Visible-light-induced cross-coupling of aryl iodides with hydrazones via EDA complex

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1. General information
All reagents were purchased from commercial sources and used without further purification unless otherwise stated. $^1$H, $^{19}$F and $^{13}$C NMR spectra were recorded at room temperature on Varian Mercury plus 300 MHz, Bruker AV400 MHz and Agilent INOVA 600 MHz with TMS as an internal standard and CDCl$_3$ (unless otherwise stated) as solvent. All reactions were carried out in argon atmosphere unless otherwise stated. Silica gel (300-400 mesh) was used for flash column chromatography, eluting (unless otherwise stated) with an ethyl acetate/ petroleum ether (v/v =1/250) mixture. GC-MS analyses were made by Thermo Scientific Trace 1300 by means of EI. HRMS analyses were made at Lanzhou University, and Technical Institute of Physics and Chemistry & University of Chinese Academy of Sciences by means of ESI and EI. Melting points were measured on micro melting point apparatus and uncorrected. All solvents were purified and dried by standard techniques.

2. Optimization of the reaction conditions

\[
\begin{align*}
\text{Base, 6w Blue LED} & \quad \text{Solvent, 24h} \\
\begin{array}{c}
\text{1a} \\
\text{2a} \\
\text{3a}
\end{array}
\end{align*}
\]

2.1) Effects of bases$^a$

| Entry | Conditions | Yield (%)$^b$ |
|-------|------------|---------------|
| 1     | DABCO      | trace         |
| 2     | DBU        | trace         |
| 3     | K$_3$CO$_3$| 4             |
| 4     | LiOH       | 23            |
| 5     | KOH        | 58            |
| 6     | NaOH       | 61            |

$^a$ General conditions: 1a (0.4 mmol), 2a (0.2 mmol) and base (1.5 equiv) in solvent (DMSO 1.0 mL) irradiated by blue LEDs (425 nm, 3W$^x$2) for 24 h under an argon atmosphere at 35 $^\circ$C. $^b$ Yields were determined by $^1$H NMR using nitromethane as internal standard.

2.2) Effects of solvent$^a$

| Entry | Conditions | Yield (%)$^b$ |
|-------|------------|---------------|

2
2.3) Effects of ratio of substrates

| Entry | Conditions | Yield (%) |
|-------|------------|-----------|
| 1     | 2:1        | 58        |
| 2     | 4:1        | 66        |
| 3     | 1:1        | 32        |
| 4     | 1:2        | 45        |
| 5     | 1:4        | 45        |

2.4) The amount of base

| Entry | Conditions | Yield (%) |
|-------|------------|-----------|
| 1     | 1.5        | 66        |
| 2     | 2.0        | 69        |

2.5) Effects of co-solvent

| Entry | Conditions          | Yield (%) |
|-------|---------------------|-----------|
| 1     | DMSO                | 69        |
| 2     | DMSO+DMF (50 µL)    | 69        |

2.6) Effects of temperature
| Entry | Conditions | Yield (%)<sup>b</sup> |
|-------|------------|---------------------|
| 1     | 35 °C      | 69                  |
| 2     | 15 °C      | 73                  |

<sup>a</sup>General conditions: 1a (0.8 mmol), 2a (0.2 mmol) and NaOH (2.0 equiv) in solvent [ DMSO (1.0 mL) + DMF (50.0 µL)] irradiated by blue LEDs (425 nm, 3W²2) for 24 h under an argon atmosphere. <sup>b</sup>Yields were determined by <sup>1</sup>H NMR using nitromethane as internal standard.

2.7) Effects of reaction time<sup>a</sup>

| Entry | Conditions | Yield (%)<sup>b</sup> |
|-------|------------|---------------------|
| 1     | 12 h       | 70                  |
| 2     | 24 h       | 73                  |
| 3     | 36 h       | 69                  |

<sup>a</sup>General conditions: 1a (0.8 mmol), 2a (0.2 mmol) and NaOH (2.0 equiv) in solvent [ DMSO (1.0 mL) + DMF (50.0 µL)] irradiated by blue LEDs (425 nm, 3W²2) for 24 h under an argon atmosphere at 15 °C. <sup>b</sup>Yields were determined by <sup>1</sup>H NMR using nitromethane as internal standard.

2.8) Effects of air<sup>a</sup>

| Entry | Conditions | Yield (%)<sup>b</sup> |
|-------|------------|---------------------|
| 1     | air atmosphere | 73              |
| 2     | argon atmosphere | 73            |

<sup>a</sup>General conditions: 1a (0.8 mmol), 2a (0.2 mmol) and NaOH (2.0 equiv) in solvent [ DMSO (1.0 mL) + DMF (50.0 µL)] irradiated by blue LEDs (425 nm, 3W²2) for 24 h at 15 °C. <sup>b</sup>Yields were determined by <sup>1</sup>H NMR using nitromethane as internal standard.

3. General procedure for C–C coupling

In the glove box, NaOH (0.4 mmol 16.0 mg) was added into a test tube (20.0 mL) charged with a magnetic stir bar. Then, the tube was moved out of the glovebox, followed by the addition of DMSO (1.0 mL), DMF (50.0 µL), hydrazone (0.8 mmol) and alkyl halide (0.2 mmol), sealed and the mixture was irradiated by 425 nm 3W²2 blue LED for 24 h under an air atmosphere at 15 °C. Brine (10.0 mL) was added to the reaction system. The mixture was extracted with EA (20.0 mL × 3), and the combined organic phase was dried over Na₂SO₄, filtered and concentrated. The product diphenylmethane (3a) was isolated by flash chromatography on silica gel with PE/EA (250/1(v/v)).
4. The promotion of light on the reaction

23% yield of 3a was obtained in dark indicating that nucleophilic substitution process was possible. To further investigate this pathway, different substrates were reacted at high temperature in absence of light, obtaining very low yield of products (2% yield of 3v, trace amounts of 3m) (Scheme S1). We increased the reaction’s temperature without light, and the yield of 3a increased at first and then decreased. The highest yield (50%) was obtained when heated at 60 °C, which was also lower than visible-light induced condition at 15 °C (73%). Further increasing the temperature lowered the yield because of competitive Wolff-Kishner-Huang reaction of 1a under basic conditions. For product 3v and 3m, when increasing the reaction temperature in dark, the yields were much lower than visible-light induced condition at 15 °C (60% for 3v and 50% for 3m, respectively). These results indicated that light was important for this transformation. On the other hand, the DFT calculations indicated that free energy barrier of an intermolecular aromatic nucleophilic substitution was as high as 30.0 kcal mol⁻¹ (see Figure S2 in SI). Therefore, in the absence of light, the experimental results can only obtain low to trace yields. These controlling experiments and DFT calculations results indicated that visible light has a great promoting effect on the reaction.

![Scheme S1 Control experiments of different substrates under dark conditions.](image-url)
5. Deuterium labelling experiment

We have carried out several deuterium labeling experiments, 0.4 mmol D$_2$O was added to the reaction system under the standard conditions (DMSO solvent), the yield was deceased to 44%. However, no deuterated product was detected. The same result was obtained using NaOD (40% in D$_2$O) instead of NaOH (Scheme S2a). Considering that the deuterium atom at the benzyl position may be exchanged with DMSO solvent under basic conditions leading to the above results, to further confirm this hypothesis, DMSO-\textit{d}$_6$ (1.0 mL) was used as solvent instead of DMSO, and obtained the deuterated product 3v-\textit{d} (70% D) in 48% yield under standard conditions (Scheme S2b). Directly using diphenylmethane 3v as starting material in DMSO-\textit{d}$_6$ (1.0 mL) under basic conditions, the hydrogen atoms at the benzylic position were completely exchanged with/without light (Scheme S2c). These results can explain why no deuterated products were obtained when adding D$_2$O or using NaOD (due to the hydrogen/deuterium atoms at the benzyl position can easily exchange with DMSO solvent under basic condition). The similar results for \textalpha-trideuteration of methylarenes have been reported with DMSO-\textit{d}$_6$ in the presence of NaOH (\textit{Org. Chem. Front.}, 2021, 8, 2981).

Scheme S2 Deuterium labeling experiments.

6. Scale-up experiment
In glovebox, NaOH (3.0 mmol, 120.0 mg) were added into a round bottom flask (25.0 mL) charged with a magnetic stir bar. Then, the flask was moved out of the glovebox, followed by the addition of DMSO (7.5 mL), DMF (0.35 mL), hydrazone 1a (6.0 mmol) and aryl halide 2a (1.5 mmol), sealed, and the mixture was irradiated by 425 nm blue LEDs (3W⁴) for 24 h under an air atmosphere at 15 °C. Brine (10.0 mL) was added to the reaction system. The mixture was extracted with EA (30.0 mL × 3), and the combined organic phase was dried over Na₂SO₄, filtered and concentrated. The product 3a (colorless liquid, 180 mg, 55% yield) was isolated by flash chromatography on silica gel with PE/EA (250/1 (v/v)).

7. Computational details

7.1 Complete reference for Gaussian 09

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; and Fox, D. J. Gaussian 09, revision D.01; Gaussian, Inc.: Wallingford, CT, 2013.

7.2 Computational methods.

All DFT calculations were carried out using Gaussian 09 program. All geometry optimizations and frequency calculations in this paper were performed with the B3LYP
functional\cite{1,2} including Grimme’s D3 (BJ-damping) dispersion corrections\cite{3} in implicit dimethylsulfoxide using at 6-31G(d) basis set (SDD basis set\cite{4} for I and Na) by using the Solvation Model Based on Density (SMD)\cite{5} with the keyword in the Gaussian code route section “SCRF=(SMD,Solvent=dimethylsulfoxide). The vibrational frequencies were computed at the same level of theory as for the geometry optimizations to confirm whether each optimized structure is an energy minimum or a transition state and to evaluate the zero-point vibrational energy (ZPVE) and thermal corrections. The single-point energies were computed with the M062X functional\cite{6} including Grimme’s D3 dispersion corrections\cite{7} using a higher-level basis set 6-311+G(d,p) basis set (SDD basis set for I and Na). The TDDFT/B3LYP-D3(BJ)/6-31G(d)-SDD/SMD(DMSO) method was applied to optimize the geometry of the lowest singlet excited state. The frontier molecular orbital (FMO) analyses were generated using VMD\cite{8} and Multiwfn\cite{9}. The 3D diagrams of molecules were generated using CYLView\cite{10}.

\[ \Delta G_{\text{M062X-D3,DMSO}} = \Delta E_{\text{B3LYP-D3(BJ),DMSO}} \]

Figure S1. Free energy profile for the homo-coupling of phenyl radical D. The energy values are in kcal mol\(^{-1}\) and represent the relative free energies calculated at M062X-D3/6-311+G(d,p)-SDD/SMD(DMSO)/B3LYP-D3(BJ)/6-31G(d)-SDD/SMD(DMSO) level of theory in DMSO solvent.
Figure S2. Free energy profile for the nucleophilic substitution of benzylidenehydrazinide 5′ with iodobenzene 2b. The energy values are in kcal mol⁻¹ and represent the relative free energies calculated at M062X-D3/6-311+G(d,p)-SDD/SMD(DMSO)//B3LYP-D3(BJ)/6-31G(d)-SDD/SMD(DMSO) level of theory in DMSO solvent.

