Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Visible Light-induced Phosphine-Catalyzed Perfluoroalkylation of Indoles

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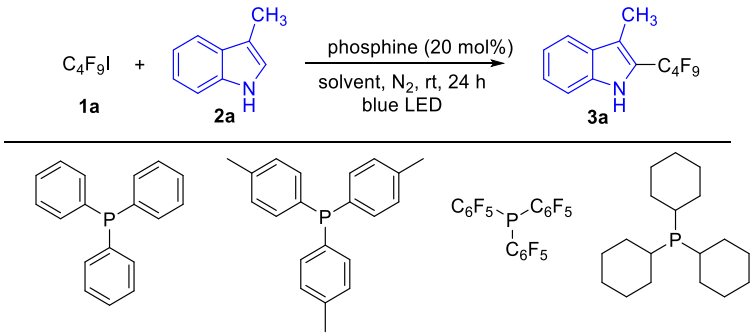
I. General information

Commercially available materials purchased from Energy Chemical were used as received. Unless otherwise specified, all reactions were carried out under an atmosphere in 10 mL dry Schlenk tube. NMR spectra were recorded on a Brüker ASCEND 400 (400 MHz) spectrometer (^{1}H: 400 MHz, ^{13}C: 101 MHz, ^{19}F: 377 MHz). Chemical shifts (δ) for ^{1}H and ^{13}C NMR spectra are given in ppm relative to TMS. The residual solvent signals were used as references for ^{1}H and ^{13}C NMR spectra and the chemical shifts converted to the TMS scale ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad, and etc. All first-order splitting patterns were assigned on the base of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). High resolution mass spectrometer analysis (HRMS) was performed on Thermo Fisher Q Exactive mass spectrometer. Melting point (m.p.): melting points were measured on a Beijing Tech Instrument X-4 digital display micro melting point apparatus and are uncorrected. Analytical thin-layer chromatography (TLC) was carried out on pre-coated silica gel plate (0.2 mm thickness). Visualization was performed using a UV lamp.

II. Experimental section: condition optimization

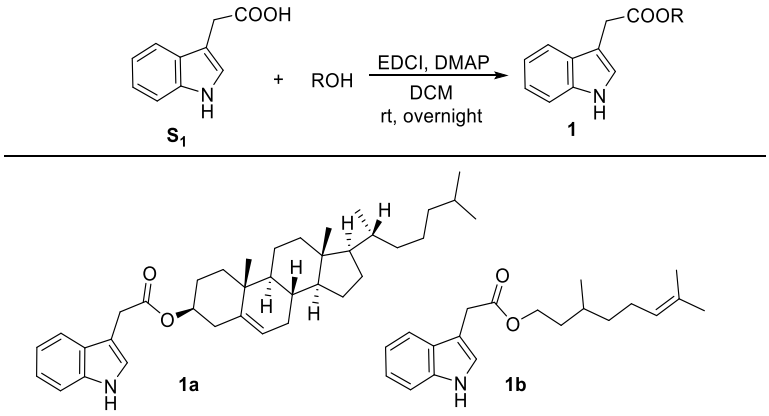
Table 1. Screening of different phosphines, light soures and solvents [a].



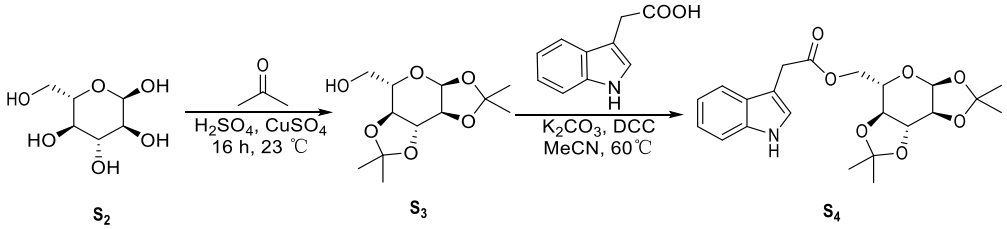
Entry	phosphine	Solvent	Light Source (nm)	Yield (%)[b]
1	PPh_3	CH_3CN	440-445	53
2	$P(p\text{-Tol})_3$	CH_3CN	440-445	34
3	$P(C_6F_5)_3$	CH_3CN	440-445	5<
4	PCy_3	CH_3CN	440-445	5<
5	-	CH_3CN	440-445	5<
6	PPh_3	THF	440-445	52
7	PPh_3	CH_3OH	440-445	80
8	PPh_3	DMF	440-445	66
9	PPh_3	CH_2Cl_2	440-445	26
10	PPh_3	CH_3OH	425-430	53
12	PPh_3	CH_3OH	460-465	27
13	PPh_3	CH_3OH	515-520	0
14	PPh_3	CH_3OH	-	0
15[c]	PPh_3	CH_3OH	440-445	0

[a]Reaction conditions: **1a** (0.11 mmol). **2a** (0.10mmol), Phosphine (20 mol%), Solvent (1.0 mL), blue LED 10 w, rt, N_2, 24 h. [b]Yields were isolated yields after purification by column chromatography. [c]**1a** (0.11 mmol). **2a** (0.10mmol), PPh_3 (20 mol%), CH_3OH (1.0 mL), blue LED 10 w, rt.

III. Preparation of indole acetate



Indole-3-acetic acid **S_1** (0.50 g, 2.85 mmol), EDCI (0.60 g, 3.13 mmol), DMAP (0.40 g, 3.13 mmol) and alcohol (1.0 equiv.) was dissolved in 15.0 mL of DCM in the round-bottom flask and further stirred overnight at room temperature. After completion of the reaction, monitored by TLC plate, filtrated and concentrated to give crude product. The crude product was purified by column chromatography on silica gel with PE / EtOAc (15:1) to afford the desired product **1a** (**1b**).[1]



Anhydrous $CuSO_4$ (5.80 g, 36.30 mmol) was dissolved in acetone (51.0 mL, dried over $MgSO_4$) and stirred under argon. To this solution was added concentrated H_2SO_4 (0.30 mL) and *D*-galactose **S_1** (4.00 g, 22.00 mmol) and stirred at room temperature overnight. As uspension of $NaHCO_3$ (7.90 g, 94 .00mmol) in water (15.00 mL) was added to the mixture. The precipitate was removed by filtration and washed with acetone. The washing and filtrate were combined, and the solution rotary evaporated to remove acetone. The product was extracted with diethyl ether (3 × 50 mL) from the aqueous phase. The combined ether solution was dried over anhydrous $MgSO_4$ and then rotary evaporated. The product was purified via a silica column chromatography on silica gel with PE/EtOAc (5:1) to afford the desired product **S_3**, Yield = 89%. Then 1,2:3,4-Di-O-isopropylidene-α-D-galactopyranose (1.00 g, 3.84 mmol), K_2CO_3 (1.00 g, 7.68 mmol), DCC (1.60 g, 7.68 mmol) and indole-3-acetic acid (2.70 g, 7.68 mmol) was dissolved in 20 mL of dry MeCN in the round-bottom flask and further stirred overnight at 60 ℃. After completion of the reaction, monitored by TLC plate, filtrated and concentrated to give crude product, The crude product was purified by column chromatography on silica gel with PE/EtOAc (15:1) to afford the desired product **S_4**.[2]

For the synthesis of other conventional indole substrates please refer to Ref..[3],[4]

References:

[1] V. A. Bobrin, S.-P. Chen, C. F. Grandes Reyes, B. Sun, C. K. Ng, Y. Kim, D. Purcell, Z. Jia, W. Gu, J. W. Armstrong, J. McAuley and M. J. Monteiro, Water-Borne Nanocoating for Rapid Inactivation of SARS-CoV-2 and Other Viruses, *ACS Nano.*, 2021, **15**, 14915-14927.

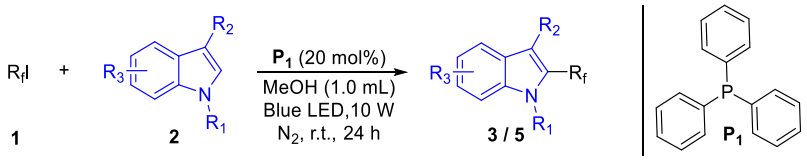
[2] W.-X. Lv, H. Chen, X. Zhang, C. C. Ho, Y. Liu, S. Wu, H. Wang, Z. Jin and Y. R. Chi, Programmable selective acylation of saccharides mediated by carbene and boronic acid, *Chem.*, 2022, **8**, 1518-1534.

[3] J. F. Bai, L. Zhao, F. Wang, F. Yan, T. Kano, K. Maruoka and Y. Li, Organocatalytic Formal (3 + 2) Cycloaddition toward Chiral Pyrrolo[1,2-*a*]indoles via Dynamic Kinetic Resolution of Allene Intermediates, *Org. Lett*., 2020, **22**, 5439-5445.

[4] R. A. Unhale, M. M. Sadhu and V. K. Singh, Chiral Bronsted Acid Catalyzed Enantioselective Synthesis of Spiro-Isoindolinone-Indolines via Formal [3 + 2] Cycloaddition, *Org. Lett.*, 2022, **24**, 3319-3324.

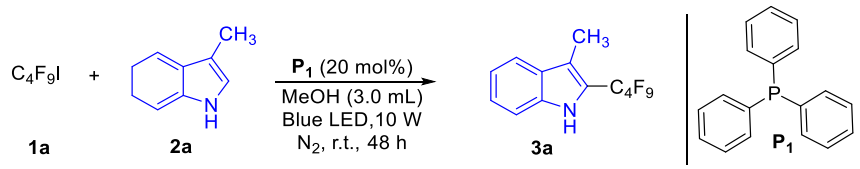
IV. General procedure

General procedure for the catalytic reactions of substrates **1** and **2** to synthesis the product **3** or **5**:



To a 4.0 mL vial equipped with a magnetic stir bar was added 3-methylindoles **1** (0.11 mmol, 38.10 mg) and $\mathbf{P_1}$, put it in a glove box filled with nitrogen to replace the nitrogen, and then perfluoroiodobutanes **2** (0.10 mmol, 13.00 mg) were added. then added CH_3OH (1.00 mL) *via* syringe, Outside the glovebox the reaction vial was transferred into the photoreactor, the irradiation was started and the reaction mixture was allowed to stirred for 24 hours at room temperature. After completion of the reaction, monitored by TLC plate, the mixture was concentrated under reduced pressure. The resulting crude residue was purified *via* column chromatography on silica gel (petroleum ether / ethyl acetate = 100:1) to afford the desired products **3** or **5**.

Procedure for synthesis of **3a** with gram scale



To a 20 mL vial equipped with a magnetic stir bar was added 3-methylindole **1a** (1.1mmol, 0.38 g, 190 μL) and $\mathbf{P_1}$ (0.20 mmol, 52.00 mg), put it in a glove box filled with nitrogen to replace the nitrogen, and then perfluoroiodobutane **2a** (1.0 mmol, 0.13 g) were added. then added CH_3OH (3.00 mL) *via* syringe, Outside the glovebox the reaction vial was transferred into the photoreactor, the irradiation was started and the reaction mixture was allowed to stirred for 48 hours at room temperature. After completion of the reaction, monitored by TLC plate, the mixture was concentrated under reduced pressure. The resulting crude residue was purified *via* column chromatography on silica gel (petroleum ether / ethyl acetate = 100:1) to afford the desired product **3a** (0.25 g, 70.4% yield).

V. Antibacterial Activity

Antibacterial Activity in Vitro: Antibacterial activities of the title compounds against Xanthomonas axonopodis pv. citri (Xac) were evaluated by using the turbidimeter test. Thiodiazole-copper (TC) and Bismerthiazol (BT) was used as the positive controls. The compound was dissolved in 150.0 μL of dimethylformamide and diluted with 0.1% (*V / V*) Tween-20 to prepare the solutions of two concentrations (100 and 50 μg/mL). 1.0 mL of the above solution was added to the non-toxic nutrient broth (NB: 1.5 g of beef extract, 2.5 g of peptone, 0.5 g of yeast powder, 5.0 g of glucose and 500 mL of distilled water, pH = 7.0 ~ 7.2) liquid medium in a 4.0 mL tube. Then, 40.0 μL of NB solution containing Xanthomonas Campestris pv. citri (Xac) was added to 5.0 mL of the NB solution containing the test compound. The inoculated test tube was incubated at (28 ± 1) °C under continuous shaking at 200 rpm for 24 h. The culture growth was monitored by measuring the optical density at 595 nm (OD_{595}) and expressed as corrected turbidity. The relative inhibitory rate was calculated as follows:

$I\ (\%) = (C_{tur} - T_{tur}) / C_{tur} \times 100\%$

C_{tur}: the corrected turbidity value of bacterial growth on untreated NB;

T_{tur}: the corrected turbidity value of bacterial growth on treated NB;

I: The relative inhibitory rate.

Table 2. In *vitro* antibacterial activity of the target compounds against ***Xac***[a]

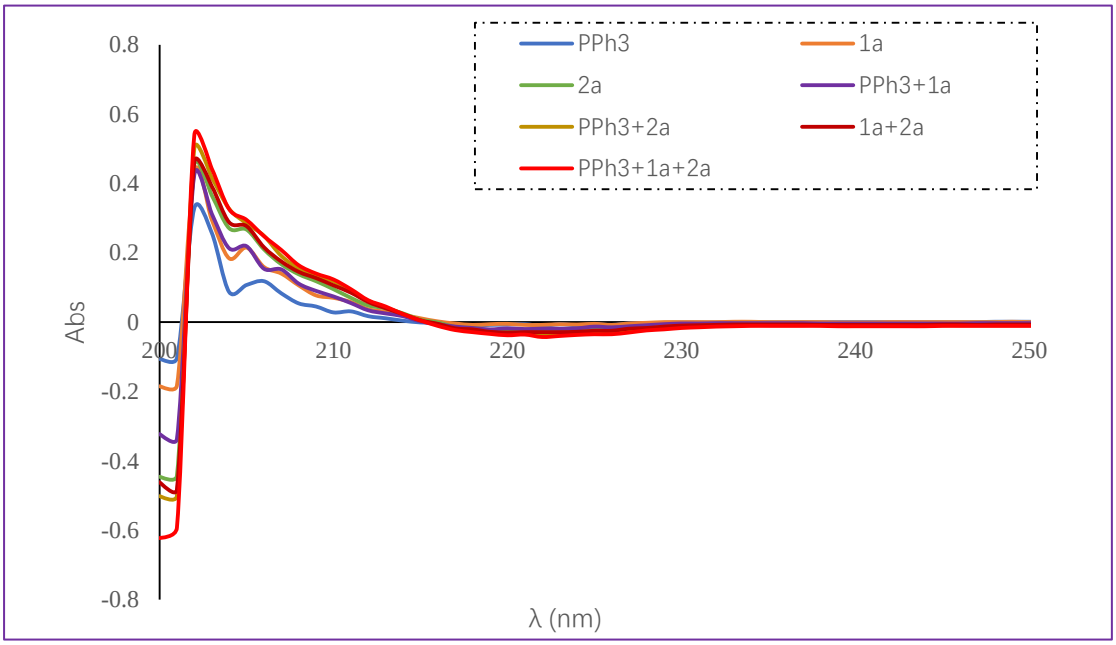
	Xac inhibition rate (%)	
compounds	100 μg/mL	50 μg/mL
3a	70.38 ±6.02	69.62 ±4.08
3b	43.82 ±8.72	44.25 ±3.07
3c	74.89 ±1.1	72.96 ±6.96
3d	75.00 ±5.24	74.46 ±1.72
3f	74.09 ±1.97	69.19 ±3.06
3g	68.06 ±0.87	56.18 ±4.03
3i	78.6 ±2.06	75.97 ±2.05
3j	40.32 ± 3.48	31.67 ±8.71
3k	79.52 ±1.21	73.49 ±3.5
3l	36.99 ±9.73	28.06 ±9.72
3m	76.99 ±2.65	65.59 ±2.1
3n	71.08 ±1.5	64.41 ±0.65
3o	80.16 ±3.08	68.06 ±1.71
3p	75.65 ±1.21	69.03 ±3.1
3r	45.54 ±8.21	38.71 ±4.52
3s	27.53 ±4.05	35.11 ±5.93
3t	34.62 ±5.4	17.63 ±3.75
3ca	33.33 ± 9.46	32.47 ± 1.53
3ea	76.24 ±0.95	75.43 ±2.2
3u	40.81 ±4.39	32.63 ±2.01
3w	59.62 ± 7.59	46.18 ± 3.91
3x	81.61 ±0.5	80.81 ±0.92
5a	79.78 ±0.93	68.82 ±0.9
5b	44.25 ±5.51	38.82 ±4.15
5c	25.75 ±3.75	18.82 ±2.25
5d	23.28 ± 2.51	17.26 ± 1.68
5e	15.7 ± 4.32	7.9 ± 3.87
Thiodiazole-copper[b]	35.91 ± 2.63	24.14 ± 5.33

Bismerthiazol[c]	80.38 ± 2.7	43.12 ± 0.55
CK	13.71 ± 7.6	11.4 ±1.26

[a] All data were average data of three replicates. [b]、[c] Commercial bactericide, used as the positive control

VI. UV-Vis-Measurements

We have carried out UV-Vis absorption experiments with both substrates and the triphenylphosphine. The bathochromic shift in the UV-vis absorbance spectra is difficult to be detected, which is in accordance with previous studies on the PPh_3/C_4F_9I EDA complex formations. Detailed data is listed below:



nm	Abs						
	PPh_3	**1a**	**2a**	PPh_3+**1a**	PPh_3+**2a**	**1a**+**2a**	PPh_3+**1a**+**2a**
660	0.002	0.003	0.002	0.003	0.001	0.002	0.001
659	0.002	0.003	0.002	0.002	0.001	0.001	0.001
658	0.002	0.003	0.002	0.002	0.001	0.001	0.001
657	0.002	0.003	0.002	0.002	0.001	0.001	0.001
656	0.002	0.003	0.002	0.002	0.001	0.001	0.001
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647	0.002	0.003	0.002	0.002	0.001	0.001	0
646	0.002	0.003	0.002	0.002	0.001	0.001	0
645	0.002	0.003	0.002	0.002	0.001	0.001	0.001
644	0.002	0.003	0.002	0.002	0.001	0.001	0.001
643	0.002	0.003	0.002	0.002	0.001	0.001	0.001
642	0.002	0.003	0.002	0.002	0.001	0.001	0
641	0.002	0.003	0.002	0.002	0.001	0.001	0.001
640	0.002	0.003	0.002	0.002	0.001	0.001	0
639	0.002	0.003	0.002	0.002	0.001	0.001	0.001

638	0.002	0.003	0.002	0.002	0.001	0.001	0.001
637	0.002	0.003	0.002	0.002	0.001	0.001	0.001
636	0.002	0.003	0.002	0.002	0.001	0.001	0.001
635	0.002	0.003	0.002	0.002	0.001	0.001	0
634	0.002	0.003	0.002	0.002	0.001	0.001	0
633	0.002	0.003	0.002	0.002	0.001	0.001	0.001
632	0.002	0.003	0.002	0.002	0.001	0.001	0
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630	0.002	0.003	0.002	0.002	0.001	0.001	0.001
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566	0.002	0.003	0.001	0.002	0.001	0.001	0
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548	0.002	0.003	0.002	0.002	0.001	0.001	0
547	0.002	0.003	0.002	0.002	0.001	0.001	0
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534	0.002	0.003	0.001	0.002	0.001	0.001	0
533	0.002	0.003	0.001	0.002	0.001	0.001	0
532	0.002	0.003	0.001	0.002	0.001	0.001	0
531	0.002	0.003	0.001	0.002	0	0.001	0
530	0.002	0.003	0.001	0.002	0	0.001	0
529	0.002	0.003	0.001	0.002	0	0.001	0
528	0.002	0.003	0.001	0.002	0	0.001	0
527	0.002	0.003	0.001	0.002	0.001	0.001	0
526	0.002	0.003	0.001	0.002	0	0.001	0
525	0.002	0.003	0.001	0.002	0.001	0.001	0
524	0.002	0.003	0.001	0.002	0.001	0.001	0
523	0.002	0.003	0.001	0.002	0	0.001	0
522	0.002	0.003	0.001	0.002	0.001	0.001	0
521	0.002	0.003	0.001	0.002	0.001	0.001	0
520	0.002	0.003	0.001	0.002	0.001	0.001	0
519	0.002	0.003	0.001	0.002	0	0.001	0
518	0.002	0.003	0.001	0.002	0.001	0.001	0
517	0.002	0.003	0.001	0.002	0.001	0.001	0
516	0.002	0.003	0.001	0.002	0	0.001	0
515	0.002	0.003	0.001	0.002	0.001	0.001	0
514	0.002	0.003	0.001	0.002	0.001	0.001	0
513	0.002	0.003	0.001	0.002	0.001	0.001	0
512	0.002	0.003	0.001	0.002	0.001	0.001	0
511	0.002	0.003	0.001	0.002	0.001	0.001	0
510	0.002	0.003	0.001	0.002	0	0.001	0
509	0.003	0.003	0.001	0.002	0.001	0.001	0
508	0.003	0.003	0.002	0.002	0.001	0.001	0
507	0.002	0.003	0.001	0.002	0.001	0.001	0
506	0.003	0.003	0.002	0.003	0.001	0.001	0
505	0.003	0.003	0.001	0.002	0.001	0.001	0
504	0.002	0.003	0.001	0.002	0	0.001	0
503	0.002	0.003	0.001	0.002	0.001	0.001	0
502	0.003	0.003	0.001	0.002	0.001	0.001	0
501	0.003	0.003	0.001	0.002	0	0.001	0
500	0.003	0.003	0.001	0.002	0	0.001	0
499	0.003	0.003	0.001	0.002	0.001	0.001	0
498	0.003	0.003	0.002	0.002	0.001	0.001	0
497	0.003	0.003	0.001	0.002	0.001	0.001	0
496	0.002	0.003	0.001	0.002	0	0.001	0
495	0.002	0.003	0.001	0.002	0	0.001	0
494	0.002	0.003	0.001	0.002	0.001	0.001	0
493	0.002	0.003	0.001	0.002	0	0.001	0
492	0.002	0.003	0.001	0.002	0	0.001	0
491	0.003	0.003	0.001	0.002	0	0.001	0
490	0.003	0.003	0.001	0.002	0	0.001	0
489	0.002	0.003	0.001	0.002	0	0.001	0

488	0.002	0.003	0.001	0.002	0	0.001	0
487	0.002	0.003	0.001	0.002	0	0.001	0
486	0.002	0.003	0.001	0.002	0	0.001	0
485	0.003	0.003	0.001	0.002	0	0.001	0
484	0.002	0.003	0.002	0.002	0.001	0.001	0
483	0.002	0.003	0.001	0.002	0.001	0.001	0
482	0.003	0.003	0.001	0.002	0.001	0.001	0
481	0.002	0.003	0.001	0.002	0	0.001	0
480	0.002	0.003	0.001	0.002	0	0.001	0
479	0.003	0.003	0.001	0.002	0	0.001	0
478	0.002	0.003	0.001	0.002	0	0.001	0
477	0.003	0.004	0.001	0.002	0.001	0.001	0
476	0.002	0.004	0.002	0.002	0.001	0.001	0
475	0.002	0.004	0.002	0.002	0.001	0.001	0
474	0.002	0.004	0.002	0.002	0.001	0.001	0
473	0.002	0.004	0.002	0.002	0.001	0.001	0
472	0.002	0.004	0.002	0.002	0.001	0.001	0
471	0.002	0.003	0.001	0.002	0	0.001	0
470	0.002	0.003	0.002	0.002	0.001	0.001	0
469	0.002	0.003	0.001	0.002	0	0.001	0
468	0.003	0.003	0.002	0.002	0.001	0.001	0
467	0.002	0.003	0.001	0.002	0	0.001	0
466	0.002	0.003	0.001	0.002	0	0.001	0
465	0.003	0.003	0.001	0.002	0	0.001	0
464	0.002	0.003	0.001	0.002	0	0	-0.001
463	0.002	0.003	0.001	0.002	0	0	-0.001
462	0.002	0.003	0.001	0.002	0	0	-0.001
461	0.002	0.003	0.001	0.002	0	0	-0.001
460	0.002	0.003	0.001	0.002	0	0	-0.001
459	0.002	0.003	0.001	0.002	0	0	-0.001
458	0.002	0.003	0.001	0.002	0	0	-0.001
457	0.002	0.003	0.001	0.002	0	0	-0.001
456	0.002	0.003	0.001	0.002	0	0	-0.001
455	0.002	0.003	0.001	0.002	0	0.001	-0.001
454	0.002	0.003	0.001	0.002	0	0	-0.001
453	0.002	0.003	0.001	0.002	0	0.001	0
452	0.003	0.003	0.001	0.002	0	0.001	0
451	0.003	0.003	0.001	0.002	0	0.001	0
450	0.002	0.003	0.001	0.002	0	0.001	0
449	0.002	0.003	0.001	0.002	0	0.001	0
448	0.002	0.003	0.001	0.002	0	0.001	0
447	0.002	0.003	0.001	0.002	0	0.001	0
446	0.002	0.004	0.002	0.002	0	0.001	0
445	0.002	0.003	0.001	0.002	0	0.001	0
444	0.002	0.004	0.002	0.002	0	0.001	0
443	0.002	0.004	0.002	0.002	0	0.001	0
442	0.002	0.004	0.002	0.002	0	0.001	0
441	0.002	0.004	0.002	0.002	0	0.001	0
440	0.002	0.004	0.002	0.002	0.001	0.001	0
439	0.003	0.004	0.002	0.002	0.001	0.001	0

438	0.001	0.002	-0.001	0	-0.002	-0.002	-0.003
437	0.001	0.002	-0.001	0	-0.002	-0.002	-0.003
436	0.001	0.002	-0.001	0	-0.002	-0.002	-0.003
435	0.001	0.002	-0.001	0	-0.002	-0.002	-0.003
434	0.001	0.002	-0.001	-0.001	-0.003	-0.002	-0.003
433	0.001	0.002	-0.002	0	-0.003	-0.002	-0.004
432	0.001	0.002	-0.001	0	-0.003	-0.002	-0.004
431	0.001	0.002	-0.002	0	-0.003	-0.002	-0.004
430	0.001	0.002	-0.002	0	-0.003	-0.002	-0.004
429	0.001	0.001	-0.002	0	-0.003	-0.003	-0.004
428	0.001	0.001	-0.002	0	-0.003	-0.003	-0.004
427	0.001	0.002	-0.002	0	-0.003	-0.002	-0.004
426	0.001	0.002	-0.002	0	-0.003	-0.003	-0.004
425	0.001	0.002	-0.002	0	-0.003	-0.003	-0.004
424	0.001	0.002	-0.002	0	-0.003	-0.003	-0.004
423	0.001	0.002	-0.002	0	-0.003	-0.003	-0.004
422	0.001	0.002	-0.002	0	-0.003	-0.003	-0.004
421	0.001	0.001	-0.002	-0.001	-0.003	-0.003	-0.004
420	0.001	0.001	-0.002	0	-0.003	-0.003	-0.004
419	0.001	0.002	-0.002	0	-0.003	-0.003	-0.004
418	0.001	0.001	-0.002	0	-0.004	-0.003	-0.005
417	0.001	0.001	-0.002	-0.001	-0.004	-0.003	-0.005
416	0.001	0.001	-0.003	-0.001	-0.004	-0.003	-0.005
415	0.001	0.001	-0.003	-0.002	-0.004	-0.003	-0.005
414	0.001	0.001	-0.003	-0.002	-0.004	-0.004	-0.005
413	0.001	0.001	-0.003	-0.001	-0.004	-0.004	-0.006
412	0.001	0.001	-0.003	-0.001	-0.005	-0.004	-0.006
411	0	0.001	-0.003	-0.001	-0.005	-0.004	-0.006
410	0	0.001	-0.004	-0.001	-0.005	-0.004	-0.006
409	0	0.001	-0.004	-0.001	-0.005	-0.004	-0.006
408	0	0.001	-0.004	-0.002	-0.005	-0.005	-0.006
407	0	0.001	-0.004	-0.002	-0.005	-0.005	-0.006
406	0	0.001	-0.004	-0.002	-0.005	-0.005	-0.006
405	0	0.001	-0.004	-0.002	-0.005	-0.005	-0.007
404	0.003	0.004	0.002	0.003	0.001	0.002	0.001
403	0.003	0.005	0.002	0.003	0.002	0.002	0.001
402	0.003	0.004	0.002	0.001	0.002	0.002	0.001
401	0.003	0.005	0.003	0.004	0.002	0.003	0.002
400	0.003	0.005	0.003	0.004	0.002	0.002	0.001
399	0.003	0.005	0.003	0.003	0.002	0.002	0.001
398	0.003	0.005	0.003	0.003	0.002	0.002	0.001
397	0.003	0.005	0.003	0.003	0.002	0.002	0.001
396	0.003	0.005	0.003	0.003	0.002	0.003	0.001
395	0.003	0.005	0.003	0.004	0.002	0.003	0.002
394	0.004	0.005	0.003	0.004	0.002	0.003	0.002
393	0.003	0.005	0.003	0.004	0.002	0.003	0.002
392	0.003	0.006	0.003	0.004	0.002	0.003	0.002
391	0.003	0.005	0.003	0.004	0.002	0.003	0.002
390	0.003	0.005	0.003	0.004	0.003	0.003	0.002
389	0.003	0.005	0.003	0.004	0.003	0.003	0.002

388	0.003	0.005	0.003	0.004	0.002	0.003	0.002
387	0.004	0.006	0.004	0.004	0.003	0.003	0.002
386	0.004	0.006	0.004	0.004	0.003	0.003	0.003
385	0.004	0.006	0.004	0.004	0.003	0.003	0.003
384	0.004	0.006	0.004	0.004	0.003	0.004	0.003
383	0.004	0.006	0.004	0.004	0.003	0.004	0.003
382	0.004	0.006	0.004	0.004	0.003	0.004	0.003
381	0.004	0.006	0.004	0.005	0.003	0.004	0.003
380	0.003	0.006	0.004	0.004	0.003	0.003	0.003
379	0.004	0.006	0.004	0.005	0.004	0.004	0.003
378	0.004	0.006	0.004	0.005	0.004	0.004	0.004
377	0.004	0.006	0.005	0.005	0.004	0.004	0.004
376	0.004	0.006	0.004	0.004	0.004	0.004	0.004
375	0.003	0.006	0.005	0.005	0.004	0.004	0.004
374	0.004	0.007	0.005	0.005	0.004	0.005	0.004
373	0.004	0.007	0.004	0.006	0.005	0.005	0.004
372	0.004	0.007	0.005	0.006	0.005	0.005	0.005
371	0.004	0.007	0.005	0.006	0.005	0.005	0.005
370	0.004	0.007	0.005	0.006	0.005	0.005	0.005
369	0.004	0.008	0.005	0.006	0.005	0.005	0.005
368	0.004	0.007	0.005	0.006	0.005	0.005	0.005
367	0.003	0.007	0.005	0.006	0.005	0.006	0.005
366	0.004	0.008	0.007	0.007	0.006	0.006	0.006
365	0.004	0.008	0.007	0.007	0.006	0.006	0.006
364	0.003	0.008	0.006	0.006	0.005	0.005	0.006
363	0.004	0.009	0.006	0.006	0.006	0.005	0.006
362	0.004	0.009	0.006	0.006	0.005	0.006	0.006
361	0.002	0.005	0.002	0.003	0.001	0.002	0.001
360	0.002	0.005	0.002	0.003	0.001	0.002	0.001
359	0.002	0.004	0.001	0.002	0.001	0.001	0
358	0.002	0.005	0.002	0.003	0.001	0.002	0
357	0.002	0.004	0.001	0.003	0.001	0.001	0
356	0.002	0.005	0.001	0.003	0.001	0.001	0
355	0.002	0.005	0.002	0.003	0.001	0.001	0
354	0.002	0.005	0.002	0.003	0.001	0.002	0
353	0.003	0.005	0.002	0.003	0.001	0.001	0
352	0.002	0.005	0.001	0.003	0.001	0.001	0
351	0.002	0.005	0.002	0.003	0.001	0.001	0
350	0.002	0.005	0.001	0.003	0	0.001	-0.001
349	0.002	0.004	0.001	0.002	0	0.001	-0.001
348	0.002	0.004	0.001	0.003	0	0.001	0
347	0.002	0.004	0.001	0.002	0	0.001	-0.001
346	0.002	0.004	0.001	0.003	0	0	-0.001
345	0.002	0.004	0.001	0.002	0	0.001	-0.001
344	0.002	0.004	0.001	0.002	0	0.001	-0.001
343	0.002	0.004	0.001	0.002	0	0	-0.001
342	0.002	0.004	0.001	0.002	0	0	-0.001
341	0.002	0.004	0.001	0.002	0	0.001	-0.001
340	0.003	0.004	0.001	0.002	0	0.001	-0.001
339	0.002	0.004	0	0.002	0	0.001	-0.001

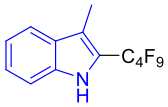
338	0.002	0.004	0.001	0.002	0	0.001	-0.001
337	0.002	0.004	0.001	0.002	0	0.001	-0.001
336	0.003	0.004	0.001	0.002	0	0.001	-0.001
335	0.003	0.004	0.001	0.002	0	0.001	-0.001
334	0.003	0.004	0.001	0.002	0	0.001	-0.001
333	0.003	0.004	0.001	0.002	0	0	-0.001
332	0.003	0.004	0.001	0.002	0	0	-0.001
331	0.003	0.004	0.001	0.002	0	0.001	-0.001
330	0.003	0.004	0.001	0.002	0	0	-0.001
329	0.003	0.004	0	0.002	0	0	-0.002
328	0.002	0.004	0.001	0.002	-0.001	0	-0.001
327	0.002	0.004	0	0.002	-0.001	0	-0.002
326	0.002	0.004	0	0.002	-0.001	0	-0.002
325	0.002	0.004	0	0.002	-0.001	0	-0.002
324	0.002	0.004	0	0.001	-0.001	0	-0.002
323	0.002	0.004	0	0.001	-0.001	-0.001	-0.002
322	0.002	0.004	0	0.001	-0.001	0	-0.002
321	0.002	0.004	0	0.001	-0.001	-0.001	-0.002
320	0.002	0.004	0	0.001	-0.002	-0.001	-0.002
319	0.002	0.003	0	0.001	-0.002	-0.001	-0.003
318	0.002	0.004	0	0.002	-0.002	-0.001	-0.002
317	0.002	0.004	0	0.001	-0.002	-0.001	-0.002
316	0.002	0.004	0	0.002	-0.002	-0.001	-0.002
315	0.002	0.004	0	0.001	-0.002	-0.001	-0.003
314	0.002	0.003	0	0.002	-0.002	-0.001	-0.003
313	0.002	0.004	0	0.001	-0.002	-0.001	-0.003
312	0.002	0.003	0	0.001	-0.002	-0.001	-0.003
311	0.002	0.003	0	0.001	-0.002	-0.001	-0.003
310	0.002	0.003	0	0.001	-0.002	-0.001	-0.003
309	0.002	0.003	-0.001	0.001	-0.002	-0.001	-0.003
308	0.002	0.003	-0.001	0.001	-0.002	-0.001	-0.003
307	0.002	0.003	-0.001	0.001	-0.002	-0.001	-0.003
306	0.002	0.003	-0.001	0.001	-0.002	-0.001	-0.003
305	0.002	0.003	0	0.001	-0.003	-0.001	-0.003
304	0.002	0.003	-0.001	0.001	-0.003	-0.002	-0.004
303	0.002	0.003	-0.001	0.001	-0.003	-0.002	-0.004
302	0.002	0.003	-0.001	0.001	-0.003	-0.002	-0.004
301	0.002	0.003	-0.001	0.001	-0.003	-0.002	-0.004
300	0.002	0.003	-0.001	0.001	-0.003	-0.002	-0.004
299	0.002	0.003	-0.001	0.001	-0.003	-0.002	-0.004
298	0.002	0.003	-0.001	0.001	-0.003	-0.002	-0.004
297	0.002	0.003	-0.001	0.001	-0.003	-0.002	-0.004
296	0	0	-0.007	-0.004	-0.01	-0.008	-0.011
295	0	-0.001	-0.007	-0.004	-0.01	-0.008	-0.012
294	0	-0.001	-0.007	-0.004	-0.01	-0.009	-0.012
293	0	-0.001	-0.007	-0.004	-0.01	-0.009	-0.012
292	0	-0.001	-0.008	-0.004	-0.011	-0.009	-0.013
291	0	-0.001	-0.008	-0.005	-0.011	-0.009	-0.013
290	0	-0.001	-0.008	-0.005	-0.012	-0.01	-0.014
289	0	-0.001	-0.008	-0.005	-0.012	-0.01	-0.014

288	-0.001	-0.001	-0.009	-0.005	-0.012	-0.011	-0.014
287	-0.001	-0.002	-0.009	-0.005	-0.012	-0.011	-0.015
286	0	-0.002	-0.009	-0.005	-0.013	-0.011	-0.015
285	-0.001	-0.002	-0.01	-0.006	-0.013	-0.011	-0.015
284	-0.001	-0.002	-0.01	-0.006	-0.013	-0.011	-0.016
283	-0.001	-0.002	-0.01	-0.006	-0.014	-0.012	-0.016
282	-0.001	-0.002	-0.01	-0.006	-0.014	-0.012	-0.017
281	-0.001	-0.002	-0.011	-0.006	-0.014	-0.012	-0.017
280	-0.001	-0.002	-0.011	-0.007	-0.014	-0.012	-0.017
279	-0.001	-0.002	-0.011	-0.007	-0.014	-0.013	-0.017
278	-0.001	-0.002	-0.011	-0.006	-0.014	-0.012	-0.017
277	-0.001	-0.002	-0.011	-0.007	-0.015	-0.013	-0.017
276	-0.001	-0.002	-0.011	-0.007	-0.015	-0.013	-0.018
275	-0.001	-0.002	-0.011	-0.007	-0.015	-0.013	-0.017
274	-0.001	-0.002	-0.011	-0.007	-0.015	-0.013	-0.018
273	-0.001	-0.002	-0.011	-0.007	-0.015	-0.013	-0.018
272	-0.001	-0.002	-0.011	-0.007	-0.015	-0.013	-0.018
271	-0.001	-0.002	-0.011	-0.007	-0.015	-0.013	-0.018
270	-0.001	-0.002	-0.011	-0.006	-0.015	-0.013	-0.018
269	-0.001	-0.002	-0.011	-0.006	-0.015	-0.013	-0.017
268	-0.001	-0.002	-0.011	-0.006	-0.015	-0.013	-0.017
267	-0.001	-0.002	-0.011	-0.006	-0.015	-0.012	-0.017
266	-0.001	-0.002	-0.011	-0.007	-0.015	-0.012	-0.017
265	-0.001	-0.002	-0.01	-0.007	-0.015	-0.012	-0.017
264	-0.001	-0.002	-0.01	-0.007	-0.015	-0.012	-0.017
263	-0.001	-0.002	-0.01	-0.007	-0.015	-0.012	-0.017
262	-0.001	-0.002	-0.01	-0.006	-0.014	-0.012	-0.017
261	0.001	0.001	-0.006	-0.003	-0.009	-0.007	-0.012
260	0.001	0	-0.006	-0.003	-0.009	-0.007	-0.011
259	0.001	0.001	-0.006	-0.003	-0.009	-0.007	-0.012
258	0.001	0.001	-0.006	-0.003	-0.009	-0.007	-0.011
257	0.001	0.001	-0.006	-0.003	-0.009	-0.007	-0.012
256	0.001	0.001	-0.006	-0.003	-0.009	-0.007	-0.011
255	0.001	0.001	-0.006	-0.003	-0.009	-0.007	-0.011
254	0.001	0.001	-0.005	-0.003	-0.009	-0.007	-0.011
253	0.001	0.001	-0.005	-0.003	-0.009	-0.007	-0.011
252	0.001	0.001	-0.006	-0.003	-0.009	-0.007	-0.011
251	0	0	-0.006	-0.003	-0.009	-0.007	-0.011
250	0.001	0	-0.006	-0.003	-0.009	-0.007	-0.011
249	0.001	0.001	-0.006	-0.003	-0.009	-0.007	-0.011
248	0.001	0	-0.006	-0.003	-0.009	-0.007	-0.011
247	0	0	-0.006	-0.003	-0.009	-0.008	-0.011
246	0	0	-0.006	-0.004	-0.009	-0.007	-0.011
245	0	0	-0.006	-0.004	-0.009	-0.007	-0.011
244	0	0	-0.006	-0.004	-0.009	-0.008	-0.012
243	0	0	-0.006	-0.004	-0.009	-0.008	-0.012
242	0	0	-0.006	-0.004	-0.009	-0.008	-0.012
241	0	-0.001	-0.006	-0.004	-0.009	-0.008	-0.012
240	0	-0.001	-0.006	-0.004	-0.009	-0.008	-0.012
239	0	-0.001	-0.006	-0.004	-0.009	-0.008	-0.012

238	0	0	-0.006	-0.004	-0.009	-0.008	-0.011
237	0	0	-0.005	-0.003	-0.008	-0.007	-0.011
236	0	0	-0.005	-0.003	-0.008	-0.007	-0.011
235	0	0	-0.005	-0.003	-0.008	-0.007	-0.011
234	0	0.001	-0.005	-0.003	-0.008	-0.007	-0.011
233	0	0.001	-0.005	-0.003	-0.008	-0.007	-0.012
232	-0.001	0	-0.005	-0.003	-0.009	-0.008	-0.013
231	-0.001	0	-0.006	-0.004	-0.011	-0.009	-0.015
230	-0.001	0	-0.007	-0.004	-0.012	-0.01	-0.017
229	-0.002	0	-0.01	-0.006	-0.014	-0.013	-0.021
228	-0.003	-0.002	-0.012	-0.009	-0.019	-0.017	-0.024
227	-0.004	-0.004	-0.015	-0.012	-0.023	-0.019	-0.03
226	-0.008	-0.008	-0.02	-0.015	-0.028	-0.025	-0.035
225	-0.006	-0.005	-0.019	-0.013	-0.029	-0.025	-0.035
224	-0.009	-0.007	-0.024	-0.018	-0.032	-0.028	-0.037
223	-0.006	-0.006	-0.022	-0.019	-0.033	-0.029	-0.04
222	-0.011	-0.008	-0.024	-0.019	-0.036	-0.029	-0.043
221	-0.006	-0.008	-0.022	-0.02	-0.033	-0.029	-0.036
220	-0.007	-0.005	-0.021	-0.018	-0.034	-0.03	-0.038
219	-0.008	-0.006	-0.023	-0.021	-0.03	-0.028	-0.034
218	-0.01	-0.008	-0.017	-0.017	-0.023	-0.021	-0.029
217	-0.008	-0.004	-0.014	-0.013	-0.02	-0.018	-0.023
216	-0.003	0.002	-0.001	-0.006	-0.006	-0.005	-0.011
215	-0.001	0.011	0.007	0.002	0.005	0.005	0.005
214	0.004	0.021	0.025	0.017	0.024	0.023	0.023
213	0.011	0.03	0.04	0.025	0.042	0.04	0.045
212	0.017	0.037	0.048	0.034	0.061	0.058	0.063
211	0.031	0.058	0.07	0.055	0.089	0.085	0.095
210	0.028	0.07	0.095	0.074	0.117	0.106	0.123
209	0.045	0.077	0.118	0.09	0.134	0.127	0.14
208	0.054	0.106	0.138	0.111	0.155	0.145	0.164
207	0.083	0.14	0.167	0.152	0.191	0.175	0.208
206	0.118	0.159	0.21	0.154	0.249	0.216	0.248
205	0.107	0.215	0.267	0.219	0.285	0.277	0.295
204	0.087	0.184	0.271	0.213	0.327	0.288	0.326
203	0.258	0.296	0.366	0.313	0.417	0.392	0.443
202	0.329	0.43	0.454	0.425	0.501	0.462	0.539
201	-0.104	-0.183	-0.443	-0.337	-0.501	-0.483	-0.593
200	-0.106	-0.185	-0.446	-0.323	-0.502	-0.462	-0.623

VII. Characterization of substrates and products

3-methyl-2-(perfluorohexyl)-1*H*-indole (3a)



White solid, 28 mg, 80% yield; m.p. 67-69 ℃;

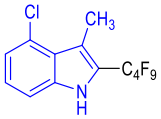
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.24 – 7.16 (m, 1H), 2.44 (t, *J* = 2.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.0, 128.4, 125.0, 120.4, 120.1, 119.4 (d, *J* = 28.3 Hz), 116.8 (t, *J* = 3.5 Hz), 111.5, 8.6 (t, *J* = 2.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.95 (t, *J* = 9.9 Hz, 3F), -108.79 to -108.89 (m, 2F), -122.98 to-123.07 (m, 2F), -125.92 to -126.04 (m, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{13}H_7F_9N^+$ $[M-H]^+$, 348.0440; found: 348.0454.

4-chloro-3-methyl-2-(perfluorobutyl)-1*H*-indole (3b)



Yellow solid, 25.3 mg, 66% yield; m.p. 54-56 ℃;

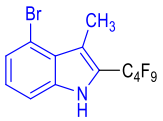
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.26 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.18 (t, *J* = 7.9 Hz, 1H), 7.12 (dd, *J* = 7.6, 1.2 Hz, 1H), 2.67 (t, *J* = 2.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.3, 128.3, 125.3, 124.9, 121.7, 120.4 (t, *J* = 27.6 Hz), 117.4 (t, *J* = 3.3 Hz), 110.4, 10.8 (t, *J* = 2.2 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -81.00 (t, *J* = 9.9 Hz, 3F), -108.70 (t, *J* = 13.1 Hz, 2F), -122.88 to -122.99 (m, 2F), -125.91 to -126.04 (m, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{13}H_6ClF_9N^+$ $[M-H]^+$, 382.0051; found: 382.0068.

4-bromo-3-methyl-2-(perfluorobutyl)-1*H*-indole (3c)



Yellow solid, 26.7 mg, 62% yield; m.p. 66-68 ℃;

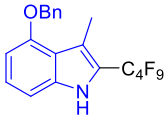
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.37 – 7.30 (m, 2H), 7.11 (t, *J* = 7.9 Hz, 1H), 2.68 (t, *J* = 1.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2, 126.0, 125.6, 125.3, 120.4 (t, *J* = 30.1 Hz), 117.9 (t, *J* = 3.2 Hz), 115.9, 111.0, 11.0 (t, *J* = 2.0 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -80.96 (t, *J* = 9.8 Hz, 3F), -108.62 (t, *J* = 13.0 Hz, 2F), -122.81 to -122.95 (m, 2F), -125.87 to -126.04 (m, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{13}H_6BrF_9N^+$ $[M-H]^+$, 425.9545; found: 425.9560.

4-(benzyloxy)-3-methyl-2-(perfluorobutyl)-1*H*-indole (3d)



White solid, 28 mg, 61% yield; m.p. 79-81 ℃;

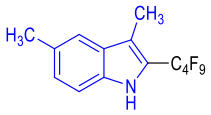
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.49 (d, *J* = 7.0 Hz, 2H), 7.40 (t, *J* = 6.8 Hz, 2H), 7.34 (t, *J* = 6.8 Hz, 1H), 7.18 (t, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.58 (d, *J* = 7.8 Hz, 1H), 5.19 (s, 2H), 2.60 (t, *J* = 2.0Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 137.7, 137.1, 128.6, 127.9, 127.3, 125.8, 118.5, 117.8 (t, *J* = 29.3 Hz), 104.7, 101.2, 69.9, 11.1, 1.0.

^{19}F NMR (377 MHz, $CDCl_3$) δ -80.98 (t, *J* = 9.8 Hz, 3F), -108.43 to -108.52 (m, 2F), -122.97 to -123.0 6 (m, 2F), -125.93 to -126.02 (m, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{20}H_{13}F_9NO^+$ $[M-H]^+$, 454.0859; found: 454.0871.

3,5-dimethyl-2-(perfluorobutyl)-1*H*-indole (3e)



Yellow solid, 29 mg, 80% yield; m.p. 60-62℃;

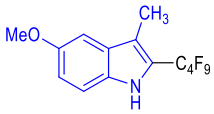
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.42 (s, 1H), 7.29 – 7.20 (m, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 2.47 (s, 3H), 2.40 (t, *J* = 2.3 Hz, 3H).

^{13}C NMR (101 MHz, CDCl3) δ 137.2, 137.1, 133.9, 133.7, 128.8, 128.6, 128.5, 31.8 (d, J = 43.7 Hz), 22.7, 14.2.

^{19}F NMR (377 MHz, $CDCl_3$) δ -80.99 (t, *J* = 9.8 Hz, 3F), -108.73 to -108.85 (m, 2F), -123.01 to -123.13 (m, 2F), -125.93 to -126.10 (m, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{14}H_9F_9N^+$ $[M-H]^+$, 362.0597; found: 362.0611.

5-methoxy-3-methyl-2-(perfluorobutyl)-1*H*-indole (3f)



White solid, 21.0 mg, 55% yield; m.p. 58-61 ℃;

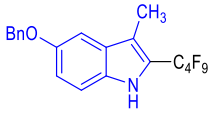
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.27 (d, *J* = 8.8 Hz, 1H), 7.04 – 6.97 (m, 2H), 3.88 (s, 3H), 2.40 (d, *J* = 2.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 131.1, 128.7, 119.9 (t, *J* = 28.3 Hz), 116.1 (t, *J* = 3.4 Hz), 116.0, 112.5, 100.7, 55.8, 8.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -80.98 (t, *J* = 9.6 Hz, 3F), -108.80 (t, *J* = 12.6 Hz, 2F), -123.03 (q, *J* = 9.2 Hz, 2F), -125.94 to -126.05 (m, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{14}H_9F_9NO^+$ $[M-H]^+$, 378.0546; found: 378.0562.

5-(benzyloxy)-3-methyl-2-(perfluorobutyl)-1*H*-indole (3g)



White solid, 19.6 mg, 43% yield; m.p. 93-95 ℃;

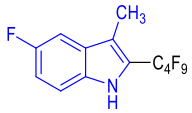
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.48 (d, *J* = 7.1 Hz, 2H), 7.44 – 7.35 (m, 2H), 7.33 (dd, *J* = 8.4, 6.1 Hz, 1H), 7.28 (d, *J* = 8.8 Hz, 1H), 7.12 (d, *J* = 2.4 Hz, 1H), 7.07 (dd, *J* = 8.8, 2.5 Hz, 1H), 5.12 (s, 2H), 2.38 (t, *J* = 2.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 137.3, 131.3, 128.7, 128.6, 128.0, 127.7, 120.0 (t, *J* = 28.6 Hz), 116.6, 116.2 (t, *J* = 3.4 Hz), 112.5, 102.4, 70.8, 8.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -80.97 (t, *J* = 9.7 Hz, 3F), -108.81 (t, *J* = 12.9 Hz, 2F), -122.89 to -123.12 (m, 2F), -125.92 to -126.04 (m, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{20}H_{13}F_9NO^+$ $[M-H]^+$, 454.0859; found: 454.087.

