

Supporting Information

Photoredox-catalyzed coupling of aryl sulfonium salts with CO₂ and amines to access *O*-aryl carbamates

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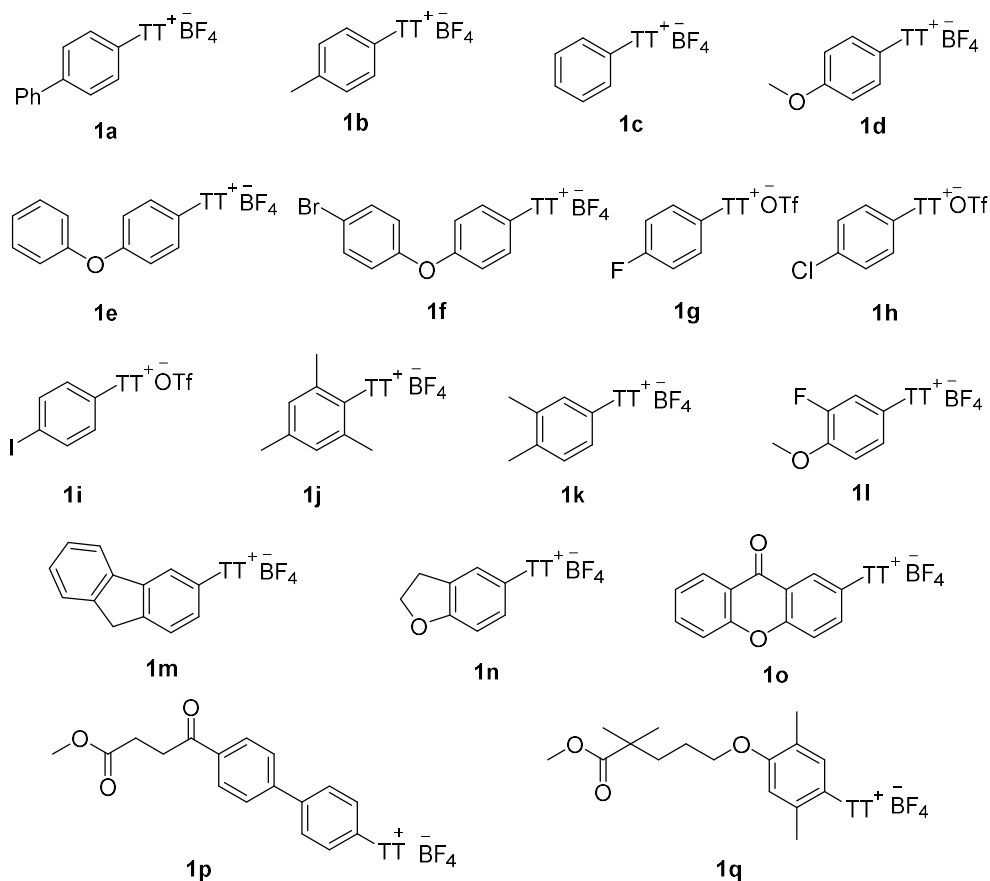
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A. General methods

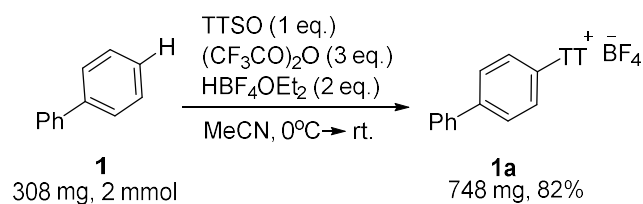
All aryl sulfonium salts **1** were synthesized according to previously described methods.¹ Other reagents were purchased from commercial sources and used directly without further treatment. ¹H and ¹³C NMR spectra were recorded in 400 MHz apparatus and using CDCl₃ as solvent and TMS as an internal standard. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively. The data of HRMS was determined on a high-resolution mass spectrometer (LCMS-IT-TOF). IR spectra were obtained either as potassium bromide plates or as liquid films between two potassium bromide plates with a Bruker TENSOR 27 spectrometer. Melting points were determined with a Büchi Melting Point B-545 instrument are uncorrected. Photoluminescence spectra were recorded on a Horiba Fluoromax-4 spectrofluorometer. Blue LED (30 W, λ_{max} = 450 nm) powered by Constant Current Modules were used for the light irradiation. The light source was placed ~ 10 mm from the reaction tube. The photoreactor was placed in an incubator, which was used to maintain the temperature at room temperature (25 °C).

B. The preparation of aryl sulfonium salts **1**

Aryl sulfonium salts **1a-1m** were prepared according to the previous reports.¹⁻²



The typical procedure for the preparation of aryl sulfonium salt **1a** was as follows:



Under an ambient atmosphere, a 20 ml round bottom flask was charged with diphenyl **1** (308 mg, 2.00 mmol, 1.00 equiv) and MeCN (2.0 ml, $c = 1.0$ M). After cooling to 0 °C, HBF₄·OEt₂ (0.55 mL, 647 mg, 4.0 mmol, 2.0 equiv) and thianthrene-S-oxide (TTSO) (464 mg, 2.00 mmol, 1.00 equiv) was added to the vial while stirring the mixture, leading to a suspension. Then trifluoroacetic anhydride (0.84 mL, 1.24 g, 6 mmol, 3.0 equiv) was added in one portion at 0 °C, resulting in a color change to deep purple. Subsequently, the reaction mixture was allowed to reach room temperature and stirred for 12 h. The solution was diluted with DCM (5 mL) and poured onto a mixture of DCM (10 mL) and saturated aqueous NaHCO₃ solution (5 mL). After stirring for 5 min at 23 °C, the mixture was poured into a separating funnel, and the layers were separated. The DCM layer was washed with aqueous NaBF₄ solution (10% w/w, 4 × ca. 20 mL). The DCM layer was dried over Na₂SO₄, filtered, and the solvent was removed under reduced pressure. The residue was purified by chromatography on silica gel eluting with DCM/MeOH (30:1 (v/v)), then the solvent was removed in vacuo to afford the thianthrenium salt **1a** (748 mg, 82%).

C. General procedure for the synthesis of *O*-aryl carbamates **3**

In a nitrogen-filled glovebox, an oven dried Schlenk tube (25 ml) was charged with the mixture of Ir[(dtbbpy)(ppy)₂][PF₆] (0.007 mmol), Cu(MeCN)₄PF₆ (0.3 mmol), aryl sulfonium salts **1** (0.1 mmol), DABCO (0.5 mmol), BF₃·OEt₂ (0.55 mmol), 4Å MS (20 mg), MeCN (1.5 ml), and a magnetic stirring bar. The tube was then evacuated, refilled with CO₂ (1 atm) three times, and charged with 0.2 mmol of amine **2** via a syringe. The reaction mixture was stirred at room temperature for 2 h under 30 W blue LED irradiation. After the reaction was completed, the tube was removed from the light source. The reaction mixture was quenched with saturated brine water (5 mL), then extracted with ethyl acetate (3 × 10 mL) three times, the organic layer was dried over anhydrous Na₂SO₄. The organic layer was filtered and concentrated under reduced pressure. The crude residue was separated by column chromatography on a silica gel column using petroleum ether/ethyl acetate as eluent to give the desired product **3**.

D. Optimization of the reaction conditions

Table S1 Optimization of the reaction conditions^a

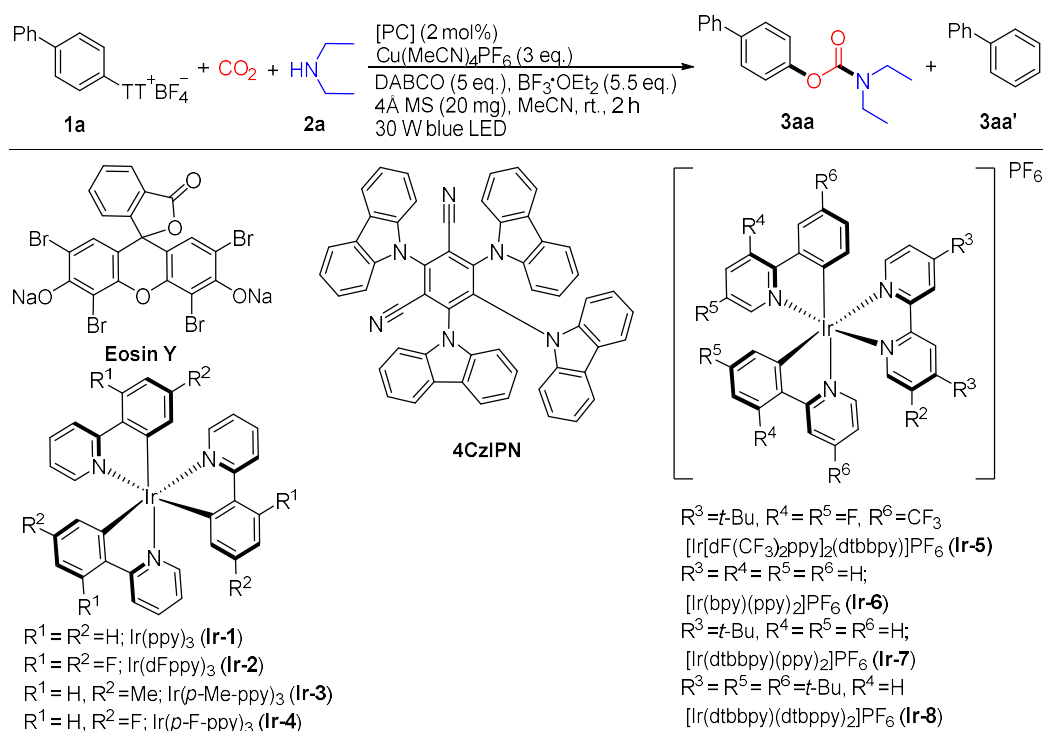
$\text{1a} + \text{CO}_2 + \text{2a} \xrightarrow[\text{DABCO (5 eq.), BF}_3 \cdot \text{OEt}_2 \text{ (5.5 eq.)}]{\text{Ir}[(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6 \text{ (7 mol\%)}
\text{Cu}[\text{MeCN}]_4\text{PF}_6 \text{ (3 eq.)}]$
 3aa

TT =

Entry	Variation from the “standard” conditions	Yield of 3aa (%) ^b
1	none	73 (69) ^b
2	No Ir[(dtbbpy)(ppy) ₂] ₂ PF ₆	0
3	No Cu(MeCN) ₄ PF ₆	0
4	No light	0
5	No DABCO	0
6	No BF ₃ ·OEt ₂	33
7	Ir(ppy) ₃ as photocatalyst	53
8	Ir[dF(CF ₃)ppy ₂](dtbpy)PF ₆ as photocatalyst	41
9	CuI instead of Cu(MeCN) ₄ PF ₆	15
10	Cu(OAc) ₂ instead of Cu(MeCN) ₄ PF ₆	8
11	Et ₃ N instead of DABCO	trace
12	DMP instead of DABCO	38
13	Quinuclidine instead of DABCO	66
14	CH ₂ Cl ₂ instead of MeCN	0
15	PhCN instead of MeCN	58

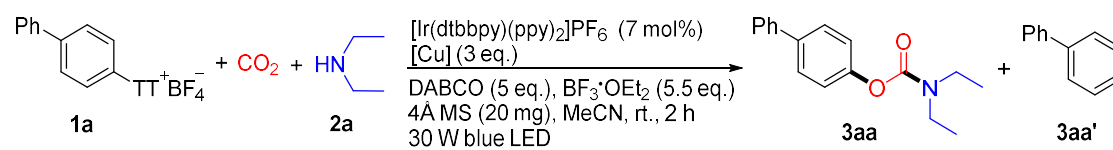
^aReaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), CO₂ (1 atm), Ir[(dtbbpy)(ppy)₂]₂PF₆ (7 mol%), Cu(MeCN)₄PF₆ (0.3 mmol), DABCO (0.5 mmol), BF₃·OEt₂ (0.55 mmol) and 4Å MS (20 mg) in MeCN (1.5 mL) at 25 °C, irradiation with 30 W blue LED for 2 h. ^bYields were determined by GC-MS analysis with *n*-dodecane as internal standard; number in parentheses is the yield of isolated product. DMP = N, N'-Dimethylpiperazine.

Table S2 The influence of different photocatalysts on the reaction^a



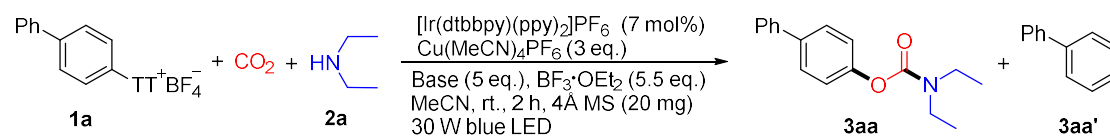
Entry	[PC]	3aa yield (%) ^b	3aa' yield (%) ^b
1	Ru[(bpy) ₃ PF ₆] ₂	35	27
2	Ru(bpy) ₃ Cl ₂	29	15
3	Eosin Y	0	0
4	4CZIPN	0	0
5	[Ir]-1	45	18
6	[Ir]-2	33	15
7	[Ir]-3	28	17
8	[Ir]-4	35	15
9	[Ir]5	38	17
10	[Ir]-6	54	12
11	[Ir]-7	60	10
12	[Ir]-8	58	14
13 ^c	[Ir]-7	73 (69) ^d	8

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol) and CO₂ (1 atm), [PC] (0.002 mmol), Cu(MeCN)₄PF₆ (0.3 mmol), DABCO (0.5 mmol), BF₃·OEt₂ (0.55 mmol) and 4 Å MS (20 mg) in MeCN (1.5 mL) at 25 °C irradiation with 30 W blue LED for 2 h. ^bGC yield with dodecane as internal standard. ^c[PC] (0.007 mmol). ^dYields of isolated product.

Table S3 The influence of different copper salts on the reaction^a

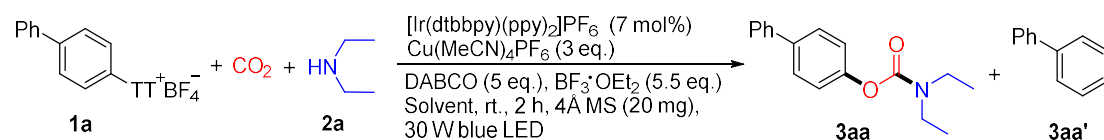
Entry	[Cu]	3aa yield (%) ^b	3aa' yield (%) ^b
1	Cu ₂ O	0	60
2	CuI	15	20
3	Cu(MeCN) ₄ PF ₆	73	8
4	Cu(MeCN) ₄ OTf	60	15
5	Cu(OAc) ₂	8	35
6	CuSO ₄	trace	30
7 ^c	Cu(MeCN) ₄ PF ₆	17	50
8 ^d	Cu(MeCN) ₄ PF ₆	36	42
9 ^e	Cu(MeCN) ₄ PF ₆	60	25
10 ^f	Cu(MeCN) ₄ PF ₆	75	11

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol) and CO₂ (1 atm), Ir[(dtbbpy)(ppy)₂]PF₆ (0.007 mmol), [Cu] (0.3 mmol), DABCO (0.5 mmol), BF₃·OEt₂ (0.55 mmol) and 4 Å MS (20 mg) in MeCN (1.5 mL) at 25 °C irradiation with 30 W blue LED for 2 h. ^bGC yield with dodecane as internal standard. ^c[Cu] (0.05 mmol). ^d[Cu] (0.1 mmol). ^e[Cu] (0.2 mmol). ^f[Cu] (0.4 mmol).

Table S4 The influence of different bases on the reaction^a

Entry	Base	3aa yield (%) ^b	3aa' yield (%) ^b
1	DBN	Trace	36
2	DMP	38	24
3	DABCO	73	8
4	Et ₃ N	Trace	35
5	Quinuclidine	66 (61) ^c	12
6	DIPEA	10	15
7	K ₂ CO ₃	Trace	Trace
8	PPh ₃	ND	Trace
9	NPh ₃	ND	Trace
10 ^d	DABCO	12	20
11 ^e	DABCO	30	15
12 ^f	DABCO	45	11
13 ^g	DABCO	56	12
14 ^h	DABCO	68	10
15 ⁱ	DABCO	75	9

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol) and CO₂ (1 atm), Ir[(dtbbpy)(ppy)₂]PF₆ (0.007 mmol), Cu(MeCN)₄PF₆ (0.3 mmol), base (0.5 mmol), BF₃·OEt₂ (0.55 mmol) and 4 Å MS (20 mg) in MeCN (1.5 mL) at 25 °C irradiation with 30 W blue LED for 2 h. ^bGC yield with dodecane as internal standard. ^cYields of isolated products. ^dDABCO (0.05 mmol). ^eDABCO (0.1 mmol). ^fDABCO (0.2 mmol). ^gDABCO (0.3 mmol). ^hDABCO (0.4 mmol). ⁱDABCO (0.6 mmol).

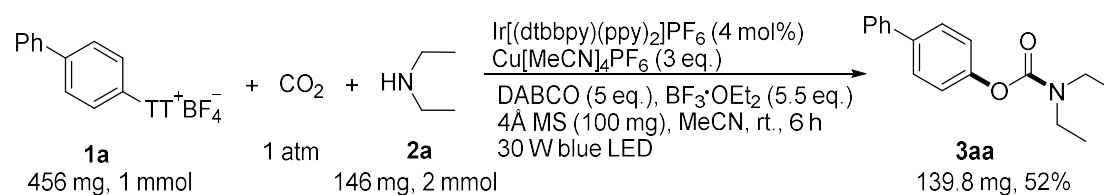
Table S5 The influence of different solvents on the reaction^a

Entry	Solvent	3aa yield (%) ^a	3aa' yield (%) ^a
1	MeCN	73	8
2	DMF	0	45
3	DMSO	0	37
4	THF	0	55
5	PhCN	58	12
6	CH_2Cl_2	0	52

Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol) and CO_2 (1 atm), $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$ (0.007 mmol), $\text{Cu}(\text{MeCN})_4\text{PF}_6$ (0.3 mmol), DABCO (0.5 mmol), $\text{BF}_3 \cdot \text{OEt}_2$ (0.55 mmol) and 4 Å MS (20 mg) in Solvent (1.5 mL) at 25 °C irradiation with 30 W blue LED for 2 h. ^aGC yield with dodecane as internal standard.

E. Larger scale synthesis and applications of **3aa**

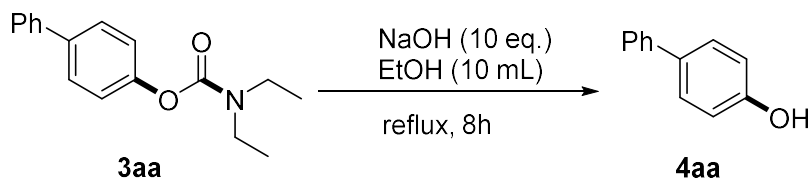
a) 1 mmol-scale experiment



In a nitrogen-filled glovebox, an oven dried Schlenk tube (100 ml) was charged with the mixture of $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$ (0.04 mmol), $\text{Cu}(\text{MeCN})_4\text{PF}_6$ (3 mmol), aryl sulfonium salts **1a** (456mg, 1 mmol), DABCO (5 mmol), $\text{BF}_3 \cdot \text{OEt}_2$ (5.5 mmol), 4Å MS (100 mg), MeCN (15 ml), and a magnetic stirring bar. The tube was then evacuated, refilled with CO_2 (1 atm) three times, and charged further with 2 mmol of amine **2a** via a syringe. The reaction mixture was stirred at room temperature for 6 h under 30 W blue LED irradiation. After the reaction was completed, the tube was removed from the light source. The reaction mixture was quenched with saturated brine water (15 mL), then extracted with ethyl acetate (3 × 20 mL) three times, the organic layer was dried over anhydrous

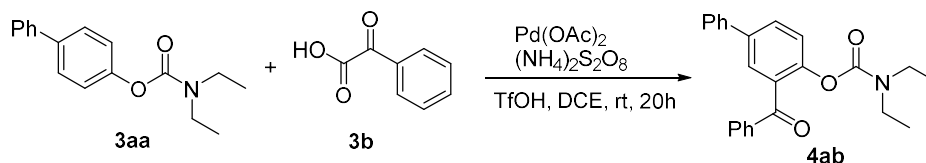
Na₂SO₄. The organic layer was filtered and concentrated under reduced pressure, the crude residue was separated by column chromatography on a silica gel column using petroleum ether/ethyl acetate(v/v=15:1) as eluent to give the desired product **3aa** (139.8 mg, 52%).

b) The synthesis of 4-phenylphenol **4aa**



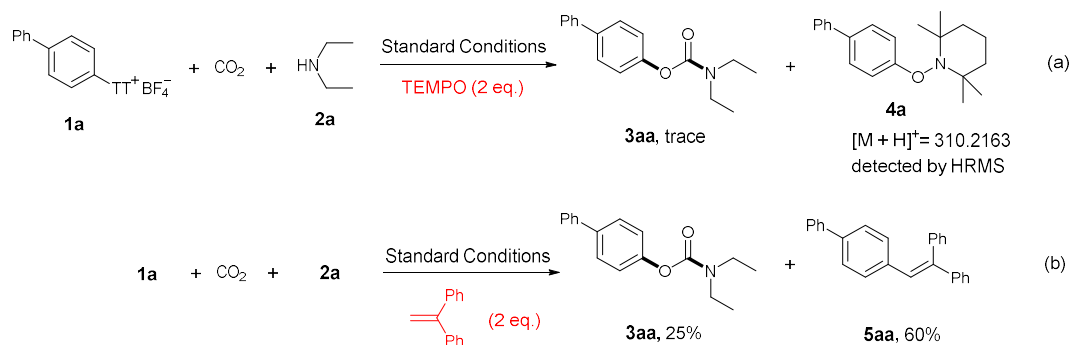
To a 25 mL round-bottom flask were added **3aa** (0.2 mmol), NaOH (10 eq.), EtOH (10 mL), then attach a reflux condenser to the flask. The reaction mixture was stirred at 78°C for 8 h. After cooling to room temperature, the solvent was removed under reduced pressure, the crude residue was separated by column chromatography on a silica gel column using petroleum ether/ethyl acetate(v/v=10:1) as eluent to give the desired product **4aa** (27.9 mg, 82%).

c) The synthesis of acylated product **4ab**



To an oven-dried sealed tube charged with [1,1'-biphenyl]-4-yl diethylcarbamate (**3aa**) (40.4 mg, 0.15 mmol, 1.0 equiv.), Pd(OAc)₂ (1.7 mg, 0.0075 mmol, 5 mol%), (NH₄)₂S₂O₈ (51.3 mg, 0.23 mmol, 1.5 equiv.), and phenylglyoxylic acid (**3b**) (45.3 mg, 0.3 mmol, 2 equiv.) in DCE (2 mL) was added TfOH (3 μL, 20 mol%). The reaction mixture was allowed to stir at room temperature for 20 h. Then the reaction mixture was diluted with EtOAc (5 mL) and washed with a saturated solution of Na₂CO₃. The aqueous layer was extracted with EtOAc (10 mL × 3). The combined organic layer was dried over Mg₂SO₄ and concentrated under vacuum. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate (v/v=10:1)) to afford product **4ab** (34.7 mg, 62%).

F. Control experiments



Scheme S1. Reaction conditions: (a) **1a** (0.1 mmol), **2a** (0.2 mmol) and CO_2 (1 atm), $\text{Ir}[(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$ (0.07 mmol), $\text{Cu}(\text{MeCN})_4\text{PF}_6$ (0.3 mmol), DABCO (0.5 mmol), $\text{BF}_3\cdot\text{OEt}_2$ (0.55 mmol), 4 Å MS (20 mg) and TEMPO (0.2 mmol) in MeCN (1.5 mL) at 25 °C irradiation with 30 W blue LED for 2 h. (b) **1a** (0.1 mmol), **2a** (0.2 mmol) and CO_2 (1 atm), $\text{Ir}[(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$ (0.07 mmol), $\text{Cu}(\text{MeCN})_4\text{PF}_6$ (0.3 mmol), DABCO (0.5 mmol), $\text{BF}_3\cdot\text{OEt}_2$ (0.55 mmol), 4 Å MS (20 mg) and diphenylethylene (0.2 mmol) in MeCN (1.5 mL) at 25 °C irradiation with 30 W blue LED for 2 h.

G. Cyclic voltammetry

Cyclic voltammetry test was performed in a three-electrode cell under nitrogen at room temperature. All cyclic voltammograms were measured using a saturated calomel electrode (SCE) as reference electrode, a platinum (Pt) wire counter electrode and a glassy carbon working electrode. The conditions of the experiments were as follows: testing compounds are in solution of 0.1 M tetrabutylammonium tetrafluoroborate ($n\text{Bu}_4\text{NBF}_4$) in MeCN at a scan rate of 100 mV/s; Prior to each measurement, solutions were purged with nitrogen (N_2) for 5 minutes to ensure the oxygen-free conditions.

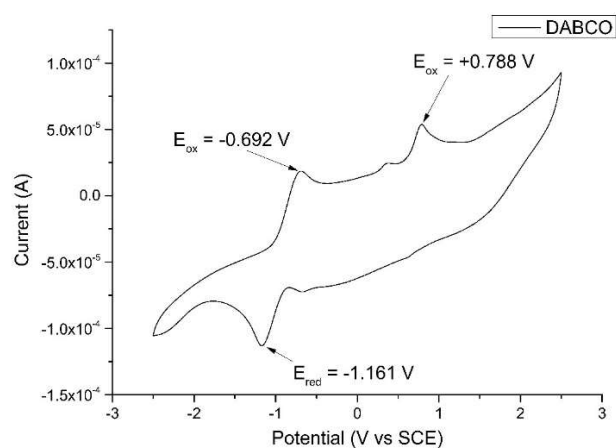


Figure S2. Cyclic voltammetry of DABCO (0.01 M) in MeCN (vs SCE) with $n\text{Bu}_4\text{NBF}_4$ (0.1 M) under nitrogen at a glassy carbon electrode at a scan rate of 100 mV/s. The oxidation and reduction potential of DABCO in MeCN was measured as -0.692 V, +0.788 V and -1.161 V (vs SCE), respectively.

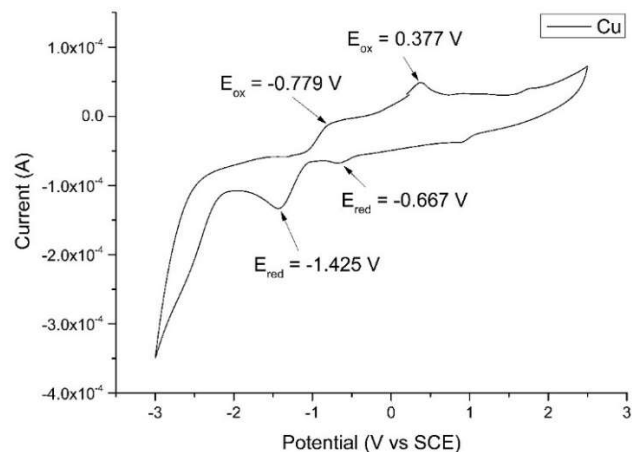


Figure S3. Cyclic voltammetry of $\text{Cu}(\text{MeCN})_4\text{PF}_6$ (0.01 M) in MeCN (vs SCE) with $n\text{Bu}_4\text{NBF}_4$ (0.1 M) under nitrogen at a glassy carbon electrode at a scan rate of 100 mV/s. The oxidation and reduction potential of $\text{Cu}(\text{MeCN})_4\text{PF}_6$ in MeCN was measured as -0.779 V, +0.377 V and -1.425 V, -0.667 V (vs SCE), respectively.

H. Stern-Volmer fluorescence quenching experiments

Fluorescence spectra were collected on Horiba Fluoromax-4 spectrofluorometer. Samples for the quenching experiments were prepared in a 4 mL glass cuvette with a septum screw cap. $\text{Ir}[(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$ was irradiated at 380 nm and the emission intensity at 585 nm was observed. In a typical experiment, the emission spectrum of a 5.0×10^{-5} M solution of $\text{Ir}[(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$ in MeCN was collected. Then, appropriate amount of quencher was added to the measured solution and the emission spectrum of the sample was collected. Here I_0 and I represent the intensities of the emission in the absence and presence of the quencher.

Stern-Volmer equation: $I_0/I = 1 + K_q\tau_0[Q]$, $\tau_0 = 0.60 \mu\text{s}$ (ref.2)

Quencher	$K_q / \text{M}^{-1}\text{S}^{-1}$
DABCO	4.2×10^8
ArTT	5.7×10^7
[Cu]	1.1×10^7

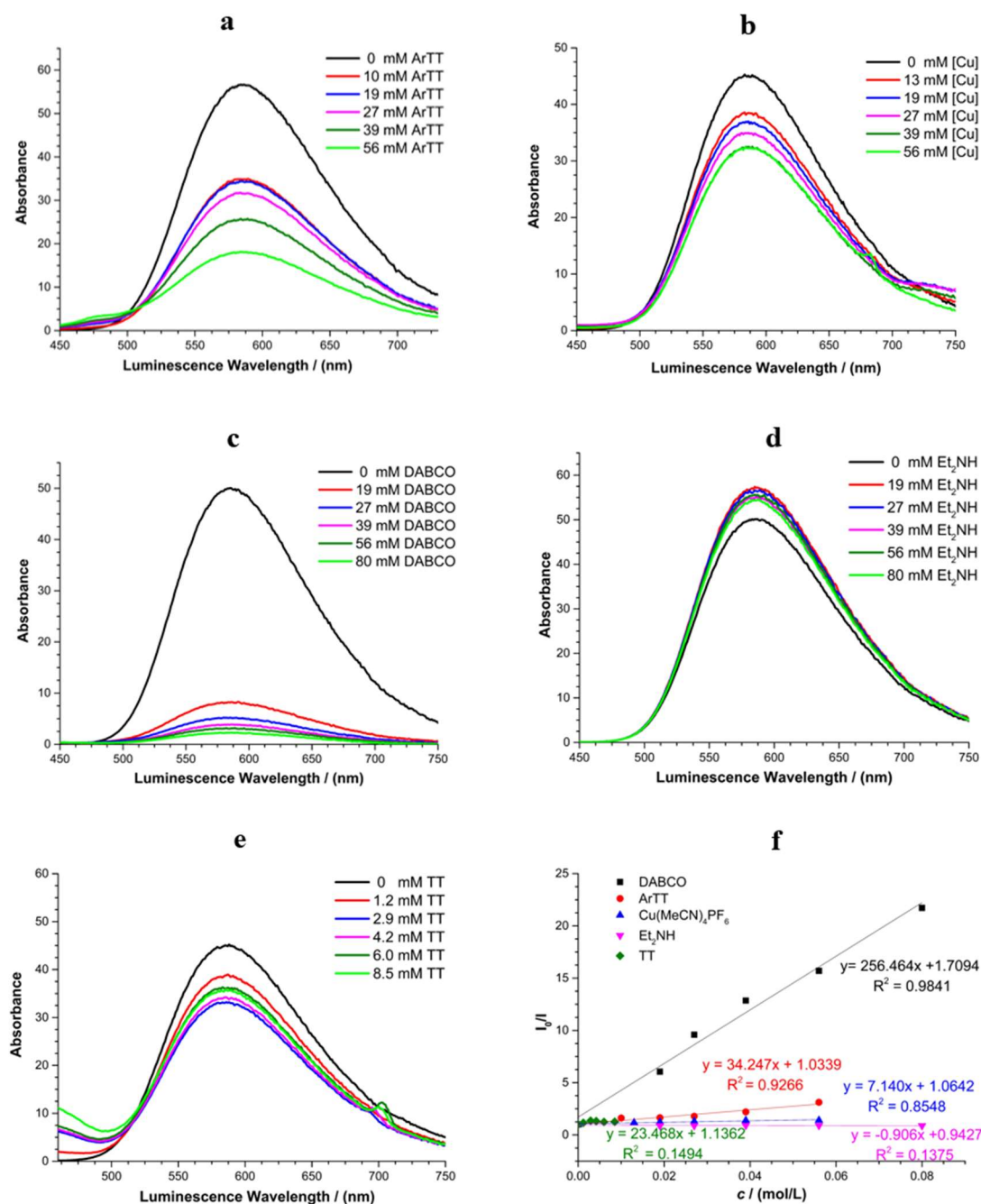
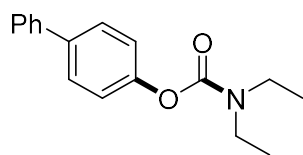


Figure S4. The emission quenching of Ir[(dtbbpy)(ppy)₂]PF₆. a) Steady-state Stern–Volmer experiment of ArTT-1a. b) Stern–Volmer fluorescence quenching experiments of Cu(MeCN)₄PF₆. c) Steady-state Stern–Volmer experiment of DABCO. d) Steady-state Stern–Volmer experiment of Et₂NH. e) Steady-state Stern–Volmer experiment of TT. f) Stern–Volmer fluorescence quenching experiments using Ir[(dtbbpy)(ppy)₂]PF₆ with ArTT-1a, Cu(MeCN)₄PF₆, DABCO, Et₂NH and TT.

I. Analytical data

[1,1'-Biphenyl]-4-yl diethylcarbamate (3aa)

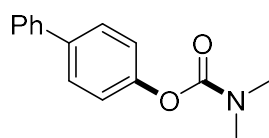


Yield: 18.6 mg (69%); Pale yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3):

$\delta = 7.65 - 7.57$ (m, 4 H), 7.46 (t, $J = 7.6$ Hz, 2 H), 7.40 – 7.34 (m, 1 H), 7.27 – 7.21 (m, 2 H), 3.59 – 3.36 (m, 4 H), 1.37 – 1.17 (m, 6 H);

$^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 154.3, 151.0, 140.7, 138.2, 128.8, 128.0, 127.2, 127.1, 122.1, 42.3, 41.9, 14.3, 13.5$; IR (KBr): 3052, 2972, 1719, 1605, 1471, 1420, 1275, 1212, 1162, 1089, 953, 865, 762, 699, 506 cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{17}\text{H}_{20}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$: 270.1489, found: 270.1484.

