Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supplementary information

Iodine mediated/Brønsted acid-catalyzed dimerization of vinylarenes: a tandem reaction through Ritter trapping to produce *N*-(4-iodo-1,3-diarylbutyl)acetamides

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General method

Reagents and solvents were obtained from commercial sources and were used without further purification. Progresses of reactions were monitored by Thin Layer Chromatography while purification was effected using silica gel column chromatography.

Acetonitrile (analytical grade) was purchased from Baishi Chemical Co., Ltd and used as received; acrylonitrile (analytical grade) was purchased from Kermel Co., Ltd and used as received; benzonitrile (chemically pure) was purchased from Aladian Corporation in China and used as received; bromoacetonitrile and phenylacetonitrile (analytical grade) were purchased from Alfa and used as received; 4-bromostyrene, 4-methylphenylene and 2-vinylnaphthalene were purchased from Alfa; 4-fluorostyrene, 4-chlorostyrene, 4-methoxystyrene were purchased from J&K Corporation in China; styrene and iodine were purchased from Yongda Chemical R&D Center; *p*-toluenesulfonic acid was purchased from Runjie Chemical Co., Ltd.

Analytical thin layer chromatography (TLC) plates and the silica gel for column chromatography were phased from Qingdao Haiyang Chemical and Special Silica Gel Co., Ltd.

Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectroscopy were performed on Bruker Advance 300 and 400 NMR spectrometers. Chemical shifts of ^{1}H NMR spectra are reported as in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (*J* = 7.264, singlet). Multiplicities were given as: s (singlet); br s (broad singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); m (multiplets), etc. The number of protons (n) for a given resonance is indicated by nH. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (*J* = 77.03, triplet).

Infrared spectra were recorded on a BRUKE Tensor 27 FTIR spectrometer. The oil samples were examined under neat conditions.

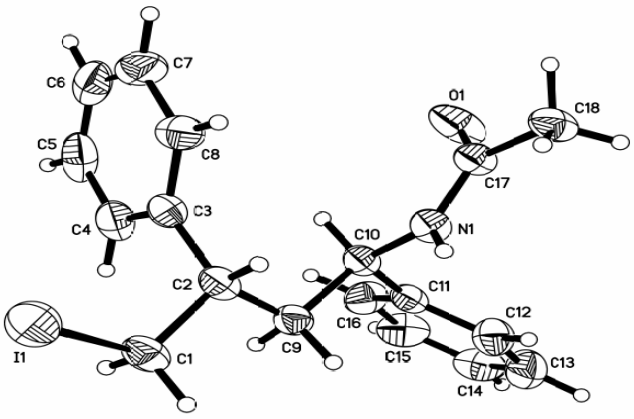
Melting points were recorded on X-4 microscope melting point apparatus.

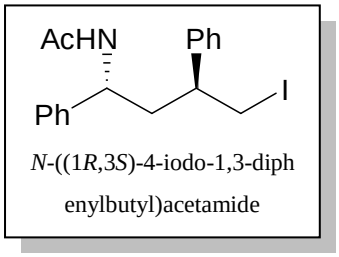
HRMS data were collected on Q-star Elite, ELI-LC-MS/MS (product from ABI, America).

Experimental procedure

General Procedure for the Reaction to Afford 3a: A mixture of PTSA (17 mg, 0.1 mmol), iodine (254 mg, 1.0 mmol) and 1 mL acetonitrile was stirred for 5 min in a round bottom flask (5 mL) at 0 °C, and then styrene (114 μL, 1 mmol) was added at 0 °C. The resulting mixture was stirred at 0 °C to room temperature for 24 h. Then, saturated $Na_2S_2O_3$ (3 mL) was added to the reaction mixture and the resulting solution was extracted with ethyl acetate (2 × 15 mL). The combined organic layer was washed with brine (5 mL), and then dried over anhydrous sodium sulfate. The organic solvent was removed on a rotary evaporator under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 2:1) and **3a** was obtained as a solid (134 mg, 68%).

X-ray Crystallography Structure of 3a





N-((1*R*,3*S*)-4-iodo-1,3-diphenylbutyl)acetamide

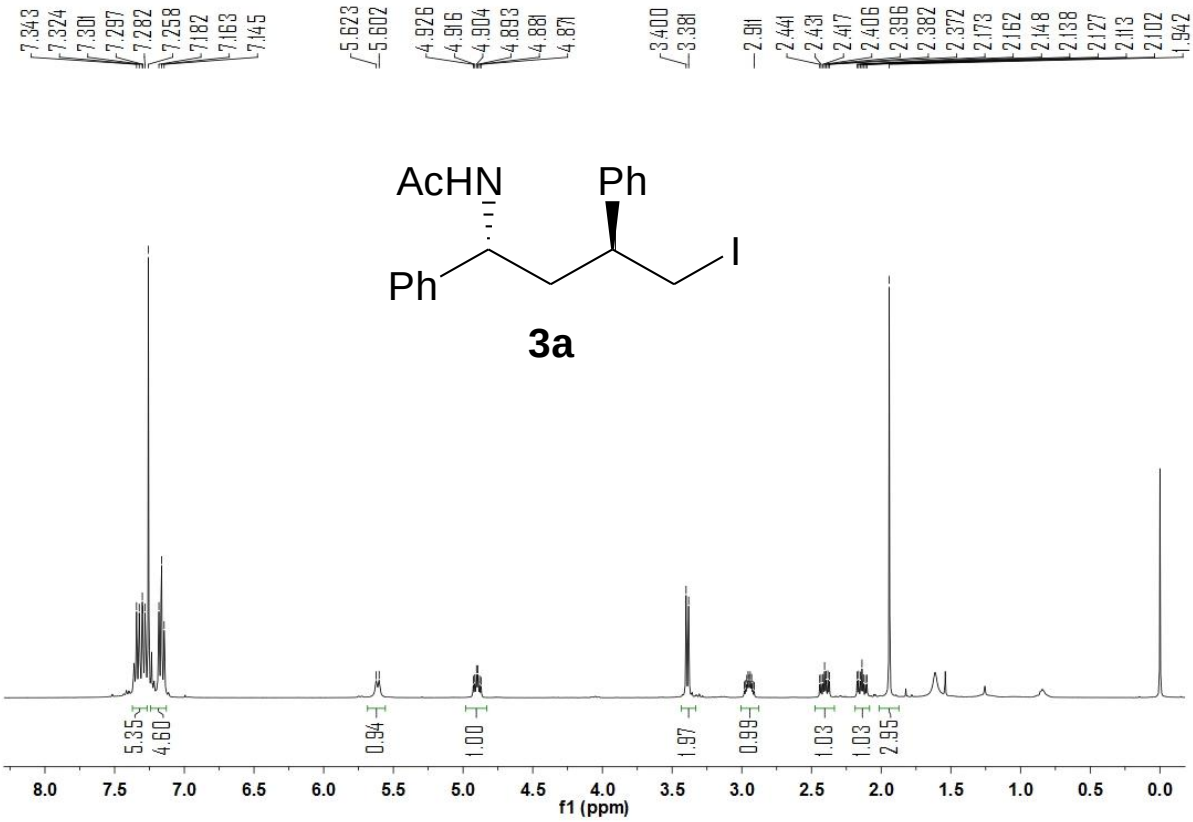
CCDC 838337 contains the supplementary crystallographic data for product **3a** (one of the major isomers). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Figure 1. X-ray crystal structure of the compound **3a** (one of the major isomers).

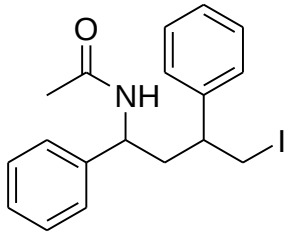
Table 1. Crystal data and structure refinement of **3a** (one of the major isomers).

Empirical formula	$C_{18}H_{20}INO$	
Formula weight	393.25	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 10.3319(4) Å	α = 90 °
	b = 21.2699(8) Å	β = 120 °
	c = 9.3647(4) Å	γ = 90 °
Volume	1770.50(12) $Å^3$	
Z	4	
Density (calculated)	1.475 Mg/m^3	
Absorption coefficient	1.808 mm^{-1}	
F(000)	784	
Crystal size	0.30 × 0.25 × 0.20 mm^3	
Theta range for data collection	1.91 to 30.52 °	
Index ranges	$-14 \le h \le 14$, $-30 \le k \le 30$, $-13 \le l \le 13$	
Reflections collected	12308	
Independent reflections	4293 [R(int) = 0.0223]	
Completeness to theta =30.52	99.6 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.7138 and 0.6131	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints /parameters	4293 / 2 / 191	
Goodness-of-fit on F^2	1.156	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0339, wR_2 =0.0975	
Rindices (all data)	R_1 = 0.0368, wR_2 = 0.1084	
Largest diff. peak and hole	1.194 and –1.047 e.$Å^{-3}$	

The ^{1}H NMR spectra of compound 3a (one of the major isomers)



Spectroscopic data of products



_N_-(4-iodo-1,3-diphenylbutyl)acetamide (3a)

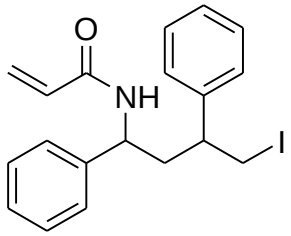
Solid (134mg, 68%); mp. 162–164°C (one of the major isomers, recrystallized from the mixture of dichloromethane and ether);

FTIR (KBr, cm^{-1}): 3272, 1648, 1549, 1295;

Major isomer, ^{1}H NMR ($CDCl_3$; 400 MHz; TMS): δ 7.34–7.10(m, 10H, 10 × *Ph*), 6.05 (d, *J* = 8.6 Hz, 1H, N*H*), 4.84 (td, *J* = 9.2, 4.2 Hz, 1H, NHC*H*), 3.35(d, *J* = 7.2 Hz, 2H, CH_2I), 3.02–2.86(m, 1H, C*H*CH_2I), 2.41–2.38 (m, 1H, 1 × CHCH_2CHCH_2I), 2.12–2.05 (m, 1H, 1 × CHCH_2CHCH_2I), 1.89 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$; 100 MHz; TMS): δ 169.27, 142.39, 142.04, 129.04, 128.84, 127.64, 127.54, 127.52, 126.29, 51.41, 45.59, 42.56, 23.51, 13.21.

Minor isomer, ^{1}H NMR ($CDCl_3$; 400 MHz; TMS): δ 7.34–7.10 (m, 10H, 10 × *Ph*), 5.94 (d, *J* = 7.7 Hz, 1H, N*H*), 4.77–4.72 (m, 1H, NHC*H*), 3.32–3.28 (m, 2H, CH_2I), 2.66–2.57 (m, 1H, C*H*CH_2I), 2.37–2.26 (m, 2H, CHCH_2CHCH_2I), 1.78 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$; 100 MHz; TMS): δ169.23, 141.74, 140.99, 128.87, 128.85, 127.85, 127.54, 127.40, 127.01, 52.43, 44.94, 40.81, 23.29, 14.12.

HRMS (ESI): *m/z* ($M+H^+$) calcd for $C_{18}H_{21}INO$, 394.0668. Found: 394.0669.



_N_-(4-iodo-1,3-diphenylbutyl)acrylamide (3b)

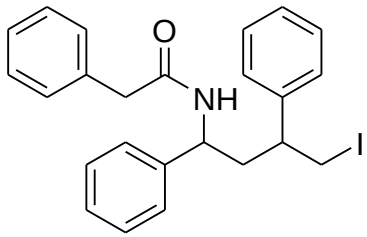
Solid (180 mg, 90%); mp. 150–152°C (one of the major isomers, recrystallized from the mixture of dichloromethane and ether);

FTIR (KBr, cm^{-1}): 3272, 1654, 1246, 1316;

Major isomer, ^{1}H NMR ($CDCl_3$; 400 MHz; TMS): δ 7.34–7.09 (m, 10H, 10 × *Ph*), 6.21–5.90 (m, 3H, CH_2=C*H*), 5.57 (d, *J* = 10.2 Hz, 1H, N*H*), 4.93 (td, *J* = 8.8, 3.9 Hz, 1H, NHC*H*), 3.35 (d, *J* = 7.1 Hz, 2H, CH_2I), 2.97–2.90 (m, C*H*CH_2I), 2.43–2.40 (m, 1H, 1 × CHCH_2CHCH_2I), 2.15–2.08 (m, 1H, 1 × CHCH_2CHCH_2I). ^{13}C NMR ($CDCl_3$; 100 MHz; TMS): δ 164.89, 142.24, 141.88, major + minor isomer (130.81, 130.72, 128.96, 128.89, 128.87, 128.73, 127.91, 127.56, 127.48, 127.46, 127.42, 127.12, 126.68, 126.60, 126.23), 51.47, 45.41, 42.57, 13.14.