5-fluoro-3-methyl-2-(perfluorobutyl)-1*H*-indole (3h)



Yellow oil, 27 mg, 74% yield;

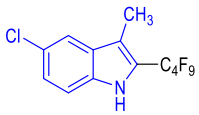
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.27 (d, *J* = 8.8 Hz, 1H), 7.04 – 6.97 (m, 2H), 3.88 (s, 3H), 2.40 (d, *J* = 2.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 156.9, 132.4, 128.7 (d, *J* = 9.5 Hz), 121.1 (t, *J* = 28.1 Hz), 113.9 (d, *J* = 26.9 Hz), 112.5 (d, *J* = 9.5 Hz), 104.8 (d, *J* = 23.6 Hz), 8.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -81.01 (t, *J* = 10.0 Hz, 3F), -109.18 (t, *J* = 12.8 Hz, 2F), -122.88 (s, 1F), -123.02 to -123.15 (m, 2F), -126.00 to -126.11 (m, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{13}H_6F_{10}N^+$ $[M-H]^+$, 366.0346; found: 366.0357.

5-chloro-3-methyl-2-(perfluorobutyl)-1*H*-indole (3i)



White solid, 26.9 mg, 70% yield; m.p. 59-61 ℃;

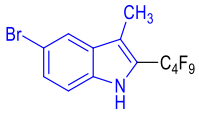
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.61 (s, 1H), 7.32 – 7.25 (m, 2H), 2.38 (t, *J* = 2.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.2, 129.4, 126.3, 125.5, 120.7 (t, *J* = 28.3 Hz), 119.6, 116.3 (t, *J* = 3.4 Hz), 112.7, 8.5.

^{19}F NMR (377 MHz, $CDCl_3$) δ -80.96 (t, *J* = 9.7 Hz, 3F), -109.04 to -109.20 (m, 2F), -122.97 to -123.09 (m, 2F), -125.93 to -126.04 (m, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{13}H_6ClF_9N^+$ $[M-H]^+$, 382.0051; found: 382.0065.

5-bromo-3-methyl-2-(perfluorobutyl)-1*H*-indole (3j)



Yellow oil, 36.4 mg, 85% yield;

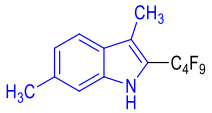
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.78 (d, *J* = 1.8 Hz, 1H), 7.41 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.27 (d, *J* = 8.8 Hz, 1H), 2.39 (t, *J* = 4.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.5, 130.0, 128.0, 122.8, 120.6 (t, *J* = 28.5 Hz), 116.2 (t, *J* = 3.5 Hz), 113.6, 113.1, 8.5 (d, *J* = 1.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.98 (t, *J* = 9.8 Hz, 3F), -109.10 to -109.21 (m, 2F), -123.01 to -123.10 (m, 2F), -125.97 to -126.06 (m, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{13}H_6BrF_9N^+$ $[M-H]^+$, 425.9545; found: 425.9555.

3,6-dimethyl-2-(perfluorobutyl)-1*H*-indole (3k)



Yellow solid, 24.0 mg, 66% yield; m.p. 64-66 ℃;

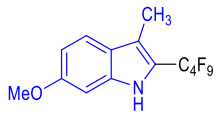
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.52 (d, *J* = 8.2 Hz, 1H), 7.15 (s, 1H), 7.02 (dd, *J* = 8.3, 1.4 Hz, 1H), 2.47 (s, 3H), 2.40 (t, *J* = 2.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.4, 135.1, 126.3, 122.3, 119.7, 118.6 (d, *J* = 28.3 Hz), 116.6 (t, *J* = 3.0 Hz), 111.3, 21.8, 8.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.98 (t, *J* = 9.7 Hz, 3F), -108.69 to -108.78 (m, 2F), -123.05 to -123.15 (m, 2F), -125.97 to -126.07 (m, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{14}H_9F_9N^+$ $[M-H]^+$, 362.0597; found: 362.0616.

6-methoxy-3-methyl-2-(perfluorobutyl)-1*H*-indole (3l)



White solid, 24 mg, 63% yield; m. p. 62-64 ℃;

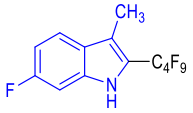
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.51 (d, *J* = 8.7 Hz, 1H), 6.88 – 6.79 (m, 2H), 3.85 (s, 3H), 2.39 (t, *J* = 2.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 136.8, 122.7, 120.9, 117.9, 116.9 (t, *J* = 2.7 Hz), 111.2, 93.9, 55.6, 8.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.98 (t, *J* = 9.8 Hz, 3F), -108.58 to -108.67 (m, 2F), -123.08 to -123.17 (m, 2F), -125.99 to -126.08 (m, 2F).

HRMS (ESI, m/z): Mass calcd. For $C_{14}H_9F_9NO^+$ $[M-H]^+$, 378.0546; found: 378.0561.

6-fluoro-3-methyl-2-((perfluorobutyl)-1*H*-indole (3m)



Yellow oil, 22.4 mg, 63% yield;

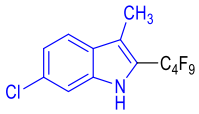
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.57 (dd, *J* = 8.8, 5.2 Hz, 1H), 7.06 (dd, *J* = 9.3, 2.2 Hz, 1H), 6.96 (td, *J* = 9.1, 2.3 Hz, 1H), 2.41 (t, *J* = 2.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 160.3, 135.9 (d, *J* = 13.0 Hz), 125.0, 121.3 (d, *J* = 10.6 Hz), 109.7 (d, *J* = 24.9 Hz), 97.7 (d, *J* = 26.3 Hz), 8.6, 1.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.94 – -81.05 (m, 3F), -109.01 (t, *J* = 12.9 Hz, 2F), -116.74 (s, 1F), -123.04 to -123.17 (m, 2F), -125.98 to -126.08 (m, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{13}H_6F_{10}N^+$ $[M-H]^+$, 366.0346; found: 366.0363.

6-chloro-3-methyl-2-(perfluorobutyl)-1*H*-indole (3n)



Yellow oil, 34.5 mg, 90% yield;

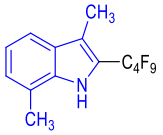
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 1.8 Hz, 2H), 7.16 (dd, *J* = 8.6, 1.8 Hz, 2H), 2.41 (t, *J* = 2.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.1, 131.0, 126.9, 121.4, 121.1, 120.0 (t, *J* = 28.4 Hz), 116.8, 111.4, 8.6.

^{19}F NMR (377 MHz, $CDCl_3$) δ -80.94 (t, *J* = 10.0 Hz, 3F), -109.21 to -109.43 (m, 2F), -123.00 (q, *J* = 9.1, 8.7 Hz, 2F), -125.89 to -126.00 (m, 2F)

HRMS (ESI, m/z): Mass calcd. for $C_{13}H_6ClF_9N^+$ $[M-H]^+$, 382.0051; found: 382.0062.

3,7-dimethyl-2-(perfluorobutyl)-1*H*-indole (3o)



White solid, 31.6 mg, 87% yield; m.p. 68-70 °C;

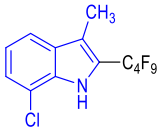
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.55 – 7.43 (m, 1H), 7.14 – 7.11 (m, 2H), 2.50 (s, 3H), 2.43 (t, *J* = 1.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7, 128.0, 125.3, 120.8 (d, *J* = 13.9 Hz), 119.2 (t, *J* = 28.1 Hz), 117.7, 117.3 (t, *J* = 3.6 Hz), 16.5, 8.8, 1.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.98 (t, *J* = 9.7 Hz, 3F), -108.68 to -108.78 (m, 2F), -122.87 to -123.01 (m, 2F), -125.93 to -126.05 (m, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{14}H_9F_9N^+$ $[M-H]^+$, 362.0597; found: 362.0615.

7-chloro-3-methyl-2-(perfluorobutyl)-1*H*-indole (3p)



Yellow oil, 25 mg, 65% yield;

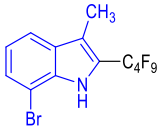
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 2.43 (t, *J* = 2.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 133.3, 129.6, 124.2, 121.2, 118.8, 117.7 (t, *J* = 3.3 Hz), 117.0, 8.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.98 (t, *J* = 9.7 Hz, 3F), -109.10 (t, *J* = 13.0 Hz, 2F), -122.89 to -122.99 (m, 2F), -125.95 to -126.04 (m, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{13}H_6ClF_9N^+$ $[M-H]^+$, 382.0051; found: 382.0060.

7-bromo-3-methyl-2-(perfluorobutyl)-1*H*-indole (3q)



White solid, 23.1 mg, 54% yield; m.p. 53-55 °C;

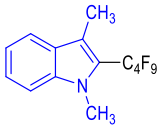
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.8 Hz, 1H), 2.43 (d, *J* = 2.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.7, 129.3, 127.3, 121.6, 120.2 (t, *J* = 28.4 Hz), 119.4, 117.8 (t, *J* = 3.5 Hz), 104.9, 8.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.97 (t, *J* = 10.4 Hz, 3F), -109.10 (t, *J* = 12.7 Hz, 2F), -122.91 (q, *J* = 9.8 Hz, 2F), -125.99 (t, *J* = 13.7 Hz, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{13}H_6BrF_9N^+$ $[M-H]^+$, 425.9545; found: 425.9555.

1,3-Dimethyl-2-(perfluorohexyl)-1*H*-indole (3r)



White solid, 20.3 mg, 56% yield; m.p. 68-70℃;

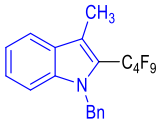
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 1H), 7.41 – 7.30 (m, 2H), 7.22 – 7.14 (m, 1H), 3.78 (s, 3H), 2.44 (t, *J* = 3.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 127.3, 124.7, 120.8, 120.1, 120.0, 117.7 (t, *J* = 3.6 Hz), 109.8, 31.6 (m), 9.1 (t, *J* = 3.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.90 to -81.00 (m, 3F), -104.16 to -104.29 (m, 2F), -122.34 to -122.47 (m, 2F), -125.97 to -126.08 (m, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{14}H_9F_9N^+$ $[M-H]^+$, 362.0597; found: 362.0587.

1-Benzyl-3-methyl-2-(perfluorobutyl)-1*H*-indole (3s)



White solid, 21.1 mg, 48% yield; m.p. 48-50 ℃;

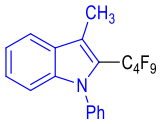
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.9 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 1H), 7.20 (dt, *J* = 15.0, 7.4 Hz, 5H), 6.93 (d, *J* = 6.9 Hz, 2H), 5.43 (s, 2H), 2.50 (t, *J* = 2.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 137.7, 128.7, 127.8, 127.3, 125.6, 125.1, 120.8 (t, *J* = 28.0 Hz), 120.4, 120.2, 118.3 (t, *J* = 3.8 Hz), 110.7, 48.8 (d, *J* = 2.2 Hz), 9.3.

^{19}F NMR (377 MHz, $CDCl_3$) δ -80.92 (t, *J* = 9.7 Hz, 3F), -103.82 to -103.95 (m, 2F), -122.22 to-122.32 (m, 2F), -125.82 to -125.93 (m, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{20}H_{15}F_9N^+$ $[M+H]^+$, 440.1055; found: 440.1048.

3-methyl-2-(perfluorobutyl)-1-phenyl-1*H*-indole (3t)



Colorless oil, 15 mg, 35% yield;

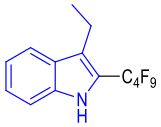
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.0, 1.6 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.32 (dd, *J* = 6.4, 3.1 Hz, 2H), 7.22 (qd, *J* = 7.6, 7.0, 1.3 Hz, 2H), 6.84 (dd, *J* = 7.5, 1.5 Hz, 1H), 2.53 (t, *J* = 2.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 137.9, 129.4, 128.9, 128.8, 127.2, 125.1, 120.6, 119.8, 118.8 (t, *J* = 3.2 Hz), 111.3, 9.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.98 (t, *J* = 9.9 Hz, 3F), -102.94 to -103.06 (m, 2F), -121.50 to -121.62 (m, 2F), -126.04 to -126.17 (m, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{19}H_{11}F_9N^+$ $[M-H]^+$, 424.0753; found: 424.0710.

3-ethyl-2-(perfluorobutyl)-1*H*-indole (3u)



White solid, 24 mg 66% yield; m.p. 49-51 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.21 – 7.16 (m, 1H), 2.90 (q, *J* = 7.5 Hz, 3H), 1.29 (t, *J* = 7.6 Hz, 3H).

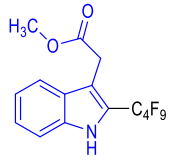
13C NMR (101 MHz, CDCl3) δ 136.2, 127.4, 124.9, 123.4 (t, J = 3.0 Hz), 120.4, 118.7 (t, J = 28.5 Hz), 111.7, 17.4, 15.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -81.00 (t, *J* = 10.0 Hz, 3F), -108.27 (t, *J* = 13.1 Hz, 2F), -122.91 to -123.04 (m, 2F), -125.89 to -125.99 (m, 2F)

(m).

HRMS (ESI, m/z): Mass calcd. for $C_{14}H_9F_9N^+$ $[M-H]^+$, 362.0597; found: 362.0614.

Methyl 2-(2-(perfluorobutyl)-1*H*-indol-3-yl)acetate (3v)



White solid, 23.6 mg, 58% yield; m.p. 61-63 ℃;

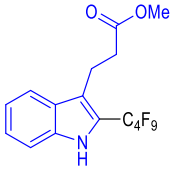
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.37 – 7.28 (m, 1H), 7.25 – 7.17 (m, 1H), 3.92 (s, 2H), 3.69 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 135.9, 127.6, 125.3, 121.1, 120.7 (d, *J* = 29.1 Hz), 120.2, 113.0 (t, *J* = 3.0 Hz), 111.8, 52.2, 29.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.94 (t, *J* = 10.1 Hz, 3F), -108.35 (t, *J* = 13.0 Hz, 2F), -122.89 (dd, *J* = 17.4, 7.7 Hz, 2F), -125.80 to -125.97 (m, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{15}H_9F_9NO_2^+$ $[M-H]^+$, 406.0495; found: 406.0508.

methyl 3-(2-(perfluorobutyl)-1*H*-indol-3-yl)propanoate (3w)



Yellow oil, 28.2 mg, 67% yield;

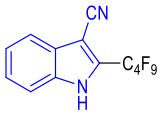
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.20 (s, 1H), 3.70 (s, 3H), 3.26 – 3.20 (m, 1H), 2.73 – 2.62 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 136.1, 127.1, 125.1, 120.7, 120.1, 119.3 (t, *J* = 2.0 Hz), 119.3 (q, *J* = 57.3 Hz, 28.9 Hz), 111.8, 51.8, 35.4, 19.6.

^{19}F NMR (377 MHz, $CDCl_3$) δ -80.98 (t, *J* = 9.9 Hz, 3F), -108.26 (t, *J* = 13.0 Hz, 2F), -122.85 (q, *J* = 9.7, 9.1 Hz, 2F), -125.86 (dd, *J* = 16.2, 10.8 Hz, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{16}H_{11}F_9NO_2^+$ $[M-H]^+$, 420.0652; found: 420.0670.

2-(perfluorobutyl)-1*H*-indole-3-carbonitrile (3x)



White solid, 22.8 mg, 61% yield; m.p. 111-113℃;

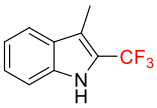
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (s, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.60 – 7.53 (m, 1H), 7.54 – 7.45 (m, 1H), 7.41 (td, *J* = 7.6, 7.0, 1.1 Hz, 1H), 1.67 – 1.63 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 135.1, 127.3, 126.9, 123.8, 122.1, 120.6, 112.7, 112.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.84 (t, *J* = 10.2 Hz, 3F), -109.87 to -109.96 (m, 2F), -122.46 (q, *J* = 9.8 Hz, 2F), -125.74 (t, *J* = 13.5 Hz, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{13}H_4F_9N_2^+$ $[M-H]^+$, 359.0236; found: 359.0251.

3-methyl-2-(trifluoromethyl)-1*H*-indole (3ba)



white solid, 11 mg, 55 % yield; m.p.76-78 ℃;

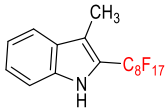
^{1}H NMR (500 MHz, CHLOROFORM-*D*) δ 8.17 (s, 1H), 7.63 (d, *J* = 6.9 Hz, 1H), 7.37 (d, *J* = 5.6 Hz, 1H), 7.31 (t, *J* = 6.2 Hz, 1H), 7.18 (t, *J* = 6.0 Hz, 1H), 2.43 (s, 3H).

^{13}C NMR (126 MHz, CHLOROFORM-*D*) δ 135.3, 128.2, 124.9, 123.3, 120.5, 120.2, 114.2 (d, *J* = 4.1 Hz), 111.6, 8.4.

^{19}F NMR (377 MHz, $CDCl_3$) δ -58.7.

HRMS (ESI, m/z): Mass calcd. for $C_{10}H_7F_3N^+$ $[M-H]^+$, 198.0536; found: 198.0540.

2-(perfluorobutyl)-3-methyl-1*H*-indole (3ca)



White solid; 39.5 mg, 72% yield; m.p. 73-75 ℃;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.25 – 7.17 (m, 1H), 2.44 (t, *J* = 2.3 Hz, 3H).

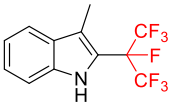
^{13}C NMR (101 MHz, $CDCl_3$) δ 135.9, 128.3, 125.0, 120.4, 120.1, 119.5 (t, *J* = 28.3 Hz), 116.7 (t,

J = 3.2 Hz), 111.5, 8.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.83 (t, *J* = 9.9 Hz, 2F), -108.69 (t, *J* = 13.8 Hz, 2F), -121.82 (d, *J* = 72.5 Hz, 7F), -122.15 (d, *J* = 10.3 Hz, 2F), -122.78 (2F), -126.12 to -126.26 (m, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{17}H_7F_{17}N^+$ $[M-H]^+$, 548.0313; found: 548.0325.

3-methyl-2-(perfluoropropan-2-yl)-1*H*-indole (3da)



colorless oil, 20.7 mg, 69%;

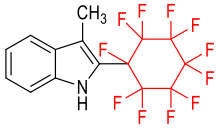
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.68 – 7.61 (m, 1H), 7.39 (dt, *J* = 8.2, 1.0 Hz, 1H), 7.36 – 7.27 (m, 1H), 7.24 – 7.16 (m, 1H), 2.44 (d, *J* = 2.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.9, 128.5, 124.6, 120.4, 119.6, 116.7 (d, *J* = 24.6 Hz), 116.0, 111.3, 29.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -75.68 (d, *J* = 8.3 Hz, 6F), -182.23 to -182.44 (m, 1F).

HRMS (ESI, m/z): Mass calcd. for $C_{12}H_7F_7N^+$ $[M-H]^+$, 298.0472; found: 298.0482

3-methyl-2-(perfluorocyclohexyl)-1*H*-indole (3ea)



White solid, 25.3 mg, 63% yield; m.p. 66-68 ℃;

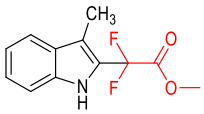
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.36 – 7.31 (m, 1H), 7.24 – 7.18 (m, 1H), 2.47 (d, *J* = 3.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.3, 128.3, 124.8, 120.4, 119.7, 118.7, 114.2 (d, *J* = 27.1 Hz), 111.4, 9.2 (d, *J* = 8.0 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -117.22 to -118.24 (m, 2F), -121.40 to -122.55 (m, 2F), -122.60 to -123.62 (m, 1F), -131.61 to -132.65 (m, 2F), -137.95 to -138.99 (m, 2F), -141.18 to -142.18 (m, 1F), -180.64 to -180.95 (m, 1F).

HRMS (ESI, m/z): Mass calcd. for $C_{15}H_7F_{11}N^+$ $[M-H]^+$, 410.0408; found: 410.0422.

methyl 2,2-difluoro-2-(3-methyl-1*H*-indol-2-yl)acetate (3fa)



Yellow siold, 15.5 mg, 65% yield; m.p. 70-72 ℃;

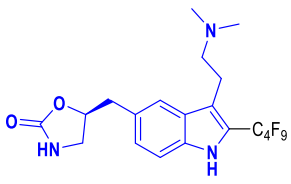
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.16 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 3.87 (s, 3H), 2.41 (t, *J* = 2.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0 (t, *J* = 36.2 Hz), 135.6, 128.5, 124.4, 123.2 (t, *J* = 29.8 Hz), 120.2, 119.8, 114.0 (q, *J* = 39.8 Hz, 28.9 Hz), 111.5, 109.0, 53.9, 8.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -101.50 (s, 2F)

HRMS (ESI, m/z): Mass calcd. for $C_{12}H_{10}F_2NO_2^+$ $[M-H]^+$, 238.0685; found: 238.0677.

(*S*)-5-((3-(2-(dimethylamino)ethyl)-2-(perfluorobutyl)-1*H*-indol-5-yl)methyl)oxazolidin-2-one (5a)



Yellow solid, 24.3 mg, 48% yield; m.p. 72-74℃;

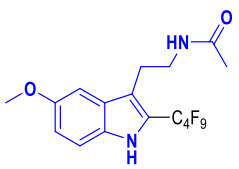
^{1}H NMR (400 MHz, DMSO) δ 12.11 (s, 1H), 7.87 (s, 1H), 7.69 (s, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.25 (dd, *J* = 8.5, 1.5 Hz, 1H), 4.30 (t, *J* = 8.2 Hz, 1H), 4.18 – 4.12 (m, 1H), 3.21 (d, *J* = 4.9 Hz, 4H), 2.90 (s, 6H), 2.52 (p, *J* = 1.8 Hz, 2H).

^{13}C NMR (101 MHz, DMSO) δ 159.2, 136.0, 128.8, 127.2, 127.0, 120.6, 119.7 (t, *J* = 28.3 Hz), 114.1, 112.9, 68.5, 57.3, 55.4, 53.2, 42.9, 19.9.

^{19}F NMR (376 MHz, DMSO) δ -80.47 (t, *J* = 9.8 Hz, 3F), -106.60 (q, *J* = 12.2 Hz, 2F), -122.33 (q, *J* = 9.5 Hz, 2F), -125.53 (t, *J* = 12.3 Hz, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{20}H_{21}F_9N_3O_2^+$, $[M+H]^+$, 506.1485; found: 506.1485.

***N*-(2-(5-methoxy-2-(perfluorobutyl)-1*H*-indol-3-yl)ethyl)acetamide (5b)**



White solid, 6.3 mg, 60% yield; m.p. 66-68 ℃;

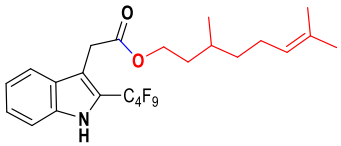
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 7.32 (d, *J* = 8.9 Hz, 1H), 7.18 (d, *J* = 2.4 Hz, 1H), 7.00 (dd, *J* = 8.9, 2.4 Hz, 1H), 5.67 (d, *J* = 7.3 Hz, 1H), 3.87 (s, 3H), 3.56 (q, *J* = 6.7 Hz, 2H), 3.07 (t, *J* = 7.0 Hz, 2H), 1.95 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 154.8, 131.3, 128.1, 120.3, 117.3 (d, *J* = 3.4 Hz), 116.6, 112.8, 100.6, 55.8, 40.2, 24.3, 23.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.94 (t, *J* = 9.8 Hz, 3F), -107.48 to -107.57 (m, 2F), -122.81 (q, *J* = 11.0, 10.4 Hz, 2F), -125.90 (t, *J* = 13.4 Hz, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{17}H_{15}F_9N_2O_2Na^+$, $[M+Na]^+$, 473.0882; found: 473.0874.

3,7-dimethyloct-6-en-1-yl-2-(2-(perfluorobutyl)-1*H*-indol-3-yl)acetate (5c)



Colorless oil, 28.2 mg, 53% yield;

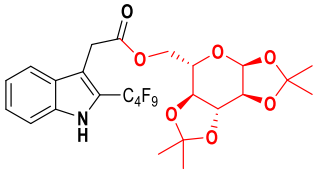
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.25 – 7.17 (m, 1H), 5.09 – 4.99 (m, 1H), 4.18 – 4.07 (m, 2H), 3.90 (s, 2H), 1.99 – 1.81 (m, 1H), 1.68 (d, *J* = 6.8 Hz, 3H), 1.59 (d, *J* = 6.1 Hz, 3H), 1.44 – 1.26 (m, 3H), 1.26 – 0.84 (m, 3H), 0.82 (t, *J* = 6.6 Hz, 3H)..

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6 (d, *J* = 4.9 Hz), 135.9, 131.3, 125.3 (d, *J* = 3.9 Hz), 124.6, 121.0, 120.4 (d, *J* = 6.6 Hz), 118.6, 111.7 (d, *J* = 2.9 Hz), 63.6, 63.2 (d, *J* = 5.7 Hz), 36.9, 35.3, 30.1, 29.6 (d, *J* = 14.4 Hz), 29.4, 25.7, 25.4, 19.2, 17.6.

^{19}F NMR (377 MHz, $CDCl_3$) δ -80.90 to -81.04 (m, 3F), -108.17 to -108.34 (m, 2F), -122.78 to -122.91 (m, 2F), -125.76 to -125.98 (m, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{24}H_{26}F_9NO_2Na^+$, $[M+Na]^+$, 554.1712; found: 554.1710.

((3a*S*,5*S*,5a*S*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl-2-(2-(perfluorobutyl)-1*H*-indol-3-yl)acetate (5d)



Colorless oil, 23.5 mg, 37% yield;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.45 – 7.38 (m, 1H), 7.39 – 7.31 (m, 1H), 7.21 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 5.71 (d, *J* = 3.6 Hz, 1H), 5.32 – 5.26 (m, 1H), 4.41 (d, *J* = 3.6 Hz, 1H), 4.14 (dd, *J* = 8.0, 3.1 Hz, 1H), 3.98 – 3.90 (m, 3H), 3.93 – 3.82 (m, 2H), 1.49 (s, 3H), 1.37 (s, 3H), 1.27 (s, 3H), 1.22 (s, 3H).

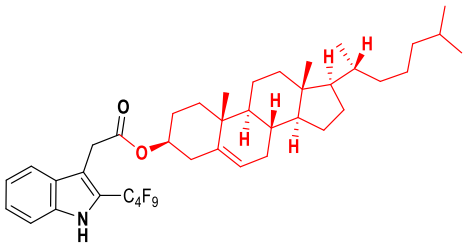
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 133.8, 125.3, 123.3, 119.0, 118.0, 110.3 (t, *J* = 2.7 Hz), 110.2, 109.7, 107.2, 102.9, 81.0, 77.8, 74.5, 70.1, 64.9, 27.9, 27.6, 24.6, 24.6, 24.0, 22.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -80.91 (t, *J* = 9.8 Hz, 3F), -108.19 (dt, *J* = 41.6, 13.0 Hz, 2F), -122.71 to -122.86 (m, 2F), -125.74 to -125.88 (m, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{26}H_{26}F_9NO_7Na^+$, $[M+Na]^+$, 658.1458; found: 658.1456.

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl 2-(2-(perfluorobutyl)-1

***H*-indol-3-yl)acetate (5e)**



Colorless oil, 31.2 mg, 41 % yield;

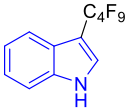
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 5.42 – 5.30 (m, 1H), 4.71 – 4.57 (m, 1H), 3.89 (d, *J* = 11.3 Hz, 2H), 2.28 (d, *J* = 5.4 Hz, 1H), 2.07 – 1.89 (m, 3H), 1.82 (d, *J* = 11.0 Hz, 3H), 1.58 – 1.42 (m, 6H), 1.36 – 1.21 (m, 6H), 1.19 – 1.02 (m, 9H), 0.99 (s, 3H), 0.91 (d, *J* = 6.4 Hz, 3H), 0.86 (dd, *J* = 6.6, 1.8 Hz, 6H), 0.67 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 139.6, 136.0, 127.7, 125.2, 122.7, 121.0, 120.5, 113.4 (t, *J* = 2.8 Hz), 111.7, 74.8, 71.0, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 37.9, 36.9, 36.6, 36.2, 35.8, 31.9 (d, *J* = 4.5 H z), 30.4, 28.2, 28.0, 27.6, 24.3, 23.8, 22.8, 22.6, 21.0, 19.3, 18.7, 11.8.

^{19}F NMR (377 MHz, $CDCl_3$) δ -80.87 – -81.11 (m, 3F), -108.28 (t, *J* = 13.1 Hz, 2F), -122.57 to -123.1 7 (m, 2F), -125.64 to -126.00 (m, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{41}H_{52}F_9NO_2Na^+$, $[M+Na]^+$, 784.3747; found: 784.3740.

3-(perfluorobutyl)-1*H*-indole (7b)



Colorless oil, 8.2 mg, 25% yield;

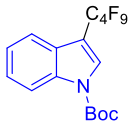
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 6.98 (s, 1H), 1.58 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 136.6, 126.9, 124.9, 124.0, 122.1, 121.2, 111.7, 106.5 (t, *J* = 5.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.97 (t, *J* = 9.7 Hz, 3F), -108.69 to -108.81 (m, 2F), -123.04 to -123.15 (m, 2F), -125.68 to -125.78 (m, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{12}H_5F_9N^+$ $[M-H]^+$, 334.0284; found: 334.0284.

tert-butyl 3-(perfluorobutyl)-1*H*-indole-1-carboxylate (7c)



Colorless oil, 9.1 mg, 21% yield;

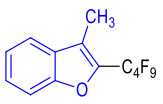
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.19 (s, 1H), 1.66 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 138.3, 127.2, 126.6, 125.3 (d, *J* = 37.6 Hz), 123.5, 122.1, 115.8, 85.6, 28.1, 27.8.

^{19}F NMR (377 MHz, $CDCl_3$) δ -80.78 to -80.90 (m, 3F), -99.93 to -100.17 (m, 2F), -118.79 to -119.02 (m, 2F), -125.21 to -125.43 (m, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{17}H_{14}F_9NO_2Na^+$ $[M+Na]^+$, 458.0773; found: 458.0762.

3-methyl-2-(perfluorobutyl)benzofuran (7d)



Colorless oil, 20.3 mg, 58% yield;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.47 – 7.41 (m, 1H), 7.36 – 7.31 (m, 1H), 2.41 (t, *J* = 2.5 Hz, 3H).

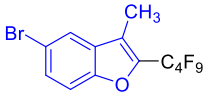
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 128.6, 127.0, 124.3, 123.4, 121.2 (t, *J* = 1.7 Hz), 120.6, 111.9, 7.8.

^{19}F NMR (377 MHz, $CDCl_3$) δ -80.93 to -81.04 (m, 3F), -111.43 to -111.56 (m, 2F), -123.57 to -

123.76 (m, 2F), -126.22 to -126.35 (m, 2F).

HRMS (APCI, m/z): Mass calcd. for $C_{13}H_8F_9O^+$ $[M+H]^+$, 351.0426; found: 351.0423.

5-bromo-3-methyl-2-(perfluorobutyl)benzofuran (7e)



Colorless oil, 8.5 mg, 21% yield;

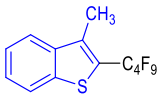
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 2.0 Hz, 1H), 7.53 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.40 (d, *J* = 8.7 Hz, 1H), 2.38 (t, *J* = 2.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 130.5, 130.1, 123.4, 120.6 (t, *J* = 2.1 Hz), 116.6, 113.5, 7.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -80.86 to -81.07 (m), -111.67 to -111.81 (m), -123.60 to -123.78 (m), -126.24 to -126.38 (m).

HRMS (APCI, m/z): Mass calcd. for $C_{13}H_7F_9BrO^+$ $[M+H]^+$, 428.9531; found: 428.9527.

3-methyl-2-(perfluorobutyl)benzo[*b*]thiophene (7f)



colorless oil, 7.3 mg, 20 % yield;

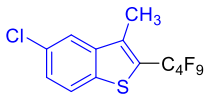
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.72 (m, 1H), 7.44 – 7.36 (m, 1H), 2.49 (t, *J* = 2.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 139.5, 136.7 (t, *J* = 4.1 Hz), 129.8, 126.6, 124.8, 123.1, 12 2.4, 12.5 (t, *J* = 2.6 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -80.94 (t, *J* = 10.0 Hz, 3F), -100.41 to -100.57 (m, 2F), -121.48 to -121.67 (m, 2F), -125.67 to -125.83 (m, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{13}H_8F_9S^+$ $[M+H]^+$, 367.0208; found: 367.0209.

5-chloro-3-methyl-2-(perfluorobutyl)benzo*[b]*thiophene (7g)



White solid, 7.6 mg, 19% yield; m.p. 69-71ºC;

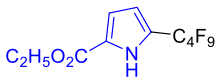
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.74 (m, 2H), 7.44 (dd, *J* = 8.6, 2.0 Hz, 1H), 2.53 (m, *J* = 2.0, 0.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 137.5 (t, *J* = 1.0 Hz), 136.0 (t, *J* = 3.9 Hz), 131.4, 127.2, 123.5, 122.9, 12.5 (t, *J* = 3.0 Hz).

^{19}F NMR (377 MHz, $CDCl_3$) δ -80.88 to -81.02 (m), -100.73 to -100.90 (m), -121.51 to -121.67 (m), -125.67 to -125.85 (m).

HRMS (APCI, m/z): Mass calcd. for $C_{13}H_7F_9ClS^+$ $[M+H]^+$, 400.9808; found: 400.9809.

ethyl 3-(perfluorobutyl)-1*H*-pyrrole-2-carboxylate (7h)



White solid, 26.4 mg, 74% yield; m.p.= 67-69°C;

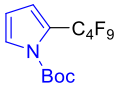
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 6.93 (ddt, *J* = 4.0, 2.6, 1.3 Hz, 1H), 6.62 (td, *J* = 2.8, 1.3 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 126.3, 122.6 (t, *J* = 30.7 Hz), 115.2, 112.9 (t, *J* = 4.1 Hz), 61.2, 14.3.

^{19}F NMR (377 MHz, $CDCl_3$) δ -80.95 to -81.08 (m), -108.74 to -108.87 (m), -123.18 to -123.32 (m), -125.70 to -125.84 (m).

HRMS (ESI, m/z): Mass calcd. for $C_{11}H_7F_9NO_2$, $[M-H]^+$, 356.0339; found: 356.0339.

tert-butyl 2-(perfluorobutyl)-1*H*-pyrrole-1-carboxylate (7i)



Colorless oil, 24 mg, 62% yield;

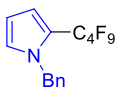
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 3.4, 1.9 Hz, 1H), 6.77 (ddt, *J* = 3.7, 1.8, 0.9 Hz, 1H), 6.25 (t, *J* = 3.4 Hz, 1H), 1.60 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 127.7, 120.2 (m), 109.8, 85.7, 29.7, 27.7.

^{19}F NMR (377 MHz, $CDCl_3$) δ -80.88 to -81.00 (m, 3F), -100.35 to -100.49 (m, 2F), -119.44 to -119.58 (m, 2F), -125.48 to -125.62 (m, 2F).

HRMS (ESI, m/z): Mass calcd. for $C_{13}H_{11}F_9NO_2$, $[M-H]^+$, 384.0652; found: 384.0653.

1-benzyl-2-(perfluorobutyl)-1*H*-pyrrole (7j)



Colorless oil, 22.4 mg, 51% yield;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 3H), 7.10 – 7.03 (m, 2H), 6.74 (t, *J* = 2.3 Hz, 1H), 6.63 (d, *J* = 3.9 Hz, 1H), 6.22 (t, *J* = 3.4 Hz, 1H), 5.17 (s, 2H).

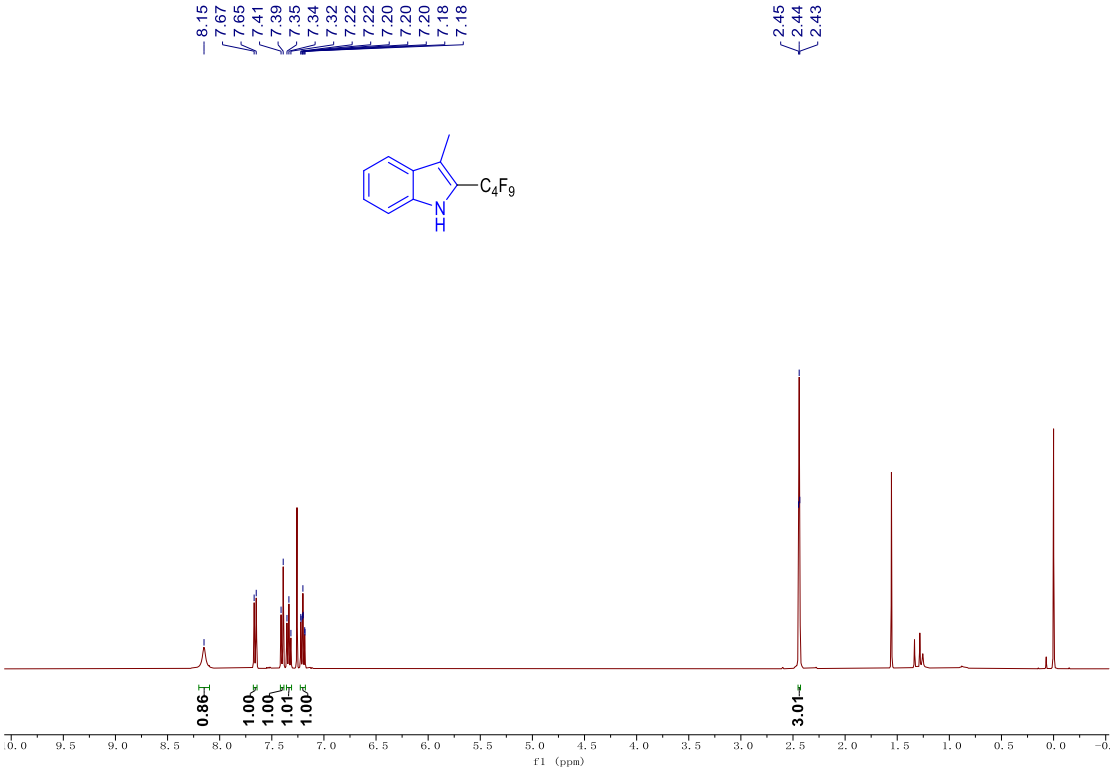
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2, 128.8, 127.9, 127.4 (t, *J* = 1.8 Hz), 126.9, 124.3, 114.5 (t, *J* = 6.0 Hz), 108.7, 52.1 (q, *J* = 3.3, 2.9 Hz).

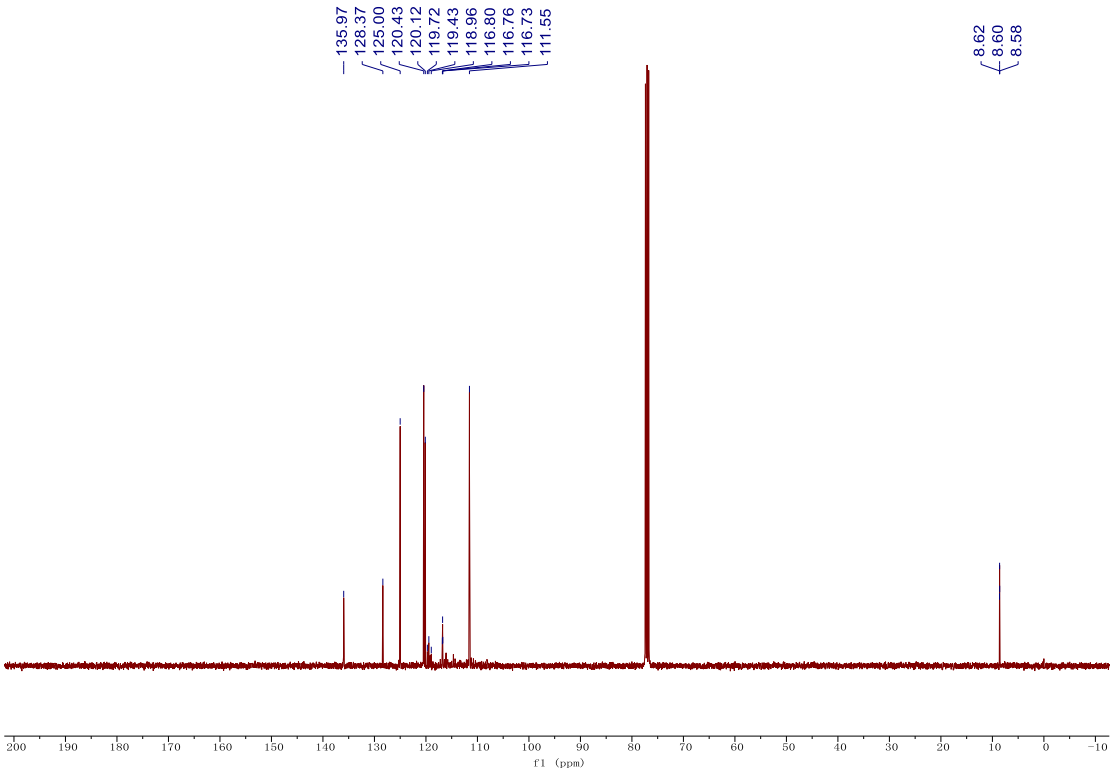
^{19}F NMR (377 MHz, $CDCl_3$) δ -80.93 to -81.10 (m, 3F), -103.32 to -103.51 (m, 2F), -121.62 to -121.80 (m, 3F), -125.61 to -125.84 (m, 2F).

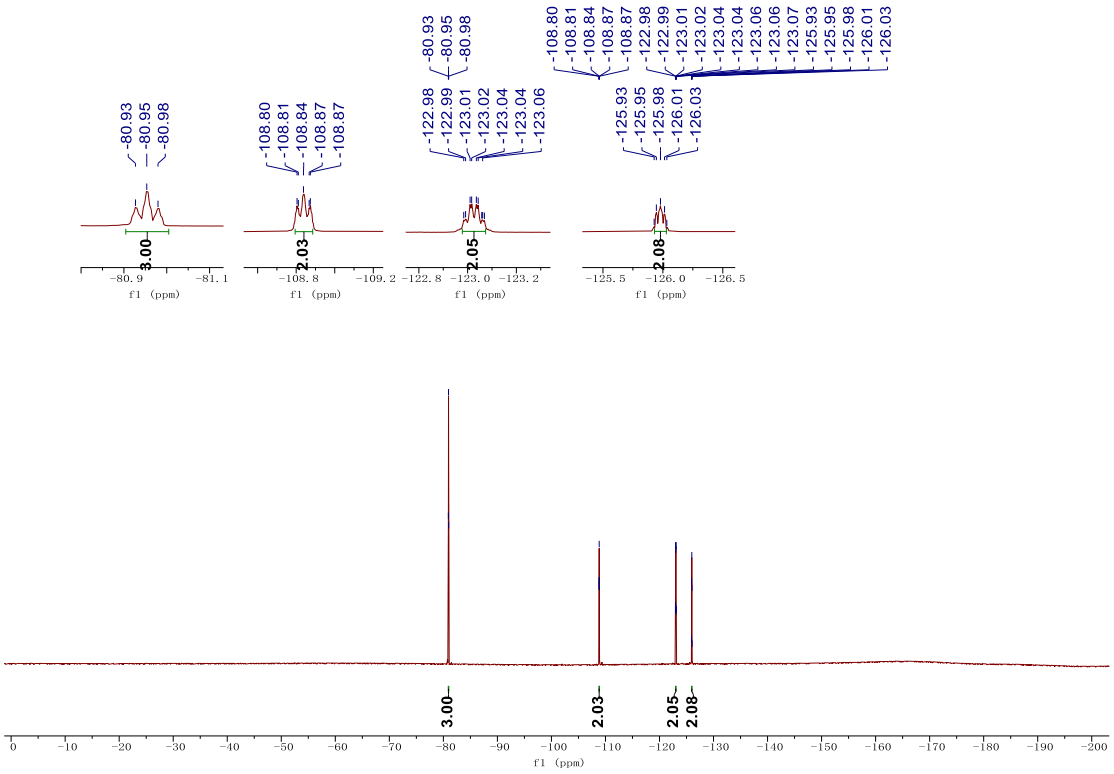
HRMS (ESI, m/z): Mass calcd. for $C_{15}H_9F_9N$, $[M-H]^+$, 374.0597; found: 374.0540.