[1,1'-Biphenyl]-4-yl dimethylcarbamate (3ab)

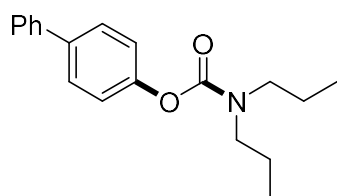


Yield: 10.8 mg (45%); Pale yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta =$

7.62 – 7.56 (m, 4 H), 7.45 (t, $J = 7.6$ Hz, 2 H), 7.39 – 7.33 (m, 1 H), 7.23 – 7.18 (m, 2 H), 3.15 (s, 3 H), 3.06 (s, 3 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3):

$\delta = 155.0, 151.0, 140.6, 138.3, 128.8, 128.0, 127.2, 127.1, 122.0, 36.8, 36.5$; IR (KBr): 2937, 2831, 1721, 1610, 1473, 1370, 1182, 862, 761, 481 cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{15}\text{H}_{16}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$: 242.1176, found: 242.1173.

[1,1'-Biphenyl]-4-yl dipropylcarbamate (3ac)

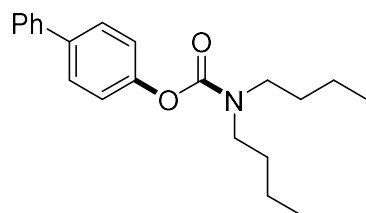


Yield: 19.0 mg (64%); Pale yellow oil; $^1\text{H NMR}$ (400 MHz,

CDCl_3): $\delta = 7.63 - 7.56$ (m, 4H), 7.49 – 7.42 (m, 2H), 7.39 – 7.33 (m, 1H), 7.24 – 7.19 (m, 2H), 3.40 (t, 2H), 3.33 (t, 2H), 1.82 – 1.60 (m, 4H), 1.07 – 0.89 (m, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3):

$\delta = 154.7, 151.1, 140.7, 138.2, 128.8, 128.0, 127.2, 127.1, 122.0, 49.6, 49.3, 22.1, 21.3, 11.3$; IR (KBr): 3049, 2970, 2880, 1719, 1621, 1469, 1417, 1215, 1158, 1009, 855, 758, 697, 506 cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{19}\text{H}_{24}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$: 298.1802, found: 298.1799.

[1,1'-Biphenyl]-4-yl dibutylcarbamate (3ad)

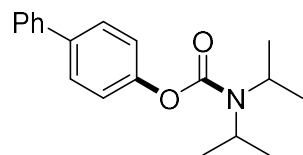


Yield: 18.9 mg (58%); Pale yellow oil; $^1\text{H NMR}$ (400 MHz,

CDCl_3): $\delta = 7.64 - 7.56$ (m, 4 H), 7.46 (t, $J = 7.6$ Hz, 2 H), 7.36 (t, $J = 7.4$ Hz, 1 H), 7.26 – 7.16 (m, 2 H), 3.43 (t, 2 H), 3.36 (t, 2 H), 1.76 – 1.58 (m, 4 H), 1.50 – 1.28 (m, 4 H), 1.00 (q, $J = 7.6$

Hz, 6 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 154.7, 151.1, 140.7, 138.2, 128.8, 128.0, 127.2, 127.1, 122.0, 47.6, 47.3, 31.0, 30.2, 20.1, 13.9$; IR (KBr): 3054, 2945, 2870, 1719, 1629, 1471, 1296, 1208, 1003, 867, 756, 693 cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{21}\text{H}_{28}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$: 326.2115, found: 326.2112.

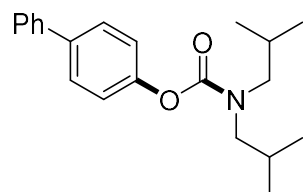
[1,1'-Biphenyl]-4-yl diisopropylcarbamate (3ae)



Yield: 15.1 mg (51%); Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.64 - 7.57$ (m, 4 H), 7.46 (t, $J = 7.8$ Hz, 2 H), 7.37 (t, $J = 7.4$ Hz, 1 H), 7.26 - 7.21 (m, 2 H), 4.08 (d, $J = 41.6$ Hz, 2 H), 1.37 (s, 12 H);

^{13}C NMR (100 MHz, CDCl_3): $\delta = 153.9, 150.9, 140.7, 138.2, 128.8, 128.0, 127.2, 127.1, 122.1, 47.0, 46.2, 21.5, 20.6$; IR (KBr): 2972, 2832, 1713, 1606, 1438, 1387, 1304, 1213, 1149, 998, 864, 763, 683, 613, 506 cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{19}\text{H}_{24}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$: 298.1802, found: 298.1798.

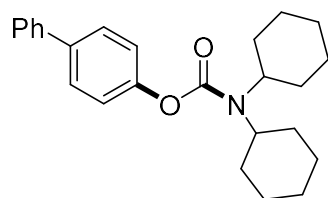
[1,1'-Biphenyl]-4-yl diisobutylcarbamate (3af)



Yield: 13.7 mg (42%); Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.64 - 7.55$ (m, 4 H), 7.46 (t, $J = 7.6$ Hz, 2 H), 7.36 (t, $J = 7.2$ Hz, 1 H), 7.24 - 7.18 (m, 2 H), 3.29 (d, $J = 7.6$ Hz, 2 H), 3.22 (d, $J = 7.6$ Hz, 2 H), 2.20 - 1.99 (m, 2 H), 1.00 (dd, $J = 14.2, J = 6.4$ Hz, 12 H); ^{13}C

NMR (100 MHz, CDCl_3): $\delta = 155.2, 151.1, 140.7, 138.2, 128.8, 128.0, 127.2, 127.1, 122.0, 55.4, 55.2, 27.6, 27.0, 20.2$; IR (KBr): 3048, 2957, 1721, 1621, 1470, 1422, 1215, 1161, 941, 854, 759, 694 cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{21}\text{H}_{28}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$: 326.2115, found: 326.2111.

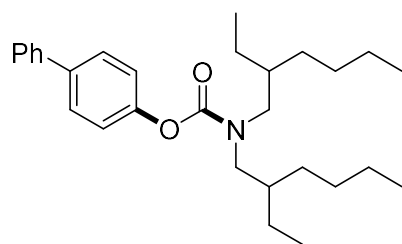
[1,1'-Biphenyl]-4-yl dicyclohexylcarbamate (3ag)



Yield: 19.2 mg (51%); Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.62 - 7.56$ (m, 4 H), 7.46 (t, $J = 7.6$ Hz, 2 H), 7.39 - 7.33 (m, 1 H), 7.25 - 7.18 (m, 2 H), 3.86 - 3.31 (m, 2 H), 2.06 - 1.55 (m, 14 H), 1.37 (q, $J = 12.8$ Hz, 4 H), 1.23 - 1.01 (m, 2 H); ^{13}C NMR (100

MHz, CDCl_3): $\delta = 154.1, 151.0, 140.7, 138.1, 128.8, 128.0, 127.1, 122.2, 56.0, 31.8, 30.6, 26.3, 25.5$; IR (KBr): 3049, 2931, 2861, 1712, 1608, 1445, 1295, 1208, 993, 881, 758, 696, 499 cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{25}\text{H}_{32}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$: 378.2428, found: 378.2421.

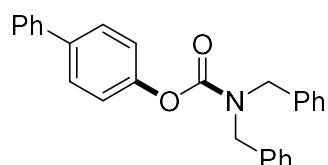
[1,1'-Biphenyl]-4-yl bis(2-ethylhexyl)carbamate (3ah).



Yield: 25.3 mg (58%); Pale yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.62 - 7.55$ (m, 4 H), 7.46 (t, $J = 7.6$ Hz, 2 H), 7.39 – 7.33 (m, 1 H), 7.22 – 7.16 (m, 2 H), 3.40 – 3.25 (m, 4 H), 1.84 – 1.74 (m, 2 H), 1.50 – 1.24 (m, 16 H), 1.01 – 0.86 (m, 12 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 155.3, 151.1,$

140.7, 138.2, 128.8, 128.0, 127.2, 127.1, 121.9, 51.1, 50.9, 38.1, 37.4, 30.6, 28.8, 23.9, 23.8, 23.1, 14.1, 10.7, 10.7; IR (KBr): 3050, 2941, 1721, 1619, 1459, 1294, 1206, 1053, 853, 757, 700, 509 cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{29}\text{H}_{44}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$: 438.3367, found: 438.3362.

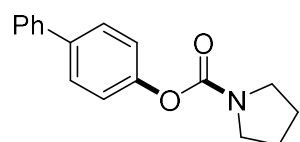
[1,1'-Biphenyl]-4-yl dibenzylcarbamate (3ai)



Yield: 19.7 mg (50%); Pale yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.57$ (t, $J = 7.8$ Hz, 4 H), 7.47 – 7.29 (m, 13 H), 7.22 (d, $J = 8.8$ Hz, 2 H), 4.57 (d, $J = 13.6$ Hz, 4 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3):

$\delta = 155.3, 150.9, 140.6, 138.6, 137.1, 137.0, 128.8, 128.5, 128.1, 127.7, 127.7, 127.7, 127.7, 127.6, 127.3, 127.2, 122.0, 50.0, 49.6$. IR (KBr): 3046, 2942, 1720, 1626, 1452, 1300, 1204, 1078, 956, 868, 702, 509 cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{27}\text{H}_{24}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$: 394.1802, found: 394.1796.

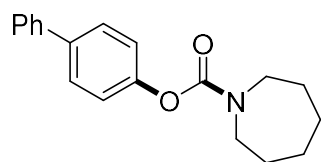
[1,1'-Biphenyl]-4-yl pyrrolidine-1-carboxylate (3aj)



Yield: 10.4 mg (39%); Pale yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.63 - 7.54$ (m, 4 H), 7.45 (t, $J = 7.6$ Hz, 2 H), 7.39 – 7.32 (m, 1 H), 7.26 – 7.19 (m, 2 H), 3.61 (t, $J = 6.6$ Hz, 2 H), 3.53 (t, $J = 6.6$ Hz, 2 H),

2.06 – 1.91 (m, 4 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 153.2, 150.9, 140.7, 138.2, 128.8, 128.0, 127.2, 127.1, 122.0, 46.5, 46.4, 25.9, 25.0$; IR (KBr): 3064, 2961, 2883, 1720, 1620, 1492, 1399, 1190, 1063, 866, 760, 688 cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{17}\text{H}_{18}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$: 268.1332, found: 268.1328.

[1,1'-Biphenyl]-4-yl azepane-1-carboxylate (3ak)

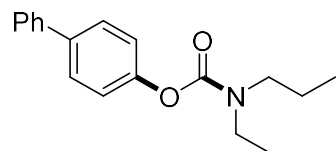


Yield: 13.9 mg (47%); Pale yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.63 - 7.56$ (m, 4 H), 7.49 – 7.43 (m, 2 H), 7.39 – 7.34 (m, 1 H), 7.25 – 7.20 (m, 2 H), 3.63 (t, $J = 6.0$ Hz, 2 H), 3.57 (t, $J = 6.0$ Hz, 2 H),

1.91 – 1.76 (m, 4 H), 1.73 – 1.62 (m, 4 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 154.7, 151.1, 140.7, 138.2, 128.8, 128.0, 127.2, 127.1, 122.1, 47.5, 47.2, 28.7, 28.1, 27.5, 26.9$; IR (KBr): 3047,

2929, 2861, 1717, 1611, 1472, 1417, 1195, 1051, 953, 758, 698, 509 cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{19}\text{H}_{22}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$: 296.1645, found: 296.1642.

[1,1'-Biphenyl]-4-yl ethyl(propyl)carbamate (3al)

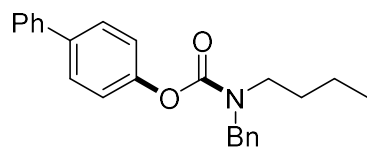


Yield: 15.0 mg (53%); Pale yellow oil; ^1H NMR (400 MHz, CDCl_3):

$\delta = 7.65 - 7.56$ (m, 4 H), $7.49 - 7.43$ (m, 2 H), $7.40 - 7.33$ (m, 1 H),
 7.22 (d, $J = 8.4$ Hz, 2 H), $3.58 - 3.24$ (m, 4 H), $1.80 - 1.58$ (m, 2

H), $1.36 - 1.19$ (m, 3 H), $1.08 - 0.91$ (m, 3 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 154.4$, 151.1 ,
 140.7 , 138.2 , 128.8 , 128.0 , 127.2 , 127.1 , 122.0 , 49.2 , 48.8 , 42.7 , 42.4 , 22.2 , 21.4 , 14.2 , 13.3 , 11.3 ;
IR (KBr): 3050 , 2963 , 2873 , 1719 , 1620 , 1473 , 1215 , 1156 , 952 , 852 , 758 , 696 , 506 cm^{-1} ; HRMS-
ESI (m/z): calcd for $\text{C}_{18}\text{H}_{22}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$: 284.1645, found: 284.1642.

[1,1'-Biphenyl]-4-yl benzyl(butyl)carbamate (3am)

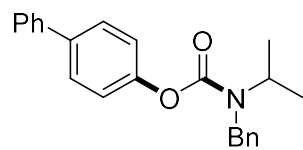


Yield: 22.6 mg (63%); Pale yellow oil; ^1H NMR (400 MHz,

CDCl_3): $\delta = 7.67 - 7.57$ (m, 4 H), 7.48 (t, $J = 7.6$ Hz, 2 H), 7.45
 $- 7.31$ (m, 6 H), $7.31 - 7.16$ (m, 2 H), 4.67 (d, $J = 32.0$ Hz, 2 H),

3.42 (t, $J = 7.2$ Hz, 2 H), $1.73 - 1.60$ (m, 2 H), $1.47 - 1.32$ (m, 2 H), 0.99 (t, $J = 7.4$ Hz, 3 H); ^{13}C
NMR (100 MHz, CDCl_3): $\delta = 155.4$, 154.7 , 151.1 , 140.6 , 138.4 , 137.6 , 128.8 , 128.7 , 128.1 , 127.6 ,
 127.2 , 127.2 , 122.0 , 50.8 , 47.3 , 46.5 , 30.4 , 29.8 , 20.0 , 13.9 ; IR (KBr): 3043 , 2947 , 2870 , 1719 , 1603 ,
 1464 , 1418 , 1297 , 1208 , 1127 , 1053 , 945 , 862 , 753 , 702 , 509 cm^{-1} ; HRMS-ESI (m/z): calcd for
 $\text{C}_{24}\text{H}_{26}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$: 360.1958, found: 360.1954.

[1,1'-Biphenyl]-4-yl benzyl(isopropyl)carbamate (3an)

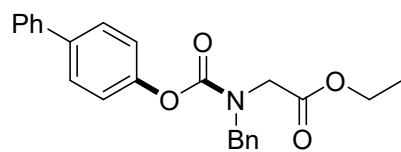


Yield: 20.4 mg (59%); Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ

$= 7.62 - 7.49$ (m, 4 H), 7.41 (t, $J = 7.6$ Hz, 2 H), $7.37 - 7.23$ (m, 7 H),
 $7.14 - 7.05$ (m, 1 H), 4.58 (s, 2 H), $4.47 - 4.20$ (m, 1 H), 1.23 (d, $J =$

6.4 Hz, 6 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 154.4$, 150.9 , 140.7 , 139.2 , 138.4 , 128.8 , 128.5 ,
 128.0 , 127.6 , 127.2 , 127.2 , 127.1 , 126.7 , 49.2 , 47.9 , 46.9 , 21.4 , 20.6 . IR (KBr): 3048 , 2969 , 1715 ,
 1608 , 1466 , 1333 , 1196 , 1044 , 849 , 741 , 508 cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{23}\text{H}_{24}\text{NO}_2$ [$\text{M} +$
 H] $^+$: 346.1802, found: 346.1797.

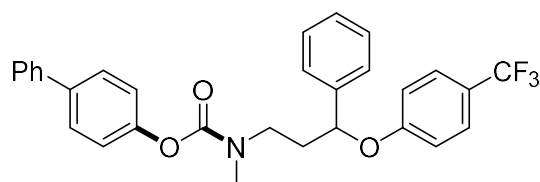
Ethyl N-(((1,1'-biphenyl]-4-yloxy)carbonyl)-N-benzylglycinate (3ao)



Yield: 20.2 mg (52%); Pale yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.61$ (t, $J = 7.3$ Hz, 4 H), 7.50 – 7.33 (m, 8 H), 7.27 – 7.22 (m, 2 H), 4.77 (d, $J = 43.6$ Hz, 2 H), 4.32 – 4.19

(m, 2 H), 4.10 (s, 2 H), 1.35 – 1.27 (m, 3 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 169.3, 155.1, 150.8, 140.5, 138.7, 136.4, 128.9, 128.8, 128.5, 128.1, 127.7, 127.3, 127.2, 122.0, 61.41, 52.05, 48.21, 14.23$; IR (KBr): 2888, 2787, 1729, 1423, 1308, 1198, 1097, 1020, 837, 741 cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{24}\text{H}_{24}\text{NO}_4$ [$\text{M} + \text{H}$] $^+$: 390.1700, found: 390.1693.

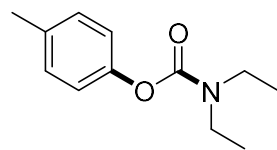
[1,1'-Biphenyl]-4-ylmethyl(3-phenyl-3-(4-(trifluoromethyl)phenoxy)propyl)carb-amate (3ap).



Yield: 22.2 mg (44%); Pale yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.63 - 7.56$ (m, 3 H), 7.55 – 7.29 (m, 11 H), 7.12 (d, $J = 8.0$ Hz, 1 H), 6.96 (t, $J = 8.4$ Hz, 3 H), 5.41 – 5.23 (m, 1 H), 3.99 –

3.40 (m, 2 H), 3.12 (d, $J = 28.4$ Hz, 3 H), 2.45 – 2.15 (m, 2 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 160.4, 154.8, 150.8, 140.7, 140.6, 138.4, 129.0$ (d, $J = 12$ Hz), 128.8, 128.2, 128.1, 128.0, 127.3, 126.89 (q, $J = 3$ Hz), 125.7 (d, $J = 15$ Hz), 121.8 (d, $J = 17$ Hz), 115.81, 115.77, 78.37, 77.74, 46.77, 46.14, 37.32, 36.47, 35.06, 34.98; $^{19}\text{F NMR}$ (376 MHz, CDCl_3): $\delta = 61.47$; IR (KBr): 3052, 2930, 1717, 1615, 1473, 1400, 1321, 1201, 1118, 834, 759, 698, 630 cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{30}\text{H}_{27}\text{F}_3\text{NO}_3$ [$\text{M} + \text{H}$] $^+$: 506.1938, found: 506.1931.

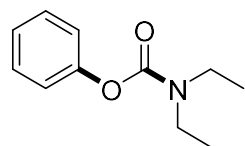
***p*-Tolyl diethylcarbamate (3ba)³**



Yield: 12.4 mg (60%); Pale yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.20 - 7.13$ (m, 2 H), 7.06 – 6.99 (m, 2 H), 3.52 – 3.33 (m, 4 H), 2.35 (s, 3 H), 1.34 – 1.13 (m, 6 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 154.5,$

149.3, 134.7, 129.7, 121.5, 42.2, 41.8, 20.8, 14.3, 13.4. IR (KBr): 2971, 1720, 1612, 1425, 1275, 1210, 1162, 1091, 1043, 1019, 964, 778, 502 cm^{-1} . HRMS-ESI (m/z): calcd for $\text{C}_{12}\text{H}_{18}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$: 208.1332, found: 208.1330.

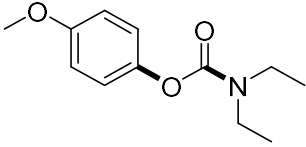
Phenyl diethylcarbamate (3ca)³



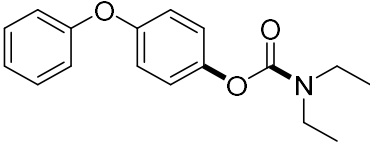
Yield: 6.9 mg (36%); Pale yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.41 - 7.34$ (m, 2 H), 7.23 – 7.18 (m, 1 H), 7.17 – 7.11 (m, 2 H), 3.53 – 3.32 (m, 4 H), 1.36 – 1.13 (m, 6 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 154.3, 151.6,$

129.2, 125.1, 121.8, 42.3, 41.9, 14.3, 13.4; IR (KBr): 2974, 1719, 1472, 1421, 1274, 1207, 1157, 1087, 955, 750, 689, 506 cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{11}\text{H}_{16}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$: 194.1176, found: 194.1174.

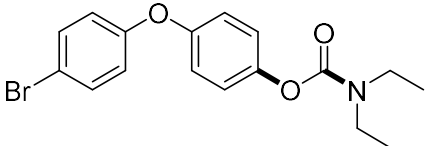
4-Methoxyphenyl diethylcarbamate (3da)³

 Yield: 11.6 mg (52%); Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.09 - 7.01$ (m, 2 H), $6.93 - 6.86$ (m, 2 H), 3.81 (s, 3 H), $3.51 - 3.32$ (m, 4 H), $1.37 - 1.12$ (m, 6 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 156.8, 154.7, 145.1, 122.6, 114.3, 55.6, 42.2, 41.8, 14.2, 13.4$; IR (KBr): 2976, 1718, 1614, 1501, 1426, 1270, 1202, 1093, 1034, 954, 848, 759, 518 cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{12}\text{H}_{18}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$: 224.1281, found: 224.1278.

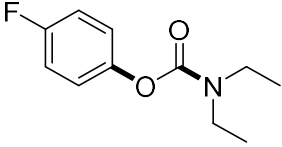
4-Phenoxyphenyl diethylcarbamate (3ea)

 Yield: 11.1 mg (39%); Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.38 - 7.31$ (m, 2 H), $7.15 - 7.08$ (m, 3 H), $7.06 - 7.00$ (m, 4 H), $3.60 - 3.25$ (m, 4 H), $1.41 - 1.07$ (m, 6 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 157.6, 154.4, 154.0, 147.2, 129.7, 123.1, 123.0, 119.8, 118.5, 42.3, 41.9, 14.3, 13.4$; IR (KBr): 3058; 2978, 2880; 1720, 1591, 1488, 1419, 1269, 1200, 1156, 1090, 1026, 957, 866, 760, 683, 506 cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{17}\text{H}_{20}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$: 286.1438, found: 286.1434.

4-(4-Bromophenoxy)phenyl diethylcarbamate (3fa)

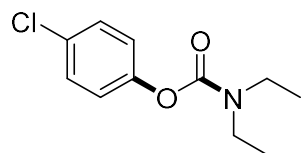
 Yield: 22.1 mg (61%); Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.47 - 7.39$ (m, 2 H), $7.16 - 7.08$ (m, 2 H), $7.04 - 6.98$ (m, 2 H), $6.92 - 6.86$ (m, 2 H), $3.54 - 3.31$ (m, 4 H), $1.37 - 1.11$ (m, 6 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 156.9, 154.3, 153.5, 147.5, 132.7, 123.1, 120.1, 119.9, 115.5, 42.3, 41.9, 14.3, 13.4$; IR (KBr): 2975, 2827, 1719, 1603, 1482, 1416, 1365, 1265, 1200, 1080, 953, 828, 764, 506 cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{17}\text{H}_{19}\text{BrNO}_3$ [$\text{M} + \text{H}$] $^+$: 364.0543, found: 364.0538.

4-Fluorophenyl diethylcarbamate (3ga)³

 Yield: 8.0 mg (38%); Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.20 - 6.96$ (m, 4 H), $3.53 - 3.33$ (m, 4 H), $1.34 - 1.13$ (m, 6 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 159.9$ ($J = 242$), $154.2, 147.4$ ($J = 2$),

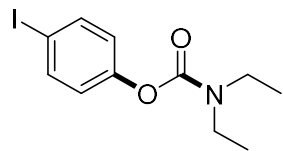
123.1 ($J = 9$), 115.8 ($J = 23$), 42.3, 41.9, 14.2, 13.4; ^{19}F NMR (376 MHz, CDCl_3): $\delta = -118.31$; IR (KBr): 2943, 2833, 1724, 1607, 1421, 1275, 1211, 1157, 1093, 1042, 1014, 952, 854, 760, 694, 502 cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{11}\text{H}_{15}\text{FNO}_2$ [$\text{M} + \text{H}$] $^+$: 212.1081, found: 212.1077.

4-Chlorophenyl diethylcarbamate (3ha)³



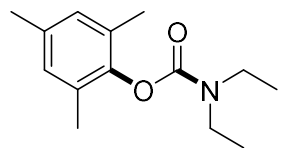
Yield: 12.0 mg (53%); Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.36 - 7.31$ (m, 2 H), $7.11 - 7.06$ (m, 2 H), $3.50 - 3.34$ (m, 4 H), $1.32 - 1.16$ (m, 6 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 153.9, 150.1, 130.3, 129.2, 123.2, 42.3, 41.9, 14.3, 13.4$; IR (KBr): 2976, 1724, 1624, 1480, 1276, 1215, 1156, 1089, 1025, 954, 854, 771, 683, 509 cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{11}\text{H}_{15}\text{ClNO}_2$ [$\text{M} + \text{H}$] $^+$: 228.0786, found: 228.0783.

4-Iodophenyl diethylcarbamate (3ia)³



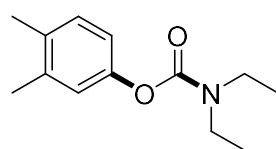
Yield: 13.7 mg (43%); Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.70 - 7.64$ (m, 2 H), $6.95 - 6.89$ (m, 2 H), $3.61 - 3.26$ (m, 4 H), $1.31 - 1.17$ (m, 6 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 153.7, 151.5, 138.2, 124.0, 88.8, 42.3, 41.9, 14.2, 13.4$; IR (KBr): 3067, 2972, 1719, 1623, 1470, 1421, 1275, 1211, 1157, 1093, 1042, 1014, 952, 854, 760, 694, 502 cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{11}\text{H}_{15}\text{INO}_2$ [$\text{M} + \text{H}$] $^+$: 320.0142, found: 320.0137.

Mesityl diethylcarbamate (3ja)³



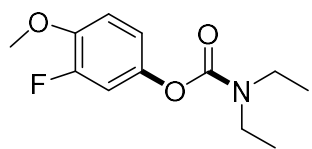
Yield: 7.1 mg (30%); Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): $\delta = 6.88$ (s, 2 H), 3.52 (q, $J = 7.2$ Hz, 2 H), 3.43 (q, $J = 7.2$ Hz, 2 H), 2.29 (s, 3 H), 2.18 (s, 6 H), 1.32 (t, $J = 7.2$ Hz, 3 H), 1.23 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 153.6, 146.5, 134.6, 130.3, 129.1, 42.2, 41.9, 20.8, 16.3, 14.4, 13.5$; IR (KBr): 2965, 1715, 1419, 1279, 1161, 1085, 955, 859, 765 cm^{-1} .

3,4-Dimethylphenyl diethylcarbamate (3ka)



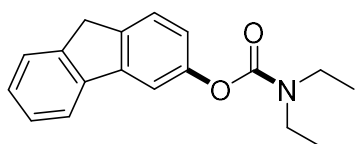
Yield: 12.2 mg (55%); Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.12$ (d, $J = 8.4$ Hz, 1 H), 6.93 (d, $J = 2.4$ Hz, 1 H), 6.87 (dd, $J = 8.0, 2.4$ Hz, 1 H), 3.43 (s, 4 H), 2.27 (s, 3 H), 2.25 (s, 3 H), $1.31 - 1.17$ (m, 6 H); ^{13}C NMR (101 MHz, CDCl_3): $\delta = 154.6, 149.5, 137.5, 133.2, 130.1, 122.8, 118.8, 42.2, 41.9, 19.8, 19.1, 14.2, 13.4$; IR (KBr): 2967, 2347, 1719, 1627, 1416, 1259, 1161, 1074, 988, 880, 773 cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{13}\text{H}_{20}\text{NO}_2$ [$\text{M} + \text{H}$] $^+$: 222.1489, found: 222.1485.

3-Fluoro-4-methoxyphenyl diethylcarbamate (3la)



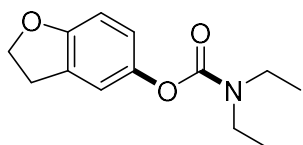
Yield: 10.8 mg (45%); Pale yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 6.97 - 6.90$ (m, 2 H), $6.89 - 6.83$ (m, 1 H), 3.89 (s, 3 H), $3.50 - 3.30$ (m, 4 H), $1.32 - 1.15$ (m, 6 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 154.1, 152.0$ (d, $J = 246$ Hz), 145.1 (d, $J = 11$ Hz), 144.8 (d, $J = 10$ Hz), 117.2 (d, $J = 4$ Hz), 113.4 (d, $J = 3$ Hz), 110.9 (d, $J = 20$ Hz), $56.7, 42.3, 41.9, 14.2, 13.4$; IR (KBr): $2976, 2352, 1720, 1602, 1514, 1423, 1262, 1158, 1033, 974, 889, 765, 591$ cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{12}\text{H}_{17}\text{FNO}_3$ $[\text{M} + \text{H}]^+$: 242.1187, found: 242.1182.

9H-fluoren-3-yl diethylcarbamate (3ma)



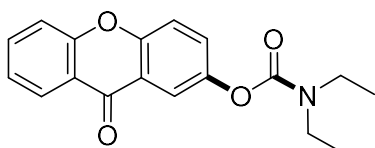
Yield: 16.3 mg (58%); Yellow solid; m.p. $97-99^\circ\text{C}$; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.78$ (d, $J = 8.4$ Hz, 2 H), 7.56 (d, $J = 7.6$ Hz, 1 H), $7.44 - 7.35$ (m, 2 H), $7.35 - 7.27$ (m, 1 H), 7.17 (dd, $J = 8.4, 2.0$ Hz, 1 H), 3.93 (s, 2 H), $3.58 - 3.40$ (m, 4 H), $1.36 - 1.20$ (m, 6 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 154.6, 150.7, 144.4, 143.3, 141.2, 138.8, 126.8, 126.4, 125.0, 120.4, 120.2, 119.7, 118.8, 42.3, 42.0, 37.0, 14.3, 13.5$; IR (KBr): $3063, 2974, 2350, 1717, 1417, 1250, 1155, 963, 874, 752$ cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{18}\text{H}_{20}\text{NO}_2$ $[\text{M} + \text{H}]^+$: 282.1489, found: 282.1484.

2,3-Dihydrobenzofuran-5-yl diethylcarbamate (3na)



Yield: 11.0 mg (47%); Pale yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 6.98$ (t, $J = 1.2$ Hz, 1 H), 6.83 (dd, $J = 8.6, 2.6$ Hz, 1 H), 6.74 (d, $J = 8.4$ Hz, 1 H), 4.59 (t, $J = 8.6$ Hz, 2 H), $3.50 - 3.32$ (m, 4 H), 3.22 (t, $J = 8.6$ Hz, 2 H), $1.31 - 1.14$ (m, 6 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 157.3, 154.9, 145.1, 127.8, 121.0, 118.8, 109.1, 71.6, 42.2, 41.8, 30.0, 14.2, 13.4$; IR (KBr): $3711, 2975, 2896, 2348, 1715, 1478, 1424, 1263, 1168, 1085, 966, 793, 676$ cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{13}\text{H}_{18}\text{NO}_3$ $[\text{M} + \text{H}]^+$: 236.1281, found: 236.1277.

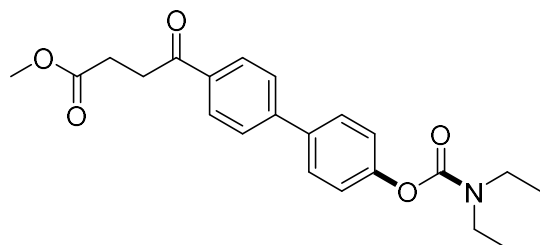
9-Oxo-9H-xanthen-2-yl diethylcarbamate (3oa)



Yield: 13.1 mg (42%); Yellow solid; m.p. $105-106^\circ\text{C}$; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 8.36$ (dd, $J = 8.0, 1.6$ Hz, 1 H), 8.05 (d, $J = 2.8$ Hz, 1 H), $7.79 - 7.72$ (m, 1 H), 7.59 (dd, $J = 8.8, 2.8$ Hz, 1 H), $7.55 - 7.49$ (m, 2 H), $7.44 - 7.38$ (m, 1 H), $3.64 - 3.23$ (m, 4 H), $1.43 - 1.11$ (m, 6 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 176.7, 156.2, 154.0, 153.4, 147.6, 134.9, 129.6, 126.8, 124.0, 122.2,$

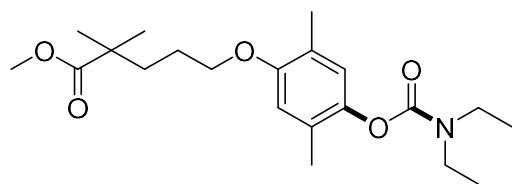
121.3, 119.0, 118.5, 118.0, 42.4, 42.0, 14.3, 13.4; IR (KBr): 3067, 2972, 2921, 2796, 1719, 1662, 1434, 1317, 1264, 1209, 1152, 1053, 951, 874, 759, 640 cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{18}\text{H}_{18}\text{NO}_4$ [$\text{M} + \text{H}$] $^+$: 312.1230, found: 312.1223.