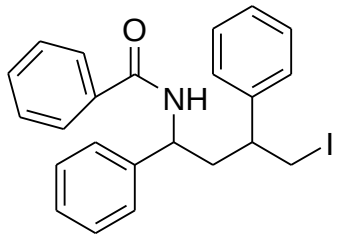
Minor isomer, ^{1}H NMR ($CDCl_3$; 400 MHz; TMS): δ 7.34–7.09 (m, 10H, 10 × *Ph*), 6.21–5.90 (m, 3H, CH_2=C*H*), 5.52 (d, *J* = 10.2 Hz, 1H, N*H*), 4.83–4.77 (m, 1H, NHC*H*), 3.32–3.26 (m, 2H, CH_2I), 2.63–2.56 (m, 1H, C*H*CH_2I), 2.39–2.30 (m, 2H, CHCH_2CHCH_2I). ^{13}C NMR ($CDCl_3$; 100 MHz; TMS): δ 164.66, 141.88, 140.72, major + minor isomer (130.81, 130.72, 128.96, 128.89, 128.87, 128.73, 127.91,

127.56, 127.48, 127.46, 127.42, 127.12, 126.68, 126.60, 126.23), 52.48, 44.78, 40.63, 14.11.
HRMS (ESI): *m/z* ($M+H^+$) calcd for $C_{19}H_{21}INO$, 406.0668. Found: 406.0673.



***N*-(4-iodo-1,3-diphenylbutyl)-2-phenylacetamide (3c)**

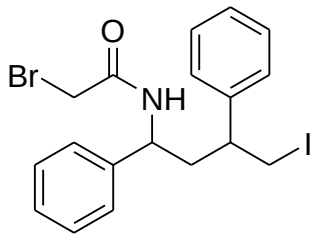
Solid (169mg, 72%); mp. 154–156°C (one of the major isomers, recrystallized from the mixture of dichloromethane and ether);
FTIR (KBr, cm^{-1}): 3287, 1645, 1543, 1254;
One isomer, ^1H NMR ($CDCl_3$; 400 MHz; TMS): δ 7.38–7.16 (m, 10H, 10 × *Ph*), 7.07–7.01 (m, 5H, 5 × *Ph*), 5.78 (d, *J* = 8.5 Hz, 1H, N*H*), 4.81–4.76 (m, 1H, NHC*H*), 3.49 (d, *J*=3.3, 2H, CH_2CO), 3.28–3.25 (m, 2H, CH_2I), 2.82–2.75 (m, 1H, C*H*CH_2I), 2.27–2.24 (m, 1H, 1 × CHC$H_2$$CHCH_2$I), 2.04–2.00 (m, 1H, 1 × CHC$H_2$$CHCH_2$I).
The other isomer, ^1H NMR ($CDCl_3$; 400 MHz; TMS): δ 7.38–7.16 (m, 10H, 10 × *Ph*), 7.07–7.01 (m, 5H, 5 × *Ph*), 5.72 (d, *J* = 7.6 Hz, 1H, N*H*), 4.81–4.76 (m, 1H, NHC*H*), 3.39 (s, 2H, CH_2CO), 3.28–3.25 (m, 2H, CH_2I), 2.57–2.51 (m, 1H, C*H*CH_2I), 2.23–2.15 (m, 2H, CHC$H_2$$CHCH_2$I).
Both of the two isomers, ^{13}C NMR ($CDCl_3$; 100 MHz; TMS): δ 170.25, 170.09, 142.11, 142.10, 141.84, 140.96, 135.03, 134.88, 129.41, 129.36, 129.35, 129.17, 128.98, 128.96, 128.89, 128.85, 128.83, 128.66, 127.55, 127.48, 127.45, 127.36, 127.34, 127.31, 126.78, 126.00, 52.31, 51.30, 45.68, 44.80, 43.98, 43.68, 42.73, 40.98, 14.07, 12.98.
HRMS (ESI): *m/z* ($M+H^+$) calcd for $C_{24}H_{25}INO$, 470.0981. Found: 470.0983.



***N*-(4-iodo-1,3-diphenylbutyl)benzamide (3d)**

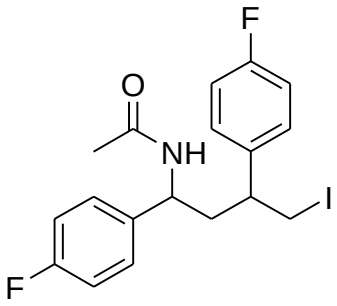
Solid (146mg, 64%); mp. 186–188°C (one of the major isomers, recrystallized from the mixture of dichloromethane and ether);
FTIR (KBr, cm^{-1}): 3293, 1636, 1533, 1278;
One isomer, ^1H NMR ($CDCl_3$; 400 MHz; TMS): δ7.63–7.14 (m, 15H, 15 × *Ph*), 6.40 (d, *J* = 8.2 Hz, 1H, N*H*), 5.14 (td, *J* = 8.7, 3.3 Hz, 1H, NHC*H*), 3.38 (d, *J* = 7.2 Hz, 2H, CH_2I), 3.03–2.97 (m, 1H, C*H*CH_2I), 2.60–2.55 (m, 1H, 1 × CHC$H_2$$CHCH_2$I), 2.28–2.21 (m, 1H, 1 × CHC$H_2$$CHCH_2$I).
The other isomer, ^1H NMR ($CDCl_3$; 400 MHz; TMS): δ 7.63–7.14 (m, 15H, 15 × *Ph*), 6.30 (d, *J* = 7.2 Hz, 1H, N*H*), 4.98–4.92 (m, 1H, NHC*H*), 3.35–3.29 (m, 2H, CH_2I), 2.73–2.65 (m, 1H, C*H*CH_2I), 2.54–2.44 (m, 2H, CHC$H_2$$CHCH_2$I).

Both of the two isomers, ^{13}C NMR ($CDCl_3$; 100 MHz; TMS): δ 166.59, 166.53, 142.40, 141.78, 141.74, 140.94, 134.24, 131.59, 131.50, 129.16, 128.97, 128.77, 128.55, 128.47, 127.96, 127.64, 127.57, 127.52, 127.51, 127.44, 127.05, 126.96, 126.89, 126.19, 53.10, 51.84, 45.42, 45.11, 42.38, 40.77, 14.15, 13.31.
HRMS (ESI): *m/z* ($M+H^+$) calcd for $C_{23}H_{23}INO$, 456.0824. Found: 456.0823.



2-bromo-*N*-(4-iodo-1,3-diphenylbutyl)acetamide (3e)

Solid (64mg, 27%); mp. 152–154°C (one of the major isomers, recrystallized from the mixture of dichloromethane and ether);
FTIR (KBr, cm^{-1}): 3266, 1649, 1540, 1283;
Major isomer, ^{1}H NMR ($CDCl_3$; 400 MHz; TMS): δ 7.36–7.24 (m, 6H, 6 × *Ph*), 7.20–7.11 (m, 4H, 4 × *Ph*), 6.79 (d, *J* = 8.3 Hz, 1H, N*H*), 4.80 (td, *J* = 9.2, 3.9 Hz, 1H, NHC*H*), 3.77 (d, *J* = 7.1 Hz, 2H, CH_2Br), 3.34 (dd, *J* = 7.2, 2.5 Hz, 2H, CH_2I), 3.91–2.80 (m, 1H, C*H*CH_2I), 2.48–2.41 (m, 1H, 1 × CHC$H_2$$CHCH_2$I), 2.17–2.10 (m, 1H, 1 × CHC$H_2$$CHCH_2$I). ^{13}C NMR ($CDCl_3$; 100 MHz; TMS): δ 164.73, 141.89, 141.21, major + minor isomer (129.08, 129.02, 128.95, 128.83, 128.16, 127.70, 127.67, 127.61, 127.49, 127.36, 126.89, 126.06), 52.12, 45.45, 42.34, 29.19, 12.82.
Minor isomer, ^{1}H NMR ($CDCl_3$; 400 MHz; TMS): δ 7.39–7.27 (m, 6H, 6 × *Ph*), 7.24–7.11 (m, 4H, 4 × *Ph*), 6.67 (d, *J* = 7.5 Hz, 1H, N*H*), 4.74–4.68 (m, 1H, NHC*H*), 3.66 (s, 2H, CH_2Br), 3.31–3.28 (m, 2H, CH_2I), 2.65–2.59 (m, 1H, C*H*CH_2I), 2.33–2.25 (m, 2H, CHC$H_2$$CHCH_2$I). ^{13}C NMR ($CDCl_3$; 100 MHz; TMS): δ 164.41, 141.45, 140.09, major + minor isomer (129.08, 129.02, 128.95, 128.83, 128.16, 127.70, 127.67, 127.61, 127.49, 127.36, 126.89, 126.06), 53.20, 45.01, 40.69, 29.71, 13.70.
HRMS (ESI): *m/z* ($M+H^+$) calcd for $C_{18}H_{20}BrINO$, 471.9773. Found: 471.9782.



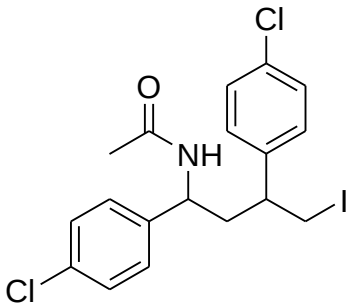
***N*-(1,3-bis(4-fluorophenyl)-4-iodobutyl)acetamide (3f)**

Gummy liquid (152mg, 71%);
FTIR (KBr, cm^{-1}): 3274, 1648, 1549, 1296;
One isomer, ^{1}H NMR ($CDCl_3$; 400 MHz; TMS): δ 7.16–6.91 (m, 8H, 8 × *Ph*), 6.24 (d, *J* = 8.5 Hz, 1H, N*H*), 4.75 (td, *J* = 9.4, 4.1 Hz, 1H, NHC*H*), 3.32 (d, *J* = 7.1 Hz, 2H, CH_2I), 2.97–2.90 (m, 1H, C*H*CH_2I), 2.38–2.33 (m, 1H, 1 × CHC$H_2$$CHCH_2$I), 2.04–1.96 (m, 1H, 1 × CHC$H_2$$CHCH_2$I), 1.93 (s, 3H, C$H_3$).

The other isomer, ^{1}H NMR ($CDCl_3$; 400 MHz; TMS): δ 7.16–6.91 (m, 8H, 8 × *Ph*), 6.07 (d, *J* = 7.7 Hz, 1H, N*H*), 4.70–4.64 (m, 1H, NHC*H*), 3.28–3.25 (m, 2H, CH_2I), 2.58–2.51 (m, 1H, C*H*CH_2I), 2.33–2.18 (m, 2H, CHCH_2CHCH_2I), 1.82 (s, 3H, CH_3).

Both of the two isomers, ^{13}C NMR ($CDCl_3$; 100 MHz; TMS): 169.50, 169.28, 162.21 (d, *J* = 246.5 Hz), 162.00 (d, *J* = 246.1 Hz), 161.93 (d, *J* = 246.0 Hz), 138.00 (d, *J* = 3.2 Hz), 137.73 (d, *J* = 3.2 Hz), 137.14 (d, *J* = 3.2 Hz), 136.56 (d, *J* = 3.2 Hz), 129.02 (d, *J* = 8.0 Hz), 128.91 (d, *J* = 8.0 Hz), 128.71 (d, *J* = 8.1 Hz), 127.84 (d, *J* = 8.0 Hz), 115.80 (d, *J* = 21.3 Hz), 115.74 (d, *J* = 21.5 Hz), 115.52 (d, *J* = 22.7 Hz), 51.57, 50.70, 44.85, 44.01, 42.74, 40.71, 23.29, 23.22, 13.82, 12.88.

