Supplementary Information (SI) for Green Chemistry.
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Reactivity under mechanochemical conditions: A new and more sustainable era for hypervalent iodine?

Pernilla Öberg,[a] Sayad Doobary,*[a,b] and Berit Olofsson*[a,b]

Supporting information

1 General information

The reader is referred to the literature for an in-depth description of mechanochemical set-ups. [1]

Solvents are listed as Green/Amber/Red according to Sneddon's *Green Chemistry* evaluation from 2016.[2] The evaluation of 2,2,2-trifluoroethanol (TFE) as Red is given on page 17 of the supporting information (SI), highlighting that TFE has especially poor grades with regard to incineration, biotreatment, health hazards and exposure potential.[2] To the best of our knowledge, hexafluoroisopropanol (HFIP) has not been reported in solvent evaluations, but has similar safety data sheet (SDS) data as TFE. Based on this, we expect TFE and HFIP to have comparable sustainability profiles, and have hence also listed the latter as Red.

Diaryliodonium salts are drawn as neutral species for symmetric structures (when $Ar^1 = Ar^2$), whereas unsymmetric salts ($Ar^1 \neq Ar^2$) are depicted as ion pairs, as such structures exist as two different T-shaped structures, with either Ar^1 or Ar^2 in the hypervalent bond. Unsymmetric salts can only be drawn with a covalent bond with support from XRDs or calculations on which aryl group is preferred in the hypervalent bond.

Safety and hazard statement

Hypervalent iodine reagents are reactive compounds and may pose an explosion risk, especially upon scale-up. Papers by the groups of Mal, Rao and Kumar describe documented exothermic events with (diacetoxyiodo)benzene (DIB), 2-iodoxybenzoic acid (IBX), and [bis(trifluoroacetoxy)iodo]benzene (PIFA) under mechanochemical conditions.[3,4,5]

A report by Waser and co-workers provides insight into thermogravimetric analysis and differential scanning calorimetry (TGA/DSC) methods to assess the decomposition profile of several common hypervalent iodine compounds and to characterize the probability of a violent thermal degradation.[6] Additionally, Browne and coworkers have proposed a safety protocol and workflow that the reader is advised to consult.[7]

2 Methods

The E-factor (Environmental Factor) was selected as the comparative metric in this study to quantify waste generation, enabling direct comparison between mechanochemical and solution-phase conditions. Metrics such as Atom Economy (AE) and Reaction Mass Efficiency (RME) were excluded, as these describe stoichiometric and reactant-to-product mass ratios, respectively, while omitting solvent use, which is central to the present comparison. Process Mass Intensity (PMI) and Mass Productivity (MP) are algebraic re-expressions of the E-factor (PMI = E-factor + 1; MP = 1 / PMI) and thus add no independent information. Eco-scale analysis was not applied due to limited descrimination between liquid-assisted grinding (LAG) additives and bulk solvent inputs, with regard to both cost and safety; moreover, key scoring inputs for milling are seldom available or subjective (e.g., in-vessel temperature and activation penalties). The GSK solvent guide was therefore instead employed to evaluate solvent sustainability, providing a solvent hazard profile alongside the E-factor assessments.

The E-factors were calculated according to the following definition:

$$E\ factor = \frac{Waste\ Mass}{Product\ Mass} = \frac{Sum\ of\ Ingoing\ Reaction\ Mass\ Components - Product\ Mass}{Product\ Mass}$$

To enable a methodology- and reactivity-focused comparison of mechanochemical and solution-based protocols, system boundaries were restricted to reaction inputs (such as reagents, additives, and solvents). Accordingly, downstream workup and purification materials were excluded from the calculations, as the reviewed literature generally lacks sufficient detail on these procedures. To ensure

a consistent computational basis for fair comparison, all masses were derived from reported molar amounts and molecular weights (or where appropriate, volumes and densities).

In cases where the reported mass and mmol values did not match in the experimental section of original publication, the reported mmol was used for substrates and reagents, and the yield of products was used for calculation of product mass, unless otherwise stated. Such discrepancies may result from rounding conventions or reporting errors; they are identified in the E-factor calculations in Section 6. Where the yield differed between the article text and the SI, the article yield is given in the review scheme, whereas the SI yield was utilized for the E-factor calculation.

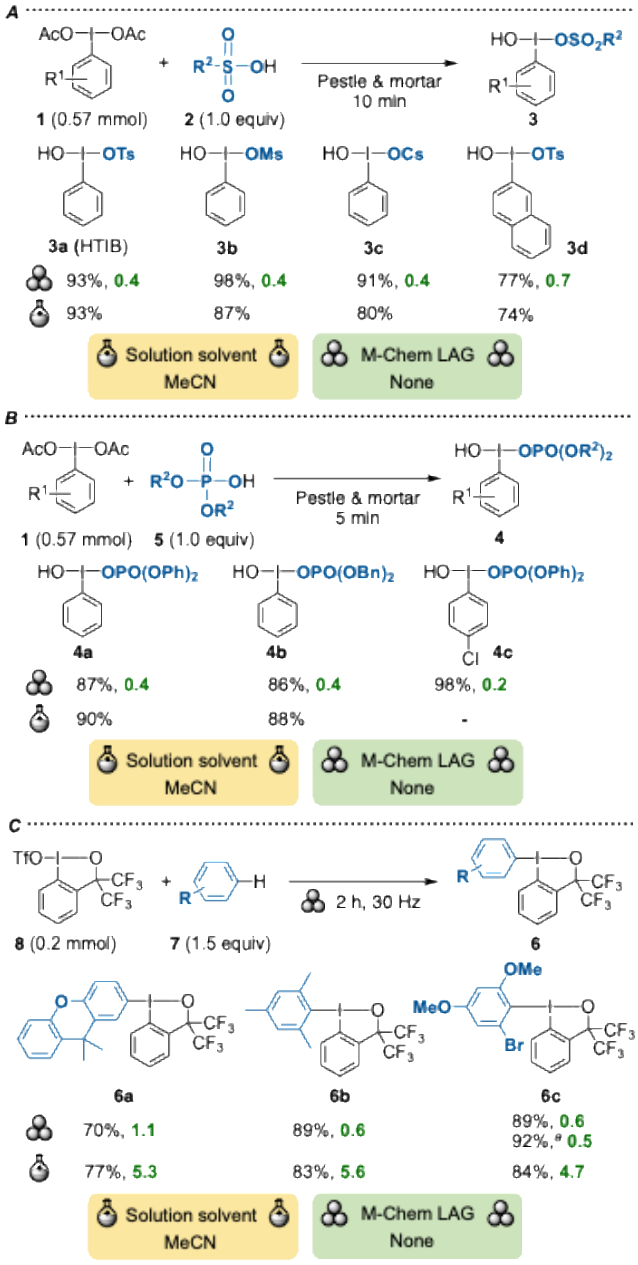
When possible, mechanochemical reactions were compared to the corresponding solution-phase reactions. The latter were selected based on:

(i) literature procedures that afforded the same target products through analogous transformations;
(ii) use of the same, or mechanistically equivalent, hypervalent iodine reagent; and
(iii) sufficiently detailed experimental data to enable E-factor calculations.

E-factor comparisons between reactions conducted at markedly different scales (e.g., mg vs g) were avoided, as E-factors may respond non-proportionally and thus preclude a meaningful comparison. The amount of liquid-assisted grinding (LAG) agent is provided as an absolute volume (μL) in the article schemes, rather than the ratio of the liquid additive to the weight of reactants (η), to illustrate the contrast in volumes between mechanochemical LAG and the solvent in solution-based protocols.

For each reaction, the reported products were selected both to illustrate the extent of the substrate scope and to facilitate direct comparison with available solution-phase data. In some cases, the solution-phase results were compiled from several literature sources to best align with the mechanochemical scope. To aid the reader, the references for the selected products are provided in Sections 3-5, together with explanations to why E-factors could not be determined in some cases. Section 6 contains the E-factor calculations.

3 References for ligand exchange reactions



References for the mechanochemical reactions:

Scheme 3A: M. S. Yusubov and T. Wirth, *Org. Lett.*, 2005, **7**, 519.[8]

Scheme 3B: M. Zhu, C. G. Cai, W. Ke and J. Shao, *Synth. Commun.*, 2010, **40**, 1371.[9]

Scheme 3C: W. Ding, C. Wang, J. R. Tan, C. C. Ho, F. León, F. García and N. Yoshikai, *Chem. Sci.*, 2020, **11**, 7356.[10]

References for the solvent-phase comparison:

Scheme 3A:

3a: G. F. Koser and R. H. Wettach, *J. Org. Chem.*, 1977, **42**, 1476**.**[11]

3b: J. S. Lodaya and G. F. Koser, *J. Org. Chem.*, 1988, **53**, 210–212.[12]

3c: E. Hatzigrigoriou, A. Varvoglis and M. Bakola-Christianopoulou, *J. Org. Chem.*, 1990, **55**, 315–318.[13]

3d: G. F. Koser and R. H. Wettach, *J. Org. Chem.*, 1980, **45**, 1542–1543.[14]

E-factors for the solvent-based syntheses were not calculated due to significant differences in reported reaction scales (**3a:** 5 mmol, 1.6 g, **3b:** 0.16 mol, ca 50 g; **3c:** 20 mmol, 6.4 g, **3d:** 1 g).

Scheme 3B

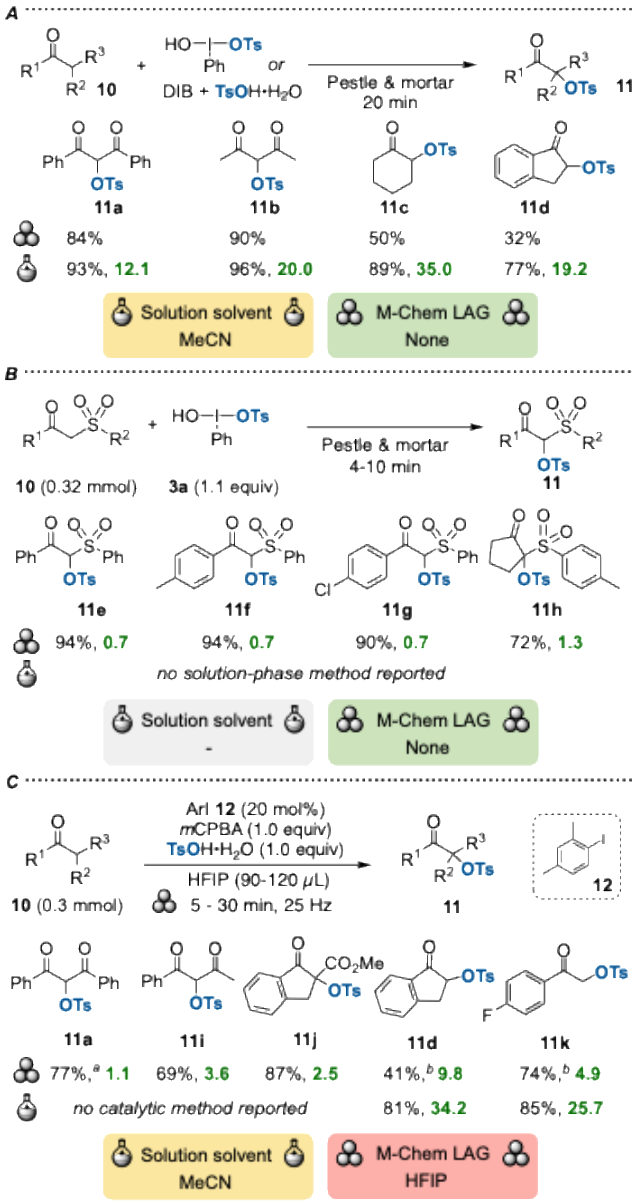
4a, 4b: G. F. Koser, J. S. Lodaya, D. G. Ray and P. B. Kokil, *J. Am. Chem. Soc.*, 1988, **110**, 2987–2988.[15]
E-factors for the solvent-based syntheses were not calculated due to significant differences in reported reaction scales (60 mmol scale).

Scheme 3C

Same reference as the mechanochemical transformation: W. Ding, C. Wang, J. R. Tan, C. C. Ho, F. León, F. García and N. Yoshikai, *Chem. Sci.*, 2020, **11**, 7356.[10]

4 References for oxidative reactions

4.1 Tosyloxylation



References for the mechanochemical reactions:

Scheme 4A: M. S. Yusubov and T. Wirth, *Org. Lett.*, 2005, **7**, 519.[8]

E-factors were not calculated due to lack of experimental details, including no reported molar or gram amounts.

Scheme 4B: D. Kumar, M. S. Sundaree, G. Patel, V. S. Rao and R. S. Varma, *Tetrahedron Lett.*, 2006, **47**, 8239.[16]

Scheme 4C: S. Doobary, M. M. de Vries Ibáñez and B. Olofsson, *Green Chem.*, 2024, **26**, 11518.[17]

References for the solvent-phase comparison:

Scheme 4A

11a, 11c: M. S. Yusubov, T. V. Funk, R. Y. Yusubova, G. Zholobova, A. Kirschning, J. Y. Park and K. W. Chi, *Synth. Commun.*, 2009, **39**, 3772–3784.[18]

11b: T. Nabana and H. Togo, *J. Org. Chem.*, 2002, **67**, 4362–4365.[19]

11d: S. T. Handy and M. Okello, *Synlett*, 2002, **3**, 489–491.[20]

Scheme 4B

No solution phase method reported.

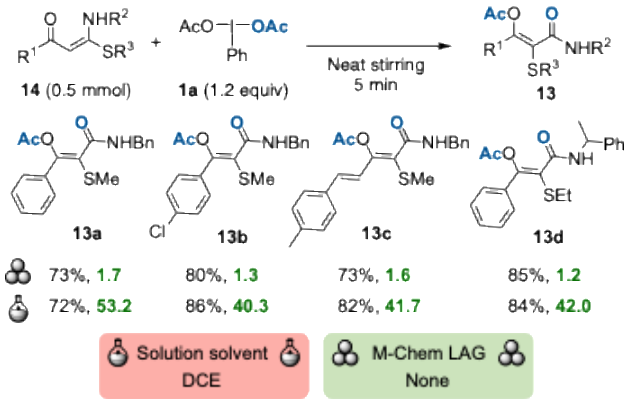
Scheme 4C

11a, 11i, 11j. *No catalytic method reported in solution. For stoichiometric HTIB reactions, see scheme 2A.*

11d: A. Boelke and B. J. Nachtsheim, *Adv. Synth. Catal.*, 2020, **362**, 184–191.[21]

11k: Rimi, B. Uttam, V.V. Zhdankin, R. Kumar, *Eur. J. Org. Chem.*, 2024, **27**, e202301191.[22]

4.2 Oxidative rearrangement



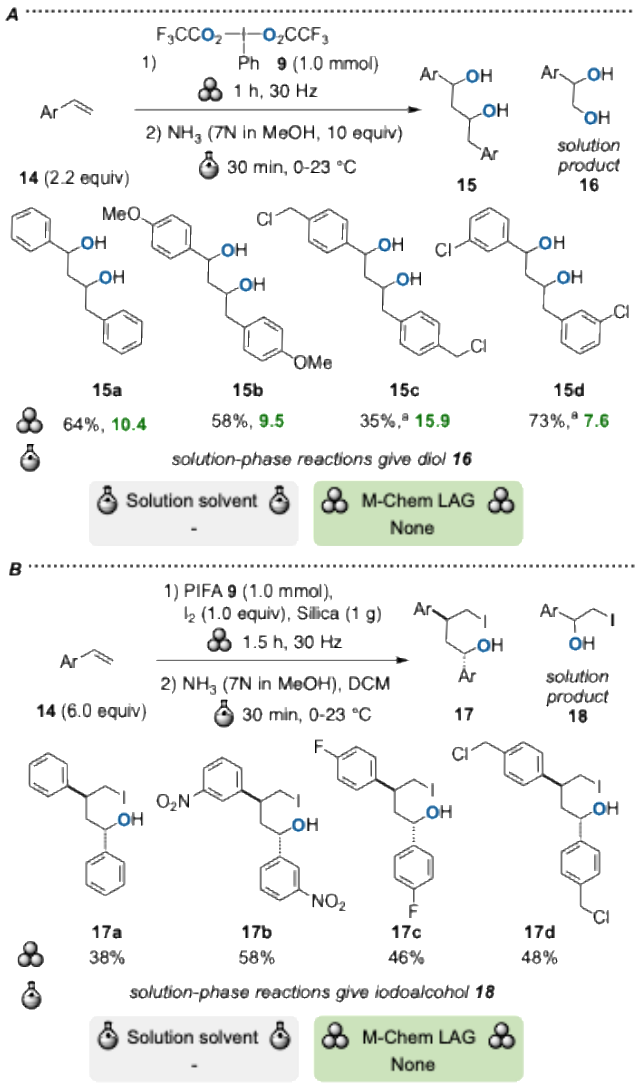
Reference for the mechanochemical reaction:

Z. Liu, F. Huang, P. Wu, Q. Wang and Z. Yu, *J. Org. Chem.*, 2018, **83**, 5731.[23]

Reference for the solvent-phase comparison:

Same reference as the mechanochemical transformation: Z. Liu, F. Huang, P. Wu, Q. Wang and Z. Yu, *J. Org. Chem.*, 2018, **83**, 5731.[23]

4.3 Oxidative functionalization of alkenes



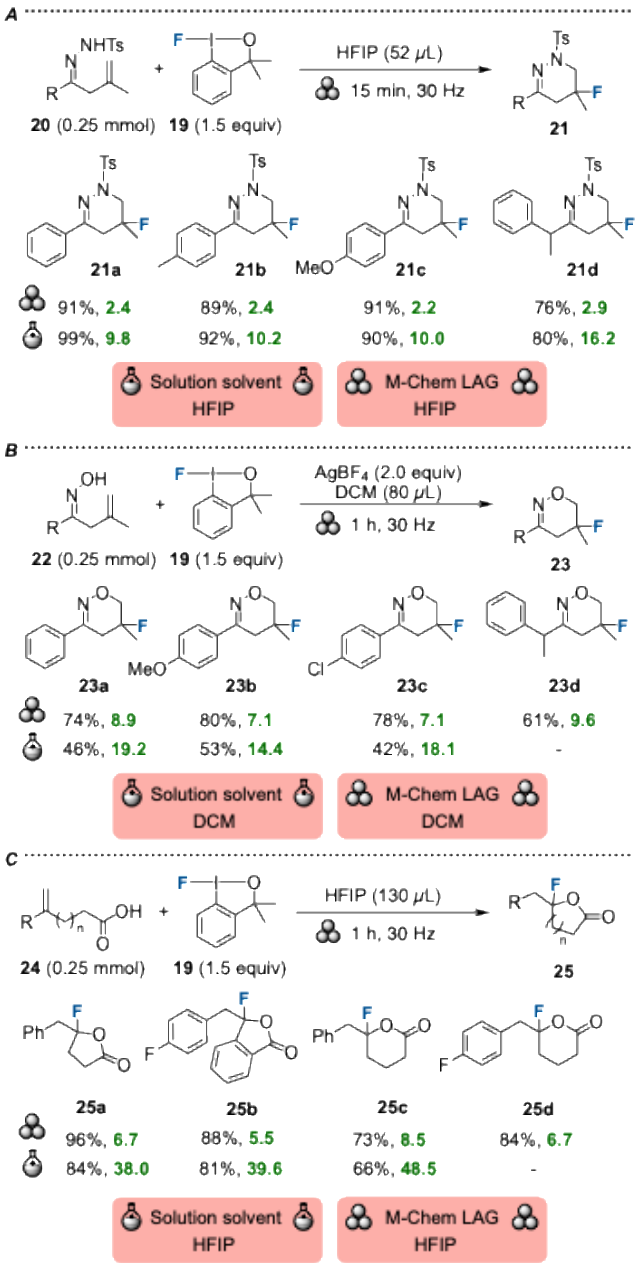
References for the mechanochemical reactions:

Scheme 6A-B: L. Pan, L. Zheng, Y. Chen, Z. Ke and Y.-Y. Yeung, *Angew. Chem. Int. Ed.*, 2022, **61**, e202207926.[24]

E-factors were not calculated for **17a-17d** due to lack of experimental details, as the amount of NH_3 in MeOH was not explicitly disclosed, nor the amount of DCM which was used to dilute the mechanochemical output prior to the 2nd synthetic step.

References for the solvent-phase comparison:

No solution phase method reported; solution-phase reactions give a different product.



Reference for the mechanochemical reactions:

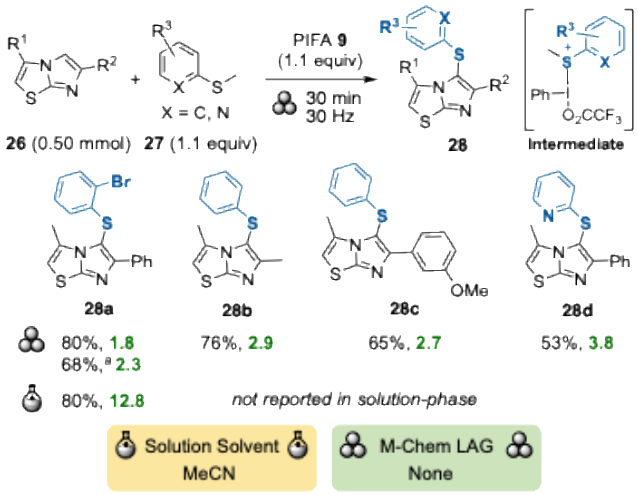
W. Riley, A. C. Jones, K. Singh, D. L. Browne and A. M. Stuart, *Chem. Commun.*, 2021, **57**, 7406.[25]

References for the solvent-phase comparison:

Scheme 7A-B: Same reference as the mechanochemical transformation, W. Riley, A. C. Jones, K. Singh, D. L. Browne and A. M. Stuart, *Chem. Commun.*, 2021, **57**, 7406.[25]

Scheme 7C: H. K. Minhas, W. Riley, A. M. Stuart and M. Urbonaite, *Org. Biomol. Chem.*, 2018, **16**, 7170.[26]

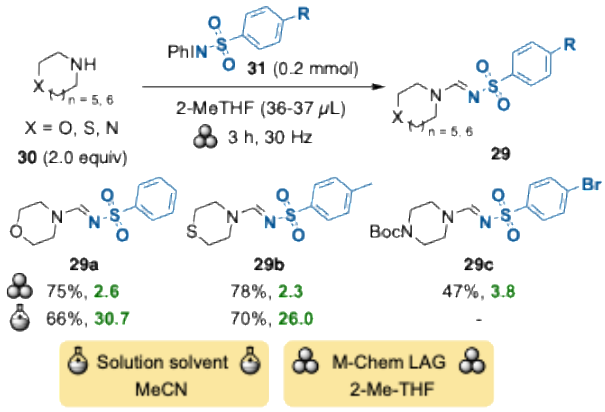
4.4 Oxidative sulfenylation



Reference for the mechanochemical reactions:
X. Liu, V. Dorokhov, O. Provot, C. Tran, P. Retailleau, J.-F. Soulé and A. Hamze, *ChemSusChem*, 2025, **18**, e202500320.[27]

References for the solvent-phase comparison:
28a: Same reference as the mechanochemical transformation: X. Liu, V. Dorokhov, O. Provot, C. Tran, P. Retailleau, J.-F. Soulé and A. Hamze, *ChemSusChem*, 2025, **18**, e202500320.[27]
28b-d: *No solution phase method reported.*

