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SUPPORTING INFORMATION

Interrupted Aza-Wittig Reactions Using Iminophosphoranes to Synthesize ^{11}C-Carbonyls

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Section 1: General Information

All chemicals and solvents used were purchased and were not further purified unless indicated otherwise. All CO_2 fixation reactions were carried out by bubbling CO_2 (balloon) through the solution. CO_2 was passed through a tube filled with Drierite to obtain anhydrous CO_2. All other reactions were routinely carried out under inert (argon or nitrogen) atmosphere. All solvents used were anhydrous. Anhydrous 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was obtained by reflux over KOH pellets, and distillation under reduced pressure. Reaction products were confirmed using ^{1}H-NMR, ^{13}C-NMR, and mass spectrometry. Purification of reaction products was carried out by flash column chromatography using silica gel unless stated otherwise. Analytical thin layer chromatography (TLC) was performed on aluminum or glass backing. ^{1}H-NMR spectra were obtained using a Bruker AVANCE 300 or a Bruker AVANCE 400. Spectral data are reported in ppm using solvent as the reference (for ^{1}H NMR $CHCl_3$ at 7.26 ppm and DMSO at 2.50 ppm). ^{1}H NMR data was reported as: multiplicity (ap = apparent, br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, and coupling constant(s) in Hz. Low resolution mass spectrometry was performed using Waters Xevo TQD with an Acquity UPLC H-Class Plus system. High resolution mass spectrometry was performed using a Kratos Concept – Magnetic Sector Electron Impact Mass Spectrometer. Radiochemical chromatograms were acquired using a Waters 2695 Alliance HPLC equipped with a Phenomenex Luna 10 µm C18(2) 100 Å column (250 x 4.6 mm, 10 µm), a Waters 996 photodiode array detector, and a Carroll & Ramsey Associates 105-S high-sensitivity radiation detector equipped with a 1 cm^3 CsI(Tl) scintillating crystal. Radiolabeled products were synthesized using Synthra MeIplus Research module. Known products generated were characterized in accordance with the literature.

Sigma-Aldrich: *N*-(triphenylphosphoranylidene)aniline; triphenylphosphine dibromide; benzyl alcohol; 2-tert-butylimino-2-diethylamino-1.3-dimethylperhydro-1,3,2-diazaphosphorine; 2-propanol; thiophenol; phenol; diethyl malonate; 4-bromoaniline; 4-fluoroaniline; furfurylamine; methylmagnesium bromide solution (3.0 M in diethyl ether); phenylmagnesium bromide solution (3.0 M in diethyl ether); benzylamine; *N*-methyl-2-phenoxyethanamine; phenylacetylene; 2-phenyl hydroquinone; phenylisocyanate; 5-chloro-2-methoxy-*N*-[2-(4-sulfamoylphenyl)ethyl]benzamide; *N*-butyllithium solution (1.6 M) in hexanes

Oakwood Chemical: 1,8-diazabicyclo[5.4.0]undec-7-ene; 2-(4-methoxyphenyl)ethanol; 4-nitroaniline; cyclohexylamine; *tert*-butylamine; triethylamine; 3-methoxybenzylamine; 1,2,4-triazole-3-thiol

Alfa Aesar: benzyl mercaptan; *tert*-butyl alcohol; *N*-*tert*-butylmethylamine; *p*-anisidine; *o*-toluidine; 4-fluorobenzylamine; 3-chloro-4-(trifluoromethyl)aniline; 4-(4-amine-3-fluorophenoxy)-*N*-methylpicolinamide; *N*-hydroxypthalamide

Acros Organics: 5-methoxytryptamine; L-phenylalanine methyl ester hydrochloride; *N*,*N*-diethylethylenediamine; 2-naphthalenethiol

Tokyo Chemical Company: glibenclamide

Section 2: Synthetic Procedures

1. Synthesis of iminophosphoranes.

A flame dried flask was equipped with a magnetic stir bar and charged with triphenylphosphine dibromide (0.6 mmol) dissolved in DCM (2.0 mL) under inert atmosphere. The flask was placed in an ice bath, and a solution containing the corresponding amine (0.6 mmol) and triethylamine (0.6 mmol) in DCM (2 mL) was added to the reactor in a dropwise manner over 10 minutes. The reaction was stirred at room temperature for 4 hours. The solvent was removed under reduced pressure, and anhydrous THF (10 mL) was added to the residue. The solution was filtered through a Celite plug, and the concentrated under reduced pressure. A sufficient volume of chloroform was added to solubilize the residue, and hexane was added to precipitate the product. The product was re-precipitated five or more times to remove unwanted triphenylphosphine oxide (TPPO).

Note: Amine hydrochlorides (0.6 mmol) were first dissolved in DCM (2.0 mL) and 1.1 equiv. of triethylamine was added. After stirring the reaction medium at room temperature for 30 min, ammonium salts were removed by adding Et_2O followed by filtration over a celite pad. Solvents were removed by rotary evaporation under reduced pressure and the afforded free amines were used without further purification.

2. Synthesis of carbamate and thiocarbamate products.

A flame dried flask was charged with the corresponding nucleophile (0.25 mmol), DBU (0.65 mmol), and ACN (2.5 mL). The mixture was brought to reflux, and CO_2 was bubbled through the solution for 10 minutes, prior to the addition of iminophosphorane (IMP). A solution containing IMP (0.25 mmol) in ACN (2 mL) was added dropwise over one hour to the reaction mixture. CO_2 was bubbled continuously throughout the reaction until completion. The contents of the flask were concentrated under reduced pressure and re-suspended in 5 mL of DCM. The solution was extracted with saturated aqueous NH_4Cl (3 × 10 mL) and dried over magnesium sulfate. The solvent was removed under reduced pressure and purified by flash column chromatography using a 0-25% hexane/ethyl acetate gradient.

Note: Blocked isocyanate products (**7–9, 11–12**) and products of alkyl iminophosphoranes (**22–23, 25**) use 2.5 mmol of nucleophile (10 equiv.) and are not subjected to solvent-solvent extraction unless mentioned otherwise. The concentrated residue is immediately purified by flash column chromatography using a 0-25% hexane/ethyl acetate gradient.

3. Synthesis of urea products.

A flame dried flask was charged with an amine nucleophile (0.50 mmol), DBU (0.25 mmol), and ACN (2.5 mL). CO_2 was bubbled through this solution for 10 minutes, followed by the addition of a solution containing iminophosphorane (0.25 mmol) in ACN (2 mL), added dropwise over 20 minutes at room temperature. The contents of the flask were concentrated under reduced pressure and purified by flash chromatography using a 0-25% hexane/ethyl acetate gradient.

4. Synthesis of amides using Grignard reagents via blocked isocyanate intermediates.

A flame dried round bottom flask was charged with the corresponding blocking nucleophile (2.5 mmol), DBU (0.65 mmol), and THF (2.5 mL). The mixture was brought to reflux, and CO_2 was bubbled through the solution for 10 minutes. A solution containing IMP (0.25 mmol) in THF (2 mL) was added dropwise over one hour to the reaction mixture. CO_2 was bubbled continuously throughout the reaction until completion. The reaction solution was sparged with argon for five minutes and added dropwise to a cooled flask containing Grignard (5 mmol) dissolved in THF (2 mL). The reaction was left to stir overnight and quenched with methanol (15 mL). The contents of the flask were concentrated under reduced

pressure, re-suspended in DCM, and extracted with saturated aqueous NH_4Cl (3 × 20 mL), water (3 × 15 mL) and brine (3 × 15 mL) and dried over magnesium sulfate. The solvent was removed under reduced pressure and purified by flash column chromatography using a 0-25% hexane/ethyl acetate gradient.

5. Synthesis of amides using phenylacetylene.

A flame dried round bottom flask was charged with phenylacetylene (2.5 mmol) dissolved in THF (5 mL) and cooled to -78 °C. n-Butyllithium (2.45 mmol) was added dropwise to the solution. The solution was left to stir for 2 hrs. The reaction was brought to room temperature, and the contents of this flask were added dropwise to a separate flask containing the prepared blocked isocyanate using procedure **4**. The reaction was left to stir at room temperature for 2 hours. The contents of the flask were concentrated under reduced pressure, resuspended in DCM (5 mL), and extracted with saturated aqueous ammonium chloride (3 × 15mL), water (3 × 15 mL), brine (1 × 15 mL) and dried over magnesium sulfate. The product was purified by flash chromatography using a hexane/ethyl acetate gradient.

6. Synthesis of amides using diethyl malonate.

A flame dried round bottom flask was charged with diethylmalonate (10 mmol) and dissolved in THF (5 mL). The flask was cooled to -78 °C, and LHMDS (2.45 mmol) was added dropwise. The reaction was left to stir for 2 h. The solution was brought to room temperature, and 1.25 mL of the solution was added to a separate flask that was charged with DBU (0.65 mmol) and THF (1.25 mL). The reaction was heated to reflux, and CO_2 was bubbled into the reaction for 5 minutes. A solution of IMP (0.25 mmol) in THF (2 mL) was added dropwise to the reaction mixture over 1 hr. CO_2 was bubbled continuously into the reaction until completion. The contents of the flask were concentrated under reduced pressure and purified by flash column chromatography using a 0-25% hexane/ethyl acetate gradient.

7. Deprotonation of alkyl iminophosphorane salts.

The iminophosphorane salt (0.25 mmol) was added to a 5-mL flame dried round bottom flask and dissolved in THF (2.5 mL). The flask was cooled to 0 °C using an ice-water bath, and KHMDS was added to the solution (0.245 mmol). The reaction was left to stir for 5 minutes and brought to room temperature for use.

8. Synthesis of carbon-11 radiolabeled products.

Using the Synthra MeIplus Research module (Figure S1), 400 µL of a DMF solution containing iminophosphorane (28.29 µmol), DBU (40 µmol), and nucleophile (483 µmol) were loaded into reactor 1. DMF or ACN (1 mL) was loaded into vial A1. Carbon-11 (CO_2) ($[^{11}C]CO_2$), generated by the bombardment of a gas target filled with pressurized N_2/O_2 mixture using a Siemens 11 MeV cyclotron, at 55 µA for 2 minutes, and was directed to a steel coil cooled at -180 °C. The coil was briefly flushed with $He_{(g)}$ prior to heating to 25 °C. $[^{11}C]CO_2$ was bubbled into the reactor (at room temperature unless otherwise stated) at 5 mL/min. The reactor was then heated to 100 °C for 10 minutes, and solvent from vial A1 was added to the reactor to dilute the mixture. The solution was transferred to a glass vial and analyzed by radioHPLC. Integration of radiation detector chromatograms on analytical HPLC informed radiochemical yields, and products were identified by co-injection of nonradioactive standards. Isolated yields were determined by decay correcting the activity to the end of synthesis (EoS). Analytical HPLC conditions for radiolabeled products (unless otherwise stated): flowrate of 1 mL/min; 50% ACN / 50% 0.1 M AMF for 2 minutes, then gradient to 95% ACN / 5% 0.1 M AMF until 10 minutes, 95% ACN / 5% 0.1 M AMF until 12 minutes, return to 50% ACN / 50% 0.1 M AMF until 13 minutes, then 2 minutes at 50% ACN / 50% 0.1 M AMF.

9. Radiosynthesis of [^{11}C]35

A solution of iminophosphorane **1o** (2.19 µmol in 200 µL of DMF) was prepared, and DBU (2.18 µmol) was added ten minutes prior to end-of-bombardment. The solution of iminophosphorane and a solution of *N*-methyl-2-phenoxyethanamine (0.12 mmol in 200 µmL of DMF) were loaded into the reaction vessel and tightly sealed two minutes prior to end-of-bombardment. [^{11}C]CO_2 was trapped at -180 ˚C. The trap was heated to 25 ˚C, and [^{11}C]CO_2 was released under a stream of helium at 3 mL/min to bubble into the reaction vessel until peak activity. The reactor was heated to 100 ˚C for 1 min and quenched with 800 µL of H_2O. The solution was injected onto an HPLC column for purification. HPLC conditions: Nucleodur C18 Pyramid 7 µm, 250 × 10 mm eluted with 30% ACN/70% 0.1 M AMF at 5 mL/min. The product was collected, and the identity was established by co-injection with the non-radioactive standard using an analytical HPLC.

10. Radiosynthesis of [^{11}C]25b ([^{11}C]URB694)

DMF was degassed using five freeze-thaw cycles prior to use. 2-Phenyl-1,4-dihydroquinone was purified by flash column chromatography (0-25% hexanes/ethyl acetate) on the day of use. A solution of iminophosphorane **1g** (2.27 µmol in 100 µL of DMF, 0.01 mg/µL) was prepared, and DBU (2.27 µmol) was added two minutes prior to end-of-bombardment. The solution was mixed under argon for one minute, and 25 µL of this solution was added to a vial containing 2-phenyl-1,4-dihydroquinone (80.5 µmol) in 125 µL of DMF. This precursor solution was loaded into the reaction vessel and tightly sealed. A stream of helium was swept through the reaction vessel after loading. [^{11}C]CO_2 was trapped at -180 ˚C. The trap was heated to 25 ˚C, and [^{11}C]CO_2 was released under a stream of helium at 3 mL/min to bubble into the reaction vessel until peak activity. The reactor was heated to 100 ˚C for 2 min and quenched with 800 µL of mobile phase. The solution was injected onto an HPLC column for purification. HPLC conditions: Nucleodur C18 Pyramid 7 µm, 250 × 10 mm eluted with 70% MeOH/30% H_2O containing 1% formic acid at 7 mL/min. The product was collected, and the identity was established by co-injection with the cold standard using an analytical HPLC.

11. Radiosynthesis of [^{11}C]36 ([^{11}C]Glibenclamide)

DMF was degassed using five freeze-thaw cycles prior to use. A solution of iminophosphorane **1g** (2.27 µmol in 100 µL of DMF) was prepared, and 27.5 µL of DABCO (1.22 µmol, 0.02 mg/µl solution in DMF) was added two minutes prior to the end-of-bombardment. The solution was stirred for 30 seconds, and 25 µL of this solution was added to the reactor. 5-Chloro-2-methoxy-*N*-[2-(4-sulfamoylphenyl)ethyl]benzamide (40.66 µmol) was dissolved in 125 µL of DMF and added to a Teflon sealed vial under inert atmosphere containing potassium *tert*-butoxide (40 µmol), also mixed 2 minutes prior to the end-of-bombardment. The solution was loaded into the reaction vessel and tightly sealed. A stream of helium was swept through the reaction vessel after loading. [^{11}C]CO_2 was trapped at -180 ˚C. The trap was heated to 25 ˚C, and [^{11}C]CO_2 was released under a stream of helium at 3 mL/min to bubble into the reaction vessel until peak activity. The reactor was heated to 100 ˚C for 2 min and quenched with 800 µL of mobile phase. The solution was injected onto an HPLC column for purification. HPLC conditions: Nucleodur C18 Pyramid 7 µm, 250 × 10 mm eluted with 55% ACN/45% H_2O containing 0.1% TFA at 5 mL/min for 10 minutes, then switched to 75% ACN/25% H_2O + 0.1% TFA for 3 minutes. The product was collected, and the identity was established by co-injection with the cold standard using an analytical HPLC.

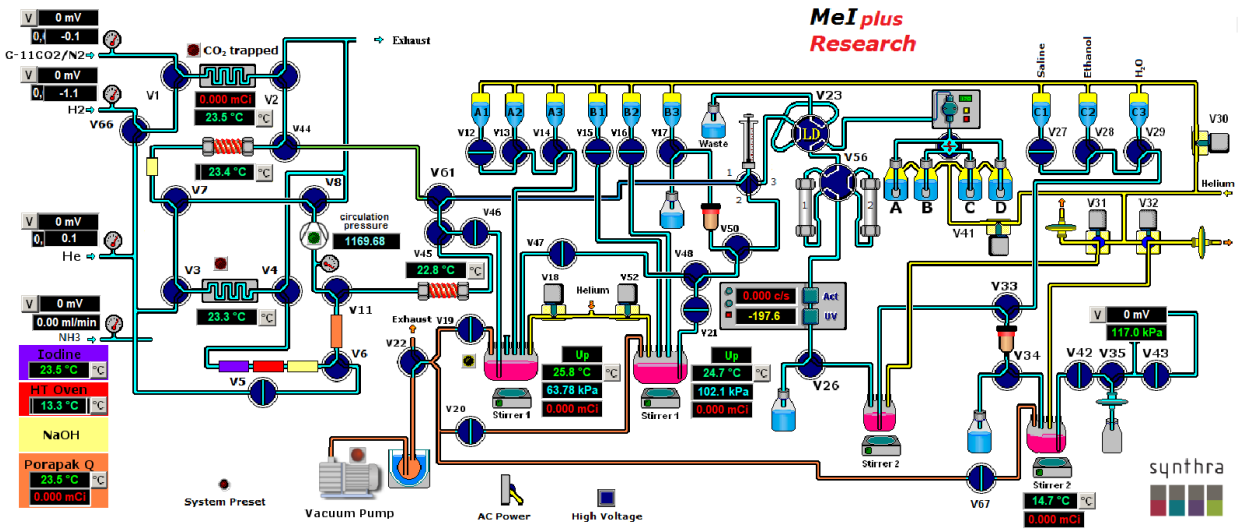
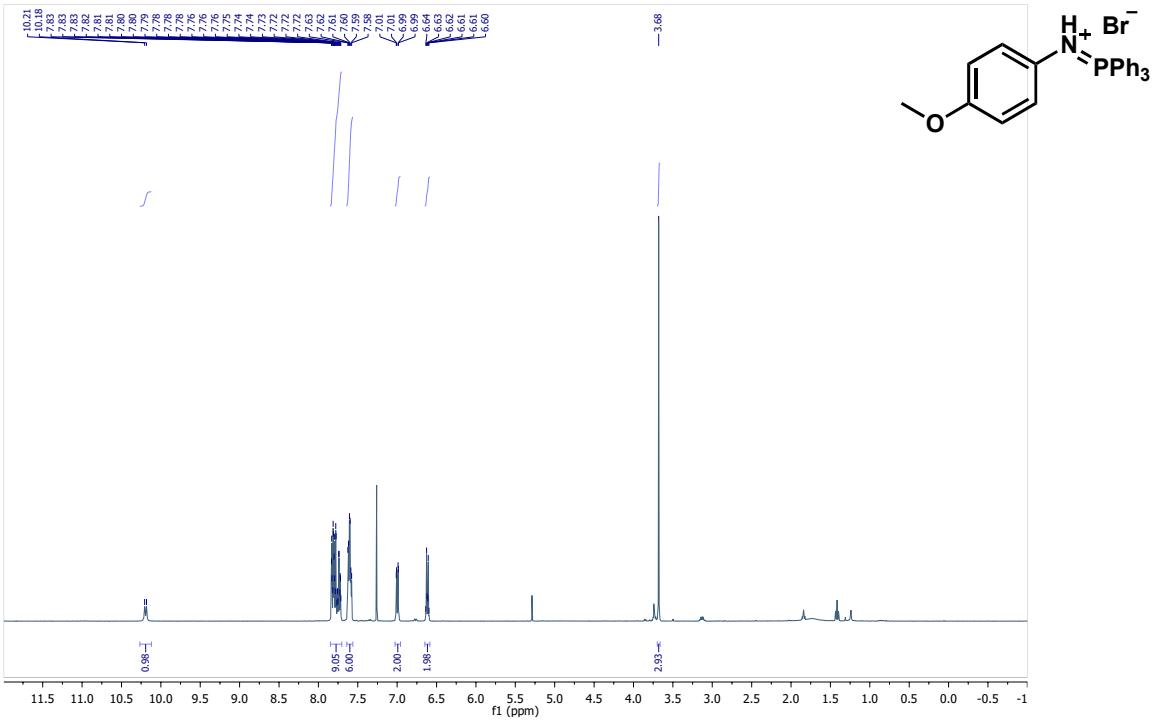


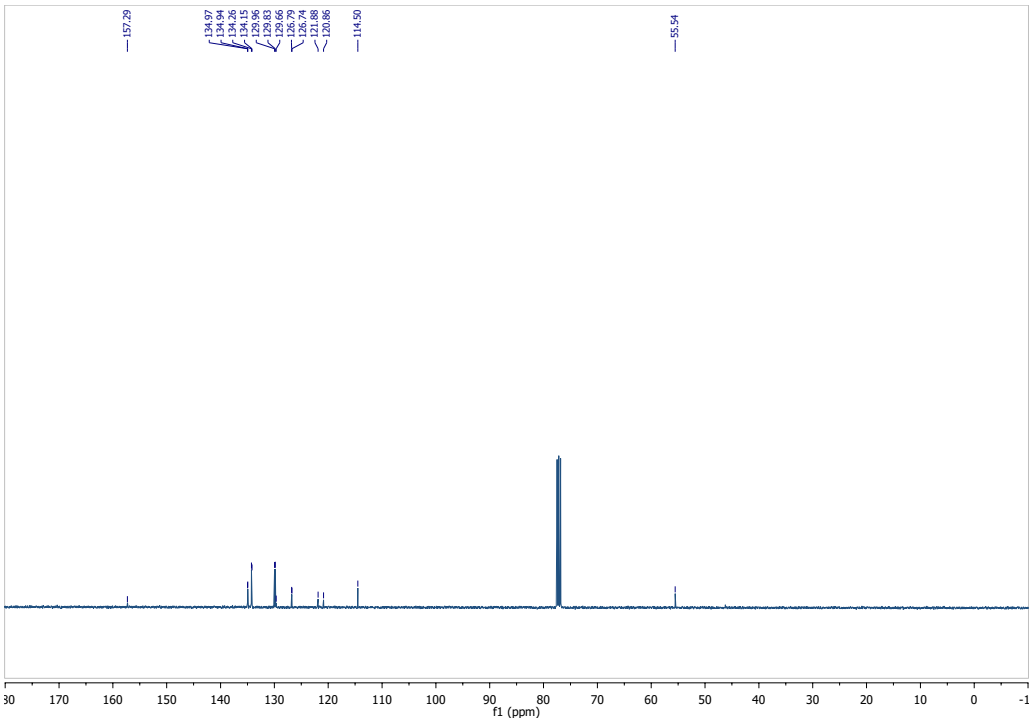
Figure S1. Synthra MeIplus Research apparatus scheme.

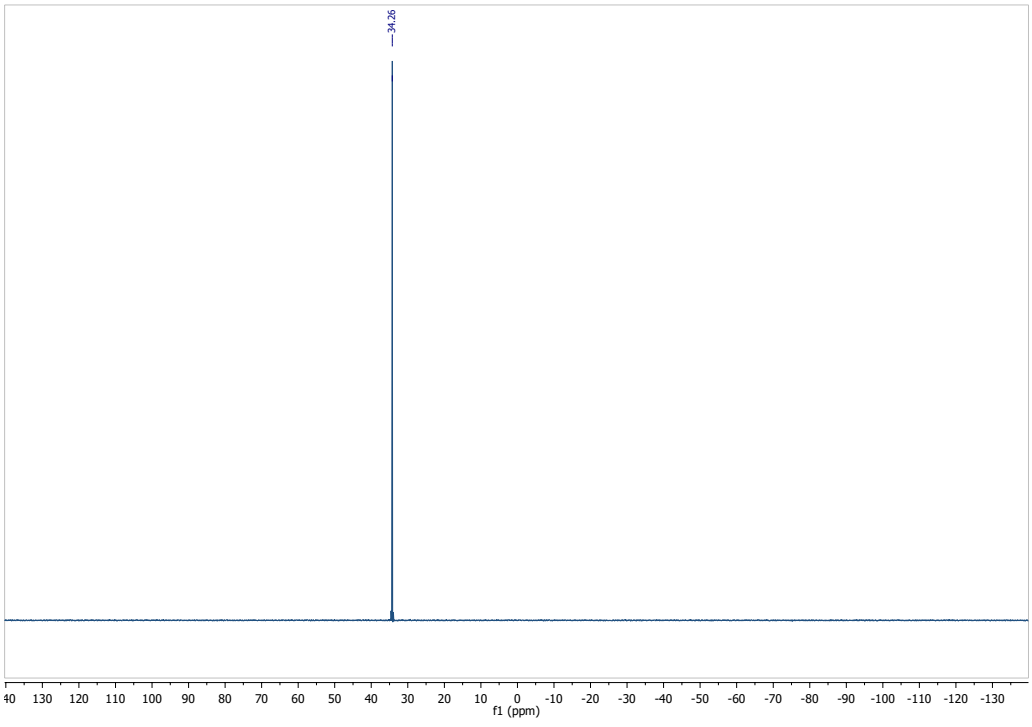
Section 3: Experimental Data

1b. 4-methoxy-*N*-(triphenylphosphanylidene)anilinium bromide

Followed the general procedure (**1**), product obtained as a light brown solid (17 mg, yield 26%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 10.20 (d, *J* = 9.3 Hz, 1H), 7.83–7.72 (m, 9H), 7.63–7.58 (m, 6H), 7.00 (d, *J* = 8 Hz, 2H), 6.62 (d, *J* = 8 Hz, 2H), 3.68 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): 157.3, 135.0 (d, *J* = 3 Hz), 134.2 (d, *J* = 11 Hz), 129.9 (d, *J* = 13 Hz), 129.7, 126.8 (d, *J* = 5 Hz), 121.4 (d, *J* = 103 Hz), 114.5, 55.5. ^{31}P-NMR (162 MHz, $CDCl_3$): δ 34.26 (s, 1P). MS (ESI+): Calculated $C_{25}H_{23}NOP$ as 384.1517, [M+H] found as 384.1535.

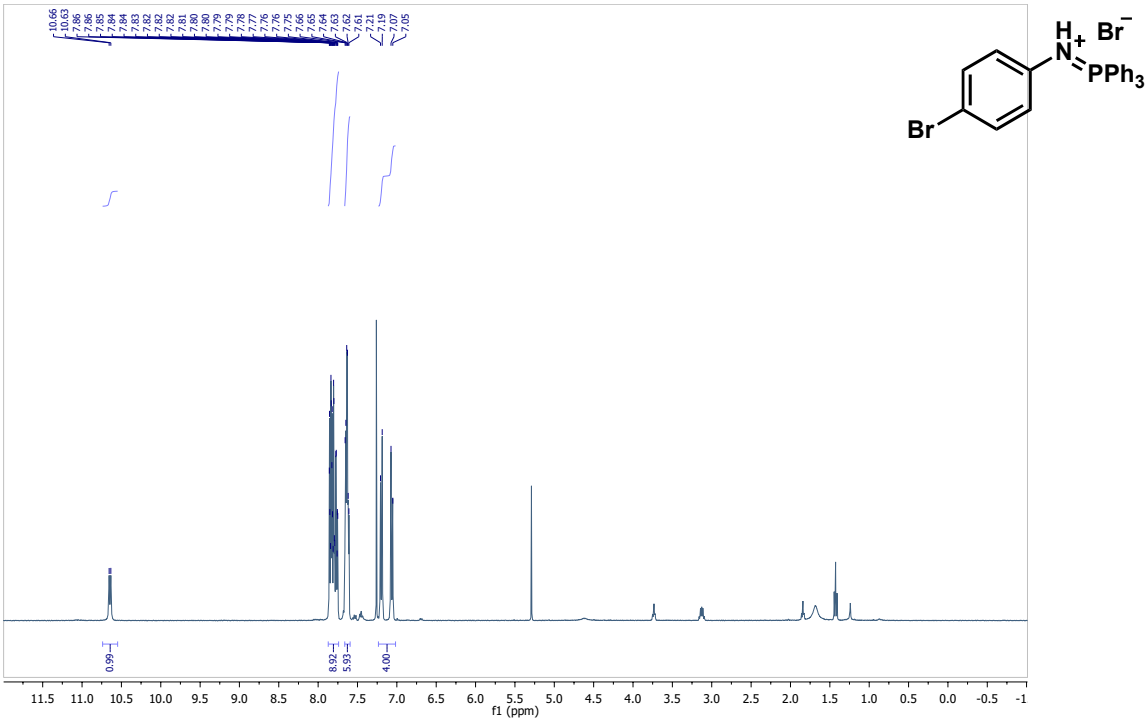


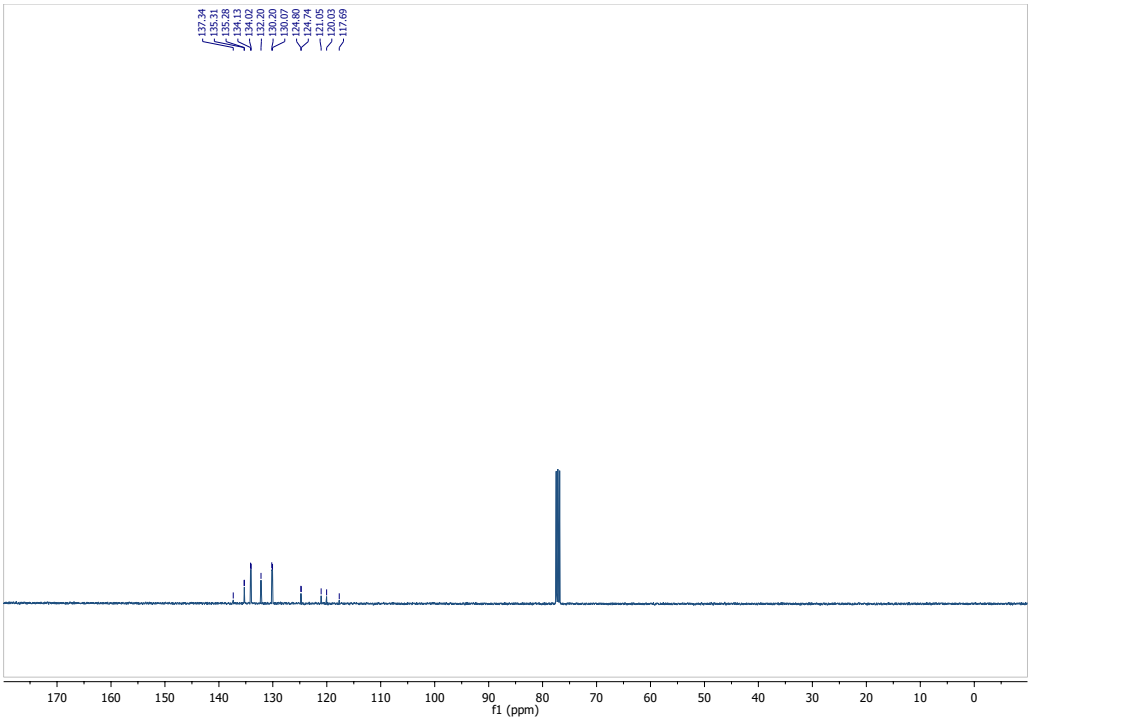

157.29
134.97
134.94
134.35
134.15
129.96
129.83
129.66
126.79
126.74
121.68
120.86
114.50
55.54
f1 (ppm)

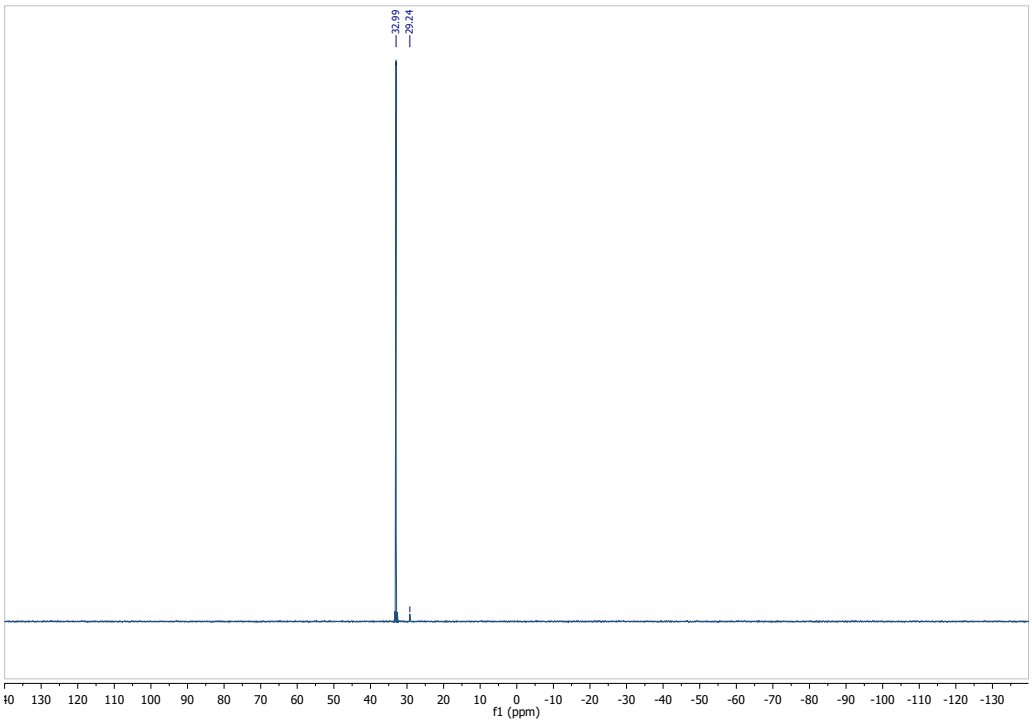

34.26
f1 (ppm)

1c. 4-bromo-*N*-(triphenylphosphanylidene)anilinium bromide

Followed the general procedure (**1**), product obtained as a white solid (209 mg, yield 68%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 10.65 (d, *J* = 8.5 Hz, 1H), 7.86–7.75 (m, 9H), 7.66–7.61 (m, 6 H), 7.20 (d, *J* = 8 Hz, 2H), 7.06 (d, *J* = 8 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): 137.3, 135.3 (d, *J* = 3 Hz), 134.1 (d, *J* = 11 Hz), 132.2, 130.1 (d, *J* = 14 Hz), 124.8 (d, *J* = 7 Hz), 120.5 (d, *J* = 103 Hz), 117.7. ^{31}P-NMR (162 MHz, $CDCl_3$): δ 32.99 (s, 1P), 29.24 (s, 1P, TPPO). MS (ESI+): Calculated $C_{24}H_{20}NBrP$ as 432.0517, [M+H] found as 432.0504.

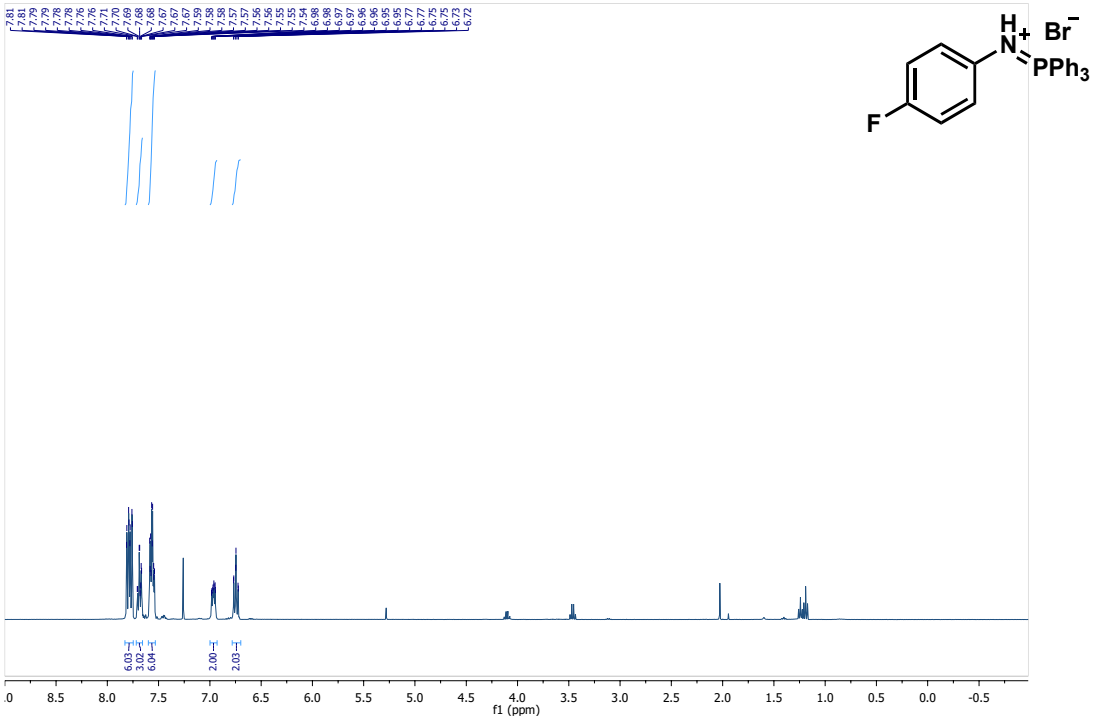


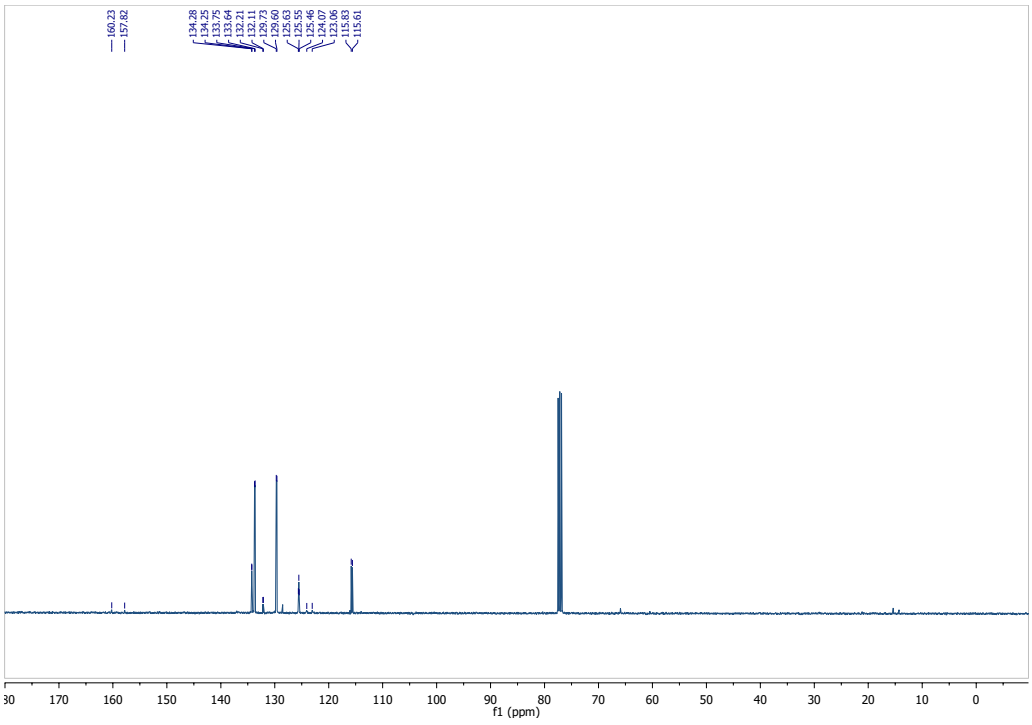



32.99
29.24
40 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

1d. 4-fluoro-*N*-(triphenylphoshanylidene)anilinium bromide

Followed the general procedure (**1**), product obtained as an off-white solid (44 mg, yield 17%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.79 (m, 6H), 7.69 (m, 3H), 7.57 (m, 6H), 6.97 (m, 2H), 6.75 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): 159.0 (d, *J* = 242 Hz), 134.3 (d, *J* = 3 Hz), 133.7 (d, *J* = 11 Hz), 132.2 (d, *J* = 10 Hz), 129.7 (d, *J* = 13 Hz), 125.5 (dd, *J* = 9, 8 Hz), 123.6 (d, *J* = 101 Hz), 115.7 (d, *J* = 22 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$): δ 34.32 (s, 1P). ^{19}F-NMR (376 MHz, $CDCl_3$): -113.46 (s, 1F, amine), -117.38 (s, 1F). MS (ESI+): Calculated $C_{24}H_{20}NFP$ as 372.1317, [M+H] found as 372.1307.