7.3 DFT calculations for the radical substitution (SRN)

As shown in Figure S3, when hydrazone radical C is formed, the calculated activation free energy for the direct radical substitution between hydrazone radical and iodobenzene 2b via 16-ts is 31.4 kcal mol⁻¹, leading to the iodine radical and benzhydryldiazene intermediate E. Moreover, the calculated activation free energy for the radical substitution between 7 and iodobenzene 2b through transition state 17-ts is as high as 28.1 kcal mol⁻¹. The activation energies of these two pathways are much higher than the corresponding radical coupling pathway via transition states 8-ts. Therefore, the radical coupling of C with D is a favorable pathway due to the low energy barriers.

Figure S3. Free energy profiles for the radical substitution of hydrazone radical C with iodobenzene 2b. The energy values are in kcal mol⁻¹ and represent the relative free energies calculated at M062X-D3/6-311+G(d,p)-SDD/SMD(DMSO)//B3LYP-D3(BJ)/6-31G(d)-SDD/SMD(DMSO) level of theory in DMSO solvent.
7.4 Computational Methods Thermal correction to Gibbs free energy, thermal correction to enthalpy, electronic energies and Gibbs free energies (in Hartree) of structures calculated at the M062X-D3/6-311+G(d,p)-SDD/SMD(DMSO)//B3LYP-D3(BJ)/6-31G(d)-SDD/SMD(DMSO) level of theory.

| Geometry | Thermal Correction to Free Energy | Thermal Correction to Enthalpy | Electronic Energy | Gibbs Free Energy | Imaginary |
|----------|----------------------------------|--------------------------------|-------------------|-------------------|-----------|
| 1b       | 0.107356                         | 0.148421                       | -380.973558       | -380.866202       |           |
| 2'       | 0.201158                         | 0.281080                       | 1897.670502       | 1897.469344       |           |
| 3'       | 0.330408                         | 0.431418                       | 2278.667380       | 2278.336972       |           |
| 4-ts     | 0.325604                         | 0.426613                       | 2278.667549       | 3439.125812       | 977.12i   |
| 5'       | 0.308207                         | 0.404252                       | 2202.228786       | 2201.920579       |           |
| DMSO     | 0.051181                         | 0.086338                       | -553.163715       | -553.112534       |           |
| A        | 0.093210                         | 0.133651                       | -380.466042       | -380.372832       |           |
| G'       | 0.268002                         | 0.356072                       | 2374.920338       | 2374.652336       |           |
| 6w       | 0.171217                         | 0.232830                       | -623.447594       | -623.276377       |           |
| 6r       | 0.165063                         | 0.229806                       | -623.378845       | -623.213782       |           |
| 2b       | 0.058570                         | 0.097170                       | -242.970170       | -242.9116         |           |
| 1'       | -0.016848                        | 0.002360                       | -11.552529        | -11.569377        |           |
| C        | 0.092795                         | 0.134204                       | -380.321994       | -380.229199       |           |
| D        | 0.059711                         | 0.093067                       | -231.518774       | -231.459063       |           |
| 7        | 0.307309                         | 0.405147                       | 2202.073839       | -2201.76653       |           |
| 8-ts     | 0.388530                         | 0.498859                       | 2374.609169       | 2433.220639       | 58.24i    |
| E        | 0.179849                         | 0.233718                       | 2433.369709       | 2433.220639       |           |
| 9-ts     | 0.359173                         | 0.511766                       | 2509.666477       | 2509.268304       | 898.28i   |
| H2O      | 0.003229                         | 0.024684                       | -76.429043        | -76.425814        |           |
| N2       | -0.012839                        | 0.008914                       | -109.515412       | -109.528251       |           |
| F        | 0.159156                         | 0.207072                       | -501.850324       | -501.850324       |           |
| 10-ts    | 0.176103                         | 0.229589                       | -578.424297       | -578.248194       | 799.43i   |
7.5 B3LYP-D3(BJ) geometries for all the optimized compounds and transition states.

1b

| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| C    | -2.781962 | 0.265004 | 0.009811 |
| C    | -1.877858 | -1.334367 | 0.000897 |
| C    | -0.506889 | -1.097256 | -0.008898 |
| C    | -0.010565 | 0.219925 | -0.008670 |
| C    | -0.925436 | 1.286054 | -0.000327 |
| H    | -3.851668 | -0.454400 | 0.016562 |
| H    | -2.246910 | -2.356573 | 0.000962 |
| C    | 1.425065 | 0.512344 | -0.012958 |
| N    | 2.307987 | -0.421959 | 0.003970 |
| H    | 1.717266 | 1.569866 | -0.030234 |
| N    | 3.268908 | -0.058793 | -0.084239 |
| H    | 4.209062 | -0.744589 | -0.000962 |

1a

| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| C    | 3.396655 | -1.673334 | 0.697536 |
| C    | 2.203121 | -0.948186 | 0.657277 |
| C    | 2.158474 | 0.309945 | 0.033790 |
| C    | 3.334110 | 0.833812 | -0.530460 |
| C    | 4.519650 | 0.102012 | -0.505790 |
| C    | 4.553196 | -1.154872 | 0.109280 |
| H    | 3.423704 | -2.645646 | 1.195328 |
| H    | 1.311160 | -1.352938 | 1.137324 |
| C    | 0.930919 | 1.175385 | 0.024438 |
| H    | 5.424129 | 0.513523 | -0.960472 |
| C    | 3.268860 | 1.824306 | -0.987850 |
| O    | 1.054442 | 2.392172 | 0.055615 |
| C    | -0.425790 | 0.555854 | -0.020100 |
| C    | -1.514593 | 1.325525 | 0.420478 |
| O    | -0.686460 | -0.723988 | -0.549763 |

C    | -2.818239 | 0.840580 | 0.373733 |
| H    | -1.316555 | 2.326159 | 0.808860 |
| C    | -1.983155 | -1.215624 | -0.617746 |
| H    | 0.129677 | -1.332070 | -0.941326 |
| C    | -3.062012 | -0.442835 | -0.149845 |
| H    | -3.635394 | 1.460888 | 0.739730 |
| H    | -2.194594 | -2.199594 | -0.104042 |
| O    | -7.621520 | 0.907386 | 0.165152 |
| C    | -5.383955 | -0.029813 | 1.024581 |
| H    | 5.484117 | -1.762908 | 0.135200 |

2'    

| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| O    | -0.937382 | -0.837109 | -1.881807 |
| H    | -0.823082 | -1.282304 | -2.733722 |
| Na   | 0.094228 | 0.286005 | -0.275488 |
| S    | 0.591923 | 2.789540 | 0.769132 |
| O    | 0.666730 | -1.306783 | 1.223363 |
| C    | -1.111803 | 3.060310 | 0.195330 |
| H    | -1.198944 | -1.004020 | -0.139114 |
| H    | -1.773899 | -2.895193 | 1.050227 |
| H    | -1.290457 | 2.633893 | -0.628301 |
| C    | 1.362887 | -2.846618 | -0.878475 |
| H    | 2.416991 | -2.579742 | -0.768540 |
| H    | 1.279889 | -3.864390 | -1.268150 |
| H    | 0.814622 | -2.129350 | -1.507110 |
| S    | -3.137451 | 1.543018 | -0.191085 |
| O    | -1.851262 | 1.403095 | 0.647510 |
| C    | -3.623458 | -1.079550 | 0.693911 |
| H    | -4.548411 | -0.060490 | -1.277172 |
| H    | -2.777017 | -0.508010 | -1.302535 |
| C    | -3.776651 | -0.742717 | 0.196715 |
| C    | -4.473476 | 1.860889 | 0.999670 |
8. Characterization data

1-(3-chlorobenzyl)-2-fluorobenzene (3a)
Colorless liquid, 32.6 mg, 74% yield. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.23 – 7.16 (m, 4H), 7.13 (t, $J$ = 7.4 Hz, 1H), 7.11 – 7.01 (m, 3H), 3.96 (s, 2H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 161.0 (d, $J_{C-F}$ = 245.1 Hz), 141.9, 134.3, 131.0 (d, $J_{C-F}$ = 4.3 Hz), 129.7, 128.9, 128.3 (d, $J_{C-F}$ = 8.1 Hz), 127.2 (d, $J_{C-F}$ = 15.9 Hz), 126.9, 126.5, 124.2 (d, $J_{C-F}$ = 3.3 Hz), 115.5 (d, $J_{C-F}$ = 21.9 Hz), 34.5 (d, $J_{C-F}$ = 2.8 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -117.70 (m, 1F). IR (KBr): 3436, 1635, 1242, 678 cm$^{-1}$. MS (EI, m/z%): 220.00 (M$^+$, 45.35), 185.05 (100.00), 165.07 (46.55), 183.04 (36.65), 91.12 (17.27), 184.07 (15.88), 222.00 (13.96), 186.07 (13.91), 109.05 (13.83), 83.01 (11.19), 91.79 (9.57), 81.08 (8.97). HRMS (EI) calcd. for C$_{13}$H$_{10}$ClF$^+$ [M$^+$]: 220.0450; Found: 220.0448.