VIII. NMR spectra

3-methyl-2-(perfluorohexyl)-1*H*-indole (3a)



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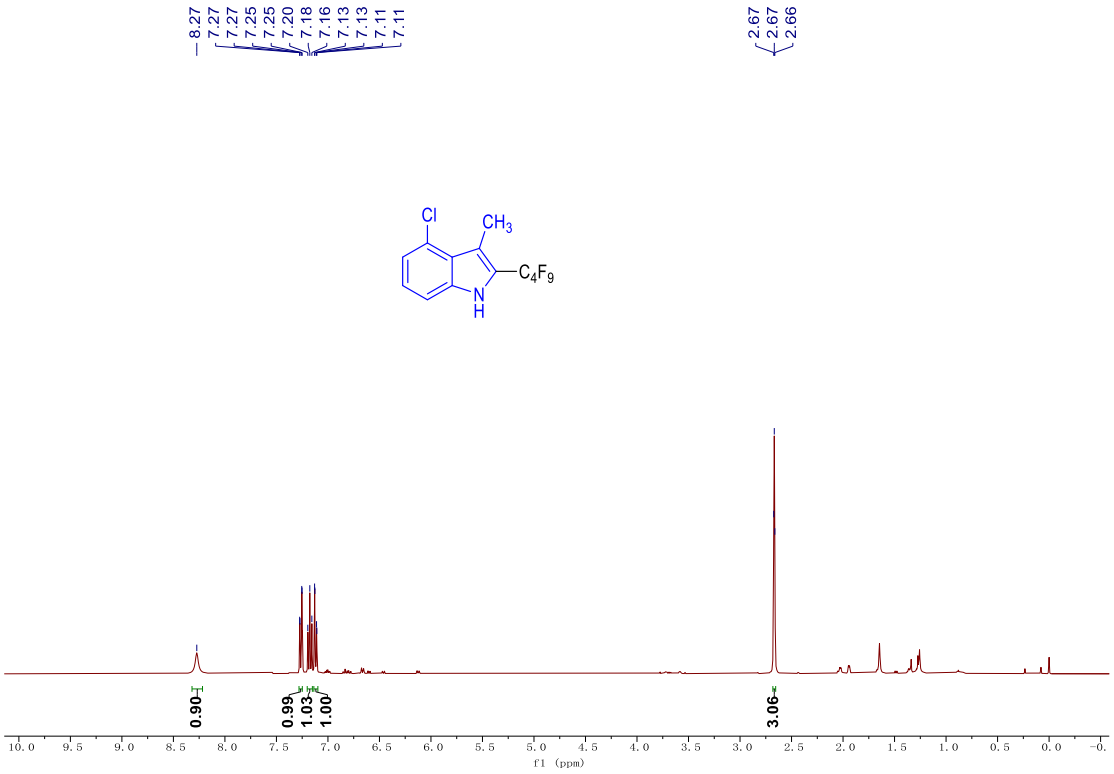
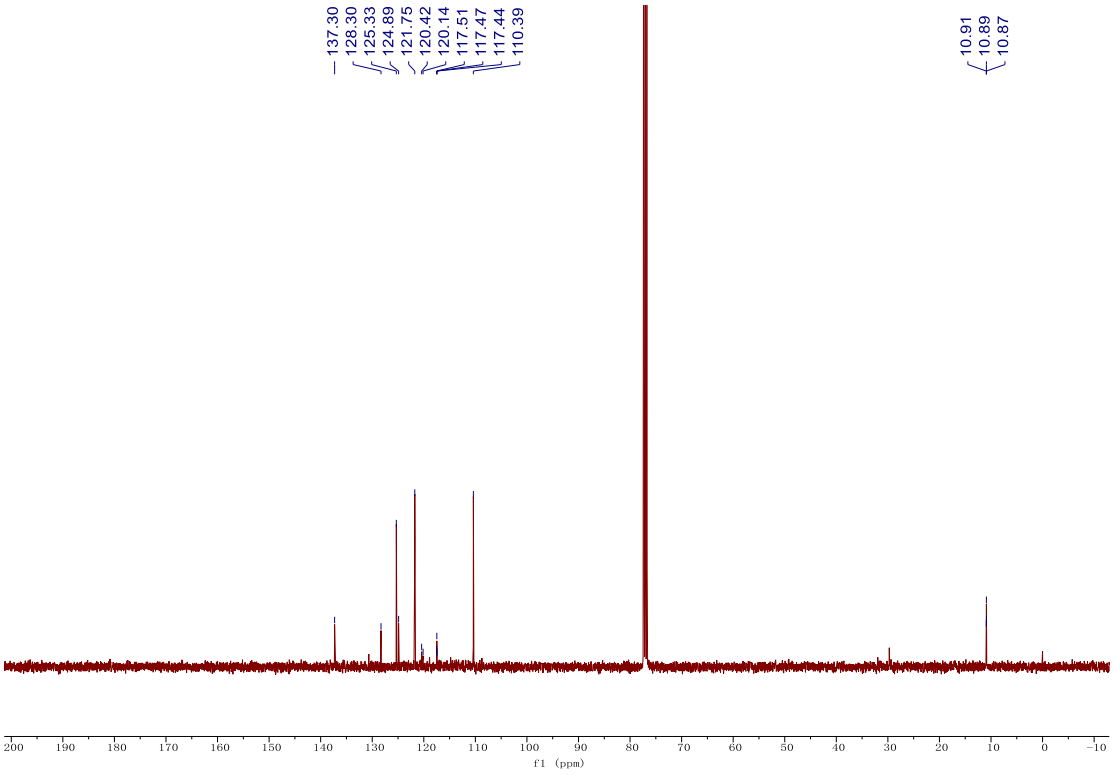
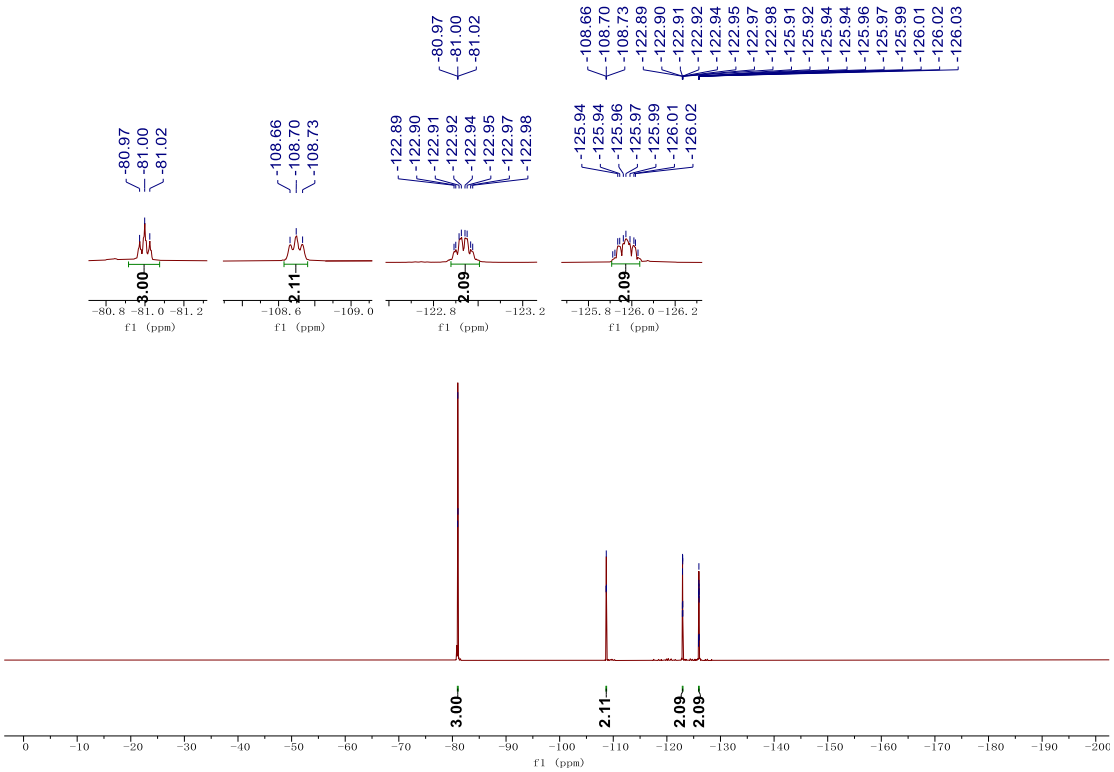
-80.95
-80.98
-108.80
-108.81
-108.84
-108.87
-108.87
-122.98
-122.99
-123.01
-123.02
-123.04
-123.04
-123.06
-123.06
-123.07
-125.93
-125.95
-125.98
-126.01
-126.03
3.00
2.03
2.05
2.08
f1 (ppm)

4-chloro-3-methyl-2-(perfluorobutyl)-1*H*-indole (3b)



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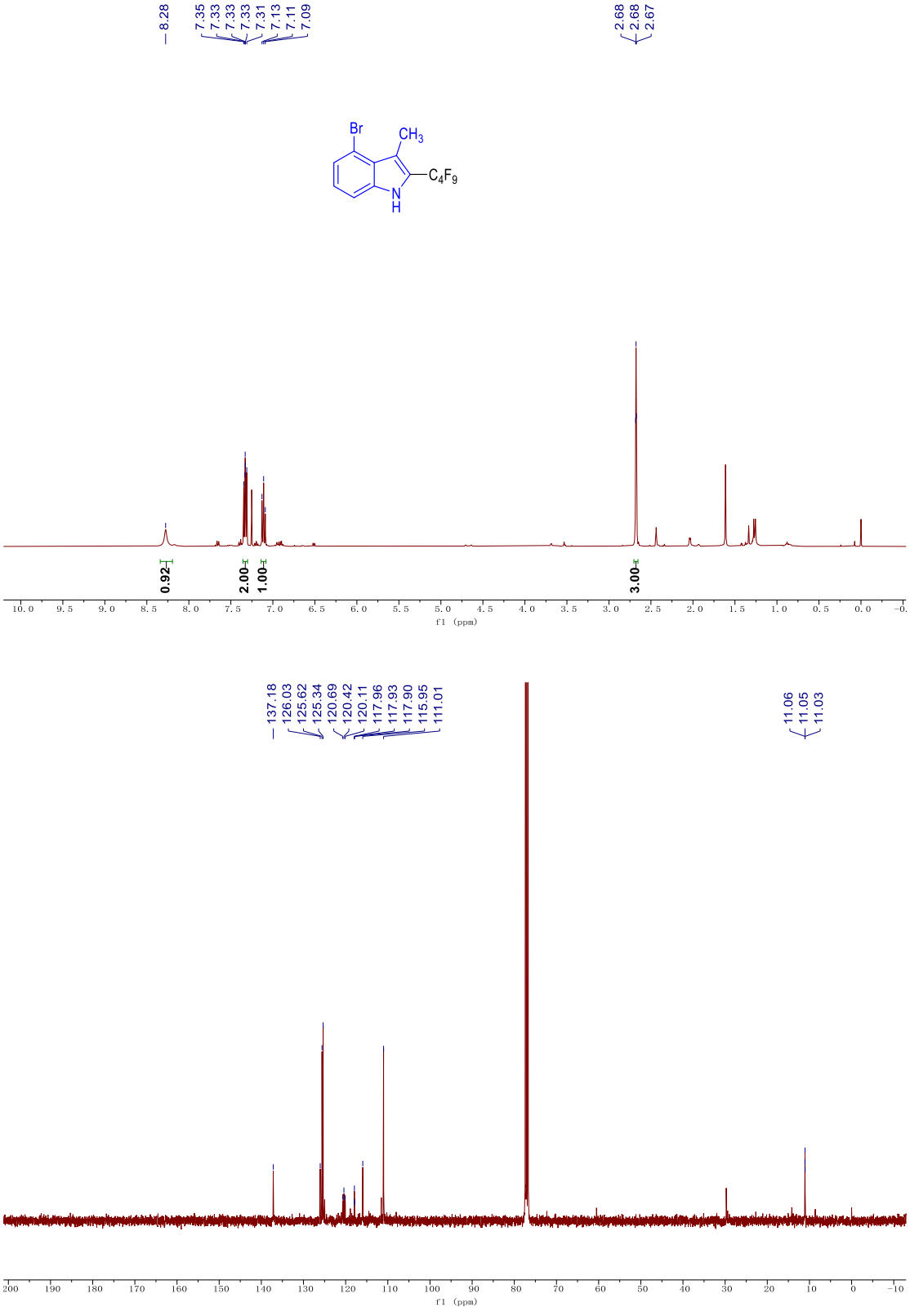
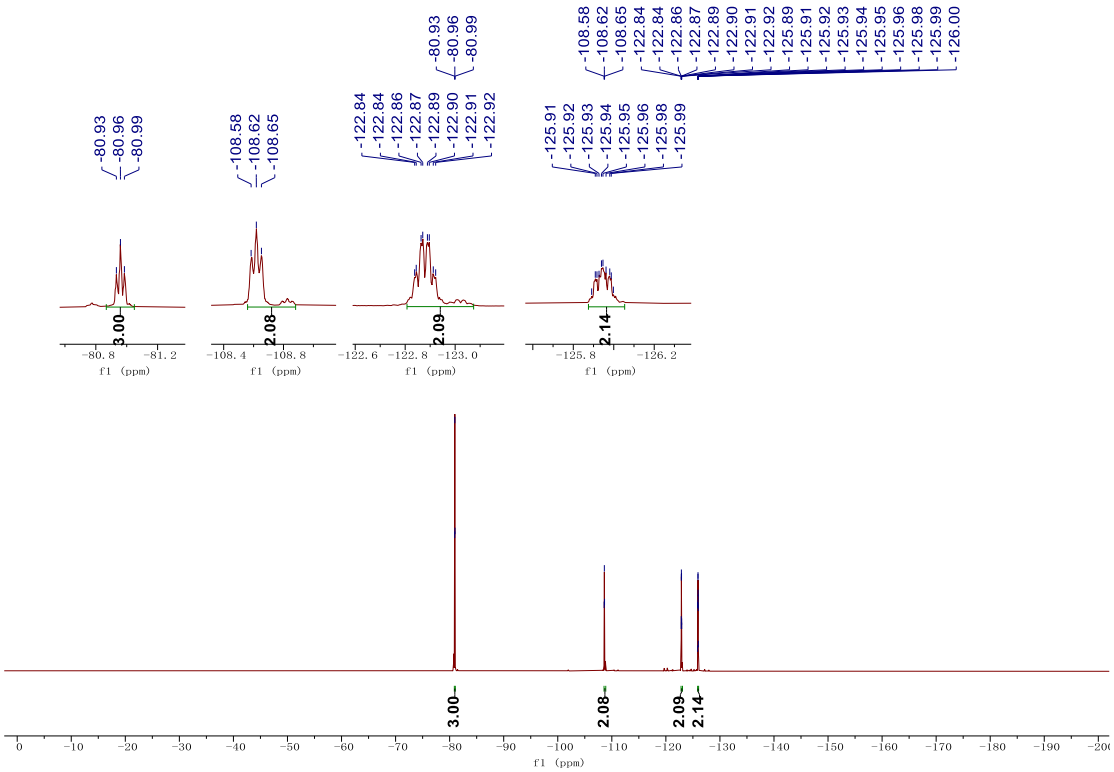
-81.02
-108.66
-108.70
-108.73
-122.89
-122.90
-122.91
-122.92
-122.94
-122.95
-122.97
-122.98
-125.91
-125.92
-125.94
-125.94
-125.96
-125.97
-125.99
-126.01
-126.02
-126.03
3.00
2.11
2.09
2.09
f1 (ppm)

4-bromo-3-methyl-2-(perfluorobutyl)-1*H*-indole (3c)




-80.93
-80.96
-80.99
-108.58
-108.62
-108.65
-122.84
-122.84
-122.86
-122.87
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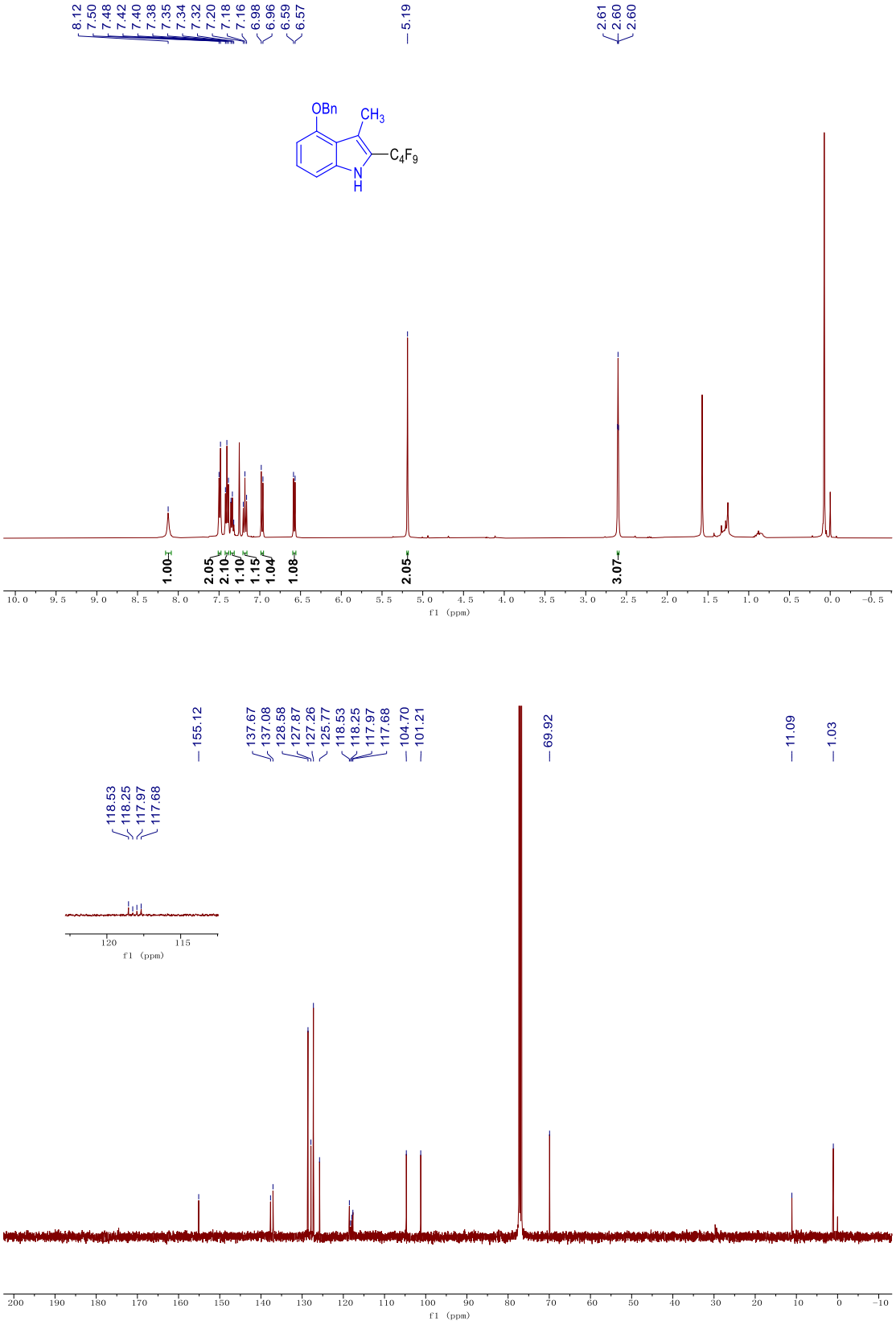
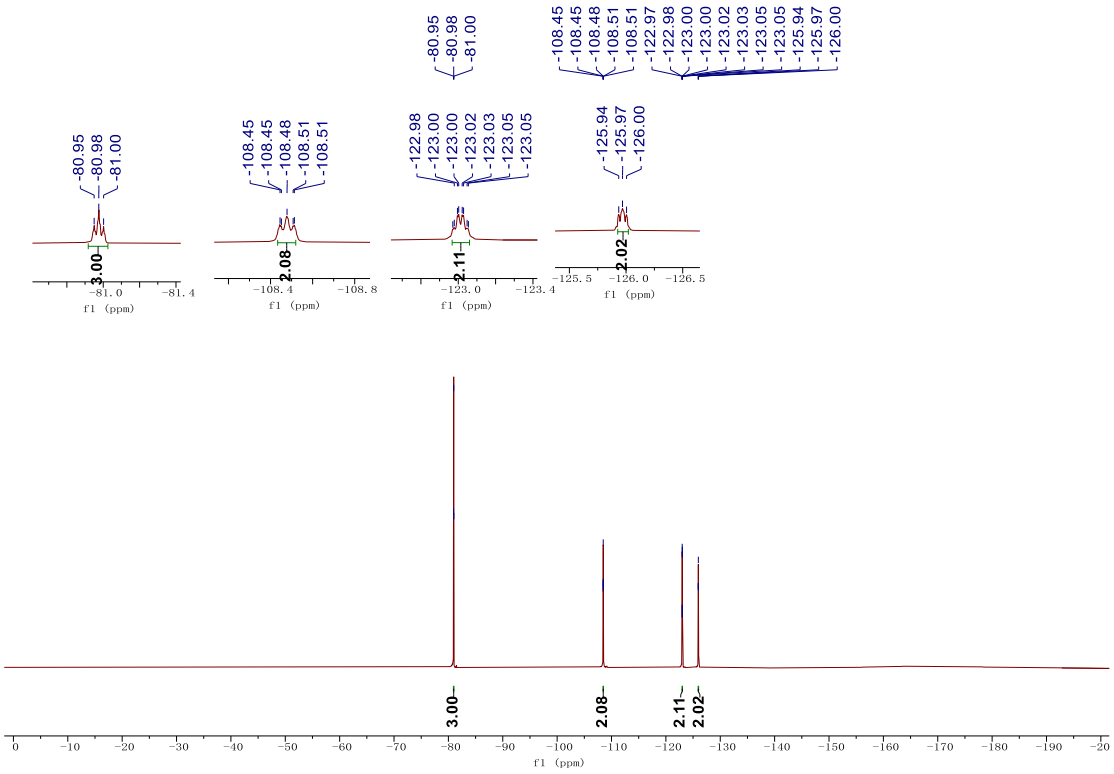
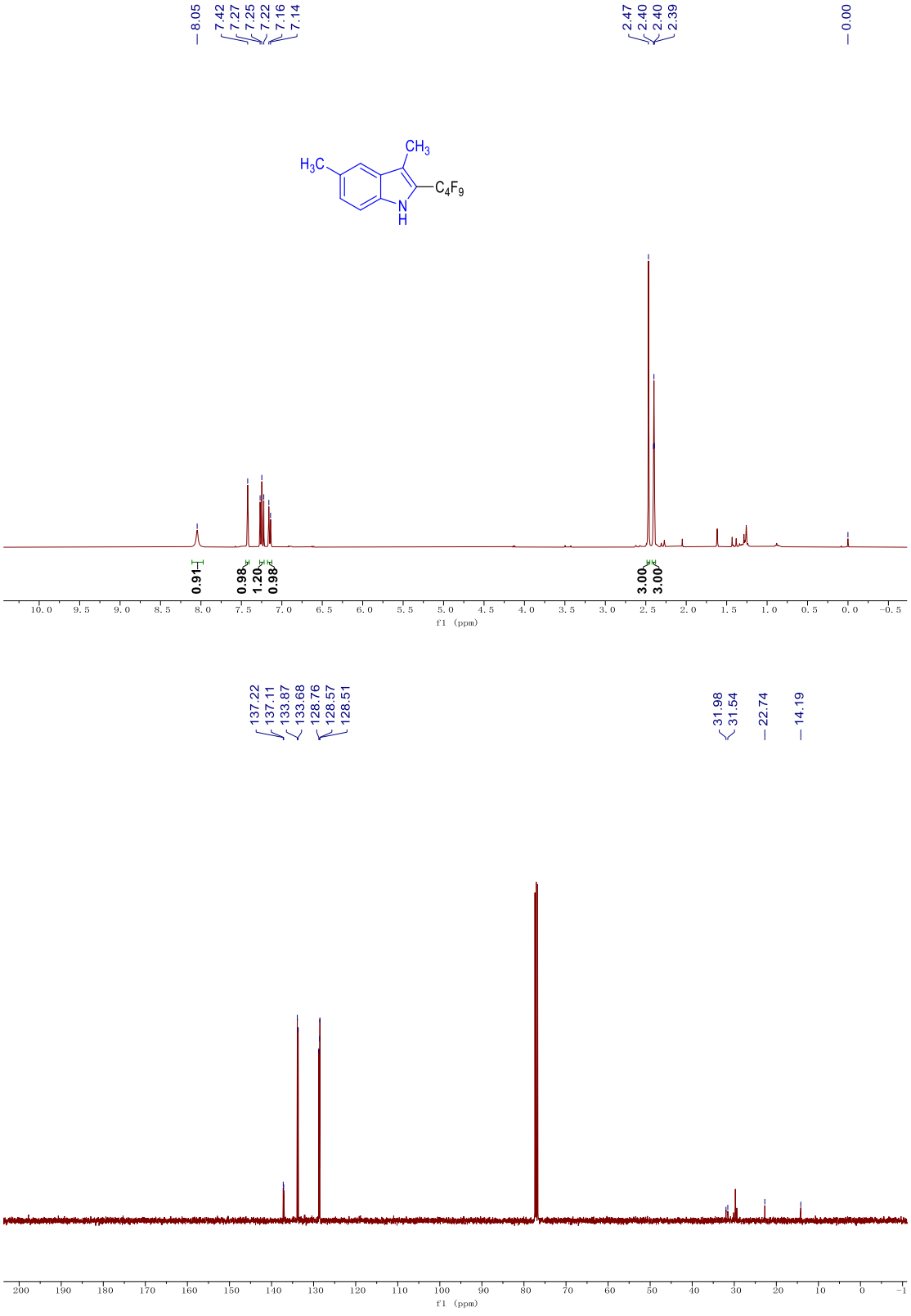
-122.90
-122.91
-122.92
-125.91
-125.92
-125.93
-125.94
-125.95
-125.96
-125.98
-125.99
-108.58
-108.62
-108.65
-122.84
-122.84
-122.86
-122.87
-122.89
-122.90
-122.91
-122.92
-125.89
-125.91
-125.92
-125.93
-125.94
-125.95
-125.96
-125.98
-125.99
-126.00
3.00
2.08
2.09
2.14
f1 (ppm)

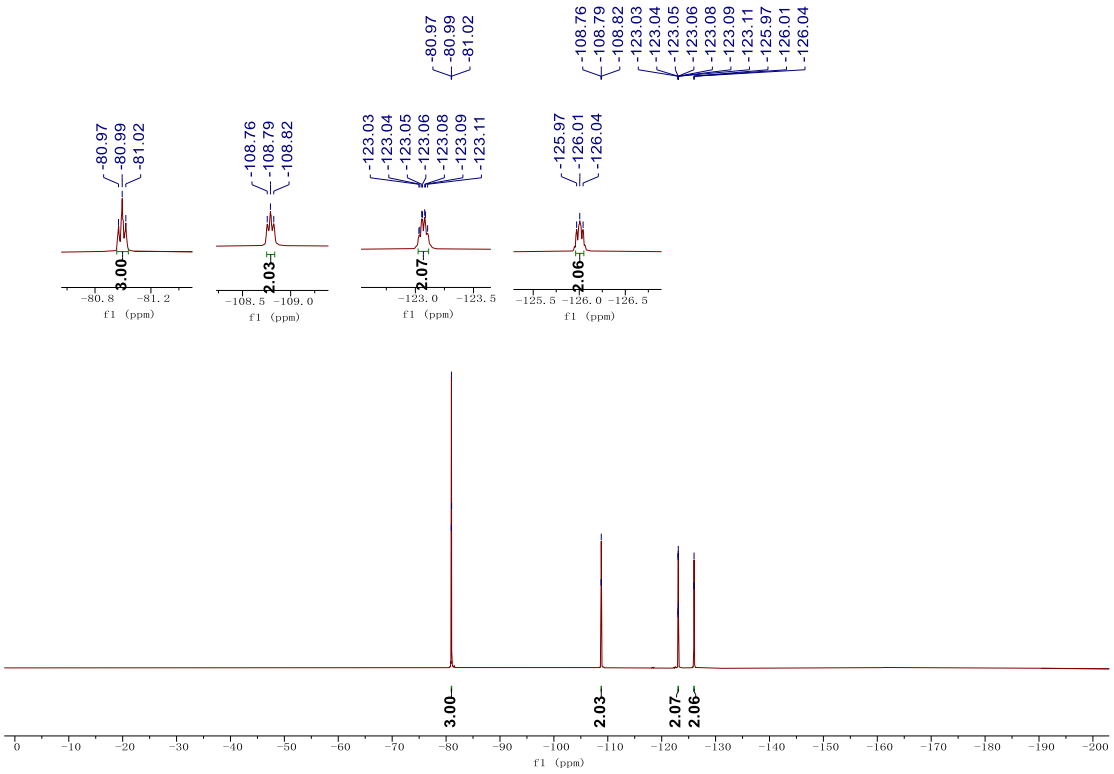
4-(benzyloxy)-3-methyl-2-(perfluorobutyl)-1*H*-indole (3d)




-80.95
-80.98
-81.00
-108.45
-108.45
-108.48
-108.51
-108.51
-122.97
-122.98
-123.00
-123.00
-123.02
-123.03
-123.05
-123.05
-125.94
-125.97
-126.00
3.00
2.08
2.11
2.02
f1 (ppm)

3,5-dimethyl-2-(perfluorobutyl)-1*H*-indole (3e)




-80.97
-80.99
-81.02
-108.76
-108.79
-108.82
-123.03
-123.04
-123.05
-123.06
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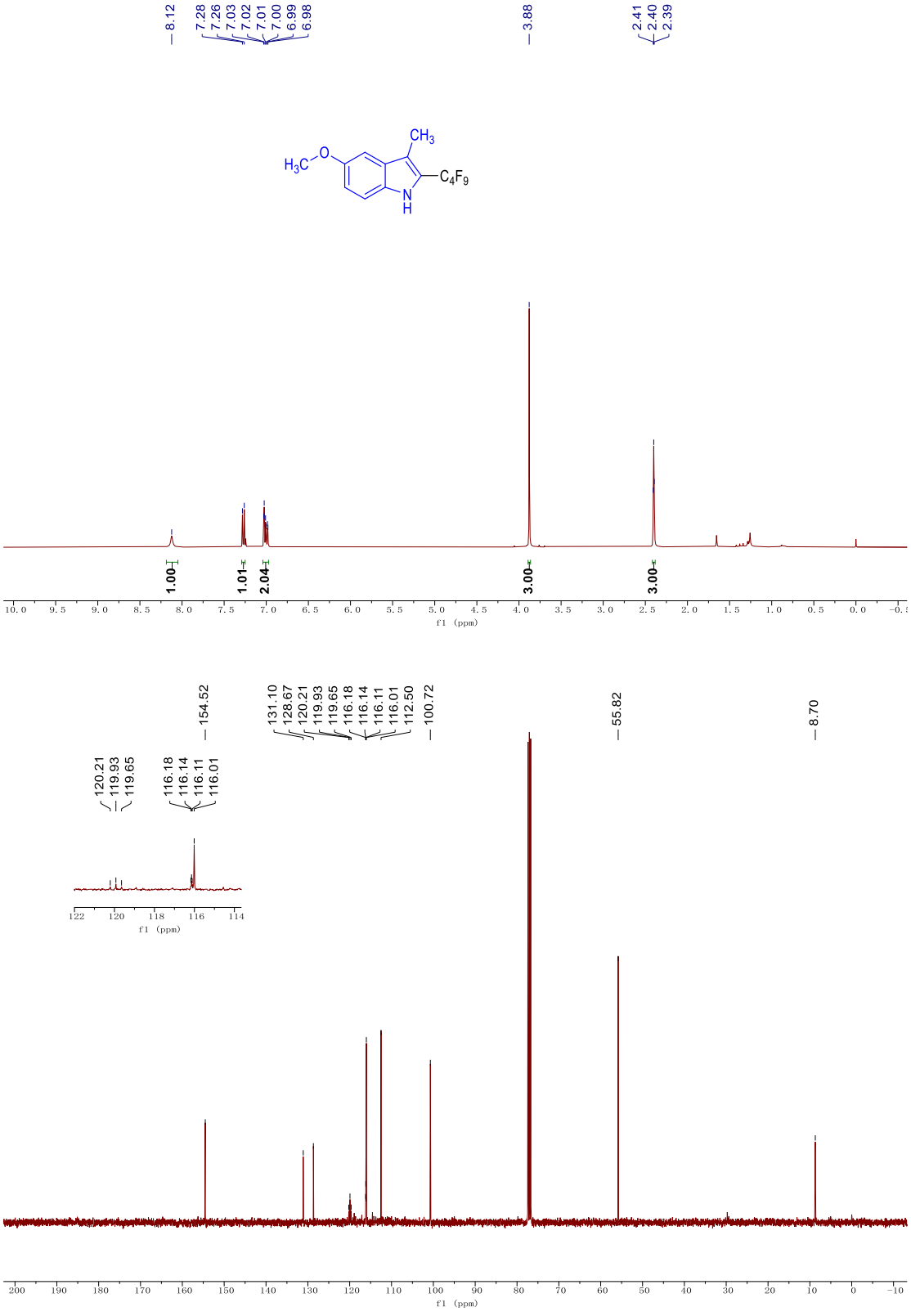
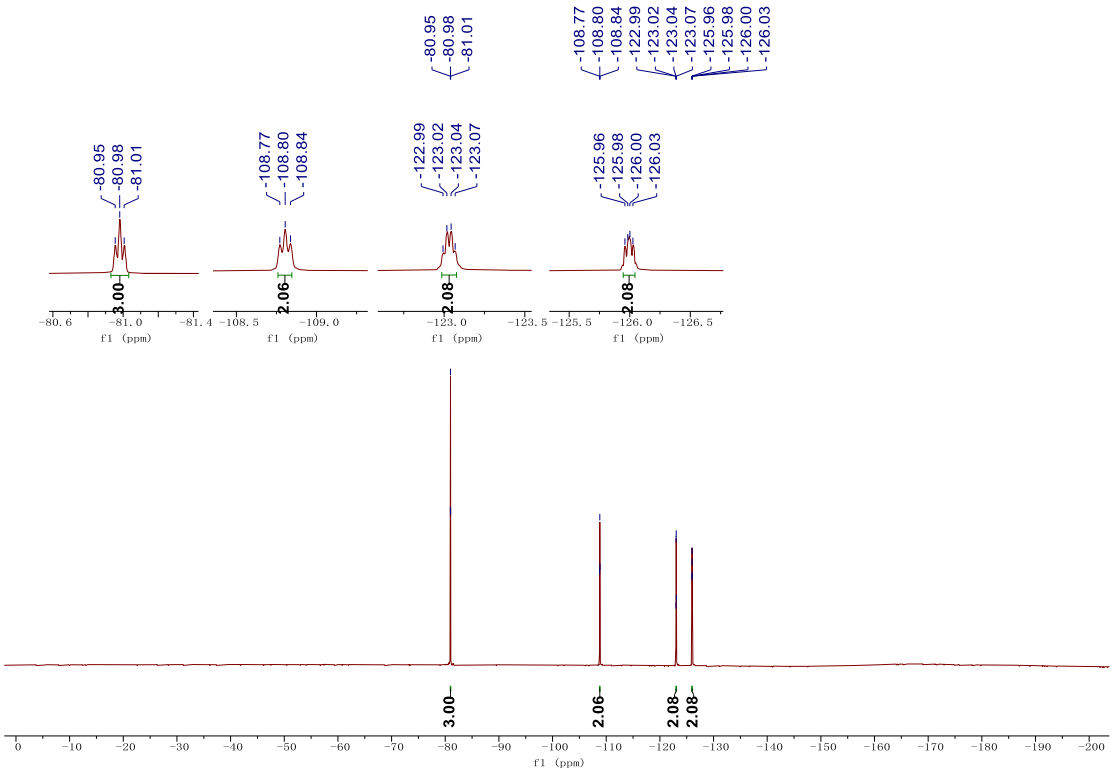
-123.09
-123.11
-125.97
-126.01
-126.04
3.00
2.03
2.07
2.06
f1 (ppm)

5-methoxy-3-methyl-2-(perfluorobutyl)-1*H*-indole (3f)




-80.95
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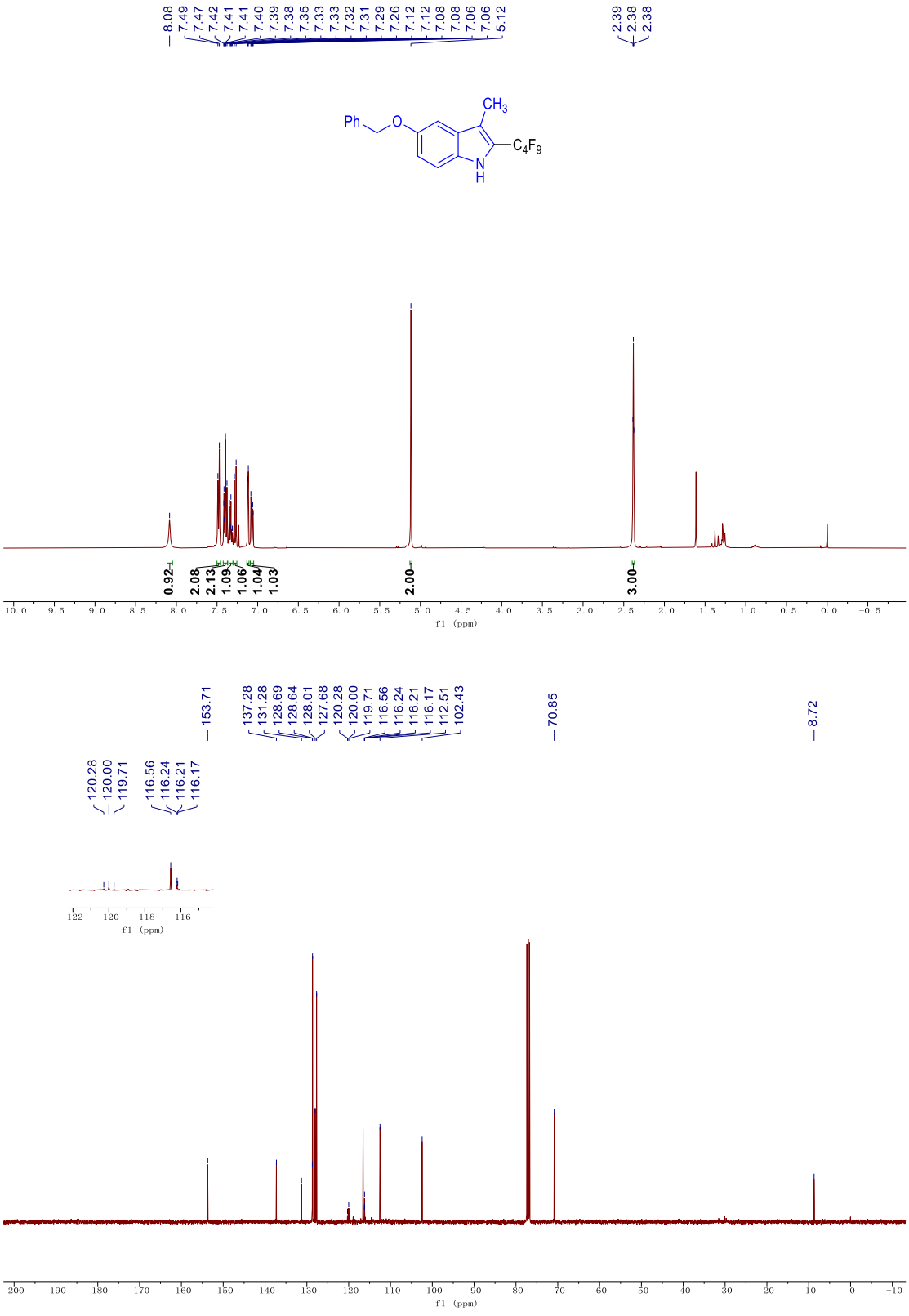
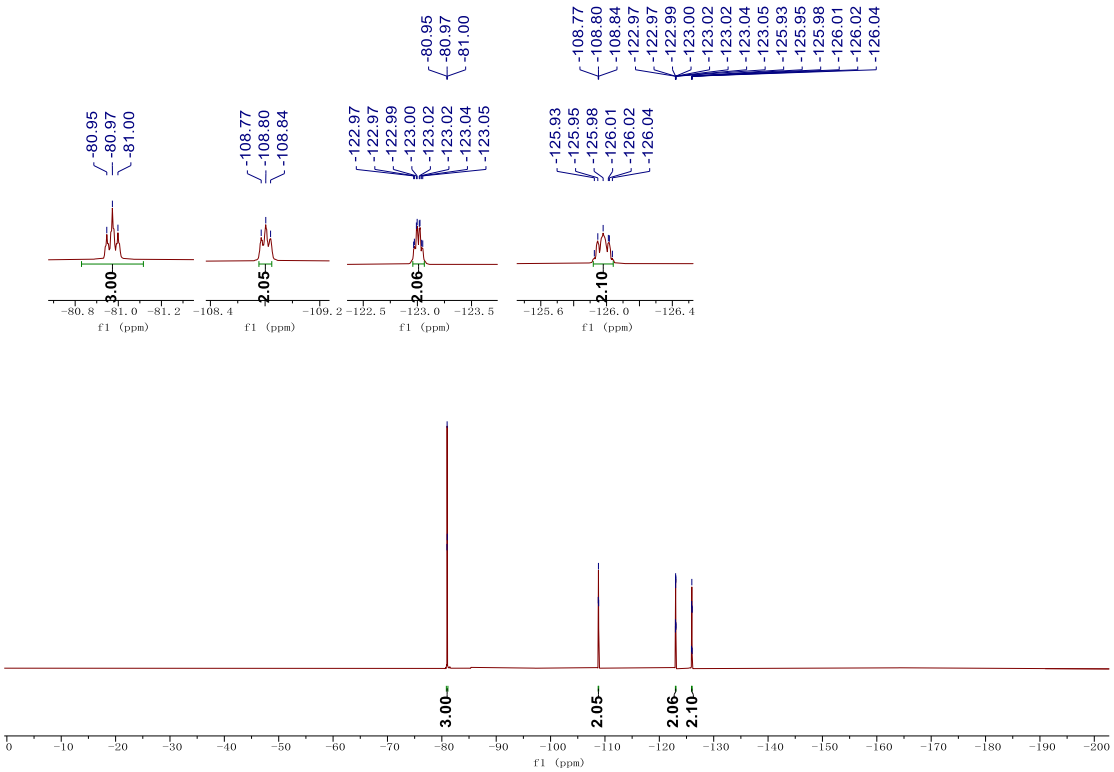
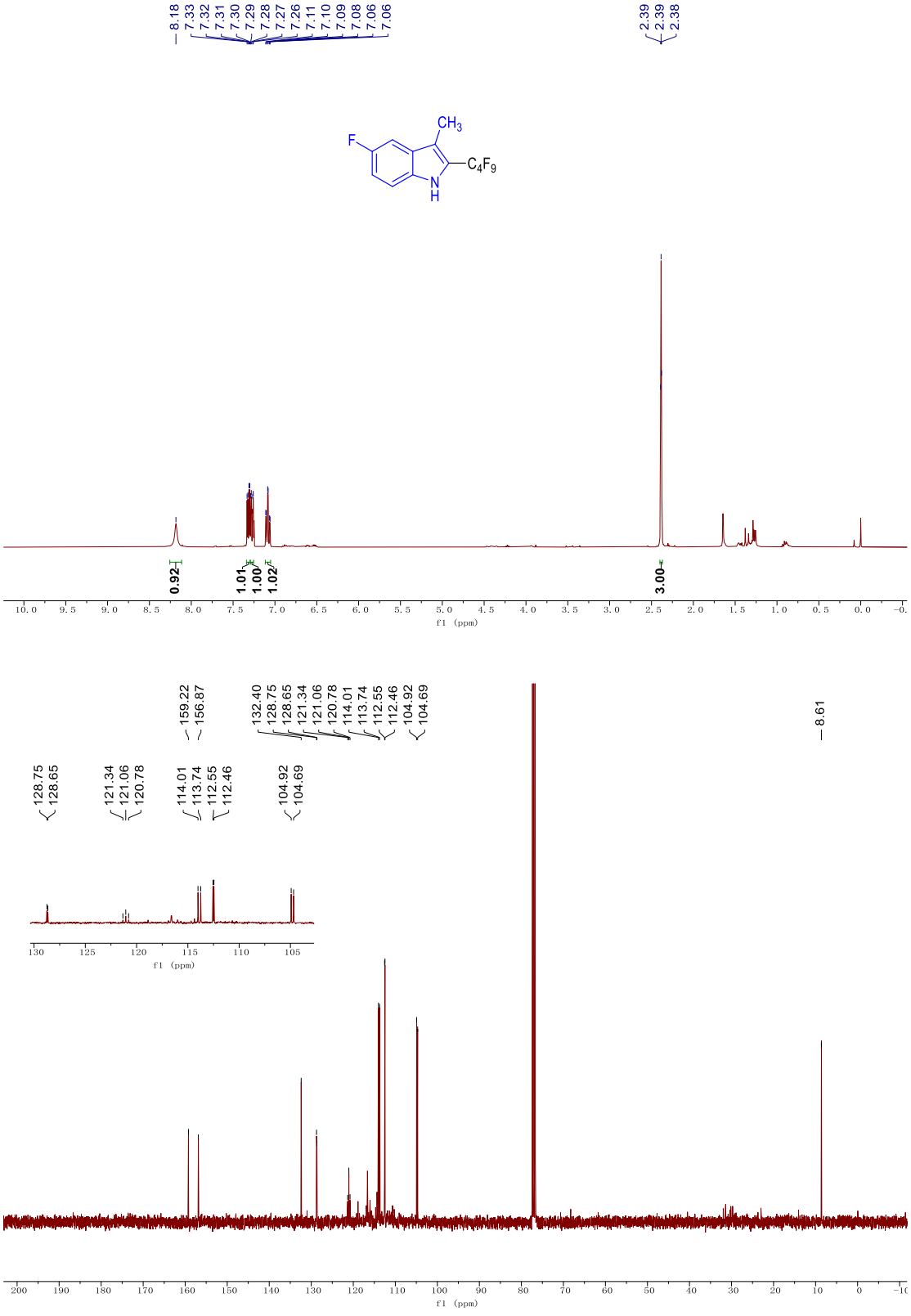
-81.01
-108.77
-108.80
-108.84
-122.99
-123.02
-123.04
-123.07
-125.96
-125.98
-126.00
-126.03
3.00
2.06
2.08
2.08
f1 (ppm)

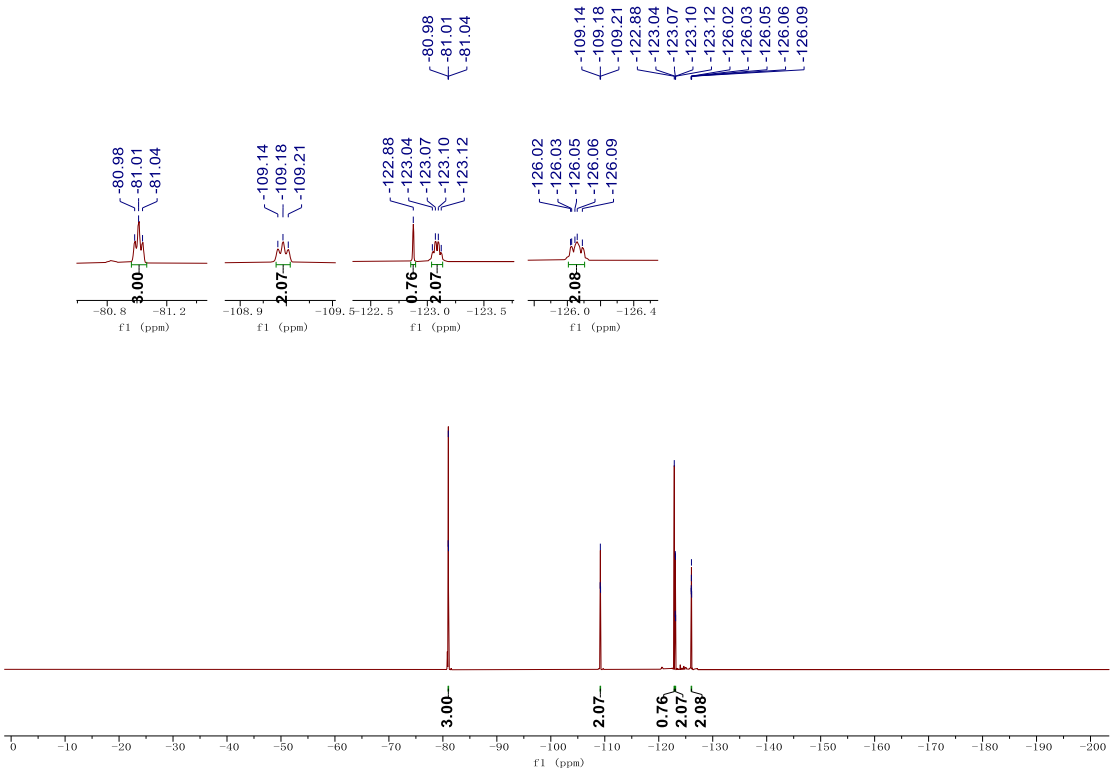
5-(benzyloxy)-3-methyl-2-(perfluorobutyl)-1*H*-indole (3g)




-80.95
-80.97
-81.00
-108.77
-108.80
-108.84
-122.97
-122.97
-122.99
-123.00
-123.02
-123.02
-123.04
-123.05
-125.93
-125.95
-125.98
-126.01
-126.02
-126.04
3.00
2.05
2.06
2.10
f1 (ppm)

5-fluoro-3-methyl-2-(perfluorobutyl)-1*H*-indole (3h)

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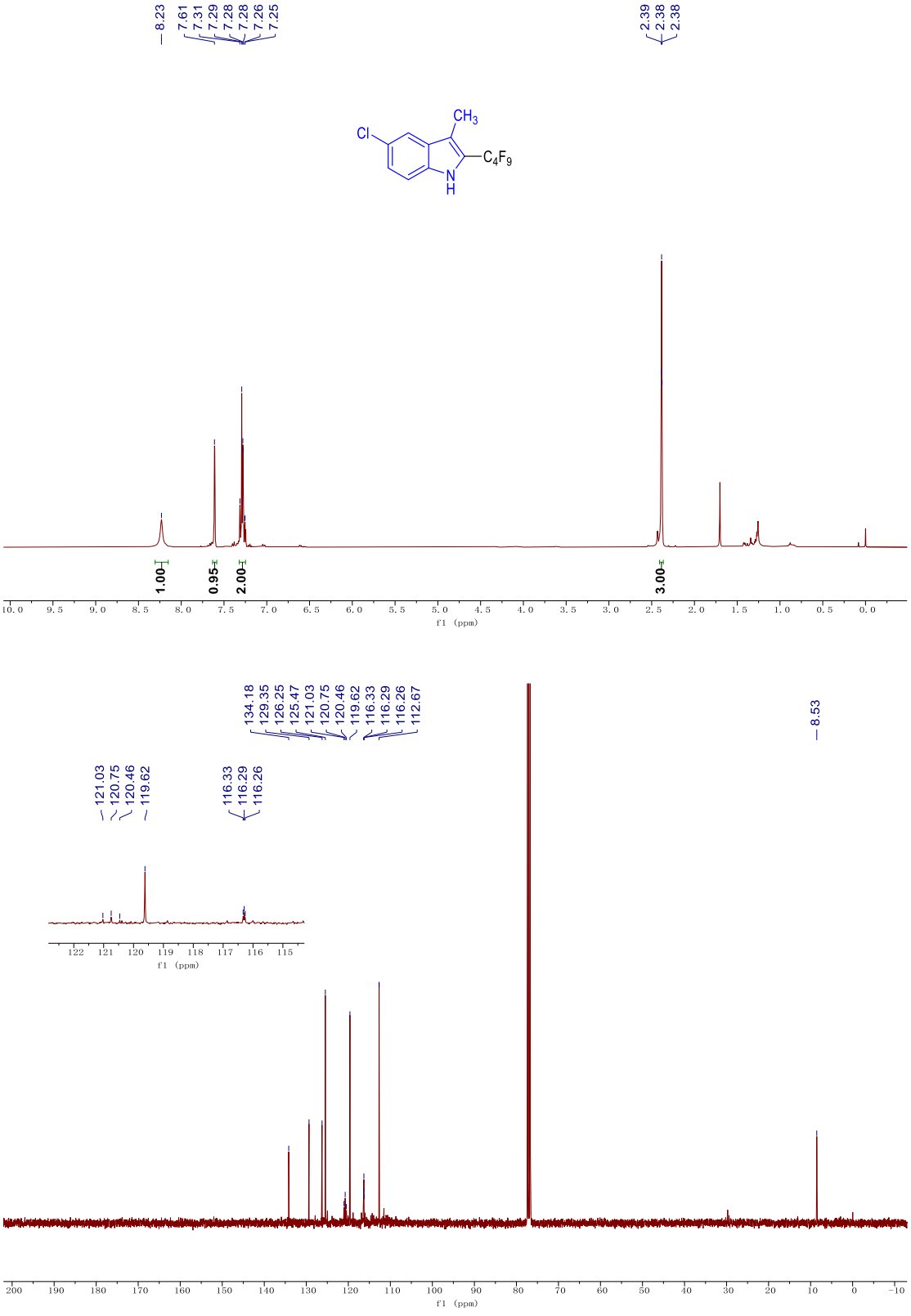
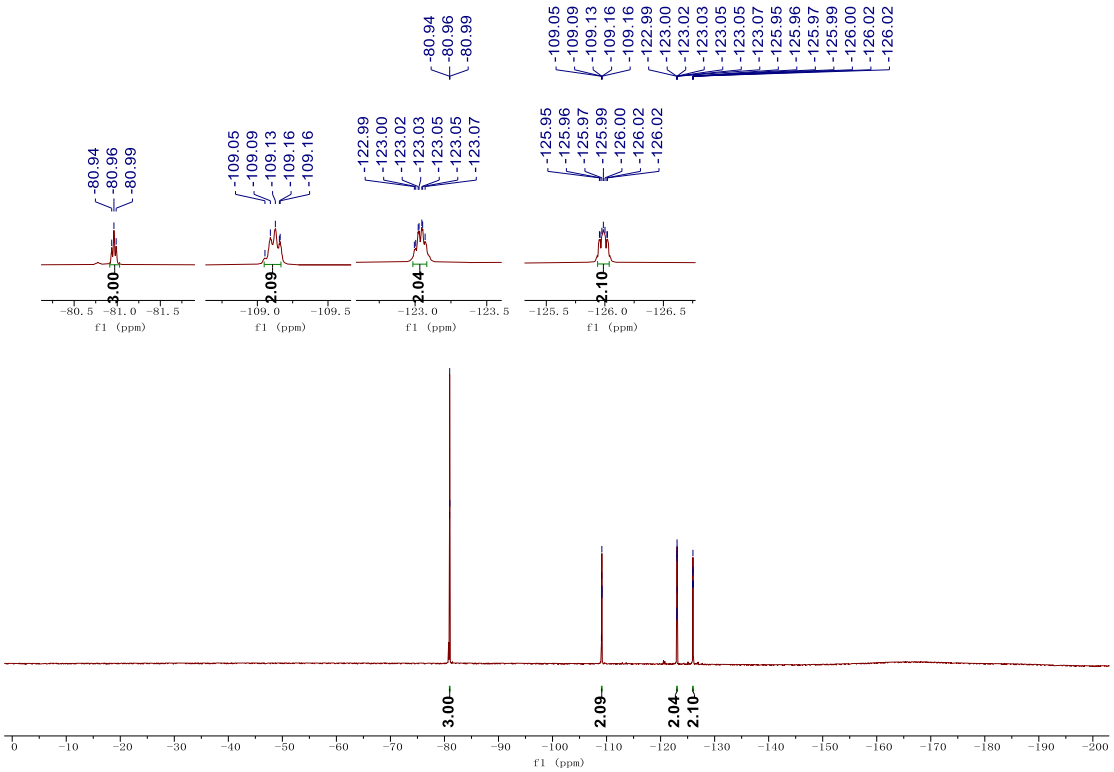
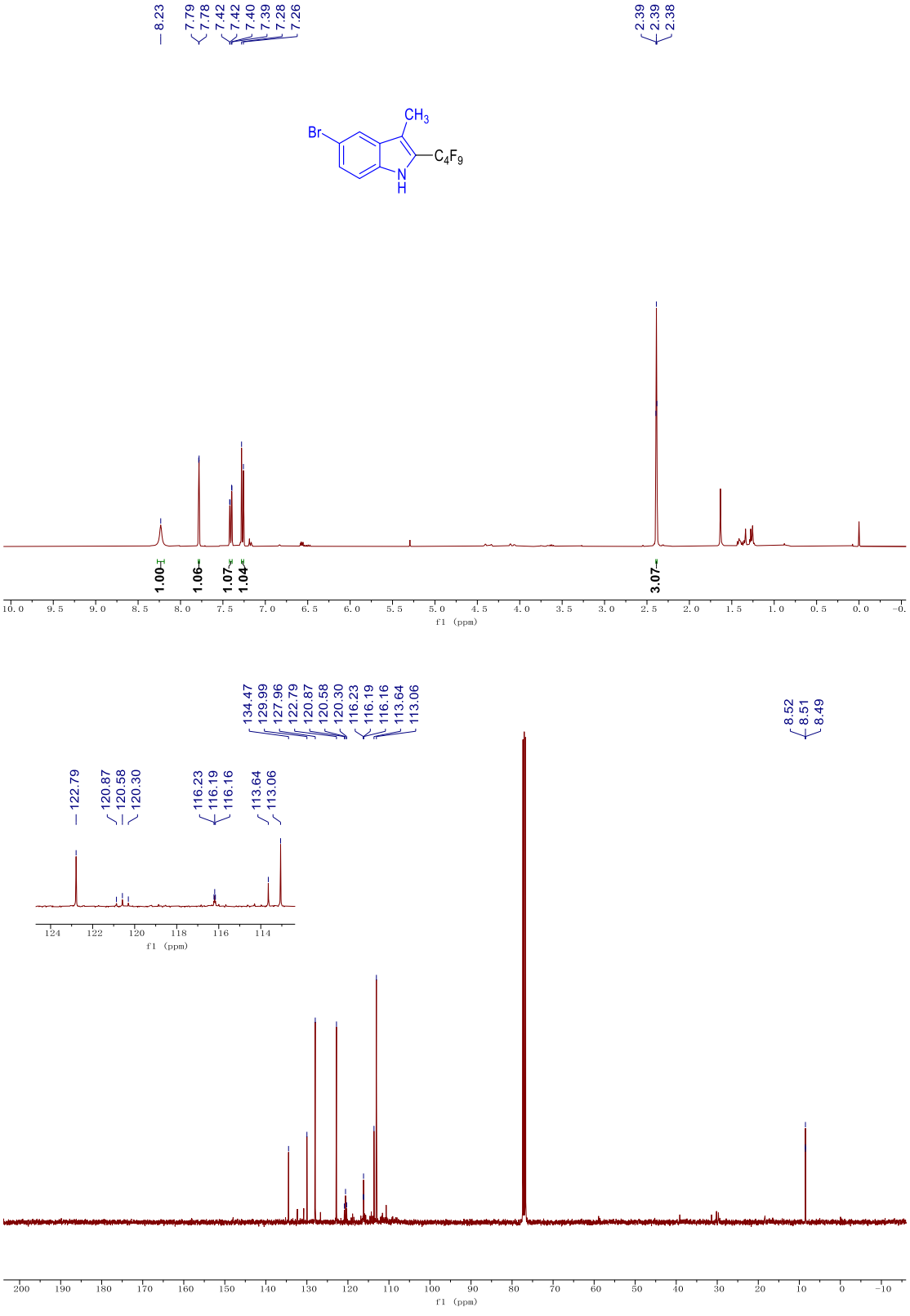
-81.04
-109.14
-109.18
-109.21
-122.88
-123.04
-123.07
-123.10
-123.12
-126.02
-126.03
-126.05
-126.06
-126.09
3.00
2.07
0.76
2.07
2.08
f1 (ppm)