160.23
157.82
134.28
134.25
133.75
133.64
132.21
132.11
129.73
129.60
125.65
125.55
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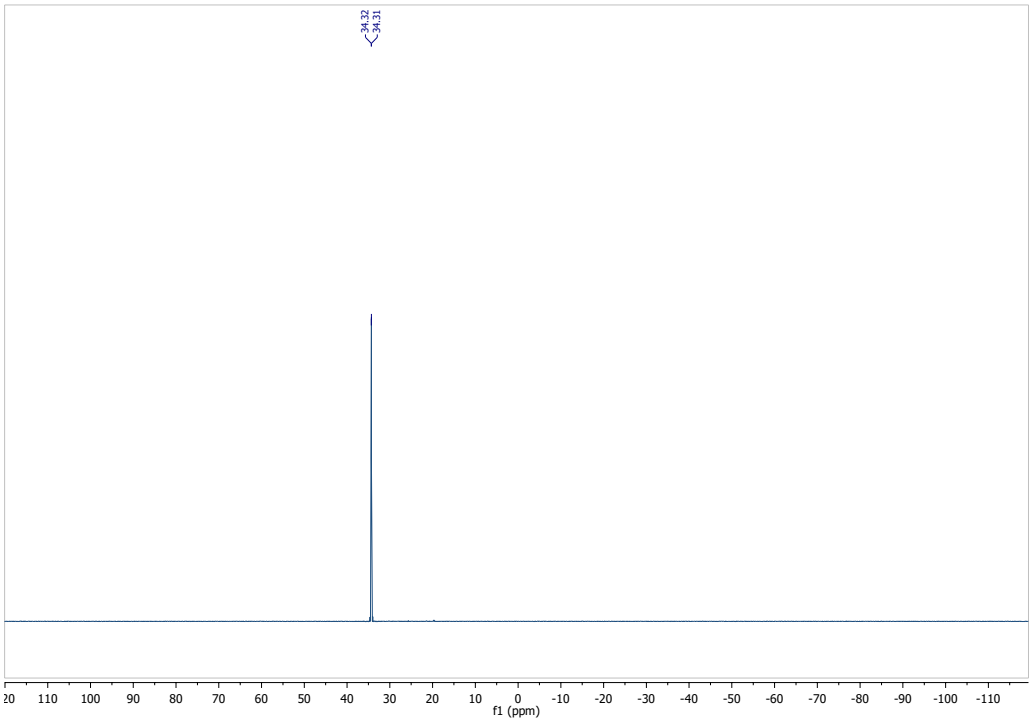
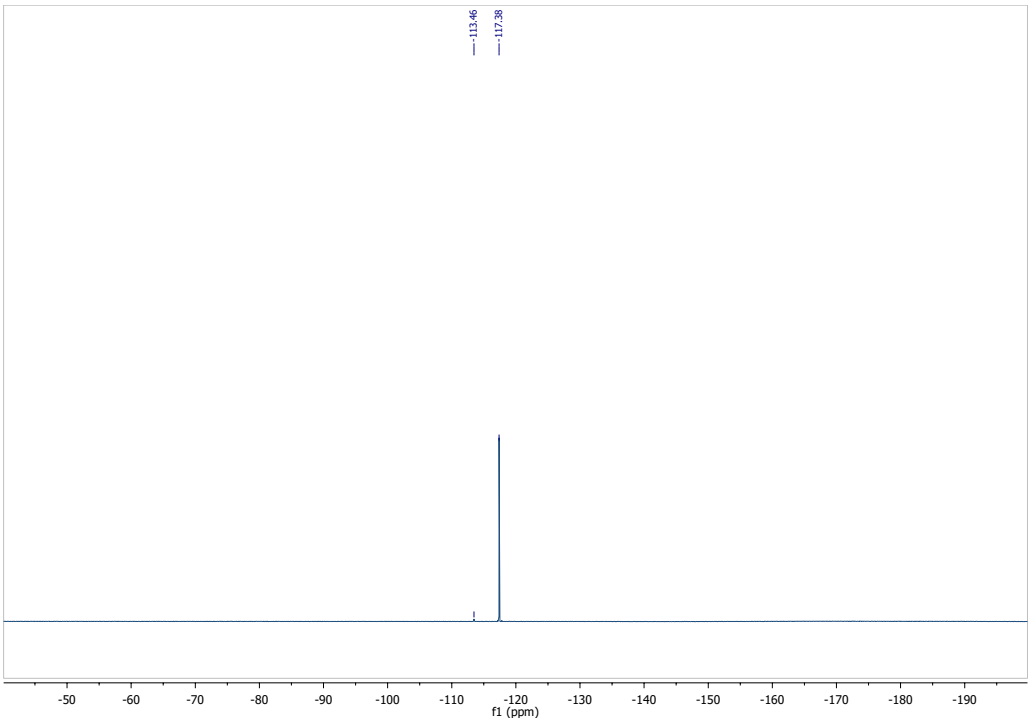
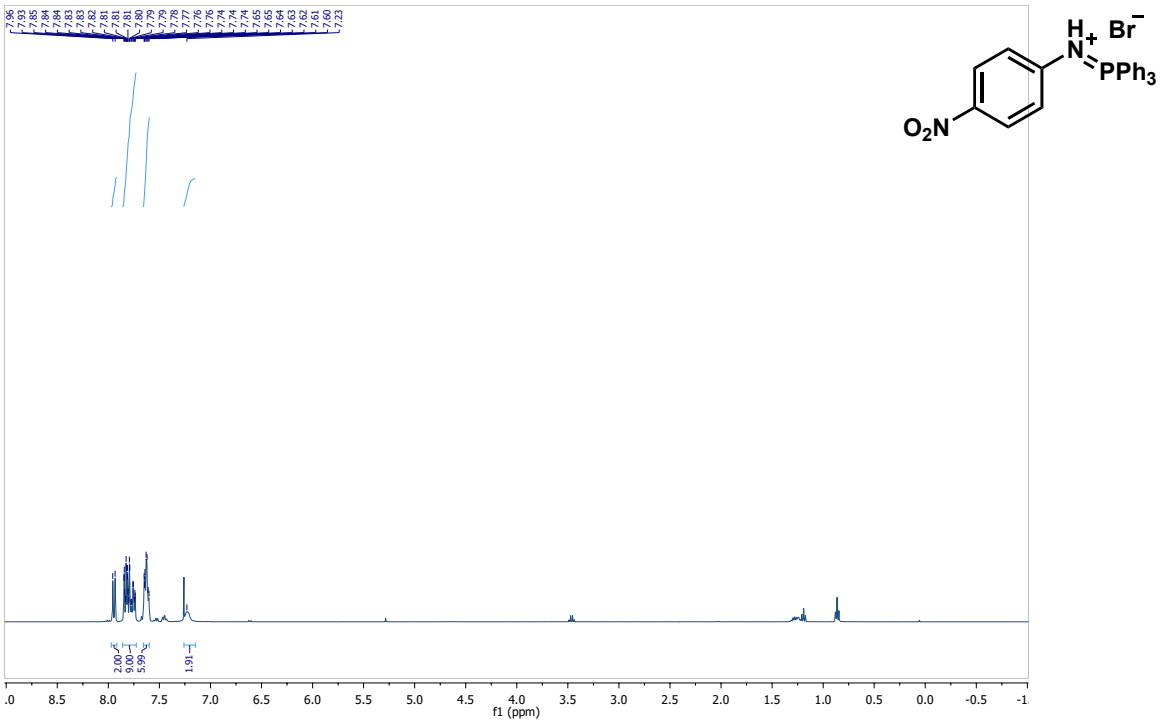
123.06
115.83
115.61
f1 (ppm)

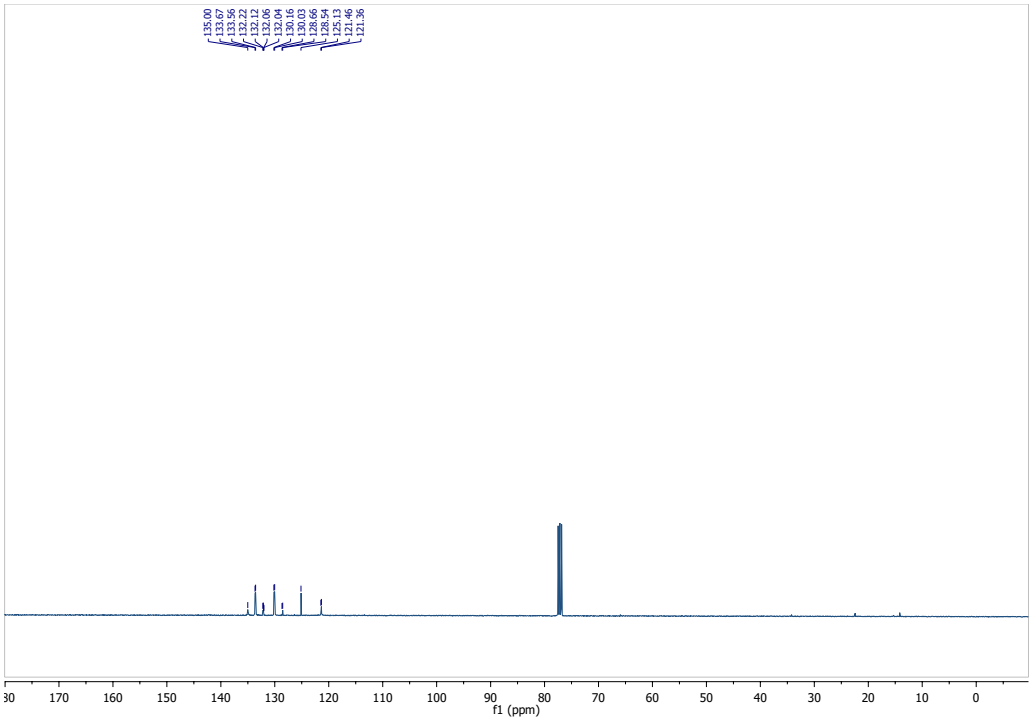

34.32
34.31
f1 (ppm)

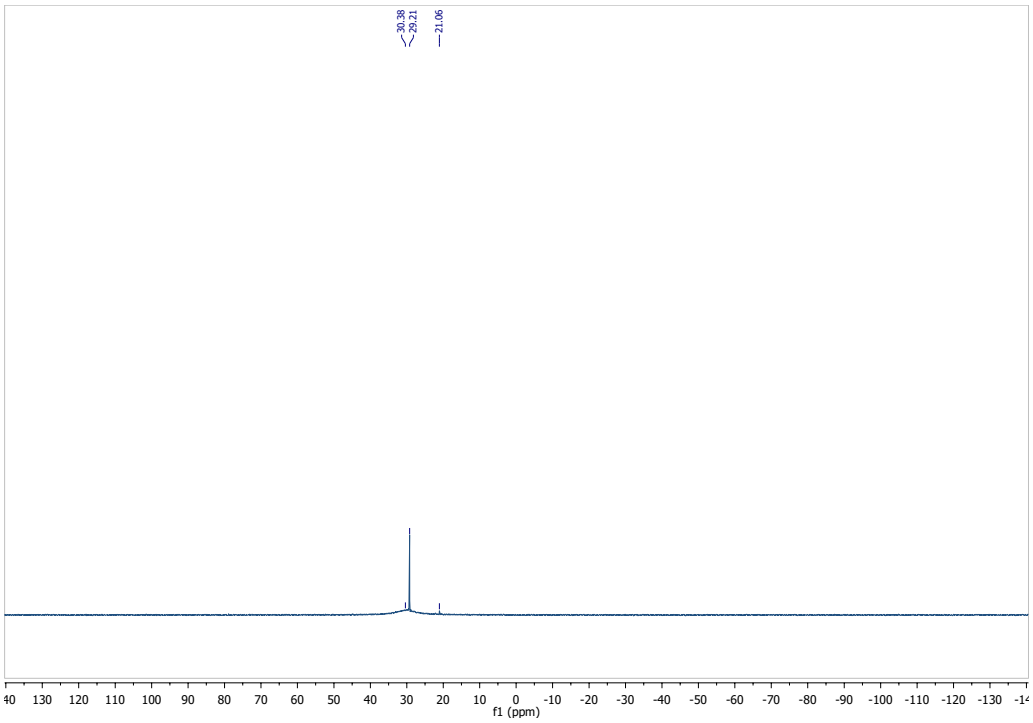

113.46
117.38
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

1e. 4-nitro-*N*-(triphenylphosphanylidene)anilinium bromide

Followed the general procedure (**1**), product obtained as a yellow solid (230 mg, yield 80%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 12 Hz, 2H), 7.85–7.74 (m, 9H), 7.63 (m, 6H), 7.23 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): 135.0, 133.6 (d, *J* = 11 Hz), 132.2 (d, *J* = 10 Hz), 132.1 (d, *J* = 3 Hz), 130.1 (d, *J* = 13 Hz), 128.6 (d, *J* = 12 Hz), 125.1, 121.4 (d, *J* = 10 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$): δ 30.38 (s, 1P), 29.21 (s, 1P, TPPO). MS (ESI+): Calculated $C_{24}H_{20}N_2O_2P$ as 399.1262, [M+H] found as 399.1248.

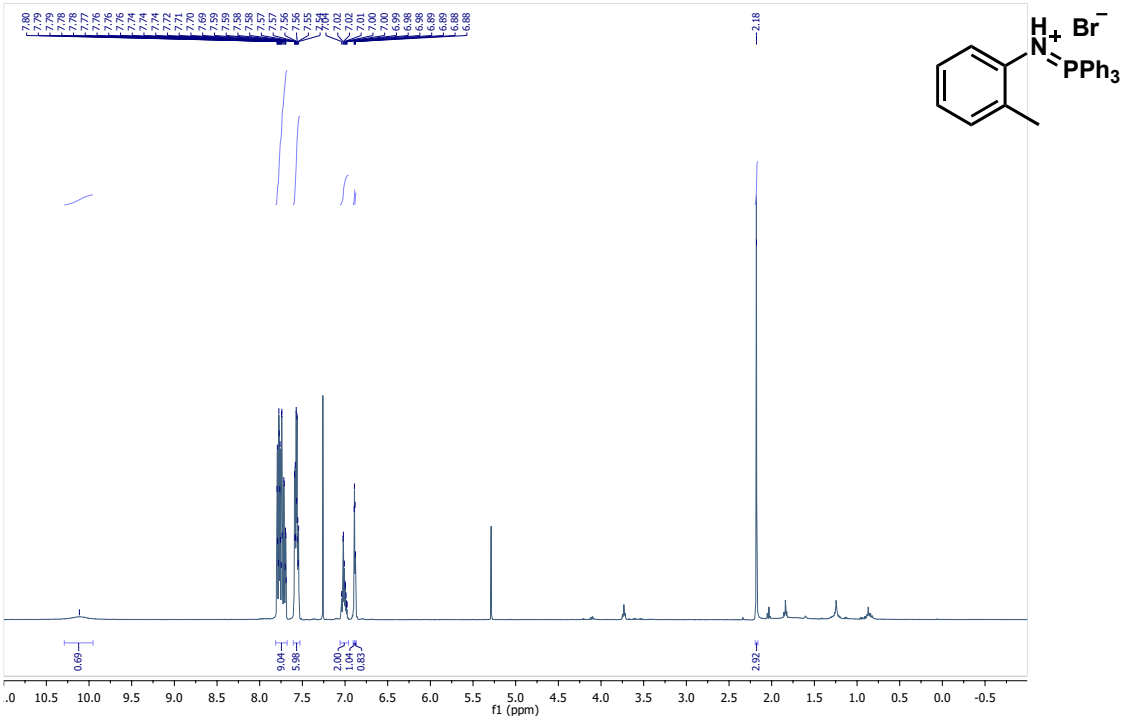


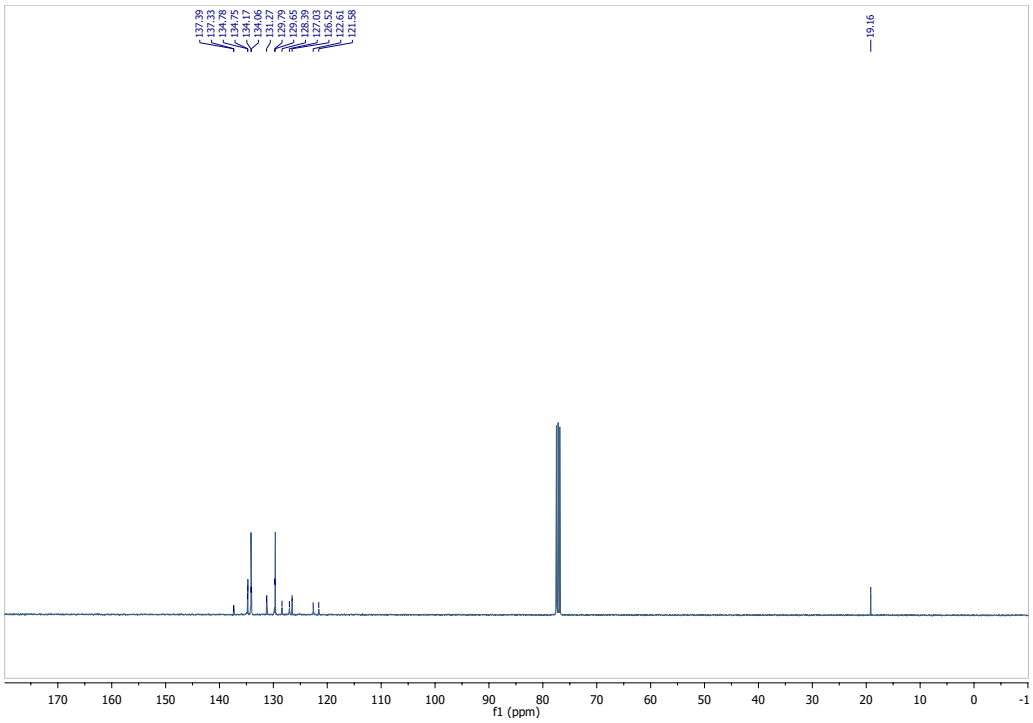


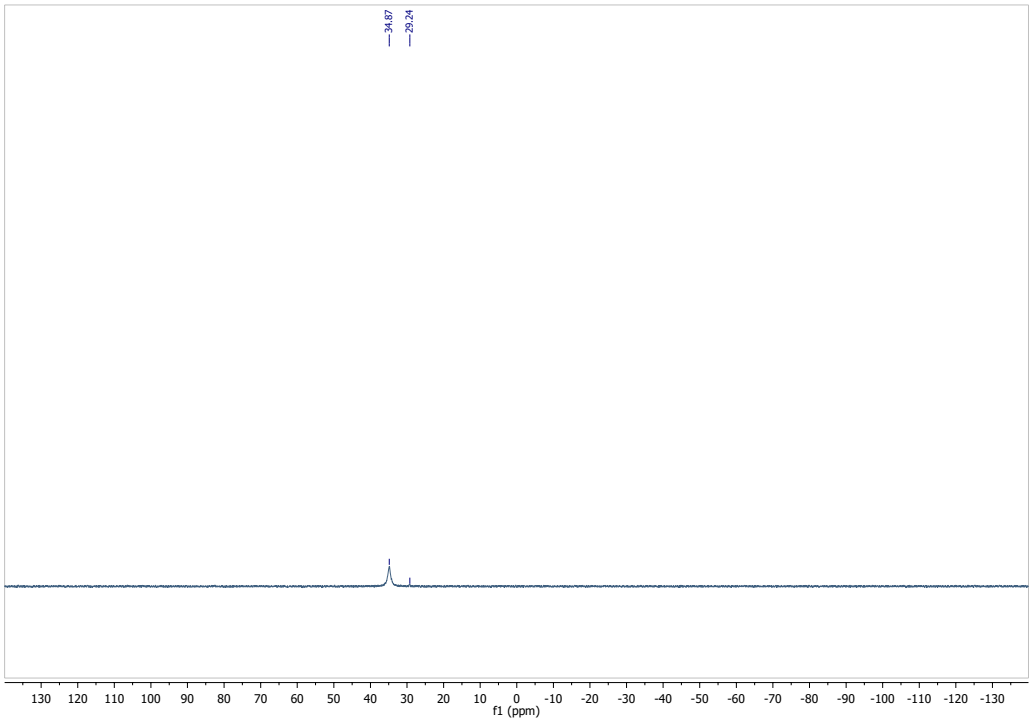

30.38
29.21
21.06
40 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -14
f1 (ppm)

1f. 2-methyl-*N*-(triphenylphosphanylidene)anilinium bromide

Followed the general procedure (**1**), product obtained as a white solid (76 mg, yield 28%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 10.11 (s, 1H), 7.80–7.58 (m, 9H), 7.59–7.54 (m, 6H), 7.04–6.98 (m, 2H), 6.89 (d, *J* = 1.5 Hz, 1H), 6.88 (d, J = 1.5 Hz, 1H), 2.18 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): 137.4 (d, *J* = 6 Hz), 134.8 (d, *J* = 3 Hz), 134.1 (d, *J* = 11 Hz), 131.3, 129.7 (d, *J* = 13 Hz), 127.7 (d, *J* = 138 Hz), 126.5, 122.1 (d, *J* = 104 Hz), 19.2. ^{31}P-NMR (162 MHz, $CDCl_3$): δ 34.87 (s, 1P), 29.24 (s, 1P, TPPO). MS (ESI+): Calculated $C_{25}H_{23}NP$ as 368.1568, [M+H] found as 368.1555.

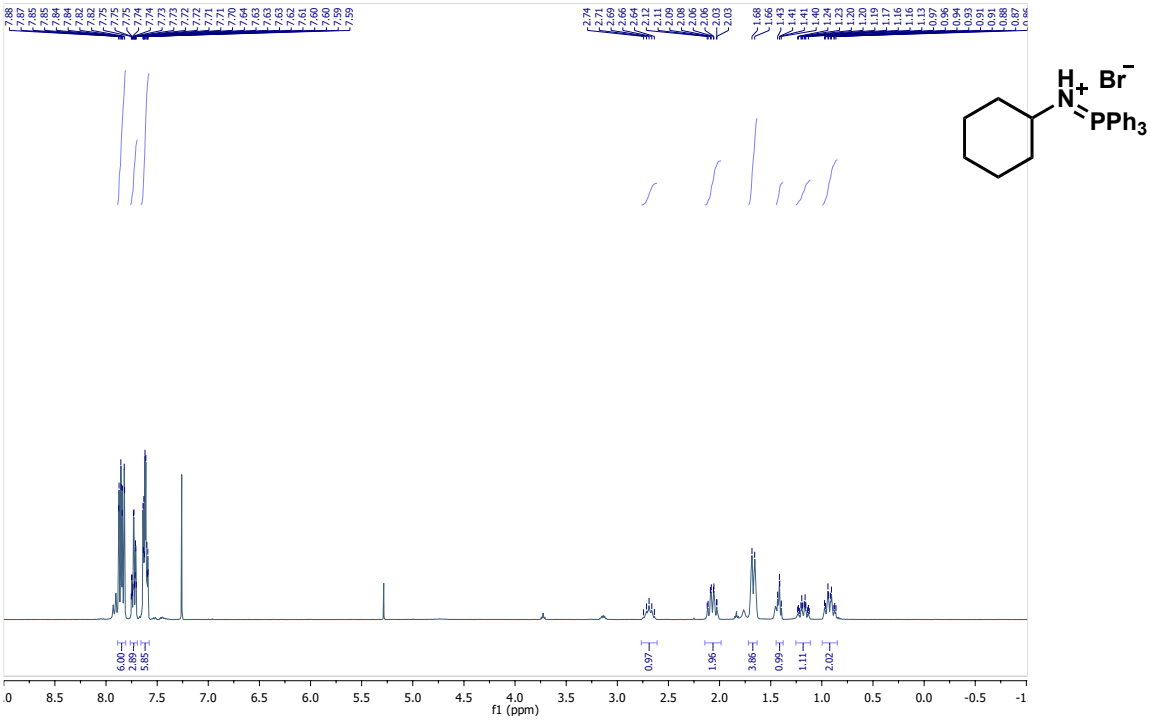


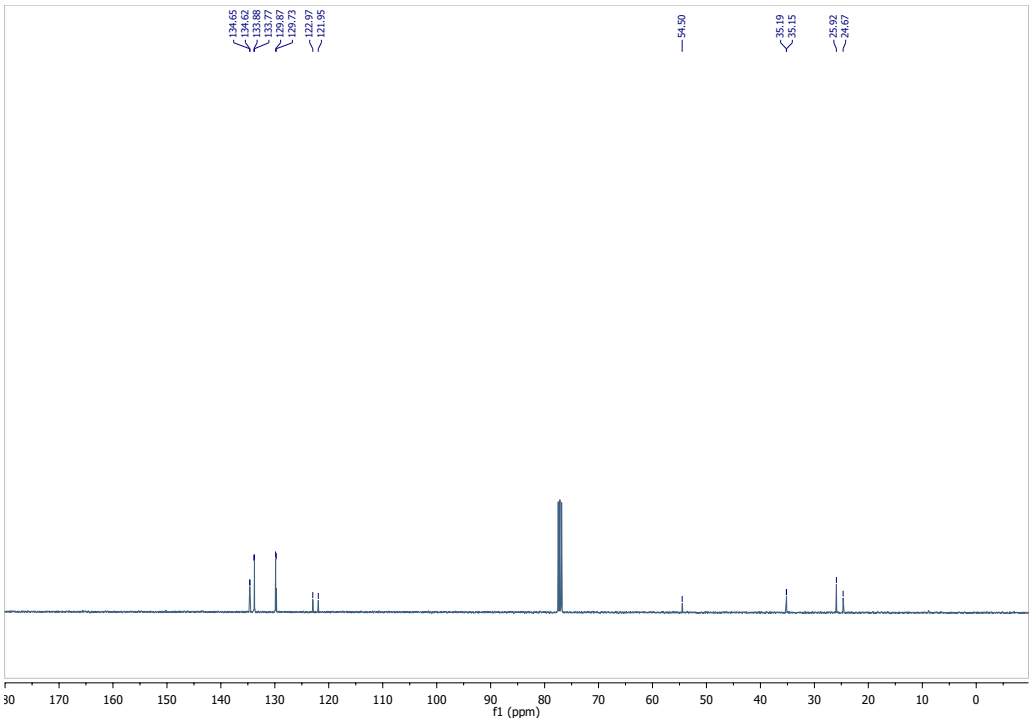

137.39
137.33
134.78
134.75
134.17
134.06
131.27
129.79
129.65
128.39
127.03
126.72
122.61
121.58
19.16
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

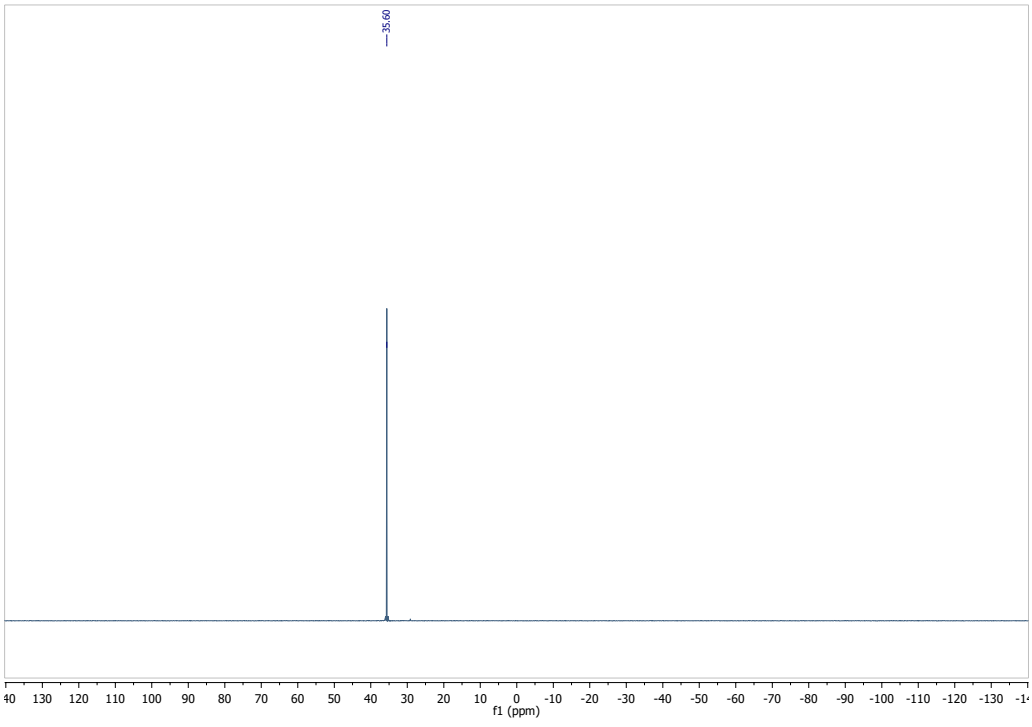

34.87
29.24
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

1g. *N*-(triphenylphosphanylidene)cyclohexanaminium bromide

Followed the general procedure (**1**), product obtained as a white solid (147 mg, yield 56%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.88–7.82 (m, 6H), 7.75–7.70 (m, 3H), 7.64–7.59 (m, 6H), 2.69 (m, 1H), 2.12–2.03 (m, 2H), 1.67 (d, *J* = 10.9 Hz, 4H), 1.42 (m, 1H), 1.18 (m, 1H), 0.92 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): 134.6 (d, *J* = 3 Hz), 133.8 (d, *J* = 11 Hz), 129.8 (d, *J* = 13 Hz), 122.5 (d, *J* = 103 Hz), 54.5, 35.2 (d, *J* = 4 Hz), 25.9, 24.7. ^{31}P-NMR (162 MHz, $CDCl_3$): δ 35.60 (s, 1P). MS (ESI+): Calculated $C_{24}H_{27}NP$ as 360.1881, [M+H] found as 360.1879.

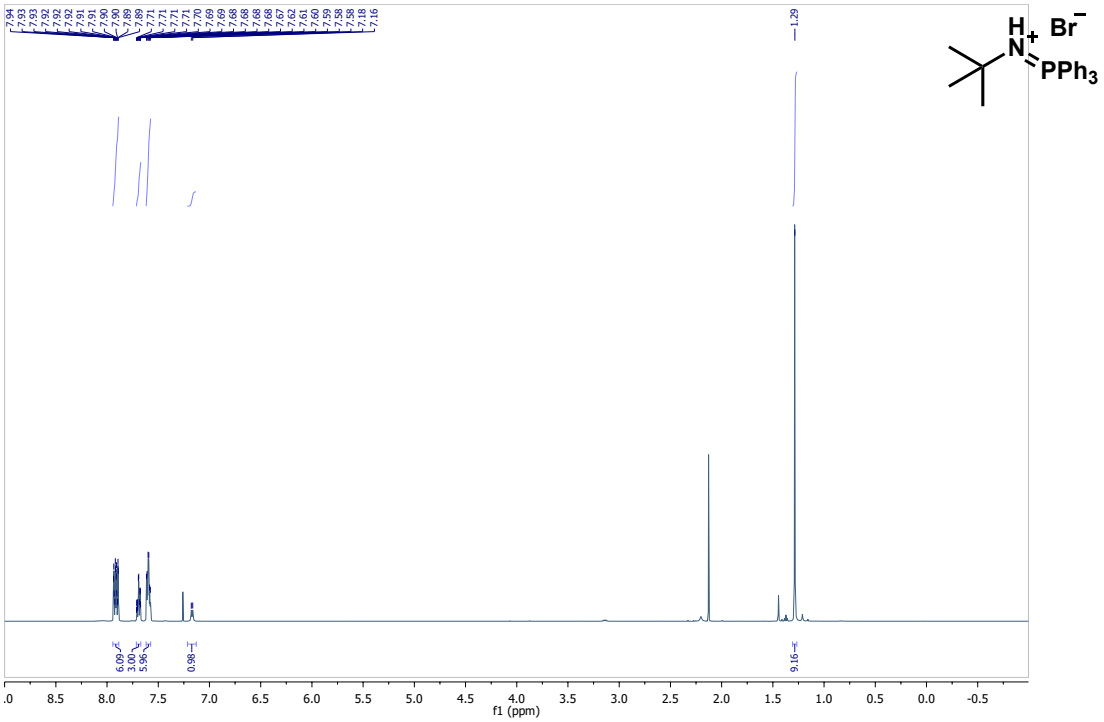


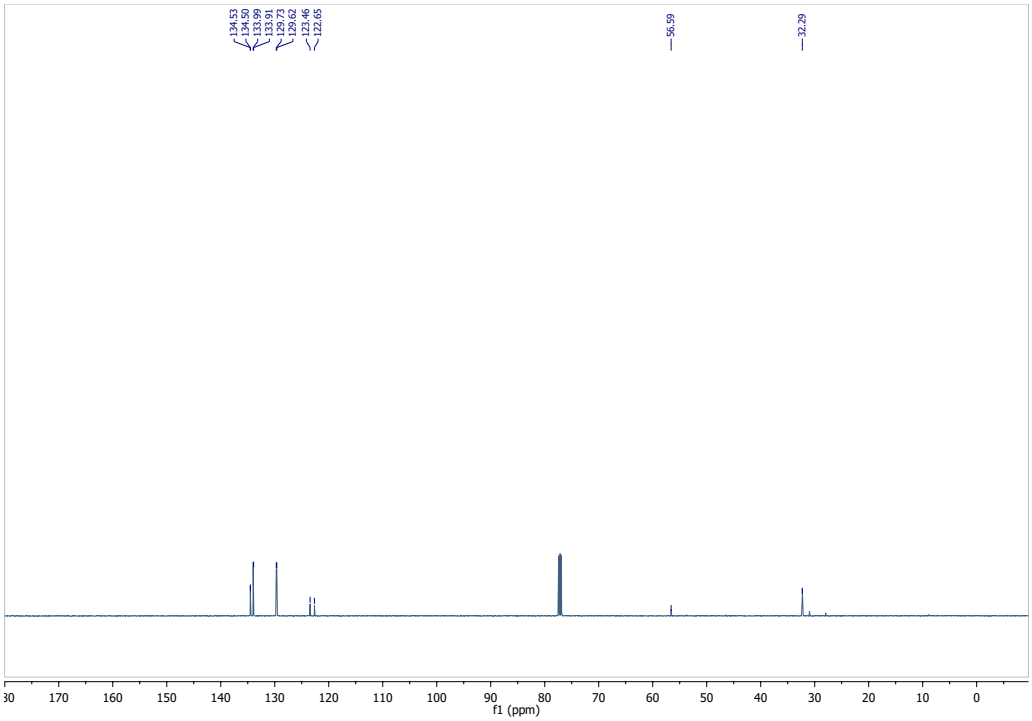

134.65
134.62
133.88
133.77
129.87
129.73
122.97
121.95
54.50
35.19
35.15
25.92
24.67
f1 (ppm)

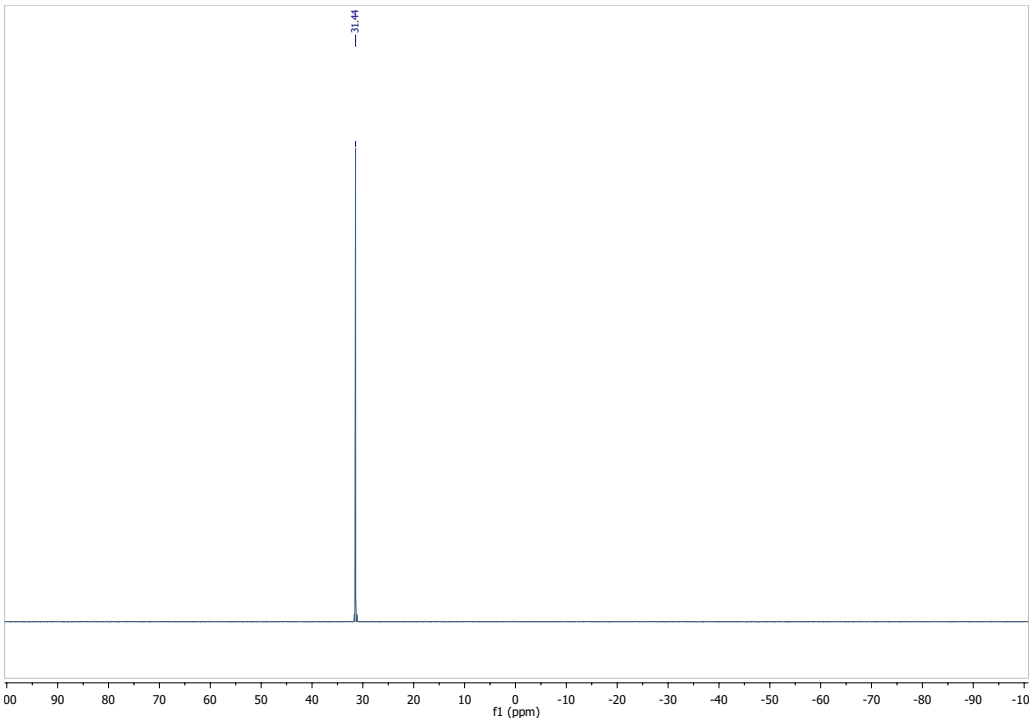

35.60
f1 (ppm)

1h. *tert*-butyl(triphenylphosphanylidene)azanium bromide

Followed the general procedure (**1**), product obtained as a white solid (47 mg, yield 19%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.94–7.89 (m, 6H), 7.71–7.67 (m, 3H), 7.62–7.58 (m, 6H), 7.17 (d, *J* = 6.9 Hz, 1H), 1.29 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): 134.5 (d, *J* = 3 Hz), 134.0 (d, *J* = 11 Hz), 129.7 (d, *J* = 13 Hz), 123.1 (d, *J* = 102 Hz), 56.6, 32.3. ^{31}P-NMR (162 MHz, $CDCl_3$): δ 31.44 (s, 1P). MS (ESI+): Calculated $C_{22}H_{25}NP$ as 334.1725, [M+H] found as 334.1703.