1-(4-chlorobenzyl)-2-fluorobenzene (3b)
Colorless liquid, 29.5 mg, 67% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32 – 7.26 (m, 2H), 7.25 – .21 (m, 1H), 7.18 – 7.14 (m, 3H), 7.13 – 7.03 (m, 2H), 4.00 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 160.9 (d, $J_{C-F}$ = 245.5 Hz), 138.3, 132.0, 130.9 (d, $J_{C-F}$ = 4.5 Hz), 130.1, 128.6, 128.2 (d, $J_{C-F}$ = 8.1 Hz), 127.5 (d, $J_{C-F}$ = 15.8 Hz), 124.2 (d, $J_{C-F}$ = 3.6 Hz), 115.4 (d, $J_{C-F}$ = 21.9 Hz), 34.2 (d, $J_{C-F}$ = 3.1 Hz). $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -117.74 – -117.82 (m, 1F). IR (KBr): 3441, 2078, 1635, 1247, 682 cm$^{-1}$. MS (EI, m/z%): 220.03 (M$^{++}$, 51.35), 185.05 (100.00), 165.06 (45.86), 183.04 (38.84), 91.93 (17.44), 82.03 (16.25), 222.01 (15.99), 184.07 (15.70), 91.11 (15.01), 186.07 (14.19), 89.06 (11.68), 83.00 (9.85), 109.06 (9.36), 81.09 (9.34), 63.05 (7.66). HRMS (EI) calcd. for C$_{13}$H$_{10}$ClF$^{++}$ [M$^{++}$]: 220.0450; Found: 220.0447.
1-(4-bromobenzyl)-2-fluorobenzene (3c)
Colorless liquid, 21.2 mg, 44% yield. \( ^1H \) NMR (600 MHz, CDCl\(_3\)) \( \delta \) 7.39 (d, \( J = 8.0 \) Hz, 2H), 7.20 (q, \( J = 7.3 \) Hz, 2H), 7.12 (t, \( J = 7.5 \) Hz, 1H), 7.10 – 7.01 (m, 4H), 3.94 (s, 2H). \( ^{13}C \) NMR (151 MHz, CDCl\(_3\)) \( \delta \) 160.9 (d, \( J_{C-F} = 245.3 \) Hz), 138.9, 131.6, 130.9 (d, \( J_{C-F} = 4.2 \) Hz), 130.5, 128.2 (d, \( J_{C-F} = 8.1 \) Hz), 127.4 (d, \( J_{C-F} = 15.9 \) Hz), 124.2, 120.1, 115.4 (d, \( J_{C-F} = 22.1 \) Hz), 34.3. \( ^19F \) NMR (282 MHz, CDCl\(_3\)) \( \delta \) -118.12 – -118.20 (m, 1F). IR (KBr): 2923, 1487, 1231, 754 cm\(^{-1}\). MS (EI, m/z %): 264.14 (M\(^+\), 20.74), 185.22 (100.00), 165.20 (98.69), 183.18 (55.18), 91.30 (35.15), 92.12 (32.09), 82.16 (28.75), 109.13 (21.37), 184.24 (20.17).

\(^1H\) and \(^{13}C\) NMR data agreed with the literature\(^{[11]}\)

\[ \begin{align*}
\text{F} & \text{F} \\
& \text{F} \\
& \text{F}
\end{align*} \]

1-fluoro-2-(3-fluorobenzyl)benzene (3d)
Colorless liquid, 29.0 mg, 71% yield. \( ^1H \) NMR (600 MHz, CDCl\(_3\)) \( \delta \) 7.24 – 7.16 (m, 2H), 7.13 (td, \( J = 7.5 \), 1.7 Hz, 1H), 7.07 – 7.01 (m, 2H), 6.98 (d, \( J = 7.6 \) Hz, 1H), 6.91 – 6.85 (m, 2H), 3.97 (s, 2H). \( ^{13}C \) NMR (151 MHz, CDCl\(_3\)) \( \delta \) 163.0(d, \( J_{C-F} = 245.7 \) Hz), 160.9 (d, \( J_{C-F} = 245.6 \) Hz), 142.4 (d, \( J_{C-F} = 7.1 \) Hz), 131.0 (d, \( J_{C-F} = 4.3 \) Hz), 129.9 (d, \( J_{C-F} = 8.2 \) Hz), 128.3 (d, \( J_{C-F} = 8.0 \) Hz), 127.3 (d, \( J_{C-F} = 15.8 \) Hz), 124.4 (d, \( J_{C-F} = 1.7 \) Hz), 124.2 (d, \( J_{C-F} = 3.3 \) Hz), 115.6 (d, \( J_{C-F} = 21.3 \) Hz), 115.4 (d, \( J_{C-F} = 22.0 \) Hz), 113.1 (d, \( J_{C-F} = 21.0 \) Hz), 34.6. \( ^19F \) NMR (376 MHz, CDCl\(_3\)) \( \delta \) -113.41 – -113.51 (m, 1F), -117.76 – -117.80 (m, 1F). IR (KBr): 3446, 2077, 1635, 750 cm\(^{-1}\). MS (EI, m/z%): 204.06 (M\(^+\), 100.00), 203.06 (81.80), 183.05 (60.94), 109.05 (43.86), 83.02 (21.25), 201.04 (21.22), 184.06 (20.95), 107.03 (14.43), 205.05 (13.51), 91.10 (10.82), 57.03 (9.89), 91.96 (9.35). HRMS (EI) calcd. for C\(_{13}H_{10}F_2\)\(^+\) [M\(^+\): 204.0745; Found: 204.0745.

\[ \begin{align*}
\text{F} & \text{F} \\
& \text{F} \\
& \text{F}
\end{align*} \]

1-fluoro-2-(4-fluorobenzyl)benzene (3e)
Colorless liquid, 26.0 mg, 64% yield. \( ^1H \) NMR (600 MHz, CDCl\(_3\)) \( \delta \) 7.20 – 7.13 (m, 3H), 7.11 (td, \( J = 7.6 \), 1.7 Hz, 1H), 7.06 – 7.00 (m, 2H), 6.97 – 6.93 (m, 2H), 3.95 (s,
Bis(2-fluorophenyl)methane (3f)

Colorless liquid, 22.8 mg, 56% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.22 – 7.13 (m, 4H), 7.07 – 7.01 (m, 4H), 4.02 (s, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 161.1 (d, J_C,F = 245.2 Hz), 132.0 (d, J_C,F = 3.02 Hz), 128.1 (d, J_C,F = 8.1 Hz), 126.7 (d, J_C,F = 15.7 Hz), 124.1, 115.3 (d, J_C,F = 21.8 Hz), 27.8. ¹⁹F NMR (376 MHz, CDCl₃) δ -117.76 – -117.82 (m, 2F). IR (KBr): 3438, 2078, 1635, 1234, 752 cm⁻¹. MS (EI, m/z%): 204.07 (M⁺, 100.00), 203.05 (78.13), 183.05 (59.29), 109.06 (40.21), 184.05 (20.96), 83.04 (19.29), 201.04 (17.50), 205.06 (14.26), 107.04 (12.85), 108.07 (10.98), 91.16 (10.01), 91.98 (8.96), 57.04 (8.34), 81.07 (8.26). HRMS (EI) calcd. for C₁₃H₁₀F₂⁺ [M⁺]: 204.0745; Found: 204.0744.

1-fluoro-2-(2-methylbenzyl)benzene (3g)

Colorless liquid, 6.0 mg, 15% yield. ¹H NMR (600 MHz, CDCl₃) δ 7.20 – 7.13 (m, 4H), 7.08 – 7.00 (m, 3H), 6.98 – 6.92 (m, 1H), 3.99 (s, 2H), 2.26 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 161.0 (d, J_C,F = 245.1 Hz), 137.5, 136.6, 130.6 (d, J_C,F = 4.5 Hz), 130.3, 129.7, 127.7 (d, J_C,F = 8.0 Hz), 127.3 (d, J_C,F = 15.8 Hz), 126.6, 126.0, 124.0 (d, J_C,F = 3.7 Hz), 115.1 (d, J_C,F = 21.9 Hz), 32.0 (d, J_C,F = 3.3 Hz), 19.5. ¹⁹F NMR (565 Hz, CDCl₃) δ -116.86 – -117.27 (m, 1F), -117.59 – -118.06 (m, 1F).

IR (KBr): 3044, 1509, 1229, 755 cm⁻¹. MS (EI, m/z%): 204.06 (M⁺, 100.00), 203.05 (79.10), 183.06 (60.01), 109.06 (50.62), 83.08 (24.48), 184.08 (22.45), 201.04 (22.16), 107.08 (16.41), 205.06 (14.13), 108.07 (13.48), 57.04 (12.19), 91.12 (11.93), 92.00 (9.71), 81.09 (9.37). HRMS (EI) calcd. for C₁₃H₁₀F₂⁺ [M⁺]: 204.0745; Found: 204.0744.
MHz, CDCl$_3$) $\delta$ -117.60 – -117.64 (m, 1F). HRMS (EI) calcd. for C$_{14}$H$_{13}$F$^+$ [M]$^+$: 200.0996; Found: 200.0997.

1-fluoro-2-(3-methylbenzyl)benzene (3h)

Colorless liquid, 18.0 mg, 45% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.21 – 7.10 (m, 3H), 7.08 – 6.95 (m, 5H), 3.96 (s, 2H), 2.31 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 160.9 (d, $J_{C,F}$ = 245.2 Hz), 139.7, 138.1, 131.0 (d, $J_{C,F}$ = 4.7 Hz), 129.6, 128.4, 128.2 (d, $J_{C,F}$ = 15.9 Hz), 127.8 (d, $J_{C,F}$ = 8.0 Hz), 127.0, 125.8, 124.0 (d, $J_{C,F}$ = 3.6 Hz), 115.3 (d, $J_{C,F}$ = 22.1 Hz), 34.7 (d, $J_{C,F}$ = 3.0 Hz), 21.4. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -117.89 – -117.95 (m, 1F). IR (KBr): 3400, 2995, 1770, 1245, 672 cm$^{-1}$. MS (EI, m/z %): 200.08 (M$^+$, 77.19), 185.04 (100.00), 165.06 (35.04), 183.04 (28.63), 184.05 (15.77), 91.09 (14.25), 199.09 (11.94), 98.10 (10.95), 201.10 (10.05), 77.06 (9.75), 83.01(9.63). HRMS (EI) calcd. for C$_{14}$H$_{13}$F$^+$ [M]$^+$: 200.0994; Found: 200.0994.

