Supporting Information

Triazole formation of phosphinyl alkynes with azides through transient protection of phosphine by copper

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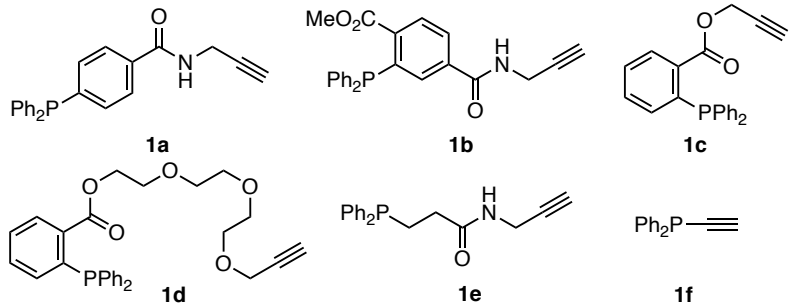
General Remarks

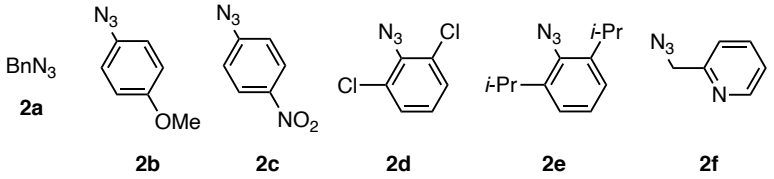
All reactions were performed in a dry glassware under atmosphere of argon otherwise noted. Analytical thin-layer chromatography (TLC) was performed on precoated (0.25 mm) silica-gel plates (Merck Chemicals, Silica Gel 60 F_{254}, Cat. No. 1.05715). Column chromatography was conducted using silica-gel (Kanto Chemical Co., Inc., Silica Gel 60N, spherical neutral, particle size 40–50 μm, Cat. No. 37563-85 or particle size 63–210 μm, Cat. No. 37565-85). Preparative thin-layer chromatography (PTLC) was performed on silica-gel (Wako Pure Chemical Industries Ltd., Wakogel B5-F, Cat. No. 230-00043). Melting points (Mp) were measured on a YANACO MP-J3 instrument or an OptiMelt MPA100 (Stanford Research Systems), and are uncorrected. ^{1}H and ^{13}C NMR spectra were obtained with a Bruker AVANCE 500 spectrometer at 500 or 126 MHz, respectively. ^{19}F NMR spectra were obtained with a Bruker AVANCE 400 spectrometer at 376 MHz. Chemical shifts (δ) are given in parts per million (ppm) downfield from $(CH_3)_4Si$ (δ 0.00 for ^{1}H NMR in $CDCl_3$) or the solvent peak (δ 77.0 for ^{13}C NMR in $CDCl_3$) as an internal reference or triphenylphosphine (δ –6.0 for ^{31}P NMR in $CDCl_3$) as an external standard with coupling constants (*J*) in hertz (Hz). The abbreviations s, d, t, q, sept, m, and br signify singlet, doublet, triplet, quartet, septet, multiplet, and broad, respectively. IR spectra were measured by diffuse reflectance method on a Shimadzu IRPrestige-21 spectrometer attached with DRS-8000A with the absorption band given in cm^{-1}. High-resolution mass spectra (HRMS) were measured on a Bruker micrOTOF mass spectrometer under positive electrospray ionization (ESI^{+}) conditions.

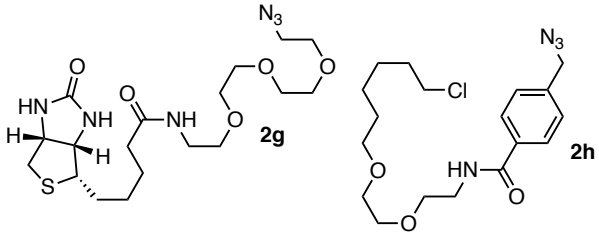
Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. SiliaMetS Thiourea (ca. 1.24 mmol/g, Cat. No. R69530B) and SiliaMetS Triamine (ca. 1.26 mmol/g, Cat. No. R48030B) were purchased from SiliCycle Inc. Resin(polystyrene)–PPh_2 (PS–TPP) (~3.0 mmol/g, Cat. No. 366455) was purchased from Sigma–Aldrich. 4-(Diphenylphosphino)benzoic acid,[S1] 2-(diphenylphosphino)benzoic acid,[S2] 4-methoxycarbonyl-3-(diphenylphosphino)benzoic acid,[S3] 4-methoxyphenyl azide (**2b**),[S4] 4-nitrophenyl azide (**2c**),[S4] 2,6-dichlorophenyl azide (**2d**),[S5] 2,6-diisopropylphenyl azide (**2e**),[S6] 2-azidomethyl pyridine (**2f**),[S7] 4-(2-(2-(6-chlorohexyloxy)ethoxy)ethylaminocarbonyl)benzyl azide (**2h**),[S8] 2-(2-(2-(2-(4-(3,6-bis(diethylamino)xanthylium-9-yl)-3-sulfonatobenzenesulfonamido)ethoxy)ethoxy)ethoxy)ethyl azide (**2j**),[S8] (11-oxo-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-pyrano[2,3-*f*]pyrido[3,2,1-*ij*]quinolin-9-

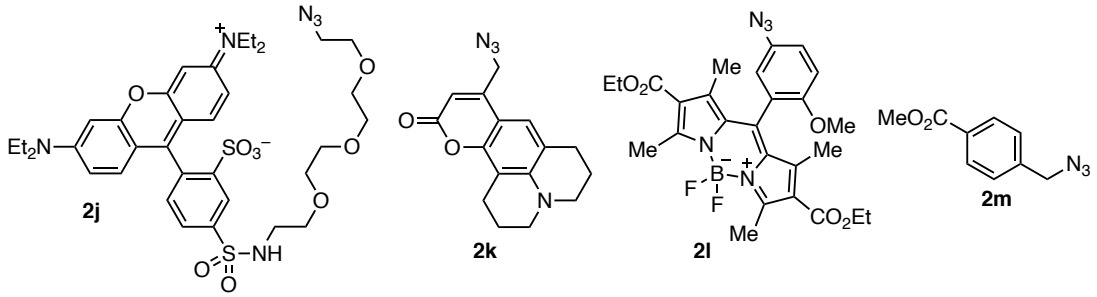
yl)methyl azide (**2k**),[S9] 3-(2,6-bis(ethoxycarbonyl)-4,4-difluoro-1,3,5,7-tetramethyl-3a,4a-diaza-4-bora-*s*-indacen-8-yl)-4-methoxyphenyl azide (**2l**),[S10] ethynyldiphenylphosphine (**1f**),[S11] methyl 3-bromo-5-iodebenzoate (**5**),[S12] 4-(methoxycarbonyl)benzyl azide (**2m**),[S13] and tris[(1-benzyl-*1H*-1,2,3-triazol-4-yl)methyl]amine (TBTA)[S14] were prepared according to the reported methods.

Structures of Phosphinyl Alkynes and Azides



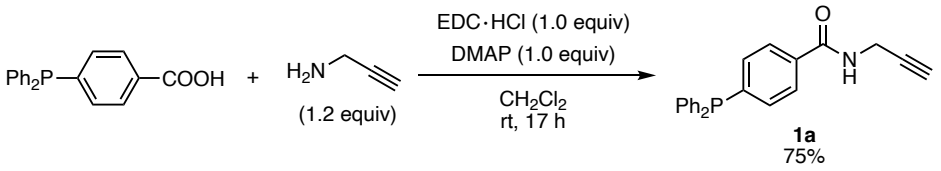






Experimental Procedures

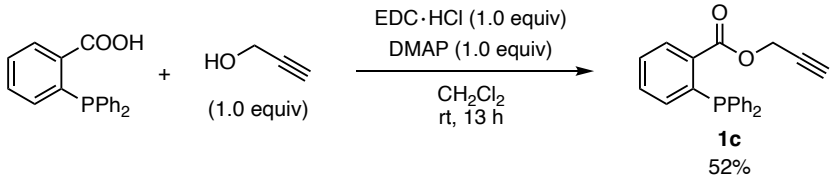
A typical procedure for the preparation of triaryl phosphine bearing terminal alkyne



To a solution of 4-(diphenylphosphino)benzoic acid (1.28 g, 4.18 mmol) dissolved in CH_2Cl_2 (20 mL) were successively added 3-amino-1-propyne (269 mg, 4.88 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (810 mg, 4.23 mmol) and 4-(dimethylamino)pyridine (508 mg, 4.16 mmol) at room temperature. After stirring for 17 h at the same temperature, to the mixture was added H_2O (10 mL). The mixture was extracted with EtOAc (20 mL × 3), and the combined organic extract was washed with brine (10 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 20 g, *n*-hexane/CH_2Cl_2 = 3/1 to 1/1) to give 4-(diphenylphosphino)-*N*-(2-propyn-1-yl)benzamide (**1a**) (1.07 g, 3.12 mmol, 75%) as a colorless solid.

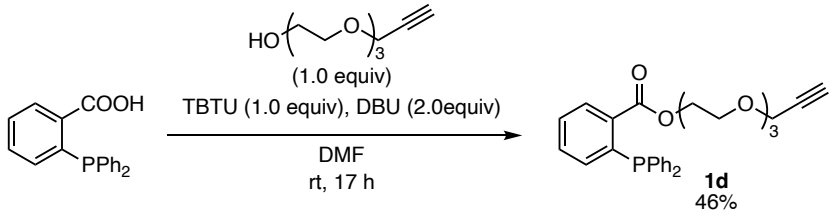
According to this procedure, *N*-(2-propyn-1-yl)-4-(methoxycarbonyl)-3-(diphenylphosphino)benzamide (**1b**) was prepared using 4-methoxycarbonyl-3-(diphenylphosphino)benzoic acid instead of 4-(diphenylphosphino)benzoic acid.

*Preparation of 2-propyn-1-yl 2-(diphenylphosphino)benzoate (**1c**)*



To a solution of 2-(diphenylphosphino)benzoic acid (221 mg, 0.721 mmol) dissolved in CH_2Cl_2 (5 mL) were successively added 2-propyne-1-ol (41.6 μL, 0.721 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (139 mg, 0.725 mmol) and 4-(dimethylamino)pyridine (87.3 mg, 0.715 mmol) at room temperature. After stirring for 13 h at the same temperature, to the mixture was added H_2O (10 mL). The mixture was extracted with EtOAc (20 mL × 3) and the combined organic extract was washed with brine (10 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 20 g, *n*-hexane/CH_2Cl_2 = 3/1 to 1/1) to give 2-propyn-1-yl 2-(diphenylphosphino)benzoate (**1c**) (129 g, 0.375 mmol, 52%) as an orange solid.

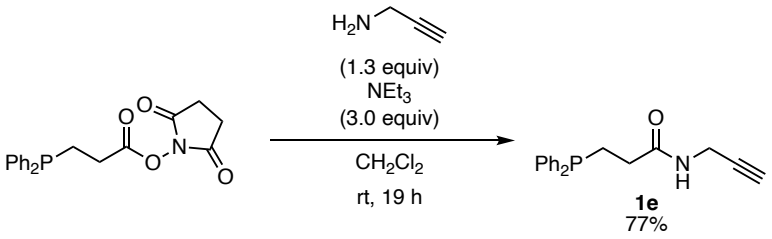
*Preparation of 2-[2-[2-(2-propynyloxy)ethoxy]ethoxy]ethyl 2-(diphenylphosphino)benzoate (**1d**)*



To a solution of 2-(diphenylphosphino)benzoic acid (338 mg, 1.10 mmol) dissolved in DMF (4.0 mL) were added 1-[bis(dimethylamino)methylene]-1*H*-benzotriazolium 3-oxide tetrafluoroborate (TBTU) (354 mg, 1.10 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (339 mg, 2.23 mmol) dissolved in DMF (1.0 mL) at room temperature. After stirring for 30 min at the same temperature,

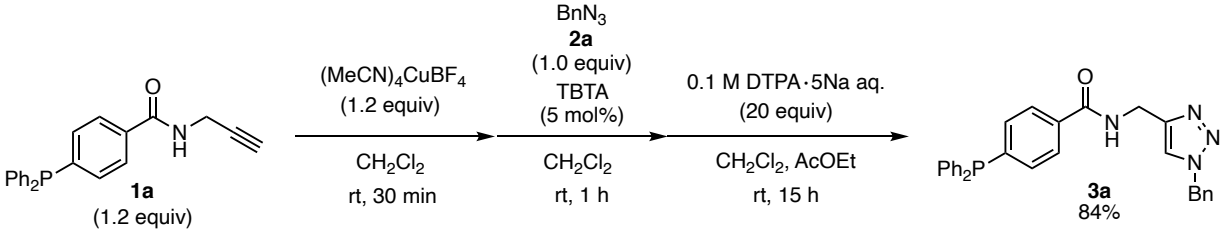
to the reaction mixture was added 2-[2-[2-(2-propynyloxy)ethoxy]ethoxy]ethanol (211 mg, 1.12 mmol) dissolved in DMF (1.0 mL). After stirring for 17 h at the same temperature, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and the resulting mixture was washed with 1M HCl (3 mL × 3), a saturated aqueous solution $NaHCO_3$ (3 mL × 3) and brine (3 mL × 3). The organic layer was collected, dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 50 g, *n*-hexane/EtOAc = 2/1) to give 2-[2-[2-(2-propynyloxy)ethoxy]ethoxy]ethyl 2-(diphenylphosphino)benzoate (**1d**) (240 mg, 0.504 mmol, 46%) as a colorless oil.

*Preparation of N-(2-propyn-1-yl)-3-(diphenylphosphino)propanamide (**1e**)*



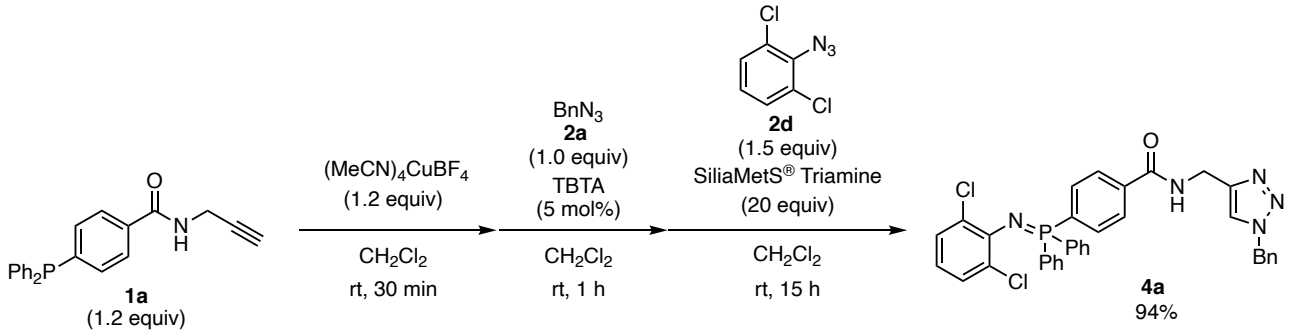
To a solution of *N*-succinimidyl 3-(diphenylphosphino)propionate (370 mg, 1.04 mmol) dissolved in CH_2Cl_2 were successively added triethylamine (416 μL, 3.00 mmol) and 3-amino-1-propyne (72.4 mg, 1.31 mmol) dissolved in CH_2Cl_2 (1.0 mL) at room temperature. After stirring for 19 h at the same temperature, to the mixture was added H_2O (10 mL) and extracted with CH_2Cl_2 (15 mL × 3). The combined organic extract was washed with brine (10 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 20 g, *n*-hexane/EtOAc = 1/1) to give *N*-(2-propyn-1-yl)-3-(diphenylphosphino)propanamide (**1e**) (250 mg, 94% purity, determined by ^{1}H NMR analysis, 0.797 mmol, 76.7%) as a colorless oil.

A typical procedure for selective click reaction of the terminal alkyne moiety of phosphine



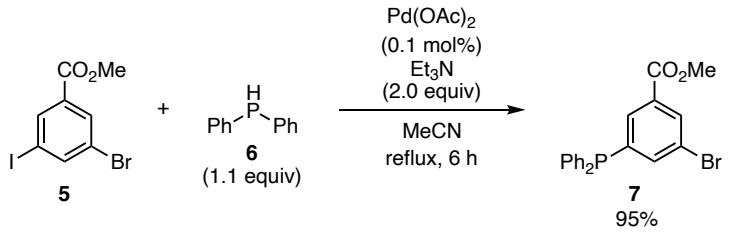
A mixture of 4-(diphenylphosphaneyl)-*N*-(2-propyn-1-yl)benzamide (**1a**) (51.3 mg, 0.149 mmol) and tetrakis(acetonitrile)copper(I) tetrafluoroborate (47.4 mg, 0.151 mmol) was dissolved in CH_2Cl_2 (2.0 mL) at room temperature. After stirring for 30 min at the same temperature, to the reaction mixture were successively added tris[(1-benzyl-*1H*-1,2,3-triazol-4-yl)methyl]amine (TBTA) (3.20 mg, 6.03 μmol) and a solution of benzyl azide (**2a**) (16.2 mg, 0.122 mmol) dissolved in CH_2Cl_2 (1.0 mL). After stirring for 1 h at the same temperature, to the mixture were added an aqueous solution of diethylenetriamine-*N*,*N*,*N′*,*N″*,*N″*-pentaacetic acid pentasodium salt (DTPA·5Na) (0.10 M, 25 mL, 2.5 mmol) and EtOAc (10 mL). After stirring for 15 h at the same temperature, the reaction mixture was extracted three times with EtOAc (20 mL × 3), and the combined organic extract was washed with brine (10 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 4 g, *n*-hexane/EtOAc = 1/1 to EtOAc) to give *N*-((1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl)-4-(diphenylphosphaneyl)benzamide (**3a**) (48.7 mg, 0.102 mmol, 84%) as a colorless solid.

*Sequential conjugation using triarylphosphine bearing terminal alkyne via CuAAC with benzyl azide (**2a**) followed by Staudinger reaction with 2,6-dichlorophenyl azide (**2d**)*



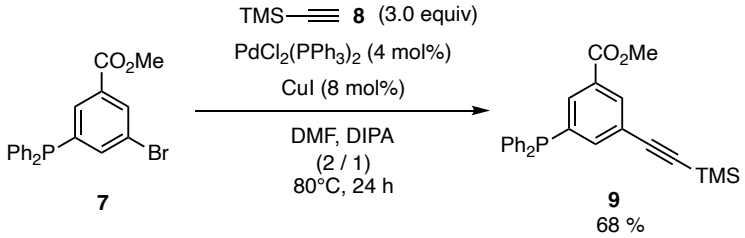
A mixture of 4-(diphenylphosphaneyl)-*N*-(2-propyn-1-yl)benzamide (**1a**) (50.5 mg, 0.147 mmol) and tetrakis(acetonitrile)copper(I) tetrafluoroborate (46.7 mg, 0.148 mmol) was dissolved in CH_2Cl_2 (2.0 mL) at room temperature. After stirring for 30 min at the same temperature, to the reaction mixture were successively added tris[(1-benzyl-*1H*-1,2,3-triazol-4-yl)methyl]amine (TBTA) (3.29 mg, 6.20 μmol) and a solution of benzyl azide (**2a**) (16.1 mg, 0.121 mmol) dissolved in CH_2Cl_2 (1.0 mL). After stirring for 1 h at the same temperature, to the mixture were successively added SiliaMetS Triamine (ca. 1.29 mmol/g, 1.94 g, ca. 2.5 mmol), CH_2Cl_2 (10 mL) and 2,6-dichlorophenyl azide (**2d**) (35.3 mg, 0.188 mmol) dissolved in CH_2Cl_2 (1.0 mL). After stirring for 15 h at the same temperature, the reaction mixture was filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 5 g, *n*-hexane/EtOAc = 1/1 to *n*-hexane/EtOAc = 1/2) to give *N*-((1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl)-4-(diphenylphosphaneyl)benzamide (**4a**) (72.2 mg, 0.113 mmol, 94%) as a colorless solid.

Synthesis of methyl 3-bromo-5-(diphenylphosphino)benzoate (7)



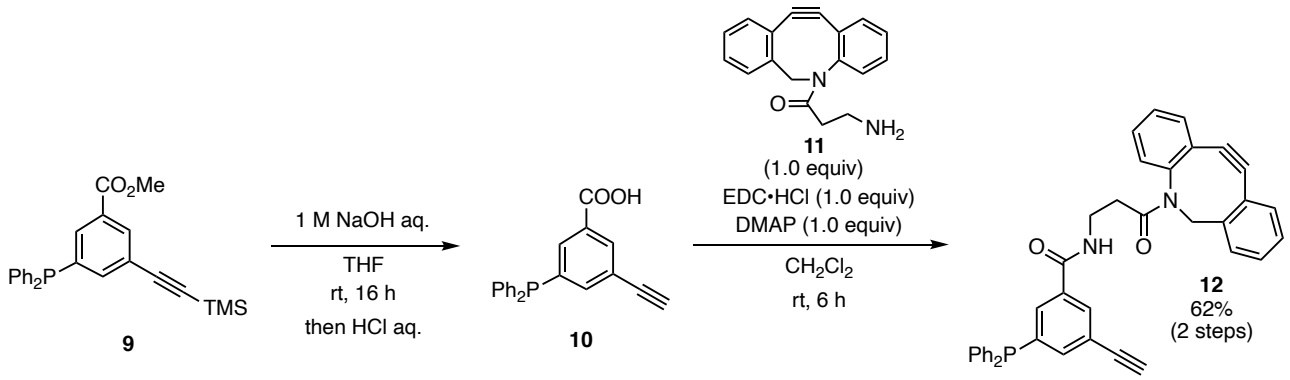
To a mixture of methyl 3-bromo-5-iodobenzoate (**5**) (4.19 g, 12.3 mmol), $Pd(OAc)_2$ (3.05 mg, 13.6 μmol), and triethylamine (3.41 mL, 24.6 mmol) dissolved in MeCN (20 mL) was added diphenylphosphine (**6**) (2.35 mL, 13.5 mmol) at room temperature. After stirring the mixture for 6 h under reflux (95 °C, bath temperature), the mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 150 g, *n*-hexane/EtOAc = 10/1) to give methyl 3-bromo-5-(diphenylphosphino)benzoate (**7**) (4.67 g, 11.7 mmol, 95%) as a colorless oil.

*Synthesis of methyl 3-(trimethylsilylethynyl)-5-(diphenylphosphino)benzoate (**9**)*



To a mixture of methyl 3-bromo-5-(diphenylphosphino)benzoate (**7**) (1.70 g, 4.26 mmol), $(Ph_3P)_2PdCl_2$ (117 mg, 0.167 mmol), and copper(I) iodide (64.9 mg, 0.341 mmol) dissolved in DMF (20 mL) and diisopropylamine (10 mL) was added trimethylsilylacetylene (**8**) (1.81 mL, 12.8 mmol) at 80 °C. After stirring for 24 h at the same temperature, the reaction mixture was extracted three times with EtOAc (20 mL × 3), and the combined organic extract was washed with brine (10 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 80 g, *n*-hexane/CH_2Cl_2 = 3/1 to *n*-hexane/EtOAc = 9/1) to give methyl 3-(trimethylsilylethynyl)-5-(diphenylphosphino)benzoate (**9**) (1.21 g, 2.90 mmol, 68%) as a colorless oil.

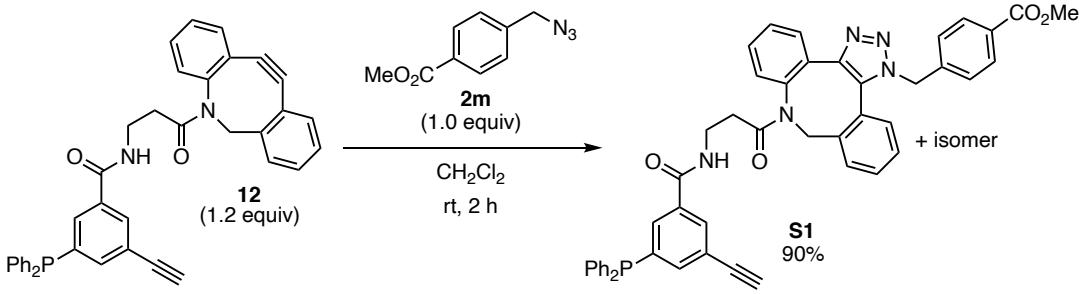
*Synthesis of platform molecule **12***



To a solution of 3-(trimethylsilylethynyl)-5-(diphenylphosphino)benzoate (**9**) (213 mg, 0.511 mmol) dissolved in THF (3.0 mL) was added aqueous NaOH (1 M, 2 mL) at room temperature. After stirring for 16 h at the same temperature, to the reaction mixture was added 1 M aqueous HCl until acidic. The mixture was extracted three times with EtOAc (15 mL × 3), and the combined organic extract was washed with brine (10 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure.