4.5 Reactions with iodonium sulfonimides

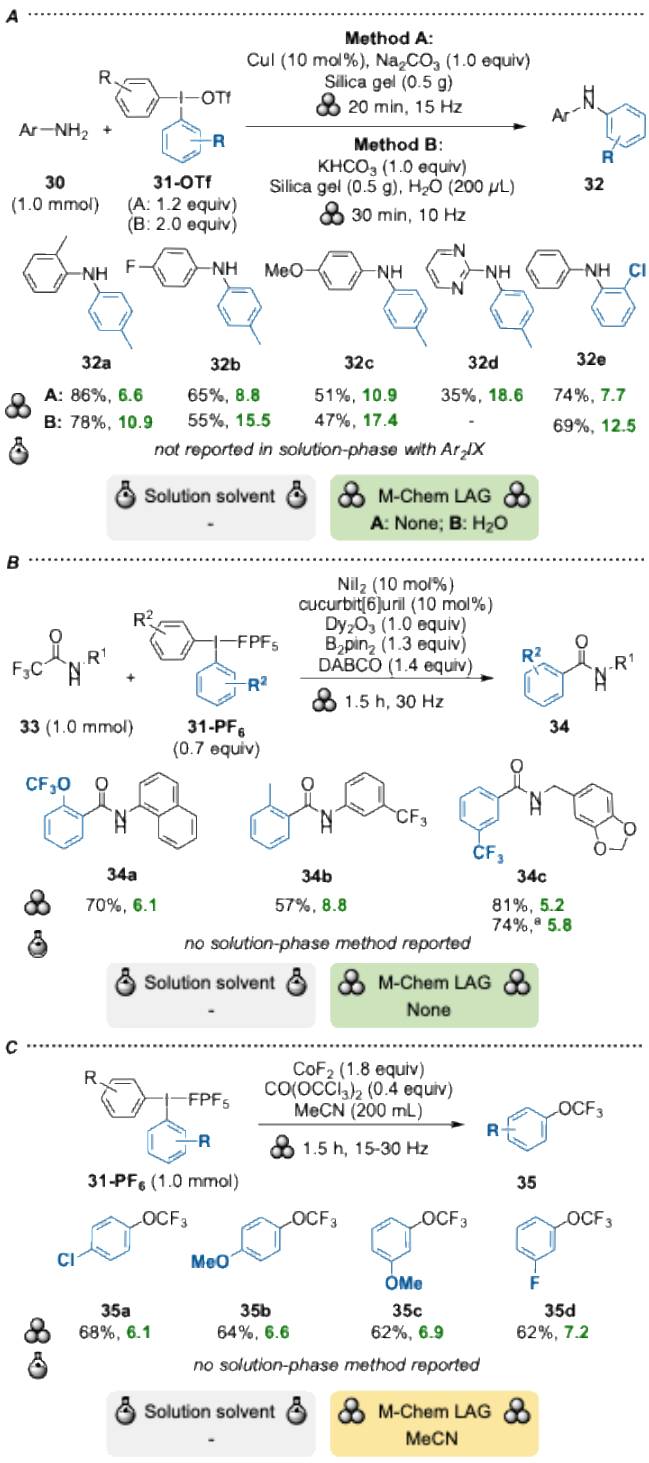


Reference for the mechanochemical reactions:
S. Guha, S. Maheshwari, M. K. Ravva, J. M. Jacob, S. Yadav and S. Sen, *Asian J. Org. Chem.*, 2023, **12**, e202300348.[28]

References for the solvent-phase comparison:
29a,b: C. S. Nishad, K. K. Haldar and B. Banerjee, *J. Org. Chem.*, 2022, **87**, 11644.[29]
29c: *No solution phase methods reported.*

5 References for transfer of carbon ligands

5.1 Arylations



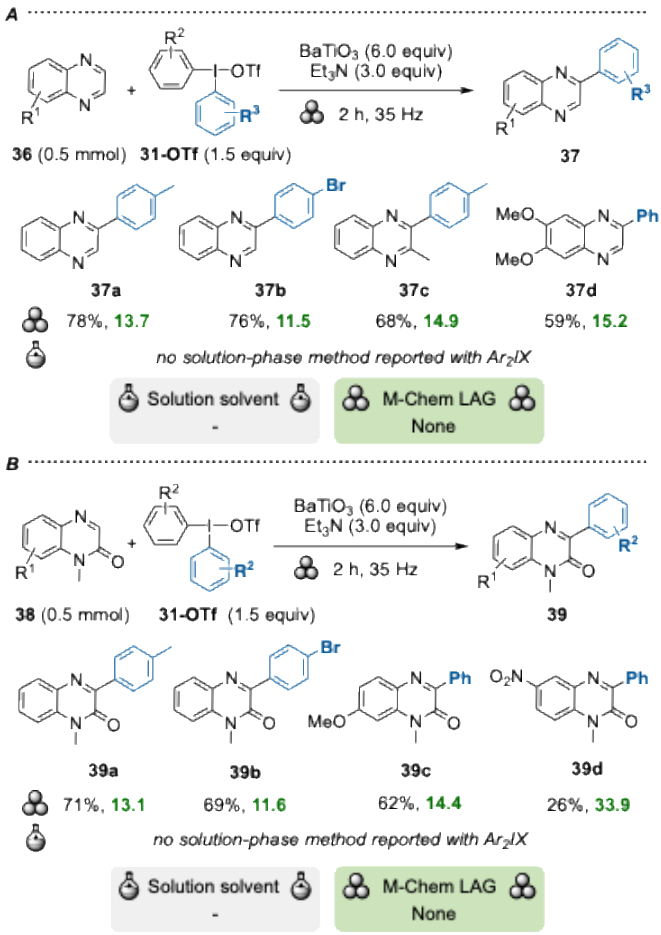
References for the mechanochemical reactions:

Scheme 10A: J. Jiang and J. Li, *ChemistrySelect*, 2020, **5**, 542.[30]

Scheme 10B: S. Mkrtchyan, M. Shkoor, M. Phanindrudu, M. Medved', O. Sevastyanova and V. O. Iaroshenko, *J. Org. Chem.*, 2023, **88**, 863.[31]

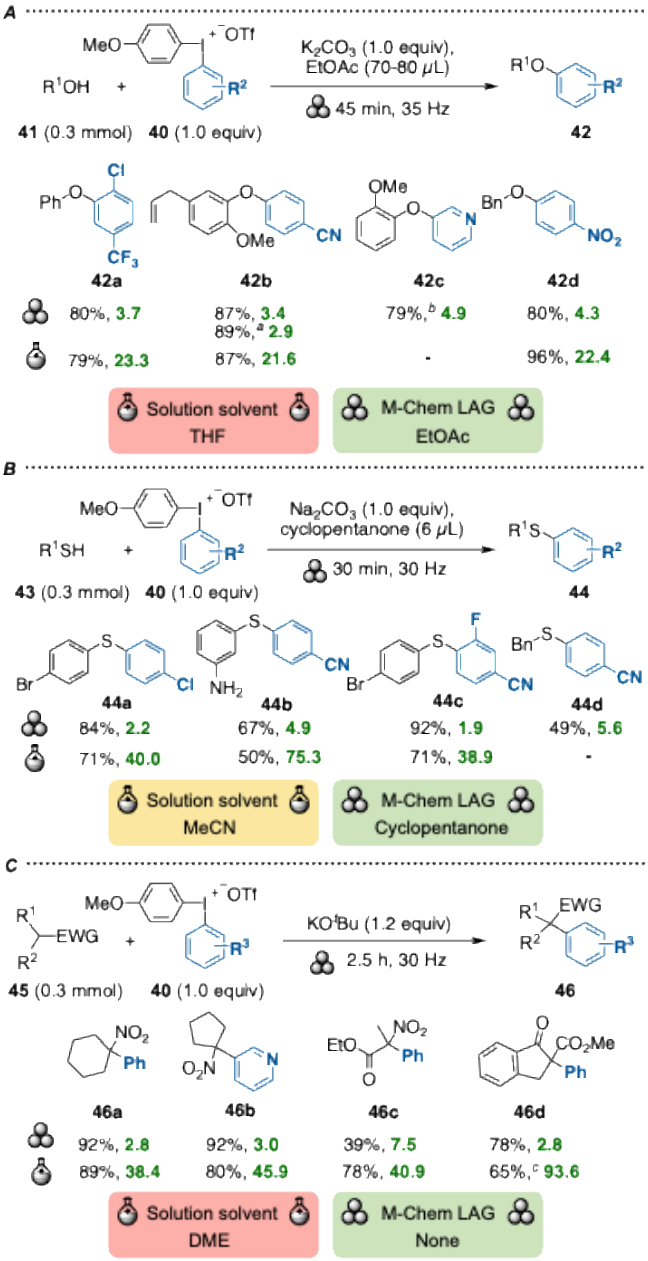
Scheme 10C: S. Mkrtchyan, V. B. Purohit, J. Zapletal, O. Shalimov, J. Nociarová, G. Addová, J. Filo, M. G. Garcia, E. Kupcová, B. Benická and V. O. Iaroshenko, *Cell Rep. Phys. Sci.*, 2024, **5**, 102118.[32]

References for the solvent-phase comparison:
No solution-phase methods reported.



References for the mechanochemical reactions:
Scheme 11A-B: J. Jiang, S. Song, J. Guo, J. Zhou and J. Li, *Tetrahedron Lett.*, 2022, **98**, 153820.[33]

References for the solvent-phase comparison:
No solution-phase methods reported with diaryliodonium salts.



References for the mechanochemical reactions:

Scheme 12A-C: S. Doobary, M. M. de Vries Ibáñez and B. Olofsson, *Green Chem.*, 2024, **26**, 11518.[17]

References for the solvent-phase comparison:

Scheme 12A

42a, 42b: Same reference as the mechanochemical reaction: S. Doobary, M. M. de Vries Ibáñez and B. Olofsson, *Green Chem.*, 2024, **26**, 11518.[17]

42c: *No solution phase method reported.*

42d: R. Ghosh, E. Lindstedt, N. Jalalian and B. Olofsson, *ChemistryOpen*, 2014, **3**, 54–57.[34]

Scheme 12B

44a-c: Same reference as the mechanochemical reaction: S. Doobary, M. M. de Vries Ibáñez and B. Olofsson, *Green Chem.*, 2024, **26**, 11518.[17]

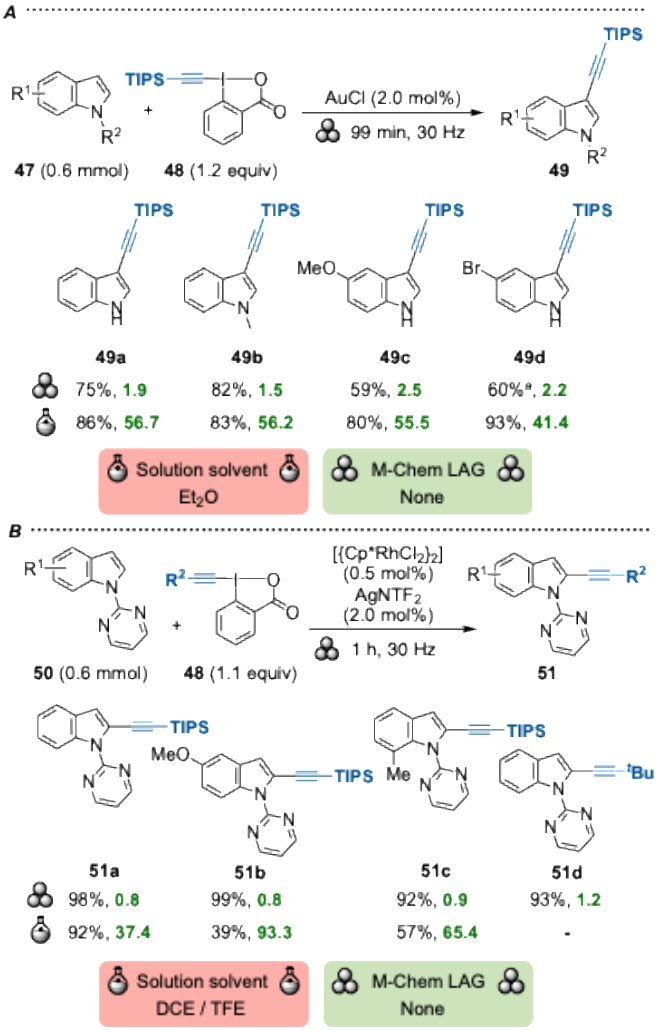
44d: *No solution phase method reported.*

Scheme 12C

46a-c: C. Dey, E. Lindstedt and B. Olofsson, *Org. Lett.*, 2015, **17**, 4554.[35]

46d: Reported in asymmetric synthesis using a chiral diaryliodonium salt: M. Ochiai, Y. Kitagawa, N. Takayama, Y. Takaoka and M. Shiro, *J. Am. Chem. Soc.*, 1999, **121**, 9233.[36]

5.2 Alkynylation



Reference for the mechanochemical reactions:

Scheme 13 A-B: G. N. Hermann, M. T. Unruh, S.-H. Jung, M. Krings and C. Bolm, *Angew. Chem. Int. Ed.*, 2018, **57**, 10723.[37]

References for the solvent-phase comparison:

Scheme 13A

J. P. Brand, J. Charpentier and J. Waser, *Angew. Chem. Int. Ed.*, 2009, **48**, 9346.[38]

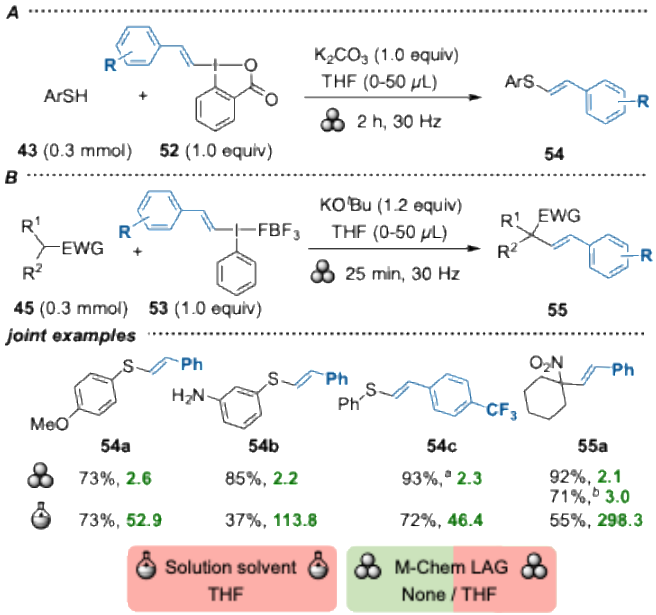
Scheme 13B

51a: F. Xie, Z. Qi, S. Yu and X. Li, *J. Am. Chem. Soc.*, 2014, **136**, 4780.[39]

51b, 51c: Z.-Z. Zhang, B. Liu, C.-Y. Wang and B.-F. Shi, *Org. Lett.*, 2015, **17**, 4094.[40]

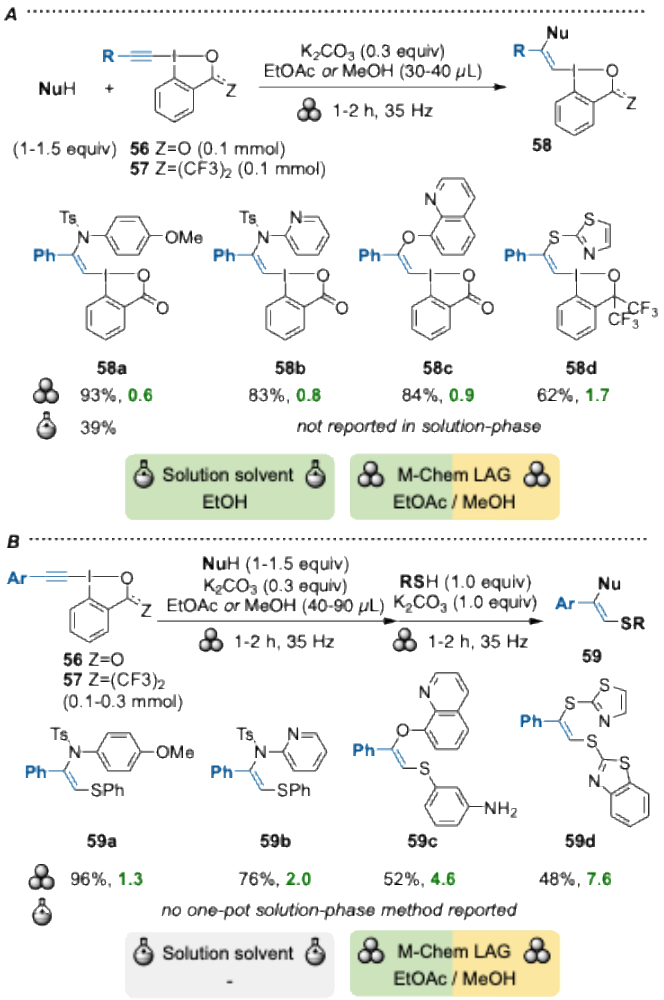
51d: *No solution phase method reported*.

5.3 Synthesis of alkenes



Reference for the mechanochemical reactions:
Scheme 14 A-B: S. Doobary, M. M. de Vries Ibáñez and B. Olofsson, *Green Chem.*, 2024, **26**, 11518.[17]

References for the solvent-phase comparison:
54a-c: L. Castoldi, E. M. Di Tommaso, M. Reitti, B. Gräfen and B. Olofsson, *Angew. Chem. Int. Ed.*, 2020, **59**, 15512.[41]
55a: E. Stridfeldt, A. Seemann, M. J. Bouma, C. Dey, A. Ertan and B. Olofsson, *Chem. Eur. J.*, 2016, **22**, 16066.[42]



Reference for the mechanochemical reactions:

Scheme 15A-B: S. Doobary, J. Braunreauther, A. K. Inge and B. Olofsson, *Angew. Chem. Int. Ed.*, 2025, e19049.[43]

References for the solvent-phase comparison:

Scheme 15A

58a: L. Castoldi, E. M. Di Tommaso, M. Reitti, B. Gräfen and B. Olofsson, *Angew. Chem. Int. Ed.*, 2020, **59**, 15512.[41]

Scheme 15B

No solution phase methods reported.

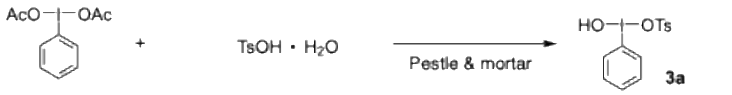
6 E-factor Calculations

The experimental procedures given in below are copied directly from the given references – hence, the compound numbers do not match those found in this review. We have added comments on differences in reaction scale, missing information in the experimental section, typos where masses do not match with reported yields, or differences between article & SI yields. The E-factor calculations were performed in Excel, and pictures of the calculation tables are provided below.

6.1 Ligand Exchange Reactions

Experimental: M. S. Yusubov and T. Wirth, *Org. Lett.*, 2005, **7**, 519.

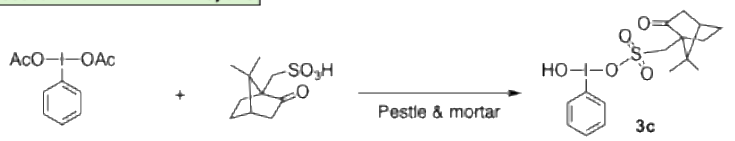
General Procedure for the Synthesis of Products 3a and 3c – 3f. A mixture of (diacetoxyiodo)arene **1** (0.571 mmol) and sulfonic acid (**3a**, **3e**: para-toluenesulfonic acid monohydrate **2a**, 111 mg, 0.584 mmol; **3c**, **3d**, **3f**: (1R)-10- camphorsulfonic acid **2c**, 135 mg, 0.581 mmol) was gently blended in an agate mortar. The resulting homogeneous mixture was then ground for 10 min. The formation of acetic acid and wetting of the reaction mixture was observed.



Molecular Weight: 322,10 Molecular Weight: 190,21 Molecular Weight: 392,21

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
DIB	1,00		322,10	0,571			0,184
TsOH•H2O	1,02		190,21	0,584			0,111
Product 3a		93%	392,21	0,531			**0,208**

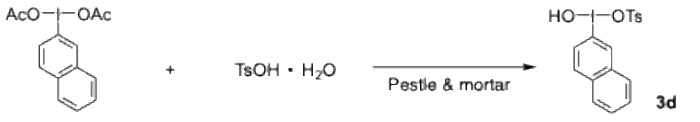
E-Factor:	**0,416**



Molecular Weight: 322,10 Molecular Weight: 232,29 Molecular Weight: 452,30

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
DIB	1,00		322,10	0,571			0,184
CSA	1,02		232,29	0,581			0,135
Product 3c		91%	452,30	0,520			**0,235**

E-Factor:	**0,357**



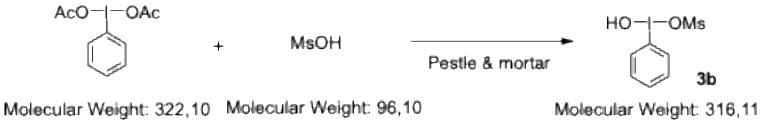
Molecular Weight: 372,16 Molecular Weight: 190,21 Molecular Weight: 442,27

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
(Diacetoxyiodo)arene	1,00		372,16	0,571			0,213
TsOH•H2O	1,02		190,21	0,584			0,111
Product 3d		77%	442,27	0,440			**0,194**

E-Factor:	**0,664**

Experimental: M. S. Yusubov and T. Wirth, *Org. Lett.*, 2005, **7**, 519.

Procedure for the Synthesis of Product 3b. Methanesulfonic acid **2b** (92 mg, 0.96 mmol) and (diacetoxyiodo)benzene **1a** (302 mg, 0.94 mmol) was placed in an agate mortar and intensively grinded. The formation of acetic acid was observed and the reaction mass turned yellow. After approximately 1 min the color of the reaction mixture changed to white and the formation of white crystals was observed. The grinding was continued for 10 min.



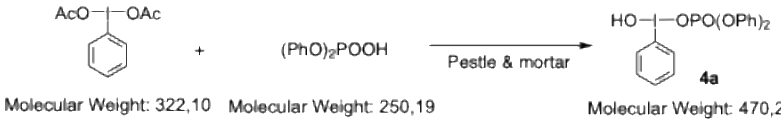
Molecular Weight: 322,10 Molecular Weight: 96,10 Molecular Weight: 316,11

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
DIB	1,00		322,10	0,940			0,303
MsOH	1,02		96,10	0,960			0,092
Product 3b		98%	316,11	0,921			**0,291**

E-Factor:	**0,357**

Experimental: M. Zhu, C. G. Cai, W. Ke and J. Shao, *Synth. Commun.*, 2010, **40**, 1371.

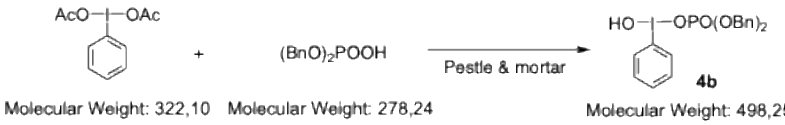
General Procedure for Synthesis of [Hydroxy(phosphoryloxy)iodo]-arenes: (Diacetoxyiodo)benzene (183 mg, 0.568 mmol, 1.0 equiv) and diphenyl phosphate (143 mg, 0.568 mmol, 1.0 equiv) was gently blended in an agate mortar. The resulting homogeneous mixture was then ground for 5 min.



Molecular Weight: 322,10 Molecular Weight: 250,19 Molecular Weight: 470,20

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
DIB	1,00		322,10	0,568			0,183
Diphenyl Phosphate	1,00		250,19	0,568			0,142
Product 4a		87%	470,20	0,494			**0,232**

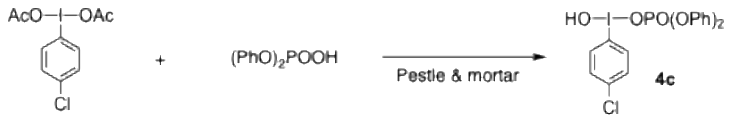
E-Factor:	**0,399**



Molecular Weight: 322,10 Molecular Weight: 278,24 Molecular Weight: 498,25

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
DIB	1,00		322,10	0,568			0,183
Diphenyl Phosphate	1,00		278,24	0,568			0,158
Product 4b		86%	498,25	0,488			**0,243**

E-Factor:	**0,401**



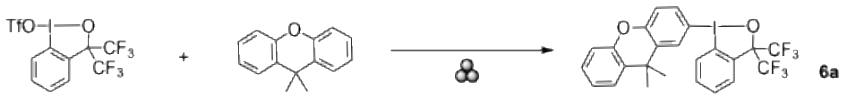
Molecular Weight: 356,54 Molecular Weight: 250,19 Molecular Weight: 504,64

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
(Diacetoxyiodo)arene	1,00		356,54	0,568			0,203
Diphenyl Phosphate	1,00		250,19	0,568			0,142
Product 4c		98%	504,64	0,557			**0,281**

E-Factor:	0,227

Experimental: W. Ding, C. Wang, J. R. Tan, C. C. Ho, F. León, F. García and N. Yoshikai, *Chem. Sci.*, 2020, **11**, 7356.

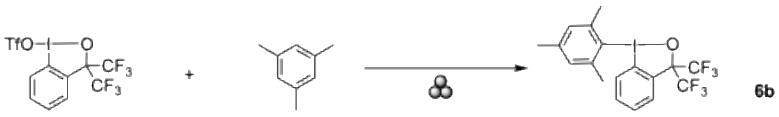
Mechanochemical Synthesis. A 15 mL stainless miller jar equipped with a 10 mm stainless steel ball was charged sequentially with aromatic compound **2** (0.30 mmol) and BXT (103.6 mg, 0.20 mmol). The jar was closed, and the mixture was subjected to 30 Hz milling for 2 h.