1-(4-(tert-butyl)benzyl)-2-fluorobenzene (3i)

Colorless liquid, 27.6 mg, 57% yield. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.32 (d, $J$ = 8.3 Hz, 2H), 7.21 – 7.15 (m, 4H), 7.08 – 7.02 (m, 2H), 3.98 (s, 2H), 1.31 (s, 9H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 161.0 (d, $J_{C,F}$ = 245.1 Hz), 149.0, 136.8, 131.1 (d, $J_{C,F}$ = 4.5 Hz), 128.4, 128.2 (d, $J_{C,F}$ = 15.8 Hz), 127.8 (d, $J_{C,F}$ = 7.9 Hz), 125.4, 124.0 (d, $J_{C,F}$ = 3.3 Hz), 115.3 (d, $J_{C,F}$ = 22.1 Hz), 34.4, 34.3 (d, $J_{C,F}$ = 2.9 Hz), 31.4. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -117.92 (m, -117.89- -117.95, 1F). IR (KBr): 2963, 1514, 1268, 754 cm$^{-1}$. MS (EI, m/z %): 242.15 (M$^+$, 22.31), 109.07 (100.00), 227.11 (89.92), 228.13 (13.83), 99.54 (10.94), 91.13 (9.89), 83.05 (8.87), 110.09 (7.93), 98.16 (7.87), 89.05 (6.25), 183.07 (6.17), 113.65 (6.10), 92.07 (5.95), 98.76 (5.77), 105.10 (5.73). HRMS (EI) calcd. for C$_{17}$H$_{19}$F$^+$ [M]$^+$: 242.1465; Found: 242.1463.
4-(2-fluorobenzyl)-1,1'-biphenyl (3j)

Colorless liquid, 31.4 mg, 60% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.56 – 7.54 (m, 2H), 7.51 – 7.49 (m, 2H), 7.42 – 7.38 (m, 2H), 7.33 – 7.26 (m, 3H), 7.22 – 7.16 (m, 2H), 7.08 – 7.02 (m, 2H), 4.03 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 161.0 (d, $J_{C-F}$ = 245.3 Hz), 140.9, 139.2, 138.9, 131.0 (d, $J_{C-F}$ = 4.5 Hz), 129.2, 128.7, 128.0 (d, $J_{C-F}$ = 8.8 Hz), 127.9 (d, $J_{C-F}$ = 16.2 Hz) 127.2, 127.1, 127.0, 124.1 (d, $J_{C-F}$ = 3.6 Hz), 115.4 (d, $J_{C-F}$ = 22.0 Hz), 34.5 (d, $J_{C-F}$ = 3.0 Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -117.82 (m, 1F). IR (KBr): 3454, 2078, 1636, 753 cm$^{-1}$. MS (EI, m/z%): 262.09 (M$^+$, 100), 165.05 (49.82), 261.11 (20.29), 109.08 (19.62), 183.04 (19.51), 167.10 (18.98), 263.14 (18.68), 152.06 (17.36), 207.02 (16.74), 115.05 (11.96), 91.16 (8.60). HRMS (EI) calcd. for C$_{19}$H$_{15}$F$^+\ [M]^+$: 262.1152; Found: 262.1152.

1-(2-fluorobenzyl)-3,5-dimethylbenzene (3k)

Colorless liquid, 24.4 mg, 57% yield. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.16 (m, 2H), 7.03 (m, 2H), 6.84 – 6.83 (m, 3H), 3.92 (s, 2H), 2.27 (s, 6H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 161.0 (d, $J_{C-F}$ = 245.7 Hz), 139.7, 138.0, 131.1 (d, $J_{C-F}$ = 4.6 Hz), 128.3 (d, $J_{C-F}$ = 15.9 Hz), 127.9, 127.8 (d, $J_{C-F}$ = 8.0 Hz), 126.6, 124.0 (d, $J_{C-F}$ = 3.4 Hz), 115.3 (d, $J_{C-F}$ = 22.1 Hz), 34.6 (d, $J_{C-F}$ = 2.4 Hz), 21.3 $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -117.77 – -118.04 (m, 1F). IR (KBr): 3449, 1640, 754 cm$^{-1}$. MS (EI, m/z%): 214.12 (M$^+$, 68.21), 199.09 (100.00), 183.09 (25.71), 184.08 (25.19), 105.10 (23.18), 179.11 (18.09), 200.10 (17.24), 77.08 (13.41), 106.10 (12.36), 215.13 (11.42), 109.06 (10.77), 91.13 (10.57), 118.12 (9.86), 83.04 (8.85), 98.10 (8.66). HRMS (EI) calcd. for C$_{15}$H$_{15}$F$^+\ [M]^+$: 214.1152; Found: 214.1150.
2-chloro-4-(2-fluorobenzyl)-1-methylbenzene (3l)
Colorless liquid, 34.2 mg, 73% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.24 - 7.15\) (m, 2H), 7.14 – 7.11 (m, 2H), 7.06 – 6.98 (m, 3H), 3.92 (s, 2H), 2.31 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 160.9\) (d, \(J_{C-F} = 245.6\) Hz), 139.1, 134.3, 133.8, 130.9 (t, \(J_{C-F} = 2.2\) Hz, 2C), 129.2, 128.1 (d, \(J_{C-F} = 8.1\) Hz), 127.5 (d, \(J_{C-F} = 15.8\) Hz), 127.0, 124.1 (d, \(J_{C-F} = 3.6\) Hz), 115.4 (d, \(J_{C-F} = 22.0\) Hz), 34.1 (d, \(J_{C-F} = 3.1\) Hz), 19.6. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta -117.74 - -117.80\) (m, 1F). IR (KBr): 3452, 2077, 1638, 752 cm\(^{-1}\). MS (EI, m/z%): 234.02 (M\(^+\), 43.63), 199.07 (100), 183.07 (36.19), 98.10 (15.70), 179.09 (15.33), 236.02 (14.72), 200.10 (14.70) 109.07 (9.66), 77.04 (9.64), 85.07 (7.87). HRMS (EI) calcd. for C\(_{14}\)H\(_{12}\)ClF\(^+\): 234.0606; Found: 234.0606.

1-fluoro-2-(4-methoxybenzyl)benzene (3m)
Colorless liquid, 23.8 mg, 55% yield. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta 7.19 - 7.16\) (m, 1H), 7.13 (m, 3H), 7.07 – 6.99 (m, 2H), 6.83 (d, \(J = 8.5\) Hz, 2H), 3.94 (s, 2H), 3.78 (s, 3H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta 160.9\) (d, \(J_{C-F} = 245.6\) Hz), 158.1, 132.0, 130.9 (d, \(J_{C-F} = 4.5\) Hz), 129.7, 128.5 (d, \(J_{C-F} = 15.8\) Hz), 127.8 (d, \(J_{C-F} = 8.0\) Hz), 124.0 (d, \(J_{C-F} = 3.5\) Hz), 115.3 (d, \(J_{C-F} = 22.1\) Hz), 114.0, 55.3, 33.9 (d, \(J_{C-F} = 3.0\) Hz). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta -112.94 - -121.65\) (m, 1F). IR (KBr): 3444, 2079, 1639, 755 cm\(^{-1}\). MS (EI, m/z%): 216.10 (M\(^+\), 100.00), 121.08 (43.47), 215.10 (36.65), 185.07 (29.67), 201.08 (20.12), 183.06 (19.94), 152.09 (16.38), 77.08 (15.35), 165.08 (15.11), 109.07 (15.05), 217.09 (14.43), 171.07 (13.90), 91.12 (12.84), 153.09 (12.44), 170.06 (11.22). HRMS (EI) calcd. for C\(_{14}\)H\(_{13}\)FO\(^+\): 216.0945; Found: 216.0942.

1-fluoro-2-(4-(trifluoromethoxy)benzyl)benzene (3n)
Colorless liquid, 35.1 mg, 65% yield. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta 7.24 - 7.18\) (m, 3H), 7.17 – 7.10 (m, 3H), 7.09 – 7.01 (m, 2H), 3.99 (s, 2H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta 160.9\) (d, \(J_{C-F} = 245.6\) Hz), 139.1, 134.3, 133.8, 130.9 (t, \(J_{C-F} = 2.2\) Hz, 2C), 129.2, 128.1 (d, \(J_{C-F} = 8.1\) Hz), 127.5 (d, \(J_{C-F} = 15.8\) Hz), 127.0, 124.1 (d, \(J_{C-F} = 3.6\) Hz), 115.4 (d, \(J_{C-F} = 22.0\) Hz), 34.1 (d, \(J_{C-F} = 3.1\) Hz), 19.6. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta -117.74 - -117.80\) (m, 1F). IR (KBr): 3452, 2077, 1638, 752 cm\(^{-1}\). MS (EI, m/z%): 234.02 (M\(^+\), 43.63), 199.07 (100), 183.07 (36.19), 98.10 (15.70), 179.09 (15.33), 236.02 (14.72), 200.10 (14.70) 109.07 (9.66), 77.04 (9.64), 85.07 (7.87). HRMS (EI) calcd. for C\(_{14}\)H\(_{12}\)ClF\(^+\): 234.0606; Found: 234.0606.
CDCl$_3$ δ 161.0 (d, $J_{C,F} = 245.6$ Hz), 147.7, 138.6, 130.9 (d, $J_{C,F} = 4.4$ Hz), 130.0, 128.3 (d, $J_{C,F} = 8.0$ Hz), 127.4 (d, $J_{C,F} = 15.8$ Hz), 124.2 (d, $J_{C,F} = 3.5$ Hz), 121.0, 120.5 (q, $J_{C,F} = 256.7$ Hz) 115.5 (d, $J_{C,F} = 22.0$ Hz), 34.2 (d, $J_{C,F} = 2.7$ Hz).

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -57.91 (s, 3F), -117.75 – -117.81 (m, 1F).

IR (KBr): 3439, 2077, 1636, 754 cm$^{-1}$.

MS (EI, m/z\%): 270.02 (M$^+$, 55.65), 185.05 (100.00), 183.07 (42.79), 165.06 (31.78), 109.06 (22.37), 186.06 (13.80), 69.01 (13.23), 83.03 (12.04), 269.01 (11.27), 170.05 (11.02), 77.07 (6.10). HRMS (EI) calcd. for C$_{14}$H$_{10}$F$_4$O$^+$ [M$^+$]: 270.0662; Found: 270.0663.