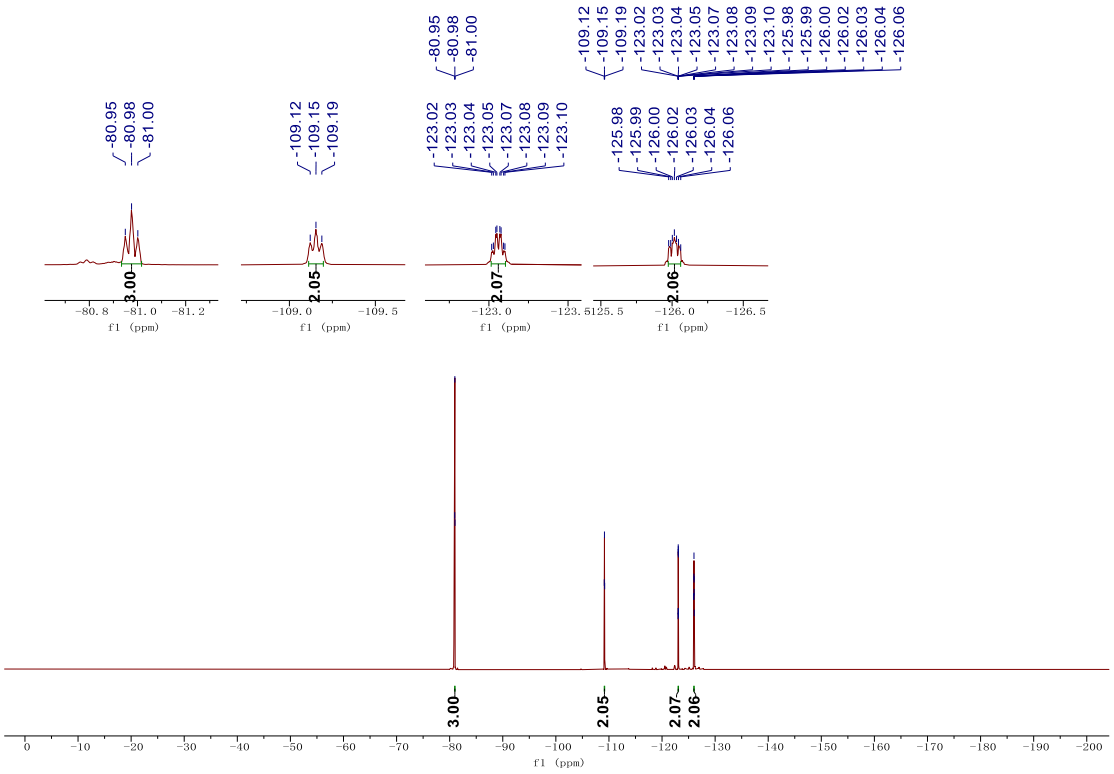
5-chloro-3-methyl-2-(perfluorobutyl)-1*H*-indole (3i)




-80.94
-80.96
-80.99
-109.05
-109.09
-109.13
-109.16
-109.16
-122.99
-123.00
-123.02
-123.03
-123.05
-123.05
-123.07
-125.95
-125.96
-125.97
-125.99
-126.00
-126.02
-126.02
3.00
2.09
2.04
2.10
f1 (ppm)

5-bromo-3-methyl-2-(perfluorobutyl)-1*H*-indole (3j)

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-81.00
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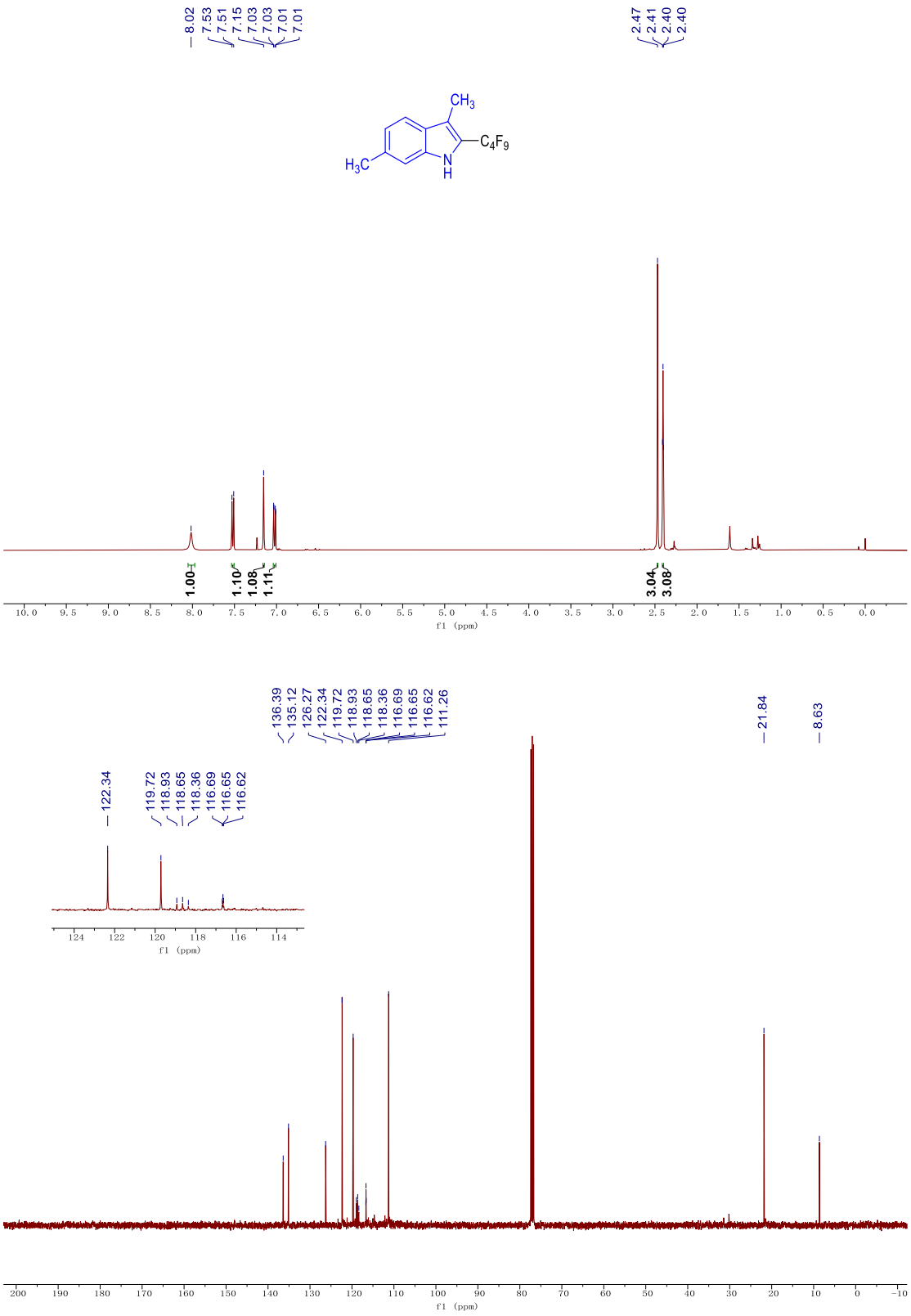
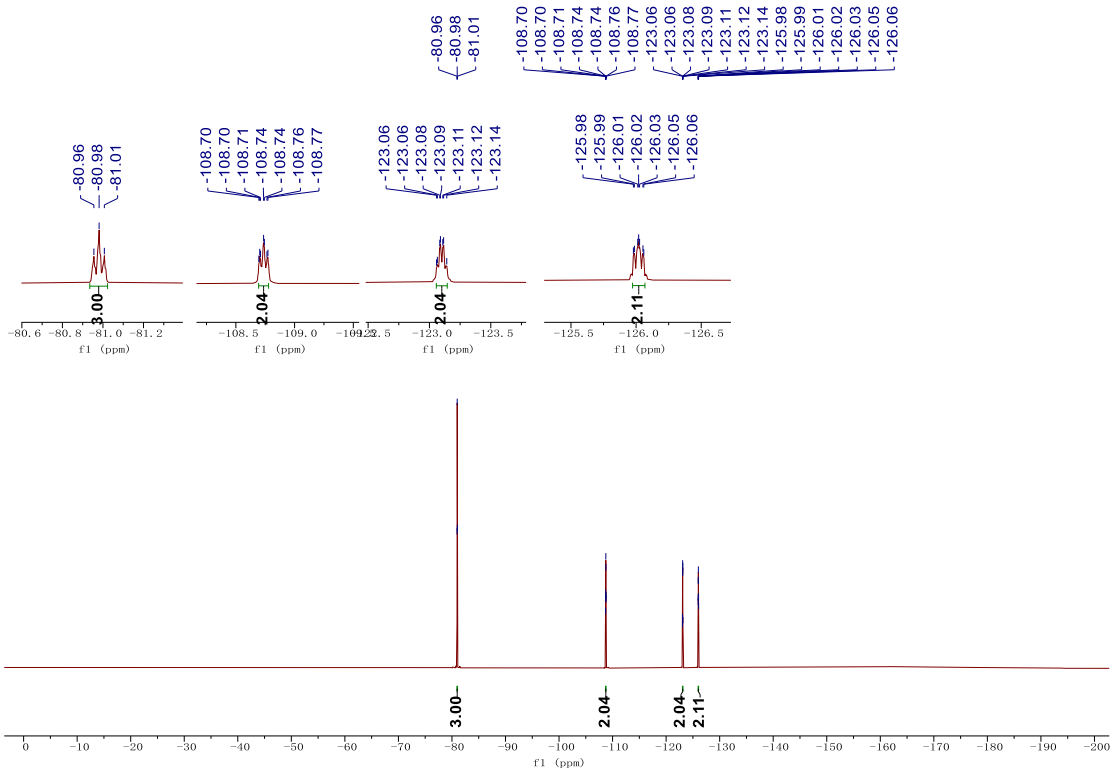
-109.15
-109.19
-123.02
-123.03
-123.04
-123.05
-123.07
-123.08
-123.09
-123.10
-125.98
-125.99
-126.00
-126.02
-126.03
-126.04
-126.06
3.00
2.05
2.07
2.06
f1 (ppm)

3,6-dimethyl-2-(perfluorobutyl)-1*H*-indole (3k)




-80.96
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-81.01
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-108.70
-108.71
-108.74
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-108.76
-108.77
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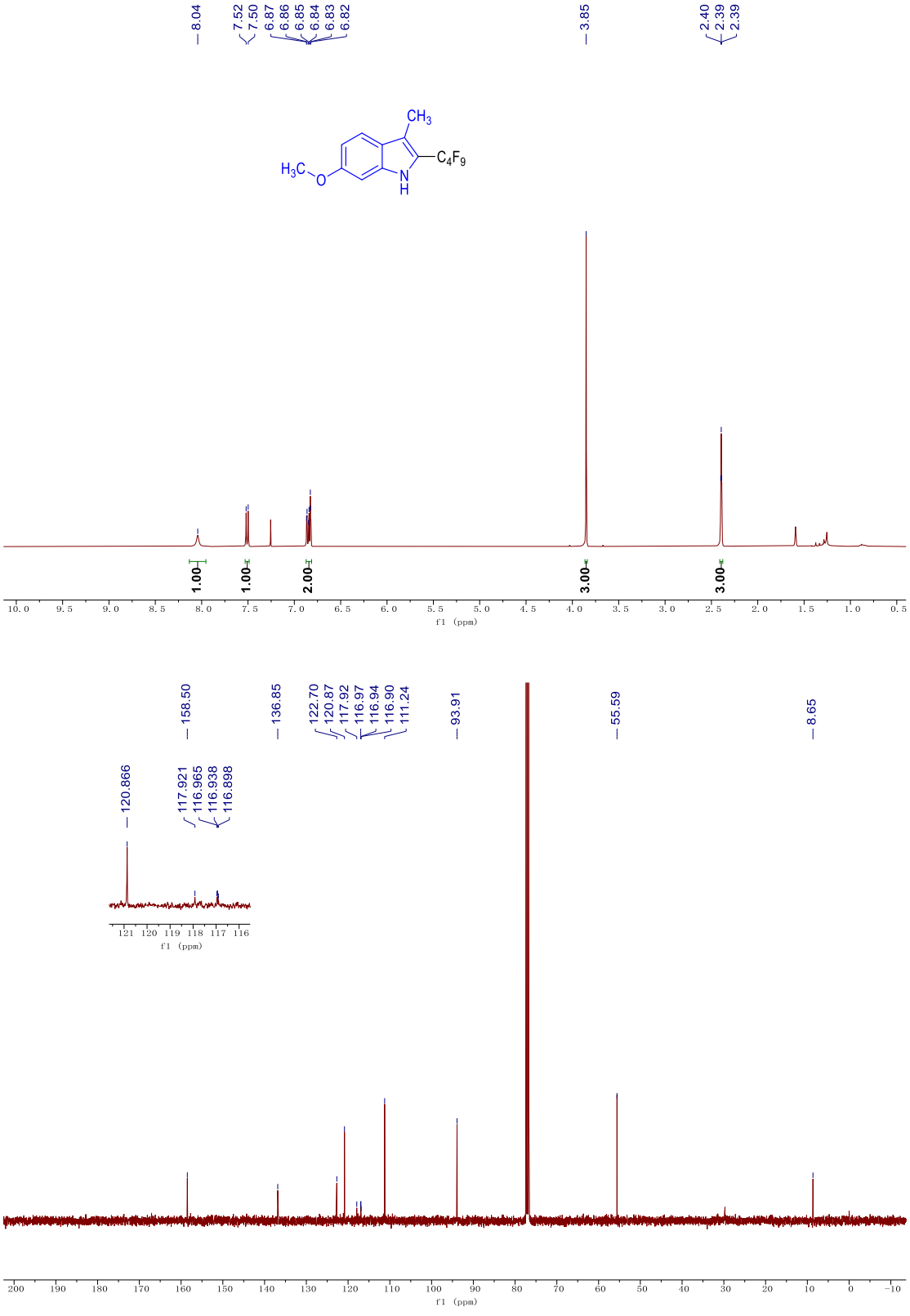
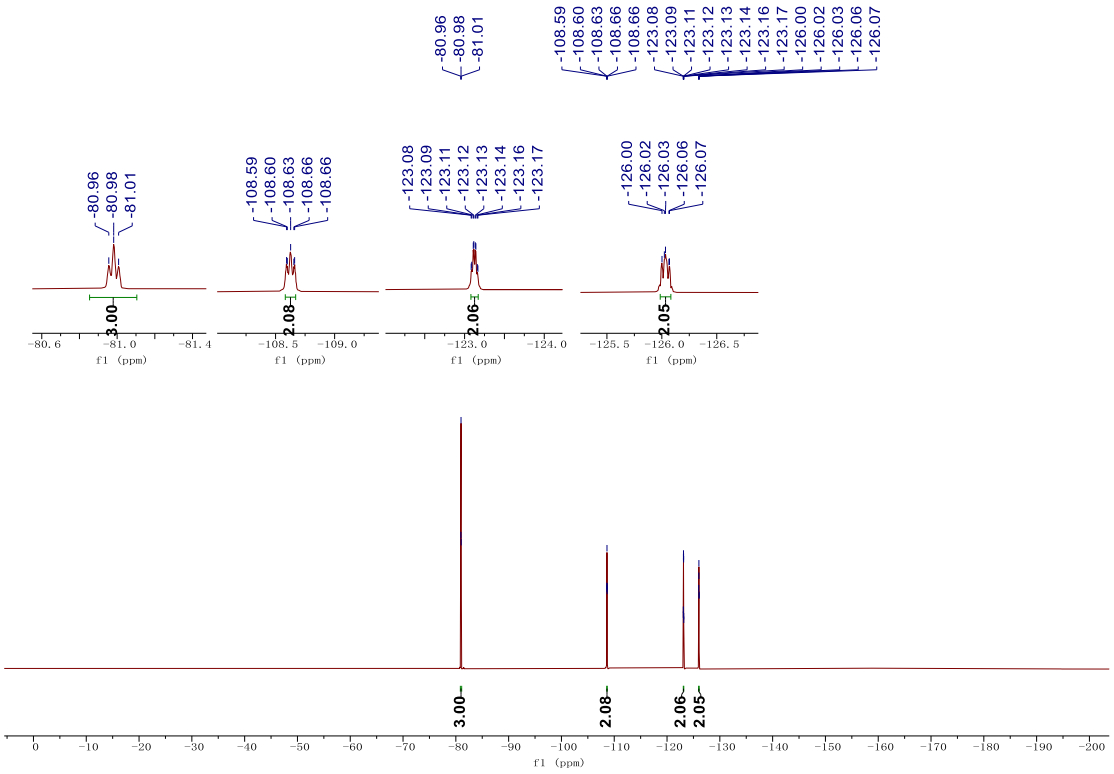
-123.06
-123.08
-123.09
-123.11
-123.12
-123.14
-125.98
-125.99
-126.01
-126.02
-126.03
-126.05
-126.06
3.00
2.04
2.04
2.11
f1 (ppm)

6-methoxy-3-methyl-2-(perfluorobutyl)-1*H*-indole (3l)

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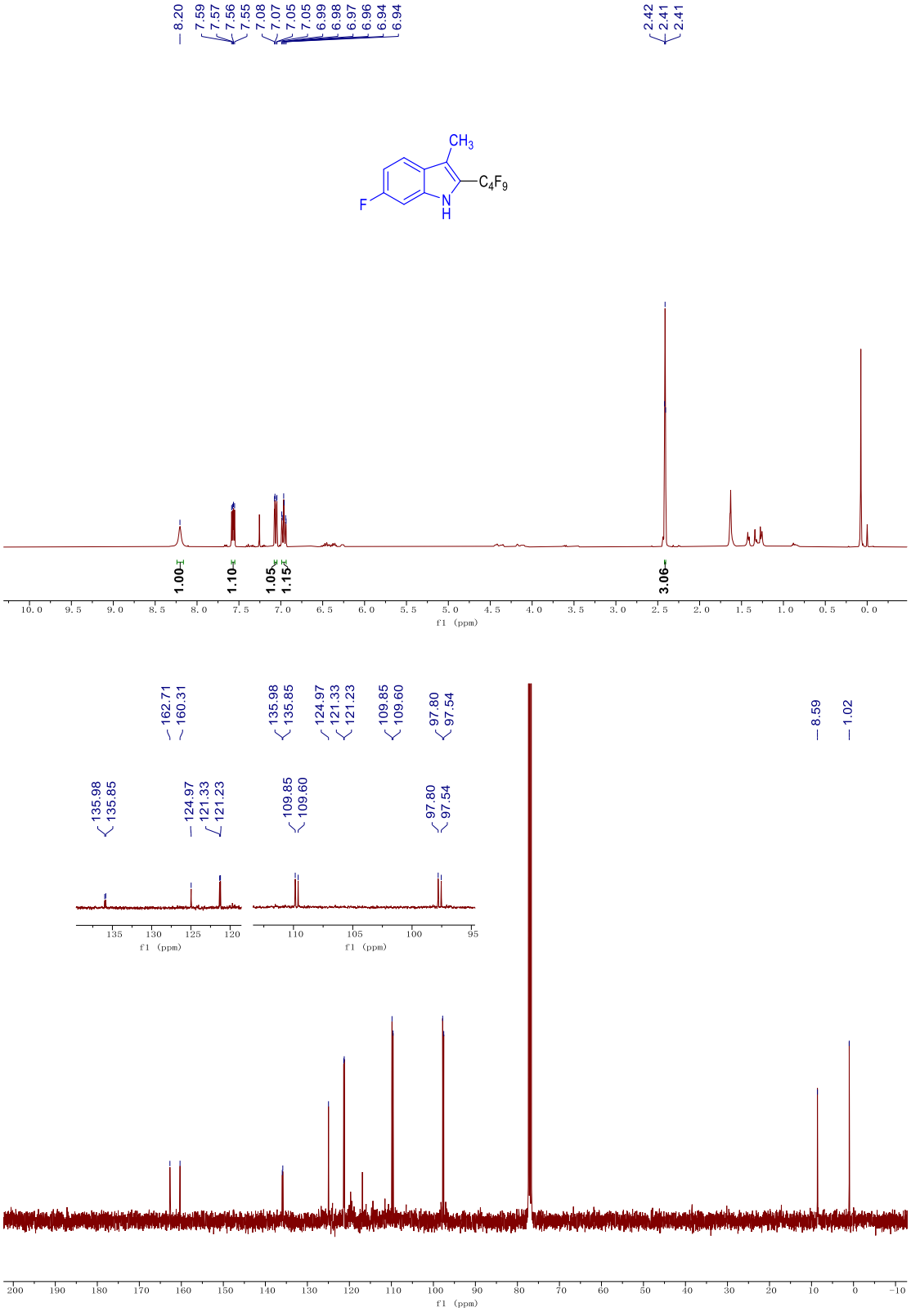
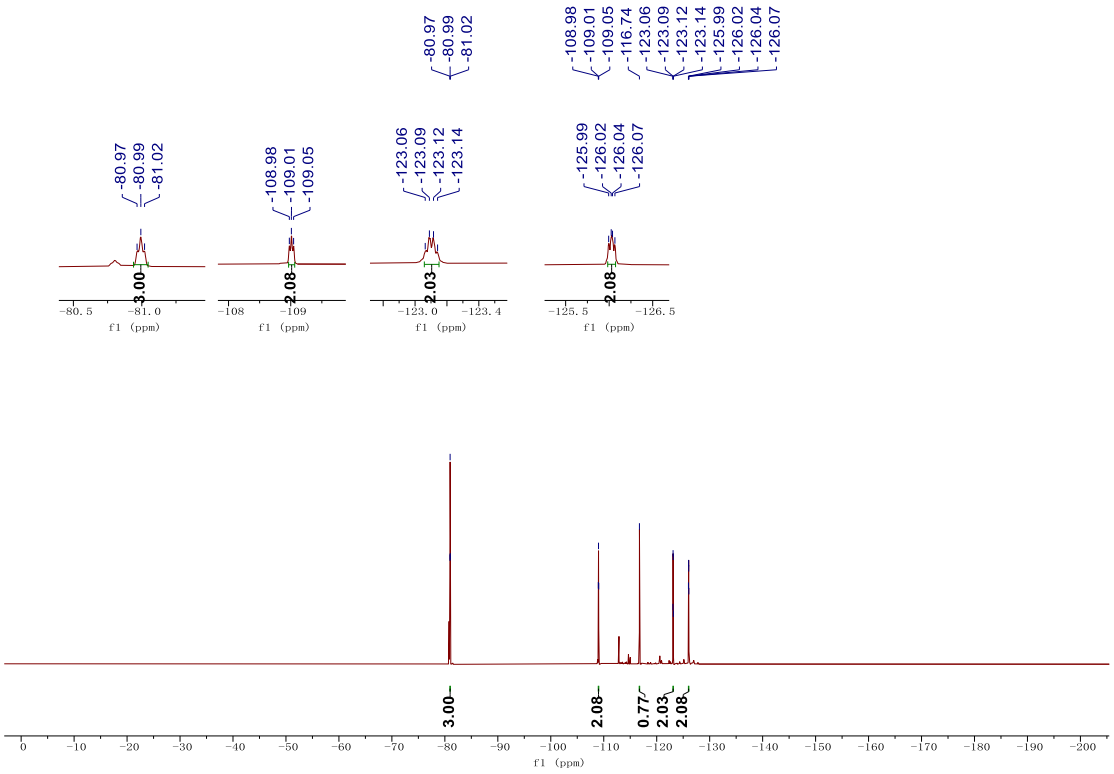
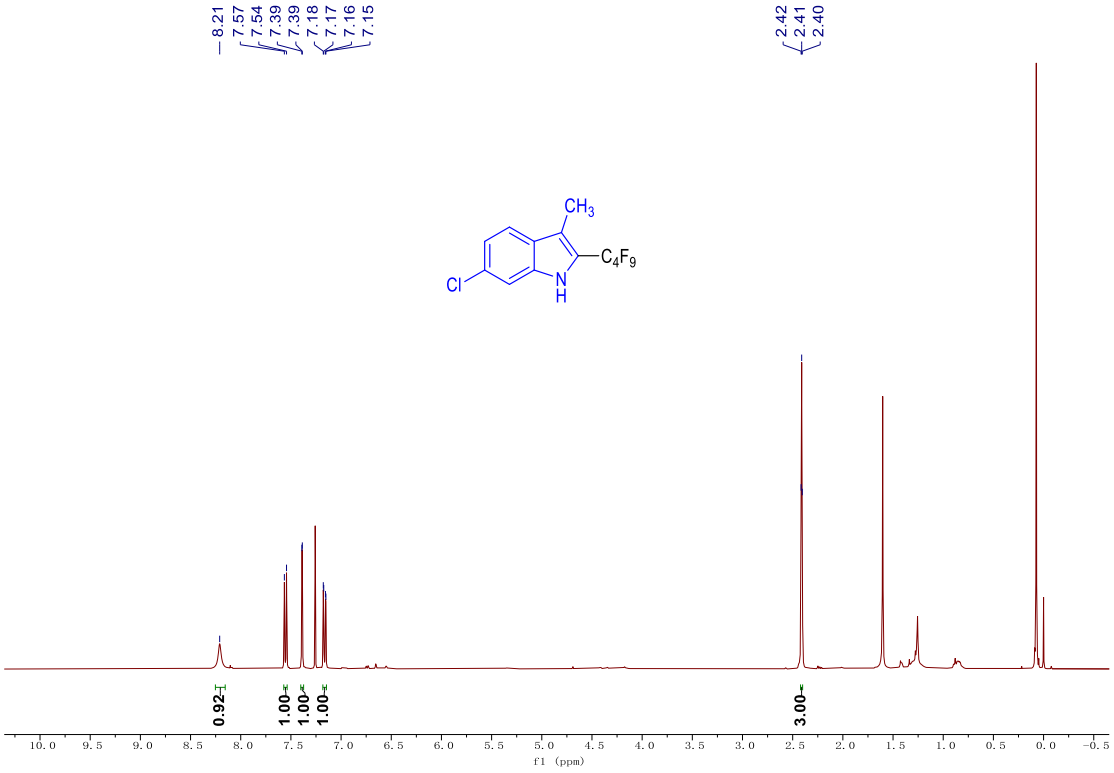
-81.01
-108.59
-108.60
-108.63
-108.66
-108.66
-123.08
-123.09
-123.11
-123.12
-123.13
-123.14
-123.16
-123.17
-126.00
-126.02
-126.03
-126.06
-126.07
3.00
2.08
2.06
2.05
f1 (ppm)

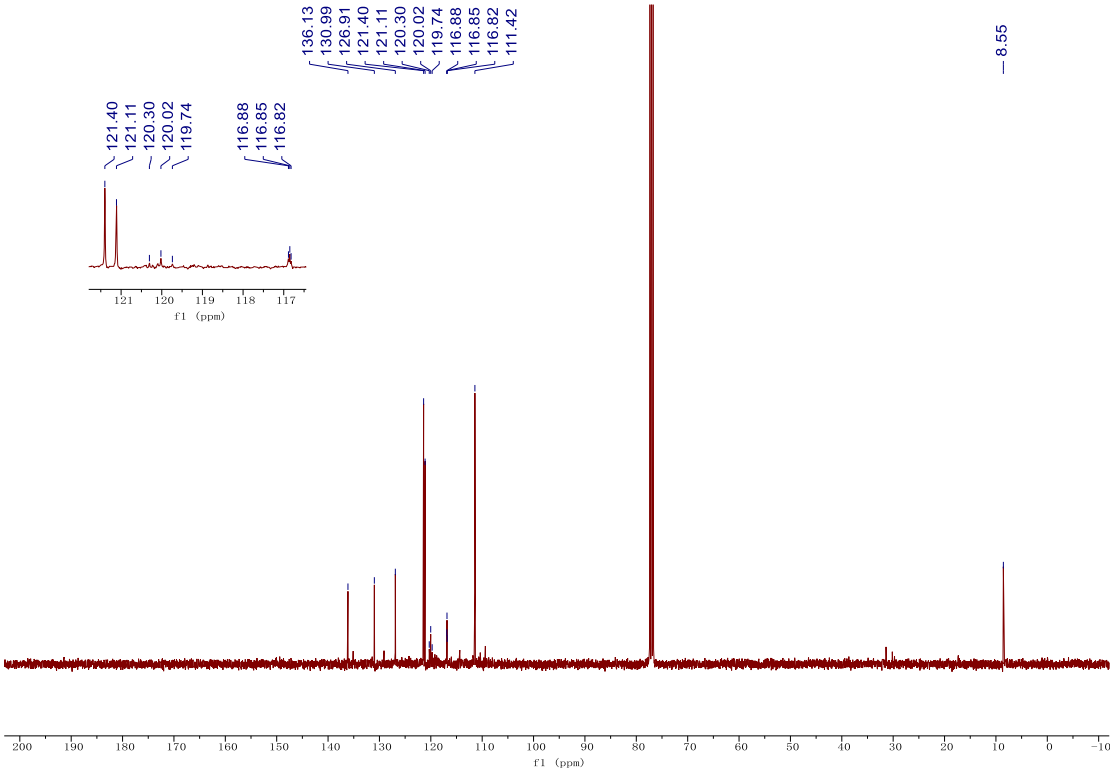
6-fluoro-3-methyl-2-((perfluorobutyl)-1*H*-indole (3m)

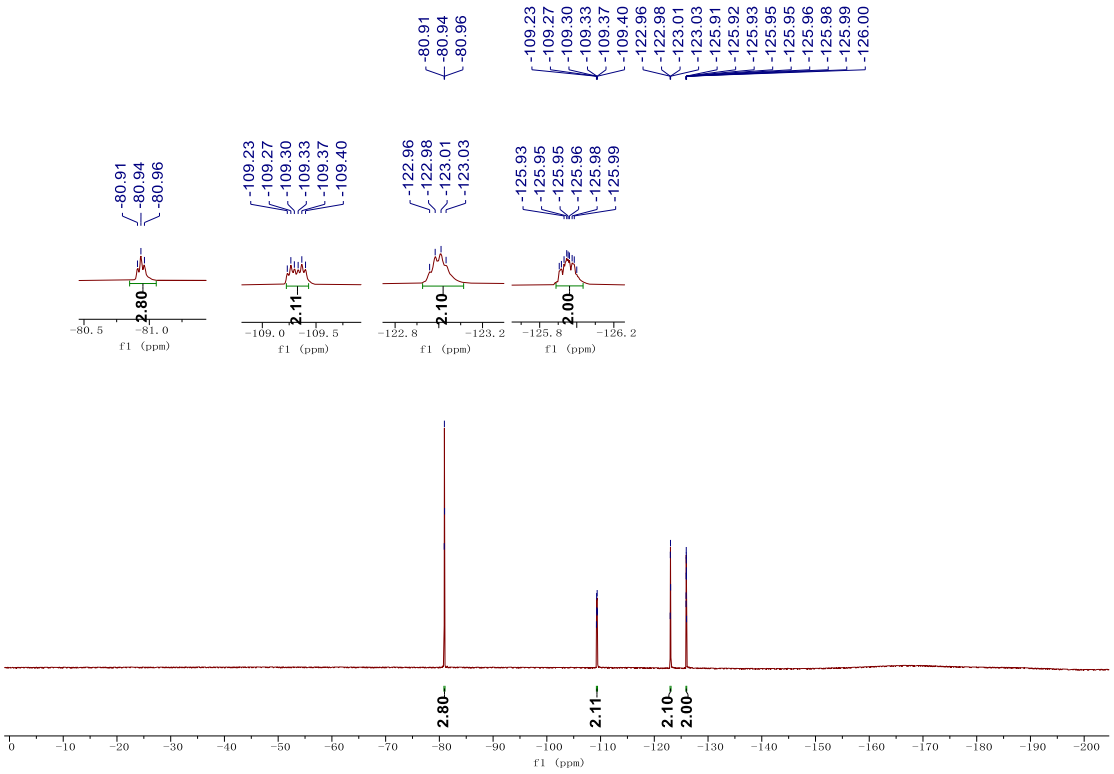



-80.97
-80.99
-81.02
-108.98
-109.01
-109.05
-116.74
-123.06
-123.09
-123.12
-123.14
-125.99
-126.02
-126.04
-126.07
3.00
2.08
2.03
2.08
f1 (ppm)
0.77

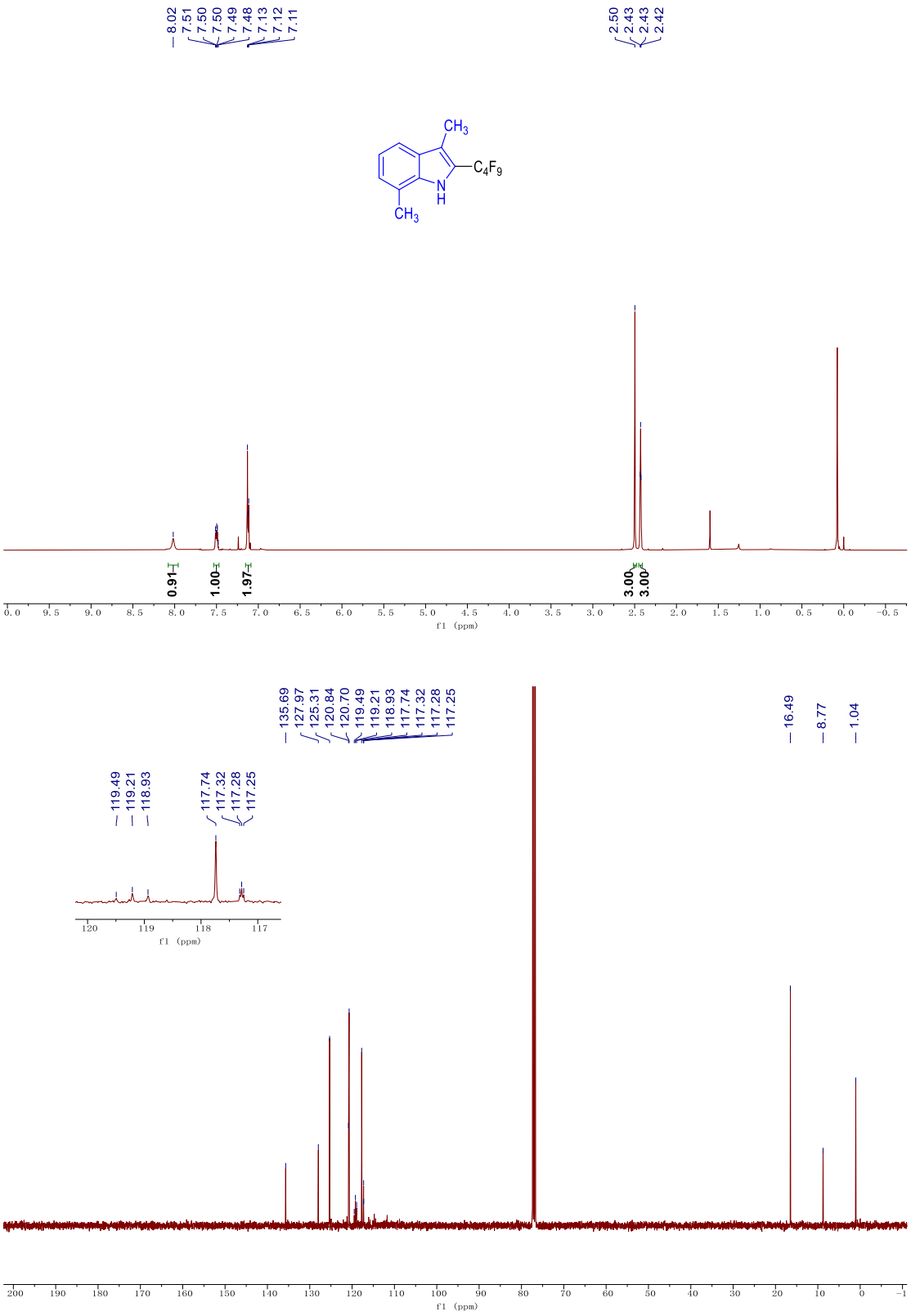
6-chloro-3-methyl-2-(perfluorobutyl)-1*H*-indole (3n)

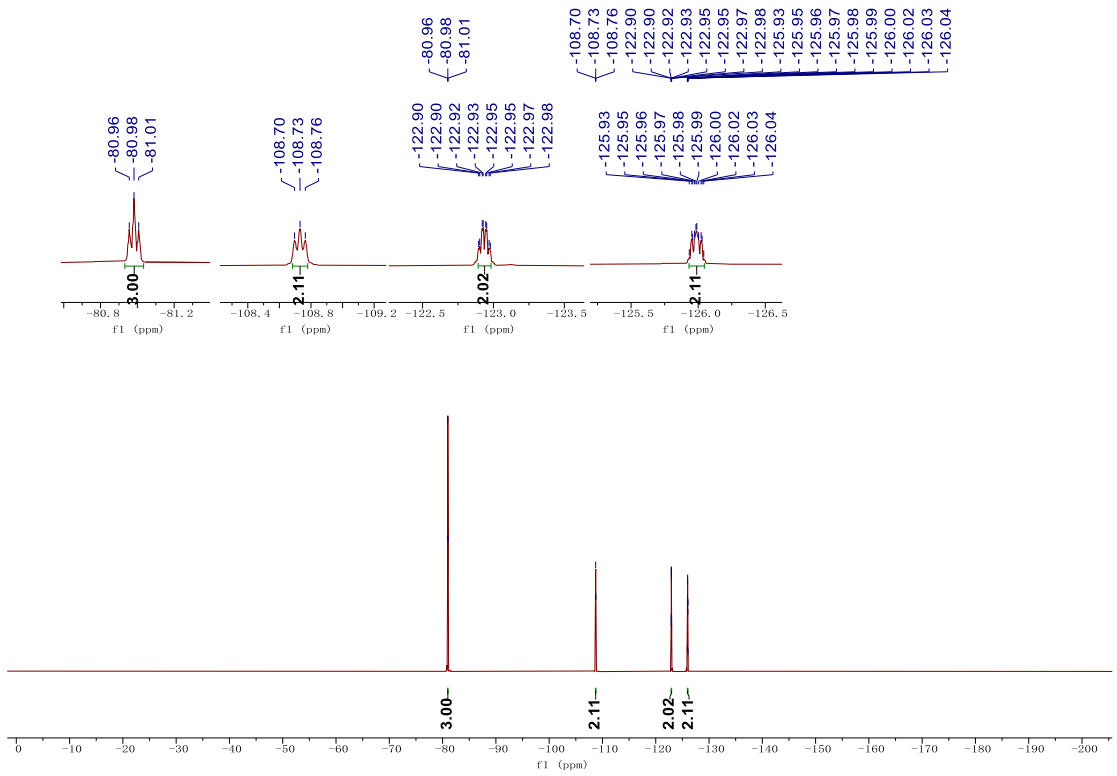




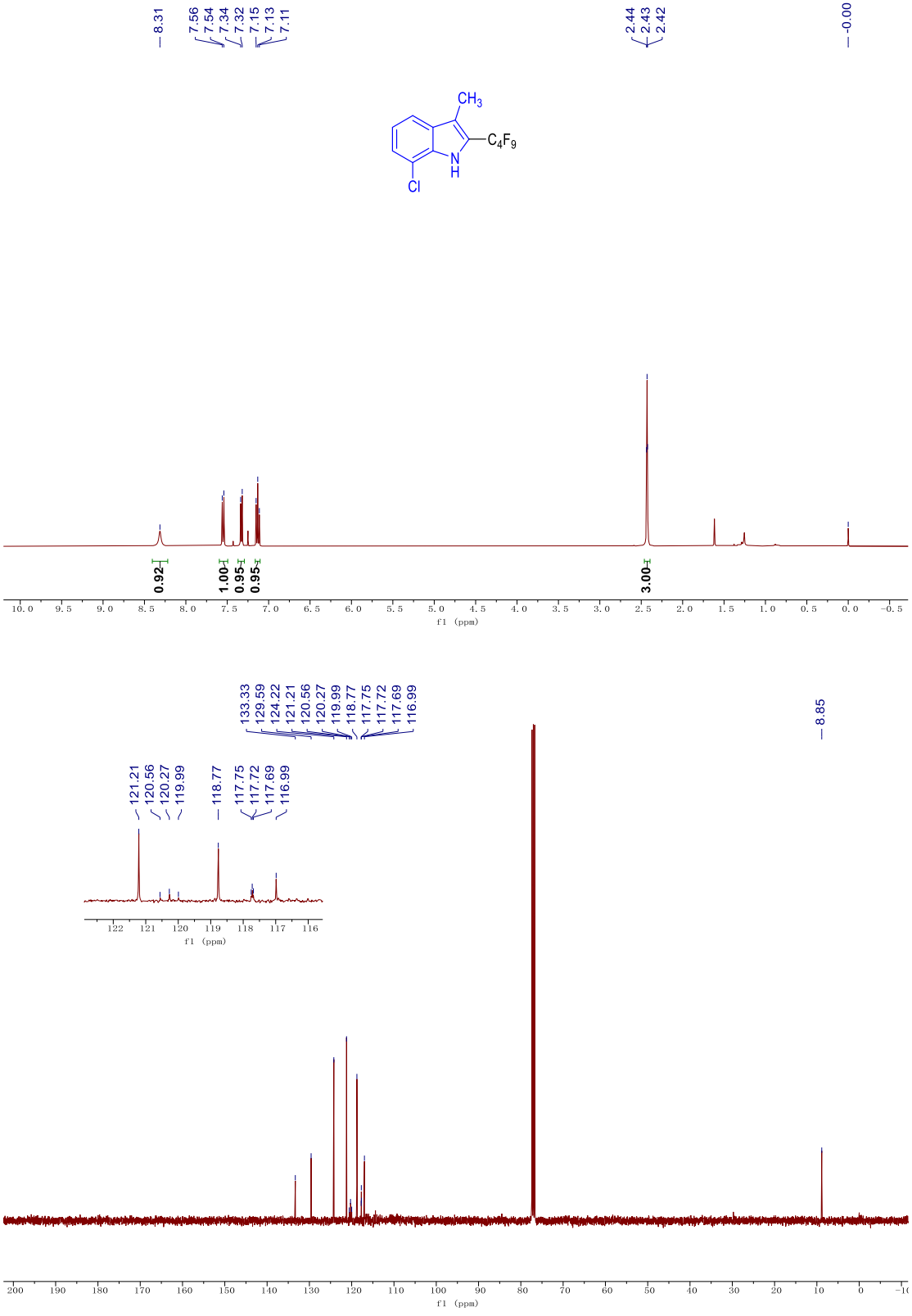

-80.91
-80.94
-80.96
-109.23
-109.27
-109.30
-109.33
-109.37
-109.40
-122.96
-122.98
-123.01
-123.03
-125.91
-125.92
-125.93
-125.95
-125.95
-125.96
-125.98
-125.99
-126.00
2.80
2.11
2.10
2.00
f1 (ppm)

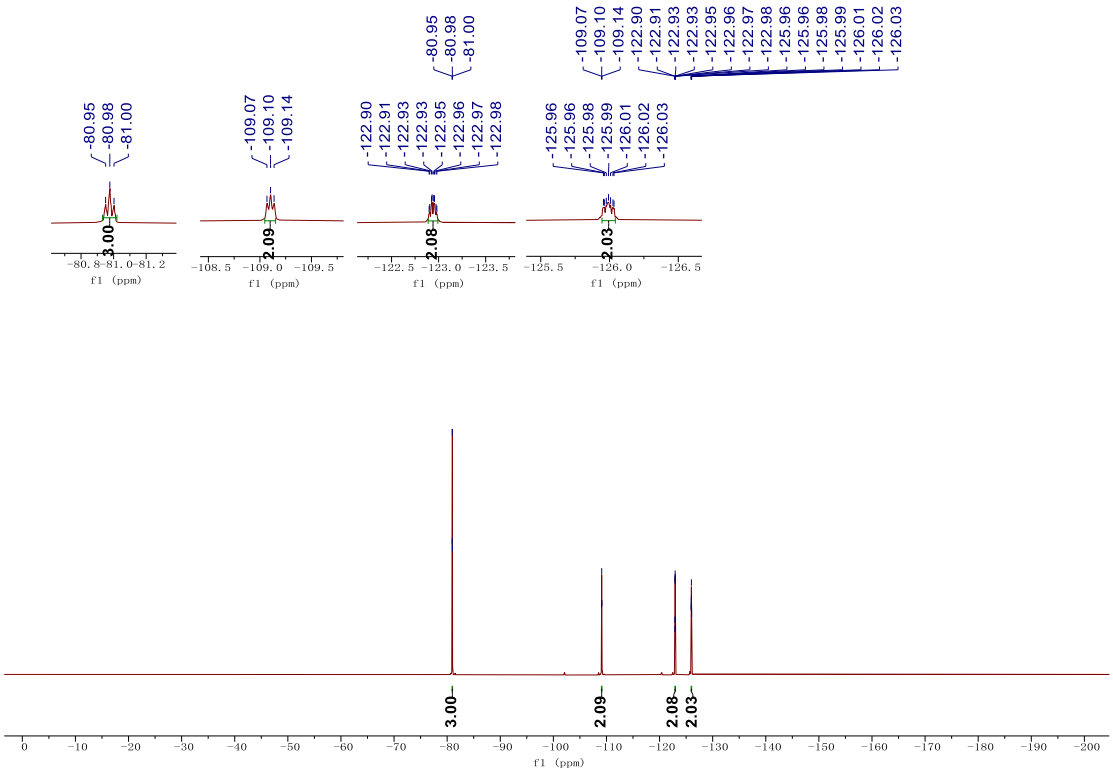
3,7-dimethyl-2-(perfluorobutyl)-1*H*-indole (3o)