Molecular Weight: 518,09 Molecular Weight: 210,28 Molecular Weight: 578,29

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Benziodoxole Triflate	1,00		518,09	0,200			0,104
Arene Substrate	1,50		210,28	0,300			0,063
Product 6a		70%	578,29	0,140			**0,081**

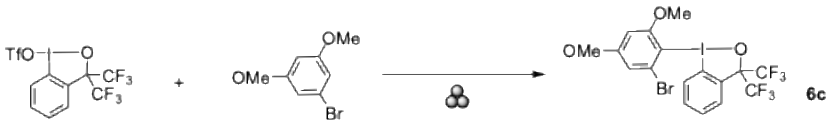
E-Factor:	1,059



Molecular Weight: 518,09 Molecular Weight: 120,20 Molecular Weight: 488,21

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Benziodoxole Triflate	1,00		518,09	0,200			0,104
Arene Substrate	1,50		120,20	0,300			0,036
Product 6b		89%	488,21	0,178			**0,087**

E-Factor:	0,607



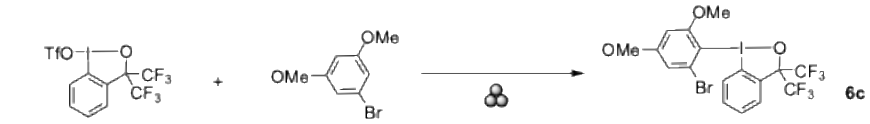
Molecular Weight: 518,09 Molecular Weight: 217,06 Molecular Weight: 585,08

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Benziodoxole Triflate	1,00		518,09	0,200			0,104
Arene Substrate	1,50		217,06	0,300			0,065
Product 6c		89%	585,08	0,178			**0,104**

E-Factor:	0,620

Experimental: W. Ding, C. Wang, J. R. Tan, C. C. Ho, F. León, F. García and N. Yoshikai, *Chem. Sci.*, 2020, **11**, 7356.

Gram-Scale Reaction: A 15 mL stainless miller jar equipped with a 10 mm stainless steel ball was charged sequentially with 1-bromo-3,5-dimethoxybenzene (**2r**, 0.52 g, 2.4 mmol) and BXT (1.04 g, 2.0 mmol). The jar was closed, and the mixture was subjected to 30 Hz milling at room temperature for 2 h.



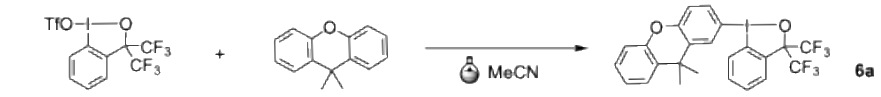
Molecular Weight: 518,09 Molecular Weight: 217,06 Molecular Weight: 585,08

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Benziodoxole Triflate	1,00		518,09	2,000			1,036
Arene Substrate	1,20		217,06	2,400			0,521
Product 6c		92%	585,08	1,840			**1,077**

E-Factor:	**0,446**

Experimental: W. Ding, C. Wang, J. R. Tan, C. C. Ho, F. León, F. García and N. Yoshikai, *Chem. Sci.*, 2020, **11**, 7356.

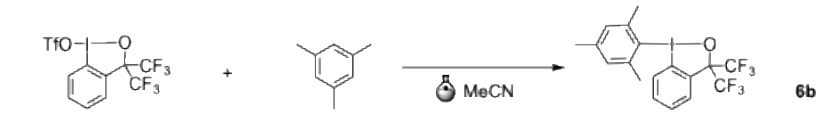
General procedure. In an argon-filled glove box, a 4 mL vial equipped with a magnetic stir bar was charged sequentially with aromatic compound **2** (0.30 mmol) and MeCN (0.5 mL), followed by the addition of BXT (**1**, 103.6 mg, 0.20 mmol). The vial was closed and taken out of the glove box. The mixture was stirred at room temperature for 24 h.



Molecular Weight: 518,09 Molecular Weight: 210,28 Molecular Weight: 578,29

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Benziodoxole Triflate	1,00		518,09	0,200			0,104
Arene Substrate	1,50		210,28	0,300			0,063
MeCN					0,500	0,786	0,393
Product 6a		77%	578,29	0,154			**0,089**

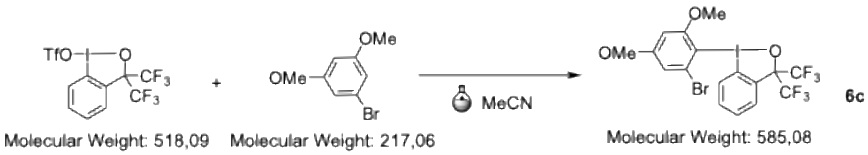
E-Factor:	**5,285**



Molecular Weight: 518,09 Molecular Weight: 120,20 Molecular Weight: 488,21

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Benziodoxole Triflate	1,00		518,09	0,200			0,104
Arene Substrate	1,50		120,20	0,300			0,036
MeCN					0,500	0,786	0,393
Product 6b		83%	488,21	0,166			**0,081**

E-Factor:	**5,573**



Molecular Weight: 518,09 Molecular Weight: 217,06 Molecular Weight: 585,08

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Benziodoxole Triflate	1,00		518,09	0,200			0,104
Arene Substrate	1,50		217,06	0,300			0,065
MeCN					0,500	0,786	0,393
Product 6c		84%	585,08	0,168			**0,098**

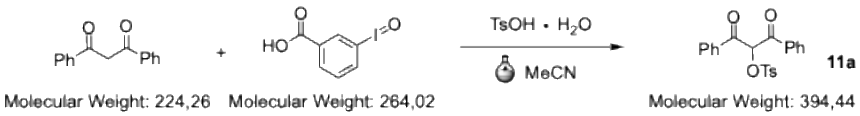
E-Factor:	**4,715**

6.2 Oxidative reactions

6.2.1 Tosyloxylations

Experimental: M. S. Yusubov, T. V. Funk, R. Y. Yusubova, G. Zholobova, A. Kirschning, J. Y. Park and K. W. Chi, *Synth. Commun*., 2009, **39**, 3772–3784.

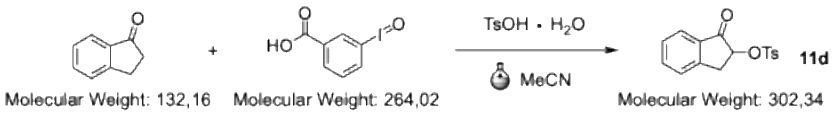
General Procedure. *m*-Iodosylbenzoic acid (**1**, 0.24 mmol) was added to a mixture of β-diketones (0.2 mmol) and *p*-toluenesulfonic acid monohydrate (or methanesulfonic acid) (0.3–0.4 mmol) in CH_3CN (1.0 mL). The reaction mixture was stirred at room temperature for 1.0–4.0 h, and the reaction was monitored by TLC.



Molecular Weight: 224,26 Molecular Weight: 264,02 Molecular Weight: 394,44

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Dibenzoylmethane	1,00		224,26	0,200			0,045
m -Iodosylbenzoic Acid	1,20		264,02	0,240			0,063
TsOH•H_2O	1,75		190,21	0,350			0,067
MeCN					1,000	0,786	0,786
Product 11a		93%	394,44	0,186			**0,073**

E-Factor:	**12,096**



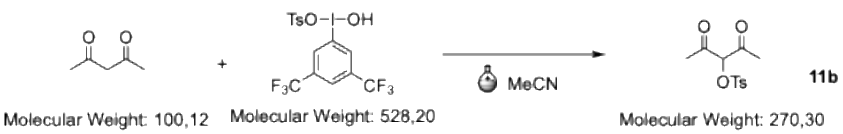
Molecular Weight: 132,16 Molecular Weight: 264,02 Molecular Weight: 302,34

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
1-Indanone	1,00		132,16	0,200			0,026
m -Iodosylbenzoic Acid	1,20		264,02	0,240			0,063
TsOH•H_2O	1,75		190,21	0,350			0,067
MeCN					1,000	0,786	0,786
Product 11d		77%	302,34	0,154			**0,047**

E-Factor:	**19,240**

Experimental: T. Nabana and H. Togo, *J. Org. Chem.*, 2002, **67**, 4362–4365.

Typical Procedure for r-Tosyloxylation of Acetophenone. To a solution of acetophenone (1 mmol) in acetonitrile (6 mL) was added 3-trifluoromethyl-1-[hydroxy(tosyloxy)iodo]ben-zene (1.2 mmol). The mixture was refluxed for 4 h under an argon atmosphere.



Molecular Weight: 100,12 Molecular Weight: 528,20 Molecular Weight: 270,30

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Acetylacetone	1,00		100,12	1,000			0,100
1,3-CF_3-HITB	1,20		528,20	1,200			0,634
MeCN					6,000	0,786	4,716
Product 11b		96%	270,30	0,960			**0,259**

E-Factor:	**20,003**

Experimental: S. T. Handy and M. Okello, *Synlett*, 2002, **3**, 489–491.

Representative Procedure. To 0.650 g (1.67 mmol) of [hydroxy(tosyloxy)iodo]benzene in a dry round-bottom flask under argon were added 2 mL of cyclohexanone and 15 mL of acetonitrile. The flask was placed in an ultrasound cleaning bath filled with warm (55 °C) water to a depth of 2 inches. The reaction mixture was sonicated for 15 minutes, during which time the suspension cleared to a yellowish- brown solution.

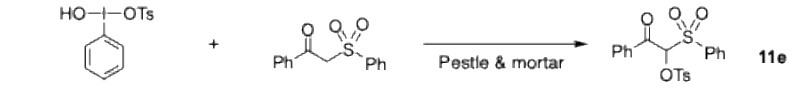
Molecular Weight: 98,15 Molecular Weight: 392,21 Molecular Weight: 268,33

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
HITB	1,00		392,21	1,670			0,655
Cyclohexanone	11,56		98,15	19,297	2,000	0,947	1,894
MeCN					15,000	0,786	11,79
Product 11c		89%	268,33	1,486			**0,399**

E-Factor:	**34,954**

Experimental: D. Kumar, M. S. Sundaree, G. Patel, V. S. Rao and R. S. Varma, *Tetrahedron Lett.*, 2006, **47**, 8239.

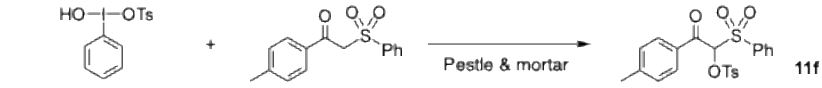
Typical experimental procedure. A mixture of *α-p*-methylbenzenesulfonyl acetophenone (0.087 g, 0.32 mmol) and [hydroxy(tosyloxy)iodo]benzene (0.140 g, 0.35 mmol) was placed in a mortar. The reaction mixture was ground together using a pestle at room temperature for 9 min wherein the contents turned to light yellow in color.



Molecular Weight: 392,21 Molecular Weight: 260,31 Molecular Weight: 430,49

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Sulfonyl Acetophenone	1,00		260,31	0,320			0,083
HITB	1,09		392,21	0,350			0,137
Product 11e		94%	430,49	0,301			**0,129**

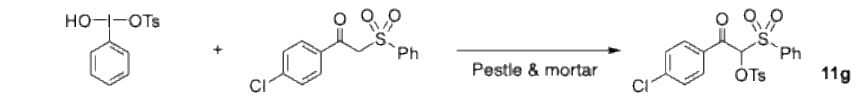
E-Factor:	**0,703**



Molecular Weight: 392,21 Molecular Weight: 274,33 Molecular Weight: 444,52

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Sulfonyl Acetophenone	1,00		274,33	0,320			0,088
HITB	1,09		392,21	0,350			0,137
Product 11f		94%	444,52	0,301			**0,134**

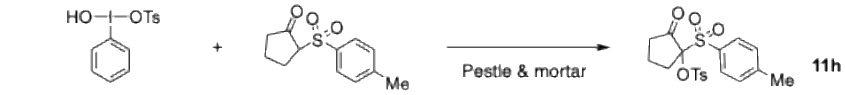
E-Factor:	**0,683**



Molecular Weight: 392,21 Molecular Weight: 294,75 Molecular Weight: 464,93

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Sulfonyl Acetophenone	1,00		294,75	0,320			0,094
HITB	1,09		392,21	0,350			0,137
Product 11g		90%	464,93	0,288			**0,134**

E-Factor:	**0,730**



Molecular Weight: 392,21 Molecular Weight: 238,30 Molecular Weight: 408,48

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Sulfonyl Ketone	1,00		238,30	0,320			0,076
HITB	1,09		392,21	0,350			0,137
Product 11h		72%	408,48	0,230			**0,094**

E-Factor:	**1,269**

Experimental: S. Doobary, M. M. de Vries Ibáñez and B. Olofsson, *Green Chem*., 2024, **26**, 11518.

General Procedure: The nucleophile (0.30 mmol, 1 equiv), 4-iodo-*m*-xylene (**9**, 9 µL, 0.30 mmol, 0.2 equiv), *m*CPBA (92% purity) (62.4 mg, 0.30 mmol, 1 equiv), *p*TsOH·H_2O (57.1 mg, 0.30 mmol, 1 equiv), HFIP (0.5 µL/mg) and one 10 mm stainless steel ball were added to a 5 mL stainless steel ball milling vessel. The vessel was closed and the mixture was milled for 5-30 minutes at 25 Hz.

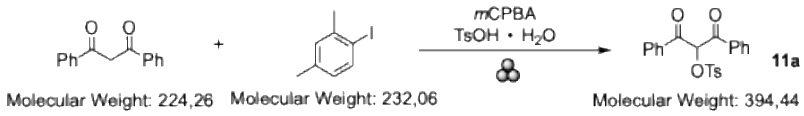
Comments:

0.2 equiv 4-iodo-*m*-xylene corresponds to 0.06 mmol, which we have used in the calculations below.

*m*CPBA of 83% purity was used in the reactions.

Product 11a: no HFIP was used.

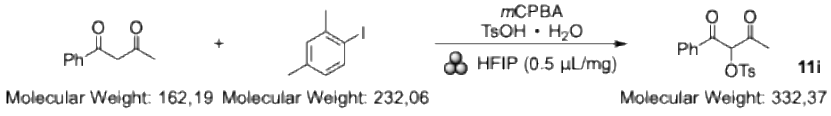
Product 11d & 11k: 0.45 mmol (1.5 equiv) *m*CPBA & TsOH•H_2O was used.



Molecular Weight: 224,26 Molecular Weight: 232,06 Molecular Weight: 394,44

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Dibenzoylmethane	1,00		224,26	0,300			0,067
4-Iodo-*m* -Xylene	0,20		232,06	0,060			0,014
m CPBA	1,00		172,57	0,300			0,062
TsOH•H_2O	1,00		190,21	0,300			0,057
Product 11a		77%	394,44	0,231			**0,091**

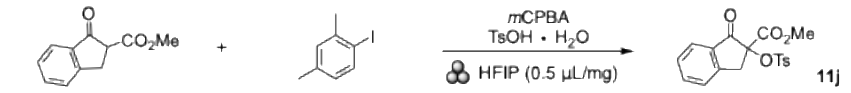
E-Factor:	**1,202**



Molecular Weight: 162,19 Molecular Weight: 232,06 Molecular Weight: 332,37

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Benzoylacetone	1,00		162,19	0,300			0,049
4-Iodo-*m* -Xylene	0,20		232,06	0,060			0,014
m CPBA	1,00		172,57	0,300			0,062
TsOH•H_2O	1,00		190,21	0,300			0,057
HFIP					0,091	1,596	0,145
Product 11i		69%	332,37	0,207			**0,069**

E-Factor:	**3,757**



Molecular Weight: 190,20 Molecular Weight: 232,06 Molecular Weight: 360,38

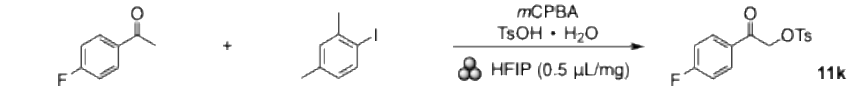
Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
2-Carbomethoxy-1-indar	1,00		190,20	0,300			0,057
4-Iodo-*m* -Xylene	0,20		232,06	0,060			0,014
m CPBA	1,00		172,57	0,300			0,062
TsOH•H_2O	1,00		190,21	0,300			0,057
HFIP					0,095	1,596	0,152
Product 11j		87%	360,38	0,261			**0,094**

E-Factor:	**2,640**

Molecular Weight: 132,16 Molecular Weight: 232,06 Molecular Weight: 302,34

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
1-Indanone	1,00		132,16	0,300			0,040
4-Iodo-*m* -Xylene	0,20		232,06	0,060			0,014
m CPBA	1,50		172,57	0,450			0,094
TsOH•H_2O	1,50		190,21	0,450			0,086
HFIP					0,116	1,596	0,186
Product 11d		41%	302,34	0,123			**0,037**

E-Factor:	**10,252**



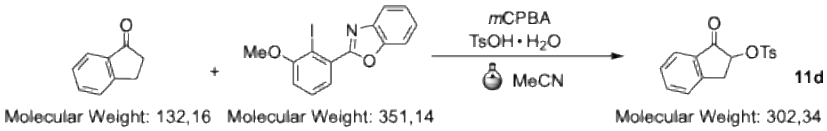
Molecular Weight: 138,14 Molecular Weight: 232,06 Molecular Weight: 308,32

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
4-Fluoroacetophenone	1,00		138,14	0,300			0,041
4-Iodo-*m* -Xylene	0,20		232,06	0,060			0,014
m CPBA	1,50		172,57	0,450			0,094
TsOH•H_2O	1,50		190,21	0,450			0,086
HFIP					0,117	1,596	0,187
Product 11k		74%	308,32	0,222			**0,068**

E-Factor:	**5,161**

Experimental: A. Boelke and B. J. Nachtsheim, *Adv. Synth. Catal.*, 2020, **362**, 184–191.

General Procedure for the α-Tosyloxylation of Carbonyl Compounds 8 with 1 mol% Catalyst 10e. To a stirred mixture of *m*CPBA (85%, 306 mg, 1.50 mmol, 1.5 equiv.), KOTs (105 mg, 0.500 mmol, 0.5 equiv.) and TsOH · H_2O (162 mg, 0.850 mmol, 0.85 equiv.) in MeCN (5 mL, 0.2 M) is added the [iodoarene]catalyst **10e** (3.5 mg, 0.010 mmol, 1 mol%) followed by the corresponding carbonyl compound **8** (1.00 mmol) and the mixture was stirred at 80 °C for 6 h.



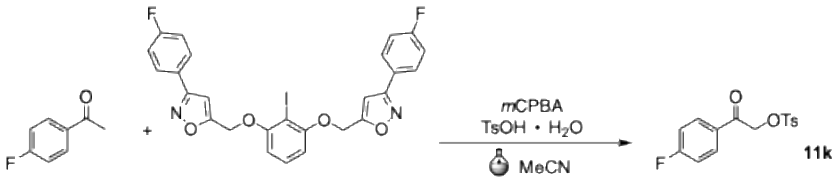
Molecular Weight: 132,16 Molecular Weight: 351,14 Molecular Weight: 302,34

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
1-Indanone	1,00		132,16	0,250			0,033
Iodoarene Catalyst	0,10		351,14	0,025			0,009
TsOH•H_2O	1,50		190,21	0,375			0,071
m CPBA	1,50		172,57	0,375			0,076
MeCN					2,500	0,786	1,965
Product 11d		81%	302,34	0,203			**0,061**

E-Factor:	**34,187**

Experimental: Rimi, B. Uttam, V.V. Zhdankin, R. Kumar, *Eur. J. Org. Chem*., 2024, **27**, e202301191.

General procedure for the α-oxytosylation of acetophenones. To a solution of acetophenone (0.2 mmol) in acetonitrile (1.5 ml), iodoarene 1b (0.02 mmol), *m*-CPBA (0.5 mmol) and *p*-TsOH•H_2O (0.5 mmol) was added and the reaction mixture was stirred at room temperature for 12 h.



Molecular Weight: 138,14 Molecular Weight: 586,33 Molecular Weight: 308,32

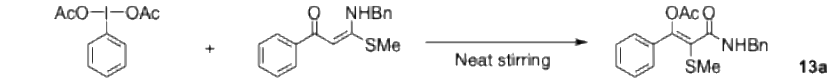
Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
4-Fluoroacetophenone	1,00		138,14	0,200			0,028
Iodoarene Catalyst	0,10		586,33	0,020			0,012
TsOH•H_2O	2,50		190,21	0,500			0,095
m CPBA	2,50		172,57	0,500			0,086
MeCN					1,500	0,786	1,179
Product 11k		85%	308,32	0,170			**0,052**

E-Factor:	**25,705**

6.2.2 Oxidative rearrangement

Experimental: Z. Liu, F. Huang, P. Wu, Q. Wang and Z. Yu, *J. Org. Chem.*, 2018, **83**, 5731.

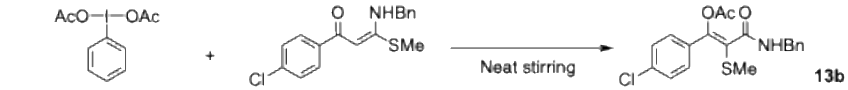
Typical Procedure for the Synthesis of α,β-Unsaturated Aamides 2 under the Solventless Mechanical Milling Conditions: A mixture of $PhI(OAc)_2$ (194 mg, 0.6 mmol) and enaminone **1a** (142 mg, 0.5 mmol) was mechanically milled in a 5 mL glass vial by a glass rod for 5 min, and the resultant yellow liquid mixture was allowed to stay in air at ambient temperature without milling for about 2 h until compound **1a** was completely consumed by TLC monitoring on silica gel.



Molecular Weight: 322,10 Molecular Weight: 283,39 Molecular Weight: 341,43

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Enaminone Substrate	1,00		283,39	0,500			0,142
DIB	1,20		322,10	0,600			0,193
Product 13a		73%	341,43	0,365			**0,125**

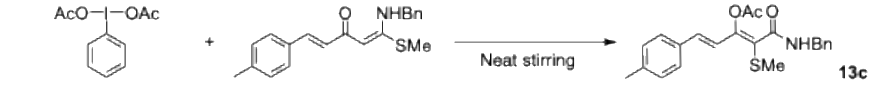
E-Factor:	**1,688**



Molecular Weight: 322,10 Molecular Weight: 317,83 Molecular Weight: 375,87

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Enaminone Substrate	1,00		317,83	0,500			0,159
DIB	1,20		322,10	0,600			0,193
Product 13b		80%	375,87	0,400			**0,150**

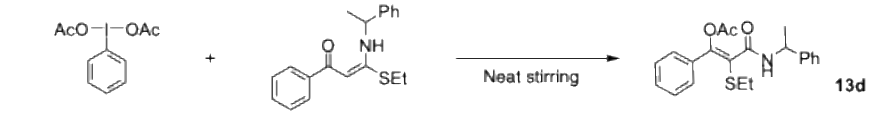
E-Factor:	**1,342**



Molecular Weight: 322,10 Molecular Weight: 323,45 Molecular Weight: 381,49

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Enaminone Substrate	1,00		323,45	0,500			0,162
DIB	1,20		322,10	0,600			0,193
Product 13c		73%	381,49	0,365			**0,139**

E-Factor:	**1,549**



Molecular Weight: 322,10 Molecular Weight: 311,44 Molecular Weight: 369,48

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Enaminone Substrate	1,00		311,44	0,500			0,156
DIB	1,20		322,10	0,600			0,193
Product 13d		85%	369,48	0,425			**0,157**

E-Factor:	**1,222**

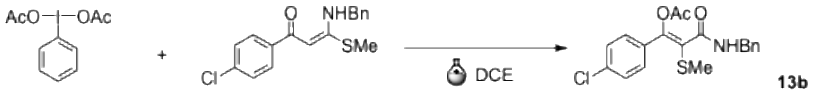
Experimental: Z. Liu, F. Huang, P. Wu, Q. Wang and Z. Yu, *J. Org. Chem.*, 2018, **83**, 5731.

Typical Procedure for the Synthesis of α,β-Unsaturated Amides (Solution): $PhI(OAc)_2$ (242 mg, 0.75 mmol) was added to a stirred solution of enaminone 1a (142 mg, 0.5 mmol) in 1,2-dichloroethane (DCE) (5 mL), and the reaction was continued at ambient temperature for 2 h until compound 1a was completely consumed by TLC monitoring on silica gel.

