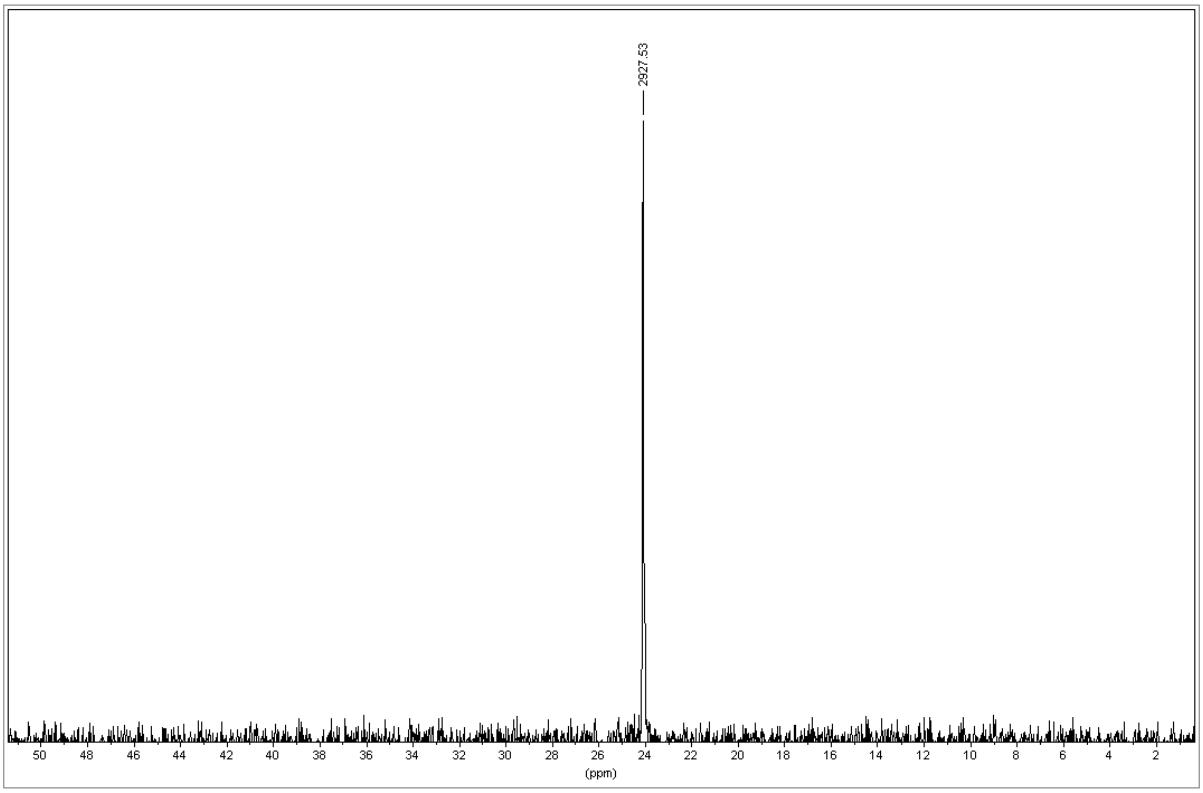

31.88.90
50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0
(ppm)

Compound 52 (^{1}H, ^{13}C and ^{31}P, CD_3OD)

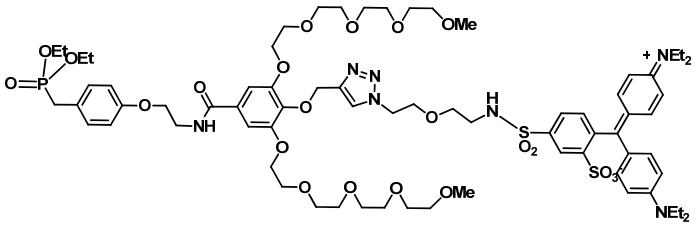


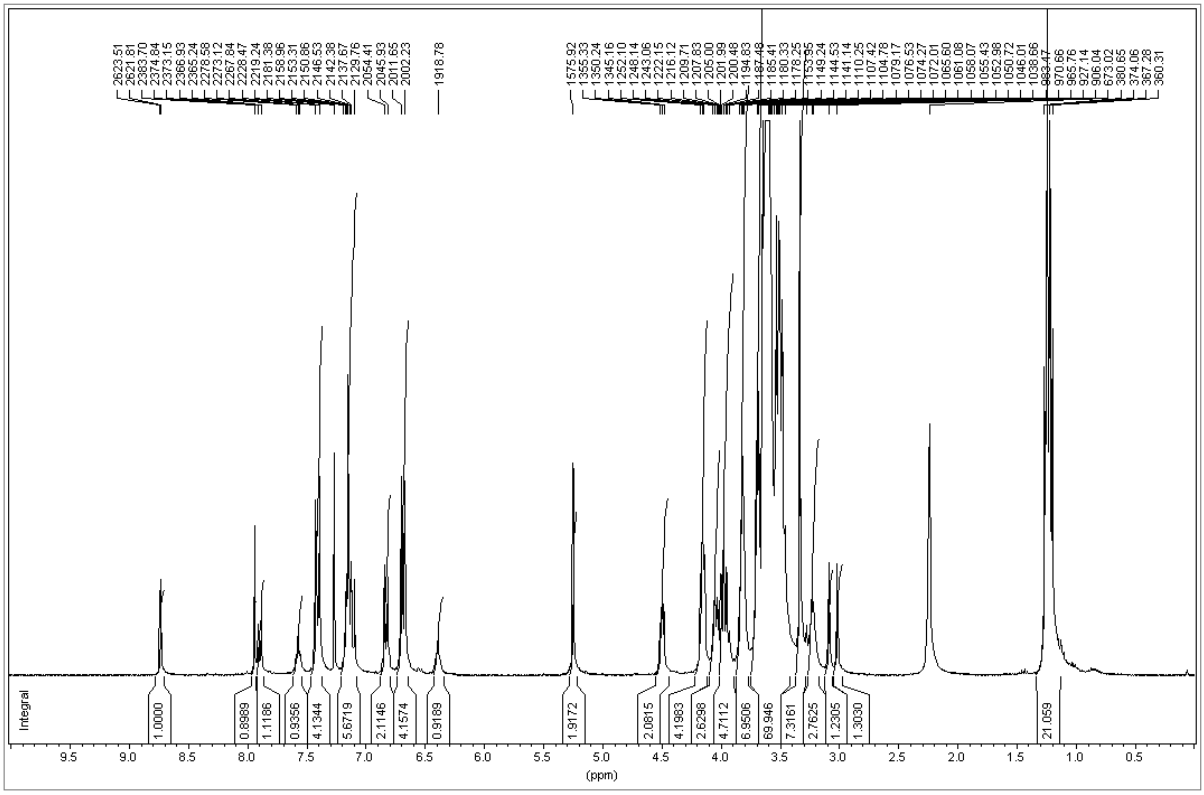


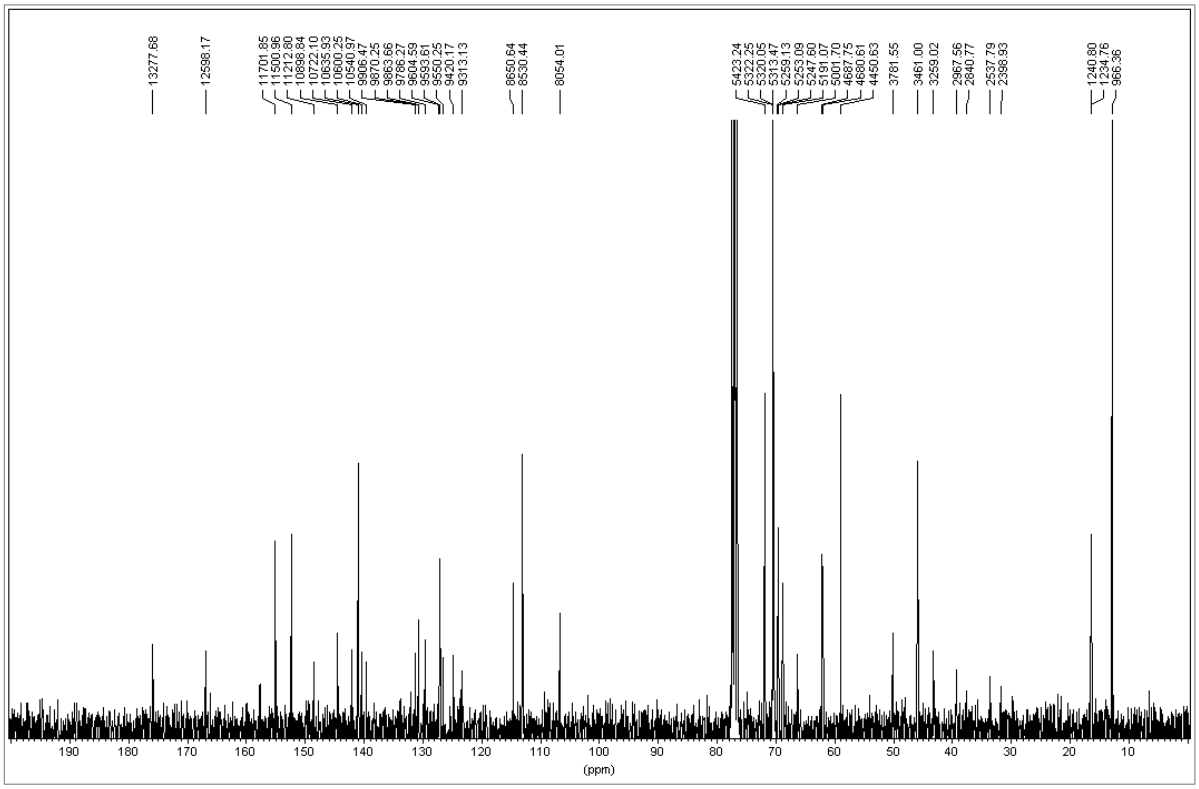

11439.72
11436.43
10973.72
10726.73
10606.72
10540.66
10501.14
10143.27
10139.43
9946.22
9783.21
9774.43
9638.30
9593.84
9504.93
8747.48
8139.32
8132.73
5412.50
5360.90
5256.62
5237.41
5197.89
5187.46
5107.48
5095.80
4720.36
4549.86
4318.04
3961.27
3187.90
2631.34
2495.76
820.59
677.88
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

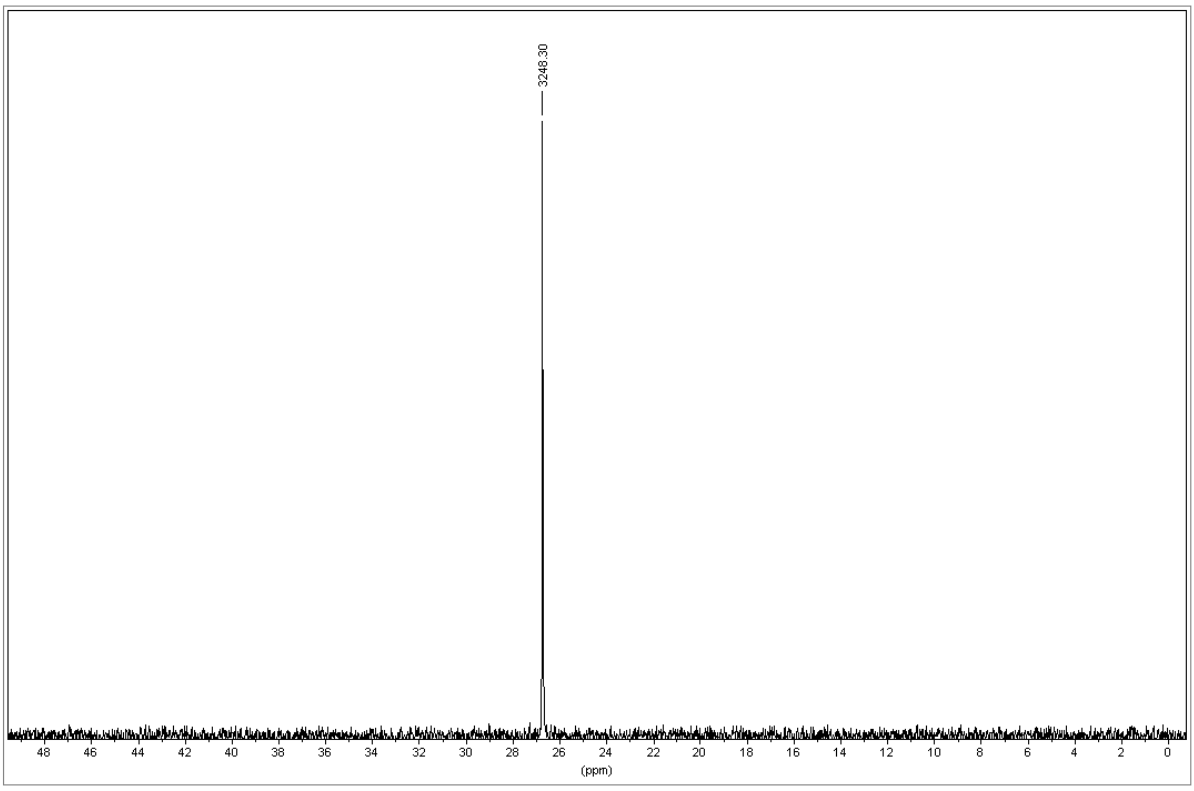

2927.53
50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2
(ppm)

Compound 53 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

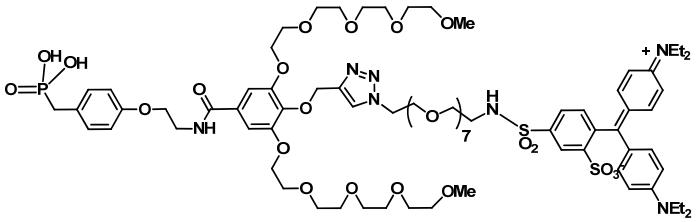


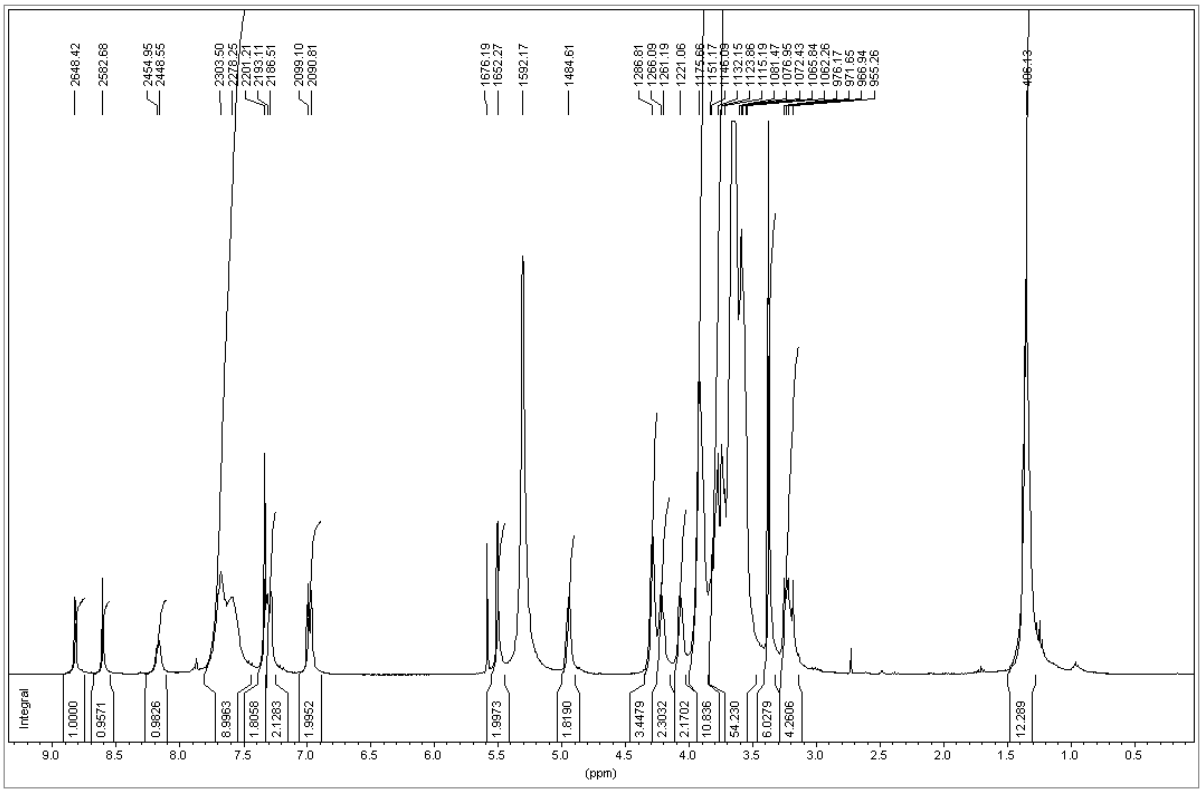


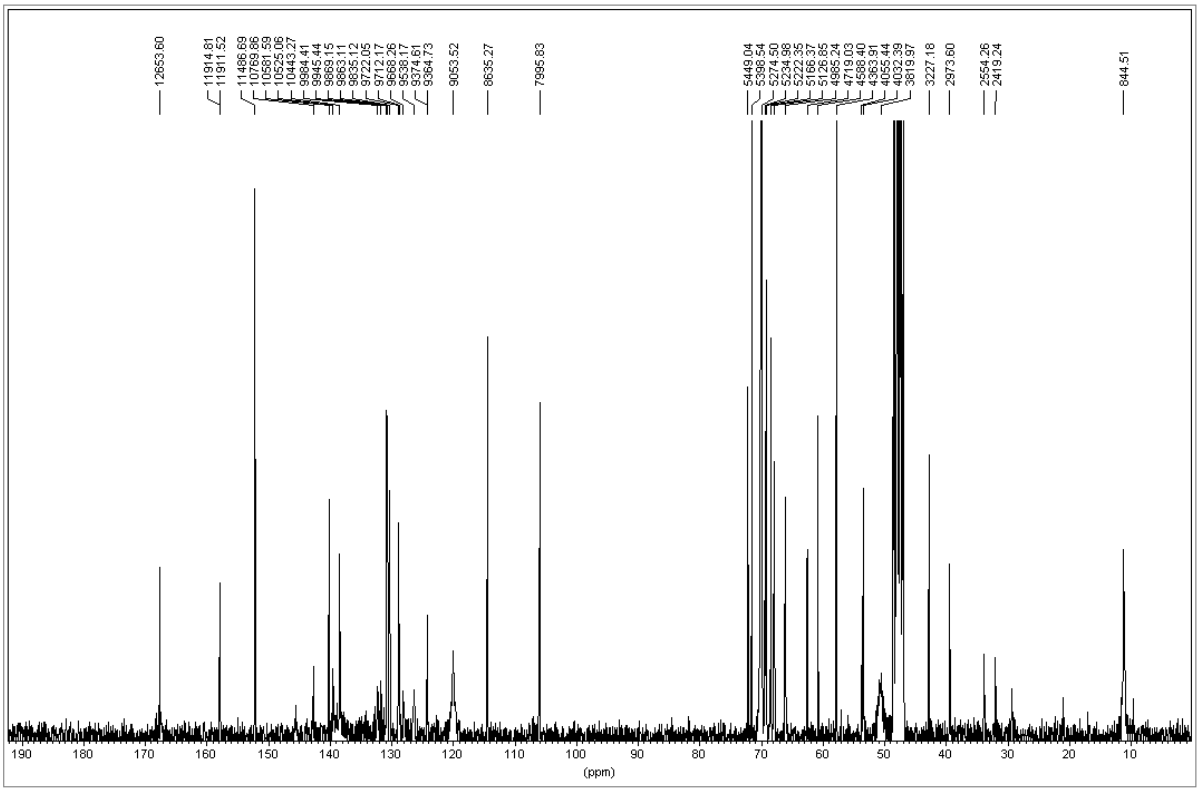

13277.68
12598.17
11701.85
11500.96
11212.80
10898.84
10722.10
10652.93
10600.25
10540.97
9906.47
9870.25
9863.86
9786.27
9604.59
9593.61
9553.25
9420.17
9313.13
8650.64
8530.44
8054.01
5423.24
5322.25
5320.05
5314.47
5253.13
5253.09
5247.60
5191.07
5001.70
4687.75
4680.61
4450.63
3781.55
3461.00
3259.02
2867.56
2840.77
2537.79
2398.93
1240.80
1234.76
966.36
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

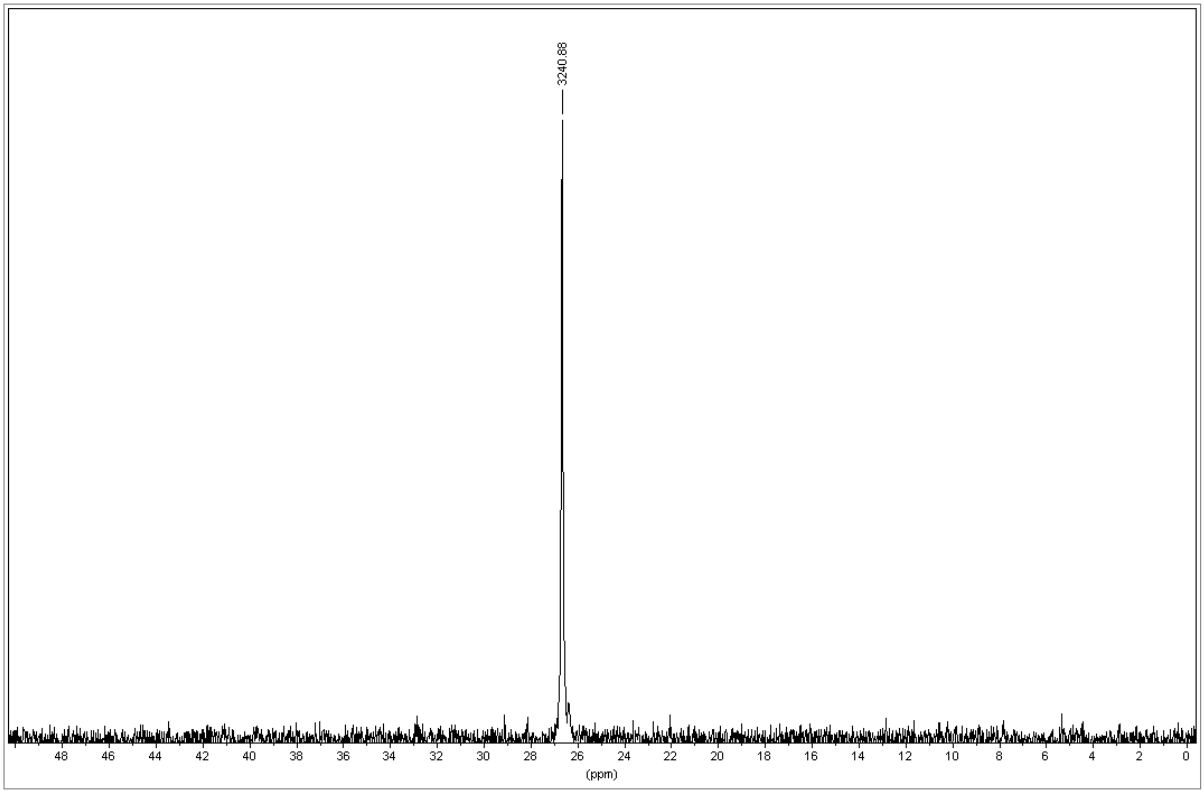

3248.30
48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0
(ppm)

Compound 54 (^{1}H, ^{13}C and ^{31}P, CD_3OD)

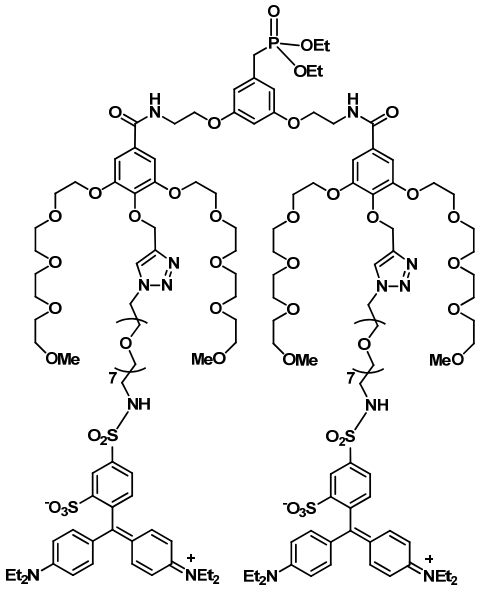


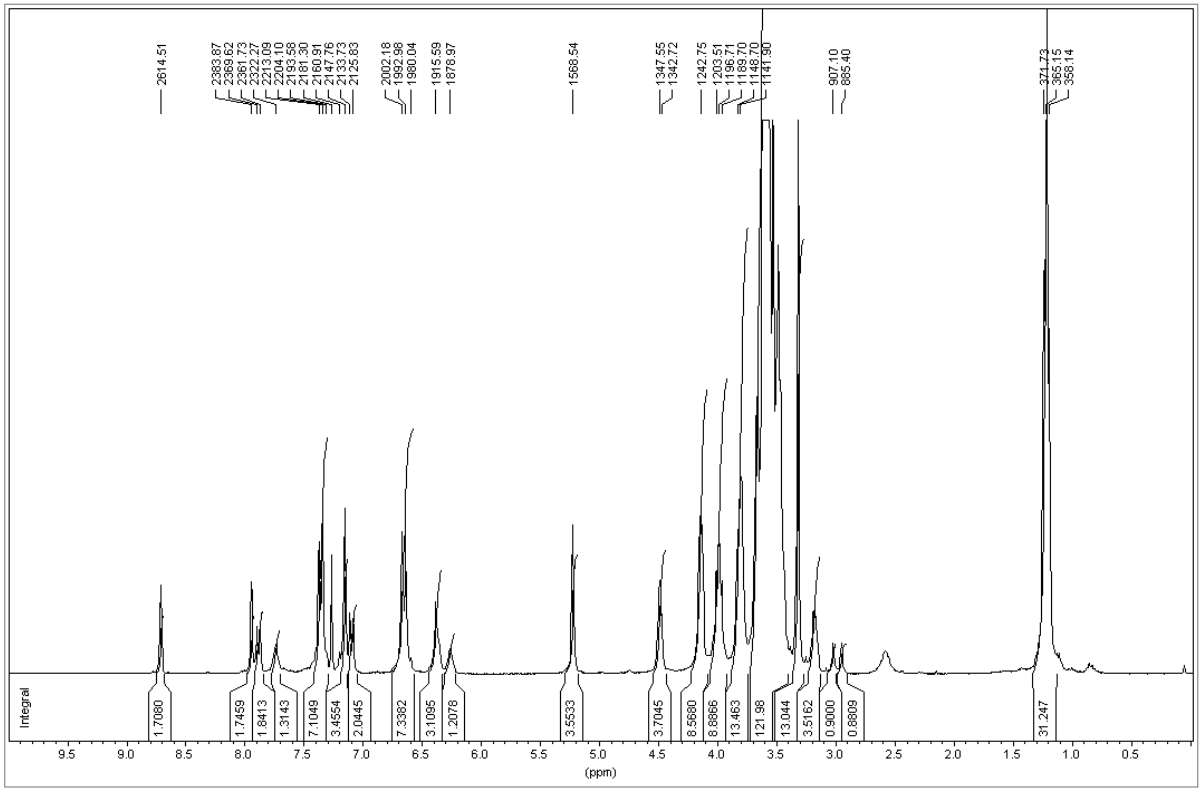


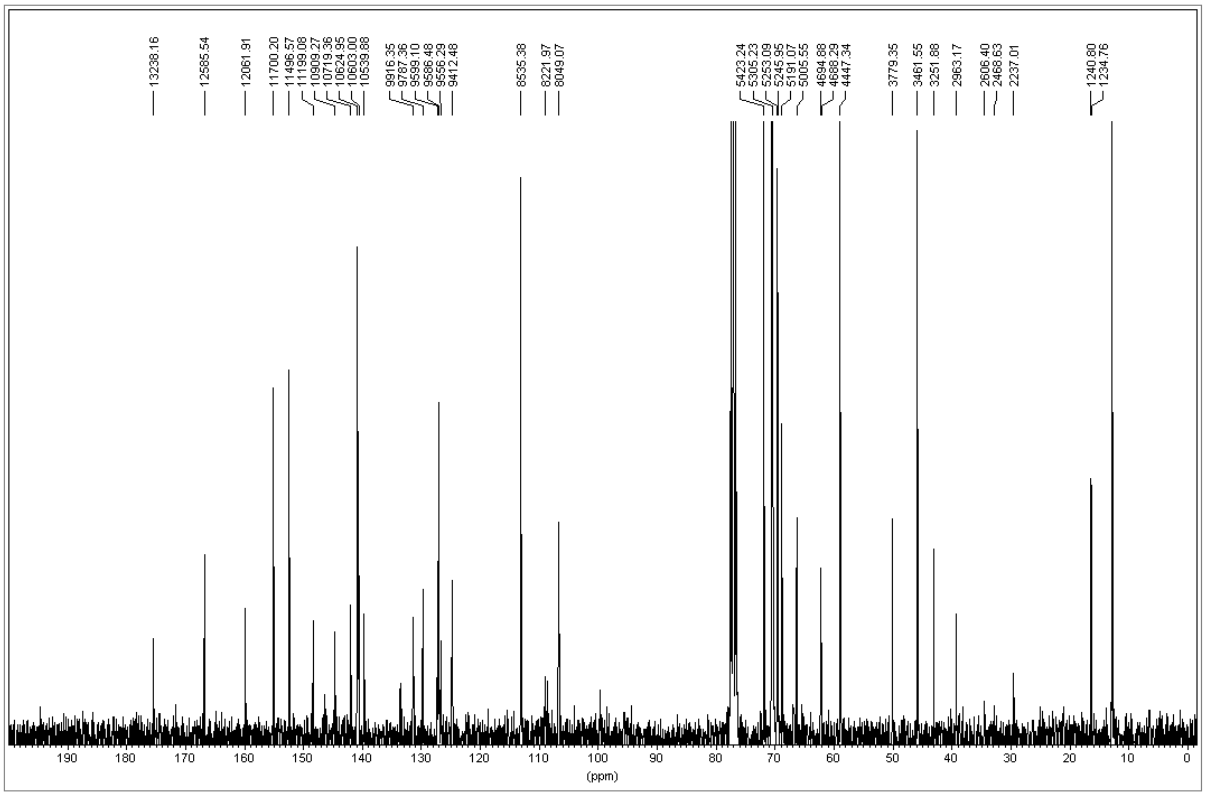

12653.60
11914.81
11911.52
11486.69
10769.86
10521.09
10251.56
10443.27
9984.41
9945.44
9869.15
9863.11
9835.12
9722.05
9672.17
9668.26
9538.17
9374.61
9364.73
9053.52
8635.27
7995.83
5449.04
5396.54
5274.50
5234.98
5222.35
5156.37
5126.85
4985.24
4719.03
4588.40
4363.91
4055.44
4032.39
3819.97
3227.18
2973.60
2554.26
2419.24
844.51
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

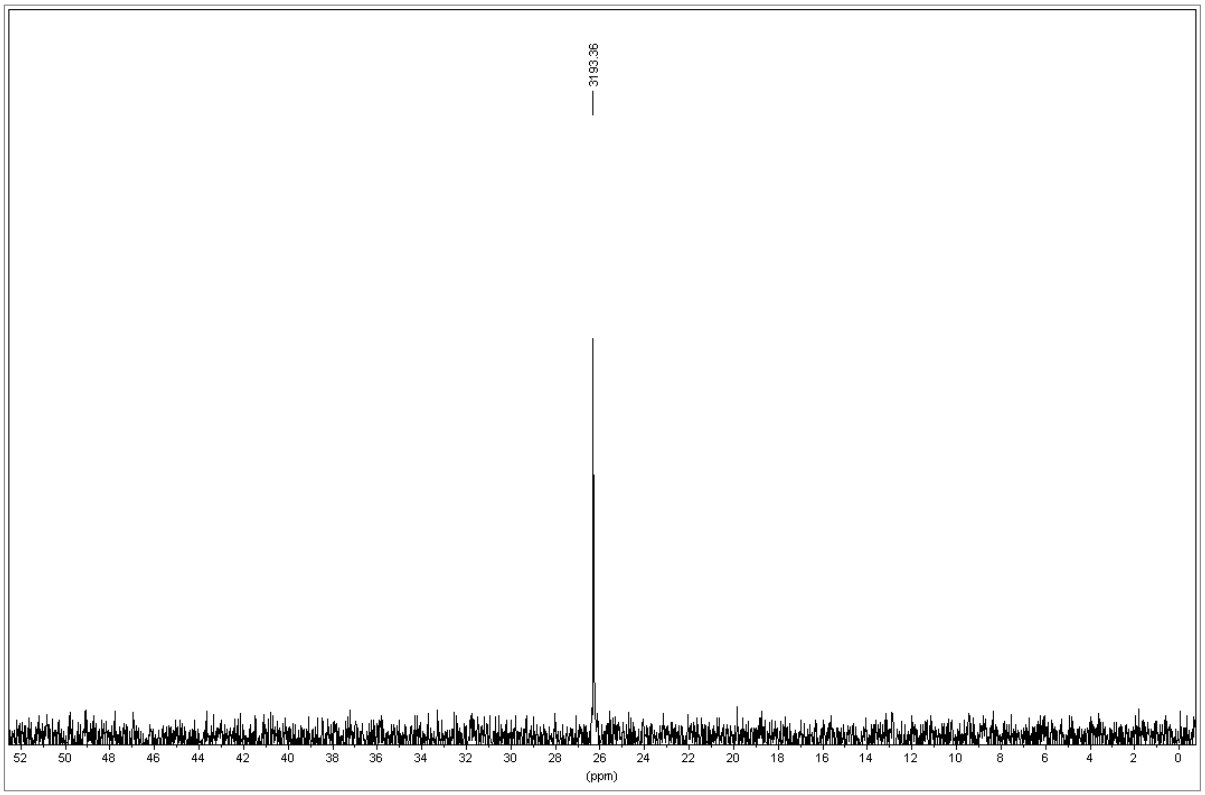

3240.88
48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0
(ppm)

Compound 55 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

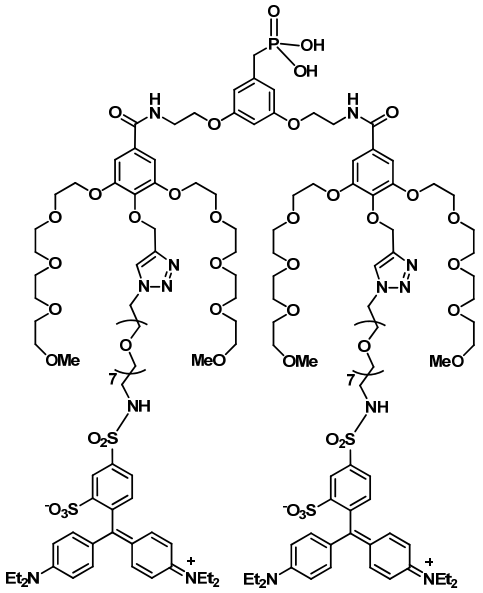


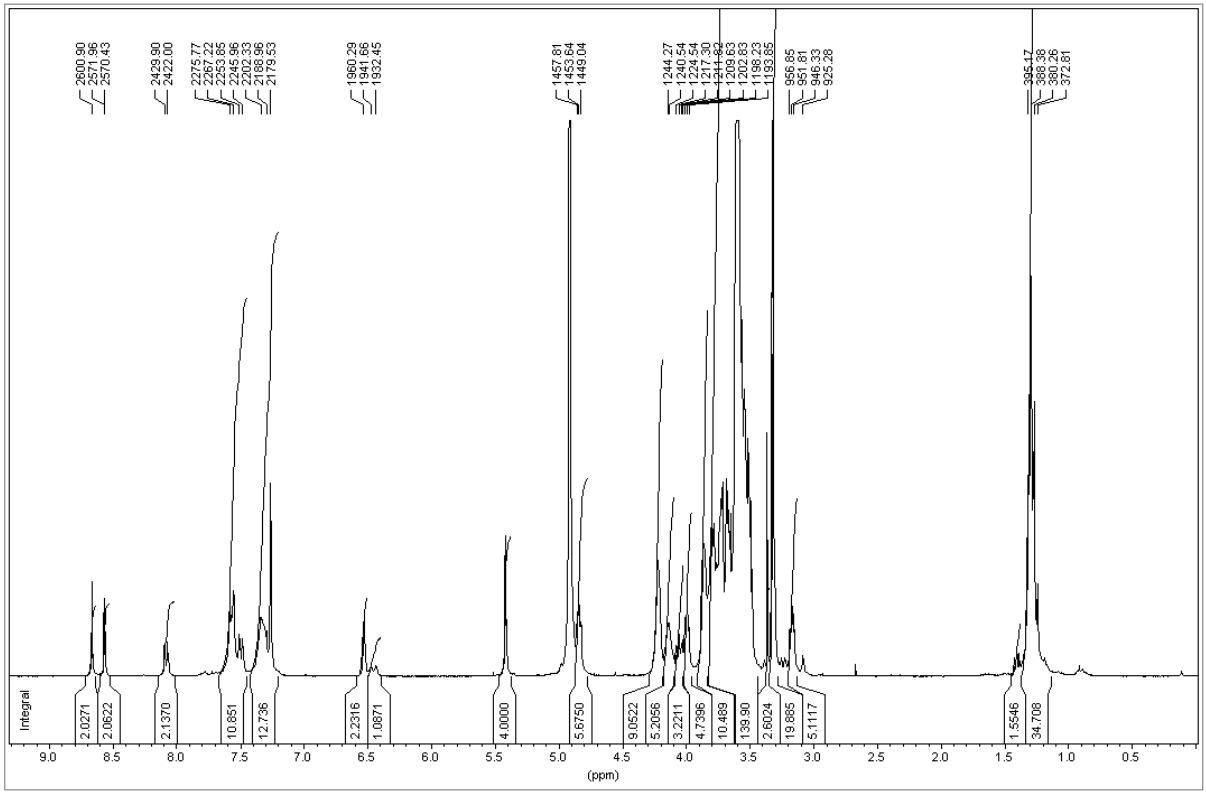


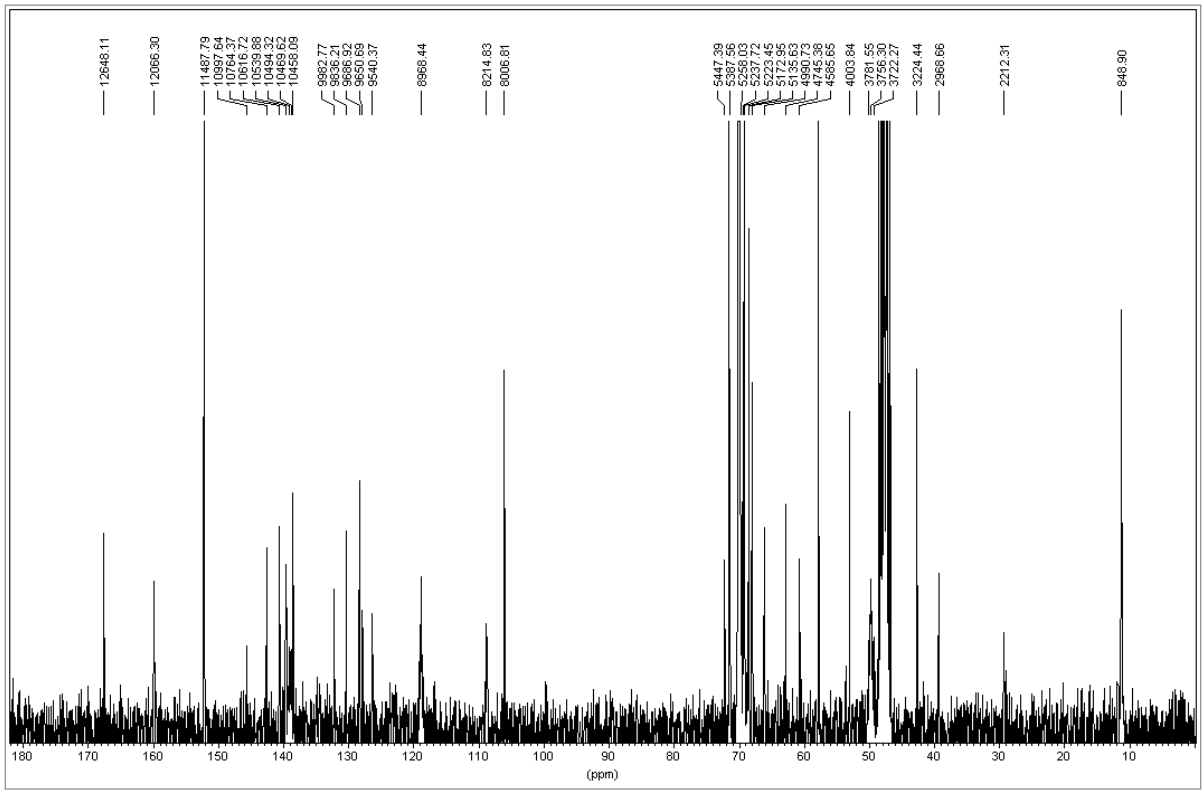

13238.16
12585.54
12061.91
11700.20
11496.57
11199.08
10909.27
10719.36
10634.15
10563.00
10539.88
9916.35
9787.36
9599.10
9566.48
9556.29
9412.48
8535.38
8221.97
8049.07
5423.24
5305.23
5253.09
5245.95
5191.07
5005.55
4694.88
4668.29
4447.34
3779.35
3461.55
3251.88
2963.17
2606.40
2468.63
2237.01
1240.80
1234.76
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