HRMS (ESI): *m/z* (M+H$^+$) calcd for $C_{18}H_{19}F_2INO$, 430.0479. Found: 430.0471.



***N*-(1,3-bis(4-chlorophenyl)-4-iodobutyl)acetamide (3g)**

Gummy liquid (143mg, 62%);

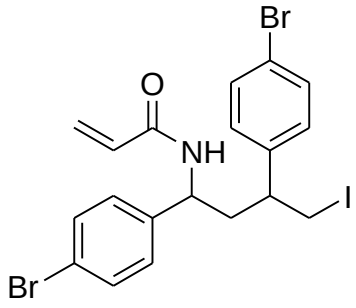
FTIR (KBr, cm^{-1}): 3276, 1649, 1545, 1291;

One isomer, ^{1}H NMR ($CDCl_3$; 400 MHz; TMS): δ 7.32–7.24 (m, 4H, 4 × *Ph*), 7.12–7.03 (m, 4H, 4 × *Ph*), 5.91 (d, *J* = 8.5 Hz, 1H, N*H*), 4.76 (td, *J* = 9.5, 4.1 Hz, 1H, NHC*H*), 3.32 (d, *J* = 7.2 Hz, 2H, CH_2I), 2.96–2.89 (m, 1H, C*H*CH_2I), 2.38–2.35 (m, 1H, 1 × CHCH_2CHCH_2I), 2.04–1.97 (m, 1H, 1 × CHCH_2CHCH_2I), 1.96 (s, 3H, CH_3).

The other isomer, ^{1}H NMR ($CDCl_3$; 400 MHz; TMS): δ 7.32–7.24 (m, 4H, 4 × *Ph*), 7.12–7.03 (m, 4H, 4 × *Ph*), 5.78 (d, *J* = 7.6 Hz, 1H, N*H*), 4.69–4.63 (m, 1H, NHC*H*), 3.27–3.25 (m, 2H, CH_2I), 2.58–2.51 (m, 1H, C*H*CH_2I), 2.34–2.19 (m, 2H, CHCH_2CHCH_2I), 1.84 (s, 3H, CH_3).

Both of the two isomers ^{13}C NMR ($CDCl_3$; 100 MHz; TMS): 169.37, 169.16, 140.50, 140.42, 139.81, 139.10, 133.77, 133.35, 133.31, 133.27, 129.13, 129.12, 129.09, 128.89, 128.84, 128.72, 128.43, 127.61, 51.68, 50.72, 45.00, 44.21, 42.49, 40.46, 23.34, 23.25, 13.18, 12.27.

HRMS (ESI): *m/z* (M+H$^+$) calcd for $C_{18}H_{19}Cl_2INO$, 461.9888. Found: 461.9887.



***N*-(1,3-bis(4-bromophenyl)-4-iodobutyl)acrylamide (3h)**

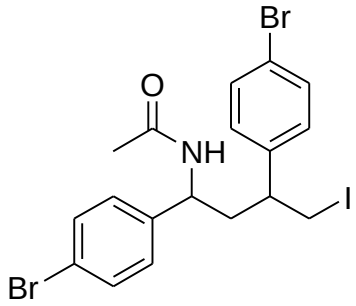
Solid (208mg, 74%); mp. 162–164°C (one of the major isomers, recrystallized from the mixture of dichloromethane and ether);

FTIR (KBr, cm^{-1}): 3271, 1656, 1541, 1244;

Major isomer, ^{1}H NMR ($CDCl_3$; 400 MHz; TMS): δ 7.51–7.34 (m, 4H, 4 × *Ph*), 7.13–6.93 (m, 4H, 4 × *Ph*), 6.42–5.90 (m, 3H, C*H*$_2$=C*H*), 5.63 (d, *J* = 10.2 Hz, 1H, N*H*), 4.81–4.75 (m, 1H, NHC*H*), 3.29 (d, *J* = 7.0 Hz, 2H, C*H*$_2$I), 2.95–2.85 (m, 1H, C*H*CH$_2$I), 2.38–2.34 (m, 1H, 1 × CHC*H*$_2$CHCH$_2$I), 2.04–1.96 (m, 1H, 1 × CHC*H*$_2$CHCH$_2$I). ^{13}C NMR ($CDCl_3$; 100 MHz; TMS): δ 165.00, major + minor isomer (140.89, 140.27, 139.44, 132.11, 132.06, 131.84, 131.79, 130.45, 130.38, 129.21, 129.11, 128.84, 127.97, 127.21, 127.05, 121.92, 121.48, 121.45, 121.37), 50.93, 45.02, 42.44, 12.07.

Minor isomer, ^{1}H NMR ($CDCl_3$; 400 MHz; TMS): δ 7.50–7.33 (m, 4H, 4 × *Ph*), 7.14–6.94 (m, 4H, 4 × *Ph*), 6.40–5.90 (m, 3H, C*H*$_2$=C*H*), 5.57 (d, *J* = 10.2 Hz, 1H, N*H*), 4.73–4.68 (m, 1H, NHC*H*), 3.27–3.20 (m, 2H, C*H*$_2$I), 2.55–2.49 (m, 1H, C*H*CH$_2$I), 2.31–2.18 (m, 2H, CHC*H*$_2$CHCH$_2$I). ^{13}C NMR ($CDCl_3$; 100 MHz; TMS): δ 164.72, major + minor isomer (140.89, 140.27, 139.44, 132.11, 132.06, 131.84, 131.79, 130.45, 130.38, 129.21, 129.11, 128.84, 127.97, 127.21, 127.05, 121.92, 121.48, 121.45, 121.37), 51.75, 44.13, 40.27, 13.07.

HRMS(ESI): *m/z* (M+H$^+$) calcd for $C_{19}H_{19}Br_2INO$, 561.8878. Found: 561.8877.



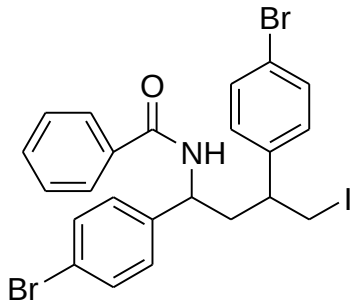
***N*-(1,3-bis(4-bromophenyl)-4-iodobutyl)acetamide (3i)**

Gummy liquid (116mg, 42%);

Major isomer, ^{1}H NMR ($CDCl_3$; 300 MHz; TMS): δ 7.49–7.40 (m, 4H, 4 × *Ph*), 7.08–6.98 (m, 4H, 4 × *Ph*), 5.73 (d, *J* = 8.5 Hz, 1H, N*H*), 4.76 (td, *J* = 9.6, 4.0 Hz, 1H, NHC*H*), 3.34 (d, *J* = 7.2 Hz, 2H, C*H*$_2$I), 2.98–2.86 (m, 1H, C*H*CH$_2$I), 2.41–2.36 (m, 1H, 1 × CHC*H*$_2$CHCH$_2$I), 2.06–2.00 (m, 1H, 1 × CHC*H*$_2$CHCH$_2$I), 1.98 (s, 3H, C*H*$_3$). ^{13}C NMR ($CDCl_3$; 75 MHz; TMS): δ 169.39, major + minor isomers (140.94, 140.92, 140.28, 139.50, 132.15, 132.13, 132.09, 131.91, 129.23, 129.10, 128.81, 128.00, 121.97, 121.51, 121.48, 121.44), 50.79, 45.09, 42.37, 23.43, 12.16.

Minor isomer, ^{1}H NMR ($CDCl_3$; 300 MHz; TMS): δ 7.49–7.40 (m, 4H, 4 × *Ph*), 7.08–6.98 (m, 4H, 4 × *Ph*), 5.62 (d, *J* = 7.5 Hz, 1H, N*H*), 4.68–4.60 (m, 1H, NHC*H*), 3.28–3.25 (m, 2H, C*H*$_2$I), 2.59–2.47 (m, 1H, C*H*CH$_2$I), 2.36–2.23 (m, 2H, CHC*H*$_2$CHCH$_2$I), 1.86 (s, 3H, C*H*$_3$). ^{13}C NMR ($CDCl_3$; 75 MHz; TMS): δ 169.18, major + minor isomers (140.94, 140.92, 140.28, 139.50, 132.15, 132.13, 132.09, 131.91, 129.23, 129.10, 128.81, 128.00, 121.97, 121.51, 121.48, 121.44), 51.82, 44.33, 40.31, 23.33, 13.04.

HRMS (ESI): *m/z* (M+H$^+$) calcd for $C_{18}H_{19}Br_2INO$, 549.8878. Found: 549.8875.



***N*-(1,3-bis(4-bromophenyl)-4-iodobutyl)benzamide (3j)**

Solid (166mg, 54%); mp. 205–207°C (one of the major isomers, recrystallized from the mixture of dichloromethane and ether);

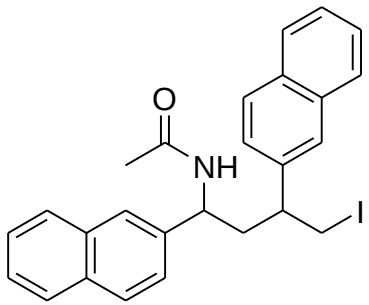
FTIR (KBr, cm^{-1}): 3295, 1637, 1533, 1290;

One isomer, ^{1}H NMR ($CDCl_3$; 400 MHz; TMS): δ 7.63 (d, *J* = 7.8 Hz, 2H, 2 × *Ph*), 7.49–7.34 (m, 9H, 9 × *Ph*), 7.13–7.00 (m, 2H, 2 × *Ph*), 6.43 (d, *J* = 8.4 Hz, 1H, N*H*), 5.02 (td, *J* = 9.0, 3.6 Hz, 1H, NHC*H*), 3.33–3.26 (m, 2H, CH_2I), 2.99–2.92 (m, 1H, C*H*CH_2I), 2.46–2.42 (m, 1H, 1 × CHC$H_2$$CHCH_2$I), 2.16–2.09 (m, 1H, 1 × CHC$H_2$$CHCH_2$I).

The other isomer, ^{1}H NMR ($CDCl_3$; 400 MHz; TMS): δ 7.58 (d, *J* = 7.9 Hz, 2H, 2 × *Ph*), 7.49–7.34 (m, 9H, 9 × *Ph*), 7.13–7.00 (m, 2H, 2 × *Ph*), 6.34 (d, *J* = 7.5 Hz, 1H, N*H*), 4.89–4.83 (m, 1H, NHC*H*), 3.33–3.26 (m, 2H, CH_2I), 2.65–2.58 (m, 1H, C*H*CH_2I), 2.39–2.34 (m, 2H, CHC$H_2$$CHCH_2$I).

Both of the two isomers ^{13}C NMR ($CDCl_3$; 100 MHz; TMS): δ 166.76, 166.65, 141.08, 140.79, 140.48, 139.79, 133.91, 133.88, 132.28, 132.13, 132.10, 131.85, 131.81, 131.73, 129.21, 129.17, 128.79, 128.69, 128.55, 127.96, 126.96, 126.89, 121.89, 121.61, 121.47, 121.34, 52.35, 51.29, 44.97, 44.51, 42.18, 40.44, 13.16, 12.22.

HRMS(ESI): *m/z* ($M+H^+$) calcd for $C_{23}H_{21}Br_2INO$, 611.9035. Found: 611.9031.