Methyl 4-(4'-((diethylcarbamoyloxy)-[1,1'-biphenyl]-4-yl)-4-oxobutanoate (3pa)



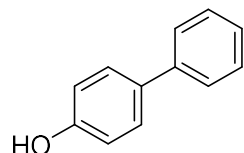
Yield: 18.1 mg (47%); Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ = 8.06 (d, J = 8.4 Hz, 2 H), 7.68 (d, J = 8.4 Hz, 2 H), 7.62 (d, J = 8.4 Hz, 2 H), 7.25 (d, J = 8.4 Hz, 2 H), 3.73 (s, 3 H), 3.53 – 3.40 (m, 4 H), 3.37 (t, J = 6.4 Hz, 2 H), 2.81 (t, J = 6.4 Hz, 2 H), 1.34 – 1.12 (m, 6 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 197.6, 173.4, 154.1, 151.8, 145.3, 136.7, 135.2, 128.7, 128.1, 127.2, 122.3, 51.9, 42.3, 42.0, 33.4, 28.1, 14.3, 13.4; IR (KBr): 2888, 2789, 1715, 1618, 1415, 1313, 1212, 1171, 959, 818, 735, 650 cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{22}\text{H}_{26}\text{NO}_5$ [$\text{M} + \text{H}$] $^+$: 384.1805, found: 384.1797.

Methyl 5-(4'-((diethylcarbamoyloxy)-2,5-dimethylphenoxy)-2,2-dimethylpentanoate (3qa).



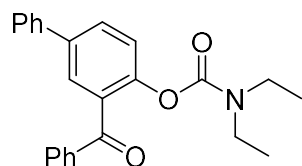
Yield: 10.6 mg (28%); Pale yellow oil; ^1H NMR (400 MHz, CDCl_3): δ = 6.84 (s, 1 H), 6.62 (s, 1 H), 3.91 (s, 2 H), 3.69 (s, 3 H), 3.51 – 3.33 (m, 4 H), 2.18 (d, J = 2.8 Hz, 6 H), 1.73 (d, J = 2.8 Hz, 4 H), 1.36 – 1.12 (m, 12 H); ^{13}C NMR (100 MHz, CDCl_3): δ = 178.3, 154.5, 154.3, 142.9, 127.9, 125.1, 124.1, 113.4, 68.5, 51.7, 42.2, 42.1, 41.8, 37.1, 25.2, 16.3, 15.8, 14.3, 13.5; IR (KBr): 3633, 3308, 2938, 1720, 1613, 1408, 1275, 1178, 1053, 962, 876, 761, 666 cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{21}\text{H}_{34}\text{NO}_5$ [$\text{M} + \text{H}$] $^+$: 380.2431, found: 380.2424.

[1,1'-Biphenyl]-4-ol (4aa)⁴



Yield: 27.9 mg (82%); ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ = 9.58 (s, 1 H), 7.57 (d, J = 7.2 Hz, 2 H), 7.48 (d, J = 8.4 Hz, 2 H), 7.40 (t, J = 7.6 Hz, 2 H), 7.27 (t, J = 7.2 Hz, 1 H), 6.85 (d, J = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ = 157.6, 140.7, 131.4, 129.3, 128.2, 126.8, 126.4, 116.2.

3-Benzoyl-[1,1'-biphenyl]-4-yl diethylcarbamate (4ab)



Yield: 34.7 mg (62%); Colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta =$

7.92 – 7.85 (m, 2 H), 7.79 – 7.71 (m, 2 H), 7.63 – 7.55 (m, 3 H), 7.50

– 7.43 (m, 4 H), 7.40 – 7.35 (m, 2 H), 3.22 (q, $J = 7.2$ Hz, 2 H), 3.05

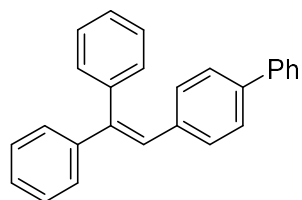
(q, $J = 7.0$ Hz, 2 H), 1.04 (t, $J = 7.2$ Hz, 3 H), 0.98 (t, $J = 7.2$ Hz, 3 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3):

$\delta = 195.1, 153.1, 148.7, 139.7, 138.2, 137.6, 133.0, 132.3, 130.4, 129.9, 128.9, 128.5, 128.4, 127.6,$

$127.1, 123.6, 42.2, 41.6, 13.8, 13.2$; IR (KBr): 2886, 2782, 1716, 1429, 1303, 948, 835, 708 cm^{-1} ;

HRMS-ESI (m/z): calcd for $\text{C}_{24}\text{H}_{24}\text{NO}_3$ [$\text{M} + \text{H}$] $^+$: 374.1751, found: 374.1743.

4-(2,2-Diphenylvinyl)-1,1'-biphenyl (5aa)



Yield: 20.0 mg (60%); Colorless oil; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta =$

7.58 (d, $J = 7.2$ Hz, 2 H), 7.47 – 7.25 (m, 15 H), 7.13 (d, $J = 8.4$ Hz, 2

H), 7.04 (s, 1 H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 143.4, 142.7, 140.6,$

$140.5, 139.3, 136.5, 130.4, 130.0, 128.8, 128.7, 128.2, 127.7, 127.6,$

$127.6, 127.5, 127.2, 126.9, 126.6$; IR (KBr): 3045, 2931, 2855, 1728, 1605, 1479, 1364, 1018, 890,

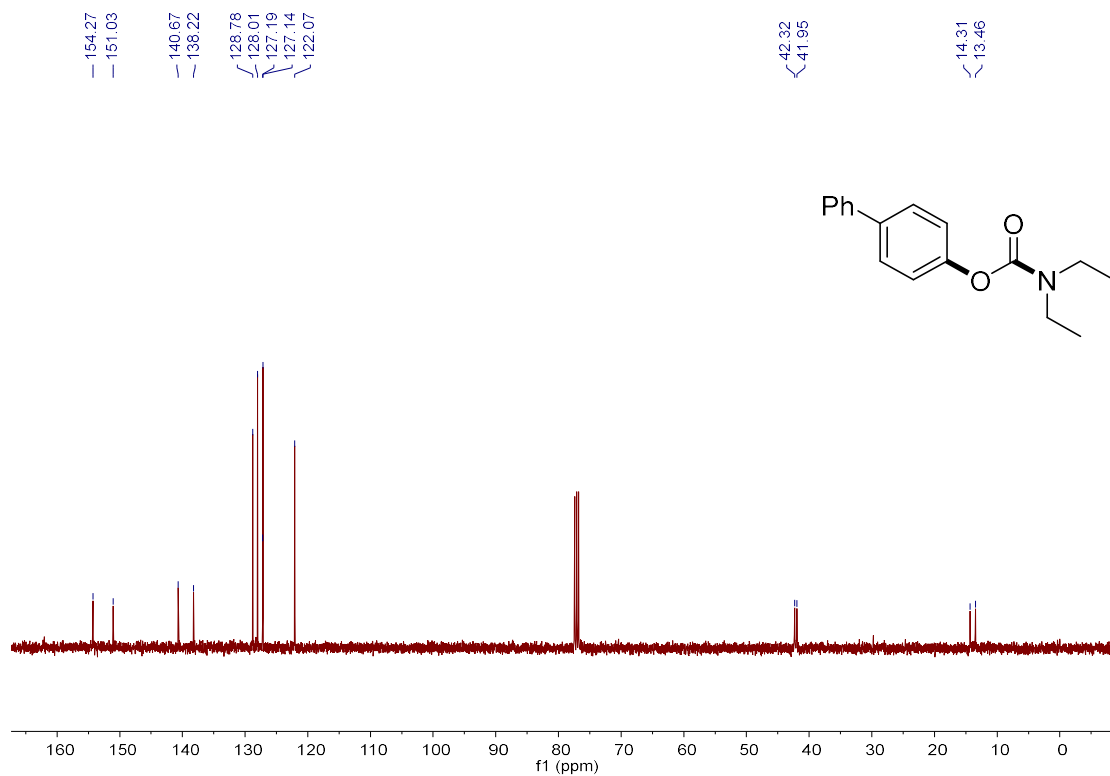
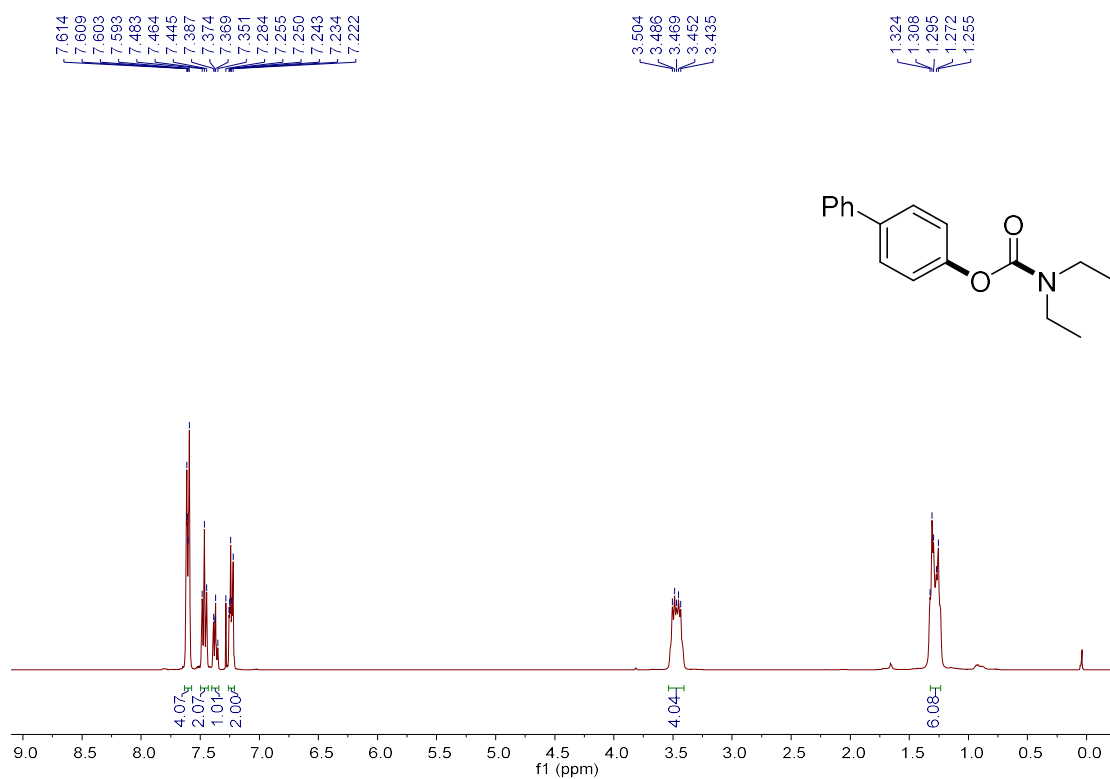
762, 698, 496 cm^{-1} ; HRMS-ESI (m/z): calcd for $\text{C}_{26}\text{H}_{21}$ [$\text{M} + \text{H}$] $^+$: 333.1638, found: 333.1634.

J. References

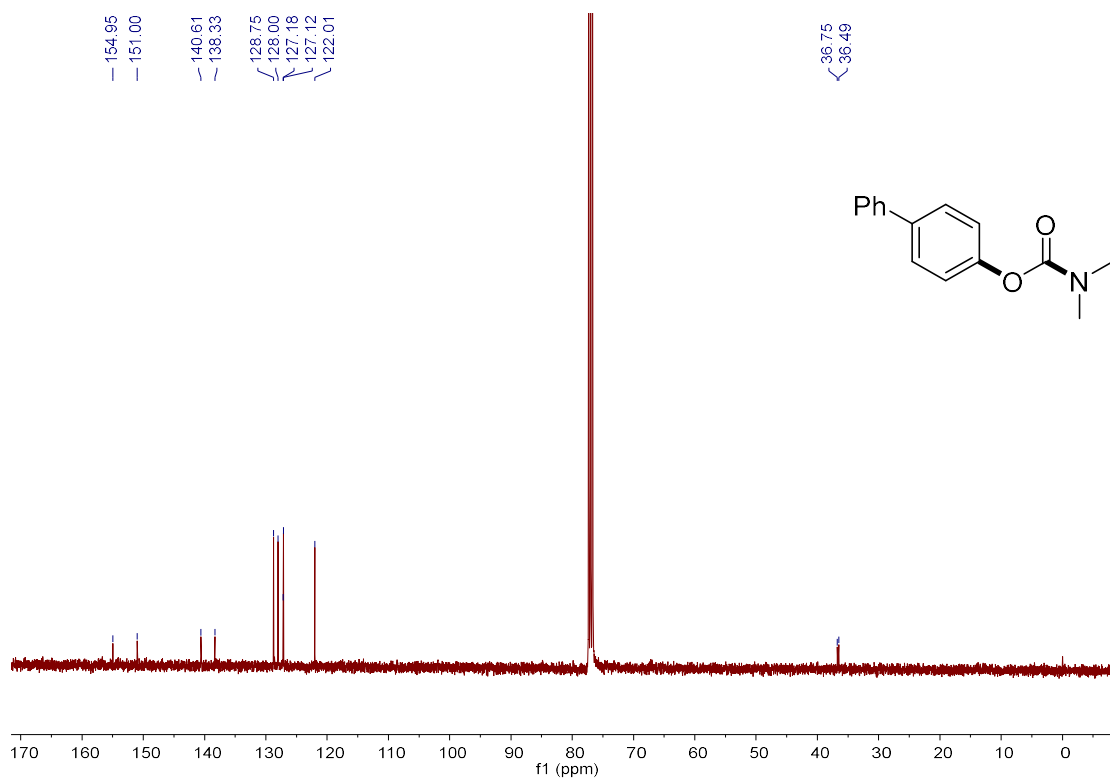
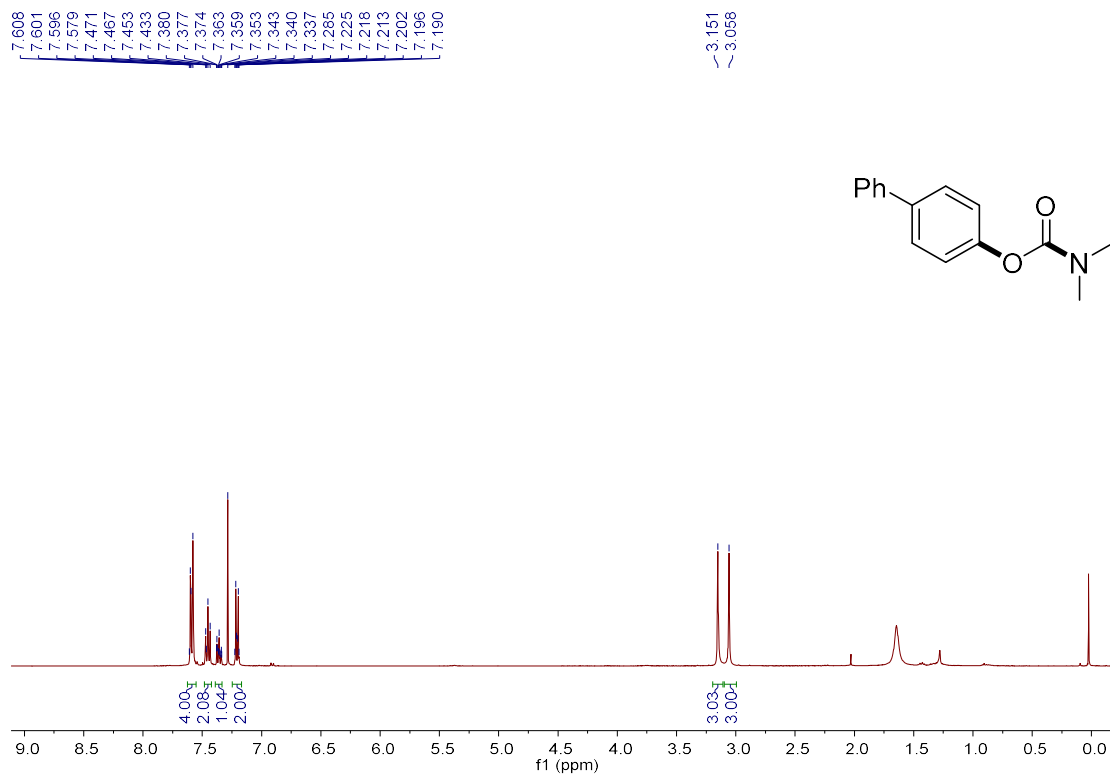
- (a). J. Li, J. Chen, R. Sang, W.-S. Ham, M. B. Plutschack, F. Berger, S. Chhabra, A. Schnegg, C. Genicot, T. Ritter, *Nat. Chem.*, 2020, **12**, 5. (b) L. Liang, H.-Y. Niu, R.-L. Li, Y.-F. Wang, J.-K. Yan, C.-G. Li, and H.-M. Guo, *Org. Lett.*, 2020, **22**, 6842. (c) Y. Wu, Y.-H. Huang, X.-Y. Chen, and P. Wang, *Org. Lett.*, 2020, **22**, 6657. (d) B. Zhao, Q. Wang, T. Zhu, B. Feng and M. Ma, *Org. Lett.*, 2022, **24**, 5608.
- M. S. Lowry, J. I. Goldsmith, J. D. Slinker, R. Rohl, R. A. Pascal, Jr., G. G. Malliaras and S. Bernhard, *Chem. Mater.*, 2005, **17**, 5712.
- W. Xiong, C. Qi, T. Guo, H. Jiang, *Green Chem.*, 2017, **19**, 1642.
- S. R. Chowdhury, S. K. Nandi, D. Halder, *ACS Omega*, 2022, **7**, 21566.

K. NMR Spectra

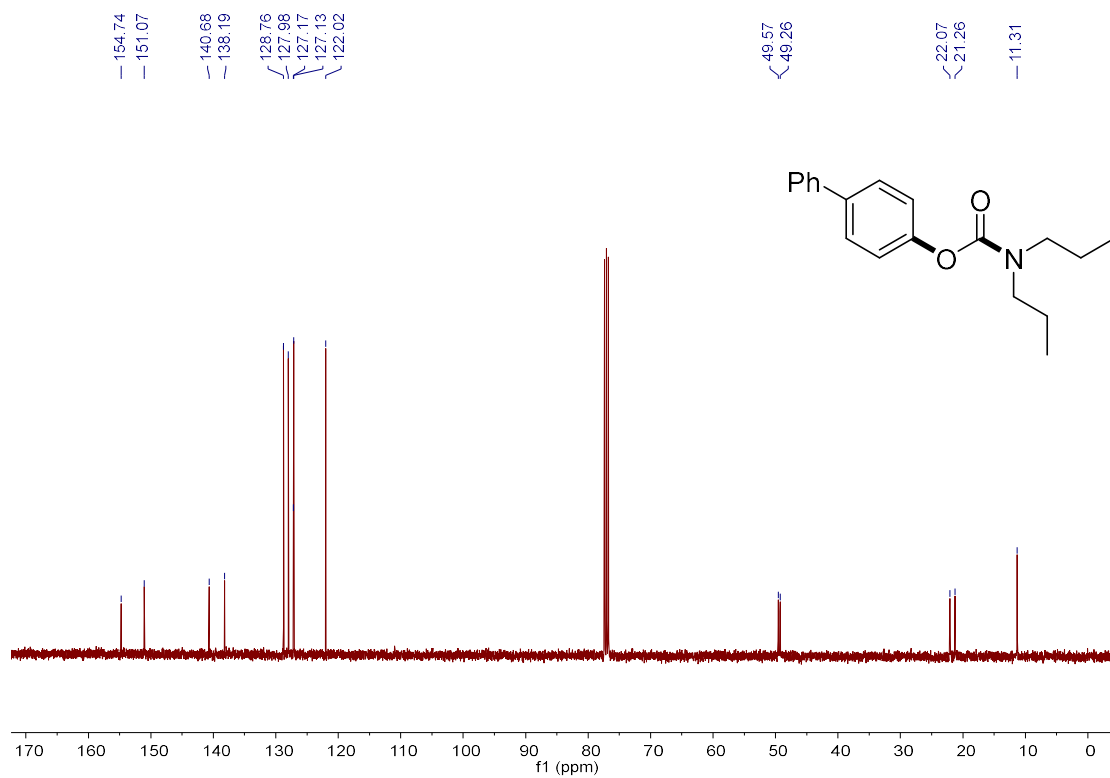
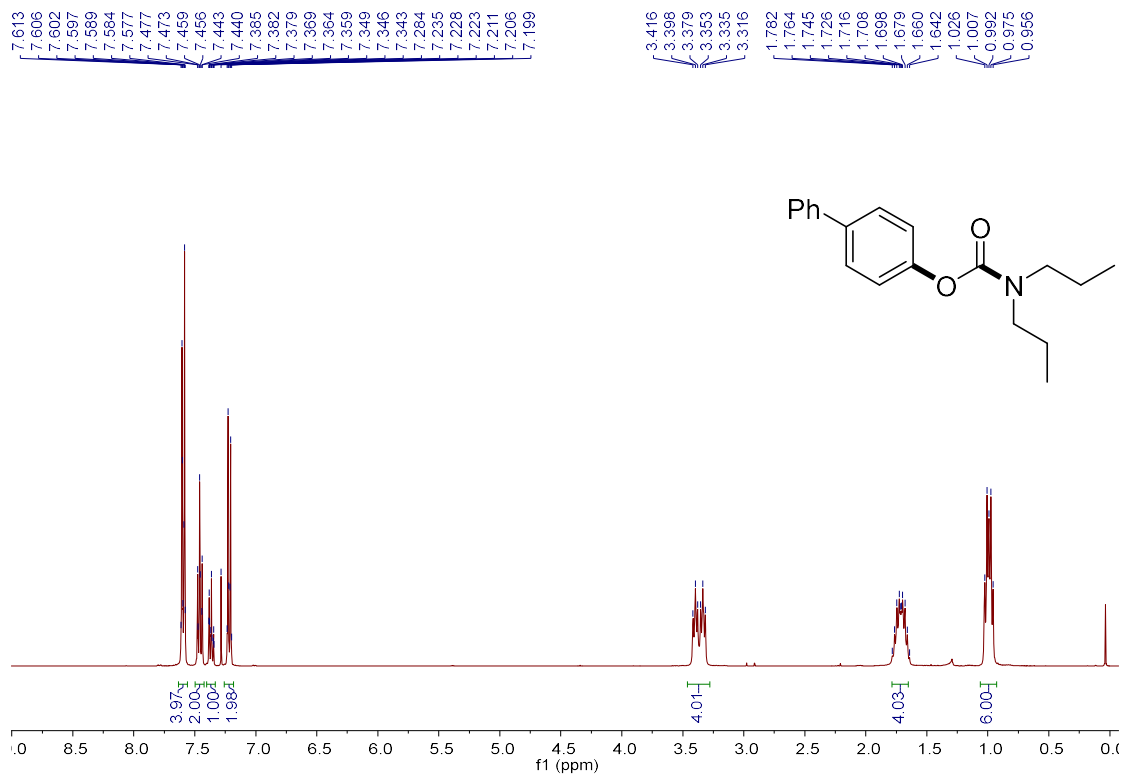
[1,1'-Biphenyl]-4-yl diethylcarbamate (3aa)



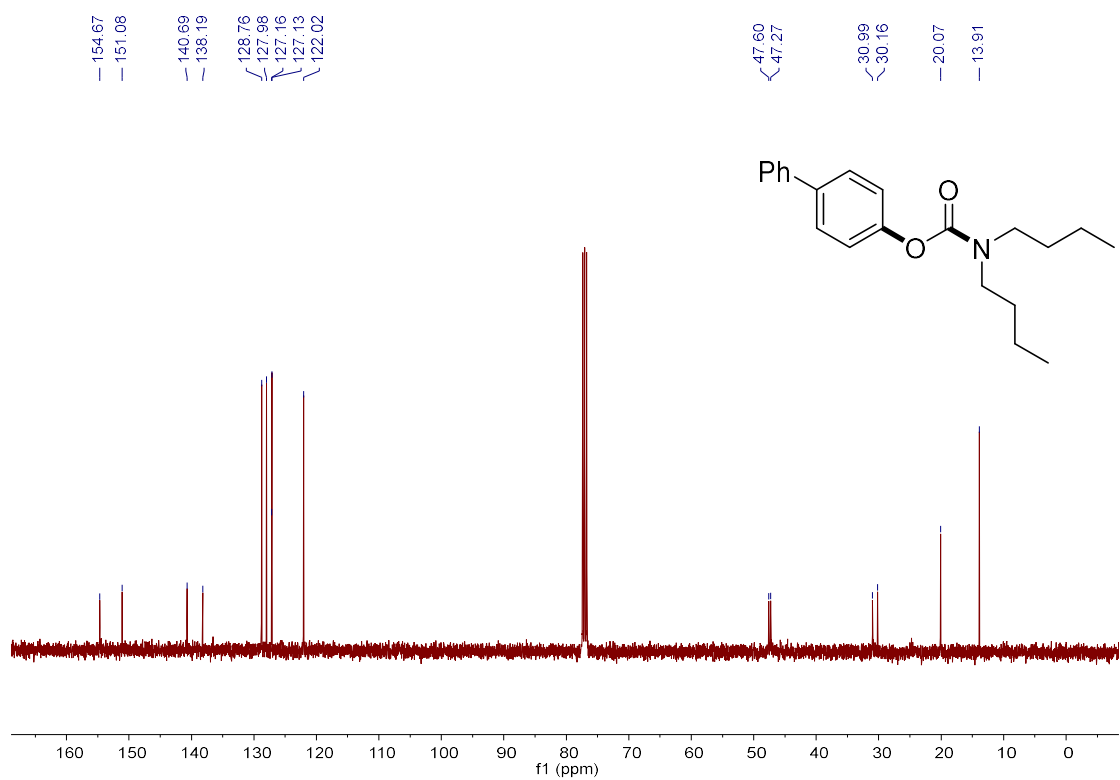
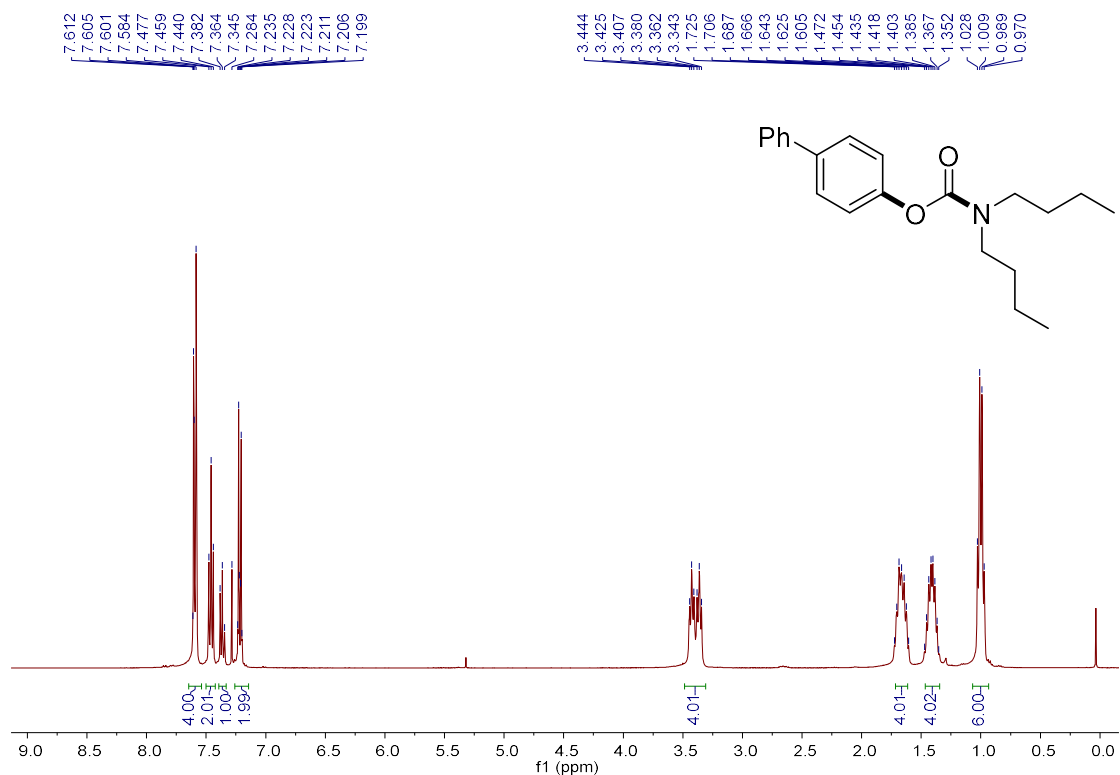
[1,1'-Biphenyl]-4-yl dimethylcarbamate (3ab)



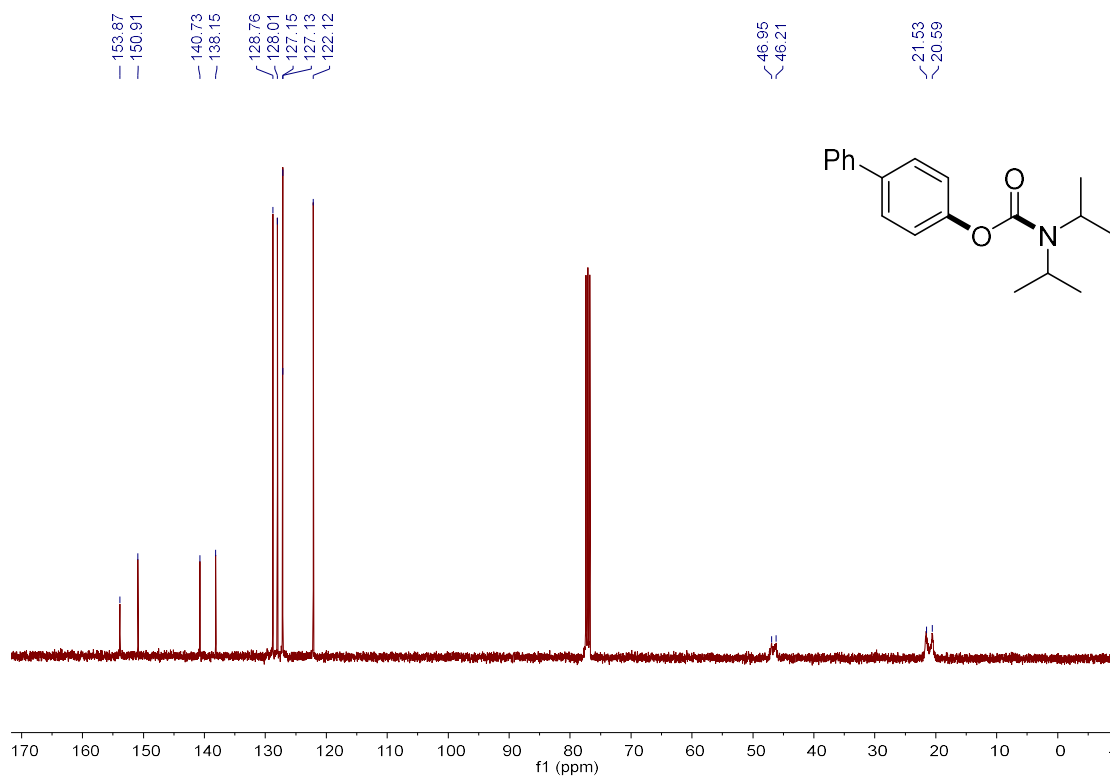
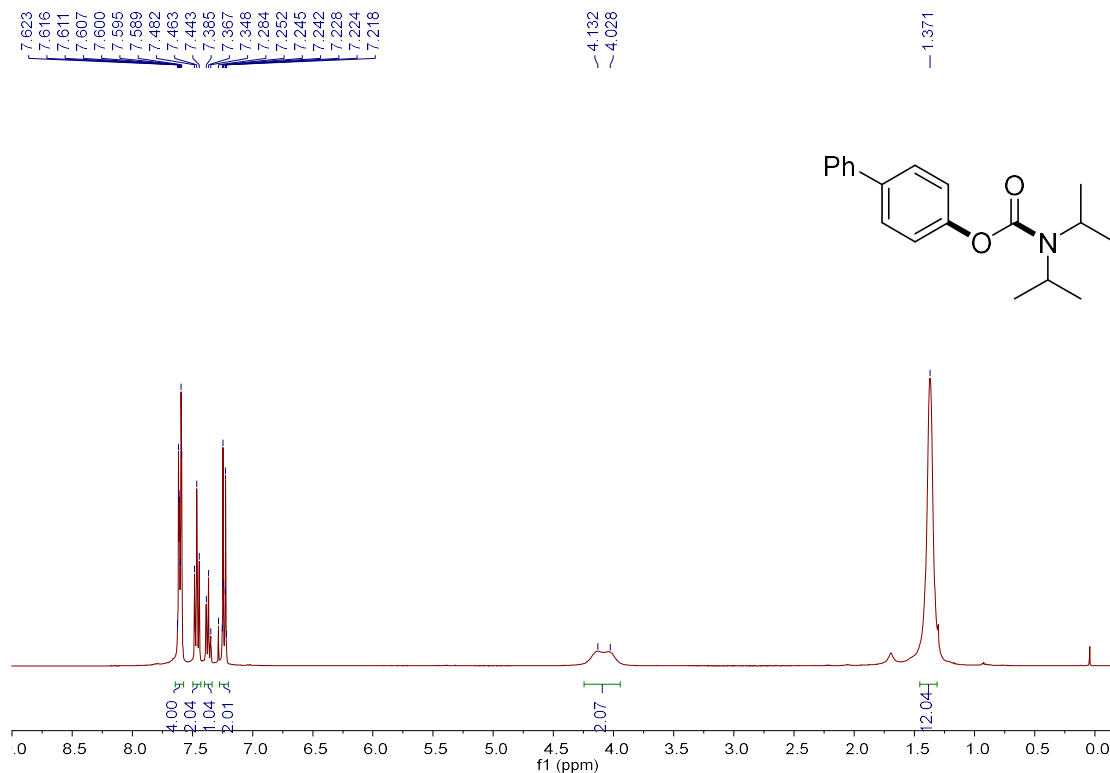
[1,1'-Biphenyl]-4-yl dipropylcarbamate (3ac)