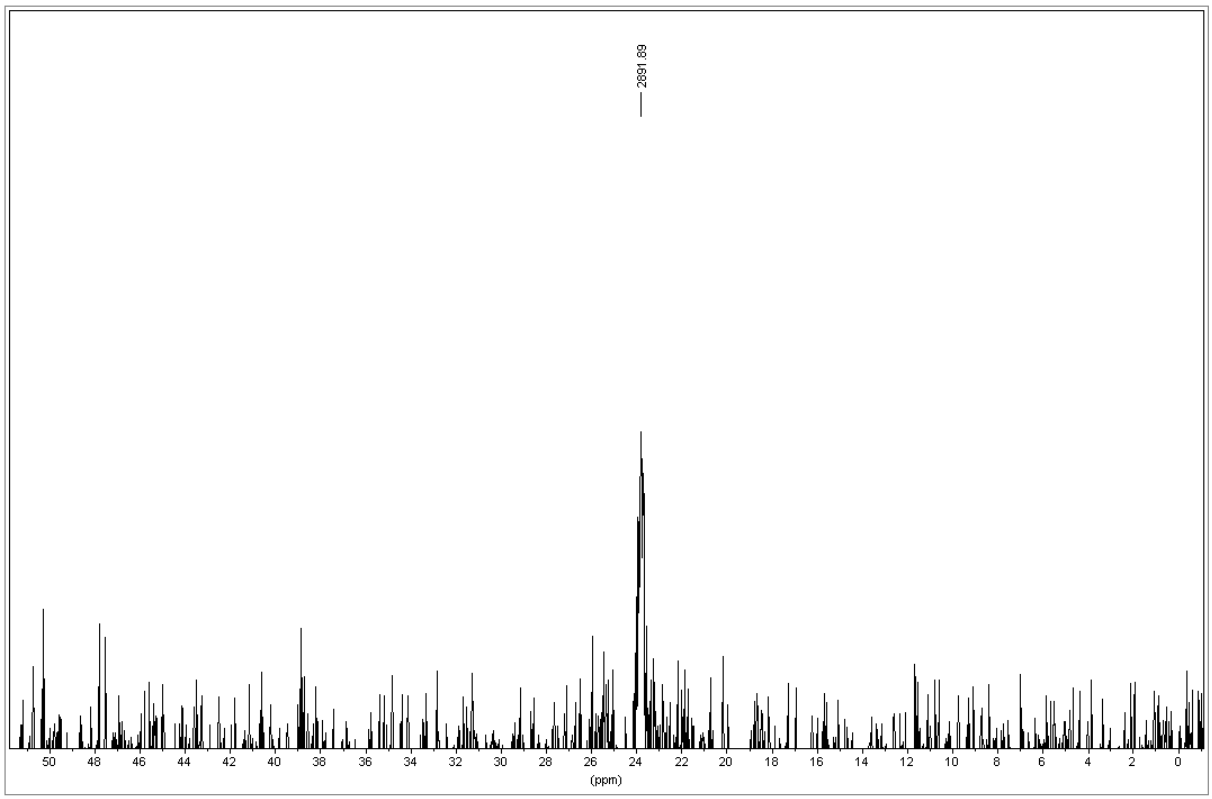

3193.36
52
50
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
(ppm)

Compound 56 (^{1}H, ^{13}C and ^{31}P, CD_3OD)

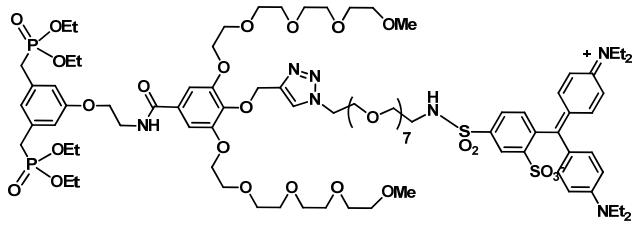


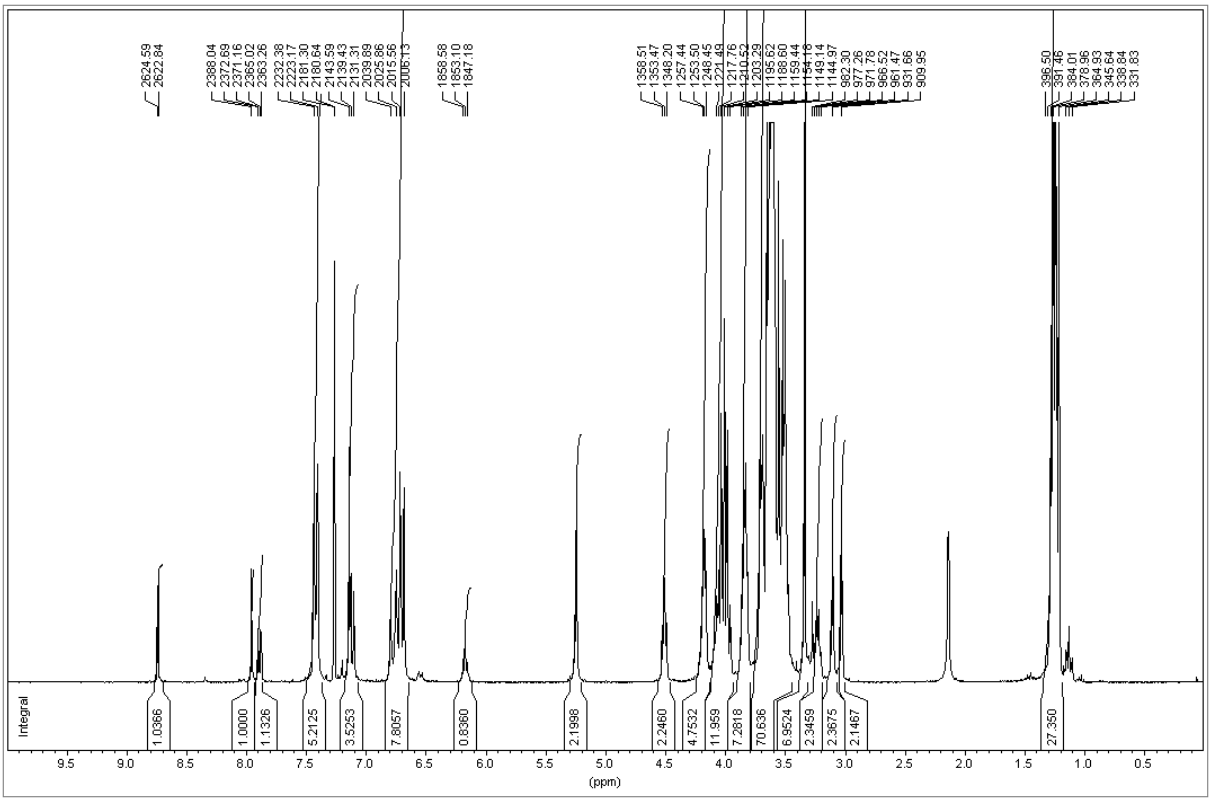


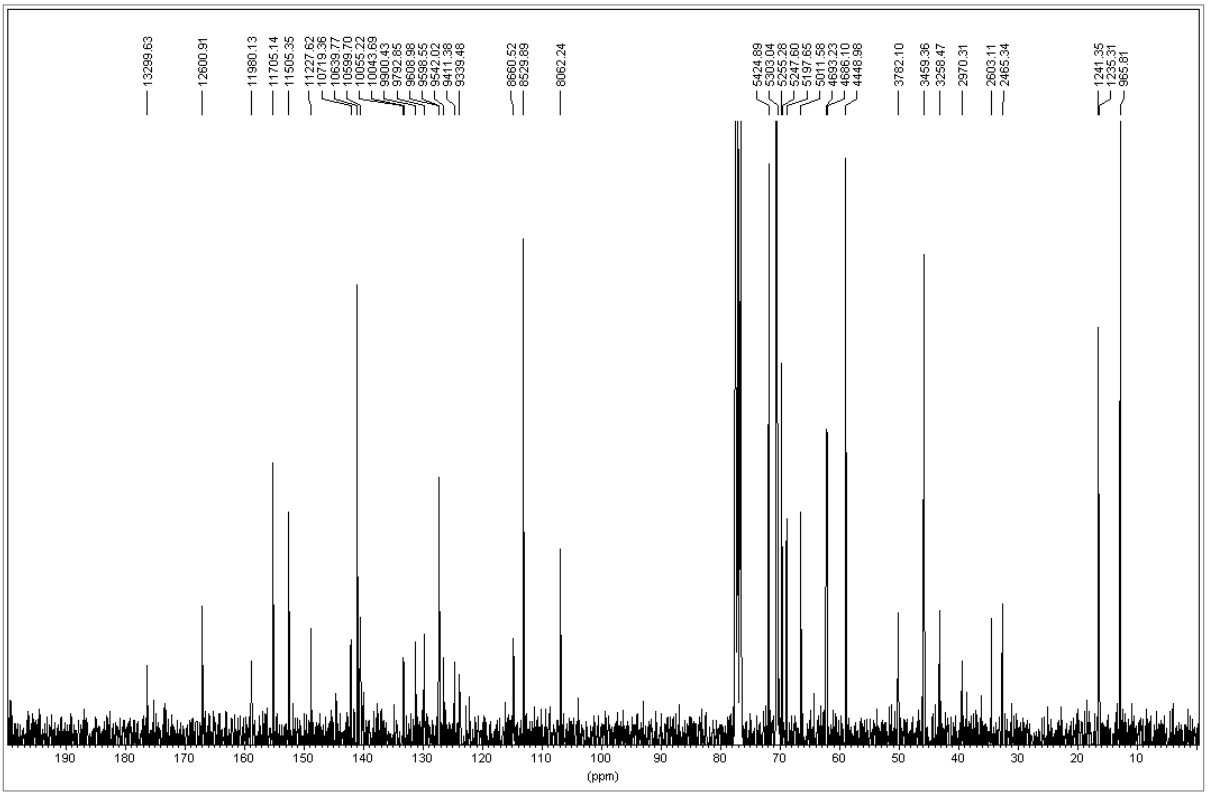

12648.11
12066.30
11487.79
10997.64
10854.37
10815.72
10539.88
10494.32
10469.62
10458.09
9982.77
9836.21
9686.92
9650.69
9540.37
8968.44
8214.83
8006.81
5447.39
5387.56
5258.03
5237.72
5223.45
5172.95
5135.63
4990.73
4745.88
4585.85
4003.84
3781.55
3756.30
3722.27
3224.44
2968.66
2212.31
848.90
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

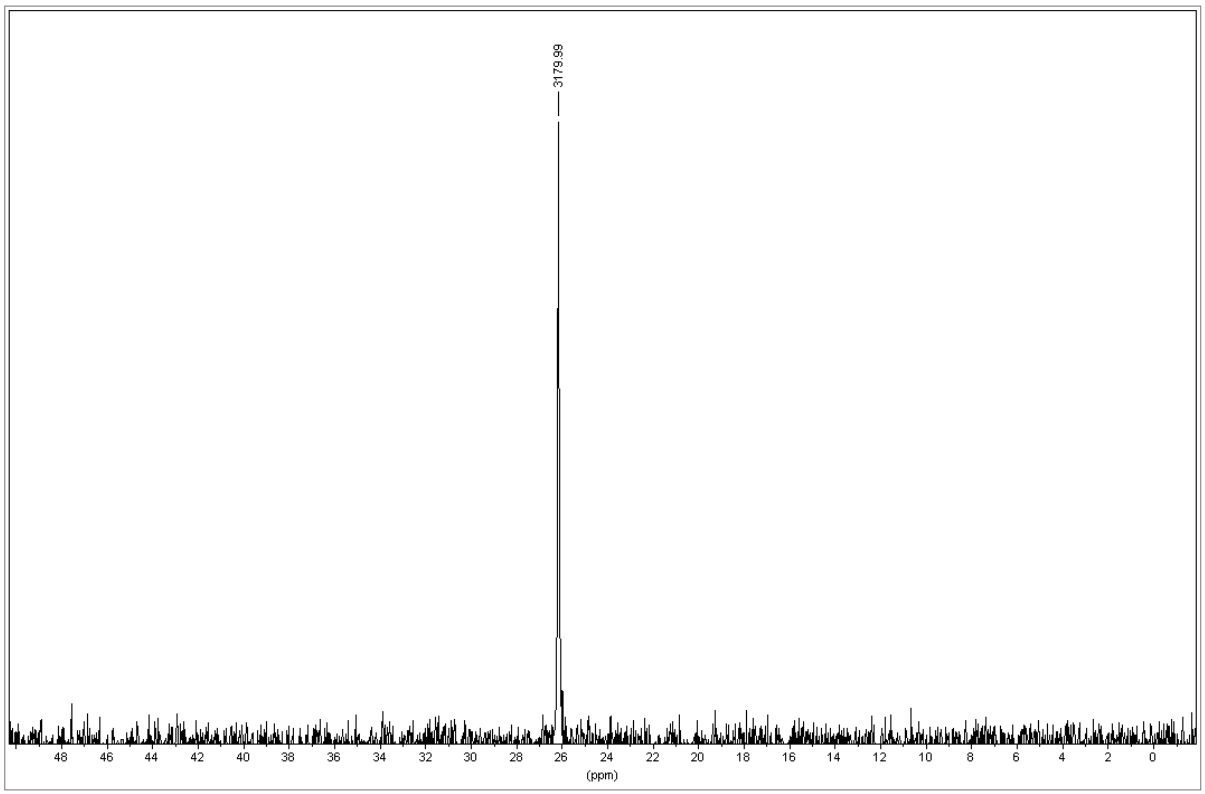

2891.89
50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0
(ppm)

Compound 57 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

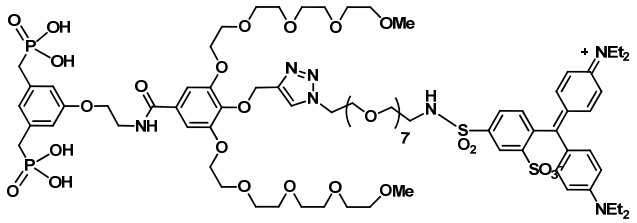


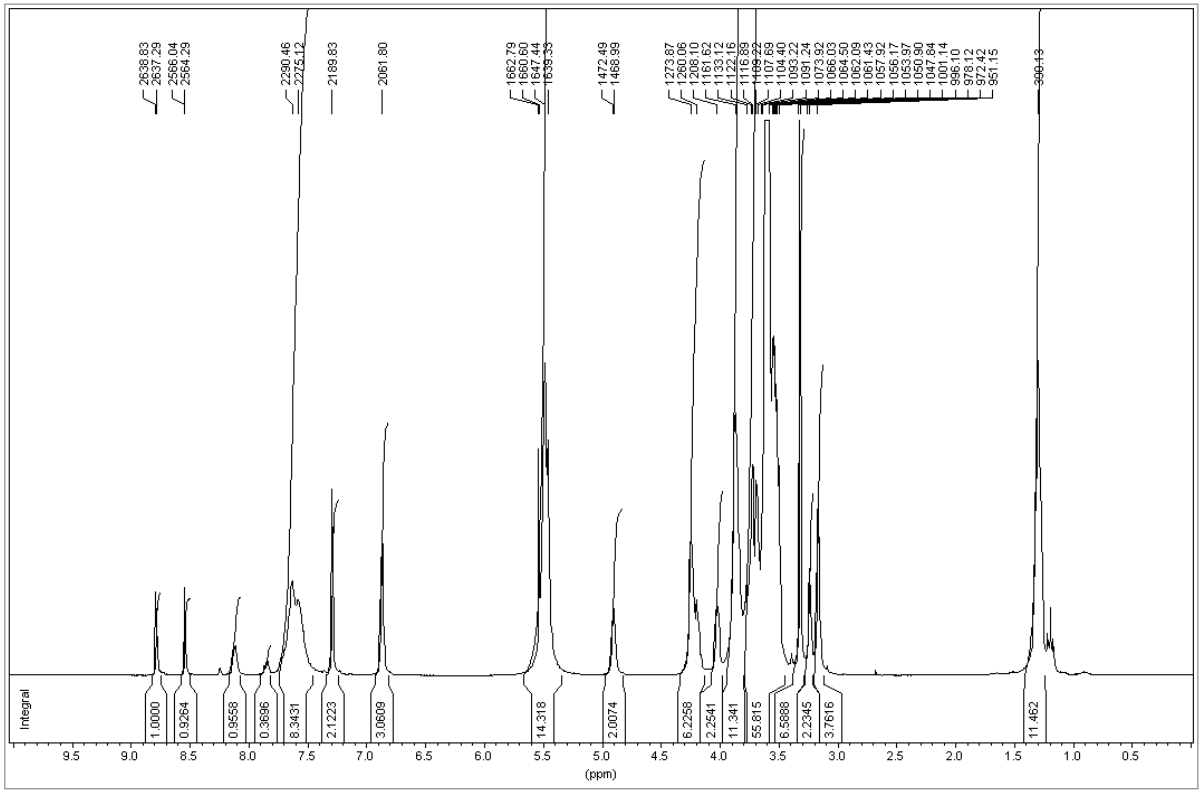


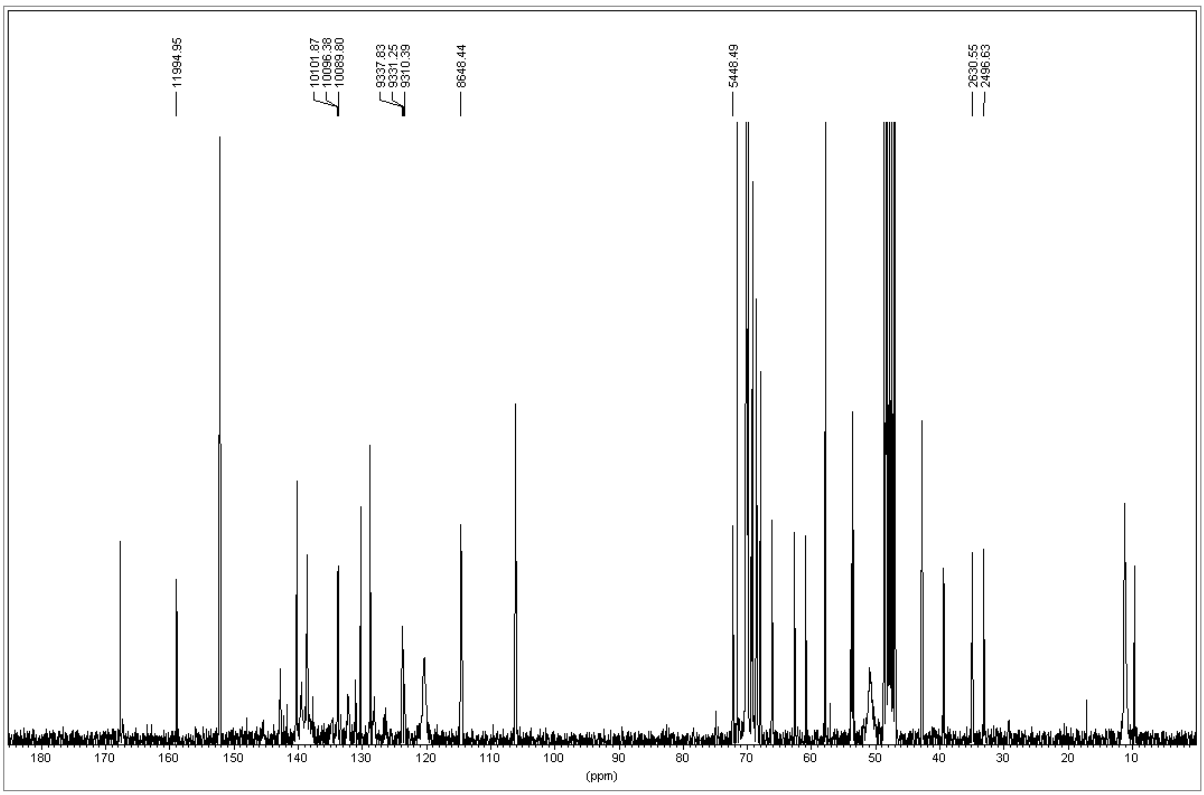

13299.63
12600.91
11980.13
11705.14
11505.35
11227.62
10719.36
10639.77
10599.70
10055.22
10043.69
9960.43
9792.85
9688.96
9608.55
9542.02
9411.38
9339.48
8660.52
8529.89
8062.24
5424.89
5303.04
5255.28
5247.60
5197.65
5011.58
4693.23
4688.10
4446.98
3782.10
3459.36
3258.47
2970.31
2603.11
2465.34
1241.35
1235.31
965.81
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

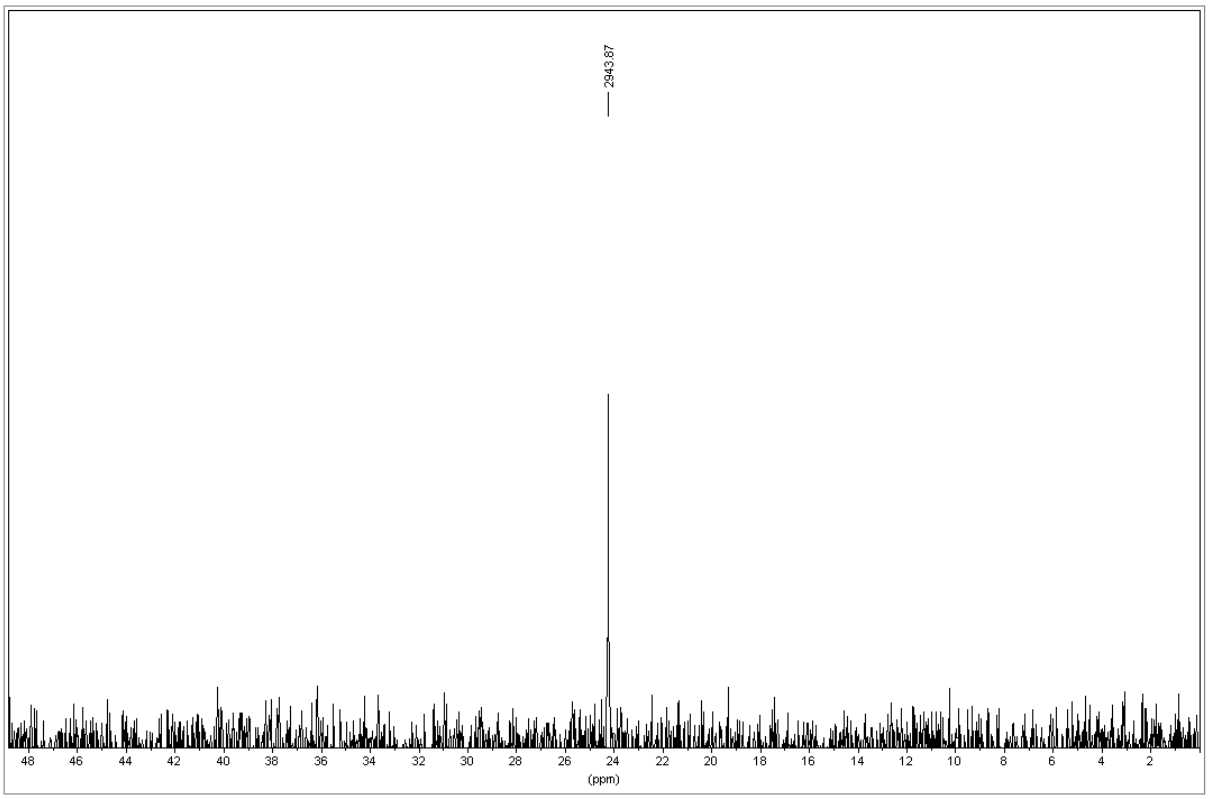

3179.99
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
(ppm)

Compound 58 (^{1}H, ^{13}C and ^{31}P, CD_3OD)

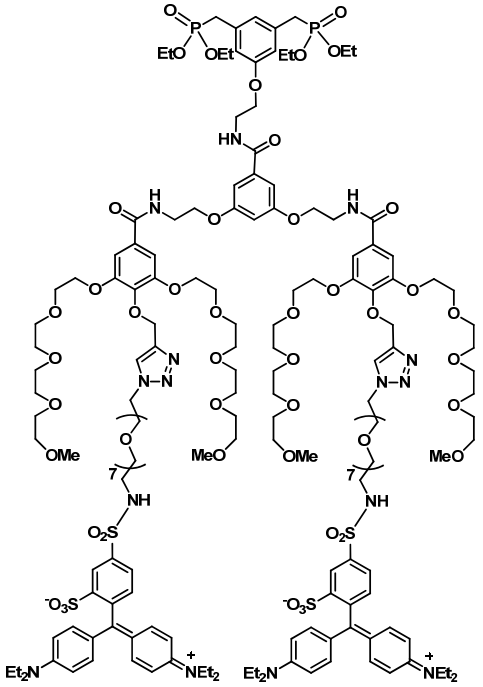


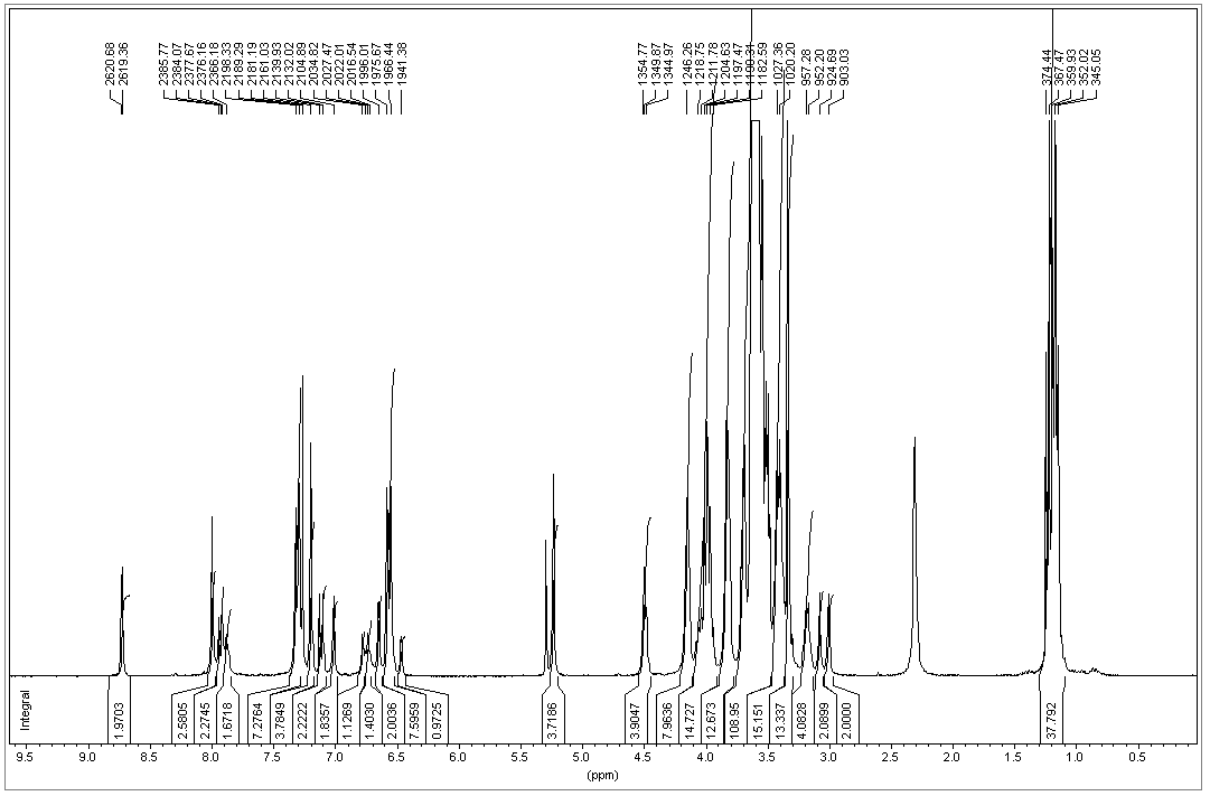


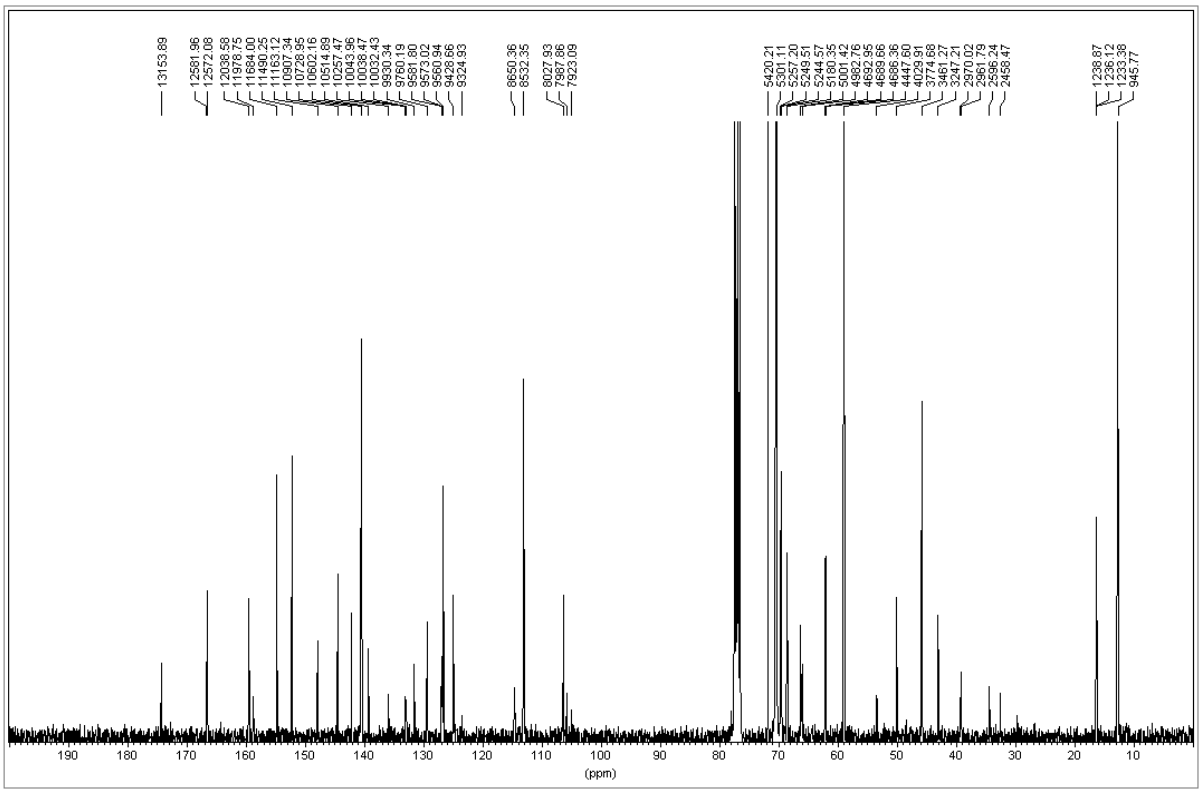

11994.95
10101.87
10096.38
10089.80
9337.83
9331.25
9310.39
8648.44
5448.49
2630.55
2496.63
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

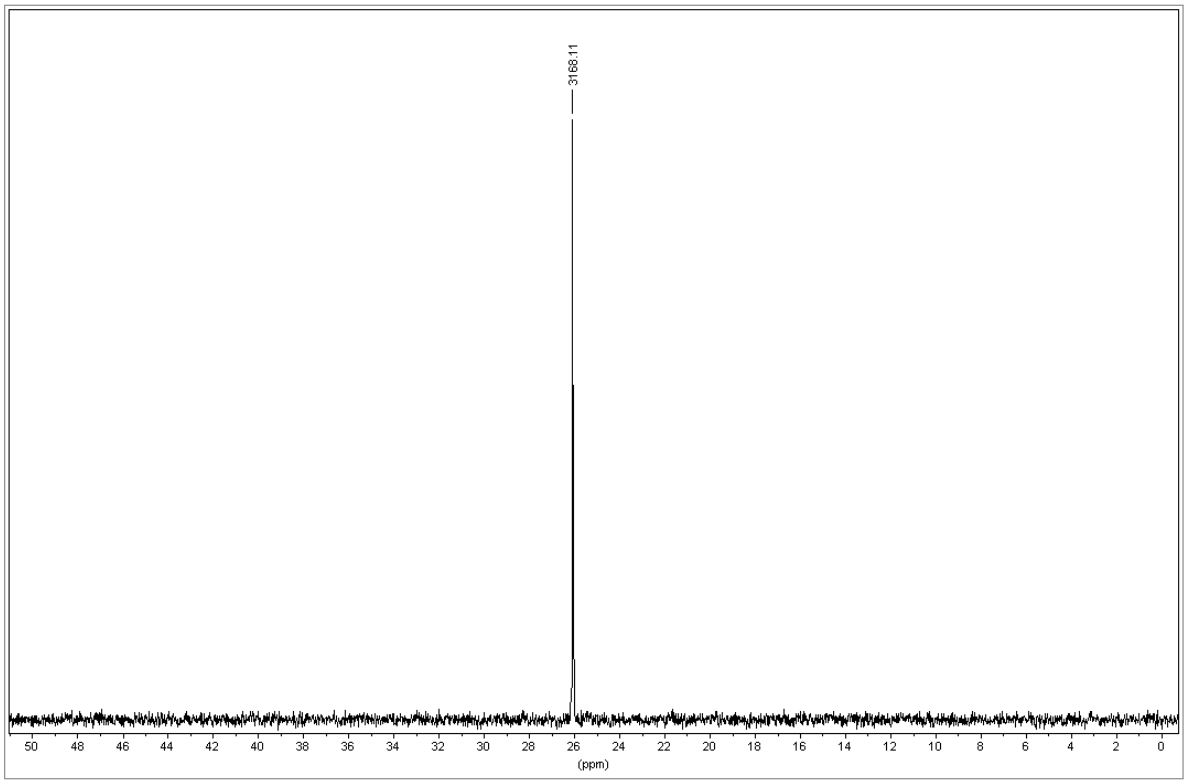

2943.87
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
(ppm)

Compound 59 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

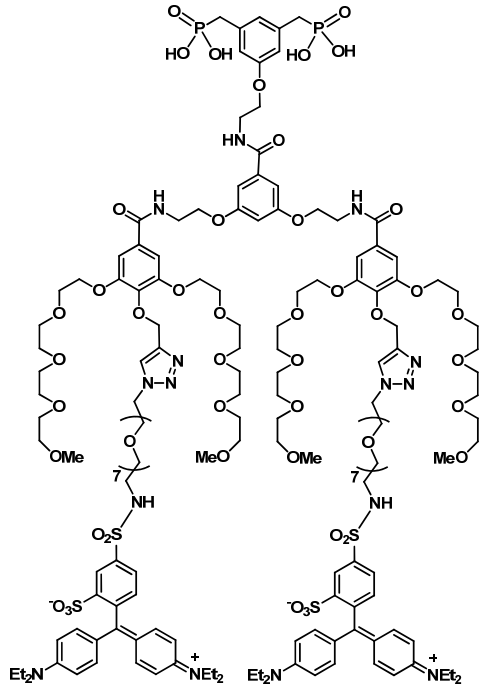


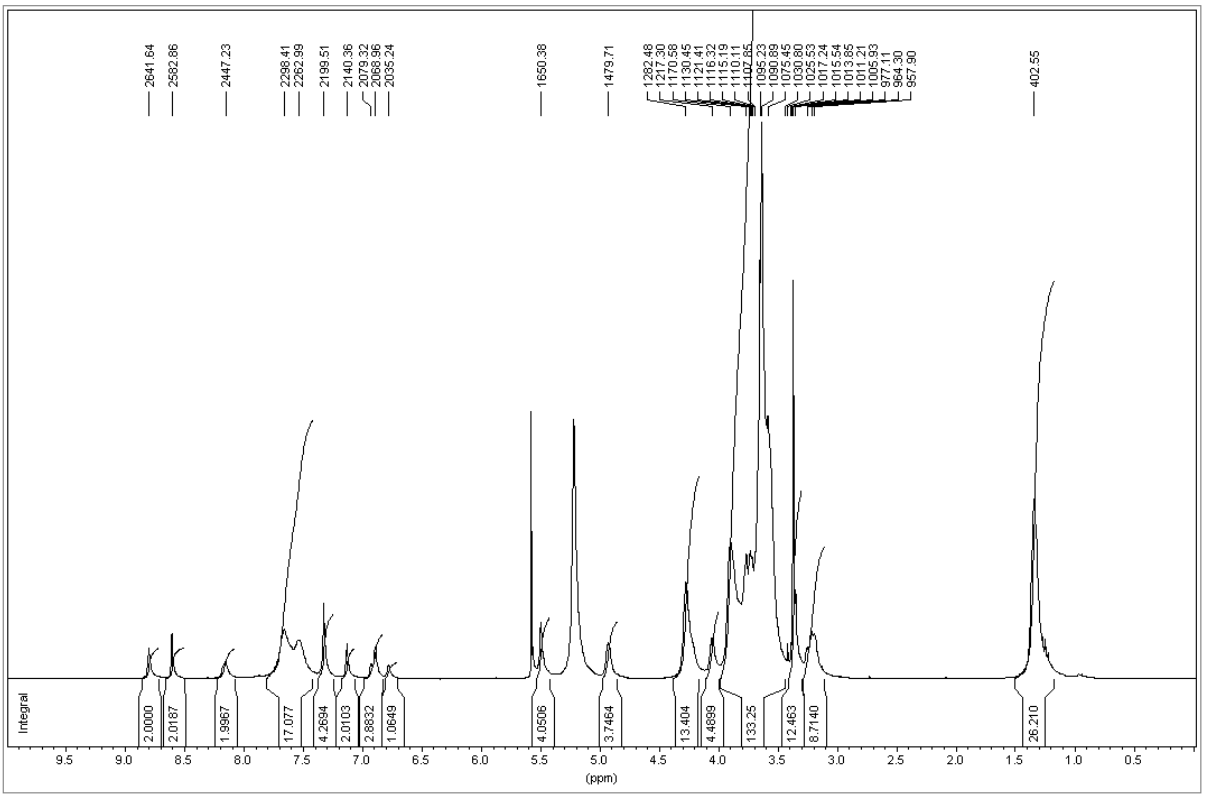


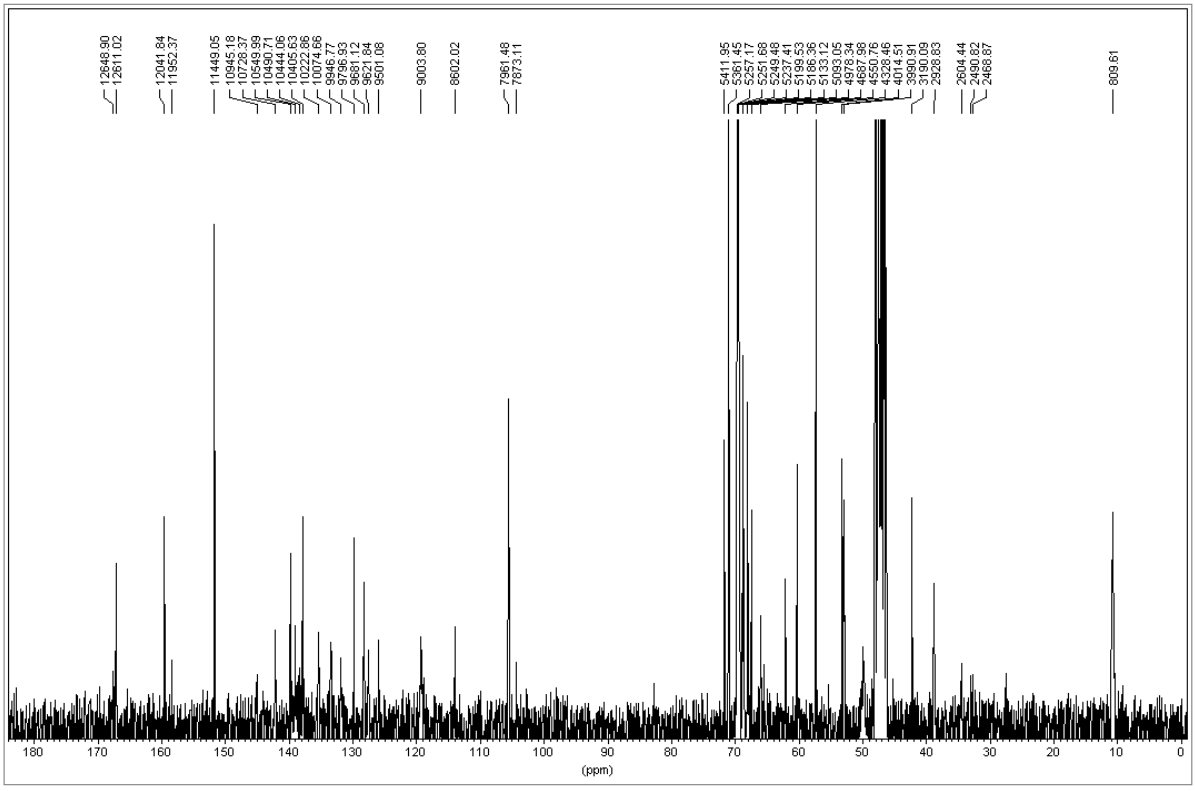

13153.89
12581.96
12572.08
12038.58
11978.75
11684.00
11490.25
11163.12
10907.34
10778.15
10602.16
10514.89
10257.47
10043.96
10038.47
10032.43
9930.34
9760.19
9571.80
9561.02
9560.94
9428.66
9324.93
8650.36
8532.35
8027.93
7987.86
7923.09
5420.21
5301.11
5257.20
5249.51
5244.57
5243.35
5001.42
4982.76
4692.95
4689.66
4686.36
4447.60
4029.91
3774.68
3745.27
3347.21
2970.02
2961.79
2596.24
2458.47
1238.87
1236.12
1233.38
945.77
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