***N*-(4-iodo-3-(naphthalen-2-yl)-1-(naphthalen-3-yl)butyl)acetamide (3k)**

Gummy liquid (94mg, 38%);

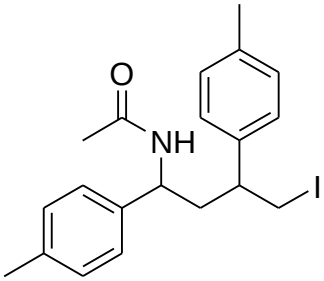
FTIR (KBr, cm^{-1}): 3274, 1648, 1545, 1271;

Major isomer, ^{1}H NMR ($CDCl_3$; 400 MHz; TMS): δ 7.87–7.74 (m, 6H, 6 × *Ph*), 7.61 (s, 2H, 2 × *Ph*), 7.51–7.44 (m, 4H, 4 × *Ph*), 7.29 (d, *J* = 12.9 Hz, 2H, 2 × *Ph*), 5.83 (d, *J* = 8.5 Hz, 1H, N*H*), 5.10 (td, *J* = 9.0, 4.4 Hz, 1H, NHC*H*), 3.50 (d, *J* = 7.0 Hz, 2H, CH_2I), 3.20–3.13 (m, 1H, C*H*CH_2I), 2.64–2.56 (m, 1H, 1 × CHC$H_2$$CHCH_2$I), 2.37–2.30 (m, 1H, 1 × CHC$H_2$$CHCH_2$I), 1.95 (s, 3H, C$H_3$). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 169.40, major + miner isomer (139.61, 139.20, 138.95, 138.00, 133.54, 133.51, 133.34, 133.28, 133.01, 132.86, 132.81, 132.73, 128.90, 128.76, 128.74, 128.66, 127.95, 127.86, 127.84, 127.74, 127.71, 127.66, 127.63, 126.82, 126.70, 126.44, 126.36, 126.34, 126.32, 126.28, 126.20, 125.99, 125.97,

125.93, 125.14, 125.01, 124.89, 124.71, 124.48, 124.46), 51.58, 45.66, 42.29, 23.41, 13.69.

Minor isomer, ^{1}H NMR ($CDCl_3$; 400 MHz; TMS): δ 7.87–7.74 (m, 6H, 6 × *Ph*), 7.56 (s, 2H, 2 × *Ph*), 7.51–7.44 (m, 4H, 4 × *Ph*), 7.34 (d, *J* = 8.5 Hz, 2H, 2 × *Ph*), 5.73 (d, *J* = 7.5 Hz, 1H, N*H*), 4.97–4.91 (m, 1H, NHC*H*), 3.41 (d, *J* = 6.9 Hz, 2H, CH_2I), 2.85–2.80 (m, 1H, C*H*CH_2I), 2.55–2.48 (m, 2H, CHCH_2CHCH_2I), 1.80 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 169.19, major + miner isomer (139.61, 139.20, 138.95, 138.00, 133.54, 133.51, 133.34, 133.28, 133.01, 132.86, 132.81, 132.73, 128.90, 128.76, 128.74, 128.66, 127.95, 127.86, 127.84, 127.74, 127.71, 127.66, 127.63, 126.82, 126.70, 126.44, 126.36, 126.34, 126.32, 126.28, 126.20, 125.99, 125.97, 125.93, 125.14, 125.01, 124.89, 124.71, 124.48, 124.46), 52.64, 45.20, 40.48, 23.28, 12.95.

HRMS(ESI): *m/z* (M+H$^+$) calcd for $C_{26}H_{25}INO$, 494.0981. Found: 494.0977.



***N*-(4-iodo-1, 3-dip-tolylbutyl)acetamide (3l)**

Gummy liquid (63mg, 30%);

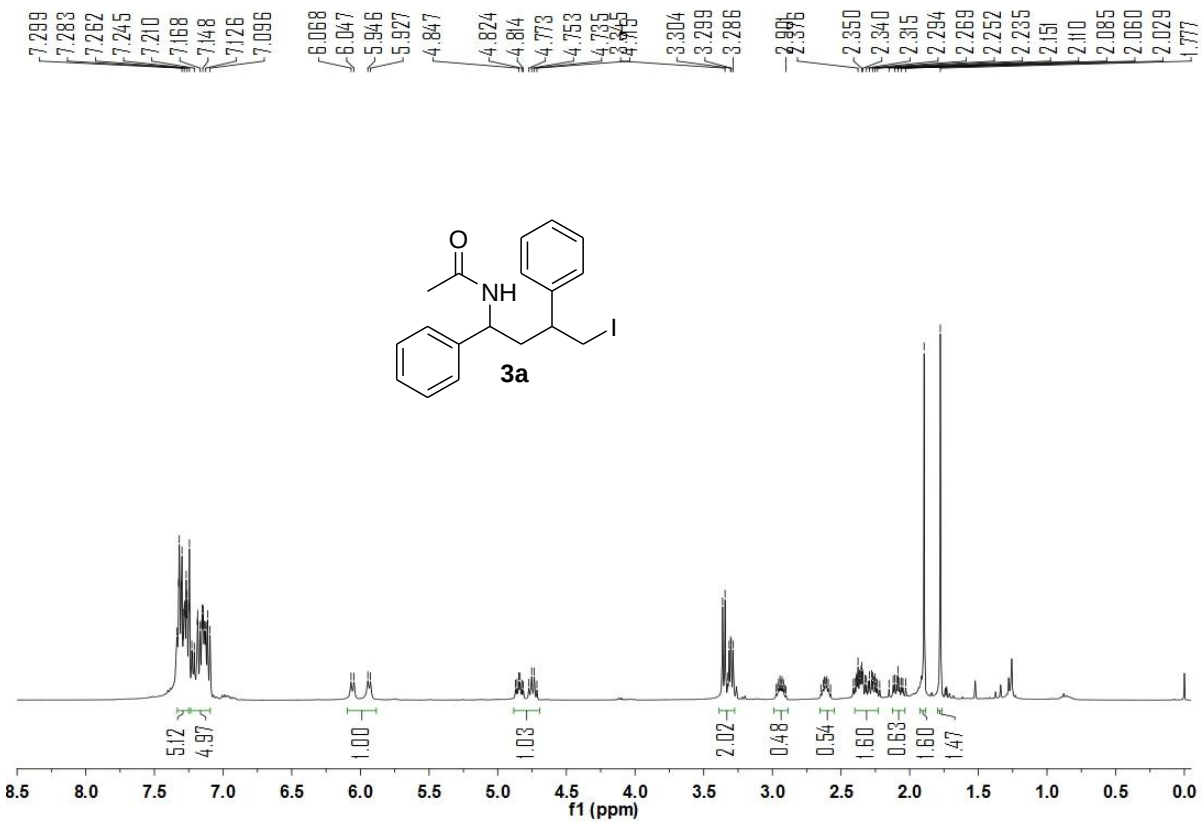
One isomer, ^{1}H NMR ($CDCl_3$; 300 MHz; TMS): δ 7.15–7.01 (m, 8H, 8 × *Ph*), 5.79 (d, *J* = 8.3 Hz, 1H, N*H*), 4.83 (td, *J* = 9.1, 4.4 Hz, 1H, NHC*H*), 3.35 (d, *J* = 7.2 Hz, 2H, CH_2I), 2.93–2.86 (m, 1H, C*H*CH_2I), 2.40–2.37 (m, 1H, 1 × CHCH_2CHCH_2I), 2.10–2.03 (m, 1H, 1 × CHCH_2CHCH_2I), 2.34 (s, 3H, CH_3), 2.33 (s, 3H, CH_3),1.91 (s, 3H, CH_3).

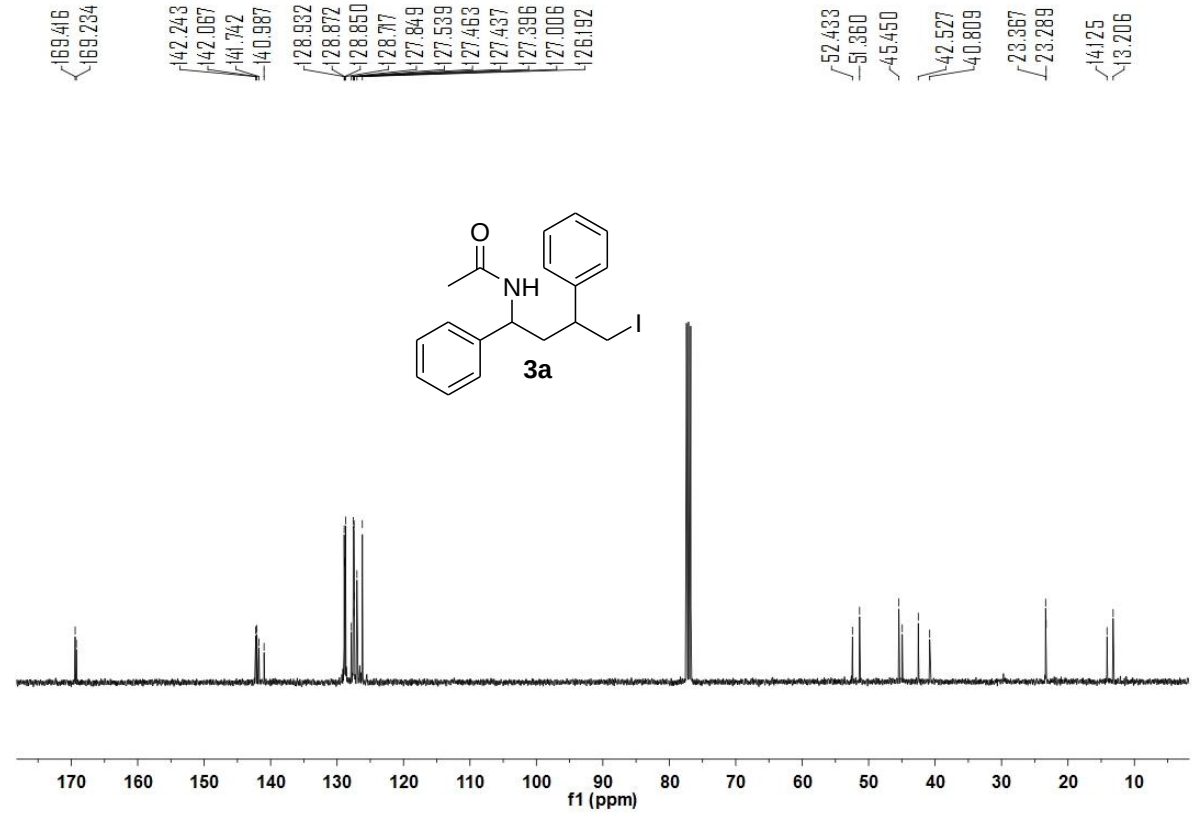
The other isomer, ^{1}H NMR ($CDCl_3$; 300 MHz; TMS): δ 7.15–7.01 (m, 8H, 8 × *Ph*), 5.70 (d, *J* = 7.5 Hz, 1H, N*H*), 4.70–4.64 (m, 1H, NHC*H*), 3.30–3.24 (m, 2H, CH_2I), 2.61–2.52 (m, 1H, C*H*CH_2I), 2.32–2.23 (m, 2H, CHCH_2CHCH_2I), 2.33 (s, 3H, CH_3), 2.31 (s, 3H, CH_3),1.81 (s, 3H, CH_3).

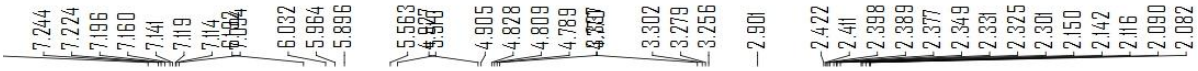
Both of the two isomers ^{13}C NMR ($CDCl_3$; 100 MHz; TMS): δ 169.23, 169.06, 139.24, 139.13, 138.61, 137.93, 137.54, 137.10, 137.02, 129.59, 129.54, 129.52, 129.36, 129.23, 127.41, 127.29, 126.97, 126.13, 52.20, 51.03, 45.00, 44.52, 42.48, 40.71, 36.69, 24.73, 23.39, 23.32, 21.15, 21.07, 14.50, 13.60.

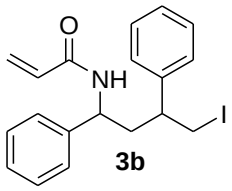
HRMS (ESI): *m/z* (M+H$^+$) calcd for $C_{20}H_{25}INO$, 422.0981. Found: 422.0984.