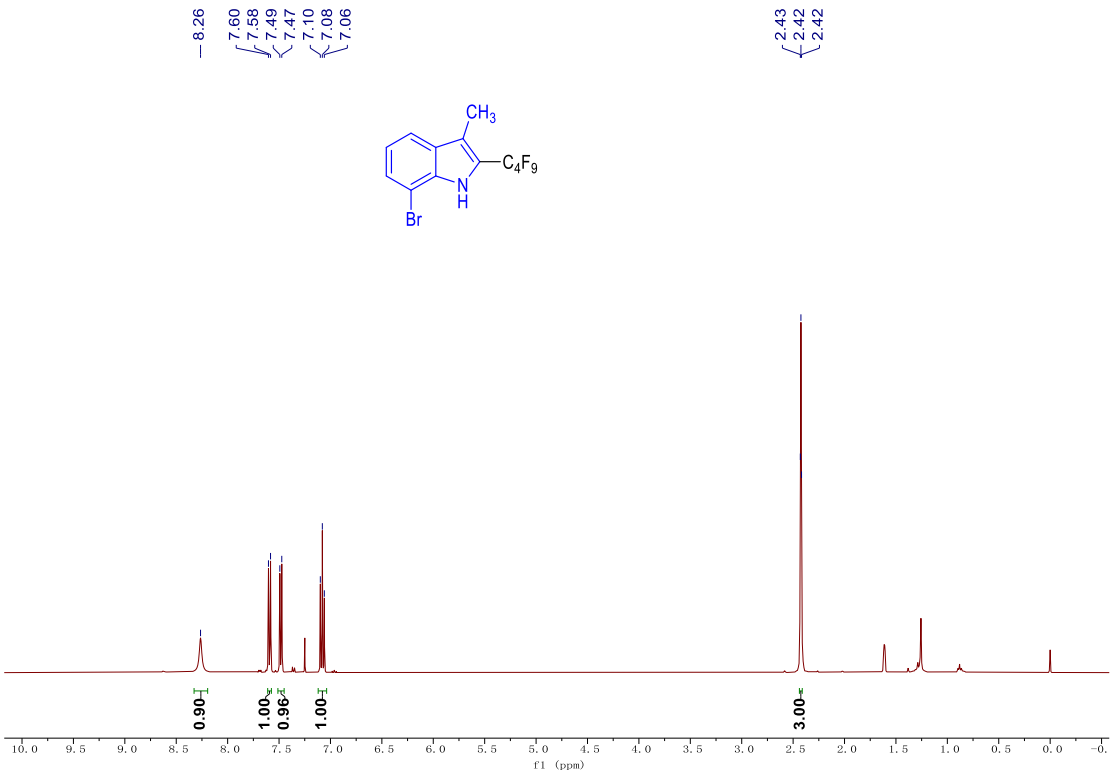

-80.96
-80.98
-81.01
-108.70
-108.73
-108.76
-122.90
-122.90
-122.92
-122.93
-122.95
-122.95
-122.97
-122.98
-125.93
-125.95
-125.96
-125.97
-125.98
-125.99
-126.00
-126.02
-126.03
-126.04
3.00
2.11
2.02
2.11
f1 (ppm)

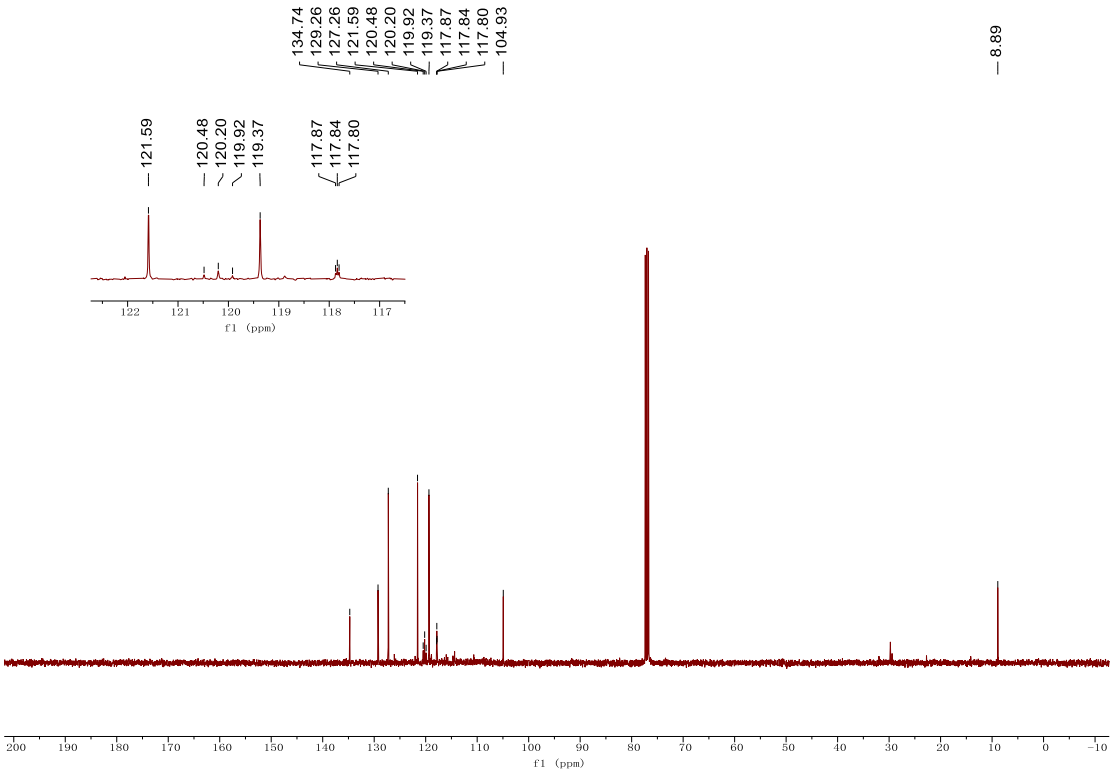
7-chloro-3-methyl-2-(perfluorobutyl)-1*H*-indole (3p)

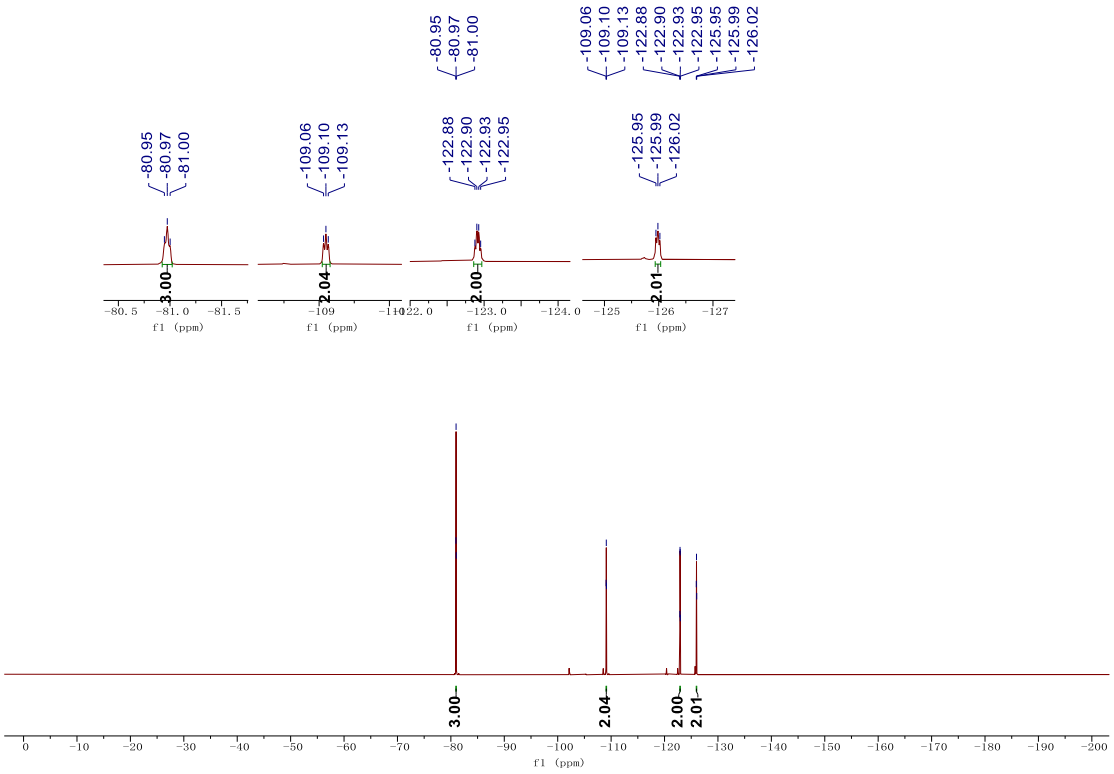



-80.95
-80.98
-81.00
-109.07
-109.10
-109.14
-122.90
-122.91
-122.93
-122.93
-122.95
-122.96
-122.97
-122.98
-125.96
-125.96
-125.98
-125.99
-126.01
-126.02
-126.03
3.00
2.09
2.08
2.03
f1 (ppm)

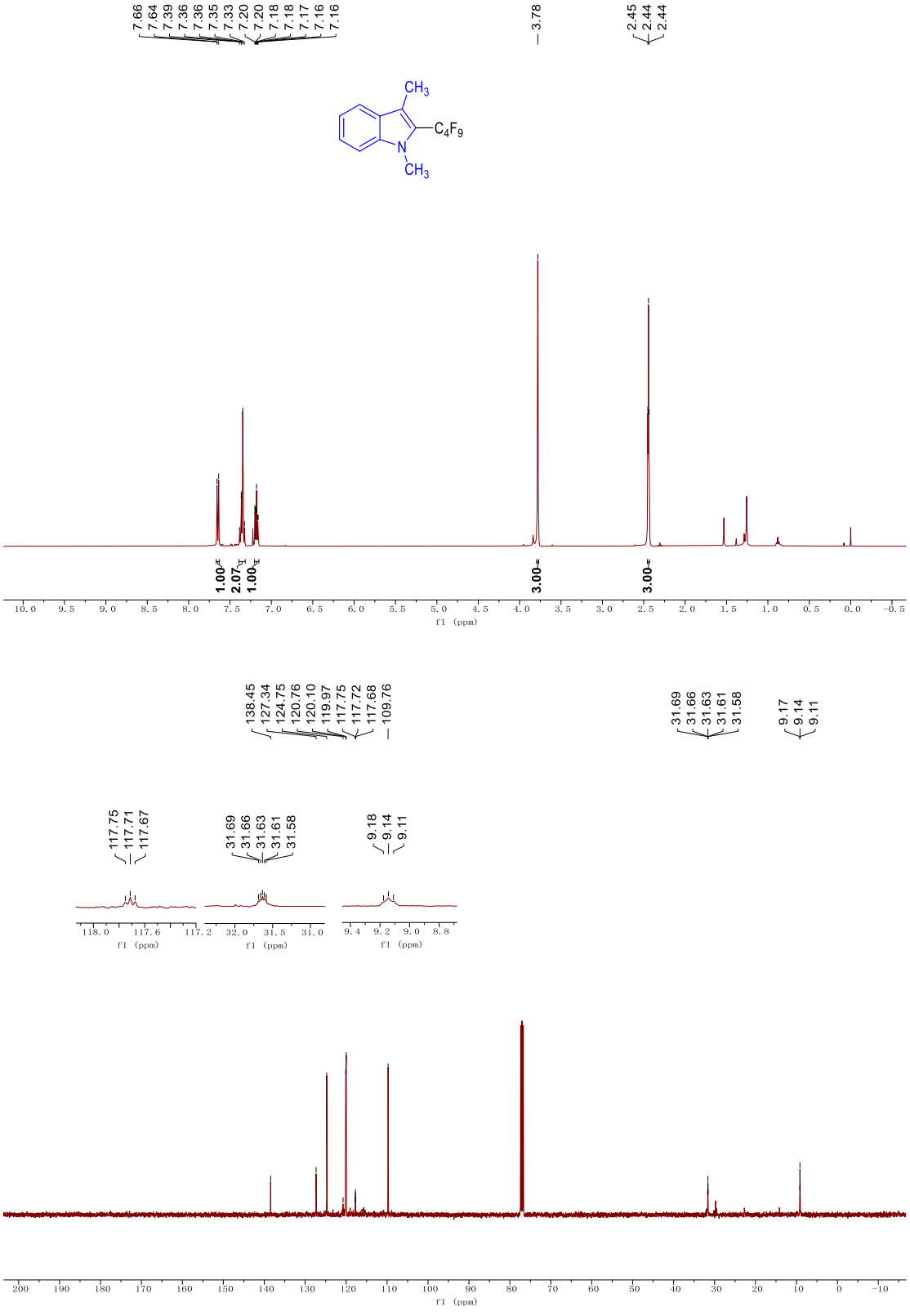
7-bromo-3-methyl-2-(perfluorobutyl)-1*H*-indole (3q)

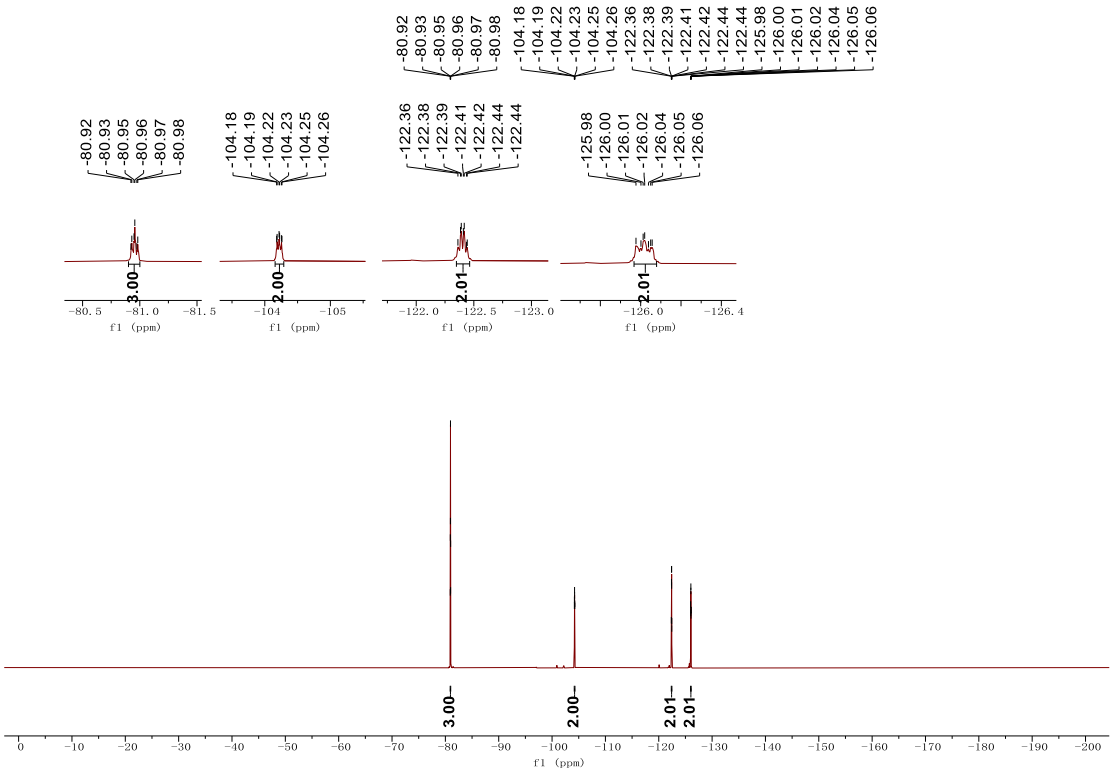




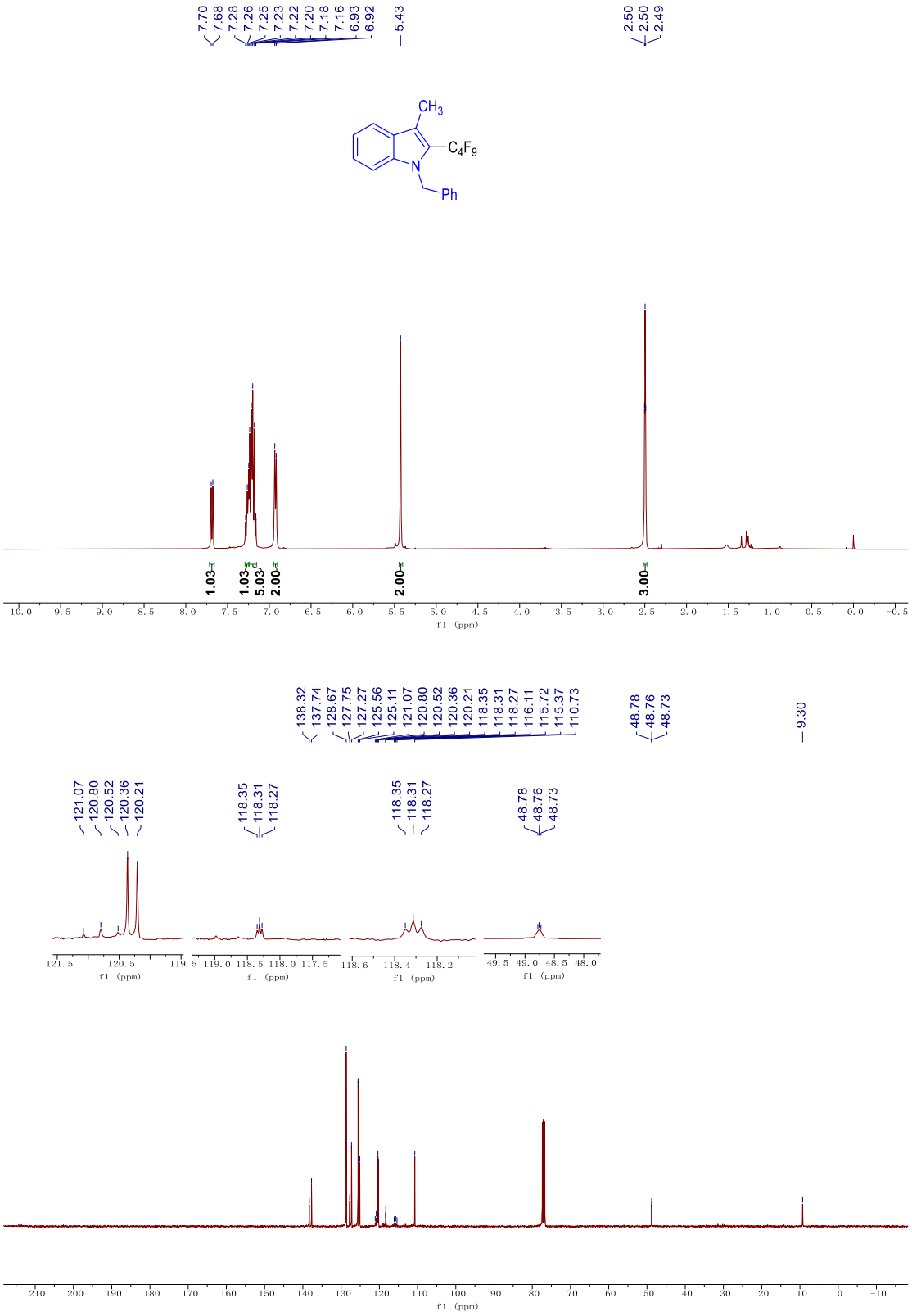

-80.95
-80.97
-81.00
-109.06
-109.10
-109.13
-122.88
-122.90
-122.93
-122.95
-125.95
-125.99
-126.02
3.00
2.04
2.00
2.01
f1 (ppm)

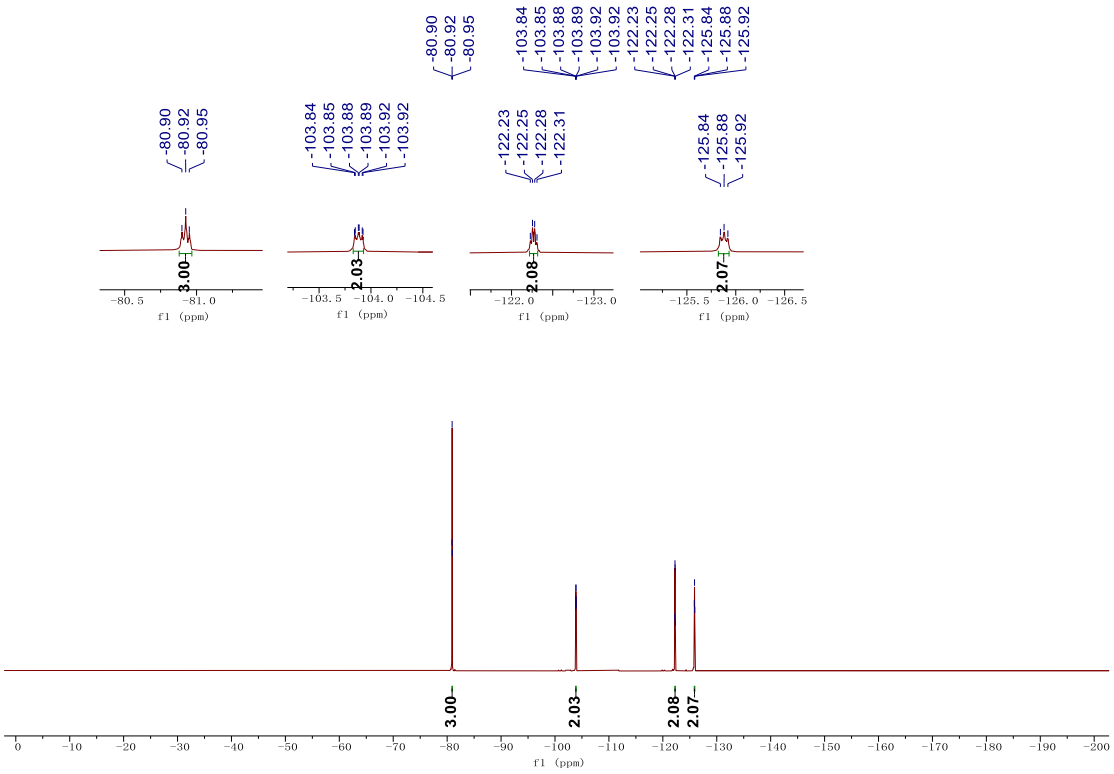
1,3-Dimethyl-2-(perfluorohexyl)-1*H*-indole (3r)



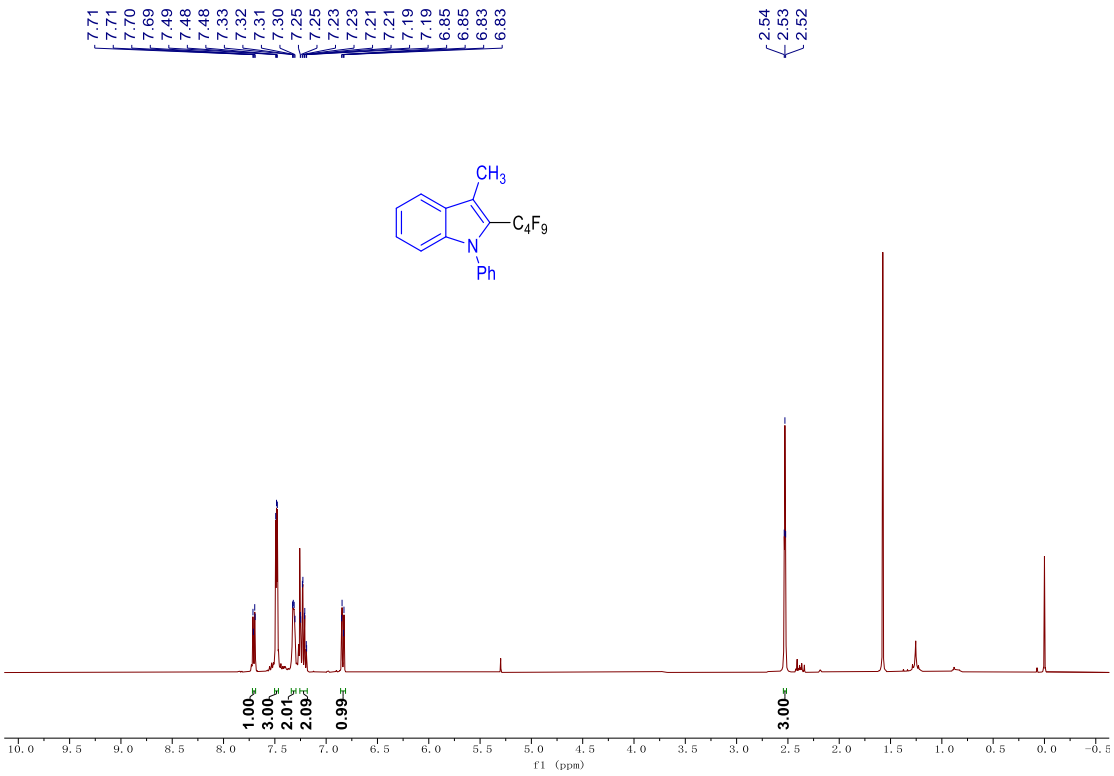

-80.92
-80.93
-80.95
-80.96
-80.97
-80.98
-104.18
-104.19
-104.22
-104.23
-104.25
-104.26
-122.36
-122.38
-122.39
-122.41
-122.42
-122.44
-122.44
-125.98
-126.00
-126.01
-126.02
-126.04
-126.05
-126.06
3.00
2.00
2.01
2.01
f1 (ppm)

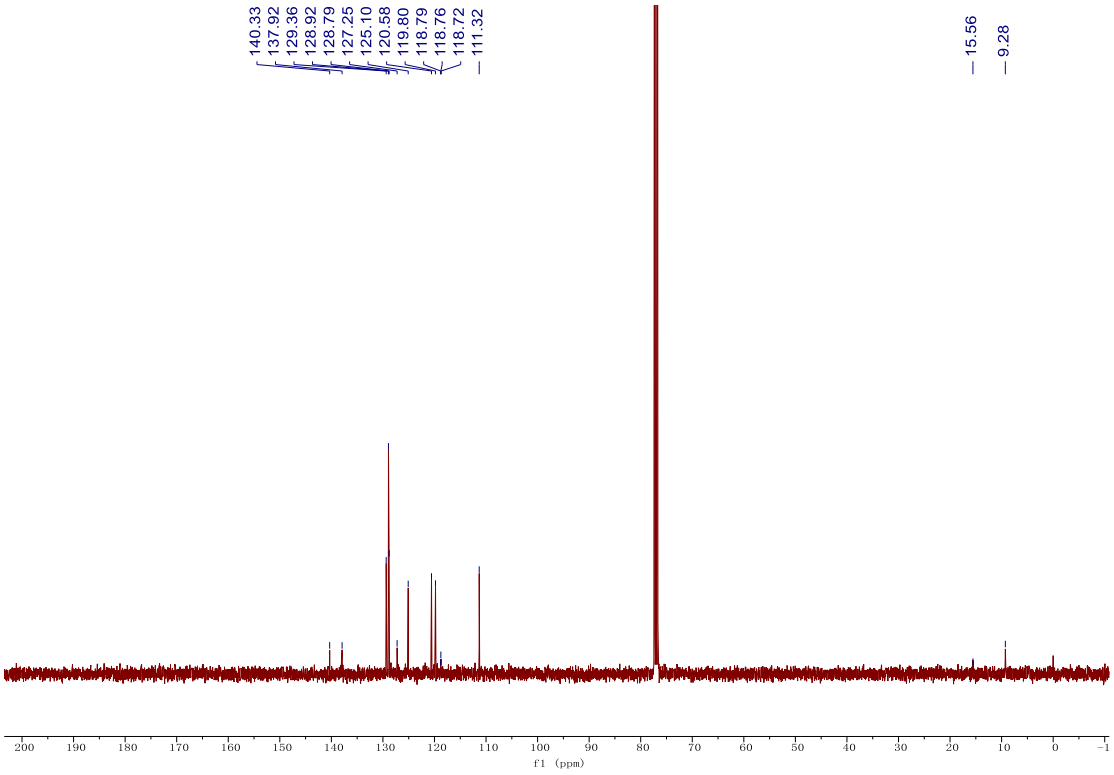
1-Benzyl-3-methyl-2-(perfluorobutyl)-1*H*-indole (3s)

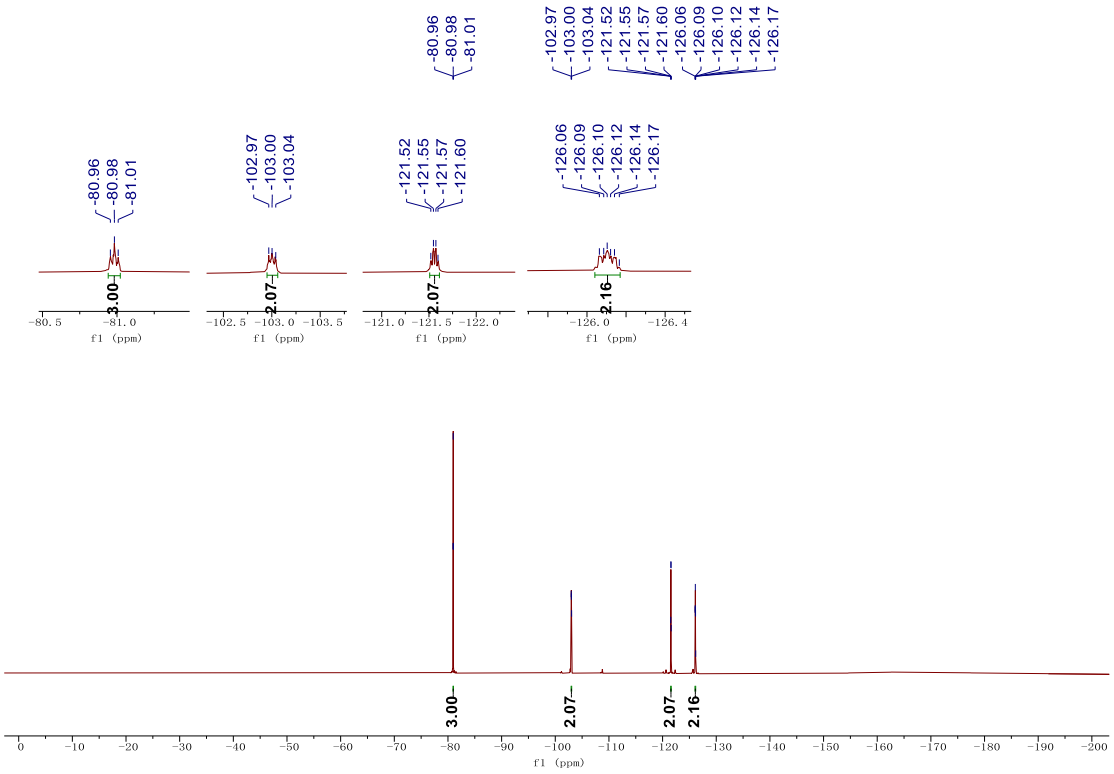



-80.90
-80.92
-80.95
-103.84
-103.85
-103.88
-103.89
-103.92
-103.92
-122.23
-122.25
-122.28
-122.31
-125.84
-125.88
-125.92
3.00
2.03
2.08
2.07
f1 (ppm)

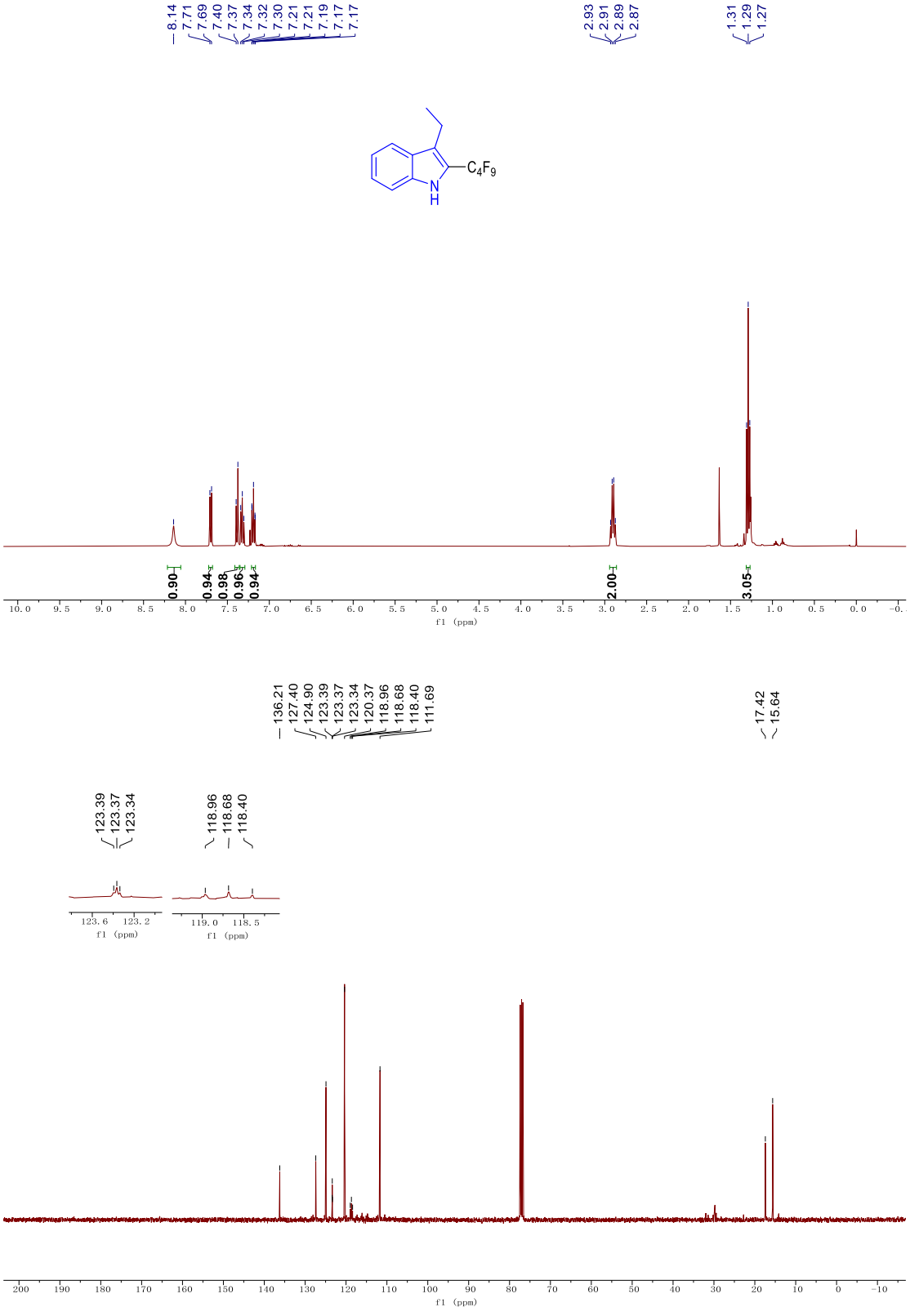
3-methyl-2-(perfluorobutyl)-1-phenyl-1*H*-indole (3t)

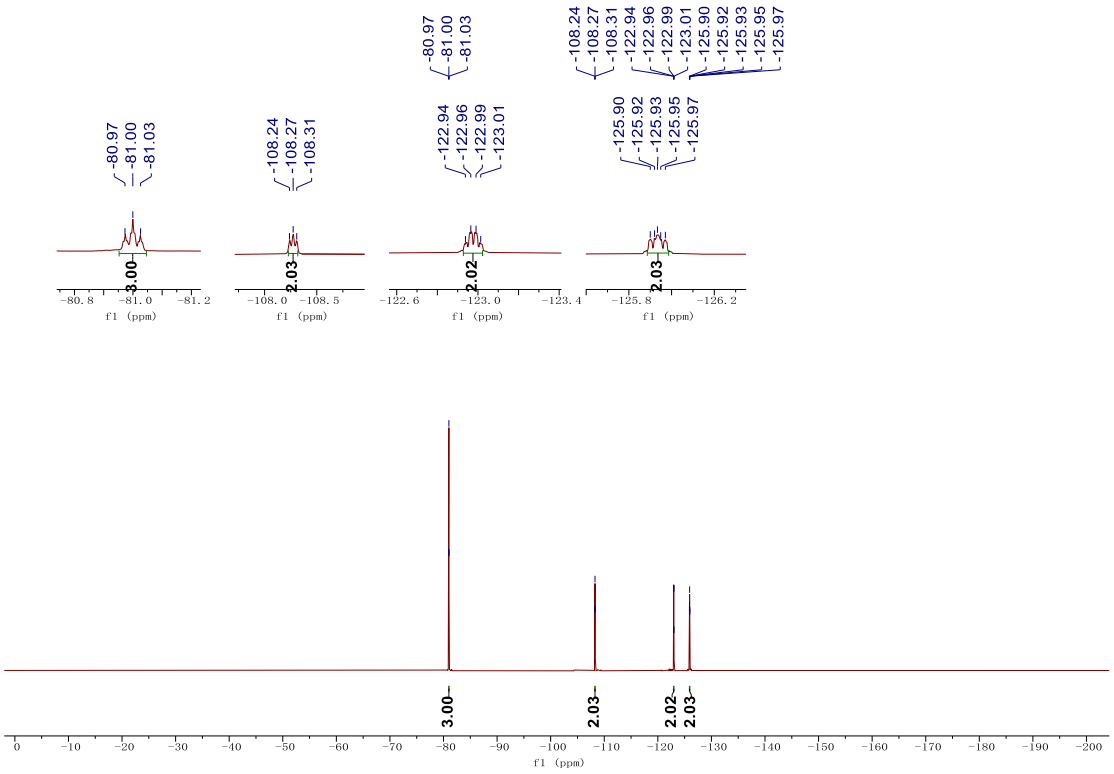




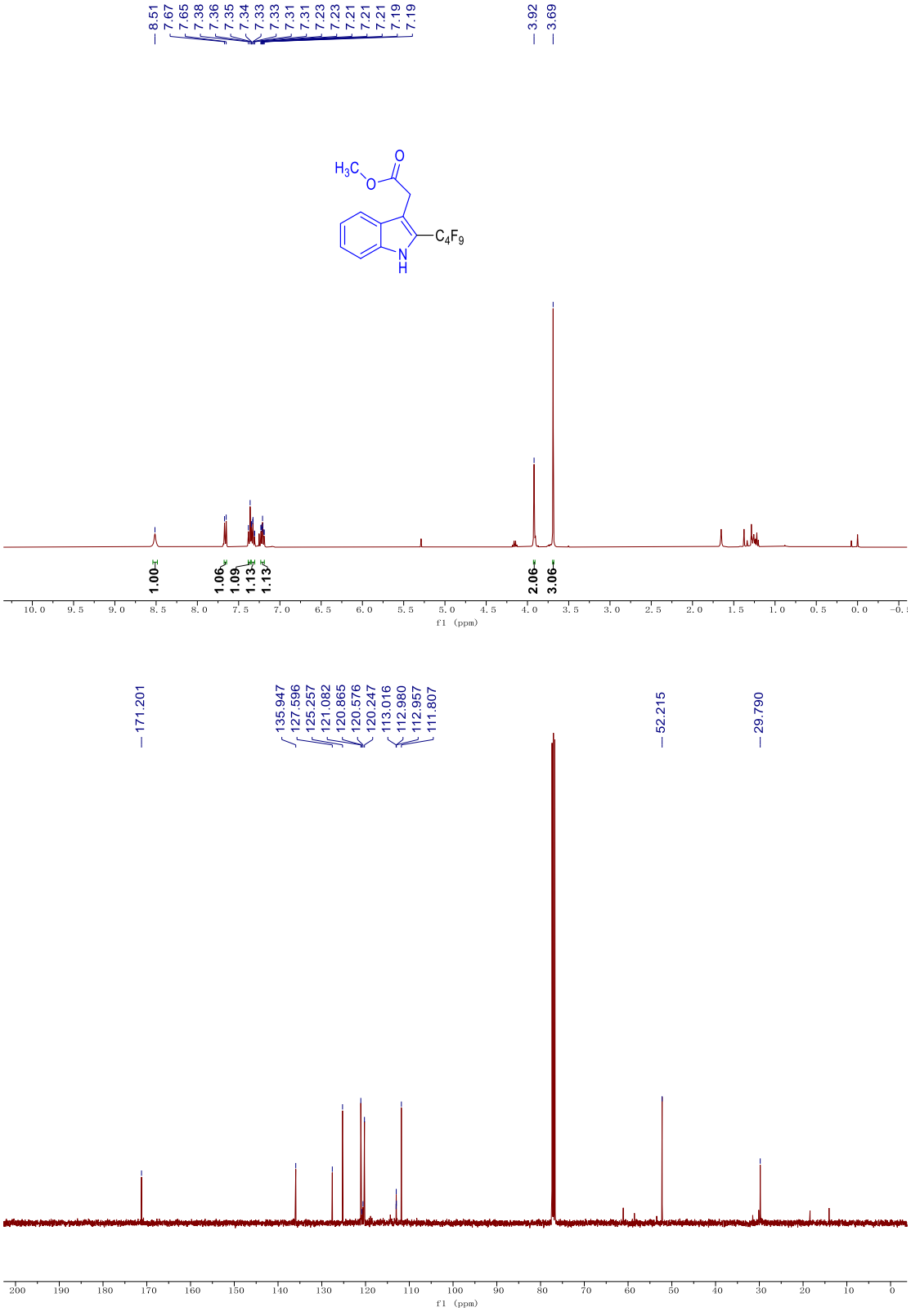

-80.96
-80.98
-81.01
-102.97
-103.00
-103.04
-121.52
-121.55
-121.57
-121.60
-126.06
-126.09
-126.10
-126.12
-126.14
-126.17
3.00
2.07
2.07
2.16
f1 (ppm)

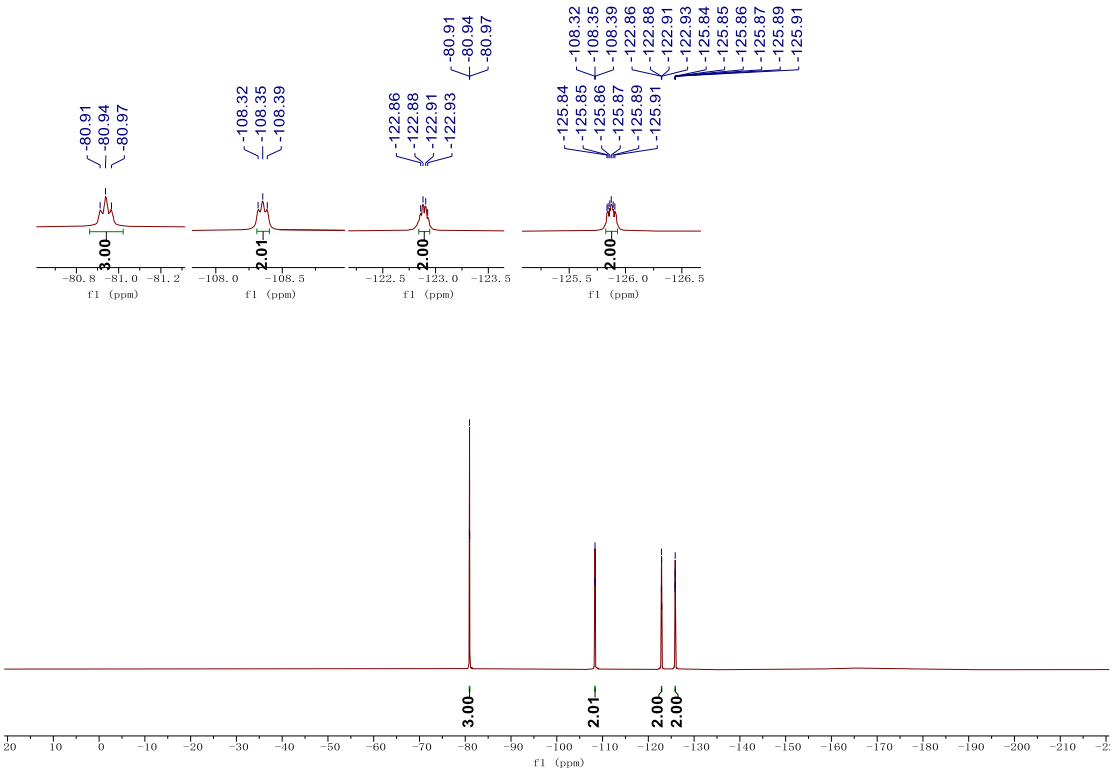
3-ethyl-2-(perfluorobutyl)-1*H*-indole (3u)



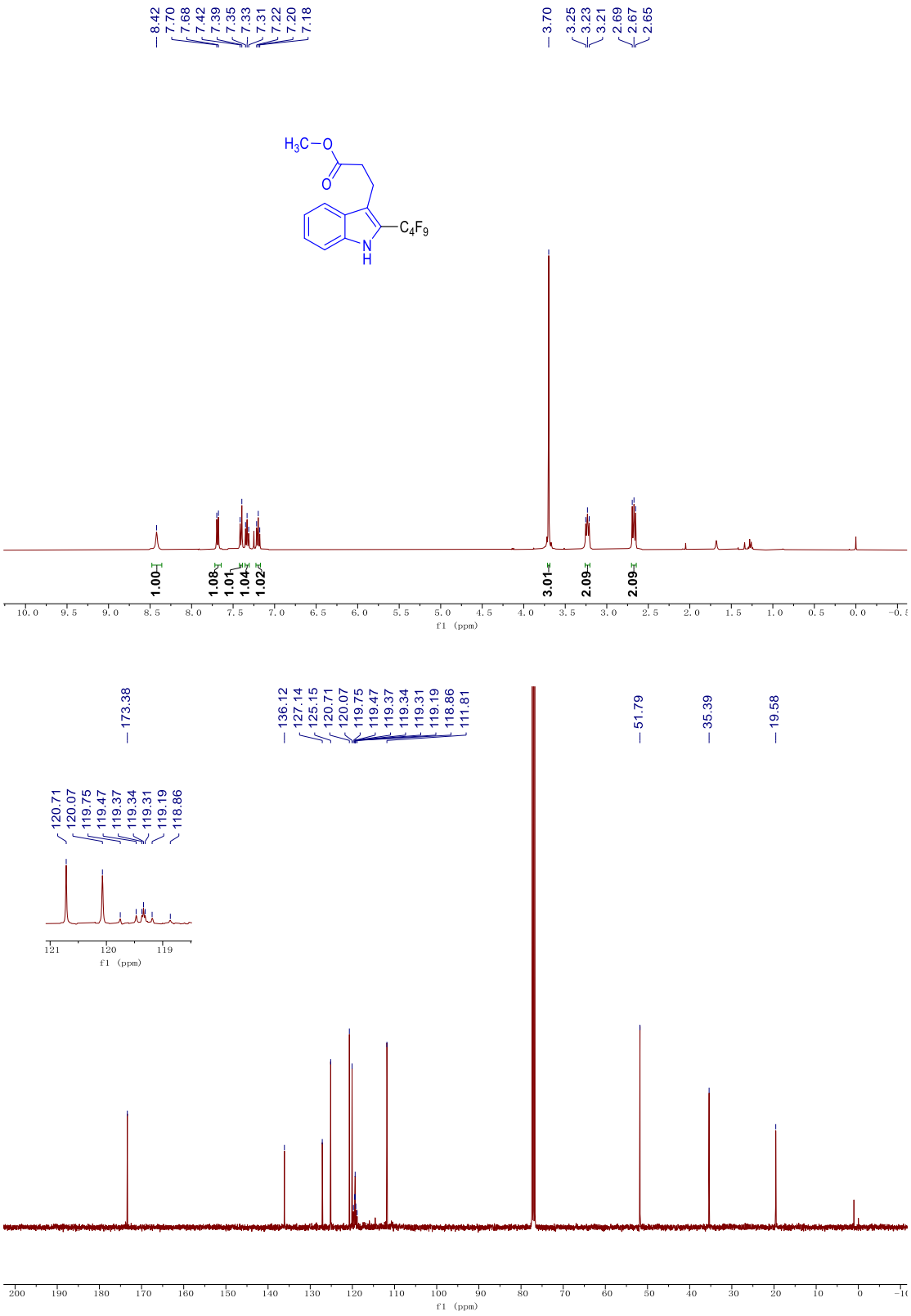

-80.97
-81.00
-81.03
-108.24
-108.27
-108.31
-122.94
-122.96
-122.99
-123.01
-125.90
-125.92
-125.93
-125.95
-125.97
3.00
2.03
2.02
2.03
f1 (ppm)

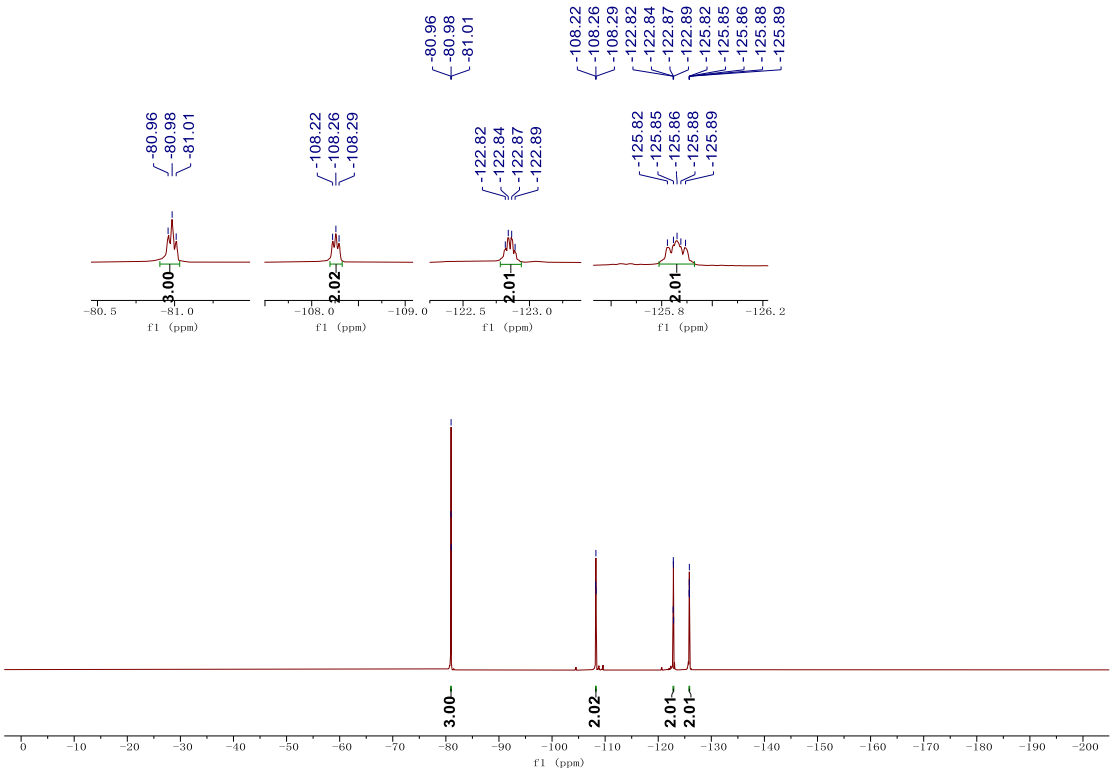
Methyl 2-(2-(perfluorobutyl)-1*H*-indol-3-yl)acetate (3v)