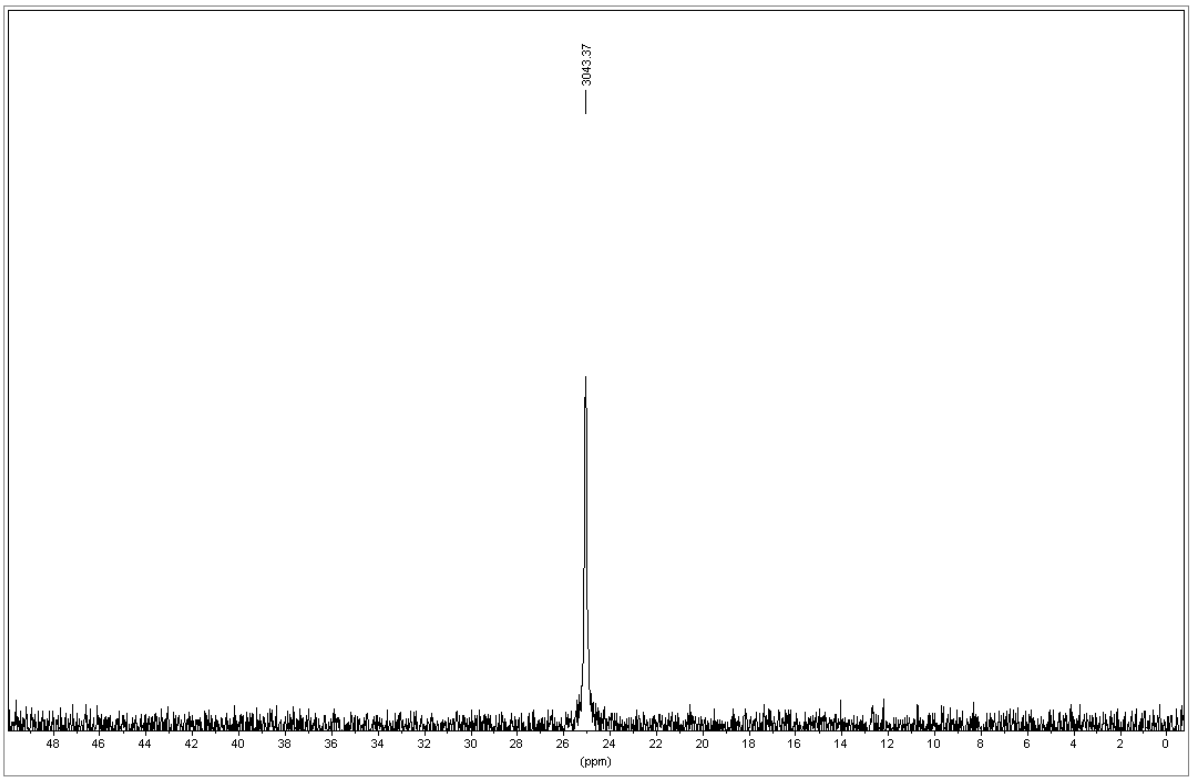

3168.11
50
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
(ppm)

Compound 60 (^{1}H, ^{13}C and ^{31}P, CD_3OD)

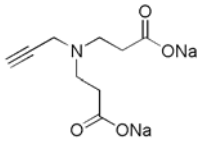


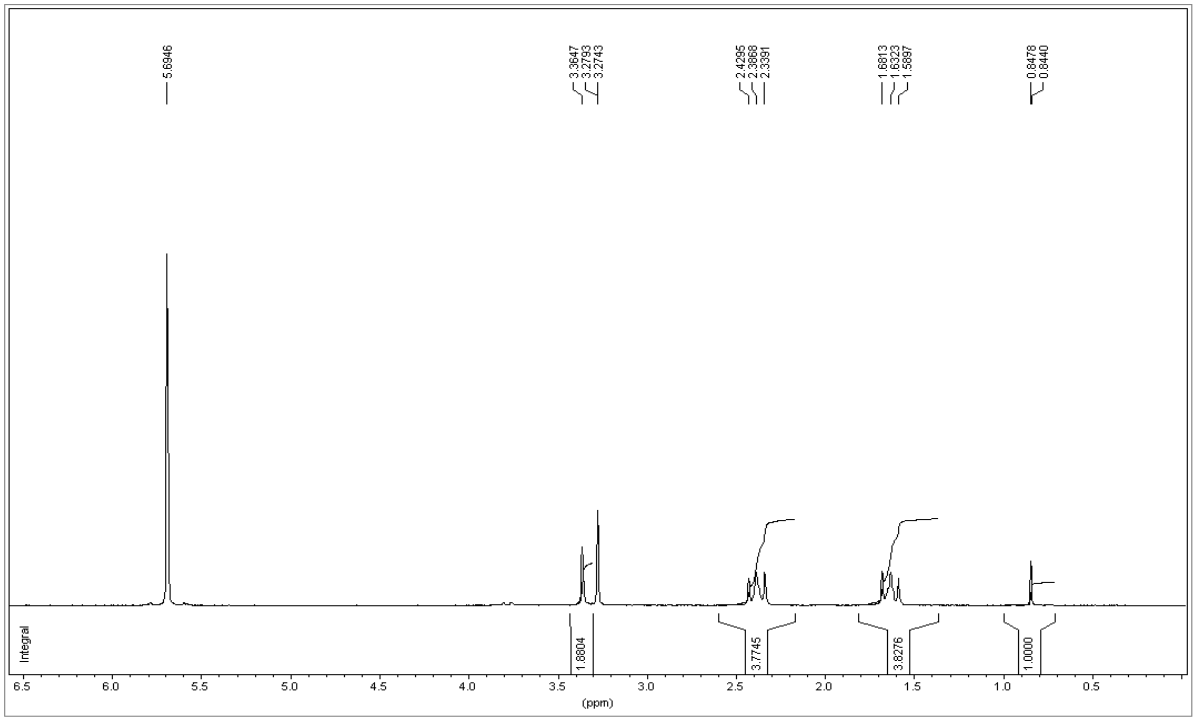


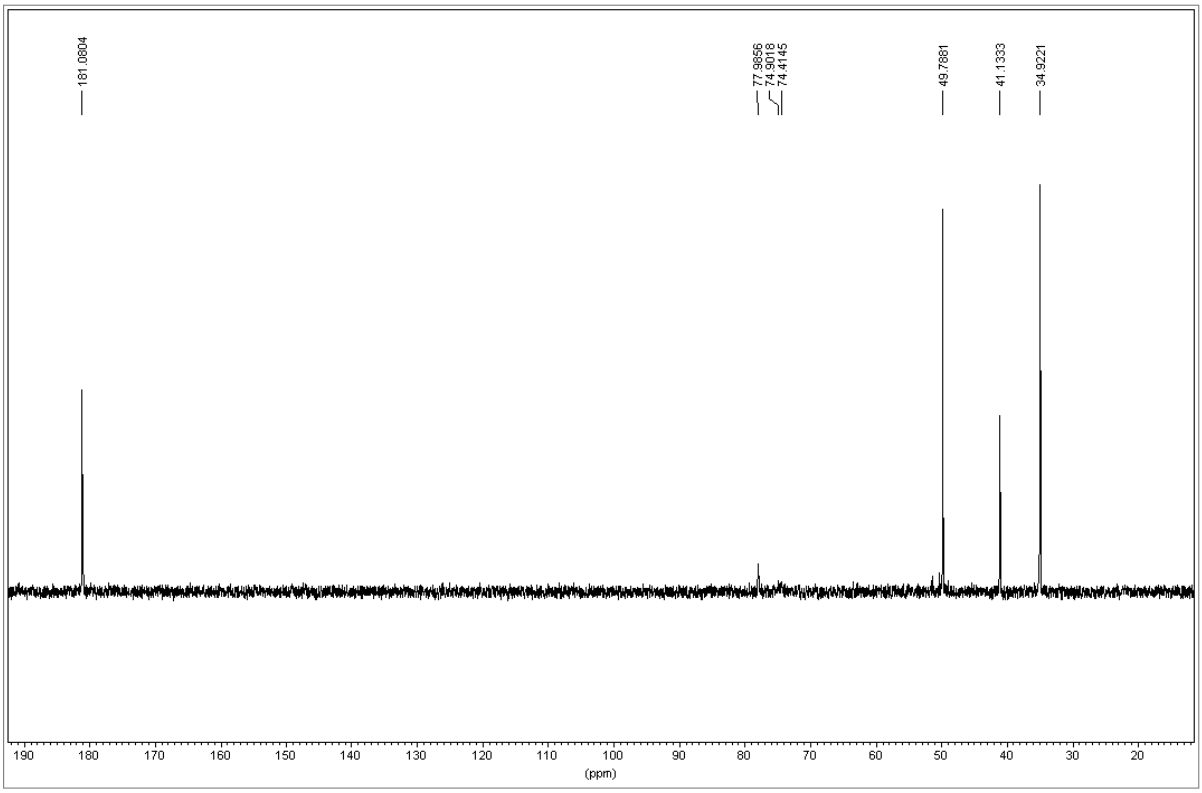

12648.90
12811.02
12041.84
11952.37
11449.05
10945.18
10728.37
10549.99
10490.71
10444.06
10405.63
10222.86
10074.66
9946.77
9796.93
9661.12
9621.84
9501.08
9003.80
8602.02
7961.48
7873.11
5411.95
5361.45
5257.17
5231.68
5209.40
5237.41
5199.53
5186.36
5133.12
5093.05
4978.34
4687.98
4550.76
4328.46
4014.51
3990.91
3190.09
2928.83
2604.44
2490.82
2468.87
809.61
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)


3043.37
48
46
44
42
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
(ppm)

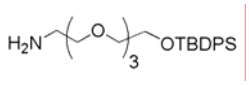
Compound 61 (^{1}H and ^{13}C, D_20)

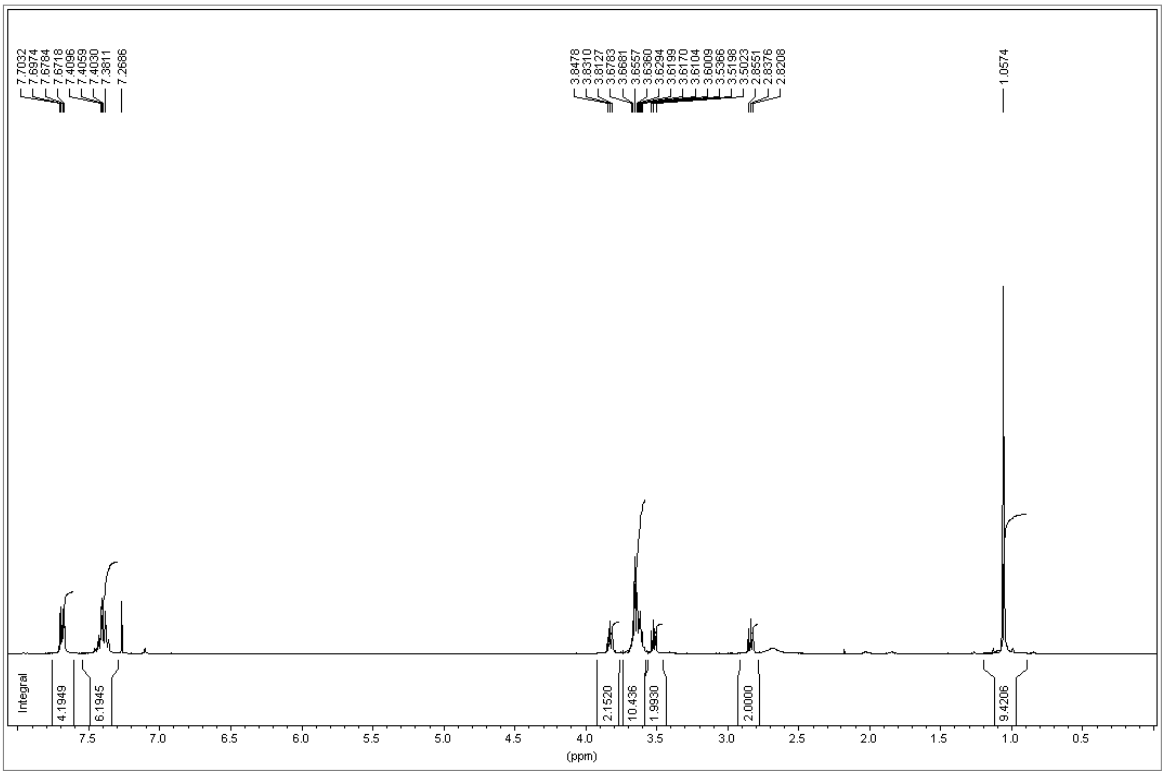


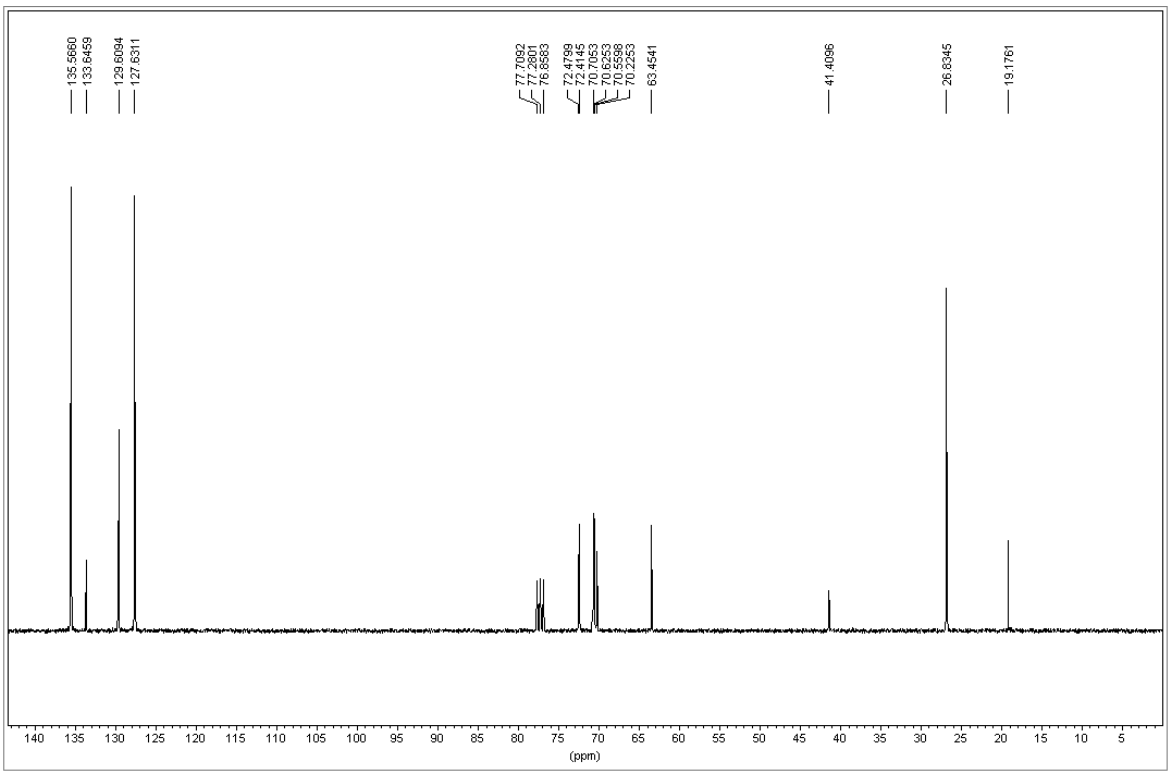




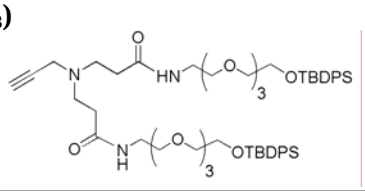
Compound 62 (^{1}H and ^{13}C, $CDCl_3$)

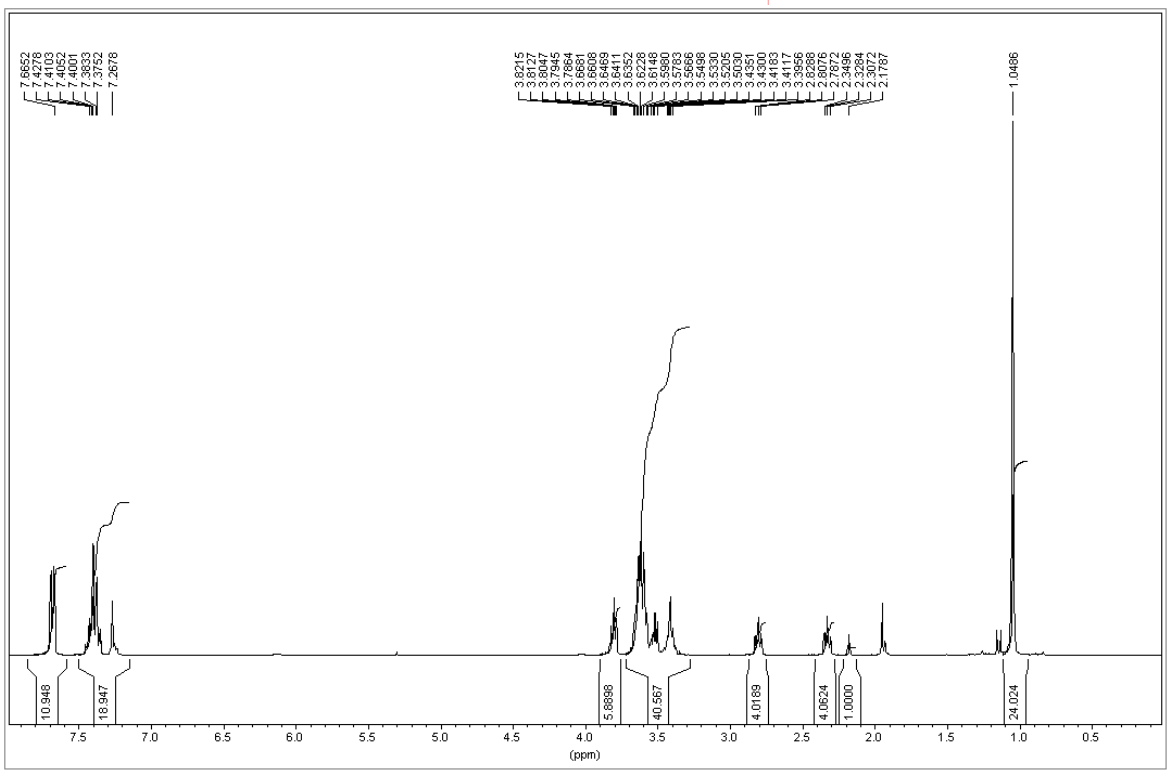


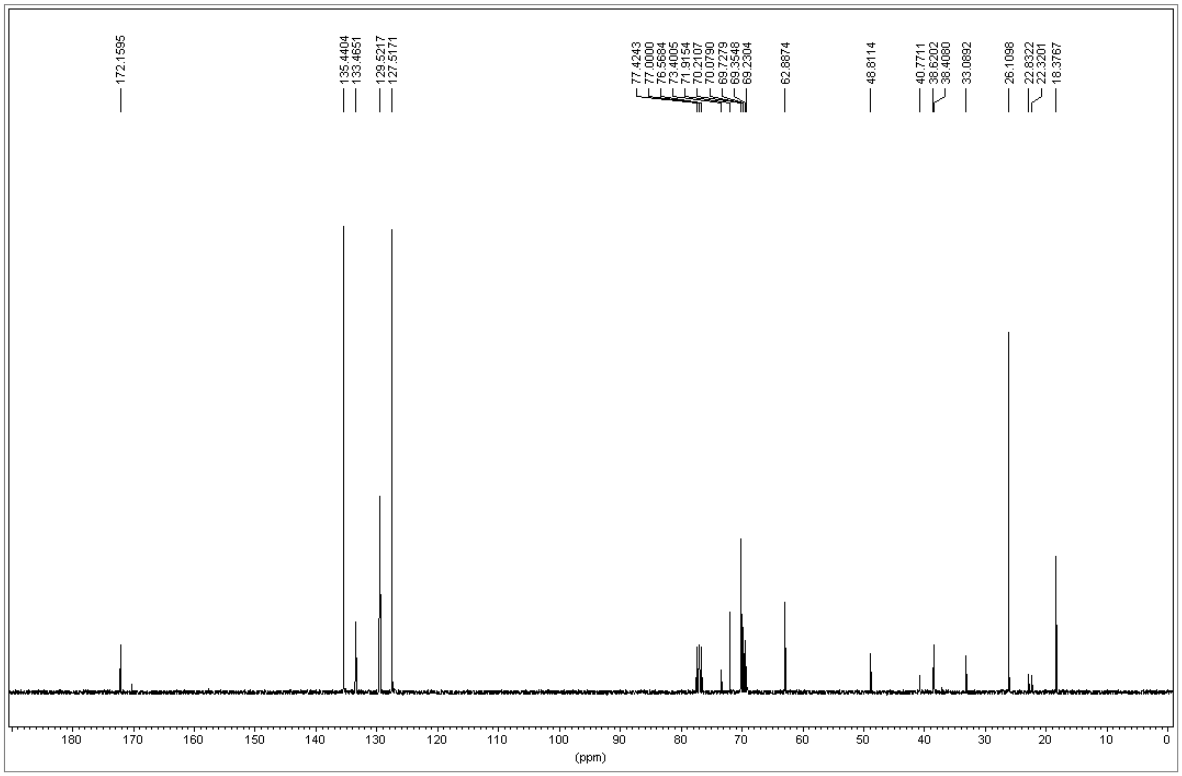




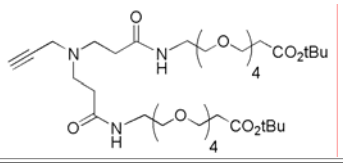
Compound 63 (^{1}H and ^{13}C, $CDCl_3$)

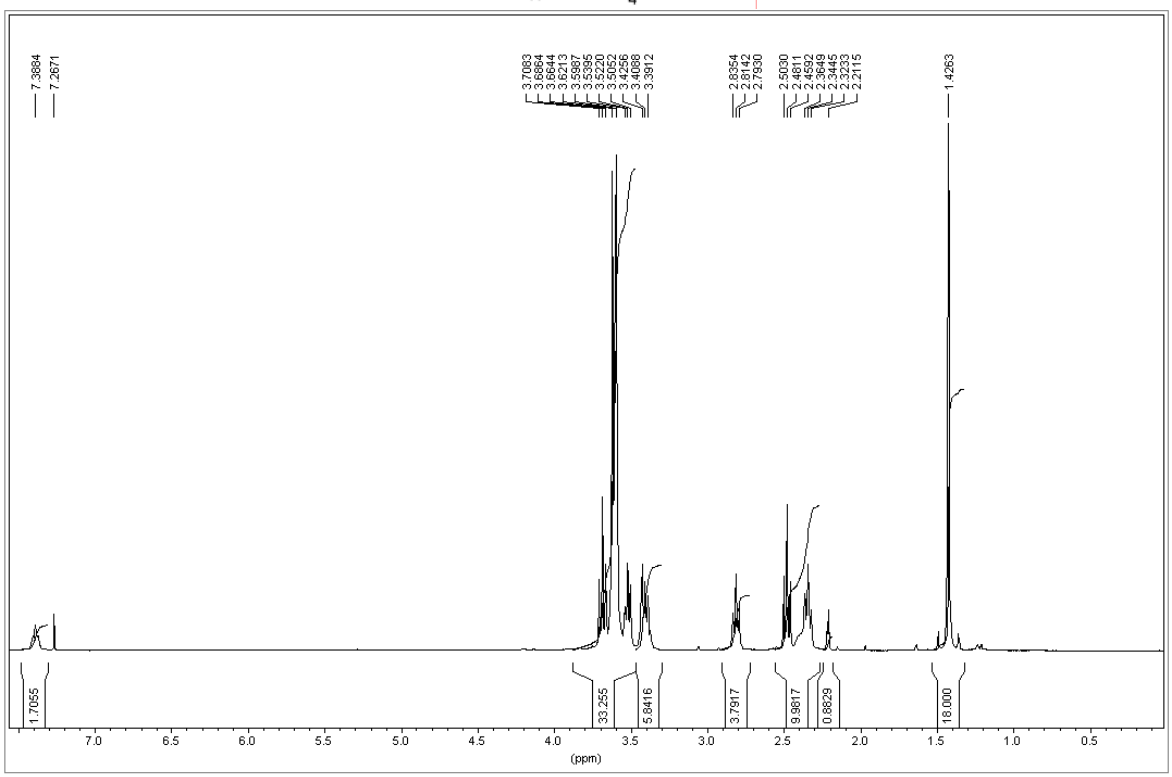


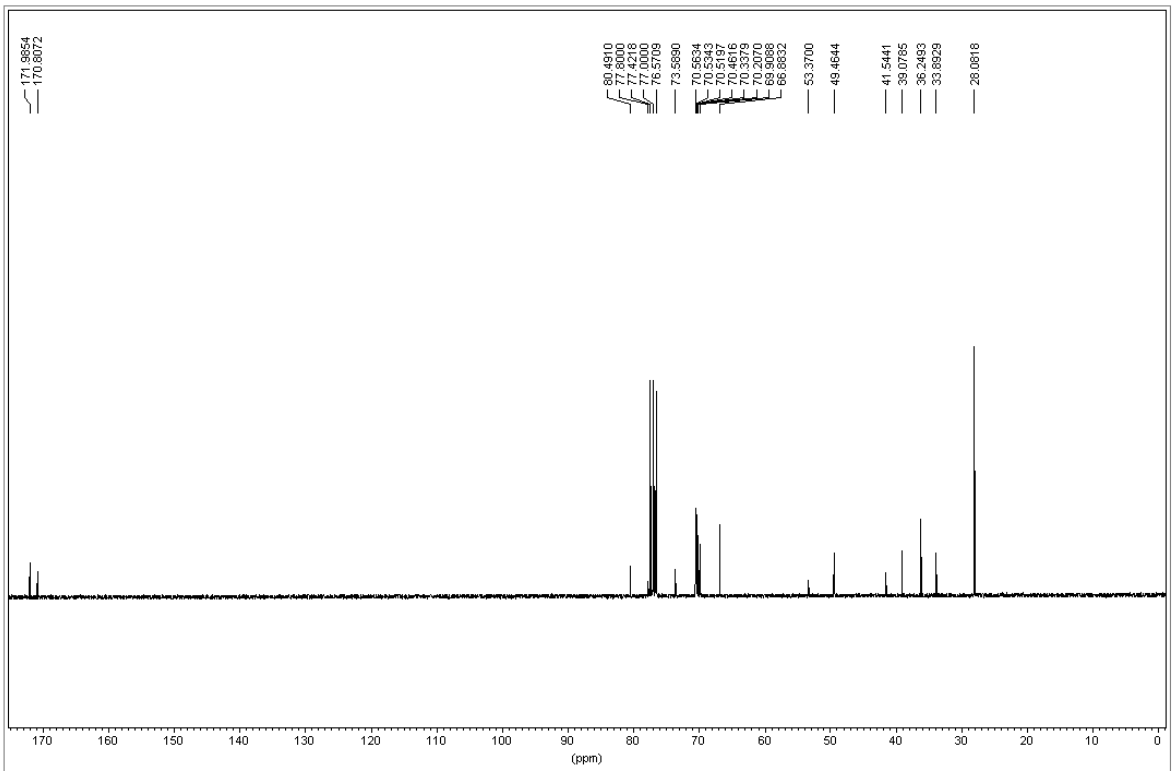




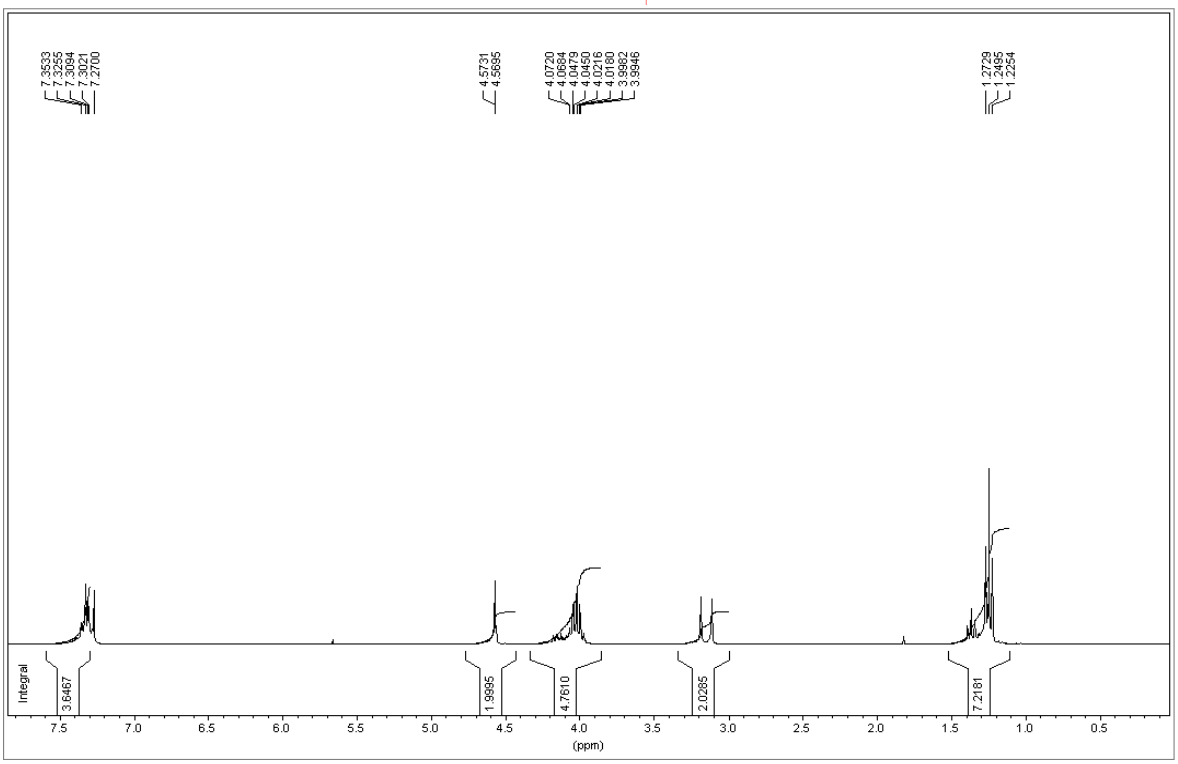
Compound 65 (^{1}H and ^{13}C, $CDCl_3$)



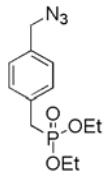


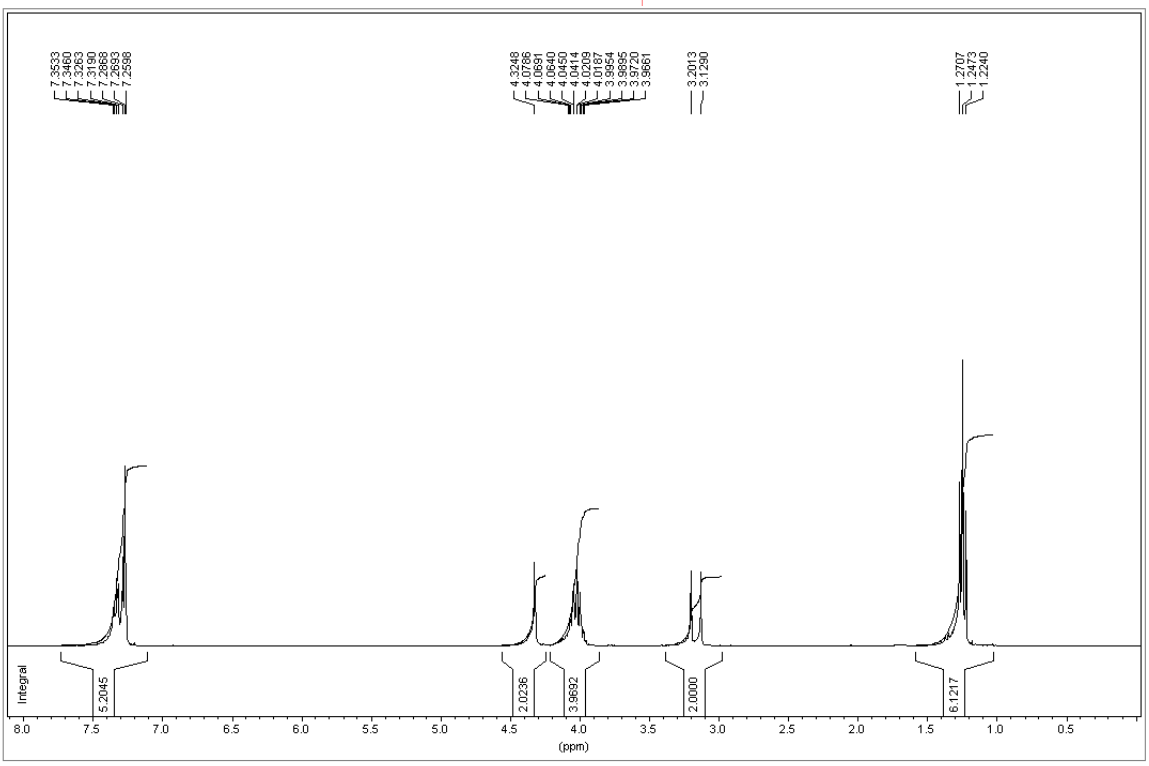


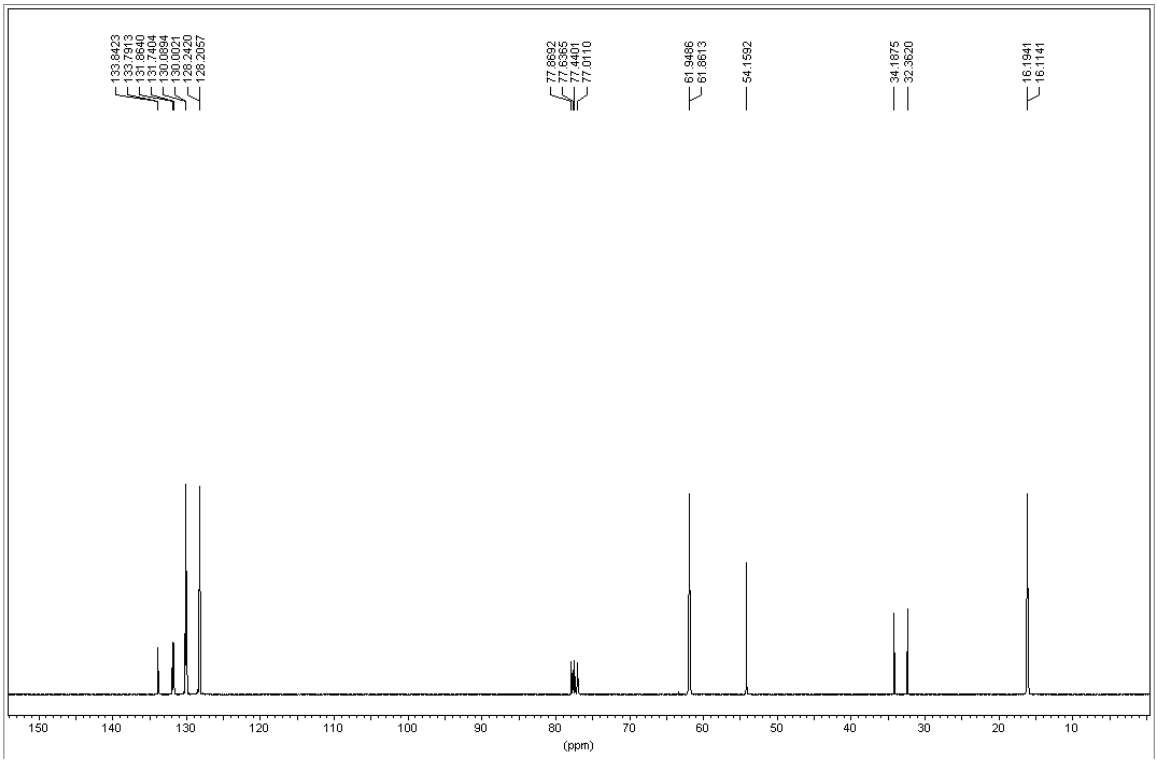
Compound 66 (^{1}H, $CDCl_3$, Tetrahedron Letters, 2006, 47, 2731-2734)

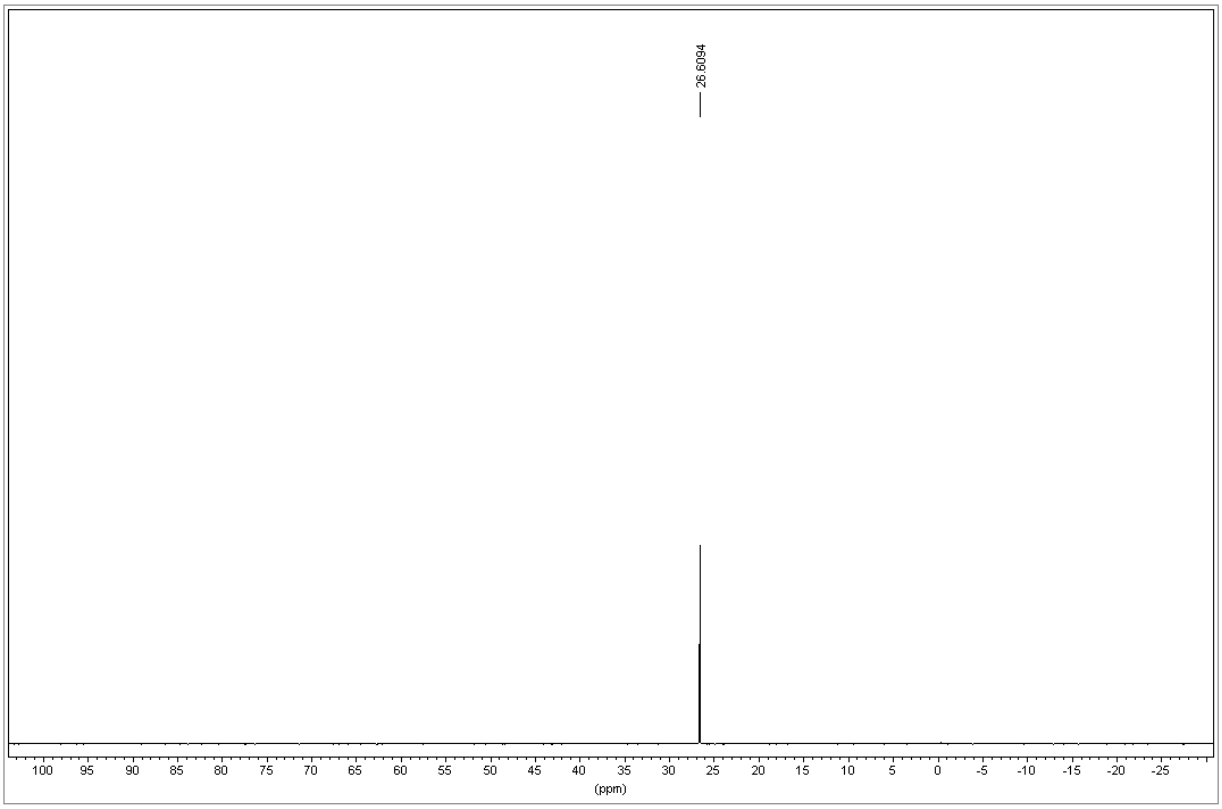


Compound 67 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

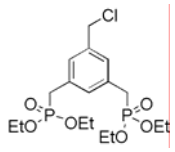


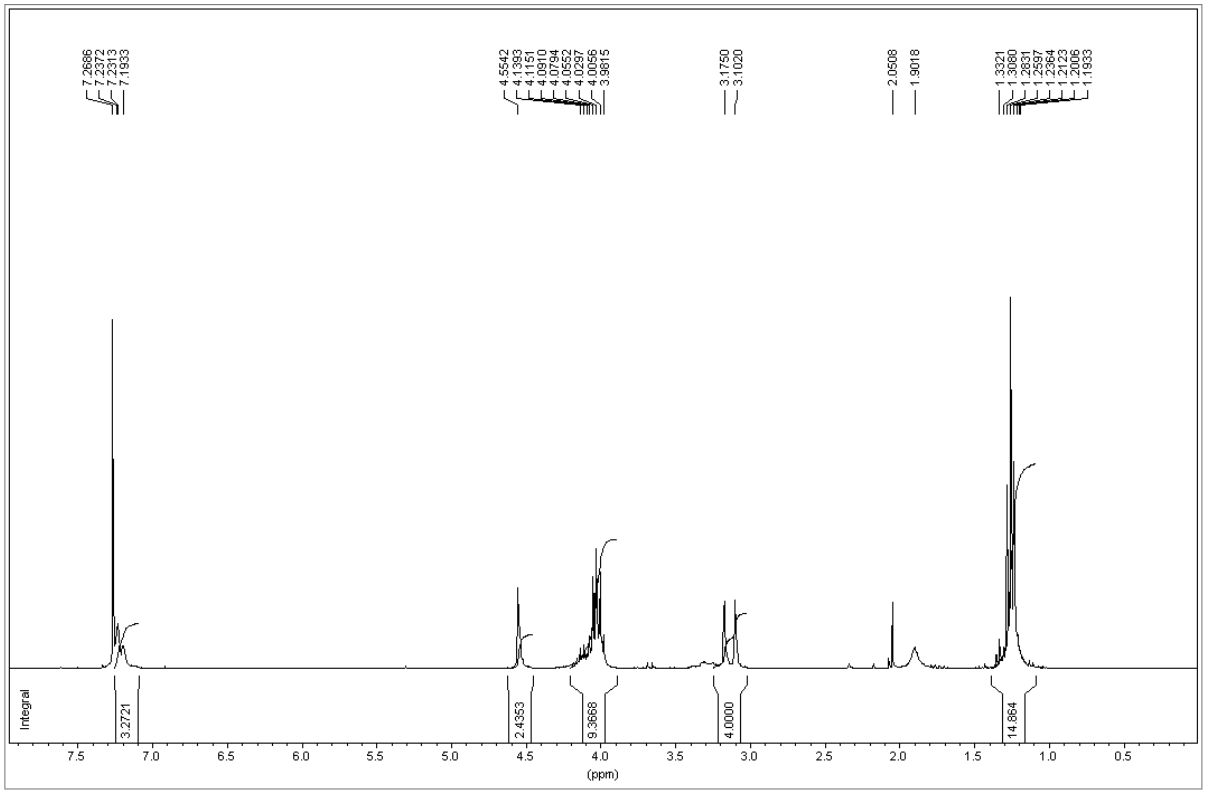


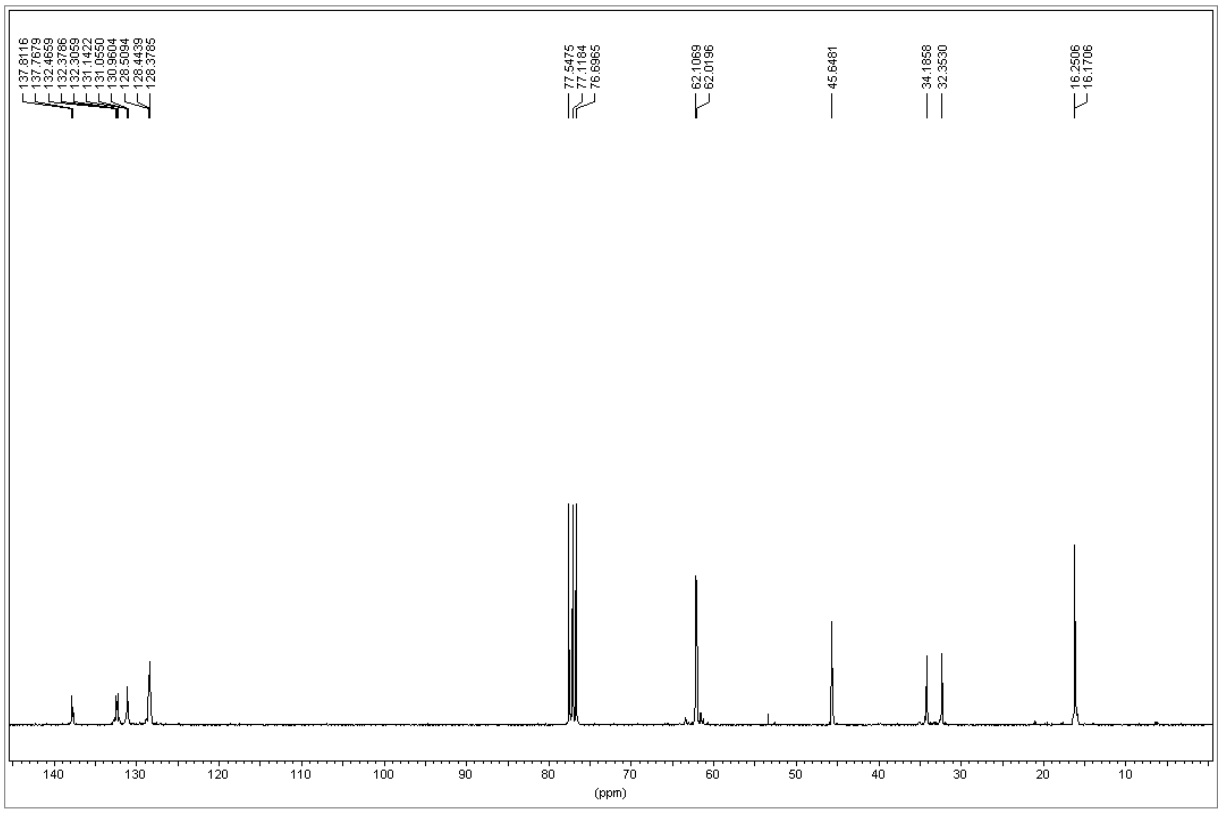




Compound 71 (^{1}H and ^{13}C, $CDCl_3$)