F$_3$CF

1-fluoro-2-(4-(trifluoromethyl)benzyl)benzene (3o)
Colorless liquid, 32.0 mg, 63% yield. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.52 (d, $J = 7.6$ Hz, 2H), 7.31 (d, $J = 7.7$ Hz, 2H), 7.23 – 7.18 (m, 1H), 7.16 – 7.12 (m, 1H), 7.08 – 7.02 (m, 2H), 4.03 (s, 2H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 161.0 (d, $J_{C,F} = 245.7$ Hz), 144.1, 131.0 (d, $J_{C,F} = 4.4$ Hz), 129.0, 128.5 (d, $J_{C,F} = 8.1$ Hz), 127.0 (d, $J_{C,F} = 15.4$ Hz), 125.4 (q, $J_{C,F} = 3.4$ Hz), 124.4 (q, 271.8 Hz), 124.3 (d, $J_{C,F} = 3.7$ Hz), 115.5 (d, $J_{C,F} = 21.9$ Hz), 34.8 (d, $J_{C,F} = 3.1$ Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) δ -62.34 – -62.35 (m, 3F), -117.59 – -117.61 (m, 1F). IR (KBr): 3049, 2935, 1328, 1067, 754 cm$^{-1}$. MS (EI, m/z\%): 254.06 (M$^+$, 57.13), 185.09 (100.00), 165.09 (39.22), 183.06 (35.95), 109.06 (31.75), 186.09 (14.77), 83.03 (13.50), 184.09 (13.44), 91.56 (10.12), 107.06 (9.21), 255.07 (8.32), 233.05 (8.32), 253.07 (7.75), 235.06 (7.56), 63.07 (6.03). HRMS (EI) calcd. for C$_{14}$H$_{10}$F$_4$O$^+$ [M$^+$]: 254.0713; Found: 254.0713.

F

1-(2-fluorobenzyl)naphthalene (3p)
Colorless liquid, 23.6 mg, 50% yield. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.98 (d, $J = 6.5$ Hz, 1H), 7.87 – 7.86 (m, 1H), 7.77 (d, $J = 8.2$ Hz, 1H), 7.64 – 7.46 (m, 2H), 7.41 (t, $J = 7.6$ Hz, 1H), 7.27 (d, $J = 6.9$ Hz, 1H), 7.17 (m, 1H), 7.08 (t, $J = 9.1$ Hz, 1H), 7.00 – 6.91 (m, 2H), 4.45 (s, 2H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 160.8 (d, $J_{C,F} = 244.9$ Hz),
135.3, 133.9, 132.1, 130.8 (d, $J_{C,F} = 4.2$ Hz), 128.7, 127.8 (d, $J_{C,F} = 8.0$ Hz), 127.4 (d, $J_{C,F} = 16.2$ Hz), 127.3, 127.1, 126.1, 125.6, 125.5, 124.0 (d, $J_{C,F} = 3.4$ Hz), 123.9, 115.1 (d, $J_{C,F} = 22.0$ Hz), 31.4 (d, $J_{C,F} = 3.1$ Hz). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -117.59 – -117.64 (m, 1F). IR (KBr): 3447, 2086, 1639, 754 cm$^{-1}$. MS (EI, m/z%): 236.10 (M$^+$, 100.00), 235.10 (48.70), 106.99 (28.00), 215.10 (26.49), 115.10 (25.57), 141.11 (21.52), 220.08 (20.83), 221.09 (20.79), 233.08 (19.69), 237.12 (17.31), 107.99 (12.84), 139.07 (10.54), 216.10 (9.04), 103.50 (8.70), 94.55 (8.69). HRMS (EI) calcd. for C$_{17}$H$_{13}$F$^+$ [M$^+$]: 236.0996; Found: 236.0994.

![9-(2-fluorobenzyl)phenanthrene (3q)]

White solid, m.p.128-129 °C, 25.8 mg, 45% yield. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.72 (d, $J = 8.3$ Hz, 1H), 8.65 (d, $J = 8.3$ Hz, 1H), 8.01 (d, $J = 8.2$ Hz, 1H), 7.78 (d, $J = 7.9$ Hz, 1H), 7.64 – 7.59 (m, 2H), 7.57 – 7.54 (m, 2H), 7.51 (s, 1H), 7.20 – 7.17 (m, 1H), 7.12 – 7.09 (m, 1H), 7.01 – 6.99 (m, 1H), 6.96 – 6.93 (m, 1H), 4.48 (s, 2H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 160.9 (d, $J_{C,F} = 245.7$ Hz), 133.5, 131.8, 131.2, 130.8 (d, $J_{C,F} = 4.7$ Hz, 2C), 130.0, 128.3, 128.0 (d, $J_{C,F} = 8.0$ Hz), 127.8, 127.1 (d, $J_{C,F} = 15.5$ Hz), 126.7, 126.7, 126.3 (d, $J_{C,F} = 2.8$ Hz, 2C), 124.7, 124.1 (d, $J_{C,F} = 3.5$ Hz), 123.2, 122.5, 115.2 (d, $J_{C,F} = 22.1$ Hz), 31.9 (d, $J_{C,F} = 3.5$ Hz). IR (KBr): 2372, 1489, 1228, 747 cm$^{-1}$. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -117.57 – -117.63 (m, 1F). MS (EI, m/z %): 286.09 (M$^+$, 100.00), 285.09 (27.26), 287.07 (20.81), 191.09 (18.00), 189.07 (15.11), 283.08 (14.88), 165.06 (14.12), 270.05 (13.96), 265.08 (13.46), 131.57 (13.40), 135.24 (12.46), 133.01 (11.10), 143.15 (10.48), 271.08 (10.35). HRMS (EI) calcd. for C$_{21}$H$_{15}$F$^+$ [M$^+$]: 286.1152; Found: 286.1151.

![4-(4-(2-fluorobenzyl)phenyl)morpholine (3r)]
Colorless liquid, 23.3 mg, 43% yield. \( ^{1}H \text{ NMR} \) (600 MHz, CDCl\(_{3}\)) \( \delta \) 7.18 – 7.14 (m, 1H), 7.12 – 7.11 (m, 3H), 7.04 – 6.99 (m, 2H), 6.84 (d, \( J = 12.0 \text{Hz} \), 2H), 3.92 (s, 2H), 3.84 (t, \( J = 6.0 \text{Hz} \), 4H), 3.11 (s, 2H). \( ^{13}C \text{ NMR} \) (151 MHz, CDCl\(_{3}\)) \( \delta \) 160.9 (d, \( J_{C,F} = 245.0 \text{Hz} \)), 149.7, 131.4, 130.9 (d, \( J_{C,F} = 4.7 \text{Hz} \)), 129.5, 128.5 (d, \( J_{C,F} = 15.9 \text{Hz} \)), 127.7 (d, \( J_{C,F} = 8.0 \text{Hz} \)), 124.0 (d, \( J_{C,F} = 3.7 \text{Hz} \)), 66.9, 49.6, 33.9 (d, \( J_{C,F} = 3.0 \text{Hz} \)). \( ^{19}F \text{ NMR} \) (376 MHz, CDCl\(_{3}\)) \( \delta \) 118.06 – 118.12 (m, 1F). IR (KBr): 3445, 1635, 1515, 756 \text{cm}^{-1}. HRMS m/z (ESI) calcd. for C\(_{17}\)H\(_{19}\)FNO\(^{+}\) [M+H\(^{+}\)]: 272.1445; found: 272.1446.

\[\begin{array}{c}
\text{F} \\
\text{N} \\
\text{6-(2-fluorobenzyl)quinoline (3s)}
\end{array}\]

Colorless liquid, 34.6 mg, 75% yield. \( ^{1}H \text{ NMR} \) (600 MHz, CDCl\(_{3}\)) \( \delta \) 8.86 (s, 1H), 8.06 – 8.03 (m, 2H), 7.59 – 7.58 (m, 2H), 7.35 – 7.34 (m, 1H), 7.22 – 7.17 (m, 2H), 7.07 – 7.04 (m, 2H), 4.17 (s, 2H). \( ^{13}C \text{ NMR} \) (151 MHz, CDCl\(_{3}\)) \( \delta \) 161.0 (d, \( J_{C,F} = 245.8 \text{Hz} \)), 149.8, 147.2, 138.3, 135.7, 131.0 (d, \( J_{C,F} = 4.4 \text{Hz} \)), 130.9, 129.5, 128.3, 128.2 (d, \( J_{C,F} = 8.1 \text{Hz} \)), 127.4 (d, \( J_{C,F} = 15.7 \text{Hz} \)), 126.7, 124.2 (d, \( J_{C,F} = 3.5 \text{Hz} \)), 121.1, 115.4 (d, \( J_{C,F} = 22.0 \text{Hz} \)), 34.8 (d, \( J_{C,F} = 2.7 \text{Hz} \)). \( ^{19}F \text{ NMR} \) (376 MHz, CDCl\(_{3}\)) \( \delta \) -117.66 – -117.73 (m, 1F). IR (KBr): 3456, 2065, 1636, 754 \text{cm}^{-1}. HRMS m/z (ESI) calcd. for C\(_{16}\)H\(_{13}\)FN\(^{+}\) [M+H\(^{+}\)]: 238.1027; found: 238.1028.

\[\begin{array}{c}
\text{F} \\
\text{S} \\
\text{3-(2-fluorobenzyl)thiophene (3t)}
\end{array}\]

Colorless liquid, 22.3 mg, 58% yield. \( ^{1}H \text{ NMR} \) (600 MHz, CDCl\(_{3}\)) \( \delta \) 7.26 (m, 1H), 7.23 – 7.14 (m, 2H), 7.11 – 7.02 (m, 2H), 6.96 – 6.95 (m, 2H), 4.01 (s, 2H). \( ^{13}C \text{ NMR} \) (151 MHz, CDCl\(_{3}\)) \( \delta \) 160.9 (d, \( J_{C,F} = 245.4 \text{Hz} \)), 140.0, 130.8 (d, \( J_{C,F} = 4.5 \text{Hz} \)), 128.3, 128.0 (d, \( J_{C,F} = 8.0 \text{Hz} \)), 127.7 (d, \( J_{C,F} = 15.7 \text{Hz} \)), 125.6, 124.1 (d, \( J_{C,F} = 3.5 \text{Hz} \)), 121.4, 115.3 (d, \( J_{C,F} = 21.9 \text{Hz} \)), 29.5 (d, \( J_{C,F} = 3.1 \text{Hz} \)). \( ^{19}F \text{ NMR} \) (376 MHz, CDCl\(_{3}\)) \( \delta \) -118.13 – -118.38 (m, 1F). IR (KBr): 3444, 1639, 753 \text{cm}^{-1}. MS (EI, m/z\%): 192.05 (M\(^{+}\), 100.00), 97.04 (85.36), 191.04 (79.12), 96.04 (71.77), 83.04 (67.2), 193.06 (15.46), 159.07 (12.88), 133.07 (12.03), 109.07 (11.41), 147.08 (11.20), 85.08 (10.24),
146.08 (9.82), 171.06 (8.57), 69.03 (8.39), 63.07 (7.99). **HRMS** (EI) calcd. for C$_{11}$H$_{19}$FS$^+$ [M$^+$]: 192.0404; Found: 192.0403.