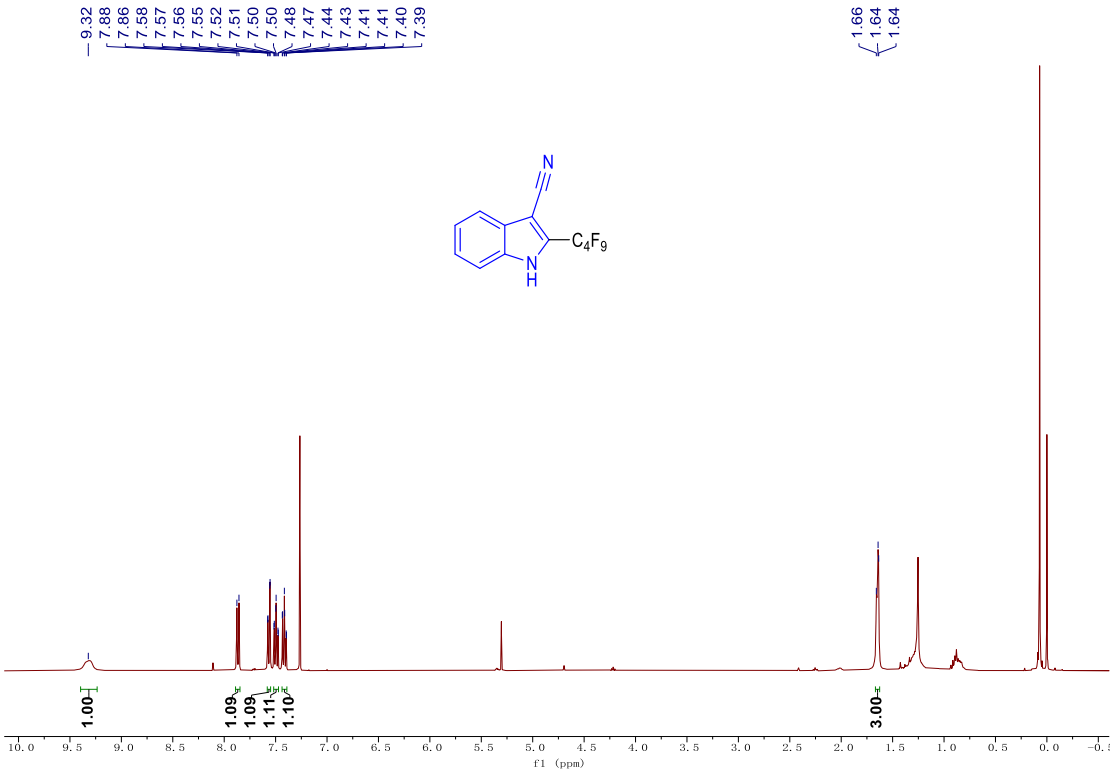

-80.91
-80.94
-80.97
-108.32
-108.35
-108.39
-122.86
-122.88
-122.91
-122.93
-125.84
-125.85
-125.86
-125.87
-125.89
-125.91
3.00
2.01
2.00
2.00
f1 (ppm)

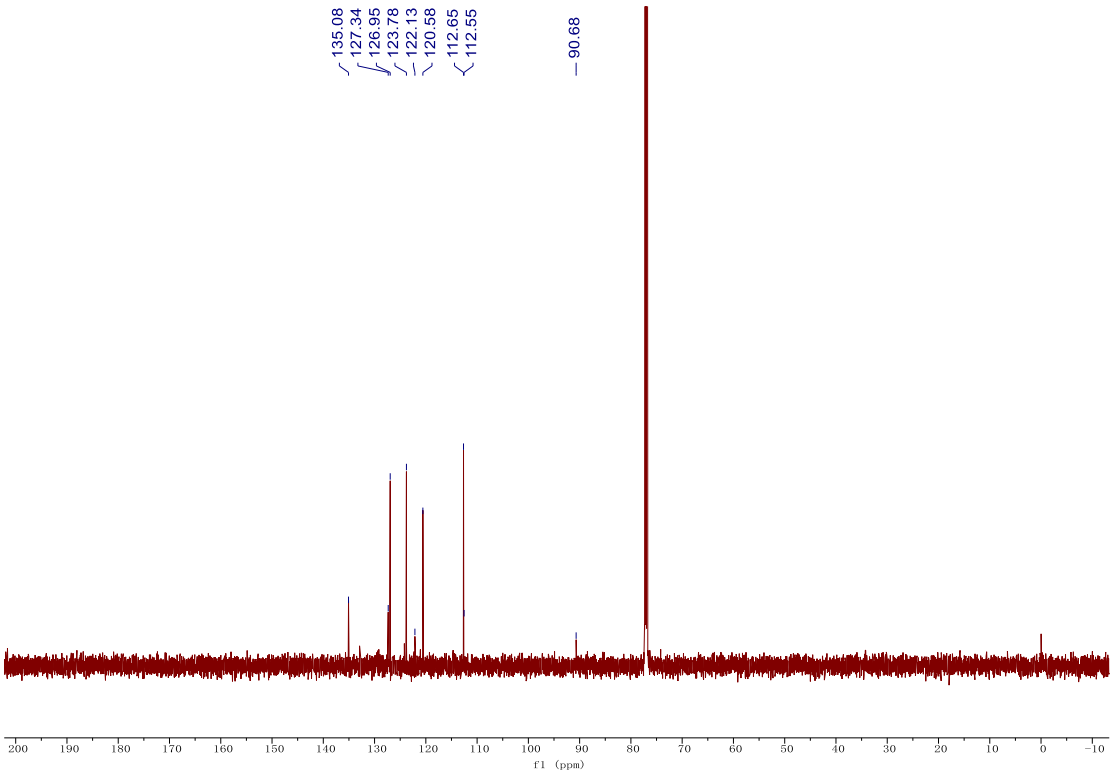
methyl 3-(2-(perfluorobutyl)-1*H*-indol-3-yl)propanoate (3w)

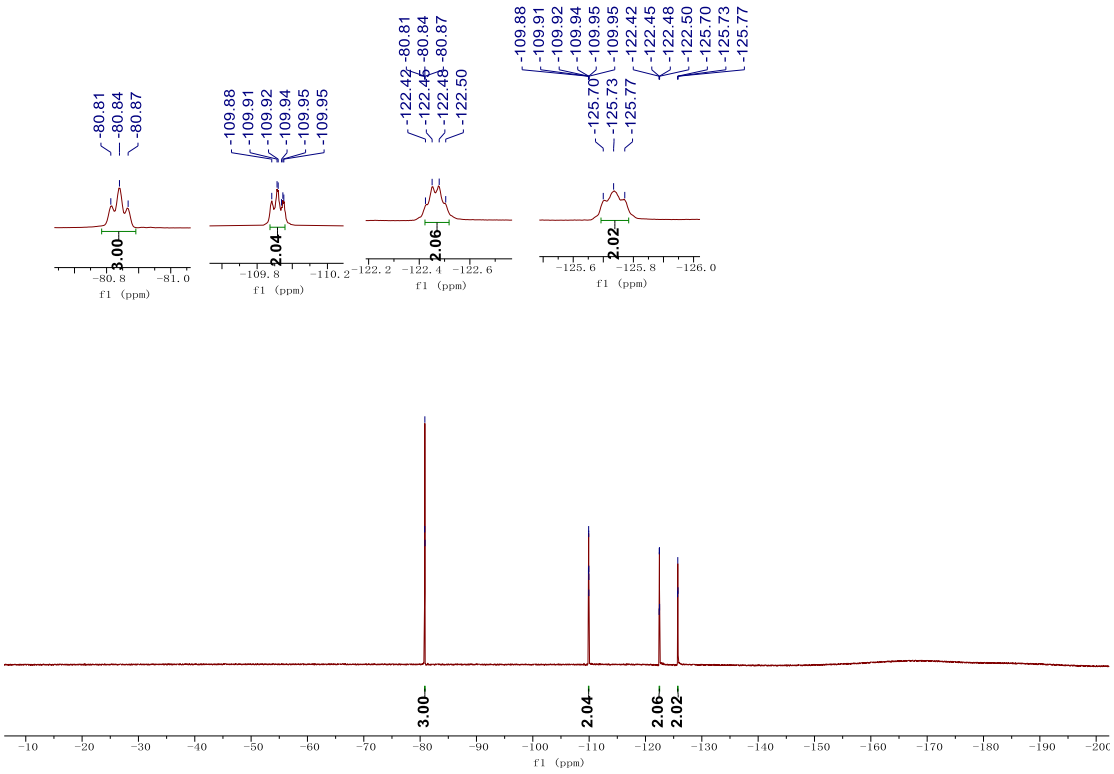



-80.96
-80.98
-81.01
-108.22
-108.26
-108.29
-122.82
-122.84
-122.87
-122.89
-125.82
-125.85
-125.86
-125.88
-125.89
3.00
2.02
2.01
2.01
f1 (ppm)

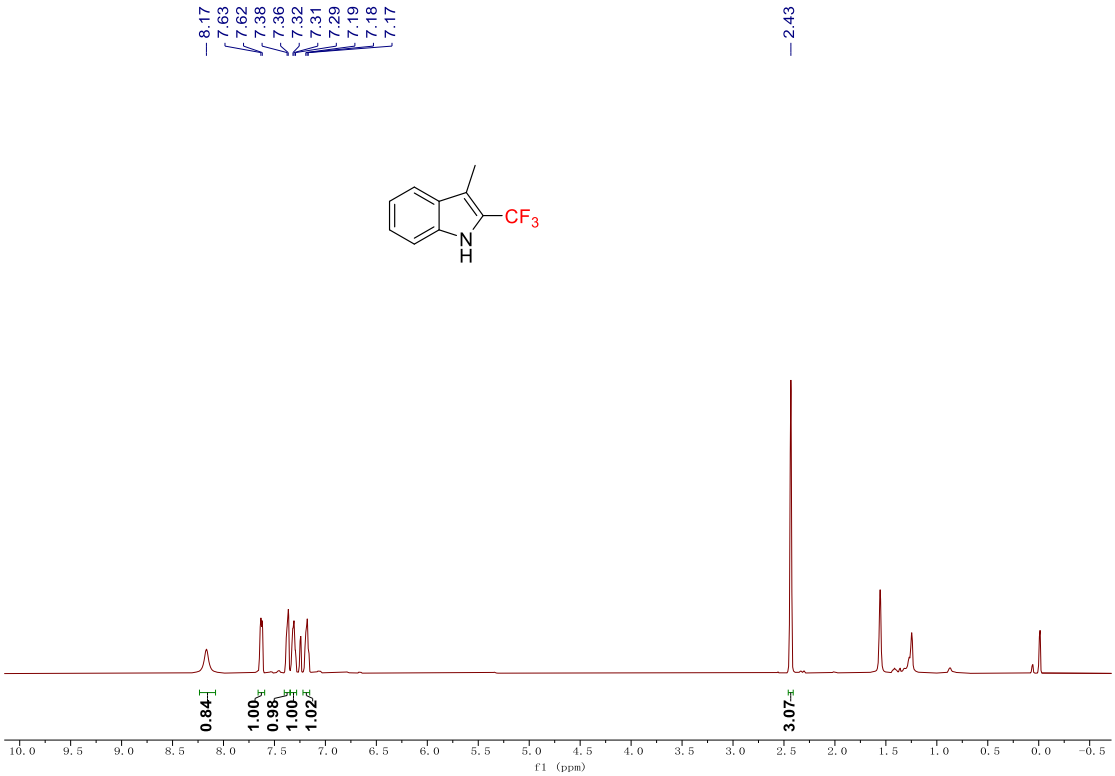
2-(perfluorobutyl)-1*H*-indole-3-carbonitrile (3x)

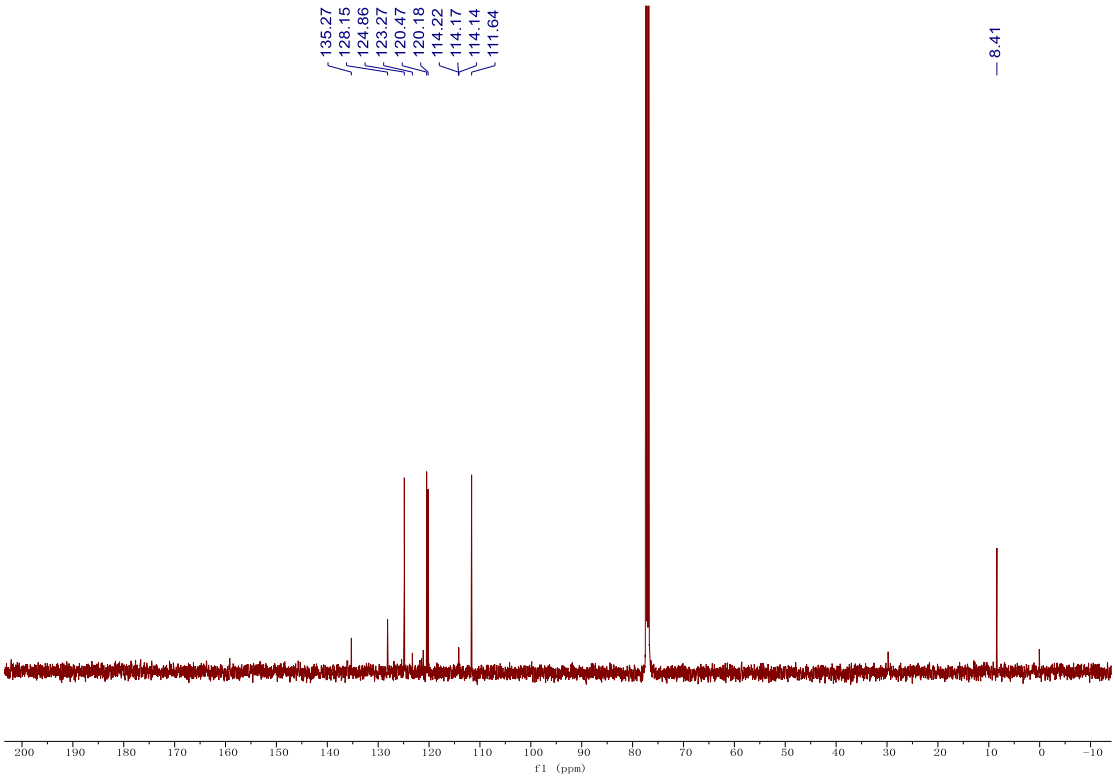


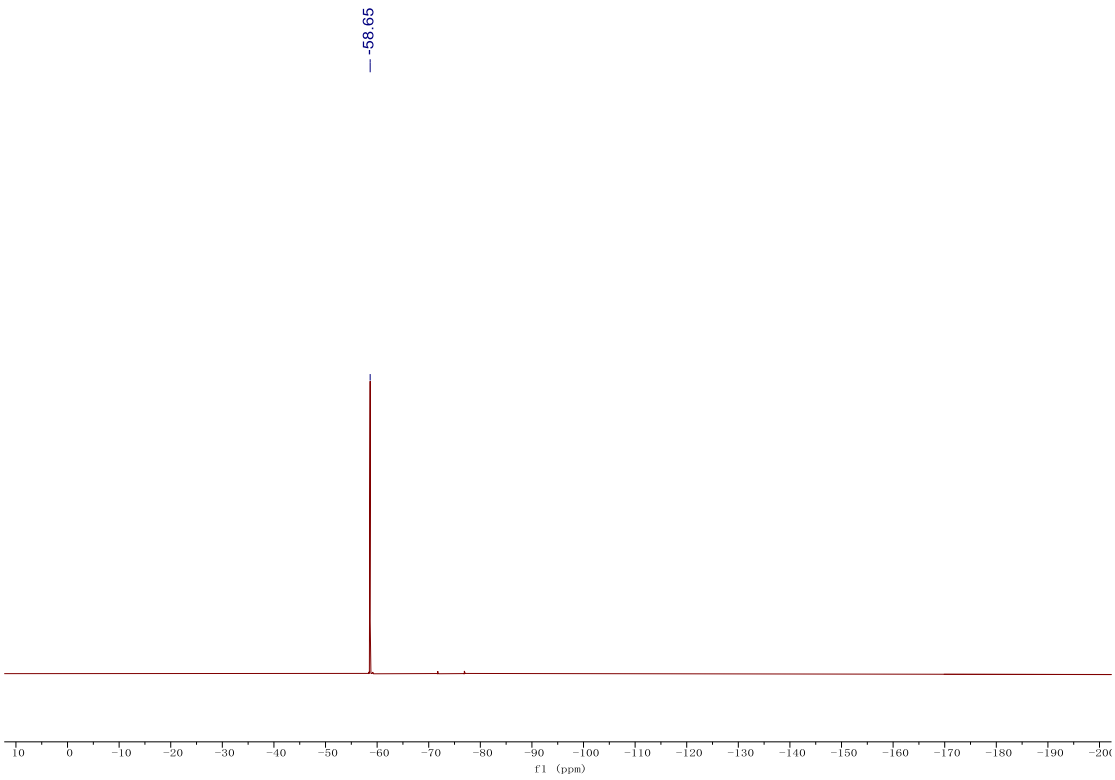



-80.81
-80.84
-80.87
-109.88
-109.91
-109.92
-109.94
-109.95
-109.95
-122.42
-122.45
-122.48
-122.50
-125.70
-125.73
-125.77
3.00
2.04
2.06
2.02
f1 (ppm)

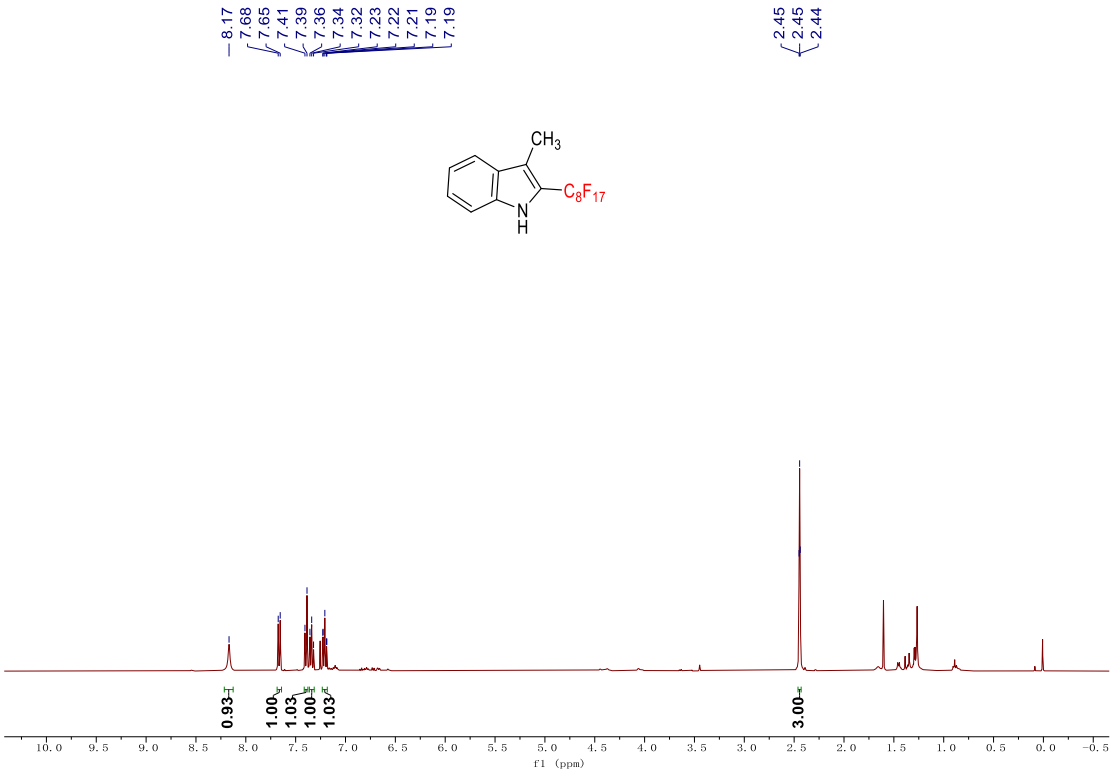
3-methyl-2-(trifluoromethyl)-1*H*-indole (3ba)

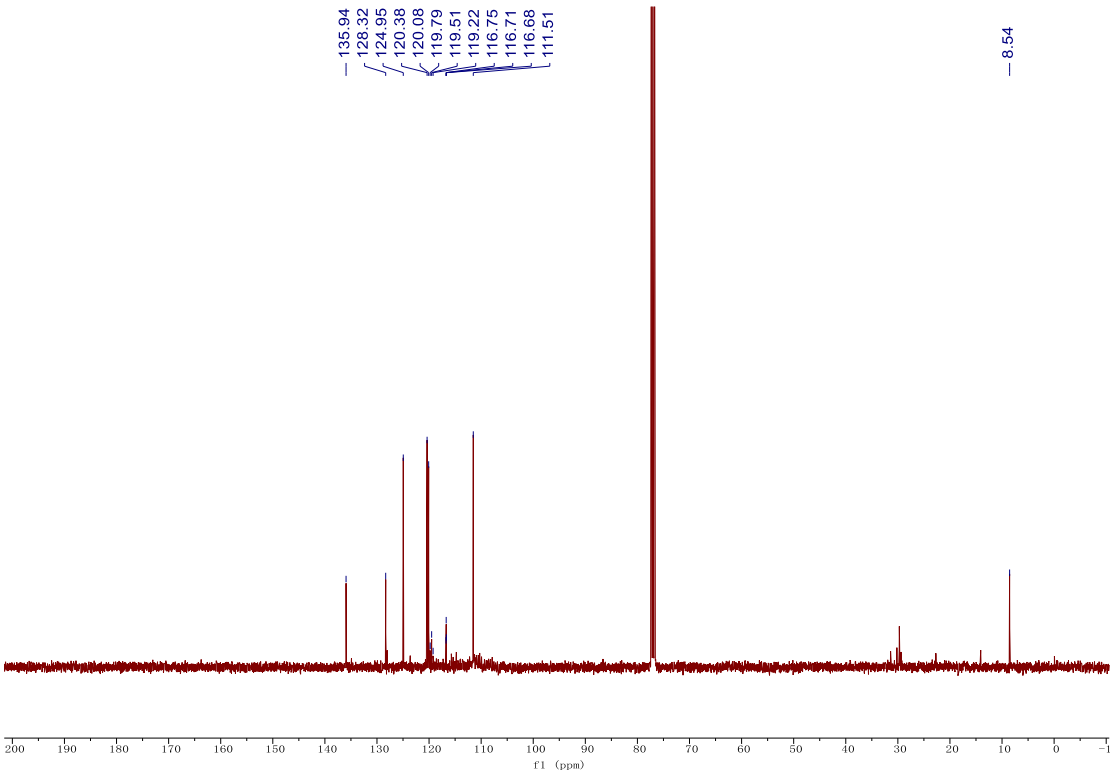


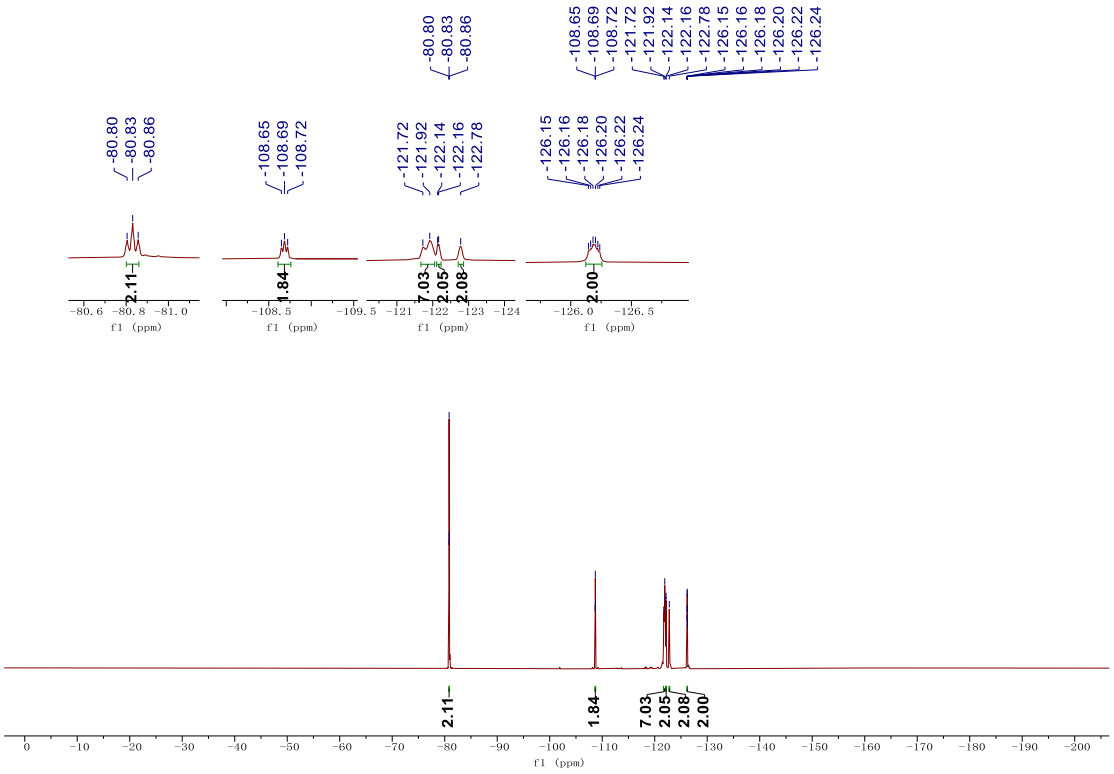



-58.65
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

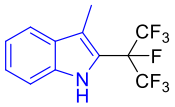
2-(perfluorobutyl)-3-methyl-1*H*-indole (3ca)

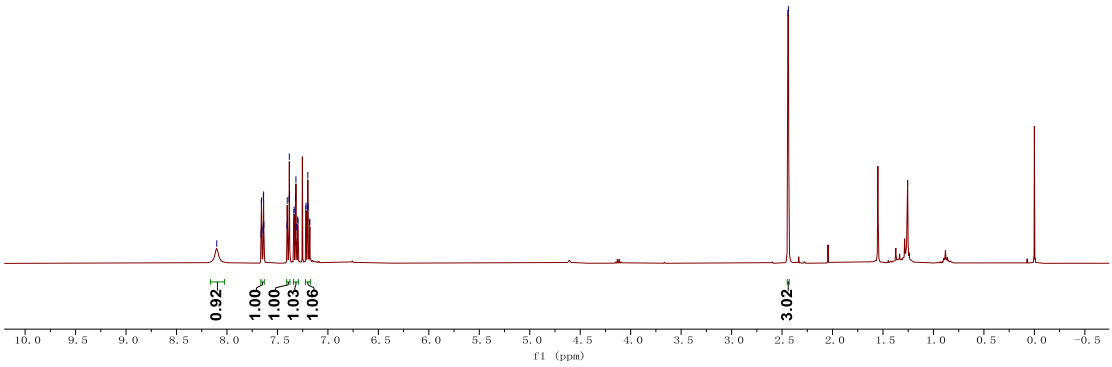


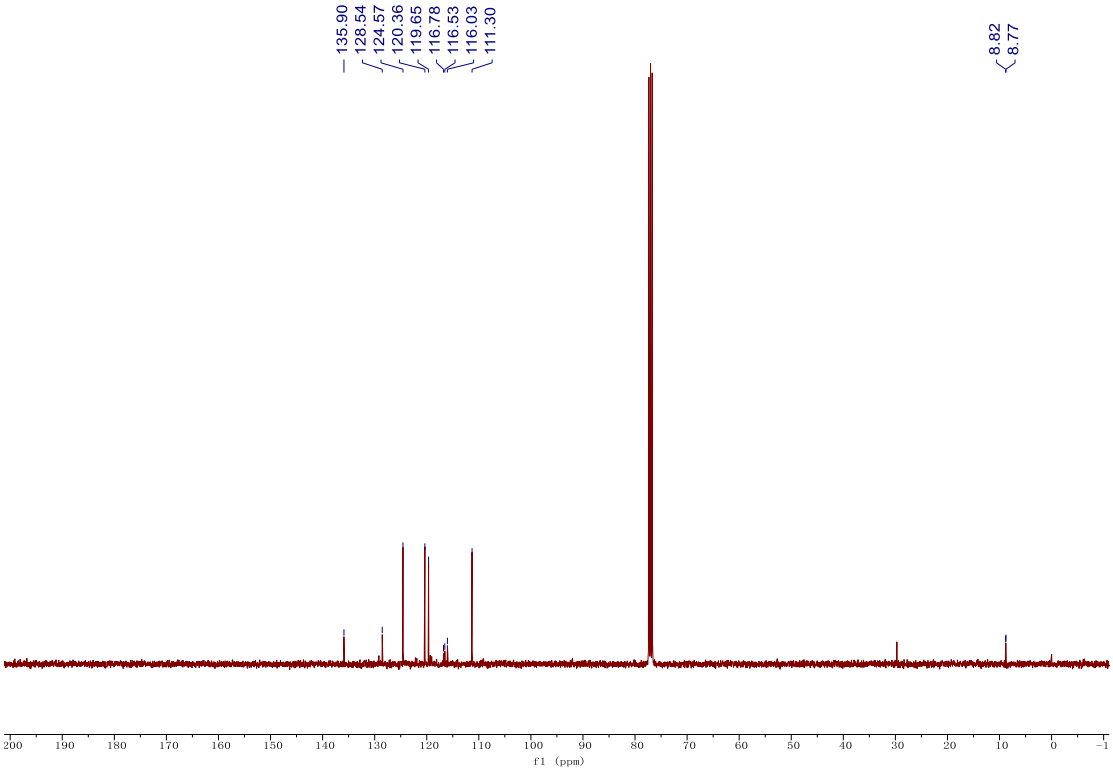


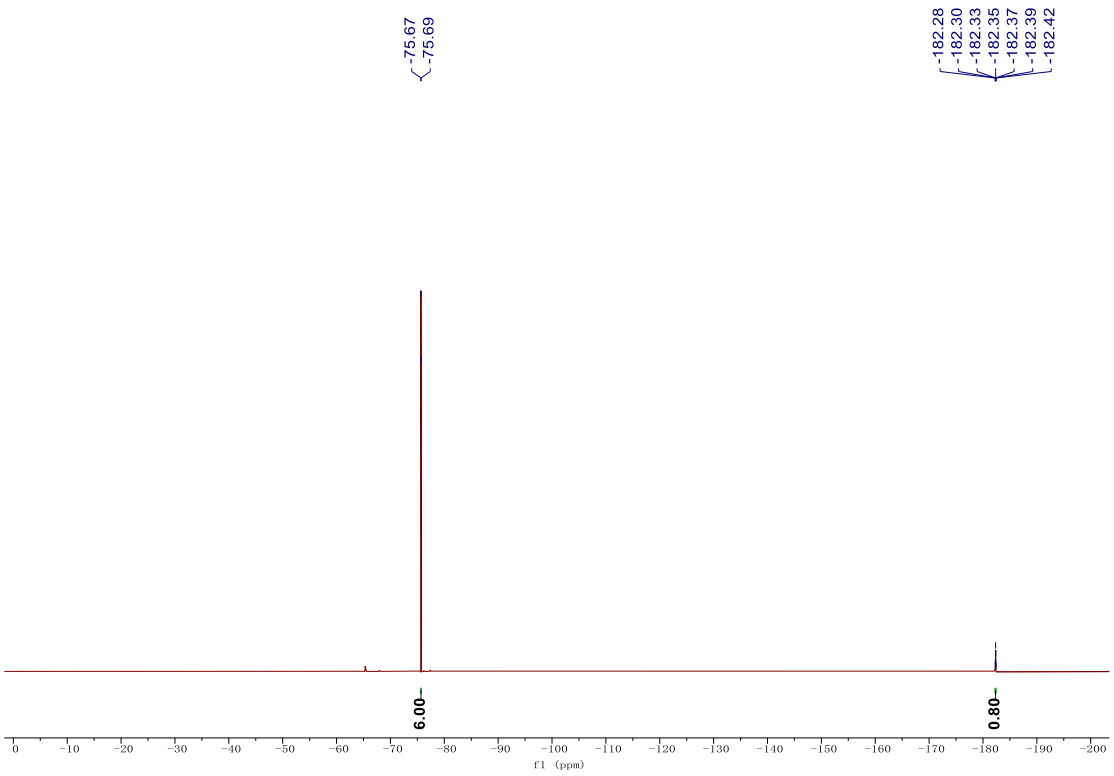

-80.80
-80.83
-80.86
-108.65
-108.69
-108.72
-121.72
-121.92
-122.14
-122.16
-122.78
-126.15
-126.16
-126.18
-126.20
-126.22
-126.24
2.11
1.84
7.03
2.05
2.08
2.00
f1 (ppm)

3-methyl-2-(perfluoropropan-2-yl)-1*H*-indole (3da)

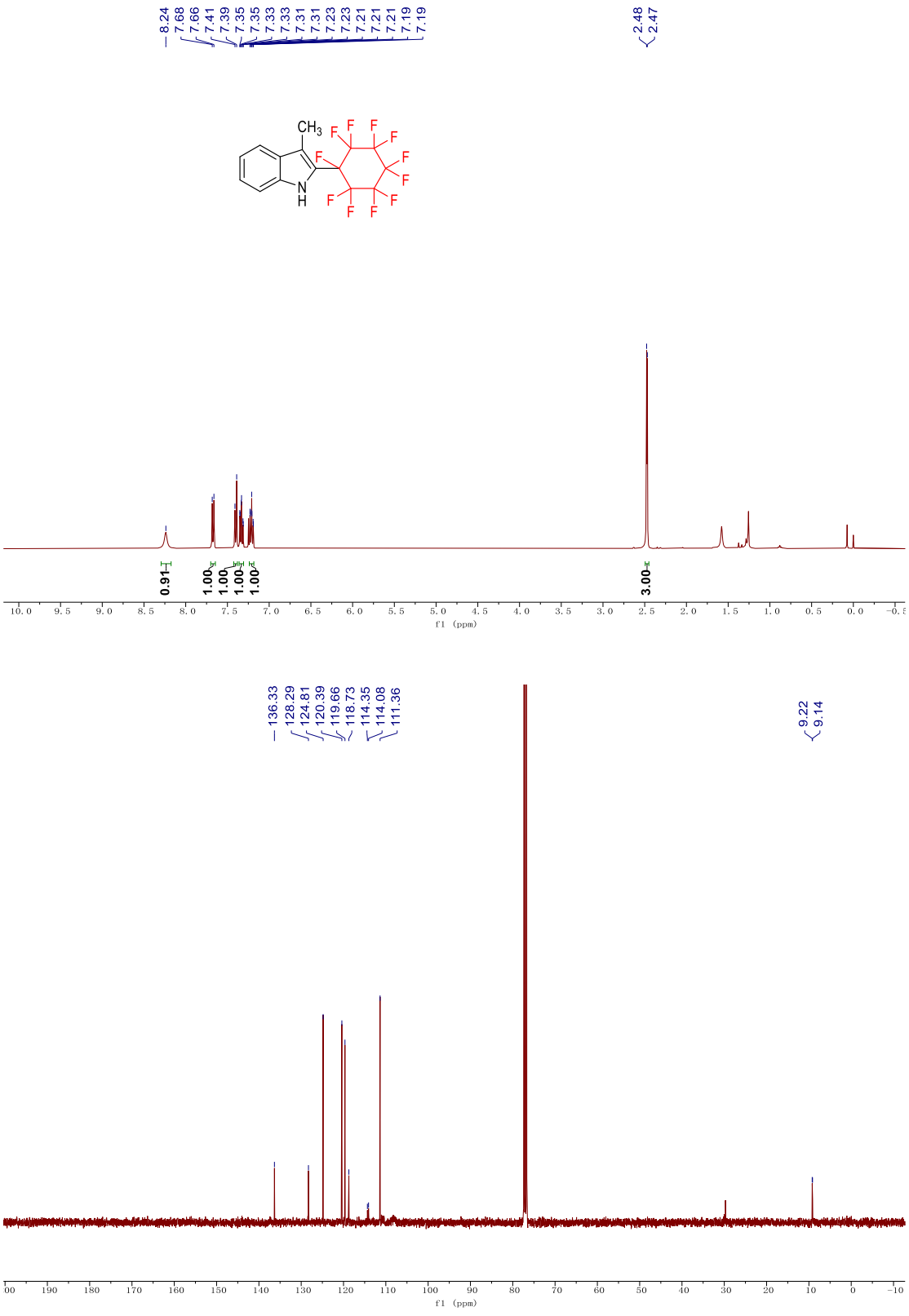


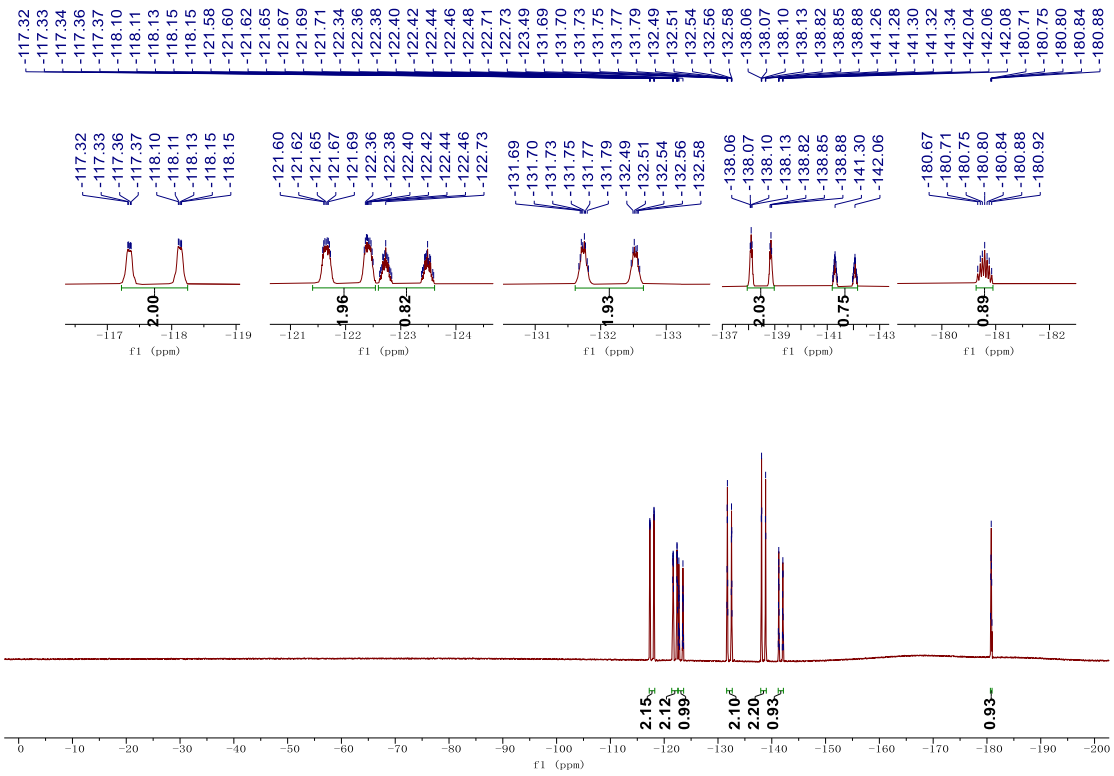




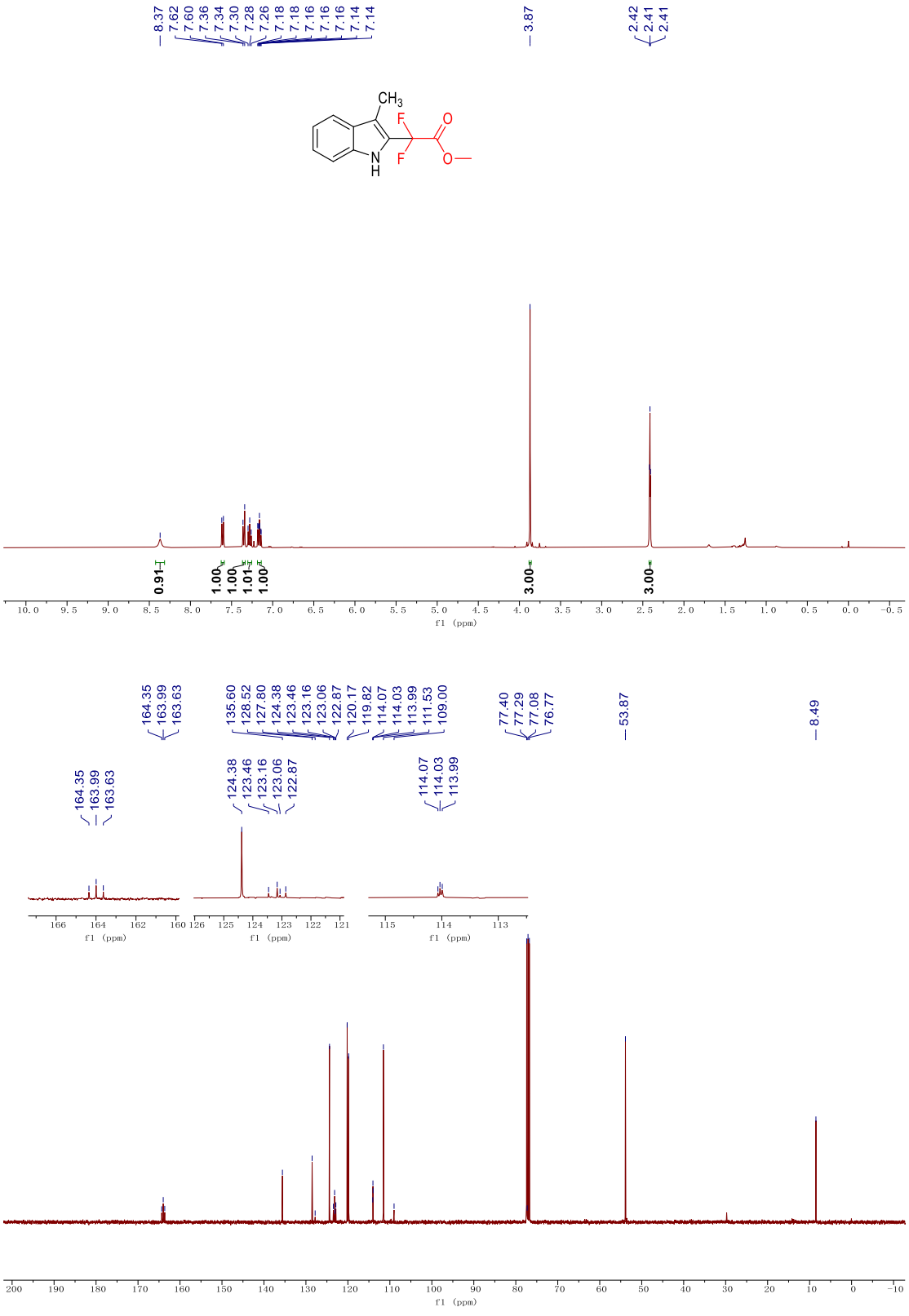

-75.67
-75.69
-182.28
-182.30
-182.33
-182.35
-182.37
-182.39
-182.42
6.00
0.80
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
f1 (ppm)

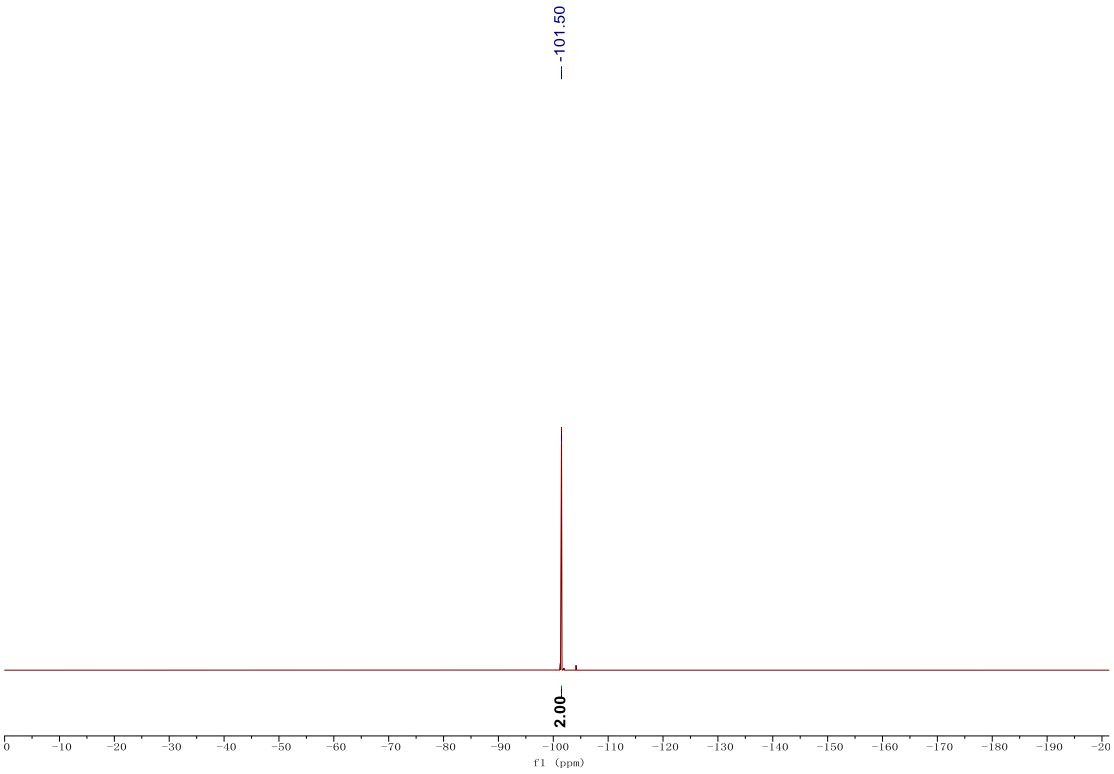
3-methyl-2-(perfluorocyclohexyl)-1*H*-indole (3ea)



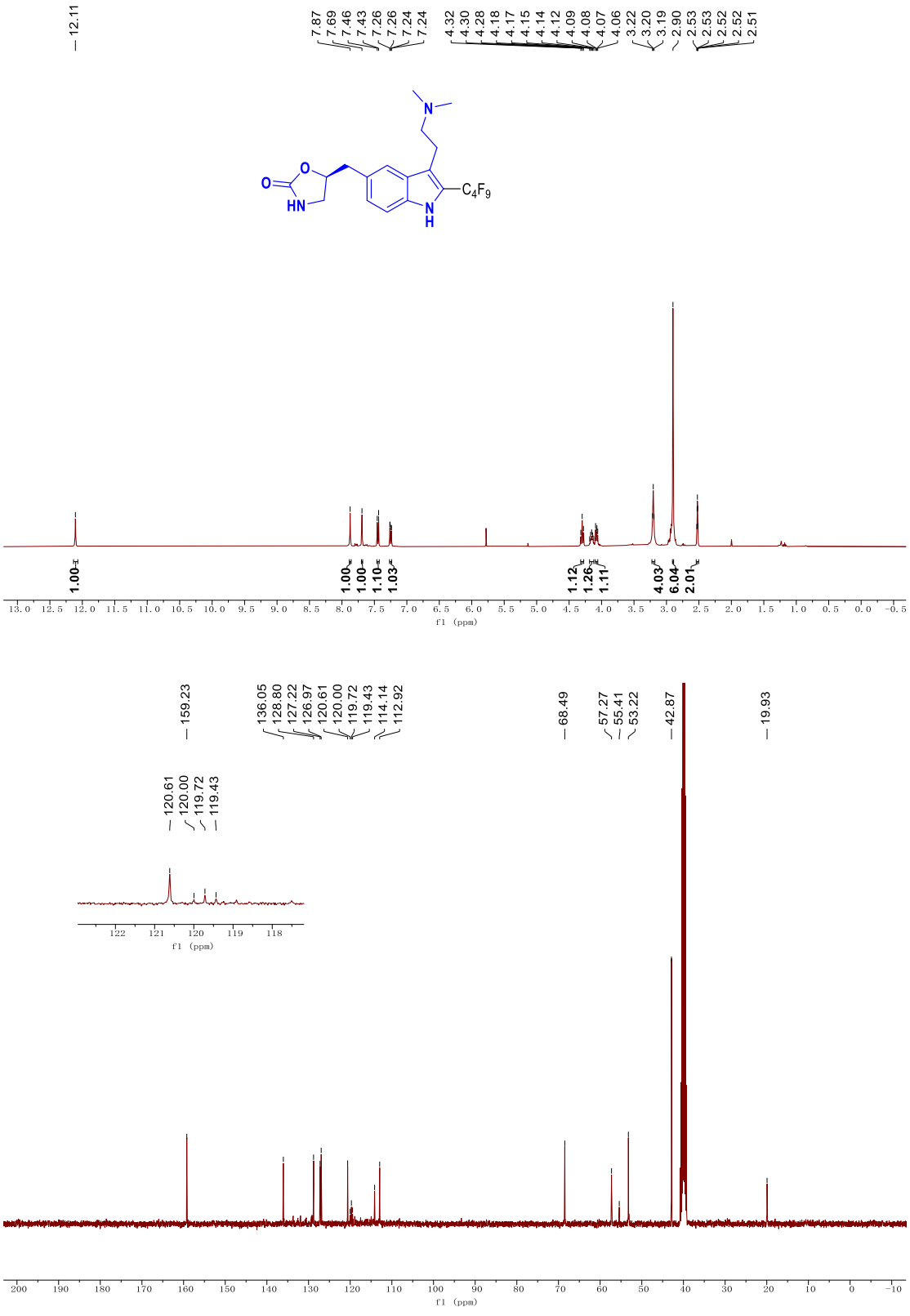

-117.32
-117.33
-117.34
-117.36
-117.37
-118.10
-118.11
-118.13
-118.15
-118.15
-121.58
-121.60
-121.62
-121.65
-121.67
-121.69
-121.71
-122.34
-122.36
-122.38
-122.40
-122.42
-122.44
-122.46
-122.48
-122.71
-122.73
-123.49
-131.69
-131.70
-131.73
-131.75
-131.77
-131.79
-132.49
-132.51
-132.54
-132.56
-132.58
-138.06
-138.07
-138.10
-138.13
-138.82
-138.85
-138.88
-141.26
-141.28
-141.30
-141.32
-141.34
-142.04
-142.06
-142.08
-180.71
-180.75
-180.80
-180.84
-180.88
2.00
1.96
0.82
1.93
2.03
0.75
0.89
f1 (ppm)
2.15
2.12
0.99
2.10
2.20
0.93
0.93
f1 (ppm)