137.8116
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132.3786
132.3059
131.1422
131.0550
130.9804
128.5094
128.4439
128.3765
77.5475
77.1184
76.8965
62.1069
62.0196
45.6481
34.1858
32.3530
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16.1706
140
130
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110
100
90
80
70
60
50
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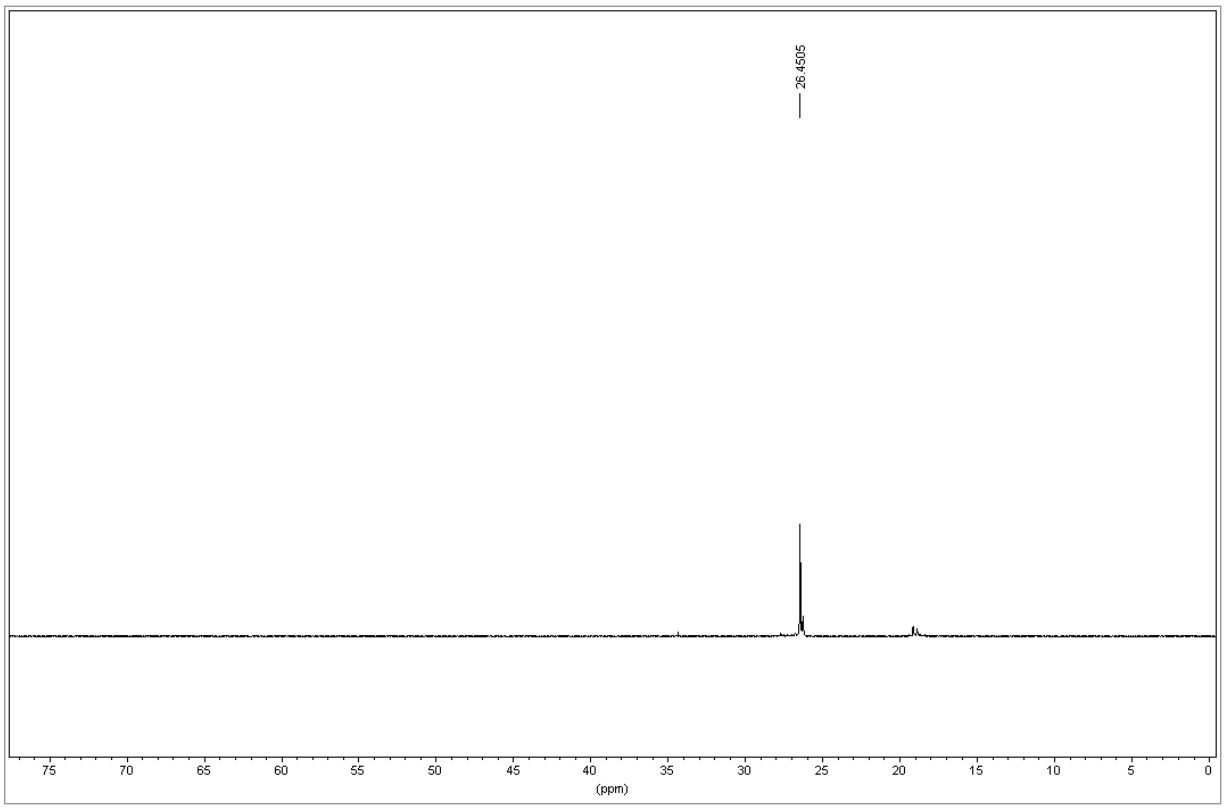
20
10
(ppm)


26.4505
75
70
65
60
55
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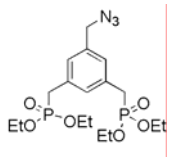
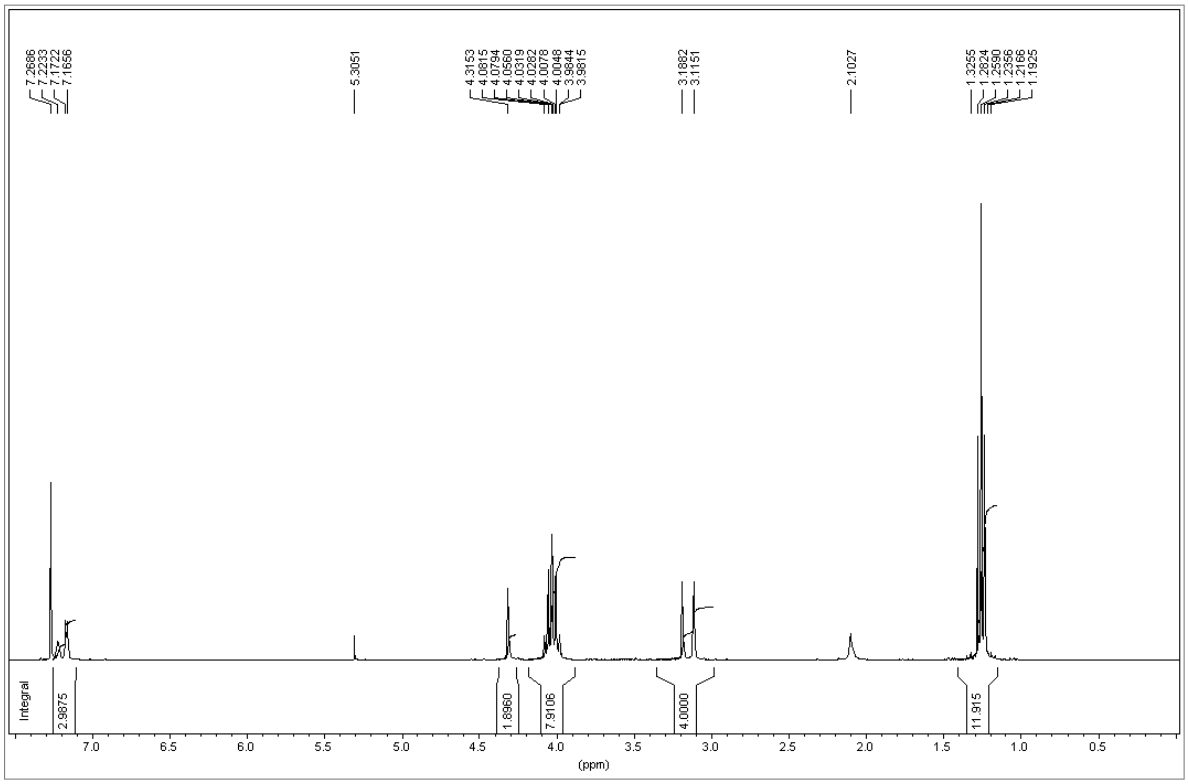
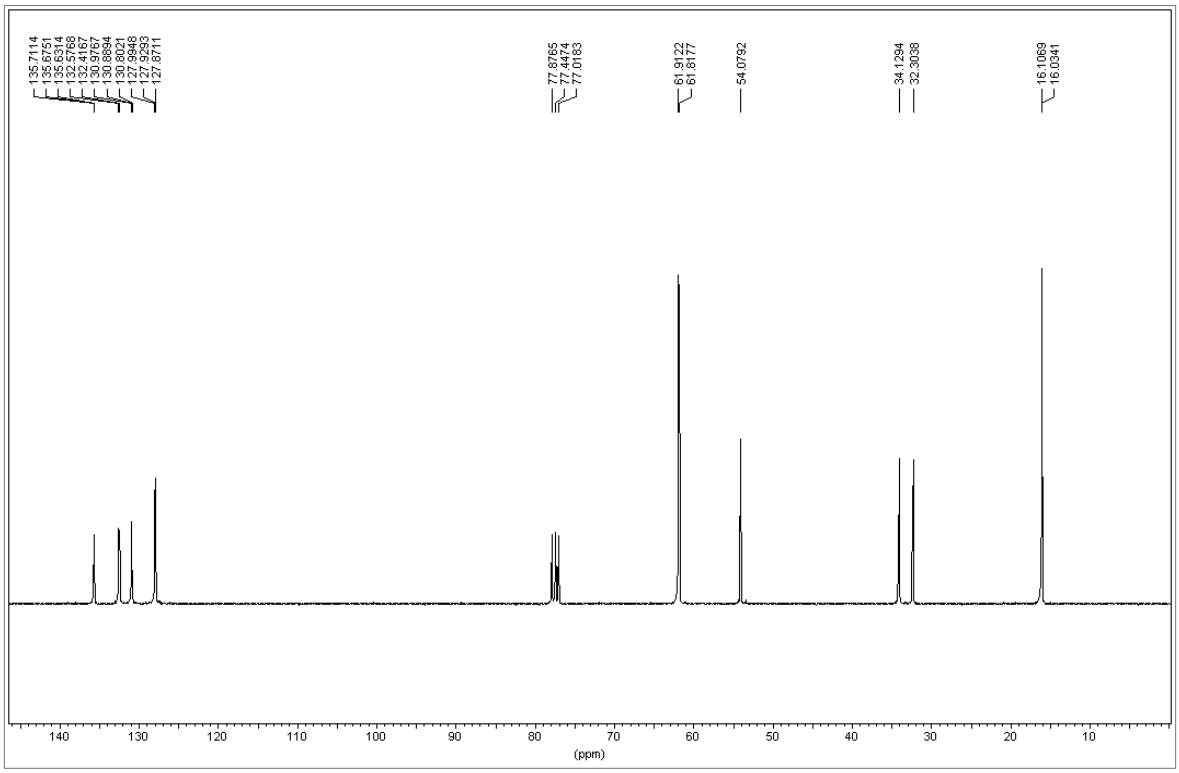
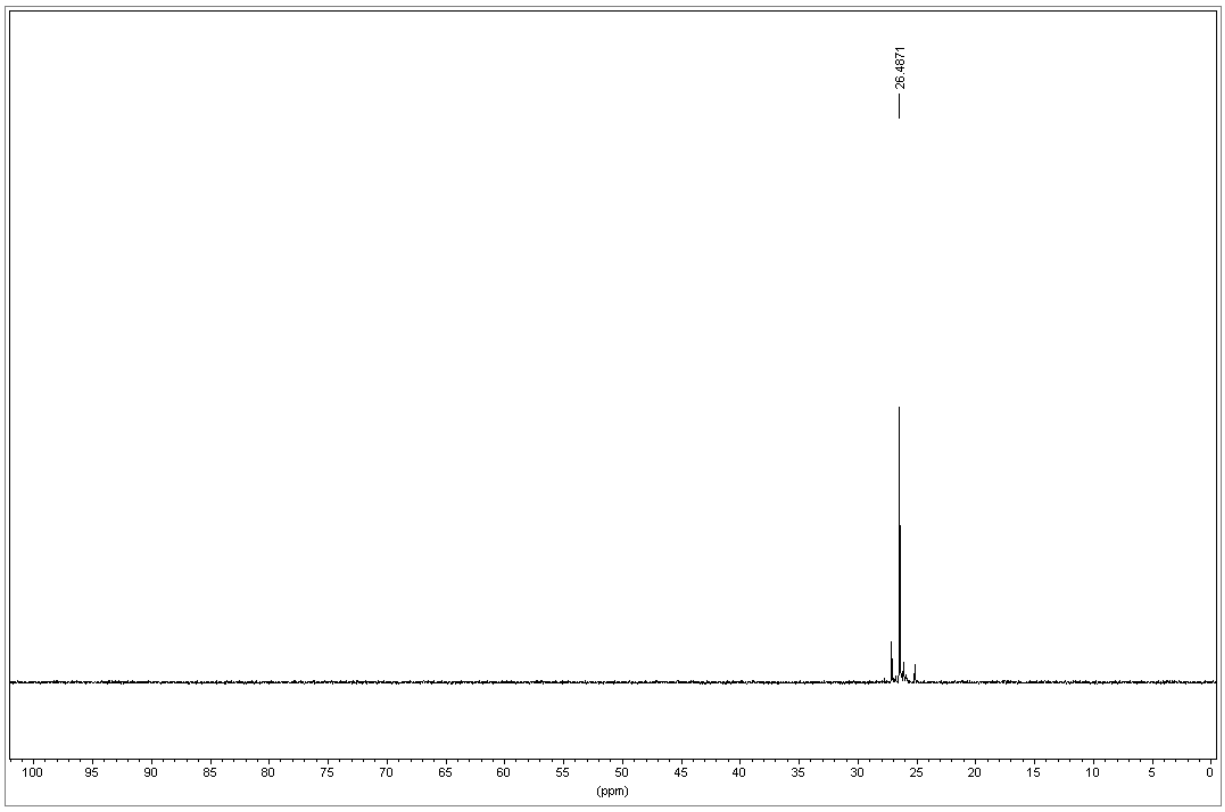
45
40
35
30
25
20
15
10
5
0
(ppm)

Compound 72 (^{1}H and ^{13}C, $CDCl_3$)

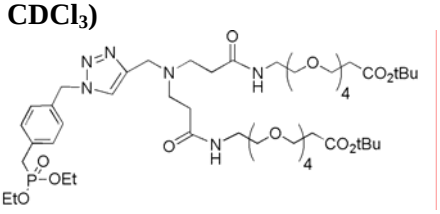


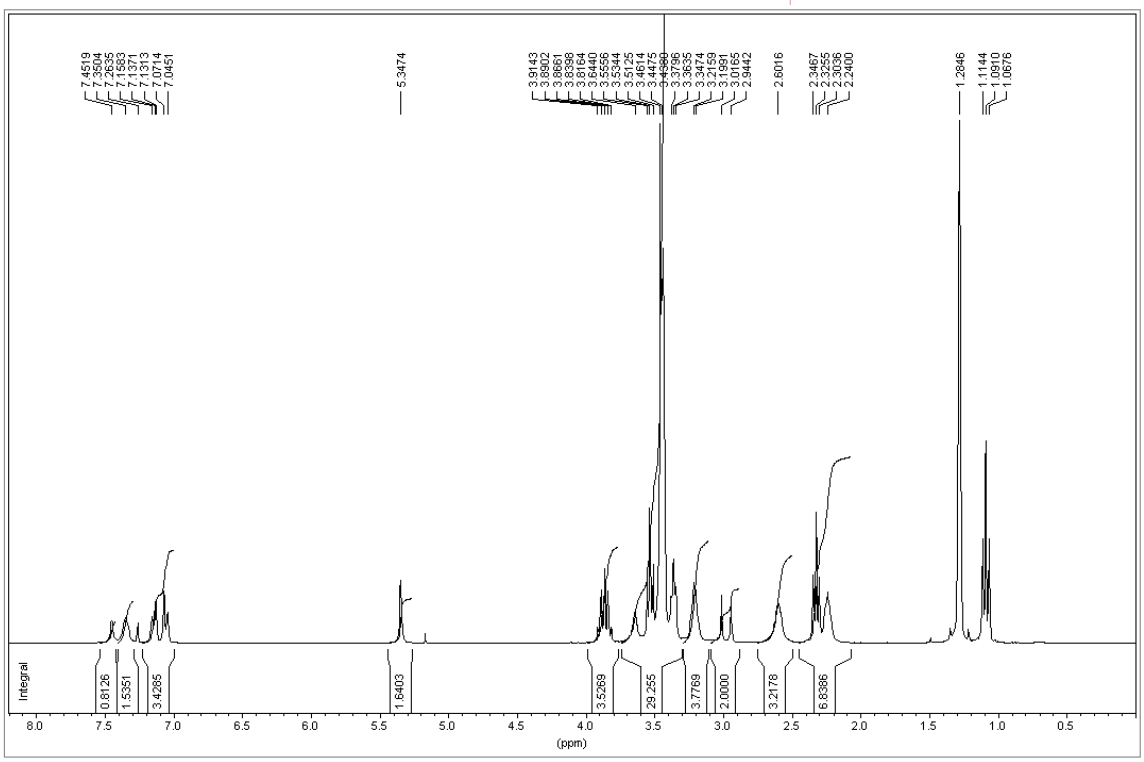


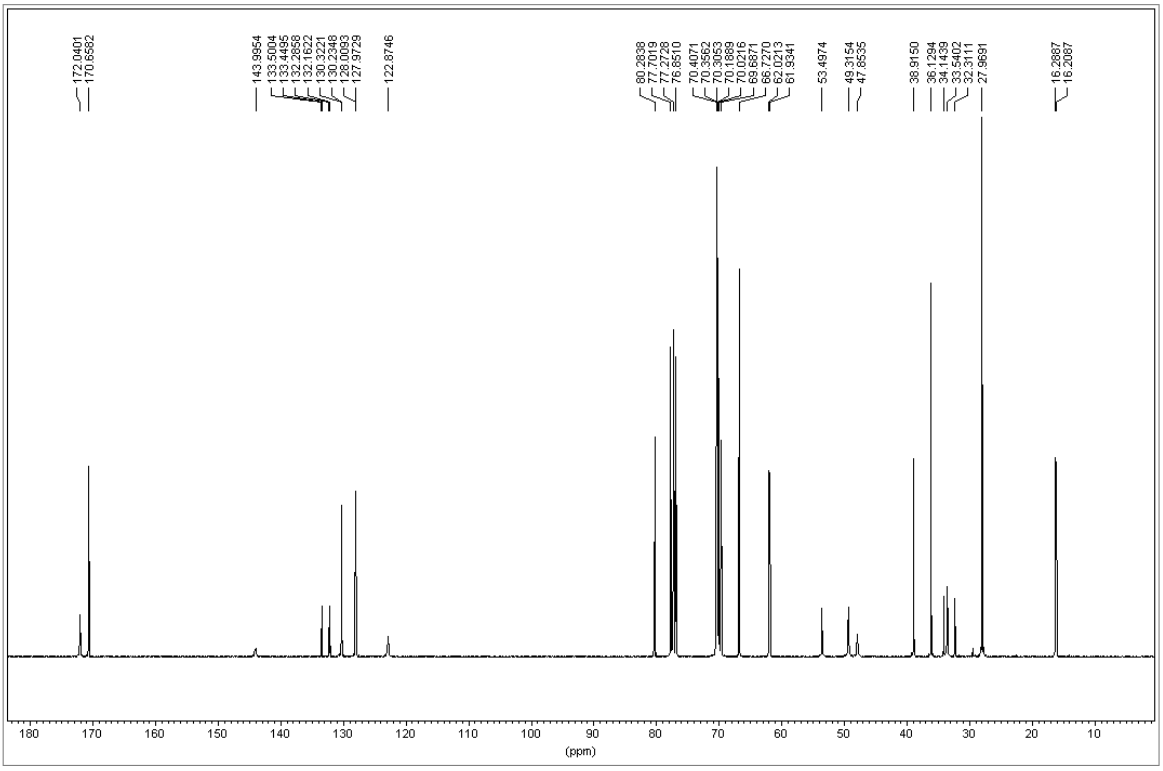


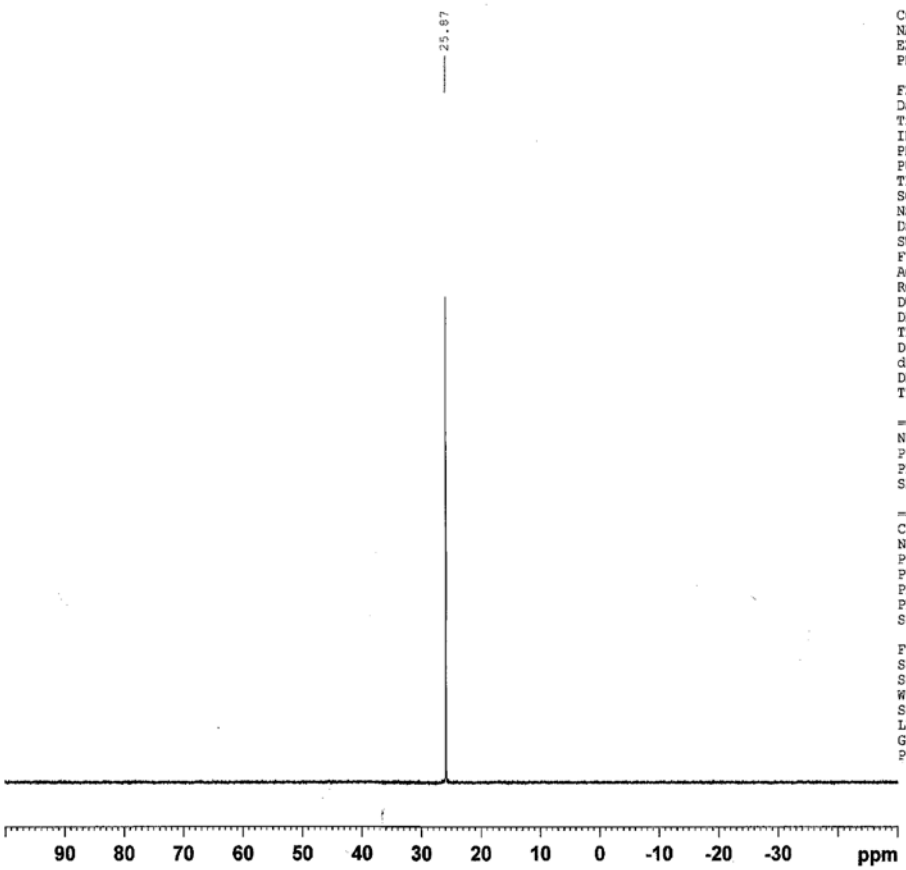


Compound 73 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)