![Structural formula of 3-(2-fluorobenzyl)pyridine (3u)](image)

**3-(2-fluorobenzyl)pyridine (3u)**
Colorless liquid, 22.4 mg, 60% yield. **$^1$H NMR** (600 MHz, CDCl$_3$) $\delta$ 8.52 (s, 1H), 8.45 (d, $J$ = 4.2 Hz, 1H), 7.50 (d, $J$ = 7.9 Hz, 1H), 7.24 – 7.17 (m, 2H), 7.14 (dd, $J$ = 7.5, 6.3 Hz, 1H), 7.09 – 7.01 (m, 2H), 3.99 (s, 2H). **$^{13}$C NMR** (151 MHz, CDCl$_3$) $\delta$ 160.9 (d, $J_{C-F}$ = 245.5 Hz), 150.0, 147.7, 136.2, 135.4, 130.8 (d, $J_{C-F}$ = 4.1 Hz), 128.5 (d, $J_{C-F}$ = 8.0 Hz), 126.8 (d, $J_{C-F}$ = 15.8 Hz), 124.3 (d, $J_{C-F}$ = 3.4 Hz), 123.4, 115.5 (d, $J_{C-F}$ = 21.9 Hz), 32.2 (d, $J_{C-F}$ = 2.8 Hz). **$^{19}$F NMR** (376 MHz, CDCl$_3$) $\delta$ -117.59 – 117.65 (m, 1F). **IR** (KBr): 3444, 2077, 1636, 754 cm$^{-1}$. **HRMS m/z** (ESI) calcd. for C$_{12}$H$_{11}$FN$^+$ [M+H]$^+$: 188.0870; found: 188.0871.

![Structural formula of Diphenylmethane (3v)](image)

**Diphenylmethane (3v)**
Colorless liquid, 16.8 mg, 60% yield. **$^1$H NMR** (300 MHz, CDCl$_3$) $\delta$ 7.30 – 7.17 (m, 4H), 7.2 – 7.1 (m, 6H), 4.0 (s, 2H). **$^{13}$C NMR** (75 MHz, CDCl$_3$) $\delta$ 141.1, 128.9, 128.4, 126.0, 41.9.

$^1$H and $^{13}$C NMR data agreed with the literature$^{[12]}$

![Structural formula of 1-benzyl-3-chlorobenzene (3w)](image)

**1-benzyl-3-chlorobenzene (3w)**
Colorless liquid, 25.0 mg, 67% yield. **$^1$H NMR** (600 MHz, CDCl$_3$) $\delta$ 7.31 (t, $J$ = 7.6 Hz, 2H), 7.25-7.18 (m, 6H), 7.08 (d, $J$ = 7.2 Hz, 2H), 7.08 (d, $J$ = 7.2 Hz, 1H), 3.96 (s, 2H). **$^{13}$C NMR** (151 MHz, CDCl$_3$) $\delta$ 143.2, 140.2, 134.3, 129.7, 129.0, 128.9, 128.6, 127.09, 126.4, 126.3, 41.6 **IR** (KBr): 3449, 2082, 1636, 681 cm$^{-1}$. **MS** (EI, m/z%): 202
(M⁺, 38.27), 167 (100), 165 (48.26), 81 (28.11), 166 (22.36), 152 (18.24), 82 (15.39).

**HRMS (EI)** calcd. for C₁₃H₁₁Cl⁺ [M]⁺: 202.0544; Found: 202.0543.

![Cl](https://example.com/structure1.png)

**1-(3-chlorobenzyl)-2-methylbenzene (3x)**

Colorless liquid, 28.5 mg, 66% yield. **¹H NMR** (400 MHz, CDCl₃) δ 7.19 – 7.13 (m, 5H), 7.11 – 7.06 (m, 2H), 7.01 – 6.97 (m, 1H), 3.95 (s, 2H), 2.22 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 142.5, 138.0, 136.6, 134.2, 130.4, 130.0, 129.6, 128.8, 126.9, 126.8, 126.2, 126.1, 39.1, 19.6. **MS (EI, m/z%):** 216.03 (M⁺, 76.82), 181.06 (100.00), 165.06 (82.56), 166.08 (79.61), 89.09 (66.98), 201.02 (43.68), 104.05 (43.56), 76.07 (31.26), 218.04 (25.24), 77.06 (22.90), 91.07 (21.05), 178.07 (17.61), 105.09 (16.58), 63.05 (16.12), 179.06 (15.70). **IR (KBr):** 3454, 2077, 1637, 740 cm⁻¹. **HRMS (EI)** calcd. for C₁₄H₁₃Cl⁺ [M]⁺: 216.0700; Found: 216.0700.

![Cl](https://example.com/structure2.png)

**1-chloro-3-(3-methylbenzyl)benzene (3y)**

Colorless liquid, 26.9 mg, 62% yield. **¹H NMR** (400 MHz, CDCl₃) δ 7.24 – 7.13 (m, 4H), 7.09 – 7.00 (m, 2H), 7.00 – 6.94 (m, 2H), 3.90 (s, 2H), 2.31 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 143.3, 140.1, 138.2, 134.2, 129.7, 129.6, 129.0, 128.5, 127.1, 126.2, 125.9, 41.5, 21.4. **IR (KBr):** 3444, 2077, 1636, 682 cm⁻¹. **MS (EI, m/z%):** 216.04 (M⁺, 67.10), 181.08 (100.00), 166.05 (73.62), 165.07 (72.24), 89.14 (60.99), 201.02 (32.00), 76.08 (26.69), 218.02 (21.15), 77.04 (17.63), 179.06 (14.28), 178.07 (14.04), 182.09 (13.82), 63.08 (13.58), 180.09 (12.29), 105.06 (11.28). **HRMS (EI)** calcd. for C₁₄H₁₃Cl⁺ [M]⁺: 216.0700; Found: 216.0699.

![Cl](https://example.com/structure3.png)

**1-chloro-3-(4-methylbenzyl)benzene (3z)**
Colorless liquid, 28.9 mg, 67% yield. \( ^1H \text{NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 7.28 – 7.13 (m, 3H), 7.13 – 7.00 (m, 5H), 3.90 (s, 2H), 2.31 (s, 3H). \( ^{13}C \text{NMR} \) (101 MHz, CDCl\(_3\)) \( \delta \) 143.4, 137.1, 135.9, 134.2, 129.6, 129.3, 128.9, 128.8, 127.0, 126.2, 41.1, 21.0. \( \text{IR} \) (KBr): 3440, 2078, 1635, 672 cm\(^{-1}\). \( \text{MS} \) (EI, m/z%): 216.05 (M\(^{+}\), 70.88), 181.09 (100.00), 166.06 (79.21), 165.05 (77.31), 89.09 (52.73), 201.02 (39.55), 76.08 (25.91), 105.10 (16.85), 63.04 (14.38), 178.07 (14.37), 203.02 (13.17), 179.08 (13.06), 182.09 (12.92), 180.11 (12.50), 91.08 (11.33). \( \text{HRMS} \) (EI) calcd. for C\(_{14}\)H\(_{13}\)Cl\(^+\) [M\(^{+}\)]: 216.0700; Found: 216.0698.

1-chloro-3-(4-ethylbenzyl) benzene (3aa)

Colorless liquid, 30.0 mg, 65% yield. \( ^1H \text{NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 7.23 – 7.03 (m, 8H), 3.90 (s, 2H), 2.61 (q, \( J \) = 7.6 Hz, 2H), 1.22 (t, \( J \) = 7.6 Hz, 3H). \( ^{13}C \text{NMR} \) (101 MHz, CDCl\(_3\)) \( \delta \) 143.4, 142.3, 137.4, 134.2, 129.6, 129.0, 128.8, 128.1, 127.1, 126.2, 41.2, 28.4, 15.6. \( \text{IR} \) (KBr): 3442, 2078, 1635, 1245, 694 cm\(^{-1}\). \( \text{MS} \) (EI, m/z%): 230.07 (M\(^{+}\), 66.04), 201.02 (100.00), 165.07 (66.69), 166.10 (50.22), 105.09 (47.13), 89.07 (33.88), 203.03 (31.99), 195.11 (20.91), 178.09 (19.36), 232.06 (19.30), 179.07 (17.57), 215.00 (16.35), 167.08 (15.12). \( \text{HRMS} \) (EI) calcd. for C\(_{15}\)H\(_{15}\)Cl\(^+\) [M\(^{+}\)]: 230.0857; Found: 230.0855.

1-(4-(tert-butyl)benzyl)-3-chlorobenzene (3ab)

Colorless liquid, 31.5 mg, 61% yield. \( ^1H \text{NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 7.34 – 7.28 (m, 2H), 7.24 – 7.14 (m, 3H), 7.12 – 7.05 (m, 3H), 3.91 (s, 2H), 1.30 (s, 9H). \( ^{13}C \text{NMR} \) (101 MHz, CDCl\(_3\)) \( \delta \) 149.2, 143.3, 137.1, 134.2, 129.6, 129.0, 128.5, 127.1, 126.2, 125.5, 41.1, 34.4, 31.4. \( \text{IR} \) (KBr): 3447, 2077, 1636, 683 cm\(^{-1}\). \( \text{MS} \) (EI, m/z%): 258.10 (M\(^{+}\), 27.79), 243.05 (100.00), 125.04 (74.80), 89.07 (45.44), 245.07 (35.17), 90.08 (33.20), 127.05 (23.64), 244.09 (19.97), 165.09 (17.80), 91.03 (15.99), 115.06 (9.41),
260.11 (9.27), 105.07 (8.86), 76.07 (8.84), 77.05 (6.67). HRMS (EI) calcd. for C\textsubscript{13}H\textsubscript{19}Cl\textsuperscript{+} [M]\textsuperscript{+}: 258.1170; Found: 258.1171.