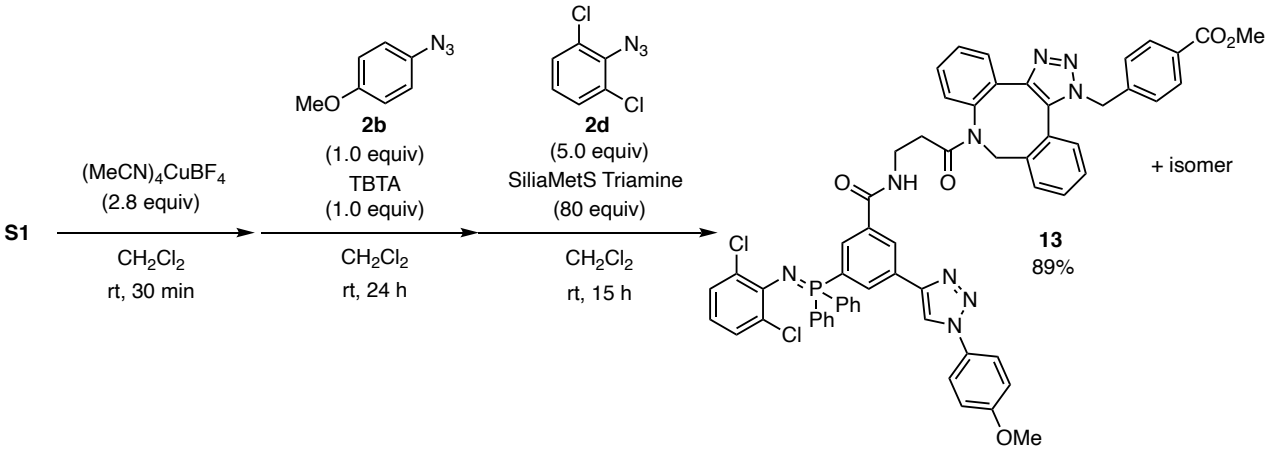
Without further purification, carboxylic acid **10** was dissolved in CH_2Cl_2 (2.0 mL). To the solution were successively added DIBAC–amine **11** (141 mg, 0.511 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (100 mg, 0.522 mmol), and 4-(dimethylamino)pyridine (63.0 mg, 0.516 mmol) at room temperature. After stirring for 6 h at the same temperature, the mixture was concentrated under reduced pressure. After the addition of H_2O (15 mL), the mixture was extracted with EtOAc (15 mL × 3), and the combined organic extract was washed with brine (10 mL), dried (Na_2SO_4), and after filtration, the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 30 g, *n*-hexane/EtOAc = 1/1) to give platform molecule **12** (185 mg, 0.314 mmol, 62%, in 2 steps from **9**) as a colorless solid.

*A procedure for the reaction of platform molecule **12** with methyl 4-azidomethylbenzoate (**S1**)*



To a solution of platform molecule **12** (8.99 mg, 15.3 μmol) dissolved in CH_2Cl_2 (1.0 mL) was added methyl 4-azidomethylbenzoate (2.49 mg, 13.0 μmol) in CH_2Cl_2 at room temperature. After stirring for 2 h at the same temperature, the mixture was concentrated under reduced pressure. The residue was purified by preparative TLC (EtOAc/*n*-hexane = 2/1) to give platform-triazole **S1** (9.09 mg, 11.7 μmol, 90%) as a colorless solid.

*A procedure for the reaction of **S1** with azides **2b** and **2d***

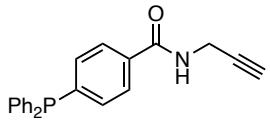


A mixture of triazole **S1** (9.09 mg, 11.7 μmol) and tetrakis(acetonitrile)copper(I) tetrafluoroborate (8.69 mg, 27.6 μmol) was dissolved in CH_2Cl_2 (1.0 mL) at room temperature. After stirring for 30 min at the same temperature, to the reaction mixture were successively added tris[(1-benzyl-*1H*-1,2,3-triazol-4-yl)methyl]amine (TBTA) (5.23 mg, 9.86 μmol) and a solution of 4-methoxyphenyl azide (**2b**) (1.48 mg, 9.92 μmol) dissolved in CH_2Cl_2 (1.0 mL). After stirring for 24 h at the same temperature, to the mixture were successively added SiliaMetS Triamine (ca. 1.29 mmol/g, 1.0 g, ca. 0.80 mmol), CH_2Cl_2 (10 mL) and 2,6-dichlorophenyl azide (**2d**) (9.50 mg, 50.5 μmol) dissolved in CH_2Cl_2 (1.0 mL). After stirring for 15 h at the same temperature, the reaction mixture was filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (silica-gel 2.5 g, *n*-hexane/EtOAc = 1/2) to give azaylide **13** (9.60 mg, 8.82 μmol, 89%) as a colorless solid.

Characterization Data of New Compounds

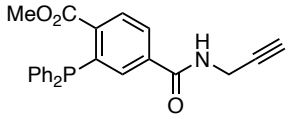
1-Benzyl-4-(diphenylphosphino)-*1H*-1,2,3-triazole (**3n**)[S15] was identical in spectra data with those reported in the literatures.

N-(2-Propyn-1-yl)-4-(diphenylphosphino)benzamide (**1a**)



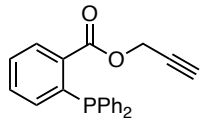
Colorless solid; Mp 112–114 ºC; TLC R_f 0.57 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.28 (t, 1H, J = 2.6 Hz), 4.25 (dd, 2H, J = 5.3, 2.6 Hz), 6.20–6.27 (br t, 1H), 7.28–7.40 (m, 12H), 7.69–7.74 (m, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 29.8 (1C), 71.9 (1C), 79.3 (1C), 126.9 (d, 2C, $J_{C–P}$ = 6.5 Hz) 128.6 (d, 4C, $J_{C–P}$ = 7.1 Hz), 129.1 (2C), 133.5 (d, 2C, $J_{C–P}$ = 18.6 Hz), 133.6 (1C), 133.9 (d, 4C, $J_{C–P}$ = 19.6 Hz), 136.2 (d, 2C, $J_{C–P}$ = 10.3 Hz), 142.6 (d, 1C, $J_{C–P}$ = 14.0 Hz), 166.8 (1C); ^{31}P NMR ($CDCl_3$, 162 MHz) δ –6.1 (t, J = 7.1 Hz); IR (KBr, cm^{-1}) 696, 743, 912, 1304, 1433, 1481, 1531, 1597, 1643, 3296; HRMS (ESI$^+$) *m*/*z* 366.1010 ([M+Na]$^+$, $C_{22}H_{18}NNaOP^+$ requires 366.1018).

N-(2-Propyn-1-yl)-4-(methoxycarbonyl)-3-(diphenylphosphino)benzamide (**1b**)



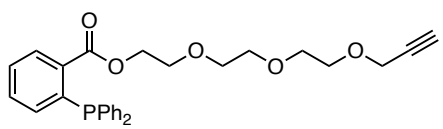
Yellow solid; Mp 47–53 ºC; TLC R_f 0.62 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.25 (t, 1H, J = 2.5 Hz), 3.75 (s, 3H), 4.12 (dd, 2H, J = 5.1, 2.5 Hz), 5.81–5.91 (br t, 1H), 7.23 (dd, 1H, J = 3.6, 1.8 Hz), 7.25–7.32 (m, 4H), 7.32–7.40 (m, 6H), 7.80 (dd, 1H, J = 8.2, 1.7 Hz), 8.11 (dd, 1H, J = 8.1, 3.7 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 29.9 (1C), 52.3 (1C), 72.1 (1C), 78.9 (1C), 126.9 (1C), 128.7 (d, 4C, $J_{C–P}$ = 7.3 Hz), 129.1 (2C), 131.0 (d, 1C, $J_{C–P}$ = 2.1 Hz), 132.4 (1C), 133.9 (d, 4C, $J_{C–P}$ = 21.0 Hz), 136.3 (1C), 137.0 (d, 1C, $J_{C–P}$ = 18.4 Hz), 137.1 (d, 2C, $J_{C–P}$ = 10.9 Hz), 141.8 (d, 1C, $J_{C–P}$ = 29.8 Hz), 165.8 (1C), 166.5 (d, 1C, $J_{C–P}$ = 2.6 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ –4.6 to –4.3 (m); IR (KBr, cm^{-1}) 696, 745, 1254, 1275, 1288, 1433, 1530, 1643, 1721; HRMS (ESI$^+$) *m*/*z* 424.1072 ([M+Na]$^+$, $C_{24}H_{20}NNaO_3P^+$ requires 424.1073).

2-Propyn-1-yl 2-(diphenylphosphino)benzoate (**1c**)



Orange solid; Mp 95 ºC (decomposition); TLC R_f 0.38 (*n*-hexane/CH_2Cl_2 = 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.44 (t, 1H, J = 2.5 Hz), 4.75 (d, 2H, J = 2.5 Hz), 6.91–6.98 (m, 1H), 7.21–7.37 (m, 10H), 7.37–7.44 (m, 2H), 8.08–8.14 (m, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 52.8 (1C), 75.1 (1C), 77.4 (1C), 128.2 (1C), 128.5 (d, 4C, $J_{C–P}$ = 7.2 Hz), 128.7 (2C), 130.9 (d, 1C, $J_{C–P}$ = 2.5 Hz), 132.3 (1C), 133.2 (d, 1C, $J_{C–P}$ = 18.8 Hz), 133.9 (d, 4C, $J_{C–P}$ = 20.5 Hz), 134.3 (1C), 137.7 (d, 2C, $J_{C–P}$ = 10.9 Hz), 141.0 (d, 1C, $J_{C–P}$ = 27.5 Hz), 165.7 (d, 1C, $J_{C–P}$ = 2.3 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ –4.98 (s); IR (KBr, cm^{-1}) 696, 745, 1057, 1101, 1250, 1265, 1433, 1721; HRMS (ESI$^+$) *m*/*z* 345.1036 ([M+H]$^+$, $C_{22}H_{18}O_2P^+$ requires 345.1039).

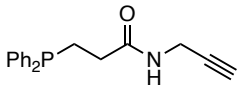
2-(2-(2-(2-Propynyloxy)ethoxy)ethoxy)ethyl 2-(diphenylphosphino)benzoate (**1d**)



Colorless oil; TLC R_f 0.64 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.41 (t, 1H, J = 2.4 Hz),

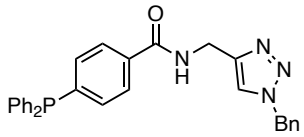
3.57–3.71 (m, 10H), 4.18 (d, 2H, J = 2.4 Hz), 4.31–4.34 (br t, 2H), 6.90–6.95 (m, 1H), 7.22–7.43 (m, 12H), 8.06–8.11 (m, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 58.4 (1C), 64.2 (1C), 68.9 (1C), 69.1 (1C), 70.4 (1C), 70.5 (1C), 70.6 (1C), 74.5 (1C), 79.6 (1C), 128.1 (1C), 128.4 (d, 4C, $J_{C–P}$ = 7.2 Hz), 128.6 (2C), 130.8 (d, 1C, $J_{C–P}$ = 2.6 Hz), 132.0 (1C), 133.9 (d, 4C, $J_{C–P}$ = 20.8 Hz), 134.2 (d, 1C, $J_{C–P}$ = 19.2 Hz), 134.3 (1C), 137.9 (d, 2C, $J_{C–P}$ = 11.1 Hz), 140.5 (d, 1C, $J_{C–P}$ = 26.6 Hz), 166.6 (d, 1C, $J_{C–P}$ = 1.8 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ –5.31 (s); IR (KBr, cm^{-1}) 698, 746, 1059, 1103, 1140, 1254, 1267, 1435, 1715, 2870; HRMS (ESI$^+$) m/z 477.1812 ([M+H]$^+$, $C_{28}H_{30}O_5P^+$ requires 477.1825).

N-(2-Propyn-1-yl)-3-(diphenylphosphino)propionamide (**1e**)



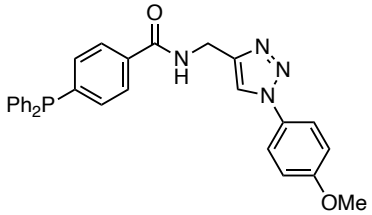
Pale yellow oil; TLC R_f 0.65 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.18 (t, 1H, J = 2.6 Hz), 2.21–2.28 (m, 2H), 2.32–2.39 (m, 2H), 3.97 (dd, 1H, J = 5.2, 2.6 Hz), 5.86–5.99 (br, 1H), 7.29–7.34 (m, 6H), 7.38–7.44 (m, 4H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 23.2 (d, 1C, $J_{C–P}$ = 11.9 Hz), 29.3 (1C), 32.4 (d, 1C, $J_{C–P}$ = 18.4 Hz), 71.7 (1C), 79.5 (1C), 128.6 (d, 4C, $J_{C–P}$ = 6.5 Hz), 128.9 (2C), 132.7 (d, 4C, $J_{C–P}$ = 18.9 Hz), 137.8 (d, 2C, $J_{C–P}$ = 12.7 Hz), 172.0 (d, 1C, $J_{C–P}$ = 13.9 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ –16.4 to –16.0 (m); IR (KBr, cm^{-1}) 1250, 1433, 1537, 1651, 3051; HRMS (ESI$^+$) m/z 296.1188 ([M+H]$^+$, $C_{18}H_{19}NOP^+$ requires 296.1199).

N-((1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl)-4-(diphenylphosphino)benzamide (**3a**)



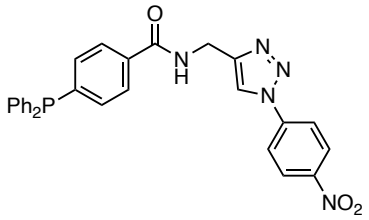
Colorless solid; Mp 177–179 ºC; TLC R_f 0.67 (EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.68 (d, 2H, J = 5.7 Hz), 5.49 (s, 2H), 6.93 (t, 1H, J = 5.4 Hz), 7.26–7.39 (m, 17H), 7.52 (s, 1H), 7.70 (d, 2H, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 35.4 (1C), 54.3 (1C), 122.2 (1C), 126.8 (d, 2C, $J_{C–P}$ = 6.5 Hz), 128.1 (2C), 128.6 (d, 4C, $J_{C–P}$ = 7.3 Hz), 128.8 (1C), 129.07 (2C), 129.15 (2C), 133.5 (d, 2C, $J_{C–P}$ = 18.9 Hz), 133.86 (d, 4C, $J_{C–P}$ = 19.6 Hz), 133.90 (1C), 134.4 (1C), 136.2 (d, 2C, $J_{C–P}$ = 10.7 Hz), 142.4 (d, 1C, $J_{C–P}$ = 13.6 Hz), 144.8 (1C), 167.1 (1C); ^{31}P NMR ($CDCl_3$, 162 MHz) δ –6.3 to –5.9 (m); IR (KBr, cm^{-1}) 696, 721, 743, 1298, 1433, 1528, 1549, 1639; HRMS (ESI$^+$) m/z 477.1830 ([M+H]$^+$, $C_{29}H_{26}N_4OP^+$ requires 477.1839).

N-((1-(4-Methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)methyl)-4-(diphenylphosphino)benzamide (**3b**)



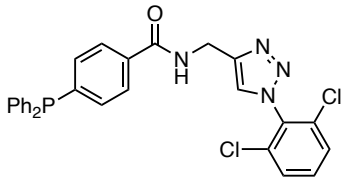
Colorless solid; Mp 151–152 ºC; TLC R_f 0.25 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.86 (s, 3H), 4.78 (d, 2H, J = 5.6 Hz), 6.97–7.03 (m, 2H), 7.10–7.18 (br, 1H), 7.27–7.40 (m, 12H), 7.57–7.63 (m, 2H), 7.73–7.79 (m, 2H), 7.98 (s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 35.4 (1C), 55.6 (1C), 114.7 (2C), 121.0 (1C), 122.2 (2C), 126.9 (d, 2C, $J_{C–P}$ = 6.5 Hz), 128.6 (d, 4C, $J_{C–P}$ = 7.2 Hz), 129.1 (2C), 130.4 (1C), 133.5 (d, 2C, $J_{C–P}$ = 18.9 Hz), 133.86 (d, 4C, $J_{C–P}$ = 20.0 Hz), 133.87 (1C), 136.2 (d, 2C, $J_{C–P}$ = 10.7 Hz), 142.4 (d, 1C, $J_{C–P}$ = 13.8 Hz), 145.0 (1C), 159.9 (1C), 167.2 (1C); ^{31}P NMR ($CDCl_3$, 162 MHz) δ –6.3 to –5.9 (m); IR (KBr, cm^{-1}) 696, 745, 831, 1042, 1256, 1304, 1433, 1483, 1518, 1639; HRMS (ESI$^+$) m/z 515.1602 ([M+Na]$^+$, $C_{29}H_{25}N_4NaO_2P^+$ requires 515.1607).

N-((1-(4-Nitrophenyl)-1*H*-1,2,3-triazol-4-yl)methyl)-4-(diphenylphosphino)benzamide (**3c**)



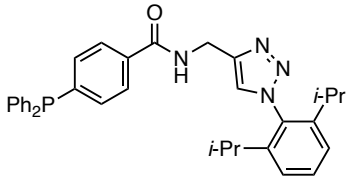
Colorless solid; Mp 160–169 ºC; TLC R_f 0.27 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.80 (d, 2H, J = 5.9 Hz), 7.12 (t, 1H, J = 5.9 Hz), 7.26–7.39 (m, 12H), 7.71–7.76 (AA'BB', 2H), 7.93–7.98 (AA'BB', 2H), 8.23 (s, 1H), 8.37–8.42 (AA'BB', 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 35.3 (1C), 120.5 (2C), 120.9 (1C), 125.5 (2C), 126.8 (d, 2C, $J_{C–P}$ = 6.5 Hz), 128.7 (d, 4C, $J_{C–P}$ = 7.1 Hz), 129.1 (2C), 133.53 (1C), 133.56 (d, 2C, $J_{C–P}$ = 18.9 Hz), 133.9 (d, 4C, $J_{C–P}$ = 20.1 Hz), 136.1 (d, 2C, $J_{C–P}$ = 10.8 Hz), 141.0 (1C), 142.9 (d, 1C, $J_{C–P}$ = 14.3 Hz), 146.3 (1C), 147.3 (1C), 167.3 (1C); ^{31}P NMR ($CDCl_3$, 162 MHz) δ –6.2 to –5.9 (m); IR (KBr, cm^{-1}) 696, 748, 854, 1342, 1506, 1526, 1597, 1643; HRMS (ESI$^+$) *m*/*z* 530.1337 ([M+Na]$^+$, $C_{28}H_{22}N_5NaO_3P^+$ requires 530.1352).

N-((1-(2,6-Dichlorophenyl)-1*H*-1,2,3-triazol-4-yl)methyl)-4-(diphenylphosphino)benzamide (**3d**)



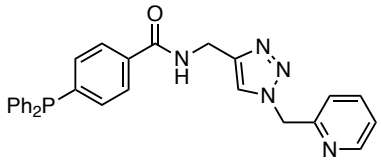
Colorless solid; Mp 153–155 ºC; TLC R_f 0.41 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.85 (d, 2H, J = 5.5 Hz), 7.09 (t, 1H, J = 5.5 Hz), 7.27–7.39 (m, 12H), 7.41–7.46 (m, 1H), 7.47–7.52 (m, 2H), 7.73–7.78 (AA'BB', 2H), 7.80 (s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 35.3 (1C), 124.7 (1C), 126.9 (d, 2C, $J_{C–P}$ = 6.5 Hz), 128.6 (d, 4C, $J_{C–P}$ = 7.3 Hz), 128.8 (2C), 129.1 (2C), 131.8 (1C), 133.0 (1C), 133.5 (d, 2C, $J_{C–P}$ = 18.7 Hz), 133.9 (d, 4C, $J_{C–P}$ = 20.0 Hz), 136.2 (d, 2C, $J_{C–P}$ = 10.3 Hz), 142.4 (d, 1C, $J_{C–P}$ = 13.7 Hz), 144.4 (1C), 167.2 (1C): Some signals were not observed clearly; ^{31}P NMR ($CDCl_3$, 162 MHz) δ –6.3 to –5.9 (m); IR (KBr, cm^{-1}) 696, 743, 795, 1298, 1435, 1489, 1533, 1647; HRMS (ESI$^+$) *m*/*z* 553.0709 ([M+Na]$^+$, $C_{28}H_{21}{}^{35}Cl_2N_4NaOP^+$ requires 553.0722).

N-((1-(2,6-Diisopropylphenyl)-1*H*-1,2,3-triazol-4-yl)methyl)-4-(diphenylphosphino)benzamide (**3e**)



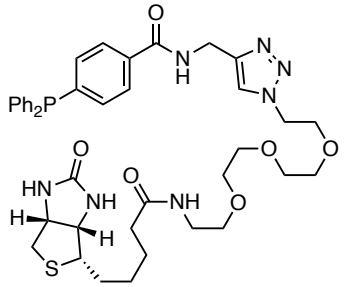
Colorless solid; Mp 182–183 ºC; TLC R_f 0.57 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.12 (dd, 12H, J = 6.8 Hz, $J_{H–P}$ = 13.3 Hz), 2.18 (sept, 2H, J = 6.8 Hz), 4.84 (d, 2H, J = 5.5 Hz), 7.02 (t, 1H, J = 5.3 Hz), 7.27–7.39 (m, 14H), 7.49 (t, 1H, J = 7.8 Hz), 7.68 (s, 1H), 7.74–7.79 (AA'BB', 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 24.0 (2C), 24.1 (2C), 28.4 (2C), 35.5 (1C), 123.8 (2C), 125.1 (1C), 126.9 (d, 2C, $J_{C–P}$ = 6.6 Hz), 128.7 (d, 4C, $J_{C–P}$ = 7.2 Hz), 129.1 (2C), 130.9 (1C), 133.0 (1C), 133.6 (d, 2C, $J_{C–P}$ = 18.7 Hz), 133.9 (d, 4C, $J_{C–P}$ = 19.8 Hz), 134.1 (1C), 136.2 (d, 2C, $J_{C–P}$ = 10.3 Hz), 142.4 (d, 1C, $J_{C–P}$ = 13.8 Hz), 143.9 (2C), 146.0 (1C), 167.2 (1C); ^{31}P NMR ($CDCl_3$, 162 MHz) δ –6.2 to –5.9 (m); IR (KBr, cm^{-1}) 696, 742, 1300, 1433, 1477, 1531, 1653, 2965; HRMS (ESI$^+$) *m*/*z* 569.2453 ([M+Na]$^+$, $C_{34}H_{35}N_4NaOP^+$ requires 569.2441).

N-((1-(2-Pyridylmethyl)-1*H*-1,2,3-triazol-4-yl)methyl)-4-(diphenylphosphino)benzamide (**3f**)



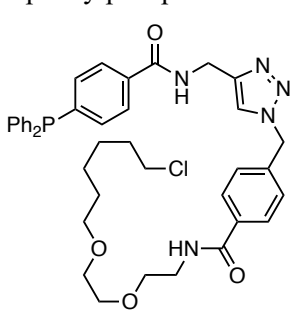
Colorless solid; Mp 167–172 ºC; TLC R_f 0.37 (CH_2Cl_2/MeOH = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.71 (d, 2H, J = 5.4 Hz), 5.63 (s, 2H), 6.88 (t, 1H, J = 5.4 Hz), 7.19 (d, 1H, J = 7.8 Hz), 7.24–7.39 (m, 13H), 7.65–7.73 (m, 3H), 7.74 (s, 1H), 8.57–8.61 (m, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 35.4 (1C), 55.7 (1C), 122.4 (1C), 122.8 (1C), 123.5 (1C), 126.8 (d, 2C, $J_{C–P}$ = 6.5 Hz), 128.0 (1C), 128.65 (d, 4C, $J_{C–P}$ = 7.3 Hz), 129.1 (2C), 133.5 (d, 2C, $J_{C–P}$ = 18.8 Hz), 133.9 (d, 4C, $J_{C–P}$ = 19.6 Hz), 136.2 (d, 2C, $J_{C–P}$ = 10.6 Hz), 137.3 (1C), 142.3 (d, 1C, $J_{C–P}$ = 14.0 Hz), 144.8 (1C), 149.9 (1C), 154.2 (1C), 167.0 (1C); ^{31}P NMR ($CDCl_3$, 162 MHz) δ –6.3 to –5.9 (m); IR (KBr, cm^{-1}) 696, 727, 744, 1300, 1433, 1479, 1531, 1595, 1643; HRMS (ESI$^+$) *m*/*z* 500.1599 ([M+Na]$^+$, $C_{28}H_{24}N_5NaOP^+$ requires 500.1611).