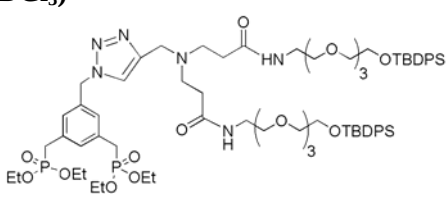


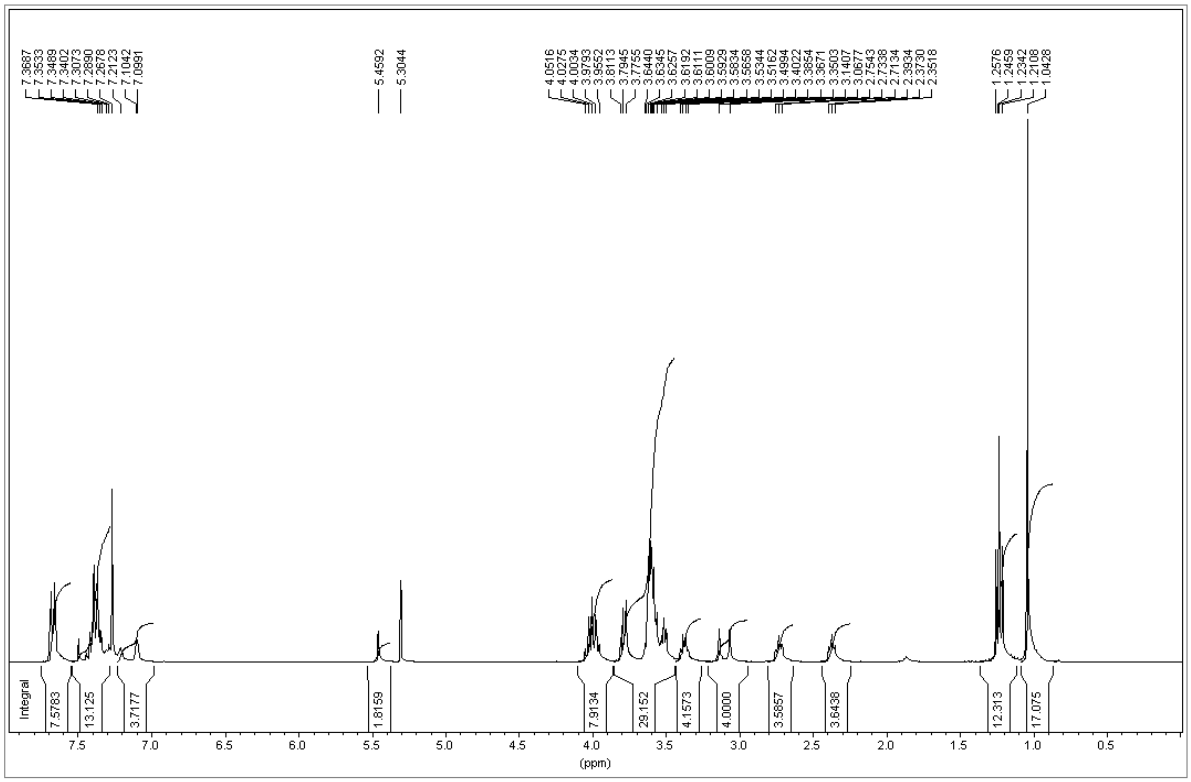


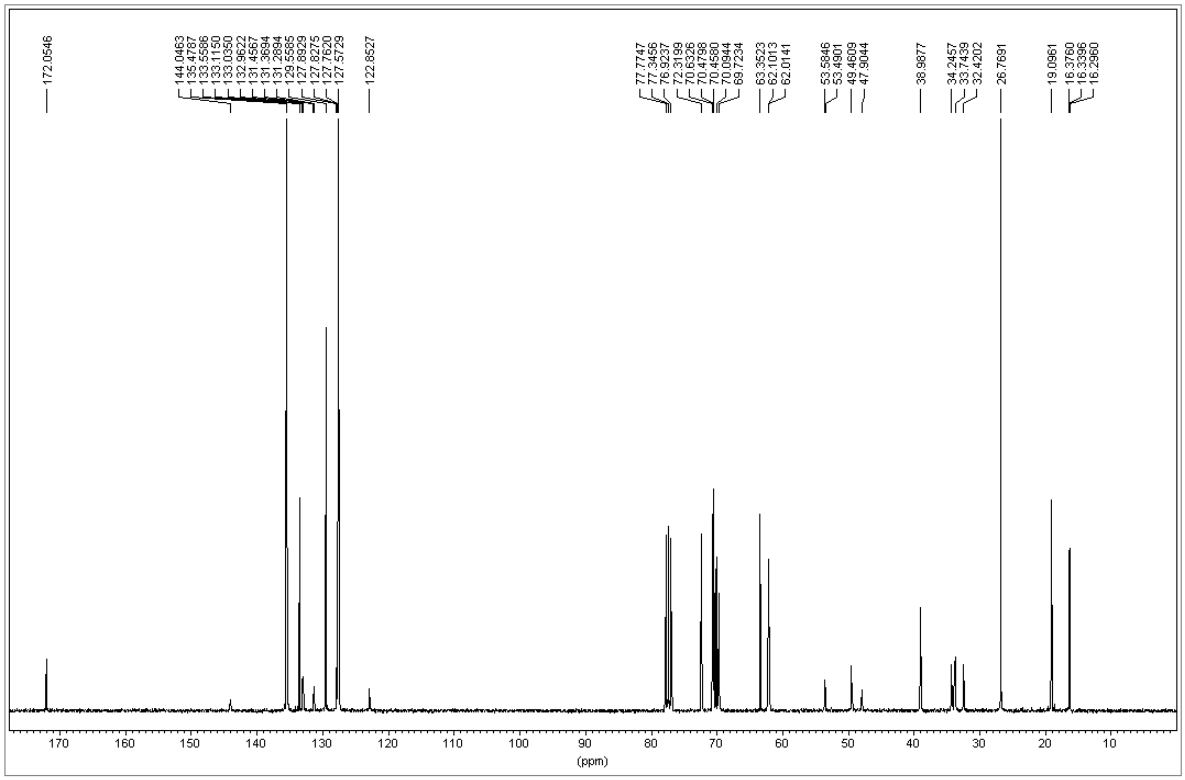

```
Current Data Parameters
NAME      ipcmsap055.1225
EXPNO                    8
PROCNO                   1

F2 - Acquisition Parameters
Date_             20120622
Time                 11.44
INSTRUM              spect
PROBHD   5 mm QNP 1H/13
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     40
DS                      2
SWH            48661.801 Hz
FIDRES          0.742520 Hz
AQ              0.6734324 sec
RG                14596.5
DW                 10.275 usec
DE                 10.00 usec
TE                 299.2 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   31P
P1                    8.00 usec
PL1                  -3.00 dB
SFO1         161.9807141 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                 120.00 dB
PL12                 18.00 dB
PL13                 18.00 dB
SFO2         400.1316000 MHz

F2 - Processing parameters
SI                     32768
SF           161.9755930 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

Compound 74 The analytical data are reported in the literature.[22c]

Compound 75 (^{1}H and ^{13}C, $CDCl_3$)



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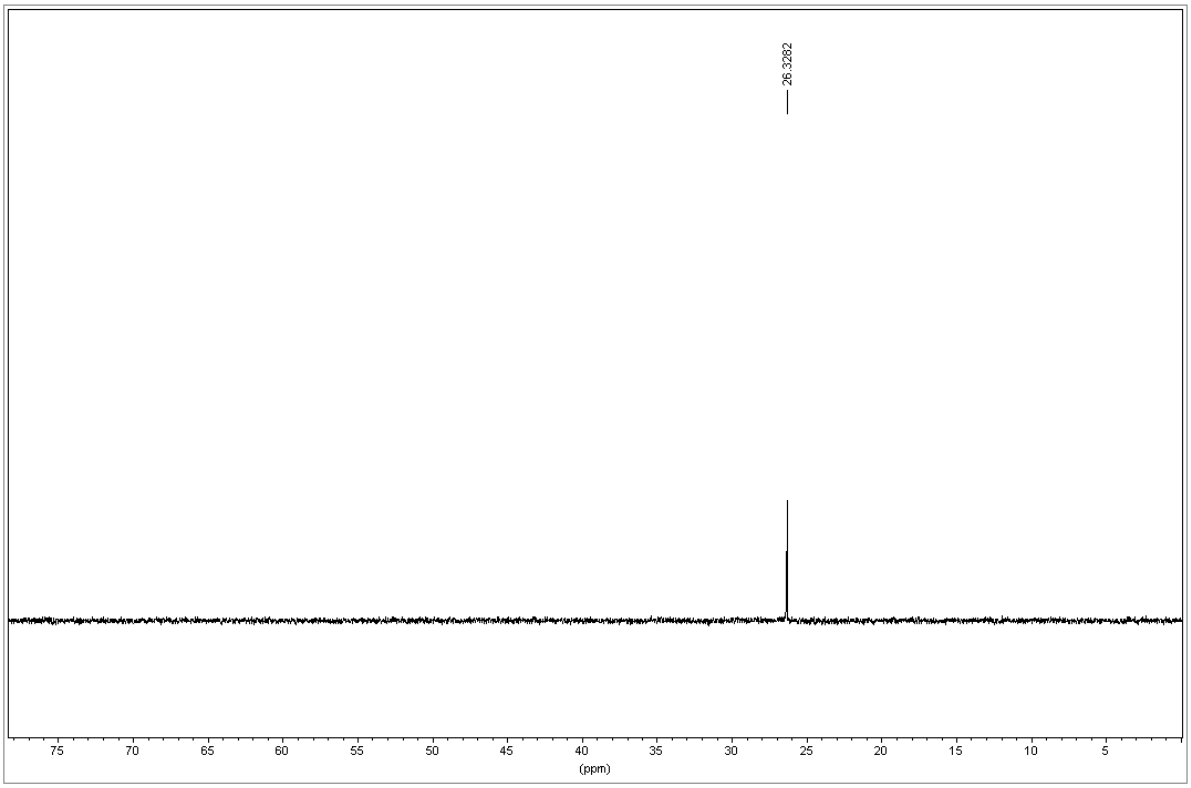
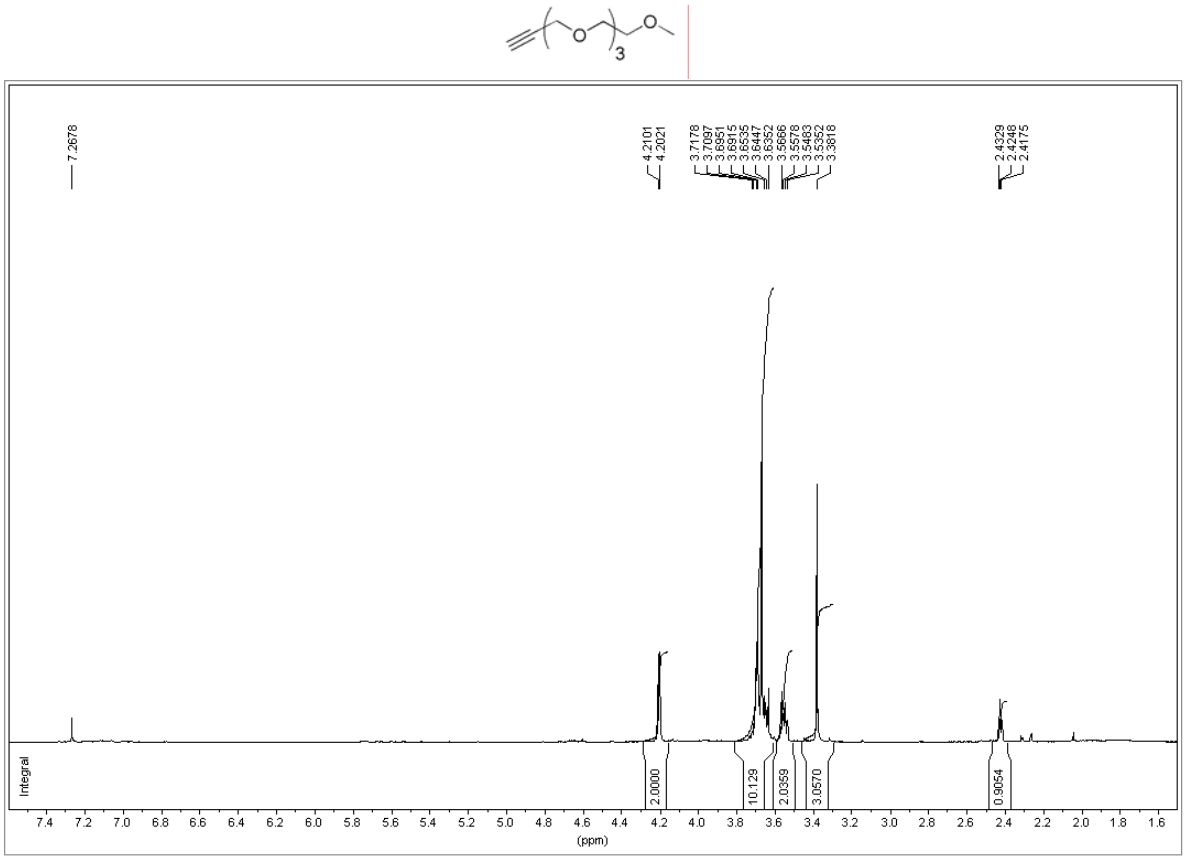
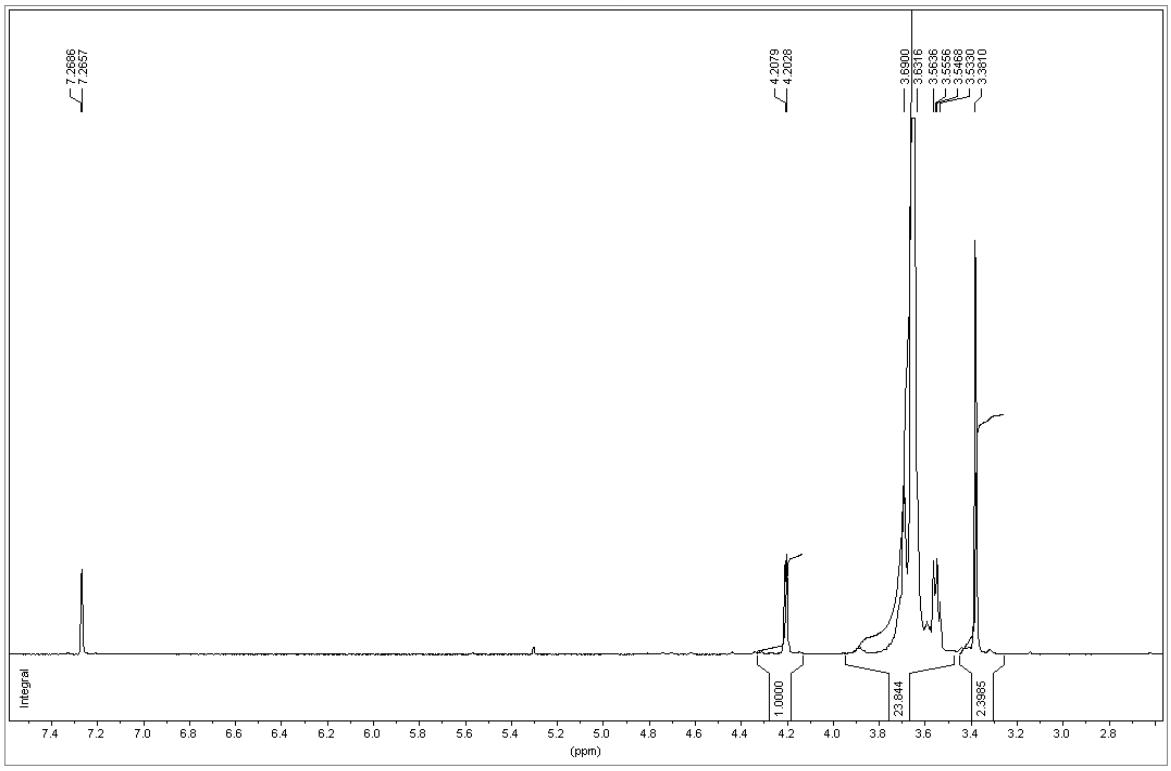
144.0463
135.4787
135.1586
133.1160
133.0350
132.9622
131.4567
131.3694
131.2894
129.5586
127.8869
127.8275
127.7620
127.5729
122.8527
77.7747
77.3456
76.9237
72.3199
70.6326
70.4798
70.4580
70.0944
69.7234
63.3523
62.1013
62.0141
53.5846
53.4901
49.4609
47.9044
38.9877
34.2457
33.7439
32.4202
26.7691
19.0961
16.3760
16.3396
16.2960
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

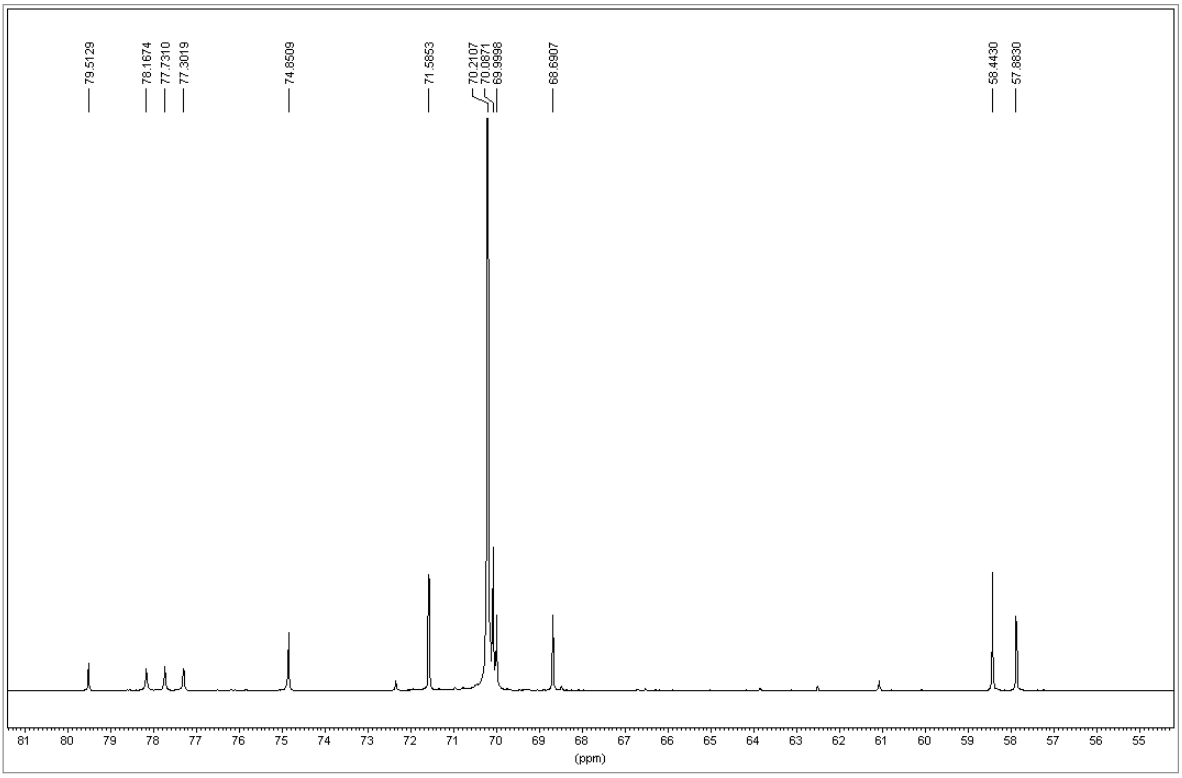

26.3282
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
(ppm)

Compound 76 (^{1}H, $CDCl_3$, literature: JACS, 2010, 132, 13928-13935)

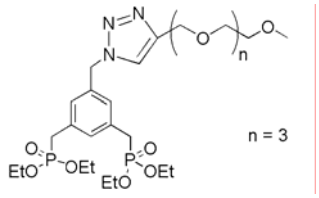


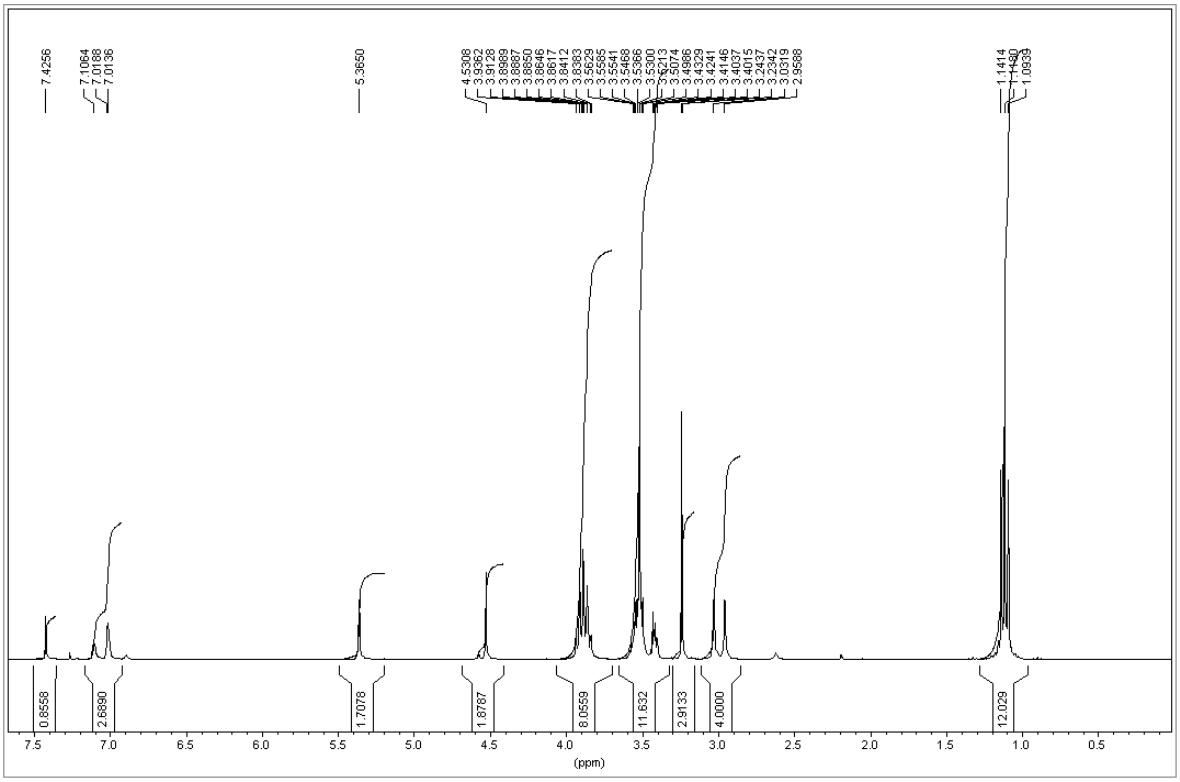
Compound 78 (^{1}H and ^{13}C, $CDCl_3$)