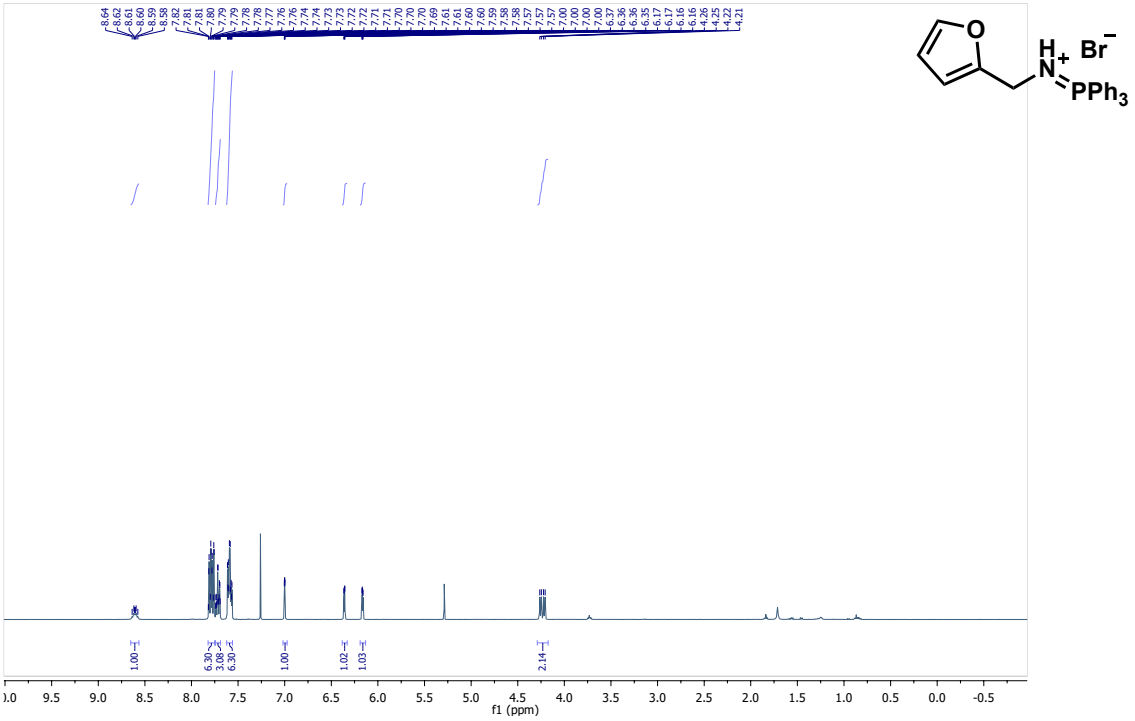


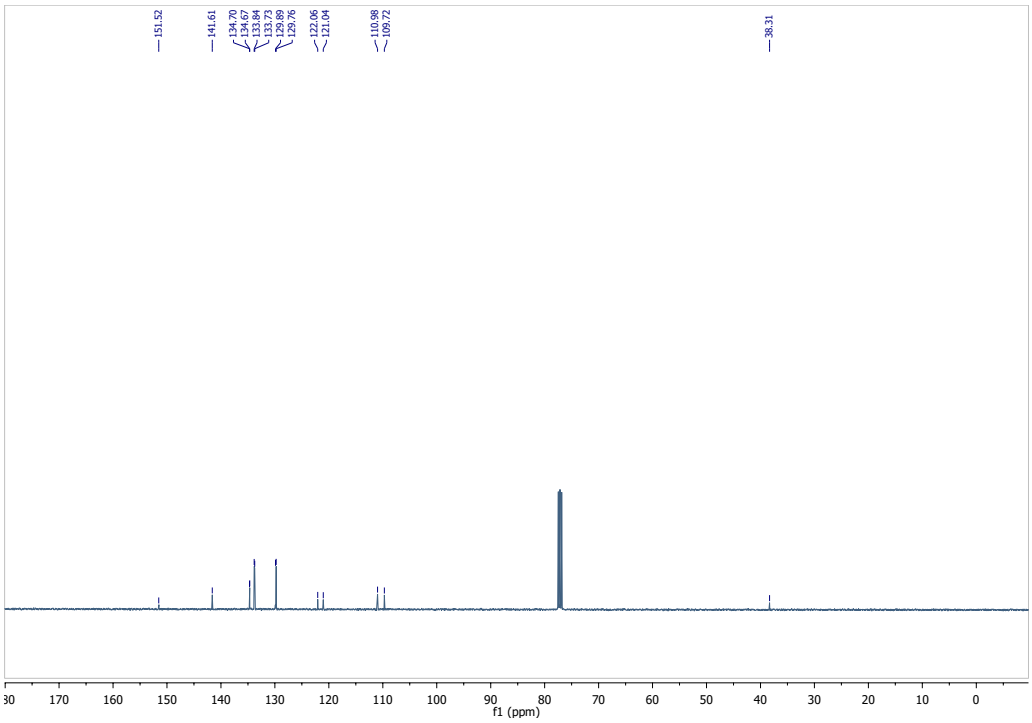


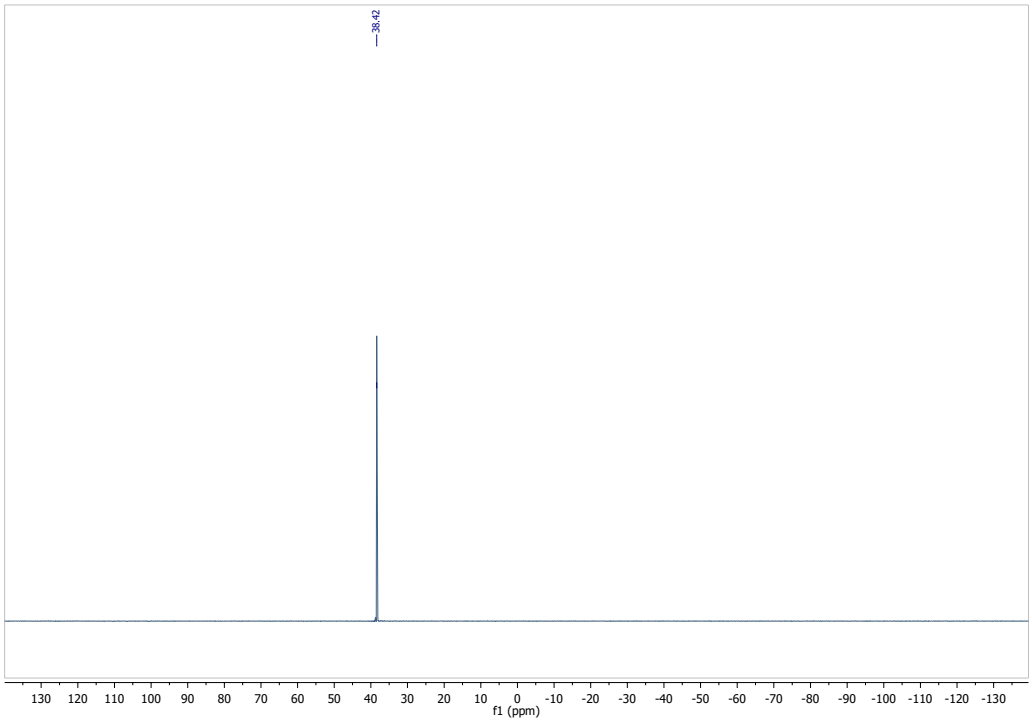

31.44
00 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -10
f1 (ppm)

1i. [(furan-2-yl)methyl](triphenylphosphanylidene)azanium bromide

Followed the general procedure (**1**), product obtained as a white solid (142 mg, yield 54%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.61 (m, 1H), 7.82–7.76 (m, 6H), 7.74–7.69 (m, 3H), 7.61–7.57 (m, 6H), 7.00 (dd, *J* = 1.9, 0.8 Hz, 1H), 6.36 (dd, *J* = 3.3, 0.8 Hz, 1H), 6.17 (dd, *J* = 3.3, 1.8 Hz, 1H), 4.24 (dd, *J* = 16.2, 6.8 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): 151.5, 141.6, 134.7 (d, *J* = 3 Hz), 133.8 (d, *J* = 11 Hz), 129.8 (d, *J* = 13 Hz), 121.6 (d, *J* = 103 Hz), 111.0, 109.7, 38.3. ^{31}P-NMR (162 MHz, $CDCl_3$): δ 38.42 (s, 1P). MS (ESI+): Calculated $C_{23}H_{21}NPO$ as 358.1361, [M+H] found as 358.1364.

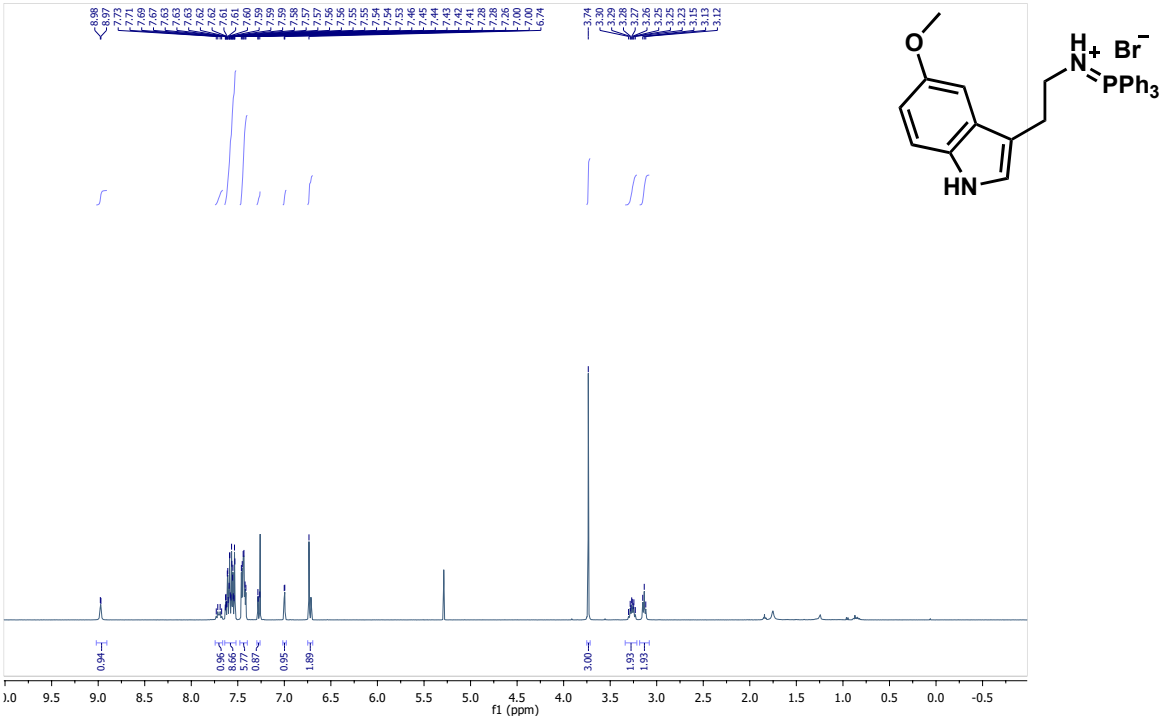


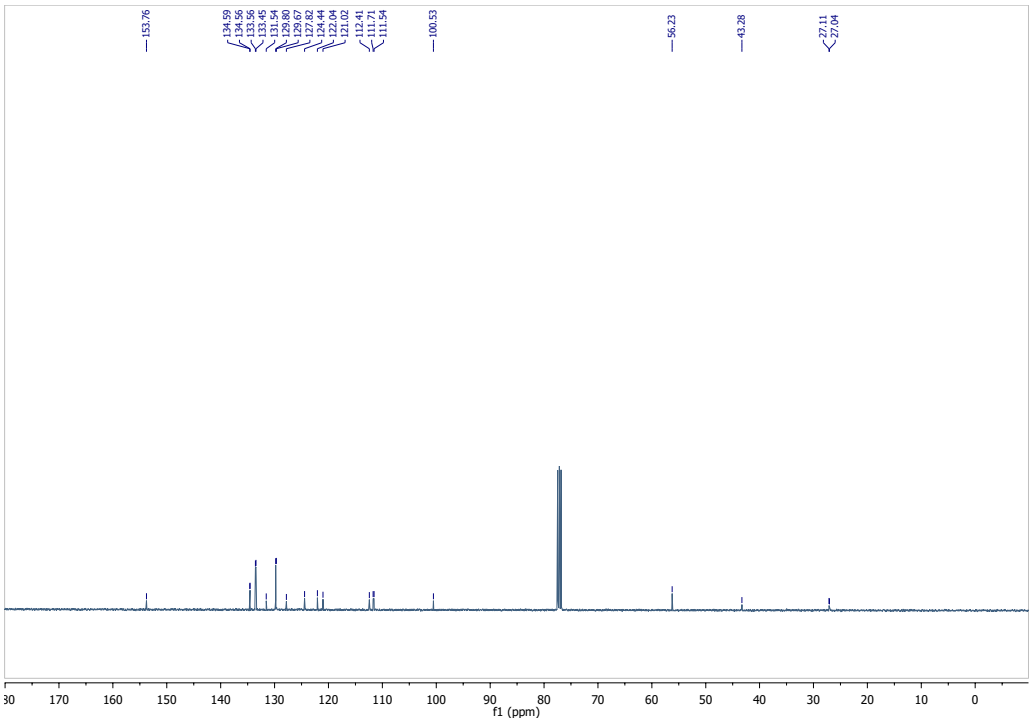

151.52
141.61
134.70
134.47
133.84
133.73
129.89
129.76
122.06
121.04
110.98
109.72
38.31
f1 (ppm)

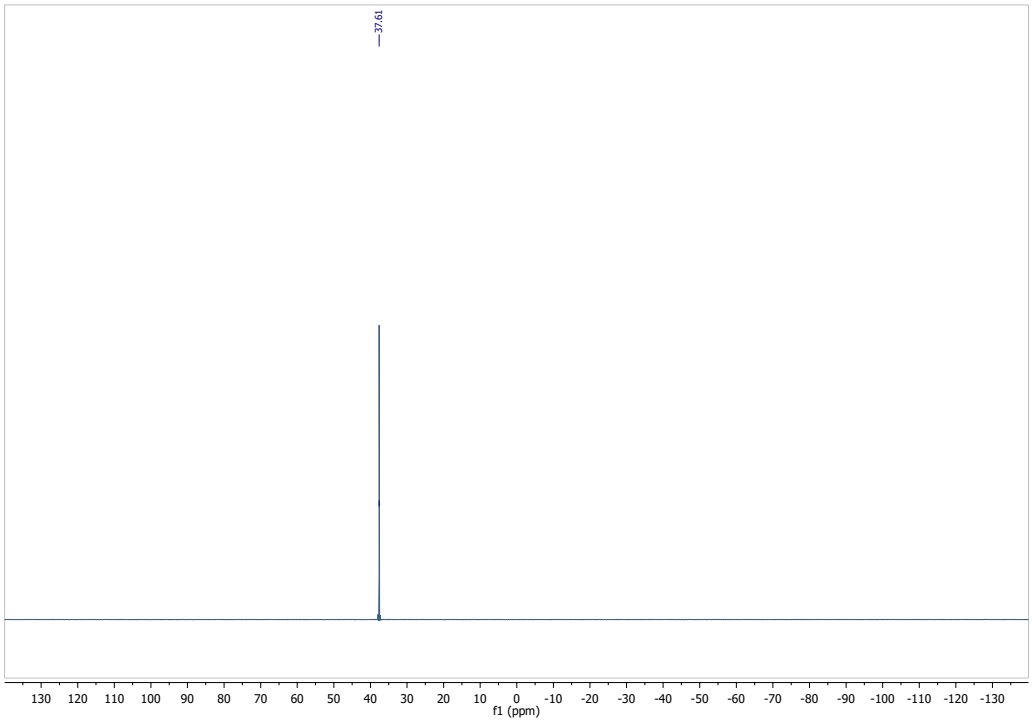

38.42
f1 (ppm)

1j. [2-(5-methoxy-1H-indol-3-yl)ethyl](triphenylphosphanylidene)azanium bromide

Followed the general procedure (**1**), product obtained as a white solid (143 mg, yield 45%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.98 (d, *J* = 2.5 Hz, 1H), 7.70 (m, 1H), 7.63–7.53 (m, 9H), 7.46–7.41 (m, 6H), 7.27 (m, 1H), 7.00 (dd, *J* = 2.4 Hz, 1H), 6.74 (s, 1H), 3.74 (s, 3H), 3.27 (m, 2H), 3.13 (t, *J* = 6.5 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): 153.8, 134.6 (d, *J* = 3 Hz), 133.5 (d, *J* = 11 Hz), 131.5, 129.7 (d, *J* = 13 Hz), 127.8, 124.4, 121.5 (d, *J* = 103 Hz), 112.4, 111.7, 111.5, 100.5, 56.2, 43.3, 27.1 (d, *J* = 7 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$): δ 37.61 (s, 1P). MS (ESI+): Calculated $C_{29}H_{28}N_2PO$ as 451.1939, [M+H] found as 451.1922.

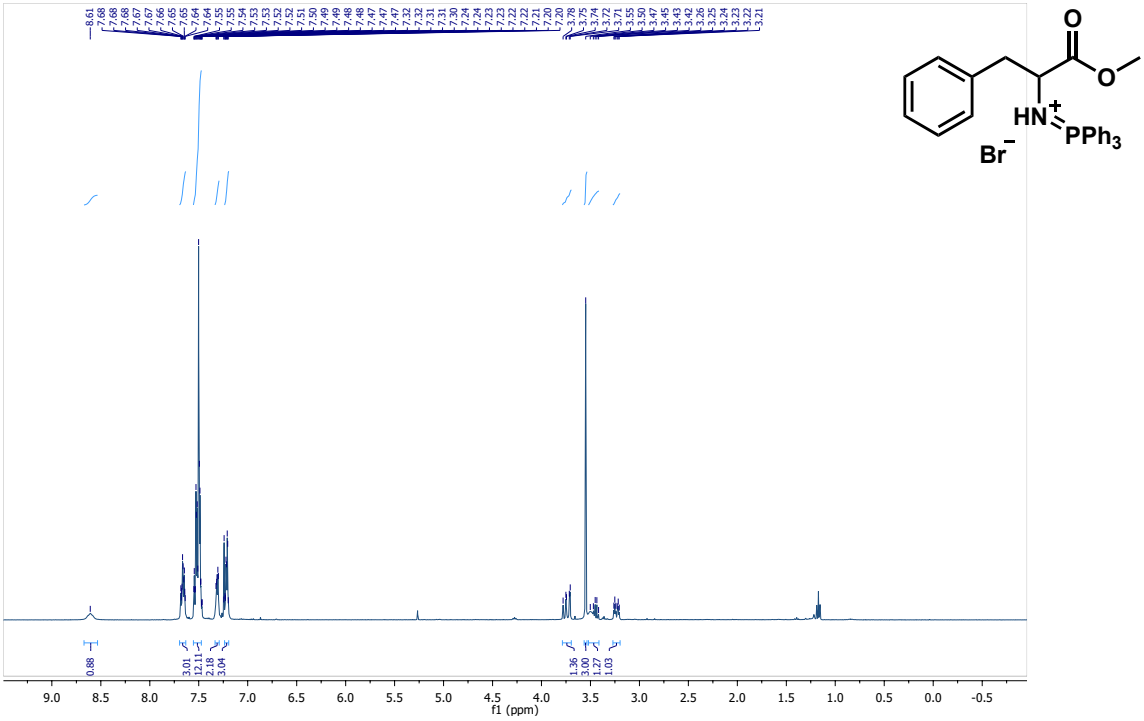


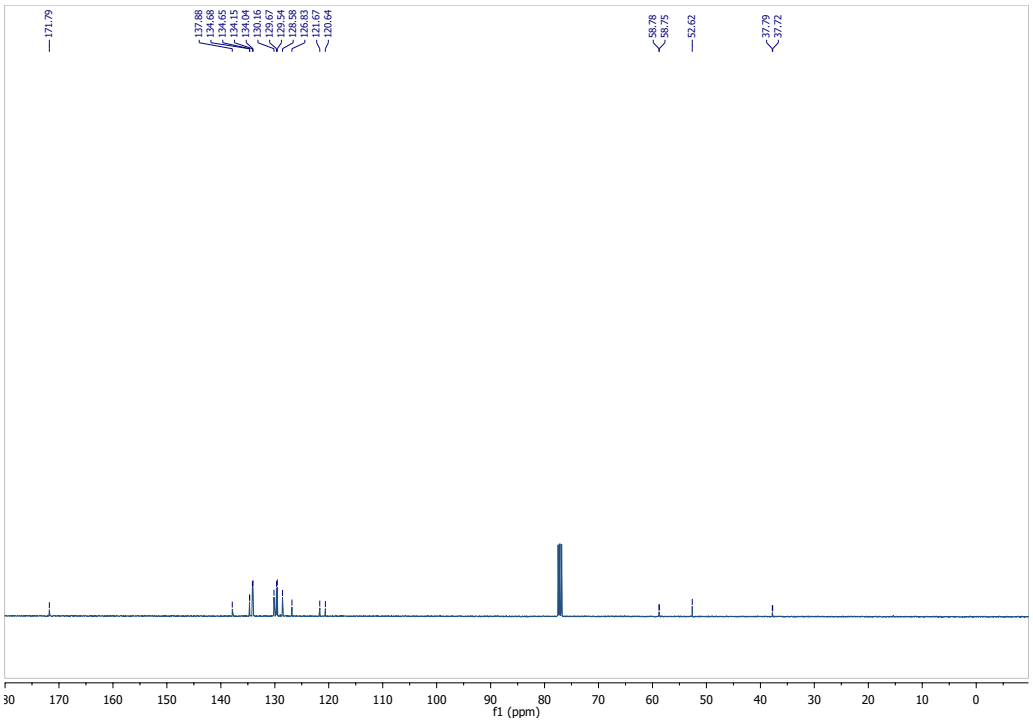

153.76
134.59
134.56
133.56
133.45
131.54
130.80
129.67
127.82
124.44
122.04
121.02
112.41
111.71
111.54
100.53
56.23
43.28
27.11
27.04
f1 (ppm)

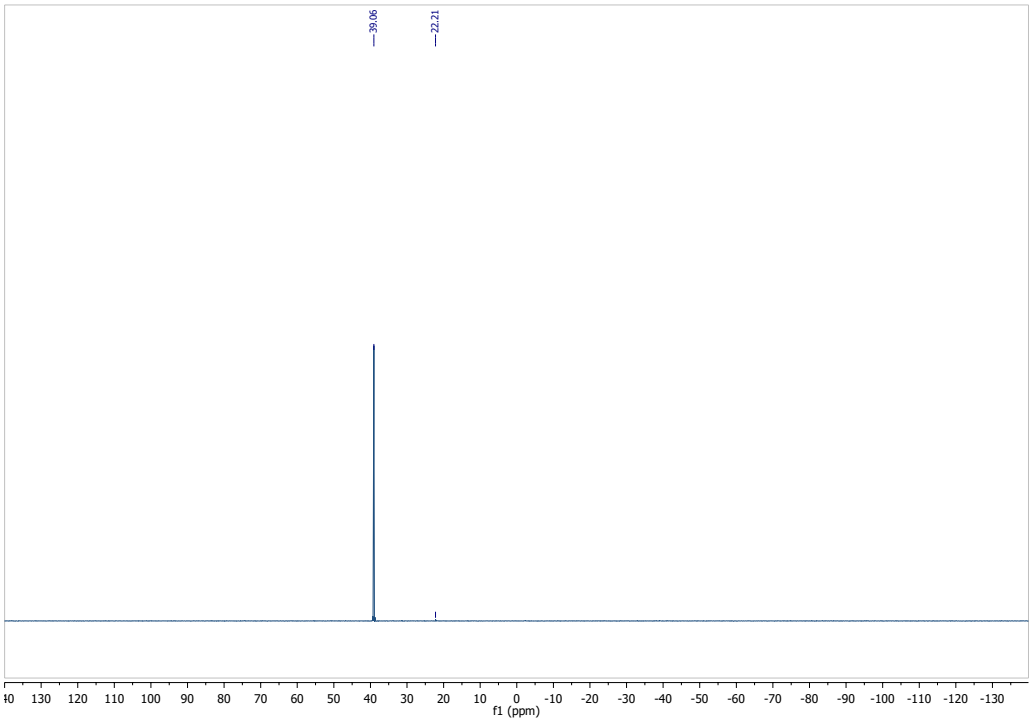

37.61
f1 (ppm)

1k. (1-methoxy-1-oxo-3-phenylpropan-2-yl)(triphenylphosphanylidene)azanium bromide

Followed the general procedure (**1**), product obtained as a white solid (78 mg, yield 25%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.61 (s, 1H), 7.66 (m, 3H), 7.51 (m, 12H), 7.31 (m, 2H), 7.22 (m, 3H), 3.75 (m, 1H), 3.55 (s, 3H), 3.46 (m, 1H), 3.24 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): 171.8, 137.9, 134.7 (d, *J* = 3 Hz), 134.1 (d, *J* = 11 Hz), 130.2, 129.6 (d, *J* = 13 Hz), 128.6, 126.9, 121.2 (d, *J* = 104 Hz), 58.8 (d, *J* = 3 Hz), 52.6, 37.8 (d, *J* = 8 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$): δ 39.06 (s, 1P), 22.21 (s, 1P, TPPO). MS (ESI+): Calculated $C_{28}H_{27}NPO_2$ as 440.1779, [M+H] found as 440.1785.

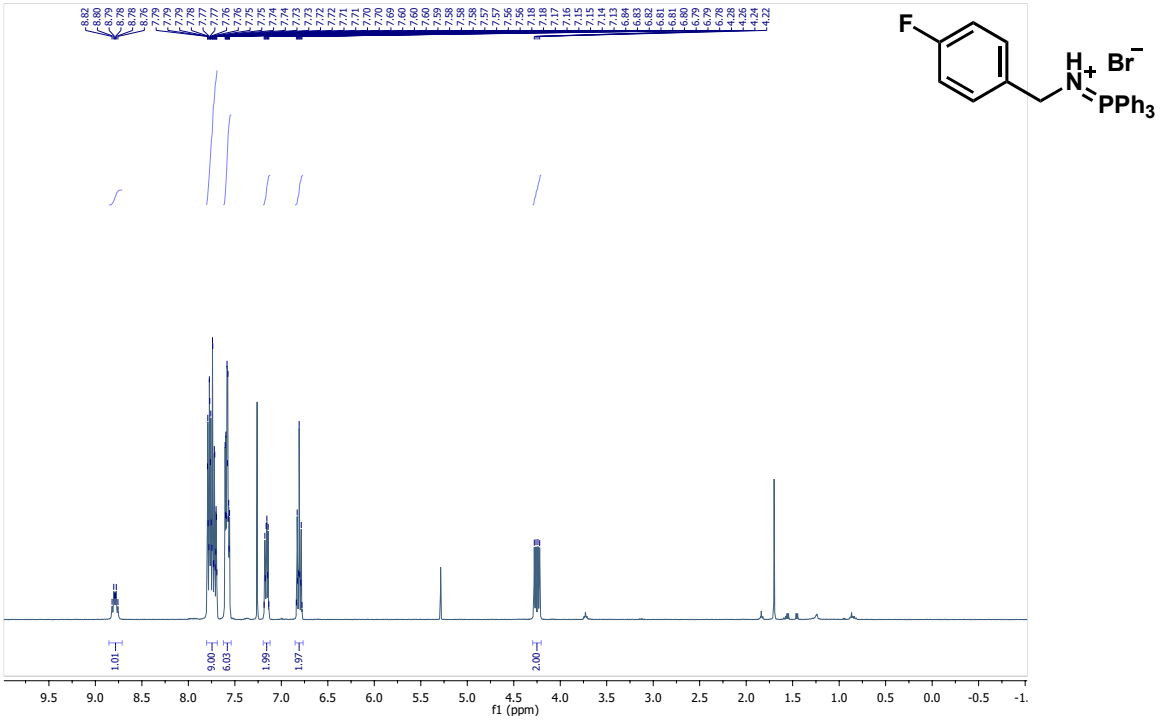


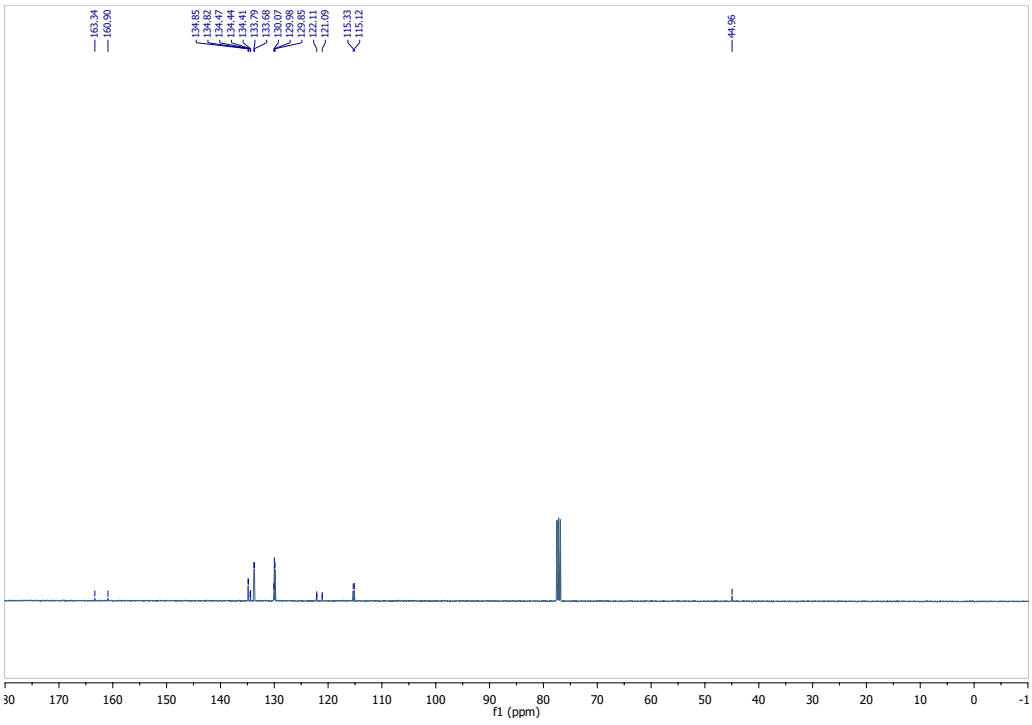

171.79
137.88
134.68
134.65
134.15
134.04
130.16
129.67
129.54
128.58
126.83
121.67
120.64
58.78
58.75
52.62
37.79
37.72
f1 (ppm)

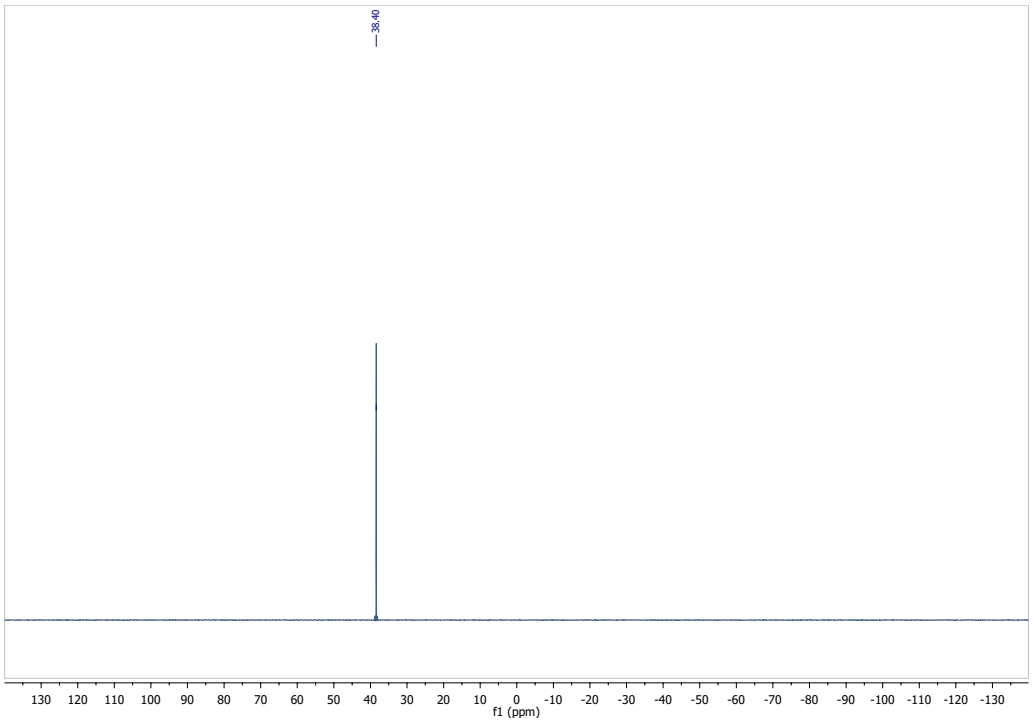

39.06
22.21
f1 (ppm)

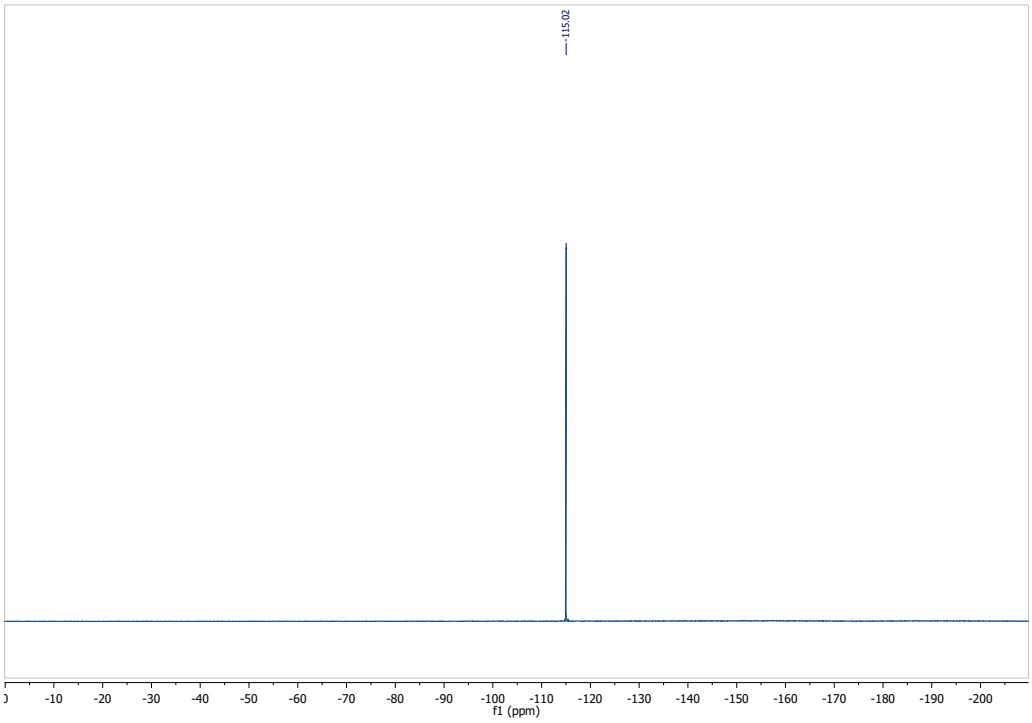
1l. [(4-fluorophenyl)methyl](triphenylphosphanylidene)azanium bromide

Followed the general procedure (**1**), product obtained as a white solid (100 mg, yield 36%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.79 (m, 1H), 7.79–7.70 (m, 9H), 7.60–7.56 (m, 6H), 7.18–7.13 (m, 2H), 6.84–6.78 (m, 2H), 4.25 (dd, *J* = 15.8, 7.3 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): 162.1 (d, *J* = 246 Hz), 134.8 (d, *J* = 3 Hz), 134.4 (dd, *J* = 3, 3), 133.7 (d, *J* = 11 Hz), 130.1, 129.9 (d, *J* = 13 Hz), 121.6 (d, *J* = 102 Hz), 115.2 (d, *J* = 21 Hz), 45.0. ^{31}P-NMR (162 MHz, $CDCl_3$): δ 38.40 (s, 1P). ^{19}F-NMR (376 MHz, $CDCl_3$): -115.02 (s, 1F). MS (ESI+): Calculated $C_{25}H_{22}NPF$ as 386.1474 [M+H] found as 386.1492.