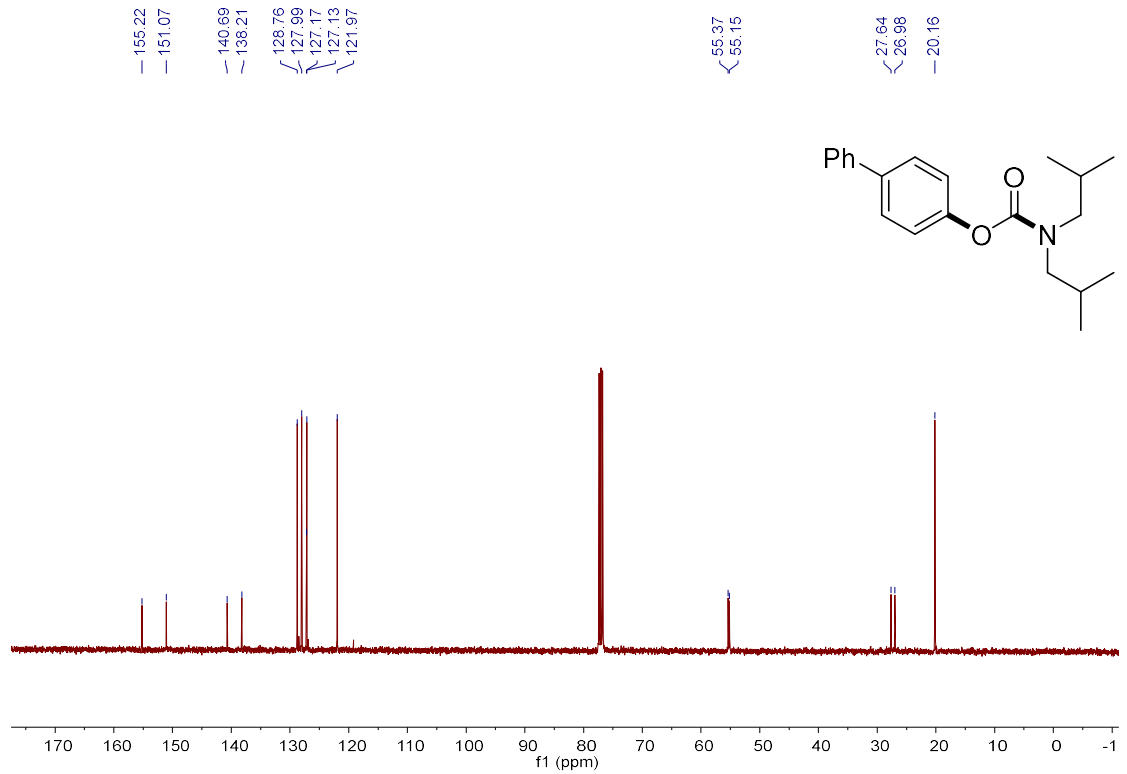
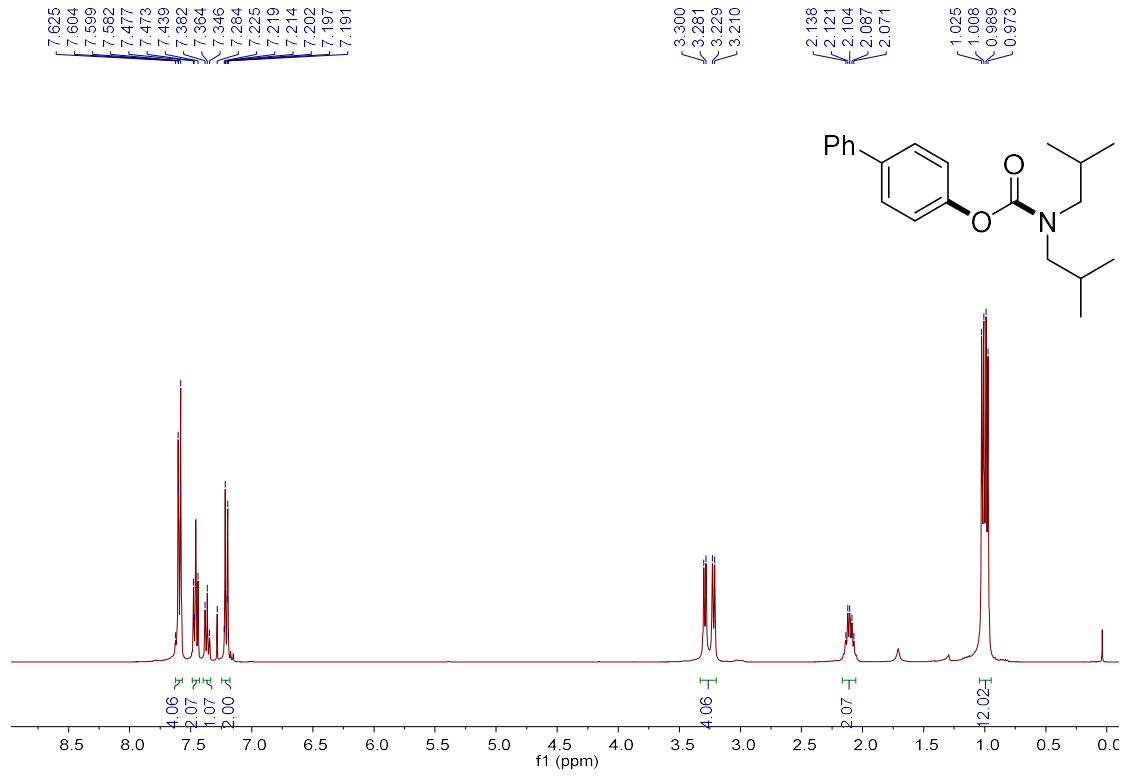
[1,1'-Biphenyl]-4-yl dibutylcarbamate (3ad)



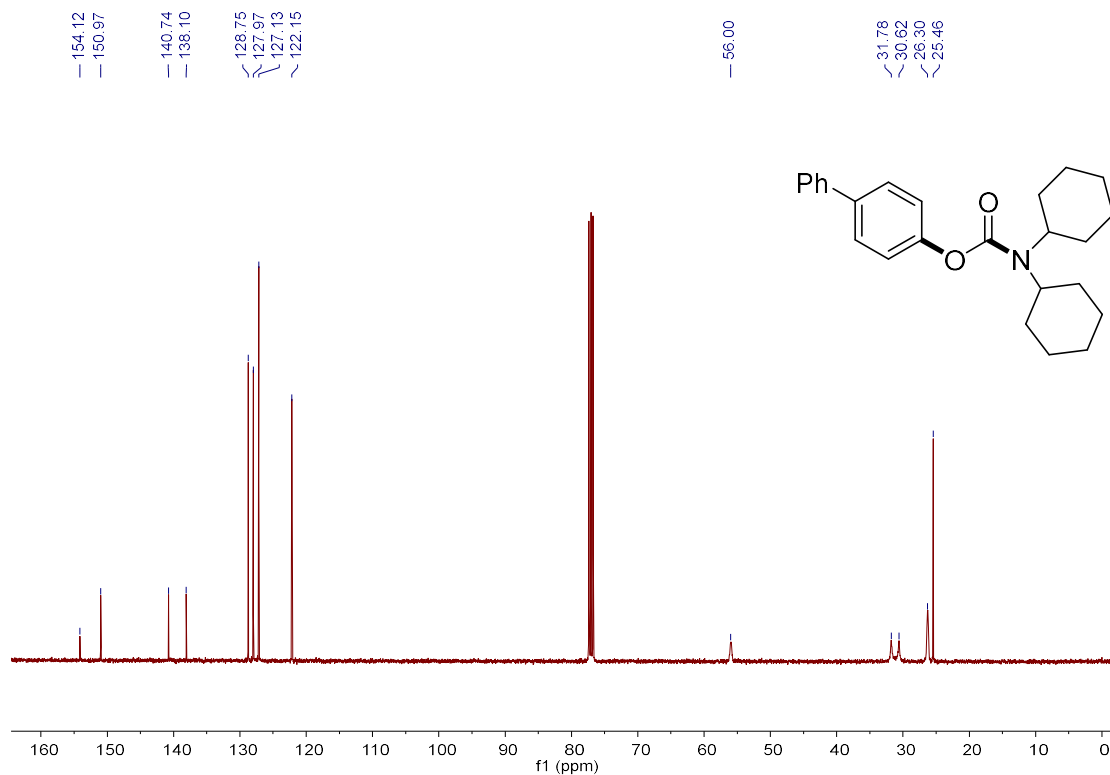
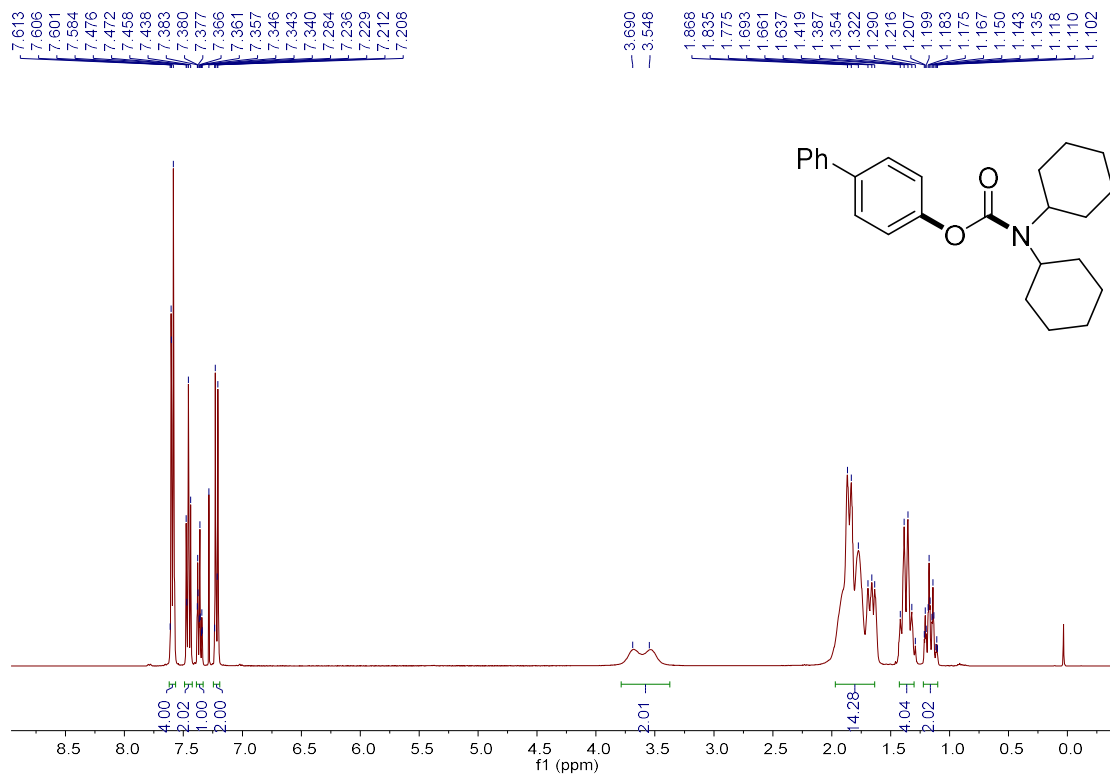
[1,1'-Biphenyl]-4-yl diisopropylcarbamate (3ae)



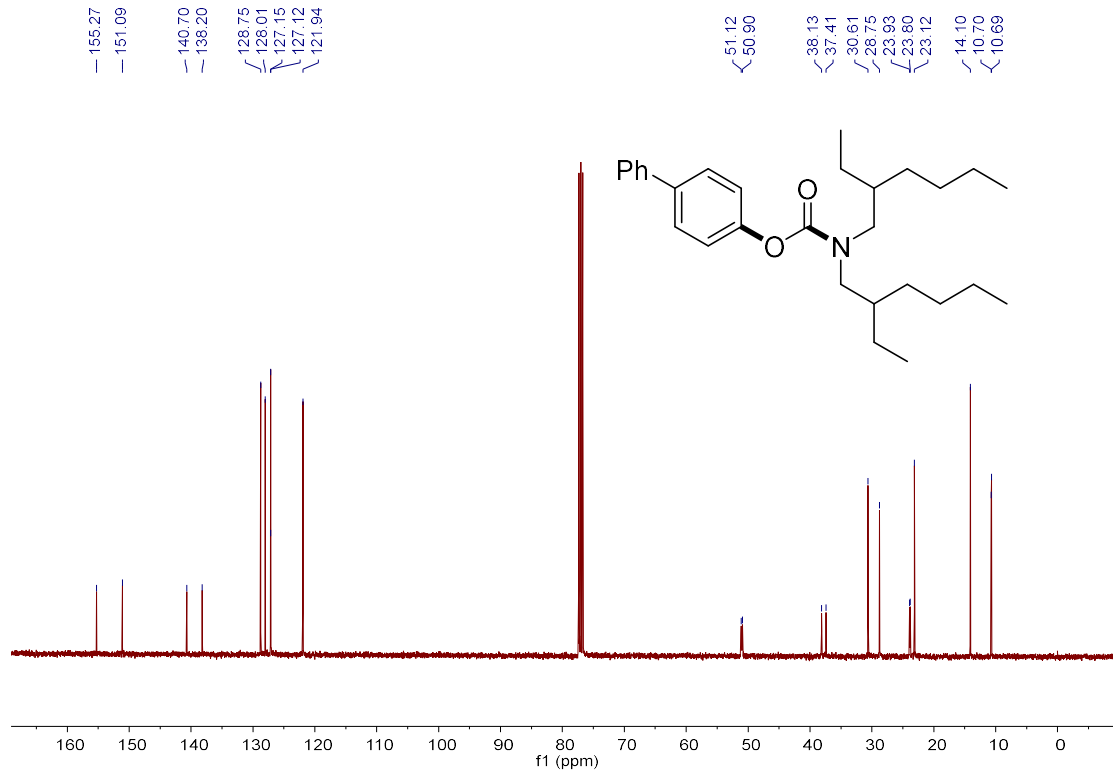
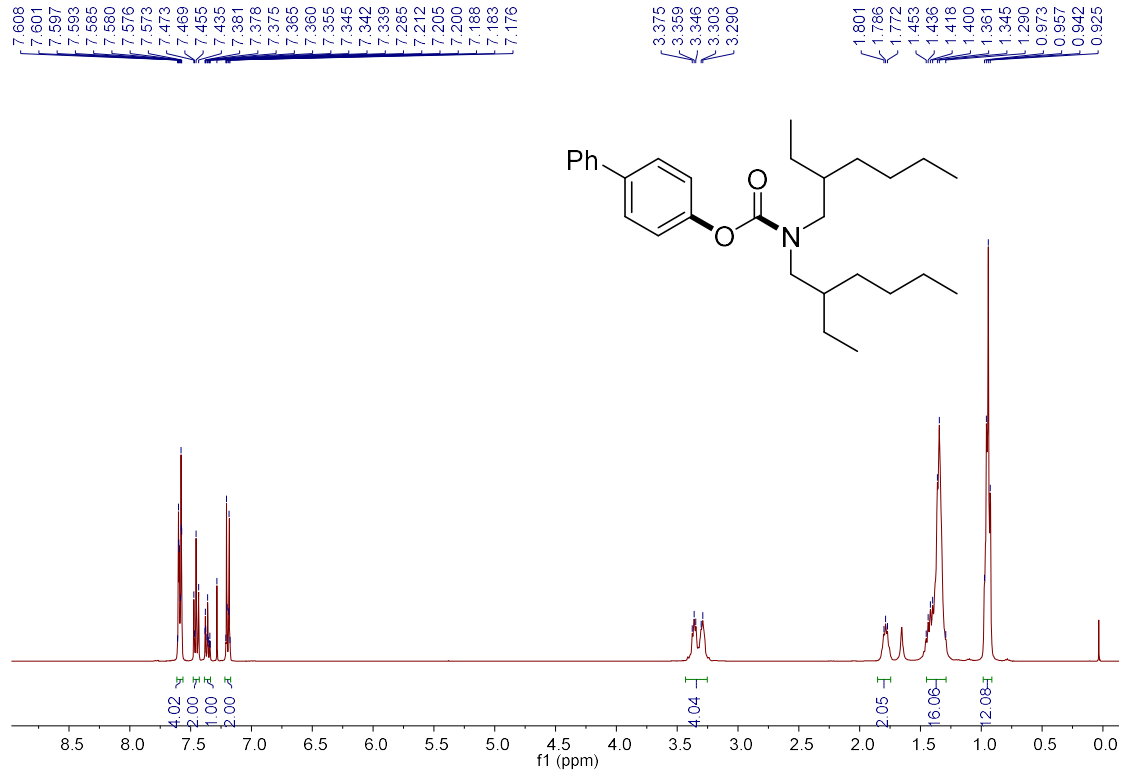
[1,1'-Biphenyl]-4-yl diisobutylcarbamate (3af)



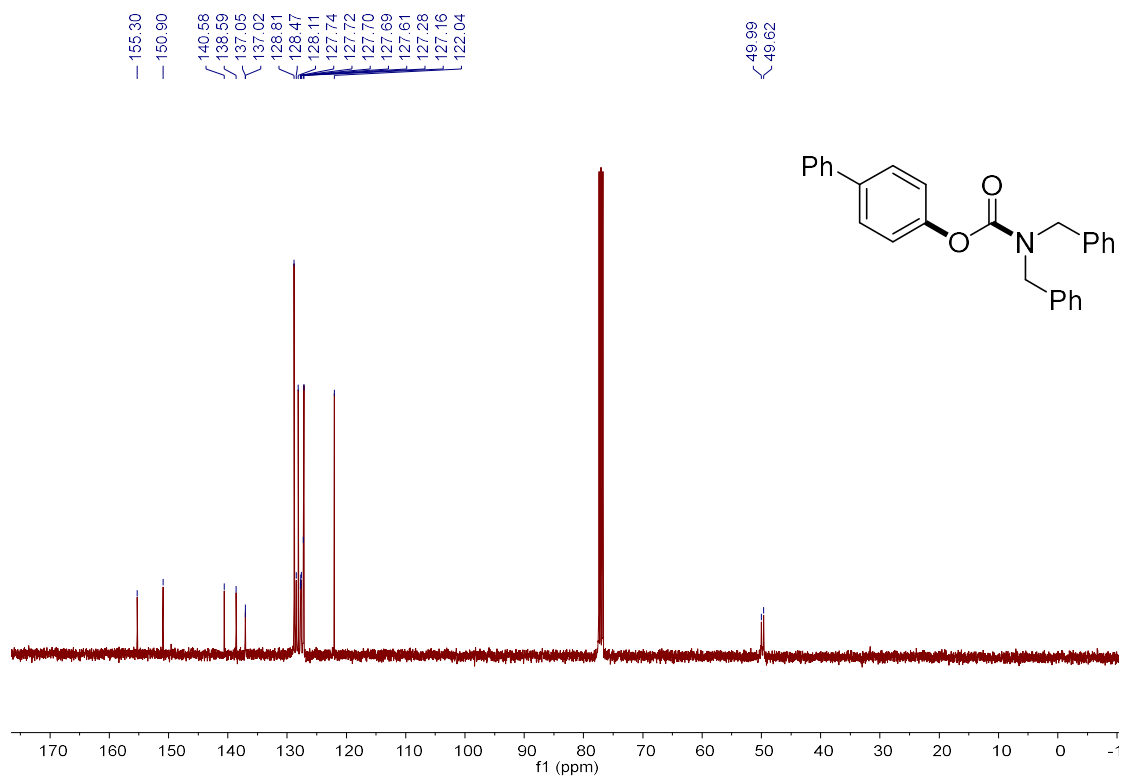
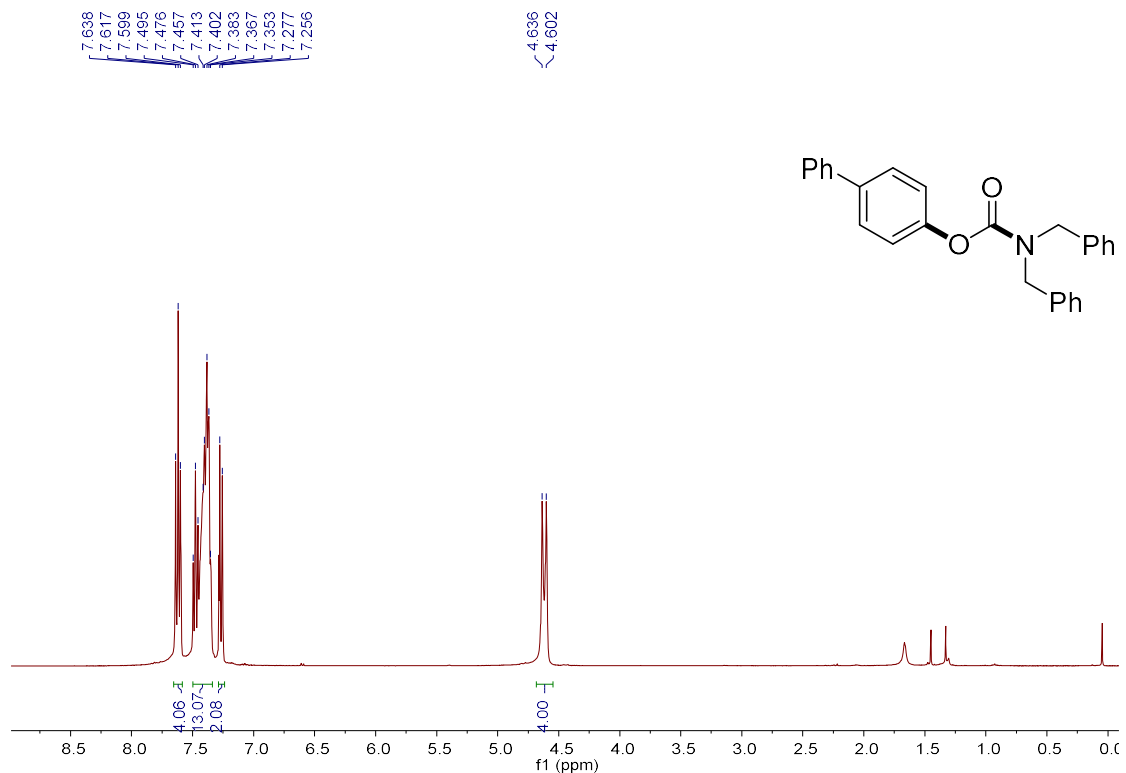
[1,1'-Biphenyl]-4-yl dicyclohexylcarbamate (3ag)



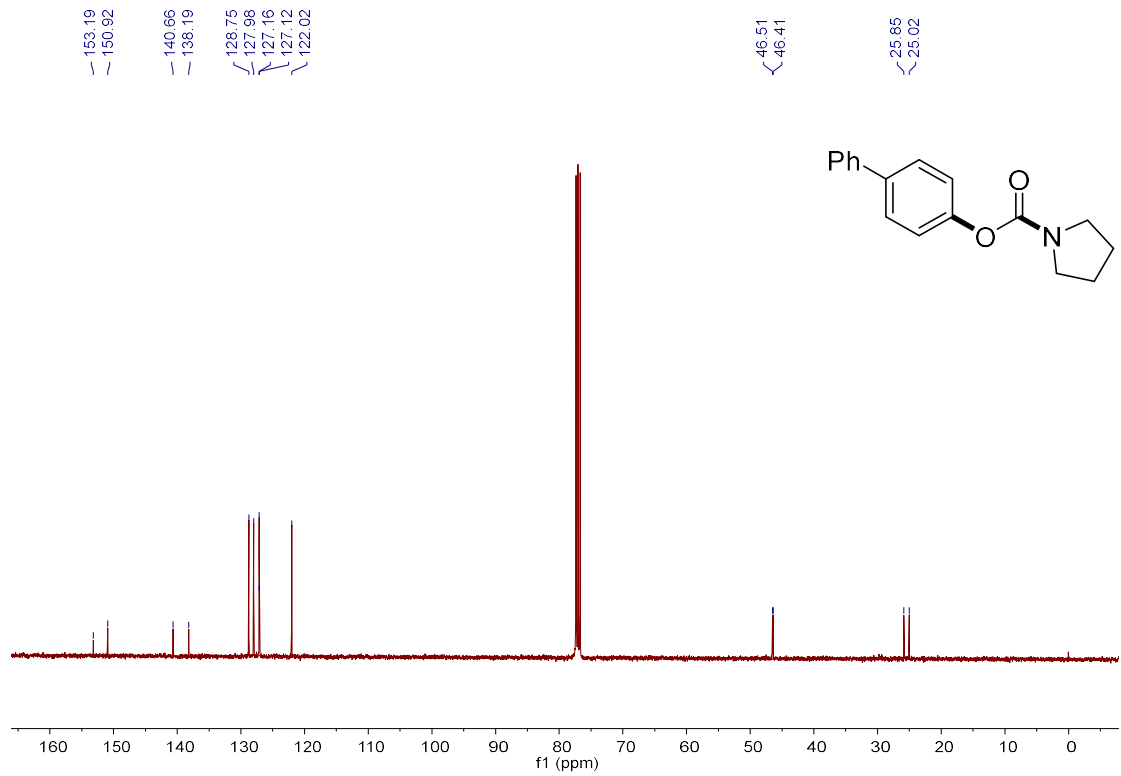
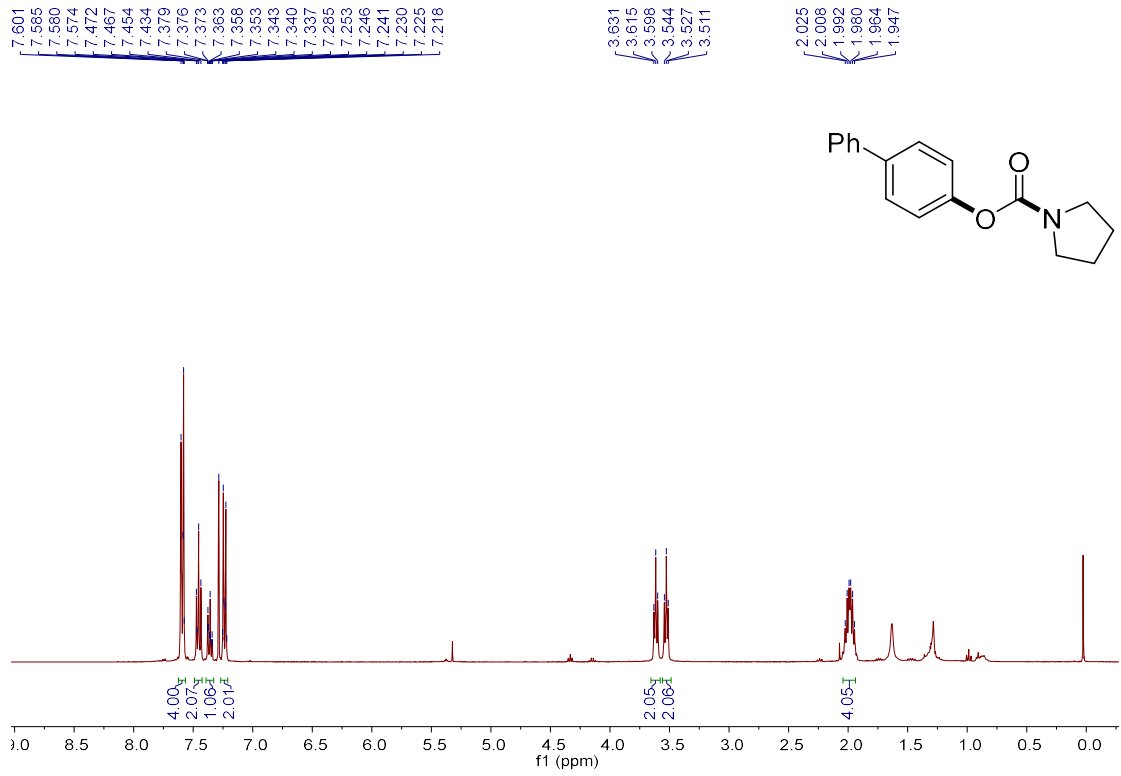
[1,1'-Biphenyl]-4-yl bis(2-ethylhexyl)carbamate (3ah).



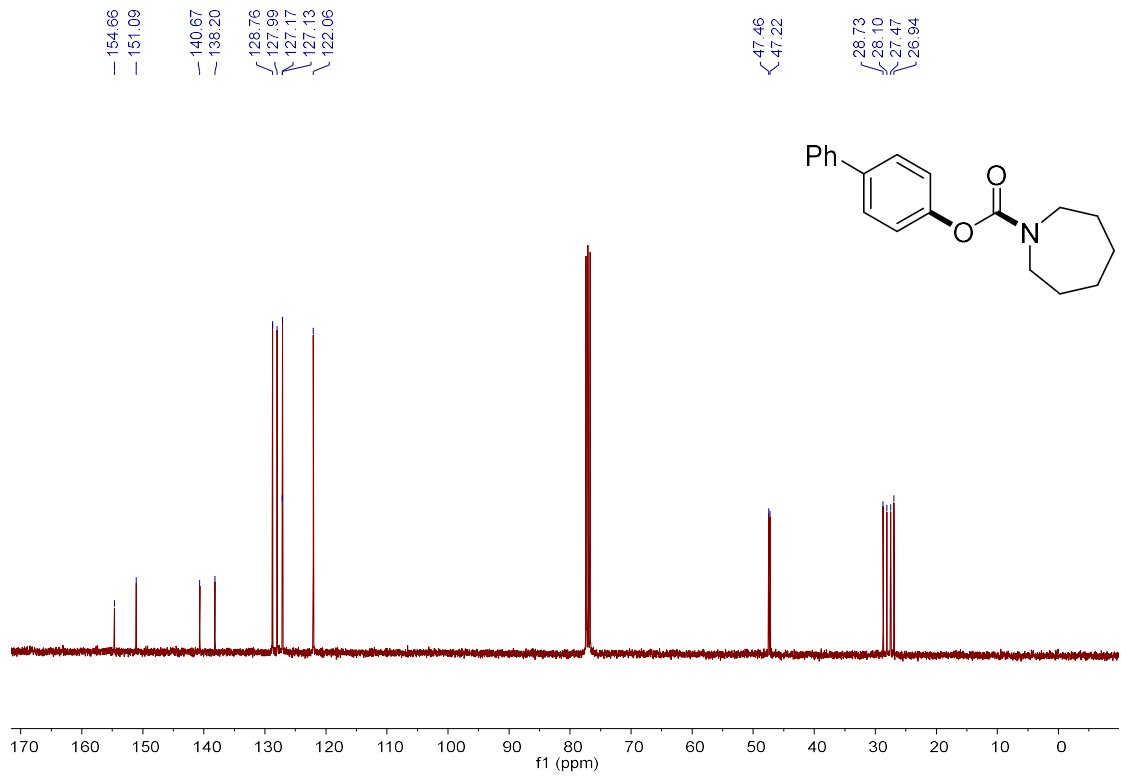
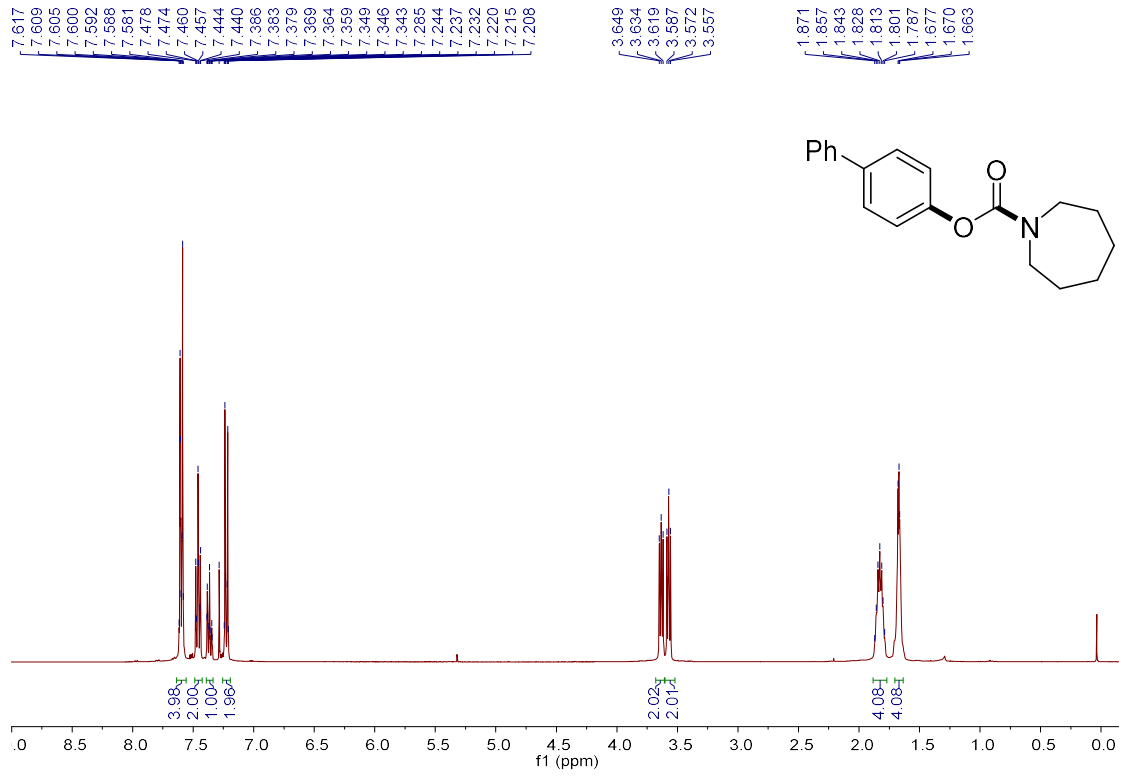
[1,1'-Biphenyl]-4-yl dibenzylcarbamate (3ai)