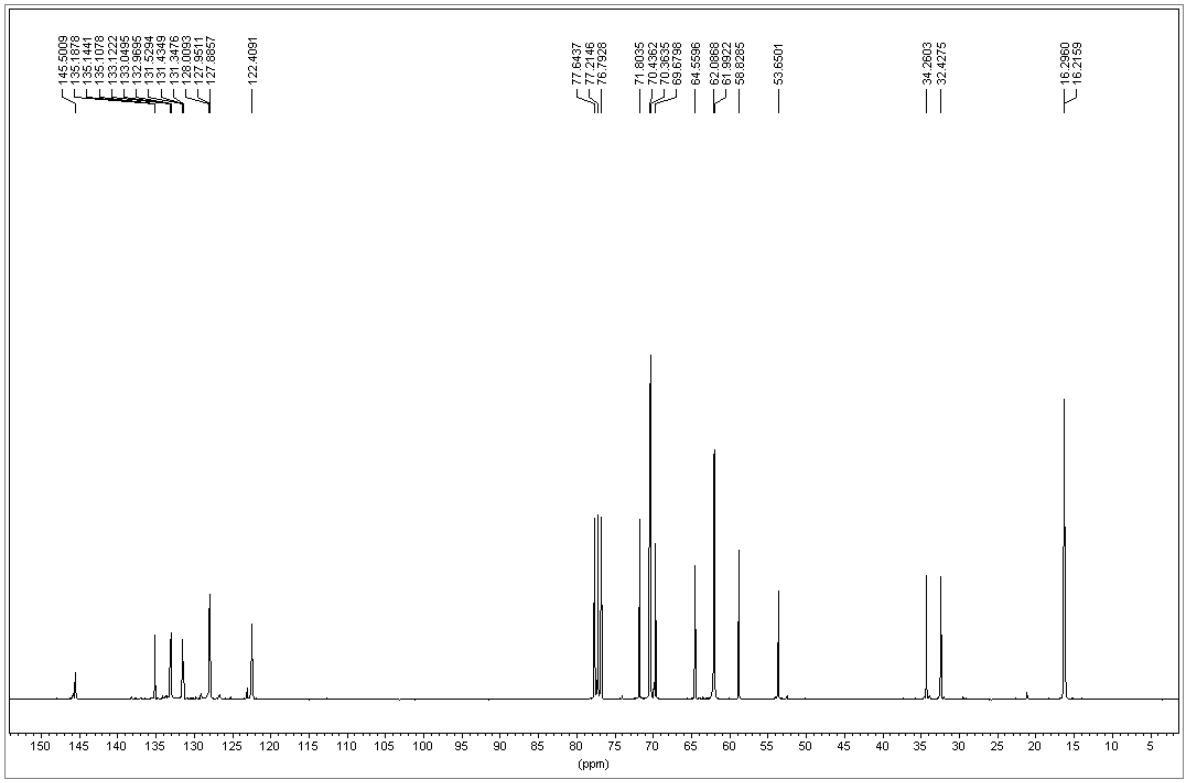


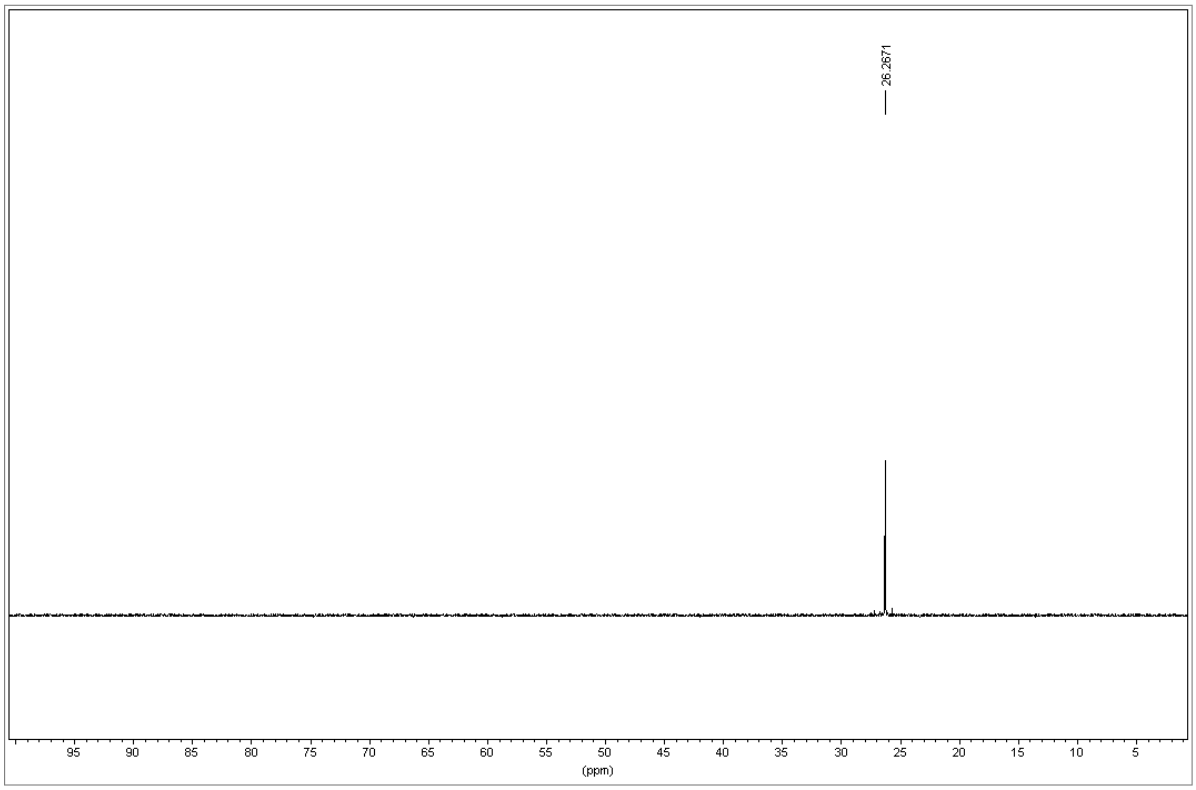


Compound 79 (^{1}H and ^{13}C, $CDCl_3$)

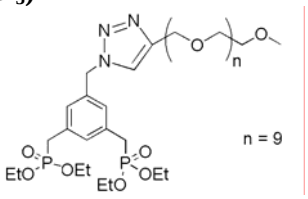


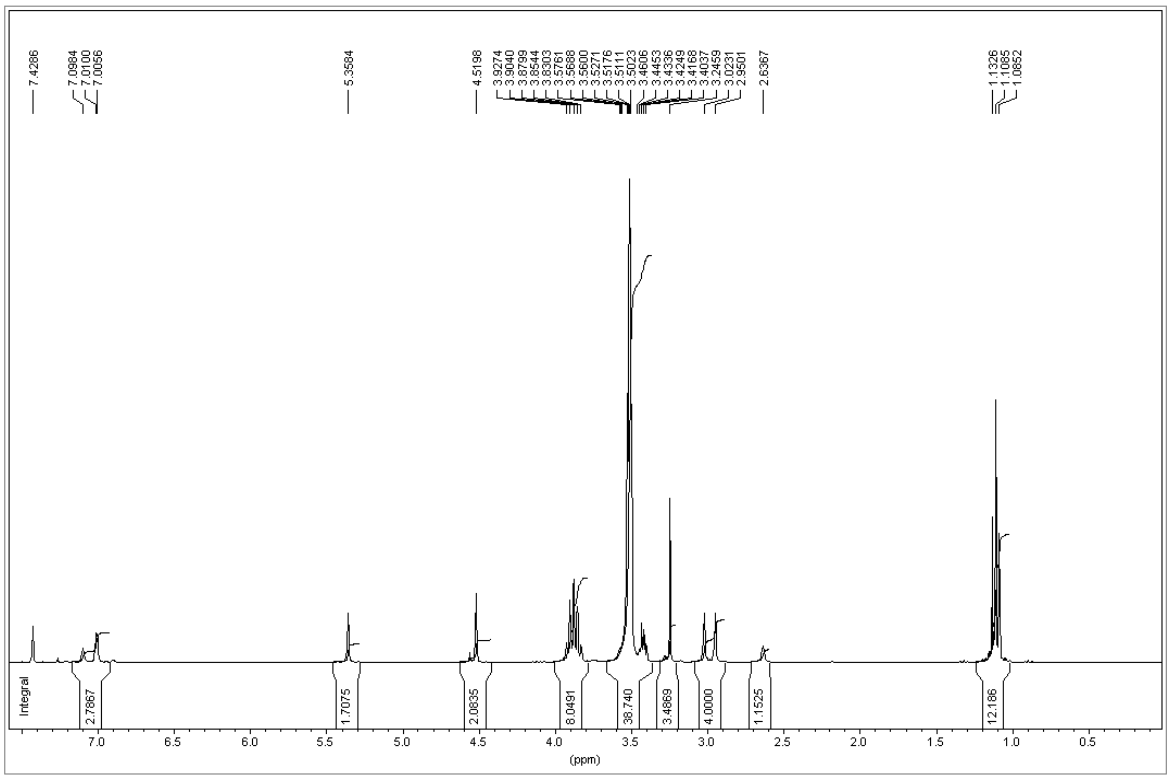


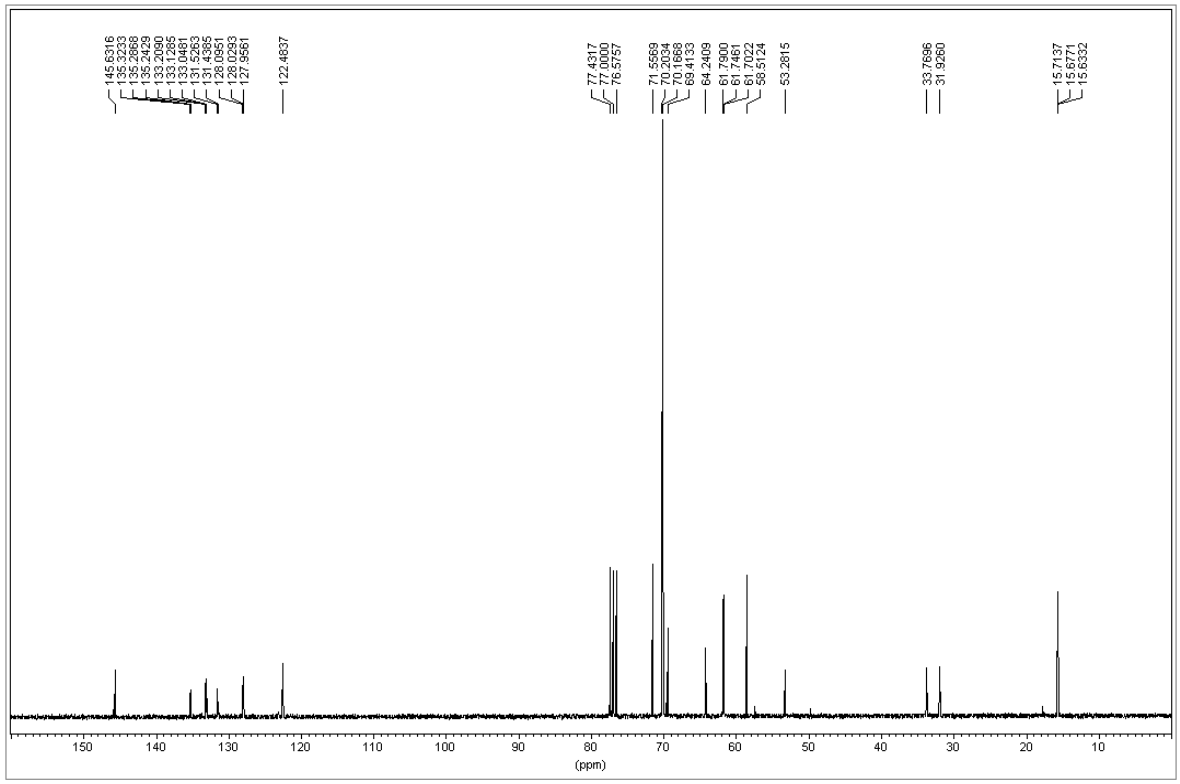

145.5009
135.1878
135.1441
135.1078
133.1222
133.0495
132.9995
131.5294
131.4349
131.3476
128.0093
127.9511
127.8857
122.4091
77.6437
77.2146
76.7928
71.8035
70.4362
70.3635
69.6798
64.5596
62.0868
61.9922
58.8285
53.6501
34.2603
32.4275
16.2960
16.2159
(ppm)

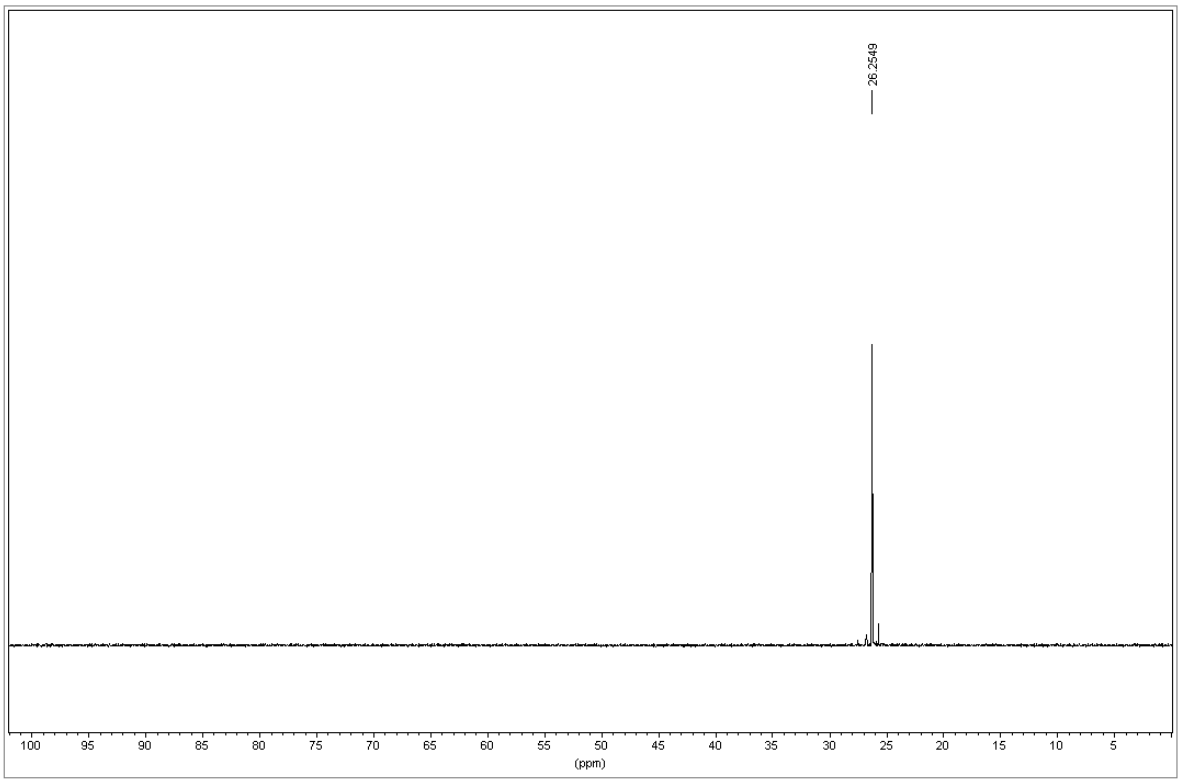

26.2671
(ppm)

Compound 80 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

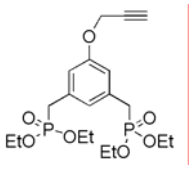


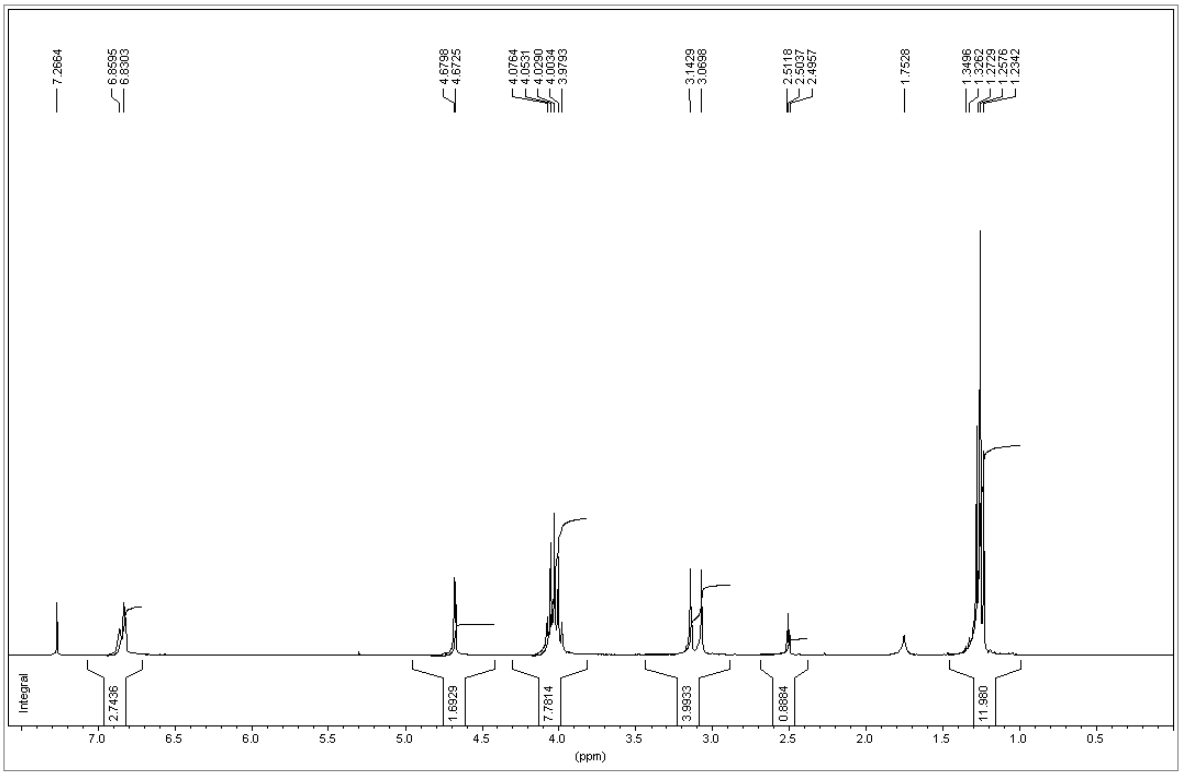


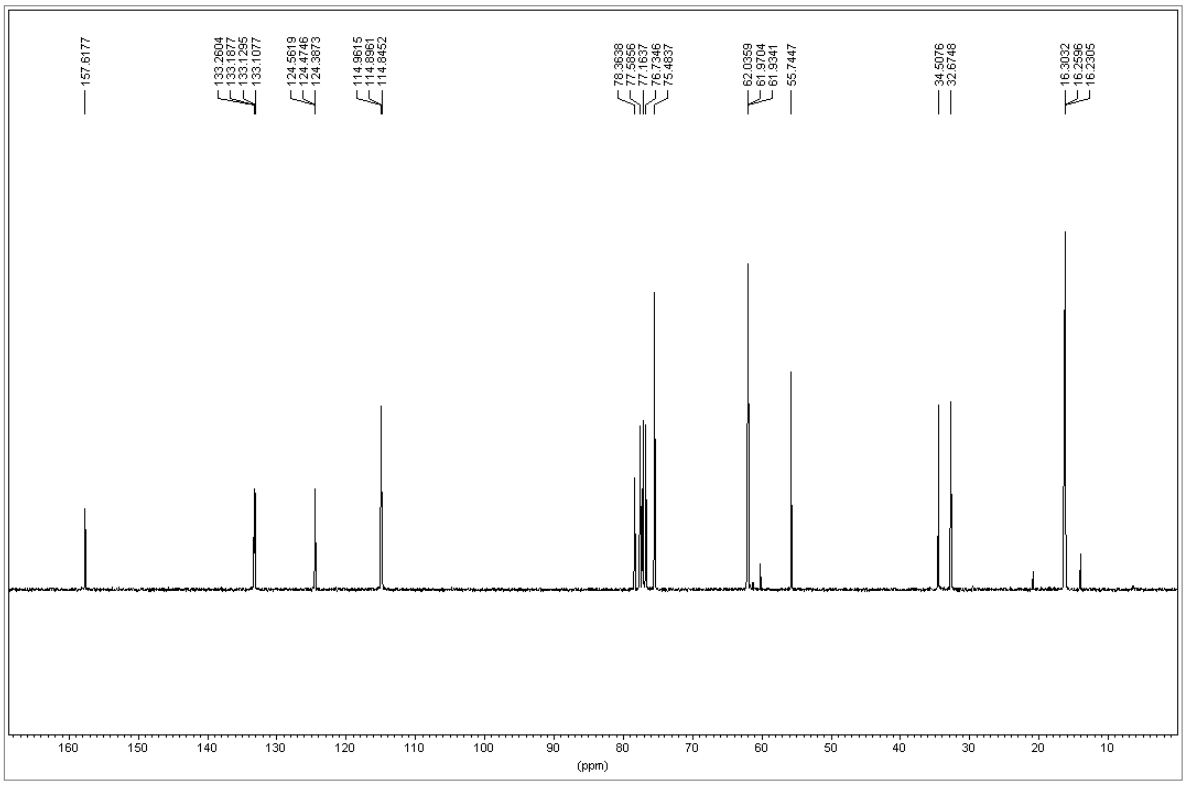


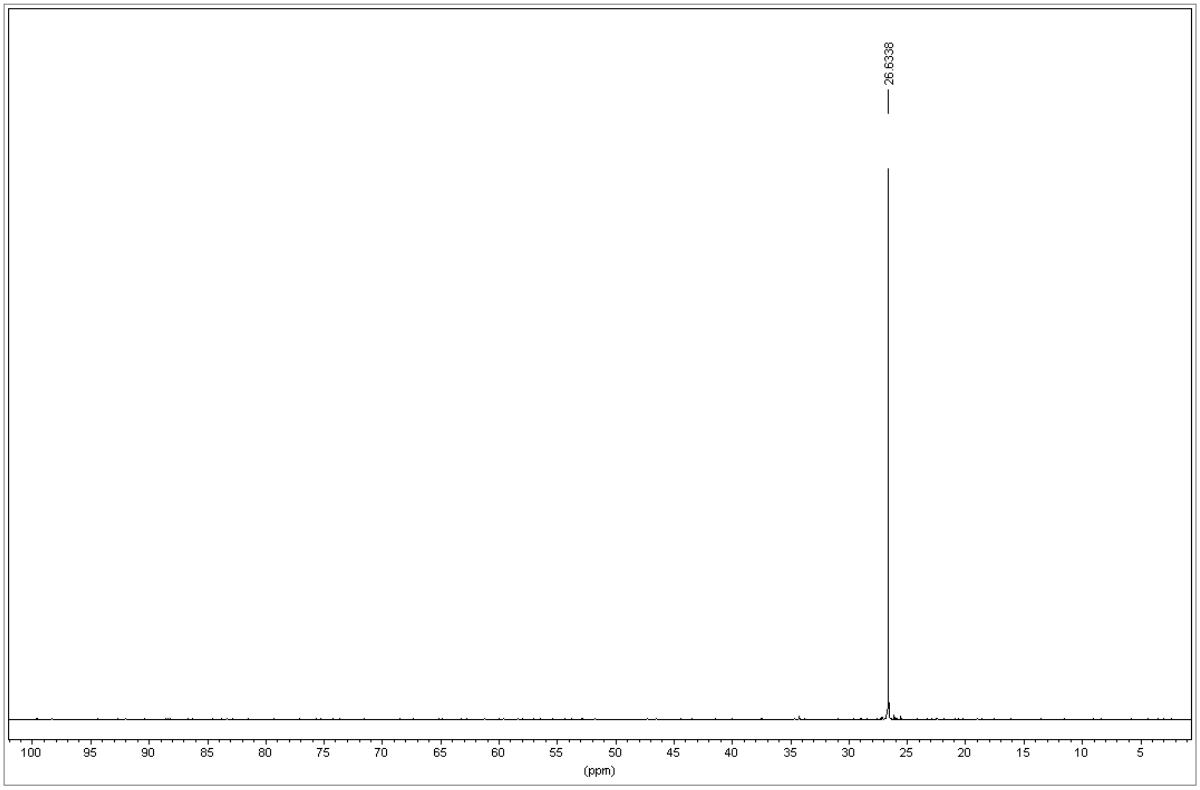


Compound 81 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

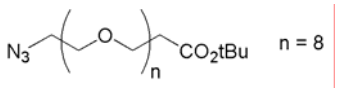


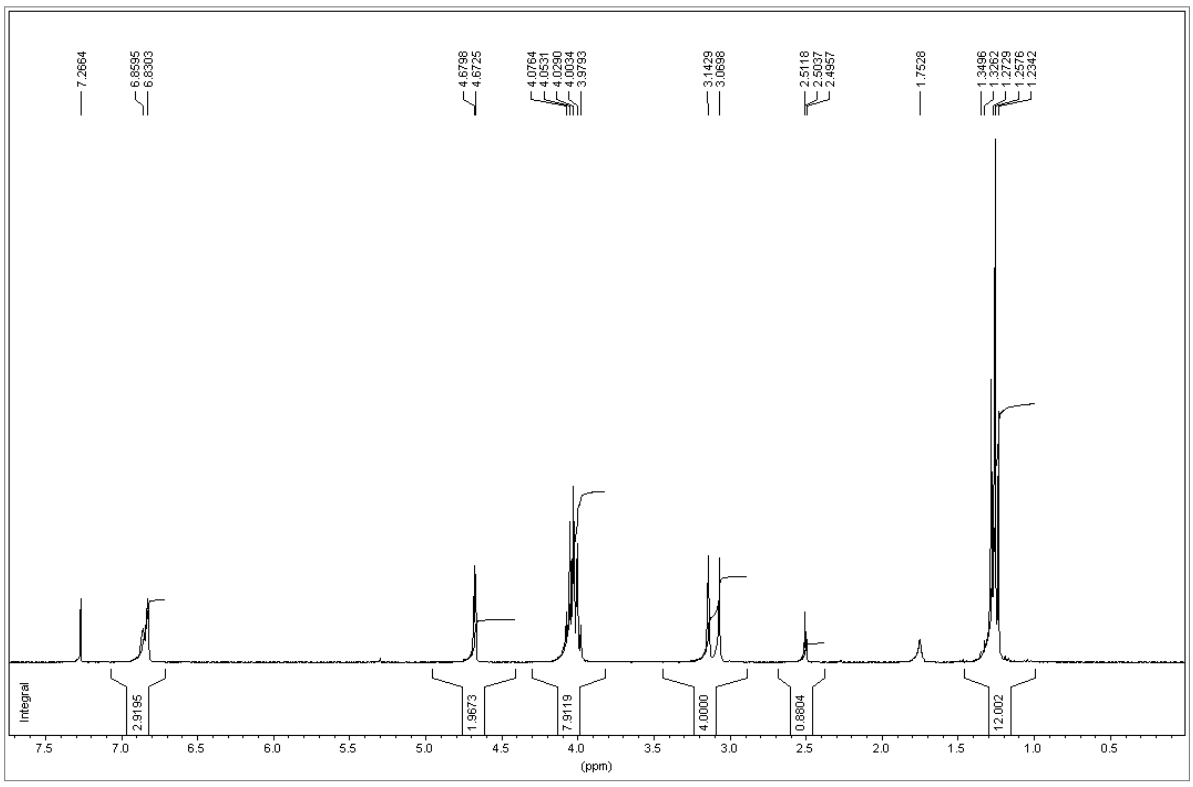


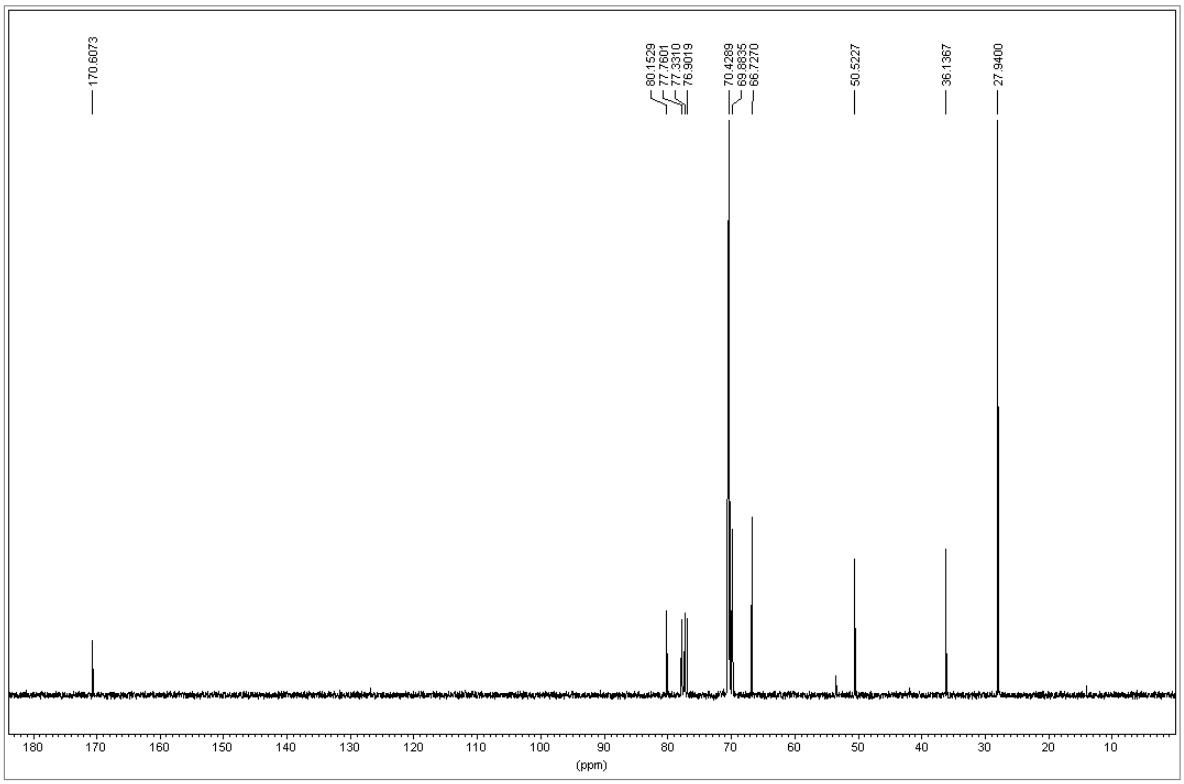

157.6177
133.2604
133.1877
133.1295
133.1077
124.5619
124.4746
124.3873
114.9615
114.8961
114.8452
79.3638
77.5856
77.1637
76.7346
75.4837
62.0359
61.9704
61.9341
55.7447
34.5076
32.6748
16.3032
16.2596
16.2305
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)


26.6338
100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
(ppm)

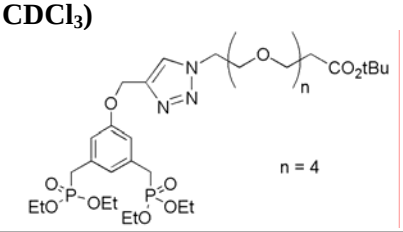
Compound 85 (^{1}H and ^{13}C, $CDCl_3$)

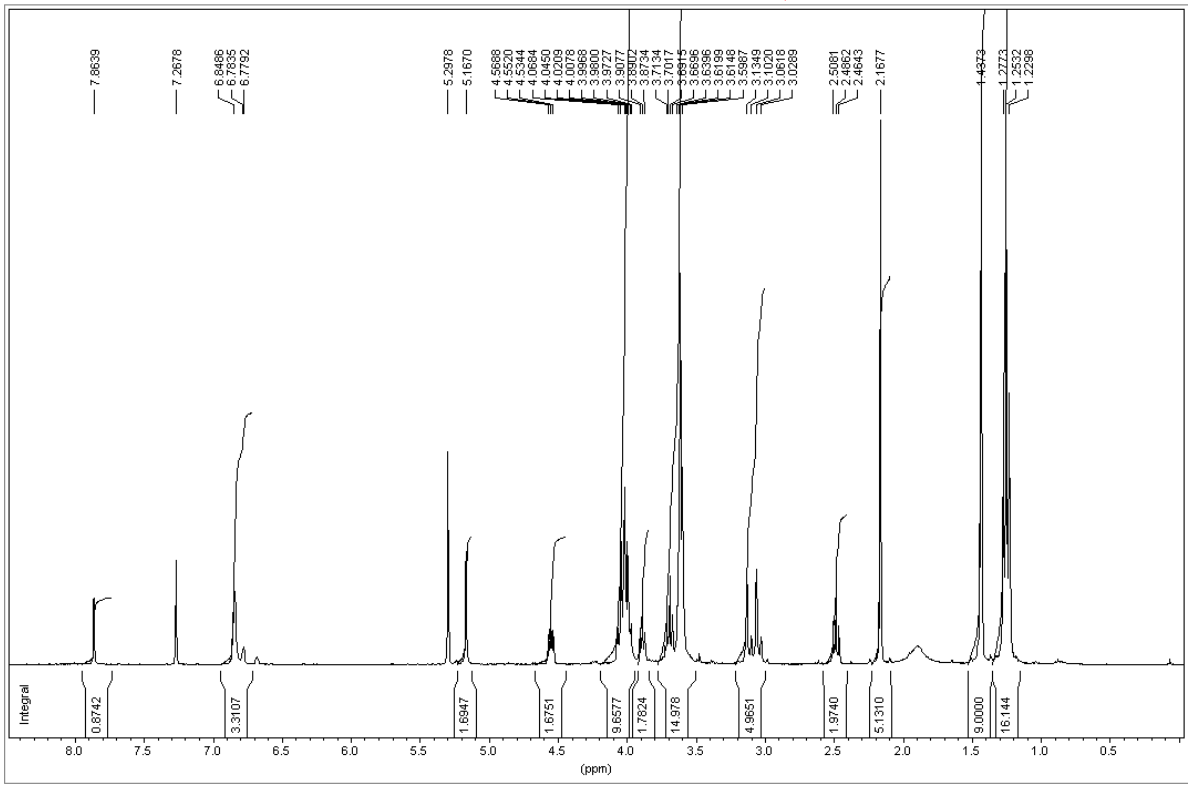


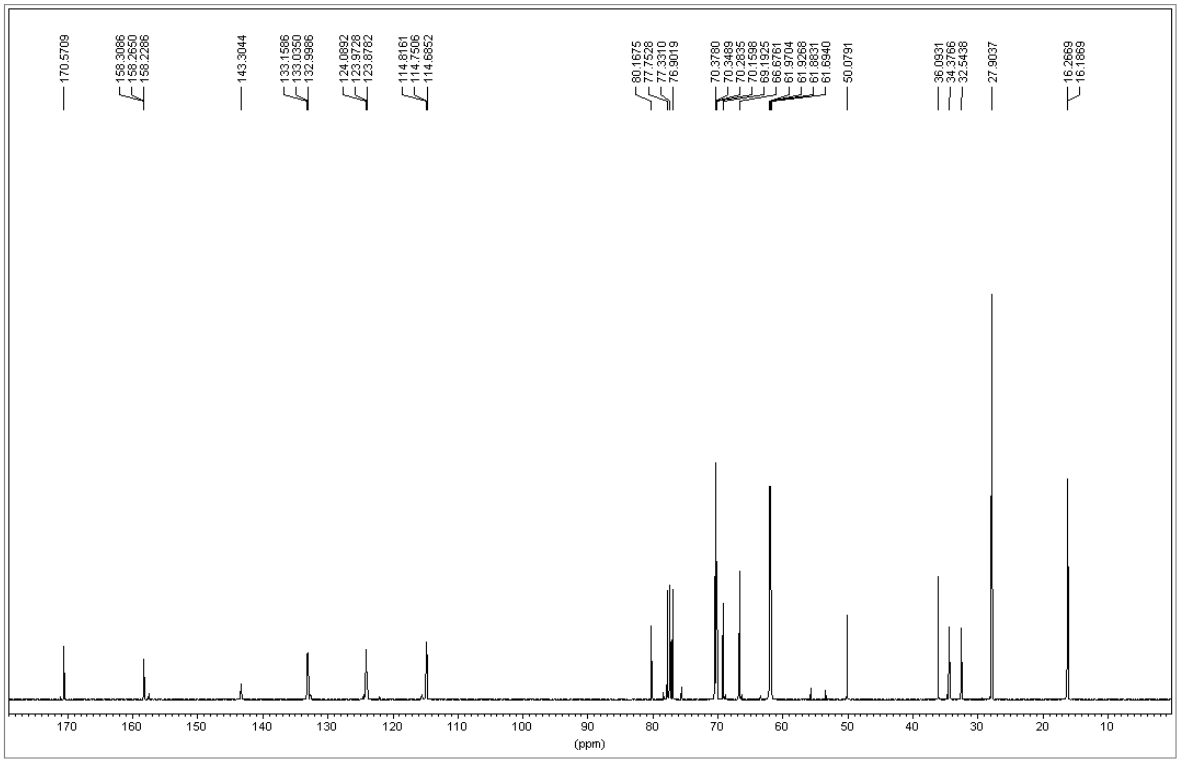


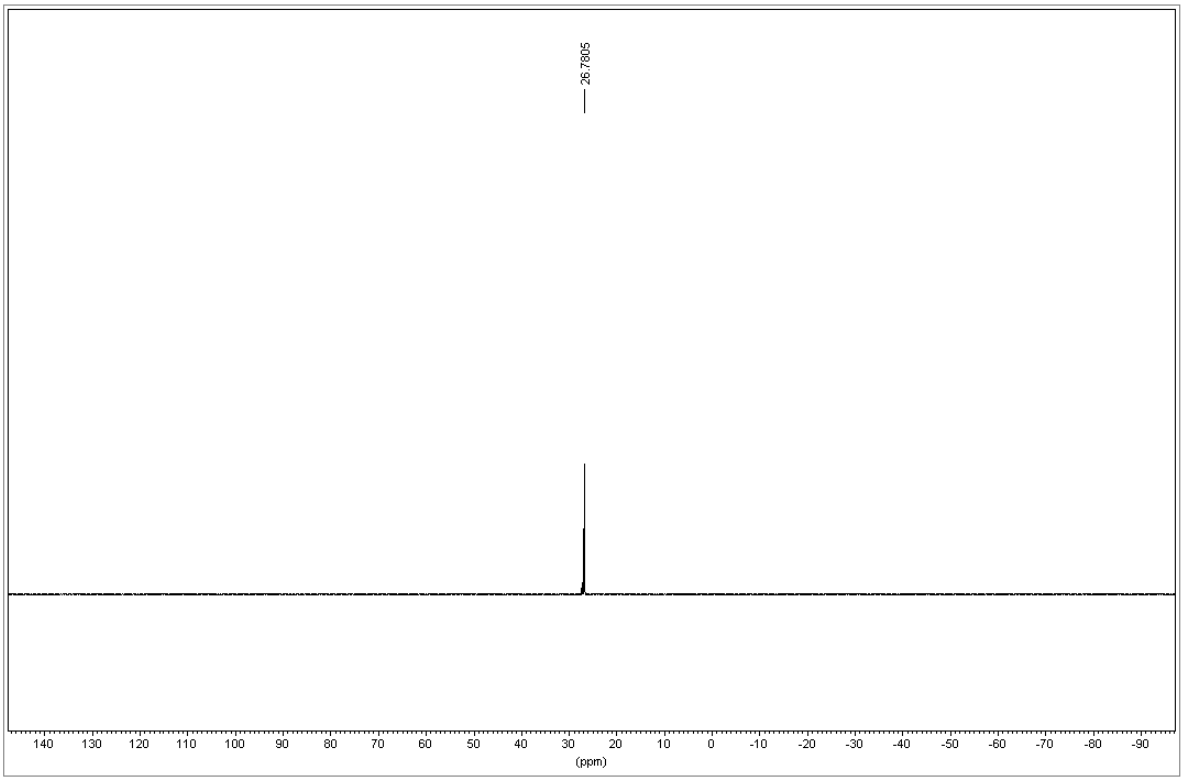


Compound 86 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

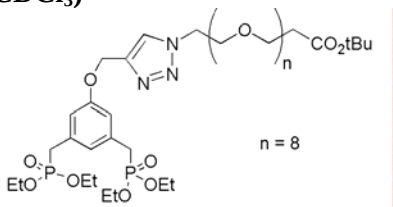


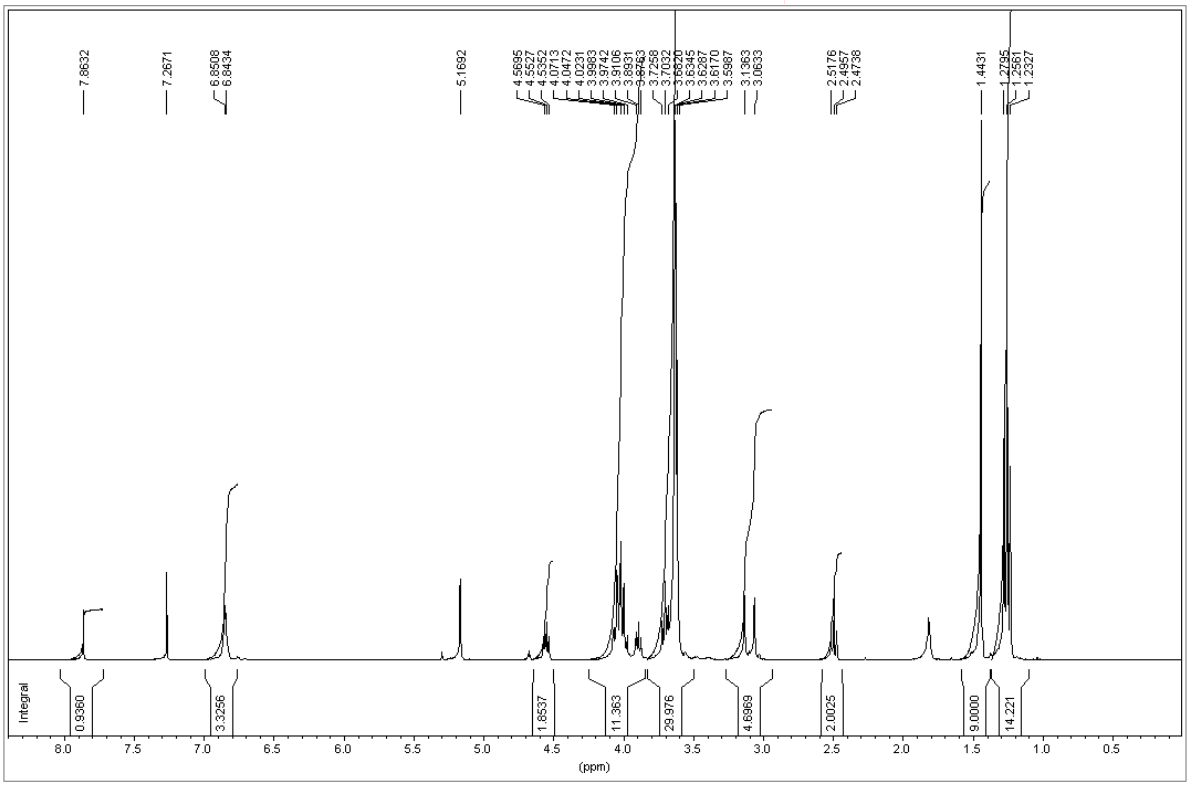


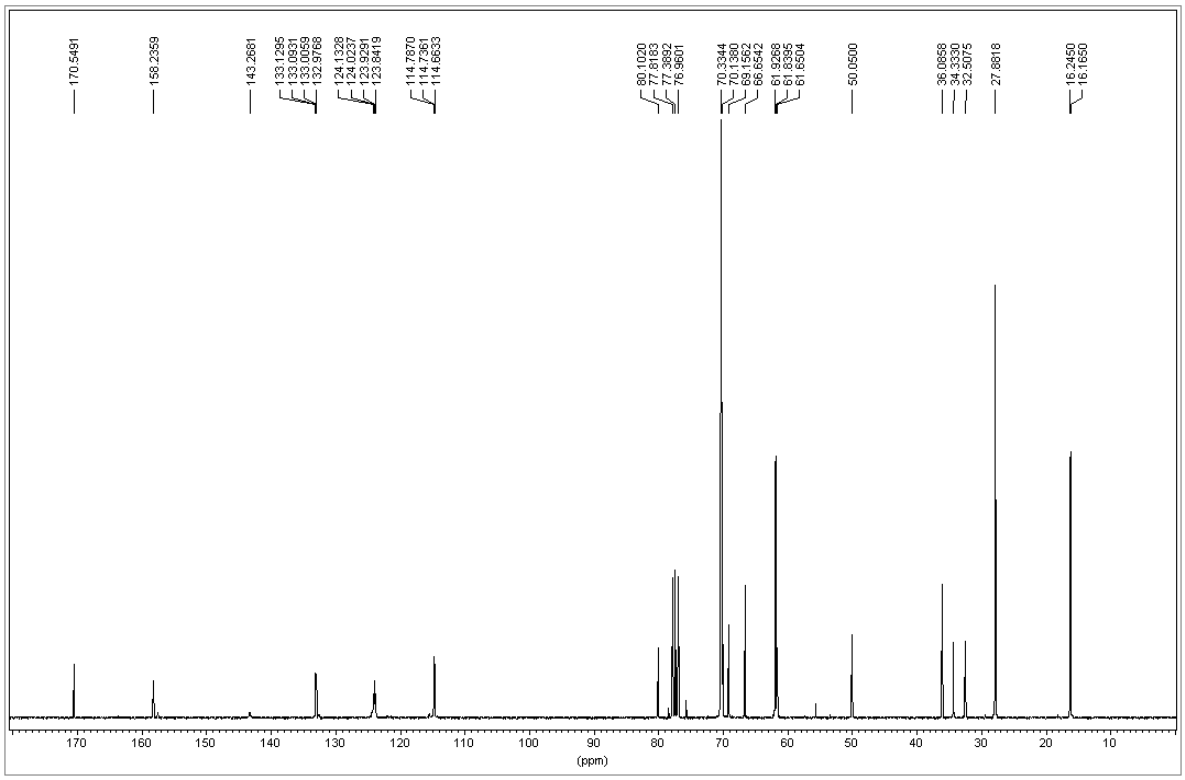


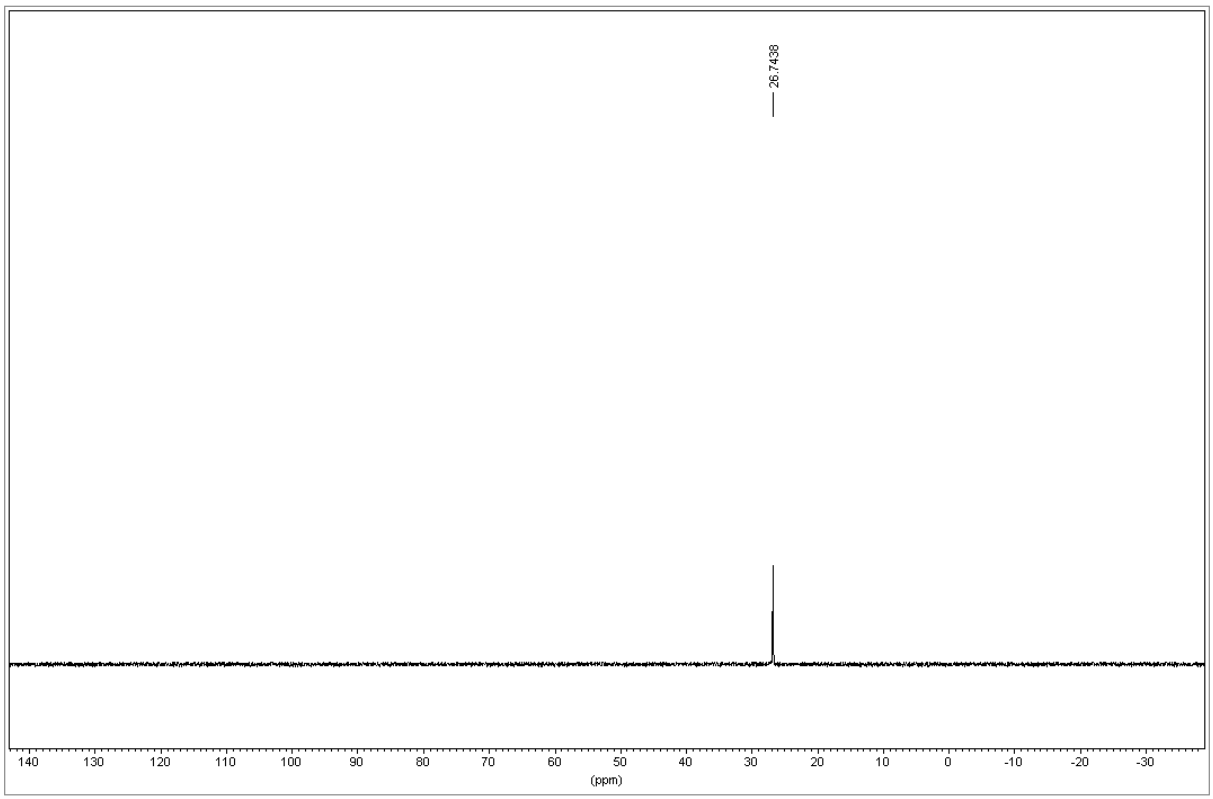


Compound 87 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

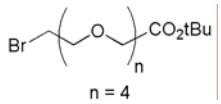


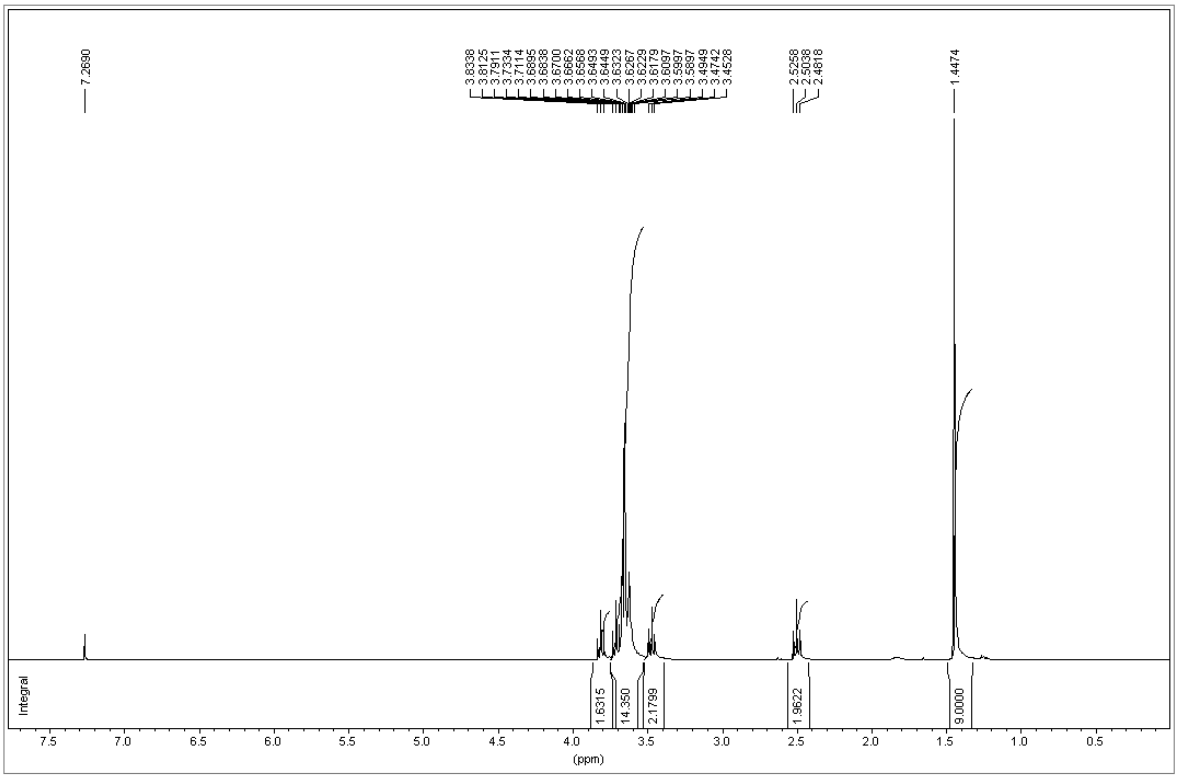


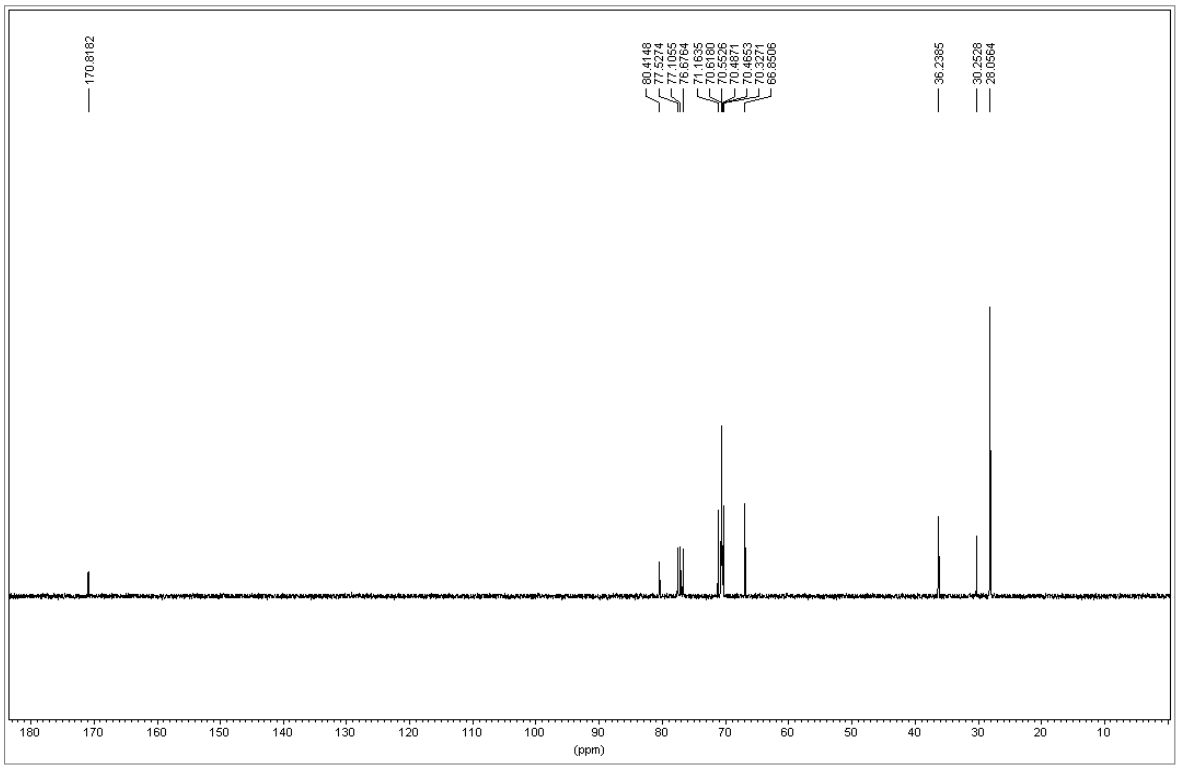

170.5491
158.2359
143.2681
133.1295
133.0931
132.9988
132.9788
124.1328
124.0237
123.9291
123.8419
114.7870