4-(4-Diphenylphosphinobenzoylaminomethyl)-1-(2-(2-(2-(2-(biotinamido)ethoxy)ethoxy)ethoxy)ethyl)-1*H*-1,2,3-triazole (**3g**)



Colorless solid; TLC R_f 0.40 (CH_2Cl_2/MeOH = 5/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.28–1.45 (m, 2H), 1.45–1.69 (m, 4H), 1.96–2.10 (m, 2H), 2.67 (d, 1H, J = 16.0 Hz), 2.84 (dd, 1H, J = 16.0, 6.1 Hz), 3.02–3.09 (m, 1H), 3.34–3.48 (m, 2H), 3.51–3.66 (m, 10H), 3.87 (t, 2H, J = 6.3 Hz), 4.20–4.26 (m, 1H), 4.39–4.46 (m, 1H), 4.50 (t, 2H, J = 6.3 Hz), 4.60 (dd, 1H, J = 18.6, 7.3 Hz), 4.74 (dd, 1H, J = 18.6, 7.3 Hz), 5.55–5.60 (br, 1H), 6.85 (t, 1H, J = 6.7 Hz), 6.96–7.01 (br, 1H), 7.24–7.39 (m, 12H), 7.78–7.85 (m, 2H), 7.89 (s, 1H), 8.40 (t, 1H, J =7.2 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 25.3 (1C), 28.0 (1C), 28.2 (1C), 35.0 (1C), 35.6 (1C), 39.2 (1C), 40.5 (1C), 50.3 (1C), 55.7 (1C), 60.0 (1C), 61.9 (1C), 69.3 (1C), 69.8 (1C), 70.1 (1C), 70.4 (1C), 70.47 (1C), 70.52 (1C), 123.9 (1C), 127.1 (d, 2C, $J_{C–P}$ = 6.5 Hz), 128.6 (d, 4C, $J_{C–P}$ = 7.2 Hz), 129.0 (d, 2C, $J_{C–P}$ = 2.2 Hz), 133.4 (d, 2C, $J_{C–P}$ = 18.8 Hz), 133.7 (d, 4C, $J_{C–P}$ = 5.3 Hz), 133.9 (d, 1C, $J_{C–P}$ = 4.8 Hz), 136.3 (d, 2C, $J_{C–P}$ = 10.6 Hz), 141.9 (d, 1C, $J_{C–P}$ = 13.6 Hz), 144.8 (1C), 164.1 (1C), 167.1 (1C), 173.3 (1C); ^{31}P NMR ($CDCl_3$, 162 MHz) δ –6.21 (t, J = 6.9 Hz); IR (KBr, cm^{-1}) 698, 1094, 1117, 1433, 1535, 1545, 1647, 1697, 2924, 3289; HRMS (ESI$^+$) *m*/*z* 810.3146 ([M+Na]$^+$, $C_{40}H_{50}N_7NaO_6PS^+$ requires 810.3173).

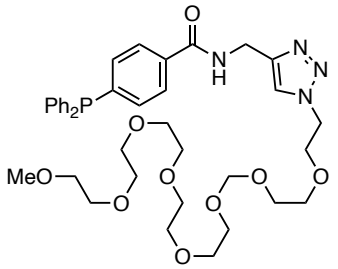
1-(4-(2-(2-(6-Chlorohexyloxy)ethoxy)ethylaminocarbonyl)benzyl)-4-(4-diphenylphosphinobenzoylaminomethyl)-1*H*-1,2,3-triazole (**3h**)



Colorless solid; TLC R_f 0.32 (EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.29–1.37 (m, 2H), 1.37–1.45 (m, 2H), 1.56 (tt, 2H, J = 7.1, 7.1 Hz), 1.73 (tt, 2H, J = 7.1, 7.1 Hz), 3.44 (t, 2H, J = 6.7 Hz), 3.50 (t, 2H, J = 6.7 Hz), 3.56–3.59 (m, 2H), 3.62–3.69 (m, 6H), 4.47 (d, 2H, J = 5.6 Hz), 5.52 (s, 2H), 6.75–6.81 (br t, 1H), 7.10 (t, 1H,

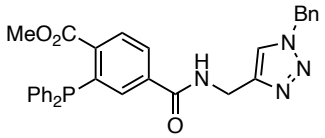
J = 5.6 Hz), 7.26–7.39 (m, 14H), 7.56 (s, 1H), 7.69–7.74 (m, 2H), 7.75–7.79 (AA'BB', 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 25.3 (1C), 26.6 (1C), 29.4 (1C), 32.4 (1C), 35.4 (1C), 39.7 (1C), 45.0 (1C), 53.7 (1C), 69.6 (1C), 70.0 (1C), 70.2 (1C), 71.2 (1C), 122.4 (1C), 126.9 (d, 2C, $J_{C–P}$ = 6.5 Hz), 127.8 (2C), 128.1 (2C), 128.6 (d, 4C, $J_{C–P}$ = 7.0 Hz), 129.1 (2C), 133.5 (d, 2C, $J_{C–P}$ = 19.1 Hz), 133.80 (1C), 133.84 (d, 4C, $J_{C–P}$ = 19.7 Hz), 135.0 (1C), 136.2 (d, 2C, $J_{C–P}$ = 10.2 Hz), 137.7 (1C), 142.4 (d, 1C, $J_{C–P}$ = 13.7 Hz), 145.1 (1C), 166.6 (1C), 167.1 (1C); ^{31}P NMR ($CDCl_3$, 162 MHz) δ –6.3 to –5.9 (m); IR (KBr, cm^{-1}) 696, 745, 1092, 1117, 1304, 1433, 1541, 1643; HRMS (ESI$^+$) m/z 748.2763 ([M+Na]$^+$, $C_{40}H_{45}{}^{35}ClN_5NaO_4P^+$ requires 748.2790).

1-(2-(2-(2-(2-(2-(2-(2-Methoxyethoxy)ethoxy)ethoxy)ethoxy)ethoxy)ethoxy)ethoxy)ethyl)-4-(4-diphenylphosphinobenzoylaminomethyl)-1*H*-1,2,3-triazole (**3i**)



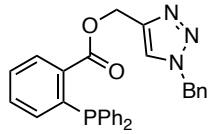
Colorless oil; TLC R_f 0.31 (CH_2Cl_2/MeOH = 9/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.37 (s, 3H), 3.51–3.65 (m, 28H), 3.86 (t, 2H, J = 5.1 Hz), 4.52 (t, 2H, J = 5.1 Hz), 4.70 (d, 2H, J = 5.6 Hz), 7.27–7.39 (m, 12H), 7.75–7.79 (m, 2H), 7.81 (s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 35.4 (1C), 50.2 (1C), 50.7 (1C), 59.0 (1C), 69.3 (1C), 70.3–70.5 (m, 12C), 71.8 (1C), 123.5 (1C), 127.0 (d, 2C, $J_{C–P}$ = 6.5 Hz), 128.6 (d, 4C, $J_{C–P}$ = 7.2 Hz), 129.0 (2C), 133.4 (d, 2C, $J_{C–P}$ = 19.1 Hz), 133.8 (d, 4C, $J_{C–P}$ = 19.8 Hz), 134.0 (1C), 136.2 (d, 2C, $J_{C–P}$ = 10.3 Hz), 142.1 (d, 1C, $J_{C–P}$ = 13.6 Hz), 144.4 (1C),167.1 (1C);^{31}P NMR ($CDCl_3$, 162 MHz) δ –6.3 to –5.9 (m); IR (KBr, cm^{-1}) 698, 746, 1107, 1298, 1350, 1435, 1479, 1533, 1655, 2872; HRMS (ESI$^+$) m/z 775.3444 ([M+Na]$^+$, $C_{39}H_{53}N_4NaO_9P^+$ requires 775.3442).

N-((1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl)-4-(methoxycarbonyl)-3-(diphenylphosphino)benzamide (**3j**)



Yellow solid; Mp 164–171 ºC; TLC R_f 0.35 (CH_2Cl_2/EtOAc = 2/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.74 (s, 3H), 4.55 (d, 2H, J = 5.4 Hz), 5.49 (s, 2H), 6.55 (t, 1H, J = 5.4 Hz), 7.22–7.41 (m, 16H), 7.44 (s, 1H), 7.77 (dd, 1H, J = 8.2, 1.7 Hz), 8.07 (dd, 1H, J = 8.1, 3.6 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 35.4 (1C), 52.3 (1C), 54.2 (1C), 122.1 (1C), 126.8 (1C), 128.1 (2C), 128.7 (d, 4C, $J_{C–P}$ = 7.3 Hz), 128.9 (1C), 129.0 (2C), 129.2 (2C), 130.9 (d, 1C, $J_{C–P}$ = 1.8 Hz), 132.4 (1C), 133.8 (d, 4C, $J_{C–P}$ = 20.7 Hz), 134.4 (1C), 136.7 (1C), 136.8 (d, 1C, $J_{C–P}$ = 18.9 Hz), 137.1 (d, 2C, $J_{C–P}$ = 10.6 Hz), 141.7 (d, 1C, $J_{C–P}$ = 29.5 Hz), 144.4 (1C), 166.3 (1C), 166.6 (d, 1C, $J_{C–P}$ = 2.6 Hz) ^{31}P NMR ($CDCl_3$, 162 MHz) δ –4.5 (s); IR (KBr, cm^{-1}) 698, 745, 1254, 1273, 1288, 1433, 1531, 1645, 1717; HRMS (ESI$^+$) m/z 535.1882 ([M+H]$^+$, $C_{31}H_{28}N_4O_3P^+$ requires 535.1894).

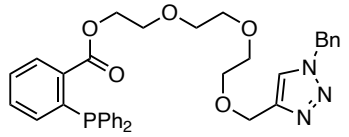
(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl 2-(diphenylphosphino)benzoate (**3k**)



Colorless solid; TLC R_f 0.70 (*n*-hexane/EtOAc = 1/2); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.29 (s, 2H), 5.45 (s, 2H), 6.86–6.93 (m, 1H), 7.17–7.42 (m, 18H), 8.02–8.08 (m, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 54.1 (1C), 58.3 (1C), 123.9 (1C), 128.0 (2C), 128.2 (1C), 128.4 (d, 4C, $J_{C–P}$ = 7.3 Hz), 128.6 (2C), 128.7 (1C), 129.1 (2C), 130.9 (d, 1C, $J_{C–P}$ = 1.9 Hz), 132.2 (1C), 133.5 (d, 1C, $J_{C–P}$ = 18.3 Hz), 133.9 (d, 4C, $J_{C–P}$ = 20.5 Hz), 134.2 (1C), 134.5 (1C), 137.8 (d, 2C, $J_{C–P}$ = 11.0 Hz), 140.7 (d, 1C, $J_{C–P}$ = 26.8 Hz), 143.2 (1C), 166.5 (d, 1C, $J_{C–P}$ =

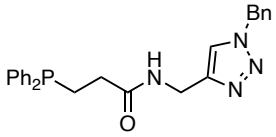
2.5 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ –4.7 (s); IR (KBr, cm^{-1}) 698, 727, 746, 1049, 1103, 1138, 1252, 1267, 1433, 1713; HRMS (ESI^+) *m/z* 500.1482 ($[M+Na]^+$, $C_{29}H_{24}N_3NaO_2P^+$ requires 500.1498).

2-(2-(2-(2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methoxy)ethoxy)ethoxy)ethyl 2-(diphenylphosphino)benzoate (**3l**)



Colorless oil; TLC R_f 0.48 (EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.54–3.68 (m, 10H), 4.29 (t, 2H, *J* = 5.0 Hz), 4.64 (s, 2H), 5.49 (s, 2H), 6.90–6.95 (m, 1H), 7.21–7.41 (m, 17H), 7.46 (s, 1H), 8.04–8.09 (m, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 54.1 (1C), 64.2 (1C), 64.7 (1C), 68.9 (1C), 69.7 (1C), 70.49 (1C), 70.51 (1C+1C, two signals overlapped), 122.5 (1C), 128.1 (2C), 128.2 (1C), 128.5 (d, 4C, $J_{C–P}$ = 7.2 Hz), 128.6 (2C), 128.7 (1C), 129.1 (2C), 130.8 (d, 1C, $J_{C–P}$ = 2.5 Hz), 132.0 (1C), 133.9 (d, 4C, $J_{C–P}$ = 20.7 Hz), 134.2 (d, 1C, $J_{C–P}$ = 19.0 Hz), 134.3 (1C), 134.6 (1C), 137.9 (d, 2C, $J_{C–P}$ = 11.0 Hz), 140.5 (d, 1C, $J_{C–P}$ = 26.9 Hz), 145.6 (1C), 166.6 (d, 1C, $J_{C–P}$ = 1.8 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ –5.34 (s); IR (KBr, cm^{-1}) 698, 748, 1103, 1254, 1267, 1715; HRMS (ESI^+) *m/z* 632.2293 ($[M+Na]^+$, $C_{35}H_{36}N_3NaO_5P^+$ requires 632.2285).

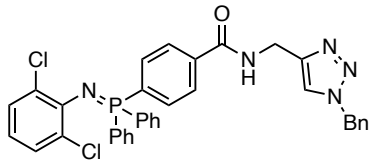
N-((1-Benzyl-1*H*-1,2,3-triazol-4-yl)methyl)-3-(diphenylphosphino)propionamide (**3m**)



Colorless oil; TLC R_f 0.29 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.20–2.27 (m, 2H), 2.31–2.37 (m, 2H), 4.42 (d, 2H, *J* = 5.7 Hz), 5.46 (s, 2H), 6.30–6.42 (br, 1H), 7.24–7.40 (m, 15H), 7.45 (s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 23.4 (d, 1C, $J_{C–P}$ = 12.0 Hz), 32.5 (d, 1C, $J_{C–P}$ = 18.2 Hz), 34.9 (1C), 54.2 (1C), 122.2 (1C), 128.1 (2C), 128.5 (d, 4C, $J_{C–P}$ = 6.6 Hz), 128.7 (2C), 128.8 (1C), 129.1 (2C), 132.7 (d, 4C, $J_{C–P}$ = 18.9 Hz), 134.4(1C), 137.8 (d, 2C, $J_{C–P}$ = 12.7 Hz), 145.0 (1C), 172.2 (d, 1C, $J_{C–P}$ = 13.5 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ –16.5 to –16.1 (m); IR (KBr, cm^{-1}) 1246, 1433, 1541, 1647, 3066; HRMS (ESI^+) *m/z* 429.1831 ($[M+H]^+$, $C_{25}H_{26}N_4OP^+$ requires 429.1839).

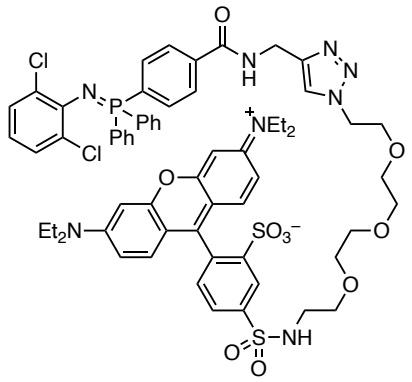
2,6-Dichloro-*N*-(4-((1-benzyl-1*H*-1,2,3-triazol-4-

yl)methyl)carbamoylphenyl)diphenylphosphoranylidene)aniline (**4a**)



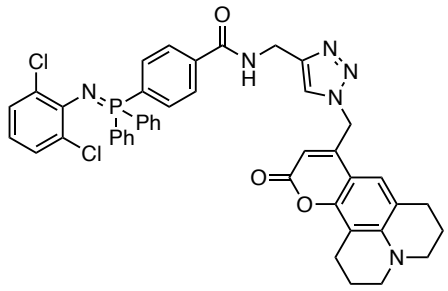
Colorless solid; Mp 193–198 ºC; TLC R_f 0.57 (EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.66 (d, 2H, *J* = 5.4 Hz), 5.47 (s, 2H), 6.52–6.58 (m, 1H), 7.08–7.13 (m, 2H), 7.17 (t, 1H, *J* = 5.4 Hz), 7.23–7.32 (m, 2H), 7.33–7.39 (m, 3H), 7.39–7.48 (m, 4H), 7.48–7.55 (m, 3H), 7.66–7.77 (m, 4H), 7.78–7.85 (m, 4H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 35.4 (1C), 54.2 (1C), 119.0 (d, 1C, $J_{C–P}$ = 2.6 Hz), 122.3 (1C), 126.8 (d, 2C, $J_{C–P}$ = 12.3 Hz), 127.8 (d, 2C, $J_{C–P}$ = 1.3 Hz), 128.1 (2C), 128.3 (d, 4C, $J_{C–P}$ = 12.4 Hz), 128.8 (1C), 129.1 (2C), 131.39 (d, 2C, $J_{C–P}$ = 104.2 Hz), 131.43 (d, 2C, $J_{C–P}$ = 9.0 Hz), 131.6 (d, 2C, $J_{C–P}$ = 2.6 Hz), 132.6 (d, 4C, $J_{C–P}$ = 10.1 Hz), 132.8 (d, 2C, $J_{C–P}$ = 10.1 Hz), 134.3 (1C), 136.2 (d, 1C, $J_{C–P}$ = 102.0 Hz),136.5 (d, 1C, $J_{C–P}$ = 2.7 Hz), 144.3 (1C), 144.7 (1C), 166.6 (1C); ^{31}P NMR ($CDCl_3$, 162 MHz) δ –0.54 (s); IR (KBr, cm^{-1}) 719, 1111, 1308, 1471, 1539, 1652; HRMS (ESI^+) *m/z* 658.1278 ($[M+Na]^+$, $C_{35}H_{28}{}^{35}Cl_2N_5NaOP^+$ requires 658.1301).

2,6-Dichloro-*N*-(4-((1-(2-(2-(2-(2-(4-(3,6-bis(diethylamino)xanthylium-9-yl)-3-sulfonatobenzenesulfonamido)ethoxy)ethoxy)ethoxy)ethyl)-1*H*-1,2,3-triazol-4-yl)methyl)carbamoylphenyl)diphenylphosphoranylidene)aniline (**4b**)



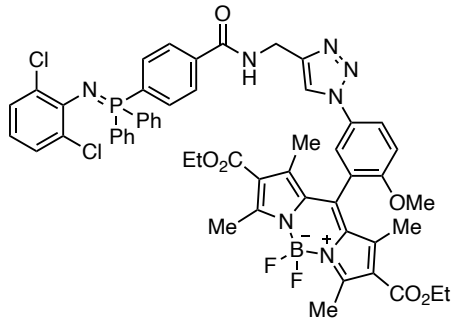
Purple solid; TLC R_f 0.21 (CH_2Cl_2/MeOH = 9/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.23 (t, 12H, J = 7.0 Hz), 3.23–3.32 (br q, 2H), 3.38–3.73 (m, 18H), 3.90 (t, 2H, J = 4.5 Hz), 4.38–4.48 (br t, 2H), 4.67 (d, 2H, J = 4.7 Hz), 6.46–6.58 (m, 3H), 6.72 (d, 2H, J = 8.7 Hz), 6.95 (t, 1H, J = 5.4 Hz), 7.02–7.14 (m, 4H), 7.17 (d, 1H, J = 7.8 Hz), 7.31–7.44 (m, 4H), 7.44–7.51 (m, 2H), 7.63–7.78 (m, 6H), 7.90 (d, 2H, J = 6.2 Hz), 7.95–8.05 (m, 2H), 8.18–8.27 (br, 1H), 8.86 (s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 12.5 (4C), 35.4 (1C), 43.1 (1C), 45.7 (4C), 50.2 (1C), 69.3 (1C+1C, two signals overlapped), 69.9 (1C), 70.49 (1C), 70.54 (1C), 70.7 (1C), 95.5 (2C), 113.5 (2C), 114.2 (2C), 118.8 (1C), 126.9 (2C), 127.1 (1C), 127.3 (d, 2C, $J_{C–P}$ = 12.5 Hz), 127.7 (2C), 128.3 (d, 4C, $J_{C–P}$ = 12.5 Hz), 129.0 (1C), 129.7 (1C), 131.5 (1C), 132.0 (d, 2C, $J_{C–P}$ = 111.4 Hz), 132.6 (d, 4C, $J_{C–P}$ = 9.7 Hz), 133.2 (1C), 133.5 (1C), 136.8 (1C), 142.4 (1C), 147.9 (1C), 155.4 (2C), 157.7 (2C), 158.6 (1C), 166.0 (1C): Some signals were not observed clearly; ^{31}P NMR ($CDCl_3$, 162 MHz) δ –0.4 to 0.2 (m); IR (KBr, cm^{-1}) 1076, 1134, 1180, 1246, 1275, 1339, 1416, 1466, 1483, 1591; HRMS (ESI$^+$) *m*/*z* 1283.3477 ([M+Na]$^+$, $C_{63}H_{67}{}^{35}Cl_2N_8NaO_{10}PS_2^+$ requires 1283.3428).

2,6-Dichloro-*N*-(4-((1-((11-oxo-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-pyrano[2,3-*f*]pyrido[3,2,1-*ij*]quinolin-9-yl)methyl)-1*H*-1,2,3-triazol-4-yl)methyl)carbamoylphenyl)diphenylphosphoranylidene)aniline (**4c**)



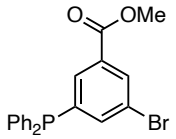
Yellow solid; TLC R_f 0.34 (CH_2Cl_2/MeOH = 9/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.89–1.98 (m, 4H), 2.71 (t, 2H, J = 6.1 Hz), 2.84 (t, 2H, J = 6.2 Hz), 3.21–3.29 (m, 4H), 4.69 (d, 2H, J = 5.6 Hz), 5.53 (s, 2H), 5.69 (s, 1H), 6.51–6.57 (m, 1H), 6.95 (s, 1H), 7.07–7.12 (m, 2H), 7.23 (t, 1H, J = 5.6 Hz), 7.38–7.44 (m, 4H), 7.47–7.53 (m, 2H), 7.64 (s, 1H), 7.68–7.75 (m, 4H), 7.78–7.85 (m, 4H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 20.3 (1C), 20.4 (1C), 21.1 (1C), 27.7 (1C), 35.4 (1C), 49.4 (1C), 49.9 (1C), 50.3 (1C), 105.7 (1C), 106.9 (1C), 107.2 (1C), 118.6 (1C), 119.1 (d, 1C, $J_{C–P}$ = 2.6 Hz), 120.4 (1C), 122.9 (1C), 126.8 (d, 2C, $J_{C–P}$ = 12.3 Hz), 127.8 (2C), 128.3 (d, 4C, $J_{C–P}$ = 12.3 Hz), 131.3 (d, 2C, $J_{C–P}$ = 103.8 Hz), 131.5 (d, 2C, $J_{C–P}$ = 8.9 Hz), 131.7 (d, 2C, $J_{C–P}$ = 2.7 Hz), 132.5 (d, 4C, $J_{C–P}$ = 10.1 Hz), 132.8 (d, 2C, $J_{C–P}$ = 10.1 Hz), 136.2 (d, 1C, $J_{C–P}$ = 101.9 Hz) 136.4 (d, 1C, $J_{C–P}$ = 2.8 Hz), 144.2 (1C), 145.1 (1C), 146.4 (1C), 148.0 (1C), 151.4 (1C), 161.7 (1C), 166.7 (1C); ^{31}P NMR ($CDCl_3$, 162 MHz) δ –0.8 to –0.2 (m); IR (KBr, cm^{-1}) 1113, 1182, 1312, 1437, 1483, 1526, 1555, 1601, 1616, 1705; HRMS (ESI$^+$) *m*/*z* 821.1955 ([M+Na]$^+$, $C_{44}H_{37}{}^{35}Cl_2N_6NaO_3P^+$ requires 821.1934).

2,6-Dichloro-*N*-(4-((1-(2,6-bis(ethoxycarbonyl)-4,4-difluoro-1,3,5,7-tetramethyl-3a,4a-diaza-4-bora-s-indacen-8-yl)-4-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)methyl)carbamoylphenyl)diphenylphosphorany lidene)aniline (**4d**)



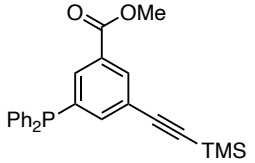
Orange solid; TLC R_f 0.86 (EtOAc); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.32 (t, 6H, J = 7.1 Hz), 1.80 (s, 6H), 2.84 (s, 6H), 3.86 (s, 3H), 4.28 (q, 4H, J = 7.1 Hz), 4.76 (d, 2H, J = 5.7 Hz), 6.52–6.58 (m, 1H), 7.07–7.18 (m, 4H), 7.38–7.45 (m, 4H), 7.48–7.54 (m, 2H), 7.56 (d, 1H, J = 2.7 Hz), 7.67–7.76 (m, 4H), 7.80–7.87 (m, 4H), 7.88 (dd, 1H, J = 8.9, 2.7 Hz), 8.03 (s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 13.2 (2C), 14.3 (2C), 15.1 (2C), 35.4 (1C), 56.3 (1C), 60.3 (2C), 112.3 (1C), 119.1 (1C), 120.7 (1C), 121.7 (1C), 122.5 (1C), 123.4 (1C), 124.7 (1C), 126.8 (d, 2C, $J_{C–P}$ = 12.6 Hz), 127.8 (d, 2C, $J_{C–P}$ = 1.9 Hz), 128.4 (d, 4C, $J_{C–P}$ = 12.3 Hz), 131.26 (2C), 131.28 (d, 2C, $J_{C–P}$ = 103.8 Hz), 131.456 (1C), 131.458 (d, 4C, $J_{C–P}$ = 12.3 Hz) 131.7 (d, 2C, $J_{C–P}$ = 2.3 Hz), 132.6 (d, 4C, $J_{C–P}$ = 10.1 Hz), 132.9 (d, 2C, $J_{C–P}$ = 10.2 Hz), 136.3 (d, 2C, $J_{C–P}$ = 8.8 Hz), 136.4 (d, 1C, $J_{C–P}$ = 102.1 Hz), 140.4 (1C), 144.2 (1C), 145.4 (1C), 146.7 (2C), 156.6 (1C), 164.2 (2C), 166.8 (1C); ^{31}P NMR ($CDCl_3$, 162 MHz) δ –0.2 to 0.7 (m); IR (KBr, cm^{-1}) 1009, 1036, 1111, 1184, 1256, 1314, 1437, 1510, 1528, 1705; HRMS (ESI$^+$) *m*/*z* 1064.2856 ([M+Na]$^+$, $C_{54}H_{49}B^{35}Cl_2F_2N_7NaO_6P^+$ requires 1064.2812).