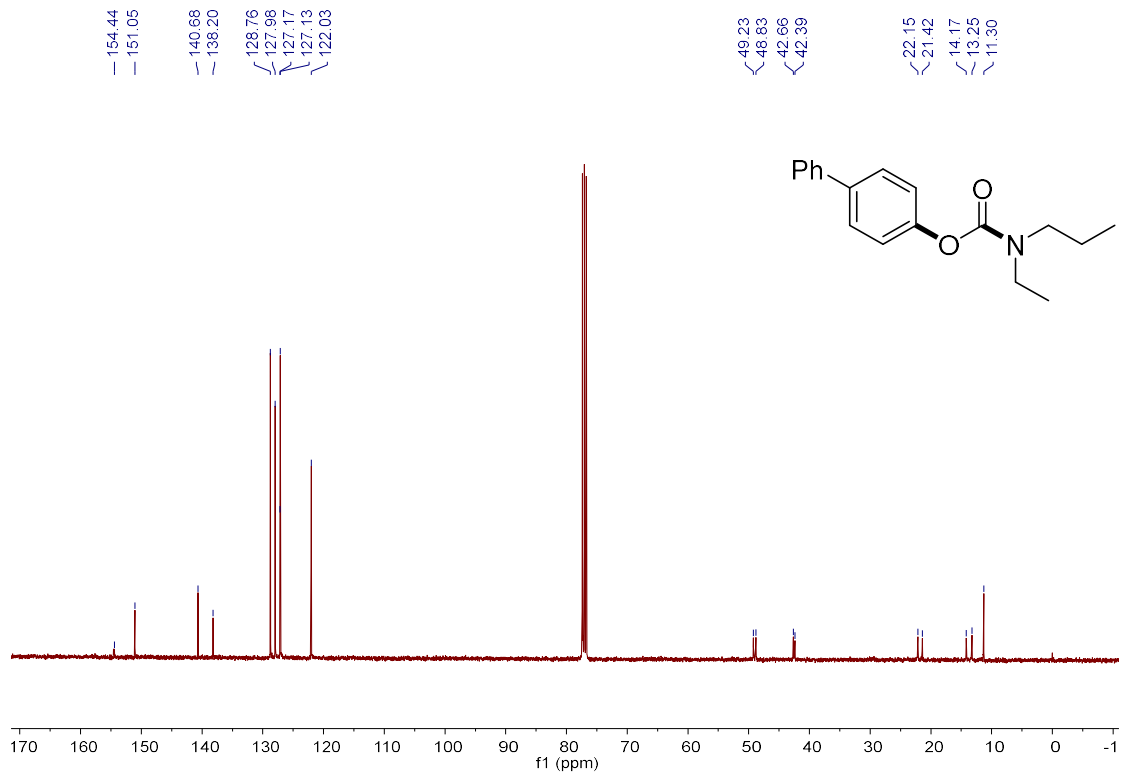
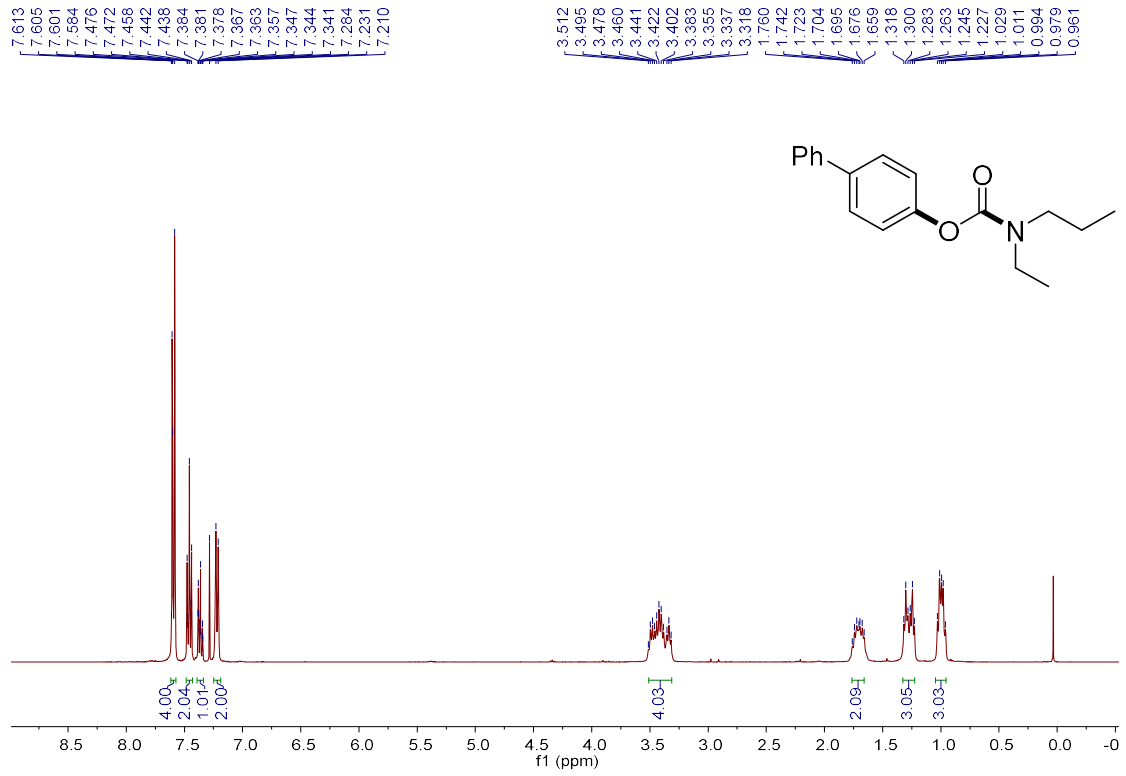
[1,1'-Biphenyl]-4-yl pyrrolidine-1-carboxylate (3aj)



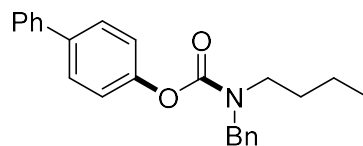
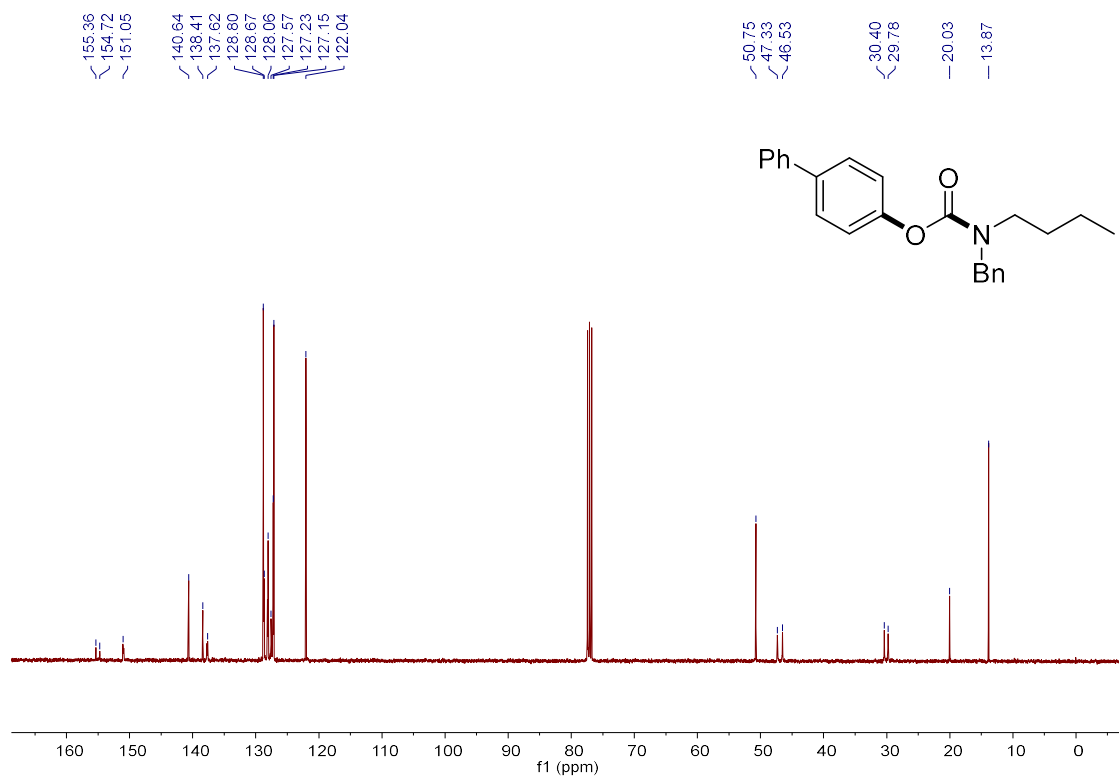
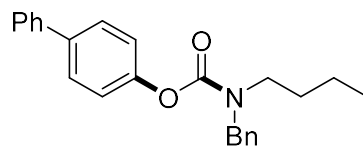
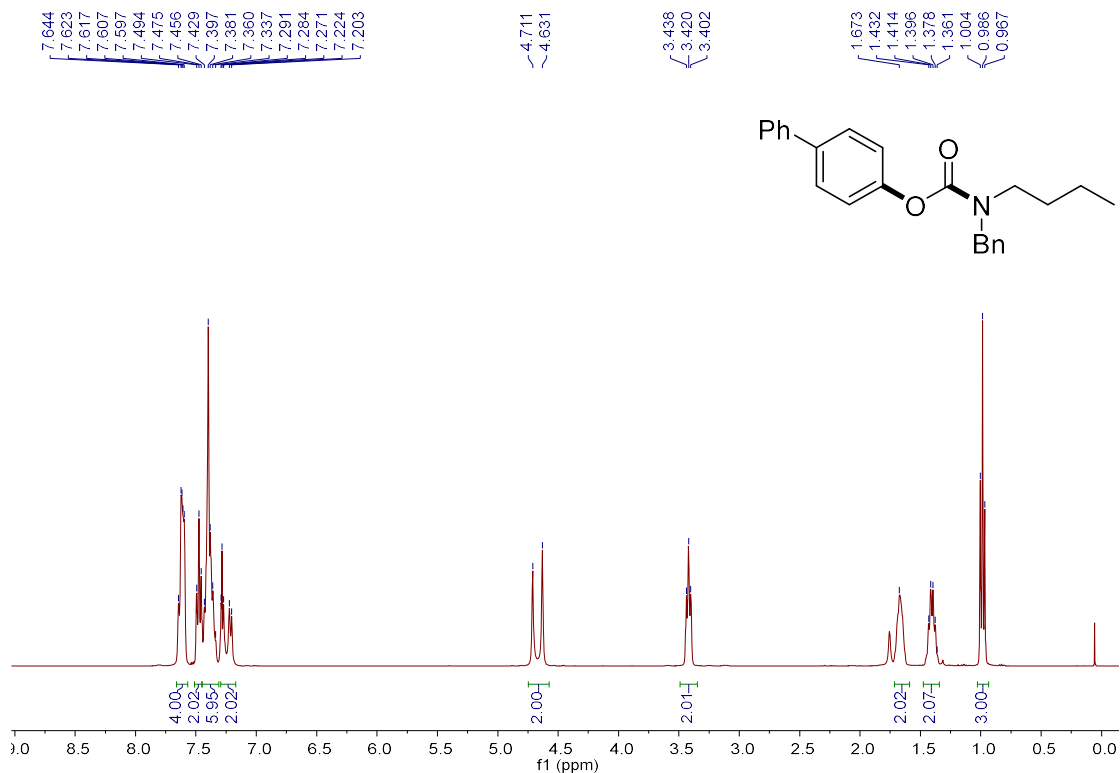
[1,1'-Biphenyl]-4-yl azepane-1-carboxylate (3ak)



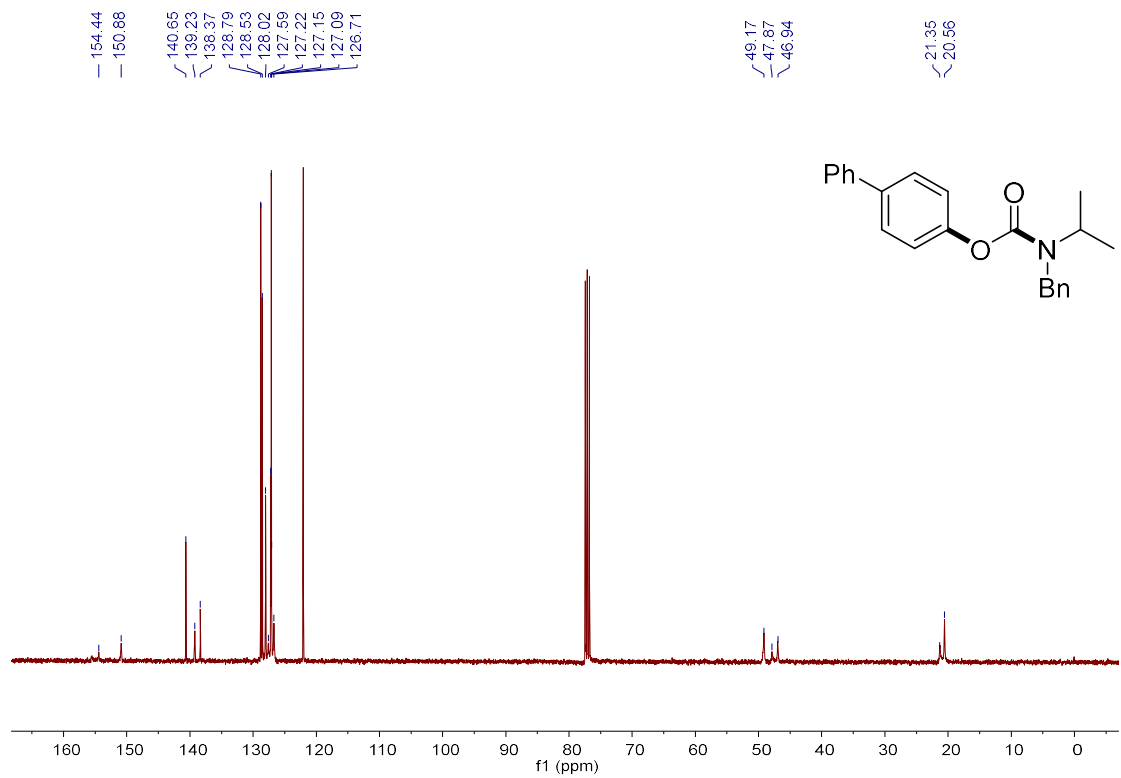
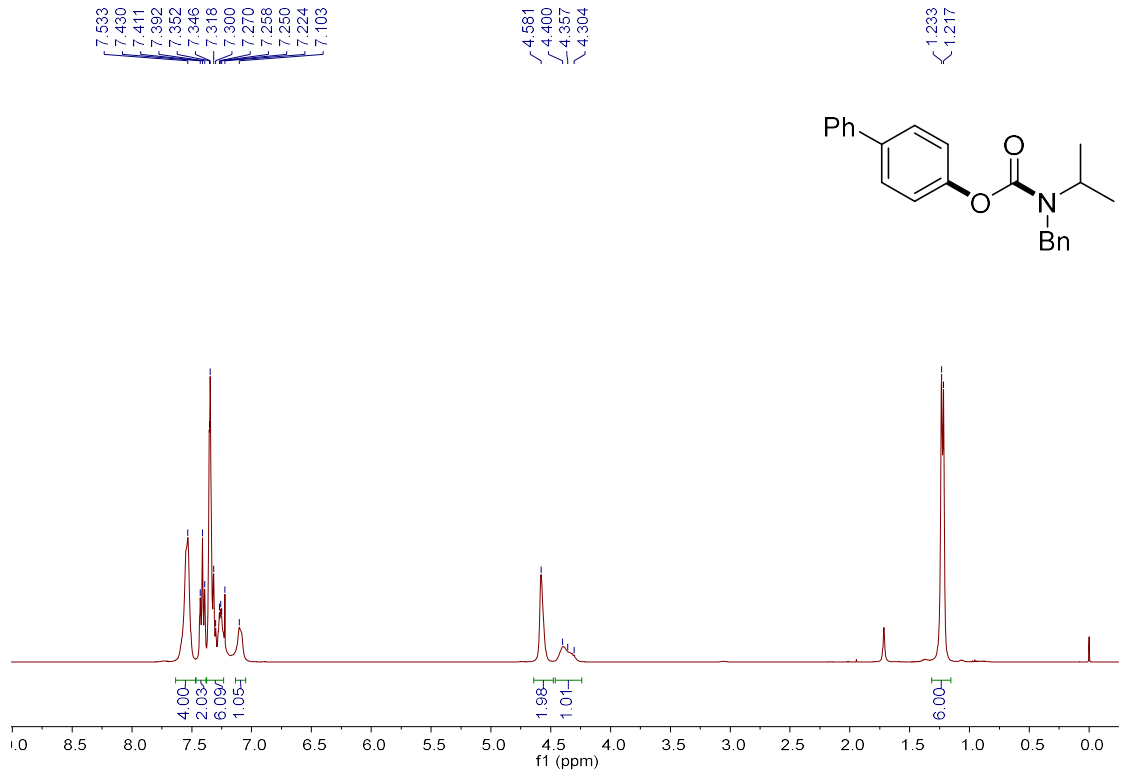
[1,1'-Biphenyl]-4-yl ethyl(propyl)carbamate (3a)



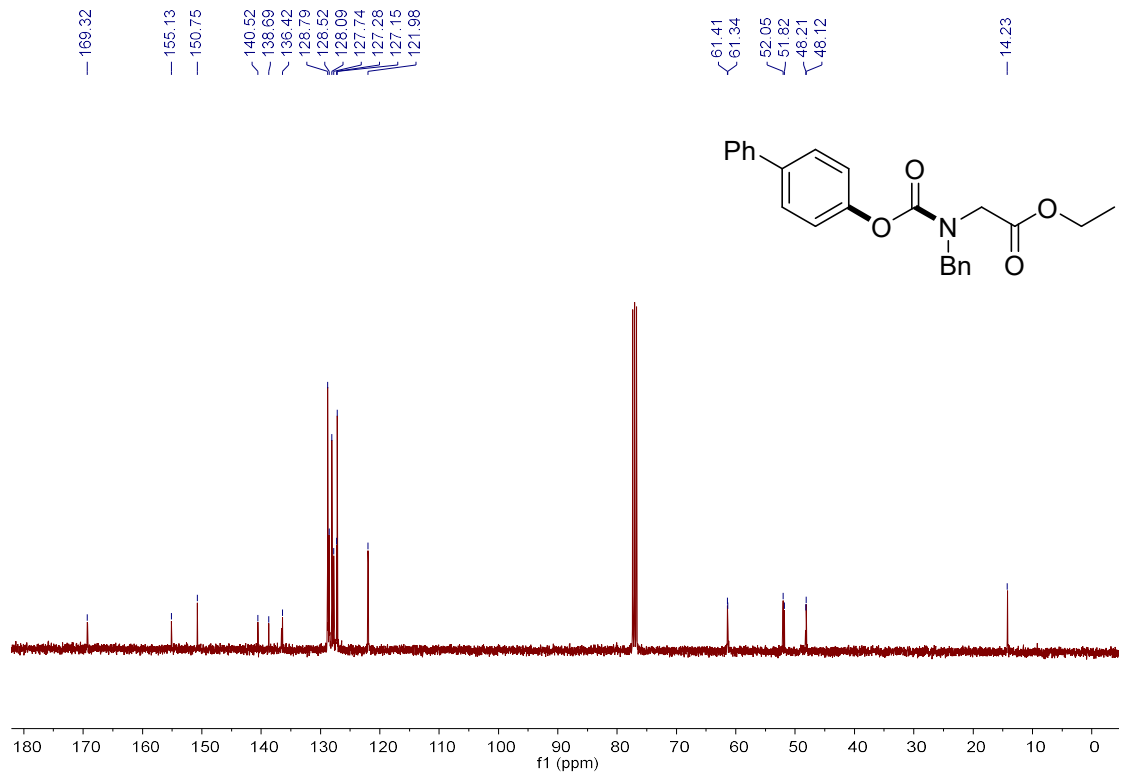
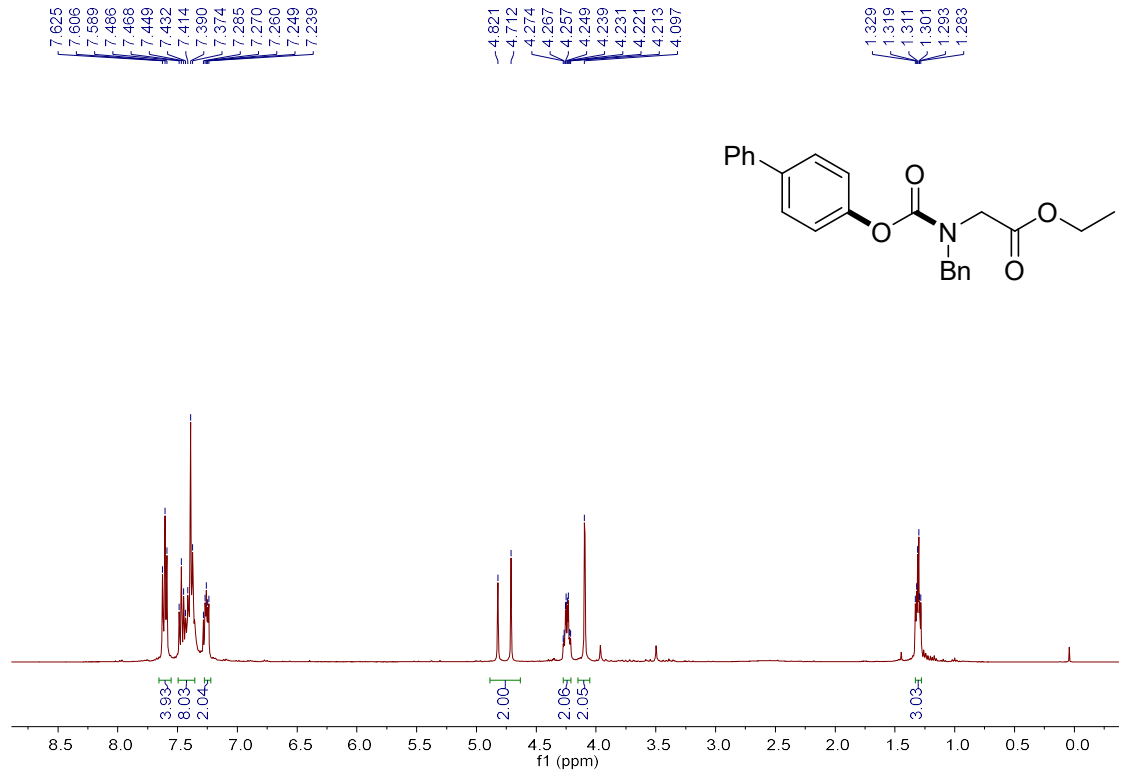
[1,1'-Biphenyl]-4-yl benzyl(butyl)carbamate (3am)



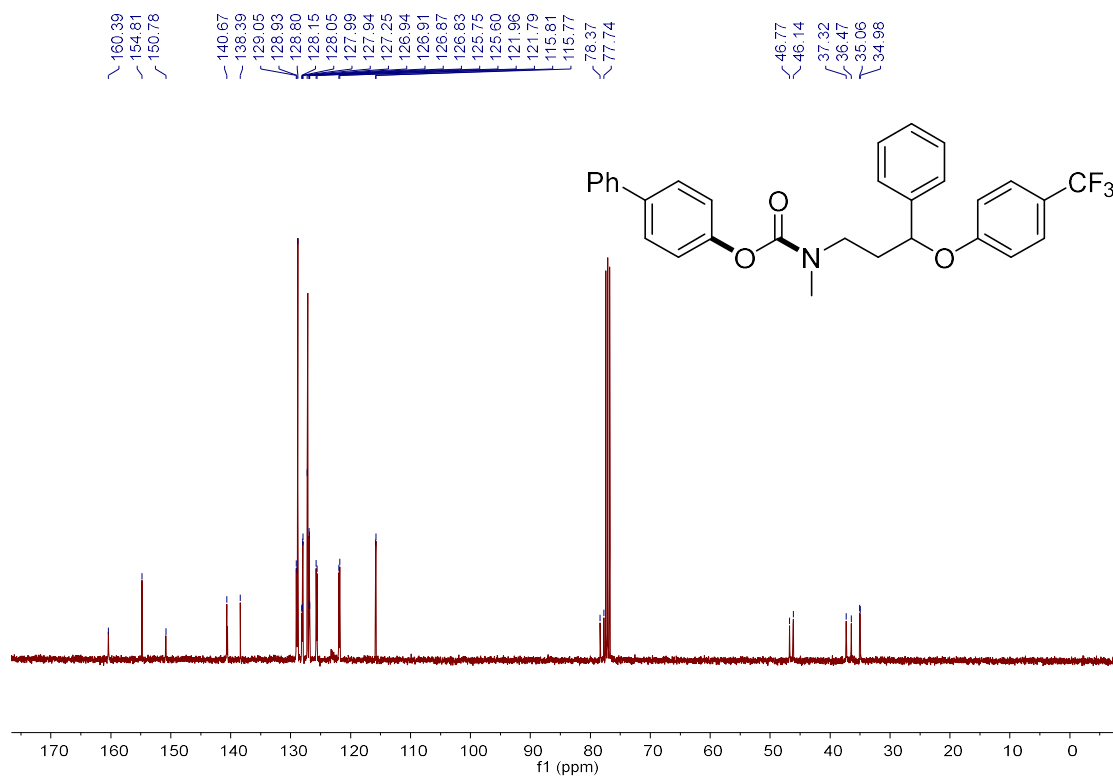
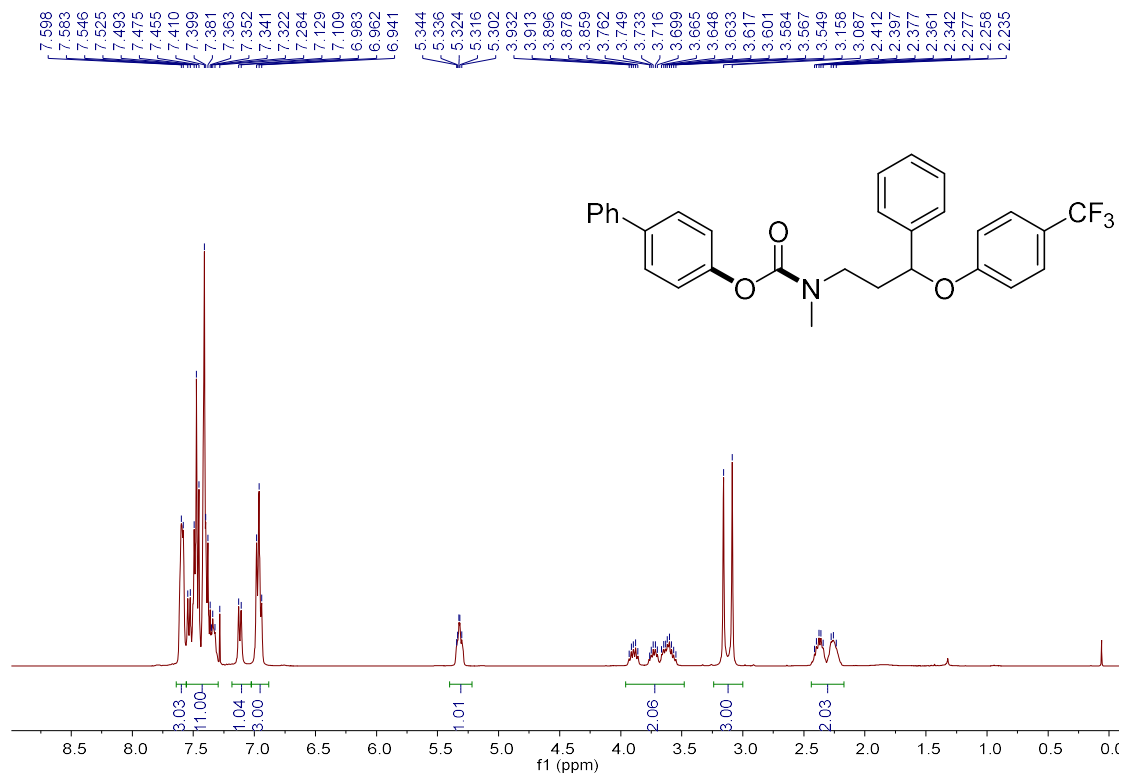
[1,1'-Biphenyl]-4-yl benzyl(isopropyl)carbamate (3an)

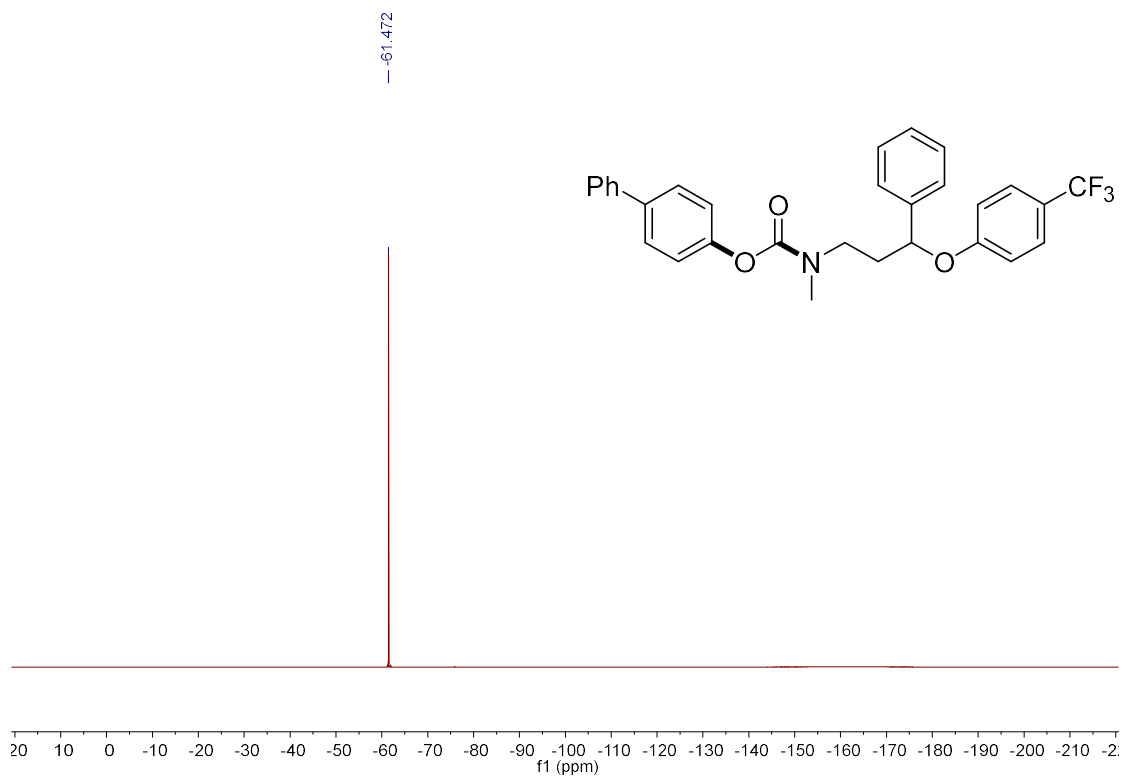


Ethyl N-([1,1'-biphenyl]-4-yloxy)carbonyl)-N-benzylglycinate (3ao)