![4-(3-chlorobenzyl)-1,1\textprime;-biphenyl (3ac)](image)

**4-(3-chlorobenzyl)-1,1\textprime;-biphenyl (3ac)**
White solid, m.p. 45-46 °C, 40.1 mg, 72% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.62 – 7.49 (m, 4H), 7.45 – 7.41 (m, 2H), 7.36 – 7.72 (m, 1H), 7.28 – 7.17 (m, 5H), 7.14 – 7.08 (m, 1H), 4.00 (s, 2H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ 143.0, 140.9, 139.4, 139.3, 134.3, 129.7, 129.3, 129.0, 128.7, 127.3, 127.2, 127.1, 127.0, 126.4, 41.2. IR (KBr): 3438, 2077, 1636, 672 cm\textsuperscript{-1}. MS (EI, m/z%): 278.03 (M\textsuperscript{+}, 85.72), 165.04 (100.00), 243.10 (50.01), 280.02 (30.74), 167.08 (28.30), 166.07 (28.16), 91.09 (24.35), 119.72 (23.48), 115.07 (23.03), 241.06 (20.66), 152.07 (20.12), 206.99 (19.45), 279.03 (18.41), 239.05 (16.28), 242.10 (16.64), 89.09 (15.22). HRMS (EI) calcd. for C\textsubscript{19}H\textsubscript{15}Cl\textsuperscript{+} [M]\textsuperscript{+}: 278.0857; Found: 278.0854.

![2-(3-chlorobenzyl)-1,3,5-trimethylbenzene (3ad)](image)

**2-(3-chlorobenzyl)-1,3,5-trimethylbenzene (3ad)**
Colorless liquid, 32.3 mg, 66% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.17 – 7.13 (m, 2H), 6.99 (s, 1H), 6.89 – 6.87 (m,3H), 3.99 (s, 2H), 2.29 (s, 3H), 2.19 (s, 6H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ 142.3, 136.9, 136.0, 134.2, 132.8, 129.5, 129.0, 127.9, 126.0, 125.9, 34.4, 20.9, 20.1. IR (KBr): 3438, 1635, 677 cm\textsuperscript{-1}. MS (EI, m/z%): 244.08 (M\textsuperscript{+}, 90.05), 229.08 (100.00), 194.08 (54.65), 133.15 (47.48), 179.08 (45.42), 119.09 (42.65), 231.08 (36.44), 178.10 (36.09), 91.12 (33.04), 132.12 (31.49), 89.08 (30.51), 193.09 (30.49), 246.07 (26.97), 115.09 (25.27), 77.08 (22.18). HRMS (EI) calcd. for C\textsubscript{16}H\textsubscript{17}Cl\textsuperscript{+} [M]\textsuperscript{+}: 244.1013; Found: 244.1013.
1-chloro-2-(3-chlorobenzyl)benzene (3ae)
Colorless liquid, 34.7 mg, 73.5% yield. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.40 – 7.34 (m, 1H), 7.25 – 7.11 (m, 6H), 7.06 (d, $J$ = 7.0 Hz, 1H), 4.06 (s, 2H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 141.6, 137.8, 134.3, 134.2, 131.0, 129.7 (2C), 128.9, 127.96, 127.1, 126.9, 126.5, 38.8. IR (KBr): 3451, 2077, 1638, 751 cm$^{-1}$. MS (EI, m/z%): 235.97 (M$^+$, 53.53), 165.05 (100.00), 165.06 (86.31), 82.03 (81.08), 201.00 (77.92), 203.02 (26.40), 89.06 (23.68), 237.96 (23.22), 82.77 (18.62), 81.12 (17.83), 63.04 (16.78), 164.07 (15.56), 163.04 (14.97), 124.99 (13.18), 75.06 (12.30). HRMS (EI) calcd. for C$_{13}$H$_{10}$Cl$_2$$^+$ [M$^+$]: 236.0154; Found: 236.0153.

Bis(3-chlorophenyl)methane (3af)
Colorless liquid, 31.2mg, 66% yield. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.24 – 7.17 (m, 4H), 7.16 – 7.14 (m, 2H), 7.06 – 7.03 (m, 2H), 3.90 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 142.2, 134.4, 129.8, 129.0 127.1, 126.6, 41.1. IR (KBr): 3449, 2082, 1636, 681 cm$^{-1}$. MS (EI, m/z%): 235.96 (M$^+$, 39.35), 165.06 (100.00), 166.07 (84.41), 201.01 (82.38), 82.04 (72.47), 237.96 (24.97), 89.05 (24.15), 81.18 (19.77), 82.77 (17.17), 63.03 (15.98), 164.08 (13.15), 75.04 (13.13), 125.01 (12.82), 202.03 (12.43), 163.05 (12.26). HRMS (EI) calcd. for C$_{13}$H$_{10}$Cl$_2$$^+$ [M$^+$]: 236.0154; Found: 236.0152.

1,2-dichloro-4-(3-chlorobenzyl)benzene (3ag)
Colorless liquid, 30.2 mg, 56% yield. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.35 (dd, $J$ = 8.2, 1.4 Hz, 1H), 7.25 – 7.20 (m, 3H), 7.14 (s, 1H), 7.03 (d, $J$ = 7.0 Hz, 1H), 6.99 (d, $J$ = 8.2 Hz, 1H), 3.89 (s, 2H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 141.7, 140.4, 134.6, 132.6, 130.8, 130.6, 130.5, 129.9, 129.0, 128.3, 127.0, 126.9, 40.6. IR (KBr): 3434, 1635, 663 cm$^{-1}$. 33
MS (EI, m/z%): 269.96 (M⁺, 30.82), 165.08 (100.00), 234.98 (80.34), 236.98 (48.01), 199.03 (41.90), 81.75 (37.84), 99.10 (34.31), 271.95 (30.58), 200.04 (30.09), 81.10 (26.98), 99.70 (23.21), 163.07 (23.19), 89.06 (20.39), 201.04 (17.63). HRMS (EI) calcd. for C₁₃H₁₉Cl₃⁺ [M⁺]: 269.9764; Found: 269.9763.

1-chloro-3-(3-fluorobenzyl)benzene (3ah)
Colorless liquid, 28.2 mg, 64% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.17 (m, 4H), 7.09 (d, J = 6.7 Hz, 1H), 7.03 – 6.84 (m, 3H), 3.97 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 163.0 (d, J_{C-F} = 246.0 Hz), 142.7 (d, J_{C-F} = 7.1 Hz), 142.3, 134.4, 130.0 (d, J_{C-F} = 8.3 Hz), 129.8, 129.0, 127.1, 126.6, 124.5 (d, J_{C-F} = 2.8 Hz), 115.8 (d, J_{C-F} = 21.3 Hz), 113.3 (d, J_{C-F} = 21.1 Hz), 41.2 (d, J_{C-F} = 1.7 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -105.62 – -116.99 (m). IR (KBr): 3441, 2078, 1635, 1247, 682 cm⁻¹. MS (EI, m/z%): 220.00 (M⁺, 53.53), 185.07 (100.00), 165.06 (48.18), 183.04 (43.76), 184.06 (20.07), 222.02 (16.54), 82.04 (13.37), 91.76 (13.29), 186.09 (12.60), 109.03 (9.39), 83.02 (9.28). HRMS (EI) calcd. for C₁₃H₁₀ClF⁺ [M⁺]: 220.0450; Found: 220.0449.

1-chloro-3-(4-methoxybenzyl)benzene (3ai)
Colorless liquid, 26.0 mg, 56% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.23 – 7.13 (m, 3H), 7.12 – 7.02 (m, 3H), 6.88 – 6.79 (m, 2H), 3.88 (s, 2H), 3.78 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 158.1, 143.6, 134.2, 132.3, 129.9, 129.6, 128.9, 126.9, 126.2, 114.0, 55.2, 40.7. IR (KBr): 3443, 2077, 1636, 1510, 1245, 681 cm⁻¹. MS (EI, m/z%): 233.0728; found: 233.0726. HRMS m/z (ESI) calcd. for C₁₄H₁₄ClO⁺ [M+H⁺]: 233.0728; found: 233.0726.

1-chloro-3-(4-phenoxybenzyl)benzene (3aj)
Colorless liquid, 35.9 mg, 61% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.32 (dd, $J$ = 8.5, 7.5 Hz, 2H), 7.26 – 7.15 (m, 3H), 7.15 – 7.03 (m, 4H), 7.03 – 6.97 (m, 2H), 6.94 (d, $J$ = 8.6 Hz, 2H), 3.92 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 157.3, 155.7, 143.2, 135.1, 134.3, 130.1, 129.7 (2C), 129.0, 127.0, 126.3, 123.1, 119.0, 118.7, 40.8. IR (KBr): 3439, 2077, 1636, 1238, 678 cm$^{-1}$. MS (EI, m/z%): 294.03 (M$^+$, 59.29), 165.06 (100.00), 166.08 (86.22), 77.05 (53.92), 201.06 (51.87), 51.06 (31.44), 153.09 (23.99), 152.07 (23.38), 296.03 (19.95), 259.10 (18.98), 183.05 (17.36), 89.08 (17.22), 107.08 (10.26). HRMS (EI) calcd. for C$_{19}$H$_{15}$ClO$^+$ [M$^+$]: 294.0806; Found: 294.0806.

5-(3-chlorobenzyl)benzo[d][1,3]dioxole (3ak)

Colorless liquid, 24.6 mg, 50% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.29 – 7.12 (m, 3H), 7.05 (d, $J$ = 7.1 Hz, 1H), 6.74 (d, $J$ = 8.4 Hz, 1H), 6.64 (d, $J$ = 7.2 Hz, 2H), 5.92 (s, 2H), 3.85 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 147.8, 146.1, 143.3, 134.2, 134.0, 129.7, 128.8, 126.9, 126.3, 121.8, 109.3, 108.3, 100.9, 41.2. IR (KBr): 3444, 2077, 1636, 682 cm$^{-1}$. HRMS m/z (ESI) calcd. for C$_{14}$H$_{12}$ClO$_2^+$ [M+H]$^+$: 247.0502; found: 247.0529.