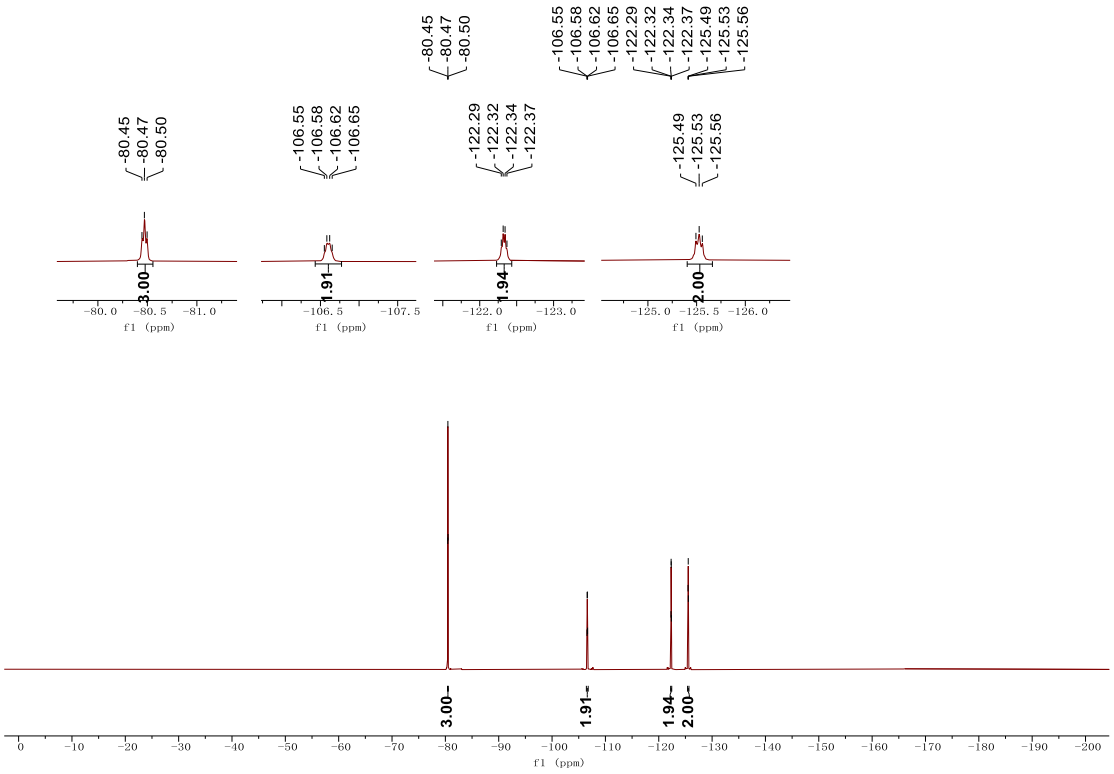
methyl 2,2-difluoro-2-(3-methyl-1H-indol-2-yl)acetate (3fa)



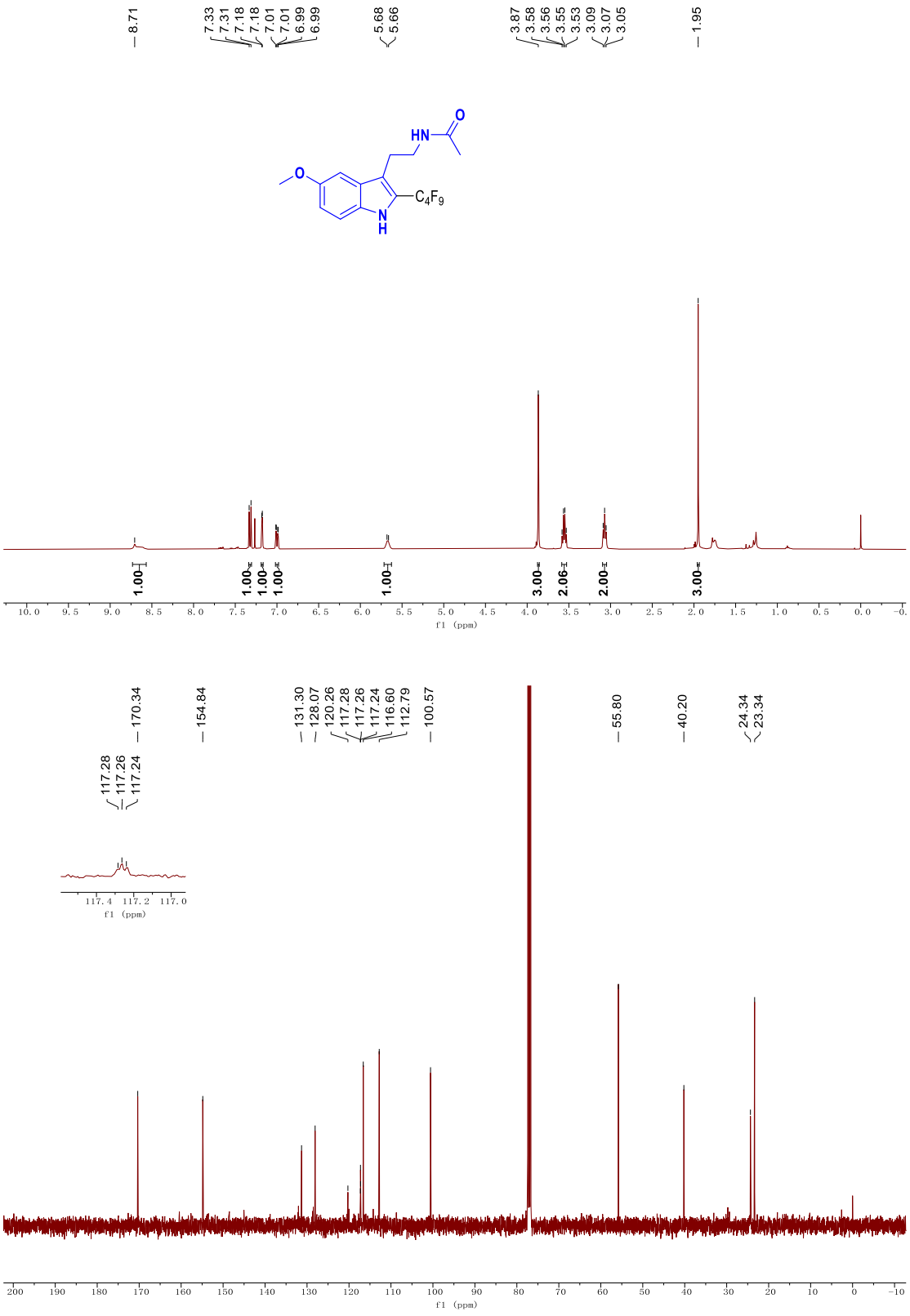

-101.50
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-20
f1 (ppm)

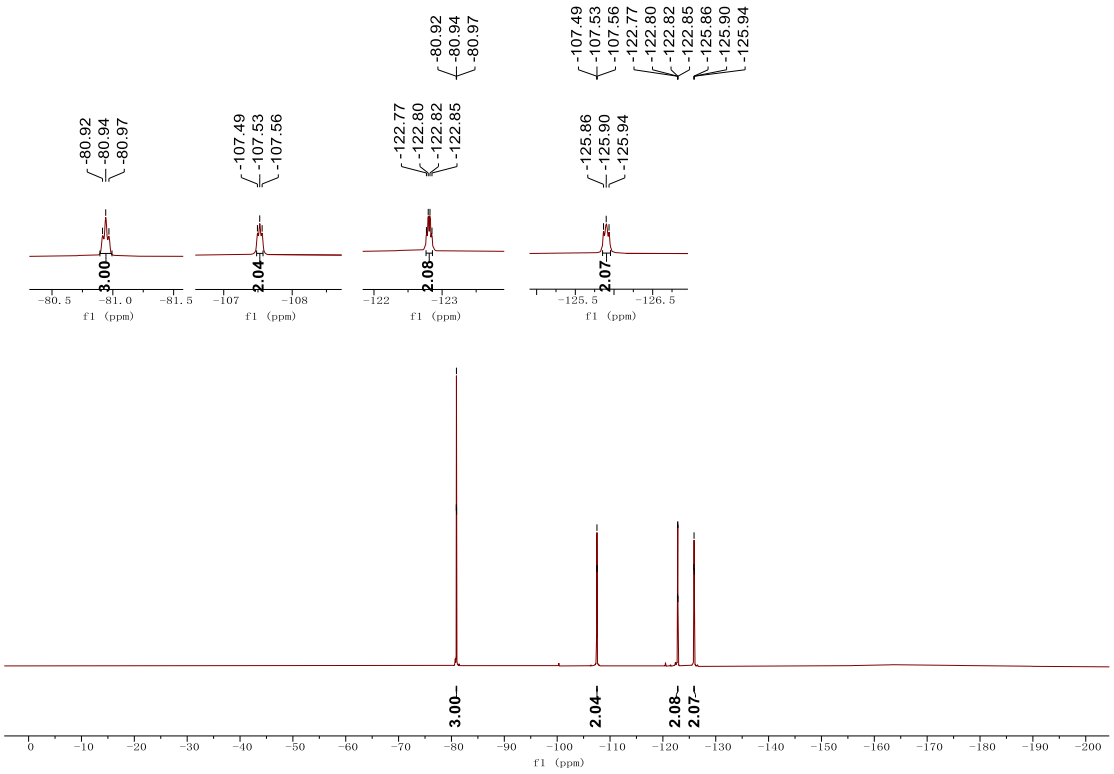
(*S*)-5-((3-(2-(dimethylamino)ethyl)-2-(perfluorobutyl)-1*H*-indol-5-yl)methyl)oxazolidin-2-one (5a)



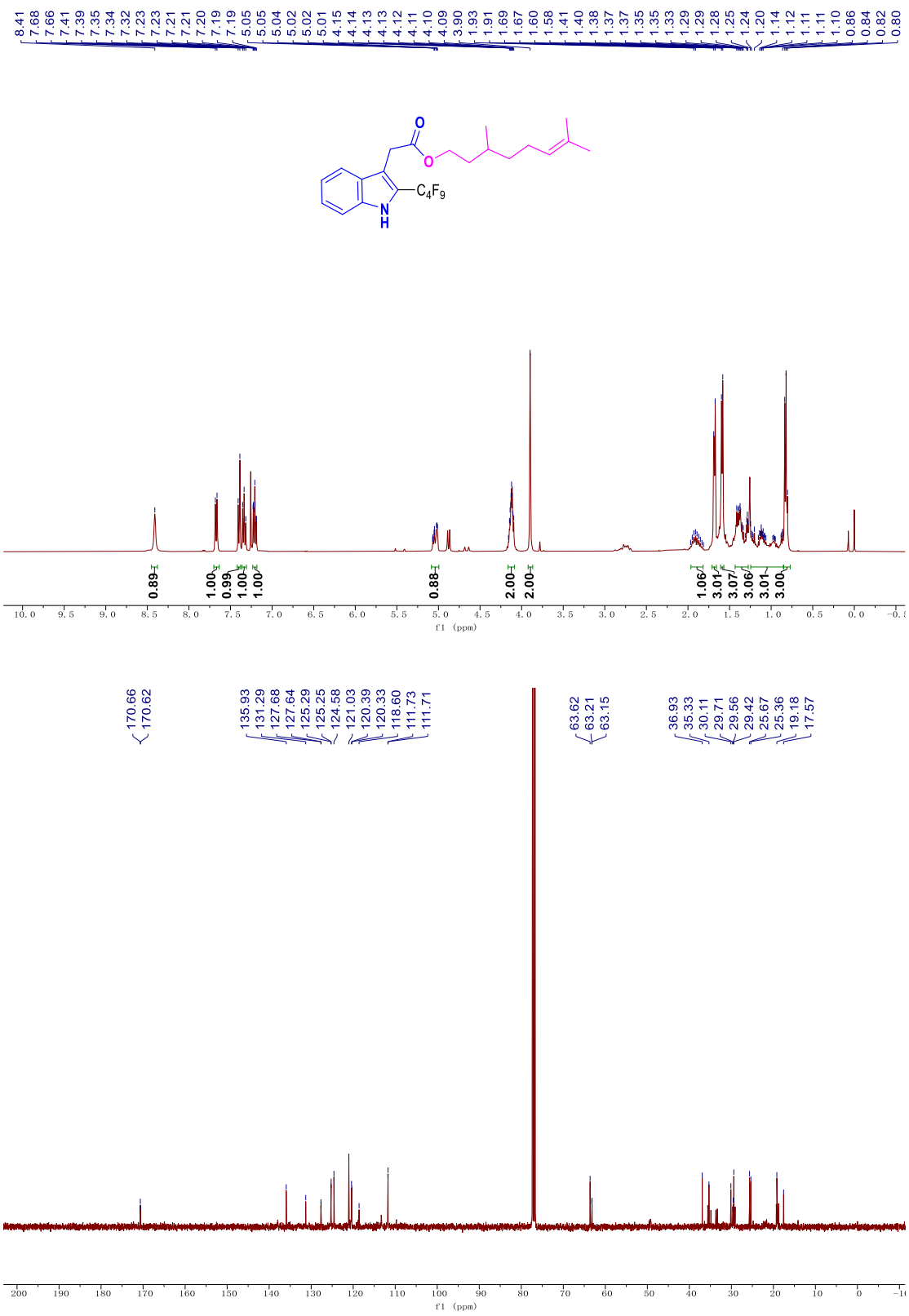

-80.45
-80.47
-80.50
-106.55
-106.58
-106.62
-106.65
-122.29
-122.32
-122.34
-122.37
-125.49
-125.53
-125.56
3.00
1.91
1.94
2.00
f1 (ppm)

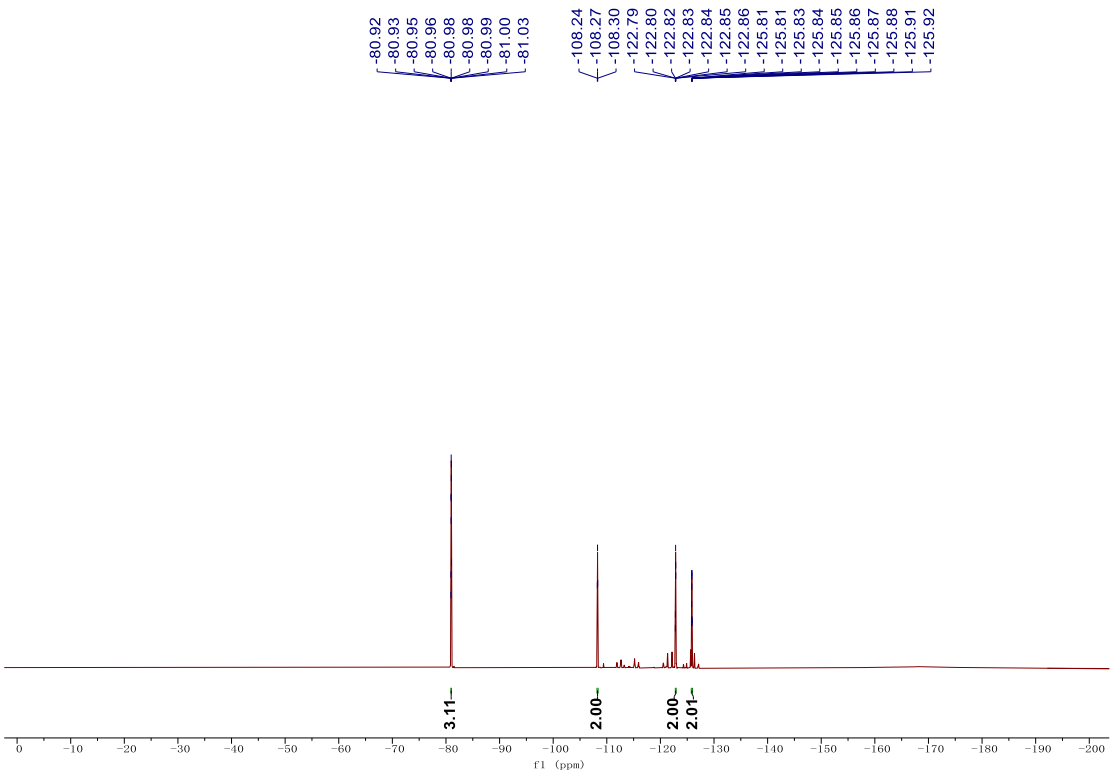
N-(2-(5-methoxy-2-(perfluorobutyl)-1*H*-indol-3-yl)ethyl)acetamide (5b)



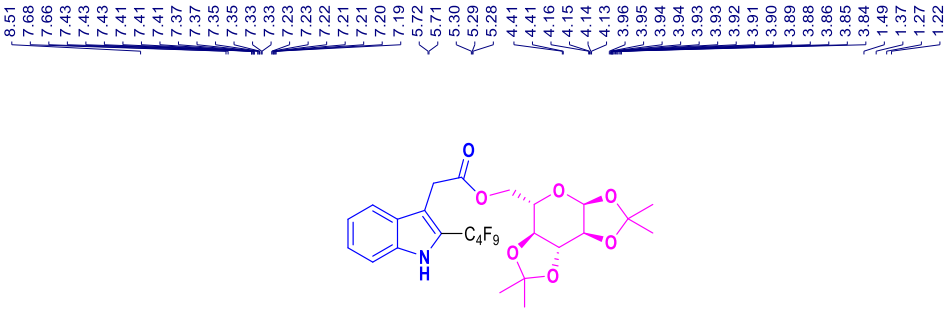

-80.92
-80.94
-80.97
-107.49
-107.53
-107.56
-122.77
-122.80
-122.82
-122.85
-125.86
-125.90
-125.94
3.00
2.04
2.08
2.07
f1 (ppm)

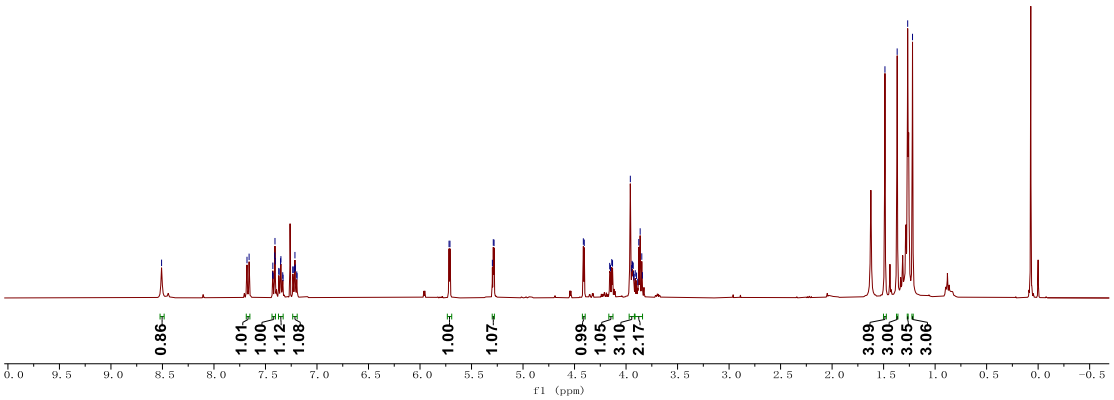
3,7-dimethyloct-6-en-1-yl-2-(2-(perfluorobutyl)-1*H*-indol-3-yl)acetate (5c)

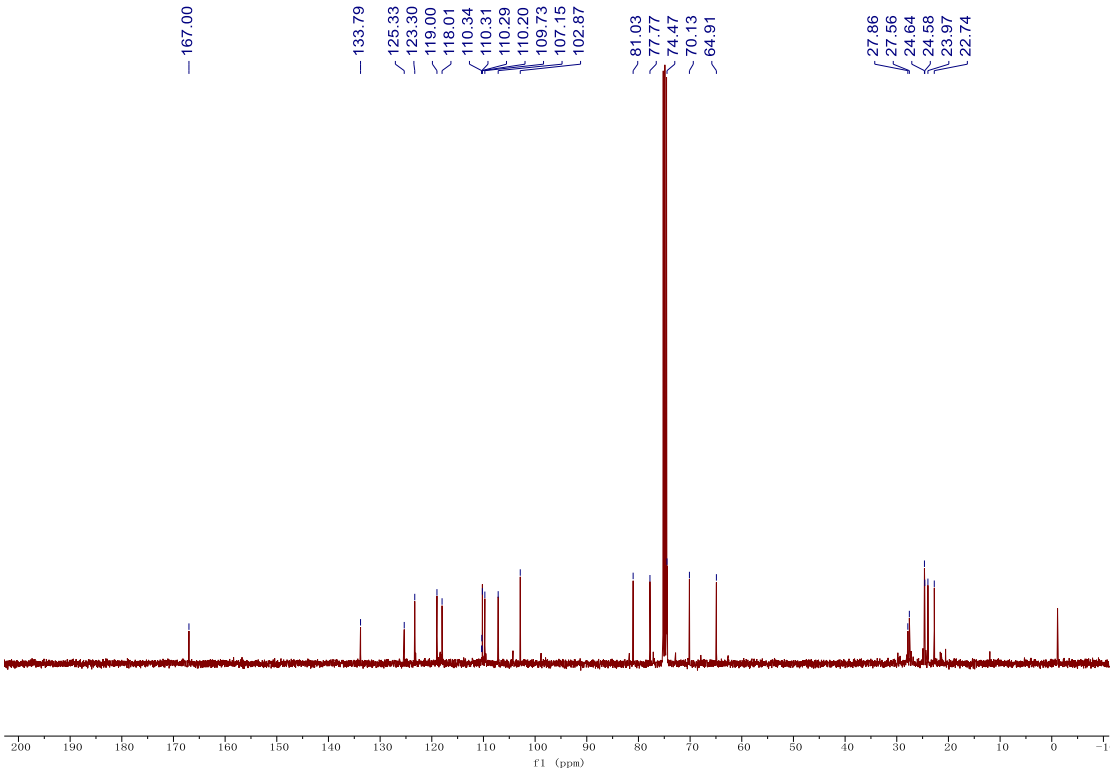


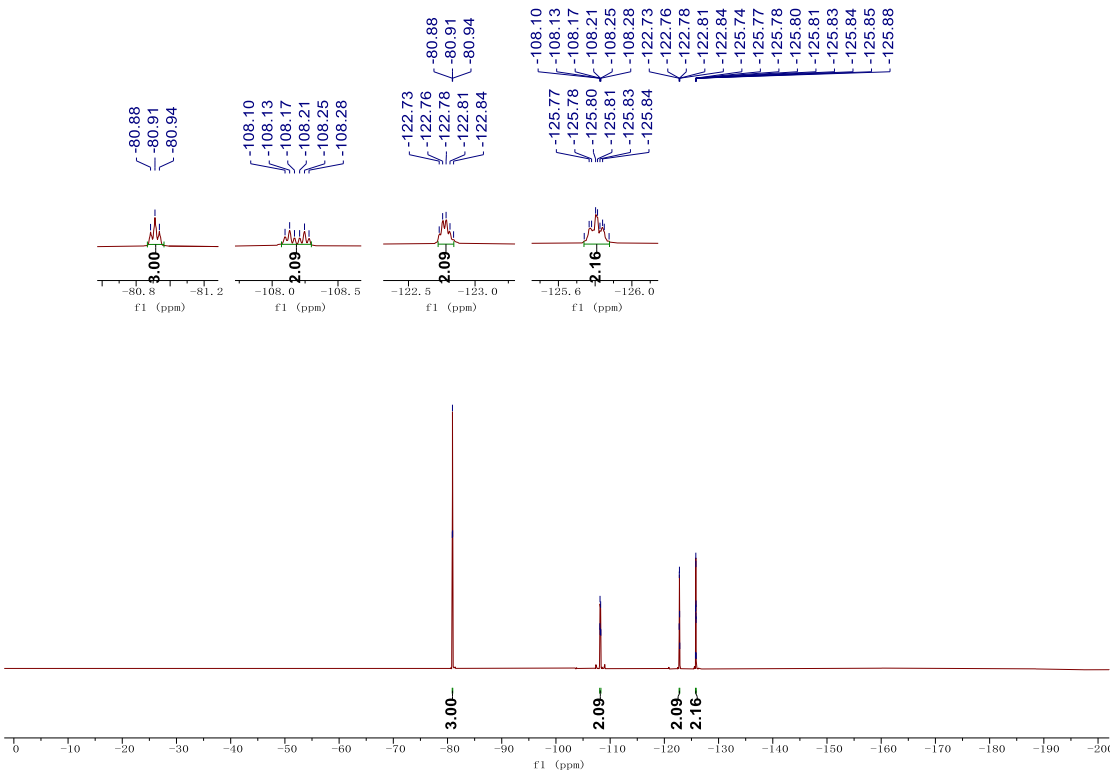

-80.92
-80.93
-80.95
-80.96
-80.98
-80.98
-80.99
-81.00
-81.03
-108.24
-108.27
-108.30
-122.79
-122.80
-122.82
-122.83
-122.84
-122.85
-122.86
-125.81
-125.81
-125.83
-125.84
-125.85
-125.86
-125.87
-125.88
-125.91
-125.92
3.11
2.00
2.00
2.01
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
f1 (ppm)

((3a*S*,5*S*,5a*S*,8a*R*,8b*S*)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl-2-(2-(perfluorobutyl)-1H-indol-3-yl)acetate (5d)

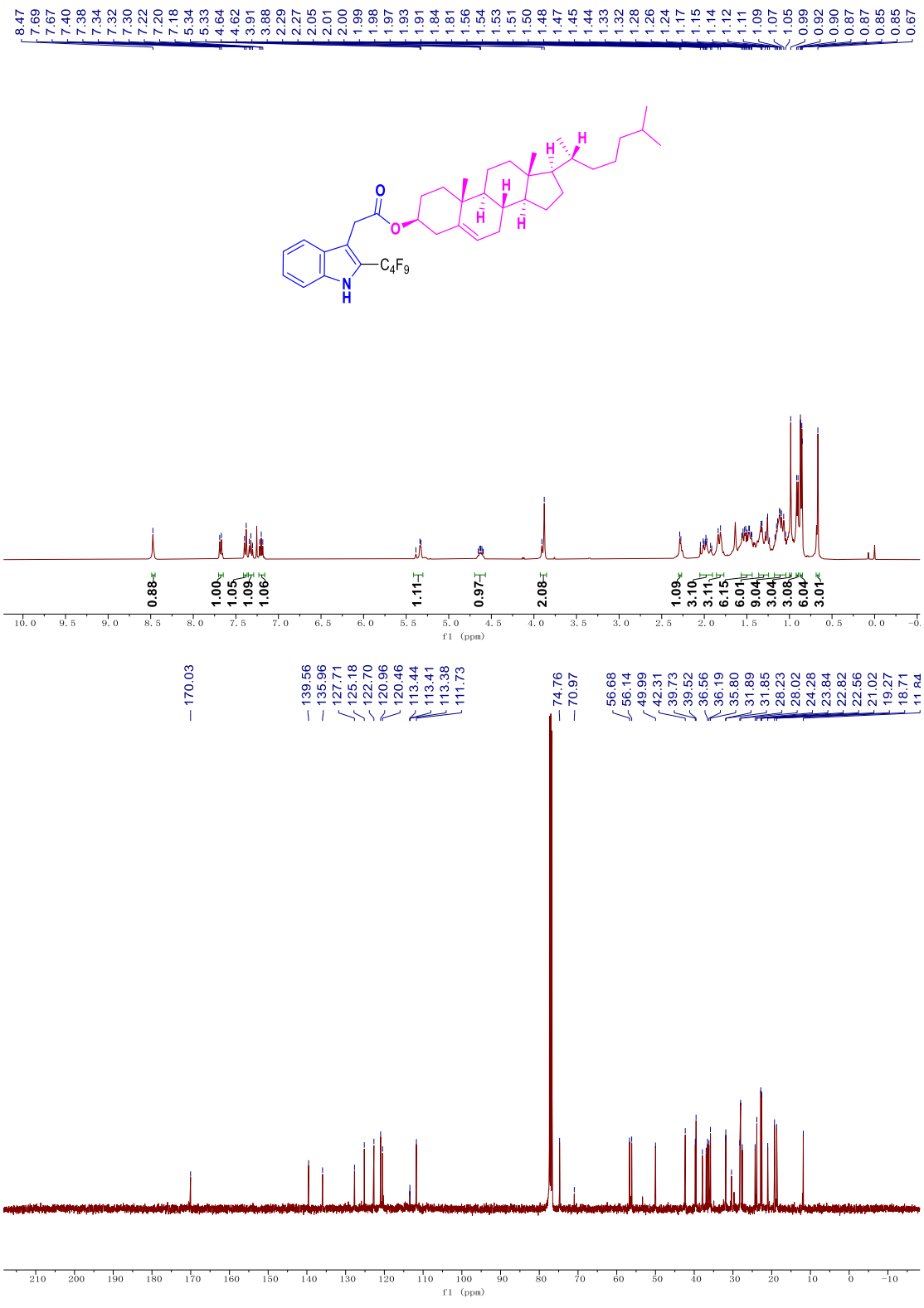


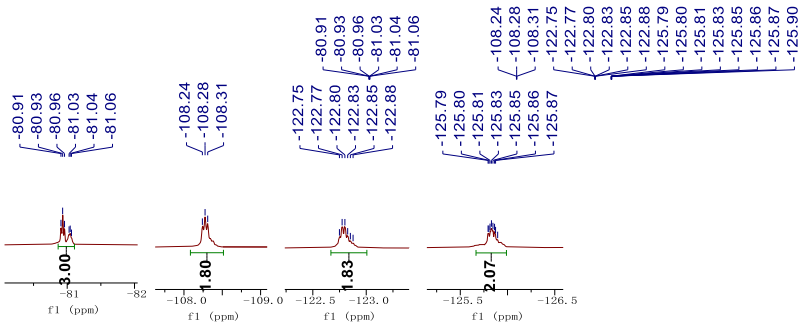


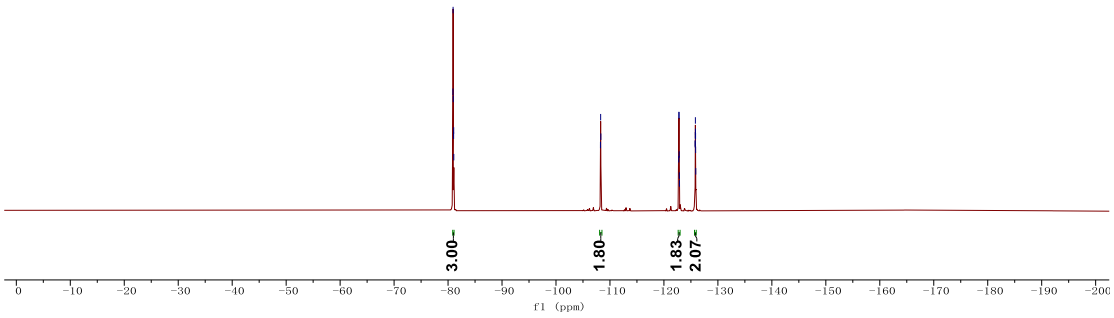



-80.88
-80.91
-80.94
-108.10
-108.13
-108.17
-108.21
-108.25
-108.28
-122.73
-122.76
-122.78
-122.81
-122.84
-125.77
-125.78
-125.80
-125.81
-125.83
-125.84
-125.85
-125.88
3.00
2.09
2.09
2.16
f1 (ppm)

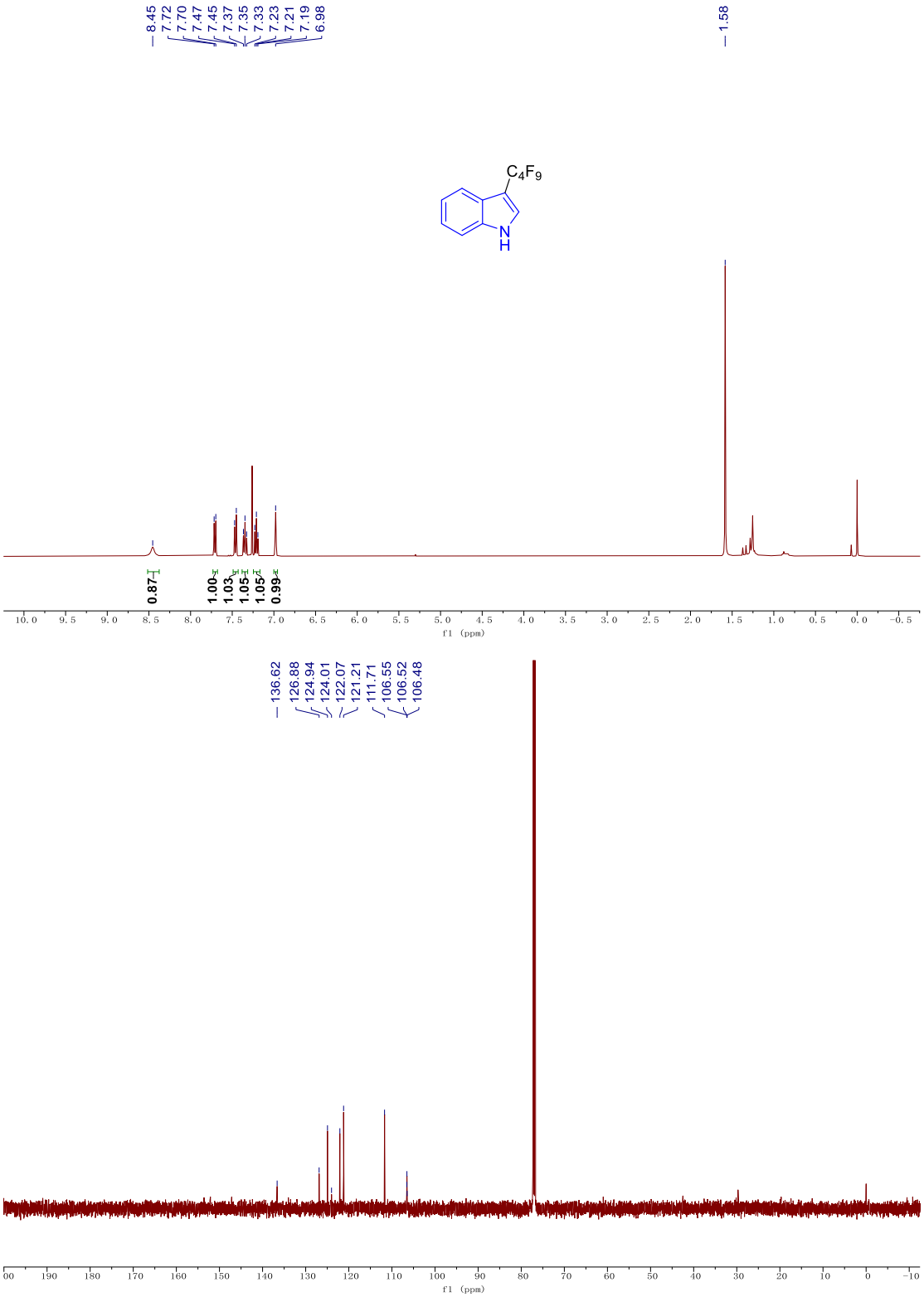
(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl 2-(2-(perfluorobutyl)-1H-indol-3-yl)acetate (5e)

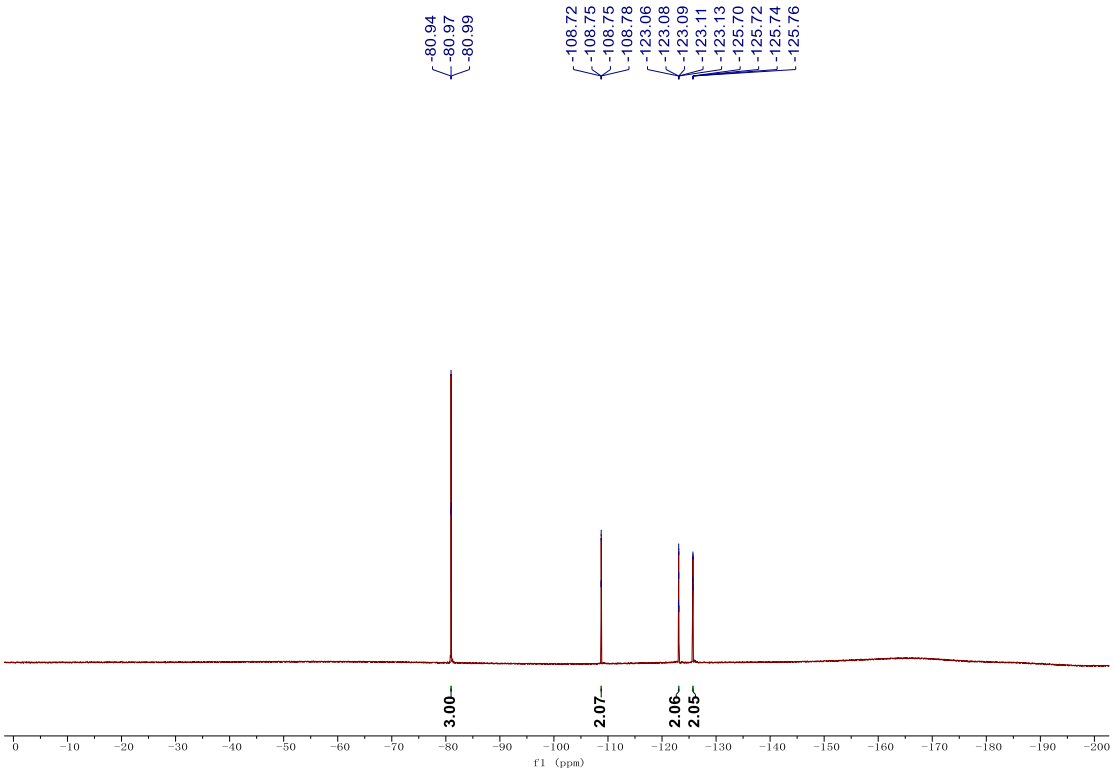



-80.91
-80.93
-80.96
-81.03
-81.04
-81.06
-108.24
-108.28
-108.31
-122.75
-122.77
-122.80
-122.83
-122.85
-122.88
-125.79
-125.80
-125.81
-125.83
-125.85
-125.86
-125.87
-125.90
3.00
1.80
1.83
2.07
f1 (ppm)

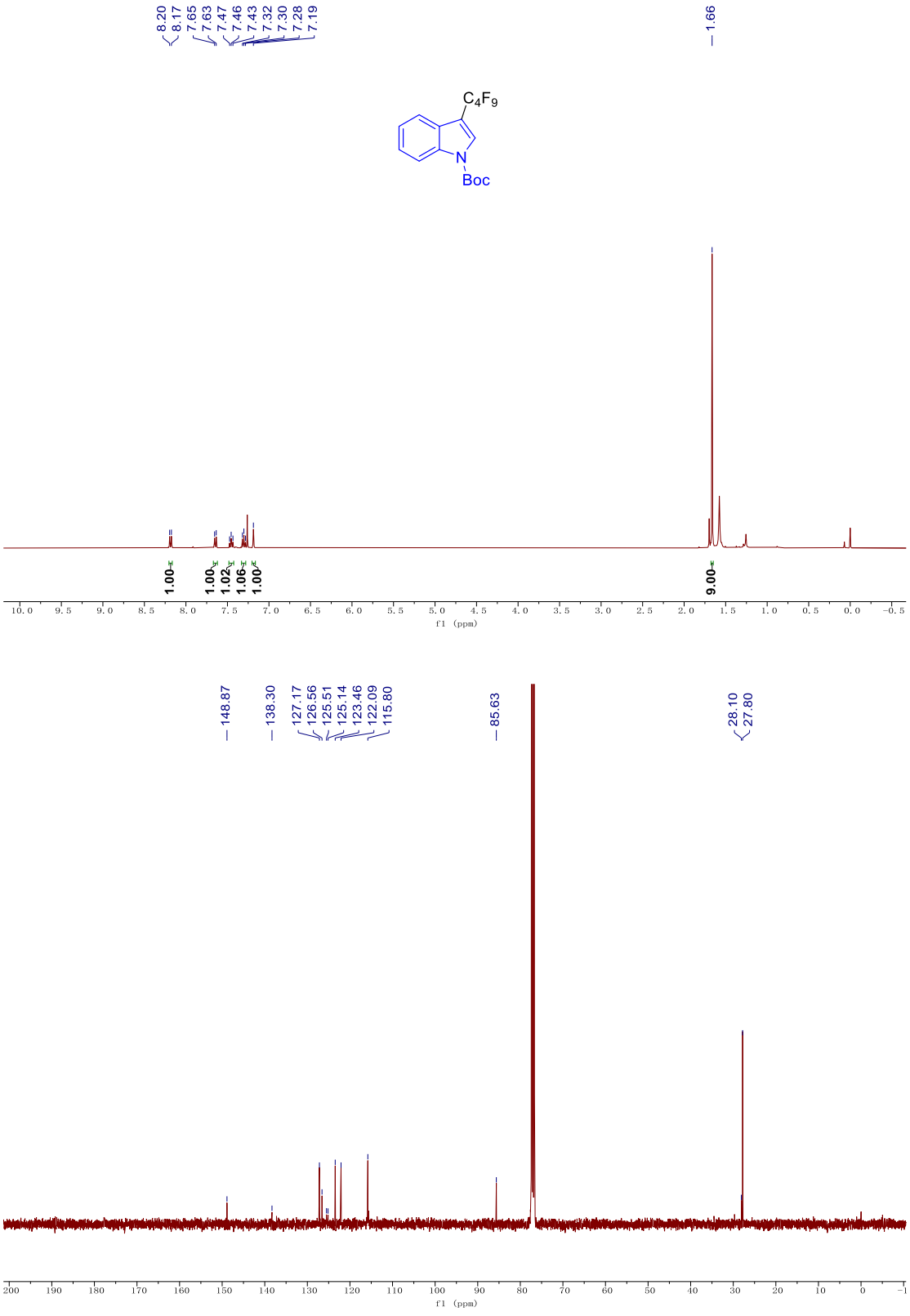

3.00
1.80
1.83
2.07
f1 (ppm)

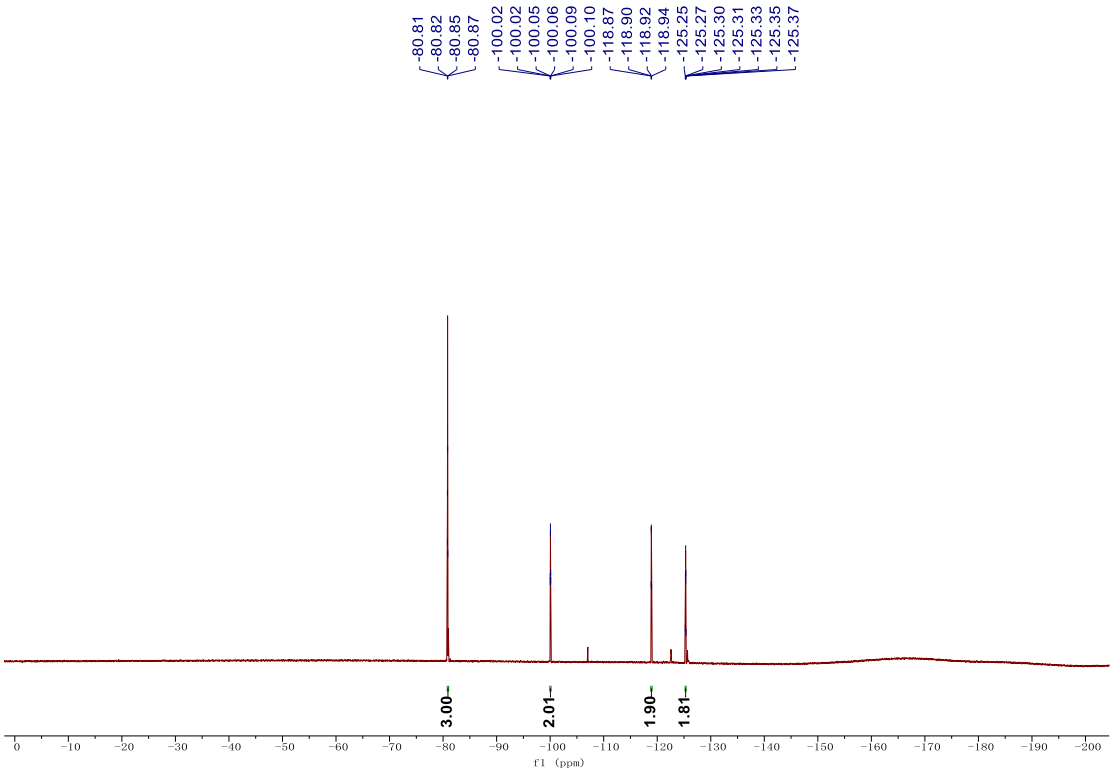
3-(perfluorobutyl)-1*H*-indole (7b)



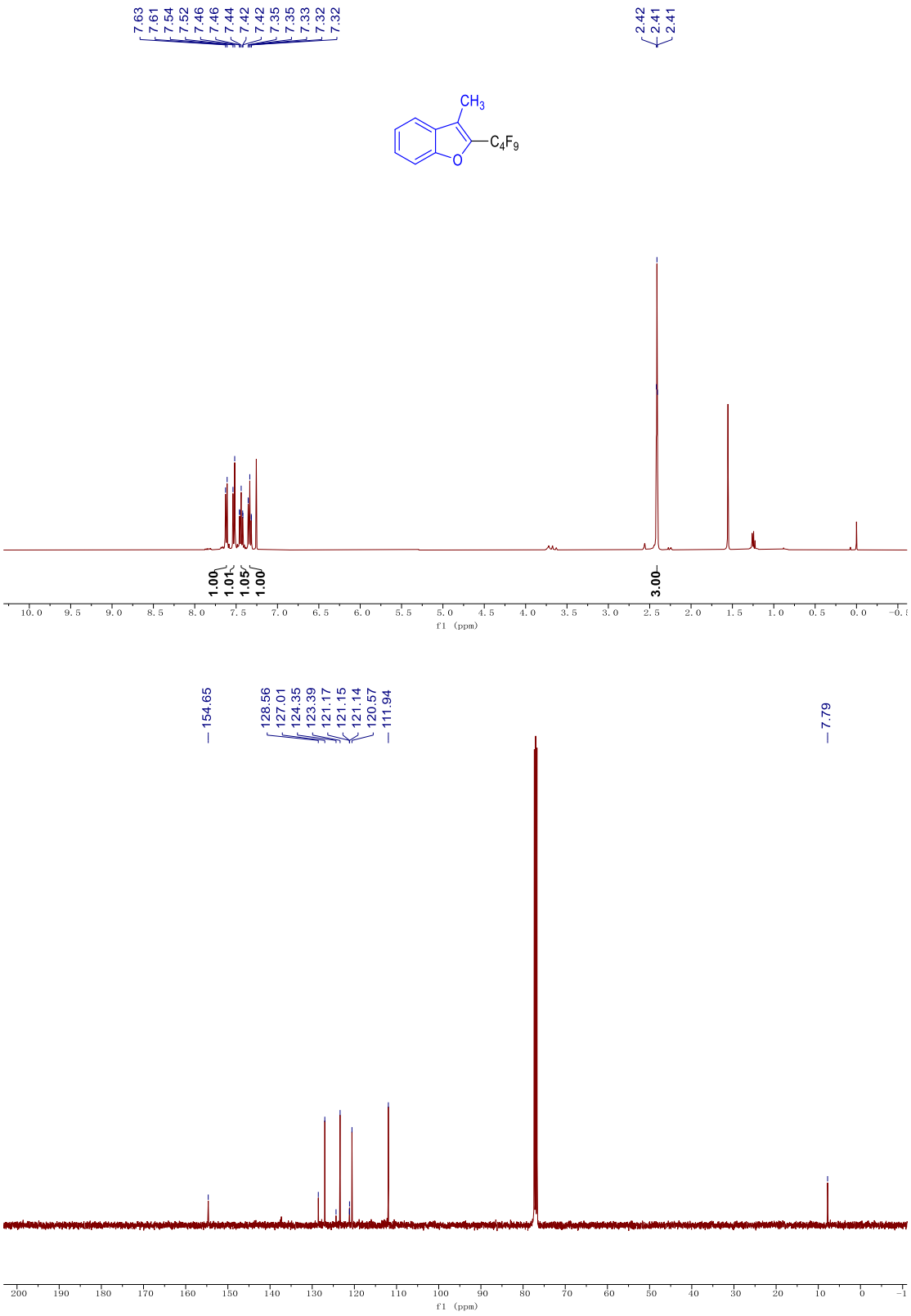

-80.94
-80.97
-80.99
-108.72
-108.75
-108.75
-108.78
-123.06
-123.08
-123.09
-123.11
-123.13
-125.70
-125.72
-125.74
-125.76
3.00
2.07
2.06
2.05
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
f1 (ppm)

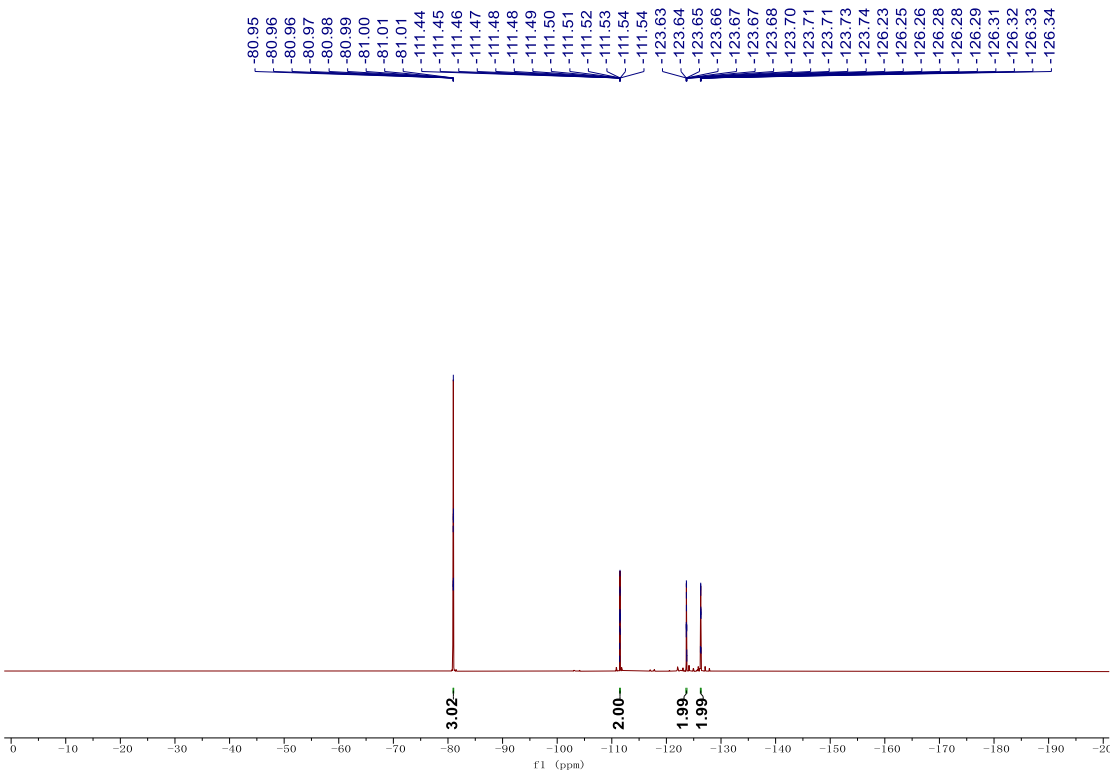
tert-butyl 3-(perfluorobutyl)-1*H*-indole-1-carboxylate (7c)