Copies of NMR spectra of products

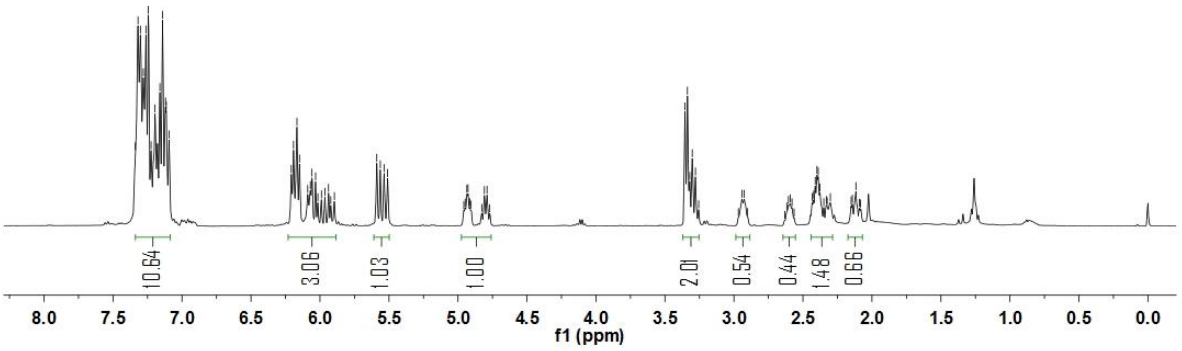


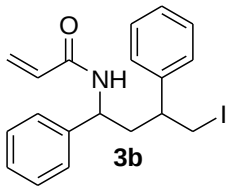






3b





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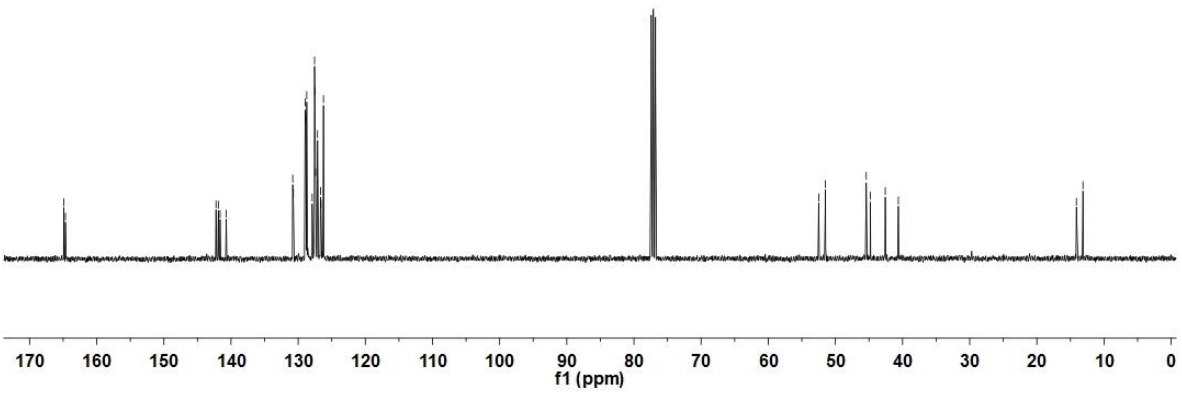

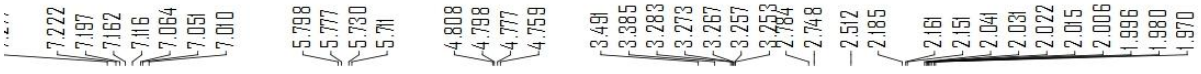

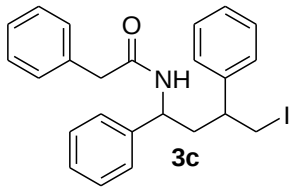

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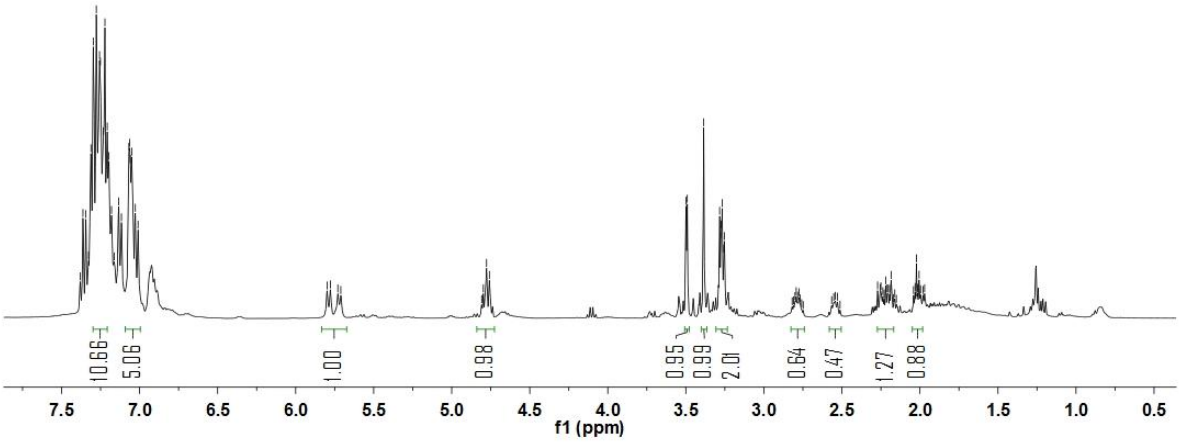

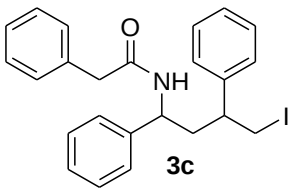

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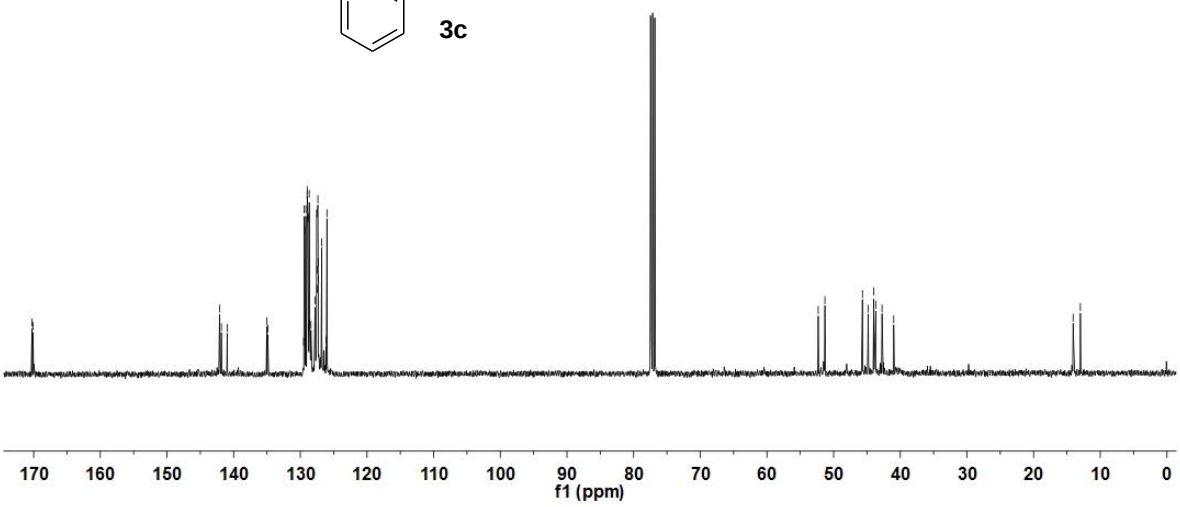

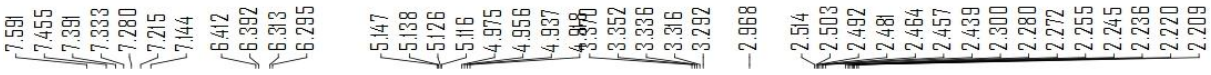
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5.126
5.116
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4.956
4.937
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3.336
3.316
3.292
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2.503
2.492
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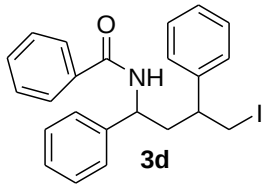
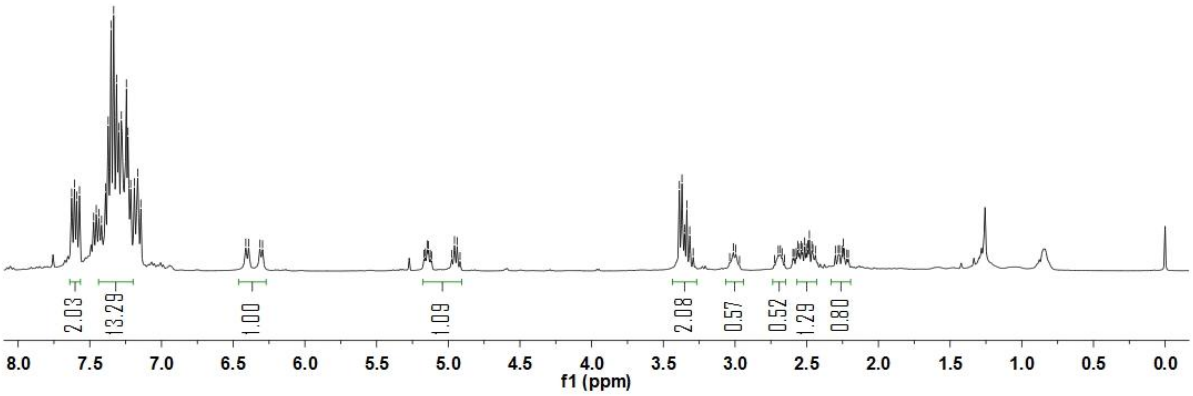

O
NH
I

3d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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


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166.533
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141.738
140.940
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128.469
127.964
127.639
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127.524
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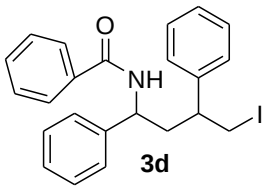
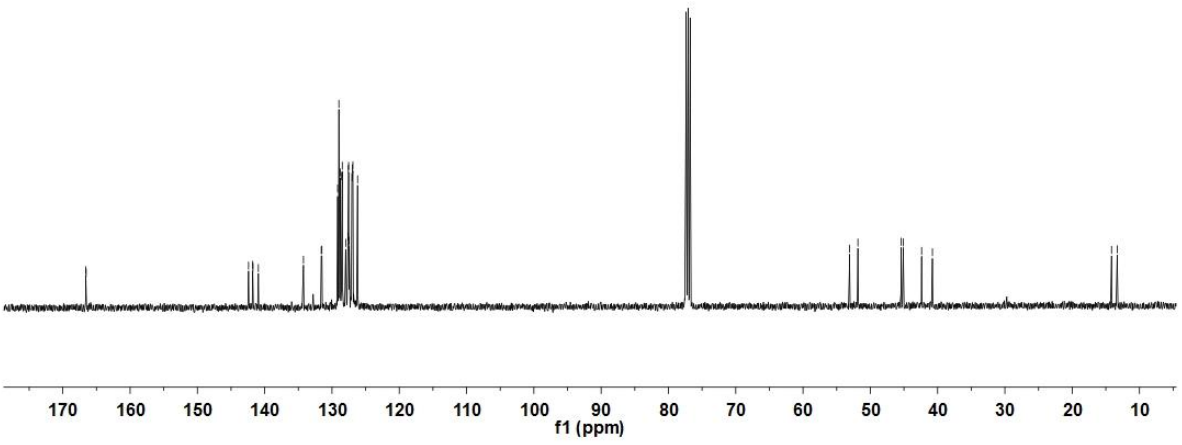

O
NH
I

3d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110
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90
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60
50
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20
10
f1 (ppm)