Molecular Weight: 322,10 Molecular Weight: 283,39 Molecular Weight: 341,43

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Enaminone Substrate	1,00		283,39	0,500			0,142
DIB	1,50		322,10	0,750			0,242
DCE					5,000	1,256	6,280
Product 13a		72%	341,43	0,360			**0,123**

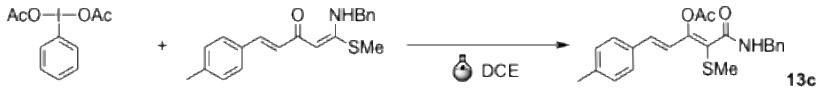
E-Factor:	**53,210**



Molecular Weight: 322,10 Molecular Weight: 317,83 Molecular Weight: 375,87

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Enaminone Substrate	1,00		317,83	0,500			0,159
DIB	1,50		322,10	0,750			0,242
DCE					5,000	1,256	6,280
Product 13b		86%	375,87	0,430			**0,162**

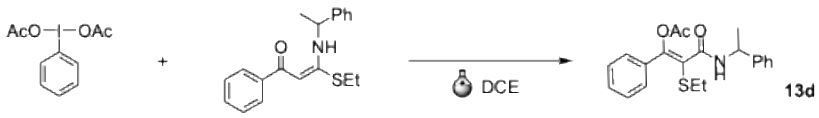
E-Factor:	**40,334**



Molecular Weight: 322,10 Molecular Weight: 323,45 Molecular Weight: 381,49

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Enaminone Substrate	1,00		323,45	0,500			0,162
DIB	1,50		322,10	0,750			0,242
DCE					5,000	1,256	6,280
Product 13c		82%	381,49	0,410			**0,156**

E-Factor:	**41,729**



Molecular Weight: 322,10 Molecular Weight: 311,44 Molecular Weight: 369,48

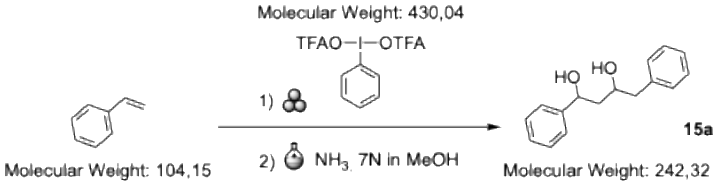
Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Enaminone Substrate	1,00		311,44	0,500			0,156
DIB	1,50		322,10	0,750			0,242
DCE					5,000	1,256	6,280
Product 13d		84%	369,48	0,420			**0,155**

E-Factor:	**42,029**

6.2.3 Oxidative functionalization of alkenes

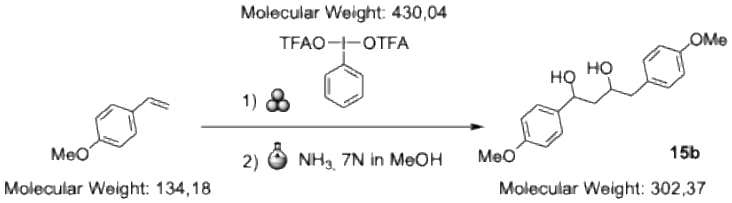
Experimental: L. Pan, L. Zheng, Y. Chen, Z. Ke and Y.-Y. Yeung, *Angew. Chem. Int. Ed*., 2022, **61**, e202207926

General procedure for the synthesis of 1,3-diol: Alkene **1** (2.2 mmol, 2.2 equiv) and PIFA (1.0 mmol, 1.0 equiv) were mixed with ball milling at 30 Hz for 60 to 99 min. The ball-milling cell was cleaned and dried before use. (Caution: although no obvious exothermic reaction or explosion was observed under these reaction conditions, it is still recommended to conduct the reaction in fumehood behind a blast shield). The reaction was then quenched with ammonia (7 N in MeOH, 10.0 equiv, 10 mmol) at 0 ℃ and stirred for another 30 min at RT.
Comment:
Product 5c: 3 equiv of alkene was used.



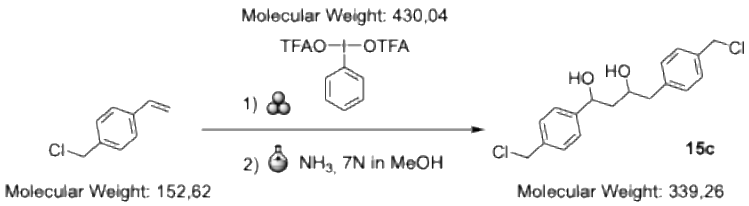
Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Normality (eq/L)	Density (g/mL)	Mass (g)
PIFA	1,00		430,04	1,000			0,430
Styrene	2,20		104,15	2,200			0,229
Ammonia/MeOH	10,00			10,000	7,000	0,779	1,113
Product 15a		64%	243,32	0,640			**0,156**

E-Factor:	**10,379**



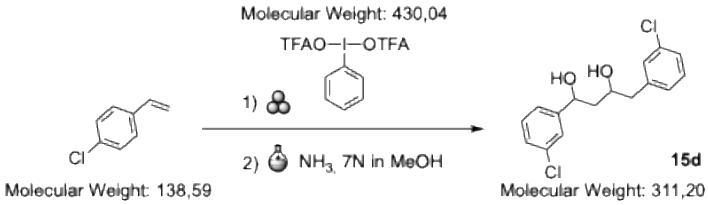
Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Normality (eq/L)	Density (g/mL)	Mass (g)
PIFA	1,00		430,04	1,000			0,430
4-Methoxystyrene	2,20		134,18	2,200			0,295
Ammonia/MeOH	10,00			10,000	7,000	0,779	1,113
Product 15b		58%	302,37	0,580			**0,175**

E-Factor:	**9,481**



Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Normality (eq/L)	Density (g/mL)	Mass (g)
PIFA	1,00		430,04	1,000			0,430
4-(Chloromethyl)styrene	3,00		152,62	3,000			0,458
Ammonia/MeOH	10,00			10,000	7,000	0,779	1,113
Product 15c		35%	339,26	0,350			**0,119**

E-Factor:	**15,850**

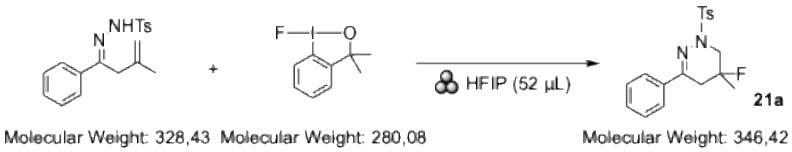


Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Normality (eq/L)	Density (g/mL)	Mass (g)
PIFA	1,00		430,04	1,000			0,430
3-Chlorostyrene	3,00		138,59	3,000			0,416
Ammonia/MeOH	10,00			10,000	7,000	0,779	1,113
Product 15d		73%	311,20	0,730			**0,227**

E-Factor:	**7,622**

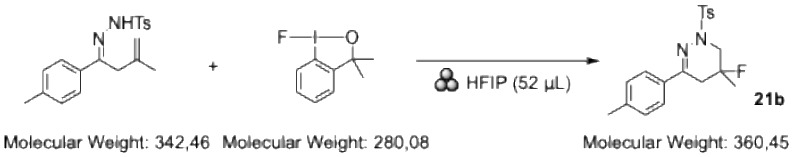
Experimental: W. Riley, A. C. Jones, K. Singh, D. L. Browne and A. M. Stuart, *Chem. Commun.*, 2021, **57**, 7406.

General Procedure C for fluorocyclisations of unsaturated tosyl hydrazones 2 using fluoroiodane in a ball-mill: To a 10 mL stainless steel jar (Retsch) was added a 2.5 g stainless steel milling ball. Unsaturated hydrazone (0.25 mmol), fluoroiodane **1** (0.1050 g, 0.375 mmol) and 1,1,1,3,3,3-hexafluoro-2-propanol (52 µL, 0.5 mmol) were added under an air atmosphere. The milling jar was then screwed closed and milled at 30 Hz for 15 minutes.



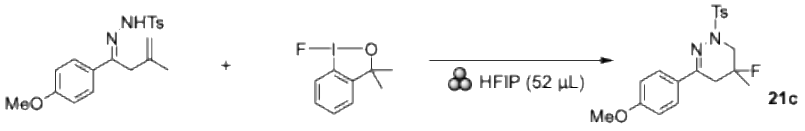
Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Unsaturated Hydrazone	1,00		328,43	0,250			0,082
Fluoroiodane	1,50		280,08	0,375			0,105
HFIP	2,00		168,04	0,500	0,052	1,596	0,083
Product 21a		91%	346,42	0,228			**0,079**

E-Factor:	**2,428**



Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Unsaturated Hydrazone	1,00		342,46	0,250			0,086
Fluoroiodane	1,50		280,08	0,375			0,105
HFIP	2,00		168,04	0,500	0,052	1,596	0,083
Product 21b		89%	360,45	0,223			**0,080**

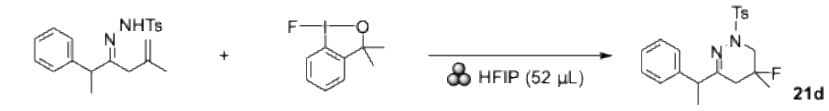
E-Factor:	**2,412**



Molecular Weight: 358,46 Molecular Weight: 280,08 Molecular Weight: 376,45

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Unsaturated Hydrazone	1,00		358,46	0,250			0,090
Fluoroiodane	1,50		280,08	0,375			0,105
HFIP	2,00		168,04	0,500	0,052	1,596	0,083
Product 21c		91%	376,45	0,228			**0,086**

E-Factor:	**2,242**



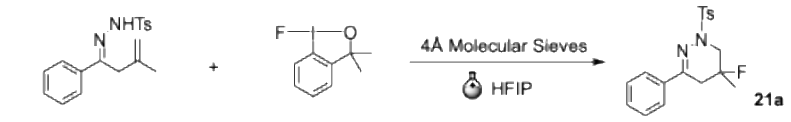
Molecular Weight: 356,48 Molecular Weight: 280,08 Molecular Weight: 374,47

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Unsaturated Hydrazone	1,00		356,48	0,250			0,089
Fluoroiodane	1,50		280,08	0,375			0,105
HFIP	2,00		168,04	0,500	0,052	1,596	0,083
Product 21d		76%	374,47	0,190			**0,071**

E-Factor:	**2,895**

Experimental: W. Riley, A. C. Jones, K. Singh, D. L. Browne and A. M. Stuart, *Chem. Commun.*, 2021, **57**, 7406.

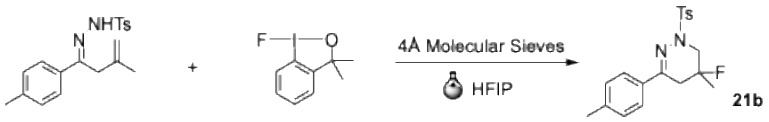
General Procedure B for fluorocyclisations of unsaturated tosyl hydrazones 2 using fluoroiodane in HFIP: A Schlenk flask was charged with unsaturated tosyl hydrazone (0.71 mmol), fluoroiodane **1** (300 mg, 1.07 mmol), 4 Å powdered molecular sieves (180 mg) and dry HFIP (1.2 mL) under an inert atmosphere. The reaction mixture was stirred for 15 minutes at room temperature.
Comment:
21d: 0.50 mmol of the hydrazone was used.



Molecular Weight: 328,43 Molecular Weight: 280,08 Molecular Weight: 346,42

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Unsaturated Hydrazone	1,00		328,43	0,710			0,233
Fluoroiodane	1,51		280,08	1,070			0,300
HFIP					1,200	1,596	1,915
Molecular Sieves							0,180
Product 21a		99%	346,42	0,703			**0,243**

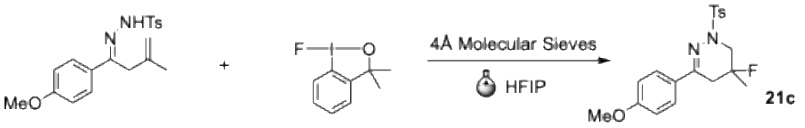
E-Factor:	**9,793**



Molecular Weight: 342,46 Molecular Weight: 280,08 Molecular Weight: 360,45

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Unsaturated Hydrazone	1,00		342,46	0,710			0,243
Fluoroiodane	1,51		280,08	1,070			0,300
HFIP					1,200	1,596	1,915
Molecular Sieves							0,180
Product 21b		92%	360,45	0,653			**0,235**

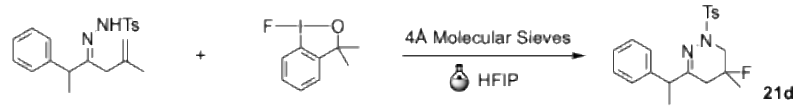
E-Factor:	**10,204**



Molecular Weight: 358,46 Molecular Weight: 280,08 Molecular Weight: 376,45

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Unsaturated Hydrazone	1,00		358,46	0,710			0,255
Fluoroiodane	1,51		280,08	1,070			0,300
HFIP					1,200	1,596	1,915
Molecular Sieves							0,180
Product 21c		90%	376,45	0,639			**0,241**

E-Factor:	**10,014**



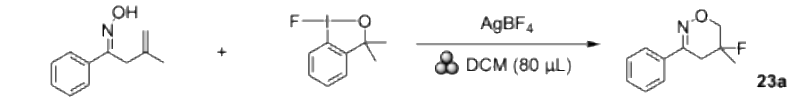
Molecular Weight: 356,48 Molecular Weight: 280,08 Molecular Weight: 374,47

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Unsaturated Hydrazone	1,00		356,48	0,500			0,178
Fluoroiodane	2,14		280,08	1,070			0,300
HFIP					1,200	1,596	1,915
Molecular Sieves							0,180
Product 21d		80%	374,47	0,400			**0,150**

E-Factor:	**16,178**

Experimental: W. Riley, A. C. Jones, K. Singh, D. L. Browne and A. M. Stuart, *Chem. Commun*., 2021, **57**, 7406.

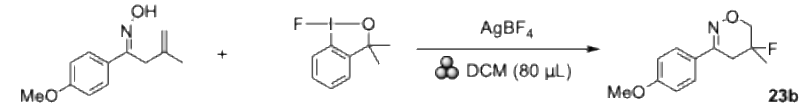
General Procedure B for intramolecular fluorocyclisations of unsaturated oximes 6 with fluoroiodane in a ball-mill: To a 10 mL stainless steel jar (Retsch) was added a 2.5 g stainless steel milling ball. Unsaturated oxime (0.25 mmol), fluoroiodane **1** (0.1050 g, 0.375 mmol) and silver tetrafluoroborate (0.0974, 0.5 mmol) were added under an air atmosphere. The milling jar was then screwed closed and milled at 30 Hz for 1 hour.
Comment:
The use of 80 µL DCM as LAG is stated in the article and schemes but not described above. E-factors are calculated with the LAG.



Molecular Weight: 175,23 Molecular Weight: 280,08 Molecular Weight: 193,22

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Unsaturated Oxime	1,00		175,23	0,250			0,044
Fluoroiodane	1,50		280,08	0,375			0,105
AgBF4	2,00		194,67	0,500			0,097
DCM					0,080	1,325	0,106
Product 23a		74%	193,22	0,185			**0,036**

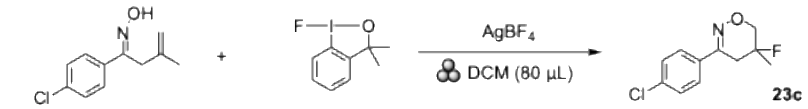
E-Factor:	**8,852**



Molecular Weight: 205,26 Molecular Weight: 280,08 Molecular Weight: 223,25

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Unsaturated Oxime	1,00		205,26	0,250			0,051
Fluoroiodane	1,50		280,08	0,375			0,105
AgBF4	2,00		194,67	0,500			0,097
DCM					0,080	1,325	0,106
Product 23b		80%	223,25	0,200			**0,045**

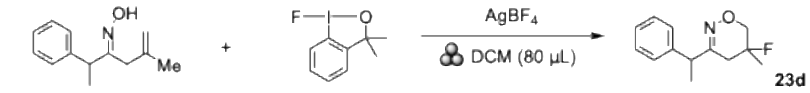
E-Factor:	**7,056**



Molecular Weight: 209,67 Molecular Weight: 280,08 Molecular Weight: 227,66

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/ml)	Mass (g)
Unsaturated Oxime	1,00		209,67	0,250			0,052
Fluoroiodane	1,50		280,08	0,375			0,105
AgBF4	2,00		194,67	0,500			0,097
DCM					0,080	1,325	0,106
Product 23c		78%	227,66	0,195			**0,044**

E-Factor:	**7,127**



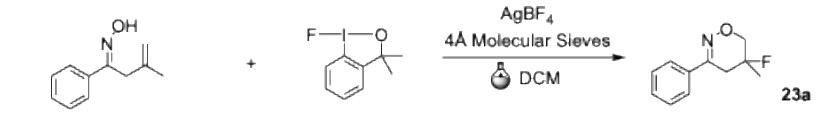
Molecular Weight: 203,29 Molecular Weight: 280,08 Molecular Weight: 221,28

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Unsaturated Oxime	1,00		203,29	0,250			0,051
Fluoroiodane	1,50		280,08	0,375			0,105
AgBF4	2,00		194,67	0,500			0,097
DCM					0,080	1,325	0,106
Product 23d		61%	221,28	0,153			**0,034**

E-Factor:	**9,644**

Experimental: W. Riley, A. C. Jones, K. Singh, D. L. Browne and A. M. Stuart, *Chem. Commun*., 2021, **57**, 7406.

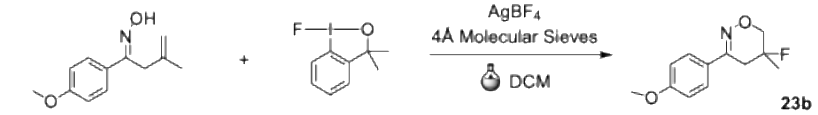
General Procedure A for intramolecular fluorocyclisations of unsaturated oximes 6 (in DCM): A Schlenk flask was charged with unsaturated oxime 6 (0.71 mmol), fluoroiodane **1** (1.07 mmol), $AgBF_4$ (0.71 mmol) and 4 Å powdered molecular sieves (180 mg) in dry dichloromethane (0.4 mL) under an inert atmosphere. The reaction mixture was stirred for 15 minutes at room temperature.



Molecular Weight: 175,23 Molecular Weight: 280,08 Molecular Weight: 193,22

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Unsaturated Oxime	1,00		175,23	0,710			0,124
Fluoroiodane	1,51		280,08	1,070			0,300
AgBF4	1,00		194,67	0,710			0,138
DCM					0,400	1,325	0,530
Molecular Sieves							0,180
Product 23a		46%	193,22	0,327			**0,063**

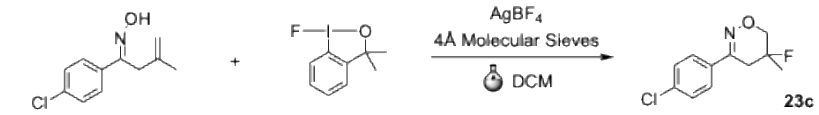
E-Factor:	**19,162**



Molecular Weight: 205,26 Molecular Weight: 280,08 Molecular Weight: 223,25

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Unsaturated Oxime	1,00		205,26	0,710			0,146
Fluoroiodane	1,51		280,08	1,070			0,300
AgBF4	1,00		194,67	0,710			0,138
DCM					0,400	1,325	0,530
Molecular Sieves							0,180
Product 23b		53%	223,25	0,376			**0,084**

E-Factor:	**14,399**



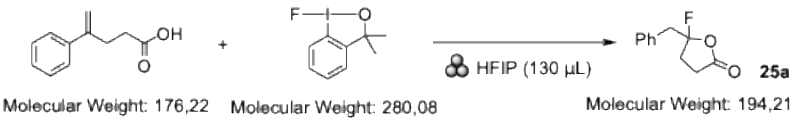
Molecular Weight: 209,67 Molecular Weight: 280,08 Molecular Weight: 227,66

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Unsaturated Oxime	1,00		209,67	0,710			0,149
Fluoroiodane	1,51		280,08	1,070			0,300
AgBF4	1,00		194,67	0,710			0,138
DCM					0,400	1,325	0,530
Molecular Sieves							0,180
Product 23b		42%	227,66	0,298			**0,068**

E-Factor:	**18,102**

Experimental: W. Riley, A. C. Jones, K. Singh, D. L. Browne and A. M. Stuart, *Chem. Commun*., 2021, **57**, 7406.

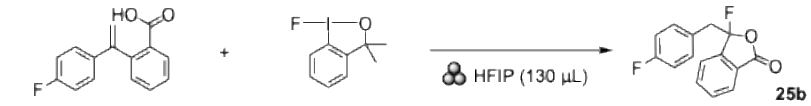
General procedure for the intramolecular fluorocyclisations of unsaturated carboxylic acids 12 in a ball-mill: To a 10 mL stainless steel jar (Retsch) was added a 2.5 g stainless steel milling ball. Unsaturated carboxylic acid (0.25 mmol), fluoroiodane **1** (0.1050 g, 0.375 mmol) and 1,1,1,3,3,3-hexafluoro-2-propanol (130 µL, 1.25 mmol) were added under an air atmosphere. The milling jar was then screwed closed and milled at 30 Hz for 1 hour.



Molecular Weight: 176,22 Molecular Weight: 280,08 Molecular Weight: 194,21

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Unsat. Carboxylic Acid	1,00		176,22	0,250			0,044
Fluoroiodane	1,50		280,08	0,375			0,105
HFIP	5,00		168,04	1,250	0,130	1,596	0,207
Product 25a		96%	194,21	0,240			**0,047**

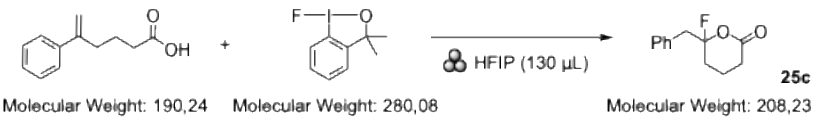
E-Factor:	**6,650**



Molecular Weight: 242,25 Molecular Weight: 280,08 Molecular Weight: 260,24

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Unsat. Carboxylic Acid	1,00		242,25	0,250			0,061
Fluoroiodane	1,50		280,08	0,375			0,105
HFIP	5,00		168,04	1,250	0,130	1,596	0,207
Product 25b		88%	260,24	0,220			**0,057**

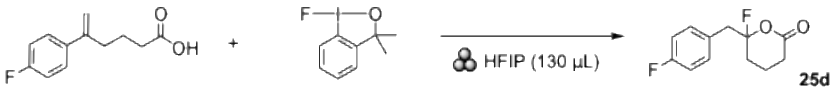
E-Factor:	**5,516**



Molecular Weight: 190,24 Molecular Weight: 280,08 Molecular Weight: 208,23

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Unsat. Carboxylic Acid	1,00		190,24	0,250			0,048
Fluoroiodane	1,50		280,08	0,375			0,105
HFIP	5,00		168,04	1,250	0,130	1,596	0,207
Product 25c		73%	208,23	0,183			**0,038**

E-Factor:	**8,475**



Molecular Weight: 208,23 Molecular Weight: 280,08 Molecular Weight: 226,22

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Unsat. Carboxylic Acid	1,00		208,23	0,250			0,052
Fluoroiodane	1,50		280,08	0,375			0,105
HFIP	5,00		168,04	1,250	0,130	1,596	0,207
Product 25d		84%	226,22	0,210			**0,048**

E-Factor:	**6,674**

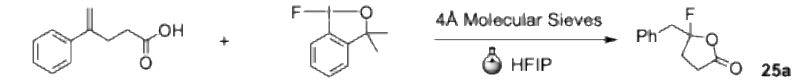
Experimental: H. K. Minhas, W. Riley, A. M. Stuart and M. Urbonaite, *Org. Biomol. Chem*., 2018, **16**, 7170.

Procedure for the intramolecular fluorocyclisations in HFIP: A small Schlenk flask was charged with powdered 4 Å molecular sieves (0.11 g), 1-fluoro-3,3-dimethyl-1,3-dihydro-λ3-benzo[d][1,2]iodoxole **1** (0.38 g, 1.36 mmol), substrate (0.9 mmol) and hexafluoroisopropanol (3 mL). The flask was then sealed and the contents were stirred at 40 °C for either one hour or four hours.

25a: 4-Phenylpent-4-enoic acid (0.15 g, 0.85 mmol) was reacted with 1-fluoro-3,3-dimethyl-1,3-dihydro-λ3 benzo[d][1,2]iodoxole (0.36 g, 1.29 mmol) in the presence of 4 Å molecular sieves (0.11 g) in hexafluoroisopropanol (3 mL) at 40 °C for 1 h following the general procedure.

25b: 2-(1-(4-Fluorophenyl)vinyl)benzoic acid **3d** (0.15 g, 0.62 mmol) was reacted with 1-fluoro-3,3-dimethyl-1,3-dihydro-λ3-benzo[d][1,2]iodoxole **1** (0.26 g, 0.93 mmol) in the presence of 4 Å molecular sieves (0.11 g) in hexafluoroisopropanol (3 mL) at 40 °C for 1 h following the general procedure.