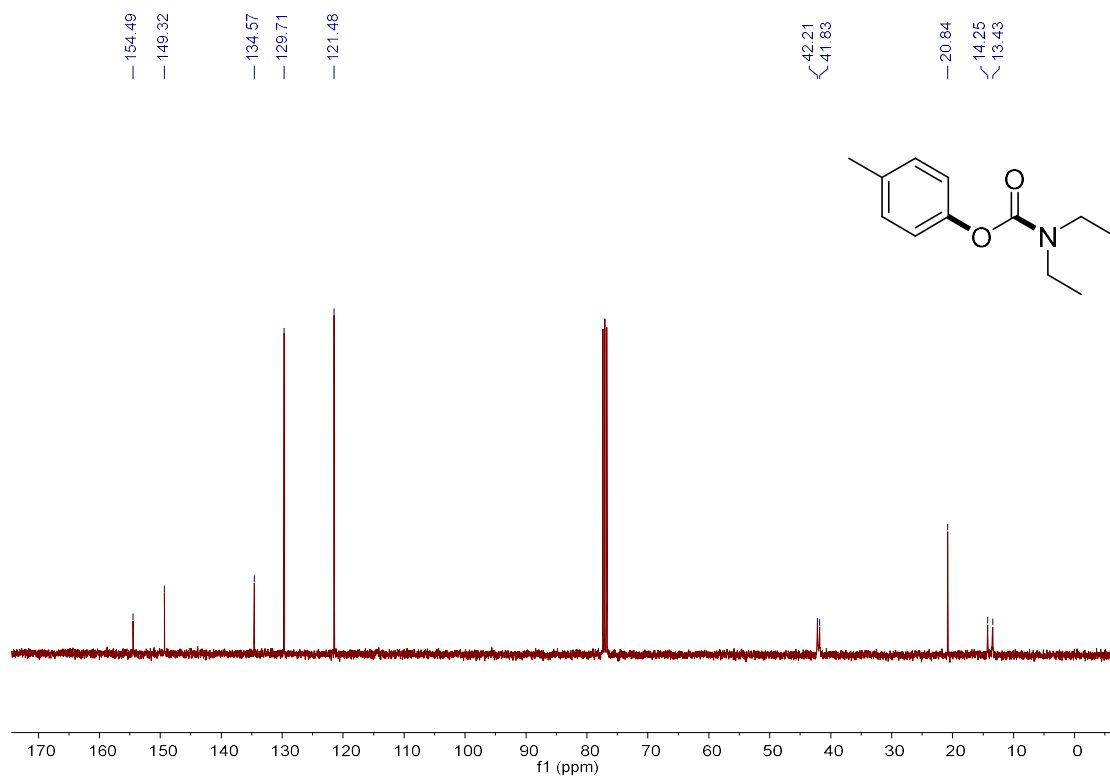
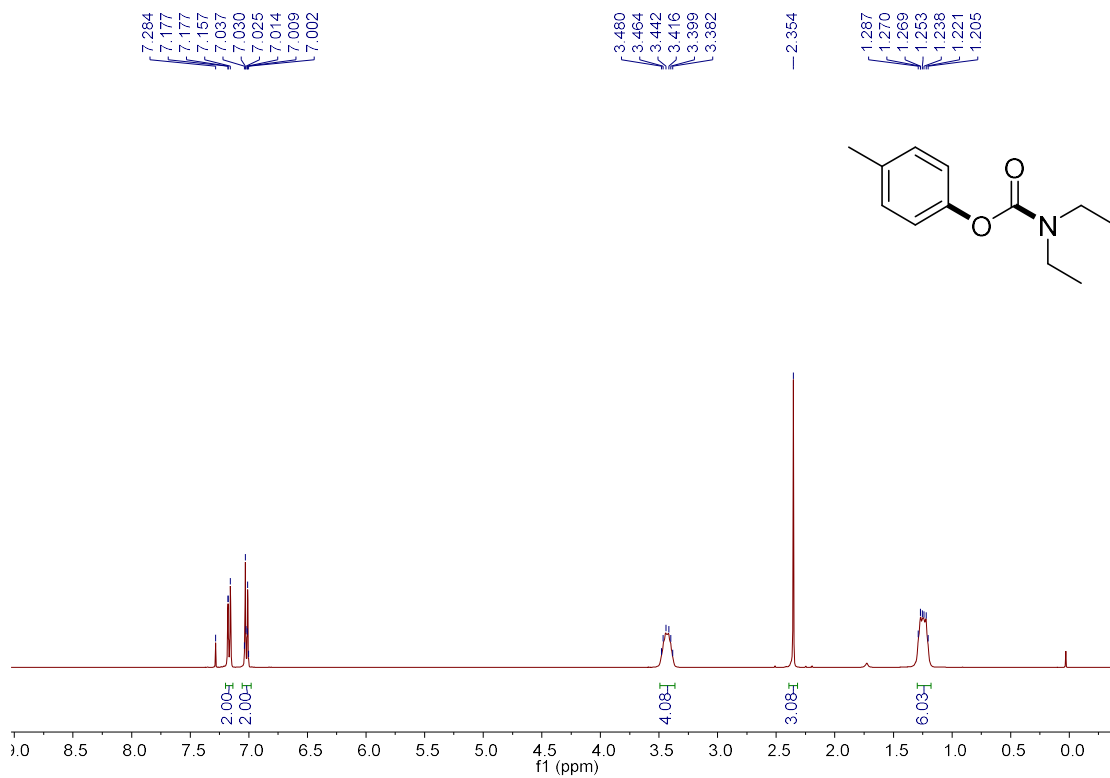


[1,1'-Biphenyl]-4-ylmethyl(3-phenyl-3-(4-(trifluoromethyl)phenoxy)propyl)carb-amate (3ap)

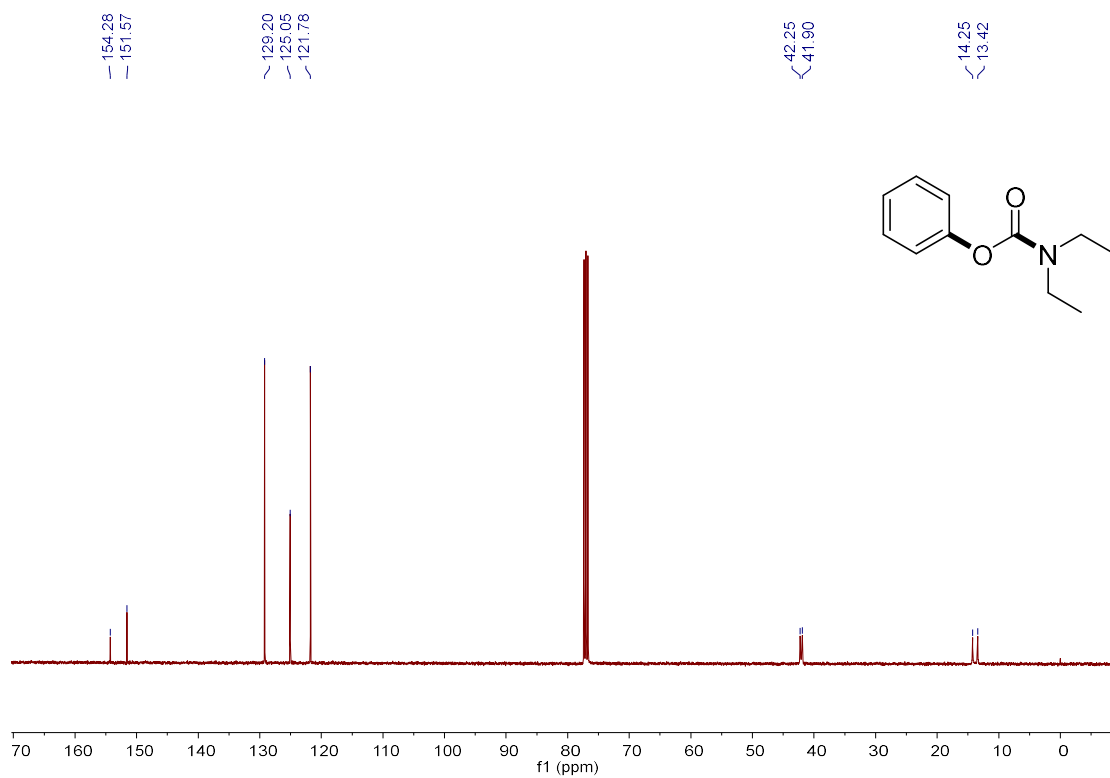
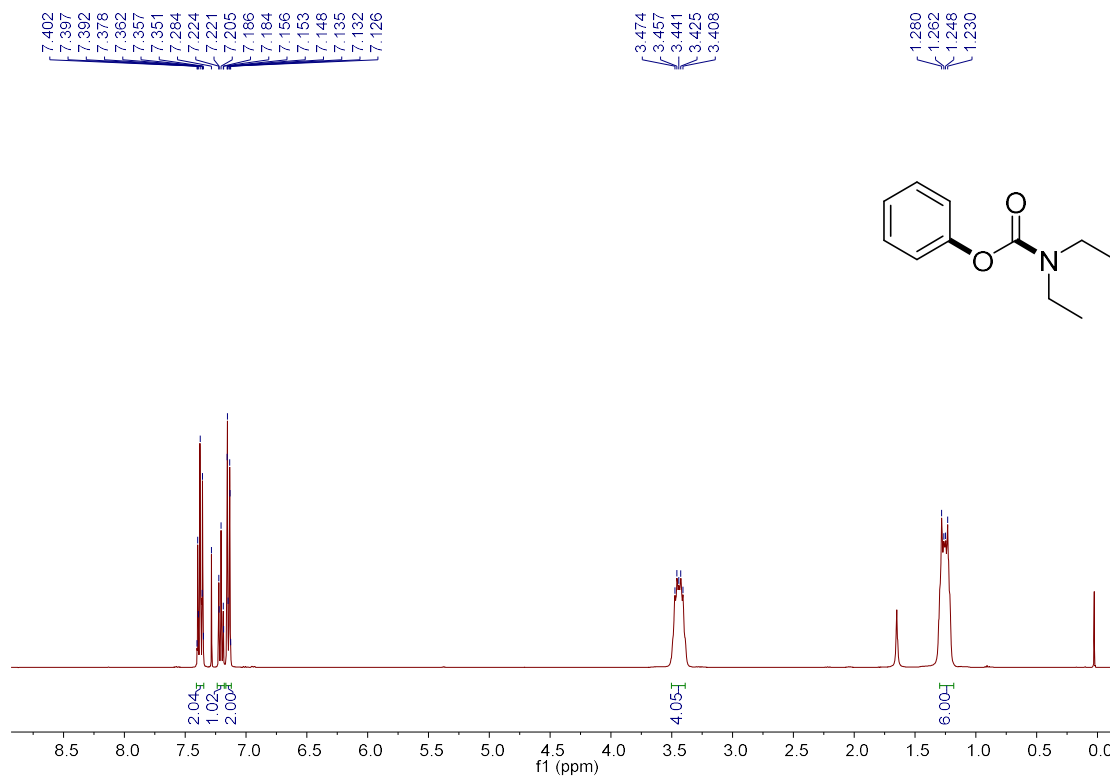




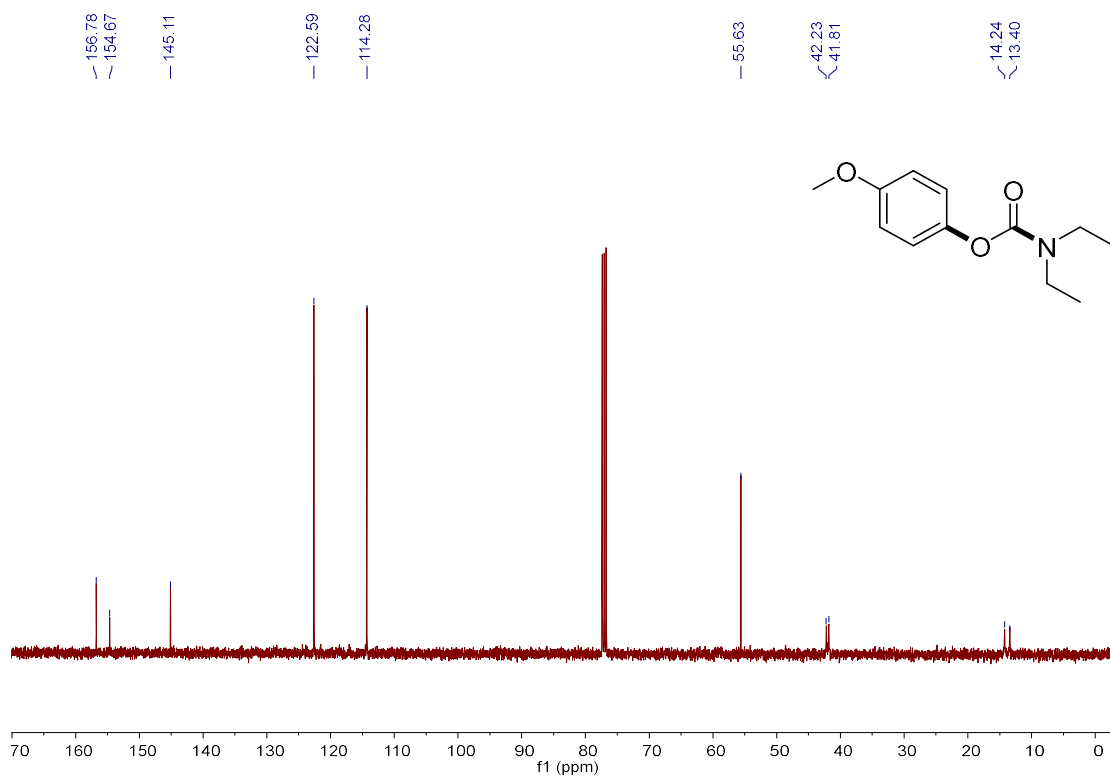
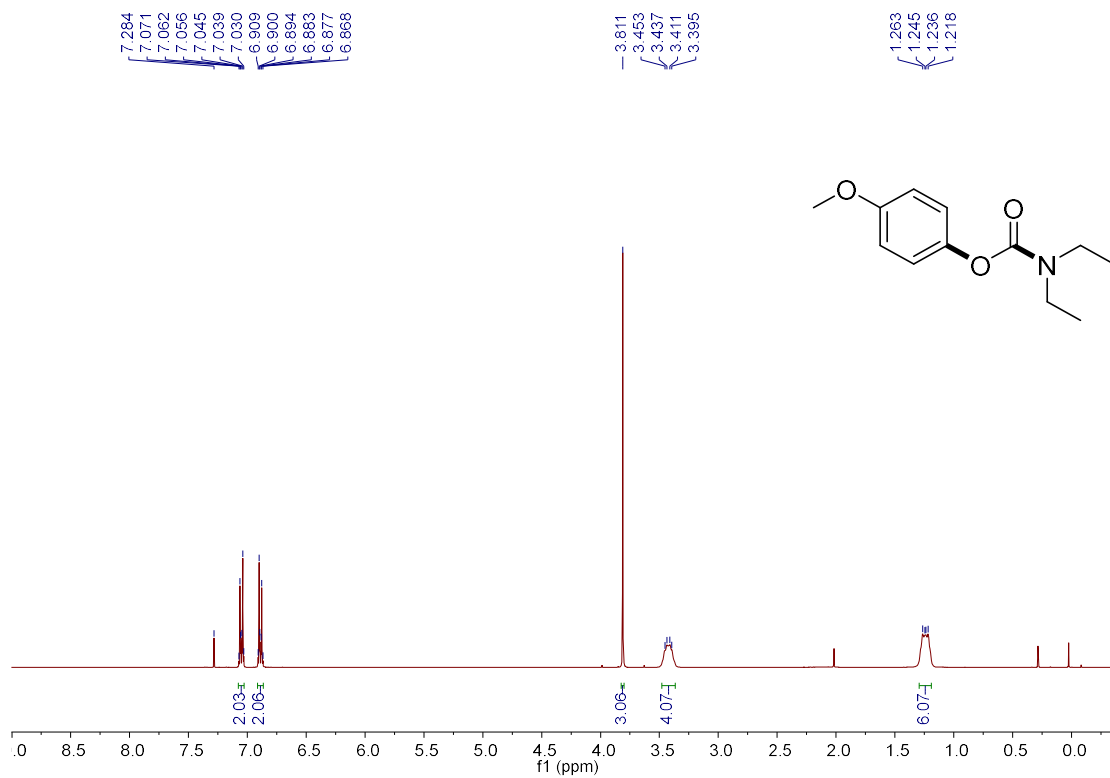
***p*-Tolyl diethylcarbamate (3ba)**



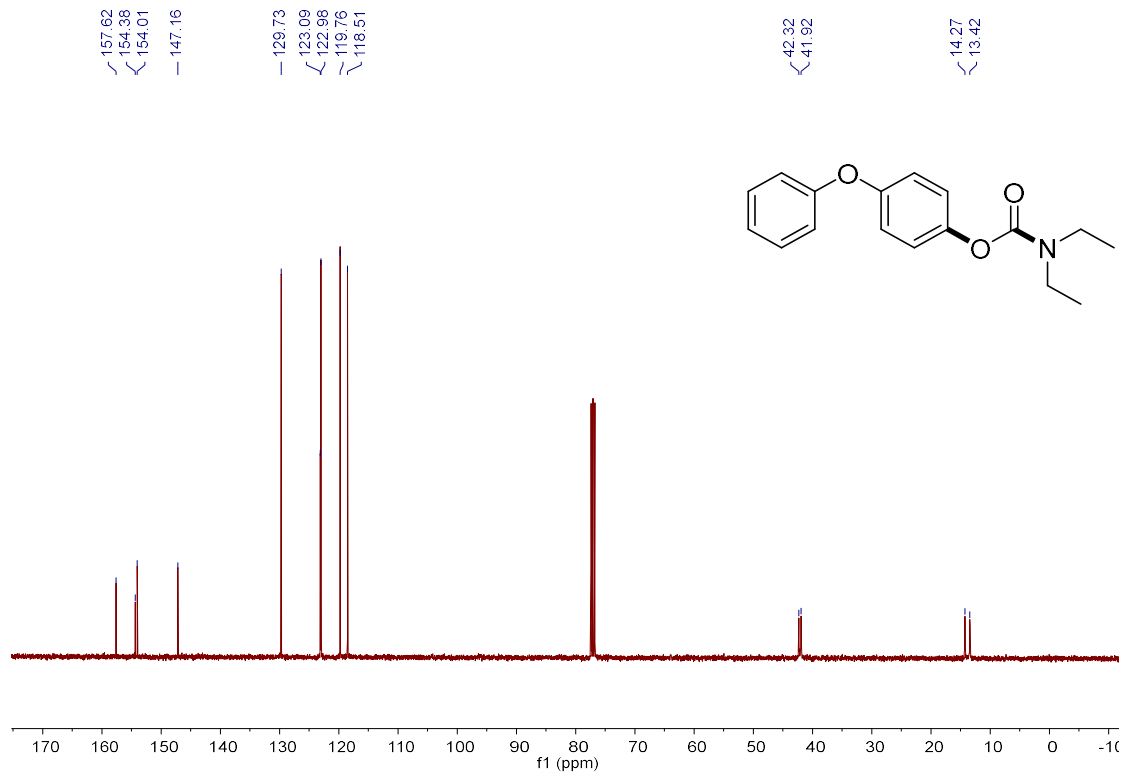
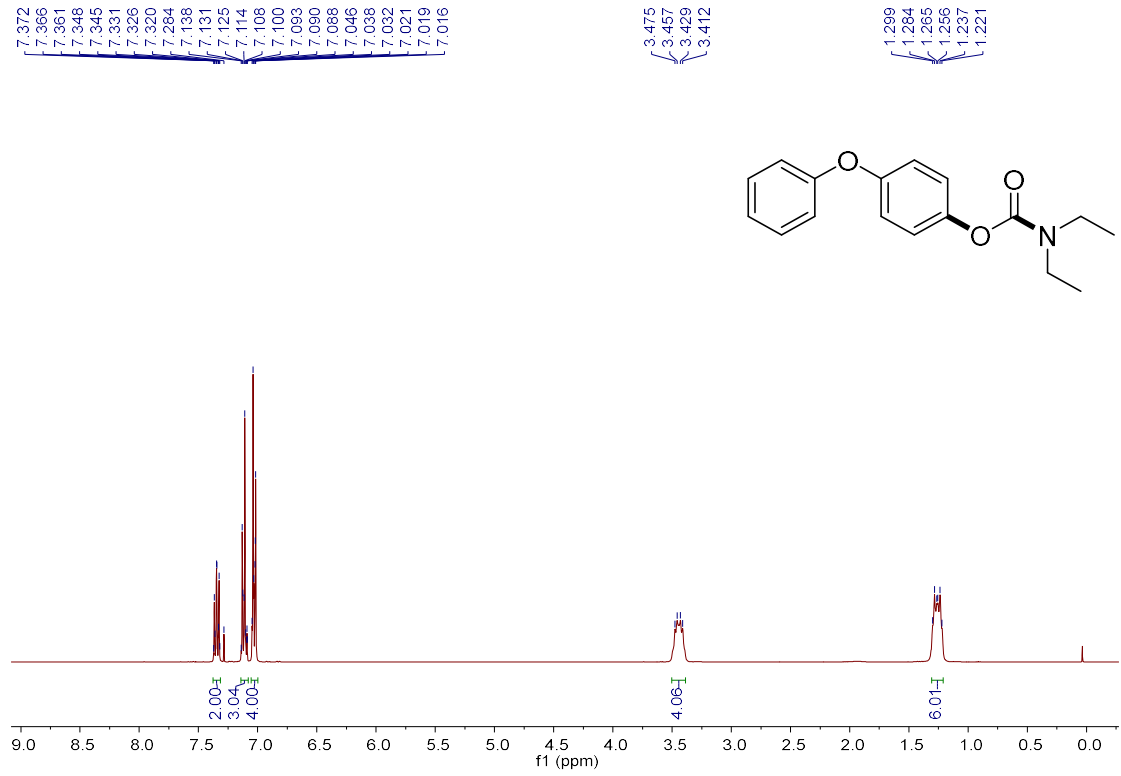
Phenyl diethylcarbamate (3ca)



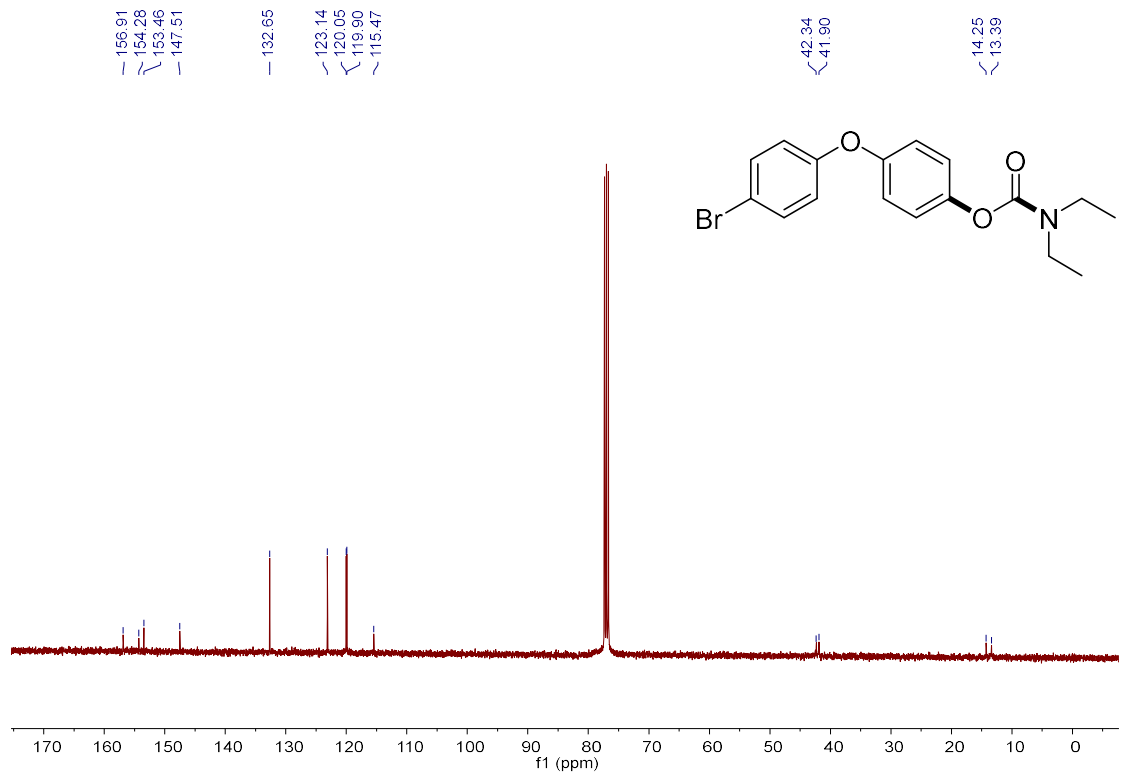
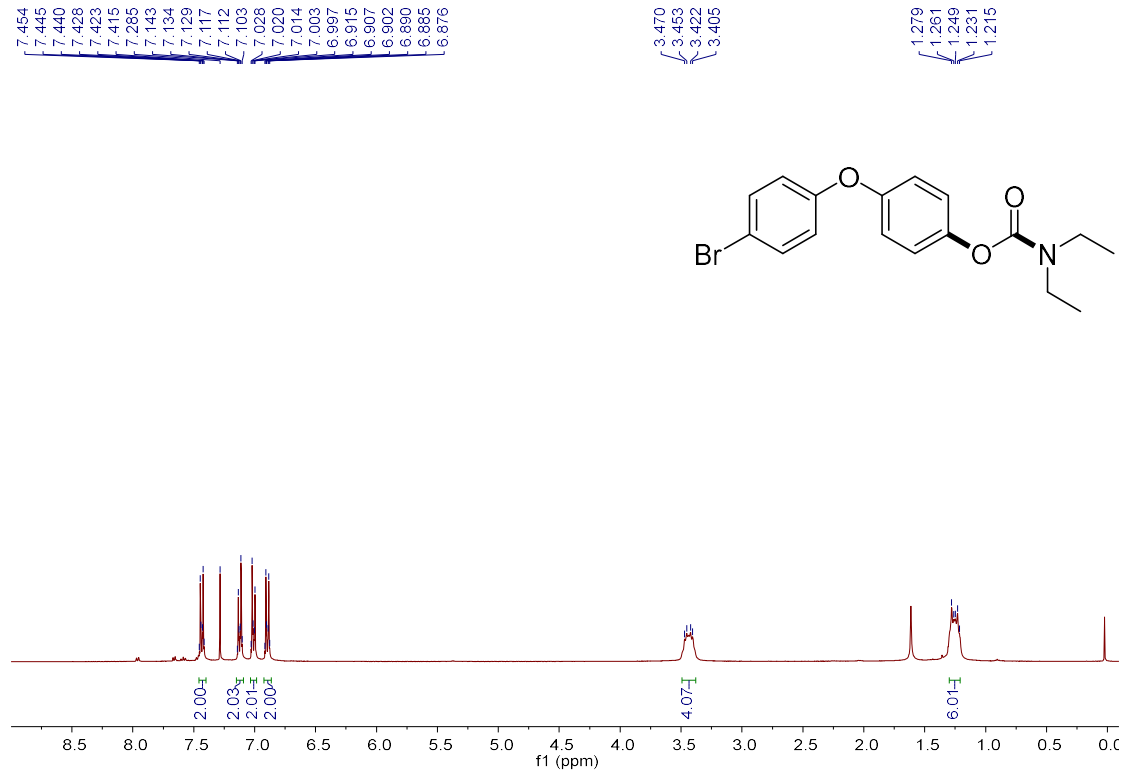
4-Methoxyphenyl diethylcarbamate (3da)



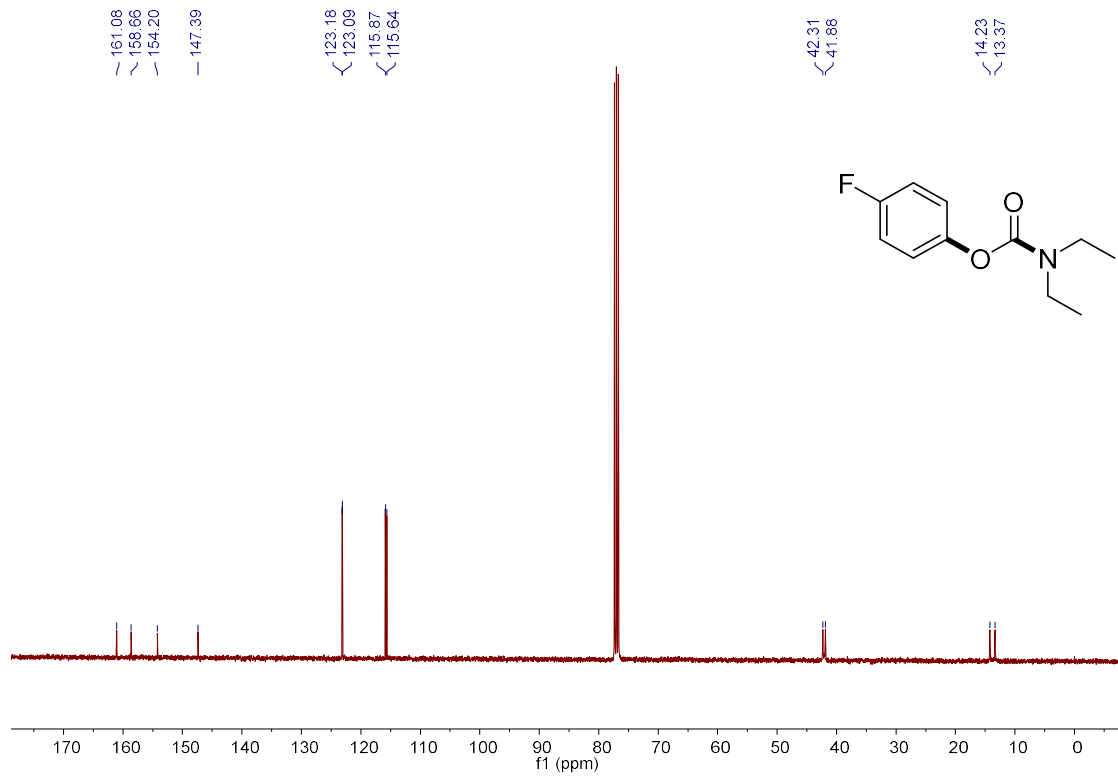
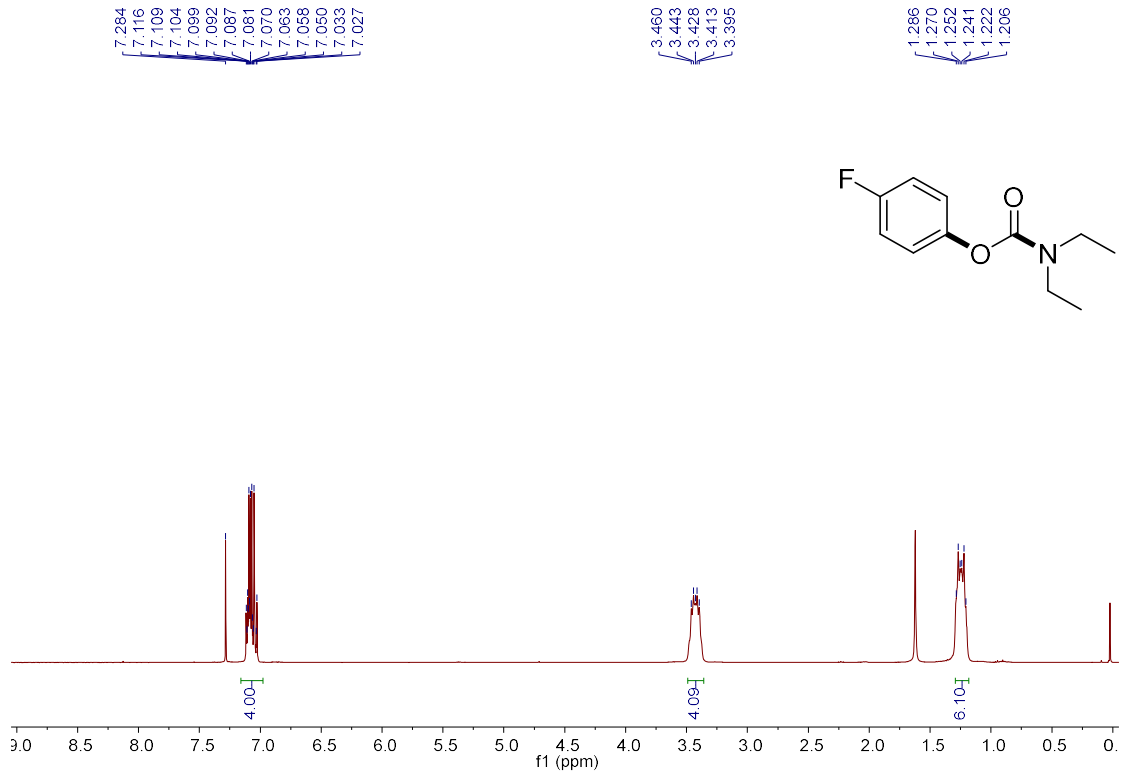
4-Phenoxyphenyl diethylcarbamate (3ea)

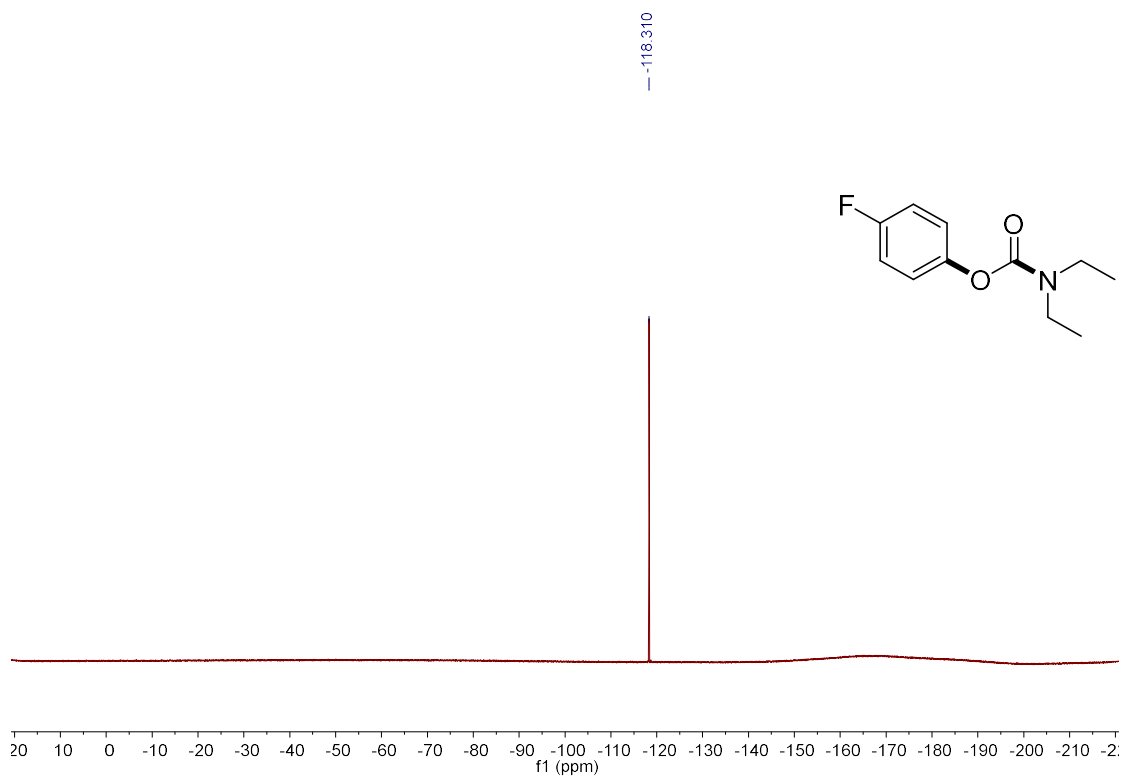


4-(4-Bromophenoxy)phenyl diethylcarbamate (3fa)