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7.152
7.102
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6.787
6.680
6.661
4.804
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4.782
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4.717
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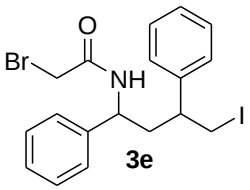
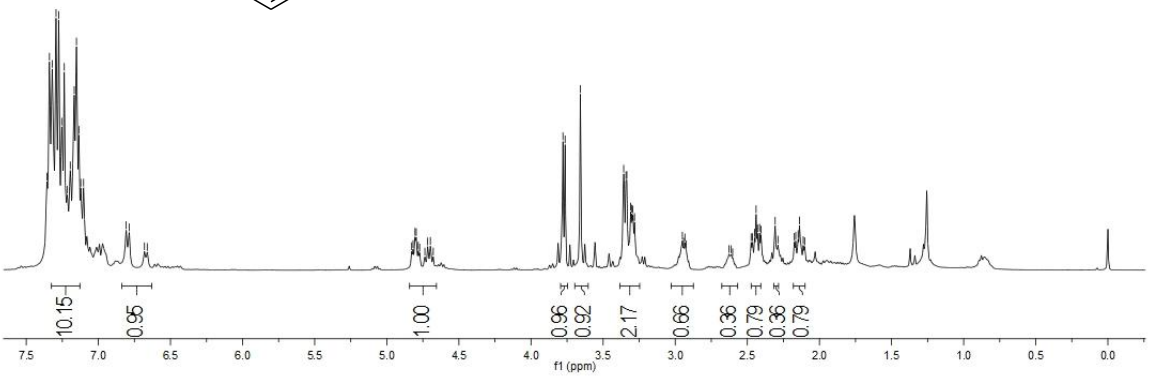

O
Br
NH
I

3e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f1 (ppm)


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40.69
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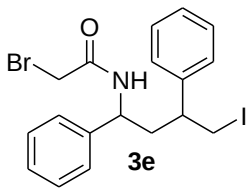
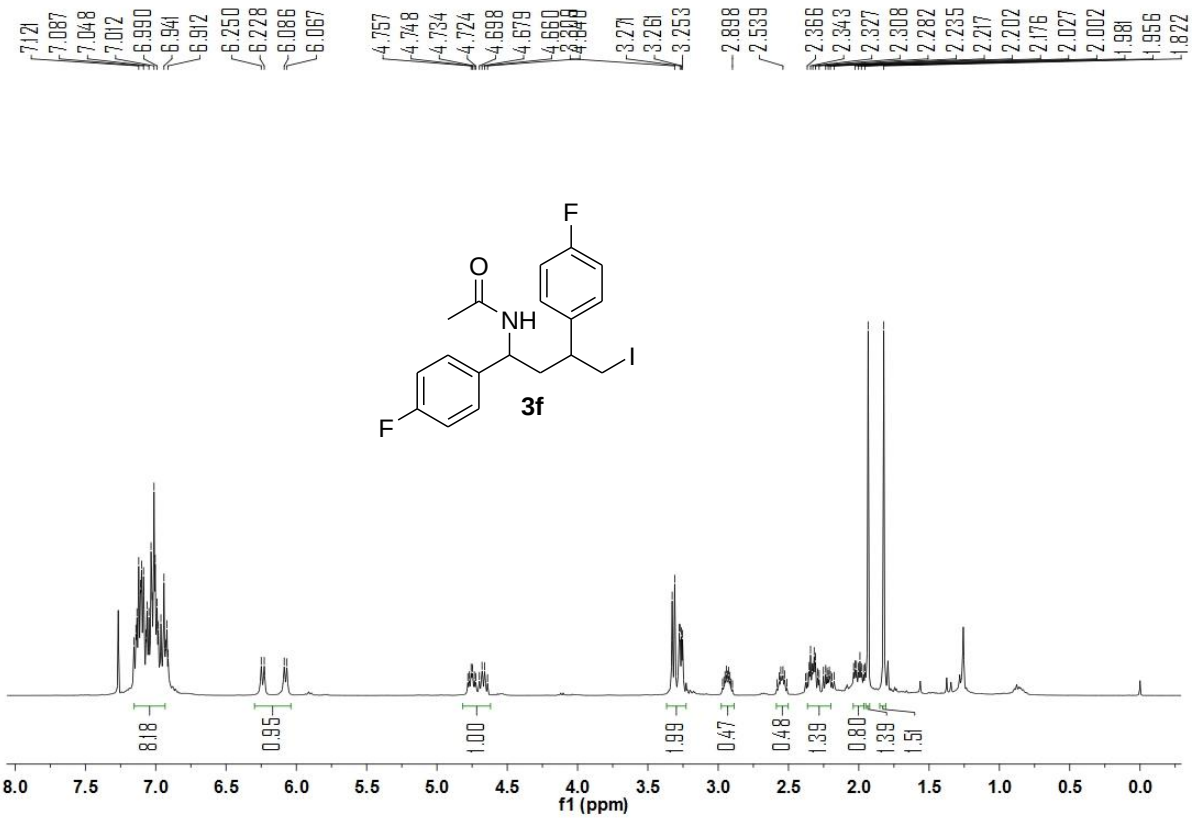
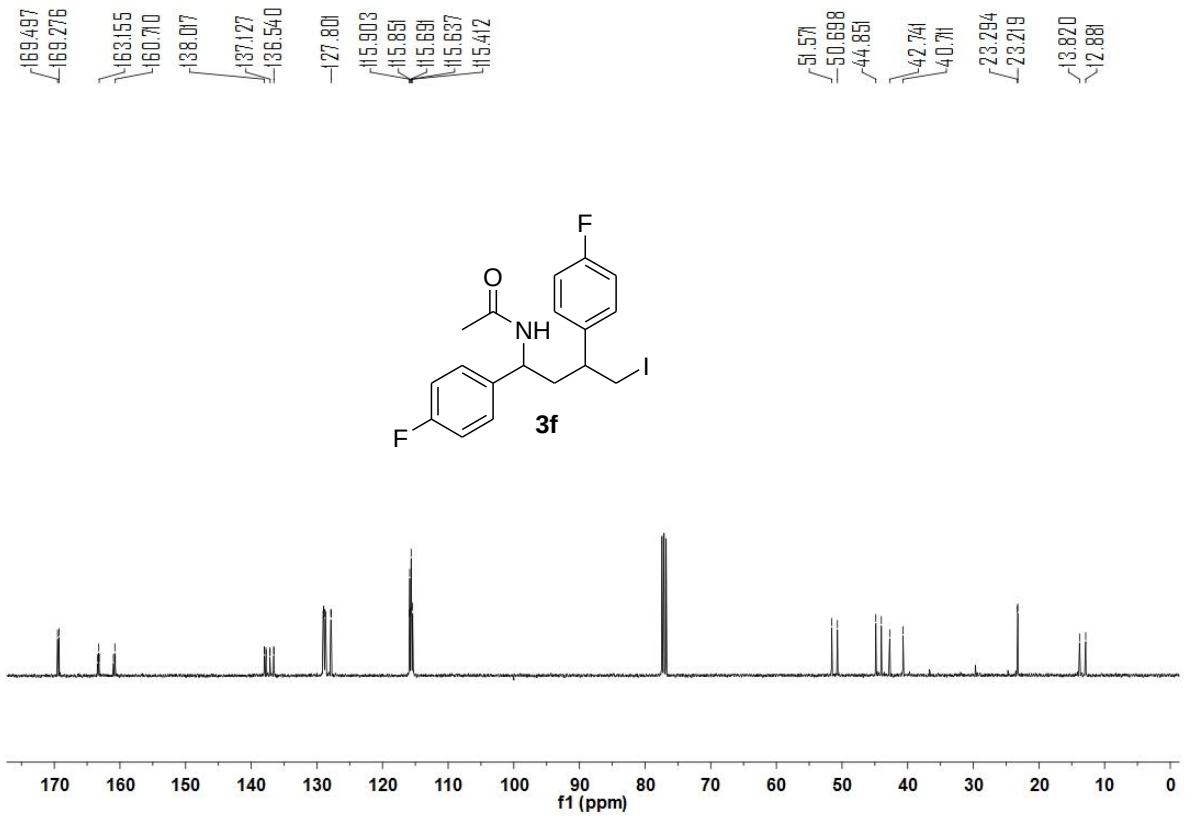
13.70
12.82


O
Br
NH
I

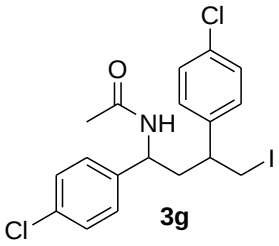
3e

f1 (ppm)

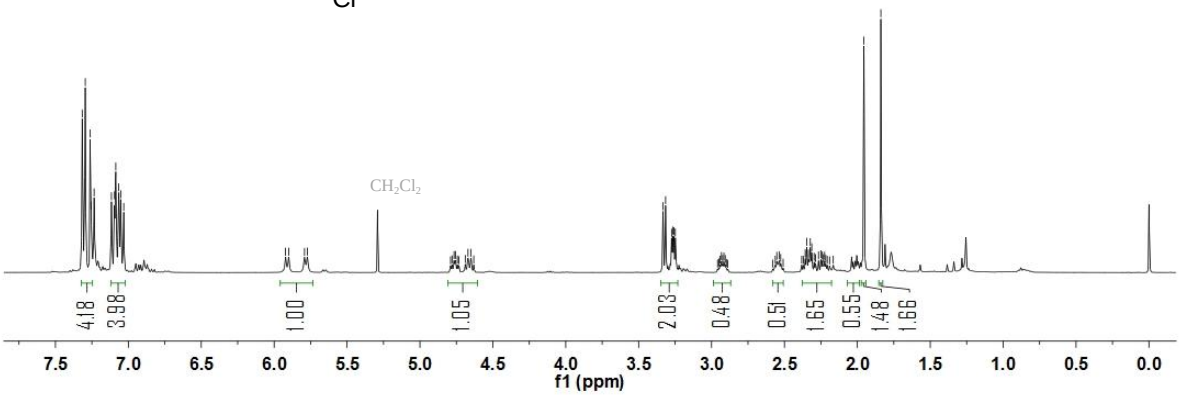




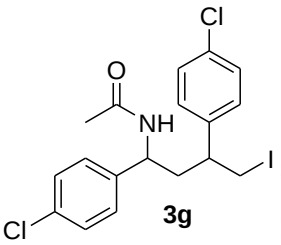

7.116
7.095
7.086
7.066
7.053
7.032
5.922
5.900
5.792
5.773
4.757
4.744
4.733
4.689
4.670
4.651
3.267
3.258
3.248
2.888
2.371
2.266
2.224
1.955
1.839


Cl
O
NH
I
Cl

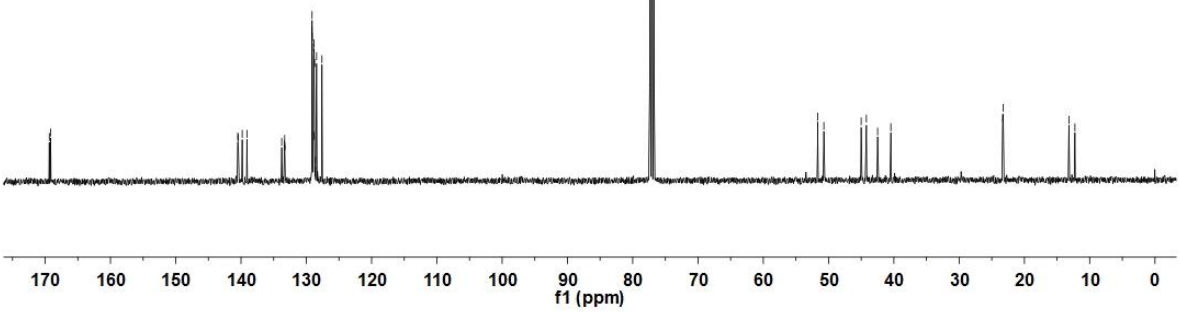
3g

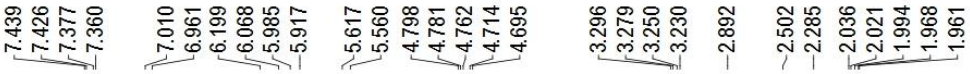

CH2Cl2
4.18
3.98
1.00
1.05
2.03
0.48
0.51
1.65
0.55
1.48
1.66
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