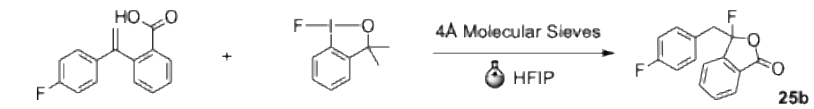
25c: 5-Phenylhex-5-enoic acid **3e** (0.15 g, 0.79 mmol) was reacted with 1-fluoro-3,3-dimethyl-1,3-dihydro-λ3-benzo[d][1,2]iodoxole **1** (0.33 g, 1.18 mmol) in the presence of 4 Å molecular sieves (0.11 g) in hexafluoroisopropanol (3 mL) at 40 °C for 1 h following the general procedure.



Molecular Weight: 176,22 Molecular Weight: 280,08 Molecular Weight: 194,21

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Unsat. Carboxylic Acid	1,00		176,22	0,850			0,150
Fluoroiodane	1,52		280,08	1,290			0,361
HFIP					3,000	1,596	4,788
Molecular Sieves							0,110
Product 25a		84%	194,21	0,714			**0,139**

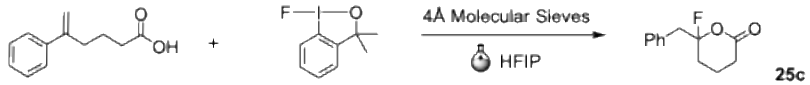
E-Factor:	**38,008**



Molecular Weight: 242,25 Molecular Weight: 280,08 Molecular Weight: 260,24

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Unsat. Carboxylic Acid	1,00		242,25	0,620			0,150
Fluoroiodane	1,50		280,08	0,930			0,260
HFIP					3,000	1,596	4,788
Molecular Sieves							0,110
Product 25b		81%	260,24	0,502			**0,131**

E-Factor:	**39,620**



25c

Molecular Weight: 190,24 Molecular Weight: 280,08 Molecular Weight: 208,23

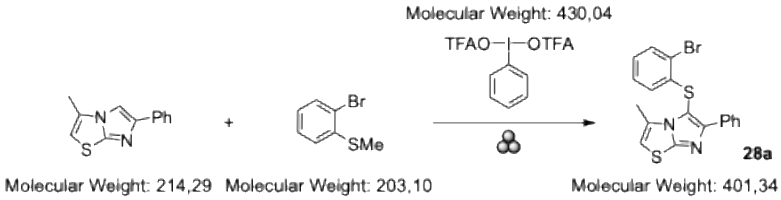
Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Unsat. Carboxylic Acid	1,00		190,24	0,790			0,150
Fluoroiodane	1,49		280,08	1,180			0,330
HFIP					3,000	1,596	4,788
Molecular Sieves							0,110
Product 25c		66%	208,23	0,521			**0,109**

E-Factor:	**48,542**

6.2.4 Oxidative sulfenylation

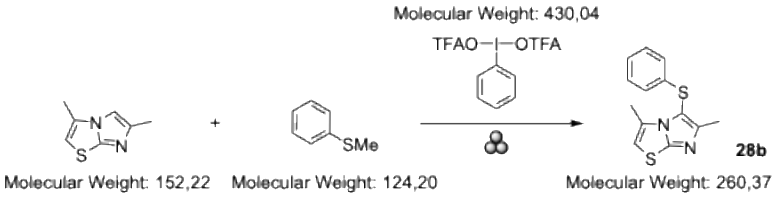
Experimental: X. Liu, V. Dorokhov, O. Provot, C. Tran, P. Retailleau, J.-F. Soulé and A. Hamze, *ChemSusChem*, 2025, **18**, e202500320.

General procedure B for the sulfenylation of imidazo[2,1-*b*]thiazoles in ball-milling conditions: One stainless-steel ball (12 mm) was added to the stainless-steel jar (10 mL) before the addition of starting materials and reagents. Then the corresponding heterocyclic substrate (0.5 mmol, 1 eq.) was added to the jar, followed by the aryl methyl sulfide (0.55 mmol, 1.1 eq.) and PIFA (0.55 mmol, 1.1 eq.), and the jar was immediately closed under air. The reaction vessel was placed on vibrational ball mill for 30 min at 30 Hz frequency.



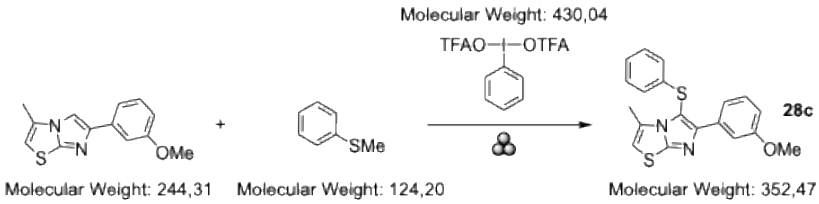
Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Imidazo[2,1-b]thiazole	1,00		214,29	0,500			0,107
Aryl Methyl Sulfide	1,10		203,10	0,550			0,112
PIFA	1,10		430,04	0,550			0,237
Product 28a		80%	401,34	0,400			**0,161**

E-Factor:	**1,837**



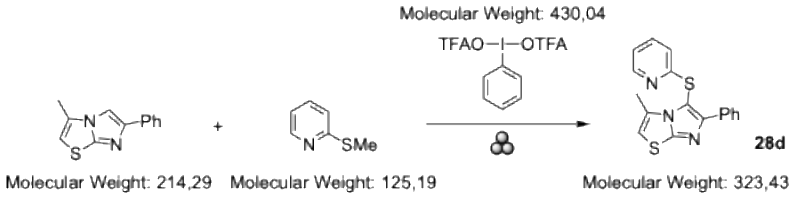
Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Imidazo[2,1-b]thiazole	1,00		152,22	0,500			0,076
Aryl Methyl Sulfide	1,10		124,20	0,550			0,068
PIFA	1,10		430,04	0,550			0,237
Product 28b		76%	260,37	0,380			**0,099**

E-Factor:	**2,850**



Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Imidazo[2,1-b]thiazole	1,00		244,31	0,500			0,122
Aryl Methyl Sulfide	1,10		124,20	0,550			0,068
PIFA	1,10		430,04	0,550			0,237
Product 28c		65%	352,47	0,325			**0,115**

E-Factor:	**2,727**

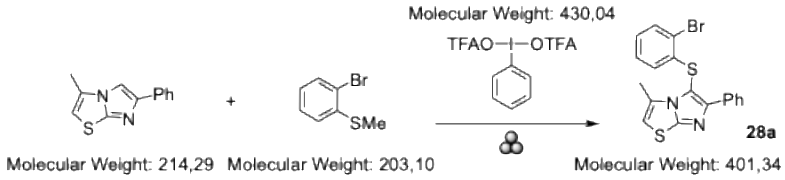


Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Imidazo[2,1-b]thiazole	1,00		214,29	0,500			0,107
Aryl Methyl Sulfide	1,10		125,19	0,550			0,069
PIFA	1,10		430,04	0,550			0,237
Product 28d		53%	323,43	0,265			**0,086**

E-Factor:	**3,813**

Experimental: X. Liu, V. Dorokhov, O. Provot, C. Tran, P. Retailleau, J.-F. Soulé and A. Hamze, *ChemSusChem*, 2025, **18**, e202500320.

Scale-up procedure for thiolation of imidazo[2,1-*b*]thiazole: The scale-up procedure was performed using General procedure B, utilizing one stainless steel ball (12 mm) in the 10 mL stainless-steel jar (second jar was empty and added for a counterbalance). 5-((2-bromophenyl)thio)-3-methyl-6-phenylimidazo[2,1-*b*]thiazole (3a) was synthesized from 1a (1.07 g, 5 mmol) and (2-bromophenyl)(methyl)sulfane (0.74 mL, 5.5 mmol) using PIFA (2.36 g, 5.5 mmol).
Comment:
General procedure B refers to the experimental given on the previous page.

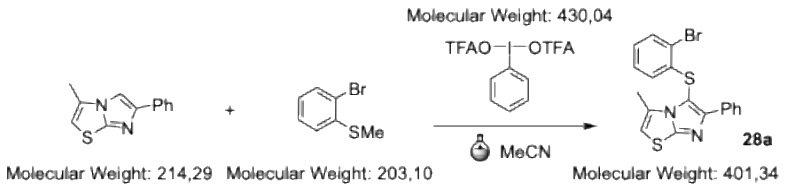


Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Imidazo[2,1-b]thiazole	1,00		214,29	5,000			1,071
Aryl Methyl Sulfide	1,10		203,10	5,500			1,117
PIFA	1,10		430,04	5,500			2,365
Product 28a		68%	401,34	3,400			**1,365**

E-Factor:	**2,337**

Experimental: X. Liu, V. Dorokhov, O. Provot, C. Tran, P. Retailleau, J.-F. Soulé and A. Hamze, *ChemSusChem*, 2025, **18**, e202500320.

Procedure in solution: To a mixture of imidazo[2,1-*b*]thiazole (0.107 g, 0.5 mmol, 1.0 equiv.), (2-bromophenyl)-(methyl)sulfane (132 mg, 0.65 mmol, 1.3 equiv.), and PIFA (0.644 g, 1.5 mmol, 3.0 equiv.), dry MeCN (1.7 mL) was added, and the resulting mixture was stirred at 50 °C for 20 min.



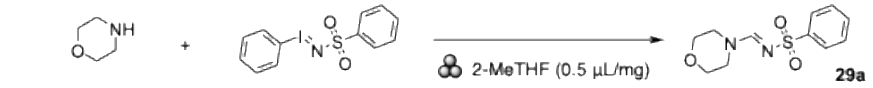
Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Imidazo[2,1-b]thiazole	1,00		214,29	0,500			0,107
Aryl Methyl Sulfide	1,30		203,10	0,650			0,132
PIFA	3,00		430,04	1,500			0,645
MeCN					1,700	0,786	1,336
Product 28a		80%	401,34	0,400			**0,161**

E-Factor:	**12,831**

6.2.5 Reactions with iodonium sulfonimides

Experimental: X. S. Guha, S. Maheshwari, M. K. Ravva, J. M. Jacob, S. Yadav and S. Sen, *Asian J. Org. Chem*., 2023, **12**, e202300348

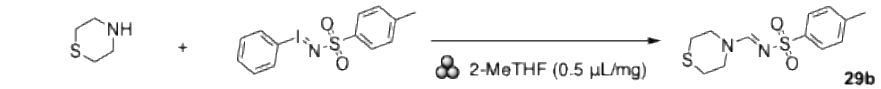
General Procedure of Sulfonyl-Amidine: Under air atmosphere, 0.2 mmol of Iminoiodinanes **1**, 6 membered cyclic base (Morpholine/ Thiomorpholine or Piperidine) **1** (0.4 mmol), and 3 stainless-steel ball (Ø = 5 mm, m_{tot} = 0.94 gm) were placed in a ball milling jar (stainless-steel, 5 mL), [N.B.: Additional 2Me-THF was added (LAG η = 0.5 µL mg^{-1}) as a grinding auxiliary]. Then, the mixture was milled at 30 Hz for 180 min.



Molecular Weight: 87,12 Molecular Weight: 359,18 Molecular Weight: 254,30

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Iminoiodinane	1,00		359,18	0,200			0,072
Morpholine	2,00		87,12	0,400			0,035
2-MeTHF					0,036	0,860	0,031
Product 29a		75%	254,30	0,150			**0,038**

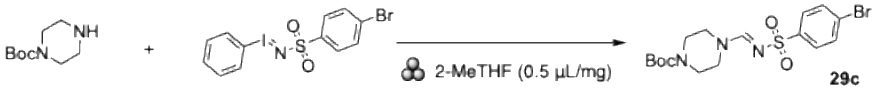
E-Factor:	2,607



Molecular Weight: 103,18 Molecular Weight: 373,21 Molecular Weight: 284,39

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Iminoiodinane	1,00		373,21	0,200			0,075
Thiomorpholine	2,00		103,18	0,400			0,041
2-MeTHF					0,037	0,860	0,032
Product 29b		78%	284,39	0,156			**0,044**

E-Factor:	2,336



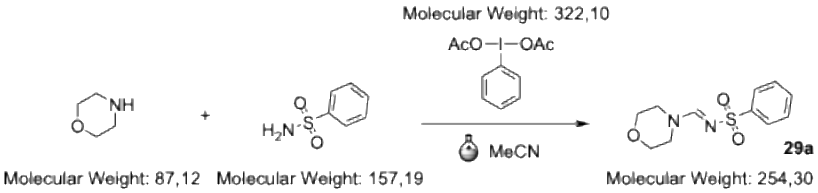
Molecular Weight: 186,26 Molecular Weight: 438,08 Molecular Weight: 432,33

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Iminoiodinane	1,00		438,08	0,200			0,088
Boc-Piperazine	2,00		186,26	0,400			0,075
2-MeTHF					0,037	0,860	0,032
Product 29c		47%	432,33	0,094			**0,0406**

E-Factor:	3,778

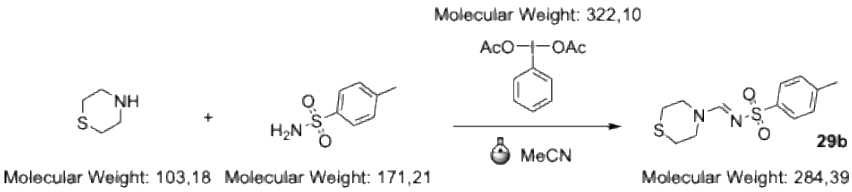
Experimental: C. S. Nishad, K. K. Haldar and B. Banerjee, *J. Org. Chem*., 2022, **87**, 11644.

General Procedure for the Synthesis of N-Sulfonyl Amidines: In a 10 ml round bottom flask 1 (0.3 mmol, 1 equiv) and 2 (0.9 mmol, 3 equiv) were taken and the mixture was dissolved in acetonitrile (1.5 ml). Then $PhI(OAc)_2$ (0.9 mmol, 3 equiv) was added and the reaction mixture was stirred at 70 °C in oil bath for 2 hr.



Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Sulfonamide	1,00		157,19	0,300			0,047
Morpholine	3,00		87,12	0,900			0,078
DIB	3,00		322,10	0,900			0,290
MeCN					1,500	0,786	1,179
Product 29a		66%	254,30	0,198			**0,050**

E-Factor:	**30,667**



Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Sulfonamide	1,00		171,21	0,300			0,051
Thiomorpholine	3,00		103,18	0,900			0,093
DIB	3,00		322,10	0,900			0,290
MeCN					1,500	0,786	1,179
Product 29b		70%	284,39	0,210			**0,060**

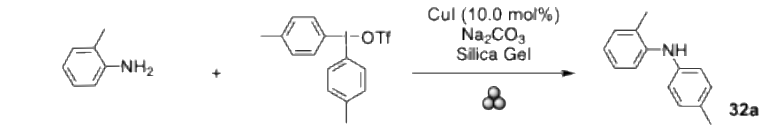
E-Factor:	**26,010**

6.3 Transfer of carbon ligands

6.3.1 Arylations

Experimental: J. Jiang and J. Li, *ChemistrySelect*, 2020, **5**, 542.

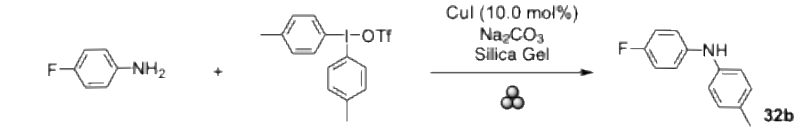
General procedure of method A:
Aniline **1a** (0.093 g, 1.0 mmol), bis(4-methylphenyl)iodonium triflate **2a** (0.550 g, 1.2 mmol), Na_2CO_3 (0.106 g, 1.0 mmol), CuI (0.019 g, 10 mol%), and silica gel (chromatography grade, 0.5 g) were mixed with stainless-steel balls (1.0 cm × 4) in a stainless-steel jar under ball milling at 15 Hz for 20 min.



Molecular Weight: 107,16 Molecular Weight: 458,23 Molecular Weight: 197,28

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
2-Methylaniline	1,00		107,16	1,000			0,107
Diaryliodonium Triflate	1,20		458,23	1,200			0,550
Na2CO3	1,00		105,99	1,000			0,106
CuI	0,10		190,45	0,100			0,019
Silica Gel							0,500
Product 32a		86%	197,28	0,860			**0,170**

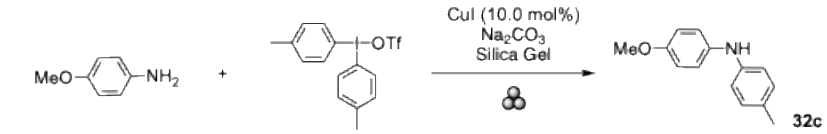
E-Factor:	**6,557**



Molecular Weight: 111,12 Molecular Weight: 458,23 Molecular Weight: 201,24

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
4-Fluoroaniline	1,00		111,12	1,000			0,111
Diaryliodonium Triflate	1,20		458,23	1,200			0,550
Na2CO3	1,00		105,99	1,000			0,106
CuI	0,10		190,45	0,100			0,019
Silica Gel							0,500
Product 32b		65%	201,24	0,650			**0,131**

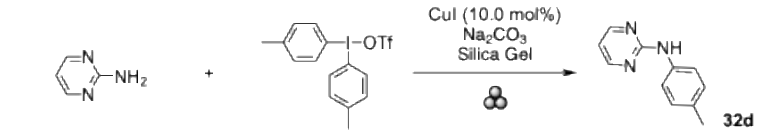
E-Factor:	**8,832**



Molecular Weight: 123,16 Molecular Weight: 458,23 Molecular Weight: 213,28

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
4-Methoxyaniline	1,00		123,16	1,000			0,123
Diaryliodonium Triflate	1,20		458,23	1,200			0,550
Na2CO3	1,00		105,99	1,000			0,106
CuI	0,10		190,45	0,100			0,019
Silica Gel							0,500
Product 32c		51%	213,28	0,510			**0,109**

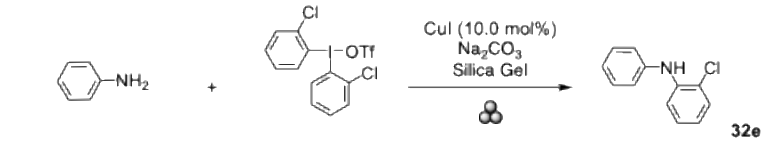
E-Factor:	**10,934**



Molecular Weight: 95,11 Molecular Weight: 458,23 Molecular Weight: 185,23

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Pyrimidinamine	1,00		95,11	1,000			0,095
Diaryliodonium Triflate	1,20		458,23	1,200			0,550
Na_2CO_3	1,00		105,99	1,000			0,106
CuI	0,10		190,45	0,100			0,019
Silica Gel							0,500
Product 32d		35%	185,23	0,350			**0,065**

E-Factor:	**18,590**



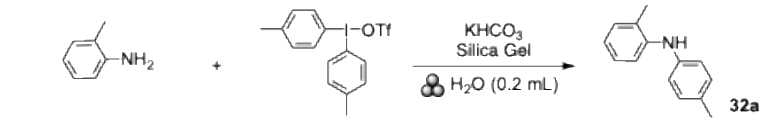
Molecular Weight: 93,13 Molecular Weight: 499,06 Molecular Weight: 203,67

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Aniline	1,00		93,13	1,000			0,093
Diaryliodonium Triflate	1,20		499,06	1,200			0,599
Na_2CO_3	1,00		105,99	1,000			0,106
CuI	0,10		190,45	0,100			0,019
Silica Gel							0,500
Product 32e		74%	203,67	0,740			**0,151**

E-Factor:	**7,739**

Experimental: J. Jiang and J. Li, *ChemistrySelect*, 2020, **5**, 542.

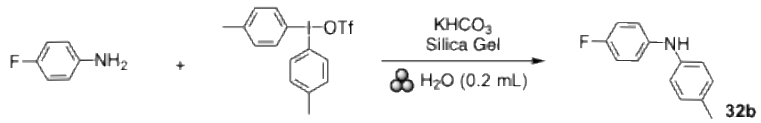
General procedure of method B: Amine **1a** (0.093 g, 1.0 mmol), diaryliodonium salt **2a** (0.916g, 2.0 mmol), $KHCO_3$ (0.100 g, 1.0 mmol), H_2O (0.2 mL), and silica gel (chromatography grade, 0.5 g) were mixed with stainless-steel balls (1.0 cm × 4) in a stainless-steel jar under ball milling at 10 Hz for 30 min.



Molecular Weight: 107,16 Molecular Weight: 458,23 Molecular Weight: 197,28

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
2-Methylaniline	1,00		107,16	1,000			0,107
Diaryliodonium Triflate	2,00		458,23	2,000			0,916
$KHCO_3$	1,00		100,11	1,000			0,100
H_2O					0,200	0,997	0,199
Silica Gel							0,500
Product 32a		78%	197,28	0,780			**0,154**

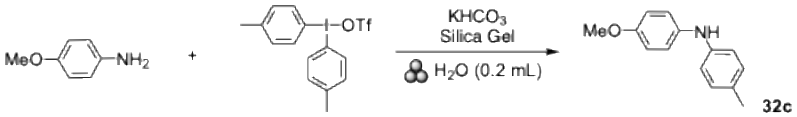
E-Factor:	**10,848**



Molecular Weight: 111,12 Molecular Weight: 458,23 Molecular Weight: 201,24

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
4-Fluoroaniline	1,00		111,12	1,000			0,111
Diaryliodonium Triflate	2,00		458,23	2,000			0,916
KHCO3	1,00		100,11	1,000			0,100
H2O					0,200	0,997	0,199
Silica Gel							0,500
Product 32b		55%	201,24	0,550			**0,111**

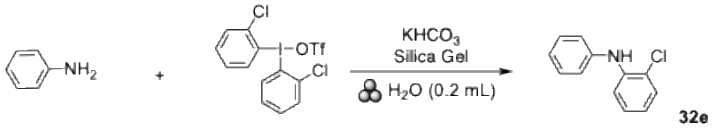
E-Factor:	**15,508**



Molecular Weight: 123,16 Molecular Weight: 458,23 Molecular Weight: 213,28

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
4-Methoxyaniline	1,00		123,16	1,000			0,123
Diaryliodonium Triflate	2,00		458,23	2,000			0,916
KHCO3	1,00		100,11	1,000			0,100
H2O					0,200	0,997	0,199
Silica Gel							0,500
Product 32c		47%	213,28	0,470			**0,100**

E-Factor:	**17,347**



Molecular Weight: 93,13 Molecular Weight: 499,06 Molecular Weight: 203,67

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Aniline	1,00		93,13	1,000			0,093
Diaryliodonium Triflate	2,00		499,06	2,000			0,998
KHCO3	1,00		100,11	1,000			0,100
H2O					0,200	0,997	0,199
Silica Gel							0,500
Product 32e		69%	203,67	0,690			**0,141**

E-Factor:	**12,454**

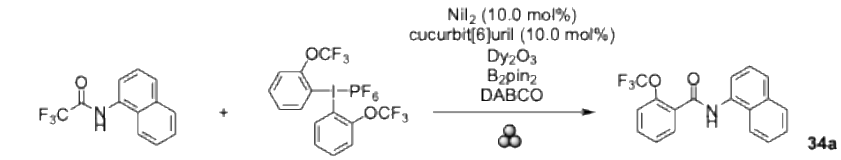
Experimental: S. Mkrtchyan, M. Shkoor, M. Phanindrudu, M. Medved, O. Sevastyanova and V. O. Iaroshenko, *J. Org. Chem*., 2023, **88**, 863.

General procedure for the synthesis of amides 3 starting from trifluoroacetamides and iodonium salts 5. In dry box, to 5 mL grinding vessel (made of stainless) equipped with two balls (made of stainless, diameter: 5 mm) was placed consequently NiI_2 (31 mg, 0.1 mmol, 10 mol%), cucurbit[6]uril (L) (100 mg, 0.1 mmol, 10 mol%), Dy_2O_3 (373 mg, 1.0 mmol, 1.0 equiv.), DABCO (157 mg, 1.4 mmol, 1.4 equiv.), bis(pinacolato)diborane (330 mg, 1.3 mmol, 1.3 equiv.); then appropriate iodonium salt **5** (0.7 mmol, 0.7 equiv.) and appropriate trifluoroacetamide **1** (1.0 mmol, 1.0 equiv.) were added and the reaction vessel was properly capped. Finally, the vessel was installed on the mill and subjected to milling at 30Hz for 90 minutes.

Comments:

34a-d: the masses given for the iodonium salts in the SI do not correspond to 0.7 mmol. We have used the latter in the E-factor calculations.

