Arylation with Unsymmetric Diaryliodonium Salts
– a Chemoselectivity Study

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1 General Experimental Conditions

Precautions to exclude air or moisture were not taken, except when mentioned. Commercial mCPBA was dried under vacuum at rt for 1 hour and subsequently the percentage of active oxidising reagent was determined by iodometric titration.[1] All other commercially available chemicals were used as supplied. For TLC analyses precoated silica gel 60 F254 plates were used; and for column chromatography 40-60 µm, 60A silica gel was used. Melting points were measured using a STUART SMP3 and are reported uncorrected. NMR spectra were recorded using a 400 MHz Bruker AVANCE II with a BBO probe at 298 K, unless otherwise mentioned, using CDCl3 and DMSO-d6 as solvents. Chemical shifts are given in ppm relative to the (residual) solvent peak (1H NMR: CHCl3 δ 7.27, DMSO-d5 δ 2.50; 13C NMR: CDCl3 δ 77.23, DMSO-d6 δ 39.52) with multiplicity (br=broad, s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, app=apparent), coupling constants (in Hz) and integration. High resolution mass analyses were obtained using a Bruker microTOF ESI with a time-of-flight-detector. Combined isolated yield refers to calculated yield based on the isolated mass of the two products and their NMR integrals.

2 Mechanistic studies

2.1 Aryl exchange study by HRMS

The aryl exchange studies were performed by setting up reactions according to the experimental protocols for arylation of 4, 5 and 6 (see the paper or Sections 5-7). A sample was taken via syringe and immediately dissolved in a mixture of MeOH and H2O (10 mL 1:1). This mixture was then further diluted (by a factor of 10) before analysis. The samples were taken after 5 min, 30 min and then once every hour up to ten hours unless otherwise noted.

Experiments with 2,5-dimethoxyphenyl-(phenyl)iodonium triflate (2d):

* Without nucleophile: 2d (0.25 mmol) was stirred in DMF at rt and under reflux. No aryl exchange was detected.

* With 3-methoxy phenol 3: Samples were taken after 5 min and 30 min respectively. The di(2,5-dimethoxyphenyl)iodonium cation 2g′ and diphenyliodonium cation 1g′ were detected after 5 min reaction time at room temperature (Figure S1).

![Diagram of the reaction](https://via.placeholder.com/150)
Figure S1. HRMS of aryl exchange after 5 min reaction of phenol 3 with salt 2d.

* With 3-methoxy aniline 6: No aryl exchange was detected.

* With diethylmethyl malonate 9: The di(2,5-diethoxyphenyl)iodonium cation 2g’ and diphenyliodonium cation 1g’ were detected. (Figure S2).

Figure S2. HRMS of aryl exchange after 5 min reaction of malonate 9 with salt 2d.
Experiments with 2,5-dimethylphenyl-(phenyl)iodonium triflate (1d):

* With diethylmethyl malonate (9): The diphenyliodonium cation 1g' and di(2,5-dimethylphenyl)iodonium cation 1h' were detected after 5 min at room temperature (Figure S3).

![Reaction scheme and HRMS spectra](image)

**Figure S3.** HRMS of aryl exchange after 5 min reaction of malonate 9 with salt 1d.

**Control experiments:**

* Malonate 9 was arylated with di(p-tolyl)iodonium triflate (1i) in the presence of 2,6-dimethyliodobenzene (1 equiv). No aryl exchange was detected.
* Di(2,5-dimethylphenyl)iodonium triflate (1h) (1 equiv) and di(4-methoxyphenyl)iodonium triflate (2h) (1 equiv) were reacted with malonate 9 (1 equiv). The corresponding unsymmetric 2,5-dimethylphenyl-(4-methoxyphenyl)iodonium cation 2i' was detected (Figure S4).

![Reaction scheme and HRMS spectra](image)

**Figure S4.** HRMS of aryl exchange after 5 min reaction of malonate 9 with salts 1h and 2h.
2.2 Aryl exchange study by NMR

An NMR study of the arylation of 9 with salt 2d was conducted in a similar manner as the HRMS study. The reaction was performed as described in the paper (or Section 7). NMR samples were taken after 15, 25, 70, 120 and 180 minutes respectively. Each sample was taken via syringe (0.1 mL) and placed in a vial containing Et₂O and H₂O (1 mL, 1:1). The organic phase was evaporated in vacuo and dissolved in CDCl₃. The product ratios (Ph: Ar) throughout the reaction were:
15 min: 2.0 : 1; 25 min: 1.9 : 1; 70 min: 1.9 : 1; 120 min: 2.0 : 1; 180 min: 2.0 : 1.

2.3 Radical trap experiments

The radical trap experiments were performed by setting up reactions according to the experimental procedure in Sections 5-7 with the addition of a radical trap, which was added as the last reagent into the reactions. The results are given in Table S1.
We have previously reported radical trap experiments with phenols and DPE.[2]

Table S1. Radical trap experiments.

| Nucleophile         | Salt | Radical trap (amount)       | Yield[8] (%) | Yield without radical trap (%) |
|---------------------|------|-----------------------------|--------------|-------------------------------|
| m-Anisidine 6       | 1a   | DPE[8] (1 equiv)            | 28           | 53                            |
| m-Anisidine 6       | 2b   | DPE (1 equiv)               | 34           | 62                            |
| m-Anisidine 6       | 2c   | DPE (10 mol%)               | 20           | 50                            |
| m-Anisidine 6       | 2c   | TEMPO[c] (10 mol%)          | 10           | 50                            |
| Diethylmethyl malonate 9 | 1a   | DPE (1 equiv)               | 54           | 54                            |

[a] Chemoselectivities were not altered. [b] 1,1-Diphenylethylene. [c] 2,2,6,6-Tetramethylpiperidin-1-oxyl.
3 Synthesis of Diaryliodonium Salts 1-2

3.1 One-pot methods

Many diaryliodonium salts are now commercially available. For convenience, we have synthesized most of the salts used in this investigation according to the one-pot methods previously developed in our group (Scheme S1).

**Scheme S1.** Our one-pot syntheses of diaryliodonium salts.
Table S2. Synthesis of diaryliodonium salts 1a-1f, 1h-j and 2a.

| Entry | Salt | Method¹ | Acid (equiv) | T (°C) | Time | Yield (%) | Ref² |
|-------|------|---------|-------------|--------|------|-----------|------|
| 1     | 1a   | I       | 2           | 0→rt   | 25 min | 90        | [3]  |
| 2     | 1b   | I       | 2           | rt     | 30 min | 52        | [3]  |
| 3     | 1c   | I       | 2           | 0      | 2 h   | 95        | -    |
| 4     | 1d   | I       | 2           | rt     | 5 h   | 69        | [3]  |
| 5     | 1e   | V       | 2.5         | rt     | 30 min + 30 min | 76 | -    |
| 6     | 1f   | I       | 2           | rt     | 1 h   | 79        | [3]  |
| 7*    | 1h   | II      | 4           | rt     | 24 h  | 40        | [3]  |
| 8     | 1i   | III     | 3           | 0→rt   | 2 h   | 60        | [3]  |
| 9[³] | 1j   | II      | 4           | rt     | 3 h   | 97        | [4]  |
| 10    | 2a   | III     | 1           | rt     | 6 h   | 100       |      |

¹ Method in Scheme S1. ² Reference to analytical data. ³ This salt was synthesized in order to selectively prepare the minor arylation product, to confirm the product ratio analysis.

2,4-Dimethyl(phenyl)iodonium triflate (1c):

Isolated as a light grey solid; mp 128-129 °C, ¹H NMR (400 MHz, DMSO-d₆) δ 8.25 (d, J = 8.0, 1H), 8.17 (appd, J = 8.0, 2H), 7.65 (t, J = 4.0, 2H), 7.51 (t, J = 8.0, 2H), 7.38 (s, 1H), 7.13 (d, J = 8.0, 1H), 2.56 (s, 3H), 2.31 (s, 3H); ¹³C NMR (100 MHz, DMSO-d₆) δ 143.3, 140.4, 137.0, 134.9, 132.0, 131.9, 131.8, 131.8, 129.9, 117.7, 115.9, 24.8, 20.7. HRMS (ESI) m/z calculated for C₁₄H₁₄I ([M-OTf]+) 309.0094, found 309.0080.

2,6-Dimethyl(phenyl)iodonium triflate (1e):
Isolated as a light grey solid; mp 137-138 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 8.01 (appd, \(J = 8.0, 2\)H), 7.69 (t, \(J = 8.0, 1\)H), 7.55-7.46 (m, 3H), 7.40 (appd, \(J = 8.0, 2\)H), 2.65 (s, 6H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 141.7, 134.6, 131.9, 131.9, 129.1, 126.2, 114.4, 26.5. HRMS (ESI) \(m/z\) calculated for \(\text{C}_{14}\text{H}_{13}\text{I} ([\text{M–OTf}^-])\) 310.0149, found 309.0135.

3.2 Stepwise methods

General procedure for anion exchange to triflate

The diaryliodonium salt (5 mmol) was dissolved in dichloromethane (30 mL) and washed with an aqueous NaOTf solution (3 x 50 mmol). The organic layer was concentrated without drying. Et\(_2\)O (20 mL) was added and the mixture was stirred at room temperature for 30 min to precipitate a solid. The solid was filtrated and washed with Et\(_2\)O and dried under vacuum to give the triflate salt. The anion exchange was confirmed by NMR analysis.

2-Methoxyphenyl(phenyl)iodonium triflate (2b):

\[
\text{Ph} \begin{array}{c} \text{MeO} \\ \text{Ph} \end{array} \text{I}^\text{OTf}^-
\]

Synthesized by a known method\(^6\) followed by anion exchange with NaOTf. Isolated as a light yellow solid; mp 148-150 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 8.30 (dd, \(J = 7.9, 1.4, 1\)H), 8.20-8.10 (m, 2H), 7.70-7.61 (m, 2H), 7.54-7.47 (m, 2H), 7.31 (dd, \(J = 1.3, 8.4, 1\)H), 7.09 (td, \(J = 7.9, 1.4, 1\)H), 3.94 (s, 3H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 156.4, 137.2, 135.1, 134.9, 131.9, 131.6, 123.4, 120.7 (q, \(^1JC=322\)), 115.8, 113.1, 106.5, 57.1; HRMS (ESI) \(m/z\) calculated for \(\text{C}_{13}\text{H}_{12}\text{IO} ([\text{M–OTf}^-])\) 310.9927, found 310.9912.

2,4-Dimethoxyphenyl(phenyl)iodonium triflate (2c):

\[
\text{Ph} \begin{array}{c} \text{MeO} \\ \text{Ph} \end{array} \text{I}^\text{OTf}^-
\]

Synthesized by a known method\(^7\) followed by anion exchange with NaOTf. Isolated as a light yellow solid; mp 92-94 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 8.18 (d, \(J = 8.8, 1\)H), 8.09-8.03 (m, 2H), 7.66-7.59 (m, 1H), 7.53-7.45 (m, 2H), 6.80 (d, \(J = 2.6, 1\)H), 6.69 (dd, \(J = 2.6, 8.8, 1\)H), 3.93 (s, 3H), 3.83 (s, 3H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 164.7, 158.2, 138.3, 134.6, 131.7, 131.5, 122.3, 120.7 (q, \(^1JC=322\)), 119.1, 116.3, 108.9, 99.7, 95.8, 57.3, 56.0; HRMS (ESI) \(m/z\) calculated for \(\text{C}_{14}\text{H}_{14}\text{IO}_2 ([\text{M–OTf}^-])\) 314.0033, found 314.0030.