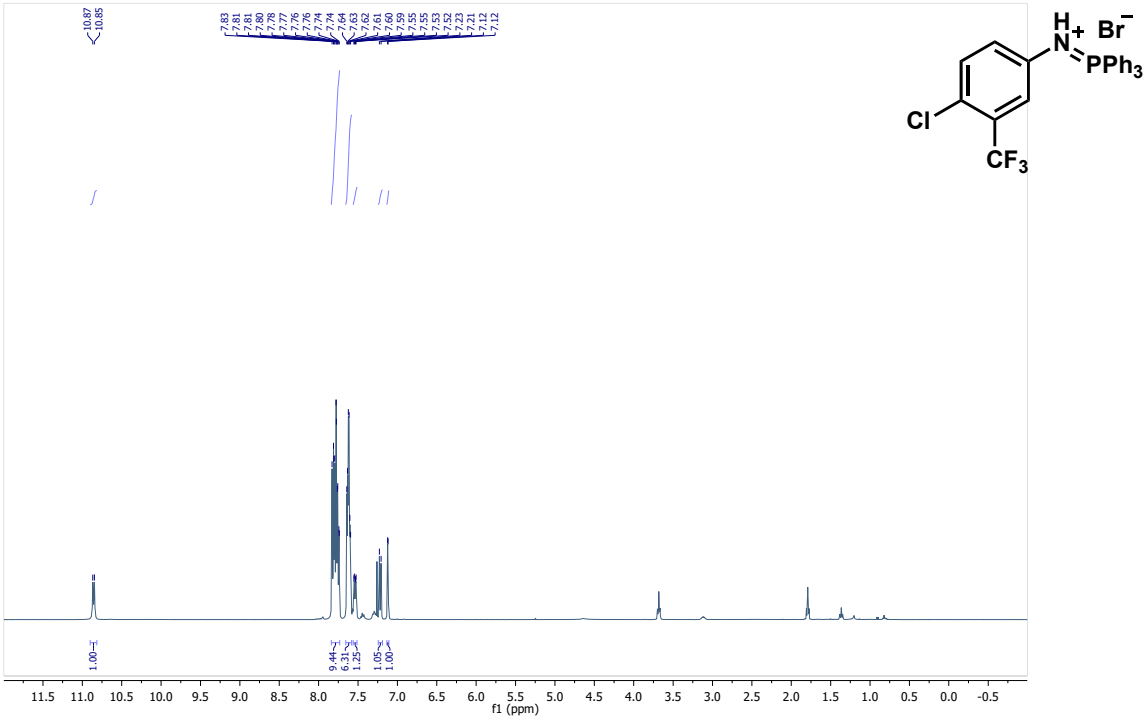

163.34
160.90
134.85
134.82
134.47
134.44
134.41
133.79
133.68
130.07
129.98
129.85
122.11
121.09
115.33
115.12
44.96
f1 (ppm)

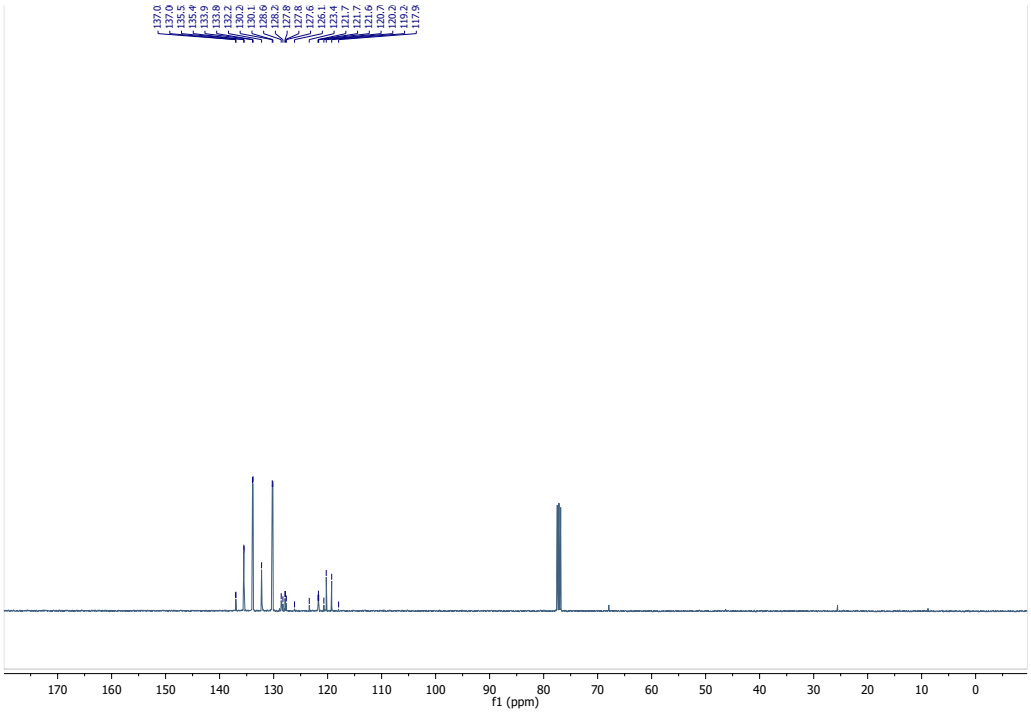

38.40
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

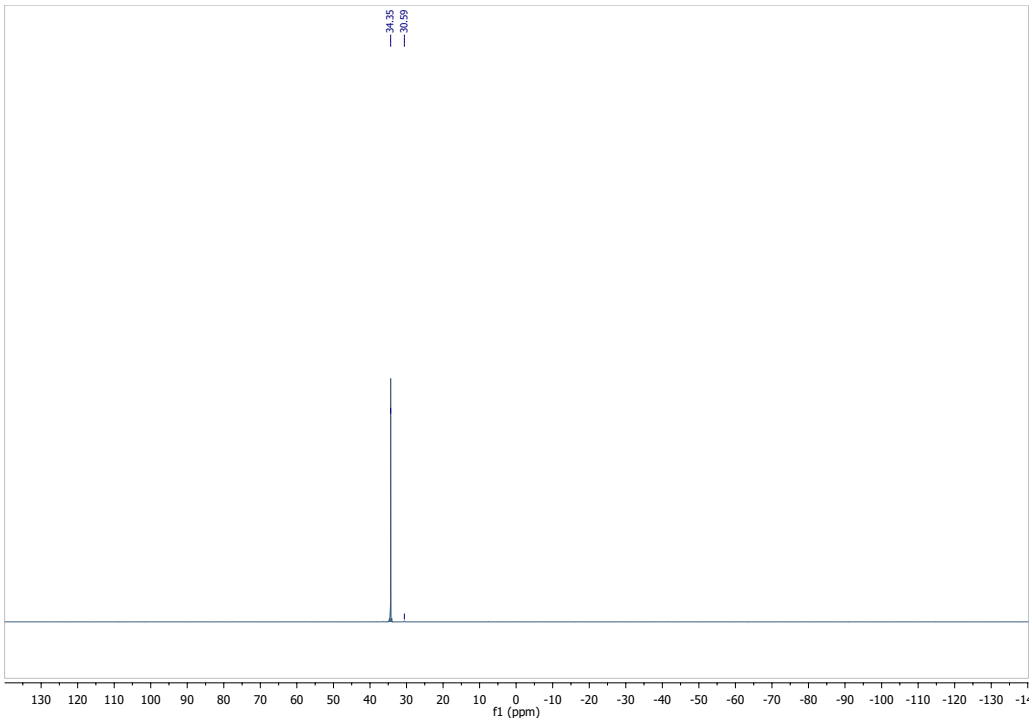

-115.02
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

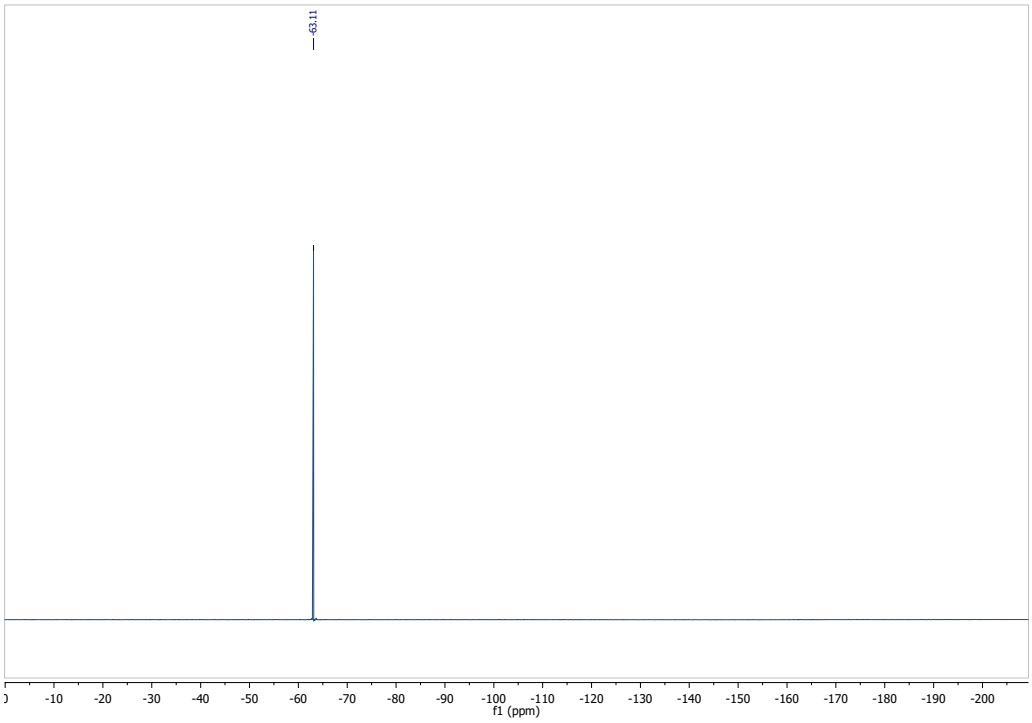
1m. 4-chloro-3-(trifluoromethyl)-*N*-(triphenylphosphanylidene)anilinium bromide

Followed the general procedure (**1**), product obtained as a white solid (171 mg, yield 53%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 10.86 (d, *J* = 7.8 Hz, 1H), 7.83–7.74 (m, 9H), 7.64–7.59 (m, 6H), 7.54 (dd, *J* = 8.7, 2.6 Hz, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 7.12 (d, *J* = 2.4 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): 137.0 (d, *J* = 2 Hz), 135.5 (d, *J* = 3 Hz), 133.9 (d, *J* = 11 Hz), 132.2, 130.2 (d, *J* = 13 Hz), 128.4 (m), 127.9 (d, *J* = 7 Hz), 127.7 (d, *J* = 6 Hz), 122.1 (q, *J* = 274 Hz), 121.7 (quin, *J* = 6 Hz), 119.8 (d, *J* = 102 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$): δ 34.35 (s, 1P), 30.59 (s, 1P, TPPO). ^{19}F-NMR (376 MHz, $CDCl_3$): -63.11 (s, 3F). MS (ESI+): Calculated $C_{25}H_{19}NF_3PCl$ as 456.0896, [M+H] found as 456.0886.



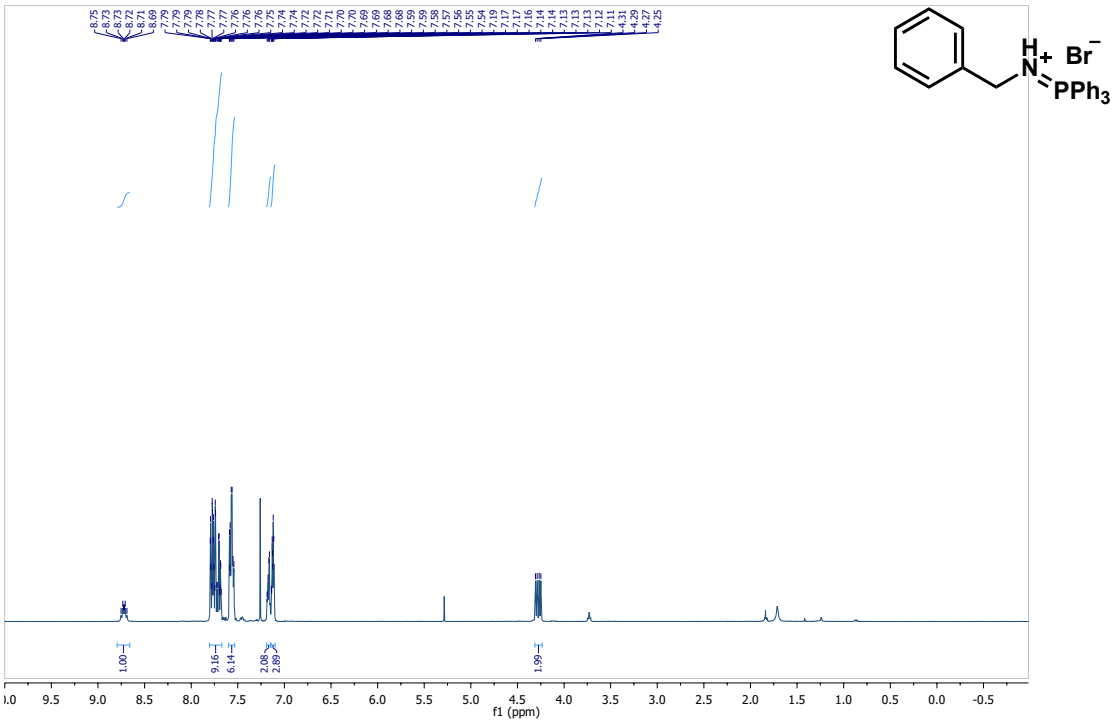

137.0
137.0
135.5
135.4
133.9
133.8
132.2
130.2
130.1
128.6
128.2
127.8
127.6
126.1
123.4
121.7
121.7
121.6
120.7
120.2
119.2
117.9
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

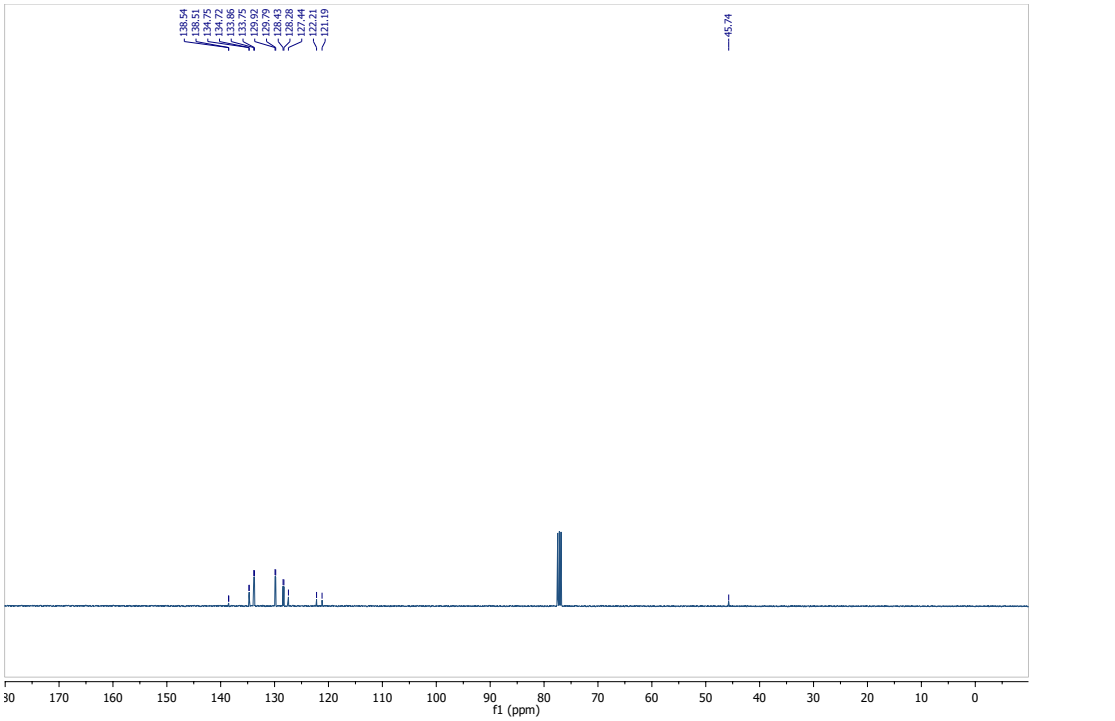

34.35
30.59
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

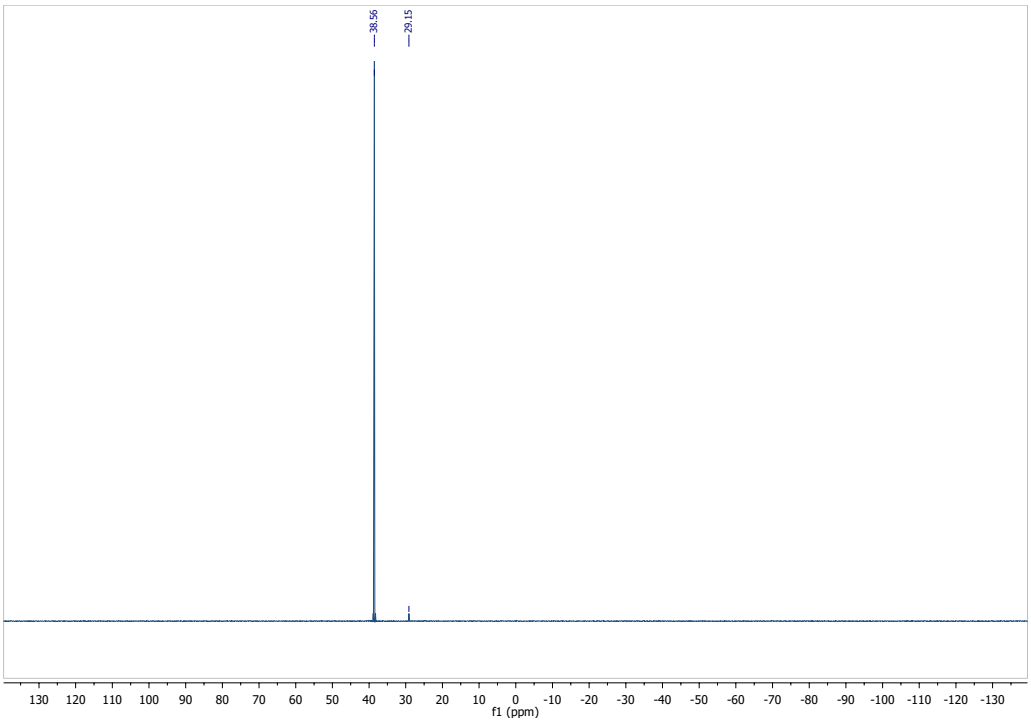

63.11
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

1n. benzyl(triphenylphosphanylidene)azanium bromide

Followed the general procedure (**1**), product obtained as a white solid (199 mg, yield 74%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.72 (m, 1H), 7.74 (m, 9H), 7.57 (m, 6H), 7.18 (m, 2H), 7.13 (m, 3H), 4.28 (dd, *J* = 15.9, 7.3 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): 138.5 (d, *J* = 3 Hz), 134.7 (d, *J* = 3 Hz), 133.8 (d, *J* = 11 Hz), 129.9 (d, *J* = 13 Hz), 128.4, 128.3, 127.4, 121.7 (d, *J* = 103 Hz), 45.7. ^{31}P-NMR (162 MHz, $CDCl_3$): δ 38.56 (s, 1P), 29.15 (s, 1P, TPPO). MS (ESI+): Calculated $C_{25}H_{23}NP$ as 368.1568, [M+H] found as 368.1574.

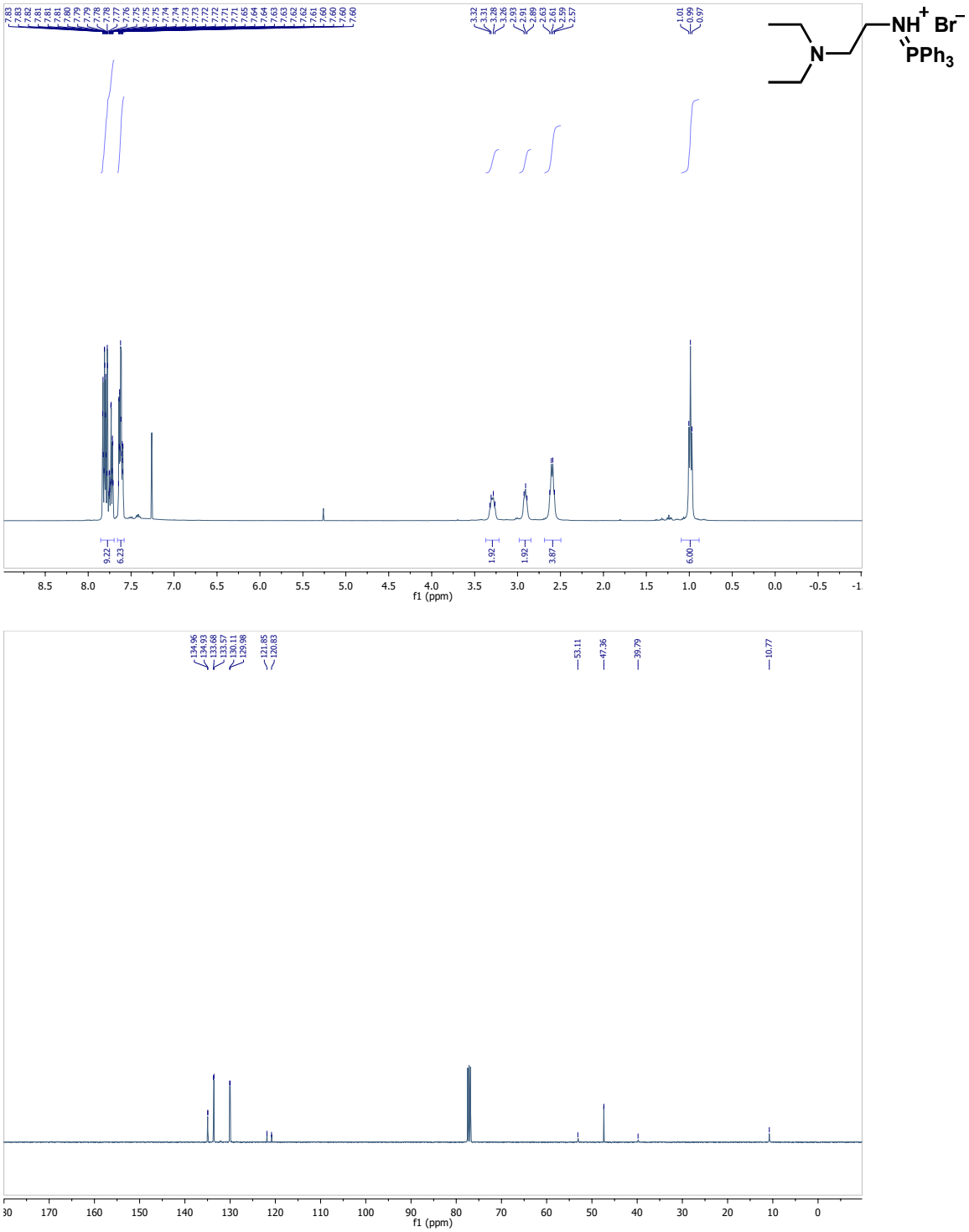


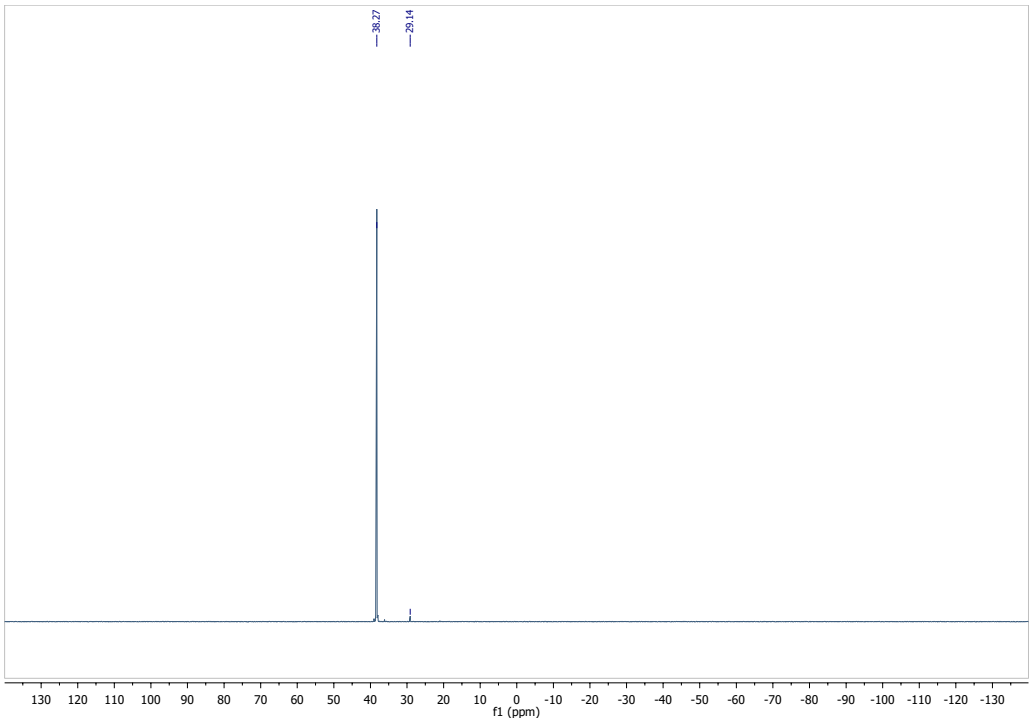



38.56
29.15
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

1o. [2-(diethylamino)ethyl](triphenylphosphanylidene)azanium bromide

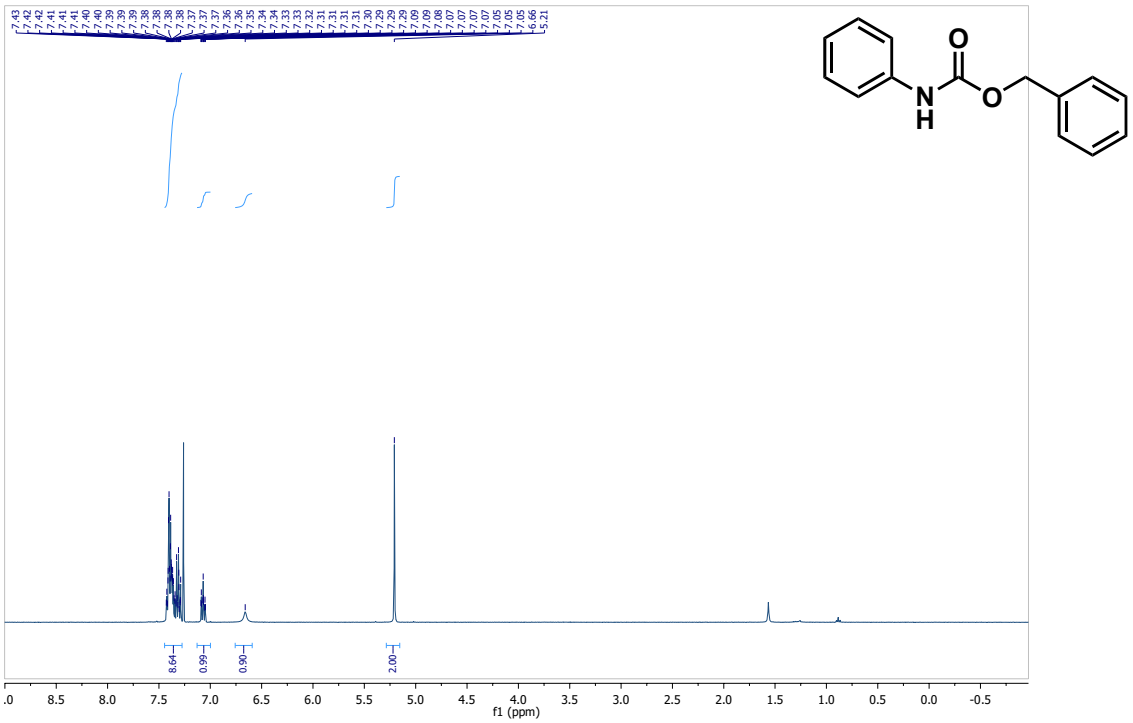
Followed the general procedure (**1**), product obtained as a sticky yellow solid (113 mg, yield 41%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.83–7.71 (m, 9H), 7.65–7.60 (m, 6H), 3.29 (q, *J* = 8.0, 7.1 Hz, 2H), 2.91 (t, *J* = 7.1 Hz, 2H), 2.60 (q, *J* = 7.4 Hz, 4H), 0.99 (t, *J* = 7.2 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): 134.9 (d, *J* = 3 Hz), 133.6 (d, *J* = 11 Hz), 130.0 (d, *J* = 13 Hz), 121.3 (d, *J* = 103 Hz), 53.1, 47.4, 39.8, 10.8. ^{31}P-NMR (162 MHz, $CDCl_3$): δ 38.27 (s, 1P), 29.14 (s, 1P, TPPO). MS (ESI+): Calculated $C_{24}H_{30}N_2P$ as 377.2147, [M+H] found as 377.2166.




38.27
29.14
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130
f1 (ppm)

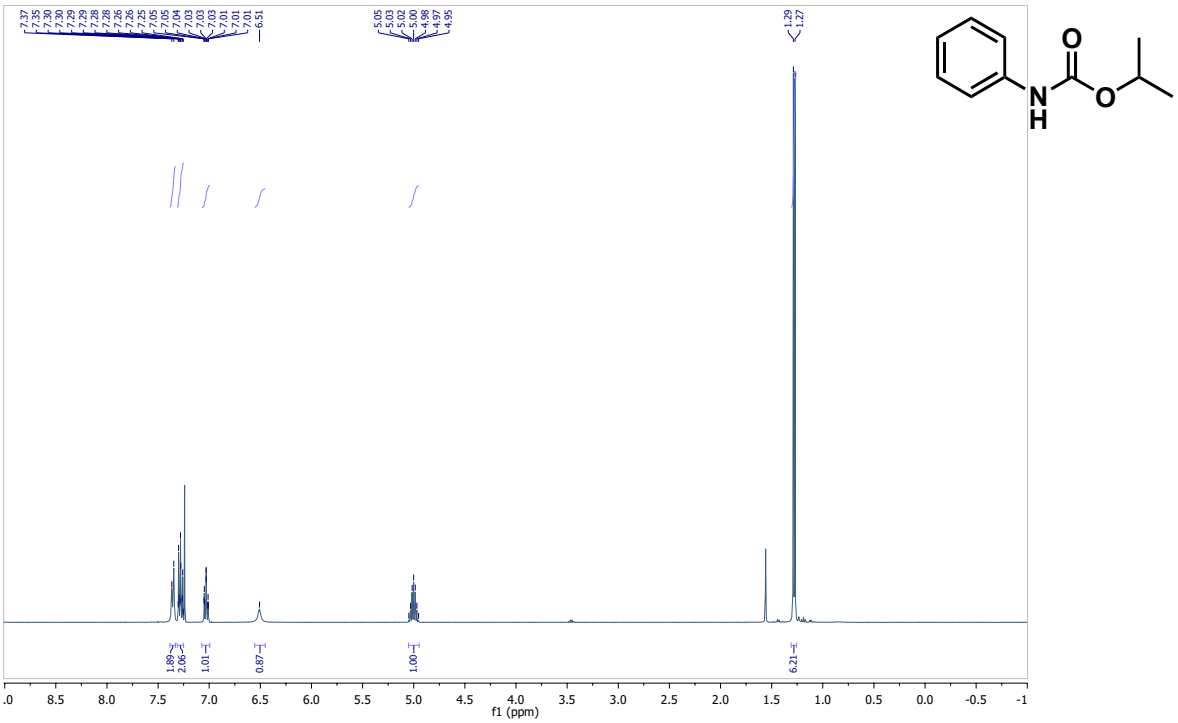
4. benzyl *N*-phenylcarbamate

Followed the general procedure (**2**), product obtained as a white powder (23 mg, yield 84%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.43–7.29 (m, 9H), 7.07 (m, 1H), 6.66 (s, 1H), 5.21 (s, 2H). MS (ESI+): Calculated $C_{14}H_{13}NO_2$ as 227.09, [M+H] found as 228.02. Characterized in accordance with the literature.[1]



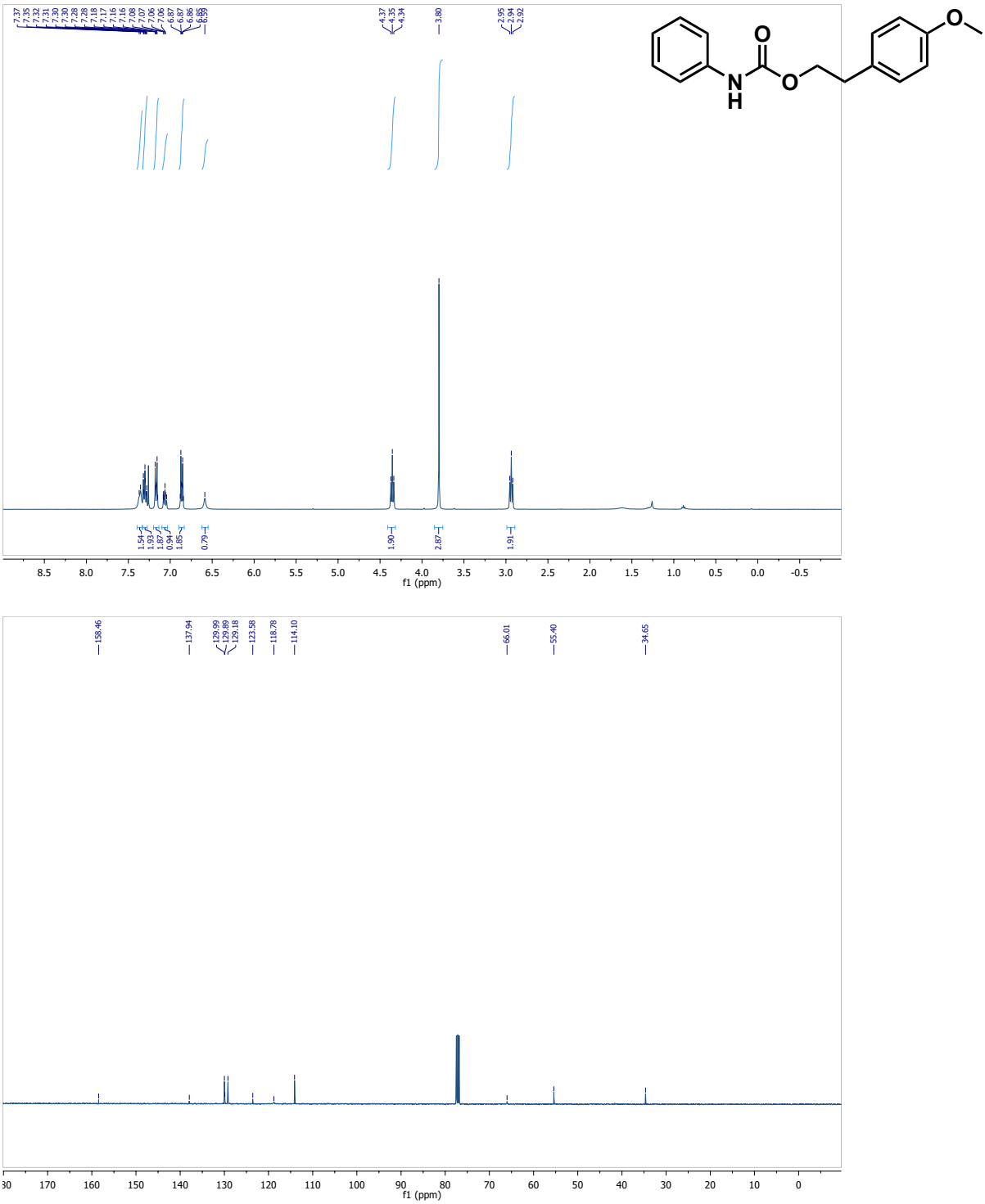
5. propan-2-yl *N*-phenylcarbamate

Followed the general procedure (**2**), product obtained as a white powder (41 mg, yield 91%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.36 (d, 2H), 7.28 (m, 2H), 7.03 (m, 1H), 6.51 (s, 1H), 5.00 (sept, *J* = 6.4 Hz, 1H), 1.28 (d, *J* = 6.3 Hz, 6H). MS (ESI+): Calculated $C_{10}H_{13}NO_2$ as 179.09, [M+H] found as 180.08. Characterized in accordance with the literature.[2]



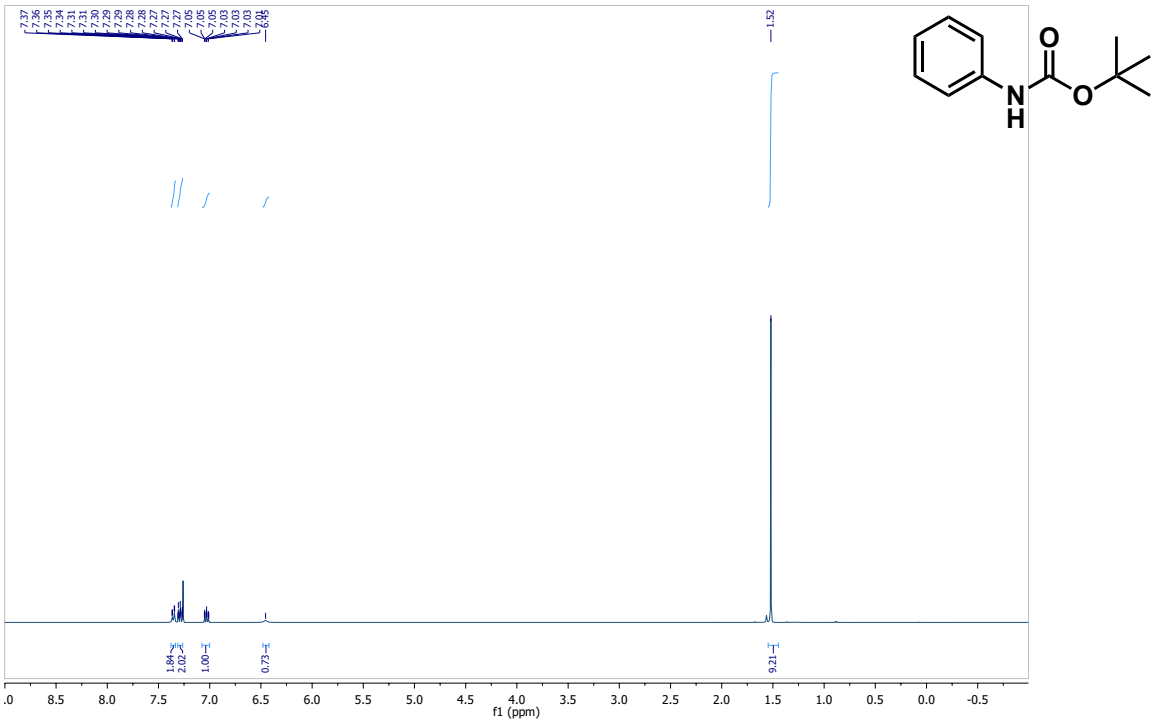
6. 2-(4-methoxyphenyl)ethyl *N*-phenylcarbamate

Followed the general procedure (**2**), product obtained as a white powder (64 mg, yield 94%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.36 (d, 2H), 7.30 (m, 2H), 7.17 (m, 2H), 7.06 (m, 1H), 6.86 (m, 2H), 6.59 (s, 1H), 3.36 (dd, 2H), 3.80 (s, 3H), 2.94 (dd, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): 158.5, 137.9, 130.0, 129.9, 129.2, 123.6, 118.8, 114.1, 66.0, 55.4, 34.7. MS (ESI+): Calculated $C_{16}H_{17}NO_3Na$ as 294.1106, [M+H] found as 294.1088.