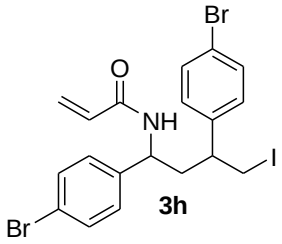

169.373
169.163
140.504
140.424
139.813
139.097
129.130
129.118
129.086
128.890
128.840
128.800
128.720
128.602
128.431
127.608
51.676
50.718
44.208
42.485
40.455
23.340
23.248
13.185
12.266


Cl
O
NH
I
Cl

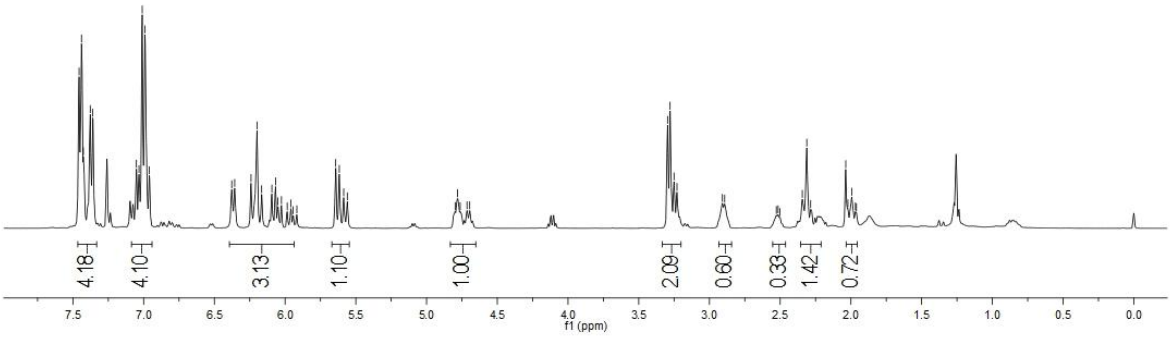
3g

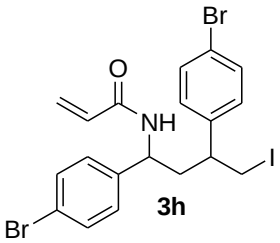

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



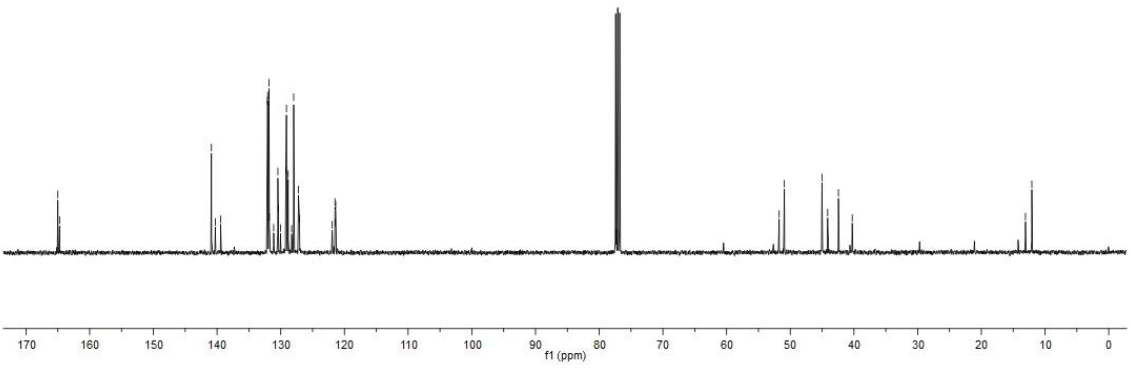


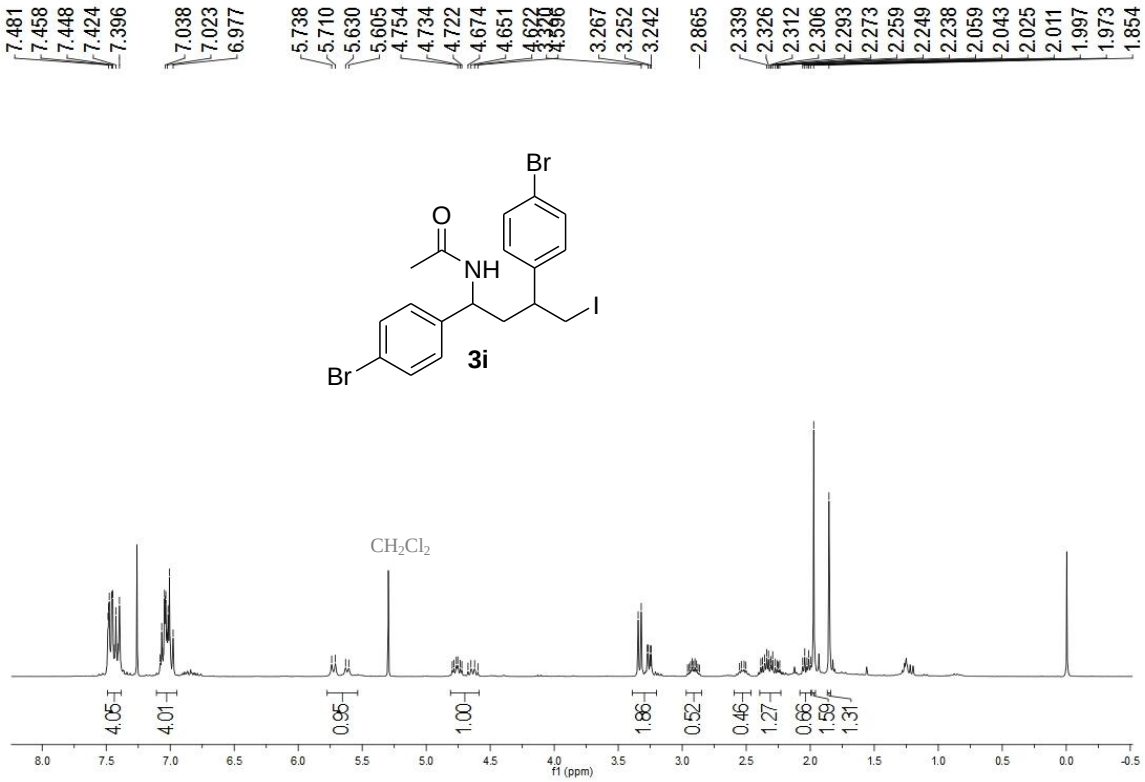
3h

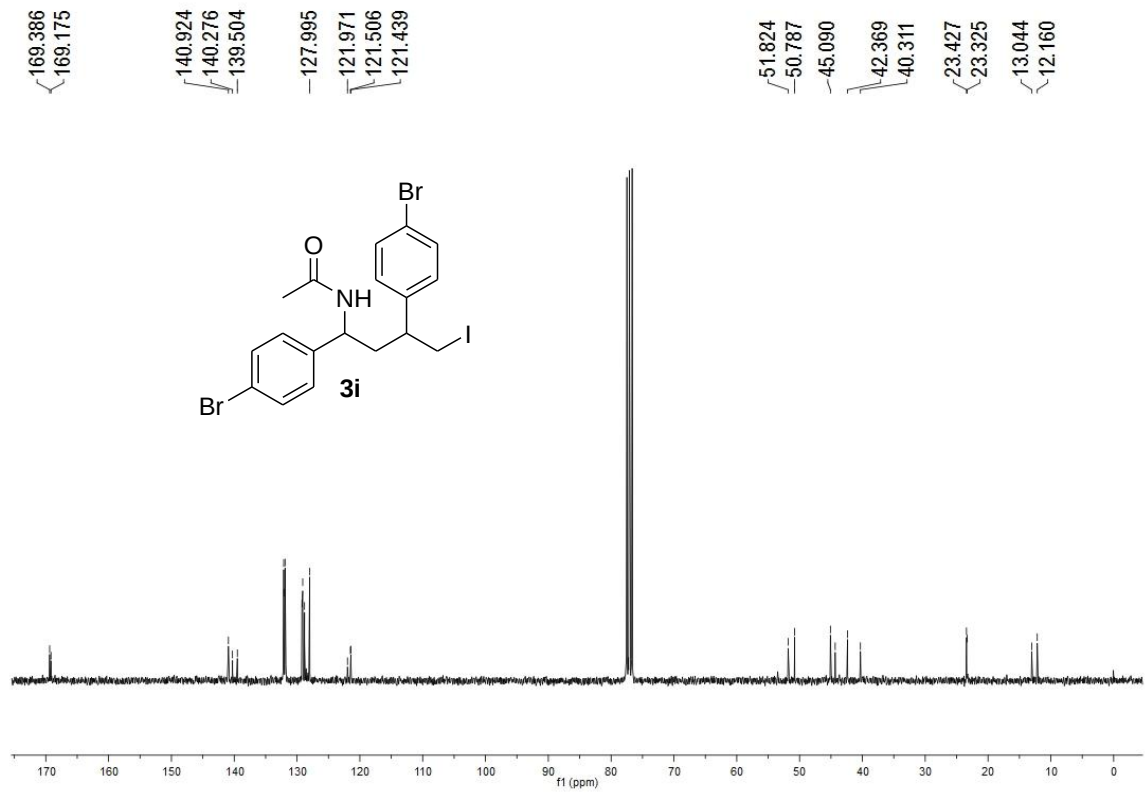


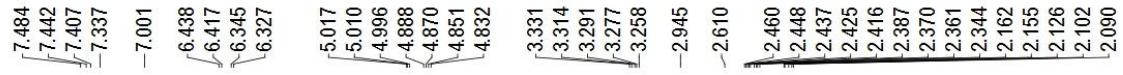


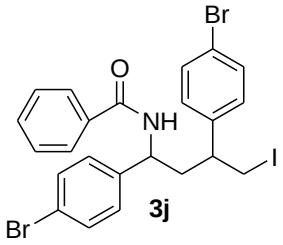
3h

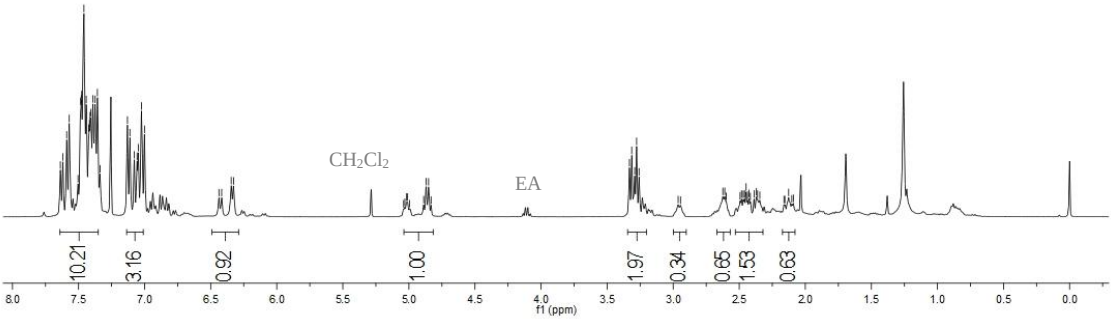


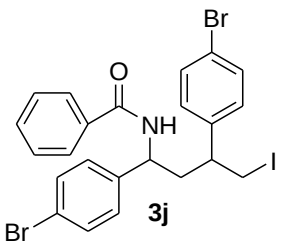

7.481
7.458
7.448
7.424
7.396
7.038
7.023
6.977
5.738
5.710
5.630
5.605
4.754
4.734
4.722
4.674
4.651
3.267
3.252
3.242
2.865
2.339
2.326
2.312
2.306
2.293
2.273
2.259
2.249
2.238
2.059
2.043
2.025
2.011
1.997
1.973
1.854
Br
O
NH
I
Br
3i
CH2Cl2
4.05
4.01
0.95
1.00
1.86
0.52
0.46
1.27
0.66
1.59
1.31
f1 (ppm)