2,5-Dimethoxyphenyl(phenyl)iodonium triflate (2d):

\[
\text{Ph} \begin{array}{c} \text{MeO} \\ \text{Ph} \end{array} \text{I}^\text{OTf}^-
\]

Synthesized by a known method\(^6\) followed by anion exchange with NaOTf. Isolated as a light yellow solid; mp 168-170 °C; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 8.12 (d, \(J = 8.0, 2\)H), 7.96 (brs, 1H), 7.65 (appt, 1H), 7.51 (appt, 2H), 7.29-7.18 (m, 2H), 3.86 (s, 3H), 3.77 (s, 3H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 154.2, 150.7, 135.0, 131.9, 131.6, 122.1, 120.7 (q, \(^1JC=322\)), 119.9, 115.9, 113.5, 106.3, 57.4, 56.2; HRMS (ESI) \(m/z\) calculated for \(\text{C}_{14}\text{H}_{14}\text{IO}_2 ([\text{M–OTf}^-])\) 314.0033, found 314.0030.
2,6-Dimethoxyphenyl(phenyl)iodonium triflate (2e):

Synthesized by a known method,[6] followed by anion exchange with NaOTf. Isolated as a light yellow solid; mp 152-153 °C; \(^1^H\) NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 7.95 (dd, \(J = 1.0, 8.3, 1\)H), 7.62-7.54 (m, 1H), 7.48-7.41 (m, 1H), 6.87 (t, \(J = 8.4, 1\)H), 3.94 (s, 3H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 158.1, 135.7, 134.6, 131.4, 131.4, 116.8, 105.3, 99.1, 57.3; HRMS (ESI) \(m/z\) calculated for C\(_{14}\)H\(_{14}\)IO\(_2\) ([M–OTf]') 314.0033, found 314.0023.

2,4,6-Trimethoxyphenyl(phenyl)iodonium triflate (2f):

Synthesized by a known method,[7] followed anion exchange with NaOTf. Isolated as a white solid in 94% yield; mp 114-116 °C; \(^1^H\) NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 7.92 (d, \(J = 7.4, 2\)H), 7.61 (t, \(J = 7.4, 1\)H), 7.47 (t, \(J = 7.8, 2\)H), 6.46 (s, 2H), 3.94 (s, 6H), 3.86 (s, 3H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta\) 166.2, 159.4, 134.4, 131.4, 128.1, 125.5, 122.31 120.7 (q, \(J_{C-F} = 322\)), 119.1, 116.1, 92.1, 87.0, 57.4, 56.2; HRMS (ESI) \(m/z\) calculated for C\(_{15}\)H\(_{16}\)IO\(_2\) ([M–OTf]') 314.0033, found 314.0023.

4 Arylation of Phenol 3 to Products 4, 5

Experimental procedure:[8] To a suspension of \(t\)BuOK (1.1 equiv, 43 mg, 0.37 mmol) in THF (1.5 mL) was added phenol 3 (1.0 equiv, 0.34 mmol) at 0 °C and the reaction was left to stir at this temperature for 15 min. Diaryliodonium salt 1 or 2 (1.2 equiv, 0.40 mmol) was added in one portion and the reaction was stirred in an oil bath preheated to 40 °C until TLC indicated complete consumption of 1 or 2. The reaction was then quenched with H\(_2\)O at 0 °C, the organic phase was separated and the water phase was extracted with CH\(_2\)Cl\(_2\) (3 × 10 mL). The combined organic phases were dried (Na\(_2\)SO\(_4\)) and concentrated in vacuo. The crude material was purified by flash chromatography to give the diaryl ethers 4 and 5. The product ratio was determined by isolating 4 and 5 respectively. The analytical data of 4[8], 5a[9] and 5b-f[4] were in agreement with previous reports.
5 Arylation of Aniline 6 to Products 7, 8

5.1 Arylation with unsymmetric diaryliodonium salts 1, 2

Experimental procedure:[¹⁰]
Diaryliodonium salt 1 or 2 (1 equiv, 0.25 mmol) was dissolved in dry DMF (2 mL). m-Anisidine (1 equiv, 0.028 mL, 0.25 mmol) was added under stirring at rt. The reaction mixture was submitted to a 130 °C oilbath and stirred for 24 h. The reaction was treated with Na₂CO₃ (1 M, 2 mL), extracted with EtOAc (3 × 5 mL) and washed with H₂O (1 × 10 mL) and brine (2 × 10 mL). The combined organic phases were dried (MgSO₄) and concentrated in vacuo. The crude material was purified with flash chromatography to give the diarylamines 7 and 8 as an inseparable mixture. The product ratio was determined by NMR from the crude mixture.

\( N-(3\text{-methoxyphenyl})\text{-aniline (7):} \)

[MeO][N][Ph]

Synthesized according to the general protocol with salt 2e to give 7 in 70% yield as a colorless oil. Analytical data were in accordance with previously reported data.[¹¹]

\( N-(3\text{-methoxyphenyl})\text{-2-methylaniline (8b):} \)

[MeO][N][Ph]

Synthesized according to the general procedure using 2-methylphenyl(phenyl)iodonium triflate (1b) to give 8b in 15% yield as a colorless oil. Analytical data were in accordance with previously reported data.[¹²]

\( N-(3\text{-methoxyphenyl})\text{-2,4,6-trimethylaniline (8f):} \)

[MeO][N][Ph]

Synthesized according to the general procedure using salt 1f. Isolated as a mixture of 7 and 8f (15:1, 50% yield). The presence of 8f was confirmed by comparing with the reported analytical data.[¹³]

\( N-(3\text{-methoxyphenyl})\text{-2,5-dimethoxyaniline (8i):} \)

[MeO][N][OMe]

Synthesized according to the general procedure using 2,5-dimethoxyphenyl(phenyl)iodonium triflate (2d) to give 7 and 8i (2.3:1, 30% combined yield). 8i was isolated by column chromatography (Pentane → pentane : EtOAc 12:1) in 9% yield as a colorless oil. \( ^1\text{H} \) NMR (400 MHz, CDCl₃) \( \delta \) 7.26 (d, \( J = 8.64, 1H \)), 7.15 (t, \( J = 8.12, 1H \)), 6.63-6.57 (m, 2H), 6.55 (d, \( J = 2.68, 1H \)), 6.47 (dd, \( J = 8.64, 2.68, 1H \)), 6.43 (appd, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 3.79 (s, 3H); \( ^{13}\text{C} \) NMR (100 MHz, CDCl₃) \( \delta \) 160.9, 155.5, 151.5, 146.3, 130.2, 125.6, 119.9, 109.3, 105.3, 104.1, 102.2, 99.7, 55.9, 55.4, 31.1; HRMS (ESI) \( m/z \) calculated for C₁₃H₁₈NO₃ ([M+H]+) 259.1281 found 259.1239.
5.2 Arylations to obtain reference products

The following compounds were synthesized separately to obtain NMR data of the pure minor products, in order to confirm the NMR analysis of the crude mixtures.

**N-(3-methoxyphenyl)-4-methylaniline (8a):**

![Chemical structure](image)

Synthesized according to the general protocol using di(4-methylphenyl)iodonium triflate (1i) to give 8a in 66% yield as a colorless oil. Analytical data were in agreement with previously reported data.\(^{[14]}\)

**N-(3-methoxyphenyl)-2,4-dimethylaniline (8c):**

![Chemical structure](image)

Synthesized according to the general protocol using di(2,4-dimethylphenyl)iodonium triflate (1j) to give 8c in 19% yield as a colorless oil. \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.19-7.10 (m, 2H), 7.05 (br s, 1H), 7.01-6.95 (app d, \(J = 8.39\), 1H), 6.44-6.39 (m, 2H), 3.77 (s, 3H), 2.32 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 161.0, 146.7, 138.1, 132.9, 131.9, 130.5, 130.2, 128.8, 127.5, 121.8, 109.1, 105.1, 102.1, 55.4, 20.9, 18.0; HRMS (ESI) \(m/z\) calculated for C\(_{15}\)H\(_{18}\)NO ([M + H]\(^{+}\)) 228.1383 found 228.1383.

**N-(3-methoxyphenyl)-2,5-dimethylaniline (8d):**

![Chemical structure](image)

Synthesized according to the general protocol using di(2,5-dimethylphenyl)iodonium triflate (1h) to give 8d in 30% yield as a colorless oil. Analytical data were in agreement with previously reported data.\(^{[15]}\)

**N-(3-methoxyphenyl)-2,6-dimethylaniline (8e):\(^{[16]}\)**

![Chemical structure](image)

t-Bu$_3$PBF$_4$ (0.005 mmol, 1.5 mg), Pd(OAc)$_2$ (0.003 mmol, 0.7 mg) and Cs$_2$CO$_3$ (3.05 mmol, 0.994 g) was added to a vial. Inert atmosphere was introduced by applying vacuum and then backfilling with argon. A mixture of \(m\)-anisidine (0.5 mmol, 0.057 mL) and 2,6-dimethylbromobenzene (3 mmol, 0.400 mL) in dry DMF (2 mL) was added to the solid compounds. The reaction vial was capped and submitted to \(\mu\)-wave irradiation at 140 °C for 1 h. The reaction mixture was filtered through a plug of SiO$_2$ (5 g). The SiO$_2$ was washed with CH$_2$Cl$_2$ (10 mL). Column chromatography (pentane \(\rightarrow\) pentane : EtOAc 9 : 1) gave 8e in 66% yield as a colorless oil. \(^{1}\)H NMR (400 MHz, CDCl$_3$) \(\delta\) 7.14-7.05 (m, 4H), 6.33 (d, \(J = 8.20\), 1H), 6.16 (d, \(J = 8.04\), 1H), 6.05 (t, \(J = 2.28\), 1H), 3.74 (s, 3H), 2.23 (s, 1H); \(^{13}\)C NMR (100 MHz, CDCl$_3$) \(\delta\) 161.1, 148.0, 138.3, 136.3, 130.2, 128.7, 126.1, 106.9, 103.4, 99.8, 55.3, 18.5; HRMS (ESI) \(m/z\) calculated for C$_{14}$H$_{18}$NO$^+$ ([M+H]$^+$) 228.1383 found 228.1360.
*N*-(*3*-methoxyphenyl)-4-methoxyaniline (8g):

![Structure](image)

Synthesized according to the same procedure as 8e using 2-methoxybromobenzene with 1.5 h reaction time. Column chromatography (pentane → pentane : EtOAc 9 : 1) gave 8g in 50% yield as a colorless oil. Analytical data were in agreement with previously reported data.\(^{[17]}\)

*N*-(*3*-methoxyphenyl)-2-methoxyaniline (8h):

![Structure](image)

Synthesized according to the same procedure as 8e with 1.5 h reaction time. Column chromatography (pentane → pentane : EtOAc 9 : 1) gave 8h in 52% yield as a colorless oil. Analytical data were in agreement with previously reported data.\(^{[18]}\)
6 Arylation of Malonate 9 to Products 10, 11

6.1 Arylation with unsymmetric diaryliodonium salts 1, 2

Experimental procedure:[19]
NaH (60% dispersed in mineral oil, 1.3 equiv, 0.33 mmol, 10 mg) was suspended in DMF (0.5 mL) and diethylmethylmalonate 9 (0.25 mmol, 44 mg) was added dropwise at 0 °C. The reaction was allowed to stir at rt for 10 min. A solution of diaryliodonium salt 1 or 2 (1.3 equiv, 0.33 mmol) in DMF (0.5 mL) was added via cannulation to the reaction mixture at 0 °C. The reaction mixture was stirred at rt until TLC indicated complete consumption of 9. The reaction was quenched with H2O at 0 °C, extracted with EtOAc (3 × 5 mL) and washed with H2O (1 × 10 mL) and brine (2 × 10 mL). The combined organic phases were dried (MgSO4) and concentrated in vacuo. The crude material was purified with flash chromatography to give products 10 and 11 as an inseparable mixture. The product ratio was determined by NMR from the crude mixture.