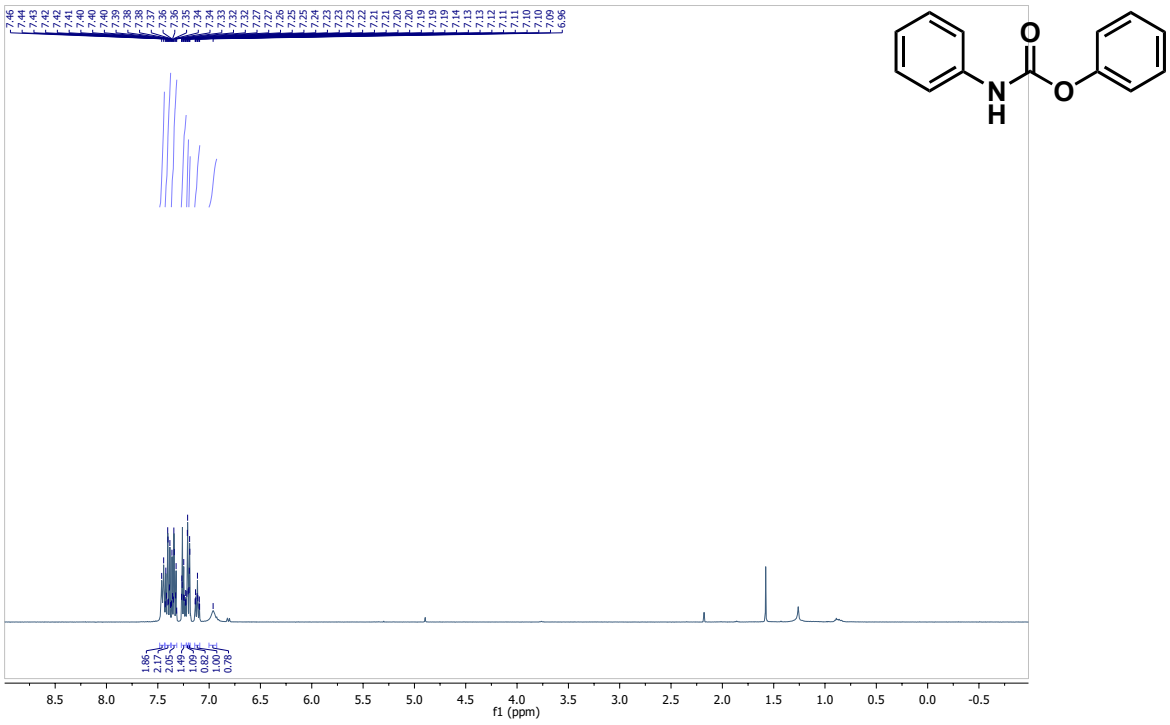
7. *tert*-butyl *N*-phenylcarbamate

Followed the general procedure (**2**), using 10 equiv. of *tert*-butyl alcohol. Product obtained as a white powder (40 mg, yield 83%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.36 (m, 2H), 7.29 (m, 2H), 7.03 (dt, *J* = 7.5, 1.2 Hz, 1H), 6.45 (s, 1H), 1.52 (s, 9H). MS (ESI+): Calculated $C_{11}H_{15}NO_2$ as 193.11, [M+H] found as 194.14. Characterized in accordance with the literature.[3]



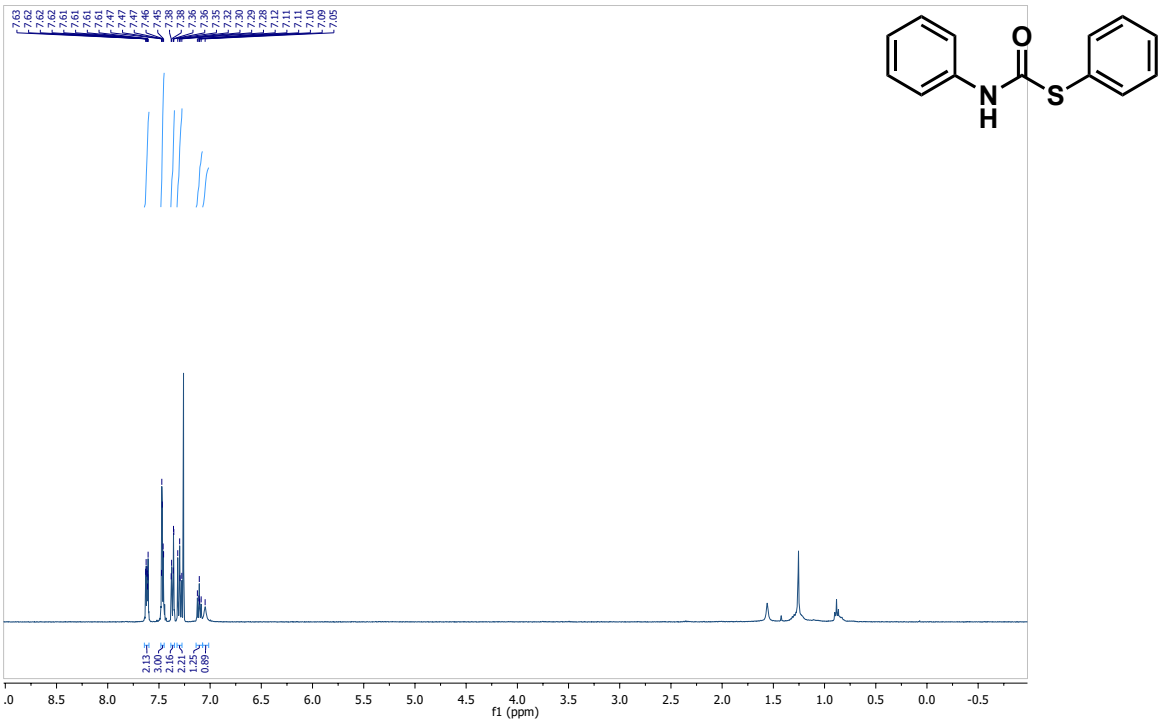
8. phenyl *N*-phenylcarbamate

Followed the general procedure (**2**), using 10 equiv. of phenol. Product obtained as a white powder (40 mg, yield 75%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 7.8 Hz, 2H), 7.41 (m, 2H), 7.35 (m, 2H), 7.25 (m, 1H), 7.21 (m, 1H), 7.20 (m, 1H), 7.12 (dt, *J* = 7.2, 1.3 Hz, 1H), 6.96 (s, 1H). MS (ESI+): Calculated $C_{13}H_{11}NO_2$ as 213.08, [M+H] found as 214.26. Characterized in accordance with the literature.[4]



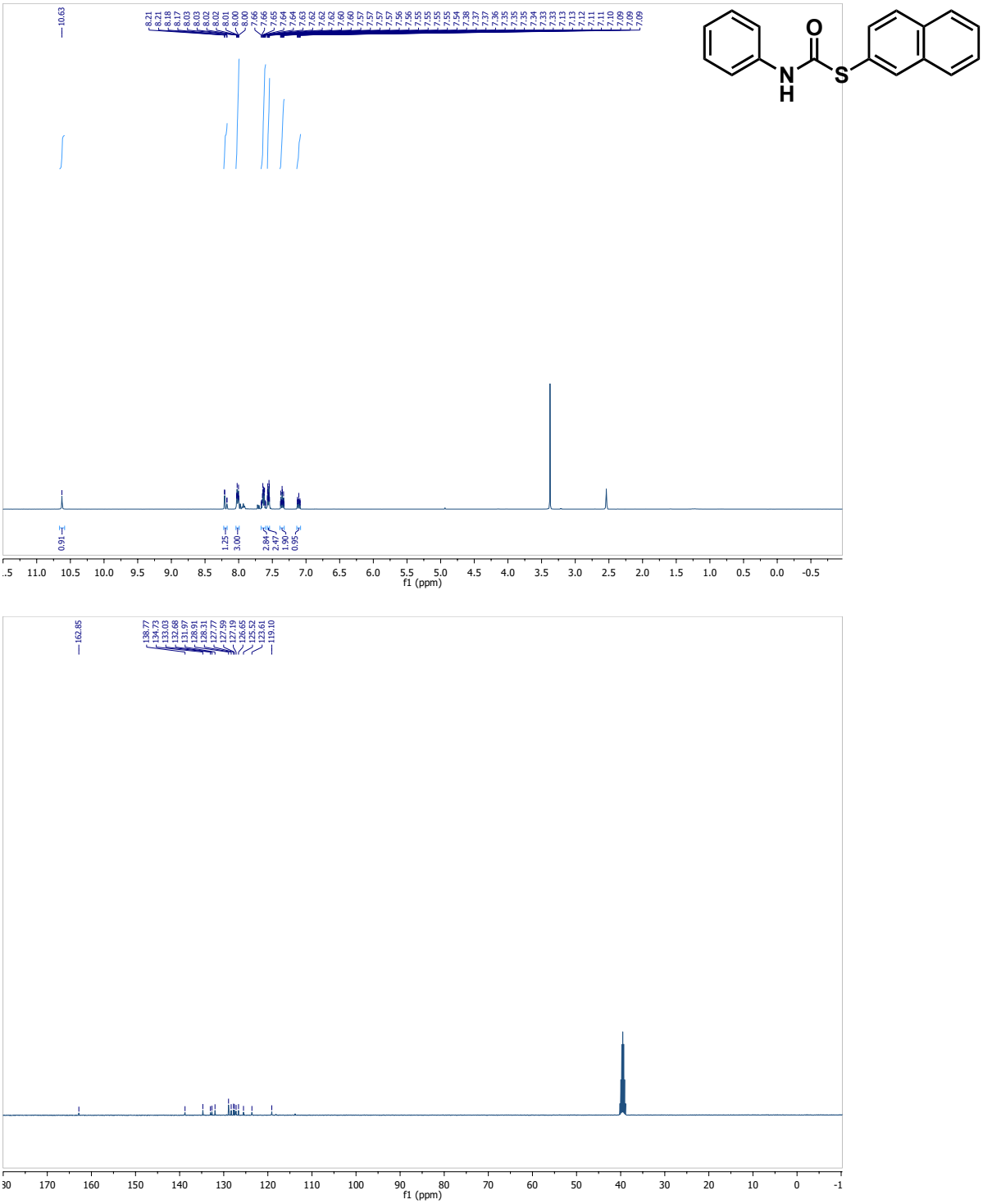
9. *N*-phenyl-1-(phenylsulfanyl)formamide

Followed the general procedure (**2**), using 10 eqv. of thiophenol. Product obtained as a white powder (43.5 mg, yield 76%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.62 (m, 2H), 7.46 (m, 3H), 7.37 (dd, *J* = 8.7, 1.3 Hz, 2H), 7.30 (dd, *J* = 8.7, 7.2 Hz, 2H), 7.11 (m, 1H), 7.05 (s, 1H). MS (ESI+): Calculated $C_{13}H_{11}NOS$ as 229.06, [M+H] found as 230.11. Characterized in accordance with the literature.[5]



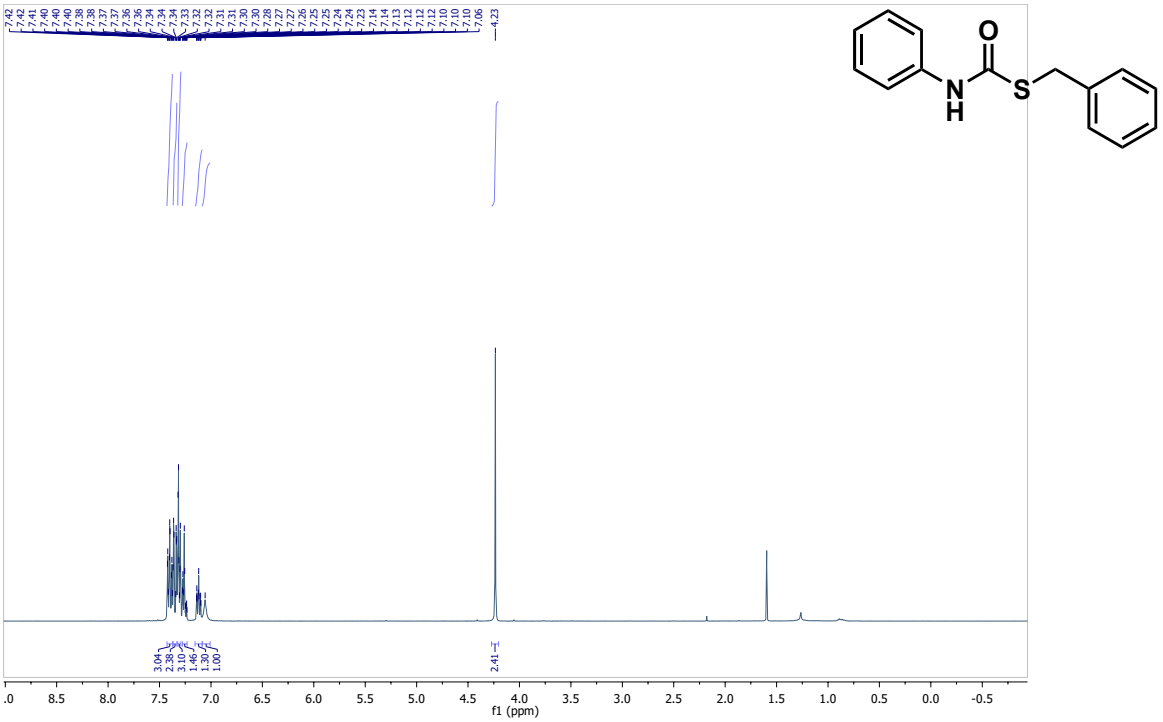
10. 1-(naphthalen-2-ylsulfanyl)-*N*-phenylformamide

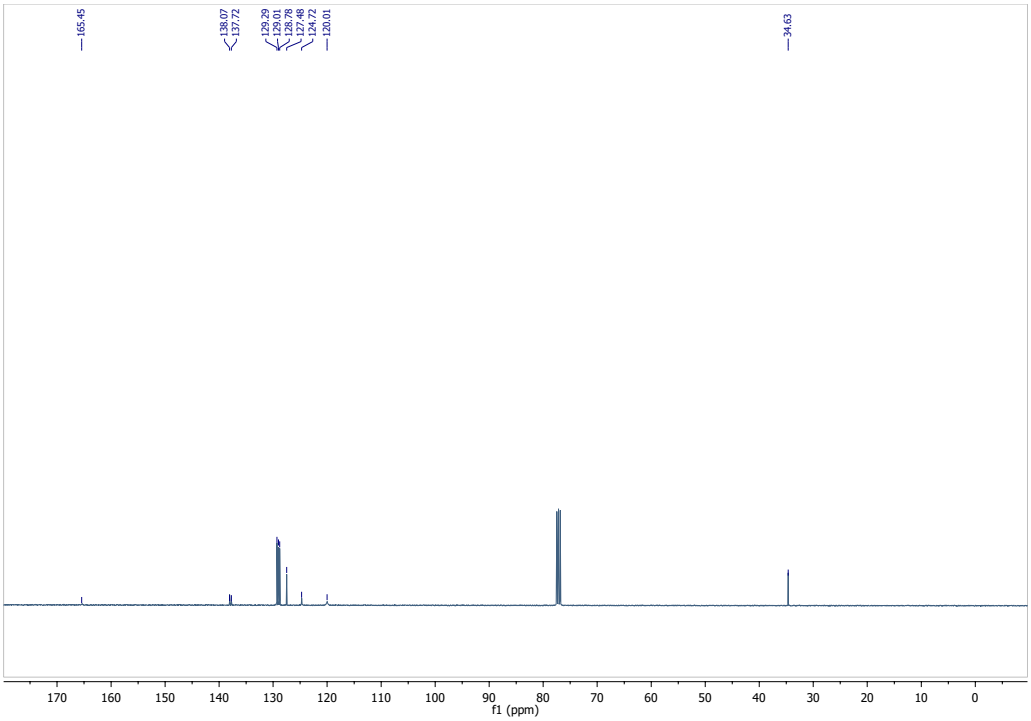
Followed the general procedure (**2**), using 10 equiv. of 2-napthalenethiol product obtained as a white powder (49 mg, yield 70%). ^{1}H-NMR (400 MHz, DMSO): δ 10.63 (s, 1H), 8.19 (dd, *J* = 13.6, 1.9 Hz, 1H), 8.02 (m, 3H), 7.63 (m, 3H), 7.56 (m, 2H), 7.36 (m, 2H), 7.11 (m, 1H). ^{13}C-NMR (100 MHz, DMSO): 162.9, 138.8, 134.7, 133.0, 132.7, 132.0, 128.9, 128.3, 127.8, 127.6, 127.2, 126.7, 125.6, 123.6, 119.1. MS (ESI+): Calculated $C_{17}H_{13}NOS$ as 279.07, [M+H] found as 280.26. Characterized in accordance with the literature.[5]



11. *N*-phenyl(benzylsulfanyl)formamide

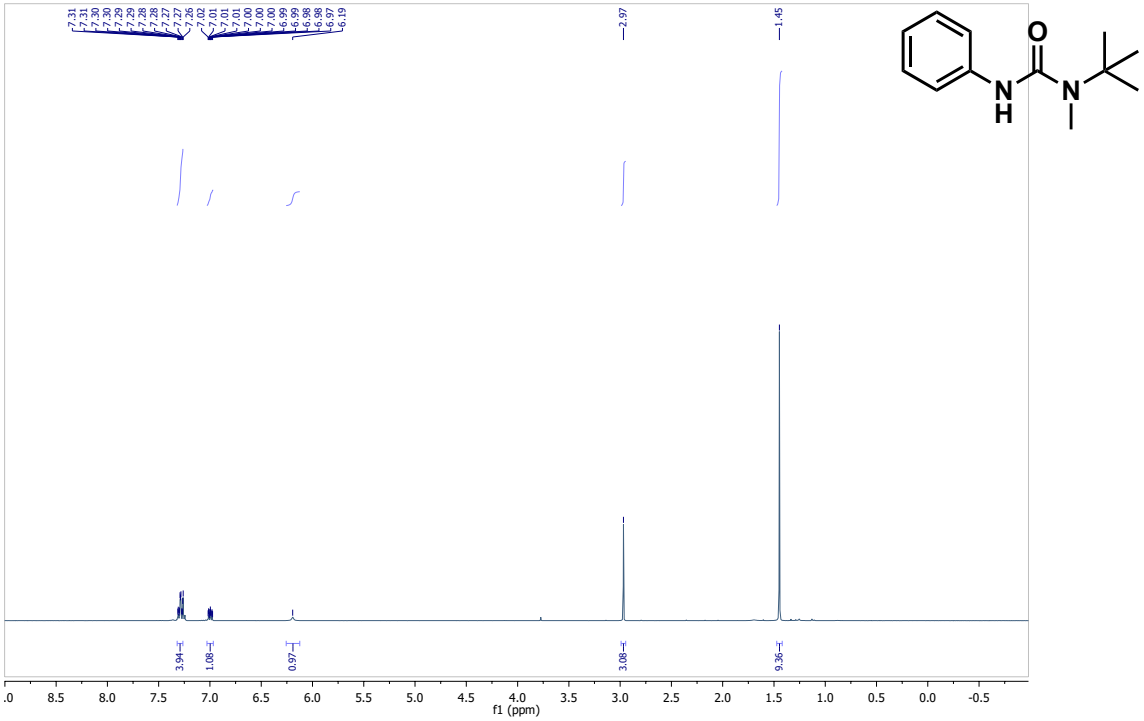
Followed the general procedure (**2**), product obtained as a white powder (66.5 mg, yield 86%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.40 (m, 3H), 7.35 (m, 2H), 7.31 (m, 3H), 7.26 (m, 1H), 7.12 (m, 1H), 7.06 (s, 1H), 4.23 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): 165.5, 138.1, 137.8, 129.3, 129.0, 128.8, 127.5, 124.7, 120.0, 34.6. MS (ESI+): Calculated $C_{14}H_{13}NOS$ as 243.07, [M+H] found as 244.13. Characterized in accordance with the literature.[5]





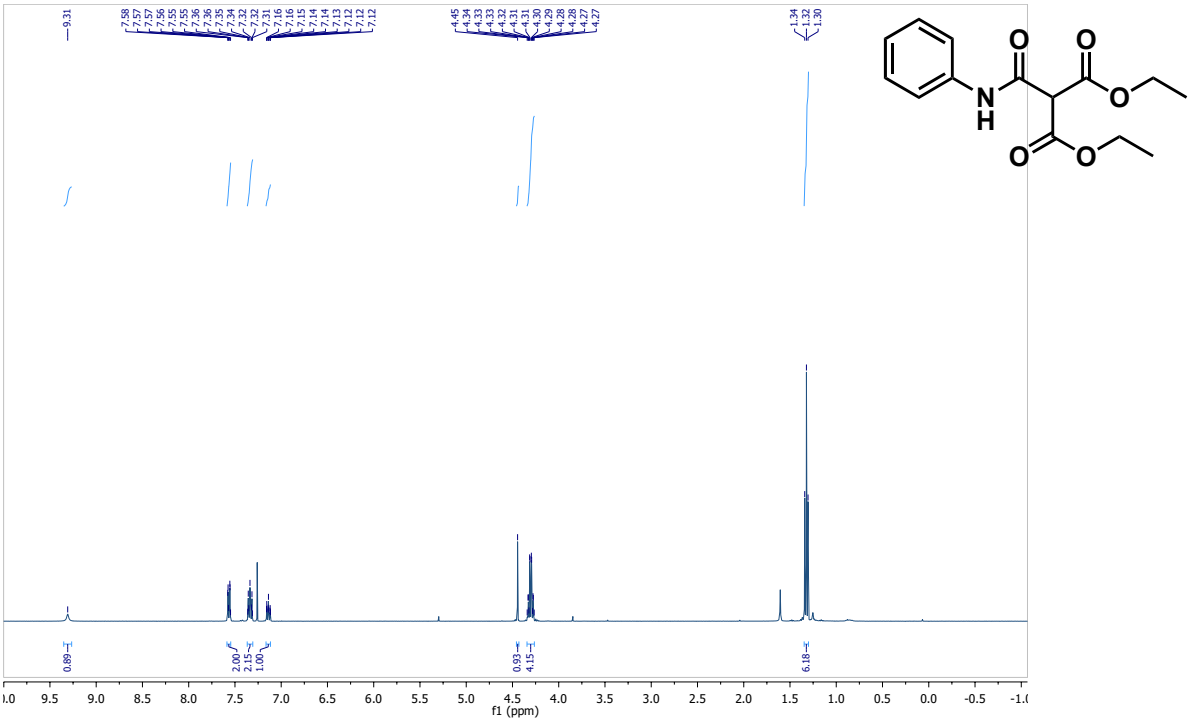
12. 3-*tert*-butyl-3-methyl-1-phenylurea

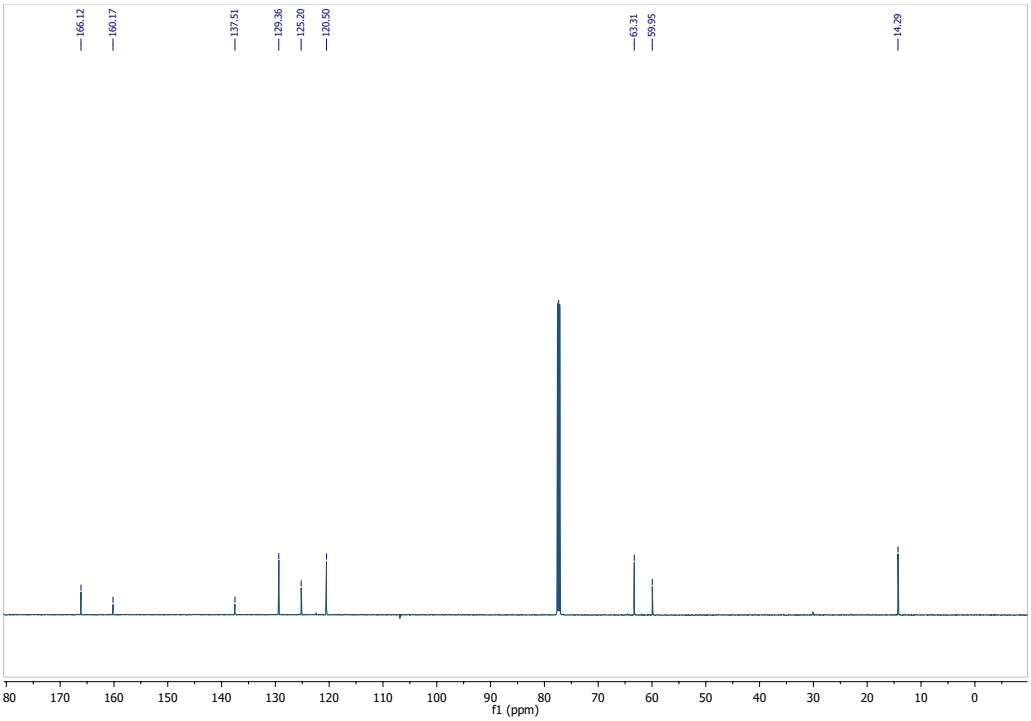
Followed the general procedure (**3**), product obtained as a white powder (40 mg, yield 78%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.29 (m, 4H), 7.00 (m, 1H), 6.19 (s, 1H), 2.97 (s, 3H), 1.45 (s, 9H). MS (ESI+): Calculated $C_{12}H_{18}N_2O$ as 206.14, [M+H] found as 207.14. Characterized in accordance with the literature.[6]



13. 1,3-diethyl 2-(phenylcarbamoyl)propanedioate

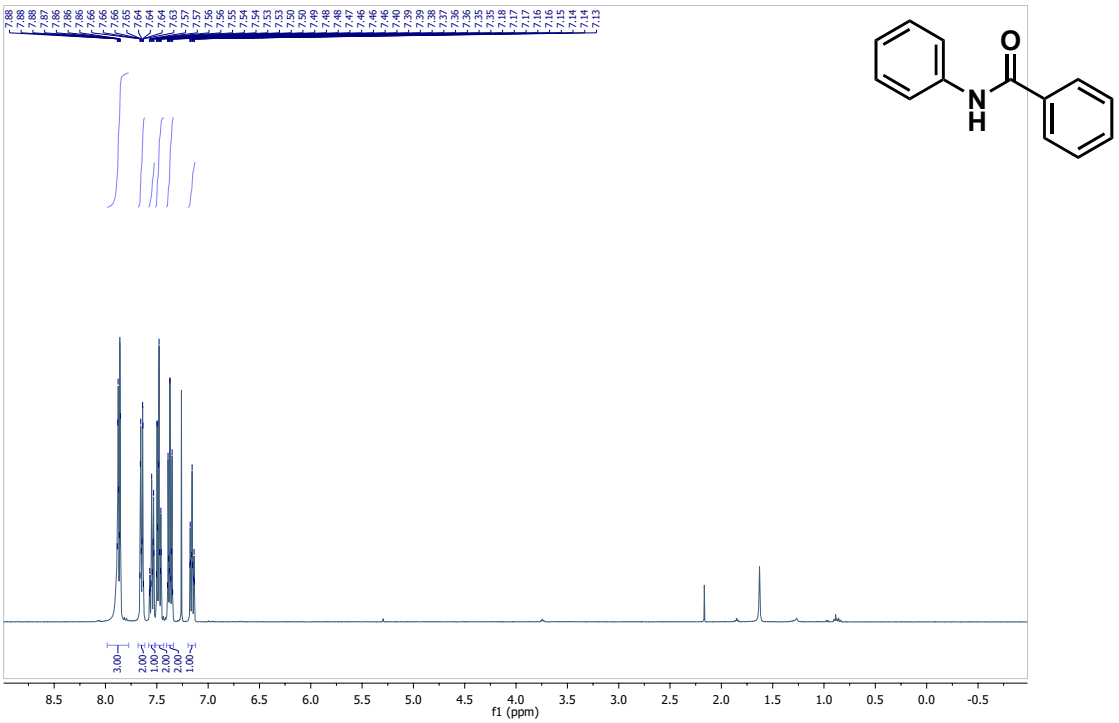
Followed the general procedure (**6**), product obtained as a white powder (57 mg, yield 82%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.31 (s, 1H), 7.57 (dd, *J* = 8.7, 1.7 Hz, 2H), 7.34 (m, 2H), 7.14 (m, 1H), 4.45 (s, 1H), 4.31 (dq, *J* = 7.1, 1.3 Hz, 4H), 1.32 (t, *J* = 7.1 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): 166.12, 160.17, 137.51, 129.36, 125.20, 120.50, 63.31, 59.95, 14.29. MS (ESI+): Calculated $C_{14}H_{17}NO_5Na$ as 302.1004, [M+H] found as 302.0982. Characterized in accordance with the literature.[7]





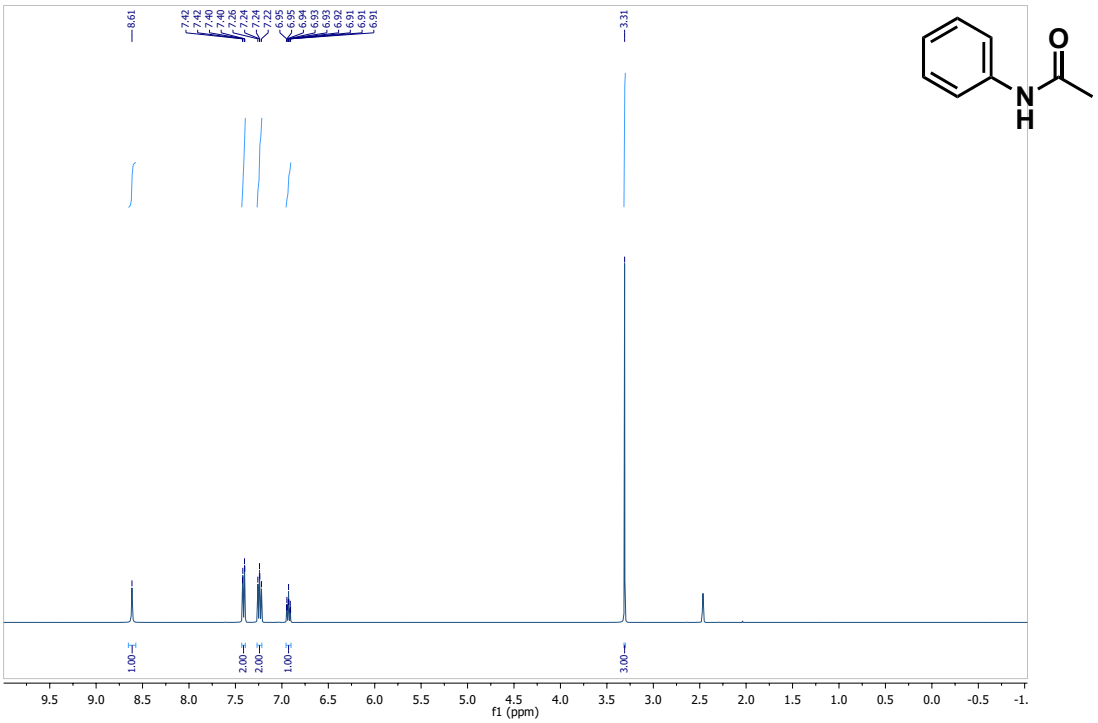
14. *N*-phenylbenzamide

Followed the general procedure (**4**), product obtained as a white powder (31 mg, yield 63%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.87 (m, 3H), 7.65 (m, 2H), 7.55 (m, 1H), 7.48 (m, 2H), 7.38 (m, 2H), 7.16 (dt, *J* = 7.1, 1.2 Hz, 1H). MS (ESI+): Calculated $C_{13}H_{11}NO$ as 197.08, [M+H] found as 198.16. Characterized in accordance with the literature.[8]



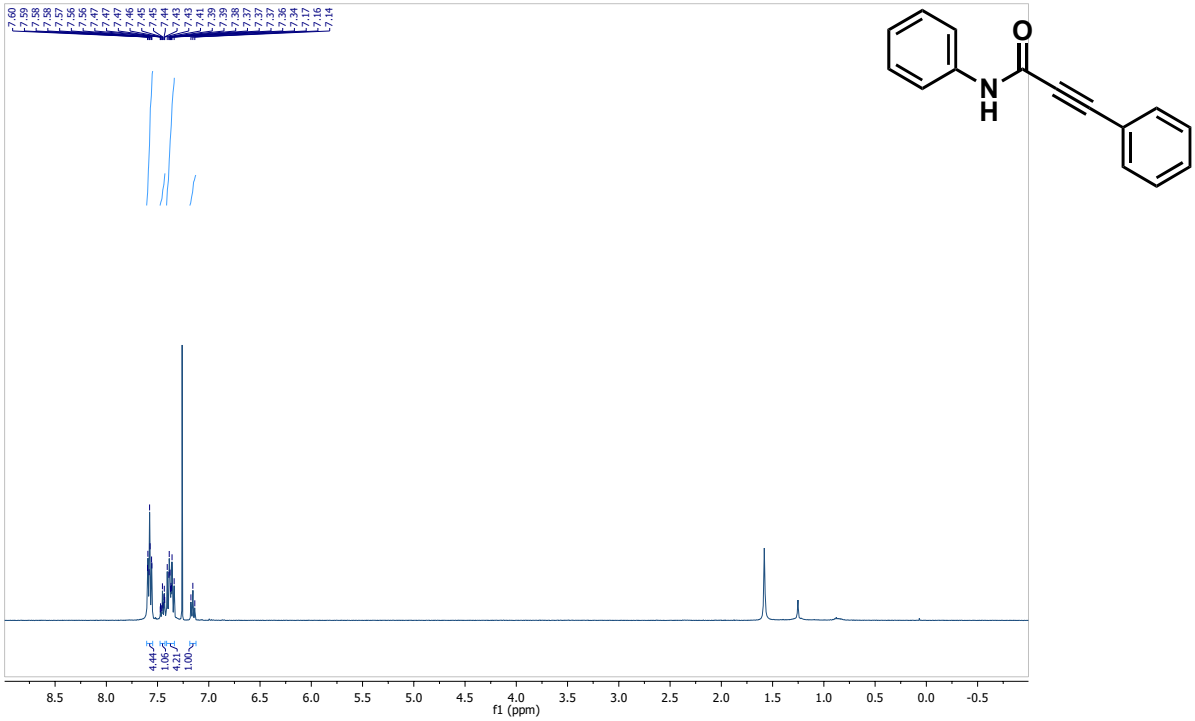
15. *N*-phenylacetamide

Followed the general procedure (**4**), product obtained as a white solid (32 mg, yield 65%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.61 (s, 1H), 7.41 (dd, *J* = 8.6, 1.2 Hz, 2H), 7.24 (dd, *J* = 8.6, 7.3 Hz, 2H), 6.93 (dt, *J* = 7.3, 1.2 Hz, 1H), 3.31 (s, 3H). MS (ESI+): Calculated C_8H_9NO as 135.07, [M+H] found as 136.14. Characterized in accordance with the literature.[9]



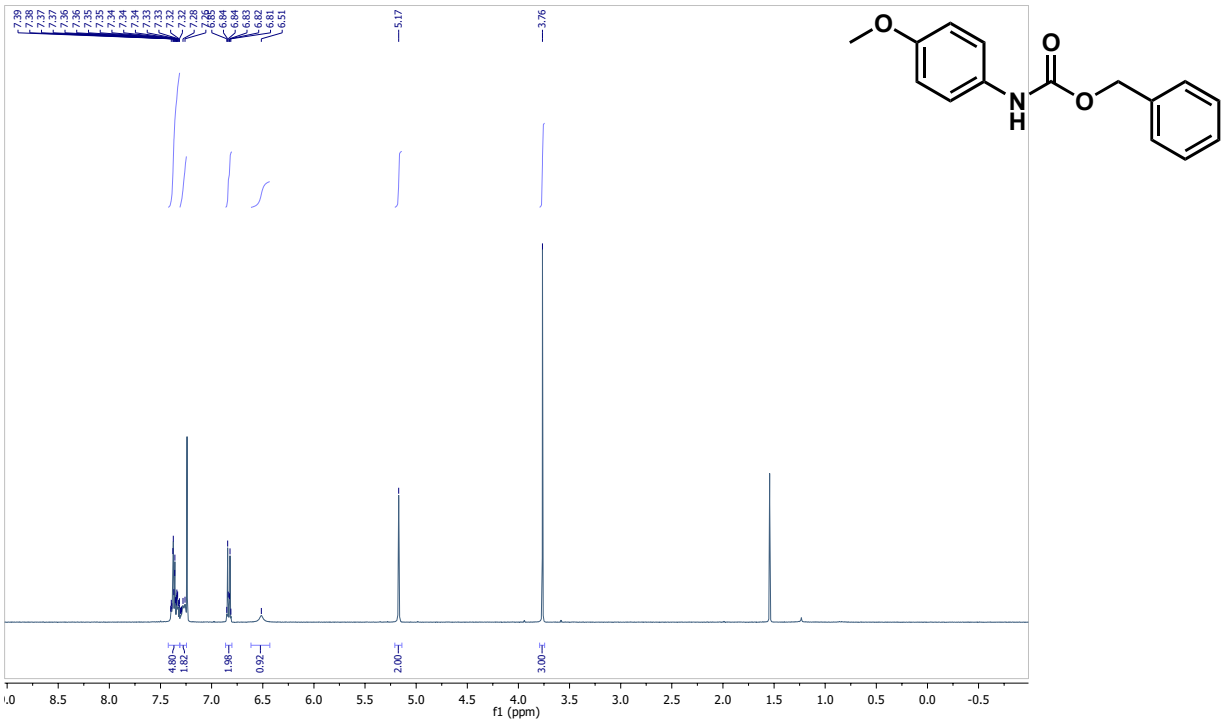
16. *N*,3-diphenylprop-2-ynamide

Followed the general procedure (**5**), product obtained as a brown solid (41.5 mg, yield 75%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.58 (m, 4H), 7.45 (m, 1H), 7.38 (m, 4H), 7.15 (t, *J* = 7.4 Hz, 1H). MS (ESI+): Calculated $C_{15}H_{11}NO$ as 221.08, [M+H] found as 222.09. Characterized in accordance with the literature.[10]



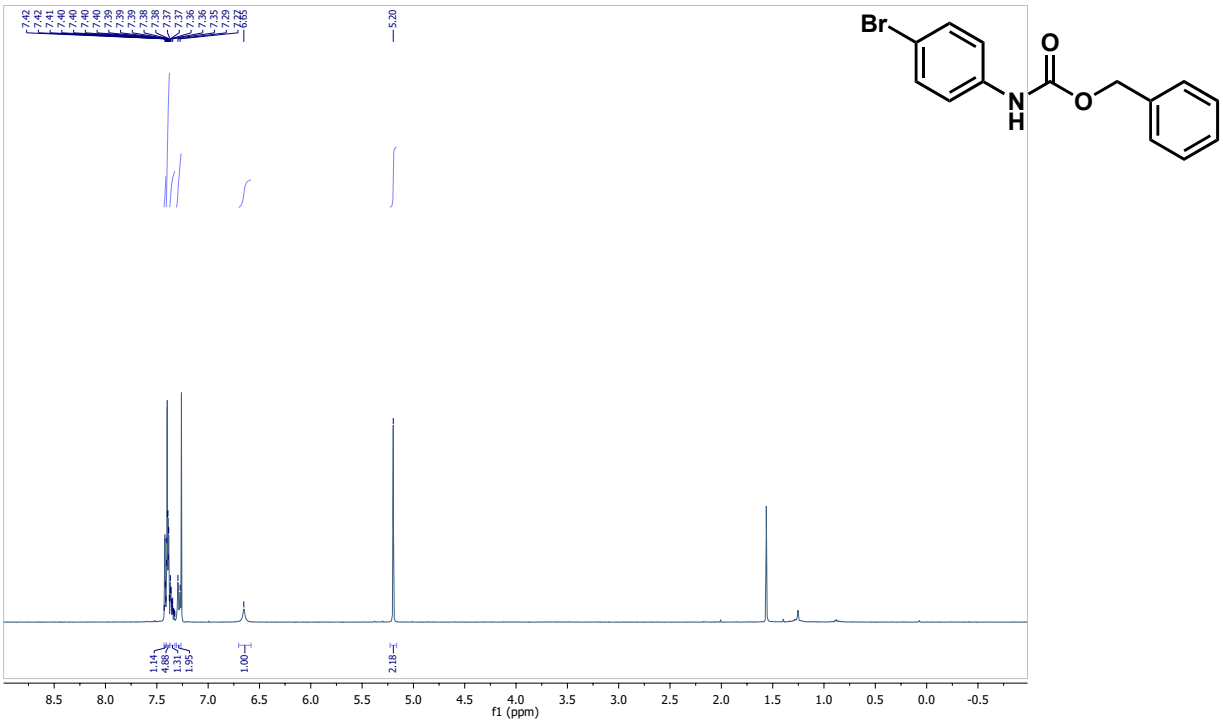
17. benzyl *N*-(4-methoxyphenyl)carbamate

