

Supporting Information.....

PIDA-I₂ Mediated Direct Vicinal Difunctionalization of Olefins: Iodoazidation, Iodoetherification and Iodoacyloxylation

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Safety issues for handling azido compounds¹

Sodium Azide (NaN₃): Sodium azide or any azide derivatives are highly toxic (similar toxicity as cyanide ion; LD₅₀ = 27 mg/kg for rats) and therefore personal protective equipment's should be always used while doing any experiments. In addition, above 275 °C, sodium azide decomposes via explosion. Chlorinated solvents (basically chloroform, dichloromethane) also should be avoided in reaction with NaN₃, because they liberates unstable tri- and di- azidomethanes which are toxic. In addition, acids should be avoided due to liberation of highly toxic HN₃.

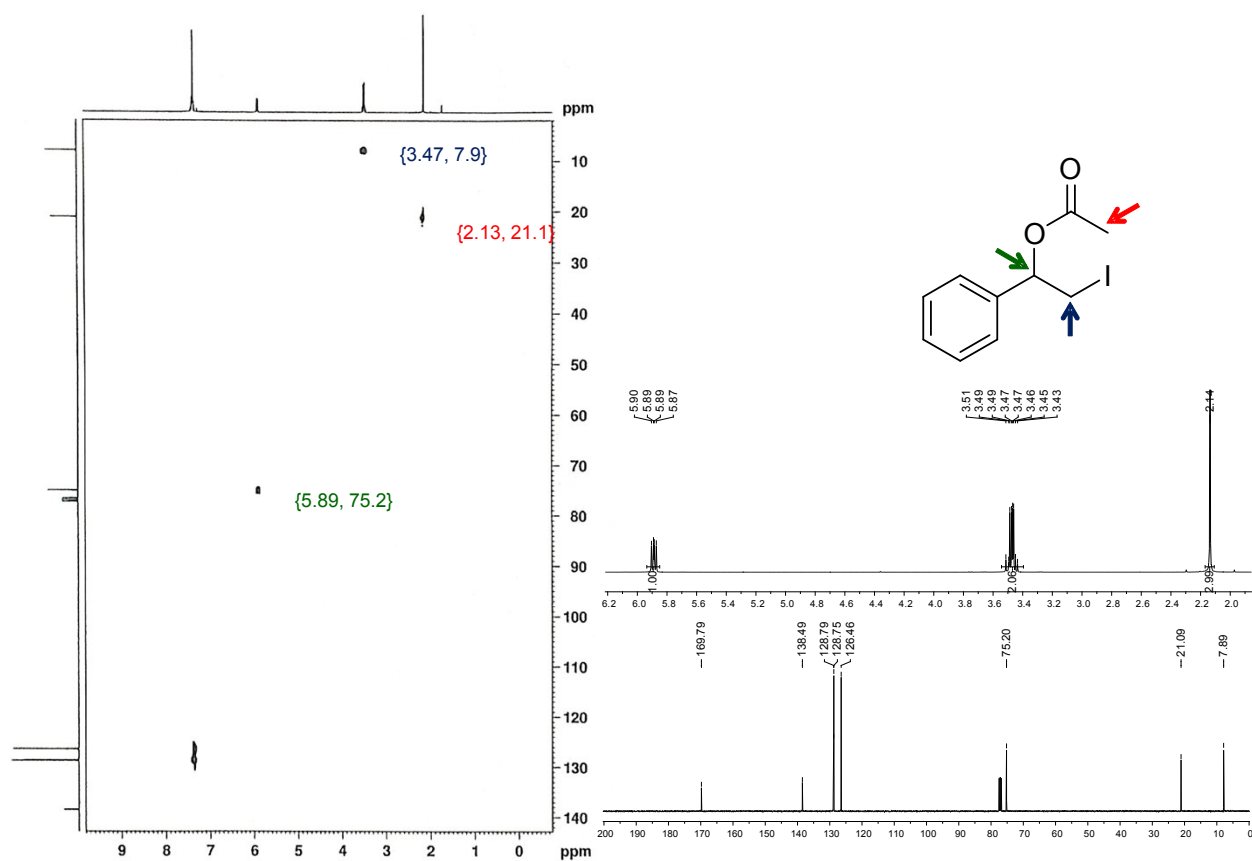
Organic Azides: Organic azides decompose with explosion in presence of heat, light and pressure. Azide should be stored under -20 °C at in the dark. The following equation was followed while synthesizing the azide molecules.

$$\frac{N_C + N_O}{N_N} \geq 3$$

N_C : Number of carbon atoms; N_O : Number of oxygen atoms; N_N : Number of nitrogen atoms in the azido group.

All organic azides were synthesized could satisfy the above equation except for **2b** and **2l**. These halogenated azide derivatives were found to be stable under -20 °C over couple of months. Still, general safety at laboratory should be carefully implemented and suggested that all reactions should be done in a well-ventilated fume hood behind a blast shield.

2D HSQC experiment of 8d



References

1. (a) T. Keicher, S. Löbbecke, In Organic Azides: Syntheses and Applications; S. Bräse, K. Banert, Eds.; Wiley: Chichester, U.K., 2010; p 3; (b) P. A. S. Smith, The Chemistry of Open-Chain Organic Nitrogen Compounds; Vol. 2, 1966, W.A. Benjamin Inc., New York, USA, p. 211.

NMR spectra of the synthesized compounds:

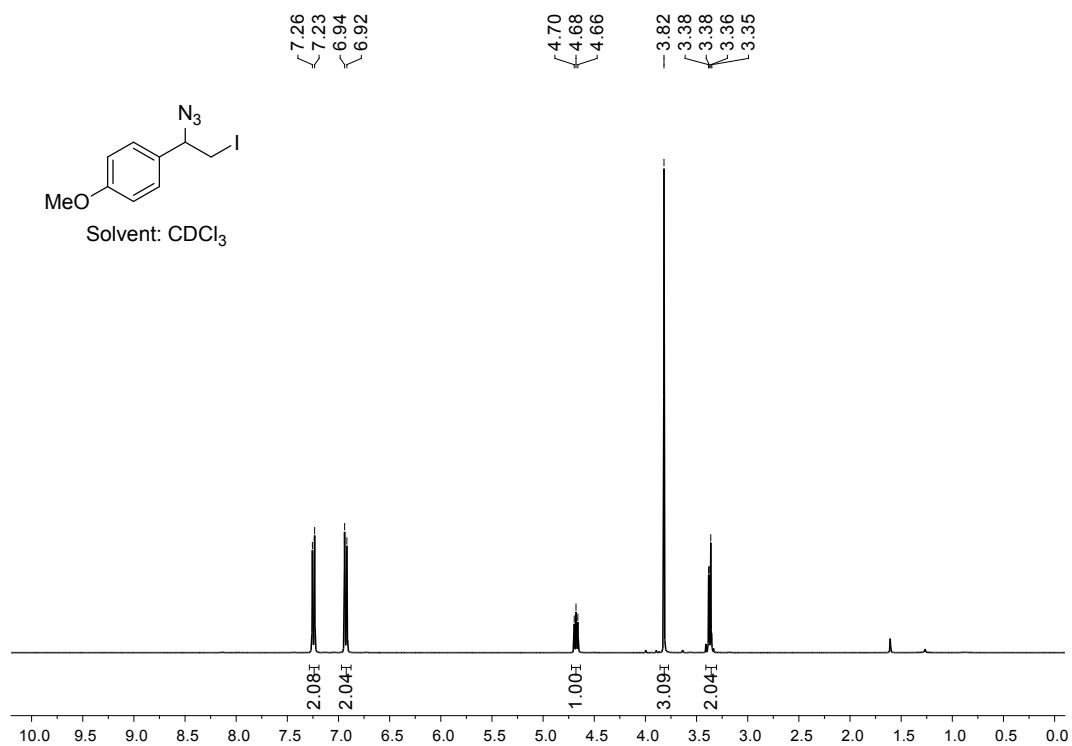


Figure S1: ¹H NMR spectrum of 1-(1-azido-2-iodoethyl)-4-methoxybenzene (2a).

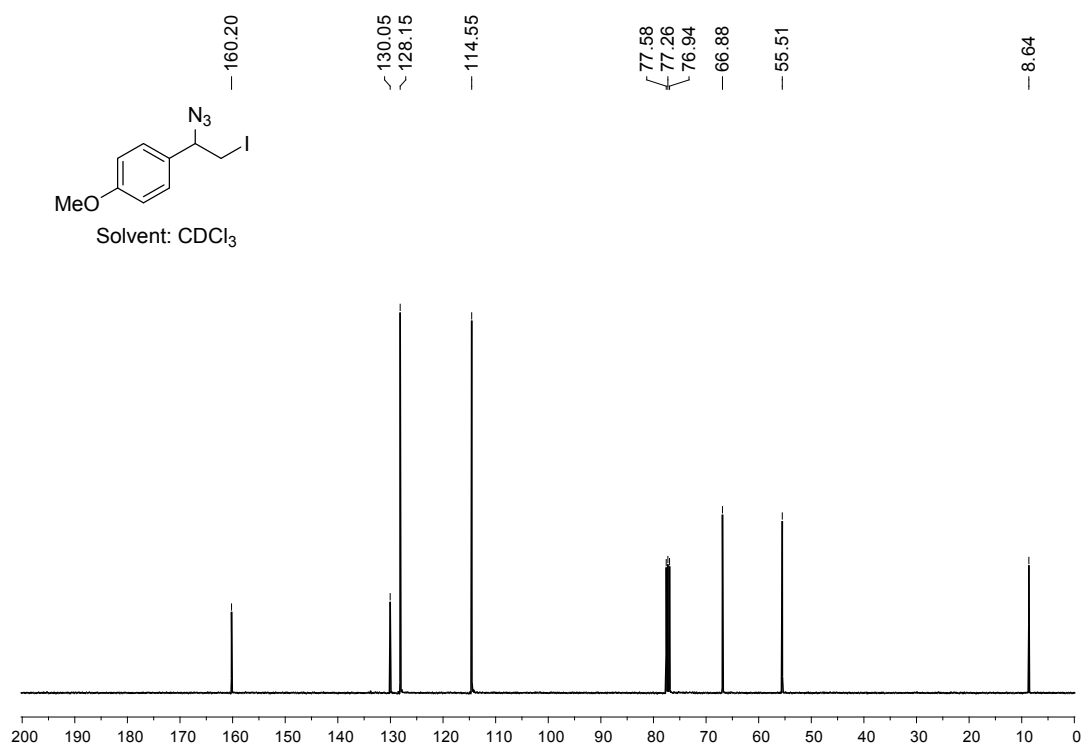


Figure S2: ¹³C NMR spectrum of 1-(1-azido-2-iodoethyl)-4-methoxybenzene (2a).

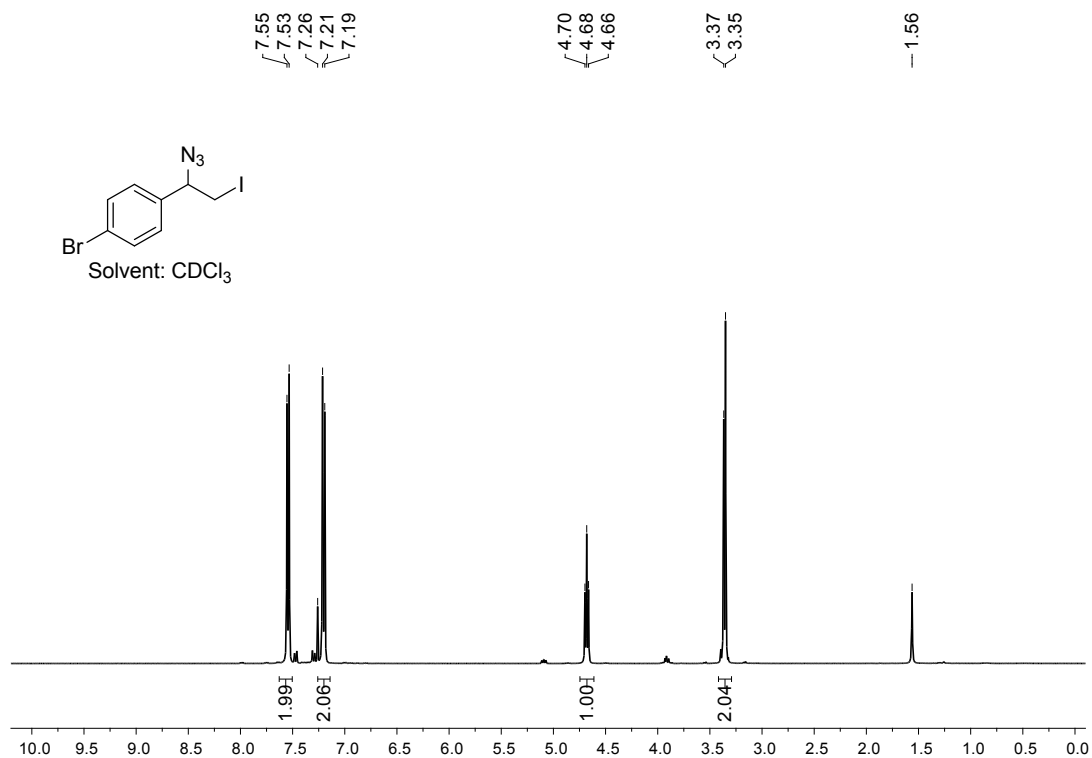


Figure S3: ¹H NMR spectrum of 1-(1-azido-2-iodoethyl)-4-bromobenzene (**2b**).

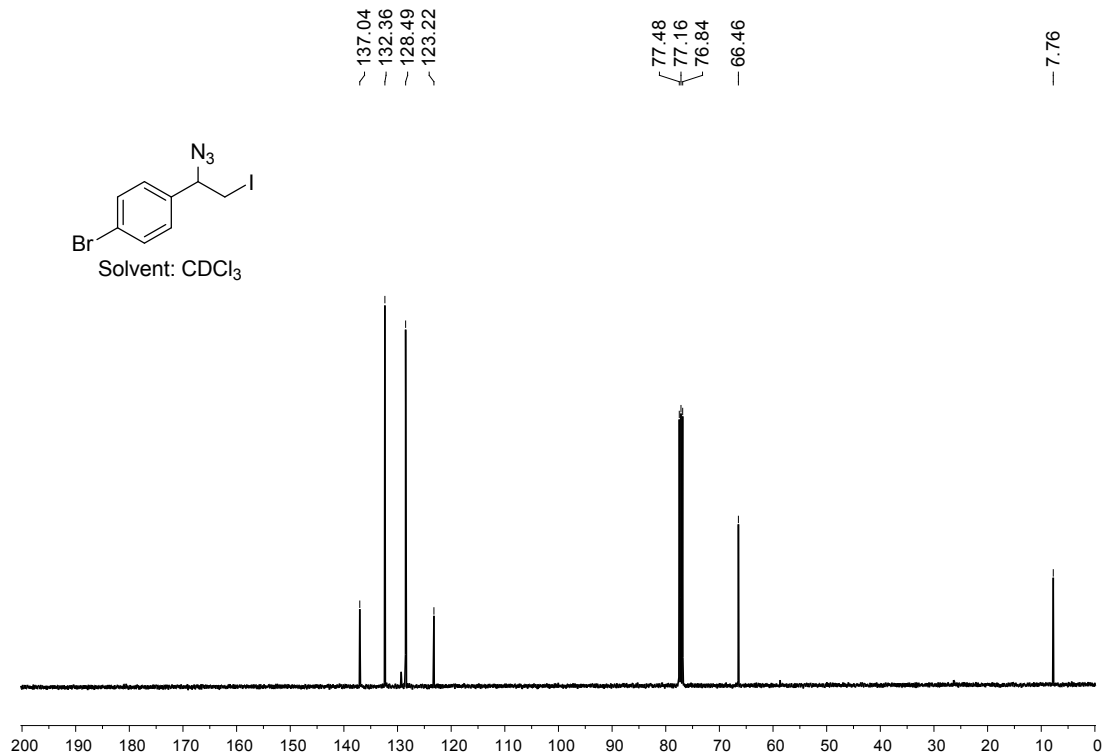


Figure S4: ¹³C NMR spectrum of 1-(1-azido-2-iodoethyl)-4-bromobenzene (**2b**).

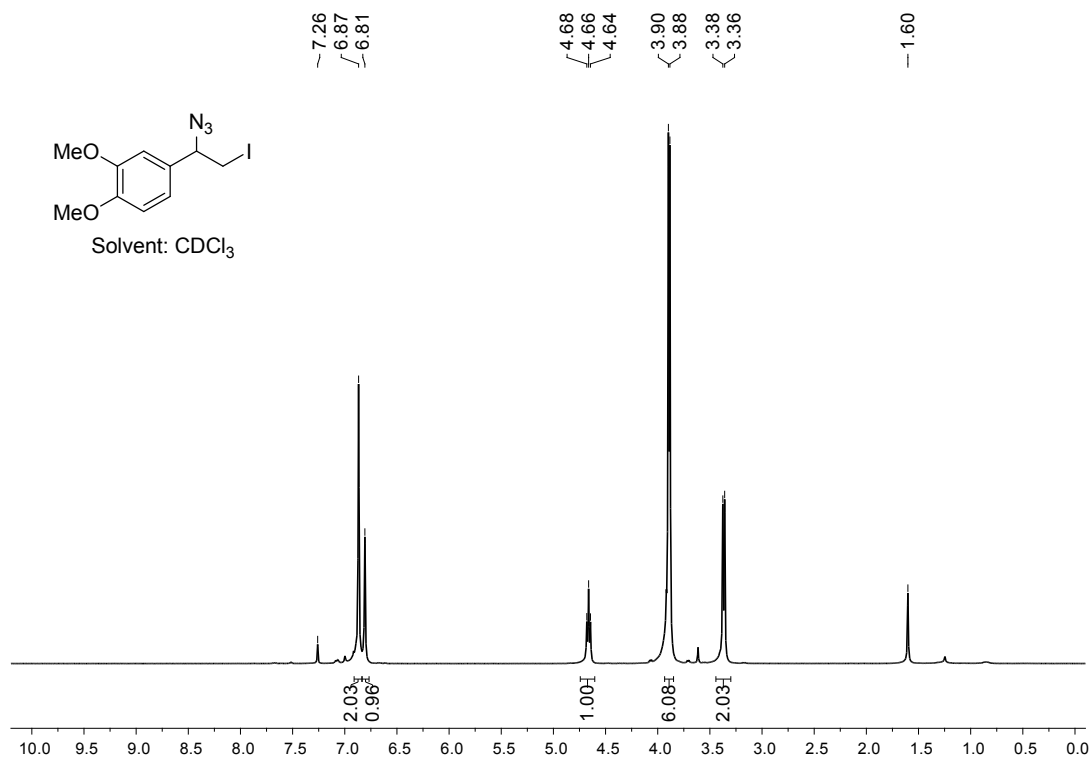


Figure S5: ^1H NMR spectrum of 4-(1-azido-2-iodoethyl)-1,2-dimethoxybenzene (**2c**).

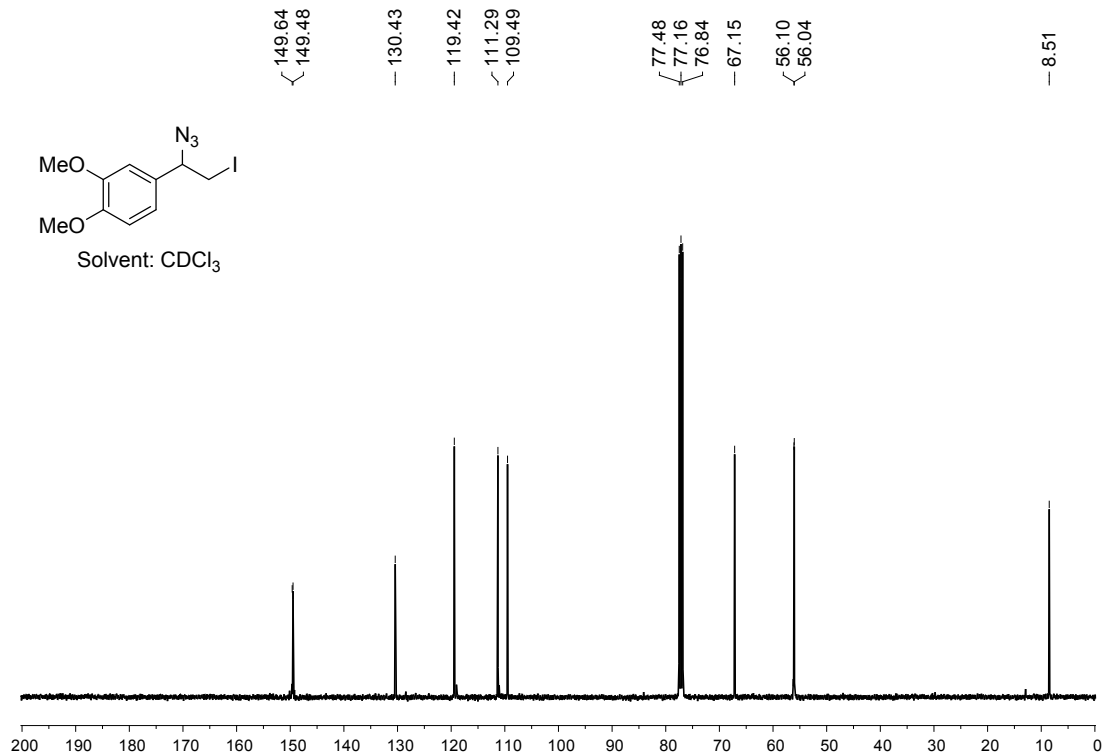


Figure S6: ^{13}C NMR spectrum of 4-(1-azido-2-iodoethyl)-1,2-dimethoxybenzene (**2c**).

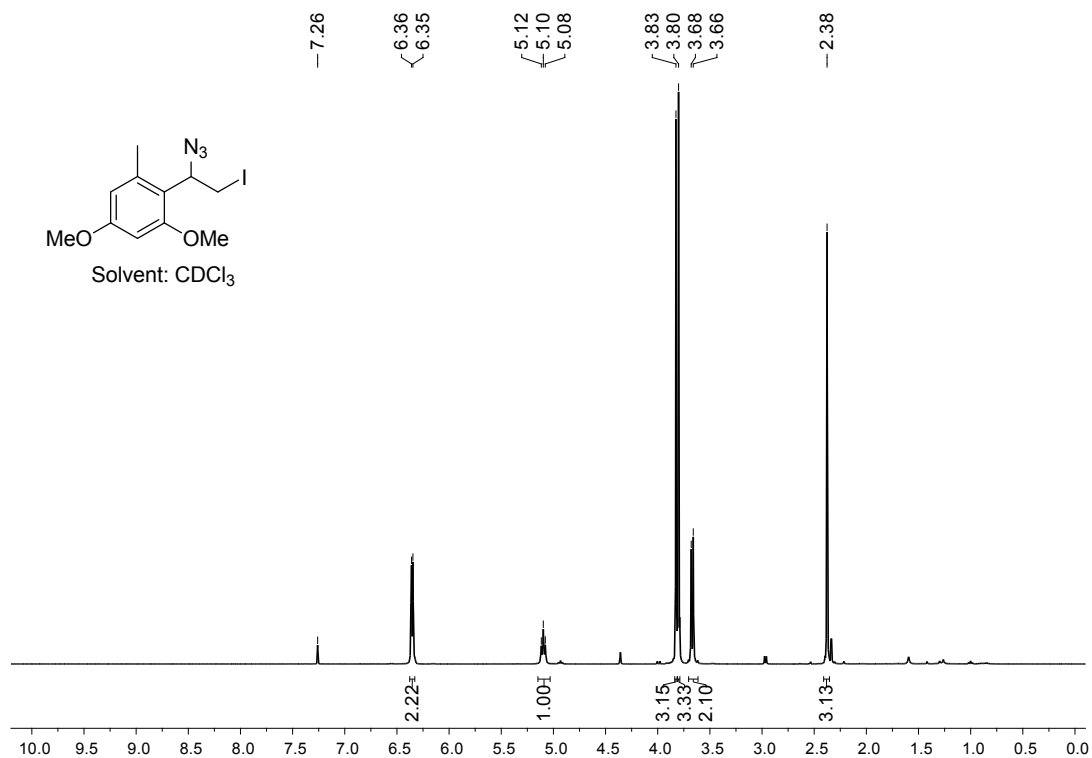


Figure S7: ^1H NMR spectrum of 2-(1-azido-2-iodoethyl)-1,5-dimethoxy-3-methylbenzene (**2d**).

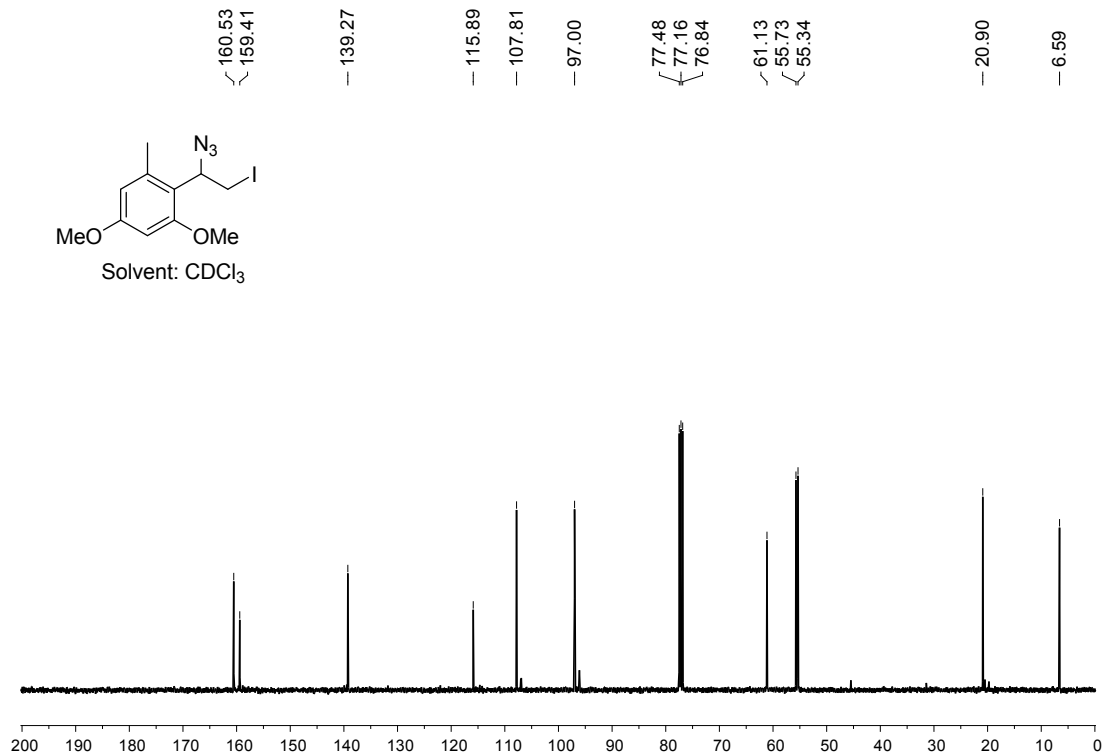


Figure S8: ^{13}C NMR spectrum of 2-(1-azido-2-iodoethyl)-1,5-dimethoxy-3-methylbenzene (**2d**).

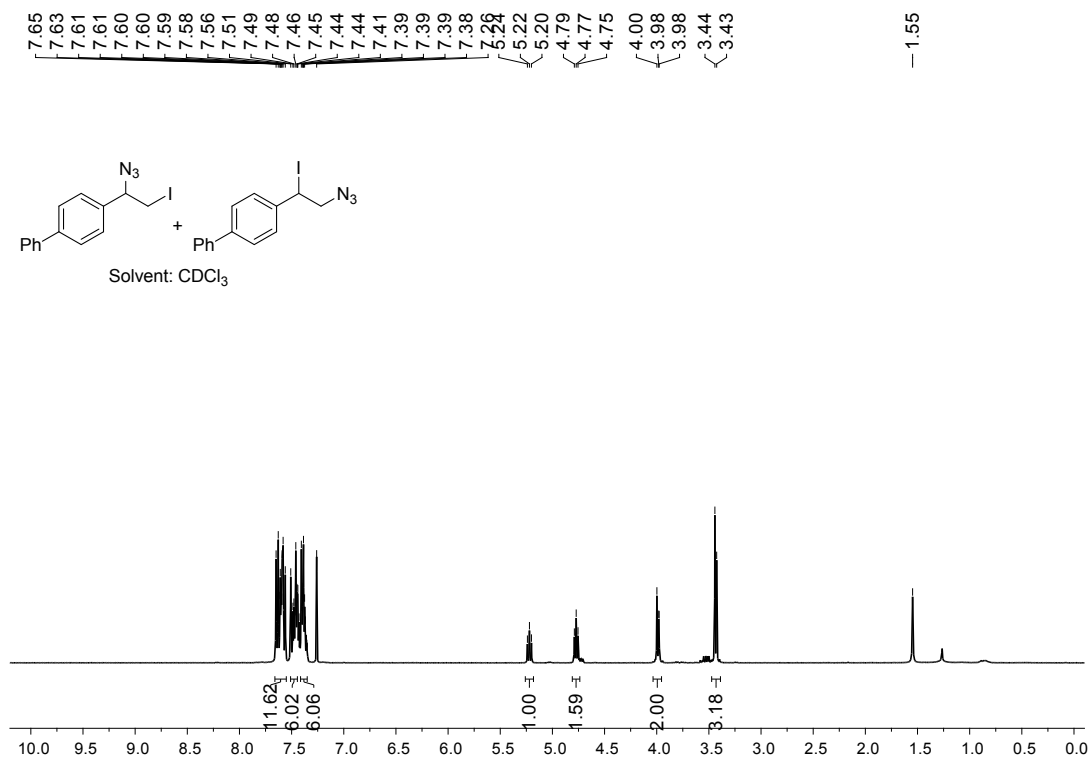


Figure S9: ¹H NMR spectrum of 4-(1-azido-2-iodoethyl)-1,1'-biphenyl (**2e**).

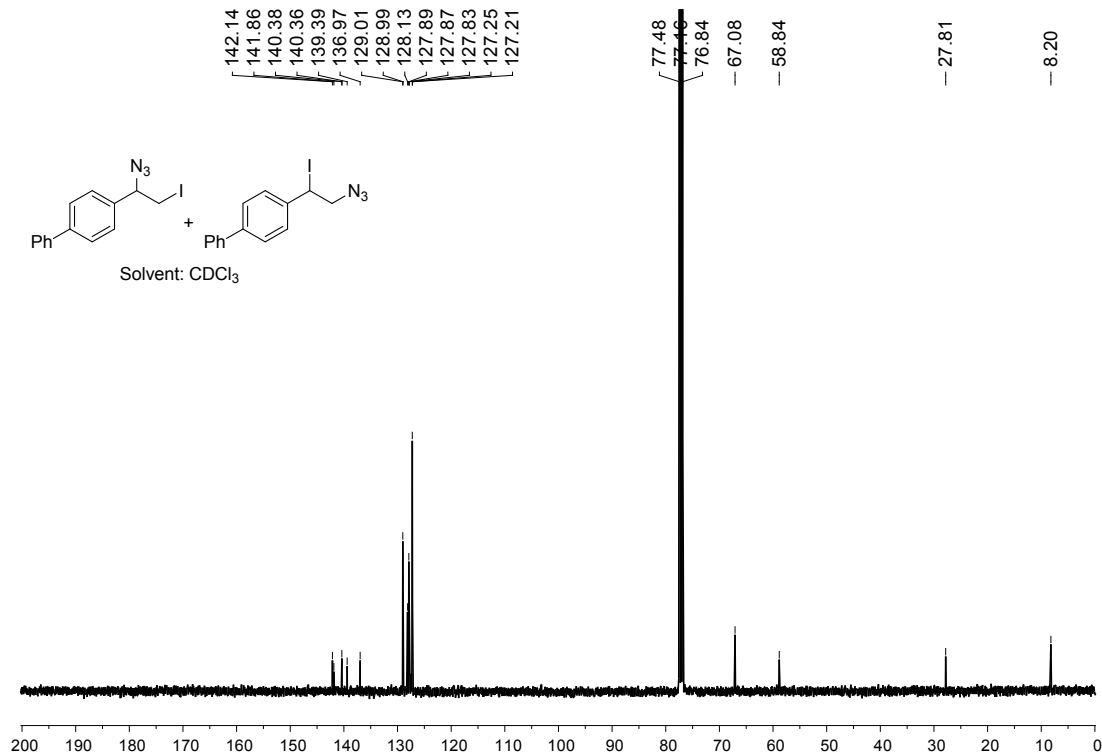


Figure S10: ¹³C NMR spectrum of 4-(1-azido-2-iodoethyl)-1,1'-biphenyl (**2e**).

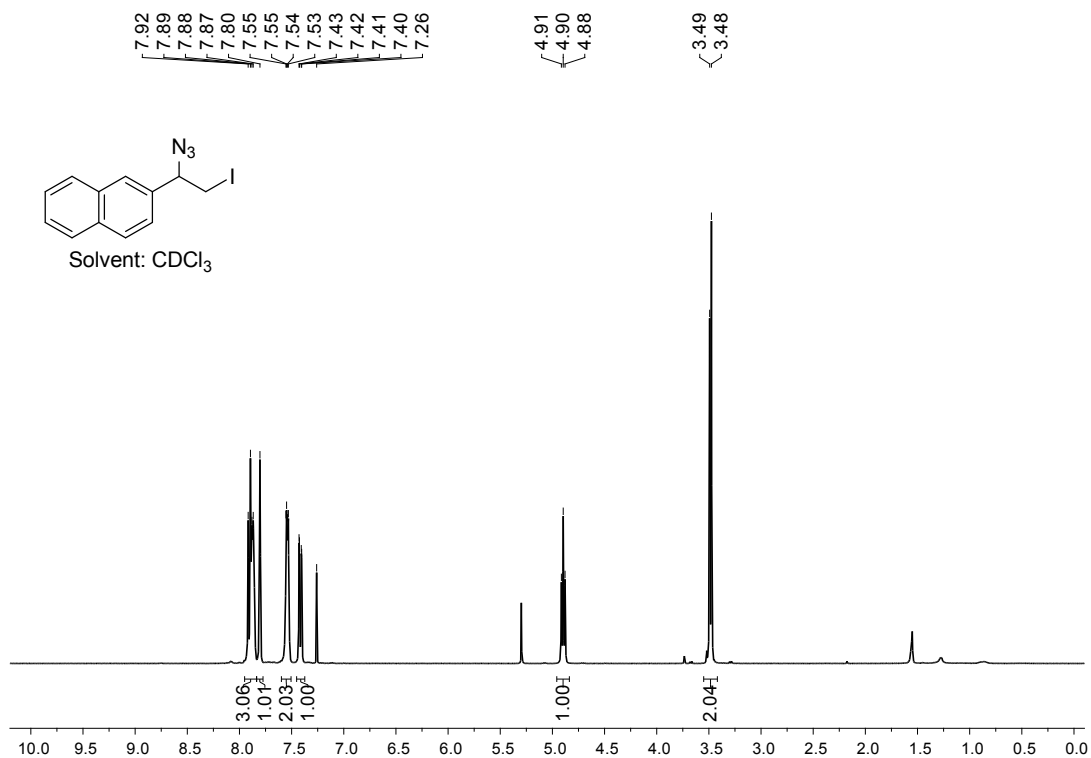


Figure S11: ¹H NMR spectrum of 2-(1-azido-2-iodoethyl)naphthalene (**2f**).