Diethyl 2-methyl-2-phenylmalonate (10):

Synthesized according to the general procedure using salt 1f, giving 10 as a colorless oil in 55% yield. Analytical data was in agreement with the reported analytical data.[20]

Diethyl 2-(2-methylphenyl)-2-methylmalonate (11b):

Synthesized according to the general procedure using salt 1b, and isolated as a mixture of 10 and 11b. The presence of 11b was confirmed by comparing with the reported analytical data.[21]

6.2 Arylations to obtain reference products

The following compounds were synthesized separately to obtain NMR data of the pure minor products, in order to confirm the NMR analysis of the crude mixtures.

Diethyl 2-(4-methylphenyl)-2-methylmalonate (11a):

Synthesized according to the general protocol using di((4-methylphenyl)iodonium triflate (1i) to give 11a in 53% yield as a colorless oil. Analytical data were in agreement with previous report.[22]
Diethyl 2-(2,4-dimethylphenyl)-2-methylmalonate (11c):

Synthesized according to the general protocol using di(2,4-dimethylphenyl)iodonium triflate (1j) to give 11c in 30% yield as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.05-6.94 (m, 3H), 4.35-4.15 (m, 4H), 2.30 (s, 3H), 2.25 (s, 3H), 1.86 (s, 3H), 1.27 (t, $J$ = 7.2, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 172.0, 137.3, 136.8, 135.2, 133.2, 126.9, 126.7, 61.9, 59.4, 23.2, 21.0, 20.9, 14.1; HRMS (ESI) $m/z$ calculated for C$_{16}$H$_{12}$NaO$_4$ ([M + Na]$^+$) 301.1410 found 301.1406.

Diethyl 2-(2,5-dimethylphenyl)-2-methylmalonate (11d):

Synthesized according to the general procedure using di(2,5-dimethylphenyl)iodonium triflate (1h) to give 11d in 41% yield as a colorless oil. Analytical data were in agreement with previous report.

Diethyl 2-(4-methoxyphenyl)-2-methylmalonate (11g):

Synthesized in a two-step procedure from diethylmalonate. CuI (0.01 g, 0.05 mmol), 2-picolinic acid (0.012 g, 0.1 mmol) and Cs$_2$CO$_3$ (0.977 g, 3 mmol) was added to a dry round-bottomed flask containing a magnetic stirrer bar, submitted to vacuum for 15 min and then backfilled with argon. Dry 1,4-dioxane (2 mL) was added via syringe followed by diethylmalonate (0.304 mL, 2 mmol) and 4-idoanisole (0.234 g, 1 mmol). The reaction was stirred at rt under argon for 24 h. Column chromatography (pentane $\rightarrow$ pentane : EtOAc 5 : 1) afforded the product in 91% yield.

Diethyl 2-(2-methoxyphenyl)methylmalonate (0.242 g, 0.91 mmol) was dissolved in dry DMF (10 mL) in a round-bottomed flask. NaH (60% dispersed in mineral oil, 0.028 g, 1.18 mmol) was added at 0 $^\circ$C and the mixture was allowed to stir at that temperature for 15 min. MeI (0.57 mL, 0.92) was added at 0 $^\circ$C and the reaction was allowed to reach rt and was stirred for 18 h. The reaction was then cooled to 0 $^\circ$C and water (2 mL) was added. After 15 min, the reaction mixture was transferred to a separatory funnel and extracted with EtOAc (3 x 40 mL). The combined organic layers where washed with water (2 x 60 mL) and brine (2 x 60 mL). Column chromatography (pentane $\rightarrow$ pentane : ethylacetate 5 : 1) afforded 11g in 30% yield as a yellow oil. Analytical data were in agreement with previous report.

Diethyl 2-(2-methoxyphenyl)-2-methylmalonate (11h):

Synthesized in a two-step procedure from diethylmalonate as described for 11g, using 2-bromoanisole and 24 h reaction time. The crude mixture was purified by column chromatography (pentane $\rightarrow$ pentane : ethylacetate 9 : 1) to give 11h in 79% yield as a yellow...
oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.31-7.25 (m, 1H), 7.11 (dd, $J = 7.72$, 1.64, 1H), 6.97-6.88 (m, 2H), 4.31-4.17 (m, 4H), 3.79 (s, 3H), 1.81 (s, 3H), 1.26 (t, $J = 7.08$, 6 H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 171.7, 157.1, 129.4, 128.9, 127.2, 120.9, 111.8, 61.7, 57.9, 55.6, 22.0, 14.2. HRMS (ESI) $m/z$ calculated for C$_{15}$H$_{20}$NaO$_5$ ([M + Na]$^+$) 303.1203 found 303.1192.

**Diethyl 2-(2,4-dimethoxyphenyl)-2-methylmalonate (11i):**

Prepared according to the general procedure using the symmetrical bis(2,4-dimethylphenyl)iodonium triflate 12b to give 11i in 57% yield as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.04-6.94 (m, 3H), 4.33-4.17 (m, 4H), 3.79 (s, 3H), 1.81 (s, 3H), 1.27 (t, $J = 7.08$, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 171.9, 160.4, 158.1, 127.6, 121.9, 104.1, 99.8, 61.6, 57.2, 55.6, 55.5, 22.1, 14.2; HRMS (ESI) $m/z$ calculated for C$_{15}$H$_{22}$NaO$_6$ ([M + Na]$^+$) 333.1309 found 333.1325.

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7 Computational details

All calculations reported in the present study were carried out using density functional theory with the B3LYP functional, as implemented in the Gaussian09 program package. For geometry optimizations, the 6-31G(d,p) basis set was used for the C, N, O, F, Cl, H elements, and the LANL2DZ pseudopotential with the corresponding basis set, augmented with d polarization and p diffuse functions, for I. Based on these optimized geometries, single-point calculations were carried out with the same basis set for I and the 6-311+G(2d,2p) basis set for all other elements. The stationary points were confirmed as minima (no imaginary frequencies) or transition states (only one imaginary frequency) by analytical frequency calculations at the same theory level as the geometry optimizations. The reported energies are Gibbs free energies, which include zero-point vibrational corrections, thermal corrections at 298 K (or 403 K for reaction with anilines), and solvation free energies. The latter are calculated as single-point corrections on the optimized structures using the conductor-like polarizable continuum model (CPCM) method with the UFF radii and with the parameters for THF or DMF, according to experiments. All energies are also corrected for dispersion effects using the B3LYP-D3 method of Grimme, with Becke and Johnson (BJ) damping.

7.1 Illustrative Figures

Figure S5: Free energy profile and optimized structures of starting complexes and transition states for the reaction of phenol 3 with 1e. Distances are in angstroms and energies are in kcal/mol. This figure is given in black and white in the paper.
**Figure S6.** Optimized TS structures of aniline 6 with salt 2b, and malonate 9 with salt 1e. Distances are in angstroms and energies are in kcal/mol. This figure is given in black and white in the paper.

**Figure S7:** Free energy profile for the reaction of malonate 9 with 1e. Energies are given in kcal/mol. TS structures are given in Figure S6.
7.2 Correlation plots between absolute barriers and Hammett $\sigma$ for the ligand coupling between phenoxide and aryl(phenyl)iodonium salts with one para-substituted aryl group.

Figure S8. Substituted aryl transfer.

Figure S9. Phenyl transfer.
7.3 Optimized structures and Cartesian coordinates of stationary points

- INT$_{3-1a}$

B3LYP/BS2 energy: -935.576772626 a.u.
ZPE: 0.3342 a.u.
Thermal correction to Gibbs Free Energy: 0.275986 a.u.
Solvation energy: -7.60 kcal/mol
Dispersion correction: -60.65 kcal/mol

I  0.48046700 -0.43620000 -0.90243900
C  0.38877000  1.61676000 -0.19824300
C  0.58395200  2.43561800 -0.76036900
C  0.64899700  3.76463300 -0.33175900
C  0.23452700  4.24393300  0.63633200
C  1.19297600  3.39238400  1.18686700
C  1.28251800  2.06042500  0.77018500
H  -1.27363500  2.02659500 -1.49069700
H  -1.40033300  4.42086200 -0.76103500
H  0.17377100  5.27714700  0.96492400
H  1.87708900  3.75020200  1.94853900
H  2.02875800  1.40294900  1.19865600
C  2.50795100 -0.67461200 -0.13038800
C  2.71153200 -1.40212200  1.04635200
C  4.00991500 -1.66642400  1.48937700
C  5.12492200 -1.21428000  0.77257200
C  4.90470400 -0.49194400 -0.41003400
C  3.61312100 -0.22487500 -0.86275600
H  1.86351200 -1.76616100  1.62071800
H  4.15638400 -2.23497100  2.40459000
H  5.75647500 -0.13942900 -0.98708700
H  3.47181600  0.33262800 -1.78487600
C  6.52760300 -1.47847000  1.26578100
H  6.56150000 -2.34427500  1.93291600
H  7.21533000 -1.66182000  0.43472600
H  6.91725000 -0.61852800  1.82738400
C -2.69359300 -0.46477100 -1.08676700
C -3.74916300 -1.07662800 -1.80583200
C -2.85556100 -0.27410300  0.29689000
C -4.90796200 -1.46341200 -1.14773100
H -3.62866600 -1.22414700 -2.87425100
C -4.02833900 -0.67881800  0.94596600
H -2.08244900  0.20543900  0.88775600
C -5.07144600 -1.27754800  0.23187800

- TS$_{isomer}$

B3LYP/BS2 energy: -935.555786091 a.u.
ZPE: 0.332919 a.u.
Thermal correction to Gibbs Free Energy: 0.274296 a.u.
Solvation energy: -11.10 kcal/mol
Dispersion correction: -57.45 kcal/mol