Followed the general procedure (**2**), product obtained as a white powder (53 mg, yield 82%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.40–7.32 (m, 5H), 7.30–7.26 (m, 2H), 6.83 (m, 2H), 6.51 (s, 1H), 5.17 (s, 2H), 3.76 (s, 3H). MS (ESI+): Calculated $C_{15}H_{15}NO_3$ as 257.11, [M+H] found as 258.20. Characterized in accordance with the literature.[1]



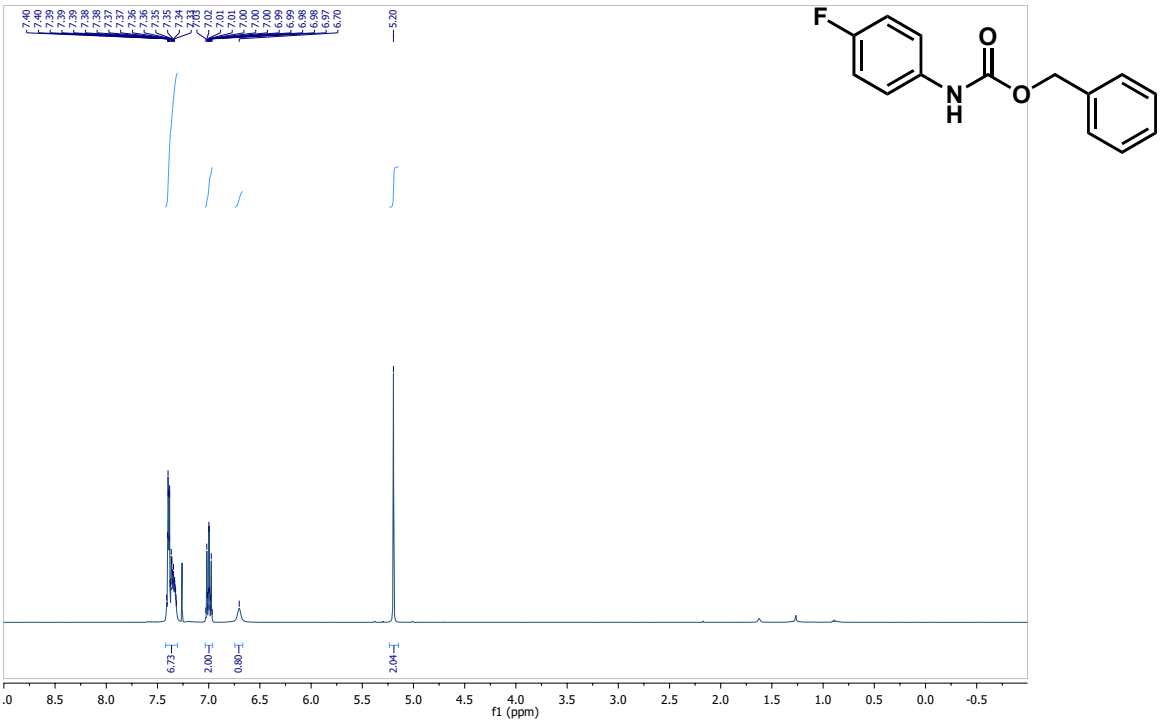
18. benzyl *N*-(4-bromophenyl)carbamate

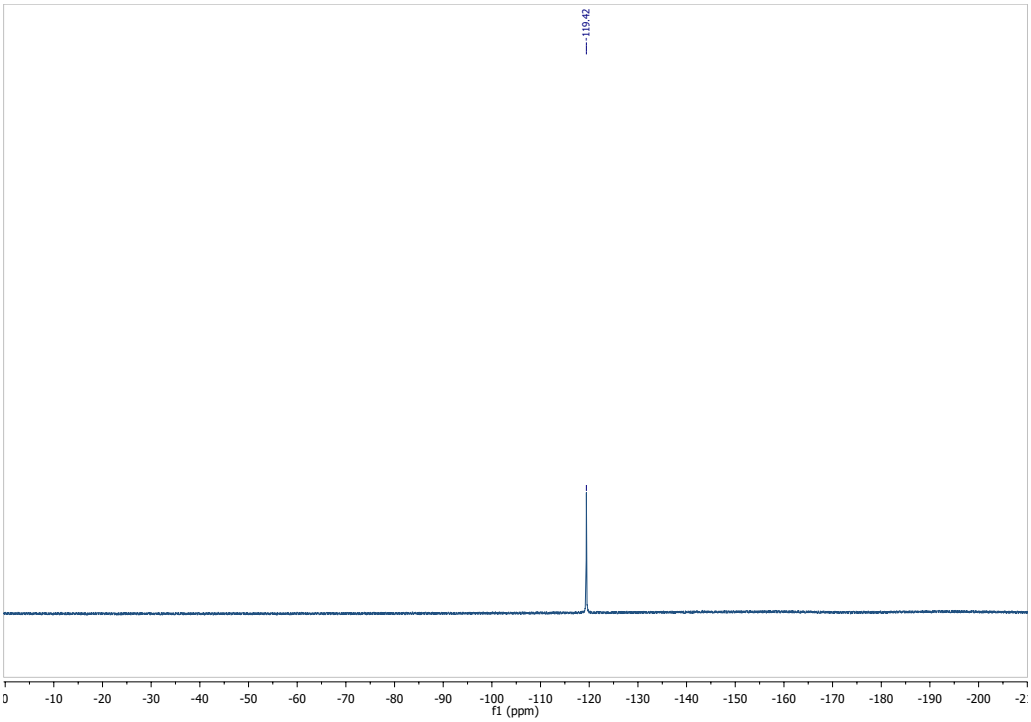
Followed the general procedure (**2**), product obtained as a white powder (64 mg, yield 83%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.42 (m, 1H), 7.39 (m, 5H), 7.35 (m, 1H), 7.28 (d, *J* = 8.5 Hz, 2H), 6.65 (s, 1H), 5.20 (s, 2H). MS (ESI+): Calculated $C_{14}H_{12}BrNO_2$ as 305.01, [M+H] found as 306.19. Characterized in accordance with the literature.[1]



19. benzyl *N*-(4-fluorophenyl)carbamate

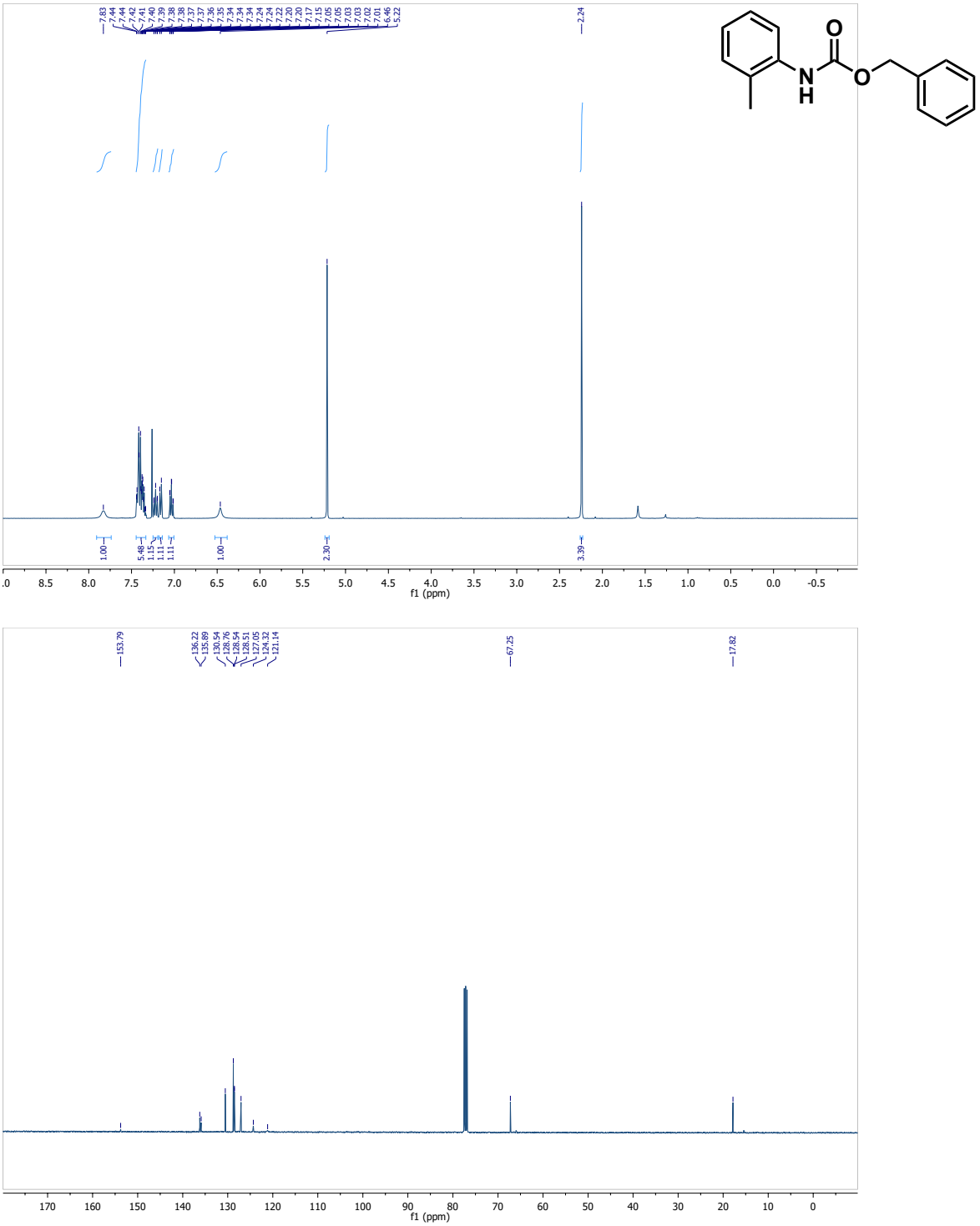
Followed the general procedure (**2**), product obtained as a white powder (35 mg, yield 57%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.41–7.32 (m, 7H), 7.00 (m, 2H), 6.70 (s, 1H), 5.20 (s, 2H). ^{19}F-NMR (376 MHz, $CDCl_3$): -119.42 (s, 1F). MS (ESI+): Calculated $C_{14}H_{12}FNO_2$ as 245.09, [M+H] found as 246.06. Characterized in accordance with the literature.[1]





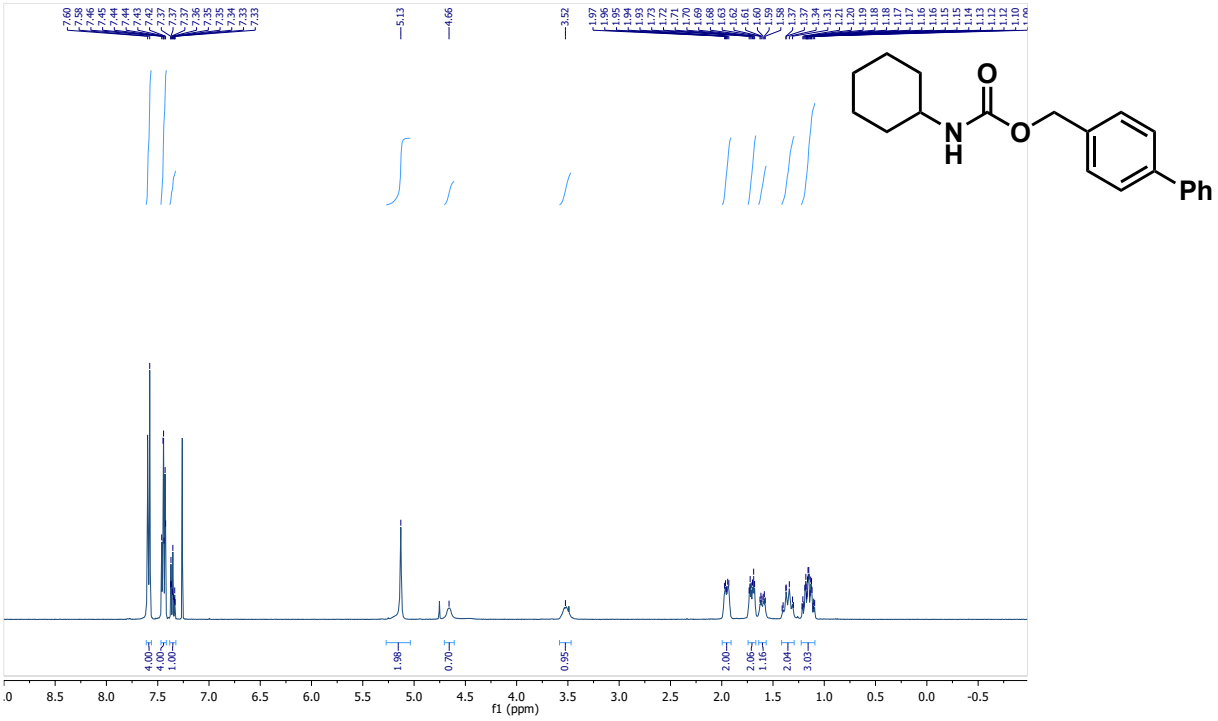
21. benzyl *N*-(2-methylphenyl)carbamate

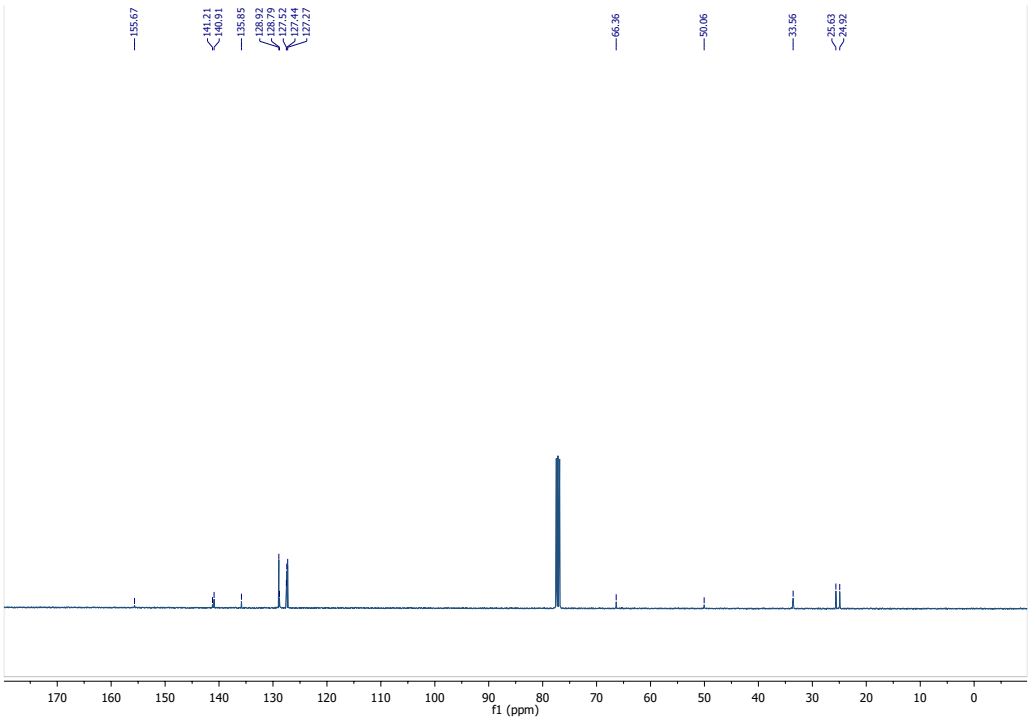
Followed the general procedure (**2**), product obtained as a white powder (51 mg, yield 84%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.83 (s, 1H), 7.44–7.34 (m, 5H), 7.22 (m, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.03 (dt, *J* = 7.4, 1.3 Hz, 1H), 6.46 (s, 1H), 5.22 (s, 2H), 2.24 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): 153.8, 136.2, 135.9, 130.5, 128.8, 128.5, 128.5, 127.1, 124.3, 121.1, 67.3, 17.8. MS (ESI+): Calculated $C_{15}H_{15}NO_2$ as 241.11, [M+H] found as 242.17. Characterized in accordance with the literature.[2]



22. [(1,1'-biphenyl)-4-yl]methyl *N*-cyclohexylcarbamate

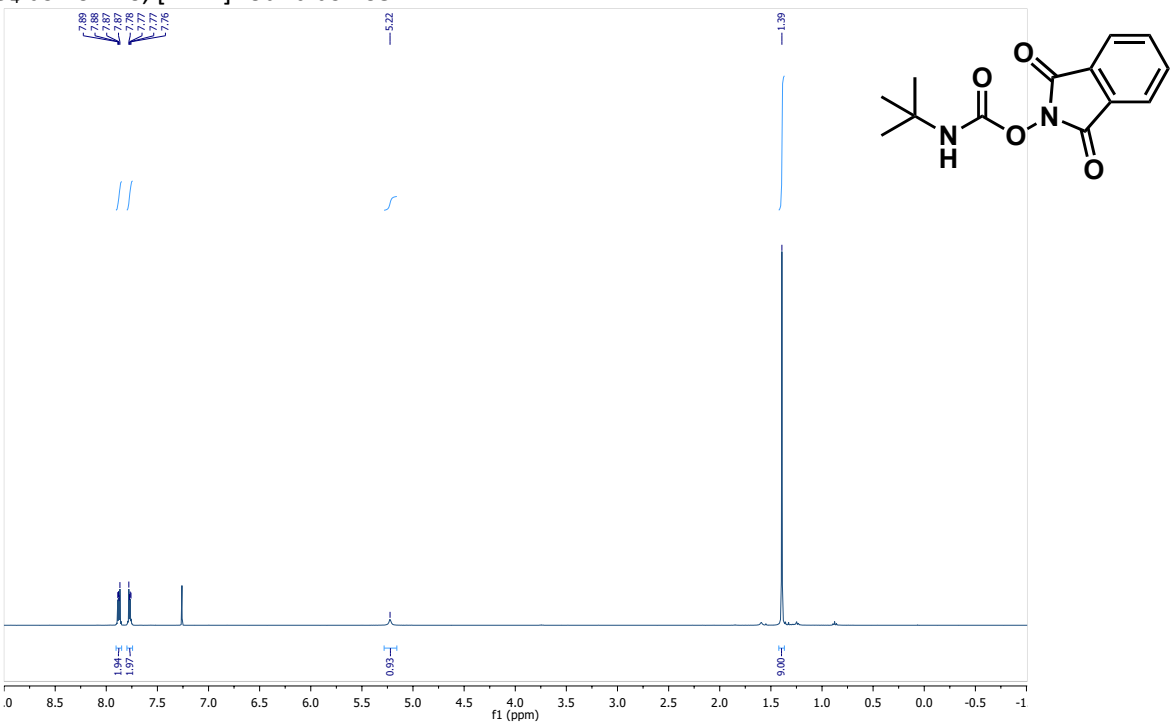
Followed the general procedure **7**, then procedure **2,** using 10 equiv. of 4-biphenylmethanol**.** The reaction was performed at reflux temperature in THF (2.5 mL). DBU was not used. Product obtained as a white powder (64 mg, yield 82%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.4 Hz, 4H), 7.44 (m, 4H), 7.35 (m, 1H), 5.13 (s, 2H), 4.66 (s, 1H), 3.52 (s, 1H), 1.95 (m, 2H), 1.71 (dt, *J* = 13.5, 3.9 Hz, 2H), 1.61 (m, 2H), 1.36 (m, 2H), 1.15 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): 155.7, 141.2, 140.9, 135.9, 128.9, 128.8, 127.5, 127.4, 127.3, 66.4, 50.1, 33.6, 25.6, 24.9. MS (ESI+): Calculated $C_{20}H_{23}NO_2Na$ as 332.1626, [M+H] found as 332.1635.

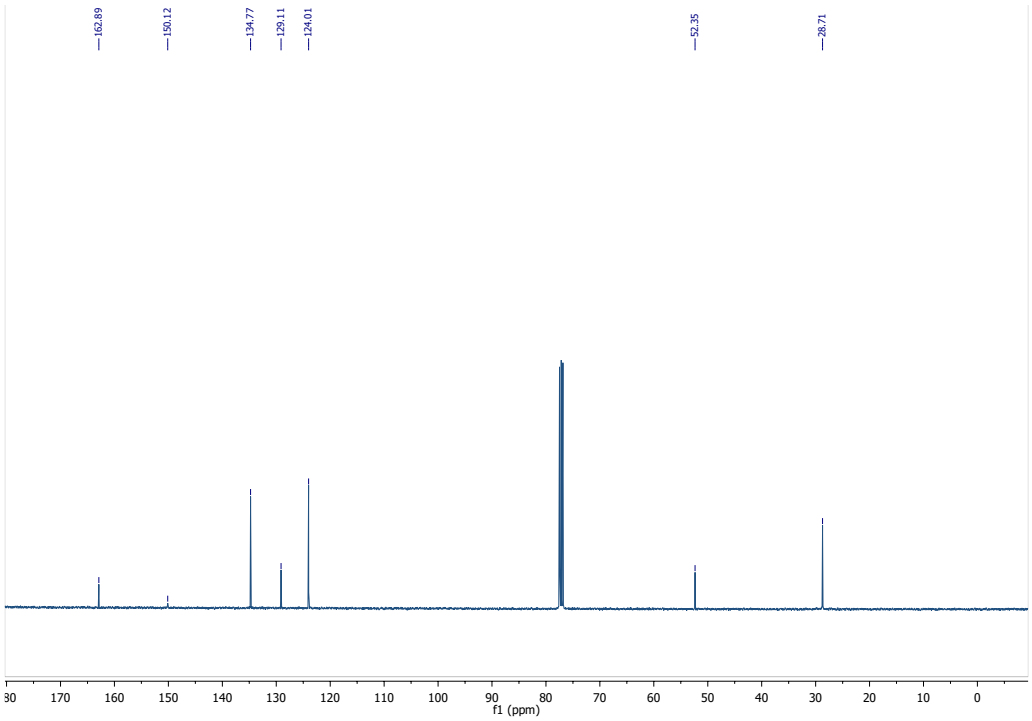



155.67
141.21
140.91
135.85
128.92
128.79
127.52
127.44
127.27
66.36
50.06
33.56
25.63
24.92
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

23. 1,3-dioxo-2,3-dihydro-1H-isoindol-2-yl *N*-tert-butylcarbamate

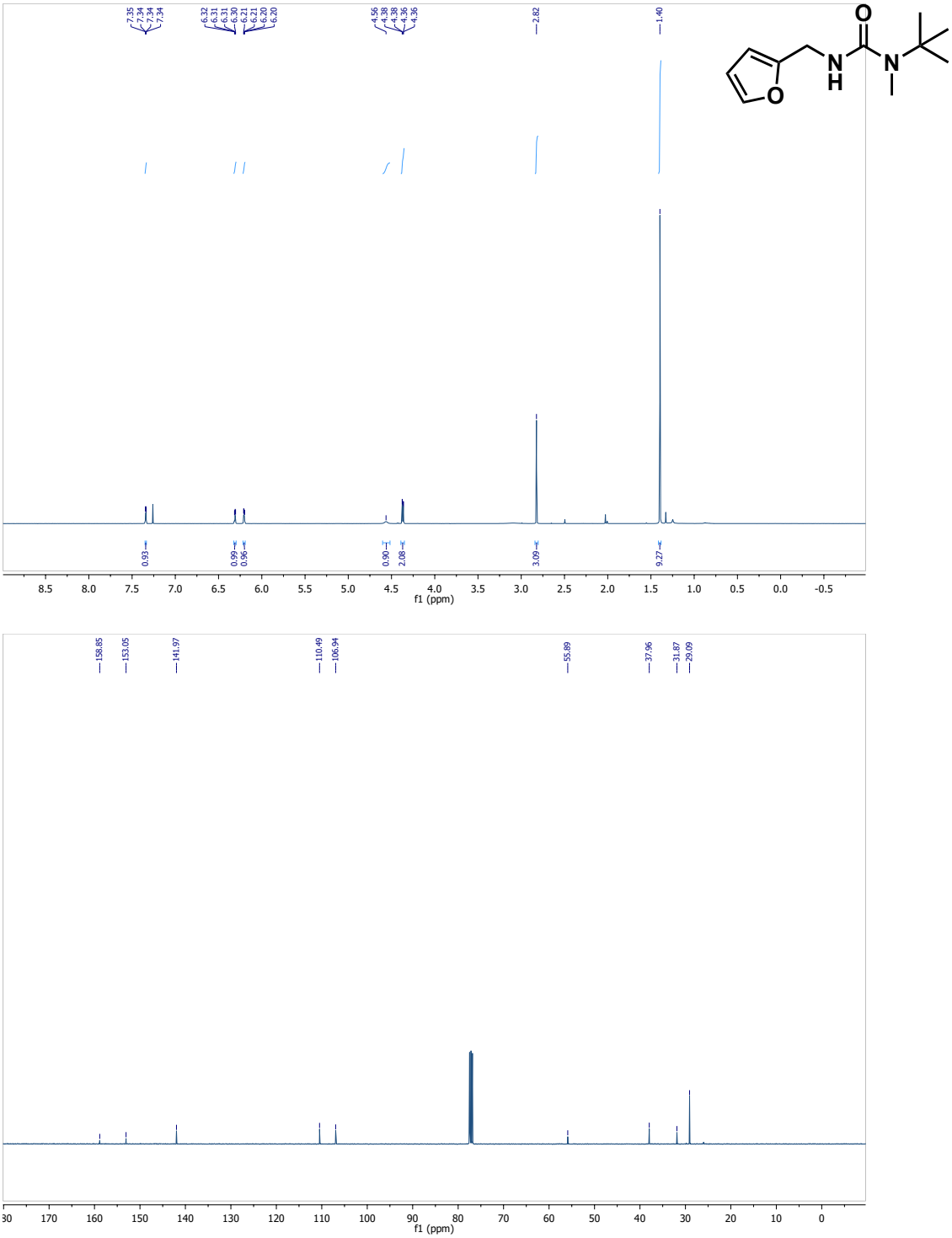
Followed the general procedure **7**, then procedure **2** using 10 equiv. of *N*-hydroxypthalimide (NHP). NHP was dissolved in THF (2.5) mL, and 10 equiv. of NEt_3 was added. The reaction was performed at reflux temperature in THF (2.5 mL). DBU was not used. The solvent was removed under reduced pressure, and the residue was dissolved in 10 mL of DCM. Solvent extraction was performed, and the organic layer was extracting using saturated aqueous NH_4Cl (3 × 5 mL), 10% Na_2CO_3 (2 × 5 mL), and water (2 × 5 mL). The solvent was removed under reduced pressure, and the product was purified by flash chromatography using silica gel (0-25% hexane/ethyl acetate). Product obtained as a white powder (54 mg, yield 81%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.88 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.77 (dd, *J* = 5.5, 3.1 Hz, 2H), 5.22 (s, 1H), 1.39 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): 162.9, 150.1, 134.8, 129.1, 124.0, 52.4, 28.7. MS (ESI+): Calculated $C_{13}H_{14}N_2O_4$ as 262.10, [M+H] found as 263.11.




162.89
150.12
134.77
129.11
124.01
52.35
28.71
f1 (ppm)

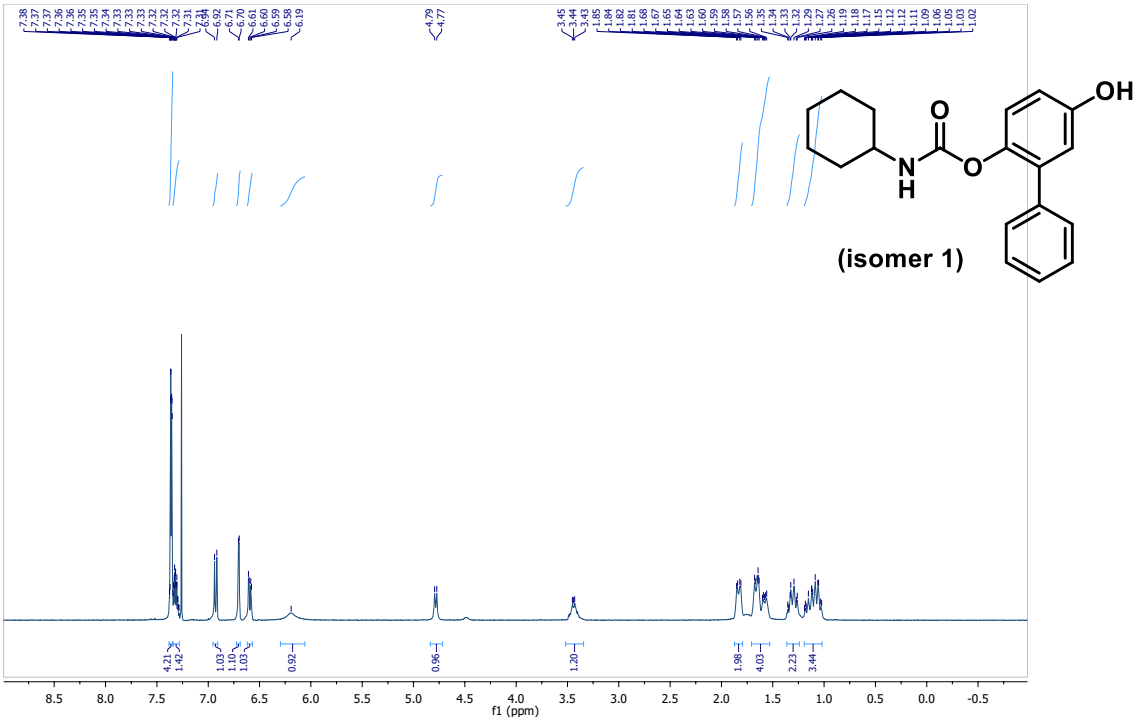
24. 3-*tert*-butyl-1-[(furan-2-yl)methyl]-3-methylurea

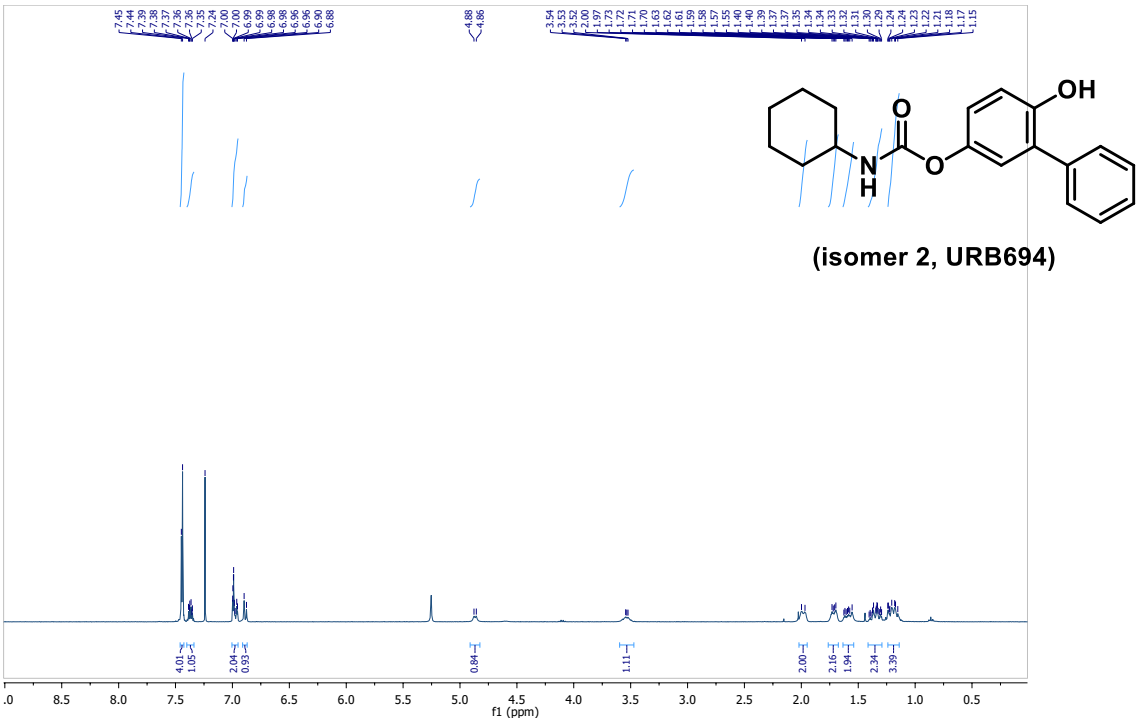
Followed the general procedure (**3**), product obtained as a white powder (37.5 mg, yield 71%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.35 (dd, *J* = 1.9, 0.9 Hz, 1H), 6.31 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.21 (dd, *J* = 3.2, 0.8 Hz, 1H), 4.56 (s, 1H), 4.37 (dd, *J* = 5.3, 0.7 Hz, 2H), 2.82 (s, 3H), 1.40 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): 158.9, 153.1, 142.0, 110.5, 106.9, 55.9, 38.0, 31.9, 29.1. MS (ESI+): Calculated $C_{11}H_{18}N_2O_2Na$ as 233.1266, [M+H] found as 233.1261.