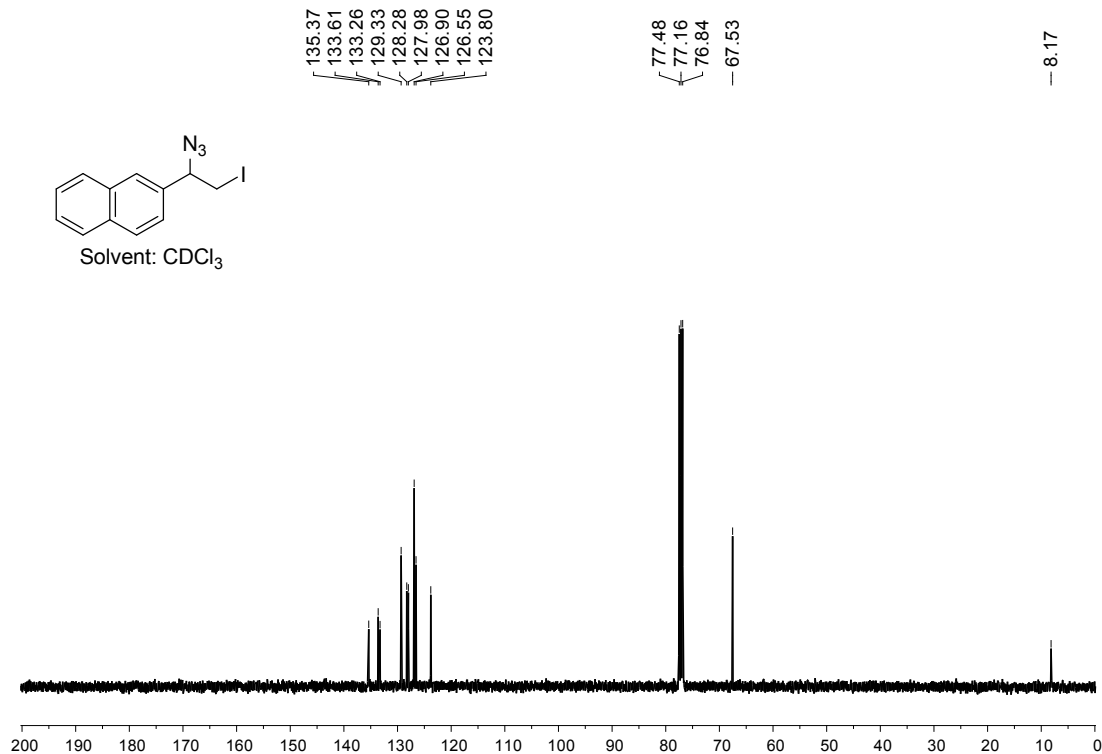


Figure S12: ¹³C NMR spectrum of 2-(1-azido-2-iodoethyl)naphthalene (**2f**).

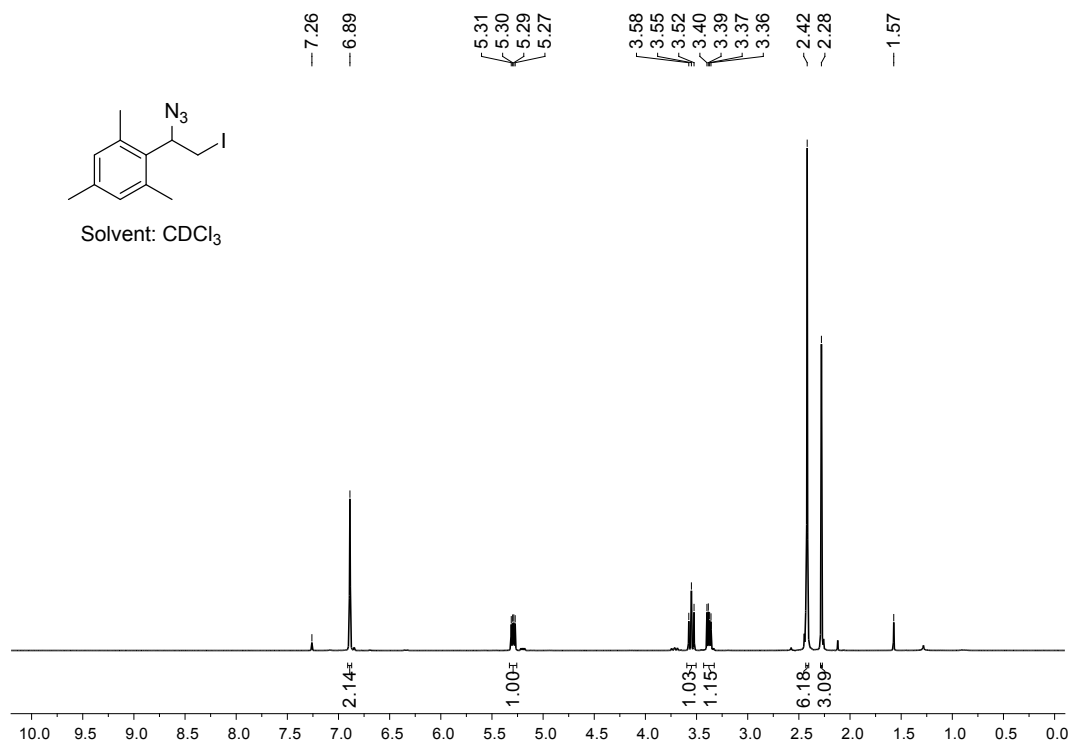


Figure S13: ¹H NMR spectrum of 2-(1-azido-2-iodoethyl)-1,3,5-trimethylbenzene (**2g**).

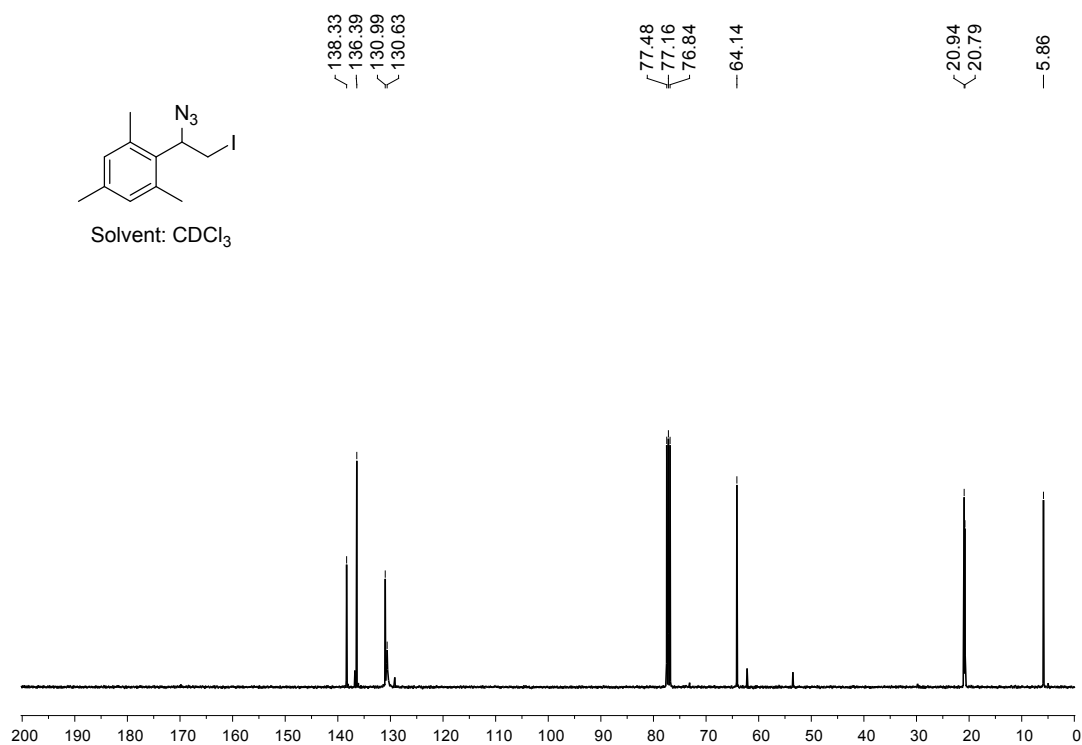


Figure S14: ¹³C NMR spectrum of 2-(1-azido-2-iodoethyl)-1,3,5-trimethylbenzene (**2g**).

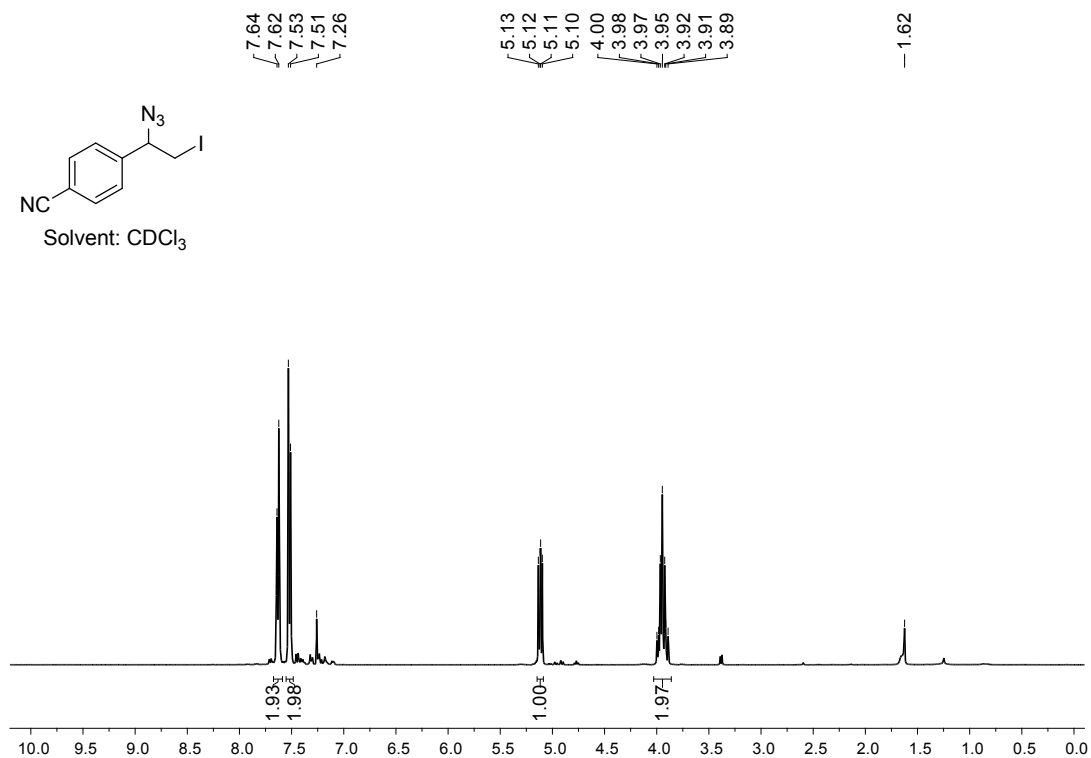


Figure S15: ¹H NMR spectrum of 4-(1-azido-2-iodoethyl)benzonitrile (**2h**).

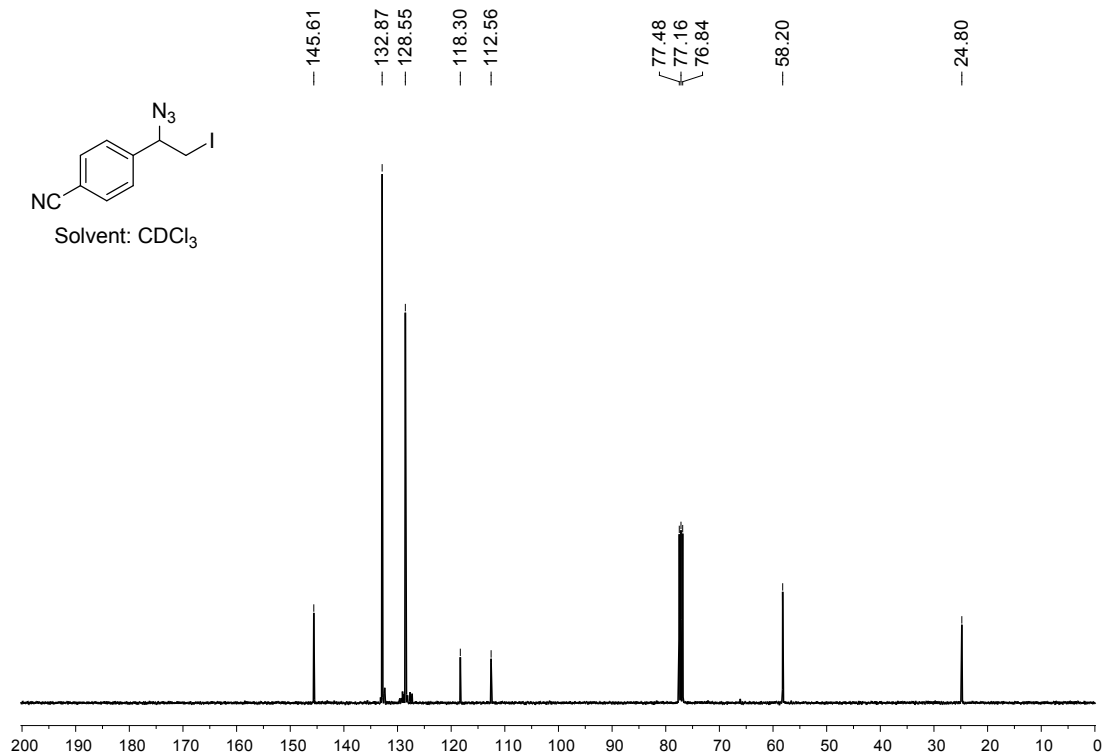


Figure S16: ¹³C NMR spectrum of 4-(1-azido-2-iodoethyl)benzonitrile (**2h**).

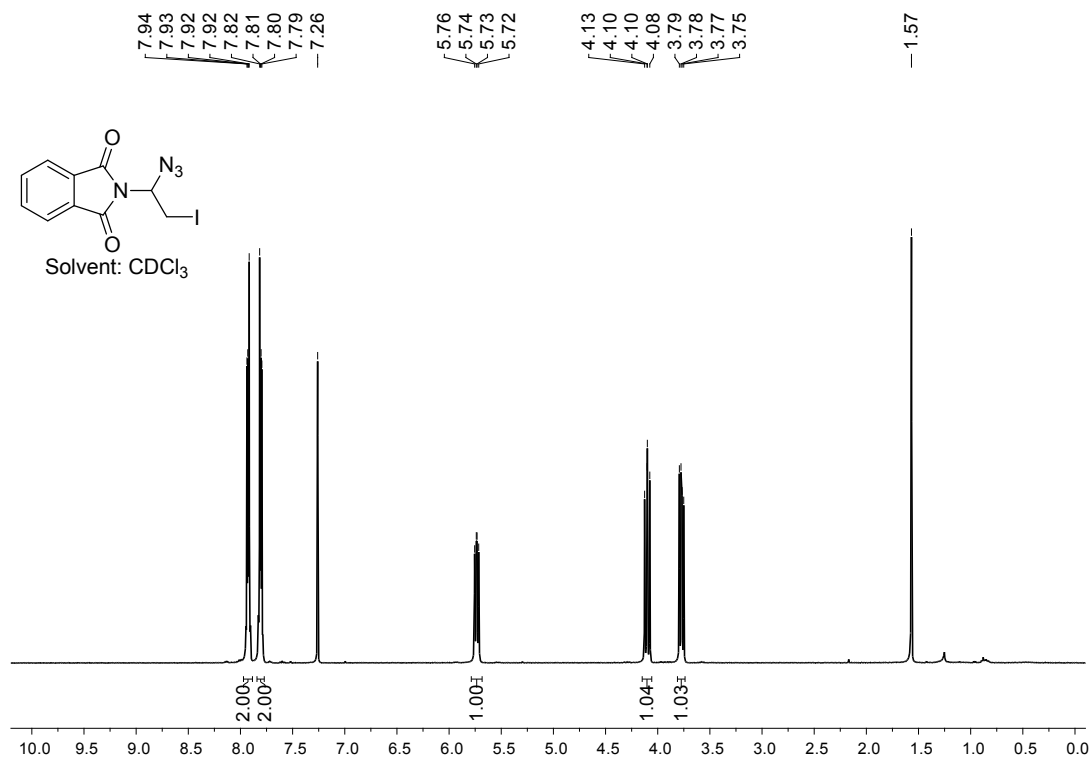


Figure S17: ¹H NMR spectrum of 2-(1-azido-2-iodoethyl)isoindoline-1,3-dione (**2i**).

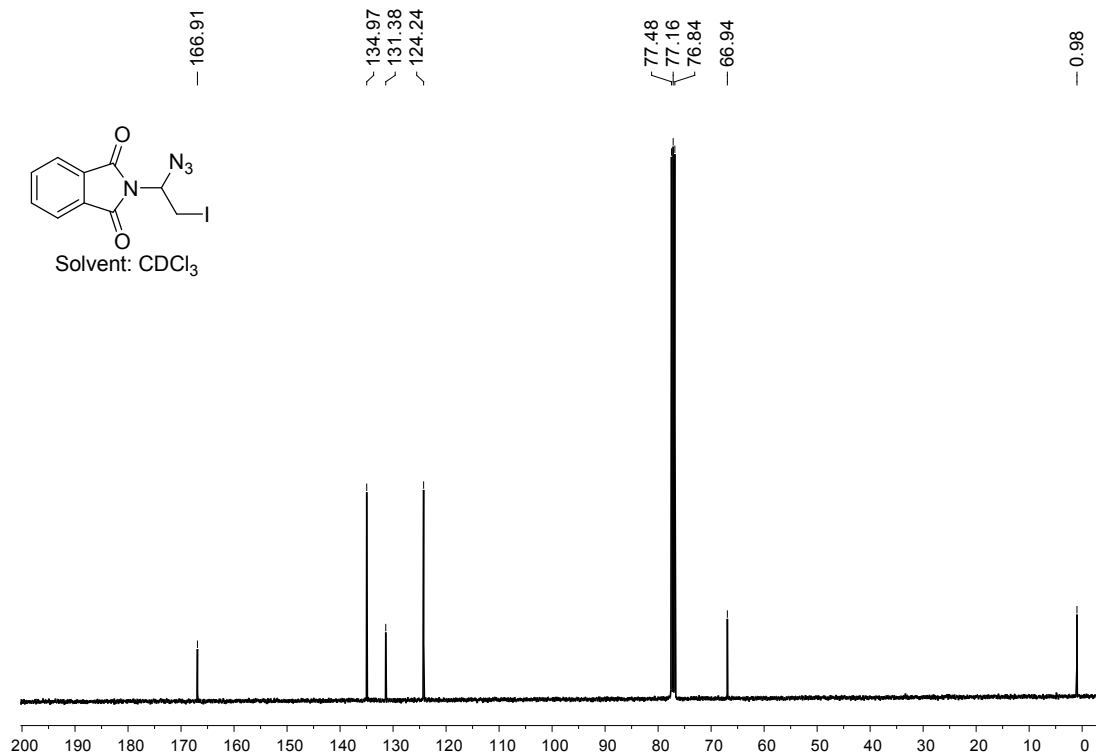


Figure S18: ¹³C NMR spectrum of 2-(1-azido-2-iodoethyl)isoindoline-1,3-dione (**2i**).

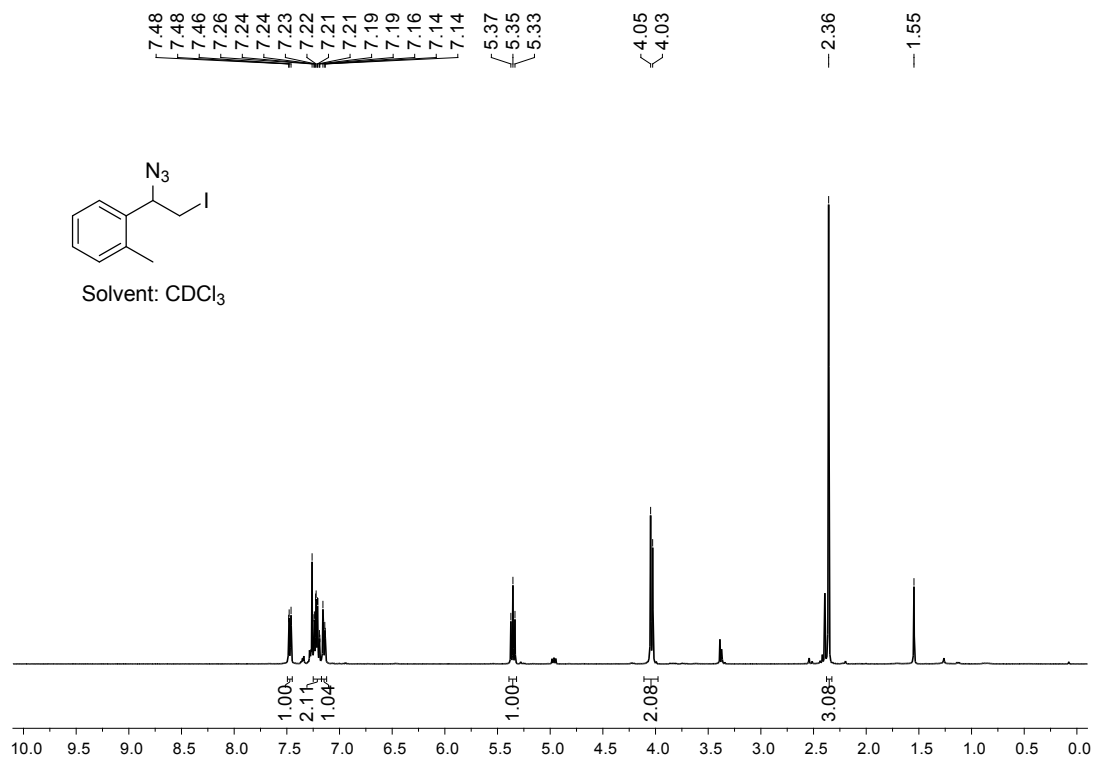


Figure S19: ^1H NMR spectrum of 1-(1-azido-2-iodoethyl)-2-methylbenzene (**2j**).

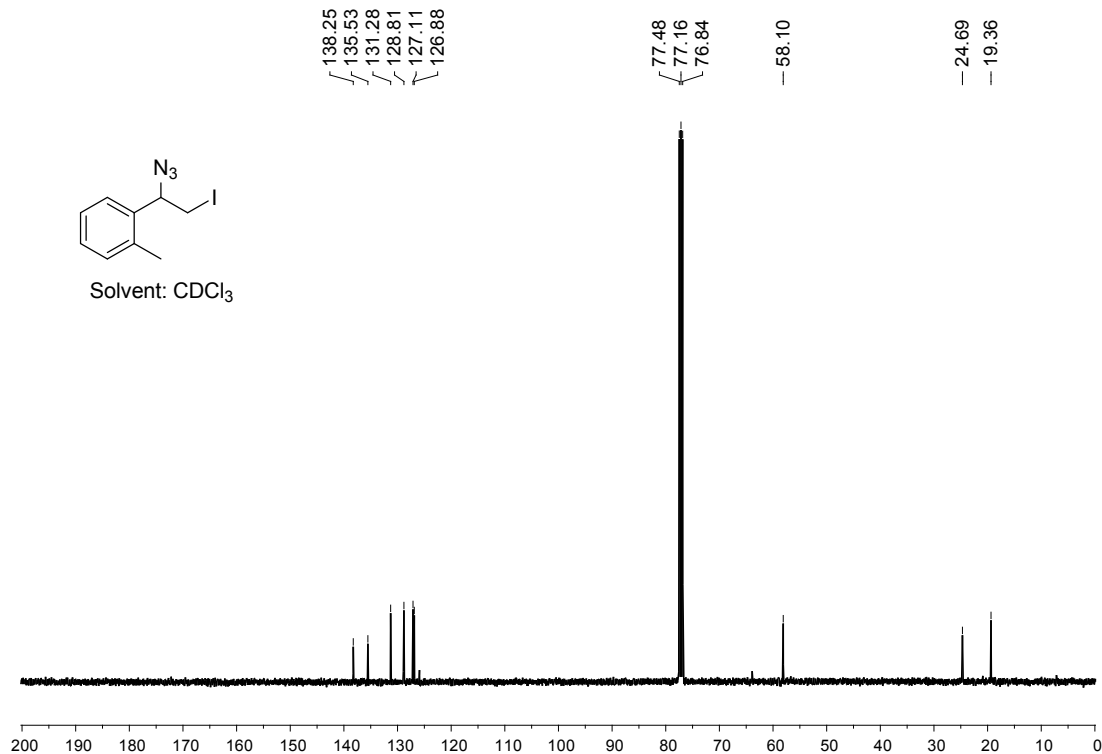


Figure S20: ^{13}C NMR spectrum of 1-(1-azido-2-iodoethyl)-2-methylbenzene (**2j**).

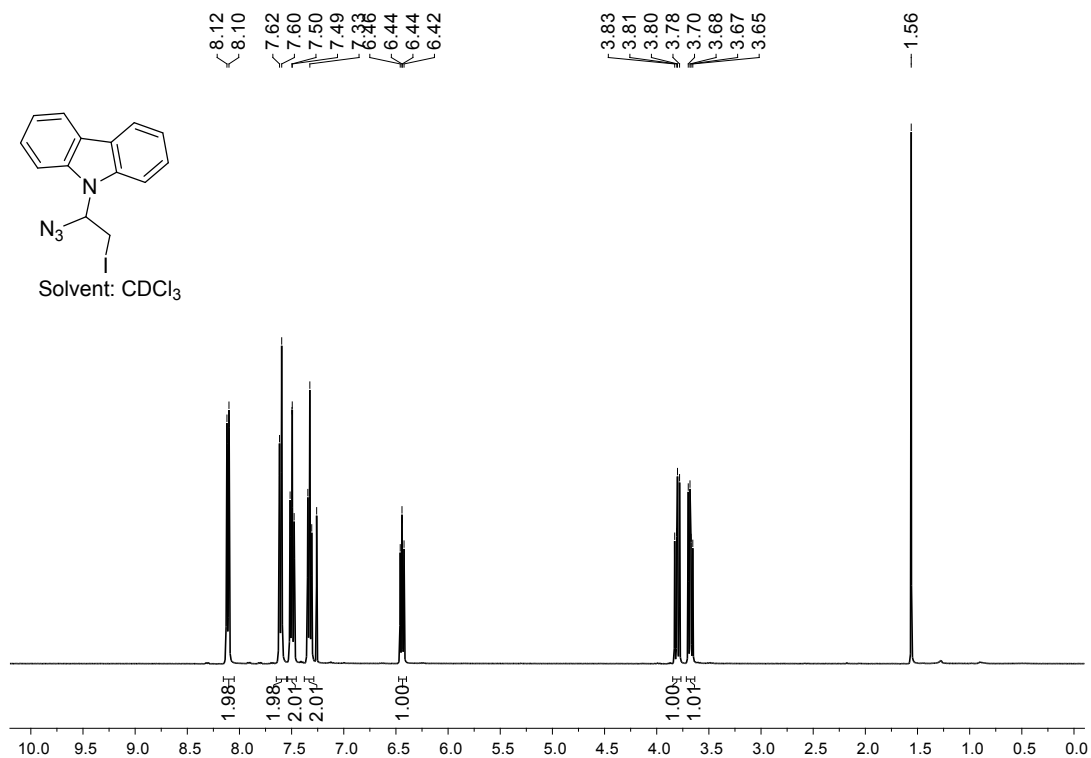


Figure S21: ¹H NMR spectrum of 9-(1-azido-2-iodoethyl)-9H-carbazole (**2k**).

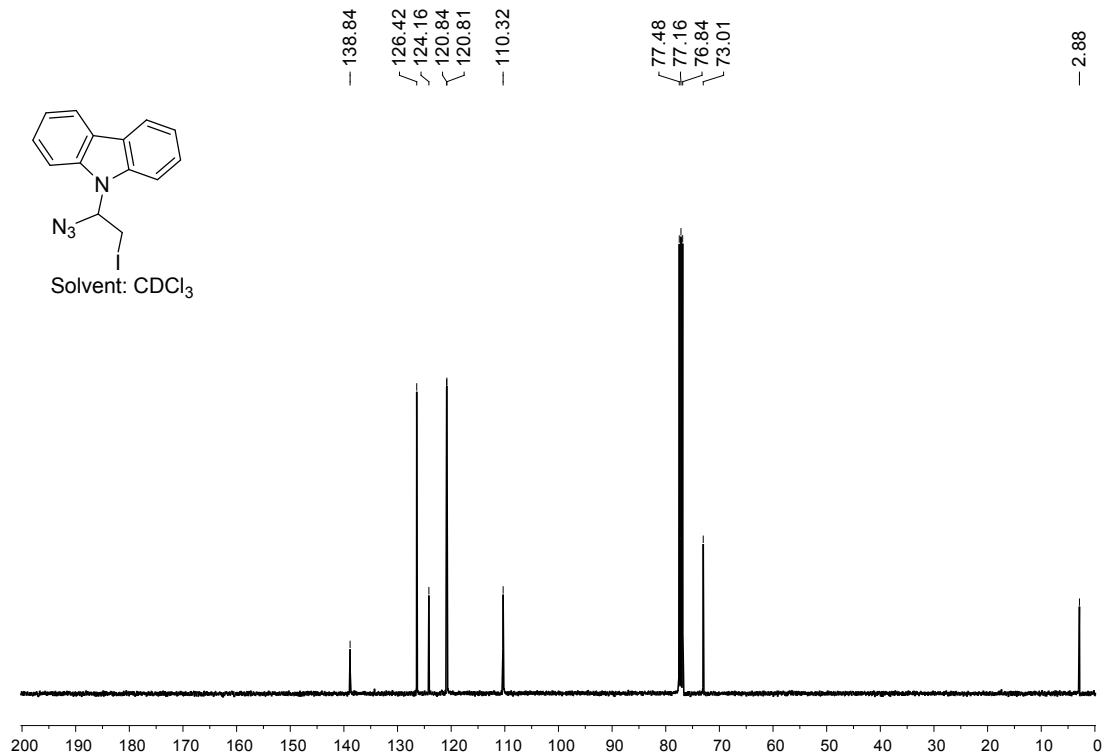


Figure S22: ¹³C NMR spectrum of 9-(1-azido-2-iodoethyl)-9H-carbazole (**2k**).

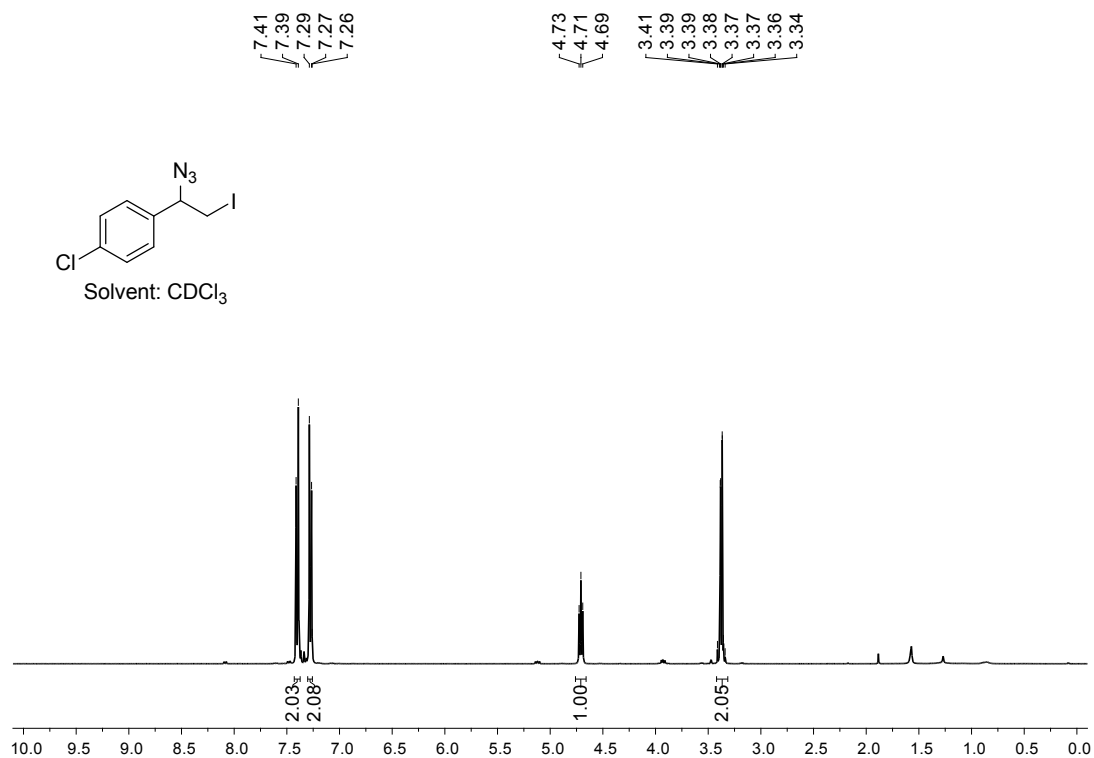


Figure S23: ¹H NMR spectrum of 1-(1-azido-2-iodoethyl)-4-chlorobenzene (**21**).