I  0.36619700  0.18774500 -0.62698900
C  1.36530700  2.01376400  0.03430000
C  2.11086600  2.75549700 -0.88216600
C  2.70430800  3.94874100 -0.46231300
C  2.53756400  4.39211100  0.85134800
C  1.77389600  3.64906000  1.75189100
C  1.17589000  2.45113000  1.34526600
H  2.23166100  2.41481700 -1.90584700
H  3.29180700  4.53198500 -1.16553200
H  2.99655100  5.32285100  1.17104000
H  1.63673800  3.99524100  2.77154100
H  0.57411000  1.87510100  2.04147300
C  2.15449900 -0.95909900 -0.11021800
C  2.26429800 -1.51215000  1.16468300
C  3.37988000 -2.29336400  1.47092300
C  4.37924300 -2.53858800  0.51916500
C  4.22939700 -1.98580700 -0.76048100
C  3.12102100 -1.20218000 -1.08551600
H  1.49530300 -1.34341700 -1.91248400
C  3.46935900 -2.72384900  2.46518200
C  4.98594100 -2.17353000 -1.51800800
H  3.01845000 -0.79357800 -2.08628300
C  5.59517500 -3.36338600  0.86747300
H  5.37608200 -4.08466200  1.65982500
H  5.96757300 -3.91411200 -0.00121300

S19
B3LYP/BS2 energy: -935.5499026890 a.u.
ZPE: 0.332506 a.u.
Thermal correction to Gibbs Free Energy: 0.275244 a.u.
Solvation energy: -7.58 kcal/mol
Dispersion correction: -60.05 kcal/mol

I  0.94862400  -0.95360100  -0.65483400
O  -1.41680300  -0.42511500  -1.17440600
C  -2.50334900  -0.74131300  -0.48279200
C  -2.55392900  -1.84664900  0.40814300
C  -3.66803800  0.04405800  -0.61181800
C  -3.69921900  -2.14395600  1.10719500
H  -1.65396900  -2.47186000  0.51055400
C  -4.82478300  -0.26223400  0.10724800
H  -3.66589900  0.89407700  -1.2848500
C  -4.85380900  -1.36406700  0.97581900
H  -3.71804300  -3.00136700  1.77561300
H  -5.74447600  -1.69116000  1.53661400
O  -5.88921500  0.57696900  -0.10495300
C  -7.09623700  0.31063200  0.58439700
H  -6.96620700  0.36346400  1.67393700
H  -7.80071000  1.08418300  0.27220800
H  -7.50783900  -0.67422100  0.32549000

B3LYP/BS2 energy: -935.548642447 a.u.
ZPE: 0.332445 a.u.
Thermal correction to Gibbs Free Energy: 0.274601 a.u.
Solvation energy: -7.49 kcal/mol
Dispersion correction: -60.05 kcal/mol

I  1.31614300  -1.15661500  -0.51519400
O  -1.04056300  -0.74404900  -1.15399700
C  -2.14300700  -1.04058000  -0.47908800
C  -2.17945300  -2.07694900  0.49086200
C  -3.32252400  -0.30121600  -0.70803000
C  -3.35968300  -2.35478600  1.16929200
H  -1.28581100  -2.66074100  0.67093200
C  -4.49642200  -0.58587600  -0.00830200
H  -3.31762700  0.49610800  -1.44269100

S20
| Atoms | B3LYP/BS2 Energy | ZPE | Thermal correction to Gibbs Free Energy | Solvation energy | Dispersion correction |
|-------|------------------|-----|----------------------------------------|------------------|----------------------|
| C     | -4.52862500      |     |                                        |                  |                      |
| H     | -3.38080600      |     |                                        |                  |                      |
| H     | -5.43237300      |     |                                        |                  |                      |
| O     | -5.57358100      |     |                                        |                  |                      |
| C     | -6.79670300      |     |                                        |                  |                      |
| H     | -6.70482000      |     |                                        |                  |                      |
| O     | -7.50852400      |     |                                        |                  |                      |
| C     | -7.17565400      |     |                                        |                  |                      |
| C     | 0.11426000       |     |                                        |                  |                      |
| C     | 0.33863600       |     |                                        |                  |                      |
| C     | -0.34133900      |     |                                        |                  |                      |
| C     | 0.07242700       |     |                                        |                  |                      |
| H     | 0.68321000       |     |                                        |                  |                      |
| C     | -0.59246600      |     |                                        |                  |                      |
| H     | -0.52705800      |     |                                        |                  |                      |
| C     | -0.39278600      |     |                                        |                  |                      |
| H     | 0.23074000       |     |                                        |                  |                      |
| C     | -0.95676700      |     |                                        |                  |                      |
| C     | 3.30510600       |     |                                        |                  |                      |
| H     | 4.23614200       |     |                                        |                  |                      |
| C     | 3.66010200       |     |                                        |                  |                      |
| C     | 5.53108700       |     |                                        |                  |                      |
| H     | 3.95832600       |     |                                        |                  |                      |
| C     | 4.95813700       |     |                                        |                  |                      |
| H     | 2.93468900       |     |                                        |                  |                      |
| C     | 5.89301500       |     |                                        |                  |                      |
| H     | 6.25590800       |     |                                        |                  |                      |
| H     | 5.23643200       |     |                                        |                  |                      |
| H     | 6.90130000       |     |                                        |                  |                      |
| C     | -0.69228200      |     |                                        |                  |                      |
| H     | 0.07951900       |     |                                        |                  |                      |
| H     | -1.64815600      |     |                                        |                  |                      |
| C     | -0.75589500      |     |                                        |                  |                      |

\[-\text{INT}_{3\text{-}1\text{-}Ar}\]

B3LYP/BS2 energy: -974.902204559 a.u.
ZPE: 0.362424 a.u.
Thermal correction to Gibbs Free Energy: 0.305344 a.u.
Solvation energy: -7.62 kcal/mol
Dispersion correction: -68.78 kcal/mol

| I     | 0.99534100     | -0.85418800 | 0.74628400 |
| O     | -1.07960400   | -0.94718600 | 1.66428600 |
| C     | -2.12355500   | -1.14562900 | 0.84869400 |
| C     | -2.35662600   | -2.40649800 | 0.24575400 |

\[-\text{INT}_{3\text{-}1\text{-}Ph}\]

B3LYP/BS2 energy: -974.901388727 a.u.
ZPE: 0.362308 a.u.
Thermal correction to Gibbs Free Energy: 0.304185 a.u.
Solvation energy: -7.47 kcal/mol
Dispersion correction: -63.30 kcal/mol

B3LYP/BS2 energy: -974.87465915 a.u.
ZPE: 0.360533 a.u.
Thermal correction to Gibbs Free Energy: 0.30235 a.u.
Solvation energy: -7.53 kcal/mol
Dispersion correction: -66.60 kcal/mol
B3LYP/BS2 energy: -974.876689458 a.u.
ZPE: 0.360557 a.u.
Thermal correction to Gibbs Free Energy: 0.302654 a.u.
Solvation energy: -6.83 kcal/mol
Dispersion correction: -67.10 kcal/mol

I  -1.25630200  -0.91905500  -0.65132400
O  1.09559100  -0.31635900  -1.15024400
C  2.23883500  -0.75517700  -0.64056800
C  2.39442800  -2.09932500  -0.20843700
C  3.34144900  0.11481600  -0.52044300
C  3.61282700  -2.53000800  0.29983000
H  1.55807200  -2.78564700  -0.30575300
C  4.55493700  -0.33324900  0.00752700
H  3.24937700  1.14533400  -0.84467900
C  4.70649500  -1.66402200  0.42298500
H  3.72483800  -3.56498600  0.61400600
H  5.64186100  -2.02860000  0.82893100
O  5.54855700  0.61022100  0.07638800
C  6.80706200  0.21624400  0.58924300
H  7.26629200  -0.57651900  -0.01660100
H  7.44136000  1.10430800  0.55386500
H  6.73501500  -0.13146300  1.62878500
C  -0.12744400  1.14399200  -0.01093000
C  0.19280800  1.22848200  1.33911500
C  -0.25148100  2.20227400  -0.90593600
C  0.37442400  2.53779000  1.82334300
C  -0.06035700  3.47808000  -0.35140000

INT_6-1a

B3LYP/BS2 energy: -916.12811498 a.u.
ZPE: 0.359608 a.u.
Thermal correction to Gibbs Free Energy: 0.297426 a.u.
Solvation energy: -37.52 kcal/mol
Dispersion correction: -60.83 kcal/mol

I  0.31655800  0.18145400  -0.18505700
C  -2.96606700  0.96063000  -0.52308100
C  -3.32825700  0.50617100  -1.81325500
C  -3.59413700  0.40736300  0.59139400
C  -4.24948000  -0.48304500  -1.96160300
C  -2.79853700  0.94343800  -2.68345500
C  -4.56690400  -0.59213500  0.42755300
H  -3.37006700  0.74812100  1.59819300
C  -4.89785600  -1.04220800  -0.85859700
H  -4.51092800  -0.82658600  -2.95782700
H  -5.64789500  -1.80823200  -1.00793400
O  -5.12194300  -1.04977400  1.57622700
C  -6.14926100  -2.03503600  1.49469100
Solvation energy:
ZPE:
B3LYP/BS2 energy:

- TS$_{6-1a}$-Ph

B3LYP/BS2 energy: -916.088077828 a.u.
ZPE: 0.35863 a.u.
Thermal correction to Gibbs Free Energy: 0.300842 a.u.
Solvation energy: -37.05 kcal/mol
Dispersion correction: -65.27 kcal/mol

I 0.13479600 -0.70828200 -0.08562000
C 2.68446700 1.34839800 0.20470100
C 2.99311100 1.25954500 1.57448100
C 3.22865800 0.43727800 -0.70904600

- TS$_{6-1a}$-Ar

B3LYP/BS2 energy: -916.087154717 a.u.
ZPE: 0.358617 a.u.
Thermal correction to Gibbs Free Energy: 0.300697 a.u.
Solvation energy: -37.02 kcal/mol
Dispersion correction: -65.22 kcal/mol

B3LYP/BS2 energy: -991.360811921 a.u.
ZPE: 0.365365 a.u.
Thermal correction to Gibbs Free Energy: 0.305086 a.u.
Solvation energy: -36.92 kcal/mol
Dispersion correction: -62.93 kcal/mol
B3LYP/BS2 energy: -991.319091906 a.u.
ZPE: 0.364112 a.u.
Thermal correction to Gibbs Free Energy: 0.305749 a.u.
Solvation energy: -36.97 kcal/mol
Dispersion correction: -67.20 kcal/mol

H 1.59058800 2.85847800 -0.35523300
H -4.32268000 -4.16929500 -1.47056400
O -2.11793600 -1.62235400 1.62958400
C -2.69084100 -2.31836000 2.74297900
H -2.26211100 -1.85592300 3.63165300
H -3.78020000 -2.20588400 2.76035100
H -2.42596300 -3.38038100 2.72079400
H -1.51872400 -1.21345100 -2.82945700