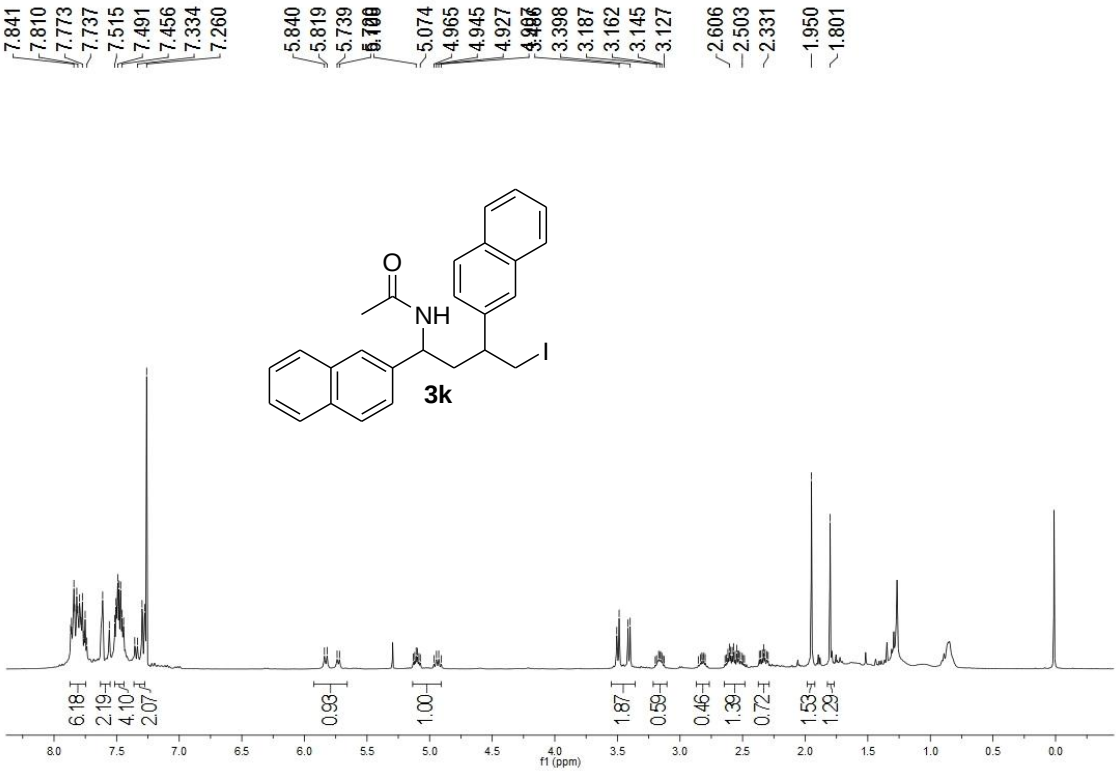

169.386
169.175
140.924
140.276
139.504
127.995
121.971
121.506
121.439
51.824
50.787
45.090
42.369
40.311
23.427
23.325
13.044
12.160
Br
O
NH
I
Br
3i
f1 (ppm)

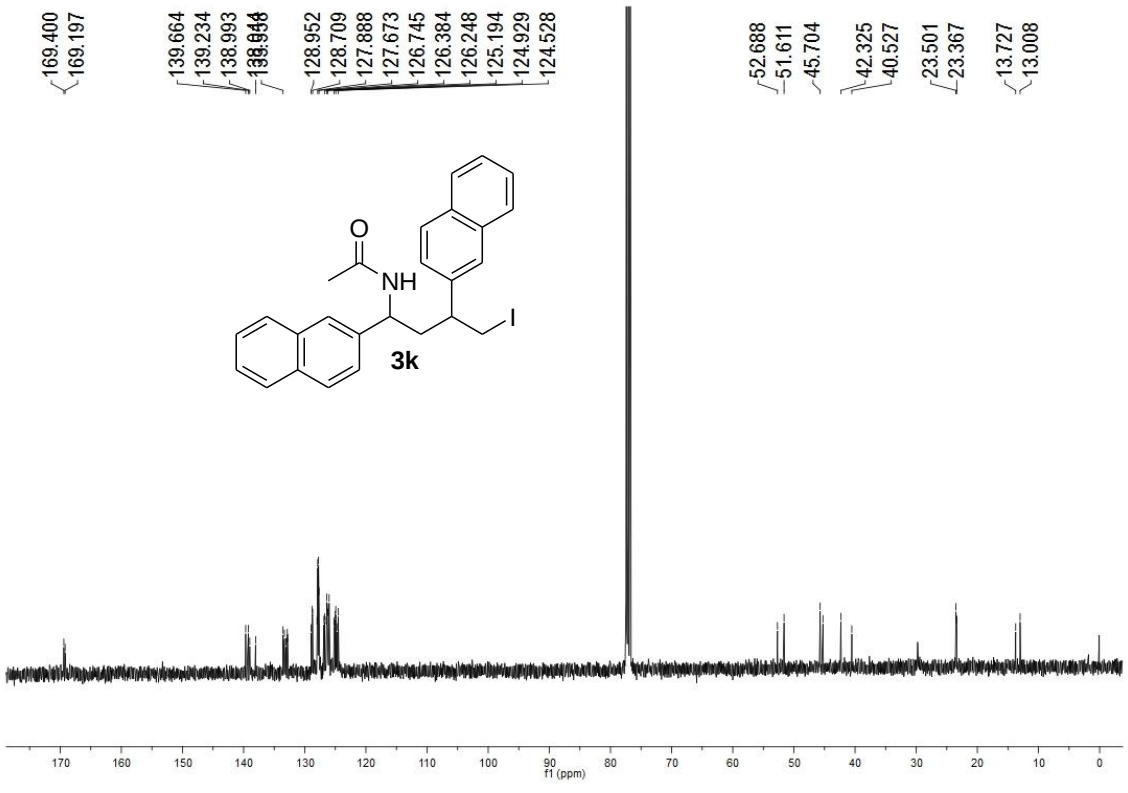


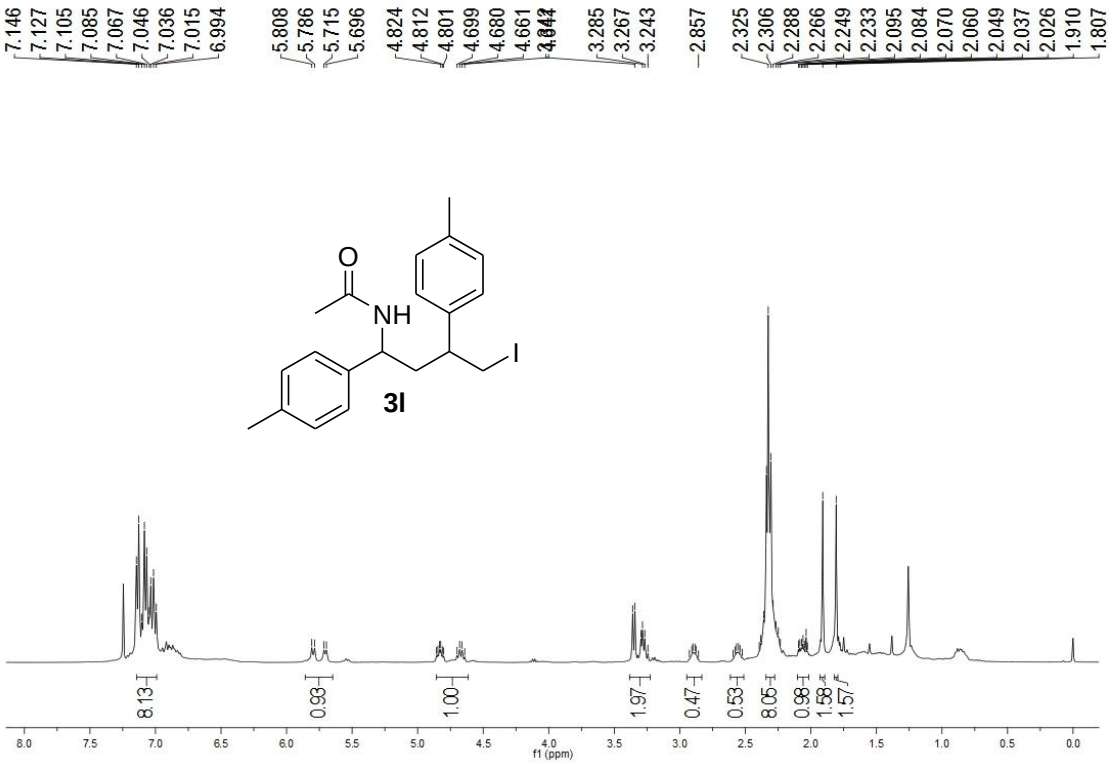


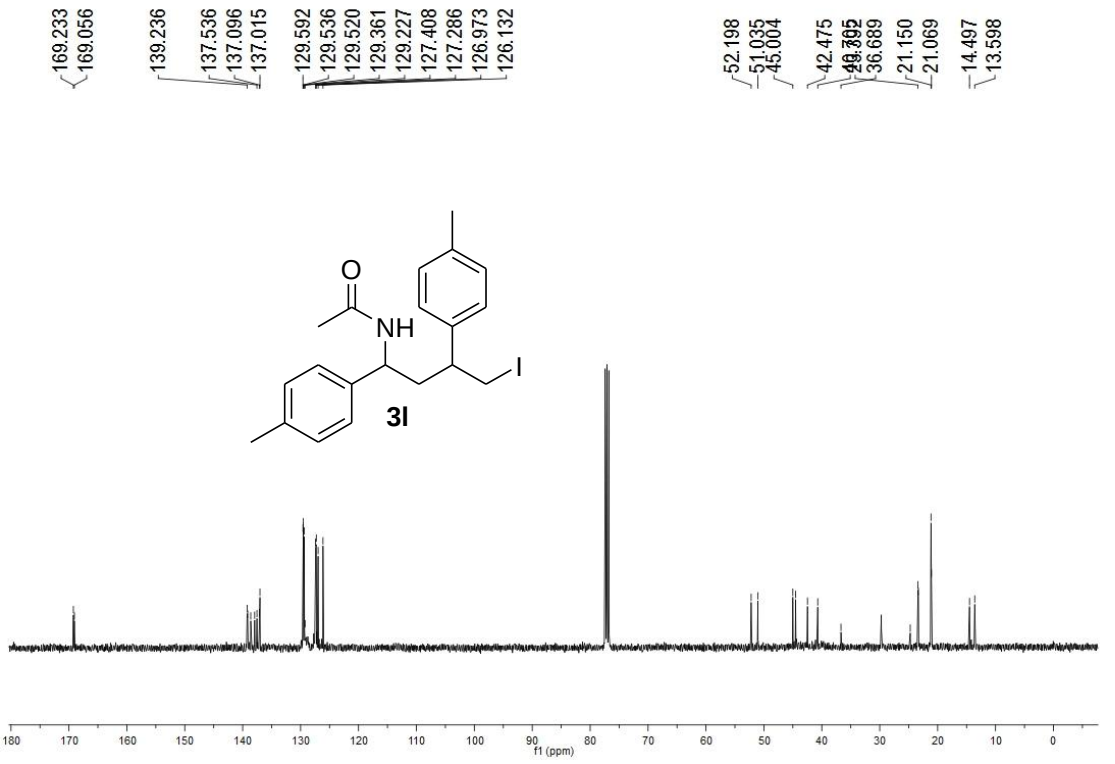









7.146
7.127
7.105
7.085
7.067
7.046
7.036
7.015
6.994
5.808
5.786
5.715
5.696
4.824
4.812
4.801
4.699
4.680
4.661
3.285
3.267
3.243
2.857
2.325
2.306
2.288
2.266
2.249
2.233
2.095
2.084
2.070
2.060
2.049
2.037
2.026
1.910
1.807
O
NH
I
3I
8.13
0.93
1.00
1.97
0.47
0.53
8.05
0.98
1.58
1.57
f1 (ppm)


169.233
169.056
139.236
137.536
137.096
137.015
129.592
129.536
129.520
129.361
129.227
127.408
127.286
126.973
126.132
52.198
51.035
45.004
42.475
36.689
21.150
21.069
14.497
13.598
O
NH
I
3I
f1 (ppm)