1-chloro-3-(4-(trifluoromethoxy)benzyl)benzene (3al)

Colorless liquid, 42.9 mg, 75% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.25 – 7.11 (m, 7H), 7.05 (dt, $J$ = 7.0, 1.7 Hz, 1H), 3.94 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 147.8, 142.4, 138.9, 134.4, 130.1, 129.8, 129.0, 127.1, 126.6, 121.1, 120.16 ($J_{C-F} = 257.6$) 40.8. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -57.90 (s, 3F). IR (KBr): 3442, 1634, 1254, 681 cm$^{-1}$. MS (EI, m/z%): 285.98 (M$^+$, 47.47), 165.07 (100.00), 251.04 (83.94), 166.08 (37.22), 152.05 (26.07), 201.03 (20.27), 153.07 (17.78), 69.06 (17.53), 287.99 (16.00), 252.06 (13.68), 89.05 (12.62), 63.06 (10.67), 175.02 (9.34). HRMS (EI) calcd. for C$_{14}$H$_{10}$ClF$_3$O$^+$ [M$^+$]: 286.0367; Found: 286.0363.
1-chloro-3-(4-(trifluoromethyl)benzyl)benzene (3am)

Colorless liquid, 28.1 mg, 52% yield. \[^1H\text{ NMR}\] (600 MHz, CDCl\textsubscript{3}) \(\delta\) 7.54 (d, \(J = 7.7\) Hz, 2H), 7.27 (d, \(J = 7.7\) Hz, 2H), 7.24 – 7.19 (m, 2H), 7.16 (s, 1H), 7.04 (d, \(J = 6.7\) Hz, 1H), 3.99 (s, 2H). \[^{13}C\text{ NMR}\] (151 MHz, CDCl\textsubscript{3}) \(\delta\) 144.3, 142.0, 134.5, 129.9, 129.2 (2C), 129.0, 127.1, 126.7, 126.2 (q, \(J_{C-F} = 271.8\) Hz) 125.6 (q, \(J_{C-F} = 3.5\) Hz), 41.3. \[^{19}F\text{ NMR}\] (376 MHz, CDCl\textsubscript{3}) \(\delta\) -62.40 (s, 3F). \(\text{IR}\) (KBr): 3436, 2077, 1635, 681 cm\(^{-1}\). \(\text{MS}\) (EI, m/z\%): 270.00 (M\(^{+}\), 51.03), 235.03 (100.00), 165.06 (77.86), 162.09 (62.64), 215.04 (25.49), 201.04 (22.20), 271.99 (17.04), 89.06 (15.95), 107.07 (14.42), 236.06 (14.07), 233.04 (11.61), 75.04 (11.35), 63.06 (11.24), 81.44 (9.40), 125.02 (9.35). \(\text{HRMS}\) (El) calcd. for C\textsubscript{14}H\textsubscript{10}ClF\textsubscript{3}\(^{+}\) [M]\(^{+}\): 270.0418; Found: 270.0414.

1-(3-chlorobenzyl)naphthalene (3an)

Yellow oil, 25.2 mg, 50% yield. \[^1H\text{ NMR}\] (600 MHz, CDCl\textsubscript{3}) \(\delta\) 7.91 (d, \(J = 7.7\) Hz, 1H), 7.85 (d, \(J = 6.8\) Hz, 1H), 7.77 (d, \(J = 8.0\) Hz, 1H), 7.50 – 7.38 (m, 3H), 7.28 (d, \(J = 6.6\) Hz, 1H), 7.20 – 7.13 (m, 3H), 7.05 (d, \(J = 5.5\) Hz, 1H), 4.39 (s, 2H). \[^{13}C\text{ NMR}\] (151 MHz, CDCl\textsubscript{3}) \(\delta\) 142.8, 135.7, 134.3, 134.0, 132.0, 129.7, 128.8 (2C), 127.5 (2C), 126.7, 126.32, 126.1, 125.7, 125.5, 124.1, 38.7. \(\text{IR}\) (KBr): 3452, 2088, 1639, 773 cm\(^{-1}\). \(\text{MS}\) (EI, m/z\%): 252.05 (M\(^{+}\), 86.96), 217.10 (100.00), 215.10 (71.77), 107.75 (46.57), 106.60 (43.66), 202.08 (43.44), 115.07 (40.56), 216.11 (40.04), 94.59 (36.46), 141.09 (33.89), 107.24 (30.54), 108.27(25.67), 254.05 (23.95), 218.13 (17.89), 253.08 (16.93), 213.07 (15.20). \(\text{HRMS}\) (El) calcd. for C\textsubscript{17}H\textsubscript{13}Cl\textsubscript{2}\(^{+}\) [M]\(^{+}\): 252.0700; Found: 252.0698.

2-(3-chlorobenzyl)pyridine (3ao)
Cl

1-chloro-3-(3-phenylpropyl)benzene (3ap)
Colorless liquid, 20.0 mg, 39% yield. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.31-7.24 (m, 2H), 7.19-7.17 (m, 6H), 7.06-7.04 (m, 1H), 2.67-2.59 (m, 4H), 2.01 – 1.85 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 144.3, 141.9, 134.0, 129.5, 128.5, 128.4, 128.3, 126.6, 125.9, 125.8, 35.3, 35.0, 32.7. IR (KBr): 2934, 1597, 1097, 697 cm$^{-1}$. MS (EI, m/z%): 230.08 (M$^+$. 21.32), 91.10 (100.00), 92.10 (60.72), 126.04 (38.58), 105.10 (24.50), 77.06 (20.73), 103.08 (16.49), 65.05 (15.25), 128.03 (9.93), 79.07 (8.75), 89.04 (8.14), 232.06 (7.53), 139.06 (7.52), 125.00 (6.44), 51.03 (6.18). HRMS (EI) calcd. for C$_{15}$H$_{15}$Cl$^+$ [M$^+$]: 230.0857; Found: 230.0857.

(Z/E)-pent-2-ene-1,2-diyl dibenzene (6)
Colorless liquid, 4.9 mg, 11% yield. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.35 – 7.32 (m, 1H), 7.25 – 7.22 (m, 4H), 7.19 – 7.13 (m, 4H), 5.97 (t, $J$ = 7.2 Hz, 1H), 3.88 (s, 2H), 2.29 – 2.24 (m, 2H), 1.08 (t, $J$ = 7.5 Hz, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 143.04, 139.96, 136.84, 132.73, 128.33, 128.17, 128.14, 126.53, 126.26, 125.78, 35.75, 22.29, 14.17. IR (KBr): 3026, 2964, 2918, 1600, 1493, 1451, 752, 722, 696 cm$^{-1}$. HRMS (EI) calcd. for C$_{17}$H$_{18}$$^+$ [M$^+$]: 222.1403; Found: 222.1402.
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10. Copies of $^1$H NMR, $^{19}$F NMR and $^{13}$C NMR spectra

$^1$H, $^{19}$F and $^{13}$C NMR spectra of compound 3a
$^1$H, $^{19}$F and $^{13}$C NMR spectra of compound 3b
$^1$H, $^{19}$F and $^{13}$C NMR spectra of compound 3c
$^1$H, $^{19}$F and $^{13}$C NMR spectra of compound 3d
$^1$H, $^{19}$F and $^{13}$C NMR spectra of compound 3e
$^1$H, $^{19}$F and $^{13}$C NMR spectra of compound 3f
$^1$H, $^{19}$F and $^{13}$C NMR spectra of compound 3g
$^1\text{H}$, $^{19}\text{F}$ and $^{13}\text{C}$ NMR spectra of compound 3h
$^1$H, $^{19}$F and $^{13}$C NMR spectra of compound 3i
$^{1}H$, $^{19}F$ and $^{13}C$ NMR spectra of compound 3j
$^1$H, $^{19}$F and $^{13}$C NMR spectra of compound 3k
$^1$H, $^{19}$F and $^{13}$C NMR spectra of compound 31
$^1$H, $^{19}$F and $^{13}$C NMR spectra of compound 3m
$^1$H, $^{19}$F and $^{13}$C NMR spectra of compound 3n
$^1$H, $^{19}$F and $^{13}$C NMR spectra of compound 30
$^{1}H$, $^{19}F$ and $^{13}C$ NMR spectra of compound 3p
$^1$H, $^{19}$F and $^{13}$C NMR spectra of compound 3q
$^1$H, $^{19}$F and $^{13}$C NMR spectra of compound 3r.
$^1$H, $^{19}$F and $^{13}$C NMR spectra of compound 3s
$^1$H, $^{19}$F and $^{13}$C NMR spectra of compound 3t
$^1$H, $^{19}$F and $^{13}$C NMR spectra of compound 3u
$^1$H and $^{13}$C NMR spectra of compound 3v

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^1$H and $^{13}$C NMR spectra of compound 3w

$^{13}$C NMR (75 MHz, CDCl$_3$)

$^1$H NMR (600 MHz, CDCl$_3$)
$^1$H and $^{13}$C NMR spectra of compound 3x
$^1$H and $^{13}$C NMR spectra of compound 3y
\( \text{\(^1H\) and \(^{13}C\) NMR spectra of compound 3z} \)

\[ \text{Diagram showing NMR spectra} \]
$^1$H and $^{13}$C NMR spectra of compound 3aa
$^1$H and $^{13}$C NMR spectra of compound 3ab
$^1$H and $^{13}$C NMR spectra of compound 3ac
\(^1\)H and \(^{13}\)C NMR spectra of compound 3ad
$^1$H and $^{13}$C NMR spectra of compound 3ae
$^1$H and $^{13}$C NMR spectra of compound 3af
$^1$H, $^{19}$F and $^{13}$C NMR spectra of compound 3ah
$^1$H and $^{13}$C NMR spectra of compound 3ai
$^1$H and $^{13}$C NMR spectra of compound 3aj
$^1$H and $^{13}$C NMR spectra of compound 3ak
$^1$H, $^{19}$F and $^{13}$C NMR spectra of compound 3al

![NMR spectra](image)
$^1$H, $^{19}$F and $^{13}$C NMR spectra of compound 3am
$^1$H and $^{13}$C NMR spectra of compound 3an
$^1$H and $^{13}$C NMR spectra of compound 3ao
$^1$H and $^{13}$C NMR spectra of compound 3ap
$^1$H and $^{13}$C NMR spectra of compound 6