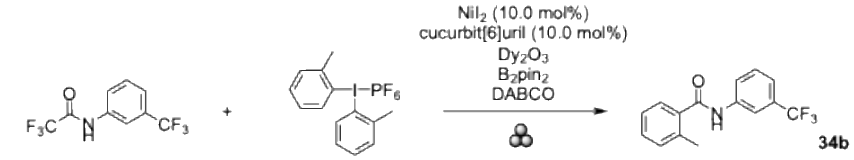
34c: The large-scale synthesis was performed using 10 mmol of starting trifluoroacetamide.



Molecular Weight: 239,20 Molecular Weight: 594,08 Molecular Weight: 331,29

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Trifluoroacetamide	1,00		239,20	1,000			0,239
Diaryliodonium Salt	0,70		594,08	0,700			0,416
NiI2	0,10		312,50	0,100			0,031
Cucurbit[6]uril	0,10		996,82	0,100			0,100
Dy2O3	1,00		373,00	1,000			0,373
Bis(pinacolato)diborane	1,30		253,94	1,300			0,330
DABCO	1,40		112,17	1,400			0,157
Product 34a		70%	331,29	0,700			**0,232**

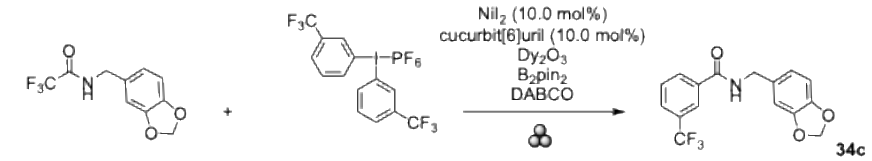
E-Factor:	**6,098**



Molecular Weight: 257,14 Molecular Weight: 454,13 Molecular Weight: 279,26

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Trifluoroacetamide	1,00		257,14	1,000			0,257
Diaryliodonium Salt	0,70		454,13	0,700			0,318
NiI2	0,10		312,50	0,100			0,031
Cucurbit[6]uril	0,10		996,82	0,100			0,100
Dy2O3	1,00		373,00	1,000			0,373
Bis(pinacolato)diborane	1,30		253,94	1,300			0,330
DABCO	1,40		112,17	1,400			0,157
Product 34b		57%	279,26	0,570			**0,159**

E-Factor:	**8,839**



Molecular Weight: 247,17 Molecular Weight: 562,08 Molecular Weight: 323,27

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Trifluoroacetamide	1,00		247,17	1,000			0,247
Diaryliodonium Salt	0,70		562,08	0,700			0,393
NiI2	0,10		312,50	0,100			0,031
Cucurbit[6]uril	0,10		996,82	0,100			0,100
Dy2O3	1,00		373,00	1,000			0,373
Bis(pinacolato)diborane	1,30		253,94	1,300			0,330
DABCO	1,40		112,17	1,400			0,157
Product 34c		81%	323,27	0,810			**0,262**

E-Factor:	**5,232**

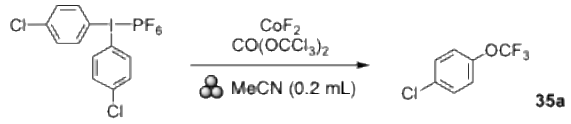
Large-scale reaction:

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Trifluoroacetamide	1,00		247,17	10,000			2,472
Diaryliodonium Salt	0,70		562,08	7,000			3,935
NiI2	0,10		312,50	1,000			0,313
Cucurbit[6]uril	0,10		996,82	1,000			0,997
Dy2O3	1,00		373,00	10,000			3,730
Bis(pinacolato)diborane	1,30		253,94	13,000			3,301
DABCO	1,40		112,17	14,000			1,570
Product 34c		74%	323,27	7,400			**2,392**

E-Factor:	**5,821**

Experimental: S. Mkrtchyan, V. B. Purohit, J. Zapletal, O. Shalimov, J. Nociarová, G. Addová, J. Filo, M. G. Garcia, E. Kupcová, B. Benická and V. O. Iaroshenko, *Cell Reports Physical Science*, 2024, **5**, 102118.

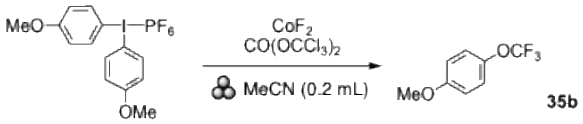
General procedure for the synthesis of trifluoromethyl ethers 3 starting from diaryliodonium salts 5.
Inside a glovebox, to 5 mL grinding vessel (made of stainless steel) equipped with two balls (made of stainless steel, diameter: 5 mm) was placed consequently appropriate diaryliodonium salt (1.0 mmol, 1 equiv.) dry CoF_2 (174 mg, 1.8 mmol, 1.8 equiv.), and triphosgene (119 mg, 0.4 mmol, 0.4 equiv.); finally, 0.2 mL acetonitrile was added and the reaction vessel was properly capped. Afterwards, the reaction vessel was installed on the mill and subjected to milling at 15Hz for 30 minutes then at 30Hz for 60 minutes.



Molecular Weight: 494,96 Molecular Weight: 196,55

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Diaryliodonium Salt	1,00		494,96	1,000			0,495
CoF2	1,80		96,93	1,800			0,174
Triphosgene	0,40		296,75	0,400			0,119
MeCN	0,00				0,200	0,786	0,157
Product 35a		68%	196,55	0,679			**0,133**

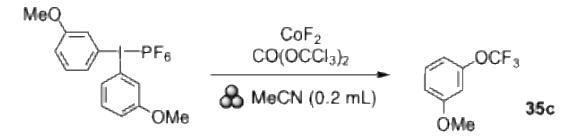
E-Factor:	**6,083**



Molecular Weight: 486,13 Molecular Weight: 192,14

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Diaryliodonium Salt	1,00		486,13	1,000			0,486
CoF2	1,80		96,93	1,800			0,174
Triphosgene	0,40		296,75	0,400			0,119
MeCN	0,00				0,200	0,786	0,157
Product 35b		64%	192,14	0,640			**0,123**

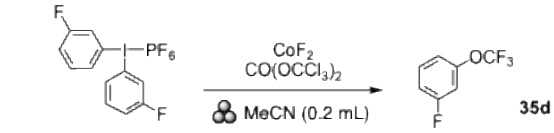
E-Factor:	**6,616**



Molecular Weight: 486,13 Molecular Weight: 192,14

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Diaryliodonium Salt	1,00		486,13	1,000			0,486
CoF2	1,80		96,93	1,800			0,174
Triphosgene	0,40		296,75	0,400			0,119
MeCN	0,00				0,200	0,786	0,157
Product 35c		62%	192,14	0,620			**0,119**

E-Factor:	**6,861**



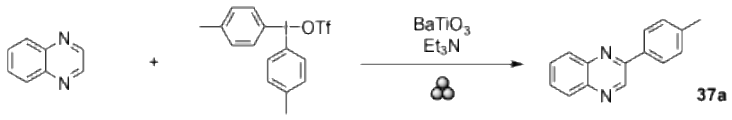
Molecular Weight: 462,06 Molecular Weight: 180,10

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Diaryliodonium Salt	1,00		462,06	1,000			0,462
CoF2	1,80		96,93	1,800			0,174
Triphosgene	0,40		296,75	0,400			0,119
MeCN	0,00				0,200	0,786	0,157
Product 35d		62%	180,10	0,620			**0,112**

E-Factor:	**7,171**

Experimental: J. Jiang, S. Song, J. Guo, J. Zhou and J. Li, *Tetrahedron Lett*., 2022, **98**, 153820.

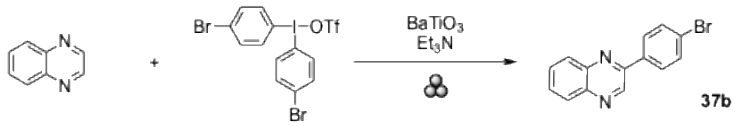
General procedure for the synthesis of 2-(4-methylphenyl)quinoxaline (3aa): Quinoxaline **1a** (0.065 g, 0.5 mmol), bis(4-methylphenyl)iodonium triflate **2a** (0.344 g, 0.75 mmol), Et_3N (0.152 g, 1.5 mmol), and $BaTiO_3$ (<4 μm) (0.699 g, 3.0 mmol) were mixed with stainless-steel balls (10 mm × 8) in a 20 mL stainless-steel jar under ball milling at 35 Hz for 2 hours.



Molecular Weight: 130,15 Molecular Weight: 458,23 Molecular Weight: 220,28

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Quinoxaline	1,00		130,15	0,500			0,065
Diaryliodonium Salt	1,50		458,23	0,750			0,344
BaTiO3	6,00		233,19	3,000			0,700
Et3N	3,00		101,19	1,500			0,152
Product 37a		78%	220,28	0,390			**0,086**

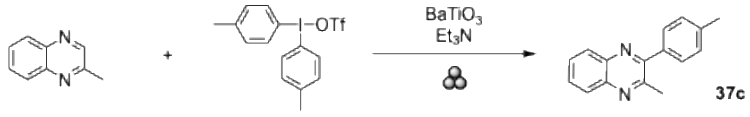
E-Factor:	**13,668**



Molecular Weight: 130,15 Molecular Weight: 587,97 Molecular Weight: 285,14

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Quinoxaline	1,00		130,15	0,500			0,065
Diaryliodonium Salt	1,50		587,97	0,750			0,441
BaTiO3	6,00		233,19	3,000			0,700
Et3N	3,00		101,19	1,500			0,152
Product 37b		76%	285,14	0,380			**0,108**

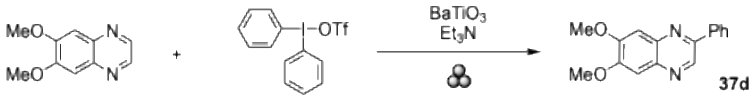
E-Factor:	**11,528**



Molecular Weight: 144,18 Molecular Weight: 458,23 Molecular Weight: 234,30

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
2-Methylquinoxaline	1,00		144,18	0,500			0,072
Diaryliodonium Salt	1,50		458,23	0,750			0,344
BaTiO3	6,00		233,19	3,000			0,700
Et3N	3,00		101,19	1,500			0,152
Product 37c		68%	234,30	0,340			**0,080**

E-Factor:	**14,906**



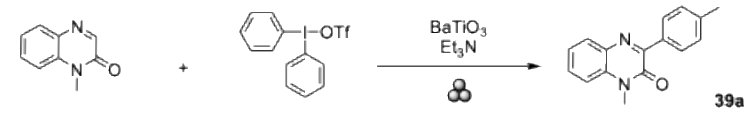
Molecular Weight: 190,20 Molecular Weight: 430,18 Molecular Weight: 266,30

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Quinoxaline Substrate	1,00		190,20	0,500			0,095
Diaryliodonium Salt	1,50		430,18	0,750			0,323
BaTiO3	6,00		233,19	3,000			0,700
Et3N	3,00		101,19	1,500			0,152
Product 37d		59%	266,30	0,295			**0,079**

E-Factor:	**15,155**

Experimental: J. Jiang, S. Song, J. Guo, J. Zhou and J. Li, *Tetrahedron Lett*., 2022, **98**, 153820.

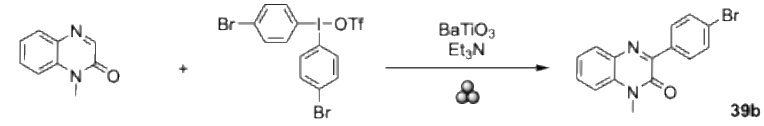
General procedure for the synthesis of 1-methyl-3-phenylquinoxalin-2(1*H*)-one(5aa): 1-Methylquinoxalinone **4a** (0.080 g, 0.5 mmol), diphenyliodonium triflate **2b** (0.322 g, 0.75 mmol), Et_3N (0.152 g, 1.5 mmol), and $BaTiO_3$ (<4 μm) (0.699 g, 3.0 mmol) were mixed with stainless-steel balls (10 mm × 8) in a 20 mL stainless-steel jar under ball milling at 35 Hz for 2 hours.



Molecular Weight: 160,18 Molecular Weight: 430,18 Molecular Weight: 250,30

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Quinoxalinone Substrate	1,00		160,18	0,500			0,080
Diaryliodonium Salt	1,50		430,18	0,750			0,323
BaTiO3	6,00		233,19	3,000			0,700
Et3N	3,00		101,19	1,500			0,152
Product 39a		71%	250,30	0,355			**0,089**

E-Factor:	**13,114**



Molecular Weight: 160,18 Molecular Weight: 587,97 Molecular Weight: 315,17

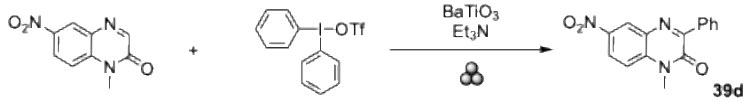
Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Quinoxalinone Substrate	1,00		160,18	0,500			0,080
Diaryliodonium Salt	1,50		587,97	0,750			0,441
BaTiO3	6,00		233,19	3,000			0,700
Et3N	3,00		101,19	1,500			0,152
Product 39b		69%	315,17	0,345			**0,109**

E-Factor:	**11,622**

Molecular Weight: 190,20 Molecular Weight: 430,18 Molecular Weight: 266,30

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Quinoxalinone Substrate	1,00		190,20	0,500			0,095
Diaryliodonium Salt	1,50		430,18	0,750			0,323
$BaTiO_3$	6,00		233,19	3,000			0,700
Et_3N	3,00		101,19	1,500			0,152
Product 39c		62%	266,30	0,310			**0,083**

E-Factor:	**14,373**



Molecular Weight: 205,17 Molecular Weight: 430,18 Molecular Weight: 281,27

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Quinoxalinone Substrate	1,00		205,17	0,500			0,103
Diaryliodonium Salt	1,50		430,18	0,750			0,323
$BaTiO_3$	6,00		233,19	3,000			0,700
Et_3N	3,00		101,19	1,500			0,152
Product 39d		26%	281,27	0,130			**0,037**

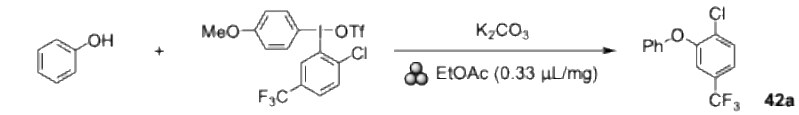
E-Factor:	**33,912**

Experimental: S. Doobary, M. M. de Vries Ibáñez and B. Olofsson, *Green Chem*., 2024, **26**, 11518.

General procedure 1: *O*-arylation: Potassium carbonate (41.5 mg, 0.30 mmol, 1 equiv), the nucleophile (0.30 mmol), one 5 mm stainless steel ball and LAG (ethyl acetate or MeCN, 0.33 µL/mg) were added to a 1.5 mL stainless steel ball milling vessel. The vessel was closed and the mixture was milled for 15 minutes at 35 Hz and then diaryliodonium salt **1** (0.30 mmol, 1 equiv) was added. This mixture was milled for 30 minutes at 35 Hz.

42b. Large scale reaction: Potassium carbonate (414.6 mg, 3.00 mmol, 1 equiv), eugenol (0.467 mL, 3.00 mmol, 1 equiv), one 10 mm stainless steel ball and LAG (0.45 mL) were added to a 5 mL stainless steel ball milling vessel. The vessel was closed and the mixture was milled for 15 minutes at 35 Hz and then diaryliodonium salt **1a** (1.455 g, 3.00 mmol, 1 equiv) was added. This mixture was milled for 30 minutes at 35 Hz.

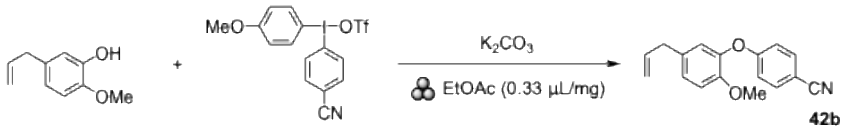
Comment:
42c & d: Product masses do not match reported yields. We have used the latter in the E-factor calculations.



Molecular Weight: 94,11 Molecular Weight: 562,65 Molecular Weight: 272,65

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Phenol	1,00		94,11	0,300			0,028
Diaryliodonium Salt	1,00		562,65	0,300			0,169
K_2CO_3	1,00		138,21	0,300			0,041
EtOAc					0,079	0,902	0,071
Product 42a		80%	272,65	0,240			**0,065**

E-Factor:	**3,730**



Molecular Weight: 164,20 Molecular Weight: 485,22 Molecular Weight: 265,31

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Eugenol	1,00		164,20	0,300			0,049
Diaryliodonium Salt	1,00		485,22	0,300			0,146
K_2CO_3	1,00		138,21	0,300			0,041
EtOAc					0,078	0,902	0,070
Product 42b		87%	265,31	0,261			**0,069**

E-Factor:	**3,428**

Large-scale reaction:

Molecular Weight: 164,20 Molecular Weight: 485,22 Molecular Weight: 265,31

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Eugenol	1,00		164,20	3,000			0,493
Diaryliodonium Salt	1,00		485,22	3,000			1,456
K_2CO_3	1,00		138,21	3,000			0,415
EtOAc					0,450	0,902	0,406
Product 42b		89%	265,31	2,670			**0,708**

E-Factor:	**2,909**

Molecular Weight: 124,14 Molecular Weight: 461,19 Molecular Weight: 201,23

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Methoxyphenol	1,00		124,14	0,300			0,037
Diaryliodonium Salt	1,00		461,19	0,300			0,138
K_2CO_3	1,00		138,21	0,300			0,041
EtOAc					0,072	0,902	0,065
Product 42c		79%	201,23	0,237			**0,048**

E-Factor:	**4,906**

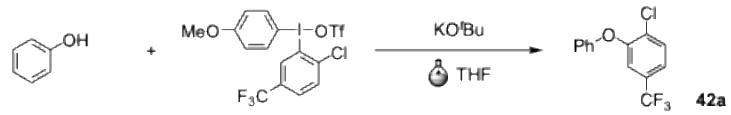
Molecular Weight: 108,14 Molecular Weight: 505,20 Molecular Weight: 229,24

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Benzyl Alcohol	1,00		108,14	0,300			0,032
Diaryliodonium Salt	1,00		505,20	0,300			0,152
K_2CO_3	1,00		138,21	0,300			0,041
EtOAc					0,074	0,902	0,067
Product 42d		80%	229,24	0,240			**0,055**

E-Factor:	**4,318**

Experimental: S. Doobary, M. M. de Vries Ibáñez and B. Olofsson, *Green Chem*., 2024, **26**, 11518.

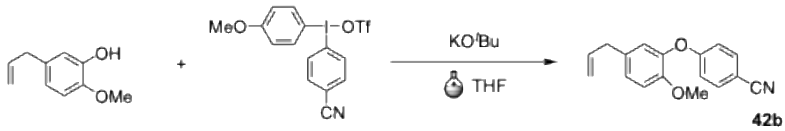
***O*-arylation (in solution) using KO*t*Bu as base**: To a solution of KO*t*Bu (37.0 mg, 0.33 mmol, 1.1 equiv) in dry THF (1.5 mL) under nitrogen atmosphere, was added the alcohol (0.30 mmol, 1 equiv). This mixture was stirred for 5 min at room temperature. Salt **1** (0.30 mmol) was added at 0 °C, and the solution was stirred for 1 h at 40 °C.



Molecular Weight: 94,11 Molecular Weight: 562,65 Molecular Weight: 272,65

	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Phenol	1,00		94,11	0,300			0,028
Diaryliodonium Salt	1,00		562,65	0,300			0,169
KO*t*Bu	1,10		112,21	0,330			0,037
THF					1,500	0,889	1,334
Product 42a		79%	272,65	0,237			**0,065**

E-Factor:	**23,259**



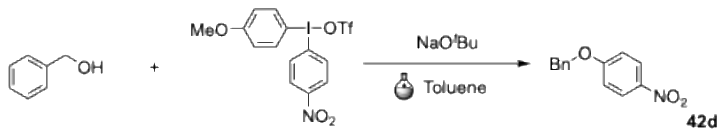
Molecular Weight: 164,20 Molecular Weight: 485,22 Molecular Weight: 265,31

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Eugenol	1,00		164,20	0,300			0,049
Diaryliodonium Salt	1,00		485,22	0,300			0,146
KO*t*Bu	1,10		112,21	0,330			0,037
THF					1,500	0,889	1,334
Product 42b		87%	265,31	0,261			**0,069**

E-Factor:	**21,606**

Experimental: R. Ghosh, E. Lindstedt, N. Jalalian and B. Olofsson, *ChemistryOpen*, 2014, **3**, 54–57.

Synthesis of alkyl aryl ethers 2: Alcohol (0.5 mmol) was added dropwise at 0 °C under argon atmosphere to a solution of *t*BuONa (0.6 mmol) in dry toluene (2.5 mL), and the solution was stirred for 15 min at RT. Diaryliodonium salt 1 (0.6 mmol) was added at 0 °C, and the solution was stirred for 0.5–1.5 h at RT.



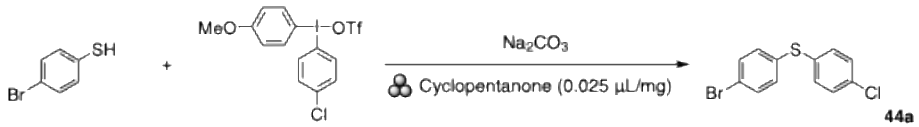
Molecular Weight: 108,14 Molecular Weight: 505,20 Molecular Weight: 229,24

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Benzyl Alcohol	1,00		108,14	0,500			0,054
Diaryliodonium Salt	1,20		505,20	0,600			0,303
NaO*t*Bu	1,20		96,10	0,600			0,058
Toluene					2,500	0,865	2,163
Product 42d		96%	229,24	0,480			**0,110**

E-Factor:	**22,423**

Experimental: S. Doobary, M. M. de Vries Ibáñez and B. Olofsson, *Green Chem*., 2024, **26**, 11518.

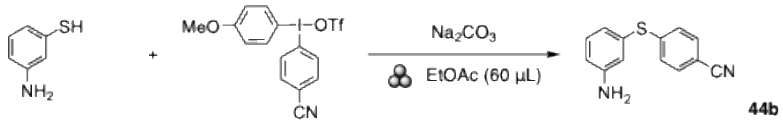
General procedure 2: *S*-arylation. Sodium carbonate (31.8 mg, 0.30 mmol, 1 equiv), nucleophile (0.30 mmol), diaryliodonium salt **1** (0.30 mmol, 1 equiv), cyclopentanone (0.025 µL/mg) and one 5 mm stainless steel ball were added to a 1.5 mL stainless steel ball milling vessel. The vessel was closed and the mixture was milled for 30 minutes at 30 Hz.
Comments:
44b. Ethyl acetate (60 µL) was used as LAG.
44c. Product mass does not match reported yield. We have used the latter in the E-factor calculation.



Molecular Weight: 189,07 Molecular Weight: 494,65 Molecular Weight: 299,61

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
4-Bromothiophenol	1,00		189,07	0,300			0,057
Diaryliodonium Salt	1,00		494,65	0,300			0,148
Na_2CO_3	1,00		105,99	0,300			0,032
Cyclopentanone					0,006	0,951	0,006
Product 44a		84%	299,61	0,252			**0,076**

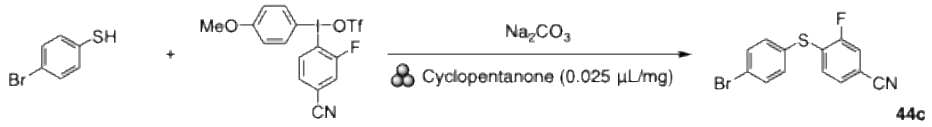
E-Factor:	**2,212**



Molecular Weight: 125,19 Molecular Weight: 485,22 Molecular Weight: 226,30

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
3-Aminothiophenol	1,00		125,19	0,300			0,038
Diaryliodonium Salt	1,00		485,22	0,300			0,146
Na_2CO_3	1,00		105,99	0,300			0,032
EtOAc					0,060	0,902	0,054
Product 44b		67%	226,30	0,201			**0,045**

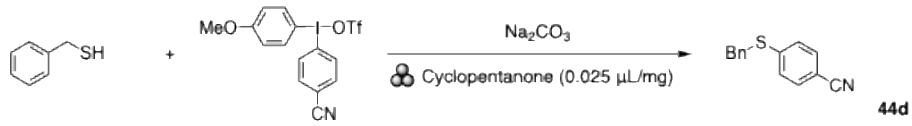
E-Factor:	**4,915**



Molecular Weight: 189,07 Molecular Weight: 503,21 Molecular Weight: 308,17

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
4-Bromothiophenol	1,00		189,07	0,300			0,057
Diaryliodonium Salt	1,00		503,21	0,300			0,151
Na_2CO_3	1,00		105,99	0,300			0,032
Cyclopentanone					0,006	0,951	0,006
Product 44c		92%	308,17	0,276			**0,085**

E-Factor:	**1,883**



44d

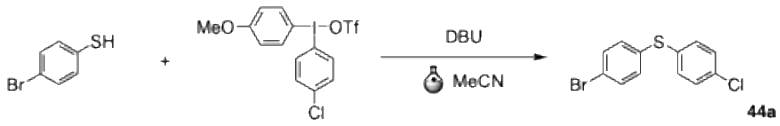
Molecular Weight: 124,20 Molecular Weight: 485,22 Molecular Weight: 225,31

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
4-Bromothiophenol	1,00		124,20	0,300			0,037
Diaryliodonium Salt	1,00		485,22	0,300			0,146
Na_2CO_3	1,00		105,99	0,300			0,032
Cyclopentanone					0,005	0,951	0,005
Product 44d		49%	225,31	0,147			**0,033**

E-Factor:	**5,634**

Experimental: S. Doobary, M. M. de Vries Ibáñez and B. Olofsson, *Green Chem*., 2024, **26**, 11518.