- TS6-2b-Ph

B3LYP/BS2 energy: -991.319759214 a.u.
ZPE: 0.364329 a.u.
Thermal correction to Gibbs Free Energy: 0.307039 a.u.
Solvation energy: -35.91 kcal/mol
Dispersion correction: -67.88 kcal/mol

I -0.02448500 -0.39614400 -0.90752700
C 2.55296900 1.43873000 -0.07639100
C 2.88386400 1.32462400 -1.44077700
C 3.13664620 0.59200100 0.87123600
C 3.81429200 0.36294400 -1.82580800
H 2.44500500 1.99662000 -2.17241600
C 4.07344700 -0.36984200 0.46850800
C 2.83283600 0.66995500 1.92645700
C 4.40969100 0.48793100 -0.89184100
H 4.09028800 0.27588600 -2.87185200
H 5.13329200 -1.22186600 -1.22302600
O 4.85803400 -1.12843900 1.46001200
C 5.57727700 -2.10822400 1.13935100
H 6.46426400 -1.64521700 0.69276600
H 5.84940700 -2.57249000 2.08680500
H 5.17711000 -2.87111400 0.46189600
C -0.64072500 1.81648700 0.40160800
C -0.94268500 1.53509100 1.71887800
C -1.30399500 2.71462400 -0.41027300
C -2.03999300 2.22285300 2.26020000
H -0.39017800 0.80785900 2.30124700
C -2.39538200 3.38220300 0.16815800
H -1.02266000 2.89327900 -1.44174100
C -2.75987200 3.14080200 1.49336000
H -2.31862200 2.02731400 3.29175100
H -2.95108400 4.09198000 -0.43778300

C -2.04807800 -0.95614200 -0.75796100
C -2.48967300 -1.63730800 0.39475900
C -2.90823200 -0.67828400 -1.82091600
C -3.83280400 -2.03593900 0.44599300
C -4.24183300 -1.08021900 -1.75014800
C -4.69247400 -1.75739200 -0.61709200
H -4.20937900 -2.56427400 1.33138400
H -4.91443000 -0.87048400 -2.57407600
H -3.60424900 3.66565700 1.92721100
N 1.55954800 2.35112700 0.32898400
H 1.60678300 2.63269000 1.29711600
H 1.46763900 3.16705800 -0.27443600
H -5.72741200 -2.07874000 -0.55378900
O -1.58422000 -1.85643100 1.37779100
C -1.97575400 -2.63880300 2.50844200
H -1.08318100 -2.72892200 3.12735700
H -2.76882000 -2.14316000 3.07942700
H -2.30907300 -3.63632100 2.20310400
H -2.53727700 -0.16051700 -2.69865000

- TS6-2b-Ar

S26
Dispersion correction:

Solvation energy:

H

C

H

C

C

C

H

C

C

H

H

C

O

C

C

H

C

H

H

C

H

H

C

H

O

S

27

B3LYP/BS2 energy: -1088.50812807 a.u.
ZPE: 0.385728 a.u.
Thermal correction to Gibbs Free Energy: 0.322089 a.u.
Solvation energy: -10.00 kcal/mol
Dispersion correction: -71.50 kcal/mol

I 0.43743100 -0.84143000 -0.53847200
C 0.33570100 1.11753500 0.32691800
C 0.28671100 2.17735800 -0.57474500
C 0.33373000 1.27814400 1.72026200
C 0.26081400 3.49704600 -0.09865100
C 0.31267300 2.60681000 2.16678200

C 0.28110900 3.68828500 1.28552300
H 0.31110300 2.79097000 3.23770200
C 2.66462100 -0.79588080 -0.27006700
C 3.25478700 -1.95013300 0.24639300
C 3.45117700 0.28632900 -0.66813400
C 4.64626400 -2.02078000 0.37148800
H 2.64209000 -2.79308100 0.55930000
C 4.84061400 0.21087900 -0.53868600
H 2.99403800 1.18836700 -1.06435800
C 5.43811100 -0.94071900 -0.02010400
H 5.10669600 -2.91659300 0.77933600
H 5.45601300 1.05260500 -0.84505800
H 0.26168300 4.69890700 1.68516400
H 6.51842500 -0.99469300 0.07815400
C 0.32209000 0.13106900 2.69682600
H -0.58692200 -0.46760000 2.56675600
H 1.18943600 -0.52371000 2.55666300
H 0.34627100 0.50423500 3.72351200
C -2.18185900 -0.90637300 -0.78342300
C -2.48388200 -1.70154600 0.42214600
C -2.61017900 0.50535200 -0.85808000
O -2.54297400 1.18365000 -1.87867600
O -2.54482400 -1.33196900 1.58546000
O -3.07316800 0.19159500 0.30778900
O -2.61752500 -3.03158400 0.10446700
C -2.23787700 -1.62531400 -2.12365800
H -3.22533600 -2.06535700 -2.30650600
H -2.02557300 -0.91530000 -2.92456200
H -1.51960300 -2.45307600 -2.17891000
C -3.52512300 2.37408000 0.23969400
H -3.90105600 2.60582000 1.23718300
H -2.70732300 3.05037100 -0.02244200
H -4.32054400 2.48537500 -0.50273400
C -2.85563500 -3.89663800 1.21829600
H -3.78702500 -3.63235600 1.72684000
H -2.92372200 -4.90309300 0.80244400
H -2.04021100 -3.83919400 1.94529600
C 2.10592000 4.65481400 -1.06749600
H 1.15233800 4.75502900 -1.62004800
H -0.58542200 4.51557300 -1.80637100
H 0.03028300 5.59927700 -0.54709300
H 0.23798600 1.98913200 -1.64128700

- TS9-1d-Ph

B3LYP/BS2 energy: -1088.48484677 a.u.
ZPE: 0.384185 a.u.

- INT9-1d
Thermal correction to Gibbs Free Energy: 0.322661 a.u.
Solvation energy: -10.40 kcal/mol
Dispersion correction: -72.56 kcal/mol

- TS$_{9.1d}$-Ar

B3LYP/BS2 energy: -1088.48586239 a.u.
ZPE: 0.384598 a.u.
Thermal correction to Gibbs Free Energy: 0.32376 a.u.
Solvation energy: -9.38 kcal/mol
Dispersion correction: -73.27 kcal/mol

I  0.72342500  -1.46524400  0.07114600
C  -0.42508900  0.67290900  0.13476600
C  -0.10410600  1.49174100  -0.93739700
C  -0.74621200  1.15663900  1.39576400
C  -0.16034500  2.87640500  -0.74237400
C  -0.79375400  2.54440100  1.56663300
C  -0.49855100  3.40307500  0.50589500
H  0.06476100  3.53675000  -1.57550600
H  -1.07562500  2.94529100  2.53617500
C  2.56564100  -0.38968500  -0.12139200
C  3.39773100  -0.60268500  -0.21341900
C  2.91878400  0.49047500  0.90471900
C  4.60069800  0.19493400  -1.26217400
C  4.12176000  1.20317500  0.85929100
C  4.95711100  1.00152800  -0.24615400
H  -0.53130800  4.47839800  0.63174200
H  5.89771600  1.54253400  -0.31392600
C  -2.70678900  -0.59175400  -0.64707700
C  -2.45103600  -1.48553300  0.42422300
C  -3.49612600  0.62304500  -0.46500000
O  -3.88717000  1.12143700  0.57899100
O  -1.60779300  -2.42437900  0.34700600
O  -3.72592200  1.23477700  -1.67569800
O  -3.09469000  1.26765900  1.59706700
C  -2.30361500  -1.00856900  -0.20358240
H  -3.17933000  -1.07211800  -2.69168400
H  -1.62712400  -0.28390300  -2.50970500
H  -1.81535400  -1.98352000  -2.01284000
C  -4.42790900  2.47490400  -1.58955400
C  -4.54926700  2.82093800  -2.61763400
H  -5.40497800  2.34393200  -1.11503600
C  -3.85957000  3.20656200  -1.00700000
C  -2.83264500  -2.20869700  2.64101800
H  -1.77603700  -2.21683200  2.29153900
H  -3.44410100  -1.88113500  3.48300000
H  -3.11663300  -3.22182100  2.34147800
H  0.16201500  1.08306400  -1.90642500
H  -1.00823200  0.49269400  2.21136800
C  3.06112200  -1.54822200  -2.36354400
C  3.00958080  -2.58861500  -2.02267200
H  2.09200100  -1.31425800  -2.81666700
H  3.82088400  -1.49405400  -3.14714700
C  4.51378800  2.13970600  1.97757000
H  3.64428500  2.44658000  2.56526800
H  5.22383100  1.66180500  2.66375200
H  4.99620300  3.04254200  1.59004800
H  2.24358500  0.64128900  1.74154900
H  5.26772700  -0.01504700  -2.11050300
B3LYP/BS2 energy: -1088.5061479 a.u.
ZPE: 0.386516 a.u.
Thermal correction to Gibbs Free Energy: 0.326000 a.u.
Solvation energy: -9.67 kcal/mol
Dispersion correction: -74.10 kcal/mol

H  2.53607400  -0.13680400  2.02285600
H  0.54451900  1.39403800  -1.64873600
H  -0.60568400  2.29701700  3.07498600
C  -0.85947900  -0.33989200  2.51938400
H  -0.73249100  -0.03582000  3.56371900
H  -1.92059000  -0.53405800  2.34166600
H  -0.30168100  1.26158200  2.35619900
C  0.66945500  4.06150800  -1.08079600
H  1.46681700  3.77609400  -1.77422800
H  -0.19587600  4.36004600  -1.68501200
H  1.00323800  4.94257100  -0.52525000

- INT_9-1e-Ar

B3LYP/BS2 energy: -1088.5061479 a.u.
ZPE: 0.386516 a.u.
Thermal correction to Gibbs Free Energy: 0.326000 a.u.
Solvation energy: -9.67 kcal/mol
Dispersion correction: -74.10 kcal/mol

H  1.38879300  1.34599600  -2.46840500
H  -0.37399500  1.47017900  -2.66649700
H  0.64464000  2.90784800  -2.83665000
C  -2.09563200  -1.03416400  -0.90287500
C  -2.34832600  -2.03062700  0.15162100
C  -2.64772500  0.32960000  -0.93015700
O  -2.66236500  1.03446300  -1.93652400
O  -2.13460800  -3.22750200  -0.01060400
O  -3.10761300  0.80011200  0.25871800
O  -2.75920800  -1.55270100  1.36256600
C  -1.95975100  -1.67217000  -2.27805500
H  -2.89277000  -2.16523700  -2.57097200
H  -1.72247000  -0.91468300  -3.02582800
H  -1.18951100  -2.45079000  -2.28424000
C  -3.62147600  2.13545100  0.21987900
H  -3.97932300  2.33971100  1.23012200
H  -2.84118000  2.84883300  -0.05819700
H  -4.44177100  2.21905100  -0.49816300
C  -2.98432200  -2.56100800  2.35472000
H  -2.06138500  -3.09841000  2.39185900
H  -3.35068300  -2.02868100  3.23385300
H  -3.72634100  -3.28745200  2.01341700