Methyl 3-bromo-5-(diphenylphosphino)benzoate (**5**)



Colorless oil; TLC R_f 0.31 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.87 (s, 3H), 7.27–7.41 (m, 10H), 7.49–7.53 (m, 1H), 7.94 (ddd, 1H, J = 7.5, 1.5, 1.5 Hz), 8.12 (dd, 1H, J = 1.5, 1.5 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 52.5 (1C), 123.0 (d, 1C, $J_{C–P}$ = 5.1 Hz), 128.8 (d, 4C, $J_{C–P}$ = 7.3 Hz), 129.3 (2C), 132.0 (d, 1C, $J_{C–P}$ = 7.1 Hz), 132.6 (1C), 133.1 (d, 2C, $J_{C–P}$ = 22.9 Hz), 133.8 (d, 4C, $J_{C–P}$ = 20.1 Hz), 135.6 (d, 1C, $J_{C–P}$ = 10.9 Hz), 139.9 (d, 1C, $J_{C–P}$ = 17.2 Hz), 141.4 (d, 1C, $J_{C–P}$ = 18.1 Hz), 165.5 (1C); ^{31}P NMR ($CDCl_3$, 162 MHz) δ –5.5 to –5.1 (m); IR (KBr, cm^{-1}) 696, 742, 766, 1132, 1273, 1435, 1557, 1728; HRMS (ESI$^+$) *m*/*z* 420.9967 ([M+Na]$^+$, $C_{20}H_{16}{}^{79}BrNaO_2P^+$ requires 420.9963).

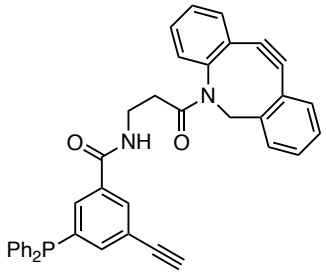
Methyl 3-(trimethylsilylethynyl)-5-(diphenylphosphino)benzoate (**7**)



Colorless solid; Mp 76–78 ºC; TLC R_f 0.31 (*n*-hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.22 (s, 9H), 3.86 (s, 3H), 7.27–7.39 (m, 10H), 7.56 (ddd, 1H, J = 7.0, 1.5, 1.5 Hz), 7.92 (ddd, 1H, J = 7.4, 1.5, 1.5 Hz), 8.09 (dd, 1H, J = 1.5, 1.5 Hz); ^{13}C NMR ($CDCl_3$, 126 MHz) δ –0.19 (3C), 52.3 (1C), 96.0 (1C), 103.6 (1C), 123.9 (d, 1C, $J_{C–P}$ = 7.1 Hz), 128.7 (d, 4C, $J_{C–P}$ = 7.2 Hz), 129.1 (2C), 130.4 (d, 1C, $J_{C–P}$ = 7.1 Hz), 133.4 (1C), 133.8 (d, 4C, $J_{C–P}$ = 20.1 Hz), 134.3 (d, 2C, $J_{C–P}$ = 20.7 Hz), 135.9 (d, 1C, $J_{C–P}$ = 10.9 Hz), 138.9 (d, 1C, $J_{C–P}$ = 15.3 Hz), 140.5 (d, 1C, $J_{C–P}$ = 19.3 Hz), 166.1 (1C); ^{31}P NMR ($CDCl_3$, 162 MHz) δ –6.1 to –5.7 (m); IR (KBr, cm^{-1}) 696, 745, 845, 1211, 1250, 1290, 1435, 1728; HRMS (ESI$^+$) *m*/*z* 439.1257 ([M+Na]$^+$,

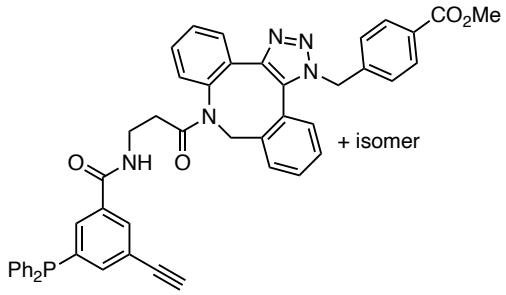
$C_{25}H_{25}NaO_2PSi^+$ requires 439.1254).

N-(3-(5*H*,6*H*-11,12-Didehydrodibenzo[*b*,*f*]azocin-5-yl)-3-oxopropyl)-3-ethynyl-5-(diphenylphosphino)benzamide (**12**)

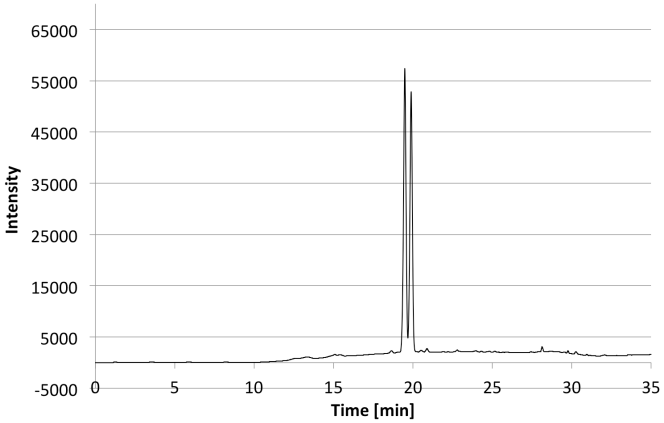


Colorless solid; Mp 120 ºC (decomp.); TLC R_f 0.38 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.05 (ddd, 1H, *J* = 16.7, 7.2, 3.6 Hz), 2.52 (ddd, 1H, *J* = 16.6, 7.9, 3.8 Hz), 3.1 (s, 1H), 3.31–3.39 (m, 1H), 3.48–3.57 (m, 1H), 3.69 (d, 1H, *J* = 13.9 Hz), 5.12 (d, 1H, *J* = 13.9 Hz), 6.67 (t, 1H, *J* = 5.8 Hz), 7.15 (d, 1H, *J* = 7.5 Hz), 7.24–7.40 (m, 16H), 7.45 (ddd, 1H, *J* = 6.4, 1.4, 1.4 Hz), 7.62 (dd, 1H, *J* = 1.4, 1.4 Hz), 7.65–7.69 (m, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 34.6 (1C), 35.9 (1C), 55.5 (1C), 78.5 (1C), 82.6 (1C), 107.6 (1C), 114.9 (1C), 122.6 (1C), 122.71 (d, 1C, $J_{C–P}$ = 5.7 Hz), 122.72 (1C), 125.6 (1C), 127.2 (1C), 127.9 (1C), 128.3 (1C), 128.4 (1C), 128.5 (1C), 128.7 (d, 4C, $J_{C–P}$ = 7.2 Hz), 129.0 (1C), 129.1 (2C), 130.5 (1C), 132.0 (1C), 132.6 (d, 1C, $J_{C–P}$ = 23.8 Hz), 133.8 (dd, 4C, $J_{C–P}$ = 19.9, 2.0 Hz), 134.9 (d, 1C, $J_{C–P}$ = 7.4 Hz), 135.9 (d, 1C, $J_{C–P}$ = 10.9, 1.7 Hz), 139.0 (1C), 139.2 (d, 2C, $J_{C–P}$ = 16.3 Hz), 147.8 (1C), 150.9 (1C), 166.0 (1C), 172.2 (1C); ^{31}P NMR ($CDCl_3$, 162 MHz) δ –6.1 to –5.7 (m); IR (KBr, cm^{-1}) 696, 750, 1398, 1435, 1479, 1506, 1522, 1636, 1647; HRMS (ESI^+) *m*/*z* 589.2057 ($[M+H]^+$, $C_{39}H_{30}N_2O_2P^+$ requires 589.2039).

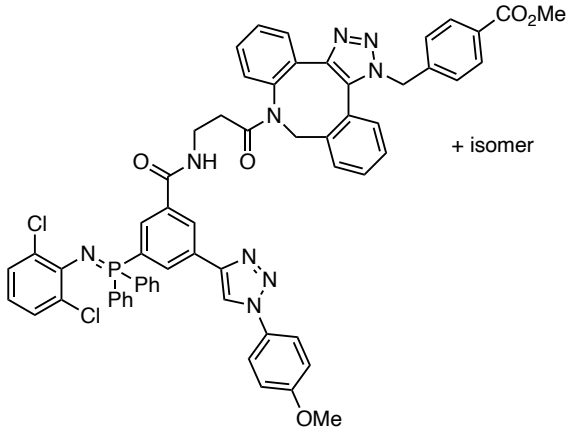
Methyl 4-((8-(3-(3-(diphenylphosphaneyl)-5-ethynylbenzamido)propanoyl)-8,9-dihydro-1*H*-dibenzo[*b*,*f*][1,2,3]triazolo[4,5-*d*]azocin-1-yl)methyl)benzoate (**S1**)



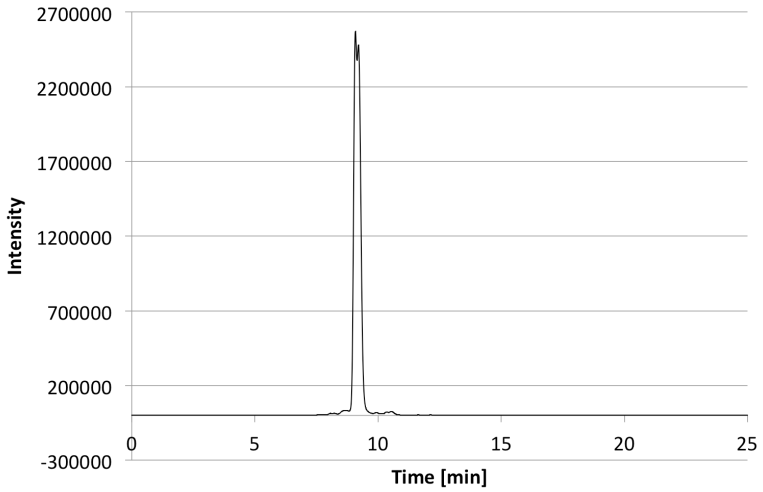
Colorless oil; TLC R_f 0.32 (*n*-hexane/EtOAc = 1/1); HPLC analysis: R*t* = 19.2 min (33%) and 19.6 (59%) [column: Shiseido CAPCELL PAK MG II (4.6 mm i.d. × 250 mm); mobile phase: CH_3CN:H_2O = 40:60 (0−5 min), linear gradient from 40:60 to 99:1 (5−25 min), 99:1 (25−35 min); flow rate: 1.00 mL/min; detection: UV at 254 nm]; ^{31}P NMR ($CDCl_3$, 162 MHz) δ –6.1 to –5.7 (m); IR (KBr, cm^{-1}) 1110, 1286, 1433, 1510, 1651, 1720, 3053; HRMS (ESI^+) *m*/*z* 780.2732 ($[M+H]^+$, $C_{48}H_{39}N_5O_4P^+$ requires 780.2734).
HPLC chart:



Methyl 4-((8-(3-(3-(*N*-(2,6-dichlorophenyl)-*P*,*P*-diphenylphosphorimidoyl)-5-(1-(4-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)benzamido)propanoyl)-8,9-dihydro-1*H*-dibenzo[*b*,*f*][1,2,3]triazolo[4,5-*d*]azocin-1-yl)methyl)benzoate (**13**)



Colorless oil; TLC R_f 0.15 (*n*-hexane/EtOAc = 1/1); HPLC analysis: R*t* = 9.0 min (47%) and 9.2 min (50%) [column: Shiseido CAPCELL PAK MG II (4.6 mm i.d. × 250 mm); mobile phase: MeOH:H_2O = 40:60 (0−5 min), linear gradient from 40:60 to 99:1 (5−10 min), 99:1 (10−25 min); flow rate: 1.00 mL/min; detection: UV at 550 nm]; ^{31}P NMR ($CDCl_3$, 162 MHz) δ –0.2 to 0.6 (m); IR (KBr, cm^{-1}) 1113, 1282, 1435, 1517, 1653, 1718, 3059; HRMS (ESI^+) *m*/*z* 1088.2999 ($[M+H]^+$, $C_{61}H_{49}Cl_2N_9O_5P^+$ requires 1088.2966).
HPLC chart:



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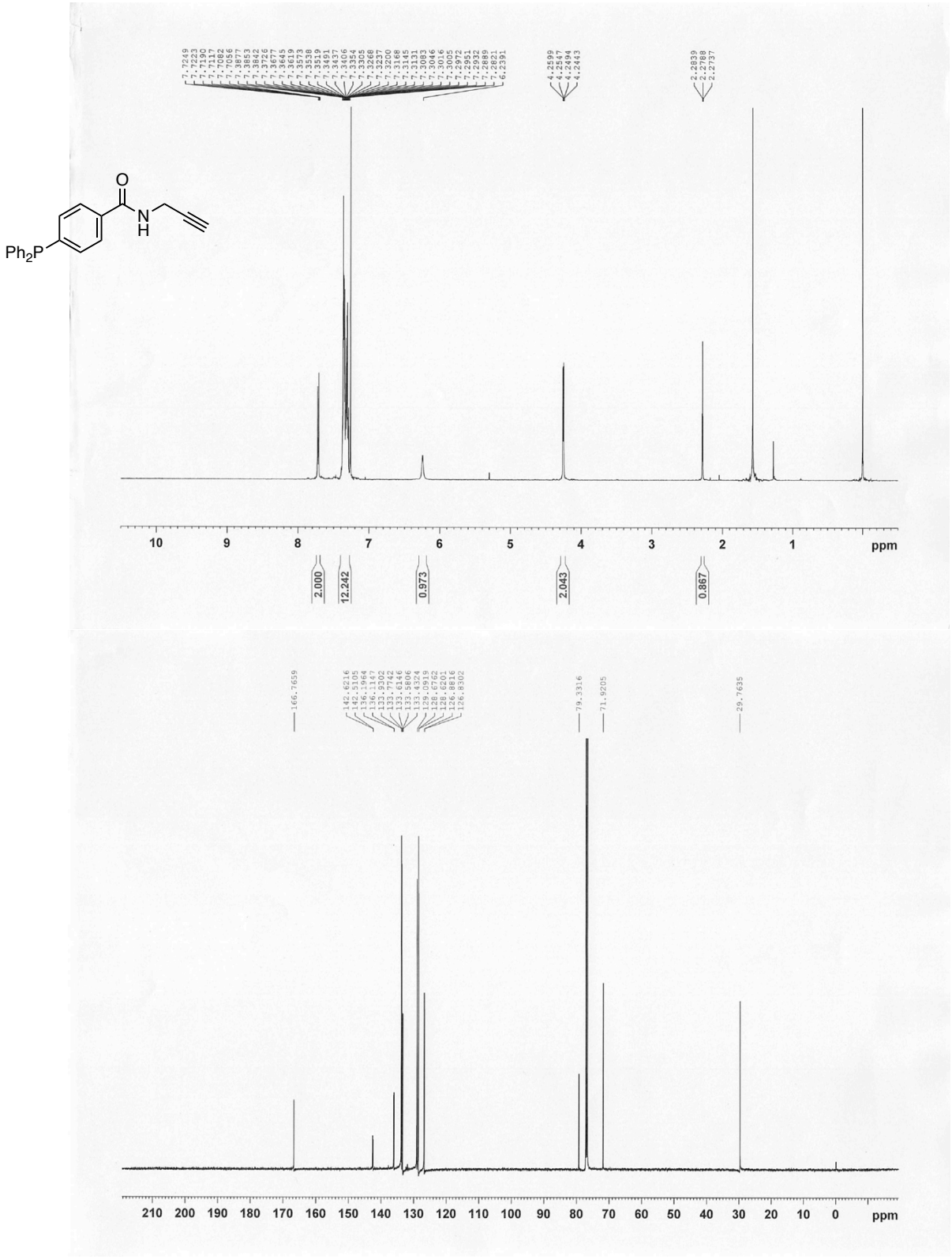
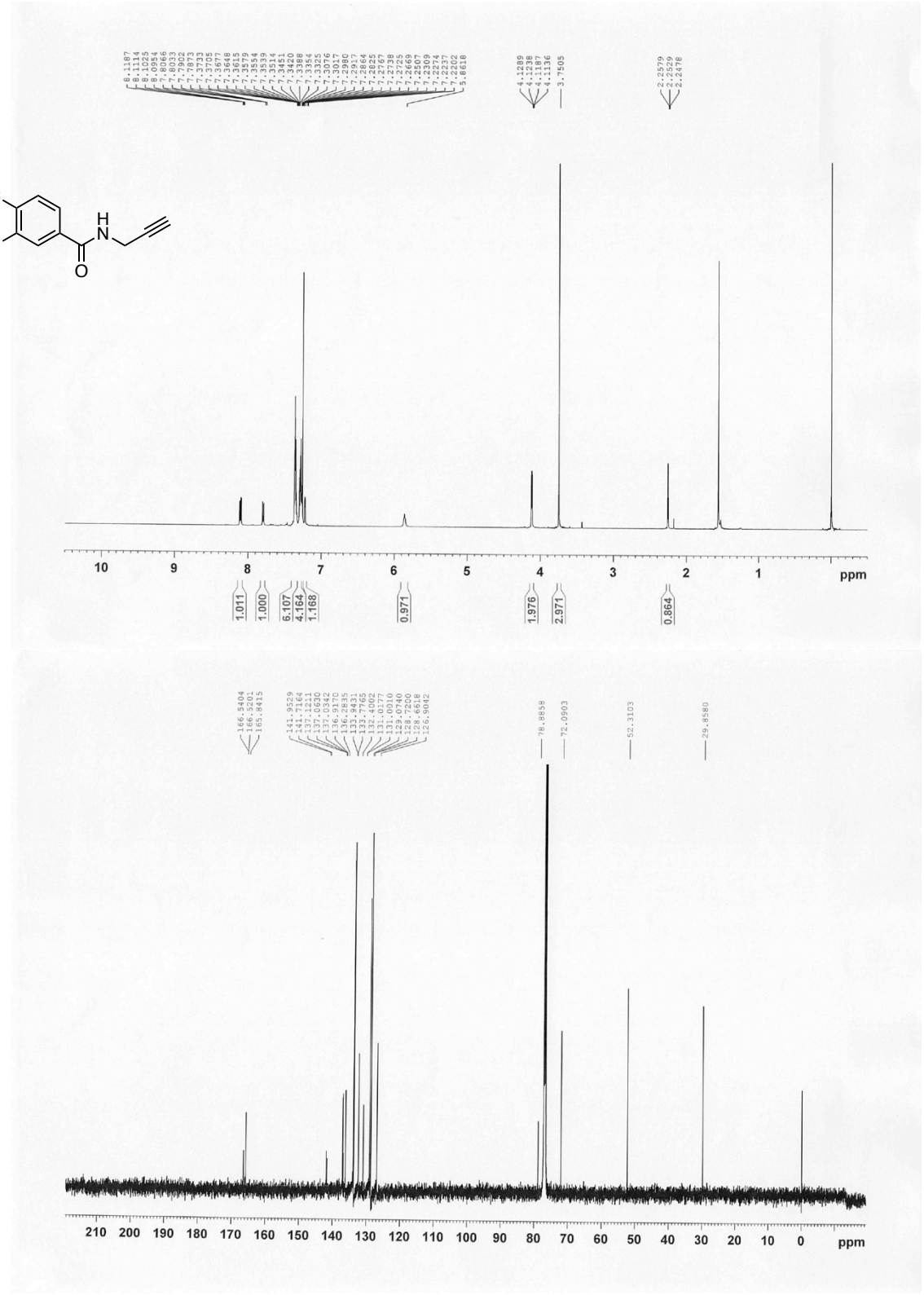
NMR Spectra of New Compounds

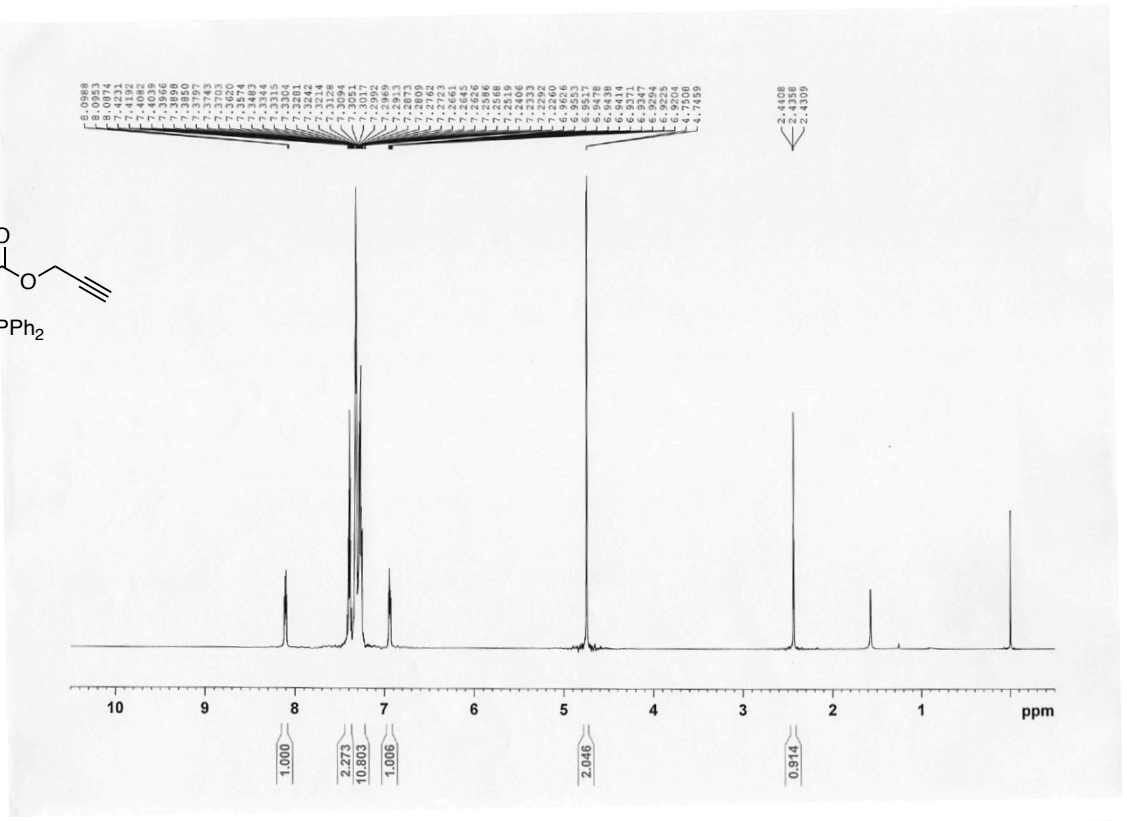
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *N*-(2-propyn-1-yl)-4-(diphenylphosphino)benzamide (**1a**) ($CDCl_3$)