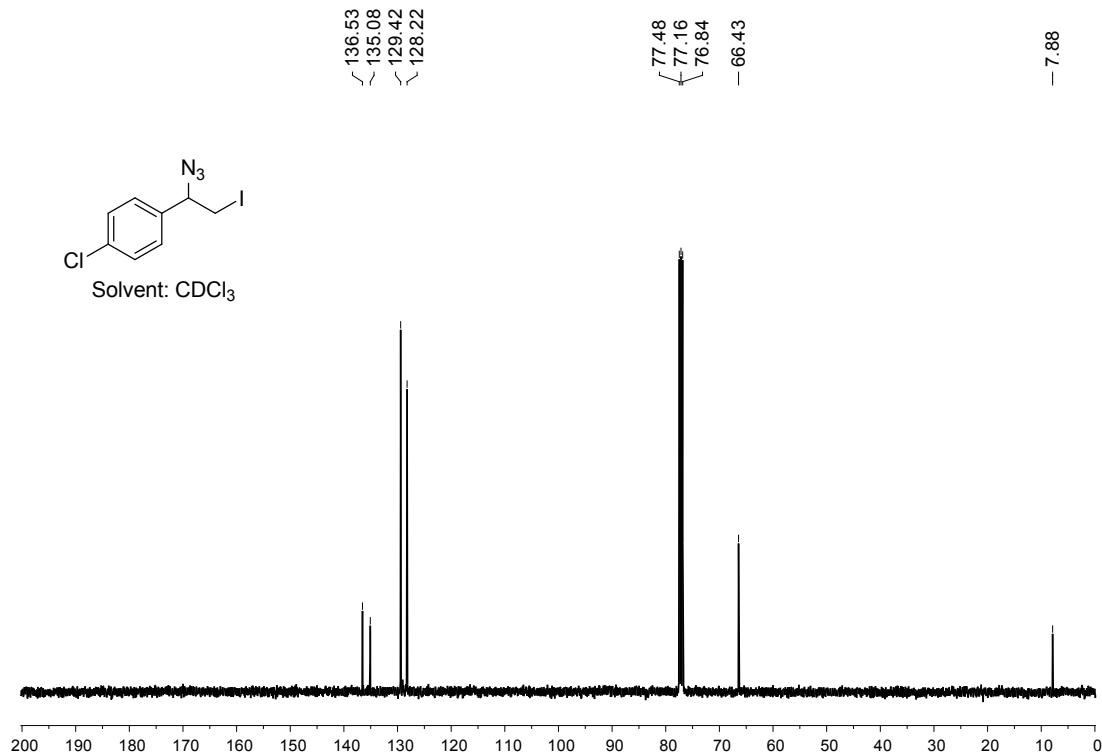


Figure S24: ¹³C NMR spectrum of 1-(1-azido-2-iodoethyl)-4-chlorobenzene (**21**).

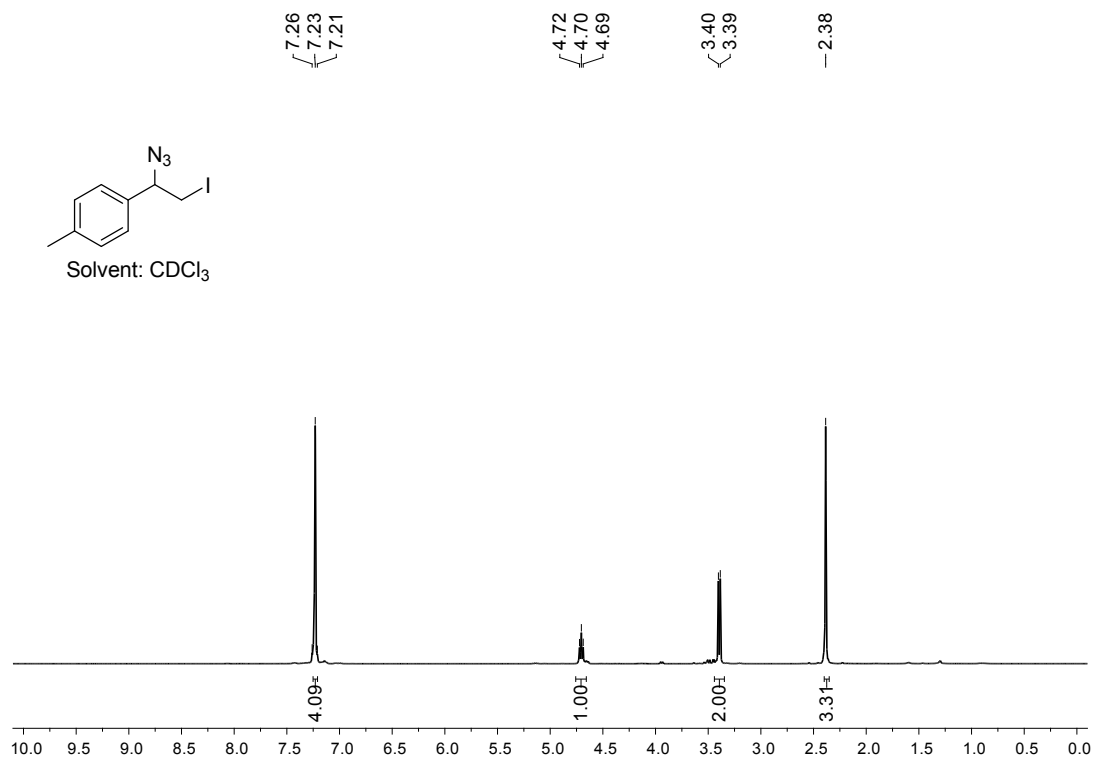


Figure S25: ¹H NMR spectrum of 1-(1-azido-2-iodoethyl)-4-methylbenzene (**2m**).

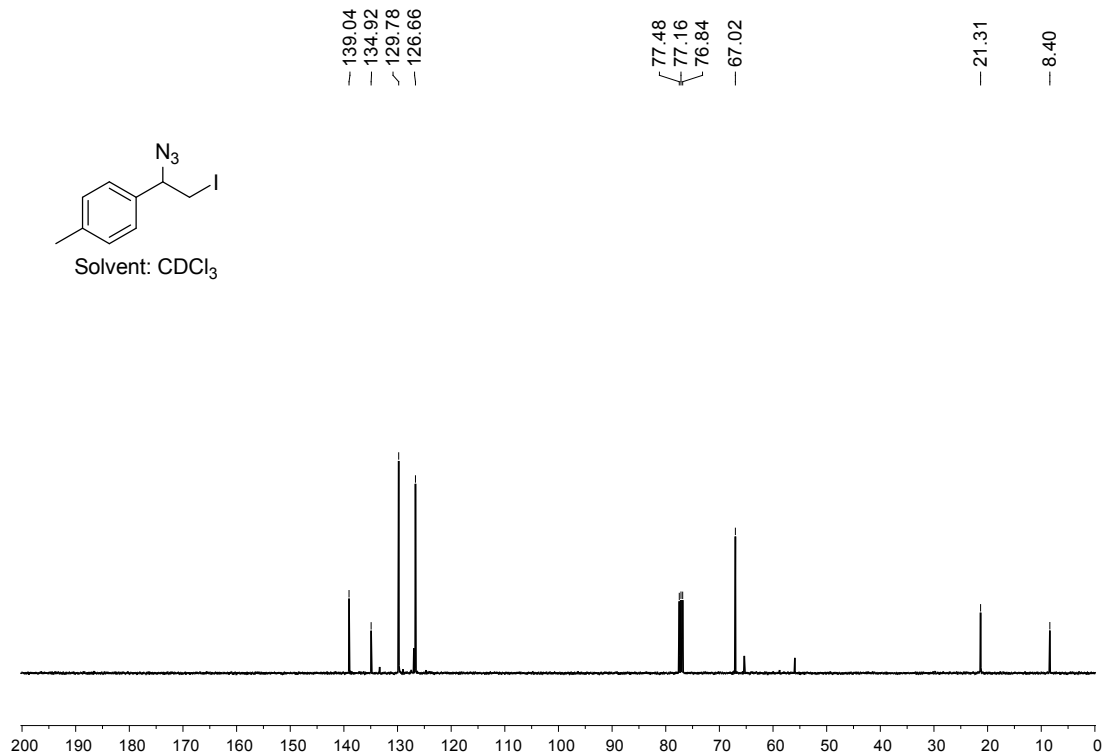


Figure S26: ¹³C NMR spectrum of 1-(1-azido-2-iodoethyl)-4-methylbenzene (**2m**).

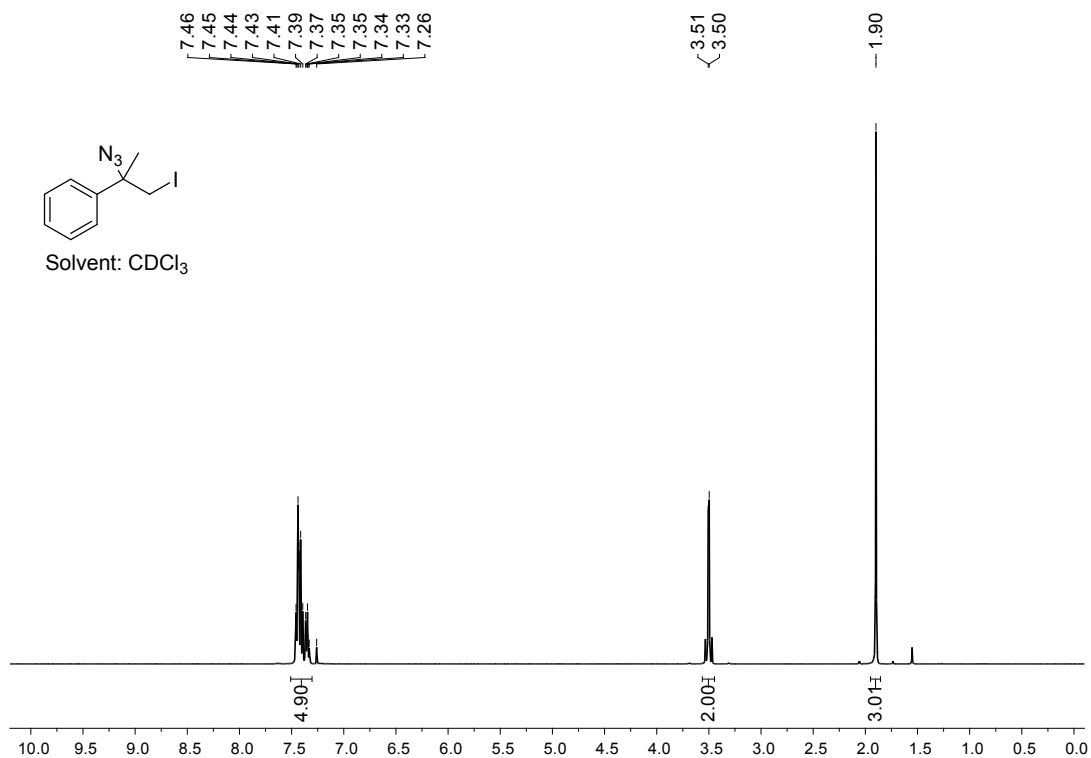


Figure S27: ^1H NMR spectrum of (2-azido-1-iodopropan-2-yl)benzene (**2n**).

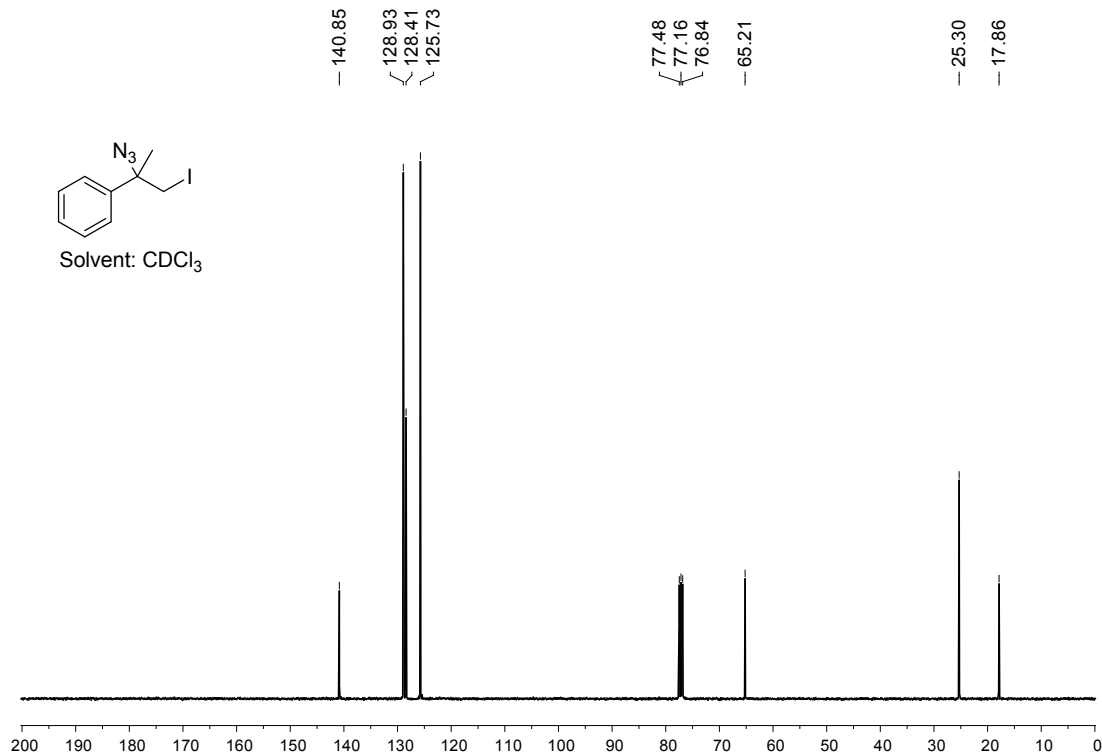


Figure S28: ^{13}C NMR spectrum of (2-azido-1-iodopropan-2-yl)benzene (**2n**).

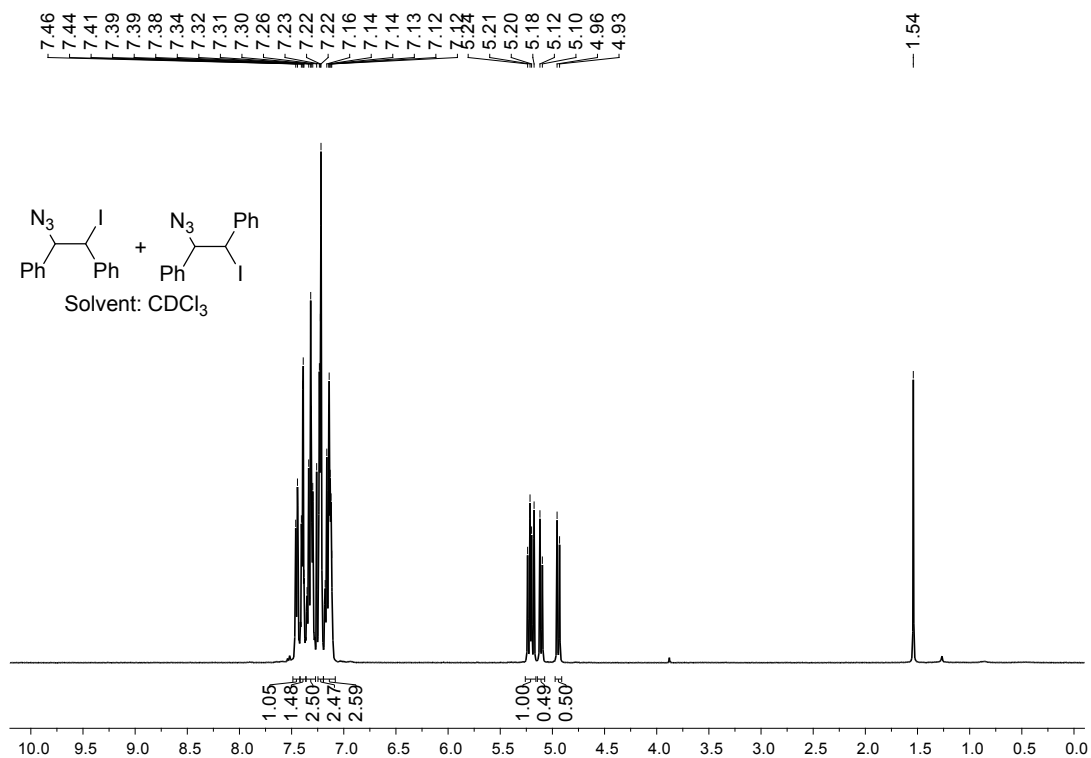


Figure S29: ¹H NMR spectrum of (1-azido-2-iodoethane-1,2-diyl)dibenzene (**2o**).

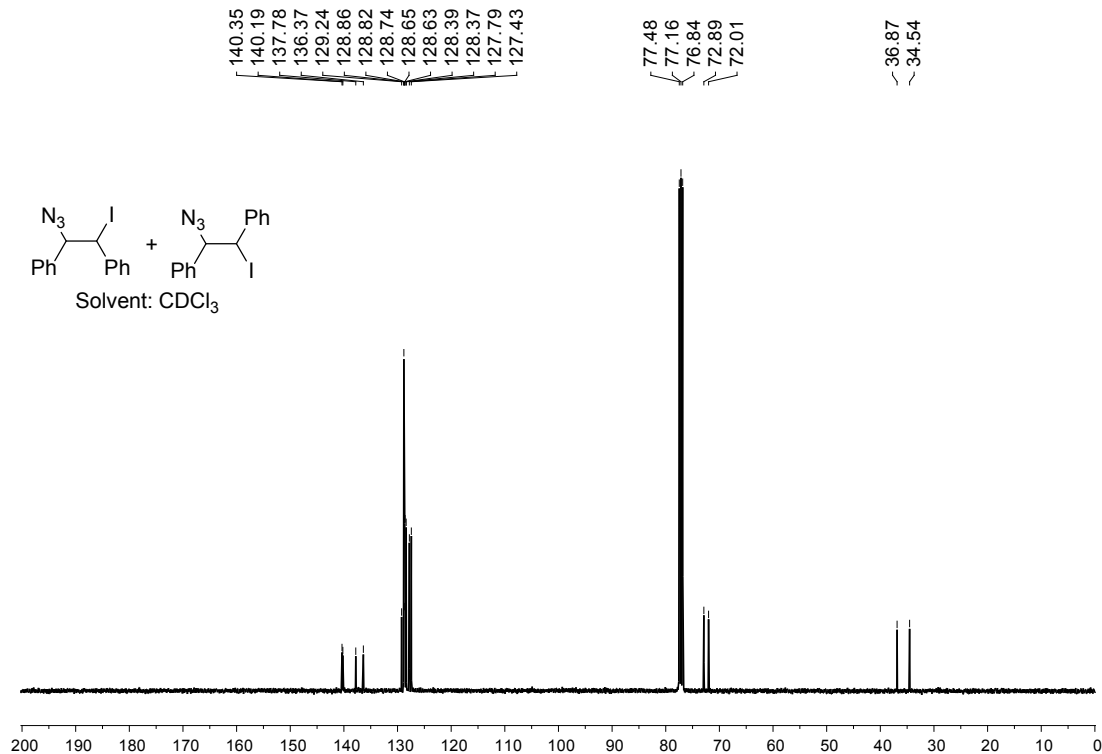


Figure S30: ¹³C NMR spectrum of (1-azido-2-iodoethane-1,2-diyl)dibenzene (**2o**).

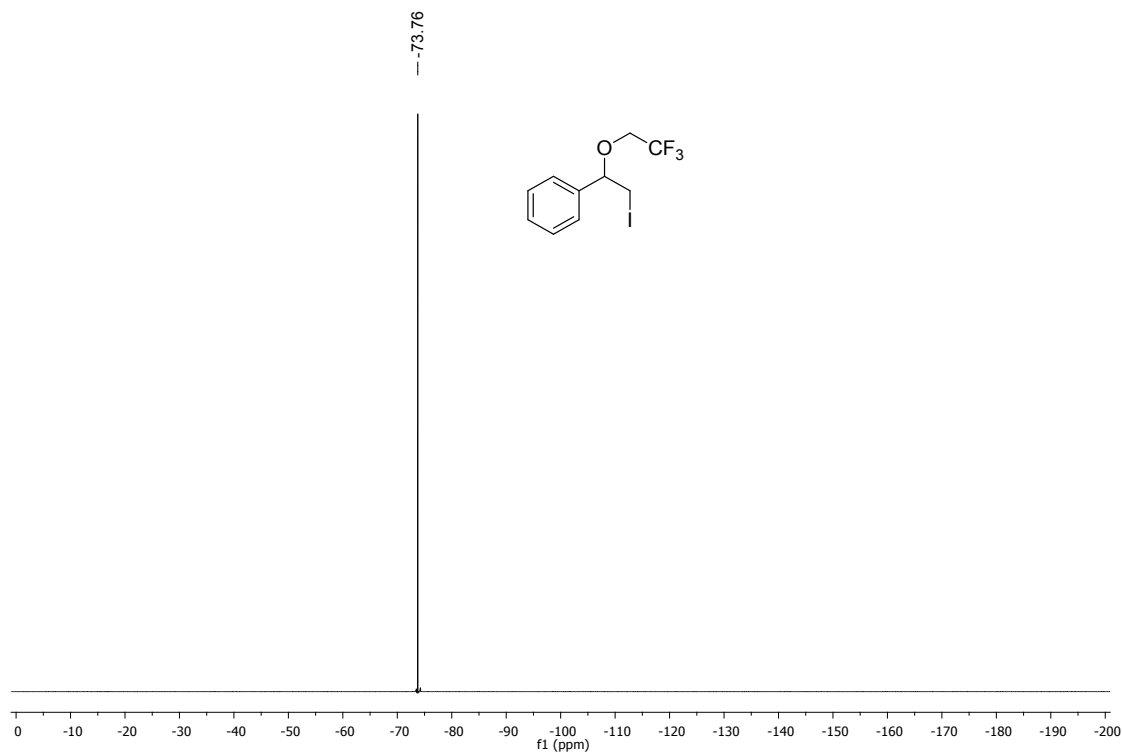


Figure 31: ^{19}F spectrum of (2-iodo-1-(2,2,2-trifluoroethoxy)ethyl)benzene (**3a**)

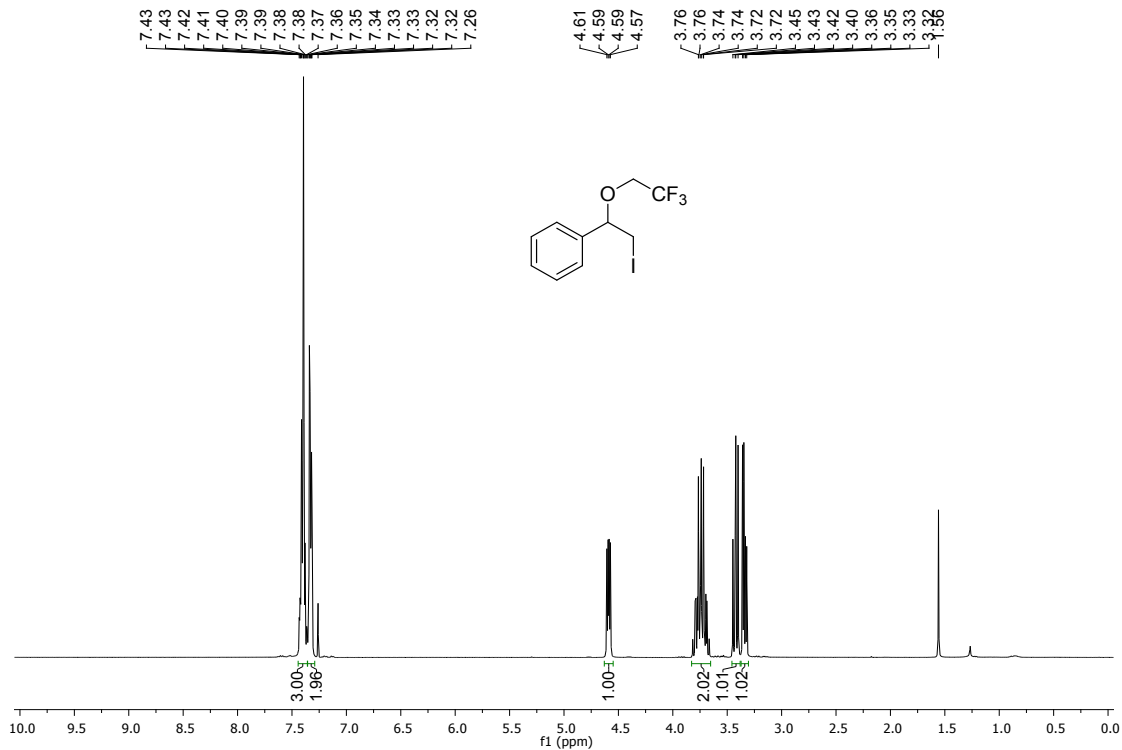


Figure 32: ^1H spectrum of (2-iodo-1-(2,2,2-trifluoroethoxy)ethyl)benzene (**3a**)

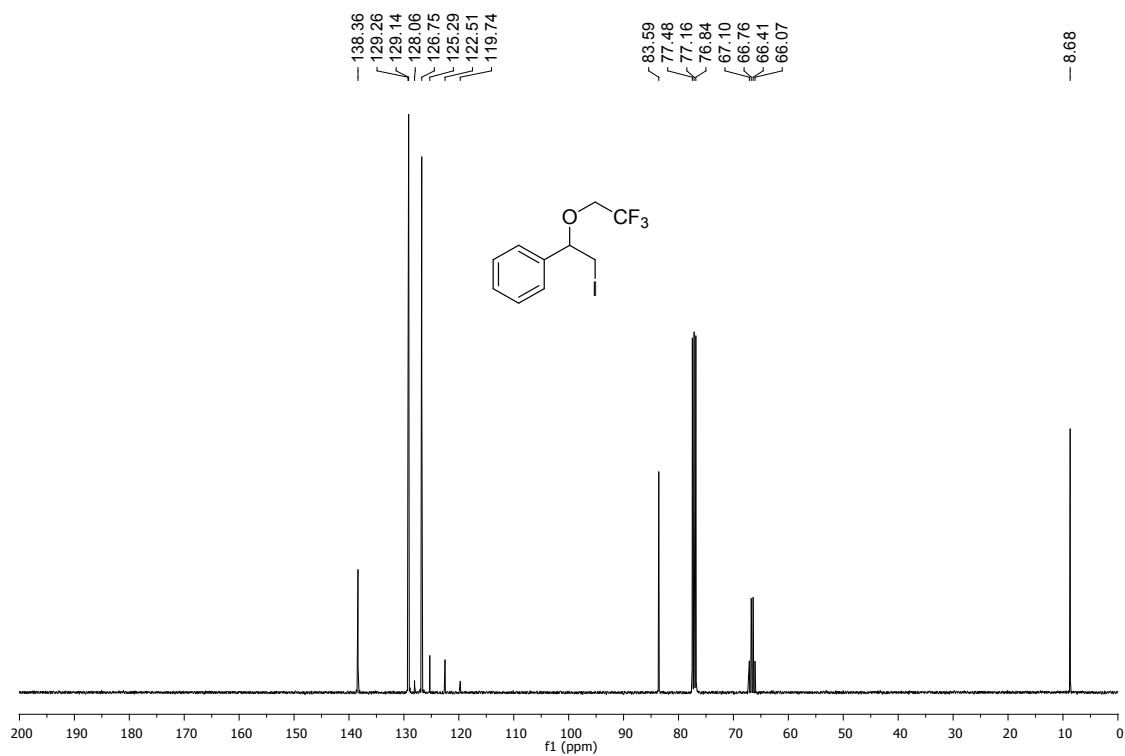


Figure 33: ¹³C spectrum of (2-iodo-1-(2,2,2-trifluoroethoxy)ethyl)benzene (**3a**)

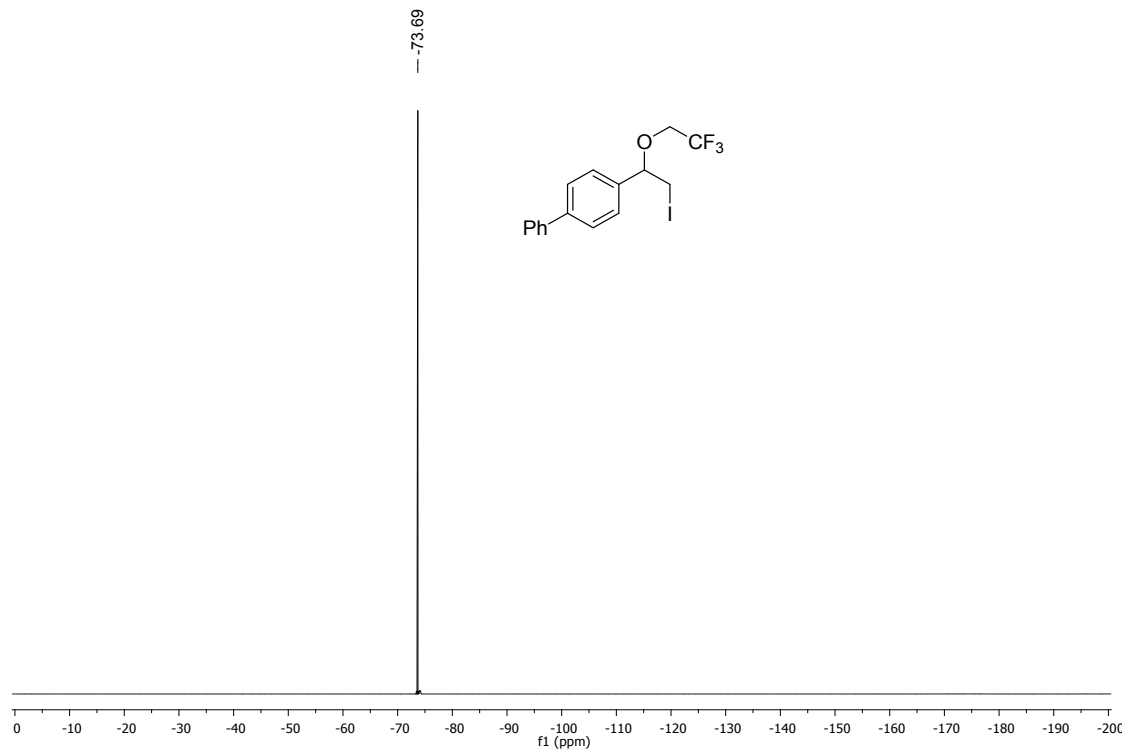


Figure 34: ¹⁹F spectrum of 4-(2-iodo-1-(2,2,2-trifluoroethoxy)ethyl)-1,1'-biphenyl (**3b**)

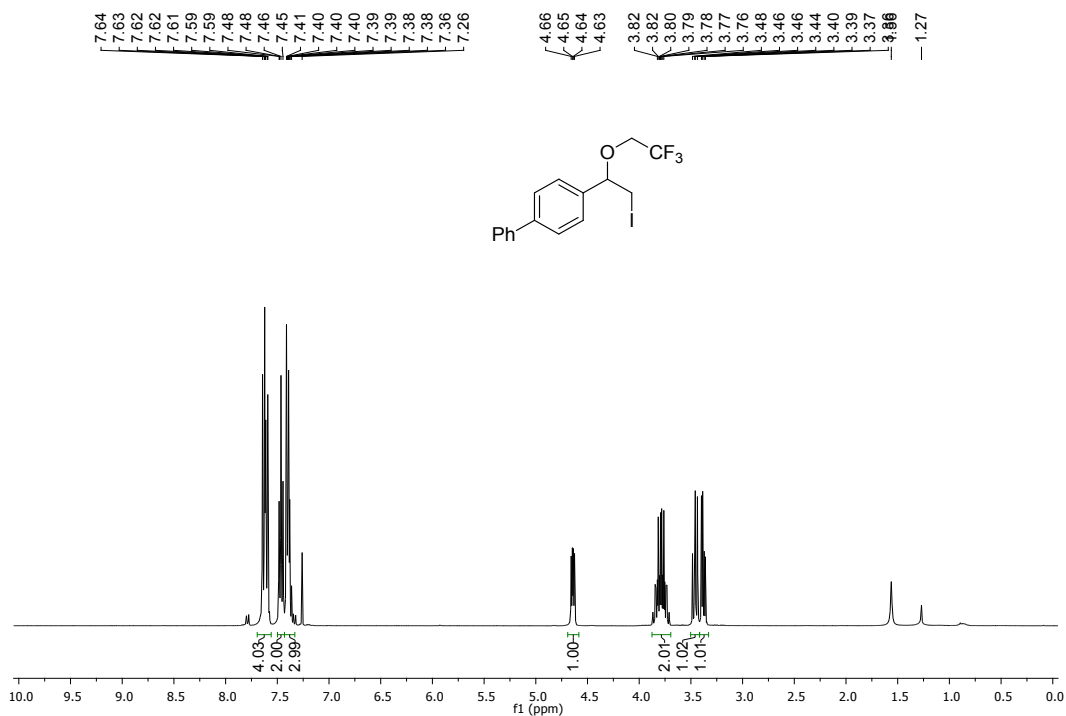


Figure 35: ¹H spectrum of 4-(2-iodo-1-(2,2,2-trifluoroethoxy)ethyl)-1,1'-biphenyl (**3b**)