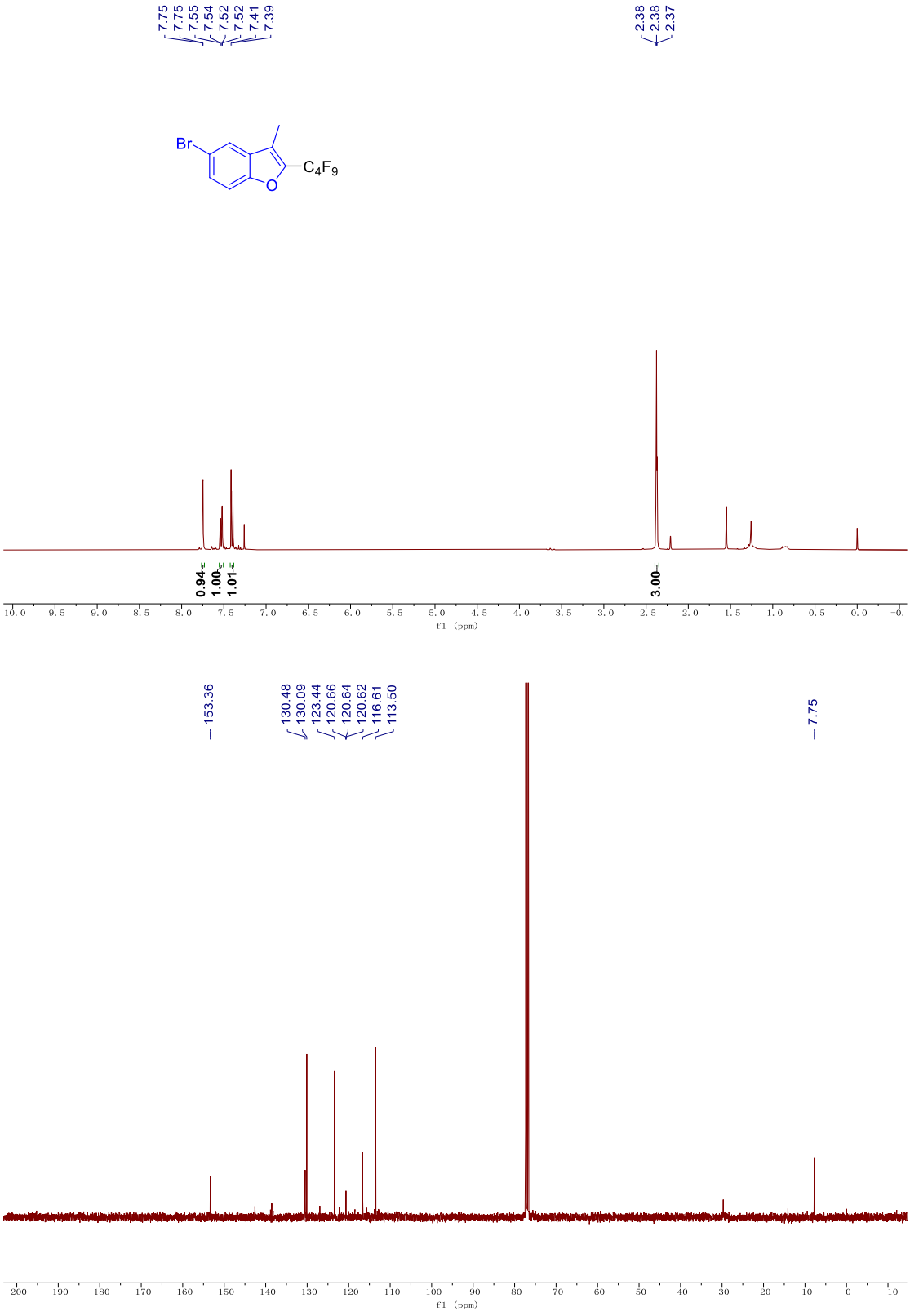

-80.81
-80.82
-80.85
-80.87
-100.02
-100.02
-100.05
-100.06
-100.09
-100.10
-118.87
-118.90
-118.92
-118.94
-125.25
-125.27
-125.30
-125.31
-125.33
-125.35
-125.37
3.00
2.01
1.90
1.81
f1 (ppm)

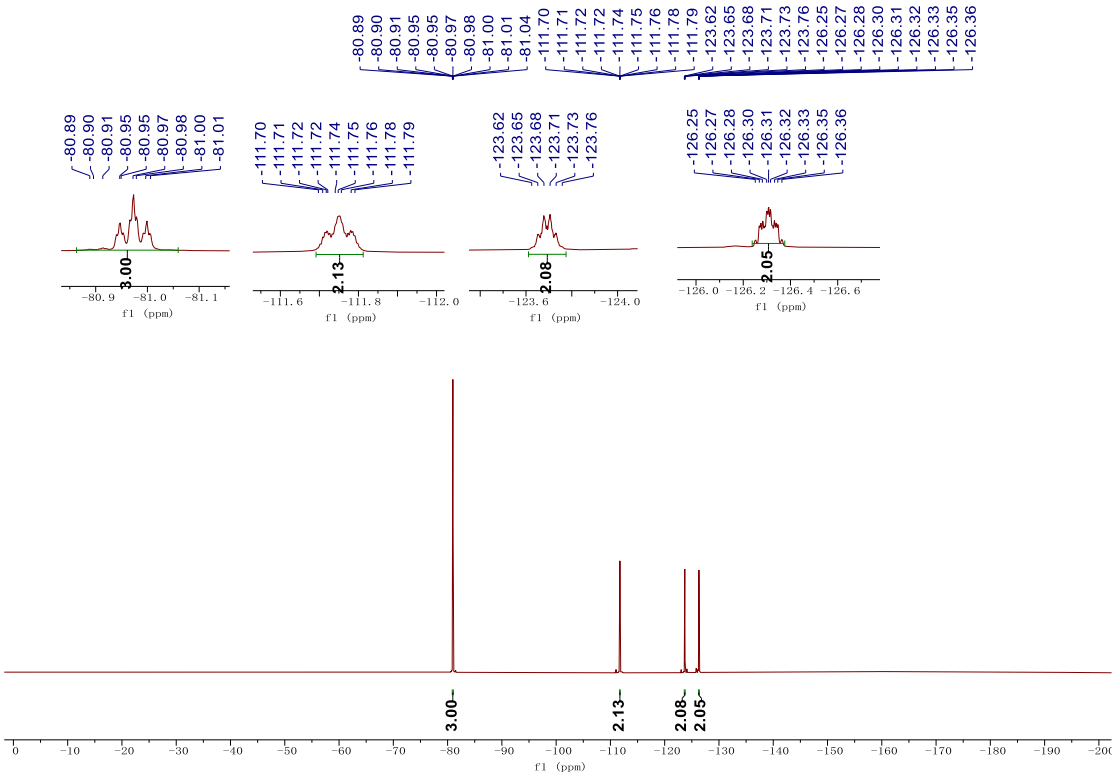
3-methyl-2-(perfluorobutyl)benzofuran (7d)



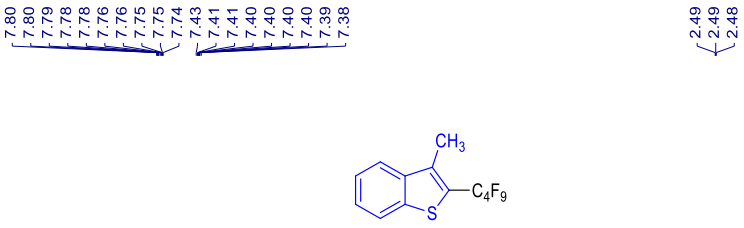

-80.95
-80.96
-80.96
-80.97
-80.98
-80.99
-81.00
-81.01
-81.01
-111.44
-111.45
-111.46
-111.47
-111.48
-111.48
-111.49
-111.50
-111.51
-111.52
-111.53
-111.54
-111.54
-123.63
-123.64
-123.65
-123.66
-123.67
-123.67
-123.68
-123.70
-123.71
-123.71
-123.73
-123.74
-126.23
-126.25
-126.26
-126.28
-126.28
-126.29
-126.31
-126.32
-126.33
-126.34
3.02
2.00
1.99
1.99
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
f1 (ppm)

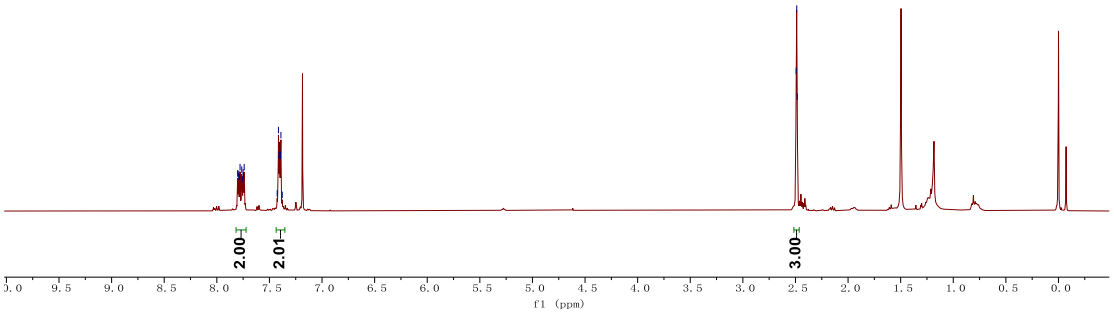
5-bromo-3-methyl-2-(perfluorobutyl)benzofuran (7e)

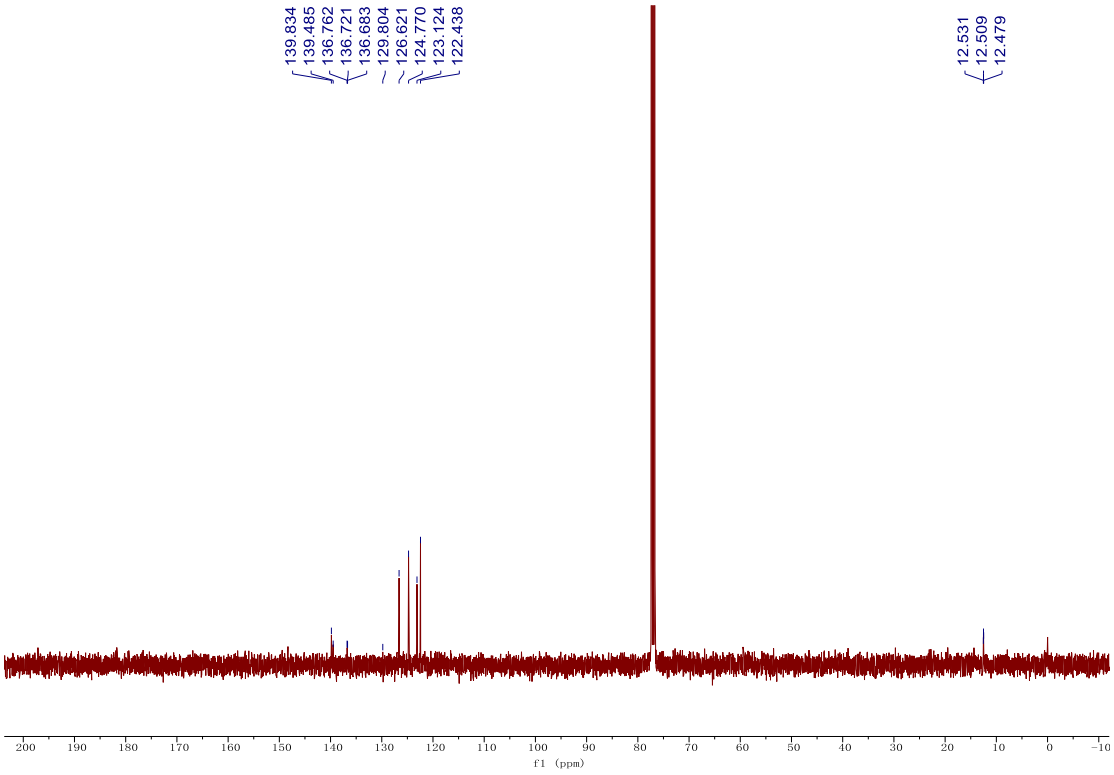


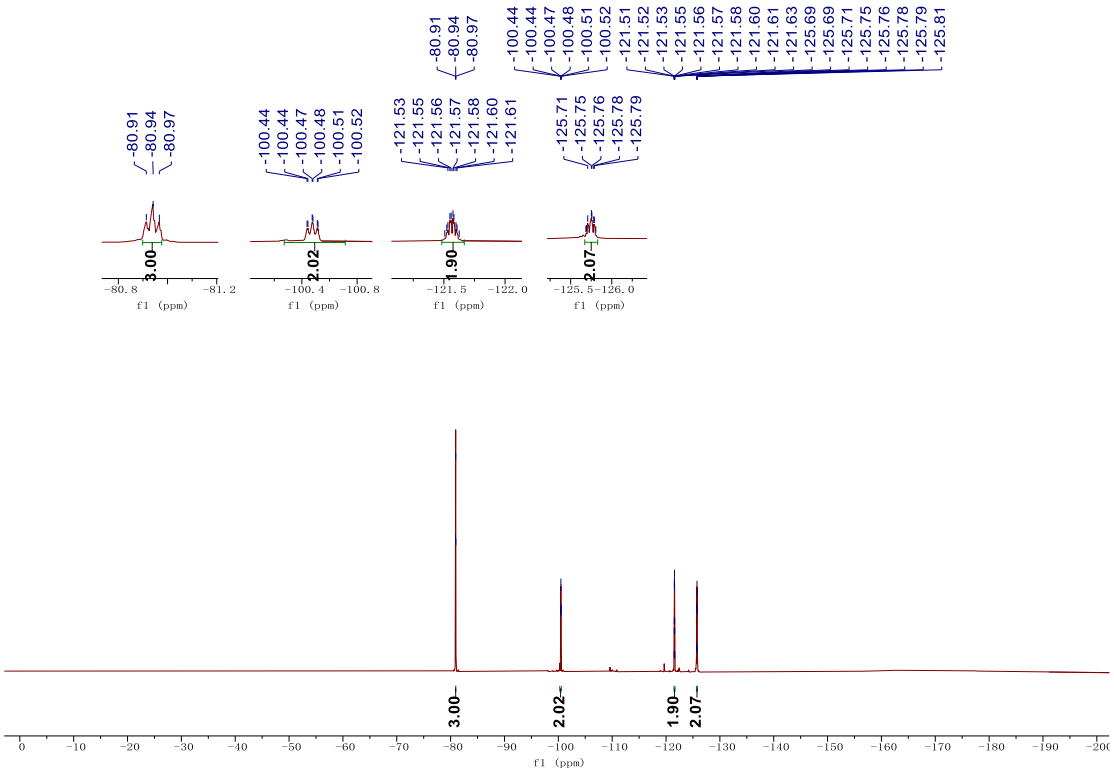

-80.89
-80.90
-80.91
-80.95
-80.95
-80.97
-80.98
-81.00
-81.01
-81.04
-111.70
-111.71
-111.72
-111.72
-111.74
-111.75
-111.76
-111.78
-111.79
-123.62
-123.65
-123.68
-123.71
-123.73
-123.76
-126.25
-126.27
-126.28
-126.30
-126.31
-126.32
-126.33
-126.35
-126.36
3.00
2.13
2.08
2.05
f1 (ppm)

3-methyl-2-(perfluorobutyl)benzo[*b*]thiophene (7f)

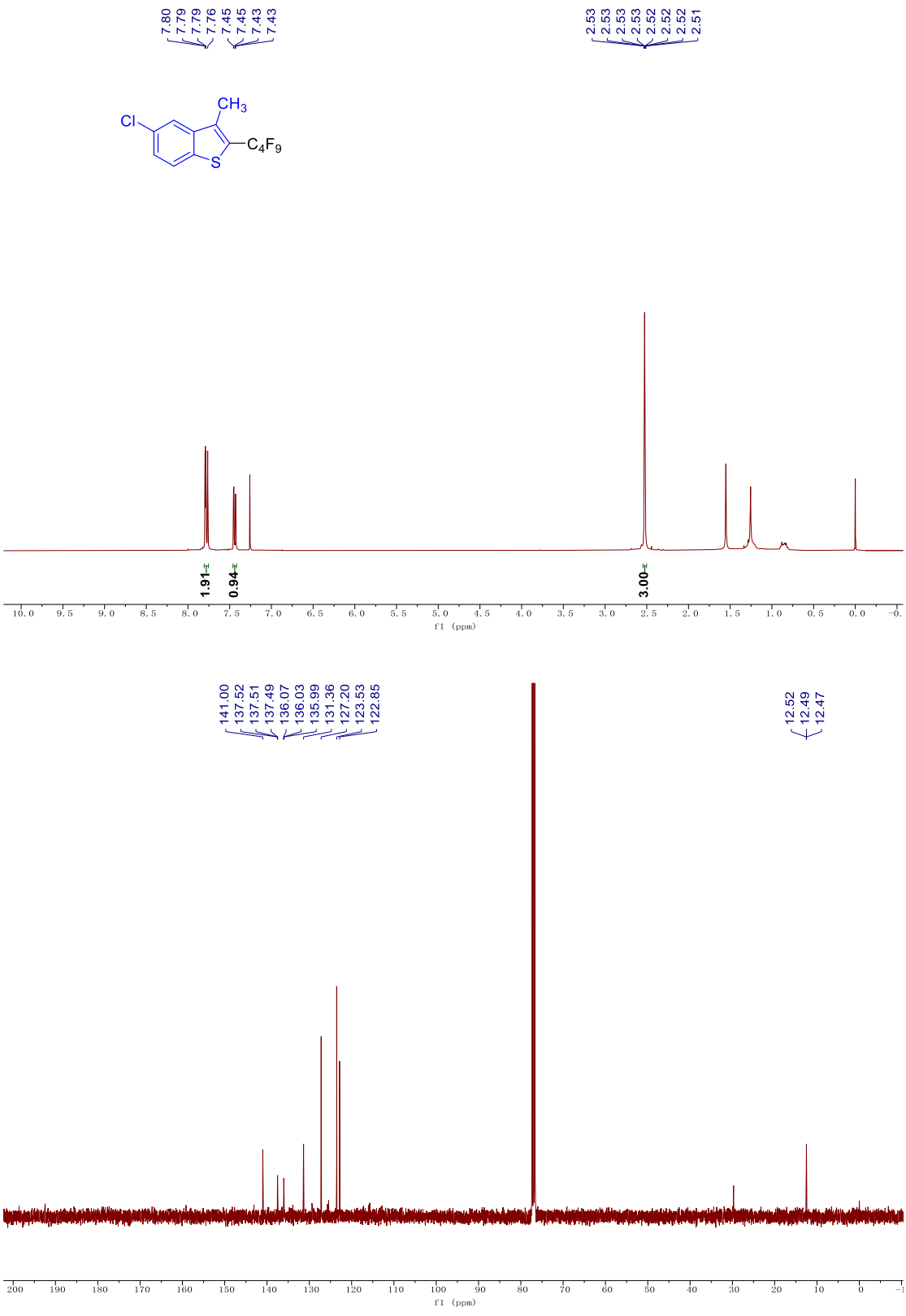


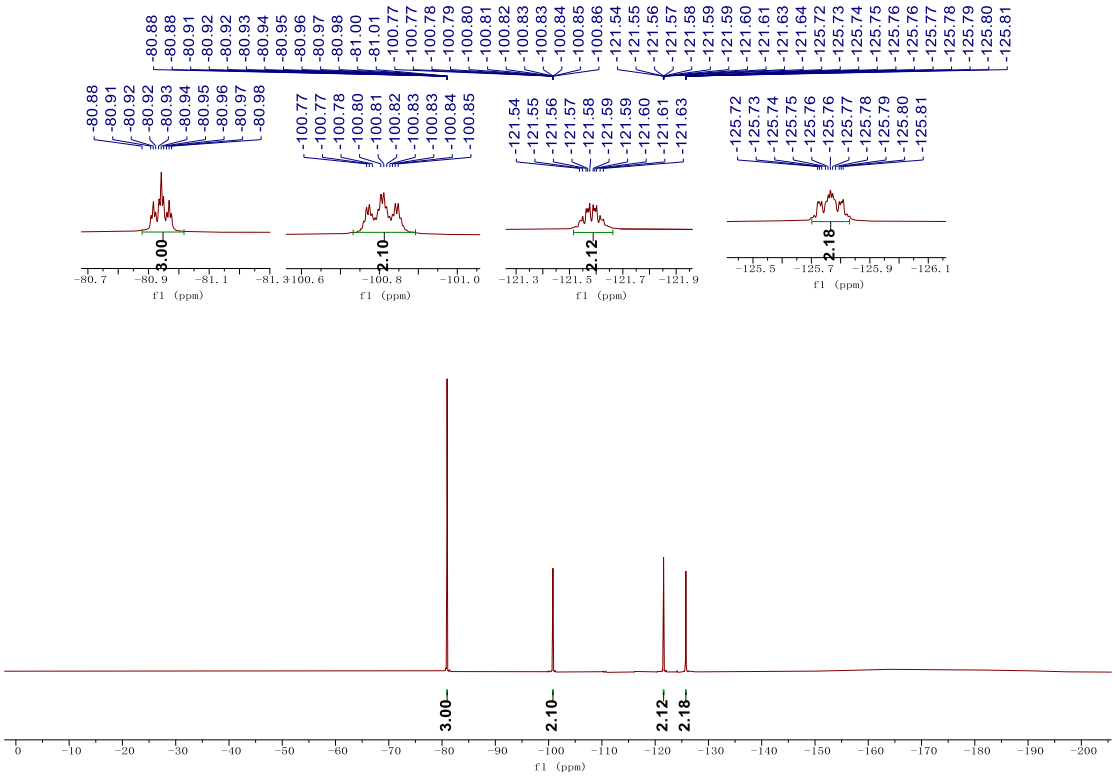




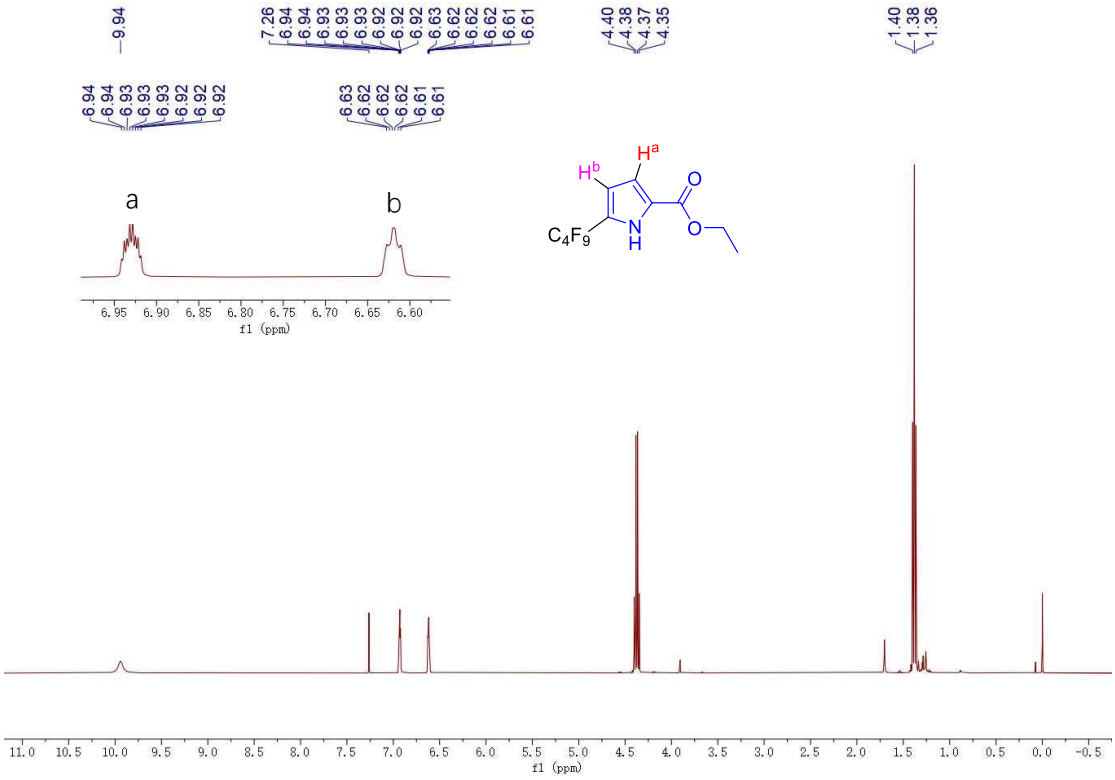

-80.91
-80.94
-80.97
-100.44
-100.44
-100.47
-100.48
-100.51
-100.52
-121.51
-121.52
-121.53
-121.55
-121.56
-121.57
-121.58
-121.60
-121.61
-121.63
-125.69
-125.69
-125.71
-125.75
-125.76
-125.78
-125.79
-125.81
3.00
2.02
1.90
2.07
f1 (ppm)

5-chloro-3-methyl-2-(perfluorobutyl)benzo*[b]*thiophene (7g)

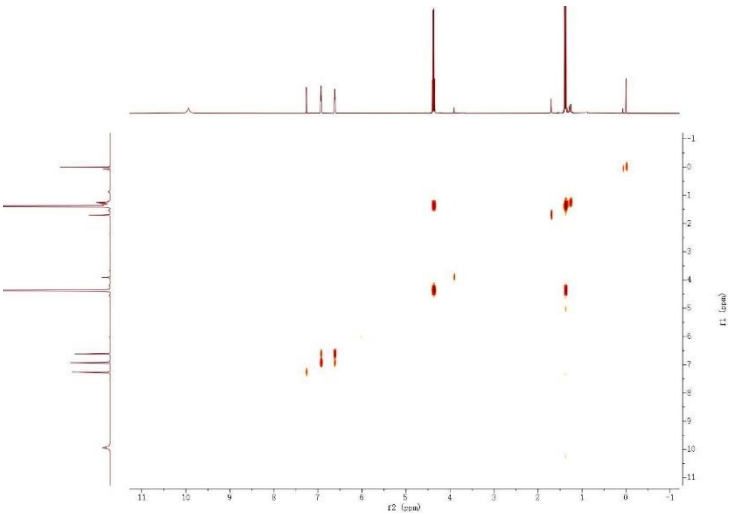



3.00
2.10
2.12
2.18
f1 (ppm)

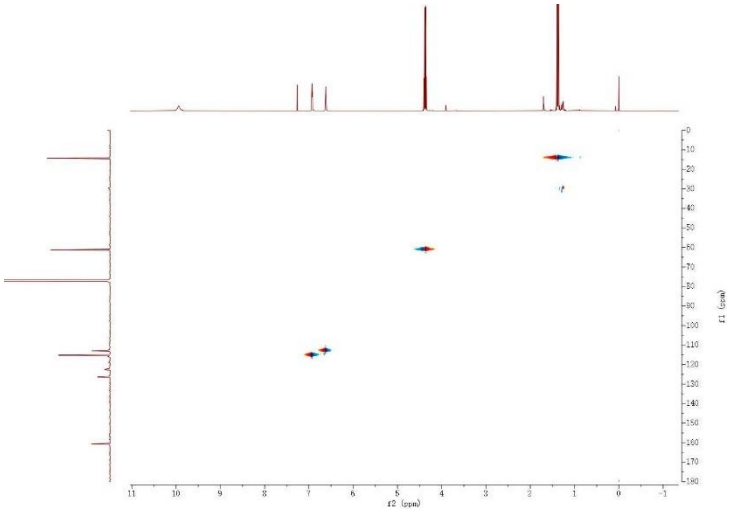
ethyl 3-(perfluorobutyl)-1H-pyrrole-2-carboxylate (7h)



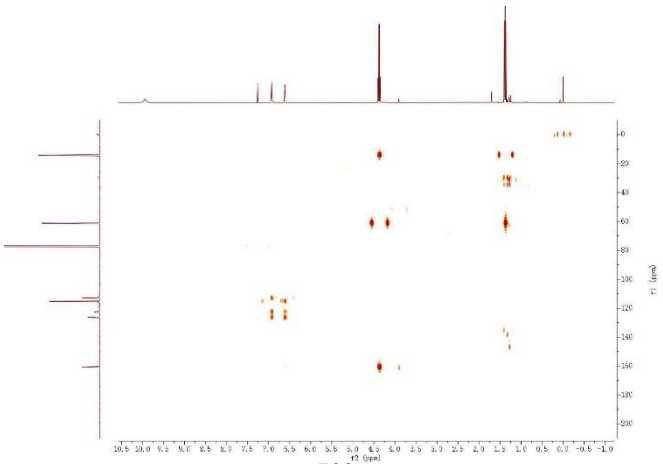
H-H COSY

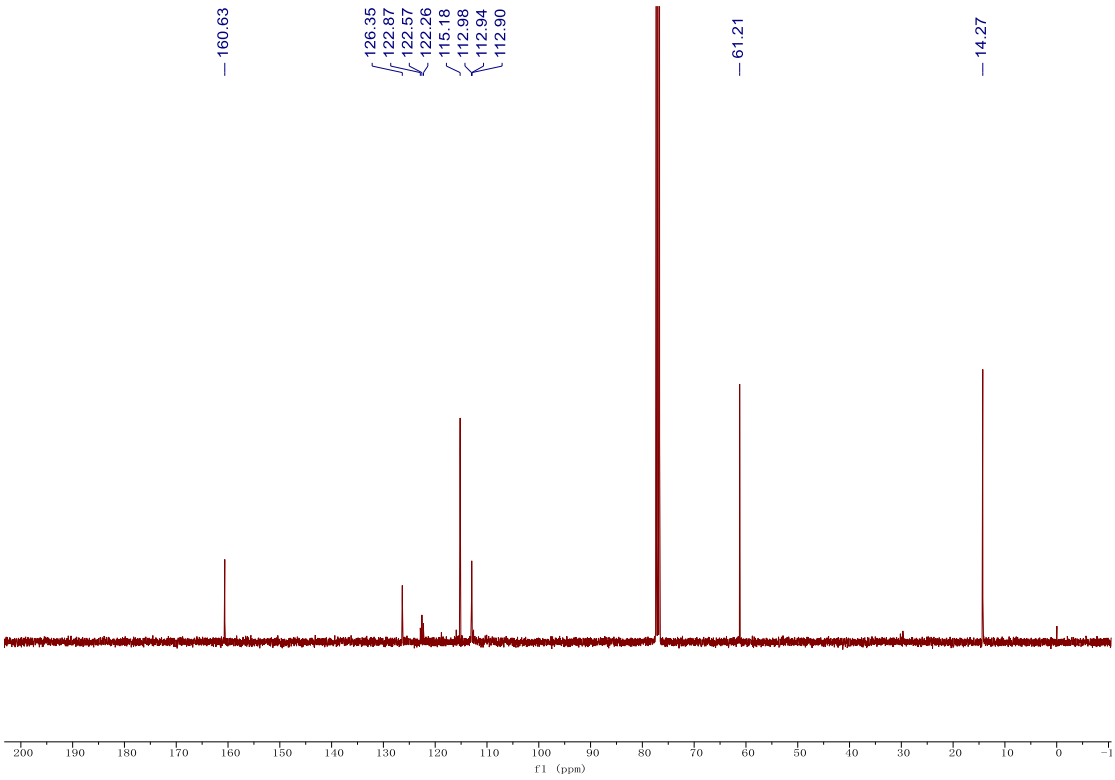


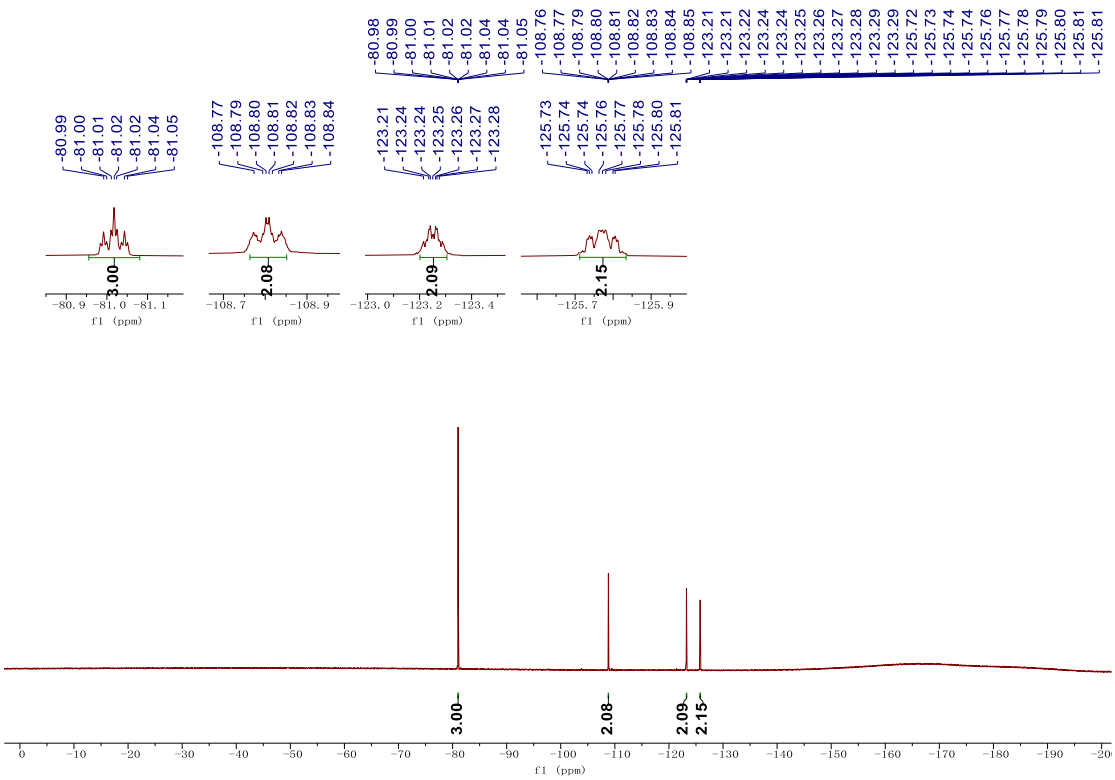
C-H HSQC



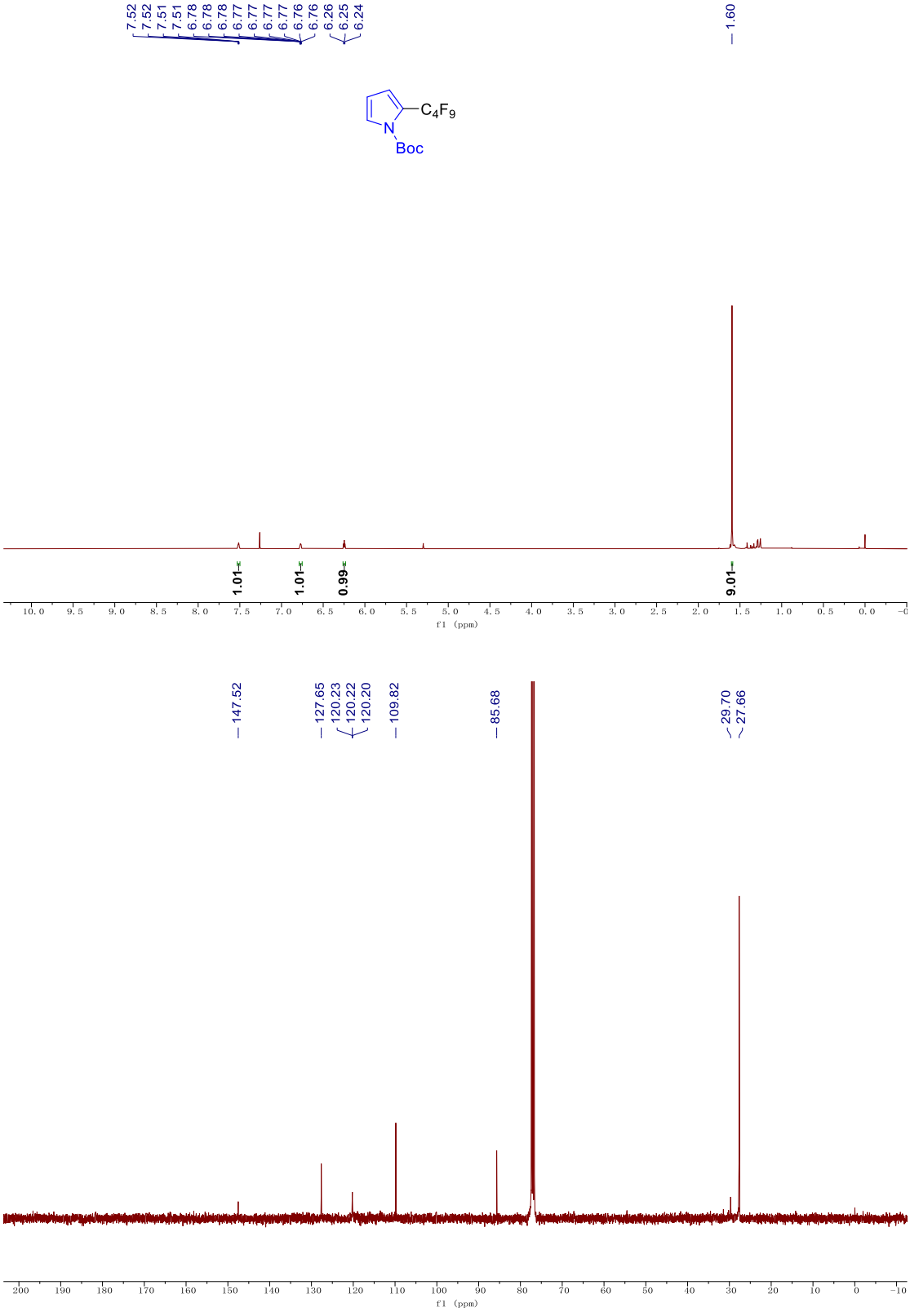
C-H HMBC

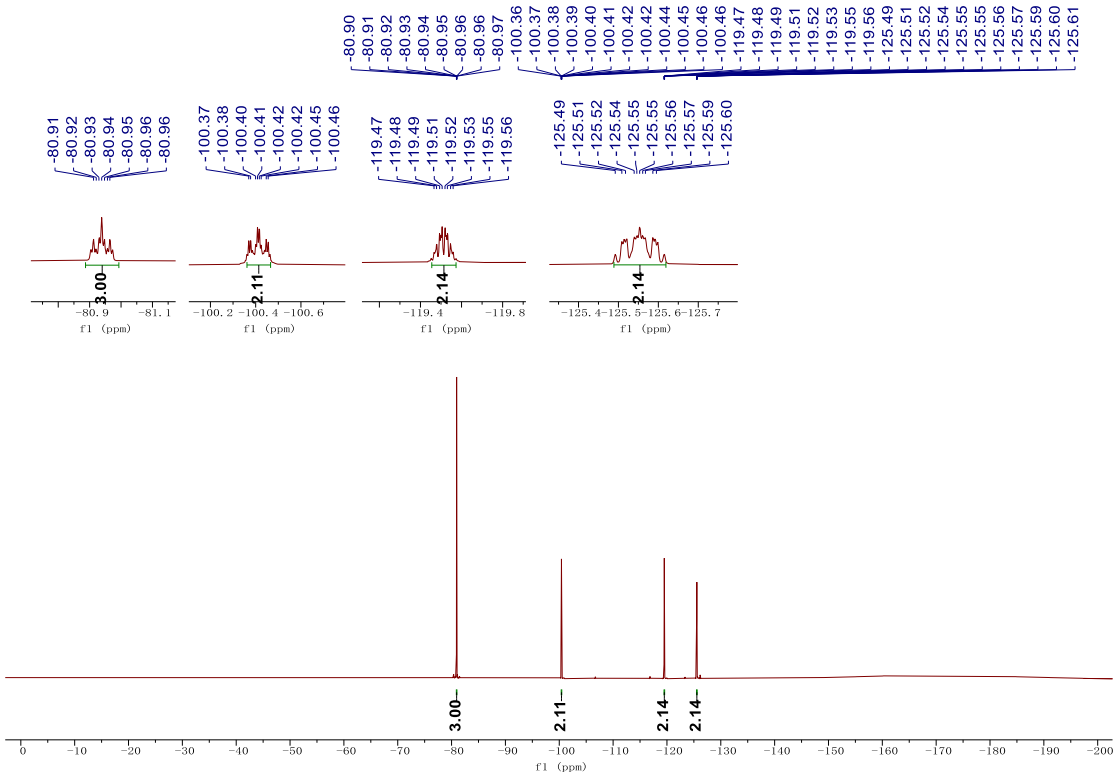



160.63
126.35
122.87
122.57
122.26
115.18
112.98
112.94
112.90
61.21
14.27
f1 (ppm)

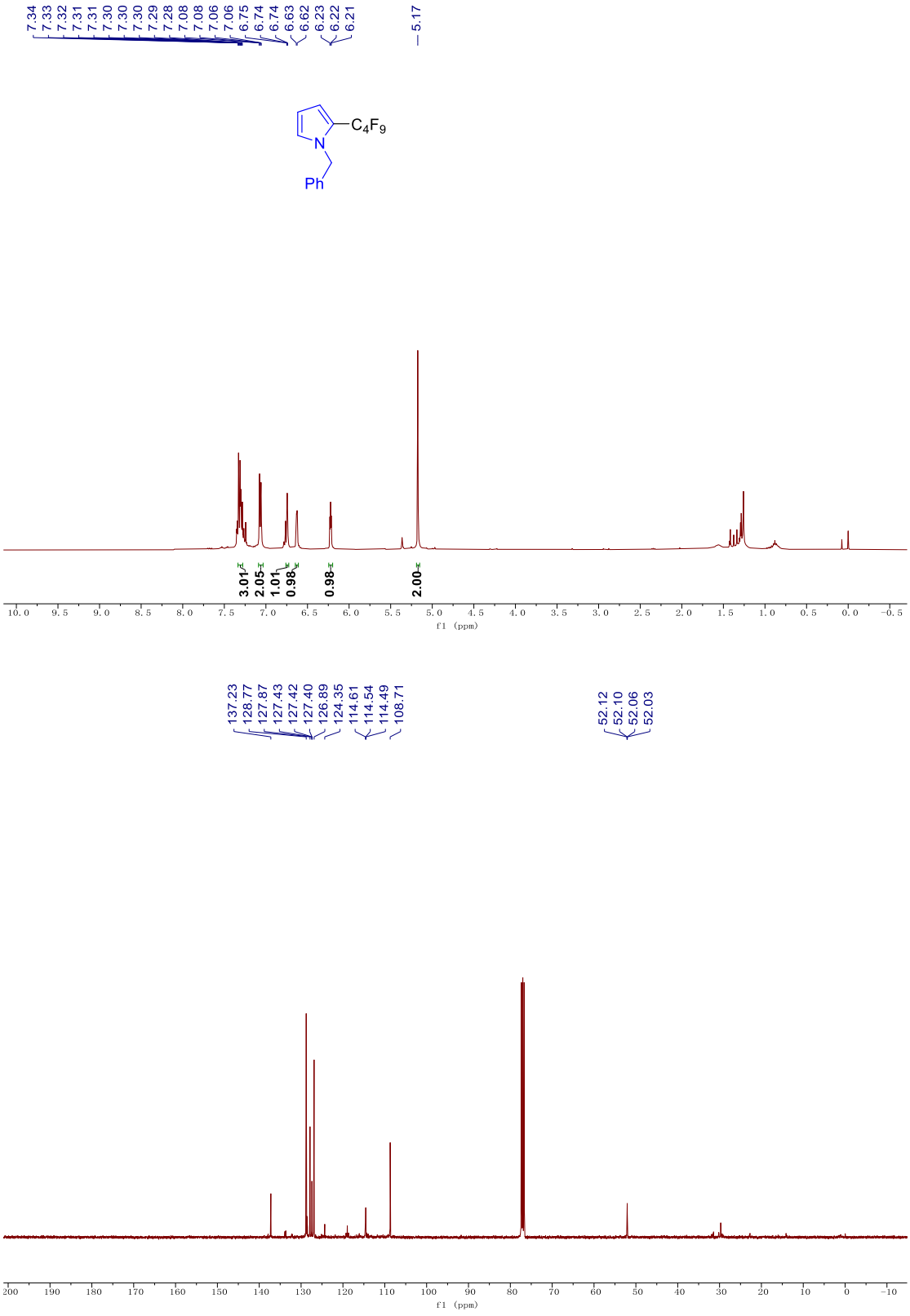

-80.98
-80.99
-81.00
-81.01
-81.02
-81.02
-81.04
-81.04
-81.05
-108.76
-108.77
-108.79
-108.80
-108.81
-108.82
-108.83
-108.84
-108.85
-123.21
-123.21
-123.22
-123.24
-123.24
-123.25
-123.26
-123.27
-123.28
-123.29
-123.29
-125.72
-125.73
-125.74
-125.74
-125.74
-125.76
-125.77
-125.78
-125.79
-125.80
-125.81
-125.81
3.00
2.08
2.09
2.15
f1 (ppm)

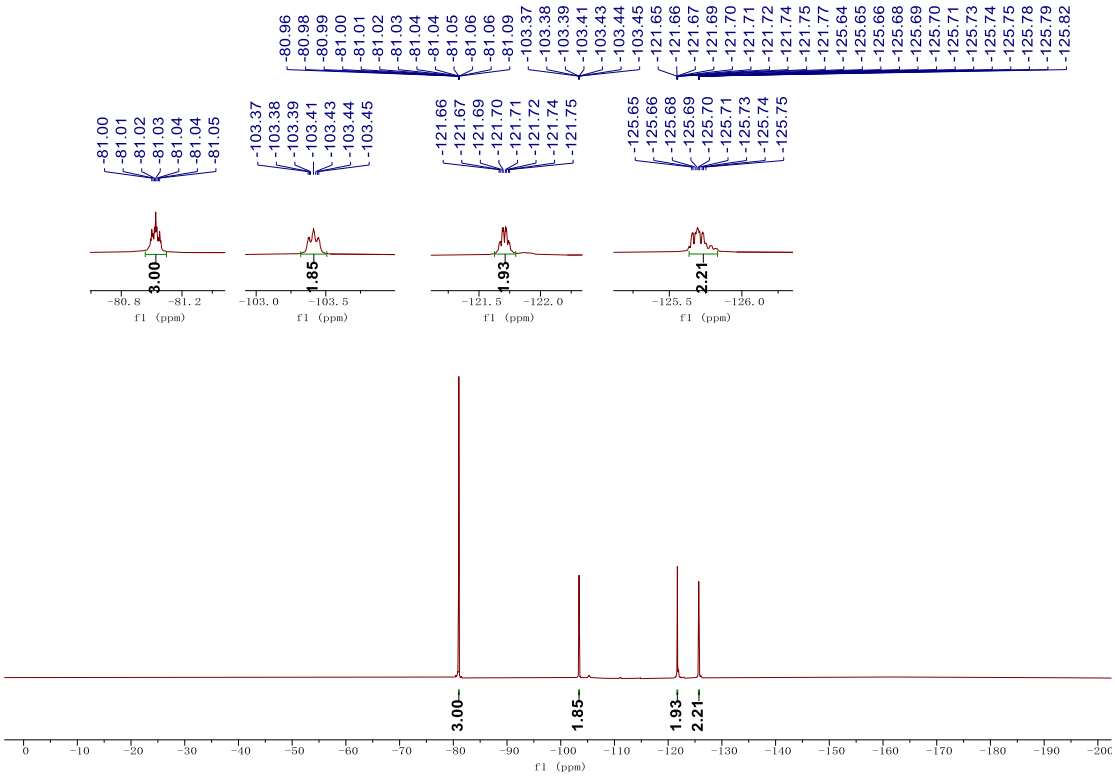
tert-butyl 2-(perfluorobutyl)-1*H*-pyrrole-1-carboxylate (7i)




-80.90
-80.91
-80.92
-80.93
-80.94
-80.95
-80.96
-80.96
-80.97
-100.36
-100.37
-100.38
-100.39
-100.40
-100.41
-100.42
-100.42
-100.44
-100.45
-100.46
-100.46
-119.47
-119.48
-119.49
-119.51
-119.52
-119.53
-119.55
-119.56
-125.49
-125.51
-125.52
-125.54
-125.55
-125.55
-125.56
-125.57
-125.59
-125.60
-125.61
3.00
2.11
2.14
2.14
f1 (ppm)

1-benzyl-2-(perfluorobutyl)-1*H*-pyrrole (7j)




-80.96
-80.98
-80.99
-81.00
-81.01
-81.02
-81.03
-81.04
-81.04
-81.05
-81.06
-81.06
-81.09
-103.37
-103.38
-103.39
-103.41
-103.43
-103.44
-103.45
-121.65
-121.66
-121.67
-121.69
-121.70
-121.71
-121.72
-121.74
-121.75
-121.77
-125.64
-125.65
-125.66
-125.68
-125.69
-125.70
-125.71
-125.73
-125.74
-125.75
-125.78
-125.79
-125.82
-81.00
-81.01
-81.02
-81.03
-81.04
-81.04
-81.05
-103.37
-103.38
-103.39
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-103.44
-103.45
-121.66
-121.67
-121.69
-121.70
-121.71
-121.72
-121.74
-121.75
-125.65
-125.66
-125.68
-125.69
-125.70
-125.71
-125.73
-125.74
-125.75
3.00
1.85
1.93
2.21
f1 (ppm)
3.00
1.85
1.93
2.21
f1 (ppm)