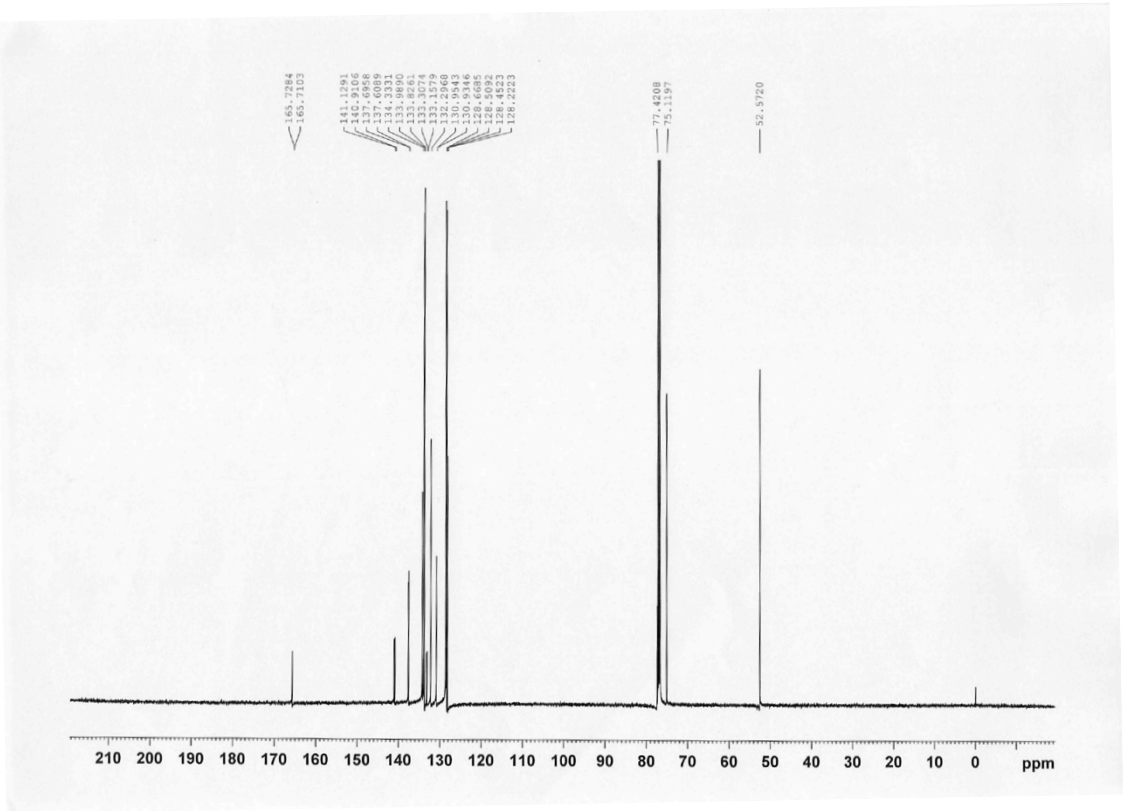


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *N*-(2-propyn-1-yl)-4-(methoxycarbonyl)-3-(diphenylphosphino)benzamide (**1b**) ($CDCl_3$)

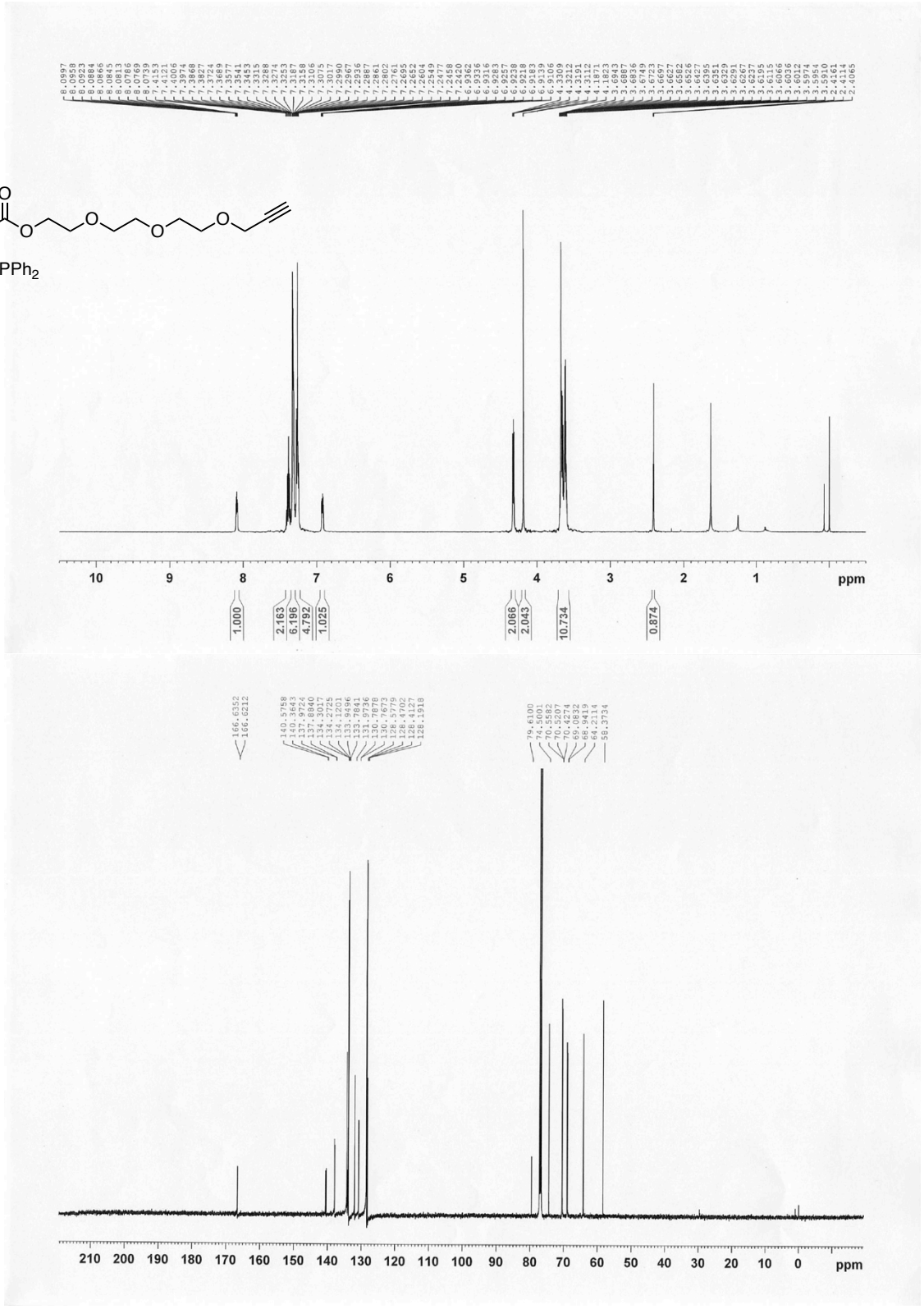


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 2-propyn-1-yl 2-(diphenylphosphino)benzoate (**1c**) ($CDCl_3$)

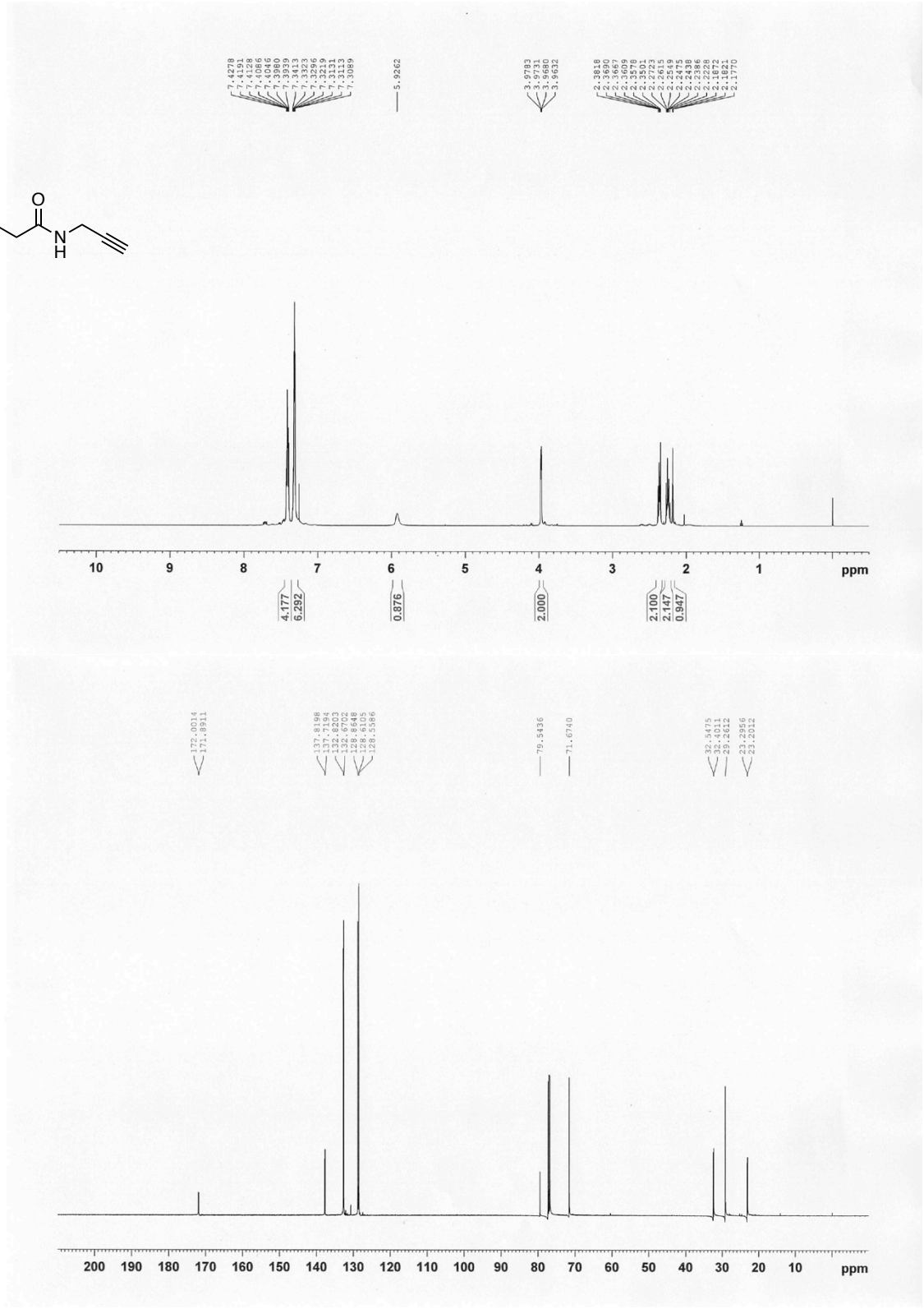




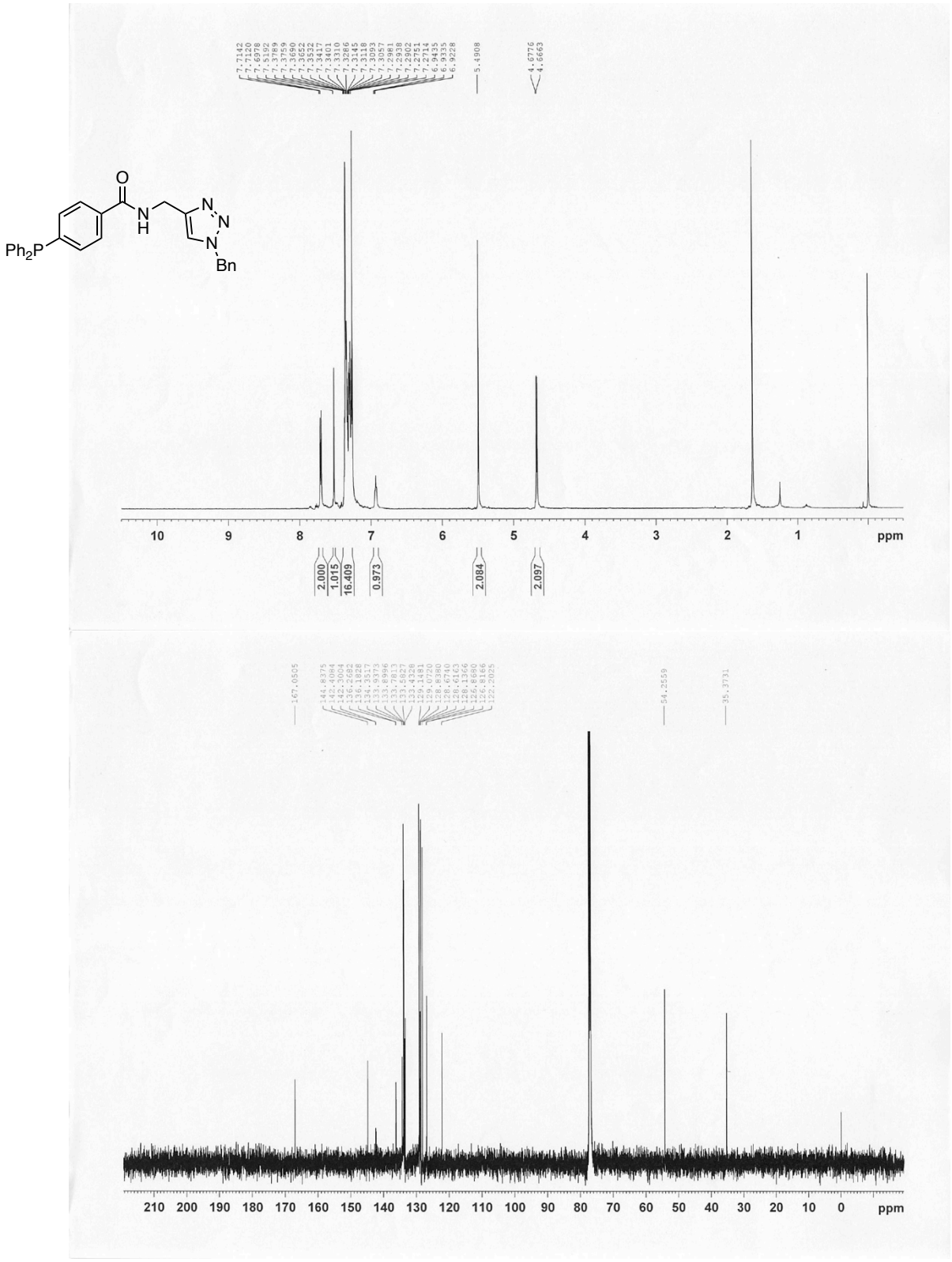
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 2-(2-(2-(2-propynyloxy)ethoxy)ethoxy)ethyl 2-(diphenylphosphino)benzoate (**1d**) ($CDCl_3$)



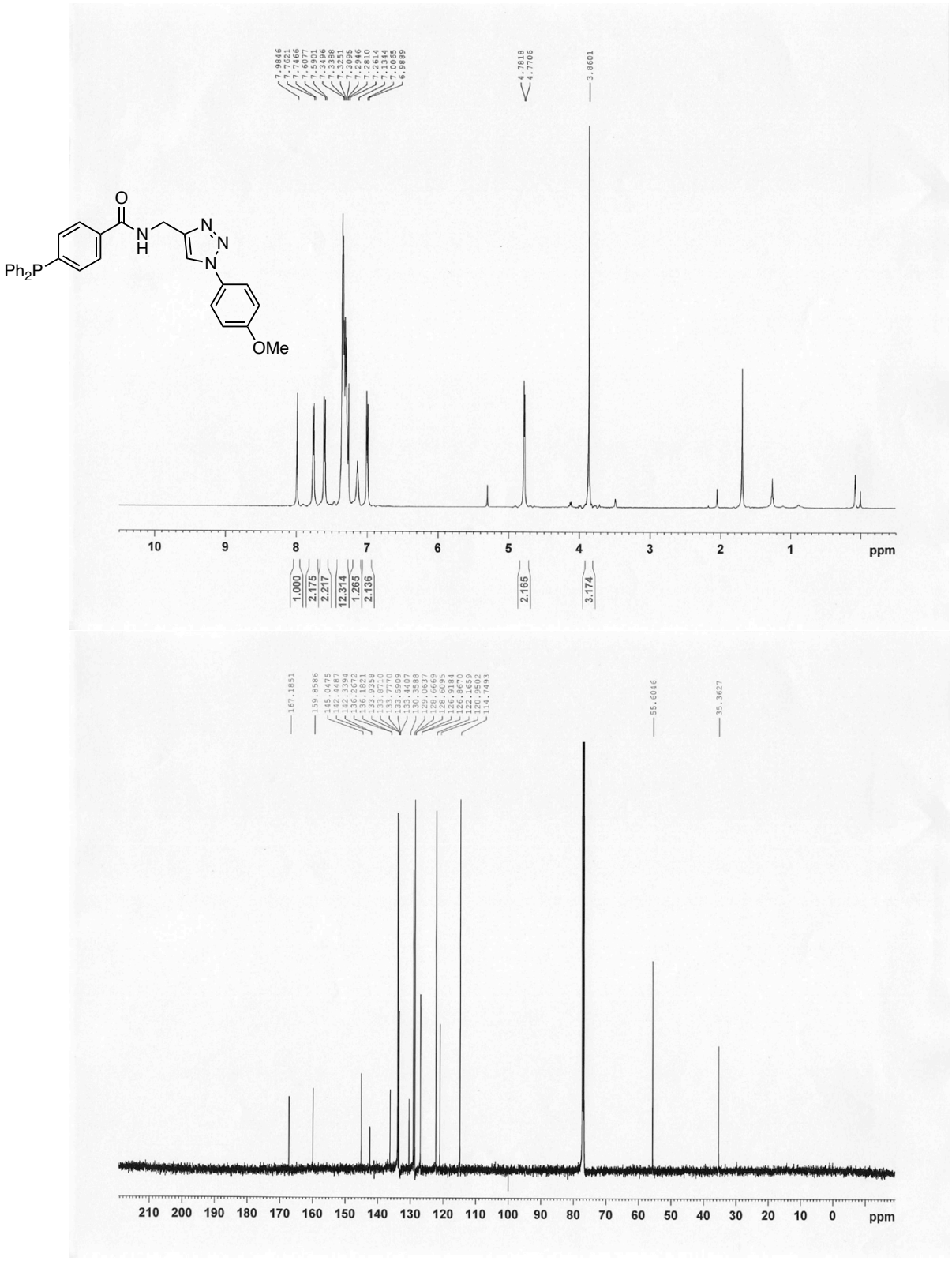
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *N*-(2-propyn-1-yl)-3-(diphenylphosphino)propionamide (**1e**) ($CDCl_3$)



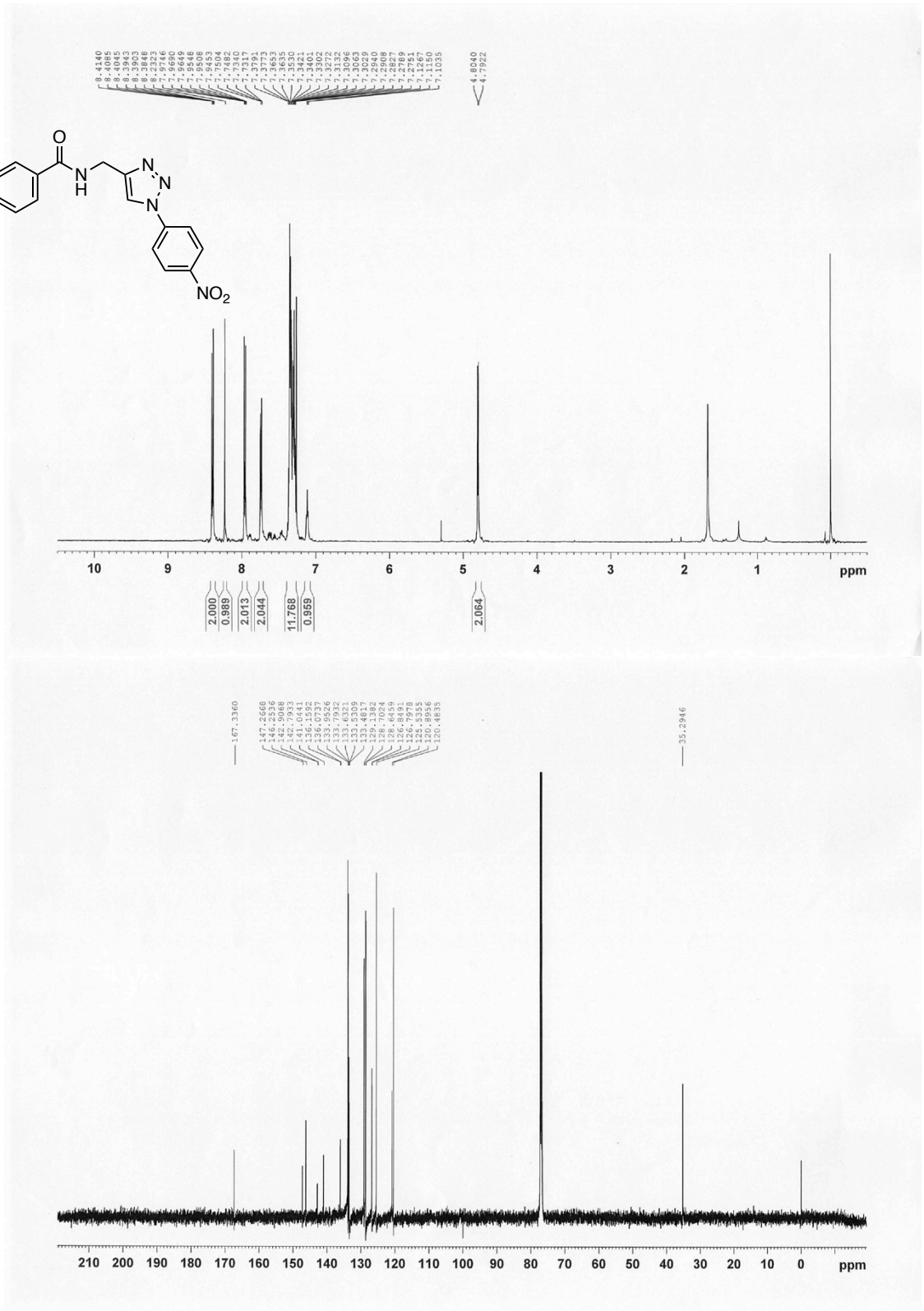
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *N*-((1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl)-4-(diphenylphosphino)benzamide (**3a**) ($CDCl_3$)



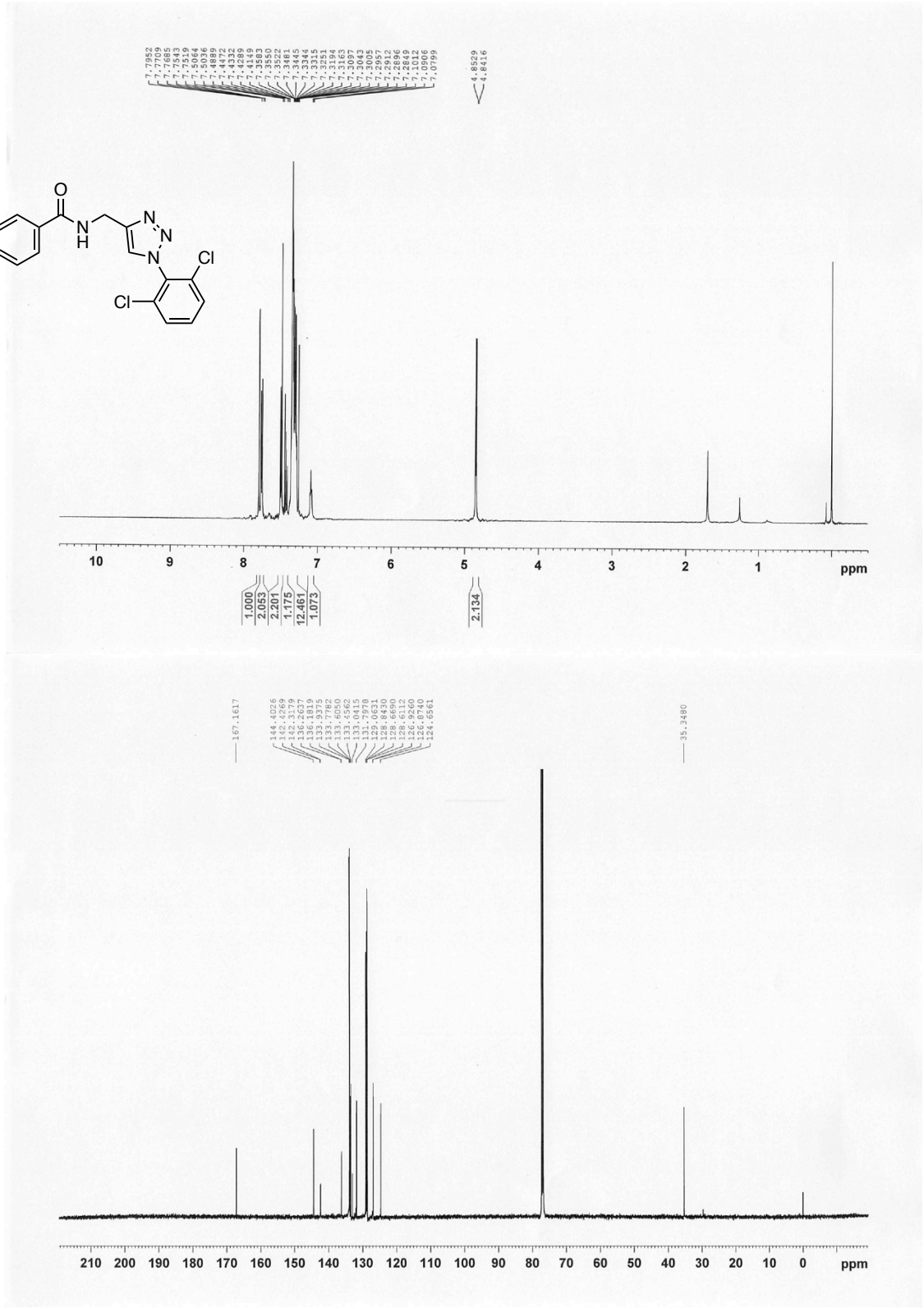
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *N*-((1-(4-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)methyl)-4-(diphenylphosphino)benzamide (**3b**) ($CDCl_3$)