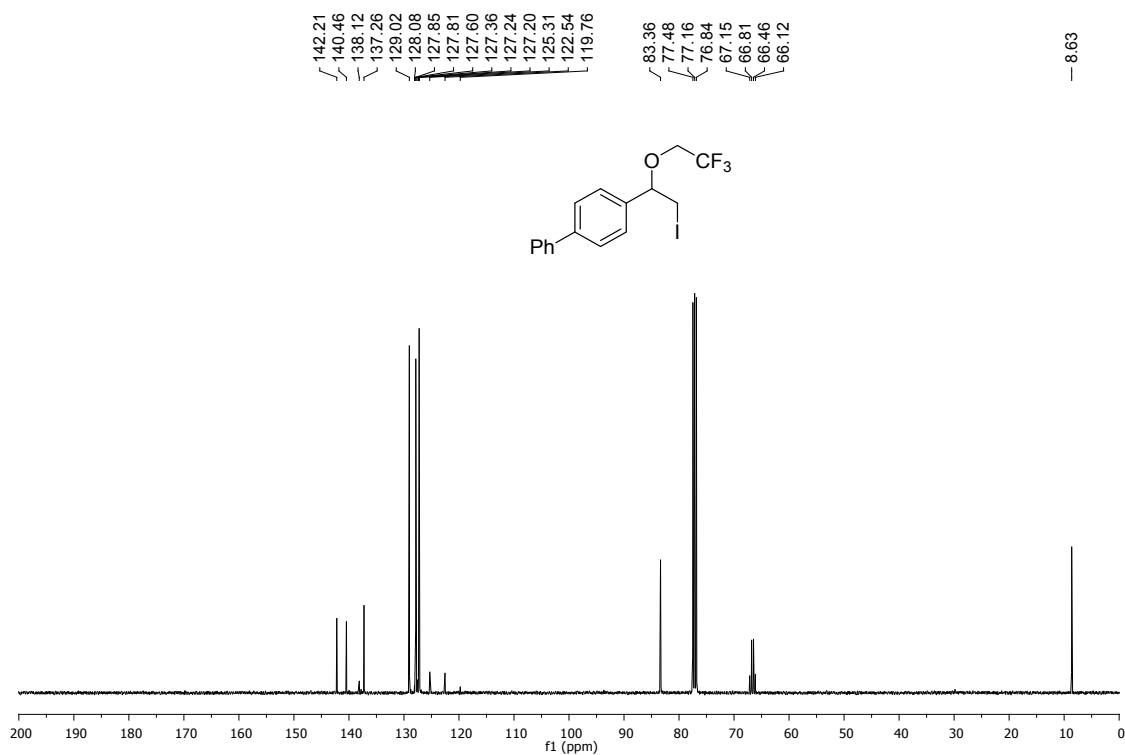


Figure 36: ¹³C spectrum of 4-(2-iodo-1-(2,2,2-trifluoroethoxy)ethyl)-1,1'-biphenyl (**3b**)

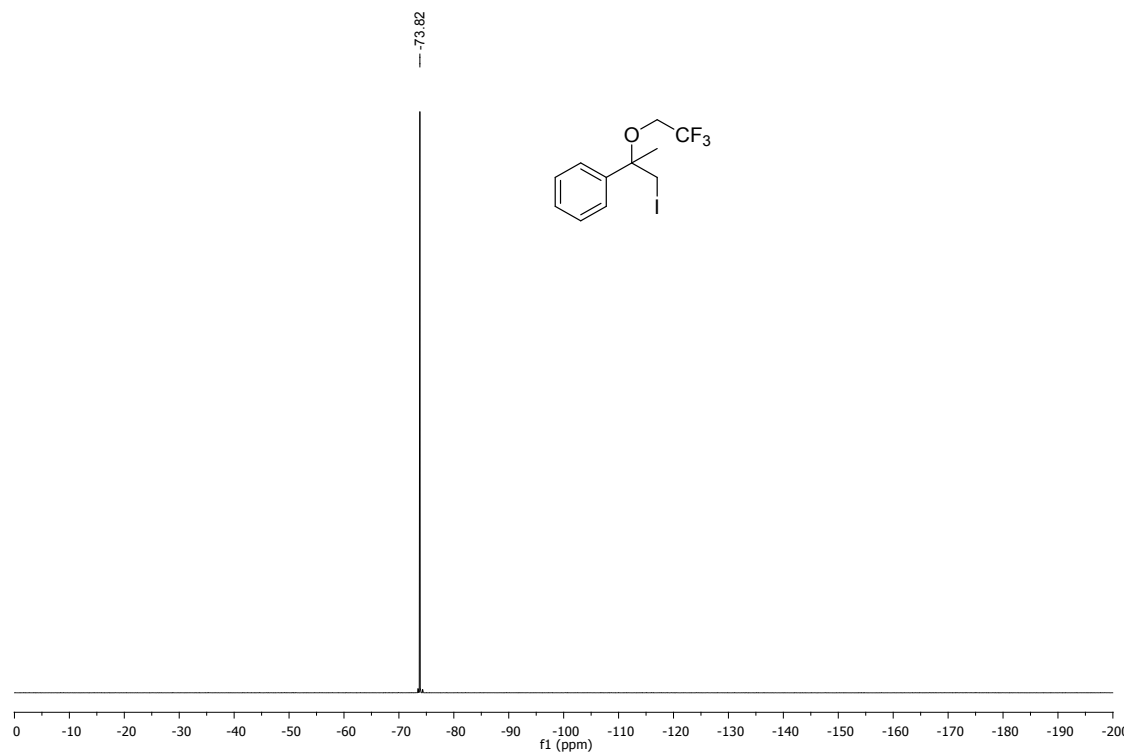


Figure 37: ^{19}F spectrum of (1-iodo-2-(2,2,2-trifluoroethoxy)propan-2-yl)benzene (**3c**)

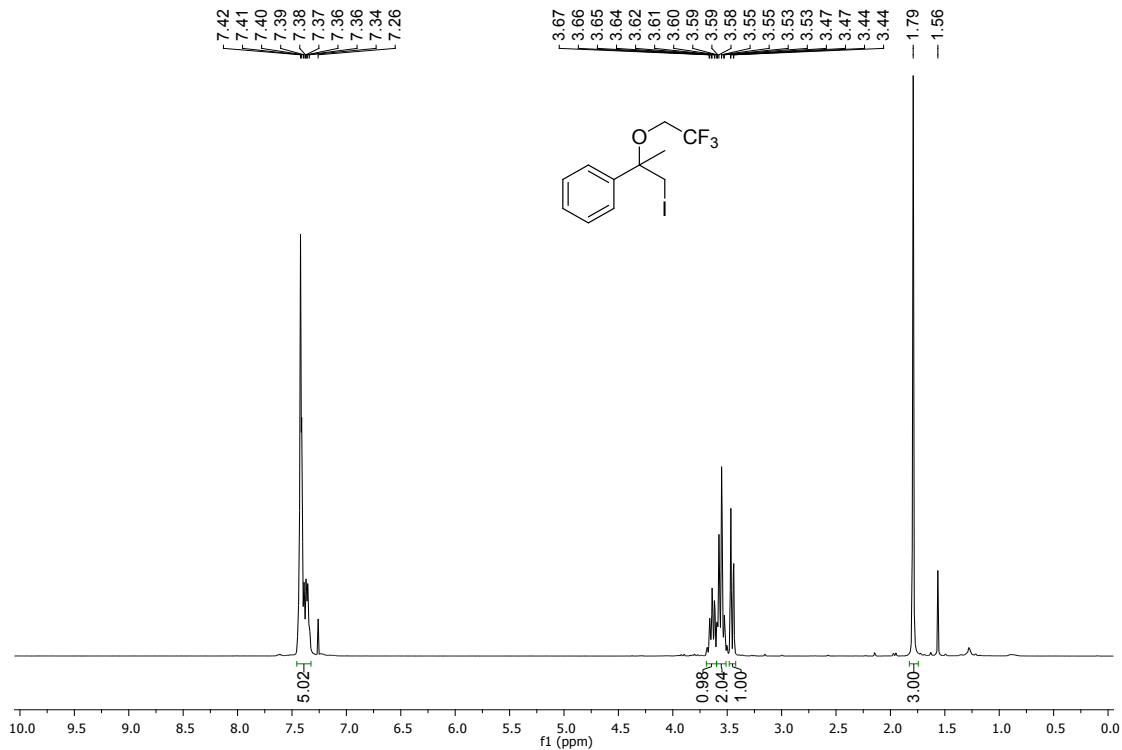


Figure 38: ^1H spectrum of (1-iodo-2-(2,2,2-trifluoroethoxy)propan-2-yl)benzene (**3c**)

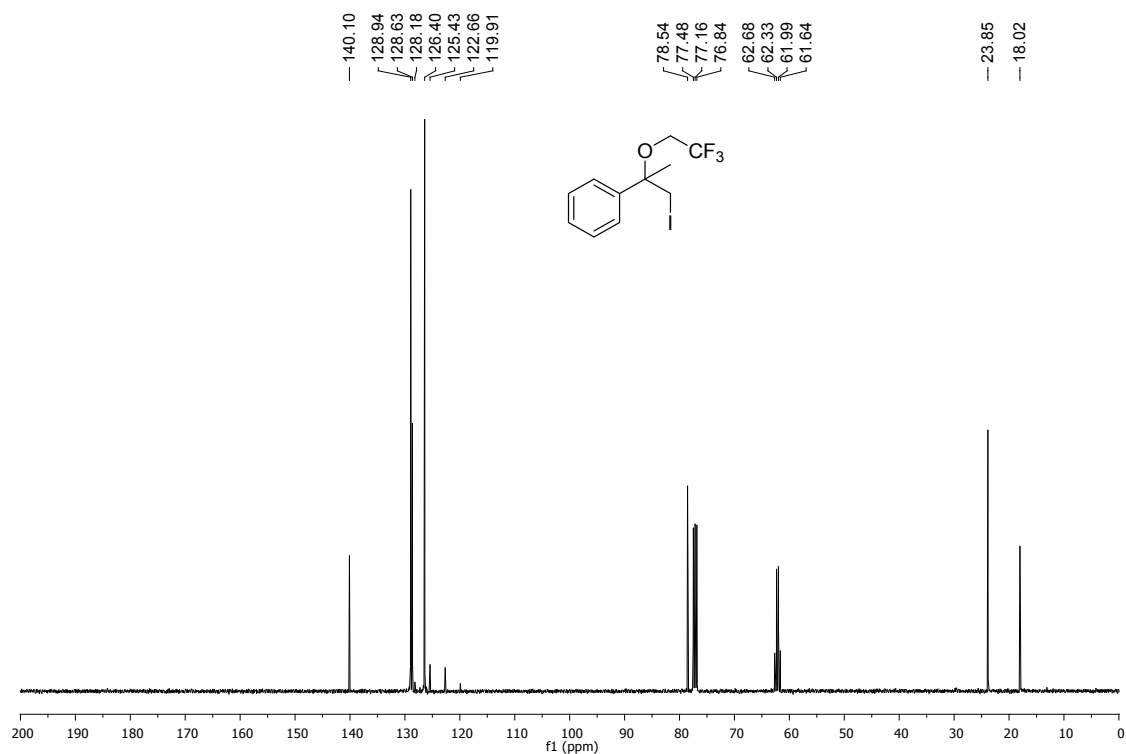


Figure 39: ¹³C spectrum of (1-iodo-2-(2,2,2-trifluoroethoxy)propan-2-yl)benzene (3c)

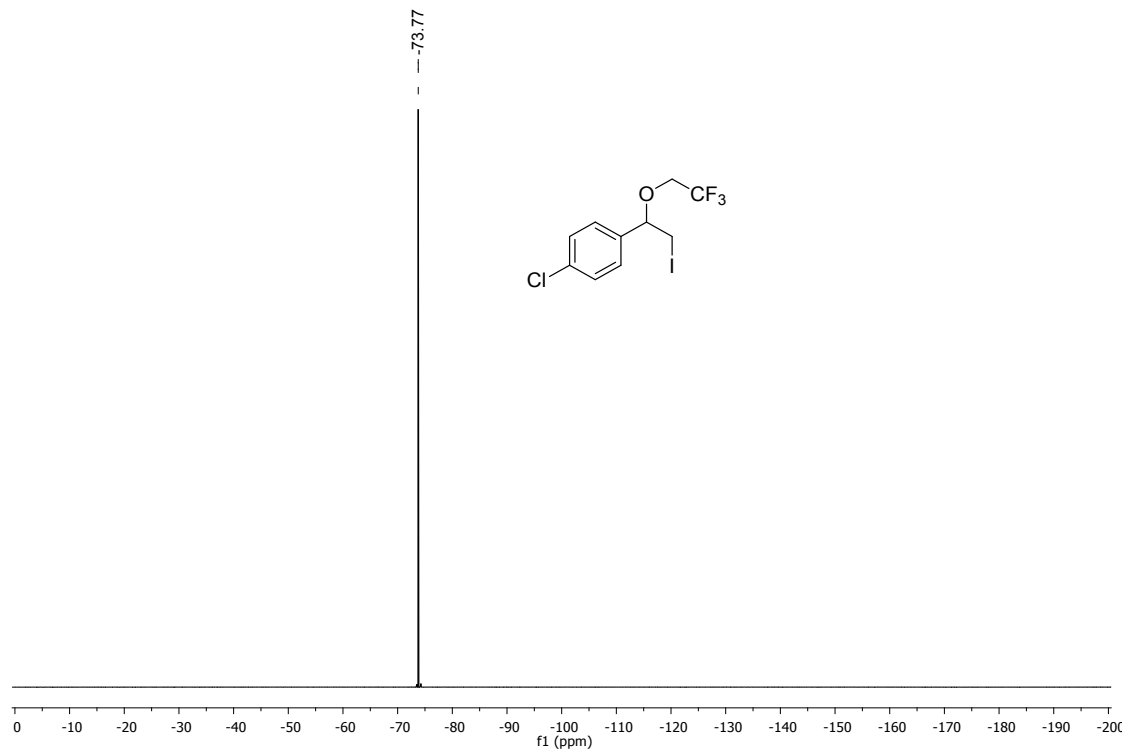


Figure 40: ¹⁹F spectrum of 1-chloro-4-(2-iodo-1-(2,2,2-trifluoroethoxy)ethyl)benzene (3d)

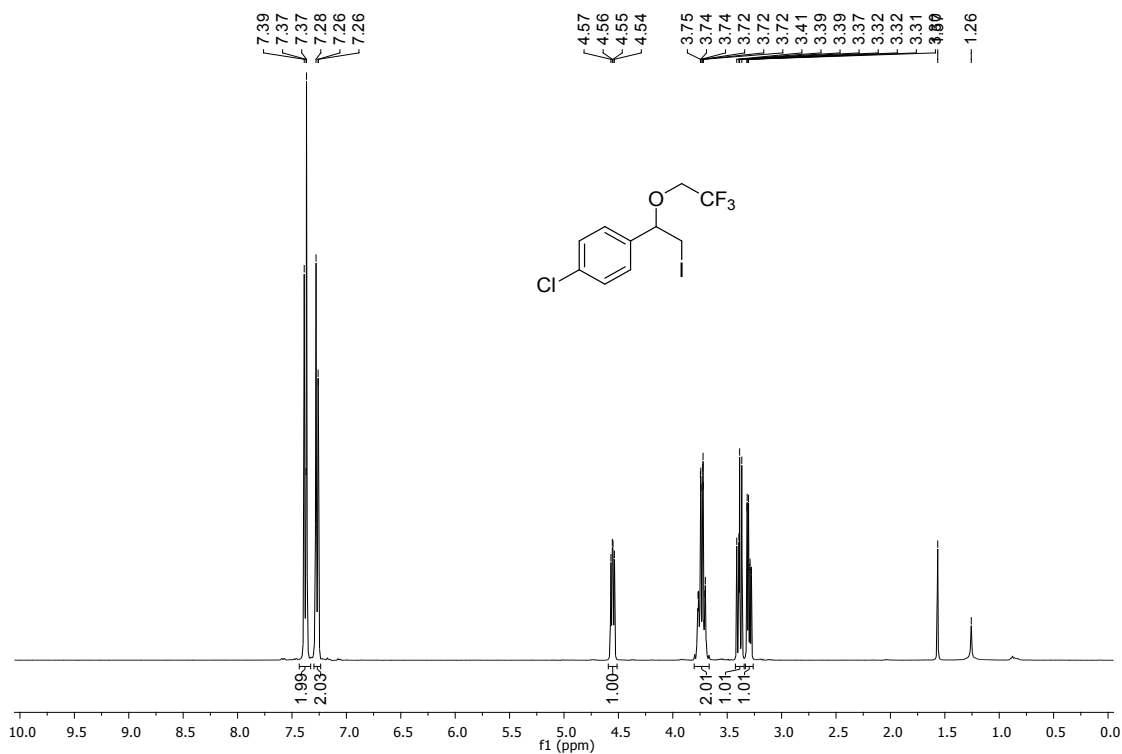


Figure 41: ¹H spectrum of 1-chloro-4-(2-iodo-1-(2,2,2-trifluoroethoxy)ethyl)benzene (**3d**)

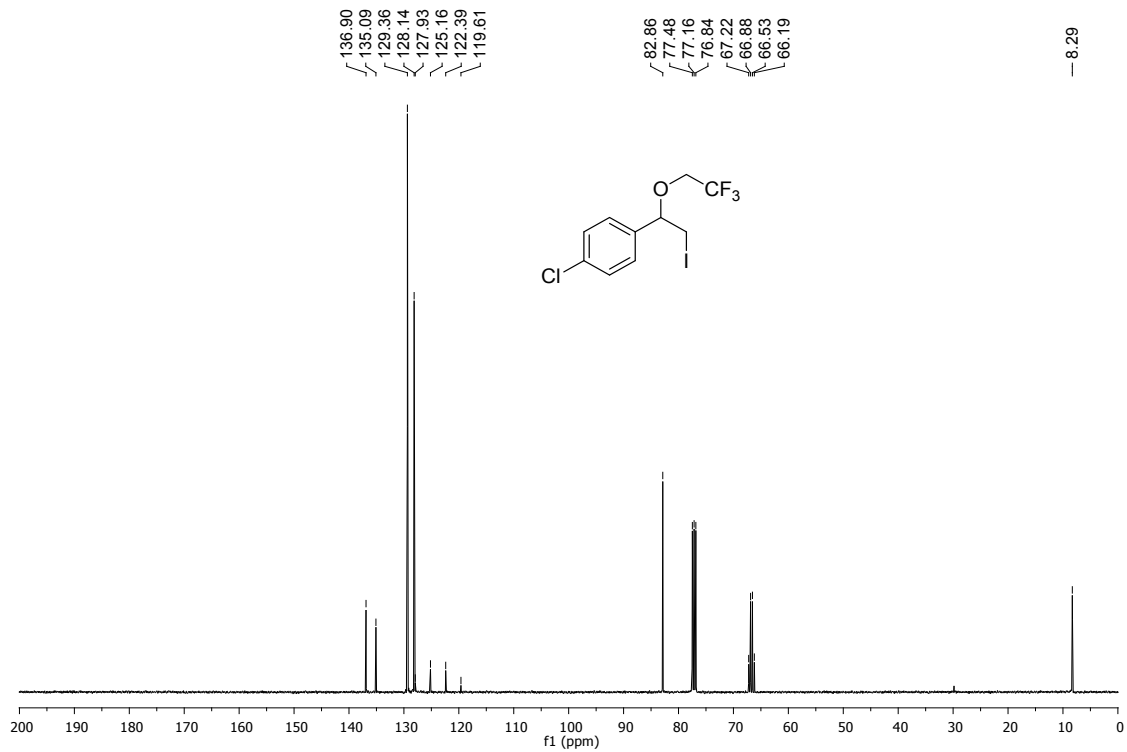


Figure 42: ¹³C spectrum of 1-chloro-4-(2-iodo-1-(2,2,2-trifluoroethoxy)ethyl)benzene (**3d**)

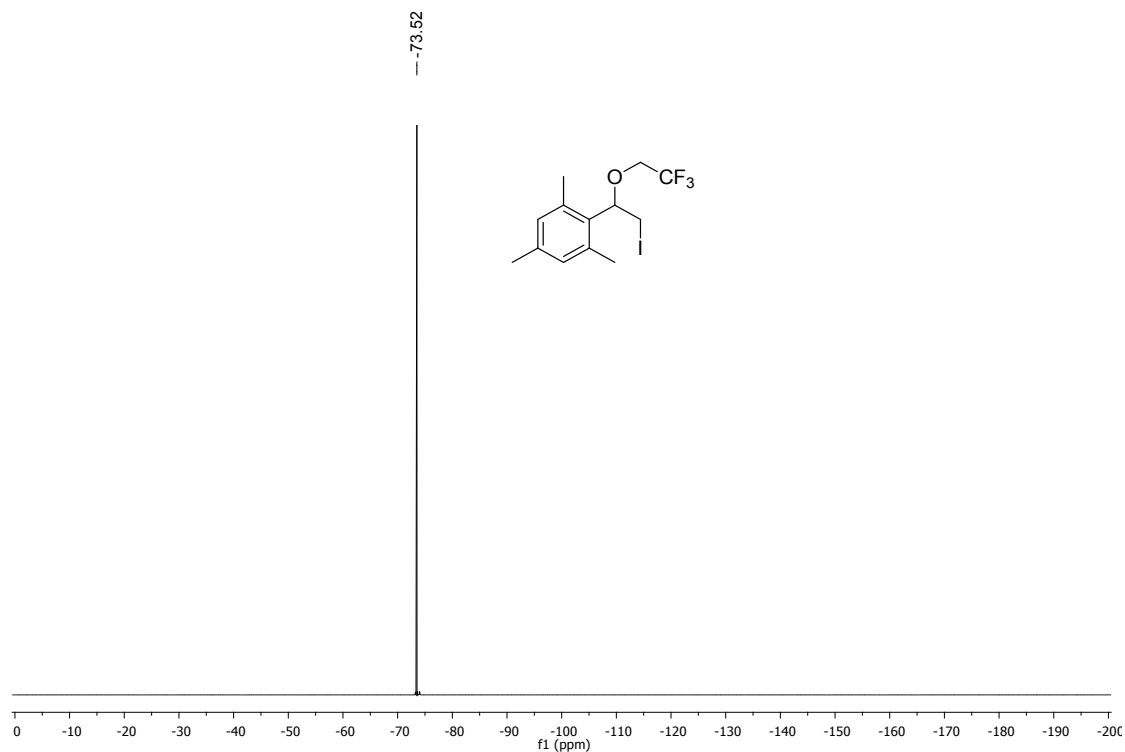


Figure 43: ^{19}F spectrum of 2-(2-iodo-1-(2,2,2-trifluoroethoxy)ethyl)-1,3,5-trimethylbenzene (**3e**)

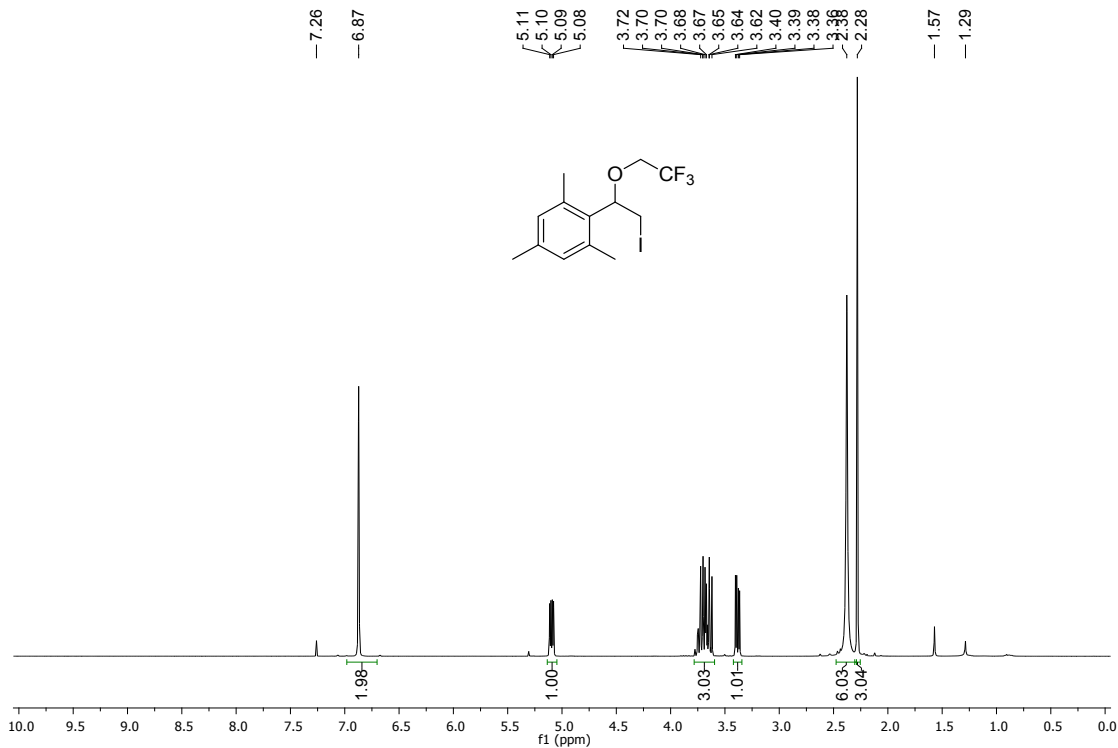


Figure 44: ^1H spectrum of 2-(2-iodo-1-(2,2,2-trifluoroethoxy)ethyl)-1,3,5-trimethylbenzene (**3e**)

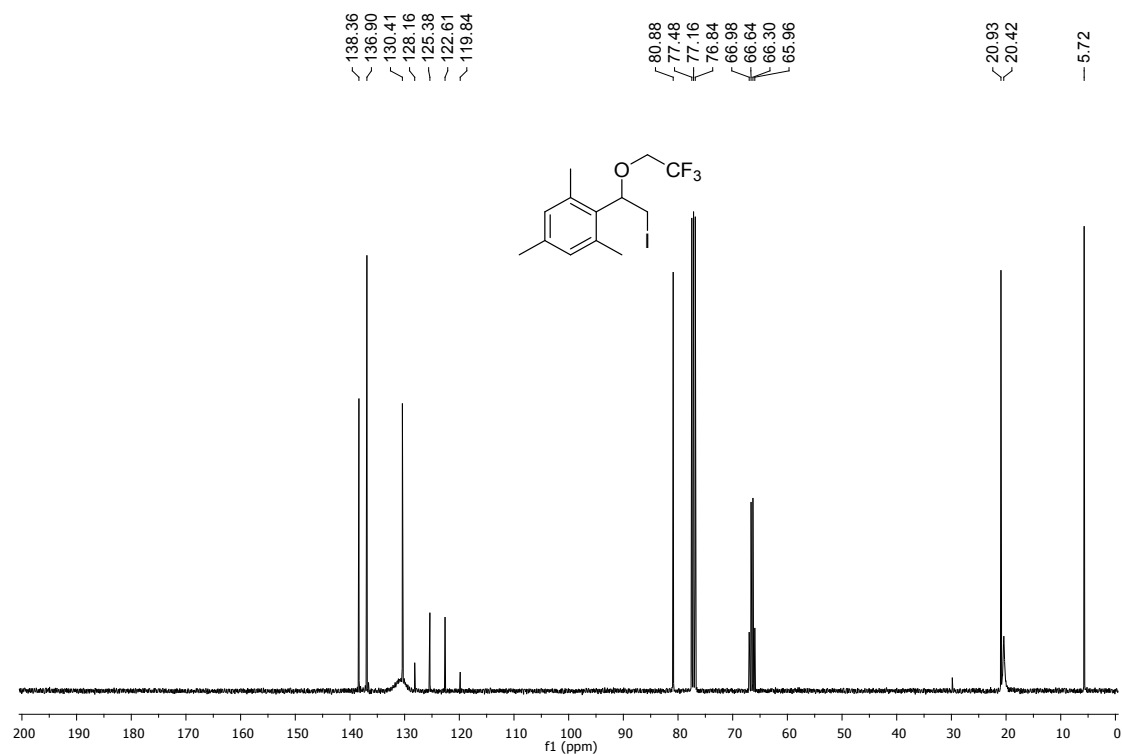


Figure 45: ¹³C spectrum of 2-(2-iodo-1-(2,2,2-trifluoroethoxy)ethyl)-1,3,5-trimethylbenzene (**3e**)



Figure 46: ¹⁹F spectrum of 1-(2-iodo-1-(2,2,2-trifluoroethoxy)ethyl)-4-isopropylbenzene (**3f**)

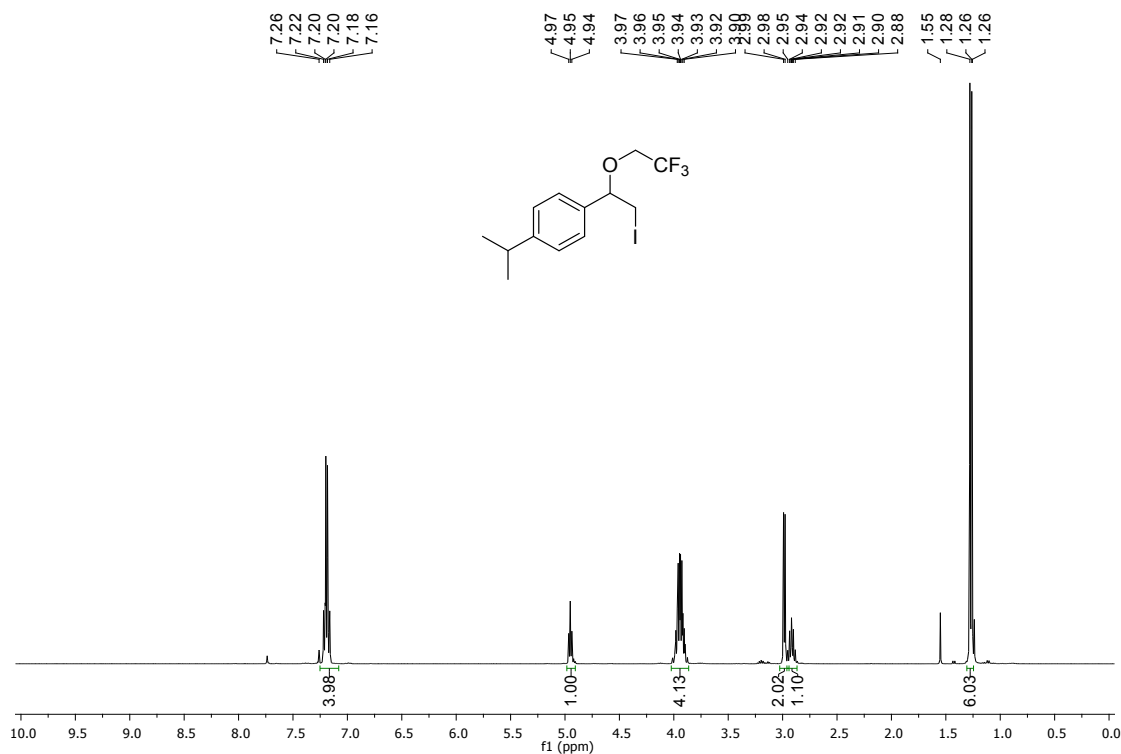


Figure 47: ¹H spectrum of 1-(2-iodo-1-(2,2,2-trifluoroethoxy)ethyl)-4-isopropylbenzene (3f)

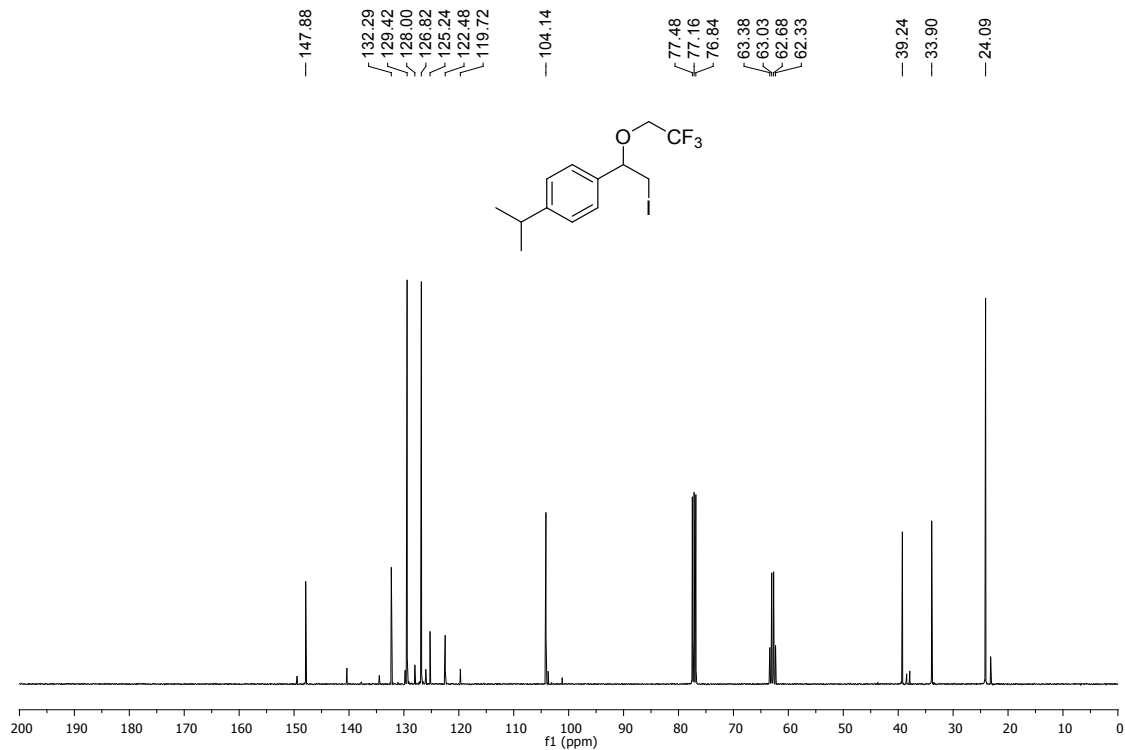


Figure 48: ¹³C spectrum of 1-(2-iodo-1-(2,2,2-trifluoroethoxy)ethyl)-4-isopropylbenzene (3f)