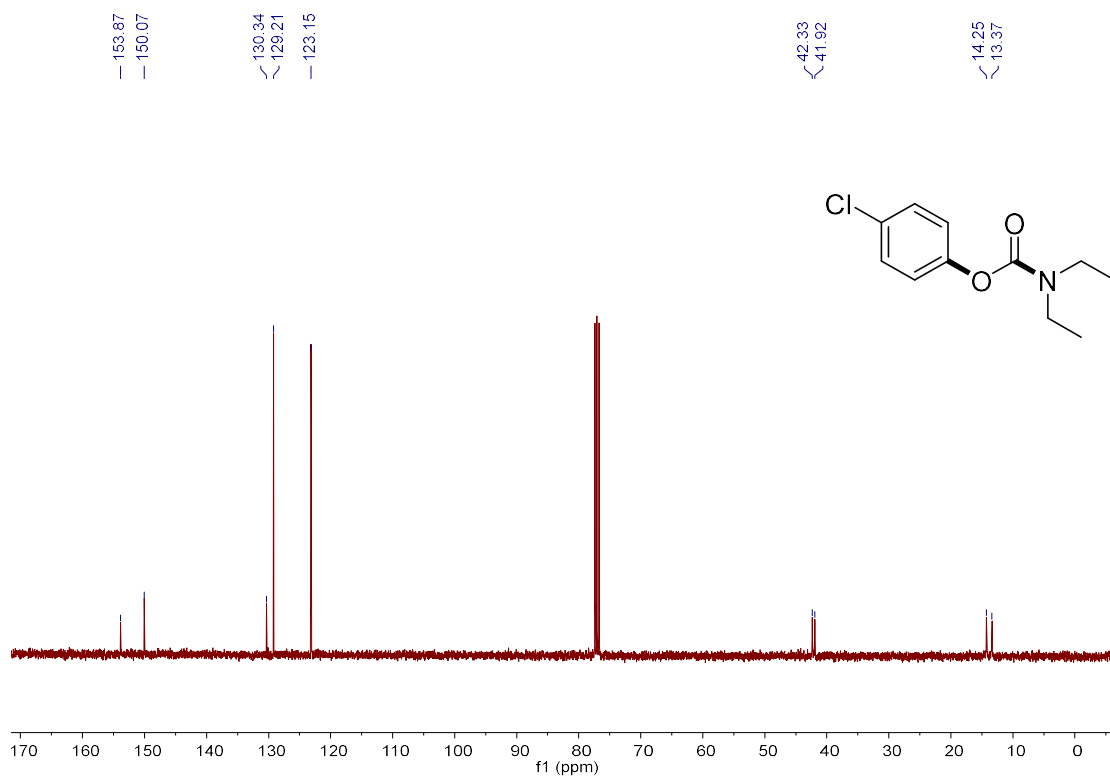
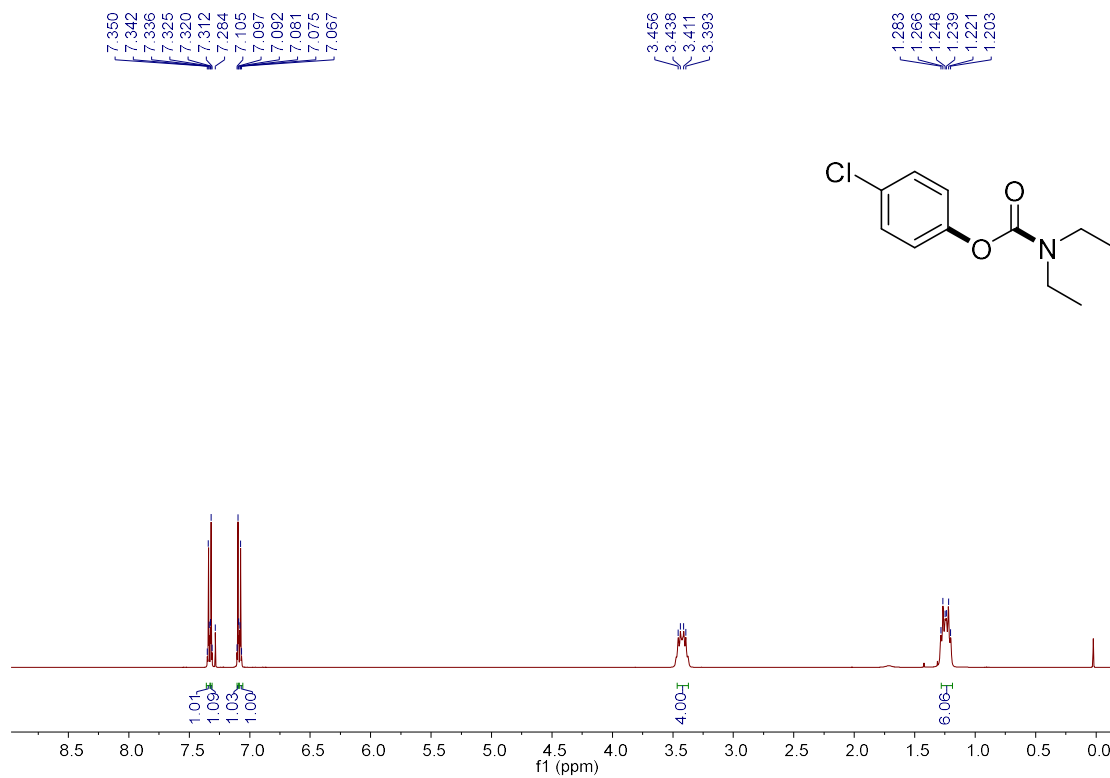


4-Fluorophenyl diethylcarbamate (3ga)

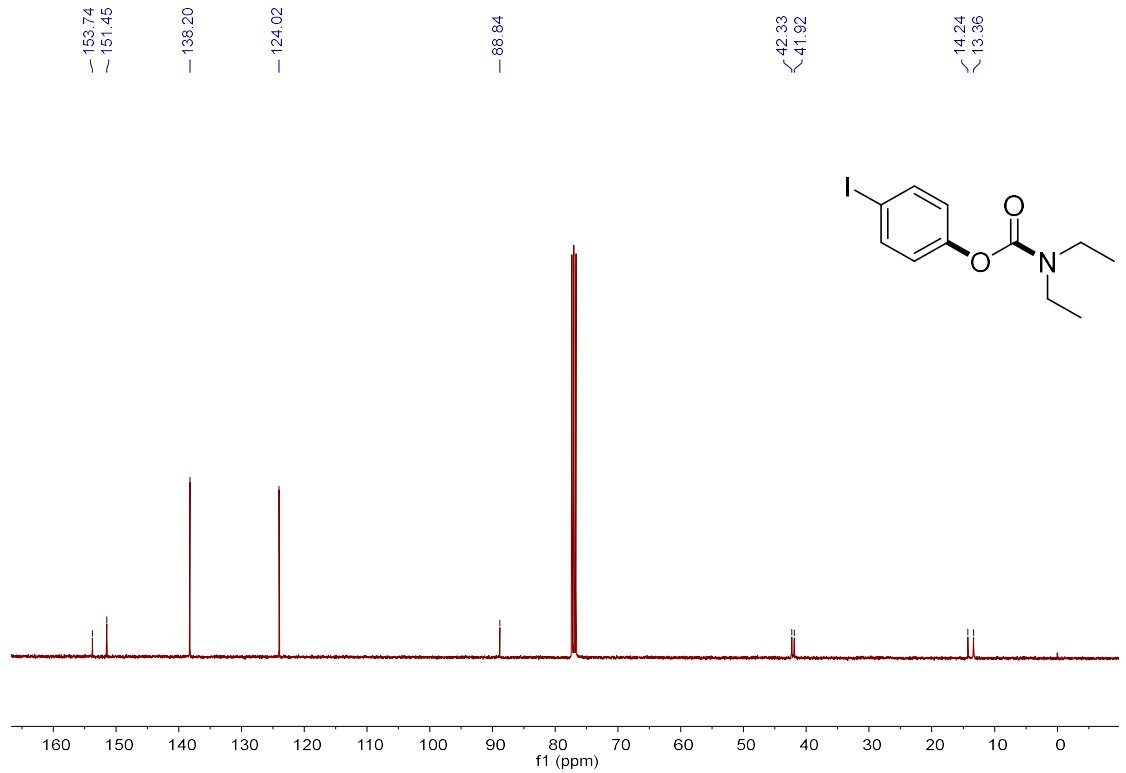
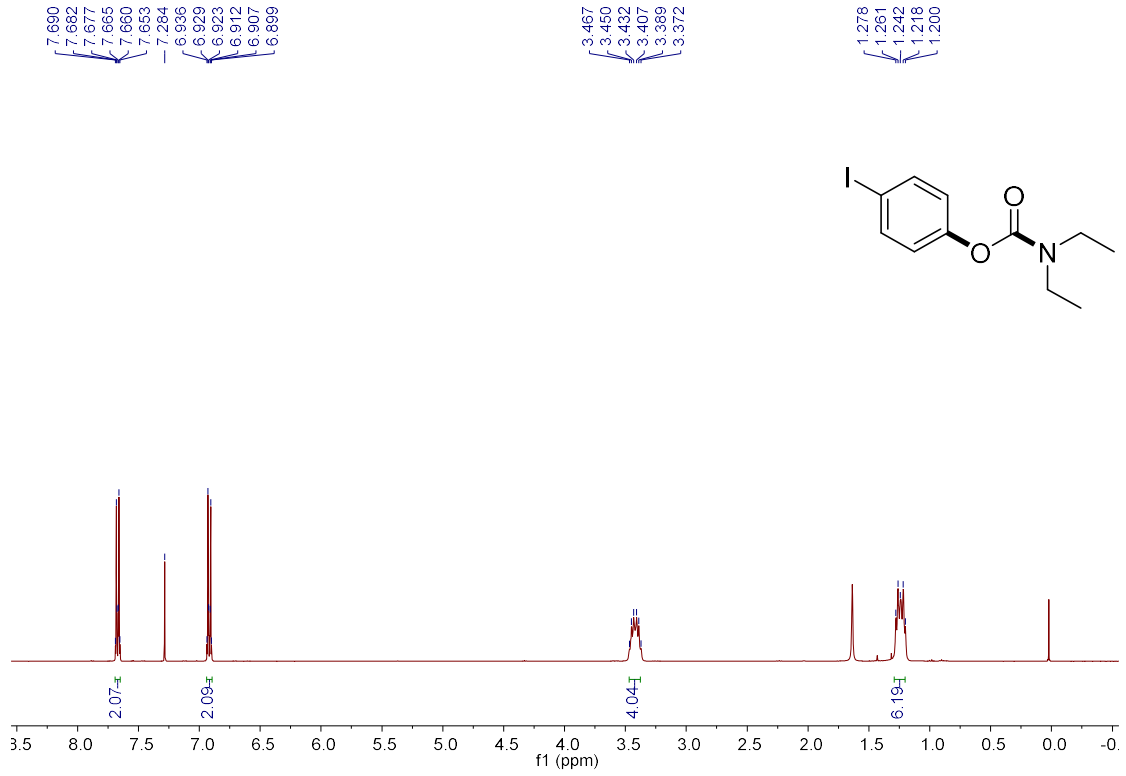




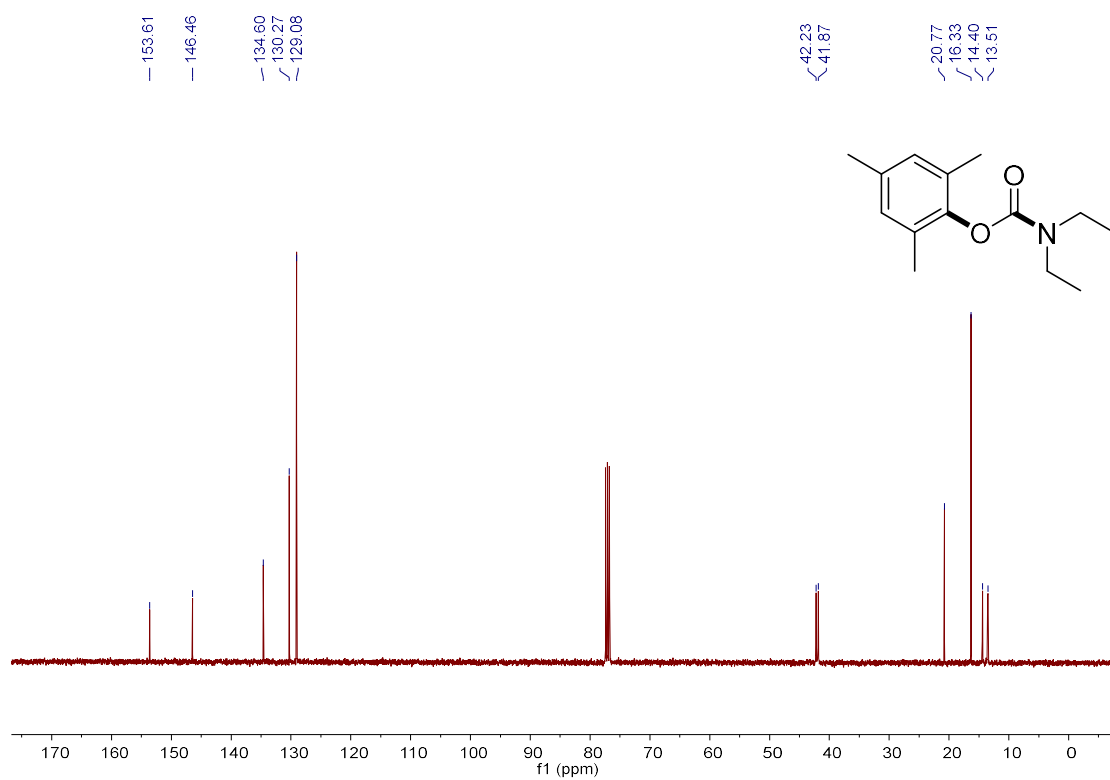
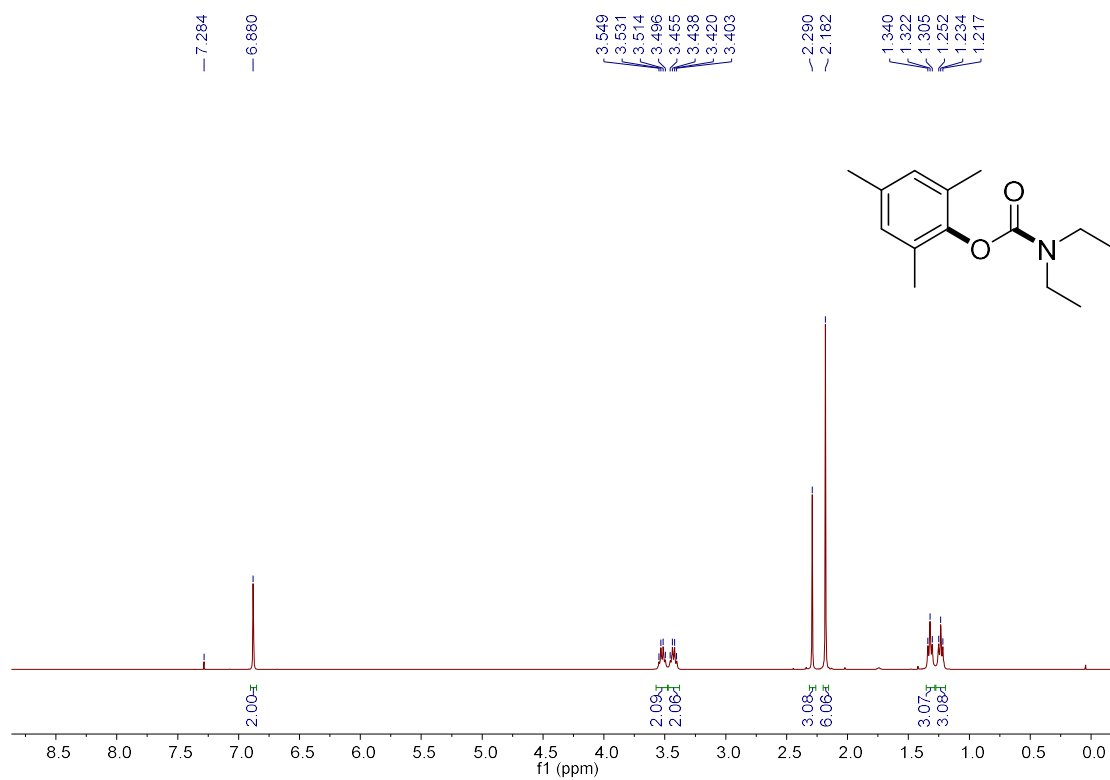
4-Chlorophenyl diethylcarbamate (3ha)



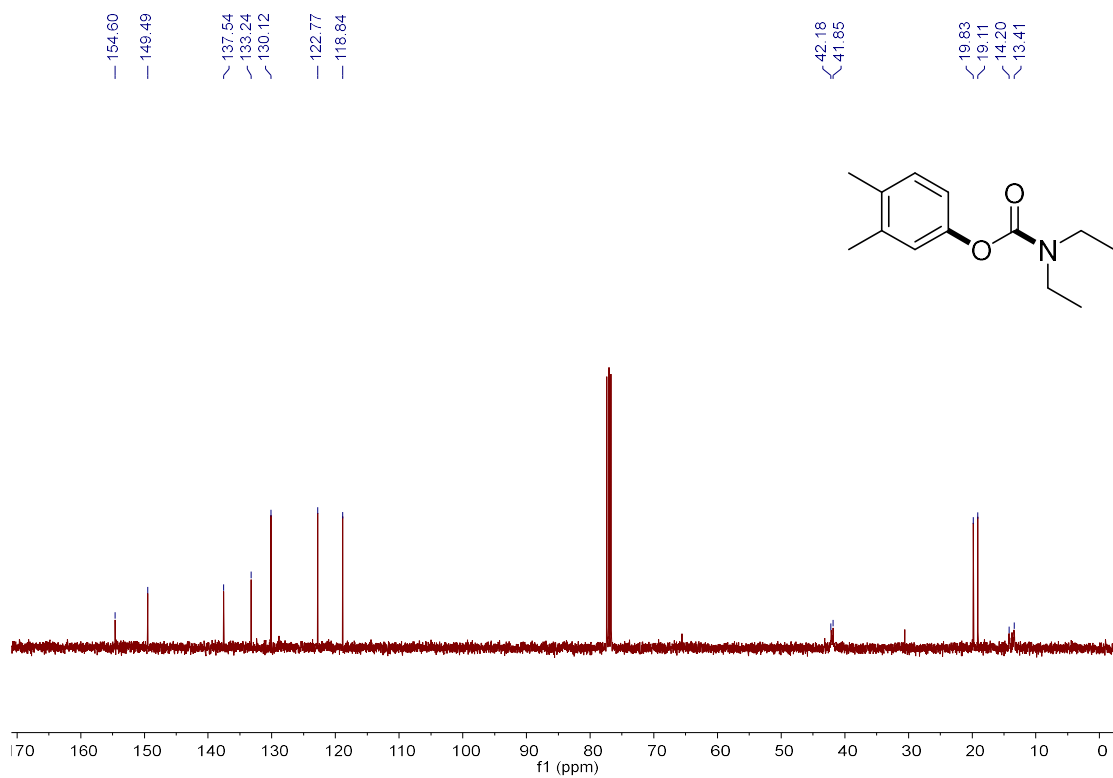
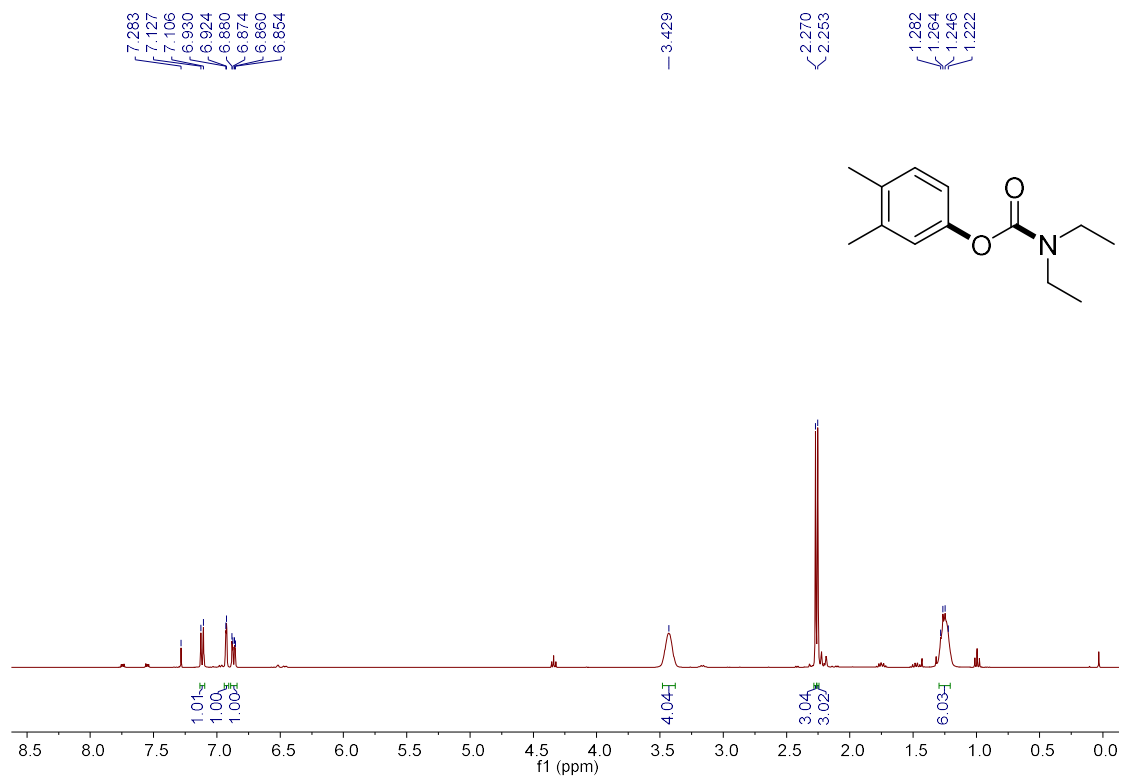
4-Iodophenyl diethylcarbamate (3ia)



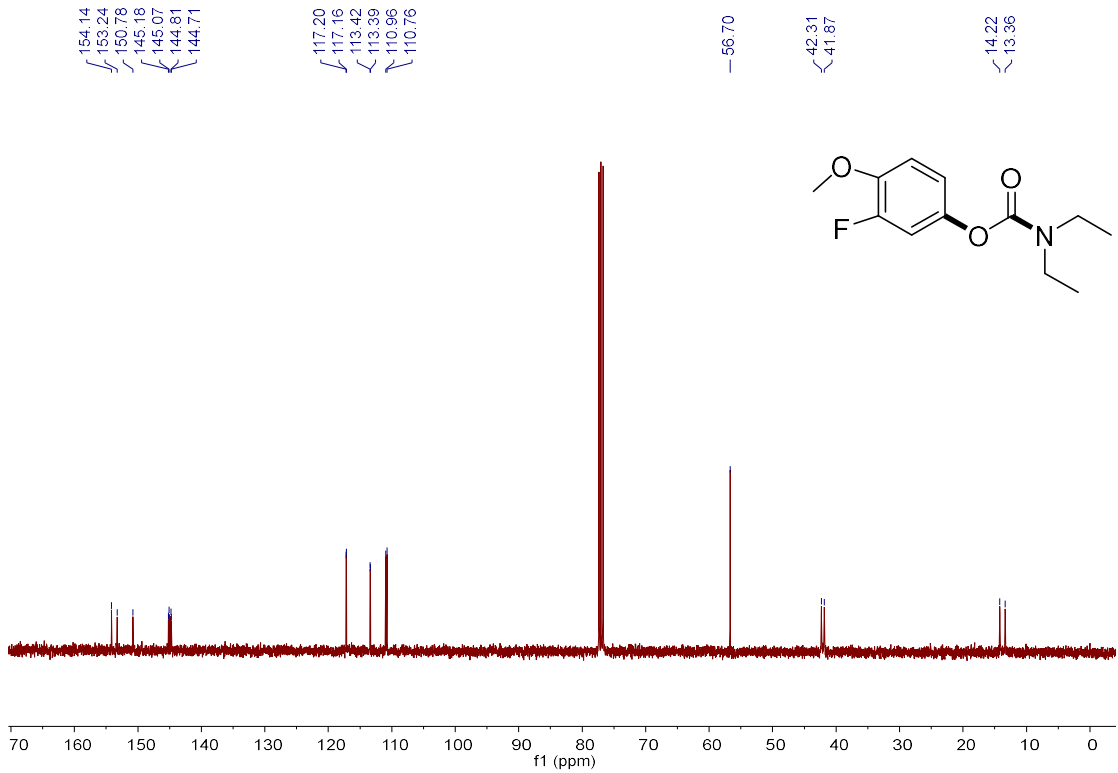
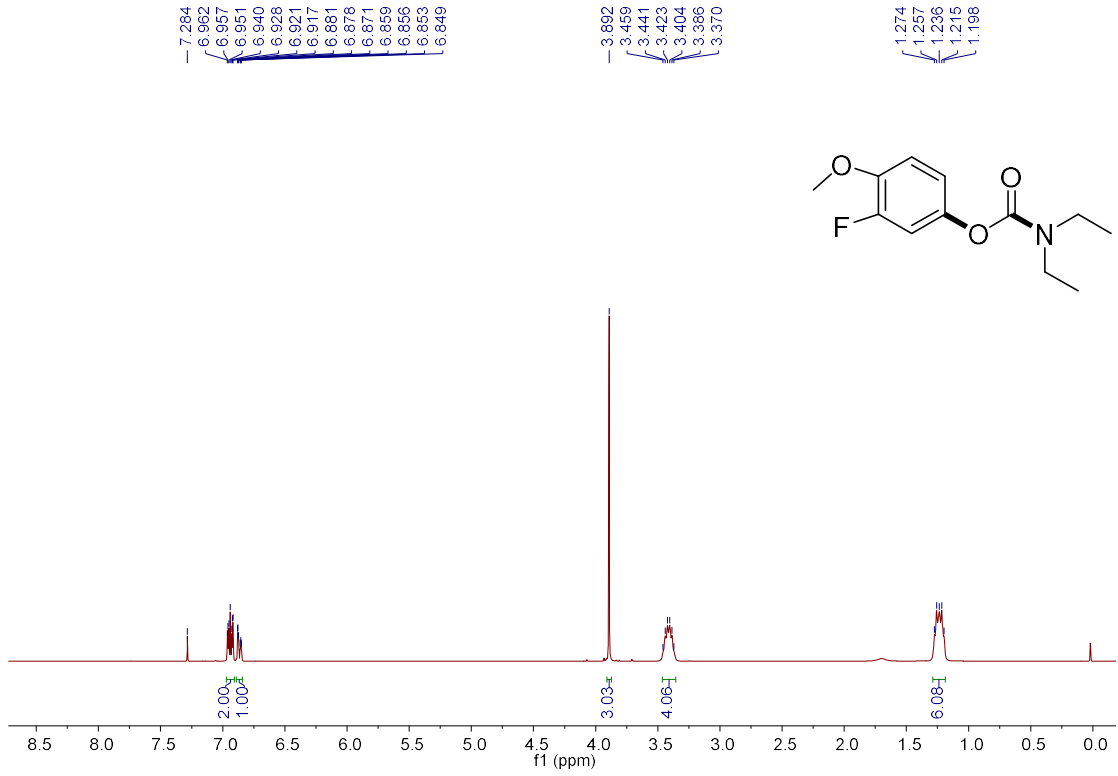
Mesityl diethylcarbamate (3ja)



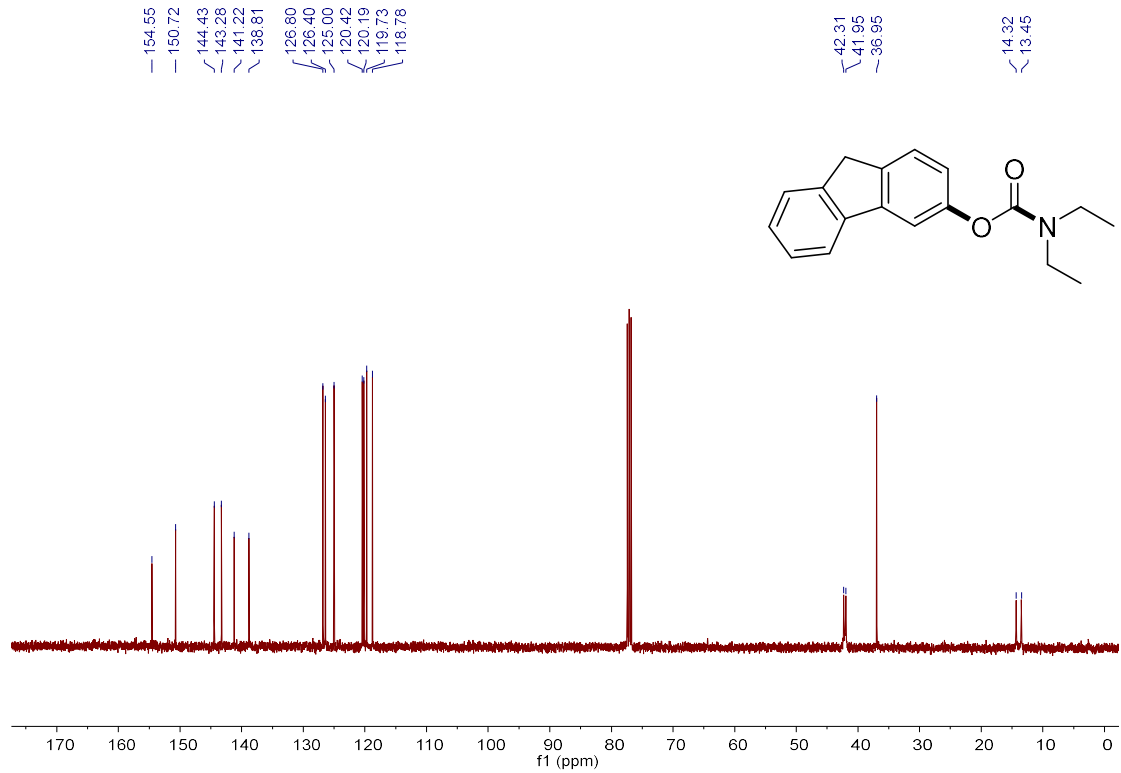
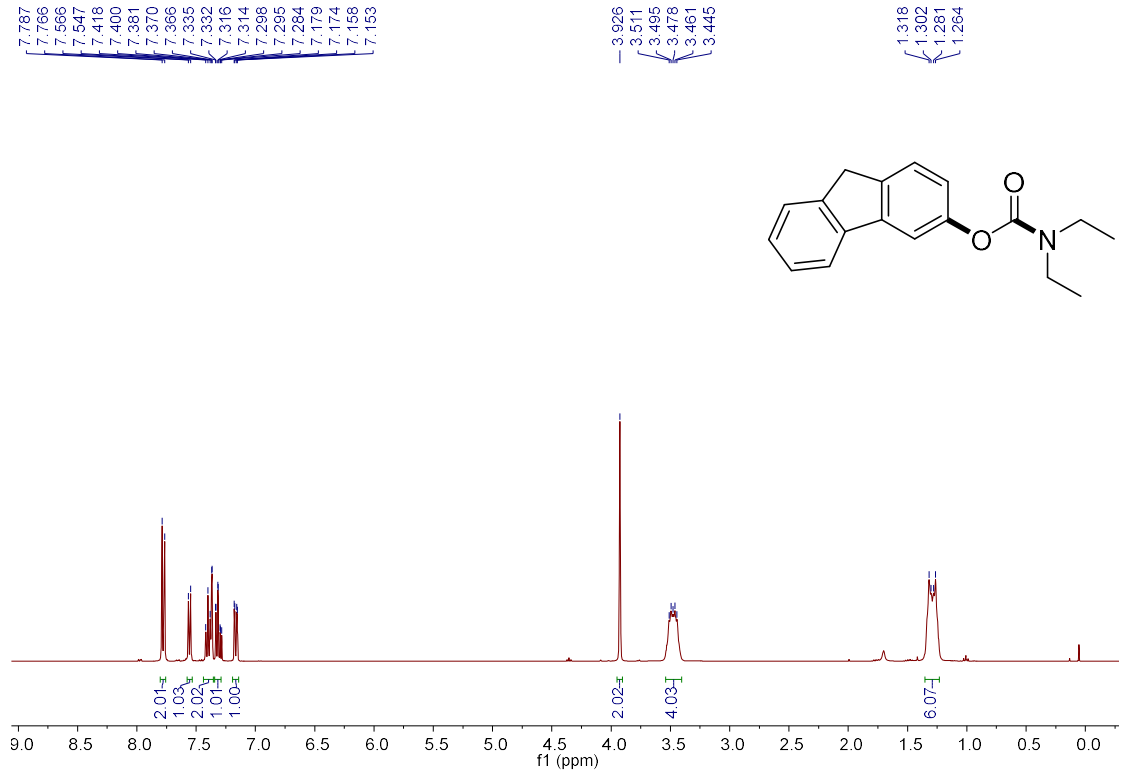
3,4-Dimethylphenyl diethylcarbamate (3ka)