25. 5-hydroxy-(1,1'-biphenyl)-2-yl *N*-cyclohexylcarbamate

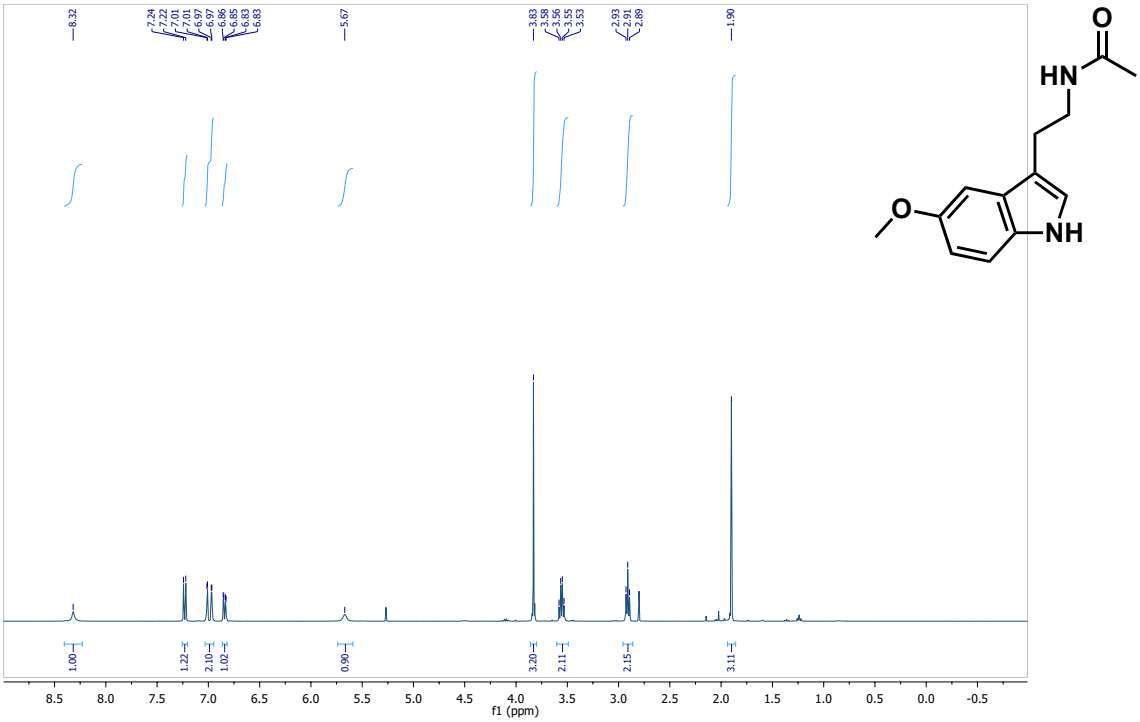
Followed the general procedure **7**, then procedure **2** using 10 equiv. of 2-phenyl-1,4-dihydroquinone. The reaction was performed at reflux temperature in THF (2.5 mL). DBU was not used. The obtained product was hydrolyzed in accordance with the literature, and a mixture of isomers was obtained (186 mg, yield 60%). Isomers were separated by prep-HPLC using a Phenomenex C18, 10 μM, 250 × 10 column with 70:30 MeOH/H_2O + 1% formic acid at 10 mL/min. Obtained isomer 1 (*N*-5-hydroxy-[1,1'-biphenyl]-2-yl cyclohexylcarbamate) as a white powder (160 mg, 85%), obtained isomer 2 (*N*-6-hydroxy-[1,1'-biphenyl]-3-yl cyclohexylcarbamate; URB694) as a white powder (26.5 mg, 14%). Isomer 1 ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.36 (m, 4H), 7.31 (m, 1H), 6.93 (d, *J* = 8.7 Hz, 1H), 6.71 (d, *J* = 3.0 Hz, 1H), 6.60 (dd, *J* = 8.7, 3.0 Hz, 1H), 6.19 (s, 1H), 4.78 (d, *J* = 8.4 Hz, 1H), 3.44 (m, 1H), 1.83 (dd, *J* = 12.6, 4.1 Hz, 2H), 1.68–1.56 (m, 4H), 1.31 (m, 2H), 1.10 (m, 2H). MS (ESI+): Calculated $C_{19}H_{21}NO_3$ as 311.15, [M+H] found as 312.20. Isomer 2 ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 4.3 Hz, 4H), 7.37 (m, 1H), 6.98 (m, 2H), 6.89 (d, *J* = 8.5 Hz, 1H), 4.87 (d, *J* = 8.2 Hz, 1H), 3.53 (m, 1H), 1.99 (d, *J* = 12.3 Hz, 2H), 1.72 (m, 2H), 1.69 (m, 2H), 1.35 (m, 2H), 1.20 (m, 2H)**.** MS (ESI+): Calculated $C_{19}H_{21}NO_3$ as 311.15, [M+H] found as 312.18. Characterized in accordance with the literature.[11]




OH
O
N
H
O
(isomer 2, URB694)
f1 (ppm)

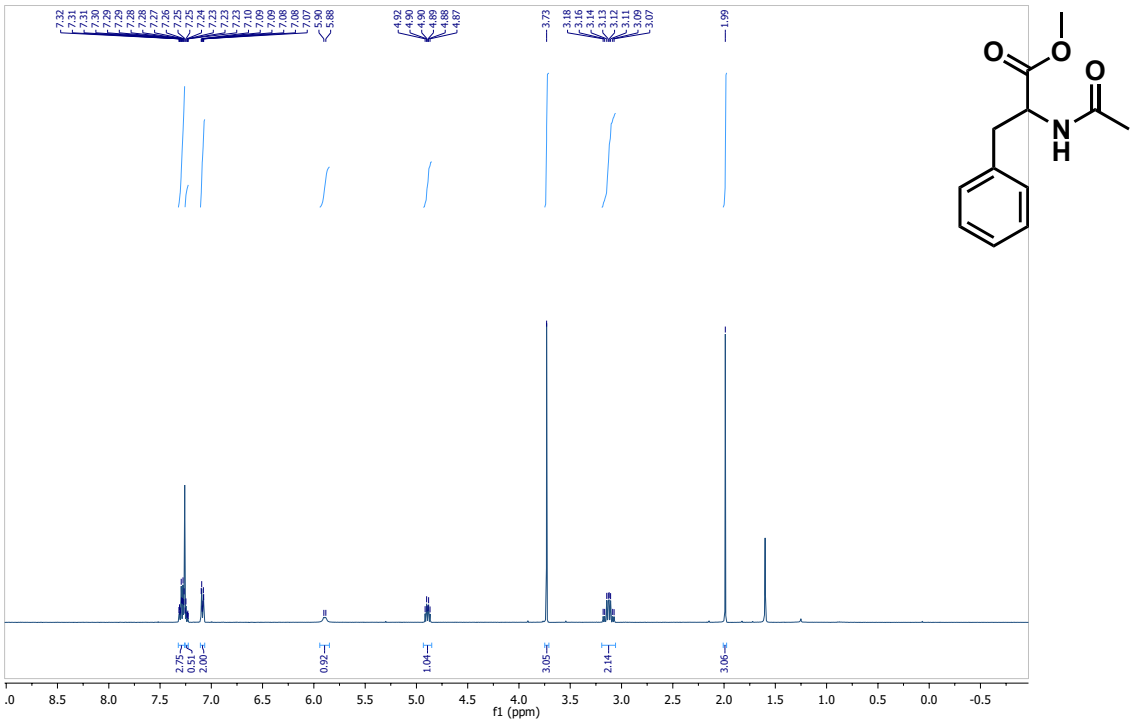
26. *N*-[2-(5-methoxy-1H-indol-3-yl)ethyl]acetamide

Followed the general procedure **7**, then procedure **4.** Flash column chromatography at 0–80% hexanes/ethyl acetate. Product obtained as a brown oil (42 mg, yield 72%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.32 (s, 1H), 7.23 (d, *J* = 8.8 Hz, 1H), 6.99 (dd, *J* = 17.0, 2.4 Hz, 2H), 6.85 (dd, *J* = 8.8, 2.5 Hz, 1H), 5.67 (s, 1H), 3.83 (s, 3H), 3.56 (dt, *J* = 6.5 Hz, 2H), 2.91 (t, *J* = 6.8 Hz, 2H), 1.90 (s, 3H). MS (ESI+): Calculated $C_{13}H_{16}N_2O_2$ as 232.12, [M+H] found as 233.15. Characterized in accordance with the literature.[12]



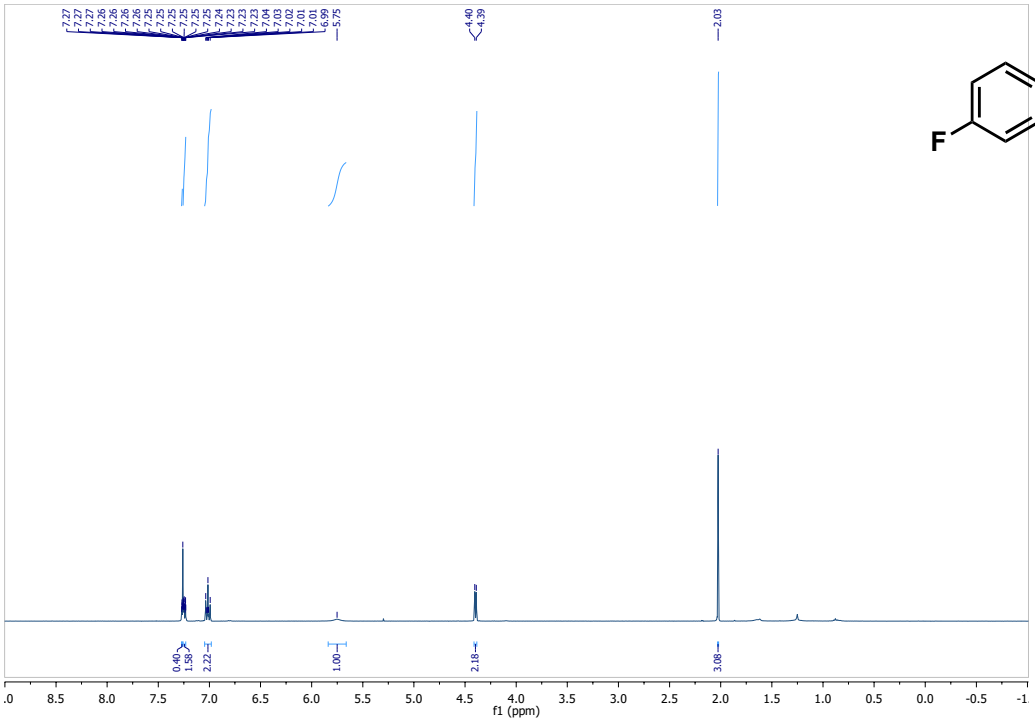
27. methyl 2-acetamido-3-phenylpropanoate

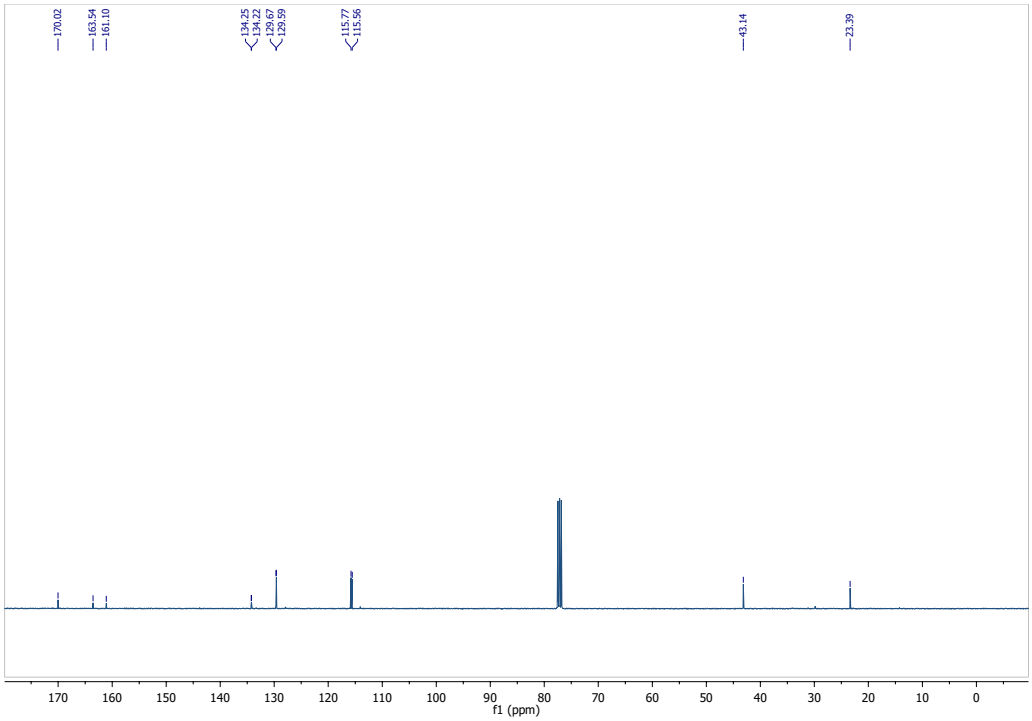
Followed the general procedure **7**, then procedure **4**. Product obtained as a white powder (46.5 mg, yield 84%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.32–7.23 (m, 3H), 7.09 (m, 2H), 5.89 (d, *J* = 7.8 Hz, 1H), 4.90 (dt, *J* = 7.8, 5.7 Hz, 1H), 3.73 (s, 3H), 3.13 (m, 2H), 1.99 (s, 3H). MS (ESI+): Calculated $C_{12}H_{15}NO_3$ as 221.11, [M+H] found as 222.09. Characterized in accordance with the literature.[13]

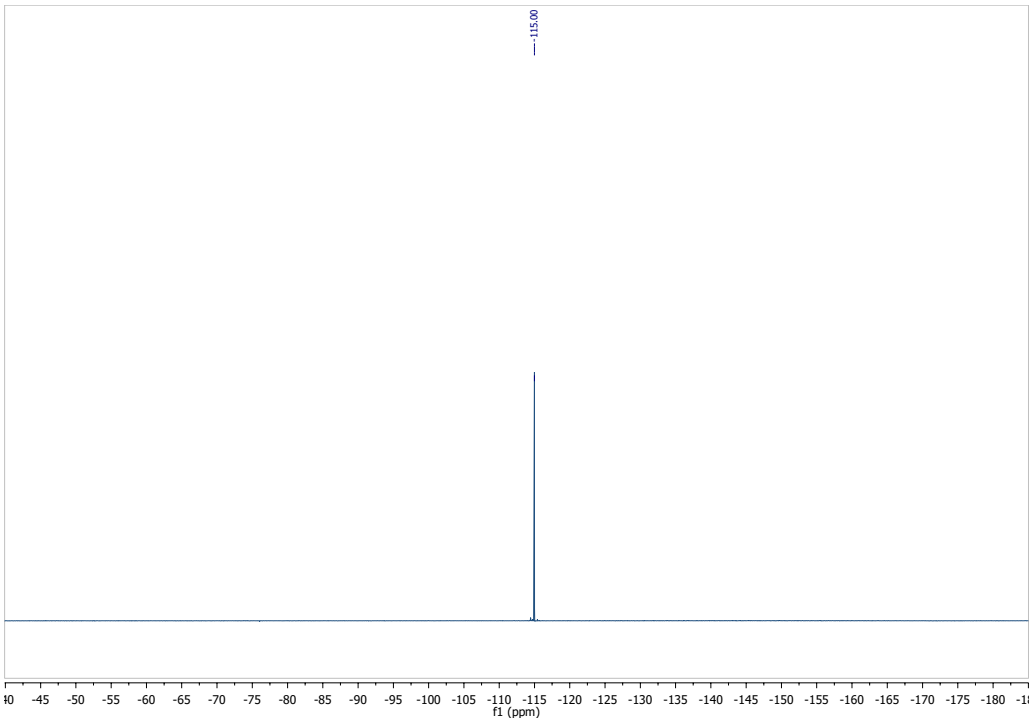


28. *N*-[(4-fluorophenyl)methyl]acetamide

Followed the general procedure **7**, then procedure **4**. Product obtained as a white powder (30.5 mg, yield 73%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.25 (m, 2H), 7.02 (m, 2H), 5.75 (s, 1H), 4.40 (d, *J* = 5.8 Hz, 2H), 2.03 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): 170.0, 162.3 (d, *J* = 246 Hz), 134.2 (d, *J* = 3 Hz), 129.6 (d, *J* = 8 Hz), 115.7 (d, *J* = 21 Hz), 43.1, 23.4. ^{19}F-NMR (376 MHz, $CDCl_3$): -115.00 (s, 1F). MS (ESI+): Calculated $C_9H_{10}FNO$ as 167.07, [M+H] found as 167.94. Characterized in accordance with the literature.[14]

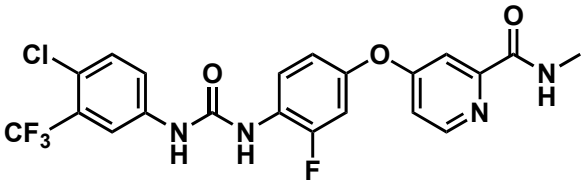


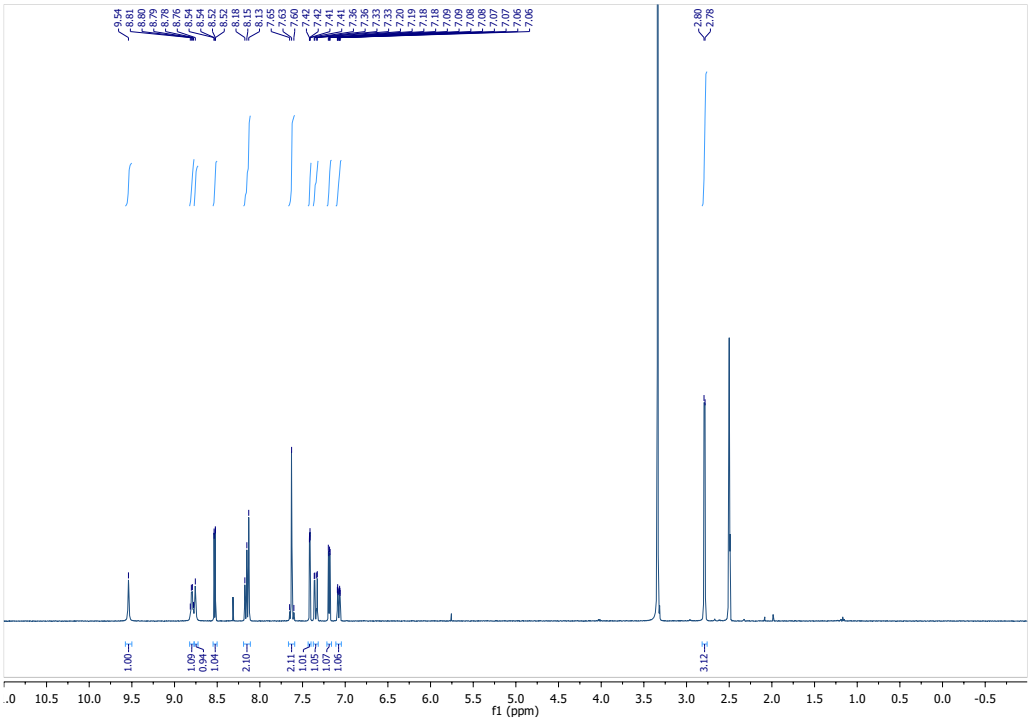


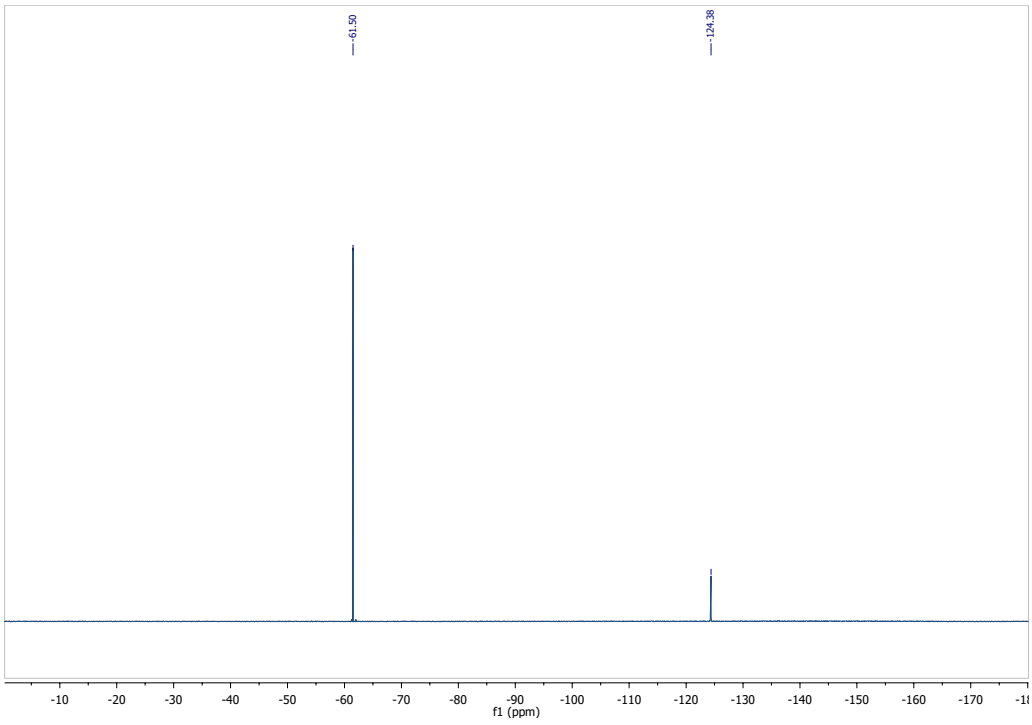

-115.00
-45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180
f1 (ppm)

29. 4-[4-({[4-chloro-3-(trifluoromethyl)phenyl]carbamoyl}amino)-3-fluorophenoxy]-*N*-methylpyridine-2-carboxamide

Followed the general procedure (**3**) to obtain the urea derived from *N*-*tert*-butylmethylamine. The intermediate was dissolved in toluene (0.25 M), and 1.5 equiv. of 4-(4-amine-3-fluorophenoxy)-*N*-methylpicolinamide was added. The reaction was heated to reflux until completion. Flash column chromatography performed using a gradient of 0–10% DCM/MeOH. The product was obtained as a white powder (85 mg, yield 71%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.54 (s, 1H), 8.80 (m, 1H), 8.76 (s, 1H), 8.53 (dd, 1H), 8.16 (m, 2H), 7.63 (m, 2H), 7.42 (dd, *J* = 2.7, 0.5 Hz, 1H), 7.35 (dd, *J* = 11.6, 2.7 Hz, 1H), 7.19 (dd, *J* = 5.6, 2.6 Hz, 1H), 7.08 (ddd, *J* = 8.9, 2.7, 1.3 Hz, 1H), 2.79 (d, *J* = 4.8 Hz, 3H). ^{19}F-NMR (376 MHz, $CDCl_3$): -61.50 (s, 3F), -124.38 (s, 1F). MS (ESI+): Calculated $C_{21}H_{15}ClF_4N_4O_3$ as 482.08, [M+H] found as 483.14. Characterized in accordance with the literature.[15]

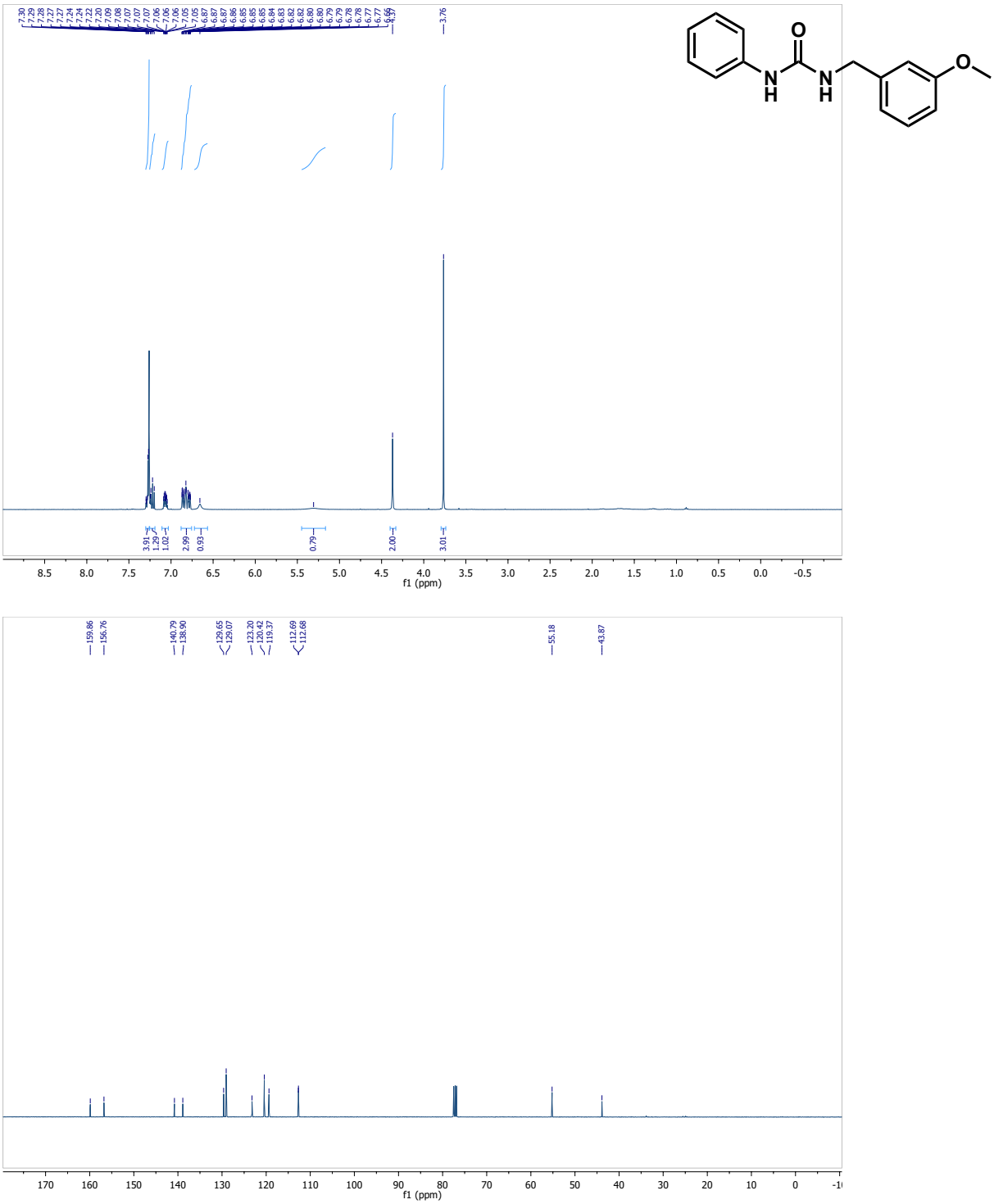





-61.50
-124.38
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

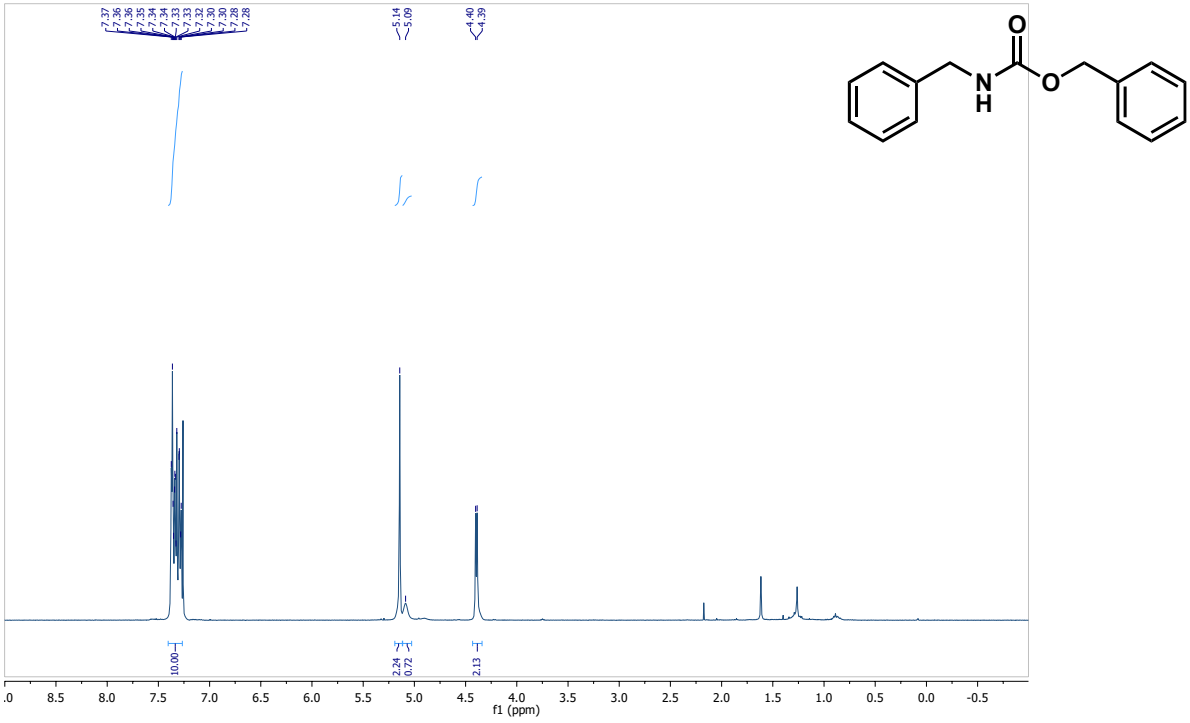
30. 1-[(3-methoxyphenyl)methyl]-3-phenylurea

Followed the procedure described by Murray et al.,[16] product obtained as a white powder (56 mg, yield 88%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.29 (m, 4H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.07 (m, 1H), 6.82 (m, 3H), 6.66 (s, 1H), 5.31 (s, 1H), 4.37 (s, 2H), 3.76 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): 159.9, 156.8, 140.8, 138.9, 129.7, 129.1, 123.2, 120.4, 119.4, 112.7, 112.7, 55.2, 43.9. MS (ESI+): Calculated $C_{15}H_{16}N_2O_2Na$ as 279.1109, [M+H] found as 279.1128.



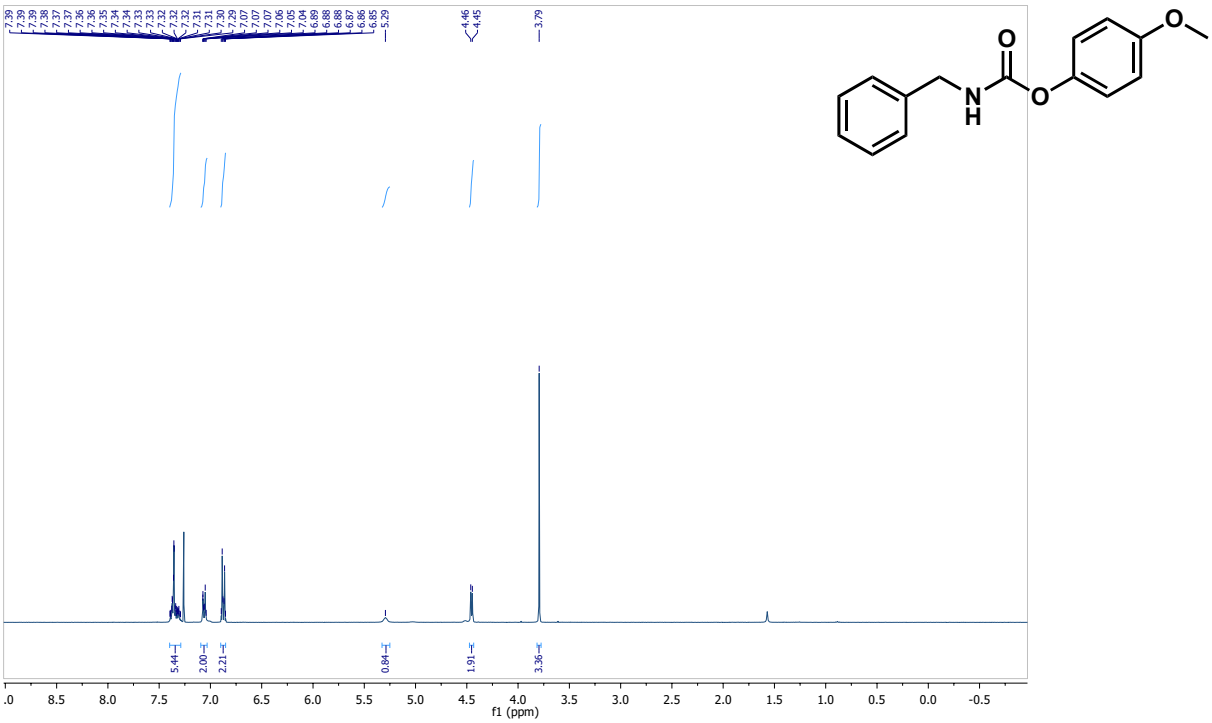
31. benzyl *N*-benzylcarbamate

Followed the general procedure (**2**), product obtained as a white powder (43 mg, yield 72%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.33 (m, 10H), 5.14 (s, 2H), 5.09 (s, 1H), 4.40 (d, *J* = 6.0 Hz, 2H). MS (ESI+): Calculated $C_{15}H_{15}NO_2$ as 241.11, [M+H] found as 242.17. Characterized in accordance with the literature.[1]



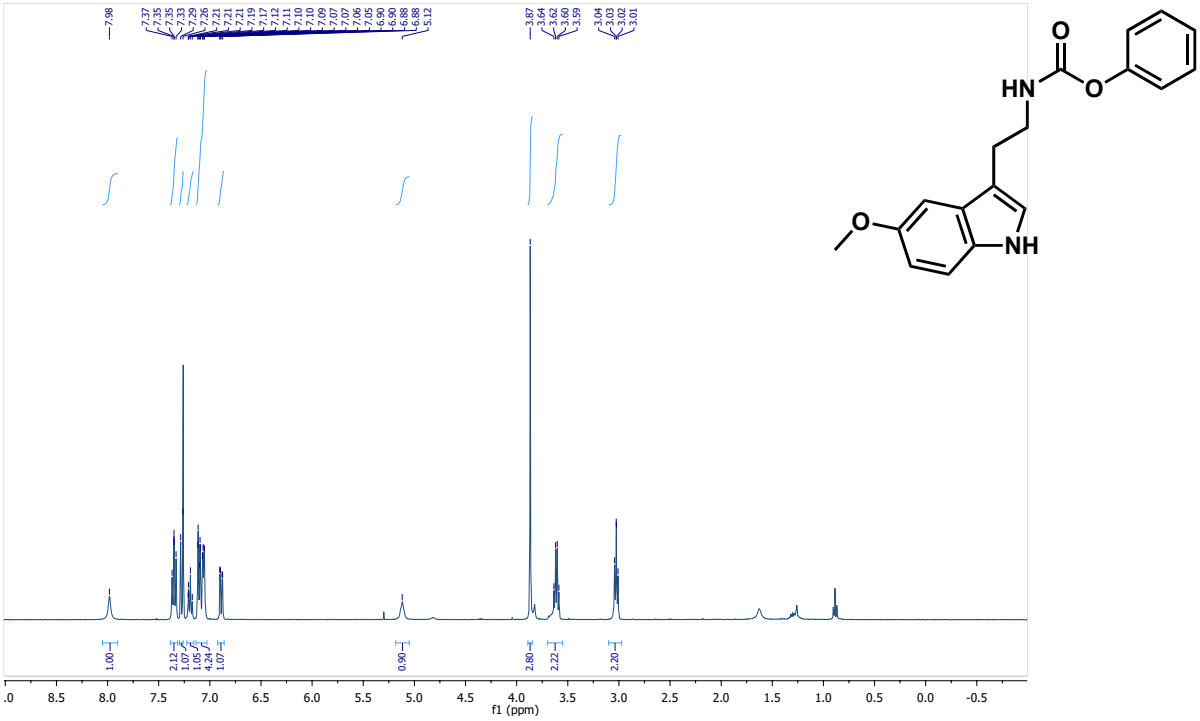
32. 4-methoxyphenyl *N*-benzylcarbamate

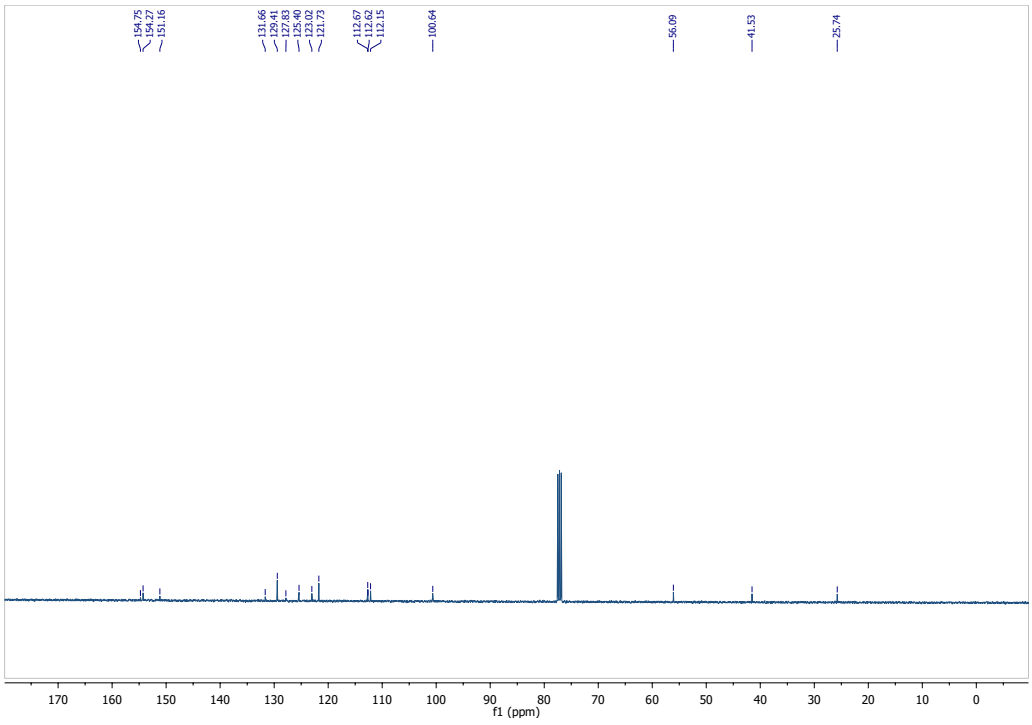
Followed the procedure described by Krátký M. et al.,[17] product obtained as a white powder (81 mg, yield 92%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.34 (m, 5H), 7.06 (m, 2H), 6.87 (m, 2H), 5.29 (s, 1H), 4.46 (d, *J* = 6.0 Hz, 2H), 3.79 (s, 3H). MS (ESI+): Calculated $C_{15}H_{15}NO_3$ as 257.11, [M+H] found as 258.16. Characterized in accordance with the literature.[18]



33. phenyl *N*-[2-(5-methoxy-1H-indol-3-yl)ethyl]carbamate

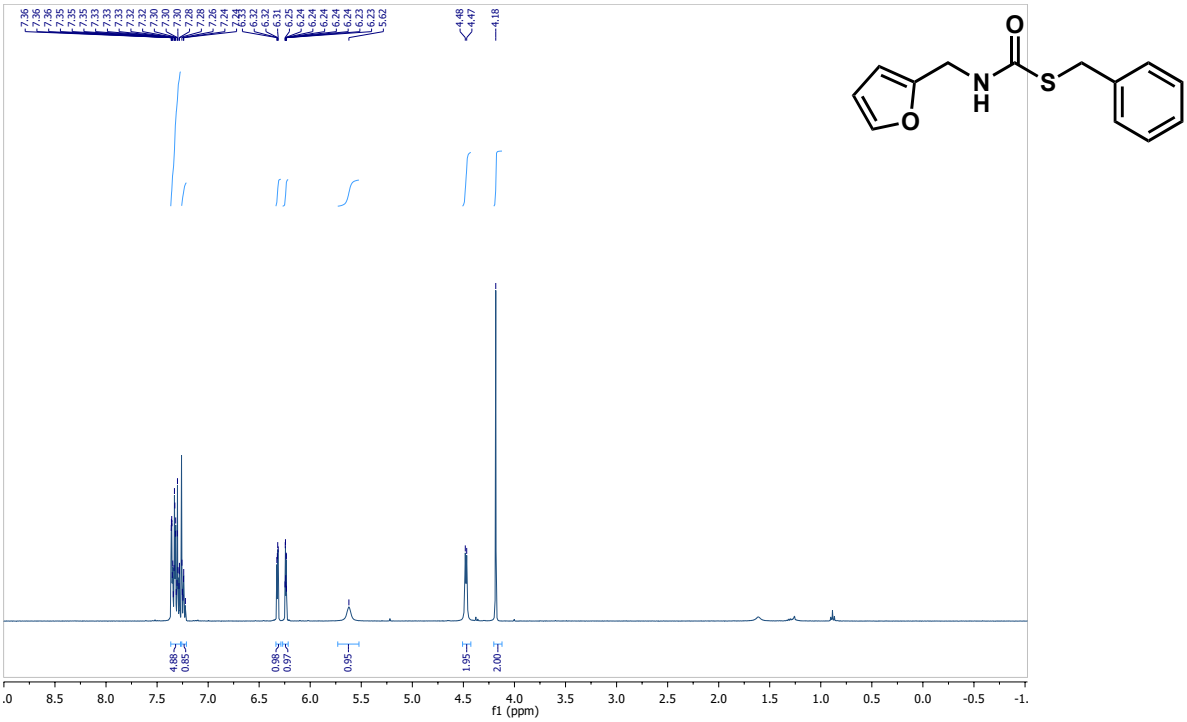
Followed the procedure described by Zhou Y. et al.,[19] product obtained as a light yellow solid (60 mg, yield 74%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.35 (dd, *J* = 8.5, 7.3 Hz, 2H), 7.26 (d, *J* = 9.0 Hz, 1H), 7.19 (m, 1H), 7.09 (m, 4H), 6.89 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.12 (s, 1H), 3.87 (s, 3H), 3.62 (dt, *J* = 6.5 Hz, 2H), 3.03 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): 154.8, 154.3, 151.2, 131.7, 129.4, 127.8, 125.4, 123.0, 121.7, 112.7, 112.6, 112.2, 100.6, 56.1, 41.5, 25.7. MS (ESI+): Calculated $C_{18}H_{18}N_2O_3Na$ as 333.1215, [M+H] found as 333.1205.