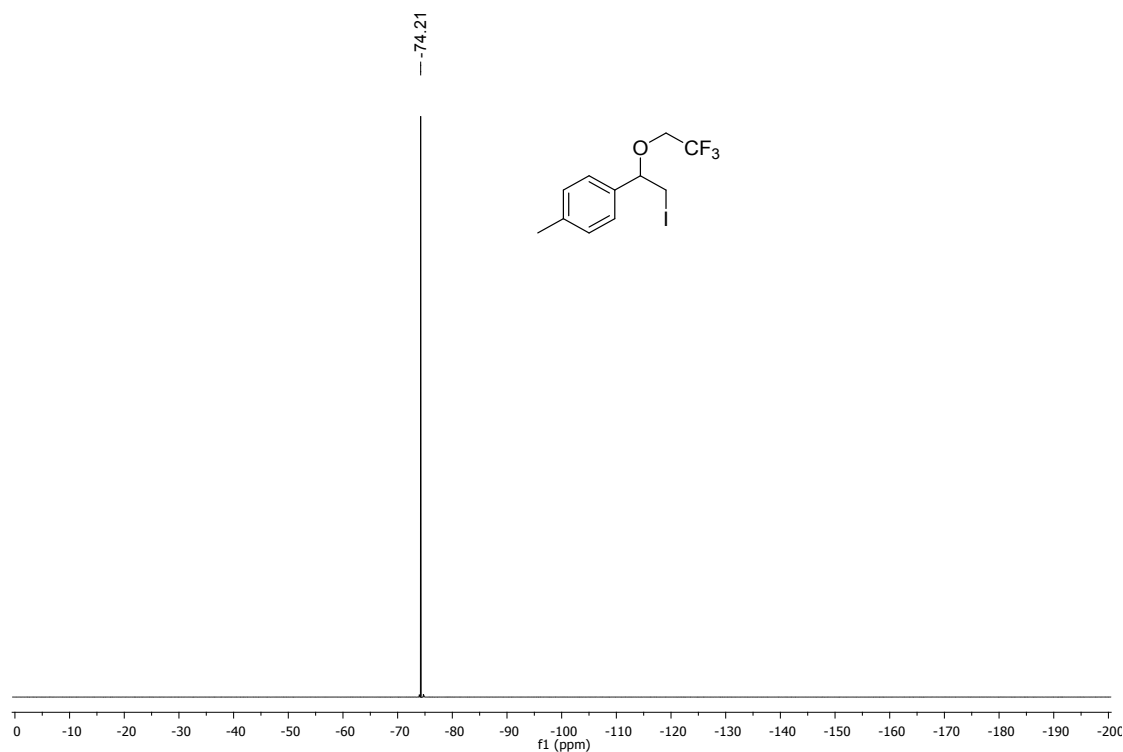


Figure 49: ^{19}F spectrum of 1-(2-iodo-1-(2,2,2-trifluoroethoxy)ethyl)-4-methylbenzene (**3g**)

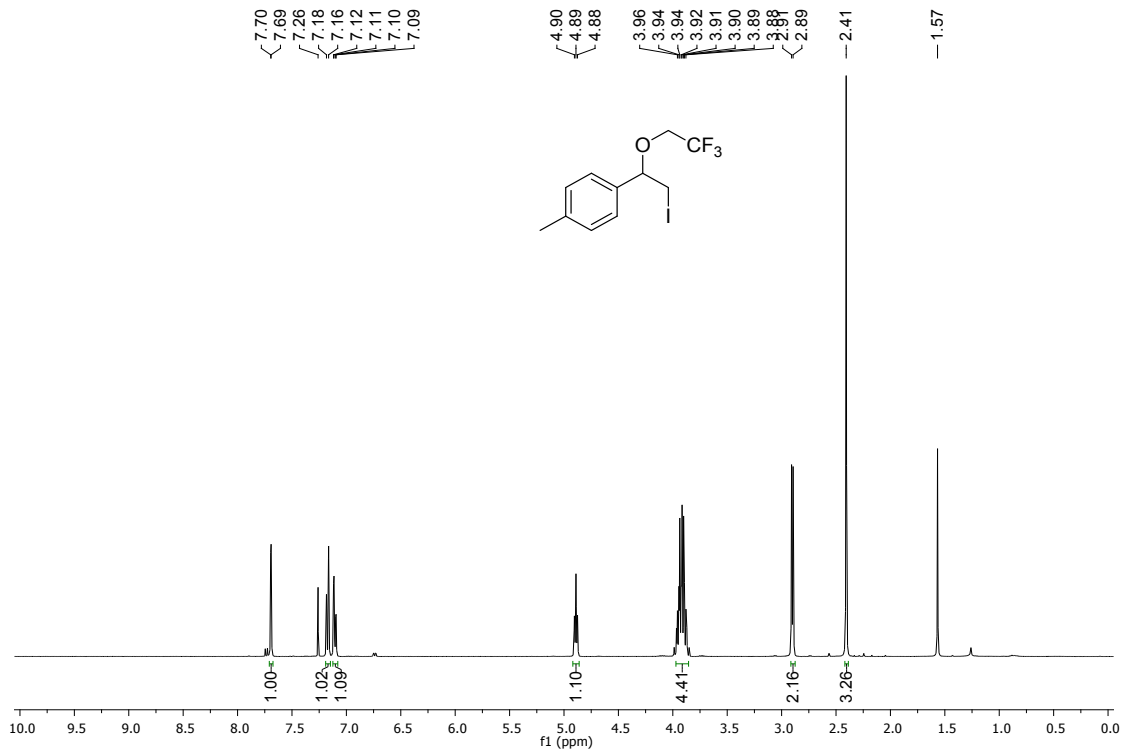


Figure 50: ^1H spectrum of 1-(2-iodo-1-(2,2,2-trifluoroethoxy)ethyl)-4-methylbenzene (**3g**)

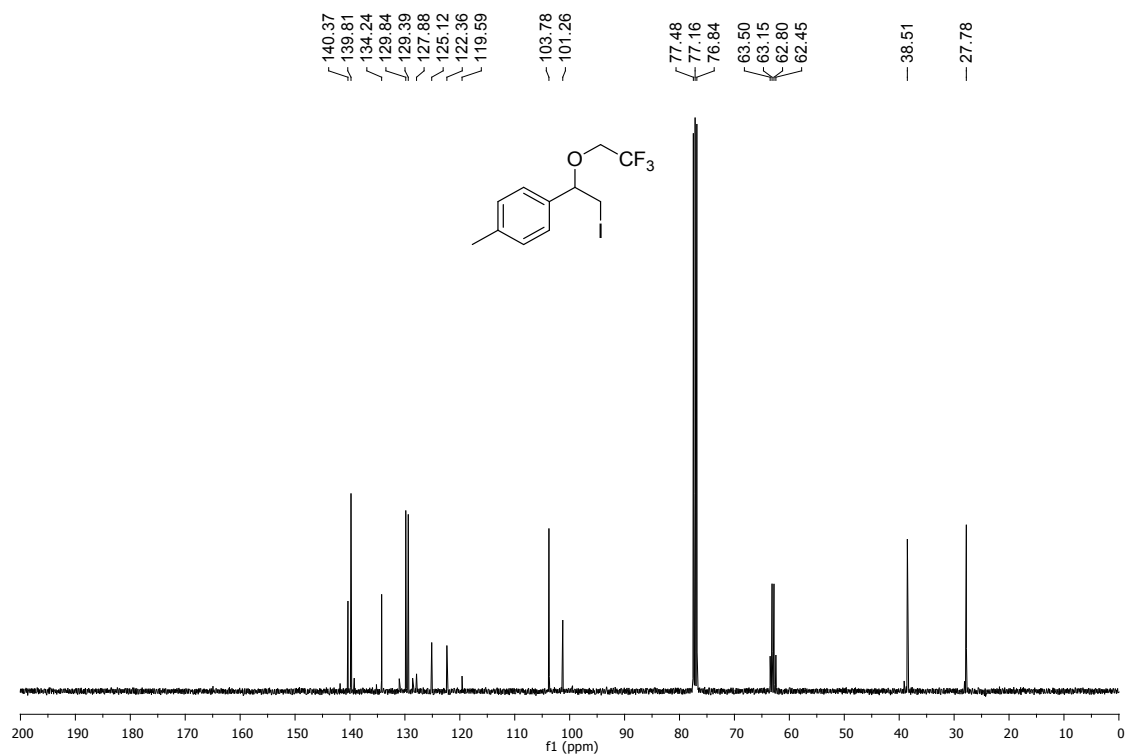


Figure 51: ¹³C spectrum of 1-(2-iodo-1-(2,2,2-trifluoroethoxy)ethyl)-4-methylbenzene (**3g**)

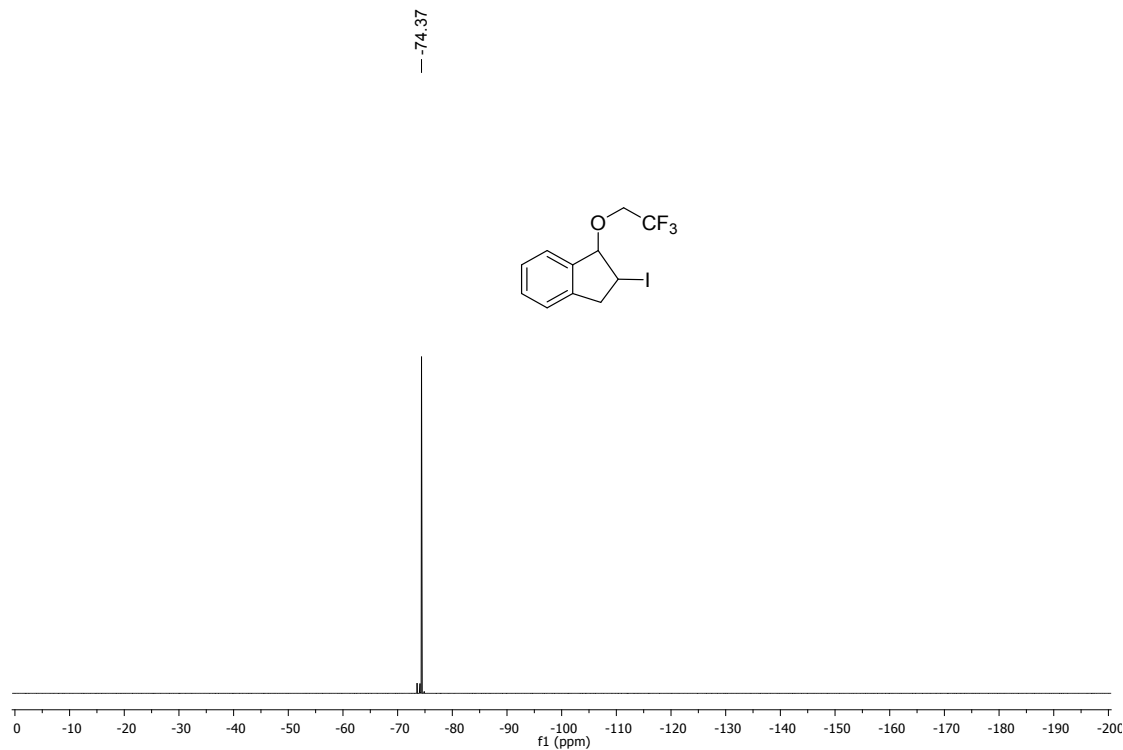


Figure 52: ¹⁹F spectrum of 2-iodo-1-(2,2,2-trifluoroethoxy)-2,3-dihydro-1H-indene (**3h**)

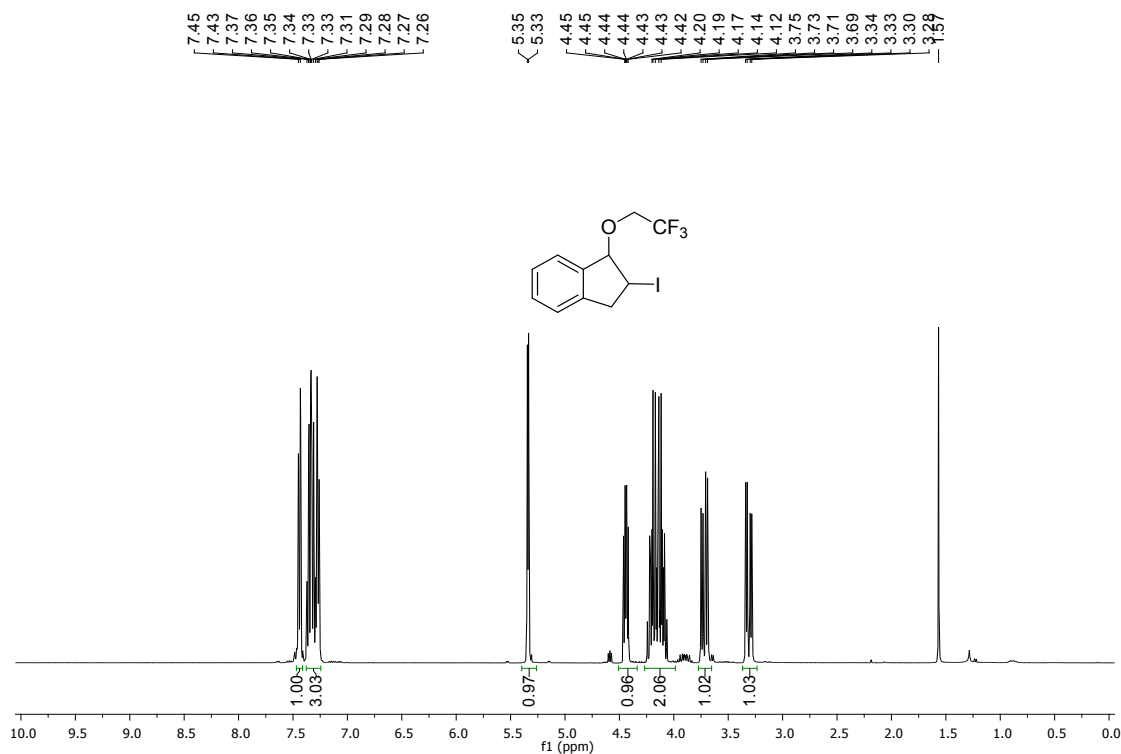


Figure 53: ¹H spectrum of 2-iodo-1-(2,2,2-trifluoroethoxy)-2,3-dihydro-1H-indene (**3h**)

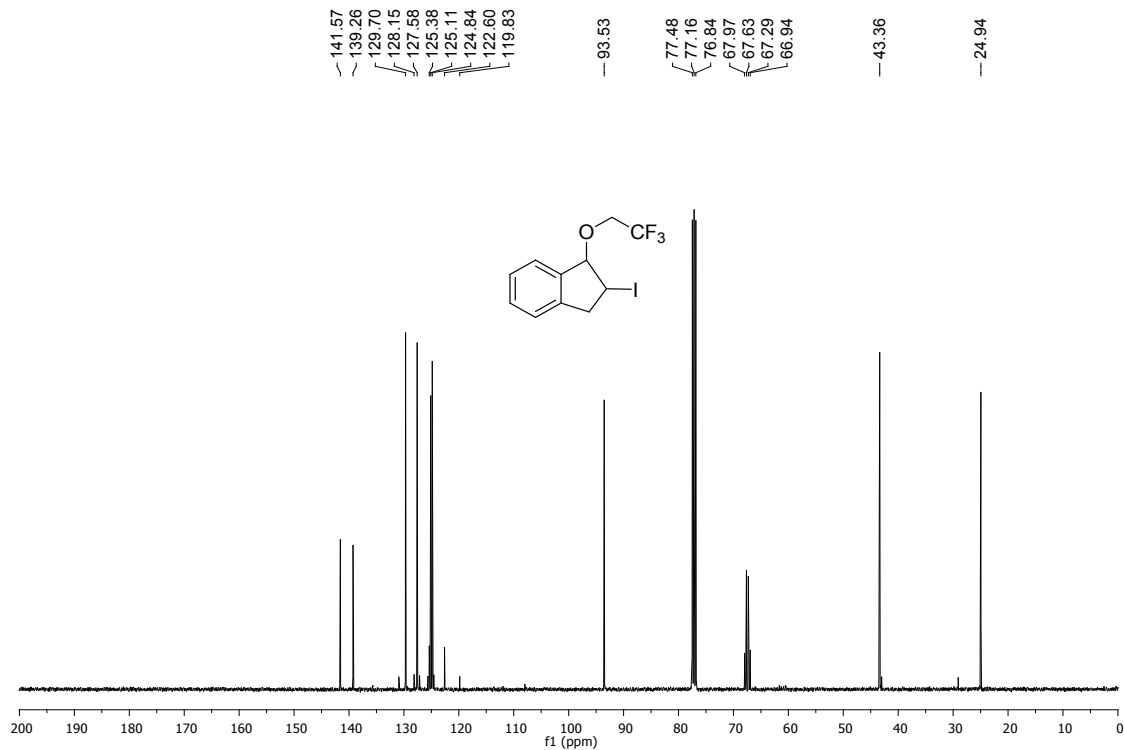


Figure 54: ¹³C spectrum of 2-iodo-1-(2,2,2-trifluoroethoxy)-2,3-dihydro-1H-indene (**3h**)

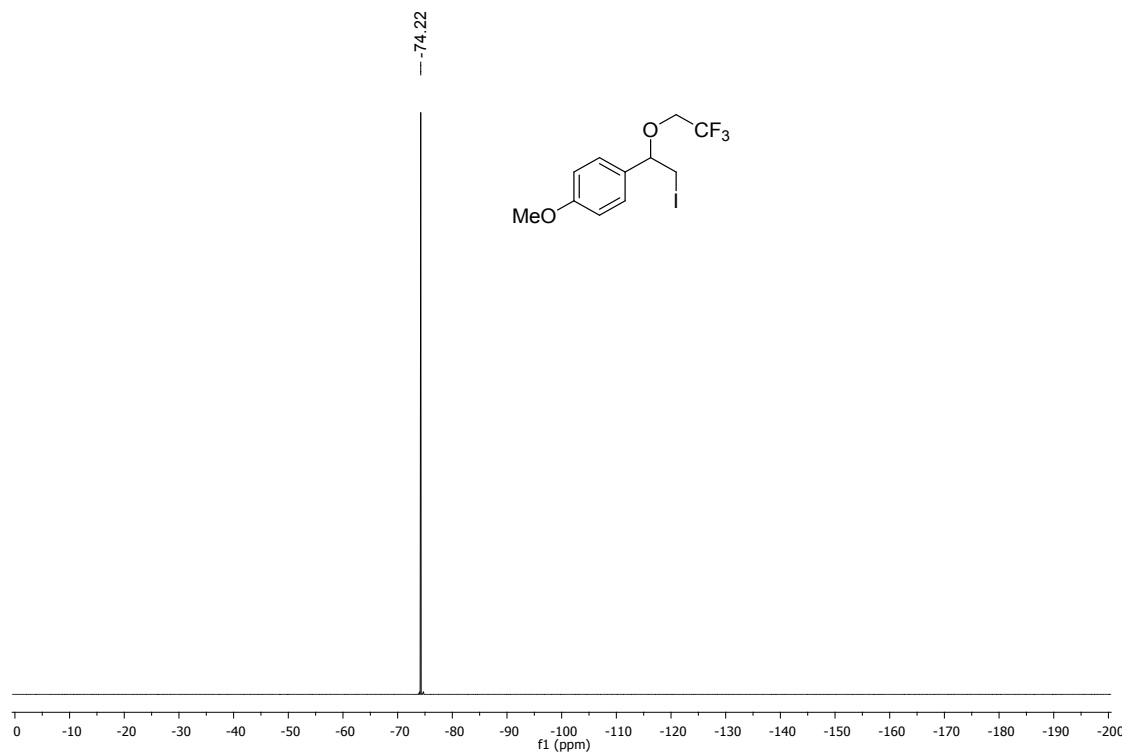


Figure 55: ^{19}F spectrum of 1-(2-iodo-1-(2,2,2-trifluoroethoxy)ethyl)-4-methoxybenzene (**3i**)

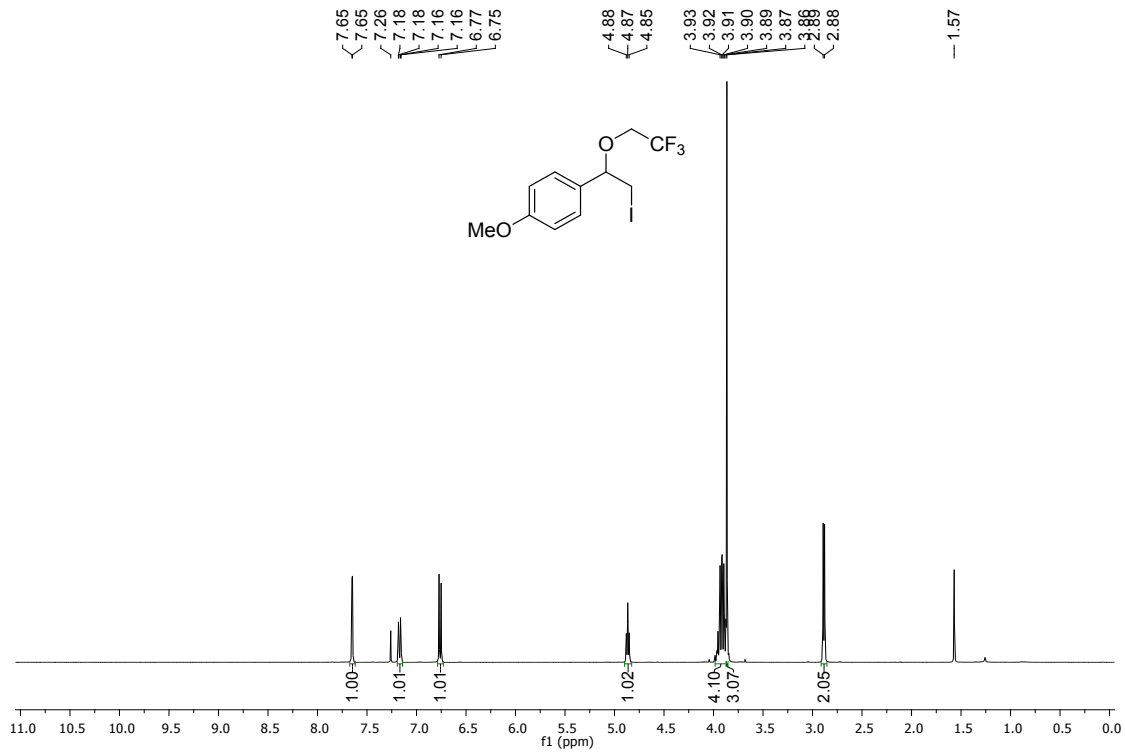


Figure 56: ^1H spectrum of 1-(2-iodo-1-(2,2,2-trifluoroethoxy)ethyl)-4-methoxybenzene (**3i**)

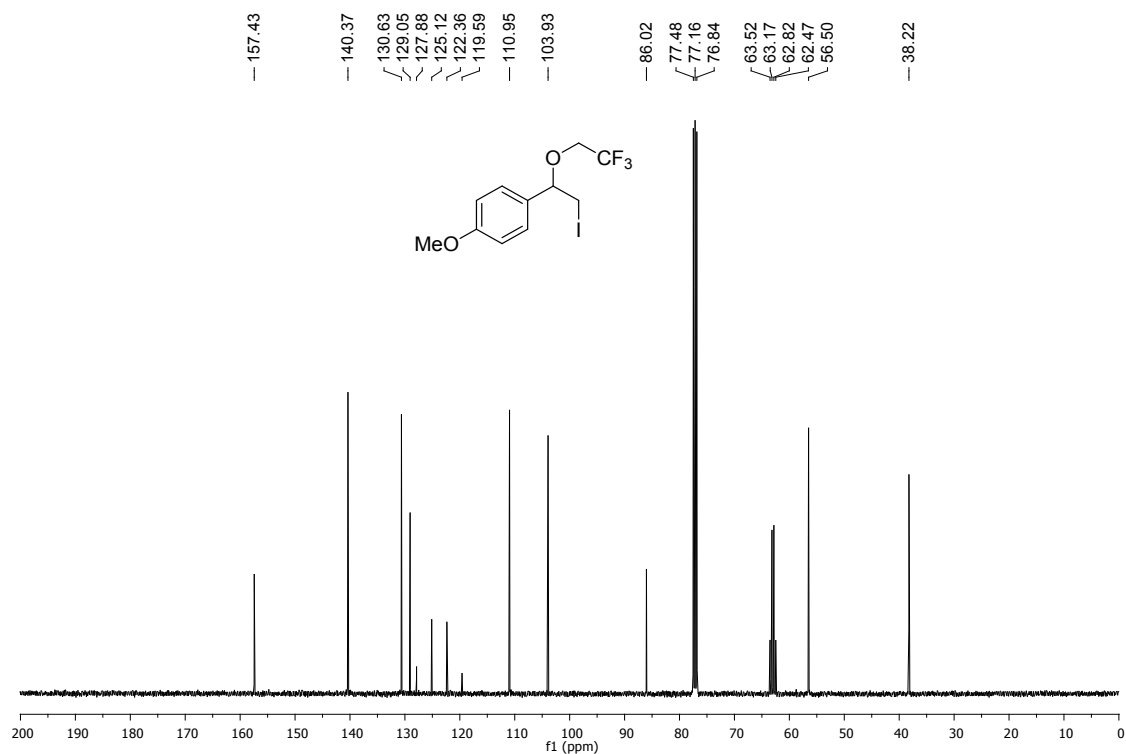


Figure 57: ¹³C spectrum of 1-(2-iodo-1-(2,2,2-trifluoroethoxy)ethyl)-4-methoxybenzene (**3i**)

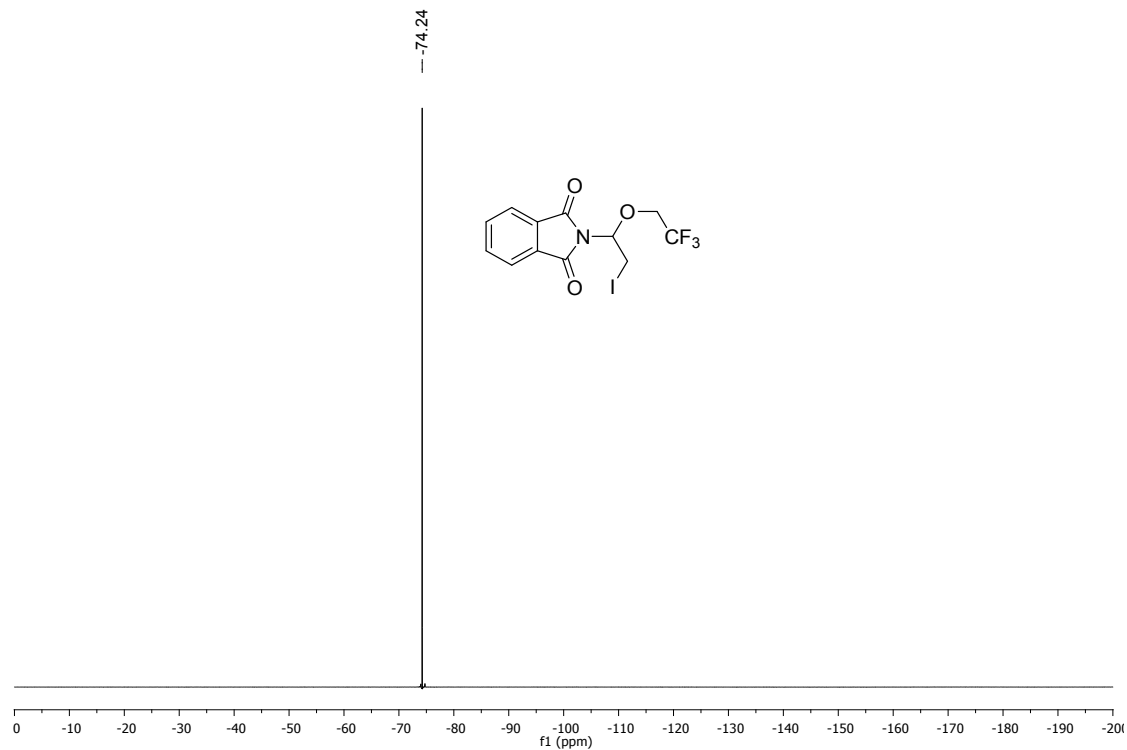


Figure 58: ¹⁹F spectrum of 2-(2-iodo-1-(2,2,2-trifluoroethoxy)ethyl)isoindoline-1,3-dione (**3j**)

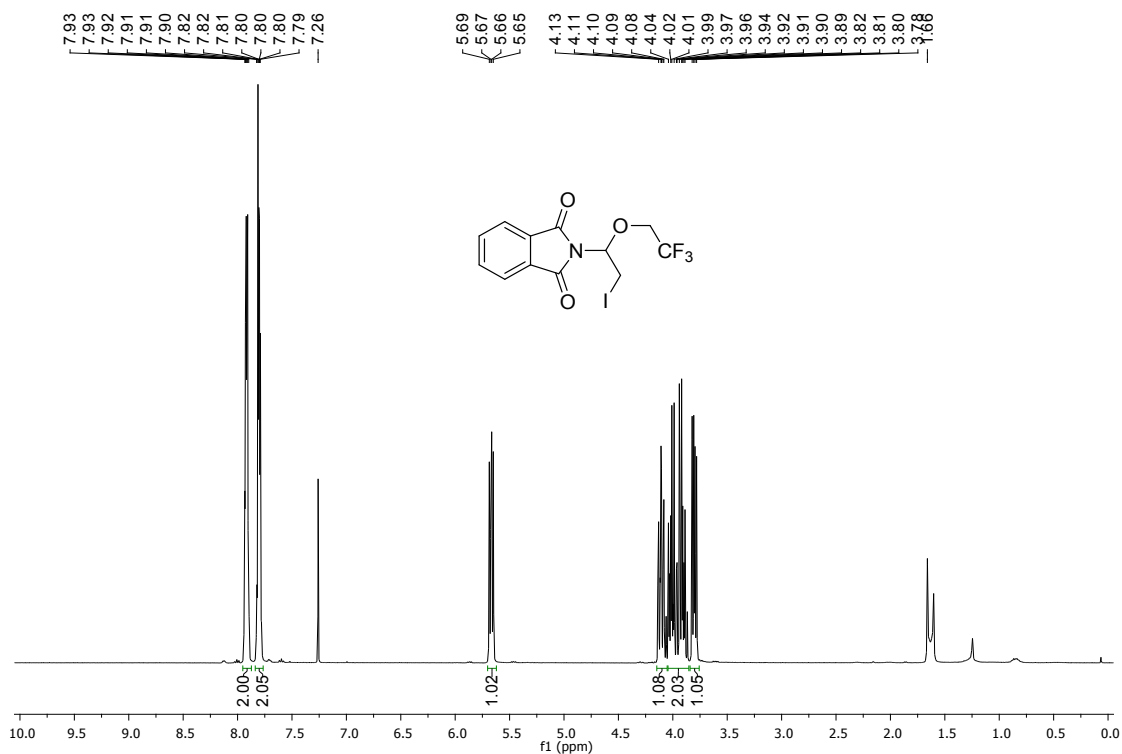


Figure 59: ¹H spectrum of 2-(2-iodo-1-(2,2,2-trifluoroethoxy)ethyl)isoindoline-1,3-dione (**3j**)

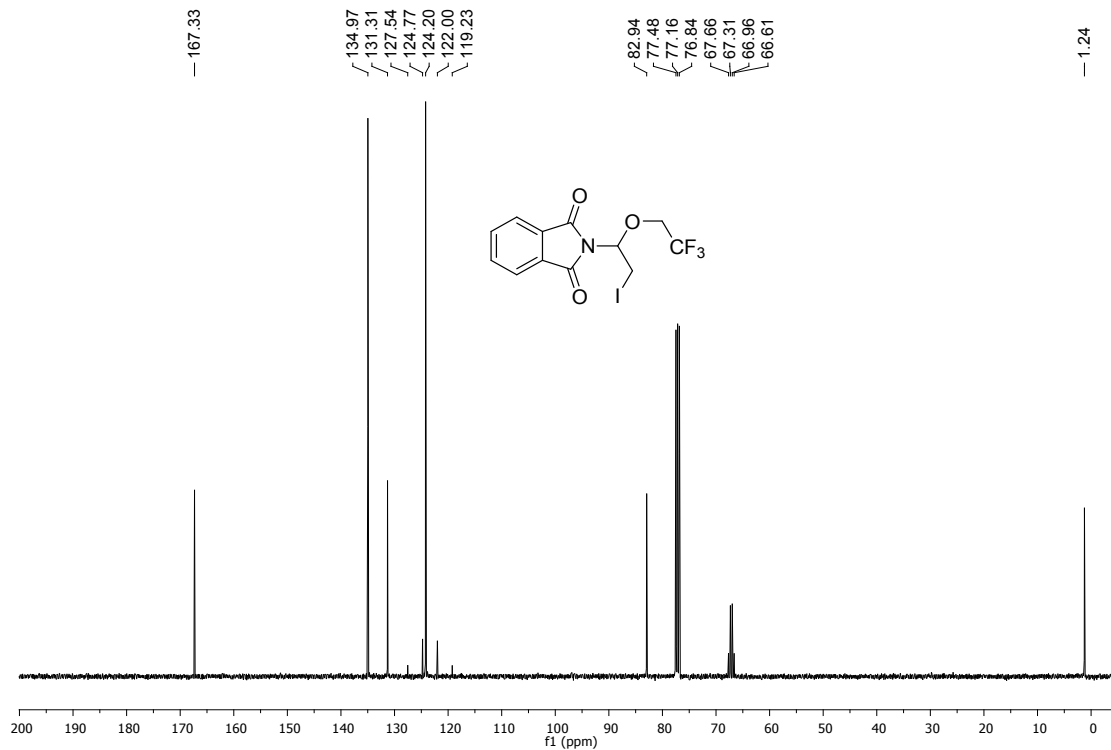


Figure 60: ¹³C spectrum of 2-(2-iodo-1-(2,2,2-trifluoroethoxy)ethyl)isoindoline-1,3-dione (**3j**)

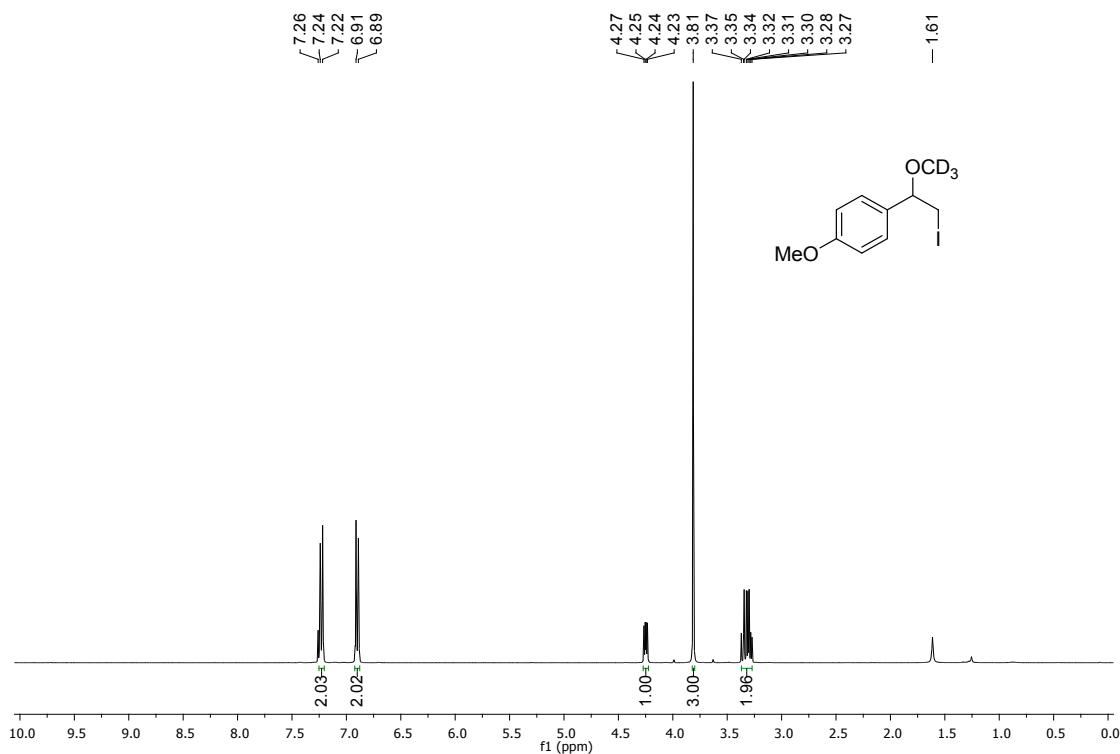


Figure 61: ¹H spectrum of 1-(2-iodo-1-trideuteriomethoxyethyl)-4-methoxybenzene (**3k**)