- INT_9-1e-Ph
H -4.99003800  -0.60691100  -2.31506400  
H  0.16487500  5.05177900  -1.51069000  
H -6.41756800  -0.53418900  -0.29074800  
C  2.28870700  -0.93099300  0.68489800  
C  2.75724100  -1.31663400  -0.65500800  
C  2.70875300  0.34887700  1.28904100  
O  2.44981300  0.67720100  2.44070000  
C  2.98521800  -0.59909600  -1.62272100  
O  3.42224000  1.16262700  0.46538800  
O  2.85321400  -2.68001700  -0.76846700  
C  2.11757300  -2.04544400  1.70592900  
H  3.04751800  -2.60736500  1.85145100  
H  1.82131000  -1.61530900  2.66401800  
H  1.64990900  -2.78371600  1.95623200  
C  3.81553900  2.40968100  1.04524200  
H  4.40423400  2.91576500  0.27862200  
H  2.94243500  3.01230300  1.31193600  
H  4.41586400  2.25236700  1.94530700  
C  3.24066400  -3.15555000  -2.06058900  
H  2.30204000  -2.78016900  -2.33552200  
H  3.25646000  -4.24371900  -1.98248200  
H  2.52786600  -2.83897400  -2.82779900  
H -1.89305800  2.03002020  0.75938800  
H  1.62889200  0.99849200  -1.53892200  
C -2.29944400  -0.61294200  -2.48739800  
H -1.63827500  0.25610700  -2.56809200  
H -1.66248100  -1.50408100  -2.51527200  
H -2.93878400  -0.63199000  -3.37314600  
C -2.77535500  -0.43331700  2.62319800  
C -2.22464600  -1.34922000  2.86502800  
H -2.07627300  0.39893400  2.75692300  
H -3.57092000  -0.32309800  3.36430700  

- TS9-1e-Phe

B3LYP/BS2 energy: -1088.48177252 a.u.  
ZPE: 0.384444 a.u.  
Thermal correction to Gibbs Free Energy: 0.324696 a.u.  
Solvation energy: -10.30 kcal/mol  
Dispersion correction: -74.67 kcal/mol  

I  0.89841000  -1.30848600  -0.30323300  
C -0.41712200  0.59590500  0.48609200  
C -0.10890400  1.78218300  -0.16000500  
C -0.86623700  0.53536500  1.79776100  

S30
B3LYP/BS2 energy: -1088.47821554 a.u.
ZPE: -9.64 kcal/mol
Dispersion correction: -75.75 kcal/mol

B3LYP/BS2 energy: -837.06414942 a.u.
ZPE: -9.87 kcal/mol
Dispersion correction: -55.76 kcal/mol
Thermal correction to Gibbs Free Energy: 0.226545 a.u.
Solvation energy: -8.69 kcal/mol
Dispersion correction: -54.17 kcal/mol

I  0.00536900  -0.54335600  -0.60648600
O  -2.17951500  -0.29128600  -1.18891700
C  -3.15237600  -0.65570300  -0.33811000
C  -4.22186000  -1.44472000  -0.81693600
C  -3.17510800  -0.26993800  1.02028400
C  -5.26611700  -1.81969100  0.02437700
H  -4.20932000  -1.74174600  -1.86165100
C  -4.22280800  -0.65883900  1.85547600
H  -2.37129900  0.34837300  1.41067600
C  -5.27676400  -1.43834800  1.36878300
H  -6.07869100  -2.42400100  -0.37242100
H  -6.09057000  -1.73316100  2.02287100
C  -0.02977500  1.57941300  -0.13629800
C  0.99303300  2.13920800  0.62118000
C  -1.09795100  2.32078700  -0.62861000
C  0.93582100  3.50988200  0.89321800
H  1.81400200  1.54095000  0.99678700
C  -1.12835100  3.69051000  -0.34964100
H  -1.88179200  1.82398200  -1.19043300
C  -0.11772600  4.85067000  0.40722100
H  1.72097700  3.96341200  1.49121100
H  -1.95279300  4.28754100  -0.72818700
C  2.12249800  -0.68465700  0.11649700
C  3.09772500  -0.36210900  -1.06695100
C  2.51859700  -1.22525500  1.11503100
C  4.44923100  -0.56247900  -0.78881800
H  2.81164600  0.05192200  -2.03000400
C  3.86620500  -1.42998500  1.40071200
H  1.77339700  -1.48801700  1.86132300
C  4.83620900  -1.09792300  0.44657000
H  5.20245100  -0.30764800  -1.53176600
H  4.18548400  -1.84654500  2.35039600
H  -0.15249100  3.54903900  0.62165600
H  -4.21355600  -0.34645400  2.89736700
O  6.13328800  -1.32022400  0.77655600
H  6.70769900  -1.06264600  0.03885400

- TS-OH-Ph

B3LYP/BS2 energy: -856.910274185 a.u.
ZPE: 0.276865 a.u.

Thermal correction to Gibbs Free Energy: 0.225072 a.u.
Solvation energy: -8.50 kcal/mol
Dispersion correction: -53.59 kcal/mol

I  0.37453600  -0.93064300  -0.62971100
O  -1.98690500  -0.32747200  -1.09463900
C  -3.08122700  -0.60198500  -0.39883100
C  -3.12672400  -1.63354900  0.57161500
C  -4.25740300  0.16282200  -0.60296600
C  -4.29668800  -1.89506900  1.28303500
H  -2.23906900  -2.23870100  0.73589200
C  -5.41511800  -0.10234100  0.11892600
H  -4.22454400  0.95652500  -1.34306200
C  -5.44720200  -1.13324100  1.06648200
H  -4.30965300  -2.70069900  2.01337600
H  -6.35618300  -1.33942900  1.62389800
C  -0.68576000  1.15712200  -0.20954900
C  -0.45180400  2.16088000  -1.13822500
C  -1.05826100  1.39170800  1.10487800
C  -0.61857900  3.48289100  -0.71181200
H  -0.17638500  1.93279700  -2.16091300
C  -1.21488300  2.72482600  1.50147100
H  -1.25655600  0.57708700  1.79221100
C  -0.99249900  3.76964400  0.60297800
H  -0.45534200  4.28775000  -1.42362100
H  -1.51346000  2.93487100  2.52497900
C  2.41466700  -0.60593100  -0.10058900
C  3.32768300  -0.16169200  -1.06236600
C  2.84816300  -0.81984900  1.21750700
C  4.65950100  0.05784400  -0.71340400
H  3.00991600  0.01263000  -2.08559300
C  4.16956300  -0.60215100  1.56863400
H  2.13975000  -1.15892200  1.97295300
C  5.08386200  -0.16182000  0.60266600
H  5.36764800  0.40015200  -1.46103000
H  4.51676900  -0.76625800  2.58300000
H  -1.11206200  4.79967800  0.92373000
H  -6.30516800  0.49696700  -0.05752200
O  6.36952300  0.03396000  1.00481700
H  6.89974500  0.33706900  0.25606600

- TS-OH-Ar

B3LYP/BS2 energy: -856.906921924 a.u.
ZPE: 0.276642 a.u.

S33
| Atom  | X   | Y   | Z   |
|-------|-----|-----|-----|
| H     | 6.39403200 | 0.17566100 | 1.16423300 |
| H     | 4.74822600  |               |       |
| H     | 3.40242000  |               |       |
| C     | 0.13788700  | 1.565         |       |
| H     |               |               |       |
| O     | 5.05623000  | 0.54552800  | 0.01164000 |
| H     | -3.86597700 | 0.49543100  | -1.47694300 |
| H     | -0.18401400 | 2.55771400  | 0.76259400  |
| C     | -0.50770000 | -1.54206300 | 0.98223550  |
| H     | -3.91470700 | -3.03885500 | 2.00699900  |
| H     | -5.99259300 | -1.75704200 | 1.52661400  |
| C     | -0.40975200 | 0.92024900  | -0.31049800 |
| C     | -0.18967700 | 1.85884500  | -1.30847000 |
| C     | -0.85367800 | 1.24724800  | 0.95793900  |
| C     | -0.43431100 | 3.20025300  | -1.01165000 |
| H     | 0.13788700  | 1.56595600  | -2.29865800 |
| H     | -1.09113100 | 2.59804700  | 1.23907700  |
| H     | -1.04708200 | 0.48825000  | 1.70742300  |
| C     | -0.87997000 | 3.57467400  | 0.26163900  |
| H     | -0.28703100 | 3.96672100  | -1.76569500 |
| H     | -1.44417900 | 2.87940800  | 2.22923300  |
| C     | 2.77445100  | -0.68059200 | 0.07945600  |
| C     | 3.69490600  | -0.22664600 | -0.87168500 |
| C     | 3.14863400  | -0.82106700 | 1.42056000  |
| H     | 4.99825300  | 0.07962600  | -0.47529300 |
| H     | 3.40242000  | -0.11537000 | -1.91112600 |
| C     | 4.45508200  | -0.51337000 | 1.80546700  |
| H     | 2.43187400  | -1.16910400 | 2.15778000  |
| C     | 5.37925300  | -0.06345700 | 0.86037000  |
| H     | 5.71464600  | 0.43028700  | -1.21277700 |
| H     | 4.74822600  | -0.62519400 | 2.84539900  |
| H     | -5.95965700 | 0.01797770  | -0.22003700 |
| O     | -1.08868000 | 4.90857500  | 0.48688800  |
| H     | -1.42137300 | 5.02943500  | 1.38534300  |
| H     | 6.39403200  | 0.17566100  | 1.16423300  |

**- INT-Me**

B3LYP/BS2 energy: -821.016487779 a.u.
ZPE: 0.301661 a.u.
Thermal correction to Gibbs Free Energy: 0.247254 a.u.

**- TS-Me-Ph**

B3LYP/BS2 energy: -820.989811644 a.u.
ZPE: 0.300003 a.u.
B3LYP/BS2 energy:

C      6.52902100    0.09435000
H      4.48941100
H      5.34632300    0.36583300
H      2.12799400
H      2.98897200
C      4.64333800    0.03451500    0.73108300
H      1.98952400    0.04466900    2.10651500
C      4.16357000    -0.60606500    1.33692000
H      2.12799400    -1.16149200    1.96080000
C      5.09176100    -0.17112100    0.58100400
H      5.34632300    0.36583300    -1.49146100
H      4.48941100    -0.77808700    2.55981200
H      -1.09369300    4.80180100    0.90232400
H      -6.31696600    0.51609800    -0.03475200
C      6.52902100    0.09435000    0.95954900
H      7.20614200    -0.09916500    0.12238400
H      6.66999000    1.14047000    1.25687300
H      6.84289600    -0.52815300    1.80243000

- TS-Me-Ar

B3LYP/BS2 energy: -820.988529752 a.u.
ZPE: 0.29993 a.u.