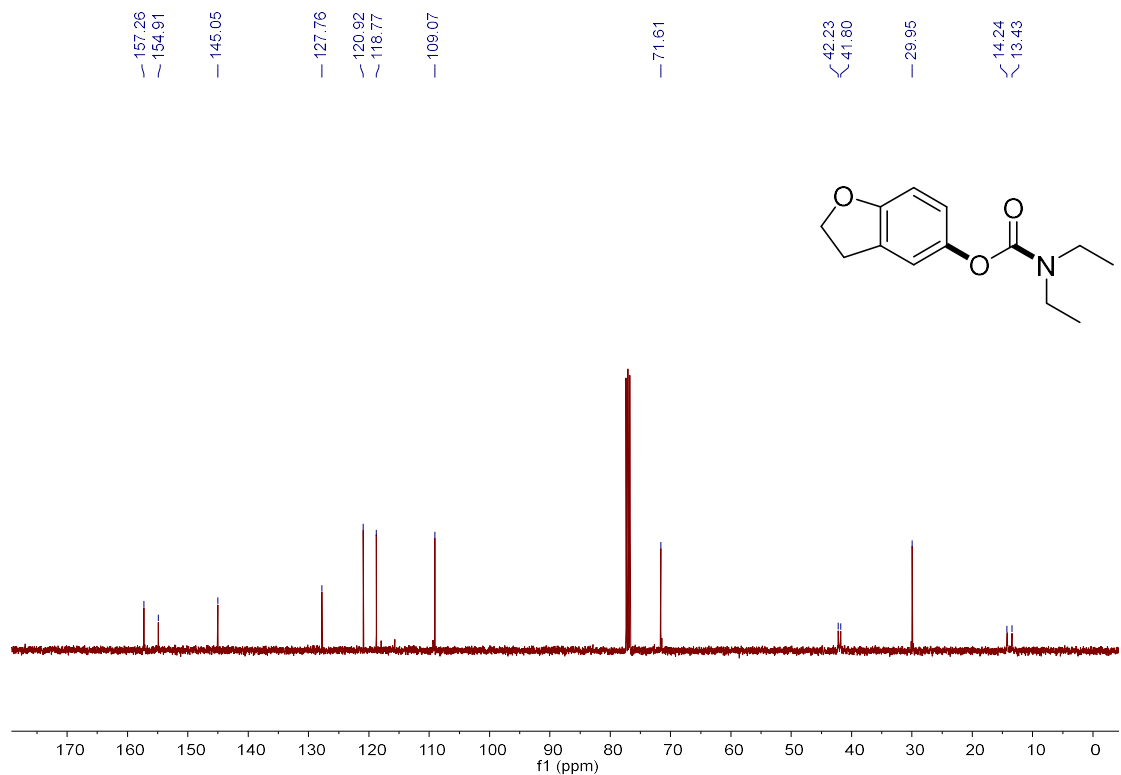
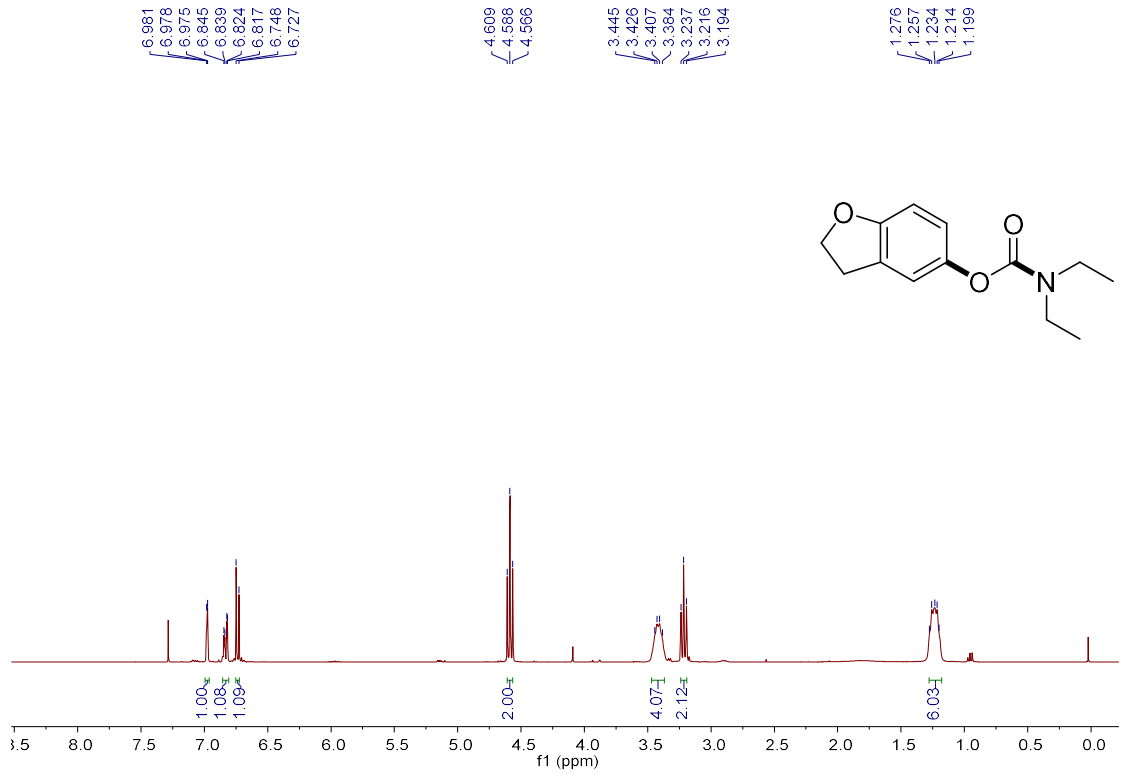
3-Fluoro-4-methoxyphenyl diethylcarbamate (31a)



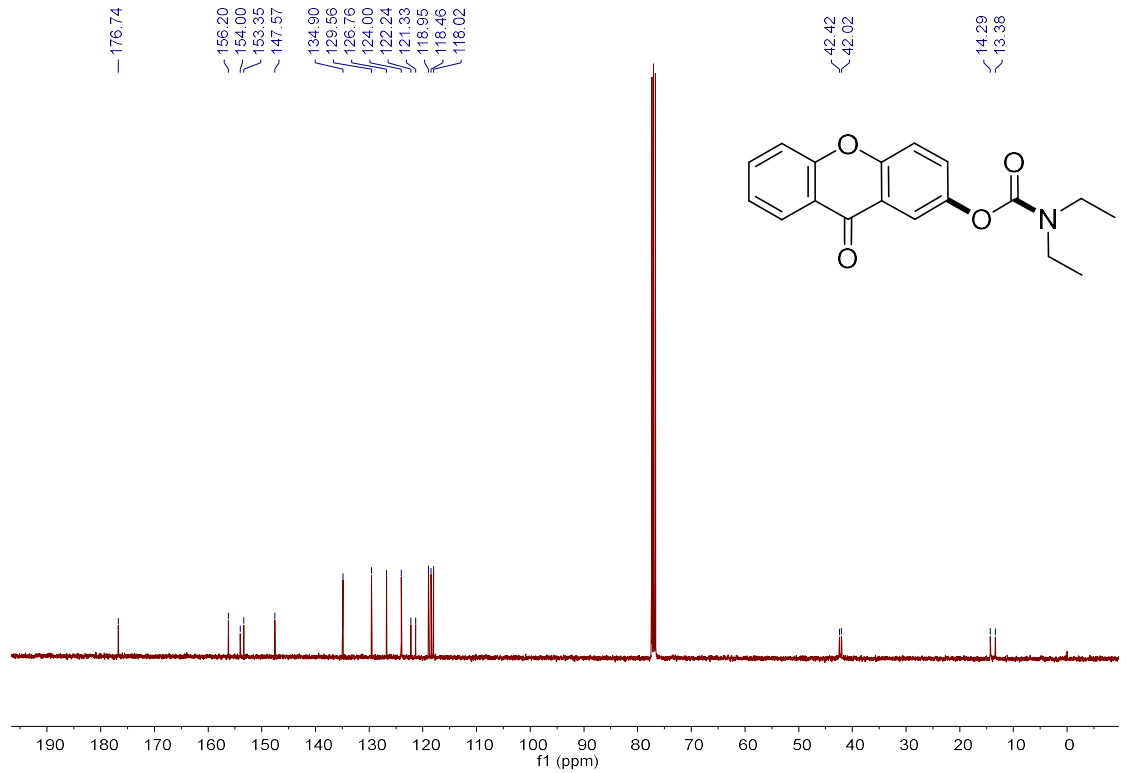
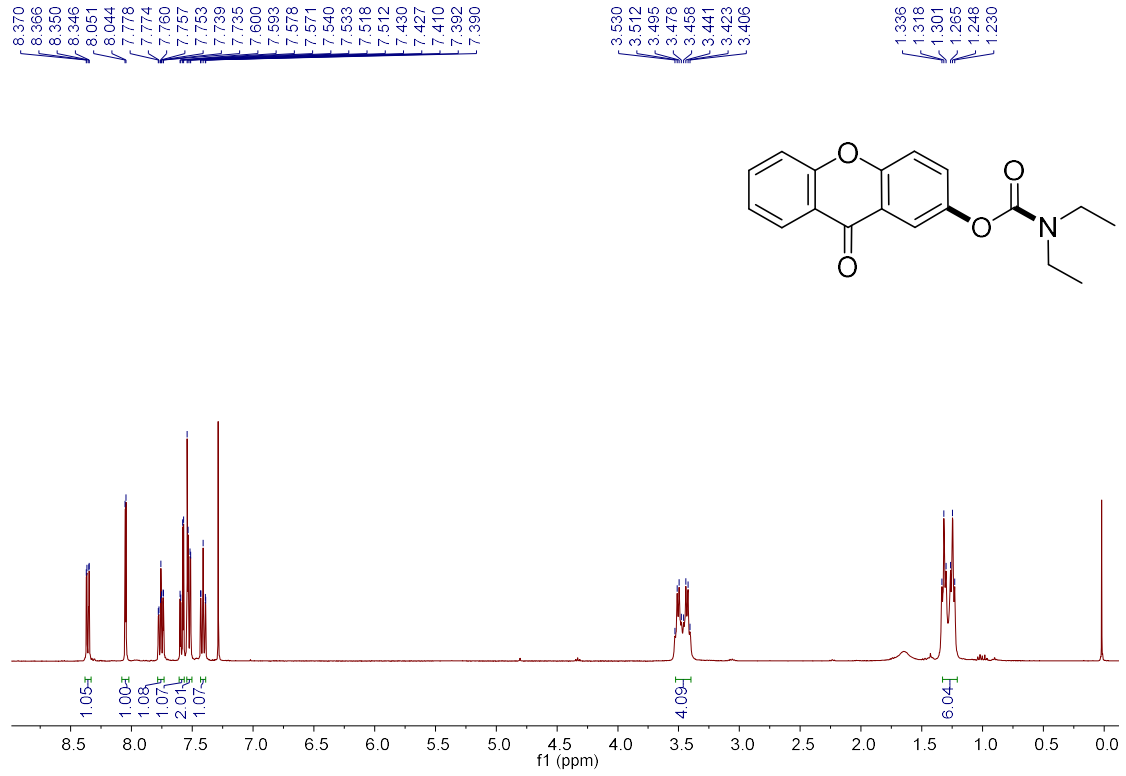
9H-fluoren-3-yl diethylcarbamate (3ma)



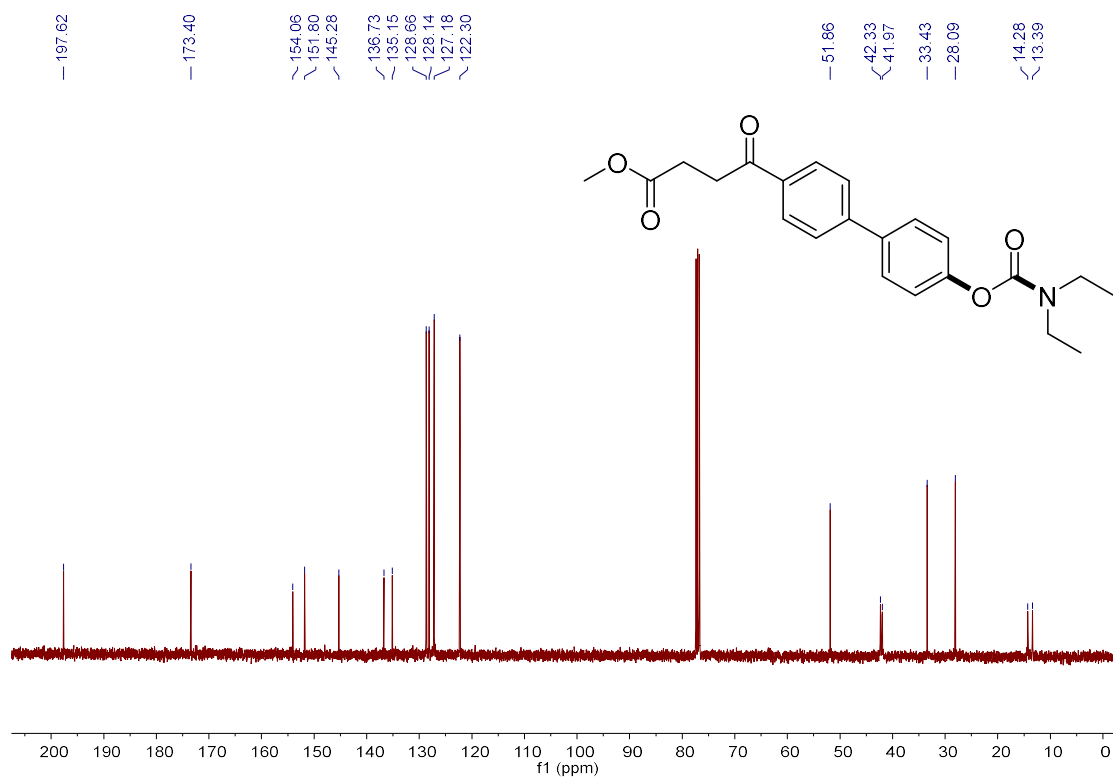
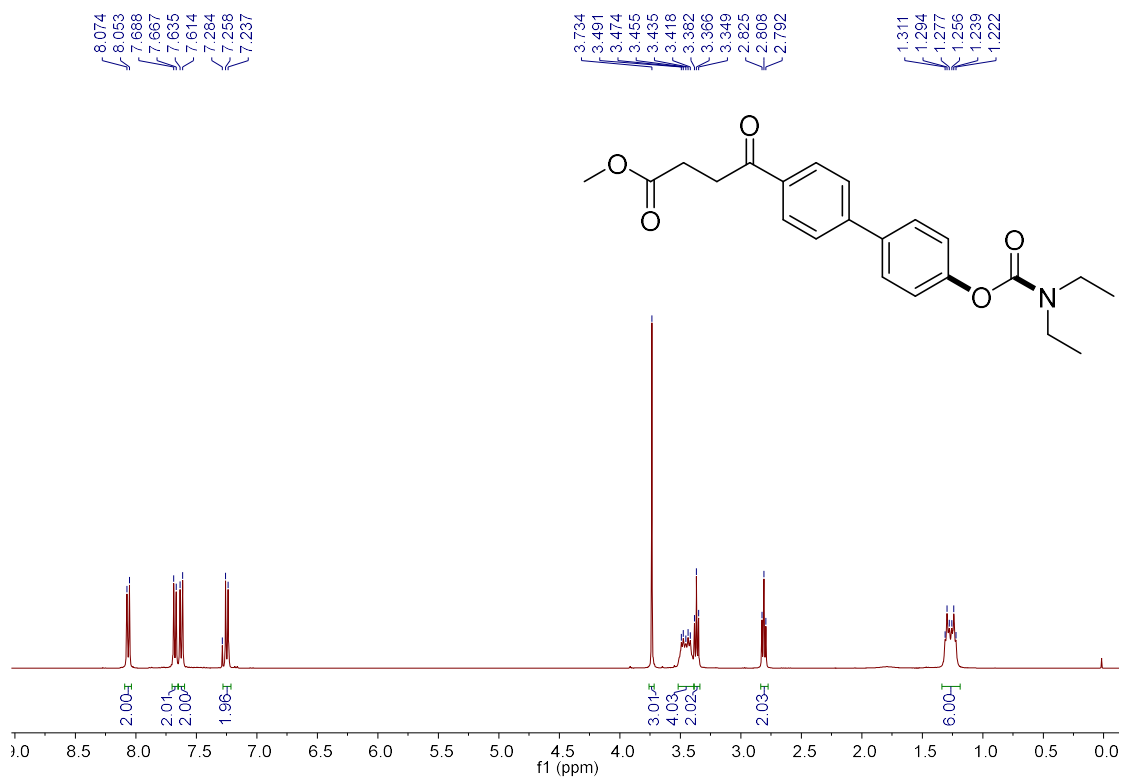
2,3-Dihydrobenzofuran-5-yl diethylcarbamate (3na)



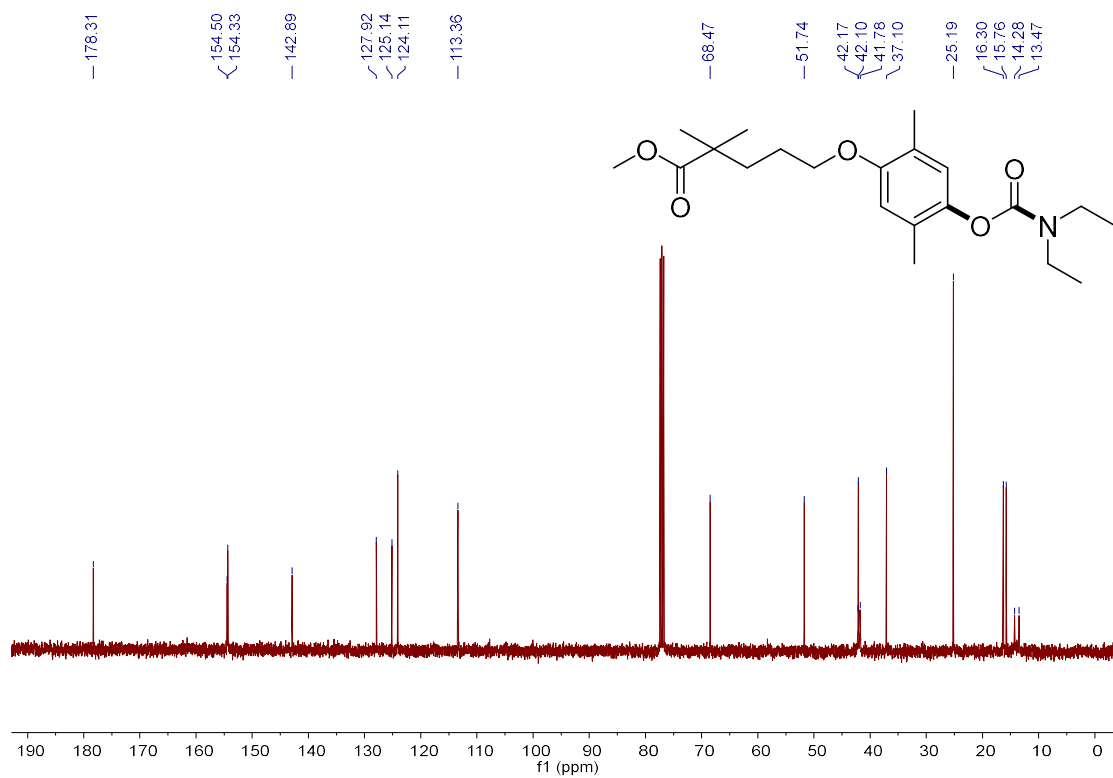
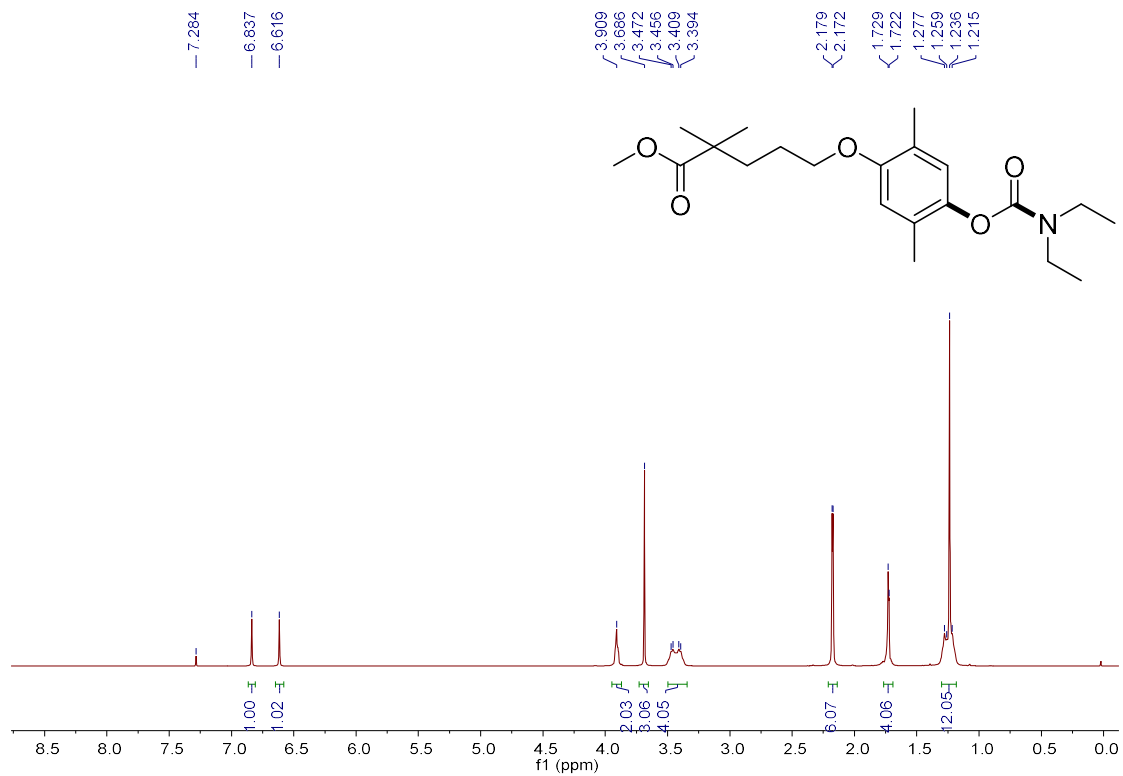
9-Oxo-9H-xanthen-2-yl diethylcarbamate (30a)



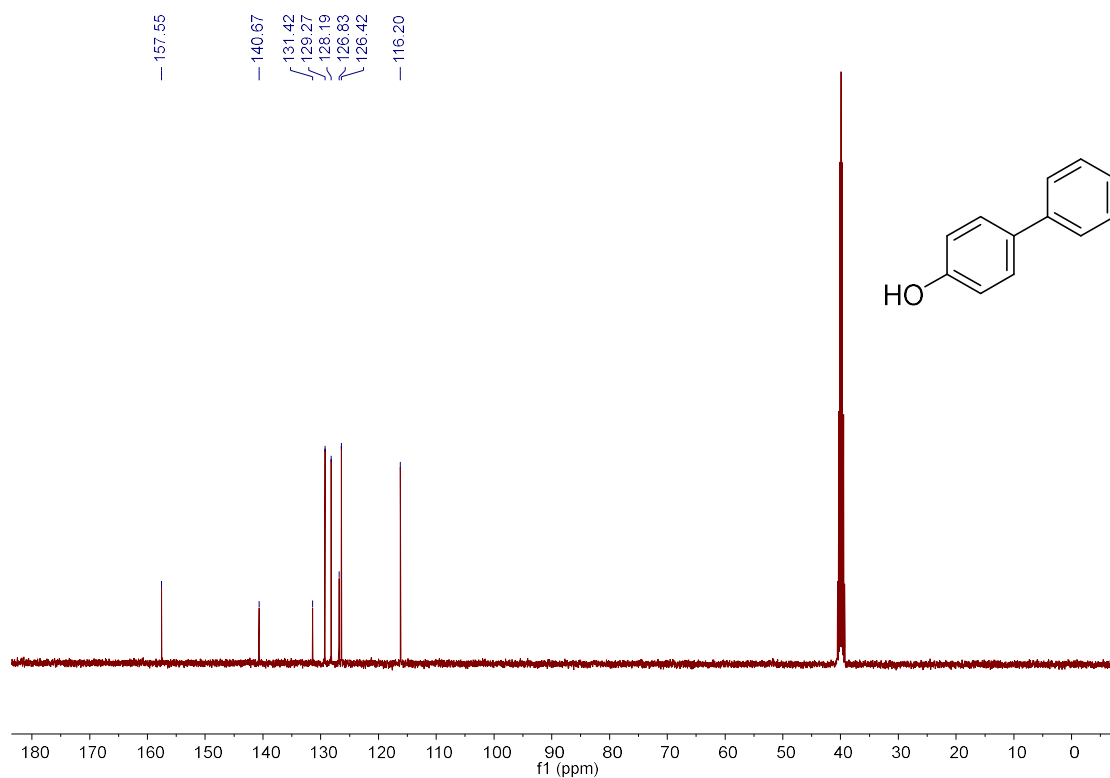
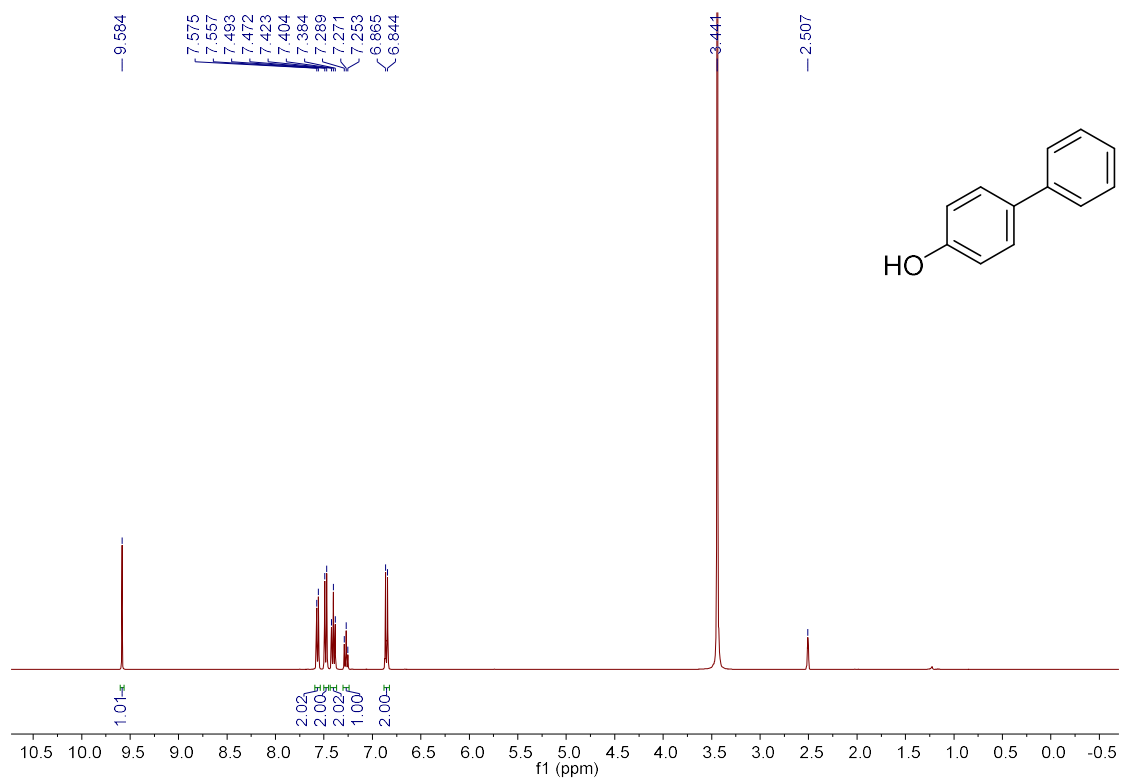
Methyl 4-(4'-((diethylcarbamoyloxy)-[1,1'-biphenyl]-4-yl)-4-oxobutanoate (3pa)



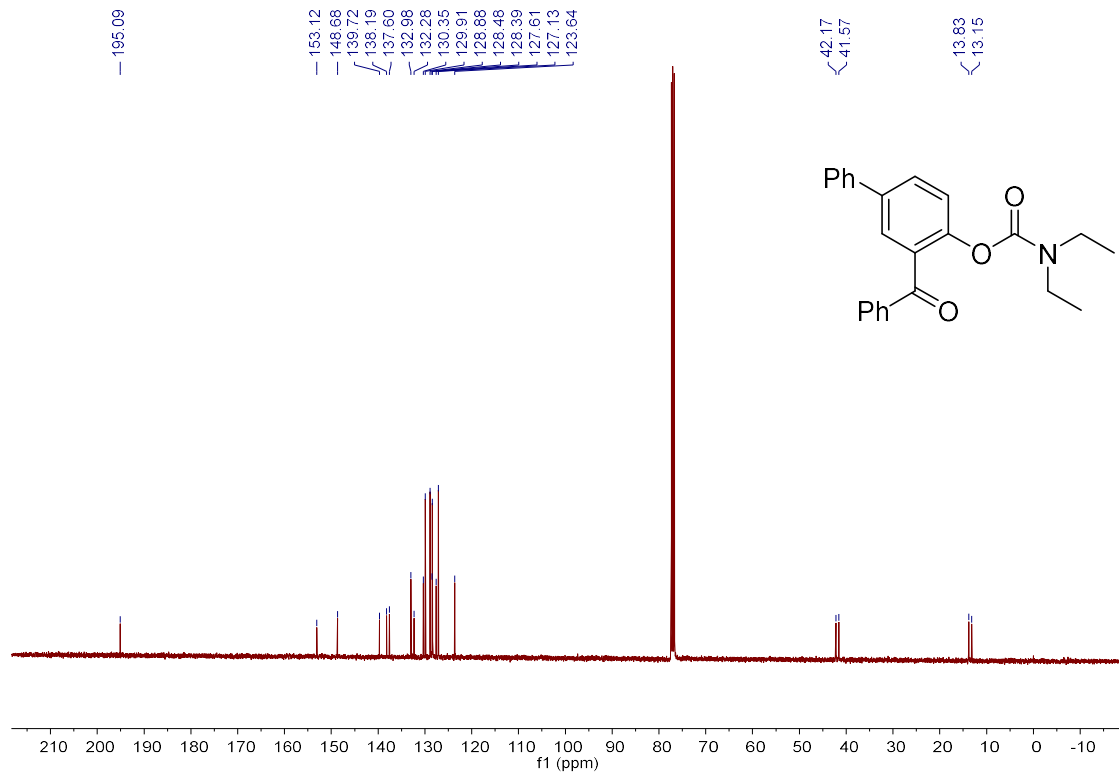
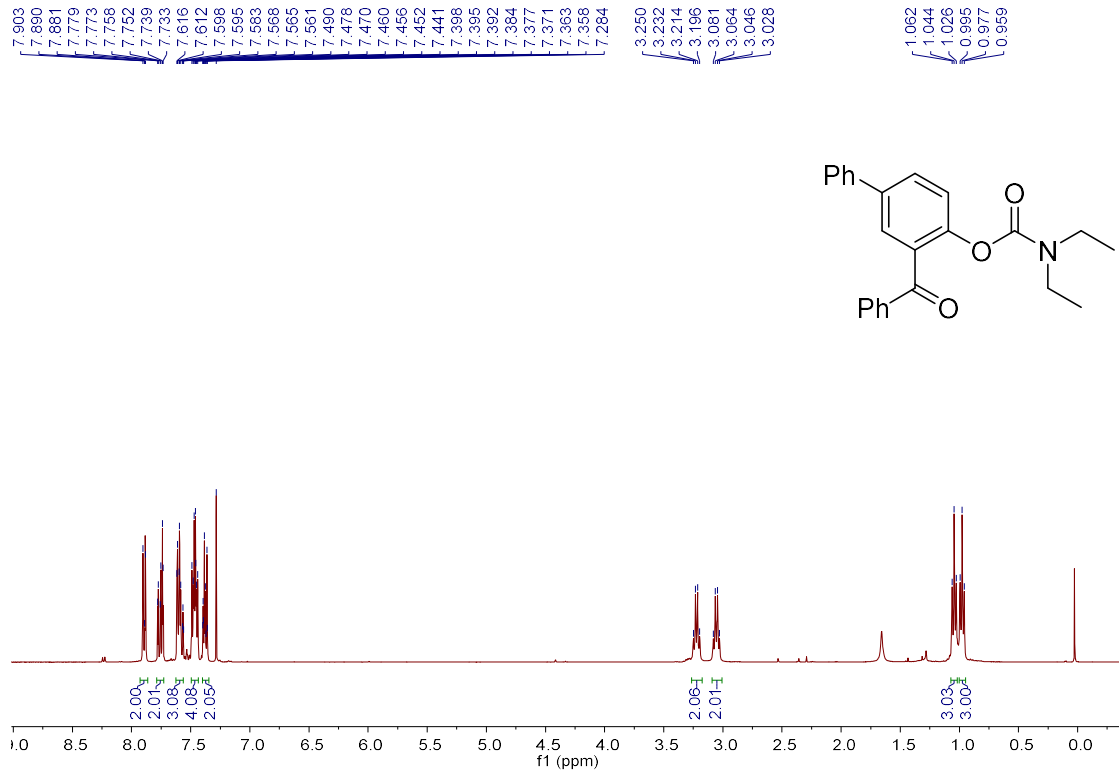
Methyl 5-(4-((diethylcarbamoyloxy)-2,5-dimethylphenoxy)-2,2-dimethylpentanoate (3qa)



[1,1'-Biphenyl]-4-ol (4aa)



3-Benzoyl-[1,1'-biphenyl]-4-yl diethylcarbamate (4ab)



4-(2,2-Diphenylvinyl)-1'-biphenyl (5aa)