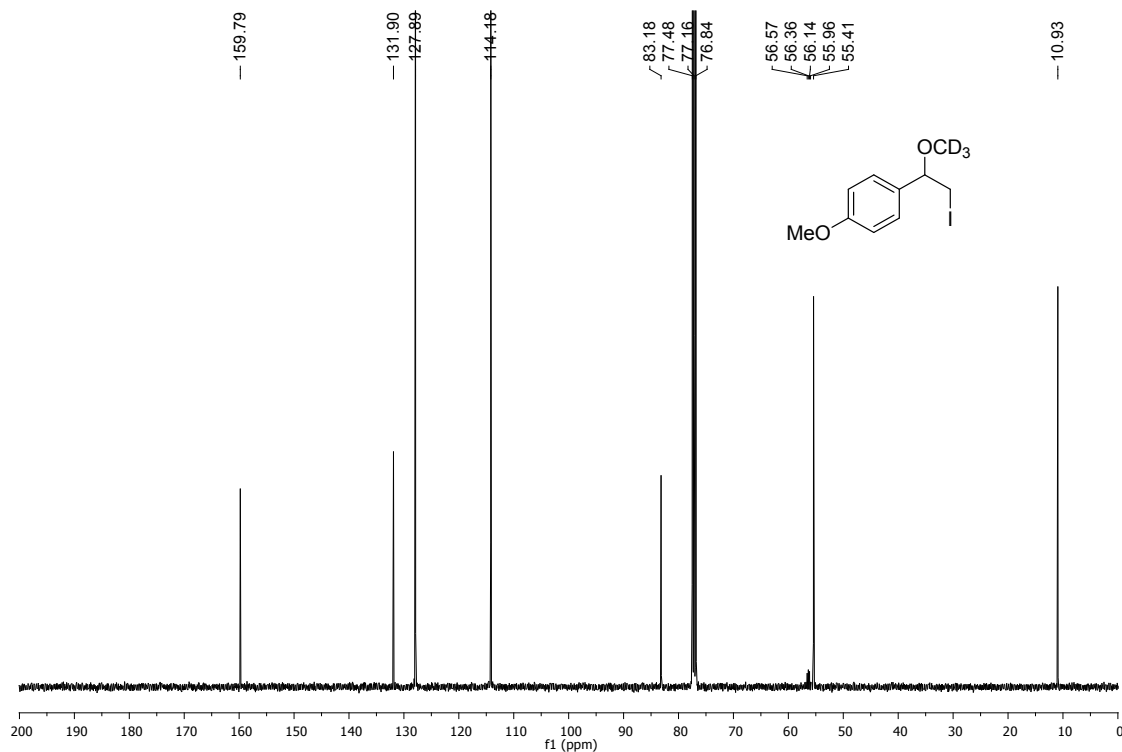


Figure 62: ¹³C spectrum of 1-(2-iodo-1-trideuteriomethoxyethyl)-4-methoxybenzene (**3k**)

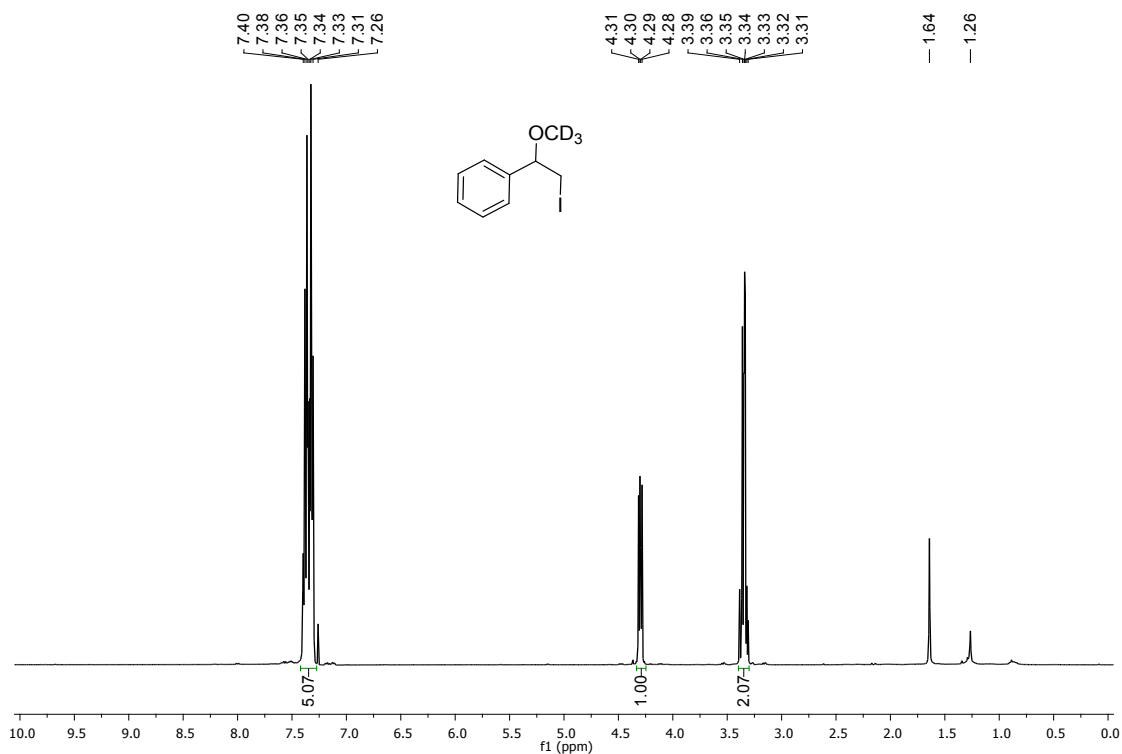


Figure 63: ¹H spectrum of (2-iodo-1-trideuteriomethoxyethyl)benzene (**31**)

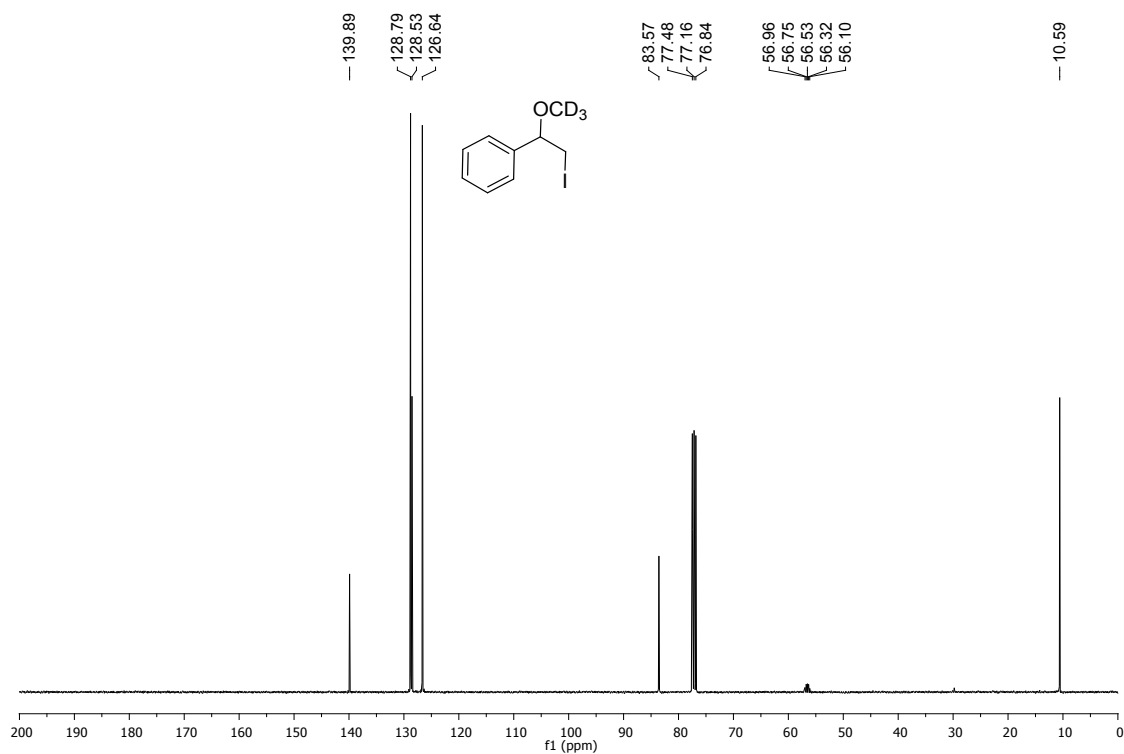


Figure 64: ¹³C spectrum of (2-iodo-1-trideuteriomethoxyethyl)benzene (**31**)

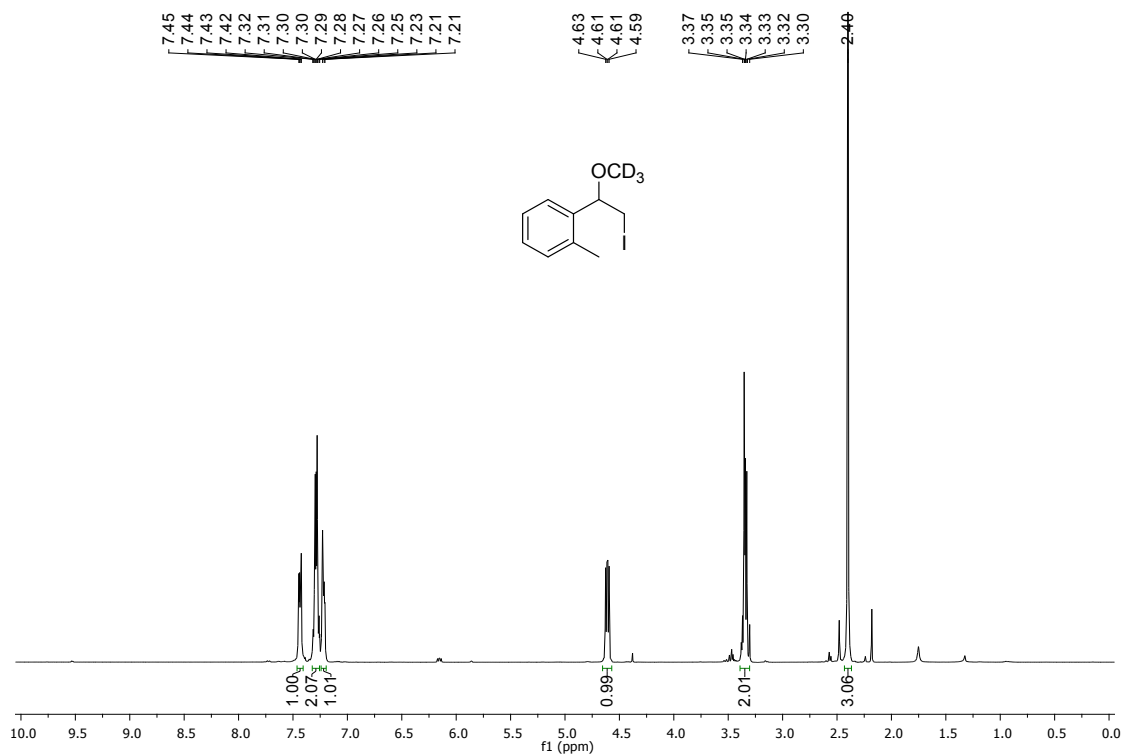


Figure 65: ¹H spectrum of 1-(2-iodo-1-trideuteriomethoxyethyl)-2-methylbenzene (**3m**)

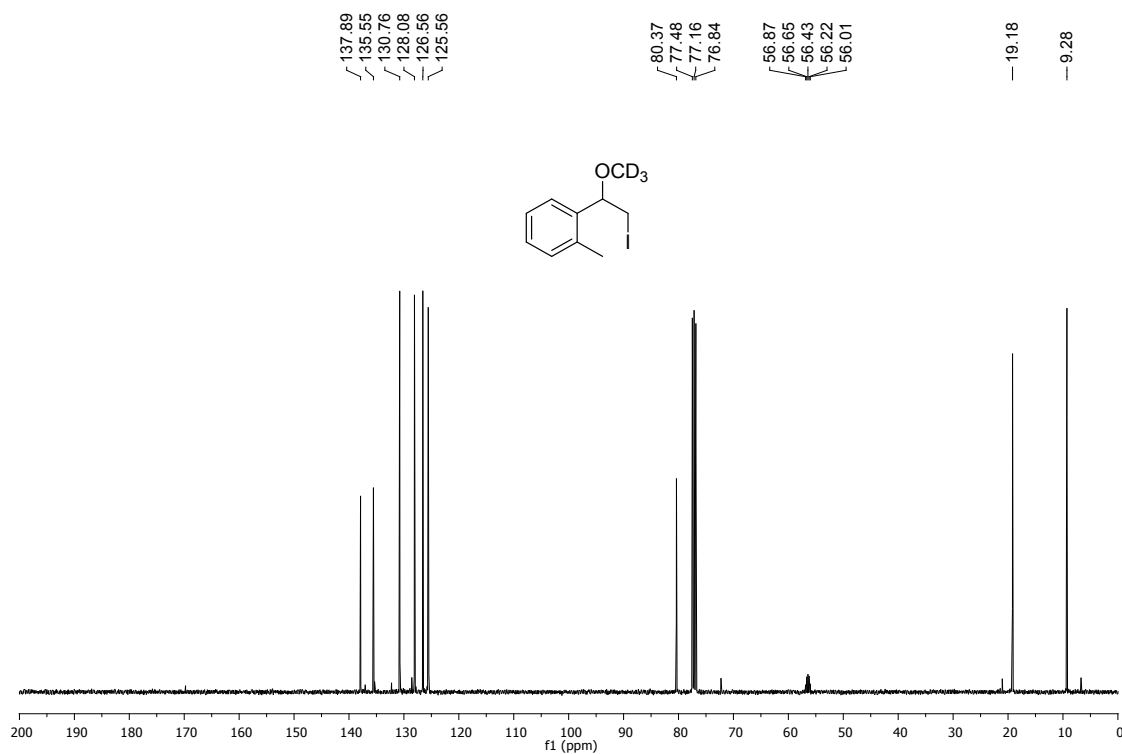


Figure 66: ¹³C spectrum of 1-(2-iodo-1-trideuteriomethoxyethyl)-2-methylbenzene (**3m**)

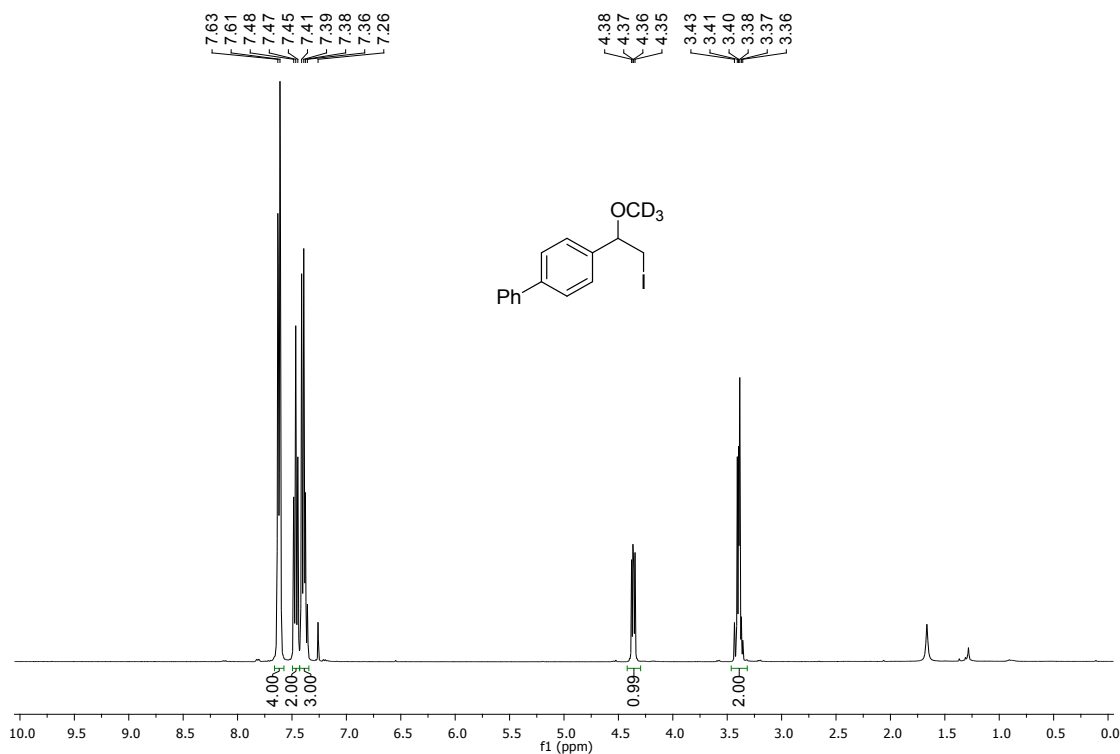


Figure 67: ¹H spectrum of 4-(2-iodo-1-trideuteriomethoxyethyl)-1,1'-biphenyl (**3n**)

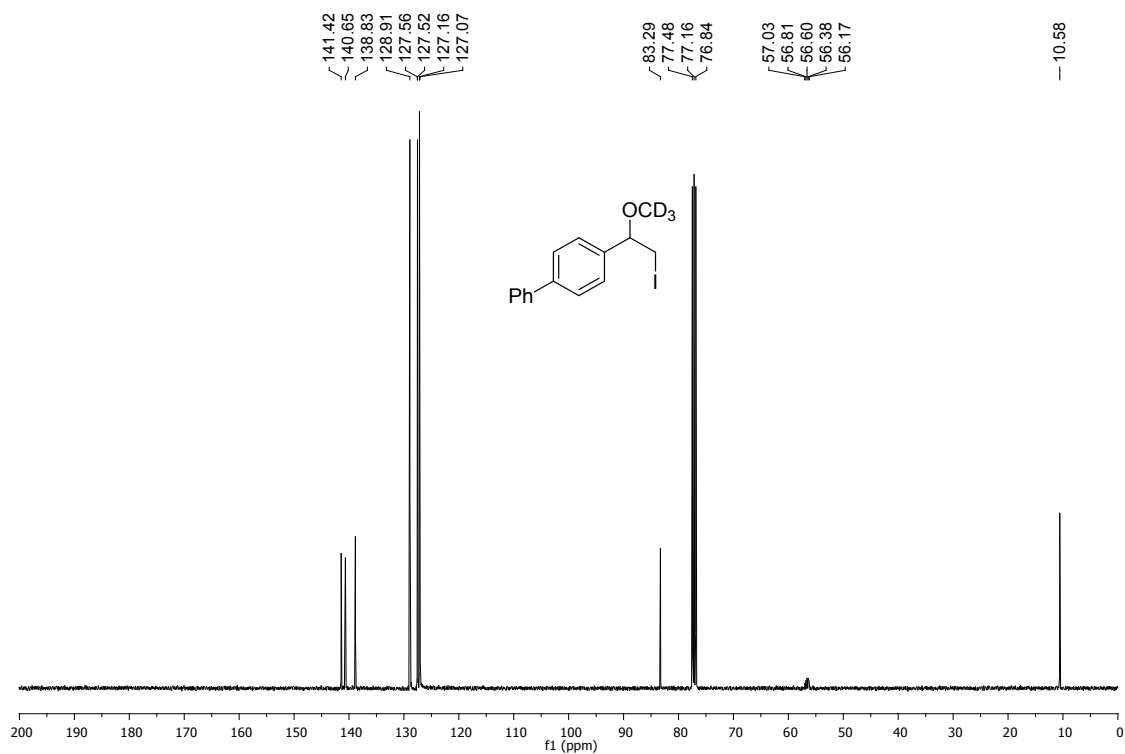


Figure 68: ¹³C spectrum of 4-(2-iodo-1-trideuteriomethoxyethyl)-1,1'-biphenyl (**3n**)

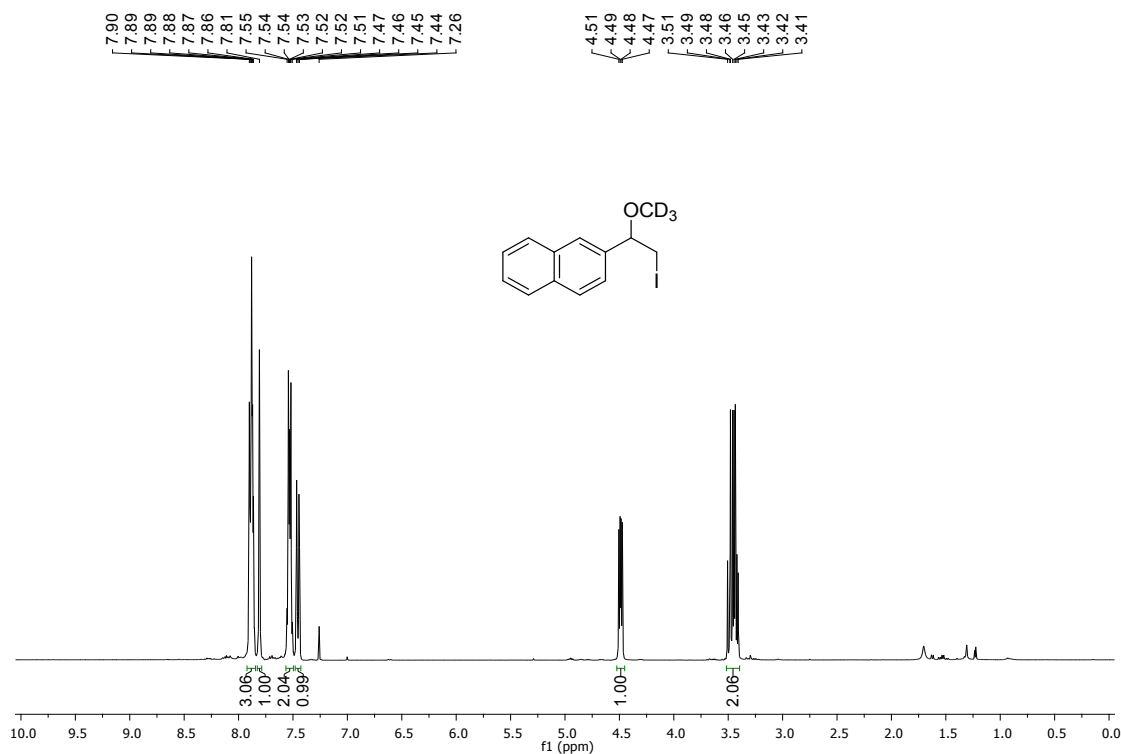


Figure 69: ¹H spectrum of 2-(2-iodo-1-trideuteriomethoxyethyl)naphthalene (**30**)

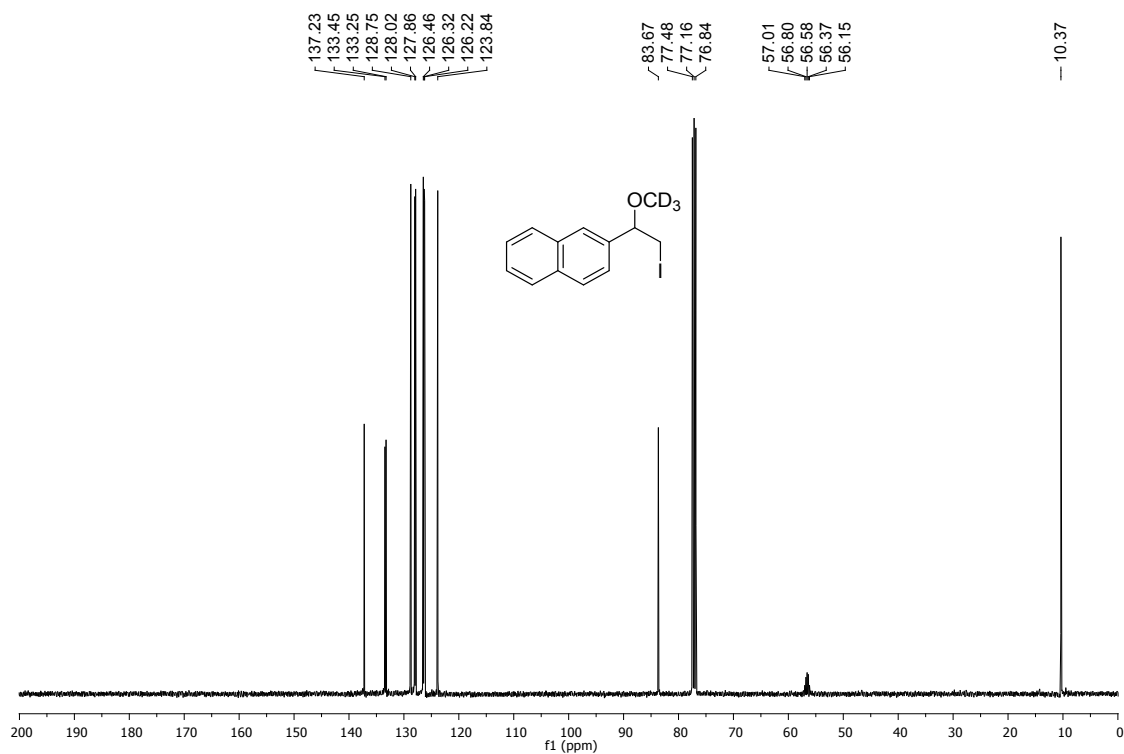


Figure 70: ¹³C spectrum of 2-(2-iodo-1-trideuteriomethoxyethyl)naphthalene (**30**)

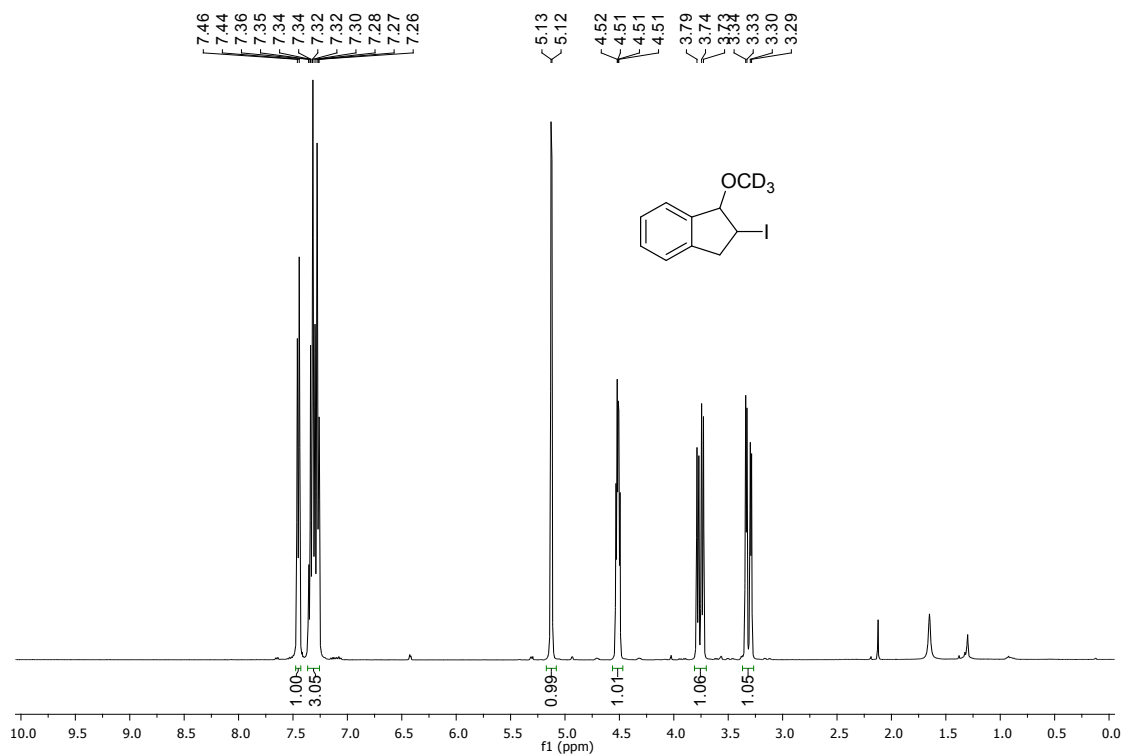


Figure 71: ¹H spectrum of 2-iodo-1-trideuteriomethoxy-2,3-dihydro-1H-indene (**3p**)

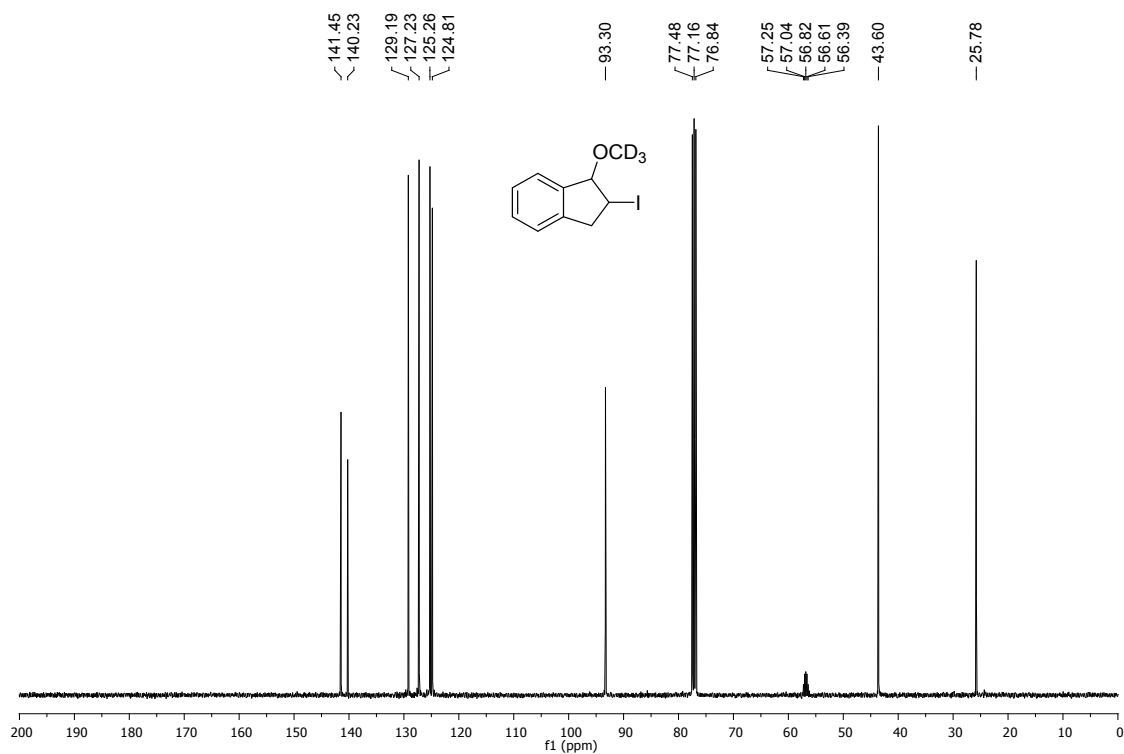


Figure 72: ¹³C spectrum of 2-iodo-1-trideuteriomethoxy-2,3-dihydro-1H-indene (**3p**)

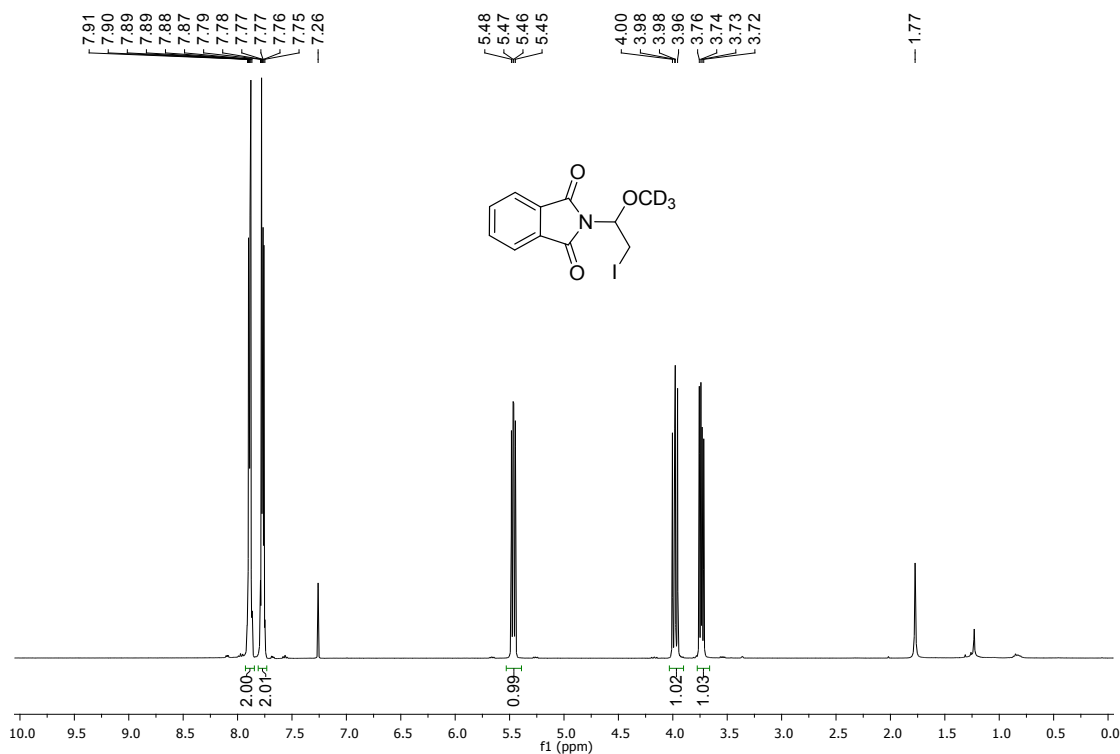


Figure 73: ¹H spectrum of 2-(2-iodo-1-trideuteriomethoxyethyl)isoindoline-1,3-dione (**3q**)