Thermal correction to Gibbs Free Energy: 0.246535 a.u.
Solvation energy: -6.41 kcal/mol
Dispersion correction: -55.66 kcal/mol

Thermal correction to Gibbs Free Energy: 0.246077 a.u.
Solvation energy: -6.36 kcal/mol
Dispersion correction: -55.66 kcal/mol

I      0.77415200    -1.15472400    -0.51495500
O      -1.58836300    -0.72273500    -1.12805100
C      -2.68724300    -1.01238000    -0.44556900
C      -2.72016400    -2.02808050    0.54933200
C      -3.88214100    -0.28994800    -0.69149100
C      -3.89551700    -2.30137700    1.24417000
H      -1.81845000    -2.59538100    0.74415000
H      -5.04437000    -0.57228100    0.01592200
H      -3.85973500    0.48508660    -1.45146300
H      -5.06414000    -1.58025800    0.98800200
H      -3.89839600    -3.08969200    1.99326900
H      -9.76975000    -1.80055100    1.53585800
C      -0.40777600    0.90308800    -0.31460500
C      -0.19046400    1.83588000    -1.31800300
C      -0.84368500    1.23453800    0.95590400
C      -0.44279700    3.17616100    -1.01624800
H      0.13800300    1.53945900    -2.30693800
H      -1.08381100    2.58842400    1.22169300
H      -1.02488500    0.47950800    1.71234400
C      -0.88758800    3.57779700    0.25213700
H      -0.28978500    3.92071100    -1.79452900
H      -1.43122400    2.86767000    2.21361800
C      2.77486000    -0.68029500    0.08229100
C      3.69793600    -0.23816200    -0.87188200
C      3.15467000    -0.80573500    1.42573800
C      5.00077600    0.07115700    -0.47607400
H      3.40793000    -0.13847500    -1.91322800
C      4.45149700    -0.49493500    1.81020600
H      2.42670300    -1.14414300    2.16528400
C      5.37842300    -0.05713900    0.86207500
C      5.71944300    0.41199500    -1.21585900
H      4.74207800    -0.59485200    2.85207200
H      -5.94899100    -0.00504100    -0.19206200
H      6.39280800    0.18420100    1.16552400
C      -1.16334300    5.03358900    0.54915100
H      -2.06494800    5.38329900    0.03149900
H      -1.31417000    5.20018600    1.69378800
H      -0.33648800    5.67439500    0.22397700

- INT-F

B3LYP/BS2 energy: -880.956546135 a.u.
ZPE: 0.266089 a.u.
Thermal correction to Gibbs Free Energy: 0.213426 a.u.
Solvation energy: -6.49 kcal/mol
Dispersion correction: -52.29 kcal/mol

I  -0.23318500  -0.18605300  -0.22485500
O  -2.31956600  0.76971900  -0.38099900
C  -3.26001100  -0.14935600  -0.13517600
C  -3.55499600  -1.16669800  -1.07197700
C  -3.99348000  -0.13238000  1.07367800
C  -4.54923600  -2.11138400  -0.81404800
H  -3.01664600  -1.17325100  -0.20164500
C  -4.98969600  -1.07410600  1.31733300
H  -3.76925100  0.64436400  1.79941000
C  -5.27382400  -2.07278100  0.37387800
H  -4.76432000  -2.87792400  -0.55480100
H  -6.04998200  -2.80655600  0.57534600
C  -0.42392200  1.87681700  -0.11135500
C  -1.72032500  2.20475500  -0.49687100
C  -0.48928100  2.82824200  0.34219200
H  -2.11808200  3.54191300  -0.40634100
C  -2.41273000  1.45919100  -0.85398700
C  -0.06683200  4.15291000  0.42568600
H  -1.50059300  2.52157900  0.58597600
C  -1.22950500  4.51345400  0.05689900
C  -3.12592000  3.81610500  -0.70402000
H  -0.76419900  4.90605000  0.78076100
C  -1.81631900  -0.90143100  0.00298000
C  -2.48972300  -1.43409300  -1.10252700
C  -2.41351700  -0.94427500  1.26908500
C  -3.75921700  -1.99765100  -0.95216400
H  -2.03294700  -1.41177300  -2.08815900
C  -3.68216000  -1.50079900  1.43127600
H  -1.89476500  -0.54234100  2.13464400
C  -4.33210100  -2.01856900  0.31443600
H  -4.30161000  -2.41506600  -1.79375000
H  -4.16664500  -1.54404700  2.40094300
H  -1.54677900  5.54986600  0.12506200
H  -5.54888500  -1.03295400  2.24913600
F  5.55599000  -2.55947000  0.46720300

- TS-F-Ph

B3LYP/BS2 energy: -880.929611399 a.u.
ZPE: 0.264458 a.u.
Thermal correction to Gibbs Free Energy: 0.212876 a.u.
Solvation energy: -6.33 kcal/mol
Dispersion correction: -52.50 kcal/mol

I  0.37111800  -0.92566200  -0.62892300
O  -1.97668500  -0.32359200  -1.09249800
C  -3.07055300  -0.60538700  -0.39775700
C  -3.10886300  -1.63011500  0.57989300
C  -4.25306900  0.14628500  -0.61259600
C  -4.27886000  -1.89759100  1.28916100
H  -2.21647200  -2.22603200  0.75181600
H  -5.41056600  -1.02463700  0.10728400
H  -4.22518800  0.93429700  -1.35887600
C  -5.43570800  -1.14854200  1.06268900
H  -4.28675300  -2.69790200  2.02529300
H  -6.34462100  -1.35940800  1.61836700
C  -0.67573700  1.17039000  -0.20627600
C  -0.43754600  2.17173500  -1.13558400
C  -1.05225300  1.40342700  1.10668800
C  -0.60350300  3.49441450  -0.70930100
H  -1.15972400  1.94305200  -2.15741700
C  -1.20786900  2.73705200  1.50253500
H  -1.25516900  0.58888000  1.79274700
C  -0.98080000  3.78113500  0.60437000
C  -0.43675100  4.29864500  -1.42057100
H  -1.50973900  2.94773200  2.52489800
C  -2.41821400  -0.60485200  -0.10010700
C  -3.33097700  -1.69449000  -1.06878000
C  -2.83793400  -0.81467500  1.21936100
C  -4.66487200  0.48481000  -0.72383000
H  3.01001200  -0.00166600  -2.09190300
C  -4.17023400  -0.59916200  1.57121600
H  2.13317800  -1.14716500  1.97472300
C  -5.06041800  -0.17080000  0.59171700
H  -5.39311700  0.38266500  -1.45483100
C  -4.52251200  -0.75684900  2.58484800
H  -1.09956800  4.81135000  0.92467700
H  -6.30583200  0.46430400  -0.07699600
F  6.34681000  0.03807700  0.92800600

- TS-F-Ar

B3LYP/BS2 energy: -880.928298169 a.u.
ZPE: 0.264395 a.u.
Thermal correction to Gibbs Free Energy: 0.212419 a.u.
Solvation energy: -6.26 kcal/mol
Dispersion correction: -52.56 kcal/mol

I  0.76026400  -1.15627500  -0.51679700

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Dispersion correction: a.u.

ZPE:

H

C

C

O

I

C

C

O

I

Solvation energy: a.u.

S

ZPE:

H

C

C

O

I

C

C

O

I

Solvation energy: a.u.

S

ZPE:

H

C

C

O

I

C

C

O

I

Solvation energy: a.u.

S

ZPE:

H

C

C

O

I

C

C

O

I

Solvation energy: a.u.

S

ZPE:

H

C

C

O

I

C

C

O

I

Solvation energy: a.u.

S

ZPE:

H

C

C

O

I

C

C

O

I

Solvation energy: a.u.
Solvation energy:
Thermal correction:
Dispersion correction:

- TS-Cl-Ar

B3LYP/BS2 energy: -1241.28332339 a.u.
ZPE: 0.263031 a.u.
Thermal correction to Gibbs Free Energy: 0.210428 a.u.
Solvation energy: -6.49 kcal/mol
Dispersion correction: -54.90 kcal/mol

I  0.89663500  -1.35906700  -0.47654200
O  -1.47788900  -1.07493200  -1.12120500
C  -2.56826600  -1.38501400  -0.43042500
C  -2.56597000  -2.37221900  0.58513800
C  -3.78440600  -0.70528500  -0.68935600
C  -3.73042500  -2.67458900  1.28921100
H  -1.64692800  -2.91595700  0.78769800
C  -4.93576900  -1.00737800  0.02871200

- INT-CF3

B3LYP/BS2 energy: -1118.84177128 a.u.
ZPE: 0.278993 a.u.
Thermal correction to Gibbs Free Energy: 0.22168 a.u.
Solvation energy: -6.62 kcal/mol
Dispersion correction: -56.32 kcal/mol

I  -0.95598800  -0.09112500  -0.25836600
O  -3.18876600  0.40116500  -0.32466200
C  -3.90973600  -0.70099300  -0.08046400
C  -3.98636600  -1.75288000  -1.02174200
C  -4.62282600  -0.84497700  1.13151000
C  -4.75291300  -2.89008500  -0.76281400
H  -3.46695400  -1.63998300  -1.97008700
C  -5.39312000  -1.97841200  1.37548200
H  -4.56685800  -0.04043000  1.85978800
C  -5.46144800  -3.01168900  0.43390500
H  -4.80338800  -3.68202200  -1.50622200
Dispersion correction: -0.84567800

TS - CF3-Ph

B3LYP/BS2 energy: -1118.81491378 a.u.
ZPE: 0.277357 a.u.
Thermal correction to Gibbs Free Energy: 0.220511 a.u.
Solvation energy: -6.42 kcal/mol
Dispersion correction: -56.48 kcal/mol

I  -0.48555400  -0.95178500  -0.72113300
O  -2.83867300  -0.32329800  -1.04082500
C  -3.88824000  -0.58648700  -0.27431700
C  -3.87048000  -1.59249400  0.72318000
C  -5.07812400  0.16797300  -0.43093500
C  -4.99608300  -1.84031500  1.50741200
H  -2.97198100  -2.19021800  0.85116100
C  -6.19041700  -0.83323200  0.36318000
H  -5.09218300  0.94164600  -1.19239400
C  -6.16128700  -1.08936600  1.33744800

TS - CF3-Ar

B3LYP/BS2 energy: -1118.81775636 a.u.
ZPE: 0.277361 a.u.
Thermal correction to Gibbs Free Energy: 0.220302 a.u.
Solvation energy: -6.57 kcal/mol
Dispersion correction: -56.90 kcal/mol

I  1.52398200  -1.33451300  -0.46129900
O  -0.80008000  -1.84444400  -1.12468400
C  -1.73660300  -2.48069700  -0.42850300
C  -1.41971700  -3.41624200  0.58558500
C  -3.10491000  -2.21725300  -0.68267500
C  -2.42719000  -4.07024300  1.29300400
H  -0.37554000  -3.64243500  0.78517900
C  -4.10032700  -2.86686200  0.03877200
H  -3.35087700  -1.49938200  -1.45901800