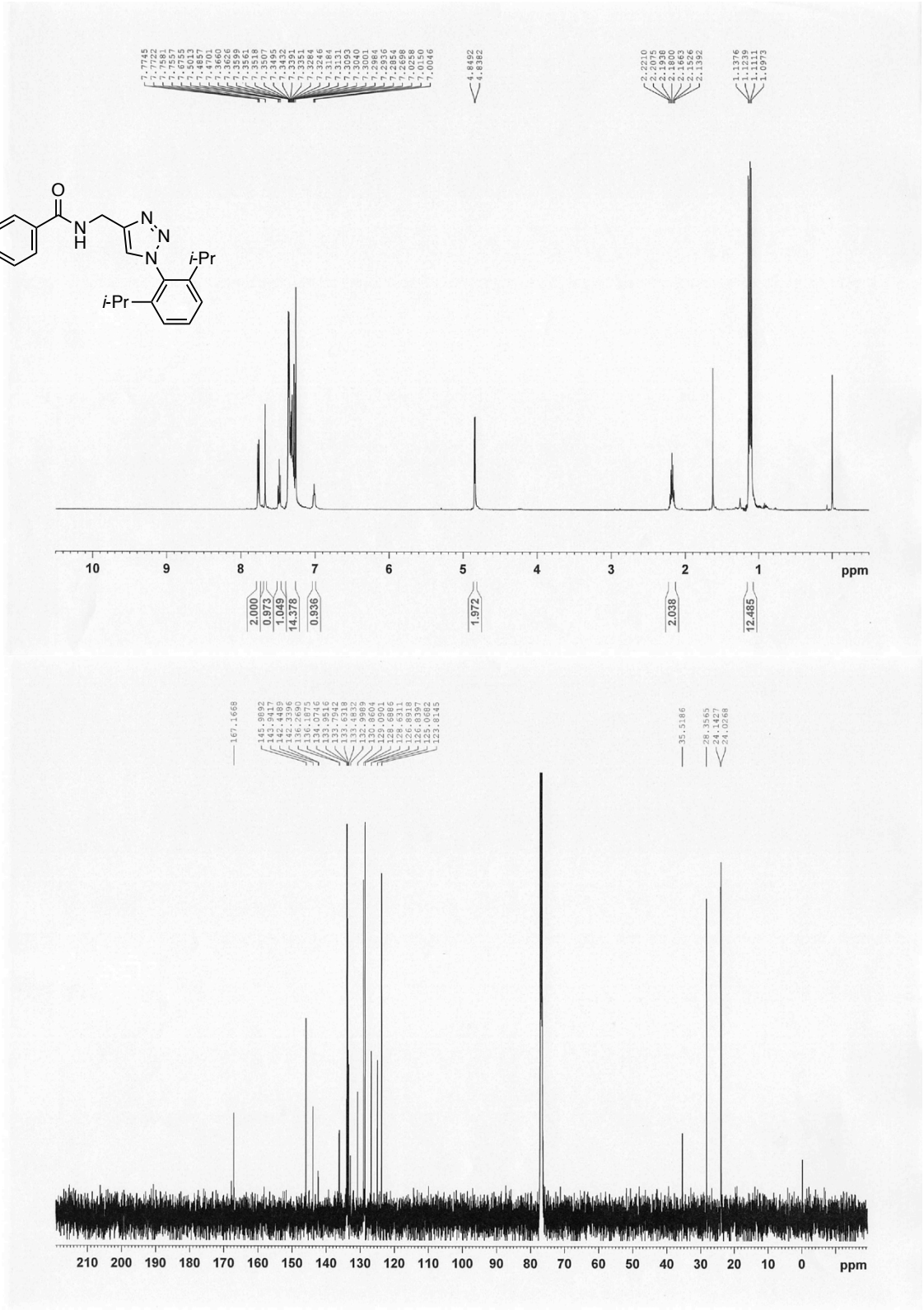
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *N*-((1-(4-nitrophenyl)-1*H*-1,2,3-triazol-4-yl)methyl)-4-(diphenylphosphino)benzamide (**3c**) ($CDCl_3$)



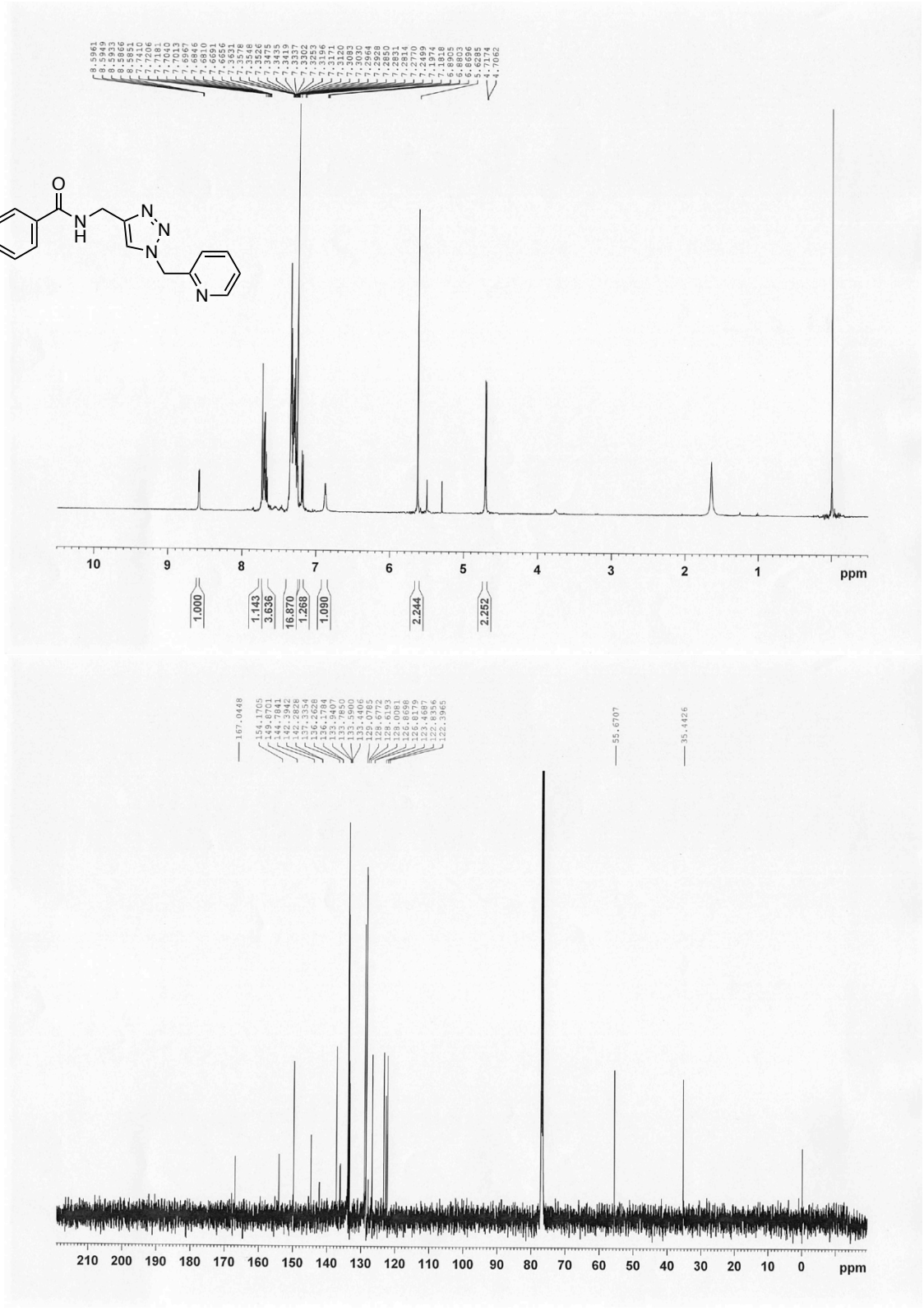
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *N*-((1-(2,6-dichlorophenyl)-1*H*-1,2,3-triazol-4-yl)methyl)-4-(diphenylphosphino)benzamide (**3d**) ($CDCl_3$)



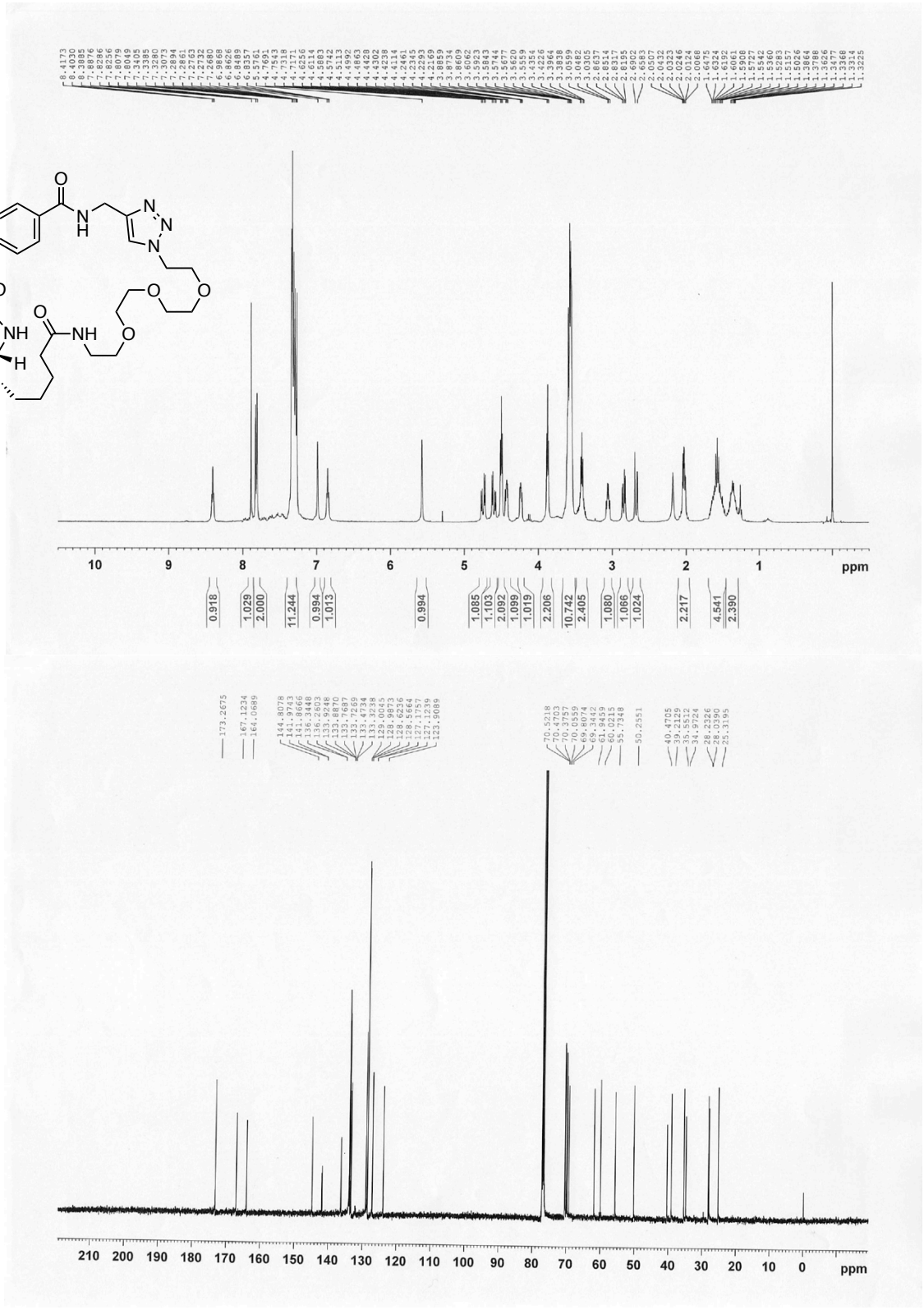
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *N*-((1-(2,6-diisopropylphenyl)-1*H*-1,2,3-triazol-4-yl)methyl)-4-(diphenylphosphino)benzamide (**3e**) ($CDCl_3$)



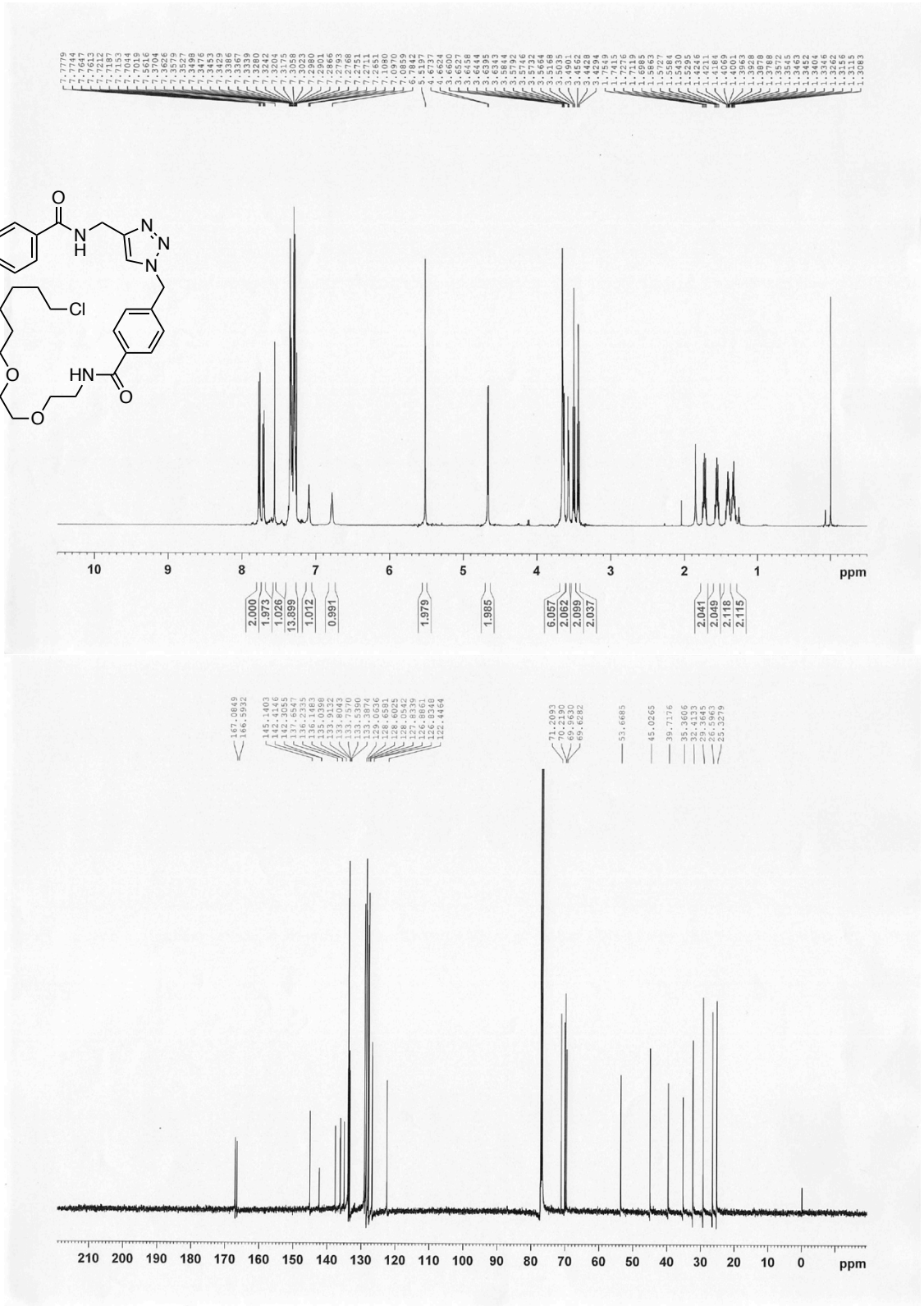
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *N*-((1-(2-pyridylmethyl)-1*H*-1,2,3-triazol-4-yl)methyl)-4-(diphenylphosphino)benzamide (**3f**) ($CDCl_3$)



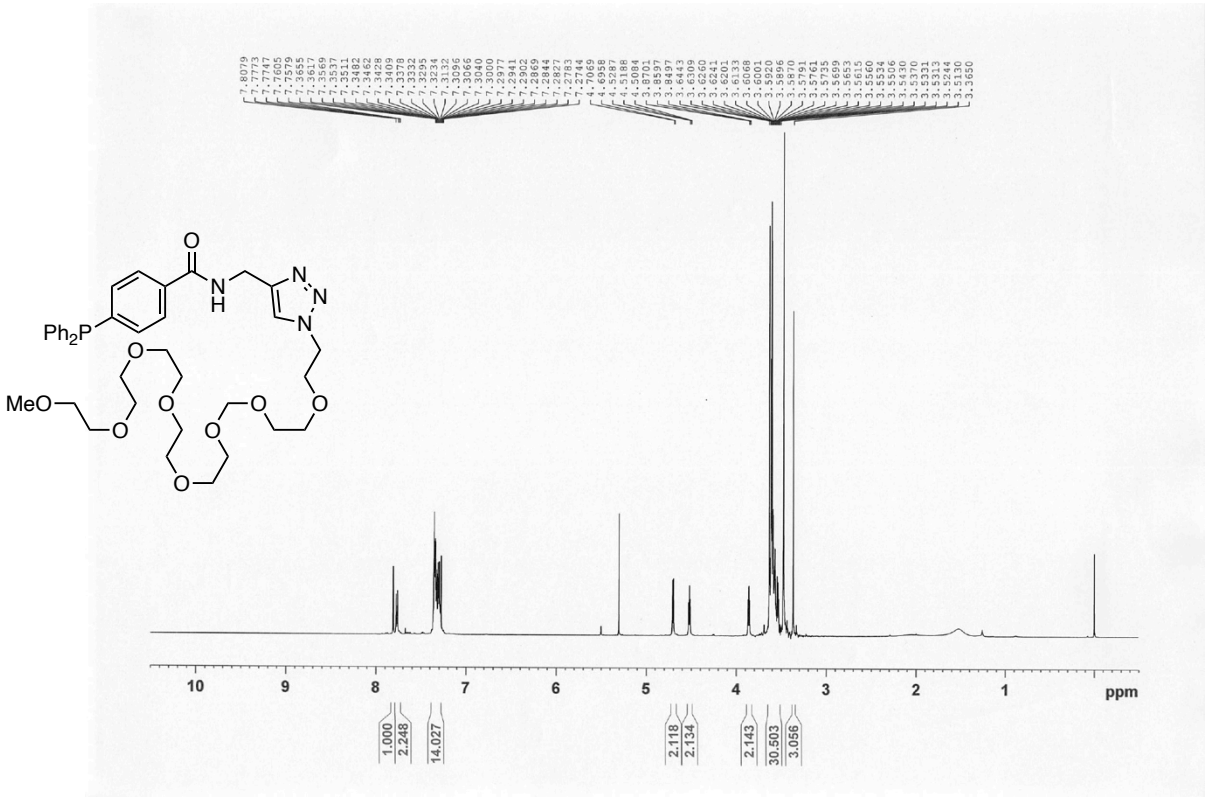
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 4-(4-diphenylphosphinobenzoylaminomethyl)-1-(2-(2-(2-(2-(biotinamido)ethoxy)ethoxy)ethoxy)ethyl)-1*H*-1,2,3-triazole (**3g**) ($CDCl_3$)

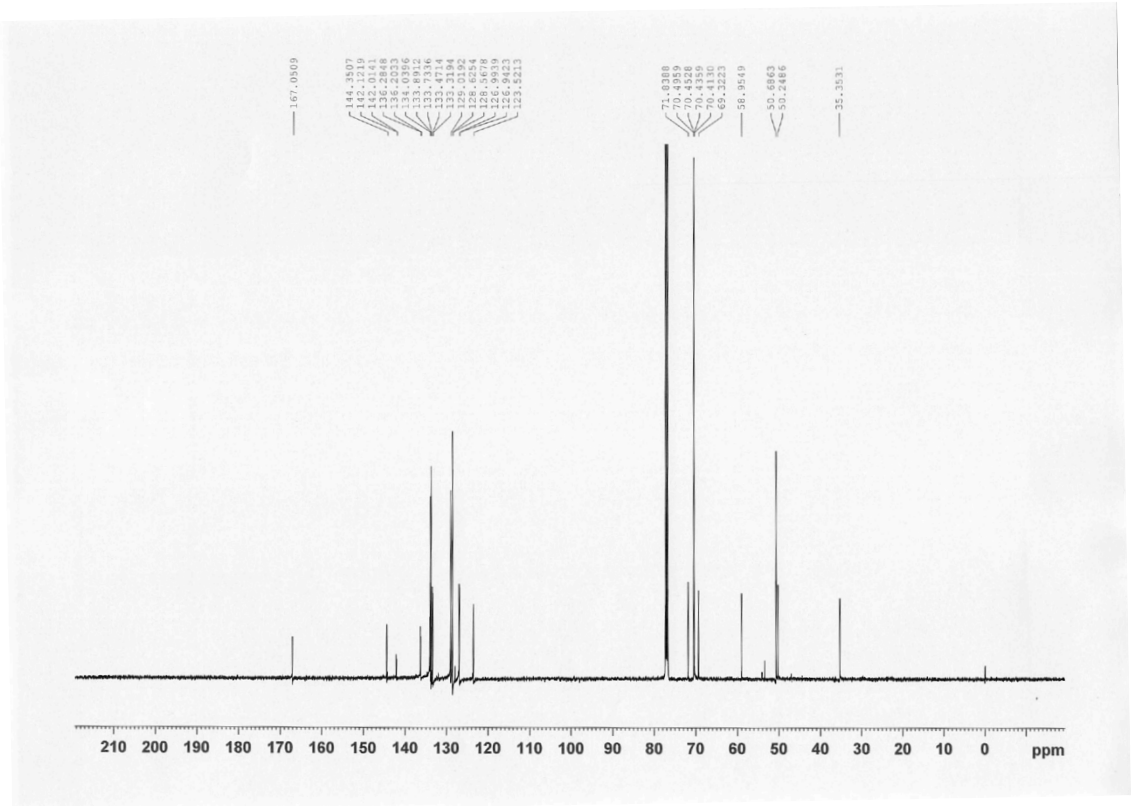


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 1-(4-(2-(2-(6-chlorohexyloxy)ethoxy)ethylaminocarbonyl)benzyl)-4-(4-diphenylphosphinobenzoylaminomethyl)-1*H*-1,2,3-triazole (**3h**) ($CDCl_3$)

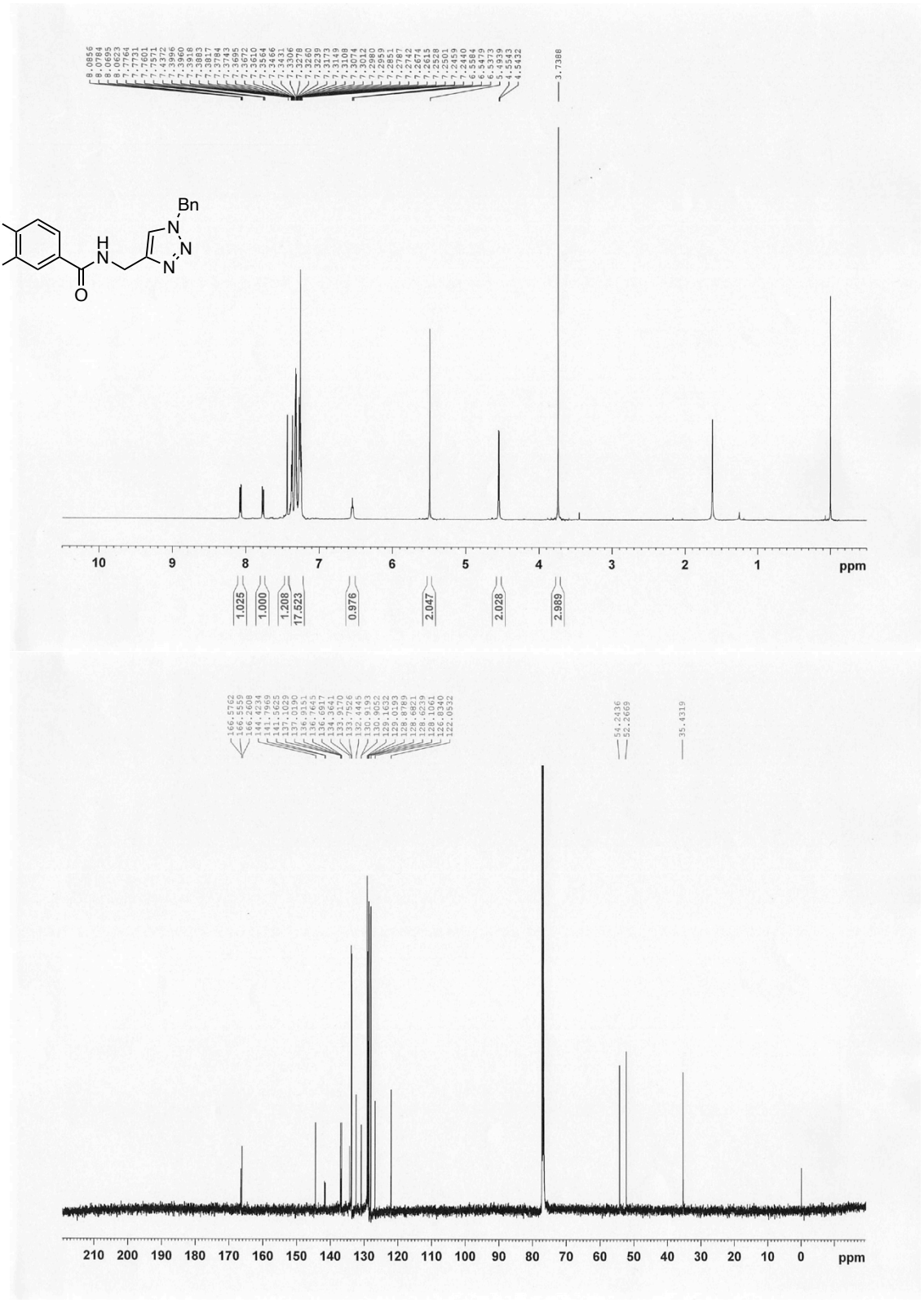


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 1-(2-(2-(2-(2-(2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)ethoxy)ethoxy)ethoxy)ethoxy)ethyl)-4-(4-diphenylphosphinobenzoylaminomethyl)-1*H*-1,2,3-triazole (**3i**) ($CDCl_3$)