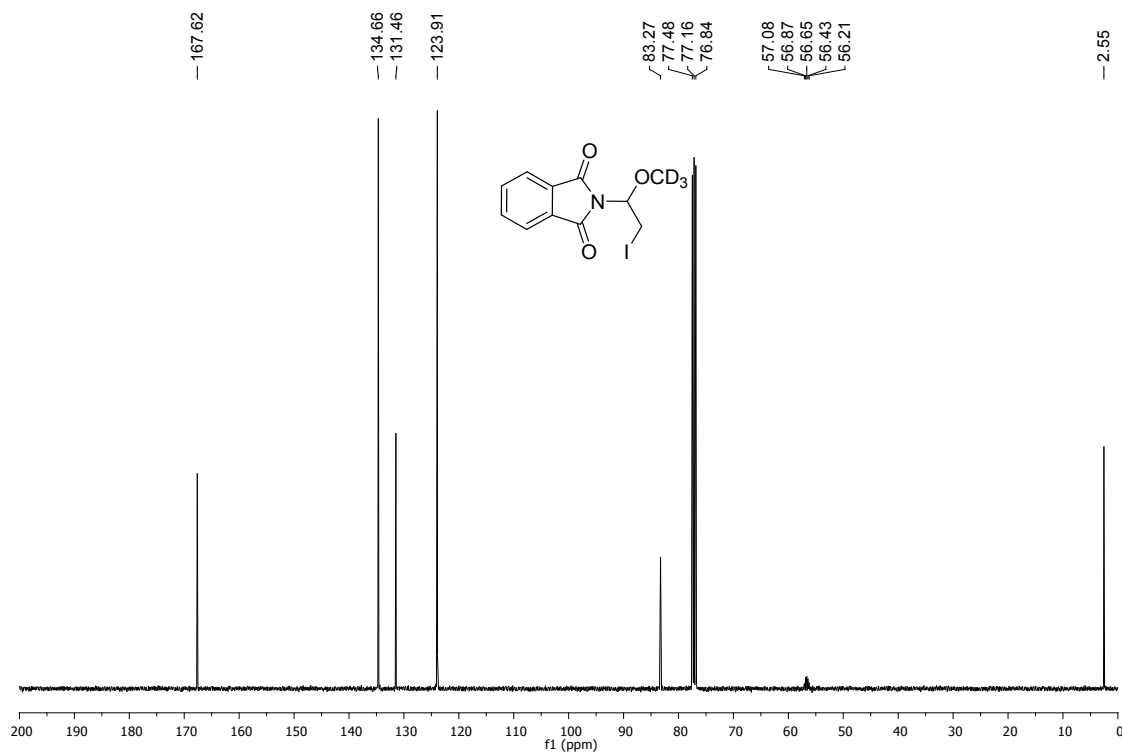


Figure 74: ¹³C spectrum of 2-(2-iodo-1-trideuteriomethoxyethyl)isoindoline-1,3-dione (**3q**)

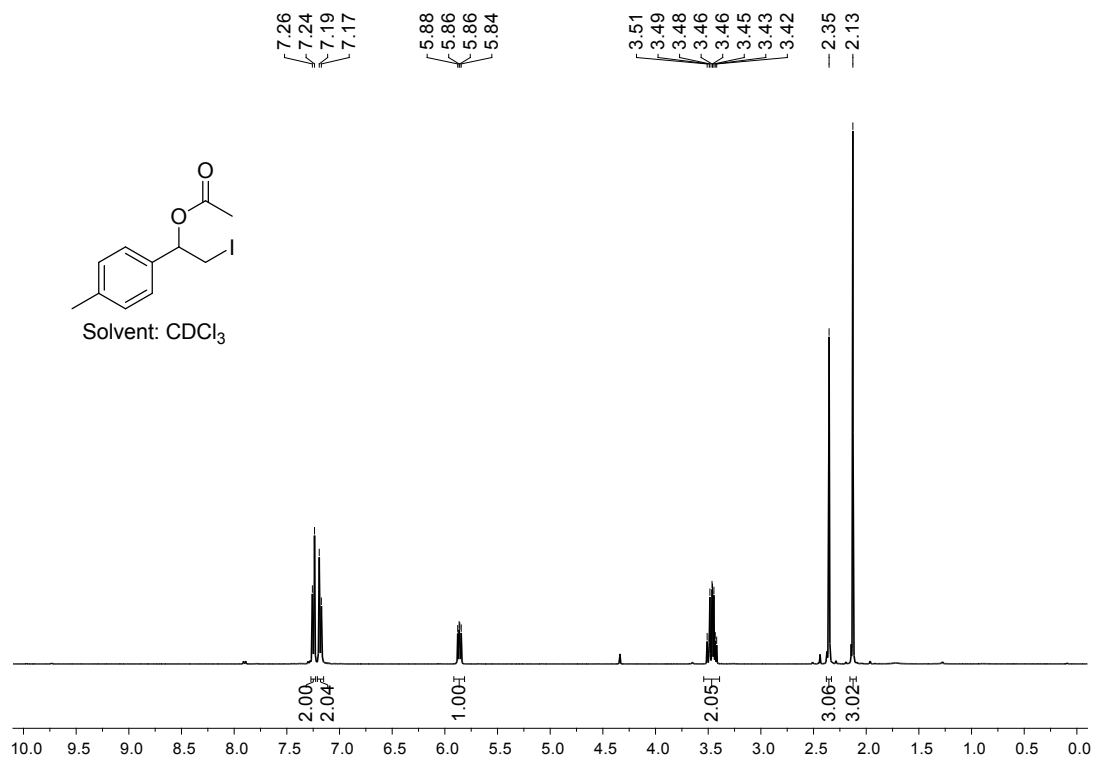


Figure S75: ¹H NMR spectrum of 2-iodo-1-(*p*-tolyl)ethyl acetate (**8a**).

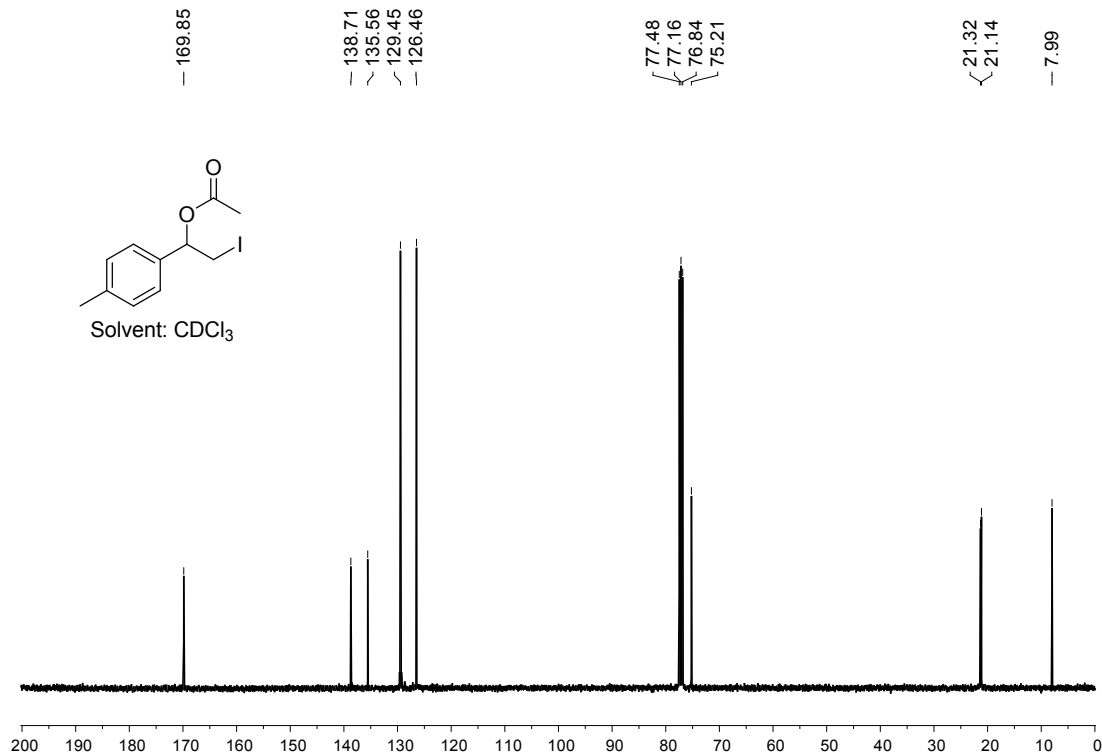


Figure S76: ¹³C NMR spectrum of 2-iodo-1-(*p*-tolyl)ethyl acetate (**8a**).

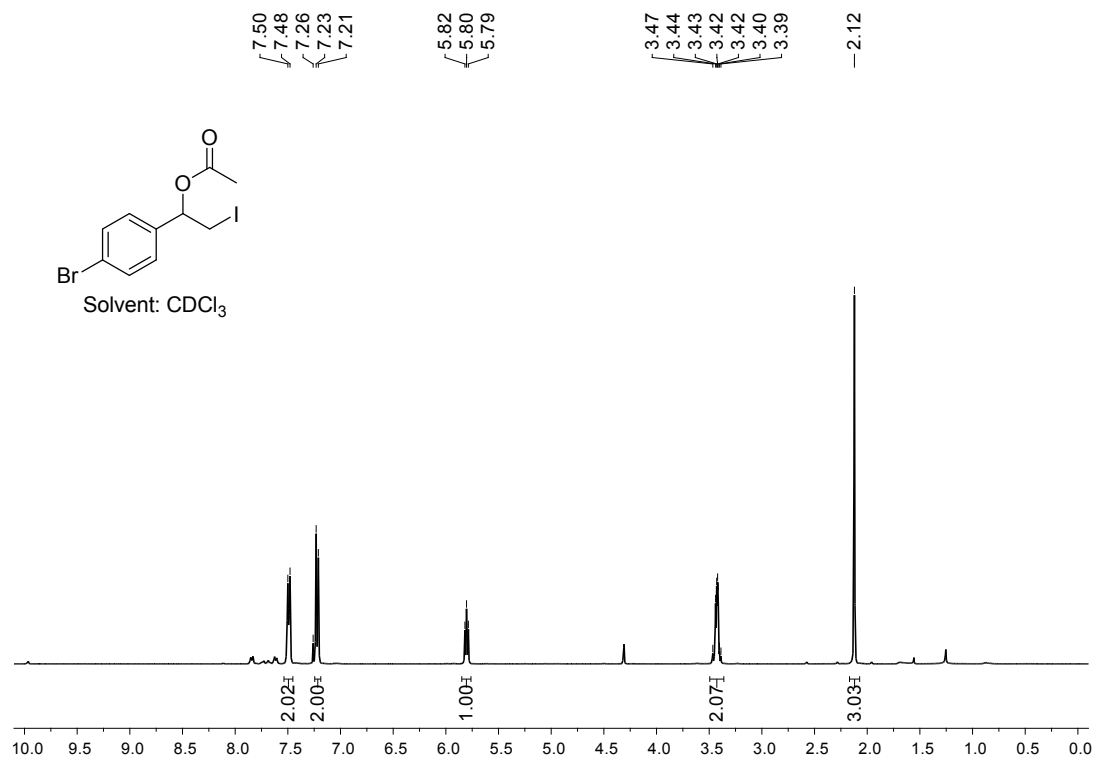


Figure S77: ¹H NMR spectrum of 1-(4-bromophenyl)-2-iodoethyl acetate (**8b**).

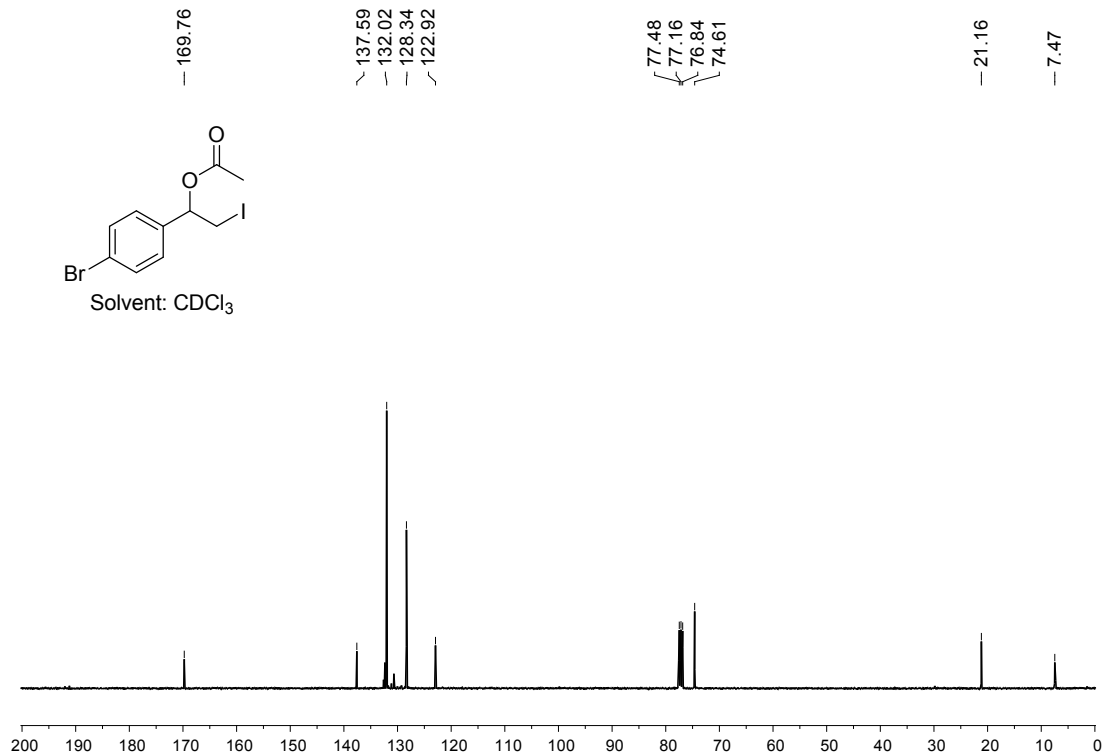


Figure S78: ¹³C NMR spectrum of 1-(4-bromophenyl)-2-iodoethyl acetate (**8b**).

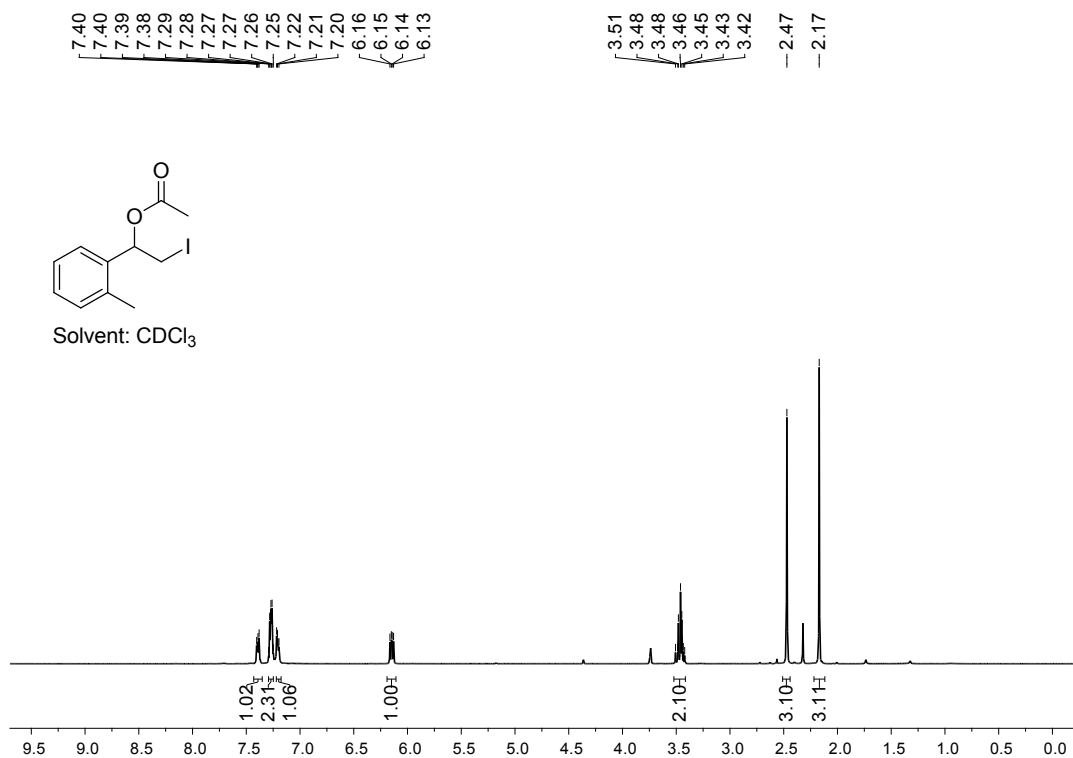


Figure S79: ¹H NMR spectrum of 2-iodo-1-(*o*-tolyl)ethyl acetate (**8c**).

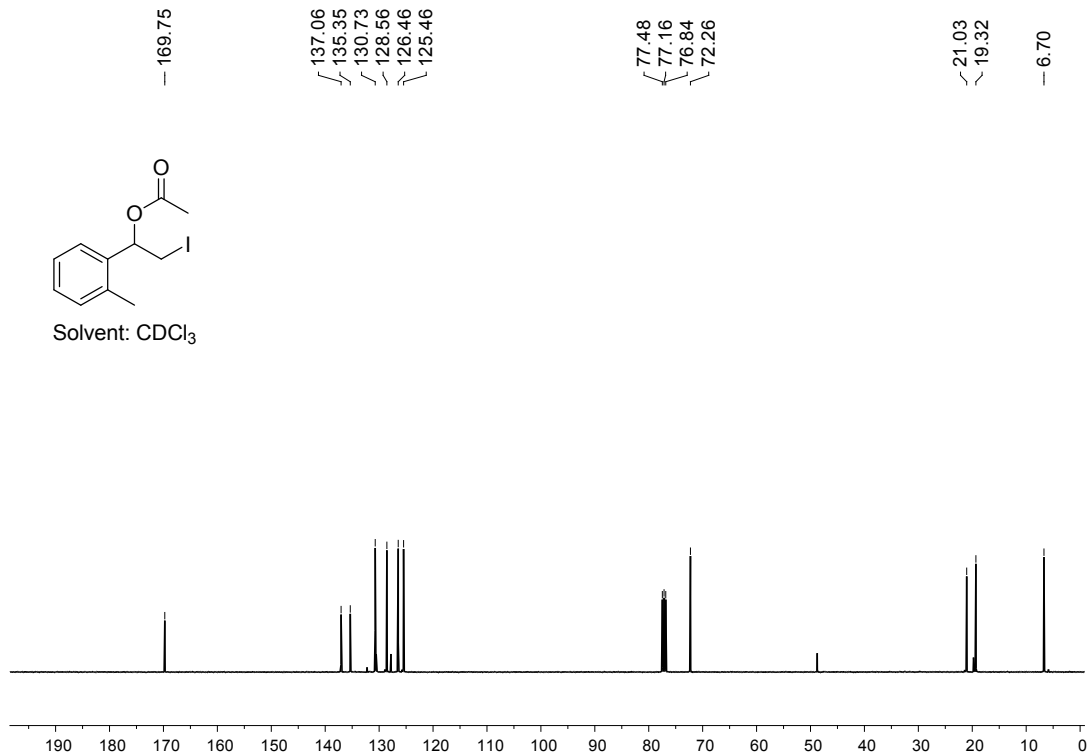


Figure S80: ¹³C NMR spectrum of 2-iodo-1-(*o*-tolyl)ethyl acetate (**8c**).

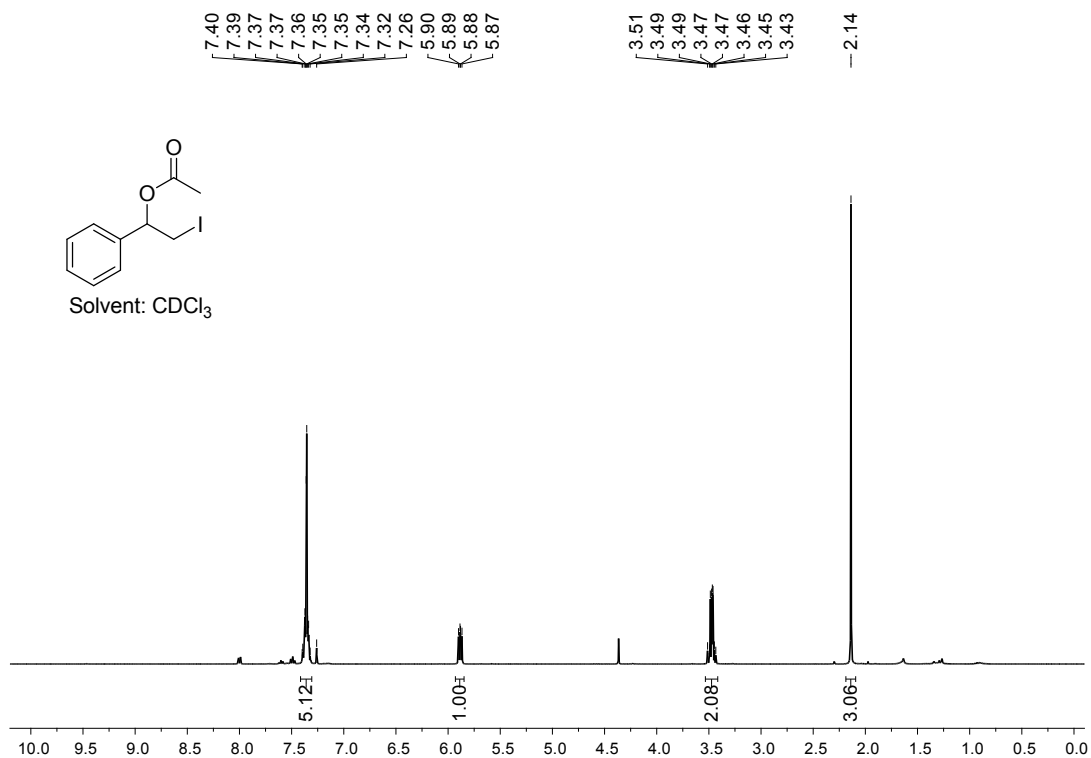


Figure S81: ¹H NMR spectrum of 2-iodo-1-phenylethyl acetate (**8d**).

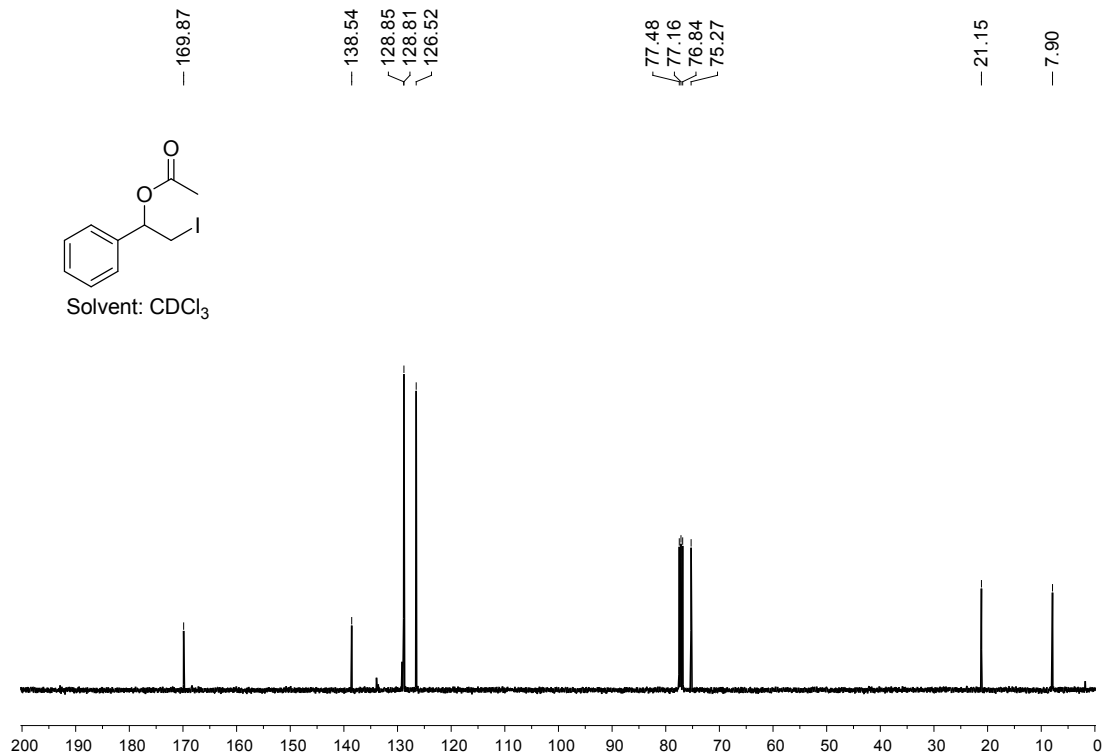


Figure S82: ¹³C NMR spectrum of 2-iodo-1-phenylethyl acetate (**8d**).

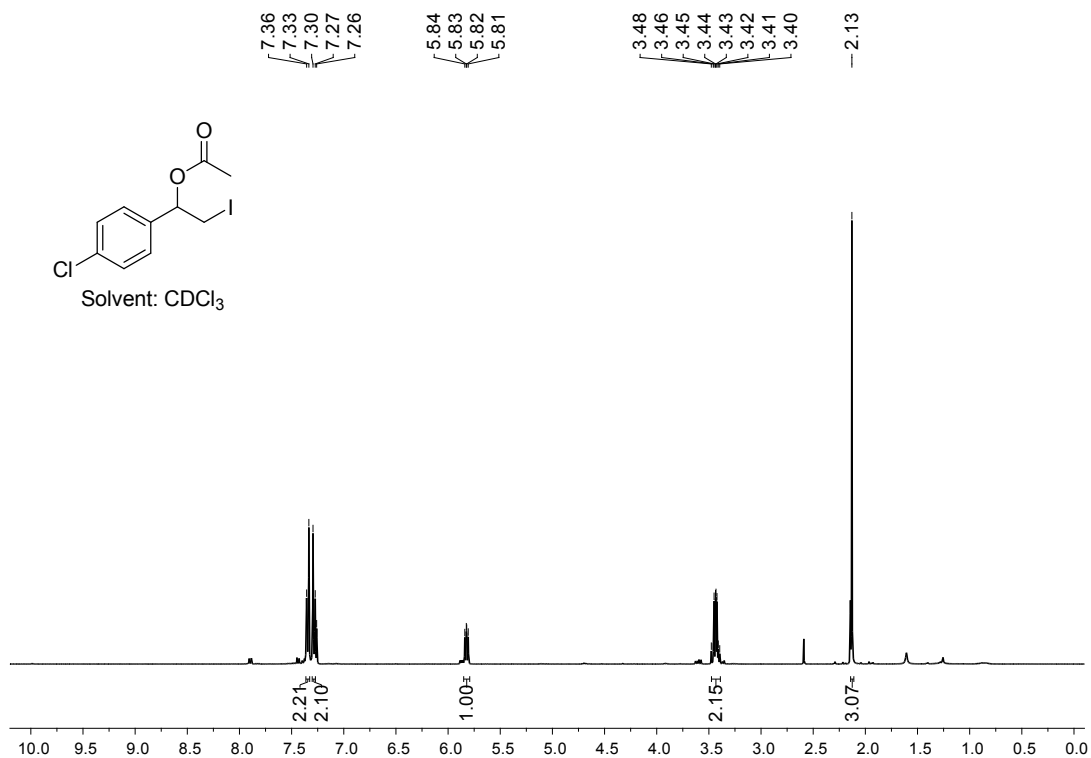


Figure S83: ^1H NMR spectrum of 1-(4-chlorophenyl)-2-iodoethyl acetate (**8e**).

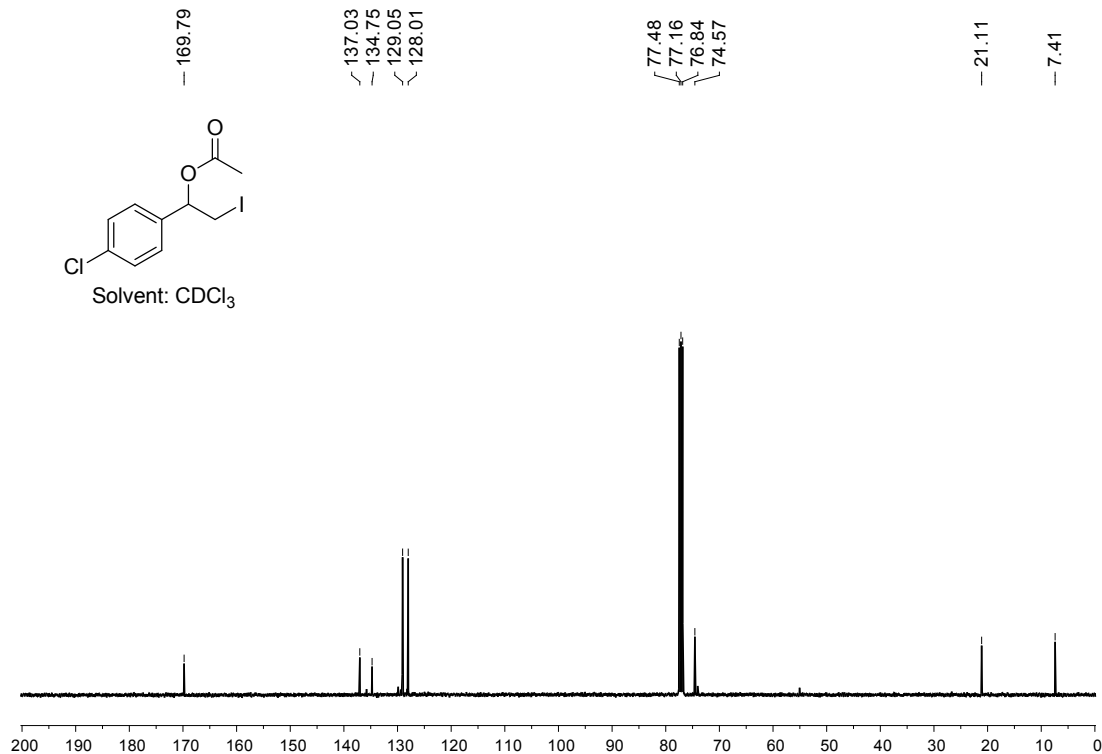


Figure S84: ^{13}C NMR spectrum of 1-(4-chlorophenyl)-2-iodoethyl acetate (**8e**).

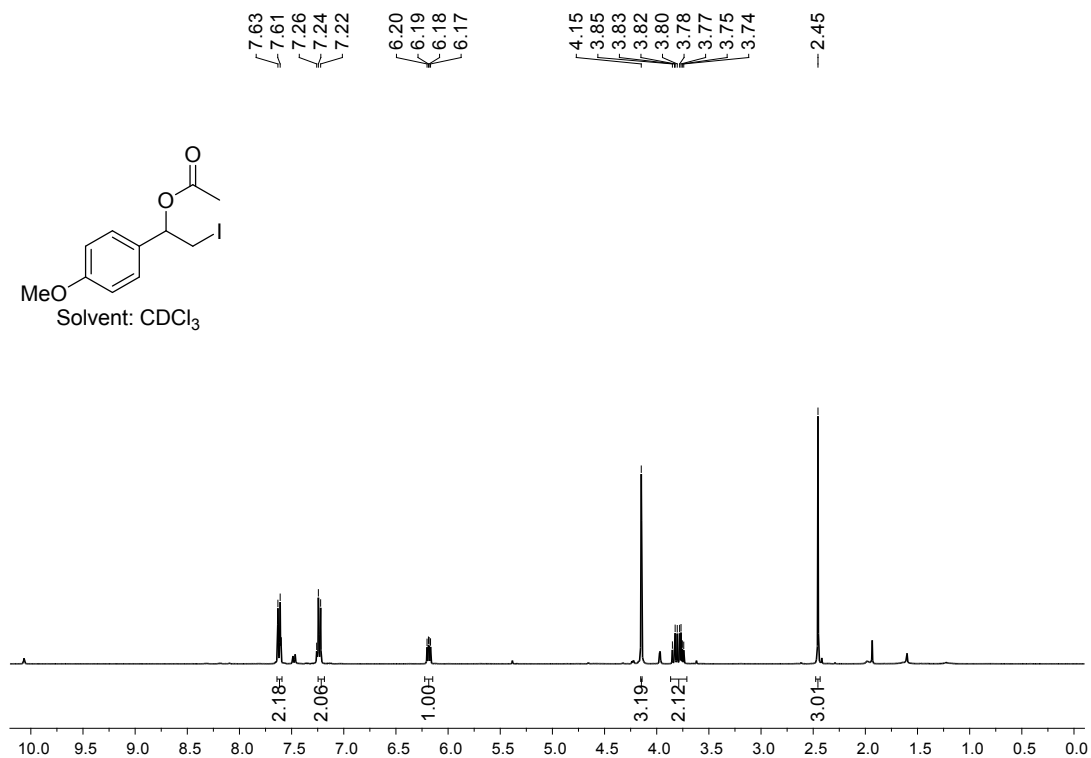


Figure S85: ¹H NMR spectrum of 2-iodo-1-(4-methoxyphenyl)ethyl acetate (**8f**).