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C -3.77206700 -3.79946700 1.03005600
H -2.15937400 -4.79601900 2.05703100
H -4.55380900 -4.30835300 1.58606500
C -0.30930800 0.10919600 -0.40790100
C -0.41256800 1.01389300 -1.46121100
C -0.88892500 0.32544700 0.83654200
C -1.15304500 2.17559100 -1.25332200
H 0.04728800 0.81430500 -2.42144000
C -1.62657500 1.49663000 1.02015400
H -0.80236200 -0.40221400 1.63507400
C -1.75534600 2.42544300 -0.01456200
H -1.25460200 2.89384600 -2.06093000
H -2.09280100 1.68723900 1.98084300
C -3.14857000 -0.06889300 0.12136000
C 3.89289200 0.59514100 -0.85976000
C 3.44446500 0.09762800 1.47852800
C 4.94645900 1.42633000 -0.47420800
H 3.65862800 0.46622900 -1.91183000
C 4.50006400 0.93177200 1.85168400
H 2.86185500 -0.41623200 2.23660200
C 5.24991700 1.59514800 0.87823800
H 5.52819500 1.94162000 -1.23295500
H 4.73426700 1.06221200 2.90416000
H -5.14395000 -2.64873400 -0.17398600
H 6.06951400 2.24344500 1.17382800
C -2.57350400 3.67054000 0.16850400
F -1.98310600 4.74527700 -0.40680300
F -2.76772600 3.96509200 1.47321200
F -3.79922900 3.55969800 -0.39682800
H -4.42441600 0.79867600 -1.16344100
C -5.58520800 -0.80939800 1.61698500
H -4.65608200 -2.54825000 2.49159100
H -6.38918500 -0.76667200 2.34575800
C -0.72759900 1.22473700 -0.36945800
C -0.20975500 2.12802700 -1.29726300
C -1.50370200 1.63112800 0.71553200
C -0.46828300 3.48802500 -1.11686600
H 0.38444900 1.78832700 -2.13830600
C -1.75251800 2.99800300 0.87484400
H -1.91567200 0.91271500 1.41153000
C -1.23657300 3.92198400 -0.03397400
H -0.07032600 4.20480400 -1.82885500
H -2.35486800 3.33176900 1.71415100
H 1.76011300 -0.51510500 -0.17540900
C 2.71048900 -1.14109500 -0.98946200
C 2.17081500 0.22271700 0.94075100
C 4.07062000 -0.92492800 -0.70010000
H 2.40164800 -1.71331700 -1.86096500
C 3.52602500 0.34608000 1.23993600
H 1.43940000 0.71272100 1.57643800
C 4.45419600 -0.28377780 0.41153300
H 4.82814400 -1.49749600 -1.31663900
C 3.87387700 0.91257900 2.09500100
H -1.43496600 4.98112500 0.99873800
H -6.27364000 0.90223700 0.50007100
N 5.88804100 -0.15449500 0.72123100
O 6.19909010 0.51031700 1.70832300
O 6.68559500 -0.71876600 -0.02650800

**- INT-NO$_2$**

B3LYP/BS2 energy: -986.250813874 a.u.
ZPE: 0.27668 a.u.
Thermal correction to Gibbs Free Energy: 0.221151 a.u.
Solvation energy: -9.18 kcal/mol
Dispersion correction: -57.24 kcal/mol

**- TS-NO$_2$-Ph**

B3LYP/BS2 energy: -986.225899137 a.u.
ZPE: 0.275212 a.u.
Thermal correction to Gibbs Free Energy: 0.220674 a.u.
Solvation energy: -8.10 kcal/mol
Dispersion correction: -56.03 kcal/mol

I -0.37359100 -0.85851600 -0.65246600
O -2.52737800 -0.97035600 -2.17733400
C -3.49375600 -0.92717200 -2.86024000
C -3.57911300 -1.87224800 0.76002300
C -4.48458700 0.07604300 -0.35516200
C -6.60901400 -1.80670600 1.69766300
H -2.84007900 -2.66798800 0.81227700
C -5.51701100 0.12525300 0.57979800
I -0.16795800 -0.91669400 -0.70957400
O -2.50594000 -2.99575000 -1.03510000
C -3.56914700 -0.59357600 -0.32180900
C -3.55662300 -1.60920000 0.66597800
C -4.67955600 0.13822200 -0.50386300
C -4.69712500 -1.88695600 1.41784900

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| Atom | X   | Y   | Z    |
|------|-----|-----|------|
| O    | -2.19079900 | 0.81232200 |
| C    | -0.14303900 | 0.25821500 |
| H    | -1.25847700 | 1.22387000 |
| H    | -2.67984800 | 2.16173000 |
| H    | -1.37676900 | 1.81250200 |
| C    | 1.20027200  | -0.20971200 |
| C    | 0.93252300  | 2.20672700  |
| C    | 1.48197500  | 1.11679000  |
| C    | -0.07163600 | -0.68711400 |
| H    | -0.69016800 | -2.16941000 |
| C    | -1.61103300 | 1.53444500  |
| H    | -1.67326800 | 1.79687800  |
| C    | -1.40276500 | 0.64183900  |
| H    | -0.92032800 | -1.39276900 |
| H    | -1.87815300 | 2.56835700  |
| O    | -0.63233100 | -0.27240000 |
| C    | -0.21437900 | -1.28374300 |
| C    | -0.84524200 | 1.03048100  |
| C    | -0.99715800 |              |
| H    | -0.4663600  | -2.29232100 |
| C    | 1.32437400  |              |
| H    | -1.16425300 | 1.81455500  |
| C    | -0.23733800 | 0.30370200  |
| C    | 0.30302100  | -1.75656400 |
| H    | -0.8072750  | 2.32050800  |
| H    | 0.97902400  |              |
| N    | 0.09943200  |              |
| O    | -0.20776700 | 0.61080100  |
| O    | -0.35351000 | -0.30846000 |

**TS-NO₂-Ar**

B3LYP/BS2 energy: -986.231432932 a.u.
ZPE: 0.275534 a.u.
Thermal correction to Gibbs Free Energy: 0.221441 a.u.
Solvation energy: -8.70 kcal/mol
Dispersion correction: -56.71 kcal/mol

Dispersion correction:
Solvation energy:
a.u.

I 1.05125500 -1.44534300 -0.46796500
O -1.31971300 -1.33968900 -1.12882200
C -2.39591800 -1.71101300 -0.43763700
C -2.34072700 -2.70587500 0.56647200
C -3.64216400 -1.09021800 -0.69161700
C -3.48808700 -3.07414700 1.26745800
H -1.39514100 -3.20424200 0.76359700
C -4.77699400 -1.45741500 0.02335100
H -3.68581400 -0.32663200 -1.46196500
C -4.71103100 -2.45204300 1.00613900
H -3.42557400 -3.85180600 2.02460700
H -5.60157400 -2.73903500 1.55717000
C -0.33555600 0.38468000 -0.40012900
C -0.22160500 1.29958100 -1.45031100
C -0.83604900 0.73551800 0.85516100
C -0.65528600 2.60329000 -1.24009400
H 0.16604800 0.99727900 -2.41552000
C -1.26622500 2.04383200 1.05277000
H -0.92460600 0.00258300 1.64842900
C -1.16611000 2.96537200 0.09924200
H -0.60467000 3.34410700 -2.02871400
H -1.67342300 2.36022800 2.00533100
C 2.93209800 -0.61907100 0.13001600
C 3.82485200 -0.16139100 -0.84491400
C 3.24742500 -0.53203800 1.49012500
C 5.04833100 0.38250500 -0.44888800
H 3.57471400 -0.22816600 -1.89904100
C 4.47355800 0.01508900 1.87294700
H 2.55000100 -0.88590000 2.24274700
C 5.37224500 0.47130600 0.90642500
H 5.74599000 0.73743800 -1.20168500
H 4.72393900 0.08414900 2.92741800
H -5.72412700 -0.96717000 -0.18792700
H 6.32424700 0.89656500 1.20939200
N -1.60204600 4.34105600 0.22899800
O -2.04151800 4.63399100 1.34338600
O -1.50489500 5.13183500

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Computational references

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8. Copies of $^1$H and $^{13}$C NMR Spectra of Novel Compounds

Start on the next page.
Parameter       Value
1 Solvent       DMSO-d$_6$
2 Temperature   297.0
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Nucleus       1H
| Parameter         | Value            |
|-------------------|------------------|
| 1 Solvent         | DMSO-d$_6$       |
| 2 Temperature     | 297.9            |
| 3 Number of Scans | 172              |
| 4 Spectrometer Frequency | 100.62        |
| 5 Nucleus         | 13C              |
Parameter | Value
--- | ---
1 Solvent | DMSO-d6
2 Temperature | 300.2
3 Number of Scans | 16
4 Spectrometer Frequency | 400.13
5 Nucleus | 1H
| Parameter          | Value         |
|--------------------|---------------|
| 1 Solvent          | DMSO-d6       |
| 2 Temperature      | 300.2         |
| 3 Number of Scans  | 172           |
| 4 Spectrometer Frequency | 100.62     |
| 5 Nucleus          | 13C           |
| Parameter   | Value            |
|-------------|------------------|
| 1 Solvent   | DMSO-d6          |
| 2 Temperature | 300.2          |
| 3 Number of Scans | 16             |
| 4 Spectrometer Frequency | 400.13       |
| 5 Nucleus   | 1H               |
Parameter | Value
--- | ---
1 Solvent | DMSO-d6
2 Temperature | 300.2
3 Number of Scans | 1024
4 Spectrometer Frequency | 100.62
5 Nucleus | $^{13}$C
| Parameter       | Value        |
|-----------------|--------------|
| 1 Solvent       | DMSO-d6      |
| 2 Temperature   | 300.1        |
| 3 Number of Scans | 16          |
| 4 Spectrometer Frequency | 400.13   |
| 5 Nucleus       | 1H           |

![Chemical Structure](image)
Parameter | Value
---|---
1 Solvent | DMSO-d6
2 Temperature | 300.2
3 Number of Scans | 16
4 Spectrometer Frequency | 400.13
5 Nucleus | 1H
| Parameter      | Value            |
|----------------|------------------|
| 1 Solvent      | DMSO             |
| 2 Temperature  | 300.2            |
| 3 Number of Scans | 172             |
| 4 Spectrometer Frequency | 100.62         |
| 5 Nucleus      | 13C              |

![Chemical Structure](image)
Parameter | Value
--- | ---
1 Solvent | DMSO-d6
2 Temperature | 298.2
3 Number of Scans | 16
4 Spectrometer Frequency | 500.13
5 Nucleus | 1H
| Parameter      | Value            |
|---------------|------------------|
| 1 Solvent     | DMSO-d6          |
| 2 Temperature | 298.1            |
| 3 Number of Scans | 6144           |
| 4 Spectrometer Frequency | 100.62        |
| 5 Nucleus     | 13C              |

![Chemical Structure](image)

**f (ppm)**

- 159.40
- 166.21
- 134.37
- 131.81
- 125.51
- 119.10
- 116.09
- 92.08
- 86.98
- 57.35
- 56.18
MeO
H

8e

CDCl$_3$
100 MHz
CDCl₃ 100 MHz
CDCl₃
100 MHz

11c

EtO

O

OEt

172.04

137.26

136.79

135.17

134.90

126.75

61.98

59.38

23.21

21.93

14.15

ppm
11h  
$^{1}$H NMR (CDCl₃, 400 MHz)
$^{11}h$ CDCl$_3$

100 MHz
CDCl₃
400 MHz

1li
11i

CDCl₃
100 MHz