Bench marking studies BM3: *S*-arylation: To a solution of thiol (0.3 mmol) and diaryliodonium salt **1** (0.3 mmol, 1 equiv) was added MeCN (3 mL) and DBU (43 μL, 0.33 mmol, 1.1 equiv). This mixture was then stirred at 80 °C for 1.5 h.

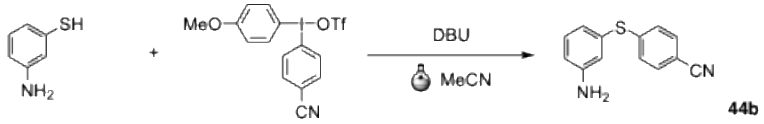


44a

Molecular Weight: 189,07 Molecular Weight: 494,65 Molecular Weight: 299,61

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
4-Bromothiophenol	1,00		189,07	0,300			0,057
Diaryliodonium Salt	1,00		494,65	0,300			0,148
DBU	1,10		152,24	0,330			0,050
MeCN					3,000	0,786	2,358
Product 44a		71%	299,61	0,213			**0,064**

E-Factor:	**39,951**

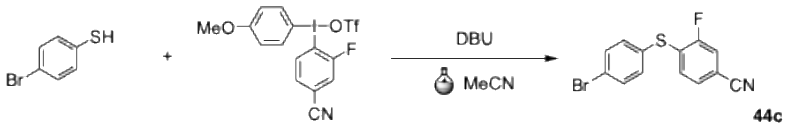


44b

Molecular Weight: 125,19 Molecular Weight: 485,22 Molecular Weight: 226,30

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
3-Aminothiophenol	1,00		125,19	0,300			0,038
Diaryliodonium Salt	1,00		485,22	0,300			0,146
DBU	1,10		152,24	0,330			0,050
MeCN					3,000	0,786	2,358
Product 44b		50%	226,30	0,150			**0,034**

E-Factor:	**75,340**



44c

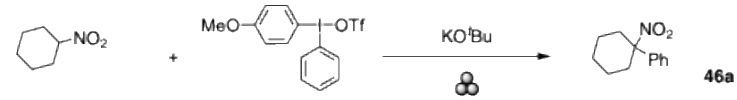
Molecular Weight: 189,07 Molecular Weight: 503,21 Molecular Weight: 308,17

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
3-Aminothiophenol	1,00		189,07	0,300			0,057
Diaryliodonium Salt	1,00		503,21	0,300			0,151
DBU	1,10		152,24	0,330			0,050
MeCN					3,000	0,786	2,358
Product 44c		71%	308,17	0,213			**0,066**

E-Factor:	**38,852**

Experimental: S. Doobary, M. M. de Vries Ibáñez and B. Olofsson, *Green Chem*., 2024, **26**, 11518.

General procedure 3: *C*-arylation. Potassium *tert*-butoxide (43.0 mg, 0.36 mmol, 1.2 equiv), nucleophile (0.30 mmol), and one 5 mm stainless steel ball were added to a 1.5 mL stainless steel ball milling vessel. The vessel was closed and the mixture was milled for 30 minutes at 30 Hz. Then diaryliodonium salt **1** (0.30 mmol, 1 equiv) was added. This mixture was milled for 120 minutes.

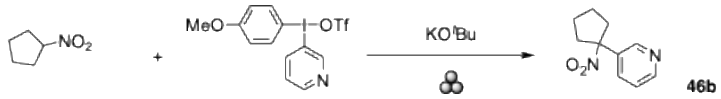


46a

Molecular Weight: 129,16 Molecular Weight: 460,21 Molecular Weight: 205,26

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Nitrocyclohexane	1,00		129,16	0,300			0,039
Diaryliodonium Salt	1,00		460,21	0,300			0,138
KO*t*Bu	1,20		112,21	0,360			0,040
Product 46a		92%	205,26	0,276			**0,057**

E-Factor:	**2,834**

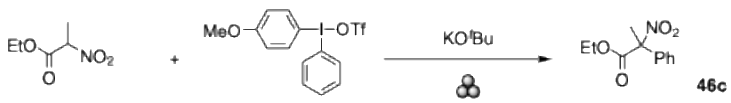


46b

Molecular Weight: 115,13 Molecular Weight: 461,19 Molecular Weight: 192,22

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Nitrocyclopentane	1,00		115,13	0,300			0,035
Diaryliodonium Salt	1,00		461,19	0,300			0,138
KO*t*Bu	1,20		112,21	0,360			0,040
Product 46b		92%	192,22	0,276			**0,053**

E-Factor:	**3,020**

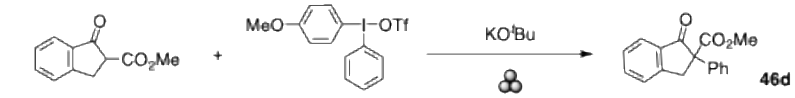


46c

Molecular Weight: 147,13 Molecular Weight: 460,21 Molecular Weight: 223,23

	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Ethyl 2-Nitropropionate	1,00		147,13	0,300			0,044
Diaryliodonium Salt	1,00		460,21	0,300			0,138
KO*t*Bu	1,20		112,21	0,360			0,040
Product 46c		39%	223,23	0,117			**0,026**

E-Factor:	**7,523**



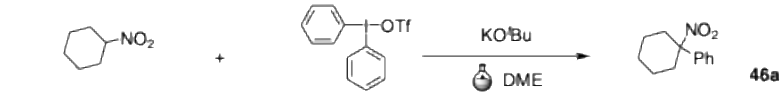
Molecular Weight: 190,20 Molecular Weight: 460,21 Molecular Weight: 266,30

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
2-Carbomethoxy-1-indanone	1,00		190,20	0,300			0,057
Diaryliodonium Salt	1,00		460,21	0,300			0,138
KO*t*Bu	1,20		112,21	0,360			0,040
Product 46d		78%	266,30	0,234			**0,062**

E-Factor:	**2,780**

Experimental: C. Dey, E. Lindstedt and B. Olofsson, *Org. Lett*., 2015, **17**, 4554.

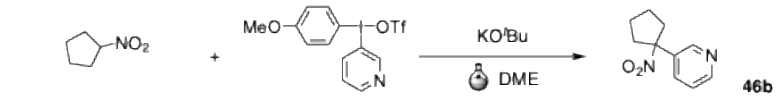
General Procedure I (C-Arylation of Nitroalkanes): Nitroalkane (0.40 mmol, 1.0 equiv), and KO*t*Bu (0.48 mmol, 1.2 equiv) were added to an oven-dried 10 mL microwave vial. The vial was capped with a rubber septum. Anhydrous DME (2 mL) was introduced to the vial by syringe at 0 °C and the solution was stirred at room temperature (RT) for 10 min. Diaryliodonium salt **2** (0.40 mmol, 1.0 equiv) was then added to the reaction mixture at ambient temperature under open air. The vial was capped again with a rubber septum and anhydrous DME (1 mL) was added at RT. The reaction mixture was stirred at RT for 16 h.



Molecular Weight: 129,16 Molecular Weight: 430,18 Molecular Weight: 205,26

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Nitrocyclohexane	1,00		129,16	0,400			0,052
Diaryliodonium Salt	1,00		430,18	0,400			0,172
KO*t*Bu	1,20		112,21	0,480			0,054
DME					3,000	0,867	2,601
Product 46a		89%	205,26	0,356			**0,073**

E-Factor:	**38,394**



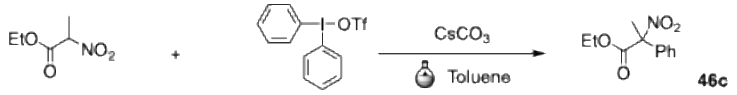
Molecular Weight: 115,13 Molecular Weight: 461,19 Molecular Weight: 192,22

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Nitrocyclopentane	1,00		115,13	0,400			0,046
Diaryliodonium Salt	1,00		461,19	0,400			0,184
KO*t*Bu	1,20		112,21	0,480			0,054
DME					3,000	0,867	2,601
Product 46b		80%	192,22	0,320			**0,062**

E-Factor:	**45,909**

Experimental: C. Dey, E. Lindstedt and B. Olofsson, *Org. Lett*., 2015, **17**, 4554.

General Procedure II (α−Arylation of Nitroesters). The ethyl-2-nitropropanoate **5** (0.40 mmol, 1.0 equiv), and Cs_2CO_3 (0.48 mmol, 1.2 equiv) were added to an oven-dry 10 mL microwave vial. The vial was capped with a rubber septum. Anhydrous PhMe (2 mL) was introduced to the vial by syringe at 0 °C and the solution was stirred at RT for 10 min. Diaryliodonium salt **2** (0.40 mmol, 1.0 equiv) was then added to the reaction mixture at RT under open air. The vial was capped again with a rubber septum and anhydrous PhMe (1 mL) was added at RT. The reaction mixture was stirred at RT for 1 h followed by 6 h at 110 °C (pre-heated oil bath).
Comment:
46c: Carried out at 0.5 mmol scale.



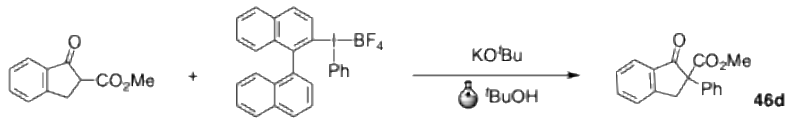
Molecular Weight: 147,13 Molecular Weight: 430,18 Molecular Weight: 223,23

	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Ethyl 2-Nitropropionate	1,00		147,13	0,500			0,074
Diaryliodonium Salt	1,00		430,18	0,500			0,215
$CsCO_3$	1,20		192,91	0,600			0,116
Toluene					3,750	0,865	3,244
Product 46c		78%	223,23	0,390			**0,087**

E-Factor:	**40,904**

Experimental: M. Ochiai, Y. Kitagawa, N. Takayama, Y. Takaoka and M. Shiro, *J. Am. Chem. Soc*., 1999, **121**, 9233.

Asymmetric a-Phenylation of 2-(Carbomethoxy)-1-indanone. To a stirred solution of freshly sublimed potassium tert-butoxide (25 mg, 0.22 mmol) in tert-butyl alcohol (4 mL) was added 2-(carbomethoxy)-1-indanone (7a) (42 mg, 0.22 mmol) under nitrogen at room temperature, and the mixture was stirred for 1 h. Binaphthylyl(phenyl)iodonium salt (S)-2 (109 mg, 0.20 mmol) was added to this mixture at room temperature, and the resulting pale yellow suspension was stirred for 20 h.



Molecular Weight: 190,20 Molecular Weight: 544,14 Molecular Weight: 266,30

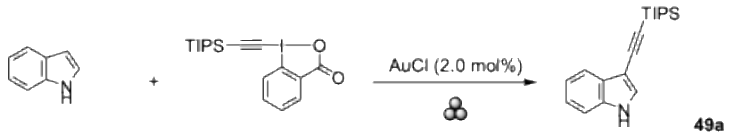
Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Diaryliodonium Salt	1,00		544,14	0,200			0,109
2-Carbomethoxy-1-indanone	1,10		190,20	0,220			0,042
KO*t*Bu	1,10		112,21	0,220			0,025
*t*BuOH					4,000	0,775	3,100
Product 46d		65%	266,3	0,130			**0,035**

E-Factor:	**93,612**

6.3.2 Alkynylations

Experimental: G. N. Hermann, M. T. Unruh, S.-H. Jung, M. Krings and C. Bolm, *Angew. Chem. Int. Ed*., 2018, **57**, 10723.

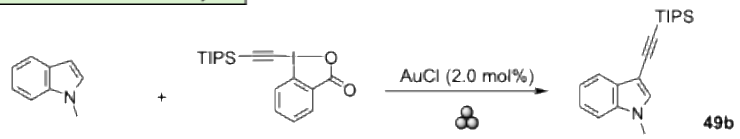
General procedure 2: Mechanochemical gold-catalyzed C–H alkynylation. The indole (**1**, 0.6 mmol, 1.0 equiv.), the hypervalent alkynyl iodine reagent (**2**, 1.2 equiv.) and AuCl (2–3 mol %) were transferred to a ball milling vessel (stainless steel, 10 mL) loaded with one grinding ball (stainless steel, diameter: 1.0 cm). The ball milling vessel was placed in the ball mill (99–198 min at 30 Hz).



Molecular Weight: 117,15 Molecular Weight: 428,39 Molecular Weight: 297,52

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Indole	1,00		117,15	0,600			0,070
TIPS-EBX	1,20		428,39	0,720			0,308
AuCl	0,02		232,42	0,012			0,003
Product 49a		75%	297,52	0,450			**0,134**

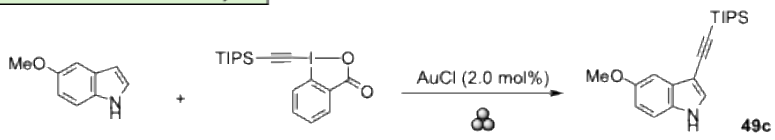
E-Factor:	**1,850**



Molecular Weight: 131,18 Molecular Weight: 428,39 Molecular Weight: 311,54

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Indole	1,00		131,18	0,600			0,079
TIPS-EBX	1,20		428,39	0,720			0,308
AuCl	0,02		232,42	0,012			0,003
Product 49b		82%	311,54	0,492			**0,153**

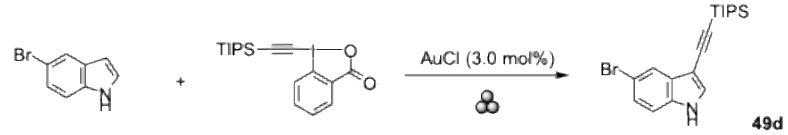
E-Factor:	**1,544**



Molecular Weight: 147,18 Molecular Weight: 428,39 Molecular Weight: 327,54

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Indole	1,00		147,18	0,600			0,088
TIPS-EBX	1,20		428,39	0,720			0,308
AuCl	0,02		232,42	0,012			0,003
Product 49c		59%	327,54	0,354			**0,116**

E-Factor:	**2,446**



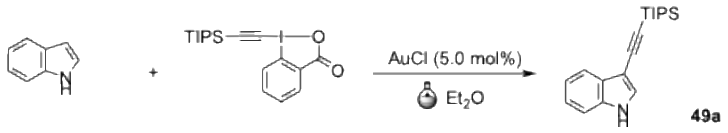
Molecular Weight: 196,05 Molecular Weight: 428,39 Molecular Weight: 376,41

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Indole	1,00		196,05	0,600			0,118
TIPS-EBX	1,20		428,39	0,720			0,308
AuCl	0,03		232,42	0,018			0,004
Product 49d		60%	376,41	0,357			**0,134**

E-Factor:	**2,202**

Experimental: J. P. Brand, J. Charpentier and J. Waser, *Angew. Chem. Int. Ed*., 2009, **48**, 9346

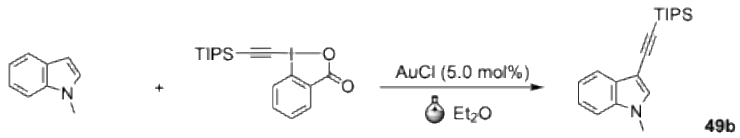
General procedure: 1d (206 mg, 0.480 mmol, 1.2 equiv) was added to a stirring solution of AuCl (4.6 mg, 0.020 mmol, 0.05 equiv) and the corresponding indole/pyrrole (0.400 mmol, 1.0 equiv) in Et_2O (8 mL) under air. The reaction was sealed and stirred at room temperature for 12-15 hrs.



Molecular Weight: 117,15 Molecular Weight: 428,39 Molecular Weight: 297,52

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Indole	1,00		117,15	0,400			0,047
TIPS-EBX	1,20		428,39	0,480			0,206
AuCl	0,05		232,42	0,020			0,005
Et2O					8,000	0,706	5,648
Product 49a		86%	297,52	0,344			**0,102**

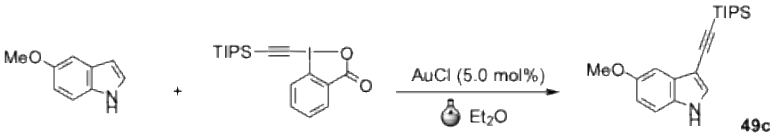
E-Factor:	**56,697**



Molecular Weight: 131,18 Molecular Weight: 428,39 Molecular Weight: 311,54

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Indole	1,00		131,18	0,400			0,052
TIPS-EBX	1,20		428,39	0,480			0,206
AuCl	0,05		232,42	0,020			0,005
Et2O					8,000	0,706	5,648
Product 49b		83%	311,54	0,332			**0,103**

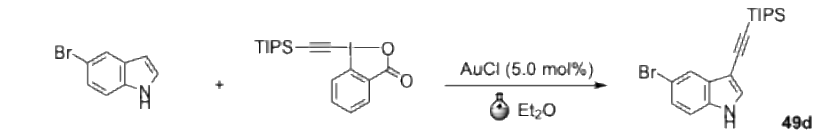
E-Factor:	**56,147**



Molecular Weight: 147,18 Molecular Weight: 428,39 Molecular Weight: 327,54

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Indole	1,00		147,18	0,400			0,059
TIPS-EBX	1,20		428,39	0,480			0,206
AuCl	0,05		232,42	0,020			0,005
Et2O					8,000	0,706	5,648
Product 49c		80%	327,54	0,320			**0,105**

E-Factor:	**55,454**



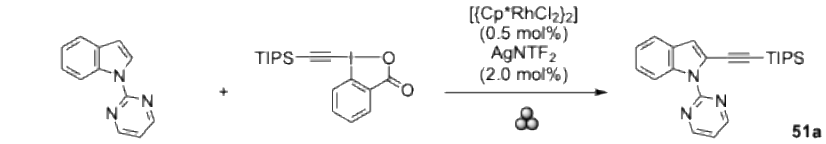
Molecular Weight: 196,05 Molecular Weight: 428,39 Molecular Weight: 376,41

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Indole	1,00		196,05	0,400			0,078
TIPS-EBX	1,20		428,39	0,480			0,206
AuCl	0,05		232,42	0,020			0,005
Et2O					8,000	0,706	5,648
Product 49d		93%	376,41	0,372			**0,140**

E-Factor:	**41,398**

Experimental: G. N. Hermann, M. T. Unruh, S.-H. Jung, M. Krings and C. Bolm, *Angew. Chem. Int. Ed*., 2018, **57**, 10723.

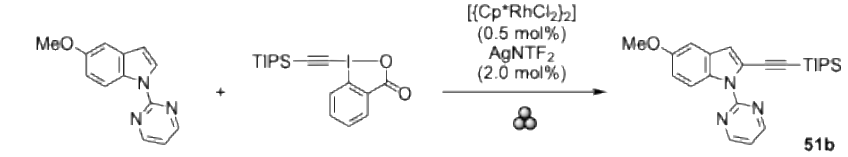
General procedure 1: Mechanochemical rhodium-catalyzed C–H alkynylation. The indole (**1**, 0.6 mmol, 1.0 equiv.), the hypervalent alkynyl iodine reagent (**2**, 1.1 equiv.), [(Cp*$RhCl_2$)$_2$] (0.5 mol %) and $AgNTf_2$ (2 mol %) were transferred to a ball milling vessel (stainless steel, 10 mL) loaded with one grinding ball (stainless steel, diameter: 1.0 cm). The ball milling vessel was placed in the ball mill (60 min by 30 Hz).
Comment:
51a: The yield is given as 98% in the article, and as 99% is the SI. The latter corresponds better to the given product mass and was thus used in the E-factor calculation.



Molecular Weight: 195,23 Molecular Weight: 428,39 Molecular Weight: 375,59

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Indole	1,00		195,23	0,600			0,117
TIPS-EBX	1,10		428,39	0,660			0,283
[{Cp*RhCl2}2]	0,005		618,08	0,003			0,002
AgNTf2	0,02		388,01	0,012			0,005
Product 51a		99%	375,59	0,594			**0,223**

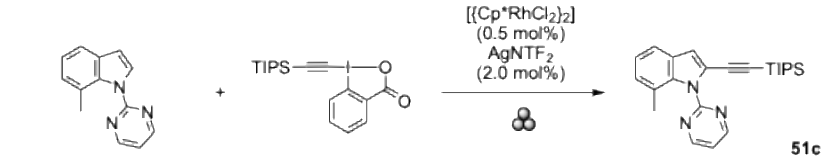
E-Factor:	**0,822**



Molecular Weight: 225,25 Molecular Weight: 428,39 Molecular Weight: 405,62

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Indole	1,00		225,25	0,600			0,135
TIPS-EBX	1,10		428,39	0,660			0,283
[{Cp*RhCl2}2]	0,005		618,08	0,003			0,002
AgNTf2	0,02		388,01	0,012			0,005
Product 51b		99%	405,62	0,596			**0,242**

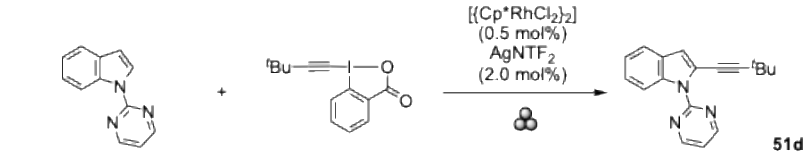
E-Factor:	**0,756**



Molecular Weight: 209,25 Molecular Weight: 428,39 Molecular Weight: 389,62

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Indole	1,00		209,25	0,600			0,126
TIPS-EBX	1,10		428,39	0,660			0,283
[{Cp*RhCl2}2]	0,005		618,08	0,003			0,002
AgNTf2	0,02		388,01	0,012			0,005
Product 51c		92%	389,62	0,553			**0,216**

E-Factor:	**0,924**



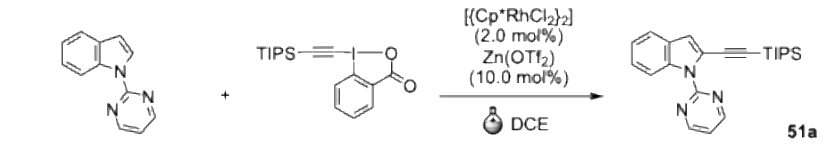
Molecular Weight: 195,23 Molecular Weight: 328,15 Molecular Weight: 275,36

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Indole	1,00		195,23	0,600			0,117
TIPS-EBX	1,10		328,15	0,660			0,217
[{Cp*RhCl2}2]	0,005		618,08	0,003			0,002
AgNTf2	0,02		388,01	0,012			0,005
Product 51d		93%	275,36	0,558			**0,154**

E-Factor:	**1,214**

Experimental: F. Xie, Z. Qi, S. Yu and X. Li, J. Am. *Chem. Soc.*, 2014, **136**, 4780

Representative synthetic procedure A. 2-Phenylpyridine derivative (1.0 eq, 0.2 mmol), alkyne **2** (0.22 mmol), [Cp*$RhCl_2$]2 (2 mol%), $Zn(OTf)_2$ (0.02 mmol, 10 mol%), and dichloroethane (2 mL) were charged into a pressure tube under argon. The reaction mixture was stirred at 25 °C for 16 h.