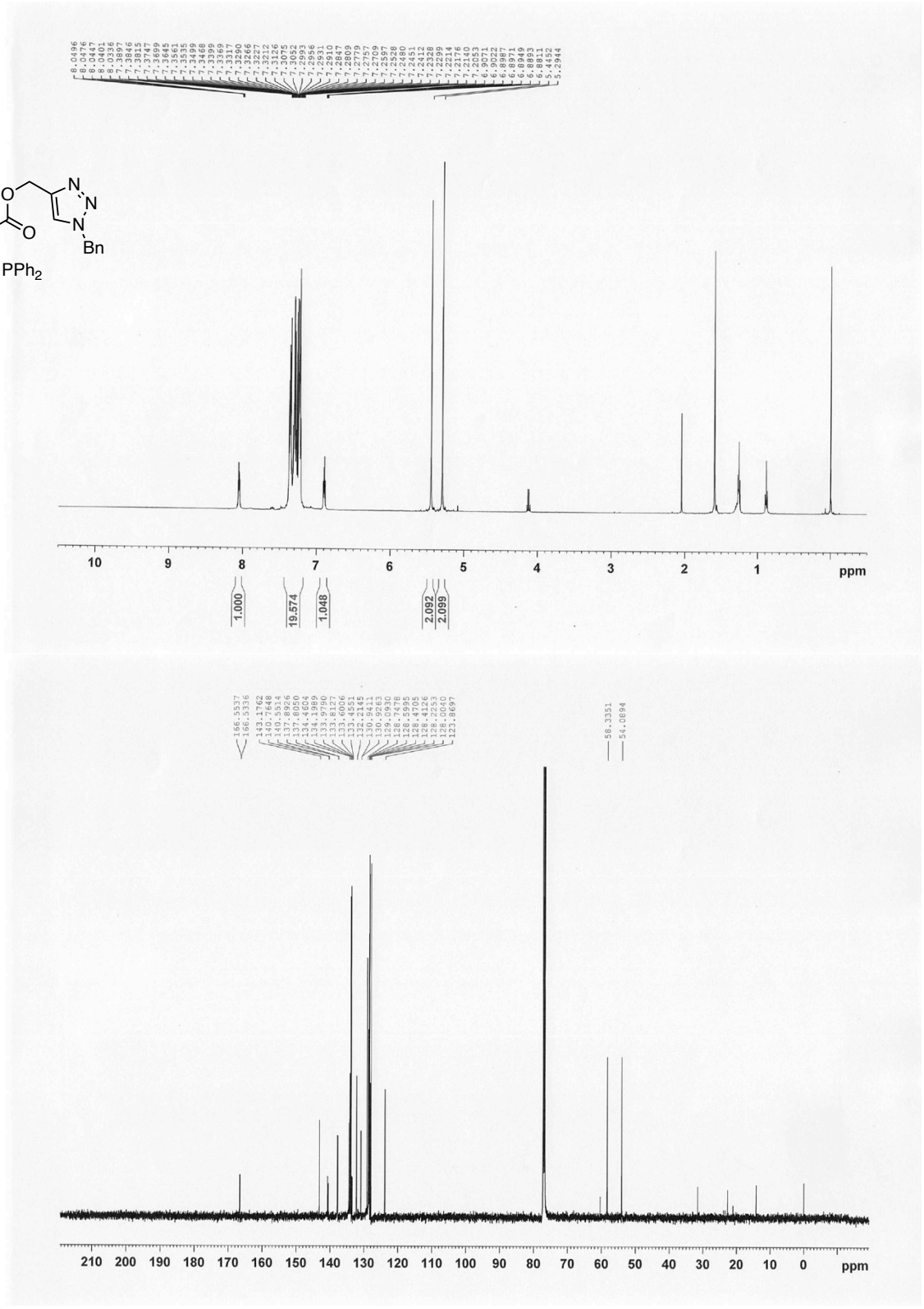




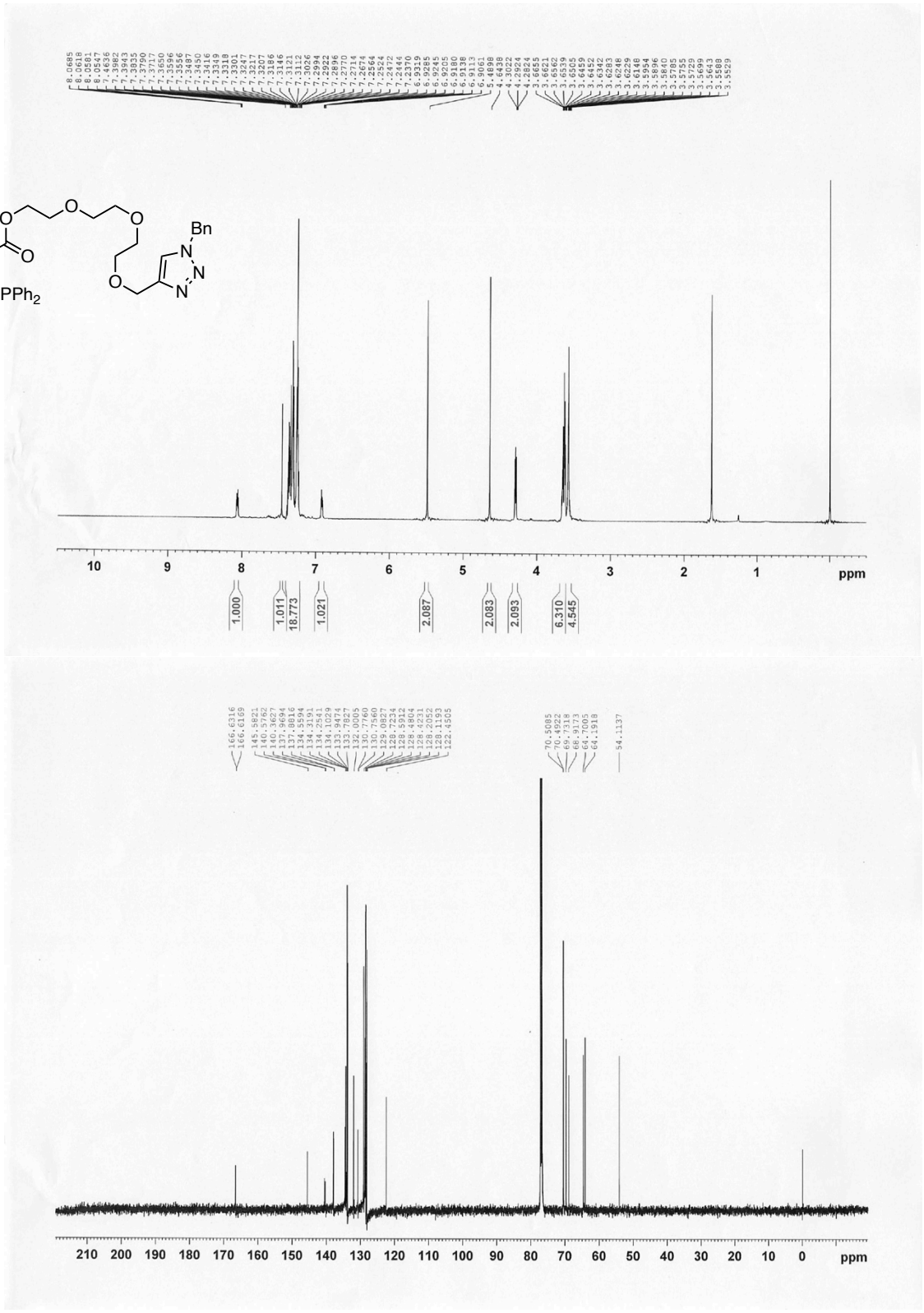
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *N*-((1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl)-4-(methoxycarbonyl)-3-(diphenylphosphino)benzamide (**3j**) ($CDCl_3$)



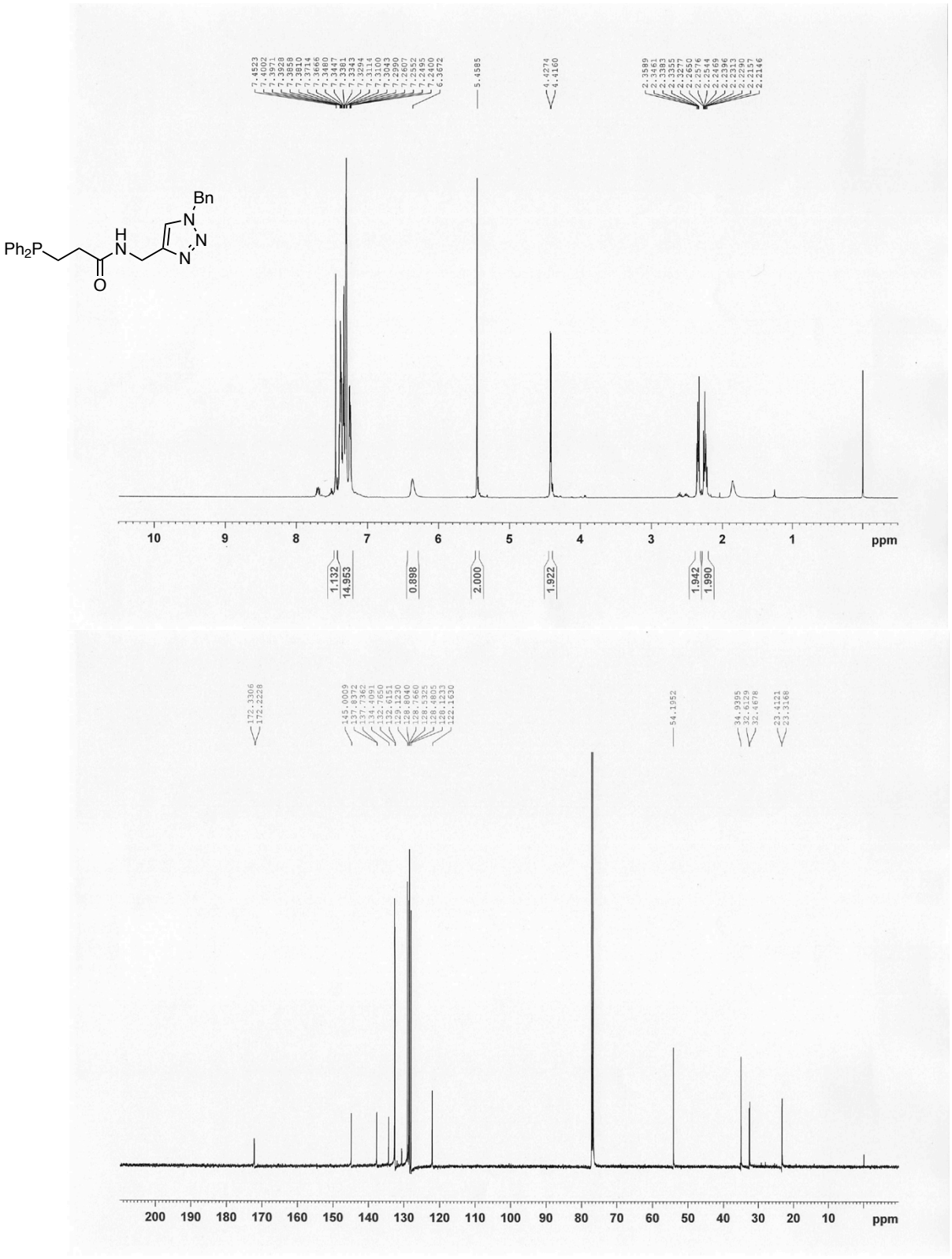
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of (1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl 2-(diphenylphosphino)benzoate (**3k**) ($CDCl_3$)



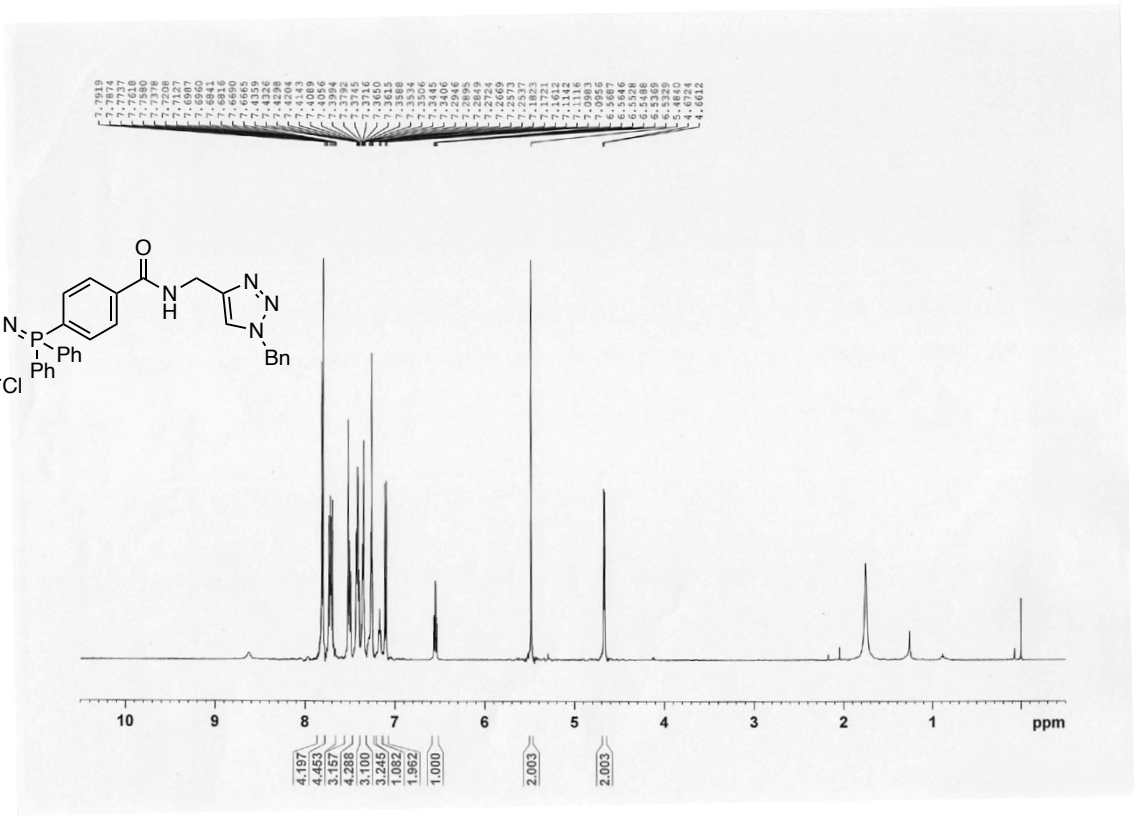
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 2-(2-(2-(2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)methoxy)ethoxy)ethoxy)ethyl 2-(diphenylphosphino)benzoate (**3l**) ($CDCl_3$)

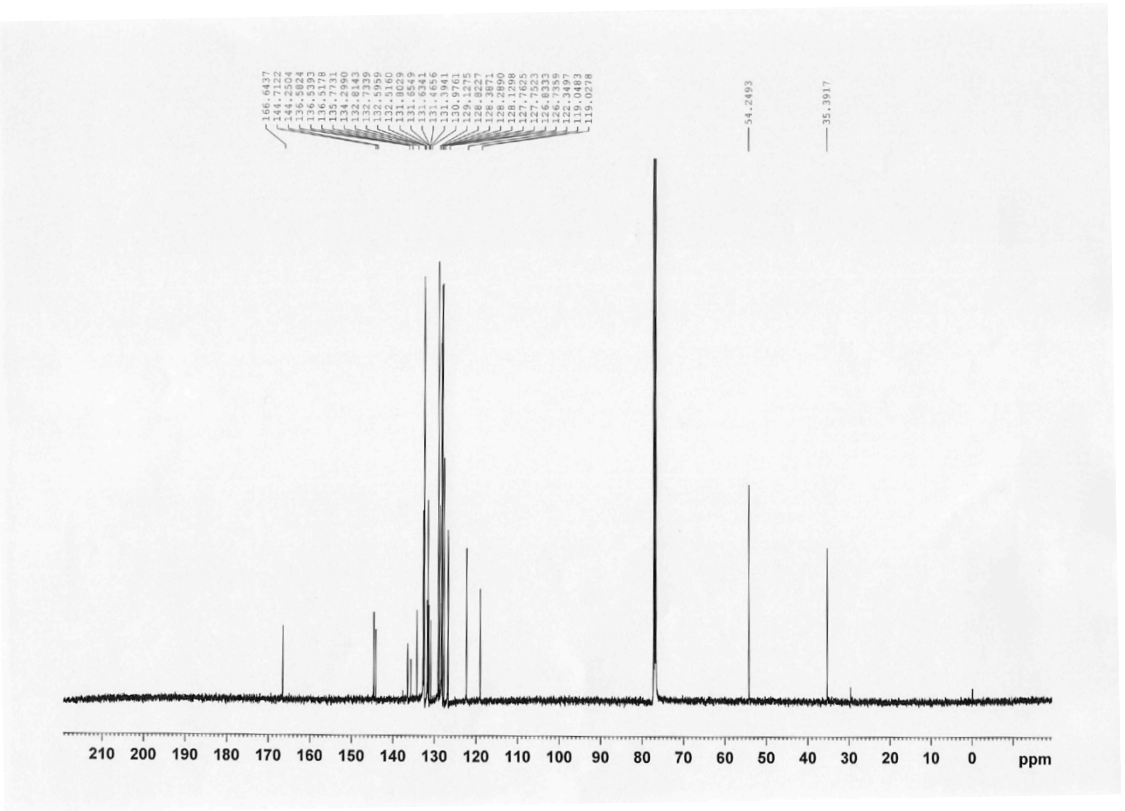


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *N*-((1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl)-3-(diphenylphosphino)propionamide (**3m**) ($CDCl_3$)

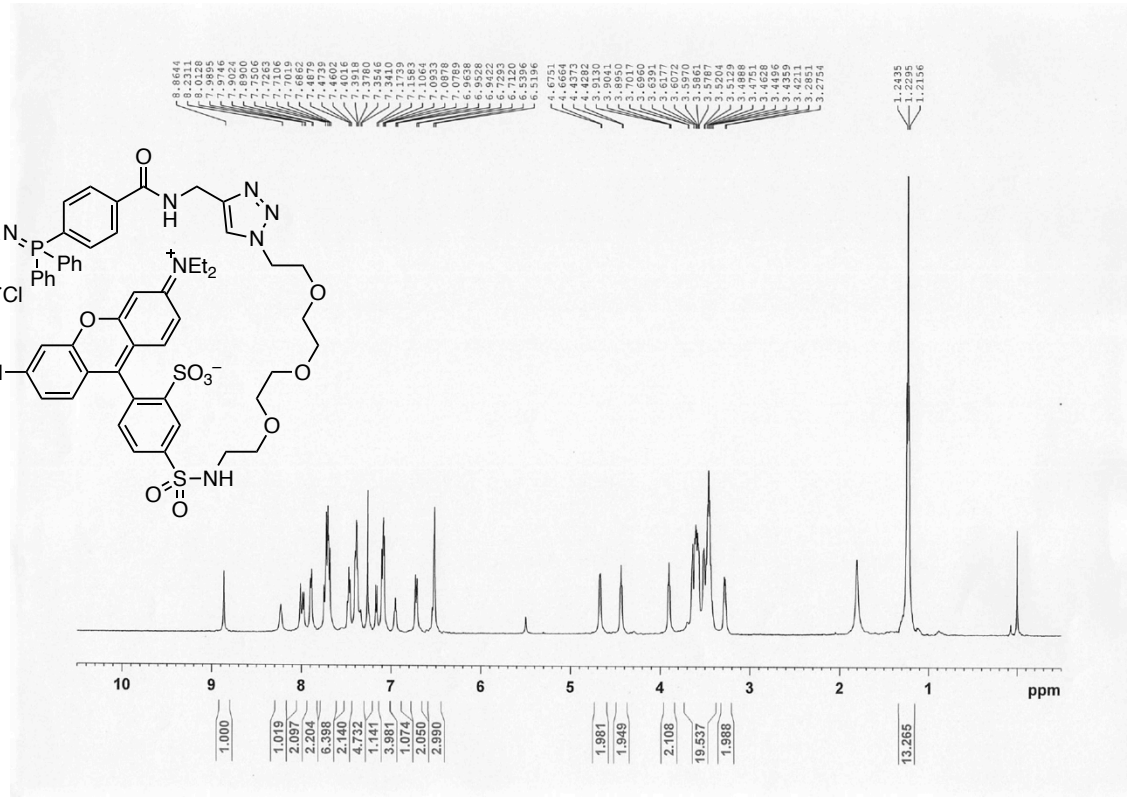


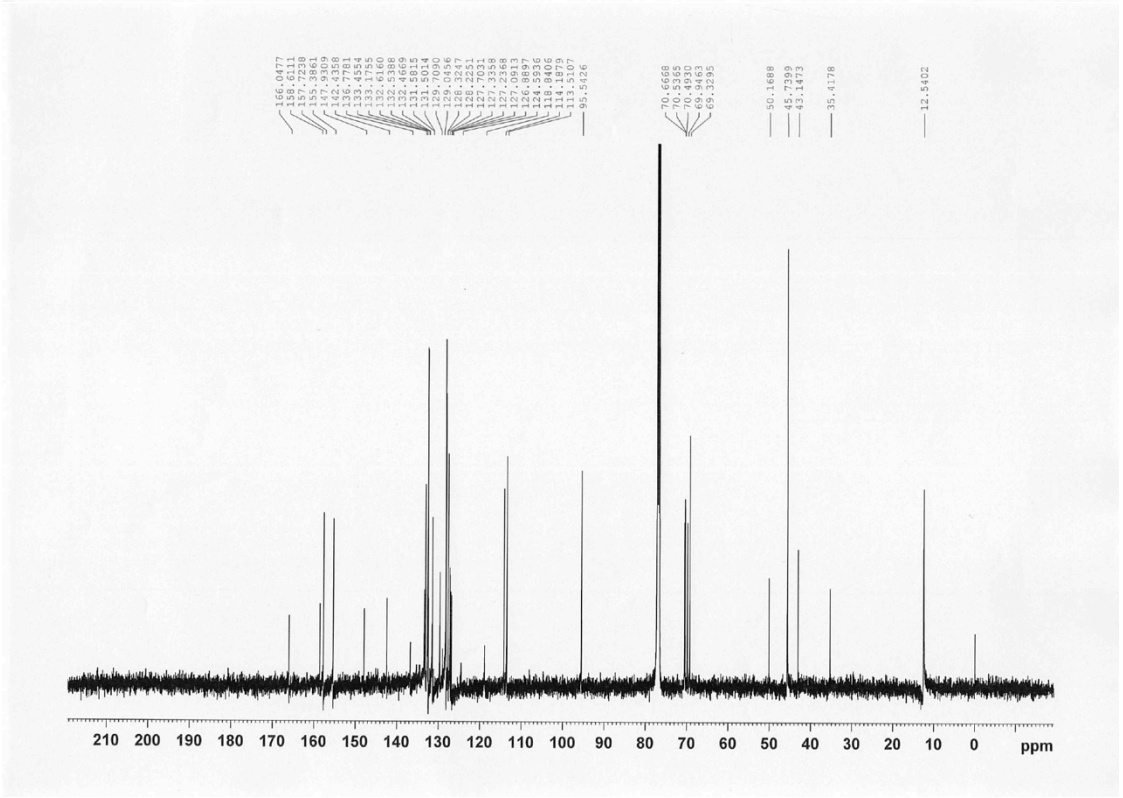
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 2,6-dichloro-*N*-(4-((1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl)carbamoylphenyl)diphenylphosphoranylidene)aniline (**4a**) ($CDCl_3$)