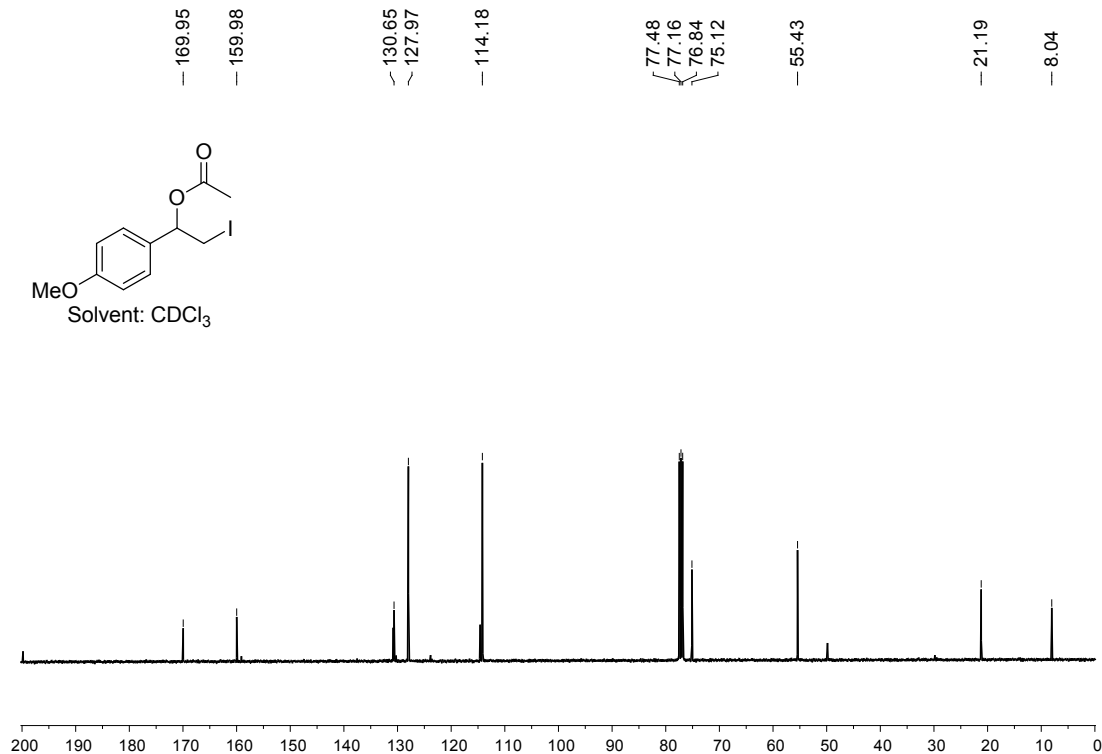


Figure S86: ¹³C NMR spectrum of 2-iodo-1-(4-methoxyphenyl)ethyl acetate (**8f**).

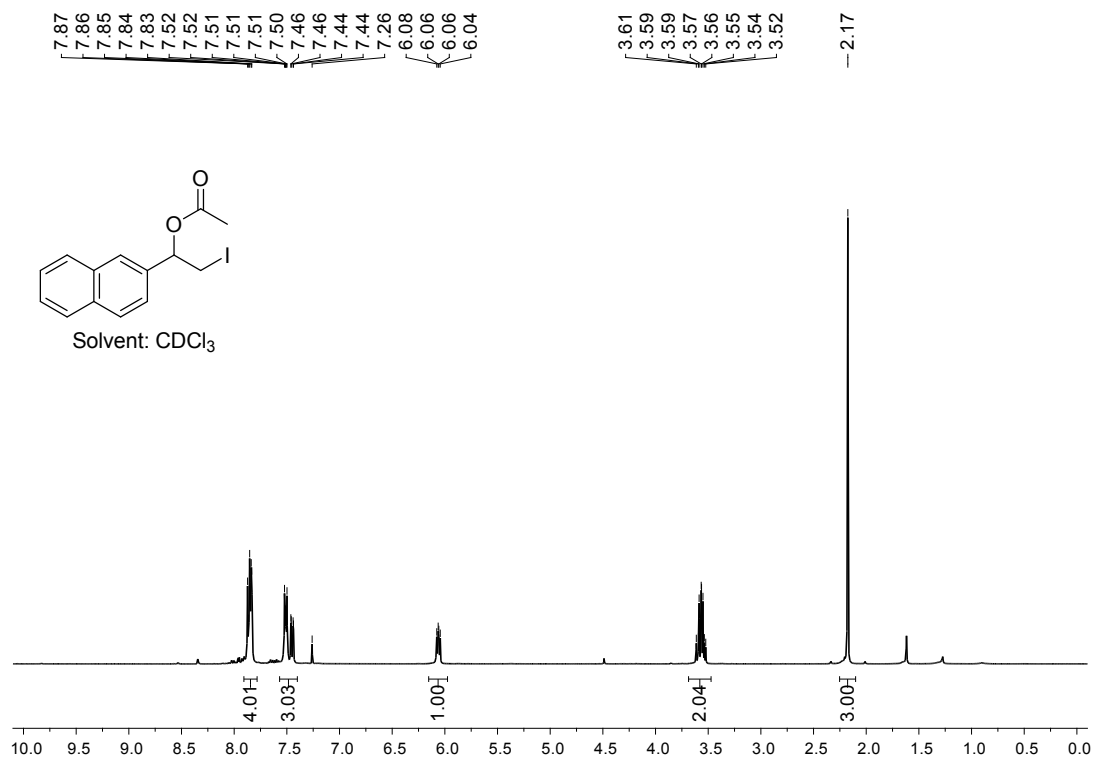


Figure S87: ^1H NMR spectrum of 2-iodo-1-(naphthalen-2-yl)ethyl acetate (**8g**).

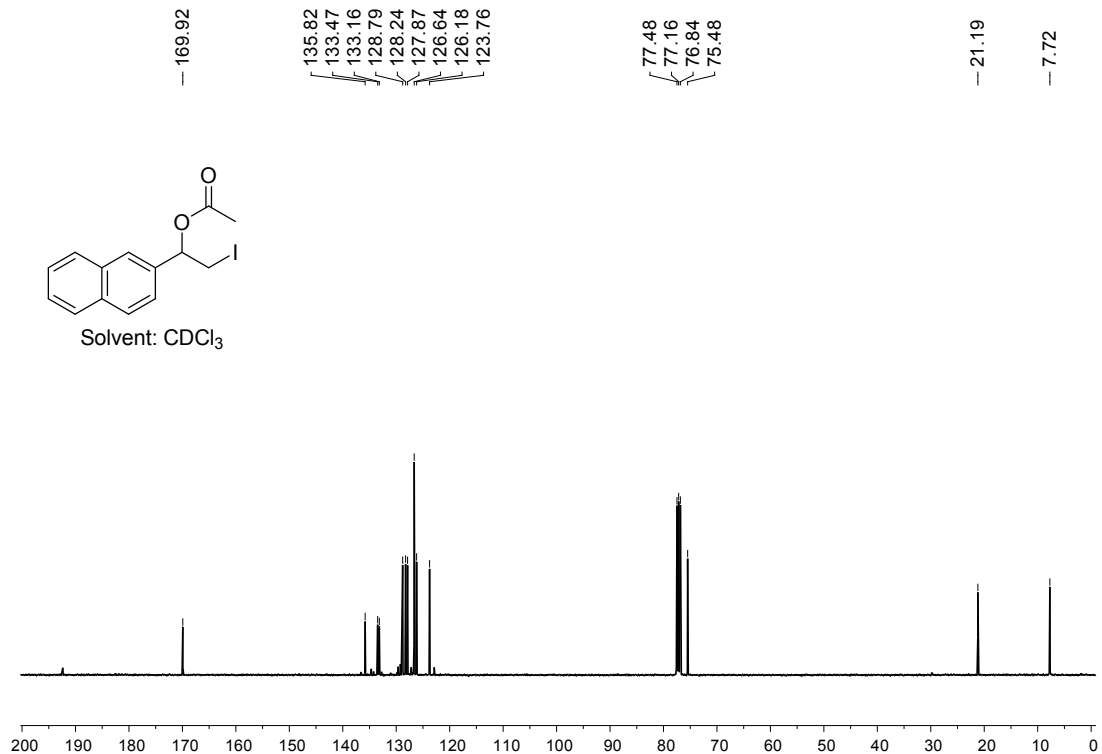


Figure S88: ^{13}C NMR spectrum of 2-iodo-1-(naphthalen-2-yl)ethyl acetate (**8g**).

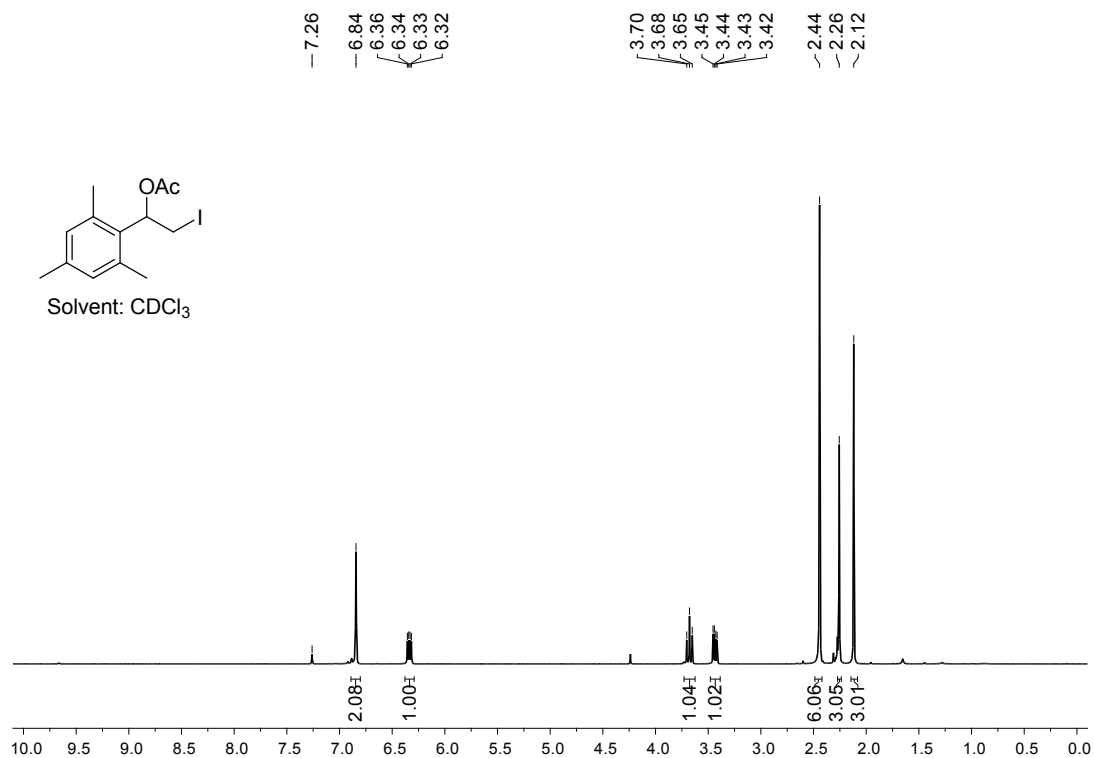


Figure S89: ¹H NMR spectrum of 2-iodo-1-mesitylethyl acetate (**8h**).

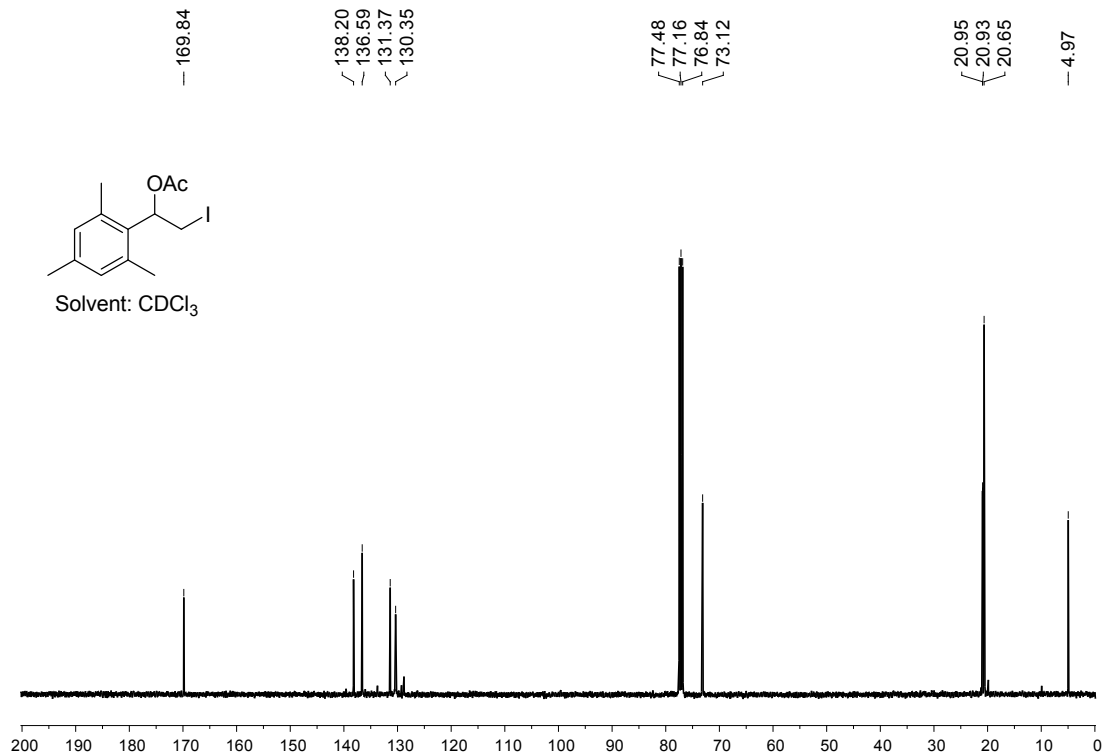


Figure S90: ¹³C NMR spectrum of 2-iodo-1-mesitylethyl acetate (**8h**).

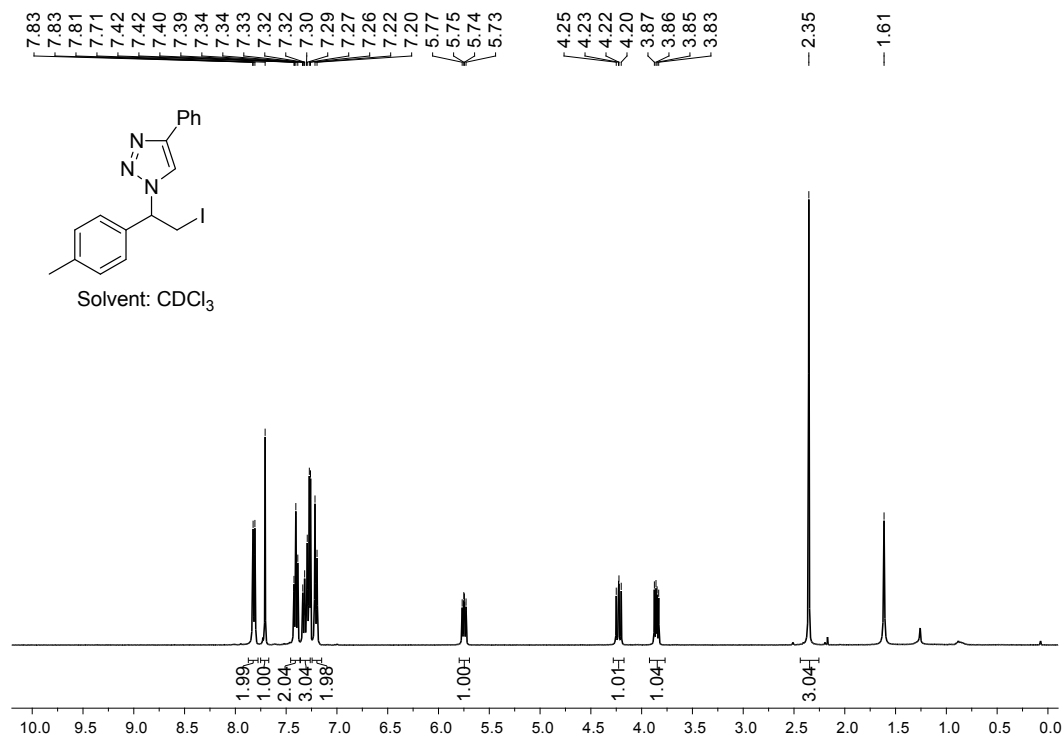


Figure S91: ¹H NMR spectrum of 1-(2-iodo-1-(*p*-tolyl)ethyl)-4-phenyl-1*H*-1,2,3-triazole (9).

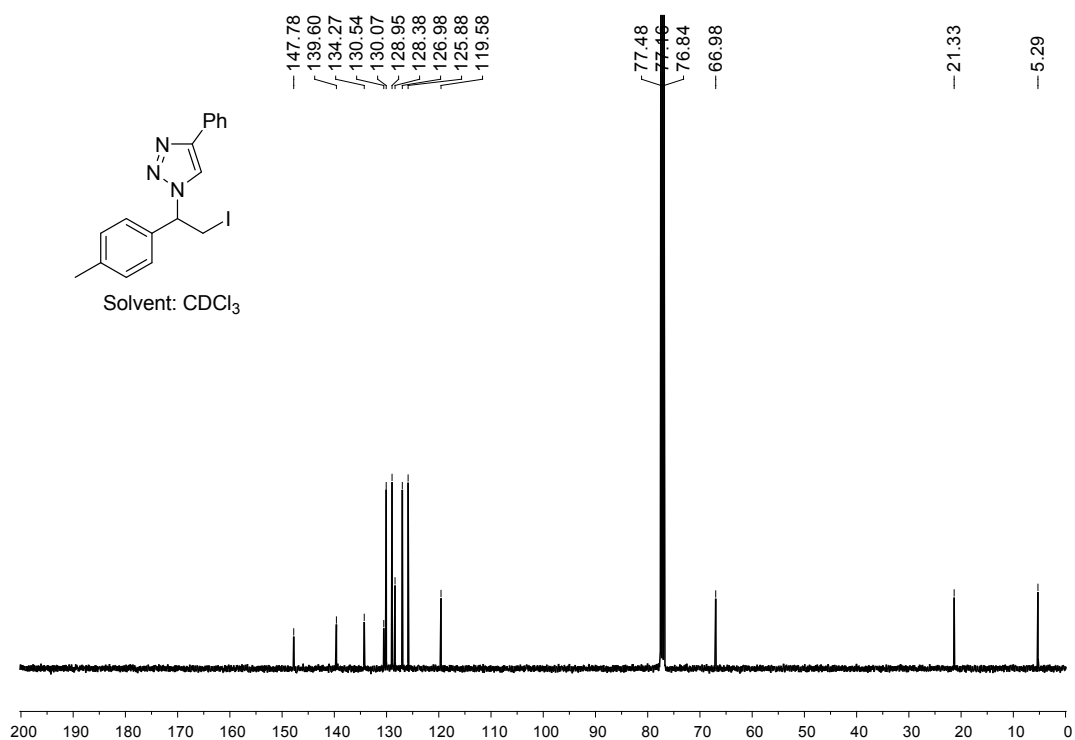


Figure S92: ¹³C NMR spectrum of 1-(2-iodo-1-(*p*-tolyl)ethyl)-4-phenyl-1*H*-1,2,3-triazole (9).

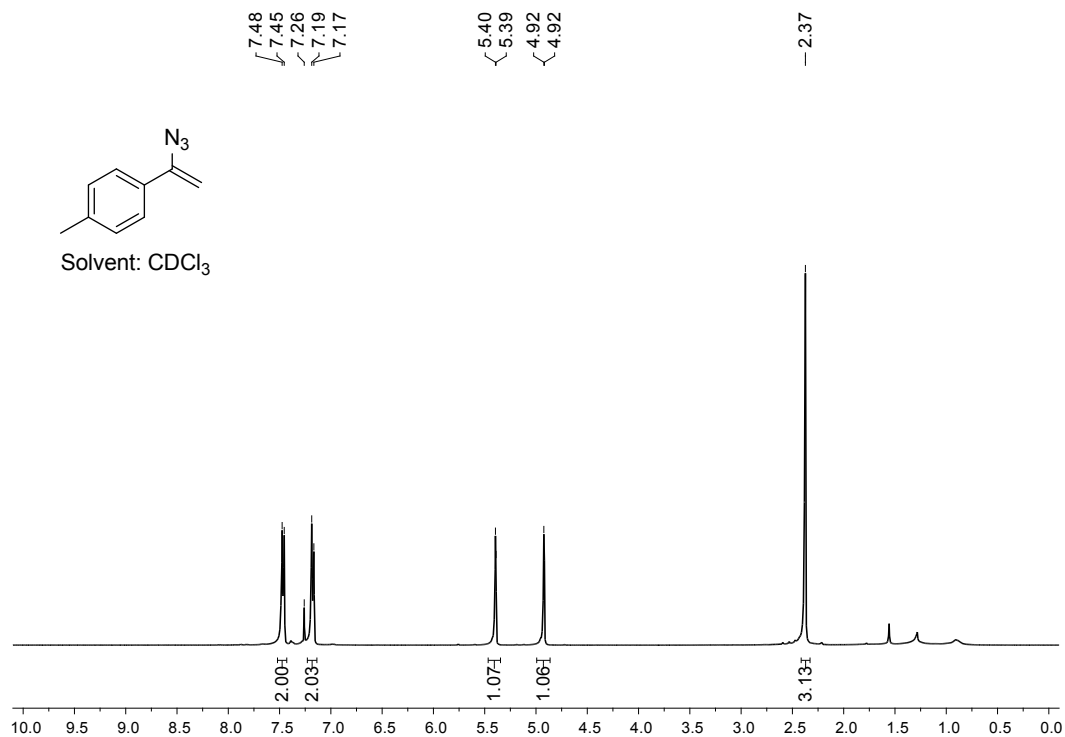


Figure S93: 1H NMR spectrum of 1-(1-azidovinyl)-4-methylbenzene (10).

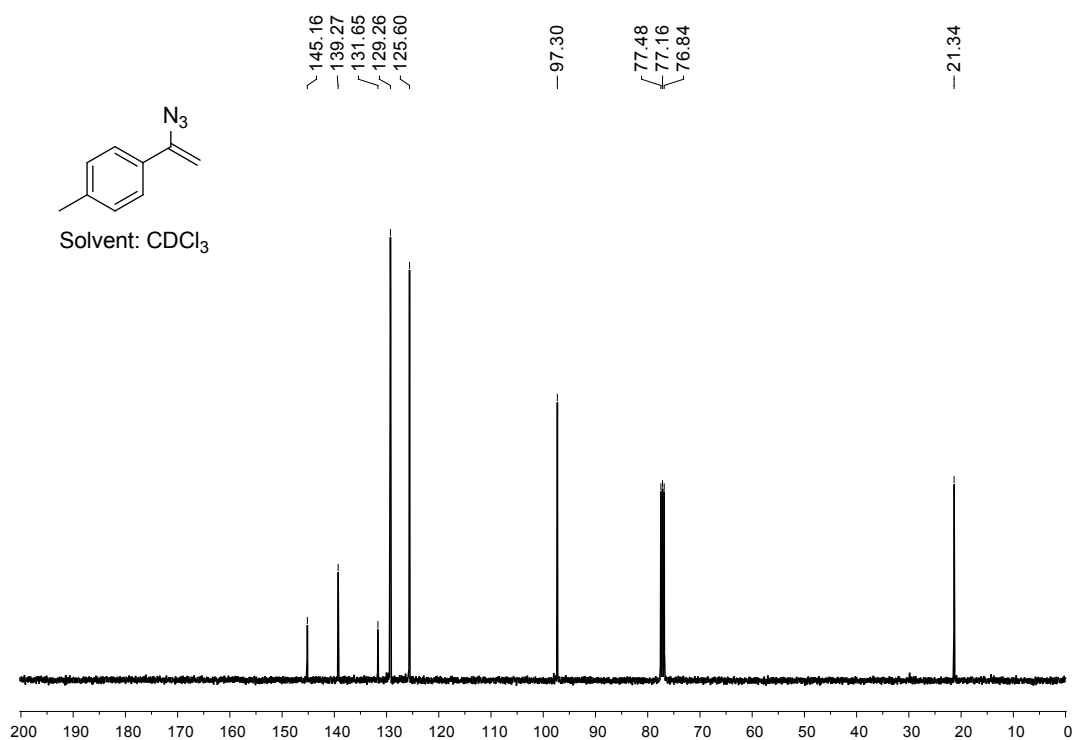


Figure S94: ^{13}C NMR spectrum of 1-(1-azidovinyl)-4-methylbenzene (10).

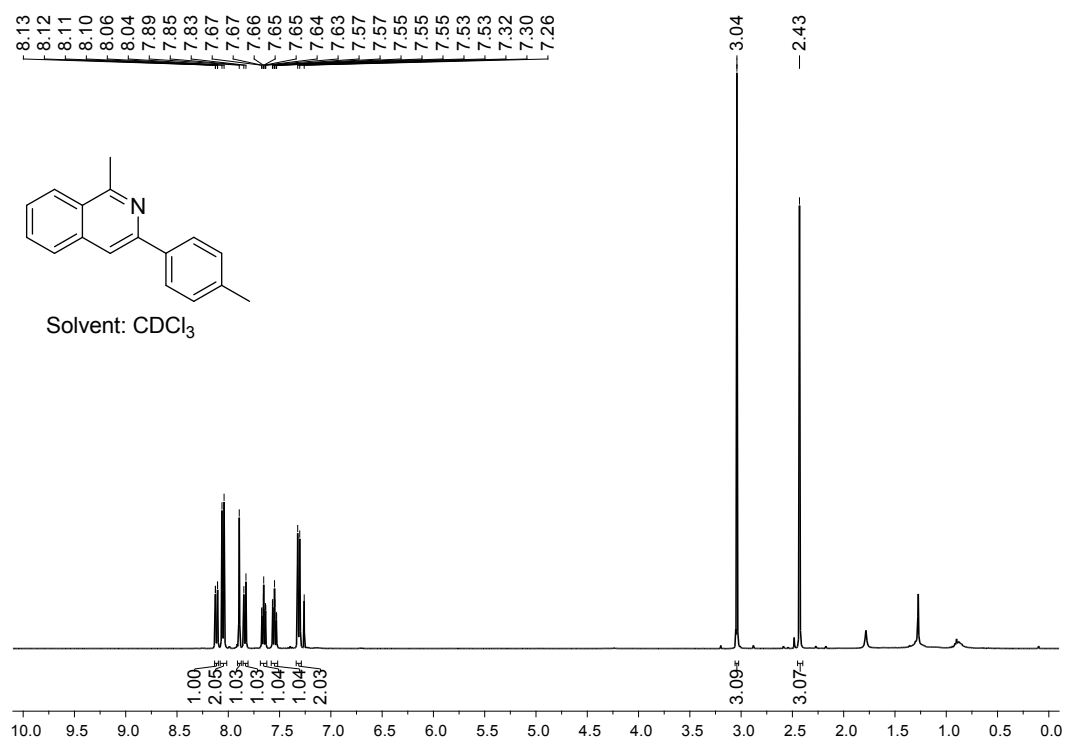


Figure S95: ¹H NMR spectrum of 1-methyl-3-(*p*-tolyl)isoquinoline (12).

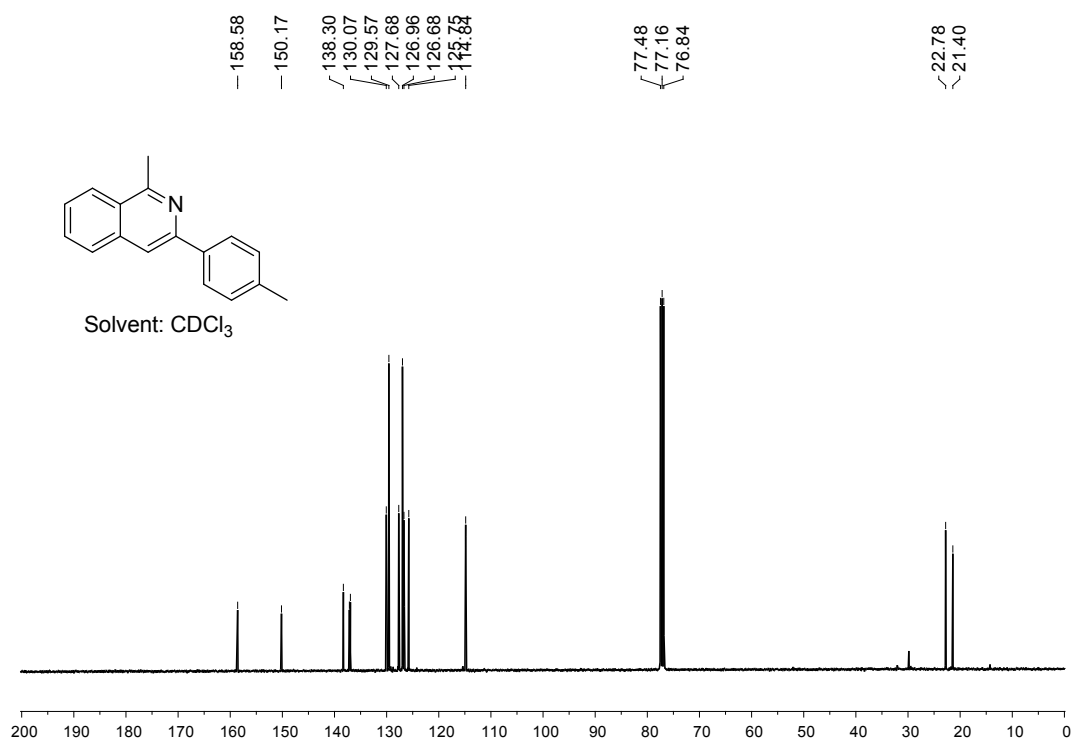


Figure S96: ¹³C NMR spectrum of 1-methyl-3-(*p*-tolyl)isoquinoline (12).

Diastereomeric ratio of compounds 3h and 3p

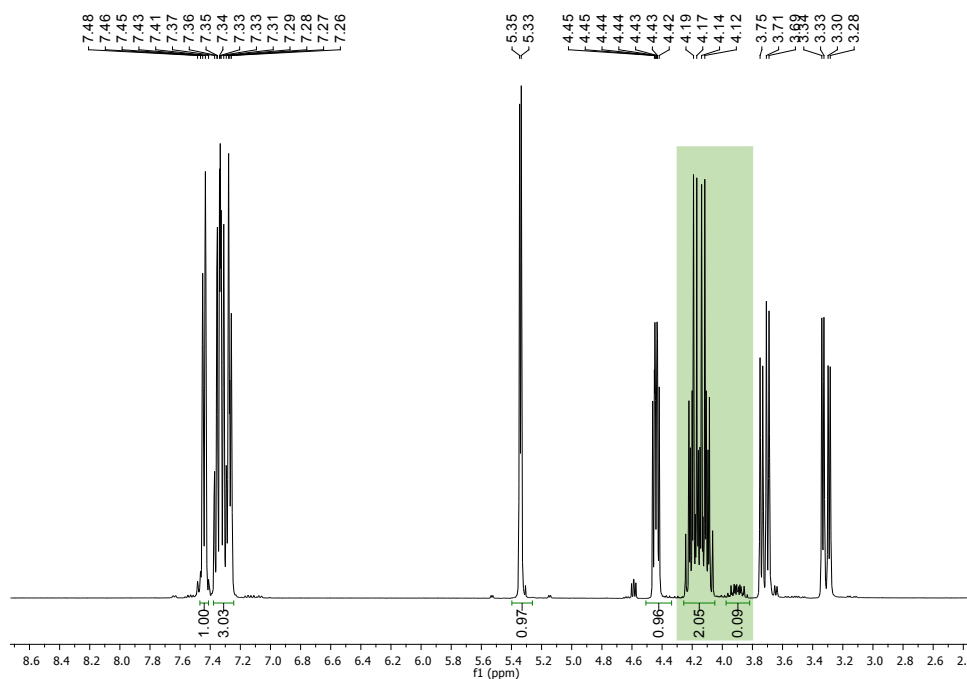


Figure S97: ¹H NMR spectrum of 2-iodo-1-(2,2,2-trifluoroethoxy)-2,3-dihydro-1H-indene (**3h**), **d.r. > 19 : 1**

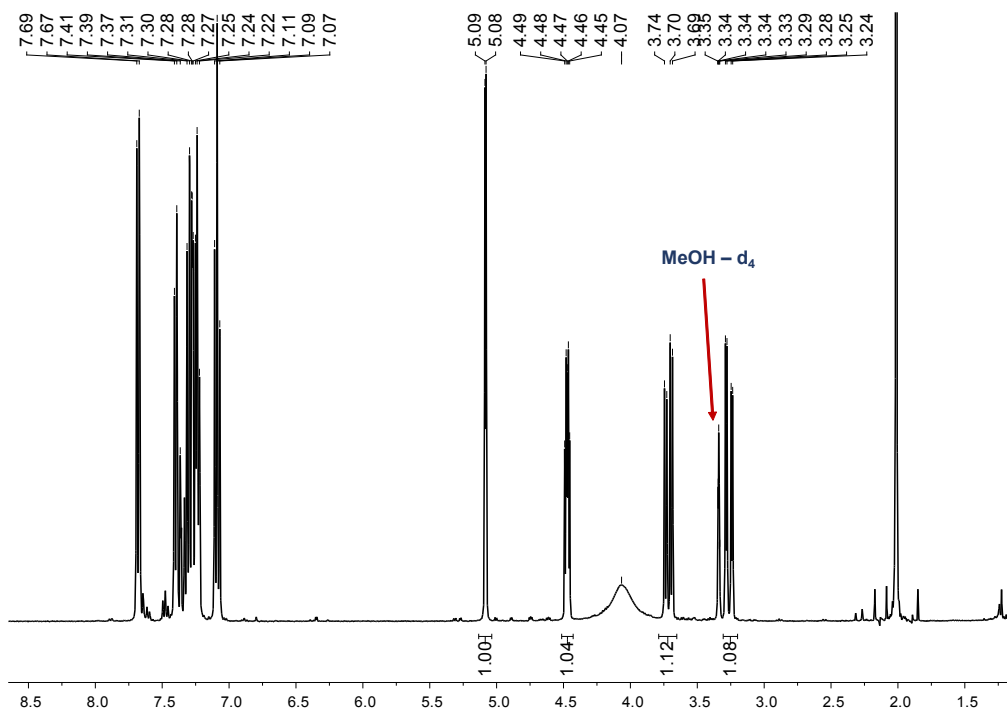


Figure S98: ¹H NMR spectrum of crude 2-iodo-1-trideuteriomethoxy-2,3-dihydro-1H-indene (**3p**).