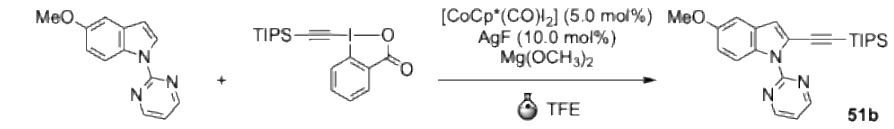
Molecular Weight: 195,23 Molecular Weight: 428,39 Molecular Weight: 375,59

	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Indole	1,00		195,23	0,200			0,039
TIPS-EBX	1,10		428,39	0,220			0,094
[{Cp*RhCl2}2]	0,02		618,08	0,004			0,002
Zn(OTf)2	0,10		363,53	0,020			0,007
DCE					2,000	1,256	2,512
Product 51a		92%	375,59	0,184			**0,069**

E-Factor:	**37,418**

Experimental: Z.-Z. Zhang, B. Liu, C.-Y. Wang and B.-F. Shi, *Org. Lett*., 2015, **17**, 4094

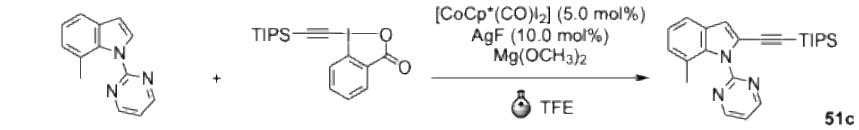
General Procedure for the Alkynylation
1-(pyrimidin-2-yl)-1H-indole **1** (0.1 mmol, 1.0 equiv), alkyne **2** (0.12 mmol, 1.2 equiv), [CoCp*(CO)I_2] (5 mol %), AgF (0.01 mmol, 10 mol %), $Mg(OCH_3)_2$ (0.3 mmol, 3 equiv) and 2,2,2-trifluoroethanol (1 mL) were charged into a pressure tube under argon. The reaction mixture was stirred for 24 h at 110 °C under N_2 followed by cooling.



Molecular Weight: 225,25 Molecular Weight: 428,39 Molecular Weight: 405,62

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Indole	1,00		225,25	0,100			0,023
TIPS-EBX	1,20		428,39	0,120			0,051
[CoCp*(CO)I2]	0,05		475,99	0,005			0,002
AgF	0,10		126,87	0,010			0,001
Mg(OCH3)2	3,00		86,37	0,300			0,026
TFE					1,000	1,373	1,373
Product 51b		39%	405,62	0,039			**0,016**

E-Factor:	**92,336**



Molecular Weight: 209,25 Molecular Weight: 428,39 Molecular Weight: 389,62

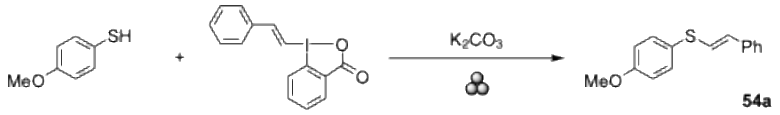
Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Indole	1,00		209,25	0,100			0,021
TIPS-EBX	1,20		428,39	0,120			0,051
[CoCp*(CO)I2]	0,05		475,99	0,005			0,002
AgF	0,10		126,87	0,010			0,001
Mg(OCH3)2	3,00		86,37	0,300			0,026
TFE					1,000	1,373	1,373
Product 51c		57%	389,62	0,057			**0,022**

E-Factor:	**65,412**

6.3.3 Synthesis of alkenes

Experimental: S. Doobary, M. M. de Vries Ibáñez and B. Olofsson, *Green Chem*., 2024, **26**, 11518.

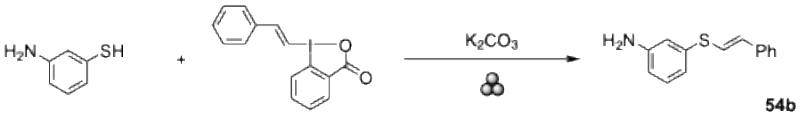
General procedure 4: *S*-vinylation
Thiol (0.30 mmol) and potassium carbonate (41.5 mg, 0.30 mmol, 1.0 equiv), and one 5 mm stainless steel ball were added to a 1.5 mL stainless steel ball milling vessel. The vessel was closed and the mixture was milled for 30 minutes at 30 Hz. Then VBX reagent **6** (0.30 mmol, 1.0 equiv) was added. This mixture was milled for 90 minutes at 30 Hz.
Comment:
54c: 0.20 mmol scale, potassium *tert*-butoxide instead of potassium carbonate and 50 µL THF as LAG.



Molecular Weight: 140,20 Molecular Weight: 350,16 Molecular Weight: 242,34

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
4-Methoxythiophenol	1,00		140,20	0,300			0,042
VBX	1,00		350,16	0,300			0,105
K2CO3	1,00		138,21	0,300			0,042
Product 54a		73%	242,34	0,219			**0,053**

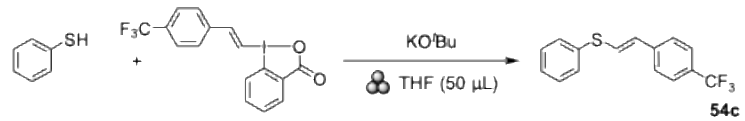
E-Factor:	**2,563**



Molecular Weight: 125,19 Molecular Weight: 350,16 Molecular Weight: 227,33

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
3-Aminothiophenol	1,00		125,19	0,300			0,038
VBX	1,00		350,16	0,300			0,105
K2CO3	1,00		138,21	0,300			0,042
Product 54b		85%	227,33	0,255			**0,058**

E-Factor:	**2,185**



Molecular Weight: 110,17 Molecular Weight: 418,15 Molecular Weight: 280,31

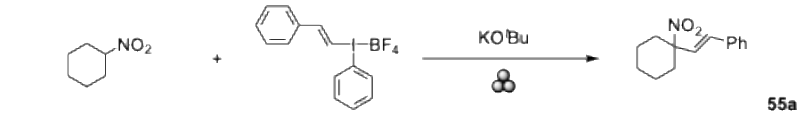
Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Thiophenol	1,00		110,17	0,200			0,022
VBX	1,00		418,15	0,200			0,084
KO*t*Bu	1,00		112,21	0,200			0,022
THF					0,050	0,889	0,044
Product 54c		93%	280,31	0,186			**0,052**

E-Factor:	**2,310**

Experimental: S. Doobary, M. M. de Vries Ibáñez and B. Olofsson, *Green Chem*., 2024, **26**, 11518

General procedure 5: *C*-vinylation. Potassium *tert*-butoxide (40.3 mg, 0.36 mmol, 1.2 equiv), the nucleophile (0.30 mmol), and one 5 mm stainless steel ball were added to a 1.5 mL stainless steel ball milling vessel. The vessel was closed and the mixture was milled for 15 minutes at 30 Hz and then vinyliodonium salt **6d** (118 mg, 0.30 mmol, 1 equiv) was added. This mixture was milled for 10 minutes at 30 Hz.

Large Scale Reaction of 55a. Potassium *tert*-butoxide (403 mg, 3.6 mmol, 1.2 equiv), nitrocyclohexane, and one 10 mm stainless steel ball were added to a 5 mL stainless steel ball milling vessel. The vessel was closed and the mixture was milled for 15 minutes at 30 Hz and then vinyliodonium salt **6d** (1.181 g, 3.00 mmol, 1.0 equiv) was added. This mixture was milled for 10 minutes at 30 Hz.



55a

Molecular Weight: 129,16 Molecular Weight: 393,96 Molecular Weight: 231,30

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Nitrocyclohexane	1,00		129,16	0,300			0,039
VBX	1,00		393,96	0,300			0,118
KO*t*Bu	1,20		112,21	0,360			0,040
Product 55a		92%	231,30	0,276			**0,064**

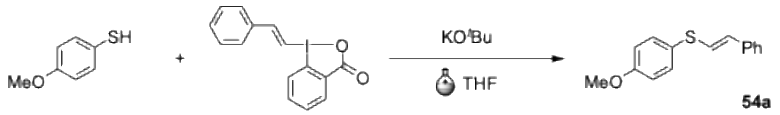
E-Factor:	**2,091**

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Nitrocyclohexane	1,00		129,16	3,000			0,387
VBX	1,00		393,96	3,000			1,182
KO*t*Bu	1,20		112,21	3,600			0,404
Product 55a		71%	231,30	2,130			**0,493**

E-Factor:	**3,005**

Experimental: L. Castoldi, E. M. Di Tommaso, M. Reitti, B. Gräfen and B. Olofsson, *Angew. Chem. Int. Ed*., 2020, **59**, 15512.

General Procedure A for Vinylation of Thiols. Thiol **1** (1.0 equiv, 0.3 mmol) was placed in an oven-dried microwave vial with magnetic stirring bar under argon, followed by the addition of dry and degassed THF (2.0 mL). Subsequently, VBX **2** (1.1 equiv) was added followed by *t*BuOK (1.0 equiv) and the vial rinsed with THF (1.0 mL), the mixture rapidly turns yellow and it was stirred at RT for 2 h.
Comment:
54c: 0.1 mmol scale in 1.0 mL THF.

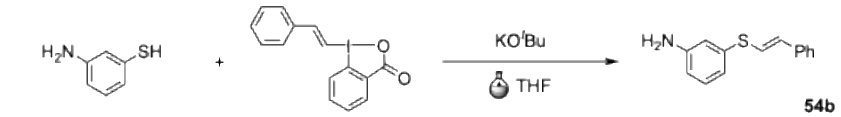


54a

Molecular Weight: 140,20 Molecular Weight: 350,16 Molecular Weight: 242,34

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
4-Methoxythiophenol	1,00		140,20	0,300			0,042
VBX	1,10		350,16	0,330			0,116
KO*t*Bu	1,00		112,21	0,300			0,034
THF					3,000	0,889	2,667
Product 54a		73%	242,34	0,219			**0,053**

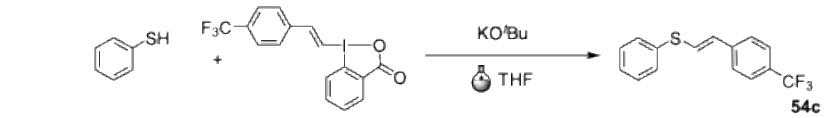
E-Factor:	**52,856**



Molecular Weight: 125,19 Molecular Weight: 350,16 Molecular Weight: 227,33

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
3-Aminothiophenol	1,00		125,19	0,300			0,038
VBX	1,50		350,16	0,450			0,158
KO*t*Bu	1,00		112,21	0,300			0,034
THF					3,000	0,889	2,667
Product 54b		37%	227,33	0,111			**0,025**

E-Factor:	**113,759**



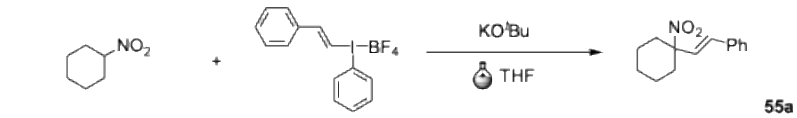
Molecular Weight: 110,17 Molecular Weight: 418,15 Molecular Weight: 280,31

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Thiophenol	1,00		110,17	0,100			0,011
VBX	1,10		418,15	0,110			0,046
KO*t*Bu	1,00		112,21	0,100			0,011
THF					1,000	0,889	0,889
Product 54c		72%	280,31	0,072			**0,020**

E-Factor:	**46,429**

Experimental: E. Stridfeldt, A. Seemann, M. J. Bouma, C. Dey, A. Ertan and B. Olofsson, *Chem. Eur. J.*, 2016, **22**, 16066.

Vinylation using THF as Solvent. *t*BuOK (0.26 mmol, 1.1 equiv) was added to a dry 10-20 mL microwave vial. The vial was capped with a rubber septum and evacuated and back-filled with argon three times. Anhydrous THF (4 mL) was added, followed by drop wise addition of nitrocyclohexane (0.24 mmol, 1 equiv). The mixture was stirred at rt for 1 h. The vial was opened and **6a** or **7** (0.26-0.48 mmol, 1.1-2.0 equiv) was added in one portion. The vial was then capped again with a rubber septum and left under a positive argon pressure. Anhydrous THF (6 mL) was added and the mixture was stirred at rt for the tabulated time.



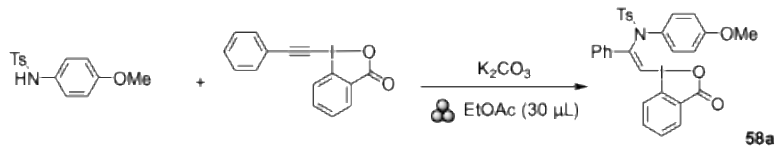
Molecular Weight: 129,16 Molecular Weight: 393,96 Molecular Weight: 231,30

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Nitrocyclohexane	1,00		129,16	0,240			0,031
VBX	2,00		393,96	0,480			0,189
KO*t*Bu	1,08		112,21	0,260			0,029
THF					10,000	0,889	8,890
Product 55a		55%	231,30	0,132			**0,031**

E-Factor:	**298,338**

Experimental: S. Doobary, J. Braunreauther, A. K. Inge and B. Olofsson, *Angew. Chem. Int. Ed.* **2025**, e19049.

General procedure 1 (GP1) to synthesize *N*-VBX 3 and *O*-VBX 4 (small vessel). Potassium carbonate (4.3 mg, 0.03 mmol, 0.3 equiv), EBX **1** (0.10 mmol, 1 equiv), nucleophile **2** (0.10 mmol, 1 equiv), ethyl acetate (30 µL) and one 7 mm stainless steel ball were added to a 1.5 mL stainless steel ball milling vessel. The vessel was closed and the mixture was milled for 60 minutes at 35 Hz.



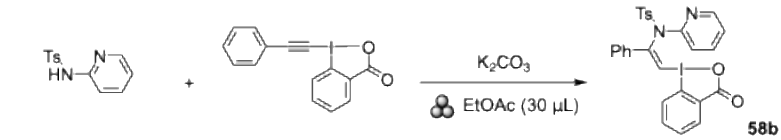
Molecular Weight: 277,34 Molecular Weight: 348,14 Molecular Weight: 625,48

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Tosylamide	1,00		277,34	0,100			0,028
EBX	1,00		348,14	0,100			0,035
K2CO3	0,30		138,21	0,030			0,004
EtOAc					0,030	0,902	0,027
Product 58a		93%	625,48	0,093			**0,058**

E-Factor:	**0,612**

Experimental: S. Doobary, J. Braunreauther, A. K. Inge and B. Olofsson, *Angew. Chem. Int. Ed.* **2025**, e19049.

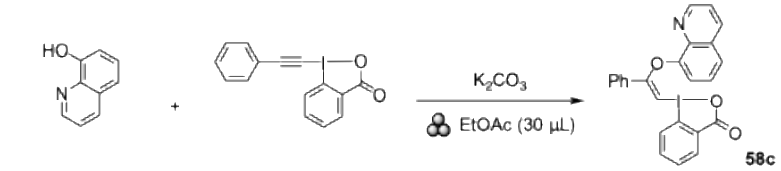
General procedure 2 (GP2) to synthesize *N*-VBX 3 and *O*-VBX 4 (large vessel). Potassium carbonate (4.3 mg, 0.03 mmol, 0.3 equiv), EBX **1** (0.10 mmol, 1 equiv), nucleophile **2** (0.10 mmol, 1 equiv), ethyl acetate (30 µL) and four 5 mm stainless steel balls were added to a 5 mL stainless steel ball milling vessel. The vessel was closed and the mixture was milled for 120 minutes at 35 Hz.



Molecular Weight: 248,30 Molecular Weight: 348,14 Molecular Weight: 596,44

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Tosylamide	1,00		248,30	0,100			0,025
EBX	1,00		348,14	0,100			0,035
K2CO3	0,30		138,21	0,030			0,004
EtOAc					0,030	0,902	0,027
Product 58b		83%	596,44	0,083			**0,050**

E-Factor:	**0,835**



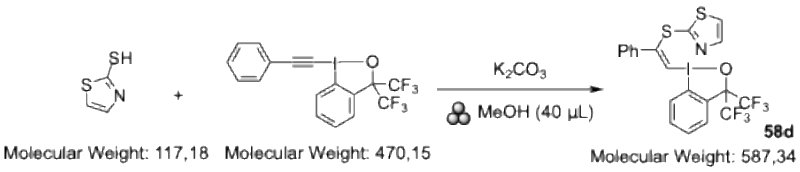
Molecular Weight: 145,16 Molecular Weight: 348,14 Molecular Weight: 493,30

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
8-Hydroxyquinoline	1,00		145,16	0,100			0,015
EBX	1,00		348,14	0,100			0,035
K2CO3	0,30		138,21	0,030			0,004
EtOAc					0,030	0,902	0,027
Product 58c		84%	493,30	0,084			**0,041**

E-Factor:	**0,944**

Experimental: S. Doobary, J. Braunreauther, A. K. Inge and B. Olofsson, *Angew. Chem. Int. Ed.* **2025**, e19049.

General procedure 3 (GP3) to synthesize *S*-VBO products 5. Potassium carbonate (4.3 mg, 0.03 mmol, 0.3 equiv), EBO **1** (0.10 mmol, 1 equiv), thiol (0.10 mmol, 1 equiv), methanol (40 µL) and one 7 mm stainless steel ball were added to a 1.5 mL stainless steel ball milling vessel. The vessel was closed and the mixture was milled for 60 minutes at 35 Hz.
Comment:
58d: 0.15 mmol 2-mercaptothiazole was used.



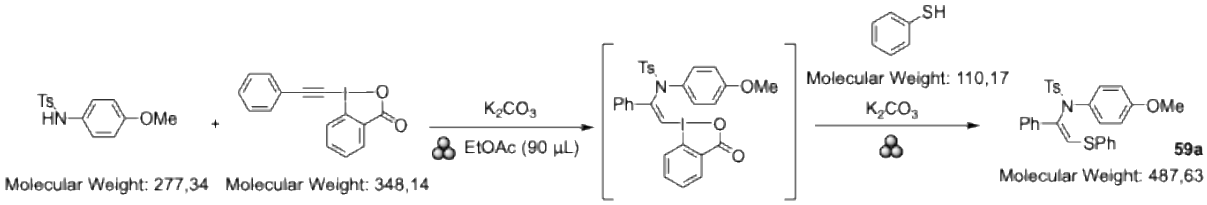
Molecular Weight: 117,18 Molecular Weight: 470,15 Molecular Weight: 587,34

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
EBO	1,00		470,15	0,100			0,047
2-Mercaptothiazole	1,50		117,18	0,150			0,018
K2CO3	0,30		138,21	0,030			0,004
MeOH					0,040	0,791	0,032
Product 58d		62%	587,34	0,062			**0,037**

E-Factor:	**1,743**

Experimental: S. Doobary, J. Braunreauther, A. K. Inge and B. Olofsson, *Angew. Chem. Int. Ed.* **2025**, e19049.

General procedure 4 (GP4): *N/O, S*-coupling with EBX (small vessel). Potassium carbonate (0.012 g, 0.09 mmol, 0.3 equiv), EBX 1 (0.3 mmol, 1 equiv), nucleophile 2 (0.30 mmol, 1 equiv), ethyl acetate (90 µL) and one 7 mm stainless steel ball were added to a 1.5 mL stainless steel ball milling vessel. The vessel was closed and the mixture was milled for 60 minutes at 35 Hz. After the vessel was opened, potassium carbonate (0.042 g, 0.3 mmol, 1.0 equiv) and thiol (0.3 mmol, 1 equiv) was added. The vessel was closed and the mixture was milled for 60 minutes at 35 Hz.



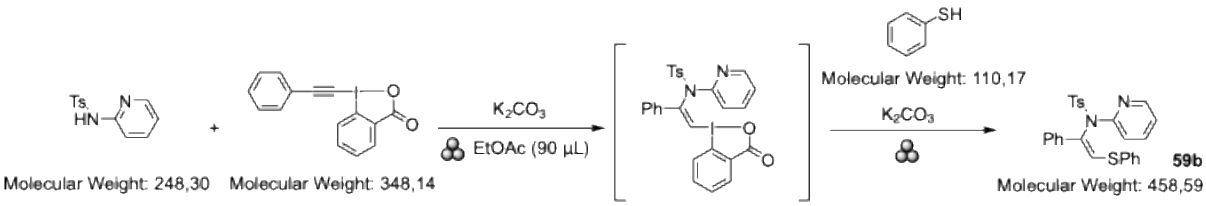
Molecular Weight: 277,34 Molecular Weight: 348,14 Molecular Weight: 487,63

Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Tosylamide	1,00		277,34	0,300			0,083
EBX	1,00		348,14	0,300			0,104
K2CO3	1,30		138,21	0,390			0,054
Thiophenol	1,00		110,17	0,300			0,000
EtOAc					0,090	0,902	0,081
Product 59a		96%	487,63	0,288			**0,140**

E-Factor:	**1,298**

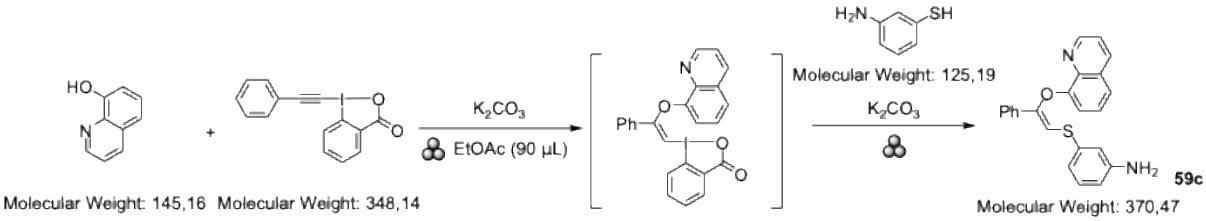
Experimental: S. Doobary, J. Braunreauther, A. K. Inge and B. Olofsson, *Angew. Chem. Int. Ed.* **2025**, e19049.

General procedure 5 (GP5): *N/O, S*-coupling with EBX (large vessel). Potassium carbonate (0.012 g, 0.09 mmol, 0.3 equiv), EBX **1** (0.3 mmol, 1 equiv), nucleophile **2** (0.30 mmol, 1 equiv), ethyl acetate (90 µL) and four 5 mm stainless steel ball were added to a 5 mL stainless steel ball milling vessel. The vessel was closed and the mixture was milled for 120 minutes at 35 Hz. After the vessel was opened, potassium carbonate (0.042 g, 0.3 mmol, 1.0 equiv) and thiol (0.3 mmol, 1 equiv) was added. The vessel was closed and the mixture was milled for 60 minutes at 35 Hz.



Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
Tosylamide	1,00		248,30	0,300			0,074
EBX	1,00		348,14	0,300			0,104
K2CO3	1,30		138,21	0,390			0,054
Thiophenol	1,00		110,17	0,300			0,000
EtOAc					0,090	0,902	0,081
Product 59b		76%	458,59	0,227			**0,104**

E-Factor:	**2,019**

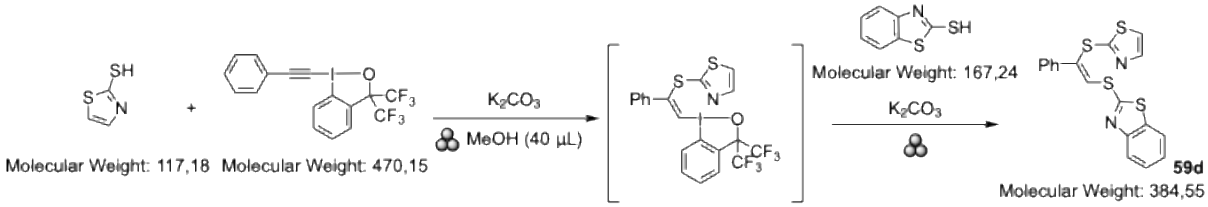


Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
8-Hydroxyquinoline	1,00		145,16	0,300			0,044
EBX	1,00		348,14	0,300			0,104
K2CO3	1,30		138,21	0,390			0,054
3-Aminothiophenol	1,00		125,19	0,300			0,038
EtOAc					0,090	0,902	0,081
Product 59c		52%	370,47	0,156			**0,058**

E-Factor:	**4,548**

Experimental: S. Doobary, J. Braunreauther, A. K. Inge and B. Olofsson, *Angew. Chem. Int. Ed.* **2025**, e19049.

General procedure 6 (GP6): Hetero-*S,S*-coupling with EBO
Potassium carbonate (4.3 mg, 0.03 mmol, 0.3 equiv), EBO 1 (0.1 mmol, 1 equiv), the first thiol (0.15 mmol, 1.5 equiv), methanol (40 mL) and one 7 mm stainless steel ball were added to a 1.5 mL stainless steel ball milling vessel. The vessel was closed and the mixture was milled for 60 minutes at 35 Hz. After the vessel was opened, potassium carbonate (0.042 g, 0.3 mmol, 1.0 equiv) and the second thiol (0.1 mmol, 1 equiv) was added. The vessel was closed and the mixture was milled for 60 minutes at 35 Hz.



Compound	Equiv	Yield	Mw (g/mol)	Moles (mmol)	Volume (mL)	Density (g/mL)	Mass (g)
EBO	1,00		470,15	0,100			0,047
2-Mercaptothiazole	1,50		117,18	0,150			0,018
K_2CO_3	3,30		138,21	0,330			0,046
2-Mercaptobenzoxazole	1,00		167,24	0,100			0,017
MeOH					0,040	0,791	0,032
Product 59d		48%	384,55	0,048			**0,018**

E-Factor:	**7,590**

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