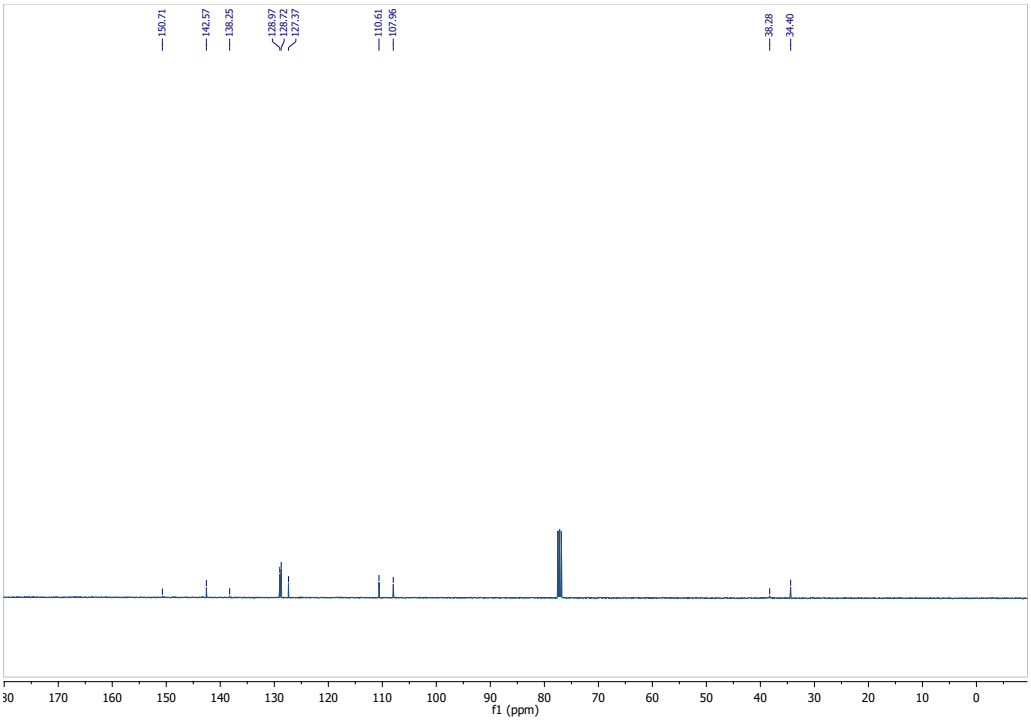



154.75
154.27
151.16
131.66
129.41
127.83
125.40
123.02
121.73
112.67
112.62
112.15
100.64
56.09
41.53
25.74
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

34. *N*-[(furan-2-yl)methyl](benzylsulfanyll)formamide

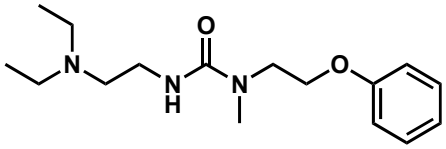
Followed the procedure described by Zhou et al.,[19] product obtained as a white powder (63 mg, yield 25%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.32 (m, 5H), 7.24 (m, 1H), 6.32 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.24 (m, 1H), 5.62 (s, 1H), 4.48 (d, *J* = 5.6 Hz, 2H), 4.18 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): 150.7, 142.6, 138.3, 129.0, 128.7, 127.4, 110.6, 108.0, 38.3, 34.4. MS (ESI+): Calculated $C_{13}H_{13}NO_2SNa$ as 270.0565, [M+H] found as 270.0571.

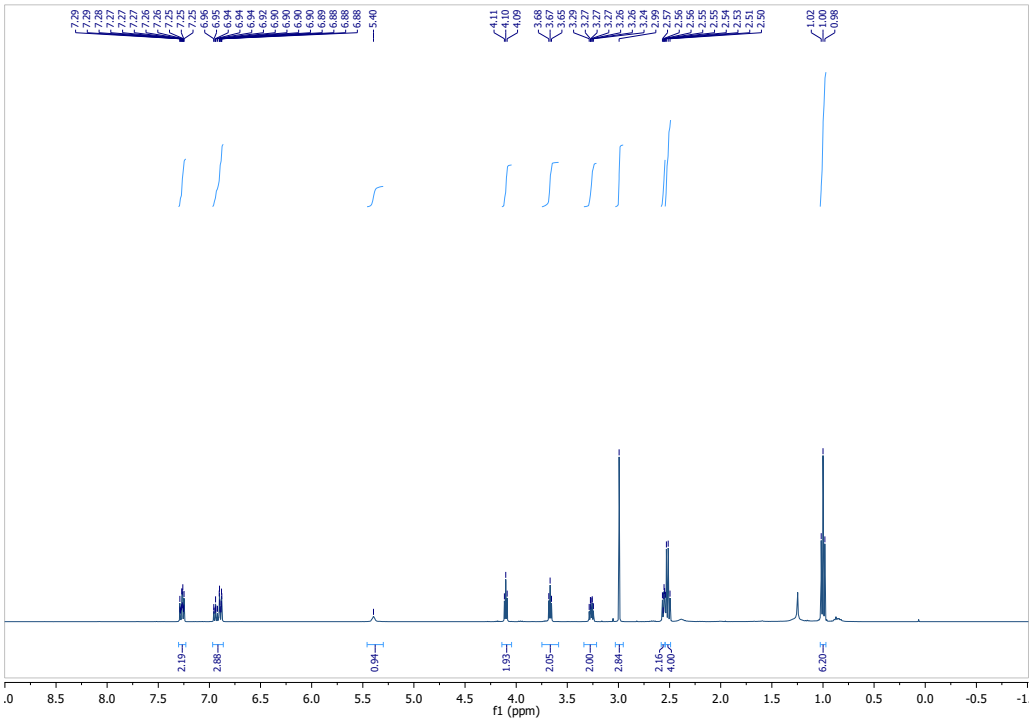




35. 3-[2-(diethylamino)ethyl]-1-methyl-1-(2-phenoxyethyl)urea

Followed the procedure described by Zhou et al.,[19] product obtained as an oil (42 mg, yield 27%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.27 (m, 2H), 6.92 (m, 3H), 5.40 (s, 1H), 4.10 (t, *J* = 5.3 Hz, 2H), 3.67 (t, *J* = 5.3 Hz, 2H), 3.27 (m, 2H), 2.99 (s, 3H), 2.56 (m, 2H), 2.52 (m, 4H), 1.00 (t, *J* = 7.1 Hz, 6H). MS (ESI+): Calculated $C_{16}H_{27}N_3O_2$ as 293.21, [M+H] found as 294.24. Characterized in accordance with the literature.[20]

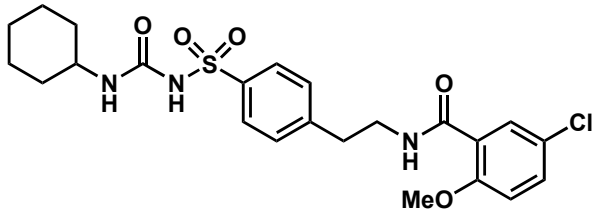




Section 4: Radiochemistry

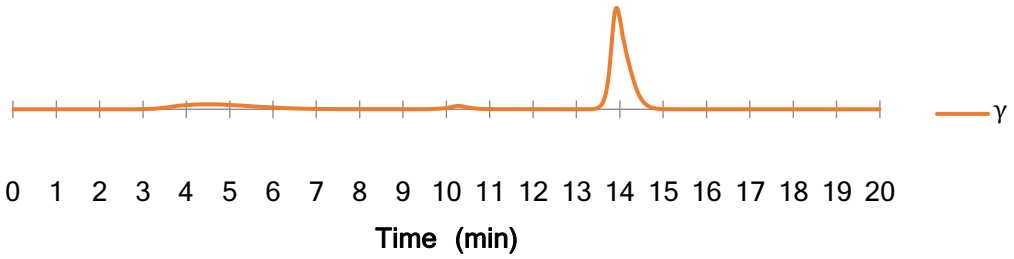
The peaks indicated by solid arrows are present in the chromatograms following co-injection of products with additional nonradioactive standard. The differences in elution times are due to UV-Vis and radiation detectors placed in series, and in all cases were consistent with delays observed at the time of acquisition. Due to modifications of the radioHPLC system, these delays have varied over the course of this project.

Example calculations:



RCY: 75 ± 14%, **TE:** 99%
***n* =** 2

Radiochemical Yield (RCY) determined based on integration of the peaks by radioHPLC.



Retention Time (min)	**Area** (μV*sec)	**% Area**	**d.c. Area**	**d.c. % Area**
4.614	5,426,465	15.60%	6,350,537	12%
10.275	905,203	2.60%	1,284,783	2%
13.927	28,444,819	81.79%	45,723,732	86%

Trapping Efficiency (TE) determined based on the activity readings collected at the reactor and the CO_2 trap.

$$TE = \frac{d.c\ A_{\text{reactor}}}{A_{\text{trap}}} x100\% = \frac{640\ mCi \text{ at } 18{:}01}{690\ mCi \text{ at } 17{:}59} x100\% = \frac{685\ mCi \text{ at } 17{:}59}{690\ mCi \text{ at } 17{:}59} x100\% = 99\%$$

Molar Activity (A_M) determined according to the activity concentration at end of synthesis.

$Area_{UV}$ = 48,108

n = $Area_{UV}$ / 298165700.87 μmol^{-1} (according to calib. curve of glibencamide, see Section 5)

= 48108 / 298165700.87 μmol^{-1}

= 0.0001613 μmol

Activity concentration:	19.14 mCi/mL	@	18:36
Injection volume:	10 μL		
Activity injected:	0.19 mCi	@	18:36
Decay-corrected activity injected:	0.26 mCi/mL	@	18:27

A_M = activity injected / n

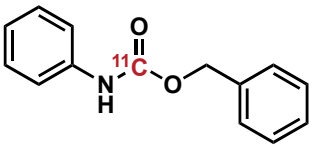
= 0.26 x 10^{-3} Ci / 1.61 x 10^{-4} μmol

= 1.61 Ci·μmol^{-1}

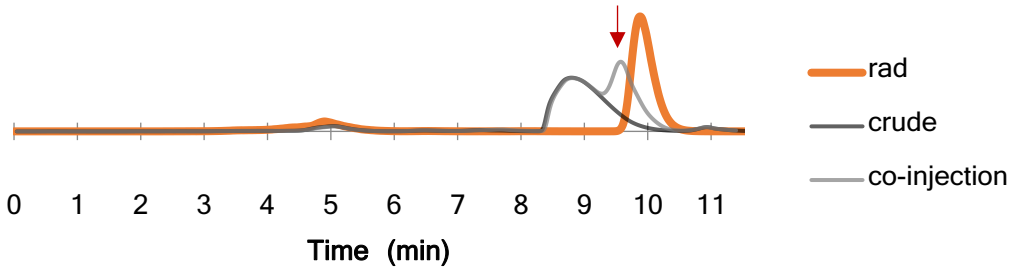
= 59.57 GBq·μmol^{-1} at end of synthesis

[^{11}C]4 (benzyl *N*-phenylcarbamate)

Compound was synthesized according to the general procedure (**8**).

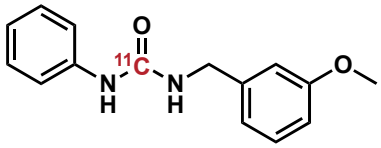


RCY: 91 ± 2%, **TE:** 99%
n = 6

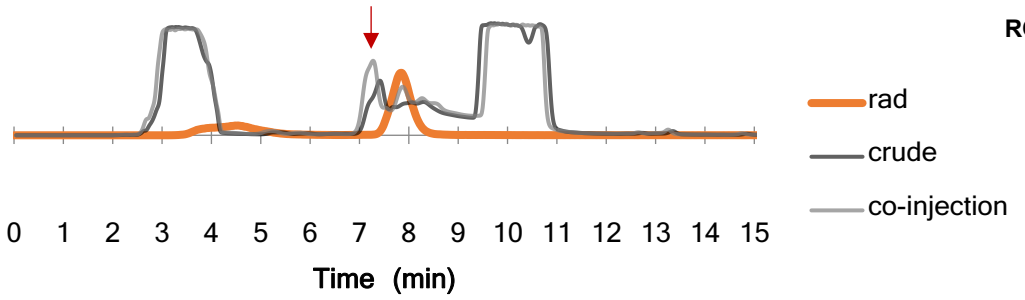


[^{11}C]30 (1-[(3-methoxyphenyl)methyl]-3-phenylurea)

Compound was synthesized according to the general procedure (**8**).

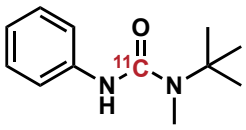


RCY: 88 ± 2%, **TE:** 83 ± 2%
n = 2

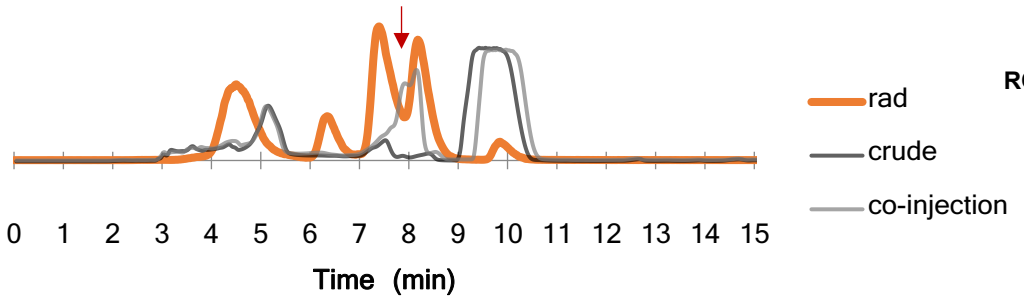


[^{11}C]12 (3-tert-butyl-3-methyl-1-phenylurea)

Compound was synthesized according to the general procedure (**8**)

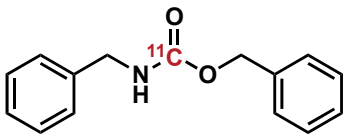


RCY: 32 ± 5%, **TE:** 70 ± 4%
n = 2

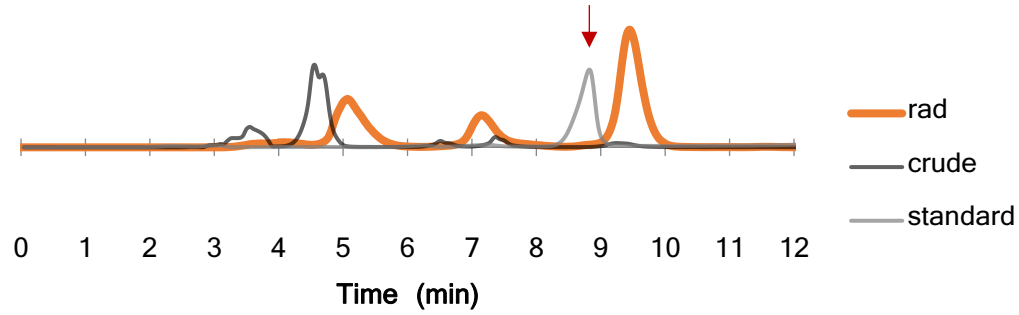


[^{11}C]31 (benzyl *N*-benzylcarbamate)

Compound was synthesized according to the general procedure (**8**).
Exceptional conditions: Iminophosphorane **1o** (7.83 µmol).

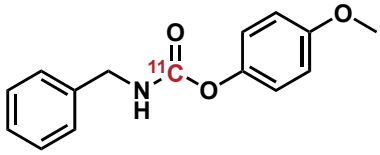


RCY: 64 ± 3%, **TE:** 98 ± 3%
n **=** 2

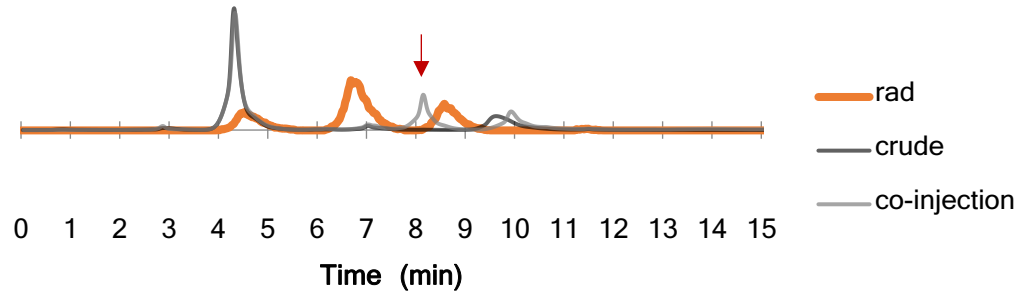


[^{11}C]32 (4-methoxyphenyl *N*-benzylcarbamate)

Compound was synthesized according to the general procedure (**8**).
Exceptional conditions: Iminophosphorane **1o** (7.83 µmol), phenol (560 µmol), DABCO (160 µmol), no DBU. CO_2 trapped at -60 °C.



RCY: 26 ± 2%, **TE:** 83 ± 2%
n **=** 2

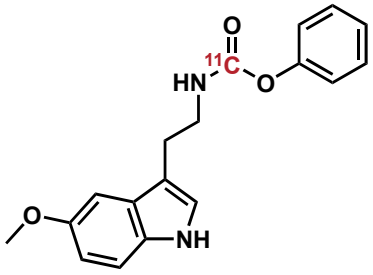


[^{11}C]33 (phenyl-*N*-[2-(5-methoxy-1H-indol-3-yl)ethyl]carbamate)

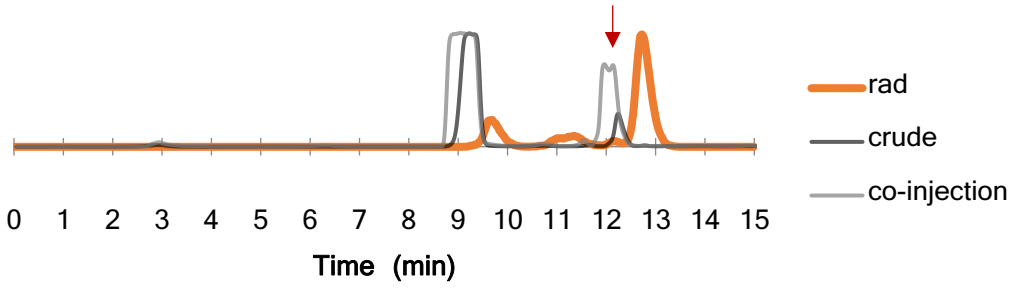
Compound was synthesized according to the general procedure (**8**).

Exceptional conditions: Iminophosphorane **1j** (7.53 µmol), phenol (1300 µmol), DABCO (16.04 µmol), no DBU. Reaction run for 2 min. CO_2 trapped at -60 °C.

Analytical HPLC Conditions: 0-2 mins at 20% ACN / 80% 0.1 M AMF. 2-10 mins gradient to 80% ACN / 20% 0.1 M AMF. 10-12 mins at 80% ACN / 20% 0.1 M AMF. 12-13 mins return to initial conditions.



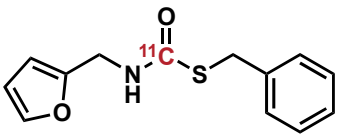
RCY: 84 ± 8%, **TE:** 58%
***n* =** 2



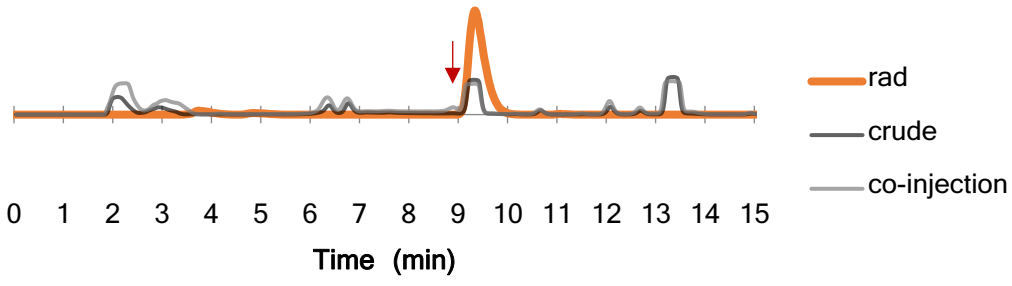
[^{11}C]34 (*N*-[(furan-2-yl)methyl](benzylsufanyl)formamide)

Compound was synthesized according to the general procedure (**8**).

Exceptional conditions: Iminophosphorane **1j** (9.13 µmol), benzyl mercaptan (510 µmol), DABCO (16.04 µmol), no DBU. CO_2 trapped at -60 °C.



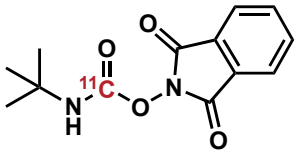
RCY: 93 ± 2%, **TE:** 53 ± 6%
***n* =** 2



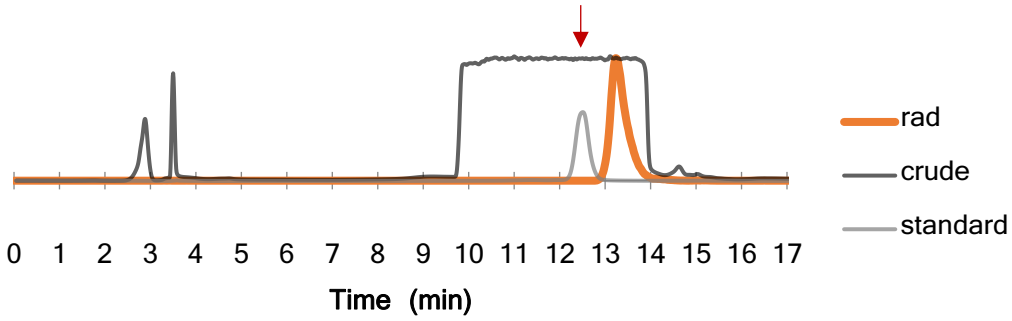
[^{11}C]23 (1,3-dioxo-2,3-dihydro-1H-isoindol-2-yl *N-tert*-butylcarbamate)

Compound was synthesized according to the general procedure (**8**).

Exceptional conditions: Iminophosphorane **1h** (11.9 µmol), LHMDS (11.7 µmol), *N*-hydroxypthalamide (510 µmol), NEt_3 (510 µmol), no DBU). CO_2 trapped at -60 °C.



RCY: 99 ± 3%, **TE:** 52 ± 6%
n **=** 2

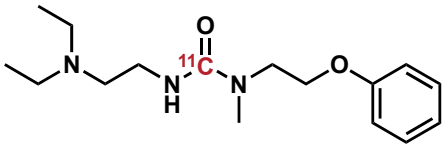


[^{11}C]35 (3-[2-(diethylamino)ethyl]-1-methyl-1-(2-phenoxyethyl)urea)

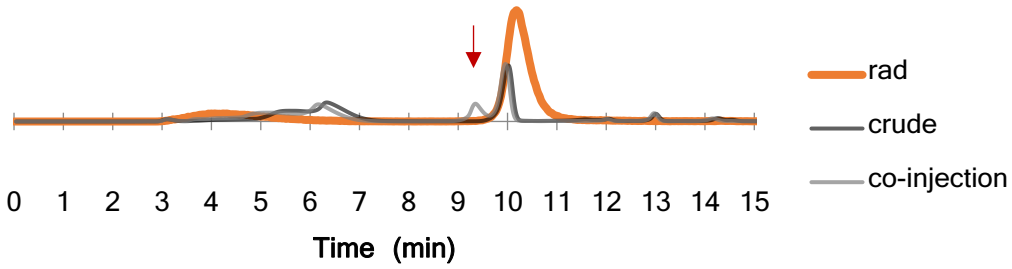
Compound was synthesized using procedure **9**.

Exceptional conditions: Iminophosphorane **1p** (8.75 µmol), *N*-methyl-2-phenoxyethanamine (87.5 µmol), DBU (8.71 µmol). CO_2 trapped at -60 °C.

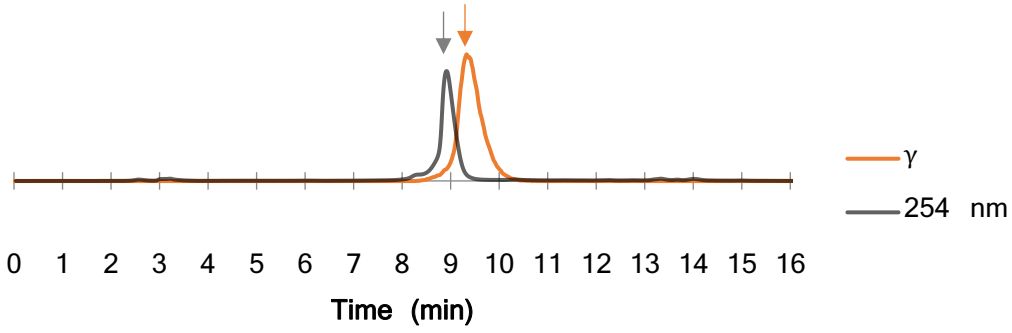
Analytical HPLC Conditions: 0-2 mins at 20% ACN / 80% 0.1 M AMF. 2-10 min gradient to 65% ACN / 35% 0.1 M AMF. 10-12 min 65% ACN / 35% 0.1 M AMF. 12-13 min return to initial conditions.



RCY: 99 ± 1%, **TE:** 99%
n **=** 2

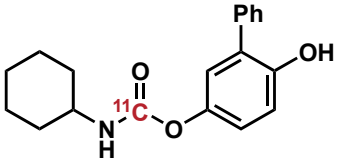


Isolated RCY: 33 ± 11%

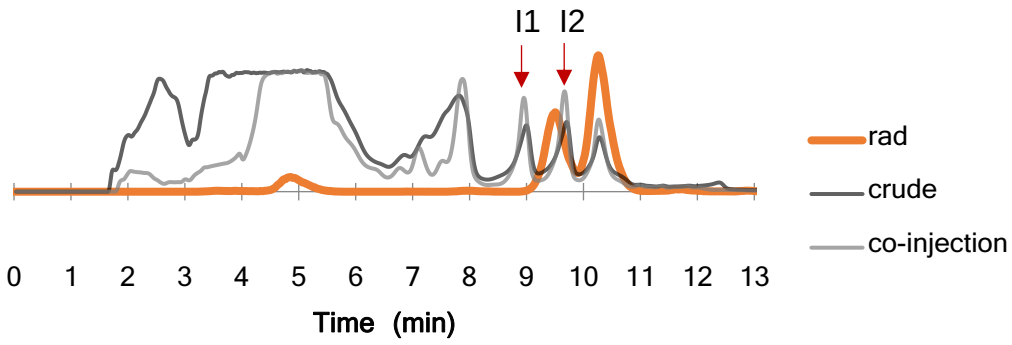


[^{11}C]25 (5-hydroxy-(1,1'-biphenyl)-2-yl-*N*-cyclohexylcarbamate)

Compound was synthesized using procedure **10**.



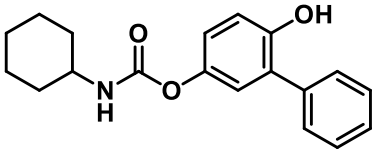
RCY: 96 ± 1%, **TE:** 64 ± 11%
(as a mixture of isomers)
***n* =** 2



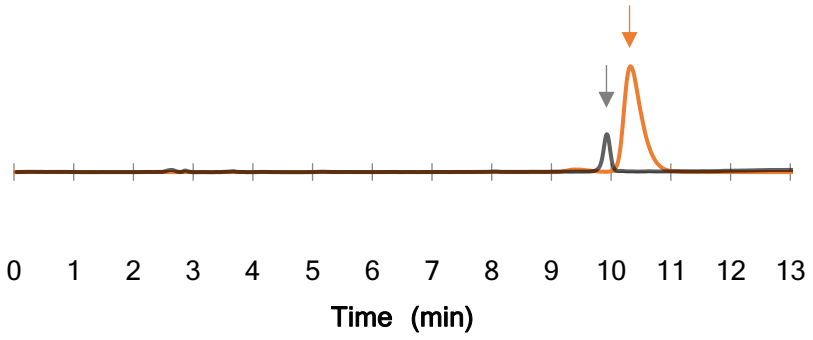
Isomer 1 → 36% area ([^{11}C]*N*-5-hydroxy-[1,1'-biphenyl]-2-yl cyclohexylcarbamate)
Isomer 2 → 64% area ([^{11}C]*N*-6-hydroxy-[1,1'-biphenyl]-3-yl cyclohexylcarbamate; [^{11}C]URB694)

[^{11}C]**URB694**:

Isolated RCY: 13 ± 2%, **Molar Activity:** 69 ± 37 GBq/μmol (*n* = 2)



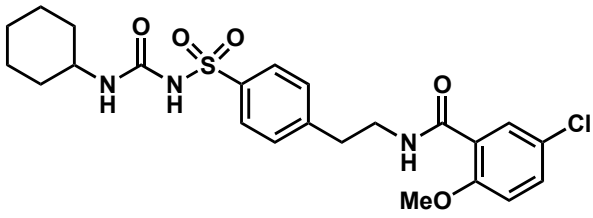
(isomer 2, URB694)



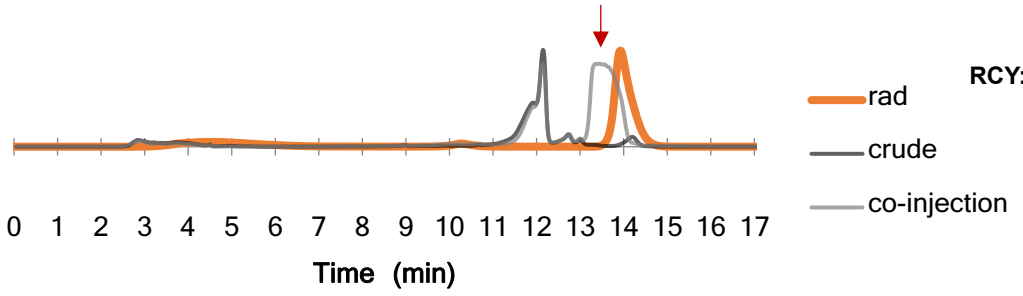
[^{11}C]36 (5-chloro-N-[2-4-{[(cyclohexylcarbamoyl)amino]sulfonyl}phenyl)ethyl]-2-methoxybenzamide)

Compound was synthesized using procedure **11**.

Analytical HPLC Conditions: 0-2 mins at 20% ACN / 80% 0.1 M AMF. 2-10 min gradient to 65% ACN / 35% 0.1 M AMF. 10-12 min 65% ACN / 35% 0.1 M AMF. 12-13 min return to initial conditions.

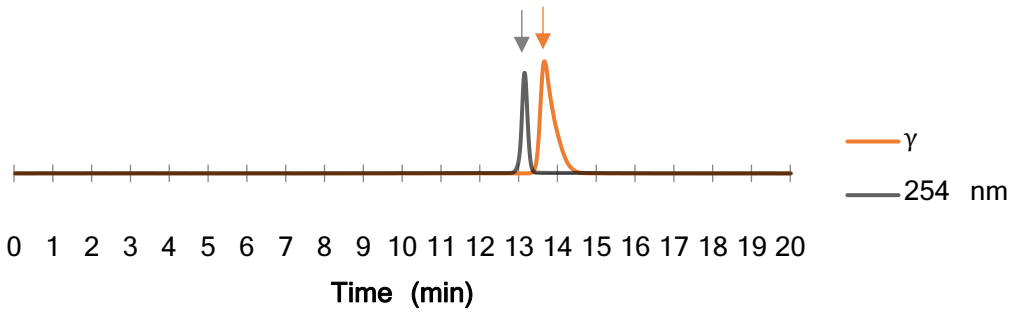


RCY: 75 ± 14%, **TE:** 99%
n **=** 2

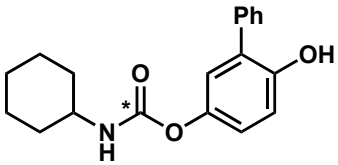


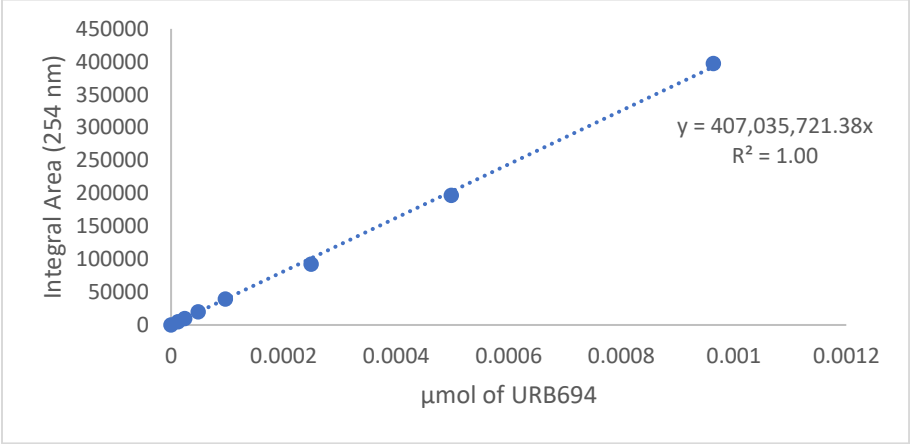
[^{11}C]**Glibenclamide**:

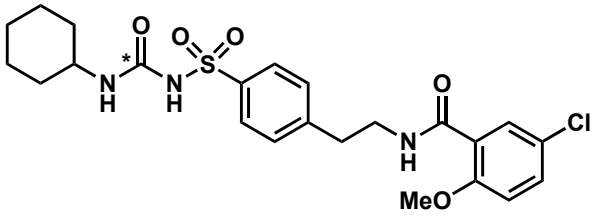
Isolated RCY: 62 ± 16%, **Molar Activity:** 59 ± 0.06 GBq/μmol (*n* = 2)

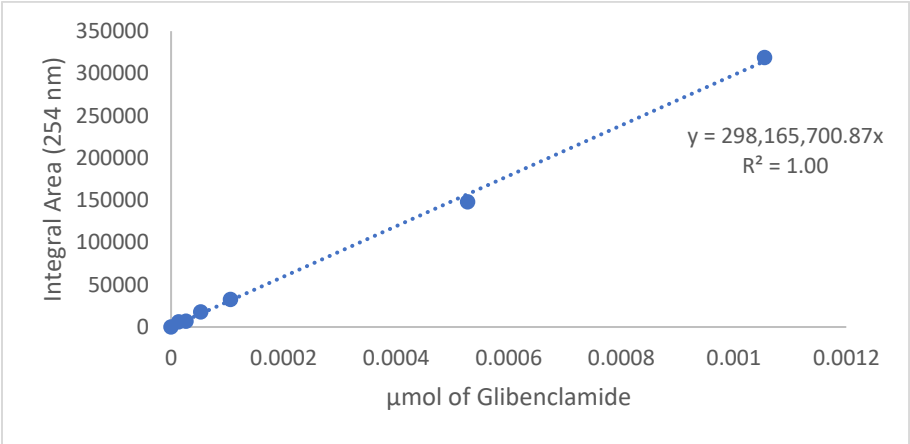


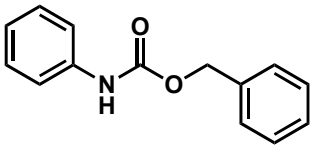
Section 5: Standard Curves

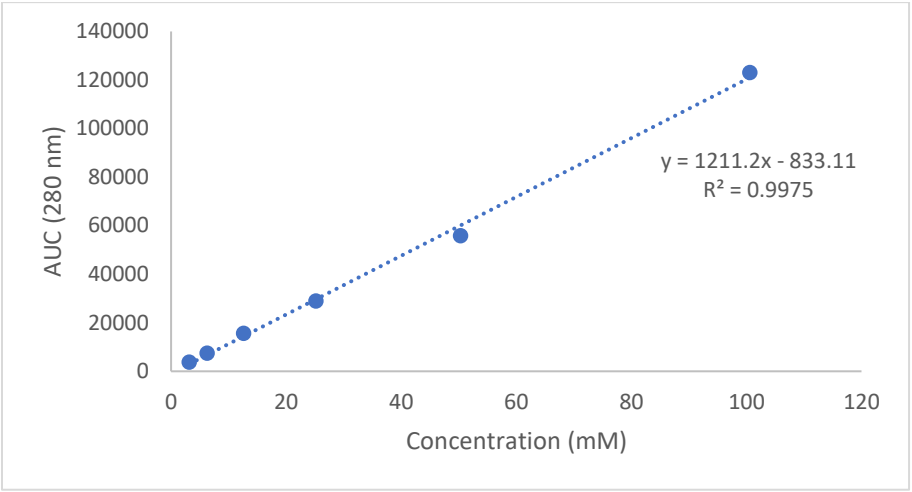


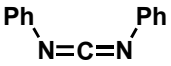


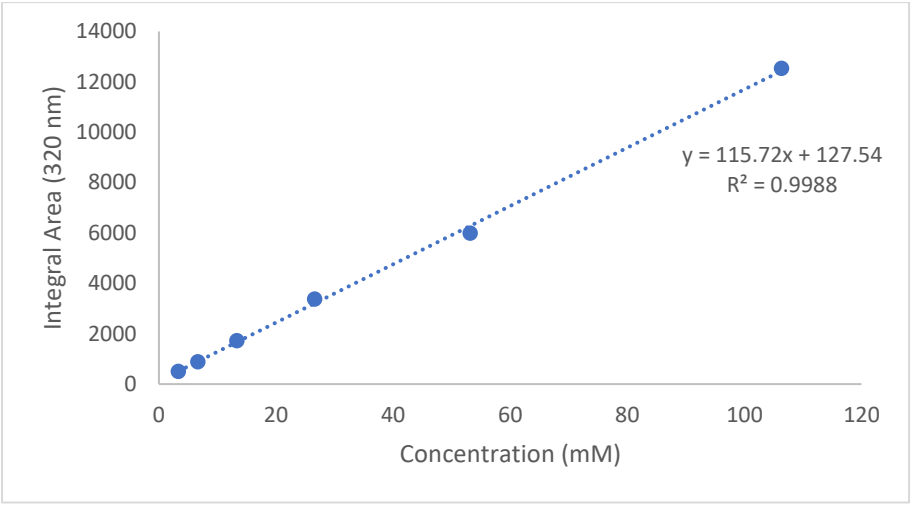





O
N
H
O

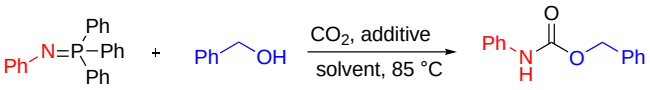

140000
120000
100000
80000
60000
40000
20000
0
AUC (280 nm)
0
20
40
60
80
100
120
Concentration (mM)
y = 1211.2x - 833.11
R² = 0.9975


Ph
Ph
N=C=N


14000
12000
10000
8000
6000
4000
2000
0
Integral Area (320 nm)
0
20
40
60
80
100
120
Concentration (mM)
y = 115.72x + 127.54
R² = 0.9988

Section 6: Optimization Table

Table S1. Solvent and additive screening[a]



1a **2** **4**

Entry	Solvent	Additive	Rxn time [b]	Yield
1	Toluene	-	2h	70%
2	Dioxane	-	2h	72%
3	DMF	-	2h	75%
4	DMSO	-	2h	64%
5	THF	-	2h	72%
6	**ACN**	**-**	**2h**	**78%**
7	**ACN**	**DBU**	**1h**	**84%**
8	ACN	BEMP	1h	70%
9	ACN	DMAP	2h	65%
10	ACN	Pyridine	2h	72%
11	ACN	K_2CO_3	2h	75%

[a]Reaction conditions: **1** (0.25mmol), **2** (1.25mmol), additives (0.55mmol), dry solvent (2.5mL). Isolated yield.

Section 7: References

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