114.7361
114.6633
80.1020
77.8183
77.3993
76.9601
70.3344
70.1380
69.1562
66.6542
61.9268
61.8395
61.6504
50.0500
36.0858
34.3330
32.5075
27.8818
16.2450
16.1650
(ppm)


26.7438
(ppm)

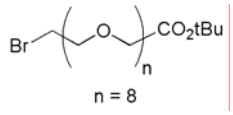
Compound 88 (^{1}H and ^{13}C, $CDCl_3$)

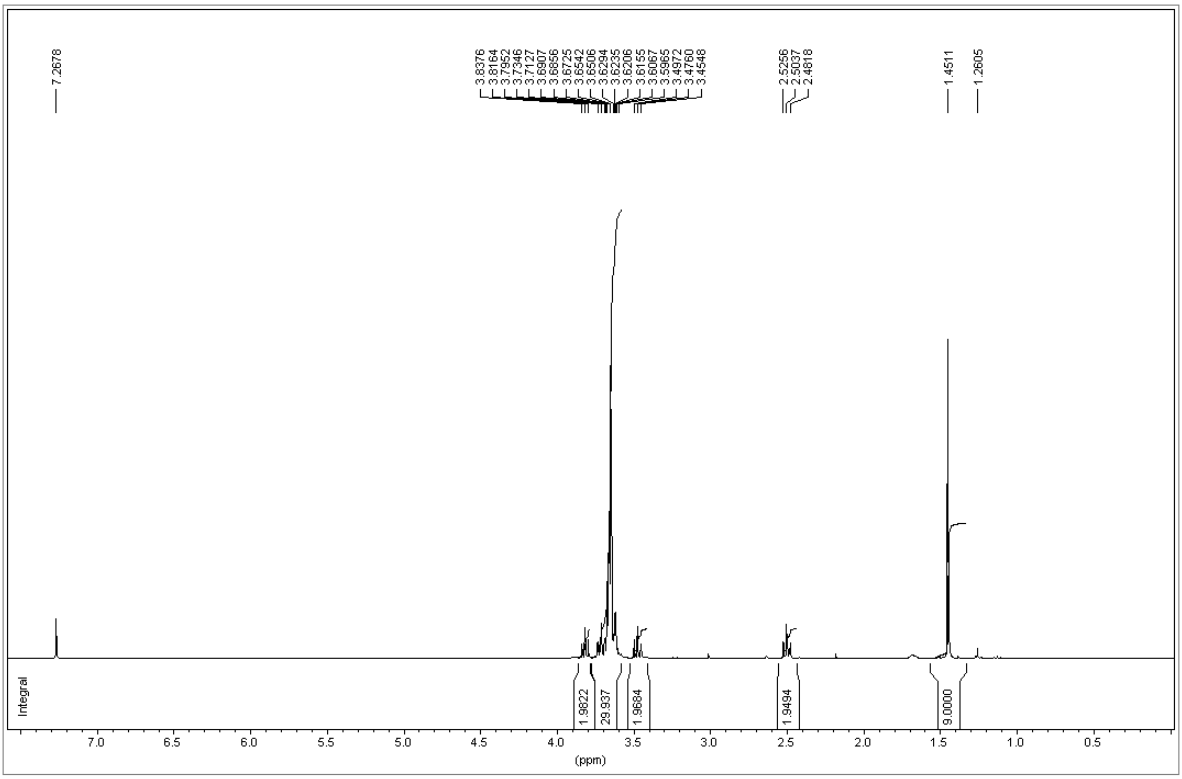


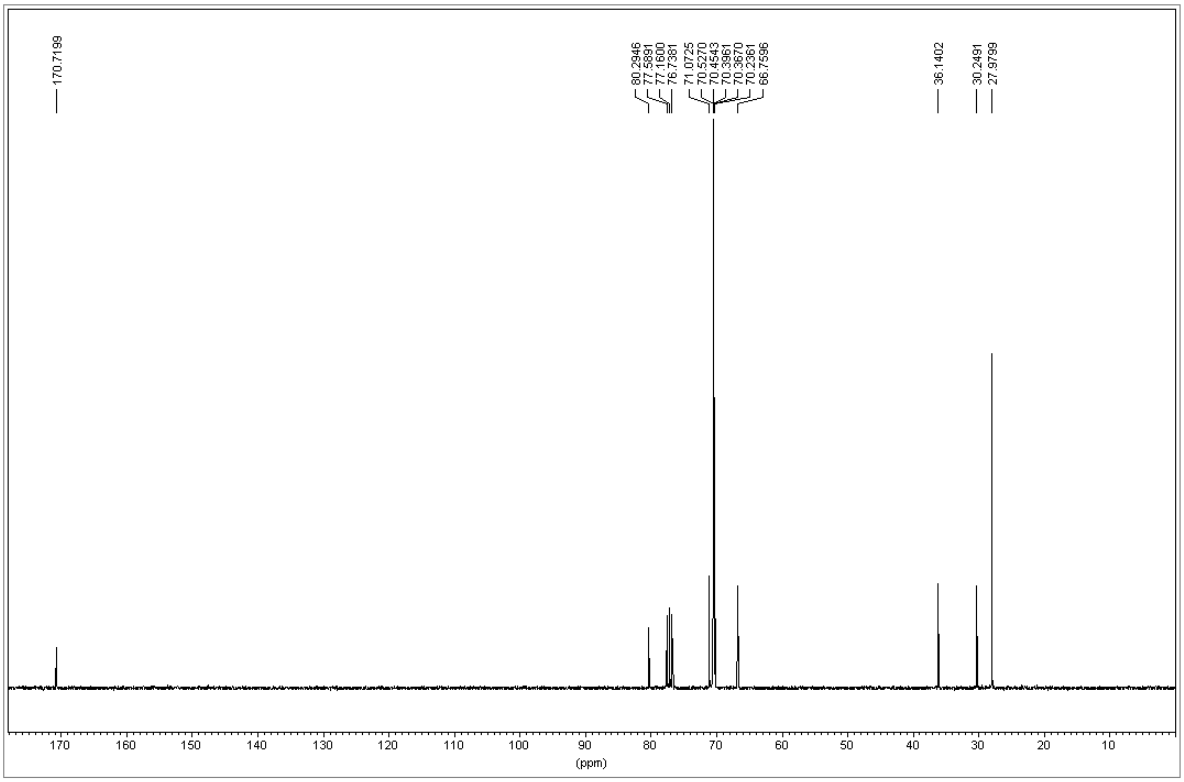




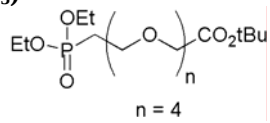
Compound 89 (^{1}H and ^{13}C, $CDCl_3$)

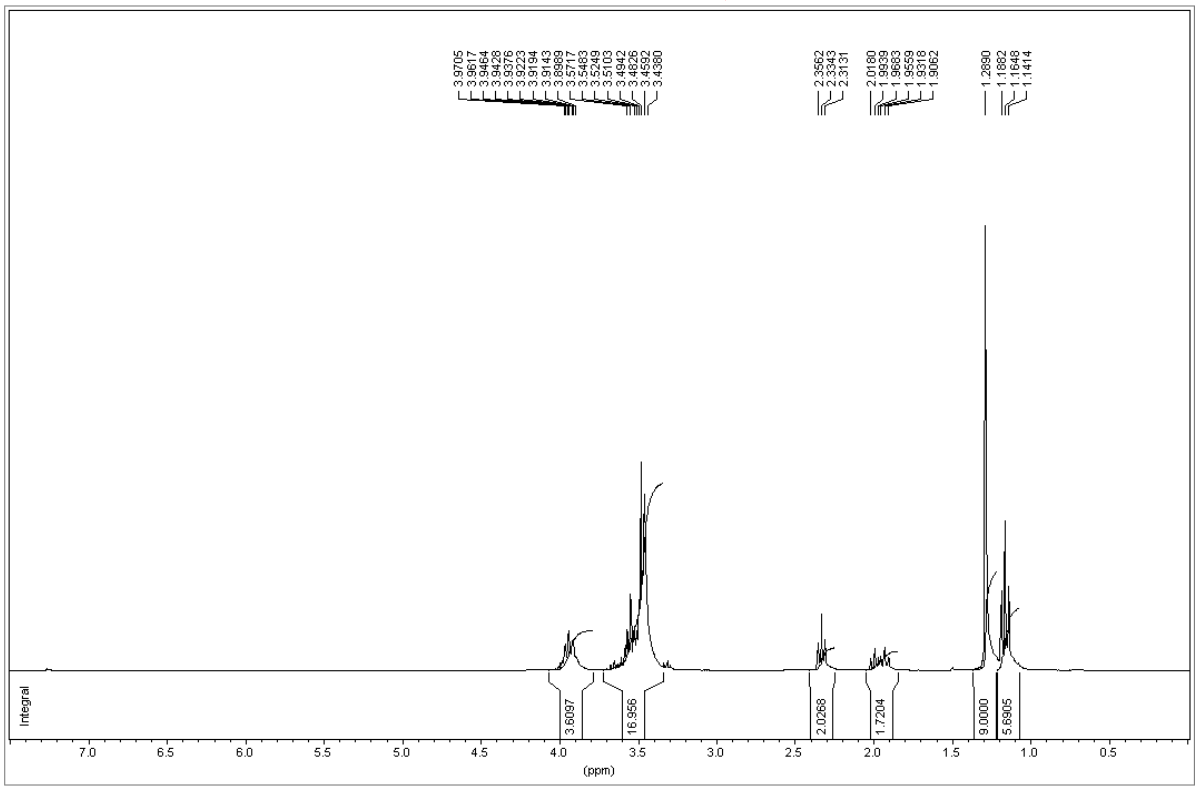


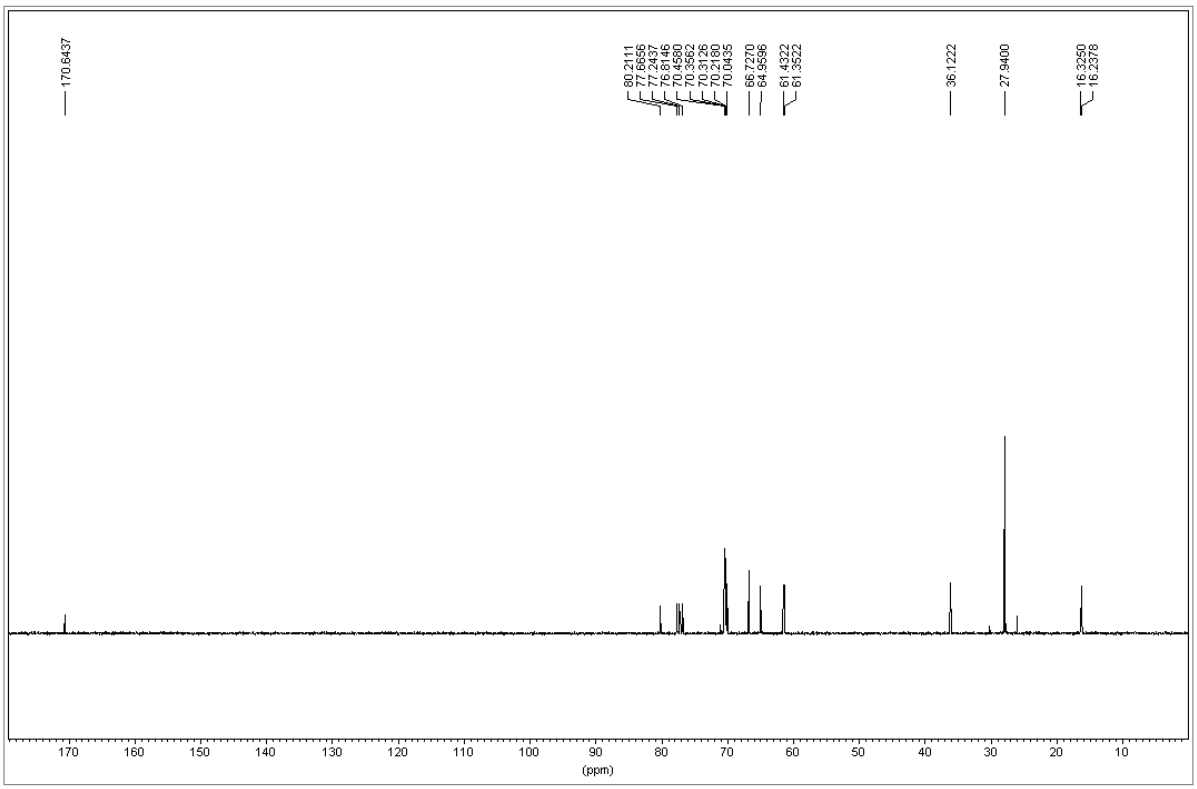


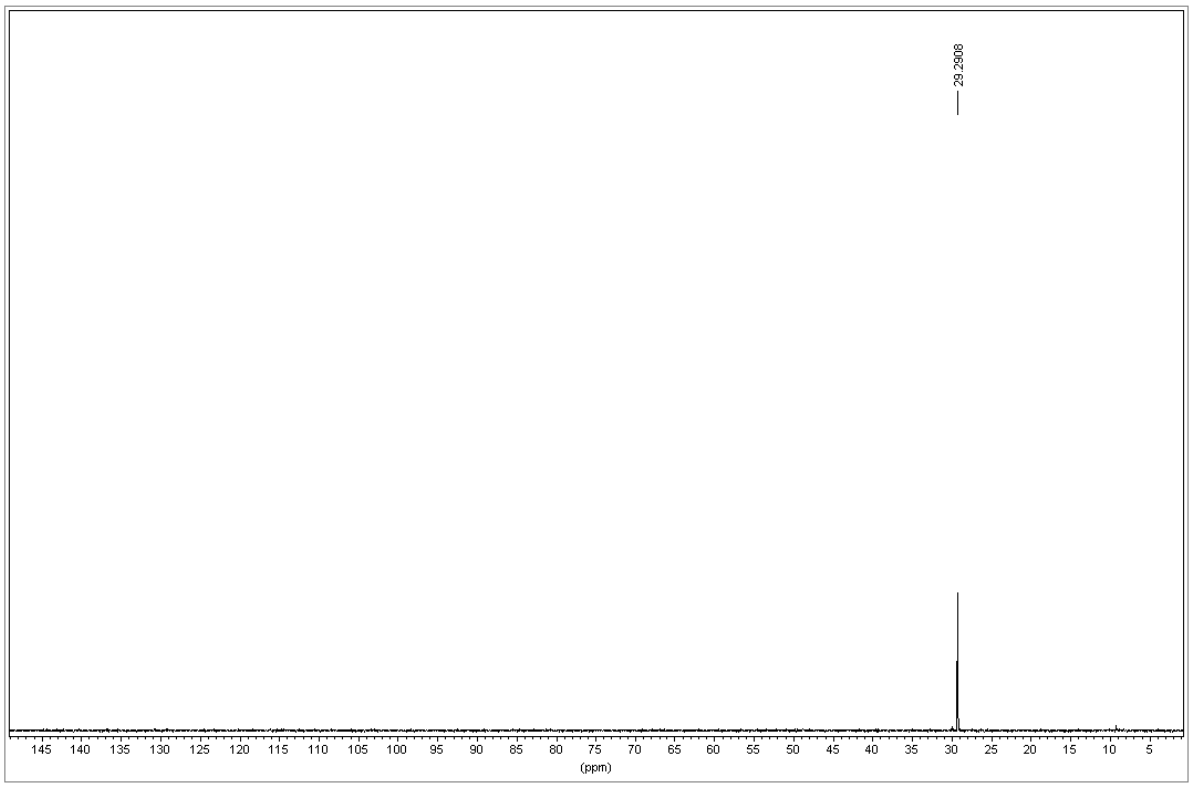


Compound 90 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

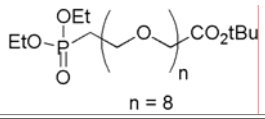


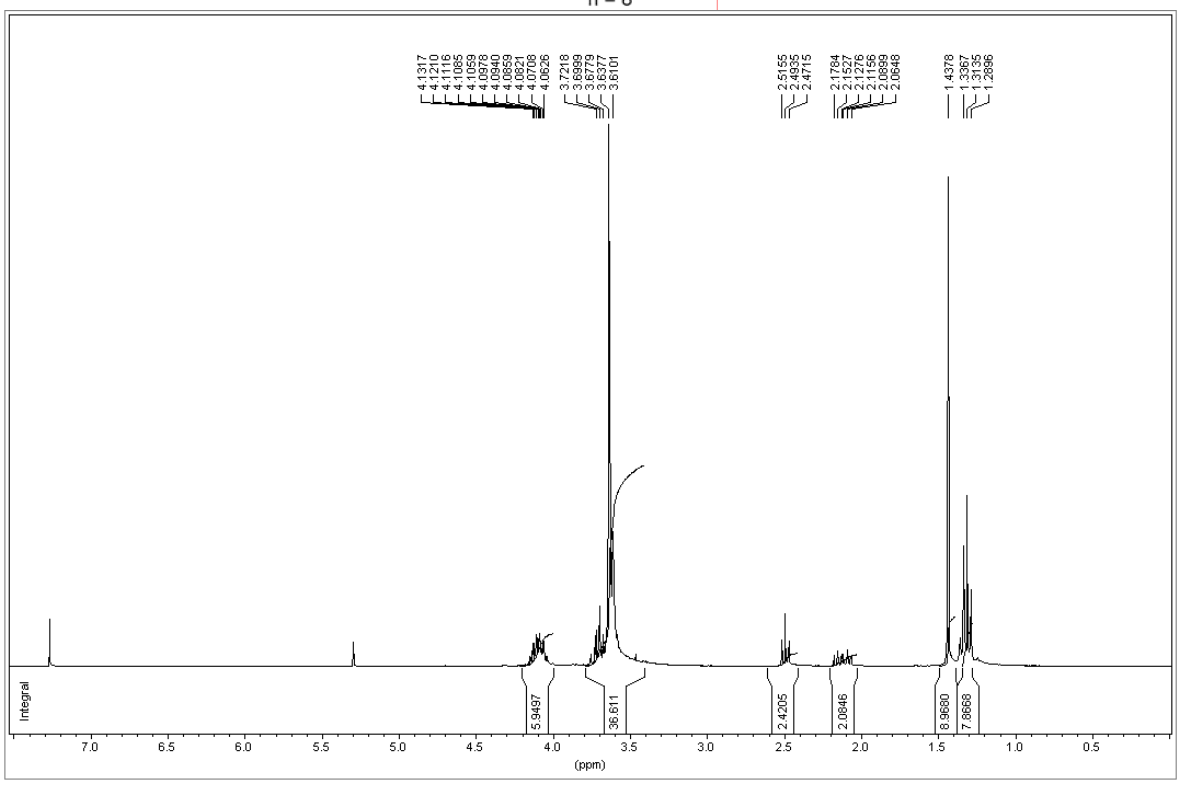


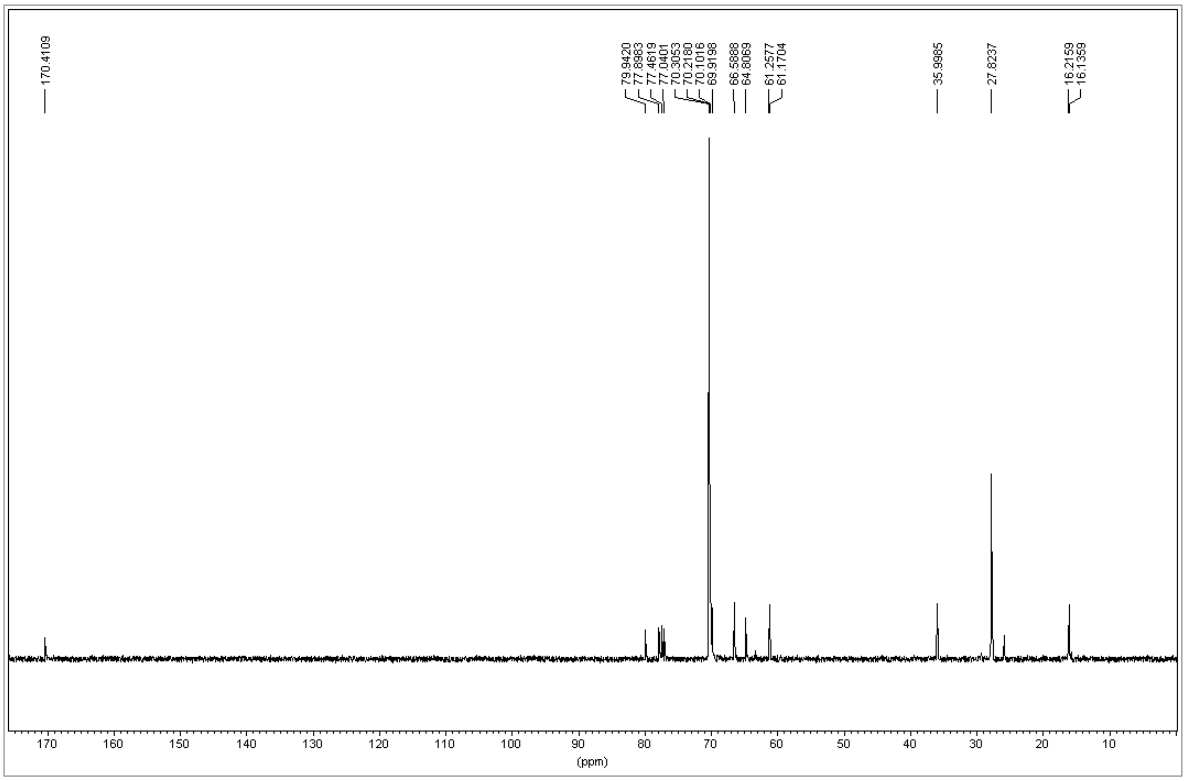


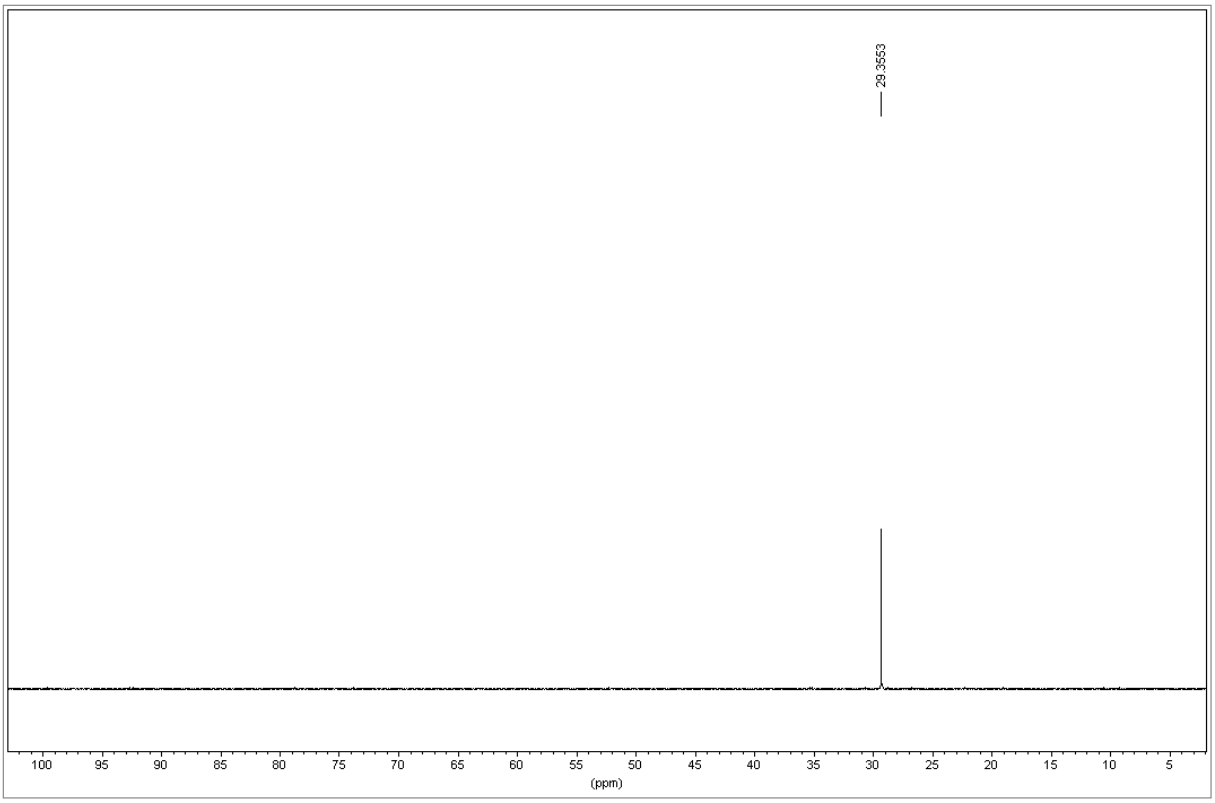


Compound 91 (^{1}H, ^{13}C and ^{31}P, $CDCl_3$)

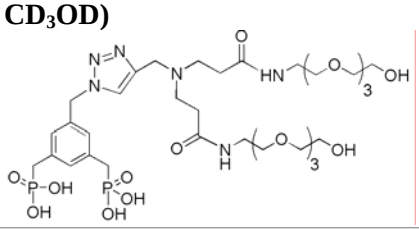


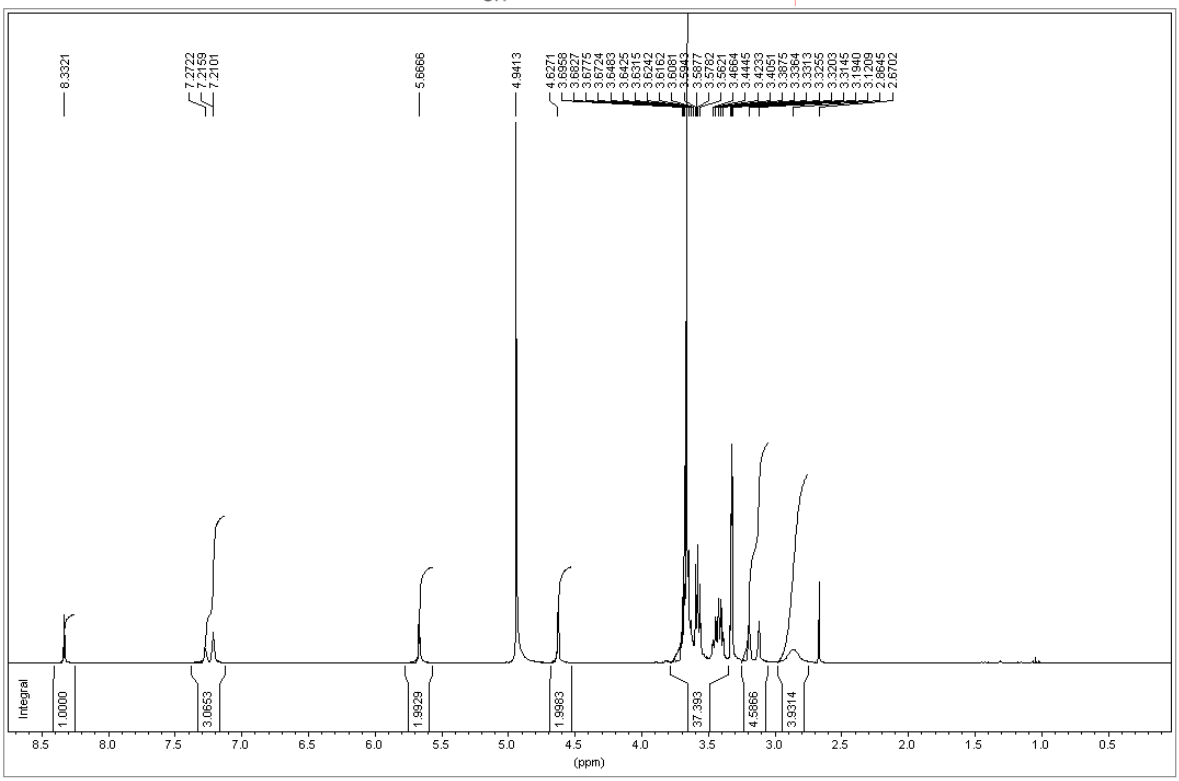


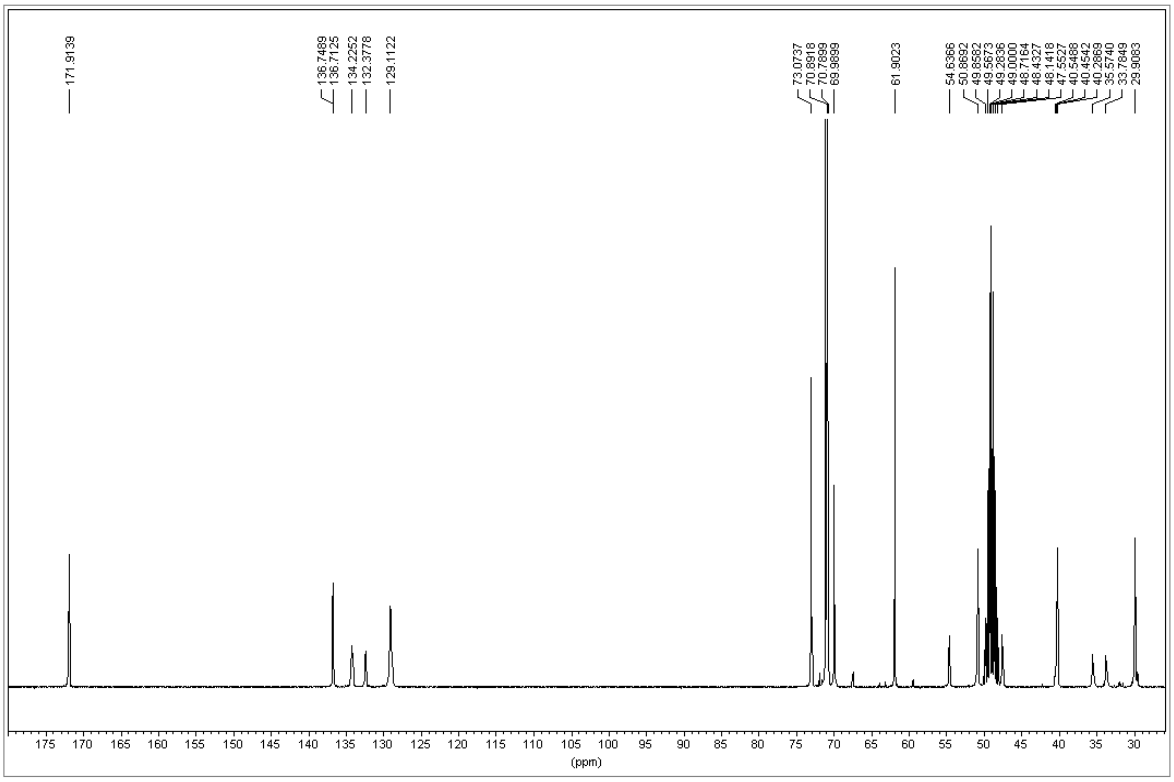

170.4109
79.9420
77.8983
77.4619
77.0401
70.3053
70.2180
70.1016
69.9198
66.5888
64.8069
61.2577
61.1704
35.9985
27.8237
16.2159
16.1359
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

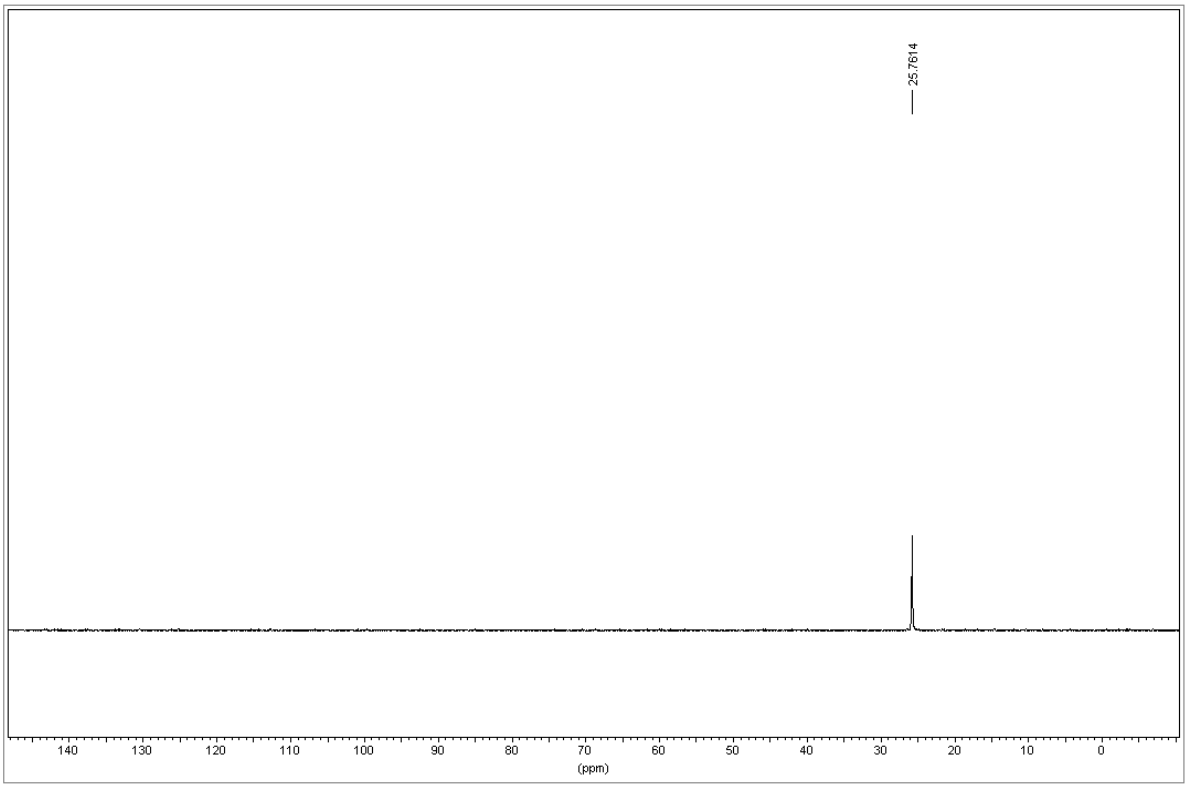

29.3553
100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
(ppm)

Compound 92 (^{1}H, ^{13}C and ^{31}P, CD_3OD)

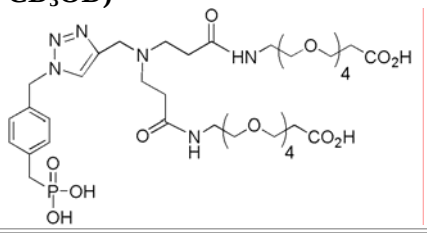


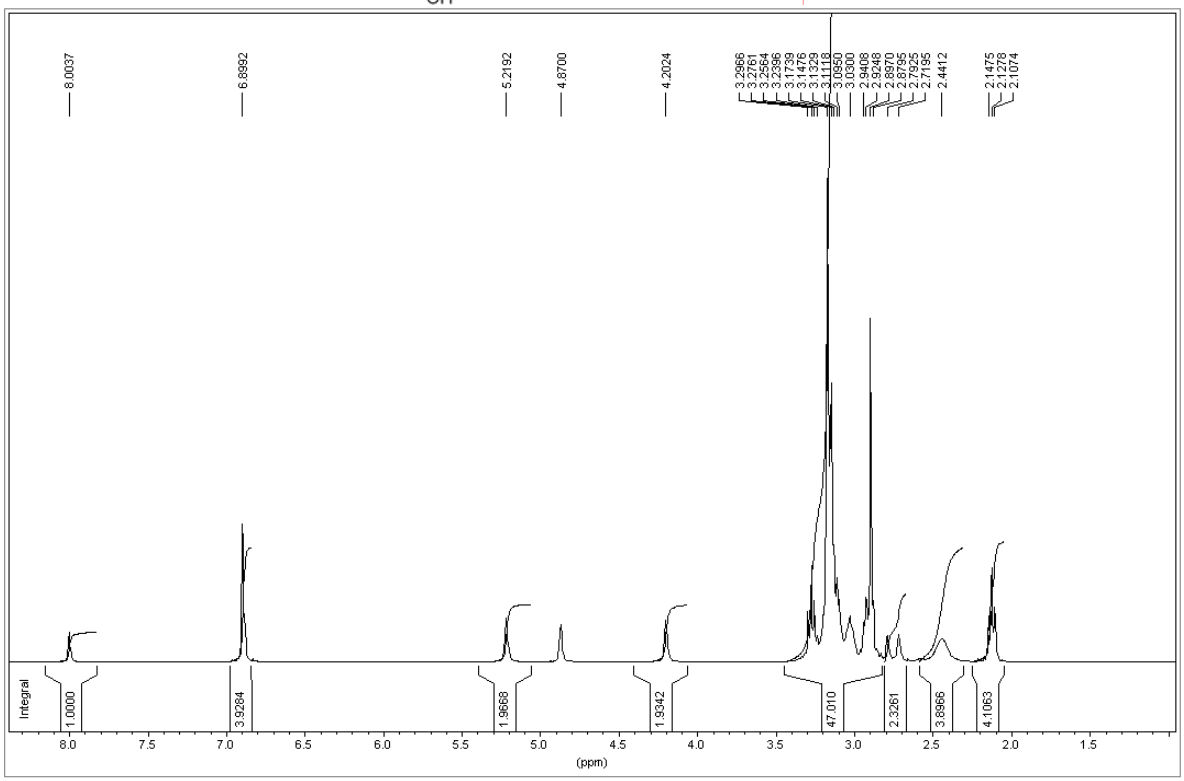


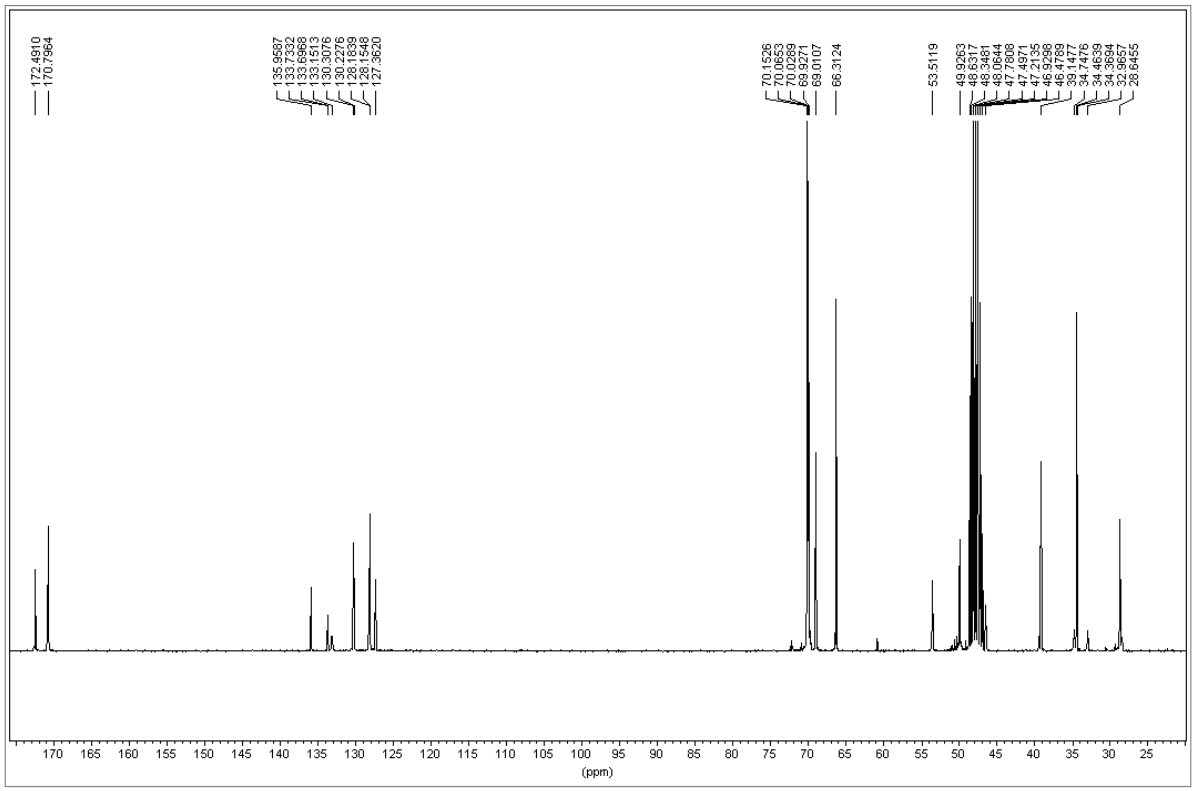


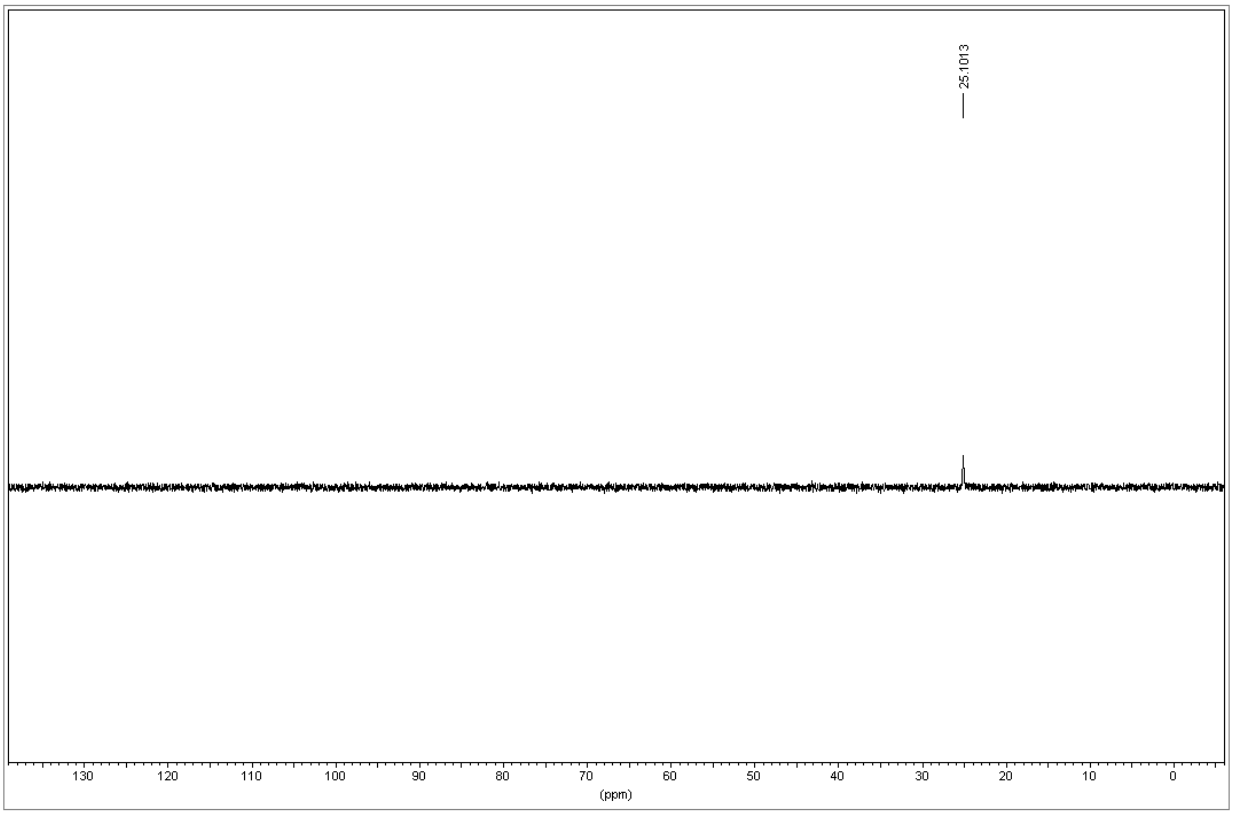


Compound 93 (^{1}H, ^{13}C and ^{31}P, CD_3OD)



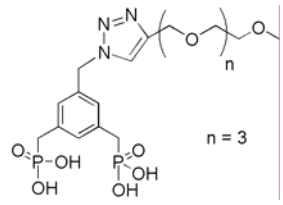


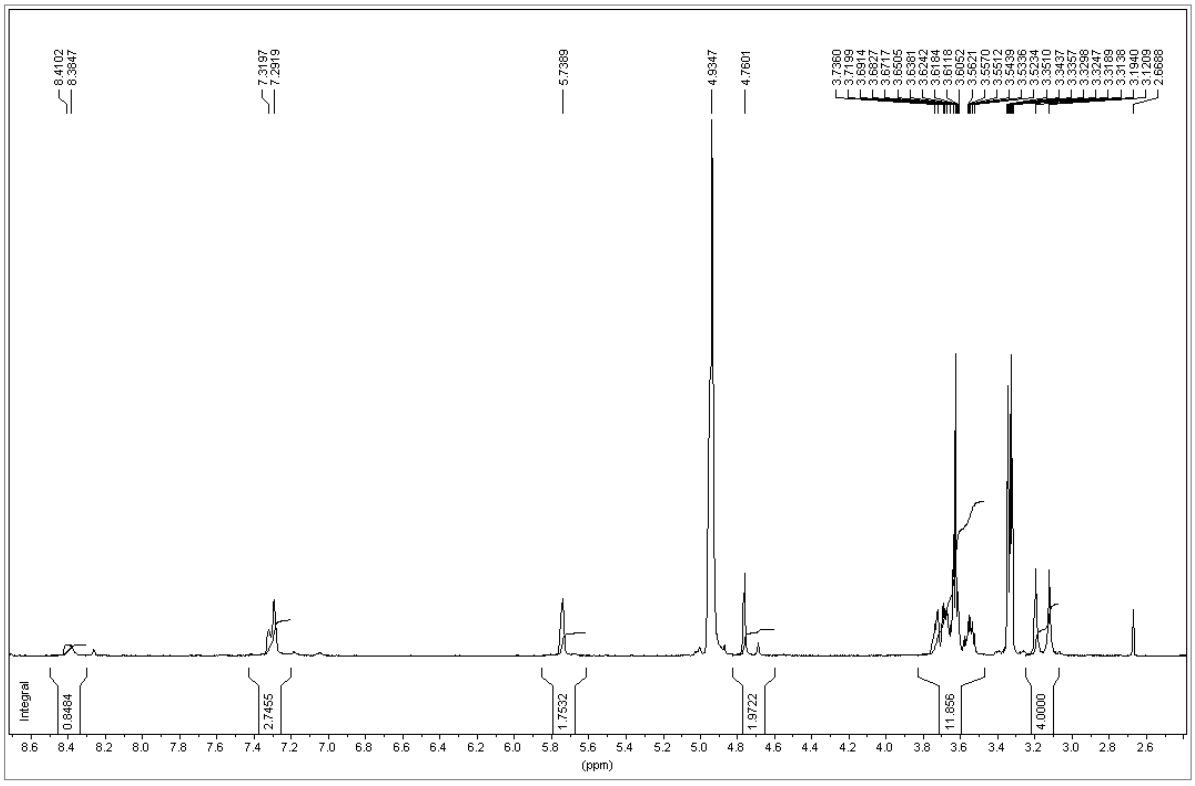


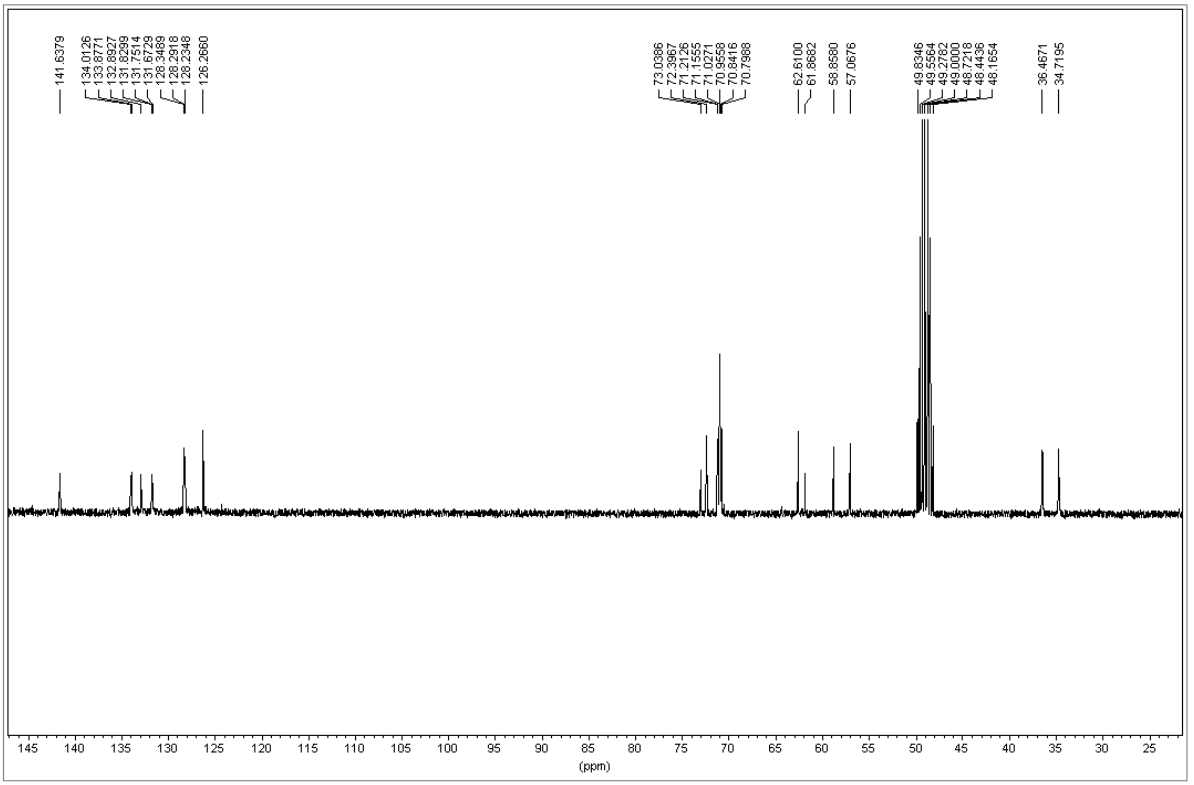


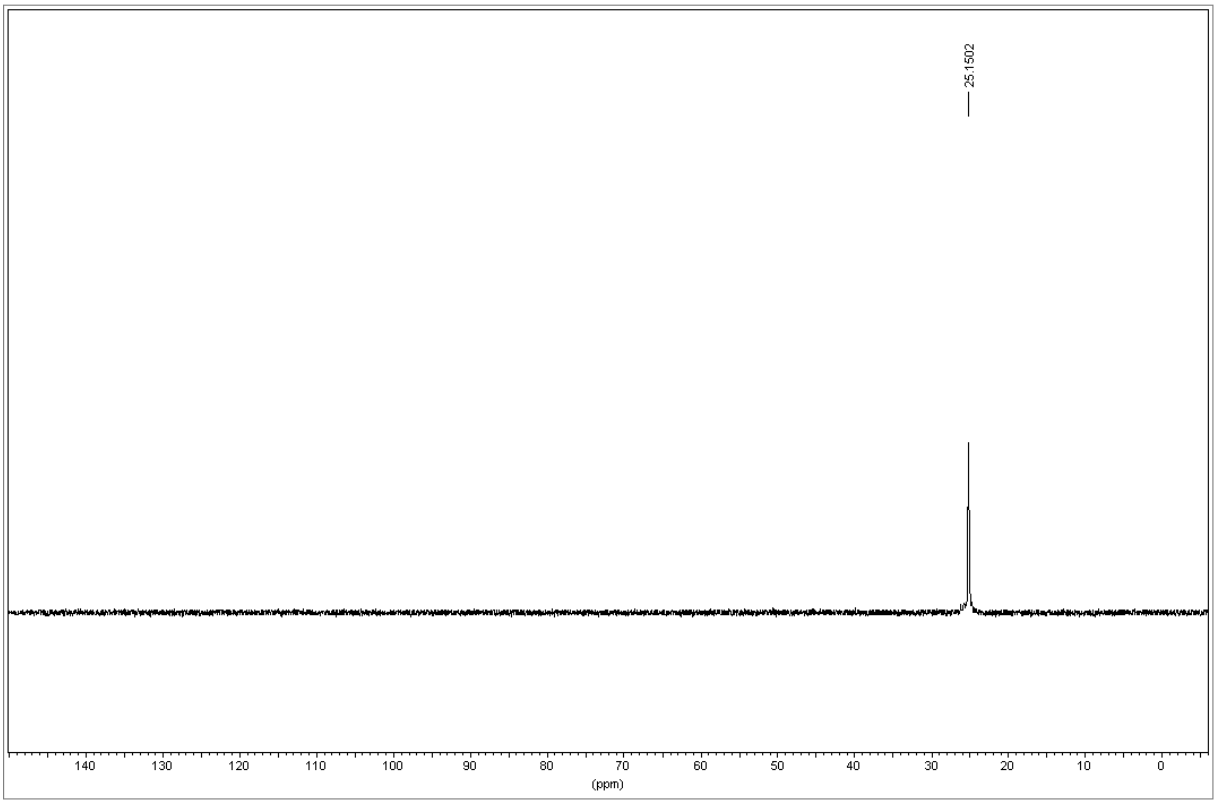
Compound 94 The analytical data are reported in the literature.[22c]

Compound 95 (^{1}H, ^{13}C and ^{31}P, CD_3OD)

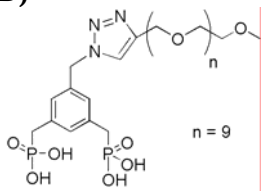


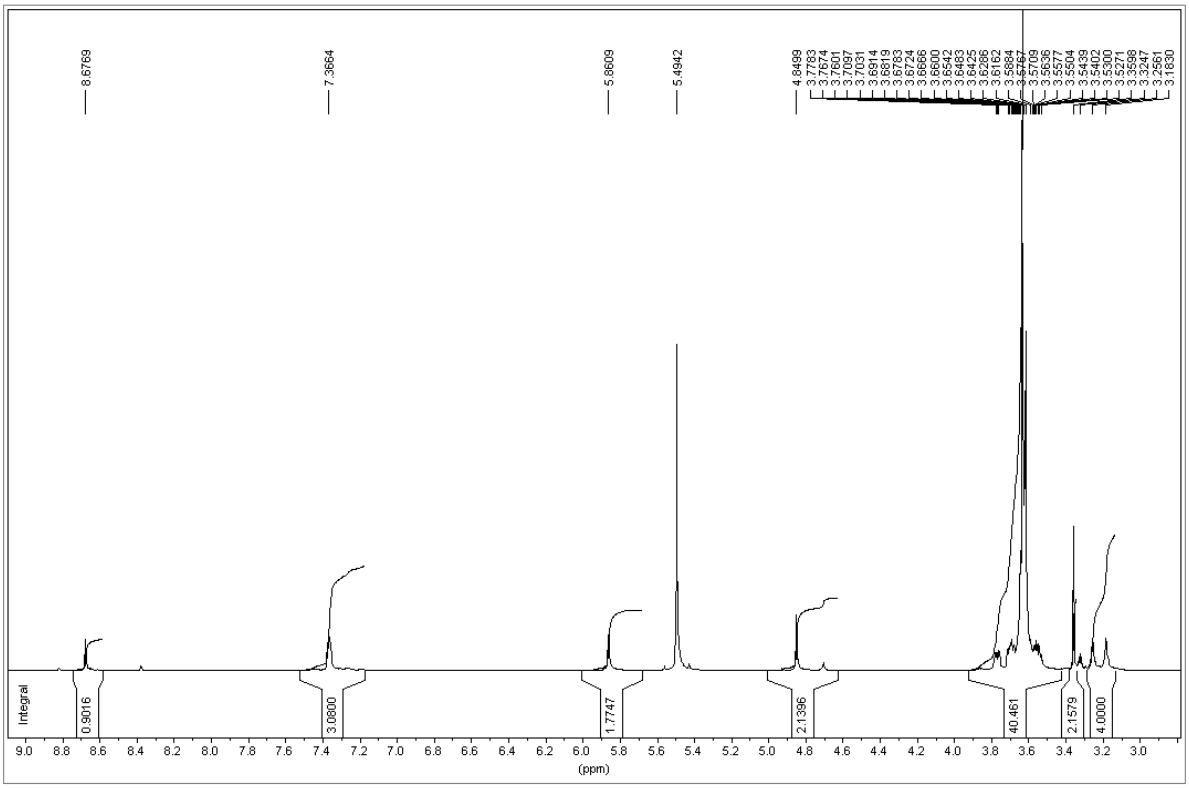


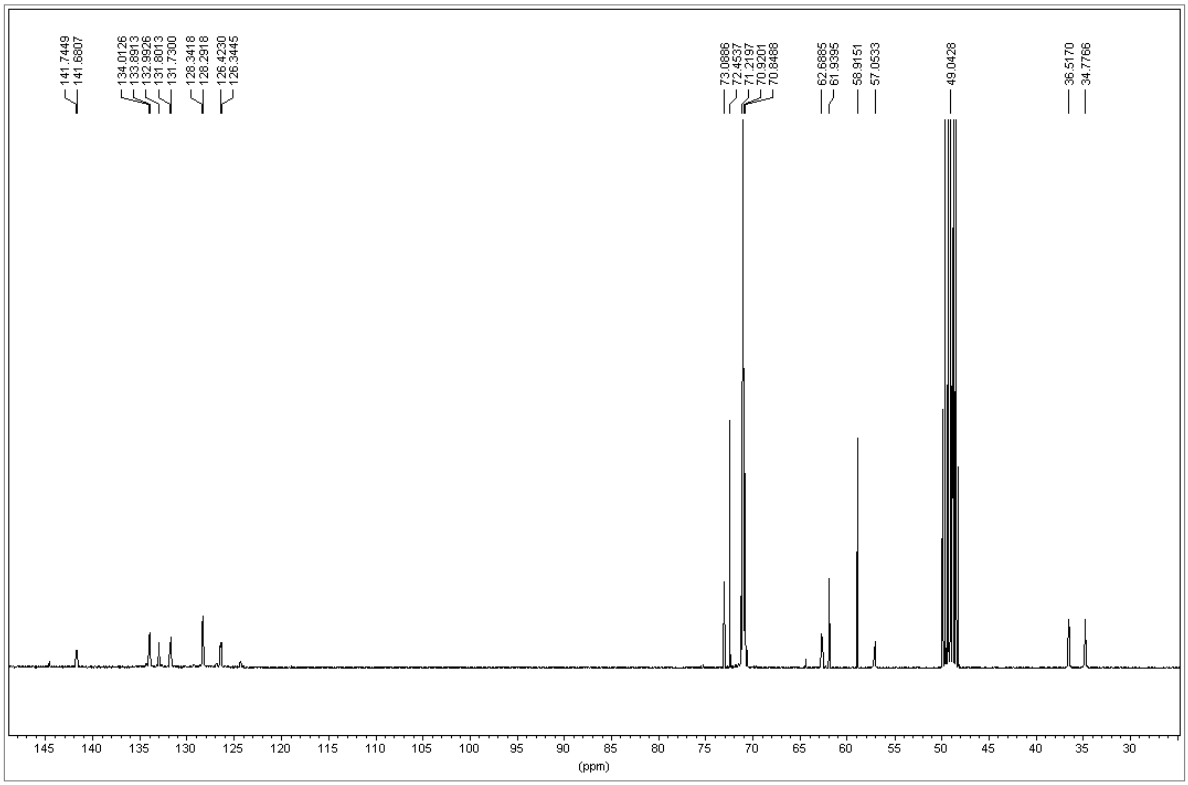


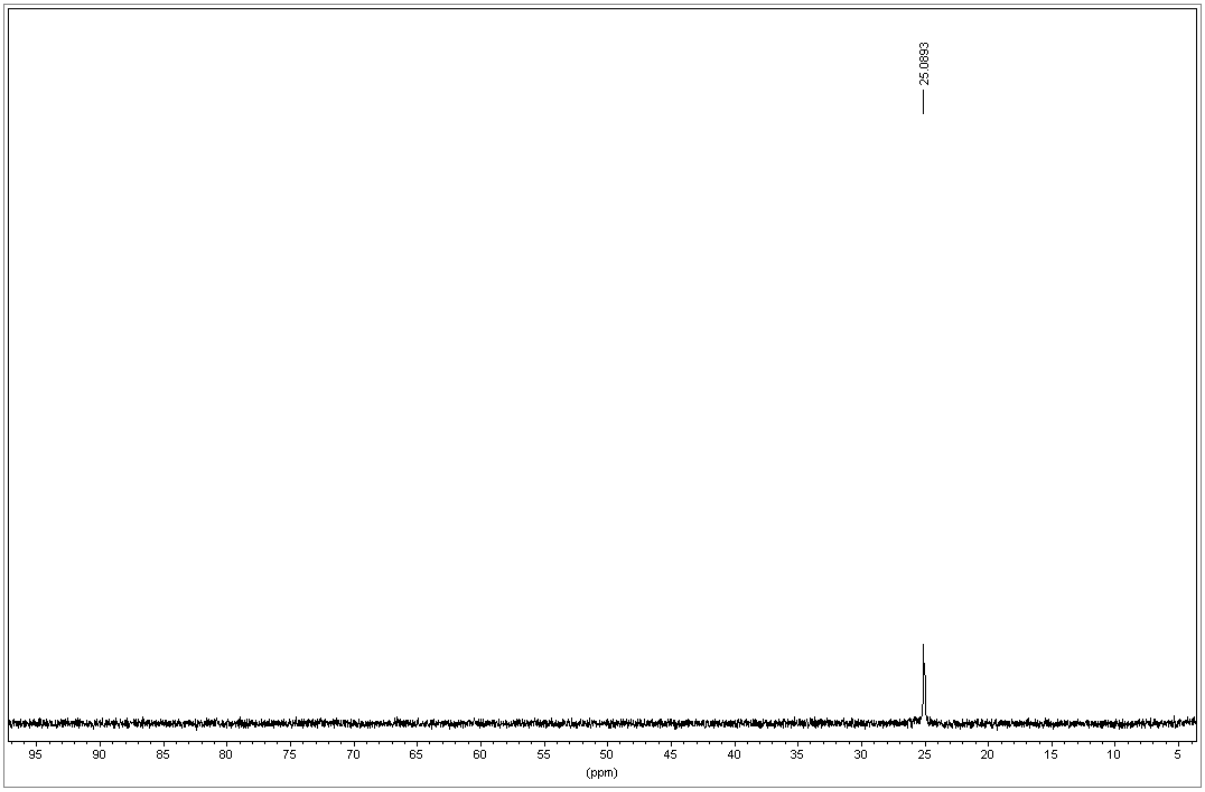


Compound 96 (^{1}H, ^{13}C and ^{31}P, CD_3OD)

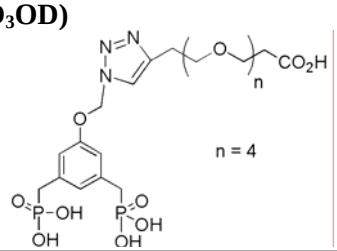