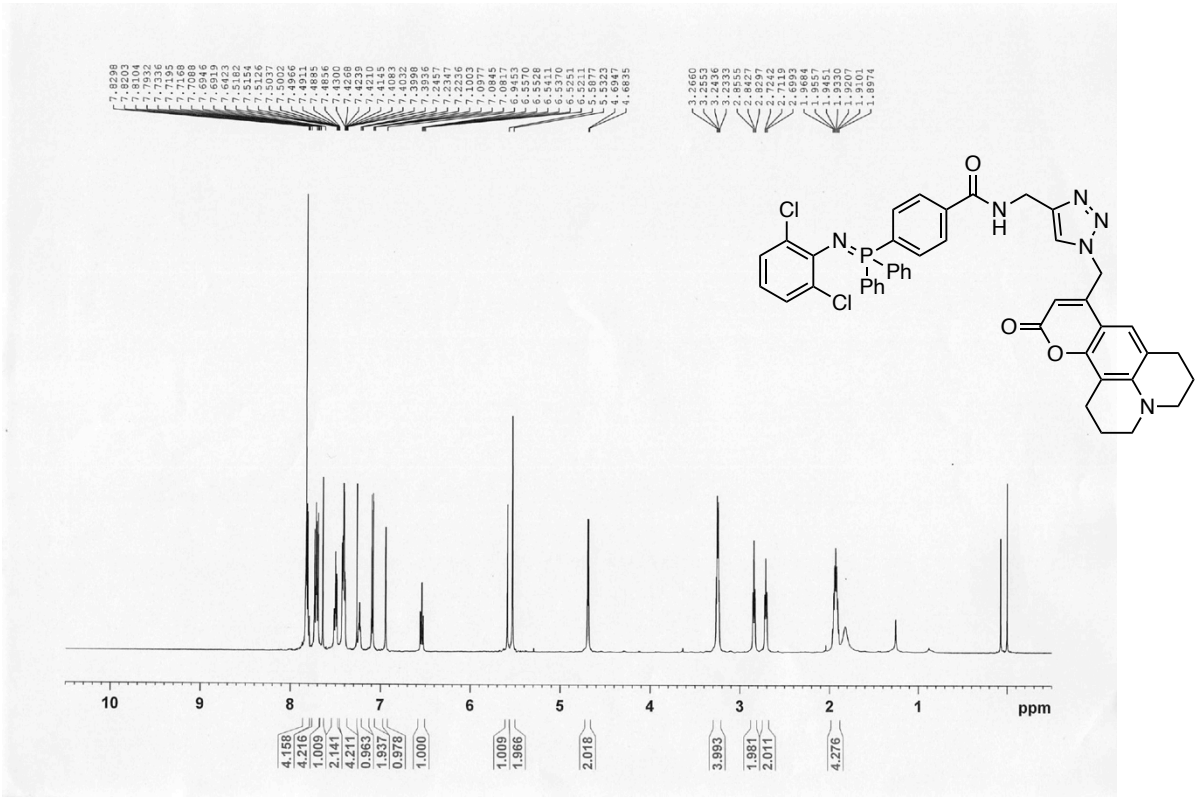


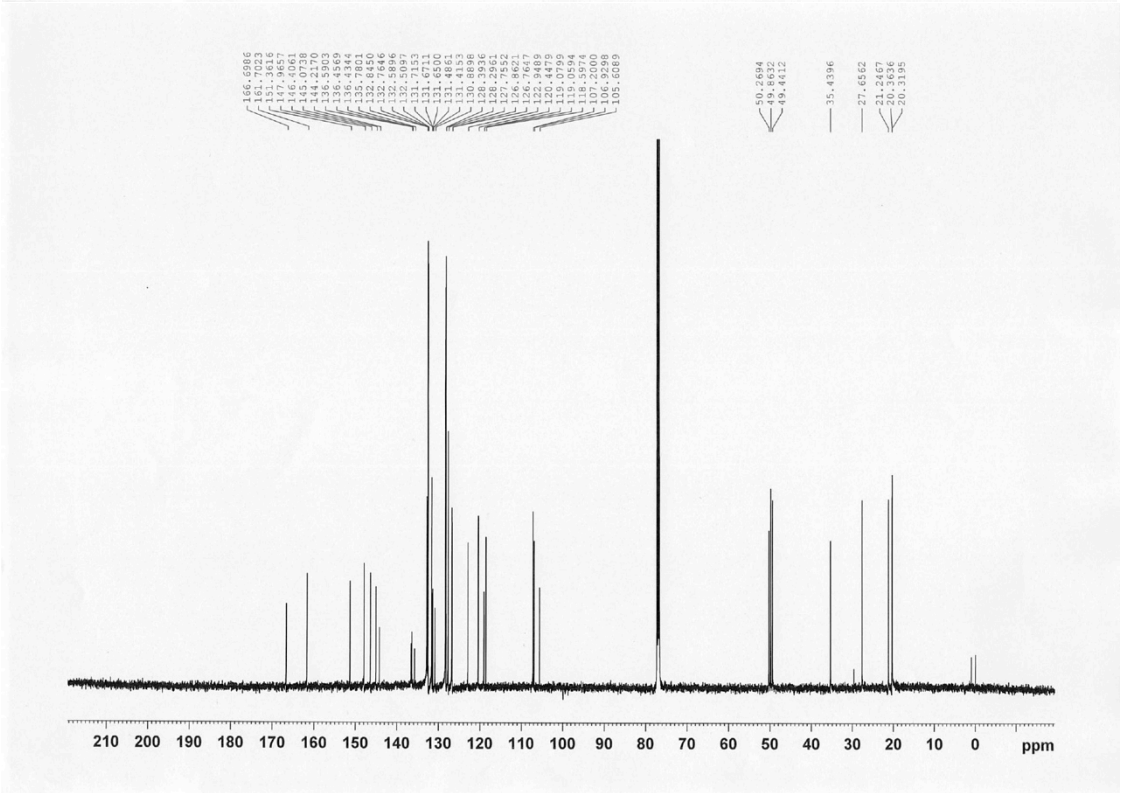
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 2,6-dichloro-*N*-(4-((1-(2-(2-(2-(2-(4-(3,6-bis(diethylamino)xanthylium-9-yl)-3-sulfonatobenzenesulfon-amido)ethoxy)ethoxy)ethoxy)ethyl)-1*H*-1,2,3-triazol-4-yl)methyl)carbamoylphenyl)diphenylphosphoranylidene)aniline (**4b**) ($CDCl_3$)



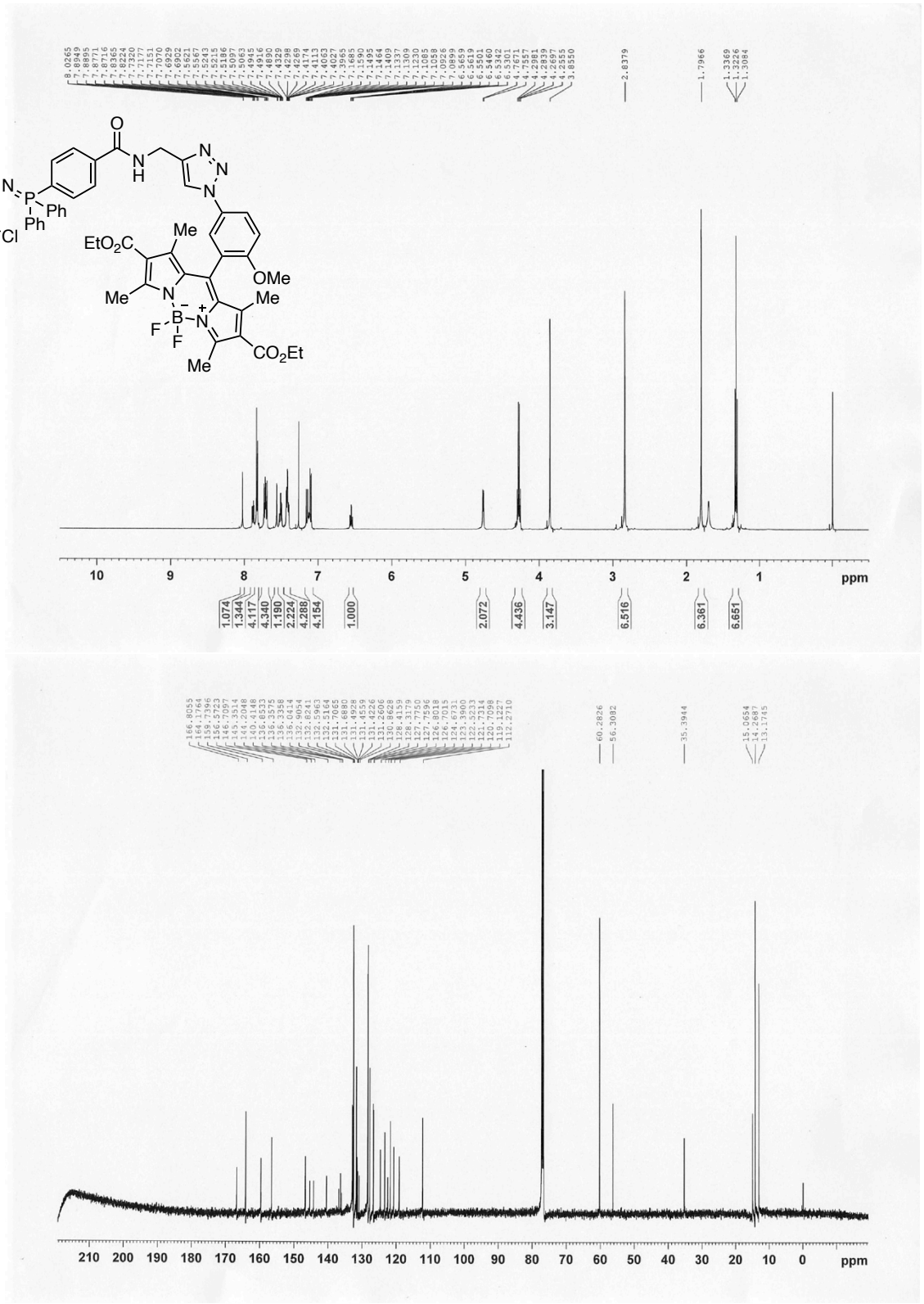


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 2,6-dichloro-*N*-(4-((1-((11-oxo-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-pyrano[2,3-*f*]pyrido[3,2,1-*ij*]quinolin-9-yl)methyl)-1*H*-1,2,3-triazol-4-yl)methyl)carbamoylphenyl)diphenylphosphoranylidene)aniline (**4c**) ($CDCl_3$)



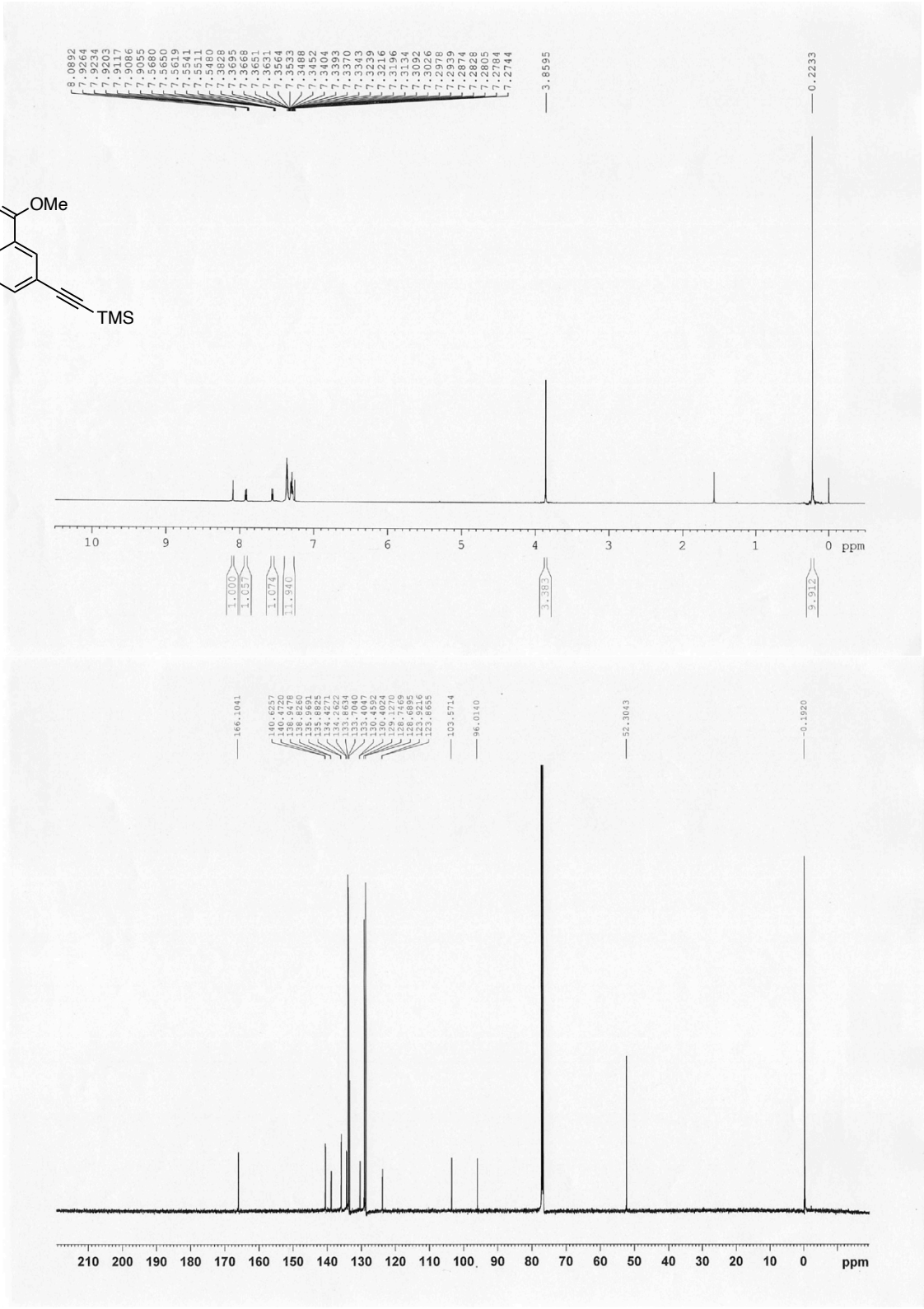


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of 2,6-dichloro-*N*-(4-((1-(2,6-bis(ethoxycarbonyl)-4,4-difluoro-1,3,5,7-tetramethyl-3a,4a-diaza-4-bora-s-indacen-8-yl)-4-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)methyl)carbamoylphenyl)diphenylphosphoranylidene)aniline (**4d**) ($CDCl_3$)

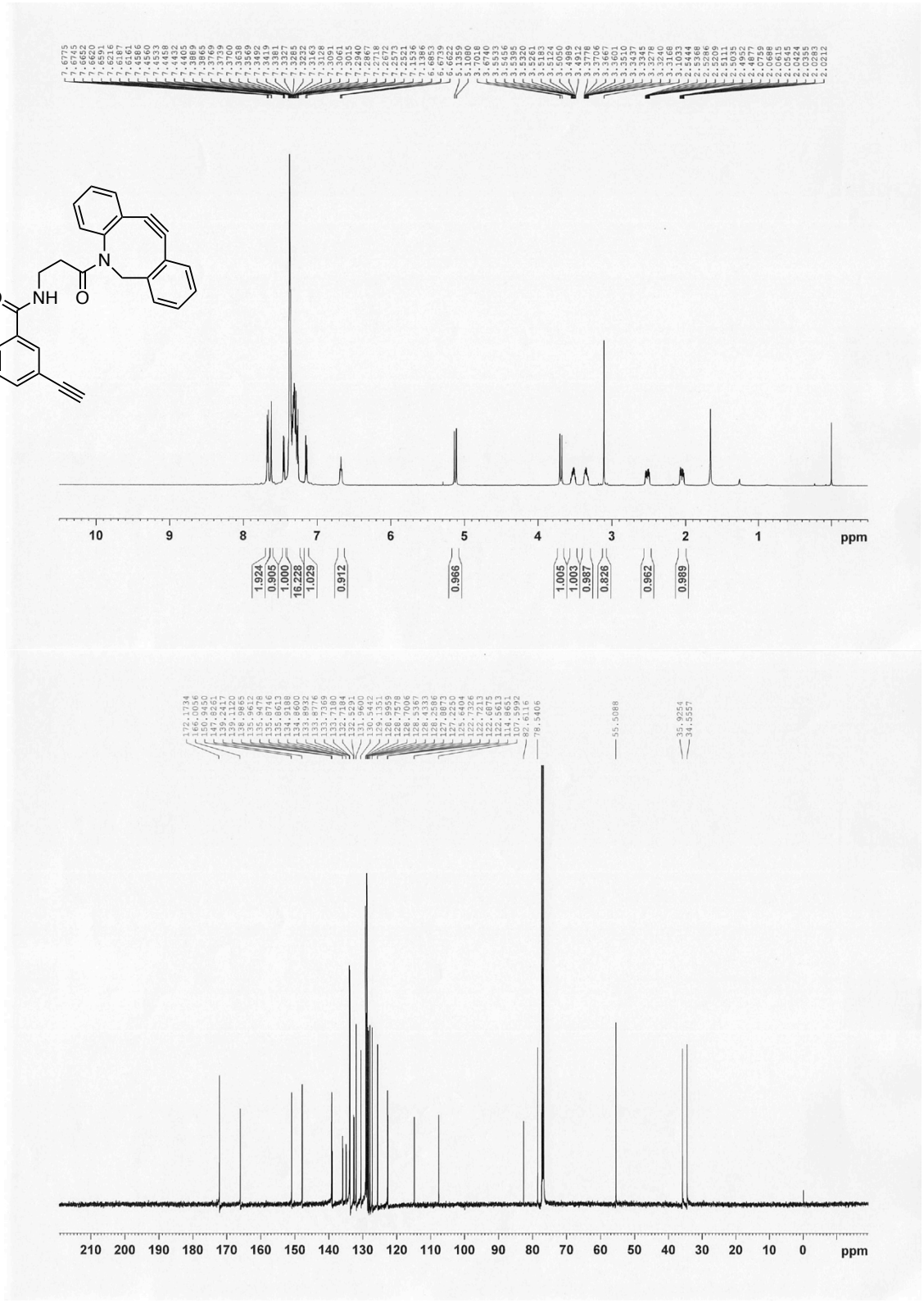


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of methyl 3-bromo-5-(diphenylphosphino)benzoate (**5**) ($CDCl_3$)

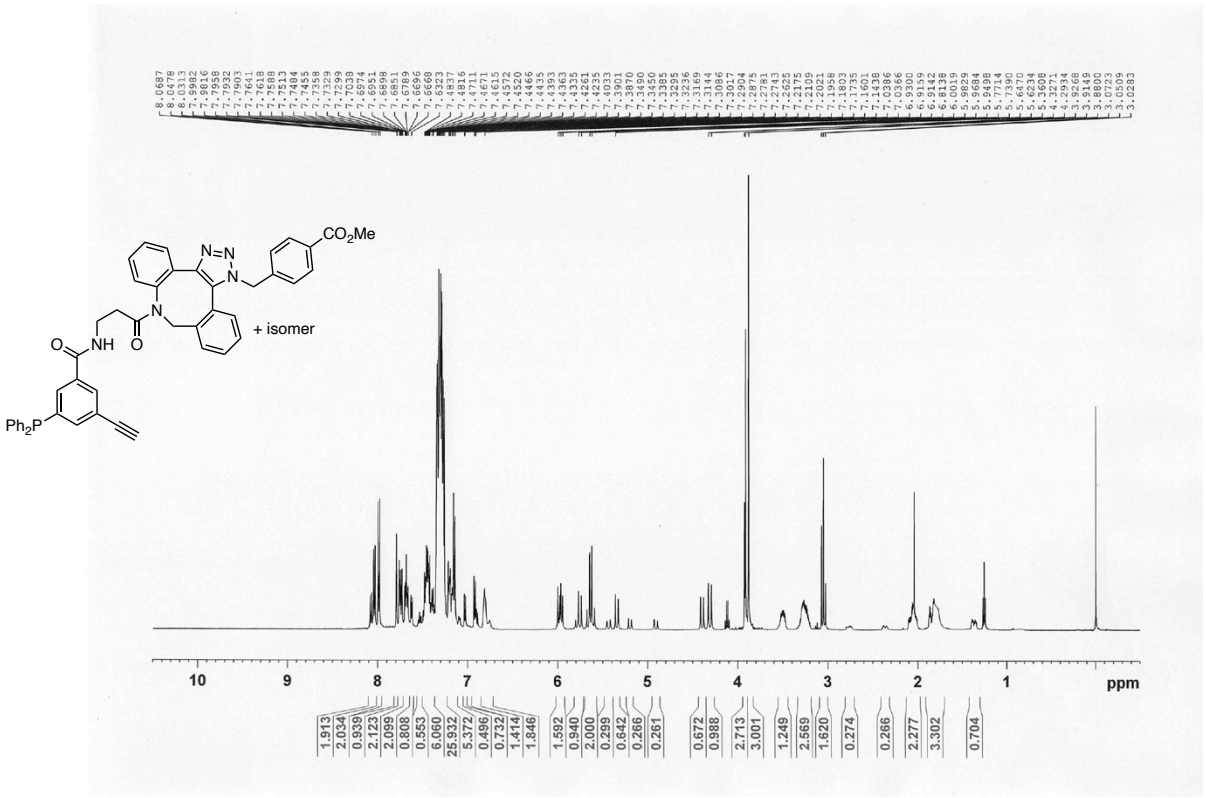
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of methyl 3-(trimethylsilylethynyl)-5-(diphenylphosphino)benzoate (**7**) ($CDCl_3$)

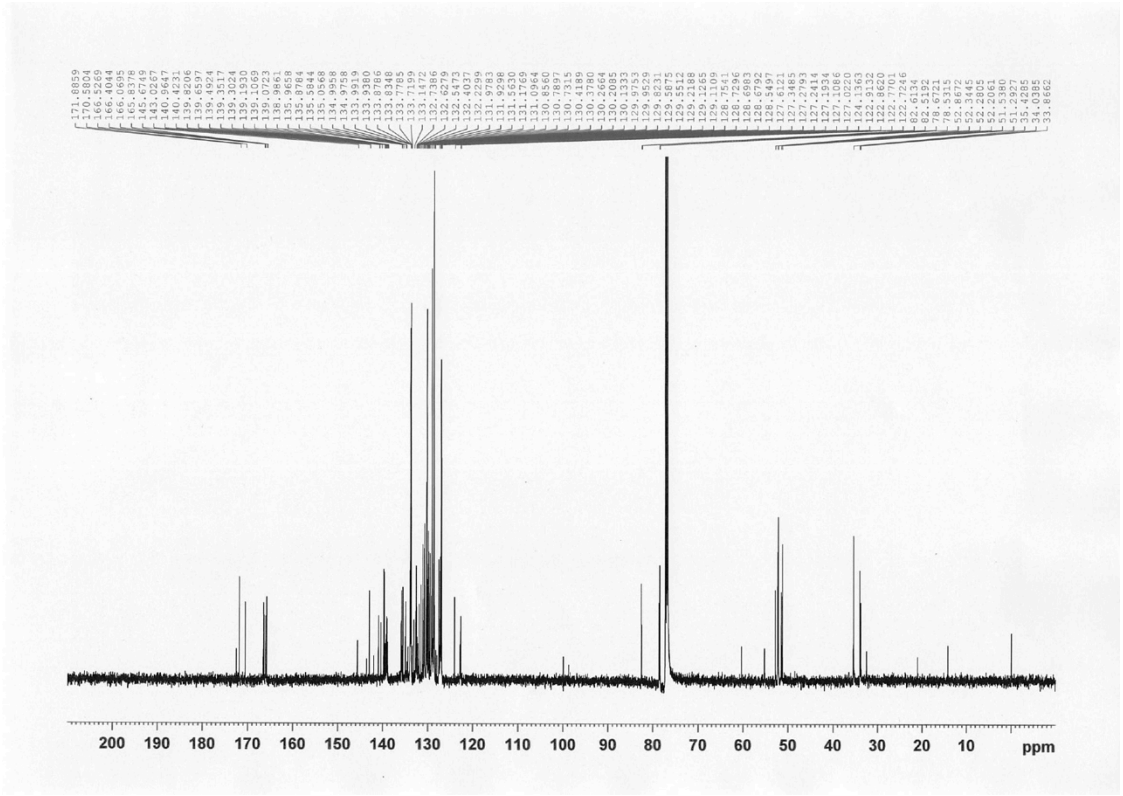


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *N*-(3-(5*H*,6*H*-11,12-didehydrodibenzo[*b*,*f*]azocin-5-yl)-3-oxopropyl)-3-ethynyl-5-(diphenylphosphino)benzamide (**12**) ($CDCl_3$)



^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of platform-triazole **S1** ($CDCl_3$)





^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra of *azaylide* **13** ($CDCl_3$)