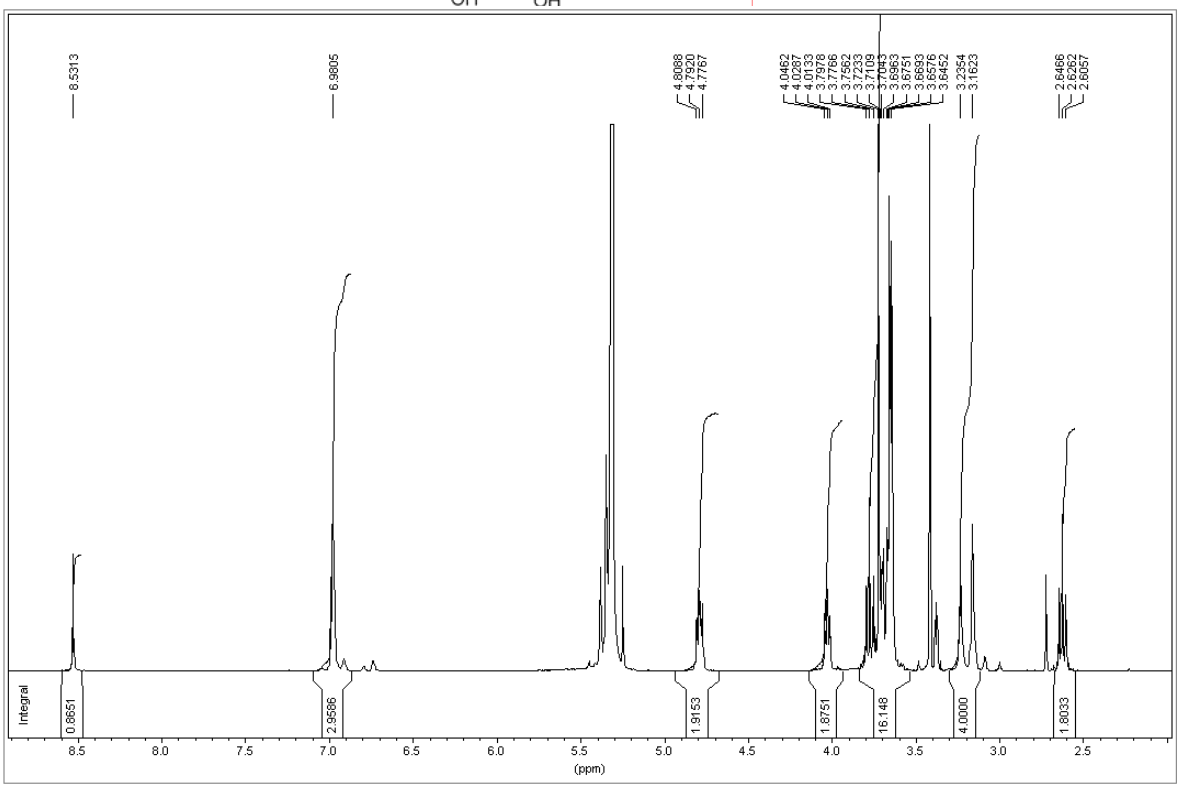


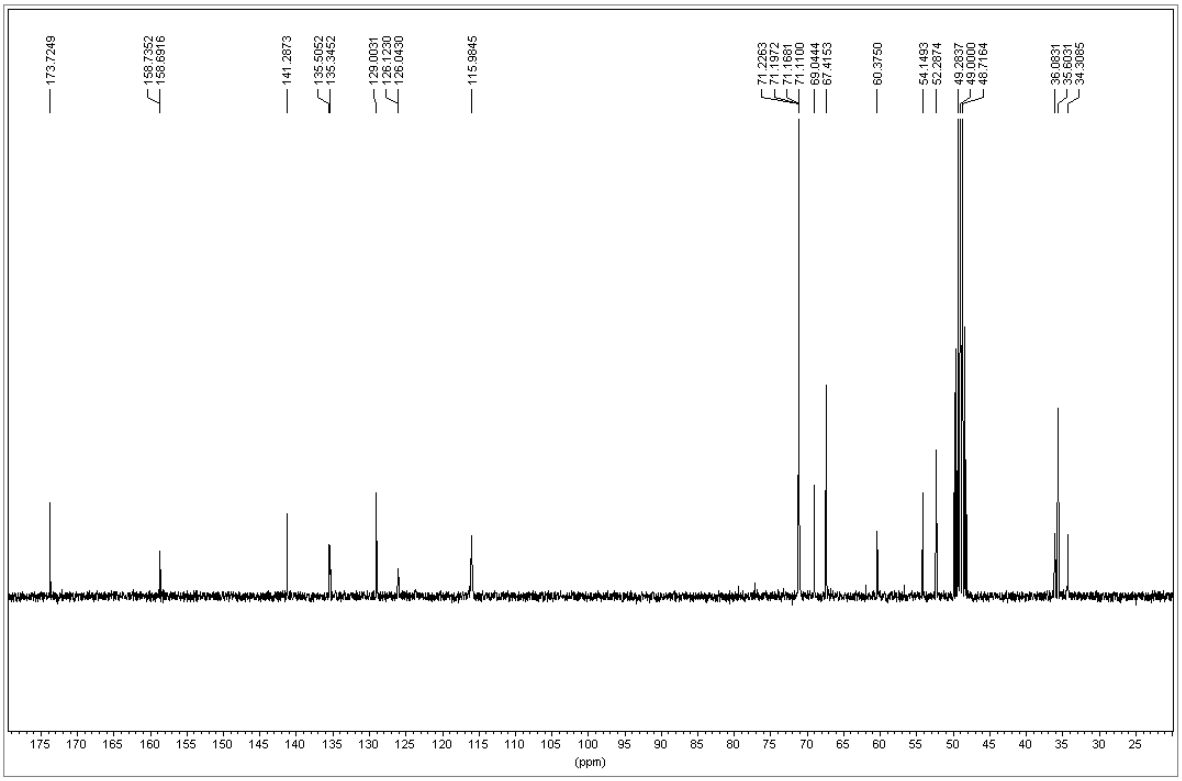

141.7449
141.6807
134.0126
133.8913
132.9926
131.8013
131.7300
128.3418
128.2918
126.4230
126.3445
73.0886
72.4537
71.2197
70.9201
70.6468
62.6885
61.9395
59.9151
57.0533
49.0428
36.5170
34.7766
(ppm)

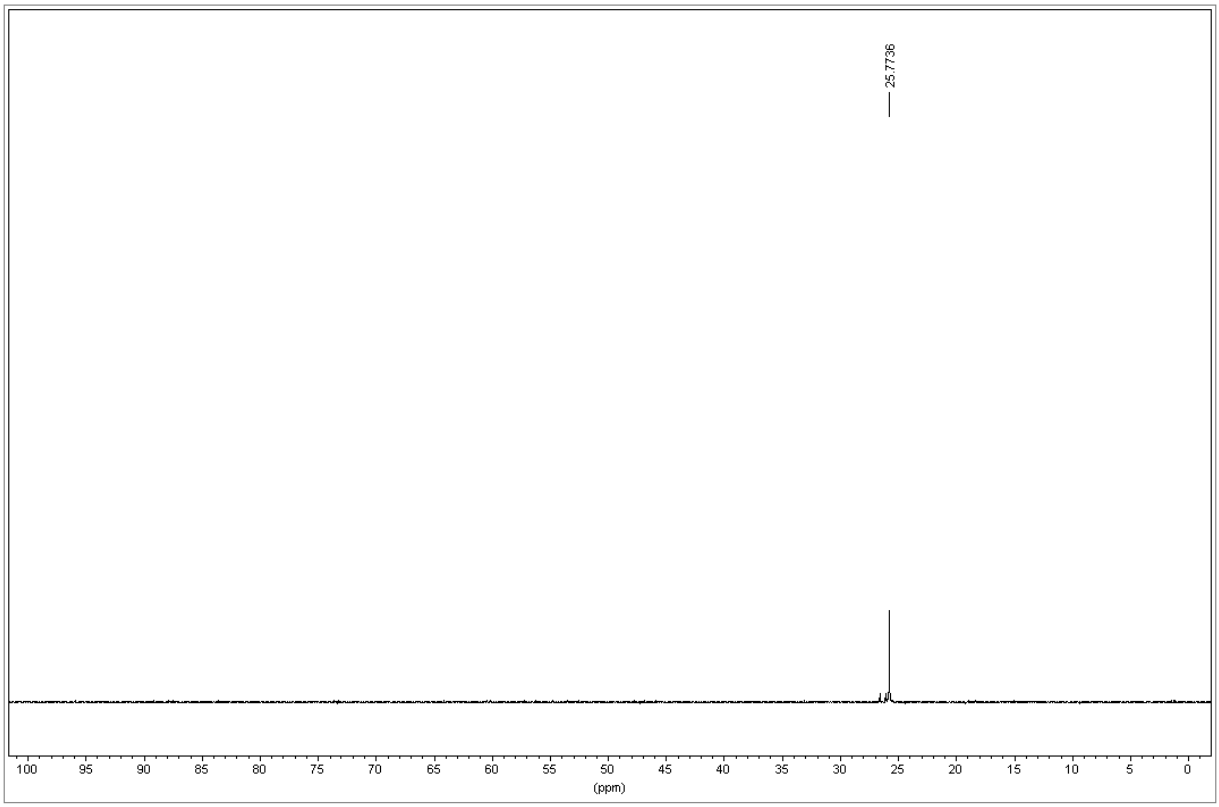

25.0893
(ppm)

Compound 97 (^{1}H, ^{13}C and ^{31}P, CD_3OD)

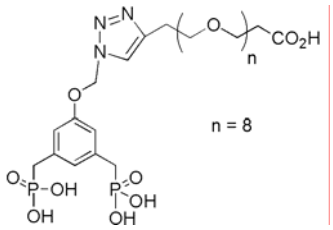


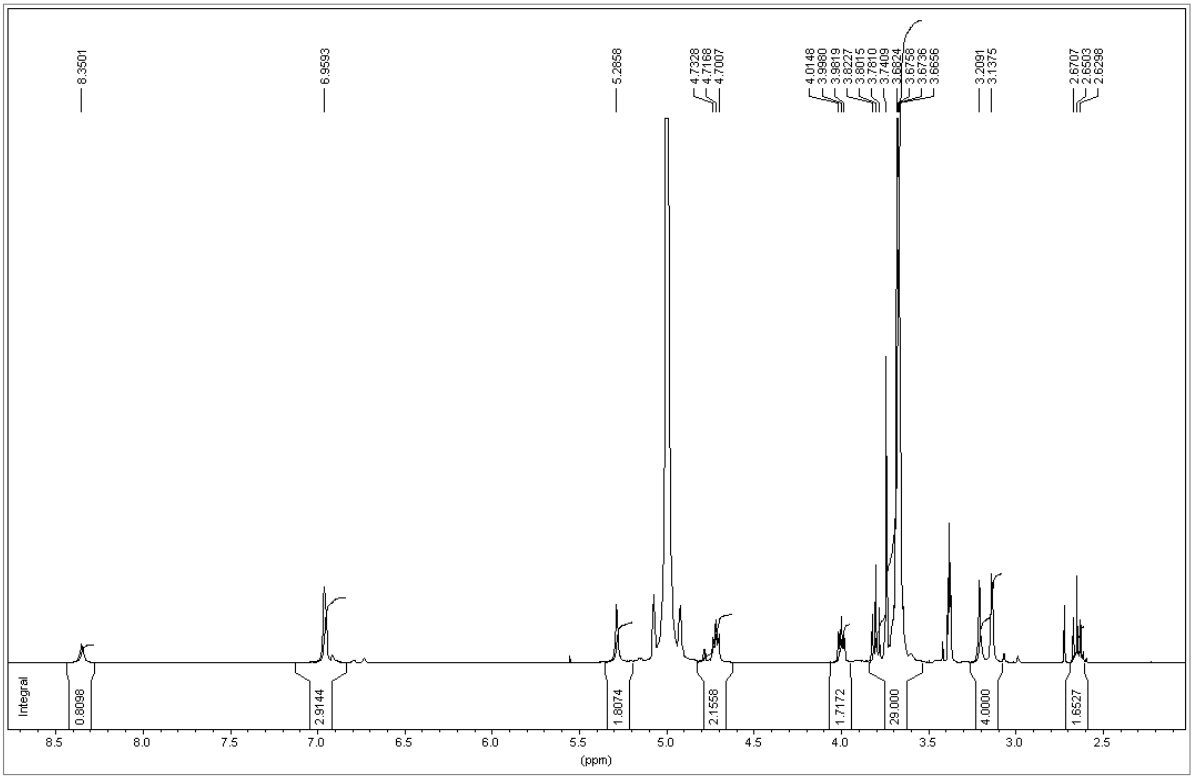


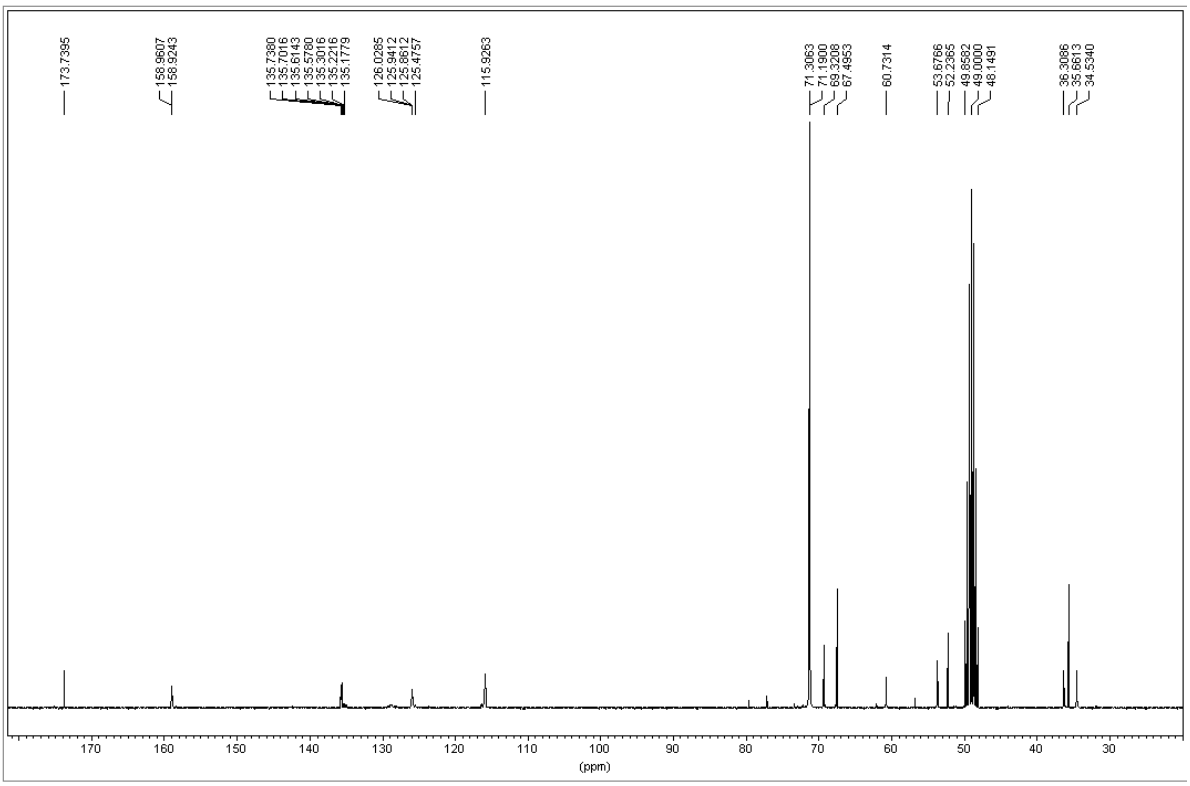


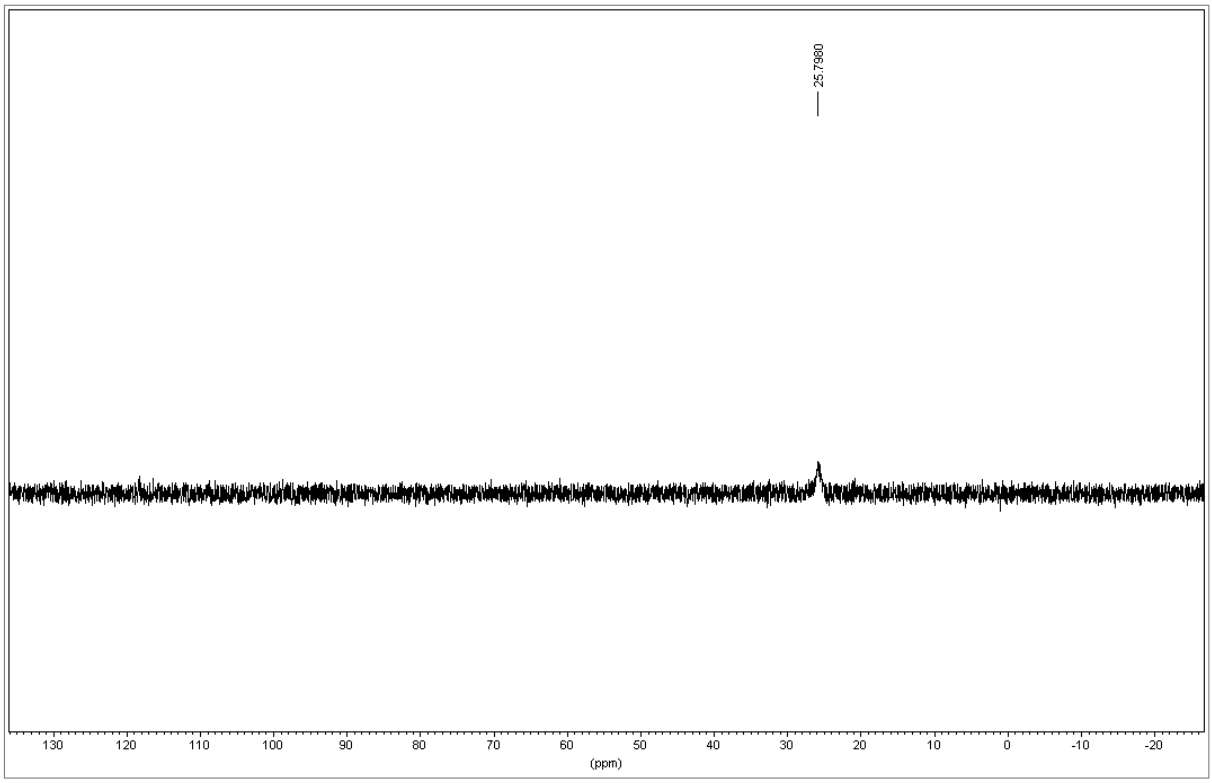


Compound 98 (^{1}H, ^{13}C and ^{31}P, CD_3OD)

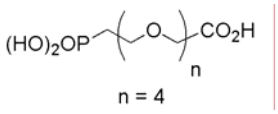


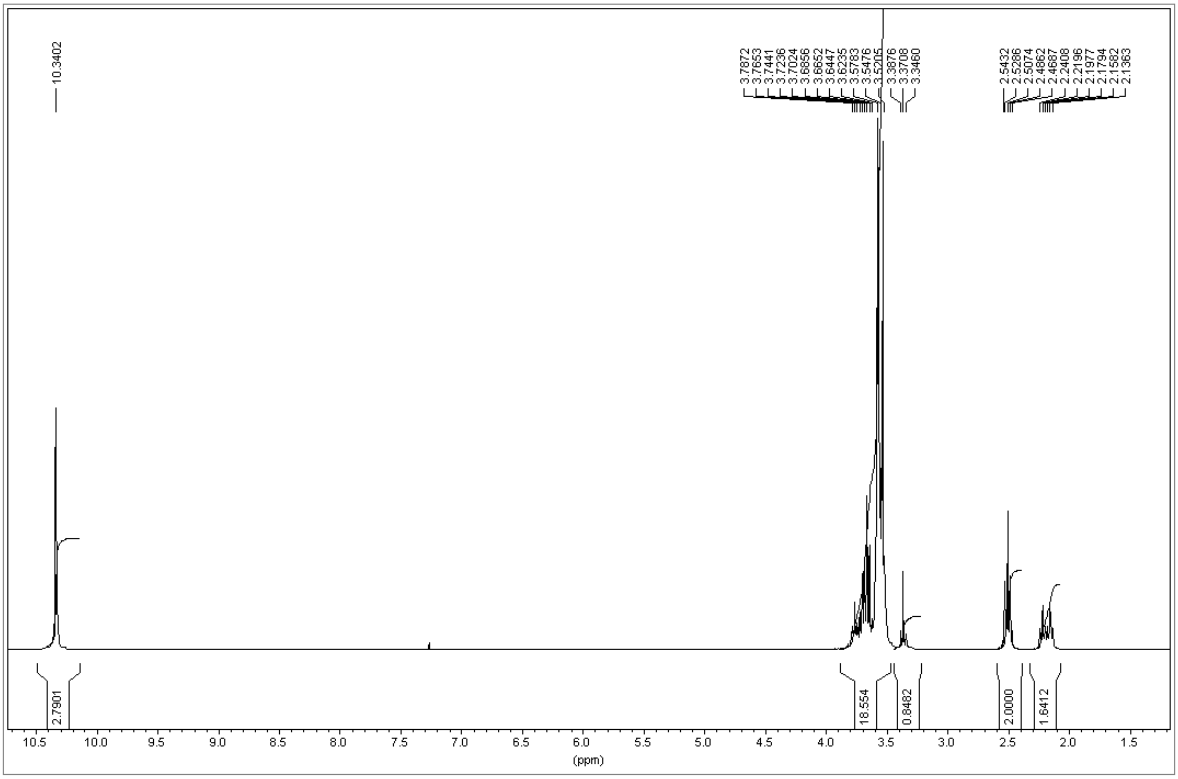

8.3501
6.9593
5.2658
4.7328
4.7168
4.7007
4.0148
3.9980
3.9819
3.8227
3.8015
3.7810
3.7409
3.7224
3.6756
3.6736
3.6656
3.2091
3.1375
2.6707
2.6503
2.6298
Integral
0.8098
2.9144
1.8074
2.1558
1.7172
29.000
4.0000
1.6527
(ppm)

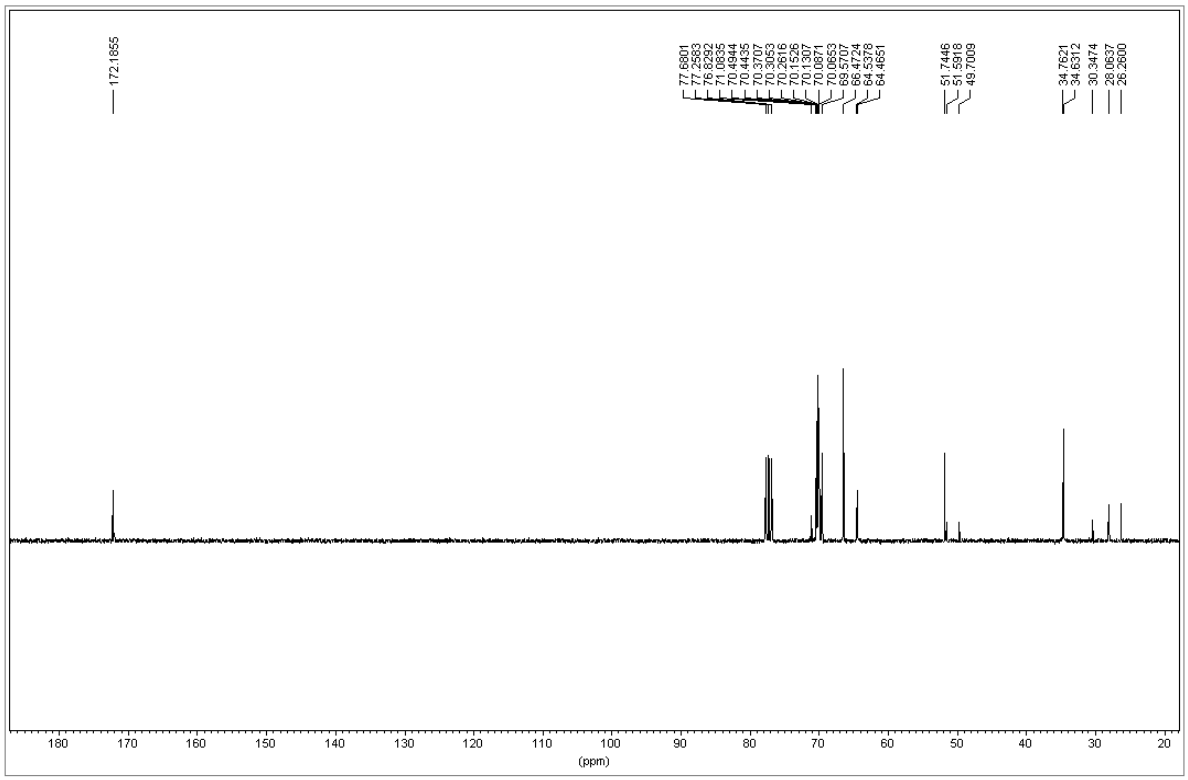

173.7395
158.9607
158.9243
135.7380
135.7016
135.6143
135.5780
135.3016
135.2216
135.1779
126.0285
125.9412
125.8612
125.4757
115.9263
71.3063
71.1900
69.3208
67.4953
60.7314
53.6766
52.2365
49.8582
49.0000
48.1491
36.3086
35.6613
34.5340
(ppm)

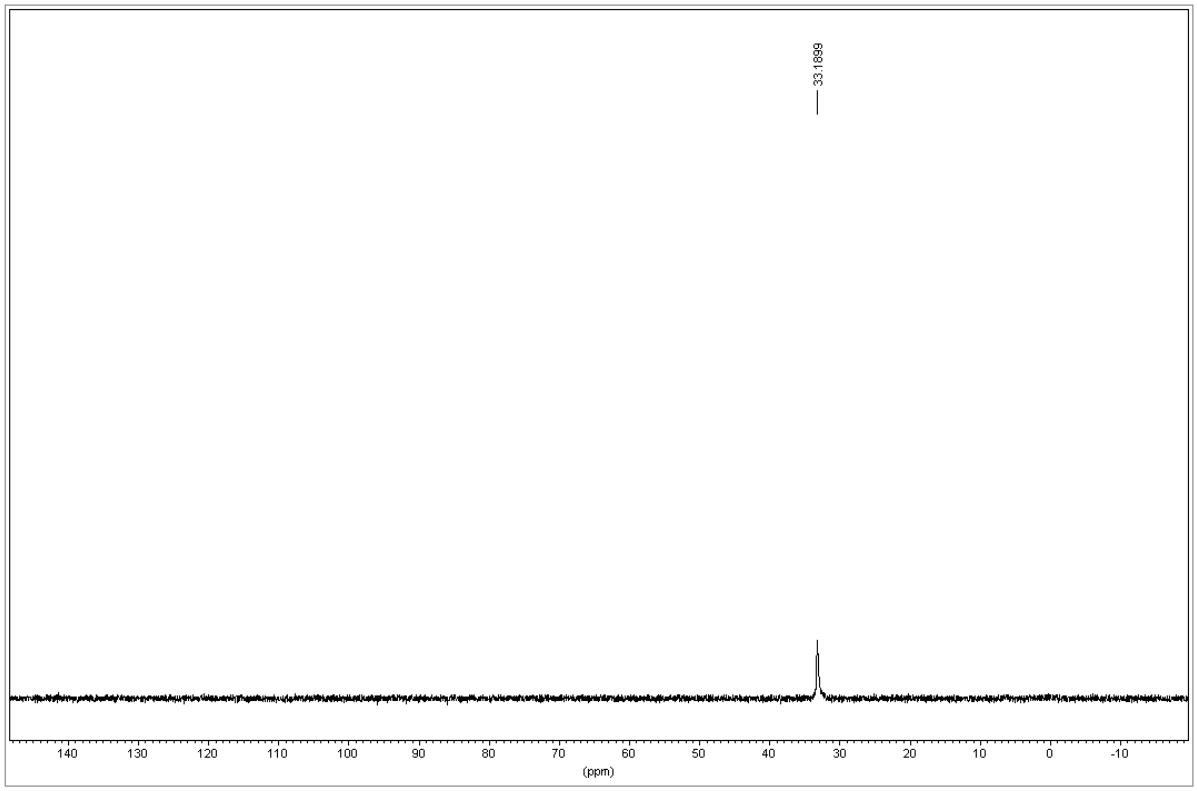


Compound 99 (^{1}H and ^{13}C, CD_3OD)

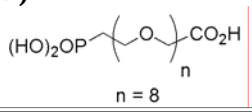


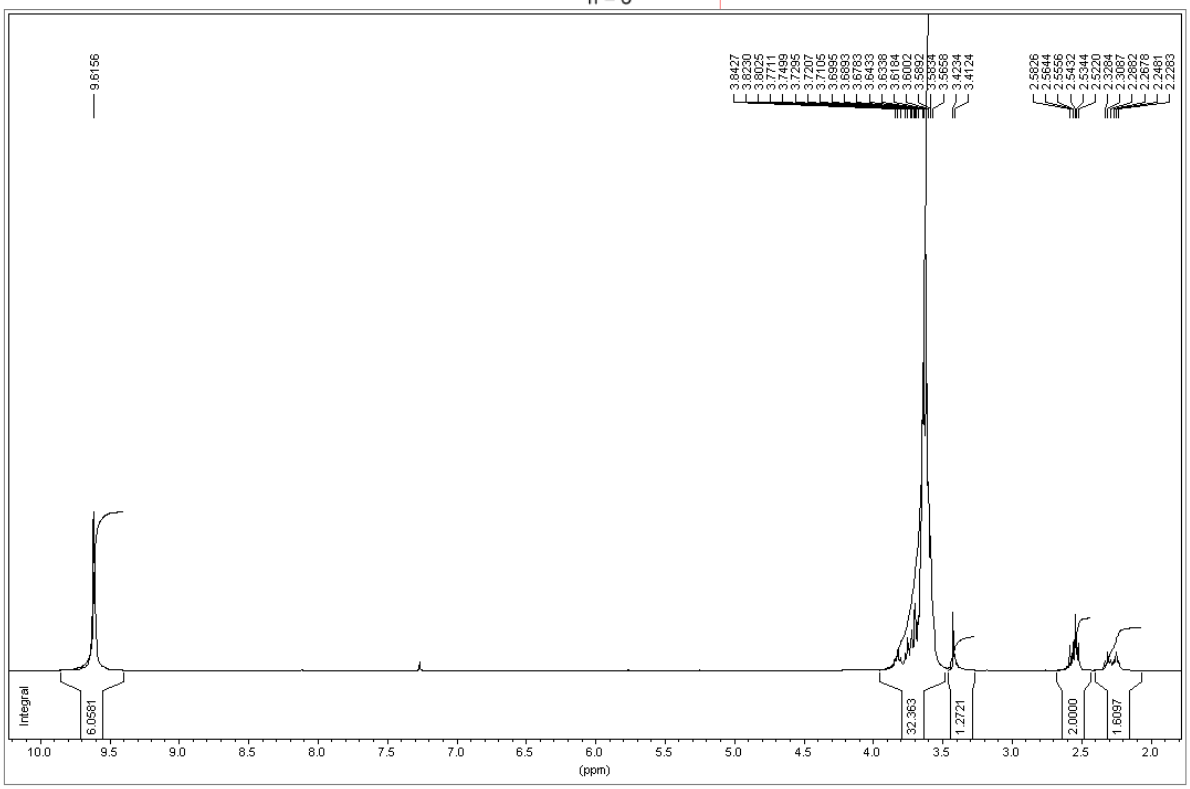


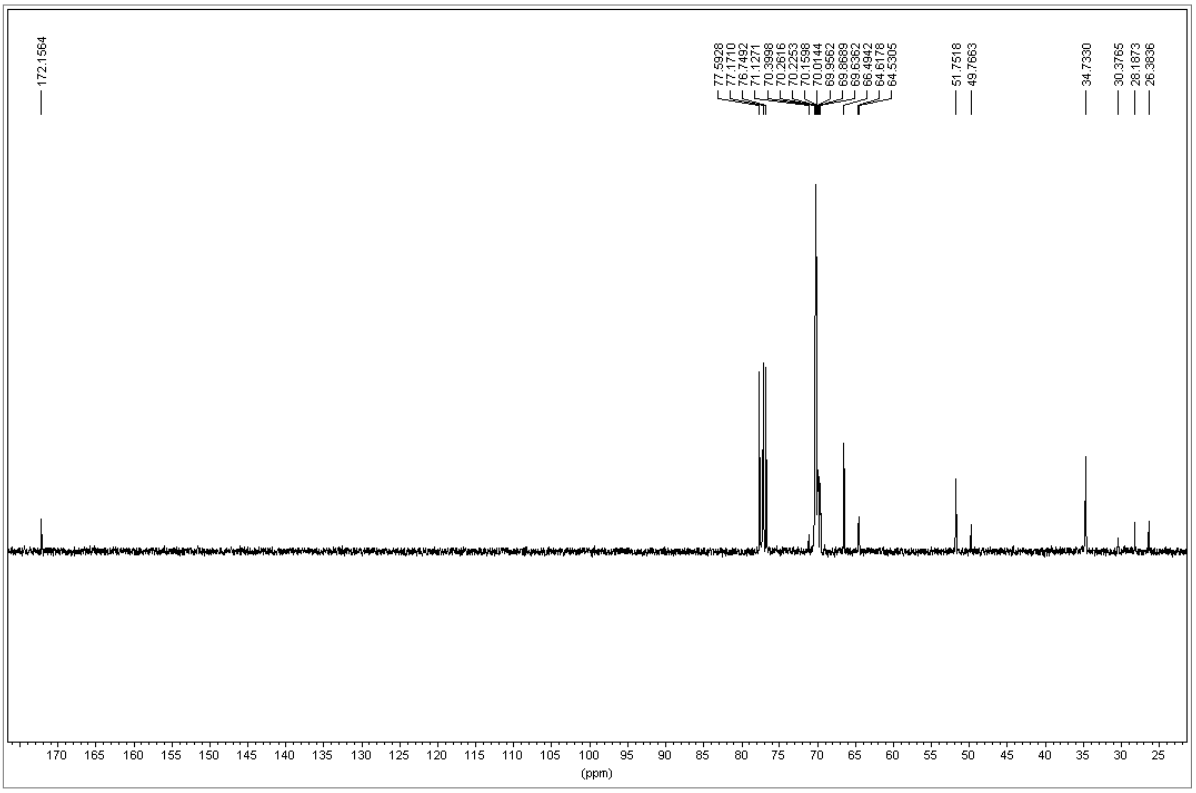

172.1855
77.6801
77.2583
76.8292
70.6635
70.4944
70.4435
70.3707
70.3053
70.2616
70.1526
70.1307
70.0871
70.0553
69.5707
66.4724
64.5378
64.4651
51.7446
51.5918
49.7009
34.7621
34.6312
30.3474
28.0637
26.2600
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
(ppm)

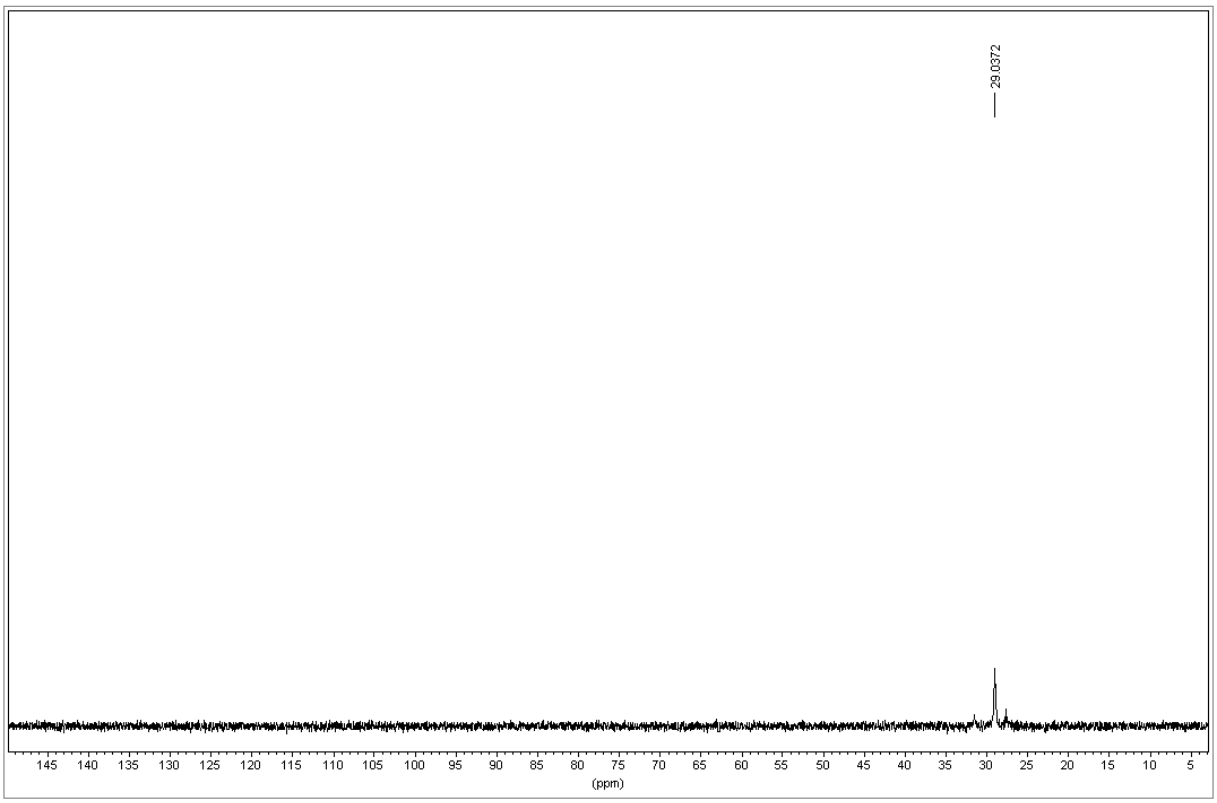

33.1899
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
(ppm)

Compound 100 (^{1}H, ^{13}C and ^{31P}, CD_3OD)

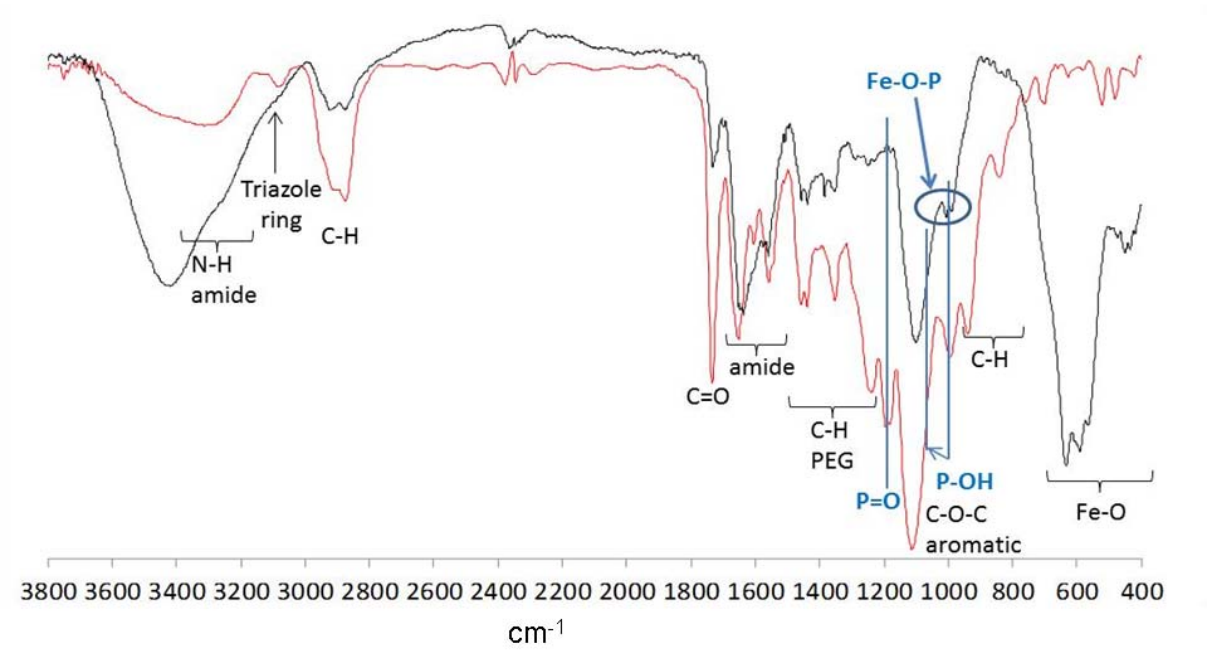








II.IR Spectra of dendronized NPs



IR spectra of 94 (red line), NP@94 (black line).

III.References used for experimental procedures

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